Supporting Information

Catalytic Asymmetric Roskamp Reaction of Silyl Diazoalkane: Synthesis of Enantioenriched α-Silyl Ketone

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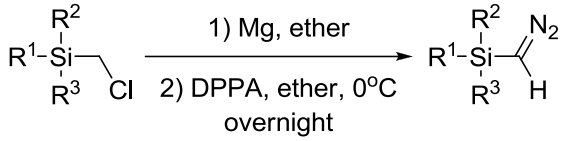
Contents

1. General Information

Unless stated otherwise, reactions were performed in vacuum-flame dried glassware under a positive pressure of dry argon atmosphere using freshly distilled solvents. Diethyl ether, tetrahydrofuran, and toluene were distilled from sodium wire. Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254}. Flash chromatography was performed using E. Merck silica gel (40-60 μm particle size). ^{1}H and ^{13}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, dq = doublet of quartets, 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). LRMS data were obtained by Bruker Impact HD quadrupole time of flight. Analytical high performance liquid chromatography (HPLC) was performed on YL 9100 HPLC system using the indicated chiral column (4.6 mm × 25 cm). Optical rotations were determined on a Perkin-Elmer polarimeter model 343 plus at 589 nm.

2. Preparation of Diazo Compound

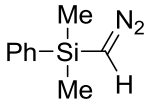
2.1 Preparation of Silyl Diazomethane[1]



To a vacuum-flame dried two-necked, round-bottomed flask was charged with crushed magnesium turnings (1.17 g, 48 mmol) in THF (30 mL). The reaction was initiated by addition of a single crystal of iodine to the magnesium turnings. (Chloromethyl)silane (40 mmol) was added dropwise over 30 min to the magnesium suspension during which time exotherms resulted in a reflux of the reaction mixture. The reaction mixture was stirred for 30 min at room temperature.

To a solution of diphenylphosphoryl azide (8.7 mL, 40 mmol) in THF (100 mL) was added (silylmethyl)magnesium chloride over 10 min at -10 °C. The reaction mixture was stirred for 16 h at 0 °C. Water (50 mL) was added to the reaction mixture and stirred for 30 min at 0 °C. The reaction mixture was filtered with diethyl ether. The filtrate was washed with water (3 x 50 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by distillation to afford desired product.

Dimethylphenylsilyldiazomethane

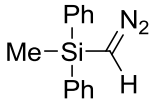


The compound was prepared according to the general procedure with (chloromethyl)dimethylphenylsilane. Purification by distillation afforded the desired product in 81% yield as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.42 – 7.36 (m, 3H), 2.81 (s, 1H), 0.43 (s, 6H)

^{13}C NMR (125MHz, $CDCl_3$) δ 137.5, 133.8, 129.7, 128.1, -2.2(2C)

Methyldiphenylsilyldiazomethane

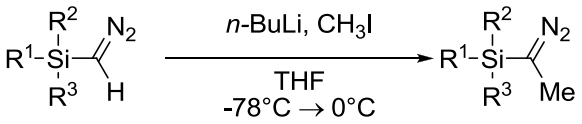


The compound was prepared according to the general procedure with (chloromethyl)diphenylmethylsilane. Purification by distillation afforded the desired product in 79% yield as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 4H), 7.47 – 7.36 (m, 6H), 3.03 (s, 1H), 0.70 (s, 3H)

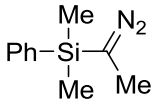
^{13}C NMR (125MHz, $CDCl_3$) δ 134.7(2C), 134.3(2C), 130.0(2C), 128.2(2C), -3.3

2.2 Preparation of Silyl Diazoethane[2]



To a stirred solution of (diazomethyl)(methyl)diphenylsilane) (5.7 g, 24 mmol) in THF (50 mL) was added *n*-BuLi (2.5 M in THF, 9.6 mL, 24 mmol) dropwise over 10 min at -78 °C. Iodomethane (1.8 mL, 29 mmol) was added to the reaction mixture at the same temperature. The reaction mixture was stirred for 30 min at -78 °C and extra 30min at 0 °C. Saturated $NaHCO_3$ solution was added to the reaction mixture. The mixture was extracted with pentane (3 x 50 mL). The combined extract was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by distillation to afford desired product.

Dimethylphenylsilyldiazomethane



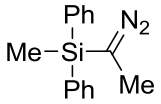
The compound was prepared according to the general procedure. Purification by distillation afforded the desired product in 79% yield as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.53 (m, 2H), 7.41 – 7.38 (m, 3H), 1.70 (s, 3H), 0.41 (s, 6H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 133.9, 129.7, 128.1, 10.6, -3.4(2C)

IR υ_{max} 3069, 3051, 3022, 3010, 2957, 2039, 1486, 1428, 1255, 1217, 1190, 1111, 958, 833, 816, 789, 728 cm^{-1}

Methyldiphenylsilyldiazoethane



The compound was prepared according to the general procedure. Purification by distillation afforded the desired product in 76% yield as a yellow oil.

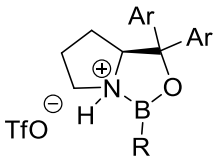
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 4H), 7.47 – 7.36 (m, 6H), 1.78 (s, 3H), 0.68 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 135.0(2C), 134.6(2C), 130.0(2C), 128.2(2C), 11.2, -4.3

IR υ_{max} 3090, 2959, 2918, 2860, 2037, 1428, 1281, 1252, 1137, 1113, 956, 833, 813, 779, 755, 732, 700 cm^{-1}

LRMS (ESI): Calcd. for $C_{16}H_{21}N_2OSi$: 285.14, found: m/z (%) = 285.16 ($[M+MeOH+H]^+$,100)

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



A 10 mL round-bottomed flask equipped with a stirring bar and a Dean-Stark trap (fully charged with activated 4Å molecular sieves) fitted on top with a reflux condenser and a argon inlet adaptor was charged with (*S*)-(-)-*α,α*-bis(3,5-dimethylphenyl)-2-pyrrolidinemethanol (0.055 mmol), 2-isopropoxybenzeneboronic acid (0.055 mmol) and 20 mL of toluene. The resulting mixture was heated to reflux under argon atmosphere. After 3

h, the reaction mixture was cooled to *ca.* 60 °C and the addition funnel and condenser were quickly replaced with a short-path distillation head. The mixture was concentrated by distillation (air-cooling) to a volume *ca.* 2.0 mL. This distillation protocol was repeated three times by re-charging with 3 x 5.0 mL of toluene. The solution was then allowed to cool to room temperature and the distillation head was quickly replaced with a vacuum adaptor. Concentration *in vacuo* (*ca.* 0.10 mmHg, 0.5 h) afforded the corresponding oxazaborolidine as clear oil.

To an aliquot of oxazaborolidine precursor (0.055 mmol) in 1.0 mL of toluene at -40 °C was added triflic acid (0.20 M solution in toluene, freshly prepared, 0.046 mmol, 0.23 mL) dropwise under argon atmosphere. After 15-20 min at -40 °C, a homogeneous catalyst solution **1** was ready for use in asymmetric synthesis *β*-hydroxysilane compounds.

4. General Procedure

4.1 Asymmetric Synthesis of *β*-hydroxysilane

To a catalyst **1f** solution prepared as described above in 1.0 mL of toluene were successively added aldehyde (0.23 mmol, 1.0 equiv.) and diazo compound (0.28 mmol, 1.2 equiv.) at -78 °C. The resulting mixture was stirred at the same temperature until complete consumption of aldehyde under argon atmosphere. After the reaction time, 1.0M DIBAL-H solution in toluene (0.58 mmol, 2.5 equiv.) was added to the reaction mixture. Then, the reaction mixture was stirred at the same temperature for 30 min under argon atmosphere. The reaction mixture was quenched with 5.0 mL of distilled water and filtered through Celite. The residue was extracted with ethyl acetate (3 x 5.0 mL). The combined extract was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (gradient elution with 20-50% dichloromethane-hexane) to afford desired *β*-hydroxysilane.

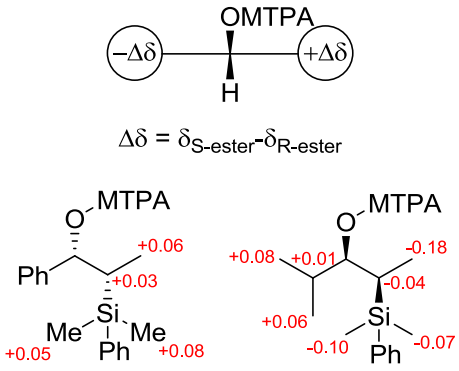
4.2 Asymmetric Synthesis of *α*-silyl ketone

To an aliquot of oxazaborolidine precursor (0.069 mmol) in 2.0 mL of toluene at -40 °C was added triflic acid (0.20 M solution in toluene, freshly prepared, 0.046 mmol, 0.23 mL) dropwise under argon atmosphere. After 15-20 min at -40 °C, a homogeneous catalyst solution **1** was ready for use in asymmetric synthesis *α*-silyl ketone compounds. To a catalyst **1f** or **1g** solution prepared as described above in 2.0 mL of toluene were successively added diazo compound solution (0.28 mmol, 1.2 equiv.) in toluene (1.0 mL) and aldehyde solution (0.23 mmol, 1.0 equiv.) in toluene (2.0 mL) at -78 °C. The resulting mixture was stirred at the same temperature until complete consumption of aldehyde under argon atmosphere. After the reaction time, the reaction mixture was quenched with 5.0 mL of distilled water and extracted with hexane (3 x 5.0 mL). The combined extract was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography

(gradient elution with 10-50% dichloromethane-hexane) to afford desired α-silyl ketone.

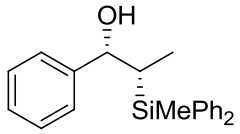
5. Absolute Configuration Determination

The absolute configuration of compounds **2a** and **5a** were confirmed by the modified Mosher ester method.[3] The *syn* configuration of *β*-hydroxysilane reduced from **5a** was confirmed by the comparison of the NMR data with literature values.[4] Details of difference in chemical shifts ($\Delta\delta^{SR}$) for the diastereomeric MTPA esters are provided in the following structures. The absolute configuration of compound **5f** was confirmed by the comparison of the optical rotation data with literature value.[5]



6. Characterization of Chiral *β*-hydroxysilane

(1*S*,2*S*)-2-(methyldiphenylsilyl)-1-phenylpropan-1-ol (4a)



Purification by column chromatography (gradient elution with 25-50% dichloromethane-hexane) afforded the desired product (267 mg, 80%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 4H), 7.40 – 7.35 (m, 6H), 7.33 – 7.26 (m, 4H), 7.26 – 7.23 (m, 1H), 4.51 (dd, J=9.6, 3.0Hz, 1H), 1.93 (dq, J=9.5, 7.6Hz, 1H), 1.75 (d, J=3.4Hz, 1H), 0.80 (d, J=7.5Hz, 3H), 0.60 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 144.7, 137.2, 137.0, 135.1, 135.1, 129.2, 129.2, 128.4, 128.0, 127.9, 127.7, 126.8, 78.2, 28.1, 12.7, -4.4

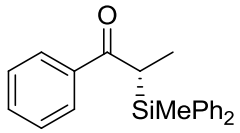
IR υ_{max} 3563, 3069, 3026, 2958, 2873, 1468, 1454, 1252, 1212, 1110, 1054, 999, 903, 788, 740 cm^{-1}.

HRMS (ESI, positive mode): Calcd. for $C_{22}H_{24}OSiNa$: m/z 355.1494 ($[M+Na]^+$), found: m/z 355.1489 ($[M+Na]^+$)

HPLC: 97% ee, OD-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 5.86 min (major) and T_R = 7.16 min (minor).

$[\alpha]^{25}_D$ = +29.4 (*c* = 1.6, $CHCl_3$).

(*S*)-2-(methyldiphenylsilyl)-1-phenylpropan-1-one



Purification by column chromatography (gradient elution with 11-33% dichloromethane-hexane) afforded the desired product (60 mg, 79%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.57 – 7.54 (m, 2H), 7.41 – 7.33 (m, 6H), 7.26 – 7.15 (m, 5H), 3.88 (q, J=6.8Hz, 1H), 1.40 (d, J=6.8Hz, 3H), 0.54 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 203.5, 138.8, 135.0, 134.8, 134.6, 134.2, 132.2, 129.8, 129.6, 128.1, 128.1, 128.1, 127.8, 34.2, 13.0, -5.5

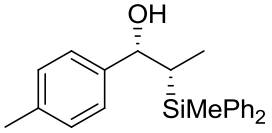
IR υ_{max} 3069, 3050, 3024, 2999, 2966, 2324, 1661, 1597, 1580, 1374, 1303, 1220, 1044, 1000, 981, 848 cm^{-1}.

HRMS (ESI, positive mode): Calcd. for $C_{22}H_{22}NaOSi$: m/z 353.1338 ($[M+Na]^+$), found: m/z 353.1332 ($[M+Na]^+$)

HPLC: 97% ee, AS-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 5.14 min (minor) and T_R = 6.46 min (major).

$[\alpha]^{25}_D$ = -126.2 (*c* = 1.4, $CHCl_3$).

(1*S*,2*S*)-2-(methyldiphenylsilyl)-1-*p*-tolylpropan-1-ol (4b)



Purification by column chromatography (gradient elution with 25-40% dichloromethane-hexane) afforded the desired product (72 mg, 90%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.38 – 7.32 (m, 6H), 7.18 – 7.13 (m, 2H), 7.12 – 7.06 (m, 2H), 4.46 (d, J=9.5Hz, 1H), 2.31 (s, 3H), 1.90 (dq, J=9.5, 7.5Hz, 1H), 1.70 (s, 1H), 0.78 (d, J=7.5Hz, 3H), 0.59 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 141.8, 137.3, 137.3 137.1, 135.1, 135.1, 129.1, 129.1, 129.0, 127.9, 127.9, 126.7, 78.0, 28.1, 21.2, 12.7, -4.3

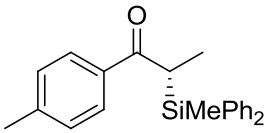
IR υ_{max} 3872, 3070, 3047, 3013, 2951, 2872, 1512, 1428, 1378, 1178, 1055, 1000, 906, 888, 792, 760 cm^{-1}.

LRMS (ESI): Calcd. for $C_{23}H_{26}NaOSi$: 369.17, found: m/z (%) = 369.17 ($[M+Na]^+$, 100)

HPLC: >99% ee, OD-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 10.2 min (major) and T_R = 17.5 min (minor).

$[\alpha]^{25}_D$ = +29.8 (*c* = 1.6, $CHCl_3$).

(*S*)-2-(methyldiphenylsilyl)-1-*p*-tolylpropan-1-one



Purification by column chromatography (gradient elution with 9-33% dichloromethane-hexane) afforded the desired product (74 mg, 93%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.43 – 7.34 (m, 5H), 7.31 – 7.27 (m, 1H), 7.23 – 7.18 (m, 2H), 7.03 (d, J=8.0Hz, 2H), 3.84 (q, J=6.8Hz, 1H), 2.32 (s, 3H), 1.38 (d, J=6.8Hz, 3H), 0.52 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 203.2, 142.9, 136.2, 135.1, 134.8(2C), 134.3, 129.8, 129.5, 128.9, 128.3, 128.1, 127.9, 33.9, 21.6, 13.1, -5.3

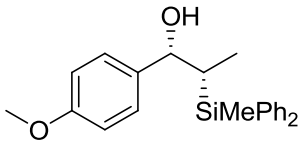
IR υ_{max} 3071, 3051, 3022, 2962, 2931, 2334, 1657, 1608, 1569, 1407, 1301, 1227, 1182, 1049, 977, 835 cm^{-1}.

HRMS (ESI, positive mode): Calcd. for $C_{23}H_{24}NaOSi$: m/z 367.1494 ($[M+Na]^+$), found: m/z 367.1489 ($[M+Na]^+$)

HPLC: >99% ee, IA-3, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 8.05 min (minor) and T_R = 9.44 min (major).

$[\alpha]^{25}_D$ = -110.9 (*c* = 1.7, $CHCl_3$).

(1*S*,2*S*)-1-(4-methoxyphenyl)-2-(methyldiphenylsilyl)propan-1-ol (4c)



Purification by column chromatography (gradient elution with 25-50% dichloromethane-hexane) afforded the desired product (79 mg, 94%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 4H), 7.43 – 7.38 (m, 6H), 7.25 – 7.22 (m, 2H), 6.90 – 6.84 (m, 2H), 4.52 (d, J=9.5Hz, 1H), 3.81 (s, 3H), 1.95 (dq, J=9.5, 7.5Hz, 1H), 1.76 (s, 1H), 0.84 (d, J=7.5Hz, 3H), 0.64 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 159.1, 137.3, 137.1, 137.0, 135.1 (2C), 129.2, 129.1, 127.9 (2C), 127.9, 113.7, 77.7, 55.3, 28.1, 12.7, -4.4

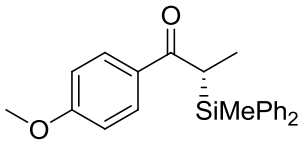
IR υ_{max} 3478, 3068, 3010, 2936, 2872, 1610, 1463, 1428, 1248, 1217, 1175, 1110, 1036, 999, 835, 792 cm^{-1}.

HRMS (ESI, positive mode): Calcd. for $C_{23}H_{26}O_2SiNa$: m/z 385.1600 ($[M+Na]^+$), found: m/z 385.1594 ($[M+Na]^+$)

HPLC: >99% ee, OD-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 15.6 min (major) and T_R = 27.6 min (minor).

$[\alpha]^{25}_D$ = +22.1 (*c* = 1.6, $CHCl_3$).

(*S*)-1-(4-methoxyphenyl)-2-(methyldiphenylsilyl)propan-1-one



Purification by column chromatography (gradient elution with 11-50% dichloromethane-hexane) afforded the desired product (81 mg, 97%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.58 – 7.55 (m, 2H), 7.42 – 7.35 (m, 5H), 7.30 – 7.26 (m, 1H), 7.22 – 7.19 (m, 2H), 3.80 (q, J=6.8Hz, 1H), 3.80 (s, 3H), 1.39 (d, J=6.8Hz, 3H), 0.55 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 201.9, 162.9, 135.1, 135.0, 134.9, 134.4, 131.7, 130.4, 129.7, 129.5, 128.1, 127.8, 113.3, 55.5, 33.5, 13.1, -5.4

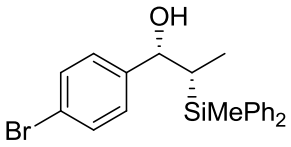
IR υ_{max} 3071, 3050, 3015, 2960, 2934, 2358, 1654, 1600, 1575, 1418, 1373, 1260, 1228, 1032, 982, 845 cm^{-1}.

LRMS (ESI): Calcd. for $C_{23}H_{24}NaO_2Si$: 383.14, found: m/z (%) = 383.15 ($[M+Na]^+$, 100)

HPLC: 98% ee, IA-3, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 12.58 min (minor) and T_R = 14.96 min (major).

$[\alpha]^{25}_D$ = -98.5 (*c* = 1.4, $CHCl_3$).

(1*S*,2*S*)-1-(4-bromophenyl)-2-(methyldiphenylsilyl)propan-1-ol (4d)



Purification by column chromatography (gradient elution with 25-50% dichloromethane-hexane) afforded the desired product (88 mg, 93%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 4H), 7.44 – 7.33 (m, 8H), 7.16 – 7.12 (m, 2H), 4.48 (dd, J=9.3, 3.2Hz, 1H), 1.85 (dq, J=9.3, 7.5Hz, 1H), 1.77 (d, J=3.4Hz, 1H), 0.79 (d, J=7.6Hz, 3H), 0.60 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 143.7, 136.9, 136.7, 135.0, 135.0, 131.4, 129.3, 129.3, 128.5, 128.0, 128.0, 121.4, 77.6, 28.3, 12.7, -4.4

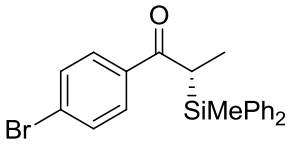
IR υ_{max} 3578, 3069, 3051, 2955, 2874, 1486, 1428, 1407, 1253, 1217, 1109, 1070, 1010, 904, 830, 738 cm^{-1}.

HRMS (ESI, positive mode): Calcd. for $C_{22}H_{23}BrOSiNa$: m/z 433.0599 ($[M+Na]^+$), found: m/z 433.0594 ($[M+Na]^+$)

HPLC: 95% ee, OZ-H, 2-propanol:*n*-Hexane=2:98, flow: 1.0mL/min, 220nm, T_R = 5.60 min (major) and T_R = 7.51 min (minor).

$[\alpha]^{25}_D$ = +14.8 (*c* = 1.6, $CHCl_3$).

(*S*)-1-(4-bromophenyl)-2-(methyldiphenylsilyl)propan-1-one



Purification by column chromatography (gradient elution with 10-25% dichloromethane-hexane) afforded the desired product (74 mg, 78%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.48 – 7.46 (m, 2H), 7.42 – 7.25 (m, 8H), 7.22 – 7.16 (m, 2H), 3.79 (q, J=6.8Hz, 1H), 1.40 (d, J=6.8Hz, 3H), 0.56 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 202.5, 137.5, 134.9, 134.8, 134.4, 134.0, 131.3, 129.9, 129.7, 129.6, 128.2, 127.9, 127.2, 34.6, 12.8, -5.8

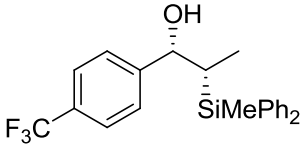
IR υ_{max} 3071, 3036, 3010, 2962, 2335, 1664, 1612, 1586, 1429, 1377, 1259, 1218, 1072, 978, 898, 850 cm^{-1}.

LRMS (ESI): Calcd. for $C_{22}H_{21}BrNaOSi$: 431.04, found: m/z (%) = 431.05 ($[M+Na]^+$, 100), 433.05 (98)

HPLC: 95% ee, IA-3, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 6.50 min (minor) and T_R = 8.30 min (major).

$[\alpha]^{25}_D$ = -77.4 (*c* = 0.9, $CHCl_3$).

(1*S*,2*S*)-2-(methyldiphenylsilyl)-1-(4-(trifluoromethyl)phenyl)propan-1-ol (4e)



Purification by column chromatography (gradient elution with 25-50% dichloromethane-hexane) afforded the desired product (69 mg, 74%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 4H), 7.57 – 7.55 (m, 2H), 7.45 – 7.37 (m, 8H), 4.62 (dd, J=9.0, 1.7Hz, 1H), 1.90 (dq, J=9.1, 7.6Hz, 1H), 1.88 (d, J=2.9Hz, 1H), 0.86 (d, J=7.6Hz, 3H), 0.65 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 148.6, 136.7, 136.6, 135.0, 135.0, 129.8 (q, J=32.0Hz), 129.4, 129.4, 128.1, 128.0, 127.1, 125.3 (q, J=3.7Hz), 124.3 (q, J=270.4Hz), 77.8, 28.5, 12.8, -4.4

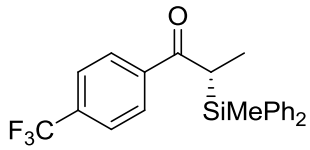
IR υ_{max} 3574, 3071, 3043, 2965, 2872, 1487, 1428, 1326, 1255, 1217, 1166, 1125, 1017, 847, 756, 701 cm^{-1}.

LRMS (ESI): Calcd. for $C_{23}H_{23}F_3NaOSi$: 423.14, found: m/z (%) = 423.14 ($[M+Na]^+$, 100)

HPLC: 88% ee, OZ-H, 2-propanol:*n*-Hexane=2:98, flow: 1.0mL/min, 220nm, T_R = 4.37 min (major) and T_R = 5.16 min (minor).

$[\alpha]^{25}_D$ = +19.7 (*c* = 1.4, $CHCl_3$).

(*S*)-2-(methyldiphenylsilyl)-1-(4-(trifluoromethyl)phenyl)propan-1-one



Purification by column chromatography (gradient elution with 11-33% dichloromethane-hexane) afforded the desired product (58 mg, 63%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 2H), 7.56 – 7.52 (m, 2H), 7.43 – 7.38 (m, 3H), 7.37 – 7.33 (m, 2H), 7.32 – 7.30 (m, 2H), 7.25 – 7.22 (m, 1H), 7.18 – 7.13 (m, 2H), 3.85 (q, J=6.7Hz, 1H), 1.43 (d, J=6.8Hz, 3H), 0.59 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 202.6, 141.7, 134.8, 134.7, 134.1, 133.8, 133.3 (q, J=32.3Hz), 130.0, 129.8, 128.3, 128.2, 127.9, 123.8 (q, J=271.0Hz), 125.1 (q, J=3.7Hz), 35.4, 12.7, -6.1

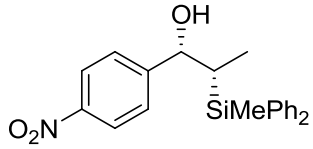
IR υ_{max} 3060, 3028, 2998, 2926, 2360, 1679, 1658, 1563, 1428, 1321, 1257, 1218, 1067, 1017, 980, 858 cm^{-1}.

HRMS (ESI, positive mode): Calcd. for $C_{23}H_{21}F_3NaOSi$: m/z 421.1212 ($[M+Na]^+$), found: m/z 421.1206 ($[M+Na]^+$)

HPLC: 94% ee, IA-3, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 5.23 min (minor) and T_R = 5.78 min (major).

$[\alpha]^{25}_D$ = -67.6 (*c* = 0.5, $CHCl_3$).

(1*S*,2*S*)-2-(methyldiphenylsilyl)-1-(4-nitrophenyl)propan-1-ol (4f)



Purification by column chromatography (gradient elution with 25-50% dichloromethane-hexane) afforded the desired product (71 mg, 81%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 2H), 7.67 – 7.59 (m, 4H), 7.44 – 7.35 (m, 8H), 4.67 (d, J=8.8Hz, 1H), 2.02 (s, 1H), 1.90 (dq, J=8.8, 7.5Hz, 1H), 0.88 (d, J=7.6Hz, 3H), 0.64 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 152.0, 147.3, 136.4, 136.3, 134.9 (2C), 134.1, 129.5, 128.1, 128.0, 127.5, 123.5, 77.4, 28.7, 12.9, -4.4

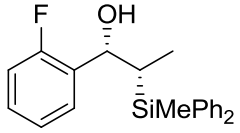
IR υ_{max} 3700, 3070, 3009, 2923, 2828, 1520, 1428, 1347, 1254, 1217, 1196, 1055, 1032, 853, 758, 740 cm^{-1}.

HRMS (ESI, positive mode): Calcd. for $C_{22}H_{23}NO_3SiNa$: m/z 400.1345 ($[M+Na]^+$), found: m/z 400.1339 ($[M+Na]^+$)

HPLC: 90% ee, OD-H, 2-propanol:*n*-Hexane=2:8, flow: 1.0mL/min, 220nm, T_R = 6.26 min (major) and T_R = 12.0 min (minor).

$[\alpha]^{25}_D$ = +8.5 (*c* = 1.5, $CHCl_3$).

(1*S*,2*S*)-1-(2-fluorophenyl)-2-(methyldiphenylsilyl)propan-1-ol (4g)



Purification by column chromatography (gradient elution with 20-33% dichloromethane-hexane) afforded the desired product (57 mg, 70%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 4H), 7.40 – 7.35 (m, 7H), 7.25 – 7.18 (m, 1H), 7.13 – 7.08 (m, 1H), 7.01 – 6.95 (m, 1H), 4.85 (dd, J=10.0, 5.1Hz, 1H), 1.99 (dq, J=9.9, 7.7Hz, 1H), 1.85 (d, J=5.2Hz, 1H), 0.83 (d, J=7.6Hz, 3H), 0.68 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 160.4 (d, J=243.8Hz), 137.0 (d, J=10.0Hz), 135.0, 135.0, 131.8 (d, J=12.5Hz), 129.3, 129.2, 128.9 (d, J=8.8Hz), 128.3, 128.3, 128.0, 128.0, 124.3 (d, J=2.5Hz), 115.4 (d, J=22.5Hz), 72.6, 28.0, 13.0, -4.5

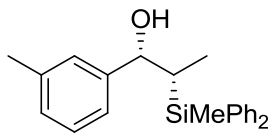
IR υ_{max} 3564, 3070, 3047, 3012, 2955, 1487, 1455, 1428, 1252, 1219, 1110, 1055, 999, 909, 833, 758, 701 cm^{-1}.

LRMS (ESI): Calcd. for $C_{22}H_{23}FNaOSi$: 373.14, found: m/z (%) = 373.15 ($[M+Na]^+$, 100)

HPLC: 97% ee, OD-H, 2-propanol:*n*-Hexane=1:9, flow: 1.0mL/min, 220nm, T_R = 4.54 min (major) and T_R = 6.77 min (minor).

$[\alpha]^{25}_D$ = +26.9 (*c* = 1.4, $CHCl_3$).

(1*S*,2*S*)-2-(methyldiphenylsilyl)-1-m-tolylpropan-1-ol (4h)



Purification by column chromatography (gradient elution with 20-33% dichloromethane-hexane) afforded the desired product (71 mg, 89%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 4H), 7.42 – 7.34 (m, 6H), 7.22 – 7.16 (m, 1H), 7.12 – 7.04 (m, 3H), 4.49 (dd, J=9.6, 3.4Hz, 1H), 2.33 (s, 3H), 1.93 (dq, J=9.5, 7.6Hz, 1H), 1.71 (d, J=3.6Hz, 1H), 0.80 (d,

J=7.6Hz, 3H), 0.61 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 144.7, 138.0, 137.3, 137.1, 135.1, 129.2(2C), 128.5, 128.3, 128.0, 127.9, 127.5, 123.9, 78.3, 28.1, 21.6, 12.8, -4.3

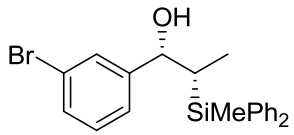
IR υ_{max} 3573, 3069, 3045, 2969, 2952, 2910, 1487, 1428, 1252, 1217, 1110, 1055, 999, 758, 701 cm^{-1}.

LRMS (ESI): Calcd. for $C_{23}H_{26}NaOSi$: 369.17, found: m/z (%) = 369.17 ($[M+Na]^+$, 100)

HPLC: 97% ee, OD-H, 2-propanol:*n*-Hexane=1:9, flow: 1.0mL/min, 220nm, T_R = 4.76 min (major) and T_R = 5.80 min (minor).

$[\alpha]^{25}_D$ = +26.1 (*c* = 1.7, $CHCl_3$).

(1*S*,2*S*)-1-(3-bromophenyl)-2-(methyldiphenylsilyl)propan-1-ol (4i)



Purification by column chromatography (gradient elution with 20-33% dichloromethane-hexane) afforded the desired product (80 mg, 84%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.43 – 7.39 (m, 1H), 7.38 – 7.33 (m, 7H), 7.18 – 7.11 (m, 2H), 4.45 (d, J=9.3Hz, 1H), 1.86 (dq, J=9.3, 7.6Hz, 1H), 1.79 (s, 1H), 0.80 (d, J=7.6Hz, 3H), 0.59 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 147.1, 136.8, 136.7, 135.0, 135.0 130.7, 129.9, 129.9 129.4, 129.3, 128.1, 128.0, 125.5, 122.6, 77.8, 28.3, 12.8, -4.4

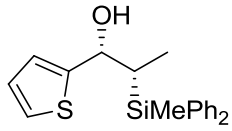
IR υ_{max} 3695, 3068, 3012, 2972, 2923, 2825, 1474, 1428, 1255, 1217, 1194, 1110, 1055, 886, 833, 757, 668 cm^{-1}.

LRMS (ESI): Calcd. for $C_{22}H_{23}BrNaOSi$: 433.06, found: m/z (%) = 433.07 ($[M+Na]^+$, 100), 435.07 (98)

HPLC: 95% ee, OZ-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 6.69 min (major) and T_R = 8.04 min (minor).

$[\alpha]^{25}_D$ = +17.9 (*c* = 2.0, $CHCl_3$).

(1*R*,2*S*)-2-(methyldiphenylsilyl)-1-(thiophen-2-yl)propan-1-ol (4j)



Purification by column chromatography (gradient elution with 20-33% dichloromethane-hexane) afforded the desired product (70 mg, 89%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 4H), 7.42 – 7.33 (m, 6H), 7.24 (dd, J=5.0, 0.7Hz, 1H), 6.91 (dd, J=5.0, 3.5Hz, 1H), 6.85 (dd, J=3.5, 0.8Hz, 1H), 4.82 (dd, J=9.2, 3.9Hz, 1H), 1.97 (dq, J=9.2, 7.5Hz, 1H), 1.88 (d, J=4.0Hz, 1H), 0.93 (d, J=7.5Hz, 3H), 0.58 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 149.1, 136.8, 136.7, 135.1(2C), 129.3(2C), 128.0, 127.9, 126.4, 124.9, 124.8, 73.8, 29.1, 12.7, -4.5

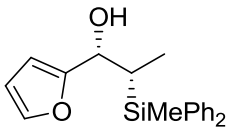
IR υ_{max} 3560, 3068, 3048, 3015, 2955, 1487, 1428, 1252, 1217, 1192, 1110, 998, 898, 832, 738, 700 cm^{-1}.

LRMS (ESI): Calcd. for $C_{20}H_{22}NaOSSi$: 361.11, found: m/z (%) = 361.11 ($[M+Na]^+$, 100)

HPLC: 94% ee, OD-H, 2-propanol:*n*-Hexane=1:9, flow: 1.0mL/min, 220nm, T_R = 5.55 min (major) and T_R = 6.82 min (minor).

$[\alpha]^{25}_D$ = +9.4 (*c* = 1.5, $CHCl_3$).

(1*S*,2*S*)-1-(furan-2-yl)-2-(methyldiphenylsilyl)propan-1-ol (4k)



Purification by column chromatography (gradient elution with 20-33% dichloromethane-hexane) afforded the desired product (70 mg, 94%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 4H), 7.40 – 7.33 (m, 7H), 6.29 (dd, J=3.2, 1.8Hz, 1H), 6.12 (d, J=3.2Hz, 1H), 4.62 (dd, J=8.7, 4.4Hz, 1H), 2.13 (dq, J=8.7, 7.5Hz, 1H), 1.80 (d, J=5.2Hz, 1H), 0.95 (d, J=7.5Hz, 3H), 0.56 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 156.5, 141.9, 136.7, 136.6, 135.0(2C), 129.3, 129.3, 128.0, 127.9, 110.2, 107.0, 71.1, 25.9, 12.1, -5.0

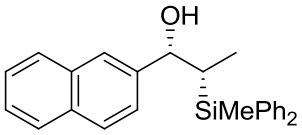
IR υ_{max} 3572, 3069, 3049, 2958, 2874, 1428, 1253, 1217, 1110, 1053, 1000, 928, 881, 757, 701 cm^{-1}.

LRMS (ESI): Calcd. for $C_{20}H_{22}NaO_2Si$: 345.13, found: m/z (%) = 345.13 ($[M+Na]^+$, 100)

HPLC: 96% ee, OJ-H, 2-propanol:*n*-Hexane=1:9, flow: 1.0mL/min, 220nm, T_R = 10.2 min (minor) and T_R = 16.3 min (major).

$[\alpha]^{25}_D$ = +14.0 (*c* = 1.6, $CHCl_3$).

(1*S*,2*S*)-2-(methyldiphenylsilyl)-1-(naphthalen-2-yl)propan-1-ol (4l)



Purification by column chromatography (gradient elution with 20-33% dichloromethane-hexane) afforded the desired product (74 mg, 84%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 3H), 7.68 – 7.62 (m, 5H), 7.54 – 7.50 (m, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 6H), 4.69 (dd, J=9.6, 2.5Hz, 1H), 2.03 (dq, J=9.6, 7.6Hz, 1H), 1.84 (d, J=3.2Hz, 1H), 0.82 (d, J=7.6Hz, 3H), 0.63 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 142.0, 137.2, 137.0, 135.1(2C), 133.2, 129.3, 129.3, 128.4, 128.1, 128.0, 127.9, 127.8, 126.2, 125.9, 125.9, 124.6(2C), 78.5, 28.0, 12.9, -4.2

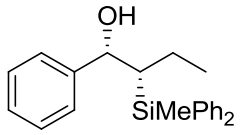
IR υ_{max} 3615, 3069, 3052, 2948, 2920, 2850, 1454, 1428, 1253, 1217, 1110, 1055, 998, 892, 857, 700, 676 cm^{-1}.

LRMS (ESI): Calcd. for $C_{26}H_{26}NaOSi$: 405.17, found: m/z (%) = 405.17 ($[M+Na]^+$, 100)

HPLC: 94% ee, OZ-H, 2-propanol:*n*-Hexane=1:9, flow: 1.0mL/min, 220nm, T_R = 4.03 min (major) and T_R = 4.39 min (minor).

$[\alpha]^{25}_{D}$ = +15.7 (*c* = 0.68, $CHCl_3$).

(1*S*,2*S*)-2-(methyldiphenylsilyl)-1-phenylbutan-1-ol (4m)



Purification by column chromatography (gradient elution with 20-33% dichloromethane-hexane) afforded the desired product (45 mg, 56%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 4H), 7.36 – 7.31 (m, 6H), 7.28 – 7.26 (m, 4H), 7.24 – 7.19 (m, 1H), 4.80 (d, J=7.8Hz, 1H), 1.84 (ddd, J=8.2, 6.1, 4.8Hz, 1H), 1.71 (s, 1H), 1.48 – 1.37 (m, 2H), 0.71 (t, J=7.4Hz, 3H), 0.59 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 145.2, 137.9, 137.8, 135.0, 135.0, 129.1, 129.0, 128.3, 127.9(2C), 127.4, 126.5, 76.2, 36.3, 21.1, 14.1, -3.5i

IR υ_{max} 3565, 3071, 3058, 2965, 2937, 2885, 2863, 1478, 1423, 1336, 1252, 1195, 1040, 1021, 918, 787 cm^{-1}.

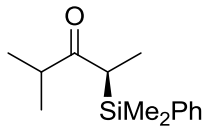
LRMS (ESI): Calcd. for $C_{23}H_{26}NaOSi$: 369.17, found: m/z (%) = 369.17 ($[M+Na]^+$, 100)

HPLC: 90% ee, OZ-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 5.97 min (major) and T_R = 7.44 min (minor).

$[\alpha]^{25}_{D}$ = +35.5 (*c* = 0.80, $CHCl_3$).

7. Characterization of Chiral α-silyl ketone

(*R*)-2-(dimethyl(phenyl)silyl)-4-methylpentan-3-one (5a)



Purification by column chromatography (gradient elution with 14-33% dichloromethane-hexane) afforded the desired product (33 mg, 60%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.39 – 7.34 (m, 3H), 2.75 (q, J=6.9Hz, 1H), 2.30 – 2.20 (m, 1H), 1.17 (d, J=6.9Hz, 3H), 0.98 (d, J=7.2Hz, 3H), 0.82 (d, J=6.6Hz, 3H), 0.37 (s, 3H), 0.35 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 216.6, 136.7, 133.9, 129.7, 128.1, 41.7, 39.3, 19.6, 16.7, 12.2, -4.5, -4.6

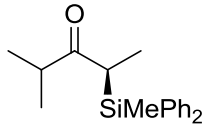
IR υ_{max} 3076, 3016, 2968, 2874, 1689, 1467, 1428, 1382, 1253, 1217, 1177, 1116, 1070, 994, 837, 819, 759 cm^{-1}.

HRMS (ESI, positive mode): Calcd. for $C_{14}H_{22}OSiNa$: m/z 257.1338 ($[M+Na]^+$), found: m/z 257.1332 ($[M+Na]^+$)

HPLC: 92% ee, OJ-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, 40°C, T_R = 5.08 min (major) and T_R = 5.88 min (minor).

$[\alpha]^{25}_{D}$ = +198.1 (*c* = 0.78, $CHCl_3$).

(*R*)-2-methyl-4-(methyldiphenylsilyl)pentan-3-one (5b)



Purification by column chromatography (gradient elution with 14-50% dichloromethane-hexane) afforded the desired product (61 mg, 89%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.55 – 7.50 (m, 2H), 7.44 – 7.33 (m, 6H), 3.16 (q, J=6.9Hz, 1H), 2.17 – 2.07 (m, 1H), 1.27 (d, J=7.0Hz, 3H), 0.99 (d, J=7.2Hz, 3H), 0.67 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 216.7, 134.9, 134.8, 134.8, 134.6, 129.8(2C), 128.2, 128.1, 42.0, 37.8, 19.6, 16.5, 12.8, -6.3

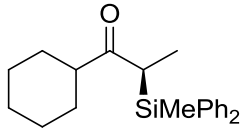
IR υ_{max} 3070, 3014, 2968, 2874, 1688, 1466, 1381, 1347, 1255, 1217, 1148, 1113, 1067, 992, 797, 756 cm^{-1}.

LRMS (ESI): Calcd. for $C_{19}H_{24}NaOSi$: 319.15, found: m/z (%) = 319.16 ($[M+Na]^+$, 100)

HPLC: 96% ee, OD-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 4.70 min (major) and T_R = 4.99 min (minor).

$[\alpha]^{25}_{D}$ = +216.7 (*c* = 1.4, $CHCl_3$).

(*R*)-1-cyclohexyl-2-(methyldiphenylsilyl)propan-1-one (5c)



Purification by column chromatography (gradient elution with 17-50% dichloromethane-hexane) afforded the desired product (62 mg, 80%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.56 – 7.52 (m, 2H), 7.43 – 7.34 (m, 6H), 3.13 (q, J=6.9Hz, 1H), 1.83 – 1.76 (m, 2H), 1.72 – 1.62 (m, 1H), 1.59 – 1.49 (m, 2H), 1.31 – 1.26 (m, 2H), 1.23 (d, J=6.9Hz, 3H), 1.17 – 1.09 (m, 2H), 1.09 – 1.00 (m, 2H), 0.65 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 216.0, 135.0, 134.9, 134.8 (2C), 129.8, 129.8, 128.2, 128.1, 52.2, 38.1, 30.1, 26.8, 26.5, 25.9, 25.1, 12.5, -6.3

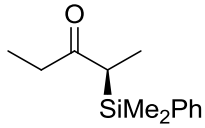
IR υ_{max} 3070, 3050, 2931, 2853, 1684, 1450, 1428, 1374, 1319, 1258, 1152, 1113, 987, 832, 757, 700 cm^{-1}.

