

## Supplementary information

### Bimetallic tandem catalysis-enabled enantioselective cycloisomerization/carbonyl-ene reaction for construction of 5-oxazoylmethyl $\alpha$ -silyl alcohol

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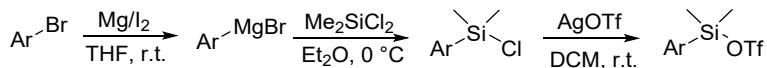
## 1. General information

<sup>1</sup>H NMR spectra were recorded at 400 MHz or 600 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiple), coupling constants (Hz), integration. <sup>13</sup>C NMR data were collected at 101 MHz with complete proton decoupling. <sup>19</sup>F NMR spectra were collected on commercial instruments (377 MHz or 565 MHz) with complete proton decoupling. Melting points (Mp) were determined using OptiMelt automated melting point system. Enantiomeric excesses (ee) were determined by chiral HPLC analysis by using the corresponding commercial chiralpak or chiralcel column as stated in the experimental procedures at 25 °C, and UPC<sup>2</sup> at 35 °C with UV detector at 254 nm or 210 nm. Optical rotations were reported as follows: [α]<sup>T</sup><sub>D</sub> (c: g/100 mL, in solvent). High resolution mass spectra (HRMS) analyses were recorded on a Thermo Scientific LTQ Orbitrap XL with positive ion mode and methanol were used to dissolve the sample. UV-vis absorbance spectra were recorded on SHIMADZU UV-2600 UV-Vis spectrophotometer in a 10.0 mm quartz cuvette. IR spectra were recorded on Pierkin Elmer 100 FT/IR spectrometer, and the wave numbers of the absorption peaks are given in cm<sup>-1</sup>. Solvents were dried and distilled prior to use according to the standard methods. Unless noted, other commercially available reagents were used without further purification. The chiral *N,N'*-dioxide ligands were synthesized by the same procedure in the literature<sup>1</sup>.

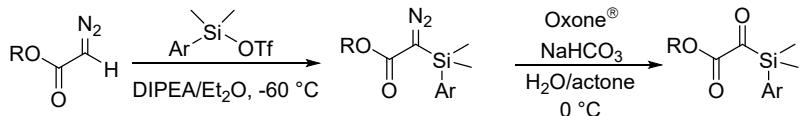
## 2. Synthesis of the substrates

### 2.1 General procedures for the preparation of silylglyoxylate A1-A12

Silylglyoxylate **A1**, **A3**, **A7-12** and were known compounds and synthesized according to the reported procedures<sup>2</sup>. Silylglyoxylate **A2**, **A4**, **A5**, **A6** were synthesized according to the following procedure:

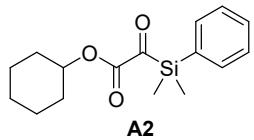


A solution of substituted bromobenzene (20 mmol, 1.0 equiv.) in THF (12 mL) was added slowly to a suspension of magnesium (20 mmol, 1.0 equiv.) in THF (8 ml) activated by I<sub>2</sub> (One grain) under N<sub>2</sub> atmosphere. The mixture was reacted at room temperature for 2 hours until the magnesium strips disappeared, and the reaction process would be violently exothermic. Then the mixture was cooled to 0 °C and added to a solution of Me<sub>2</sub>SiCl<sub>2</sub> in Et<sub>2</sub>O (5 mL), the mixture was stirred at r.t. for 24 h. The solvent was evaporated and added hexane, filtered, concentrated and purified by vacuum distillation. A solution of chlorodimethylarylilsilane<sup>3</sup> (12 mmol, 1.2 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added to a suspension of AgOTf (12 mmol, 1.2 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The resulting mixture was left stirring at room temperature in the dark for 24 h. The AgCl precipitate was removed by filtration and the solvent was removed in vacuo and used without purification<sup>4</sup>.



Under a nitrogen atmosphere, to a solution of diazoacetate<sup>5</sup> (10 mmol, 1.0 equiv.) and *i*Pr<sub>2</sub>NEt (14 mmol, 1.4 equiv.) was added Et<sub>2</sub>O (15 mL) under N<sub>2</sub>. This solution was cooled to -78 °C and ArMe<sub>2</sub>SiOTf (13 mmol, 1.3 equiv.) in DCM (10 mL) was added slowly via syringe over the course of 20 min. The resultant solution was stirred at -60 °C for 36 h and the ammonium salts were removed by filtration. The filtrate was concentrated in vacuo to afford the crude silyl diazoacetate. Oxone® (92 g, 150 mmol, 15.0 equiv.) was added in portions to a stirred solution of NaHCO<sub>3</sub> (50.4 g, 600 mmol, 60.0 equiv.) in H<sub>2</sub>O/acetone (300 ml, 1.5:1) at 0 °C. After 20 min, a solution of the crude silyl diazoacetate in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added slowly over 30 min via syringe. Once addition was complete, the reaction was warmed to room temperature and stirring was continued for an additional 15 min (bright yellow solution). The organic phase was decanted into a separatory funnel and was washed with H<sub>2</sub>O and dried (Na<sub>2</sub>SO<sub>4</sub>). Concentration of the organic phase by rotary evaporation afforded the crude silylglyoxylate which was purified by flash chromatography using the specified solvent system (PE/Et<sub>2</sub>O = 40 : 1).

#### cyclohexyl 2-(dimethyl(phenyl)silyl)-2-oxoacetate (A2)



Bright yellow liquid; 14% yield.

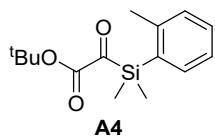
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.55 (m, 2H), 7.44 – 7.36 (m, 3H), 4.91 – 4.71 (m, 1H), 1.85 – 1.77 (m, 2H), 1.74 – 1.61 (m, 3H), 1.57 – 1.49 (m, 1H), 1.45 – 1.30 (m, 4H), 0.59 (s, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 161.4, 134.5, 133.0, 130.4, 128.3, 75.1, 31.5, 25.3, 23.9, -4.4.

**HRMS** (ESI+) *m/z* calcd for C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>Si [M+H]<sup>+</sup>: 291.1411, found: 291.1419.

**IR** (neat): 2938, 1711, 1252, 1116, 1037, 1009, 833, 789, 699 cm<sup>-1</sup>.

#### Tert-butyl 2-(2-dimethylphenyl) dimethylsilyl)-2-oxoacetate (A4)



Bright yellow liquid; 17% yield.

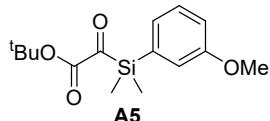
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.46 (m, 1H), 7.37 – 7.29 (m, 1H), 7.25 – 7.15 (m, 2H), 2.30 (s, 3H), 1.32 (s, 9H), 0.58 (s, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 161.5, 143.9, 135.1, 132.6, 130.5, 130.1, 125.5, 83.7, 27.8, 23.1, -3.4.

**HRMS** (ESI+)  $m/z$  calcd for  $C_{15}H_{22}O_3Si$  [M+H]<sup>+</sup>: 279.1411, found: 279.1410.

**IR** (neat): 2963, 1711, 1371, 1257, 1024, 792 cm<sup>-1</sup>.

**Tert-butyl 2-( (3-methoxyphenyl) dimethylsilyl)-2-oxoacetate (A5)**



Bright yellow liquid; 20% yield.

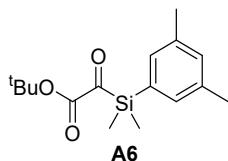
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.28 (m, 1H), 7.16 – 7.11 (m, 1H), 7.10 – 7.06 (m, 1H), 6.98 – 6.91 (m, 1H), 3.8 (s, 3H), 1.4 (s, 9H), 0.6 (s, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 161.6, 159.3, 134.7, 129.5, 126.7, 119.8, 115.7, 83.8, 55.3, 28.0, -4.4.

**HRMS** (ESI+)  $m/z$  calcd for  $C_{15}H_{22}O_4Si$  [M+H]<sup>+</sup>: 295.1360, found: 295.1356.

**IR** (neat): 2978, 1709, 1369, 1283, 1245, 1041, 782 cm<sup>-1</sup>.

**Tert-butyl 2-( (3,5-dimethylphenyl) dimethylsilyl)-2-oxoacetate (A6)**



Bright yellow liquid; 23% yield.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.19 – 7.12 (m, 2H), 7.08 – 7.02 (m, 1H), 2.33 – 2.29 (m, 6H), 1.43 (s, 9H), 0.56 (s, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 161.8, 137.6, 132.8, 132.1, 132.1, 83.7, 28.0, 21.5, -4.3.

**HRMS** (ESI+)  $m/z$  calcd for  $C_{16}H_{24}O_3Si$  [M+H]<sup>+</sup>: 293.1567, found: 293.1569.

**IR** (neat): 2977, 1739, 1369, 1247, 1038, 787 cm<sup>-1</sup>.

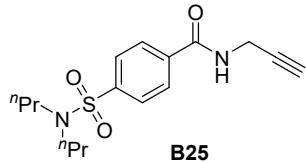
## 2.2 General procedures for the preparation of propargyl amides

Propargyl amides **B1-B10**<sup>6a-c</sup>, **B11**<sup>6g</sup>, **B12-B14**<sup>6a-c</sup>, **B15-B22**<sup>6f</sup>, **B23**<sup>6e</sup>, **B24**<sup>6d</sup>, **B28**<sup>6h</sup>, **B29**<sup>6c</sup>, **B30**<sup>6d</sup>, **B31**<sup>6d</sup>, **B32**<sup>6h</sup> were prepared according to the reported literature.

**General procedure for propargyl amide synthesis via EDC coupling:** To a solution of the appropriate carboxylic acid (5.0 mmol, 1.0 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added EDC hydrochloride (1.15 g, 6.0 mmol, 1.2 equiv.) and stirred for 2 min, then HOBr (0.74 g, 5.5 mmol, 1.1 equiv.) was added and stirred for a further 2 min. Propargylamine (0.35 mL, 5.5 mmol, 1.1 equiv.) was then added and the mixture stirred at r.t. for 24 h (monitored by TLC). The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL), washed with saturated aqueous Na<sub>2</sub>CO<sub>3</sub> solution (20 mL), 1 N aqueous HCl solution (20 mL), saturated NaCl solution in sequence and dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced

pressure after filtration. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give pure product.

**4-(*N,N*-dipropylsulfamoyl)-*N*-(prop-2-yn-1-yl) benzamide (B25)**



51% yield, white solid; mp: 90–95 °C.

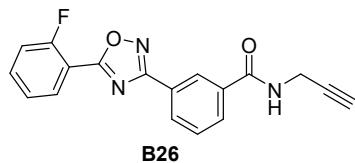
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.84 (m, 2H), 7.78 – 7.67 (m, 2H), 7.51 (s, 1H), 4.15 (dd, *J* = 5.2, 2.4 Hz, 2H), 3.08 – 2.91 (m, 4H), 2.20 (t, *J* = 2.4 Hz, 1H), 1.46 (m, 4H), 0.78 (t, *J* = 7.2 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 166.1, 142.7, 137.3, 128.1, 127.1, 79.3, 71.6, 49.9, 29.7, 21.9, 11.1.

**HRMS** (ESI+) *m/z* calcd for C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup>: 323.1424, found: 323.1423.

**IR** (neat): 3289, 2967, 2876, 1649, 1533, 1486, 1465, 1334, 1146, 1089, 990, 856, 797, 740, 603 cm<sup>-1</sup>.

**3-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl)-*N*-(prop-2-yn-1-yl)benzamide (B26)**



67% yield, white solid; mp: 169–173 °C.

**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.26 (t, *J* = 5.6 Hz, 1H), 8.59 (m, 1H), 8.32 – 8.18 (m, 2H), 8.16 – 8.07 (m, 1H), 7.86 – 7.77 (m, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.62 – 7.44 (m, 2H), 4.22 – 4.11 (m, 2H), 3.42 (s, 1H), 3.21 (s, 1H).

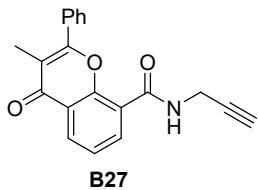
**<sup>13</sup>C NMR** (101 MHz, DMSO-*d*<sub>6</sub>) δ 173.1 (d, *J* = 4.3 Hz), 168.0, 165.6, 161.7, 159.1, 136.2 (d, *J* = 8.9 Hz), 135.2, 131.3, 130.8, 130.3, 130.0, 126.6 (d, *J* = 8.8 Hz), 125.9 (d, *J* = 3.4 Hz), 117.7 (d, *J* = 20.6 Hz), 112.1 (d, *J* = 11.4 Hz), 81.6, 73.5, 29.1.

**<sup>19</sup>F NMR** (377 MHz, DMSO-*d*<sub>6</sub>) δ -109.31.

**HRMS** (ESI+) *m/z* calcd for C<sub>18</sub>H<sub>12</sub>FN<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 322.0986, found: 322.0982.

**IR** (neat): 3300, 1647, 1621, 1591, 1536, 1517, 1468, 1369, 1348, 1294, 1268, 1227, 1165, 1110, 920, 824, 749, 722, 682 cm<sup>-1</sup>.

**3-methyl-4-oxo-2-phenyl-*N*-(prop-2-yn-1-yl)-4*H*-chromene-8-carboxamide (B27)**



35% yield, white solid; mp: 200–204 °C.

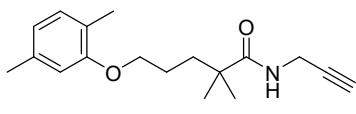
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.45 (dd, J = 7.6, 2.0 Hz, 1H), 8.38 (dd, J = 7.6, 1.6 Hz, 1H), 7.75 – 7.64 (m, 2H), 7.62 – 7.50 (m, 4H), 7.47 (t, J = 8.0 Hz, 1H), 4.25 (dd, J = 4.8, 2.4 Hz, 2H), 2.21 (t, J = 2.4 Hz, 1H), 2.19 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 178.0, 163.1, 160.1, 153.3, 136.4, 132.6, 130.7, 130.1, 129.0, 128.9, 124.8, 122.7, 122.1, 118.1, 79.0, 72.1, 29.9, 11.7.

**HRMS** (ESI+) *m/z* calcd for C<sub>20</sub>H<sub>15</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 318.1125, found: 318.1119.

**IR** (neat): 3239, 2360, 1626, 1540, 1478, 1439, 1389, 1301, 1234, 1132, 1076, 761, 697 cm<sup>-1</sup>.

### 5-(2,5-dimethylphenoxy)-2,2-dimethyl-N-(prop-2-yn-1-yl)pentanamide (B33)



64% yield, white solid; mp: 55–60 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.01 (d, J = 7.6 Hz, 1H), 6.69 – 6.64 (m, 1H), 6.63 – 6.59 (m, 1H), 5.91 (s, 1H), 4.05 (dd, J = 5.2, 2.4 Hz, 2H), 3.92 (t, J = 5.6 Hz, 2H), 2.31 (s, 3H), 2.23 (t, J = 2.8 Hz, 1H), 2.19 (s, 3H), 1.80 – 1.67 (m, 4H), 1.24 (s, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 177.2, 156.9, 136.5, 130.3, 123.5, 120.8, 112.1, 71.6, 67.9, 41.9, 37.5, 29.4, 25.4, 25.1, 21.4, 15.9.

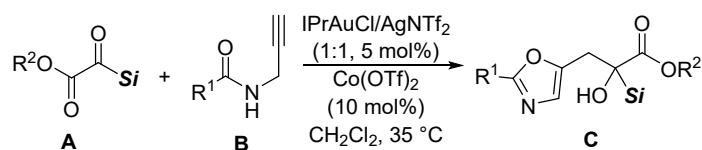
**HRMS** (ESI+) *m/z* calcd for C<sub>18</sub>H<sub>25</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 288.1958, found: 288.1956.

**IR** (neat): 3307, 2951, 1643, 1583, 1509, 1475, 1415, 1390, 1262, 1156, 1129, 1040, 804, 750, 651, 448 cm<sup>-1</sup>.

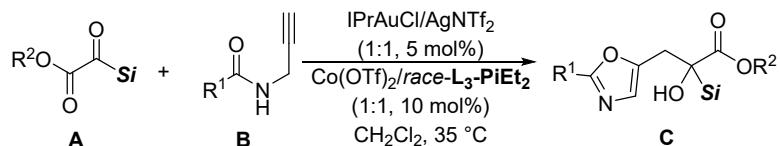
## 3. General procedures for the catalytic asymmetric reaction

### 3.1 General procedures for the preparation of racemic products

Representative experimental procedure for the reaction of silylglyoxylate **A** and propargyl amides **B**.



**Procedure A:** IPrAuCl (3.1 mg, 5 mol%), AgNTf<sub>2</sub> (1.9 mg, 5 mol%), Co(OTf)<sub>2</sub> (3.5 mg, 10 mol%), silylglyoxylate **A** (0.10 mmol) and propargyl amides **B** (0.10 mmol) are successively added into a dry catalytic tube. CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added and the mixture was stirred at 35 °C until the solution becomes to be colorless. After the silylglyoxylate **A** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product **C**.

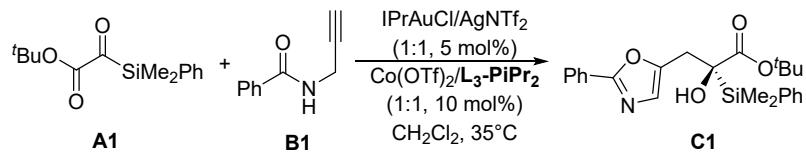


**Procedure B:** IPrAuCl (3.1 mg, 5 mol%), AgNTf<sub>2</sub> (1.9 mg, 5 mol%), Co(OTf)<sub>2</sub> (3.5 mg, 10 mol%), *race*-L<sub>3</sub>-PiEt<sub>2</sub> (5.9 mg, 10 mol%), silylglyoxylate **A** (0.10 mmol) and propargyl amides **B** (0.10 mmol) are successively added into a dry catalytic tube. CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added and the mixture was stirred at 35 °C until the solution becomes to be colorless. After the silylglyoxylate **A** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product **C**.

The racemic products **C25** were prepared with procedure **B**.

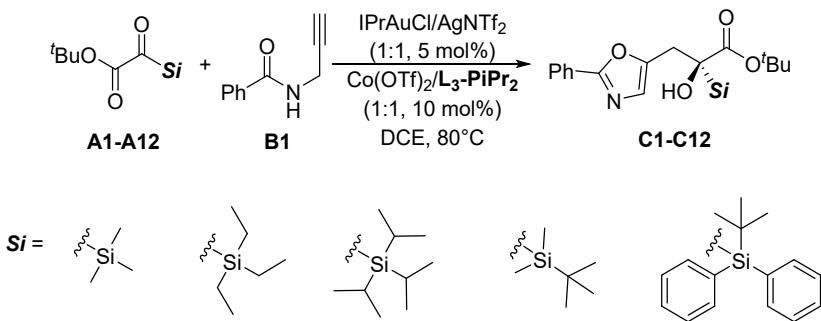
### 3.2 General procedures for the catalytic asymmetric reaction

Representative experimental procedure for the reaction of silylglyoxylate **A1** and propargyl amides **B1**.

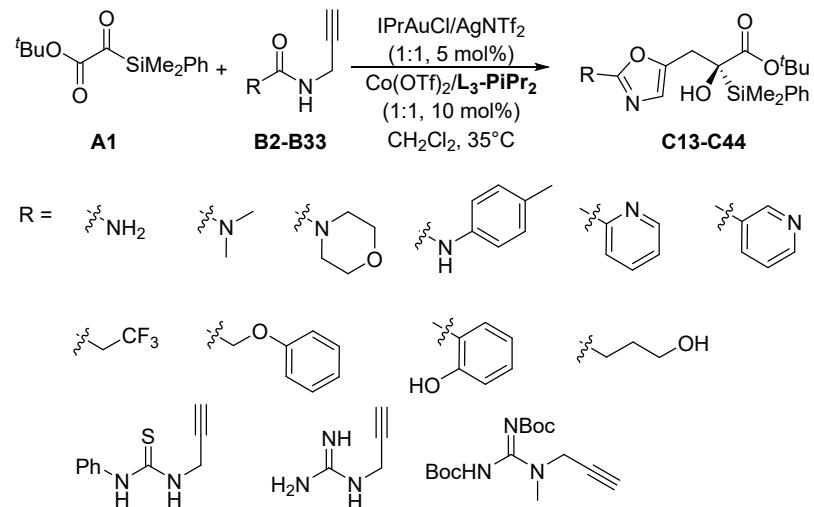


**Procedure for the synthesis of the adduct **C**:** Under an atmosphere of nitrogen, IPrAuCl (3.1 mg, 5 mol%), AgNTf<sub>2</sub> (1.9 mg, 5 mol%), Co(OTf)<sub>2</sub> (3.5 mg, 10 mol%), L<sub>3</sub>-PiPr<sub>2</sub> (6.5 mg, 10 mol%), silylglyoxylate **A1** (0.10 mmol) and propargyl amides **B1** (0.12 mmol) were stirred in DCM (1 mL) at 35 °C. The mixture was stirred until **A1** disappeared (bright orange faded, or TLC monitor). the residue was purified by column chromatography (petroleum ether:ethyl acetate = 8.5 : 1) on silica gel to afford the product **C1**.

## 4. Scope limitation



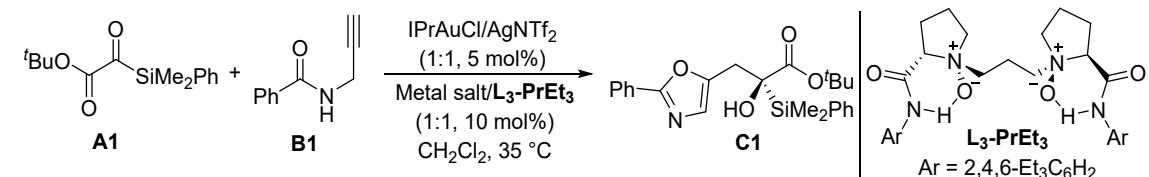
**Figure S1.** Unsuccessful substrate scope of silyl glyoxylate.



**Figure S2.** Unsuccessful substrate scope of *N*-propargylamides.

## 5. Optimization of the reaction conditions

**Table S1.** The screening of metal salts



Entry <sup>a</sup>	Metal salts	C1 yield (%) <sup>b</sup>	C1 ee (%) <sup>c</sup>
1	Mg(OTf) <sub>2</sub>	50	66
2	Sc(OTf) <sub>3</sub>	49	32
3	Y(OTf) <sub>3</sub>	65	45
4	La(OTf) <sub>3</sub>	64	47

5	Al(OTf) <sub>3</sub>	26	2
6	In(OTf) <sub>3</sub>	18	10
7	Fe(OTf) <sub>2</sub>	25	39
8	Zn(OTf) <sub>2</sub>	65	96
9	Ni(OTf) <sub>2</sub>	74	98
10	Co(OTf) <sub>2</sub>	84	99

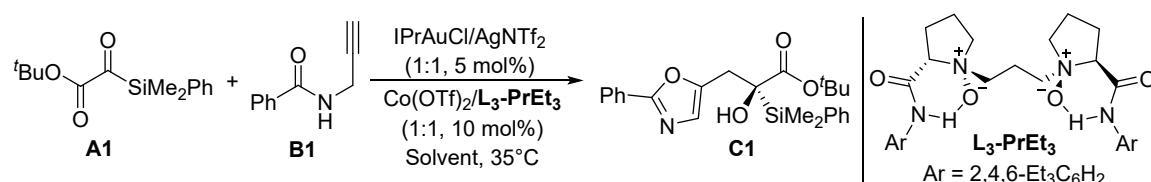
<sup>a</sup> Unless otherwise noted, all reactions were performed with metal salt/**L<sub>3</sub>-PrEt<sub>3</sub>** (1:1, 10 mol%), IPrAuCl/AgNTf<sub>2</sub> (1:1, 5 mol%), **A1** (0.10 mmol), **B1** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) under N<sub>2</sub> atmosphere at 35 °C for 5 h. <sup>b</sup> Yield of isolated product. <sup>c</sup> ee values were determined by UPC<sup>2</sup> on a chiral stationary phase. N.D. = no detected.

**Table S2.** The screening of counterbalance ions in cobalt metal salts

Entry <sup>a</sup>	Metal salts	C1 yield (%) <sup>b</sup>	C1 ee (%) <sup>c</sup>
1	Co(OTf) <sub>2</sub>	84	99
2	Co(NTf <sub>2</sub> ) <sub>2</sub>	82	99
3	Co(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	79	98
4	Co(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	68	97
5	Co(acac) <sub>2</sub>	N.D.	-
6	CoCl <sub>2</sub>	N.D.	-

<sup>a</sup> Unless otherwise noted, all reactions were performed with metal salt/**L<sub>3</sub>-PrEt<sub>3</sub>** (1:1, 10 mol%), IPrAuCl/AgNTf<sub>2</sub> (1:1, 5 mol%), **A1** (0.10 mmol), **B1** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) under N<sub>2</sub> atmosphere at 35 °C for 5 h. <sup>b</sup> Yield of isolated product. <sup>c</sup> ee values were determined by UPC<sup>2</sup> on a chiral stationary phase. N.D. = no detected.

**Table S3.** The screening of solvent

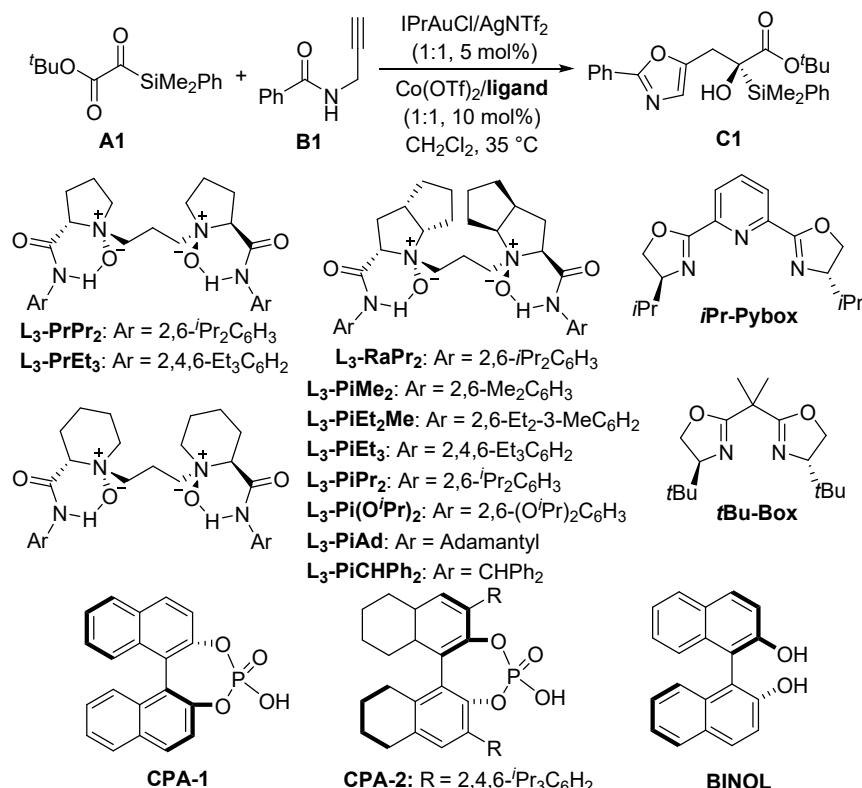


Entry <sup>a</sup>	Solvent	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	THF	19	72
2	CH <sub>3</sub> CN	44	76
3	Toluene	31	84
4	EA	47	93
5	Et <sub>2</sub> O	56	93
6	CHCl <sub>3</sub>	73	99
7	CH <sub>2</sub> Cl <sub>2</sub> CH <sub>2</sub> Cl	74	99

8	CH <sub>2</sub> Cl <sub>2</sub>	84	99
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<sup>a</sup> Unless otherwise noted, all reactions were performed with Co(OTf)<sub>2</sub>/**L<sub>3</sub>-PrEt<sub>3</sub>** (1:1, 10 mol%), IPrAuCl/AgNTf<sub>2</sub> (1:1, 5 mol%), **A1** (0.10 mmol), **B1** (0.12 mmol) in solvent (1.0 mL) under N<sub>2</sub> atmosphere at 35 °C for 5 h. <sup>b</sup> Yield of isolated product. <sup>c</sup> ee values were determined by UPC<sup>2</sup> on a chiral stationary phase.

**Table S4.** The screening of ligands



Entry <sup>a</sup>	Ligand	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	<b>L<sub>3</sub>-PrPr<sub>2</sub></b>	73	97
2	<b>L<sub>3</sub>-PrEt<sub>3</sub></b>	84	99
3	<b>L<sub>3</sub>-RaPr<sub>2</sub></b>	68	98
4	<b>L<sub>3</sub>-PiPr<sub>2</sub></b>	88	99
5	<b>L<sub>3</sub>-PiAd</b>	13	20
6	<b>L<sub>3</sub>-PiCHPh<sub>2</sub></b>	38	83
7	<b>L<sub>3</sub>-PiMe<sub>2</sub></b>	74	99
8	<b>L<sub>3</sub>-PiEt<sub>2</sub>Me</b>	77	99
9	<b>L<sub>3</sub>-PiEt<sub>3</sub></b>	85	99
9	<b>L<sub>3</sub>-Pi(O'Pr)<sub>2</sub></b>	64	96
10 <sup>d</sup>	<b>CPA-1</b>	N.D.	-
11 <sup>d</sup>	<b>CPA-2</b>	N.D.	-
12	<b>tBu-Box</b>	39	4
13	<b>iPr-PyBox</b>	14	0

14	BINOL	56	0
<sup>a</sup> Unless otherwise noted, all reactions were performed with Co(OTf) <sub>2</sub> / <b>Ligand</b> (1:1, 10 mol%), IPrAuCl/AgNTf <sub>2</sub> (1:1, 5 mol%), <b>A1</b> (0.10 mmol), <b>B1</b> (0.12 mmol) in CH <sub>2</sub> Cl <sub>2</sub> (1.0 mL) under N <sub>2</sub> atmosphere at 35 °C for 5 h. <sup>b</sup> Yield of isolated product. <sup>c</sup> ee values were determined by UPC <sup>2</sup> on a chiral stationary phase. <sup>d</sup> without Co(OTf) <sub>2</sub> .			

**Table S5.** The screening of additives

Entry <sup>a</sup>	Additives		Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	-		88	99
2	3 Å M.S. (20 mg)		75	99
3	4 Å M.S. (20 mg)		84	99
4	5 Å M.S. (20 mg)		83	99
5	Et <sub>3</sub> N (30 mol%)		N.D.	-
6	K <sub>2</sub> CO <sub>3</sub> (10 mol%)		N.D.	-
7	PhCO <sub>2</sub> H (10 mol%)		83	99
8	NaBAr <sup>F</sup> <sub>4</sub> (10 mol%)		83	98

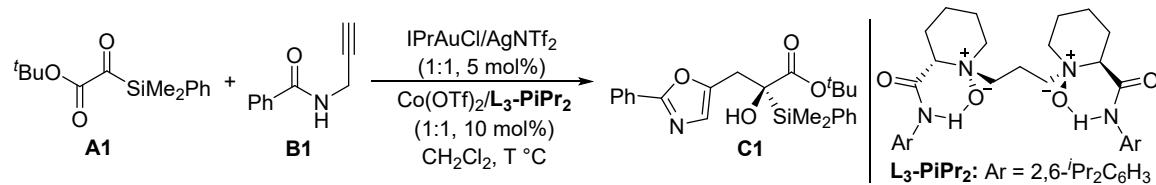
<sup>a</sup> Unless otherwise noted, all reactions were performed with Co(OTf)<sub>2</sub>/**L<sub>3</sub>-PiPr<sub>2</sub>** (1:1, 10 mol%), IPrAuCl/AgNTf<sub>2</sub> (1:1, 5 mol%), **A1** (0.10 mmol), **B1** (0.12 mmol) and additives in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) under N<sub>2</sub> atmosphere at 35 °C for 5 h. <sup>b</sup> Yield of isolated product. <sup>c</sup> ee values were determined by UPC<sup>2</sup> on a chiral stationary phase.

**Table S6.** The screening of the ratio of substrates

Entry <sup>a</sup>	<b>B1/A1</b>		Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	3.0		78	99
2	2.0		83	99
3	1.5		86	99
4	1.2		88	99
5	1.0		80	99

<sup>a</sup> Unless otherwise noted, all reactions were performed with Co(OTf)<sub>2</sub>/**L<sub>3</sub>-PiPr<sub>2</sub>** (1:1, 10 mol%), IPrAuCl/AgNTf<sub>2</sub> (1:1, 5 mol%), **A1** (0.10 mmol), **B1** (x mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) under N<sub>2</sub> atmosphere at 35 °C for 5 h. <sup>b</sup> Yield of isolated product. <sup>c</sup> ee values were determined by UPC<sup>2</sup> on a chiral stationary phase.

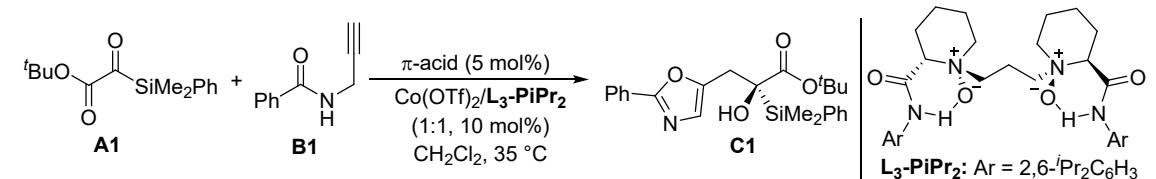
**Table S7.** The screening of temperature



Entry <sup>a</sup>	Temperature ( $^\circ\text{C}$ )	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	0	26	99
2	10	51	99
3	20	74	99
4	35	88	99

<sup>a</sup> Unless otherwise noted, all reactions were performed with  $\text{Co}(\text{OTf})_2/\text{L}_3\text{-PiPr}_2$  (1:1, 10 mol%),  $\text{IPrAuCl/AgNTf}_2$  (1:1, 5 mol%), **A1** (0.10 mmol), **B1** (0.12 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) under  $\text{N}_2$  atmosphere at  $T^\circ\text{C}$  for 5 h. <sup>b</sup> Yield of isolated product. <sup>c</sup> ee values were determined by UPC<sup>2</sup> on a chiral stationary phase.

**Table S8.** The screening of  $\pi$ -acid



Entry <sup>a</sup>	$\pi$ -acid	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	$\text{AuCl}\cdot\text{PPh}_3$	20	99
2	$\text{IPrAuCl}$	48	99
3	$\text{AuCl}_3$	61	98
4	$\text{AuCl}(\text{CH}_3\text{SCH}_3)/\text{AgNTf}_2$	8	99
5	$\text{AuCl}\cdot\text{PPh}_3/\text{AgNTf}_2$	84	99
6	$\text{Me}_4'\text{BuXPhOSAuCl/AgNTf}_2$	86	99
7	$\text{IPrAuCl/AgNTf}_2$	88	99
8	$\text{IPrAuCl/AgNO}_3$	42	92
9	$\text{IPrAuCl/AgOAc}$	73	99
10	$\text{IPrAuCl/AgBF}_4$	73	99
11	$\text{IPrAuCl/AgOTf}$	84	99
12	Cyclohexyl JohnPhos AuNTf <sub>2</sub>	63	99

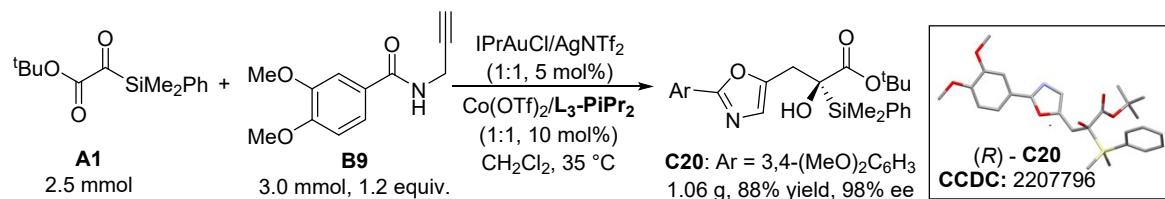
<sup>a</sup> Unless otherwise noted, all reactions were performed with  $\text{Co}(\text{OTf})_2/\text{L}_3\text{-PiPr}_2$  (1:1, 10 mol%),  $\pi$ -acid (5 mol%), **A1** (0.10 mmol), **B1** (0.12 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) under  $\text{N}_2$  atmosphere at  $35^\circ\text{C}$  for 5 h. <sup>b</sup> Yield of isolated product. <sup>c</sup> ee values were determined by UPC<sup>2</sup> on a chiral stationary phase.

**Table S9.** Screening of the the amount of the **L<sub>3</sub>-PiPr<sub>2</sub>**/Co(OTf)<sub>2</sub>

Entry <sup>a</sup>	x	Reaction time (h)	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	1.0	18	75	90
2	2.0	18	77	93
3	5.0	8	81	99
4	10.0	5	88	99

<sup>a</sup> Unless otherwise noted, all reactions were performed with Co(OTf)<sub>2</sub>/**L<sub>3</sub>-PiPr<sub>2</sub>** (1:1, x mol%), IPrAuCl/AgNTf<sub>2</sub> (1:1, 5 mol%), **A1** (0.10 mmol), **B1** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) under N<sub>2</sub> atmosphere at 35 °C for 5 h. <sup>b</sup> Yield of isolated product. <sup>c</sup> ee values were determined by UPC<sup>2</sup> on a chiral stationary phase.

## 6. Gram-scale synthesis

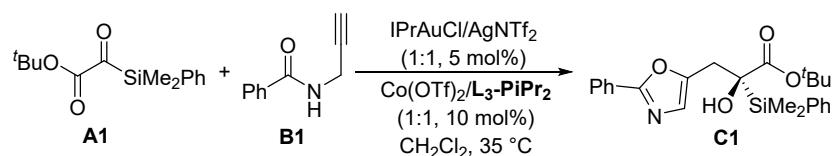


A 100 mL of dry round-bottom flask was charged with the IPrAuCl (77.6 mg, 5 mol%), AgNTf<sub>2</sub> (48.5 mg, 5 mol%), Co(OTf)<sub>2</sub> (89.3 mg, 10 mol%), *N,N'*-dioxide ligand **L<sub>3</sub>-PiPr<sub>2</sub>** (162.5 mg, 10 mol%) and silyl glyoxylate **A1** (660.0 mg, 2.50 mmol, 1.0 equiv.) under nitrogen atmosphere. DCM (25 mL) was added and the mixture were stirred at 35 °C for 5 h. Then, **B9** (657.0 mg, 3.0 mmol, 1.2 equiv.) was added. The mixture was stirred at 35 °C for 15 h (detection by TLC). The residue was purified by column chromatography (petroleum ether: ethyl acetate: = 4 : 1) on silica gel to afford the desired product **C20** in 88% yield (1.06 g) with 98% ee as a white solid.

## 7. Control experiments and mechanistic studies

### 7.1 Control experiments

**Table S10.** Control experiments

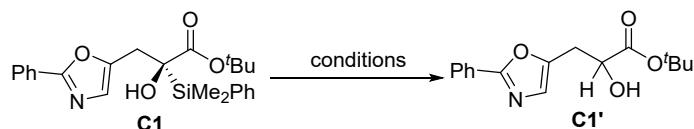


Entry <sup>a</sup>	variation from the standard conditions	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	-	88	99
2	No Co(OTf) <sub>2</sub> / <b>L<sub>3</sub>-PiPr<sub>2</sub></b>	7	0
3	No AgNTf <sub>2</sub>	48	99
4	No IPrAuCl	3	99
5	No Co(OTf) <sub>2</sub>	trace	0
6	No <b>L<sub>3</sub>-PiPr<sub>2</sub></b>	70	0
7	No IPrAuCl/AgNTf <sub>2</sub> and Zn(OTf) <sub>2</sub> instead of Co(OTf) <sub>2</sub>	48	94

<sup>a</sup> Unless otherwise noted, all reactions were performed with Co(OTf)<sub>2</sub>/L<sub>3</sub>-PiPr<sub>2</sub> (1:1, 10 mol%), IPrAuCl/AgNTf<sub>2</sub>

(1:1, 5 mol%), **A1** (0.10 mmol), **B1** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) under N<sub>2</sub> atmosphere at 35 °C for 5 h. <sup>b</sup> Yield of isolated product. <sup>c</sup> ee values were determined by UPC<sup>2</sup> on a chiral stationary phase.

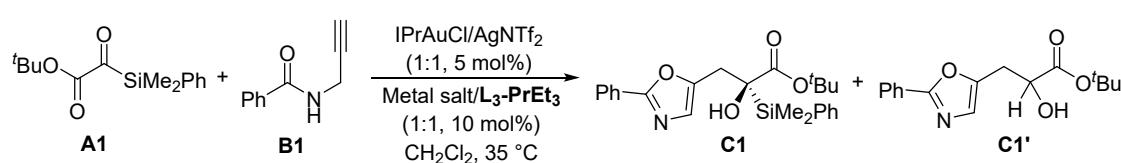
**Table S11**



Entry <sup>a</sup>	conditions	Yield of <b>C1'</b> <sup>b</sup>
1	In(OTf) <sub>3</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%)	0
2	Sc(OTf) <sub>3</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%)	0
3	Co(OTf) <sub>2</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%)	0
4	IPrAuCl/AgNTf <sub>2</sub> (1:1, 5 mol%), In(OTf) <sub>3</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%)	0
5	IPrAuCl/AgNTf <sub>2</sub> (1:1, 5 mol%), Sc(OTf) <sub>3</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%)	0
6	IPrAuCl/AgNTf <sub>2</sub> (1:1, 5 mol%), Co(OTf) <sub>2</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%)	0
7	IPrAuCl/AgNTf <sub>2</sub> (1:1, 5 mol%), In(OTf) <sub>3</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%) + 10 uL H <sub>2</sub> O	0
8	IPrAuCl/AgNTf <sub>2</sub> (1:1, 5 mol%), Sc(OTf) <sub>3</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%) + 10 uL H <sub>2</sub> O	0
9	IPrAuCl/AgNTf <sub>2</sub> (1:1, 5 mol%), Co(OTf) <sub>2</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%) + 10 uL H <sub>2</sub> O	0

<sup>a</sup> Unless otherwise noted, all reactions were performed in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) under N<sub>2</sub> atmosphere at 35 °C for 5 h. <sup>b</sup> Yield of isolated product.

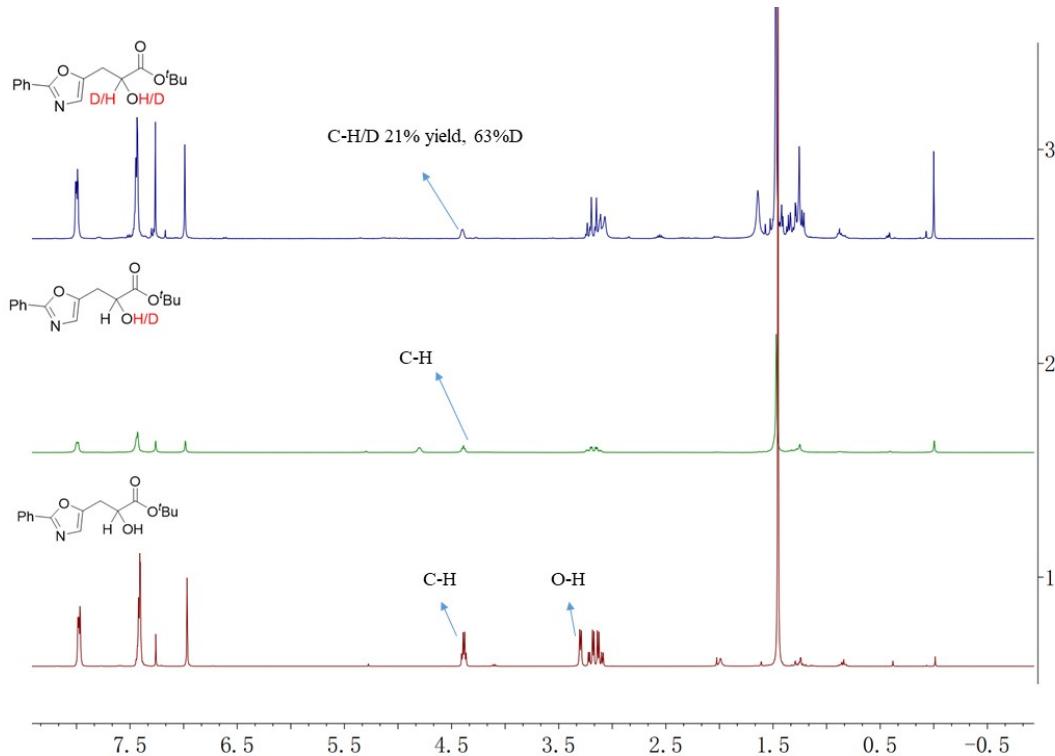
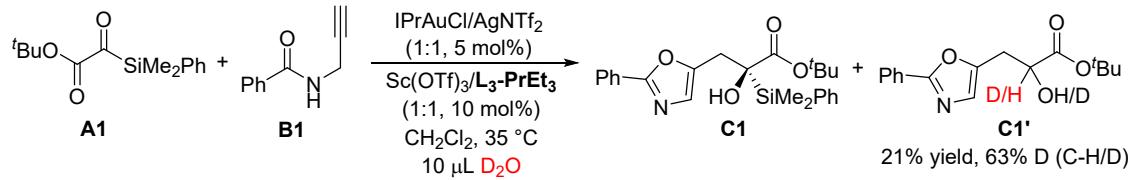
**Table S12**

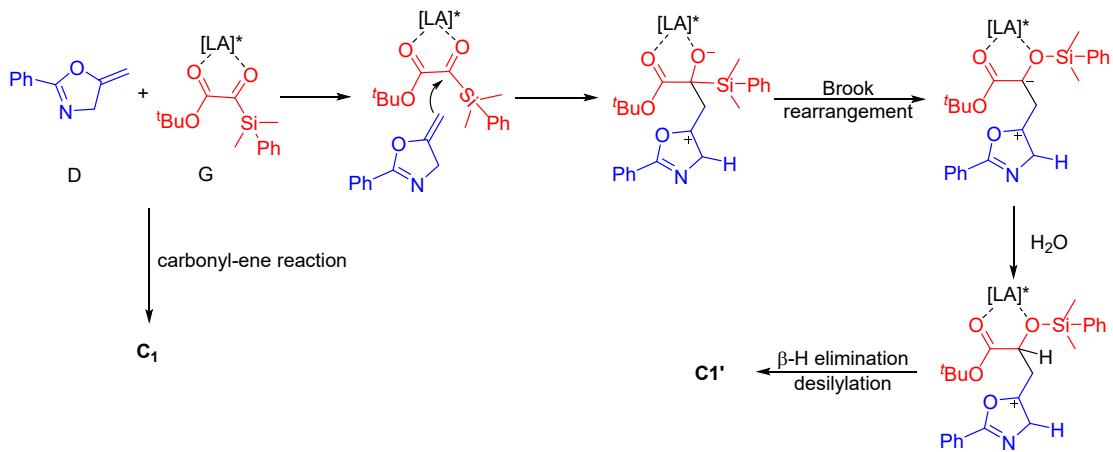


Entry <sup>a</sup>	conditions	Yield of <b>C1</b> <sup>b</sup>	Yield of <b>C1'</b> <sup>b</sup>
1	Sc(OTf) <sub>3</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%)	49	0
2	Sc(OTf) <sub>3</sub> / <b>L<sub>3</sub>-PrEt<sub>3</sub></b> (1:1, 10 mol%) + 10 uL H <sub>2</sub> O	16	21

<sup>a</sup> Unless otherwise noted, all reactions were performed with Metal salts / $\text{L}_3\text{-PrEt}_3$  (1:1, 10 mol%), IPrAuCl/AgNTf<sub>2</sub> (1:1, 5 mol%), **A1** (0.10 mmol), **B1** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) under N<sub>2</sub> atmosphere at 35 °C for 5 h. <sup>b</sup> Yield of isolated product.

To make clear the  $\alpha$ -proton source of **C1'**, the deuterium labeling experiment was carried out with addition of D<sub>2</sub>O. Under an atmosphere of nitrogen, IPrAuCl (3.1 mg, 5 mol%), AgNTf<sub>2</sub> (1.9 mg, 5 mol%), Sc(OTf)<sub>3</sub> (4.9 mg, 10 mol%),  $\text{L}_3\text{-PrEt}_3$  (6.2 mg, 10 mol%), silylglyoxylate **A1** (0.10 mmol) and propargyl amides **B1** (0.12 mmol) were stirred in DCM (1 mL) and D<sub>2</sub>O (10  $\mu\text{L}$ ) at 35 °C for 5 h. **C1'** was observed with 63% deuterated ratio, suggesting the  $\alpha$ -proton of **C1'** might come from water. Based on the above control experimental results, a possible mechanism for the production of **C1'** was also proposed in Figure S3.



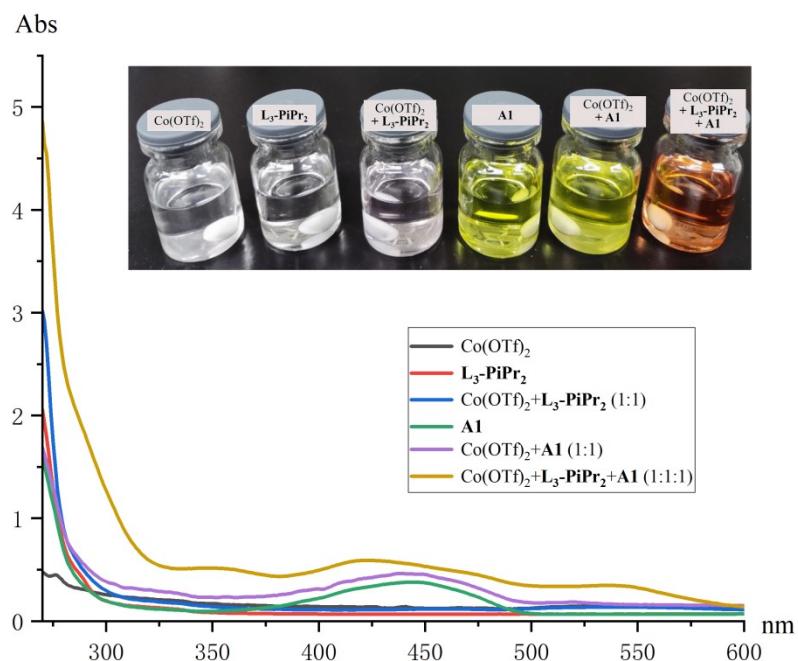


**Figure S3.** The two competing reaction processes

## 7.2 Mechanistic studies

### 7.2.1 UV-Vis spectroscopy

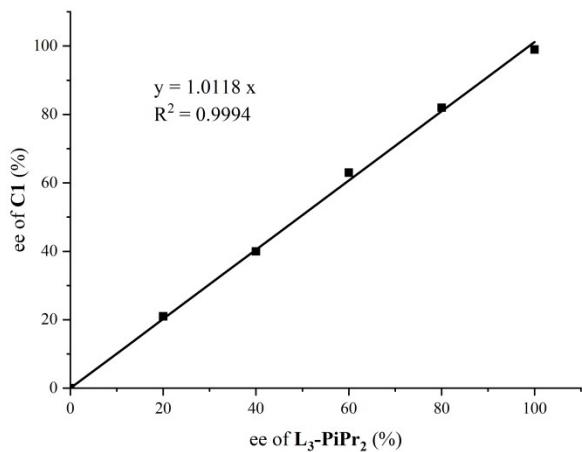
General:  $\text{Co}(\text{OTf})_2$  (0.01 mmol),  $\text{L}_3\text{-PiPr}_2$  (0.01 mmol),  $\text{Co}(\text{OTf})_2 + \text{L}_3\text{-PiPr}_2$  (1:1, 0.01 mmol), **A1** (0.01 mmol),  $\text{Co}(\text{OTf})_2 + \text{A1}$  (1:1, 0.01 mmol),  $\text{Co}(\text{OTf})_2 + \text{L}_3\text{-PiPr}_2 + \text{A1}$  (1:1:1, 0.01 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (1.0 mL), separately. The above solution (0.01 M) stirred at room temperature for 3 hours, then diluted to 0.002 M and analyzed by UV-Vis spectroscopy using a 10.0 mm quartz cuvette. (The concentration shown in below picture is 0.002 M).



**Figure S4.** UV-Vis spectroscopy of the catalytical components

### 7.2.2 The relationship of the ee values of product **C1** and $\text{L}_3\text{-PiPr}_2$

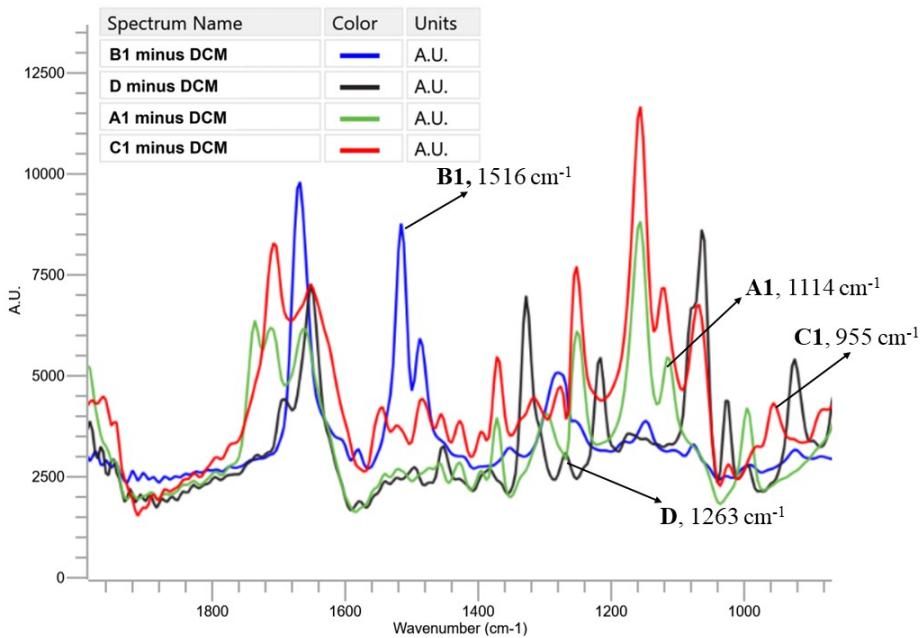
Combined certain amount of optically pure (*S*)-**L<sub>3</sub>-PiPr<sub>2</sub>** with pure (*R*)-**L<sub>3</sub>-PiPr<sub>2</sub>** led to **L<sub>3</sub>-PiPr<sub>2</sub>** with specified ee values. Six different control reactions were performed in parallel by using **L<sub>3</sub>-PiPr<sub>2</sub>** with 0% ee, 20% ee, 40% ee, 60% ee, 80% ee, and 100% ee. Under an atmosphere of nitrogen, the IPrAuCl (3.1 mg, 5 mol%), AgNTf<sub>2</sub> (1.9 mg, 5 mol%), Co(OTf)<sub>2</sub> (3.5 mg, 10 mol%), **L<sub>3</sub>-PiPr<sub>2</sub>** (6.5 mg, 10 mol%), silylglyoxylate **A1** (0.10 mmol) and propargyl amides **B1** (0.12 mmol) were stirred in DCM (1 mL) at 35 °C for 5 h. The residue was purified by column chromatography (petroleum ether : ethyl acetate = 8.5:1) on silica gel to afford the product **C1**. The ee values were determined by UPC<sup>2</sup> on a chiral stationary phase.



