Catalytic asymmetric addition of thiols to silyl glyoxylates for synthesis of multi-hetero-atom substituted carbon stereocenter

Mingming Guan, Shiyu Wang, Yao Luo, Weidi Cao,* Xiaohua Liu and Xiaoming Feng*

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China

E-mail: wdcao@scu.edu.cn; xmfeng@scu.edu.cn

Contents

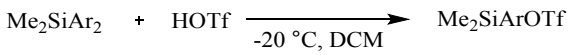
1. General information

Unless otherwise reported, the reaction was performed under nitrogen atmosphere and all reagents were obtained from commercial sources and used without further purification. Purification of the reaction products was carried out by flash filtration with a thin silica gel or flash chromatography using silica gel at -60℃. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$, CD_3COCD_3 or CD_2Cl_2 on a bruker ASCEND™ (400MHz or 600MHz). Chemical shifts were given in parts per million (ppm). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), coupling constants (Hz), integration and assignment. HRMS was recorded on a Thermo Q-Exactive Focus (FTMS+c ESI). Enantiomeric excesses (ee) were determined by HPLC and UPC^2 analysis using the corresponding commercial chiral column as stated in the experimental procedures at 23 °C with UV detector. Optical rotations were reported as follows: $[\alpha]_{\lambda}^{T}$ = (c = g/100 mL, in CH_2Cl_2, unless otherwise noted, λ = 436 nm). IR was detected by Bruker Tensor II spectrometer with Plantium ATR accessory. Solvents were dried and distilled prior to use according to the standard methods. The silylglyoxylates were prepared according to previously published synthetic strategies[1]. Silyl triflates were prepared according to Uhlig's method[2]. The chiral *N,N′*-dioxide ligands were synthesized by the same procedure in the literature[3].

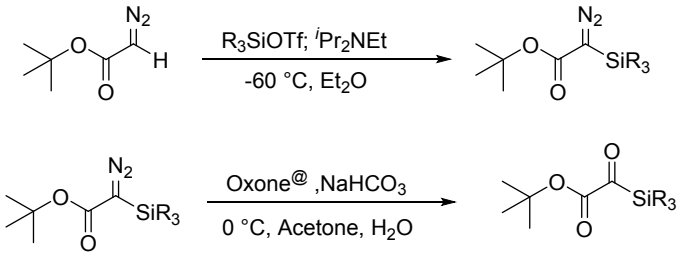
2. General procedures for the preparation of silylglyoxylate

Silylglyoxylate **1a**, **1b**, **1g** and **1h** were known compounds and synthesized according to the reported procedures.[1] Silylglyoxylate **1c-f** were synthesized according to the following procedure:

General Procedure.



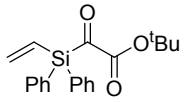
Under a nitrogen atmosphere, 10 ml of DCM was added to a 50 ml round bottom flask containing Me_2SiAr_2[4,5,6] (13 mmol, 1.3 equivalents). The solution was cooled to -20°C. The HOTf (12 mmol, 1.2 equivalent) was carefully added dropwise via a glass syringe within 3 minutes. The resulting solution was stirred for 24 hours at room temperature and used without purification.



Under a nitrogen atmosphere, to a solution of *tert*-butyl diazoacetate[7] (10 mmol, 1.0 equiv) and $^{i}Pr_2NEt$ (14 mmol, 1.4 equiv) was added 15 ml Et_2O under N_2. This solution was cooled to -78 °C and R_3SiOTf (13 mmol, 1.3 equiv) in 10 ml DCM mixture solution 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 $NaHCO_3$ (50.4 g, 600 mmol, 60.0 equiv) in H_2O/acetone (300 ml, v/v, 1.5:1) at 0 °C. After 20 min, a solution of the crude silyl diazoacetate in 40 ml of CH_2Cl_2 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_2O, brine, and dried (Na_2SO_4). 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_2O = 40 : 1).

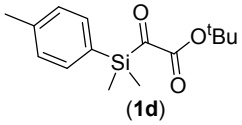
***Tert*-butyl (diphenyl(vinyl)silyl)-glyoxylate (1c)**



(**1c**)

Bright orange liquid. 44% yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.49 – 7.43 (m, 2H), 7.40 (dd, *J* = 7.9, 6.5 Hz, 4H), 6.63 (dd, *J* = 20.3, 14.7 Hz, 1H), 6.39 (dd, *J* = 14.7, 3.2 Hz, 1H), 5.89 (dd, *J* = 20.3, 3.2 Hz, 1H), 1.35 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 228.1, 162.0, 139.5, 136.0, 130.6, 130.3, 130.0, 128.3, 84.2, 27.9.
HRMS (ESI+) m/z calcd for $C_{20}H_{22}O_3Si$ $[M+Na]^+$: 361.1230, found: 361.1229.
IR (neat) 3743, 3053, 2980, 2362, 1737, 1715, 1665, 1481, 1429, 1399, 1370, 1255, 1156, 1115, 991, 842, 703, 664, 552, 507.

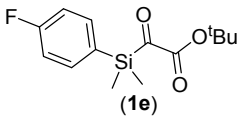
***Tert*-butyl (dimethyl(p-tolyl)silyl)-glyoxylate (1d)**



(**1d**)

Bright orange liquid. 32% yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.44 (s, 9H), 0.56 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 230.0, 160.6, 139.2, 133.3, 128.3, 127.9, 127.5, 127.2, 82.5, 26.8, -0.0, -5.5.
HRMS (ESI+) *m/z* calcd for $C_{15}H_{22}O_3Si$ $[M+Na]^+$: 317.0970, found: 317.0987.
IR (neat) 2978, 2362, 0739, 1711, 1664, 1602, 1456, 1395, 1370, 1290, 1253, 1158, 1108, 1037, 994, 839, 793, 701, 674, 601, 493.

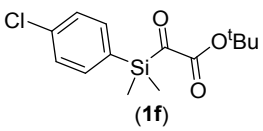
***Tert*-butyl ((4-fluorophenyl)dimethylsilyl)-glyoxylate (1e)**



(**1e**)

Bright orange liquid. 15% yield, 0.45 g. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.09 (t, J = 8.9 Hz, 2H), 1.44 (s, 9H), 0.58 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) 230.5, 164.6 ($J_{C\text{-}F}$ = 250.0 Hz), 161.7, 136.7 ($J_{C\text{-}F}$ = 7.7 Hz), 128.8 ($J_{C\text{-}F}$ = 12 Hz), 115.7 ($J_{C\text{-}F}$ = 20.0 Hz), 83.9, 28.0, -4.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ -109.9. **HRMS** (ESI+) *m/z* calcd for $C_{14}H_{19}FO_3Si$ $[M+Na]^+$: 305.0980, found: 305.0980.
IR (neat) 2978, 2362, 1738, 1711, 1661, 1588, 1501, 1458, 1392, 1370, 1253, 1160, 1107, 995, 834, 794, 674, 601, 615, 421.

***Tert*-butyl ((4-chlorophenyl)dimethylsilyl)-glyoxylate (1f)**



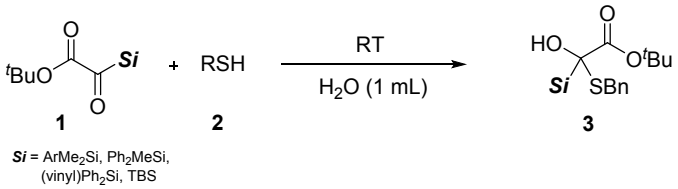
(**1f**)

Bright orange liquid. 10% yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, H), 7.39 – 7.35 (m, 2H), 1.44 (s, 9H), 0.57 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 230.2, 161.6, 136.8, 135.8, 135.1, 131.6, 128.5, 128.3, 84.0, 28.0, -4.4.
HRMS (ESI+) *m/z* calcd for $C_{14}H_{19}ClO_3Si$ $[M+Na]^+$: 353.0405 and 355.0375, found: 353.0405 and 355.0374.

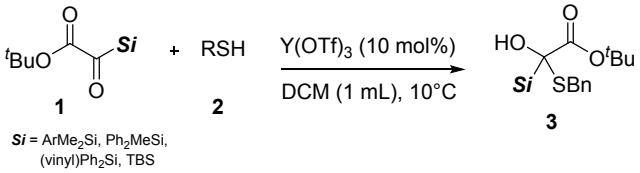
IR (neat) 2977, 2362, 1738, 1712, 1665, 1577, 1501, 1482, 1374, 1370, 1253, 1156, 1085, 1014, 834, 797, 742, 663, 494.

3. General procedures for the preparation of racemic products

Representative experimental procedure for the reaction of silylglyoxylate **1** and mercaptan **2**[8].



Procedure A: Silylglyoxylate **1** (0.1 mmol) were stirred in water (1.0 mL) at RT. Then mercaptan **2** (0.10 mmol) was added. The mixture was stirred until **1** disappeared (bright orange faded). Then the crude product was subjected to column chromatography on silica gel to afford product **3**.



Procedure B: Silylglyoxylate **1** (0.1 mmol) and $Y(OTf)_3$ (10 mol%) were stirred in DCM (1.0 mL) at 10℃. Then mercaptan **2** (0.10 mmol) was added. The mixture was stirred until **1** disappeared (bright orange faded). Then the crude product was subjected to column chromatography on silica gel to afford product **3**.

The racemic products **3l** and **3r** were prepared with **procedure B**.

4. General procedures for the catalytic asymmetric reaction

Representative experimental procedure for the reaction of silylglyoxylate **1a** and benzyl mercaptan **2a.**

Procedure A: Under an atmosphere of nitrogen, the $Y(OTf)_3$ (0.01 mmol), **L_5-$PrPr_2$** (0.01 mmol) and Silylglyoxylate **1a** (0.1 mmol, 26.4 mg) were stirred in DCM (1 mL) at 35 °C for 30 min. Then benzyl mercaptan **2a** (0.1 mmol) was added at -60 ℃.

The mixture was stirred until **1a** disappeared (bright orange faded, or TLC monitor). Purification of the reaction products was carried out by flash chromatography on silica gel at -60℃ and eluted with petroleum ether and ethyl ether (v/v, 20:1) to afford **3a** as a colorless liquid, or flash filtration with a thin silica gel [9] and washed with 8 mL Et_2O (DCM or EA can also be used) to afford the desired product.

Procedure B: Under an atmosphere of nitrogen, the $Y(OTf)_3$ (0.01 mmol), **L_5-$PrPr_2$** (0.01 mmol) were stirred in DCM (1 mL) at 35 °C for 30 min, and then concentrated in vacuo. Mercaptan **2** (0.1 mmol) were added at RT under an air atmosphere. The mixture was dissolved in 1.0 mL of DCM. Silylglyoxylate **1** was added at -60 ℃.

The mixture was stirred until **1** disappeared (bright orange faded, or TLC monitor). Purification of the reaction products was carried out by flash chromatography on silica gel at -60℃, or flash filtration with a thin silica gel and washed with 8 mL Et_2O (DCM or EA can also be used) to afford the desired product.

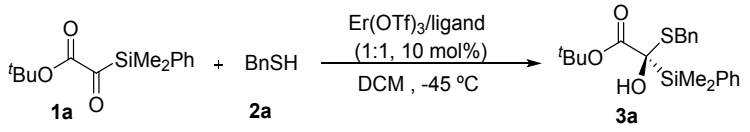
When the mercaptan is solid, **procedure B** is used for the reaction(**3l**, **3r and 3ae**).

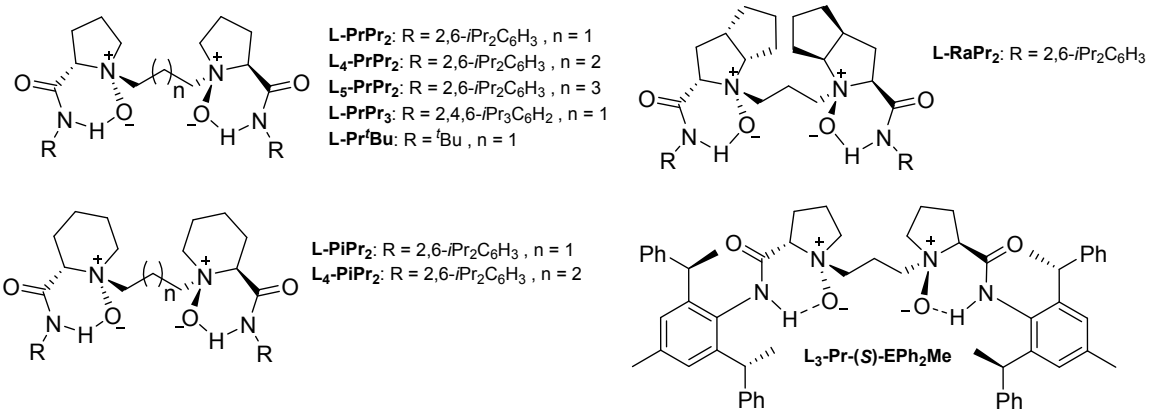
By the way, the product suffered somewhat racemization and decomposition after the chromatography on silica gel at room temperature. To avoid racemization and decomposition, **3a-3d**, **3h-3y**, **3aa-3ah** were purification by flash filtration with a thin silica gel, **3e**, **3f** and **3g** were purification by flash chromatography on silica gel at -60℃.

The products can be stored stably for a long time (at least half a year) at low temperature (-20 ℃), they will not decompose and the ee values can maintain. However, they will decompose very slowly at room temperature. It is worth mentioning that the product will decompose and racemize rapidly when dissolved in strong protonic solvent (such as methanol). However, they (configuration) will not be affected during the HPLC analysis. Moreover, the products can exist stably in non-protonic solvents, and the enantioselectivity value of the products will not decrease.

5. Optimization of the reaction conditions

Table S1. Screening of chiral *N*,*N*′-dioxide ligands

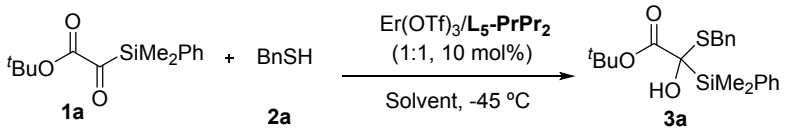




entry[a]	ligand	yield of **3a** (%)[b]	ee (%)[c]
1	-	85	-
2	**L-PrPr$_2$**	85	49
3	**L-RaPr$_2$**	50	0
4	**L-PiPr$_2$**	88	55
5	**L-Pr^{t}Bu**	74	12
6	**L-PrPr$_3$**	76	38
7	**L$_4$-PiPr$_2$**	99	77
8	**L$_4$-PrPr$_2$**	86	81
9	**L$_5$-PrPr$_2$**	87	87

[a] Unless otherwise noted, all reactions were performed with Er(OTf)$_3$/ligand (1:1, 10 mol%), **1a** (0.10 mmol), **2a** (0.10 mmol) in DCM (1.0 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S2. The screening of solvents.

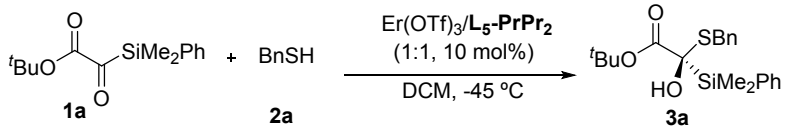


entry[a]	Solvent	yield of **3a** (%)[b]	ee[c] (%)
1	DCM	87	87
2	Toluene	no reaction	
3	CH_3CN	86	0
4	TCM	87	83
5	n-Hexane	57	-8
6	THF	85	10

7	Et_2O	no reaction

[a] Unless otherwise noted, all reactions were performed with $Er(OTf)_3$/**L_5-PrPr$_2$** (1:1, 10 mol%), **1a** (0.10 mmol), **2a** (0.10 mmol) in Solvent (1.0 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

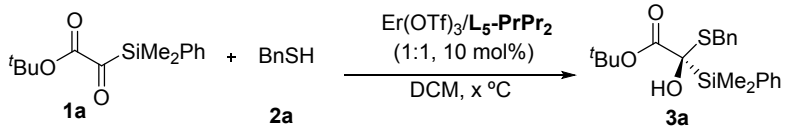
Table S3. The screening of concentration.



entry[a]	x	yield of **3a** (%)[b]	ee (%)[c]
1	0.5	88	86
2	1.0	87	87
3	1.5	87	86

[a] Unless otherwise noted, all reactions were performed with $Er(OTf)_3$/**L_5-PrPr$_2$** (1:1, 10 mol%), **1a** (0.10 mmol), **2a** (0.10 mmol) in DCM (x mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

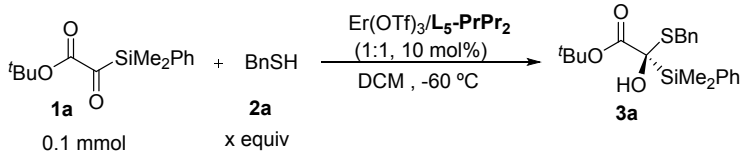
Table S4. Temperature effect.



entry[a]	x	yield of **3a** (%)[b]	ee[c] (%)
1	-78	NR	-
2	-70	95	83
3	-65	99	83
4	-60	95	89
5	-55	91	86
6	-50	95	86
7	-45	87	87
8[d]	-20	99	68
9[d]	0	99	66

[a] Unless otherwise noted, all reactions were performed with $Er(OTf)_3$/**L_5-PrPr$_2$** (1:1, 10 mol%), **1a** (0.10 mmol), **2a** (0.10 mmol) in DCM (1.0 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] $Y(OTf)_3$ was used instead of $Er(OTf)_3$.

Table S5. Optimization of condition for substrate ratio.

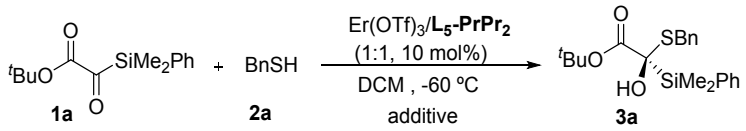


entry[a]	x	yield of **3a** (%)[b]	ee (%)[c]
1	1.2	90	85
2	1.1	88	86

3	1	95	89
4	0.91	83	87

[a] Unless otherwise noted, all reactions were performed with $Er(OTf)_3$/ligand (1:1, 10 mol%), **1a** (0.10 mmol), **2a** (x^{-1} mmol) in DCM (1.0 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

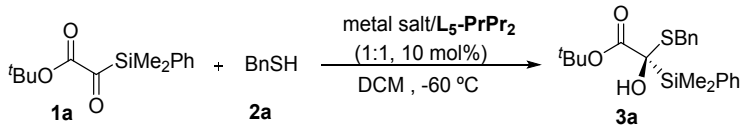
Table S6. The screening of additives.



entry[a]	additive	yield of **3a** (%)[b]	ee (%)[c]
1	-	95	89
2	3 Å M.S. (20 mg)	71	73
3	4 Å M.S. (20 mg)	69	69
4	5 Å M.S. (20 mg)	79	68
5	Et_3N (30 mol%)	70	1
6	H_2O (2 ul)	82	77
7	H_2O (5 ul)	82	64
8	$NaBArF_4$ (10 mg)	91	88
9	PhCOOH (10 mol%)	80	12

[a] Unless otherwise noted, all reactions were performed with $Er(OTf)_3$/**L_5-PrPr$_2$** (1:1, 10 mol%), additive, **1a** (0.10 mmol), **2a** (0.10 mmol) in CH_2Cl_2 (1.0 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

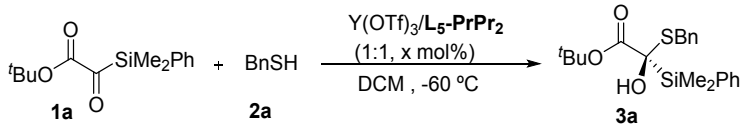
Table S7. Screening of metal salts.



entry[a]	metal salt	yield of **3a** (%)[b]	ee (%)[c]
1	-	87	5
2	$Er(OTf)_3$	95	87
3	$La(OTf)_3$	88	51
4	$Zn(OTf)_2$	83	0
5	$Ni(OTf)_2$	80	10
6	$Al(OTf)_3$	no reaction	
7	$Pr(OTf)_3$	no reaction	
8	$Y(OTf)_3$	99	91
9	YCl_3	95	1
10	$Y(^iPrO)_3$	93	33

[a] Unless otherwise noted, all reactions were performed with Metal salt/**L_5-PrPr$_2$** (1:1, 10 mol%), **1a** (0.10 mmol), **2a** (0.10 mmol) in CH_2Cl_2 (1.0 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

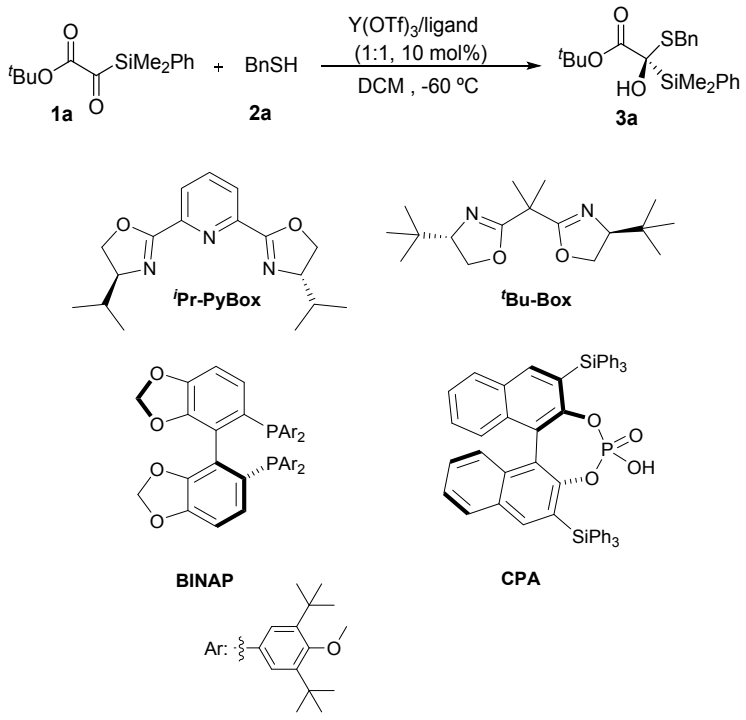
Table S8. Screening of the the amount of the **L_5-PrPr$_2$**/$Y(OTf)_3$.



entry[a]	x	yield of **3a** (%)[b]	ee (%)[c]
1	1	no reaction	
2	2	96	90
3	5	>99	91
4	10	>99	91

[a] Unless otherwise noted, all reactions were performed with $Y(OTf)_3$/**L_5-PrPr$_2$** (1:1, x mol%), **1a** (0.10 mmol), **2a** (0.10 mmol) in CH_2Cl_2 (1.0 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

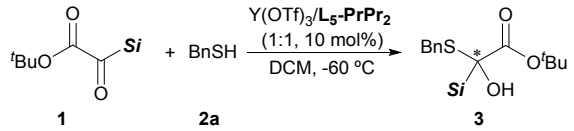
Table S9. Screening of chiral ligands



entry[a]	ligand	yield of **3a** (%)[b]	ee (%)[c]
1	**^{i}Pr-PyBox**	74	4
2	**^{t}Bu-Box**	73	3
3	**BINAP**	66	0
4	**CPA**[d]	77	0

[a] Unless otherwise noted, all reactions were performed with $Y(OTf)_3$/ligand (1:1, 10 mol%), **1a** (0.10 mmol), **2a** (0.10 mmol) in DCM (1.0 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] **CPA** was used instead of $Y(OTf)_3$/**CPA**.

Table S10. Screening of silyl groups

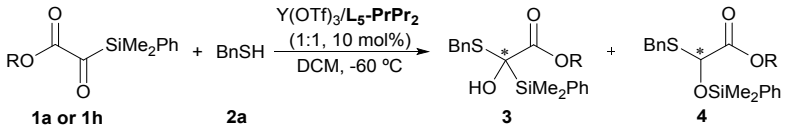


1 2a 3

Entry [a]	***Si***	Yield (%)[b]	ee (%)[c]
1	$PhMe_2Si$	99	91
2[d]	TBS	90	40
3 [d]	TES	91	20
4 [e]	TMS	93	25

[a] Unless otherwise noted, all reactions were performed with $Y(OTf)_3$/**L_5-PrPr$_2$** (1:1, 10 mol%), **1** (0.10 mmol), **2a** (0.10 mmol) in DCM (1.0 mL) at -60 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Run at -45 °C. [e] Run at -20 °C.

Table S11. Screening of ester moiety

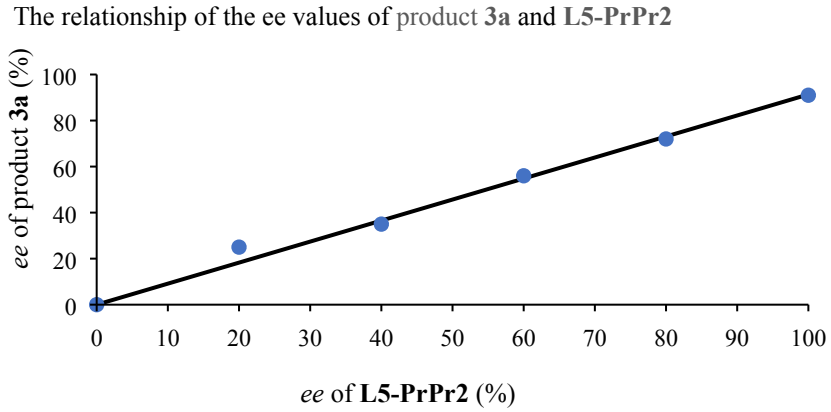


1a or 1h 2a 3 4

Entry [a]	**R**	Yield (%)[b]	ee (%)[c]	4[d]
1	^{t}Bu	99	91	N.D.
2	Bn	94	61	N.D.

[a] Unless otherwise noted, all reactions were performed with $Y(OTf)_3$/**L_5-PrPr$_2$** (1:1, 10 mol%), **1** (0.10 mmol), **2a** (0.10 mmol) in DCM (1.0 mL) at -60 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Determined by NMR.

6. The relationship of the ee values of product 3a and L_5-$PrPr_2$

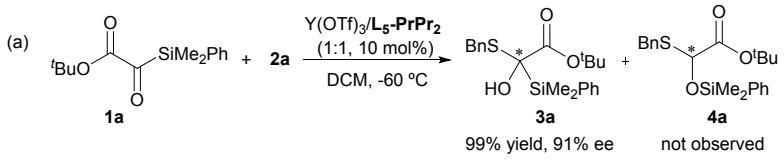


ee of L_5-PrPr	0	20	40	60	80	100
ee of product **3a**	0	25	35	56	72	91

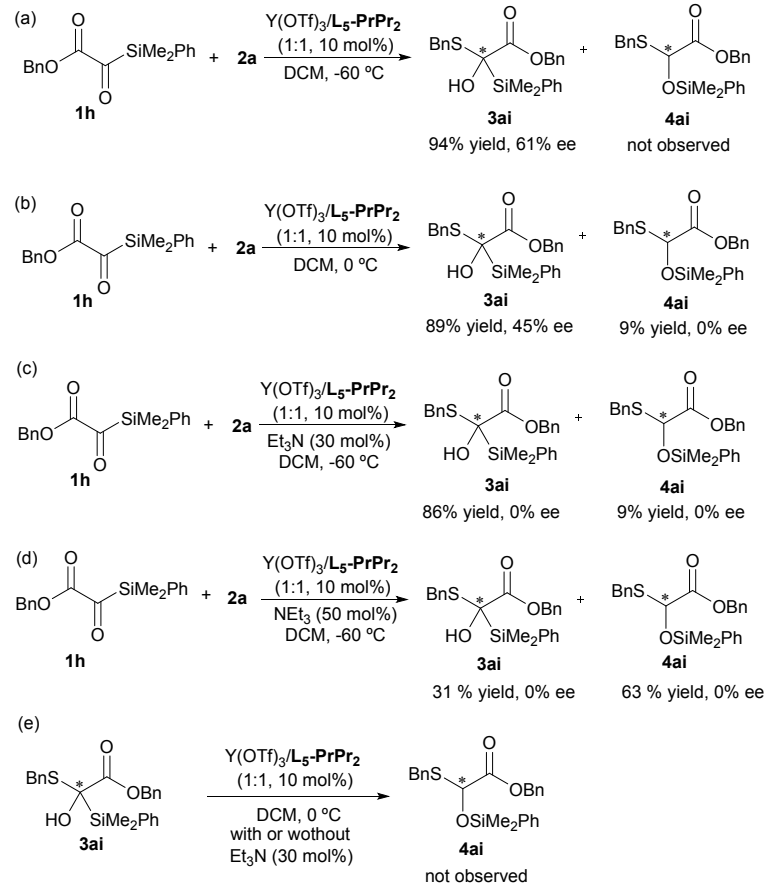
To gain mechanistic insight into the reaction, the relationship between the ee values of the product **3a** and ligand L_5-$PrPr_2$ was explored. A self-evident linear effect was observed, which indicates that the monomeric catalyst of L_5-$PrPr_2$ and $Y(OTf)_3$ may be the main catalytically active species.

7. Control experiments

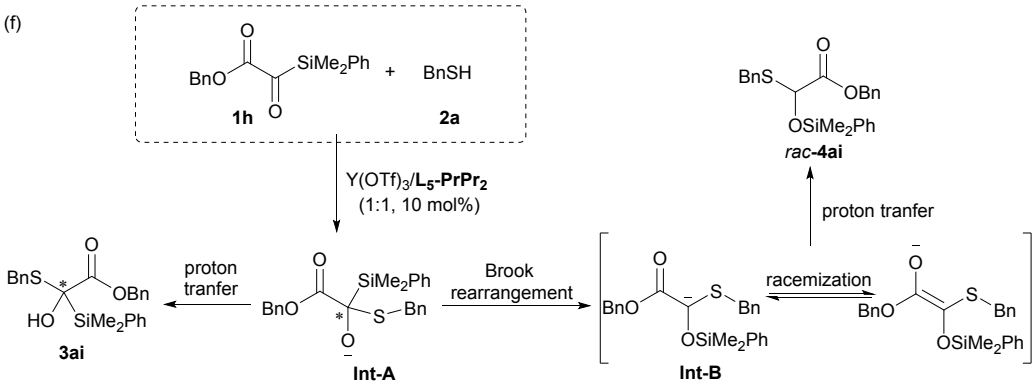
For the reaction between **1a** and **2a**



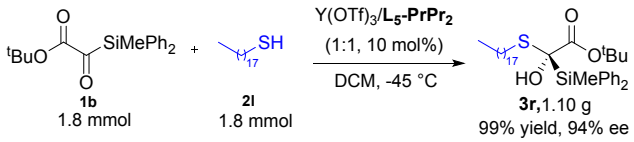
For the reaction between **1h** and **2a**



(f)


1h
2a
Y(OTf)3/L5-PrPr2
(1:1, 10 mol%)
3ai
proton tranfer
Int-A
Brook rearrangement
Int-B
racemization
proton tranfer
rac-4ai

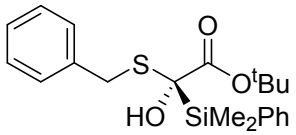
8. Scale-up version of the asymmetric reaction



A 100 mL of dry round-bottom flask was charged with *N,N'*-dioxide ligand **L_5-PrPr$_2$** (10 mol %, 0.18 mmol) and $Y(OTf)_3$ (10 mol %, 0.18 mmol) under nitrogen atmosphere. The DCM (18 mL) was added and the mixture were stirred at 35 °C for 6 h. Then, **2l** (1.8 mmol) and **1b** (1.8 mmol)was added at -45℃. The mixture was stirred at -45 °C for 48 h (detection by TLC). Purification of the reaction products was carried out by flash filtration with a thin silica gel and washed with 15 mL DCM to afford the desired product in 99% yield (1.10 g) with 94% ee as a colorless solid.

8. Characterization of the products

Tert-butyl (*R*)-2-(benzylthio)-2-(dimethyl(phenyl)silyl)-2-hydroxyacetate (**3a**)



3a

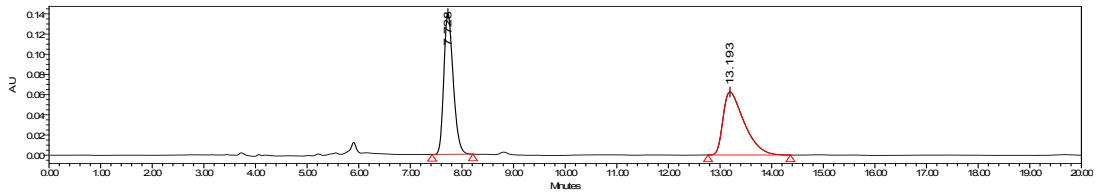
Colorless oil. 38.8 mg, 99% yield, 91% ee. **Specific rotation** $[\alpha]^{25}_D$ = -21 (*c* = 3.68, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral ODH column, *i*-PrOH/*n*-hexane = 1/99, flow rate: 1.0 mL/min, 254 nm): tr (minor) = 7.63 min, tr (major) = 13.93 min.

^{1}H NMR (400 MHz, $CDCl_3$)δ 7.67 – 7.60 (m, 2H), 7.40 – 7.32 (m, 3H), 7.30 – 7.24 (m, 4H), 7.23 – 7.16 (m, 1H), 3.88 (s, 1H), 3.84 (d, *J* = 11.8 Hz, 1H), 3.59 (d, *J* = 11.8 Hz, 1H), 1.33 (s, 9H), 0.53 (d, *J* = 7.0 Hz, 6H).

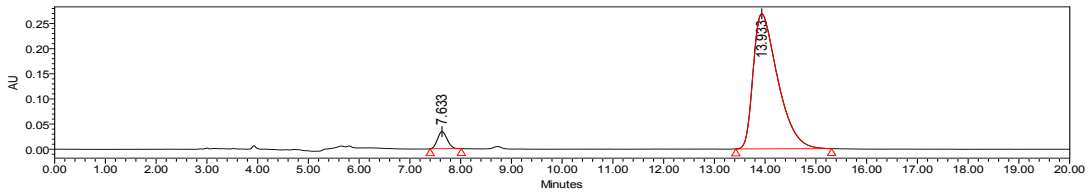
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.4, 137.3, 134.8, 134.7, 130.0, 129.4, 128.6, 127.8, 127.2, 83.4, 32.3, 27.9, -4.2.

HRMS (ESI+) *m/z* calcd for $C_{21}H_{28}O_3SSi$ $[M+Na]^+$: 411.1421, found: 411.1421.

IR (neat) 3442, 2975, 2926, 2361, 3696, 1492, 1455, 1427, 1394, 1368, 1250, 1154, 1114, 1050, 966, 916, 838, 780, 736, 699, 645, 565, 521, 469.

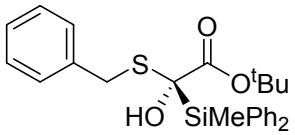


	Retention Time	Area	% Area
1	7.728	1767628	49.95
2	13.193	1771168	50.05



	Retention Time	Area	% Area
1	7.633	449468	4.75
2	13.933	9011224	95.25

Tert-butyl (*R*)-2-(benzylthio)-2-hydroxy-2-(methyldiphenylsilyl)acetate (**3b**)



3b

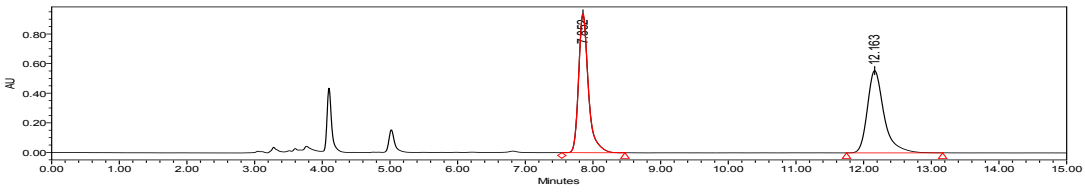
Colorless oil. 45.0 mg, 99% yield, 95% ee. **Specific rotation** $[\alpha]^{25}_D$ = +47 (*c* = 0.95, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 5/95, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 7.78 min, tr (major) = 12.01 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (ddd, *J* = 7.7, 5.7, 1.6 Hz, 4H), 7.41 – 7.31 (m, 6H), 7.28 – 7.23 (m, 4H), 7.20 (m, 1H), 3.98 (s, 1H), 3.85 (d, *J* = 11.9 Hz, 1H), 3.62 (d, *J* = 12.0 Hz, 1H), 1.21 (s, 9H), 0.83 (s, 3H).

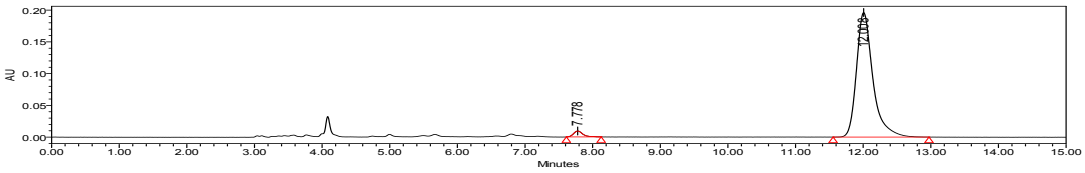
^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$) δ 174.0, 137.2, 135.7, 135.5, 133.8, 133.1, 130.1, 130.0, 129.5, 128.6, 127.9, 127.8, 127.2, 83.6, 77.4, 32.4, 27.7, -4.3.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{30}O_3SSi$ $[M+Na]^+$: 473.1577, found: 473.1576.

IR (neat) 3439, 3067, 2977, 2928, 2361, 1698, 1595, 1491, 1455, 1428, 1394, 1369, 1257, 1155, 1113, 1051, 964, 843, 790, 732, 670, 522, 488.

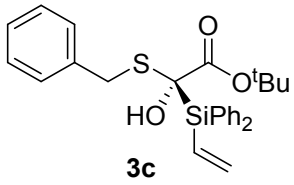


	Retention Time	Area	% Area
1	7.852	9380714	49.82
2	12.163	9449673	50.18



	Retention Time	Area	% Area
1	7.778	88344	2.61
2	12.008	3301514	97.39

Tert-butyl (*R*)-2-(benzylthio)-2-(diphenyl(vinyl)silyl)-2-hydroxyacetate (**3c**)



3c

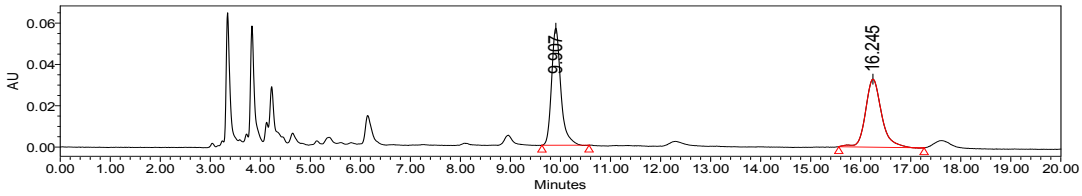
Colorless oil. 44.9 mg, 97% yield, 96% ee. **Specific rotation** $[\alpha]^{25}_D$ = +57 (*c* = 0.87, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 9.91 min, tr (major) = 16.06 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (ddd, *J* = 7.7, 5.7, 1.6 Hz, 4H), 7.41 – 7.31 (m, 6H), 7.28 – 7.23 (m, 4H), 7.20 (m, 1H), 3.98 (s, 1H), 3.85 (d, *J* = 11.9 Hz, 1H), 3.62 (d, *J* = 12.0 Hz, 1H), 1.21 (s, 9H), 0.83 (s, 3H).

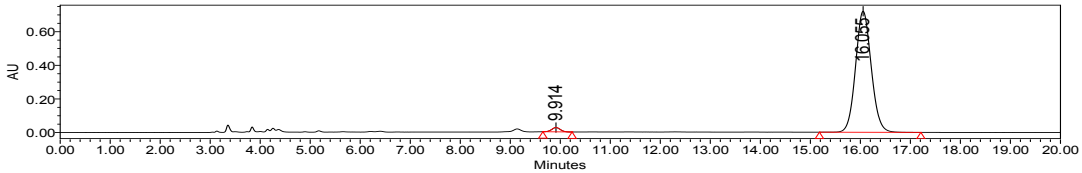
^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$) δ 174.0, 137.2, 135.7, 135.5, 133.8, 133.1, 130.1, 130.0, 129.5, 128.6, 127.9, 127.8, 127.2, 83.6, 77.4, 32.4, 27.7, -4.3.

HRMS (ESI+) *m/z* calcd for $C_{27}H_{30}O_3SSi$ $[M+Na]^+$: 485.1577, found: 485.1576.

IR (neat) 3439, 3067, 2977, 2928, 2361, 1698, 1595, 1491, 1455, 1428, 1394, 1369, 1257, 1155, 1113, 1051, 964, 843, 790, 732, 670, 522, 488.

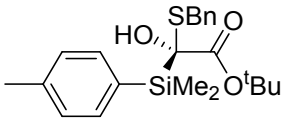


	Retention Time	Area	% Area
1	9.907	732157	49.90
2	16.245	735206	50.10



	Retention Time	Area	% Area
1	9.914	307067	1.92
2	16.055	15684587	98.08

Tert-butyl (*R*)-2-(benzylthio)-2-(dimethyl(p-tolyl)silyl)-2-hydroxyacetate (**3d**)



3d

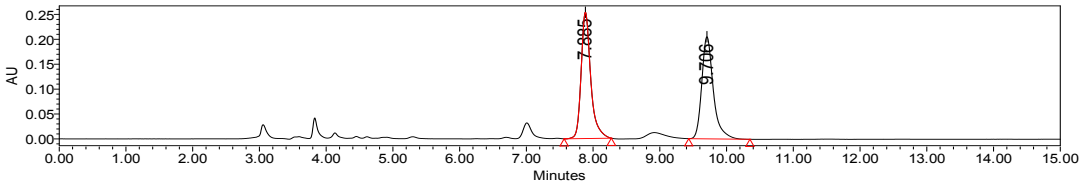
Colorless oil. 35.4 mg, 88% yield, 85% ee. **Specific rotation** $[\alpha]^{25}_{D}$ = -13 (*c* = 0.55, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 8.10 min, tr (major) = 10.22 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.60 – 7.53 (m, 2H), 7.34 – 7.25 (m, 4H), 7.20 (dd, *J* = 16.5, 7.2 Hz, 3H), 4.64 (s, 1H), 3.87 (d, *J* = 11.7 Hz, 1H), 3.64 (d, *J* = 11.8 Hz, 1H), 2.31 (s, 3H), 1.36 (s, 9H), 0.50 (s, 3H), 0.46 (s, 3H).

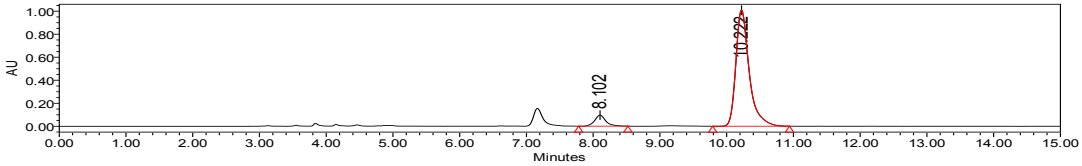
^{13}C{^{1}H} NMR (Acetone-d_6) δ 174.4, 140.3, 138.6, 135.6, 135.6, 132.2, 130.1, 129.3, 129.1, 127.7, 83.1, 78.1, 32.5, 28.1, 21.5, -3.8, -3.9.

HRMS (ESI+) *m/z* calcd for $C_{22}H_{30}O_3SSi$ $[M+Na]^+$: 425.1567, found: 425.1557.

IR (neat) 3444, 2974, 2925, 1697, 1602, 1495, 1454, 1394, 1369, 1251, 1155, 1108, 1051, 967, 894, 785, 701, 602, 493.

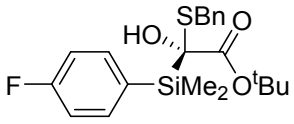


	Retention Time	Area	% Area
1	7.885	2529828	50.57
2	9.706	2472311	49.43



	Retention Time	Area	% Area
1	8.102	1116389	7.40
2	10.222	13968317	92.60

Tert-butyl (*R*)-2-(benzylthio)-2-((4-fluorophenyl)dimethylsilyl)-2-hydroxyacetate (**3e**)



3e

Colorless oil. 31.0 mg, 76% yield, 80% ee. **Specific rotation** $[\alpha]^{25}_{D}$ = -9.5 (*c* = 0.28, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 7.57 min, tr (major) = 8.76 min.

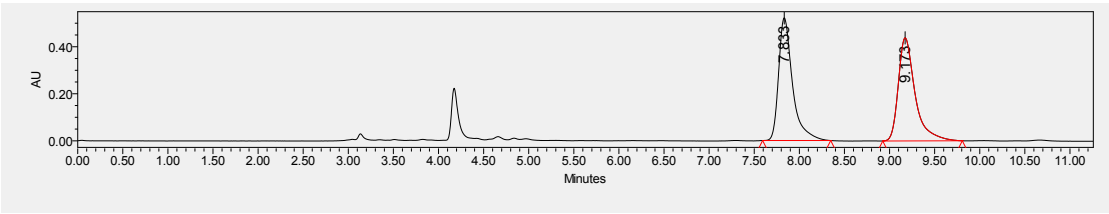
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.77 – 7.69 (m, 2H), 7.33 – 7.25 (m, 4H), 7.25 – 7.18 (m, 1H), 7.17 - 7.10 (m, 2H), 4.75 (s, 1H), 3.88 (d, *J* = 11.8 Hz, 1H), 3.66 (d, *J* = 11.7 Hz, 1H), 1.36 (s, 9H), 0.53 (s, 3H), 0.48 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.3, 165.17 ($J_{C\text{-}F}$ = 247.2 Hz), 138.7, 138.1 ($J_{C\text{-}F}$ = 7.6 Hz), 132.1 ($J_{C\text{-}F}$ = 3.8 Hz), 130.3, 129.5, 128.0, 115.51 ($J_{C\text{-}F}$ = 19.8 Hz), 83.4, 78.1, 32.7, 28.2, -3.7.

^{19}F NMR (376 MHz, Acetone-d_6) δ -112.7.

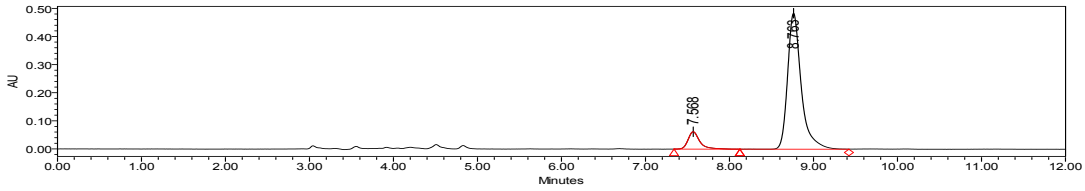
HRMS (ESI+) *m/z* calcd for $C_{21}H_{27}O_3FSSi$ $[M+Na]^+$: 429.1326, found: 429.1326.

IR (neat) 2977, 2362, 1712, 1665, 1577, 1483, 1374, 1253, 1156, 1085, 1014, 834, 797, 742, 663, 494.4



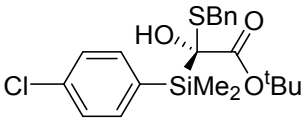
	Retention Time	Area	% Area
1	7.833	5593732	49.80
2	9.173	5638667	50.20

The mixture was purified by flash chromatography on silica gel at -60℃:



	Retention Time	Area	% Area
1	7.568	599685	9.92
2	8.763	5447913	90.08

Tert-butyl (*R*)-2-(benzylthio)-2-((4-chlorophenyl)dimethylsilyl)-2-hydroxyacetate (**3f**)



3f

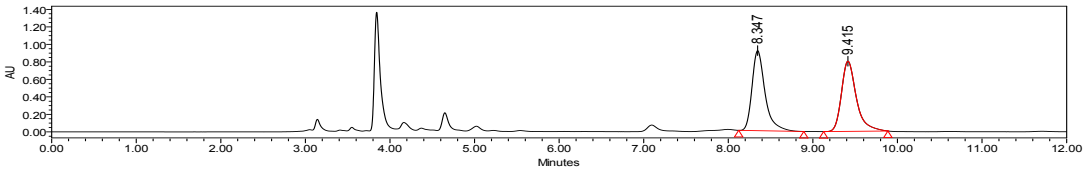
Colorless oil. 35.5 mg, 84% yield, 91% ee. **Specific rotation** $[\alpha]^{25}_{D}$ = -20 (*c* = 0.33, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 254 nm): tr (minor) = 8.34 min, tr (major) = 9.43 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.72 – 7.67 (m, 2H), 7.43 – 7.39 (m, 2H), 7.33 – 7.26 (m, 4H), 7.22 (m, 1H), 4.78 (s, 1H), 3.89 (d, *J* = 11.8 Hz, 1H), 3.66 (d, *J* = 11.8 Hz, 1H), 1.37 (s, 9H), 0.53 (s, 3H), 0.49 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.1, 138.4, 137.3, 136.4, 136.3, 134.9, 130.1, 129.3, 128.7, 128.5, 127.8, 83.3, 77.86, 32.6, 28.0, -4.0, -4.1.

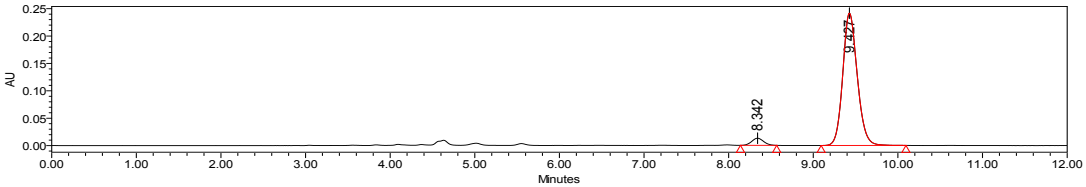
HRMS (ESI+) *m/z* calcd for $C_{21}H_{27}O_3ClSSi$ $[M+Na]^+$: 445.1031 and 447.1001, found: 445.1031 and 447.1000.

IR (neat) 2979, 2363, 1738, 1711, 1665, 1589, 1502, 1458, 1370, 1253, 1160, 1107, 995, 834, 794, 674, 601, 515, 421.



