

# Supporting Information

## **Enantioselective Acyloin Rearrangement of Acyclic Aldehydes Catalyzed by Chiral Oxazaborolidinium Ion**

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## 1. General Information

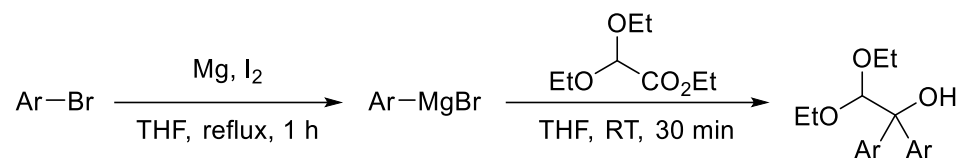
Unless stated otherwise, reactions were carried out under a dry argon atmosphere in vacuum-flame dried glassware. Dichloromethane was distilled from calcium hydride. Toluene was distilled from sodium wire. Thin layer chromatography was carried out on Merck silica gel 60 F254. Flash chromatography was 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 at 500 and 125 MHz. Chemical shift values are reported in ppm from tetramethylsilane as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), and coupling constants (Hz). Infrared spectra were recorded on a Bruker Vertex 70. HRMS were recorded on ESI-Q-TOF mass spectrometer (compact, Bruker Daltonics Inc., Bremen Germany). 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.

Unless stated otherwise, all aldehyde compounds were prepared according to previously reported procedures.<sup>1-3</sup>

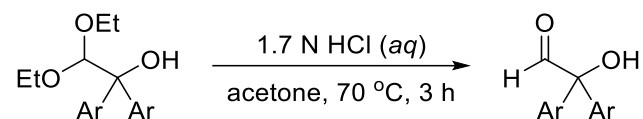
## 2. Preparation of Aldehyde Compounds

### 2.1 Preparation of $\alpha,\alpha$ -Diaryl- $\alpha$ -Hydroxy Aldehyde (Procedure A)

General procedure for synthesis of  $\alpha,\alpha$ -diaryl- $\alpha$ -hydroxy aldehydes

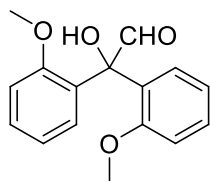


To a two-neck round bottom flask was added crushed magnesium (0.30 g, 13 mmol, 2.5 equiv), a small crystal of I<sub>2</sub> (50mg, 0.24 mmol, 0.050 equiv) and THF (13 mL). While stirring, the appropriate aryl bromide (13 mmol, 2.5 equiv) was added via a syringe (for solid bromides, a solution was prepared by dissolving in a minimal amount of THF). After introduced aryl bromide, the mixture was heated to reflux in an oil bath under argon atmosphere for 1 hour and cooled down until room temperature. Ethyl 2,2-diethoxyacetate (0.89 mL, 5.0 mmol, 1.0 equiv) dissolved in THF (7.2 mL) was added dropwise to the Grignard solution under argon at 0 °C, and the reaction mixture was stirred for 30 min at room temperature. After completion of the reaction, the mixture was quenched with saturated aqueous NH<sub>4</sub>Cl solution and extracted with diethyl ether (3 x 25 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The combined crude product was used without purification in the next deprotection step.



To a stirred solution of 2,2-diethoxy-1,1-diarylethanol (5.0 mmol, 1.0 equiv) in acetone (18 mL) was added 1.7 N HCl aqueous solution (0.90 mL, 1.5 mmol, 0.30 equiv) at room temperature. After solution clear, the mixture was stirred for 3 hours at 70 °C in an oil bath. After completion of the reaction, the reaction mixture was cooled down until room temperature and diluted with dichloromethane (DCM). Separate organic layer 1 time and wash with saturated aqueous NaHCO<sub>3</sub> solution and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by flash column chromatography and recrystallization to afford desired product.

### 2-hydroxy-2,2-bis(2-methoxyphenyl)acetaldehyde (1e)



According to the general procedure, the reaction of 2,2-diethoxy-1,1-bis(4-methoxyphenyl)ethan-1-ol (1.7 g, 5.0 mmol, 1.0 equiv) with 1.7 N HCl aqueous solution (0.90 mL, 1.5 mmol, 0.30 equiv) was performed. Column chromatography (silica gel, 1:20 ethyl acetate/*n*-hexane) and recrystallization from 1:20 dichloromethane/*n*-hexane afforded the desired product (0.82 g, 60%) as white solid.

**R<sub>f</sub>**: 0.23 (1:5 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.13 (d, *J* = 1.2 Hz, 1H), 7.38 – 7.28 (m, 4H), 6.97 (td, *J* = 7.5, 1.2 Hz, 2H), 6.92 (d, *J* = 1.1 Hz, 1H), 6.91 (d, *J* = 1.1 Hz, 1H), 4.60 (d, *J* = 1.2 Hz, 1H), 3.74 (s, 6H)

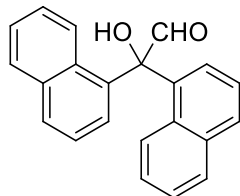
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 199.0, 156.3, 130.0, 129.0, 128.9, 121.5, 111.7, 81.4, 55.8

**IR** ν<sub>max</sub> 3465, 3005, 2962, 1717, 1598, 1587, 1488, 1464, 1437, 1245, 1220, 1137, 1028, 911 cm<sup>-1</sup>

**HRMS** (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd. for C<sub>16</sub>H<sub>16</sub>O<sub>4</sub>Na 295.0941; Found 295.0944

**mp**: 119 - 121 °C

### 2-hydroxy-2,2-di(naphthalen-1-yl)acetaldehyde (1l)



According to the general procedure, the reaction of 2,2-diethoxy-1,1-di(naphthalen-1-yl)ethan-1-ol (1.9 g, 5.0 mmol, 1.0 equiv) with 1.7 N HCl aqueous solution (0.90 mL, 1.5 mmol, 0.30 equiv) was performed. Column chromatography (silica gel, 1:20 ethyl acetate/*n*-hexane) and recrystallization from 1:20 dichloromethane/*n*-hexane afforded the desired product (0.78 g, 50%) as white solid.

**R<sub>f</sub>**: 0.38 (1:5 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.43 (d, *J* = 1.2 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.27 (m, 2H), 4.67 (d, *J* = 1.2 Hz, 1H)

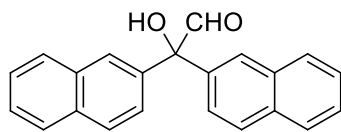
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 199.7, 135.9, 134.9, 131.2, 130.3, 129.2, 126.6, 126.4, 126.0, 126.0, 125.4, 85.4

**IR** ν<sub>max</sub> 3474, 2980, 2920, 1721, 1670, 1597, 1541, 1443, 1347, 1329, 1220, 1163, 1074, 913 cm<sup>-1</sup>

**HRMS** (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd. for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>Na 335.1043; Found 335.1045

**mp**: 156 - 158 °C

**2-hydroxy-2,2-di(naphthalen-2-yl)acetaldehyde (1m)**



According to the general procedure, the reaction of 2,2-diethoxy-2,2-di(naphthalen-1-yl)ethan-1-ol (1.9 g, 5.0 mmol, 1.0 equiv) with 1.7 N HCl aqueous solution (0.90 mL, 1.5 mmol, 0.30 equiv) was performed. Column chromatography (silica gel, 1:20 ethyl acetate/*n*-hexane) and recrystallization from 1:20 dichloromethane/*n*-hexanes afforded the desired product (0.73 g, 47%) as white solid.

**R<sub>f</sub>**: 0.37 (1:5 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.21 (d, *J* = 1.4 Hz, 1H), 7.92 (s, 2H), 7.89 – 7.82 (m, 6H), 7.55 – 7.49 (m, 4H), 7.47 (dd, *J* = 8.6, 1.7 Hz, 2H), 4.54 (d, *J* = 1.4 Hz, 1H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 198.3, 136.9, 133.3, 133.2, 129.0, 128.5, 127.9, 127.0, 127.0, 126.8, 125.1, 84.0

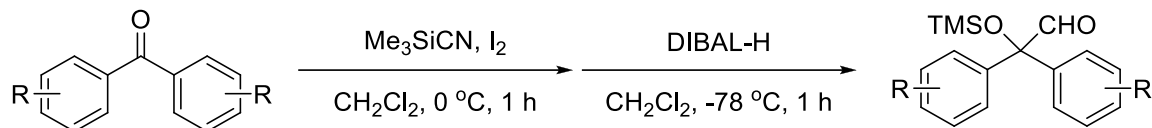
**IR** ν<sub>max</sub> 3492, 3059, 2910, 1725, 1631, 1620, 1530, 1503, 1328, 1220, 1127, 1056, 913 cm<sup>-1</sup>

**HRMS** (ESI) *m/z*: [M+Na+MeOH]<sup>+</sup> Calcd. for C<sub>23</sub>H<sub>20</sub>O<sub>3</sub>Na 367.1305; Found 367.1303

**mp**: 135 - 137 °C

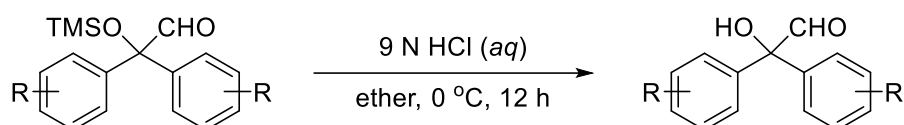
## 2.2 Preparation of $\alpha,\alpha$ -Diaryl- $\alpha$ -Hydroxy Aldehyde (Procedure B)

### General procedure for synthesis of $\alpha,\alpha$ -diaryl- $\alpha$ -hydroxy aldehydes

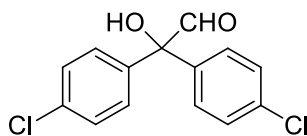


To a stirred solution of  $\alpha,\alpha$ -diaryl ketone (5.0 mmol, 1.0 equiv) in DCM (15 mL) were added trimethylsilyl cyanide (0.75 mL, 6.0 mmol, 1.2 equiv) and a small crystal of I<sub>2</sub> (0.13 g, 0.50 mmol, 0.10 equiv) at 0 °C dropwise. Under argon atmosphere, the mixture was stirred for 1 hour at 0 °C. After completion of the reaction, the reaction mixture was quenched with saturated aqueous Na<sub>2</sub>SO<sub>3</sub> solution and extracted with diethyl ether (3 x 25 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*.

To the crude solution in DCM (10 mL) was added DIBAL-H solution (1.0 M in toluene, 10 mL, 10 mmol, 2.0 equiv) under argon atmosphere at -78 °C, and the reaction mixture was stirred for 1 hour at same temperature. The reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl solution at -78 °C, and filtered using celite pad with diethyl ether. After evaporation of solvent under vacuum, the crude mixture was extracted with diethyl ether (3 x 25 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The product was purified by column chromatography (1:20 diethyl ether/*n*-hexane) to afford desired product.



To a stirred solution of  $\alpha,\alpha$ -diaryl- $\alpha$ -trimethylsiloxy aldehyde (3.0 mmol, 1.0 equiv) in diethyl ether (3.0 mL) was added 9 N HCl aqueous solution (3.0 mL, 27 mmol, 9.0 equiv) at 0 °C. The reaction mixture was stirred vigorously for 12 hours at 0 °C. After completion of the reaction, the mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography to obtain desired products.

**2,2-bis(4-chlorophenyl)-2-hydroxyacetaldehyde (1g)**

According to the general procedure, the reaction of 2,2-bis(4-chlorophenyl)-2-((trimethylsilyl)oxy)acetaldehyde (1.1 g, 3.0 mmol, 1.0 equiv) with 9.0 N HCl aqueous solution (3.0 mL, 27 mmol, 9.0 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired product (0.70 g, 83%) as colorless oil.

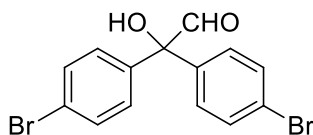
**R<sub>f</sub>**: 0.37 (1:5 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.92 (d, *J* = 1.3 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 4H), 7.29 (d, *J* = 8.6 Hz, 4H), 4.38 (d, *J* = 1.5 Hz, 1H)

**<sup>13</sup>C NMR** (125MHz, CDCl<sub>3</sub>) δ 197.1, 137.6, 135.1, 129.3, 128.9, 82.8

**IR** ν<sub>max</sub> 3474, 2921, 2850, 2096, 1723, 1639, 1592, 1490, 1403, 1299, 1220, 1131, 1093, 1012, 928 cm<sup>-1</sup>

**HRMS** (ESI) *m/z*: [M+Na+MeOH]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>3</sub>Na 335.0212; Found 335.0215

**2,2-bis(4-bromophenyl)-2-hydroxyacetaldehyde (1h)**

According to the general procedure, the reaction of 2,2-bis(4-bromophenyl)-2-((trimethylsilyl)oxy)acetaldehyde (1.3 g, 3.0 mmol, 1.0 equiv) with 9.0 N HCl aqueous solution (3.0 mL, 27 mmol, 9.0 equiv) was performed. Column chromatography purification with 1:30 diethyl ether/*n*-hexane afforded the desired product (0.83 g, 75%) as colorless oil.

**R<sub>f</sub>**: 0.37 (1:5 ethyl acetate/*n*-hexane)

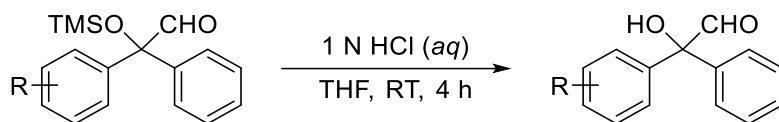
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.91 (d, *J* = 1.4 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 4H), 7.23 (d, *J* = 8.6 Hz, 4H), 4.37 (d, *J* = 1.4 Hz, 1H)

**<sup>13</sup>C NMR** (125MHz, CDCl<sub>3</sub>) δ 197.0, 138.1, 132.3, 129.1, 123.2, 82.9

**IR** ν<sub>max</sub> 3476, 3086, 2962, 1723, 1656, 1587, 1486, 1442, 1277, 1174, 1093, 1074, 925 cm<sup>-1</sup>

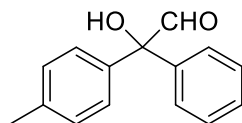
**HRMS** (ESI) *m/z*: [M+Na+MeOH]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>14</sub>Br<sub>2</sub>O<sub>3</sub>Na 422.9202; Found 422.9200





To a stirred solution of  $\alpha,\alpha$ -differently diaryl- $\alpha$ -trimethylsiloxy aldehyde (3.0 mmol, 1.0 equiv) in THF (30 mL) at room temperature, a 1 N HCl aqueous solution (15 mL, 15 mmol, 5.0 equiv) was added to reaction mixture. The reaction mixture was stirred vigorously for 4 hours at room temperature. After completion of the reaction, the mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  solution and extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. The product was purified by column chromatography and recrystallization to afford the desired product.

### 2-hydroxy-2-phenyl-2-(*p*-tolyl)acetaldehyde (1n)



According to the general procedure, the reaction of 2-phenyl-2-(*p*-tolyl)-2-((trimethylsilyl)oxy)acetaldehyde (0.90 g, 3.0 mmol, 1.0 equiv) with 1.0 N HCl aqueous solution (15 mL, 15 mmol, 5.0 equiv) was performed. Column chromatography (1:20 ethyl acetate/*n*-hexane) and recrystallization (1:20 dichloromethane/*n*-hexane) afforded the desired product (0.63 g, 93%) as white solid.

**R<sub>f</sub>**: 0.42 (1:5 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.96 (d,  $J$  = 1.4 Hz, 1H), 7.44 – 7.32 (m, 5H), 7.25 (d,  $J$  = 8.4 Hz, 2H), 7.21 (d,  $J$  = 8.2 Hz, 2H), 4.35 (d,  $J$  = 1.4 Hz, 1H), 2.36 (s, 3H)

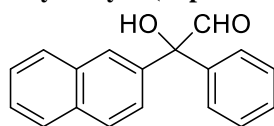
**<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ )  $\delta$  198.2, 139.5, 138.6, 136.5, 129.7, 128.9, 128.6, 127.6, 127.5, 83.5, 21.3

**IR**  $\nu_{\text{max}}$  3485, 3030, 2962, 1723, 1656, 1602, 1511, 1492, 1449, 1338, 1220, 1175, 1102, 1048, 913  $\text{cm}^{-1}$

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}+\text{MeOH}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{18}\text{O}_3\text{Na}$  281.1148; Found 281.1151

**mp**: 49 – 51  $^{\circ}\text{C}$

### 2-hydroxy-2-(naphthalen-2-yl)-2-phenylacetaldehyde (1o)



According to the general procedure, the reaction of 2-(naphthalen-2-yl)-2-phenyl-2-((trimethylsilyl)oxy)acetaldehyde (1.0 g, 3.0 mmol, 1.0 equiv) with 1.0 N HCl aqueous solution (15 mL, 15 mmol, 5.0 equiv) was performed. Column chromatography (1:20 ethyl acetate/*n*-hexane) and recrystallization (1:20 dichloromethane/*n*-hexane) afforded the desired product (0.52 g, 66%) as white solid.

**R<sub>f</sub>**: 0.33 (1:5 ethyl acetate/*n*-hexane)

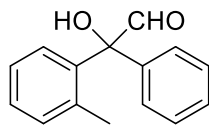
**<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.10 (d,  $J$  = 1.4 Hz, 1H), 7.91 – 7.78 (m, 4H), 7.67 – 7.48 (m, 2H), 7.44 (d,  $J$  = 1.8 Hz, 1H), 7.43 – 7.32 (m, 5H), 4.46 (d,  $J$  = 1.4 Hz, 1H)

**<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ )  $\delta$  198.3, 139.5, 136.9, 133.2, 133.2, 129.1, 128.9, 128.8, 128.5, 127.8, 127.7, 126.9, 126.8, 126.7, 125.1, 83.8

**IR**  $\nu_{\text{max}}$  3473, 3059, 2979, 1723, 1635, 1599, 1559, 1493, 1448, 1273, 1220, 1168, 1129, 1026, 912  $\text{cm}^{-1}$

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}+\text{MeOH}]^+$  Calcd. for  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{Na}$  317.1148; Found 317.1150

**mp**: 74 – 76  $^{\circ}\text{C}$

**2-hydroxy-2-phenyl-2-(*o*-tolyl)acetaldehyde (1p)**

According to the general procedure, the reaction of 2-phenyl-2-(*o*-tolyl)-2-((trimethylsilyl)oxy)acetaldehyde (0.90 g, 3.0 mmol, 1.0 equiv) with 1.0 N HCl aqueous solution (15 mL, 15 mmol, 5.0 equiv) was performed. Column chromatography (1:20 ethyl acetate/*n*-hexane) and recrystallization (1:20 dichloromethane/*n*-hexane) afforded the desired product (0.48 g, 70%) as a white solid.

**R<sub>f</sub>**: 0.50 (1:5 ethyl acetate/*n*-hexane)

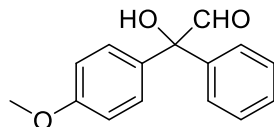
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.02 (d, *J* = 1.5 Hz, 1H), 7.38 (d, *J* = 3.4 Hz, 4H), 7.36 – 7.31 (m, 1H), 7.27 (td, *J* = 7.3, 1.4 Hz, 1H), 7.20 (ddd, *J* = 10.9, 6.9, 2.2 Hz, 2H), 7.15 (dd, *J* = 7.6, 1.5 Hz, 1H), 4.38 (d, *J* = 1.4 Hz, 1H), 2.06 (s, 3H)

**<sup>13</sup>C NMR** (125MHz, CDCl<sub>3</sub>) δ 198.6, 139.3, 138.9, 138.6, 133.2, 129.0, 128.8, 128.4, 127.5, 127.0, 125.8, 84.2, 20.9

**IR**  $\nu_{\text{max}}$  3476, 3063, 2968, 2923, 1723, 1670, 1661, 1489, 1449, 1382, 1337, 1220, 1175, 1121, 1037, 913 cm<sup>-1</sup>

**HRMS** (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>Na 249.0886; Found 249.0883

**mp**: 72 – 74 °C

**2-hydroxy-2-(4-methoxyphenyl)-2-phenylacetaldehyde (1q)**

According to the general procedure, the reaction of 2-(4-methoxyphenyl)-2-phenyl-2-((trimethylsilyl)oxy)acetaldehyde (0.94 g, 3.0 mmol, 1.0 equiv) with 1.0 N HCl aqueous solution (15 mL, 15 mmol, 5.0 equiv) was performed. Column chromatography (1:20 ethyl acetate/*n*-hexane) and recrystallization (1:20 dichloromethane/*n*-hexane) afforded the desired product (0.68 g, 93%) as a white solid.

**R<sub>f</sub>**: 0.27 (1:5 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.94 (s, 1H), 7.44 – 7.34 (m, 5H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.33 (s, 1H), 3.82 (s, 3H)

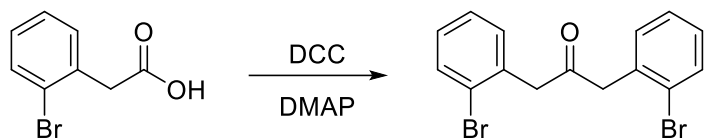
**<sup>13</sup>C NMR** (125MHz, CDCl<sub>3</sub>) δ 198.1, 159.8, 139.5, 131.5, 129.0, 128.9, 128.6, 127.6, 114.4, 83.3, 55.5

**IR**  $\nu_{\text{max}}$  3472, 2963, 2936, 2839, 1723, 1610, 1583, 1512, 1448, 1336, 1304, 1254, 1220, 1175, 1036, 913 cm<sup>-1</sup>

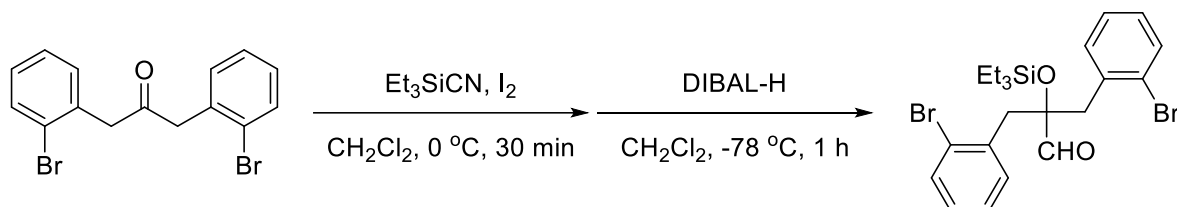
**HRMS** (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>Na 265.0835; Found 265.0832

**mp**: 74 – 76 °C

## 2.3 Preparation of 2-(2-Bromobenzyl)-3-(2-Bromophenyl)-2-((Triethylsilyl)oxy)propanal



To a stirred solution of dicyclohexylcarbodiimide (DCC, 2.2 g, 11 mmol, 1.1 equiv) and dimethylaminopyridine (DMAP, 0.37g, 3.0 mmol, 0.30 equiv) in THF (20 mL) was added 2-(2-bromophenyl)acetic acid (2.2g, 10 mmol, 1.0 equiv) at room temperature. Under argon atmosphere, the mixture was stirred for 2 hours at room temperature. After completion of the reaction, the reaction mixture was filtered using silica gel with DCM. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, 1:20 ethyl acetate/*n*-hexane) and recrystallization (1:20 dichloromethane/*n*-hexane) to afford desired product (2.2 g, 61%) as a white solid.



To a stirred solution of 1,3-bis(2-bromophenyl)propan-2-one (1.8 g, 5.0 mmol, 1.0 equiv) in DCM (15 mL) were added triethylsilyl cyanide (1.4 mL, 8.0 mmol, 1.6 equiv) and a small crystal of  $\text{I}_2$  (0.13 g, 0.50 mmol, 0.10 equiv) at 0 °C dropwise. Under argon atmosphere, the mixture was stirred for 1 hour at 0 °C. After completion of the reaction, the reaction mixture was quenched with saturated aqueous  $\text{Na}_2\text{SO}_3$  solution and extracted with diethyl ether (3 x 25 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*.

To the crude solution in DCM (10 mL) was added DIBAL-H solution (1.0 M in toluene, 10 mL, 10 mmol, 2.0 equiv) under argon atmosphere at -78 °C, and the reaction mixture was stirred for 1 hour at same temperature. The reaction mixture was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  solution at -78 °C, and filtered using celite pad with diethyl ether. After evaporation of solvent under vacuum, the crude mixture was extracted with diethyl ether (3 x 25 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. The product was purified by column chromatography (1:20 diethyl ether/*n*-hexane) to afford desired product (1.6 g, 61%) as a white solid.

**R<sub>f</sub>**: 0.62 (1:10 diethyl ether/*n*-hexane)

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.77 (s, 1H), 7.53 (dd,  $J$  = 8.0, 1.3 Hz, 2H), 7.33 (dd,  $J$  = 8.0, 1.8 Hz, 2H), 7.23 (td,  $J$  = 7.5, 1.3 Hz, 2H), 7.09 (td,  $J$  = 7.5, 1.8 Hz, 2H), 3.28 (d,  $J$  = 14.2 Hz, 2H), 3.25 (d,  $J$  = 14.1 Hz, 2H), 0.85 (t,  $J$  = 8.0 Hz, 9H), 0.51 (q,  $J$  = 8.0 Hz, 6H)

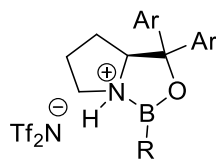
**$^{13}\text{C}$  NMR** (125MHz,  $\text{CDCl}_3$ )  $\delta$  201.4, 135.5, 133.1, 133.0, 128.7, 127.2, 125.9, 84.5, 42.6, 7.4, 7.0

**IR**  $\nu_{\text{max}}$  3472, 2958, 2917, 2355, 2339, 1740, 1670, 1595, 1472, 1440, 1381, 1220, 1150, 1116, 1047, 943  $\text{cm}^{-1}$

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd. for  $\text{C}_{22}\text{H}_{28}\text{Br}_2\text{O}_2\text{SiNa}$  533.0118; Found 533.0114

**mp**: 44 - 46 °C

### 3. Preparation of (S)-Oxazaborolidinium Catalyst



A 10 mL round-bottomed flask equipped with a stirring bar and a Dean-Stark trap fitted on top with a reflux condenser and a argon inlet adaptor was charged with (S)-(-)- $\alpha,\alpha$ -diphenyl-2-pyrrolidinemethanol (0.048 mmol), triphenylboroxine (0.016 mmol) and 20 mL of toluene. The resulting mixture was heated to reflux in an oil bath under argon atmosphere. After 3 hours, 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 *ca.* 2.0 mL. This distillation protocol was repeated three times by re-charging with 3 x 6.0 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* (*ca.* 0.10 mmHg, 10 min) afforded the corresponding oxazaborolidine as clear oil.

To an aliquot of oxazaborolidine precursor (0.048 mmol) in 0.8 mL of DCM at -40 °C was added triflimide (0.20 M solution in DCM freshly prepared, 0.040 mmol, 0.20 mL) dropwise under argon atmosphere. After 15-20 min at -40 °C, a homogeneous catalyst solution **3a** was ready for use in enantioselective synthesis of acyloin compounds.

## 4. General Procedure for Asymmetric Acyloin Rearrangement of Aldehydes

### 4.1 General Procedure for Acyloin Rearrangement of $\alpha,\alpha$ -Diaryl- $\alpha$ -Hydroxy Aldehydes

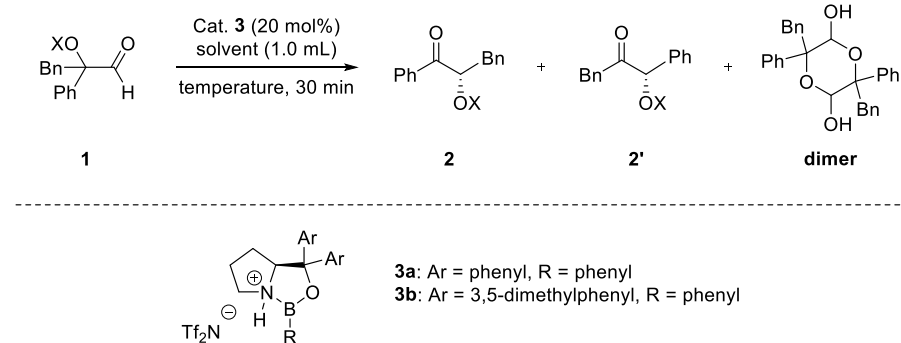
To a catalyst **3a** solution in 1.0 mL of DCM prepared as described above was added the corresponding aldehyde **1** (0.20 mmol, 1.0 equiv) at -40 °C. The resulting mixture was stirred at the same temperature until complete consumption of aldehyde compounds under argon atmosphere. The reaction mixture was quenched with 5.0 mL of distilled water and extracted with DCM (3 x 5.0 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography to obtain desired acyloin products **2**.

### 4.2 General Procedure for Acyloin Rearrangement of $\alpha,\alpha$ -Dialkyl- $\alpha$ -Siloxy Aldehydes

To a catalyst **3b** solution in 1.0 mL of toluene prepared as described above was added the corresponding aldehyde **4** (0.20 mmol, 1.0 equiv) at -20 °C. The resulting mixture was stirred at the same temperature until complete consumption of aldehyde compounds under argon atmosphere. The reaction mixture was quenched with 5.0 mL of distilled water and extracted with DCM (3 x 5.0 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography to obtain desired acyloin products **5**.

## 5. Enantioselective Acyloin Rearrangement of $\alpha$ -Benzyl- $\alpha$ -Phenyl Aldehydes

**Table S2.** Enantioselective acyloin rearrangement of  $\alpha$ -benzyl- $\alpha$ -phenyl aldehyde **1**<sup>a</sup>

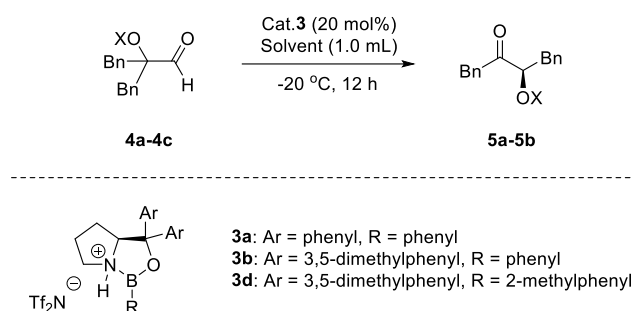


Entry	X	<b>2</b>	<b>3</b>	Solvent	Temperature	<b>2</b> : <b>2'</b>	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1 <sup>d</sup>	H	<b>2r</b>	<b>3a</b>	CH <sub>2</sub> Cl <sub>2</sub>	-40 °C	>20 : 1	25	62
2 <sup>d</sup>	H	<b>2r</b>	<b>3b</b>	PhMe	-40 °C	>20 : 1	28	98
3 <sup>e</sup>	H	<b>2r</b>	<b>3b</b>	PhMe	-40 °C	>20 : 1	26	-
4 <sup>f</sup>	TES	<b>2s</b>	<b>3b</b>	PhMe	-20 °C	10 : 1	55	22

<sup>a</sup>The reactions were performed with aldehydes **1** (0.2 mmol) in the presence of catalyst **3** (20 mol%) in solvent (1.0 mL) for 30 minutes at -40 °C. <sup>b</sup>Isolated yield of **2**. <sup>c</sup>Determined by chiral HPLC analysis. <sup>d</sup>70% of dimer was obtained. <sup>e</sup>The reaction was performed in 10 mL of toluene. 60% of dimer was obtained. <sup>f</sup>The reaction was performed for 4 hours. 40% of starting aldehyde **1** was recovered and dimer was not obtained.

## 6. Optimization of the Enantioselective Acyloin Rearrangement of Aldehydes **4**

**Table S1.** Optimization of the enantioselective acyloin rearrangement of aldehydes **4**.<sup>a</sup>

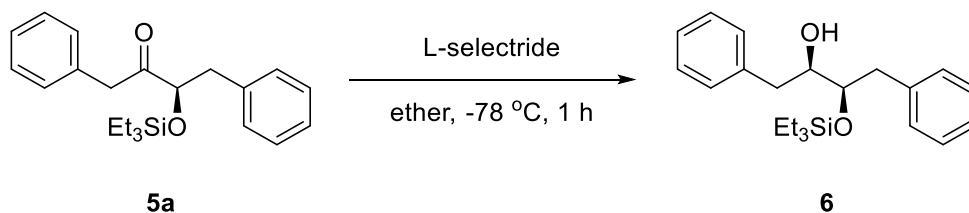


Entry	X	<b>5</b>	<b>3</b>	Solvent	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1 <sup>d,e</sup>	H	<b>5a</b>	<b>3a</b>	CH <sub>2</sub> Cl <sub>2</sub>	<10	-
2 <sup>d,e</sup>	TMS	<b>5a'</b>	<b>3a</b>	CH <sub>2</sub> Cl <sub>2</sub>	94	73
3 <sup>d,e</sup>	TMS	<b>5a'</b>	<b>3a</b>	PhMe	88	77
4	TMS	<b>5a'</b>	<b>3b</b>	PhMe	84	81
5 <sup>f</sup>	TMS	<b>5a'</b>	<b>3d</b>	PhMe	55	46
6	TES	<b>5b</b>	<b>3b</b>	PhMe	92	86

<sup>a</sup>The reactions were performed with aldehydes **4** (0.2 mmol) in the presence of catalyst **3** (20 mol%) in solvent (1.0 mL) for 12 hours at -20 °C. <sup>b</sup>Isolated yield. <sup>c</sup>Determined by chiral HPLC analysis. <sup>d</sup>The reaction was conducted for 18 hours. <sup>e</sup>The reaction was conducted at -40 °C. <sup>f</sup>The reaction was conducted at 0 °C.

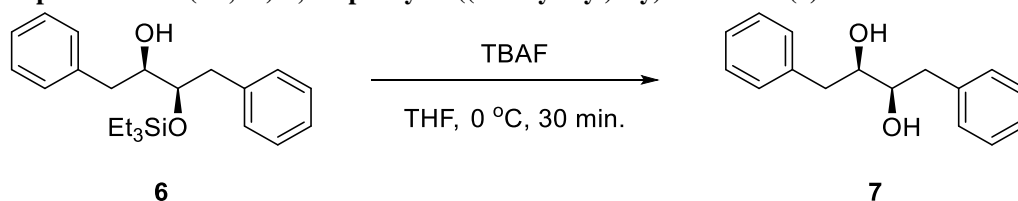
## 7. Transformation of 5b and Absolute Configuration Determination

### Reduction of (*R*)-1,4-diphenyl-3-((triethylsilyl)oxy)butan-2-one (5b)



To a stirred solution of (*R*)-1,4-diphenyl-3-((triethylsilyl)oxy)butan-2-one (65 mg, 0.18 mmol, 1.0 equiv) in diethyl ether (2.0 mL) was added L-Selectride solution (1.0 M in THF, 0.37 mL, 0.37 mmol, 2.0 equiv) at  $-78\text{ }^{\circ}\text{C}$  dropwise. Under argon atmosphere, the mixture was stirred for 1 hour at  $-78\text{ }^{\circ}\text{C}$ . After completion of the reaction, the reaction mixture was quenched with distilled water (5.0 mL) and extracted with DCM (3 x 5.0 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. The residue was purified by column chromatography (1:30 diethyl ether/*n*-hexane) to obtain desired product **6** (51 mg, 80%, d.r.=12:1).

### Deprotection of (2*R*,3*R*)-1,4-diphenyl-3-((triethylsilyl)oxy)butan-2-ol (6)



To a stirred solution of (2*R*,3*R*)-1,4-diphenyl-3-((triethylsilyl)oxy)butan-2-ol (51 mg, 0.14 mmol, 1.0 equiv) in THF (0.75 mL) was added TBAF solution (1.0 M in THF, 0.14 mL, 0.14 mmol, 1.0 equiv) at  $0\text{ }^{\circ}\text{C}$ . Under argon atmosphere, the mixture was stirred for 30 min at  $0\text{ }^{\circ}\text{C}$ . After completion of the reaction, the reaction mixture was quenched with distilled water (5.0 mL) and extracted with ethyl acetate (3 x 5.0 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. The residue was purified by column chromatography (1:5 ethyl acetate/*n*-hexane) to obtain desired product **7** (29 mg, 82%). Analytical data are consistent with reported values.<sup>4</sup>

**R<sub>f</sub>**: 0.30 (1:3 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (t,  $J = 7.4$  Hz, 4H), 7.27 – 7.19 (m, 6H), 3.75 (td,  $J = 8.2, 3.3$  Hz, 2H), 2.92 (dd,  $J = 13.7, 4.3$  Hz, 2H), 2.85 (dd,  $J = 13.8, 8.1$  Hz, 2H), 2.09 (bs, 2H)

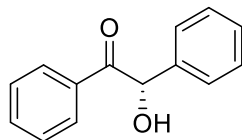
**<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.2, 129.5, 128.8, 126.7, 74.2, 40.5

**HPLC**: ee = 86%, Chiralpak<sup>®</sup> ID, 2-propanol:*n*-hexane=20:80, flow: 1.0mL/min, 220nm,  $t_R = 6.79$  min (major) and  $t_R = 7.49$  min (minor)

$[\alpha]_D^{20} = -1.8$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ) [lit.<sup>4</sup>  $[\alpha]_D^{20} = -2.0$  ( $c = 0.5$ ,  $\text{CHCl}_3$ , >99% ee) for (2*R*,3*R*)-enantiomer]

## 8. Characterization of Chiral Acyloins

### (S)-2-hydroxy-1,2-diphenylethan-1-one (2c)



According to the general procedure, the reaction of 2-hydroxy-2,2-diphenylacetaldehyde **1c** (42 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired product (38 mg, 90%) as white solid. Analytical data are consistent with reported values.<sup>5</sup>

**R<sub>f</sub>**: 0.47 (1:3 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.26 (m, 5H), 5.95 (d, *J* = 6.1 Hz, 1H), 4.55 (d, *J* = 6.1 Hz, 1H)

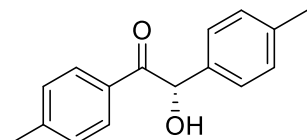
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 199.1, 139.2, 134.1, 133.6, 129.3, 129.3, 128.8, 128.7, 127.9, 76.4

**HPLC**: ee = 98%, Chiralpak® IA-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 15.11 min (minor) and *t<sub>R</sub>* = 18.05 min (major)

[α]<sub>D</sub><sup>20</sup> = +104.9 (*c* = 1.0, acetone) [lit.<sup>5</sup> [α]<sub>D</sub><sup>34</sup> = -104.7 (*c* = 1.5, acetone, 87% ee) for (*R*)-enantiomer]

**Procedure for 1.0 mmol scale reaction**: To a catalyst **3a** solution in 5.0 mL of DCM prepared as described above was added the 2-hydroxy-2,2-diphenylacetaldehyde **1c** (210 mg, 1.0 mmol, 1.0 equiv) at -40 °C. The resulting mixture was stirred at the same temperature for 3 h under argon atmosphere. The reaction mixture was quenched with 10 mL of distilled water and extracted with DCM (3 x 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography to afford corresponding products **2c** (180 mg, 86%) with 98% ee as white solid.

### (S)-2-hydroxy-1,2-di-*p*-tolylethan-1-one (2d)



According to the general procedure, the reaction of 2-hydroxy-2,2-di-*p*-tolylacetaldehyde **1d** (48 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired product (42 mg, 88%) as white solid. Analytical data are consistent with reported values.<sup>6</sup>

**R<sub>f</sub>**: 0.30 (1:5 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.89 (d, *J* = 6.1 Hz, 1H), 4.53 (d, *J* = 6.1 Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H)

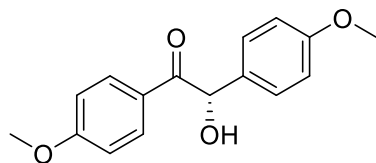
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 198.7, 145.0, 138.5, 136.5, 131.1, 129.9, 129.5, 129.4, 127.8, 75.9, 21.9, 21.3

**HPLC**: ee = 98%, Chiralpak® IA-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 18.10 min (minor) and *t<sub>R</sub>* = 21.93 min (major)

[α]<sub>D</sub><sup>20</sup> = +115.3 (*c* = 1.0, MeOH) [lit.<sup>6</sup> [α]<sub>D</sub><sup>20</sup> = -130.8 (*c* = 1.0, MeOH, 82% ee) for (*R*)-enantiomer]



**(S)-2-hydroxy-1,2-bis(4-methoxyphenyl)ethan-1-one (2e)**



According to the general procedure, the reaction of 2-hydroxy-2,2-bis(4-methoxyphenyl)acetaldehyde **1e** (54 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:10 ethyl acetate/*n*-hexane afforded the desired product (45 mg, 83%) as white solid. Analytical data are consistent with reported values.<sup>5</sup>

**R<sub>f</sub>**: 0.47 (1:1 ethyl acetate/*n*-hexane)

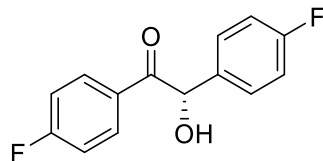
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H) 6.84 (d, *J* = 8.8 Hz, 2H), 5.85 (d, *J* = 5.8 Hz, 1H), 4.57 (d, *J* = 5.8 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 197.5, 164.1, 159.8, 132.0, 131.7, 129.2, 126.5, 114.6, 114.1, 75.4, 55.6, 55.4

**HPLC**: ee = 95%, Chiralpak® IA-3, 2-propanol:*n*-hexane=20:80, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 22.44 min (minor) and *t<sub>R</sub>* = 26.14 min (major)

[α]<sup>20</sup><sub>D</sub> = +83.1 (*c* = 0.5, MeOH) [lit.<sup>5</sup> [α]<sup>24</sup><sub>D</sub> = -85.2 (*c* = 1.0, MeOH, 93% ee) for (*R*)-enantiomer]

**(S)-1,2-bis(4-fluorophenyl)-2-hydroxyethan-1-one (2f)**



According to the general procedure, the reaction of 2,2-bis(4-fluorophenyl)-2-hydroxyacetaldehyde **1f** (50 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired product (42 mg, 85%) as white solid. Analytical data are consistent with reported values.<sup>7</sup>

**R<sub>f</sub>**: 0.17 (1:5 ethyl acetate/*n*-hexane)

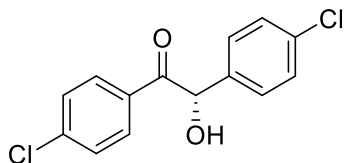
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 5.5 Hz, 1H), 7.92 (d, *J* = 5.5 Hz, 1H), 7.31 (d, *J* = 5.6 Hz, 1H), 7.29 (d, *J* = 5.6 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 5.89 (d, *J* = 3.8 Hz, 1H), 4.50 (d, *J* = 3.8 Hz, 1H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 197.3, 166.2 (C-F, <sup>1</sup>*J* C-F = 257.3 Hz), 162.9 (C-F, <sup>1</sup>*J* C-F = 248.4 Hz), 135.0 (C-F, <sup>4</sup>*J* C-F = 3.1 Hz), 132.0 (C-F, <sup>3</sup>*J* C-F = 9.5 Hz), 129.8 (C-F, <sup>4</sup>*J* C-F = 3.0 Hz), 129.7 (C-F, <sup>3</sup>*J* C-F = 8.4 Hz), 116.4 (C-F, <sup>2</sup>*J* C-F = 20.8 Hz), 116.2 (C-F, <sup>2</sup>*J* C-F = 21.3 Hz), 75.5

**HPLC**: ee = 95%, Chiralpak® IA-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 15.72 min (minor) and *t<sub>R</sub>* = 17.25 min (major)

[α]<sup>20</sup><sub>D</sub> = +152.0 (*c* = 0.5, CHCl<sub>3</sub>) [lit.<sup>7</sup> [α]<sup>25</sup><sub>D</sub> = -128.2 (*c* = 0.24, CHCl<sub>3</sub>, 99% ee) for (*R*)-enantiomer]

**(S)-1,2-bis(4-chlorophenyl)-2-hydroxyethan-1-one (2g)**



According to the general procedure, the reaction of 2,2-bis(4-chlorophenyl)-2-hydroxyacetaldehyde **1g** (56 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired product (45 mg, 80%) as colorless oil. Analytical data are consistent with reported values.<sup>5</sup>

**R<sub>f</sub>**: 0.23 (1:5 ethyl acetate/*n*-hexane)

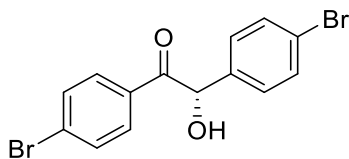
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 5.88 (d, *J* = 5.7 Hz, 1H), 4.48 (d, *J* = 5.7 Hz, 1H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 197.6, 140.9, 137.3, 134.9, 131.7, 130.6, 129.6, 129.3, 129.2, 75.6

**HPLC**: ee = 96%, Chiralpak® IA-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 17.37 min (minor) and *t<sub>R</sub>* = 19.35 min (major)

[α]<sub>D</sub><sup>20</sup> = +14.7 (*c* = 1.0, MeOH) [lit.<sup>5</sup> [α]<sub>D</sub><sup>20</sup> = -28.4 (*c* = 0.1, MeOH, 97% ee) for (*R*)-enantiomer]

**(S)-1,2-bis(4-bromophenyl)-2-hydroxyethan-1-one (2h)**



According to the general procedure, the reaction of 2,2-bis(4-bromophenyl)-2-hydroxyacetaldehyde **1h** (74 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired product (52 mg, 70%) as colorless oil. Analytical data are consistent with reported values.<sup>8</sup>

**R<sub>f</sub>**: 0.23 (1:5 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.86 (d, *J* = 5.9 Hz, 1H), 4.46 (d, *J* = 5.9 Hz, 1H)

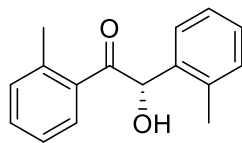
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 197.8, 137.8, 132.6, 132.4, 132.1, 130.6, 129.7, 129.5, 123.1, 75.7

**HRMS** (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd. for C<sub>14</sub>H<sub>10</sub>Br<sub>2</sub>O<sub>2</sub>Na 390.8940; Found 390.8942

**HPLC**: ee = 95%, Chiralpak® IA-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 19.71 min (minor) and *t<sub>R</sub>* = 21.43 min (major)

[α]<sub>D</sub><sup>20</sup> = +9.9 (*c* = 1.0, MeOH) [lit.<sup>8</sup> [α]<sub>D</sub><sup>25</sup> = +9.1 (*c* = 1.0, MeOH, 88% ee) for (*S*)-enantiomer]

**(S)-2-hydroxy-1,2-di-*o*-tolylethan-1-one (2i)**



According to the general procedure, the reaction of 2-hydroxy-2,2-di-*o*-tolylacetaldehyde **1i** (48 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired product (45 mg, 93%) as colorless oil. Analytical data are consistent with reported values.<sup>8</sup>

**R<sub>f</sub>**: 0.37 (1:5 ethyl acetate/*n*-hexane)

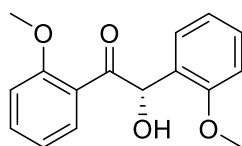
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.38 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.31 (td, *J* = 7.5, 1.4 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.16 – 7.08 (m, 5H), 6.02 (d, *J* = 5.3 Hz, 1H), 4.48 (d, *J* = 5.3 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 3H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 203.2, 138.9, 136.5, 136.5, 134.9, 132.0, 132.0, 131.3, 128.6, 128.4, 127.9, 126.6, 125.6, 75.0, 20.8, 19.5

**HPLC**: ee = 98%, Chiralpak® IA-3, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 15.11 min (major) and *t<sub>R</sub>* = 16.18 min (minor)

[α]<sup>20</sup><sub>D</sub> = +176.5 (*c* = 1.0, MeOH) [lit.<sup>8</sup> [α]<sup>25</sup><sub>D</sub> = +47.5 (*c* = 0.5, MeOH, 41% ee) for (*S*)-enantiomer]

**(S)-2-hydroxy-1,2-bis(2-methoxyphenyl)ethan-1-one (2j)**



According to the general procedure, the reaction of 2-hydroxy-2,2-bis(2-methoxyphenyl)acetaldehyde **1j** (54 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired product (48 mg, 88%) as colorless oil. Analytical data are consistent with reported values.<sup>5</sup>

**R<sub>f</sub>**: 0.47 (1:1 ethyl acetate/*n*-hexane)

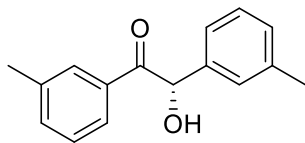
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.22 – 7.12 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.10 (d, *J* = 5.5 Hz, 1H), 4.46 (d, *J* = 5.5 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 201.8, 158.3, 157.4, 134.0, 130.8, 130.1, 129.7, 127.7, 125.4, 120.6, 120.6, 111.3, 111.0, 76.0, 55.4, 55.3

**HPLC**: ee = 90%, Chiralpak® IA-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 21.81 min (minor) and *t<sub>R</sub>* = 26.83 min (major)

[α]<sup>20</sup><sub>D</sub> = +76.0 (*c* = 1.0, CHCl<sub>3</sub>) [lit.<sup>5</sup> [α]<sup>24</sup><sub>D</sub> = -107.2 (*c* = 1.0, CHCl<sub>3</sub>, 86% ee) for (*R*)-enantiomer]

**(S)-2-hydroxy-1,2-di-*m*-tolylethan-1-one (2k)**



According to the general procedure, the reaction of 2-hydroxy-2,2-di-*m*-tolylacetaldehyde **1k** (48 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired product (41 mg, 86%) as colorless oil. Analytical data are consistent with reported values.<sup>9</sup>

**R<sub>f</sub>**: 0.33 (1:5 ethyl acetate/*n*-hexane)

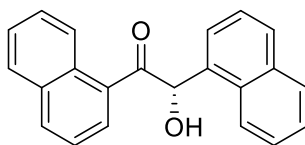
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.76 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 1H), 7.12 (s, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 5.90 (d, *J* = 6.2 Hz, 1H), 4.52 (d, *J* = 6.2 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 3H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 199.3, 139.1, 139.0, 138.7, 134.8, 133.6, 129.7, 129.4, 129.1, 128.6, 128.4, 126.6, 125.1, 76.3, 21.5, 21.4

**HPLC**: ee = 98%, Chiralpak® IA-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 10.60 min (minor) and *t<sub>R</sub>* = 14.18 min (major)

**[α]<sup>20</sup><sub>D</sub>** = +137.9 (*c* = 1.0, MeOH) [lit.<sup>9</sup> **[α]<sup>25</sup><sub>D</sub>** = -127.8 (*c* = 1.0, MeOH, 95% ee) for (*R*)-enantiomer]

**(S)-2-hydroxy-1,2-di(naphthalen-1-yl)ethan-1-one (2l)**



According to the general procedure, the reaction of 2-hydroxy-2,2-di(naphthalen-1-yl)acetaldehyde **1l** (62 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography (0 °C)<sup>10</sup> purification with 1:10 ethyl acetate/*n*-hexane afforded the desired product (59 mg, 95%) as colorless form. Analytical data are consistent with reported values.<sup>11</sup>

**R<sub>f</sub>**: 0.20 (1:5 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.71 (d, *J* = 8.7 Hz, 1H), 8.31 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.78 (dd, *J* = 8.1, 3.1 Hz, 2H), 7.75 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.60 (ddd, *J* = 8.6, 6.9, 1.4 Hz, 1H), 7.55 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.46 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.37 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.33 – 7.21 (m, 2H), 6.71 (d, *J* = 5.0 Hz, 1H), 4.72 (d, *J* = 5.0 Hz, 1H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 203.1, 135.0, 134.4, 134.0, 133.9, 131.8, 131.5, 130.7, 129.5, 129.0, 129.0, 128.7, 128.6, 127.1, 127.0, 126.8, 126.1, 125.6, 125.5, 124.2, 123.6, 75.4