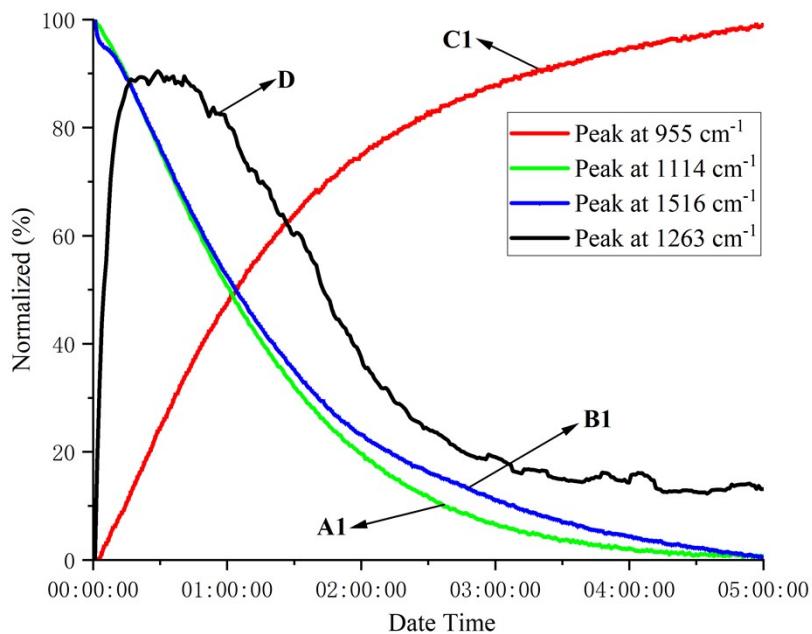
**Figure S5.** The relationship of the ee values of product **C1** and **L<sub>3</sub>-PiPr<sub>2</sub>**

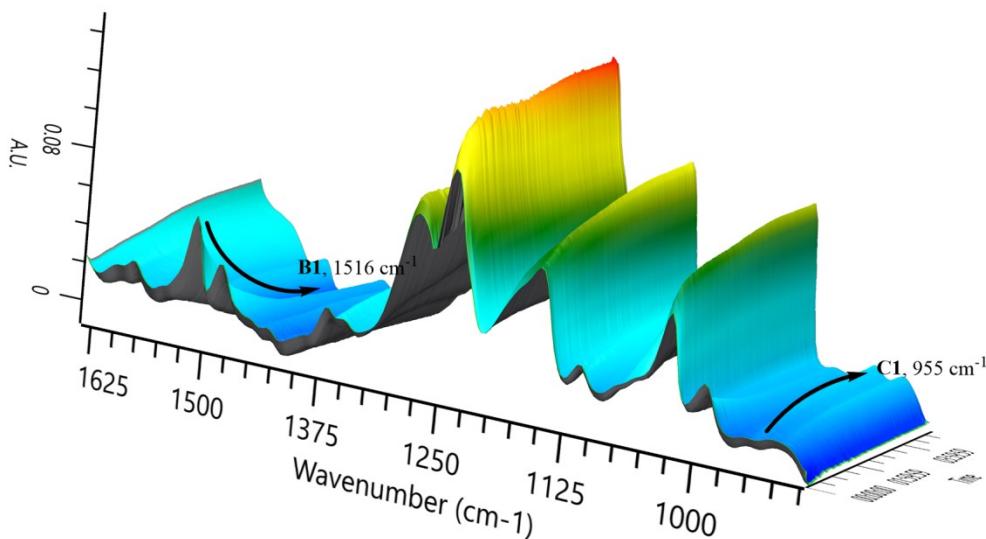
### 7.2.3 The operando IR experiment

General: The reaction was monitored by the operando IR spectrometer using a Mettler Toledo ReactIR™. First, the infrared absorption spectra of each reactants **A1** and **B1**, intermediate **D** and product **C1** in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) were collected. The following figure shows the absorption of each participant minus the absorption of solvent. Peak at 1516 cm<sup>-1</sup> was identified as the characteristic absorption of reactant **B1**, 1114 cm<sup>-1</sup> for **A1**, 1263 cm<sup>-1</sup> for **D**, and 955 cm<sup>-1</sup> for **C1**.



Then, an oven-dried flask with three necks was equipped with a stir bar and attached to a React IR probe. And then the system was charged with 5.0 mL of a stock solution containing the 0.025 mmol (IPrAuCl /AgNTf<sub>2</sub>, 1:1, 5 mol%), 0.05 mmol catalyst (Co(OTf)<sub>2</sub>/**L<sub>3-PiPr<sub>2</sub></sub>**, 1:1, 10 mol%), 0.6 mmol propargyl amides (**B1**) and 0.5 mmol silylglyoxylate (**A1**) in CH<sub>2</sub>Cl<sub>2</sub>. The reaction was heated to 35 °C using a water bath. Then staring to collect data. The React IR spectra were recorded over the process of the reaction. The reaction progress is monitored by the absorbance of **D** increased and then decreased at 1263 cm<sup>-1</sup>.

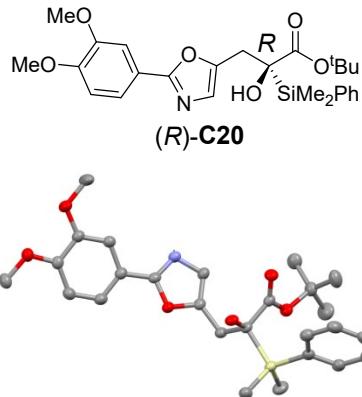




**Figure S6.** The operando IR experiment

## 8. X-ray crystal structure

The crystal of product **C20** was obtained in the solvents of PE and CH<sub>2</sub>Cl<sub>2</sub>. CCDC: 2207796 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via <https://www.ccdc.cam.ac.uk/structures/>.



**Figure S7.** X-ray crystal structure of product **C20**

Crystallographic Data for C<sub>26</sub>H<sub>33</sub>N O<sub>6</sub> Si.

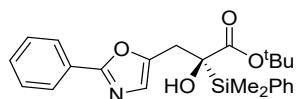
Formula	C <sub>26</sub> H <sub>33</sub> N O <sub>6</sub> Si
Formula mass (amu)	483.62
Space group	C 2 2 21
<i>a</i> (Å)	12.5846(4)
<i>b</i> (Å)	22.3829(7)

$c$ (Å)	20.1826(6)
$\alpha$ (deg)	90
$\beta$ (deg)	90
$\gamma$ (deg)	90
$V$ (Å <sup>3</sup> )	5685.0(3)
$Z$	8
$\lambda$ (Å)	1.54178
$T$ (K)	142 K
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.130
$\mu$ (mm <sup>-1</sup> )	1.031
Transmission factors	0.766-0.928
$\theta_{\max}$ (deg)	68.349
No. of unique data, including $F_o^2 < 0$	5225
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	5021
No. of variables	318
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ <sup>a</sup>	0.0252
$R_w(F_o^2)$ <sup>b</sup>	0.0644
Goodness of fit	1.037

<sup>a</sup>  $R(F) = \sum|F_o| - |F_c| / \sum|F_o|.$

<sup>b</sup>  $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum w F_o^4]^{1/2}; w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp],$  where  $p = [\max(F_o^2, 0) + 2F_c^2] / 3.$

## 9. The analytical and spectral characterization data for the products



### **Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-phenyloxazol-5-yl)propanoate (C1)**

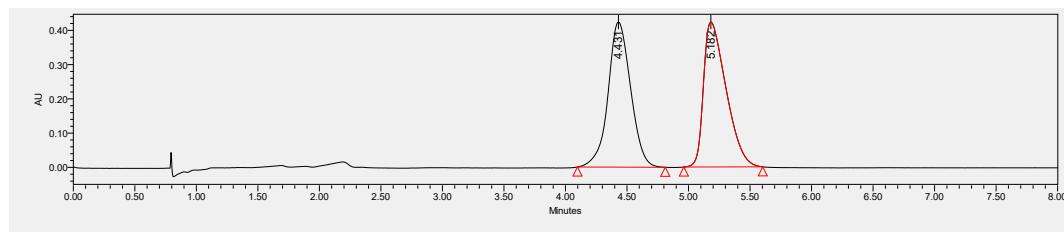
(C<sub>24</sub>H<sub>29</sub>NO<sub>4</sub>Si) 37.3 mg, 88% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>24</sup> = -8.2 (c = 1.60, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiraldak IA-3, CO<sub>2</sub>/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 4.54 min, tr (major) = 4.93 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.92 (m, 2H), 7.67 – 7.60 (m, 2H), 7.44 – 7.36 (m, 6H), 6.94 – 6.88 (m, 1H), 3.29 (d, *J* = 15.6 Hz, 1H), 3.23 (s, 1H), 3.13 (d *J* = 15.6, 1H), 1.33 (s, 9H), 0.49 (d, *J* = 6.4 Hz, 6H).

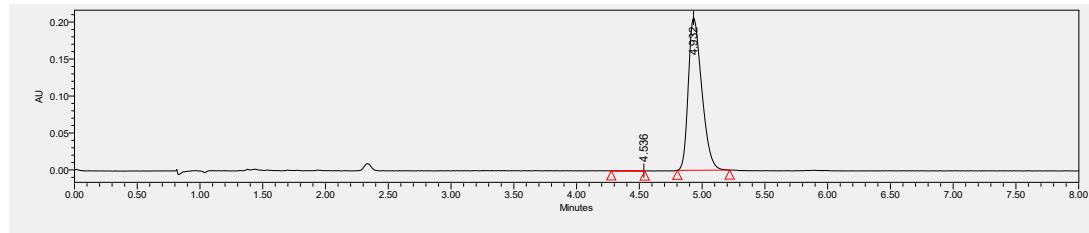
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.4, 160.9, 148.6, 134.7, 134.4, 130.0, 129.9, 128.7, 127.8, 127.6, 126.1, 126.0, 82.8, 72.0, 31.9, 28.0, -5.4, -5.4.

**HRMS (ESI+)** *m/z* calcd for C<sub>24</sub>H<sub>29</sub>NO<sub>4</sub>Si [M+H]<sup>+</sup>: 424.1939, found: 424.1933.

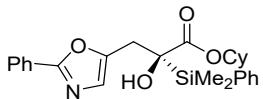
**IR** (neat): 2974, 1706, 1539, 1547, 1482, 1426, 1368, 1249, 1152, 1120, 1065, 954, 833, 810, 779, 735, 692 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	4.431	5394795	50.08
2	5.182	5377490	49.92



Entry	Retention Time	Area	% Area
1	4.536	2159	0.14
2	4.932	1535827	99.86



**Cyclohexyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-phenyloxazol-5-yl)propanoate (C2)**

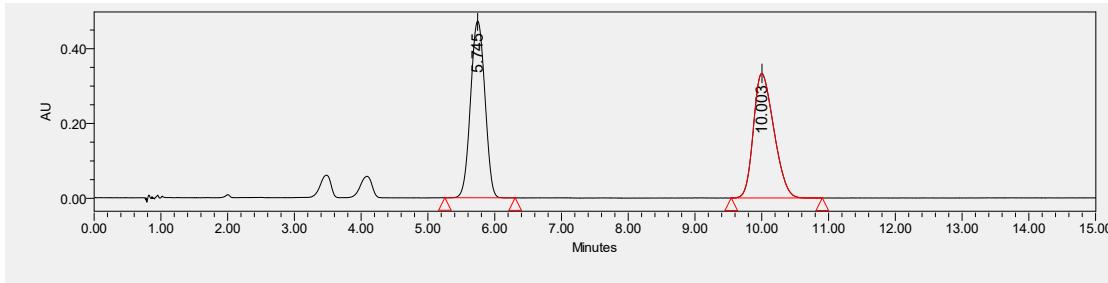
(C<sub>26</sub>H<sub>31</sub>NO<sub>4</sub>Si) 36.4 mg, 81% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>24</sup> = -9.7 (c = 0.91, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 5.72 min, tr (major) = 9.84 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.98 – 7.88 (m, 2H), 7.65 – 7.58 (m, 2H), 7.46 – 7.34 (m, 6H), 6.90 (s, 1H), 4.88 – 4.66 (m, 1H), 3.44 – 3.25 (d, *J* = 15.2 Hz, 1H), 3.23 – 3.07 (m, 2H), 1.85 – 1.59 (m, 5H), 1.54 – 1.47 (m, 1H), 1.40 – 1.28 (m, 4H), 0.50 (d, *J* = 1.6 Hz, 6H).

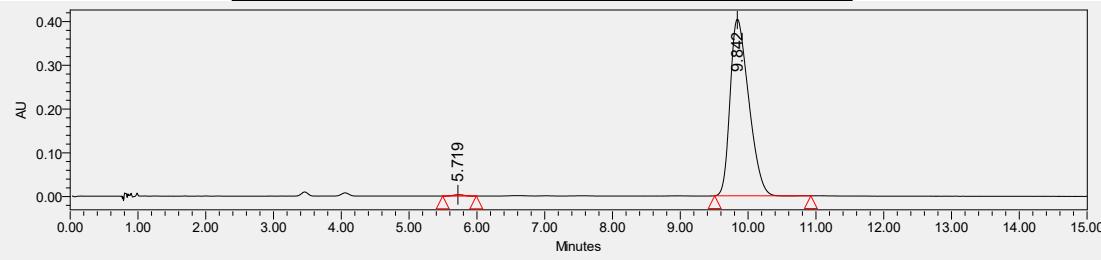
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.9, 161.1, 148.6, 134.8, 134.3, 130.1, 130.1, 128.8, 128.0, 127.8, 126.3, 126.2, 74.9, 72.2, 32.1, 31.9, 27.1, 25.4, 23.9, 23.8, -5.3, -5.3.

**ESI-HRMS:** calcd for C<sub>26</sub>H<sub>32</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 450.2095, found: 450.2100.

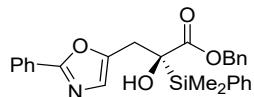
**IR** (neat): 2937, 1709, 1548, 1450, 1427, 1247, 1121, 1067, 1011, 811, 780, 735, 701 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	5.745	7052429	49.95
2	10.003	7067453	50.05



Entry	Retention Time	Area	% Area
1	5.719	30582	0.40
2	9.842	7700711	99.60



**Benzyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-phenyloxazol-5-yl)propanoate (C3)**

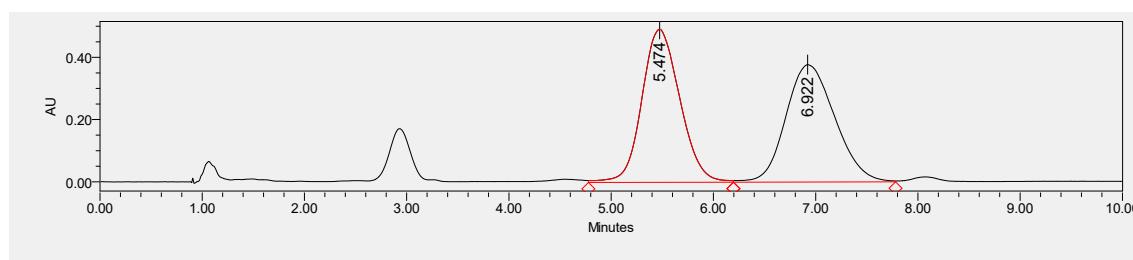
(C<sub>27</sub>H<sub>27</sub>NO<sub>4</sub>Si) 26.1 mg, 57% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>24</sup> = -19.4 (c = 0.66, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiralkpak AY-3, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 6.84 min, tr (major) = 5.49 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.92 – 7.85 (m, 2H), 7.53 – 7.47 (m, 2H), 7.42–7.37 (m, 4H), 7.36 – 7.30 (m, 5H), 7.27 – 7.23 (m, 2H), 6.85–6.82 (m, 1H), 5.17 – 5.05 (m, 2H), 3.34 (d, *J* = 15.6 Hz, 1H), 3.13 (dd, *J* = 15.6, 0.8 Hz, 1H), 3.08 (s, 1H), 0.44 (d, *J* = 4.4 Hz, 6H).

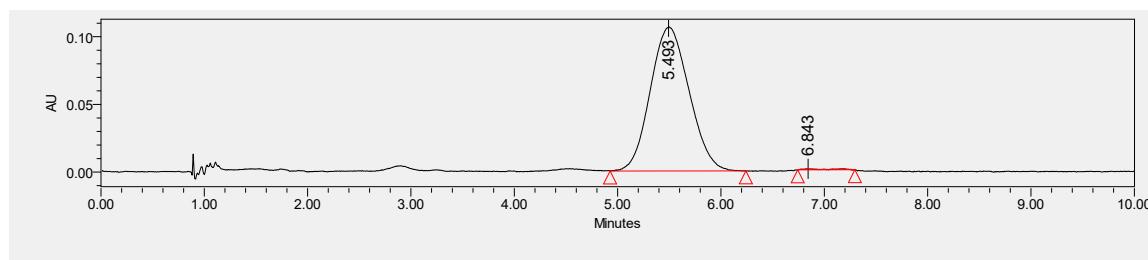
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 176.4, 161.2, 148.4, 135.1, 134.7, 134.0, 130.2, 130.2, 128.9, 128.8, 128.0, 127.7, 126.4, 126.2, 72.7, 67.9, 32.0, -5.4, -5.6.

**ESI-HRMS:** calcd for C<sub>27</sub>H<sub>28</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 458.1782, found: 458.1780.

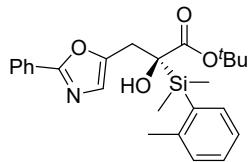
**IR** (neat): 2958, 1718, 1593, 1548, 1485, 1249, 1214, 1174, 1069, 952, 836, 815, 780, 696 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	5.474	12735225	50.33
2	6.922	12566080	49.67



Entry	Retention Time	Area	% Area
1	5.493	2772671	99.51
2	6.843	13706	0.49



**Tert-butyl (R)-2-(dimethyl(o-tolyl)silyl)-2-hydroxy-3-(2-phenyloxazol-5-yl)propanoate (C4)**

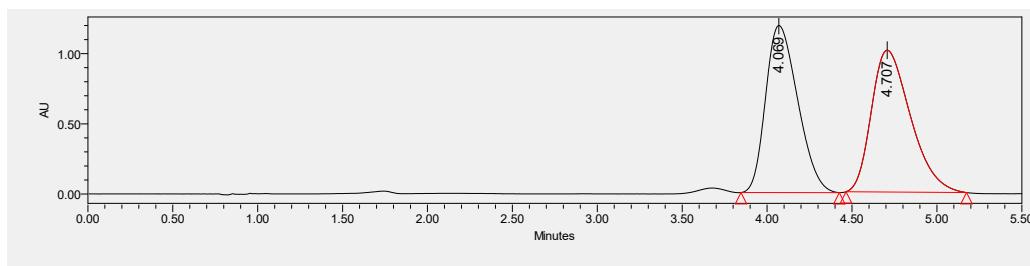
(C<sub>25</sub>H<sub>31</sub>NO<sub>4</sub>Si) 31.1 mg, 71% yield, 88% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>23</sup> = -8.1 (c = 0.78, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiraldak AZ-3, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (major) = 4.91 min, tr (minor) = 4.00 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 – 7.92 (m, 2H), 7.57 – 7.49 (m, 1H), 7.44 – 7.39 (m, 3H), 7.33 – 7.26 (m, 1H), 7.22 – 7.12 (m, 2H), 6.93 (s, 1H), 3.33 (d, *J* = 15.6 Hz, 1H), 3.23 (s, 1H), 3.14 (d, *J* = 15.6 Hz, 1H), 2.55 (s, 3H), 1.29 (s, 9H), 0.57 (d, *J* = 6.8 Hz, 6H).

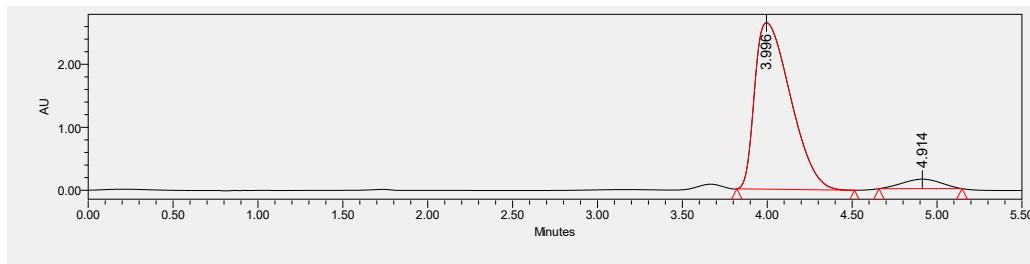
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 161.0, 148.8, 145.1, 136.2, 133.0, 130.5, 130.2, 130.1, 128.8, 127.8, 126.3, 124.9, 83.0, 72.5, 32.6, 28.1, 24.2, -2.4, -2.6.

ESI-HRMS: calcd for C<sub>25</sub>H<sub>32</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 438.2095, found: 438.2093.

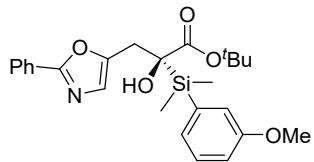
IR (neat): 2975, 1710, 1592, 1450, 1368, 1155, 1126, 1068, 952, 838, 779, 747, 713, 690 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	4.069	15613317	49.11
2	4.707	16177185	50.89



Entry	Retention Time	Area	% Area
1	3.996	38713264	94.24
2	4.914	2366028	5.76



**Tert-butyl (R)-2-hydroxy-2-((3-methoxyphenyl)dimethylsilyl)-3-(2-phenyloxazol-5-yl)propanoate (C5)**

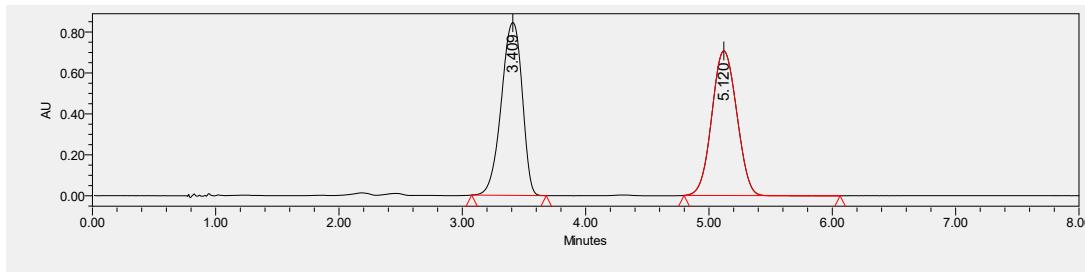
( $C_{25}\text{H}_{31}\text{NO}_5\text{Si}$ ) 36.7 mg, 81% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{25} = -8.6$  ( $c = 0.92$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**,  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm), retention time: tr (minor) = 3.39 min, tr (major) = 4.92 min.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 – 7.91 (m, 2H), 7.46 – 7.37 (m, 3H), 7.35 – 7.28 (m, 1H), 7.23 – 7.14 (m, 2H), 6.97 – 6.91 (m, 2H), 3.82 (s, 3H), 3.28 (d,  $J = 15.2$  Hz, 1H), 3.22 (s, 1H), 3.13 (d,  $J = 15.6$  Hz, 1H), 1.34 (s, 9H), 0.47 (d,  $J = 5.2$  Hz, 6H).

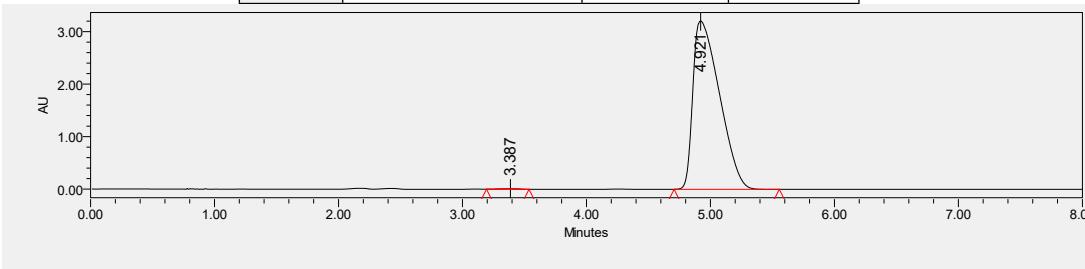
**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.6, 161.0, 159.0, 148.8, 136.1, 130.1, 129.2, 128.8, 127.8, 127.1, 126.3, 126.2, 120.6, 115.0, 83.0, 72.1, 55.3, 32.1, 28.2, -5.2, -5.2.

**ESI-HRMS:** calcd for  $C_{25}\text{H}_{32}\text{NO}_5\text{Si}^+ ([M + H]^+) = 454.2044$ , found: 454.2044.

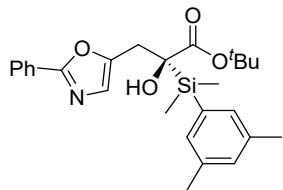
**IR** (neat): 2974, 1709, 1570, 1481, 1407, 1368, 1248, 1155, 1068, 955, 806, 779, 712, 692  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	3.409	9892569	49.99
2	5.120	9896733	50.01



Entry	Retention Time	Area	% Area
1	3.387	112021	0.23
2	4.921	47741720	99.77



**Tert-butyl (R)-2-((3,5-dimethylphenyl)dimethylsilyl)-2-hydroxy-3-(2-phenyloxazol-5-yl)propanoate (C6)**

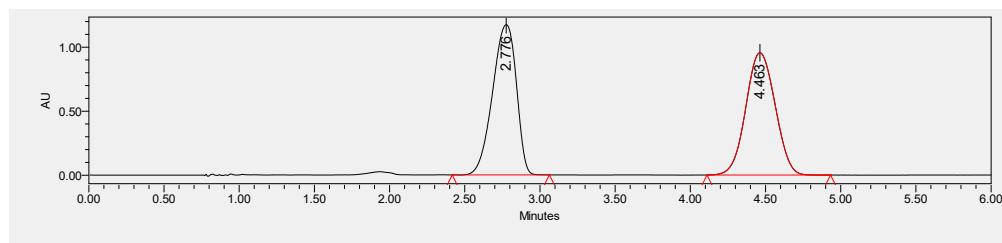
( $\text{C}_{26}\text{H}_{33}\text{NO}_4\text{Si}$ ) 37.0 mg, 82% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{24} = -9.4$  ( $c = 0.93$ , in  $\text{CH}_2\text{Cl}_2$ ). Colorless oil; 82% yield, 99% ee. Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiralcel OZ-3,  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 254 \text{ nm}$ ), retention time: tr (minor) = 2.76 min, tr (major) = 4.36 min.

<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.88 (m, 2H), 7.47 – 7.37 (m, 3H), 7.23 – 7.18 (m, 2H), 7.08 – 7.00 (m, 1H), 6.92 (s, 1H), 3.28 (d,  $J = 15.6$ , 1H), 3.19 (s, 1H), 3.14 (d,  $J = 15.6$  Hz, 1H), 2.33 (s, 6H), 1.35 (s, 9H), 0.46 (d,  $J = 5.2$  Hz, 6H).

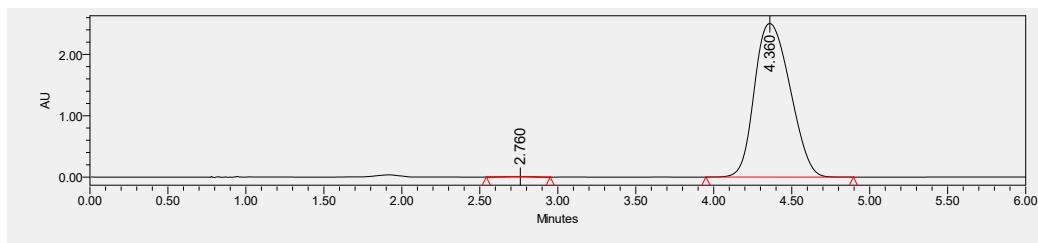
<sup>13</sup>C NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 161.0, 148.9, 137.2, 134.2, 132.5, 131.8, 130.1, 128.8, 127.8, 126.2, 126.1, 82.8, 72.2, 32.0, 28.2, 21.5, -5.2.

ESI-HRMS: calcd for  $\text{C}_{26}\text{H}_{34}\text{NO}_4\text{Si}^+ ([\text{M} + \text{H}]^+) = 452.2252$ , found: 452.2254.

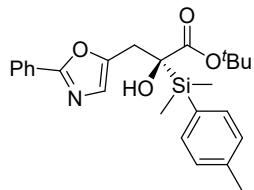
IR (neat): 2975, 1708, 1594, 1481, 1368, 1250, 1155, 1067, 952, 869, 833, 799, 779, 712, 692  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	2.776	12903108	49.94
2	4.463	12932711	50.06



Entry	Retention Time	Area	% Area
1	2.760	110098	0.28
2	4.360	39753475	99.72



**Tert-butyl (R)-2-(dimethyl(p-tolyl)silyl)-2-hydroxy-3-(2-phenyloxazol-5-yl)propanoate (C7)**

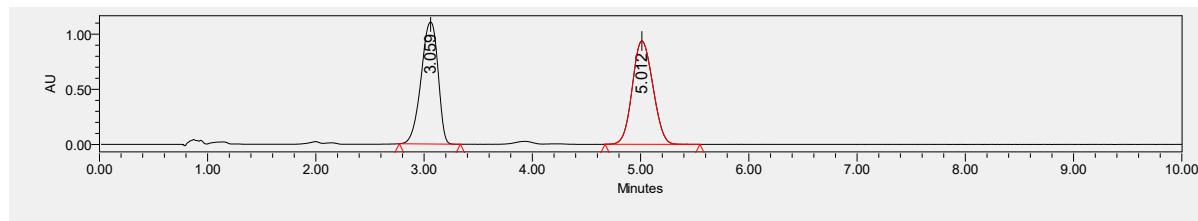
(C<sub>25</sub>H<sub>31</sub>NO<sub>4</sub>Si) 36.3 mg, 83% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>23</sup> = -7.3 (c = 0.91, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiralcel OZ-3, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 3.12 min, tr (major) = 5.00 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.99 – 7.90 (m, 2H), 7.56 – 7.48 (m, 2H), 7.45–7.38 (m, 3H), 7.23 – 7.17 (m, 2H), 6.94–6.89 (m, 1H), 3.28 (dd, *J* = 15.6, 0.8 Hz, 1H), 3.20 (s, 1H), 3.12 (d, *J* = 15.6 Hz, 1H), 2.35 (s, 3H), 1.35 (s, 9H), 0.46 (d, *J* = 1.6 Hz, 6H).

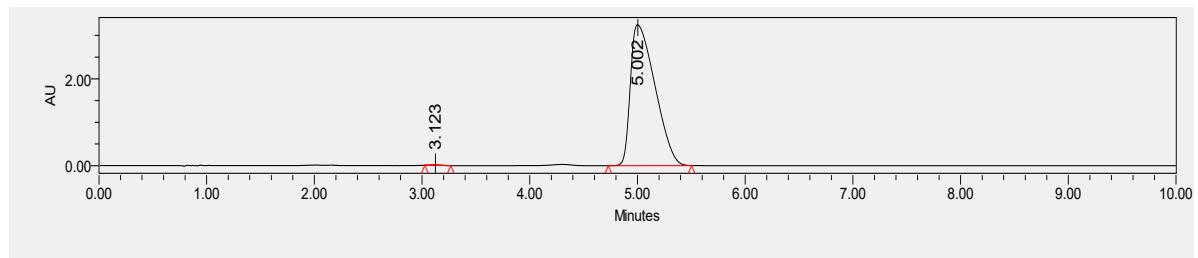
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.7, 161.0, 148.9, 140.0, 134.9, 130.8, 130.1, 128.8, 127.8, 126.3, 126.1, 82.9, 72.2, 32.0, 28.2, 21.7, -5.2, -5.3.

**ESI-HRMS:** calcd for C<sub>25</sub>H<sub>32</sub>NO<sub>4</sub>SiK<sup>+</sup> ([M + K]<sup>+</sup>) = 476.1654, found: 476.1647.

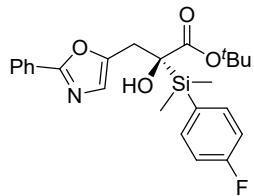
**IR** (neat): 2975, 1708, 1548, 1482, 1368, 1250, 1155, 1107, 1067, 954, 836, 795, 712, 691 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	3.059	11967854	49.27
2	5.012	12323274	50.73



Entry	Retention Time	Area	% Area
1	3.123	61883	0.12
2	5.002	51285007	99.88



**Tert-butyl (R)-2-((4-fluorophenyl)dimethylsilyl)-2-hydroxy-3-(2-phenyloxazol-5-yl)propanoate (C8)**

( $C_{24}\text{H}_{28}\text{FNO}_4\text{Si}$ ) 38.9 mg, 88% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{24} = -9.6$  ( $c = 0.97$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**,  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm), retention time:  $t_r$  (minor) = 2.65 min,  $t_r$  (major) = 3.47 min.

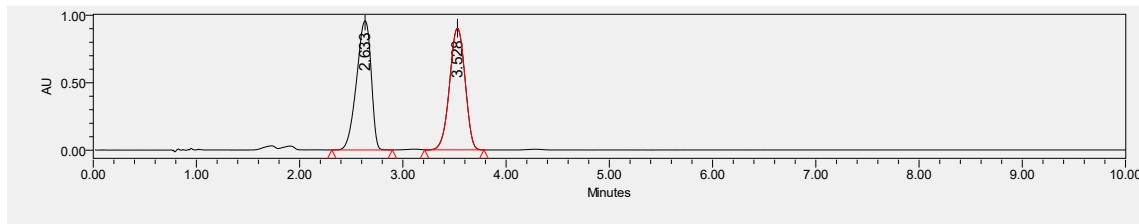
**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 – 7.90 (m, 2H), 7.64–7.55 (m, 2H), 7.46–7.36 (m, 3H), 7.13 – 7.02 (m, 2H), 6.94–6.89 (m, 1H), 3.32 – 3.18 (m, 2H), 3.10 (d,  $J = 15.2$  Hz, 1H), 1.34 (s, 9H), 0.47 (d,  $J = 3.2$  Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 165.6, 163.2, 161.1, 148.6, 136.8 (d,  $J = 7.1$  Hz), 130.1 (d,  $J = 8.1$  Hz), 128.8, 127.7, 126.3, 115.3, 115.1, 83.1, 72.0, 32.1, 28.2, -5.0, -5.1.

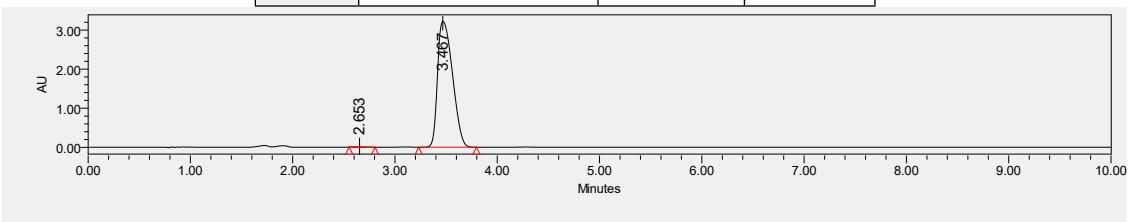
**<sup>19</sup>F NMR** (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -110.51.

**ESI-HRMS:** calcd for  $C_{24}\text{H}_{29}\text{FNO}_4\text{Si}^+ ([M + H]^+) = 442.1844$ , found: 442.1842.

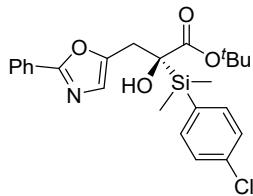
**IR** (neat): 2976, 1710, 1589, 1499, 1369, 1251, 1159, 1105, 1068, 955, 836, 781, 713, 691  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	2.633	9357737	50.01
2	3.528	9352999	49.99



Entry	Retention Time	Area	% Area
1	2.653	44319	0.14
2	3.467	32610094	99.86



**Tert-butyl (R)-2-((4-chlorophenyl)dimethylsilyl)-2-hydroxy-3-(2-phenyloxazol-5-yl)propanoate (C9)**

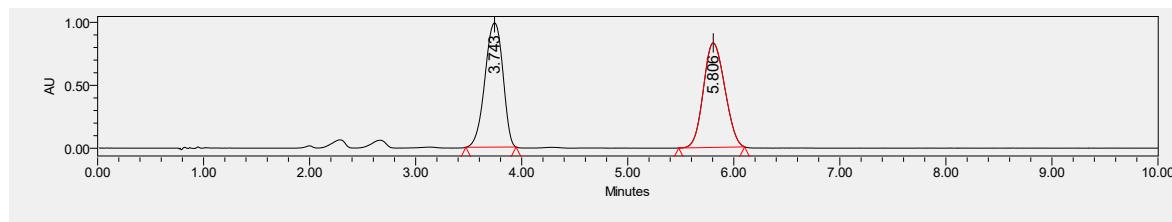
( $\text{C}_{24}\text{H}_{28}\text{ClNO}_4\text{Si}$ ) 35.3 mg, 77% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{24} = -4.1$  ( $c = 0.88$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**,  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm), retention time: tr (minor) = 3.71 min, tr (major) = 5.51 min.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.90 (m, 2H), 7.58 – 7.51 (m, 2H), 7.45 – 7.38 (m, 3H), 7.38 – 7.32 (m, 2H), 6.94 – 6.87 (m, 1H), 3.25 (dd,  $J = 15.6, 0.8$  Hz, 1H), 3.22 (s, 9H), 3.10 (d,  $J = 15.2$  Hz, 1H), 1.35 (s, 9H), 0.47 (d,  $J = 1.6$  Hz, 6H).

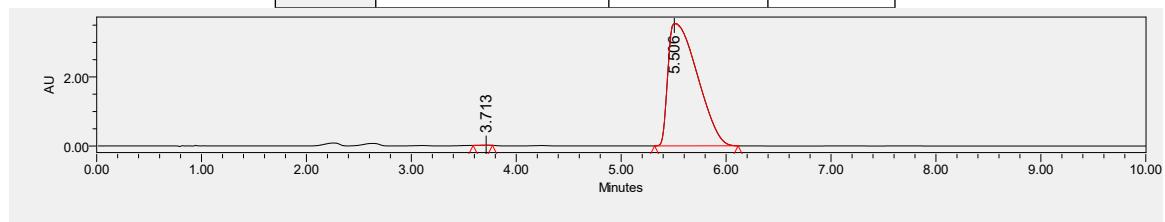
**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.4, 161.1, 148.5, 136.5, 136.2, 132.9, 130.2, 128.9, 128.2, 127.7, 126.3, 83.2, 72.0, 32.1, 28.2, -5.1, -5.2.

**ESI-HRMS:** calcd for  $\text{C}_{24}\text{H}_{29}^{35}\text{ClNO}_4\text{Si}^+$  ( $[\text{M} + \text{H}]^+$ ) = 458.1549, found: 458.1546.  $\text{C}_{24}\text{H}_{29}^{37}\text{ClNO}_4\text{Si}^+$  ( $[\text{M} + \text{H}]^+$ ) = 460.1519, found: 460.1519.

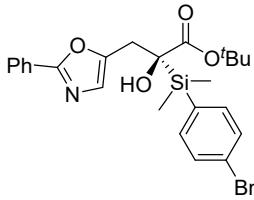
**IR** (neat): 2976, 1711, 1577, 1484, 1369, 1252, 1154, 1083, 955, 835, 806, 781, 712, 691  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	3.743	11589790	50.00
2	5.806	11589488	50.00



Entry	Retention Time	Area	% Area
1	3.713	37005	0.05
2	5.506	68879175	99.95



**Tert-butyl (R)-2-((4-bromophenyl)dimethylsilyl)-2-hydroxy-3-(2-phenyloxazol-5-yl)propanoate (C10)**

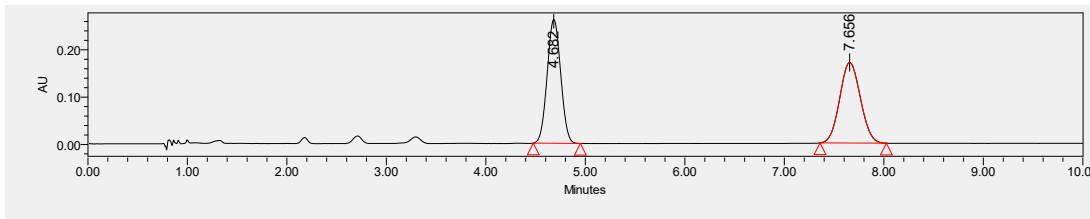
(C<sub>24</sub>H<sub>28</sub>BrNO<sub>4</sub>Si) 41.7 mg, 83% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>365</sub><sup>25</sup> = -12.6 (c = 0.46, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 4.63 min, tr (major) = 7.44 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.99 – 7.91 (m, 2H), 7.56 – 7.45 (m, 4H), 7.44 – 7.37 (m, 3H), 6.91 (s, 1H), 3.37 – 3.18 (m, 2H), 3.10 (d, *J* = 15.2 Hz, 1H), 1.35 (s, 9H), 0.46 (s, 6H).

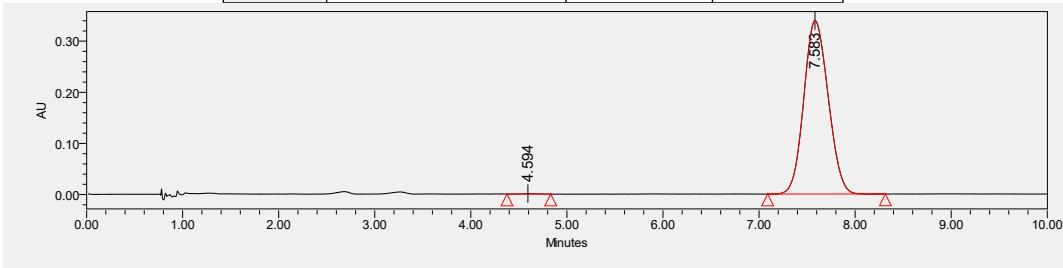
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.4, 161.1, 148.5, 136.4, 133.4, 131.2, 130.2, 128.9, 127.7, 126.3, 126.3, 125.1, 83.2, 72.0, 32.1, 28.2, -5.2, -5.3.

**ESI-HRMS:** calcd for C<sub>24</sub>H<sub>29</sub><sup>79</sup>BrNO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 502.1044, found: 502.1041. C<sub>24</sub>H<sub>29</sub><sup>81</sup>BrNO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 504.1023, found: 504.1021.

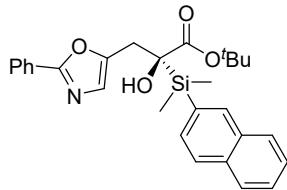
**IR** (neat): 2923, 2360, 1713, 1572, 1370, 1252, 1370, 1154, 1067, 1011, 834, 804, 782, 713, 691 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	4.682	2470448	50.14
2	7.656	2456173	49.86



Entry	Retention Time	Area	% Area
1	4.594	8824	0.15
2	7.583	5981474	99.85



**Tert-butyl (R)-2-(dimethyl(naphthalen-2-yl)silyl)-2-hydroxy-3-(2-phenyloxazol-5-yl)propanoate (C11)**

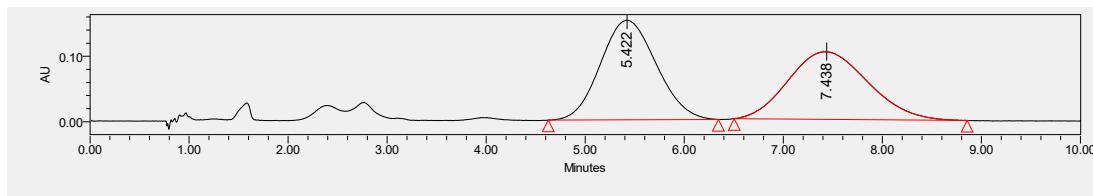
( $\text{C}_{28}\text{H}_{31}\text{NO}_4\text{Si}$ ) 38.8 mg, 82% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{24} = -5.1$  ( $c = 0.97$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiraldak **AY-3**,  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm), retention time: tr (major) = 7.50 min, tr (minor) = 5.14 min.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.07 (m, 1H), 8.00 – 7.91 (m, 2H), 7.89 – 7.81 (m, 3H), 7.71 (dd,  $J = 8.4, 1.2$  Hz, 1H), 7.55 – 7.48 (m, 2H), 7.42 – 7.36 (m, 3H), 6.92 (s, 1H), 3.38 – 3.25 (m, 2H), 3.17 (d,  $J = 15.6$  Hz, 1H), 1.33 (s, 9H), 0.58 (d,  $J = 2.4$  Hz, 6H).

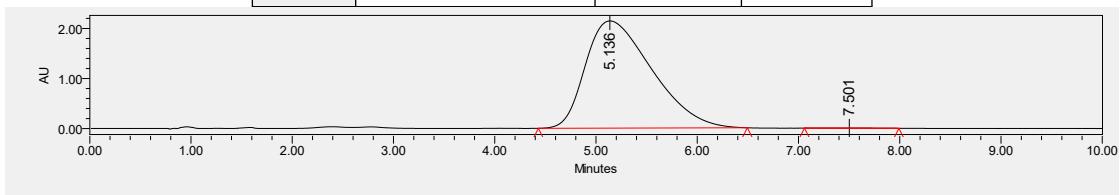
**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.6, 161.0, 148.8, 135.9, 134.2, 132.9, 132.1, 130.7, 130.1, 128.8, 128.3, 127.9, 127.7, 127.2, 126.9, 126.2, 126.2, 83.0, 72.3, 32.1, 28.2, -5.1, -5.2.

**ESI-HRMS:** calcd for  $\text{C}_{28}\text{H}_{32}\text{NO}_4\text{Si}^+ ([\text{M} + \text{H}]^+) = 474.2095$ , found: 474.2092.

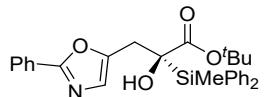
**IR** (neat): 2975, 1708, 1592, 1548, 1482, 1368, 1250, 1154, 1085, 953, 857, 806, 780, 743, 712, 691  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	5.422	5953886	50.83
2	7.438	5759733	49.17



Entry	Retention Time	Area	% Area
1	5.136	97536583	99.93
2	7.501	73112	0.07



**Tert-butyl (R)-2-hydroxy-2-(methyldiphenylsilyl)-3-(2-phenyloxazol-5-yl)propanoate (C12)**

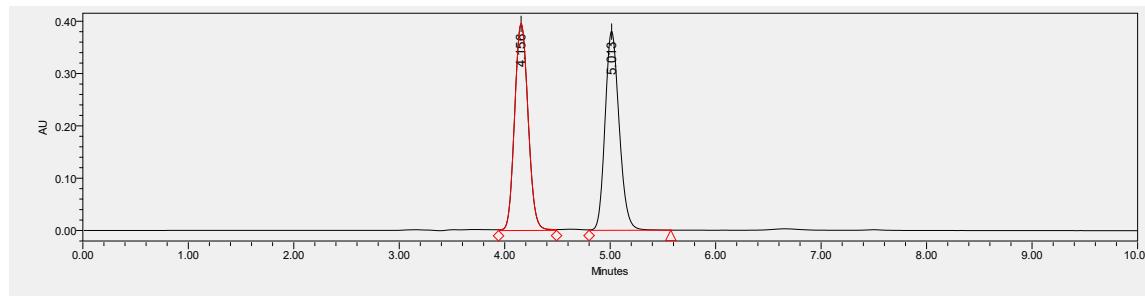
( $\text{C}_{29}\text{H}_{31}\text{NO}_4\text{Si}$ ) 35.6 mg, 73% yield, 29% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{23} = +2.6$  ( $c = 0.89$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in *i*-PrOH for HPLC (Daicel Chiralcel **OZH**, *i*-PrOH/*n*-hexane = 20/80, flow rate = 1.0 mL/min,  $\lambda = 254$  nm), retention time: tr (major) = 5.02 min, tr (minor) = 4.16 min.

**$^1\text{H NMR}$**  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 – 7.89 (m, 2H), 7.78 – 7.70 (m, 4H), 7.45 – 7.37 (m, 9H), 6.91 (s, 1H), 3.42 (s, 1H), 3.38 (d,  $J = 10.4$  Hz, 1H), 3.26 (d,  $J = 10.4$  Hz, 1H), 1.21 (s, 9H), 0.80 (s, 3H).

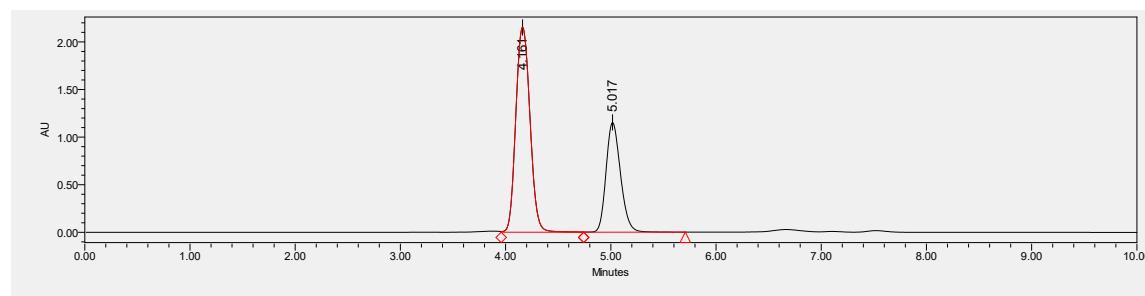
**$^{13}\text{C NMR}$**  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  175.4, 161.1, 148.5, 135., 133.4, 133.0, 130.2, 130.1, 128.8, 128.1, 128.1, 127.7, 126.4, 126.3, 83.2, 72.6, 32.9, 27.9, -5.5.

**ESI-HRMS:** calcd for  $\text{C}_{29}\text{H}_{32}\text{NO}_4\text{Si}^+ ([\text{M} + \text{H}]^+) = 486.2095$ , found: 486.2094.

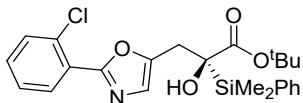
**IR** (neat): 2917, 1745, 1549, 1483, 1428, 1368, 1255, 1118, 793, 736, 698  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	4.156	3514660	49.93
2	5.013	3524187	50.07



Entry	Retention Time	Area	% Area
1	4.161	20142056	64.71
2	5.017	10985070	35.29



**Tert-butyl (R)-3-(2-(2-chlorophenyl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C13)**

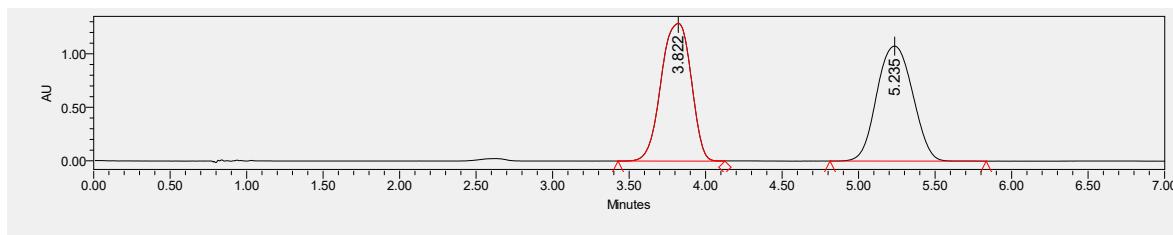
(C<sub>24</sub>H<sub>28</sub>ClNO<sub>4</sub>Si) 34.8 mg, 76% yield, 96% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>27</sup> = -12.5 (c = 0.87, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 3.95 min, tr (major) = 5.19 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.81 (m, 1H), 7.65 – 7.59 (m, 2H), 7.49 – 7.44 (m, 1H), 7.42 – 7.34 (m, 3H), 7.34 – 7.27 (m, 2H), 7.00 (s, 1H), 3.30 (d, *J* = 15.6 Hz, 1H), 3.24 (s, 1H), 3.14 (d, *J* = 15.2 Hz, 1H), 1.30 (s, 9H), 0.48 (d, *J* = 5.2 Hz, 6H).

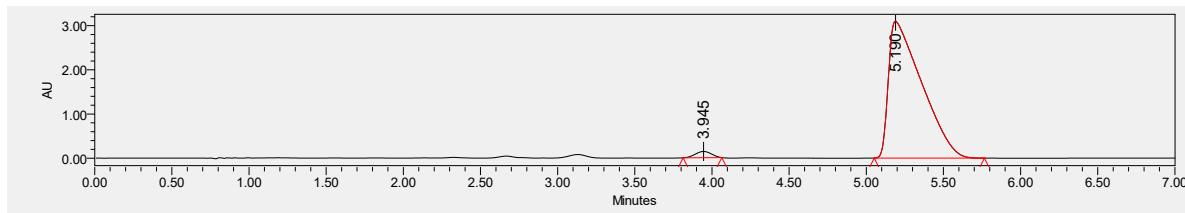
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.4, 149.1, 134.7, 134.4, 132.2, 131.1, 130.7, 129.9, 127.8, 126.7, 126.0, 82.9, 72.0, 31.9, 27.9, -5.4, -5.4.

**ESI-HRMS:** calcd for C<sub>24</sub>H<sub>29</sub><sup>35</sup>ClNO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 458.1549, found: 458.1546. C<sub>24</sub>H<sub>29</sub><sup>37</sup>ClNO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 459.1582, found: 459.1573.

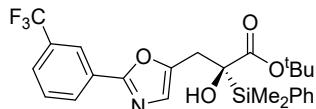
**IR** (neat): 2975, 1707, 1474, 1428, 1368, 1250, 1155, 1114, 1066, 955, 835, 811, 783, 736, 701, 654 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	3.822	17464410	50.16
2	5.235	17354240	49.84



Entry	Retention Time	Area	% Area
1	3.945	1030393	2.18
2	5.190	46138656	97.82



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-(trifluoromethyl)phenyl)oxazol-5-ylpropanoate (C14)**

( $\text{C}_{25}\text{H}_{28}\text{F}_3\text{NO}_4\text{Si}$ ) 42.8 mg, 87% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{24} = -1.9$  ( $c = 1.07$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in *i*-PrOH for HPLC (Daicel Chiralcel **OZH**, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1.0 mL/min,  $\lambda = 254$  nm), retention time: tr (minor) = 4.35 min, tr (major) = 5.14 min.

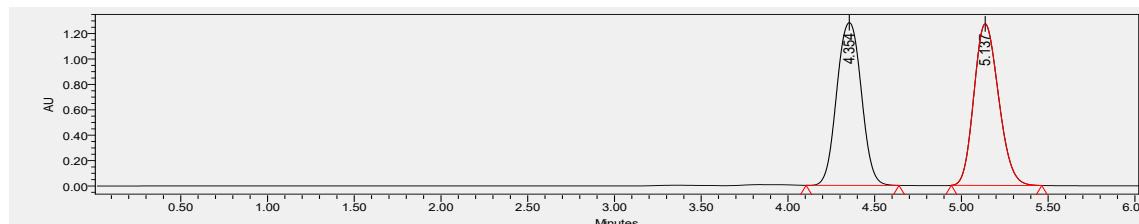
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 – 8.17 (m, 1H), 8.14 (d,  $J = 7.6$  Hz, 1H), 7.69 – 7.59 (m, 3H), 7.54 (t,  $J = 7.6$  Hz, 1H), 7.45 – 7.31 (m, 3H), 6.95 (s, 1H), 3.30 (d,  $J = 15.2$  Hz, 1H), 3.21 (s, 1H), 3.14 (d,  $J = 15.6$  Hz, 1H), 1.35 (s, 9H), 0.49 (d,  $J = 3.2$  Hz, 6H).

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.6, 159.7, 149.6, 134.8, 134.4, 131.3, 130.1, 129.5, 129.3, 128.5, 128.0, 126.6, 126.6 (dd,  $J = 7.5, 3.7$  Hz), 123.1 (dd,  $J = 7.9, 4.0$  Hz), 122.6, 83.1, 72.0, 32.0, 28.2, -5.3, -5.3.

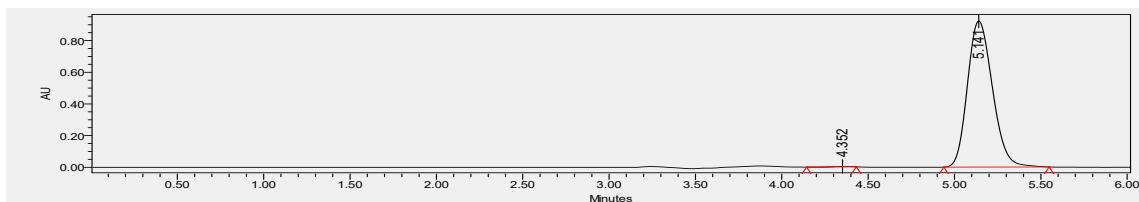
**$^{19}\text{F NMR}$**  (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.89.

**ESI-HRMS:** calcd for  $\text{C}_{25}\text{H}_{29}\text{F}_3\text{NO}_4\text{Si}^+$  ( $[\text{M} + \text{H}]^+$ ) = 492.1812, found: 492.1808.

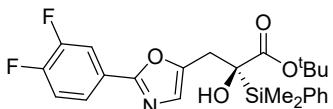
**IR** (neat): 2076, 1712, 1426, 1369, 1325, 1250, 1155, 1126, 1066, 957, 835, 808, 783, 697, 654  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	4.354	12605323	50.11
2	5.137	12551818	49.89



Entry	Retention Time	Area	% Area
1	4.352	22349	0.24
2	5.141	9270575	99.76



**Tert-butyl (R)-3-(2-(3,4-difluorophenyl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C15)**

(C<sub>24</sub>H<sub>27</sub>F<sub>2</sub>NO<sub>4</sub>Si) 39.5 mg, 86% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>26</sup> = -9.0 (c = 0.99, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiralcel OZ-3, CO<sub>2</sub>/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 2.83 min, tr (major) = 4.08 min.