HRMS (ESI, positive mode): Calcd. for $C_{22}H_{28}OSiNa$: m/z 359.1807 ($[M+Na]^+$), found: m/z 359.1802 ($[M+Na]^+$)

HPLC: 85% ee, OD-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 5.07 min (major) and T_R = 5.86 min (minor).

$[\alpha]^{25}_{D}$ = +145.1 (*c* = 0.95, $CHCl_3$).

(*R*)-2-(dimethyl(phenyl)silyl)pentan-3-one (5d)



Purification by column chromatography (gradient elution with 14-33% dichloromethane-hexane) afforded the desired product (37 mg, 73%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.41 – 7.34 (m, 3H), 2.62 (q, J=6.9Hz, 1H), 2.15 – 2.02 (m, 2H), 1.17 (d, J=6.9Hz, 3H), 0.87 (t, J=7.3Hz, 3H), 0.37 (s, 3H), 0.35 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 213.4, 136.6, 133.9, 129.7, 128.1, 40.7, 36.9, 11.6, 7.9, -4.4, -4.6

IR υ_{max} 3072, 3054, 3000, 2972, 2883, 1692, 1462, 1428, 1375, 1253, 1217, 1151, 1114, 984, 837, 823, 763 cm^{-1}.

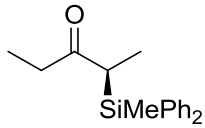
HRMS (ESI, positive mode): Calcd. for $C_{13}H_{20}OSiNa$: m/z 243.1181 ($[M+Na]^+$), found: m/z 243.1176 ($[M+Na]^+$)

HPLC: 95% ee, OD-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 4.70 min (major) and T_R = 5.00 min (minor).

$[\alpha]^{25}_D$ = +197.0 (*c* = 2.0, C_6H_6).

[lit. $[\alpha]^{22}_D$ = -201.4 (*c* = 1.25 C_6H_6, >96% ee) for *S*-enantiomer]; Enders, D.; Lohray, B. B.; Burkamp, F.; Bhushan, V.; Hett, R. *Liebigs Ann.* **1996**, 189.

(*R*)-2-(methyldiphenylsilyl)pentan-3-one (5e)



Purification by column chromatography (gradient elution with 11-33% dichloromethane-hexane) afforded the desired product (56 mg, 85%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.53 – 7.48 (m, 2H), 7.43 – 7.33 (m, 6H), 3.00 (q, J=7.0Hz, 1H), 2.05 (dq, J=17.6, 7.3Hz, 1H), 1.91 (dq, J=17.6, 7.2Hz, 1H), 1.23 (d, J=6.9Hz, 3H), 0.78 (t, J=7.3Hz, 3H), 0.64 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 213.5, 134.9, 134.8, 134.8, 134.4, 129.9(2C), 128.2, 128.2, 39.3, 37.3, 12.2, 7.8, -6.2

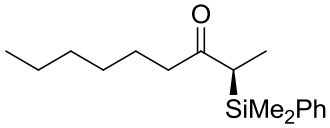
IR υ_{max} 3071, 3060, 3019, 2880, 1691, 1460, 1411, 1375, 1304, 1217, 1155, 1113, 1042, 948, 810, 740 cm^{-1}.

LRMS (ESI): Calcd. for $C_{18}H_{22}NaOSi$: 305.13, found: m/z (%) = 305.14 ($[M+Na]^+$, 100)

HPLC: 83% ee, OD-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 5.64 min (major) and T_R = 6.55 min (minor).

$[\alpha]^{25}_D$ = +150.7 (*c* = 1.4, $CHCl_3$).

(*R*)-2-(dimethyl(phenyl)silyl)nonan-3-one (5f)



Purification by column chromatography (gradient elution with 10-25% dichloromethane-hexane) afforded the desired product (47 mg, 73%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.42 – 7.35 (m, 3H), 2.61 (q, J=6.9Hz, 1H), 2.12 – 1.98 (m, 2H), 1.49 – 1.39 (m, 1H), 1.38 – 1.29 (m, 1H), 1.28 – 1.19 (m, 2H), 1.16(d, J=6.9Hz, 3H), 1.18 – 1.06 (m, 4H), 0.85 (t, J=7.2Hz, 3H), 0.37 (s, 3H), 0.35 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 213.2, 136.7, 133.9, 129.7, 128.1, 44.0, 41.0, 31.7, 29.0, 24.0, 22.6, 14.2, 11.6, -4.3, -4.6

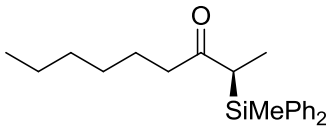
IR υ_{max} 3046, 3017, 2958, 2932, 2861, 1688, 1462, 1428, 1374, 1253, 1217, 1149, 1114, 986, 836, 816, 759 cm^{-1}.

LRMS (ESI): Calcd. for $C_{17}H_{28}NaOSi$: 299.18, found: m/z (%) = 299.19 ($[M+Na]^+$, 100)

HPLC: 93% ee, OD-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 4.42 min (major) and T_R = 4.84 min (minor).

$[\alpha]^{25}_D$ = +133.2 (*c* = 1.1, $CHCl_3$).

(*R*)-2-(methyldiphenylsilyl)nonan-3-one (5g)



Purification by column chromatography (gradient elution with 14-33% dichloromethane-hexane) afforded the desired product (60 mg, 77%) as colorless oil.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.53 – 7.50 (m, 2H), 7.44 – 7.34 (m, 6H), 3.01 (q, J=6.9Hz, 1H), 2.02 (ddd, J=16.7, 9.1, 5.9Hz, 1H), 1.88 (ddd, J=16.8, 9.2, 5.9Hz, 1H), 1.44 – 1.34 (m, 1H), 1.22 (d, J=7.0Hz, 3H), 1.27 – 1.15 (m, 3H), 1.11 – 1.04 (m, 2H), 1.01 – 0.94 (m, 2H), 0.84 (t, J=7.3Hz, 3H), 0.66 (s, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 213.2, 134.8(2C), 134.5(2C), 129.9, 129.9, 128.2, 128.2, 44.4, 39.5, 31.6, 28.9, 23.8, 22.6, 14.2, 12.1, -6.2

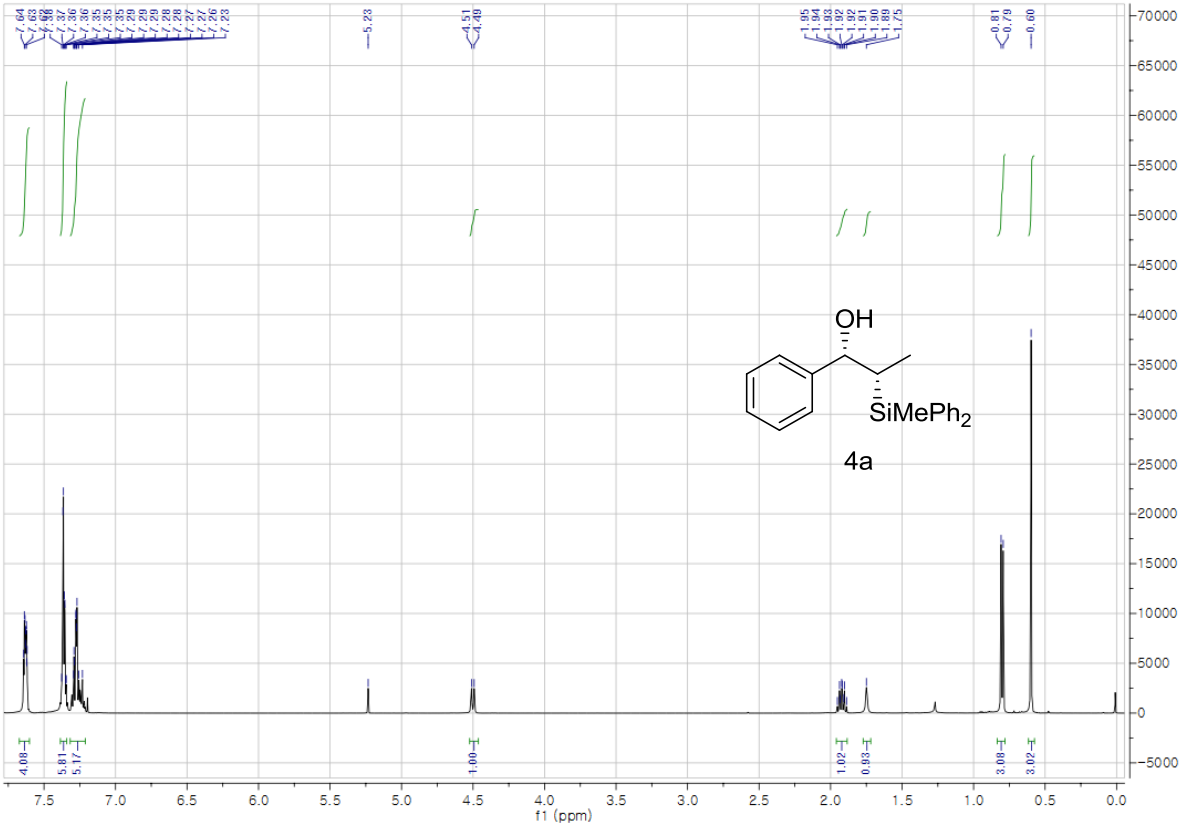
IR υ_{max} 3071, 3051, 3018, 2958, 2873, 1689, 1459, 1428, 1256, 1216, 1149, 1112, 1067, 987, 832, 757 cm^{-1}.

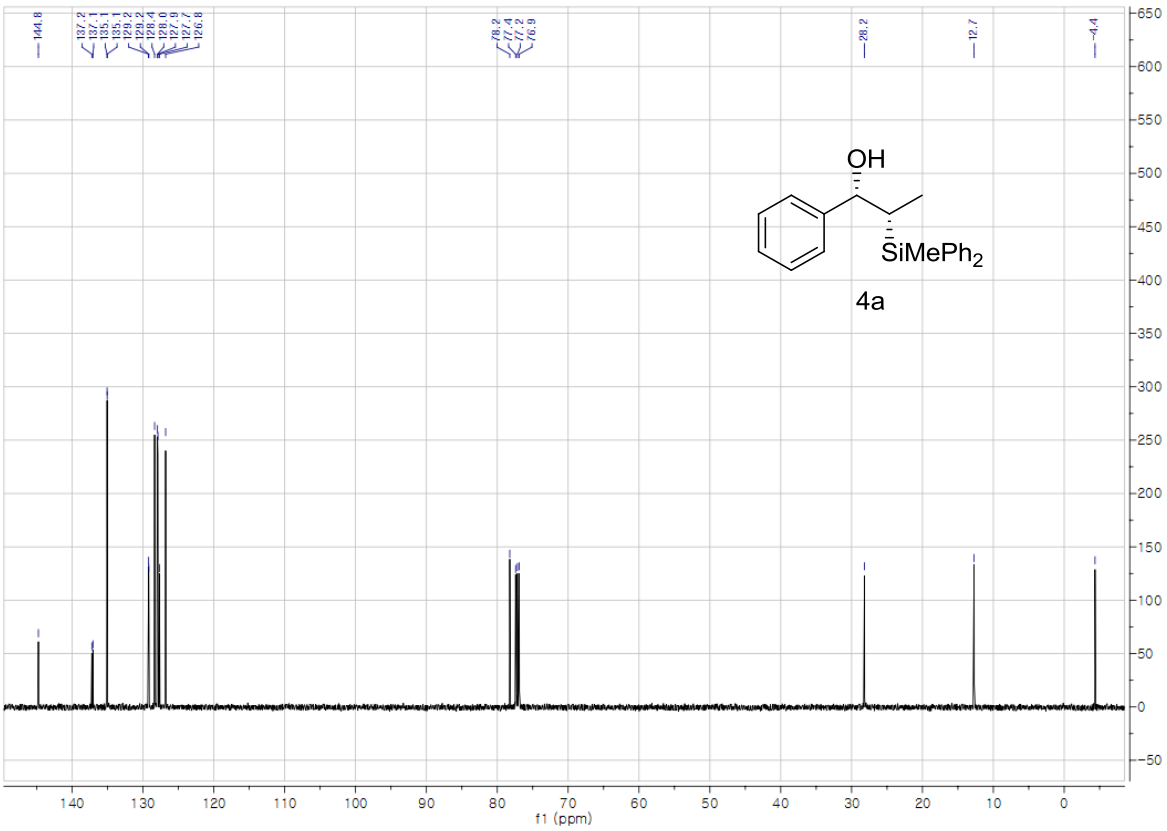
HRMS (ESI, positive mode): Calcd. for $C_{22}H_{30}OSiNa$: m/z 361.1964 ($[M+Na]^+$), found: m/z 361.1958 ($[M+Na]^+$)

HPLC: 85% ee, OD-H, 2-propanol:*n*-Hexane=1:99, flow: 1.0mL/min, 220nm, T_R = 4.90 min (major) and T_R = 5.70 min (minor).

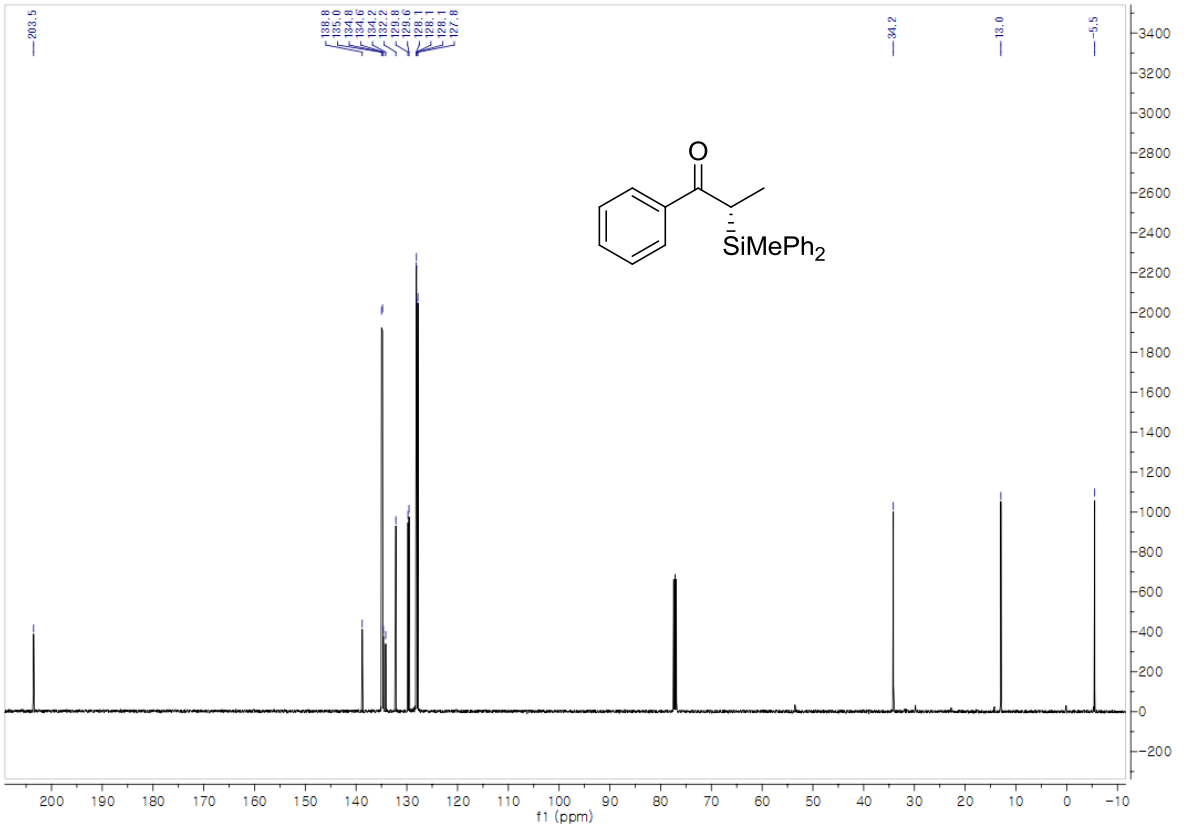
$[\alpha]^{25}_D$ = +138.8 (*c* = 1.6, $CHCl_3$).

8. ^{1}H NMR and ^{13}C NMR Spectra






O
SiMePh2
f1 (ppm)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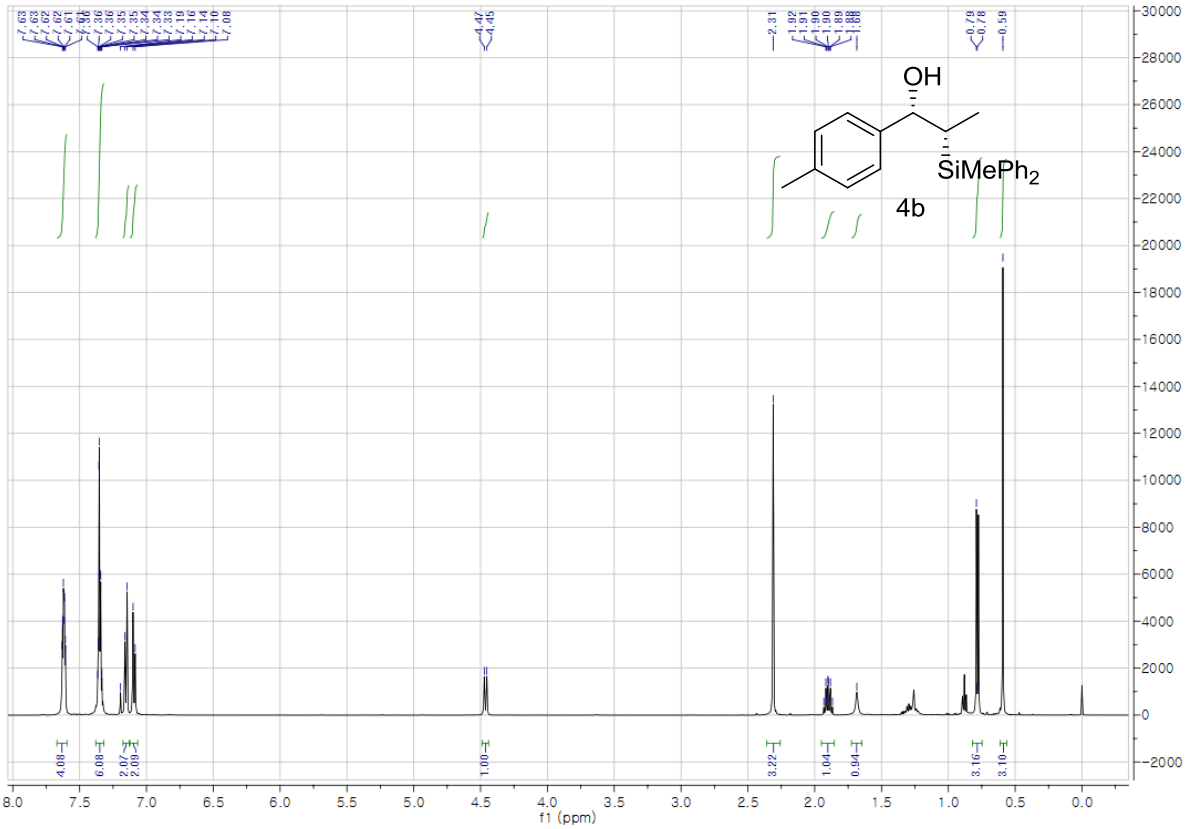
f1 (ppm)


OH
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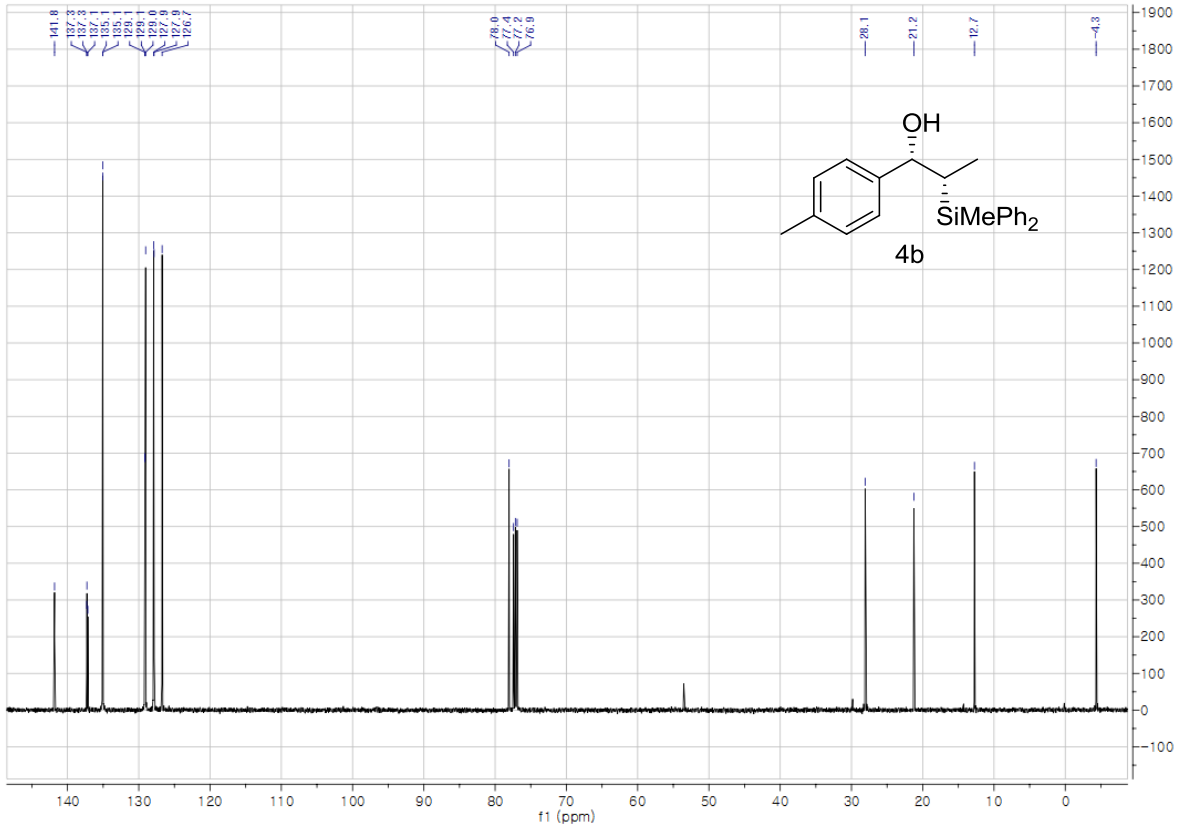
4b
f1 (ppm)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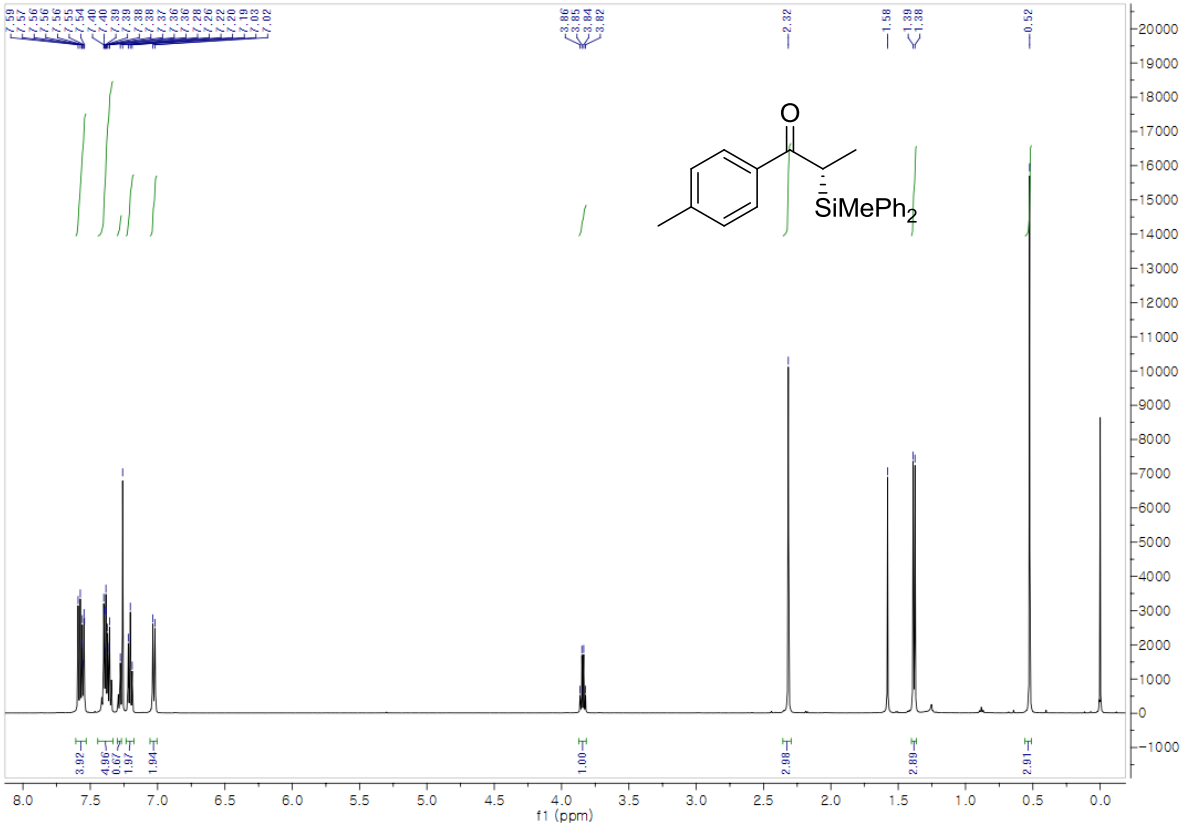
SiMePh2
4b
f1 (ppm)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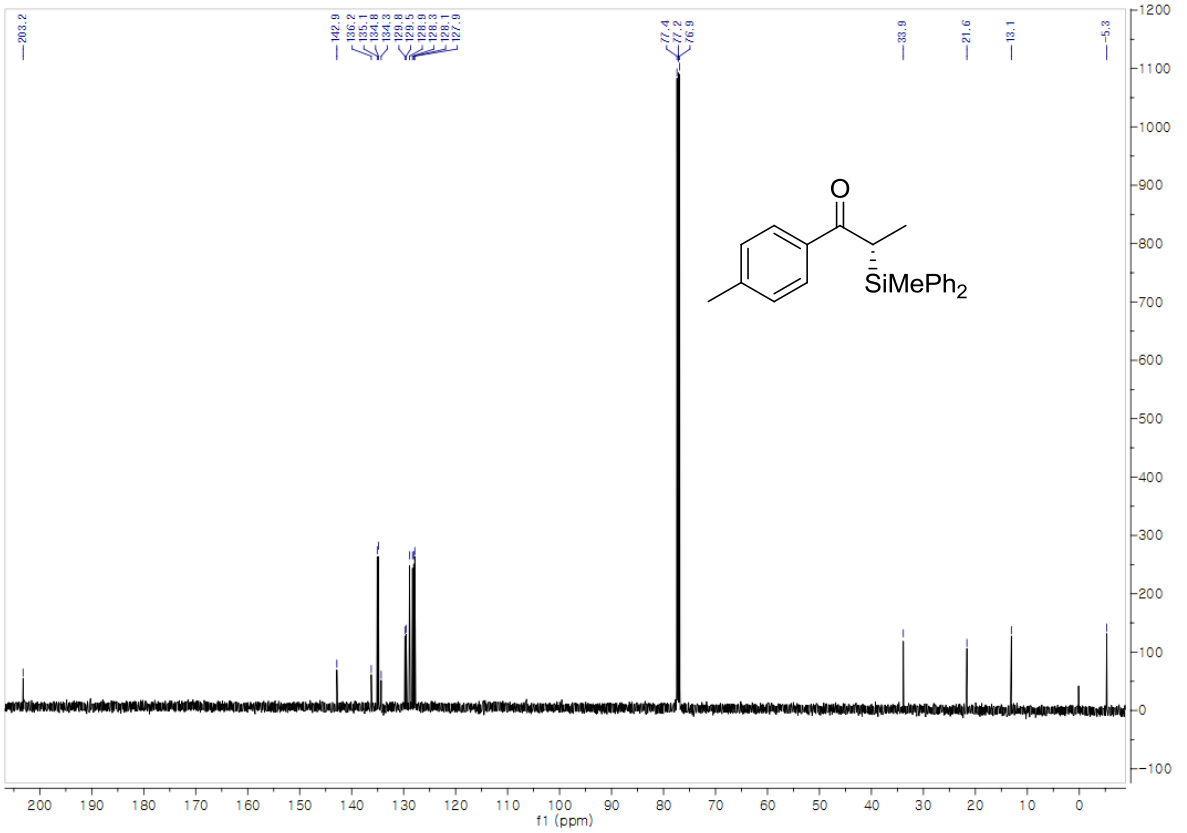
f1 (ppm)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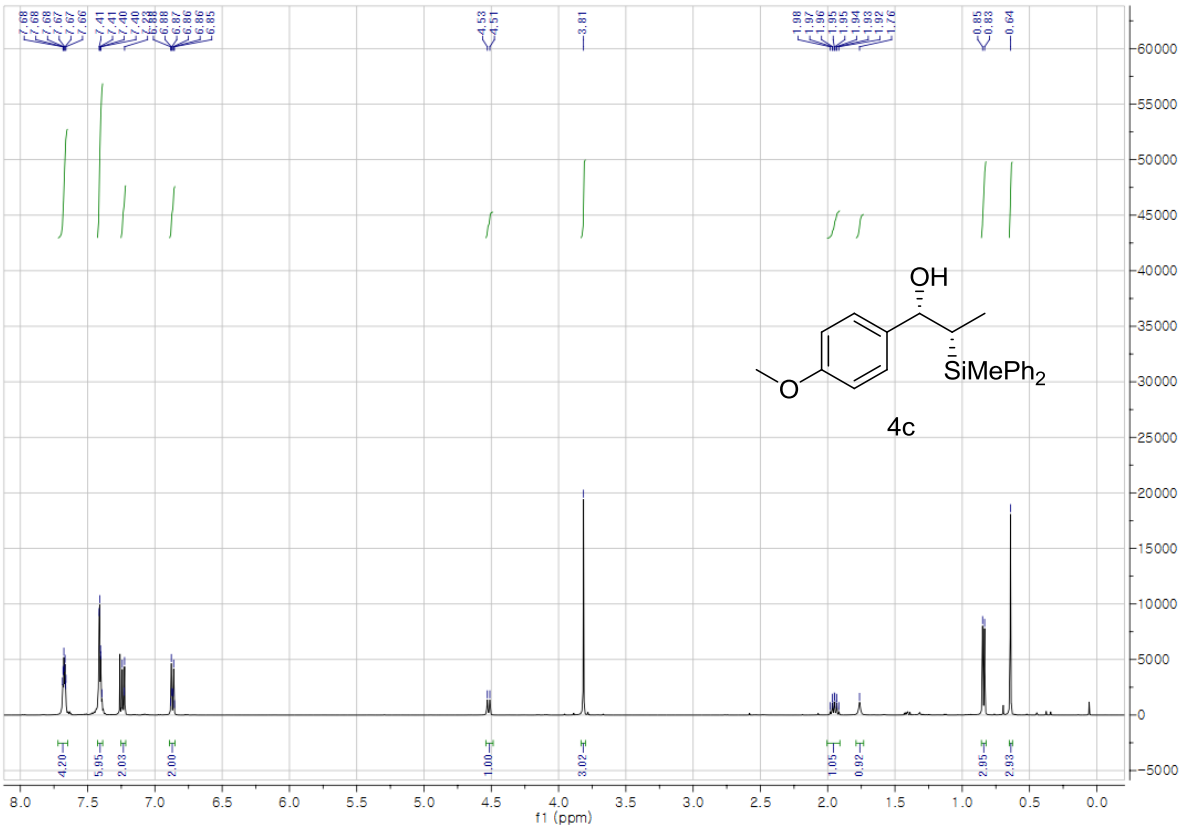
f1 (ppm)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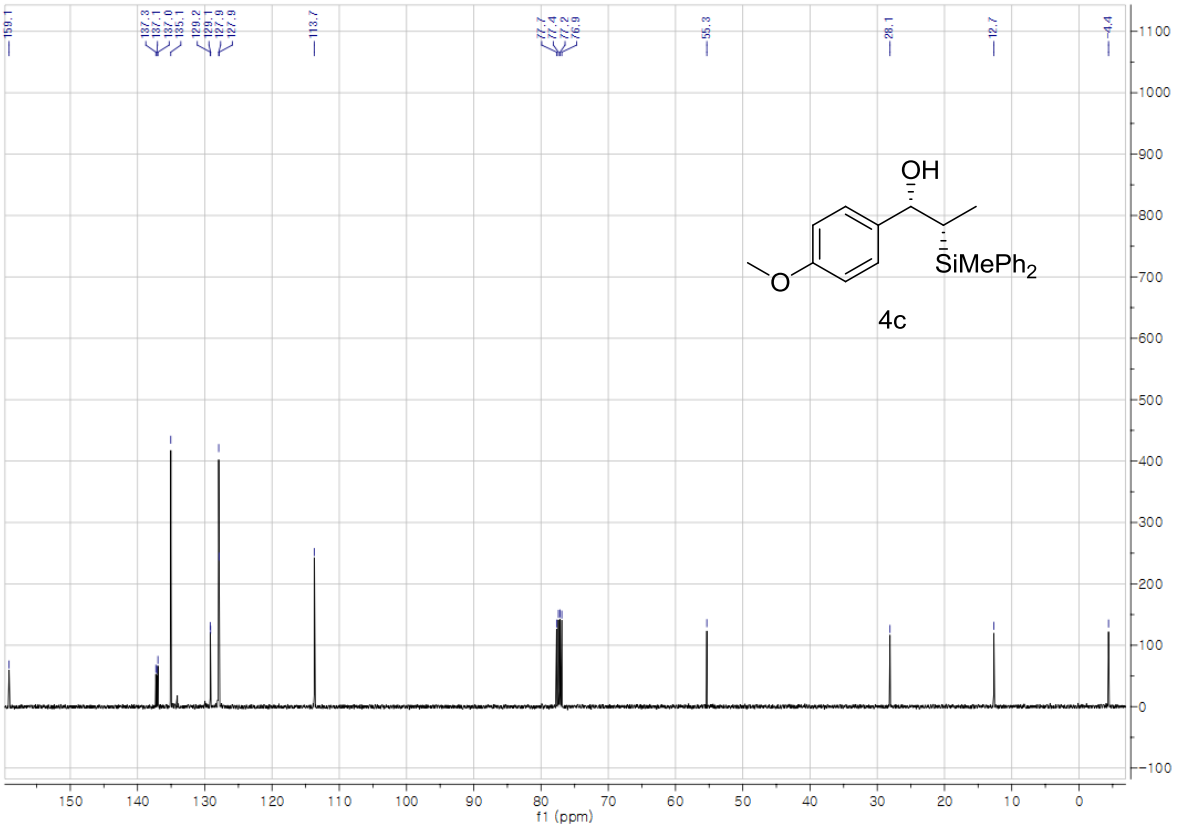
O
4c
f1 (ppm)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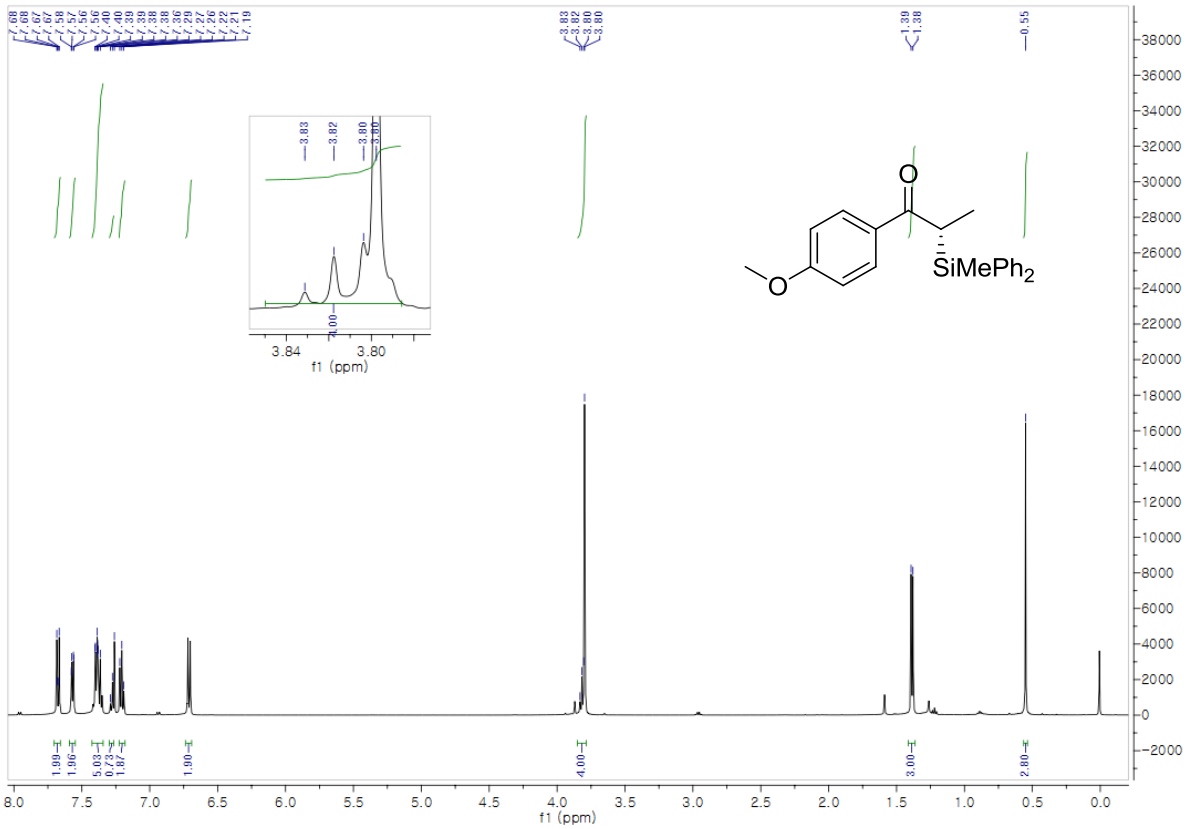
SiMePh2
O
4c
f1 (ppm)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7.27
7.26
7.22
7.21
7.19
3.83
3.82
3.80
3.80
1.39
1.38
0.55
3.84
3.80
f1 (ppm)
O
O
SiMePh2
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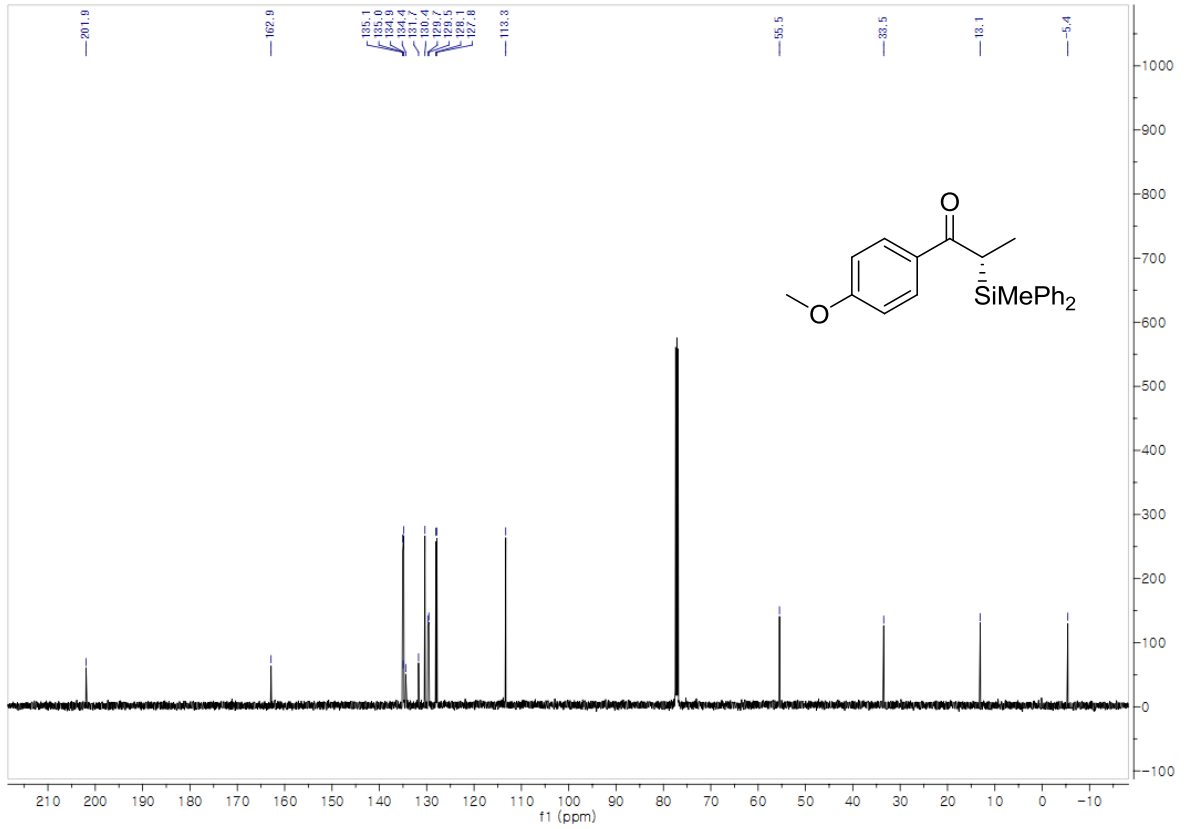
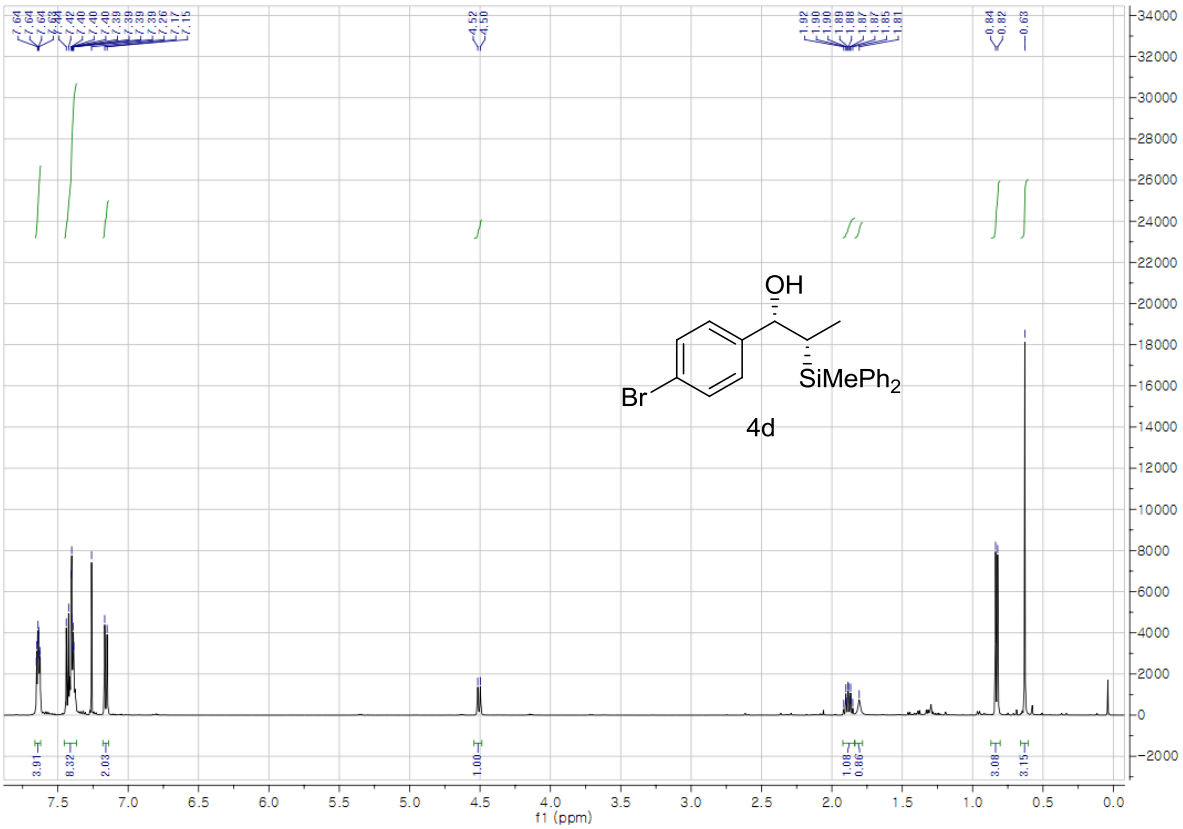
0.73
1.87
1.90
4.00
3.00
2.80
f1 (ppm)