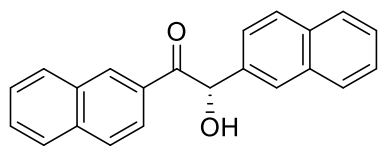
**IR** *ν*<sub>max</sub> 1677, 1595, 1574, 1510, 1055, 940, 772, 754, 668, 568, 529 cm<sup>-1</sup>

**HRMS** (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd. for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>Na 335.1043; Found 335.1044

**HPLC**: ee = 94%, Chiralpak® IA-3, 2-propanol:*n*-hexane=30:70, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 11.68 min (minor) and *t<sub>R</sub>* = 14.35 min (major)

**[α]<sup>20</sup><sub>D</sub>** = +392.2 (*c* = 1.0, CHCl<sub>3</sub>) [lit.<sup>11</sup> **[α]<sup>26</sup><sub>D</sub>** = +75.4 (*c* = 0.50, CHCl<sub>3</sub>, 83% ee) for (*S*)-enantiomer]

**(S)-2-hydroxy-1,2-di(naphthalen-2-yl)ethan-1-one (2m)**



According to the general procedure, the reaction of 2-hydroxy-2,2-di(naphthalen-2-yl)acetaldehyde **1m** (62 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:10 ethyl acetate/*n*-hexane afforded the desired product (53 mg, 85%) as colorless solid. Analytical data are consistent with reported values.<sup>7</sup>

**R<sub>f</sub>**: 0.30 (1:3 ethyl acetate/*n*-hexane)

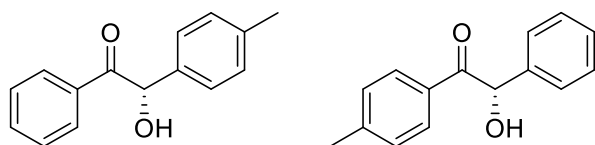
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.50 (s, 1H), 7.99 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.91 (s, 1H), 7.85 (s, 1H), 7.84 – 7.71 (m, 5H), 7.55 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.49 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.47 – 7.41 (m, 3H), 6.27 (d, *J* = 5.9 Hz, 1H), 4.72 (d, *J* = 6.0 Hz, 1H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 198.9, 136.6, 135.8, 133.5, 133.2, 133.2, 131.4, 130.9, 129.7, 129.2, 129.1, 128.7, 128.1, 127.8, 127.7, 127.5, 127.0, 126.5, 126.4, 124.9, 124.3, 76.5

**HPLC**: ee = 92%, Chiralpak® IA-3, 2-propanol:*n*-hexane=30:70, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 14.74 min (minor) and *t<sub>R</sub>* = 22.89 min (major)

[α]<sub>D</sub><sup>20</sup> = -54.0 (*c* = 0.25, MeOH) [lit.<sup>7</sup> [α]<sub>D</sub><sup>25</sup> = +52.4 (*c* = 0.37, MeOH, 93% ee) for (*R*)-enantiomer]

**(S)-2-hydroxy-1-phenyl-2-(p-tolyl)ethan-1-one (2n) and (S)-2-hydroxy-2-phenyl-1-(p-tolyl)ethan-1-one (2n')**



According to the general procedure, the reaction of 2-hydroxy-2-phenyl-2-(*p*-tolyl)acetaldehyde **1n** (45 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired products (18 mg, 40%) as white solid. **2n** and **2n'** did not be separated. Analytical data are consistent with reported values.<sup>12</sup>

**R<sub>f</sub>**: 0.50 (1:2 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR of 2n** (500 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.92 (d, *J* = 6.1 Hz, 1H), 4.62 (d, *J* = 6.1 Hz, 1H), 2.28 (s, 3H)

**<sup>1</sup>H NMR of 2n'** (500 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.24 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.92 (d, *J* = 6.1 Hz, 1H), 4.53 (d, *J* = 6.1 Hz, 1H), 2.34 (s, 3H)

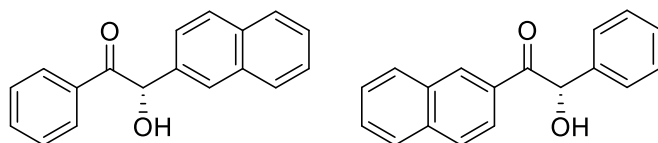
**<sup>13</sup>C NMR of 2n** (125 MHz, CDCl<sub>3</sub>) δ 199.1, 138.6, 136.2, 134.0, 133.6, 129.9, 129.5, 128.8, 127.8, 76.1, 21.3

**<sup>13</sup>C NMR of 2n'** (125 MHz, CDCl<sub>3</sub>) δ 198.5, 145.1, 139.4, 131.0, 129.4, 129.3, 129.2, 128.6, 127.9, 76.1, 21.8

**HPLC**: ee (**2n**) = 96%, Chiralcel® OX-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 17.78 min (minor) and *t<sub>R</sub>* = 20.60 min (major)

**HPLC**: ee (**2n'**) = 98%, Chiralcel® OX-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 15.79 min (minor) and *t<sub>R</sub>* = 19.34 min (major)

**(S)-2-hydroxy-2-(naphthalen-2-yl)-1-phenylethan-1-one (2o) and (S)-2-hydroxy-1-(naphthalen-2-yl)-2-phenylethan-1-one (2o')**



According to the general procedure, the reaction of 2-hydroxy-2-(naphthalen-1-yl)-2-phenylacetaldehyde **1o** (52 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired products (36 mg, 69%) as white solid. **2o** and **2o'** did not be separated. Analytical data are consistent with reported values.<sup>13</sup>

**R<sub>f</sub>**: 0.47 (1:2 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR of 2o** (500 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.76 (m, 5H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 3H), 6.10 (d, *J* = 8.6 Hz, 1H), 4.68 (d, *J* = 8.9 Hz, 1H)

**<sup>1</sup>H NMR of 2o'** (500 MHz, CDCl<sub>3</sub>) δ 8.43 (s, 1H), 7.94 (d, *J* = 7.9 Hz, 4H), 7.44 (dd, *J* = 9.1, 5.4 Hz, 2H), 7.38 (dt, *J* = 6.5, 3.2 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.10 (d, *J* = 8.6 Hz, 1H), 4.68 (d, *J* = 8.9 Hz, 1H)

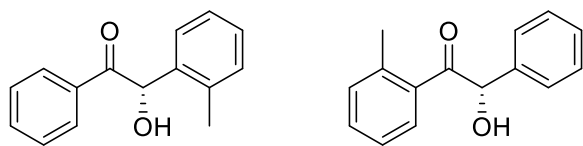
**<sup>13</sup>C NMR of 2o** (125 MHz, CDCl<sub>3</sub>) δ 199.0, 136.5, 134.0, 133.6, 133.5, 133.3, 129.2, 129.2, 128.8, 128.2, 127.8, 127.6, 126.6, 126.5, 124.9, 76.4

**<sup>13</sup>C NMR of 2o'** (125 MHz, CDCl<sub>3</sub>) δ 199.0, 139.3, 135.9, 132.3, 131.4, 130.9, 129.8, 129.2, 129.1, 128.7, 128.7, 127.9, 127.8, 127.1, 124.3, 76.4

**HPLC**: ee (**2o**) = 95%, Chiralpak® ID, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 30.82 min (minor) and *t<sub>R</sub>* = 43.87 min (major)

**HPLC**: ee (**2o'**) = 97%, Chiralpak® ID, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 34.77 min (minor) and *t<sub>R</sub>* = 37.60 min (major)

**(S)-2-hydroxy-1-phenyl-2-(*o*-tolyl)ethan-1-one (2p) and (S)-2-hydroxy-2-phenyl-1-(*o*-tolyl)ethan-1-one (2p')**



According to the general procedure, the reaction of 2-hydroxy-2-phenyl-2-(*o*-tolyl)acetaldehyde **1p** (45 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired products (18 mg, 40%) as white solid. **2p** and **2p'** did not be separated. Analytical data are consistent with reported values.<sup>14</sup>

**R<sub>f</sub>**: 0.33 (1:5 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR of 2p** (500 MHz, CDCl<sub>3</sub>) δ 7.54 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H), 7.28 – 7.19 (m, 6H), 7.16 (d, *J* = 7.7 Hz, 1H), 5.88 (d, *J* = 5.8 Hz, 1H), 4.59 (d, *J* = 5.8 Hz, 1H), 2.26 (s, 3H)

**<sup>1</sup>H NMR of 2p'** (500 MHz, CDCl<sub>3</sub>) δ 7.83 – 7.77 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 3H), 7.19 (s, 1H), 7.10 (td, *J* = 7.3, 1.8 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.04 (d, *J* = 5.3 Hz, 1H), 4.40 (d, *J* = 5.3 Hz, 1H), 2.53 (s, 3H)

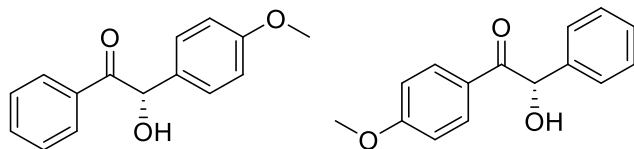
**<sup>13</sup>C NMR of 2p** (125 MHz, CDCl<sub>3</sub>) δ 202.5, 139.0, 138.1, 134.8, 132.0, 131.9, 128.9, 128.5, 128.4, 127.4, 125.6, 77.6, 20.7

**<sup>13</sup>C NMR of 2p'** (125 MHz, CDCl<sub>3</sub>) δ 200.1, 137.5, 136.7, 133.9, 133.8, 131.6, 129.0, 128.9, 128.8, 128.5, 126.8, 74.5, 19.4

**HPLC**: ee (**2p**) = 96%, Chiralpak<sup>®</sup> IC, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 8.65 min (minor) and *t<sub>R</sub>* = 9.99 min (major)

**HPLC**: ee (**2p'**) = 93%, Chiralpak<sup>®</sup> IC, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 11.07 min (minor) and *t<sub>R</sub>* = 11.89 min (major)

**(S)-2-hydroxy-2-(4-methoxyphenyl)-1-phenylethan-1-one (2q) and (S)-2-hydroxy-1-(4-methoxyphenyl)-2-phenylethan-1-one (2q')**



According to the general procedure, the reaction of 2-hydroxy-2-(2-methoxyphenyl)-2-phenylacetaldehyde **1q** (48 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3a** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired products (28 mg, 58%) as white solid. **2q** and **2q'** did not be separated. Analytical data are consistent with reported values.<sup>5,12b</sup>

**R<sub>f</sub>**: 0.23 (1:3 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR of 2q** (500 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 6.7 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.91 (d, *J* = 5.5 Hz, 1H), 4.49 (d, *J* = 6.0 Hz, 1H), 3.74 (s, 3H)

**<sup>1</sup>H NMR of 2q'** (500 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.8, 2H), 7.35-7.26 (m, 5H), 6.91 (d, *J* = 8.8, 2H), 5.89 (d, *J* = 6.1 Hz, 1H), 4.65 (d, *J* = 6.1 Hz, 1H), 3.80 (s, 3H)

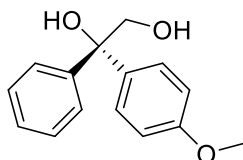
**<sup>13</sup>C NMR of 2q** (125 MHz, CDCl<sub>3</sub>) δ 199.2, 159.8, 133.9, 133.7, 131.4, 129.2, 129.2, 128.8, 114.7, 75.8, 55.3

**<sup>13</sup>C NMR of 2q'** (125 MHz, CDCl<sub>3</sub>) δ 198.1, 164.1, 139.6, 131.7, 128.9, 128.9, 127.8, 127.5, 114.1, 75.9, 55.4

**HPLC**: ee (**2q**) = 92%, Chiralcel® OX-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 28.63 min (minor) and *t<sub>R</sub>* = 34.42 min (major)

**HPLC**: ee (**2q'**) = 99%, Chiralcel® OX-3, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 30.41 min (minor) and *t<sub>R</sub>* = 39.88 min (major)

**(S)-1-(4-methoxyphenyl)-1-phenylethane-1,2-diol (1q')**



The compound was synthesized from recovered **1q** (17 mg, 0.070 mmol) according to the known procedure.<sup>3</sup> Column chromatography purification with 1:3 ethyl acetate/*n*-hexane afforded the desired product (15 mg, 87%) as white solid.

**R<sub>f</sub>**: 0.40 (1:1 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.38 (m, 2H), 7.34 – 7.29 (m, 4H), 7.26 – 7.23 (m, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.07 (s, 2H), 3.77 (s, 3H), 3.23 (bs, 1H), 2.11 (bs, 1H)

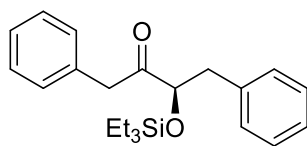
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 158.9, 144.2, 136.1, 128.5, 127.9, 127.5, 126.5, 113.9, 78.4, 69.6, 55.4

**HPLC**: ee = 99%, Chiralpak® ID, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 15.99 min (minor) and *t<sub>R</sub>* = 16.77 min (major)

**[α]<sub>D</sub><sup>20</sup>** = -23.6 (*c* = 1.0, CHCl<sub>3</sub>)



**(R)-1,4-diphenyl-3-((triethylsilyl)oxy)butan-2-one (5b)**



According to the general procedure, the reaction of 2-benzyl-3-phenyl-2-((triethylsilyl)oxy)propanal **4b** (71 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3b** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:20 diethyl ether/*n*-hexane afforded the desired product (65 mg, 92%) as white solid. Analytical data are consistent with reported values.<sup>3</sup>

**R<sub>f</sub>**: 0.27 (1:20 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.22 (m, 6H), 7.18 (d, *J* = 6.7 Hz, 2H), 7.07 (d, *J* = 7.1 Hz, 2H), 4.37 (dd, *J* = 7.5, 4.4 Hz, 1H), 3.78 (d, *J* = 16.9 Hz, 1H), 3.66 (d, *J* = 16.9 Hz, 1H), 2.94 (dd, *J* = 13.5, 4.4 Hz, 1H), 2.84 (dd, *J* = 13.5, 7.5 Hz, 1H), 0.87 (t, *J* = 8.0 Hz, 9H), 0.47 (m, 6H)

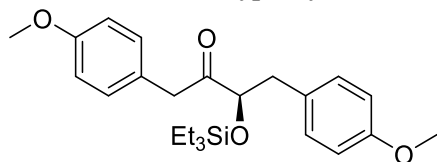
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 210.6, 137.0, 134.0, 130.1, 129.9, 128.6, 128.4, 126.9, 126.9, 79.7, 45.0, 41.8, 6.9, 4.7

**HPLC**: ee = 86%, Chiralpak® ID, 2-propanol:*n*-hexane=1:99, flow: 1.0mL/min, 220nm, *t<sub>R</sub>* = 5.57 min (minor) and *t<sub>R</sub>* = 5.95 min (major)

[α]<sub>D</sub><sup>20</sup> = +63.7 (*c* = 1.0, CHCl<sub>3</sub>) [lit.<sup>3</sup> [α]<sub>D</sub><sup>21</sup> = -58.7 (*c* = 1.1, CHCl<sub>3</sub>, 86% ee) for (*S*)-enantiomer]

**Procedure for 1.0 mmol scale reaction**: To a catalyst **3b** solution in 5.0 mL of toluene was added the aldehyde **4b** (350 mg, 1.0 mmol, 1.0 equiv) at -20 °C. The resulting mixture was stirred at -20 °C for 12 h under argon atmosphere. The reaction mixture was quenched with 10 mL of distilled water and extracted with DCM (3 x 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography to afford products **5b** (320 mg, 90%) with 86% ee as white solid.

**(R)-1,4-bis(4-methoxyphenyl)-3-((triethylsilyl)oxy)butan-2-one (5c)**



According to the general procedure, the reaction of 2-(4-methoxybenzyl)-3-(4-methoxyphenyl)-2-((triethylsilyl)oxy)propanal **4c** (83 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3b** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:10 diethyl ether/*n*-hexane afforded the desired product (70 mg, 84%) as colorless oil. Analytical data are consistent with reported values.<sup>3</sup>

**R<sub>f</sub>**: 0.47 (1:5 ethyl acetate/*n*-hexane)

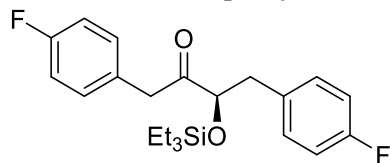
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 7.5 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 2H), 4.32 (dd, *J* = 7.1, 4.6 Hz, 1H), 3.78 (s, 3H), 3.78 (s, 3H), 3.69 (d, *J* = 17.0 Hz, 1H), 3.59 (d, *J* = 17.0 Hz, 1H), 2.87 (dd, *J* = 13.7, 4.6 Hz, 1H), 2.79 (dd, *J* = 13.7, 7.1 Hz, 1H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.49 (qd, *J* = 8.0, 4.7 Hz, 6H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 211.1, 158.6, 158.6, 131.0, 130.9, 129.0, 126.0, 114.0, 113.8, 79.7, 55.4, 55.4, 44.2, 40.9, 6.9, 4.8

**HPLC**: ee = 76%, Chiralpak® ID, 2-propanol:*n*-hexane=1:99, flow: 1.0mL/min, 220nm, *t<sub>R</sub>* = 18.32 min (minor) and *t<sub>R</sub>* = 21.24 min (major)

[α]<sub>D</sub><sup>20</sup> = +43.6 (*c* = 1.0, CHCl<sub>3</sub>) [lit.<sup>3</sup> [α]<sub>D</sub><sup>29</sup> = -197.9 (*c* = 1.5, CHCl<sub>3</sub>, 85% ee) for (*S*)-enantiomer]

**(R)-1,4-bis(4-fluorophenyl)-3-((triethylsilyl)oxy)butan-2-one (5d)**



According to the general procedure, the reaction of 2-(4-fluorobenzyl)-3-(4-fluorophenyl)-2-((triethylsilyl)oxy)propanal **4d** (78 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3b** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:30 diethyl ether/*n*-hexane afforded the desired product (70 mg, 90%) as colorless oil. Analytical data are consistent with reported values.<sup>3</sup>

**R<sub>f</sub>**: 0.63 (1:5 ethyl acetate/*n*-hexane)

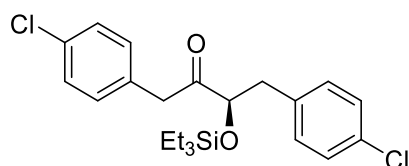
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.13 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 7.02 – 6.92 (m, 6H), 4.34 (dd, *J* = 7.0, 4.5 Hz, 1H), 3.73 (d, *J* = 17.2 Hz, 1H), 3.62 (d, *J* = 17.2 Hz, 1H), 2.90 (dd, *J* = 13.7, 4.5 Hz, 1H), 2.83 (dd, *J* = 13.7, 7.0 Hz, 1H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.50 (m, 6H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 210.5, 162.1 (C-F, <sup>1</sup>*J* C-F = 244.8 Hz), 162.0 (C-F, <sup>1</sup>*J* C-F = 245.0 Hz), 133.0 (C-F, <sup>4</sup>*J* C-F = 3.3 Hz), 132.0 (C-F, <sup>3</sup>*J* C-F = 7.8 Hz), 131.4 (C-F, <sup>3</sup>*J* C-F = 8.0 Hz), 130.0 (C-F, <sup>4</sup>*J* C-F = 3.2 Hz), 115.4 (C-F, <sup>2</sup>*J* C-F = 21.4 Hz), 115.2 (C-F, <sup>2</sup>*J* C-F = 21.3 Hz), 79.6, 44.0, 40.9, 6.9, 4.7

**HPLC**: ee = 86%, Chiralpak® IA, 2-propanol:*n*-hexane=1:99, flow: 1.0mL/min, 220nm, *t<sub>R</sub>* = 5.32 min (minor) and *t<sub>R</sub>* = 6.15 min (major)

[α]<sub>D</sub><sup>20</sup> = +43.5 (*c* = 1.0, CHCl<sub>3</sub>) [lit.<sup>3</sup> [α]<sub>D</sub><sup>29</sup> = -66.4 (*c* = 1.1, CHCl<sub>3</sub>, 90% ee) for (*S*)-enantiomer]

**(R)-1,4-bis(4-chlorophenyl)-3-((triethylsilyl)oxy)butan-2-one (5e)**



According to the general procedure, the reaction of 2-(4-chlorobenzyl)-3-(4-chlorophenyl)-2-((triethylsilyl)oxy)propanal **4e** (85 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3b** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:30 diethyl ether/*n*-hexane afforded the desired product (68 mg, 80%) as colorless oil. Analytical data are consistent with reported values.<sup>3</sup>

**R<sub>f</sub>**: 0.47 (1:10 ethyl acetate/*n*-hexane)

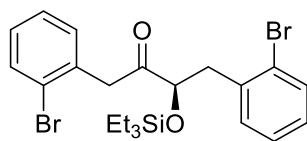
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.26 (d, *J* = 6.1 Hz, 2H), 7.24 (d, *J* = 6.1 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.34 (dd, *J* = 6.8, 4.7 Hz, 1H), 3.72 (d, *J* = 17.1 Hz, 1H), 3.62 (d, *J* = 17.1 Hz, 1H), 2.89 (dd, *J* = 13.6, 4.7 Hz, 1H), 2.84 (dd, *J* = 13.6, 6.8 Hz, 1H), 0.90 (t, *J* = 8.0 Hz, 9H), 0.52 (qd, *J* = 8.0, 4.3 Hz, 6H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 210.2, 135.2, 133.0, 132.9, 132.2, 131.4, 131.2, 128.7, 128.5, 79.4, 44.2, 41.0, 6.9, 4.8

**HPLC**: ee = 82%, Chiralpak® IA, 2-propanol:*n*-hexane=1:99, flow: 1.0mL/min, 220nm, *t<sub>R</sub>* = 5.71 min (minor) and *t<sub>R</sub>* = 6.27 min (major)

[α]<sub>D</sub><sup>20</sup> = +62.3 (*c* = 1.0, CHCl<sub>3</sub>) [lit.<sup>3</sup> [α]<sub>D</sub><sup>26</sup> = -67.9 (*c* = 1.0, CHCl<sub>3</sub>, 86% ee) for (*S*)-enantiomer]

**(R)-1,4-bis(2-bromophenyl)-3-((triethylsilyl)oxy)butan-2-one (5f)**



According to the general procedure, the reaction of 2-(2-bromobenzyl)-3-(2-bromophenyl)-2-((triethylsilyl)oxy)propanal **4f** (100 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3b** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:30 diethyl ether/*n*-hexane afforded the desired product (90 mg, 88%) as white solid.

**R<sub>f</sub>**: 0.43 (1:10 ethyl acetate/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.56 (t, *J* = 7.9 Hz, 2H), 7.26 (ddd, *J* = 8.6, 5.5, 1.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.06 (m, 3H), 4.58 (dd, *J* = 9.3, 4.1 Hz, 1H), 4.18 (d, *J* = 17.9 Hz, 1H), 4.05 (d, *J* = 17.9 Hz, 1H), 3.28 (dd, *J* = 13.5, 4.1 Hz, 1H), 2.99 (dd, *J* = 13.5, 9.3 Hz, 1H), 0.84 (t, *J* = 8.0 Hz, 9H), 0.42 (m, 6H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 207.7, 136.7, 134.4, 133.0, 132.9, 132.9, 132.0, 128.8, 128.6, 127.6, 127.3, 125.3, 125.0, 77.9, 45.3, 41.6, 6.8, 4.6

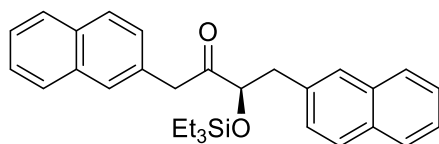
**IR**  $\nu_{\text{max}}$  2956, 2877, 1726, 1471, 1441, 1219, 1141, 1096, 975, 772, 747, 671 cm<sup>-1</sup>

**HRMS** (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd. for C<sub>22</sub>H<sub>28</sub>Br<sub>2</sub>O<sub>2</sub>SiNa 533.0118; Found 533.0120

**HPLC**: ee = 89%, Chiralpak® IA, 2-propanol:*n*-hexane=1:99, flow: 1.0mL/min, 220nm, *t<sub>R</sub>* = 6.27 min (minor) and *t<sub>R</sub>* = 7.00 min (major)

[ $\alpha$ ]<sub>D</sub><sup>20</sup> = +38.9 (*c* = 1.5, CHCl<sub>3</sub>)

**(R)-1,4-di(naphthalen-2-yl)-3-((triethylsilyl)oxy)butan-2-one (5g)**



According to the general procedure, the reaction of 3-(naphthalen-2-yl)-2-(naphthalen-2-ylmethyl)-2-((triethylsilyl)oxy)propanal **4b** (91 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3b** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:30 diethyl ether/*n*-hexane afforded the desired product (79 mg, 87%) as white solid. Analytical data are consistent with reported values.<sup>3</sup>

**R<sub>f</sub>**: 0.60 (1:5 ethyl acetate/*n*-hexane)

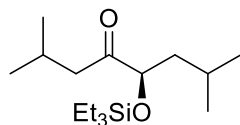
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.85 – 7.79 (m, 1H), 7.76 (dd, *J* = 8.7, 4.0 Hz, 2H), 7.71 (dd, *J* = 9.0, 5.2 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.57 (s, 1H), 7.45 (t, *J* = 4.3 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 4.52 (dd, *J* = 6.7, 4.7 Hz, 1H), 3.86 (d, *J* = 16.9 Hz, 1H), 3.79 (d, *J* = 16.9 Hz, 1H), 3.11 (dd, *J* = 13.5, 4.7 Hz, 1H), 3.07 (dd, *J* = 13.5, 6.7 Hz, 1H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.51 (m, 6H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 210.8, 134.3, 133.5, 133.5, 132.5, 132.5, 131.5, 128.7, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.7, 126.1, 126.0, 125.7, 125.7, 79.6, 45.3, 42.0, 6.9, 4.8

**HPLC**: ee = 86%, Chiralpak® IA, 2-propanol:*n*-hexane=1:99, flow: 1.0mL/min, 220nm, *t<sub>R</sub>* = 9.74 min (minor) and *t<sub>R</sub>* = 11.04 min (major)

[ $\alpha$ ]<sub>D</sub><sup>20</sup> = +73.7 (*c* = 1.0, CHCl<sub>3</sub>) [lit.<sup>3</sup> [ $\alpha$ ]<sub>D</sub><sup>23</sup> = -81.0 (*c* = 1.1, CHCl<sub>3</sub>, 85% ee) for (*S*)-enantiomer]

**(R)-2,7-dimethyl-5-((triethylsilyl)oxy)octan-4-one (5h)**



According to the general procedure, the reaction of 2-isobutyl-4-methyl-2-((triethylsilyl)oxy)pentanal **4b** (57 mg, 0.20 mmol, 1.0 equiv) solution and catalyst **3b** solution (0.040 M, 1.0 mL, 0.20 equiv) was performed. Column chromatography purification with 1:100 diethyl ether/*n*-hexane afforded the desired product (50 mg, 87%) as colorless oil. Analytical data are consistent with reported values.<sup>3</sup>

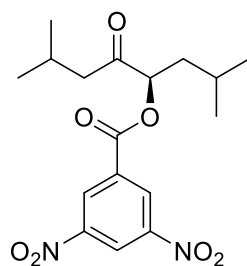
**R<sub>f</sub>**: 0.33 (1:30 diethyl ether/*n*-hexane)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 4.05 (dd, *J* = 8.3, 5.2 Hz, 1H), 2.41 (d, *J* = 6.9 Hz, 2H), 2.16 (h, *J* = 6.7 Hz, 1H), 1.76 – 1.64 (m, 1H), 1.47 (ddd, *J* = 13.9, 8.4, 5.8 Hz, 1H), 1.36 (ddd, *J* = 13.5, 8.0, 5.2 Hz, 1H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.91 (dd, *J* = 12.4, 6.8 Hz, 12H), 0.61 (q, *J* = 7.9 Hz, 6H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 213.3, 77.6, 45.9, 44.0, 24.2, 23.7, 23.4, 22.9, 22.7, 22.3, 6.9, 5.0

**[α]<sup>20</sup><sub>D</sub>** = +13.7 (*c* = 1.0, CHCl<sub>3</sub>) [lit.<sup>3</sup> **[α]<sup>71</sup><sub>D</sub>** = -13.3 (*c* = 1.0, CHCl<sub>3</sub>, 74% ee) for (*S*)-enantiomer]

**(S)-2,7-dimethyl-5-oxooctan-4-yl 3,5-dinitrobenzoate (5h')**



The compound was synthesized from **5h** (50 mg, 0.17 mmol) according to the known procedure.<sup>3</sup> Column chromatography purification with 1:20 ethyl acetate/*n*-hexane afforded the desired product (59 mg, 90%) as colorless oil. Analytical data are consistent with reported values.<sup>3</sup>

**R<sub>f</sub>**: 0.53 (1:5 ethyl acetate/*n*-hexane)

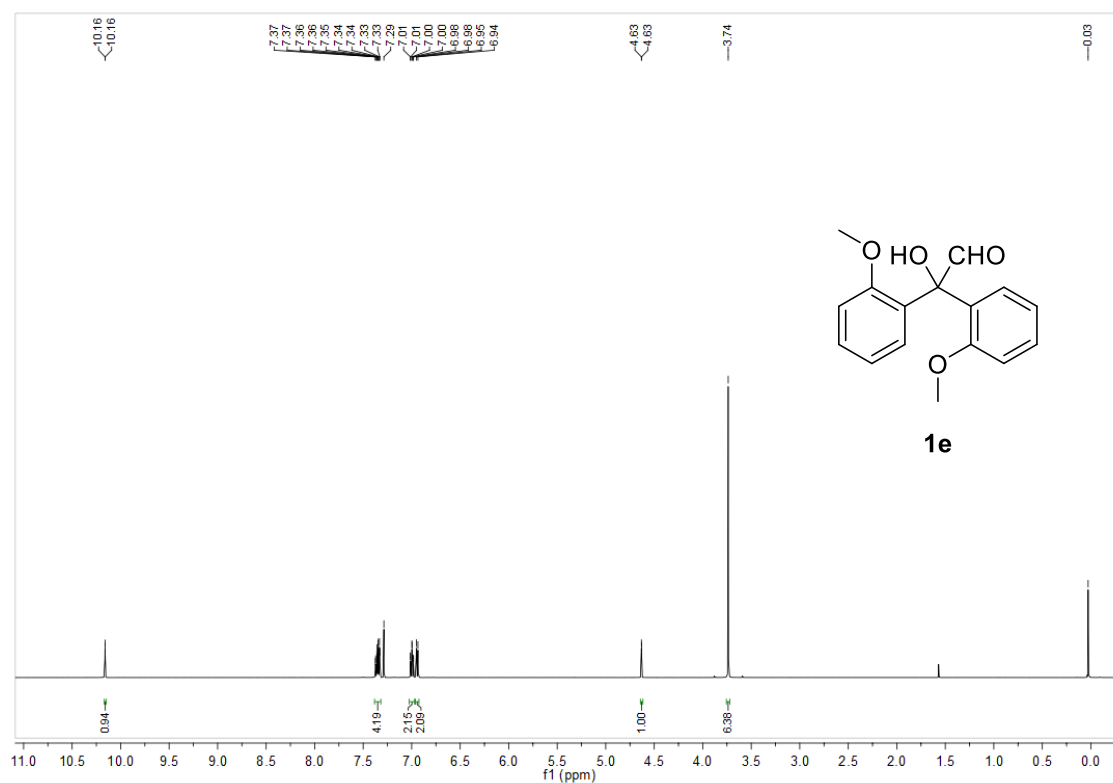
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.26 (t, *J* = 2.2 Hz, 1H), 9.18 (d, *J* = 2.1 Hz, 2H), 5.46 – 5.17 (dd, *J* = 10.2, 3.0 Hz, 1H), 2.47 (dd, *J* = 16.6, 6.6 Hz, 1H), 2.35 (dd, *J* = 16.6, 7.0 Hz, 1H), 2.23 (dp, *J* = 13.4, 6.6 Hz, 1H), 1.96 – 1.81 (m, 2H), 1.75 – 1.65 (m, 1H), 1.04 (dd, *J* = 13.9, 6.6 Hz, 6H), 0.97 (dd, *J* = 12.2, 6.6 Hz, 6H)

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 205.1, 162.4, 148.9, 133.5, 129.7, 122.8, 79.7, 47.7, 38.7, 25.3, 24.5, 23.4, 22.7, 22.7, 21.5

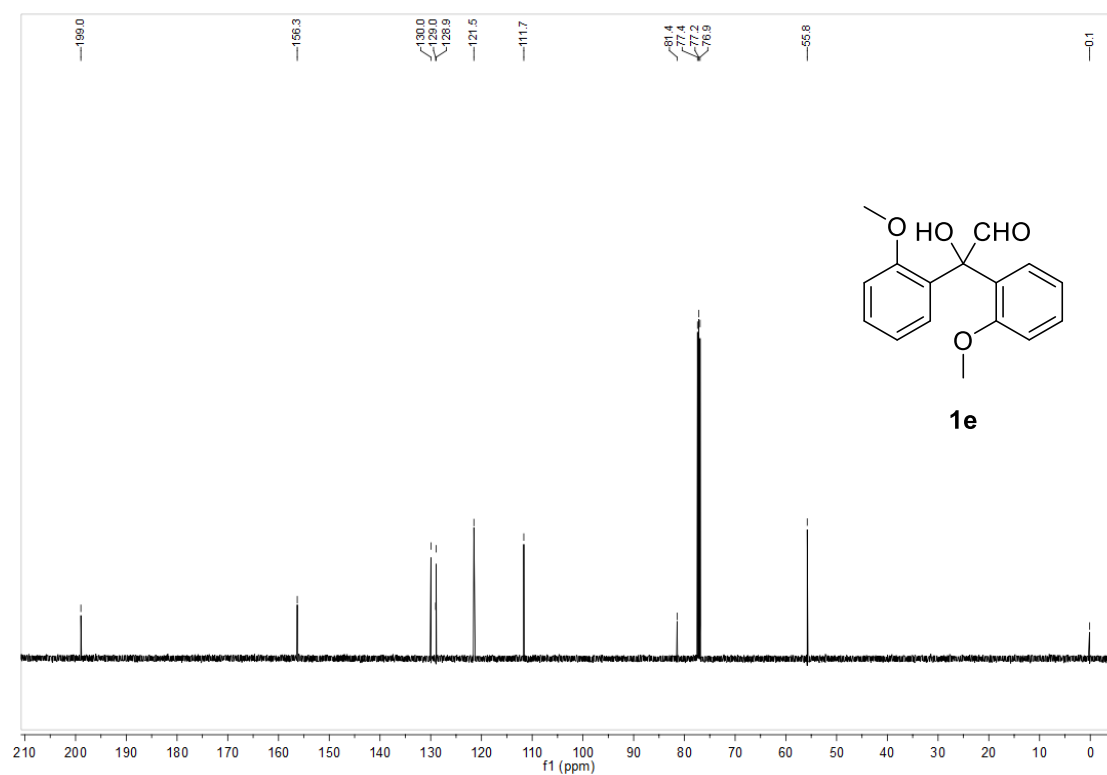
**HPLC**: ee = 78%, Chiralpak AD-H, 2-propanol:*n*-hexane=10:90, flow: 1.0mL/min, 254nm, *t<sub>R</sub>* = 5.84 min (major) and *t<sub>R</sub>* = 7.74 min (minor)

**[α]<sup>20</sup><sub>D</sub>** = -7.2 (*c* = 1.0, MeOH)

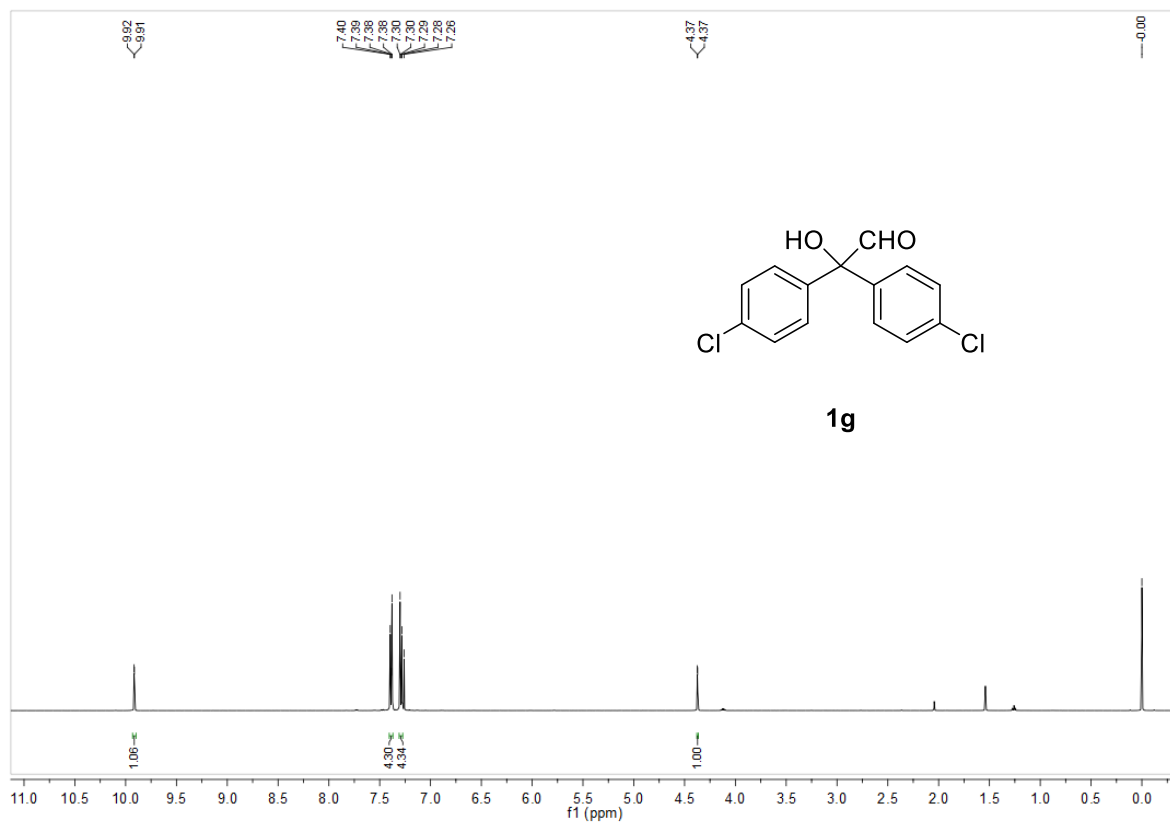
## 9. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra



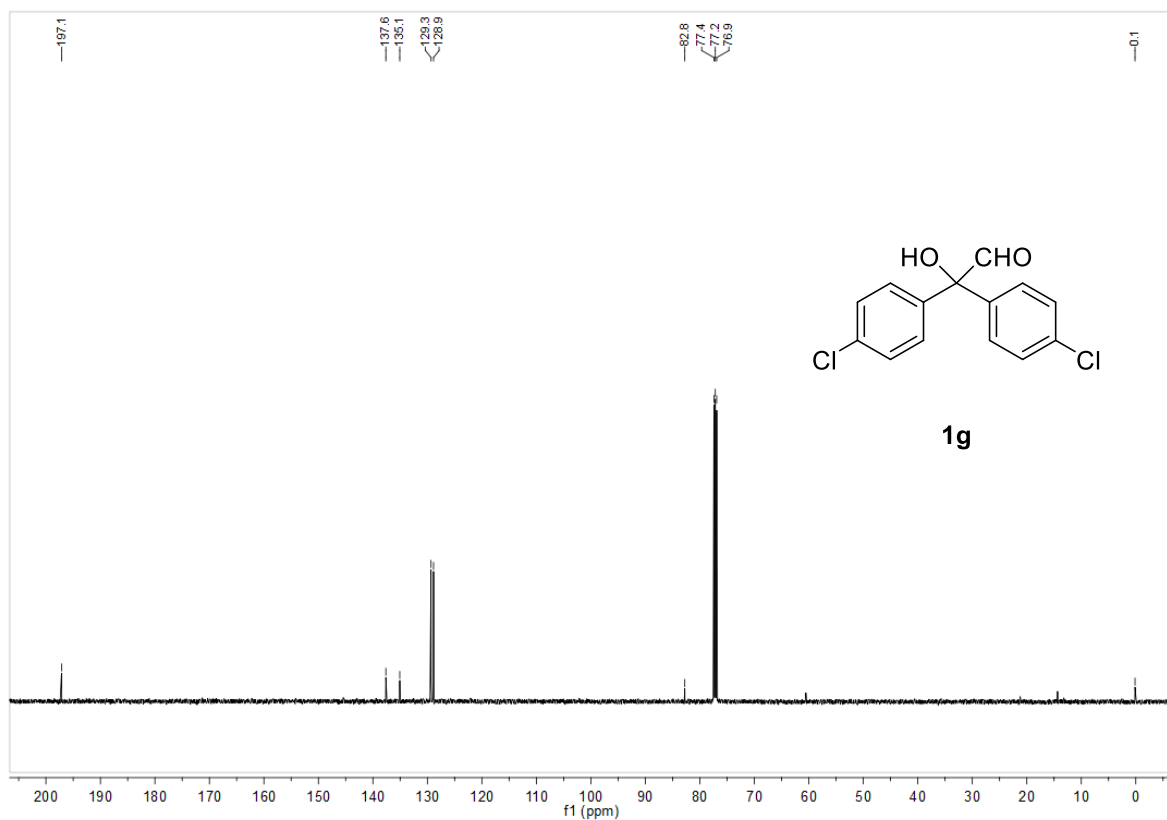
$^1\text{H}$  NMR spectrum of compound **1e** (500 MHz,  $\text{CDCl}_3$ )



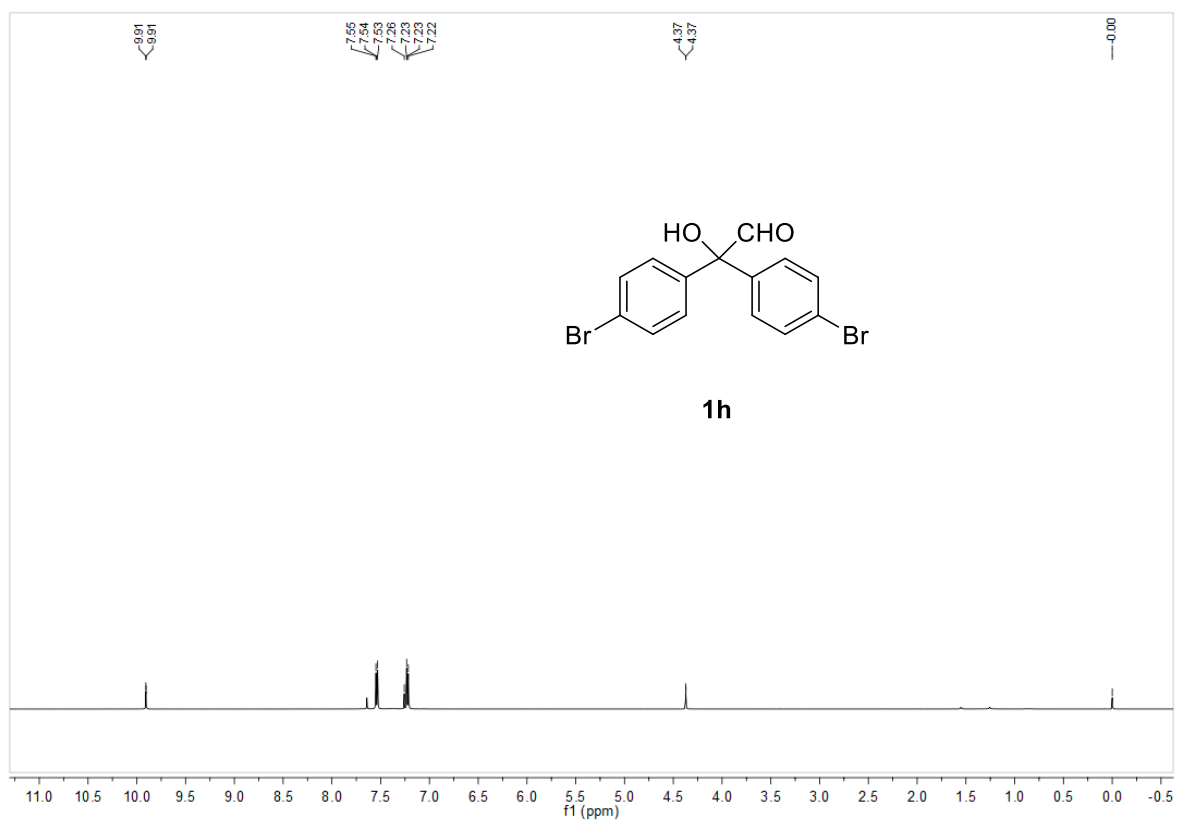
$^{13}\text{C}$  NMR spectrum of compound **1e** (125 MHz,  $\text{CDCl}_3$ )



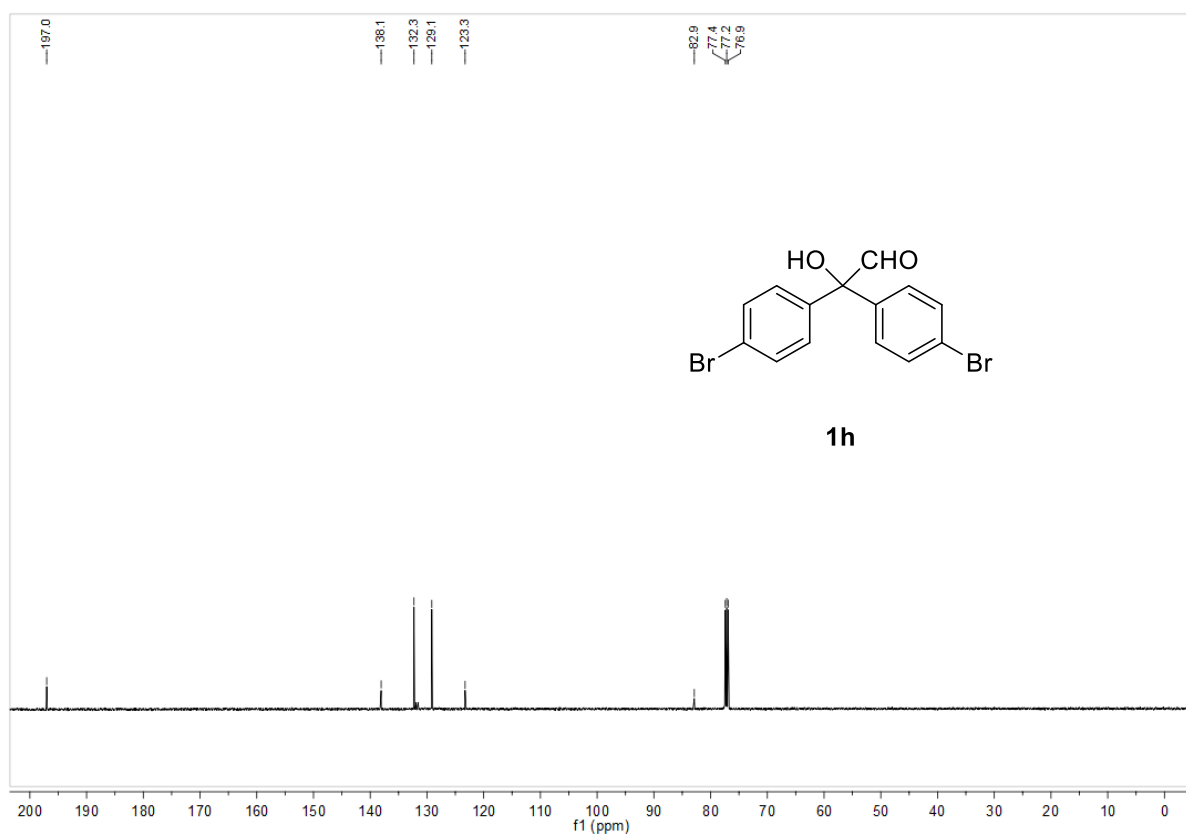
$^1\text{H}$  NMR spectrum of compound **1g** (500 MHz,  $\text{CDCl}_3$ )



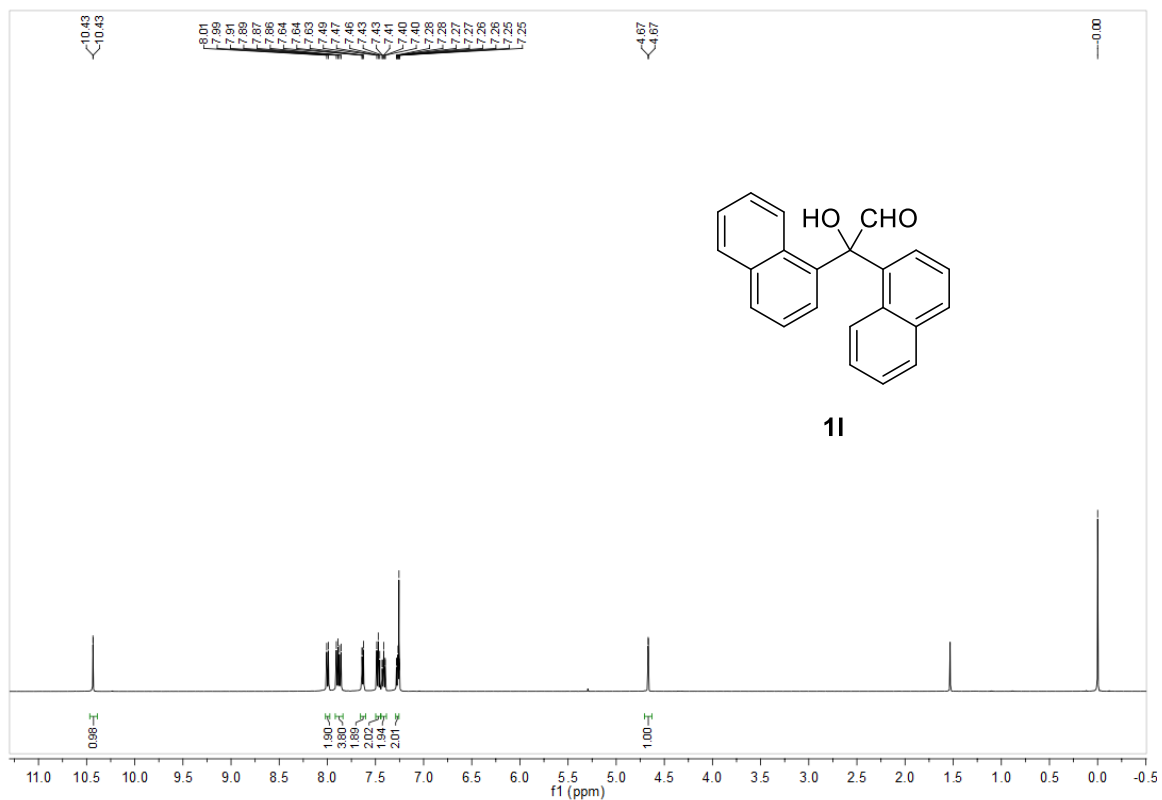
$^{13}\text{C}$  NMR spectrum of compound **1g** (125 MHz,  $\text{CDCl}_3$ )