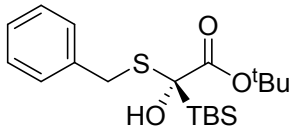
	Retention Time	Area	% Area
1	8.347	9802761	49.99
2	9.415	9805506	50.01

The mixture was purified by flash chromatography on silica gel at -60℃:



	Retention Time	Area	% Area
1	8.341	186913	4.31
2	9.427	4153436	95.69

Tert-butyl (*R*)-2-(benzylthio)-2-(tert-butyldimethylsilyl)-2-hydroxyacetate (**3g**)



3g

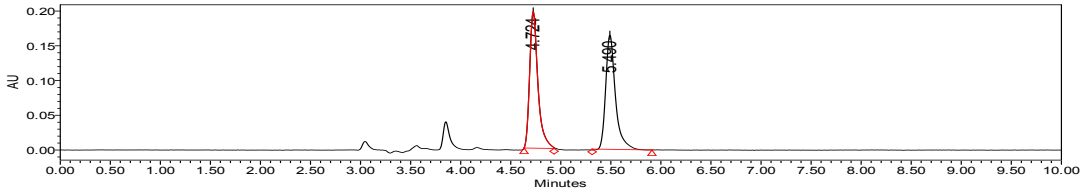
Colorless oil. 32.1 mg, 87% yield, 80% ee. **Specific rotation** $[\alpha]^{25}_{D}$ = +16 (*c* = 0.44, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 4.65 min, tr (major) = 5.35 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.13 (m, 5H), 3.91 (s, 1H), 3.80 (d, *J* = 11.6 Hz, 1H), 3.51 (d, *J* = 11.6 Hz, 1H), 1.51 (s, 9H), 0.96 (s, 9H), 0.23 (s, 3H), 0.13 (s, 3H).

^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$) δ 175.4, 137.3, 129.4, 128.6, 127.2, 83.6, 78.7, 32.0, 28.2, 27.7, 18.8, -5.9, -6.2.

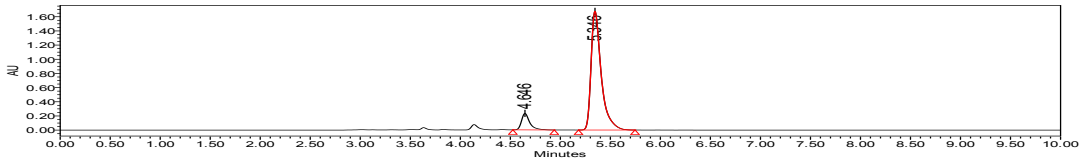
HRMS (ESI+) *m/z* calcd for $C_{19}H_{32}O_3SSi$ $[M+Na]^+$: 391.1734, found: 391.1730.

IR (neat) 3448, 2932, 2858, 2361, 1694, 1464, 1393, 1368, 1253, 1157, 1051, 964, 840, 798, 772, 702, 573, 454.



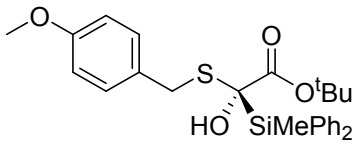
	Retention Time	Area	% Area
1	4.724	1120405	50.05
2	5.490	1118363	49.95

The mixture was purified by flash chromatography on silica gel at -60℃:



	Retention Time	Area	% Area
1	4.646	1323163	10.07
2	5.346	11819788	89.93

Tert-butyl (*R*)-2-(dimethyl(phenyl)silyl)-2-hydroxy-2-((4-methoxybenzyl)thio)acetate (**3h**)



3h

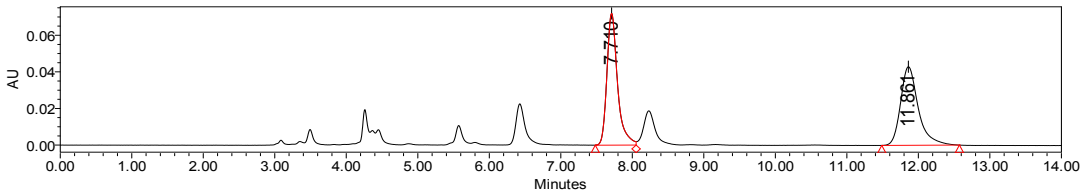
Colorless oil. 48.0 mg, 99% yield, 94% ee. **Specific rotation** $[\alpha]^{25}_D$ = +20 (*c* = 0.04, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane =10/90, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 7.82 min, tr (major) = 11.81 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.82 – 7.74 (m, 4H), 7.45 – 7.31 (m, 6H), 7.24 – 7.18 (m, 2H), 6.87 – 6.80 (m, 2H), 4.88 (s, 1H), 3.85 (d, *J* = 11.7 Hz, 1H), 3.75 (s, 3H), 3.63 (d, *J* = 11.6 Hz, 1H), 1.26 (s, 9H), 0.83 (s, 3H).

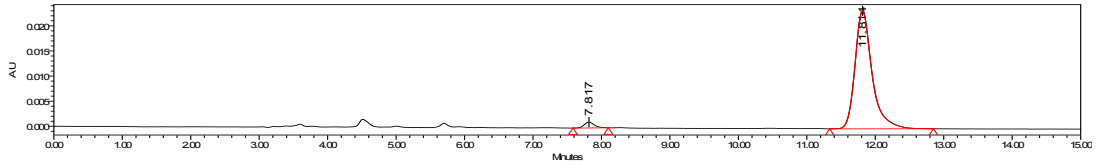
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.0, 159.9, 136.6, 136.3, 135.4, 134.7, 131.3, 130.7, 130.5, 130.0, 128.6, 128.4, 114.8, 83.5, 78.4, 55.6, 32.3, 28.0, -3.8.

HRMS (ESI+) *m/z* calcd for $C_{27}H_{32}O_4SSi$ [M+Na]$^+$: 503.1683, found: 503.1683.

IR (neat) 3438, 2975, 2099, 1697, 1610, 1511, 1461, 1430, 1369, 1249, 1155, 1112, 1035, 964, 838, 788, 733, 699, 490.

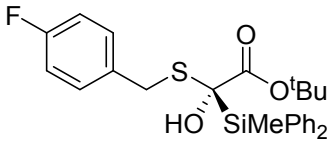


	Retention Time	Area	% Area
1	7.710	740488	50.17
2	11.861	735417	49.83



	Retention Time	Area	% Area
1	7.817	12028	2.87
2	11.814	407561	97.13

Tert-butyl (*R*)-2-(dimethyl(phenyl)silyl)-2-((4-fluorobenzyl)thio)-2-hydroxyacetate (**3i**)



3i

Colorless oil. 46.7 mg, 99% yield, 93% ee. **Specific rotation** $[\alpha]^{25}_D$ = +18 (*c* = 0.90, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane =3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 9.78 min, tr (major) = 17.11 min.

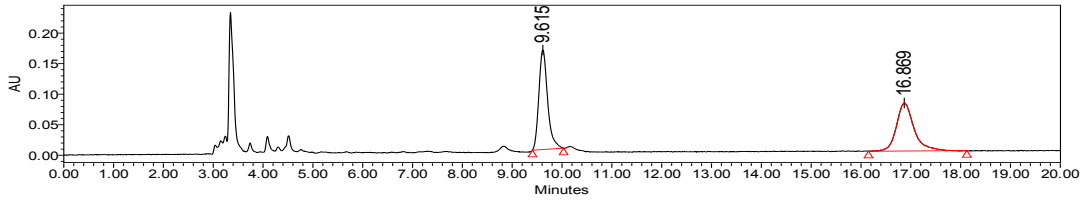
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.80 – 7.69 (m, 4H), 7.41 – 7.26 (m, 8H), 7.03 – 6.96 (m, 2H), 4.92 (s, 1H), 3.83 (d, *J* = 12.1 Hz, 1H), 3.66 (d, *J* = 12.1 Hz, 1H), 1.20 (s, 9H), 0.80 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.0, 162.7 ($J_{C\text{-}F}$ = 243.6 Hz), 136.6, 136.3, 135.2, 134.7 ($J_{C\text{-}F}$ = 3.1 Hz), 134.6, 132.1 ($J_{C\text{-}F}$ = 8.2 Hz), 130.8, 130.5, 128.6, 128.4, 116.0 ($J_{C\text{-}F}$ = 21.6 Hz), 83.5, 78.2, 32.0, 27.9, -3.9.

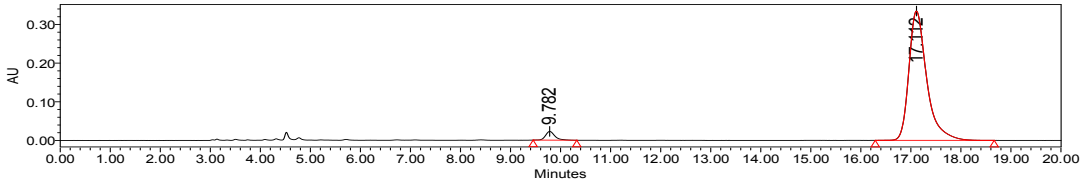
^{19}F NMR (376 MHz, Acetone-d_6) δ -117.37.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{29}FO_3SSi$ $[M+Na]^+$: 491.1488, found: 491.1489.

IR (neat) 3436, 3048, 2978, 1697, 1600, 1508, 1458, 1394, 1369, 1255, 1225, 1155, 1111, 1052, 964, 841, 788, 732, 699.

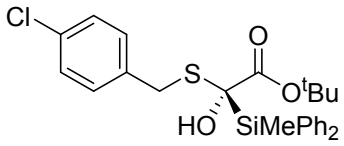


	Retention Time	Area	% Area
1	9.615	1999525	51.04
2	16.869	1917804	48.96



	Retention Time	Area	% Area
1	9.782	290451	3.40
2	17.112	8257782	96.60

Tert-butyl (*R*)-2-((4-chlorobenzyl)thio)-2-(dimethyl(phenyl)silyl)-2-hydroxyacetate (**3j**)



3j

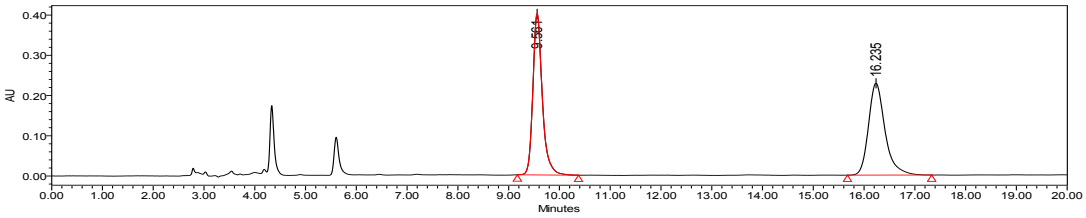
Colorless oil. 48.0 mg, 99% yield, 93% ee. **Specific rotation** $[\alpha]^{25}_D$ = +22 (*c* = 0.98, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane =3/97, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 9.49 min, tr (major) = 15.94 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.82 – 7.73 (m, 4H), 7.44 – 7.33 (m, 6H), 7.30 (d, *J* = 0.8 Hz, 4H), 4.97 (s, 1H), 3.86 (d, *J* = 12.2 Hz, 1H), 3.69 (d, *J* = 12.2 Hz, 1H), 1.23 (s, 9H), 0.83 (s, 3H).

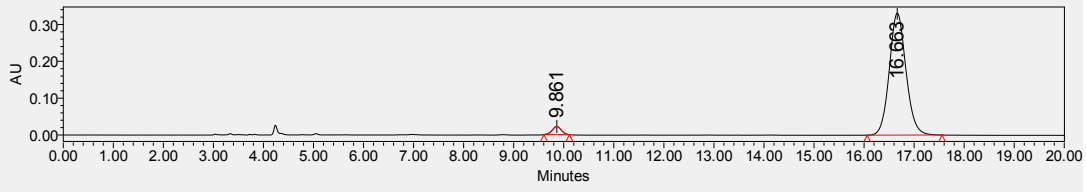
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.0, 137.8, 136.6, 136.6, 135.2, 134.6, 133.2, 132.0, 130.8, 130.6, 129.4, 128.6, 128.5, 83.6, 78.2, 32.1, 27.9, -3.9.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{29}ClO_3SSi$ $[M+Na]^+$: 507.1187 and 509.1157, found: 507.1187 and 509.1157.

IR (neat) 3438, 3049, 2977, 2930, 1697, 1592, 1489, 1428, 1398, 1369, 1255, 1155, 1111, 1053, 964, 841, 789, 732, 699, 490.

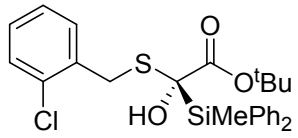


	Retention Time	Area	% Area
1	9.561	5171679	50.06
2	16.235	5158853	49.94



	Retention Time	Area	% Area
1	9.861	280462	3.53
2	16.663	7664487	96.47

Tert-butyl (*R*)-2-((2-chlorobenzyl)thio)-2-(dimethyl(phenyl)silyl)-2-hydroxyacetate (**3k**)



3k

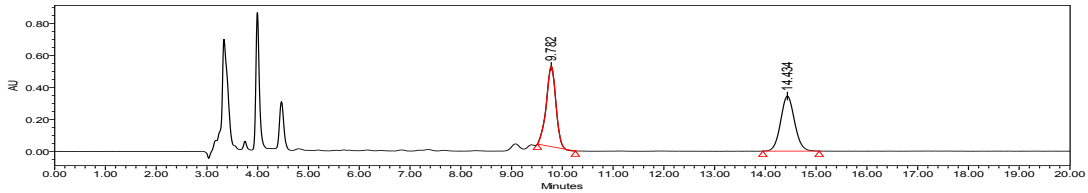
Colorless oil. 48.1 mg, 99% yield, 92% ee. **Specific rotation** $[\alpha]^{25}_D$ = +26 (*c* = 0.71, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane =3/97, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 9.95 min, tr (major) = 14.74 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.76 (ddd, *J* = 13.1, 7.9, 1.7 Hz, 4H), 7.44 – 7.29 (m, 8H), 7.26 – 7.17 (m, 2H), 4.97 (s, 1H), 3.95 (d, *J* = 11.9 Hz, 1H), 3.86 (d, *J* = 11.8 Hz, 1H), 1.21 (s, 9H), 0.82 (s, 3H).

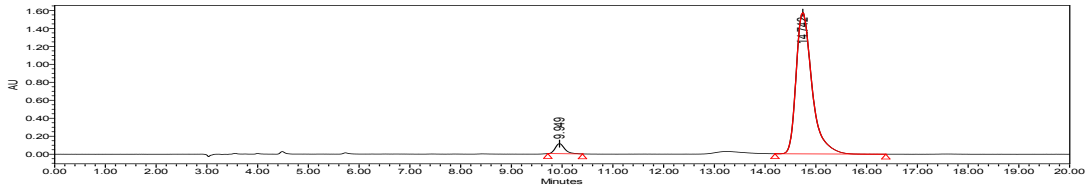
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.0, 136.6, 136.3, 136.3, 135.3, 134.8, 134.6, 132.7, 130.8, 130.5, 130.4, 129.7, 128.6, 128.5, 128.2, 83.7, 78.1, 30.5, 27.9, -3.9.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{29}ClO_3SSi$ $[M+Na]^+$: 507.1187 and 509.1157, found: 507.1187 and 509.1157.

IR (neat) 3435, 3051, 2977, 2929, 2362, 1696, 1590, 1472, 1429, 1394, 1369, 1255, 1155, 1111, 11046, 963, 842, 790, 733, 699, 523, 490, 450.

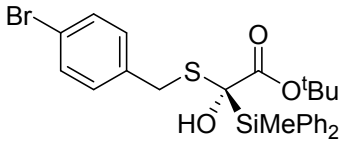


	Retention Time	Area	% Area
1	9.782	6522564	50.61
2	14.434	6364976	49.39



	Retention Time	Area	% Area
1	9.949	1452658	4.08
2	14.742	34170351	95.92

Tert-butyl (*R*)-2-((4-bromobenzyl)thio)-2-(dimethyl(phenyl)silyl)-2-hydroxyacetate (**3l**)



3l

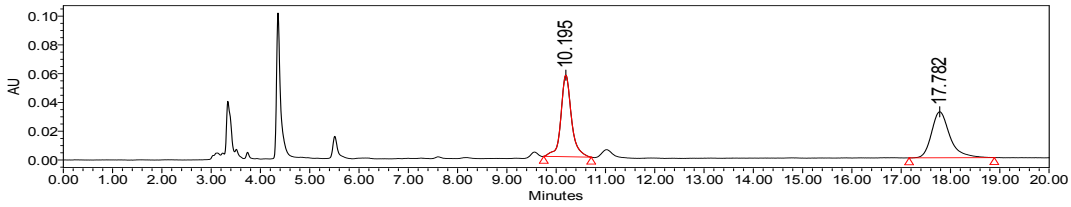
Colorless oil. 49.8 mg, 93% yield, 93% ee. **Specific rotation** $[\alpha]^{20}_D$ = +26 (*c* = 1.00, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane =3/97, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 10.12 min, tr (major) = 17.65 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.77 (ddt, *J* = 15.2, 6.7, 1.5 Hz, 4H), 7.47 – 7.32 (m, 8H), 7.29 – 7.22 (m, 2H), 4.97 (s, 1H), 3.84 (d, *J* = 12.2 Hz, 1H), 3.68 (d, *J* = 12.2 Hz, 1H), 1.22 (s, 9H), 0.83 (s, 3H).

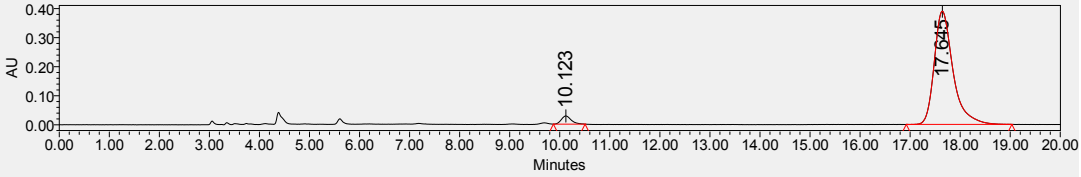
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.0, 138.3, 136.6, 136.3, 135.2, 134.6, 132.4, 132.3, 130.8, 130.6, 128.6, 128.5, 121.2, 83.6, 78.2, 32.1, 27.9, -3.9.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{29}BrO_3SSi$ $[M+Na]^+$: 551.0682 and 553.0662, found: 551.0684 and 553.0662.

IR (neat) 3432, 2977, 1698, 1487, 1428, 1394, 1369, 1253, 1154, 1113, 1070, 1011, 964, 843, 798, 729, 699, 489.

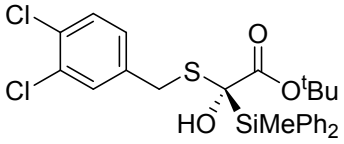


	Retention Time	Area	% Area
1	10.195	844758	50.59
2	17.782	825068	49.41



	Retention Time	Area	% Area
1	10.123	387094	3.68
2	17.645	10136719	96.32

Tert-butyl (*R*)-2-((3,4-dichlorobenzyl)thio)-2-hydroxy-2-(methyldiphenylsilyl)acetate (**3m**)



3m

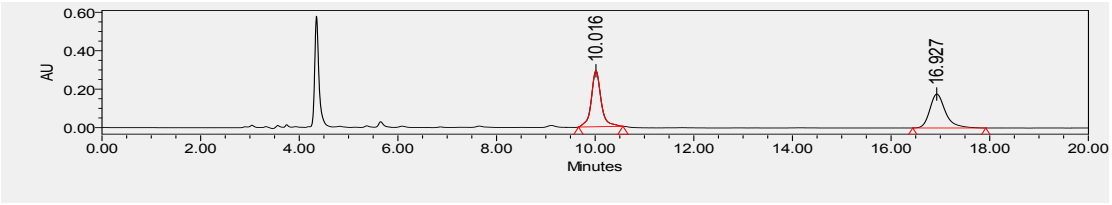
Colorless oil. 51.1 mg, 98% yield, 93% ee. **Specific rotation** $[\alpha]^{20}_{D}$ = +11 (*c* = 0.33, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 9.99 min, tr (major) = 17.15 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.74 (ddt, *J* = 16.6, 6.6, 1.6 Hz, 4H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.46 – 7.29 (m, 7H), 7.25 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.05 (s, 1H), 3.76 (q, *J* = 18.4 Hz, 2H), 1.16 (s, 9H), 0.81 (s, 3H).

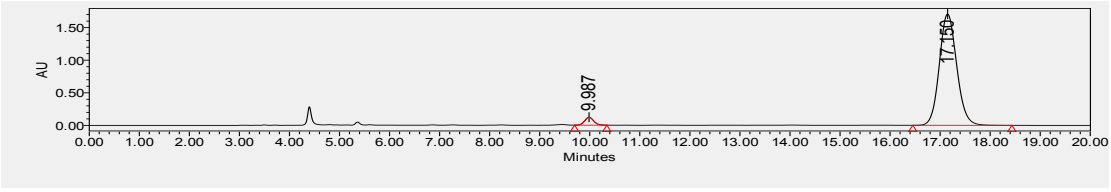
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 173.9, 140.5, 136.6, 136.3, 135.1, 134.4, 132.5, 132.2, 131.4, 131.1, 130.8, 130.6, 130.3, 128.6, 128.5, 83.6, 77.9, 31.5, 27.8, -4.0.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{28}Cl_2O_3SSi$ $[M+Na]^+$: 541.0798 and 542.0831, found: 541.0798 and 542.0814.

IR (neat) 3430, 3051, 2978, 2930, 1697, 1590, 1471, 1428, 1393, 1370, 1255, 1155, 1112, 964, 842, 786, 732, 699, 490.

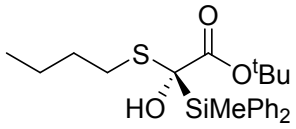


	Retention Time	Area	% Area
1	10.016	3998717	50.78
2	16.927	3875634	49.22



	Retention Time	Area	% Area
1	9.987	1523918	3.58
2	17.150	41102716	96.42

Tert-butyl (*R*)-2-(butylthio)-2-hydroxy-2-(methyldiphenylsilyl)acetate (**3n**)



3n

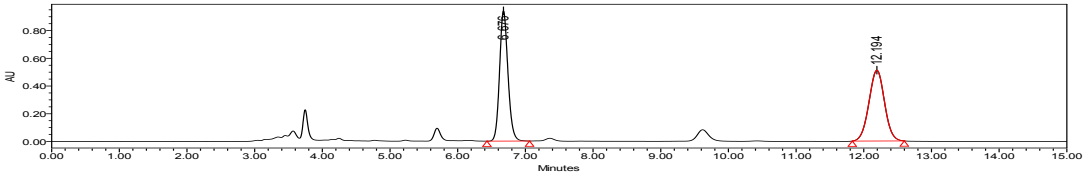
Colorless oil. 40.0 mg, 96% yield, 97% ee. **Specific rotation** $[\alpha]^{20}_D$ = +18 (*c* = 0.80, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 6.84 min, tr (major) = 12.88 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.77 (td, *J* = 8.2, 1.6 Hz, 4H), 7.37 (m, 6H), 4.69 (s, 1H), 2.63 (m, 1H), 2.52 (m, 1H), 1.56 – 1.46 (m, 2H), 1.41 – 1.31 (m, 2H), 1.24 (s, 9H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.82 (s, 3H).

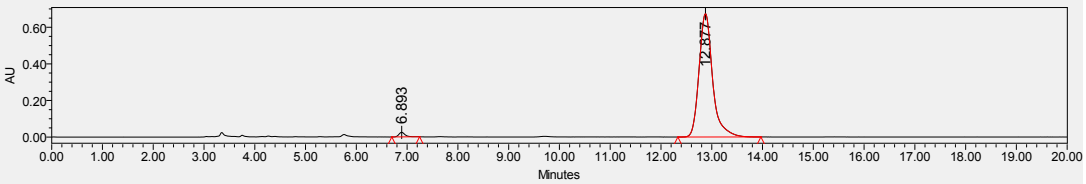
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.5, 136.6, 136.3, 135.5, 134.9, 130.7, 130.4, 83.4, 77.6, 32.4, 28.0, 27.9, 23.0, 14.0, -3.7.

HRMS (ESI+) *m/z* calcd for $C_{23}H_{32}O_3SSi$ [M+Na]$^+$: 439.1734, found: 439.1733.

IR (neat) 3445, 2961, 2930, 1689, 1450, 1429, 1369, 1255, 1157, 1111, 1047, 693, 845, 790, 731, 699, 490.

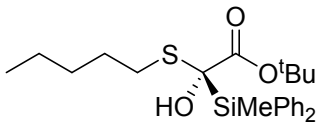


	Retention Time	Area	% Area
1	6.676	8076072	49.78
2	12.194	8148102	50.22



	Retention Time	Area	% Area
1	6.893	211908	1.67
2	12.877	12463411	98.33

Tert-butyl (*R*)-2-hydroxy-2-(methyldiphenylsilyl)-2-(pentylthio)acetate (**3o**)



3o

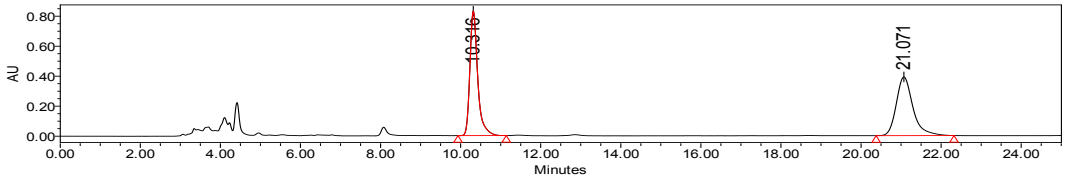
Colorless oil. 42.5 mg, 99% yield, 98% ee. **Specific rotation** $[\alpha]^{25}_D$ = +28 (*c* = 0.44, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 1/99, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 10.34 min, tr (major) = 20.90 min.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 7.9 Hz, 4H), 7.37 – 7.27 (m, 6H), 3.89 (s, 1H), 2.45 (m, 2H), 1.51 – 1.44 (m, 2H), 1.28 – 1.21 (m, 4H), 1.18 (s, 9H), 0.82 (t, *J* = 7.0 Hz, 3H), 0.76 (s, 3H).

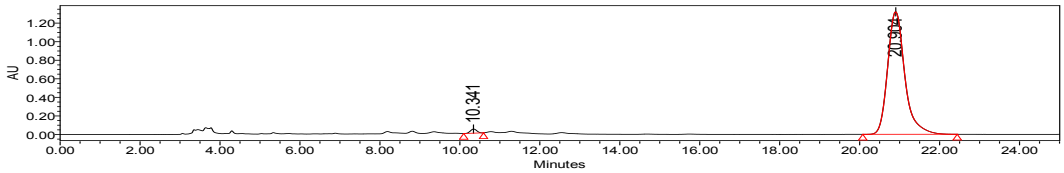
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 174.7, 136.2, 135.9, 134.6, 133.9, 130.5, 130.3, 128.3, 128.1, 84.0, 77.3, 31.9, 29.6, 28.0, 28.0, 22.8, 14.3, -4.1.

HRMS (ESI+) *m/z* calcd for $C_{24}H_{34}O_3SSi$ $[M+Na]^+$: 453.1890, found: 453.1893.

IR (neat) 3442, 2958, 2927, 1697, 1460, 428, 1369, 1253, 1155, 1111, 1036, 962, 844, 786, 729, 698, 527, 487.

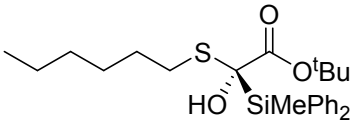


	Retention Time	Area	% Area
1	10.316	11227929	49.95
2	21.071	11250065	50.05



	Retention Time	Area	% Area
1	10.341	493760	1.24
2	20.904	39192279	98.76

Tert-butyl (*R*)-2-(hexylthio)-2-hydroxy-2-(methyldiphenylsilyl)acetate (**3p**)



3p

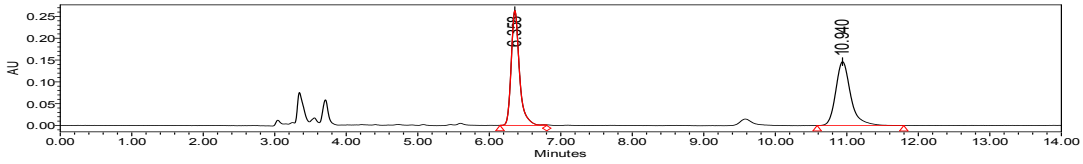
Colorless oil. 44 mg, 99% yield, 94% ee. **Specific rotation** $[\alpha]^{25}_{D} = +22$ ($c = 0.86$, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 6.42 min, tr (major) = 11.21 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.77 (td, $J = 7.8$, 1.6 Hz, 4H), 7.45 – 7.31 (m, 6H), 4.67 (s, 1H), 2.68 – 2.44 (m, 2H), 1.53 (m, 2H), 1.39 – 1.26 (m, 6H), 1.25 (s, 9H), 0.87 (t, $J = 6.8$ Hz, 3H), 0.82 (s, 3H).

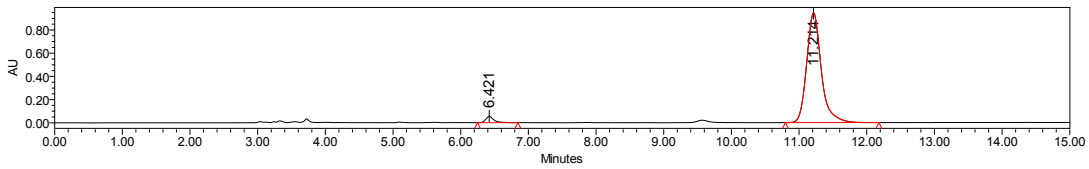
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.6, 136.7, 136.4, 135.6, 135.0, 130.8, 130.5, 128.6, 128.5, 83.5, 77.7, 32.3, 30.4, 29.7, 28.3, 28.1, 23.4, 14.5, -3.7.

HRMS (ESI+) *m/z* calcd for $C_{25}H_{36}O_3SSi$ $[M+Na]^+$: 467.2047, found: 467.2049.

IR (neat) 3444, 3050, 2958, 2927, 2856, 1698, 1461, 1429, 1369, 1254, 1157, 1111, 1050, 961, 845, 790, 731, 699, 490.

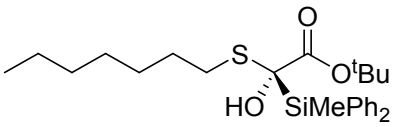


	Retention Time	Area	% Area
1	6.358	2116525	50.01
2	10.940	2115910	49.99



	Retention Time	Area	% Area
1	6.421	450953	3.08
2	11.214	14174021	96.92

Tert-butyl (*R*)-2-(heptylthio)-2-hydroxy-2-(methyldiphenylsilyl)acetate (**3q**)



3q

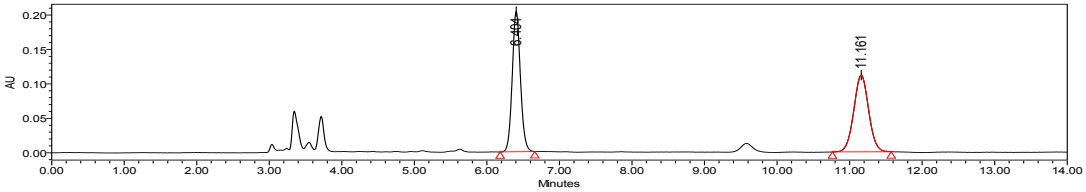
Colorless oil. 45.8 mg, 99% yield, 91% ee. **Specific rotation** $[\alpha]^{25}_{D}$ = +22 (*c* = 0.94, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 6.32 min, tr (major) = 11.03 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.77 (td, *J* = 7.8, 1.7 Hz, 4H), 7.44 – 7.31 (m, 6H), 4.67 (s, 1H), 2.56 (ddt, *J* = 46.6, 12.0, 7.4 Hz, 2H), 1.52 (h, *J* = 6.8 Hz, 2H), 1.39 – 1.25 (m, 7H), 1.25 (s, 9H), 0.87 (t, *J* = 6.7 Hz, 3H), 0.82 (s, 3H).

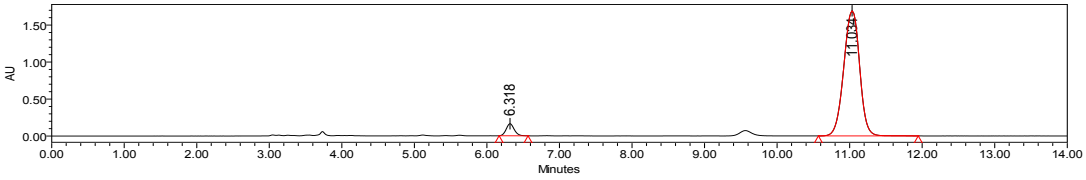
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.5, 136.7, 136.4, 135.6, 135.0, 130.7, 130.5, 128.6, 128.4, 83.4, 77.6, 32.2, 30.3, 29.7, 28.3, 28.0, 23.3, 14.5, -3.7.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{38}O_3SSi$ $[M+Na]^+$: 481.2203, found: 481.2206.

IR (neat) 3443, 2926, 2855, 1698, 1461, 1429, 1369, 1254, 1157, 1111, 1050, 962, 845, 791, 731, 699, 490.

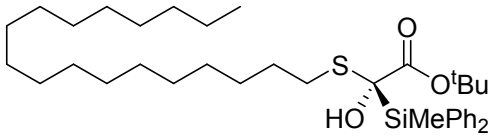


	Retention Time	Area	% Area
1	6.404	1598280	50.26
2	11.161	1581876	49.74



	Retention Time	Area	% Area
1	6.318	1257681	4.67
2	11.034	25681981	95.33

Tert-butyl (*R*)-2-hydroxy-2-(methyldiphenylsilyl)-2-(octadecyl lthio)acetate (**3r**)



3r

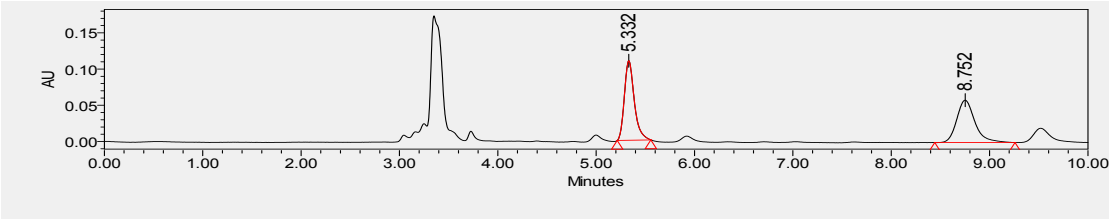
Colorless oil. 61.0 mg, 99% yield, 94% ee. **Specific rotation** $[\alpha]^{20}_{D}$ = +18 (*c* = 1.22, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 254 nm): tr (minor) = 5.41 min, tr (major) = 9.18 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.76 (ddt, *J* = 8.2, 6.6, 1.6 Hz, 4H), 7.45 – 7.29 (m, 6H), 4.69 (s, 1H), 2.61 (dt, *J* = 12.0, 7.5 Hz, 1H), 2.49 (dt, *J* = 11.9, 7.4 Hz, 1H), 1.56 – 1.47 (m, 2H), 1.28 (d, *J* = 3.9 Hz, 32H), 1.23 (s, 9H), 0.92 – 0.84 (t, 3H), 0.81 (s, 3H).

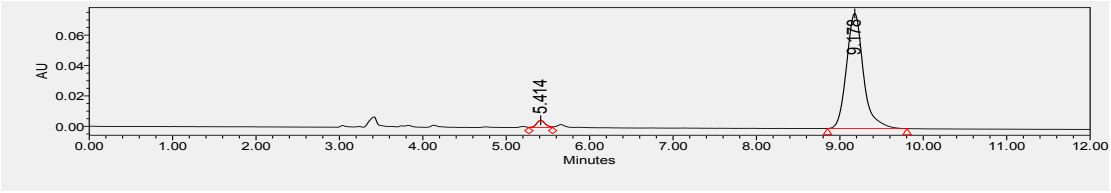
^{13}C{^{1}H} NMR (101 MHz, Acetone) δ 174.3, 136.5, 136.2, 135.4, 134.7, 130.6, 130.3, 128.4, 128.2, 83.2, 77.4, 32.6, 30.4, 30.4, 30.3, 30.1, 30.1, 29.8, 28.0, 27.8, 23.3, 14.4, -3.8.

HRMS (ESI+) *m/z* calcd for $C_{37}H_{60}O_3SSi$ [M+Na]$^+$: 635.3925, found: 635.3925.

IR (neat) 2923, 2853, 1743, 1700, 1462, 1429, 1369, 1254, 1114, 959, 835, 793, 731, 699, 490.

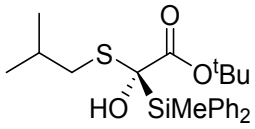


	Retention Time	Area	% Area
1	5.332	767980	50.62
2	8.752	749198	49.38



	Retention Time	Area	% Area
1	5.414	34577	3.14
2	9.178	1065469	96.86

Tert-butyl (*R*)-2-hydroxy-2-(isobutylthio)-2-(methyldiphenylsilyl)acetate (**3s**)



3s

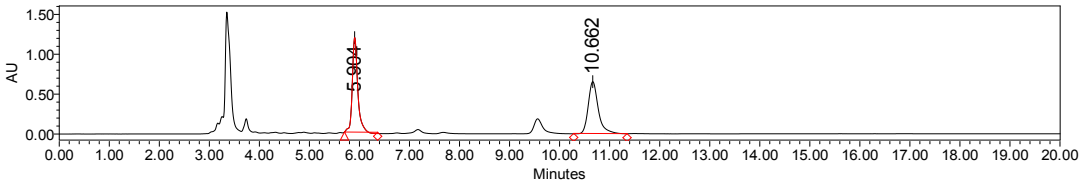
Colorless oil. 41.0 mg, 99% yield, 96% ee. **Specific rotation** $[\alpha]^{20}_D$ = +23 (*c* = 0.71, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 5.91 min, tr (major) = 10.63 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.77 (tt, *J* = 6.7, 1.6 Hz, 4H), 7.45 – 7.29 (m, 6H), 4.67 (s, 1H), 2.50 (dd, *J* = 12.1, 6.9 Hz, 1H), 2.40 (dd, *J* = 12.1, 6.8 Hz, 1H), 1.74 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.24 (s, 9H), 0.93 (dd, *J* = 6.7, 2.2 Hz, 6H), 0.83 (s, 3H).

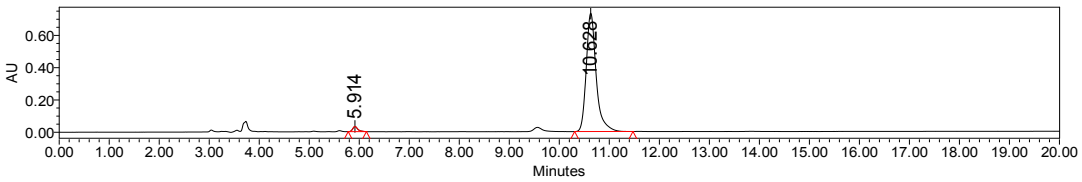
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.5, 136.7, 136.4, 135.6, 134.9, 130.7, 130.5, 128.6, 128.4, 83.4, 77.4, 37.0, 29.5, 28.0, 22.7, -3.7.

HRMS (ESI+) *m/z* calcd for $C_{23}H_{32}O_3SSi$ [M+Na]$^+$: 439.1734, found: 439.1732.

IR (neat) 3443, 3050, 2960, 2871, 1698, 1590, 1461, 1428, 1390, 1369, 1252, 1155, 1112, 1049, 963, 844, 791, 731, 699.

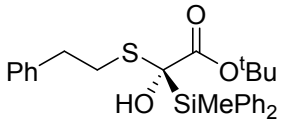


	Retention Time	Area	% Area
1	5.904	9049934	50.05
2	10.662	9030271	49.95



	Retention Time	Area	% Area
1	5.914	227584	2.20
2	10.628	10113388	97.80

Tert-butyl (*R*)-2-hydroxy-2-(methyldiphenylsilyl)-2-(phenethylthio)acetate (**3t**)



3t

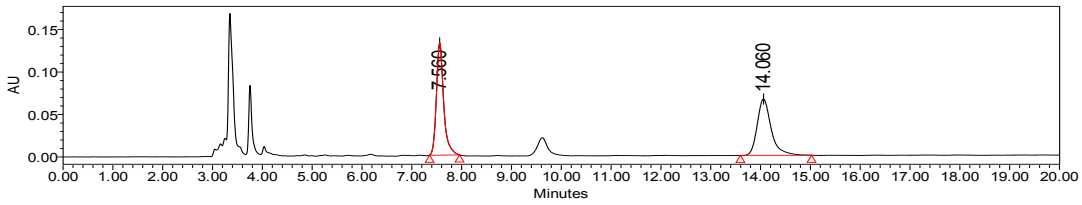
Colorless oil. 46.0 mg, 99% yield, 97% ee. **Specific rotation** $[\alpha]^{25}_D$ = +50 (*c* = 0.98, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 7.65 min, tr (major) = 14.43 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.73 (ddt, *J* = 6.2, 4.4, 1.6 Hz, 4H), 7.44 – 7.32 (m, 6H), 7.28 – 7.23 (m, 2H), 7.21 – 7.11 (m, 3H), 3.93 (s, 1H), 2.90 – 2.80 (m, 3H), 2.73 – 2.63 (m, 1H), 1.21 (s, 9H), 0.83 (s, 3H).

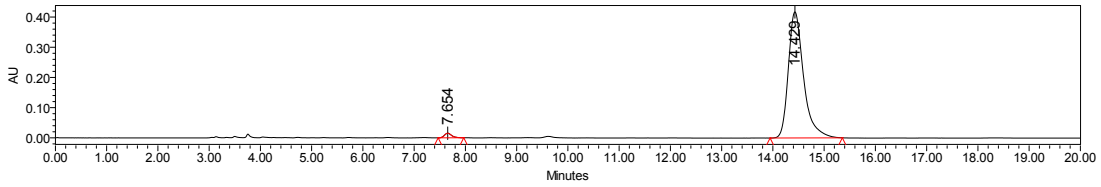
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.2, 140.7, 135.7, 135.5, 133.8, 133.2, 130.1, 129.9, 128.6, 128.5, 127.9, 127.8, 126.4, 83.6, 76.9, 36.1, 29.3, 27.7, -4.3.

HRMS (ESI+) *m/z* calcd for $C_{27}H_{32}O_3SSi$ $[M+Na]^+$: 487.1733, found: 487.1733.

IR (neat) 3439, 2977, 2928, 1697, 1454, 1428, 1393, 1369, 1255, 1156, 1111, 1052, 959, 844, 788, 731, 699, 524, 490.

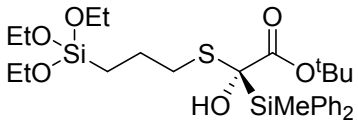


	Retention Time	Area	% Area
1	7.560	1331764	50.81
2	14.060	1289506	49.19



	Retention Time	Area	% Area
1	7.654	147882	1.69
2	14.429	8620821	98.31

Tert-butyl (*R*)-2-hydroxy-2-(methyldiphenylsilyl)-2-((3-(triethoxysilyl)propyl)thio)acetate (**3u**)



3u

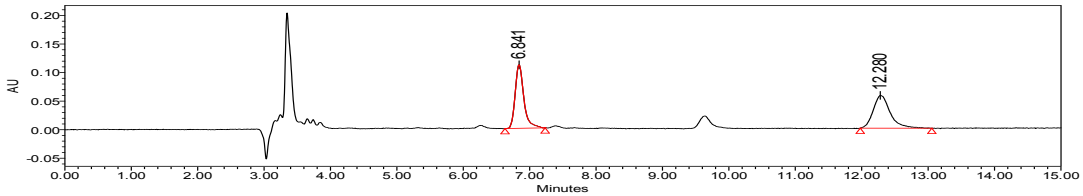
Colorless oil. 56.1 mg, 99% yield, 91% ee. **Specific rotation** $[\alpha]^{25}_{D}$ = +20 (*c* = 0.98, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 210 nm): tr (minor) = 6.90 min, tr (major) = 12.52 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.77 (td, *J* = 8.3, 1.6 Hz, 4H), 7.37 (m, 6H), 4.67 (s, 1H), 3.79 (q, *J* = 7.0 Hz, 6H), 2.59 (m, 2H), 1.64 (m, 2H), 1.25 (s, 9H), 1.18 (t, *J* = 7.0 Hz, 9H), 0.82 (s, 3H), 0.70 – 0.63 (m, 2H).

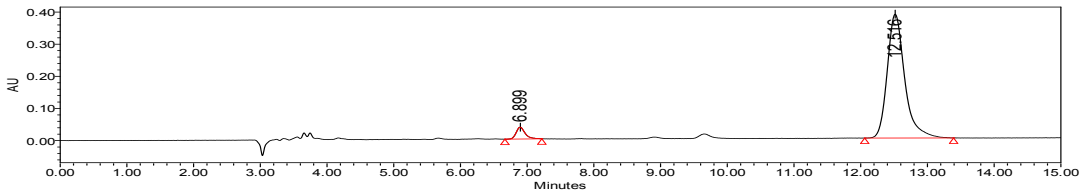
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.6, 136.7, 136.4, 135.6, 134.9, 130.8, 130.5, 128.6, 128.4, 83.5, 77.5, 59.0, 31.4, 28.0, 24.5, 18.9, 11.2, -3.7.

HRMS (ESI+) *m/z* calcd for $C_{28}H_{44}O_6SSi_2$ $[M+Na]^+$: 587.2289, found: 587.2289.

IR (neat) 2973, 1699, 1429, 1369, 1251, 1158, 1075, 957, 844, 784, 730, 699, 487.

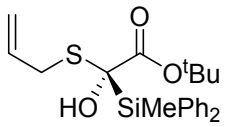


	Retention Time	Area	% Area
1	6.841	1010584	49.84
2	12.280	1017071	50.16



	Retention Time	Area	% Area
1	6.899	344910	4.69
2	12.516	7008305	95.31

Tert-butyl (*R*)-2-(allylthio)-2-(dimethyl(phenyl)silyl)-2-hydroxyacetate (**3v**)



3v

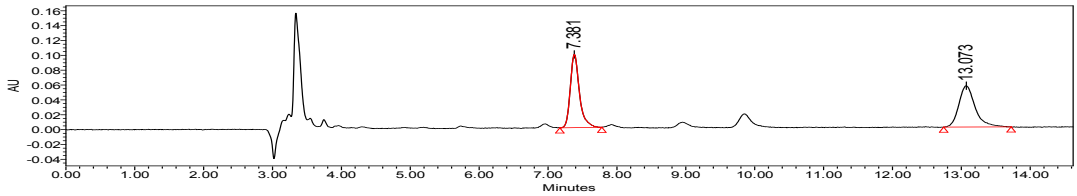
Yellowish oil. 38.0 mg, 95% yield, 93% ee. **Specific rotation** $[\alpha]^{20}_{D}$ = +22 (*c* = 0.76, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane =3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 7.13 min, tr (major) = 12.52 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.77 (m, 4H), 7.45 – 7.31 (m, 6H), 5.82 (m, 1H), 5.16 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.01 (dd, *J* = 10.0, 1.5 Hz, 1H), 4.78 (s, 1H), 3.34 – 3.25 (m, 1H), 3.23 – 3.08 (m, 1H), 1.25 (s, 9H), 0.83 (s, 3H).

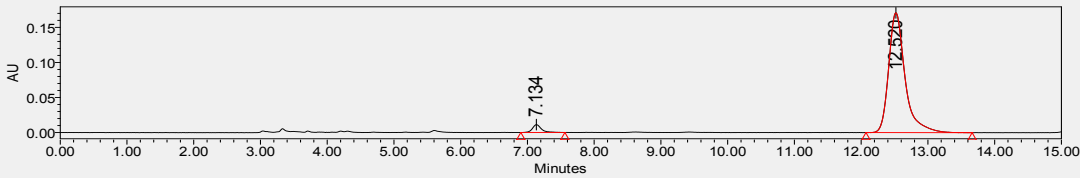
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.0, 136.5, 136.2, 135.2, 135.2, 134.5, 130.6, 130.4, 128.5, 128.3, 117.8, 83.4, 77.8, 31.5, 27.8, -4.0

HRMS (ESI+) *m/z* calcd for $C_{22}H_{28}O_3SSi$ $[M+Na]^+$: 423.1421, found: 423.1422.

IR (neat) 3439, 2977, 2362, 1698, 1428, 1396, 1369, 1254, 1155, 1112, 1050, 991, 920, 843, 789, 731, 699, 489.

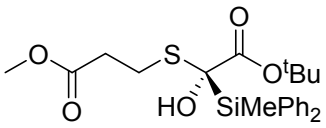


	Retention Time	Area	% Area
1	7.381	910329	49.97
2	13.073	911334	50.03



	Retention Time	Area	% Area
1	7.134	104650	3.47
2	12.520	2907918	96.53

Methyl (*R*)-3-((2-(*tert*-butoxy)-1-hydroxy-1-(methyldiphenylsilyl)-2-oxoethyl)thio)propanoate (**3w**)



3w

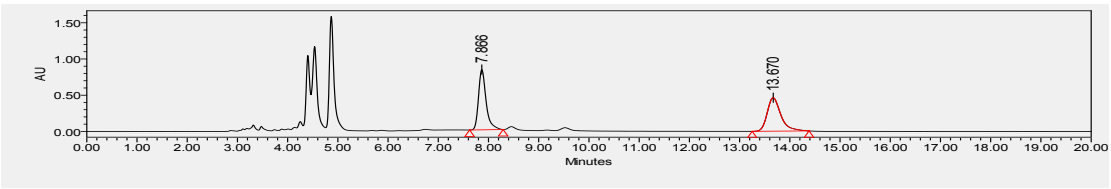
White solid. **m.p.** 92-93 °C. 44.6 mg, 99% yield, 86% ee. **Specific rotation** $[\alpha]^{20}_{D}$ = +25 (*c* = 0.53, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 10/90, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 7.86 min, tr (major) = 13.22 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.76 (ddt, *J* = 12.9, 6.6, 1.6 Hz, 4H), 7.45 – 7.32 (m, 6H), 4.87 (s, 1H), 3.62 (s, 3H), 2.81 (d, *J* = 7.2 Hz, 2H), 2.57 (td, *J* = 7.2, 1.4 Hz, 2H), 1.25 (s, 9H), 0.82 (s, 3H).