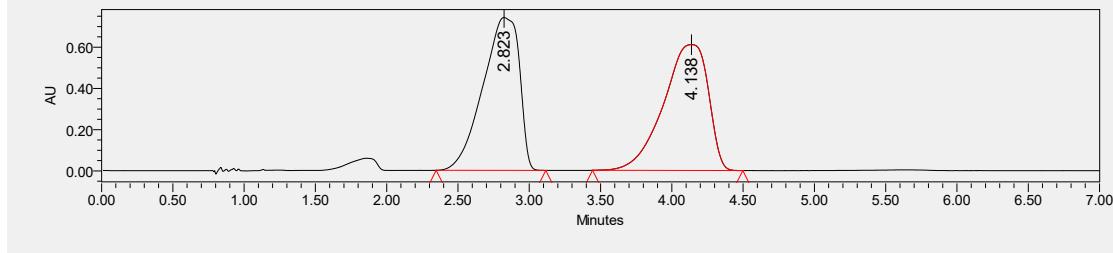
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 – 7.72 (m, 1H), 7.71 – 7.66 (m, 1H), 7.65 – 7.57 (m, 2H), 7.48 – 7.33 (m, 3H), 7.24 – 7.14 (m, 1H), 6.90 (s, 1H), 3.27 (d, *J* = 15.6 Hz, 1H), 3.21 (s, 1H), 3.12 (d, *J* = 15.6 Hz, 1H), 1.33 (s, 9H), 0.48 (d, *J* = 4.4 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.6, 159.1, 152.8 (d, *J* = 13.0 Hz), 151.9 (d, *J* = 13.1 Hz), 150.4 (d, *J* = 12.7 Hz), 149.5, 134.8, 134.4, 130.1, 128.0, 126.4, 122.7 (dd, *J* = 7.0, 3.8 Hz), 118.0 (d, *J* = 18.2 Hz), 115.5 (d, *J* = 19.6 Hz), 83.0, 72.1, 32.0, 28.2, -5.3, -5.3.

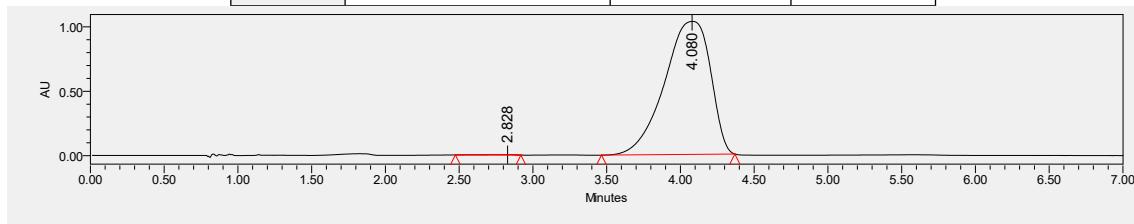
<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -134.88 (d, *J* = 22.0 Hz), -136.68 (d, *J* = 22.0 Hz).

ESI-HRMS: calcd for C<sub>24</sub>H<sub>28</sub>F<sub>2</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 460.1750, found: 460.1748.

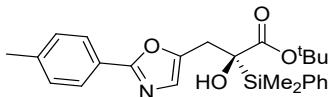
IR (neat): 2923, 1713, 1560, 1510, 1443, 1369, 1254, 1155, 1114, 1071, 961, 834, 776, 701 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	2.823	13221097	49.80
2	4.138	13327646	50.20



Entry	Retention Time	Area	% Area
1	2.828	56369	0.25
2	4.080	22415741	99.75



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-(p-tolyl)oxazol-5-yl)propanoate (C16)**

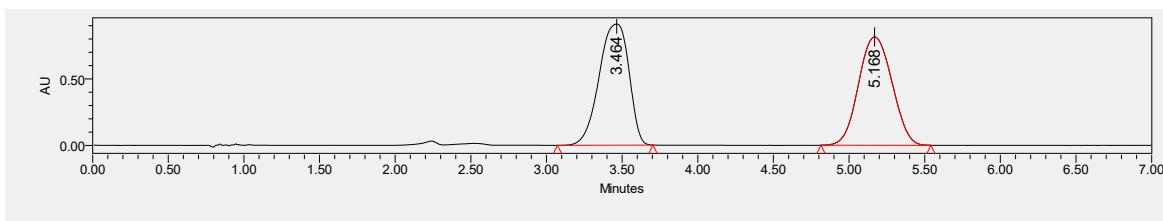
(C<sub>25</sub>H<sub>31</sub>NO<sub>4</sub>Si) 37.6 mg, 86% yield, 98% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>25</sup> = -8.7 (c = 0.94, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiralcel OZ-3, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 3.57 min, tr (major) = 4.98 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.67 – 7.57 (m, 2H), 7.45 – 7.34 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 2H), 6.89 (s, 1H), 3.27 (d, *J* = 15.2 Hz, 1H), 3.21 (s, 1H), 3.12 (d, *J* = 15.2 Hz, 1H), 2.38 (s, 3H), 1.32 (s, 9H), 0.48 (d, *J* = 6.8 Hz, 6H).

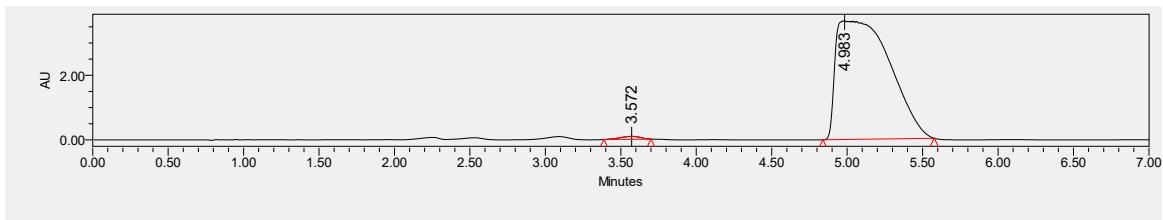
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.6, 161.2, 148.4, 140.3, 134.8, 134.6, 130.0, 129.5, 128.0, 126.2, 126.0, 125.1, 82.9, 72.1, 32.0, 28.2, 21.6, -5.2, -5.3.

ESI-HRMS: calcd for C<sub>25</sub>H<sub>32</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 438.2095, found: 438.2090.

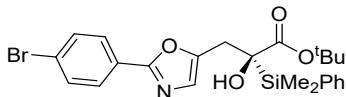
IR (neat): 2975, 1708, 1498, 1427, 1368, 1250, 1155, 1117, 1069, 955, 827, 783, 734, 701, 648 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	3.464	12457869	49.93
2	5.168	12494010	50.07



Entry	Retention Time	Area	% Area
1	3.572	838804	0.90
2	4.983	91868787	99.10



**Tert-butyl (R)-3-(2-(4-bromophenyl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C17)**

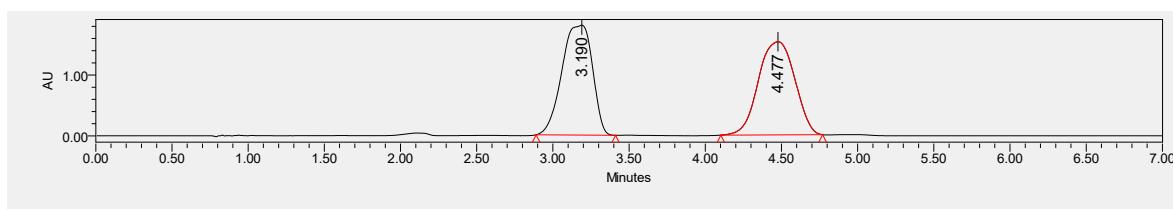
( $\text{C}_{24}\text{H}_{28}\text{BrNO}_4\text{Si}$ ) 44.2 mg, 88% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{25} = -9.0$  ( $c = 1.10$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**,  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm), retention time: tr (minor) = 3.25 min, tr (major) = 4.60 min.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 – 7.76 (m, 2H), 7.69 – 7.58 (m, 2H), 7.57 – 7.49 (m, 2H), 7.46 – 7.33 (m, 3H), 6.91 (s, 1H), 3.27 (d,  $J = 15.6$  Hz, 1H), 3.22 (s, 1H), 3.12 (d,  $J = 15.2$  Hz, 1H), 1.32 (s, 9H), 0.48 (d,  $J = 4.8$  Hz, 6H).

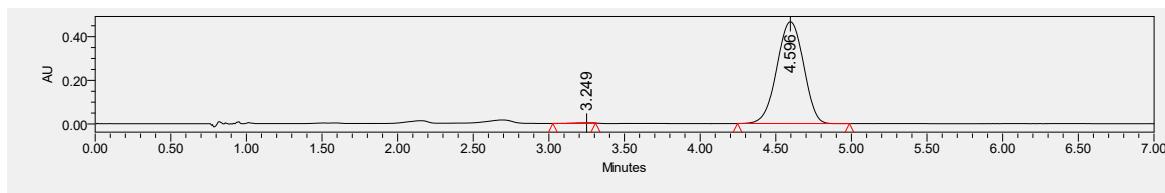
**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 160.1, 149.2, 134.8, 134.5, 132.1, 130.1, 128.0, 127.7, 126.7, 126.3, 124.5, 83.0, 72.1, 32.0, 28.2, -5.3, -5.3.

**ESI-HRMS:** calcd for  $\text{C}_{24}\text{H}_{29}^{79}\text{BrNO}_4\text{Si}^+ ([M + H]^+) = 502.1044$ , found: 502.1041.  $\text{C}_{24}\text{H}_{29}^{81}\text{BrNO}_4\text{Si}^+ ([M + H]^+) = 504.1023$ , found: 504.1022.

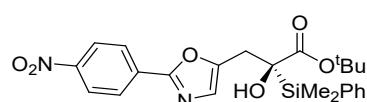
**IR** (neat): 2975, 1710, 1604, 1479, 1427, 1401, 1368, 1250, 1154, 1071, 955, 834, 783, 733, 700  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	3.190	25172390	49.77
2	4.477	25400224	50.23



Entry	Retention Time	Area	% Area
1	3.249	8586	0.15
2	4.596	5713714	99.85



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-(4-nitrophenyl)oxazol-5-yl)propanoate (C18)**

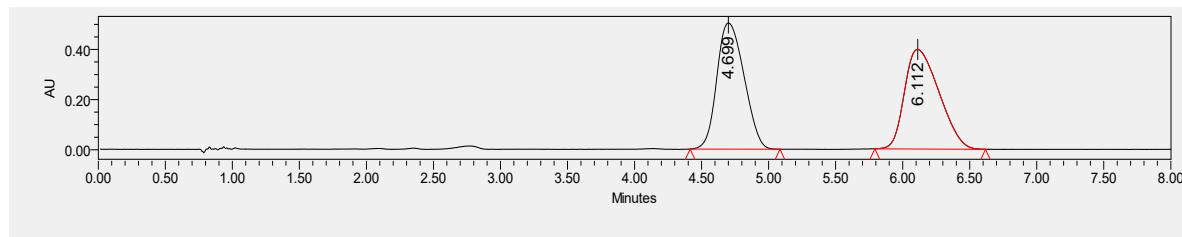
(C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub>Si) 38.9 mg, 83% yield, 98% ee; Light yellow solid, mp: 107–111 °C; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>25</sup> = -13.1 (c = 0.97, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in i-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 4.77 min, tr (major) = 5.99 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.32 – 8.22 (m, 2H), 8.14 – 8.15 (m, 2H), 7.66 – 7.58 (m, 2H), 7.47 – 7.33 (m, 3H), 7.03–6.97 (m, 1H), 3.30 (d, J = 15.2 Hz, 1H), 3.23 (s, 1H), 3.15 (d, J = 15.6 Hz, 1H), 1.34 (s, 9H), 0.49 (d, J = 2.4 Hz, 6H).

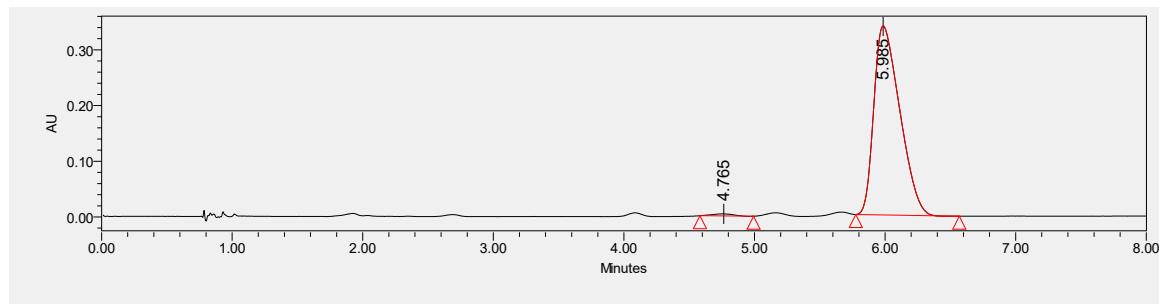
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.5, 158.9, 150.8, 148.5, 134.8, 134.3, 133.1, 130.2, 128.0, 127.2, 126.9, 124.3, 83.2, 72.1, 32.0, 28.2, -5.3, -5.3.

**ESI-HRMS:** calcd for C<sub>24</sub>H<sub>29</sub>N<sub>2</sub>O<sub>6</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 469.1789, found: 469.1786.

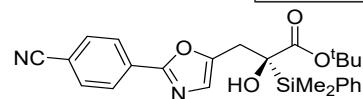
**IR** (neat): 2975, 1709, 1520, 1427, 1337, 1251, 1154, 1110, 1063, 955, 836, 811, 784, 737, 714 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	4.699	7100273	50.03
2	6.112	7091262	49.97



Entry	Retention Time	Area	% Area
1	4.765	40933	0.87
2	5.985	4680981	99.13



**Tert-butyl (R)-3-(2-(4-cyanophenyl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C19)**

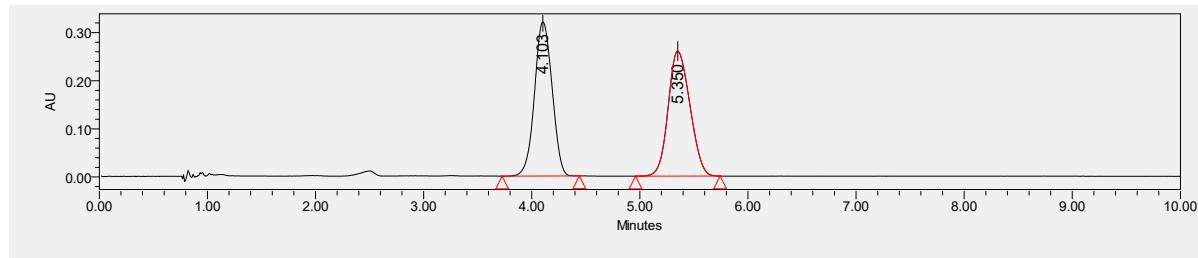
(C<sub>25</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>Si) 42.6 mg, 95% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>24</sup> = -8.4 (c = 1.06, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 4.16 min, tr (major) = 5.34 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.08 – 8.00 (m, 2H), 7.74 – 7.67 (m, 2H), 7.66 – 7.57 (m, 2H), 7.45 – 7.34 (m, 3H), 6.99 – 6.95 (m, 1H), 3.29 (d, *J* = 15.6 Hz, 1H), 3.21 (s, 1H), 3.14 (d, *J* = 15.6 Hz, 1H), 1.33 (s, 9H), 0.48 (d, *J* = 2.8 Hz, 6H).

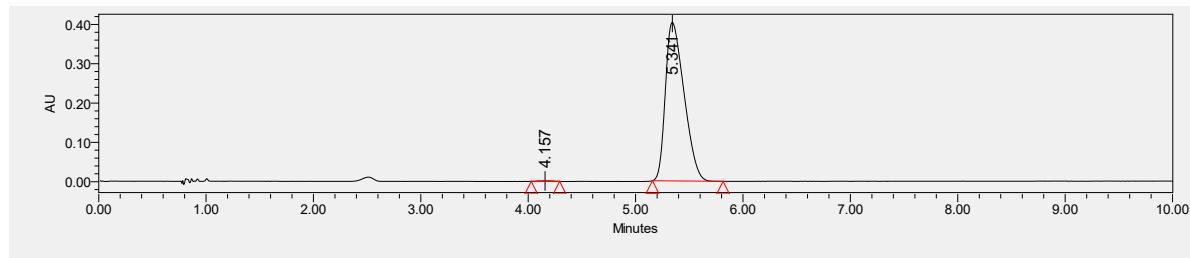
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.5, 159.2, 150.4, 134.8, 134.4, 132.7, 131.5, 130.1, 128.0, 127.0, 126.6, 118.6, 113.4, 83.1, 72.2, 32.0, 28.2, -5.3, -5.3.

**ESI-HRMS:** calcd for C<sub>25</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 449.1891, found: 449.1889.

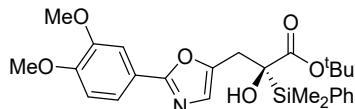
**IR** (neat): 2976, 2228, 1711, 1592, 1490, 1427, 1369, 1251, 1155, 1069, 840, 784, 740, 702, 552 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	4.103	3617325	49.92
2	5.350	3629564	50.08



Entry	Retention Time	Area	% Area
1	4.157	9321	0.19
2	5.341	4860305	99.81



**Tert-butyl (R)-3-(2-(3,4-dimethoxyphenyl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C20)**

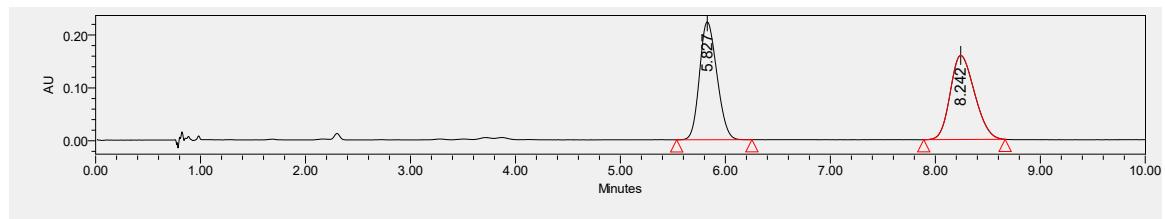
(C<sub>26</sub>H<sub>33</sub>NO<sub>6</sub>Si) 44.0 mg, 91% yield, 99% ee; Light yellow solid, mp: 78-82 °C; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 2:1). [α]<sub>436</sub><sup>26</sup> = -2.4 (c = 1.20, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in i-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 5.84 min, tr (major) = 8.20 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.59 (m, 2H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 7.48 (d, J = 2.0 Hz, 1H), 7.45 – 7.34 (m, 3H), 6.90 (s, 1H), 6.88 (s, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.28 (d, J = 15.6 Hz, 1H), 3.21 (s, 1H), 3.12 (d, J = 15.6 Hz, 1H), 1.33 (s, 9H), 0.49 (d, J = 6.4 Hz, 6H).

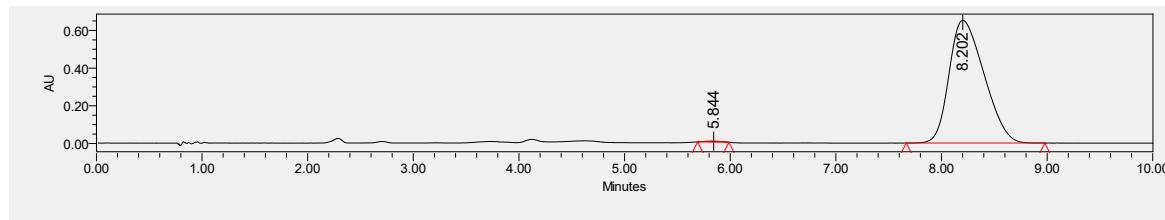
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.6, 161.1, 150.8, 149.2, 148.3, 134.8, 134.6, 130.1, 128.0, 126.0, 120.8, 119.4, 111.1, 109.0, 82.9, 72.1, 56.2, 56.1, 32.1, 28.2, -5.2, -5.3.

**ESI-HRMS:** calcd for C<sub>26</sub>H<sub>34</sub>NO<sub>6</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 484.2150, found: 484.2148.

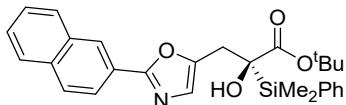
**IR** (neat): 2971, 1717, 1603, 1553, 1502, 1425, 1368, 1269, 1248, 1152, 1025, 813, 784, 702, 646 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	5.827	2573439	50.16
2	8.242	2557072	49.84



Entry	Retention Time	Area	% Area
1	5.844	53583	0.36
2	8.202	14951457	99.64



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-(naphthalen-2-yl)oxazol-5-yl)propanoate (C21)**

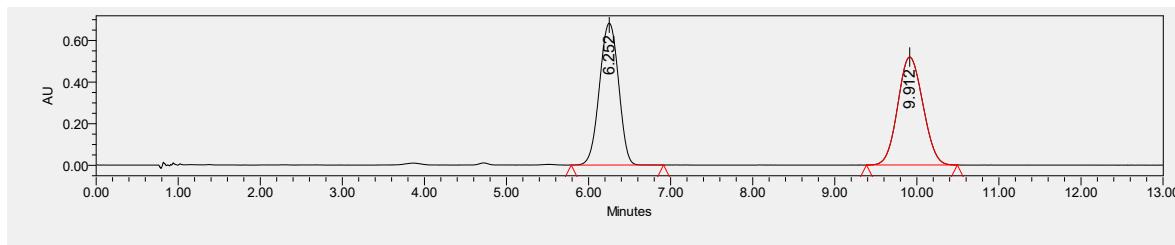
( $\text{C}_{28}\text{H}_{31}\text{NO}_4\text{Si}$ ) 39.3 mg, 83% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{25} = -3.6$  ( $c = 0.98$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**,  $\text{CO}_2/\text{MeOH} = 90/10$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm), retention time: tr (minor) = 6.24 min, tr (major) = 9.73 min.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 (s, 1H), 8.06 (dd,  $J = 8.4, 1.6$  Hz, 1H), 7.92 – 7.86 (m, 2H), 7.86 – 7.81 (m, 1H), 7.70 – 7.60 (m, 2H), 7.56 – 7.48 (m, 2H), 7.46 – 7.34 (m, 3H), 6.97 (s, 1H), 3.33 (d,  $J = 15.6$  Hz, 1H), 3.26 (s, 1H), 3.17 (d,  $J = 15.2$  Hz, 1H), 1.35 (s, 9H), 0.50 (d,  $J = 5.6$  Hz, 6H).

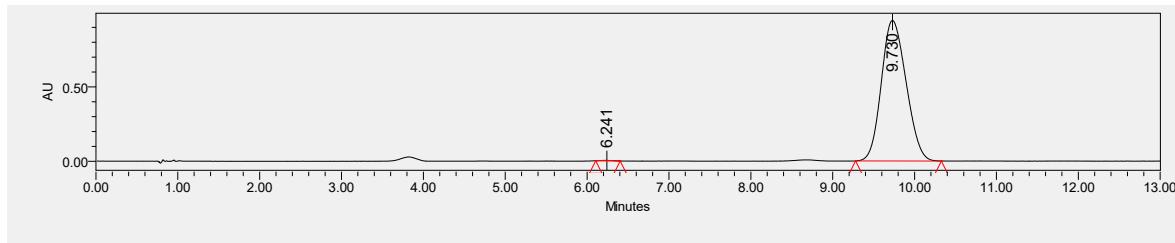
**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.6, 161.2, 149.0, 134.8, 134.6, 134.1, 133.2, 130.1, 128.8, 128.7, 128.0, 127.2, 126.8, 126.4, 126.0, 125.1, 123.4, 83.0, 72.2, 32.1, 28.2, -5.2, -5.3.

**ESI-HRMS:** calcd for  $\text{C}_{28}\text{H}_{32}\text{NO}_4\text{Si}^+ ([\text{M} + \text{H}]^+) = 474.2095$ , found: 474.2095.

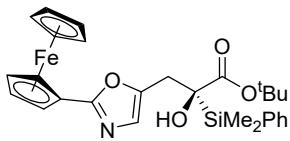
**IR** (neat): 2924, 1712, 1592, 1459, 1369, 1252, 1155, 1118, 1070, 960, 834, 784, 754, 701  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	6.252	11003093	49.99
2	9.912	11006018	50.01



Entry	Retention Time	Area	% Area
1	6.241	31313	0.16
2	9.730	19841325	99.84



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-(Ferrocene)oxazol-5-yl)propanoate (C22)**

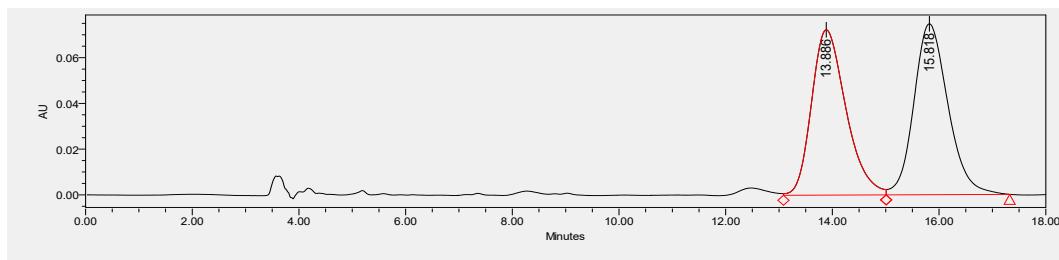
(C<sub>28</sub>H<sub>33</sub>FeNO<sub>4</sub>Si) 47.8 mg, 90% yield, 99% ee; Brown yellow oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 5:1). [α]<sub>365</sub><sup>25</sup> = -19.7 (c = 0.21, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for HPLC (Daicel Chiralcel OZH, *i*-PrOH/n-hexane = 15/85, flow rate = 1.0 mL/min, λ = 254 nm), retention time: tr (minor) = 13.84 min, tr (major) = 15.47 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69-7.60 (m, 2H), 7.46-7.34 (m, 3H), 6.77 (s, 1H), 4.82 (d, *J* = 6.4 Hz, 2H), 4.36-4.31 (m, 2H), 4.12 (s, 5H), 3.30-3.15 (m, 2H), 3.08 (d, *J* = 15.2 Hz, 1H), 1.37 (s, 9H), 0.49 (d, *J* = 8.0 Hz, 6H).

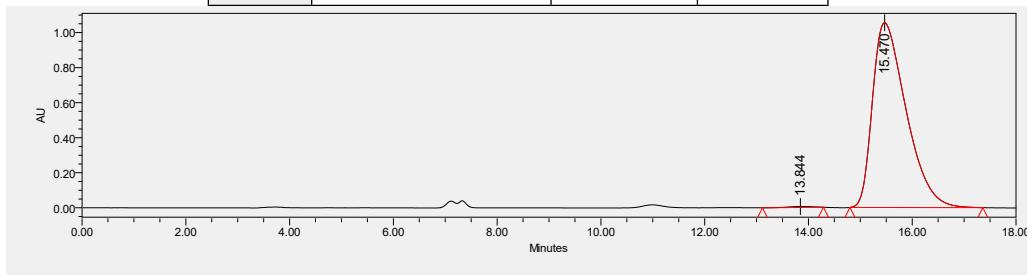
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 163.0, 147.5, 134.8, 134.7, 130.0, 128.0, 125.9, 82.8, 72.0, 71.4, 70.0, 70.0, 69.7, 67.4, 67.4, 32.1, 28.3, -5.2, -5.2.

ESI-HRMS: calcd for C<sub>28</sub>H<sub>34</sub>FeNO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 532.1601, found: 532.1604.

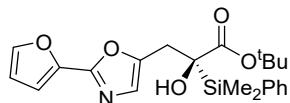
IR (neat): 2974, 1707, 1584, 1426, 1369, 1249, 1154, 1119, 1064, 957, 811, 700, 642 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	13.886	3232057	49.34
2	15.818	3319158	50.66



Entry	Retention Time	Area	% Area
1	13.844	177704	0.37
2	15.470	47418241	99.63



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-3-(2-(furan-2-yl)oxazol-5-yl)-2-hydroxypropanoate (C23)**

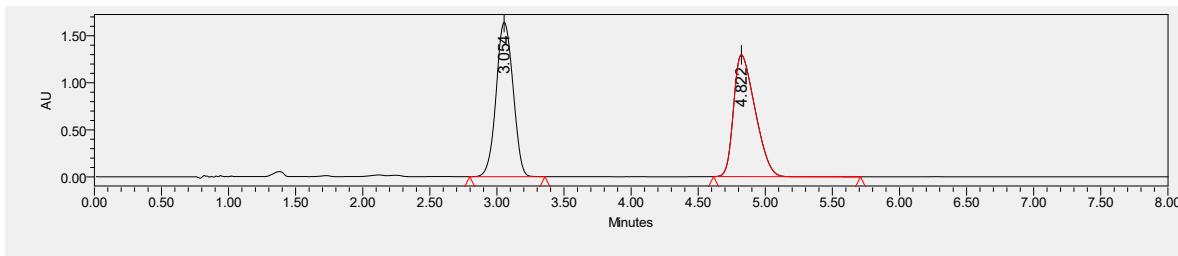
(C<sub>22</sub>H<sub>27</sub>NO<sub>5</sub>Si) 33.0 mg, 80% yield, 98% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 4:1). [α]<sub>D</sub><sup>25</sup> = -4.8 (c = 0.67, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiralcel OZ-3, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 3.10 min, tr (major) = 4.90 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.58 (m, 2H), 7.52 – 7.47 (m, 1H), 7.44 – 7.32 (m, 3H), 6.95 – 6.82 (m, 2H), 6.49 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.26 (d, *J* = 15.6 Hz, 1H), 3.18 (s, 1H), 3.09 (d, *J* = 15.6 Hz, 1H), 1.35 (s, 9H), 0.47 (d, *J* = 4.0 Hz, 6H).

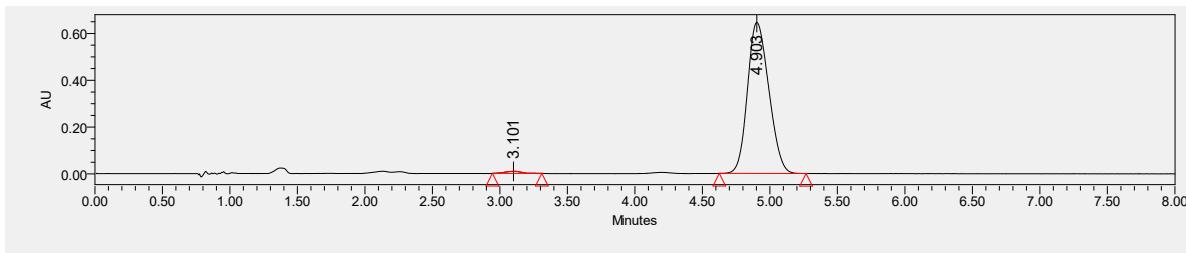
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.5, 153.9, 148.3, 144.1, 143.3, 134.8, 134.5, 130.1, 128.0, 126.1, 111.9, 110.8, 83.1, 72.0, 31.9, 28.1, -5.3, -5.3.

**ESI-HRMS:** calcd for C<sub>22</sub>H<sub>28</sub>NO<sub>5</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 414.1731, found: 414.1727.

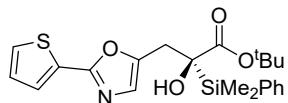
**IR** (neat): 2976, 1708, 1534, 1455, 1369, 1252, 1155, 1117, 1011, 955, 835, 812, 784, 740, 702 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	3.054	14382942	50.01
2	4.822	14377393	49.99



Entry	Retention Time	Area	% Area
1	3.101	74924	1.05
2	4.903	7084825	98.95



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-(thiophen-2-yl)oxazol-5-yl)propanoate (C24)**

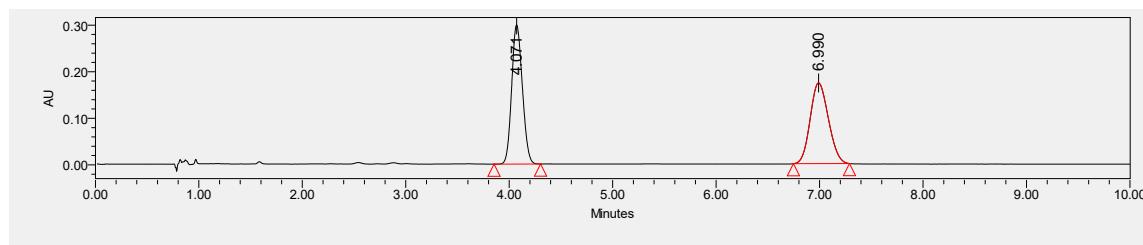
(C<sub>22</sub>H<sub>27</sub>NO<sub>4</sub>SSi) 32.7 mg, 76% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>25</sup> = -1.4 (c = 0.83, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 4.03 min, tr (major) = 6.82 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.60 (m, 2H), 7.55 (dd, *J* = 4.0, 1.6 Hz, 1H), 7.42 – 7.34 (m, 4H), 7.06 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.88 – 6.83 (m, 1H), 3.26 (d, *J* = 15.2 Hz, 1H), 3.19 (s, 1H), 3.09 (d, *J* = 15.6 Hz, 1H), 1.34 (s, 9H), 0.48 (d, *J* = 4.8 Hz, 6H).

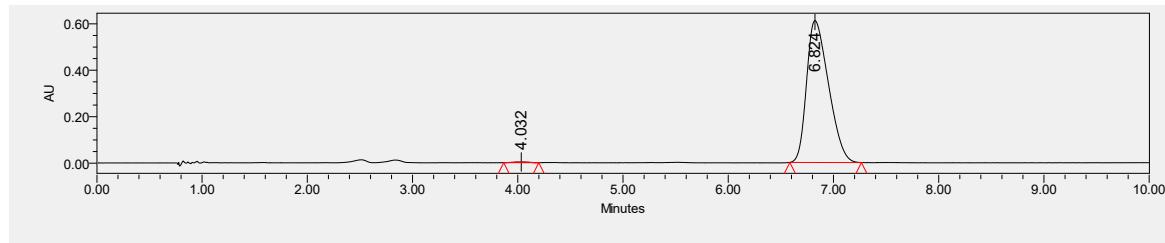
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.5, 157.2, 148.2, 134.8, 134.5, 130.4, 130.1, 128.0, 127.9, 127.3, 126.2, 83.0, 72.0, 32.0, 28.2, -5.2, -5.3.

**ESI-HRMS:** calcd for C<sub>22</sub>H<sub>28</sub>NO<sub>4</sub>SSi<sup>+</sup> ([M + H]<sup>+</sup>) = 430.1503, found: 430.1504.

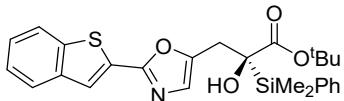
**IR** (neat): 2976, 1709, 1596, 1426, 1369, 1249, 1155, 1117, 1066, 954, 836, 811, 784, 724, 702 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	4.071	2143798	50.33
2	6.990	2116017	49.67



Entry	Retention Time	Area	% Area
1	4.032	27655	0.31
2	6.824	8824815	99.69



**Tert-butyl (R)-3-(2-(benzo[b]thiophen-2-yl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C25)**

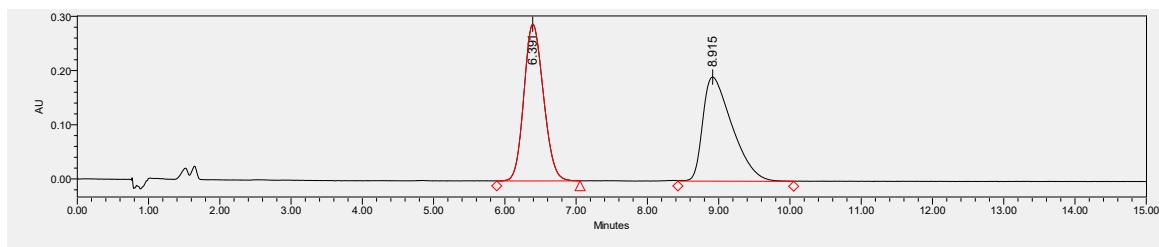
( $\text{C}_{26}\text{H}_{30}\text{NO}_4\text{SSi}$ ) 43.2 mg, 90% yield, 99% ee; white solid; mp: 94–98 °C;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{25} = +0.9$  ( $c = 1.08$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralpak **AD-3**,  $\text{CO}_2/\text{MeOH} = 80/20$ , flow rate = 1.5 mL/min,  $\lambda = 254 \text{ nm}$ ), retention time: tr (major) = 6.61 min, tr (minor) = 9.41 min.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.82 (m, 1H), 7.81 – 7.77 (m, 2H), 7.66 – 7.60 (m, 2H), 7.43 – 7.34 (m, 5H), 6.94 (s, 1H), 3.30 (d,  $J = 15.6 \text{ Hz}$ , 1H), 3.24 (s, 1H), 3.13 (d,  $J = 15.2 \text{ Hz}$ , 1H), 1.36 (s, 9H), 0.50 (d,  $J = 4.0 \text{ Hz}$ , 6H).

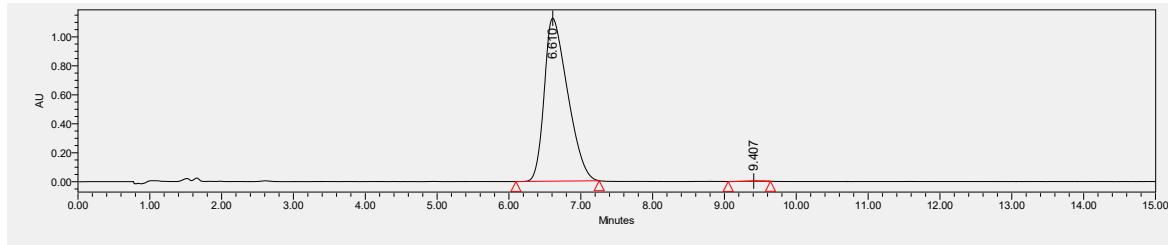
**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 157.1, 149.2, 140.4, 139.7, 134.8, 134.5, 130.1, 130.0, 128.0, 126.6, 125.8, 125.0, 124.6, 123.8, 122.6, 83.1, 72.1, 32.0, 28.2, -5.3, -5.3.

**ESI-HRMS:** calcd for  $\text{C}_{26}\text{H}_{30}\text{NO}_4\text{SSi}^+ ([\text{M} + \text{H}]^+) = 480.1659$ , found: 480.1657.

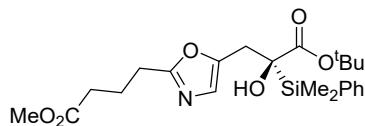
**IR** (neat): 2975, 1709, 1598, 1456, 1368, 1252, 1155, 1116, 1068, 835, 811, 784, 747, 702  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	6.391	5507392	50.05
2	8.915	5497137	49.95



Entry	Retention Time	Area	% Area
1	6.610	25392529	99.87
2	9.407	34184	0.13



**Methyl (R)-4-(5-(3-(tert-butoxy)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-oxopropyl)oxazol-2-yl)butanoate (C26)**

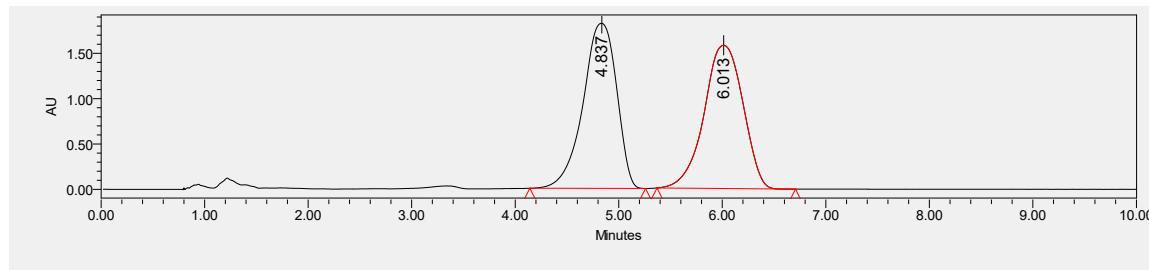
( $\text{C}_{23}\text{H}_{33}\text{NO}_6\text{Si}$ ) 21.9 mg, 49% yield, 88% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4:1).  $[\alpha]_D^{23} = -16.1$  ( $c = 0.36$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in  $i\text{-PrOH}$  for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**,  $\text{CO}_2/\text{MeOH} = 95/5$ , flow rate = 1.5 mL/min,  $\lambda = 210$  nm), retention time:  $\text{tr}$  (minor) = 4.67 min,  $\text{tr}$  (major) = 5.82 min.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.52 (m, 2H), 7.44 – 7.32 (m, 3H), 6.72–6.61 (m, 1H), 3.65 (s, 3H), 3.20–3.10 (m, 2H), 2.99 (d,  $J = 15.2$  Hz, 1H), 2.71 (t,  $J = 7.2$  Hz, 2H), 2.37 (t,  $J = 7.6$  Hz, 2H), 2.08–1.98 (m, 2H), 1.34 (s, 9H), 0.45 (d,  $J = 5.6$  Hz, 6H).

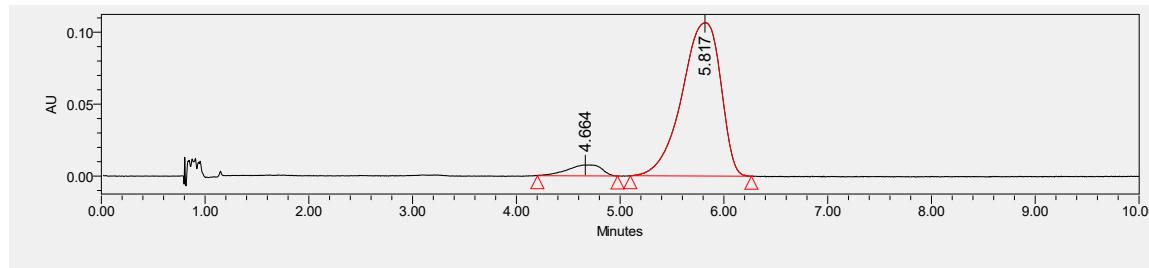
**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.6, 173.5, 163.2, 148.2, 134.8, 130.0, 127.9, 124.7, 82.9, 72.1, 51.8, 33.1, 31.9, 29.9, 28.1, 27.5, 22.3, -5.3, -5.3.

**ESI-HRMS:** calcd for  $\text{C}_{23}\text{H}_{34}\text{NO}_6\text{Si}^+ ([\text{M} + \text{H}]^+) = 448.2150$ , found: 448.2147.

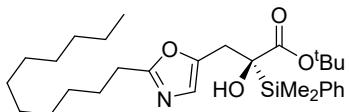
**IR** (neat): 2927, 1737, 1568, 1430, 1369, 1252, 1155, 1113, 1067, 836, 812, 783, 737, 702  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	4.837	41116409	49.93
2	6.013	41232818	50.07



Entry	Retention Time	Area	% Area
1	4.664	175874	5.99
2	5.817	2762199	94.01



**Tert-butyl (*R*)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-undecyloxazol-5-yl)propanoate (C27)**

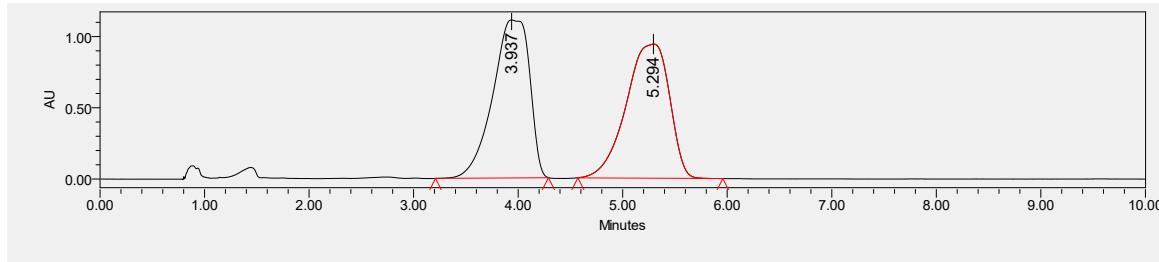
(C<sub>29</sub>H<sub>47</sub>NO<sub>4</sub>Si) 20.1 mg, 40% yield, 90% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 5:1). [α]<sub>D</sub><sup>25</sup> = -13.3 (c = 0.51, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiralcel OZ-3, CO<sub>2</sub>/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 210 nm), retention time: tr (minor) = 4.05 min, tr (major) = 5.27 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.55 (m, 2H), 7.43-7.32 (m, 3H), 6.66 (s, 1H), 3.16 (d, *J* = 15.2 Hz, 1H), 2.99 (d, *J* = 15.6 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.73-1.63 (m, 3H), 1.34 (s, 9H), 1.29-1.22 (m, 15H), 0.89-0.84 (m, 3H), 0.45 (d, *J* = 6.4 Hz, 6H).

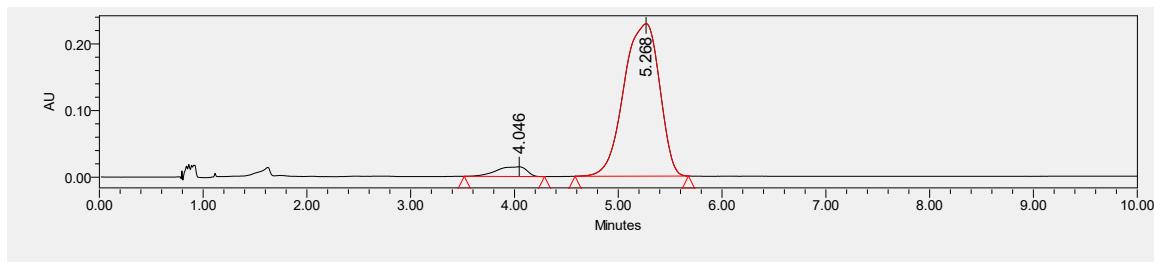
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.6, 164.4, 147.8, 134.8, 134.7, 130.0, 127.9, 124.6, 82.8, 72.1, 32.1, 31.9, 29.8, 29.6, 29.5, 29.4, 29.3, 28.3, 28.1, 27.1, 22.9, 14.3, -5.3, -5.3.

**ESI-HRMS:** calcd for C<sub>29</sub>H<sub>48</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 502.3347, found: 502.3339.

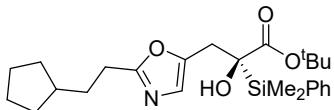
**IR** (neat): 2925, 1711, 1568, 1461, 1369, 1252, 1155, 1066, 967, 835, 811, 783, 736, 701 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	3.937	27082412	50.00
2	5.294	27079061	50.00



Entry	Retention Time	Area	% Area
1	4.046	294663	5.14
2	5.268	5437206	94.86



**Tert-butyl (R)-3-(2-(2-cyclopentylethyl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C28)**

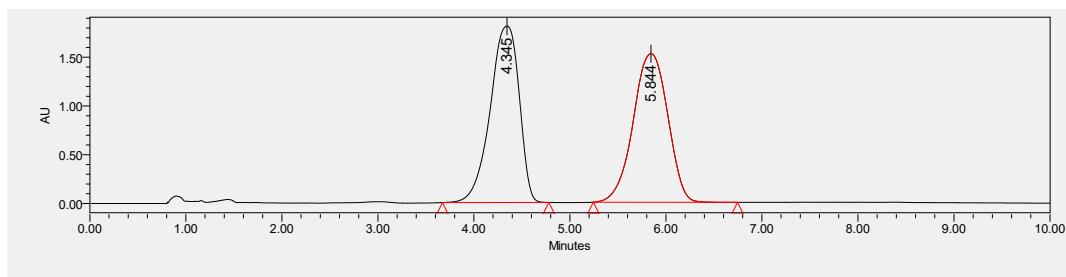
(C<sub>25</sub>H<sub>37</sub>NO<sub>6</sub>Si) 19.5 mg, 44% yield, 94% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 5:1). [α]<sub>D</sub><sup>24</sup> = -13.5 (c = 0.48, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in i-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 210 nm), retention time: tr (minor) = 4.44 min, tr (major) = 5.96 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.56 (m, 2H), 7.43 – 7.34 (m, 3H), 6.66 (s, 1H), 3.18–3.13 (d, J = 15.2, 1H), 3.12 (s, 1H), 2.99 (dd, J = 15.2, 0.8 Hz, 1H), 2.72 – 2.59 (m, 2H), 1.77 – 1.67 (m, 5H), 1.62 – 1.55 (m, 2H), 1.53 – 1.45 (m, 2H), 1.34 (s, 9H), 1.13 – 1.02 (m, 2H), 0.45 (d, J = 5.6 Hz, 6H).

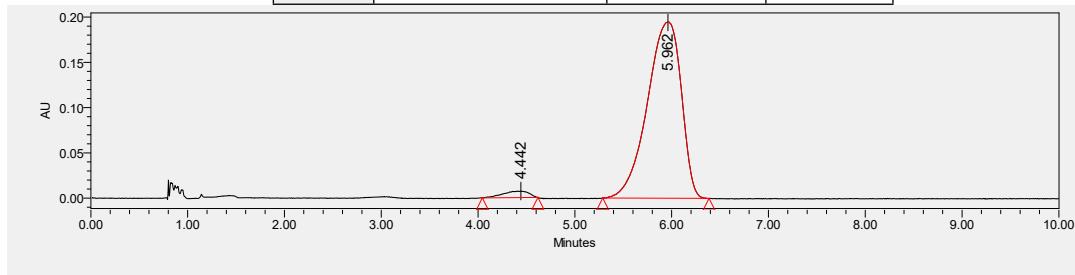
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.6, 164.5, 147.8, 134.8, 134.7, 130.0, 127.9, 124.6, 82.8, 72.1, 39.8, 33.4, 32.5, 31.9, 28.1, 27.6, 25.3, -5.2, -5.3.

**ESI-HRMS:** calcd for C<sub>25</sub>H<sub>38</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 444.2565, found: 444.2557.

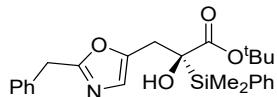
**IR** (neat): 2952, 1710, 1568, 1455, 1368, 1251, 1156, 1115, 1068, 969, 836, 812, 783, 735, 701 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	4.345	38012897	49.92
2	5.844	38128163	50.08



Entry	Retention Time	Area	% Area
1	4.442	134239	2.76
2	5.962	4737353	97.24



**Tert-butyl (R)-3-(2-benzyloxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C29)**

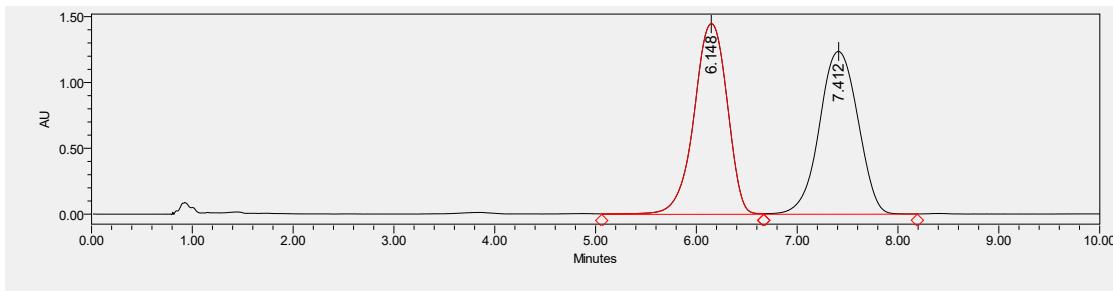
(C<sub>25</sub>H<sub>31</sub>NO<sub>4</sub>Si) 19.3 mg, 44% yield, 93% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 5:1). [α]<sub>D</sub><sup>23</sup> = -12.4 (c = 0.48, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 210 nm), retention time: tr (minor) = 6.32 min, tr (major) = 7.55 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.55 (m, 2H), 7.42 – 7.33 (m, 3H), 7.32 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 6.74 – 6.68 (m, 1H), 4.00 (d, *J* = 15.6, 18.0 Hz, 2H), 3.22 – 3.09 (m, 2H), 2.99 (d, *J* = 15.6 Hz, 1H), 1.27 (s, 9H), 0.43 (d, *J* = 6.4 Hz, 6H).

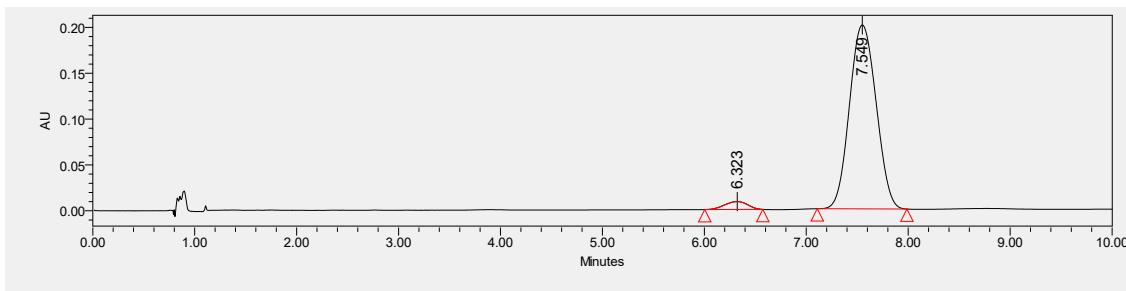
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.6, 162.3, 148.6, 135.8, 134.8, 134.6, 130.0, 128.9, 128.8, 127.9, 127.1, 125.0, 82.8, 72.0, 34.8, 31.9, 28.0, -5.3, -5.3.

**ESI-HRMS:** calcd for C<sub>25</sub>H<sub>32</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 438.2095, found: 438.2095.

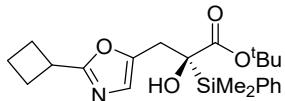
**IR** (neat): 2926, 1709, 1563, 1427, 1369, 1266, 1155, 1109, 1067, 968, 836, 735, 700 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	6.148	33139527	50.18
2	7.412	32897832	49.82



Entry	Retention Time	Area	% Area
1	6.323	135606	3.59
2	7.549	3645680	96.41



**Tert-butyl (R)-3-(2-cyclobutyloxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoaten (C30)**

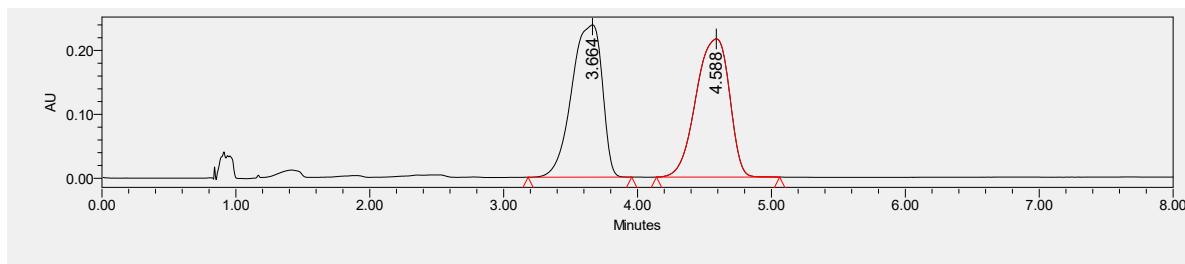
(C<sub>22</sub>H<sub>31</sub>NO<sub>4</sub>Si) 13.7 mg, 34% yield, 95% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 5:1). [α]<sub>D</sub><sup>23</sup> = -16.2 (c = 0.68, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in i-PrOH for UPC<sup>2</sup> (Daicel Chiralcel OZ-3, CO<sub>2</sub>/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 210 nm), retention time: tr (minor) = 3.70 min, tr (major) = 4.66 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.55 (m, 2H), 7.43 – 7.33 (m, 3H), 6.69 (s, 1H), 3.57 – 3.45 (m, 1H), 3.17 (dd, J = 15.2, 0.8 Hz, 1H), 3.12 (s, 1H), 3.00 (d, J = 15.2 Hz, 1H), 2.41 – 2.22 (m, 4H), 2.09 – 1.95 (m, 1H), 1.94 – 1.84 (m, 1H), 1.33 (s, 9H), 0.45 (d, J = 7.6 Hz, 6H).

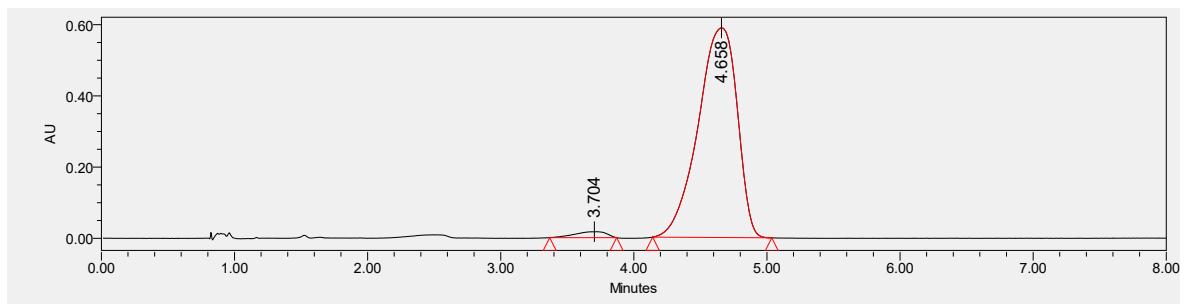
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.6, 166.5, 147.8, 134.8, 134.7, 130.0, 127.9, 124.7, 82.8, 72.0, 33.2, 32.0, 28.1, 27.4, 27.3, 18.7, -5.3, -5.3.