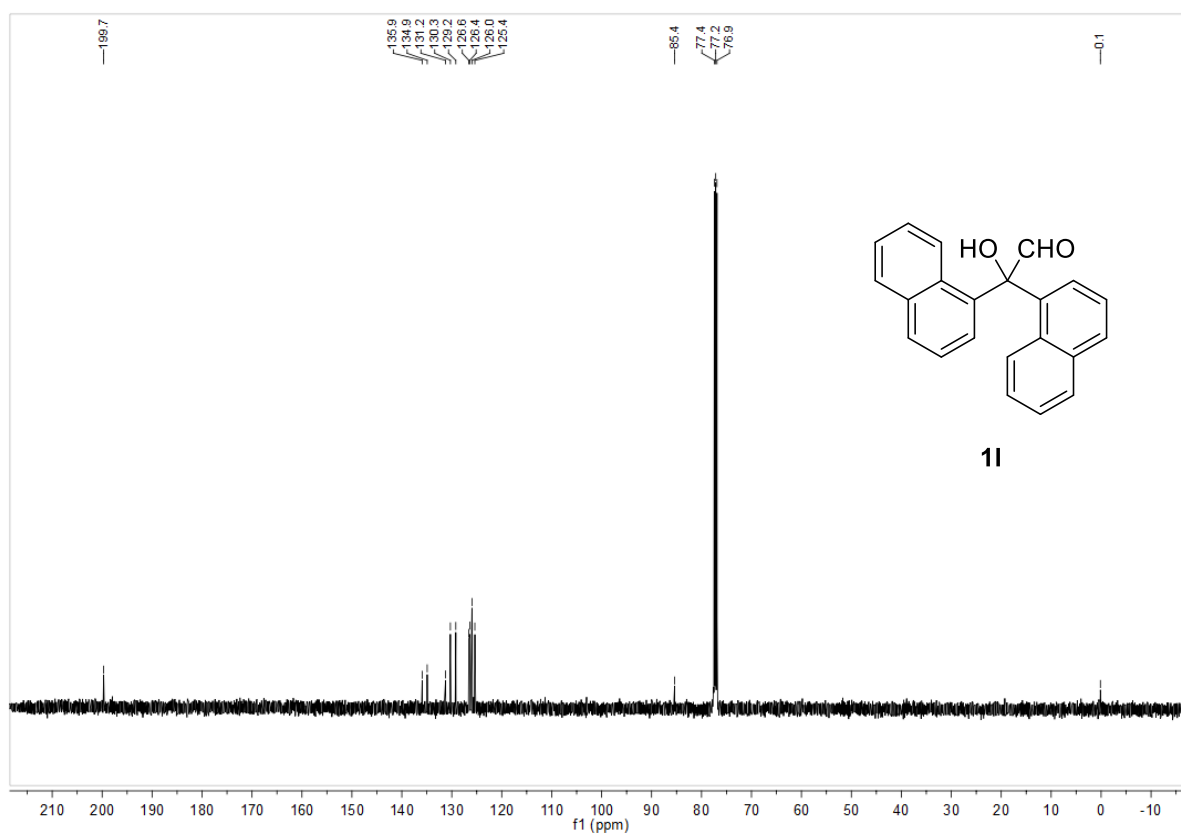
<sup>1</sup>H NMR spectrum of compound **1h** (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR spectrum of compound **1h** (125 MHz, CDCl<sub>3</sub>)

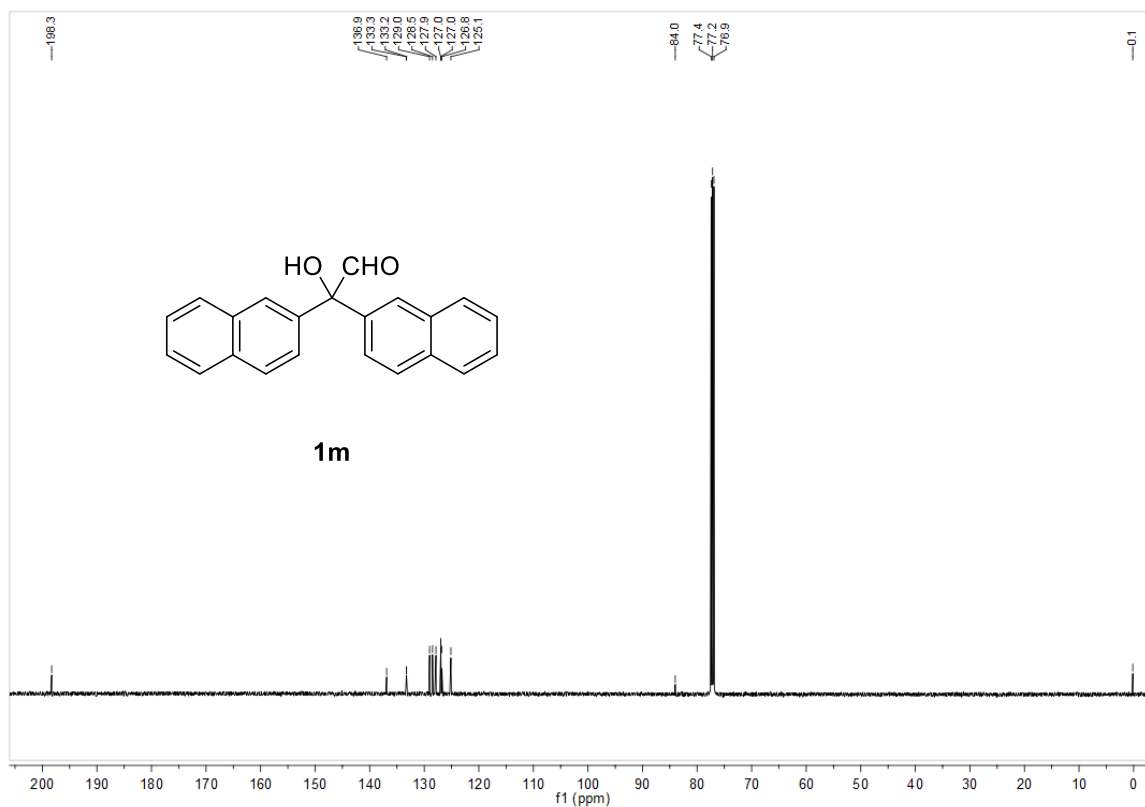
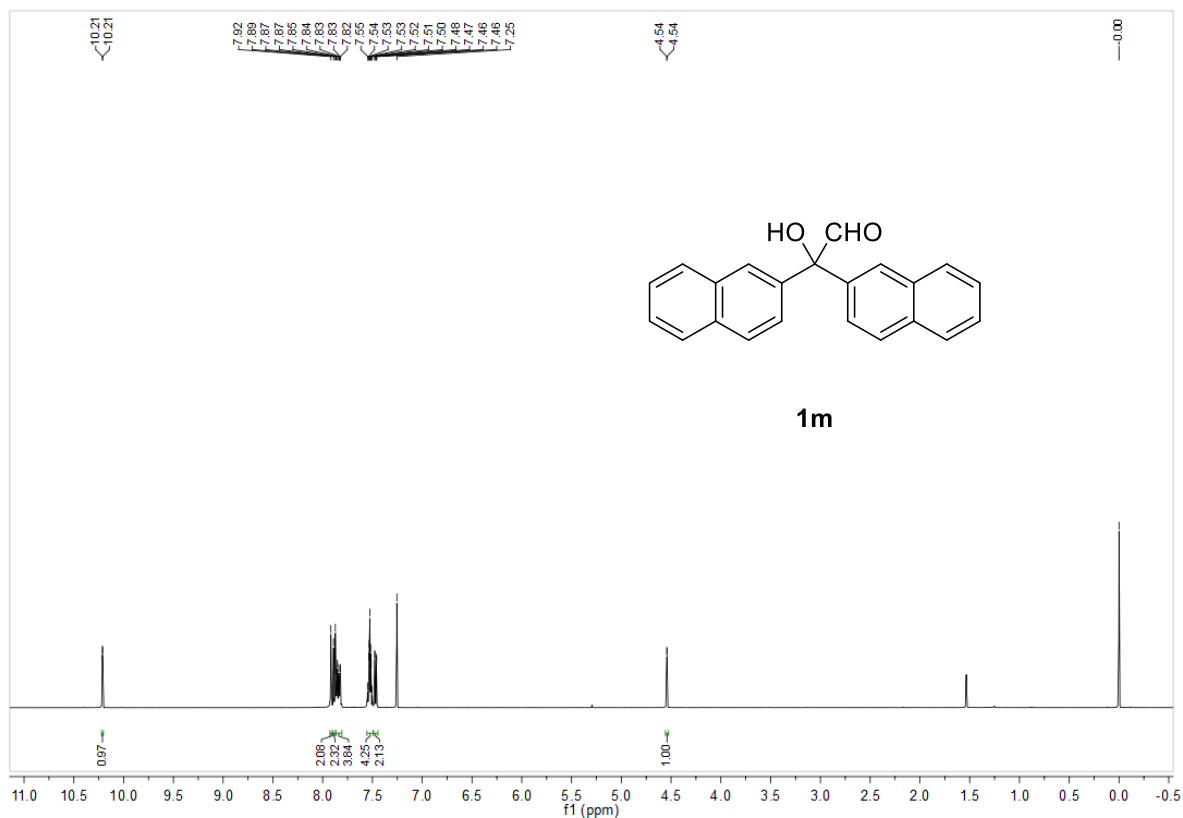


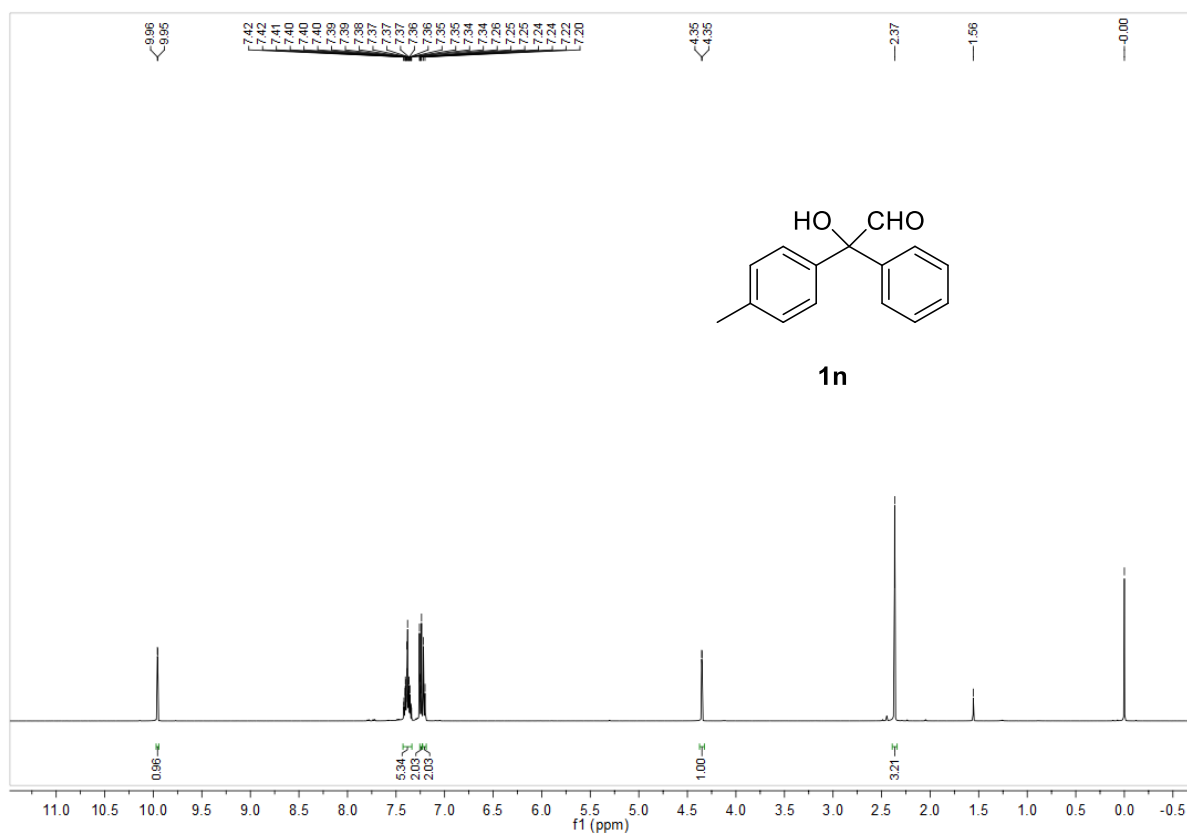
<sup>1</sup>H NMR spectrum of compound **11** (500 MHz, CDCl<sub>3</sub>)



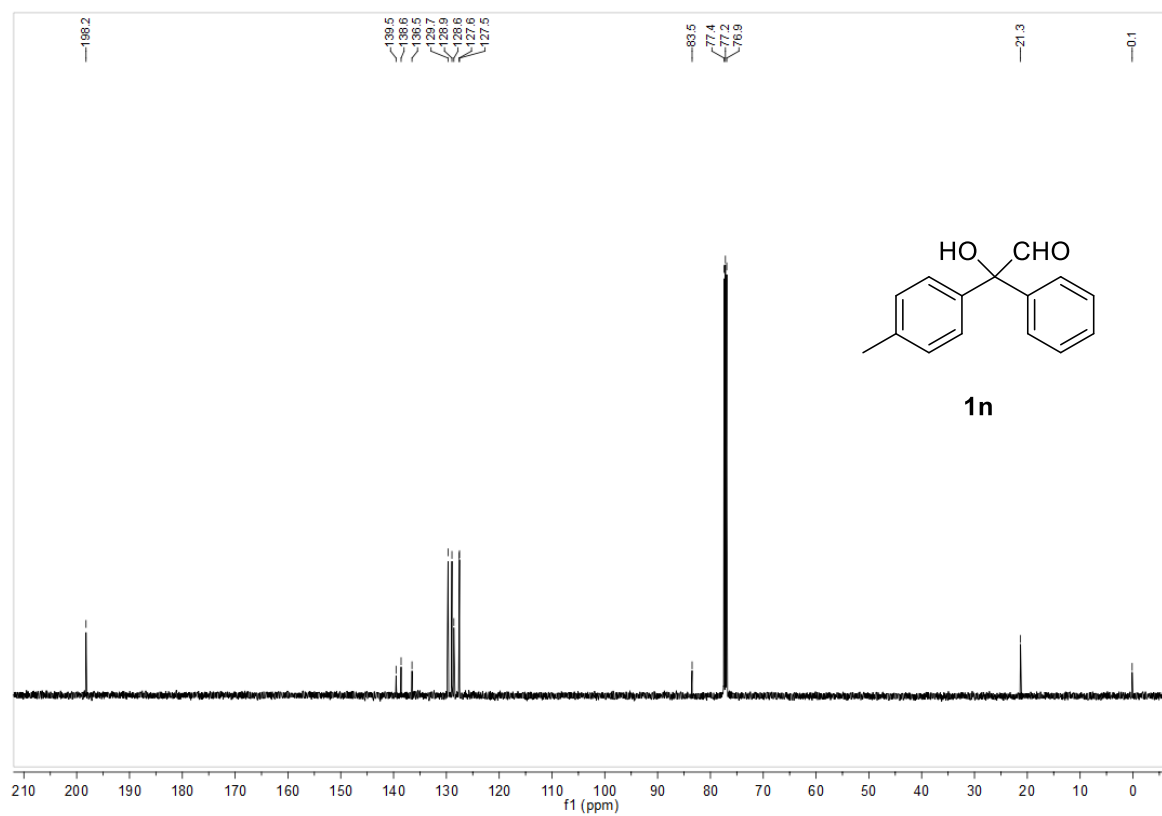
<sup>13</sup>C NMR spectrum of compound **11** (125 MHz, CDCl<sub>3</sub>)



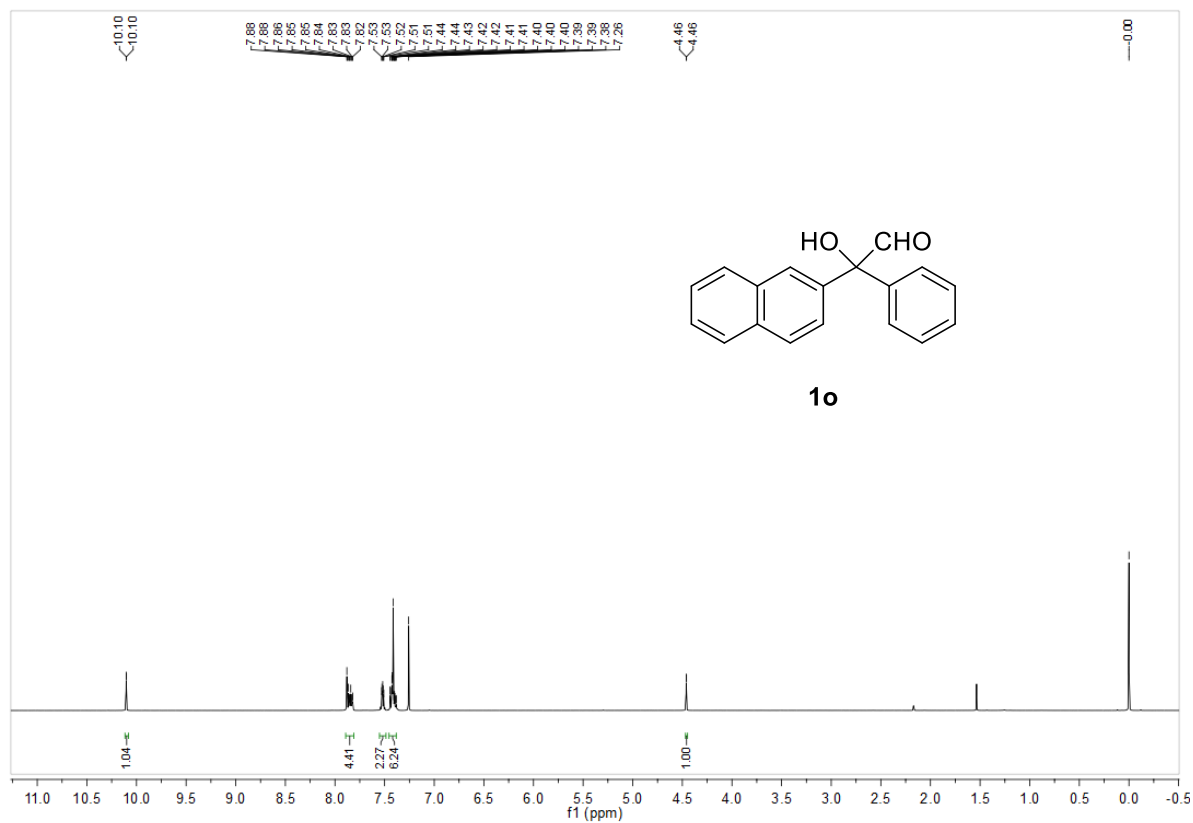




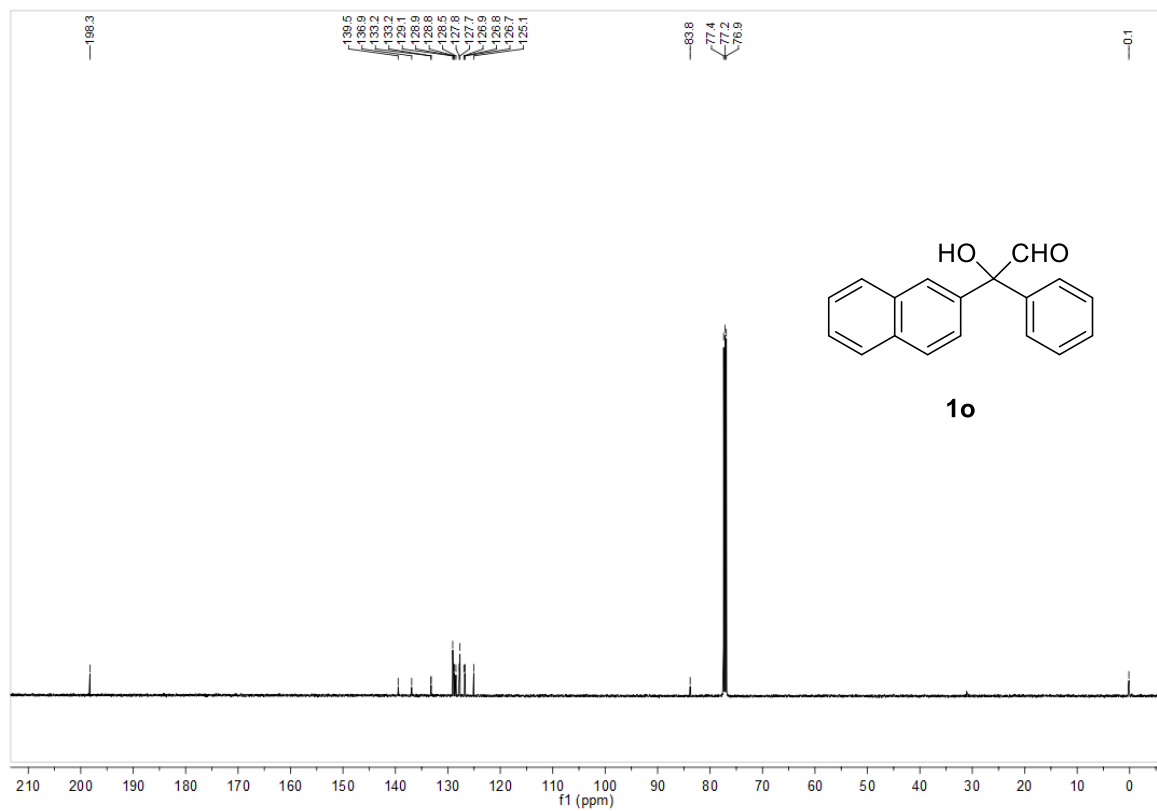
<sup>1</sup>H NMR spectrum of compound **1n** (500 MHz, CDCl<sub>3</sub>)



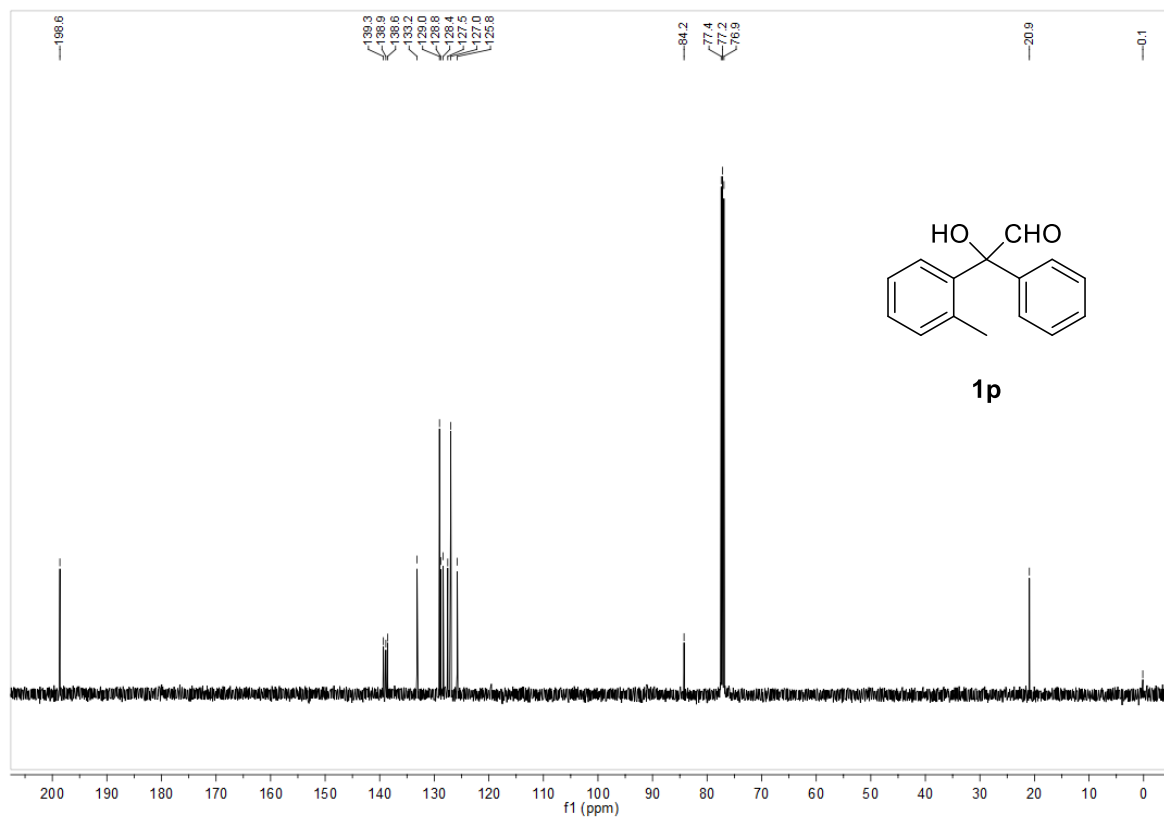
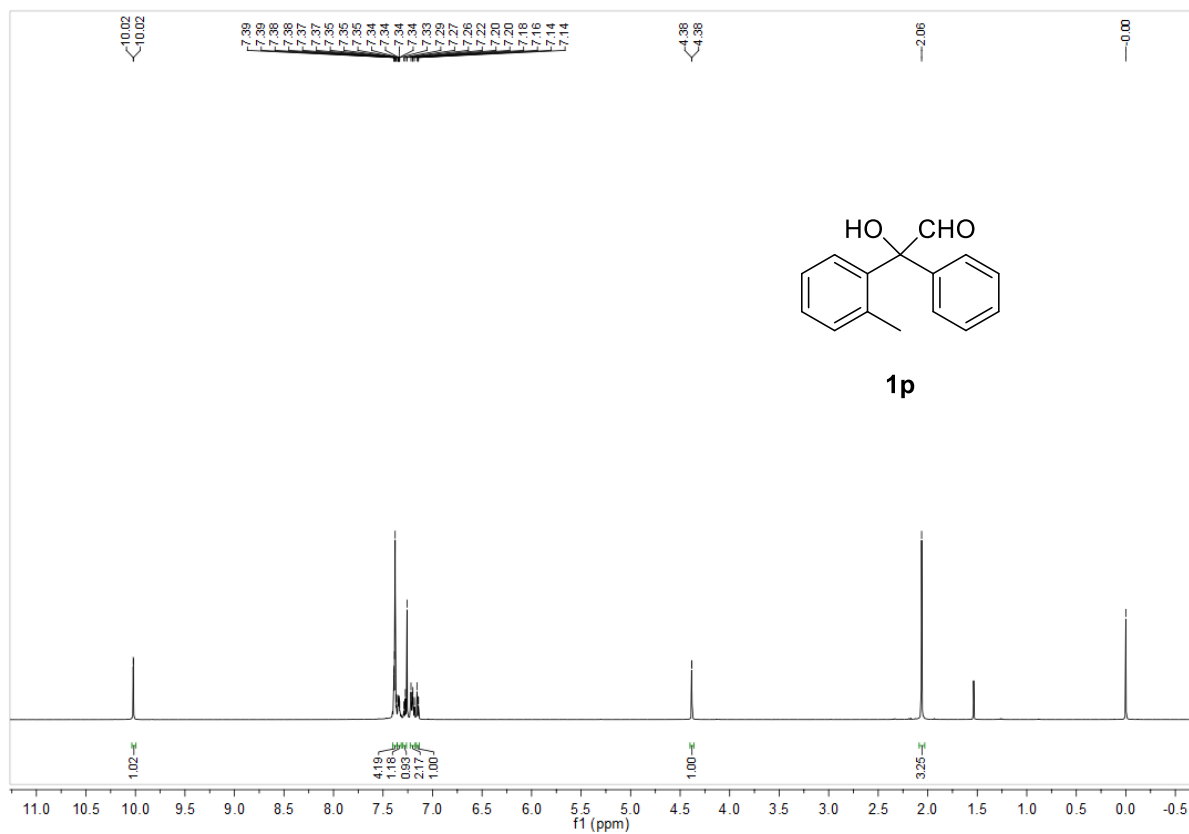
<sup>13</sup>C NMR spectrum of compound **1n** (125 MHz, CDCl<sub>3</sub>)

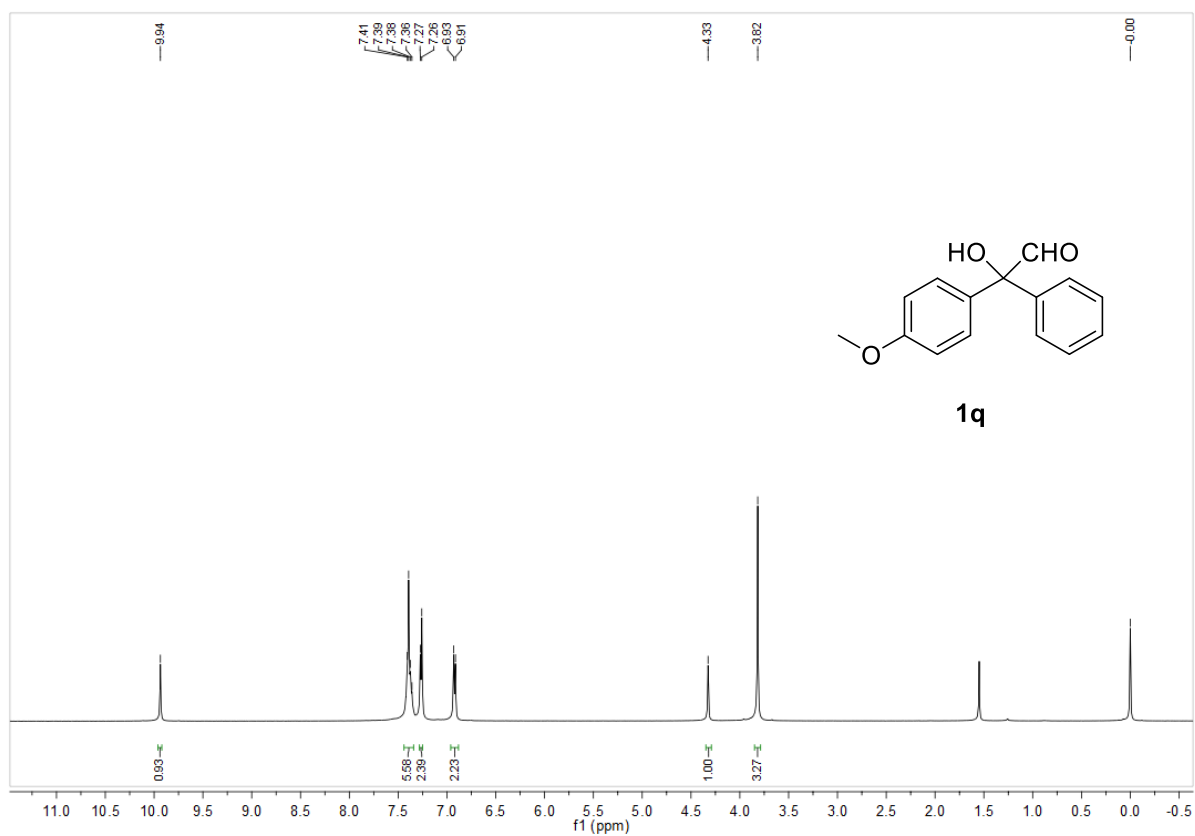


<sup>1</sup>H NMR spectrum of compound **1o** (500 MHz, CDCl<sub>3</sub>)

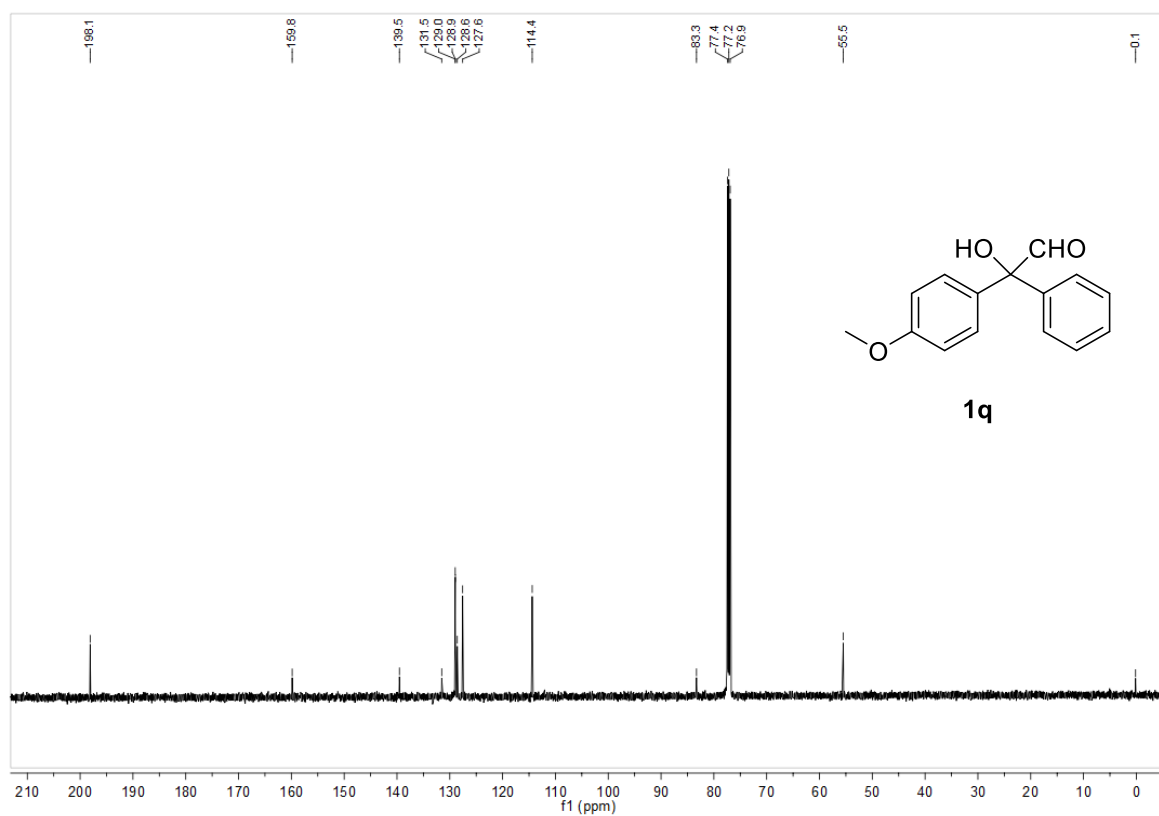


<sup>13</sup>C NMR spectrum of compound **1o** (125 MHz, CDCl<sub>3</sub>)

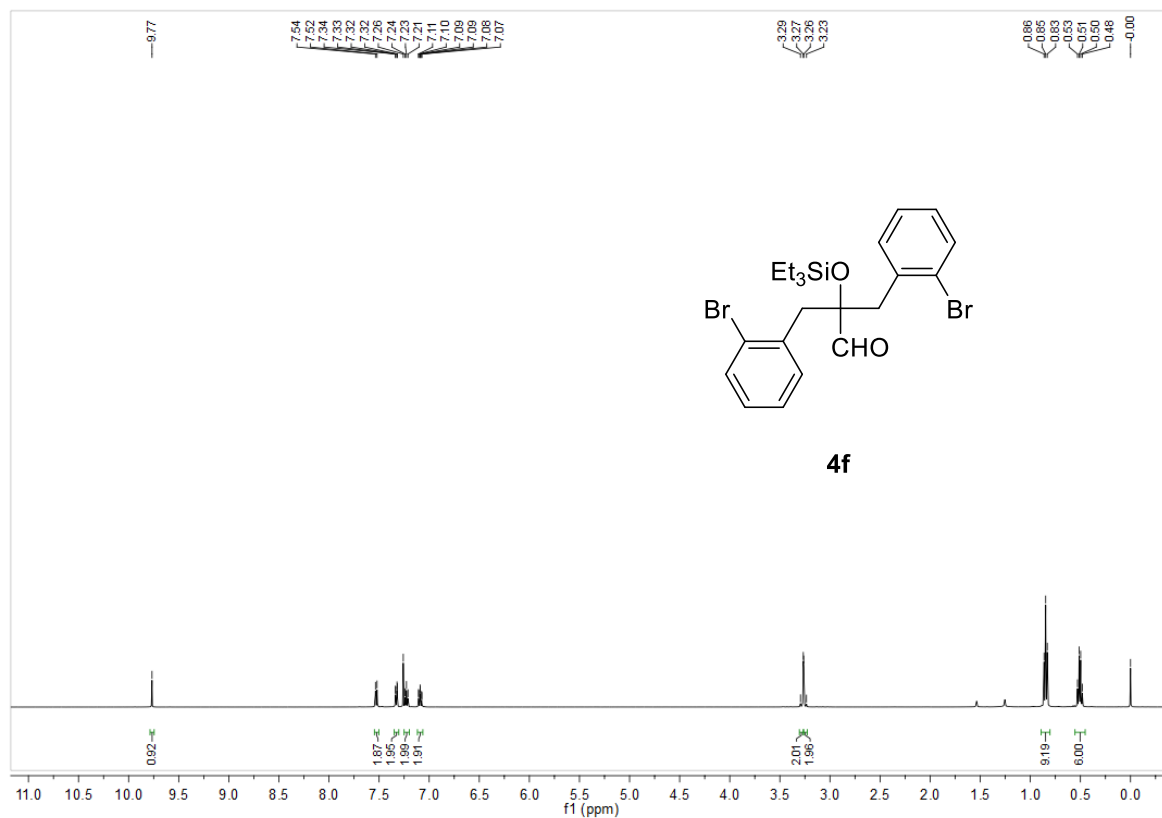




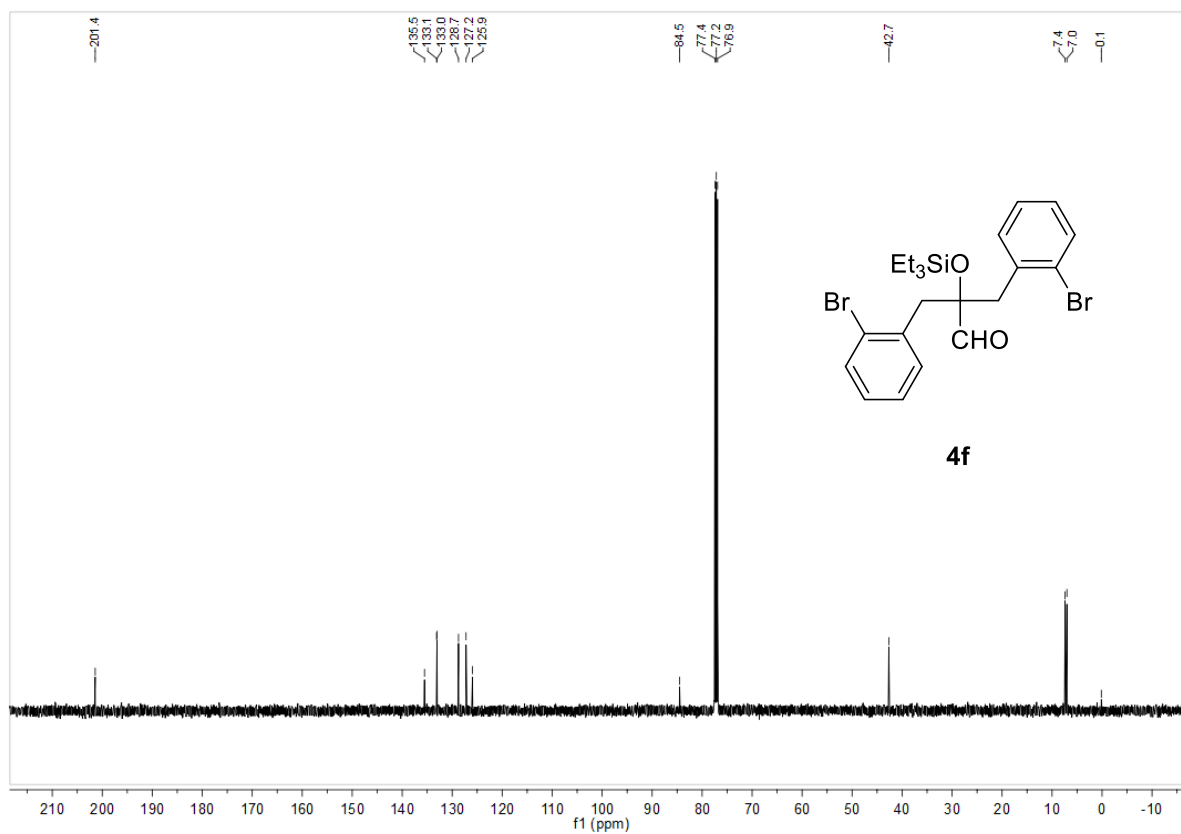
<sup>1</sup>H NMR spectrum of compound **1q** (500 MHz, CDCl<sub>3</sub>)



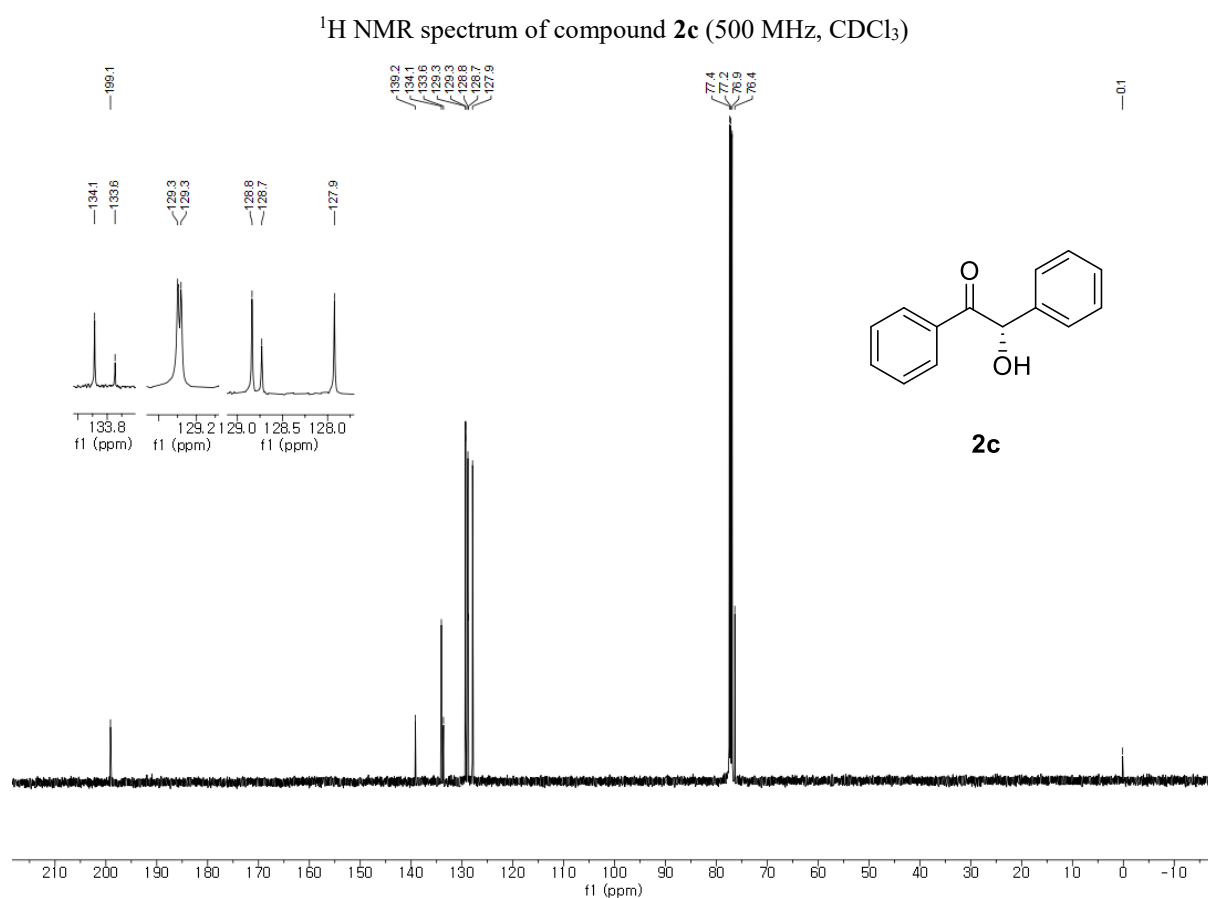
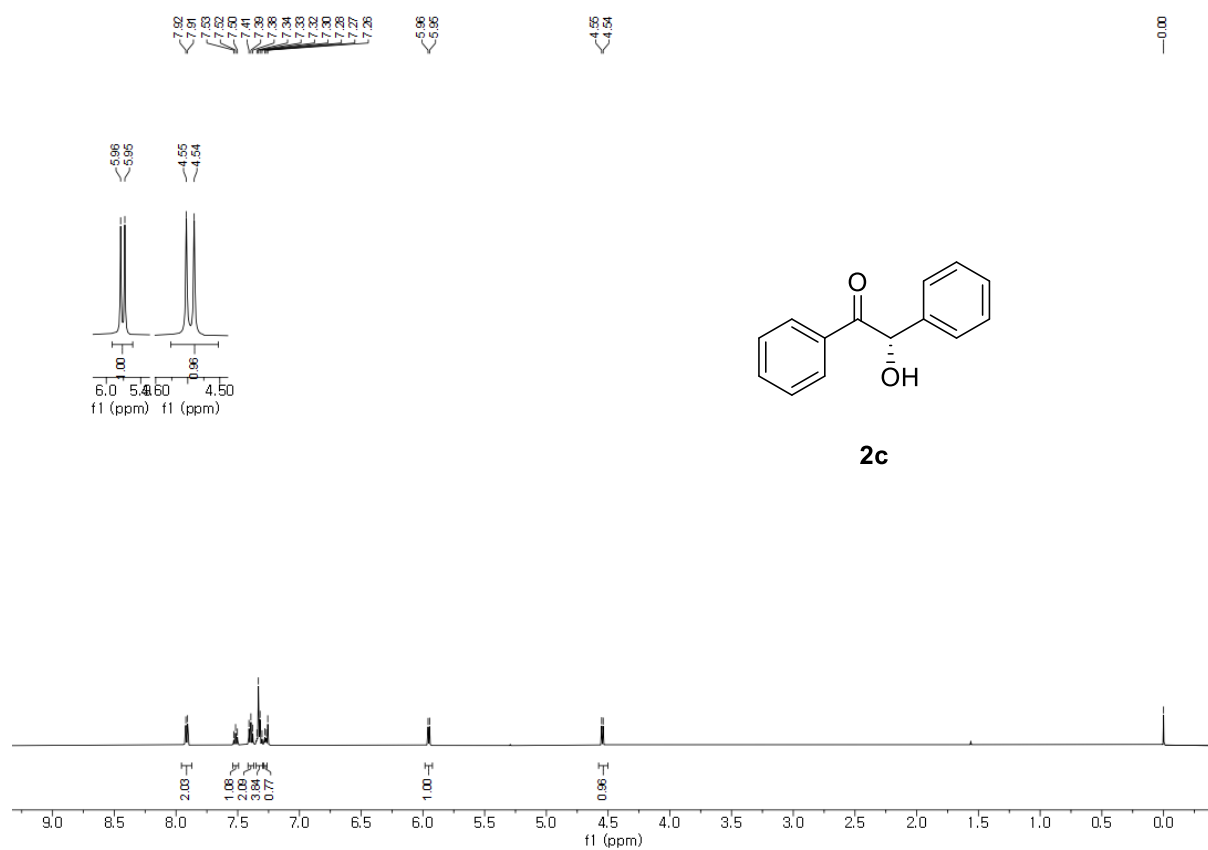
<sup>13</sup>C NMR spectrum of compound **1q** (125 MHz, CDCl<sub>3</sub>)

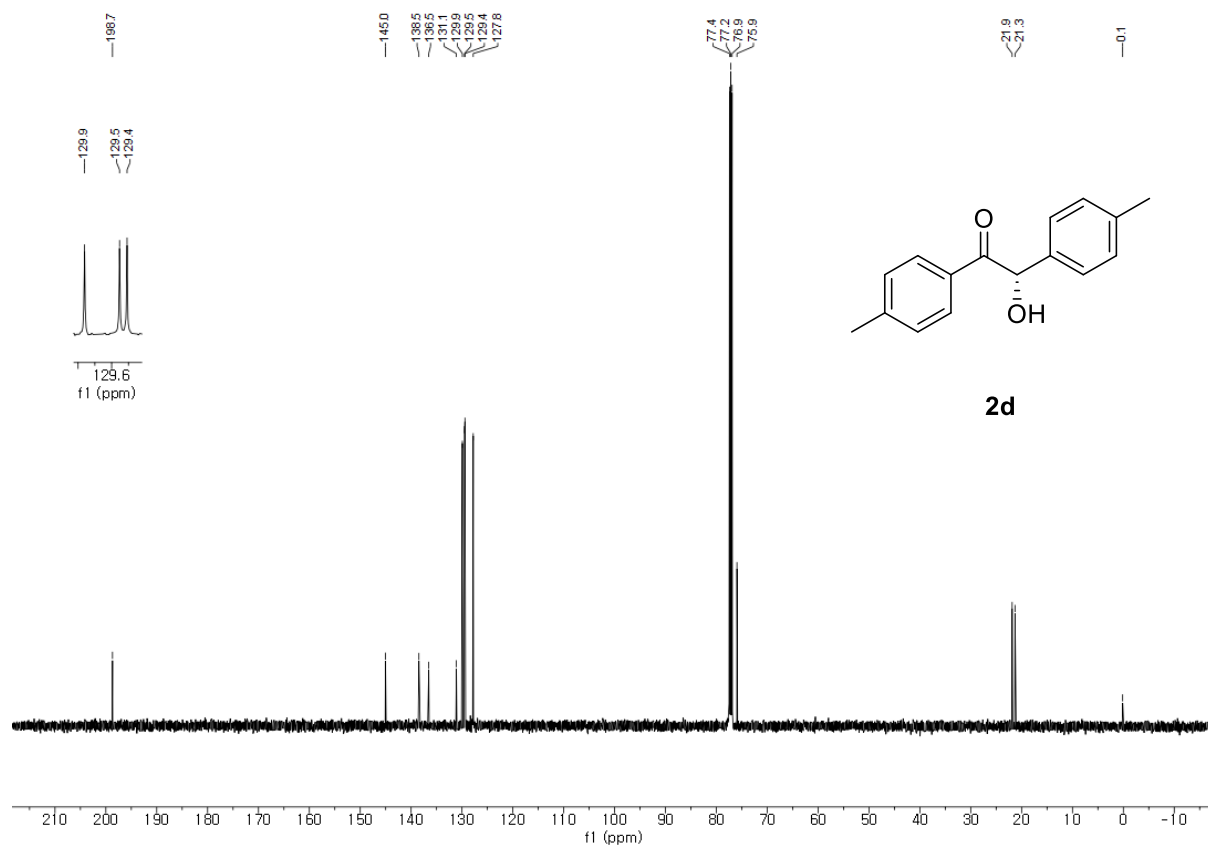
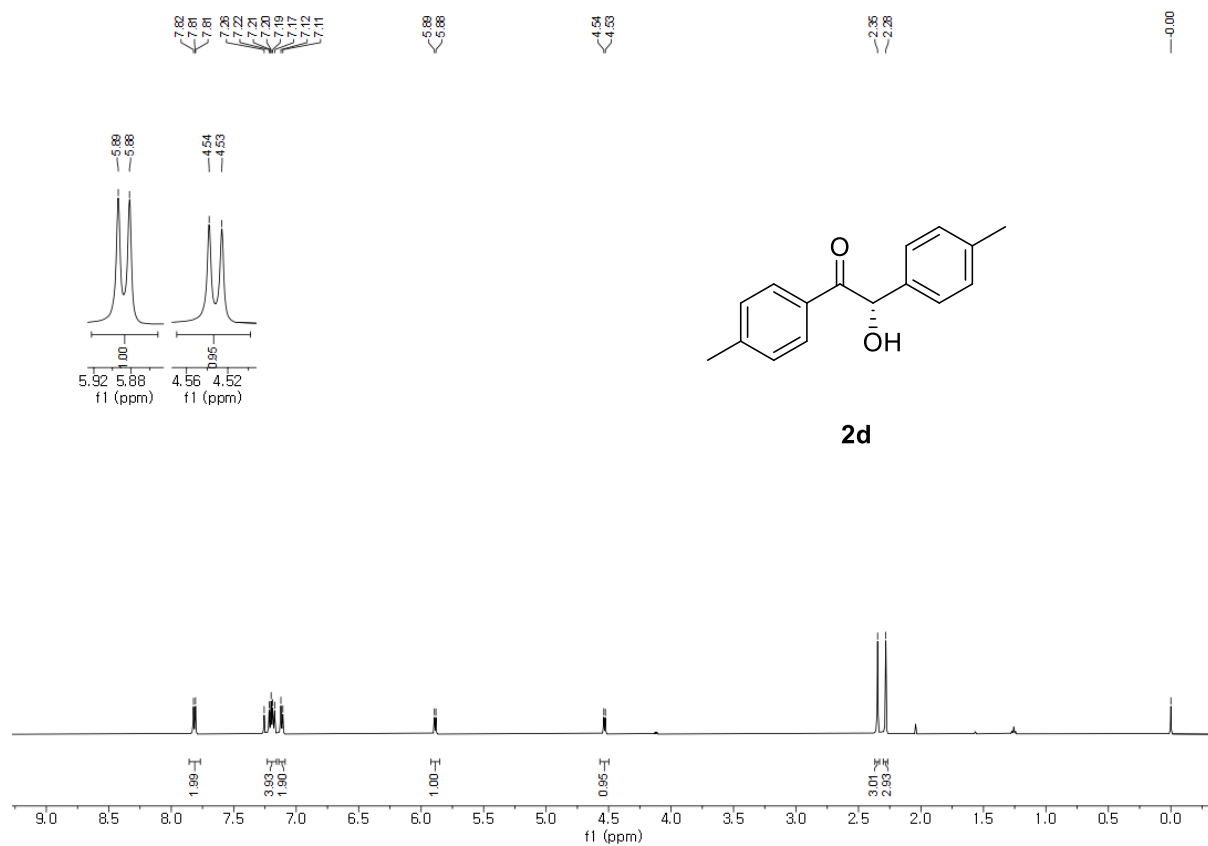