201.9
162.9
135.1
135.0
134.9
134.4
131.7
130.4
129.7
129.5
128.1
127.8
113.3
55.5
33.5
13.1
-5.4
O
O
SiMePh2
f1 (ppm)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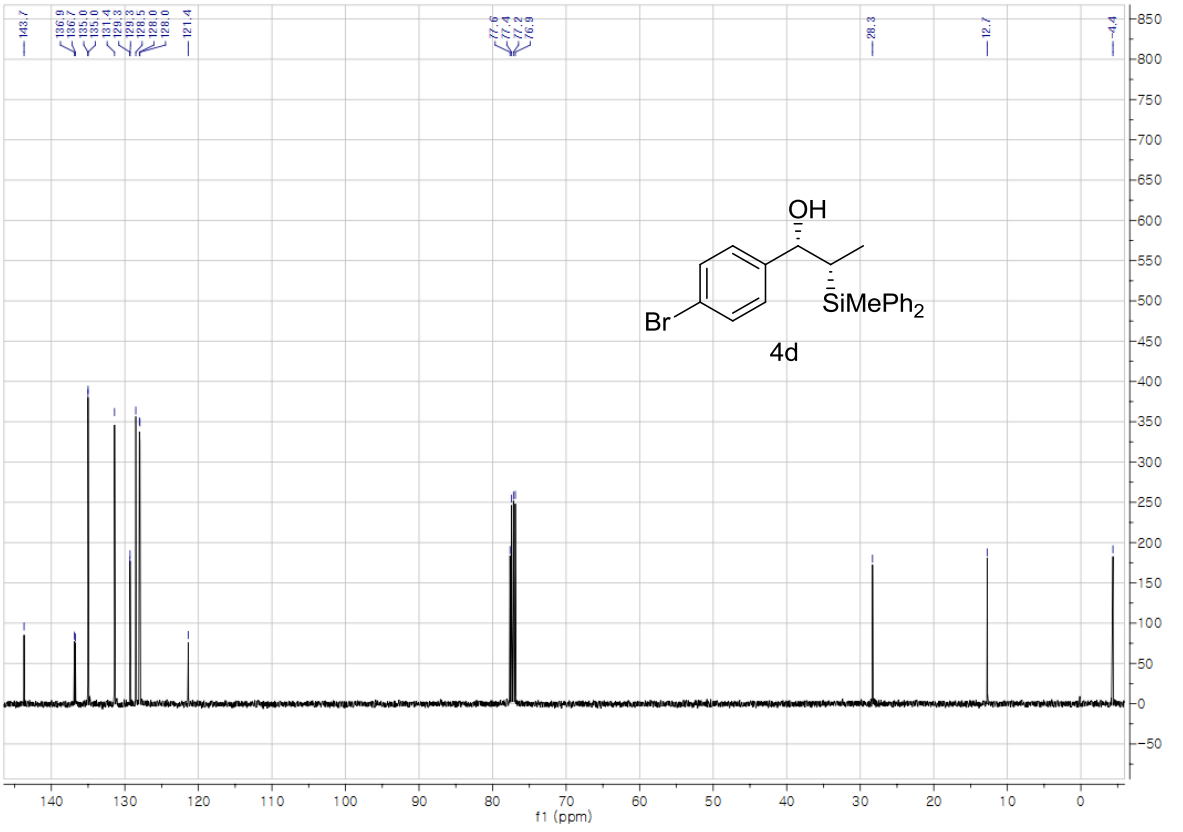
SiMePh2
Br
4d
f1 (ppm)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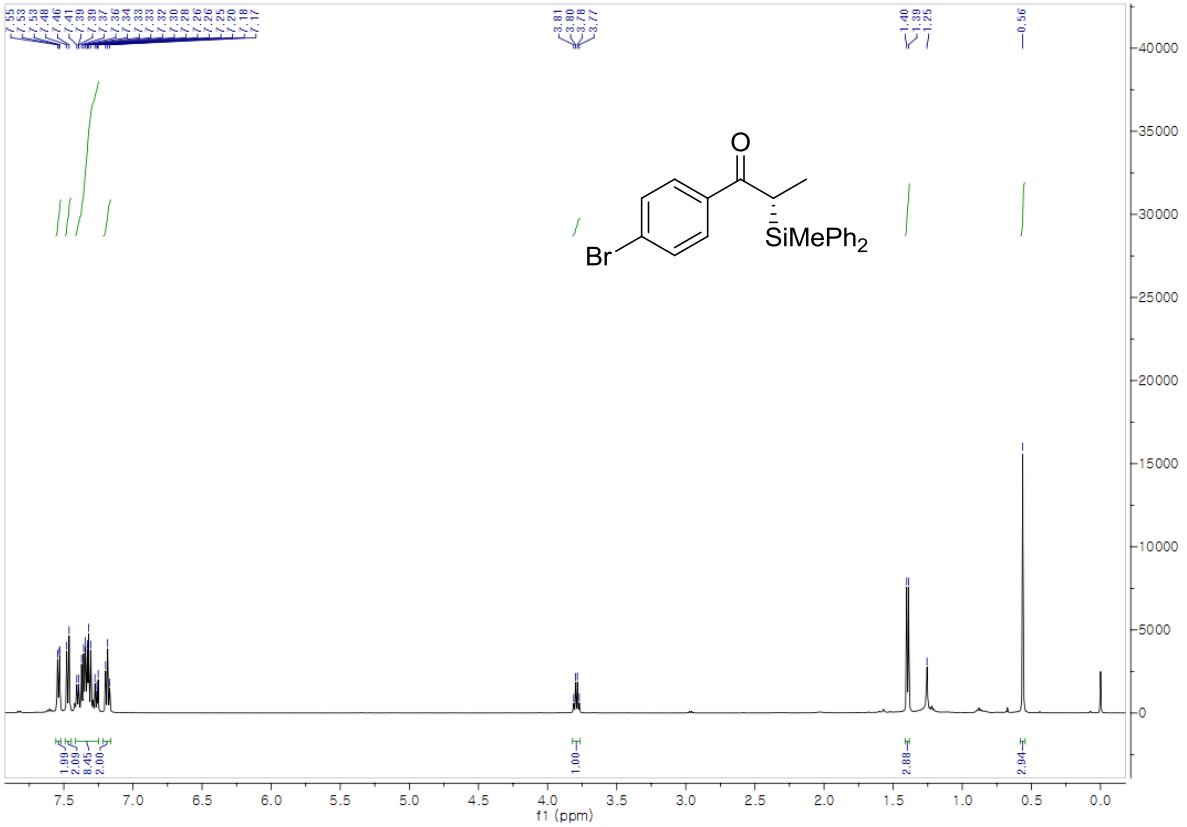
Br
4d
f1 (ppm)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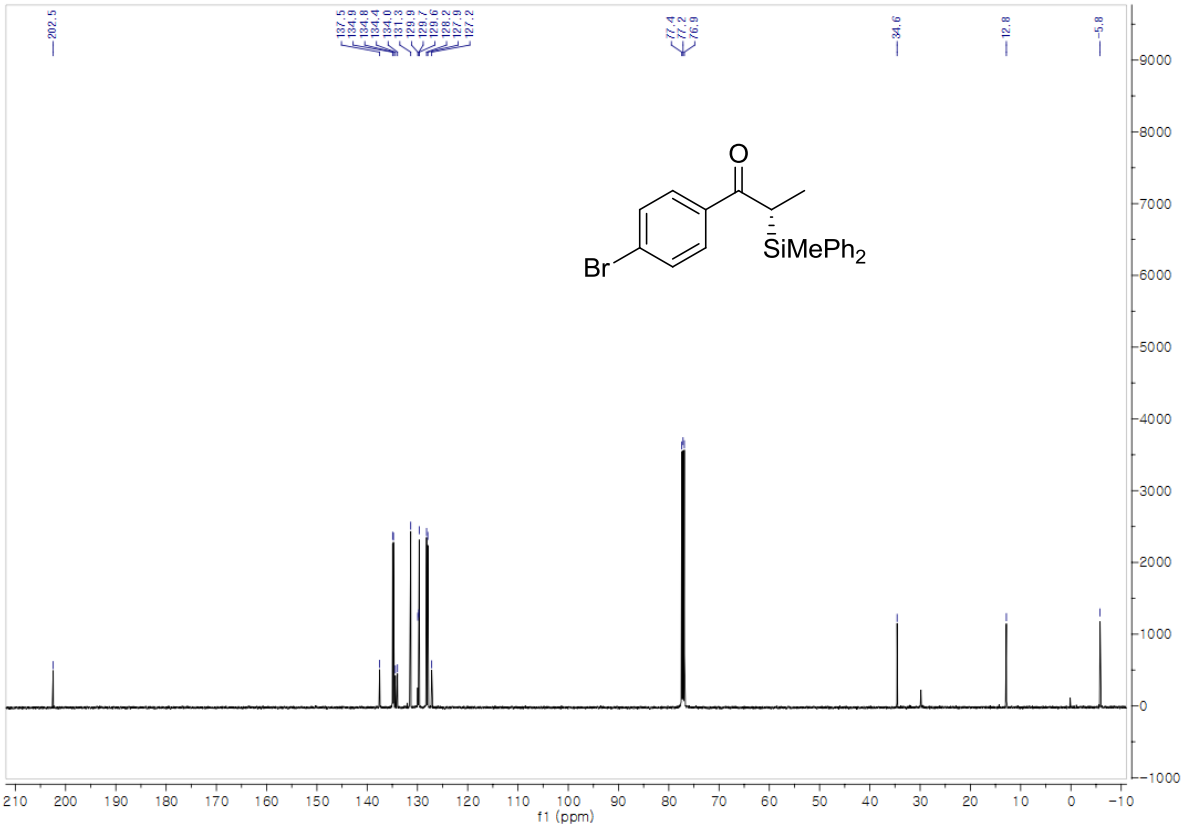
Br
SiMePh2
f1 (ppm)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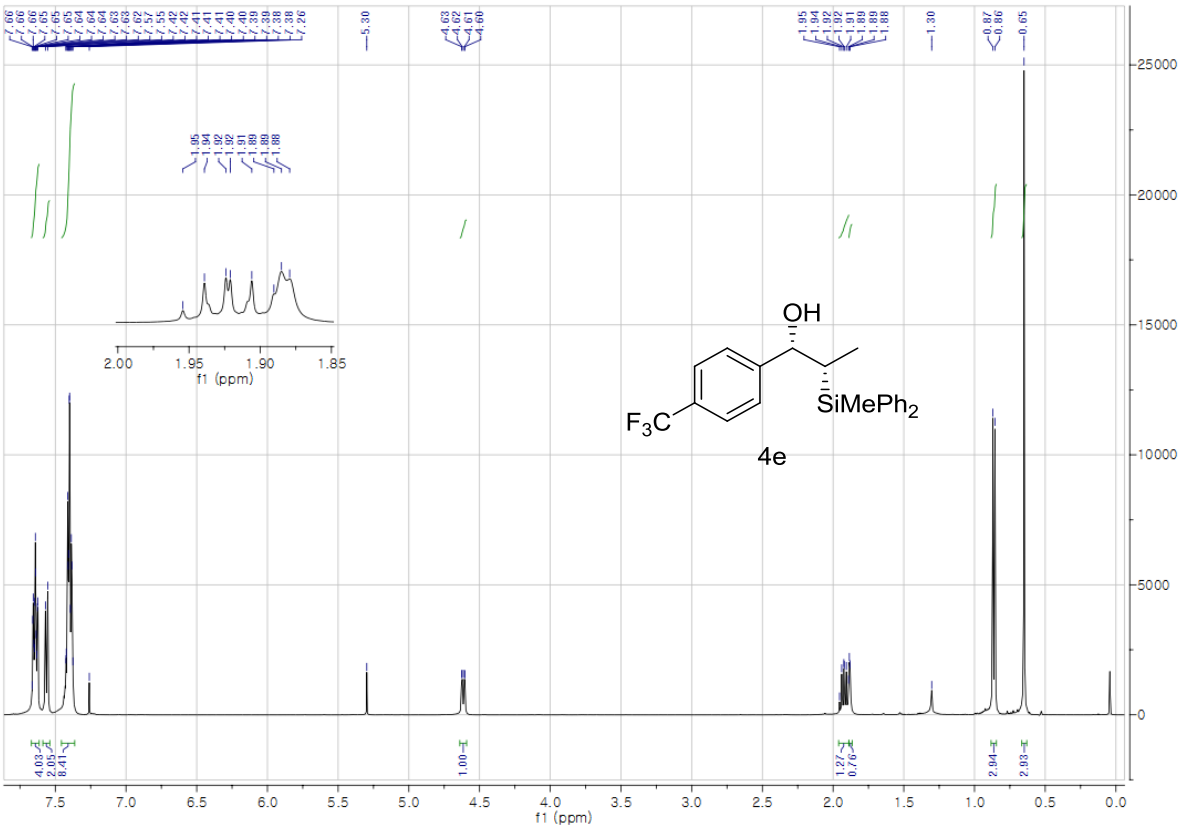
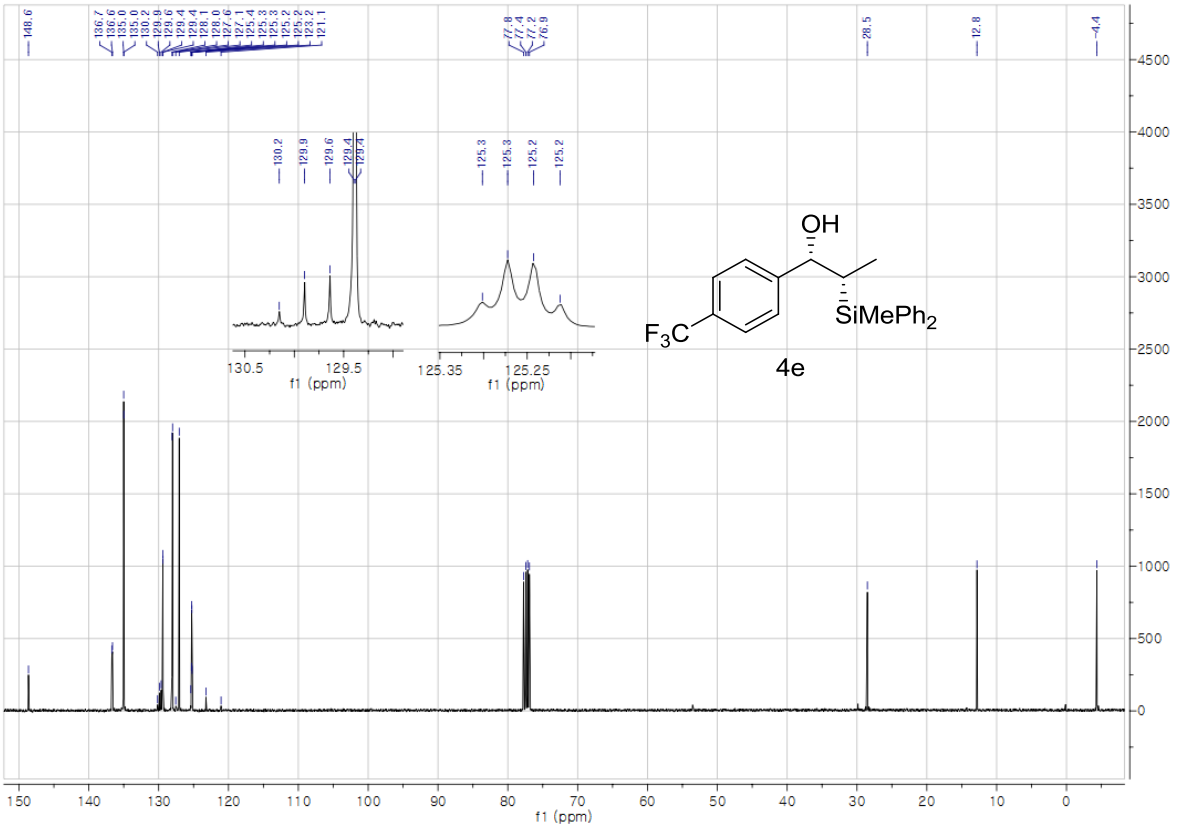
Br
SiMePh2
f1 (ppm)


OH
SiMePh2
F3C
4e
f1 (ppm)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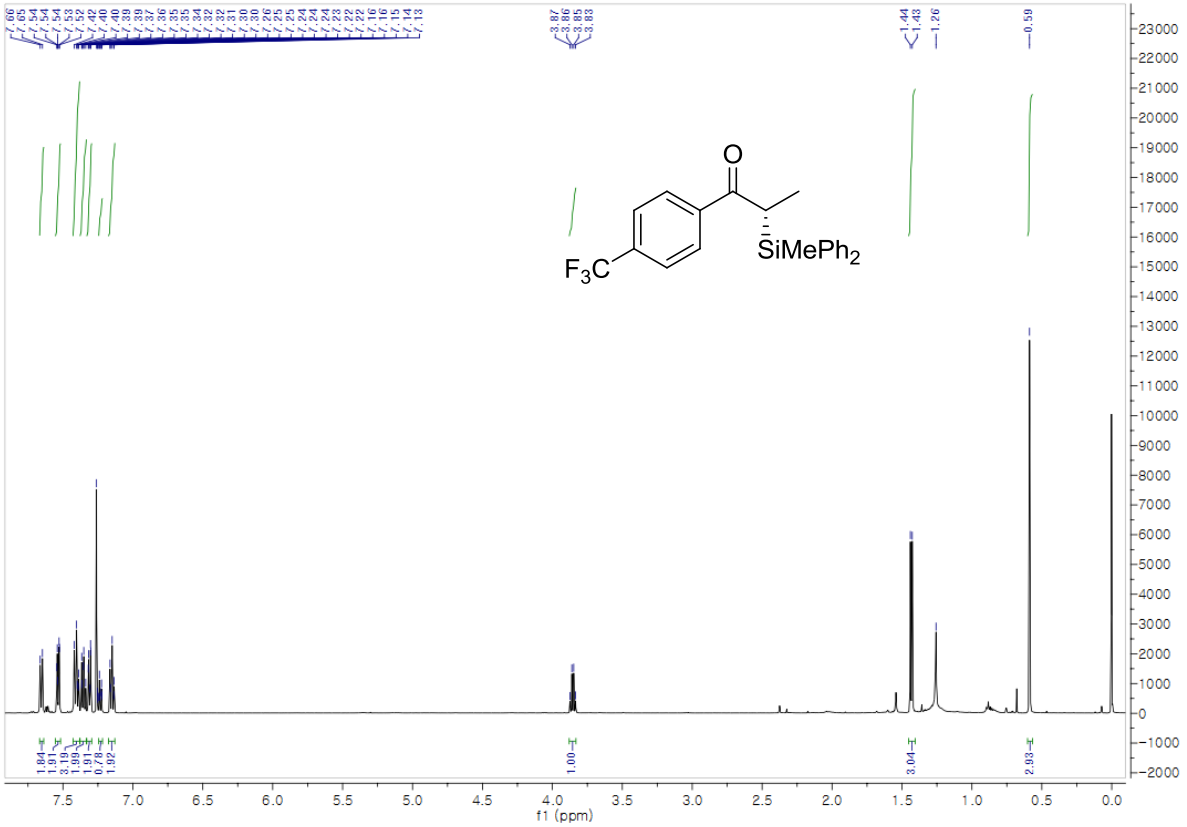
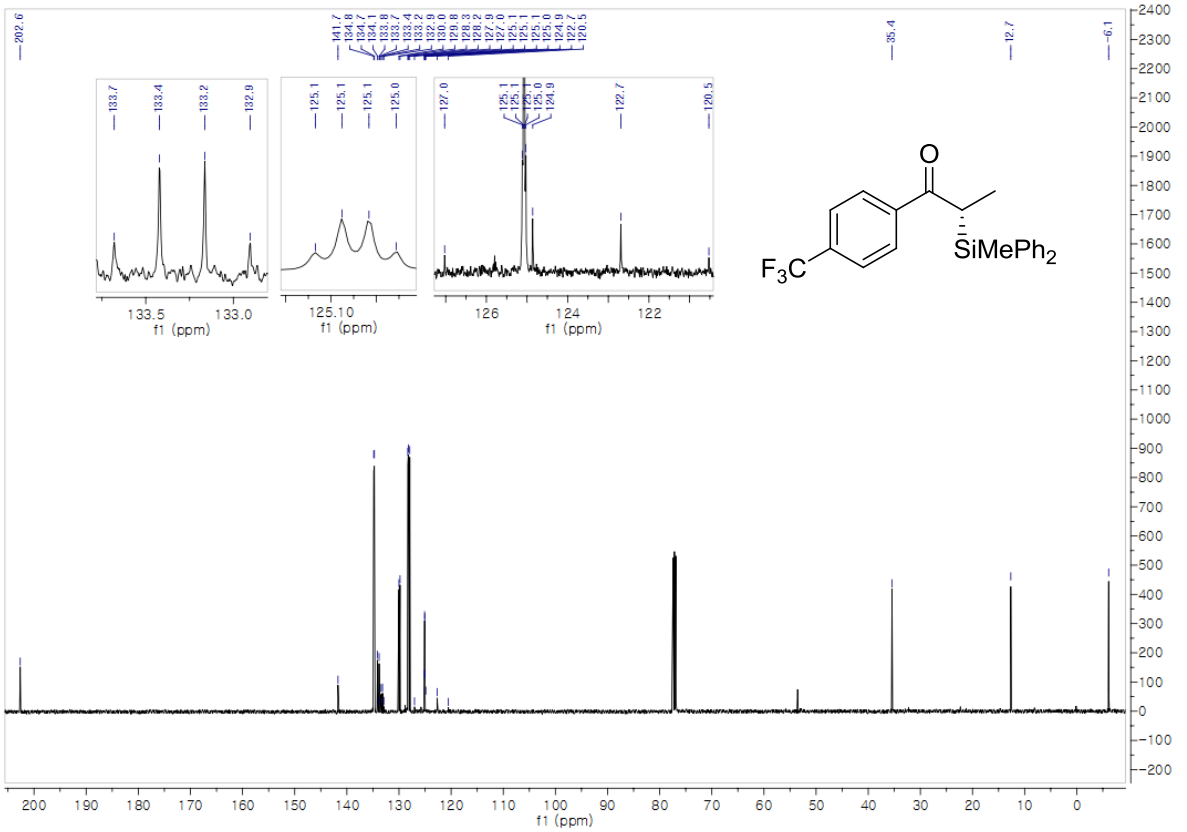
SiMePh2
F3C
4e
f1 (ppm)


O
F3C
SiMePh2
f1 (ppm)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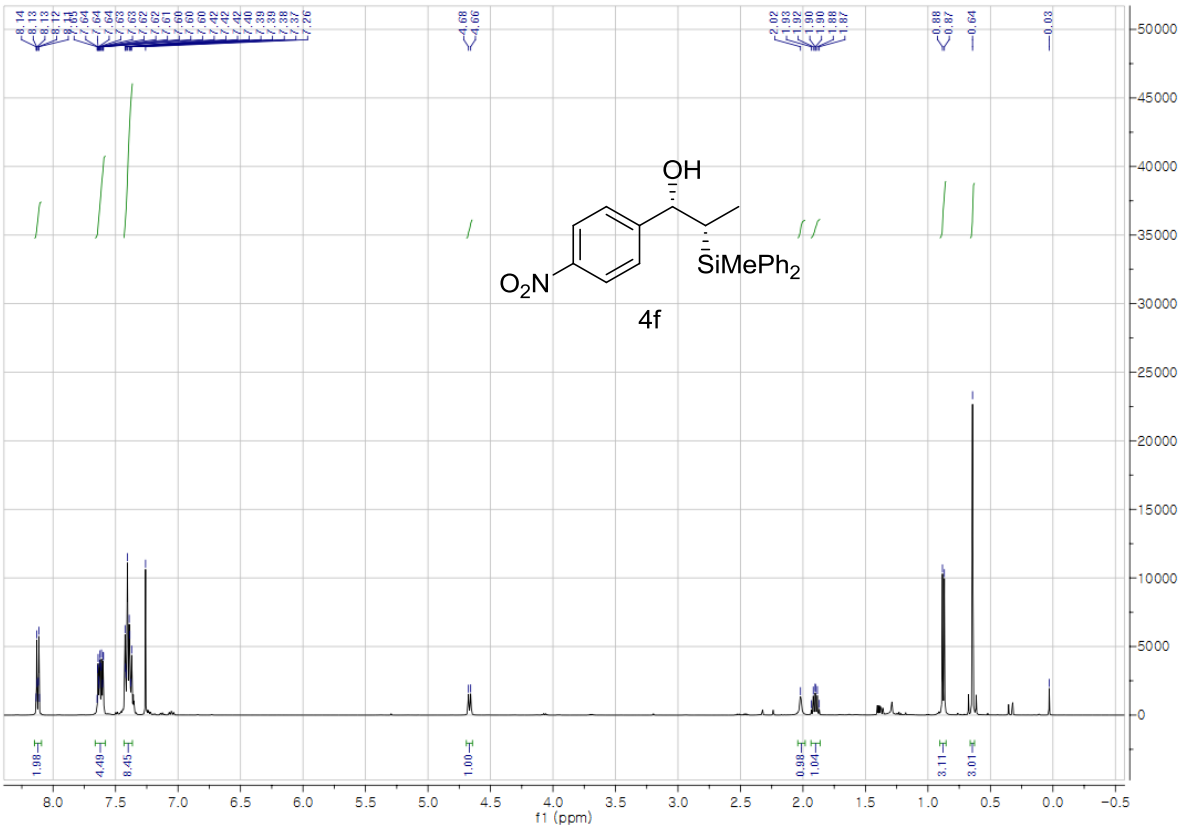
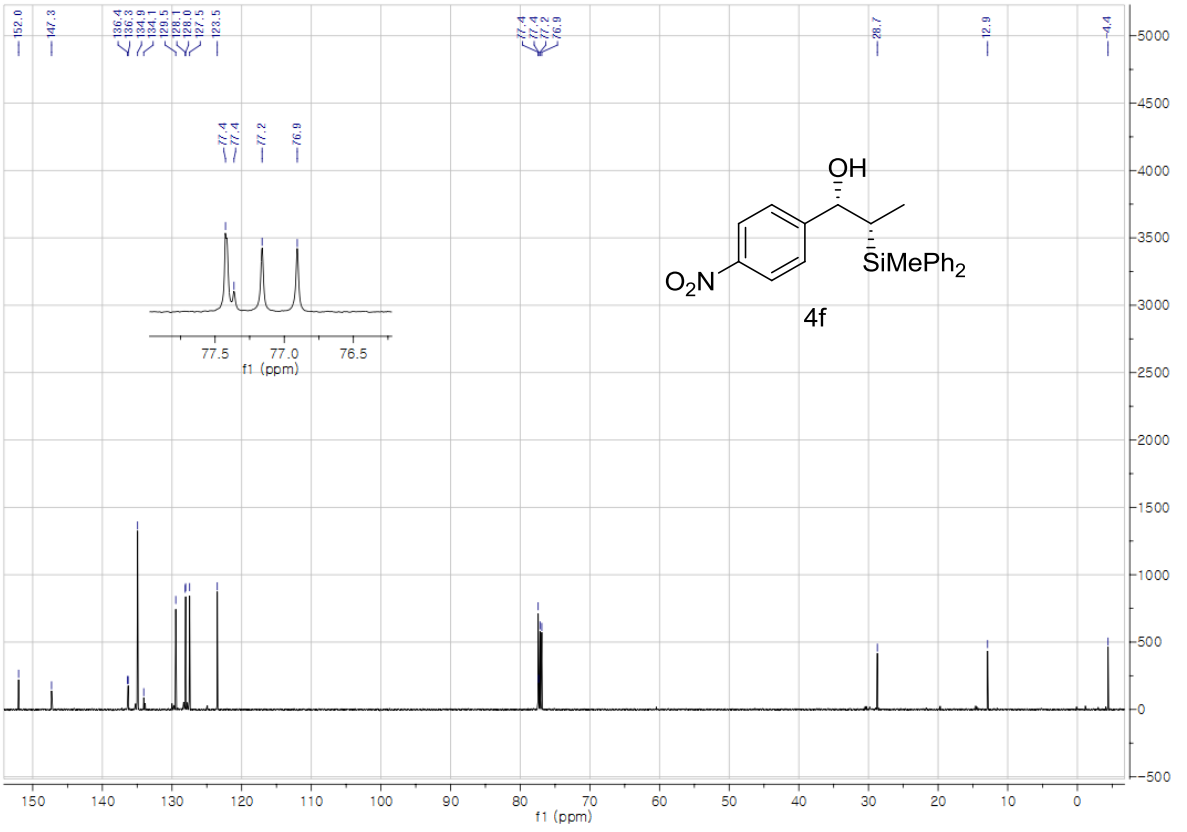
F3C
SiMePh2
f1 (ppm)


OH
SiMePh2
O2N
4f
f1 (ppm)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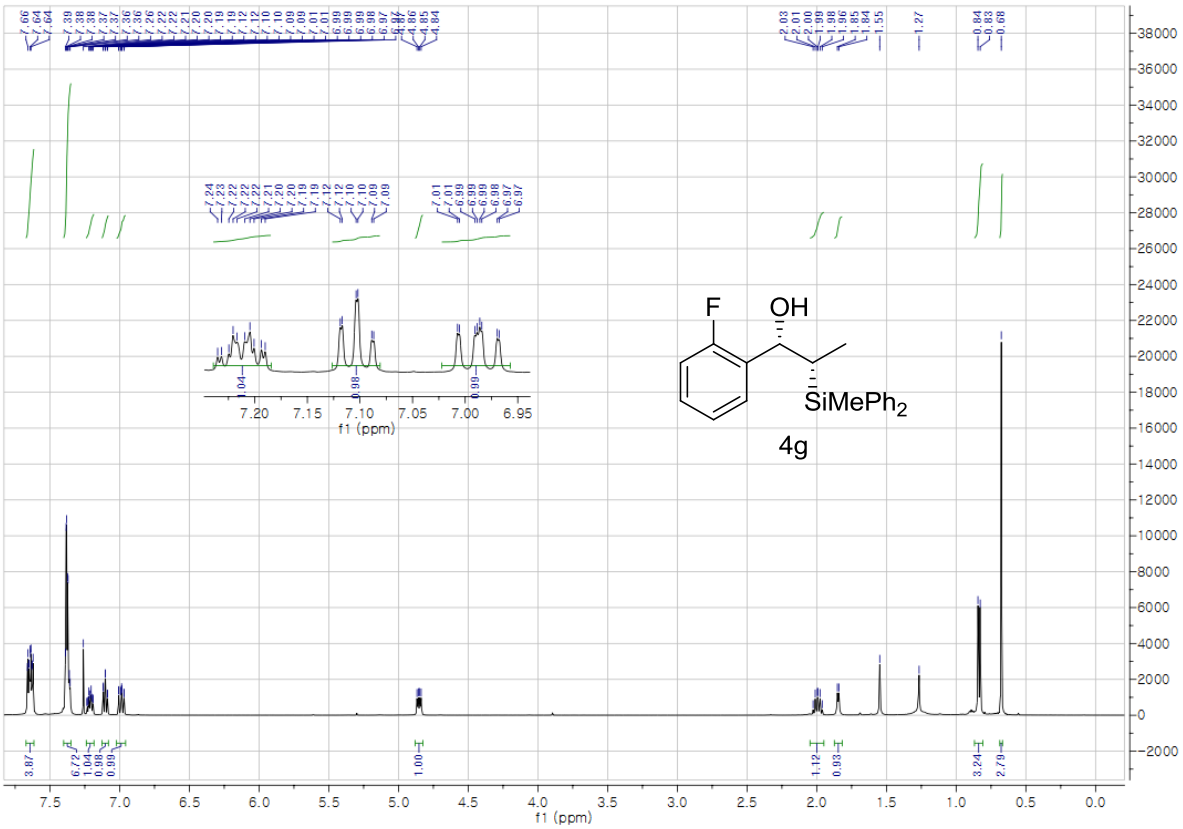
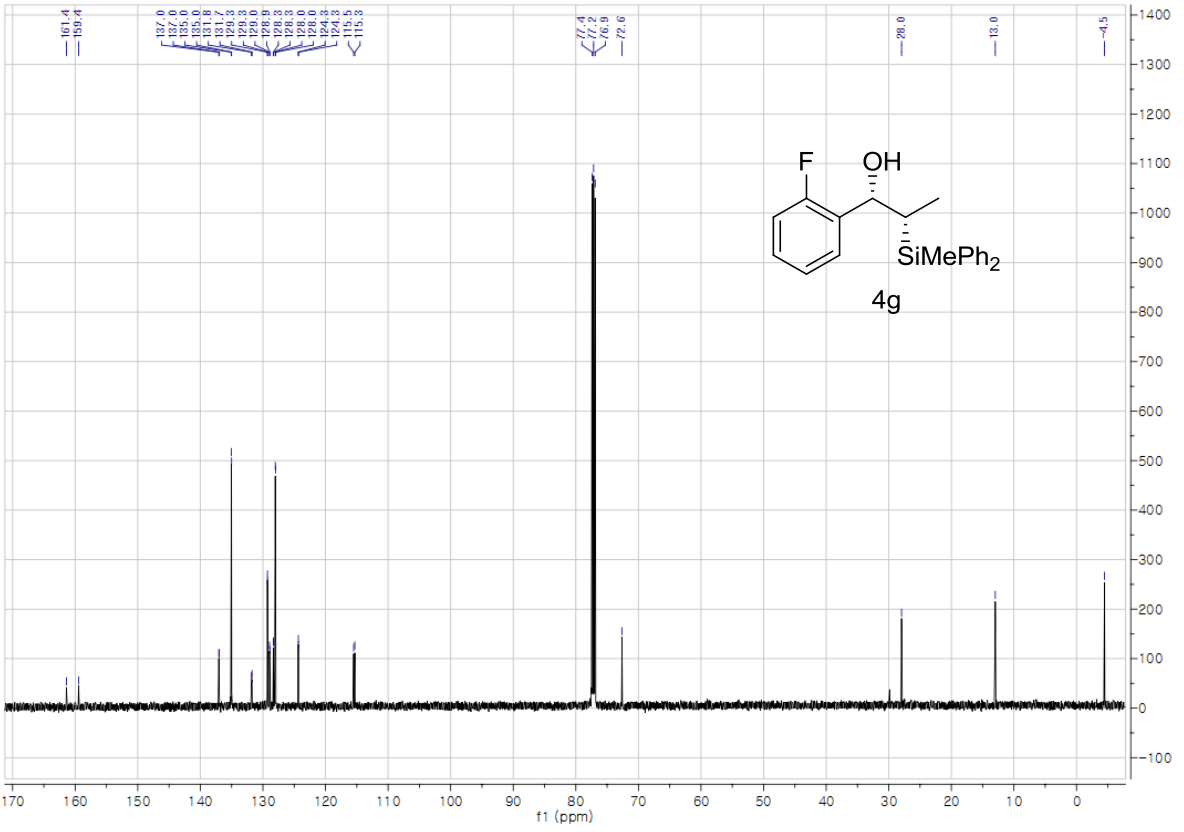
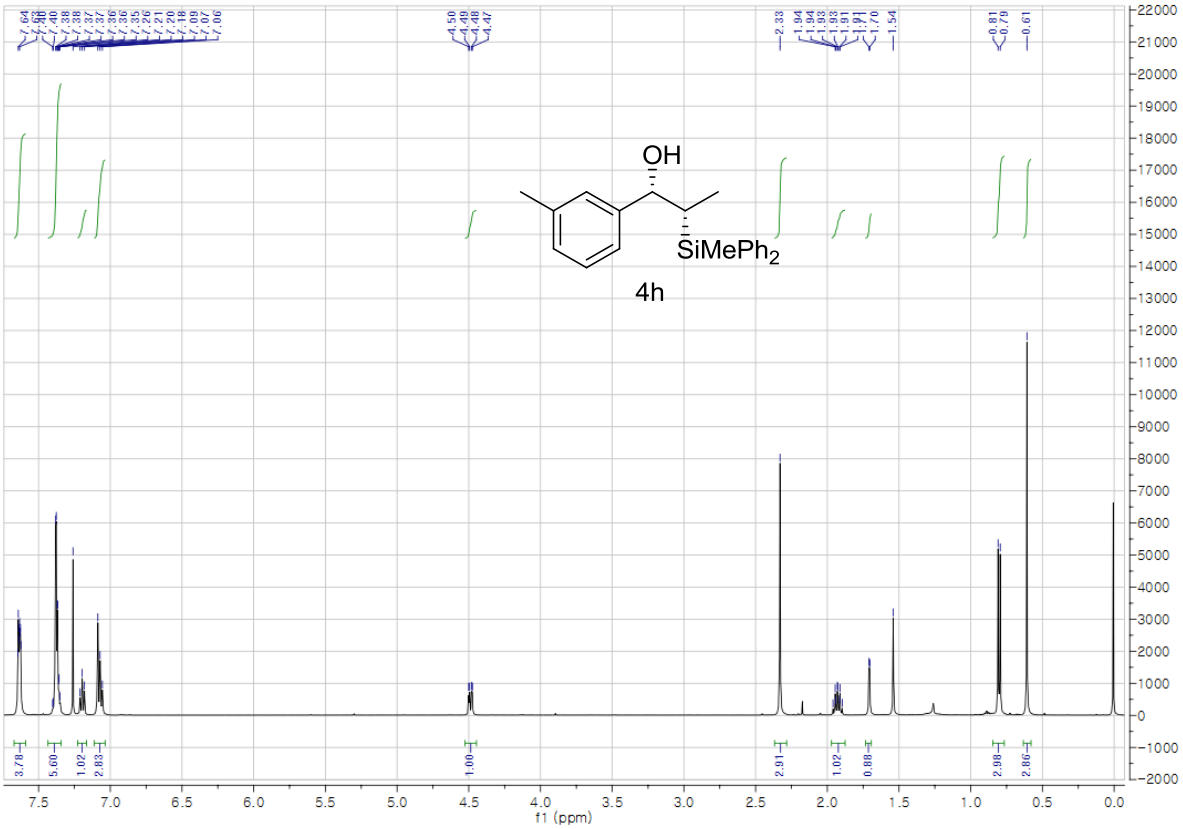
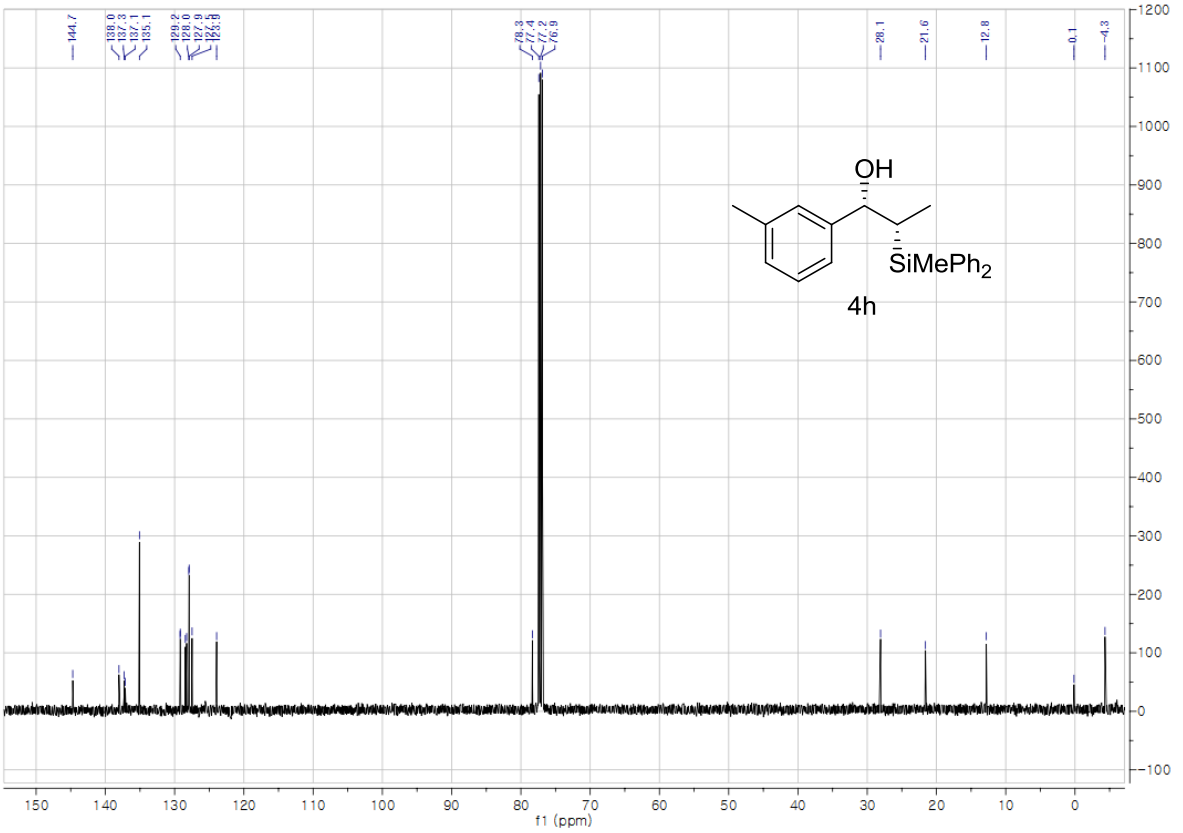
SiMePh2
O2N
4f
77.5
77.0
76.5
f1 (ppm)
f1 (ppm)