ESI-HRMS: calcd for C<sub>22</sub>H<sub>32</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 402.2095, found: 402.2100.

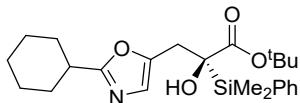
IR (neat): 2976, 1709, 1564, 1427, 1369, 1250, 1155, 1117, 1066, 961, 835, 811, 783, 737, 701 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	3.664	3773771	50.19
2	4.588	3745313	49.81



Entry	Retention Time	Area	% Area
1	3.704	278366	2.26
2	4.658	12026396	97.74



**Tert-butyl (R)-3-(2-cyclohexyloxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C31)**

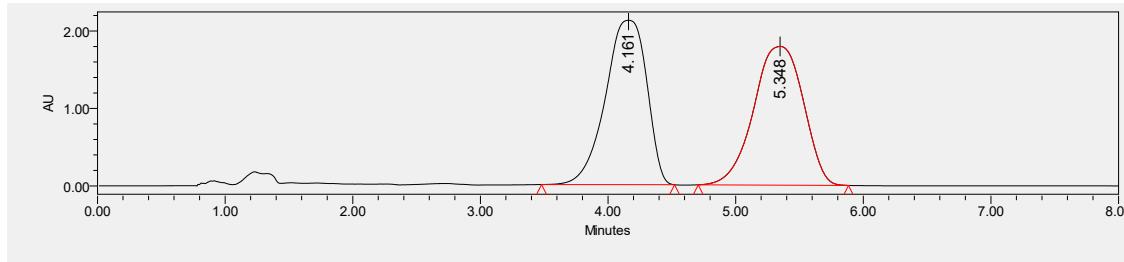
( $\text{C}_{24}\text{H}_{35}\text{NO}_4\text{Si}$ ) 32.2 mg, 75% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 5:1).  $[\alpha]_D^{25} = -16.0$  ( $c = 0.80$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in  $i\text{-PrOH}$  for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**,  $\text{CO}_2/\text{MeOH} = 95/5$ , flow rate = 1.5 mL/min,  $\lambda = 210$  nm), retention time: tr (minor) = 4.39 min, tr (major) = 5.58 min.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.56 (m, 2H), 7.42 – 7.33 (m, 3H), 6.68 – 6.63 (m, 1H), 3.21 – 3.09 (m, 2H), 3.00 (d,  $J = 15.2$  Hz, 1H), 2.74 – 2.59 (m, 1H), 2.03 – 1.93 (m, 2H), 1.81 – 1.71 (m, 3H), 1.70 – 1.61 (m, 1H), 1.55 – 1.44 (m, 2H), 1.32 (s, 9H), 1.28 – 1.20 (m, 2H), 0.44 (d,  $J = 9.6$  Hz, 6H).

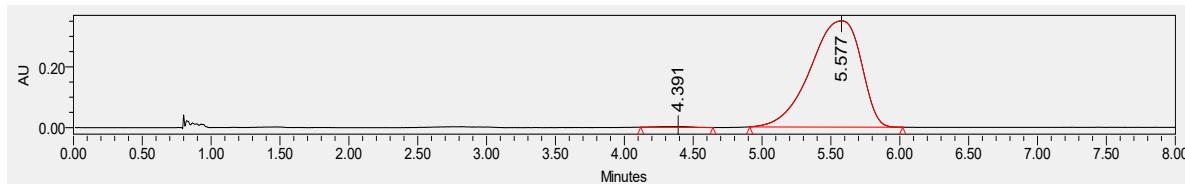
**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 167.5, 147.6, 134.8, 130.0, 127.9, 124.4, 82.7, 72.1, 37.6, 32.0, 30.7, 30.6, 28.1, 25.9, 25.8, -5.3, -5.3.

**ESI-HRMS:** calcd for  $\text{C}_{24}\text{H}_{36}\text{NO}_4\text{Si}^+ ([\text{M} + \text{H}]^+) = 430.2408$ , found: 430.2406.

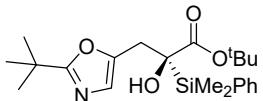
**IR** (neat): 2930, 1710, 1562, 1451, 1427, 1368, 1251, 1156, 1110, 1067, 962, 836, 811, 783, 737, 701  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	4.161	47785429	49.64
2	5.348	48469725	50.36



Entry	Retention Time	Area	% Area
1	4.391	39602	0.44
2	5.577	8941836	99.56



**Tert-butyl (R)-3-(2-(tert-butyl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C32)**

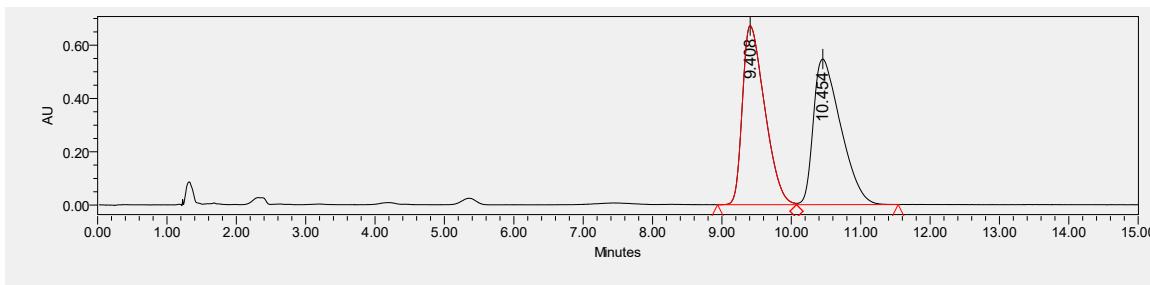
( $C_{22}H_{33}NO_4Si$ ) 33.9 mg, 84% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 7:1).  $[\alpha]_D^{24} = -23.5$  ( $c = 0.85$ , in  $CH_2Cl_2$ ). Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiraldpak IE-3,  $CO_2/EtOH = 95/5$ , flow rate = 1.0 mL/min,  $\lambda = 210$  nm), retention time: tr (major) = 9.72 min, tr (minor) = 10.69 min.

<sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.65 – 7.55 (m, 2H), 7.43 – 7.32 (m, 3H), 6.66 (s, 1H), 3.16 (m, 2H), 3.03 (d,  $J = 15.6$  Hz, 1H), 1.31 (s, 18H), 0.45 (d,  $J = 12.8$  Hz, 6H).

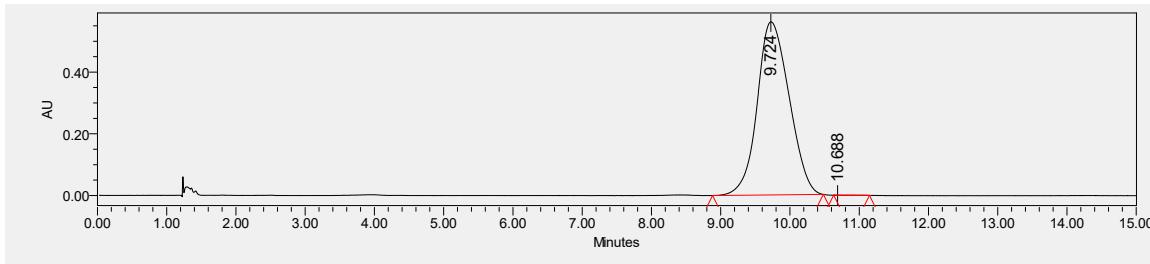
<sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )  $\delta$  175.7, 170.4, 147.9, 134.8, 134.7, 130.0, 127.9, 124.2, 82.7, 72.0, 33.7, 32.0, 28.7, 28.2, -5.2, -5.3.

ESI-HRMS: calcd for  $C_{22}H_{34}NO_4Si^+ ([M + H]^+) = 404.2252$ , found: 404.2249.

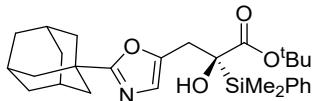
IR (neat): 2973, 1710, 1560, 1368, 1251, 1156, 1114, 1067, 960, 836, 811, 783, 734, 701  $cm^{-1}$ .



Entry	Retention Time	Area	% Area
1	9.408	14964782	50.06
2	10.454	14929035	49.94



Entry	Retention Time	Area	% Area
1	9.724	17989412	99.98
2	10.688	3475	0.02



**Tert-butyl (R)-3-(2-((3R,5R)-adamantan-1-yl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C33)**

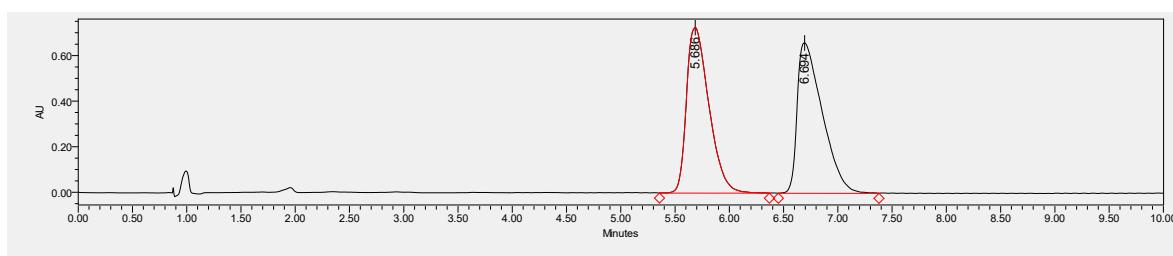
(C<sub>28</sub>H<sub>40</sub>NO<sub>4</sub>Si) 29.4 mg, 61% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 5:1). [α]<sub>D</sub><sup>24</sup> = -20.0 (c = 0.74, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in i-PrOH for **UPC<sup>2</sup>** (Daicel Chiralpak **IA-3**, CO<sub>2</sub>/MeOH = 95/5, flow rate = 1.5 mL/min, λ = 210 nm), retention time: tr (major) = 5.47 min, tr (minor) = 6.61 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.57 (m, 2H), 7.42 – 7.32 (m, 3H), 6.67 (s, 1H), 3.24 – 3.09 (m, 2H), 3.05 (d, J = 15.6 Hz, 1H), 2.03 (s, 3H), 1.96 (m, 6H), 1.76 – 1.69 (m, 6H), 1.31 (s, 9H), 0.44 (d, J = 13.6 Hz, 6H).

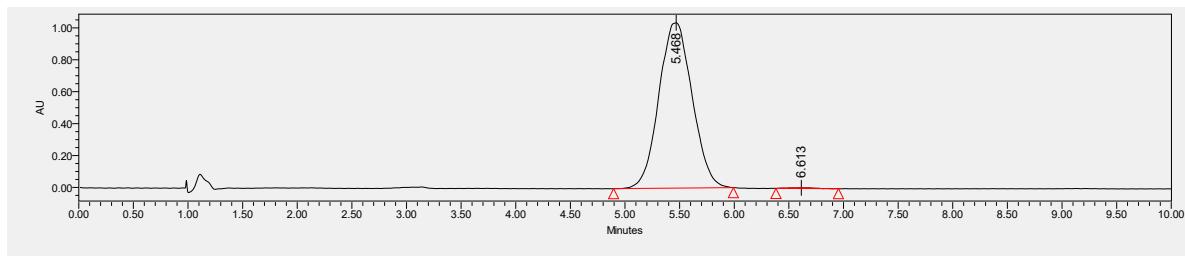
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.7, 170.2, 147.5, 134.8, 134.7, 130.0, 127.9, 124.1, 82.7, 72.1, 40.4, 36.6, 35.6, 32.0, 28.2, 28.1, -5.2, -5.3.

**ESI-HRMS:** calcd for C<sub>28</sub>H<sub>40</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 482.2721, found: 482.2726.

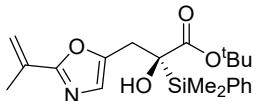
**IR** (neat): 2906, 1710, 1555, 1453, 1368, 1252, 1155, 1115, 1068, 955, 835, 811, 783, 736, 701 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	5.686	10466847	49.68
2	6.694	10603254	50.32



Entry	Retention Time	Area	% Area
1	5.468	21913028	99.69
2	6.613	67305	0.31



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-(prop-1-en-2-yl)oxazol-5-yl)propanoate (C34)**

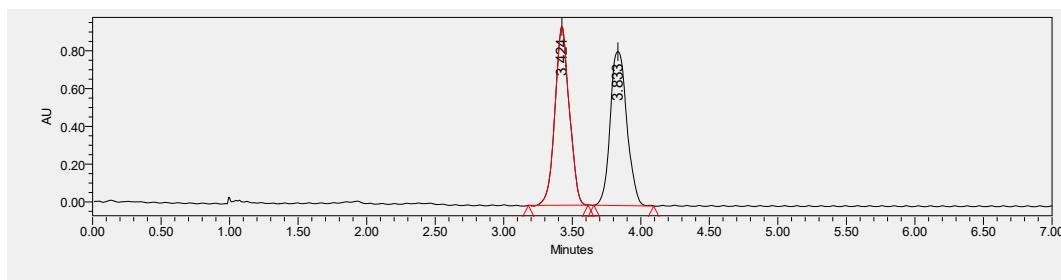
(C<sub>21</sub>H<sub>30</sub>NO<sub>4</sub>Si) 35.7 mg, 92% yield, 83% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>365</sub><sup>24</sup> = +11.8 (c = 0.89, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiraldak **IE-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (major) = 3.37 min, tr (minor) = 3.83 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.57 (m, 2H), 7.43 – 7.34 (m, 3H), 6.82 (s, 1H), 5.80 (s, 1H), 5.28 (s, 1H), 3.21 (d, *J* = 15.6 Hz, 1H), 3.16 (s, 1H), 3.05 (d, *J* = 15.6 Hz, 1H), 2.10 (s, 3H), 1.32 (s, 9H), 0.46 (d, *J* = 5.6 Hz, 6H).

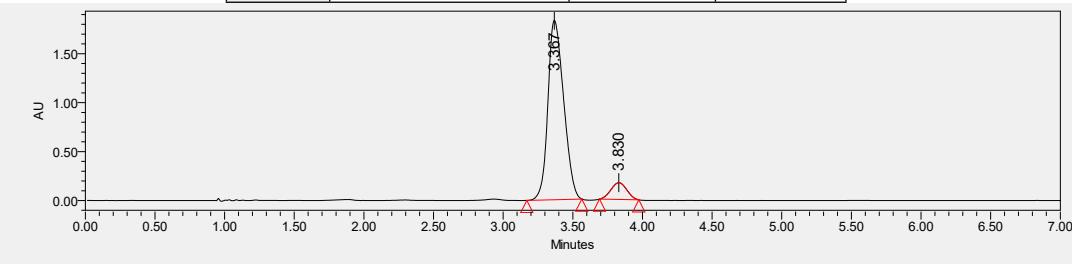
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.5, 162.0, 148.4, 134.8, 134.6, 131.8, 130.0, 127.9, 125.9, 117.3, 82.9, 72.0, 32.0, 28.1, 19.2, -5.3, -5.3.

**ESI-HRMS:** calcd for C<sub>21</sub>H<sub>30</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 388.1939, found: 388.1932.

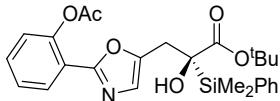
**IR** (neat): 2976, 1707, 1526, 1368, 1252, 1154, 1117, 1066, 836, 782, 701, 650 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	3.424	6890082	49.96
2	3.833	6899772	50.04



Entry	Retention Time	Area	% Area
1	3.367	14407064	91.37
2	3.830	1361548	8.63



**Tert-butyl (R)-3-(2-(2-acetoxyphenyl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C35)**

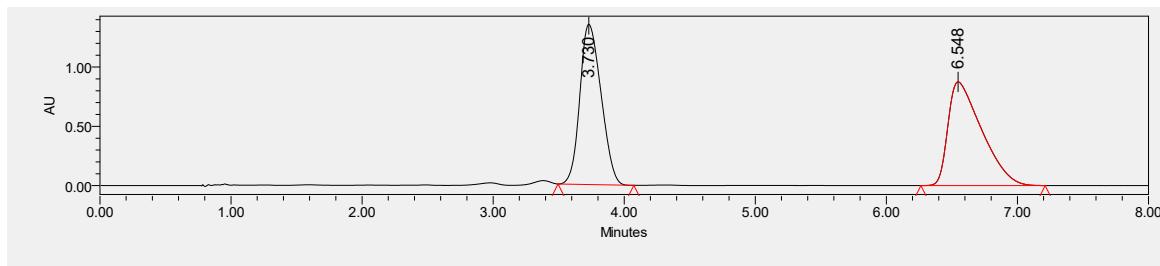
(C<sub>26</sub>H<sub>31</sub>NO<sub>6</sub>Si) 38.5 mg, 80% yield, 96% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>24</sup> = -29.3 (c = 1.93, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in i-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 3.35 min, tr (major) = 6.03 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.01 (dd, J = 8.0, 2.0 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.45 – 7.35 (m, 4H), 7.32 – 7.27 (m, 1H), 7.12 (dd, J = 8.0, 1.2 Hz, 1H), 6.91 (s, 1H), 3.25 (d, J = 15.6 Hz, 1H), 3.19 (s, 1H), 3.09 (d, J = 15.2 Hz, 1H), 2.34 (s, 3H), 1.32 (s, 9H), 0.48 (d, J = 4.0 Hz, 6H).

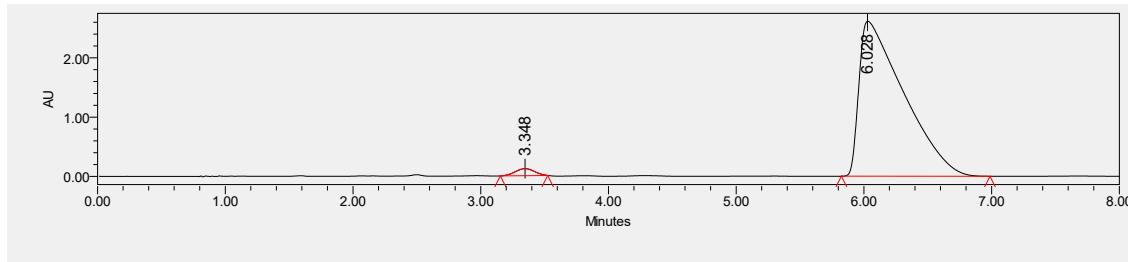
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.4, 170.2, 157.9, 148.8, 148.1, 134.8, 134.5, 131.1, 130.0, 129.1, 127.9, 126.4, 126.0, 124.0, 120.9, 83.0, 72.4, 31.9, 28.1, 21.3, -5.3, -5.4.

**ESI-HRMS:** calcd for C<sub>26</sub>H<sub>32</sub>NO<sub>6</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 482.1993, found: 482.1992.

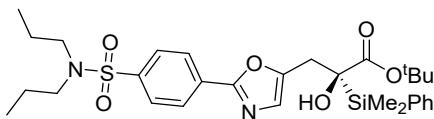
**IR** (neat): 2974, 1768, 1708, 1487, 1368, 1250, 1191, 1155, 1063, 955, 835, 784, 704, 654 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	3.730	15222515	49.37
2	6.548	15608458	50.63



Entry	Retention Time	Area	% Area
1	3.348	1246327	1.92
2	6.028	63515629	98.08



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-3-(2-(4-(N,N-dipropylsulfamoyl)phenyl)oxazol-5-yl)-2-hydroxypropanoate (C36)**

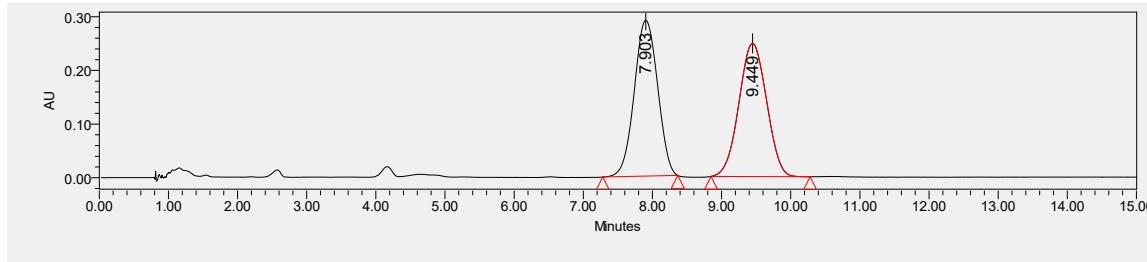
(C<sub>30</sub>H<sub>42</sub>N<sub>2</sub>O<sub>6</sub>SSi) 39.3 mg, 67% yield, 97% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 5:1). [α]<sub>D</sub><sup>23</sup> = -1.0 (c = 1.95, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for UPC<sup>2</sup> (Daicel Chiralcel OZ-3, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 8.18 min, tr (major) = 9.08 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.66 – 7.55 (m, 2H), 7.46 – 7.33 (m, 3H), 6.96 (s, 1H), 3.29 (d, *J* = 15.6 Hz, 1H), 3.22 (s, 1H), 3.14 (d, *J* = 15.2 Hz, 1H), 3.11 – 3.06 (m, 4H), 1.58 – 1.50 (m, 4H), 1.33 (s, 9H), 0.86 (t, *J* = 7.2 Hz, 6H), 0.48 (d, *J* = 3.6 Hz, 6H).

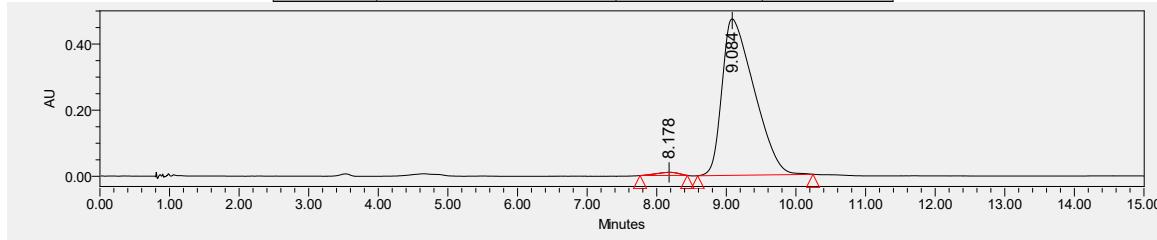
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.5, 159.5, 150.0, 141.3, 134.8, 134.4, 131.0, 130.1, 128.0, 127.6, 126.8, 126.6, 83.1, 72.1, 50.0, 32.0, 28.1, 22.0, 11.3, -5.3, -5.3.

ESI-HRMS: calcd for C<sub>30</sub>H<sub>43</sub>N<sub>2</sub>O<sub>6</sub>SSi<sup>+</sup> ([M + H]<sup>+</sup>) = 587.2606, found: 587.2601.

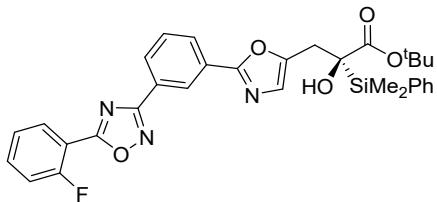
IR (neat): 2967, 1732, 1593, 1462, 1368, 1340, 1252, 1154, 1117, 991, 835, 781, 702, 602, 567 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	7.903	6813953	49.74
2	9.449	6884826	50.26



Entry	Retention Time	Area	% Area
1	8.178	210706	1.38
2	9.084	15075991	98.62



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-3-(2-(3-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl)phenyl)oxazol-5-yl)-2-hydroxypropanoate (C37)**

( $\text{C}_{32}\text{H}_{32}\text{FN}_3\text{O}_5\text{Si}$ ) 50.4 mg, 86% yield, 99% ee; Colorless oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 5:1).  $[\alpha]_D^{23} = +3.7$  ( $c = 1.26$ , in  $\text{CH}_2\text{Cl}_2$ ). Dissolved in  $i\text{-PrOH}$  for **UPC<sup>2</sup>** (Daicel Chiraldak **AD-3**,  $\text{CO}_2/\text{MeOH} = 85/15$ , flow rate = 1.5 mL/min,  $\lambda = 254$  nm), retention time: tr (major) = 6.47 min, tr (minor) = 8.54 min.

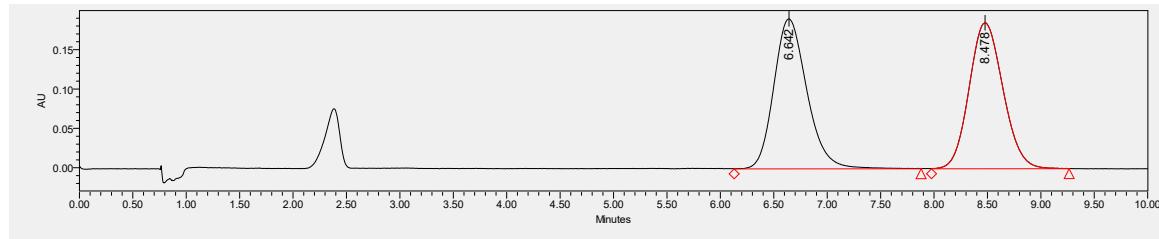
**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79–8.71 (m, 1H), 8.31 – 8.19 (m, 2H), 8.16–8.10 (m, 1H), 7.71 – 7.53 (m, 4H), 7.44 – 7.36 (m, 3H), 7.35 – 7.26 (m, 2H), 6.98 (s, 1H), 3.33 (d,  $J = 15.6$  Hz, 1H), 3.26 (s, 1H), 3.20 – 3.13 (m, 1H), 1.36 (s, 9H), 0.50 (d,  $J = 4.0$  Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.6, 173.1 (d,  $J = 4.0$  Hz), 168.3, 162.2, 160.2, 159.6, 149.3, 134.9, 134.8, 134.5, 131.2, 130.1, 129.5, 128.9 (d,  $J = 7.1$  Hz), 128.5, 128.0, 127.6, 126.5, 125.3, 124.9 (d,  $J = 4.0$  Hz), 117.3 (d,  $J = 21.2$  Hz), 112.9 (d,  $J = 11.1$  Hz), 83.1, 72.0, 32.1, 28.2, -5.2, -5.3.

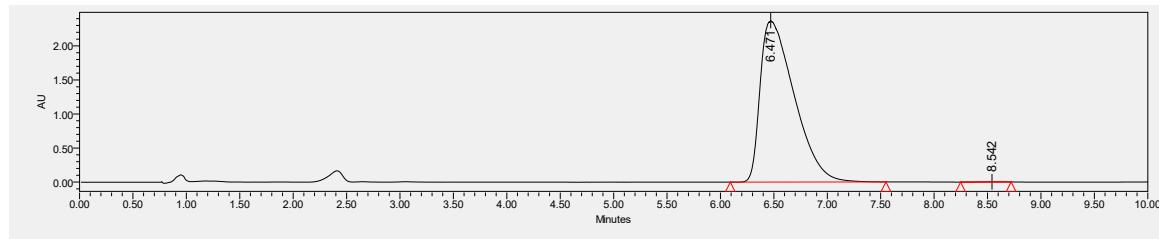
**<sup>19</sup>F NMR** (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -108.17.

**ESI-HRMS:** calcd for  $\text{C}_{32}\text{H}_{33}\text{FN}_3\text{O}_5\text{Si}^+ ([M + H]^+) = 586.2168$ , found: 586.2166.

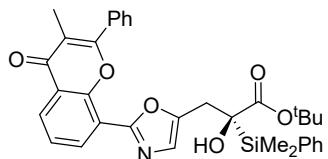
**IR** (neat): 2976, 1709, 1621, 1466, 1368, 1251, 1155, 1116, 1066, 955, 830, 811, 757, 719  $\text{cm}^{-1}$ .



Entry	Retention Time	Area	% Area
1	6.642	4106926	50.15
2	8.478	4082284	49.85



Entry	Retention Time	Area	% Area
1	6.471	52468500	99.93
2	8.542	34950	0.07



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-(3-methyl-4-oxo-2-phenyl-4H-chromen-8-yl)oxazol-5-yl)propanoate (C38)**

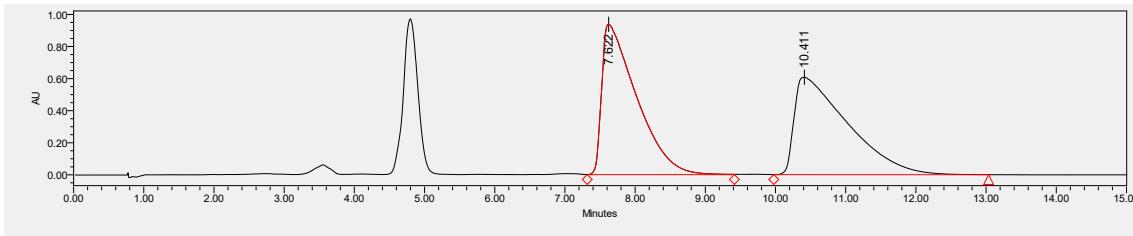
(C<sub>34</sub>H<sub>35</sub>NO<sub>6</sub>Si) 52.9 mg, 91% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 3:1). [α]<sub>D</sub><sup>24</sup> = +8.0 (c = 1.33, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in i-PrOH for UPC<sup>2</sup> (Daicel Chiraldak IA-3, CO<sub>2</sub>/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (major) = 7.87 min, tr (minor) = 10.53 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 (dd, J = 7.6, 1.6 Hz, 1H), 8.28 (dd, J = 7.6, 1.6 Hz, 1H), 7.91 – 7.83 (m, 2H), 7.65 – 7.57 (m, 2H), 7.52 – 7.36 (m, 7H), 7.01 (s, 1H), 3.27 (d, J = 15.6 Hz, 1H), 3.22 (s, 1H), 3.13 (d, J = 15.2 Hz, 1H), 2.28 (s, 3H), 1.24 (s, 9H), 0.47 (d, J = 3.6 Hz, 6H).

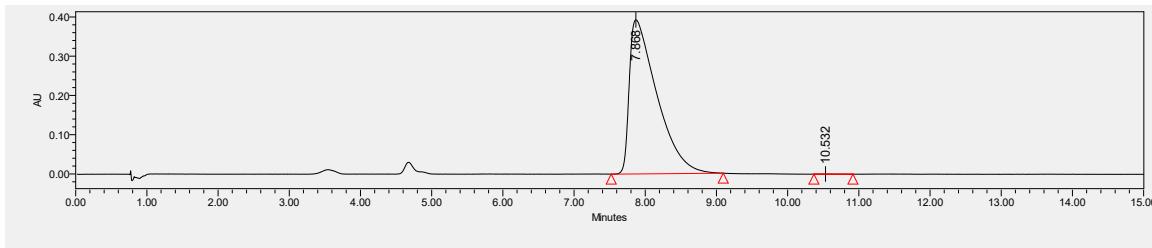
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.7, 175.5, 161.0, 157.6, 152.9, 149.6, 134.8, 134.5, 133.6, 133.2, 130.6, 130.1, 129.8, 128.5, 128.1, 128.0, 126.2, 124.6, 123.3, 117.8, 117.6, 83.0, 72.2, 32.0, 28.0, 12.1, -5.2, -5.3.

**ESI-HRMS:** calcd for C<sub>34</sub>H<sub>36</sub>NO<sub>6</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 582.2306, found: 582.2307.

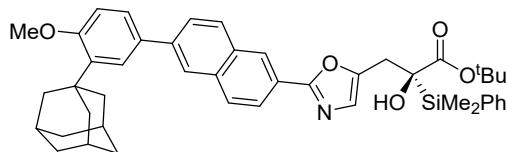
**IR** (neat): 2974, 1710, 1631, 1580, 1438, 1390, 1252, 1153, 1112, 1064, 1020, 947, 835, 762, 736, 698, 645 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	7.622	32233922	50.08
2	10.411	32131765	49.92



Entry	Retention Time	Area	% Area
1	7.868	10556446	99.95
2	10.532	5238	0.05



**Tert-butyl (R)-3-(2-(6-(3-(3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)oxazol-5-yl)-2-(dimethyl(phenyl)silyl)-2-hydroxypropanoate (C39)**

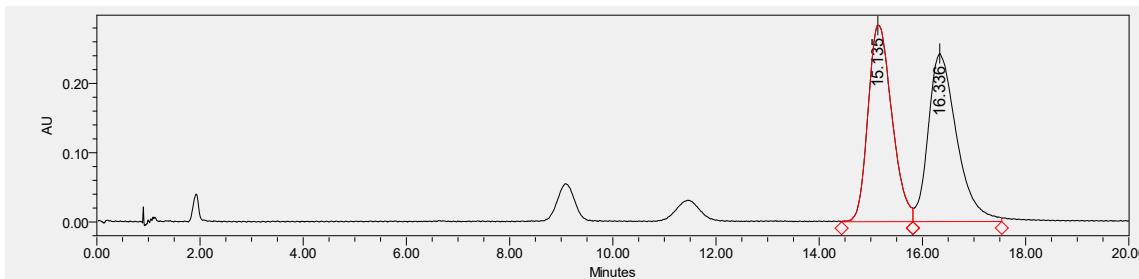
(C<sub>45</sub>H<sub>51</sub>NO<sub>5</sub>Si) 57.1 mg, 80% yield, 98% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>23</sup> = -4.2 (c = 2.87, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in i-PrOH for UPC<sup>2</sup> (Daicel Chiralcel OZ-3, CO<sub>2</sub>/MeOH = 85/15, flow rate = 1.5 mL/min, λ = 254 nm), retention time: tr (minor) = 15.17 min, tr (major) = 16.47 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.50 – 8.43 (m, 1H), 8.09 (dd, J = 8.8, 1.6 Hz, 1H), 8.03 – 7.97 (m, 1H), 7.93 (dd, J = 8.4, 2.4 Hz, 2H), 7.78 (dd, J = 8.4, 1.6 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.61 (d, J = 2.4 Hz, 1H), 7.54 (dd, J = 8.4, 2.0 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.07 – 6.94 (m, 2H), 3.90 (s, 3H), 3.35 (d, J = 15.2 Hz, 1H), 3.30 (s, 1H), 3.23 – 3.16 (m, 1H), 2.26 – 2.16 (m, 6H), 2.16 – 2.08 (m, 3H), 1.85 – 1.78 (m, 6H), 1.37 (s, 9H), 0.53 (d, J = 5.6 Hz, 6H).

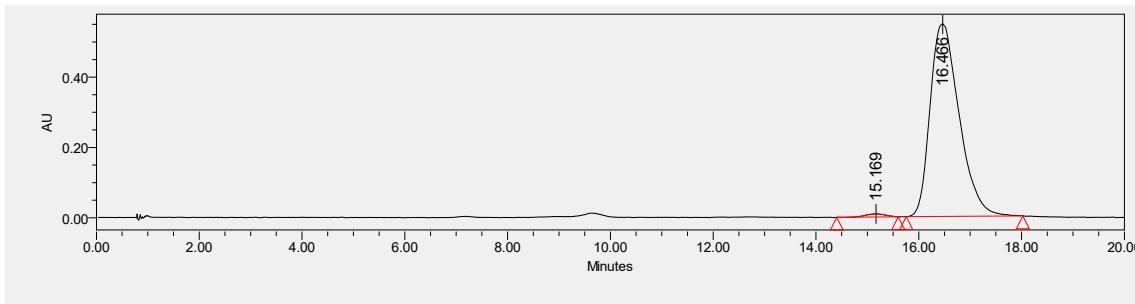
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.6, 161.3, 158.9, 148.9, 140.3, 139.1, 134.8, 134.6, 134.5, 132.9, 131.9, 130.1, 129.1, 128.8, 128.0, 126.6, 126.4, 126.1, 125.8, 125.0, 124.6, 123.7, 112.2, 83.0, 72.2, 55.3, 40.8, 37.3, 37.3, 32.1, 29.3, 28.2, -5.2, -5.3.

**HRMS (ESI+)** m/z calcd for C<sub>45</sub>H<sub>52</sub>NO<sub>5</sub>Si [M+H]<sup>+</sup>: 714.3609, found: 714.3611.

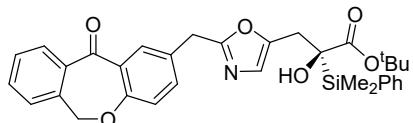
**IR (neat):** 2903, 1711, 1598, 1492, 1368, 1238, 1155, 1118, 1063, 884, 810, 784, 735, 702 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	15.135	9122657	49.58
2	16.336	9278946	50.42



Entry	Retention Time	Area	% Area
1	15.169	235928	1.09
2	16.466	21479011	98.91



**Tert-butyl (*R*)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-((11-oxo-6,11-dihydrodibenz[b,e]oxepin-2-yl)methyl)oxazol-5-yl)propanoate (C40)**

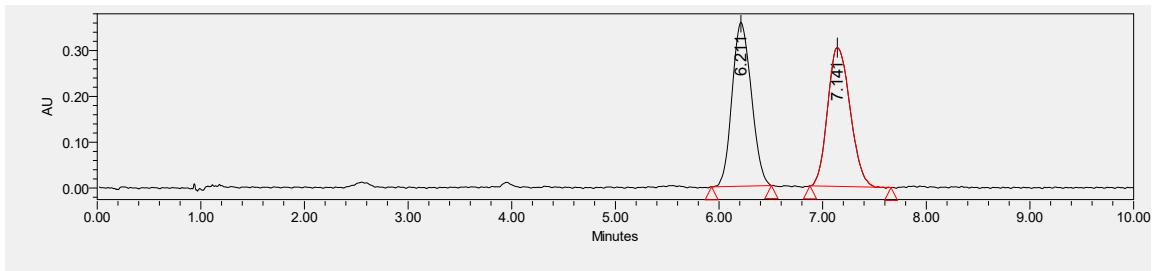
(C<sub>33</sub>H<sub>35</sub>NO<sub>6</sub>Si) 22.8 mg, 40% yield, 90% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 2:1). [α]<sub>D</sub><sup>24</sup> = -4.3 (c = 1.15, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 210 nm), retention time: tr (minor) = 6.79 min, tr (major) = 7.73 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 2.4 Hz, 1H), 7.87 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.49 – 7.43 (m, 1H), 7.42 – 7.32 (m, 5H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.72 (s, 1H), 5.16 (s, 2H), 4.01 (s, 2H), 3.19 – 3.12 (m, 2H), 2.99 (d, *J* = 15.6 Hz, 1H), 1.28 (s, 9H), 0.43 (d, *J* = 5.6 Hz, 6H).

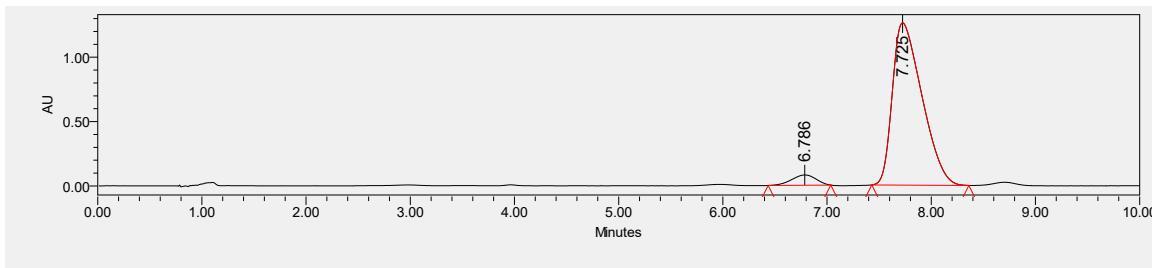
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 191.0, 175.6, 162.0, 160.6, 148.8, 140.6, 136.0, 135.7, 134.8, 134.6, 132.9, 132.1, 130.0, 129.7, 129.5, 129.4, 128.0, 127.9, 125.3, 125.1, 121.4, 82.9, 73.8, 72.0, 33.9, 31.9, 28.1, -5.3, -5.3.

**ESI-HRMS:** calcd for C<sub>33</sub>H<sub>36</sub>NO<sub>6</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 570.2306, found: 570.2314.

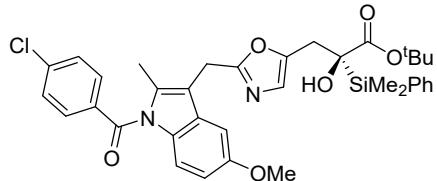
**IR** (neat): 2972, 1712, 1648, 1611, 1567, 1489, 1455, 1369, 1299, 1254, 1155, 1069, 1017, 834, 701 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	6.211	4606500	50.22
2	7.141	4566824	49.78



Entry	Retention Time	Area	% Area
1	6.786	1296576	4.97
2	7.725	24804345	95.03



**Tert-butyl (R)-3-(2-((1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)methyl)oxazol-5-yl)-2-(dimethylphenylsilyl)-2-hydroxypropanoate (C41)**

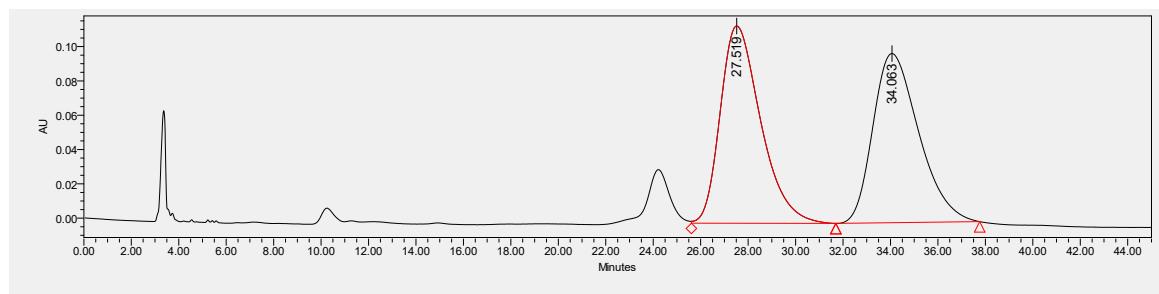
(C<sub>36</sub>H<sub>39</sub>ClN<sub>2</sub>O<sub>6</sub>Si) 34.9 mg, 53% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 3:1). [α]<sub>D</sub><sup>24</sup> = -3.0 (c = 1.73, in CH<sub>2</sub>Cl<sub>2</sub>). Colorless oil; 53% yield, 99% ee. Dissolved in *i*-PrOH for HPLC (Daicel Chiralcel OZH, *i*-PrOH/*n*-hexane = 15/85, flow rate = 1.0 mL/min, λ = 254 nm), retention time: tr (minor) = 27.66 min, tr (major) = 33.66 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.62 (m, 2H), 7.61–7.53 (m, 2H), 7.49 – 7.42 (m, 2H), 7.42 – 7.30 (m, 3H), 6.90 (d, *J* = 2.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.70 (s, 1H), 6.63 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.04 (s, 2H), 3.78 (s, 3H), 3.16–3.07 (m, 2H), 3.02–2.94 (m, 1H), 2.38 (s, 3H), 1.23 (s, 9H), 0.42 (d, *J* = 8.0 Hz, 6H).

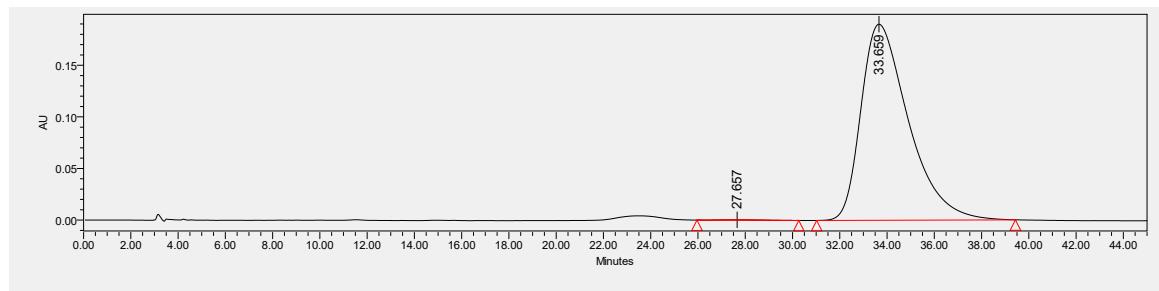
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.5, 168.5, 161.3, 156.1, 148.7, 139.4, 135.5, 134.8, 134.1, 131.4, 131.0, 130.6, 130.0, 129.3, 127.9, 124.8, 115.1, 113.8, 112.0, 101.4, 82.8, 72.0, 55.8, 31.9, 28.0, 24.0, 13.5, -5.3, -5.4.

**ESI-HRMS:** calcd for C<sub>36</sub>H<sub>40</sub><sup>35</sup>ClN<sub>2</sub>O<sub>6</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 659.2339, found: 659.2330. C<sub>36</sub>H<sub>40</sub><sup>37</sup>ClN<sub>2</sub>O<sub>6</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 660.2372, found: 660.2372.

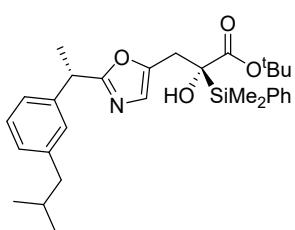
**IR** (neat): 2928, 1683, 1593, 1478, 1397, 1367, 1319, 1250, 1152, 1065, 1015, 835, 811, 701 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	27.519	13603938	50.71
2	34.063	13223039	49.29



Entry	Retention Time	Area	% Area
1	27.657	44768	0.17
2	33.659	26481225	99.83



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-((S)-1-(3-isobutylphenyl)ethyl)oxazol-5-yl)propanoate (C42)**

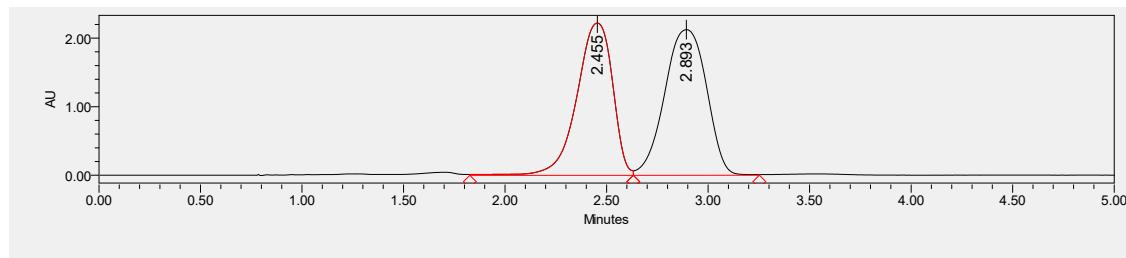
(C<sub>30</sub>H<sub>41</sub>NO<sub>4</sub>Si) 39.1 mg, 77% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 5:1). [α]<sub>D</sub><sup>20</sup> = -9.3 (c = 0.85, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 210 nm), retention time: tr (major) = 2.55 min, tr (minor) = 2.99 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.62–7.54 (m, 2H), 7.43 – 7.32 (m, 3H), 7.13 – 7.01 (m, 4H), 6.73 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 1H), 3.20 – 3.07 (m, 2H), 2.99 (d, *J* = 15.2 Hz, 1H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.85 – 1.79 (m, 1H), 1.63 (d, *J* = 7.6 Hz, 3H), 1.22 (s, 9H), 0.88 (d, *J* = 6.4 Hz, 6H), 0.43 (d, *J* = 8.4 Hz, 6H).

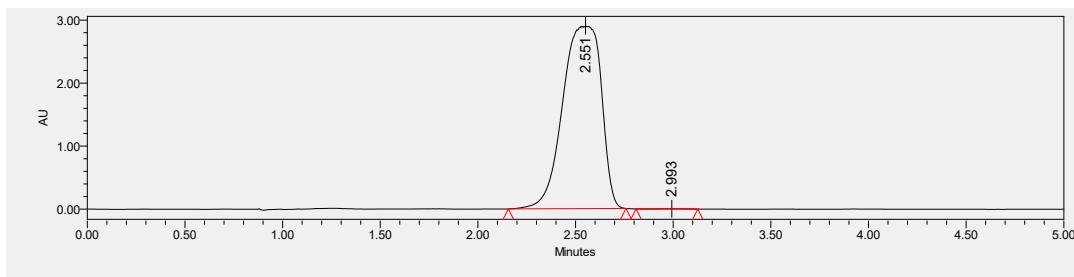
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.5, 166.0, 148.2, 140.3, 139.4, 134.8, 134.6, 130.0, 129.5, 127.9, 127.1, 124.6, 82.7, 72.0, 45.2, 39.3, 31.9, 30.3, 28.0, 22.5, 22.5, 20.3, -5.3, -5.4.

**ESI-HRMS:** calcd for C<sub>30</sub>H<sub>42</sub>NO<sub>4</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 508.2878, found: 508.2878.

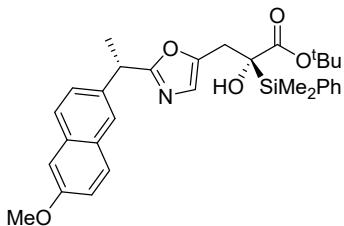
**IR** (neat): 2956, 1709, 1560, 1512, 1458, 1368, 1251, 1155, 1117, 1065, 957, 835, 810, 783, 700, 654 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	2.455	27282132	47.22
2	2.893	30490394	52.78



Entry	Retention Time	Area	% Area
1	2.551	39885882	99.90
2	2.993	38074	0.10



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-2-hydroxy-3-(2-((S)-1-(6-methoxynaphthalen-2-yl)ethyl)oxazol-5-yl)propanoate (C43)**

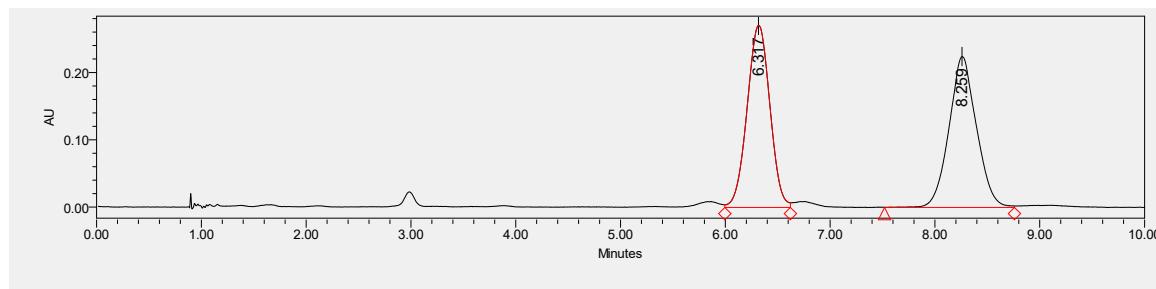
(C<sub>31</sub>H<sub>37</sub>NO<sub>5</sub>Si) 38.8 mg, 73% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 5:1). [α]<sub>D</sub><sup>20</sup> = -20.5 (c = 1.00, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in i-PrOH for **UPC<sup>2</sup>** (Daicel Chiralcel **OZ-3**, CO<sub>2</sub>/MeOH = 90/10, flow rate = 1.5 mL/min, λ = 210 nm), retention time: tr (minor) = 6.62 min, tr (major) = 8.33 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.67 (dd, J = 8.8, 3.2 Hz, 2H), 7.61-7.55 (m, 3H), 7.42 – 7.28 (m, 4H), 7.15 – 7.06 (m, 2H), 6.76 (s, 1H), 4.30 (q, J = 3.2 Hz, 1H), 3.90 (s, 3H), 3.20 – 3.08 (m, 2H), 2.99 (d, J = 15.6 Hz, 1H), 1.72 (d, J = 7.2 Hz, 3H), 1.16 (s, 9H), 0.42 (d, J = 8.0 Hz, 6H).

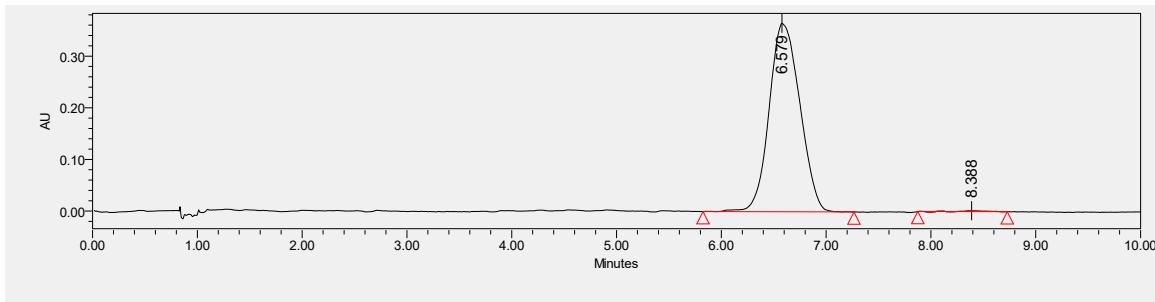
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.5, 165.9, 157.6, 148.4, 137.3, 134.7, 134.6, 133.7, 130.0, 129.4, 129.1, 127.9, 127.3, 126.2, 125.7, 124.6, 119.0, 105.7, 82.7, 72.0, 55.4, 39.6, 31.8, 27.9, 20.2, -5.3, -5.4.

**ESI-HRMS:** calcd for C<sub>31</sub>H<sub>38</sub>NO<sub>5</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 532.2514, found: 532.2505.

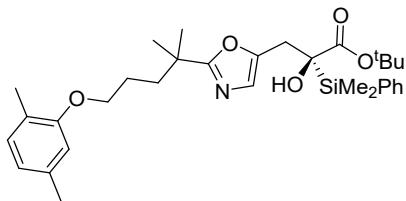
**IR** (neat): 2976, 1709, 1606, 1559, 1505, 1426, 1369, 1264, 1156, 1117, 1067, 836, 811, 702 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	6.317	4971026	50.34
2	8.259	4903171	49.66



Entry	Retention Time	Area	% Area
1	6.579	7426376	99.58
2	8.388	31513	0.42



**Tert-butyl (R)-2-(dimethyl(phenyl)silyl)-3-(2-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)oxazol-5-yl)-2-hydroxypropanoate (C44)**

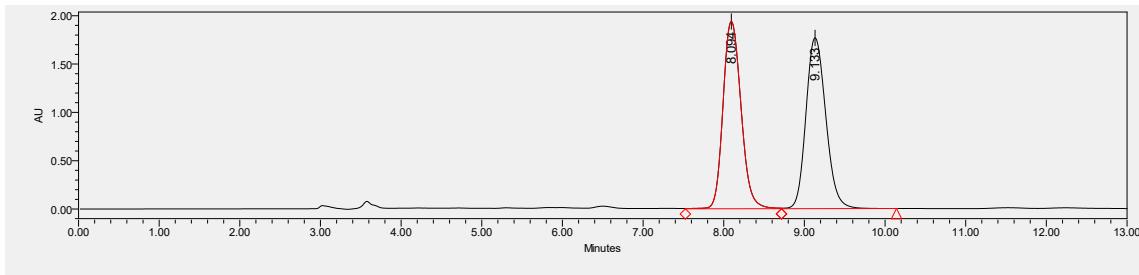
(C<sub>32</sub>H<sub>45</sub>NO<sub>5</sub>Si) 46.4 mg, 84% yield, 99% ee; Colorless oil; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 7:1). [α]<sub>D</sub><sup>23</sup> = -18.0 (c = 1.16, in CH<sub>2</sub>Cl<sub>2</sub>). Dissolved in *i*-PrOH for HPLC (Daicel Chiralpak **IA**, *i*-PrOH/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm), retention time: tr (major) = 8.27 min, tr (minor) = 9.33 min.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.58 (m, 2H), 7.45 – 7.33 (m, 3H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.69 (s, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.58 (s, 1H), 3.86 (t, *J* = 6.0 Hz, 2H), 3.20 – 3.12 (m, 2H), 3.08 – 2.96 (m, 1H), 2.30 (s, 3H), 2.16 (s, 3H), 1.85 – 1.79 (m, 2H), 1.66 – 1.57 (m, 2H), 1.35 (s, 6H), 1.31 (s, 9H), 0.46 (d, *J* = 11.2 Hz, 6H).

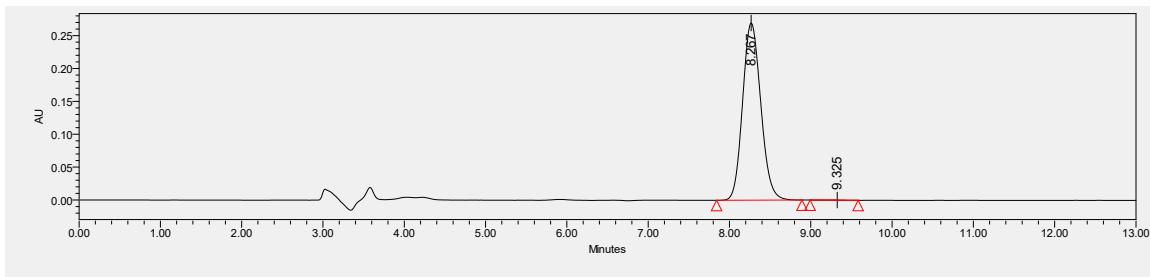
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.7, 169.5, 157.1, 148.0, 136.6, 134.8, 134.7, 130.4, 130.0, 127.9, 124.2, 123.7, 120.7, 112.1, 82.7, 72.0, 68.0, 38.4, 36.9, 31.9, 28.1, 26.5, 26.4, 25.1, 21.6, 15.9, -5.2, -5.3.