<sup>1</sup>H NMR spectrum of compound **4f** (500 MHz, CDCl<sub>3</sub>)

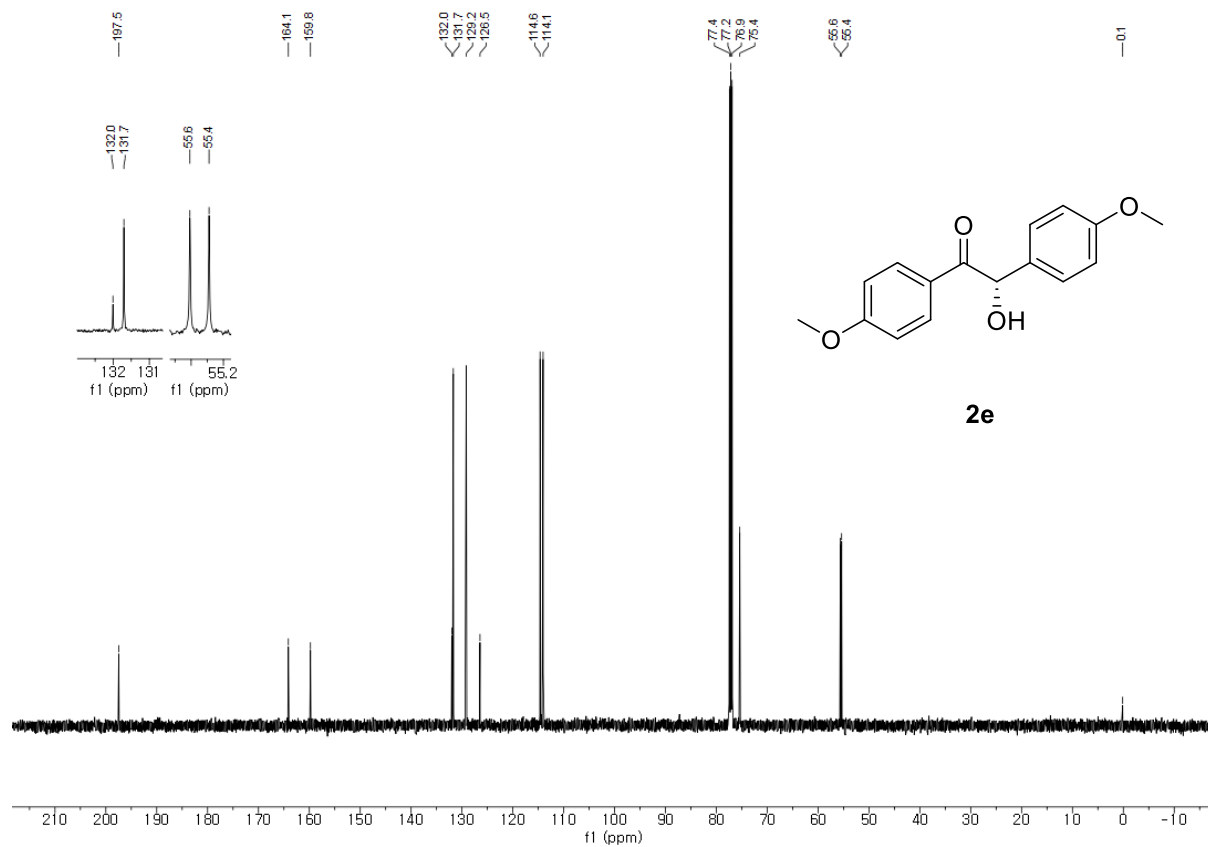
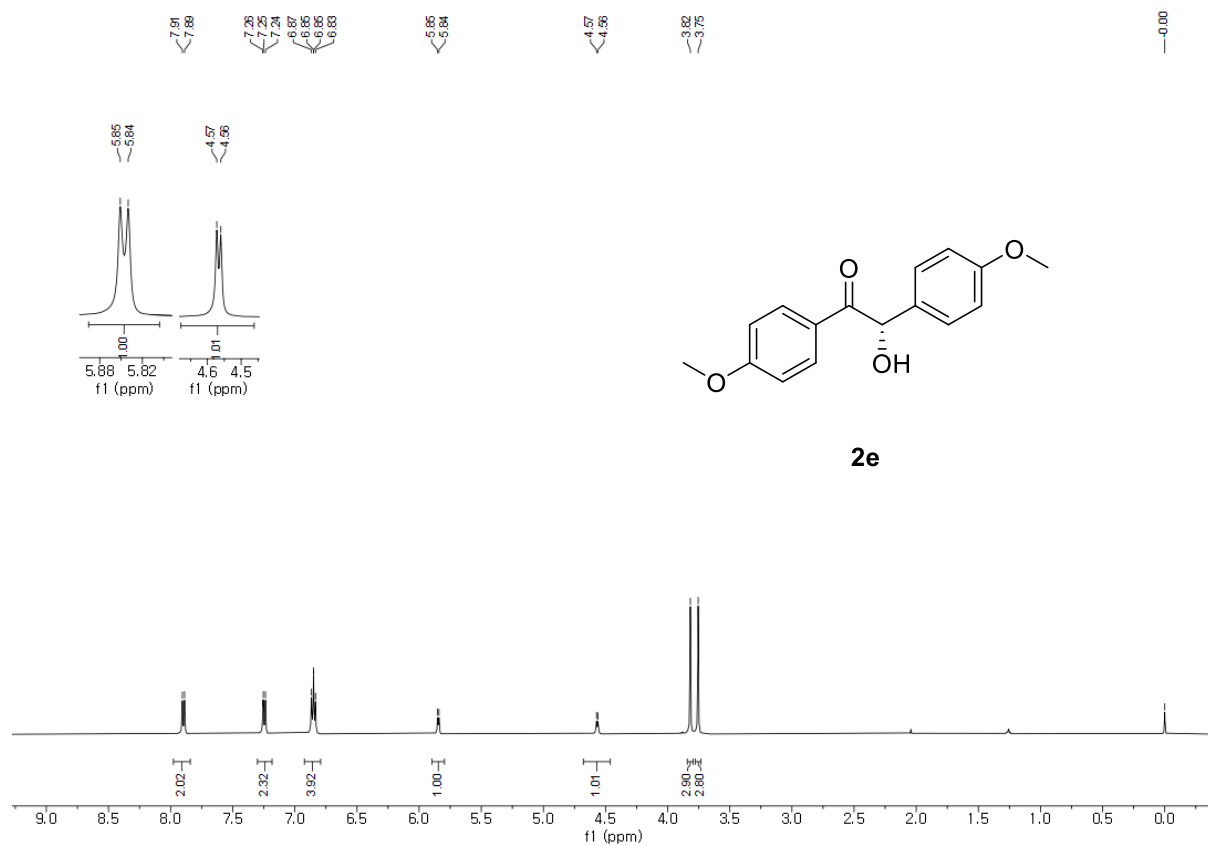


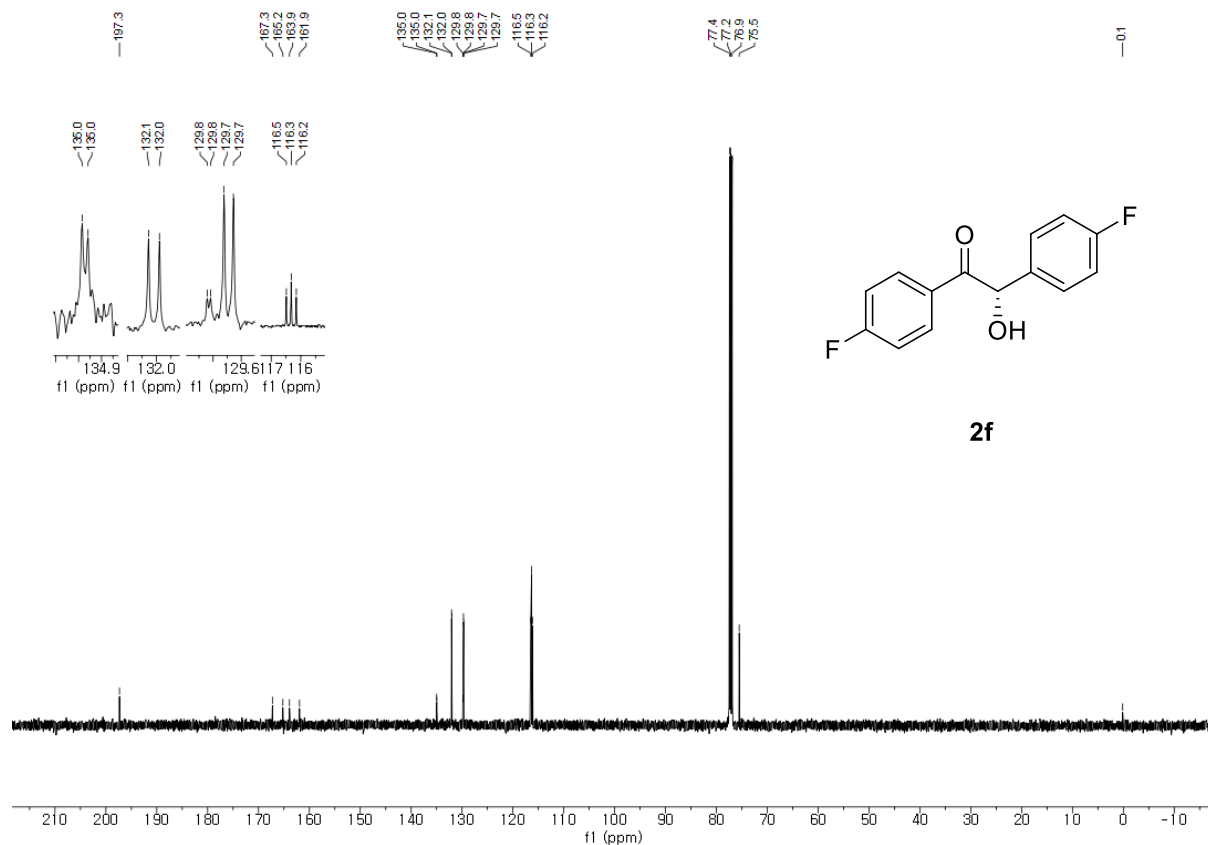
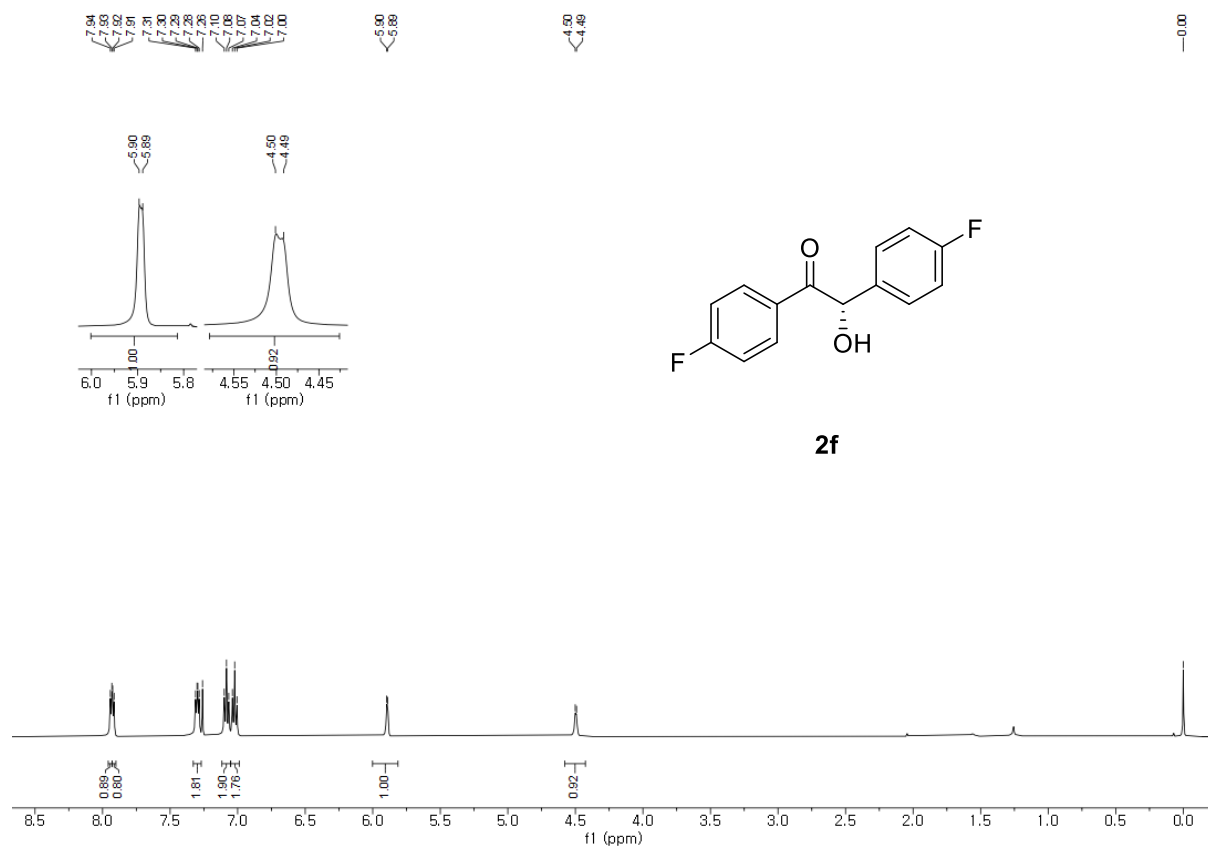
<sup>13</sup>C NMR spectrum of compound **4f** (125 MHz, CDCl<sub>3</sub>)

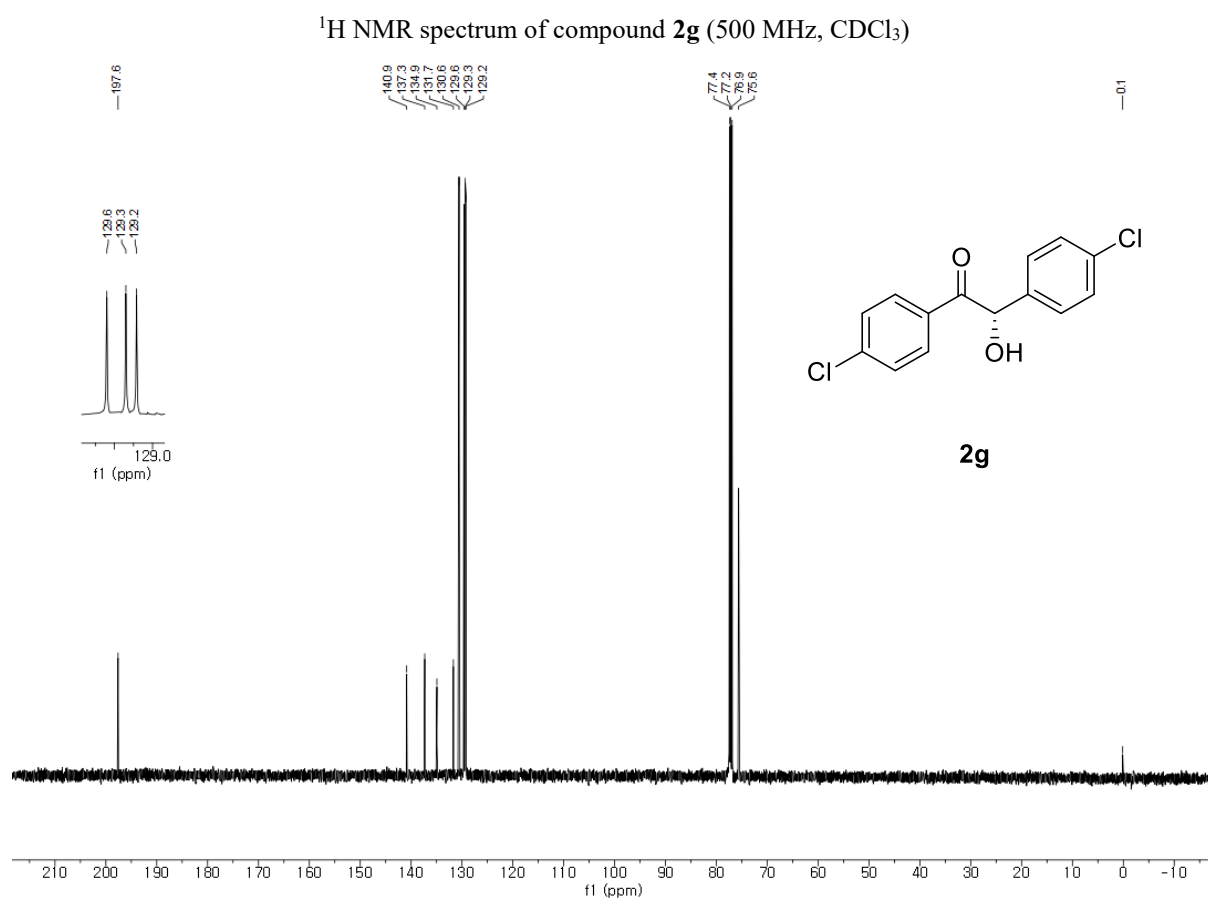
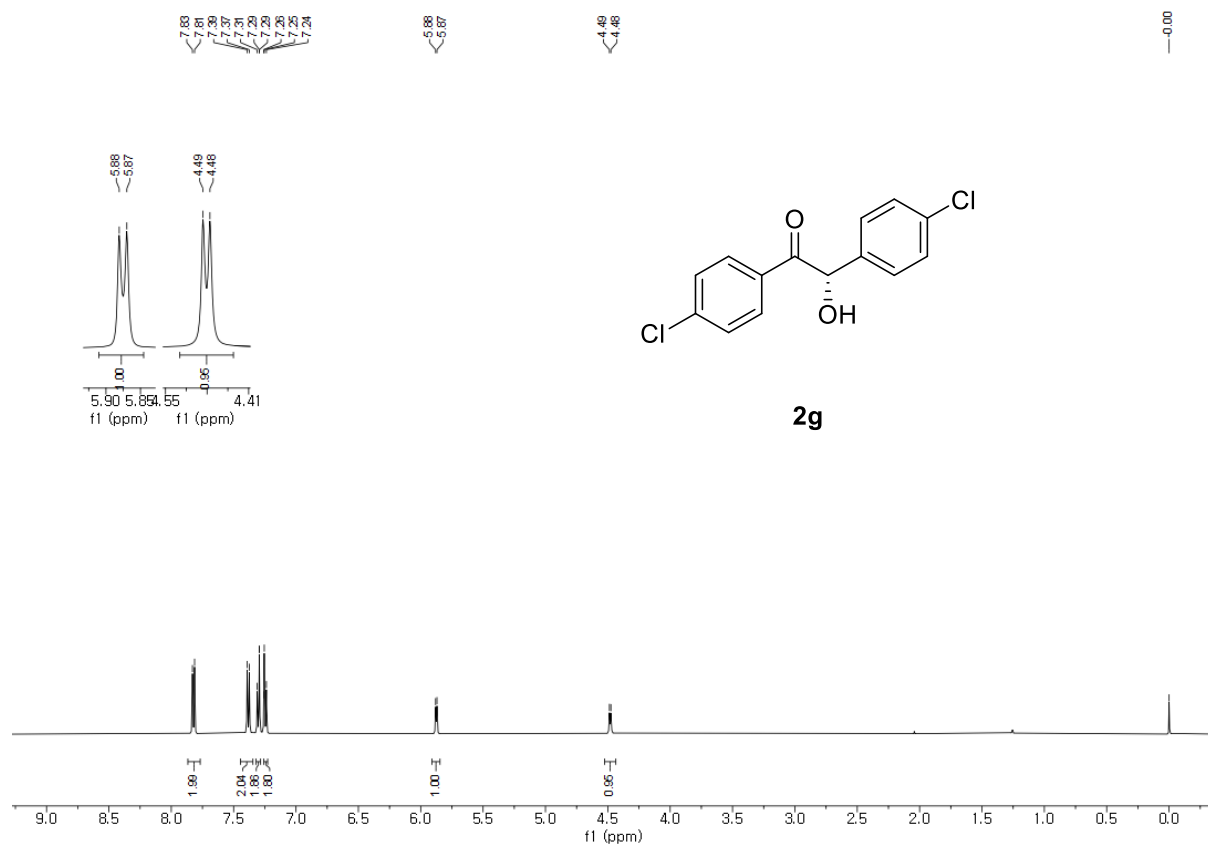


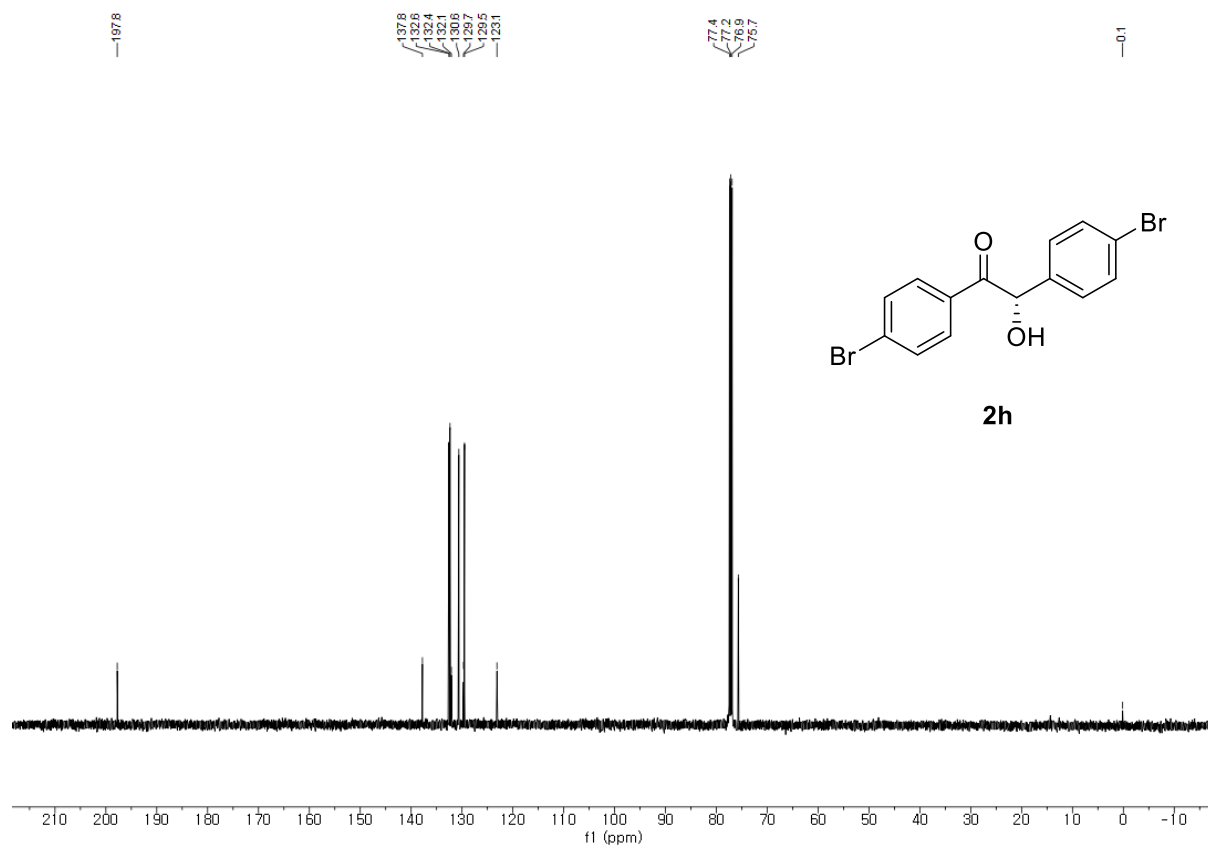
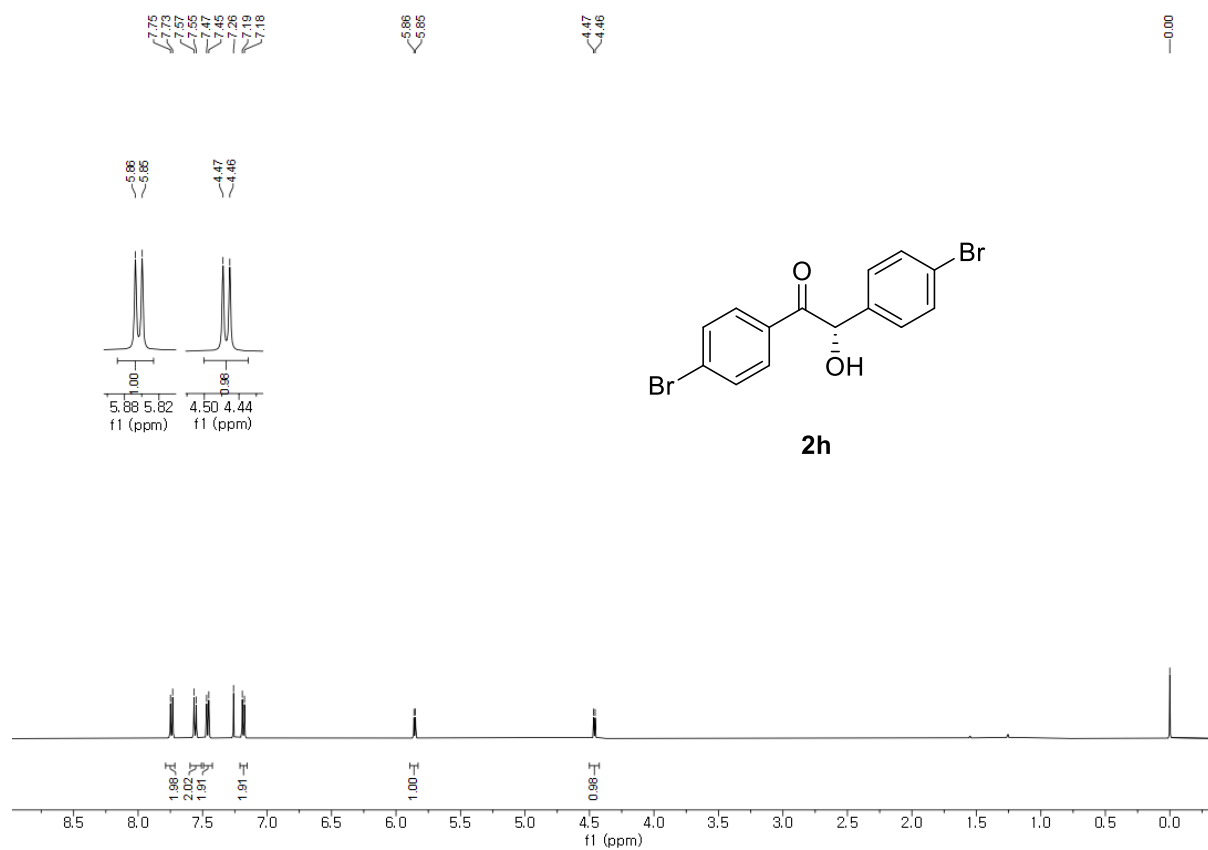


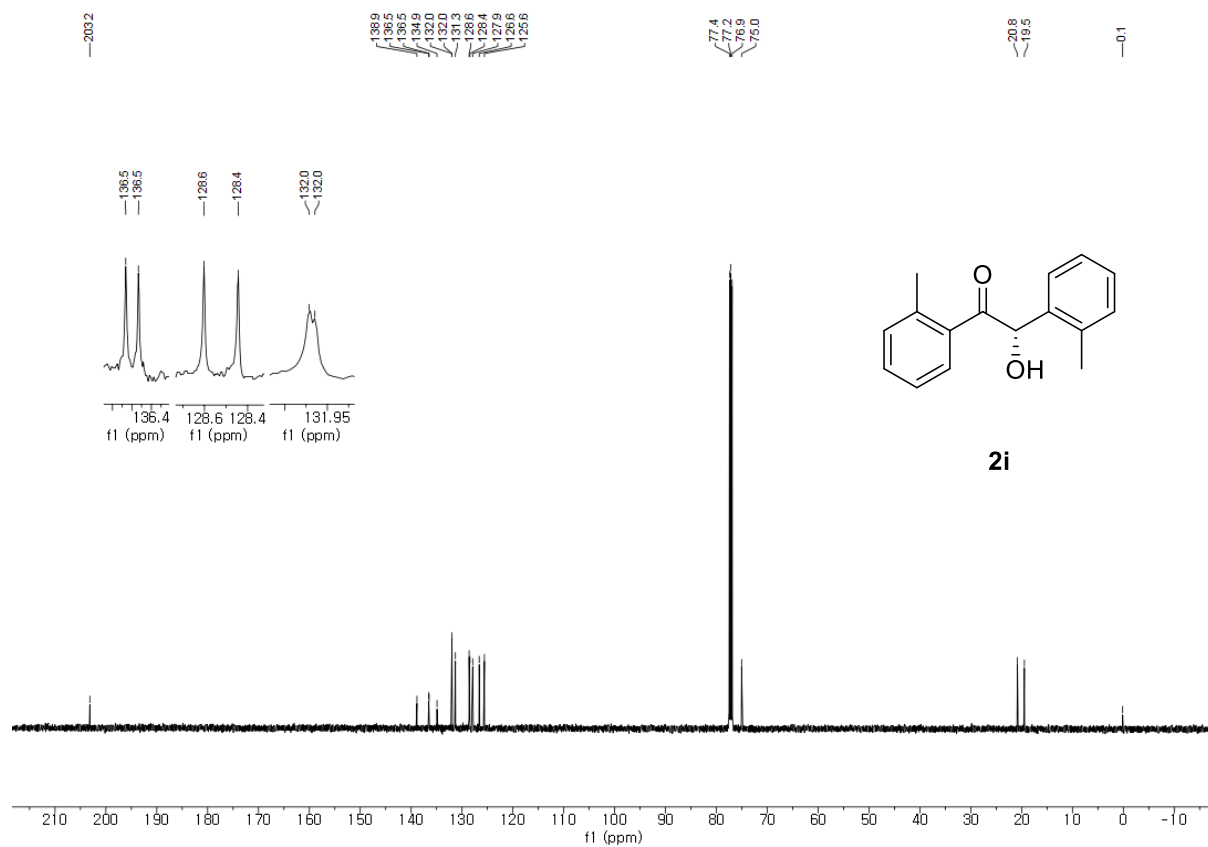
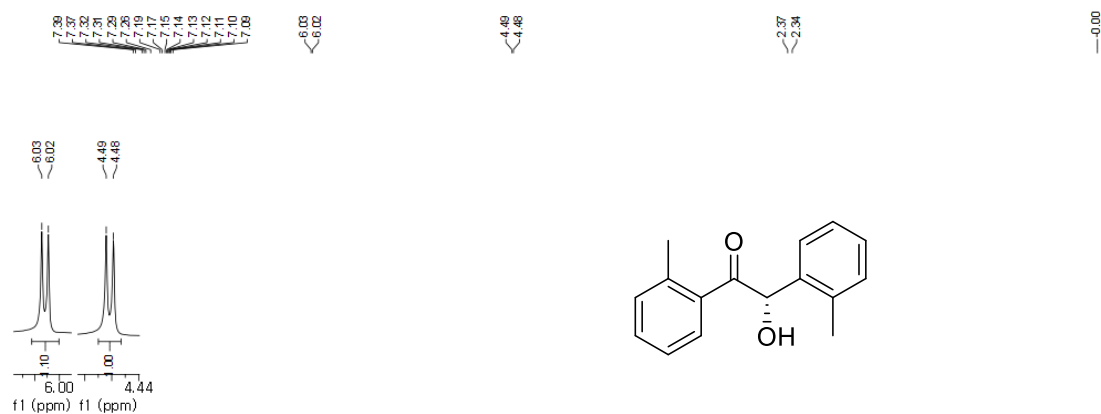


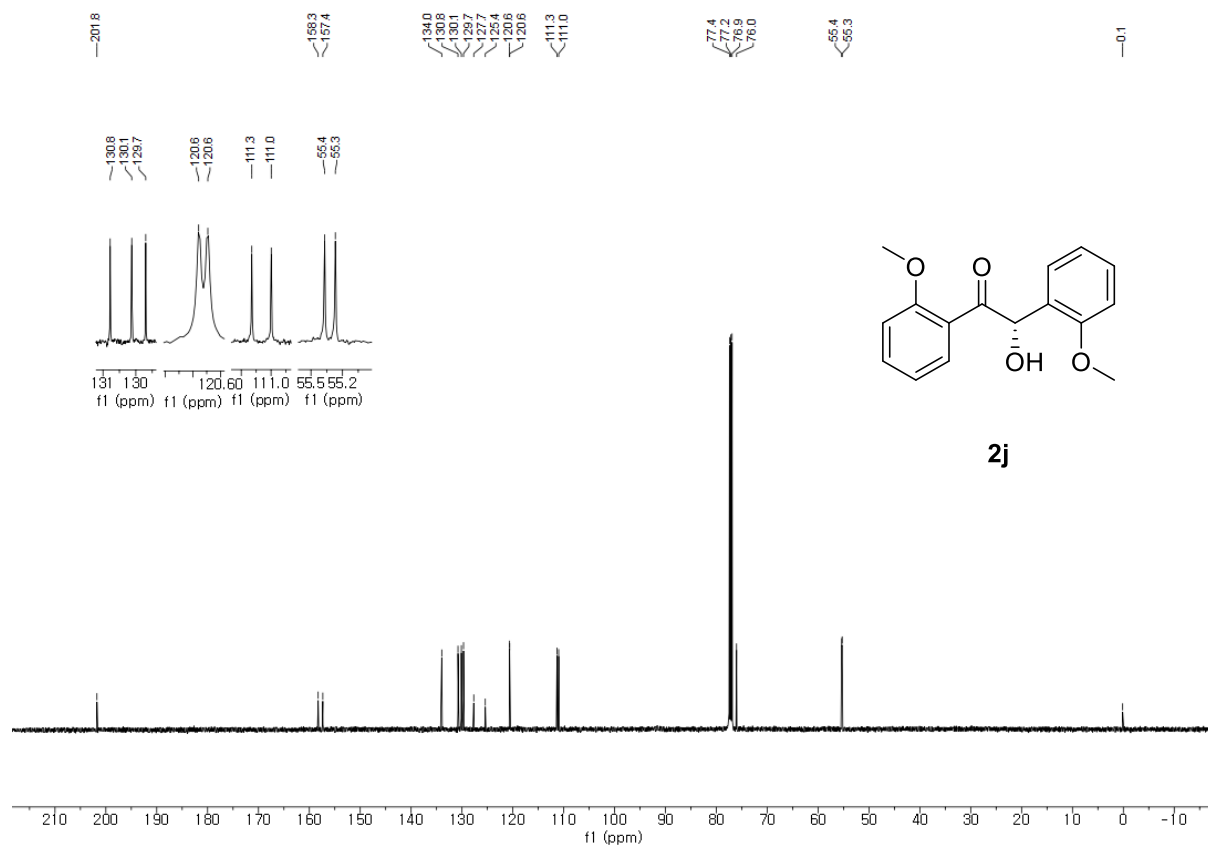
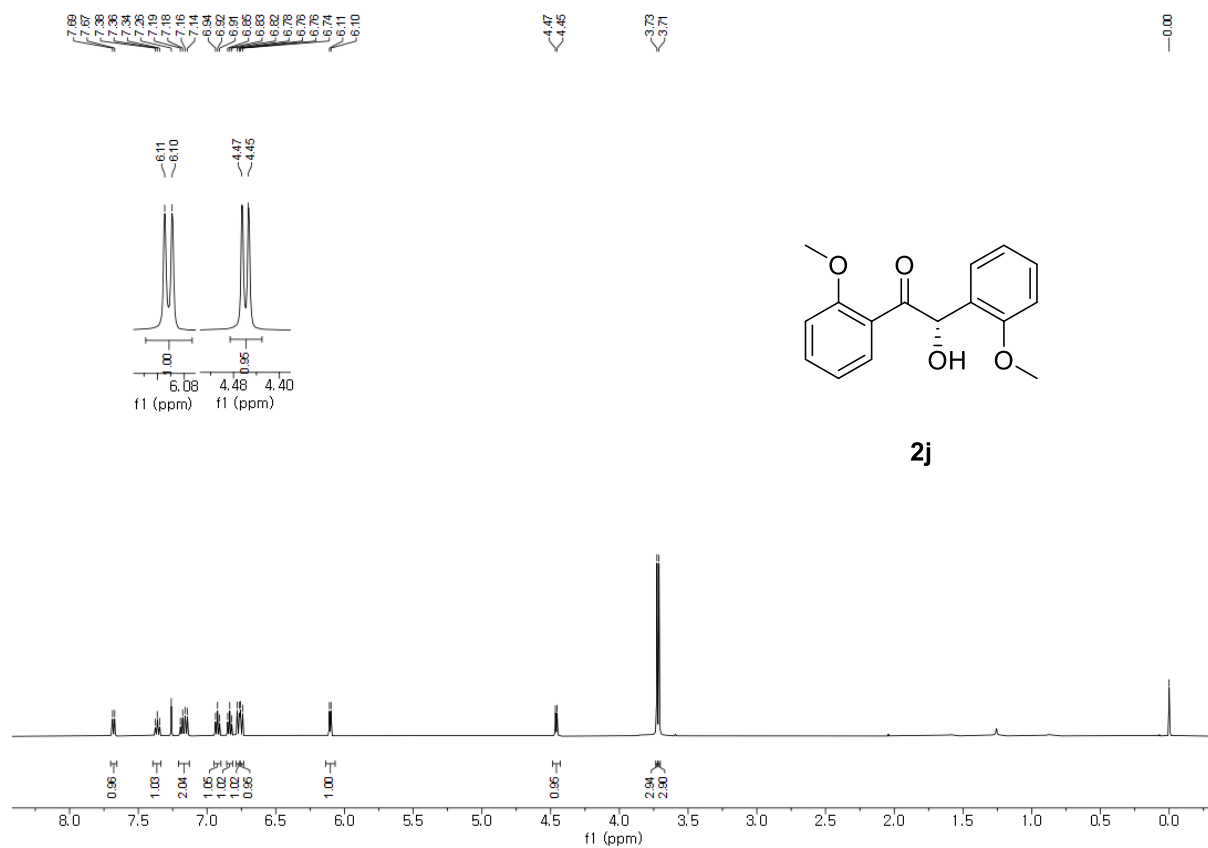


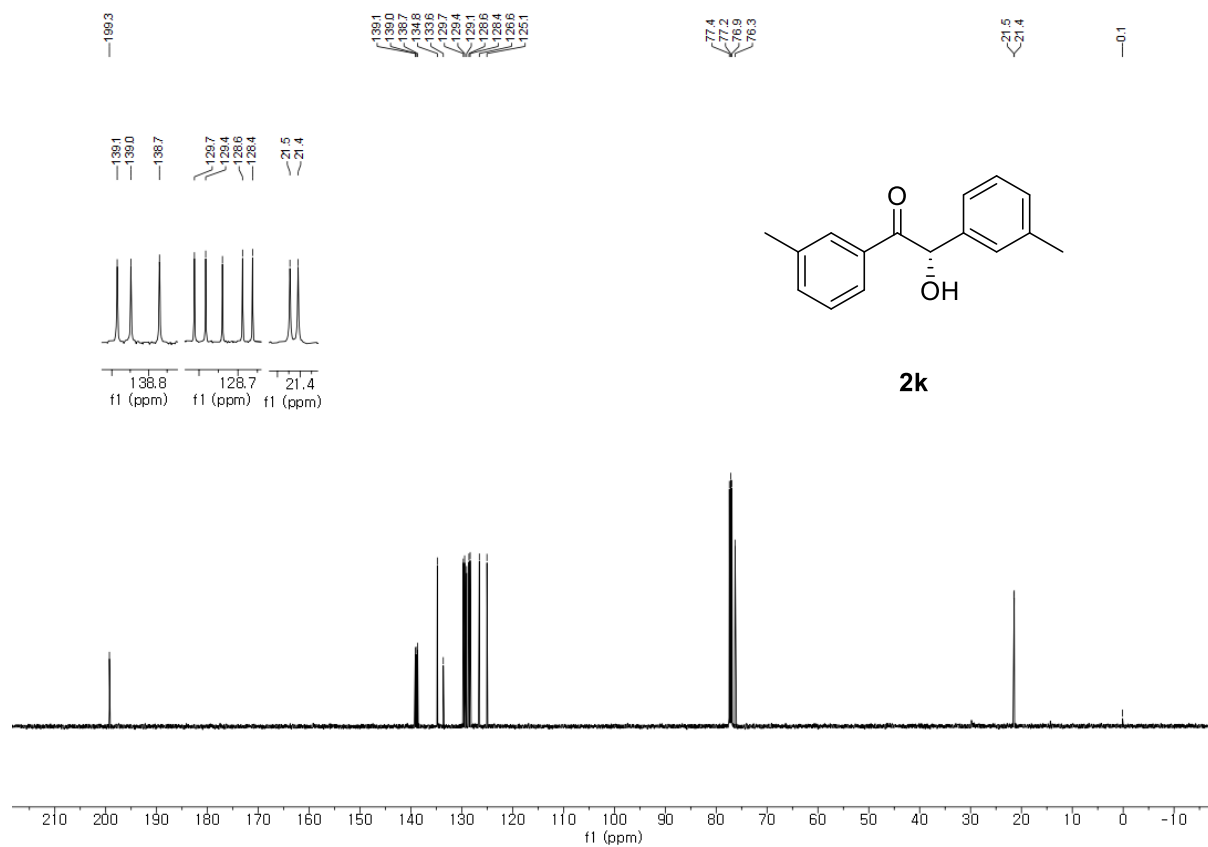
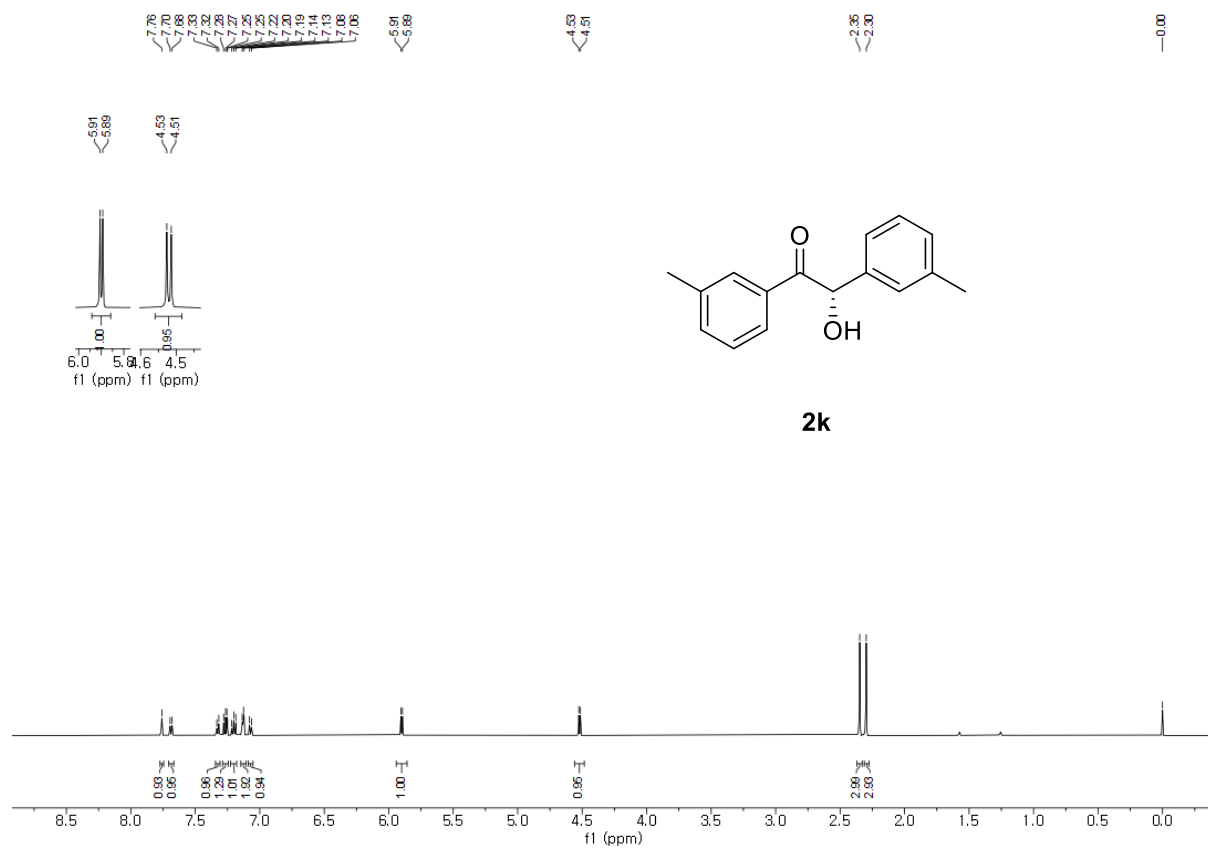


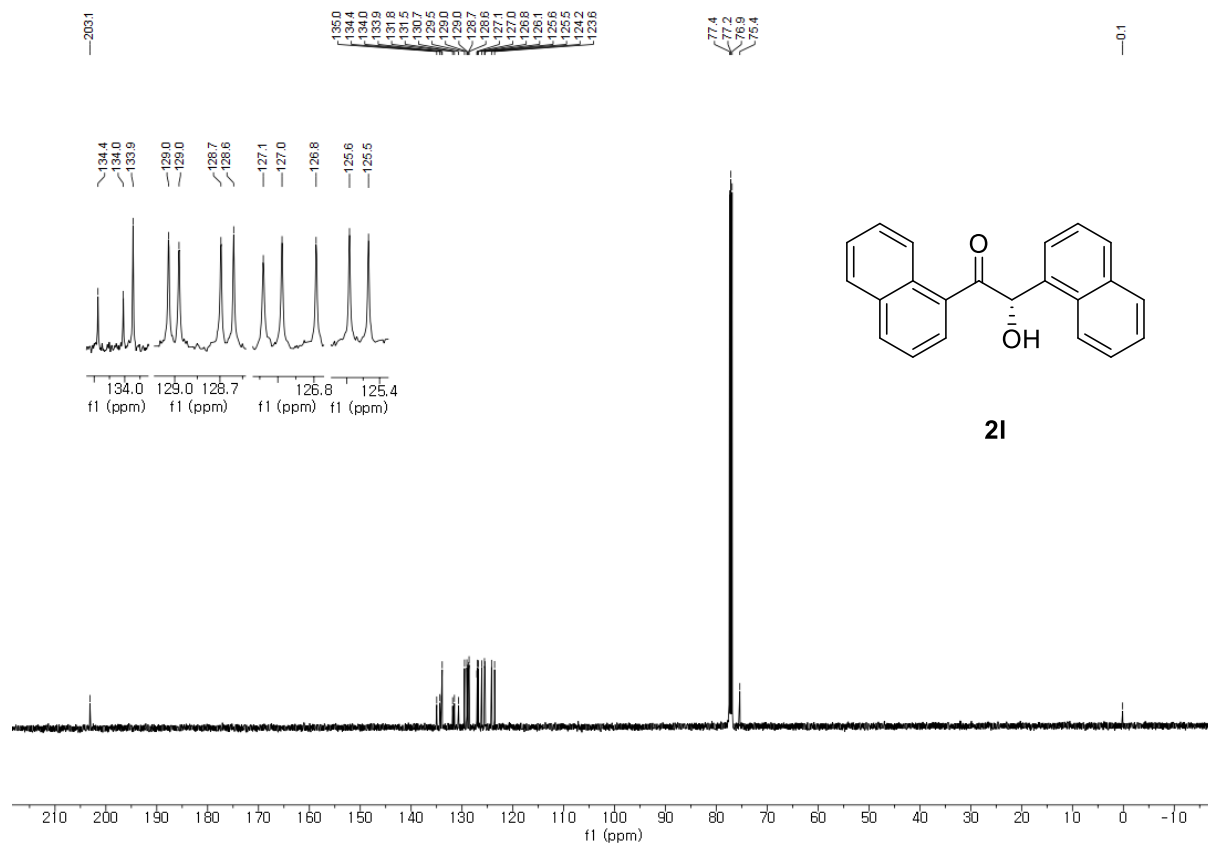
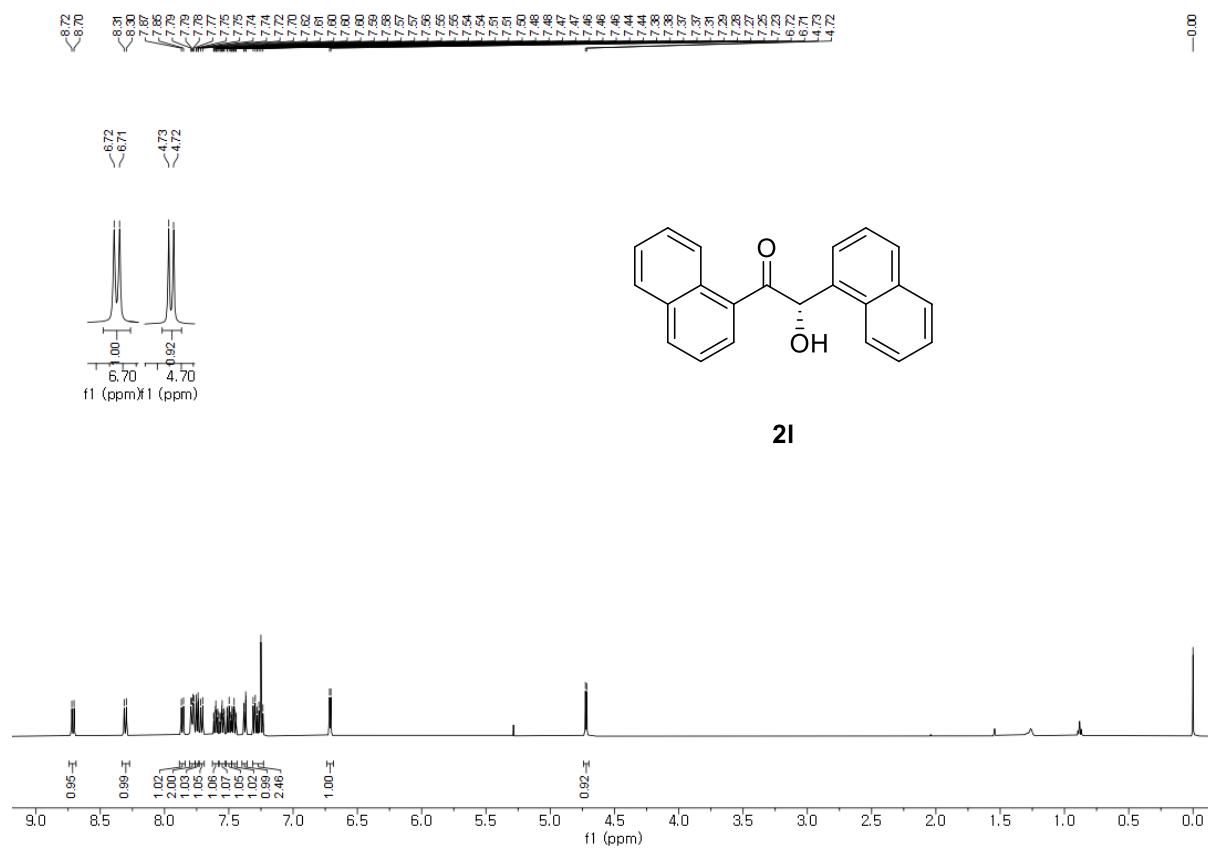