F
OH
SiMePh2
4g
f1 (ppm)


F
OH
SiMePh2
4g
f1 (ppm)


OH
SiMePh2
4h
f1 (ppm)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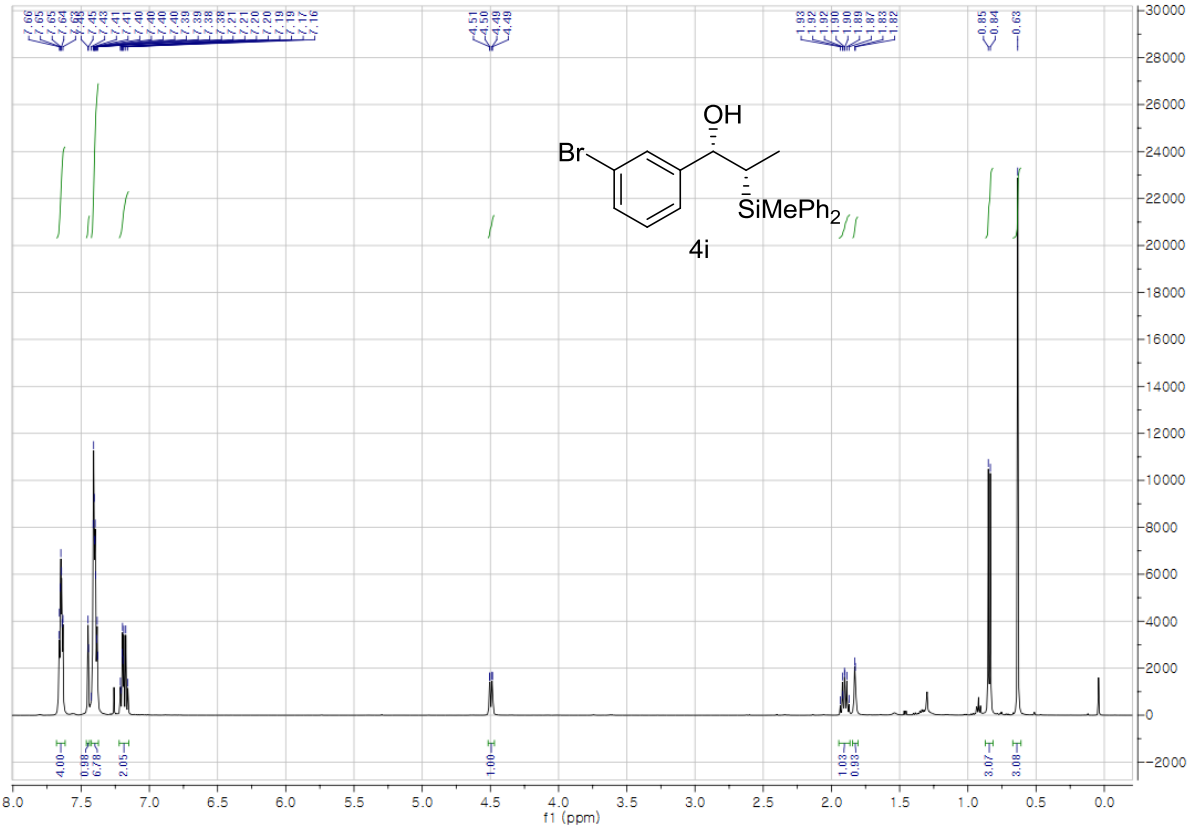
4h
f1 (ppm)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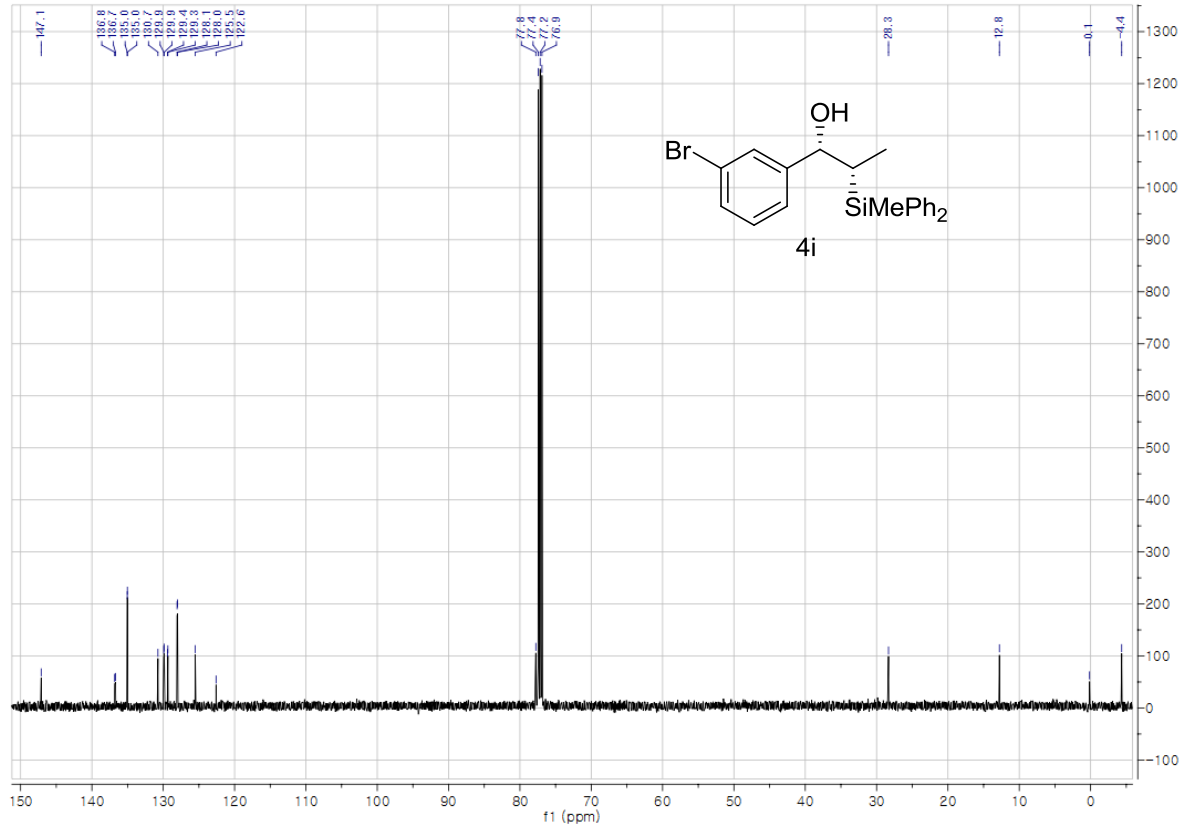
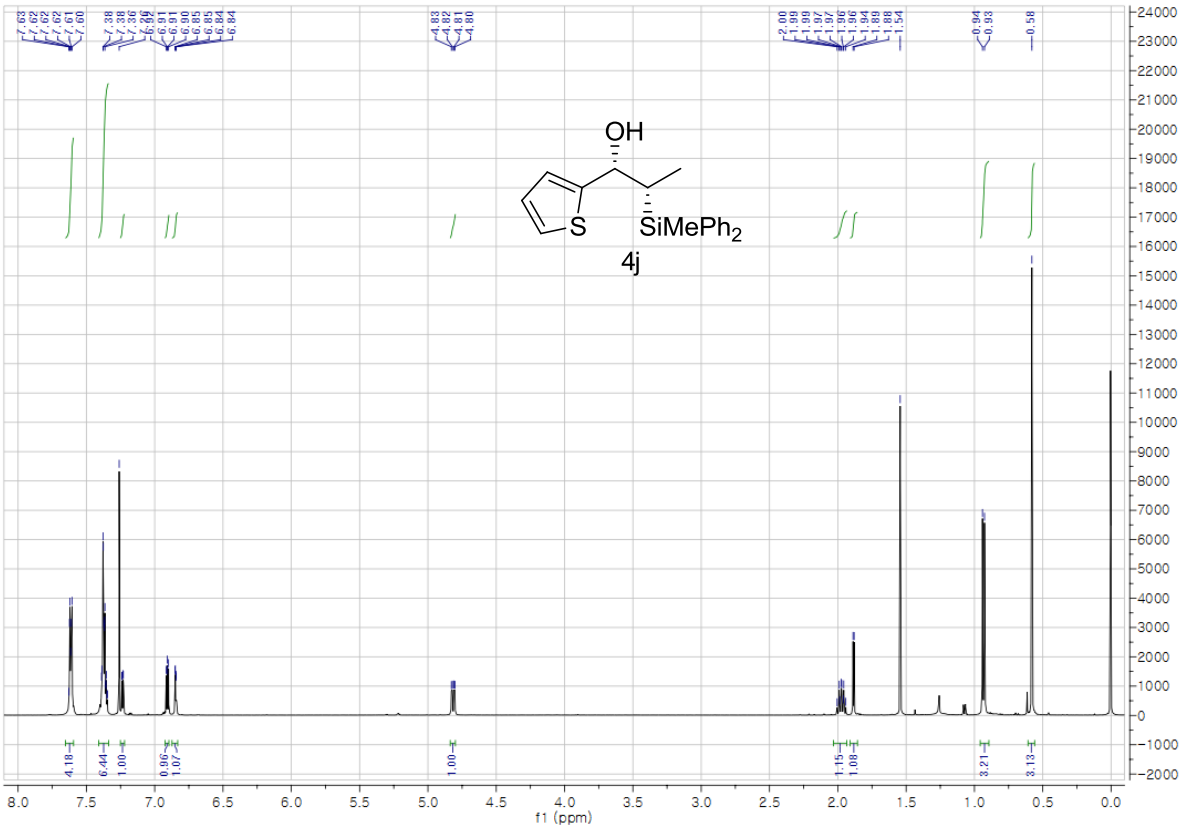
Br
SiMePh2
4i
f1 (ppm)


OH
Br
SiMePh2
4i
f1 (ppm)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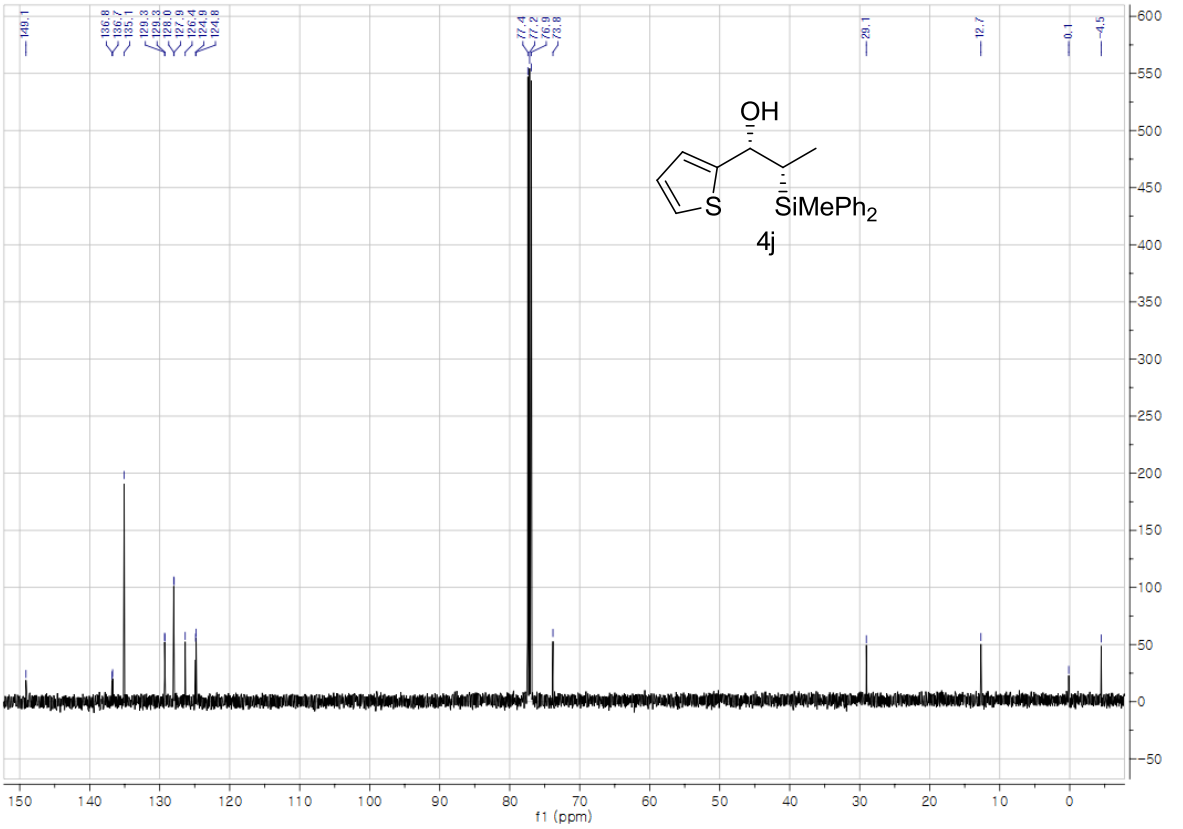
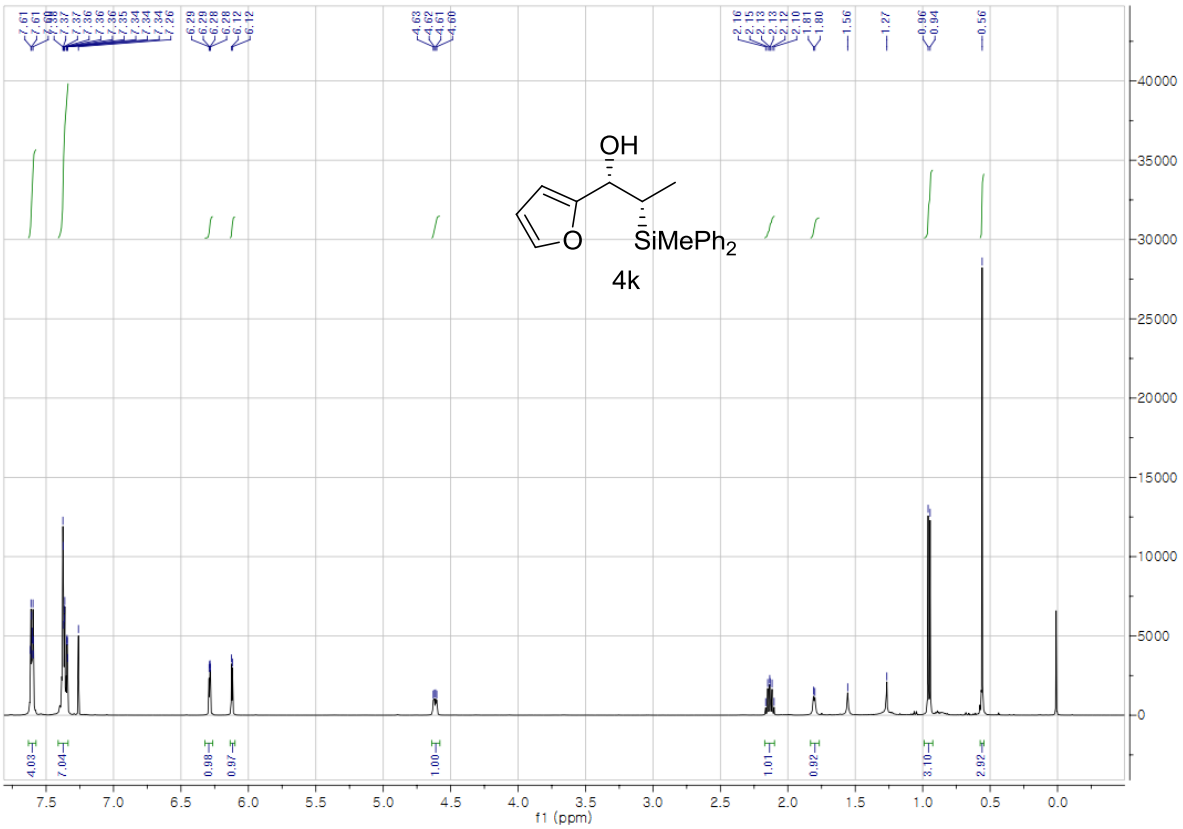
S
SiMePh2
4j
f1 (ppm)