**ESI-HRMS:** calcd for C<sub>32</sub>H<sub>46</sub>NO<sub>5</sub>Si<sup>+</sup> ([M + H]<sup>+</sup>) = 552.3140, found: 552.3146.

**IR (neat):** 2972, 1710, 1557, 1509, 1458, 1369, 1252, 1156, 1129, 1066, 836, 809, 783, 701 cm<sup>-1</sup>.



Entry	Retention Time	Area	% Area
1	8.094	30027675	49.87
2	9.133	30188215	50.13



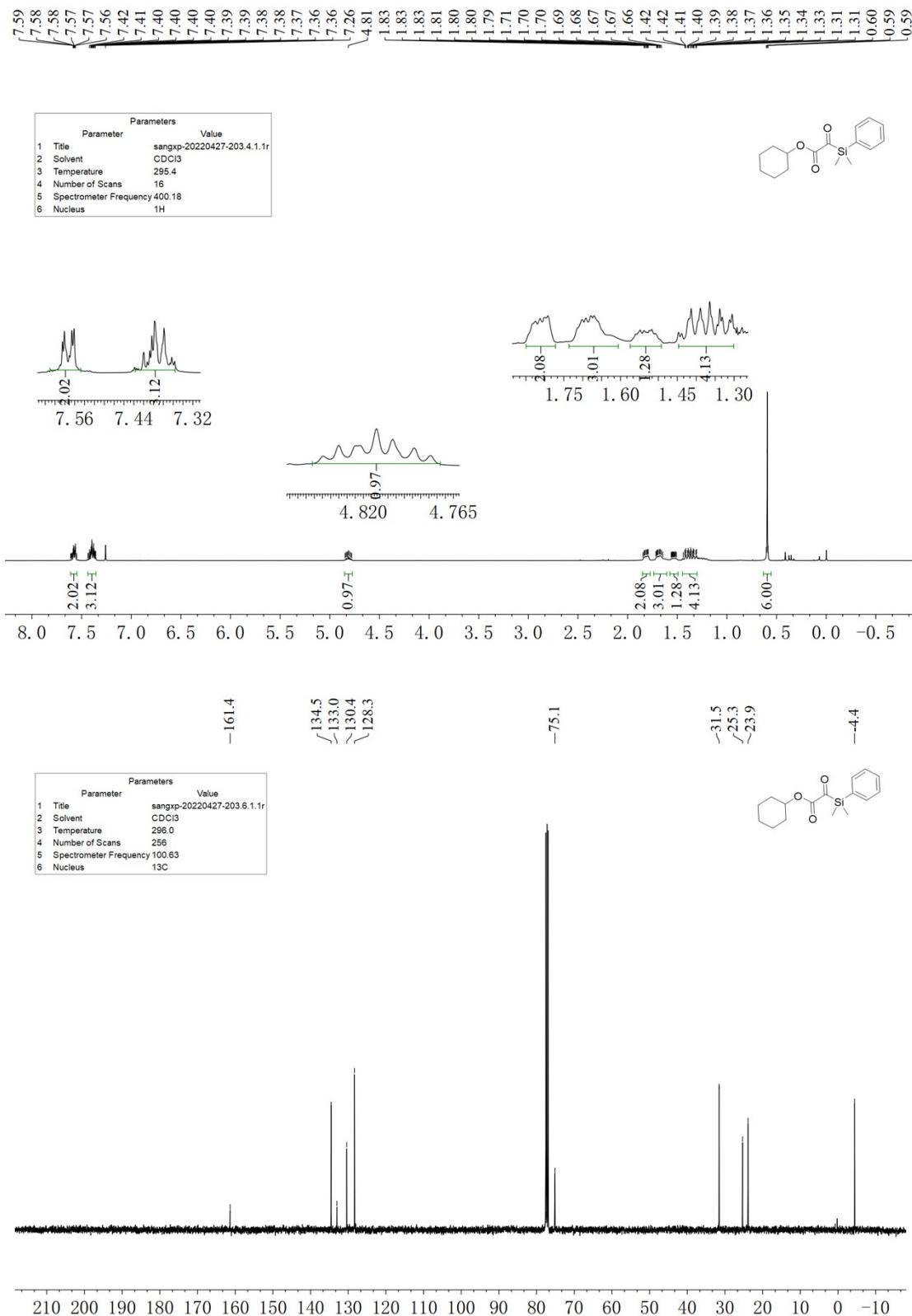
Entry	Retention Time	Area	% Area
1	8.267	4183849	99.96
2	9.325	1529	0.04

## 10. References

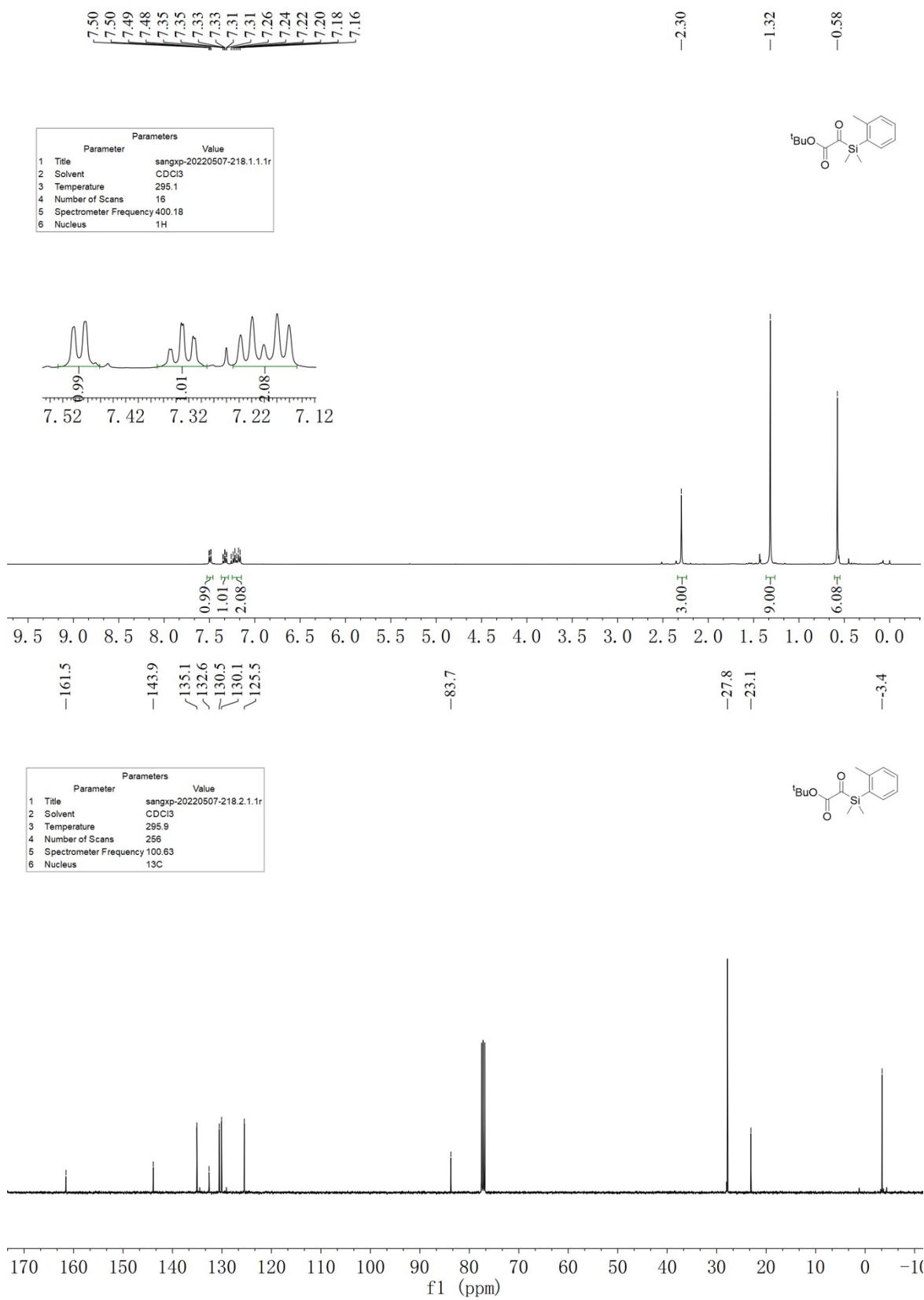
- 1 (a) Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie and X. M. Feng, *Angew. Chem. Int. Ed.*, 2008, **47**, 1308-1311; (b) X. Zhou, D. J. Shang, Q. Zhang, L. L. Lin, X. H. Liu and X. M. Feng, *Org. Lett.*, 2009, **11**, 1401-1404.
- 2 (a) D. A. Nicewicz and J. S. Johnson, *J. Am. Chem. Soc.*, 2005, **127**, 6170-6171; (b) C. Bolm, A. Kasyan, P. Heider, S. Saladin, K. Drauz, K. Günther and C. Wagner, *Org. Lett.*, 2002, **4**, 2265-2267; (c) M. M. Guan, S. Y. Wang, Y. Luo, W. D. Cao, X. H. Liu and X. M. Feng, *Chem. Sci.* 2021, **12**, 7498-7503.
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- 5 (a) S. K. Ray, M. M. Sadhu, R. G. Biswas, R. A. Unhale and V. K. Singh, *Org. Lett.*, 2019, **21**, 417-422; (b) J. Kim and E. J. Yoo, *Org. Lett.* 2021, **23**, 4256-4260.
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- 7.....Y. H. Mo, Q. Y. Chen, J. Z. Li, D. Ye, Y. Q. Zhou, S. X. Dong, X. H. Liu, and X. M. Feng, *ACS Catal.*, 2023, **13**, 877–886.
- 8.....(a) G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei and D. W. Stephan, *Dalton Trans.*, 2007, 3407–3414; (b) J. J. Tian, N. Liu, Q. F. Liu, W. Sun and X. C. Wang, *J. Am. Chem. Soc.*, 2021, **143**, 3054-3059.

## 11. Copies of the NMR spectra for new compounds

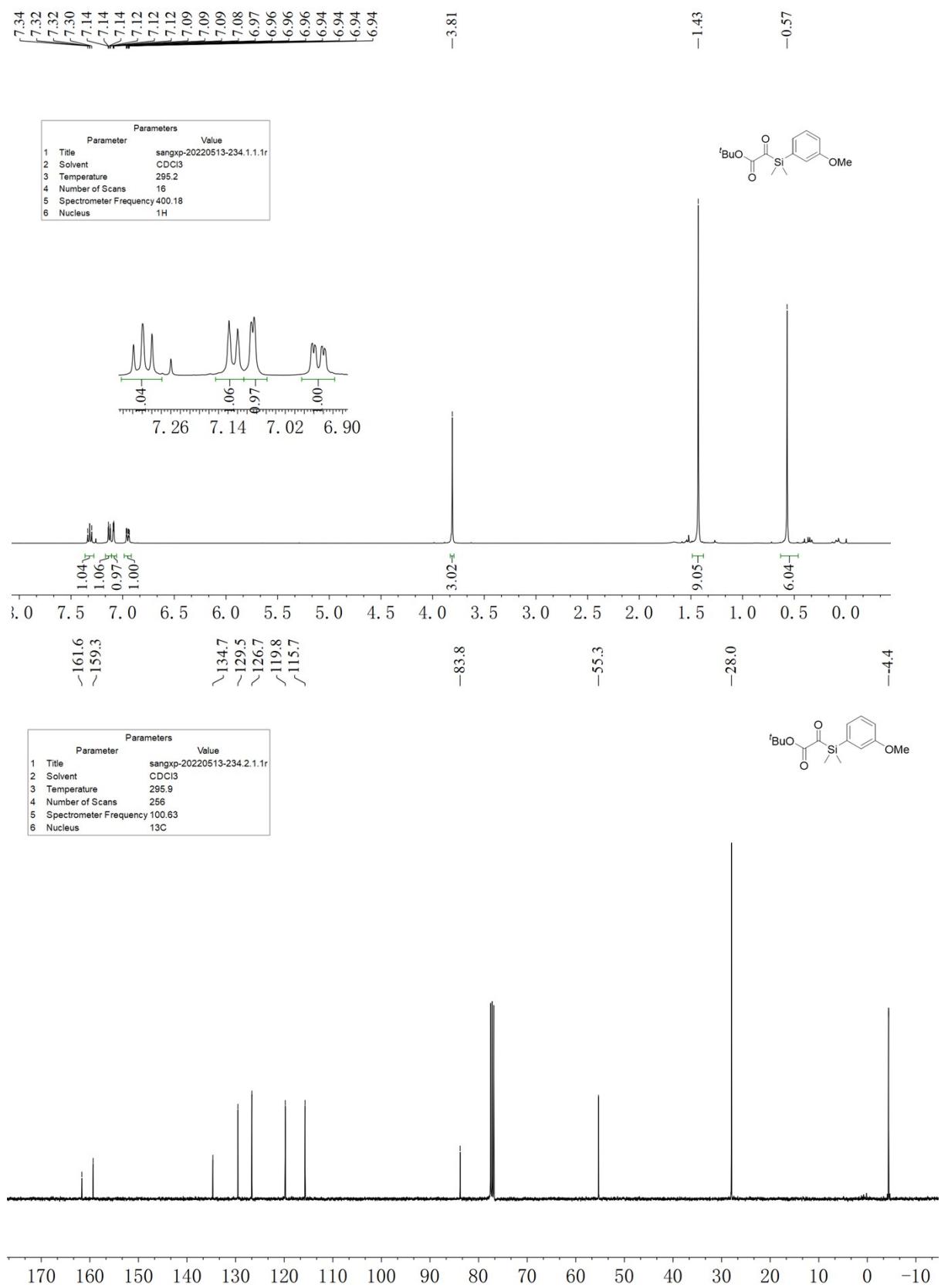
A2

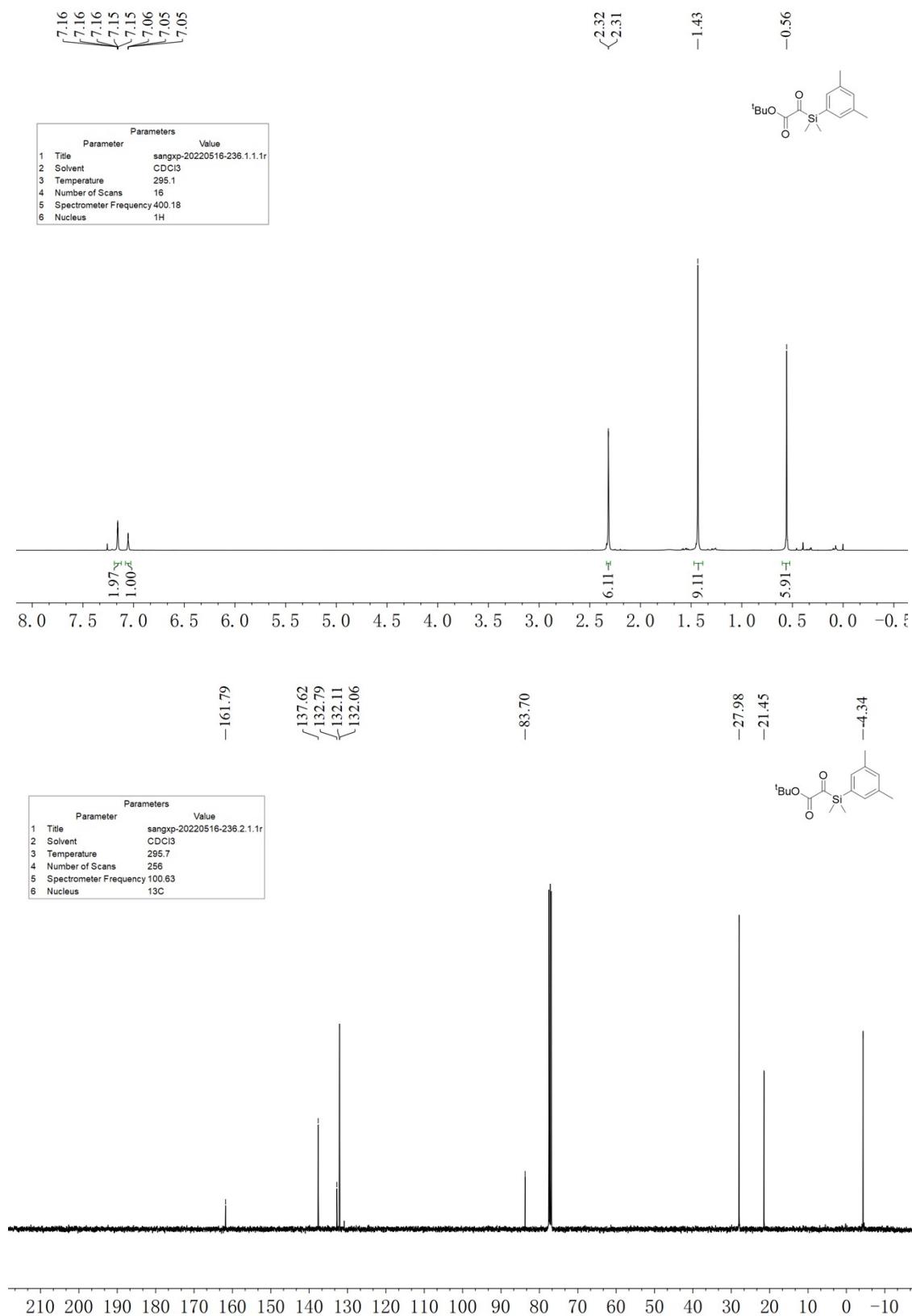


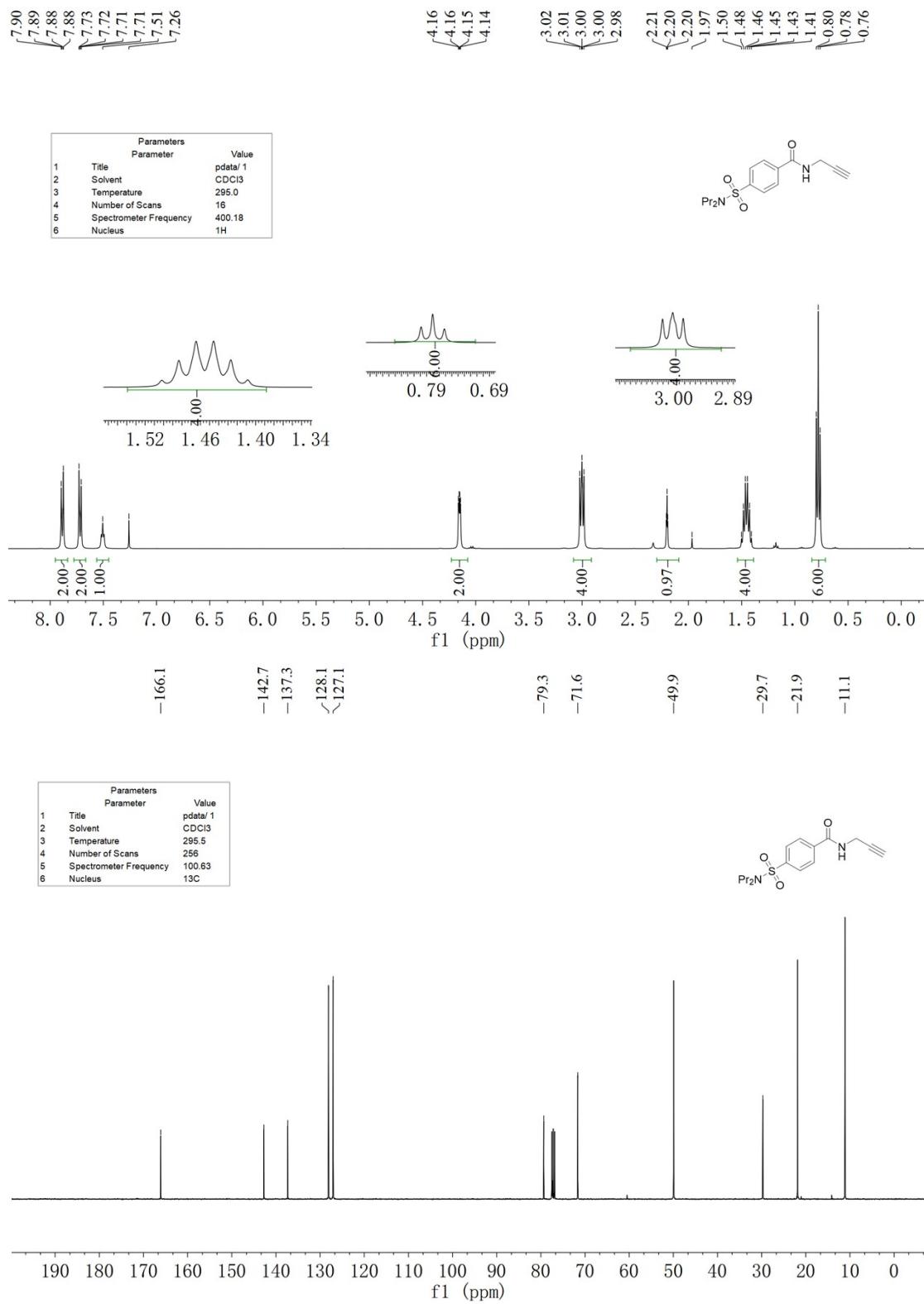
A4

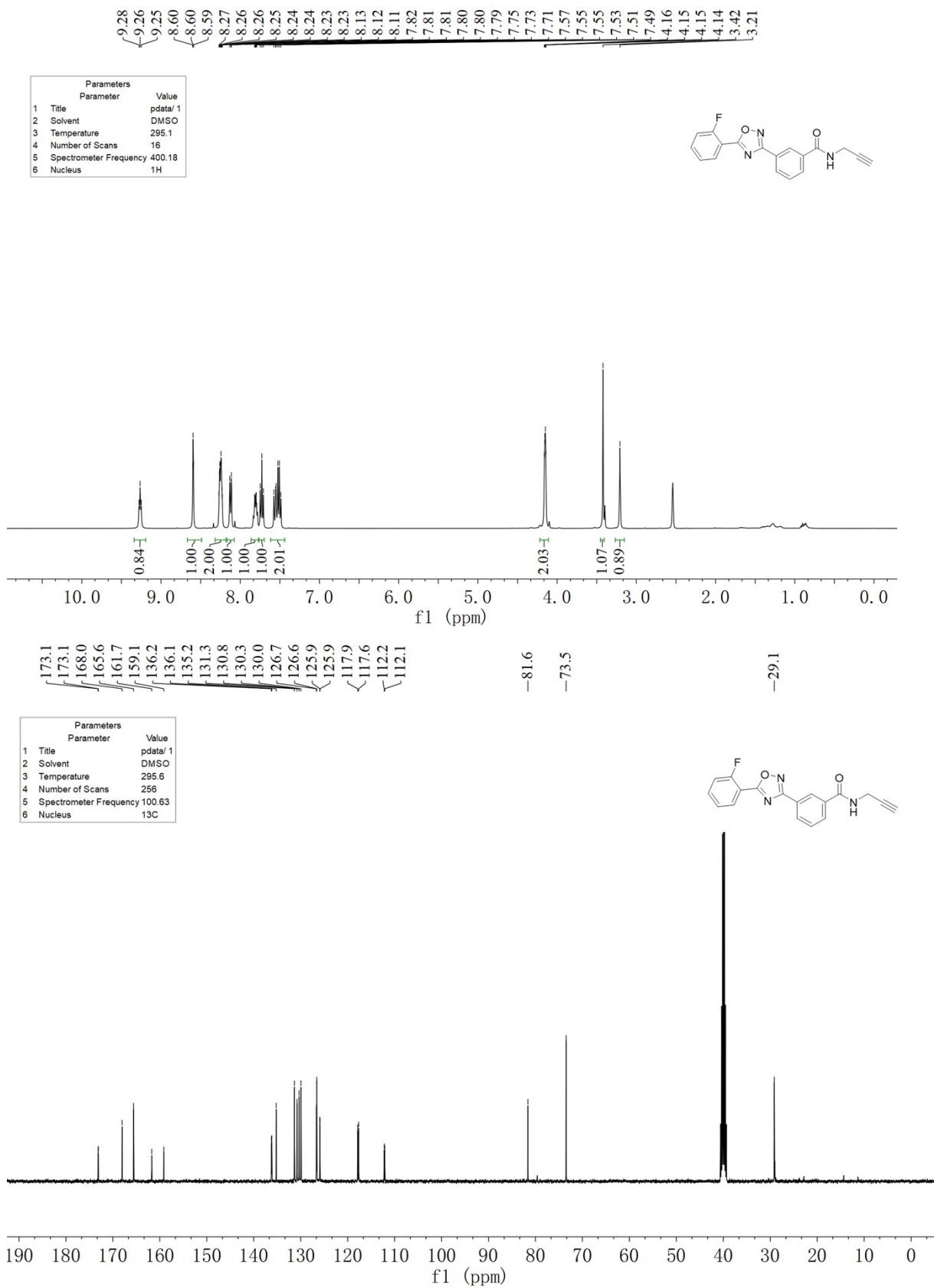


A5



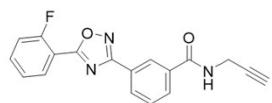
**A6**

**B25**

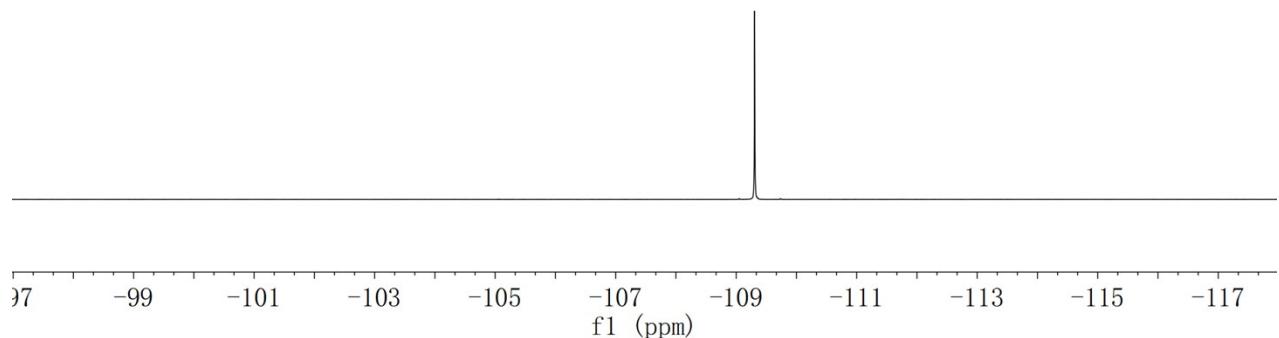
**B26**

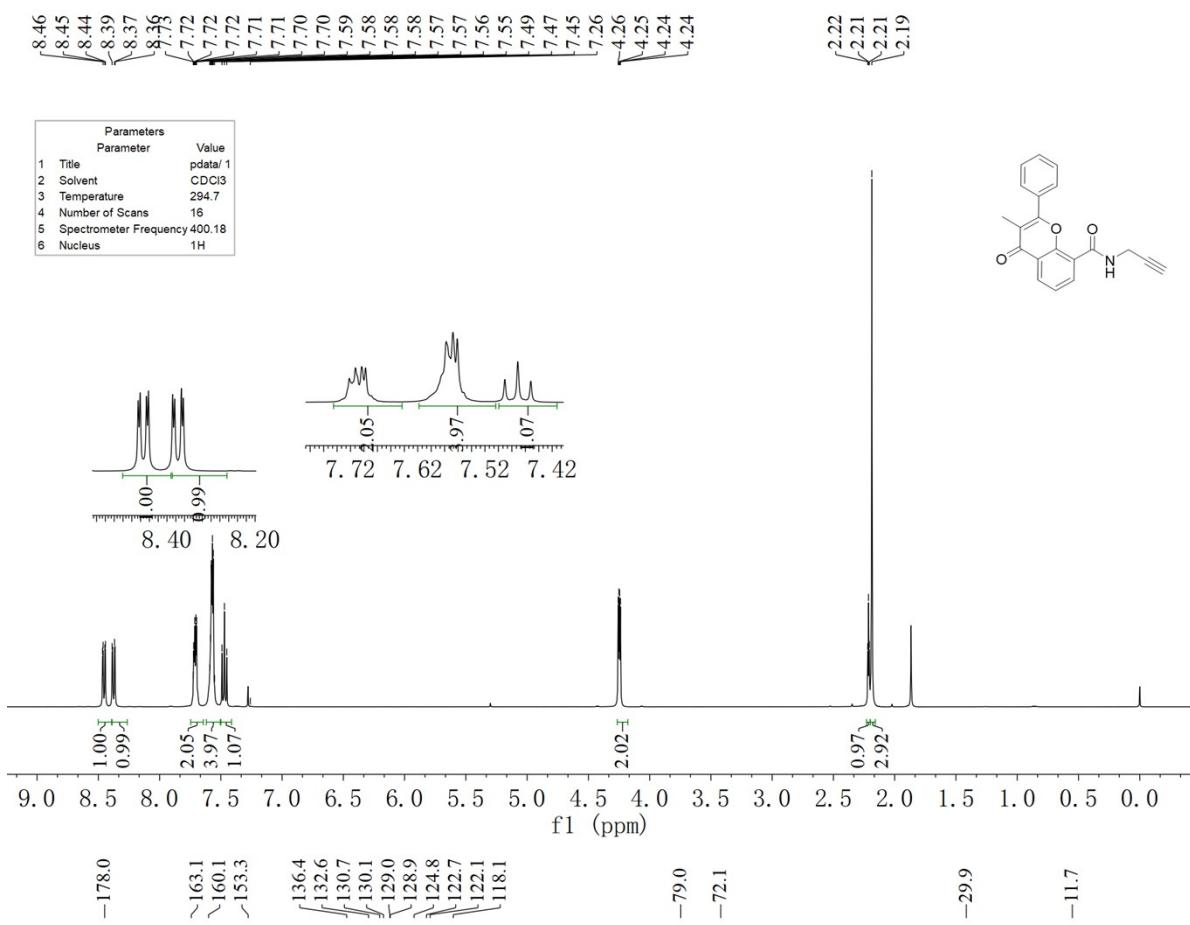


-109.31

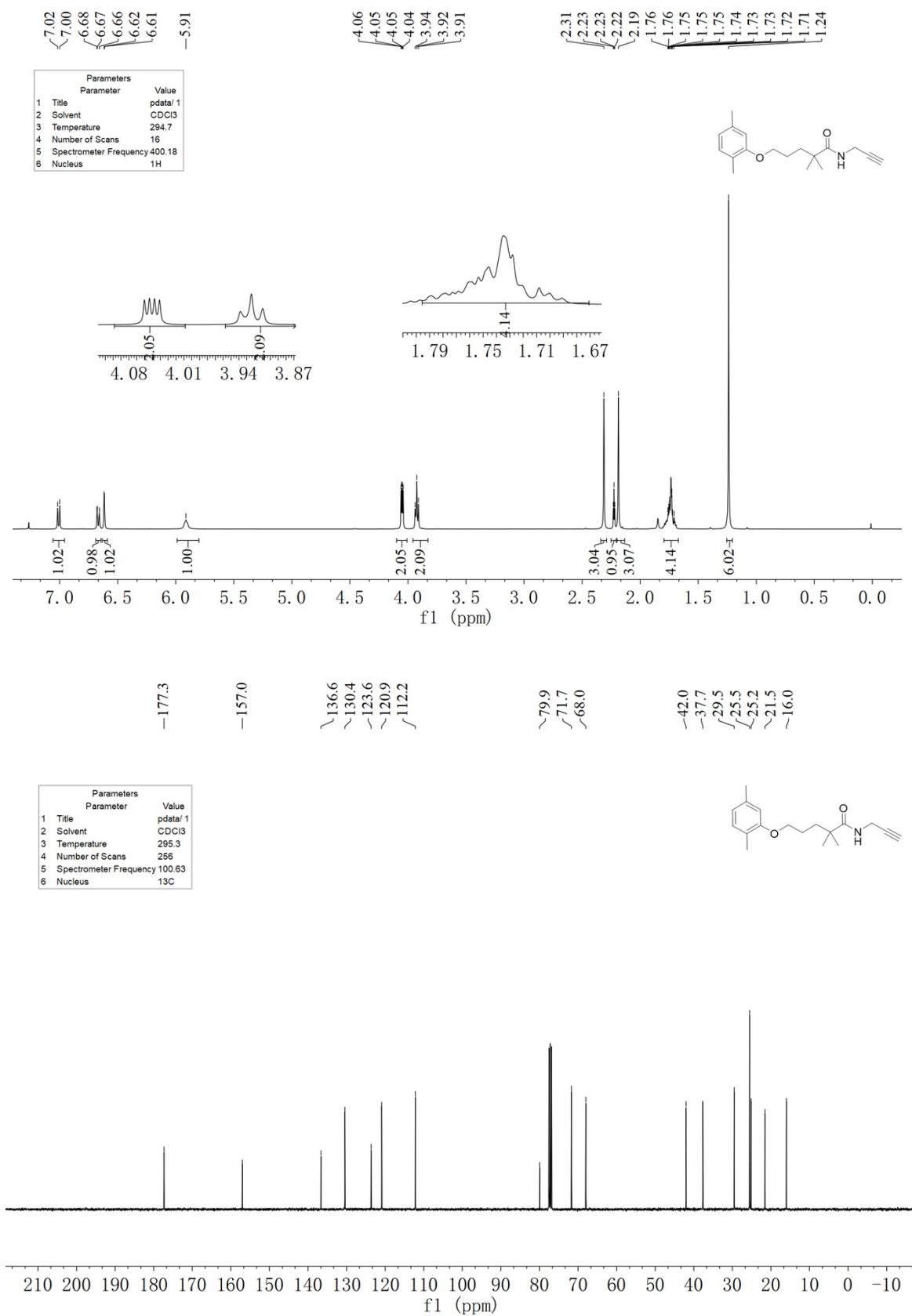


Parameters		
Parameter	Value	
1 Title	pdata/1	
2 Solvent	DMSO	
3 Temperature	295.3	
4 Number of Scans	16	
5 Spectrometer Frequency	376.55	
6 Nucleus	19F	