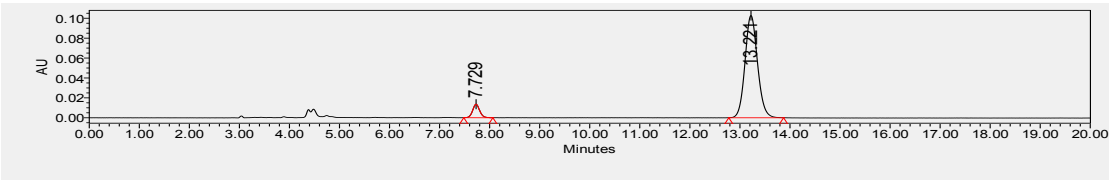
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 174.3, 172.8, 136.6, 136.3, 135.3, 134.7, 130.8, 130.5, 128.6, 128.44, 83.6, 77.5, 51.9, 35.5, 27.9, 23.6, -3.9.

HRMS (ESI+) *m/z* calcd for $C_{23}H_{30}O_5SSi$ $[M+Na]^+$: 469.1475, found: 469.1475.

IR (neat) 3735, 3448, 2980, 2288, 2190, 2180, 2146, 2077, 2046, 1996, 1966, 1900, 1429, 1369, 1251, 1156, 1112, 793, 731, 699, 580, 531, 445, 410.

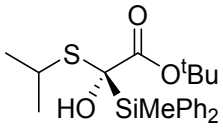


	Retention Time	Area	% Area
1	7.866	8727134	50.05
2	13.670	8710778	49.95



	Retention Time	Area	% Area
1	7.729	133174	6.94
2	13.221	1786673	93.06

Tert-butyl (*R*)-2-hydroxy-2-(isopropylthio)-2-(methyldiphenylsilyl)acetate (**3x**)



3x

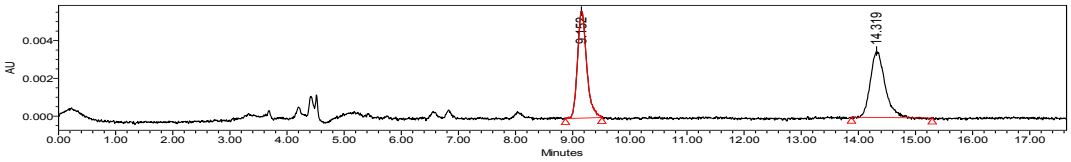
Colorless oil. 36.2 mg, 90% yield, 94% ee. **Specific rotation** $[\alpha]^{20}_D$ = +29 (*c* = 0.72, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 1/99, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 9.25 min, tr (major) = 14.74 min.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.75 – 7.63 (m, 4H), 7.39 – 7.27 (m, 6H), 3.88 (s, 1H), 3.08 (td, *J* = 6.8, 1.8 Hz, 1H), 1.23 (d, *J* = 6.7 Hz, 3H), 1.18 (s, 9H), 1.15 (d, *J* = 7.8 Hz, 3H), 0.75 (s, 3H).

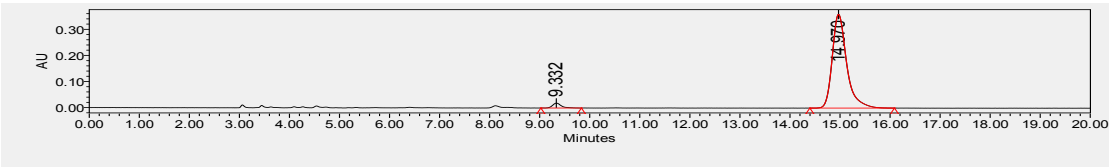
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 175.1, 136.3, 136.0, 134.7, 133.9, 130.5, 130.3, 128.3, 128.1, 84.1, 78.1, 34.5, 28.0, 26.1, 24.9, -4.1.

HRMS (ESI+) *m/z* calcd for $C_{22}H_{30}O_3SSi$ $[M+Na]^+$: 425.1577, found: 425.1577.

IR (neat) 3442, 2973, 1696, 1455, 1428, 1369, 1253, 1155, 1111, 1033, 960, 844, 786, 730, 698, 488, 443.

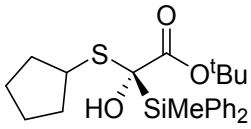


	Retention Time	Area	% Area
1	9.154	60461	50.01
2	14.320	60428	49.99



	Retention Time	Area	% Area
1	9.332	223620	3.02
2	14.970	7170961	96.98

Tert-butyl (*R*)-2-(cyclopentylthio)-2-hydroxy-2-(methyldiphenylsilyl)acetate (**3y**)



3y

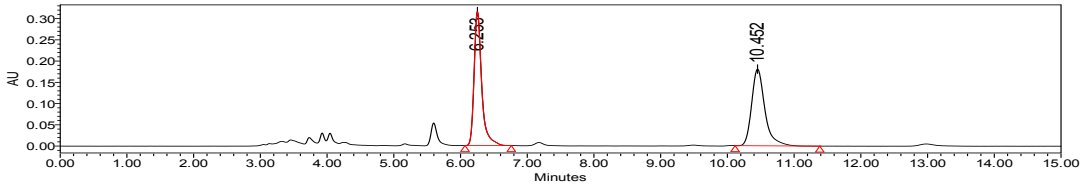
Colorless oil. 41.9 mg, 98% yield, 96% ee. **Specific rotation** $[\alpha]^{25}_{D}$ = +48 (*c* = 0.84, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 6.27 min, tr (major) = 10.44 min.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (ddd, *J* = 8.0, 4.4, 1.6 Hz, 4H), 7.39 – 7.26 (m, 6H), 3.89 (s, 1H), 3.14 (p, *J* = 7.5 Hz, 1H), 1.94 (dddd, *J* = 15.8, 12.3, 9.7, 6.6 Hz, 2H), 1.70 – 1.57 (m, 2H), 1.56 – 1.34 (m, 4H), 1.18 (s, 9H), 0.76 (s, 3H).

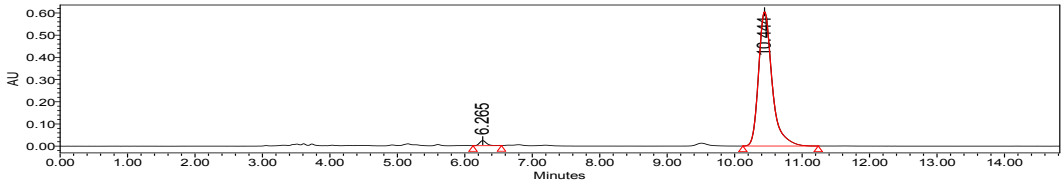
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 175.0, 136.1, 135.8, 134.6, 133.8, 130.3, 130.1, 128.1, 128.0, 83.8, 78.0, 41.7, 35.8, 34.8, 27.8, 25.4, 25.1, -4.2.

HRMS (ESI+) *m/z* calcd for $C_{24}H_{32}O_3SSi$ $[M+Na]^+$: 451.1734, found: 451.1727.

IR (neat) 3446, 3050, 2960, 2867, 2361, 2040, 1967, 1699, 1455, 1428, 1394, 1369, 1257, 1157, 1114, 1048, 962, 844, 791, 732, 699, 489.

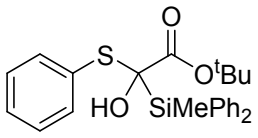


	Retention Time	Area	% Area
1	6.253	2486260	50.06
2	10.452	2480130	49.94



	Retention Time	Area	% Area
1	6.265	162887	1.89
2	10.444	8438317	98.11

Tert-butyl (*R*)-2-hydroxy-2-(methyldiphenylsilyl)-2-(phenylthio)acetate (**3aa**)



3aa

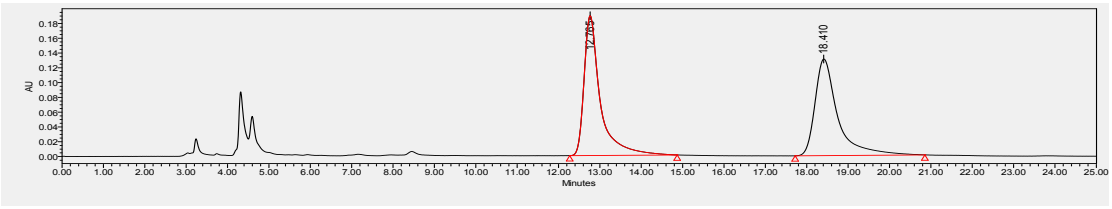
Colorless oil. 43.6 mg, 99% yield, 94% ee. **Specific rotation** $[\alpha]^{20}_{D}$ = +94.3 (*c* = 0.88, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral ADH column, *i*-PrOH/*n*-hexane = 1/99, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 12.79 min, tr (major) = 18.15 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.79 (ddt, *J* = 8.0, 3.3, 1.8 Hz, 4H), 7.53 – 7.47 (m, 2H), 7.43 – 7.29 (m, 9H), 4.55 (s, 1H), 1.08 (s, 9H), 0.88 (s, 3H).

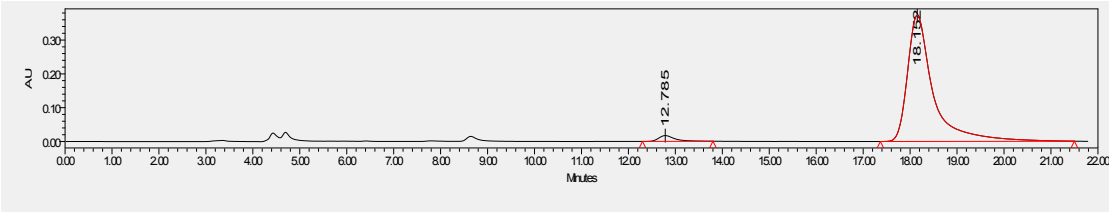
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 173.0, 136.7, 136.6, 136.4, 135.1, 134.4, 132.0, 130.9, 130.6, 129.9, 129.6, 128.6, 128.5, 83.7, 81.1, 27.9, -3.7.

HRMS (ESI+) *m/z* calcd for $C_{25}H_{28}O_3SSi$ $[M+Na]^+$: 459.1242, found: 459.1418.

IR (neat) 3440, 3051, 2978, 1705, 1585, 1473, 1430, 1393, 1369, 1253, 1155, 1111, 963, 844, 787, 731, 697, 526, 489.

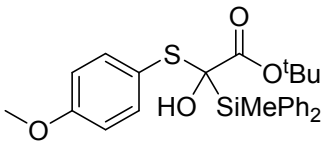


	Retention Time	Area	% Area
1	12.765	5160118	50.89
2	18.410	4979144	49.11



	Retention Time	Area	% Area
1	12.785	411336	2.83
2	18.152	14128533	97.17

Tert-butyl (*R*)-2-hydroxy-2-((4-methoxyphenyl)thio)-2-(methyldiphenylsilyl)acetate (**3ab**)



3ab

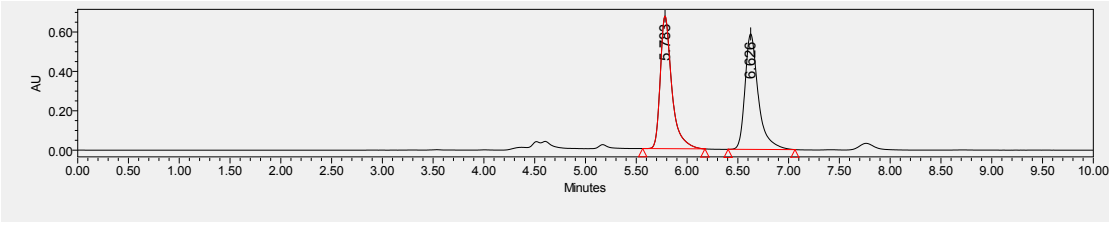
Colorless oil. 46.2 mg, 99% yield, 95% ee. **Specific rotation** $[\alpha]^{20}_{D}$ = +152.8 (*c* = 0.92, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 10/90, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 5.79 min, tr (major) = 6.57 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.82 – 7.74 (m, 4H), 7.44 – 7.31 (m, 8H), 6.90 – 6.83 (m, 2H), 4.36 (s, 1H), 3.76 (s, 3H), 1.12 (s, 9H), 0.87 (s, 3H).

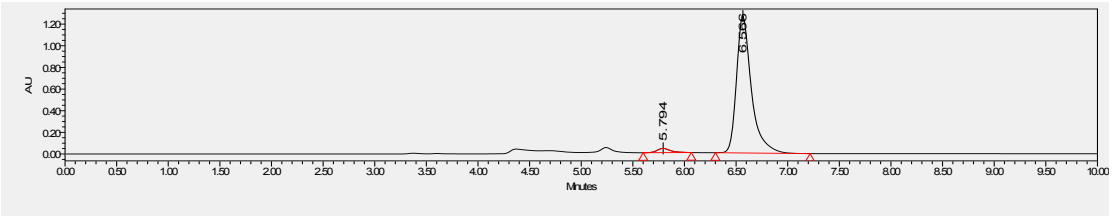
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 173.2, 161.8, 138.8, 136.6, 136.4, 135.3, 134.5, 130.8, 130.5, 128.6, 128.5, 121.6, 115.1, 83.6, 80.7, 55.7, 28.0, -3.7.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{30}O_4SSi$ $[M+Na]^+$: 489.1526, found: 489.1256.

IR (neat) 3444, 2977, 1706, 1591, 1492, 1461, 1429, 1394, 1369, 1248, 1156, 1110, 1032, 964, 830, 798, 731, 699, 523, 489.

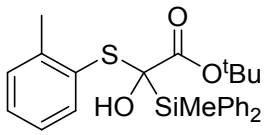


	Retention Time	Area	% Area
1	5.783	5327130	49.92
2	6.626	5344606	50.08



	Retention Time	Area	% Area
1	5.794	354683	2.72
2	6.566	12684174	97.28

Tert-butyl (*R*)-2-hydroxy-2-(methyldiphenylsilyl)-2-(*o*-tolylthio)acetate (**3ac**)



3ac

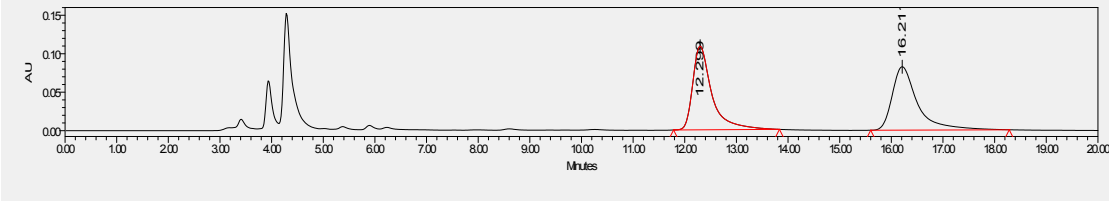
Colorless oil. 44.1 mg, 98% yield, 93% ee. **Specific rotation** $[\alpha]^{20}_D$ = +64 (*c* = 0.90, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral ADH column, *i*-PrOH/*n*-hexane = 1/99, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 11.60 min, tr (major) = 15.23 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.90 – 7.76 (m, 4H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.35 (m, 6H), 7.22 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 4.64 (s, 1H), 2.42 (s, 3H), 1.04 (s, 9H), 0.93 (s, 3H).

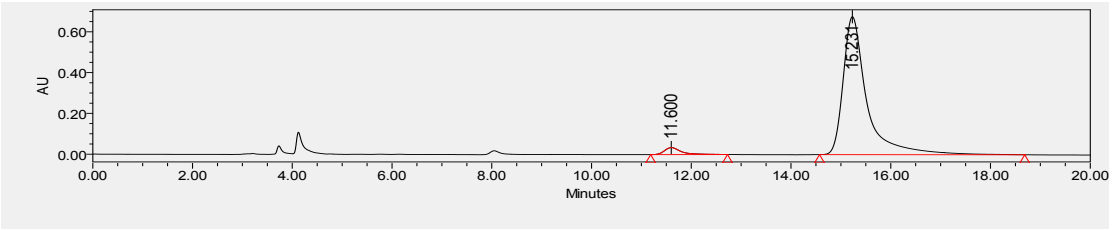
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 173.1, 143.3, 137.4, 136.8, 136.5, 135.0, 134.5, 132.3, 131.2, 130.9, 130.7, 129.9, 128.7, 128.5, 127.0, 83.8, 81.9, 27.8, 22.0, -3.8.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{30}O_3SSi$ $[M+Na]^+$: 473.1577, found: 473.1577.

IR (neat) 3435, 3052, 2978, 1704, 1589, 1469, 1428, 1393, 1370, 1253, 1156, 1111, 1033, 963, 844, 787, 731, 699, 676.

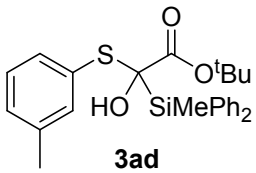


	Retention Time	Area	% Area
1	12.299	2808218	50.00
2	16.211	2808207	50.00



	Retention Time	Area	% Area
1	11.600	800112	3.46
2	15.231	22313953	96.54

Tert-butyl (*R*)-2-hydroxy-2-(methyldiphenylsilyl)-2-(*m*-tolylthio)acetate (**3ad**)



3ad

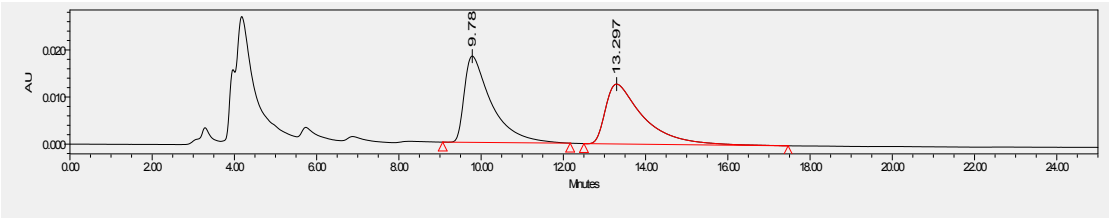
Colorless oil. 44.3 mg, 98% yield, 90% ee. **Specific rotation** $[\alpha]^{20}_D$ = +76.2 (*c* = 0.90, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral ADH column, *i*-PrOH/*n*-hexane = 1/99, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 10.22 min, tr (major) = 13.84 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.80 (dq, *J* = 6.6, 1.4 Hz, 4H), 7.43 – 7.36 (m, 6H), 7.34 – 7.28 (m, 2H), 7.21 – 7.14 (m, 2H), 4.55 (s, 1H), 2.27 (s, 3H), 1.10 (s, 9H), 0.89 (s, 3H).

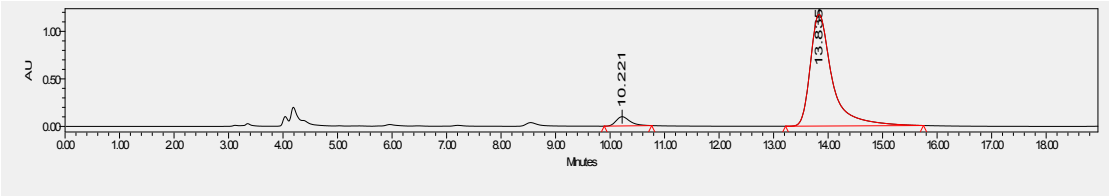
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 173.0, 139.3, 137.2, 136.7, 136.4, 135.2, 134.5, 133.7, 131.6, 130.9, 130.6, 129.4, 128.6, 128.5, 83.7, 81.1, 27.9, 21.3, -3.7.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{30}O_3SSi$ $[M+Na]^+$: 473.1577, found: 473.1577.

IR (neat) 3443, 3050, 2977, 1705, 1591, 1474, 1428, 1394, 1369, 1253, 1155, 1111, 1052, 693, 846, 783, 730, 697, 520, 489.

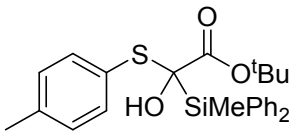


	Retention Time	Area	% Area
1	9.785	837229	50.75
2	13.297	812539	49.25



	Retention Time	Area	% Area
1	10.221	1729927	5.00
2	13.835	32868762	95.00

Tert-butyl (*R*)-2-hydroxy-2-(methyldiphenylsilyl)-2-(*p*-tolylthio)acetate (**3ae**)



3ae

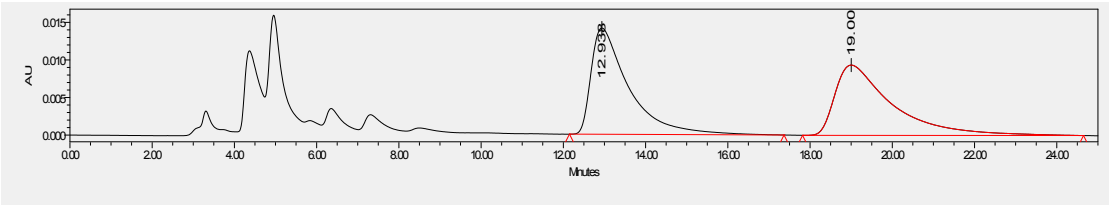
Colorless oil. 45.0 mg, 99% yield, 90% ee. **Specific rotation** $[\alpha]^{20}_D$ = +117.8 (*c* = 0.90, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral ADH column, *i*-PrOH/*n*-hexane = 1/99, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 13.35 min, tr (major) = 19.50 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.82 – 7.75 (m, 4H), 7.43 – 7.33 (m, 8H), 7.12 (d, *J* = 7.9 Hz, 2H), 4.43 (s, 1H), 2.29 (s, 3H), 1.11 (s, 9H), 0.88 (s, 3H).

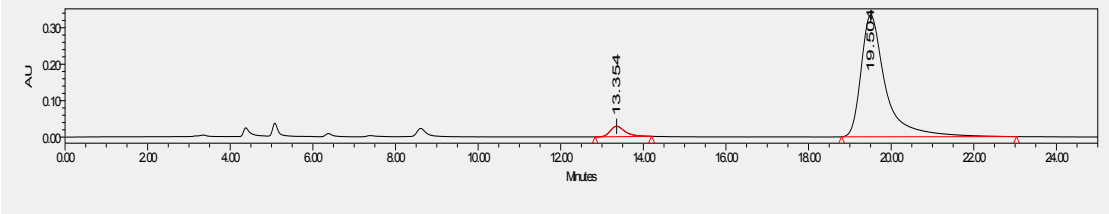
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 173.1, 140.0, 137.0, 136.7, 136.4, 135.2, 134.5, 130.9, 130.6, 130.3, 128.6, 128.5, 128.0, 83.7, 80.9, 27.9, 21.3, -3.7.

HRMS (ESI+) *m/z* calcd for $C_{26}H_{30}O_3SSi$ $[M+Na]^+$: 473.1577, found: 473.1577.

IR (neat) 3443, 3049, 2977, 2926, 1706, 1593, 1489, 1428, 1395, 1369, 1253, 1157, 1111, 1056, 964, 845, 799, 731, 699, 489.

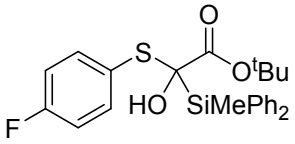


	Retention Time	Area	% Area
1	12.938	899498	49.99
2	19.002	899986	50.01



	Retention Time	Area	% Area
1	13.354	718412	4.97
2	19.504	13739491	95.03

Tert-butyl (*R*)-2-((4-fluorophenyl)thio)-2-hydroxy-2-(methyldiphenylsilyl)acetate (**3af**)



3af

Colorless oil. 39.9 mg, 88% yield, 87% ee. **Specific rotation** $[\alpha]^{20}_D$ = +99 (*c* = 0.80, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral ADH column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 7.69 min, tr (major) = 11.28 min.

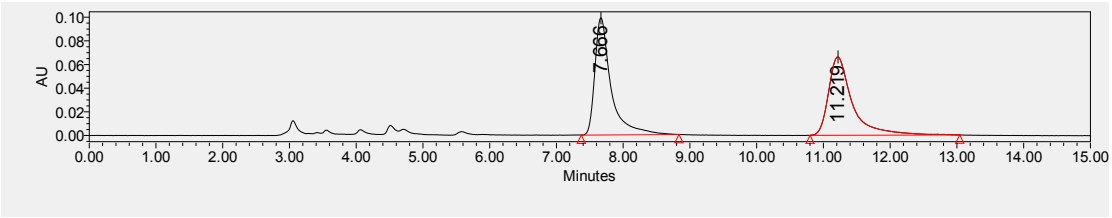
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 4H), 7.49 – 7.36 (m, 8H), 7.01 – 6.94 (m, 2H), 3.86 (s, 1H), 1.13 (s, 9H), 0.90 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.8, 163.72 ($J_{C\text{-}F}$ = 249.3 Hz), 138.20 ($J_{C\text{-}F}$ = 8.4 Hz), 135.75, 135.55, 133.73, 132.96, 130.18, 129.99, 127.93, 127.86, 125.5 ($J_{C\text{-}F}$ = 3.3 Hz), 115.9 ($J_{C\text{-}F}$ = 21.8 Hz)., 83.64, 79.48, 31.73, 27.71, 22.80, 14.26, -4.24.

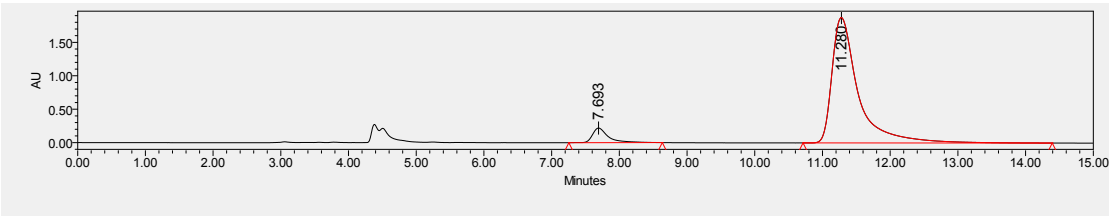
^{19}F NMR (376 MHz, $CDCl_3$) δ -111.9.

HRMS (ESI+) *m/z* calcd for $C_{25}H_{27}FO_3SSi$ $[M+K]^+$: 493.1066, found: 493.1068.

IR (neat) 3434, 2977, 2926, 1702, 1587, 1486, 1428, 1394, 1369, 1253, 1223, 1153, 1110, 1055, 963, 911, 833, 784, 729, 698, 633, 515, 488.

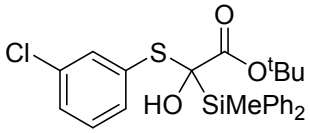


	Retention Time	Area	% Area
1	7.666	1669020	50.40
2	11.219	1642269	49.60



	Retention Time	Area	% Area
1	7.693	3567298	6.59
2	11.280	50587657	93.41

Tert-butyl (*R*)-2-((3-chlorophenyl)thio)-2-hydroxy-2-(methyldiphenylsilyl)acetate (**3ag**)



3ag

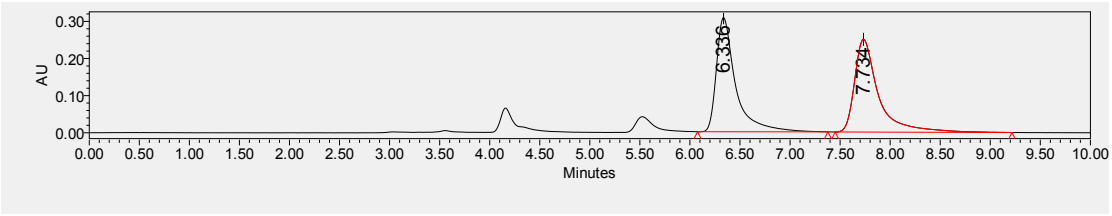
Colorless oil. 45.8 mg, 97% yield, 81% ee. **Specific rotation** $[\alpha]^{20}_{D}$ = +63 (*c* = 0.92, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral ADH column, *i*-PrOH/*n*-hexane = 3/97, flow rate: 1.0 mL/min, 230 nm): tr (minor) = 6.32 min, tr (major) = 7.69 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (ddd, *J* = 8.0, 3.4, 1.6 Hz, 4H), 7.49 (t, *J* = 1.9 Hz, 1H), 7.46 – 7.36 (m, 7H), 7.30 (ddd, *J* = 8.1, 2.1, 1.1 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 1H), 3.98 (s, 1H), 1.12 (s, 10H), 0.90 (s, 3H).

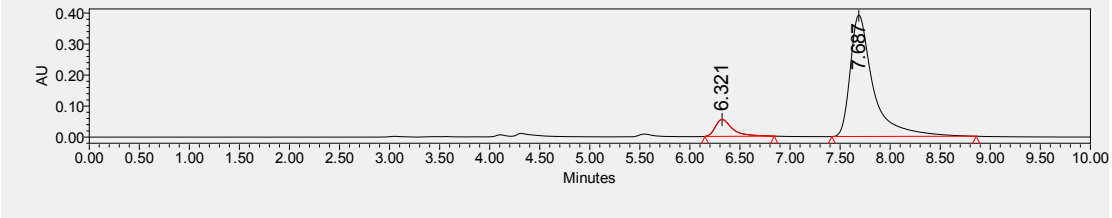
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6, 135.8, 135.6, 135.5, 134.2, 133.9, 133.5, 132.8, 132.6, 130.2, 130.1, 129.7, 129.3, 128.0, 127.9, 83.9, 80.0, 27.7, -4.3.

HRMS (ESI+) *m/z* calcd for $C_{25}H_{27}O_3ClSSi$ [M+Na]$^+$: 493.1031 and 495.1001, found: 493.1033 and 495.1001.

IR (neat) 3433, 3051, 2977, 1702, 1568, 1459, 1428, 1397, 1369, 1253, 1111, 1064, 962, 842, 780, 730, 698, 520, 488.

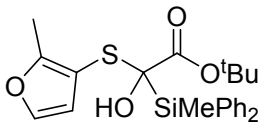


	Retention Time	Area	% Area
1	6.336	4109538	49.81
2	7.734	4140716	50.19



	Retention Time	Area	% Area
1	6.321	648728	9.39
2	7.687	6258118	90.61

Tert-butyl 2-hydroxy-2-(methyldiphenylsilyl)-2-((2-methylfuran-3-yl)thio)acetate (**3ah**)



3ah

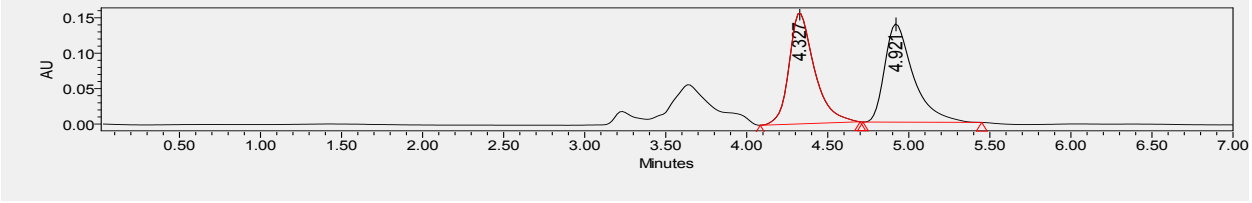
Colorless oil. 44.0 mg, 99% yield, 94% ee. **Specific rotation** $[\alpha]^{20}_D$ = +93.3 (*c* = 0.614, CH_2Cl_2). Dissolved in *n*-hexane for HPLC; HPLC (Chiral ADH column, *i*-PrOH/*n*-hexane = 2/98, flow rate: 1.0 mL/min, 254 nm): tr (major) = 4.54 min, tr (minor) = 4.12 min.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.82 – 7.77 (m, 4H), 7.45 – 7.35 (m, 7H), 6.32 (d, *J* = 2.0 Hz, 1H), 2.28 (s, 3H), 1.29 (s, 1H), 1.18 (s, 9H), 0.89 (s, 3H).

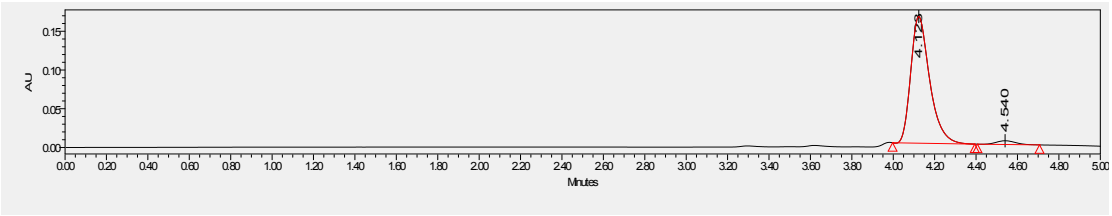
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 173.4, 158.7, 141.6, 136.6, 136.4, 135.3, 134.5, 130.9, 130.6, 128.7, 128.5, 117.3, 106.6, 83.6, 80.3, 27.9, 12.5, -3.8.

HRMS (ESI+) *m/z* calcd for C24H28O4SSi $[M+Na]^+$: 463.1370, found: 463.1370.

IR (neat) 3447, 3050, 2977, 2926, 1707, 1584, 1515, 1457, 1429, 1391, 1369, 1254, 1225, 1157, 1113, 1087, 965, 887, 845, 787, 731, 699,488.

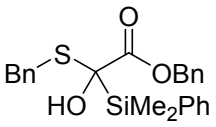


	Retention Time	Area	% Area
1	4.327	1704560	50.04
2	4.921	1701689	49.96



	Retention Time	Area	% Area
1	4.123	1036749	97.09
2	4.540	31047	2.91

Benzyl 2-(benzylthio)-2-(dimethyl(phenyl)silyl)-2-hydroxyacetate (**3ai**)



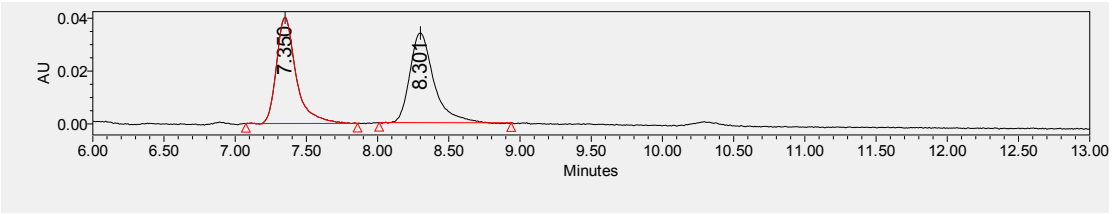
3ai

Colorless oil. 40.0 mg, 94% yield, 61% ee. Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 10/90, flow rate: 1.0 mL/min, 230 nm): tr (major) = 7.35 min, tr (minor) = 8.32 min.

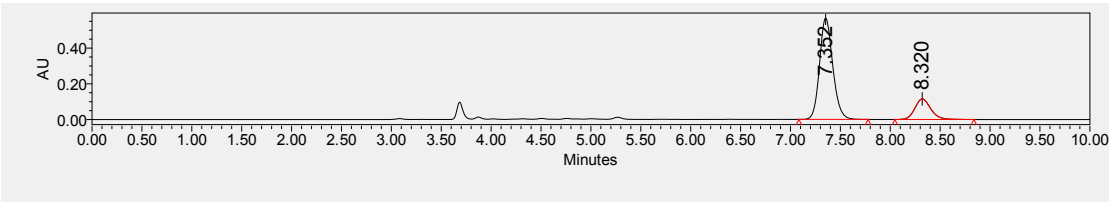
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.38 – 7.33 (m, 4H), 7.30 – 7.20 (m, 8H), 4.93 (d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 3.75 (d, *J* = 12.6 Hz, 1H), 3.73 (s, 1H), 3.56 (d, *J* = 12.6 Hz, 1H), 0.48 (s, 3H), 0.44 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.1, 137.2, 135.0, 134.6, 133.8, 130.0, 129.4, 128.7, 128.6, 128.6, 128.4, 127.7, 127.1, 77.2, 67.9, 32.3, -4.7, -4.8.

HRMS (ESI+) *m/z* calcd for C24H26O3SSi $[M+Na]^+$: 445.1264, found: 445.1217.

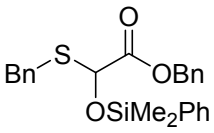


	Retention Time	Area	% Area
1	7.350	385428	49.19
2	8.301	398147	50.81



	Retention Time	Area	% Area
1	7.352	5212121	80.65
2	8.320	1250225	19.35

Benzyl 2-(benzylthio)-2-((dimethyl(phenyl)silyl)oxy)acetate (**4ai**)



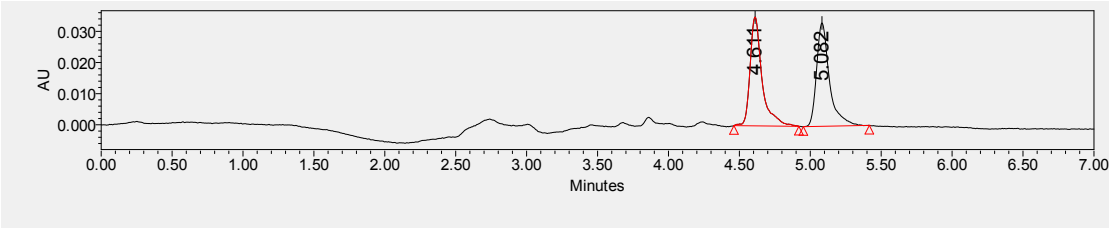
4ai

Colorless oil. Dissolved in *n*-hexane for HPLC; HPLC (Chiral IF column, *i*-PrOH/*n*-hexane = 10/90, flow rate: 1.0 mL/min, 230 nm): tr = 4.61 min, tr = 5.01 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.42 – 7.38 (m, 1H), 7.36 – 7.31 (m, 6H), 7.25 – 7.18 (m, 4H), 7.17 – 7.13 (m, 2H), 5.16 (s, 1H), 5.08 (q, *J* = 12.2 Hz, 2H), 3.82 (d, *J* = 12.8 Hz, 1H), 3.72 (d, *J* = 12.5 Hz, 1H), 0.46 (s, 3H), 0.44 (s, 4H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.3, 137.2, 136.2, 135.5, 133.8, 130.2, 129.3, 128.8, 128.7, 128.5, 128.5, 128.4, 128.1, 128.1, 127.2, 127.2, 33.1, -1.1, -1.3.

HRMS (ESI+) *m/z* calcd for C24H26O3SSi $[M+H]^+$: 423.1445, found: 423.1445

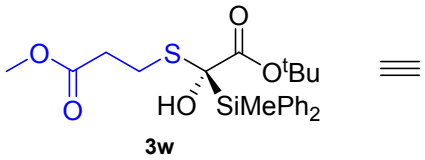


	Retention Time	Area	% Area
1	4.611	206878	49.67
2	5.082	209600	50.33

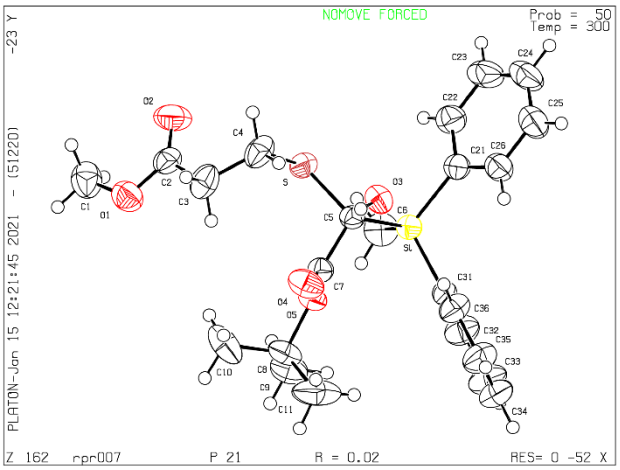
9. The X-ray data for 3w and *N,N'*-Dioxide/Y(OTf)$_3$ complexes

The colourless crystal in block-shape, with approximate dimensions of 0.486 × 0.179 × 0.136 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 300(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved, and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[a,b,c,d]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[e].

The crystal suitable for X-ray structure analysis was obtained from the solution of **3w** in THF and Et_2O at 10℃. The data has been deposited at the Cambridge Crystallographic Data Center (CCDC 2056433).



3w



Crystallographic Data for C23H30O5SSi.

Formula	C23H30O5SSi
Formula mass (amu)	446.62
Space group	P 21
a (Å)	9.2424(3)
b (Å)	8.7534(3)
c (Å)	15.2178(4)
α (deg)	90
β (deg)	96.7840(10)
γ (deg)	90
V (Å^3)	1222.54(7)
Z	2
λ (Å)	1.54178
T (K)	300 K

ρ_{calcd} (g cm^{-3})	1.213
μ (mm^{-1})	1.889
Transmission factors	0.580-0.848
$2\theta_{max}$ (deg)	68.300
No. of unique data, including $F_o^2 < 0$	4408
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	4343
No. of variables	280
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$	0.0240
$R_w(F_o^2)$	0.0659
Goodness of fit	1.071

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

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

References:

a Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122.

b Sheldrick, G. M. Acta Cryst. 2015, A71, 3–8.

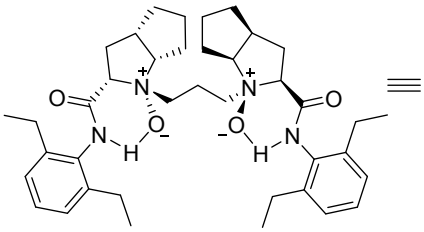
c Sheldrick, G. M. Acta Cryst. 2015, C71, 3–8.

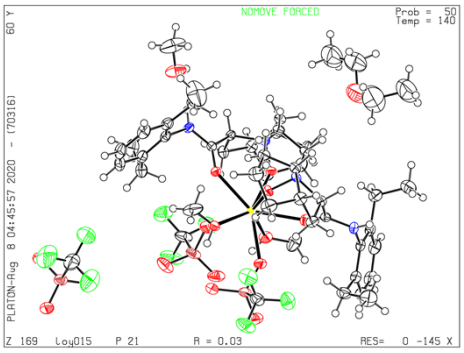
d Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J. A. K., Puschmann, H. J. Appl. Cryst. 2009, 42, 339-341.

e Spek, A. L. J. Appl. Cryst. 2003, 36, 7–13.

The colourless crystal in block-shape, with approximate dimensions of 0.389 × 0.283 × 0.163 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 140(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[a,b,c,d]. The value observed herein is indicative of racemic twinning and was accommodated during the refinement (using the SHELXL TWIN instruction). In this case, the relatively large standard uncertainty indicates that the structural data alone should not be used to confirm absolute stereochemistry, but should be used in conjunction with the established stereochemistry of the precursor compound. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[e].

The crystal of **L-RaEt$_2$**/Y(OTf)$_3$ was obtained in the solvents of MeOH and Et_2O. The data has been deposited at the Cambridge Crystallographic Data Center (CCDC 2064772).





Crystallographic Data for C39H56N4O4Y.

Formula	C39H56N4O4Y
Formula mass (amu)	1351.24
Space group	P 21
a (Å)	11.9751(5)
b (Å)	20.8149(9)
c (Å)	12.9319(6)
α (deg)	90
β (deg)	106.231(1)
γ (deg)	90
V (Å^3)	3094.9(2)
Z	2
λ (Å)	1.54178
T (K)	140 K

ρ_{calcd} (g cm^{-3})	1.450
μ (mm^{-1})	3.102
Transmission factors	0.642-0.898
$2\theta_{max}$ (deg)	80.719
No. of unique data, including $F_o^2 < 0$	13286
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	13233
No. of variables	776
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$	0.0265
$R_w(F_o^2)$	0.1760
Goodness of fit	1.050

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

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

References:

a Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122.

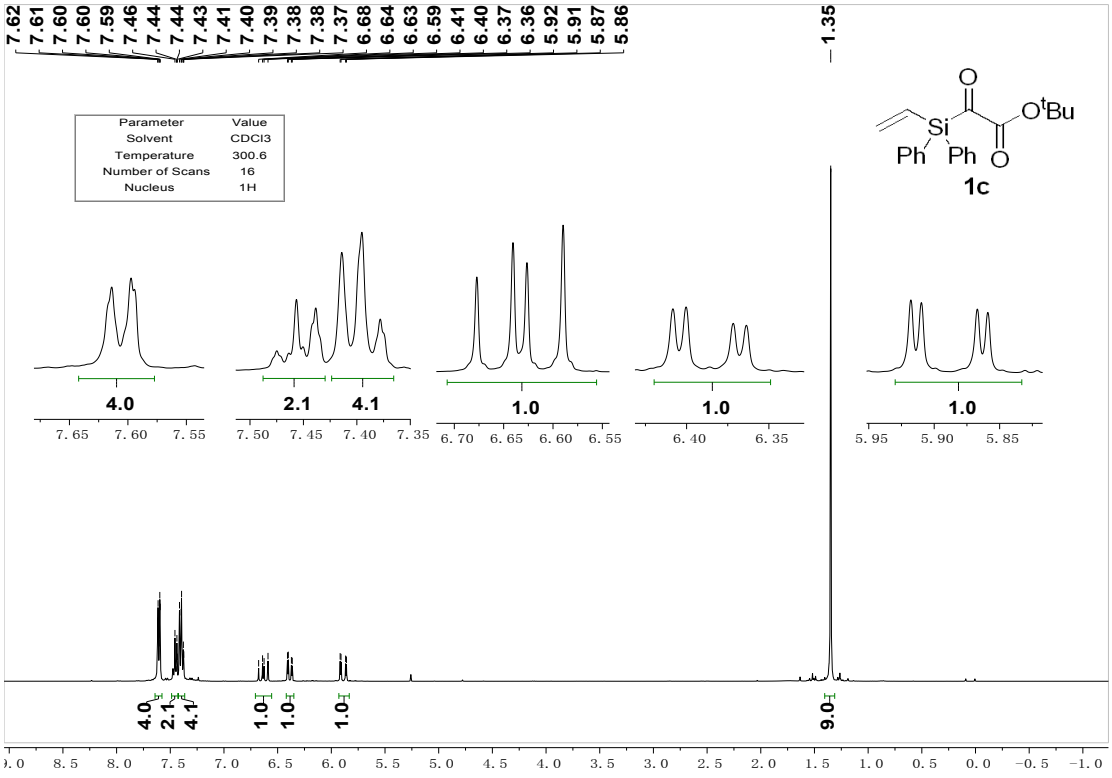
b Sheldrick, G. M. Acta Cryst. 2015, A71, 3–8.

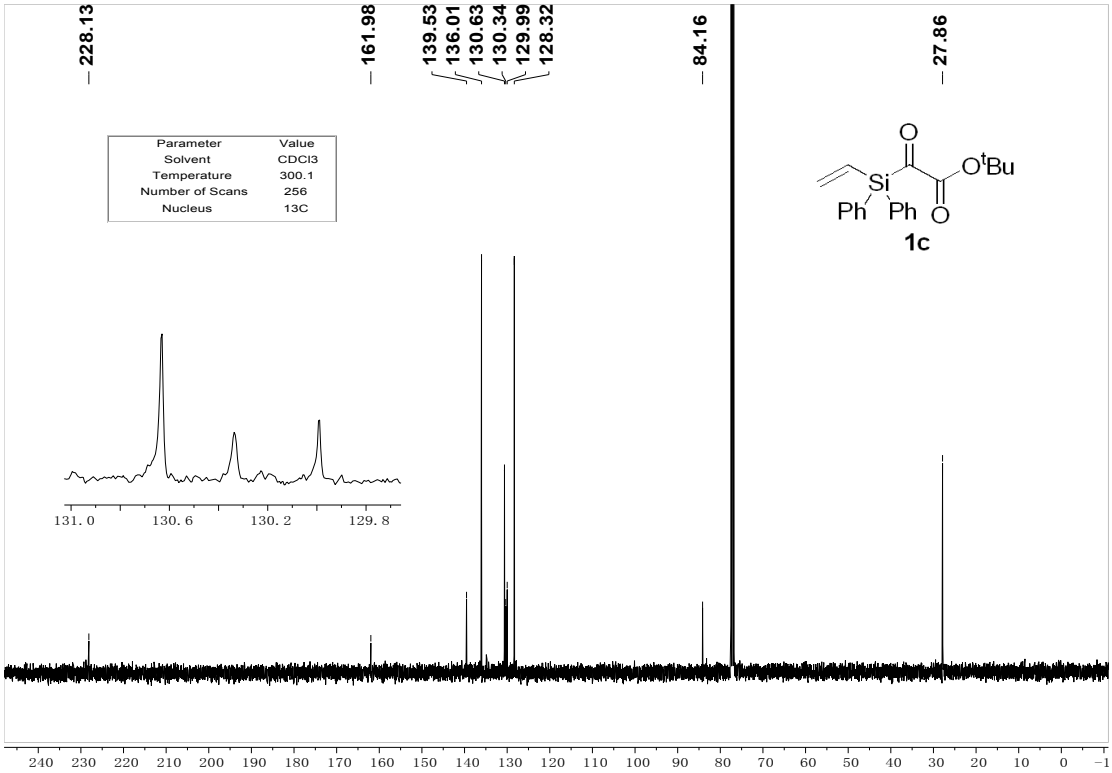
c Sheldrick, G. M. Acta Cryst. 2015, C71, 3–8.

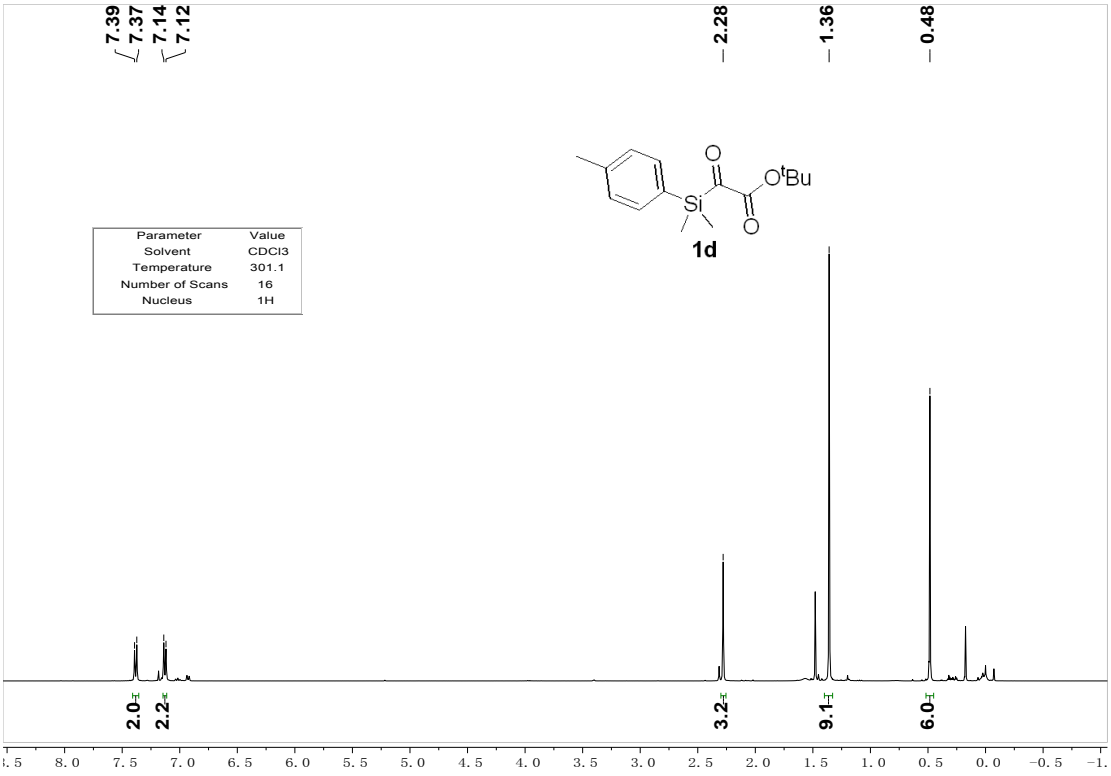
d Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J. A. K., Puschmann, H. J. Appl. Cryst. 2009, 42, 339-341.