OH
S
SiMePh2
4j
f1 (ppm)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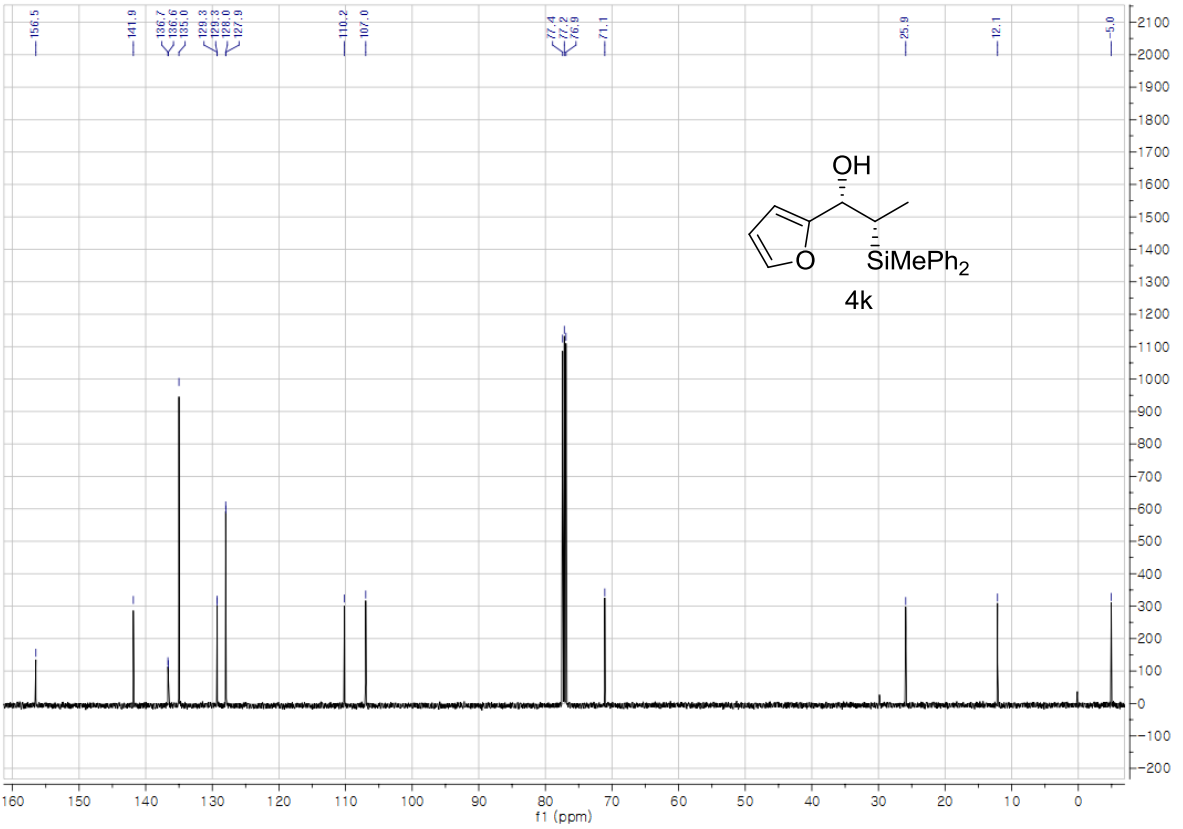
f1 (ppm)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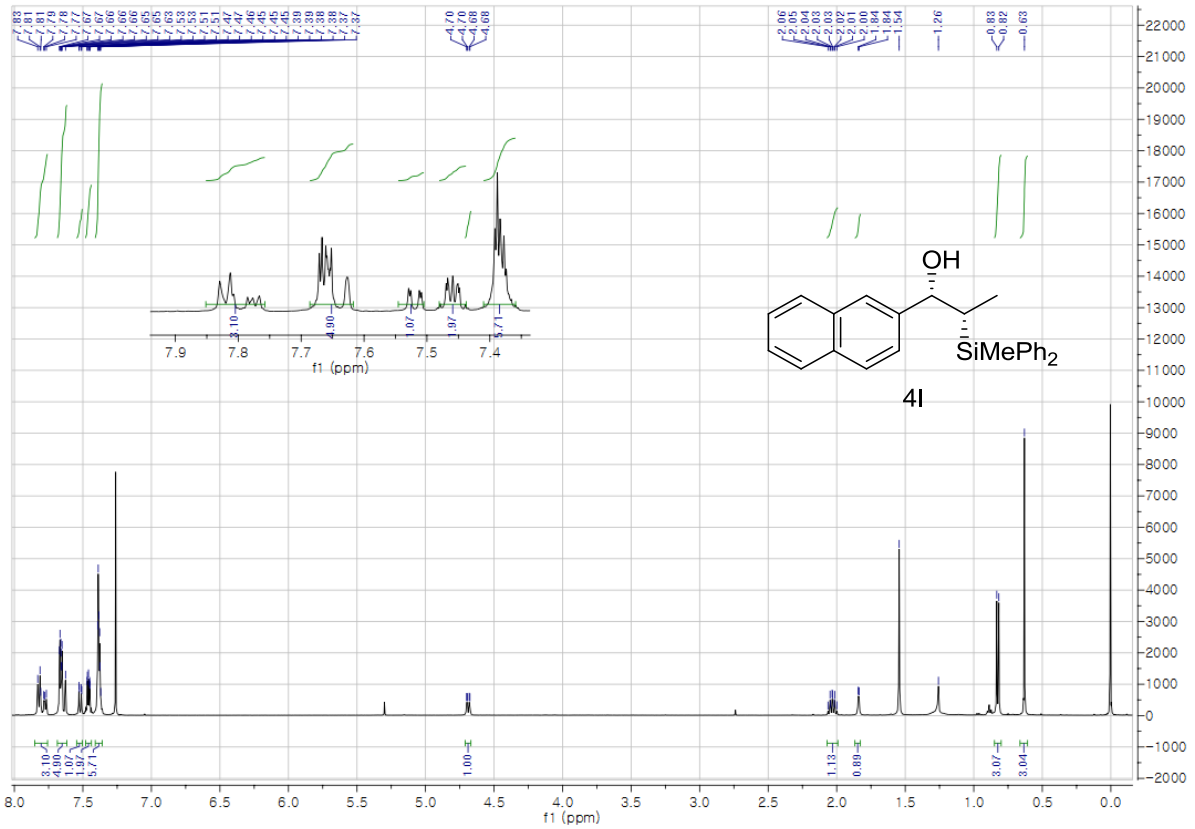
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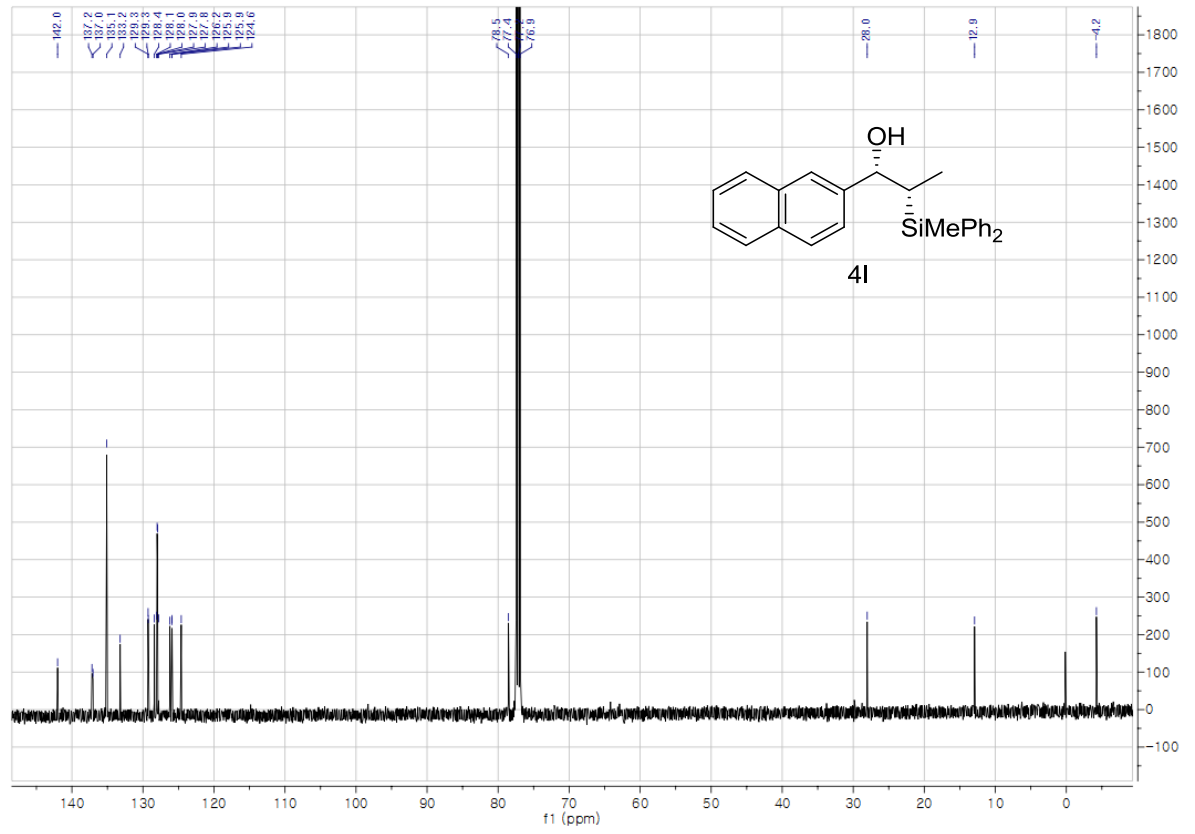
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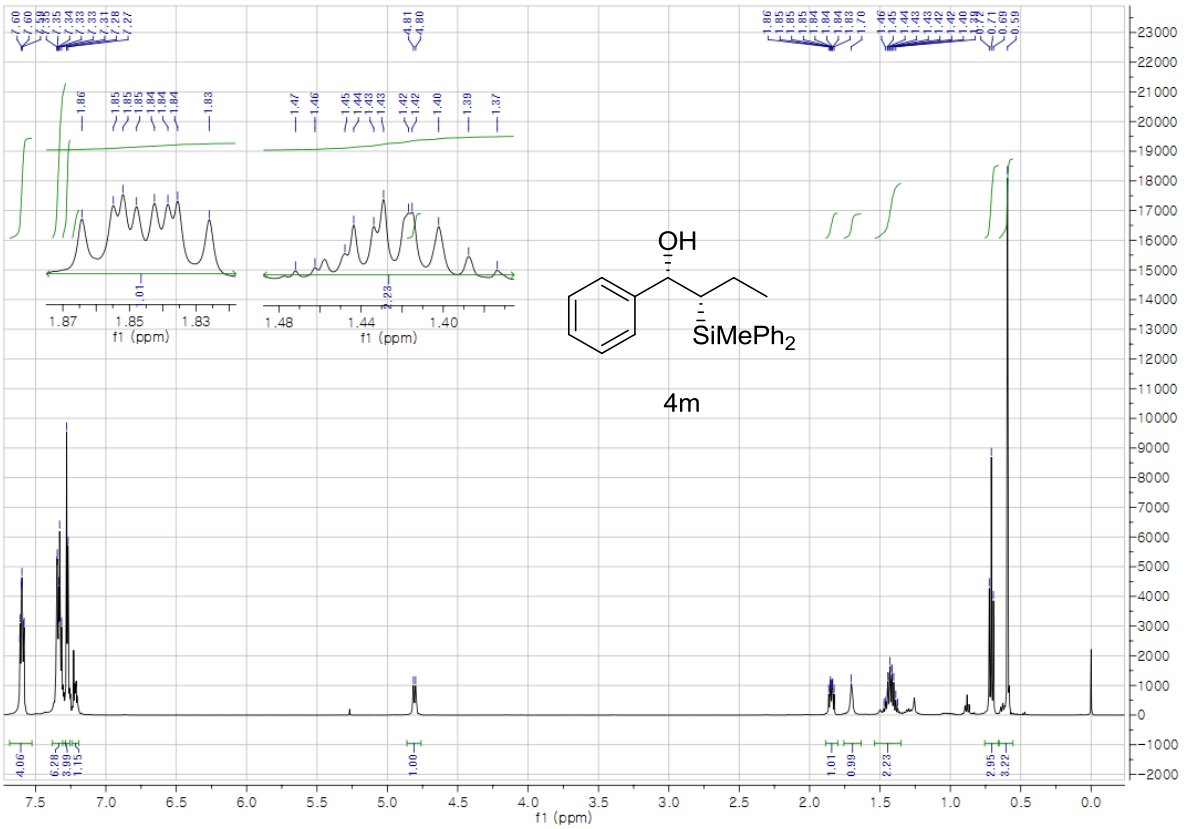
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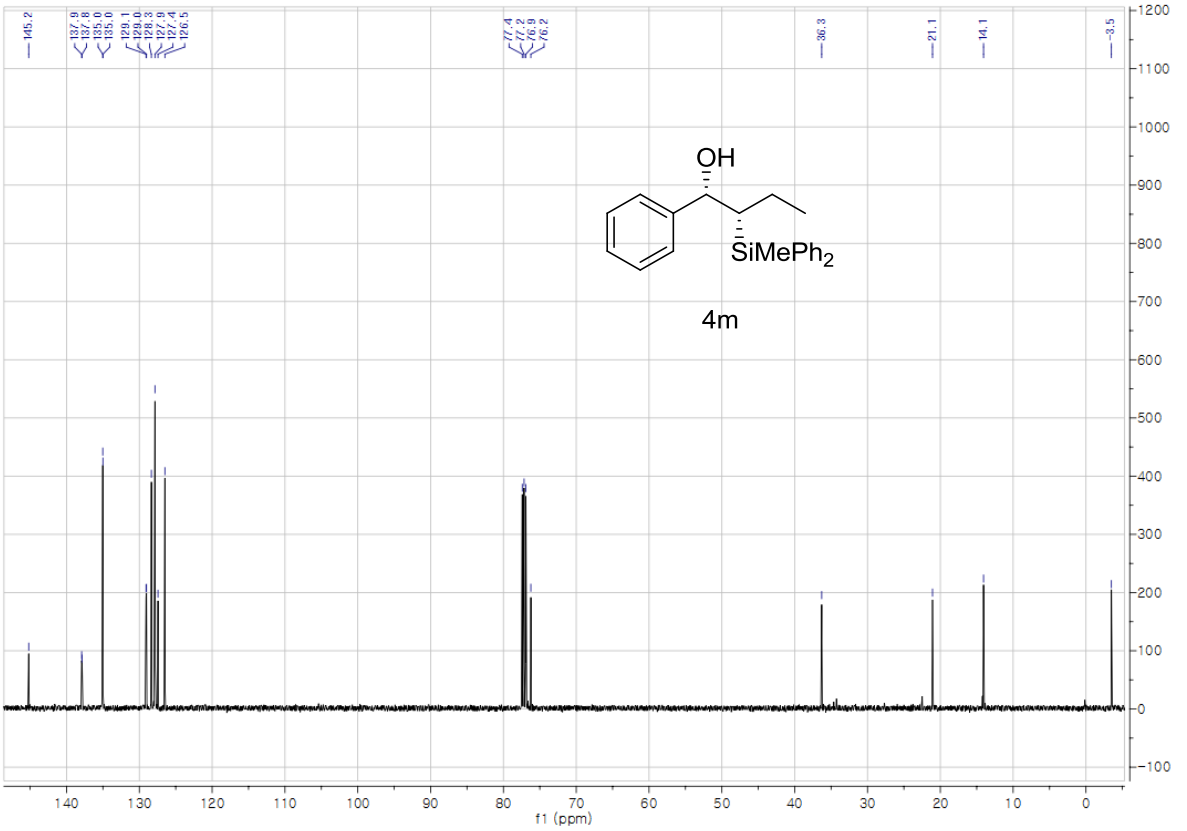
4m
f1 (ppm)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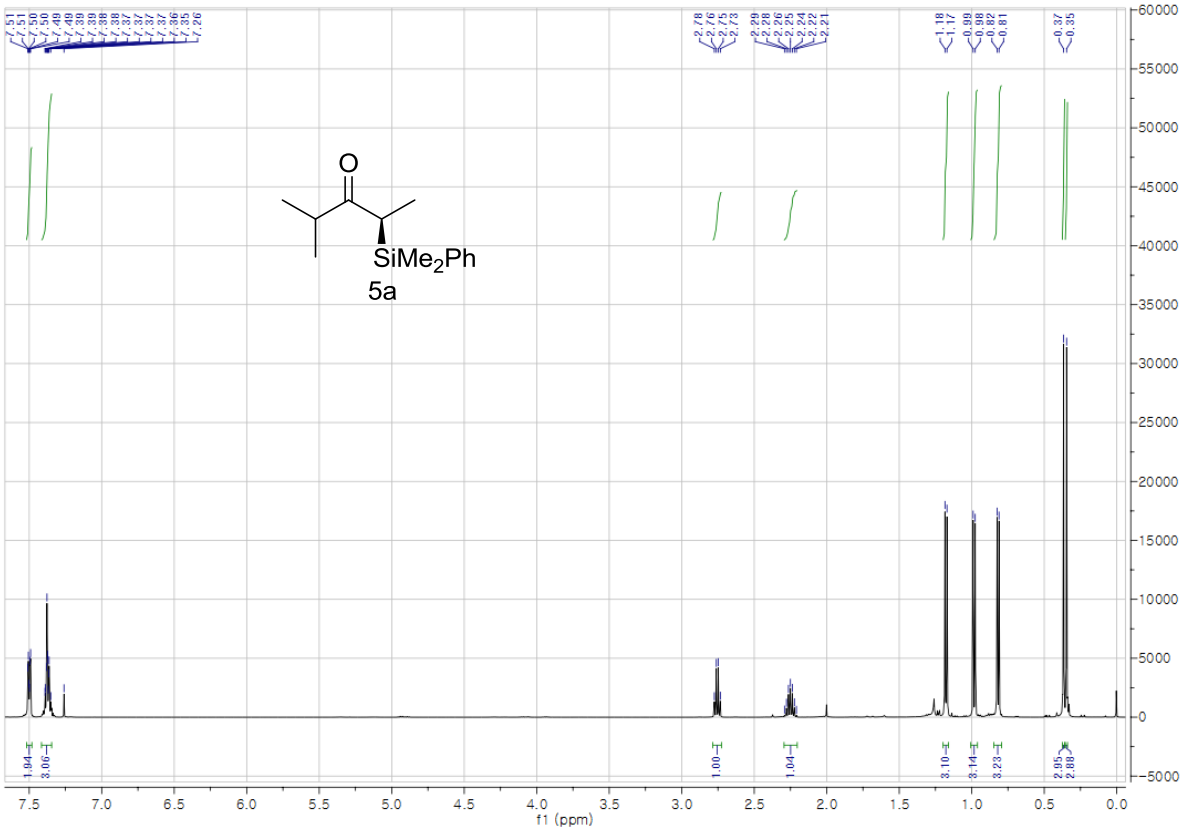
4m
f1 (ppm)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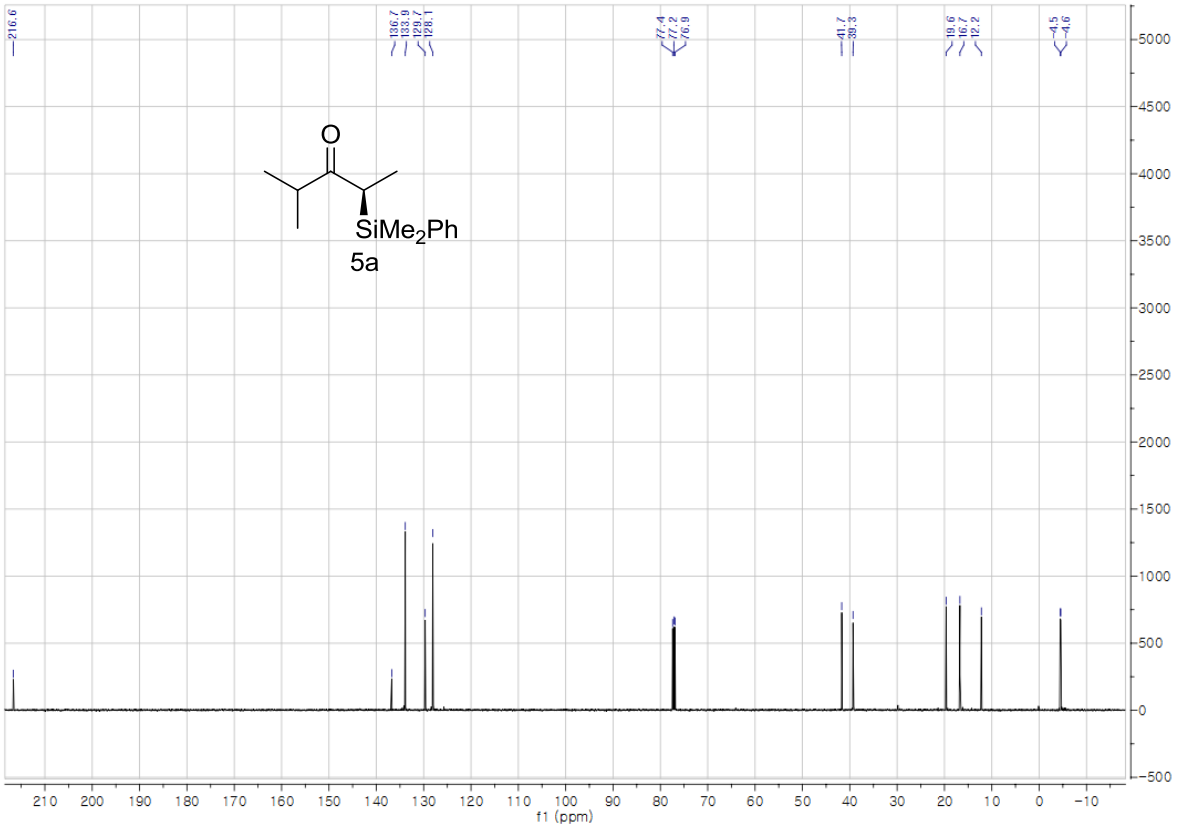
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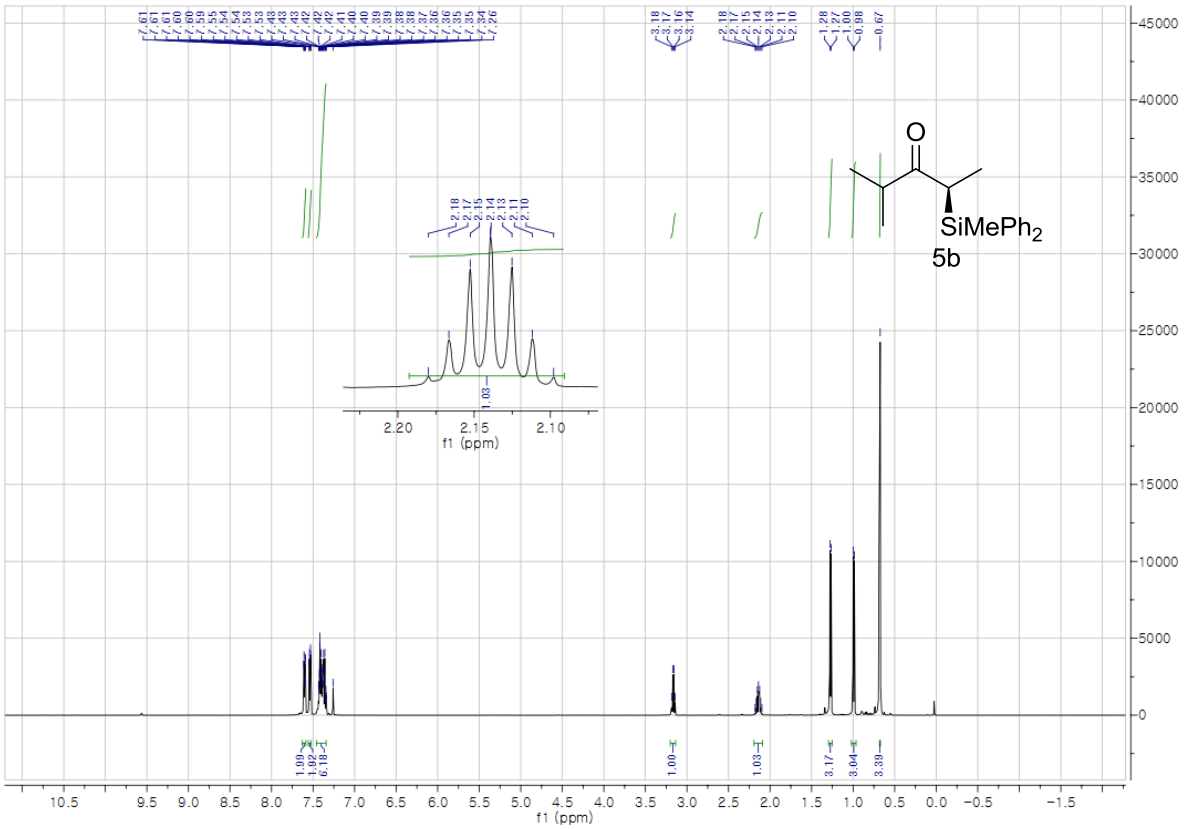
f1 (ppm)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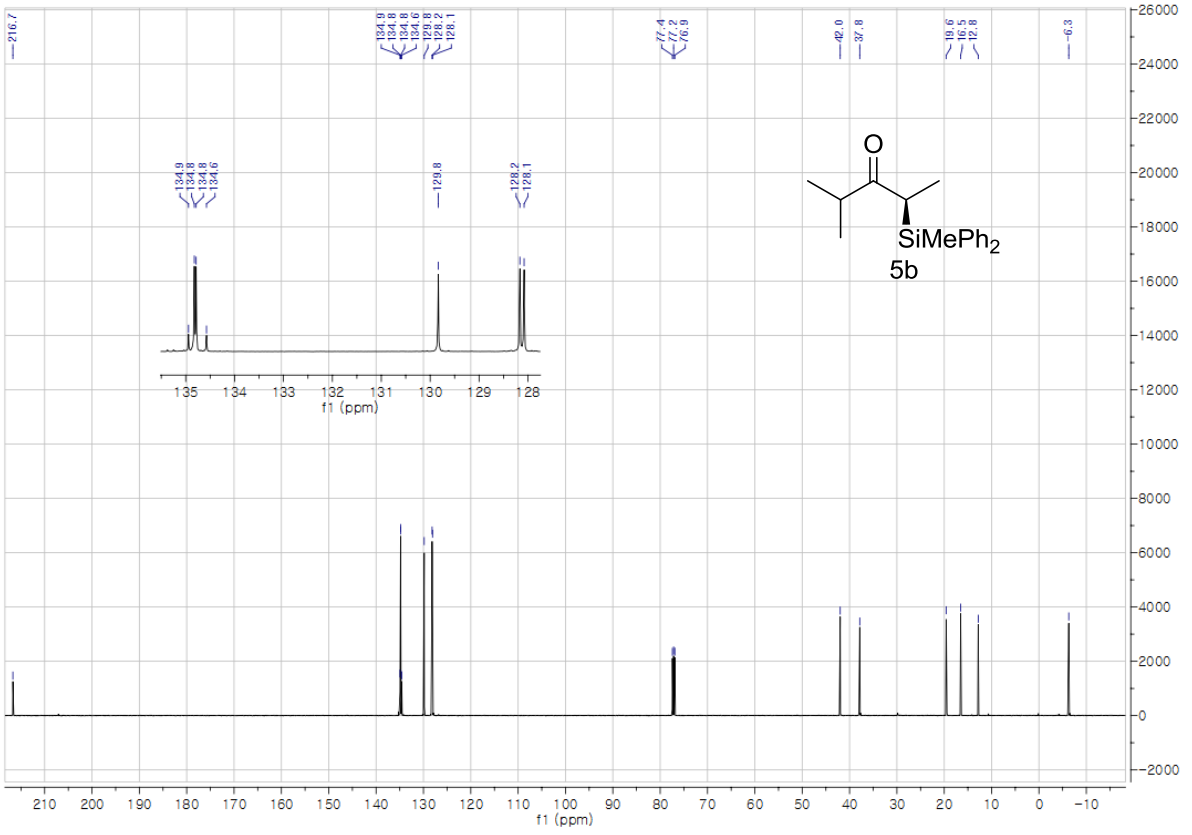
f1 (ppm)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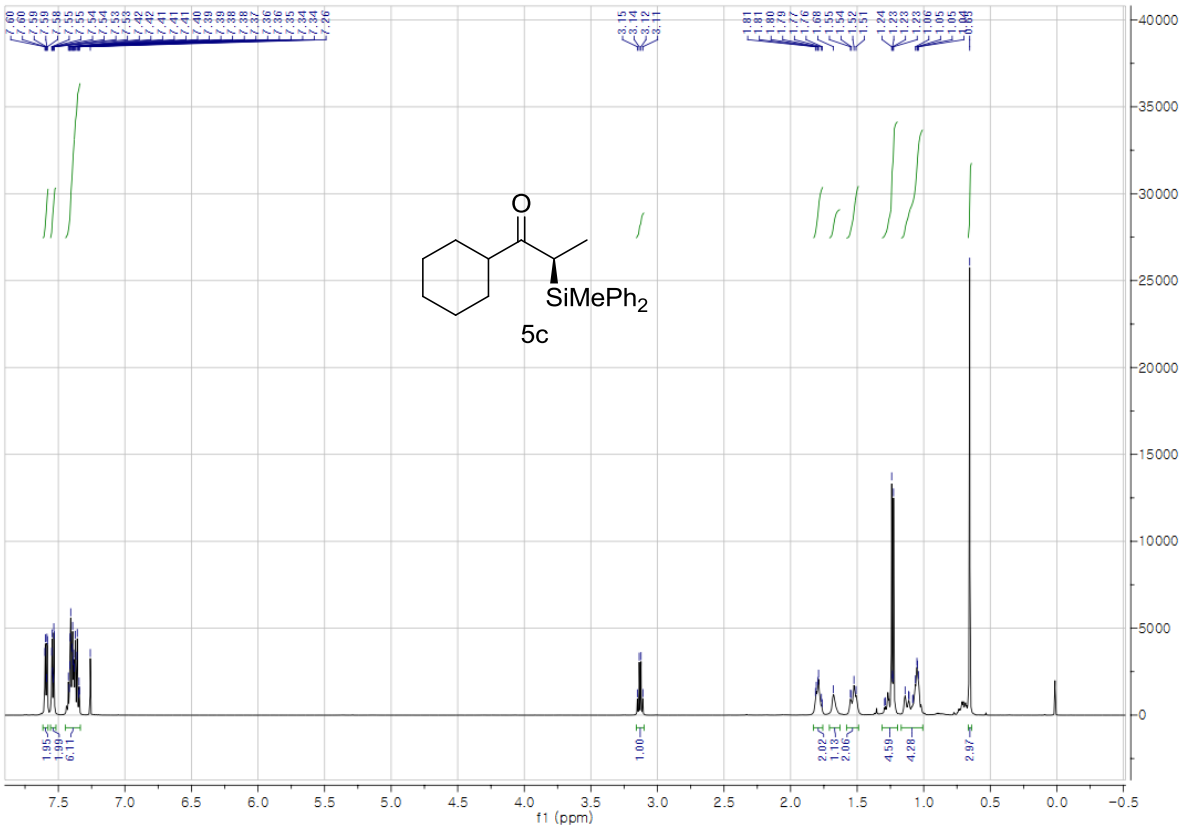
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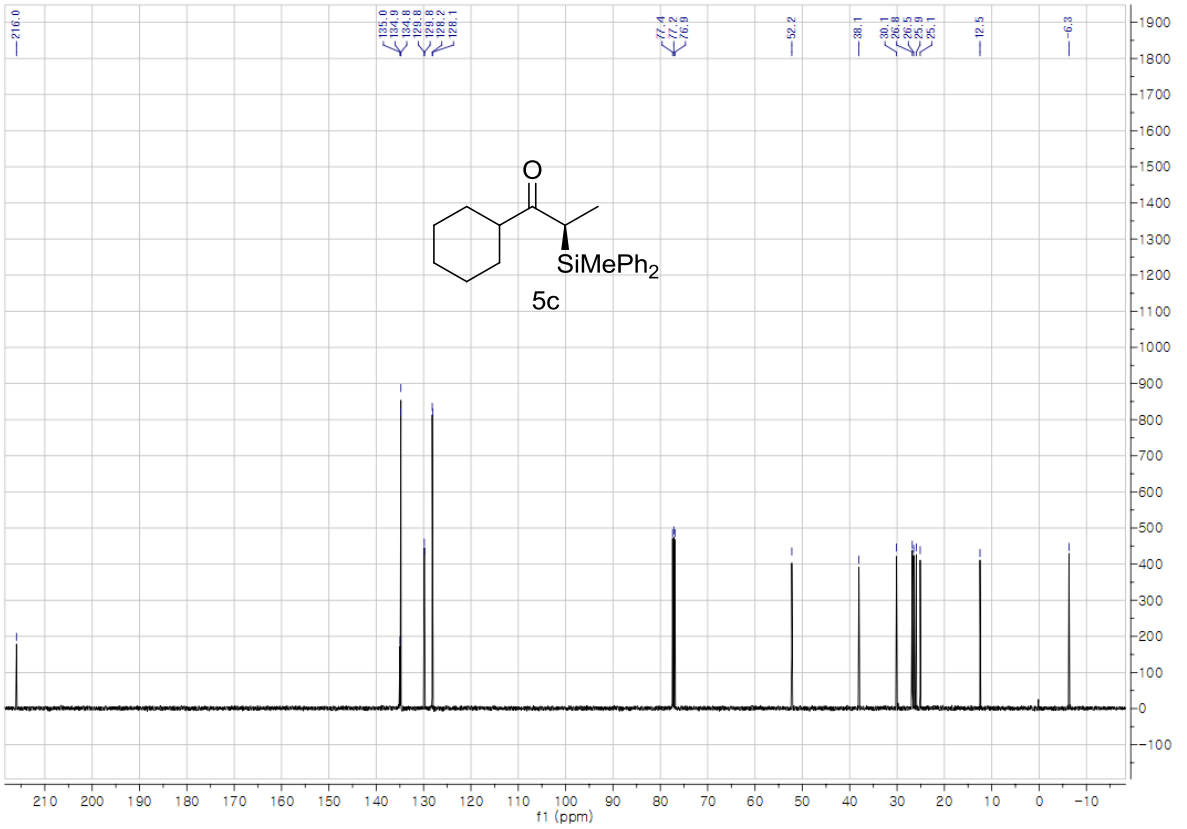
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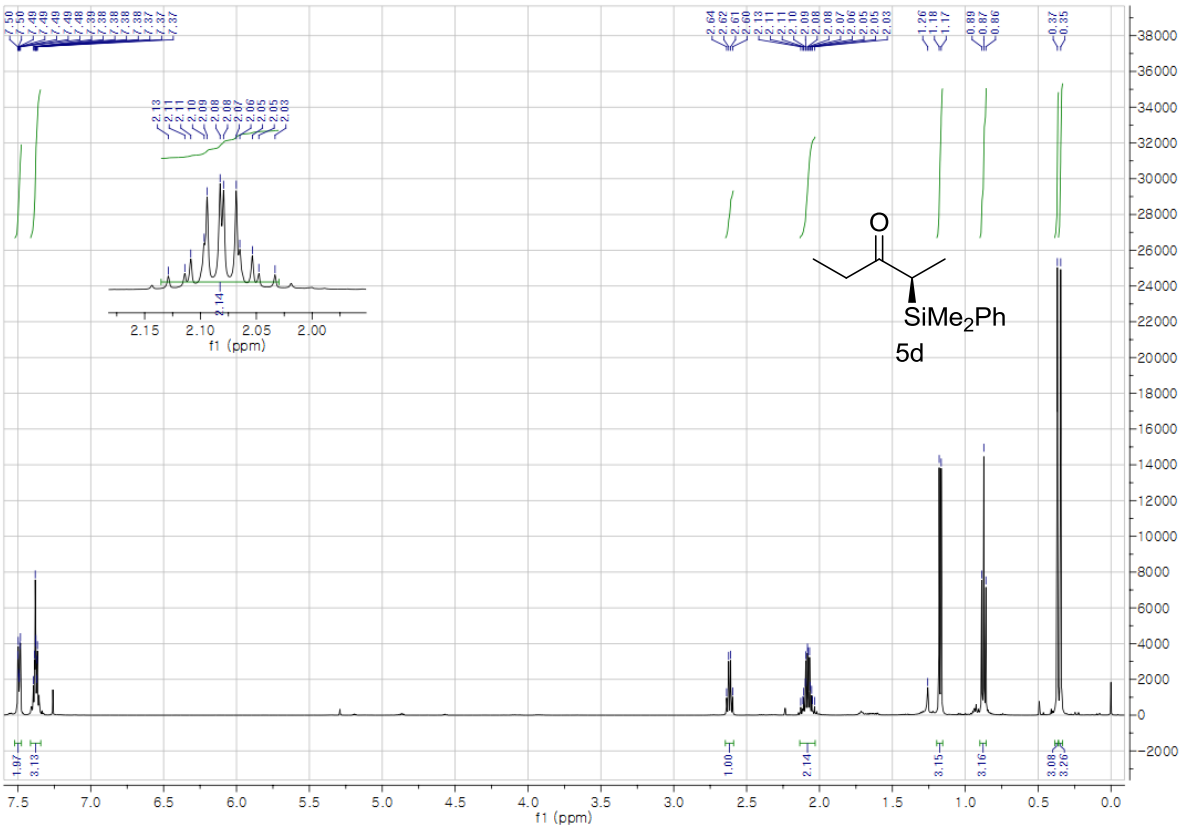
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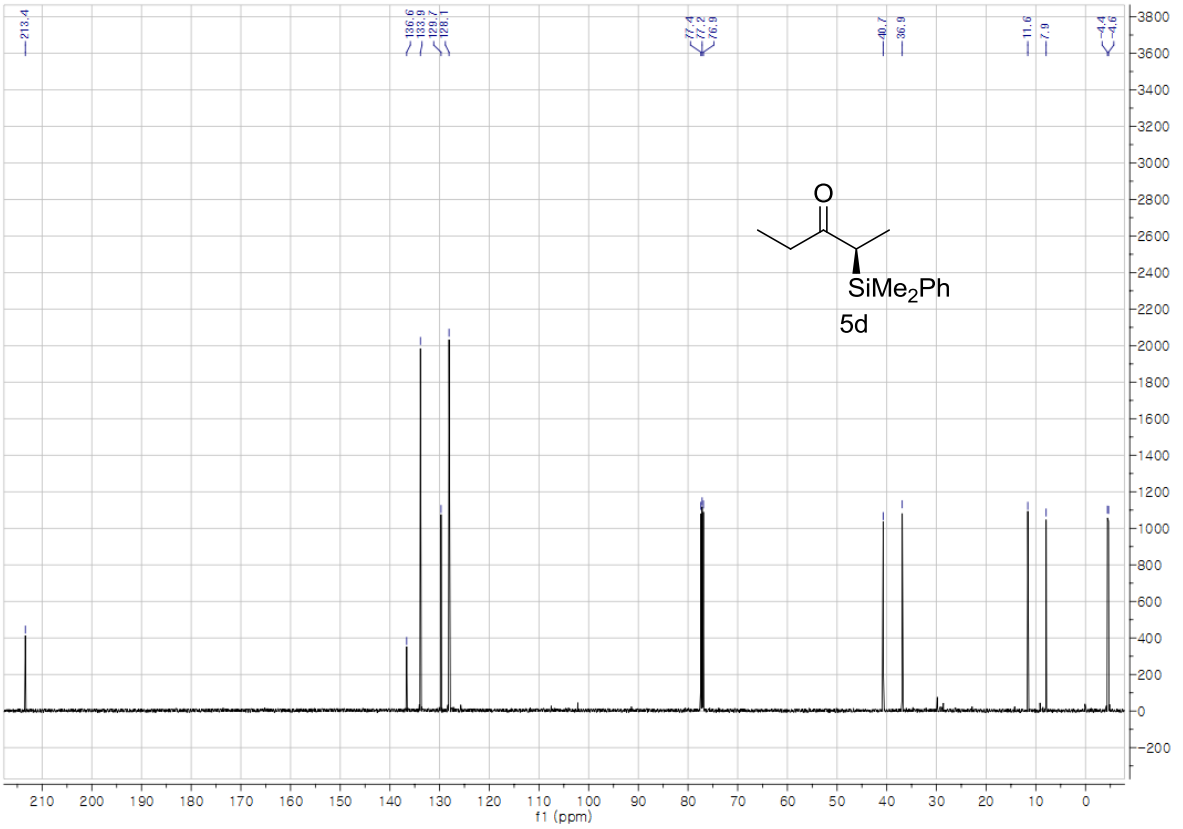
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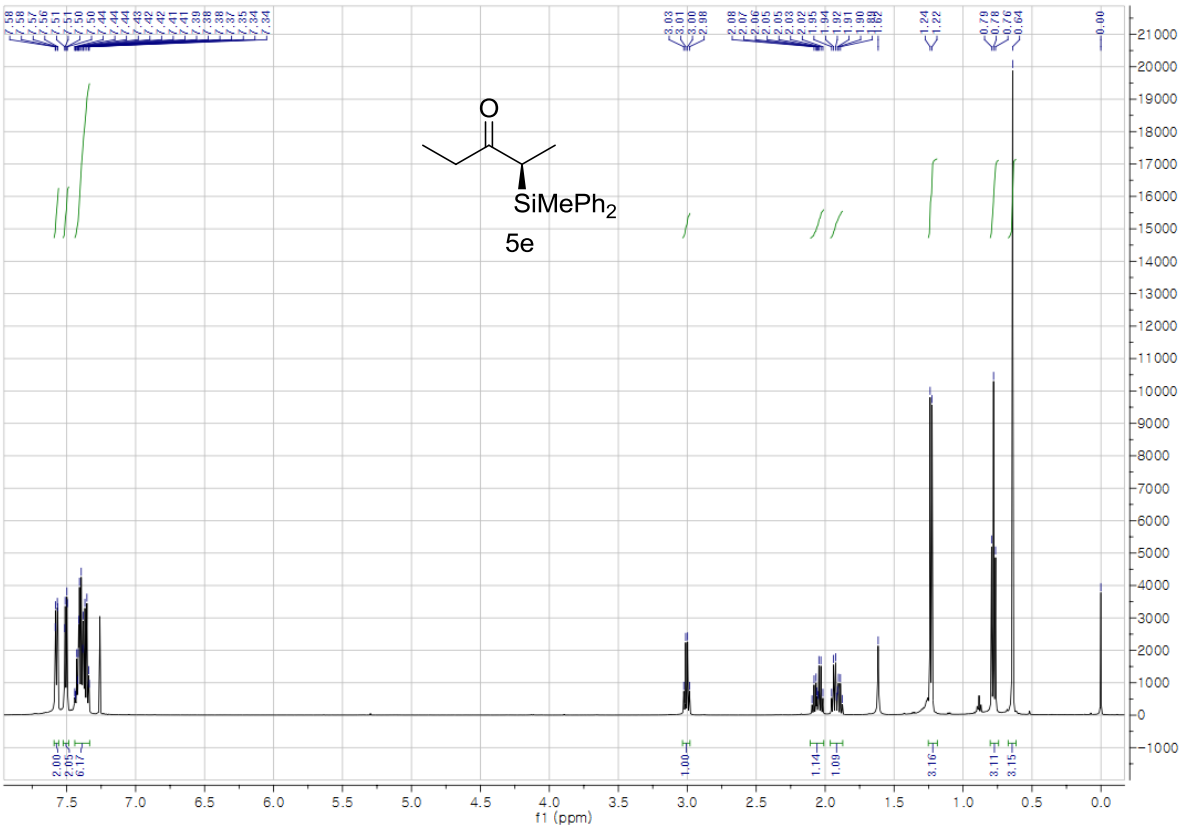
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5e
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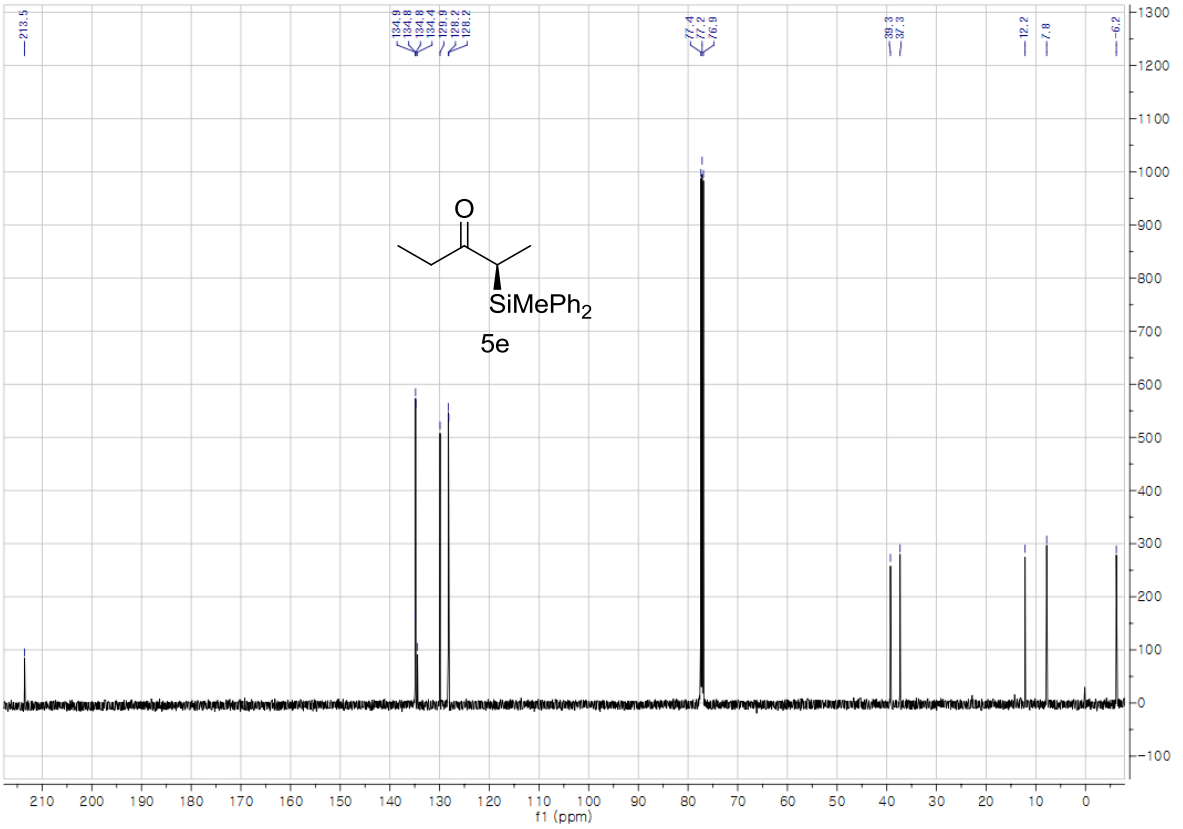
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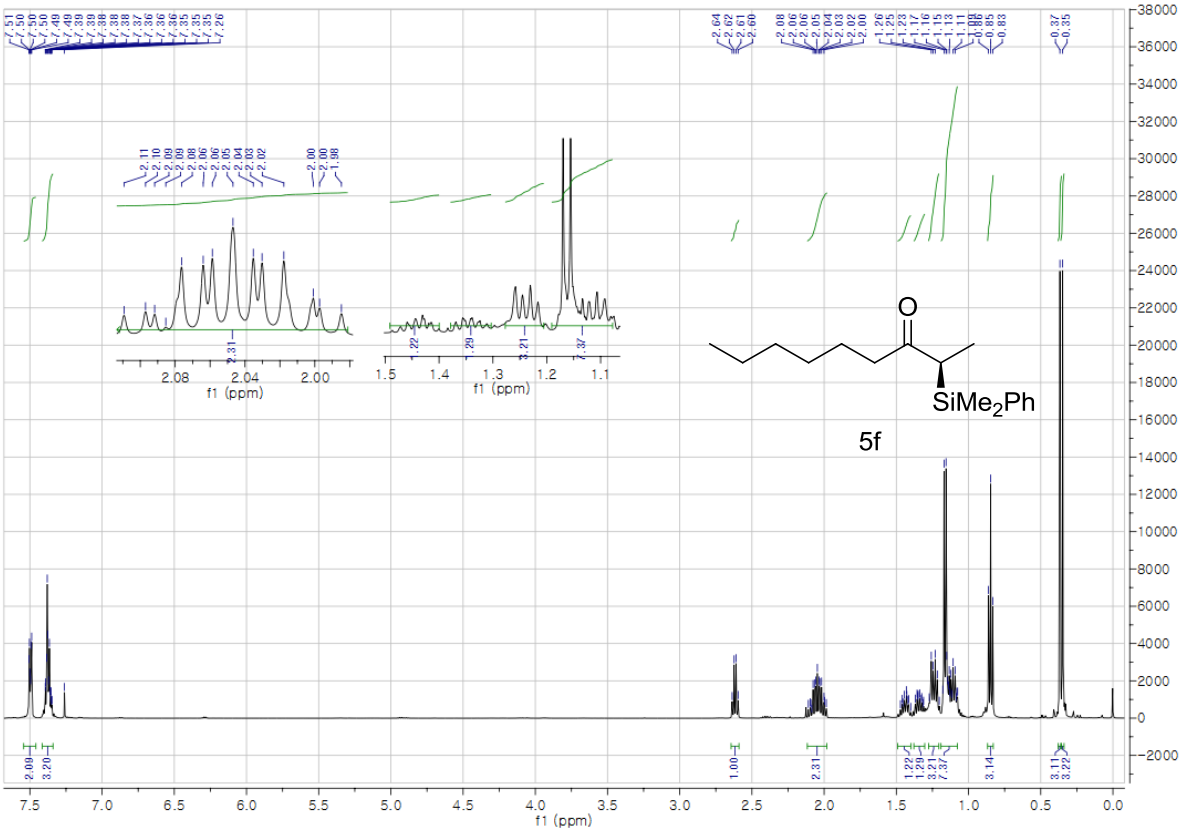
f1 (ppm)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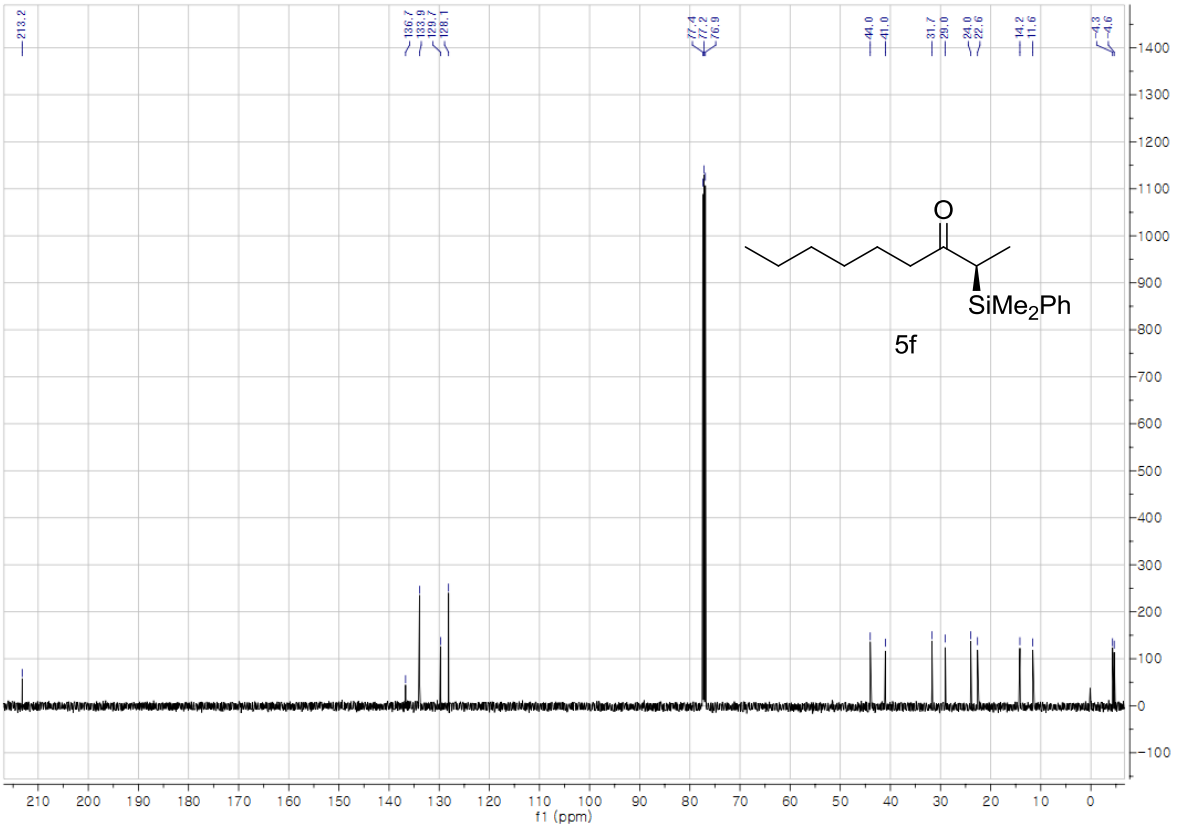
5f
f1 (ppm)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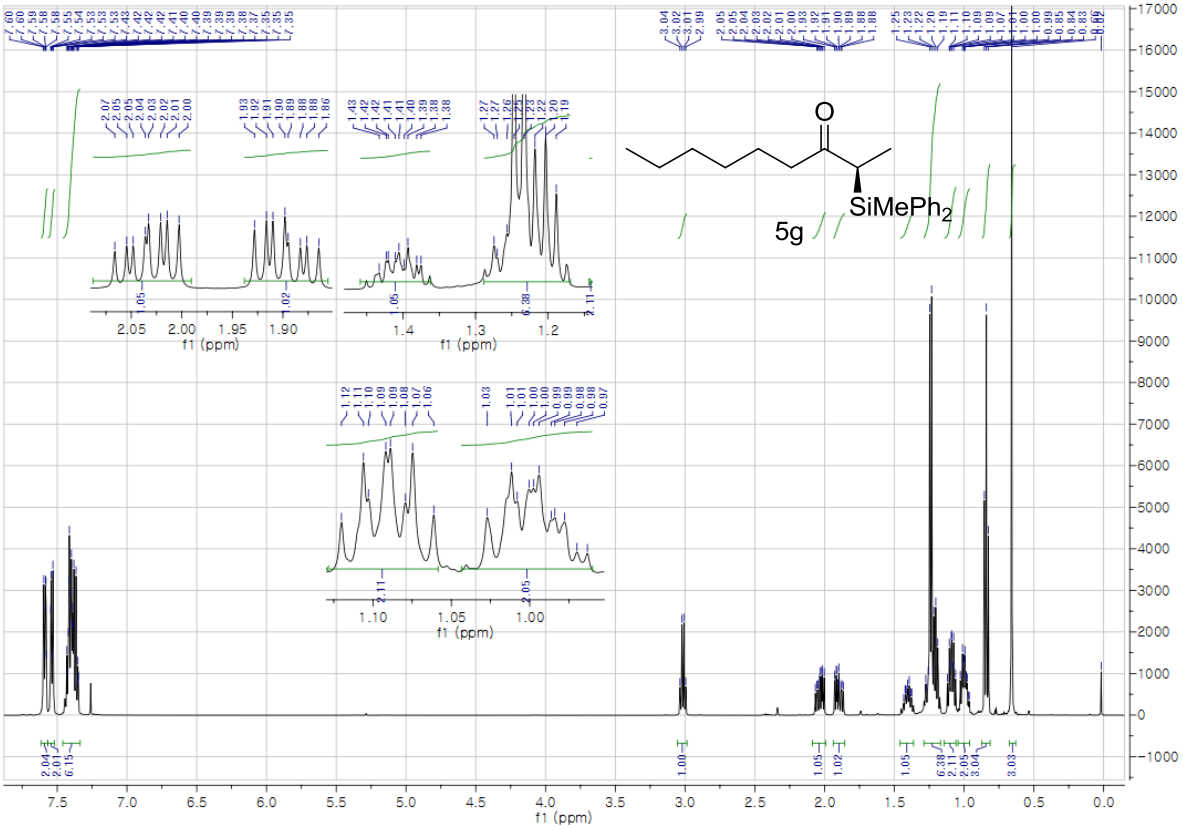
5f
f1 (ppm)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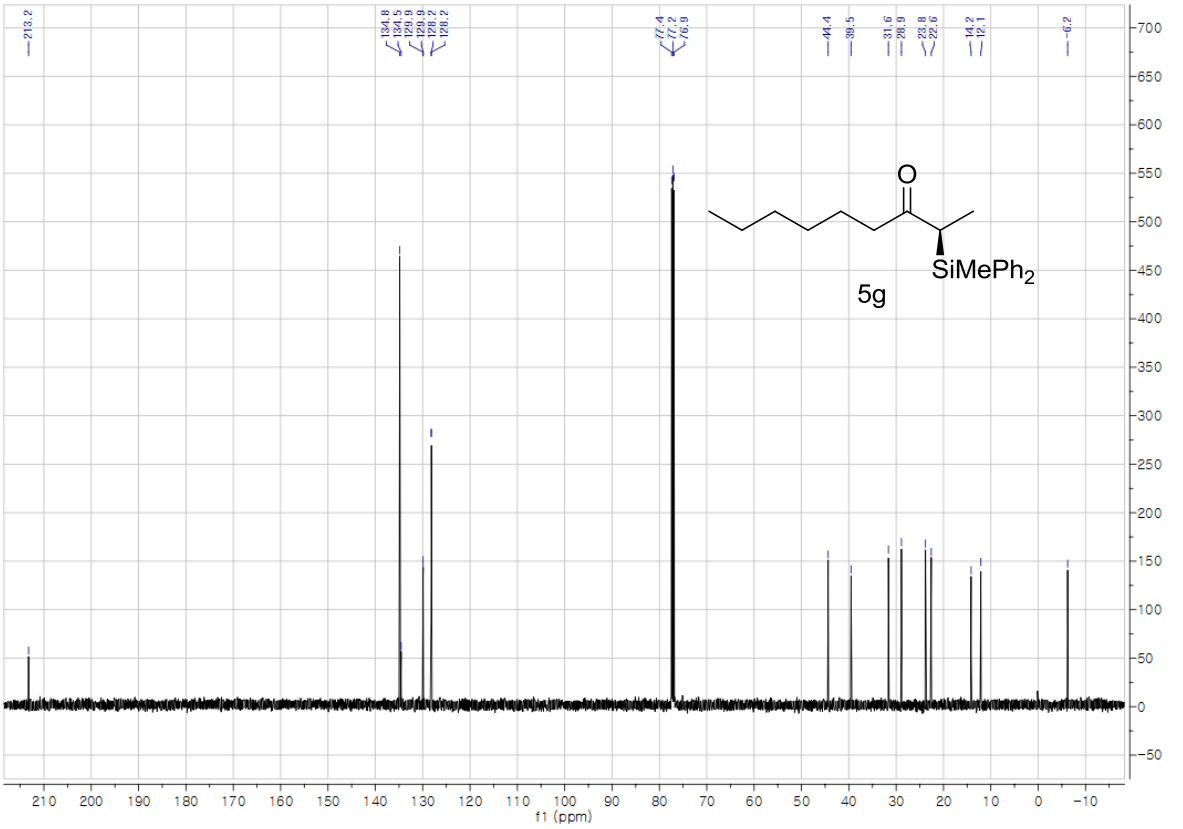
5g
f1 (ppm)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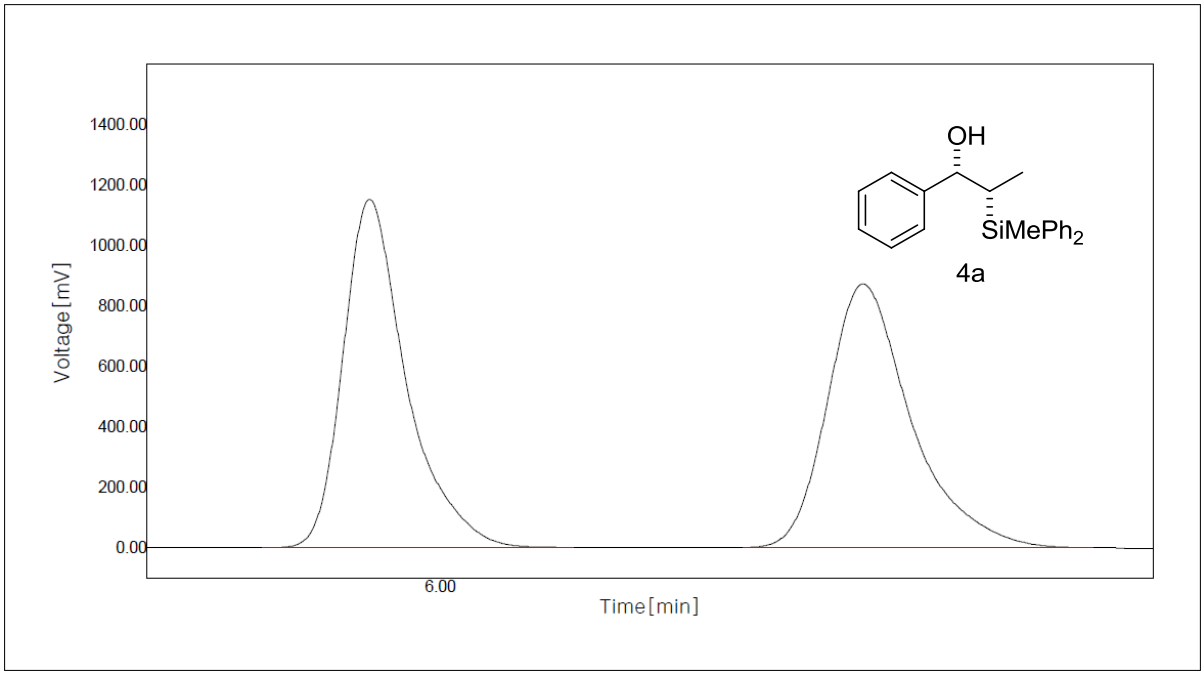
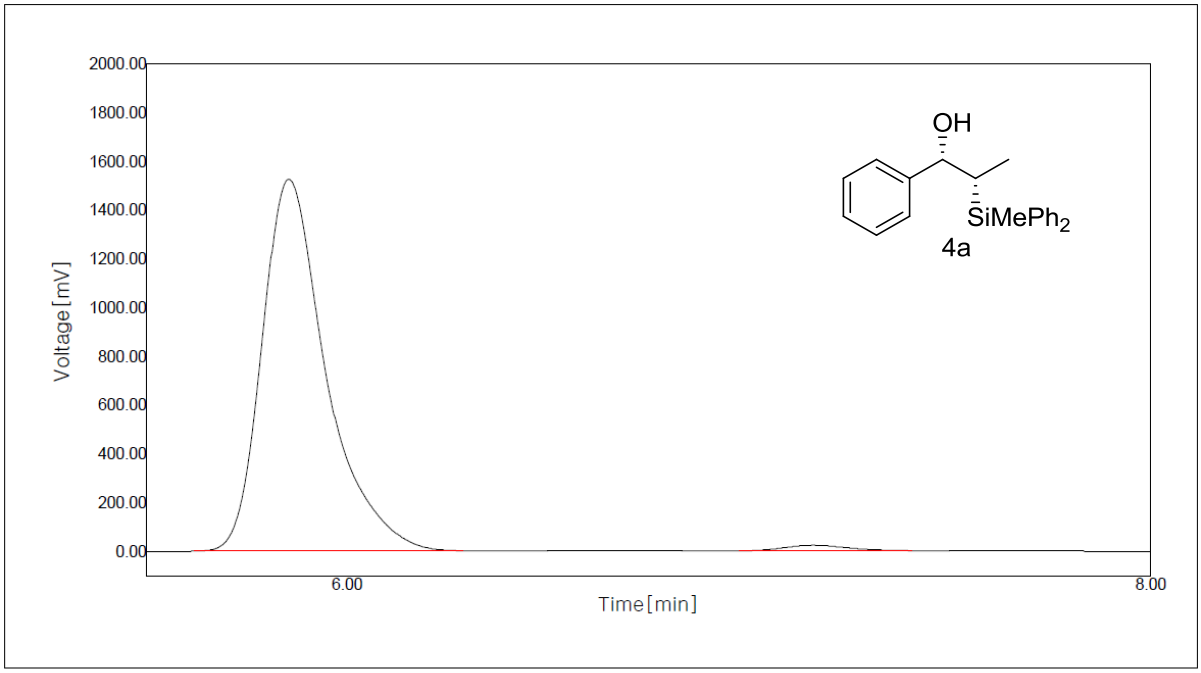
SiMePh2
5g
f1 (ppm)