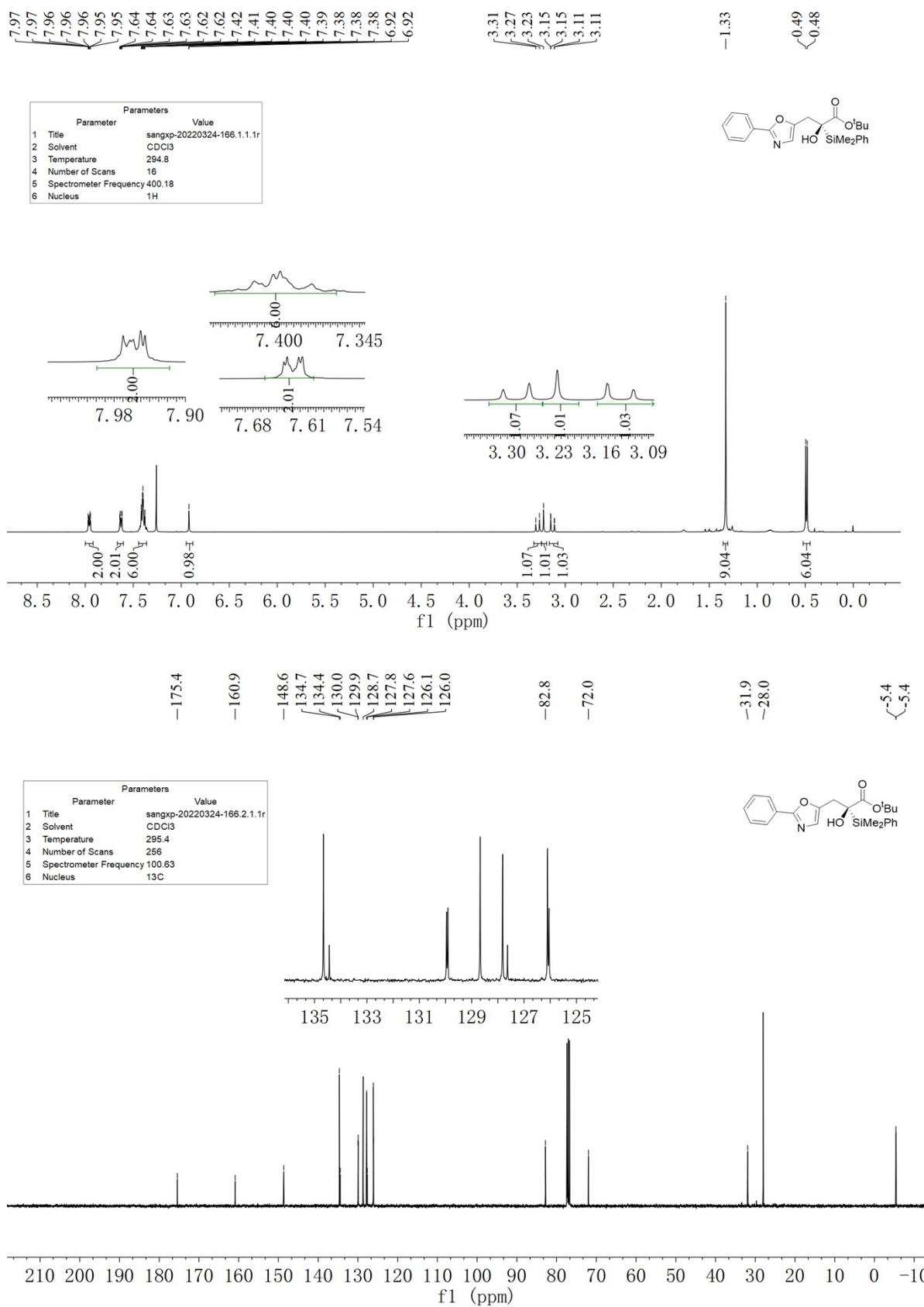


**B27**

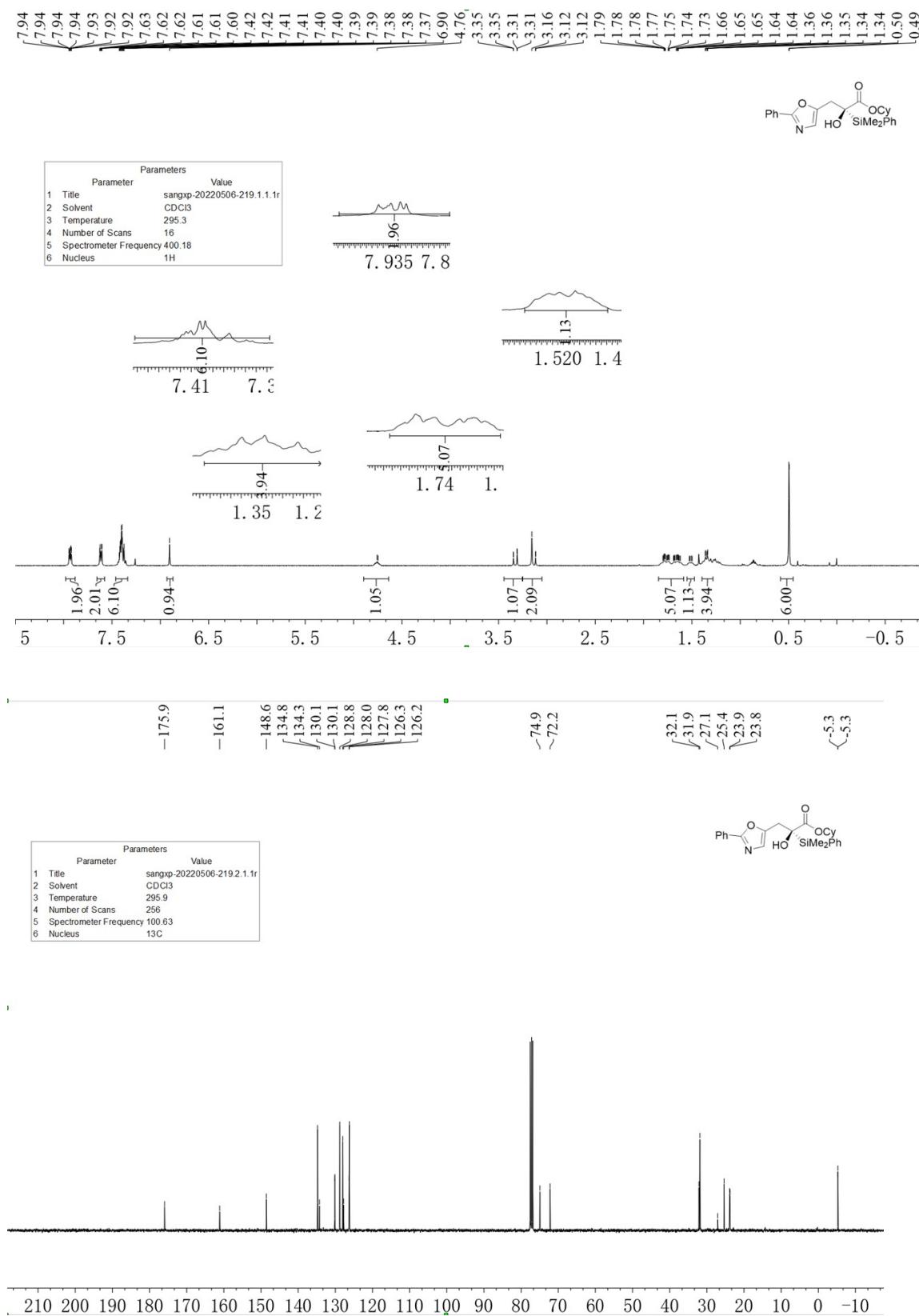
**B33**



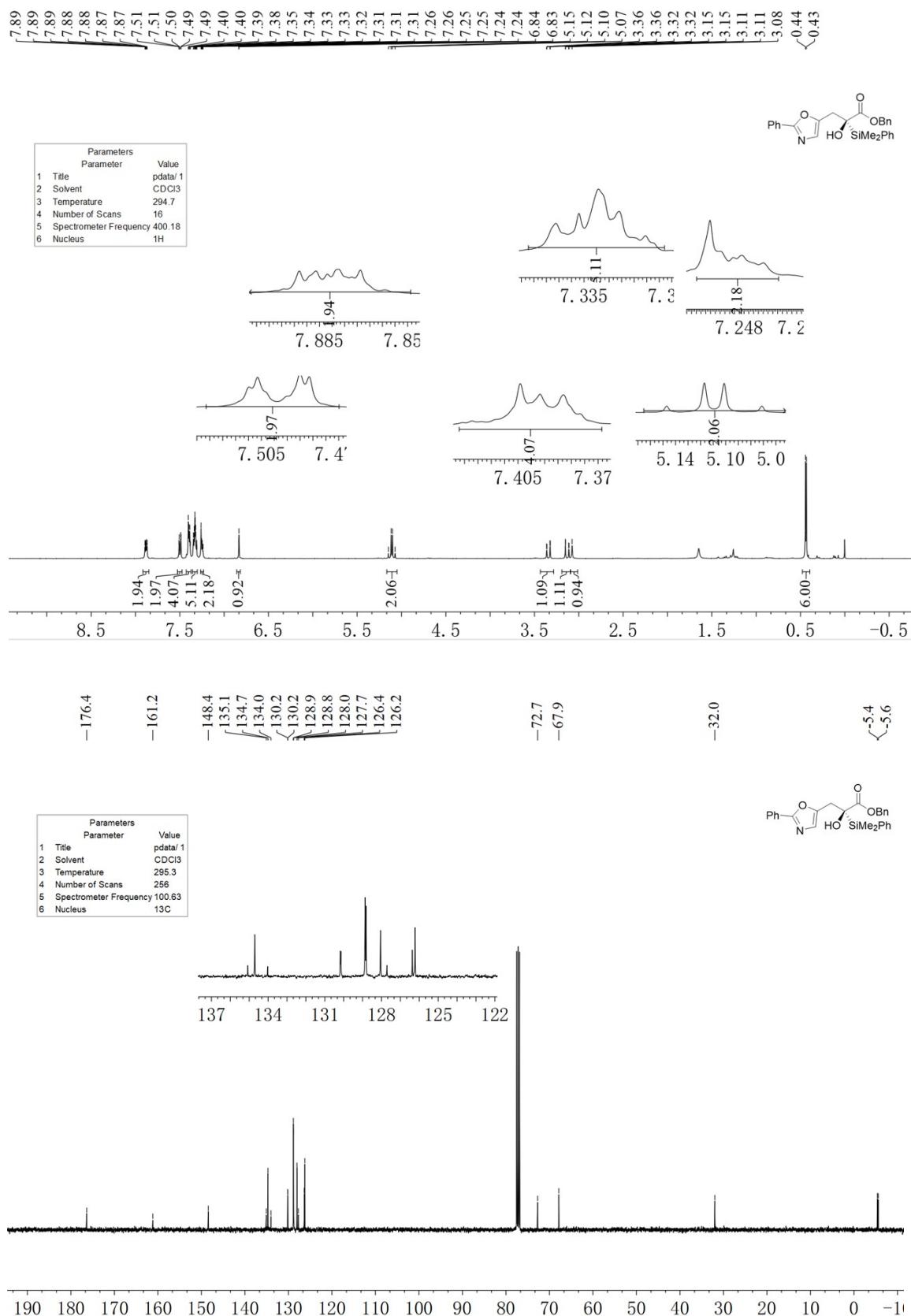
C1



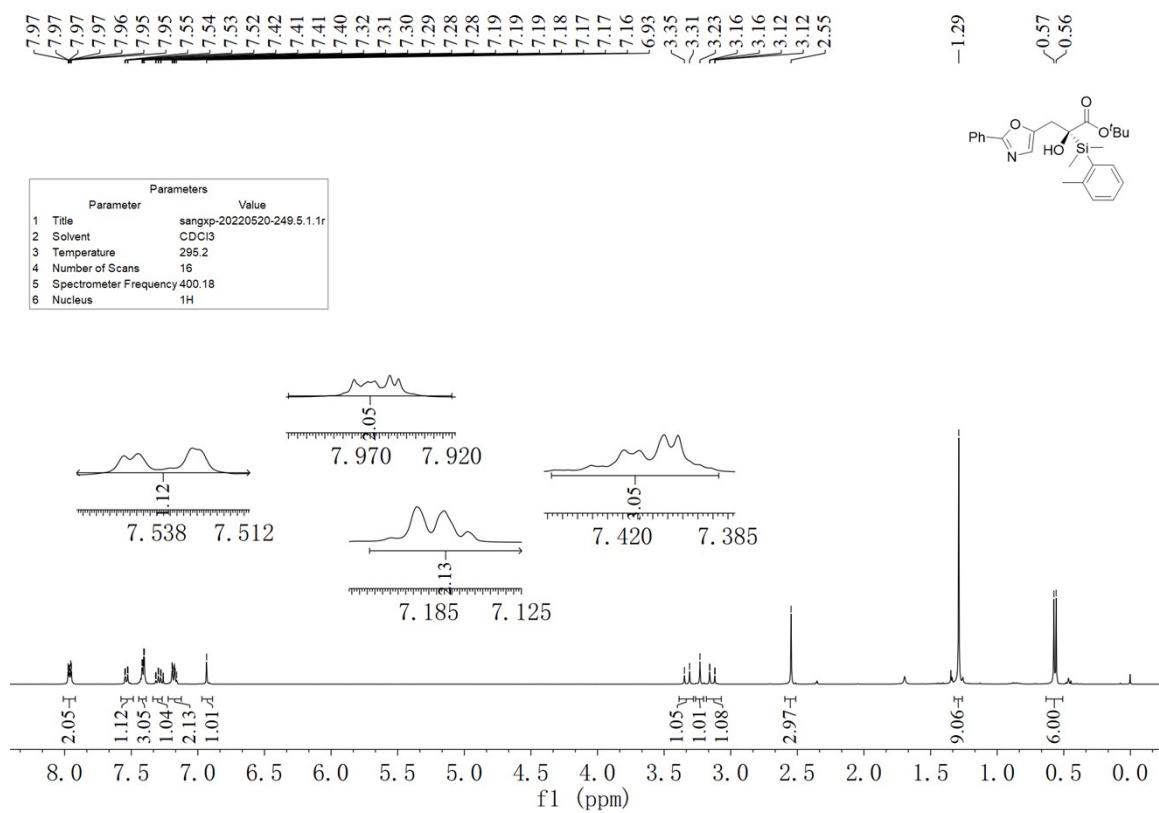
C2

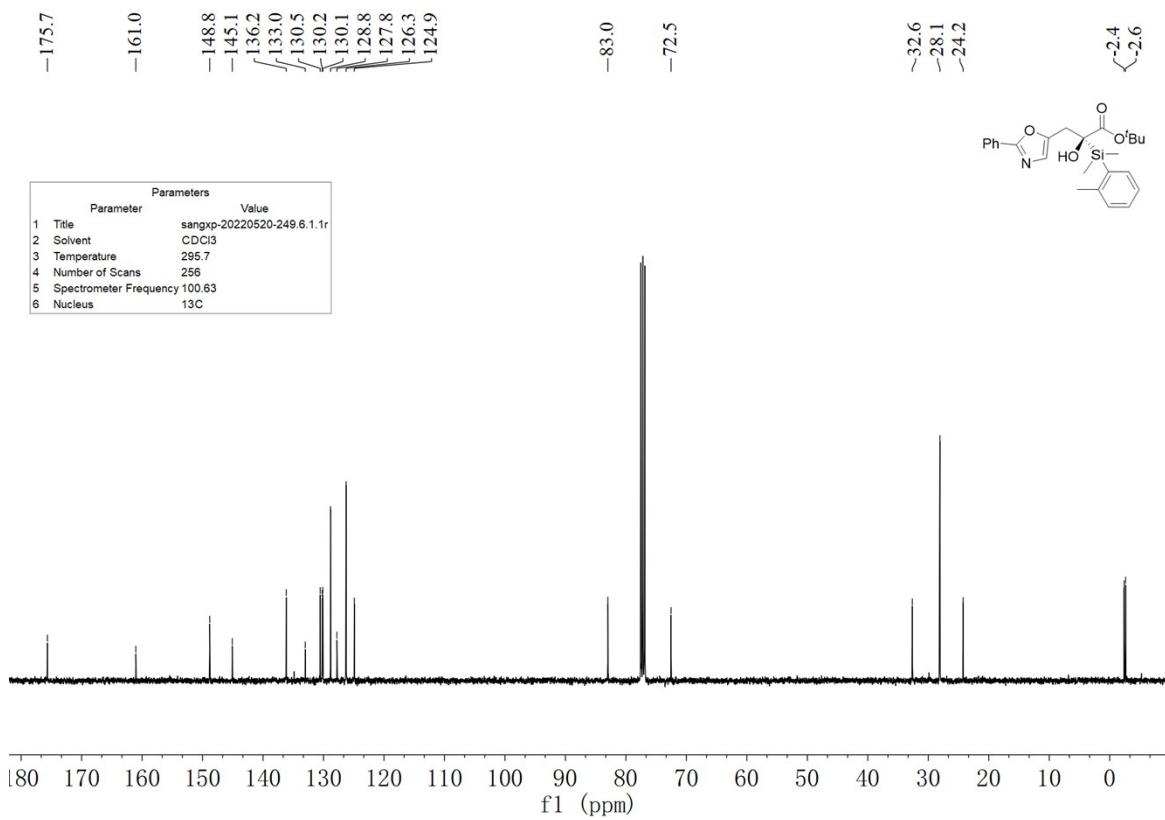


C3

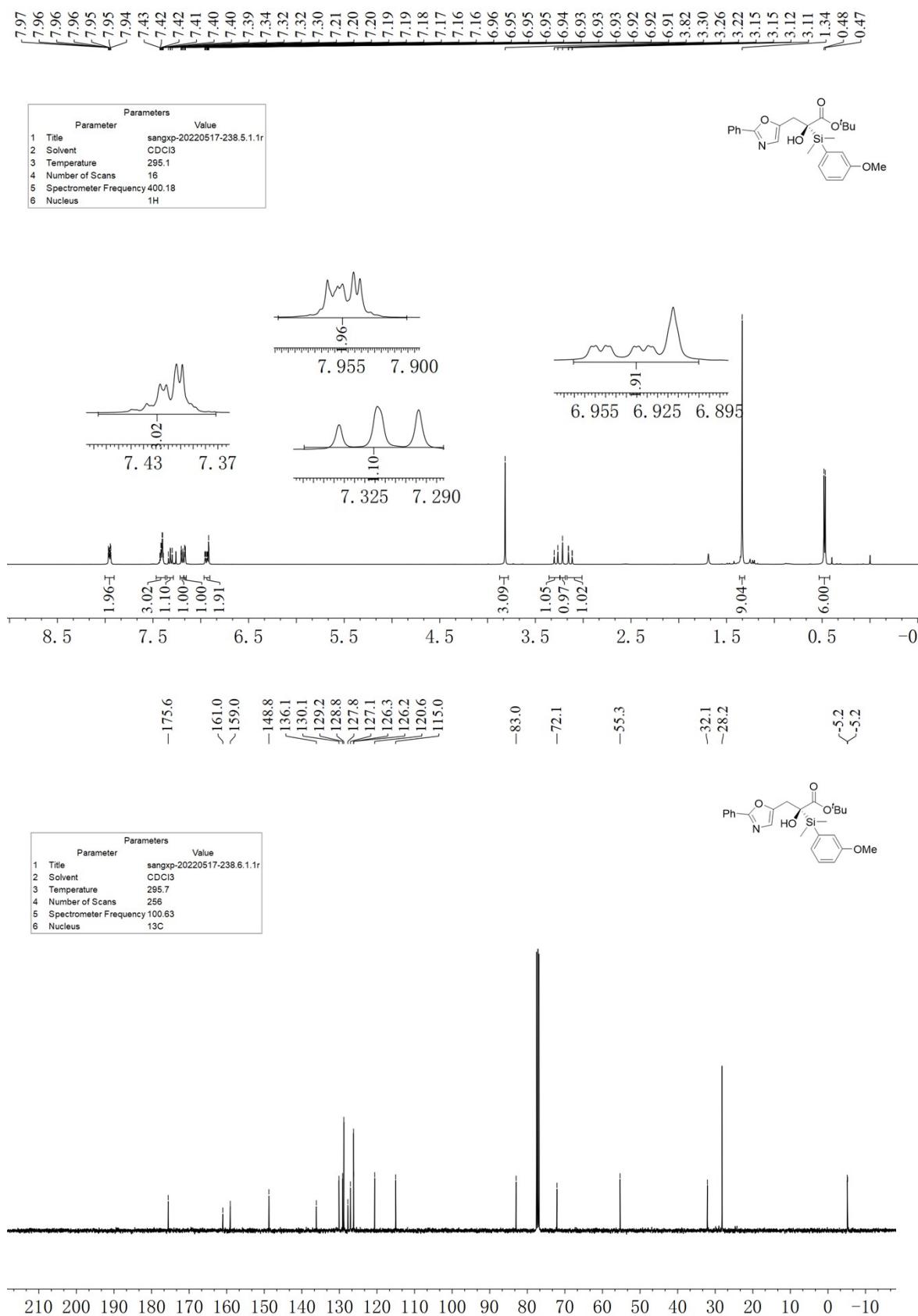


**C4**

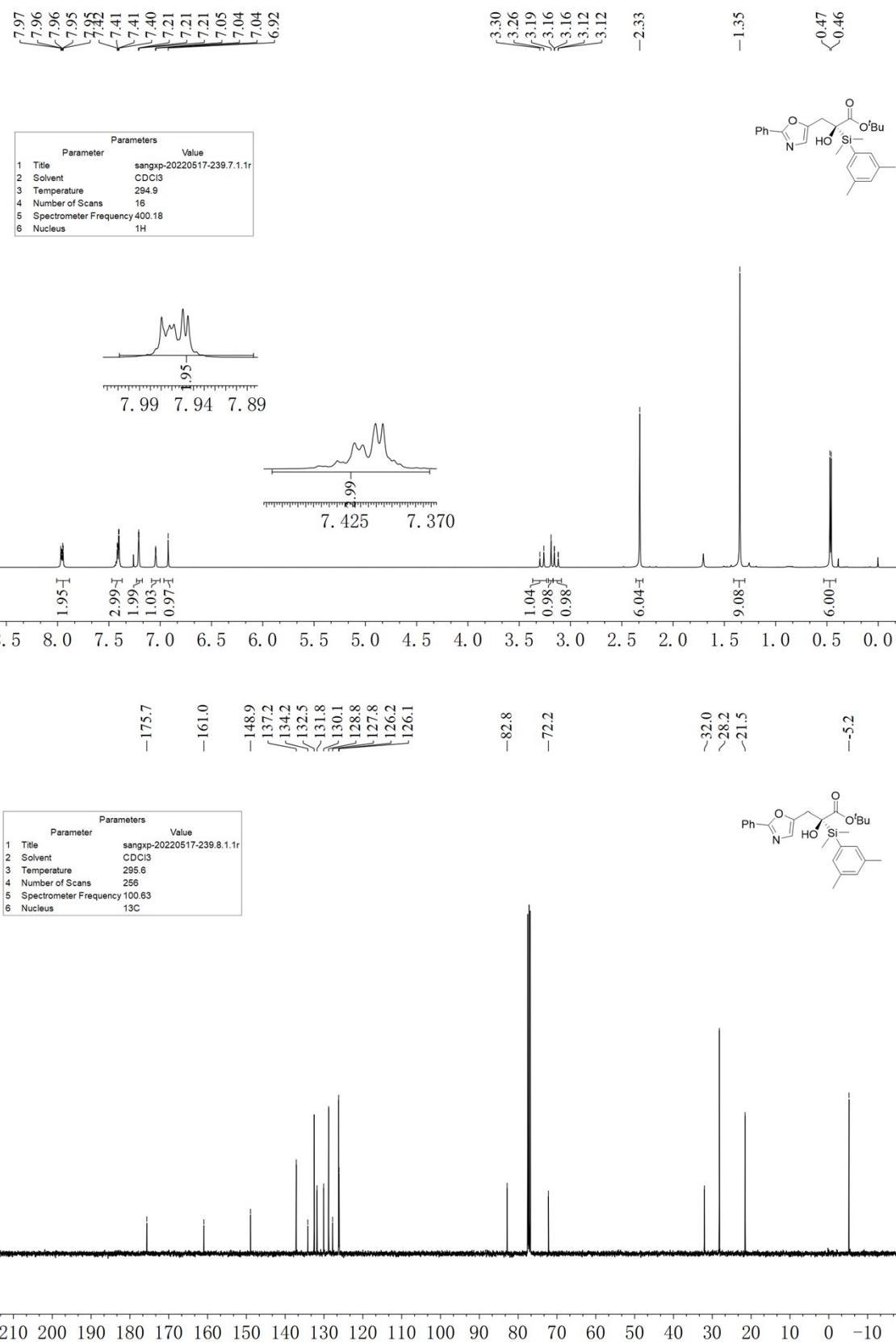




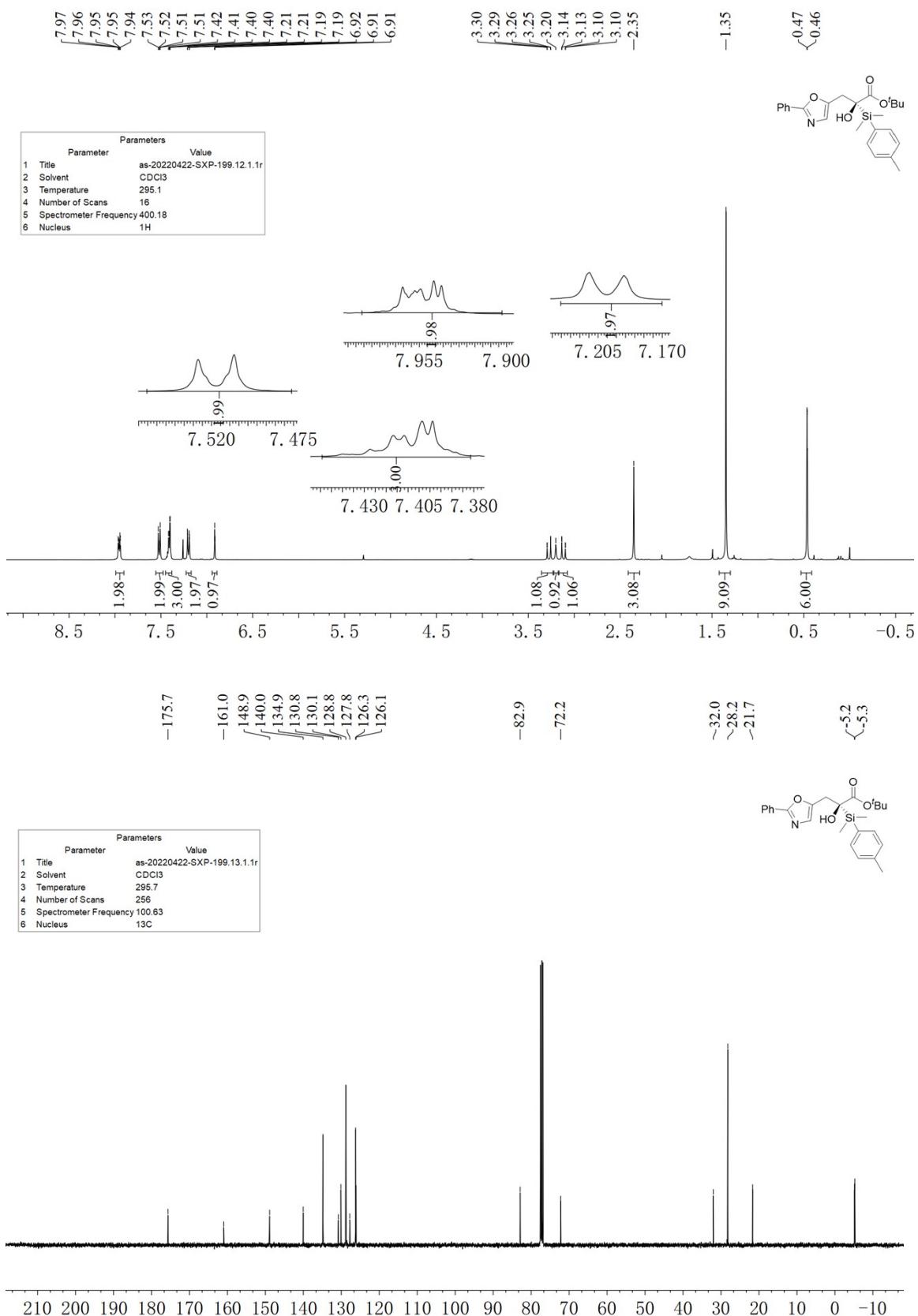
C5

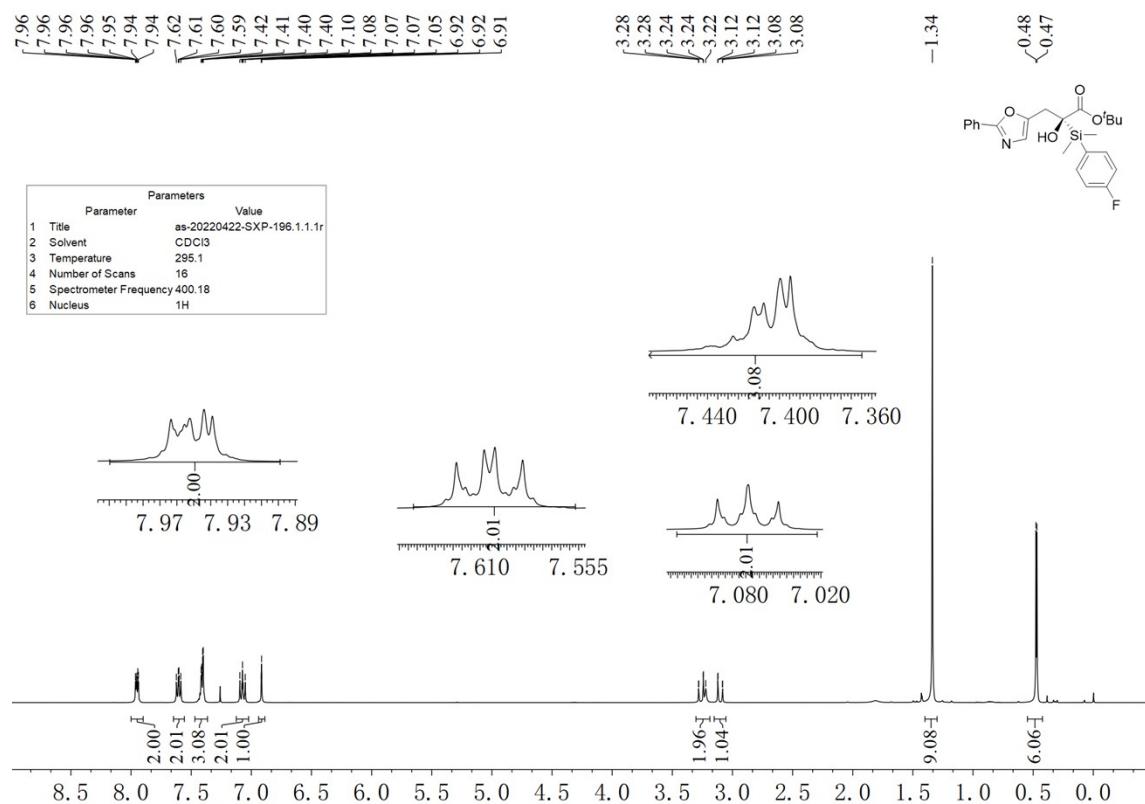


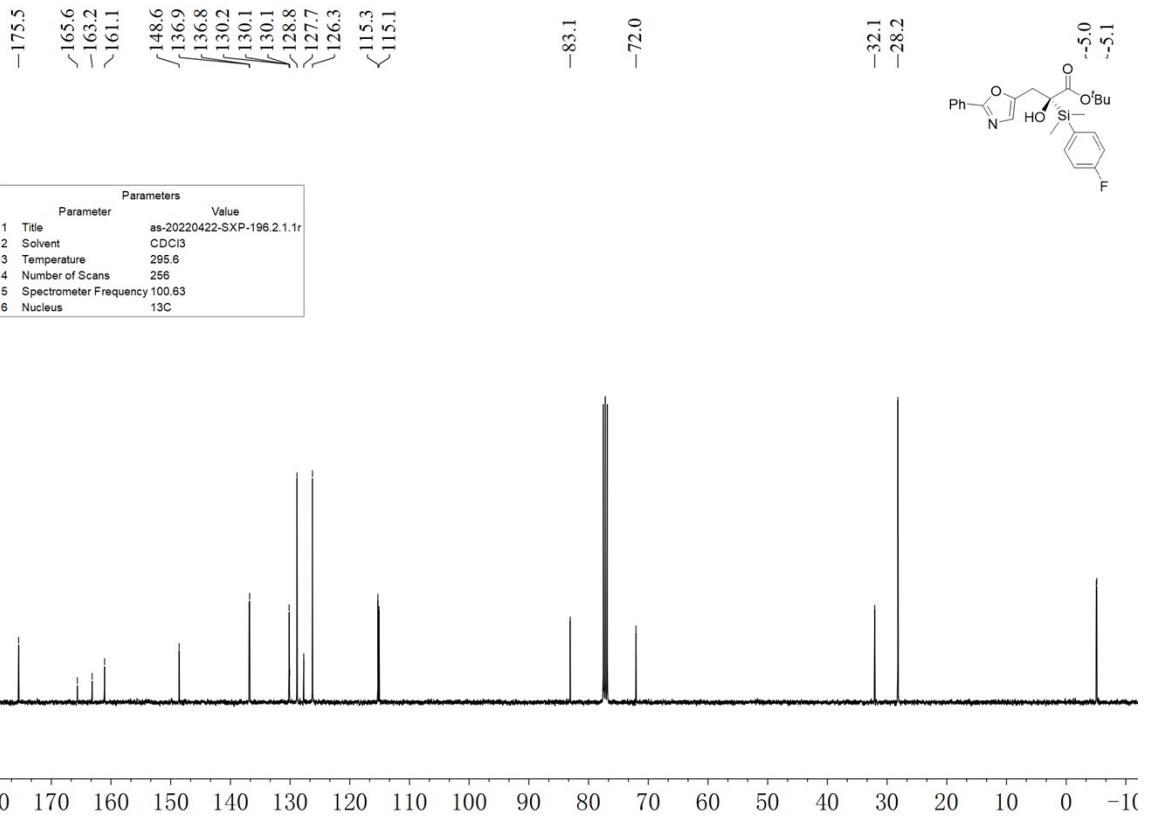
**C6**



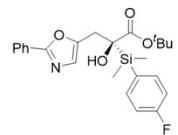
C7



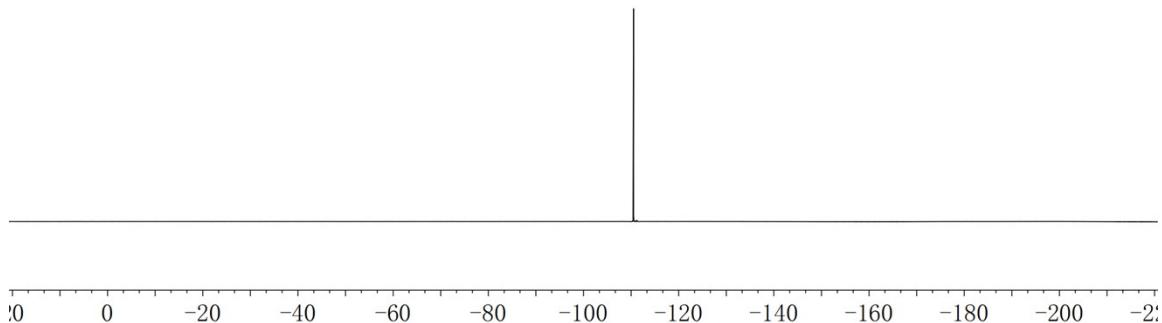
**C8**

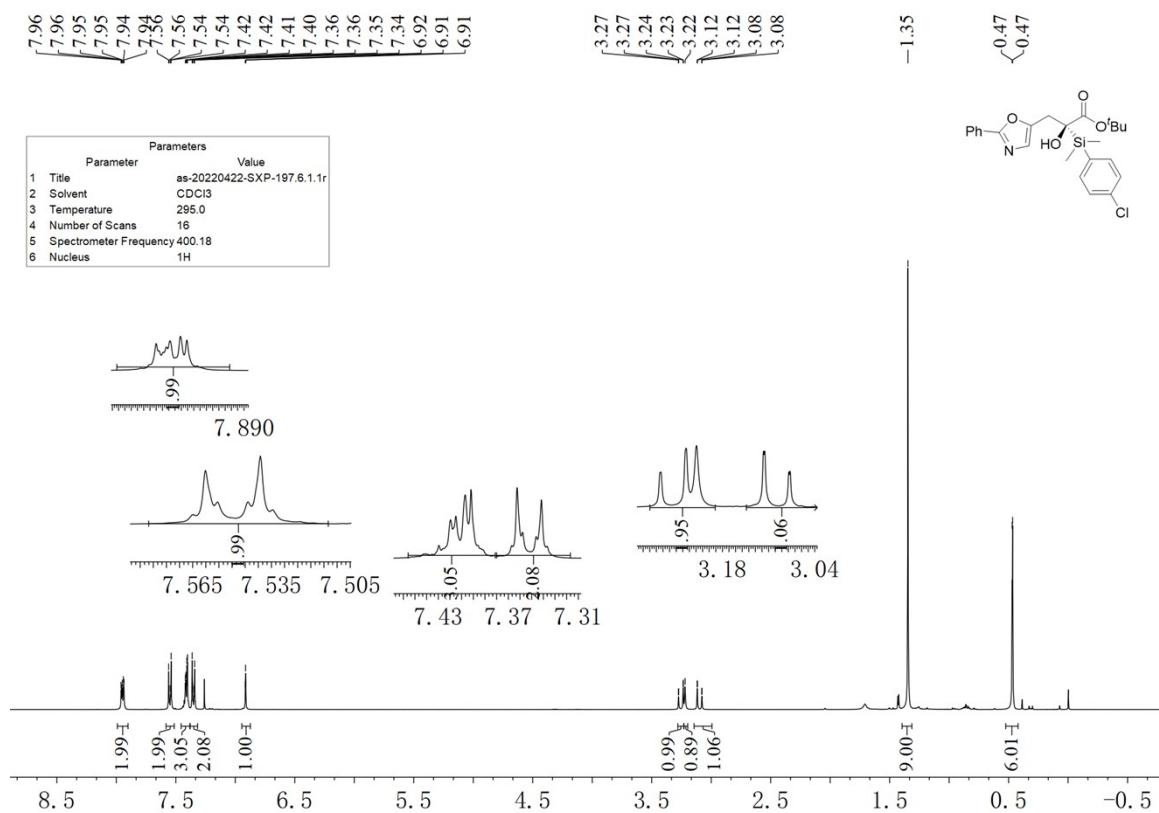


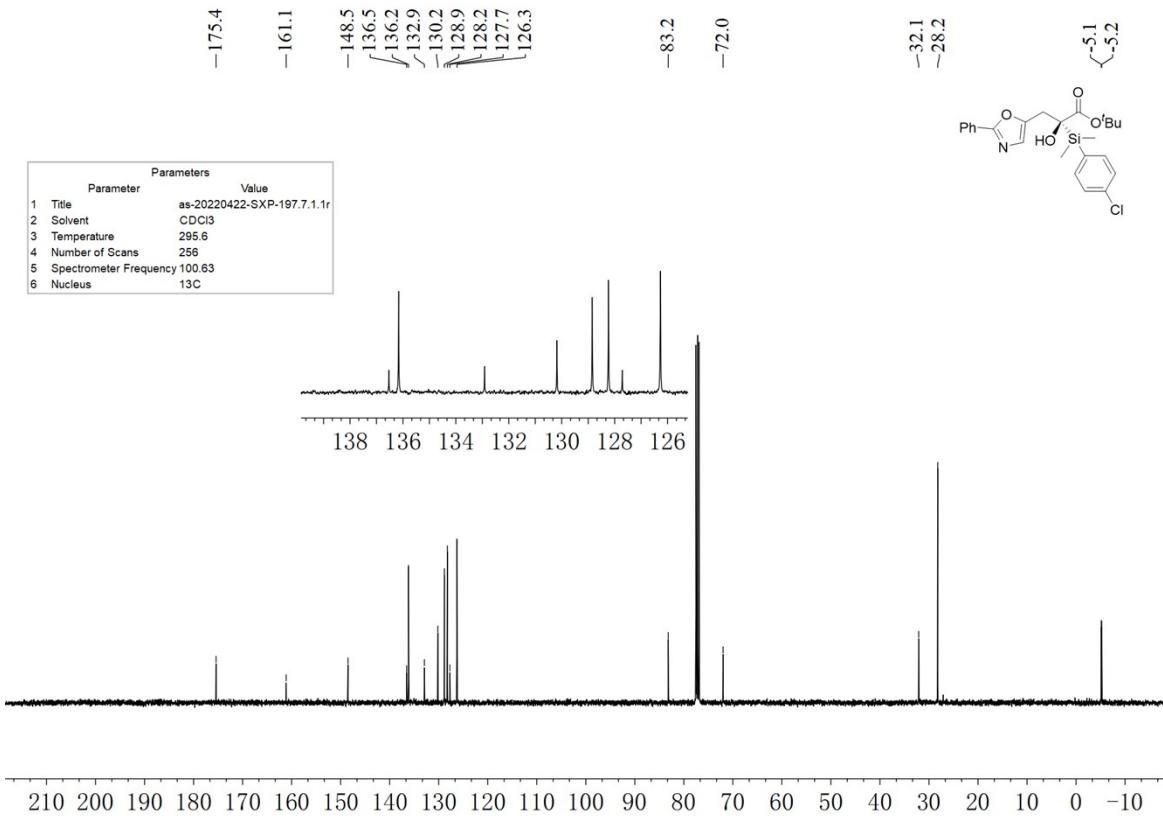
-110.51



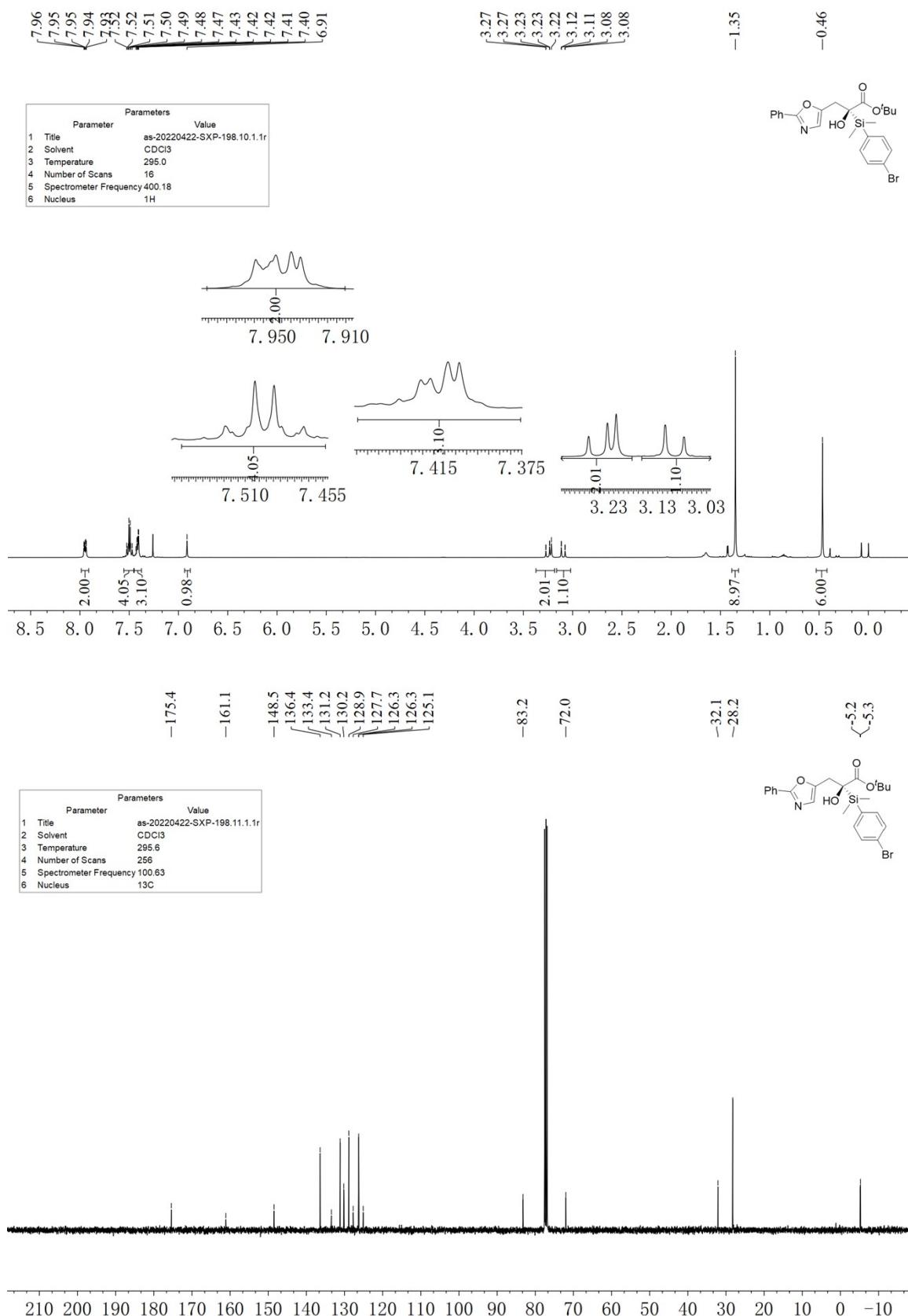
Parameters	
Parameter	Value
1 Title	as-20220422-SXP-196.3.1.r
2 Solvent	CDCl <sub>3</sub>
3 Temperature	295.3
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	<sup>19</sup> F



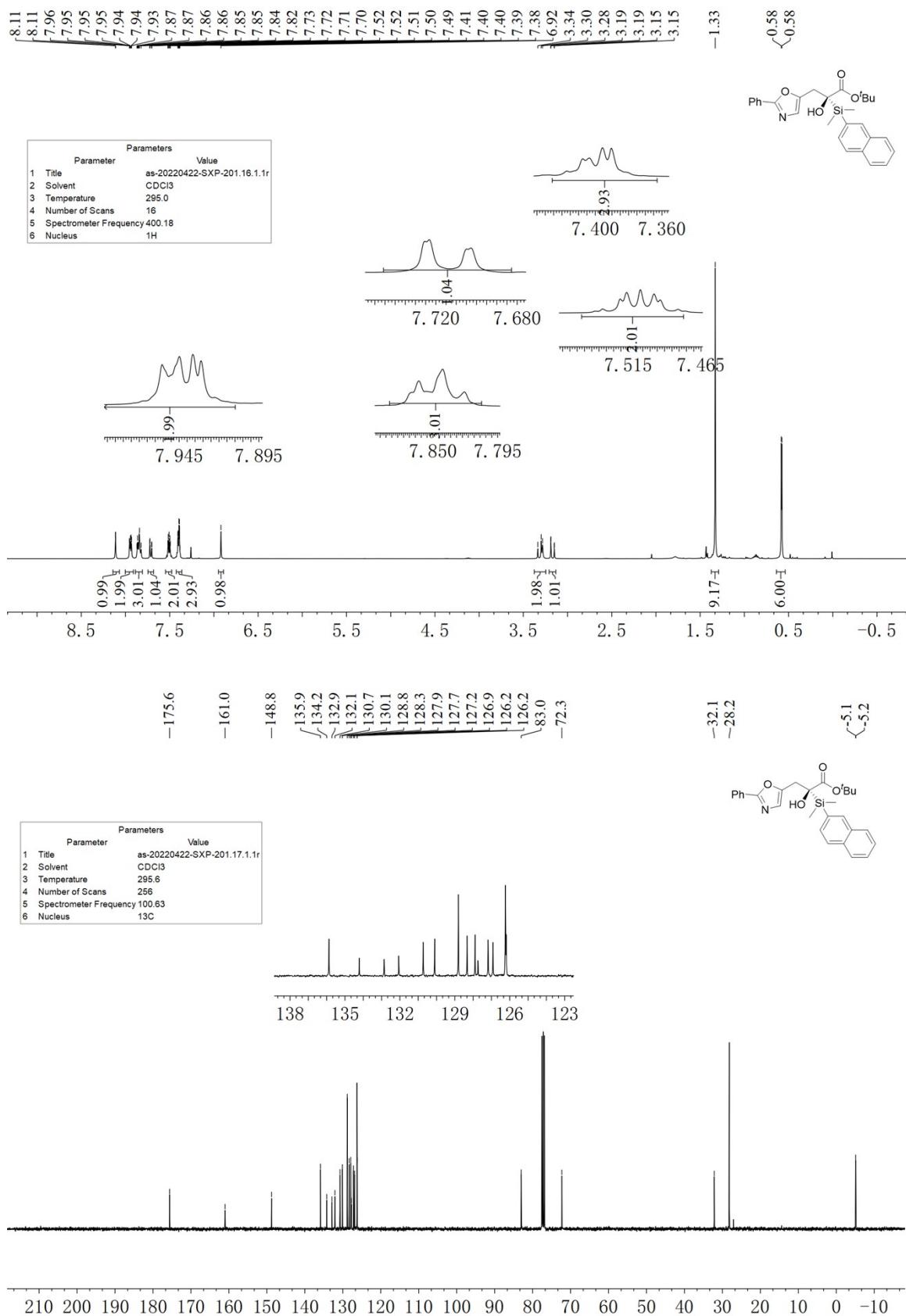
**C9**



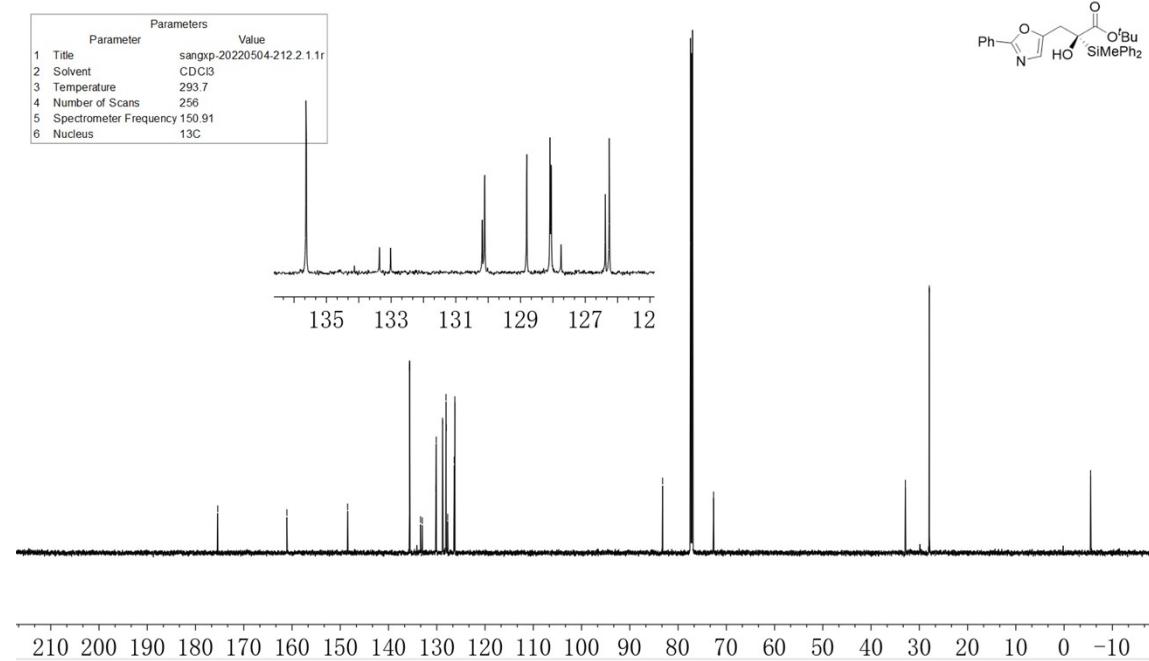
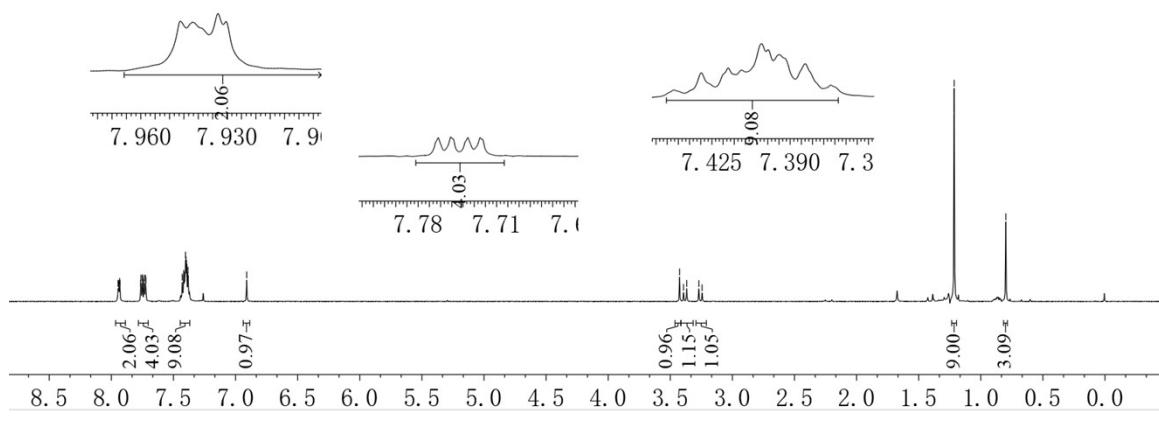
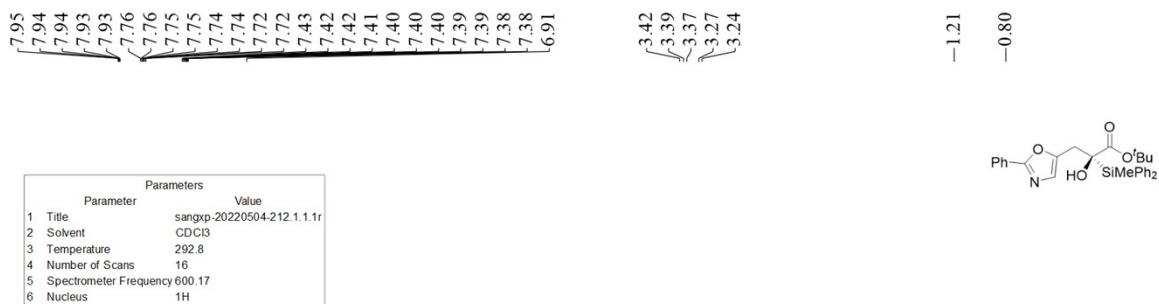
**C10**



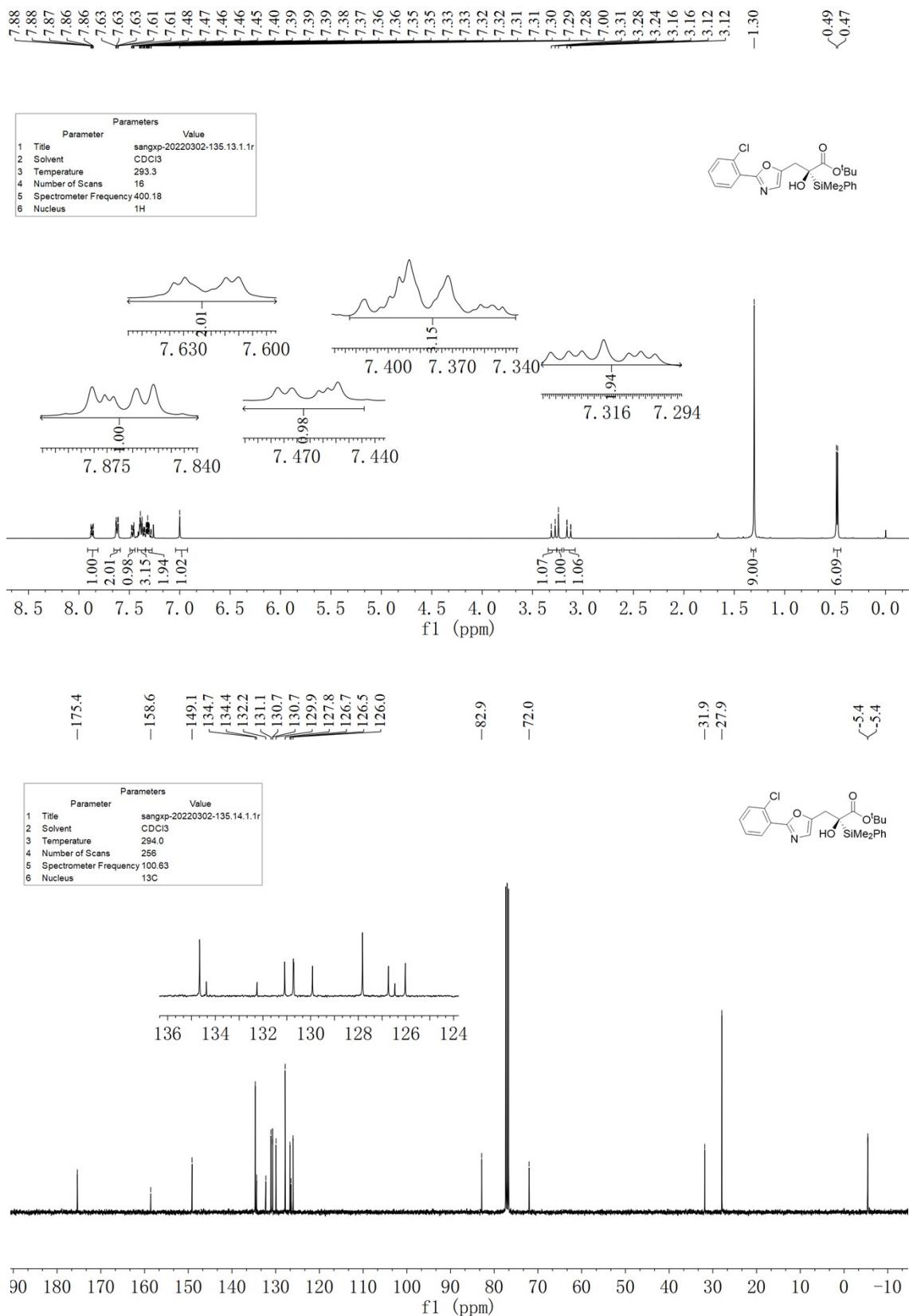
## C11



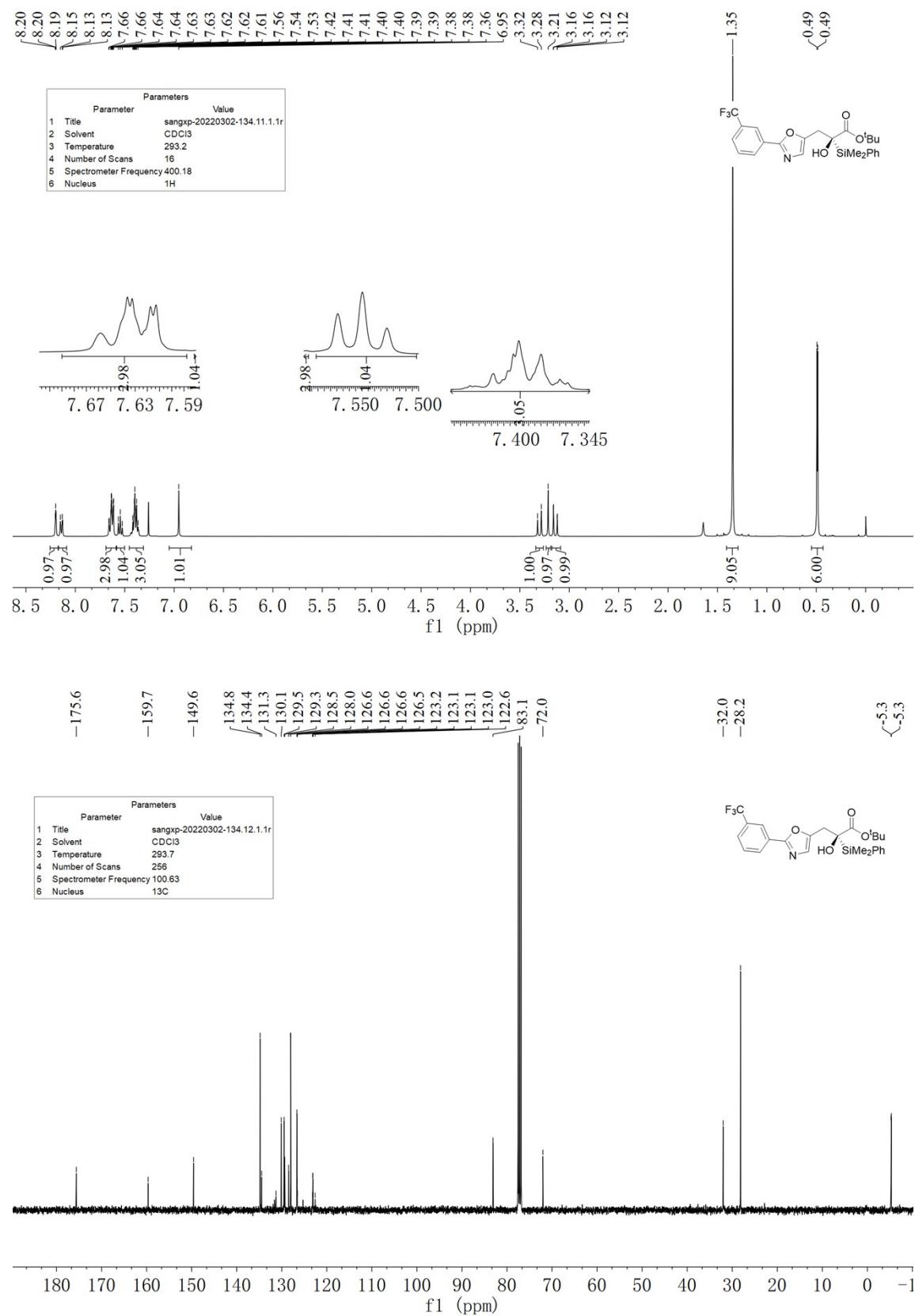
**C12**



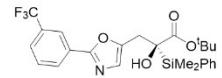
**C13**



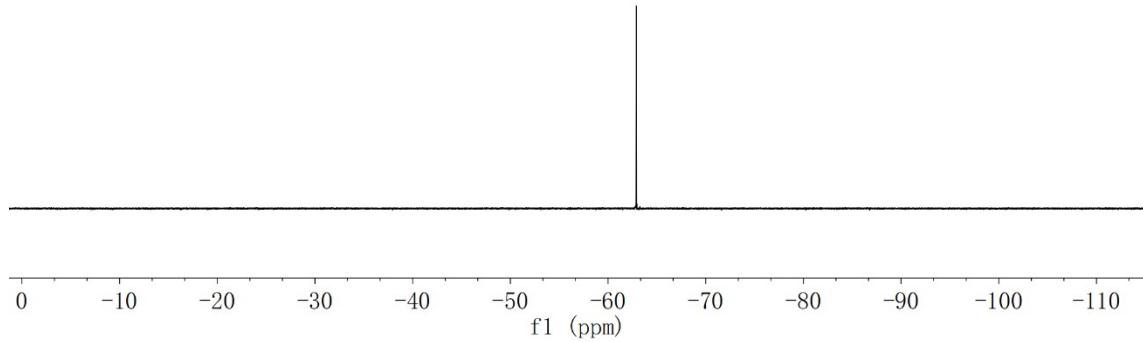
**C14**



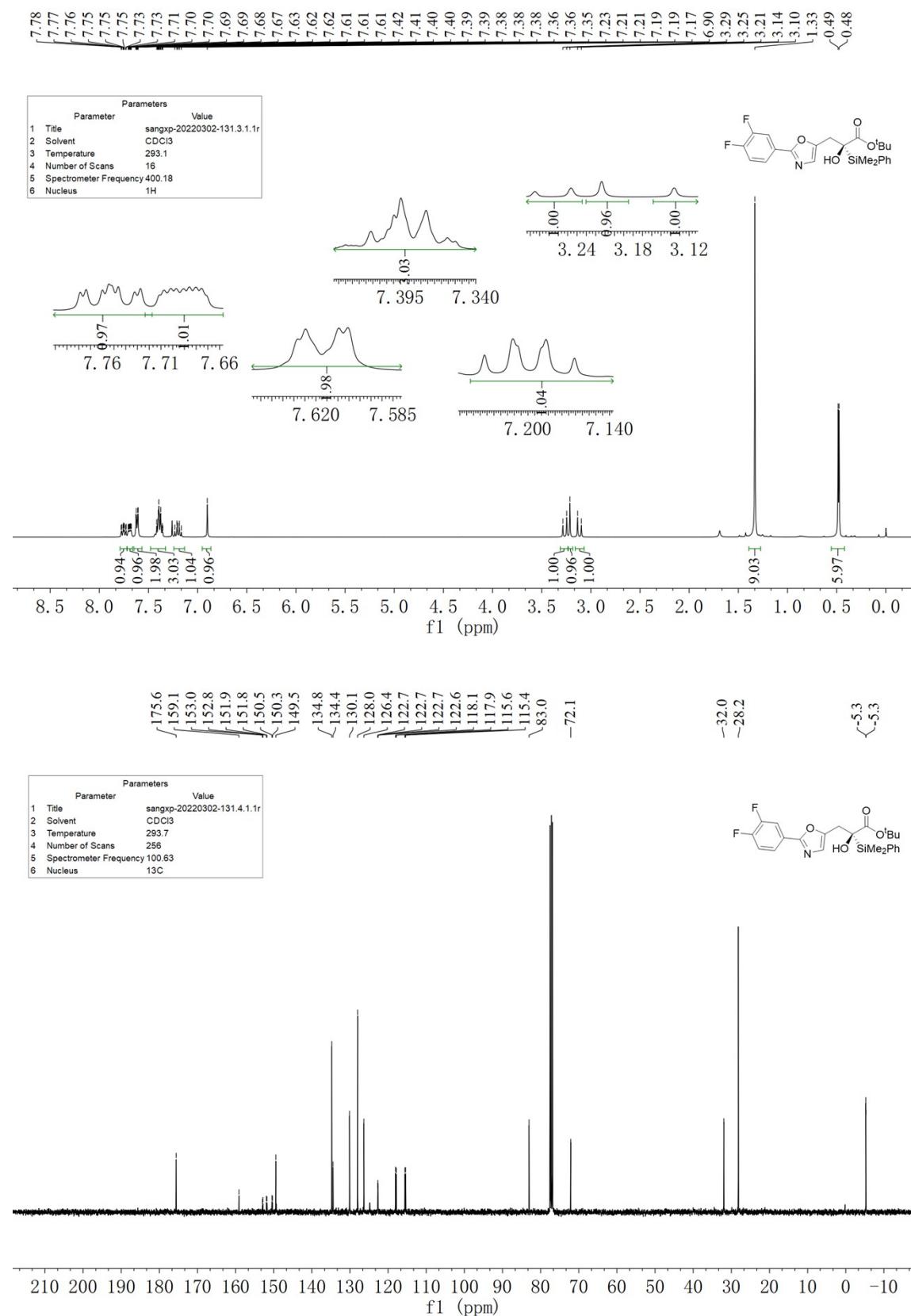
-62.89



Parameters	
Parameter	Value
1 Title	as-20220331-SXP-170.3.1.1r
2 Solvent	CDCl3
3 Temperature	293.5
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	19F

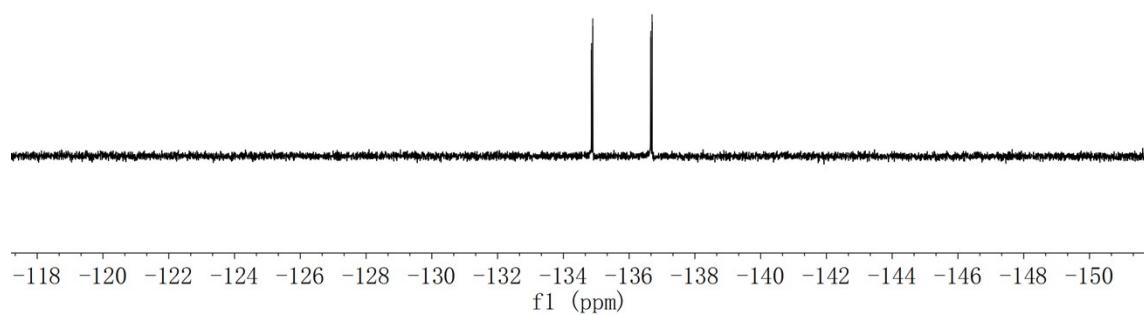
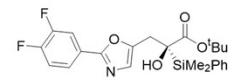


**C15**

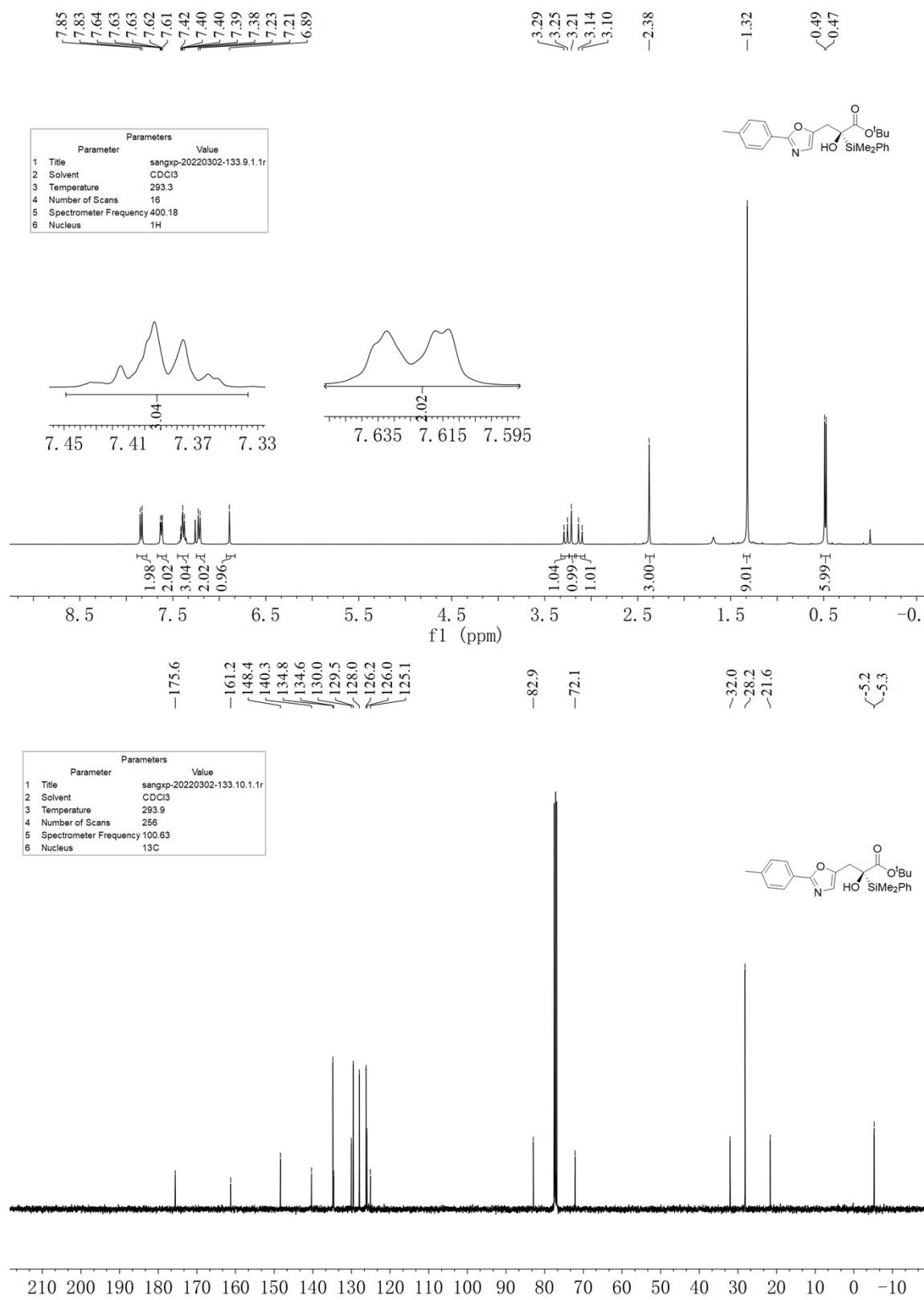


$\left\langle^{-134.86}\right.$   
 $\left\langle^{-134.89}\right.$   
 $\left\langle^{-136.66}\right.$   
 $\left\langle^{-136.70}\right.$

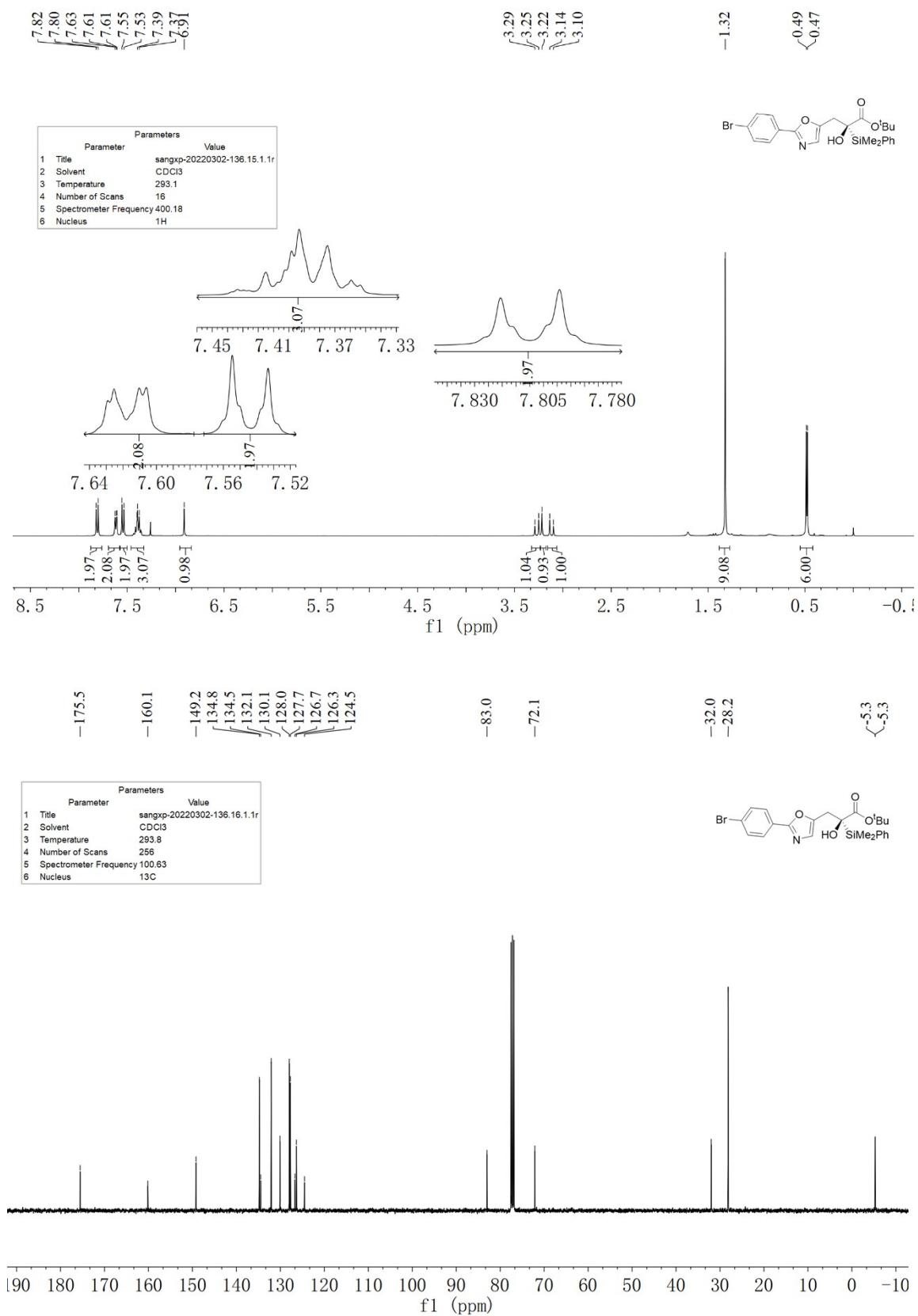
Parameters	
Parameter	Value
1 Title	as-20220331-SXP-171.9.1.r
2 Solvent	CDCl <sub>3</sub>
3 Temperature	293.4
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	<sup>19</sup> F