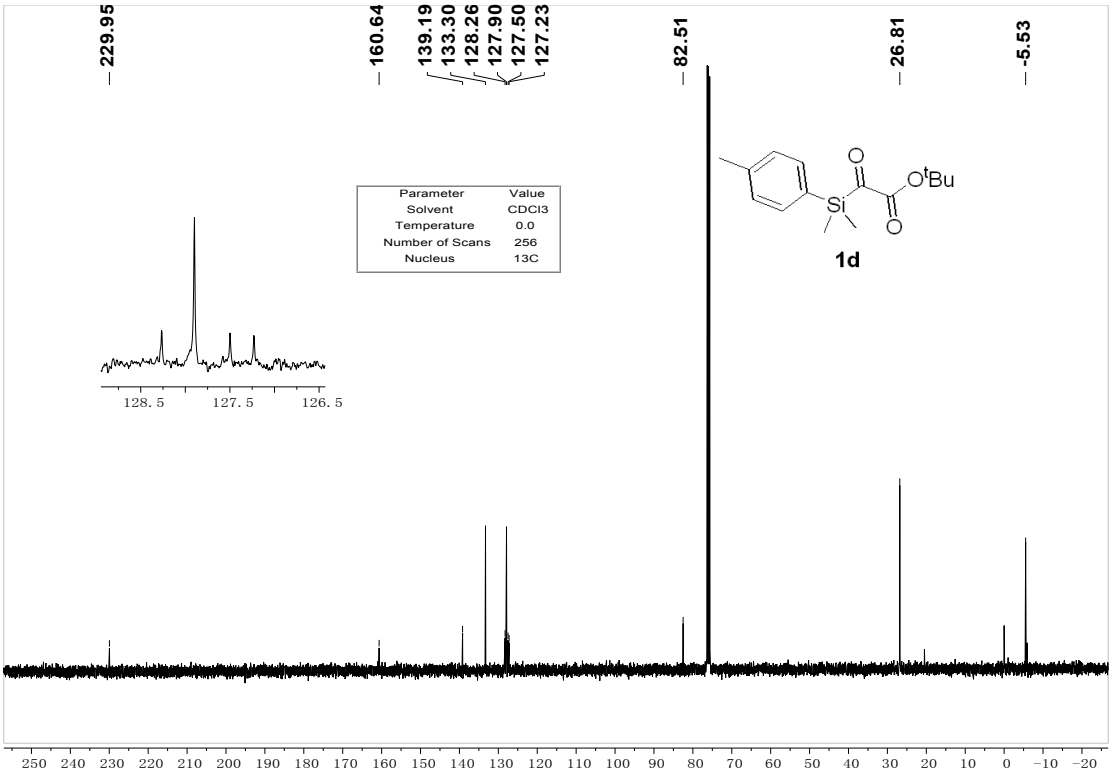
e Spek, A. L. J. Appl. Cryst. 2003, 36, 7–13.

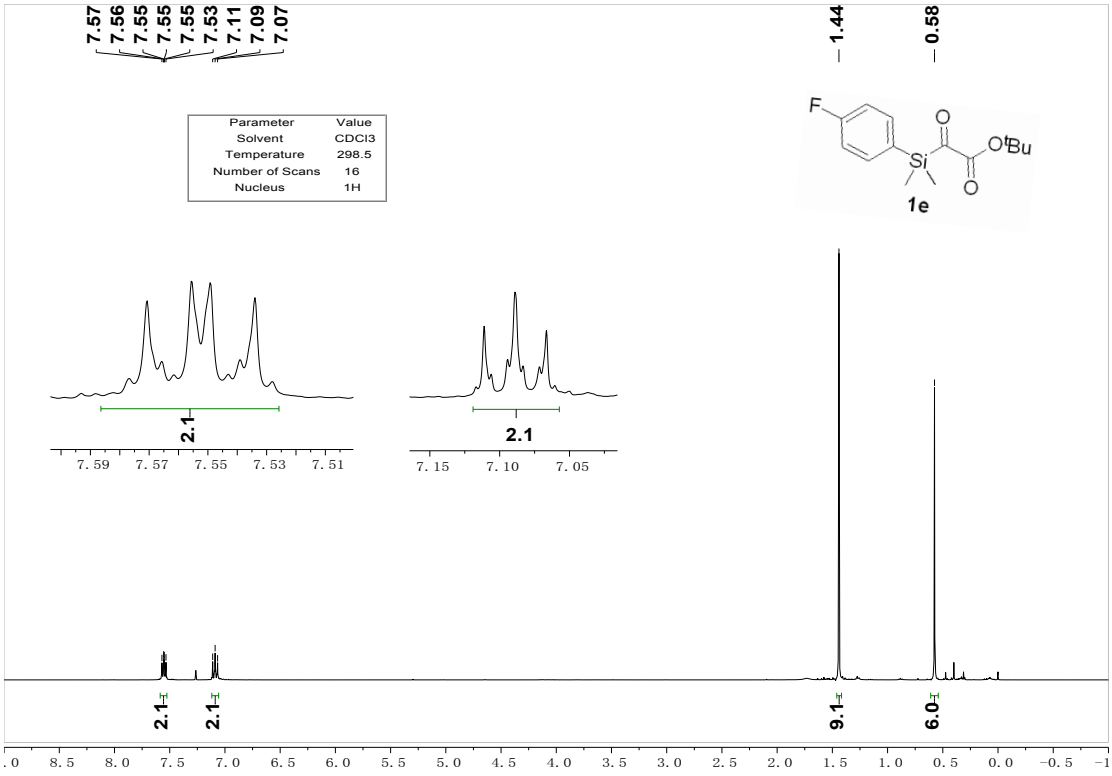
10. Copy of ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR Spectra.

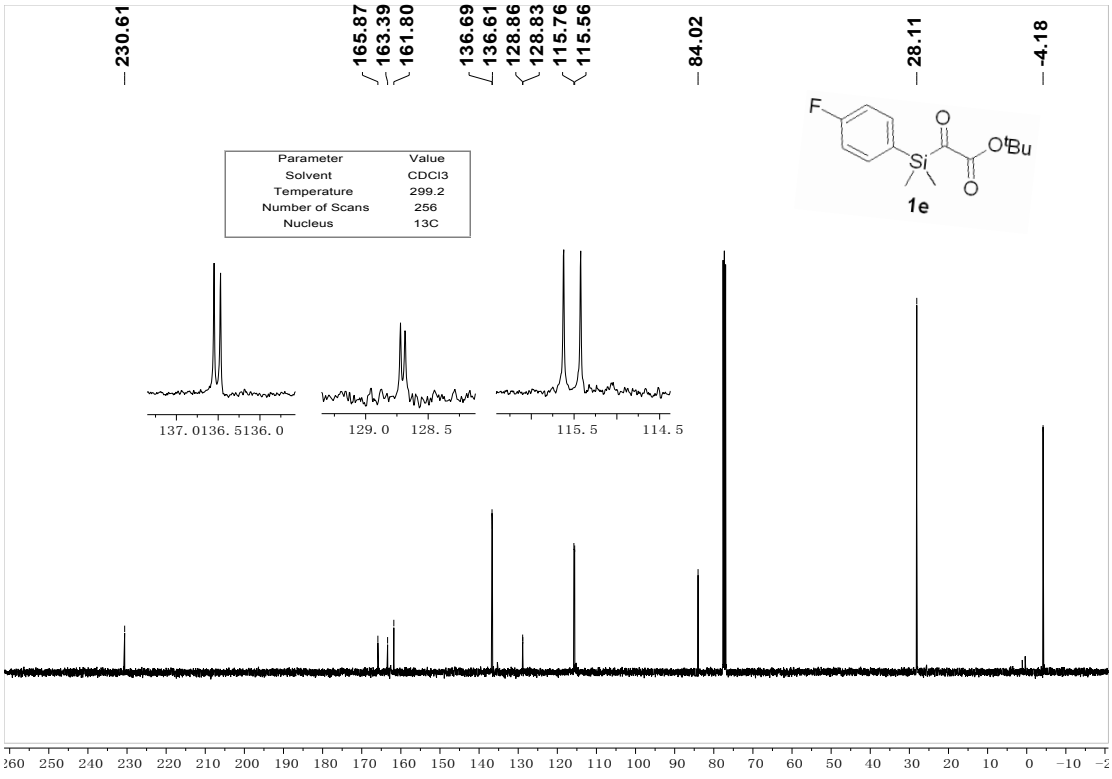


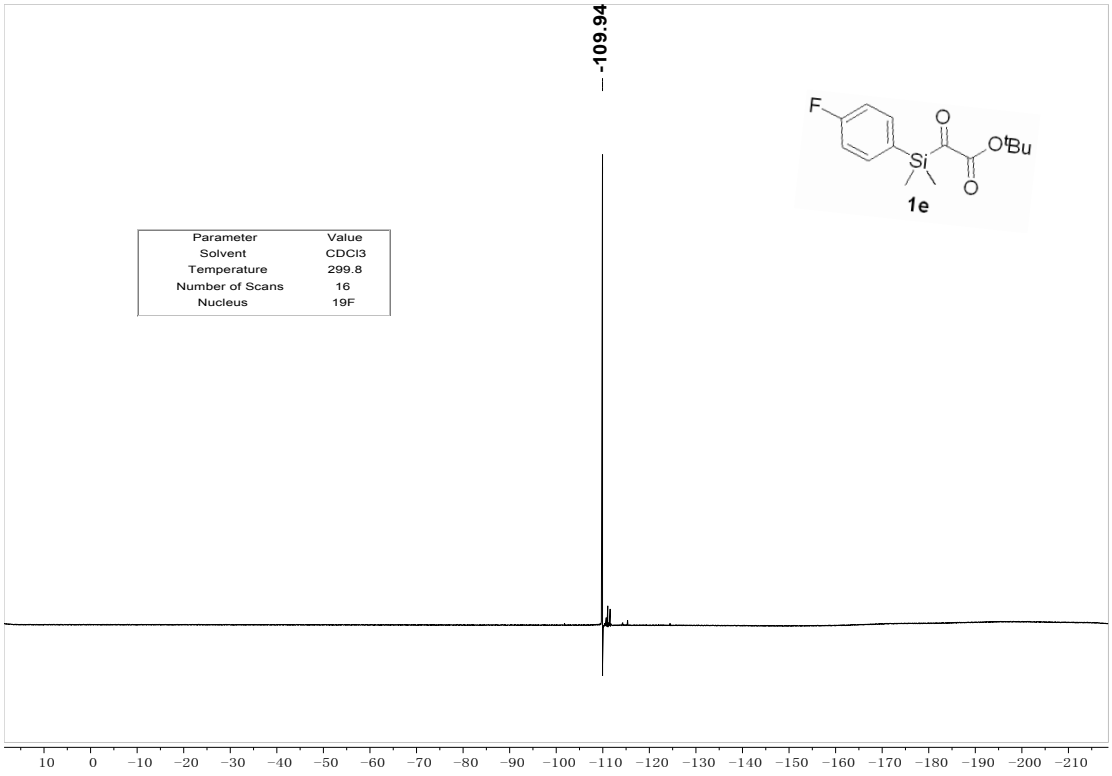


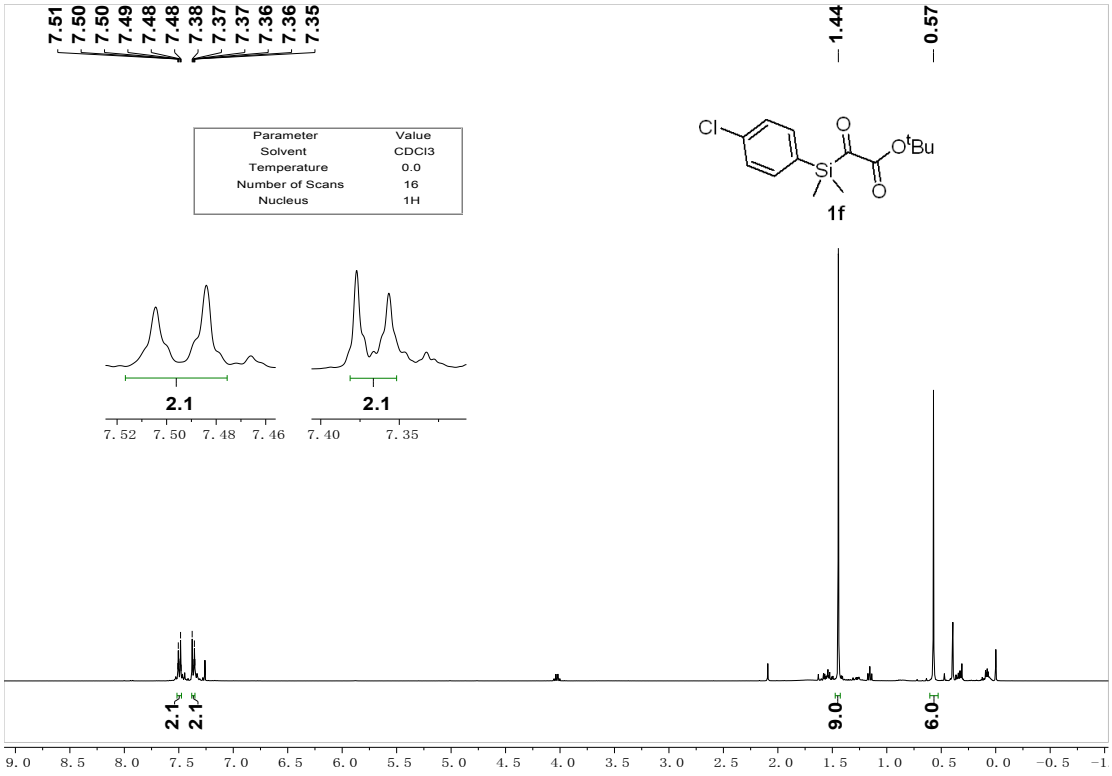

7.39
7.37
7.14
7.12
2.28
1.36
0.48
Parameter Value
Solvent CDCl3
Temperature 301.1
Number of Scans 16
Nucleus 1H
O
O
OtBu
Si
1d
2.0
2.2
3.2
9.1
6.0

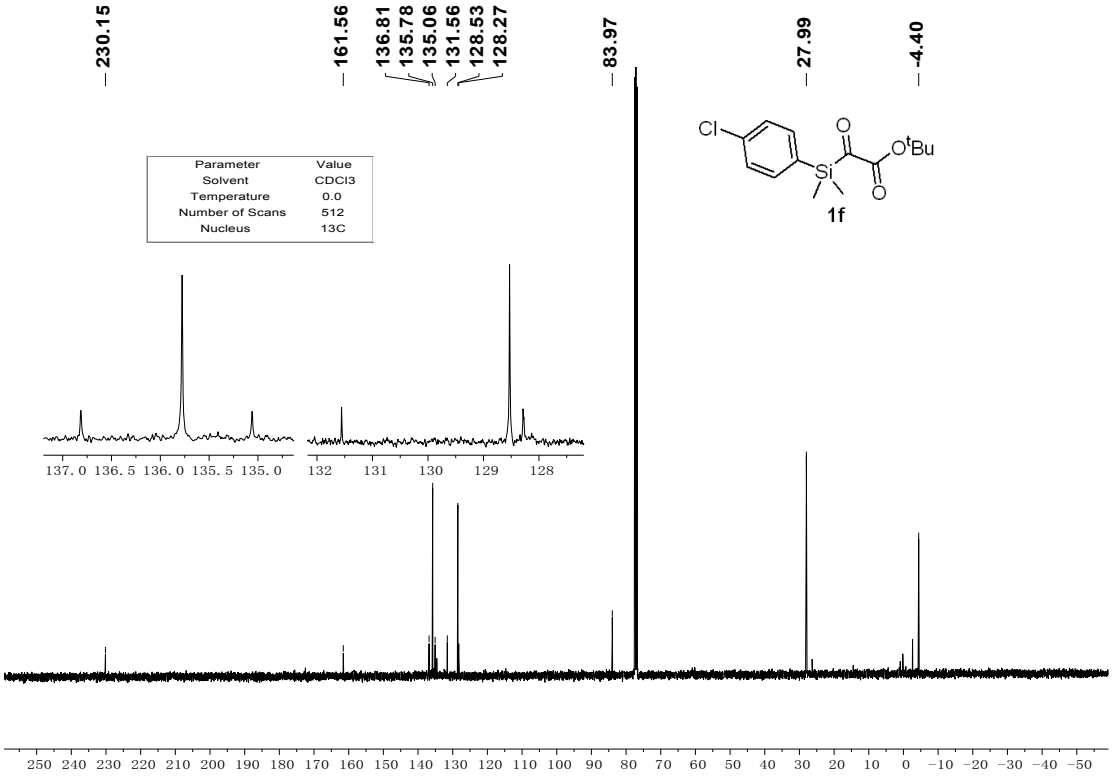

229.95
160.64
139.19
133.30
128.26
127.90
127.50
127.23
82.51
26.81
-5.53
Parameter Value
Solvent CDCl3
Temperature 0.0
Number of Scans 256
Nucleus 13C
O
O
OtBu
Si
1d

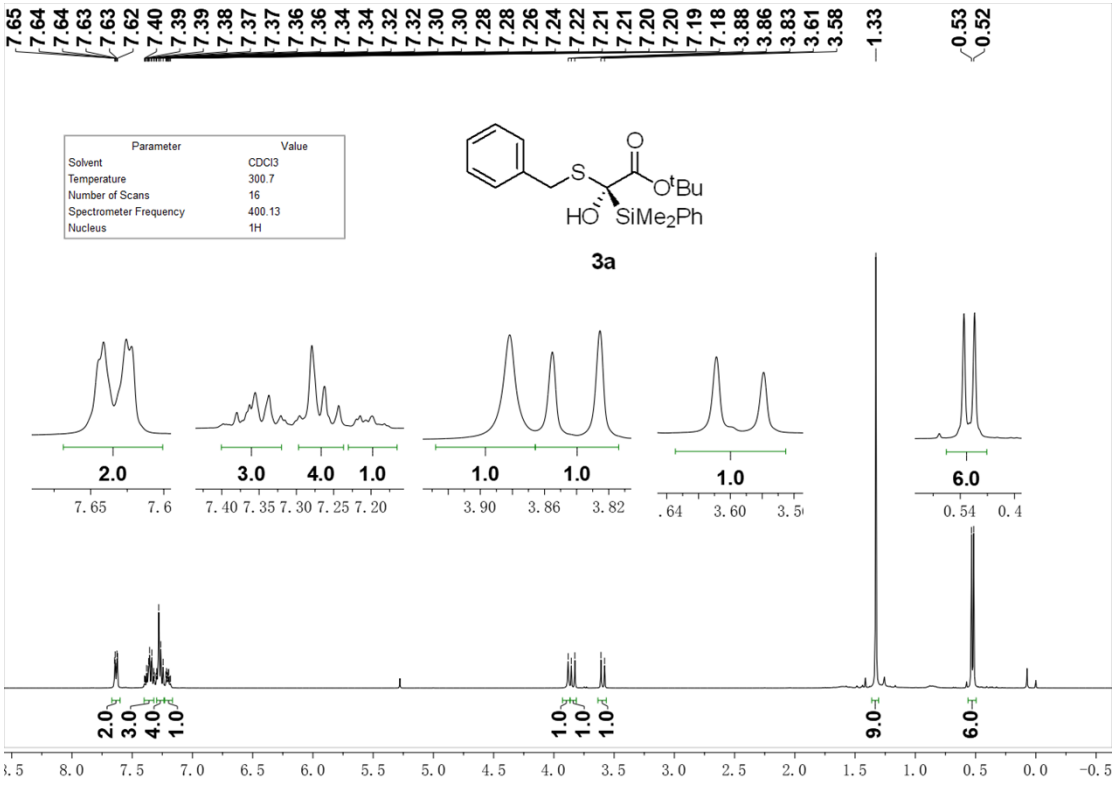

7.57
7.56
7.55
7.55
7.55
7.53
7.11
7.09
7.07
1.44
0.58
Parameter Value
Solvent CDCl3
Temperature 298.5
Number of Scans 16
Nucleus 1H
F
O
OtBu
Si
O
1e
2.1
2.1
2.1
2.1
9.1
6.0

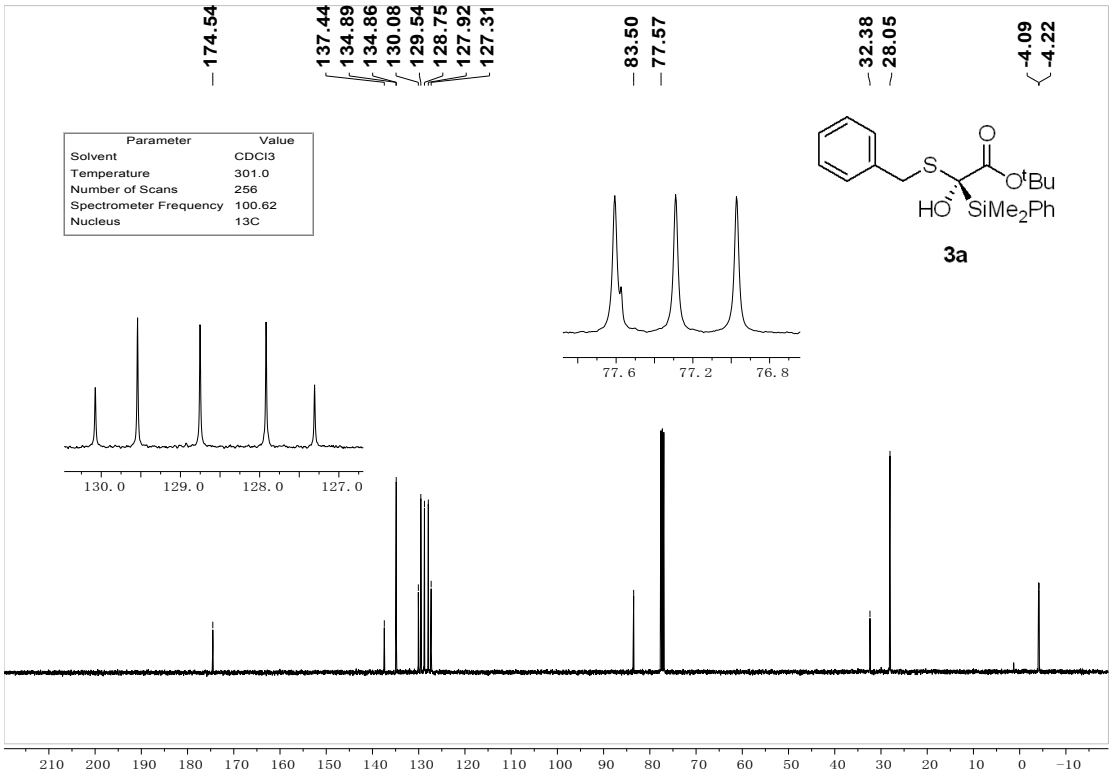

230.61
165.87
163.39
161.80
136.69
136.61
128.86
128.83
115.76
115.56
84.02
28.11
-4.18
Parameter Value
Solvent CDCl3
Temperature 299.2
Number of Scans 256
Nucleus 13C
F
O
OtBu
Si
O
1e

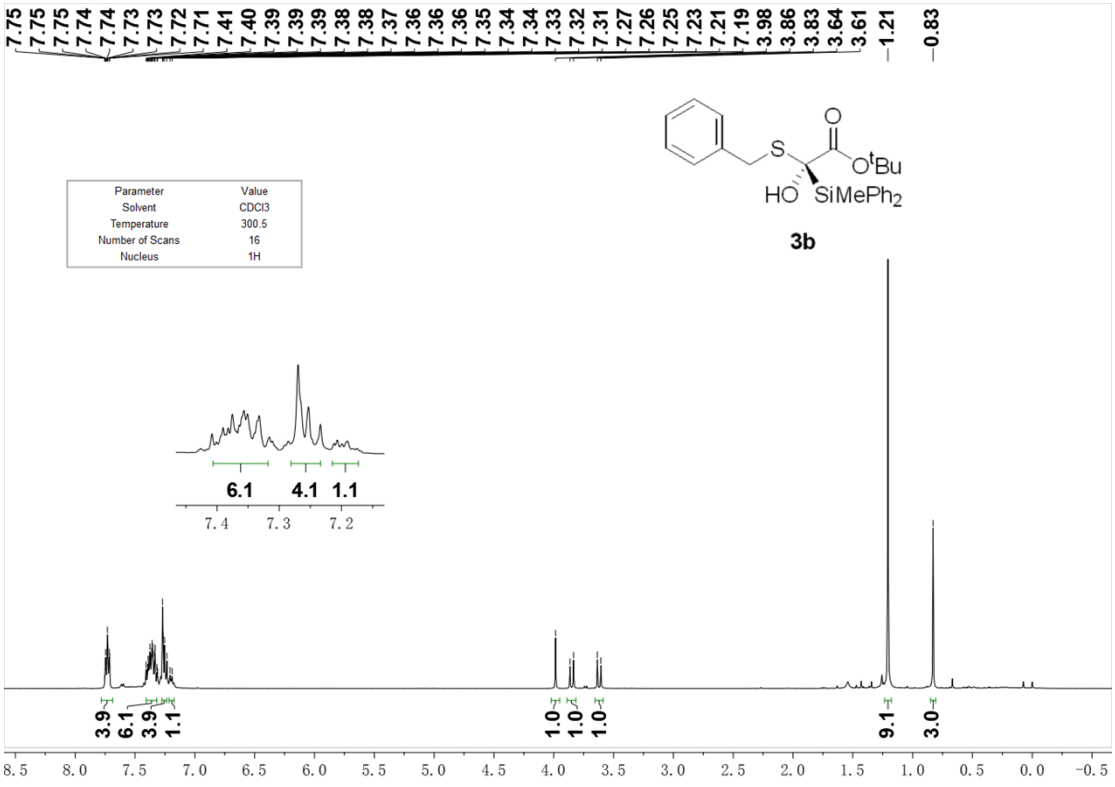

-109.94
F
O
OtBu
Si
O
1e
Parameter Value
Solvent CDCl3
Temperature 299.8
Number of Scans 16
Nucleus 19F
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210

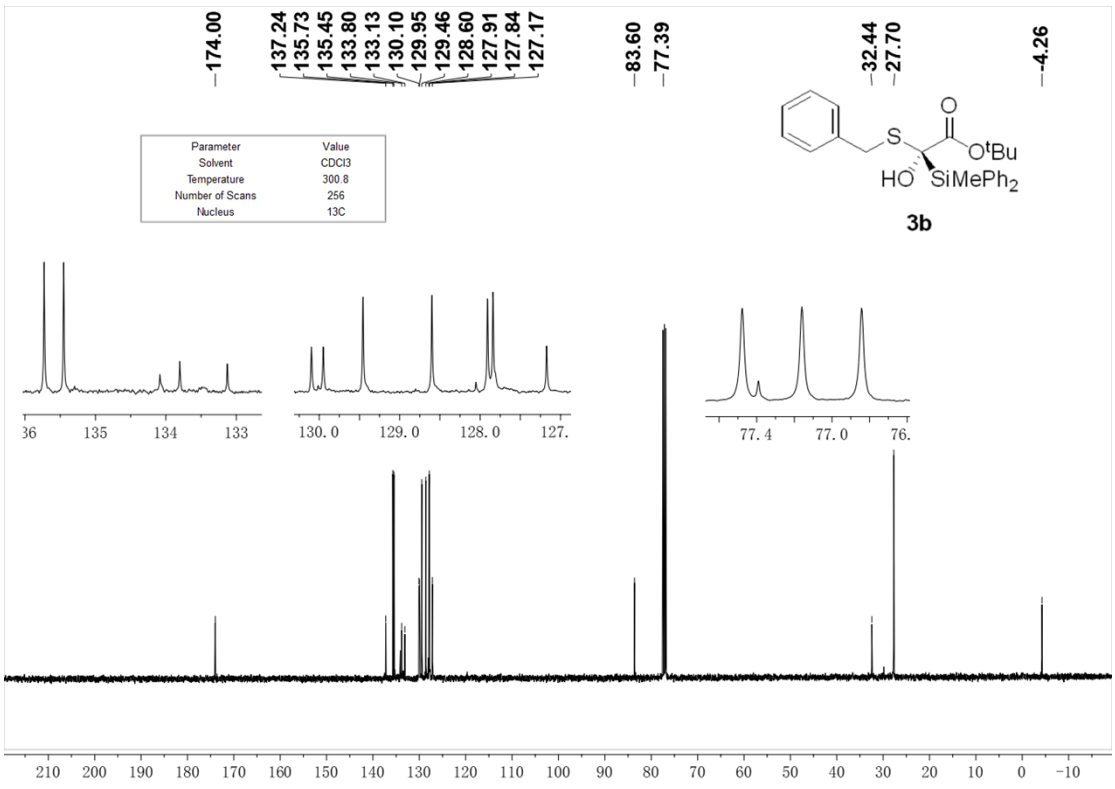

7.51
7.50
7.50
7.49
7.48
7.48
7.38
7.37
7.37
7.36
7.36
7.35
1.44
0.57
Parameter Value
Solvent CDCl3
Temperature 0.0
Number of Scans 16
Nucleus 1H
Cl
O
O
tBu
Si
O
1f
2.1
2.1
7.52 7.50 7.48 7.46
7.40 7.35
2.1
2.1
9.0
6.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1

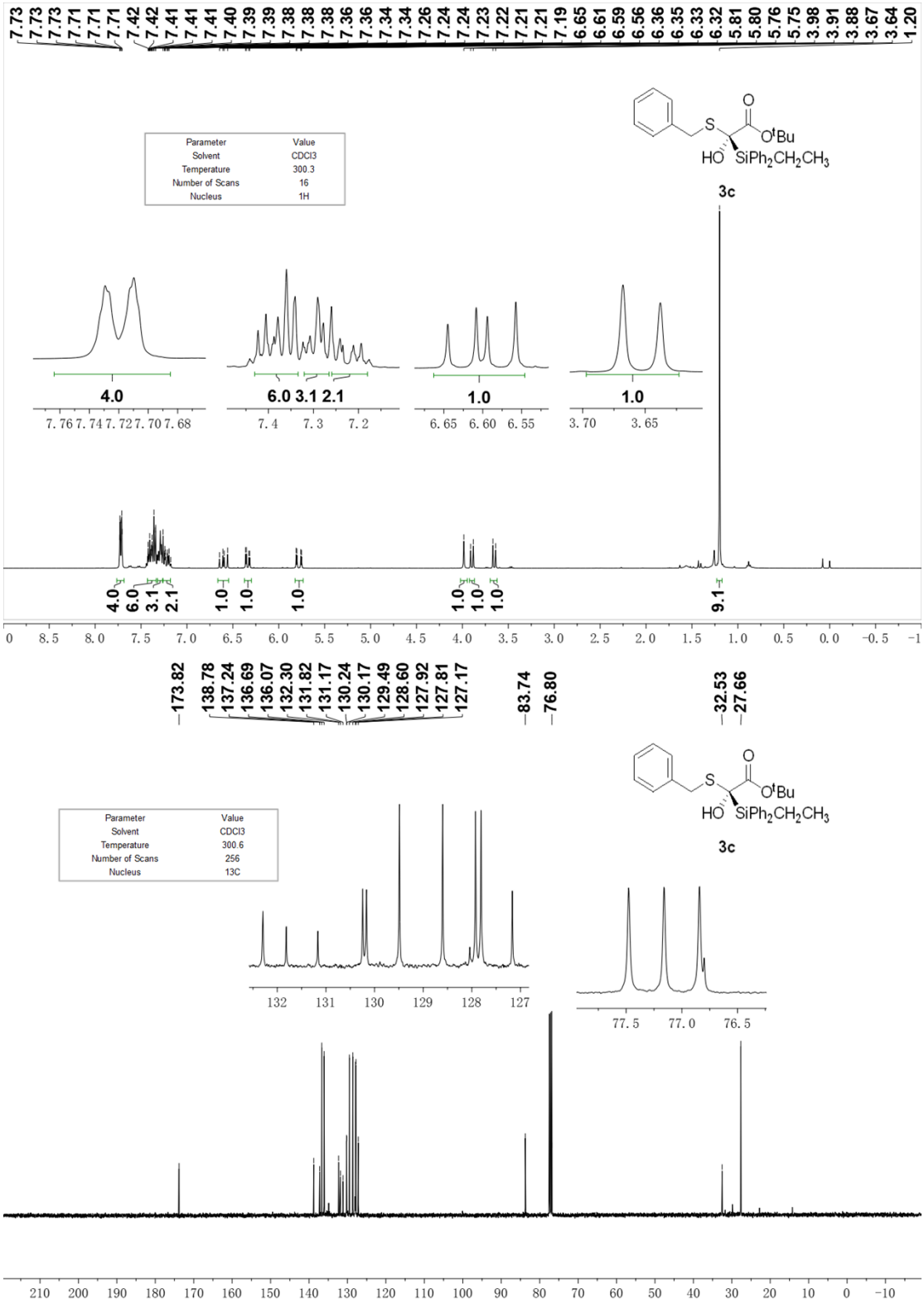

230.15
161.56
136.81
135.78
135.06
131.56
128.53
128.27
83.97
27.99
-4.40
Parameter Value
Solvent CDCl3
Temperature 0.0
Number of Scans 512
Nucleus 13C
Cl
O
O
tBu
Si
O
1f
137.0 136.5 136.0 135.5 135.0
132 131 130 129 128
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50

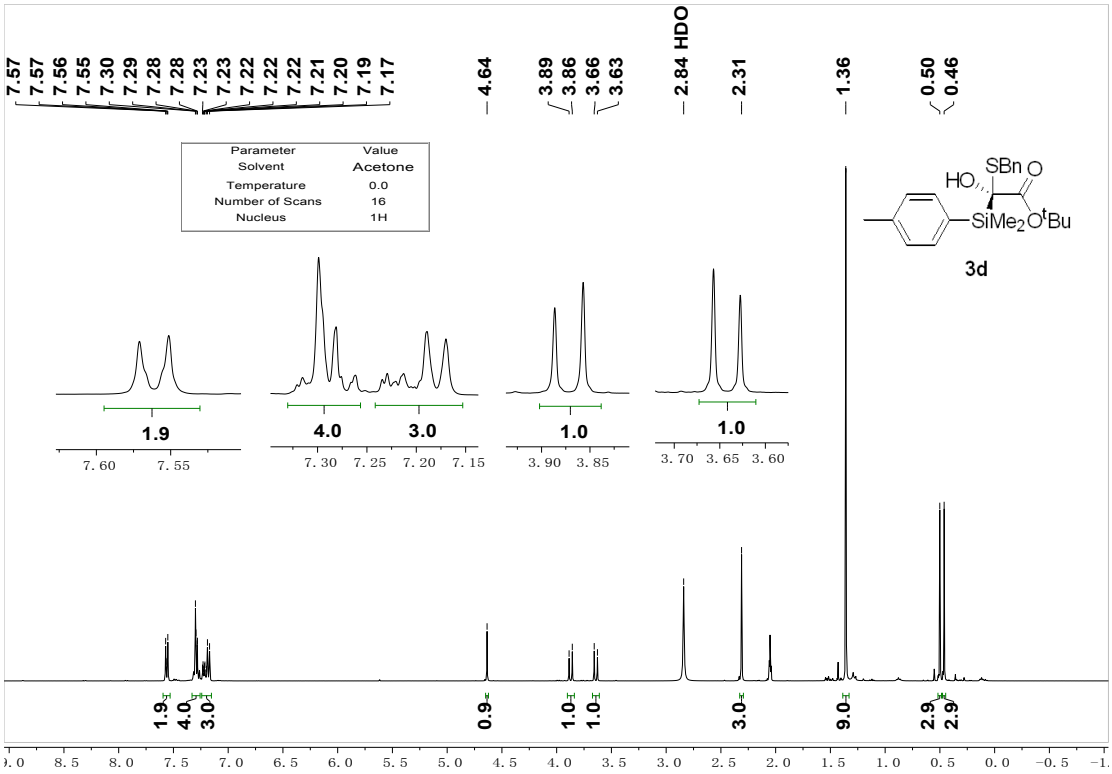

7.65 7.64 7.64 7.63 7.63 7.62 7.40 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.34 7.34 7.32 7.32 7.30 7.30 7.28 7.28 7.26 7.24 7.22 7.21 7.21 7.20 7.20 7.19 7.18 3.88 3.86 3.83 3.61 3.58 1.33 0.53 0.52
Parameter Value
Solvent CDCl3
Temperature 300.7
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
3a
2.0 3.0 4.0 1.0 1.0 1.0 1.0 6.0
2.0 3.0 4.0 1.0 1.0 1.0 9.0 6.0

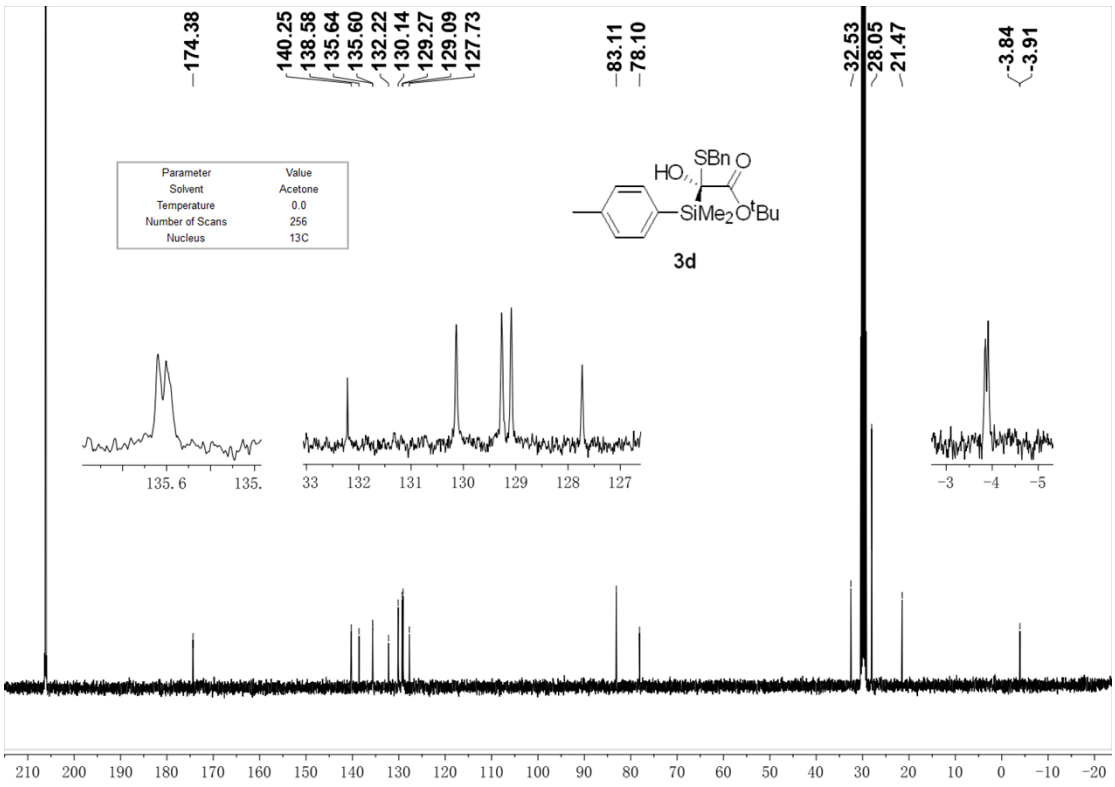

174.54 137.44 134.89 134.86 130.08 129.54 128.75 127.92 127.31 83.50 77.57 32.38 28.05 -4.09 -4.22
Parameter Value
Solvent CDCl3
Temperature 301.0
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C
3a

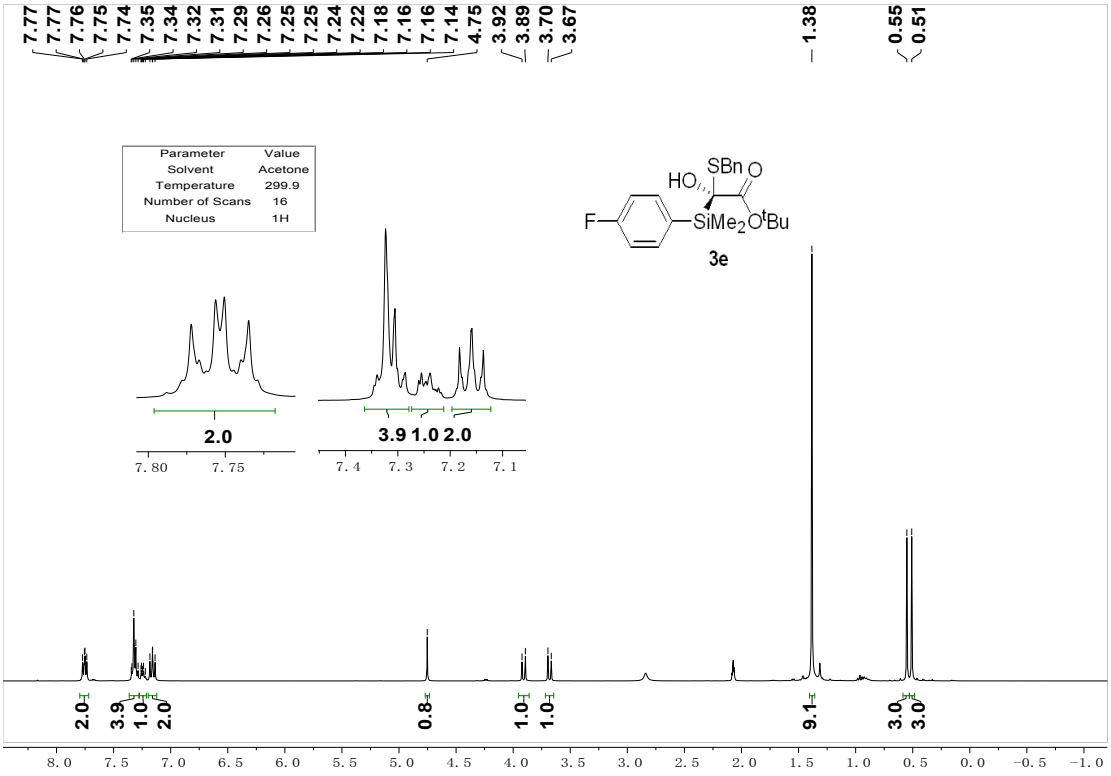

7.75 7.75 7.75 7.74 7.74 7.73 7.73 7.72 7.71 7.41 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.31 7.27 7.26 7.25 7.23 7.21 7.19 3.98 3.86 3.83 3.64 3.61 1.21 0.83
Parameter Value
Solvent CDCl3
Temperature 300.5
Number of Scans 16
Nucleus 1H
3b
6.1 4.1 1.1
3.9 6.1 3.9 1.1 1.0 1.0 1.0 9.1 3.0

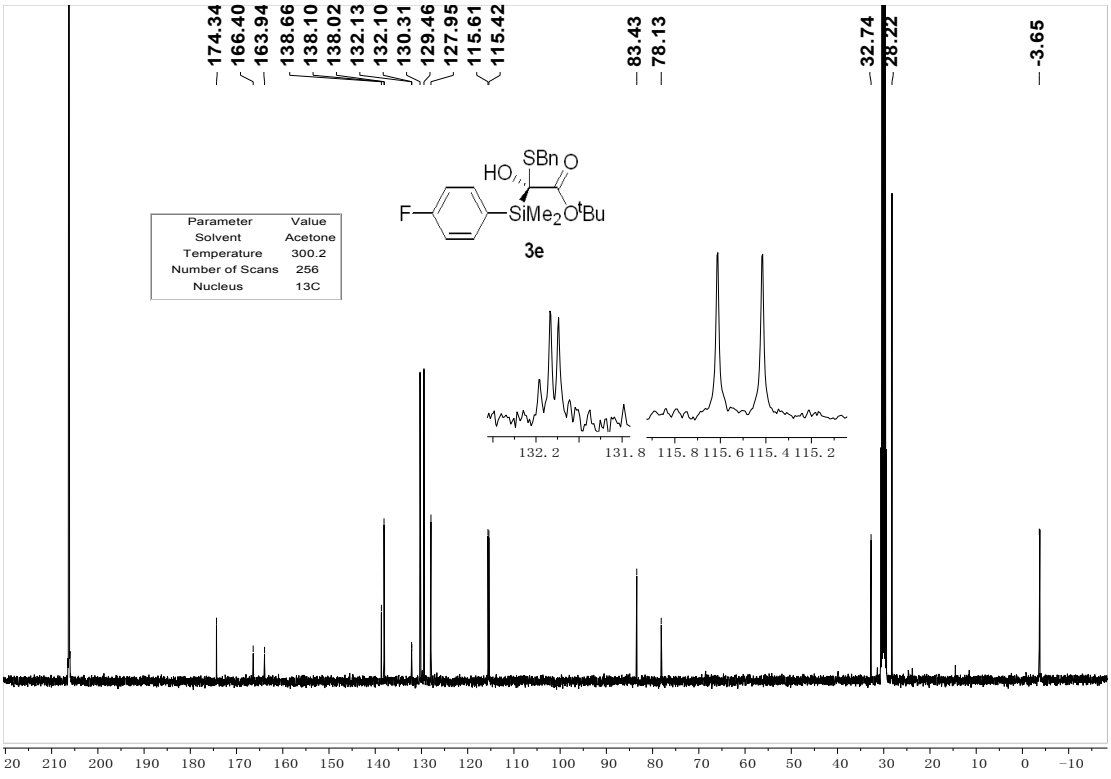

174.00 137.24 135.73 135.45 133.80 133.13 130.10 129.95 129.46 128.60 127.91 127.84 127.17 83.60 77.39 32.44 27.70 -4.26
Parameter Value
Solvent CDCl3
Temperature 300.8
Number of Scans 256
Nucleus 13C
3b


7.73 7.73 7.73 7.71 7.71 7.71 7.42 7.42 7.41 7.41 7.41 7.40 7.39 7.39 7.38 7.38 7.38 7.36 7.36 7.34 7.34 7.26 7.24 7.24 7.23 7.22 7.21 7.21 7.19 6.65 6.61 6.59 6.56 6.36 6.35 6.33 6.32 5.81 5.80 5.76 5.75 3.98 3.91 3.88 3.67 3.64 1.20
Parameter Value
Solvent CDCl3
Temperature 300.3
Number of Scans 16
Nucleus 1H
O
S
O^{t}Bu
HO SiPh$_2$CH$_2$CH$_3$
3c
4.0
6.0 3.1 2.1
1.0
1.0
7.76 7.74 7.72 7.70 7.68
7.4 7.3 7.2
6.65 6.60 6.55
3.70 3.65
4.0 6.0 3.1 2.1 1.0 1.0 1.0 1.0 1.0 1.0 9.1
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
173.82 138.78 137.24 136.69 136.07 132.30 131.82 131.17 130.24 130.17 129.49 128.60 127.92 127.81 127.17 83.74 76.80 32.53 27.66
Parameter Value
Solvent CDCl3
Temperature 300.6
Number of Scans 256
Nucleus 13C
O
S
O^{t}Bu
HO SiPh$_2$CH$_2$CH$_3$
3c
132 131 130 129 128 127
77.5 77.0 76.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

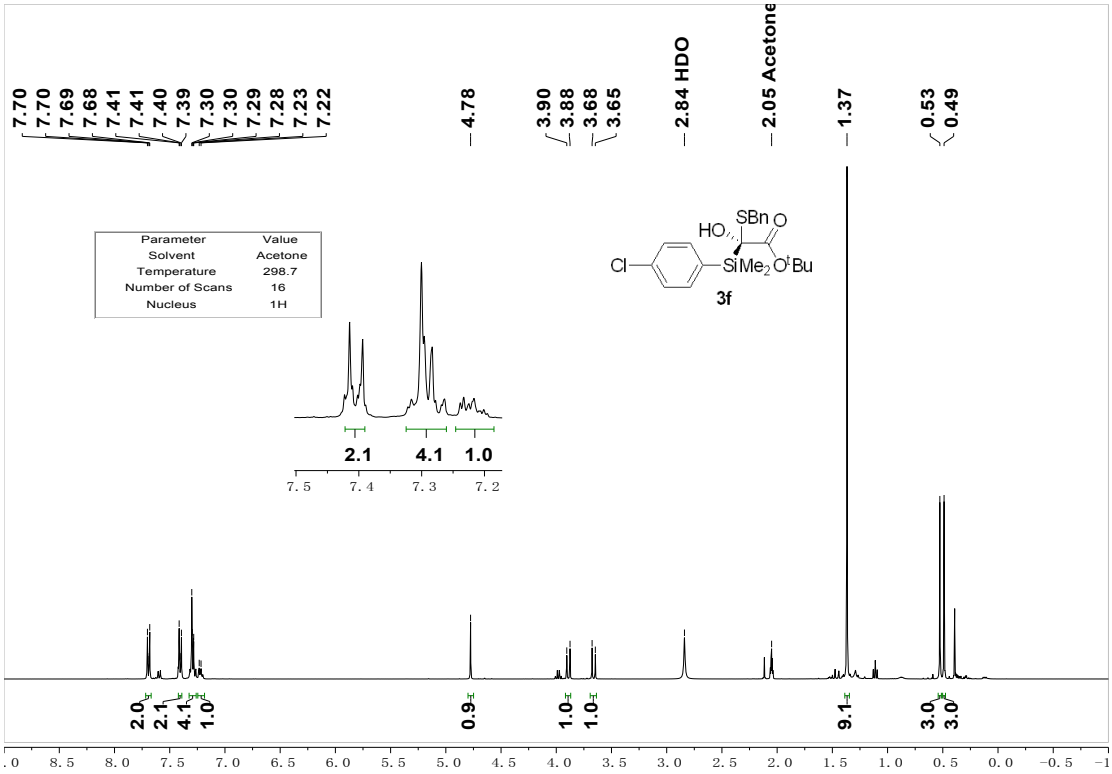

7.57 7.57 7.56 7.55 7.30 7.29 7.28 7.28 7.23 7.23 7.22 7.22 7.22 7.21 7.20 7.19 7.17
4.64
3.89 3.86 3.66 3.63
2.84 HDO
2.31
1.36
0.50 0.46
Parameter Value
Solvent Acetone
Temperature 0.0
Number of Scans 16
Nucleus 1H
SBn O
HO
SiMe2OtBu
3d
1.9
4.0 3.0
1.0
1.0
1.9 4.0 3.0 0.9 1.0 1.0 3.0 9.0 2.9 2.9