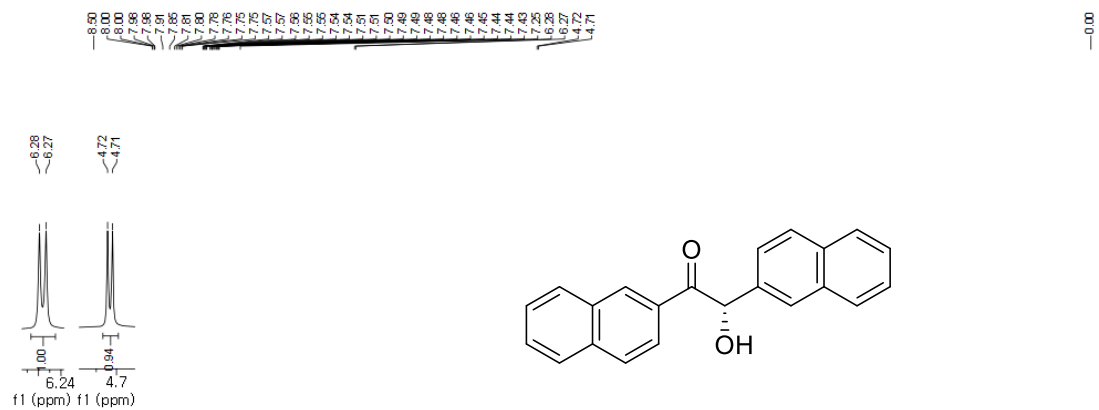






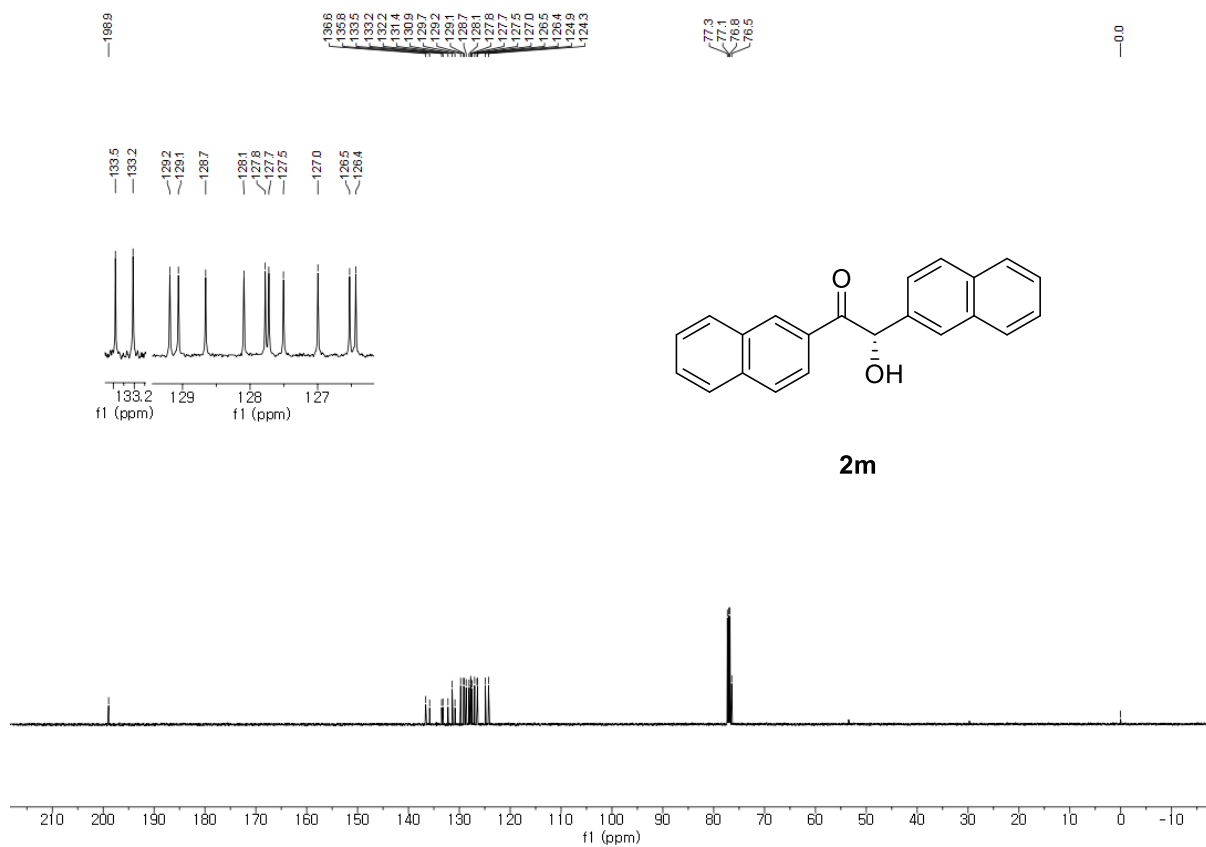






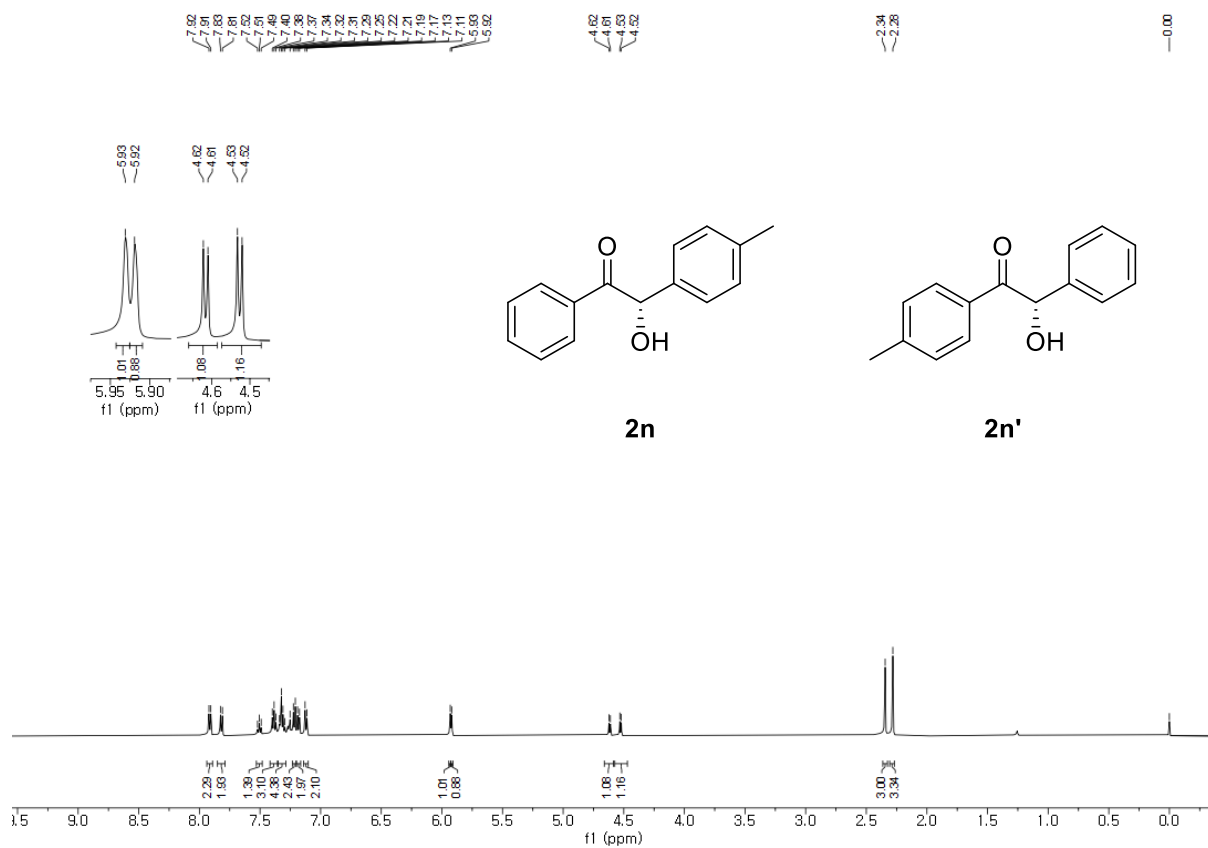
**2m**

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

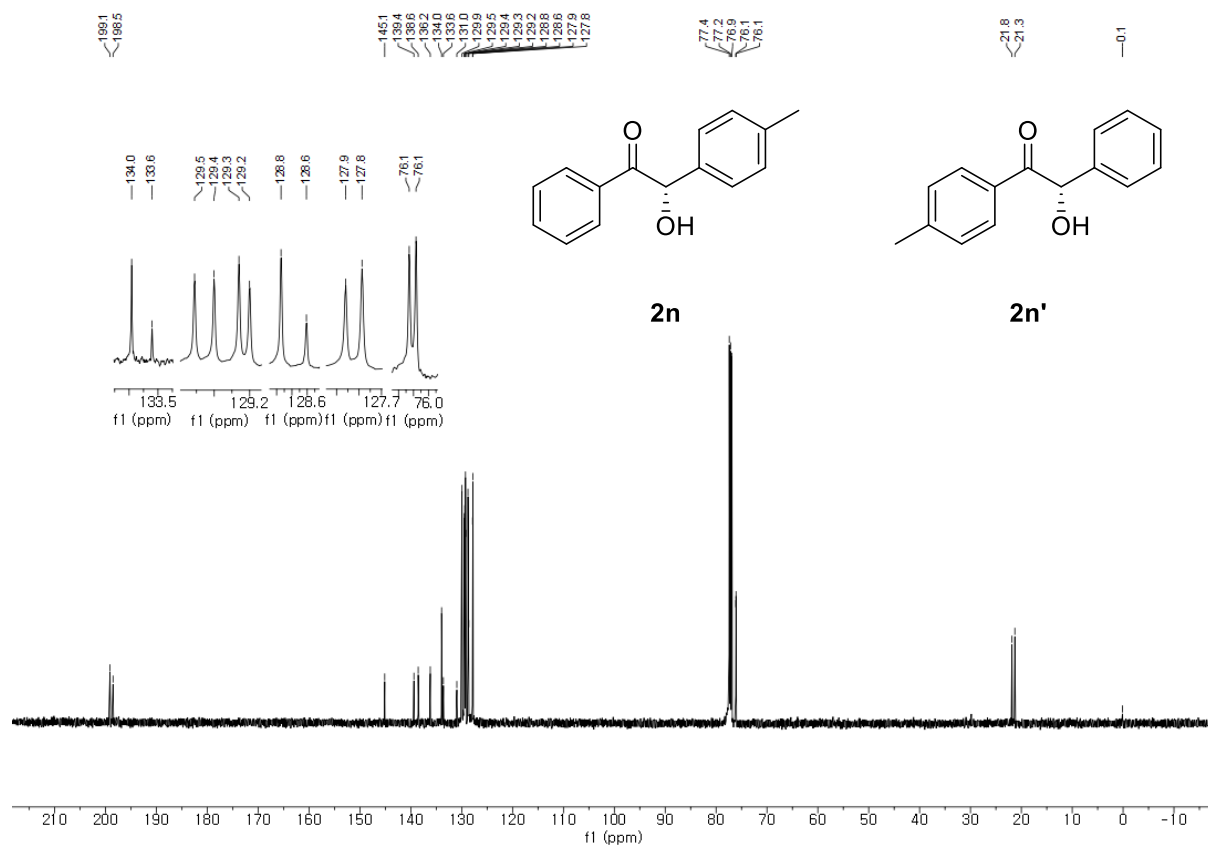


**2m**

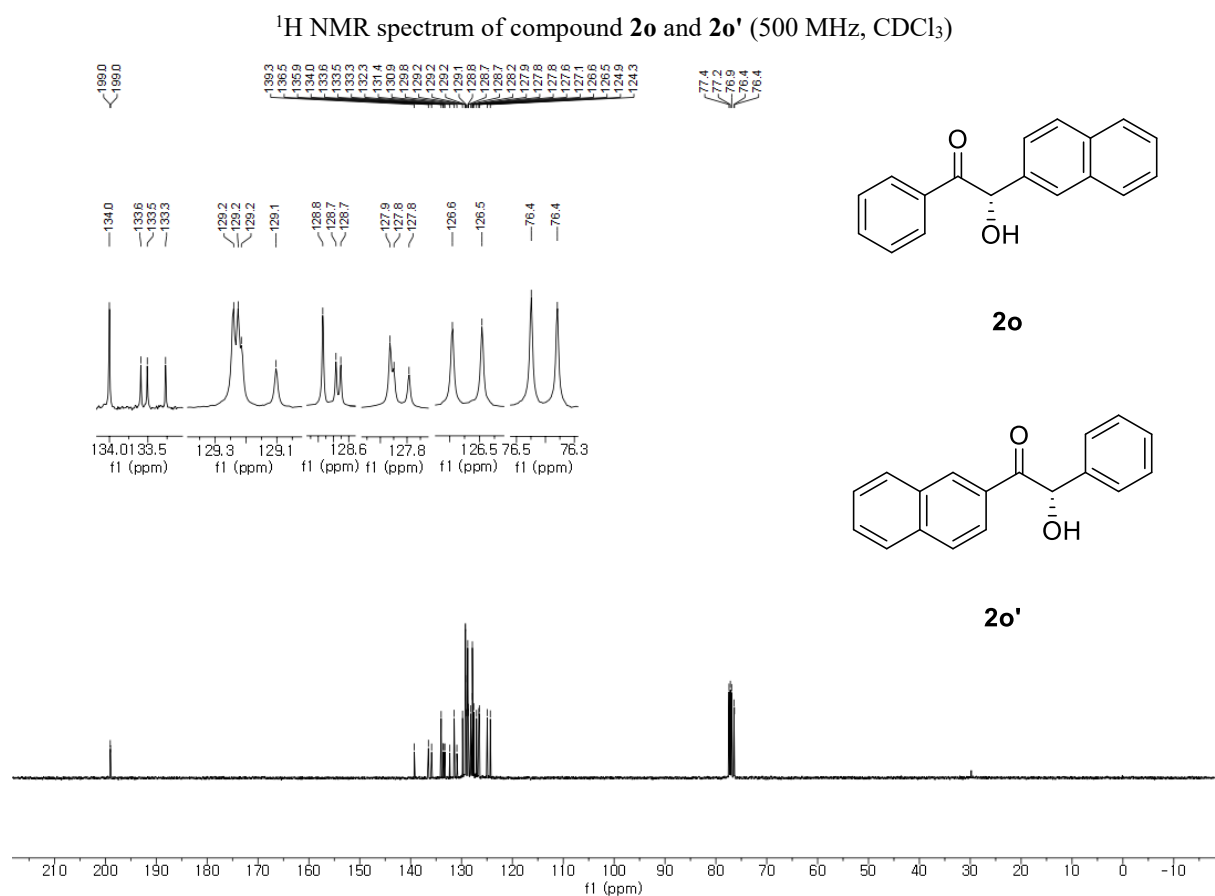
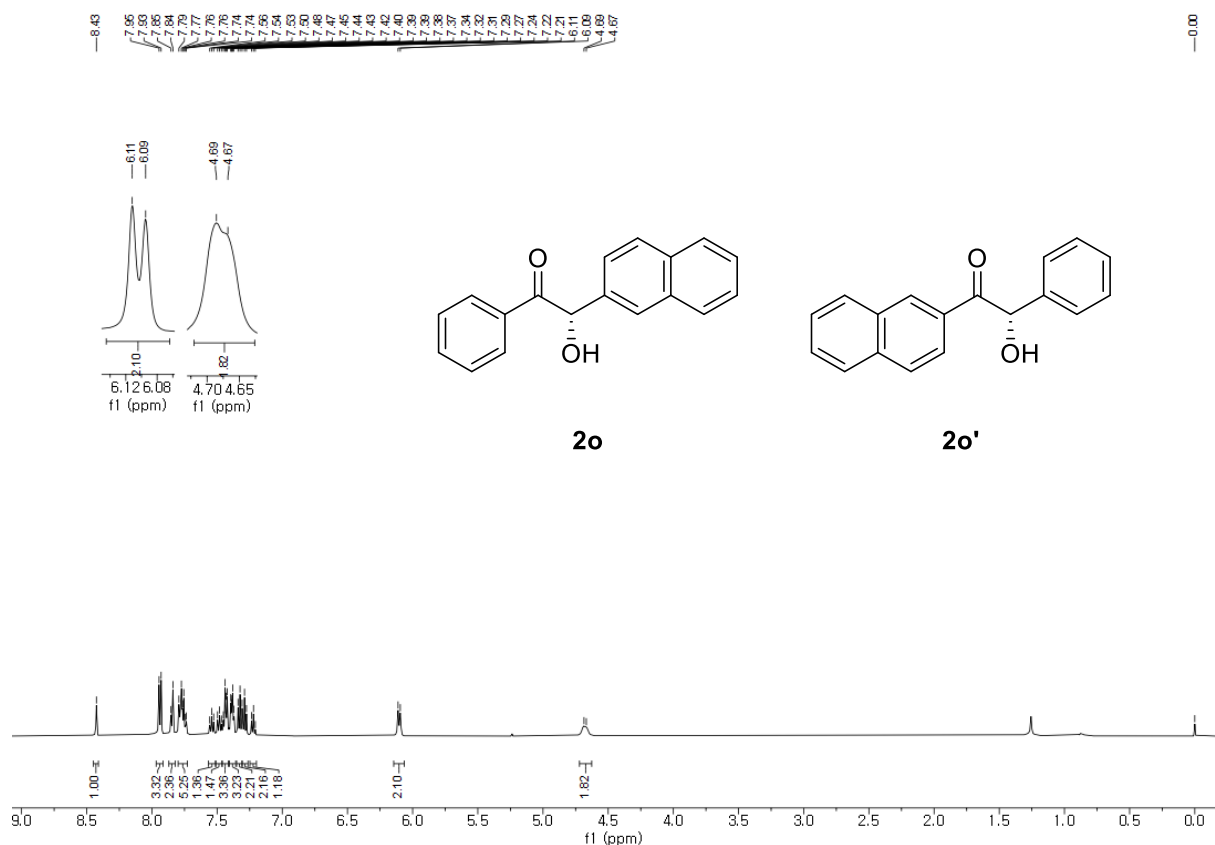
<sup>13</sup>C NMR spectrum of compound **2m** (125 MHz, CDCl<sub>3</sub>)

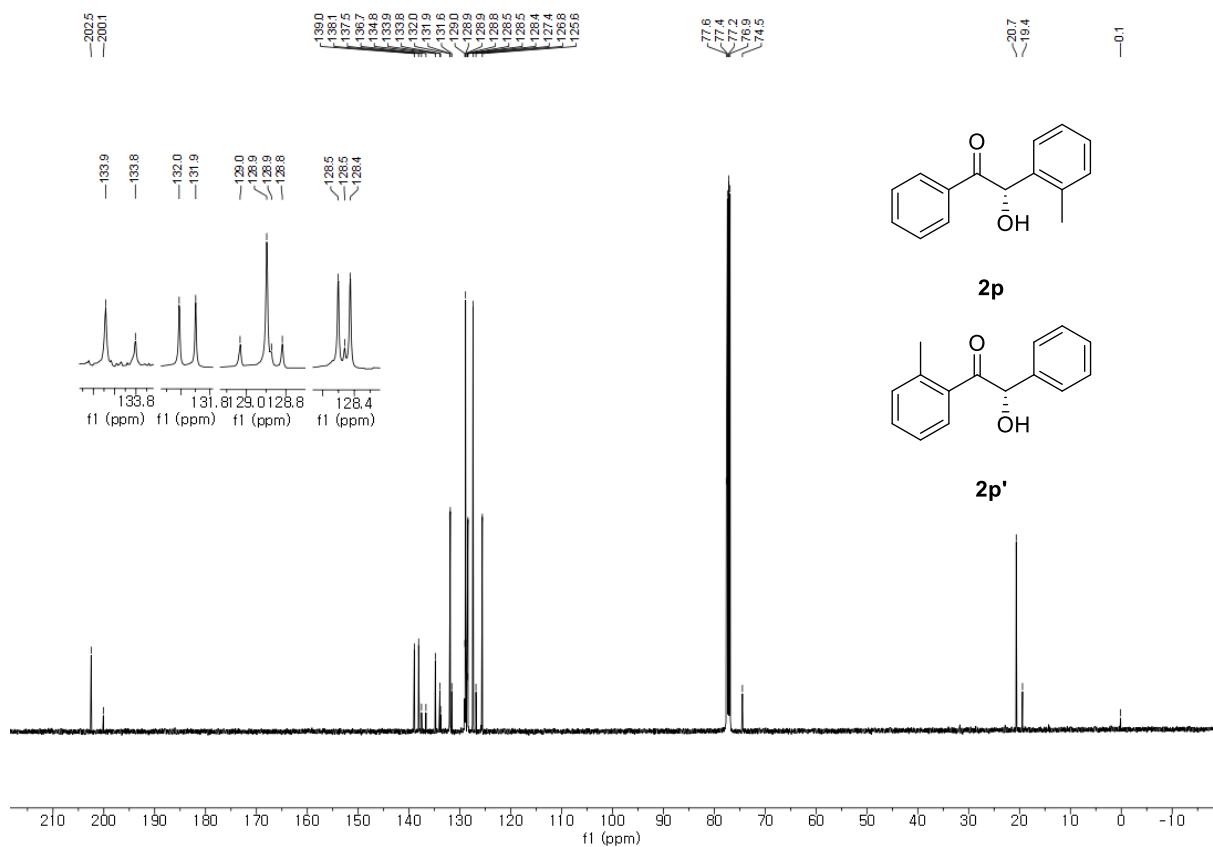
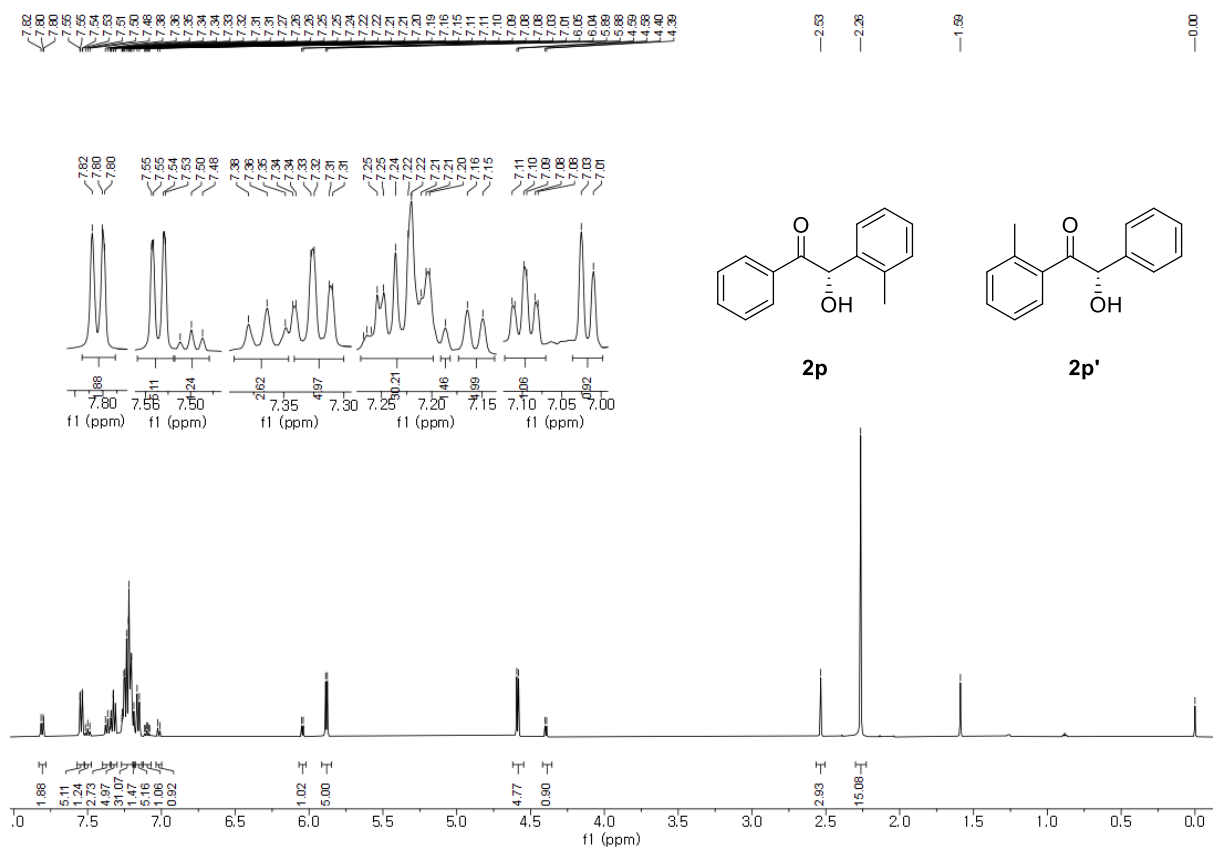


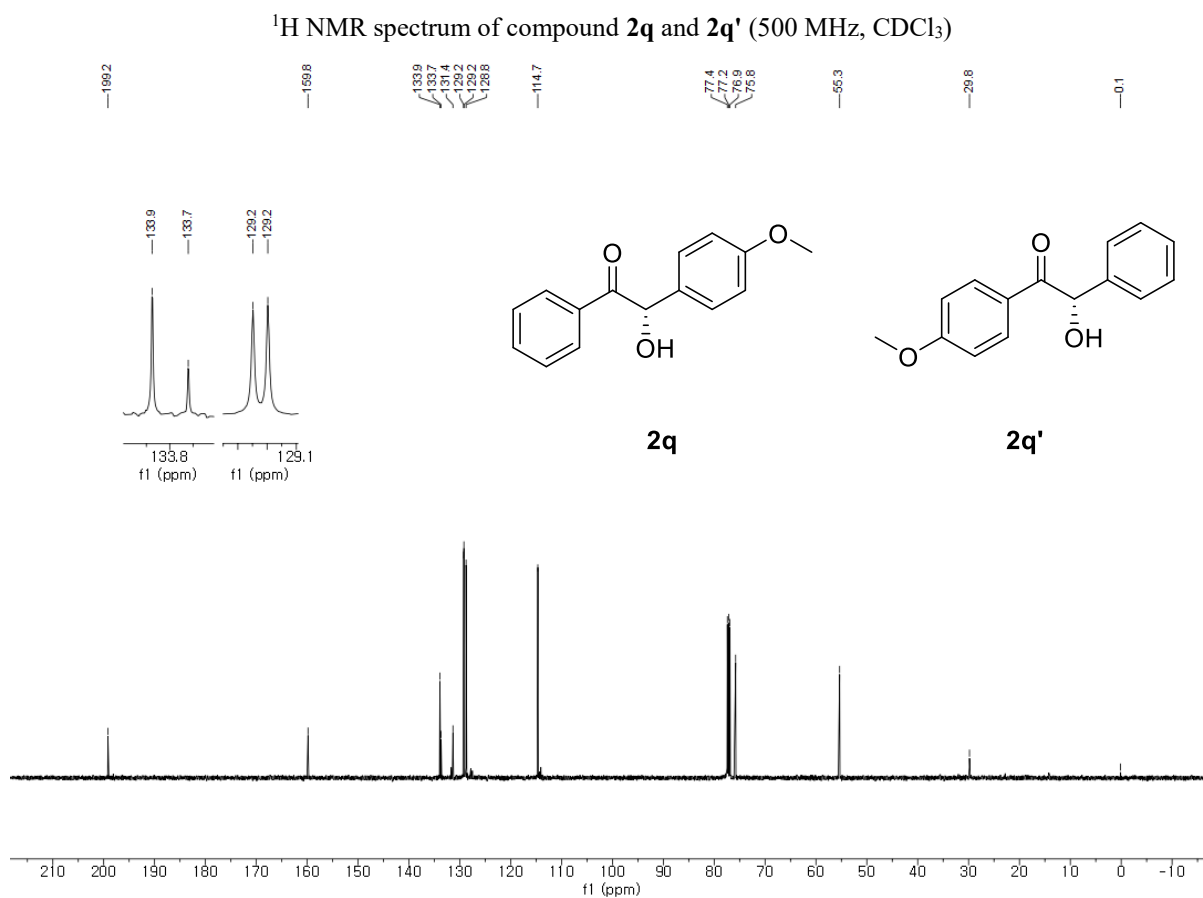
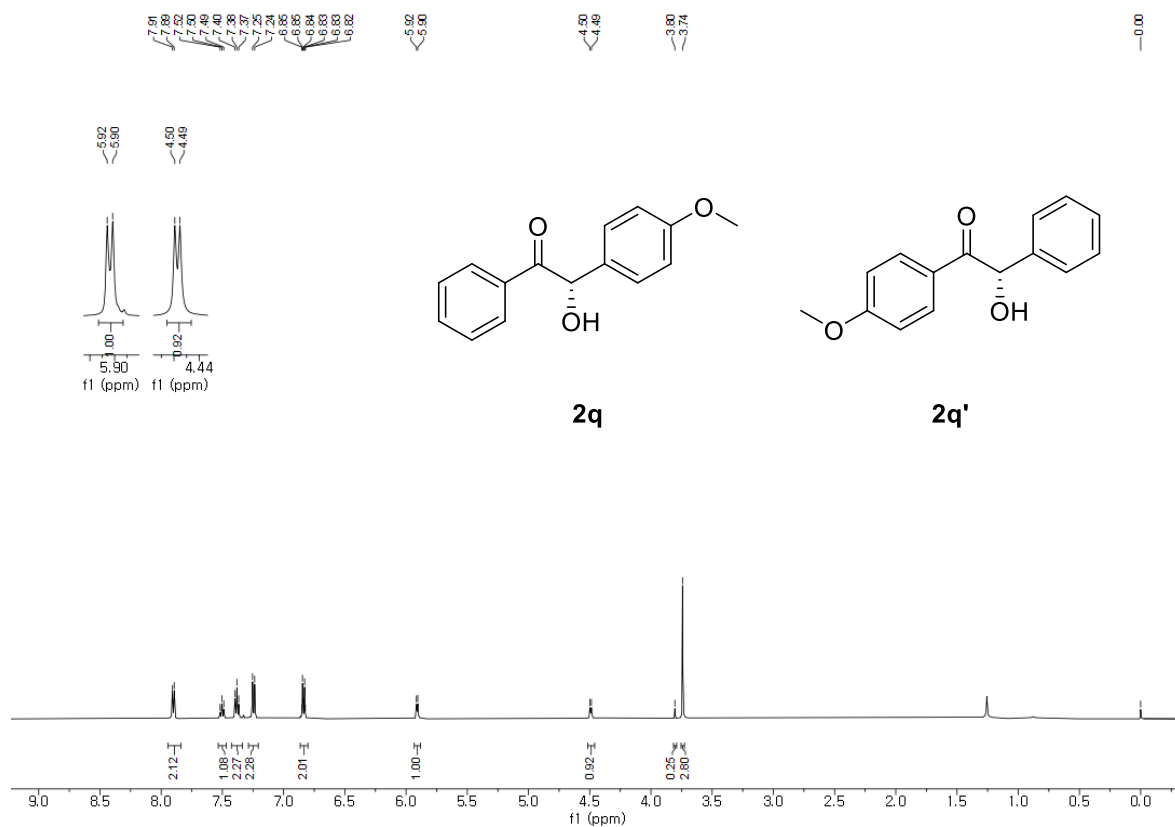
$^1\text{H}$  NMR spectrum of compound **2n** and **2n'** (500 MHz,  $\text{CDCl}_3$ )

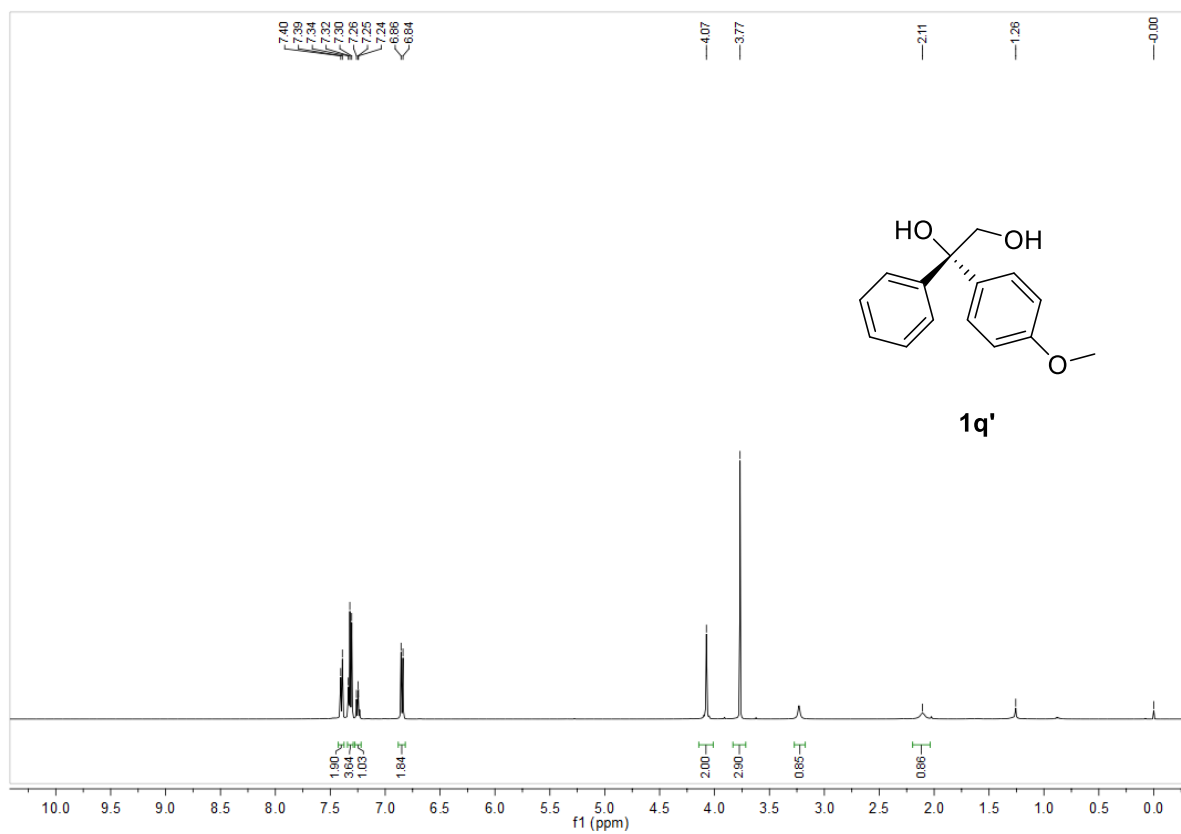


$^{13}\text{C}$  NMR spectrum of compound **2n** and **2n'** (125 MHz,  $\text{CDCl}_3$ )

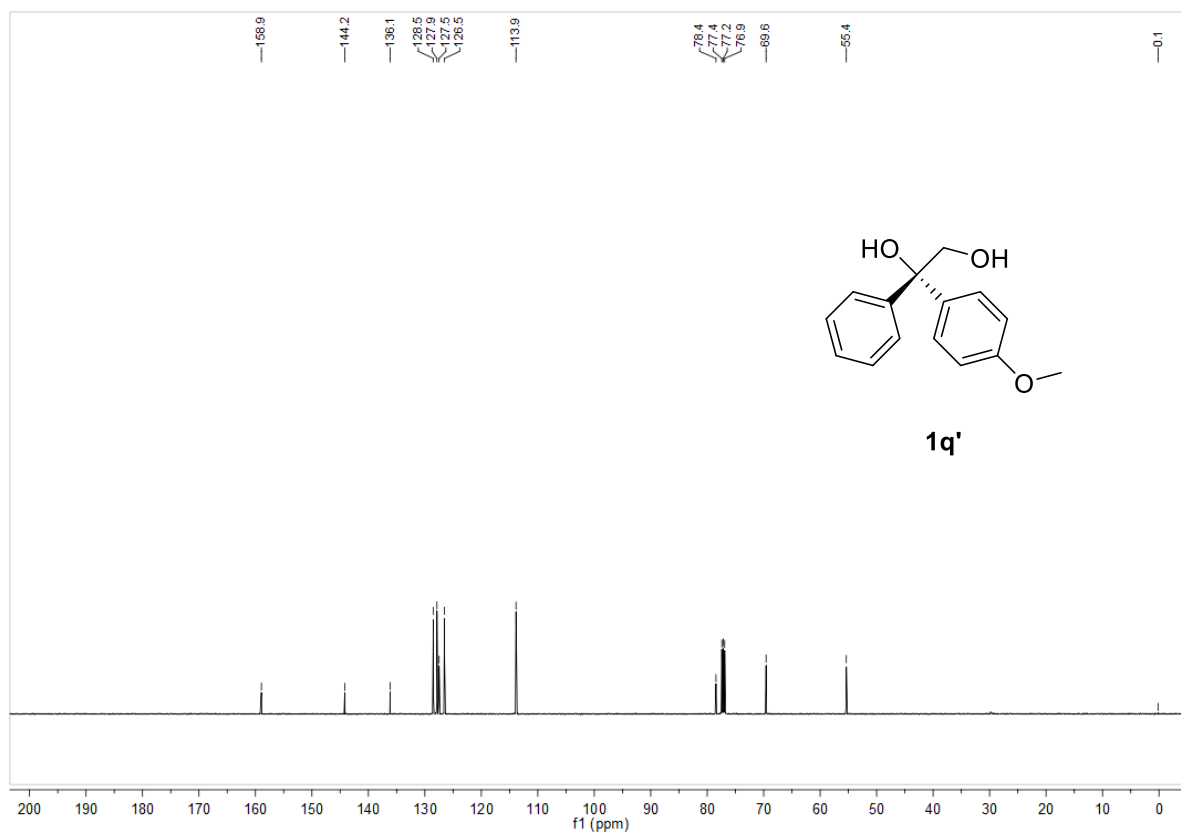




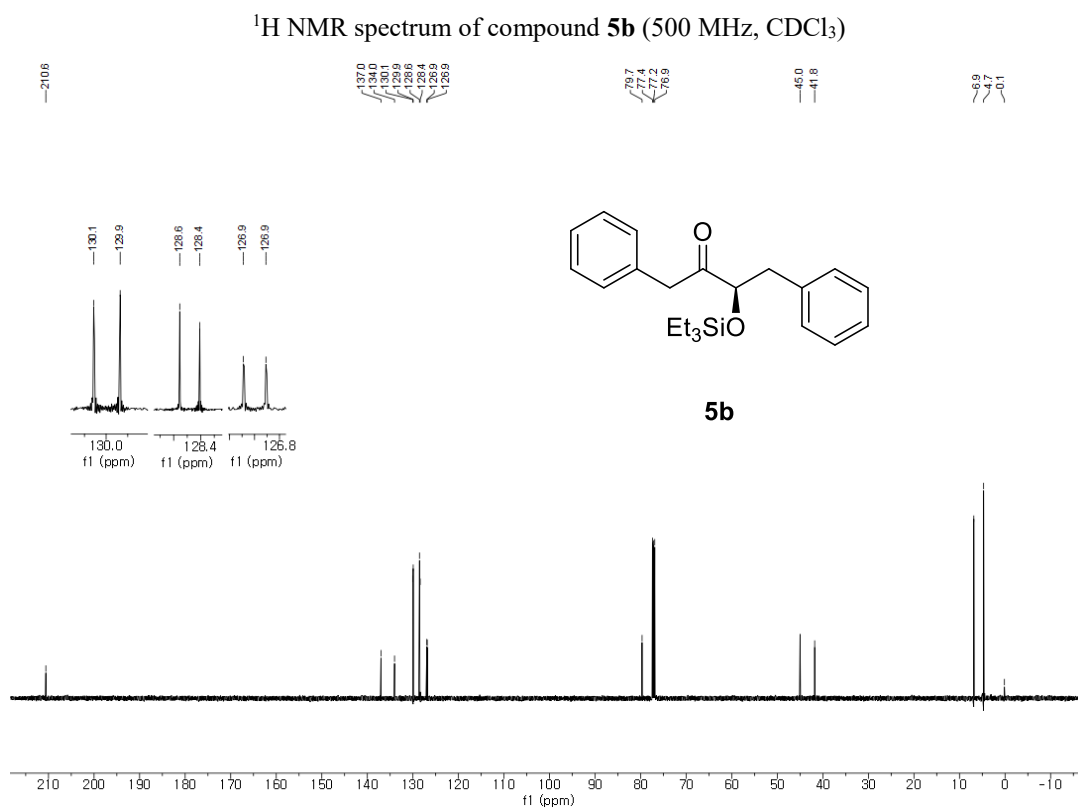
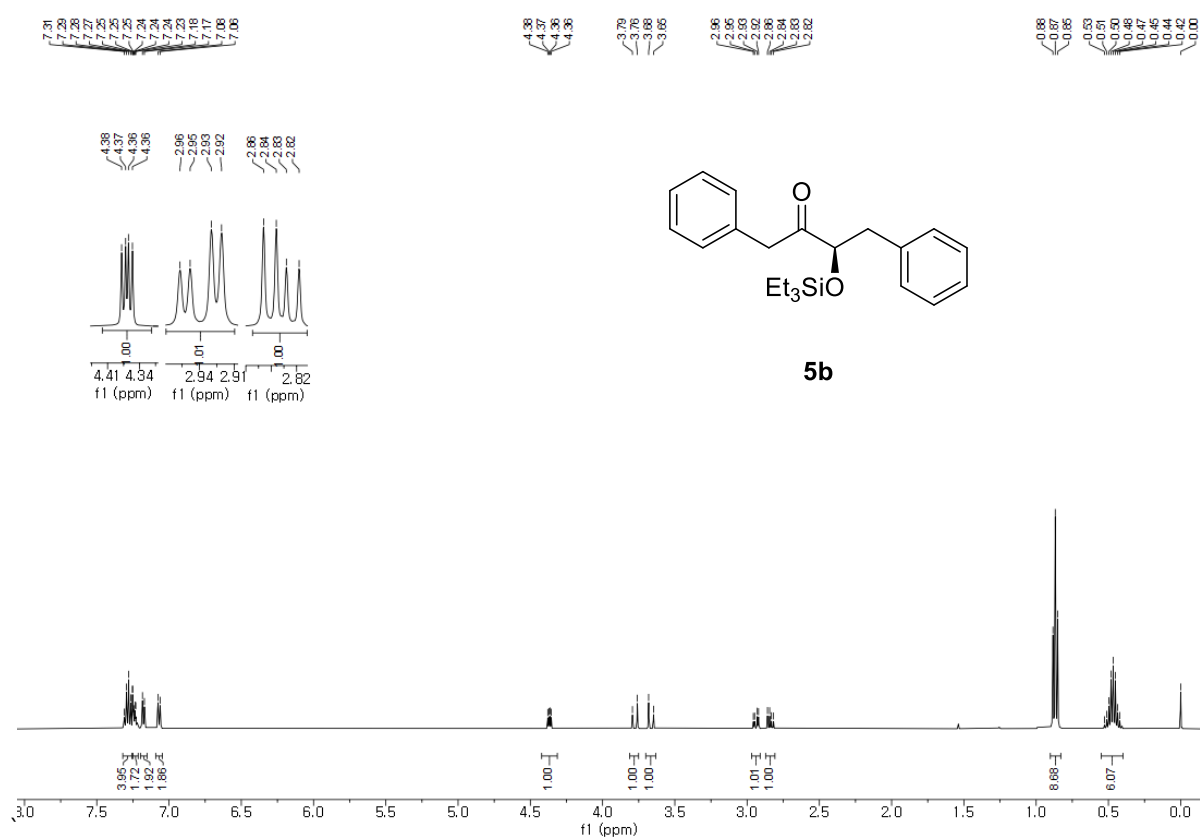


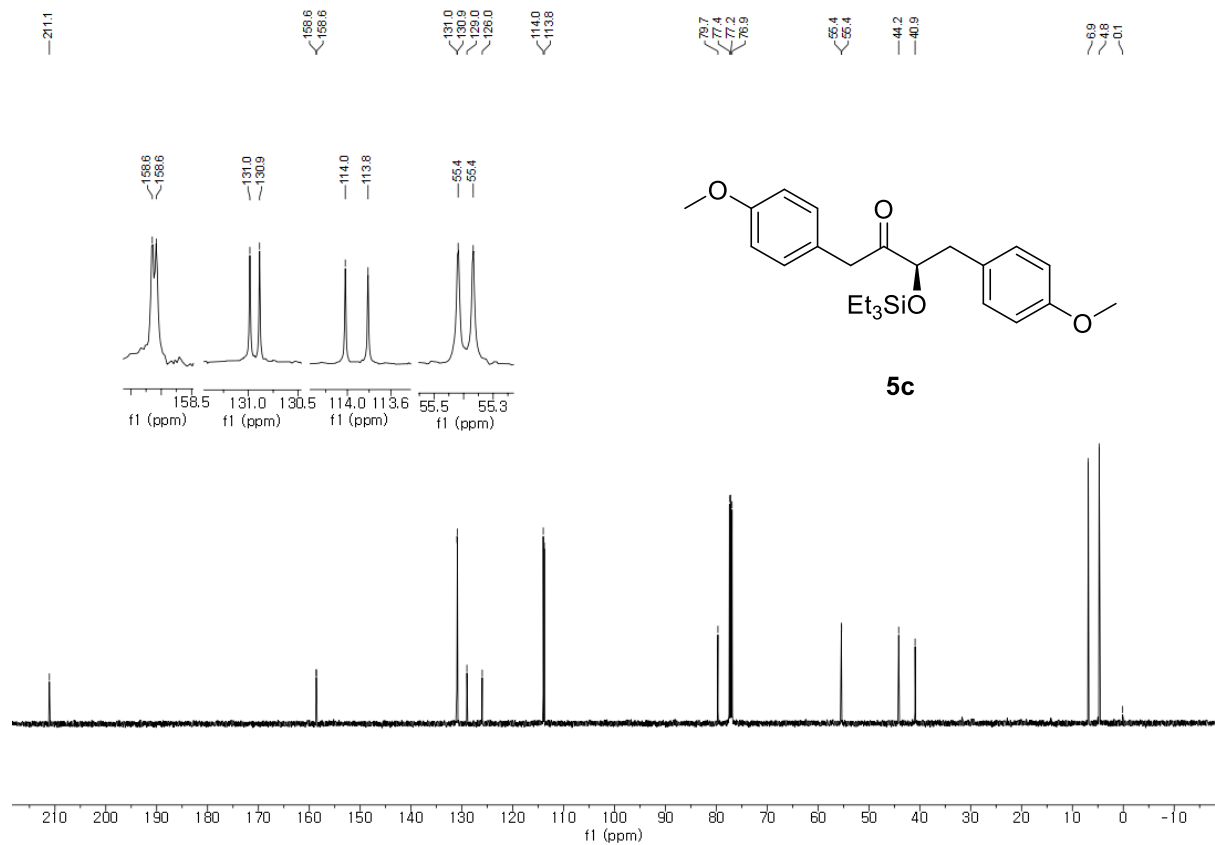


<sup>1</sup>H NMR spectrum of compound **1q'** (500 MHz, CDCl<sub>3</sub>)

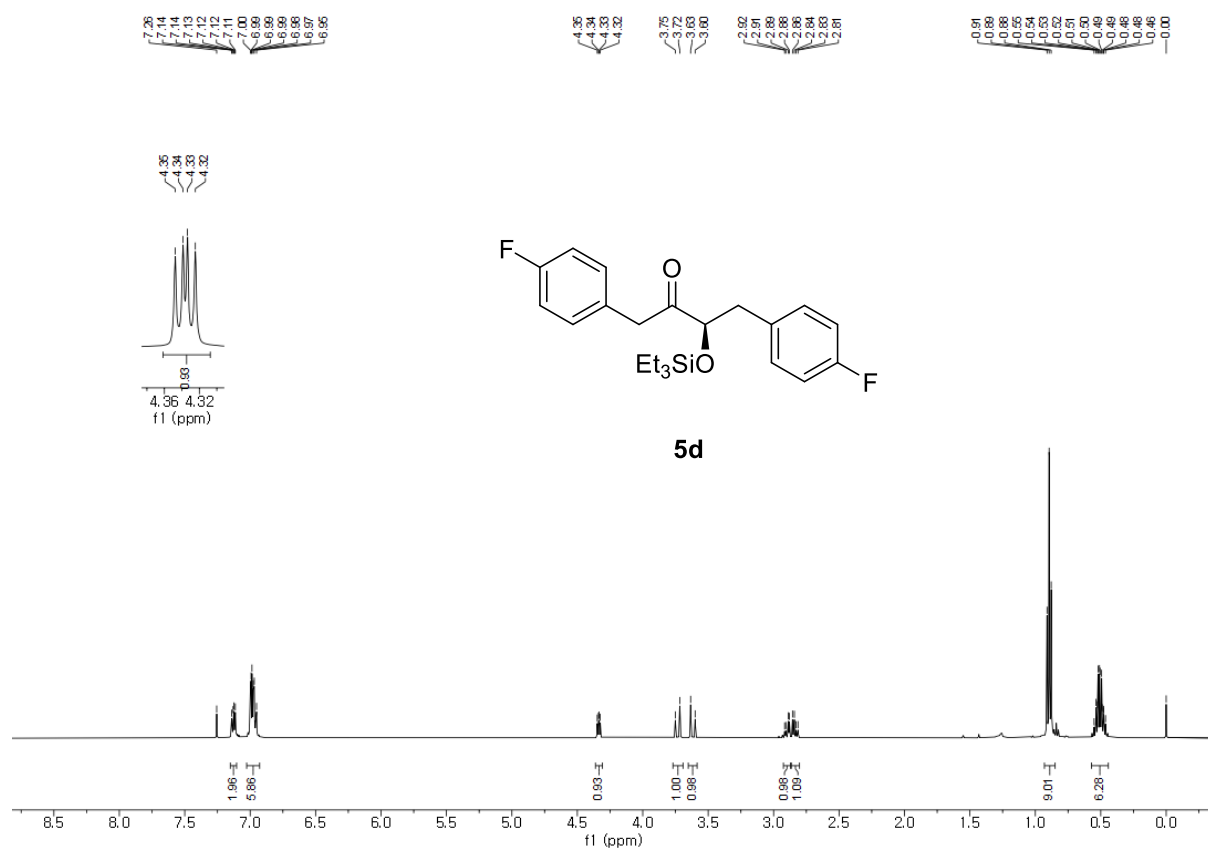


<sup>13</sup>C NMR spectrum of compound **1q'** (125 MHz, CDCl<sub>3</sub>)