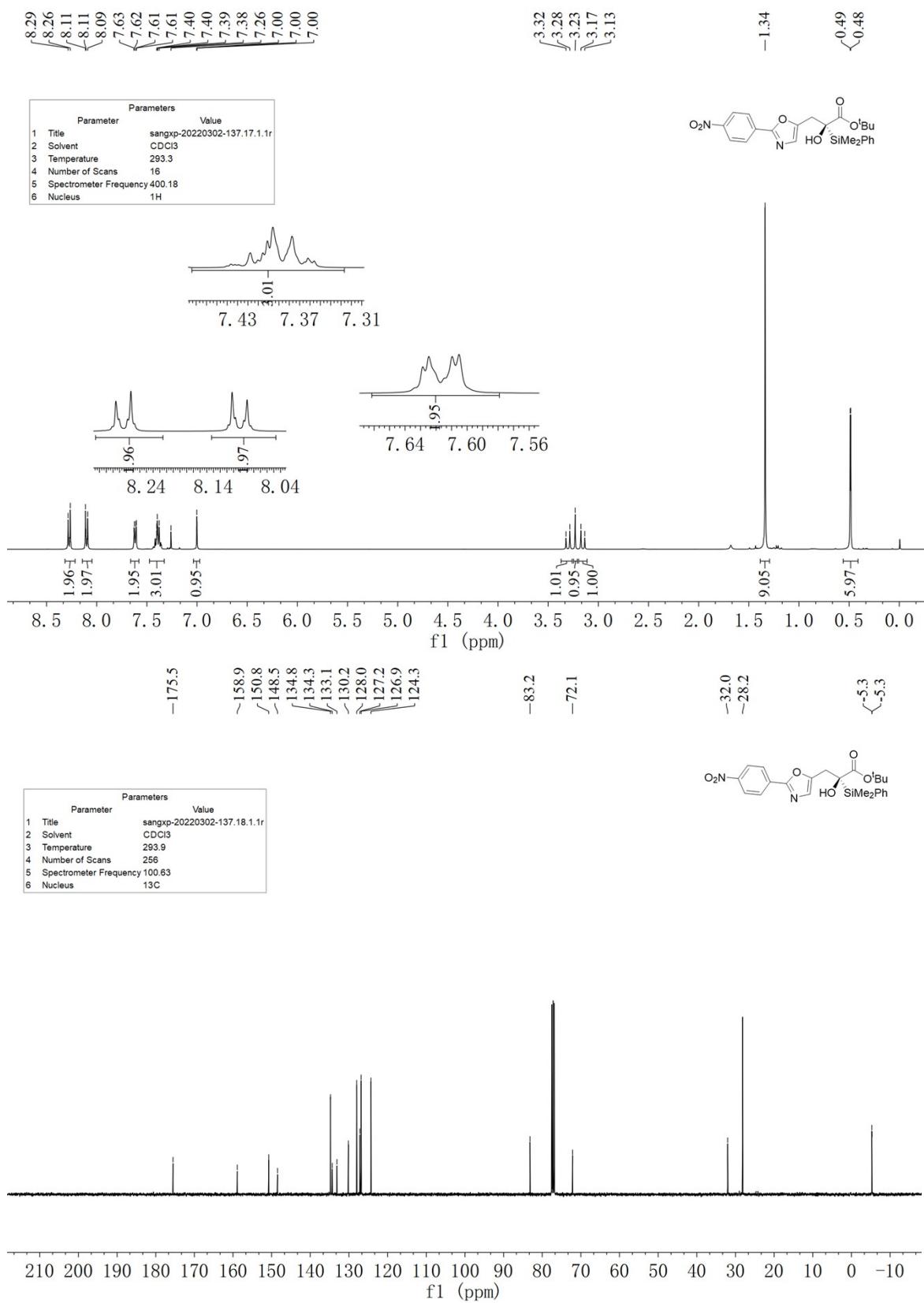
**C16**



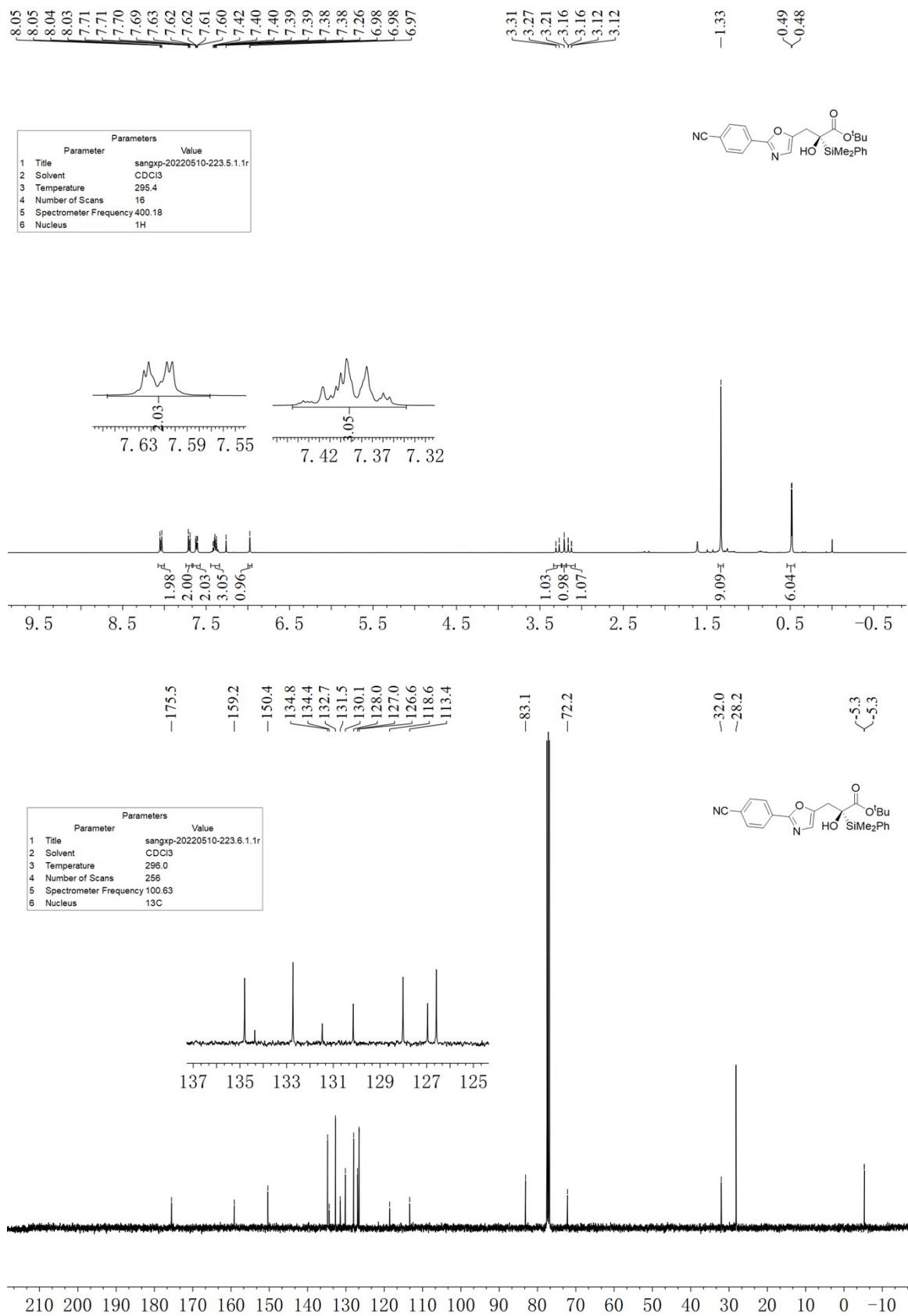
**C17**



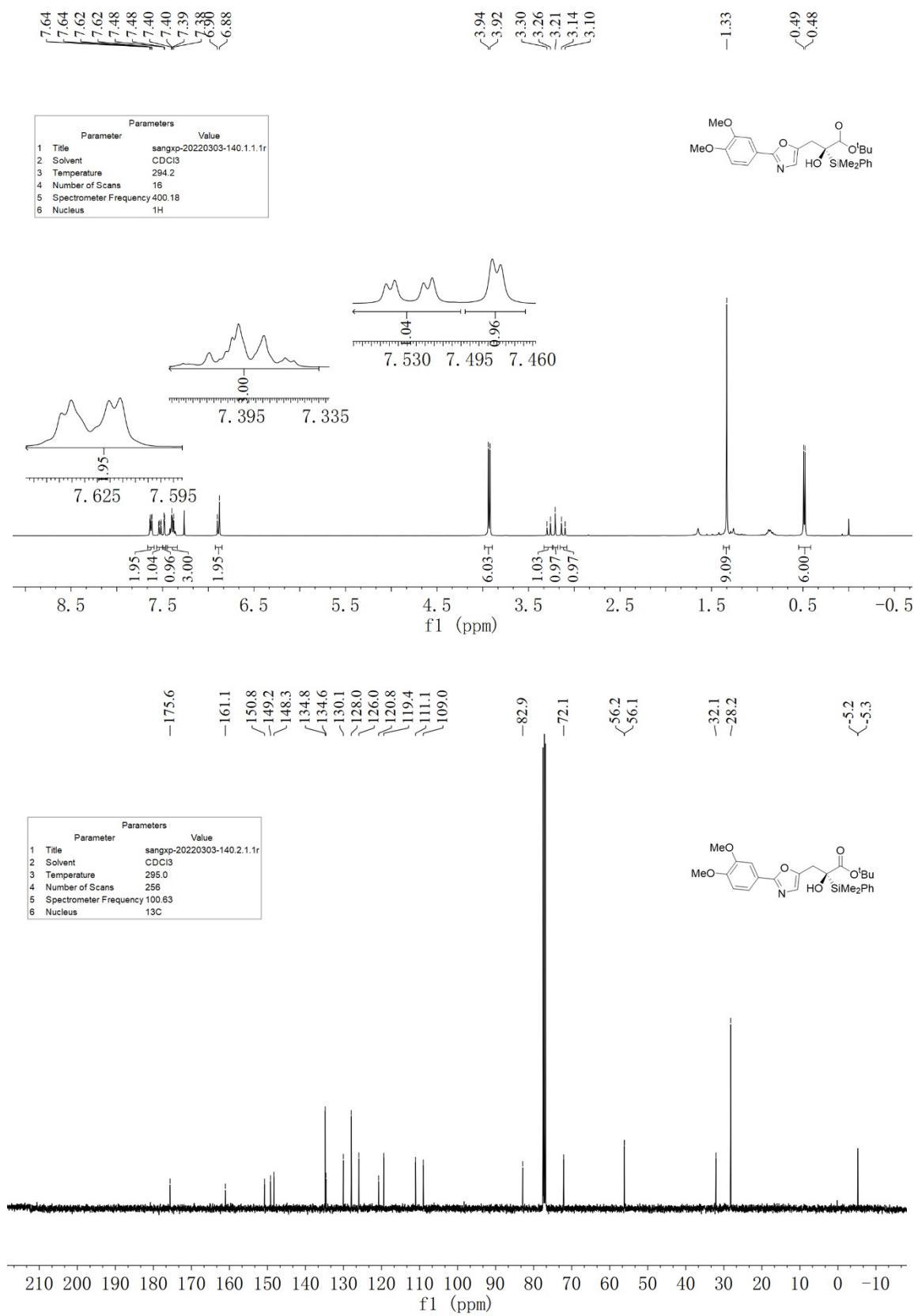
## C18



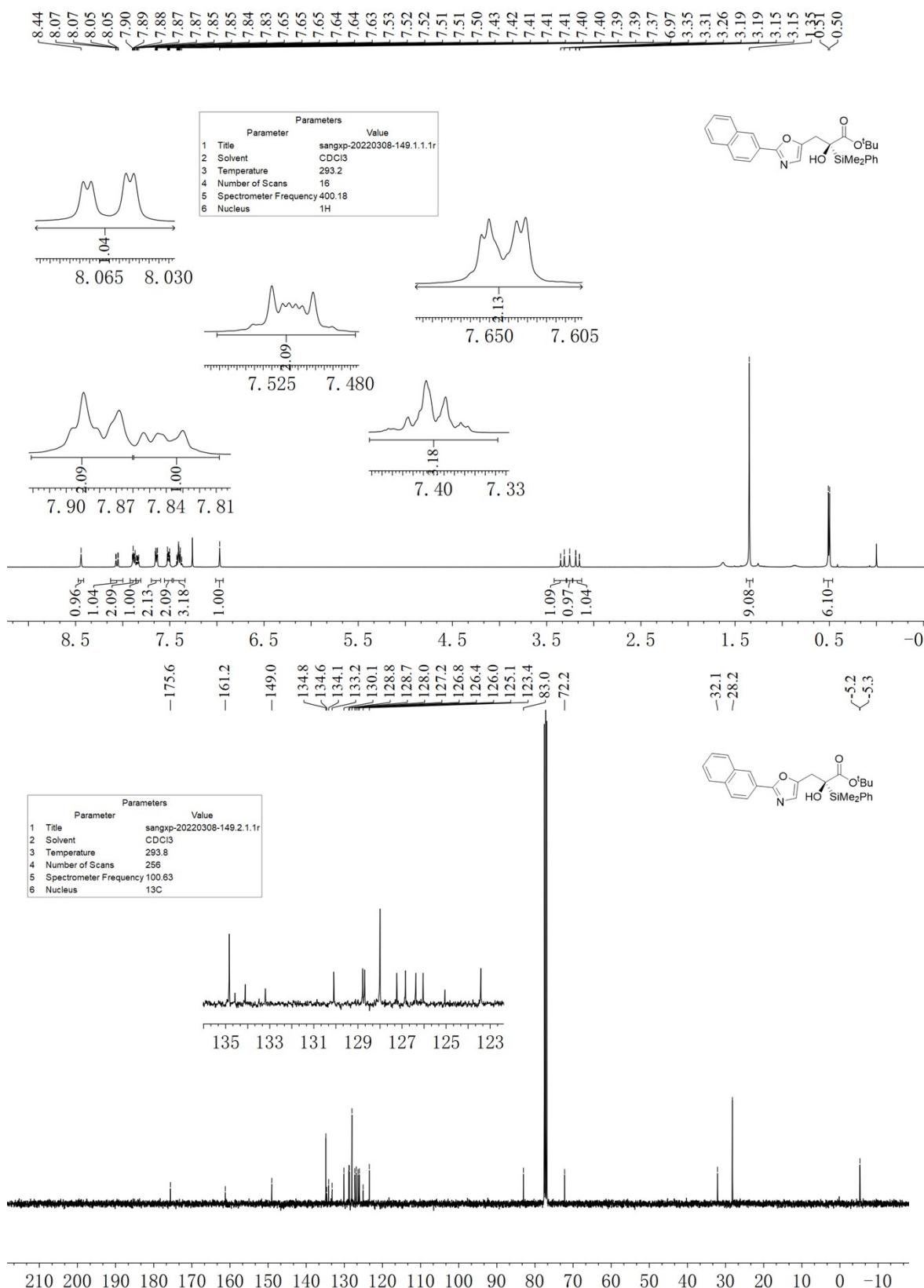
**C19**



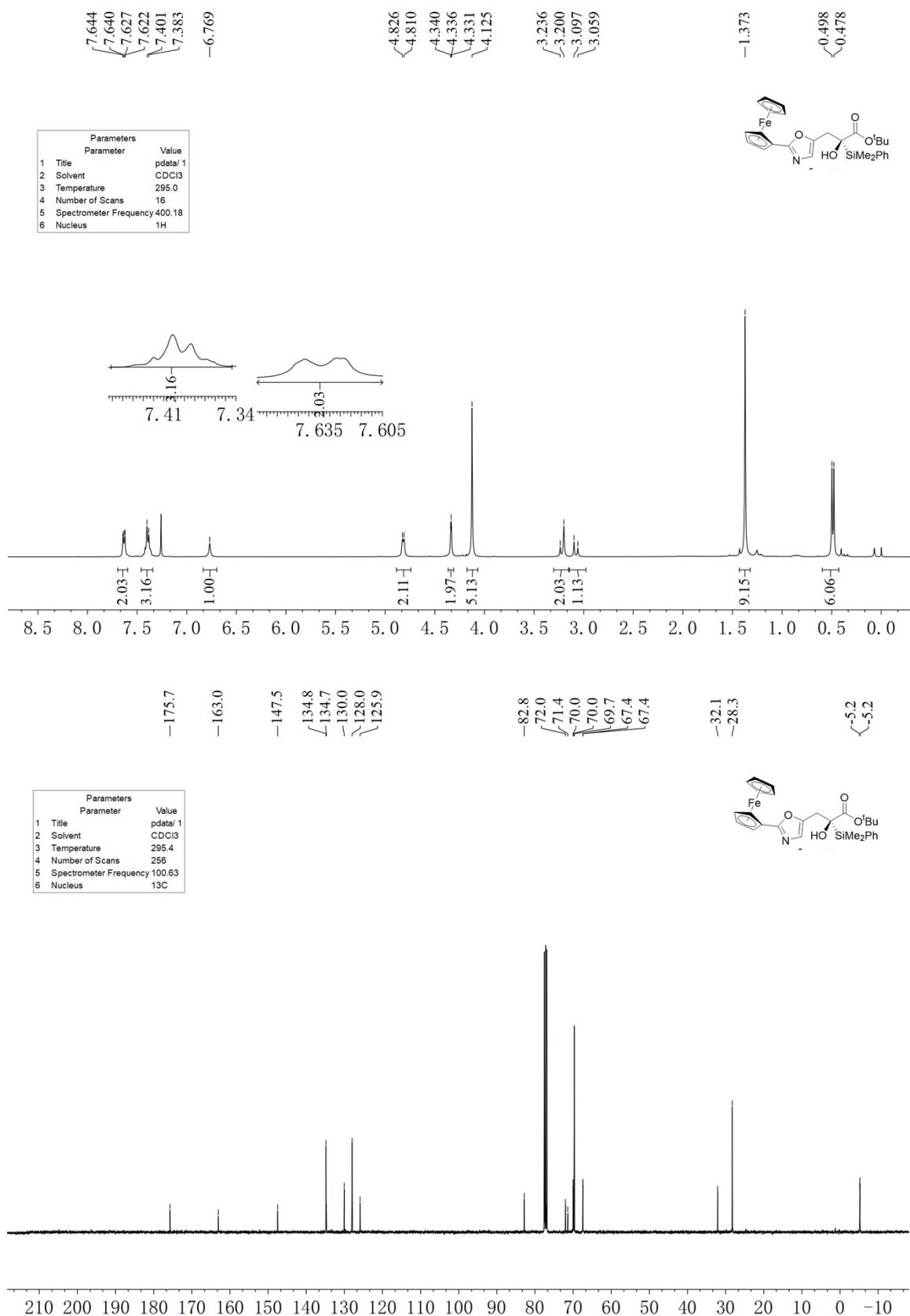
**C20**



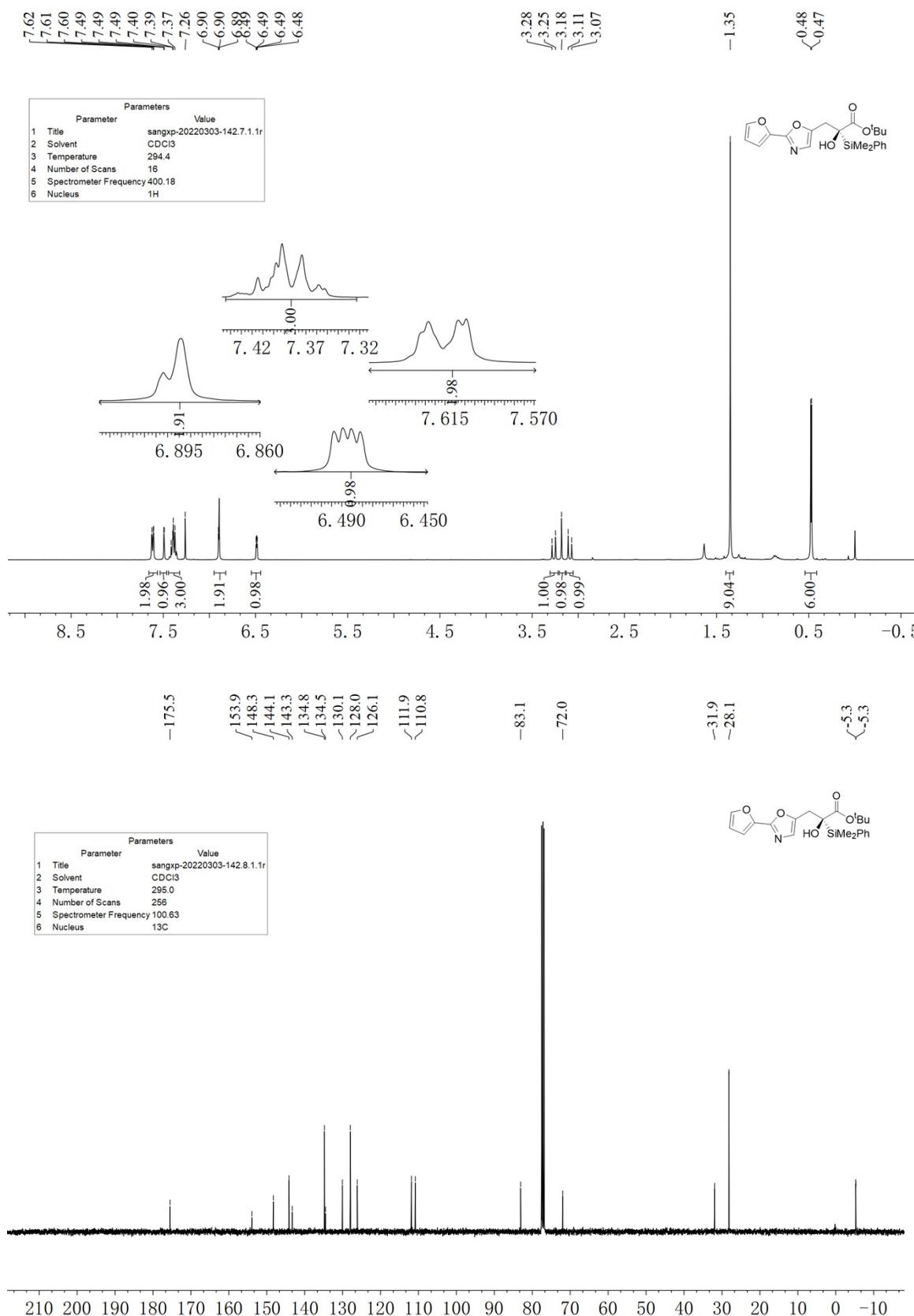
C21



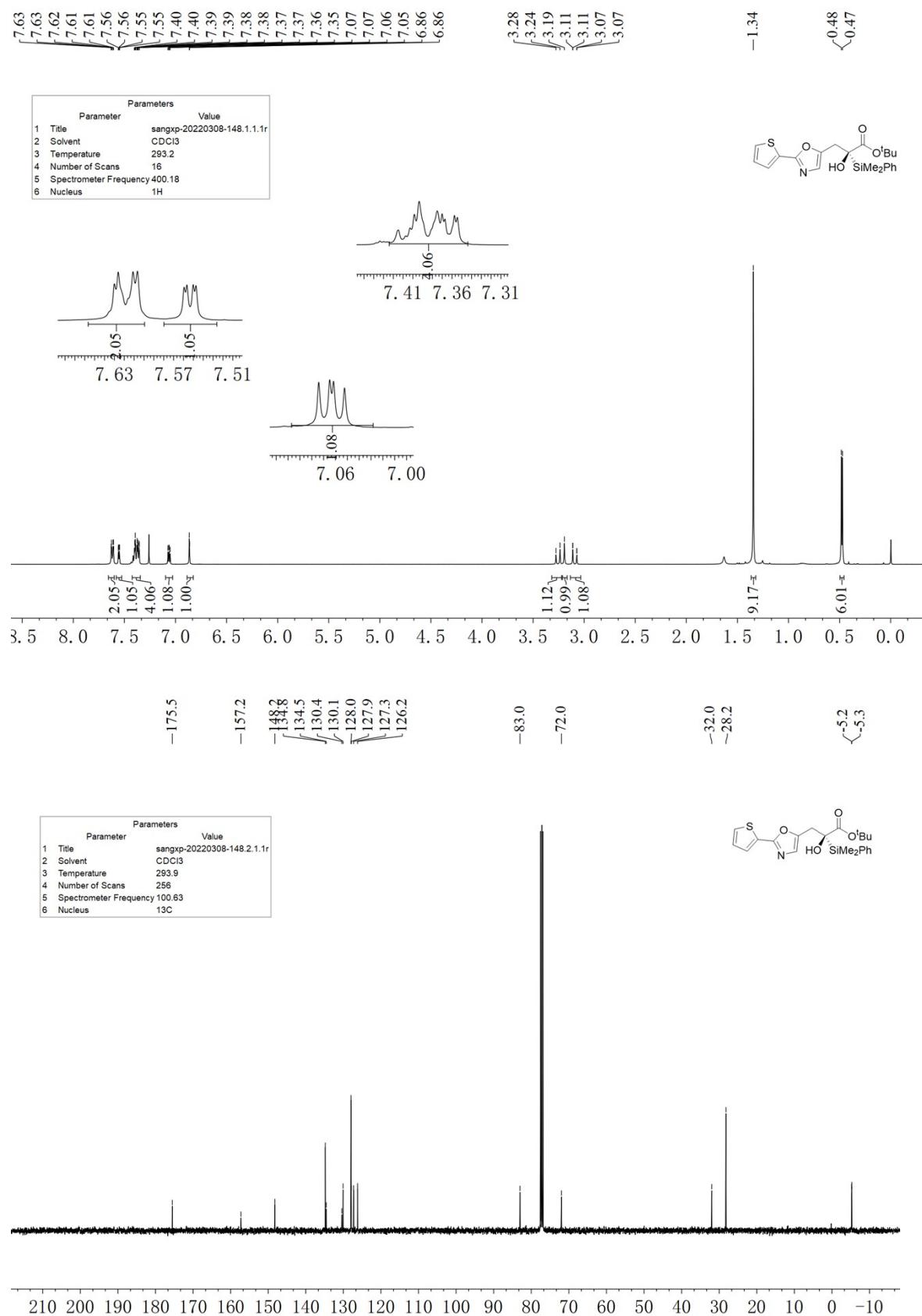
C22



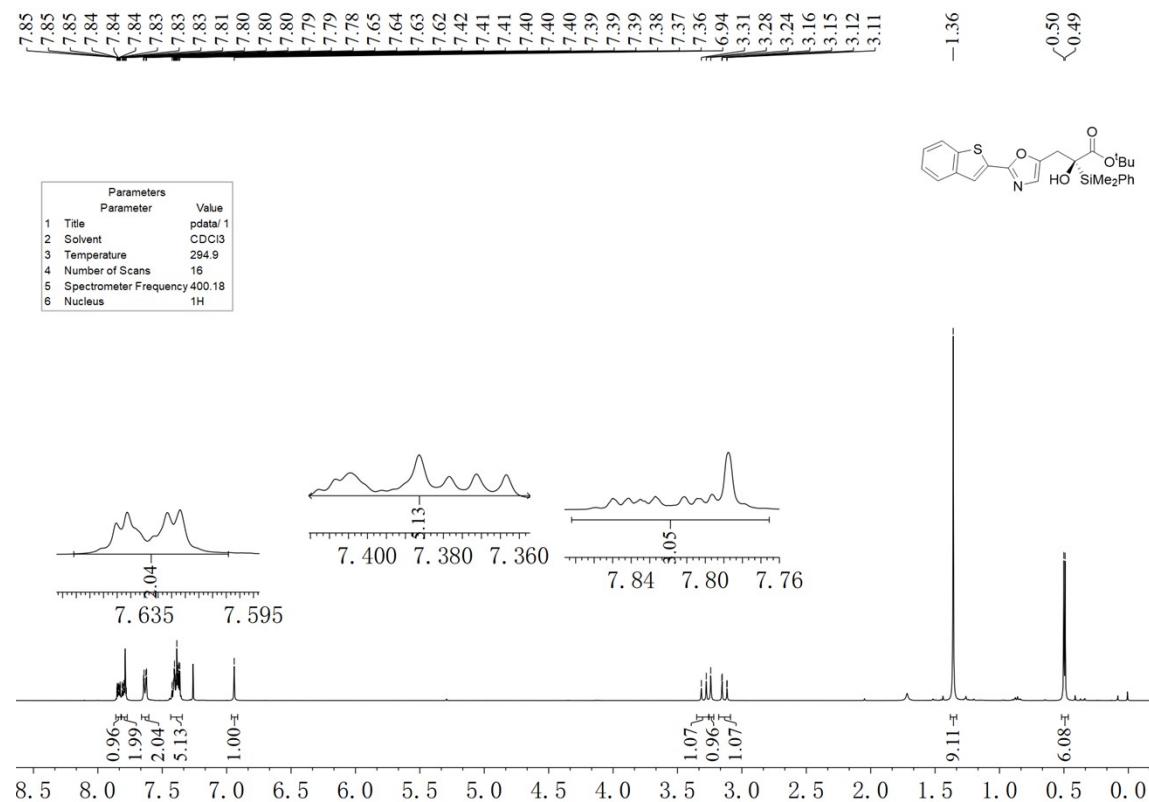
C23

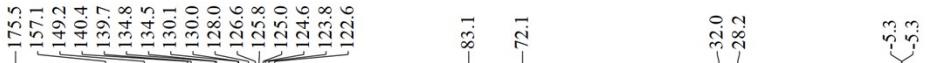


C24

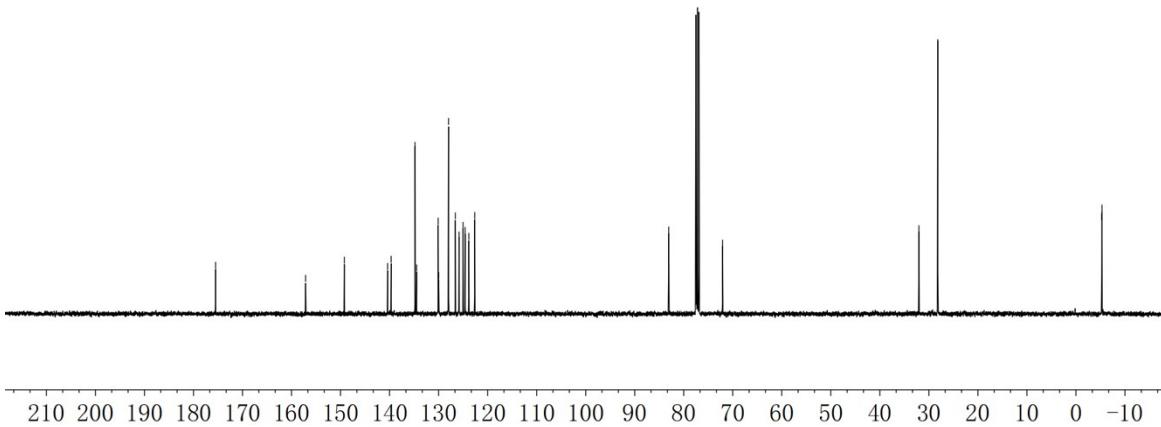


**C25**

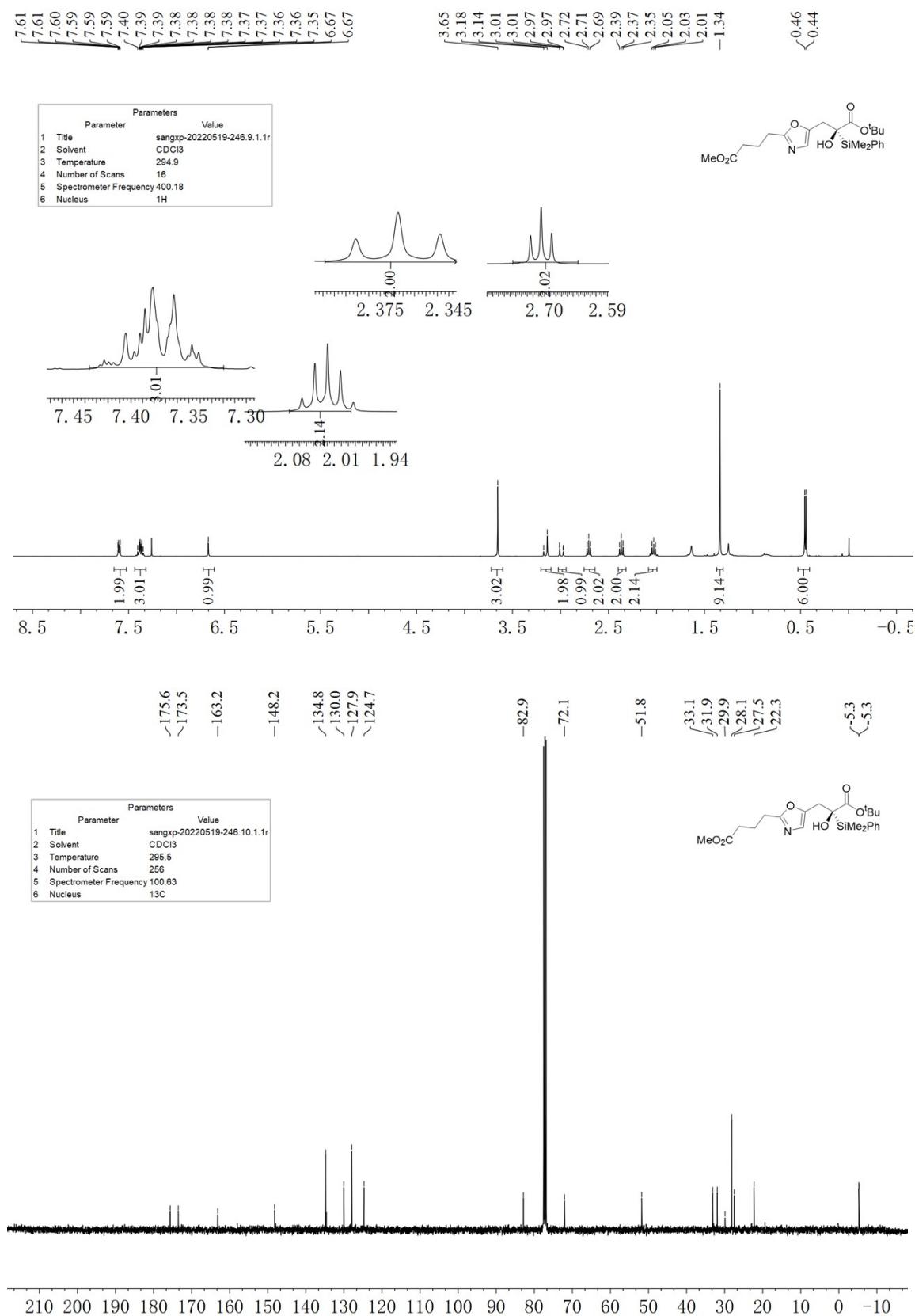




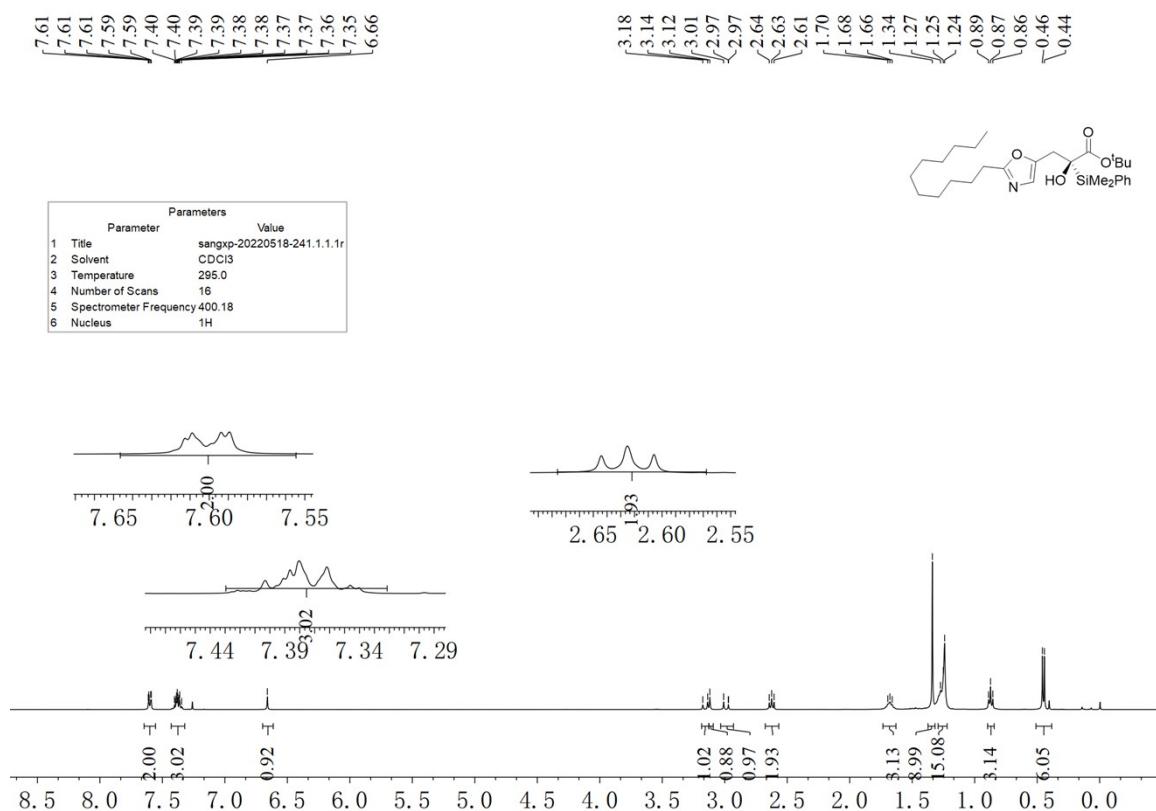
Parameters		
Parameter		Value
1 Title	pdata/1	
2 Solvent	CDCl <sub>3</sub>	
3 Temperature	295.2	
4 Number of Scans	256	
5 Spectrometer Frequency	100.63	
6 Nucleus	<sup>13</sup> C	