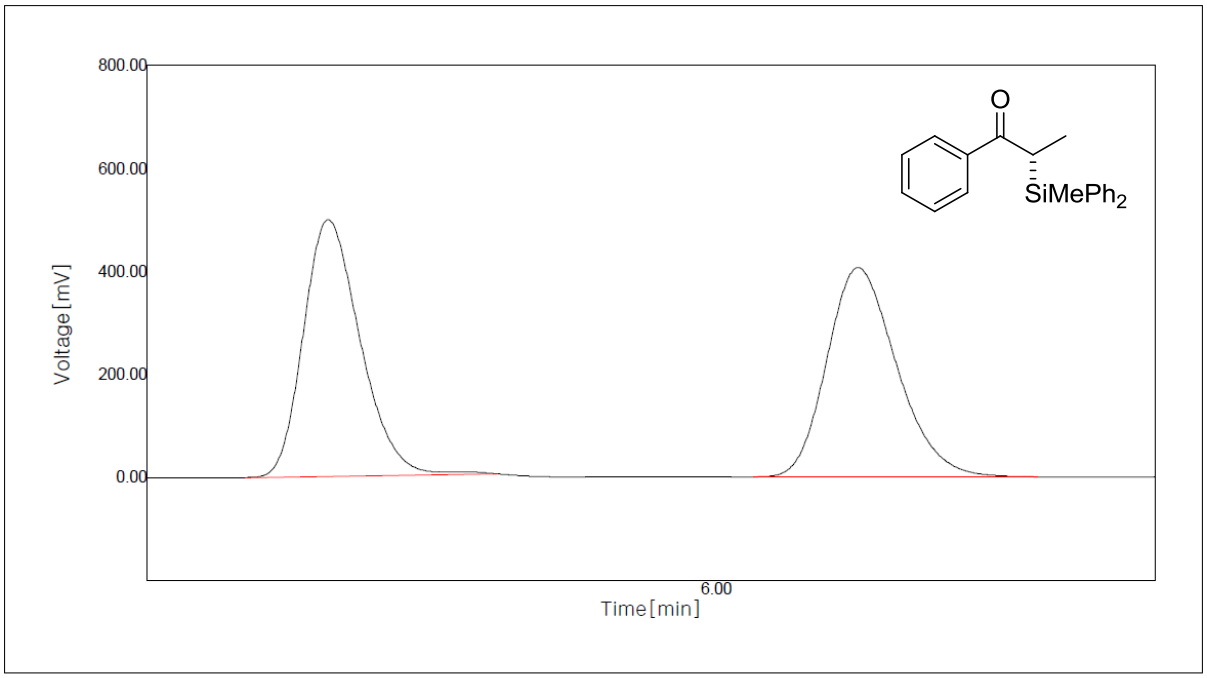
9. HPLC Spectra



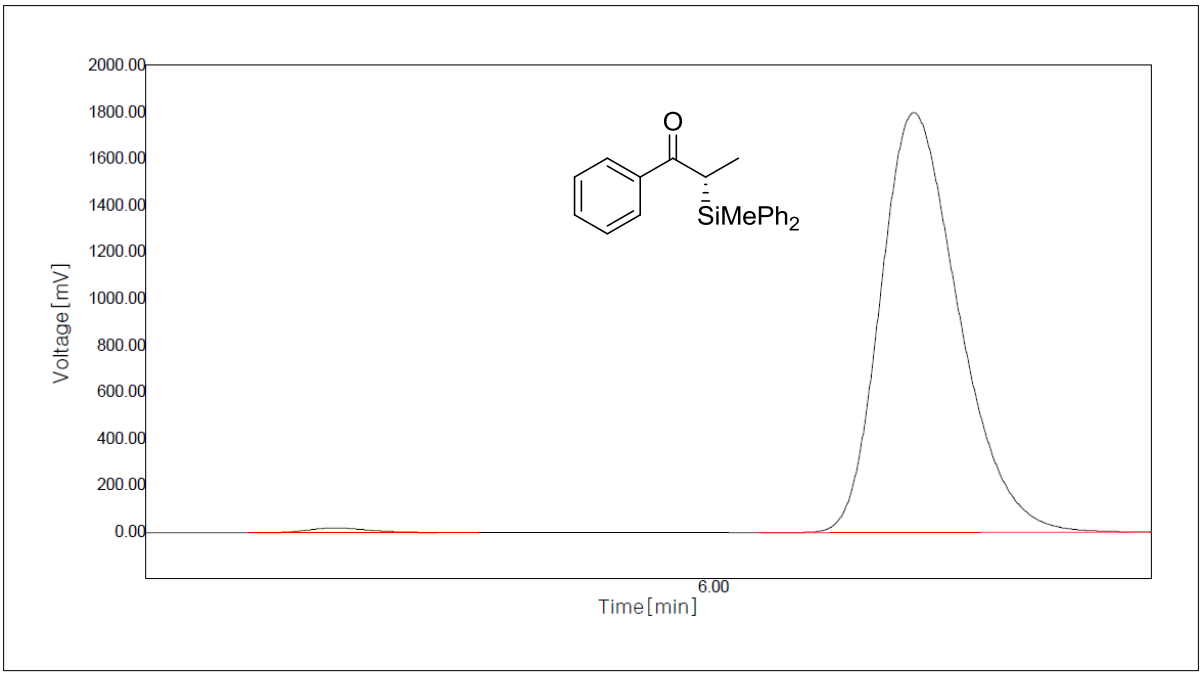
No.	Time(min)	Area ratio (%)
1	5.8317	49.93
2	7.0083	50.07



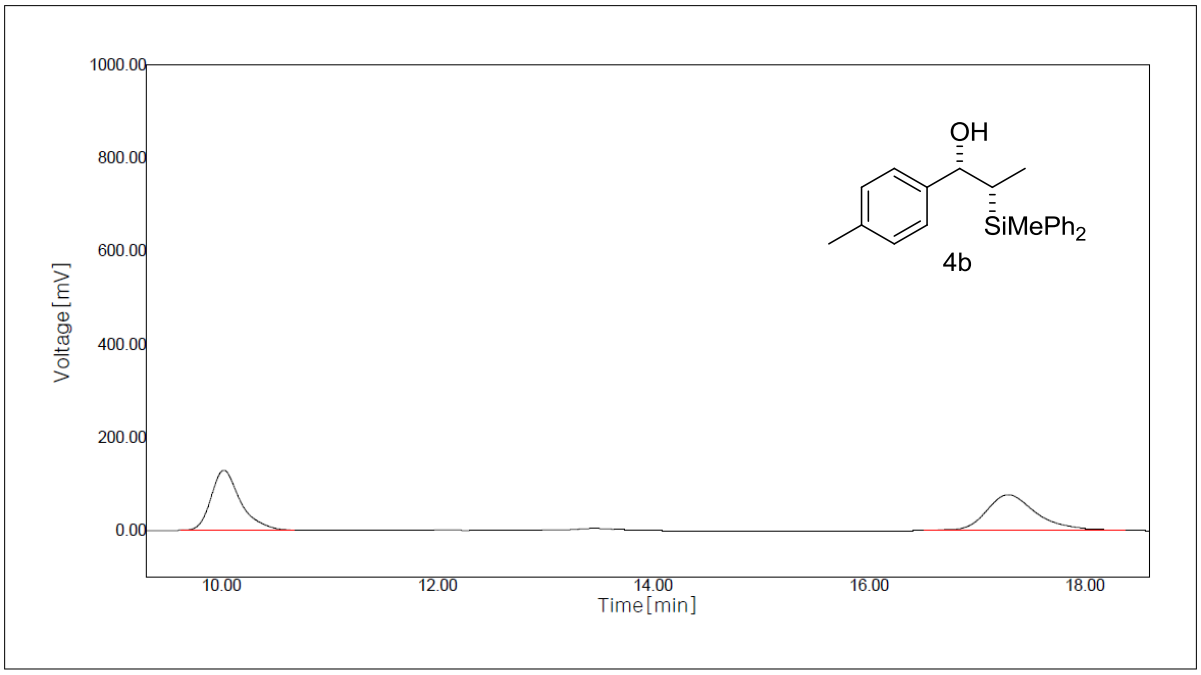
No.	Time(min)	Area ratio (%)
1	5.8550	98.51
2	7.1617	1.49



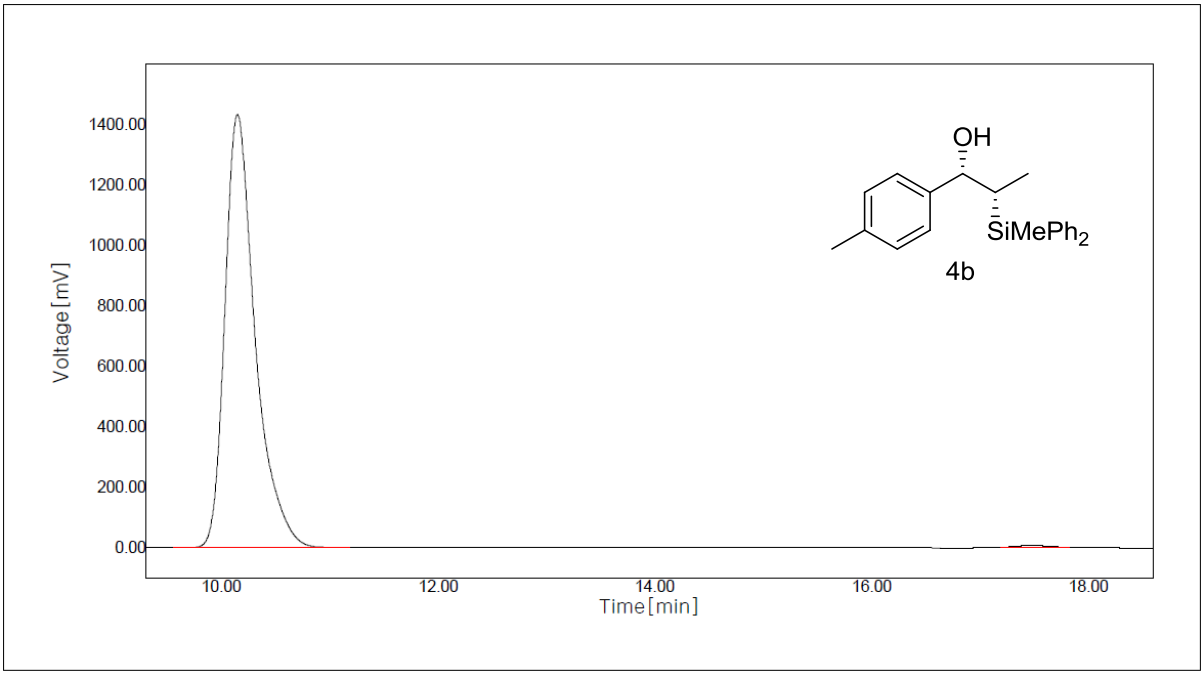
Peak #	Time (min)	Area (%)
1	5.1133	49.95
2	6.3217	50.05



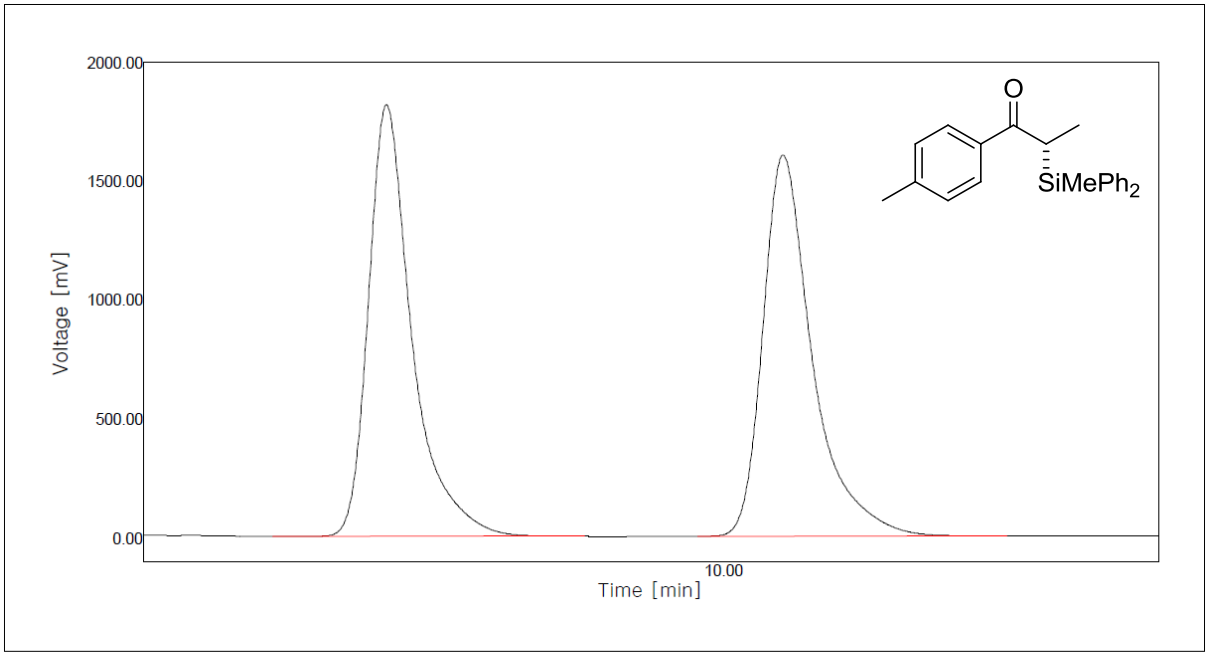
Peak #	Time (min)	Area (%)
1	5.1350	0.85
2	6.4567	99.15



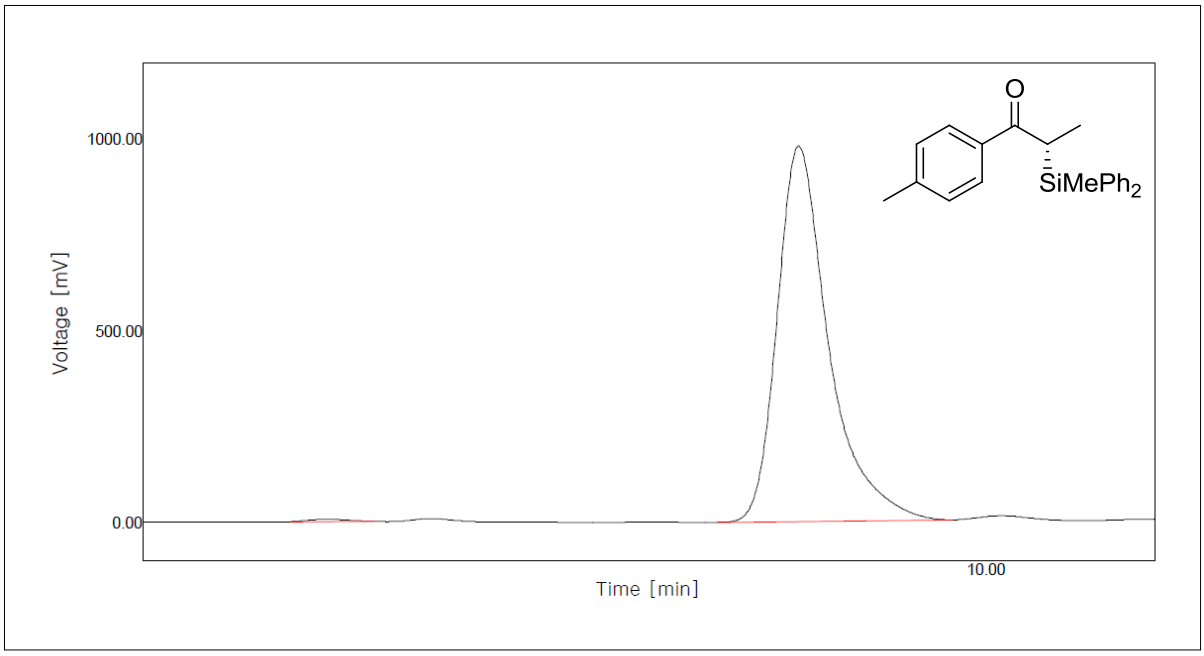
No.	Time(min)	Area ratio (%)
1	10.0217	50.03
2	17.2917	49.97



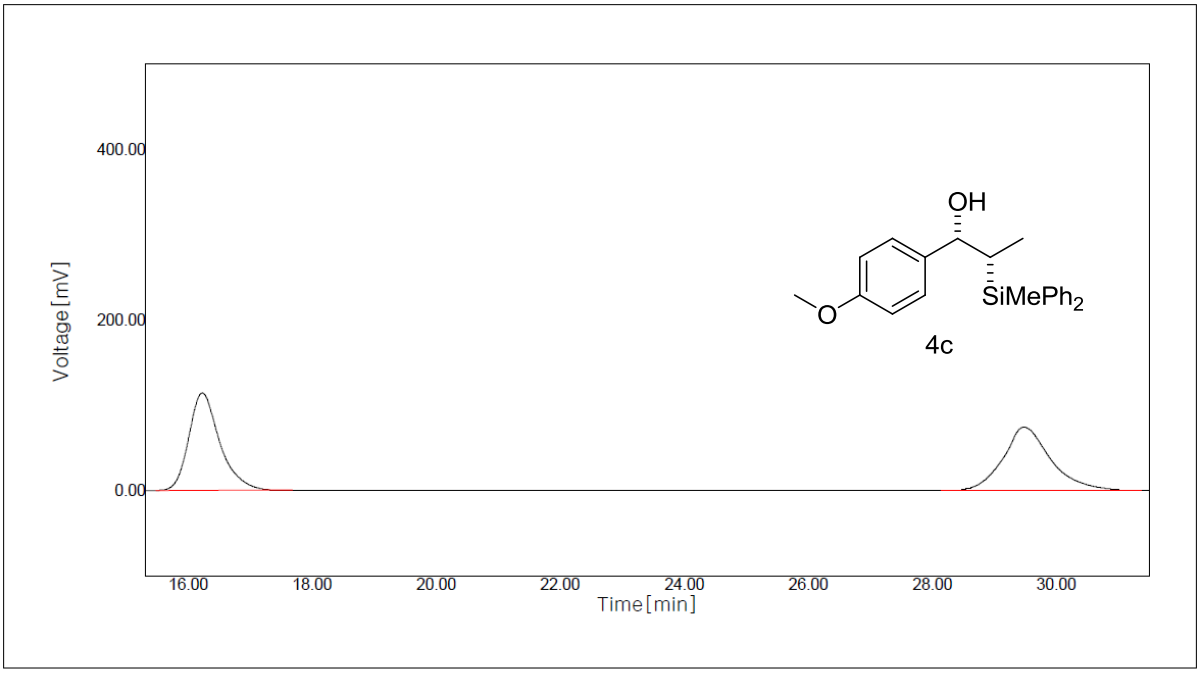
No.	Time(min)	Area ratio (%)
1	10.1500	99.63
2	17.4833	0.37



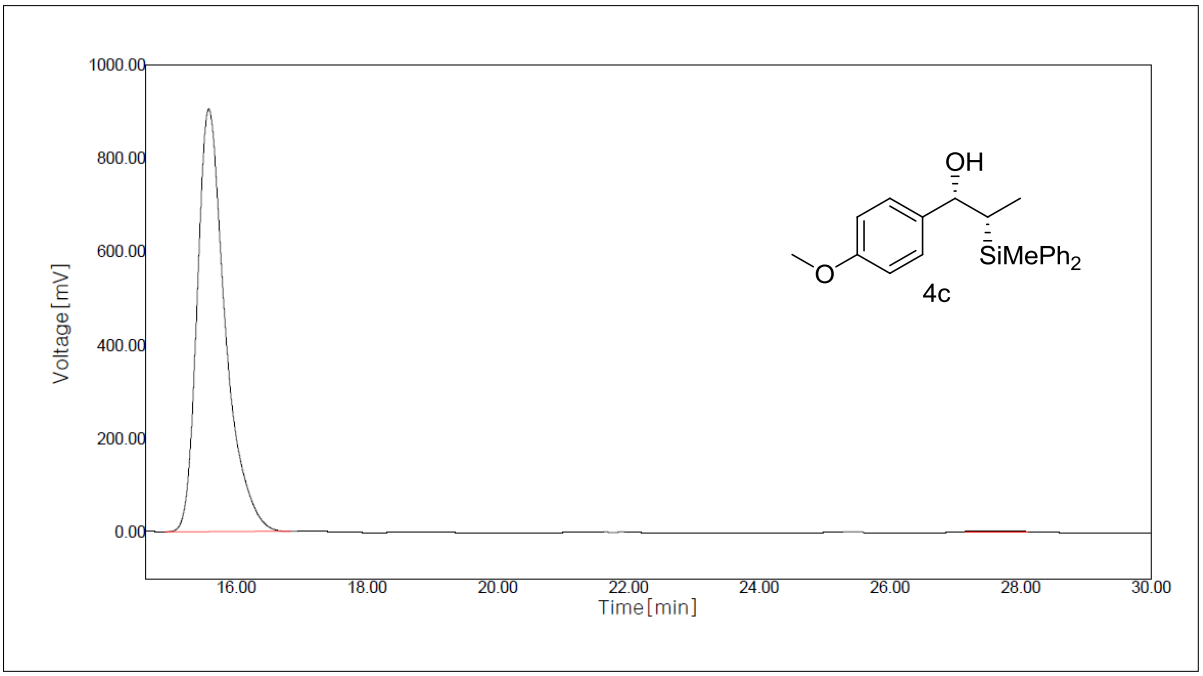
No.	Time(min)	Area ratio (%)
1	8.8400	49.87
2	10.2067	50.13



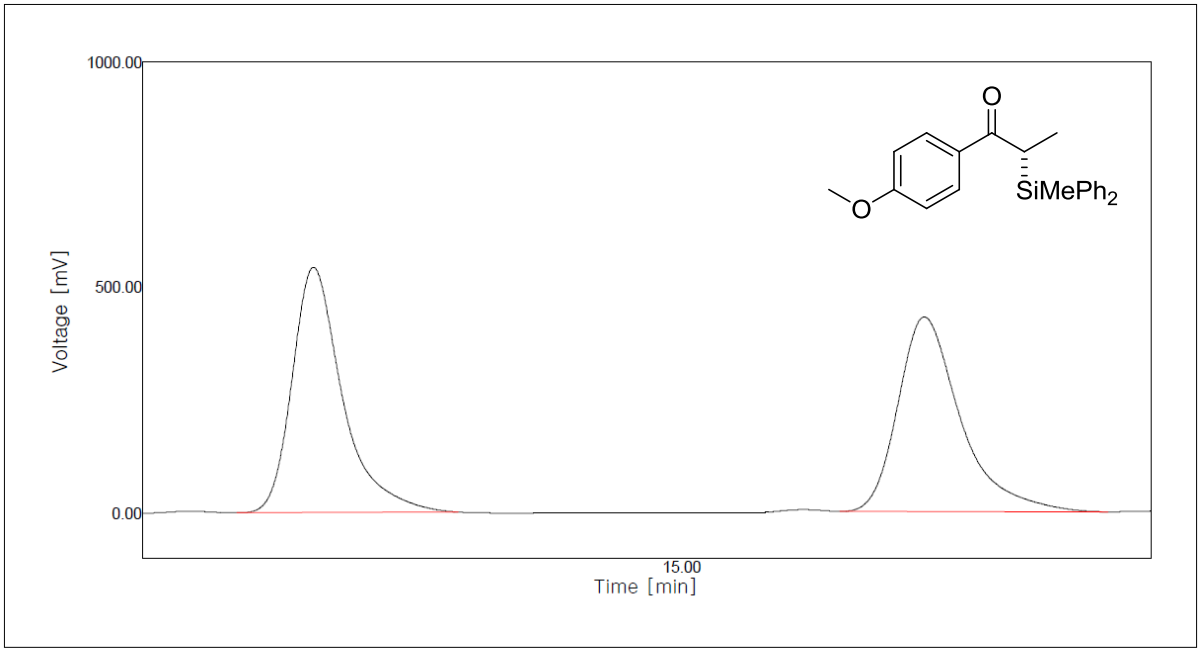
No.	Time(min)	Area ratio (%)
1	8.0483	0.45
2	9.4450	99.55



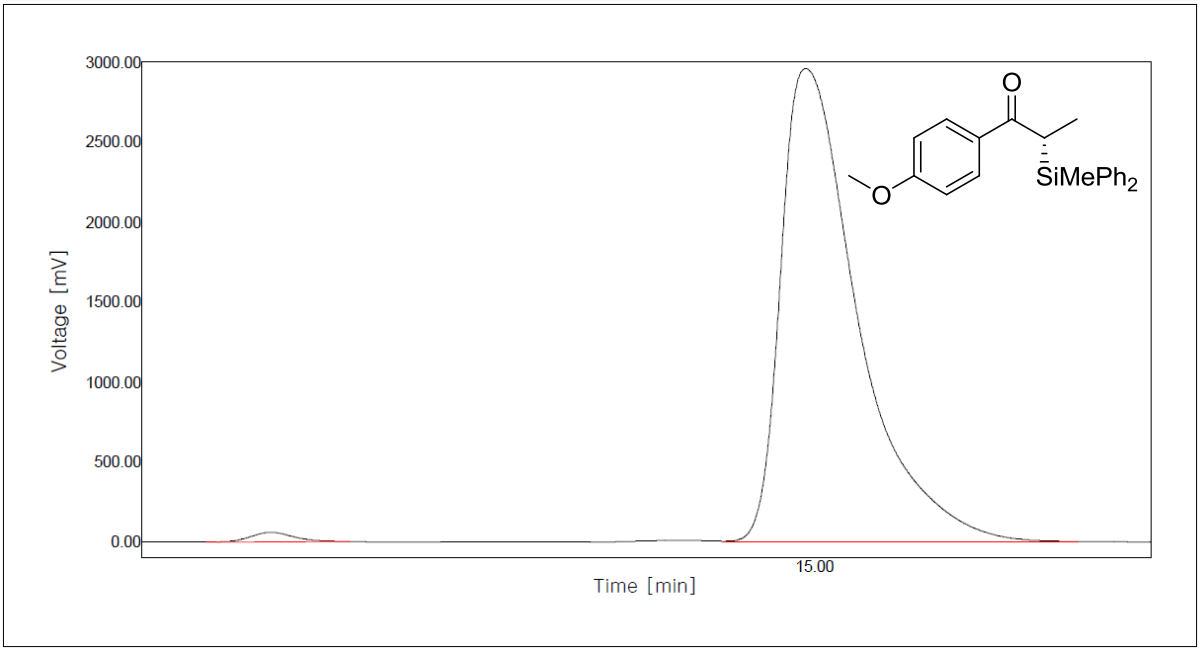
No.	Time(min)	Area ratio (%)
1	16.2250	49.83
2	29.4817	50.17



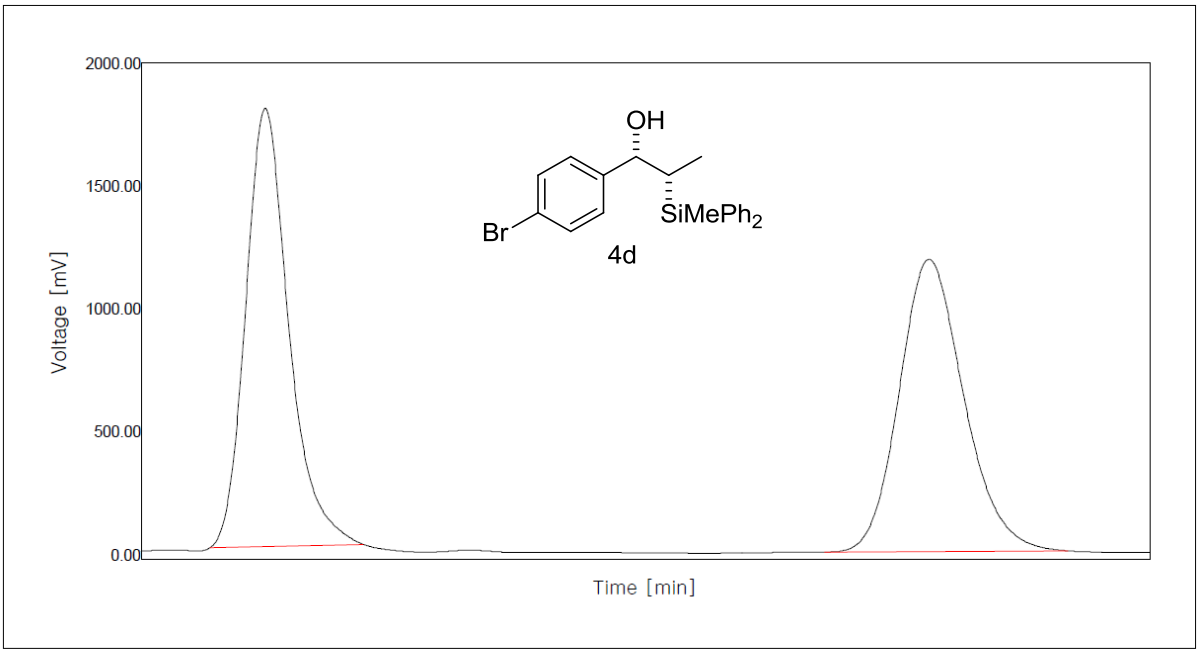
No.	Time(min)	Area ratio (%)
1	15.5750	99.70
2	27.5700	0.30



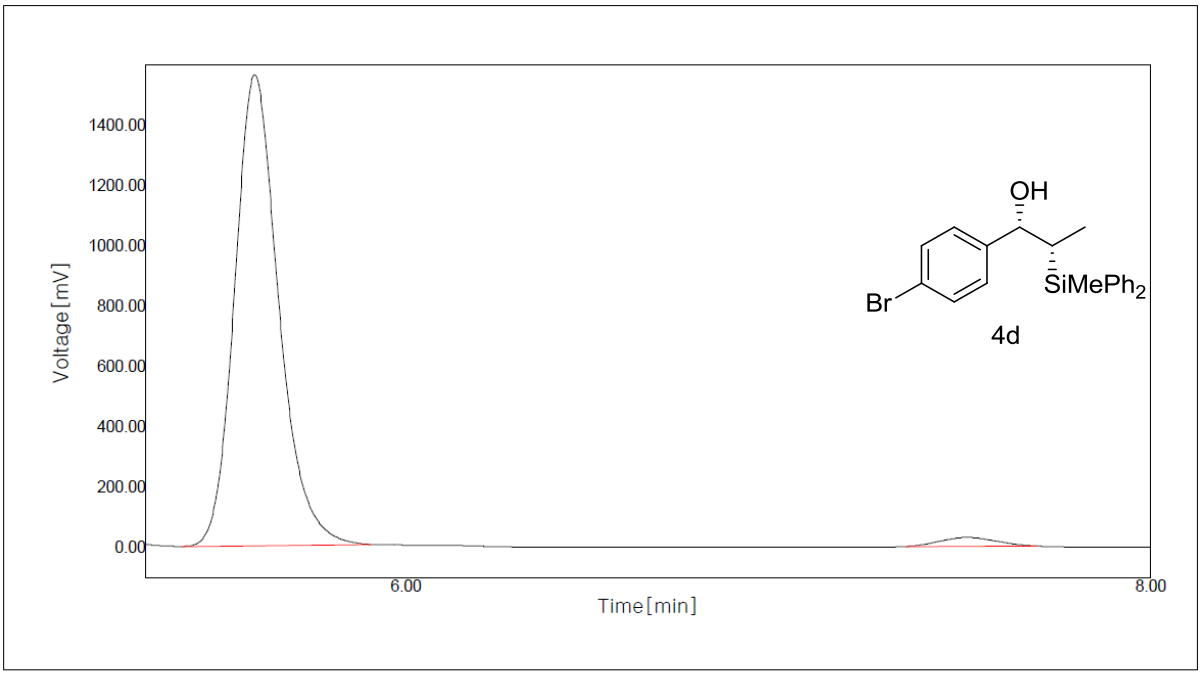
No.	Time(min)	Area ratio (%)
1	13.4317	50.35
2	16.0333	49.65



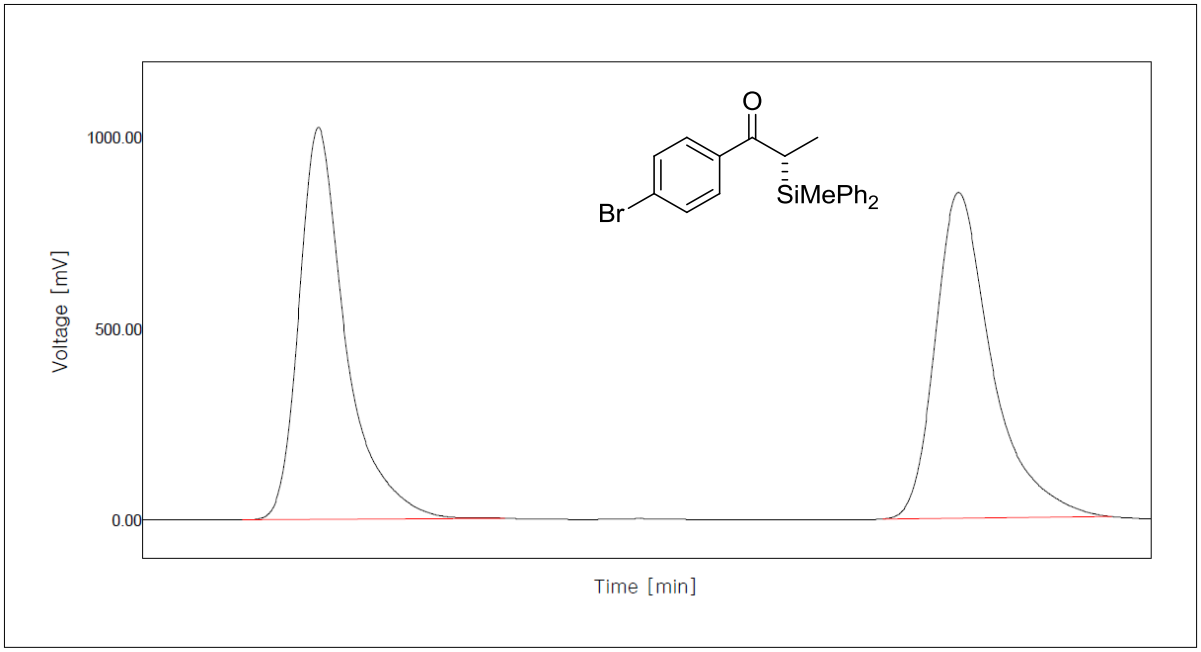
No.	Time(min)	Area ratio (%)
1	12.5783	1.13
2	14.9617	98.87



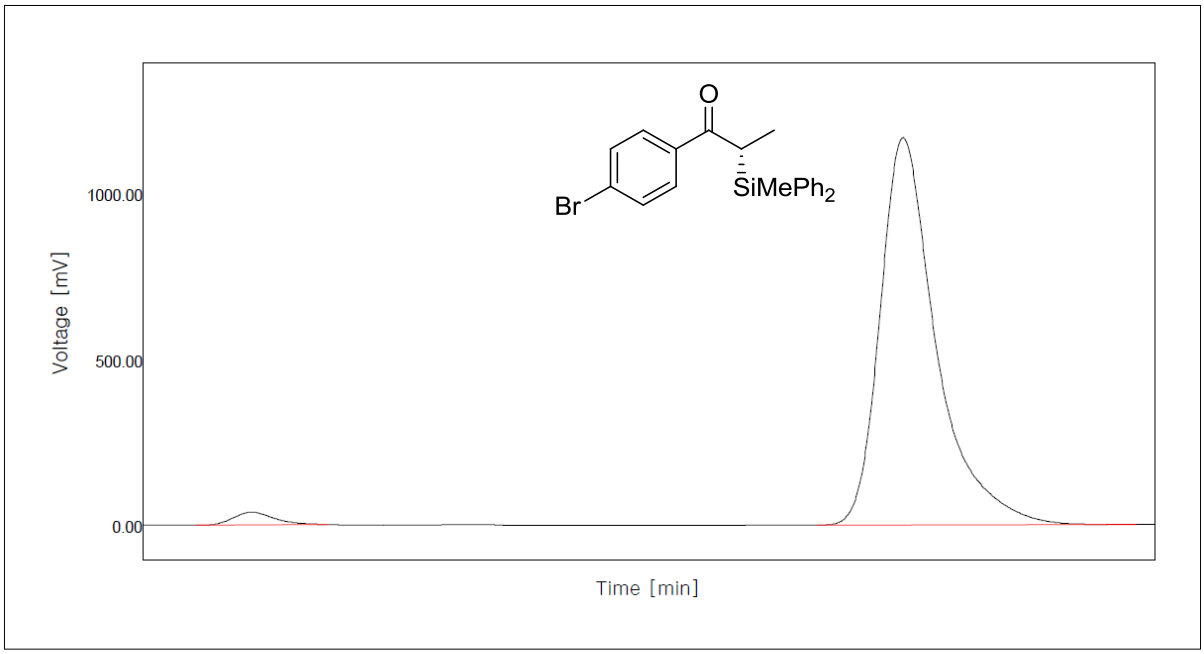
No.	Time(min)	Area ratio (%)
1	5.5450	50.04
2	7.3867	49.96



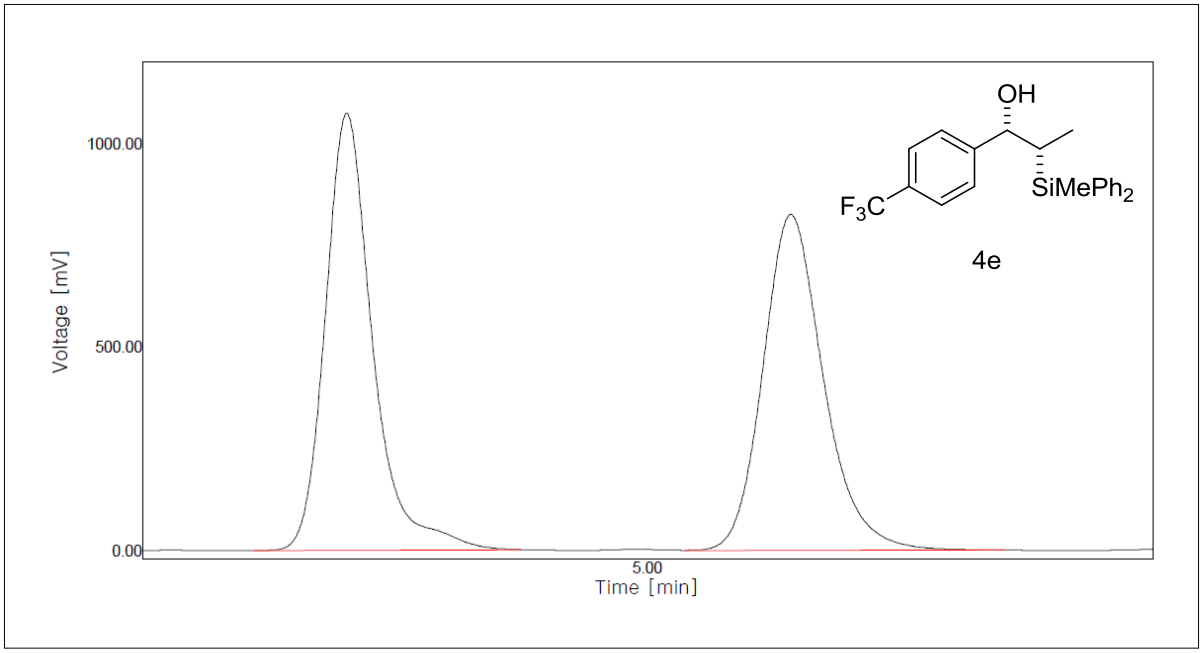
No.	Time(min)	Area ratio (%)
1	5.5950	97.66
2	7.5083	2.34



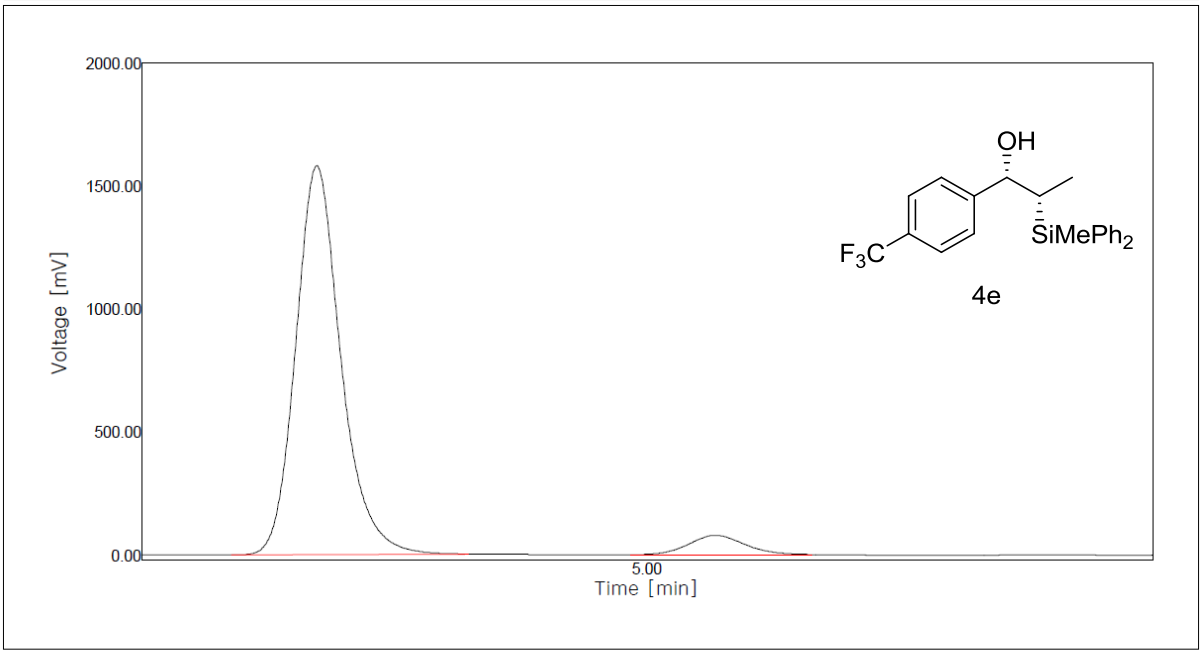
No.	Time(min)	Area ratio (%)
1	7.2717	49.69
2	8.9850	50.31



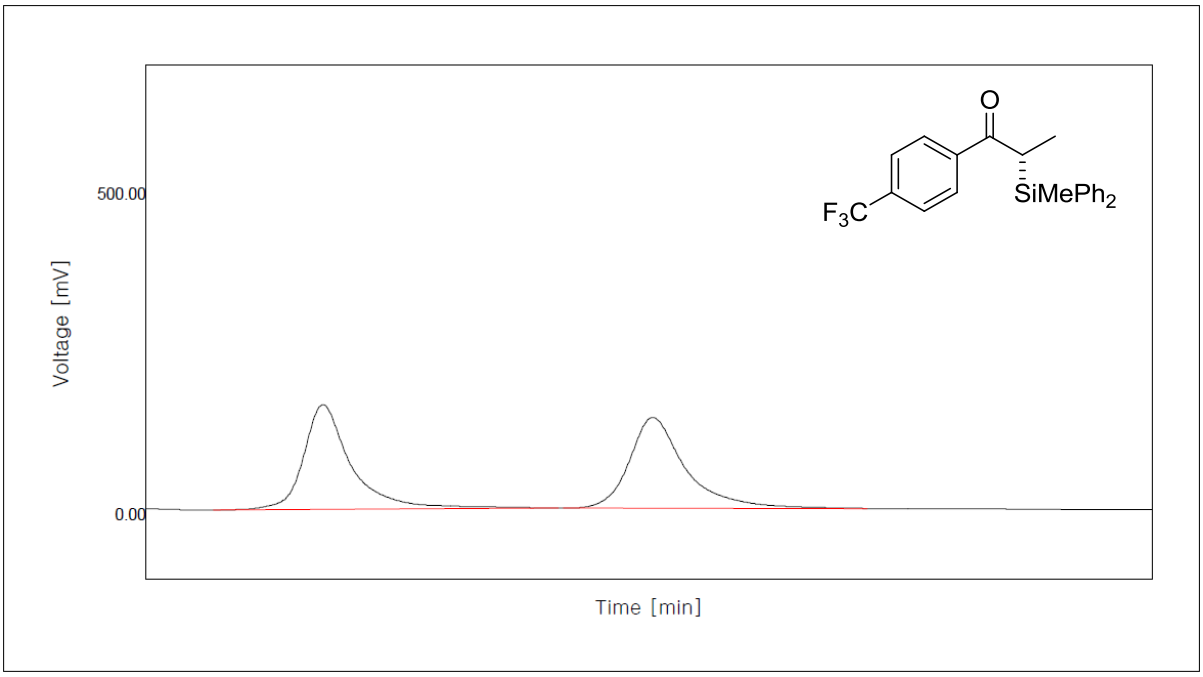
No.	Time(min)	Area ratio (%)
1	6.5017	2.40
2	8.3033	97.60