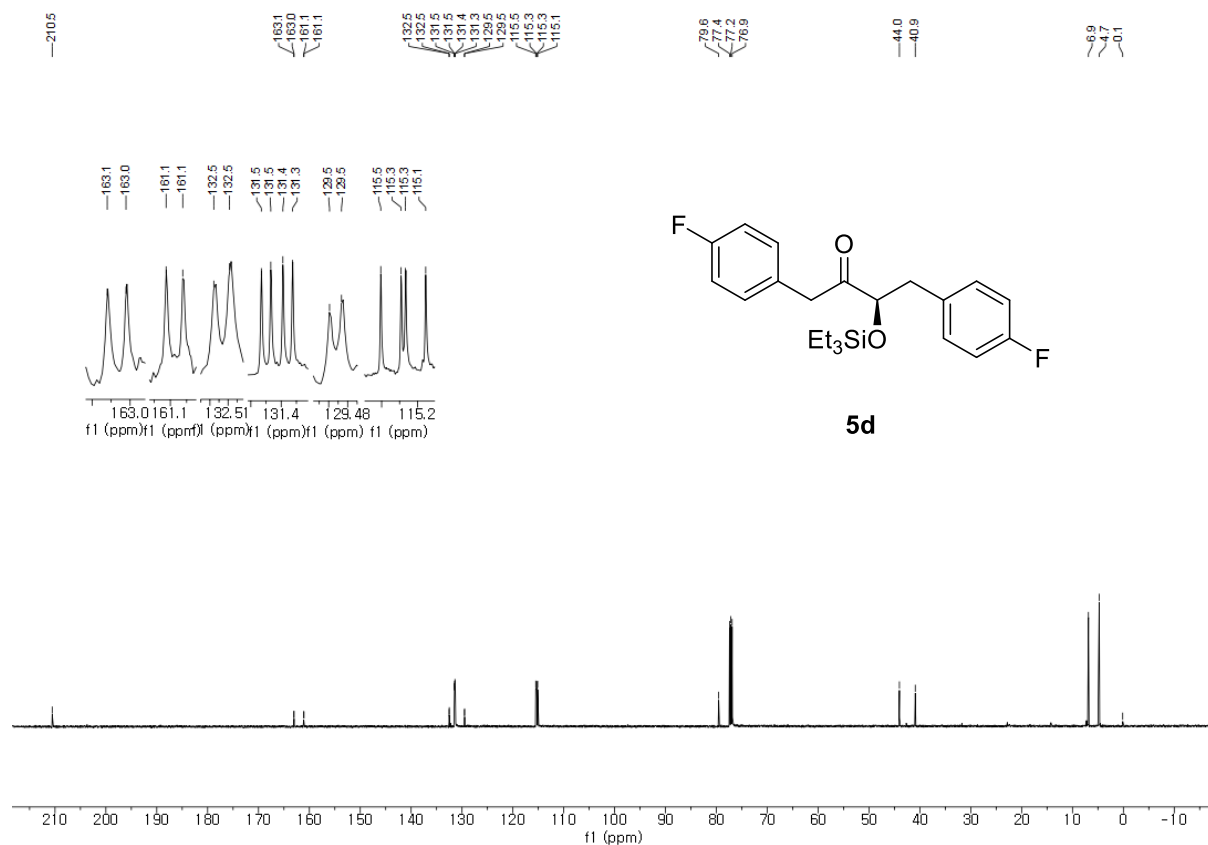




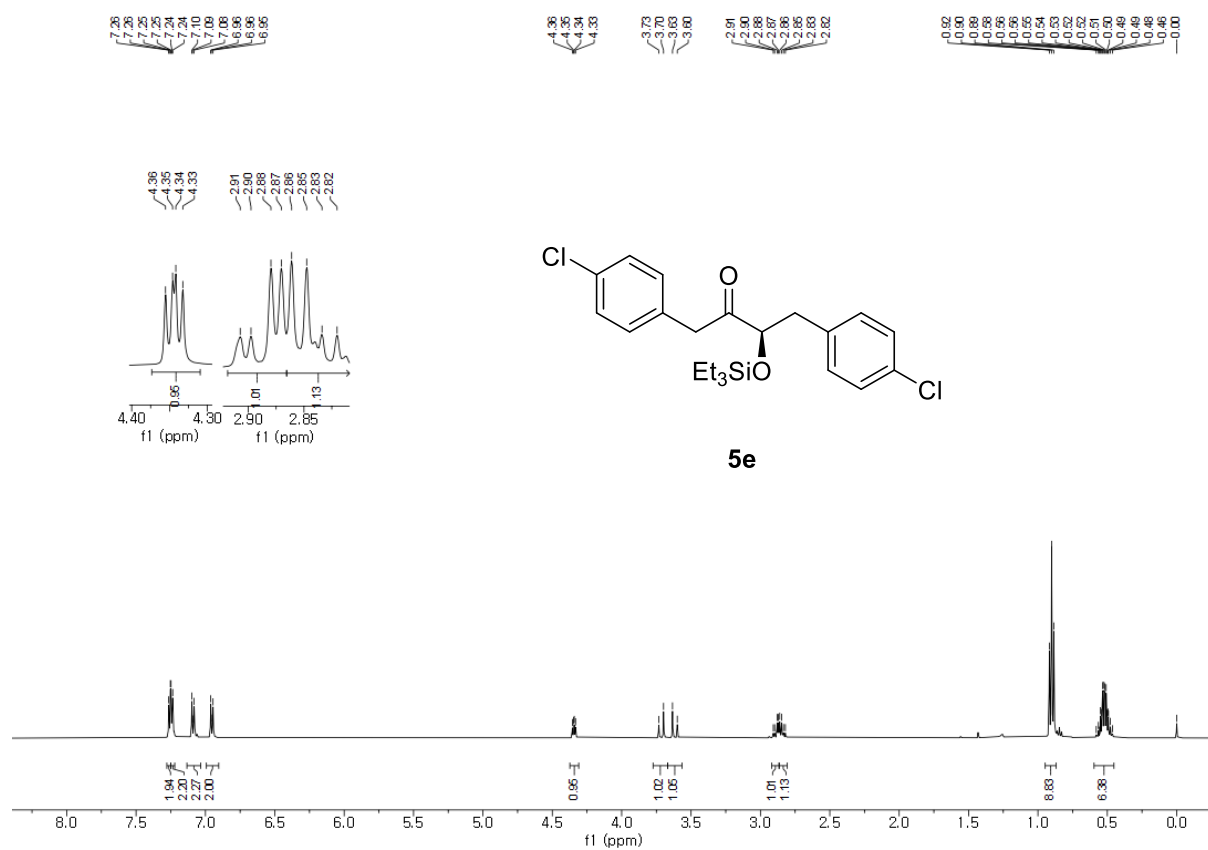




<sup>1</sup>H NMR spectrum of compound **5d** (500 MHz, CDCl<sub>3</sub>)



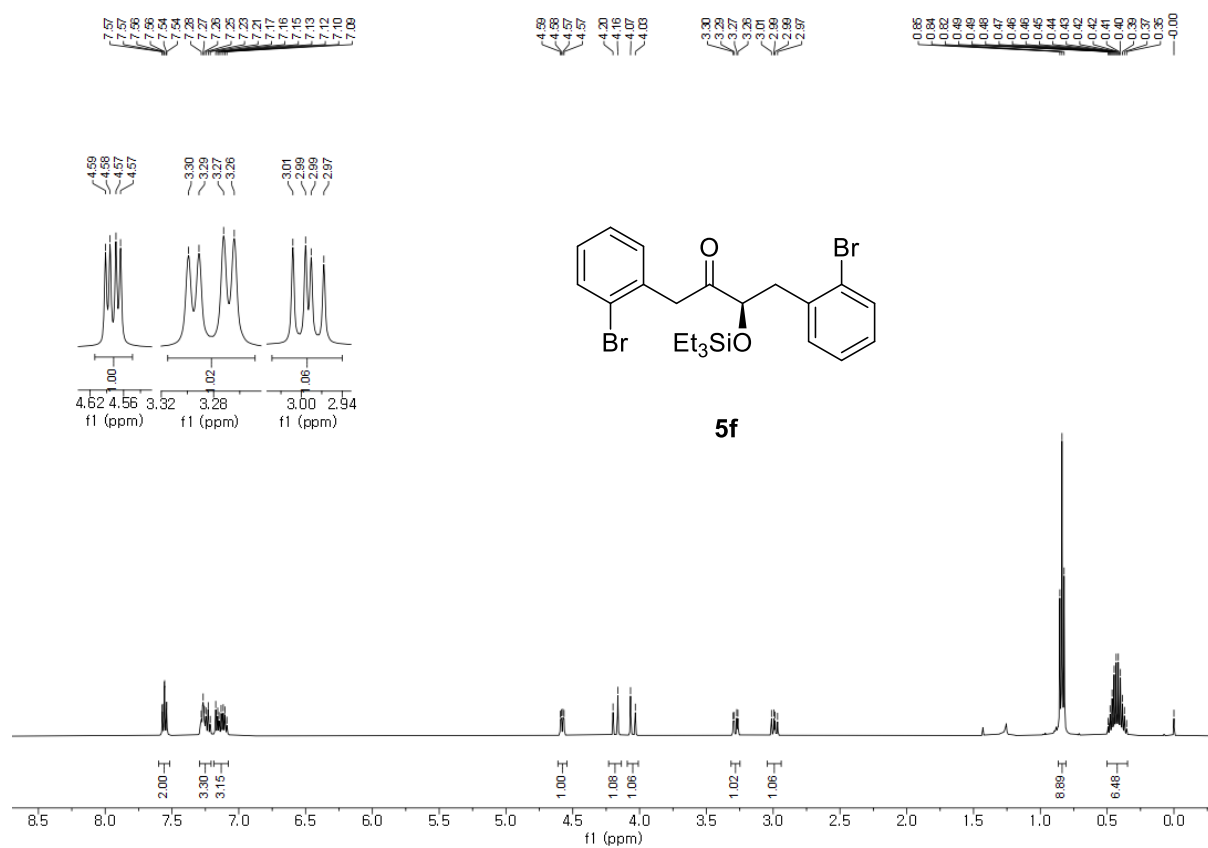
<sup>13</sup>C NMR spectrum of compound **5d** (125 MHz, CDCl<sub>3</sub>)



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



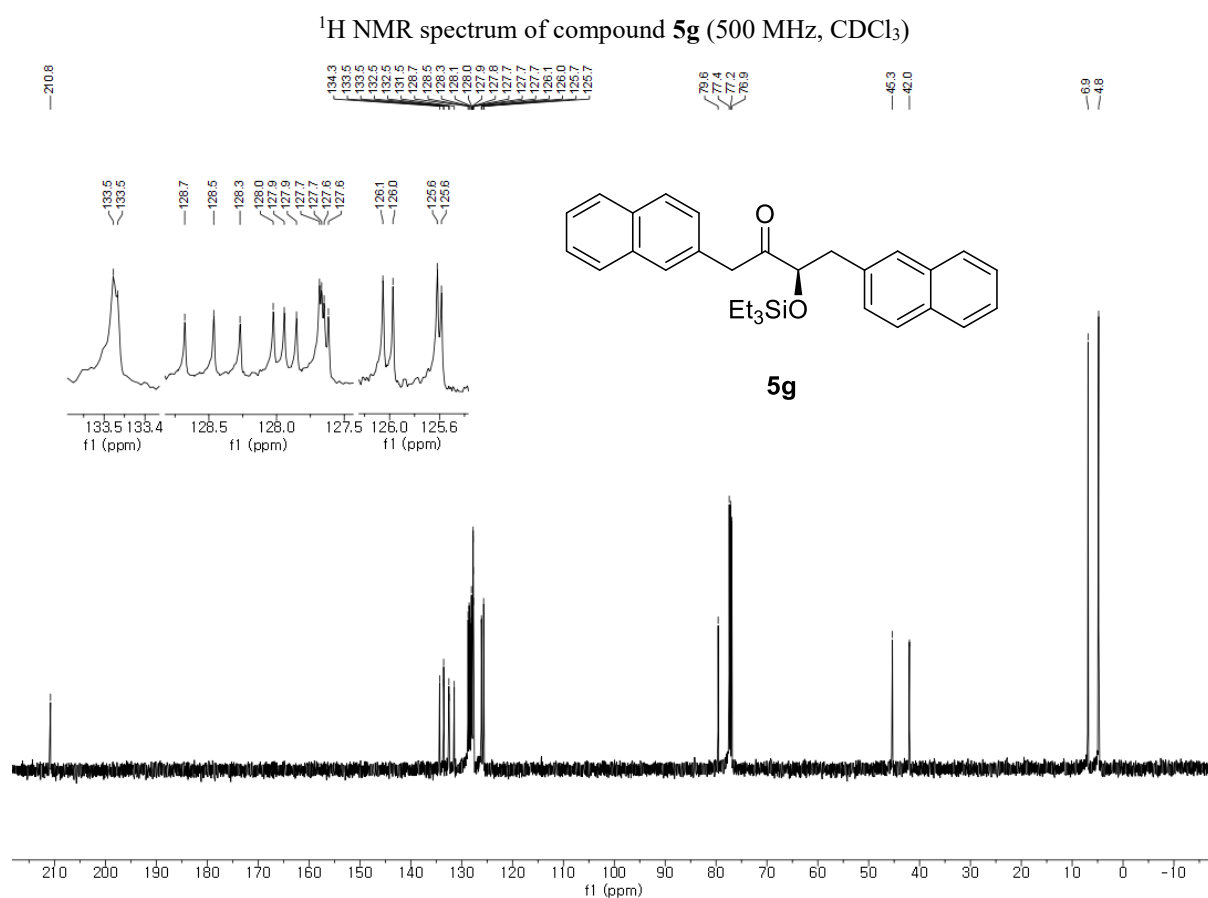
<sup>13</sup>C NMR spectrum of compound **5e** (125 MHz, CDCl<sub>3</sub>)

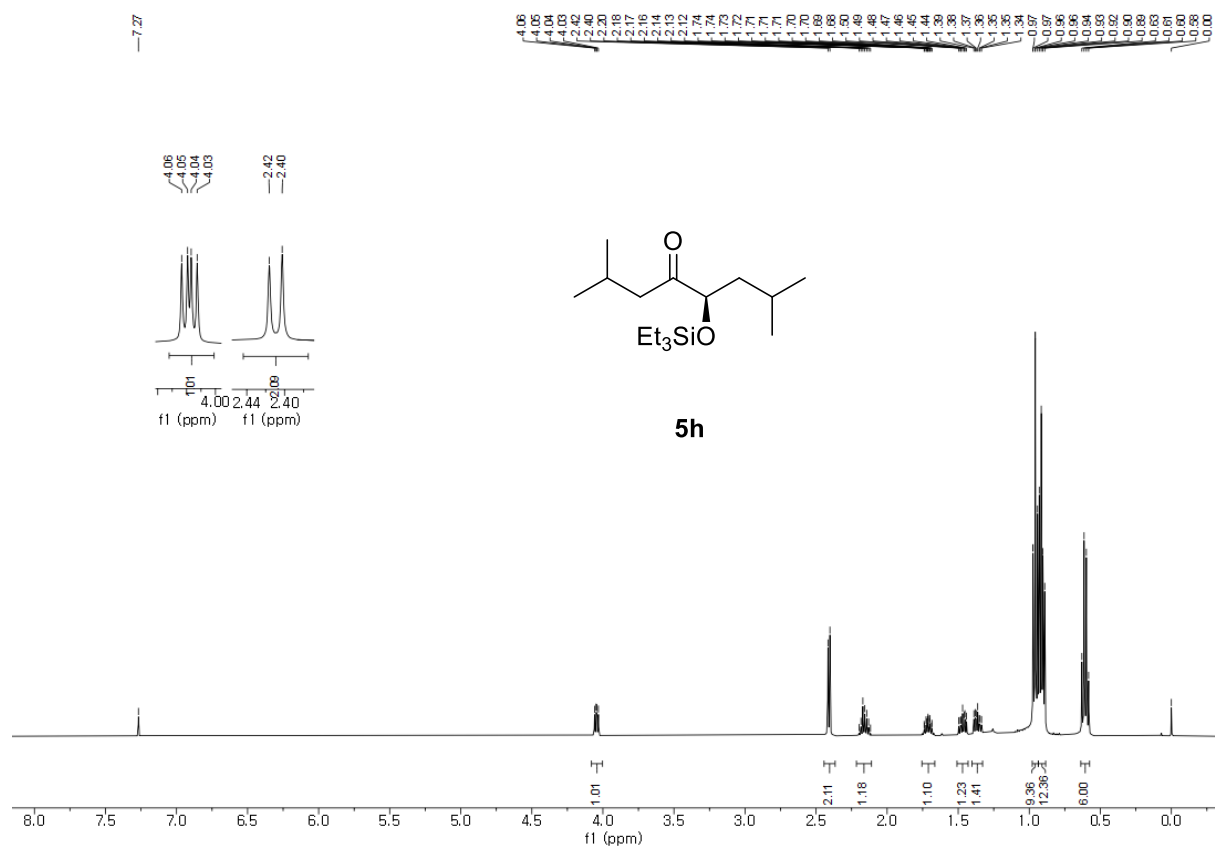


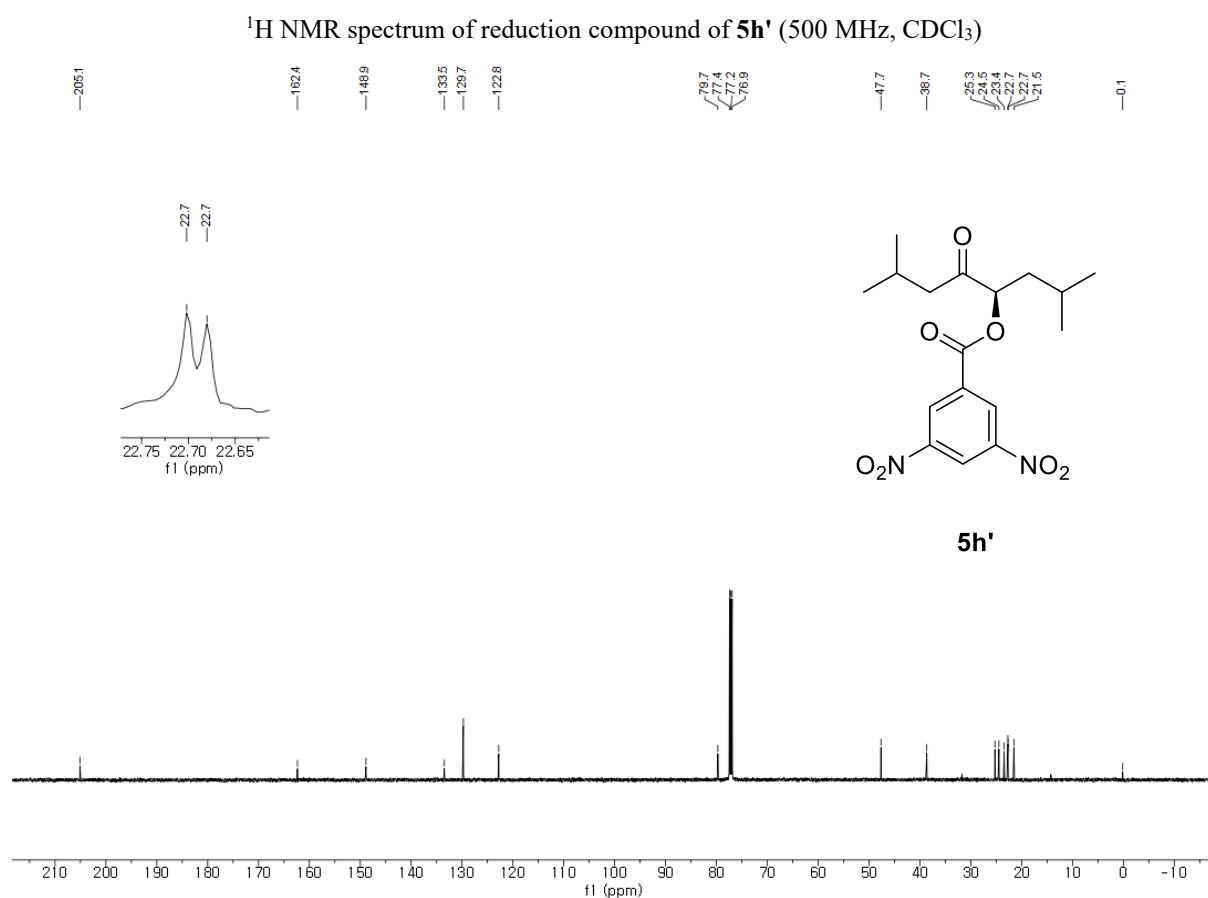
<sup>1</sup>H NMR spectrum of compound **5f** (500 MHz, CDCl<sub>3</sub>)

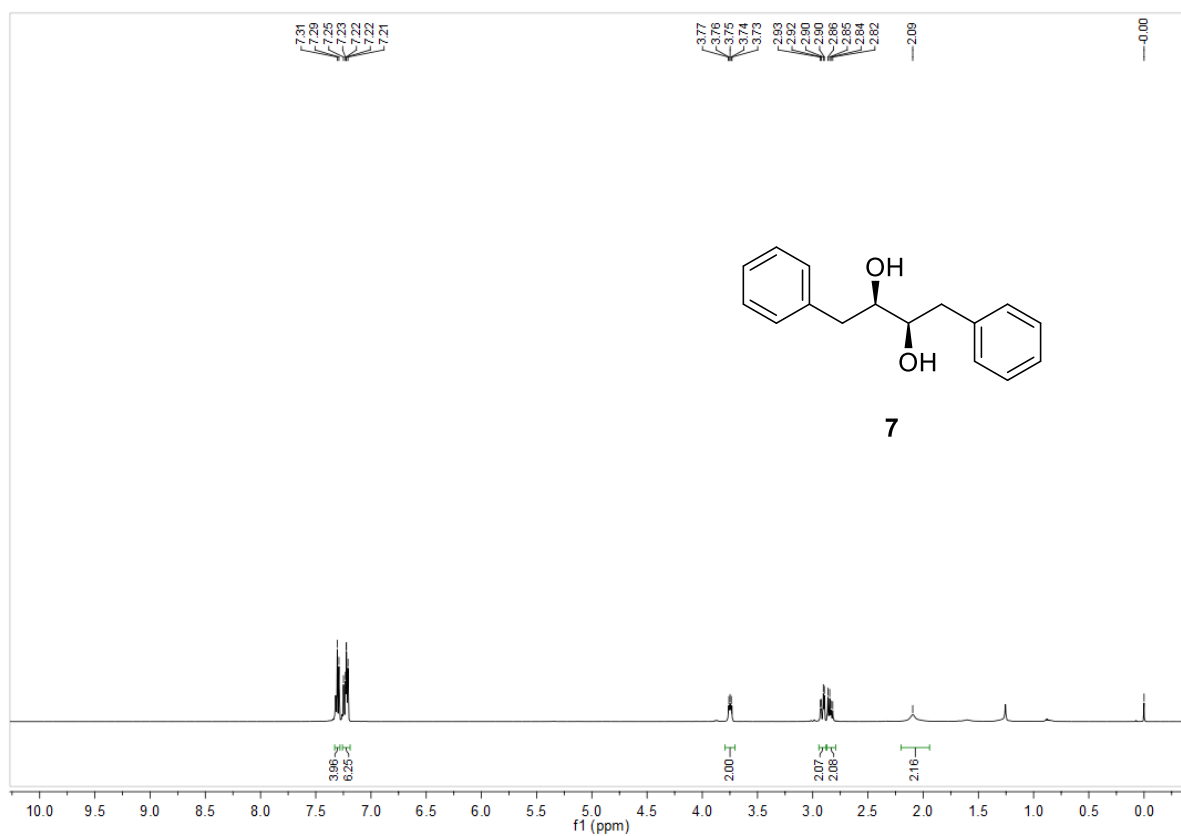


<sup>13</sup>C NMR spectrum of compound **5f** (125 MHz, CDCl<sub>3</sub>)

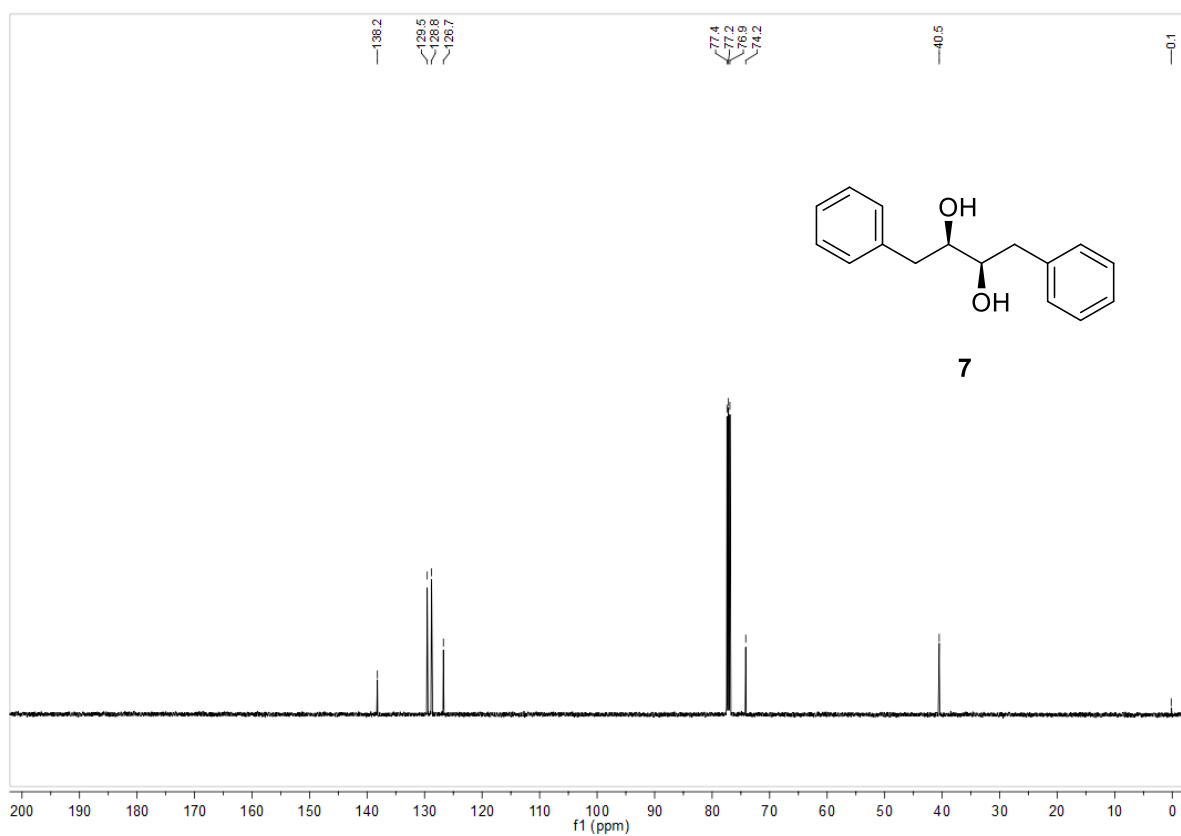






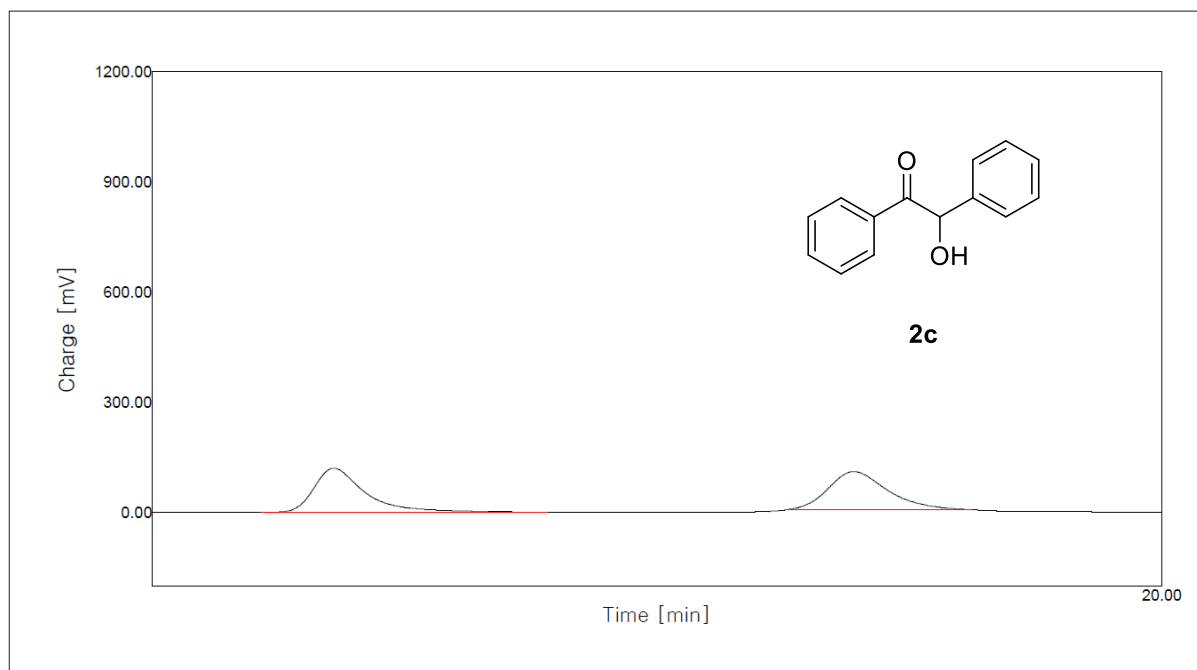


<sup>1</sup>H NMR spectrum of compound 7 (500 MHz, CDCl<sub>3</sub>)



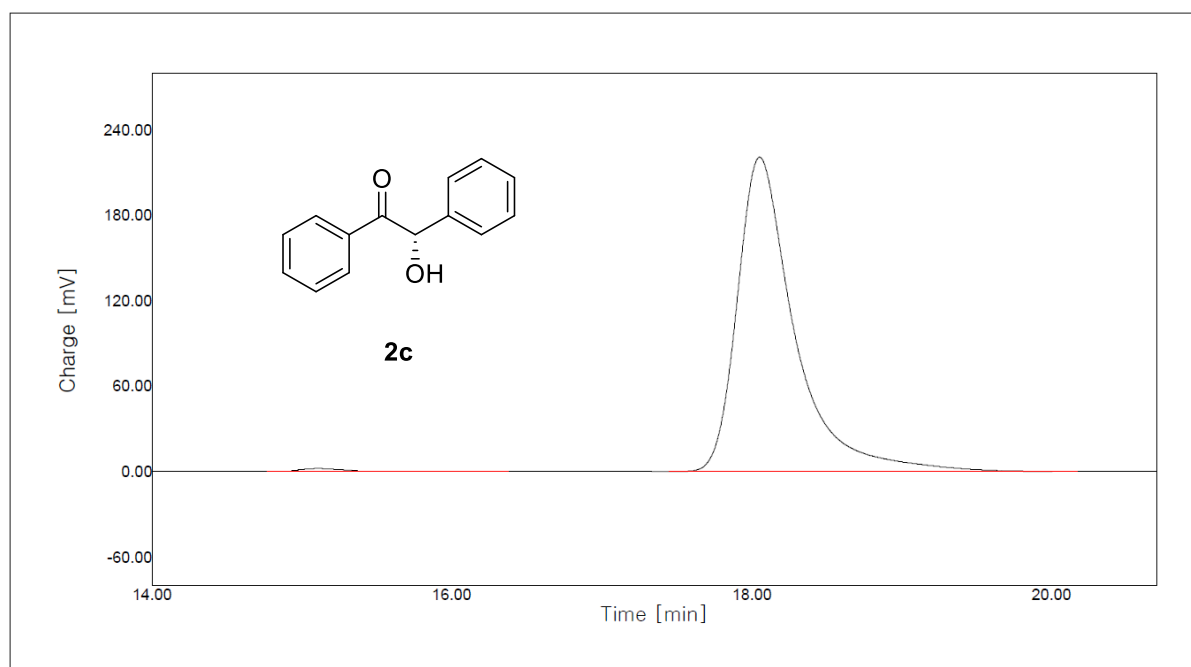
<sup>13</sup>C NMR spectrum of compound 7 (125 MHz, CDCl<sub>3</sub>)

## 10. HPLC Spectra



### Result

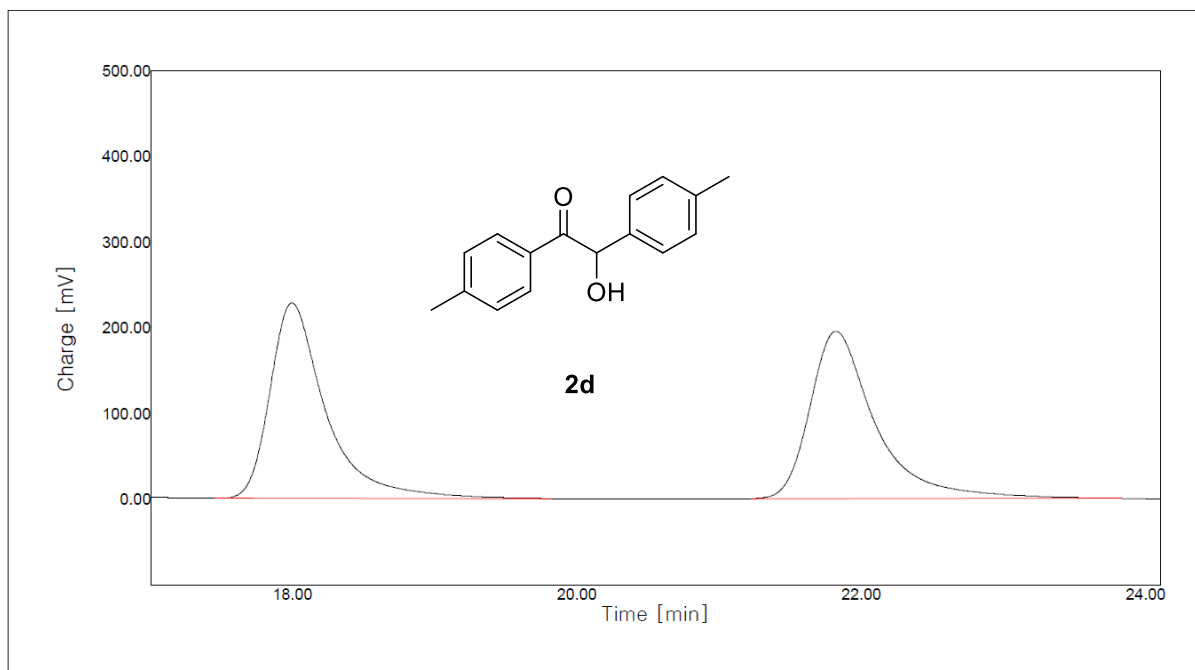
Number	Time (min)	Area (%)
1	15.0833	49.69
2	18.1733	50.31



### Result

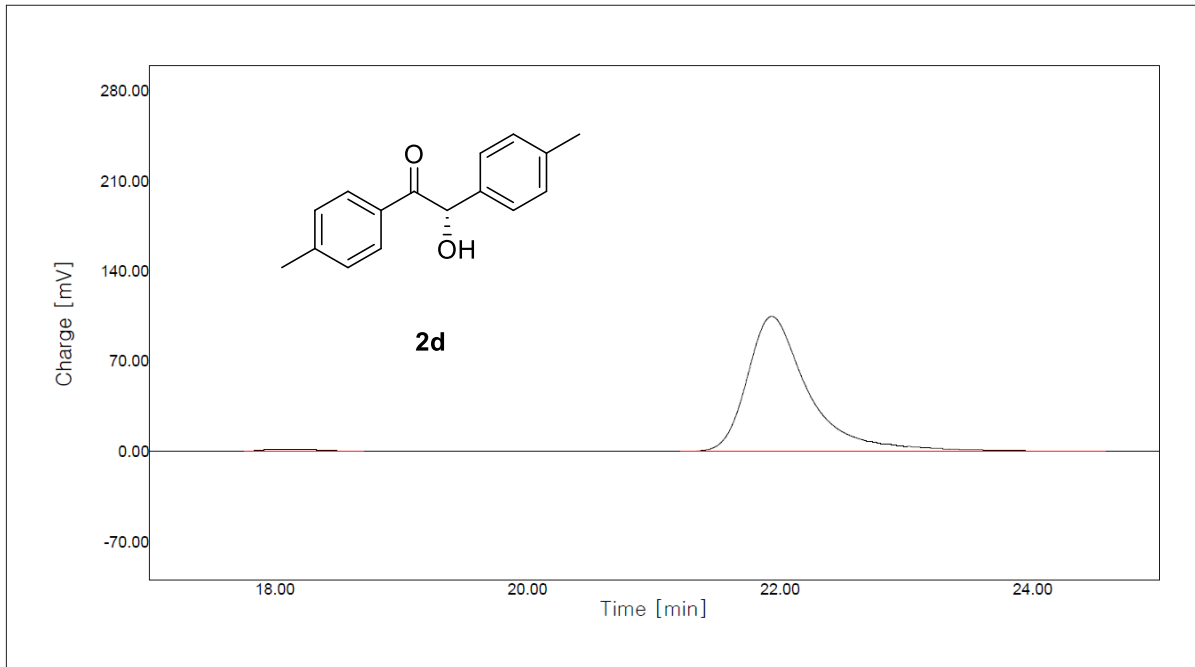
Number	Time (min)	Area (%)
1	15.1100	0.88
2	18.0533	99.12