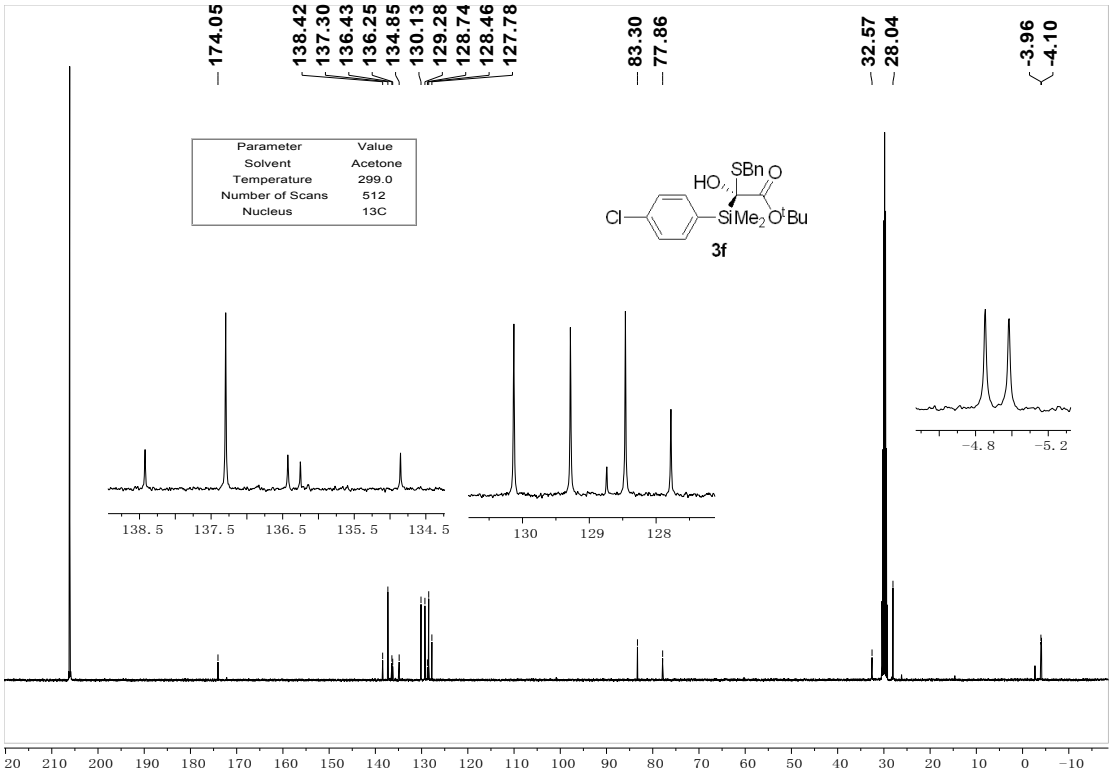

174.38
140.25 138.58 135.64 135.60 132.22 130.14 129.27 129.09 127.73
83.11 78.10
32.53 28.05 21.47
-3.84 -3.91
Parameter Value
Solvent Acetone
Temperature 0.0
Number of Scans 256
Nucleus 13C
SBn O
HO
SiMe2OtBu
3d

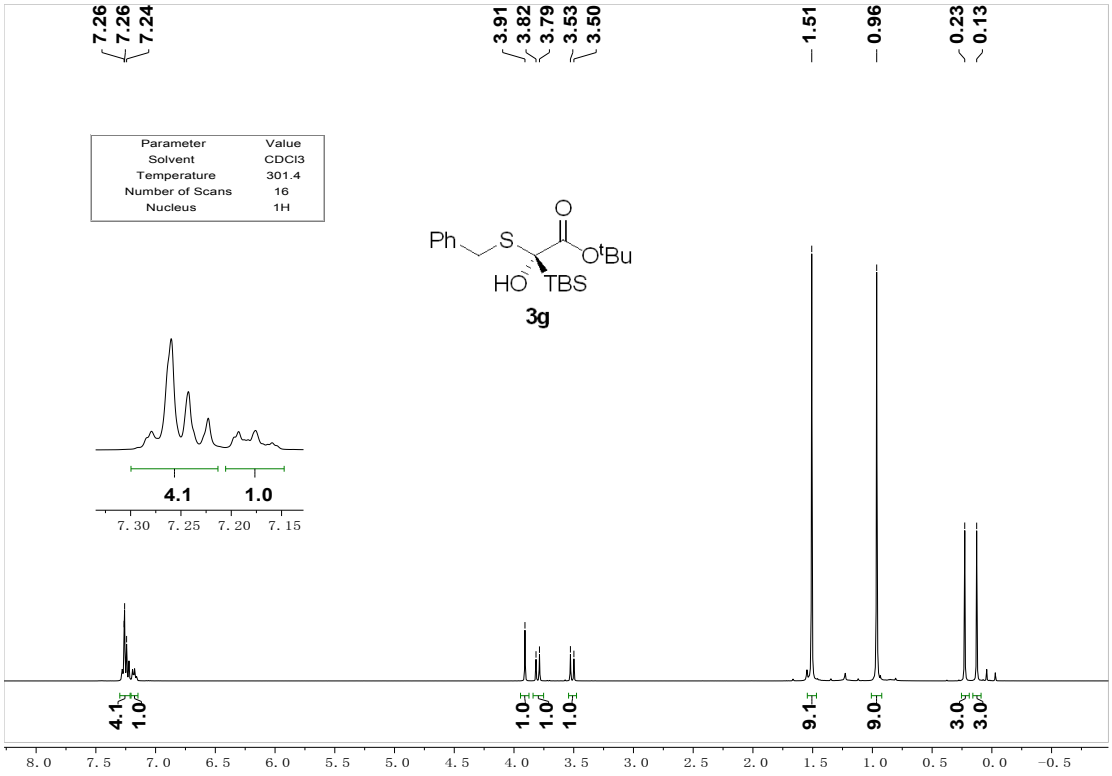

7.77 7.77 7.76 7.75 7.74 7.35 7.34 7.32 7.31 7.29 7.26 7.25 7.25 7.24 7.22 7.18 7.16 7.16 7.14 4.75 3.92 3.89 3.70 3.67
1.38
0.55 0.51
Parameter Value
Solvent Acetone
Temperature 299.9
Number of Scans 16
Nucleus 1H
HO SBn O
F SiMe2OtBu
3e
2.0
3.9 1.0 2.0
2.0 3.9 1.0 2.0 0.8 1.0 1.0 9.1 3.0 3.0

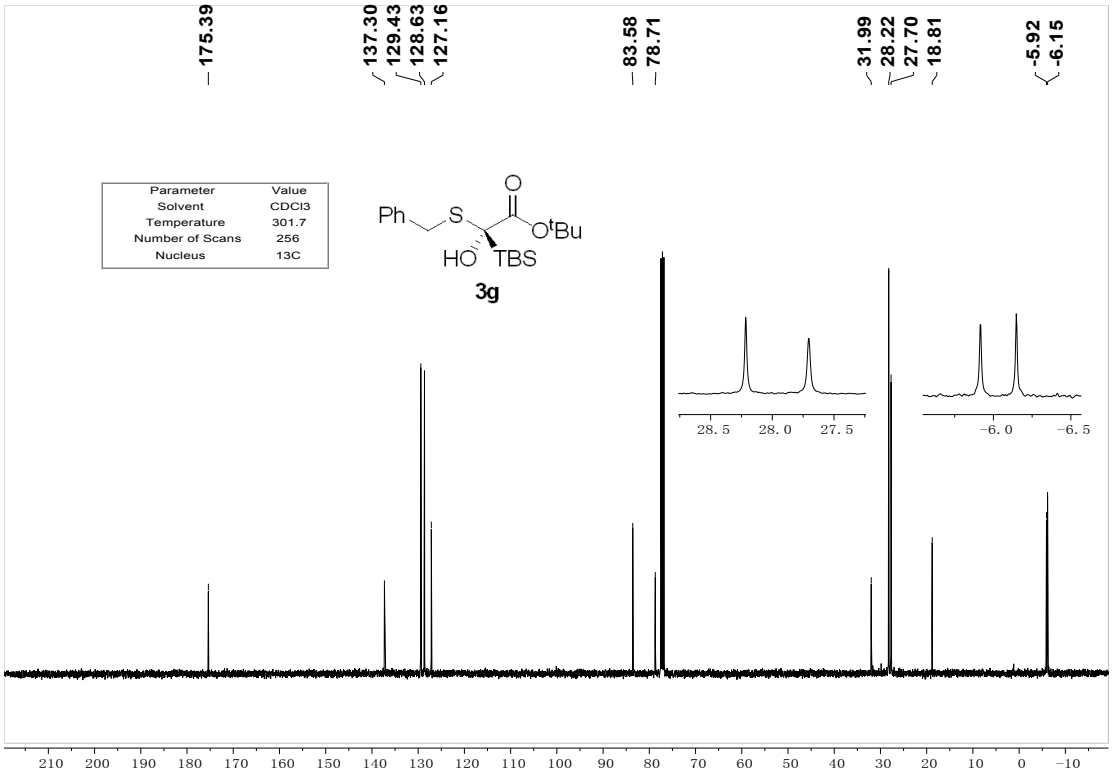

174.34 166.40 163.94 138.66 138.10 138.02 132.13 132.10 130.31 129.46 127.95 115.61 115.42
83.43 78.13
32.74 28.22
-3.65
Parameter Value
Solvent Acetone
Temperature 300.2
Number of Scans 256
Nucleus 13C
HO SBn O
F SiMe2OtBu
3e

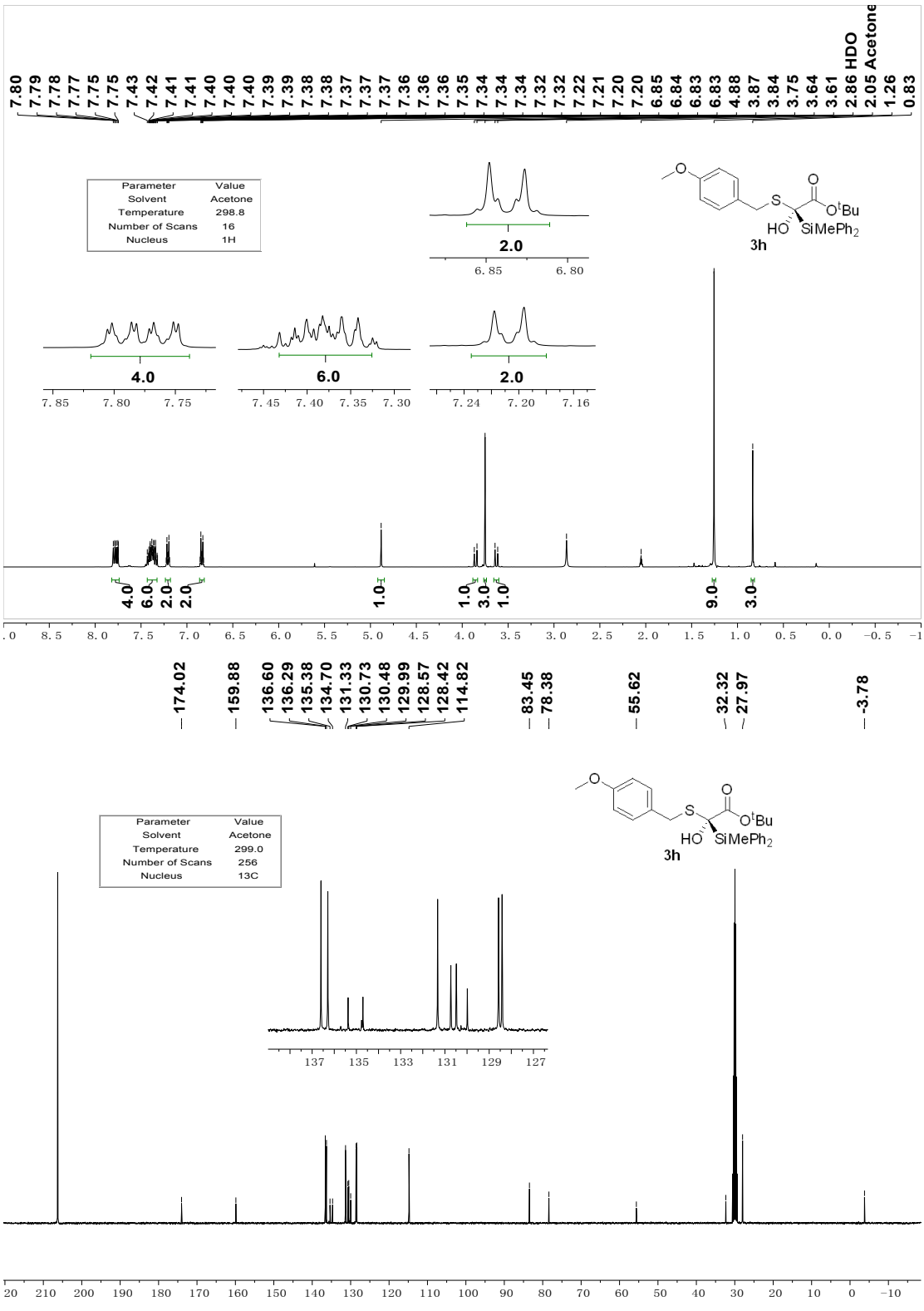

-112.67
Parameter Value
Solvent Acetone
Temperature 298.8
Number of Scans 16
Nucleus 19F
HO
SBn
O
F
SiMe2OtBu
3e
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210

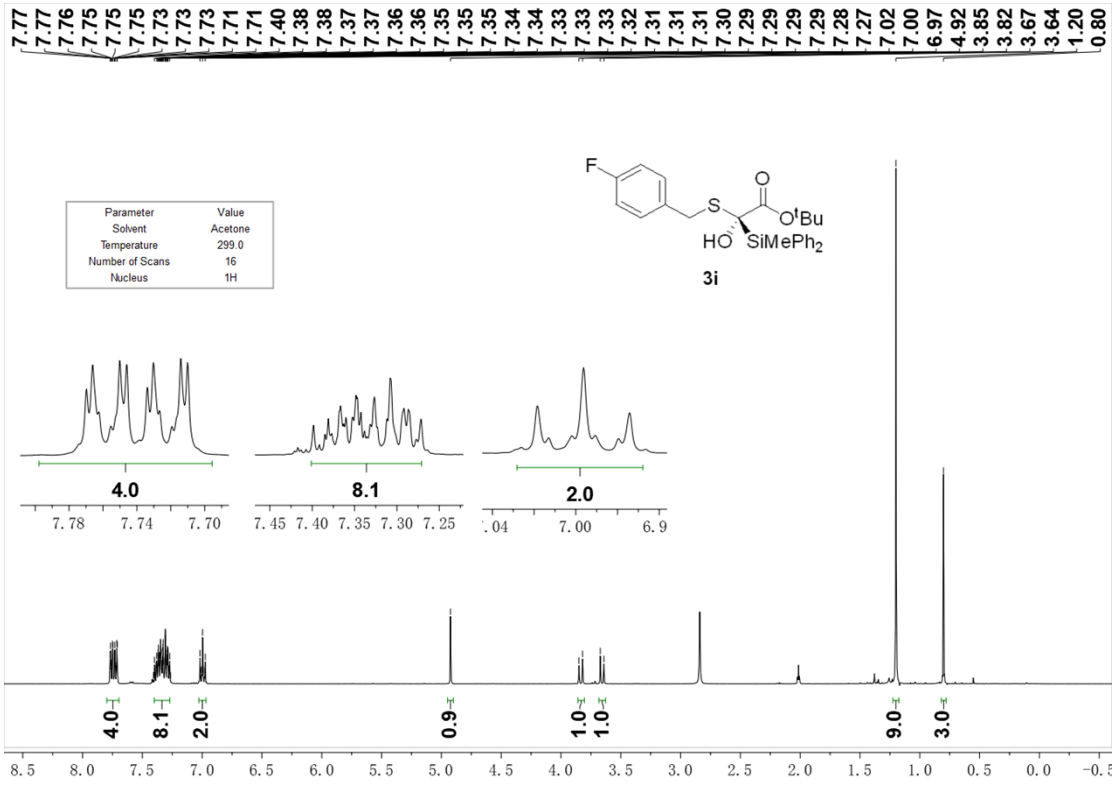

7.70
7.70
7.69
7.68
7.41
7.41
7.40
7.39
7.30
7.30
7.29
7.28
7.23
7.22
4.78
3.90
3.88
3.68
3.65
2.84 HDO
2.05 Acetone
1.37
0.53
0.49
Parameter Value
Solvent Acetone
Temperature 298.7
Number of Scans 16
Nucleus 1H
HO
SBn
O
Cl
SiMe2
O
tBu
3f
2.1
4.1
1.0
2.0
2.1
4.1
1.0
0.9
1.0
1.0
9.1
3.0
3.0

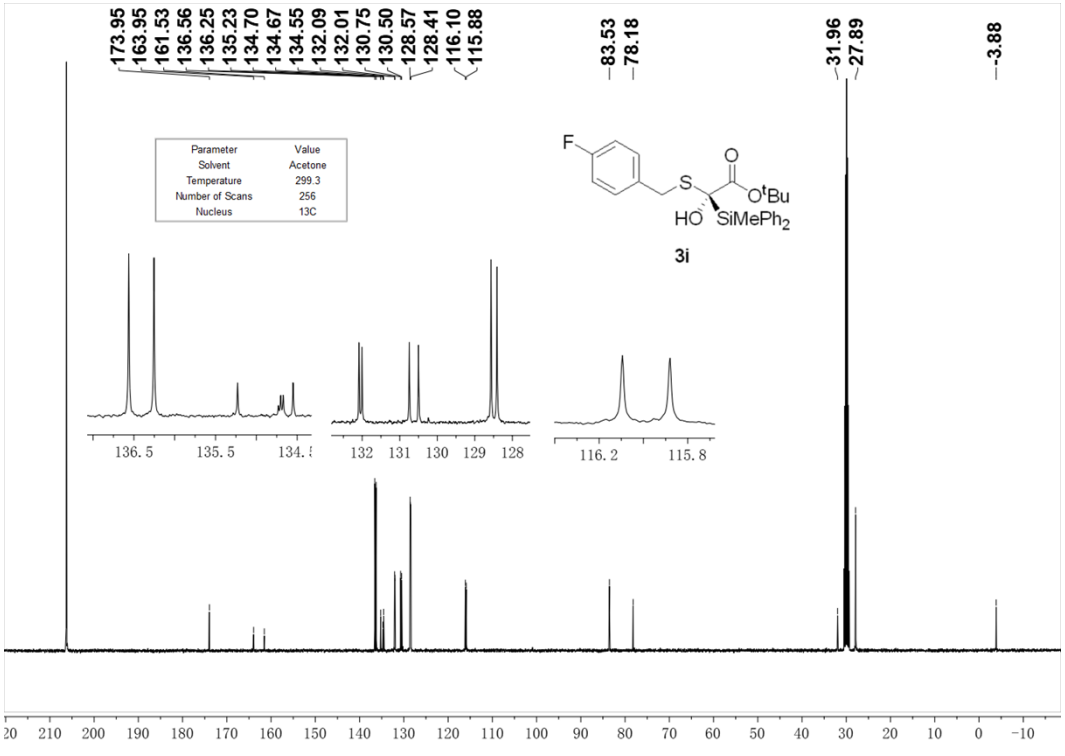

174.05
138.42
137.30
136.43
136.25
134.85
130.13
129.28
128.74
128.46
127.78
83.30
77.86
32.57
28.04
-3.96
-4.10
Parameter Value
Solvent Acetone
Temperature 299.0
Number of Scans 512
Nucleus 13C
HO
SBn
O
Cl
SiMe2
O
tBu
3f

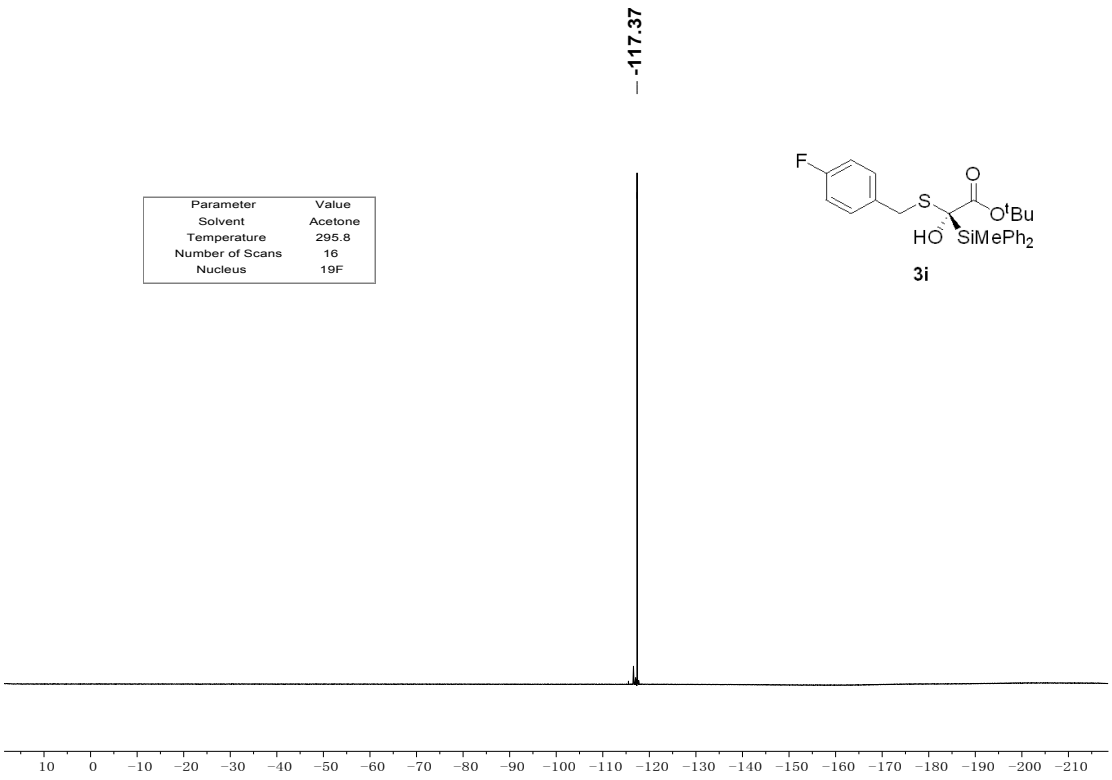

7.26
7.26
7.24
3.91
3.82
3.79
3.53
3.50
1.51
0.96
0.23
0.13
Parameter Value
Solvent CDCl3
Temperature 301.4
Number of Scans 16
Nucleus 1H
Ph
S
O
O^tBu
HO
TBS
3g
4.1
1.0
7.30 7.25 7.20 7.15
4.1
1.0
1.0
1.0
1.0
9.1
9.0
3.0
3.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5

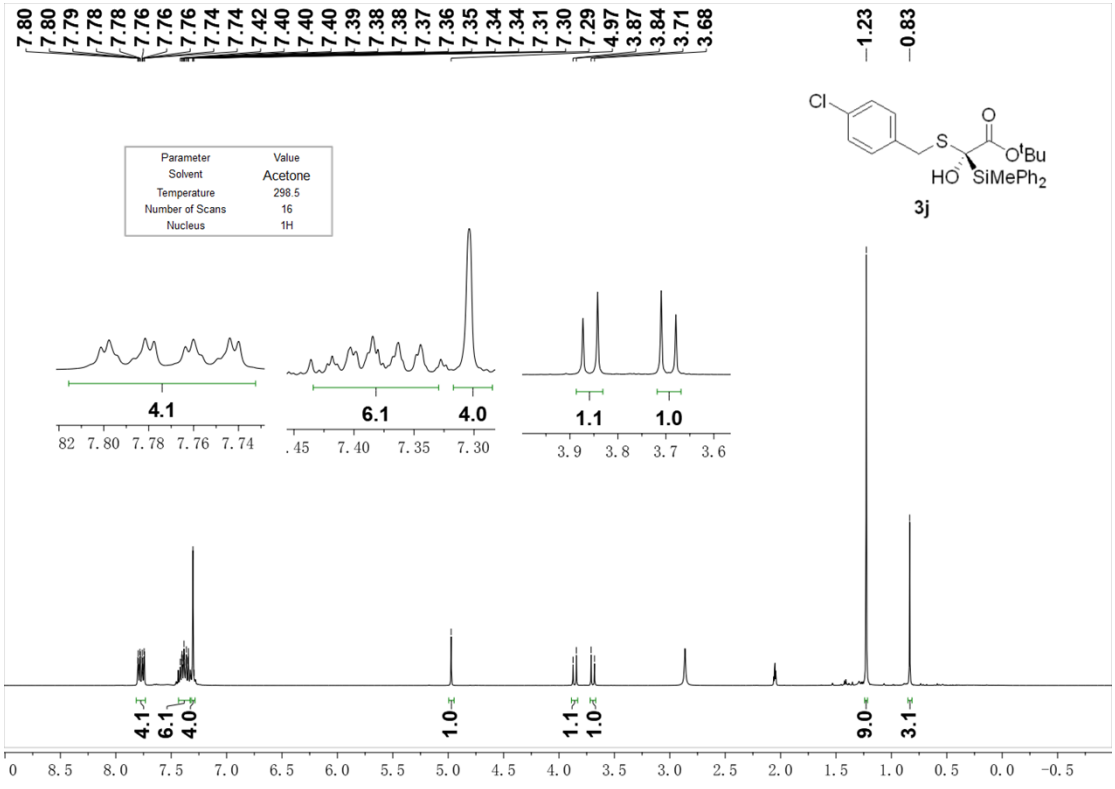

175.39
137.30
129.43
128.63
127.16
83.58
78.71
31.99
28.22
27.70
18.81
-5.92
-6.15
Parameter Value
Solvent CDCl3
Temperature 301.7
Number of Scans 256
Nucleus 13C
Ph
S
O
O^tBu
HO
TBS
3g
28.5 28.0 27.5
−6.0 −6.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

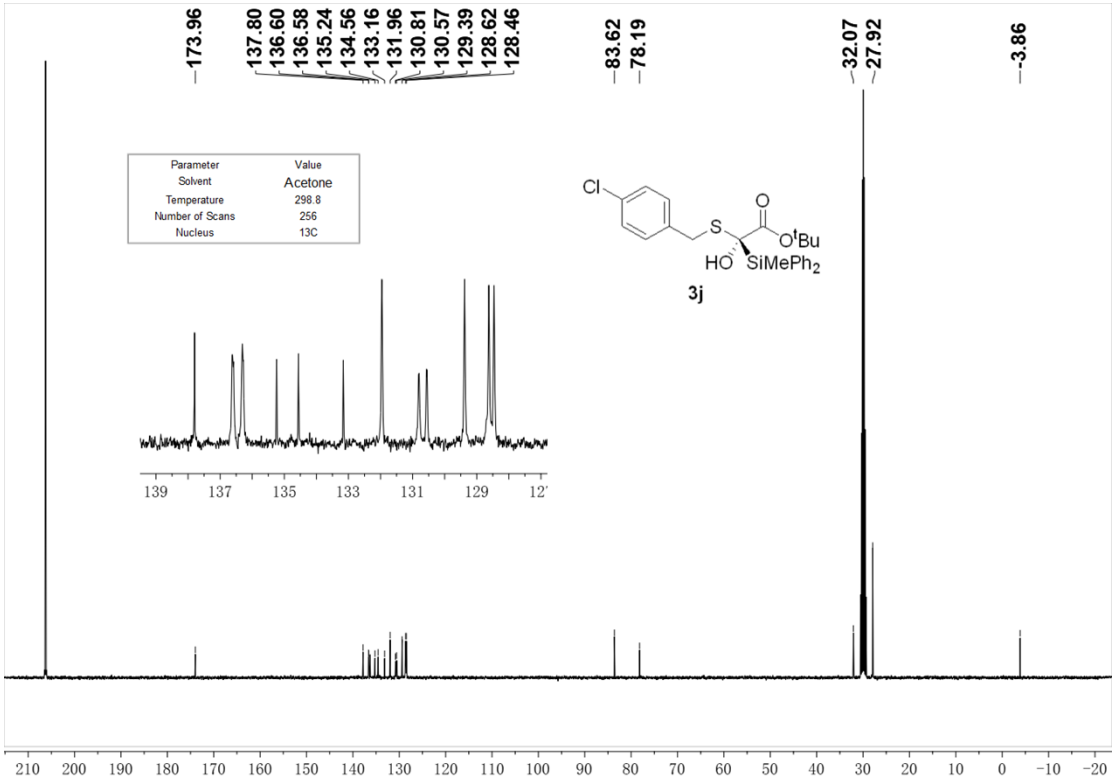

7.80 7.79 7.78 7.77 7.75 7.75 7.43 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.34 7.32 7.32 7.22 7.21 7.20 7.20 6.85 6.84 6.83 6.83 4.88 3.87 3.84 3.75 3.64 3.61 2.86 HDO 2.05 Acetone 1.26 0.83
Parameter Value
Solvent Acetone
Temperature 298.8
Number of Scans 16
Nucleus 1H
2.0
4.0
6.0
2.0
3h
4.0 6.0 2.0 2.0 1.0 1.0 3.0 1.0 9.0 3.0
174.02 159.88 136.60 136.29 135.38 134.70 131.33 130.73 130.48 129.99 128.57 128.42 114.82 83.45 78.38 55.62 32.32 27.97 -3.78
Parameter Value
Solvent Acetone
Temperature 299.0
Number of Scans 256
Nucleus 13C
3h

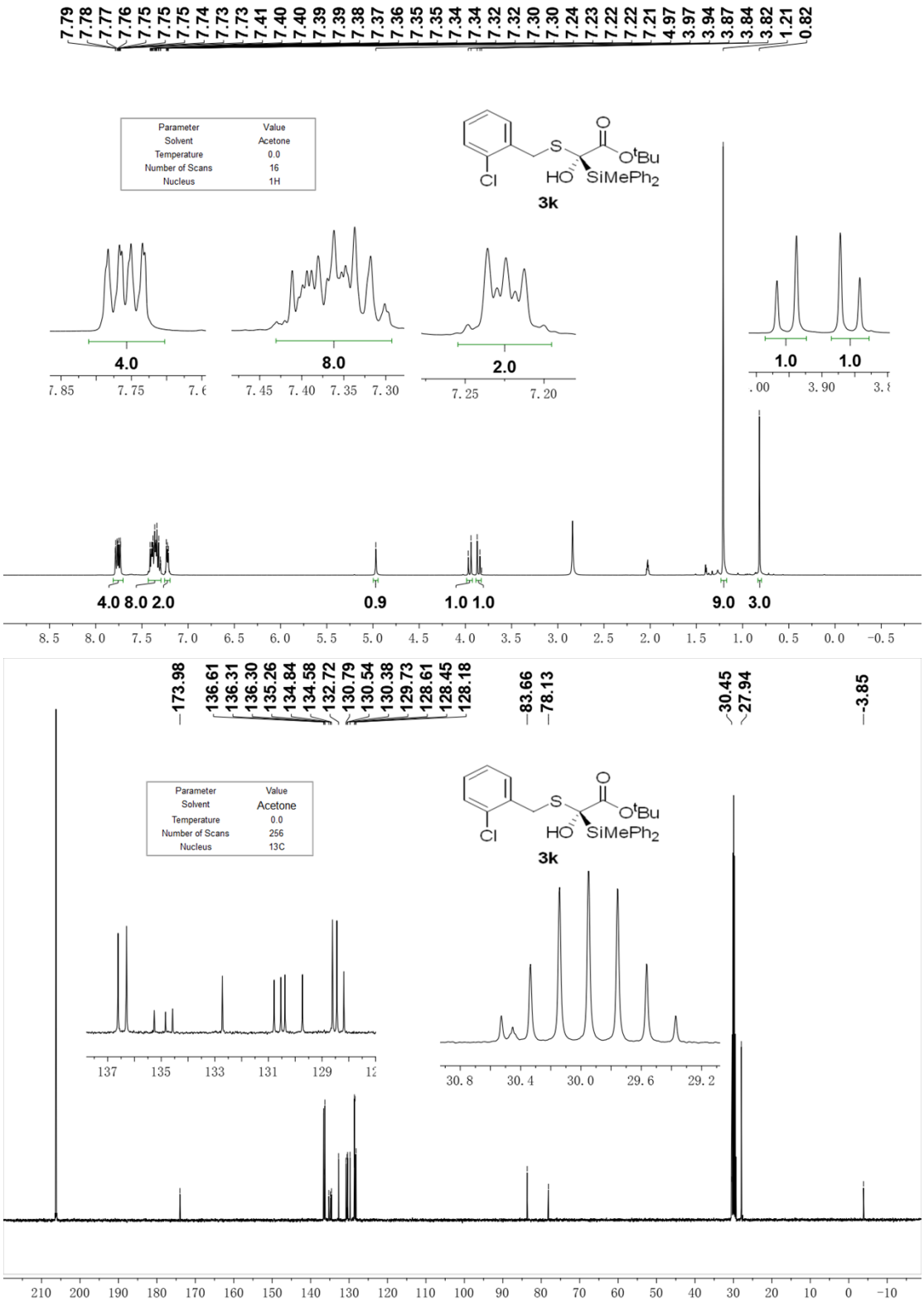

7.77 7.77 7.76 7.75 7.75 7.73 7.73 7.73 7.71 7.71 7.40 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.27 7.02 7.00 6.97 4.92 3.85 3.82 3.67 3.64 1.20 0.80
Parameter Value
Solvent Acetone
Temperature 299.0
Number of Scans 16
Nucleus 1H
F
S
O
O^{t}Bu
HO
SiMePh$_2$
3i
4.0
8.1
2.0
4.0 8.1 2.0 0.9 1.0 1.0 9.0 3.0

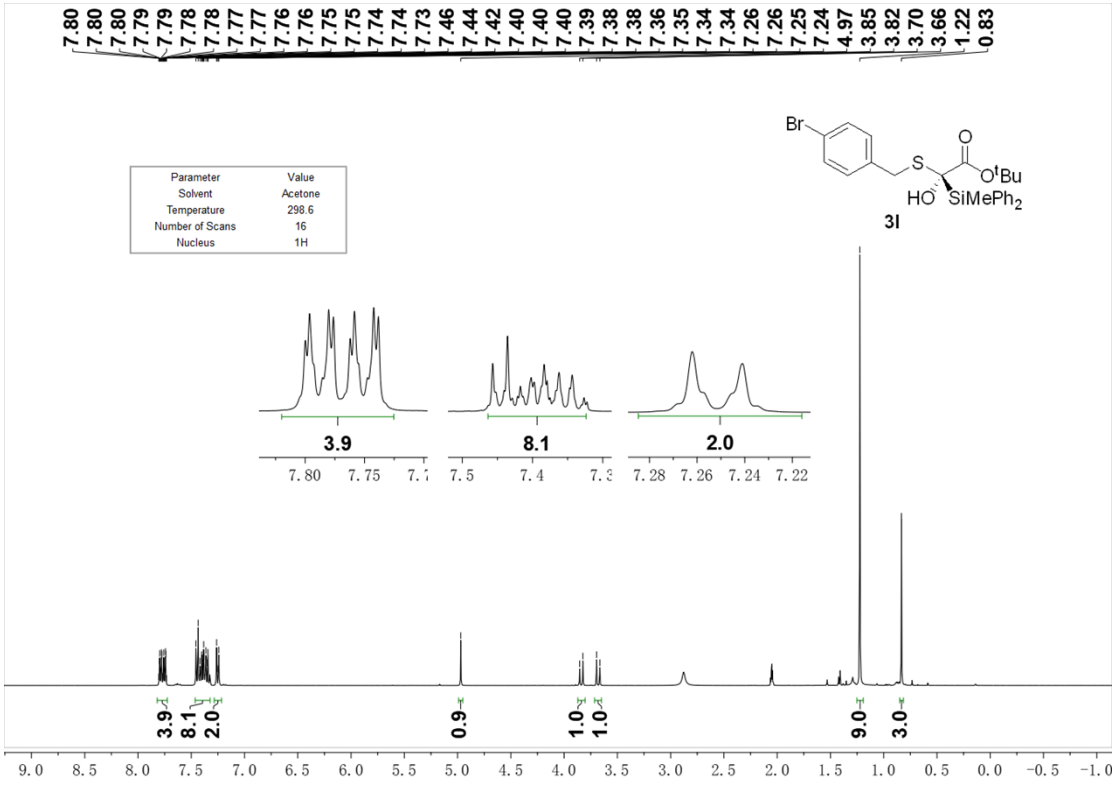

173.95 163.95 161.53 136.56 136.25 135.23 134.70 134.67 134.55 132.09 132.01 130.75 130.50 128.57 128.41 116.10 115.88
83.53 78.18
31.96 27.89
-3.88
Parameter Value
Solvent Acetone
Temperature 299.3
Number of Scans 256
Nucleus 13C
F
S
O
O^{t}Bu
HO
SiMePh$_2$
3i

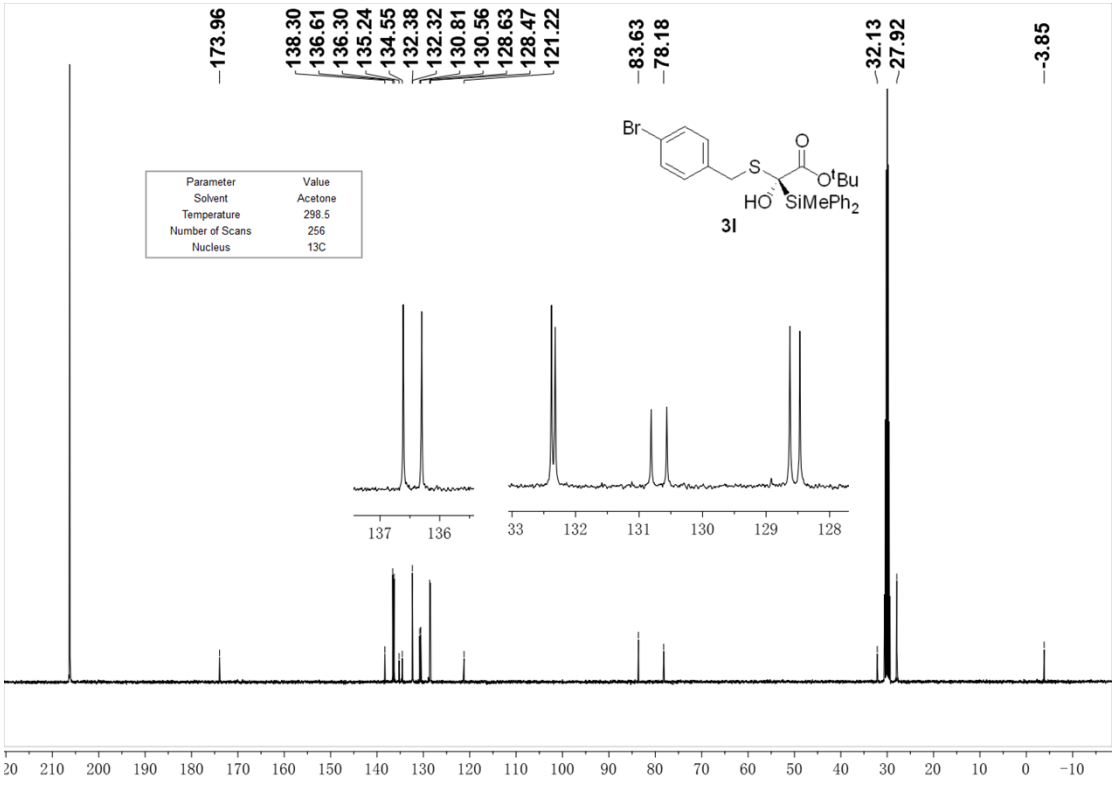

-117.37
Parameter Value
Solvent Acetone
Temperature 295.8
Number of Scans 16
Nucleus 19F
F
S
O
O^{t}Bu
HO SiMePh$_2$
3i
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210

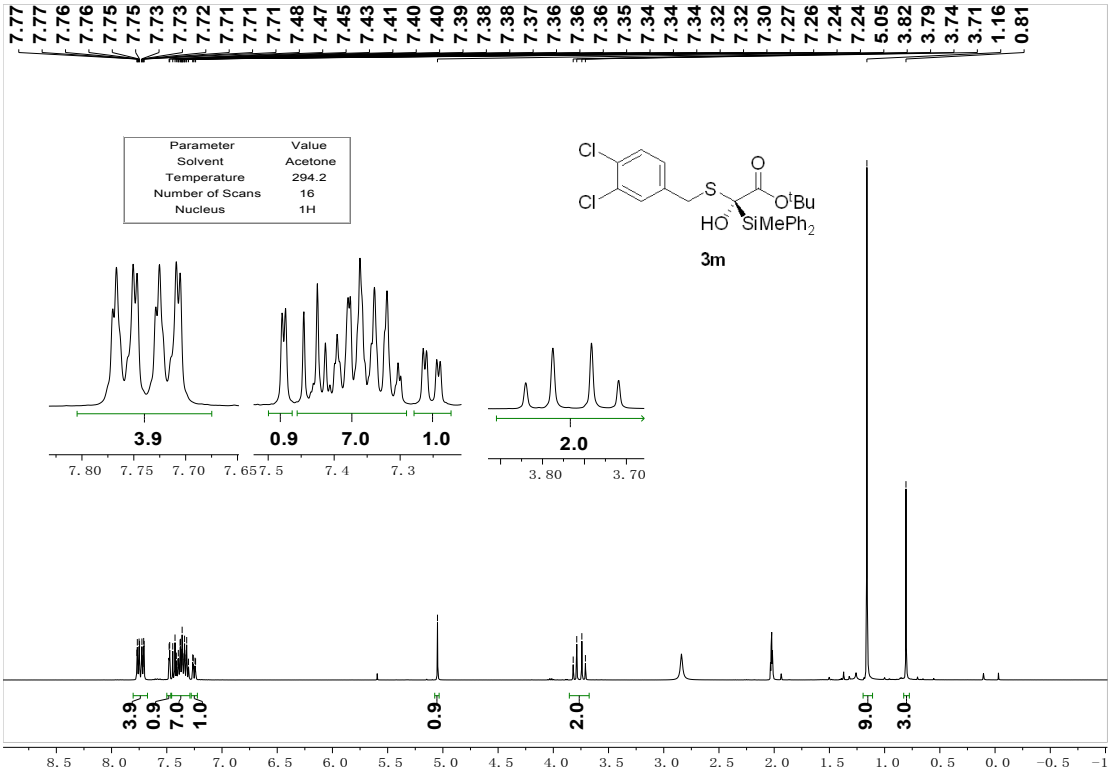

7.80 7.80 7.79 7.78 7.78 7.76 7.76 7.76 7.74 7.74 7.42 7.40 7.40 7.40 7.39 7.38 7.38 7.37 7.36 7.35 7.34 7.34 7.31 7.30 7.29 4.97 3.87 3.84 3.71 3.68
1.23 0.83
Parameter Value
Solvent Acetone
Temperature 298.5
Number of Scans 16
Nucleus 1H
Cl
S
O
O^{t}Bu
HO SiMePh$_2$
3j
4.1
6.1
4.0
1.1
1.0
4.1 6.1 4.0 1.0 1.1 1.0 9.0 3.1

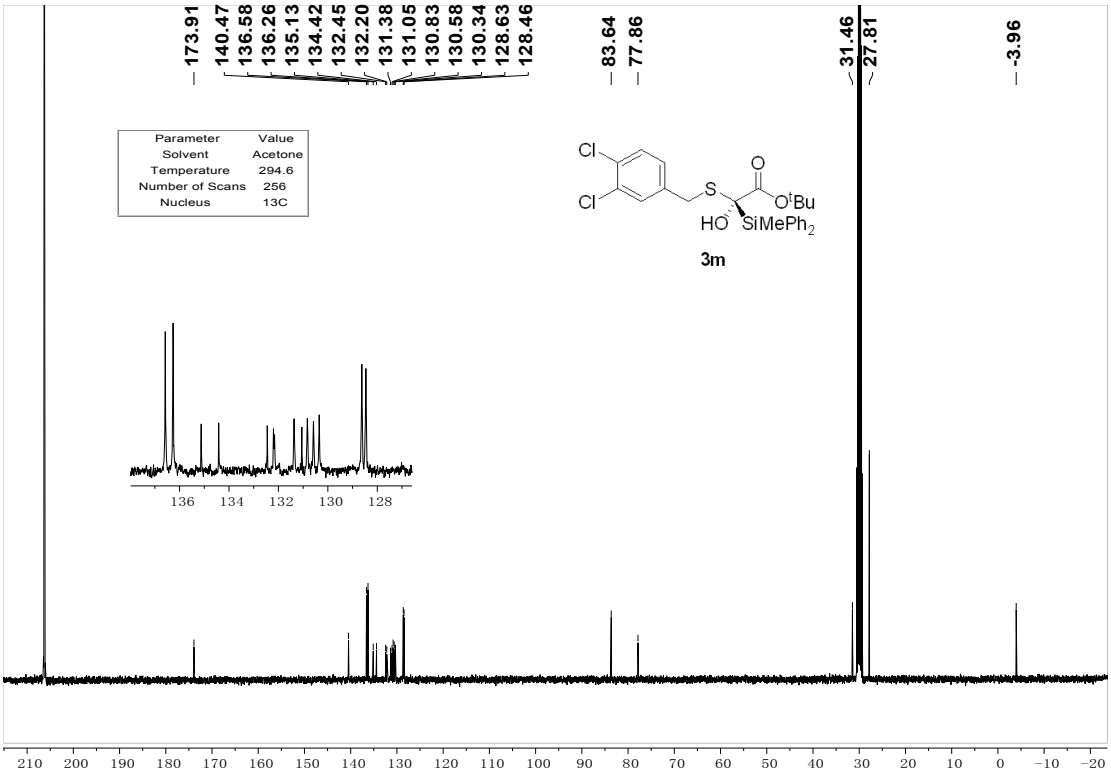

173.96
137.80 136.60 136.58 135.24 134.56 133.16 131.96 130.81 130.57 129.39 128.62 128.46
83.62 78.19
32.07 27.92
-3.86
Parameter Value
Solvent Acetone
Temperature 298.8
Number of Scans 256
Nucleus 13C
Cl
S
O
O^{t}Bu
HO SiMePh$_2$
3j

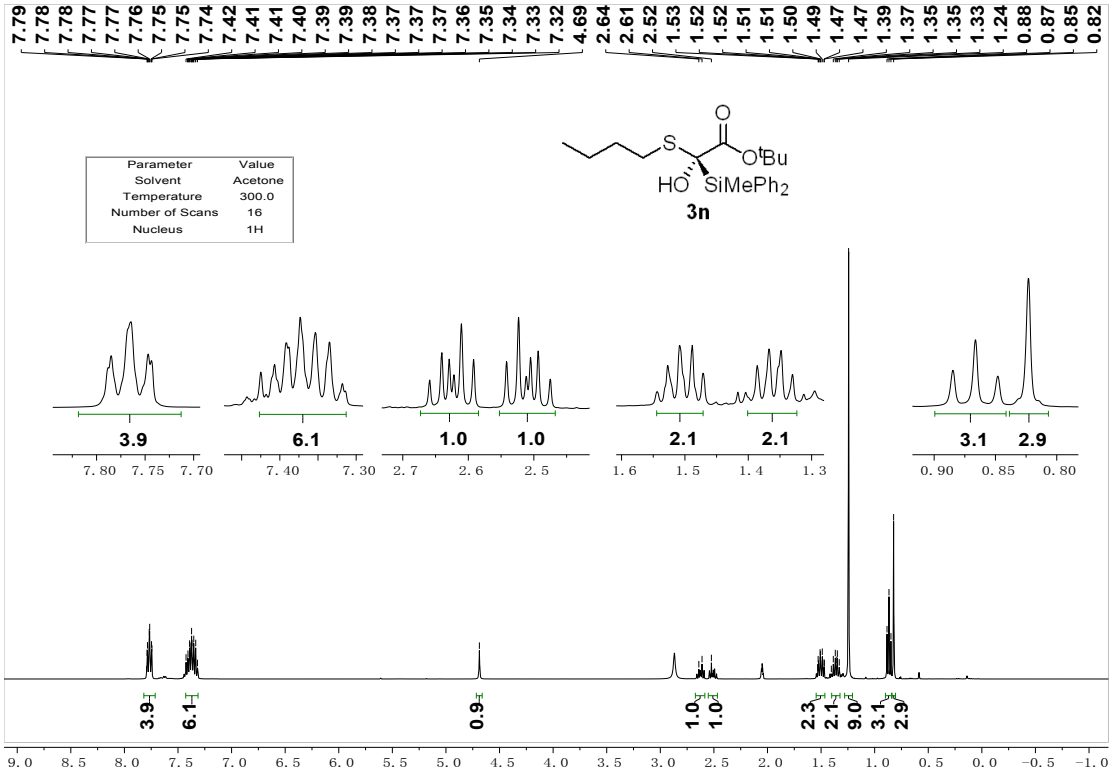

7.79 7.78 7.77 7.76 7.75 7.75 7.75 7.74 7.73 7.73 7.41 7.40 7.40 7.39 7.39 7.38 7.37 7.36 7.35 7.34 7.34 7.32 7.32 7.30 7.30 7.24 7.23 7.22 7.22 7.21 4.97 3.97 3.94 3.87 3.84 3.82 1.21 0.82
Parameter Value
Solvent Acetone
Temperature 0.0
Number of Scans 16
Nucleus 1H
3k
4.0 8.0 2.0 0.9 1.0 1.0 9.0 3.0
173.98 136.61 136.31 136.30 135.26 134.84 134.58 132.72 130.79 130.54 130.38 129.73 128.61 128.45 128.18 83.66 78.13 30.45 27.94 -3.85
Parameter Value
Solvent Acetone
Temperature 0.0
Number of Scans 256
Nucleus 13C
3k