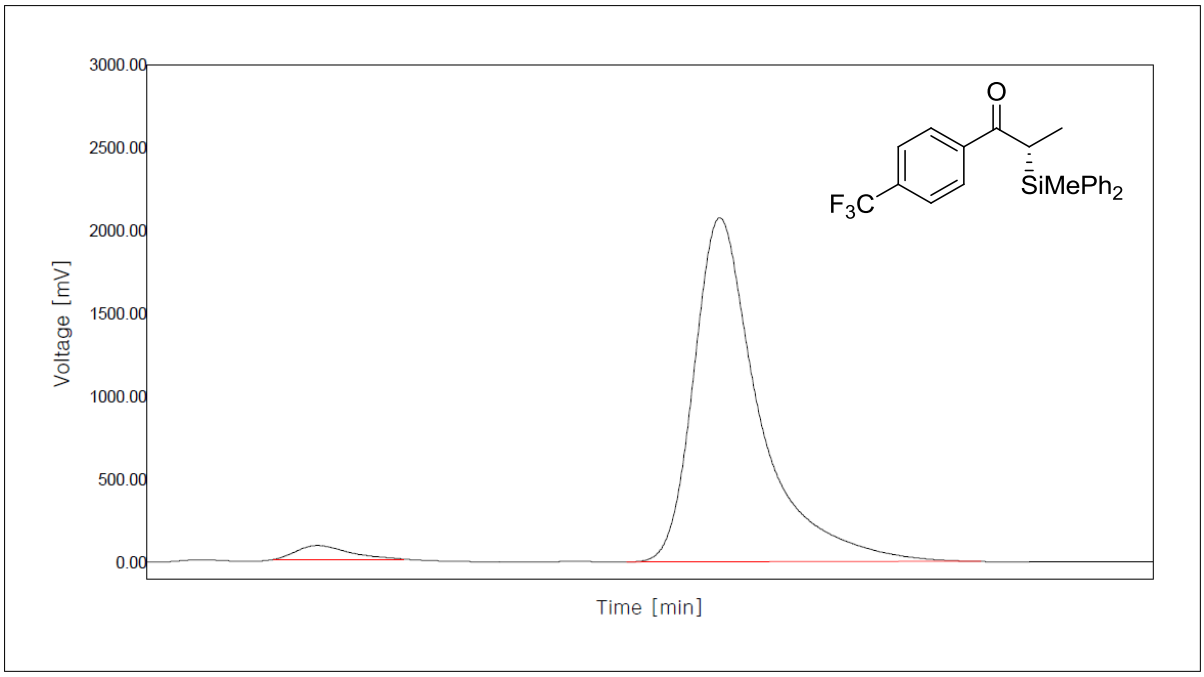
No.	Time(min)	Area ratio (%)
1	4.4050	50.48
2	5.2833	49.52



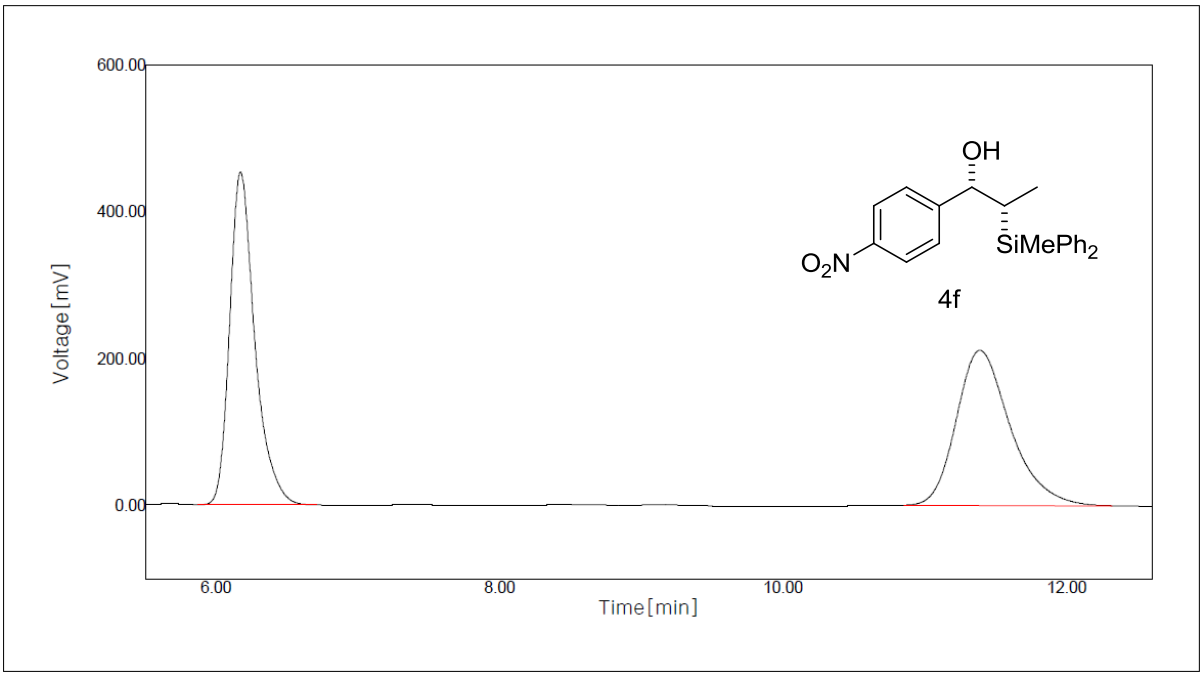
No.	Time(min)	Area ratio (%)
1	4.3467	94.12
2	5.1350	5.88



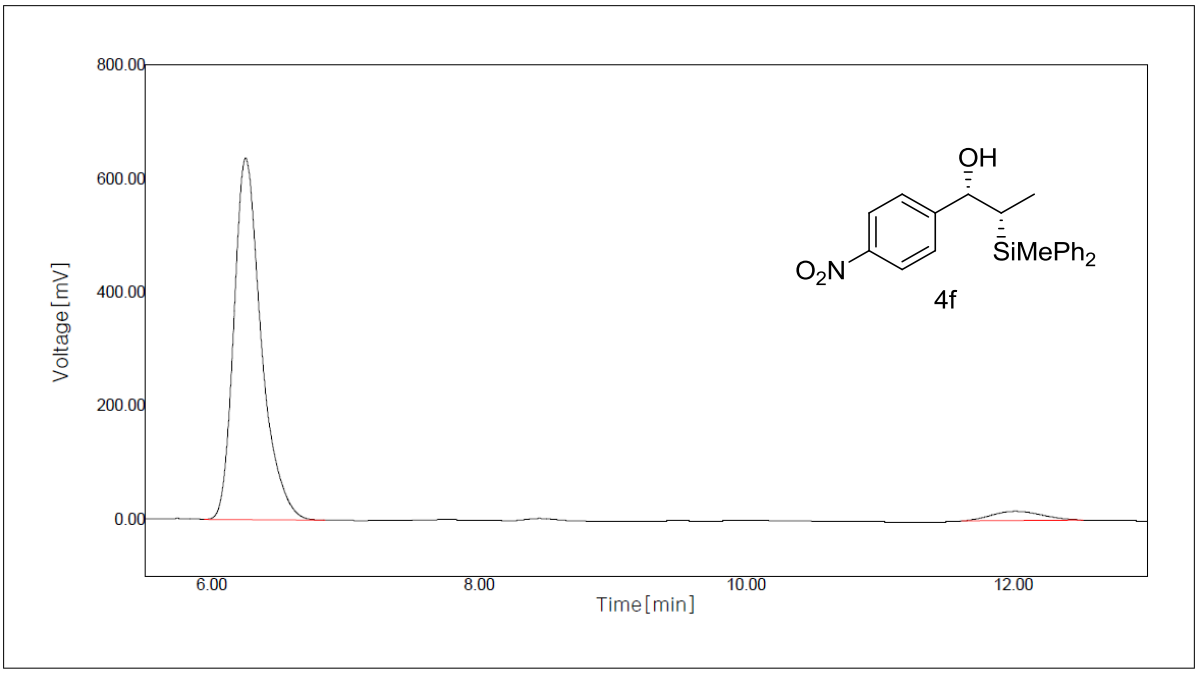
No.	Time(min)	Area ratio (%)
1	5.6883	49.74
2	6.4083	50.26



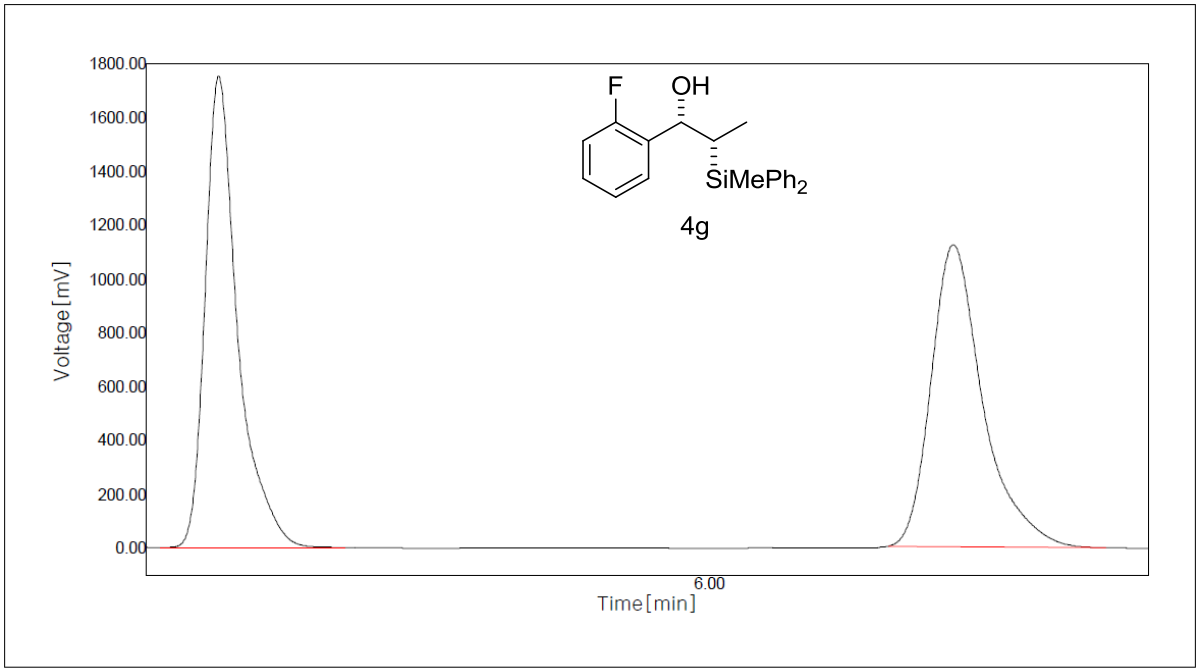
No.	Time(min)	Area ratio (%)
1	5.9233	3.08
2	6.6817	96.92



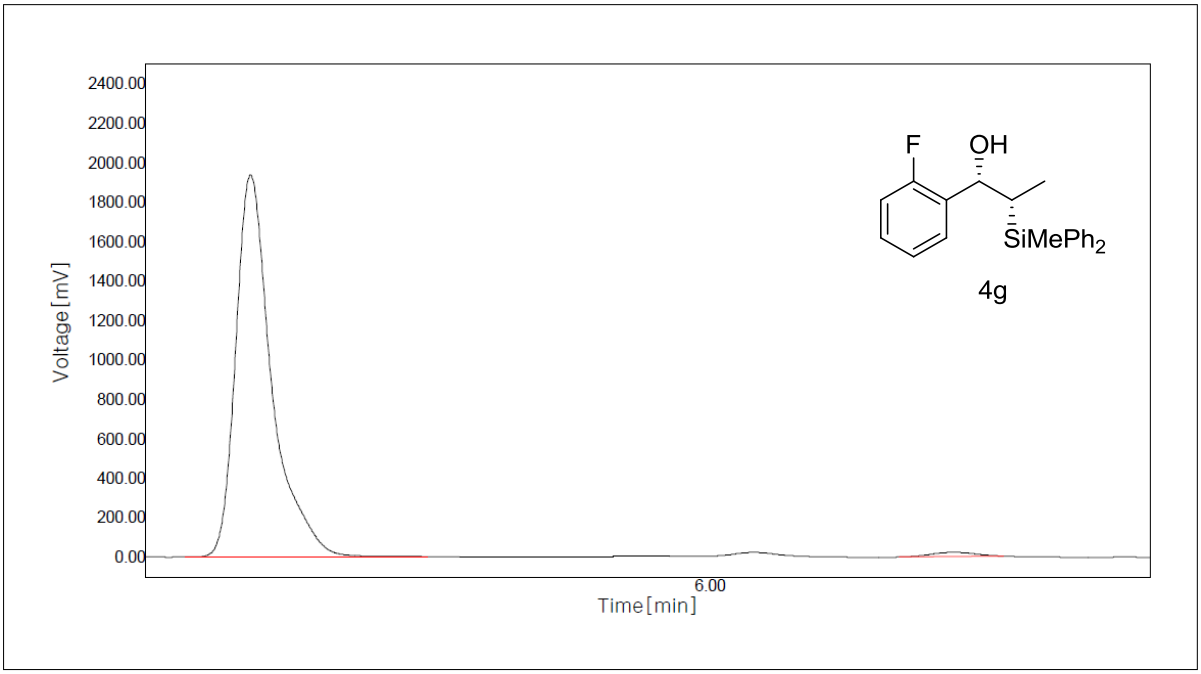
No.	Time(min)	Area ratio (%)
1	6.1717	50.03
2	11.3850	49.97



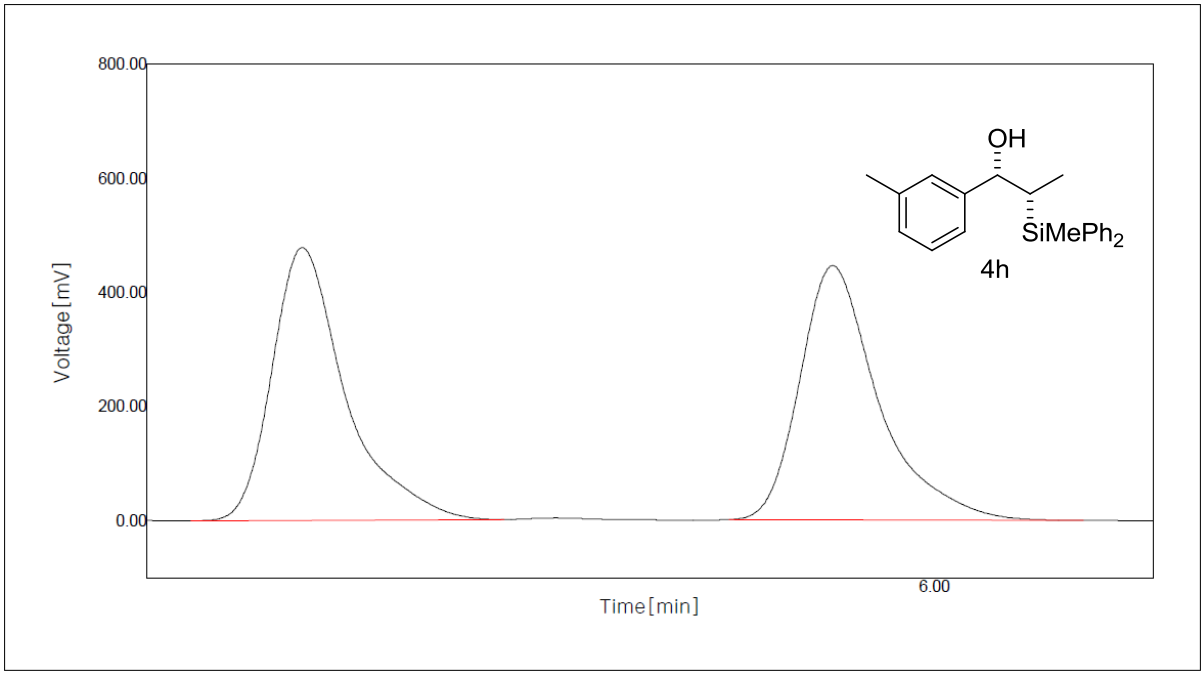
No.	Time(min)	Area ratio (%)
1	6.2550	95.39
2	12.0133	4.61



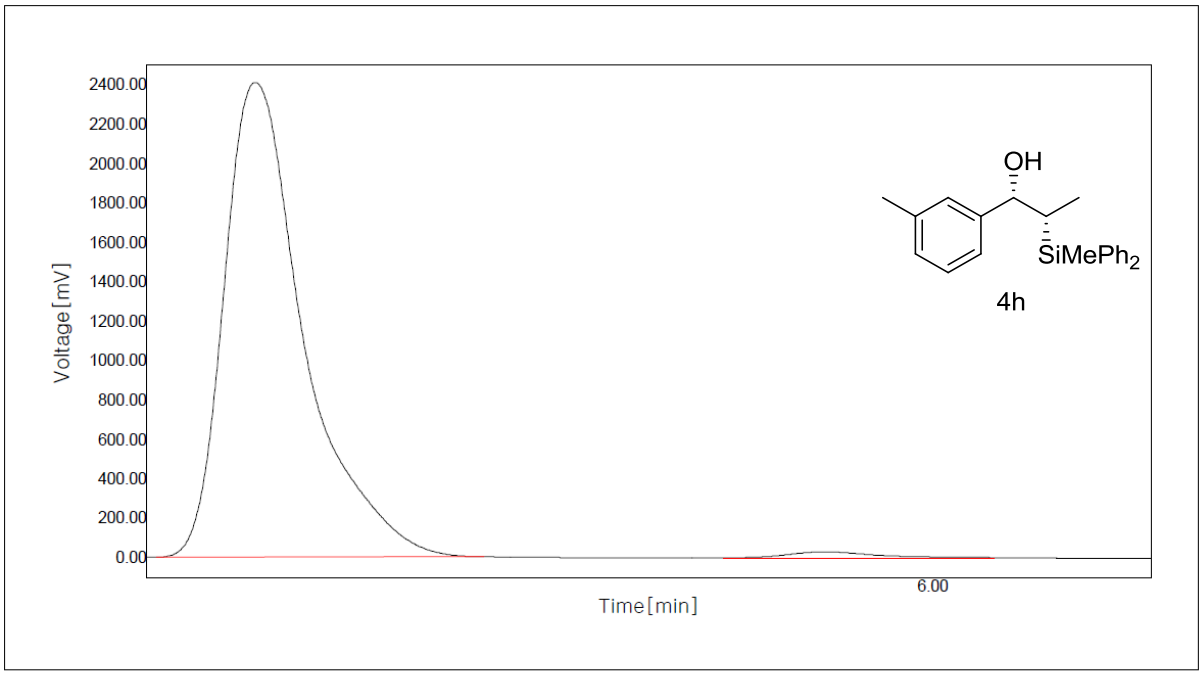
No.	Time(min)	Area ratio (%)
1	4.4333	49.48
2	6.7767	50.52



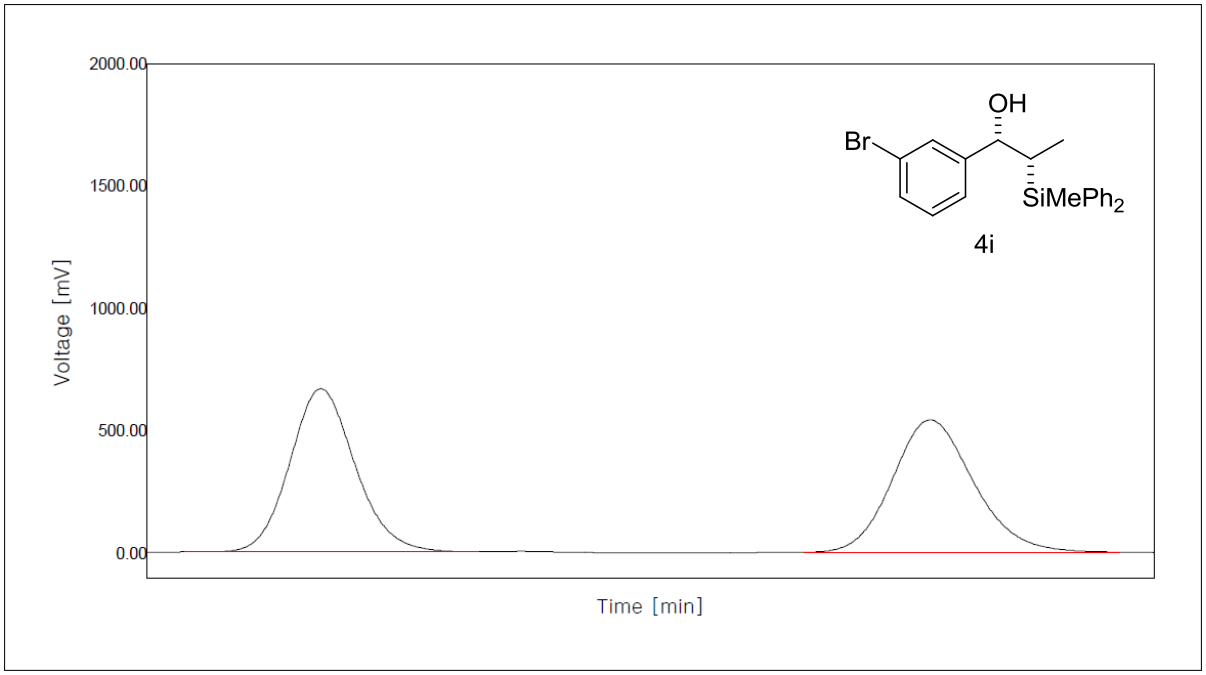
No.	Time(min)	Area ratio (%)
1	4.5350	98.64
2	6.7733	1.36



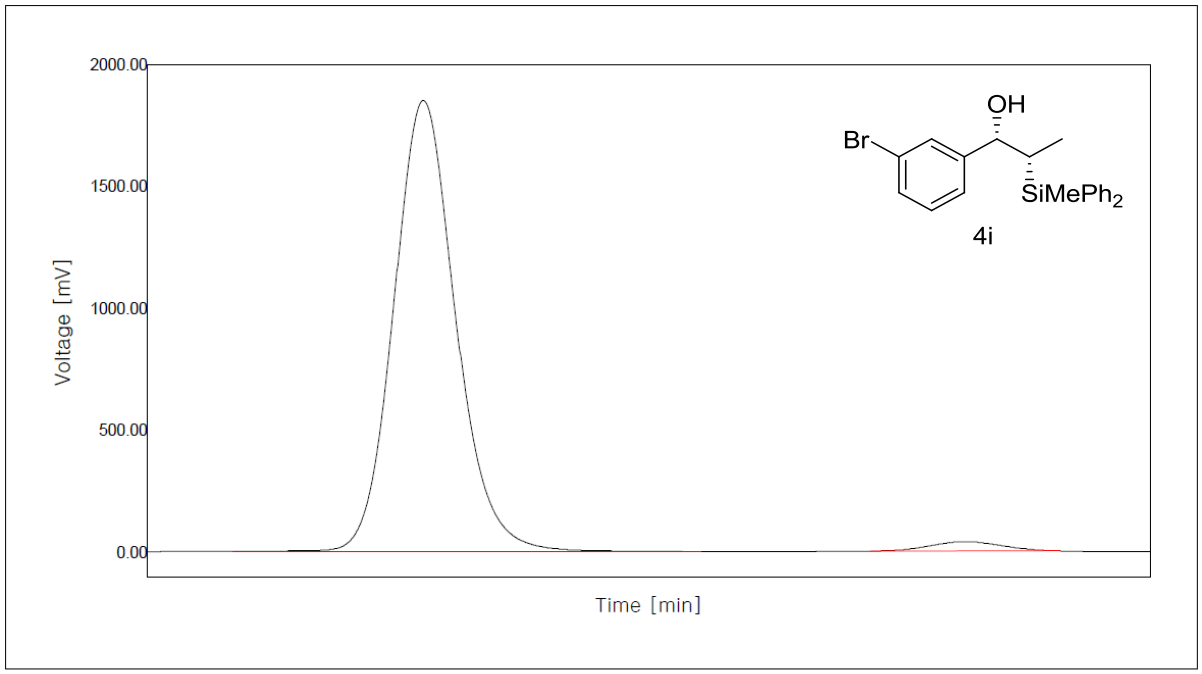
No.	Time(min)	Area ratio (%)
1	4.8450	50.06
2	5.8150	49.94



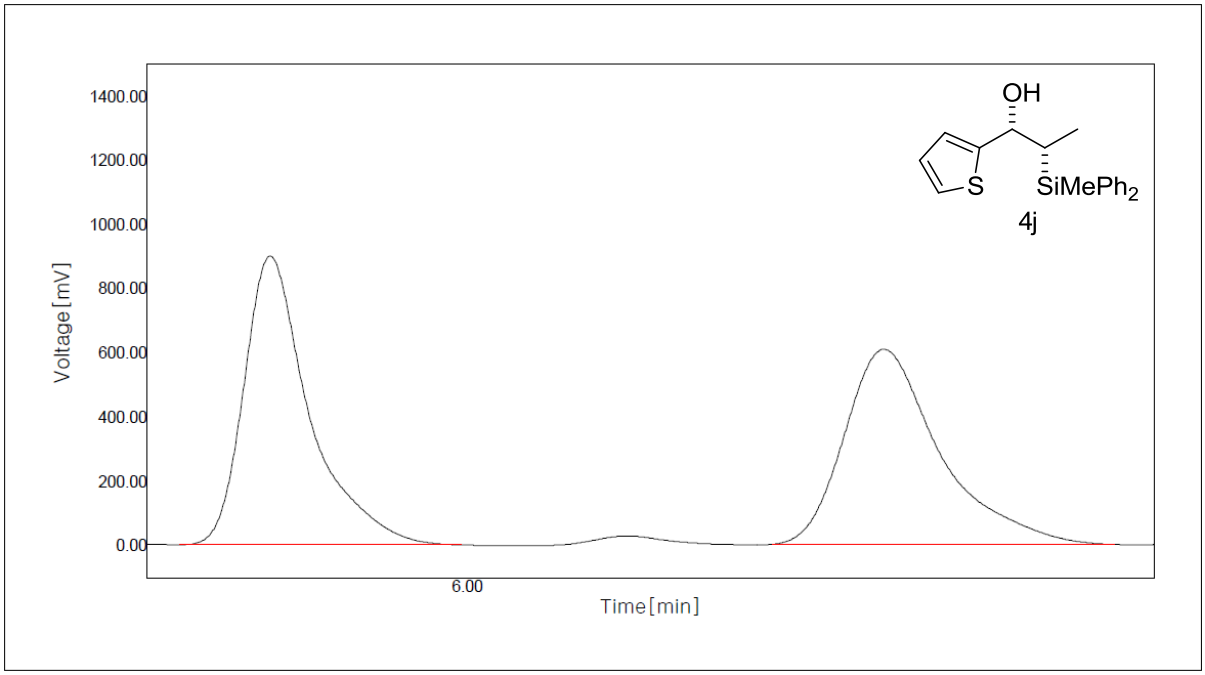
No.	Time(min)	Area ratio (%)
1	4.7600	98.70
2	5.8033	1.30



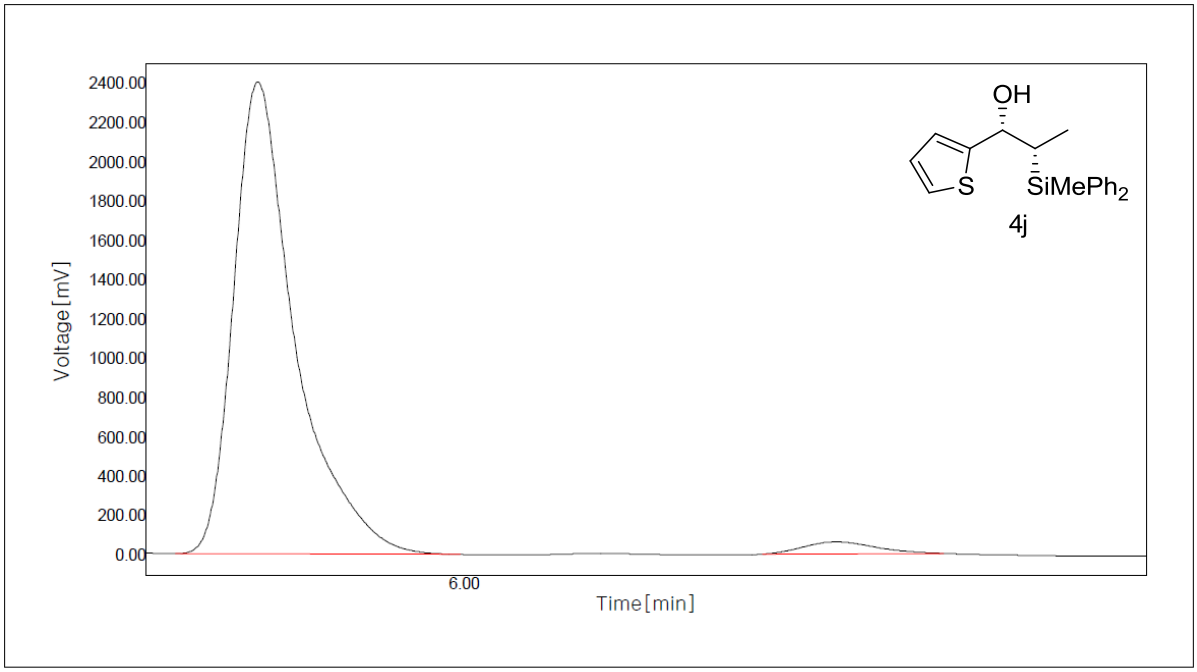
No.	Time(min)	Area ratio (%)
1	6.5983	49.83
2	7.9883	50.17



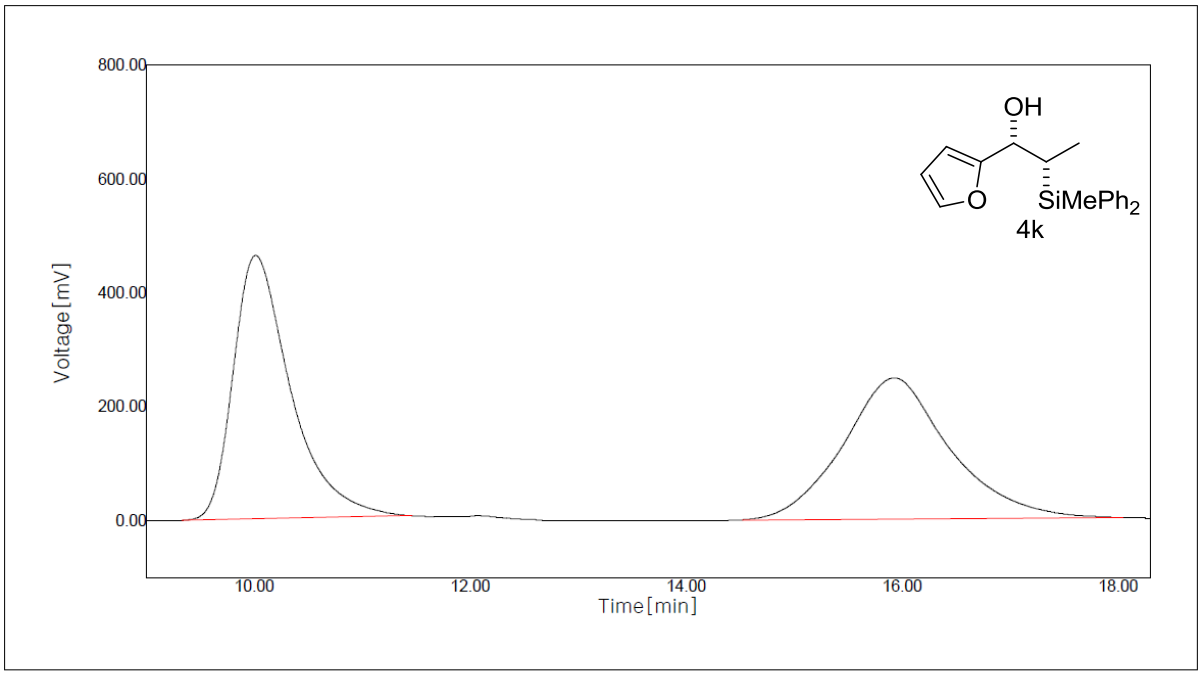
No.	Time(min)	Area ratio (%)
1	6.6883	97.65
2	8.0400	2.35



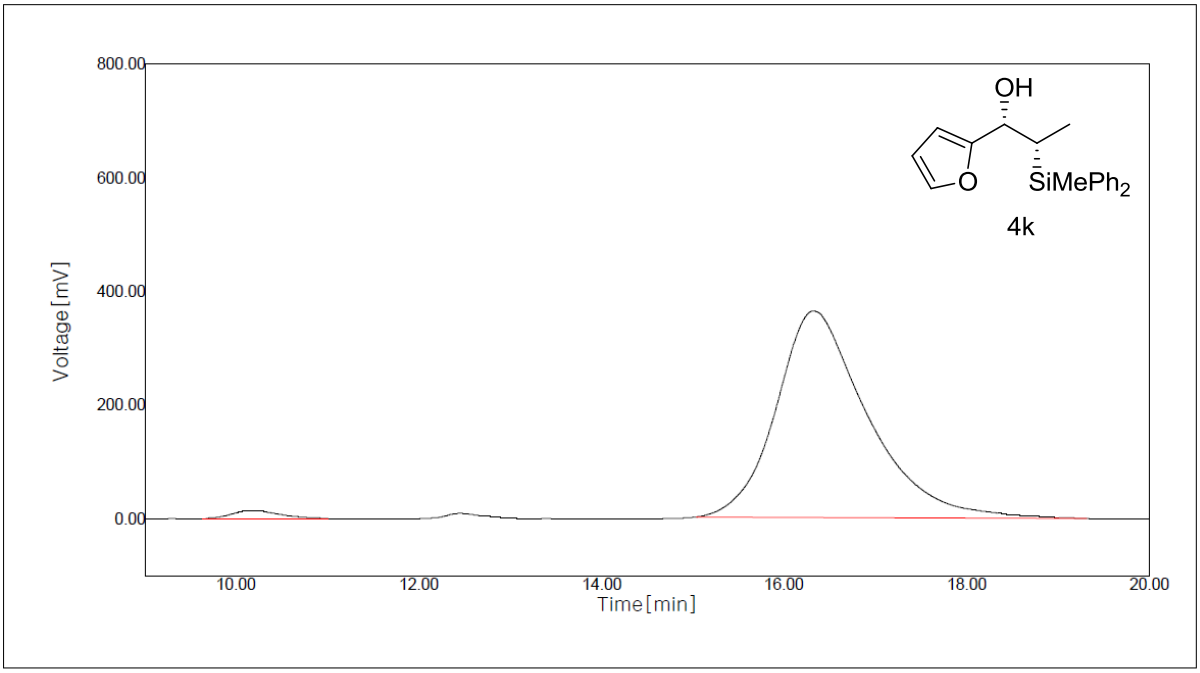
No.	Time(min)	Area ratio (%)
1	5.5700	50.39
2	6.9100	49.61



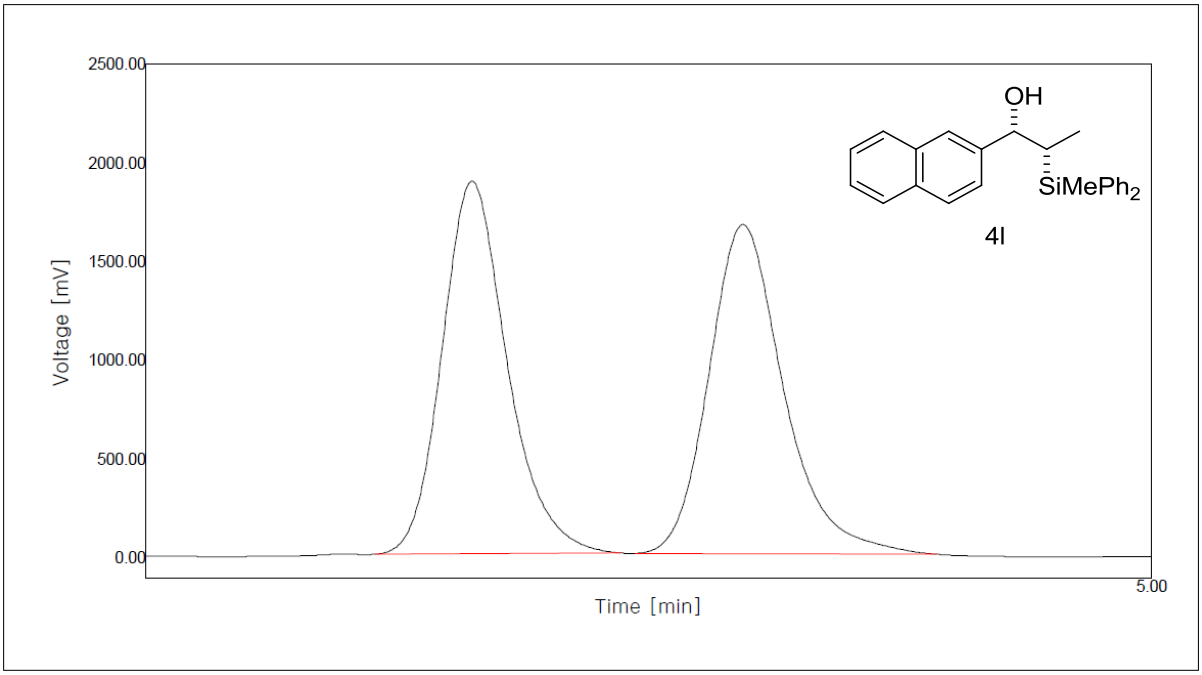
No.	Time(min)	Area ratio (%)
1	5.5467	97.08
2	6.8183	2.92



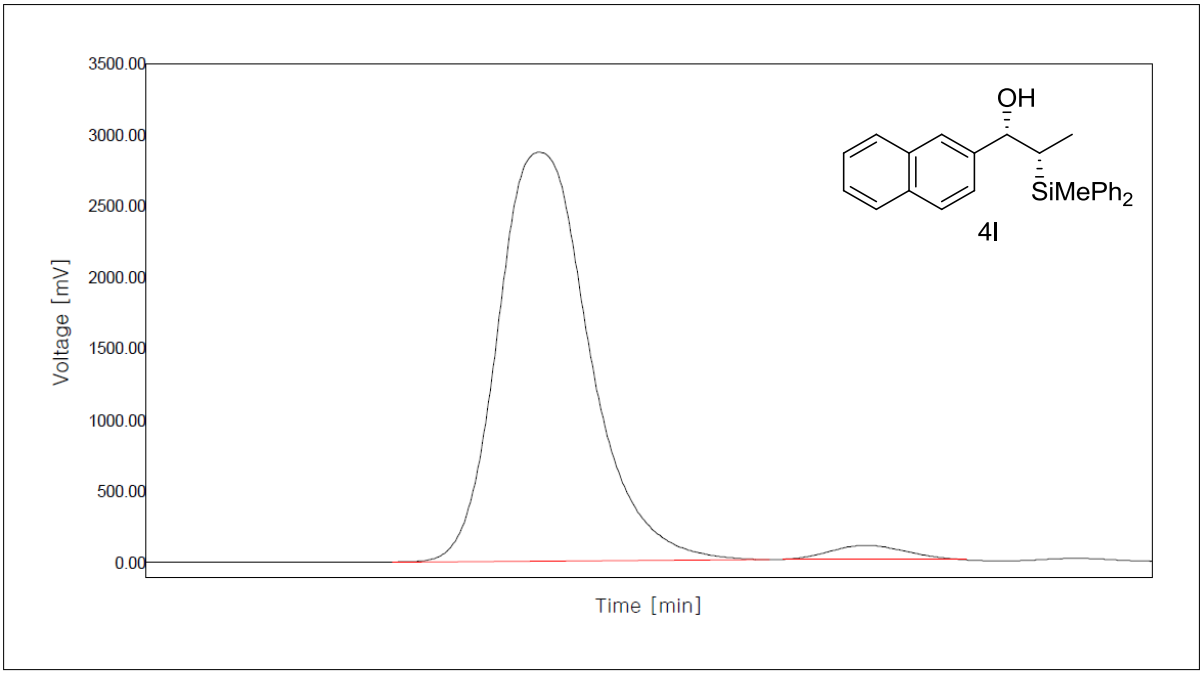
No.	Time(min)	Area ratio (%)
1	10.0167	50.12
2	15.9283	49.88



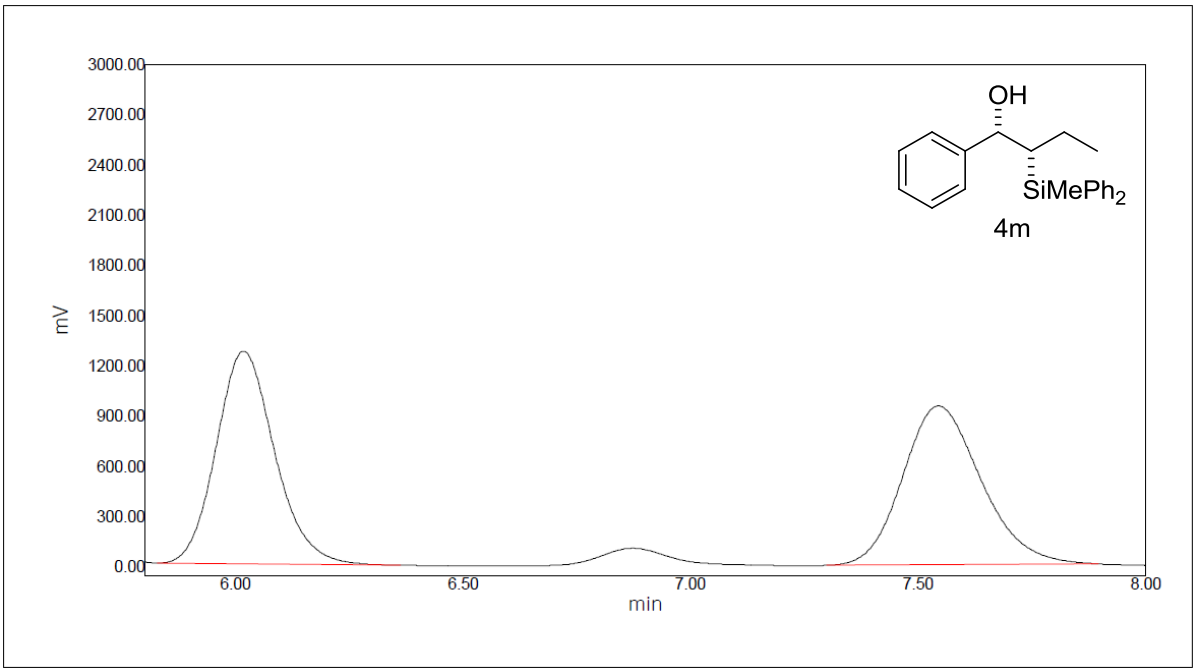
No.	Time(min)	Area ratio (%)
1	10.1733	1.86
2	16.3200	98.14