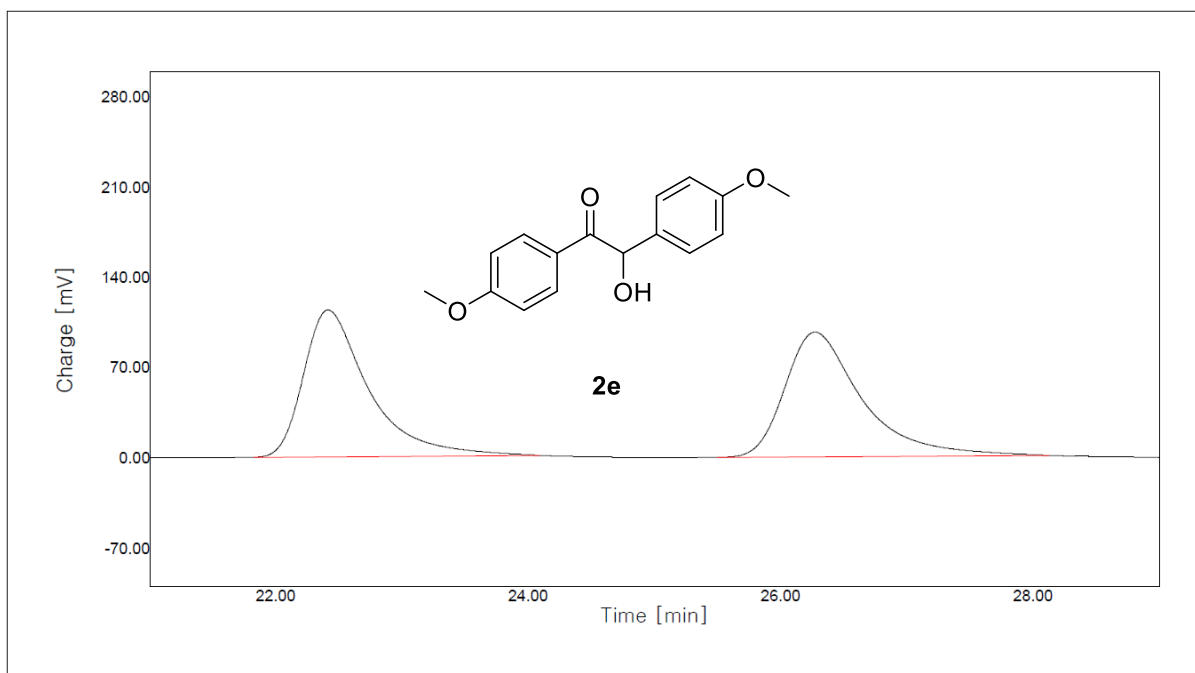
## Result

Number	Time (min)	Area (%)
1	17.9950	49.96
2	21.8200	50.04



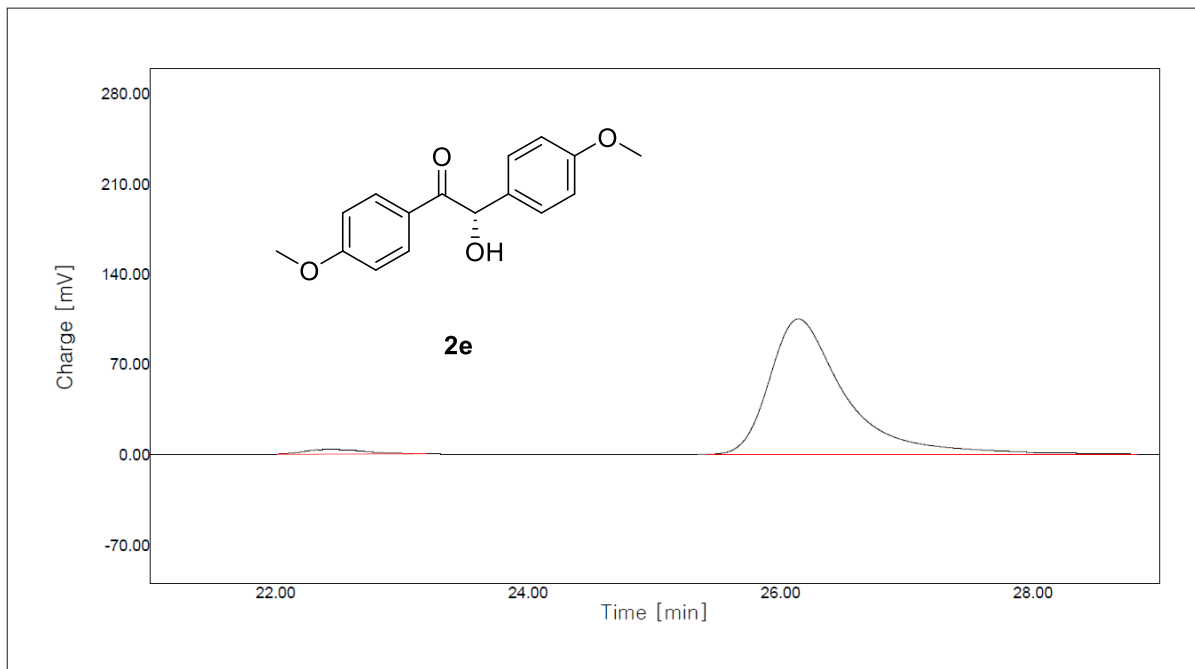
## Result

Number	Time (min)	Area (%)
1	18.0950	1.22
2	21.9333	98.78



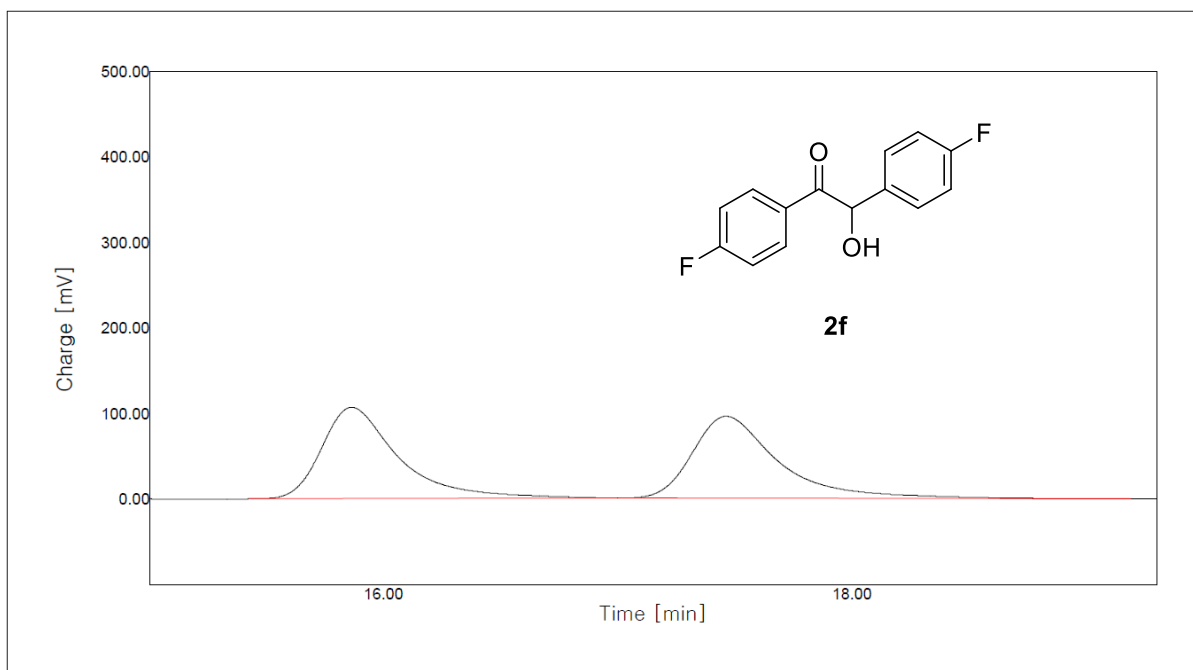
## Result

Number	Time (min)	Area (%)
1	22.4150	49.98
2	26.2733	50.02



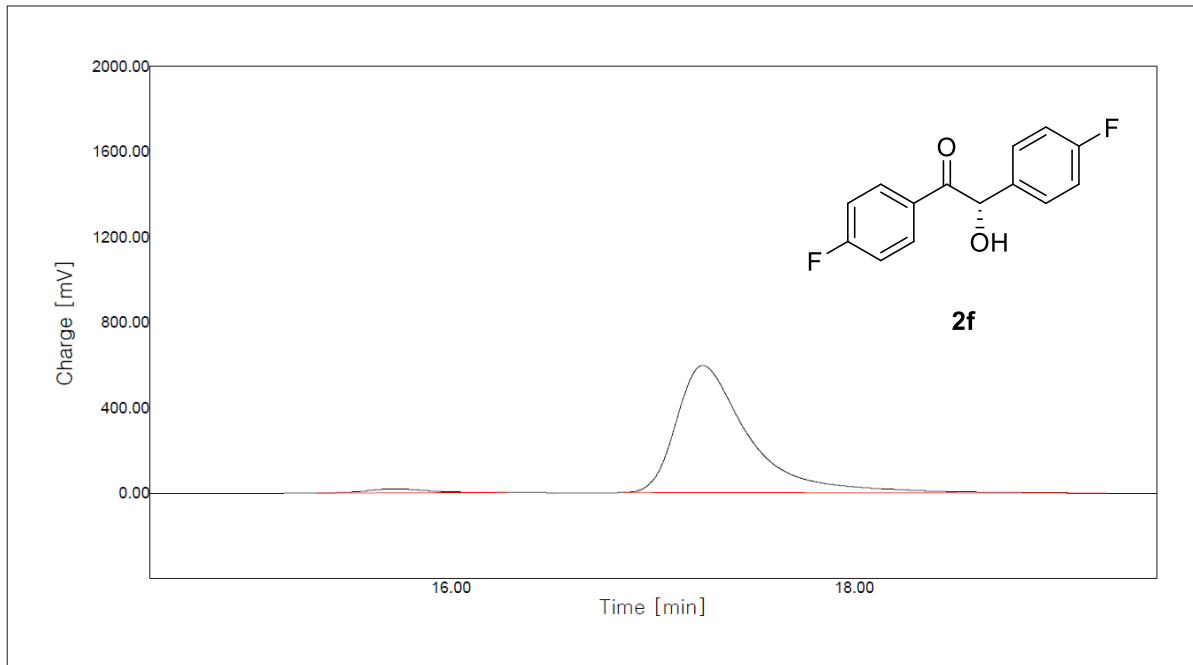
## Result

Number	Time (min)	Area (%)
1	22.4383	2.68
2	26.1417	97.32



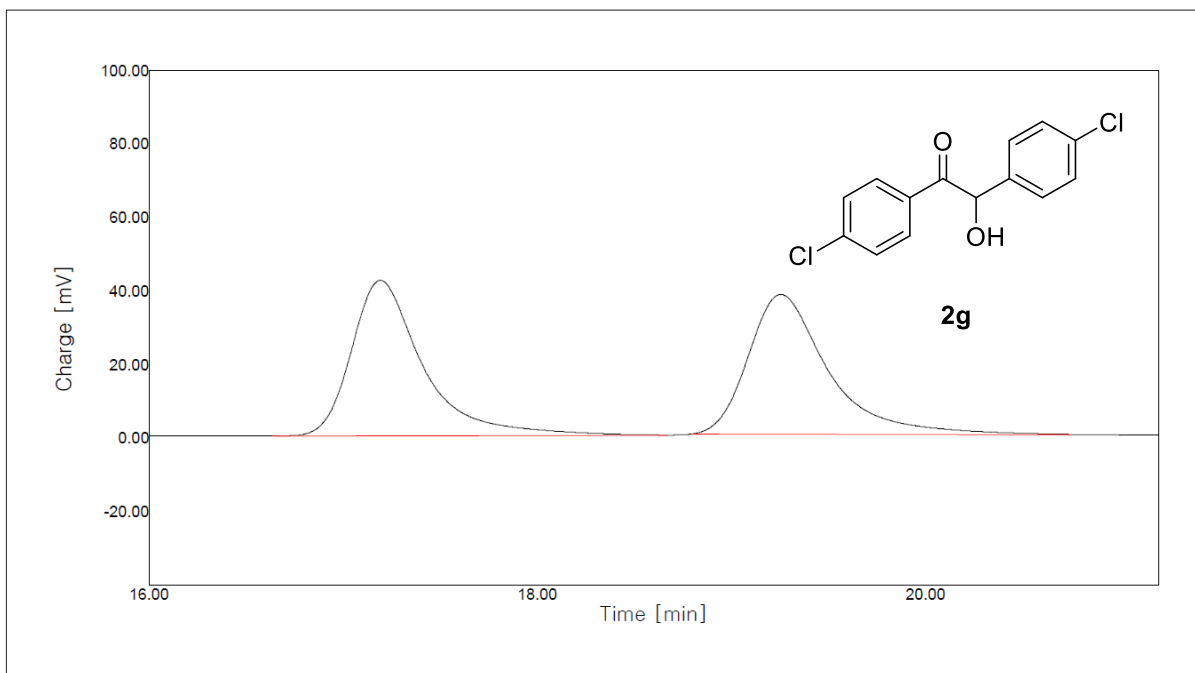
## Result

Number	Time (min)	Area (%)
1	15.8650	49.92
2	17.4633	50.08



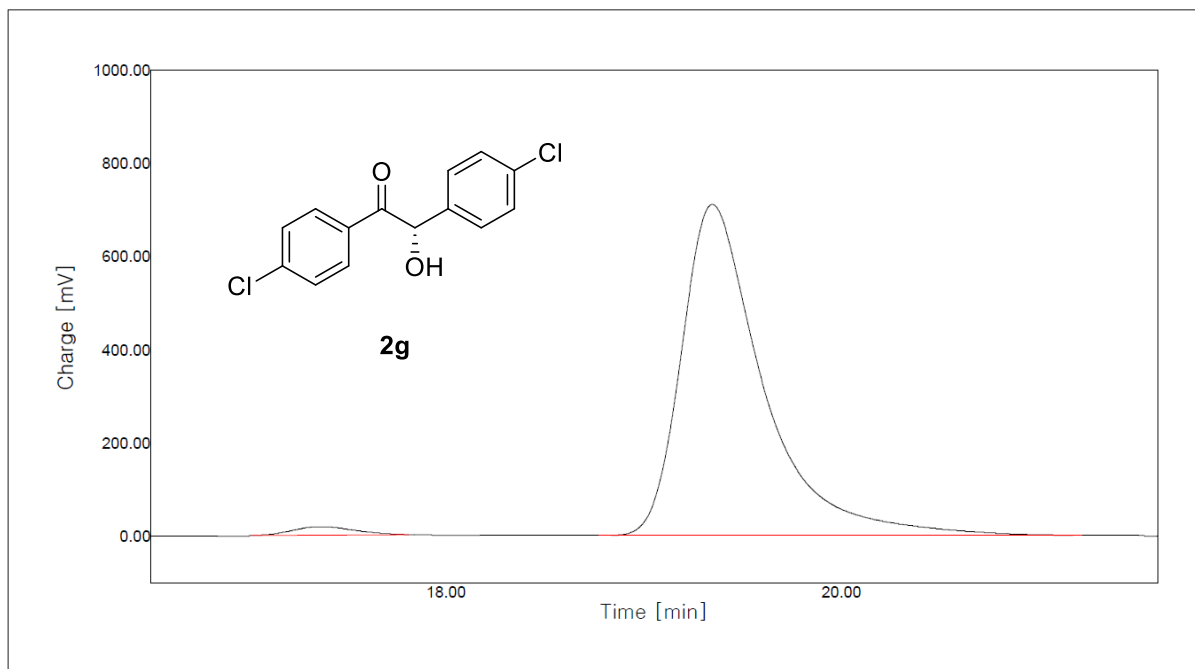
## Result

Number	Time (min)	Area (%)
1	15.7183	2.49
2	17.2483	97.51



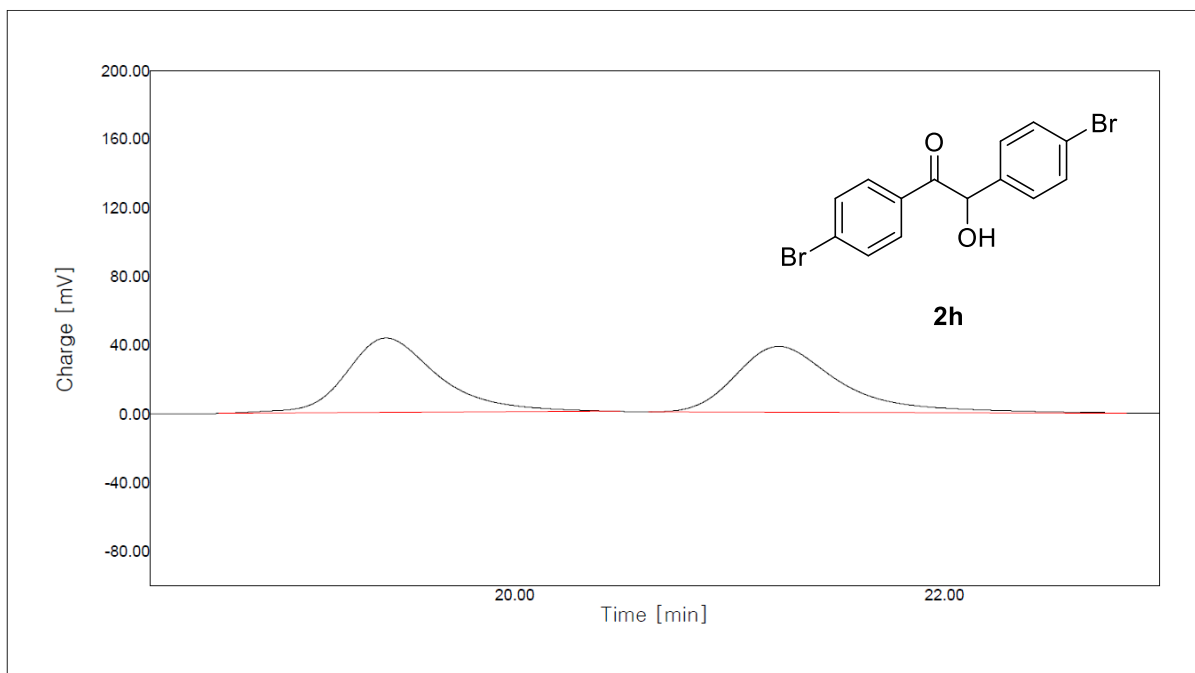
### Result

Number	Time (min)	Area (%)
1	17.1933	49.97
2	19.2567	50.03



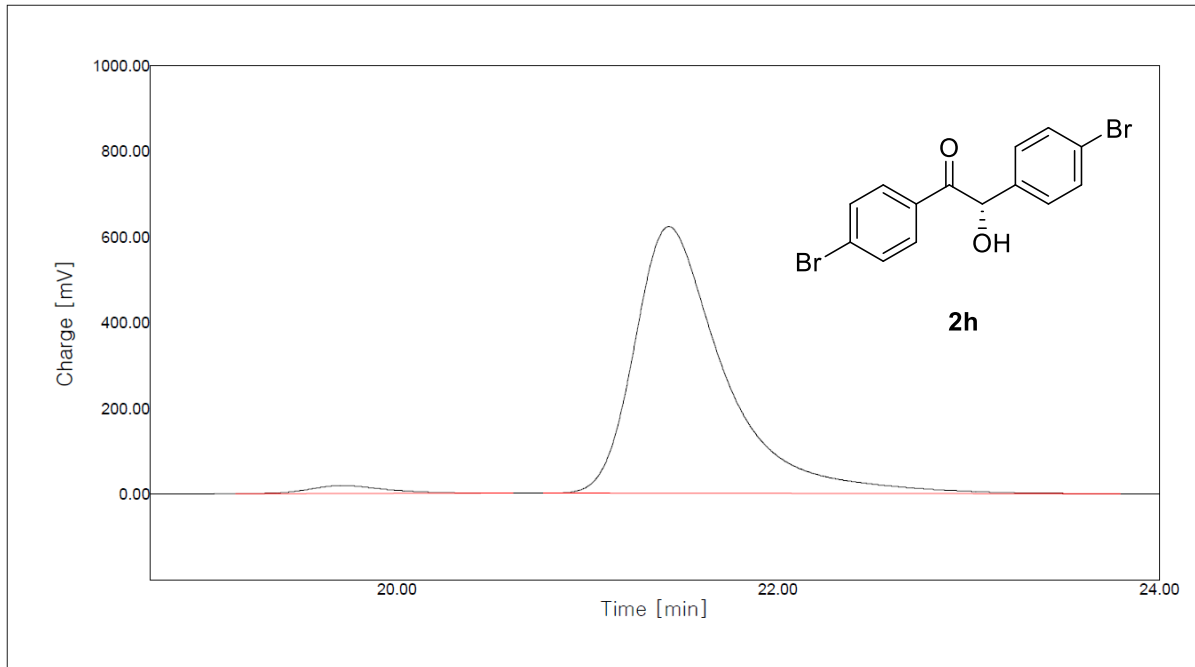
### Result

Number	Time (min)	Area (%)
1	17.3667	1.95
2	19.3450	98.05



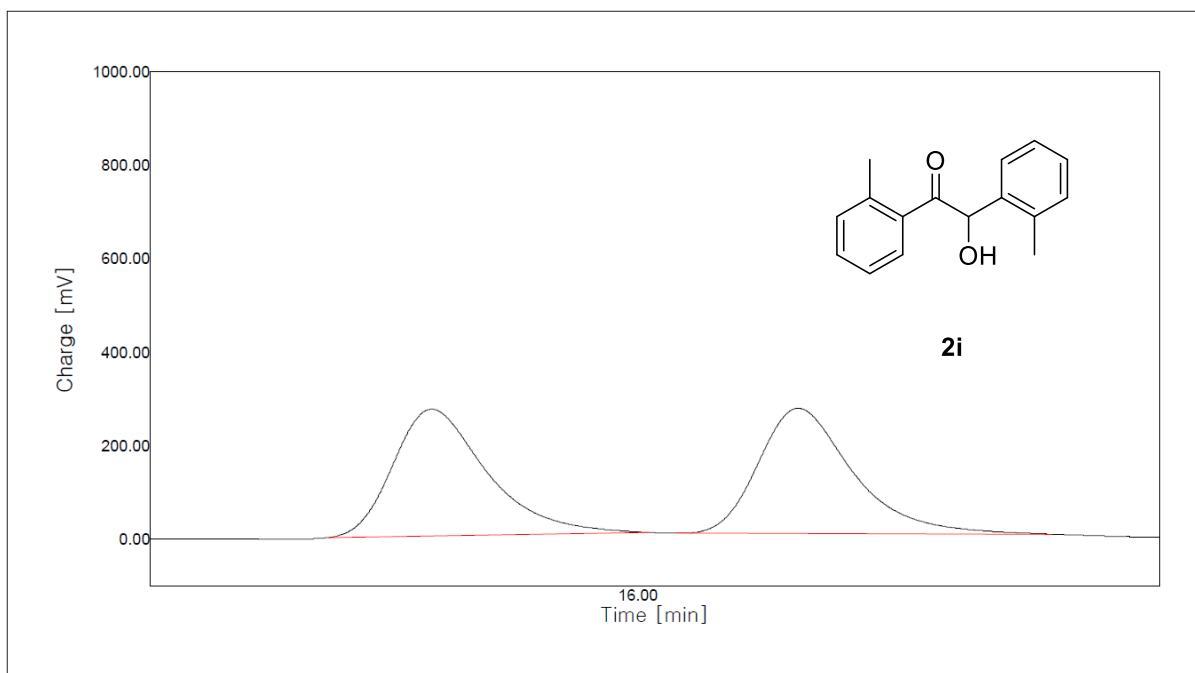
## Result

Number	Time (min)	Area (%)
1	19.4017	50.24
2	21.2283	49.76



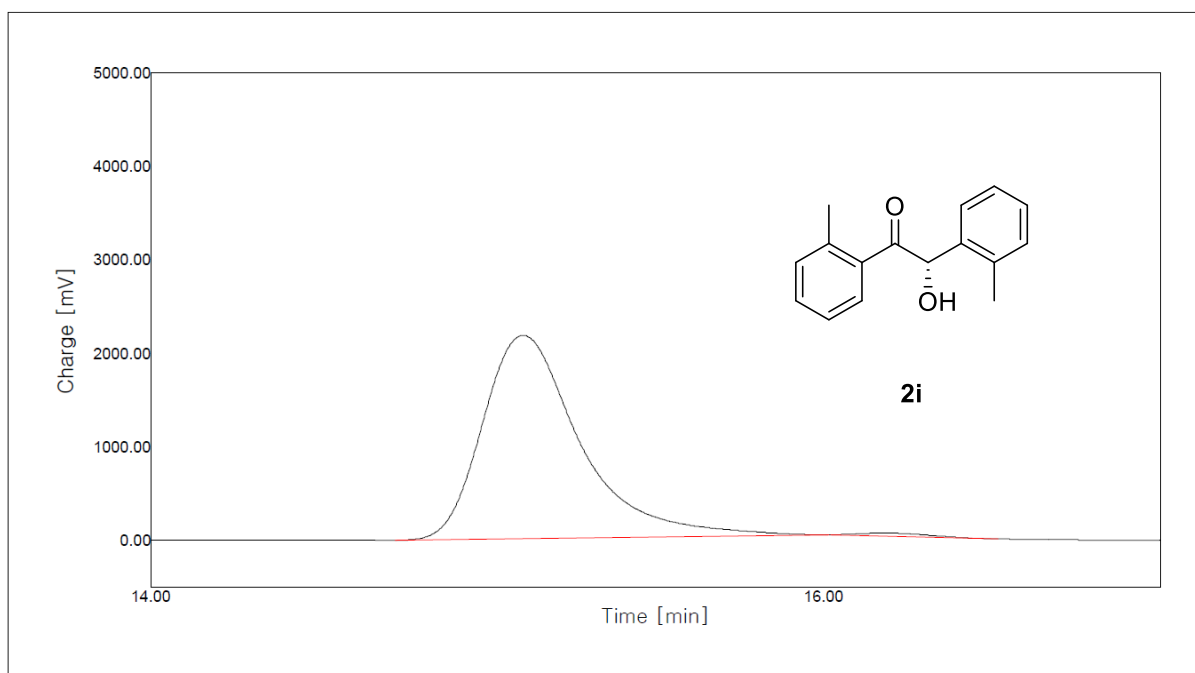
## Result

Number	Time (min)	Area (%)
1	19.7133	2.44
2	21.4267	97.56



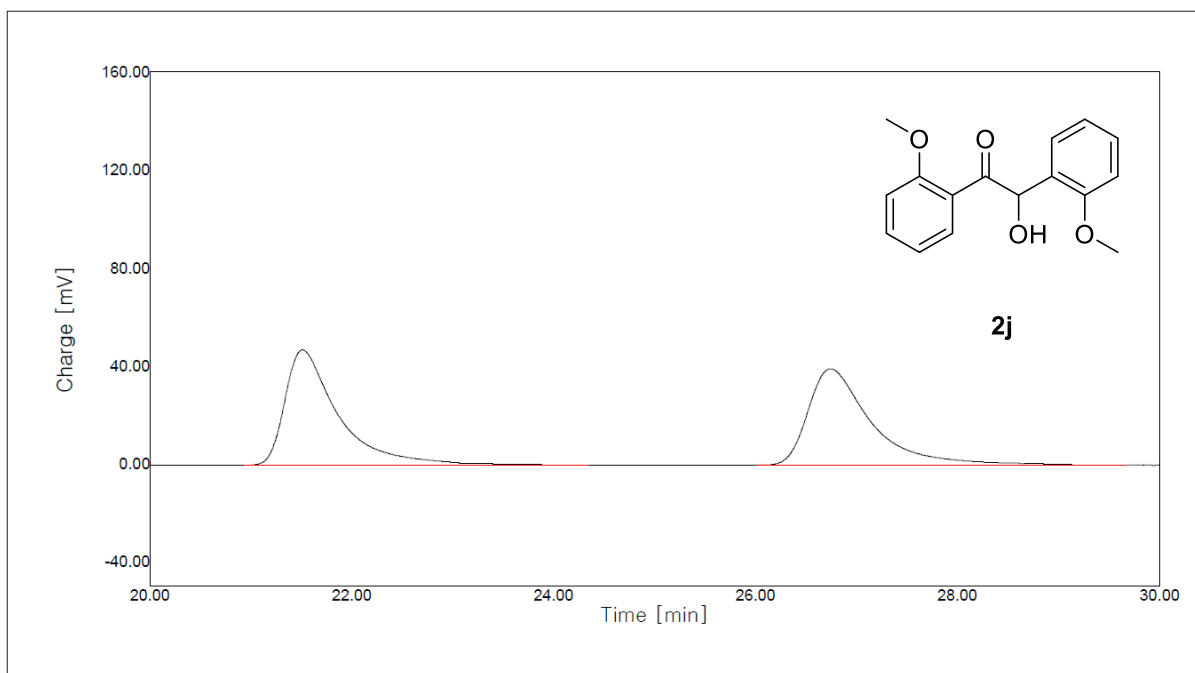
## Result

Number	Time (min)	Area (%)
1	15.3667	50.05
2	16.4917	49.95



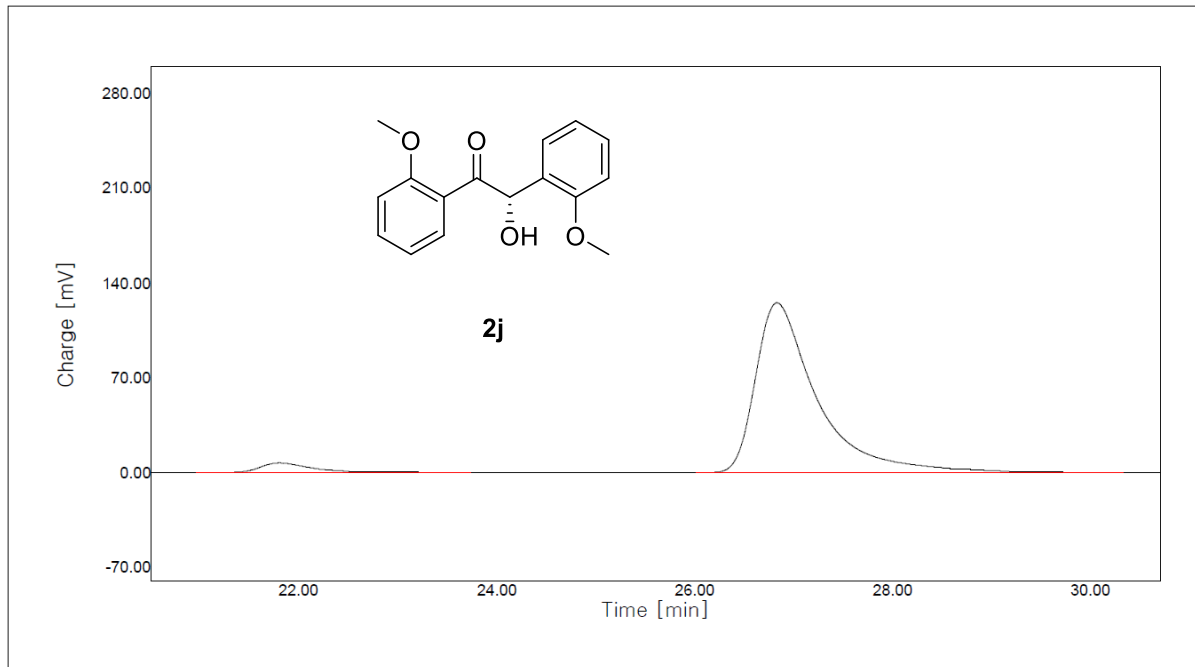
## Result

Number	Time (min)	Area (%)
1	15.1067	98.87
2	16.1800	1.13



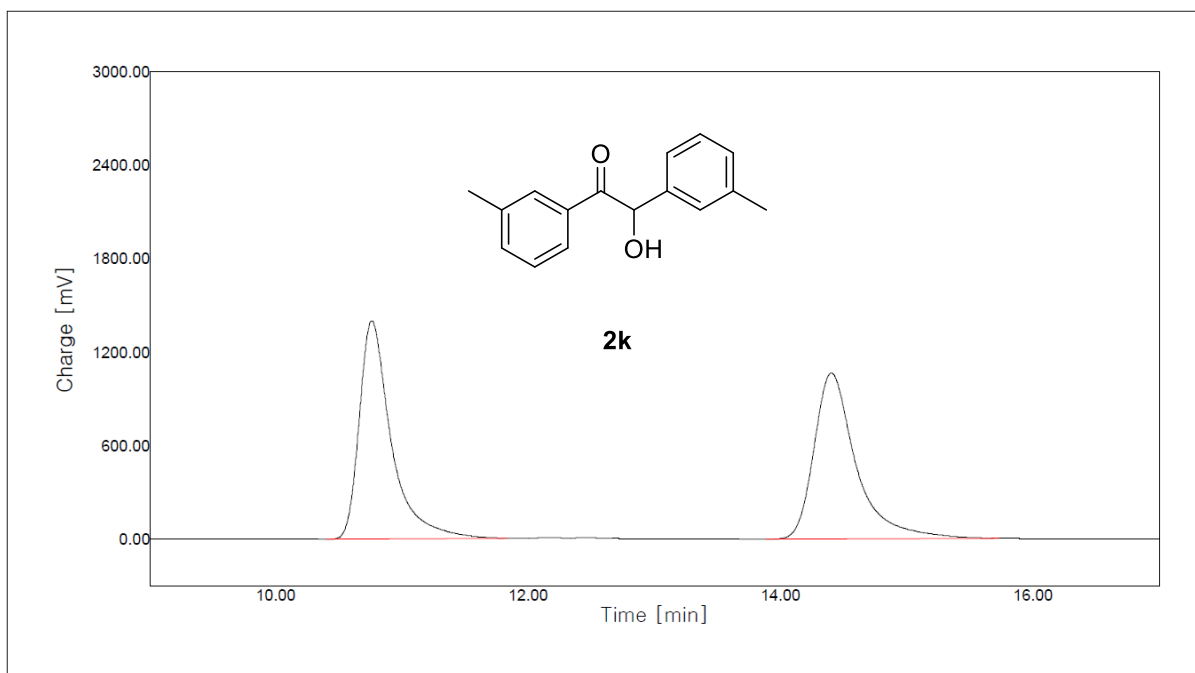
## Result

Number	Time (min)	Area (%)
1	21.5150	50.11
2	26.7467	49.89



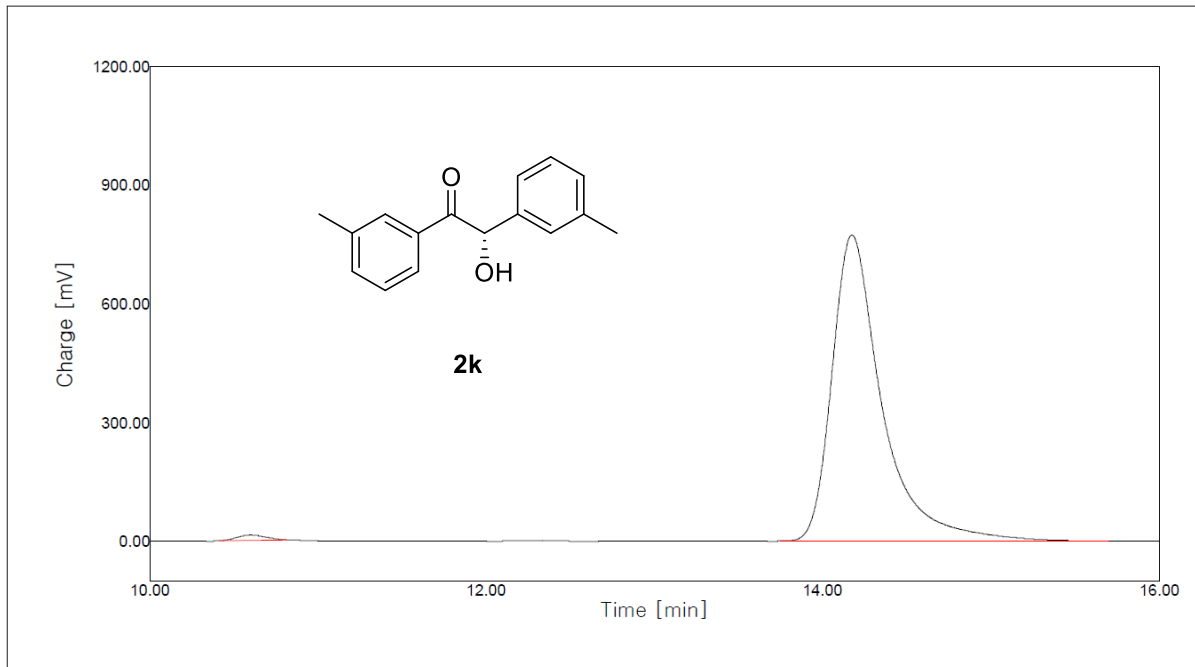
## Result

Number	Time (min)	Area (%)
1	21.8050	4.74
2	26.8300	95.26



## Result

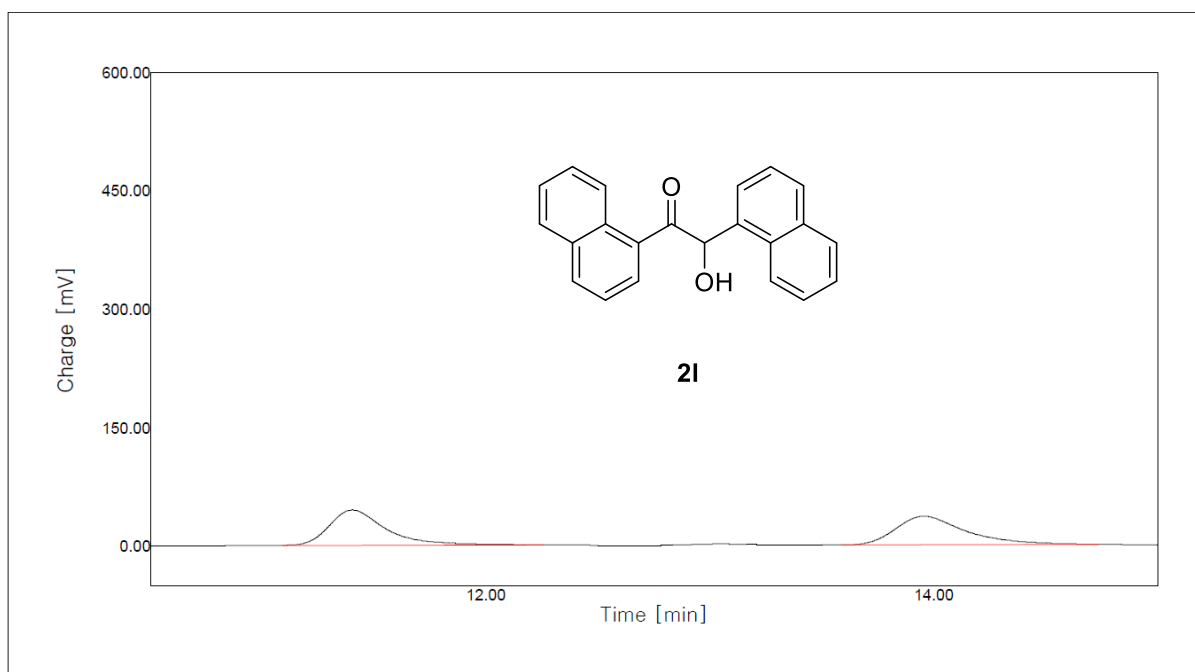
Number	Time (min)	Area (%)
1	10.7617	50.00
2	14.4033	50.00



## Result

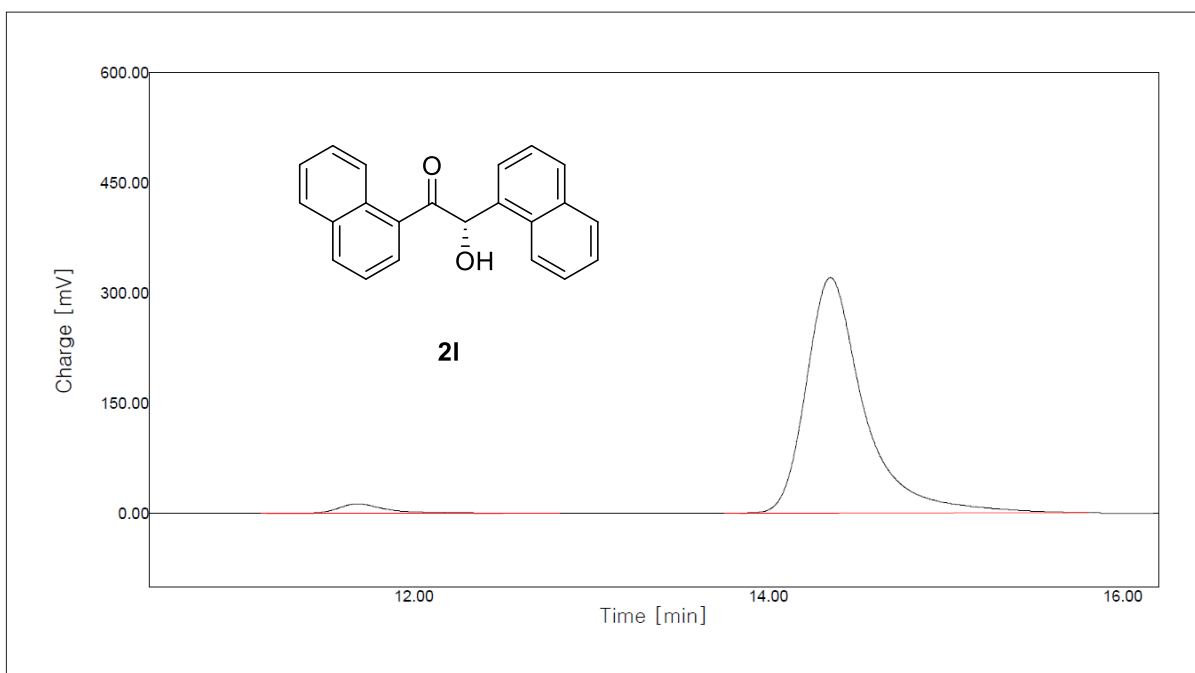
Number	Time (min)	Area (%)
1	10.6017	0.99
2	14.1750	99.01





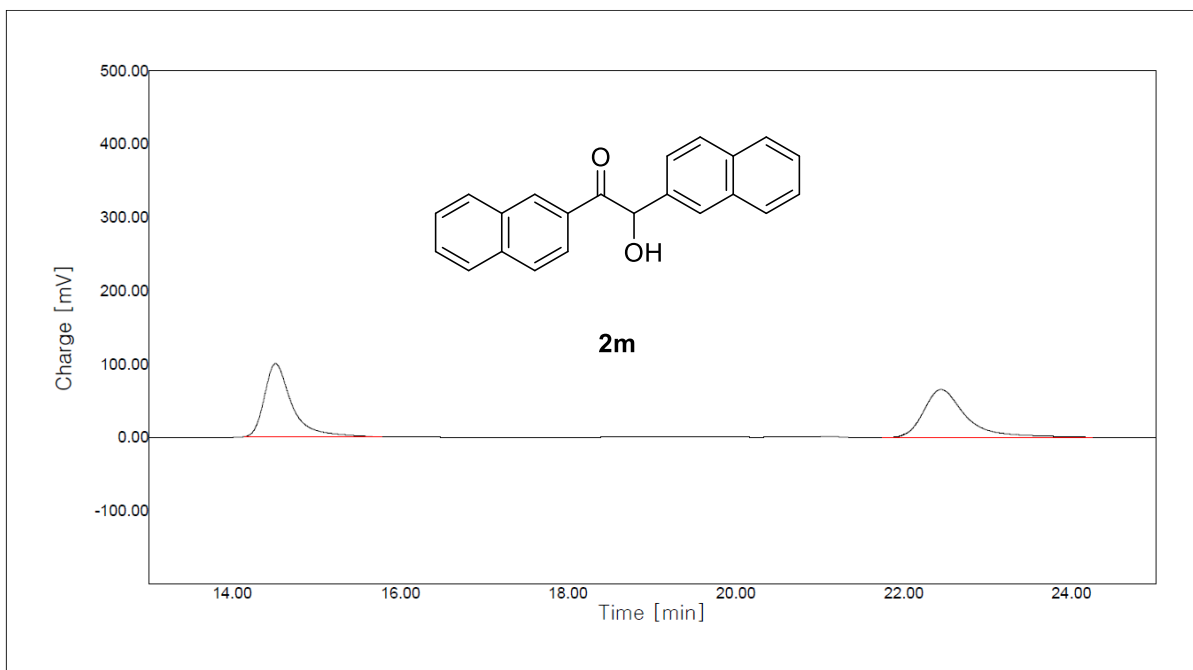
## Result

Number	Time (min)	Area (%)
1	11.4033	49.95
2	13.9567	50.05



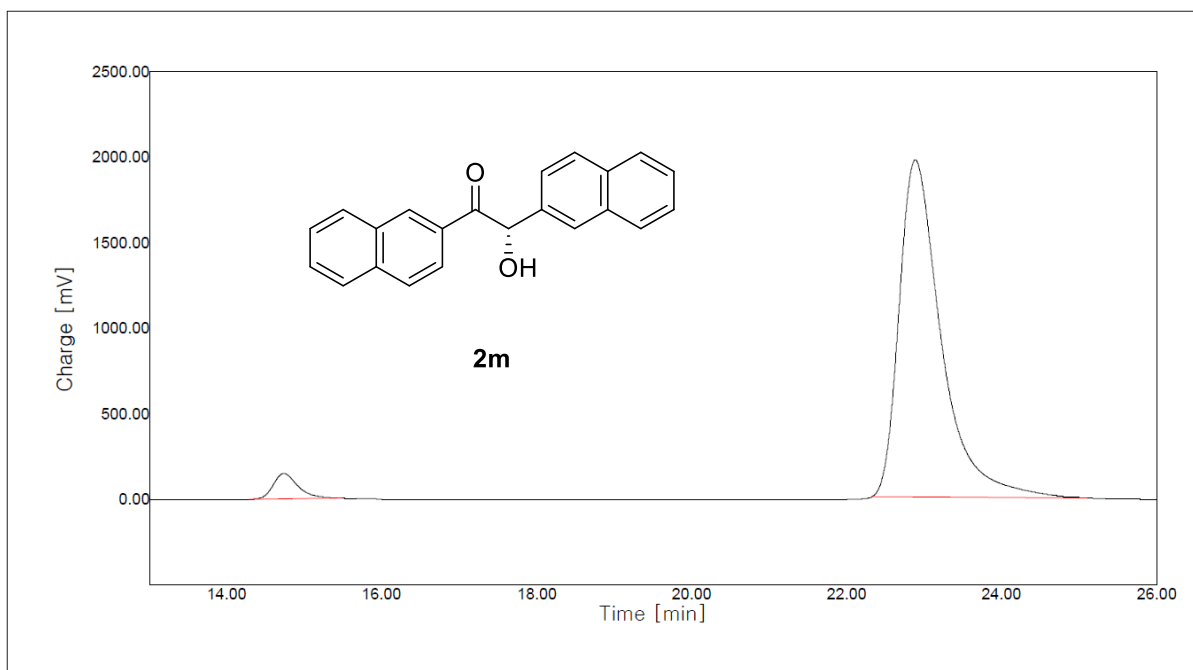
## Result

Number	Time (min)	Area (%)
1	11.6800	3.16
2	14.3483	96.84



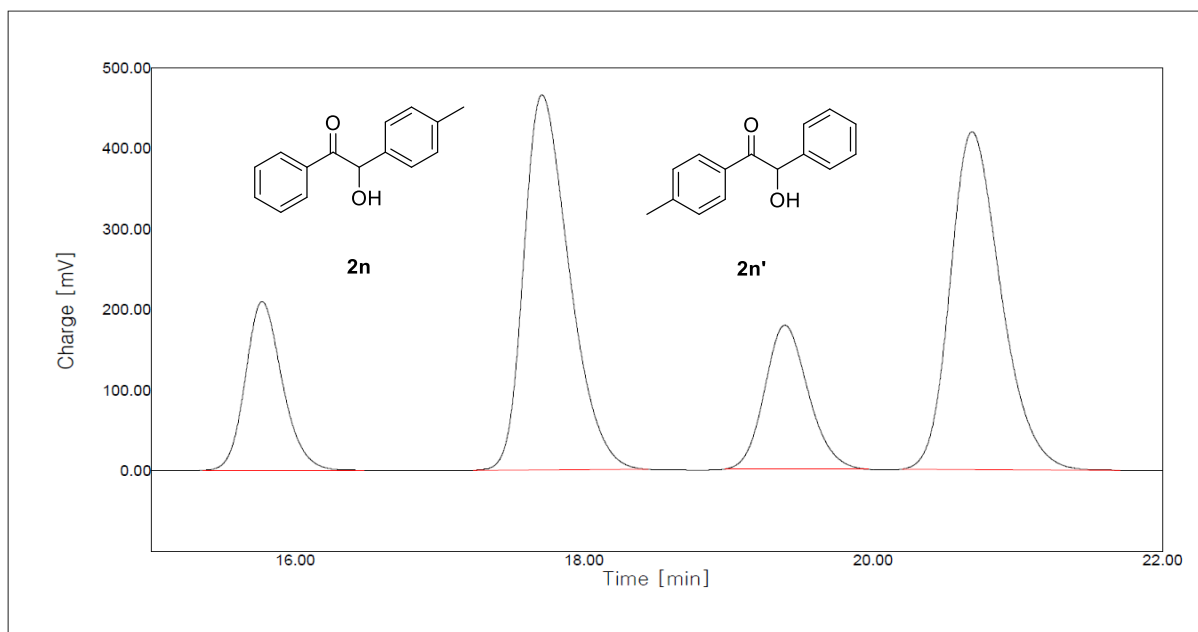
## Result

Number	Time (min)	Area (%)
1	14.5167	50.22
2	22.4433	49.78



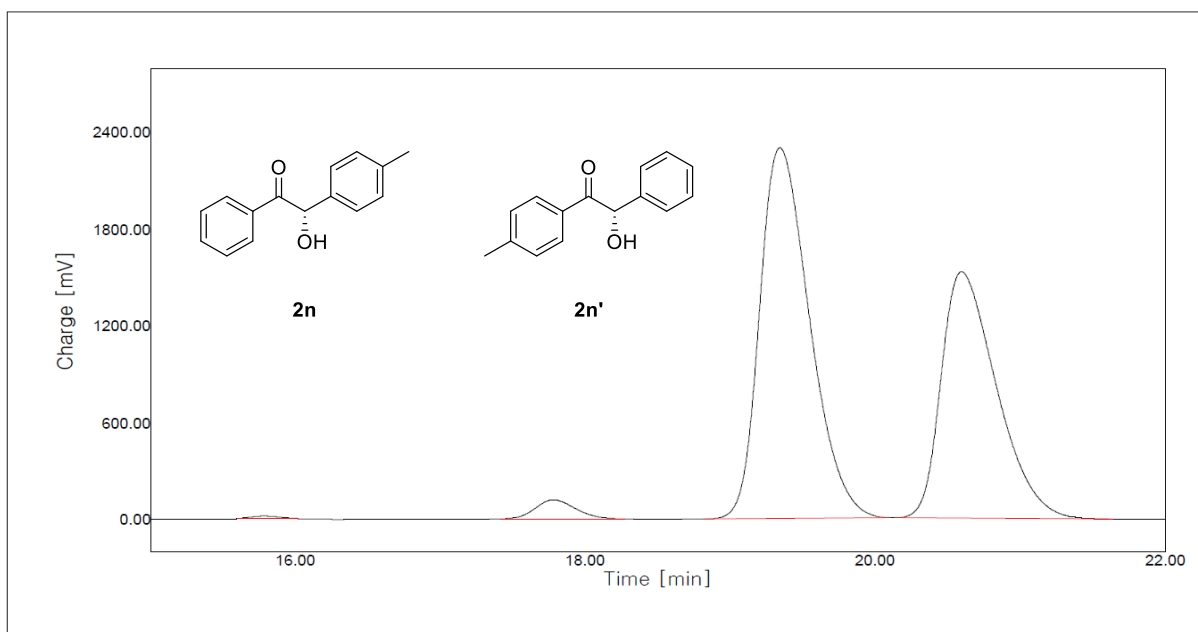
## Result

Number	Time (min)	Area (%)
1	14.7383	4.23
2	22.8867	95.77



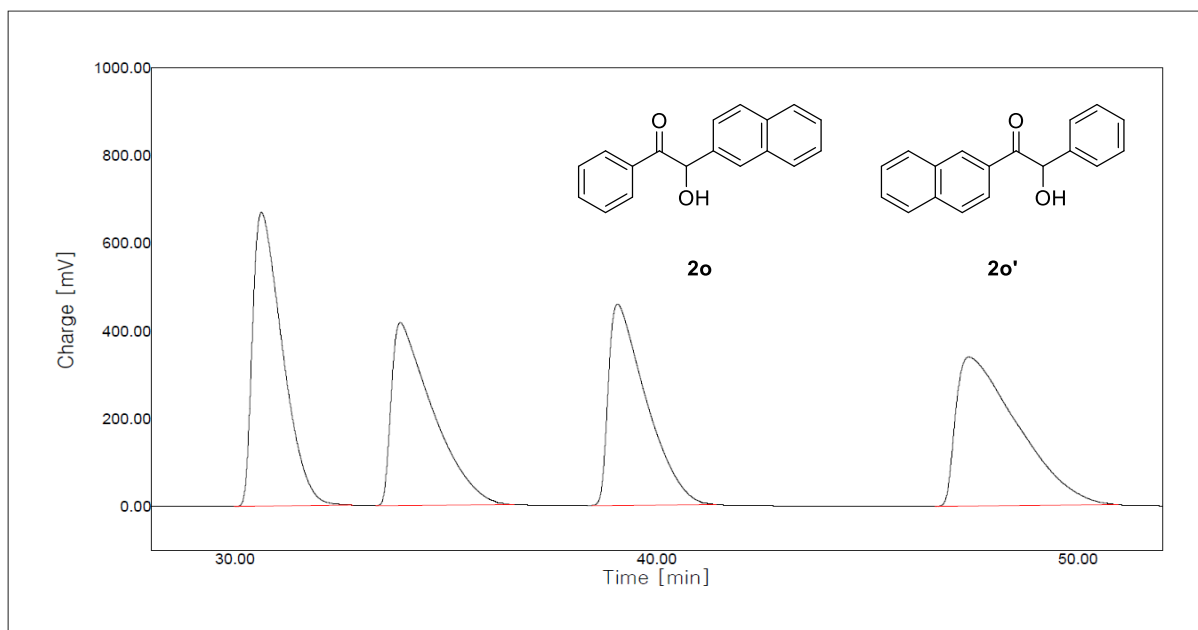
## Result

Number	Time (min)	Area (%)
1	15.7717	13.34
2	17.7083	36.51
3	19.3883	13.44
4	20.6833	36.72



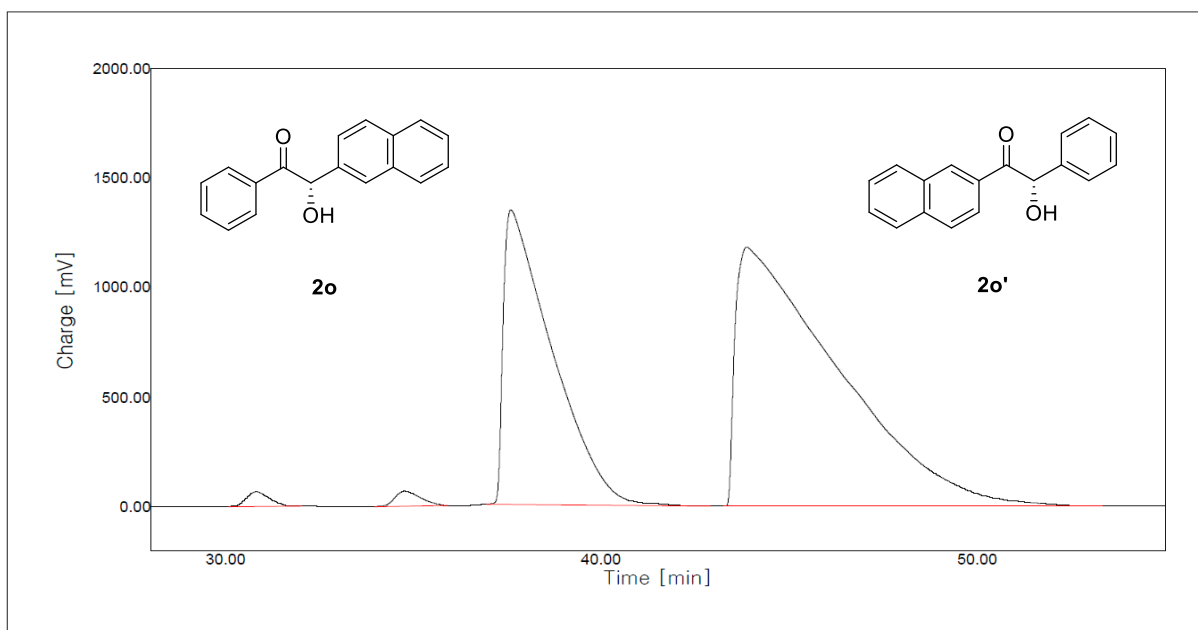
## Result

Number	Time (min)	Area (%)
1	15.7867	0.22
2	17.7817	2.33
3	19.3433	56.16
4	20.5967	41.30



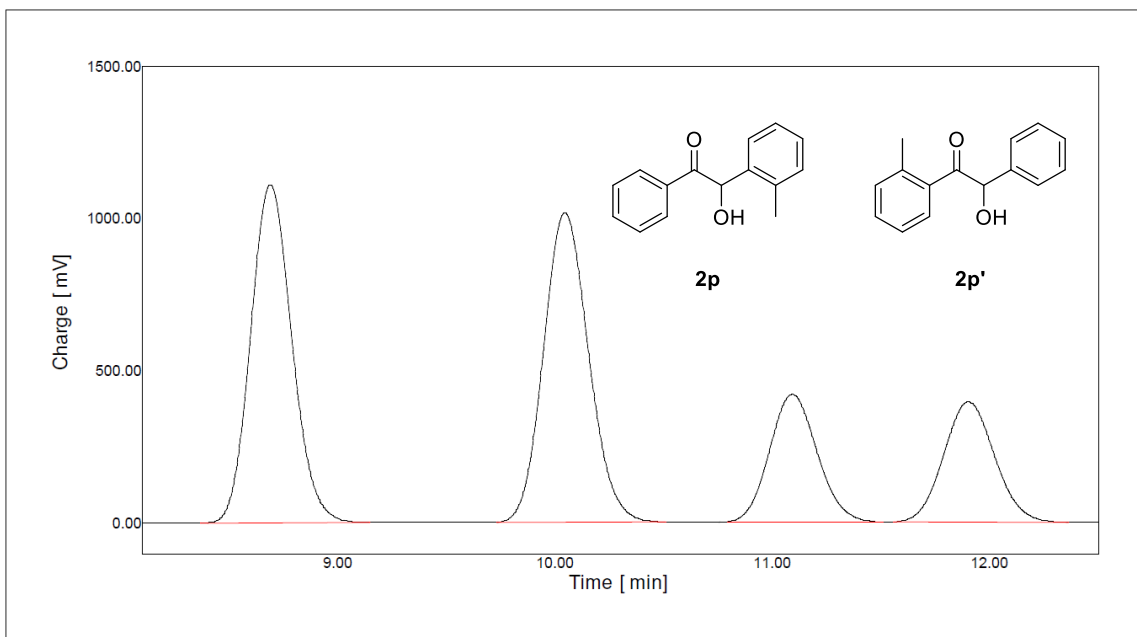
## Result

Number	Time (min)	Area (%)
1	30.6317	26.52
2	33.9217	22.82
3	39.0767	22.90
4	47.4133	27.75



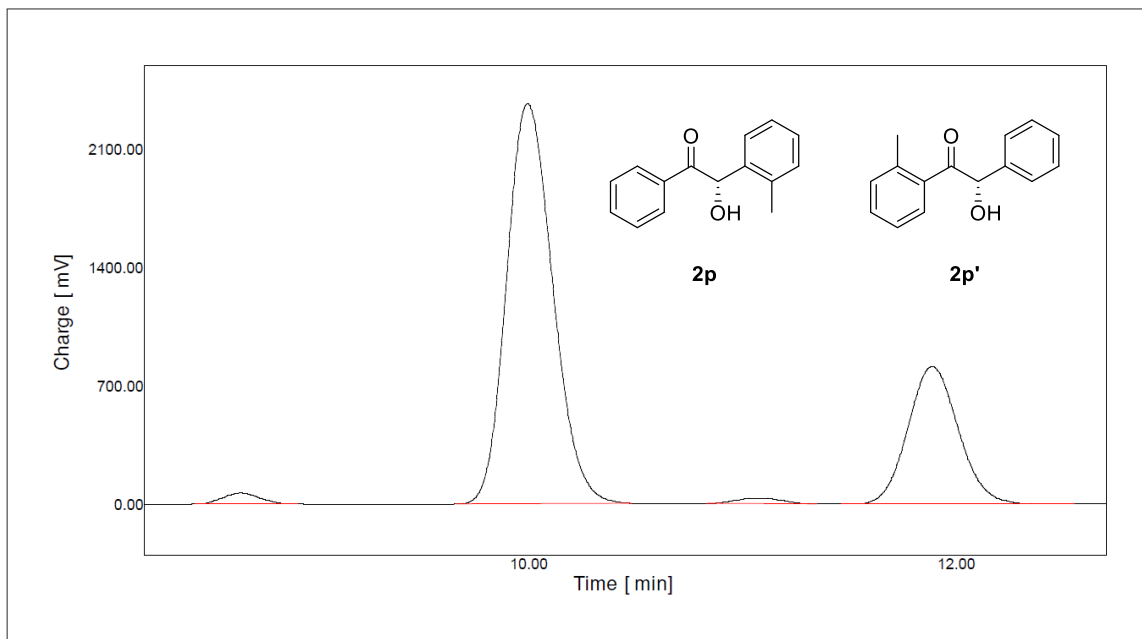
## Result

Number	Time (min)	Area (%)
1	30.8233	0.82
2	34.7717	0.90
3	37.5967	34.48
4	43.8717	63.79



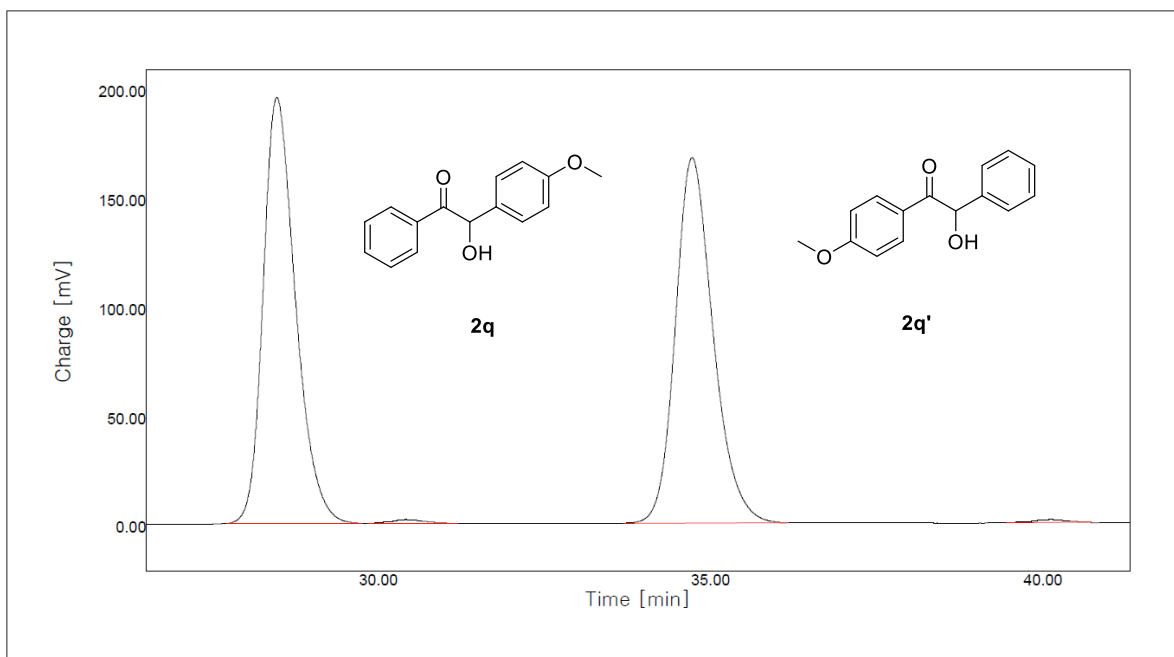
## Result

번호	피크이름	RT[ 분]	면적비[ %]
1		8.6900	34.84
2		10.0450	34.80
3		11.0917	15.09
4		11.9017	15.28