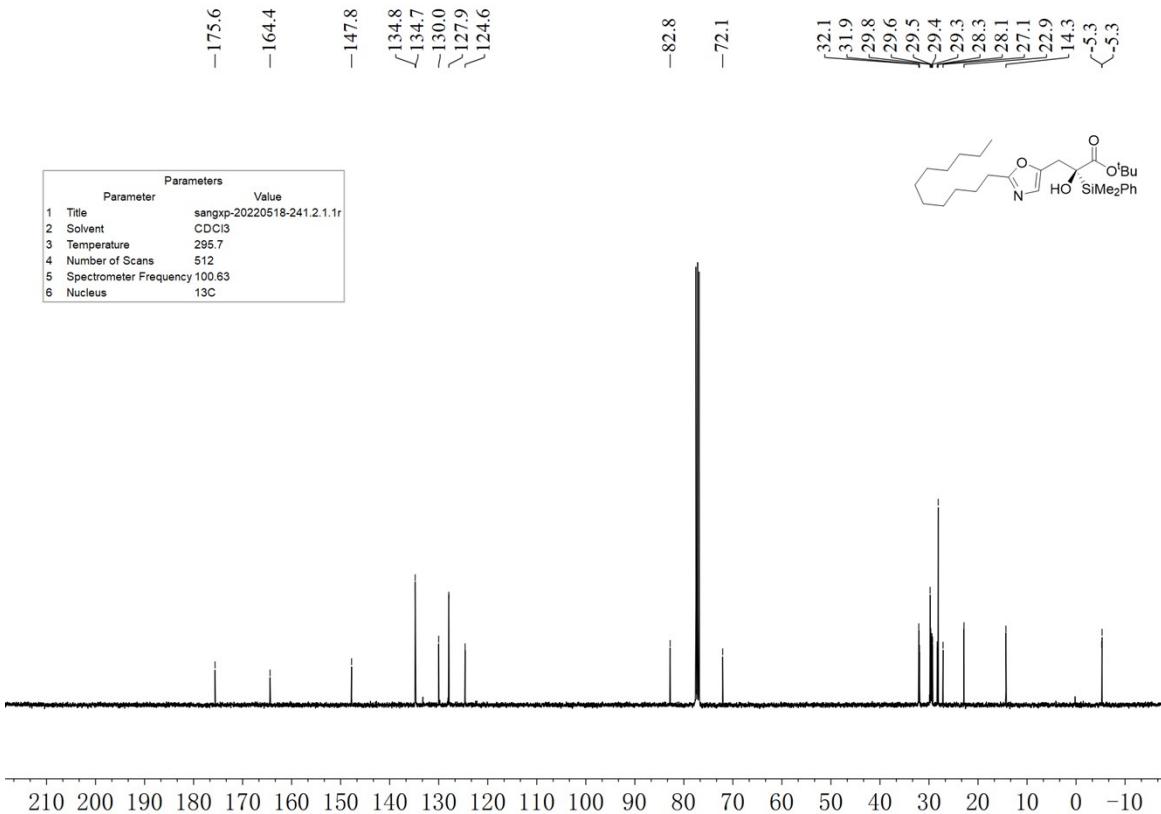


C26

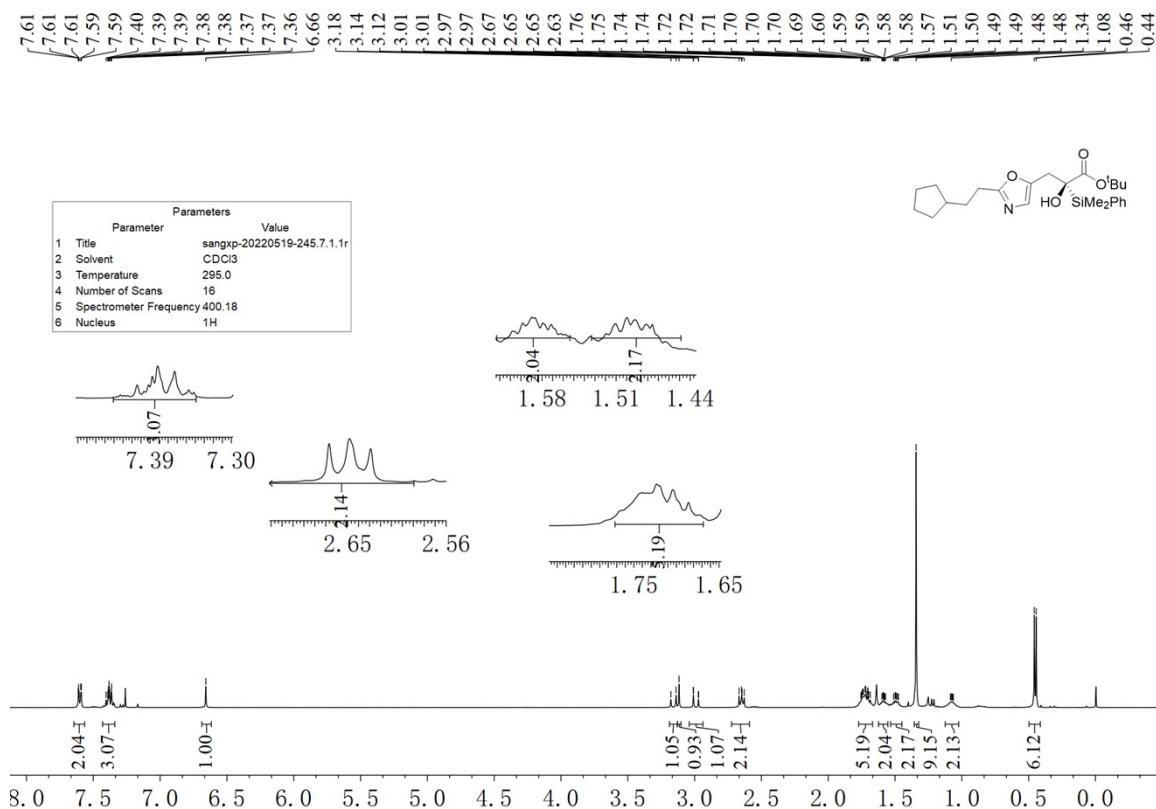


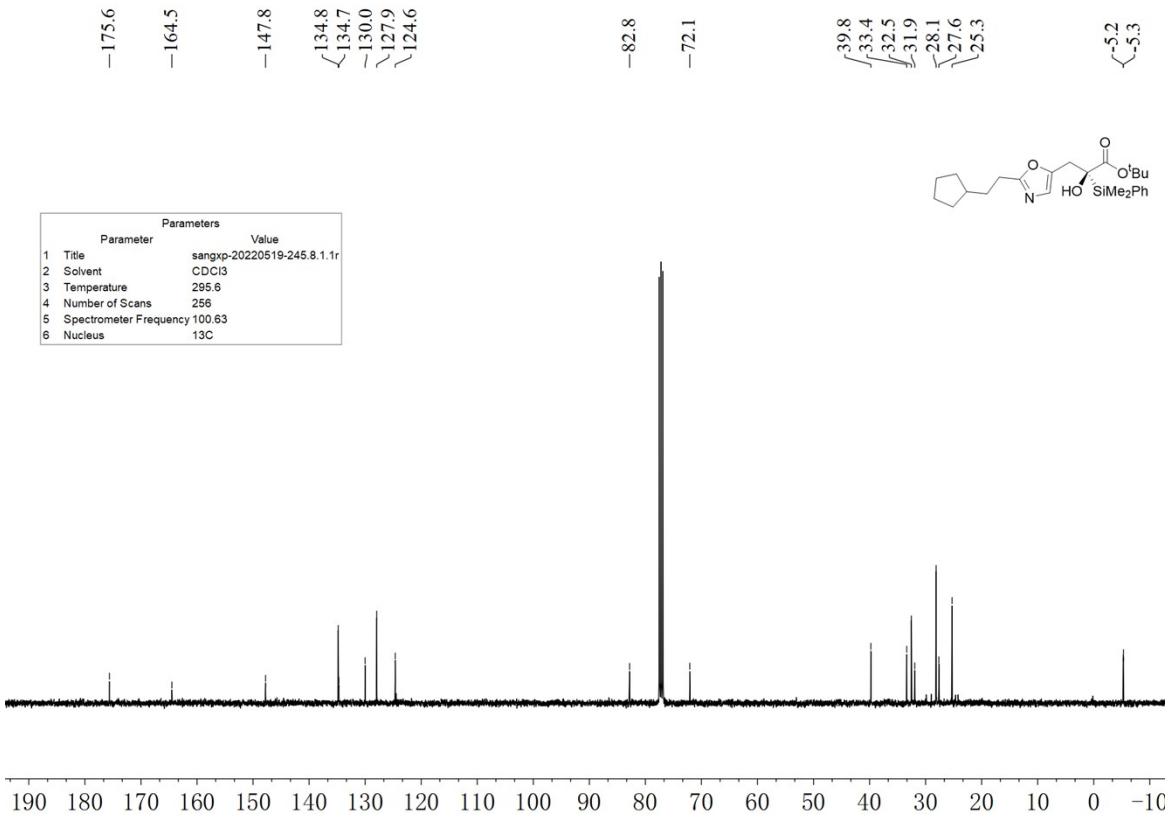
C27



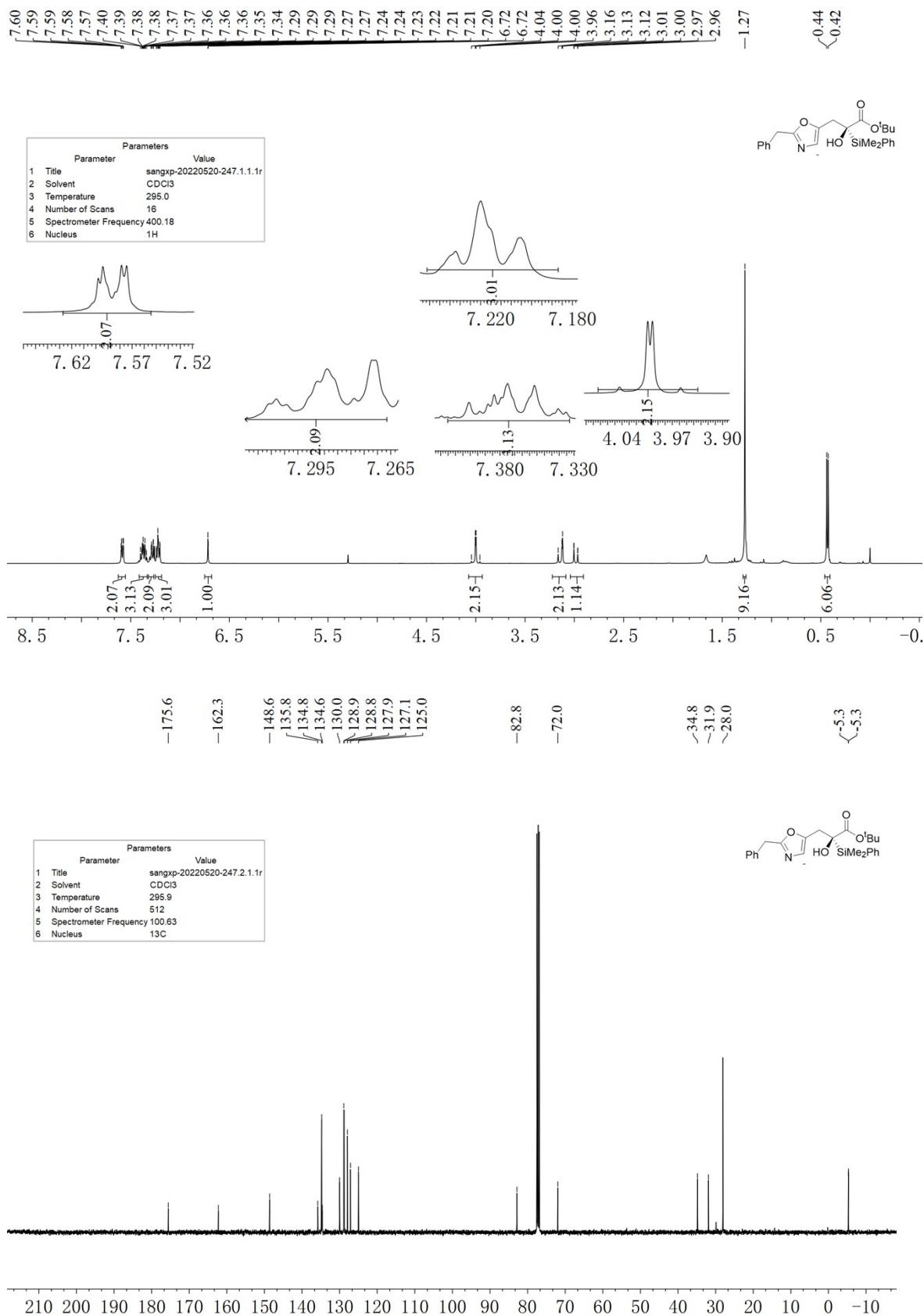


C28

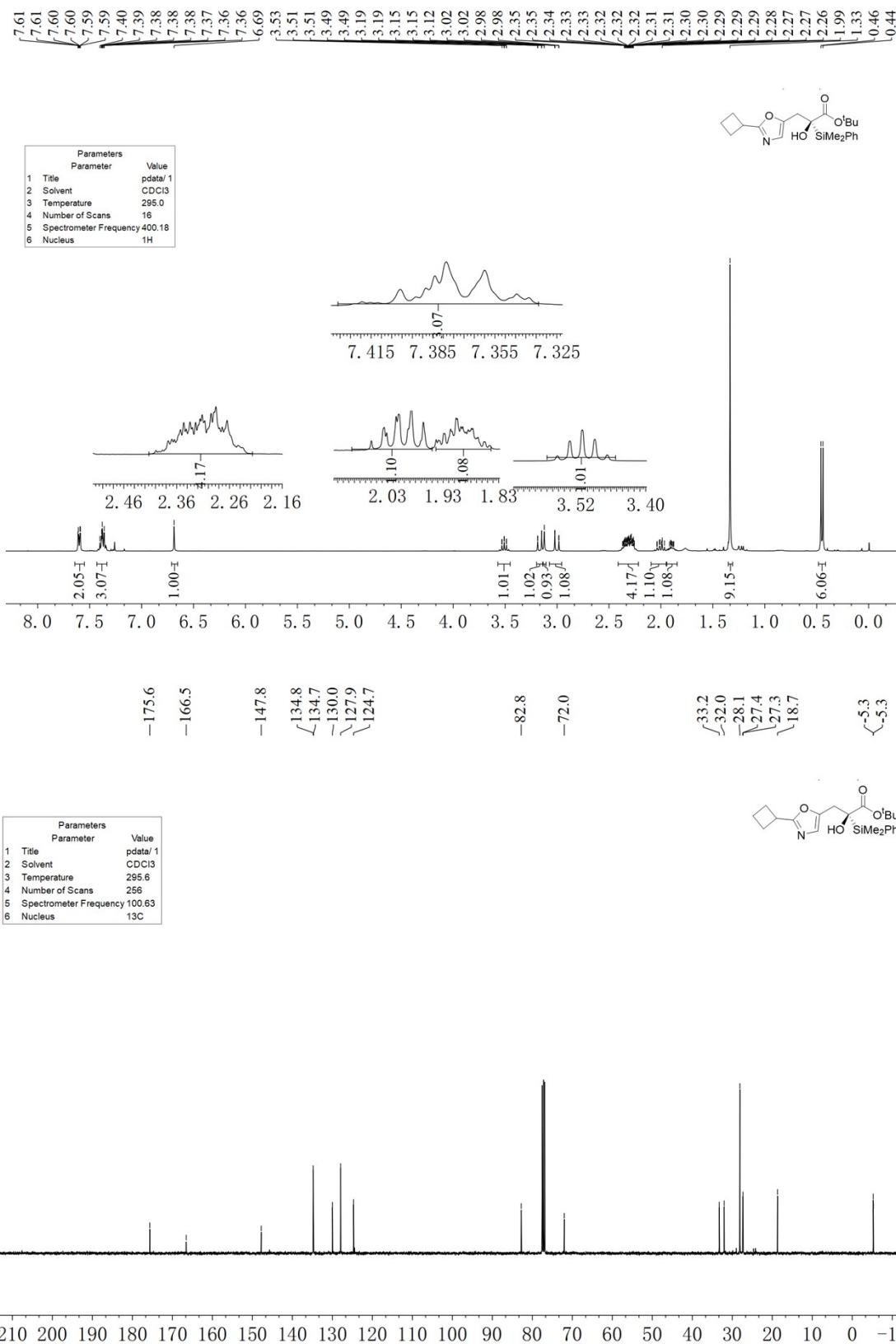




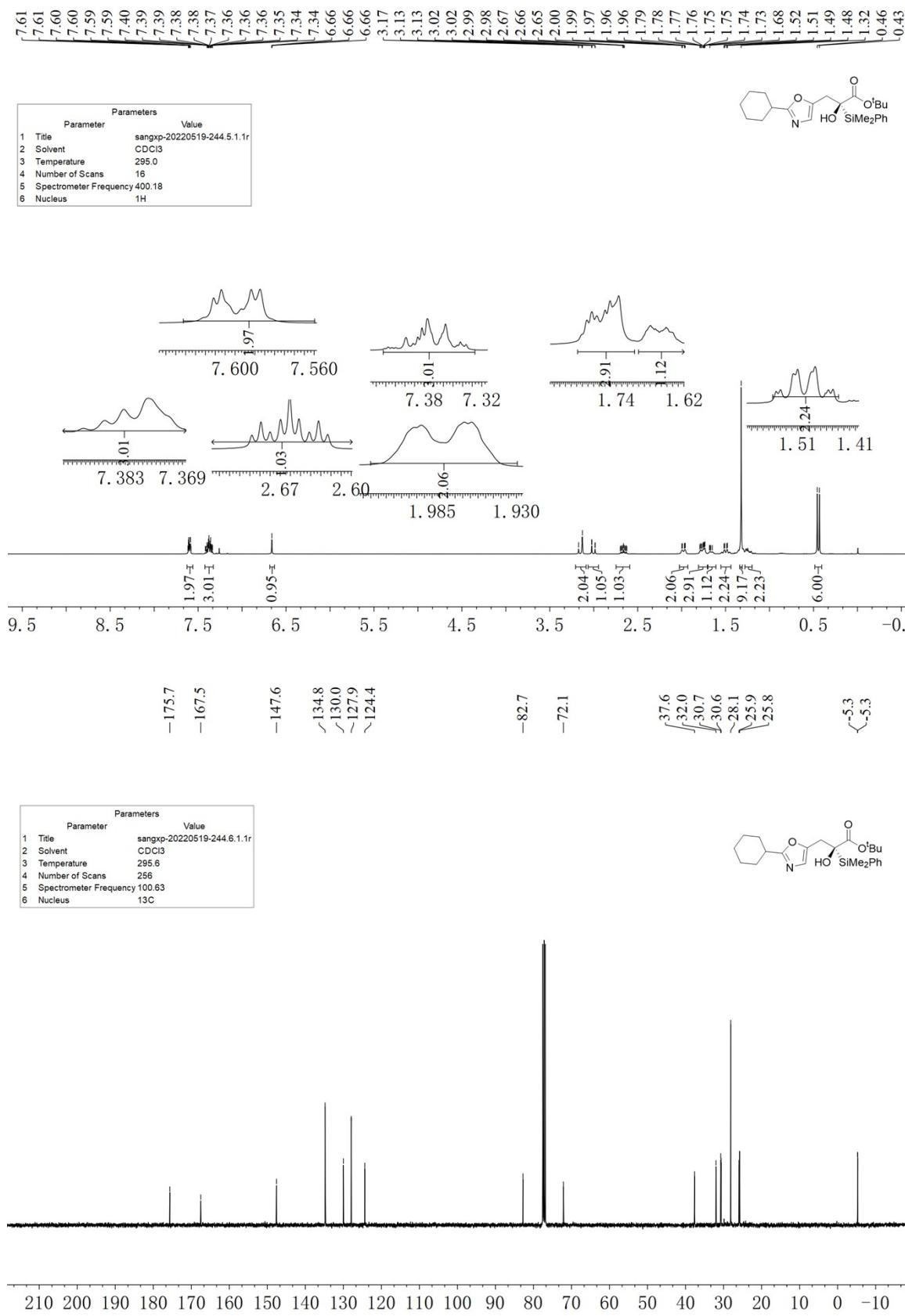
C29



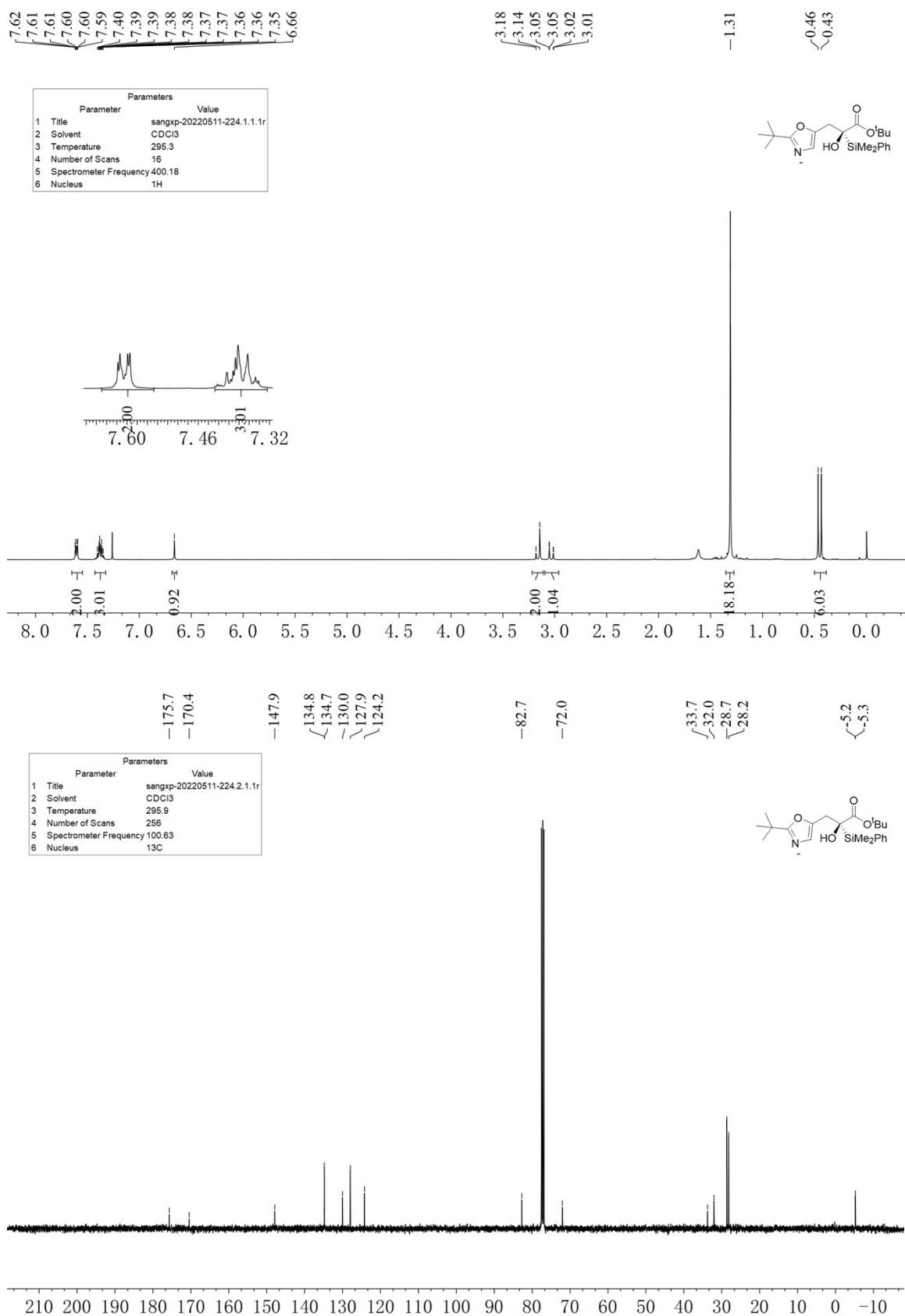
C30



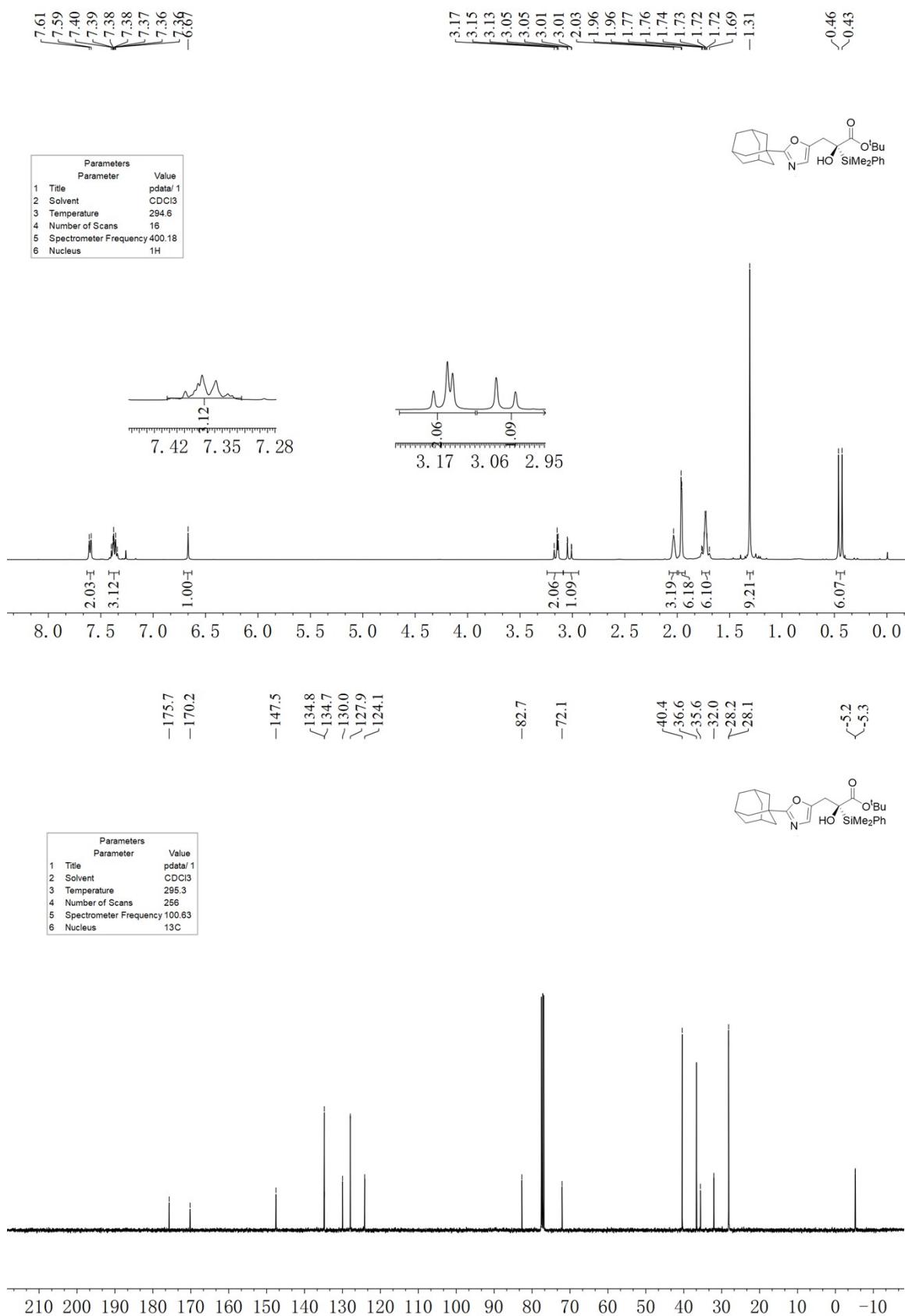
C31



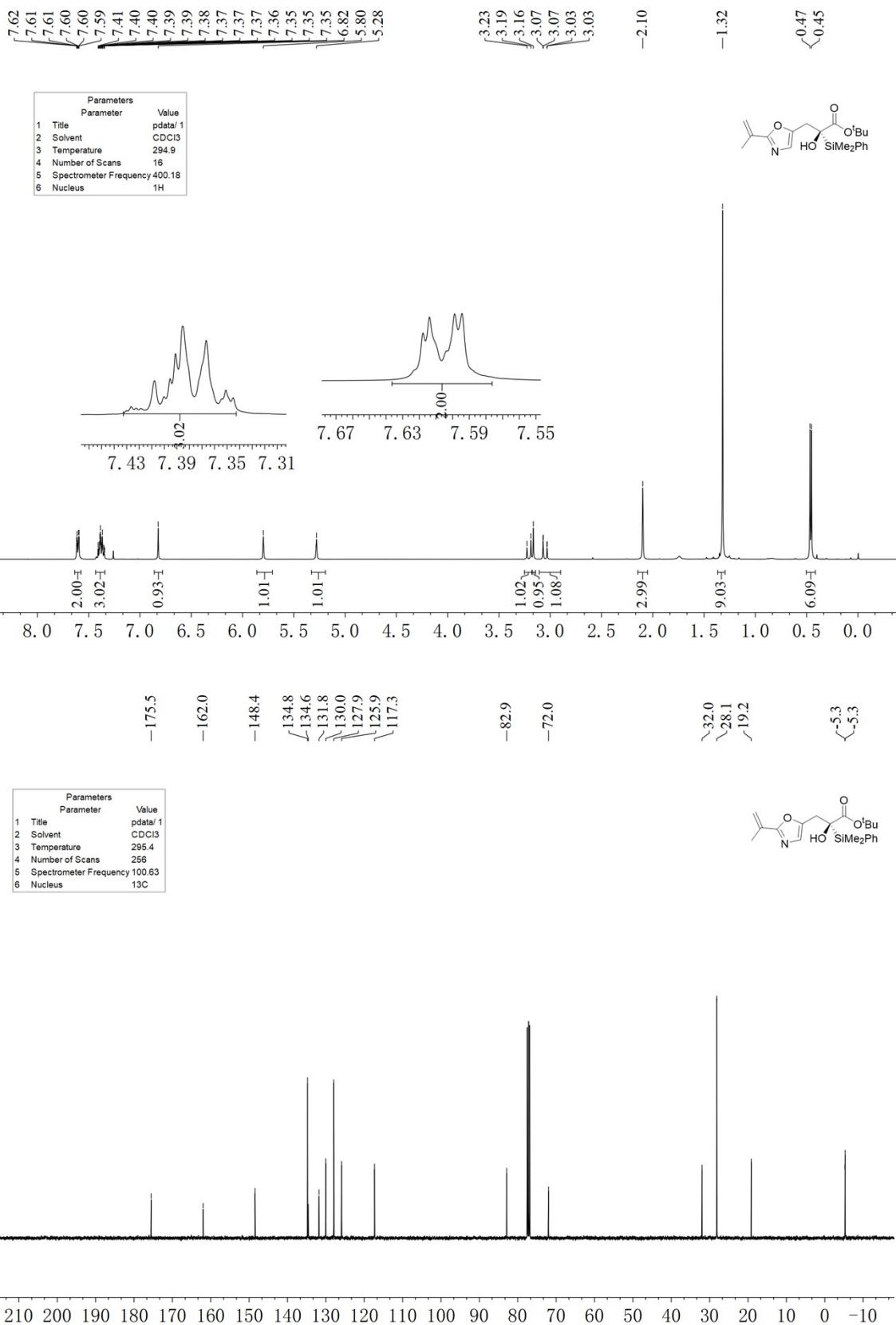
C32



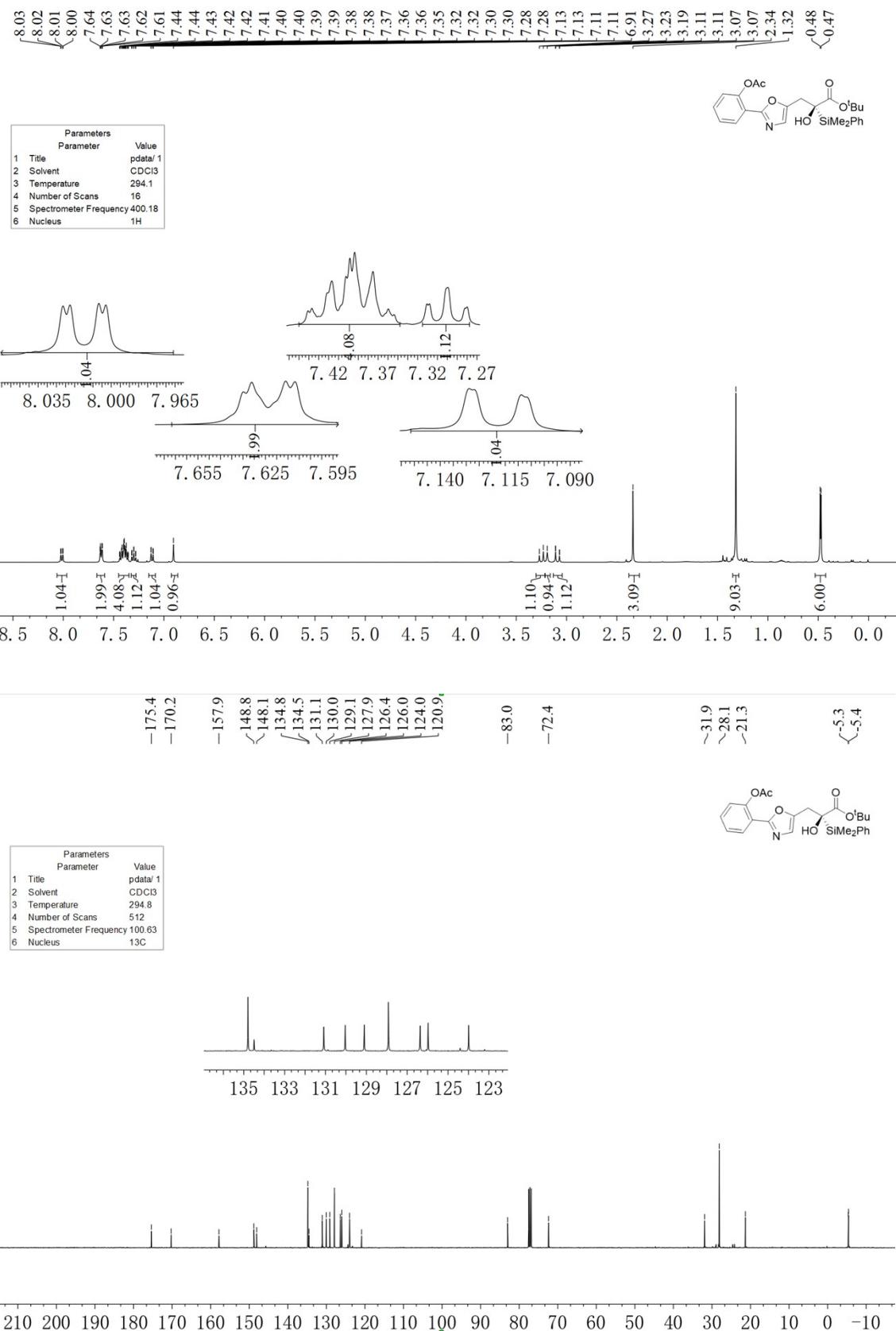
C33



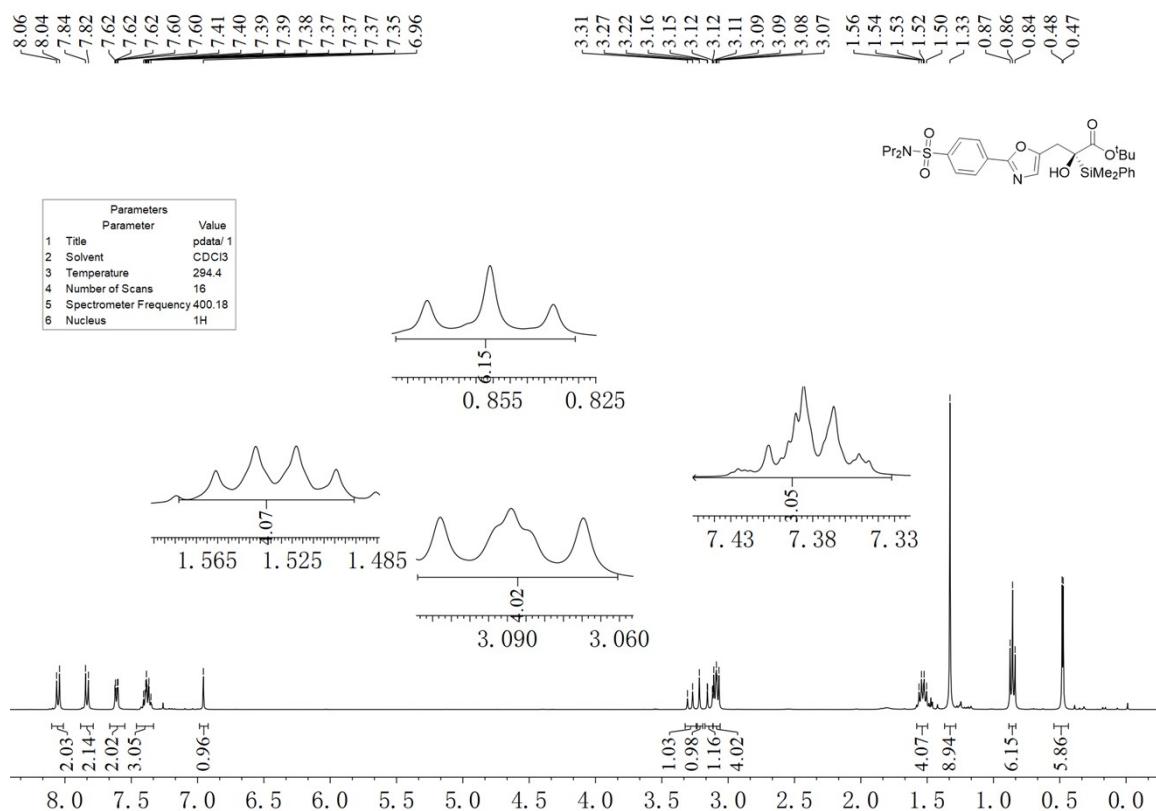
C34

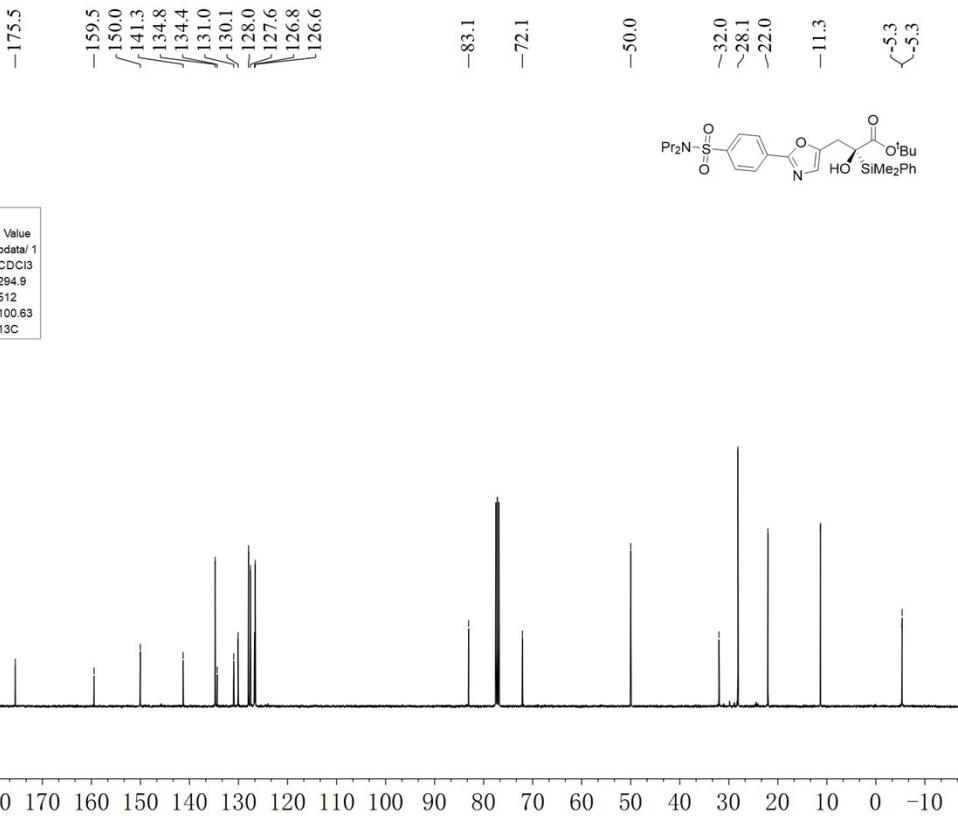


C35

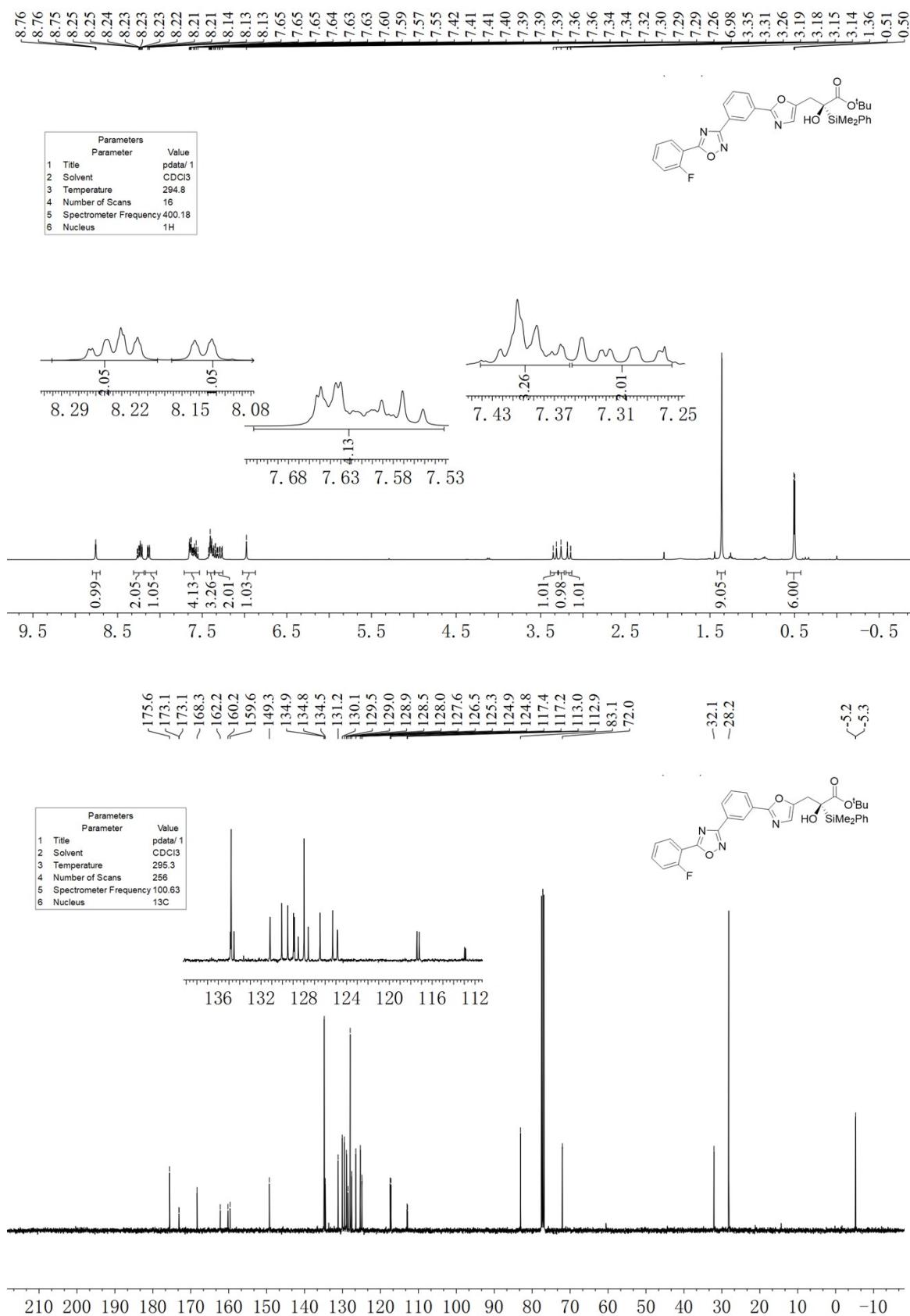


**C36**

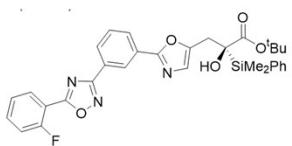




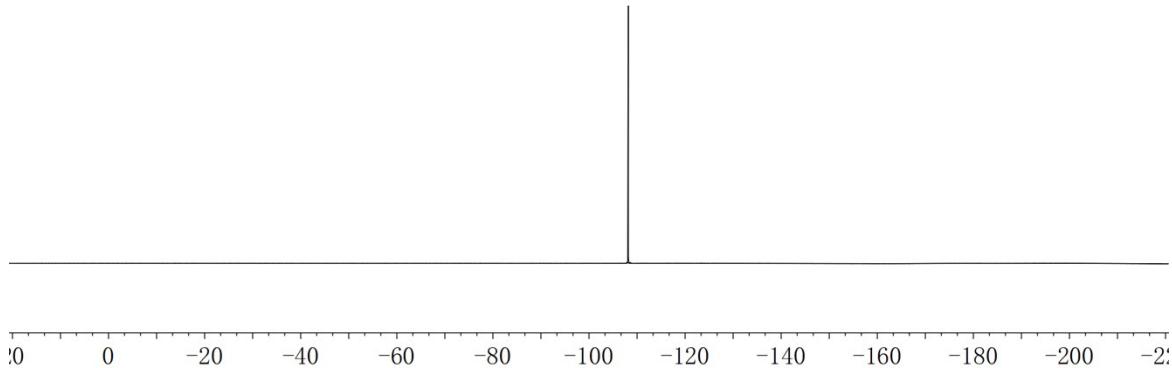
C37



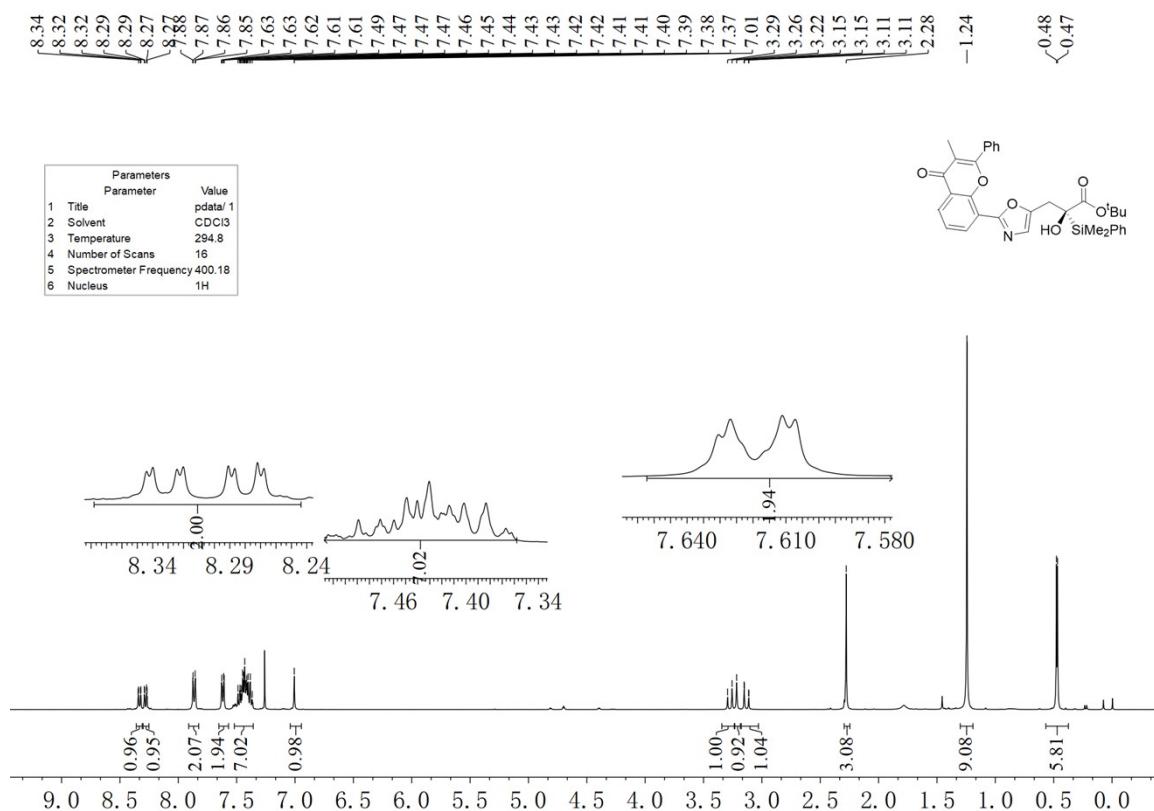
-108.17

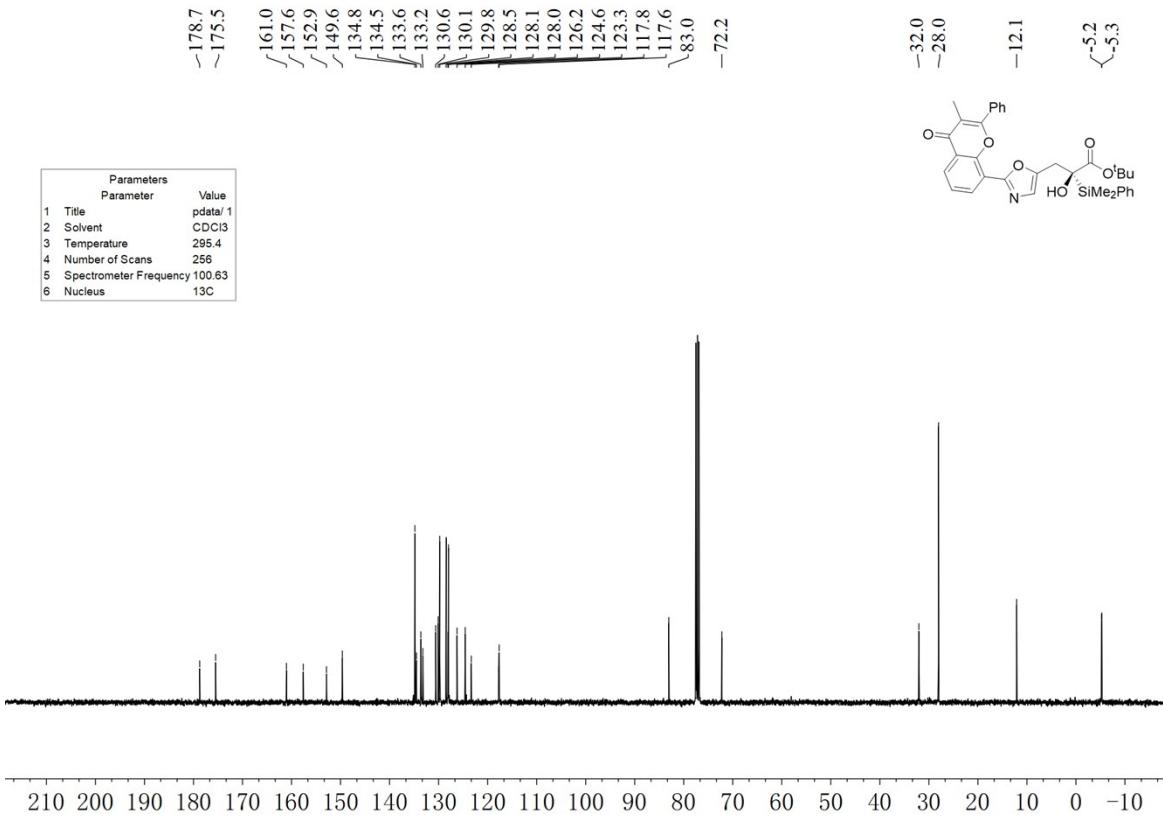


Parameters	
Parameter	Value
1 Title	pdata/1
2 Solvent	CDCl <sub>3</sub>
3 Temperature	295.1
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	<sup>19</sup> F

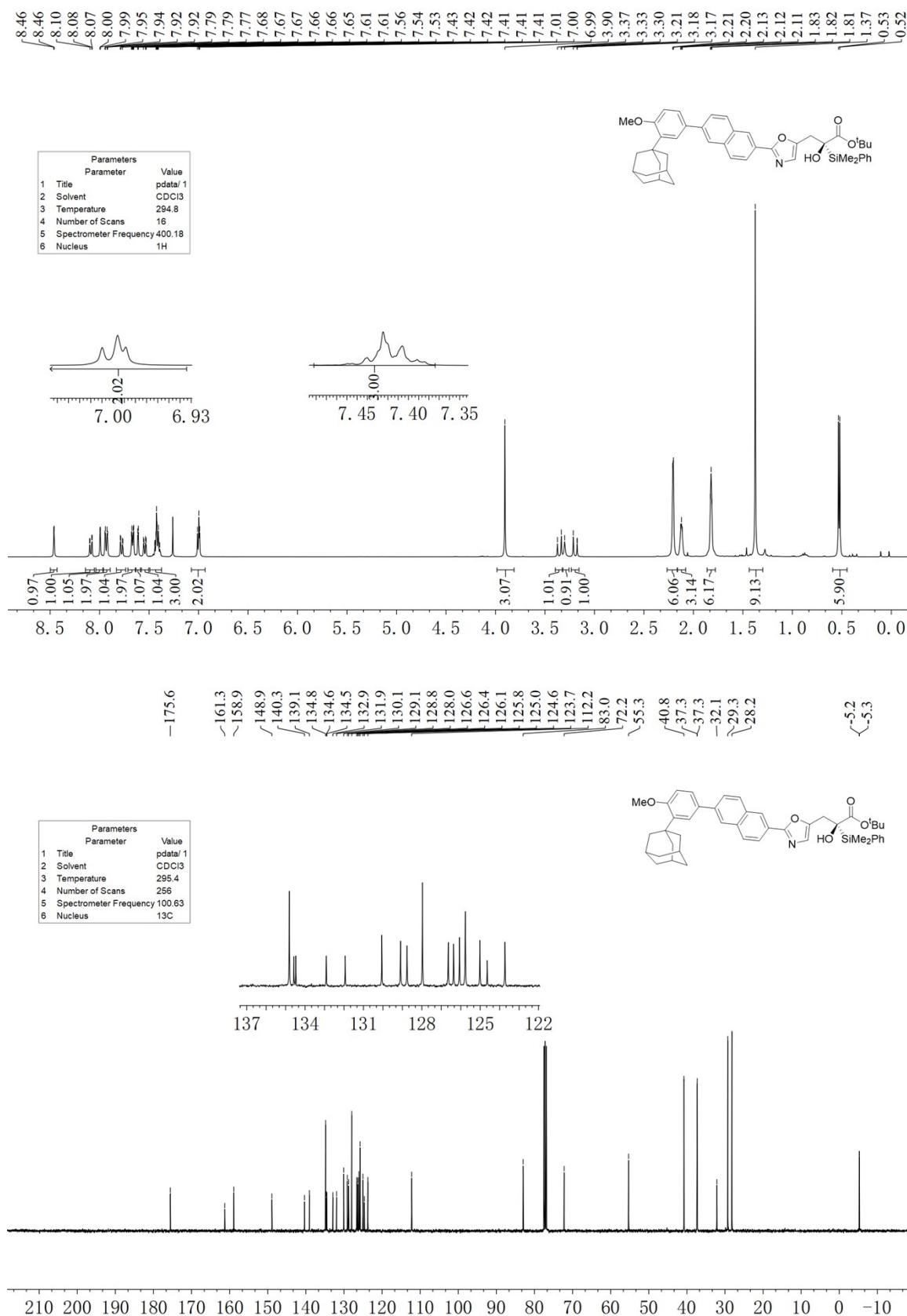


**C38**

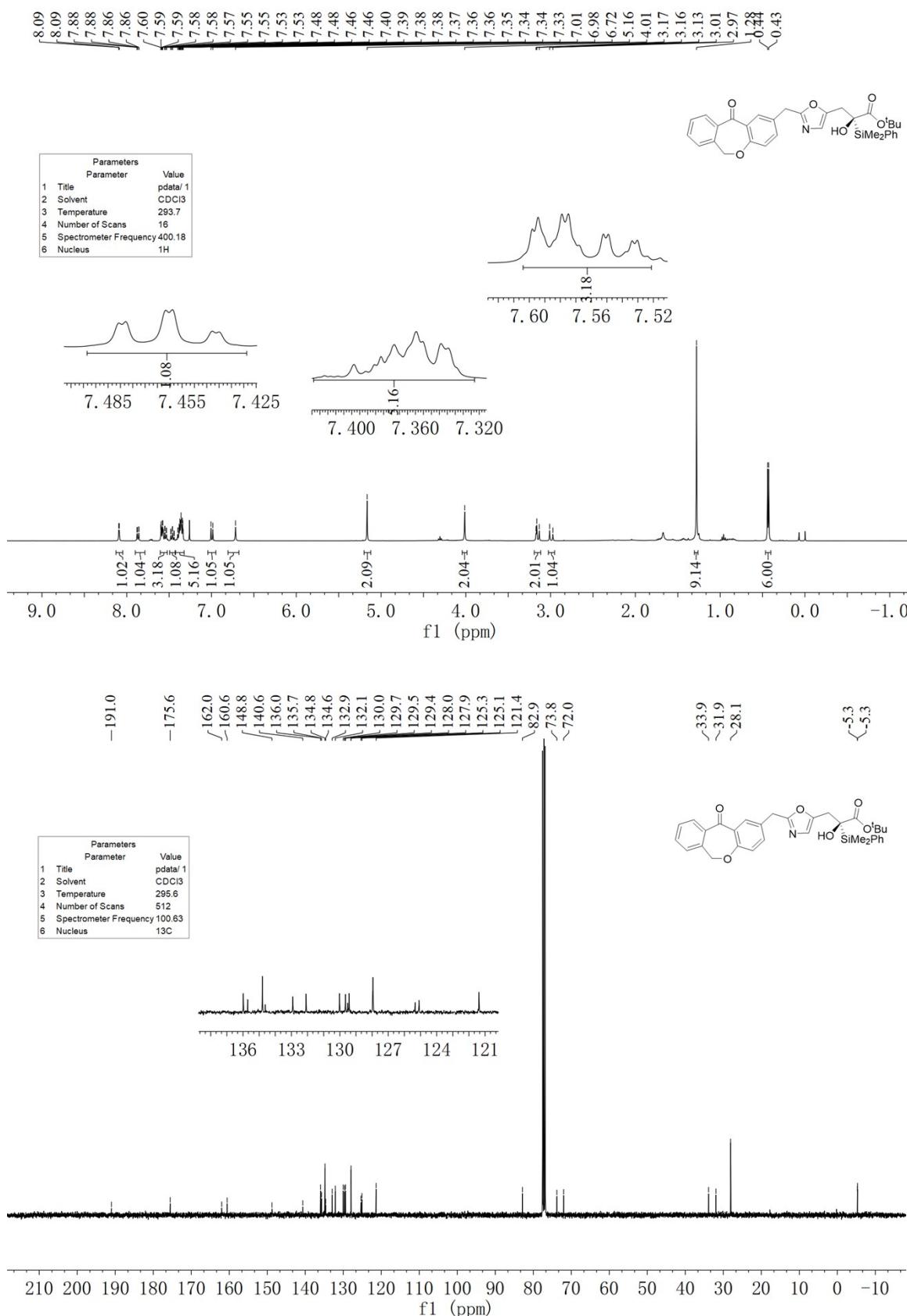




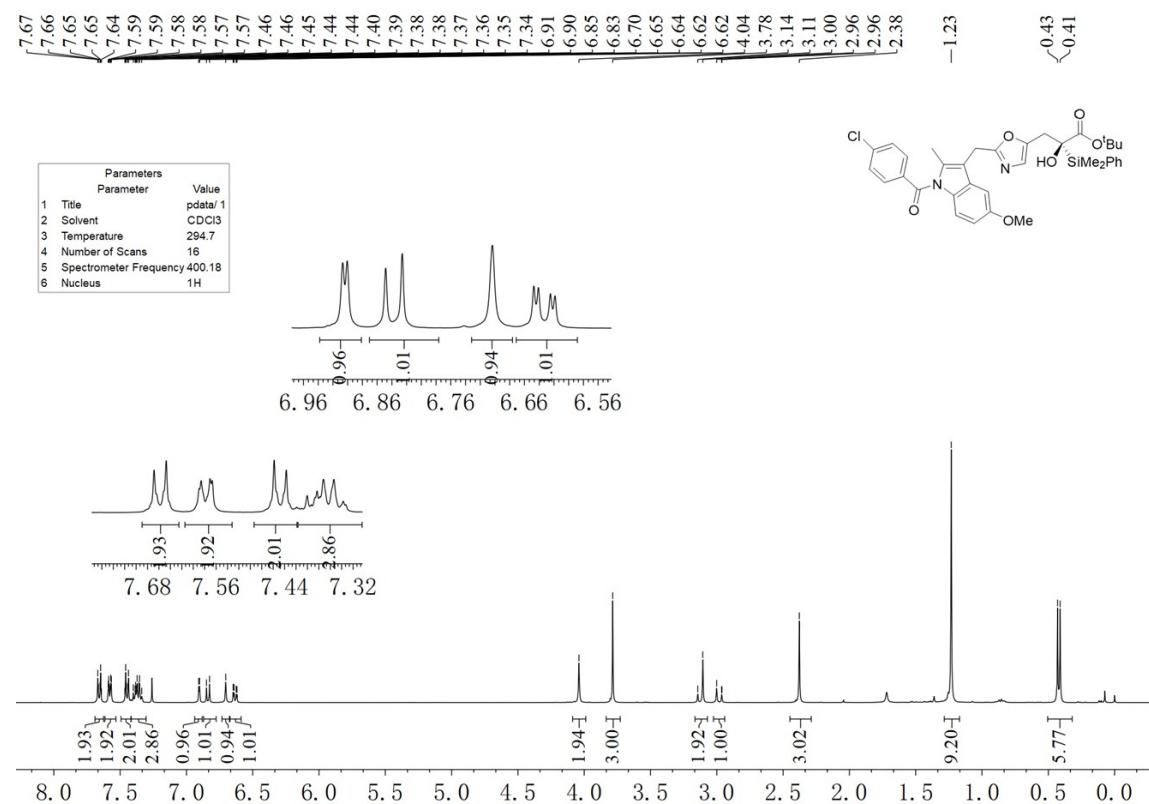
C39

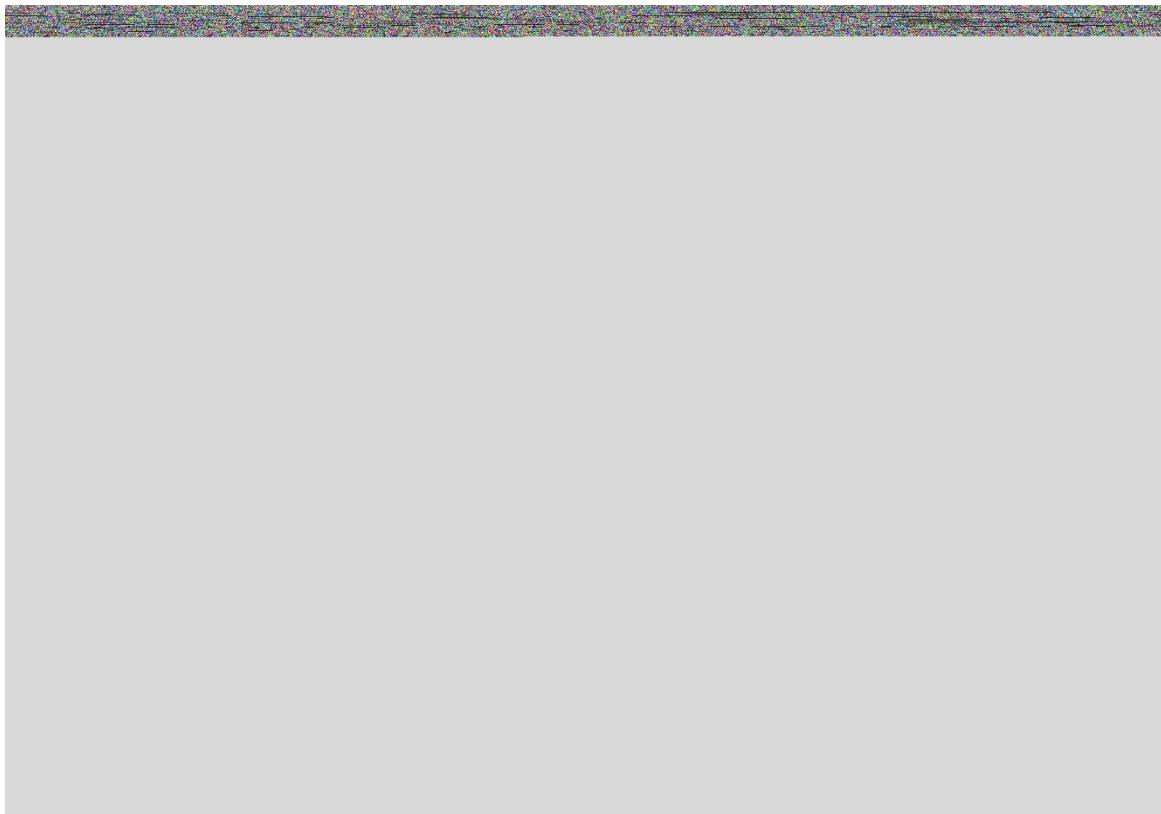


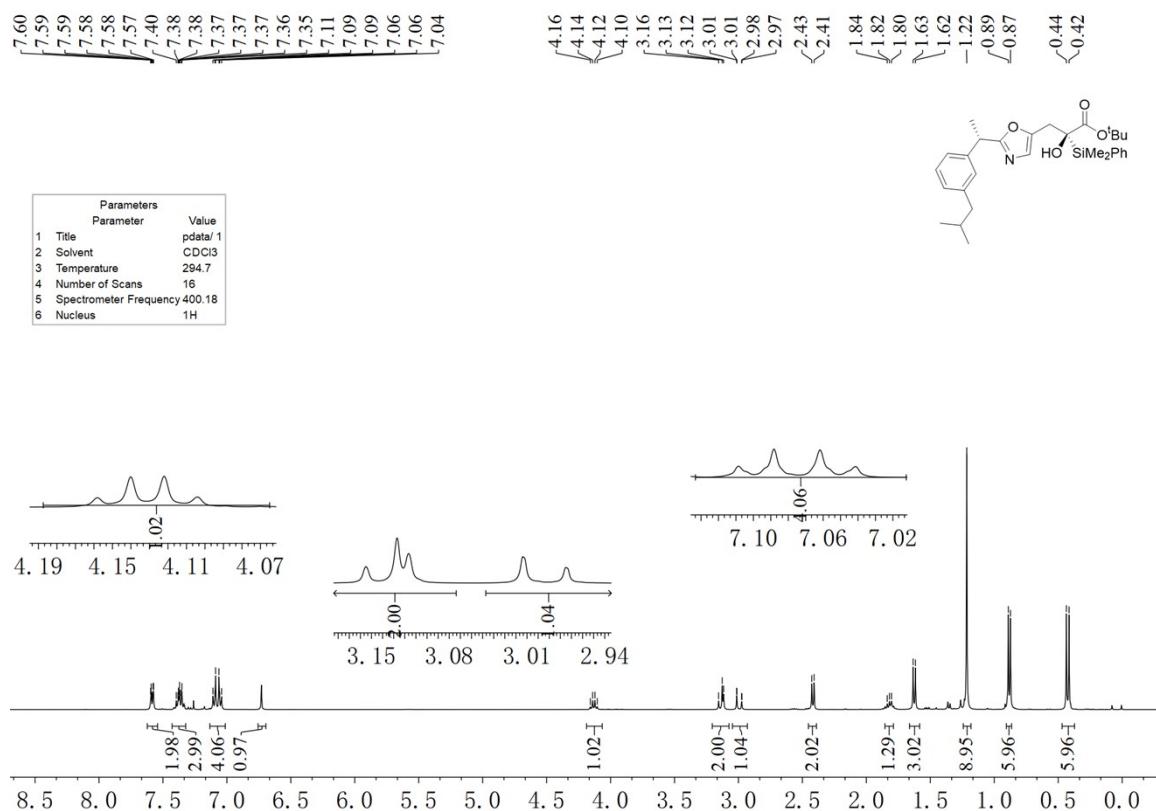
C40

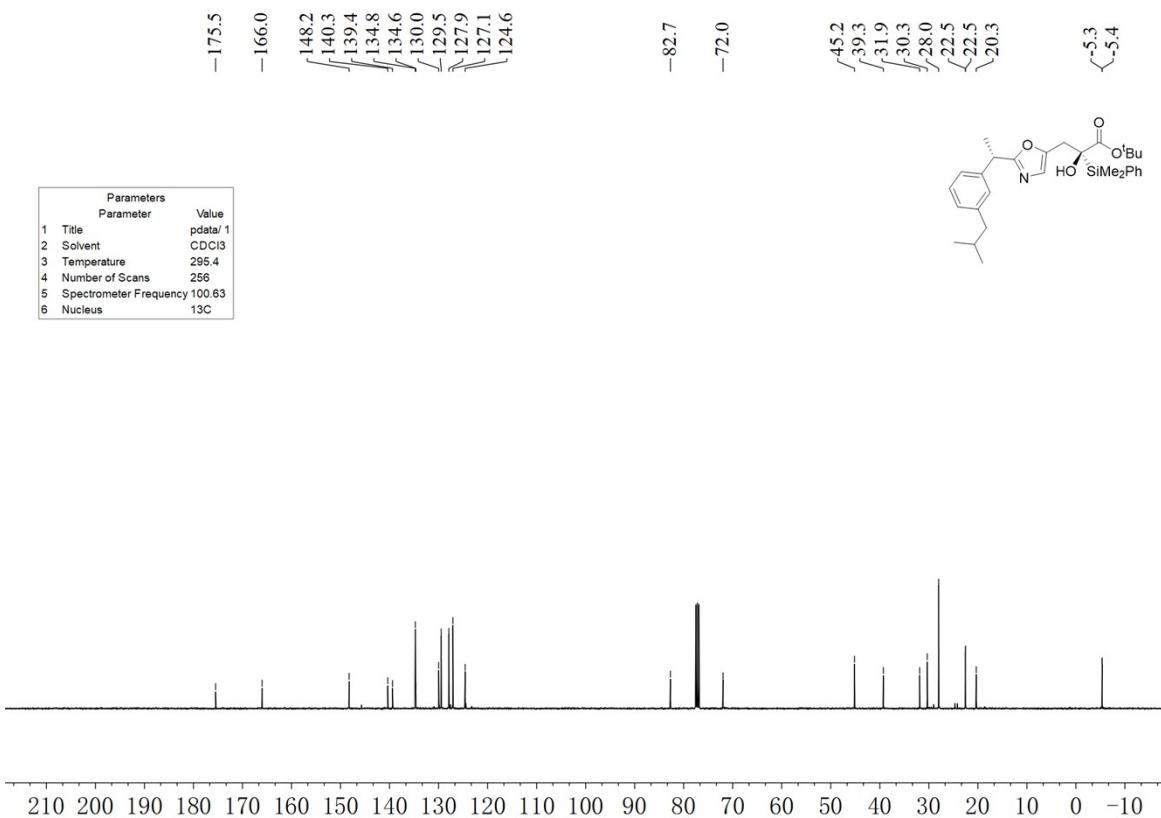


C41

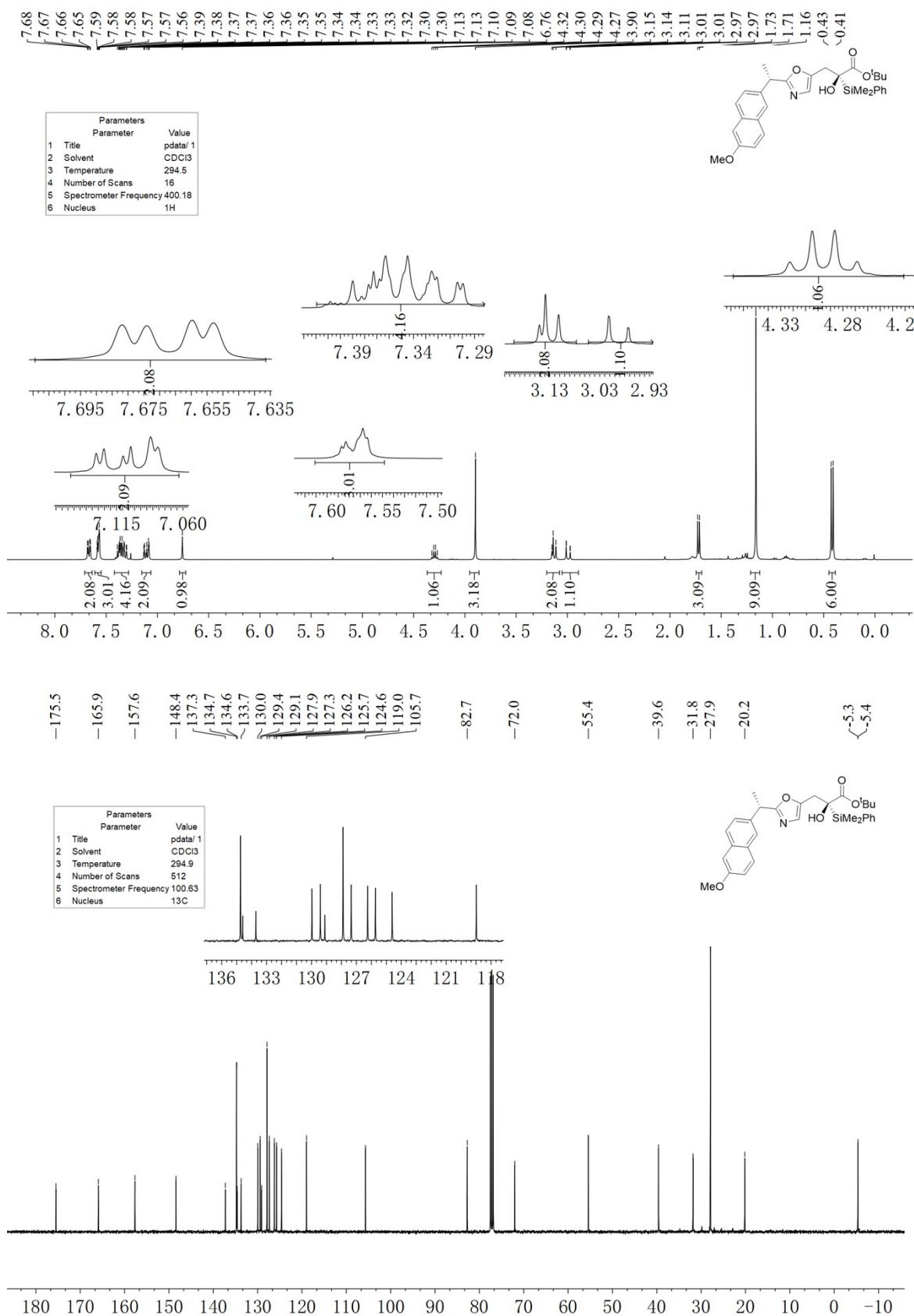




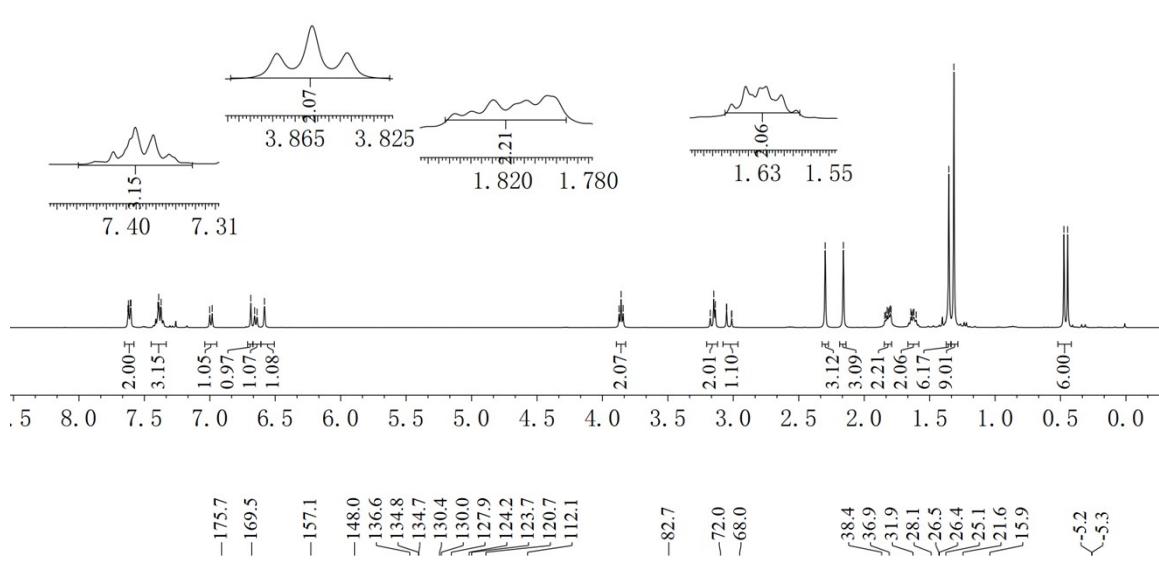
**C42**



C43



C44



Parameters	
Parameter	Value
1 Title	pdata/1
2 Solvent	CDCl <sub>3</sub>
3 Temperature	295.4
4 Number of Scans	256
5 Spectrometer Frequency	100.63
6 Nucleus	<sup>13</sup> C