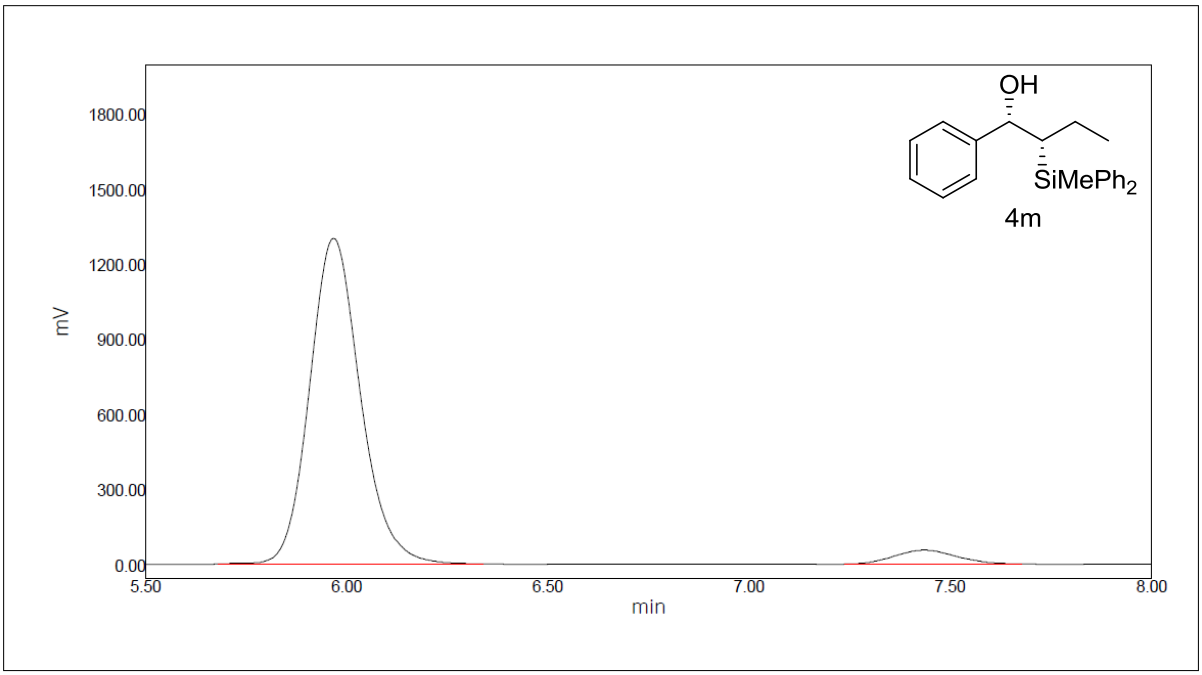
No.	Time(min)	Area ratio (%)
1	4.0550	49.62
2	4.4317	50.38



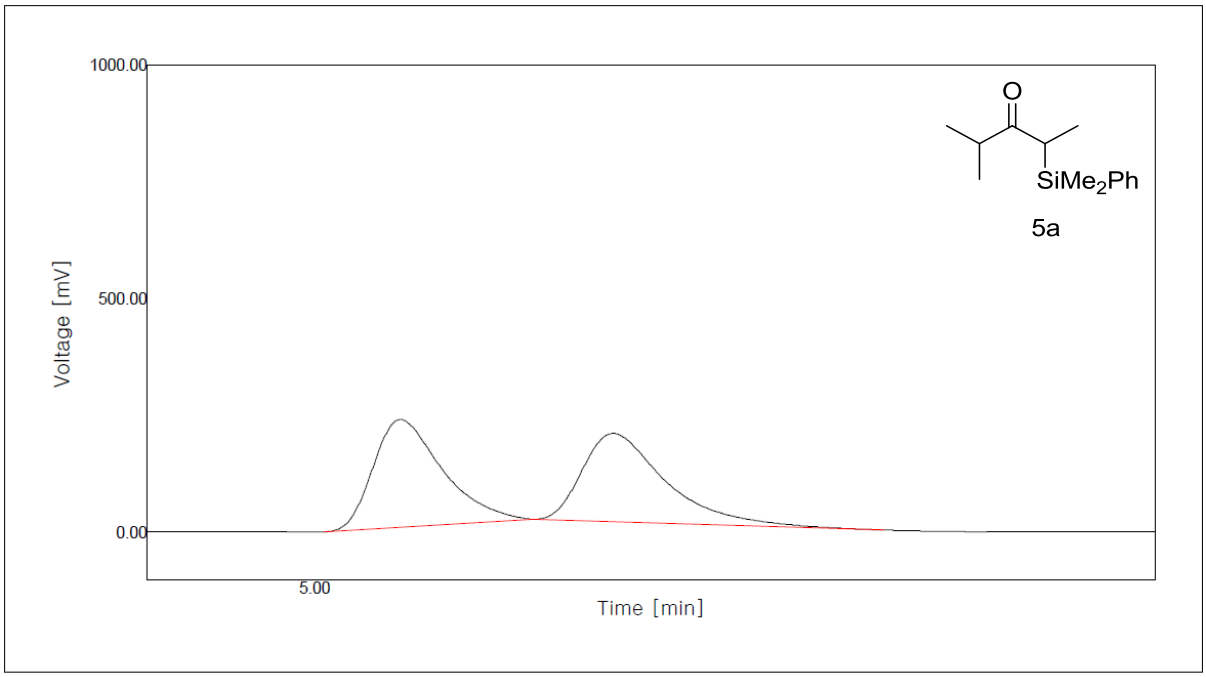
No.	Time(min)	Area ratio (%)
1	4.0300	97.19
2	4.3867	2.81



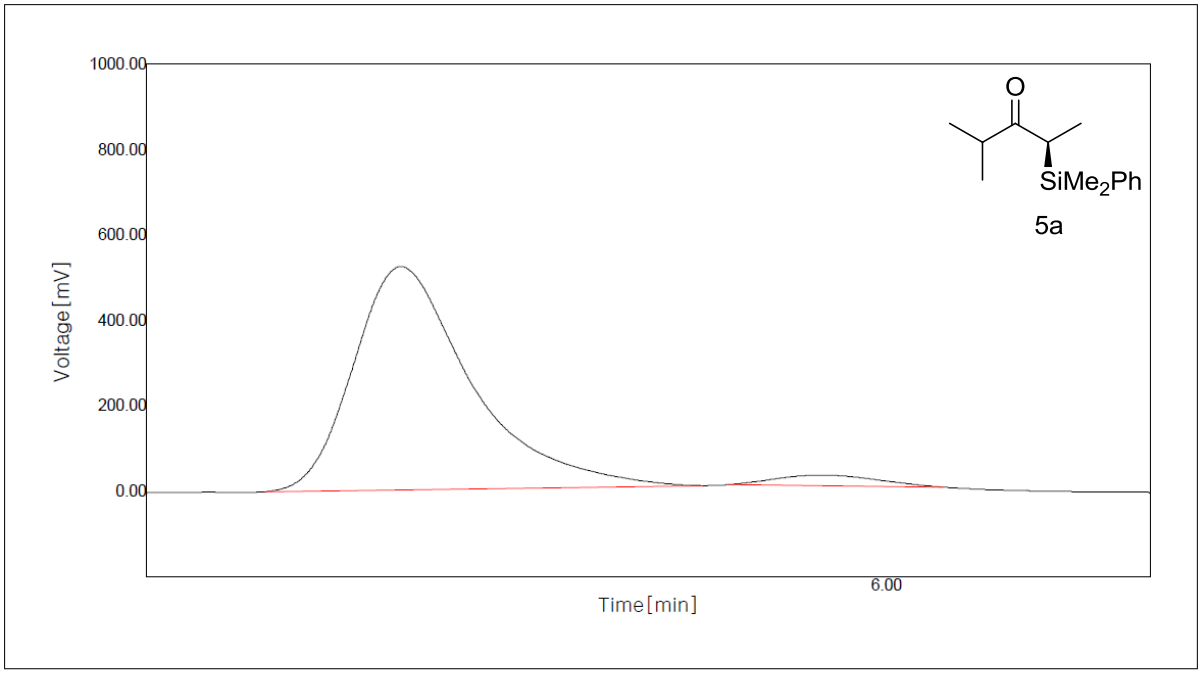
#	RT (min)	Area (mV*s)	Area (%)
1	6.0183	11364.5930	49.97
2	7.5450	11376.6914	50.03
		22741.2844	



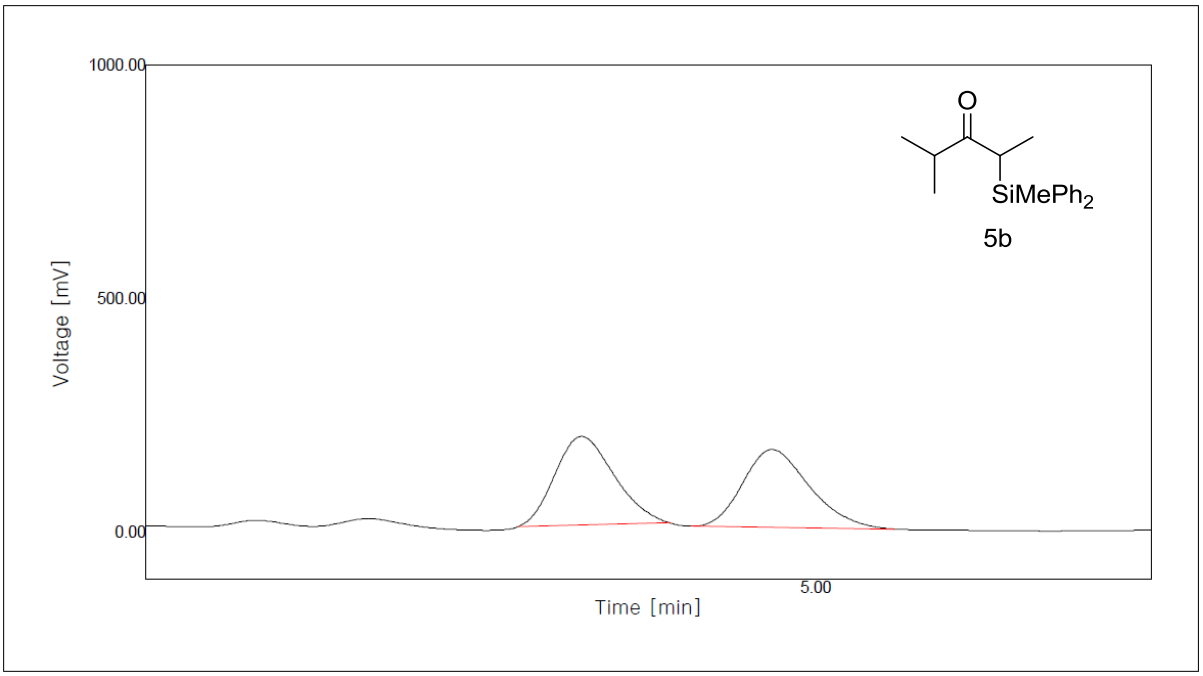
#	RT (min)	Area (mV*s)	Area (%)
1	5.9683	11398.0219	94.99
2	7.4350	601.0670	5.01
		11999.0891	



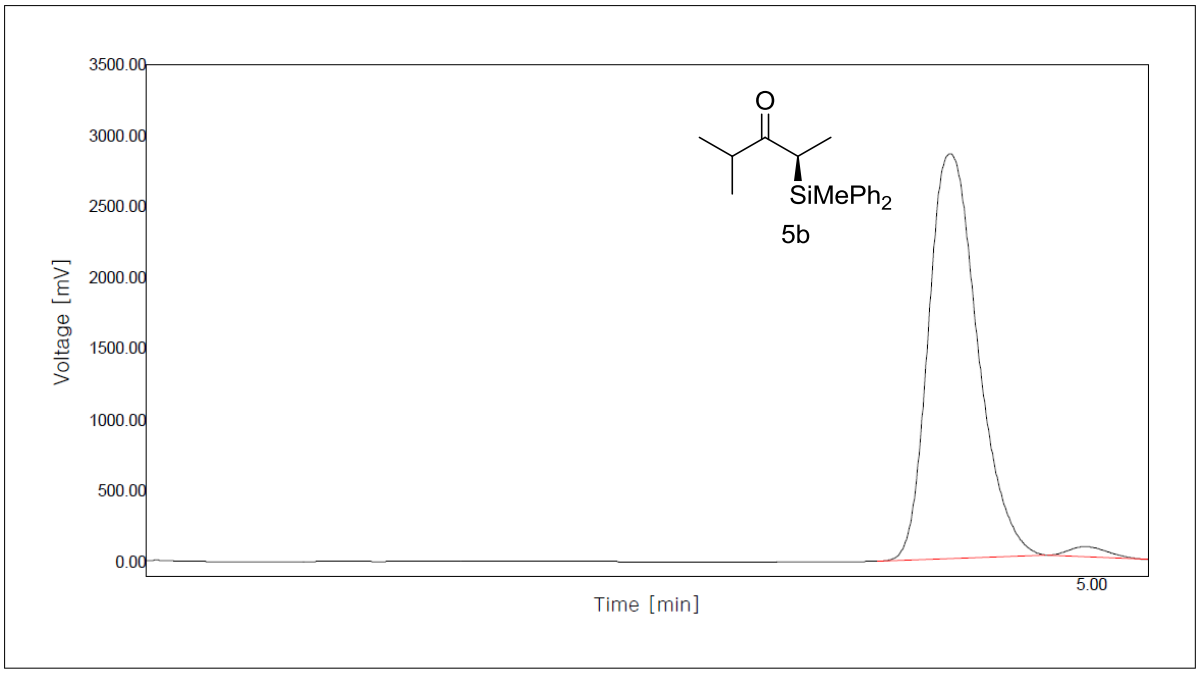
No.	Time(min)	Area ratio (%)
1	5.2050	50.33
2	5.7100	49.67



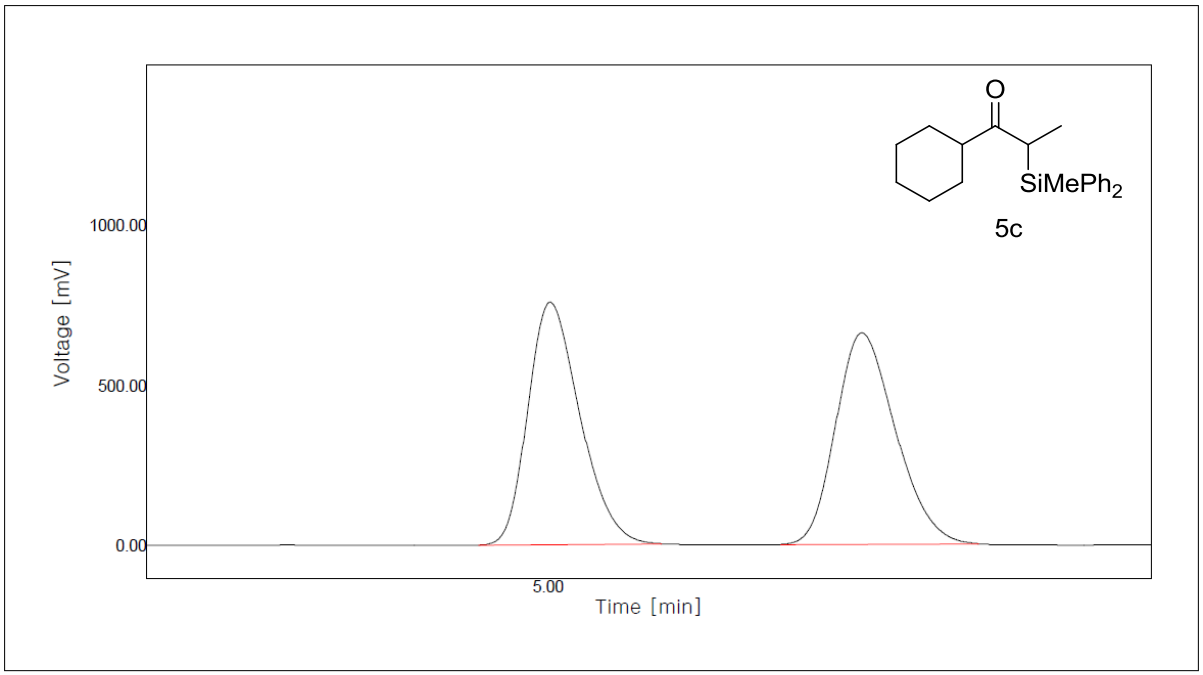
Peak #	Time (min)	Area (%)
1	5.0817	96.05
2	5.8783	3.95



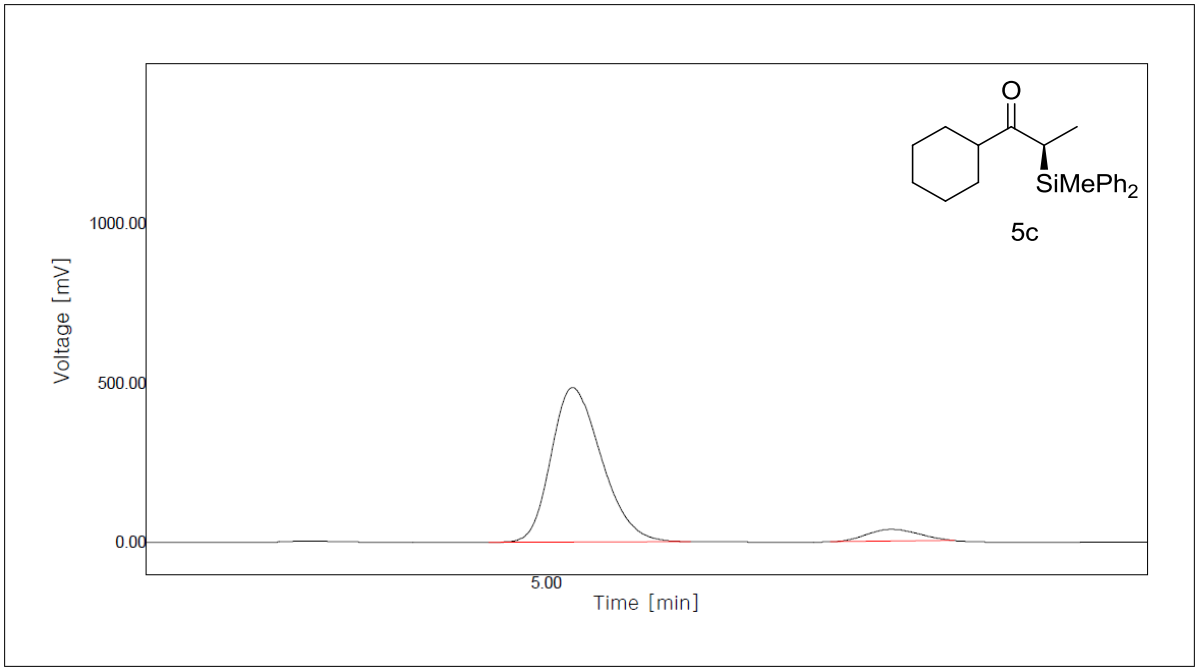
No.	Time(min)	Area ratio (%)
1	4.6500	50.31
2	4.9350	49.69



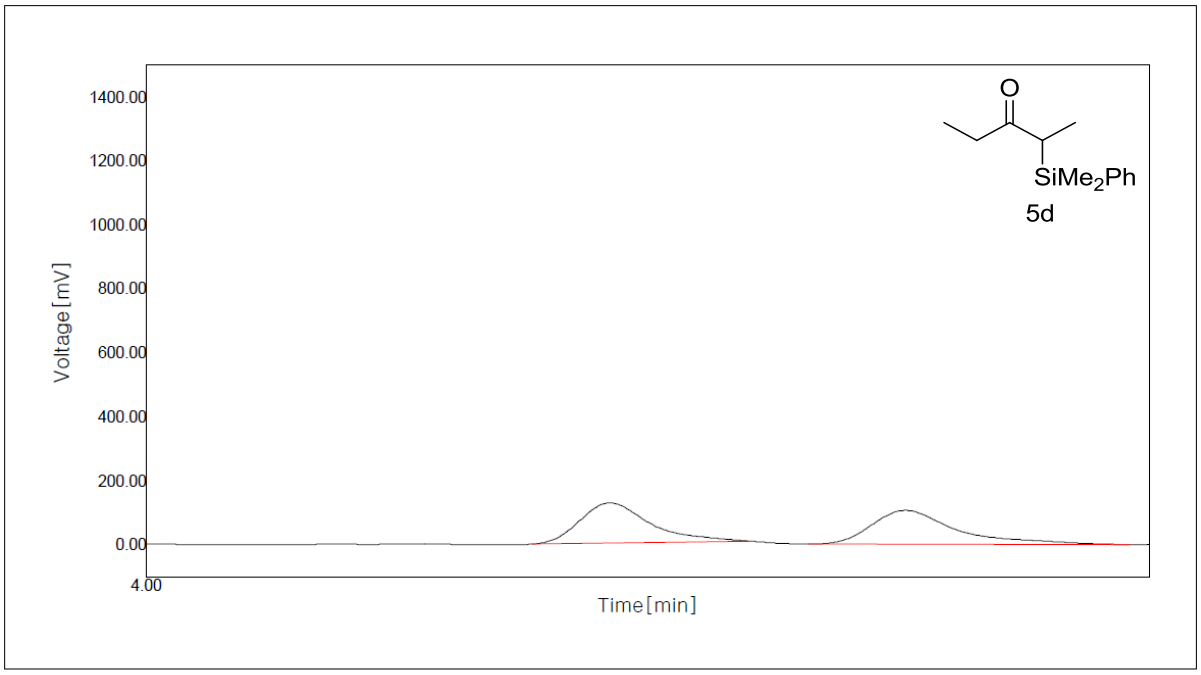
No.	Time(min)	Area ratio (%)
1	4.7000	98.04
2	4.9867	1.96



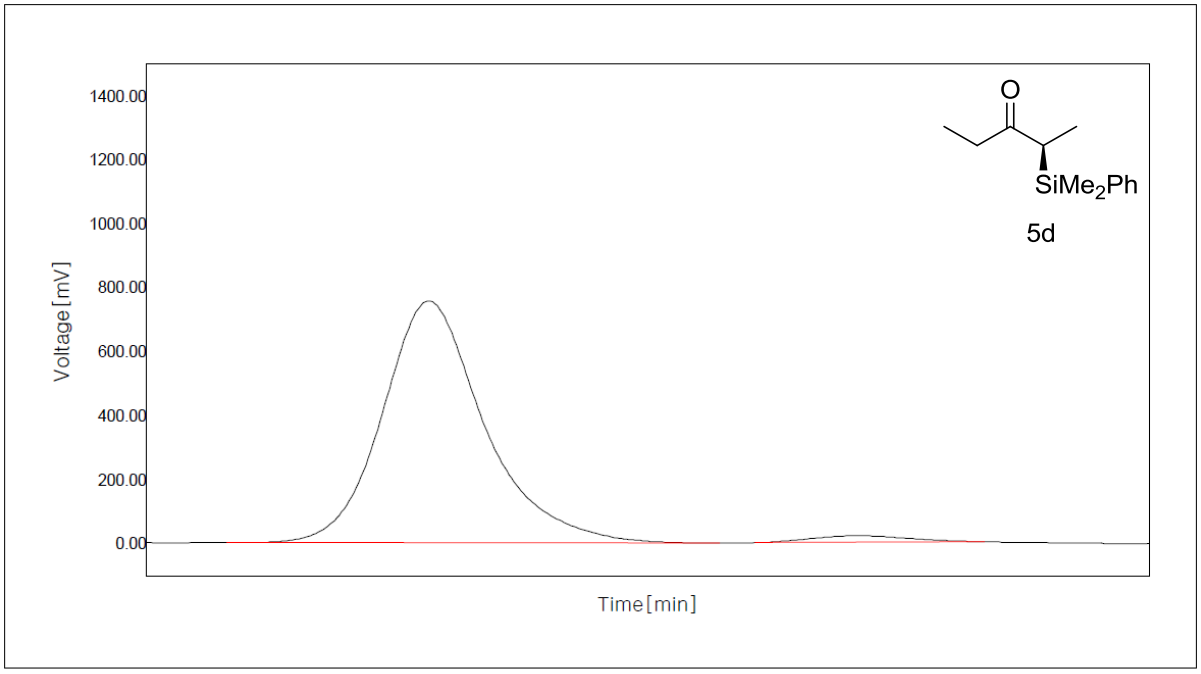
No.	Time(min)	Area ratio (%)
1	5.0050	49.96
2	5.7800	50.04



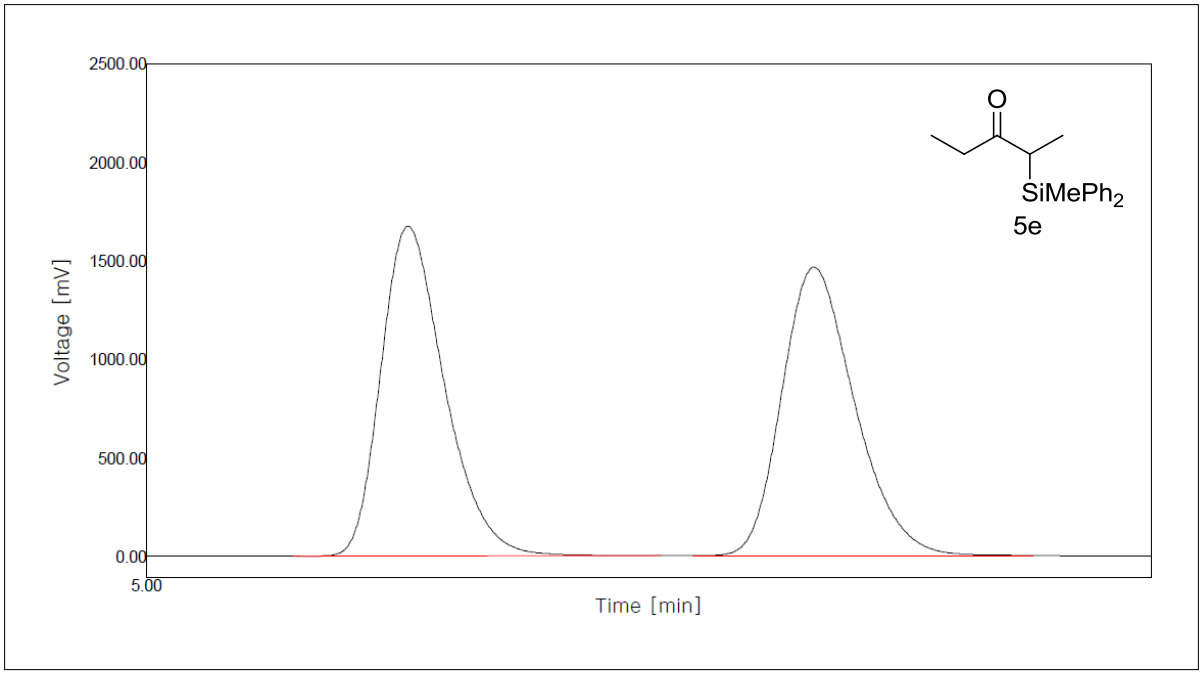
No.	Time(min)	Area ratio (%)
1	5.0667	92.68
2	5.8617	7.32



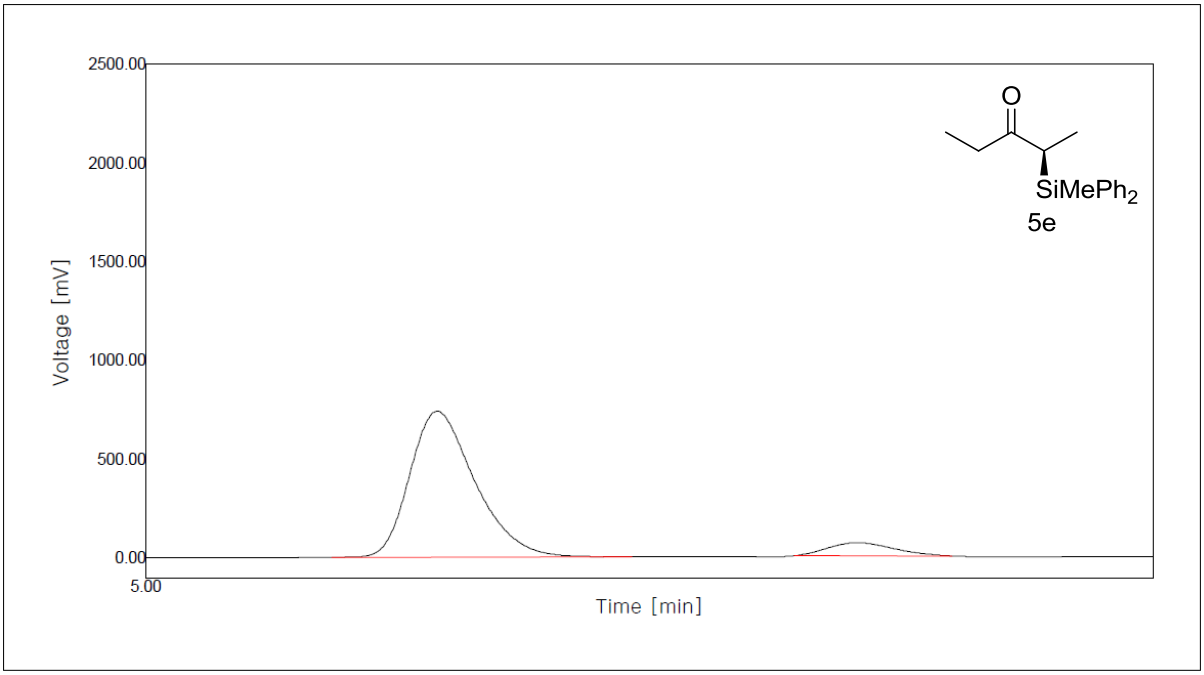
No.	Time(min)	Area ratio (%)
1	4.5550	49.54
2	4.9083	50.46



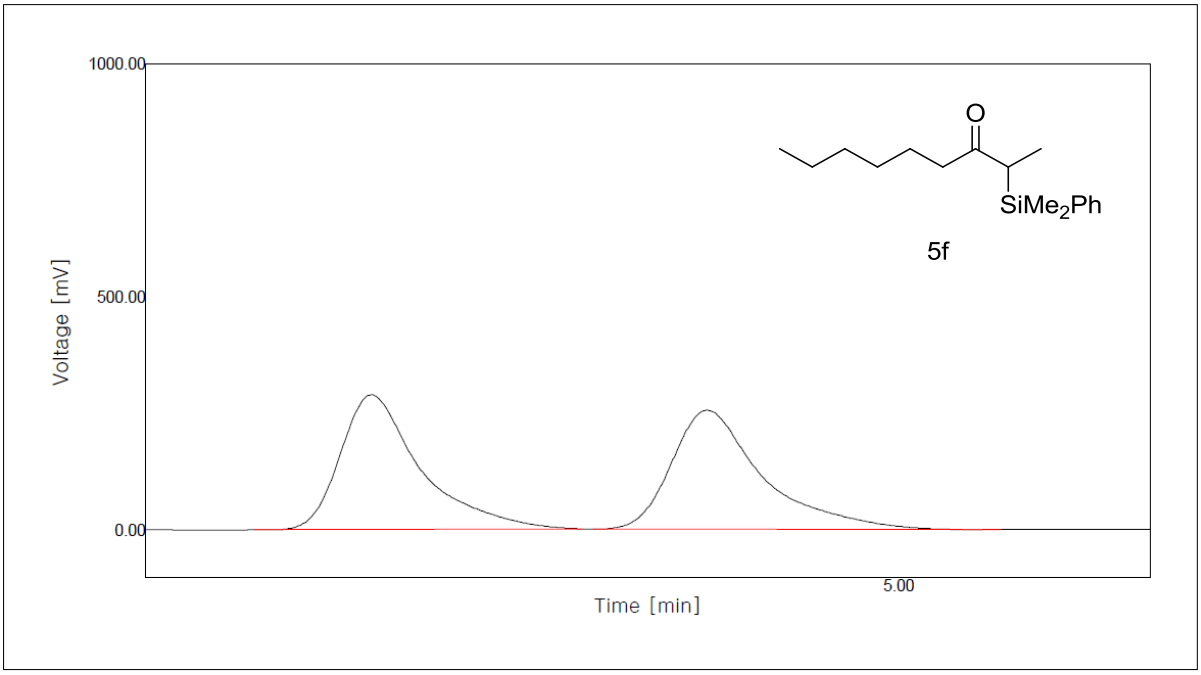
No.	Time(min)	Area ratio (%)
1	4.6967	97.50
2	4.9967	2.50



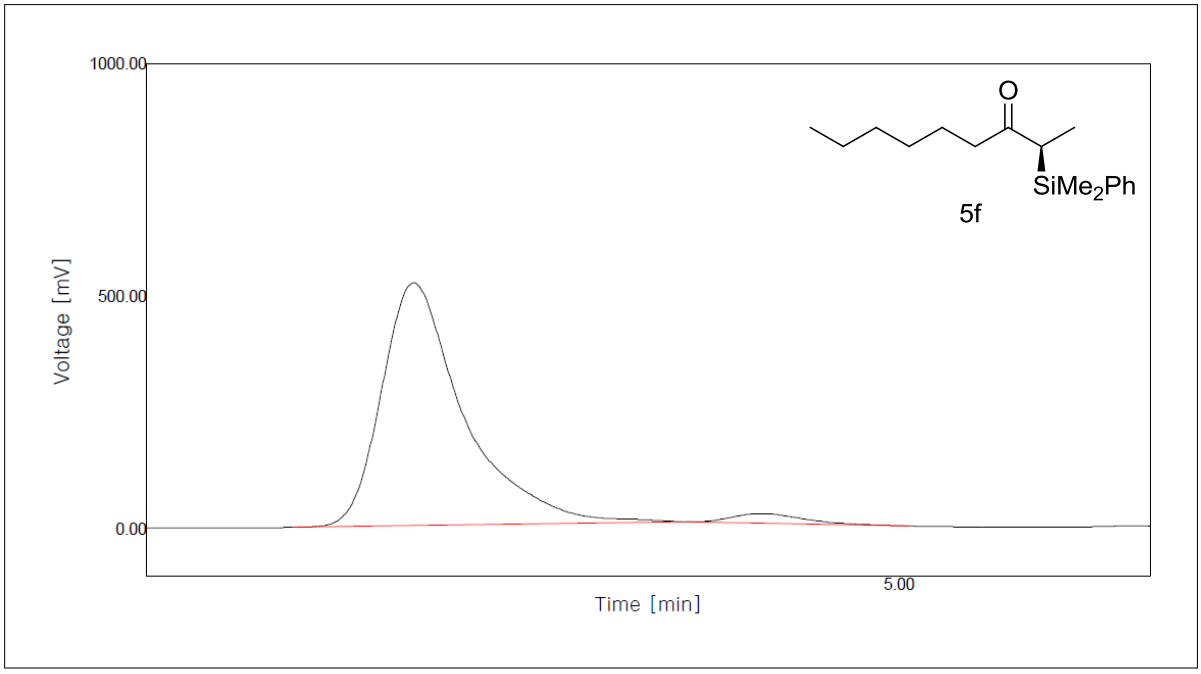
No.	Time(min)	Area ratio (%)
1	5.5733	50.00
2	6.4617	50.00



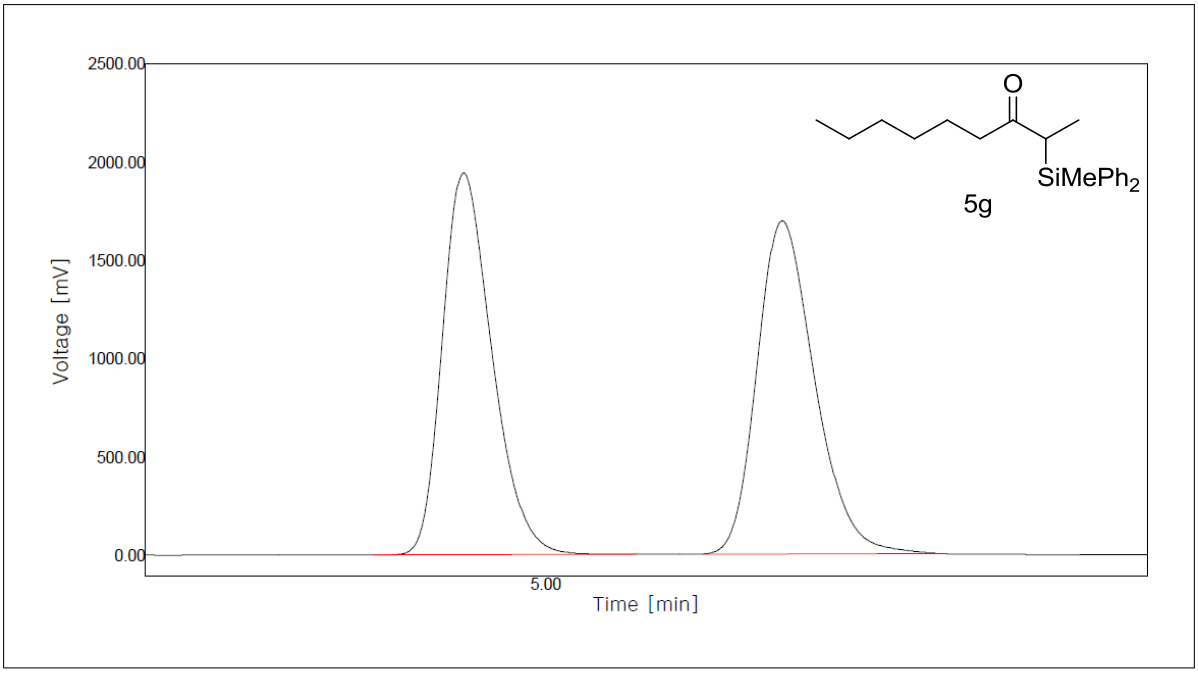
No.	Time(min)	Area ratio (%)
1	5.6367	91.67
2	6.5533	8.33



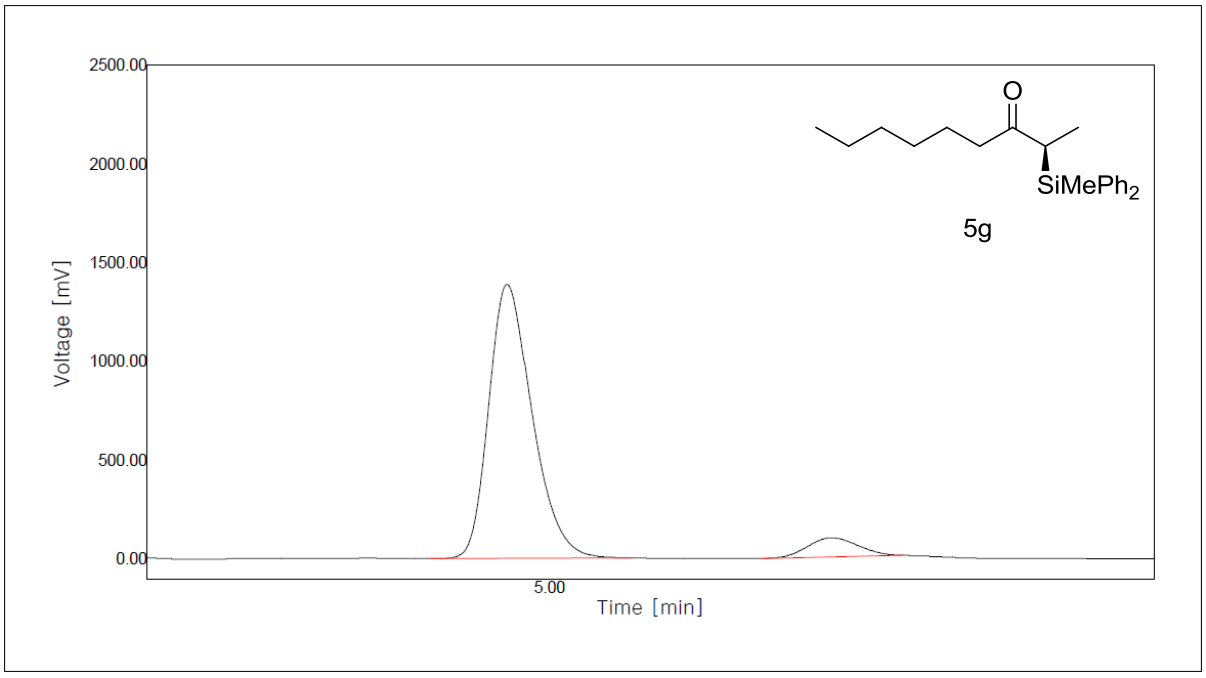
No.	Time(min)	Area ratio (%)
1	4.3700	49.95
2	4.7717	50.05



No.	Time(min)	Area ratio (%)
1	4.4200	96.63
2	4.8350	3.37



No.	Time(min)	Area ratio (%)
1	4.7950	49.62
2	5.5883	50.38



No.	Time(min)	Area ratio (%)
1	4.8950	92.52
2	5.7000	7.48

10. Reference

(1) Shioiri, T.; Aoyama, T.; Mori, S. *Org. Synth.* **1990**, *68*, 1.

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(4) Fleming, I.; Lawrence, N. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3309.

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