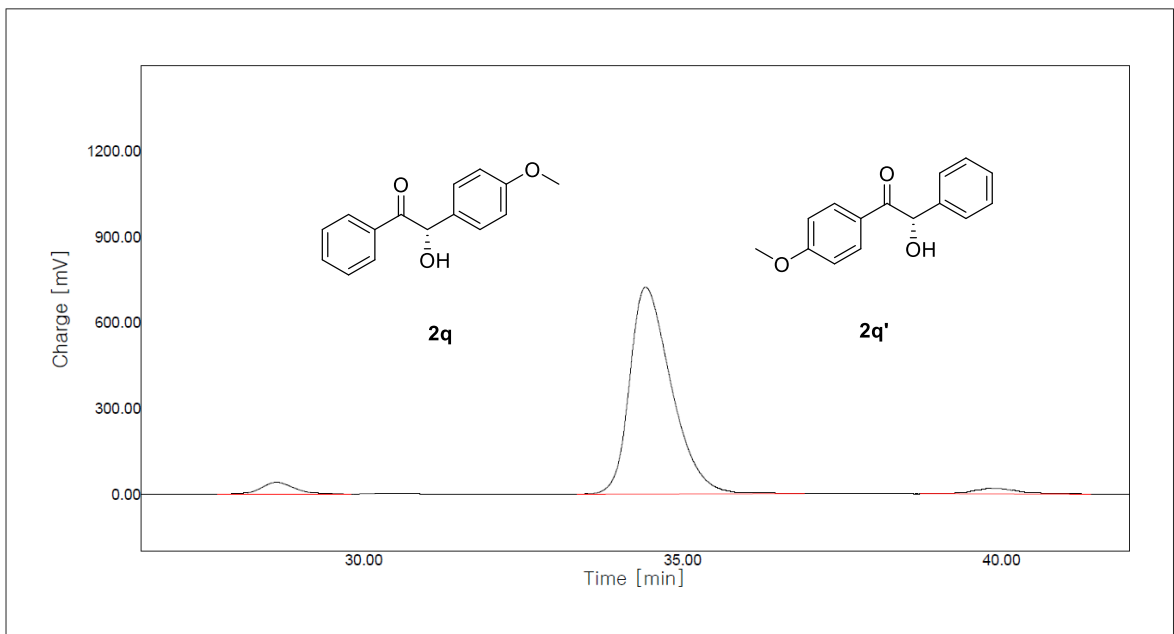
## Result

Number	Name	Time (min)	Area (%)
1		8.6517	1.56
2		9.9933	70.84
3		11.0733	0.95
4		11.8850	26.66



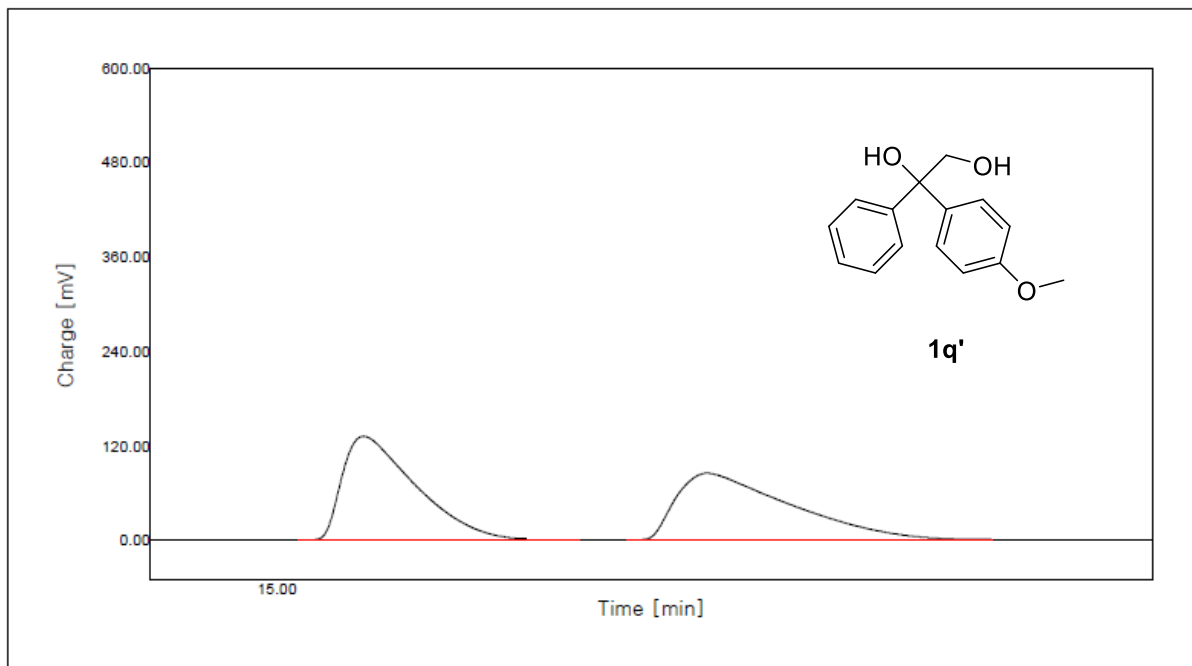
## Result

Number	Time (min)	Area (%)
1	28.4750	49.63
2	30.4133	0.40
3	34.7200	49.60
4	40.1150	0.36



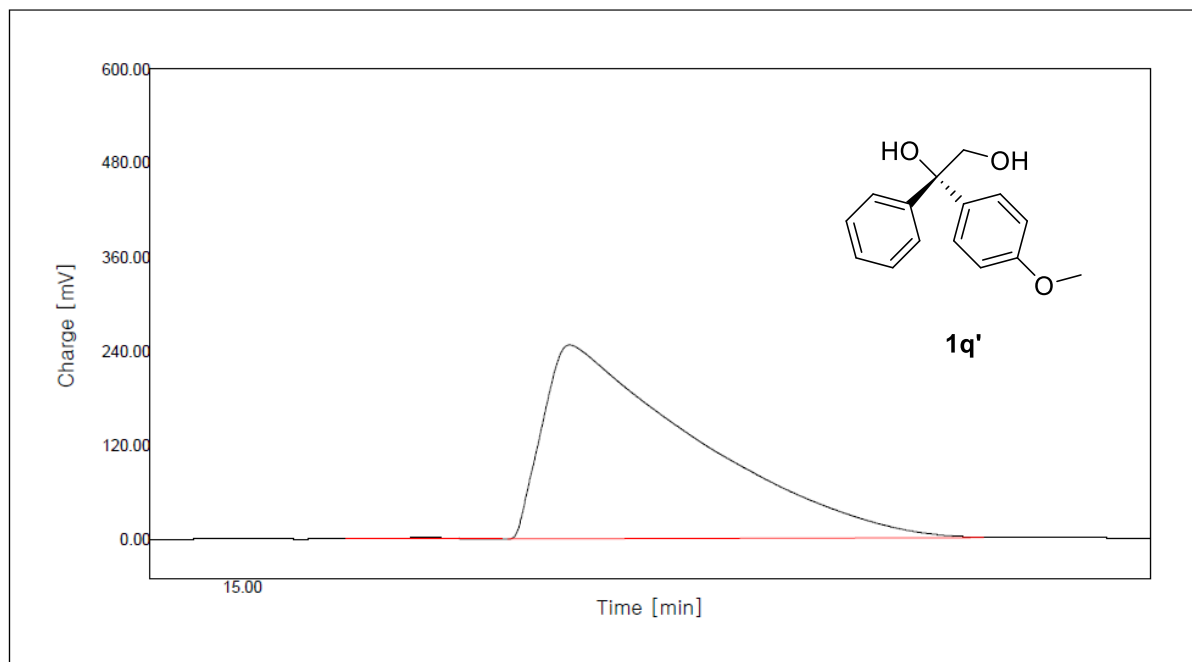
## Result

Number	Time (min)	Area (%)
1	28.6317	4.04
2	34.4183	93.36
3	39.8783	2.60



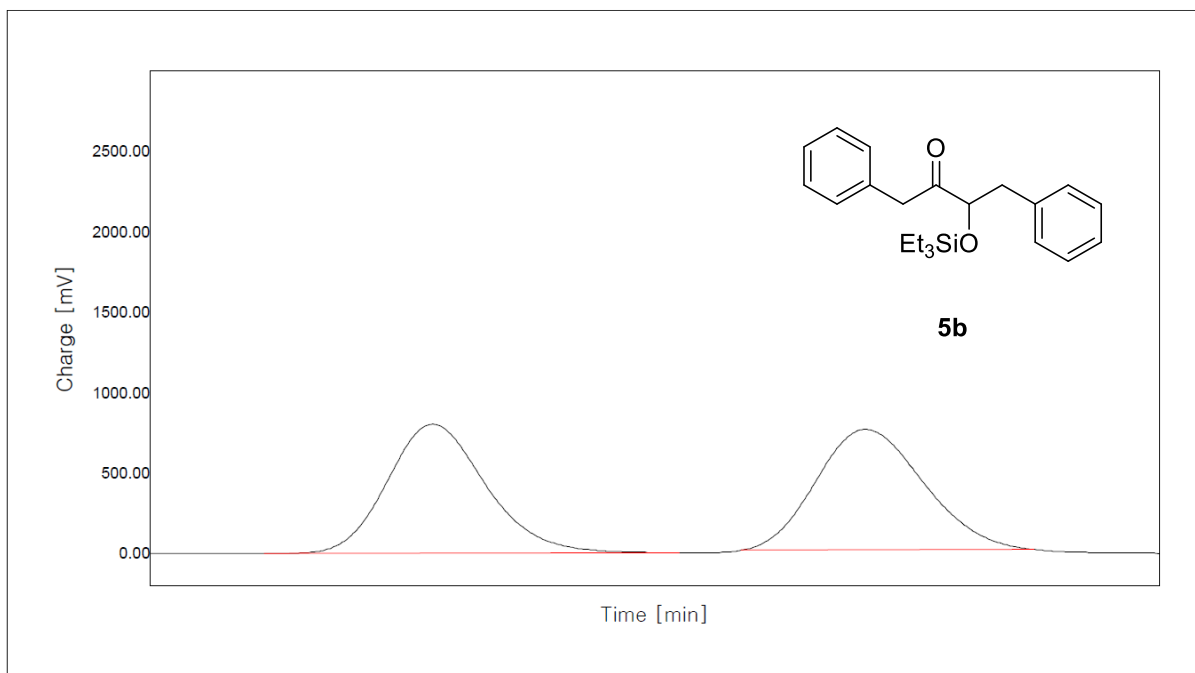
## Result

Number	Time (min)	Area (%)
1	15.4717	50.07
2	17.3550	49.93
합계		



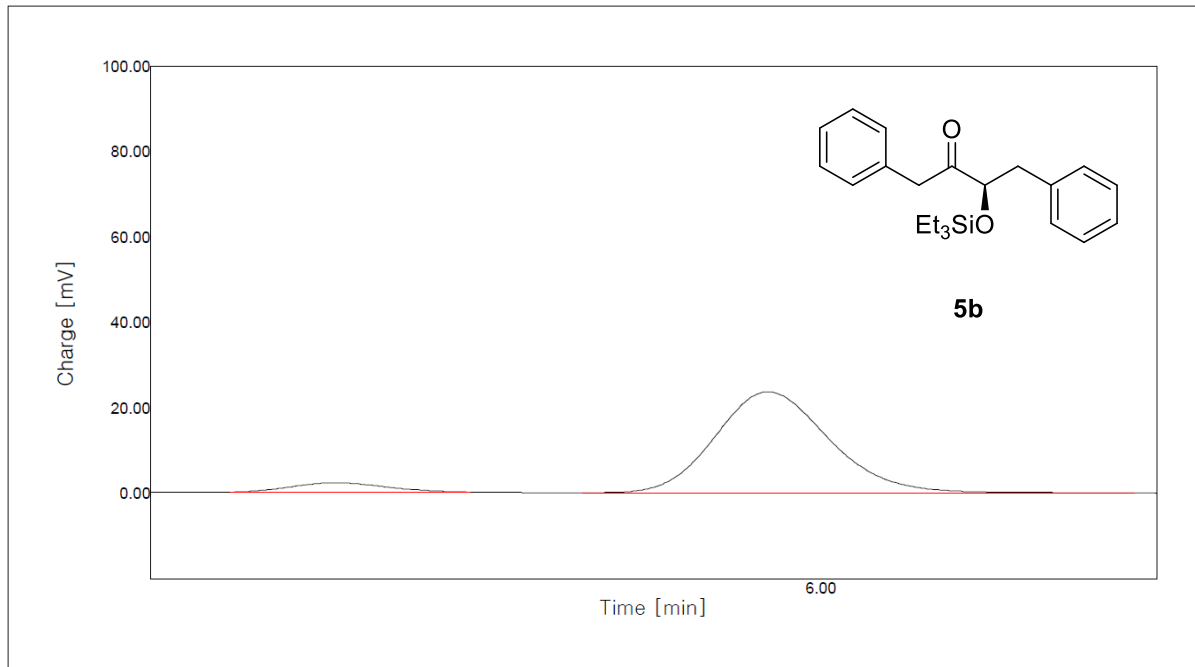
## Result

Number	Time (min)	Area (%)
1	15.9883	0.26
2	16.7667	99.74
합계		



### Result

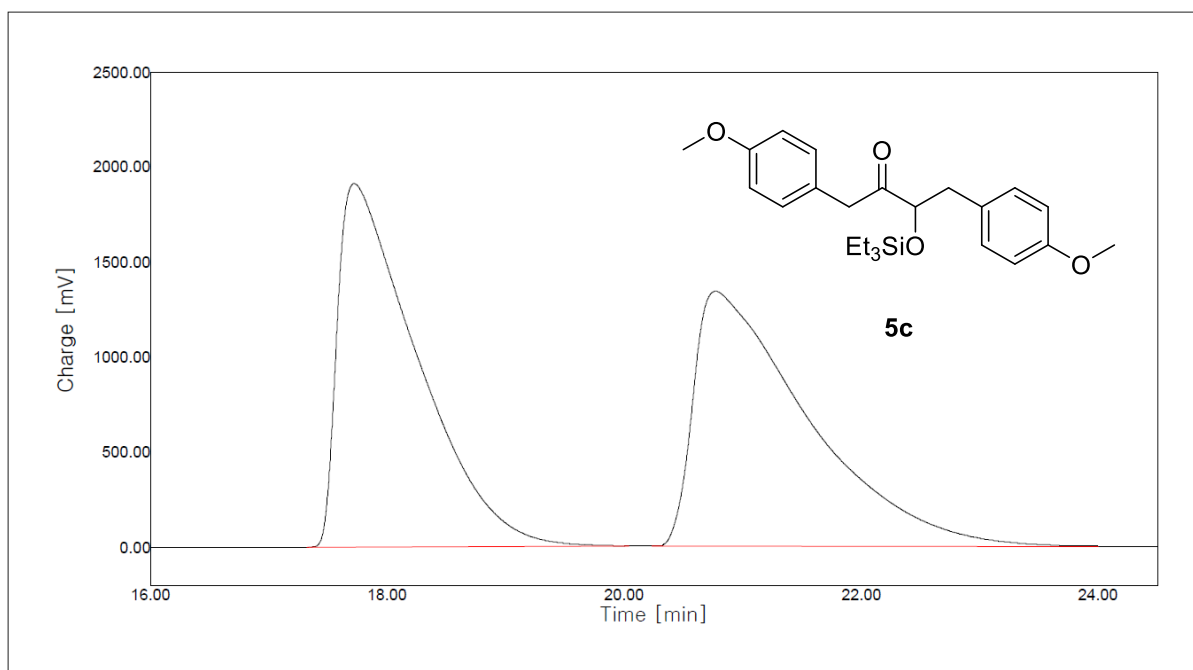
Number	Time (min)	Area (%)
1	5.6167	49.50
2	6.0233	50.50



### Result

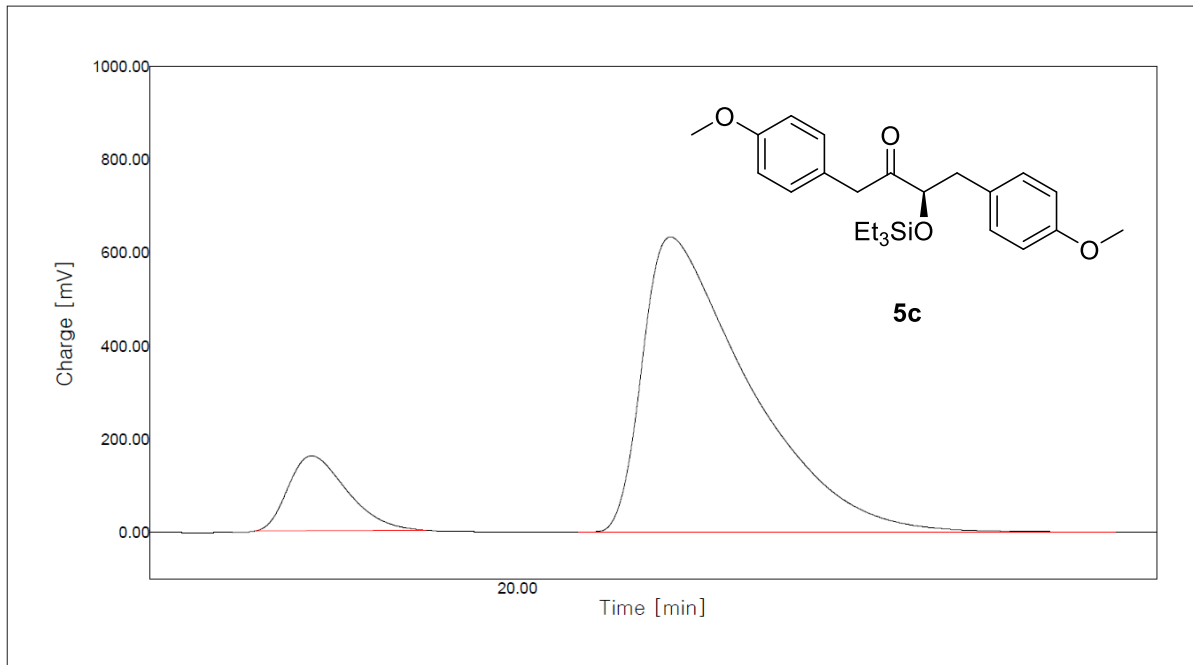
Number	Time (min)	Area (%)
1	5.5667	6.99
2	5.9533	93.01





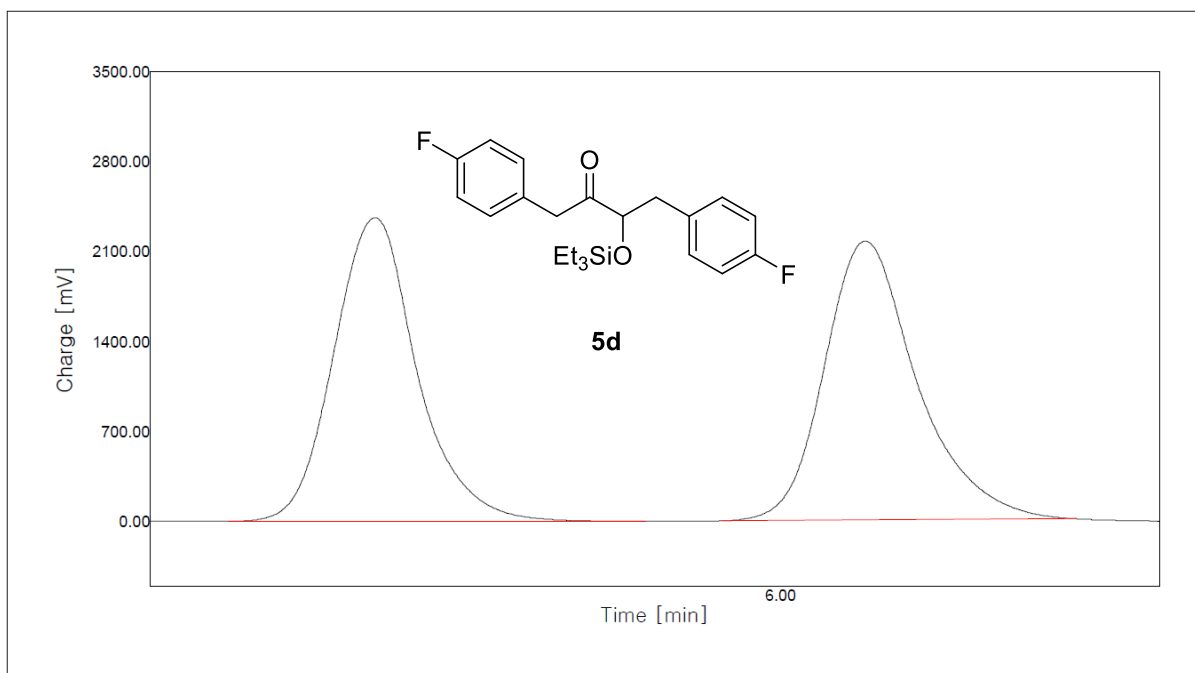
## Result

Number	Time (min)	Area (%)
1	17.7217	49.80
2	20.7700	50.20



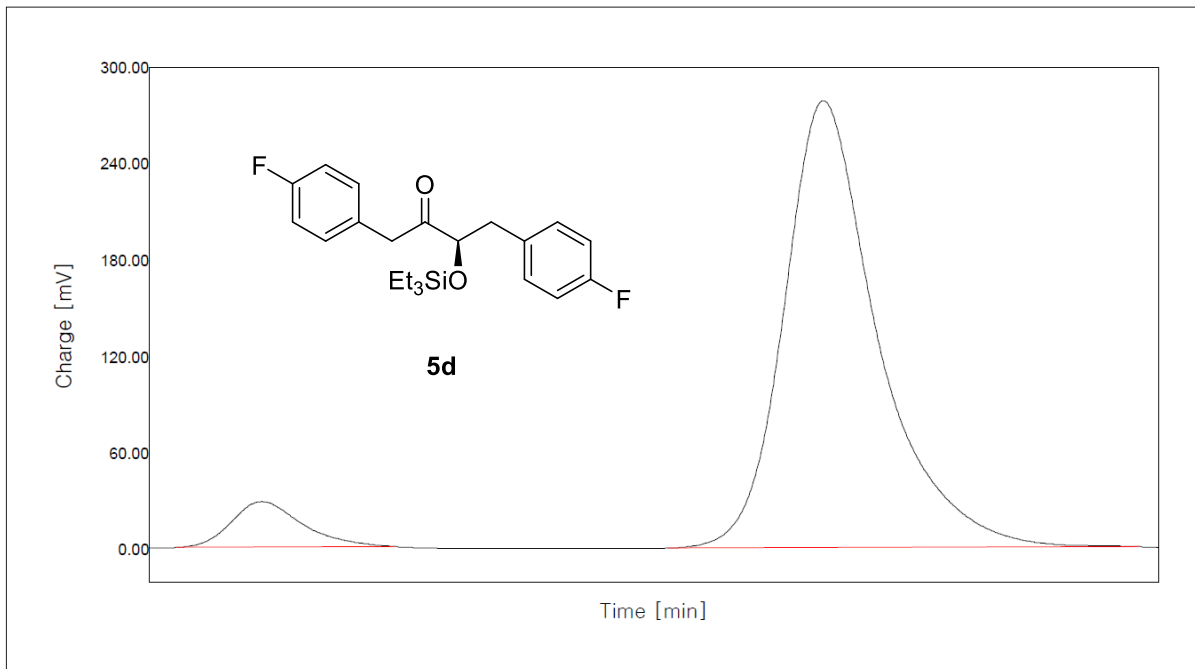
## Result

Number	Time (min)	Area (%)
1	18.3217	12.19
2	21.2433	87.81



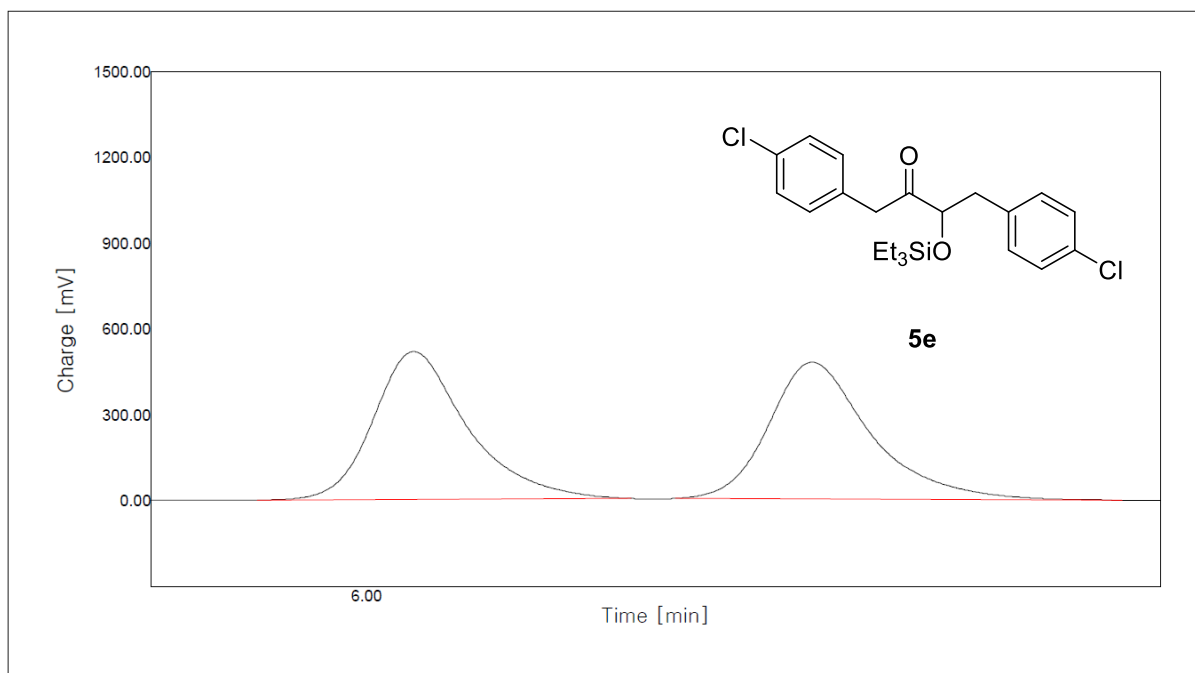
## Result

Number	Time (min)	Area (%)
1	5.3567	49.47
2	6.1350	50.53



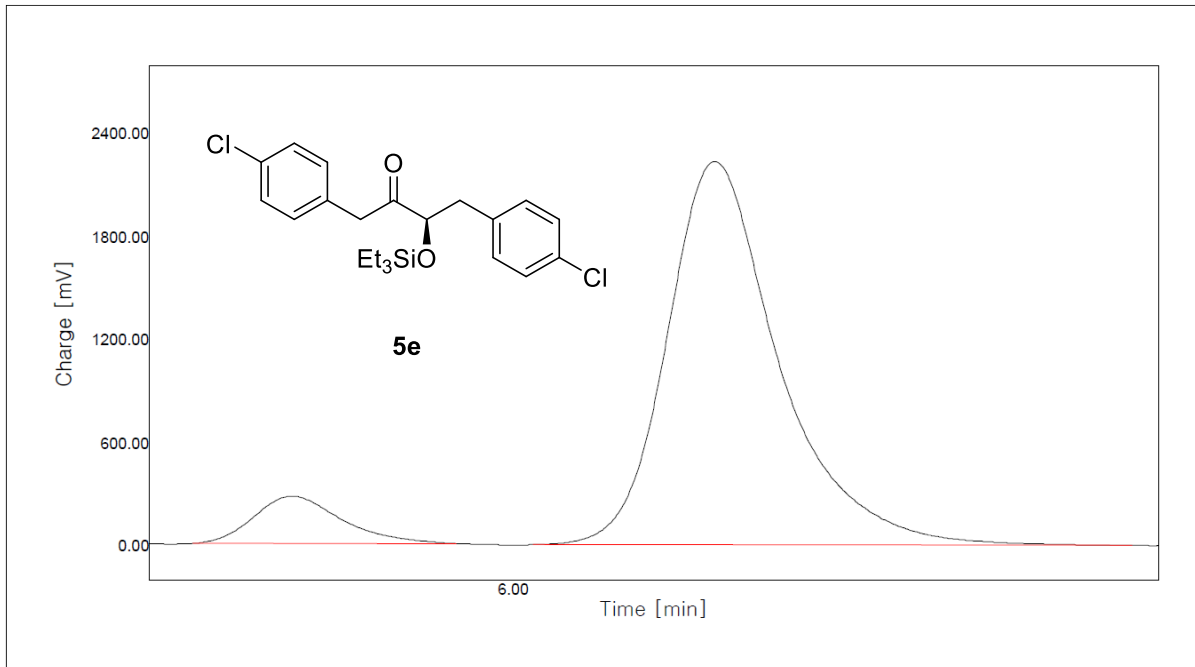
## Result

Number	Time (min)	Area (%)
1	5.3183	7.20
2	6.1517	92.80



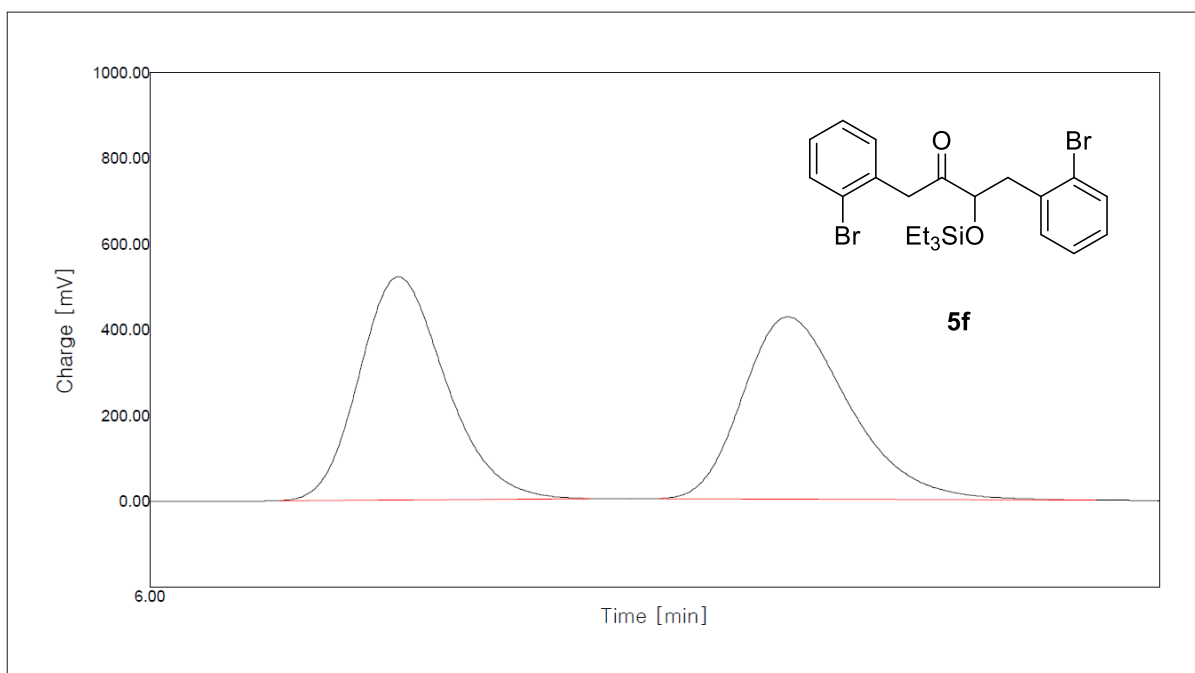
## Result

Number	Time (min)	Area (%)
1	6.0650	50.08
2	6.6167	49.92



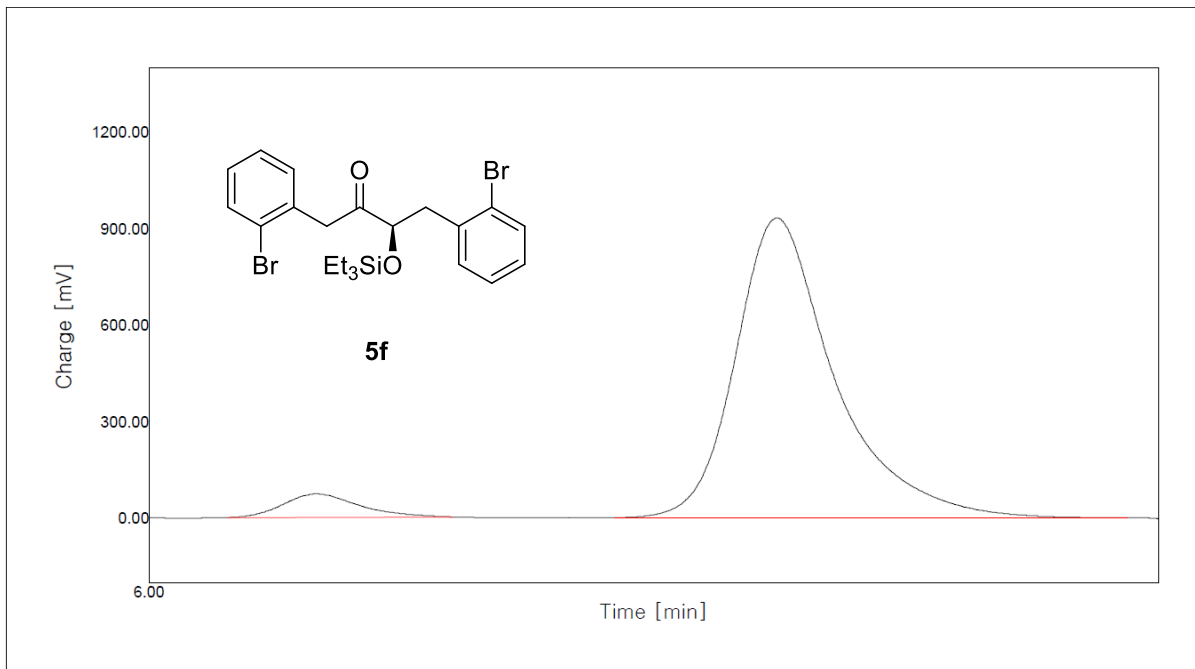
## Result

Number	Time (min)	Area (%)
1	5.7083	8.82
2	6.2667	91.18



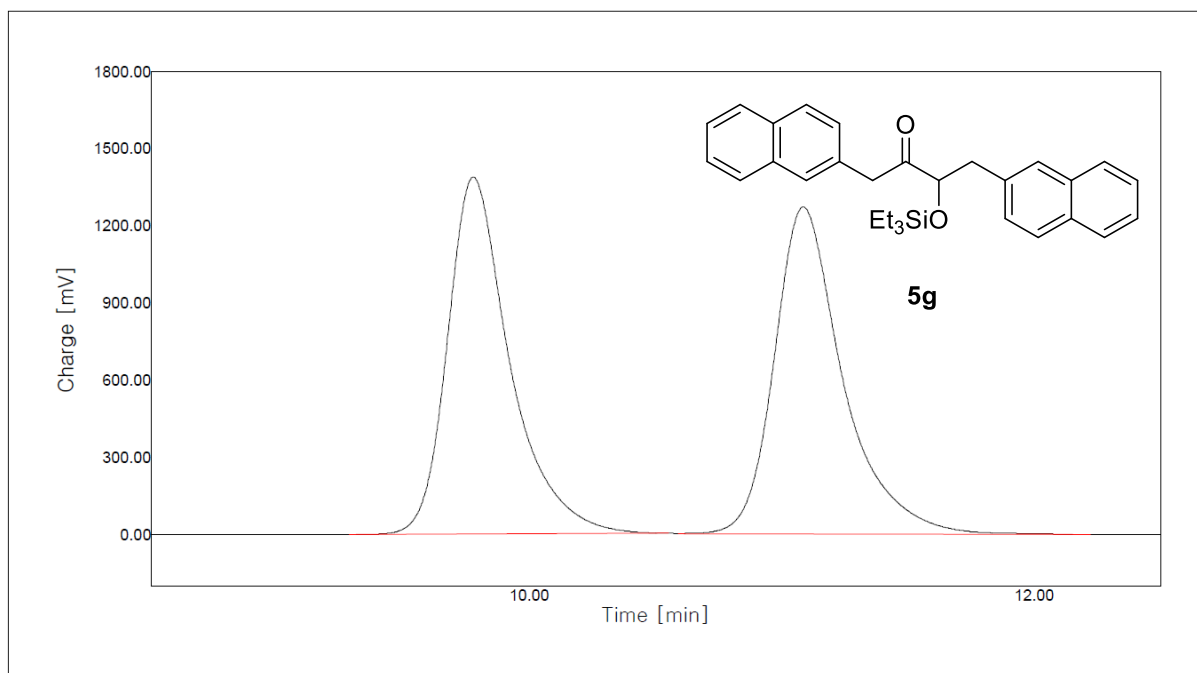
### Result

Number	Time (min)	Area (%)
1	6.3450	49.98
2	6.8850	50.02



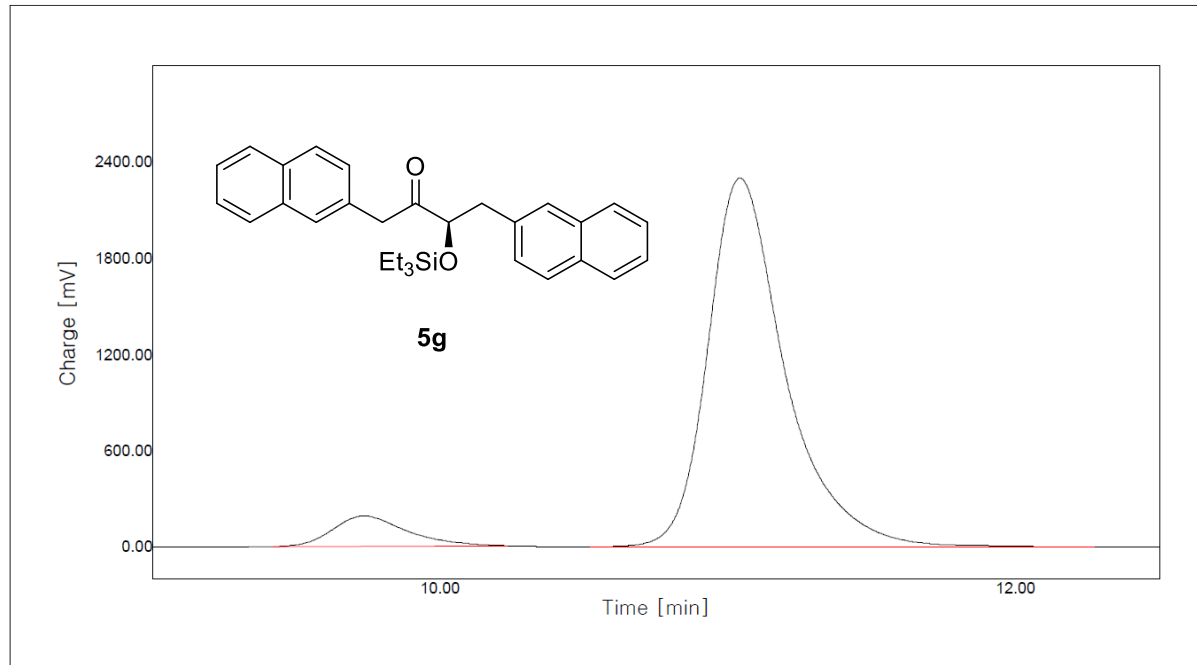
### Result

Number	Time (min)	Area (%)
1	6.2667	5.57
2	6.9950	94.43



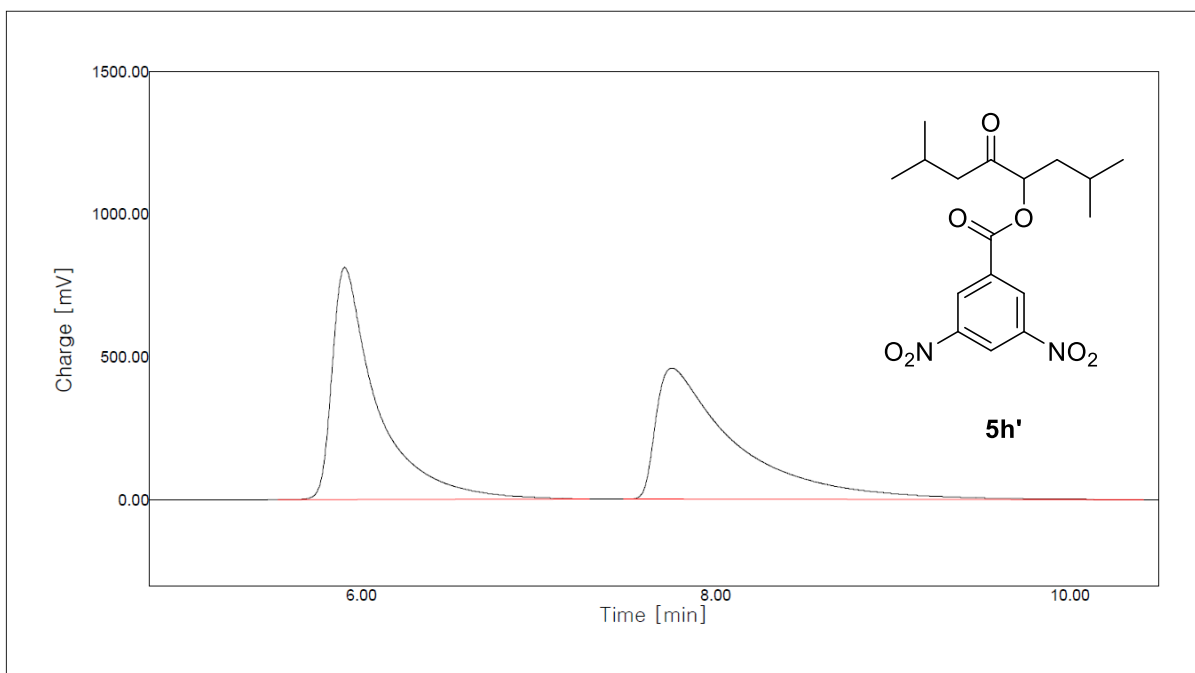
## Result

번호	time(min)	mV
1	9.7783	49.87
2	11.0850	50.13



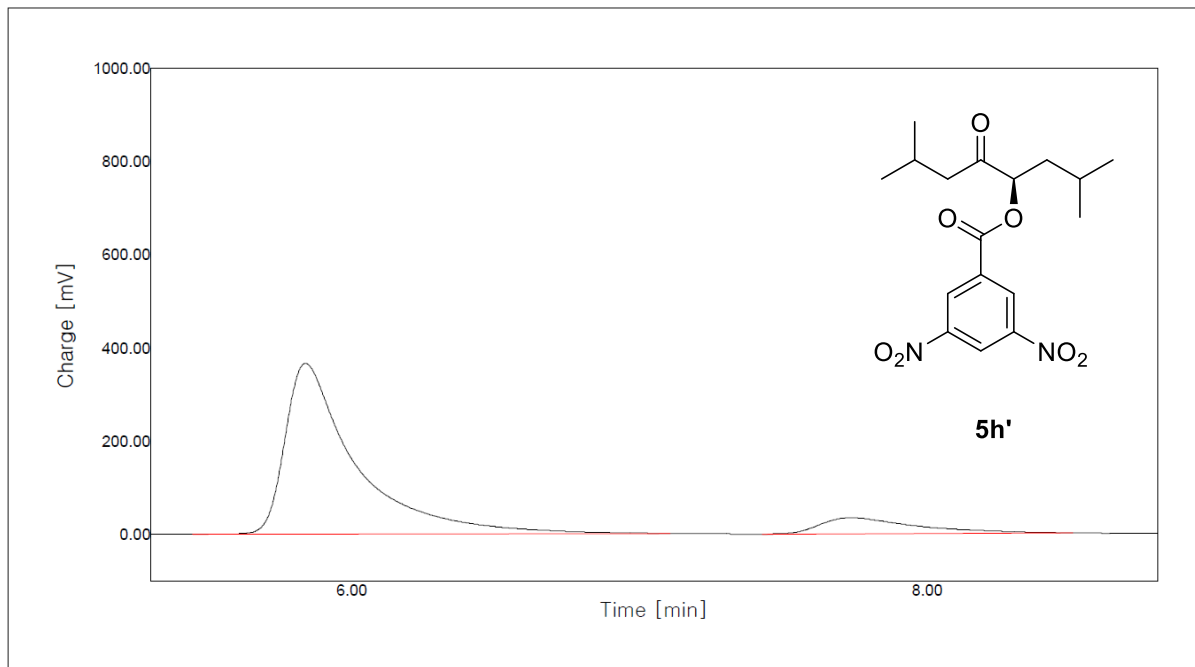
## Result

Number	Name	Time (min)	Area (%)
1		9.7367	7.27
2		11.0433	92.73



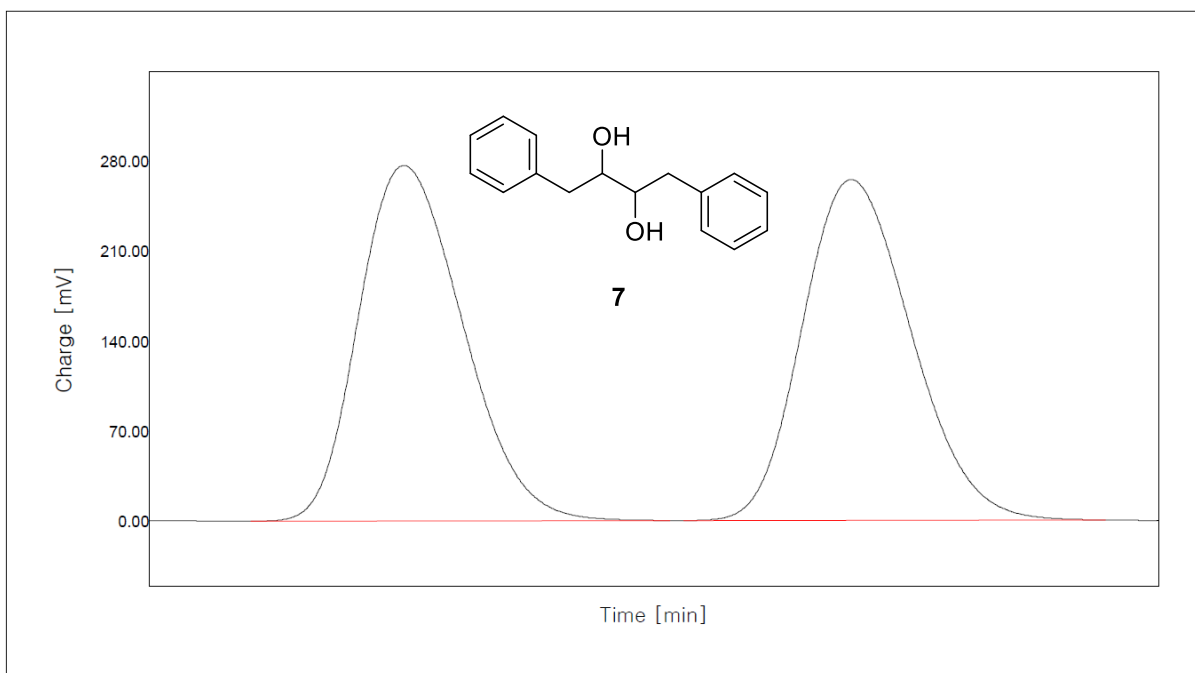
## Result

Number	Time (min)	Area (%)
1	5.9067	49.94
2	7.7533	50.06



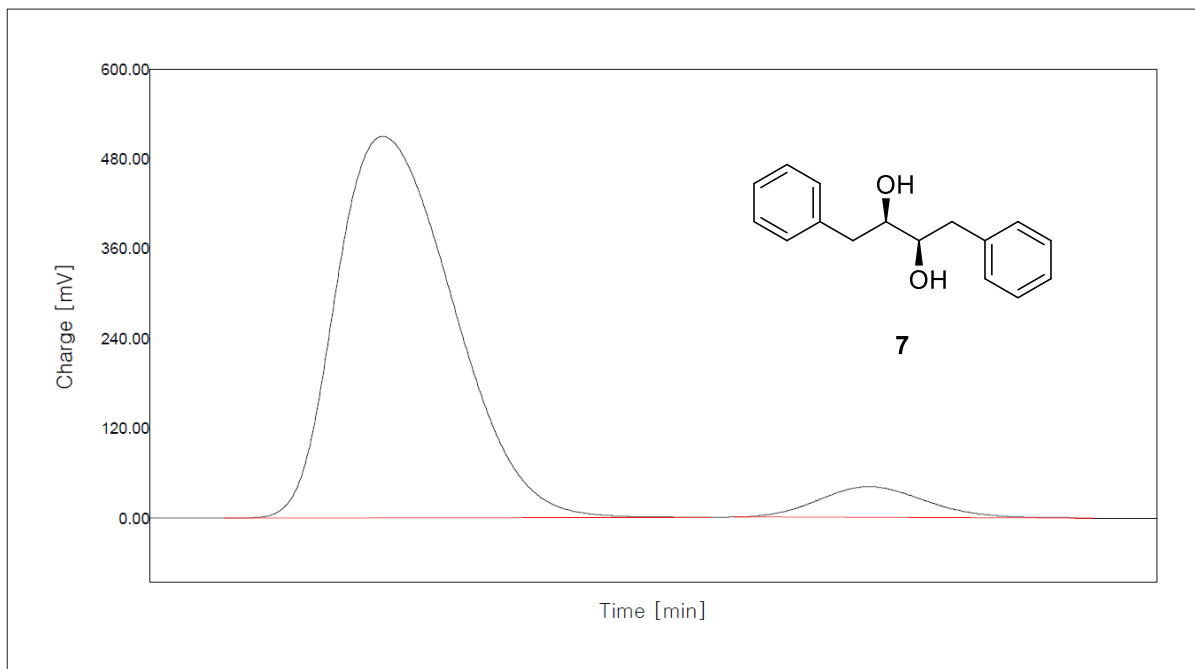
## Result

Number	Time (min)	Area (%)
1	5.8400	88.85
2	7.7350	11.15



## Result

Number	Time (min)	Area (%)
1	6.9450	49.92
2	7.6350	50.08



## Result

Number	Time (min)	Area (%)
1	6.7867	93.19
2	7.4850	6.81

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