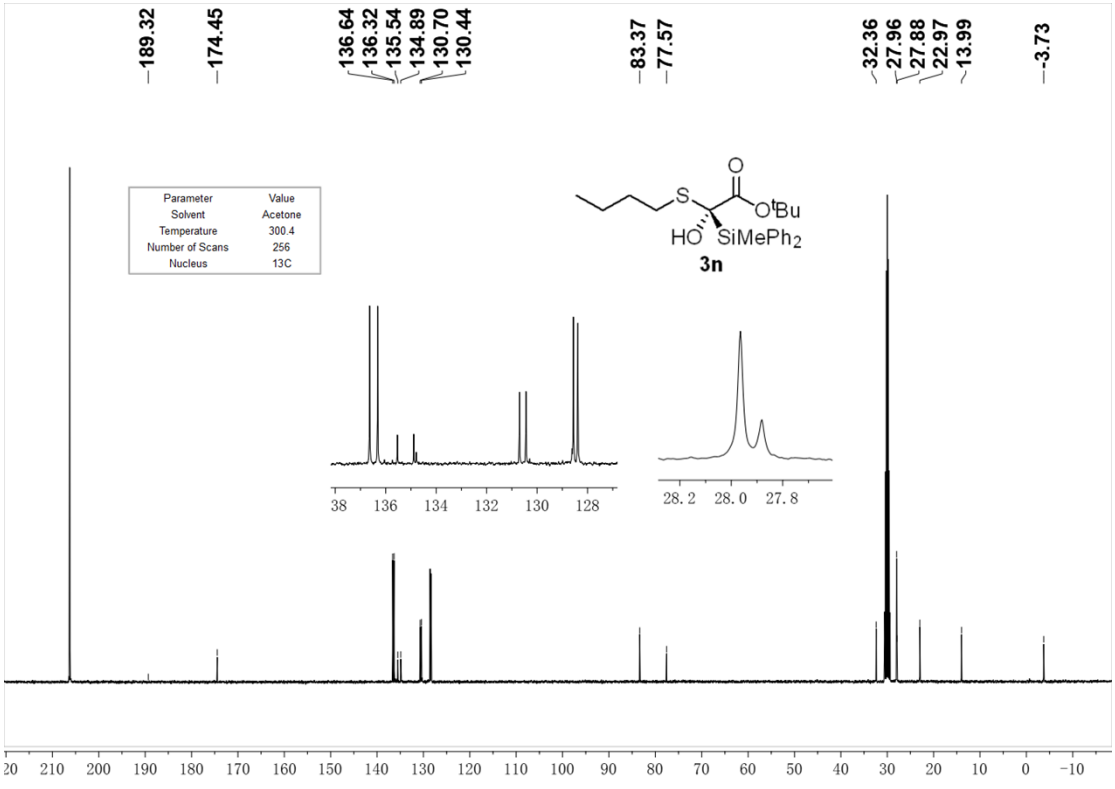

7.80 7.80 7.80 7.79 7.79 7.78 7.78 7.77 7.77 7.76 7.76 7.75 7.75 7.74 7.74 7.73 7.46 7.44 7.42 7.40 7.40 7.40 7.39 7.38 7.38 7.36 7.35 7.34 7.34 7.26 7.26 7.25 7.24 4.97 3.85 3.82 3.70 3.66 1.22 0.83
Parameter Value
Solvent Acetone
Temperature 298.6
Number of Scans 16
Nucleus 1H
Br
S
O
O'Bu
HO SiMePh2
3l
3.9
8.1
2.0
3.9 8.1 2.0 0.9 1.0 1.0 9.0 3.0

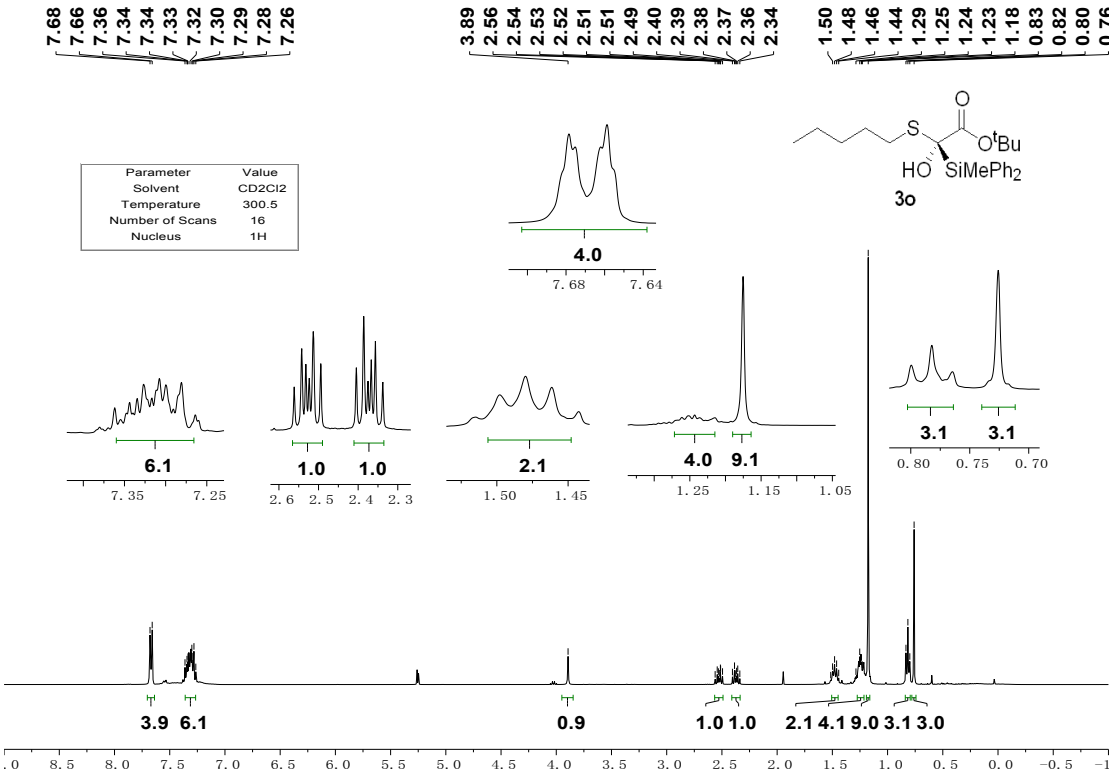

173.96
138.30 136.61 136.30 135.24 134.55 132.38 132.32 130.81 130.56 128.63 128.47 121.22
83.63 78.18
32.13 27.92
-3.85
Parameter Value
Solvent Acetone
Temperature 298.5
Number of Scans 256
Nucleus 13C
Br
S
O
O'Bu
HO SiMePh2
3l

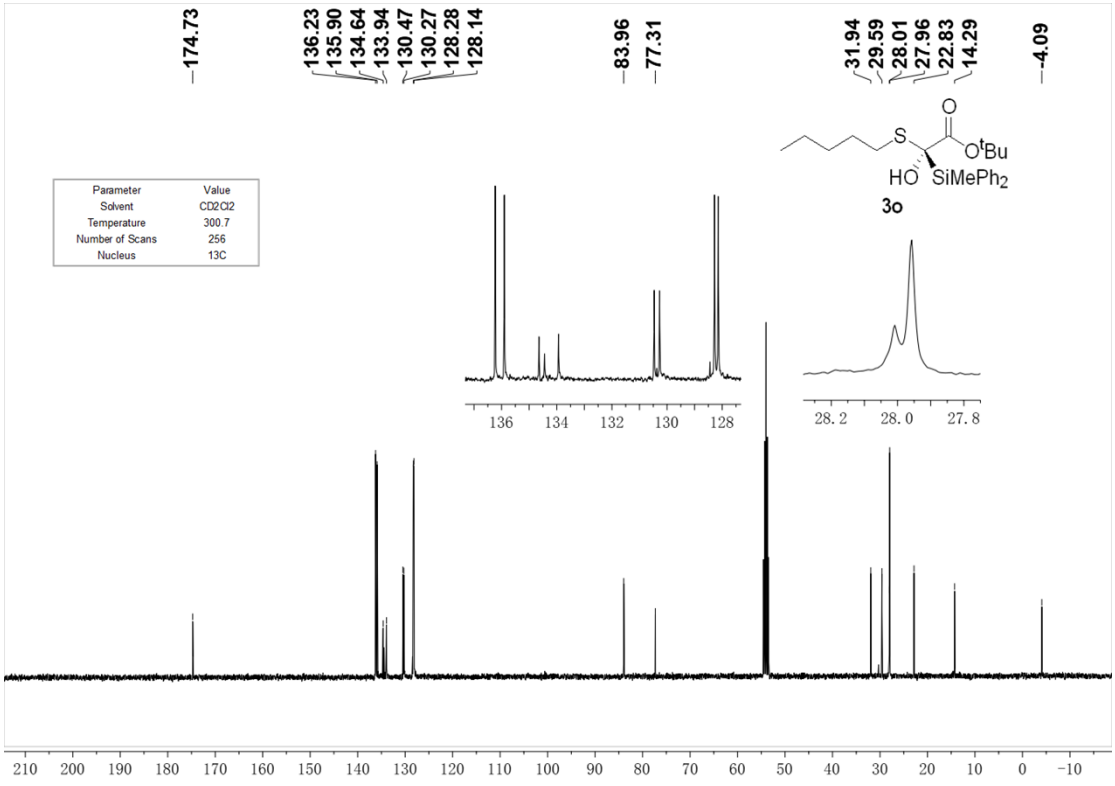

7.77 7.77 7.76 7.76 7.75 7.75 7.73 7.73 7.72 7.71 7.71 7.71 7.48 7.47 7.45 7.43 7.41 7.40 7.40 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.34 7.32 7.32 7.30 7.27 7.26 7.24 7.24 5.05 3.82 3.79 3.74 3.71 1.16 0.81
Parameter Value
Solvent Acetone
Temperature 294.2
Number of Scans 16
Nucleus 1H
3m
3.9 0.9 7.0 1.0 0.9 2.0 9.0 3.0

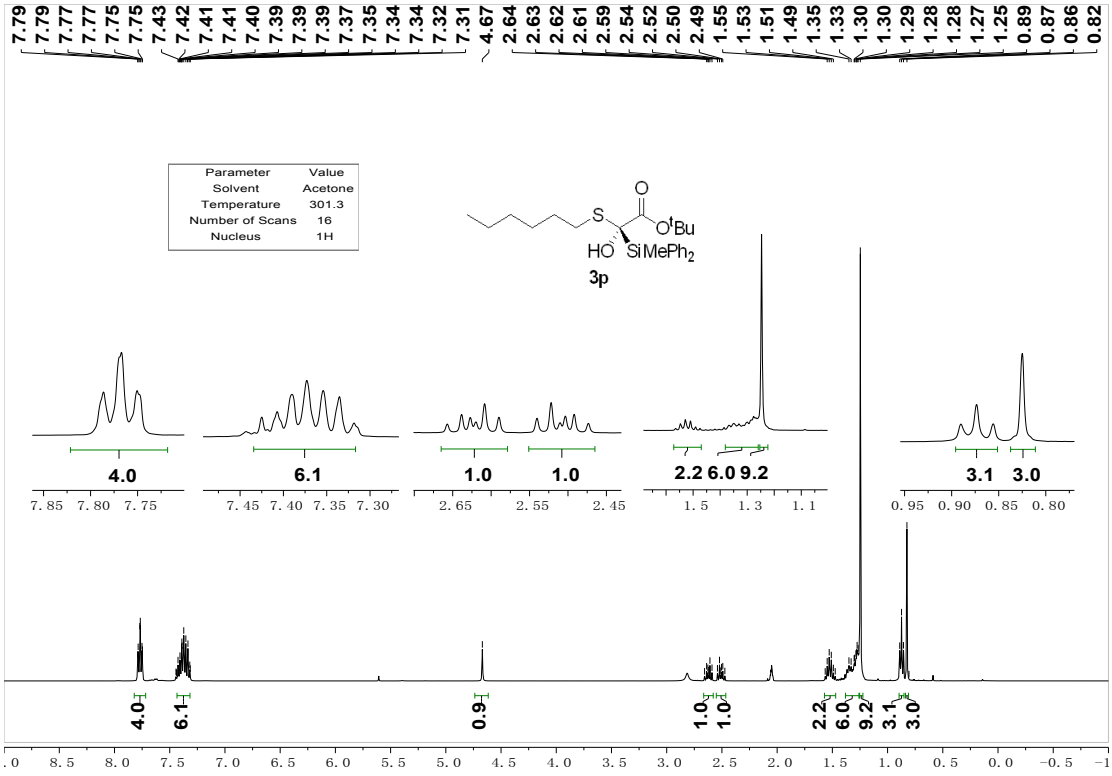

173.91 140.47 136.58 136.26 135.13 134.42 132.45 132.20 131.38 131.05 130.83 130.58 130.34 128.63 128.46 83.64 77.86 31.46 27.81 -3.96
Parameter Value
Solvent Acetone
Temperature 294.6
Number of Scans 256
Nucleus 13C
3m

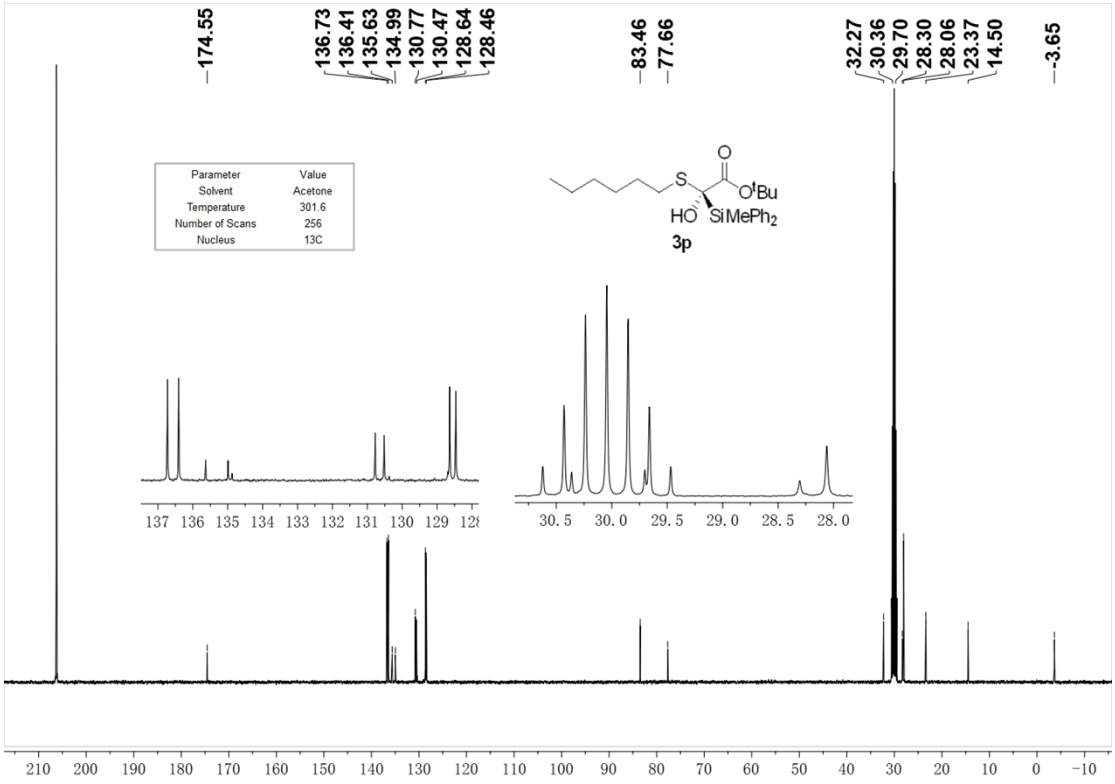

7.79 7.78 7.78 7.77 7.77 7.76 7.75 7.75 7.74 7.42 7.41 7.41 7.40 7.39 7.39 7.38 7.37 7.37 7.37 7.36 7.35 7.34 7.33 7.32 4.69 2.64 2.61 2.52 1.53 1.52 1.52 1.51 1.51 1.50 1.49 1.47 1.47 1.39 1.37 1.35 1.35 1.33 1.24 0.88 0.87 0.85 0.82
Parameter Value
Solvent Acetone
Temperature 300.0
Number of Scans 16
Nucleus 1H
3n
3.9 6.1 1.0 1.0 2.1 2.1 3.1 2.9
3.9 6.1 0.9 1.0 1.0 2.3 2.1 9.0 3.1 2.9

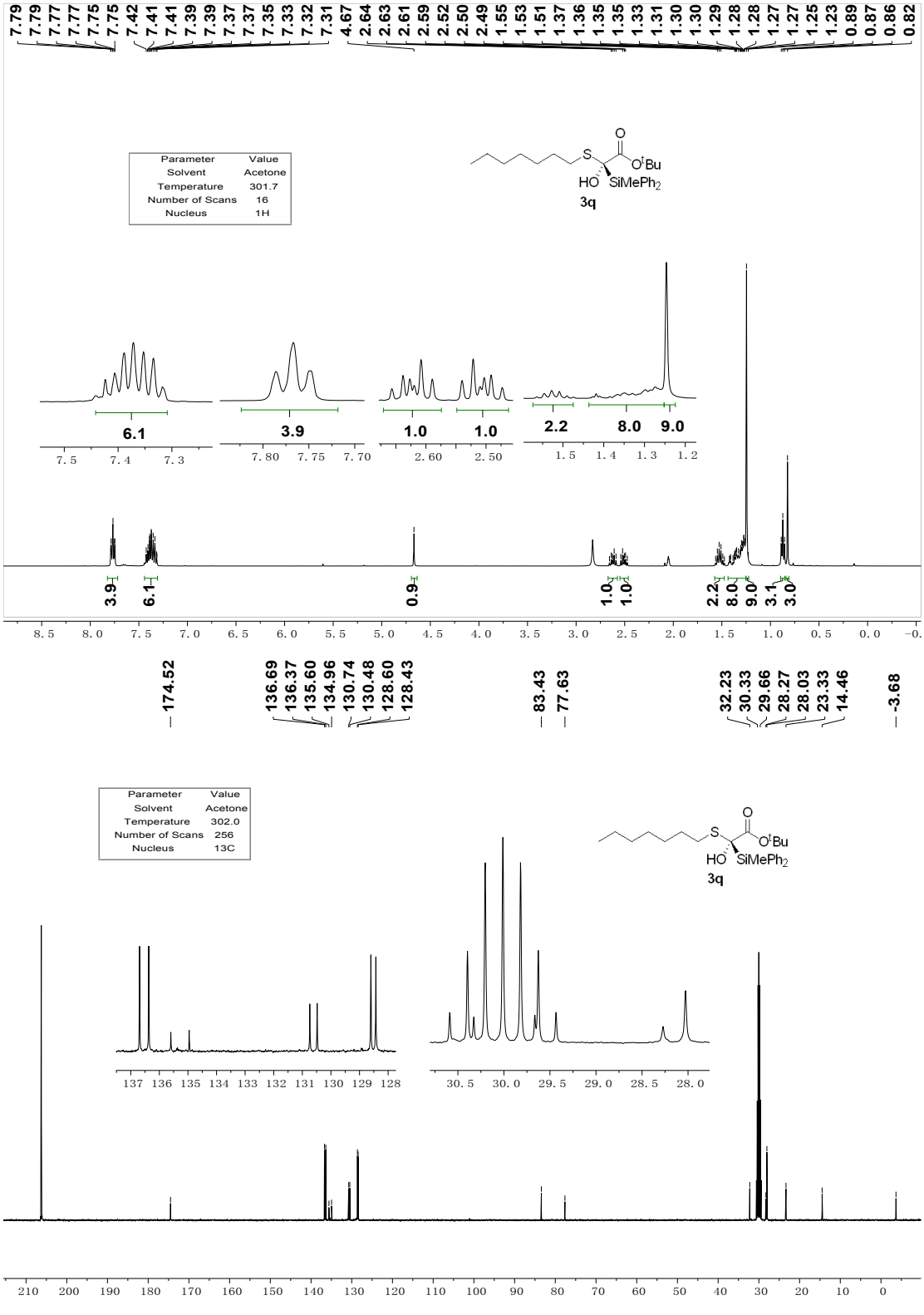

189.32 174.45 136.64 136.32 135.54 134.89 130.70 130.44 83.37 77.57 32.36 27.96 27.88 22.97 13.99 -3.73
Parameter Value
Solvent Acetone
Temperature 300.4
Number of Scans 256
Nucleus 13C
3n

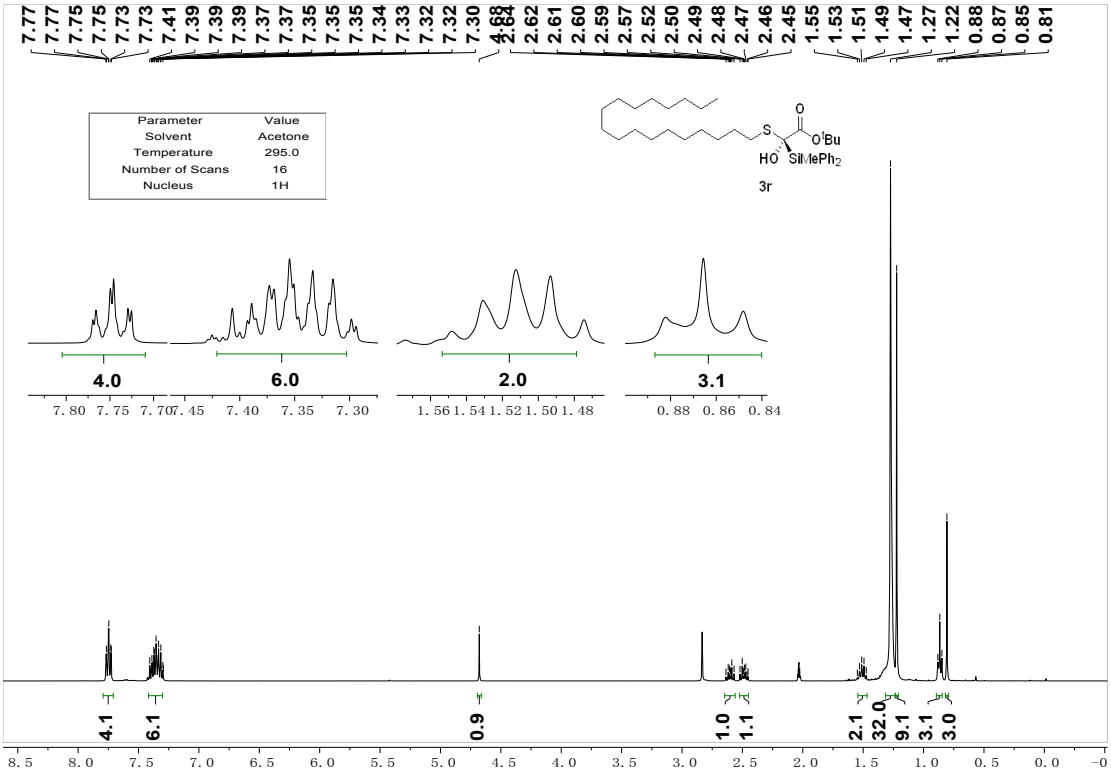

7.68 7.66 7.36 7.34 7.34 7.33 7.32 7.30 7.29 7.28 7.26
3.89 2.56 2.54 2.53 2.52 2.51 2.51 2.49 2.40 2.39 2.38 2.37 2.36 2.34
1.50 1.48 1.46 1.44 1.29 1.25 1.24 1.23 1.18 0.83 0.82 0.80
Parameter Value
Solvent CD2Cl2
Temperature 300.5
Number of Scans 16
Nucleus 1H
O
S
O^{t}Bu
HO SiMePh$_2$
3o
4.0
6.1
1.0 1.0
2.1
4.0 9.1
3.1 3.1
3.9 6.1 0.9 1.0 1.0 2.1 4.1 9.0 3.1 3.0

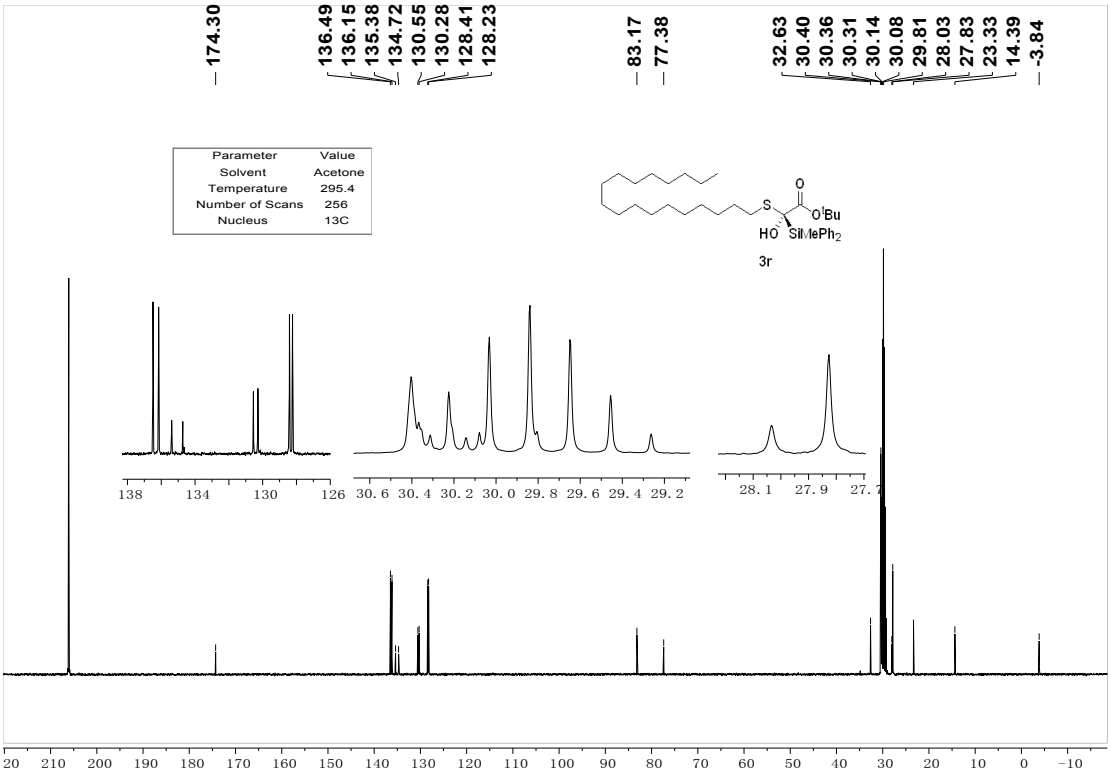

174.73
136.23 135.90 134.64 133.94 130.47 130.27 128.28 128.14
83.96 77.31
31.94 29.59 28.01 27.96 22.83 14.29
-4.09
Parameter Value
Solvent CD2Cl2
Temperature 300.7
Number of Scans 256
Nucleus 13C
O
S
O^{t}Bu
HO SiMePh$_2$
3o

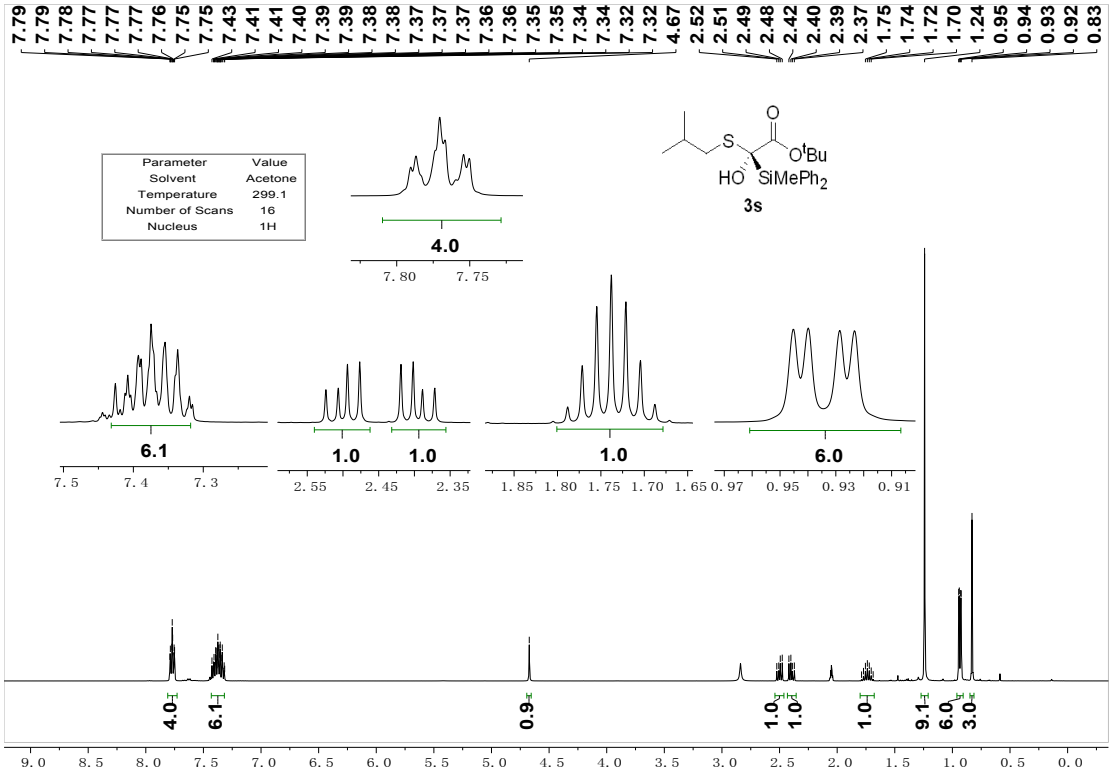

7.79 7.79 7.77 7.77 7.75 7.75 7.43 7.42 7.41 7.41 7.40 7.39 7.39 7.39 7.37 7.35 7.34 7.34 7.32 7.31 4.67 2.64 2.63 2.62 2.61 2.59 2.54 2.52 2.50 2.49 1.55 1.53 1.51 1.49 1.35 1.33 1.30 1.30 1.29 1.28 1.28 1.27 1.25 0.89 0.87 0.86 0.82
Parameter Value
Solvent Acetone
Temperature 301.3
Number of Scans 16
Nucleus 1H
O
S
O^{t}Bu
HO SiMePh$_2$
3p
4.0
6.1
1.0
1.0
2.2 6.0 9.2
3.1 3.0
4.0 6.1 0.9 1.0 1.0 2.2 6.0 9.2 3.1 3.0

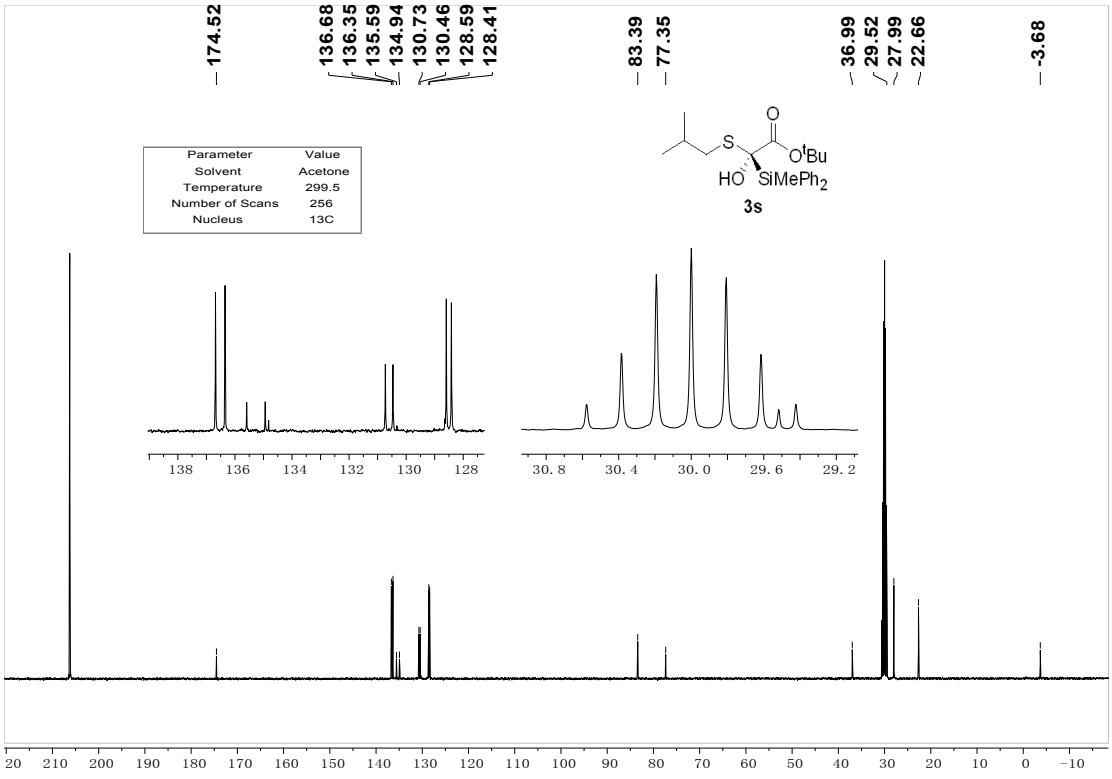

174.55
136.73 136.41 135.63 134.99 130.77 130.47 128.64 128.46
83.46 77.66
32.27 30.36 29.70 28.30 28.06 23.37 14.50
-3.65
Parameter Value
Solvent Acetone
Temperature 301.6
Number of Scans 256
Nucleus 13C
O
S
O^{t}Bu
HO SiMePh$_2$
3p

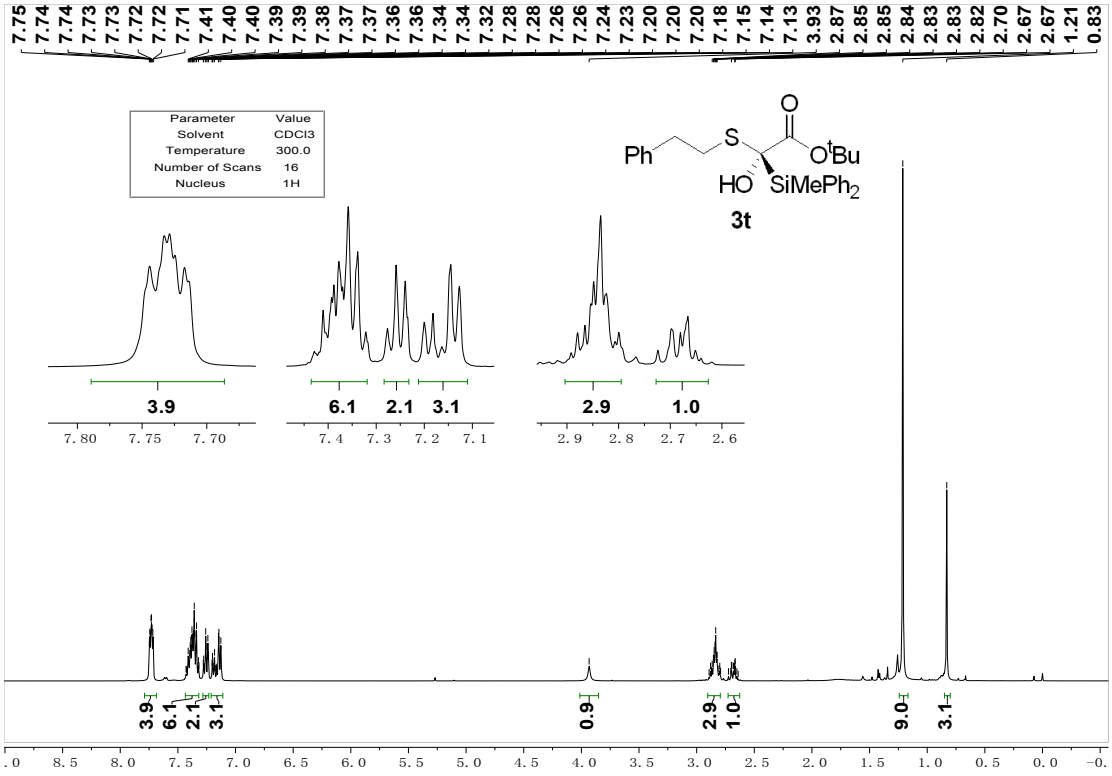

Parameter Value
Solvent Acetone
Temperature 301.7
Number of Scans 16
Nucleus 1H
3q
Parameter Value
Solvent Acetone
Temperature 302.0
Number of Scans 256
Nucleus 13C
3q

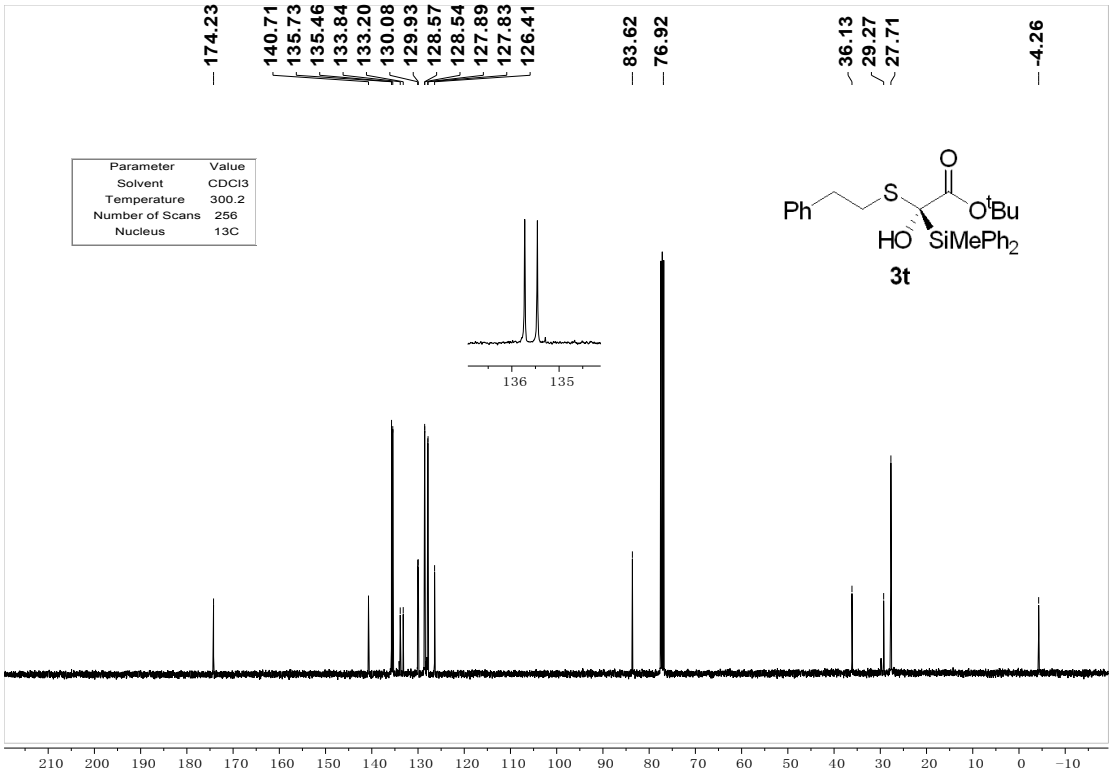

7.77 7.77 7.75 7.75 7.73 7.73 7.41 7.39 7.39 7.39 7.37 7.37 7.35 7.35 7.35 7.34 7.33 7.32 7.32 7.30 4.68 4.64 2.62 2.61 2.60 2.59 2.57 2.52 2.50 2.49 2.48 2.47 2.46 2.45 1.55 1.53 1.51 1.49 1.47 1.27 1.22 0.88 0.87 0.85 0.81
Parameter Value
Solvent Acetone
Temperature 295.0
Number of Scans 16
Nucleus 1H
3r
4.0
6.0
2.0
3.1
4.1 6.1 0.9 1.0 1.1 2.1 32.0 9.1 3.1 3.0

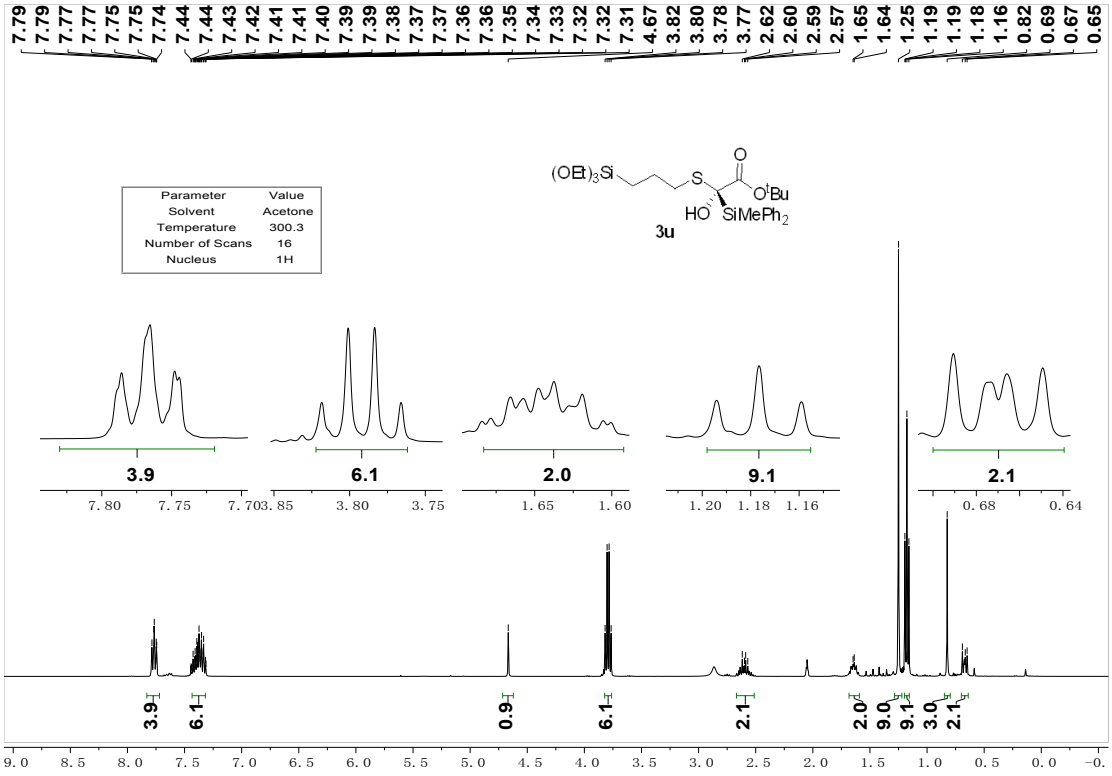

174.30 136.49 136.15 135.38 134.72 130.55 130.28 128.41 128.23 83.17 77.38 32.63 30.40 30.36 30.31 30.14 30.08 29.81 28.03 27.83 23.33 14.39 -3.84
Parameter Value
Solvent Acetone
Temperature 295.4
Number of Scans 256
Nucleus 13C
3r

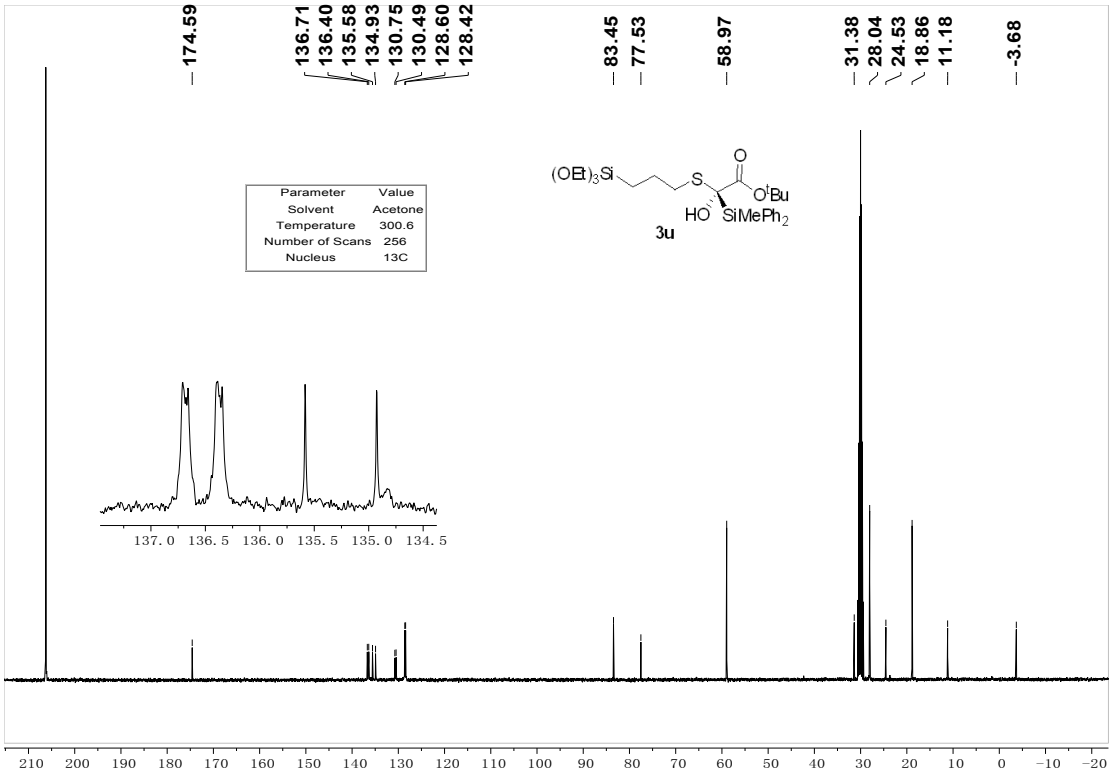

7.79 7.79 7.78 7.77 7.77 7.77 7.76 7.75 7.75 7.43 7.41 7.41 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.32 7.32 4.67 2.52 2.51 2.49 2.48 2.42 2.40 2.39 2.37 1.75 1.74 1.72 1.70 1.24 0.95 0.94 0.93 0.92 0.83
Parameter Value
Solvent Acetone
Temperature 299.1
Number of Scans 16
Nucleus 1H
3s
4.0
6.1
1.0
1.0
1.0
6.0
4.0 6.1 0.9 1.0 1.0 1.0 9.1 6.0 3.0

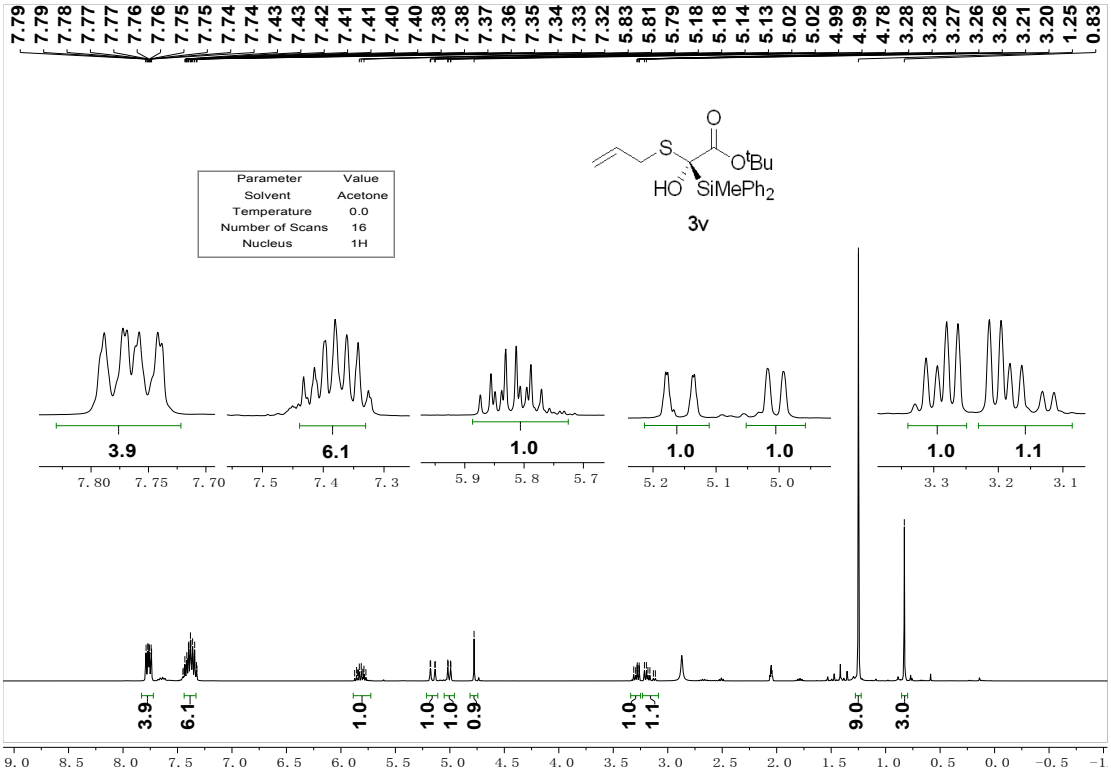

174.52 136.68 136.35 135.59 134.94 130.73 130.46 128.59 128.41 83.39 77.35 36.99 29.52 27.99 22.66 -3.68
Parameter Value
Solvent Acetone
Temperature 299.5
Number of Scans 256
Nucleus 13C
3s

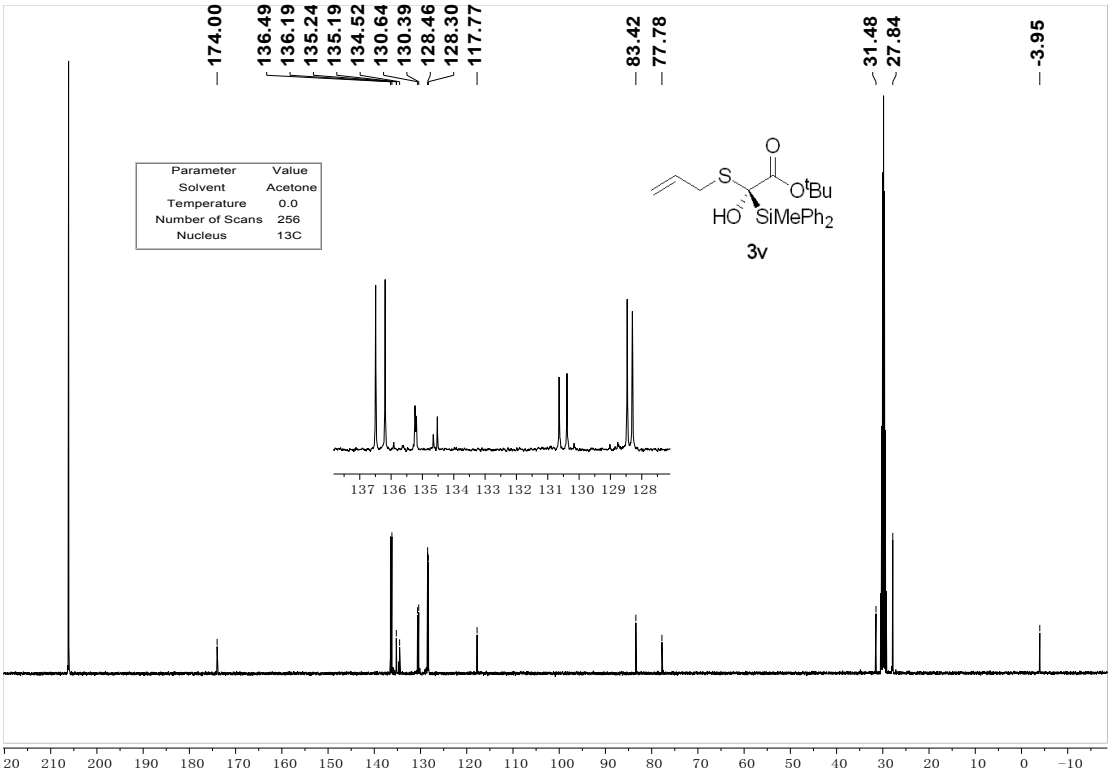

7.75 7.74 7.74 7.73 7.73 7.72 7.72 7.71 7.41 7.40 7.40 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.34 7.34 7.32 7.28 7.28 7.26 7.26 7.24 7.23 7.20 7.20 7.20 7.18 7.15 7.14 7.13 3.93 2.87 2.85 2.85 2.84 2.83 2.83 2.82 2.70 2.67 2.67 1.21 0.83
Parameter Value
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Nucleus 1H
Ph
S
O
O^{t}Bu
HO
SiMePh$_2$
3t
3.9
6.1 2.1 3.1
2.9 1.0
3.9 6.1 2.1 3.1 0.9 2.9 1.0 9.0 3.1

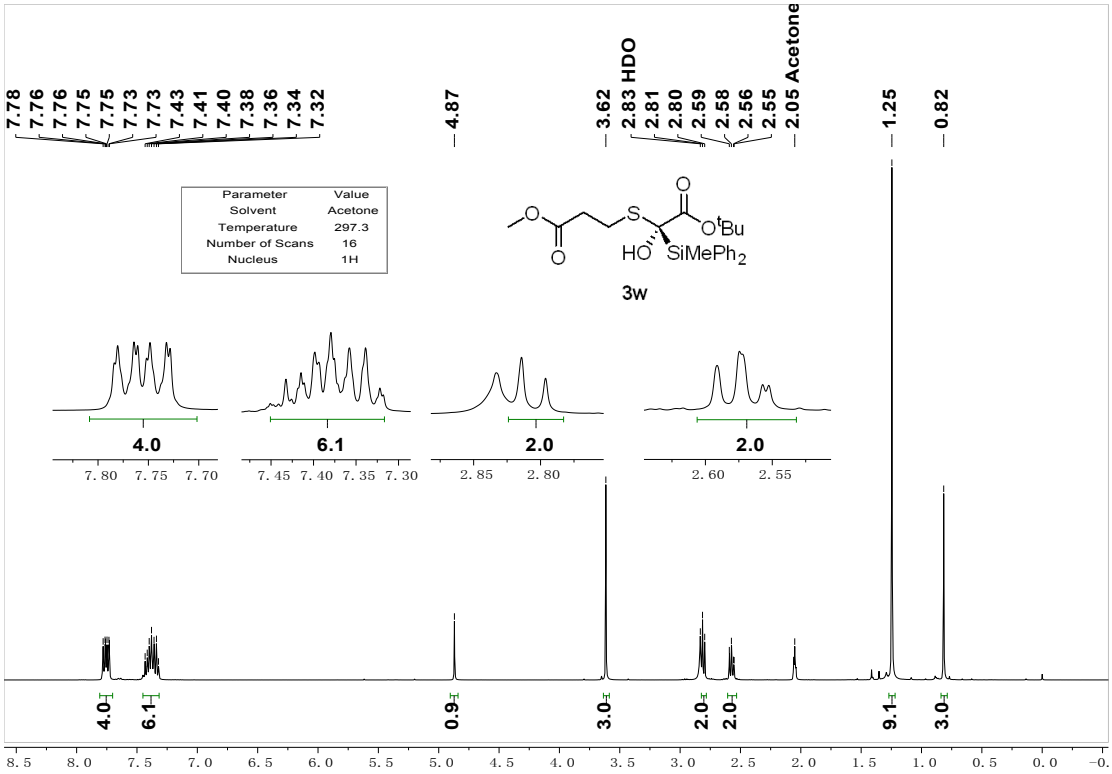

174.23 140.71 135.73 135.46 133.84 133.20 130.08 129.93 128.57 128.54 127.89 127.83 126.41 83.62 76.92 36.13 29.27 27.71 -4.26
Parameter Value
Solvent CDCl3
Temperature 300.2
Number of Scans 256
Nucleus 13C
Ph
S
O
O^{t}Bu
HO
SiMePh$_2$
3t

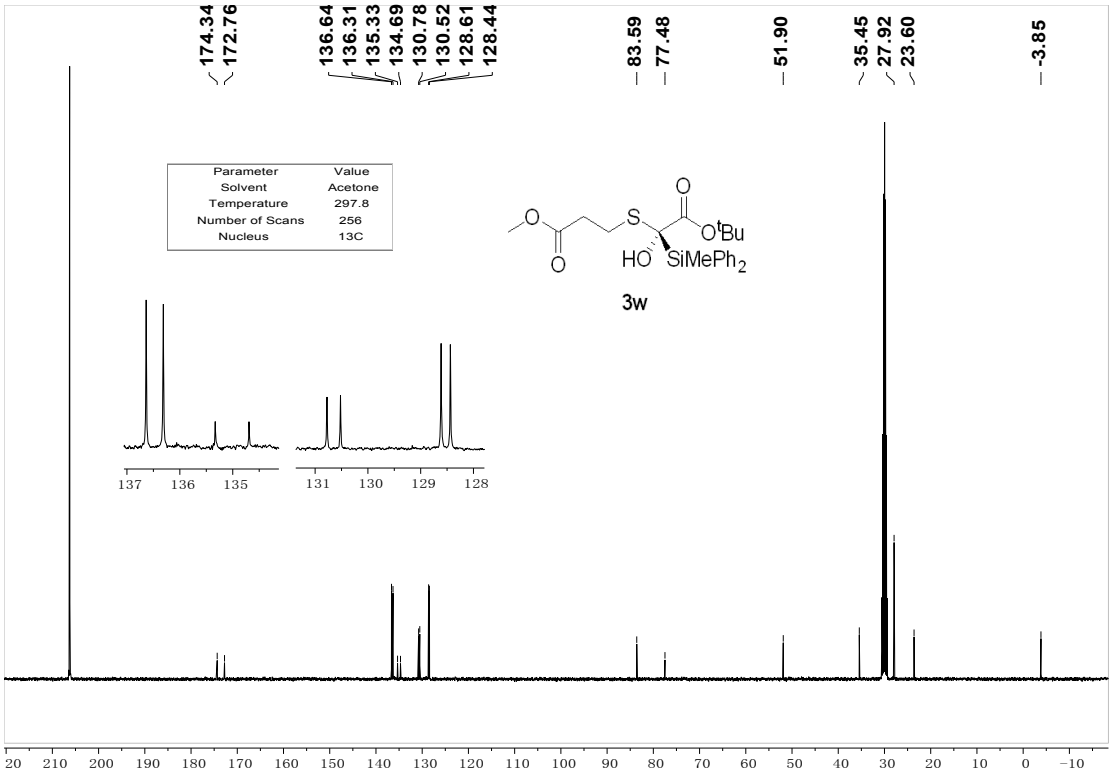

7.79 7.79 7.77 7.77 7.75 7.75 7.74 7.44 7.44 7.43 7.42 7.41 7.41 7.40 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.33 7.32 7.32 7.31 4.67 3.82 3.80 3.78 3.77 2.62 2.60 2.59 2.57 1.65 1.64 1.25 1.19 1.19 1.18 1.16 0.82 0.69 0.67 0.65
Parameter Value
Solvent Acetone
Temperature 300.3
Number of Scans 16
Nucleus 1H
3u
3.9
6.1
2.0
9.1
2.1
3.9 6.1 0.9 6.1 2.1 2.0 9.0 9.1 3.0 2.1

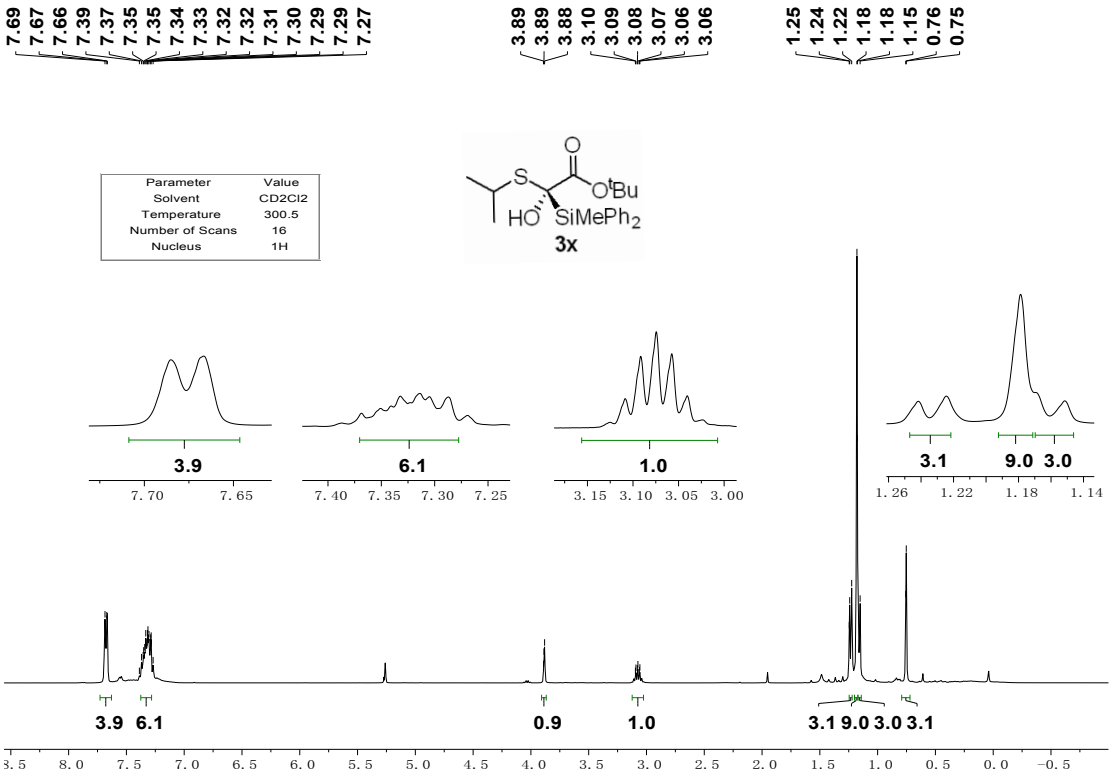

174.59
136.71 136.40 135.58 134.93 130.75 130.49 128.60 128.42
83.45 77.53 58.97
31.38 28.04 24.53 18.86 11.18 -3.68
Parameter Value
Solvent Acetone
Temperature 300.6
Number of Scans 256
Nucleus 13C
3u

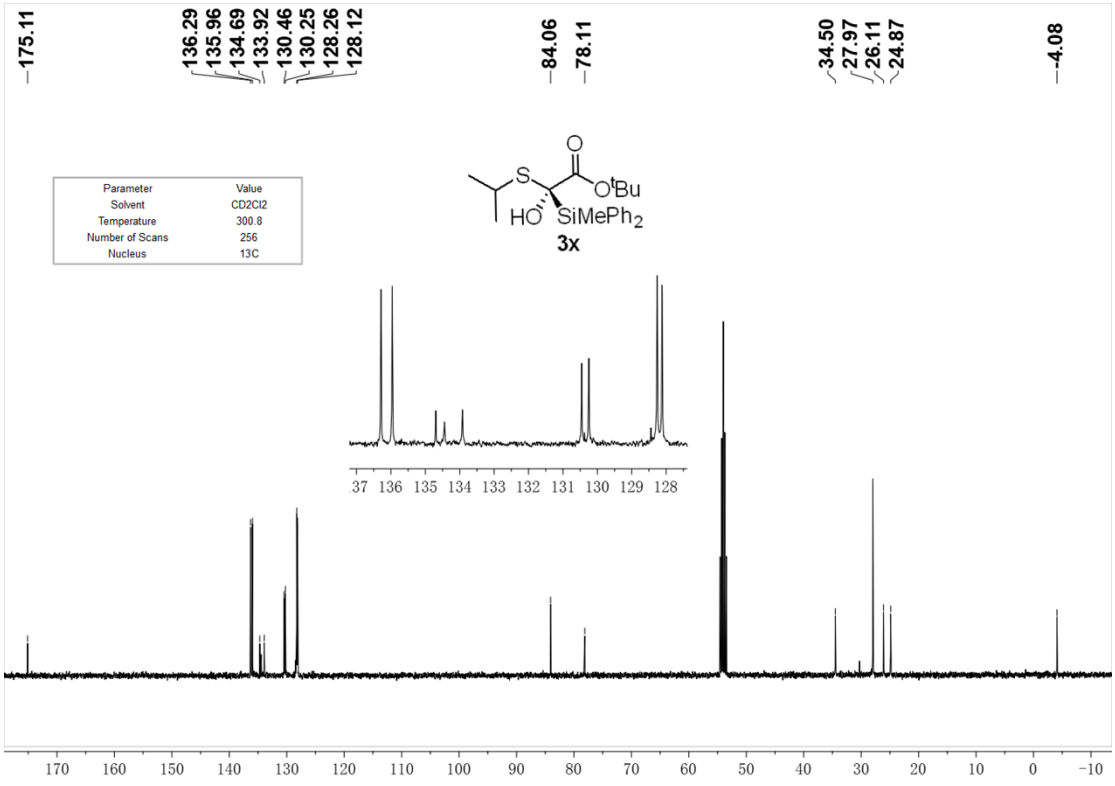

7.79 7.79 7.78 7.77 7.77 7.76 7.76 7.75 7.75 7.74 7.74 7.43 7.43 7.42 7.41 7.41 7.40 7.40 7.38 7.38 7.37 7.36 7.35 7.34 7.33 7.32 5.83 5.81 5.79 5.18 5.18 5.14 5.13 5.02 5.02 4.99 4.99 4.78 3.28 3.28 3.27 3.26 3.26 3.21 3.20 1.25 0.83
Parameter Value
Solvent Acetone
Temperature 0.0
Number of Scans 16
Nucleus 1H
O
S
O^{t}Bu
HO SiMePh$_2$
3v
3.9
6.1
1.0
1.0
1.0
1.0
1.1
3.9
6.1
1.0
1.0
1.0
0.9
1.0
1.1
9.0
3.0

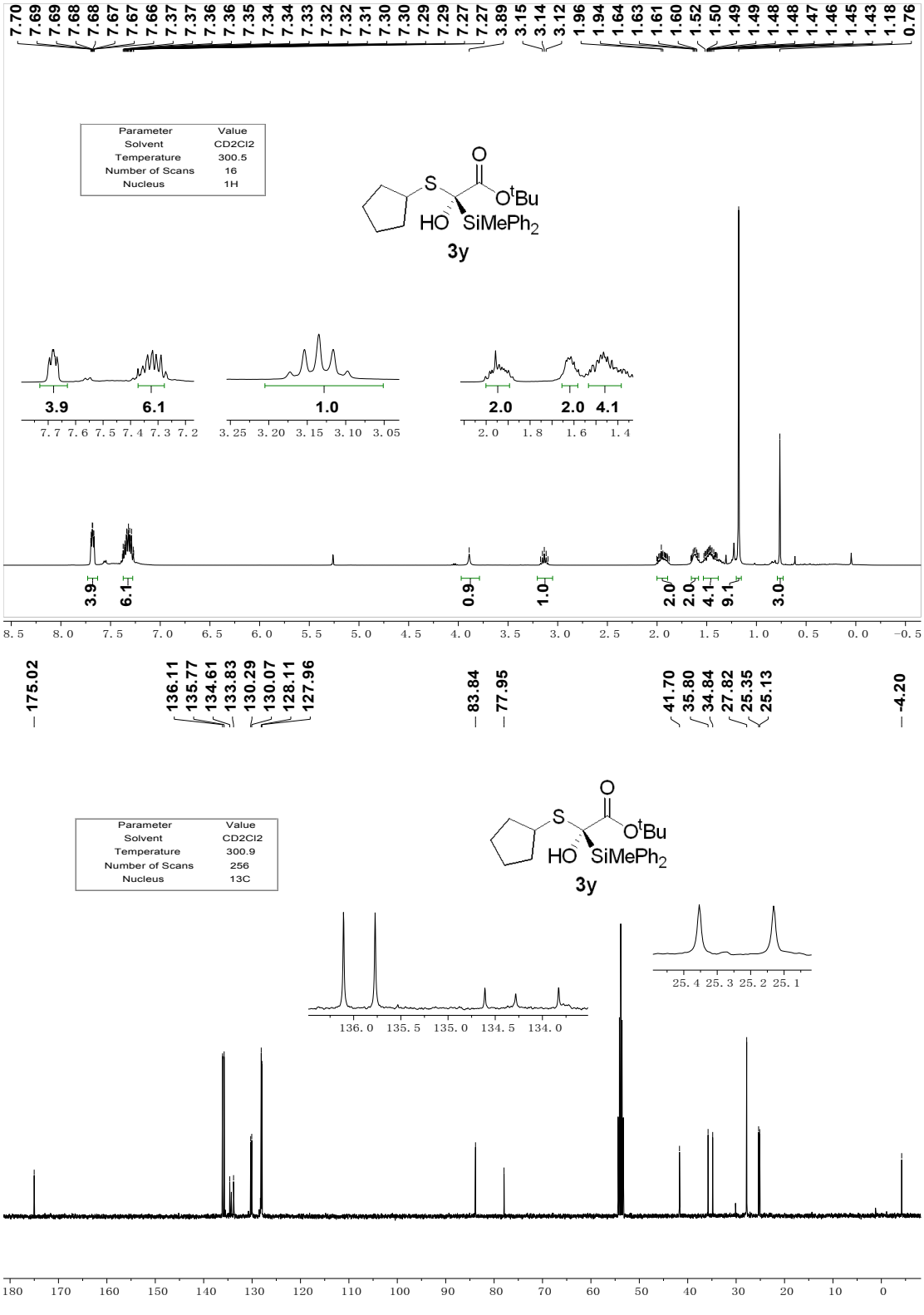

174.00 136.49 136.19 135.24 135.19 134.52 130.64 130.39 128.46 128.30 117.77 83.42 77.78 31.48 27.84 -3.95
Parameter Value
Solvent Acetone
Temperature 0.0
Number of Scans 256
Nucleus 13C
O
S
O^{t}Bu
HO SiMePh$_2$
3v

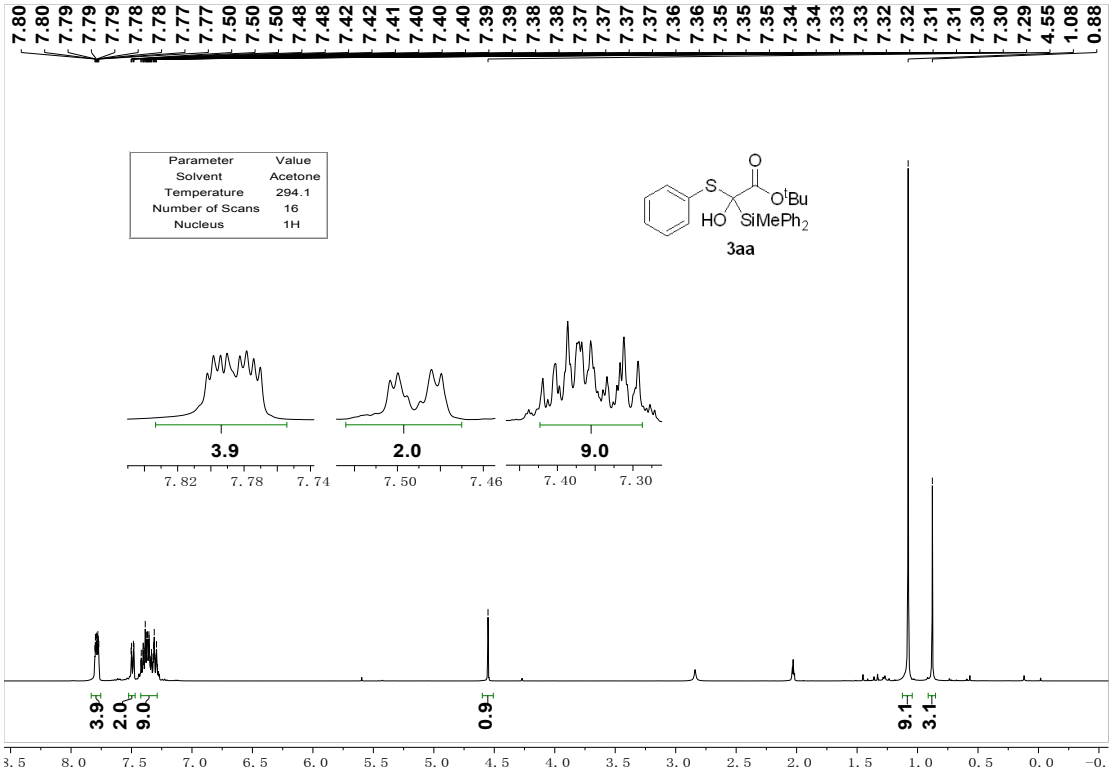

7.78
7.76
7.76
7.75
7.75
7.73
7.73
7.43
7.41
7.40
7.38
7.36
7.34
7.32
4.87
3.62
2.83 HDO
2.81
2.80
2.59
2.58
2.56
2.55
2.05 Acetone
1.25
0.82
Parameter Value
Solvent Acetone
Temperature 297.3
Number of Scans 16
Nucleus 1H
3w
4.0
6.1
2.0
2.0
4.0
6.1
0.9
3.0
2.0
2.0
9.1
3.0

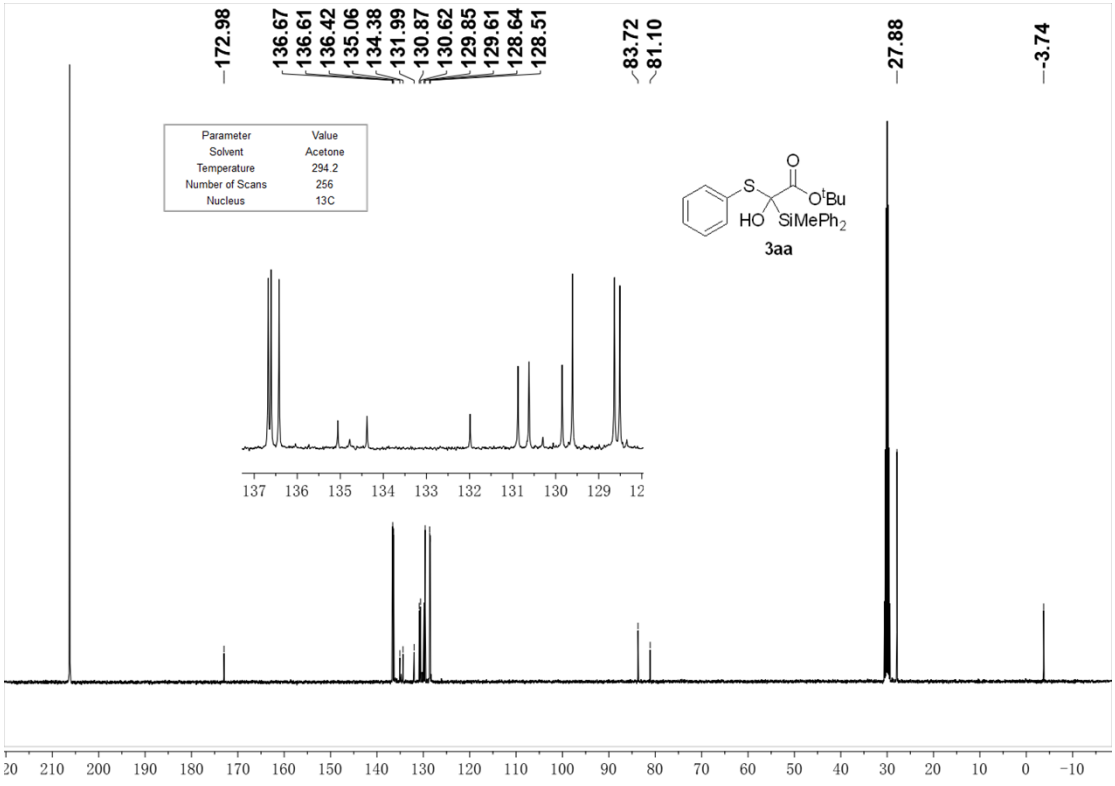

174.34
172.76
136.64
136.31
135.33
134.69
130.78
130.52
128.61
128.44
83.59
77.48
51.90
35.45
27.92
23.60
-3.85
Parameter Value
Solvent Acetone
Temperature 297.8
Number of Scans 256
Nucleus 13C
3w

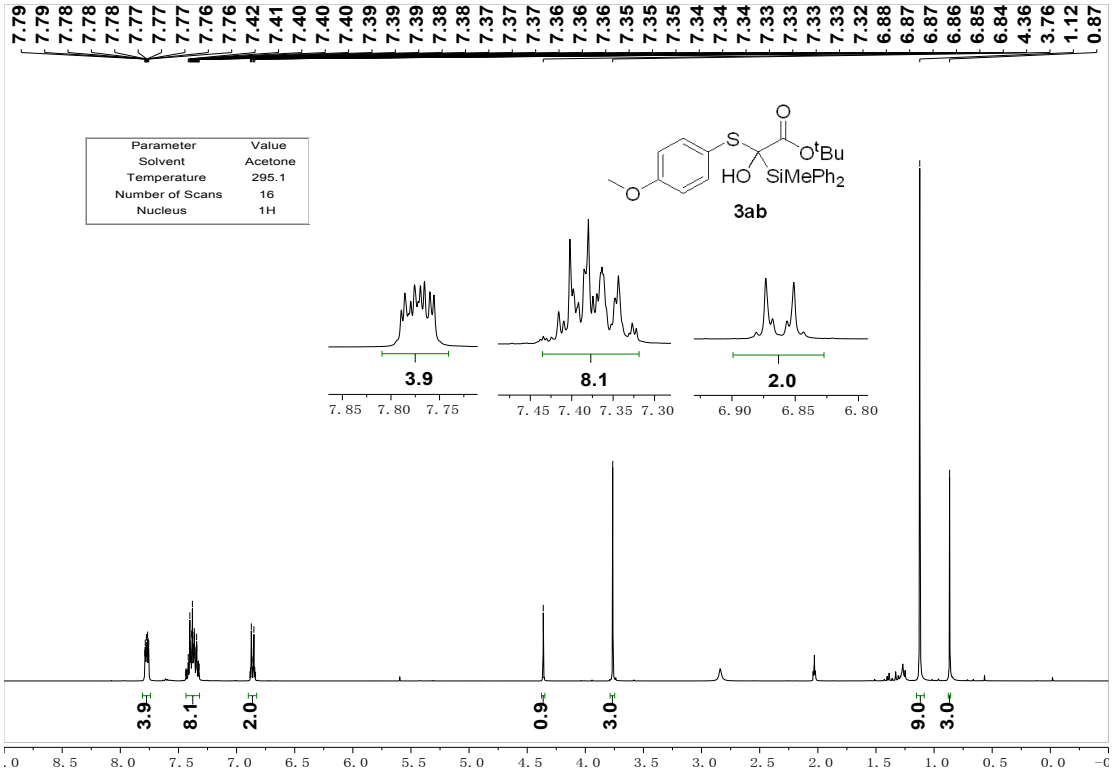

7.69 7.67 7.66 7.39 7.37 7.35 7.35 7.34 7.33 7.32 7.32 7.31 7.30 7.29 7.29 7.27
3.89 3.89 3.88 3.10 3.09 3.08 3.07 3.06 3.06
1.25 1.24 1.22 1.18 1.18 1.15 0.76 0.75
Parameter Value
Solvent CD2Cl2
Temperature 300.5
Number of Scans 16
Nucleus 1H
3x
3.9 6.1 0.9 1.0 3.1 9.0 3.0 3.1

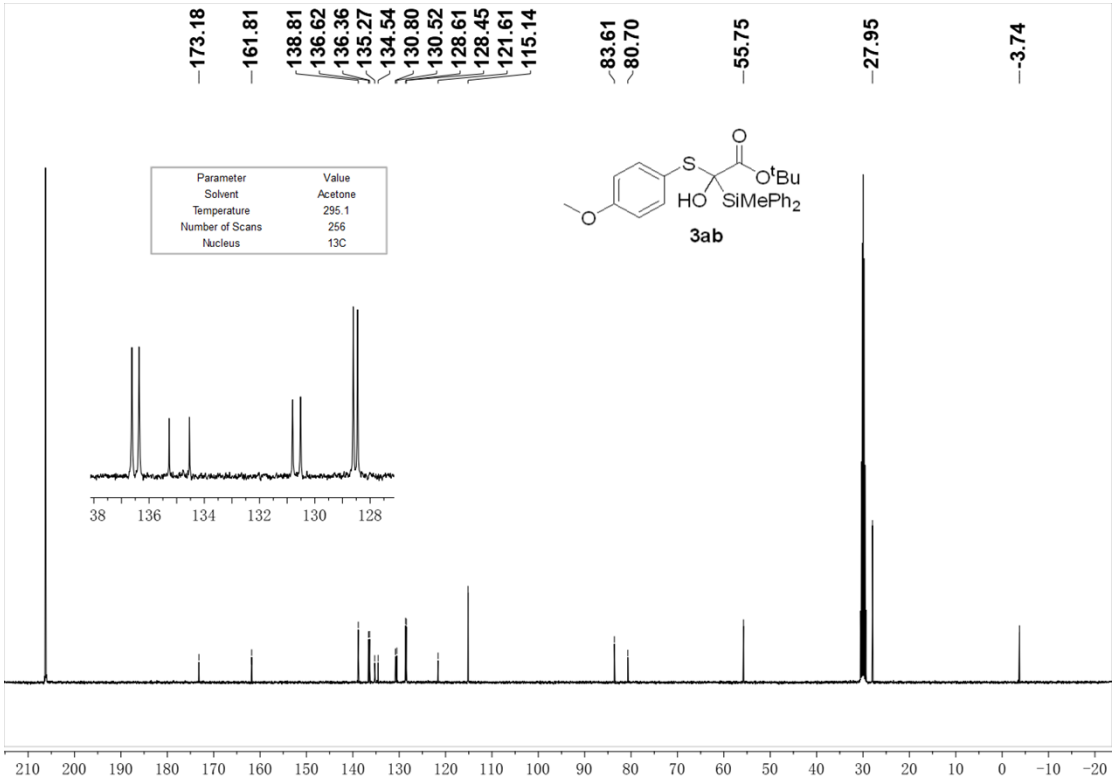

175.11
136.29 135.96 134.69 133.92 130.46 130.25 128.26 128.12
84.06 78.11
34.50 27.97 26.11 24.87
-4.08
Parameter Value
Solvent CD2Cl2
Temperature 300.8
Number of Scans 256
Nucleus 13C
3x

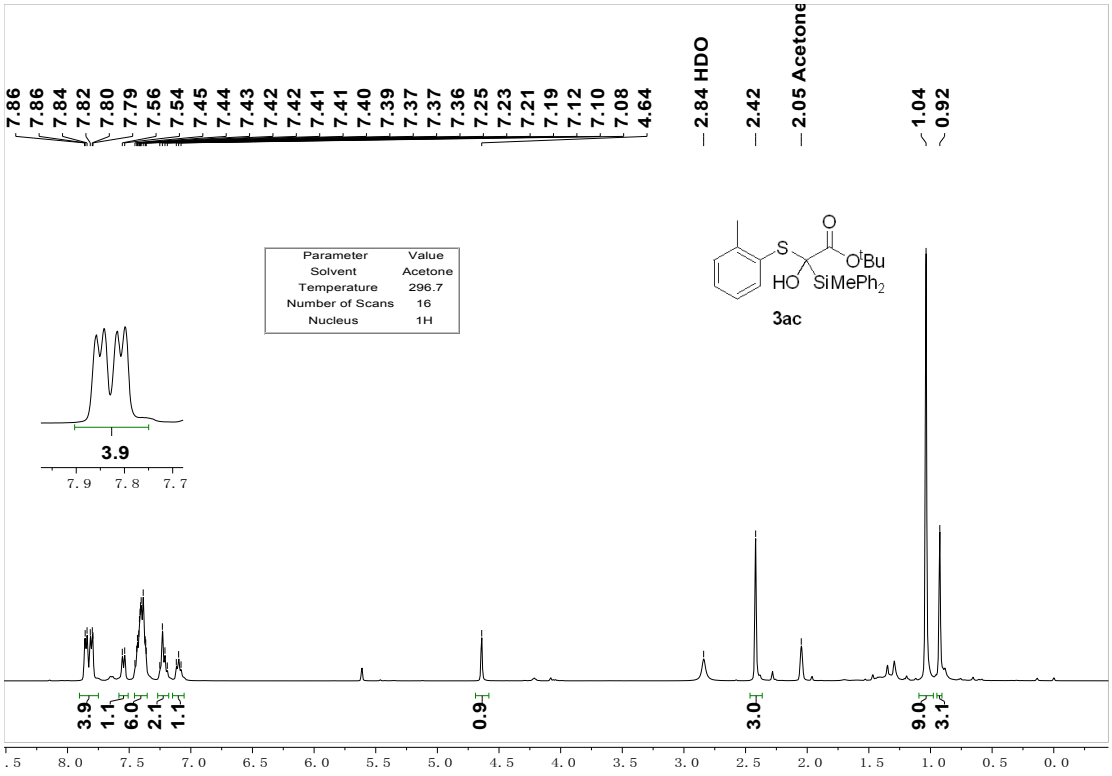

7.70 7.69 7.69 7.68 7.68 7.67 7.67 7.66 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.27 7.27 3.89 3.15 3.14 3.12 1.96 1.94 1.64 1.63 1.61 1.60 1.52 1.50 1.49 1.49 1.48 1.48 1.47 1.46 1.45 1.43 1.18 0.76
Parameter Value
Solvent CD2Cl2
Temperature 300.5
Number of Scans 16
Nucleus 1H
3y
3.9 6.1 1.0 2.0 2.0 4.1
3.9 6.1 0.9 1.0 2.0 2.0 4.1 9.1 3.0
175.02 136.11 135.77 134.61 133.83 130.29 130.07 128.11 127.96 83.84 77.95 41.70 35.80 34.84 27.82 25.35 25.13 -4.20
Parameter Value
Solvent CD2Cl2
Temperature 300.9
Number of Scans 256
Nucleus 13C
3y

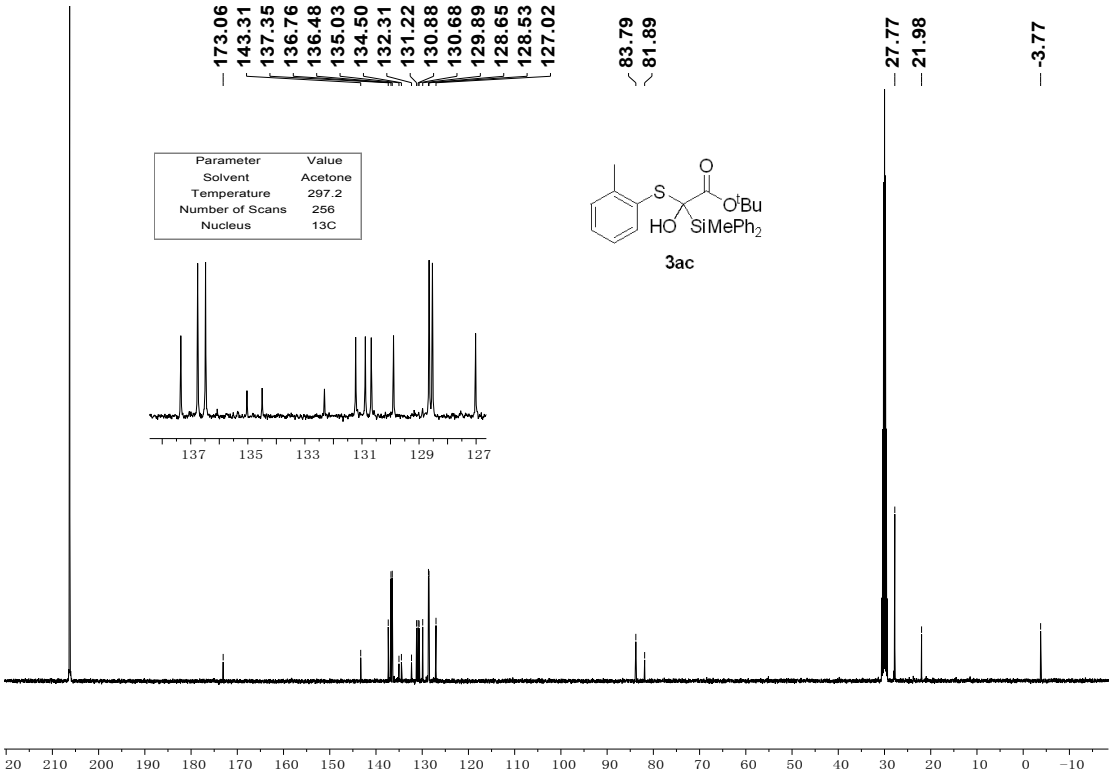

7.80 7.80 7.79 7.79 7.79 7.78 7.78 7.77 7.77 7.50 7.50 7.48 7.48 7.42 7.42 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 4.55 1.08 0.88
Parameter Value
Solvent Acetone
Temperature 294.1
Number of Scans 16
Nucleus 1H
3aa
3.9
2.0
9.0
3.9 2.0 9.0 0.9 9.1 3.1

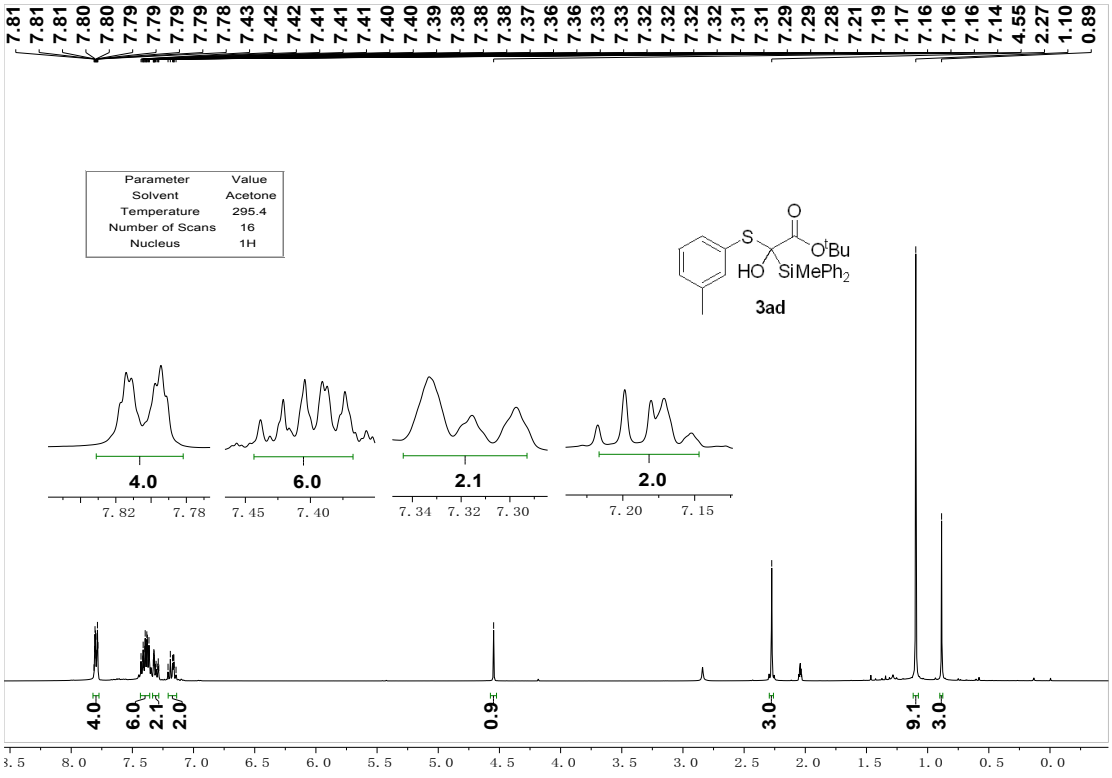

172.98 136.67 136.61 136.42 135.06 134.38 131.99 130.87 130.62 129.85 129.61 128.64 128.51 83.72 81.10 27.88 -3.74
Parameter Value
Solvent Acetone
Temperature 294.2
Number of Scans 256
Nucleus 13C
3aa

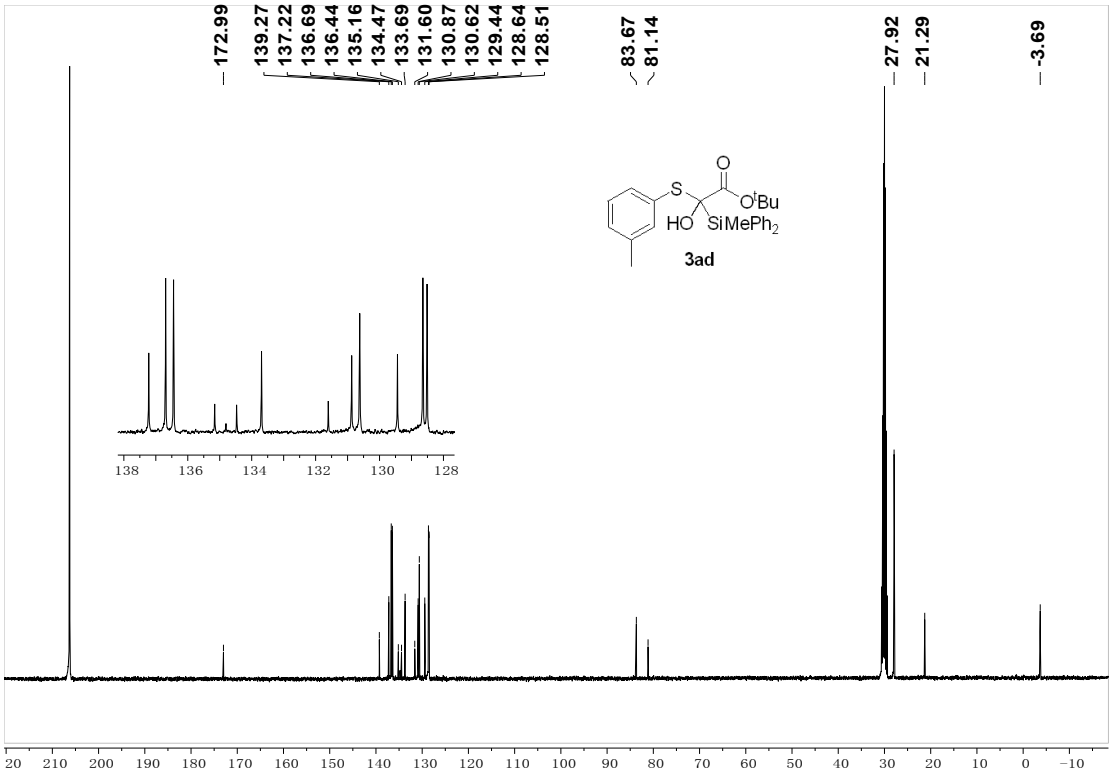

7.79 7.79 7.78 7.78 7.78 7.77 7.77 7.77 7.76 7.76 7.42 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.32 6.88 6.87 6.87 6.86 6.85 6.84 4.36 3.76 1.12 0.87
Parameter Value
Solvent Acetone
Temperature 295.1
Number of Scans 16
Nucleus 1H
3ab
3.9
8.1
2.0
3.9 8.1 2.0 0.9 3.0 9.0 3.0

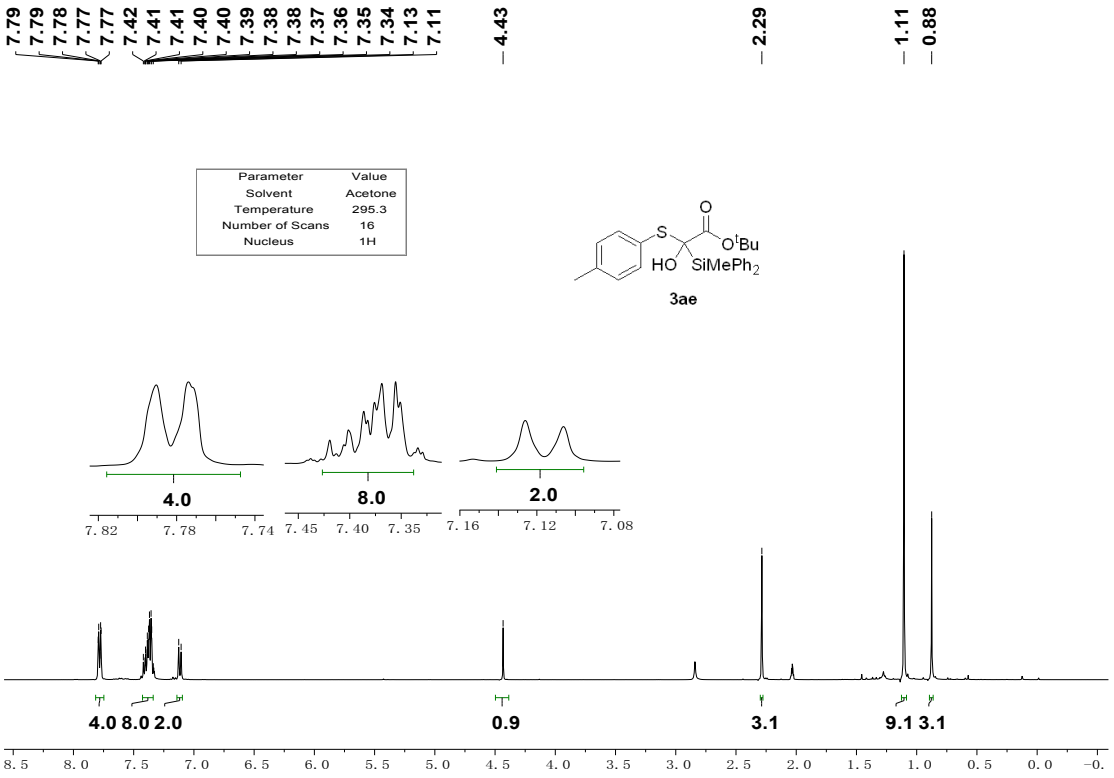

173.18 161.81 138.81 136.62 136.36 135.27 134.54 130.80 130.52 128.61 128.45 121.61 115.14 83.61 80.70 55.75 27.95 -3.74
Parameter Value
Solvent Acetone
Temperature 295.1
Number of Scans 256
Nucleus 13C
3ab

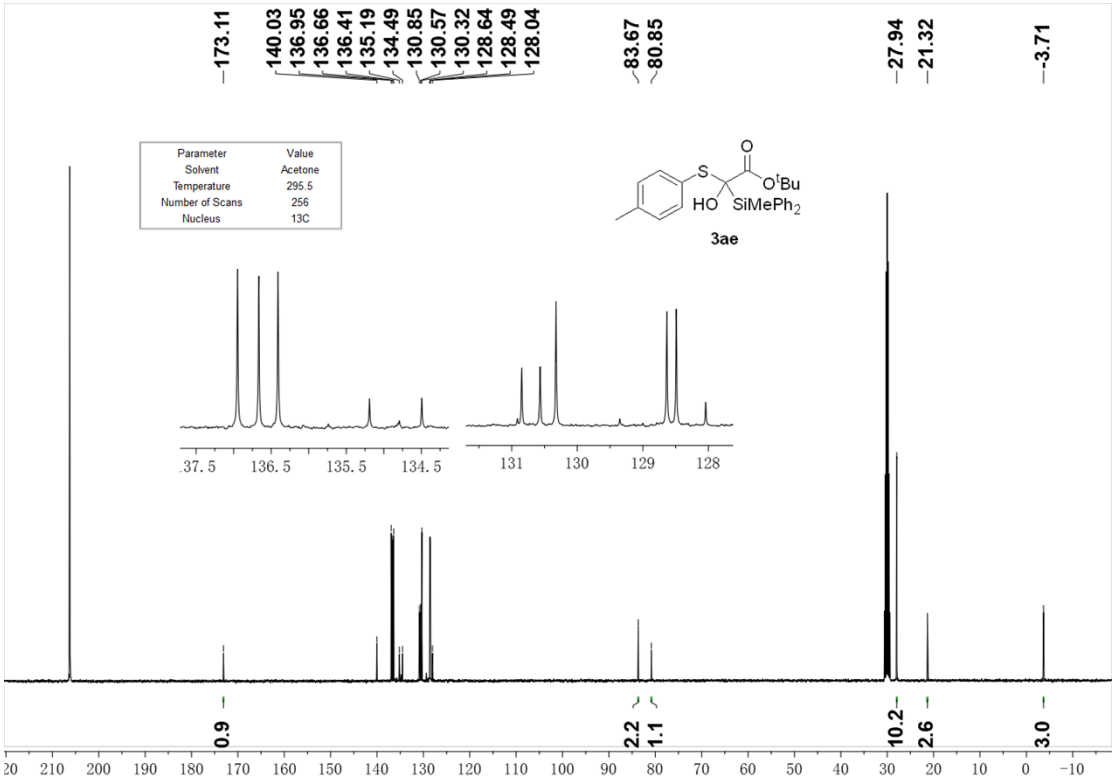

7.86 7.86 7.84 7.82 7.80 7.79 7.56 7.54 7.45 7.44 7.43 7.42 7.42 7.41 7.41 7.40 7.39 7.37 7.37 7.36 7.25 7.23 7.21 7.19 7.12 7.10 7.08 4.64
2.84 HDO
2.42
2.05 Acetone
1.04
0.92
Parameter Value
Solvent Acetone
Temperature 296.7
Number of Scans 16
Nucleus 1H
3ac
3.9
3.9 1.1 6.0 2.1 1.1
0.9
3.0
9.0 3.1

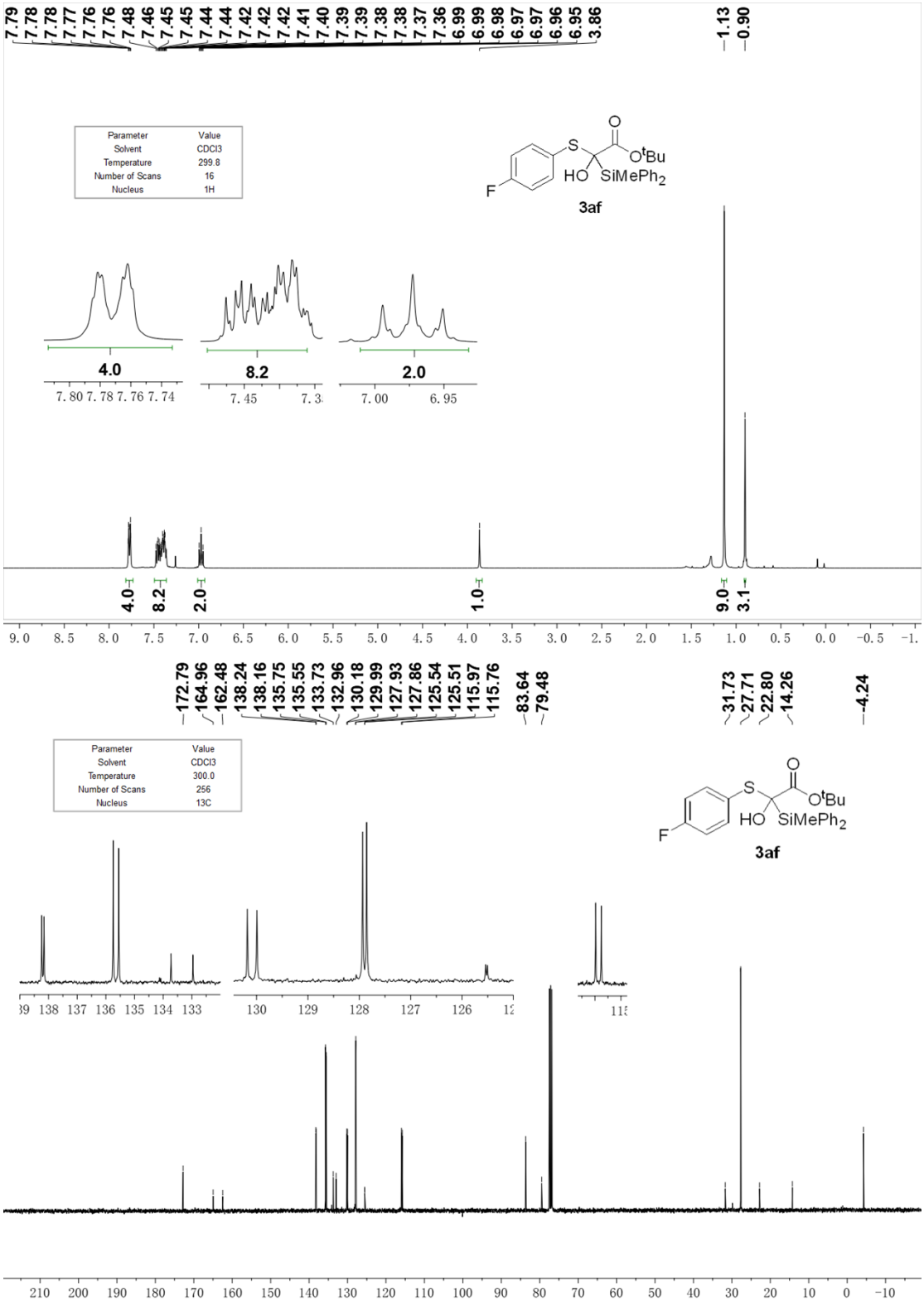

173.06 143.31 137.35 136.76 136.48 135.03 134.50 132.31 131.22 130.88 130.68 129.89 128.65 128.53 127.02
83.79 81.89
27.77 21.98
-3.77
Parameter Value
Solvent Acetone
Temperature 297.2
Number of Scans 256
Nucleus 13C
3ac

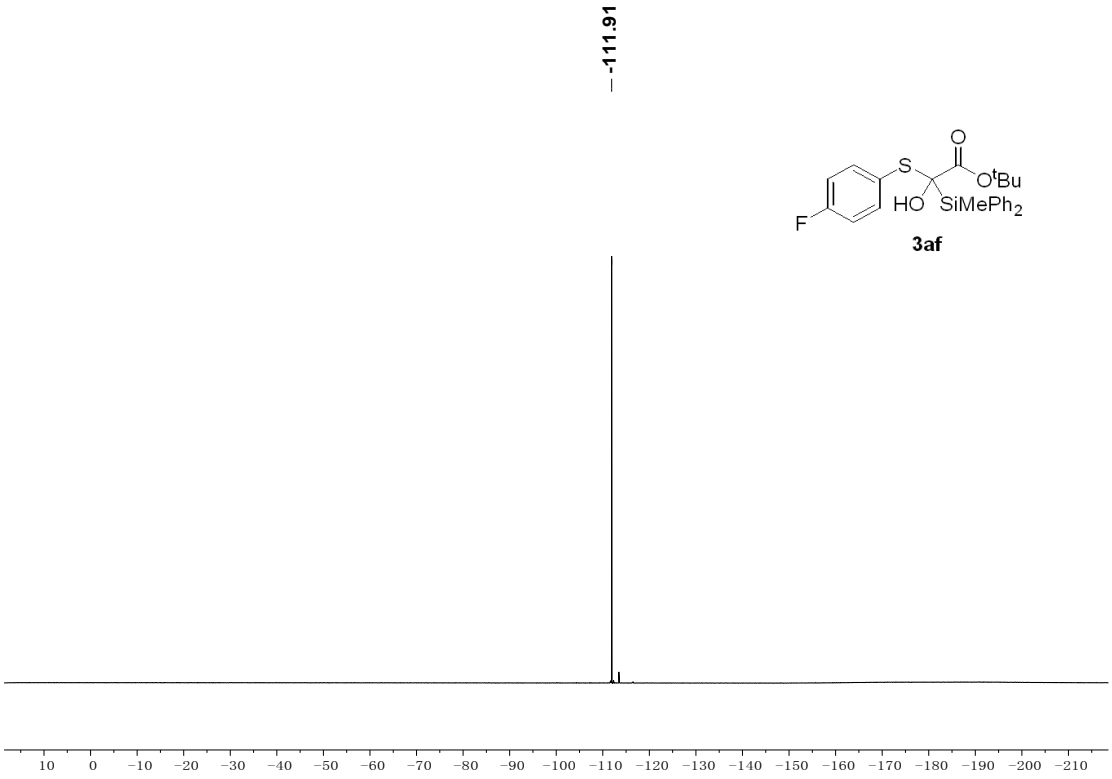

7.81 7.81 7.81 7.80 7.80 7.79 7.79 7.79 7.79 7.78 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.29 7.29 7.28 7.21 7.19 7.17 7.16 7.16 7.16 7.14 4.55 2.27 1.10 0.89
Parameter Value
Solvent Acetone
Temperature 295.4
Number of Scans 16
Nucleus 1H
3ad
4.0
6.0
2.1
2.0
7.82 7.78
7.45 7.40
7.34 7.32 7.30
7.20 7.15
4.0 6.0 2.1 2.0 0.9 3.0 9.1 3.0

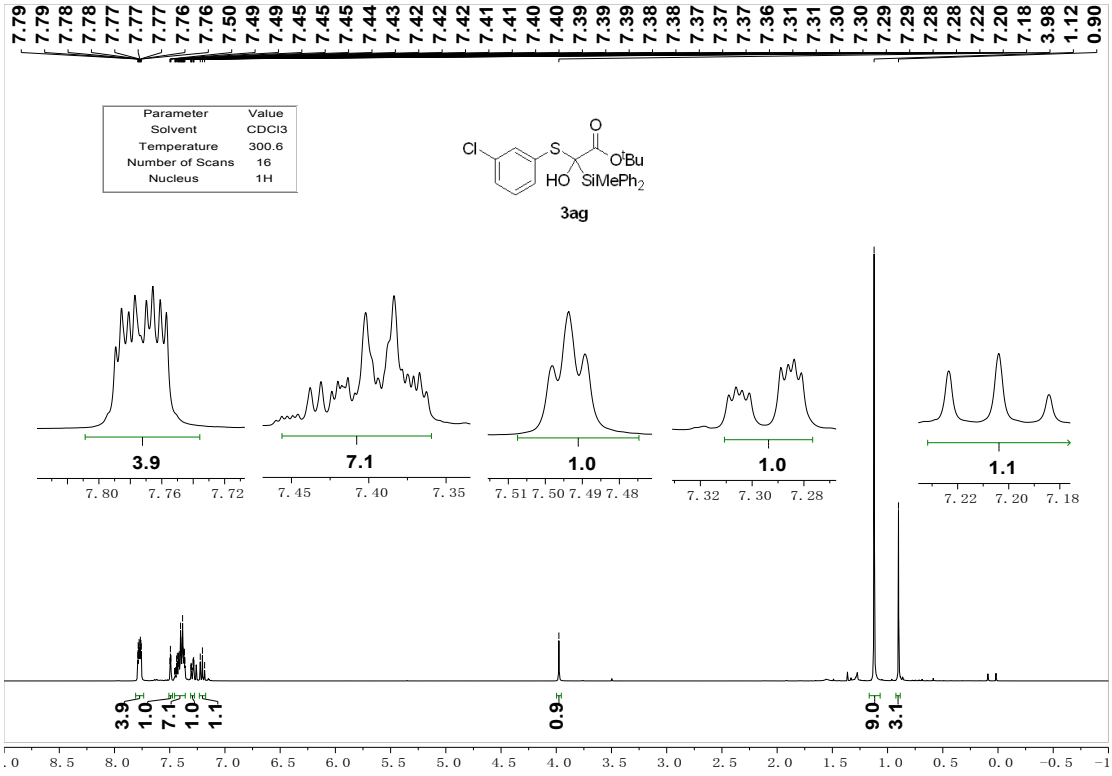

172.99 139.27 137.22 136.69 136.44 135.16 134.47 133.69 131.60 130.87 130.62 129.44 128.64 128.51 83.67 81.14 27.92 21.29 -3.69
3ad
138 136 134 132 130 128

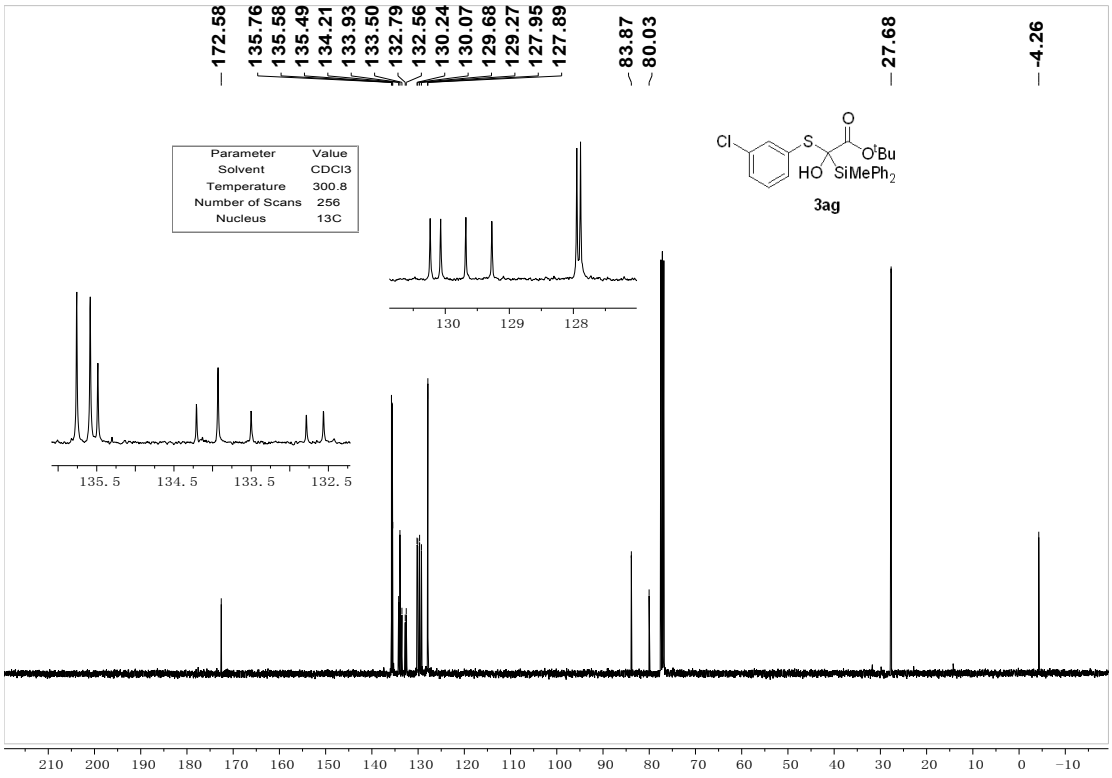

7.79 7.79 7.78 7.77 7.77 7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.37 7.36 7.35 7.34 7.13 7.11
4.43
2.29
1.11 0.88
Parameter Value
Solvent Acetone
Temperature 295.3
Number of Scans 16
Nucleus 1H
3ae
4.0 8.0 2.0
0.9
3.1
9.1 3.1

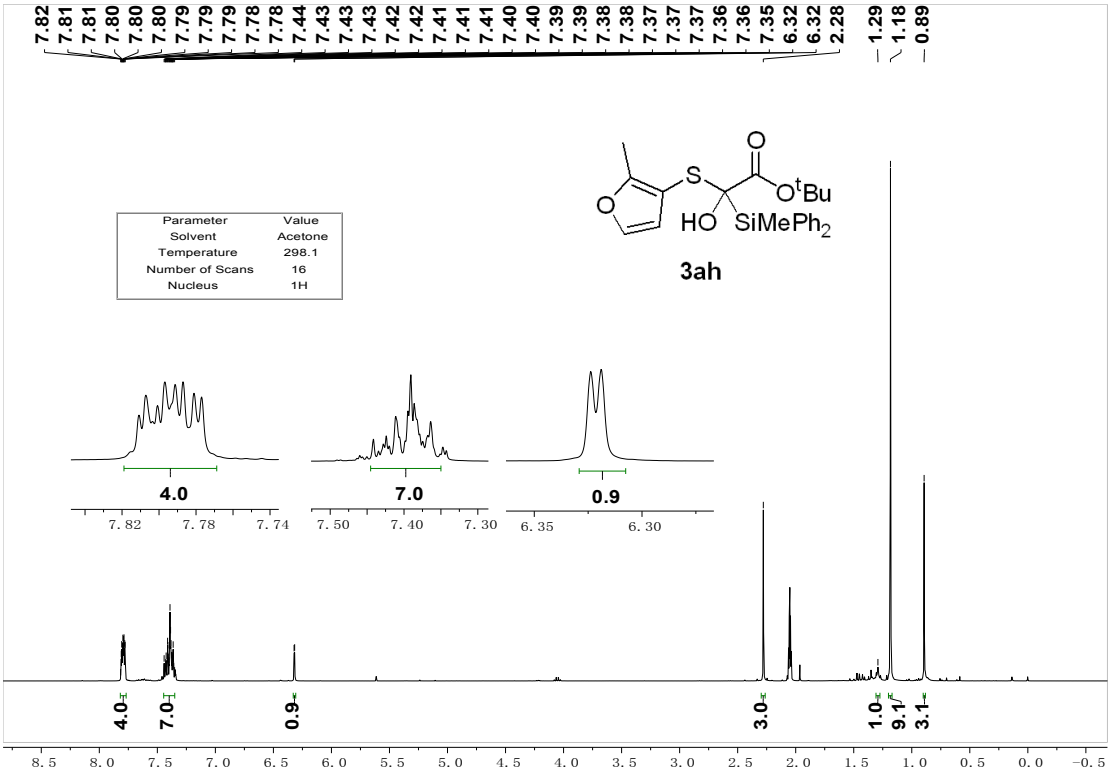

173.11
140.03 136.95 136.66 136.41 135.19 134.49 130.85 130.57 130.32 128.64 128.49 128.04
83.67 80.85
27.94 21.32
-3.71
Parameter Value
Solvent Acetone
Temperature 295.5
Number of Scans 256
Nucleus 13C
3ae
0.9
2.2 1.1
10.2 2.6 3.0

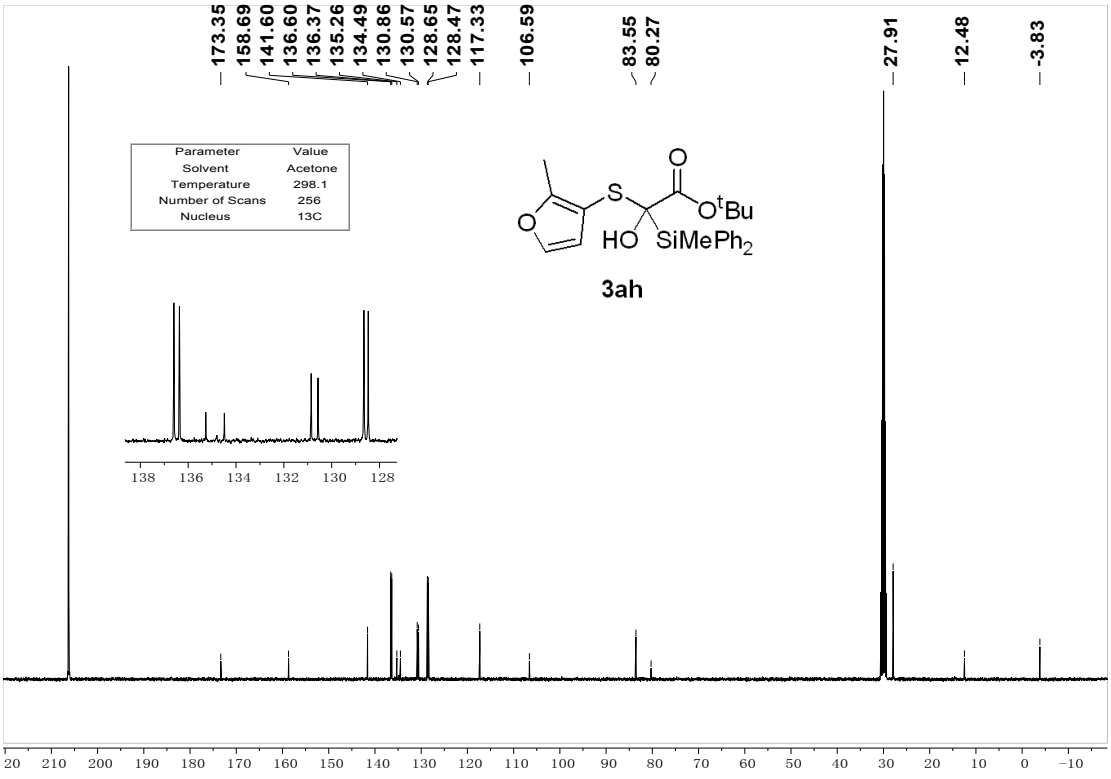

7.79 7.78 7.78 7.77 7.76 7.76 7.48 7.46 7.45 7.45 7.44 7.44 7.42 7.42 7.42 7.41 7.40 7.39 7.39 7.38 7.38 7.37 7.36 6.99 6.99 6.98 6.97 6.97 6.96 6.95 3.86
1.13 0.90
Parameter Value
Solvent CDCl3
Temperature 299.8
Number of Scans 16
Nucleus 1H
3af
4.0 8.2 2.0
4.0 8.2 2.0 1.0 9.0 3.1
172.79 164.96 162.48 138.24 138.16 135.75 135.55 133.73 132.96 130.18 129.99 127.93 127.86 125.54 125.51 115.97 115.76 83.64 79.48 31.73 27.71 22.80 14.26 -4.24
Parameter Value
Solvent CDCl3
Temperature 300.0
Number of Scans 256
Nucleus 13C
3af

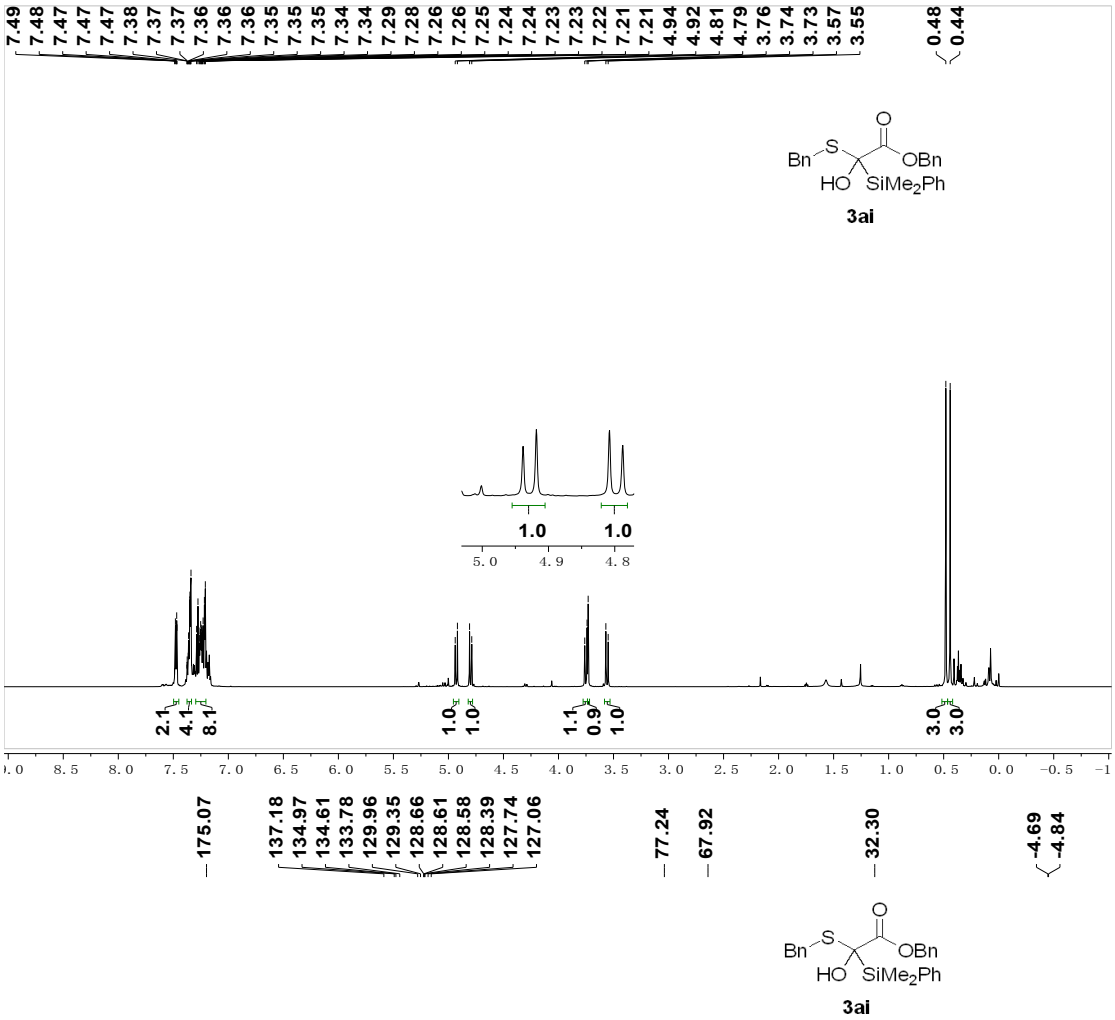

-111.91
O
S
O^{t}Bu
HO
SiMePh$_2$
F
3af
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210

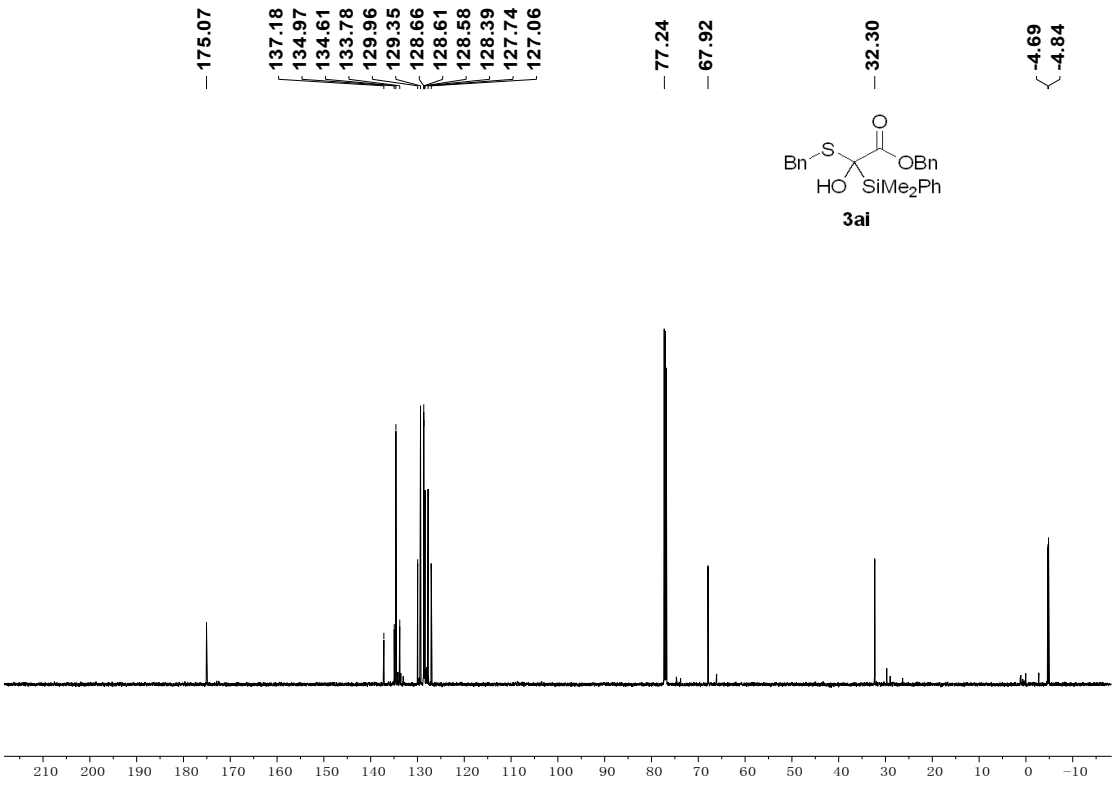

7.79 7.79 7.78 7.78 7.77 7.77 7.77 7.76 7.76 7.50 7.49 7.49 7.45 7.45 7.45 7.44 7.43 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.22 7.20 7.18 3.98 1.12 0.90
Parameter Value
Solvent CDCl3
Temperature 300.6
Number of Scans 16
Nucleus 1H
Cl
S
O
O'Bu
HO
SiMePh2
3ag
3.9
7.1
1.0
1.0
1.1
3.9 1.0 7.1 1.0 1.1
0.9
9.0 3.1

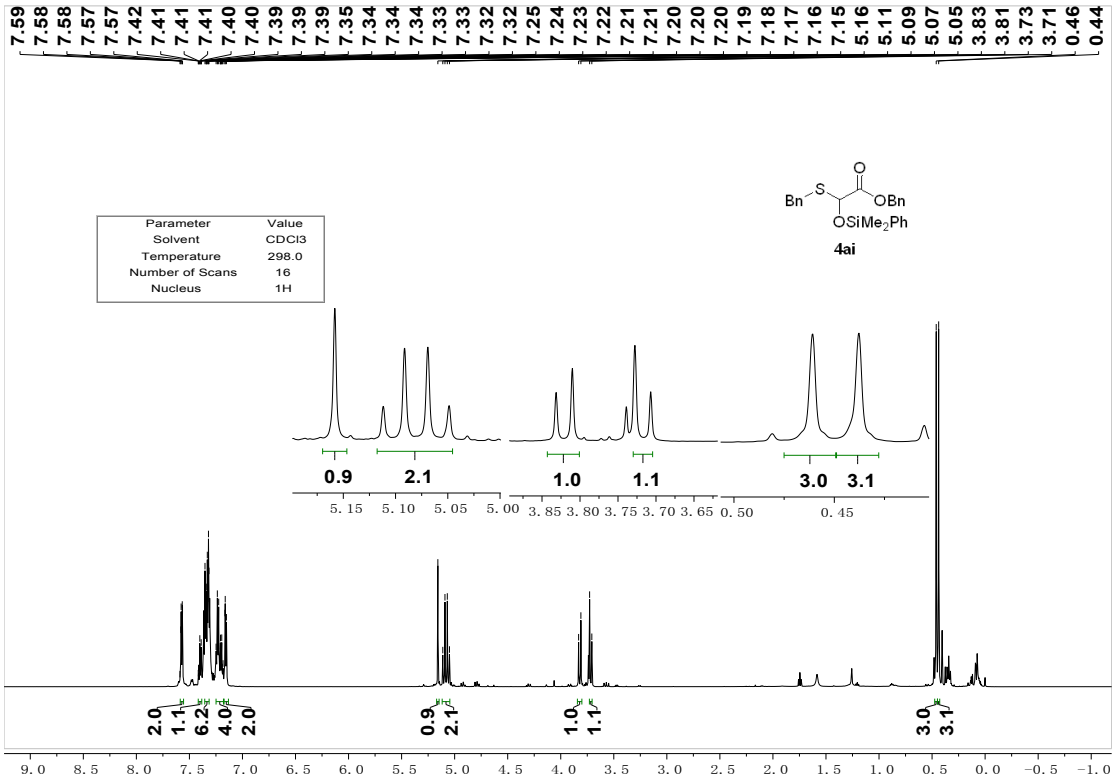

172.58 135.76 135.58 135.49 134.21 133.93 133.50 132.79 132.56 130.24 130.07 129.68 129.27 127.95 127.89 83.87 80.03 27.68 -4.26
Parameter Value
Solvent CDCl3
Temperature 300.8
Number of Scans 256
Nucleus 13C
Cl
S
O
O'Bu
HO
SiMePh2
3ag

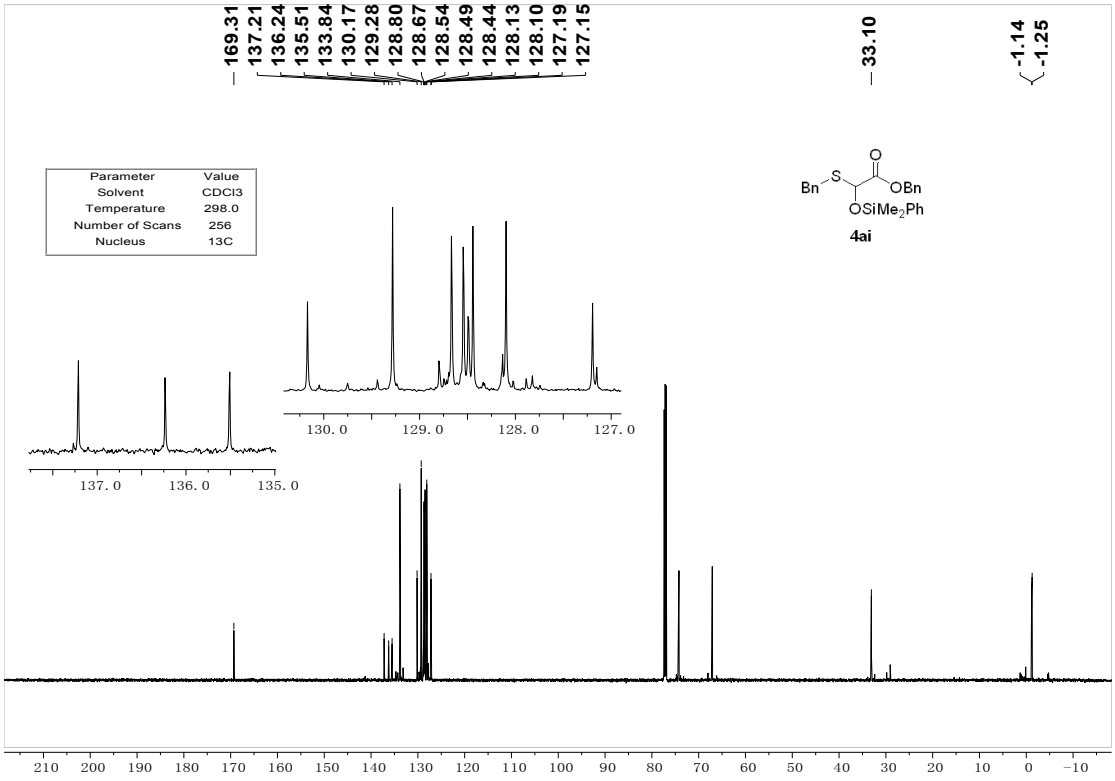

7.82 7.81 7.81 7.80 7.80 7.80 7.79 7.79 7.79 7.78 7.78 7.44 7.43 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 6.32 6.32 2.28 1.29 1.18 0.89
Parameter Value
Solvent Acetone
Temperature 298.1
Number of Scans 16
Nucleus 1H
3ah
4.0
7.0
0.9
4.0 7.0 0.9 3.0 1.0 9.1 3.1


173.35 158.69 141.60 136.60 136.37 135.26 134.49 130.86 130.57 128.65 128.47 117.33 106.59 83.55 80.27 27.91 12.48 -3.83
Parameter Value
Solvent Acetone
Temperature 298.1
Number of Scans 256
Nucleus 13C
3ah


7.49 7.48 7.47 7.47 7.47 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.29 7.28 7.26 7.26 7.25 7.24 7.24 7.23 7.23 7.22 7.21 7.21 4.94 4.92 4.81 4.79 3.76 3.74 3.73 3.57 3.55
0.48 0.44
Bn S O OBn HO SiMe2Ph
3ai
1.0 1.0
2.1 4.1 8.1 1.0 1.0 1.1 0.9 1.0 3.0 3.0

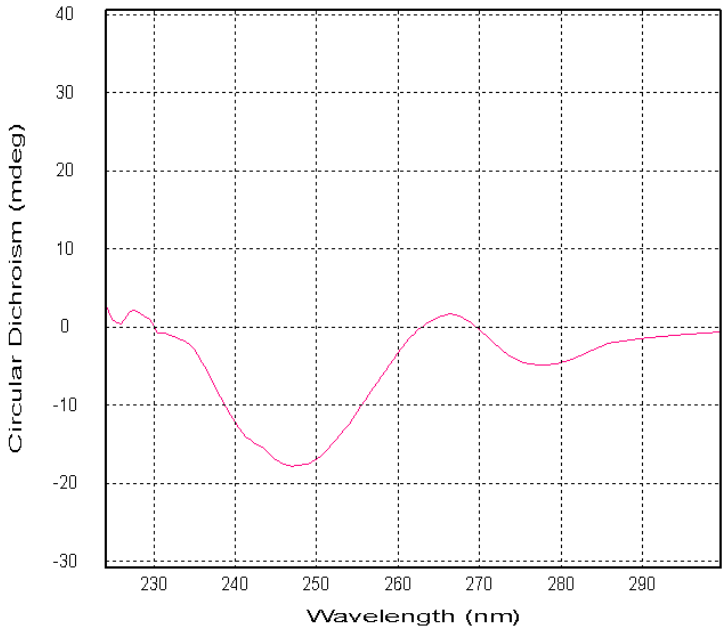

175.07
137.18 134.97 134.61 133.78 129.96 129.35 128.66 128.61 128.58 128.39 127.74 127.06
77.24
67.92
32.30
-4.69 -4.84
Bn S O OBn HO SiMe2Ph
3ai


Parameter Value
Solvent CDCl3
Temperature 298.0
Number of Scans 16
Nucleus 1H
Bn S OBn
OSiMe2Ph
4ai


Parameter Value
Solvent CDCl3
Temperature 298.0
Number of Scans 256
Nucleus 13C
Bn S OBn
OSiMe2Ph
4ai

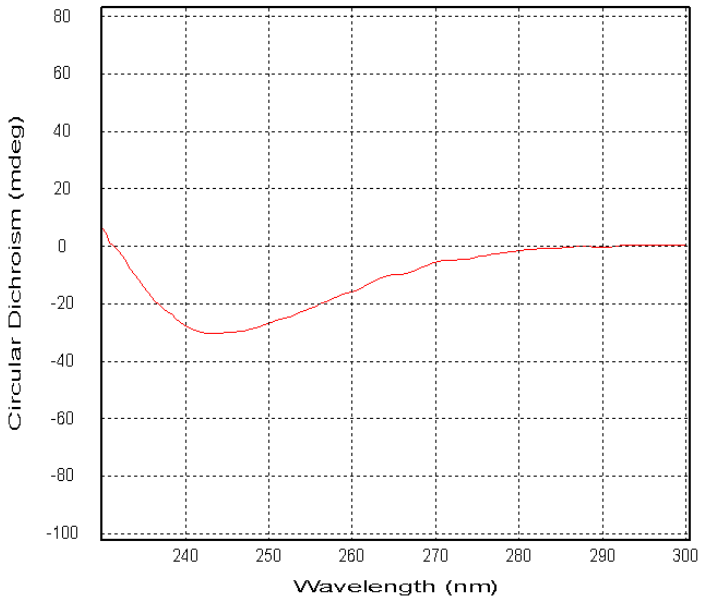
11. Copy of CD spectra in n-Hexane

3w



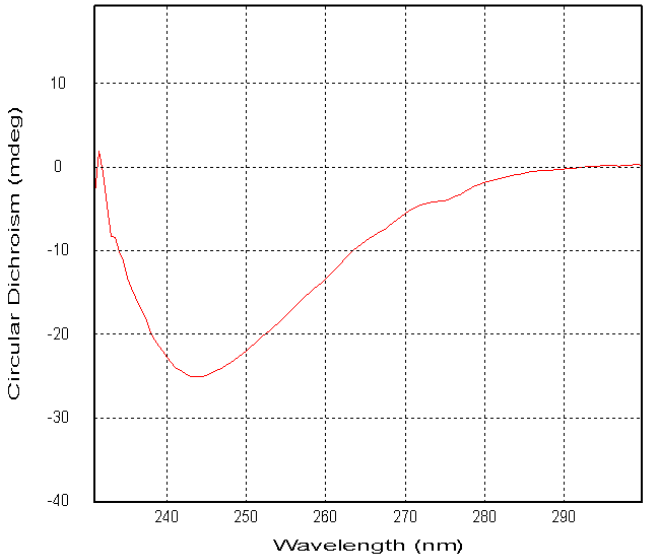
CD spectra for product 3w (Characterized in DCM)

3a



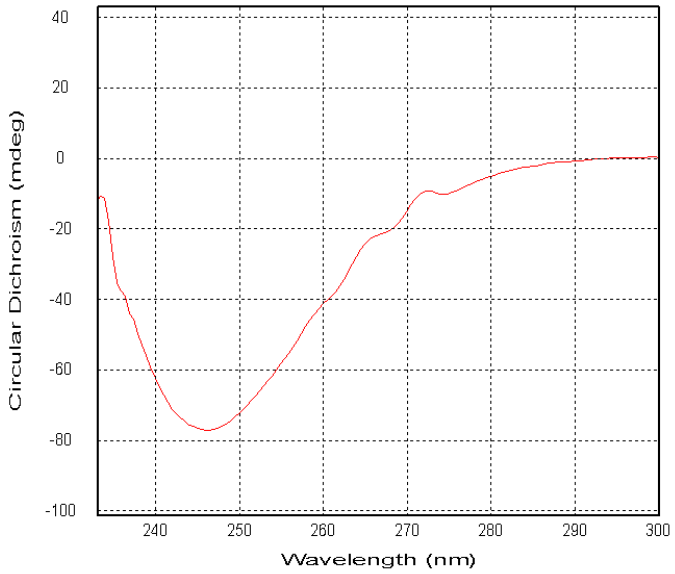
CD spectra for product 3a

3b



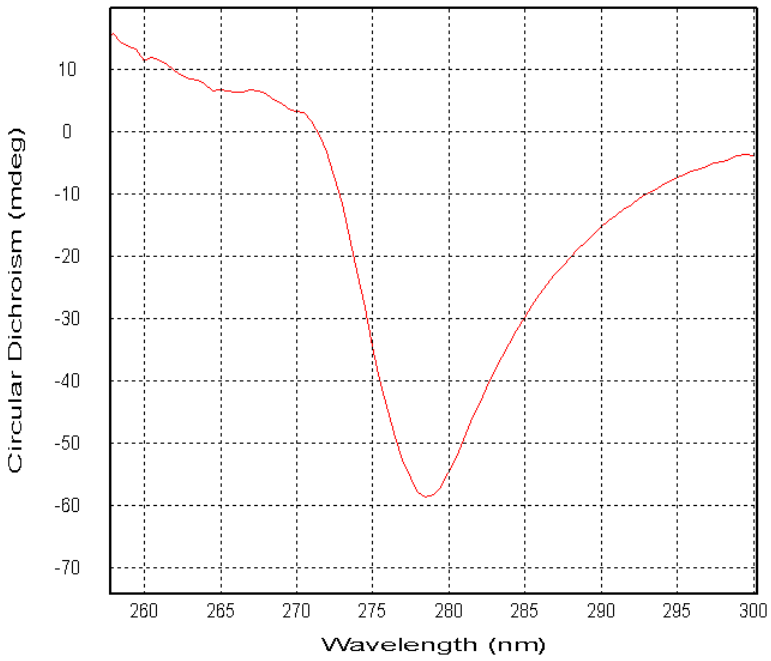
CD spectra for product 3b

3c



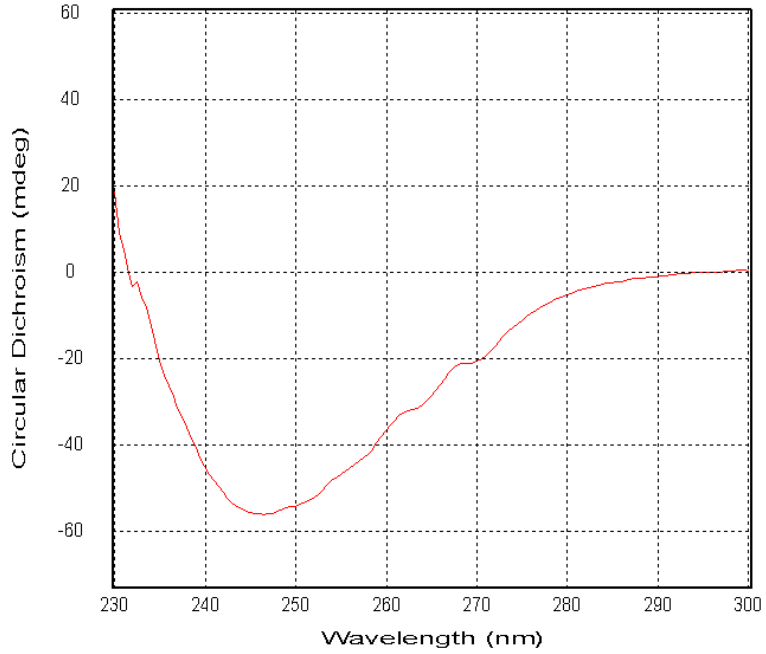
CD spectra for product 3c

3d



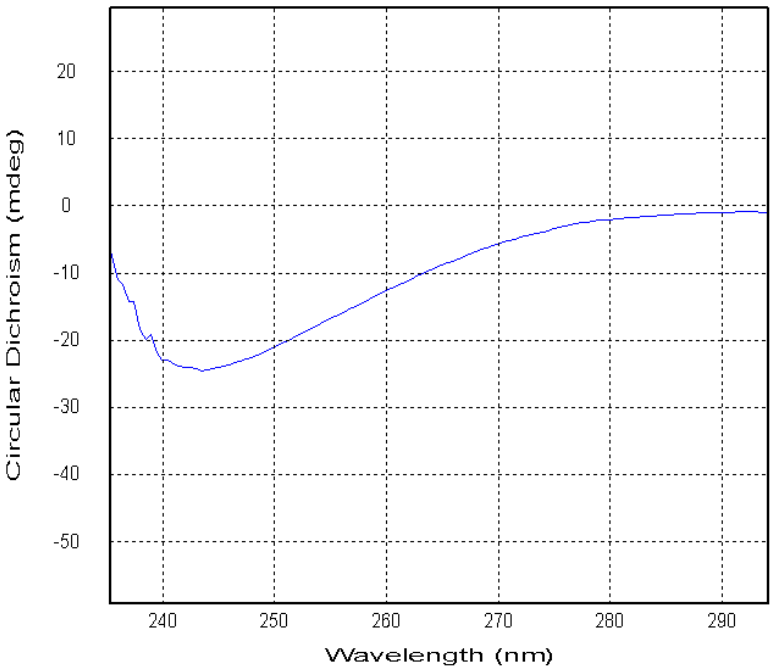
CD spectra for product 3d

3e



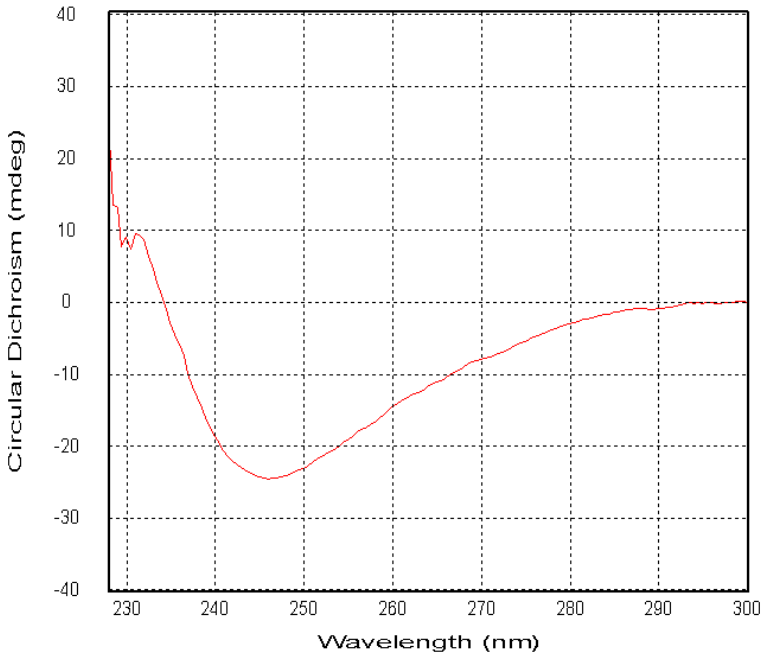
CD spectra for product 3e

3f



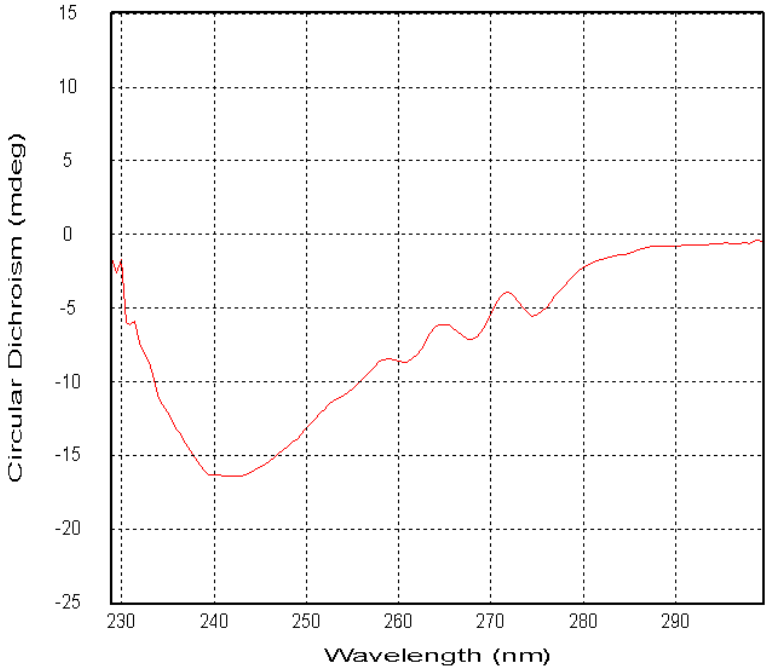
CD spectra for product 3f

3g



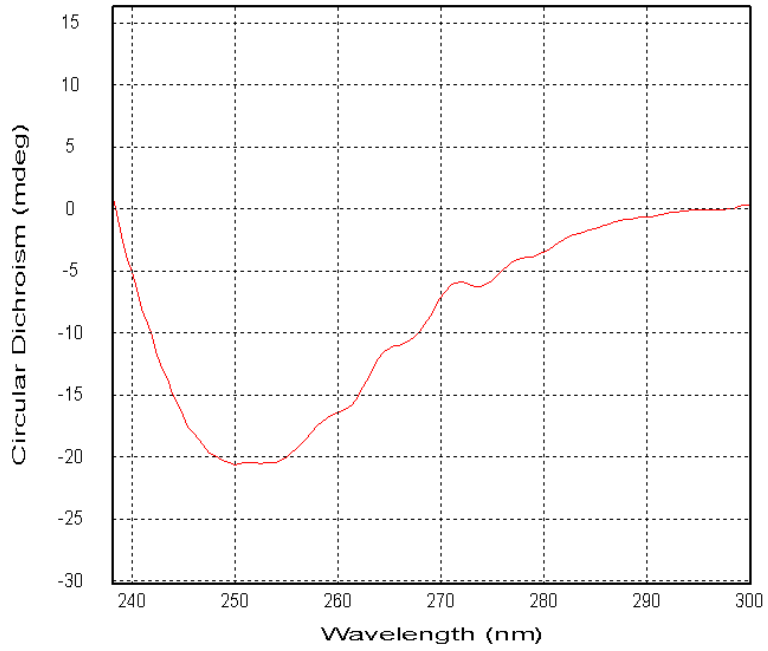
CD spectra for product 3g

3i



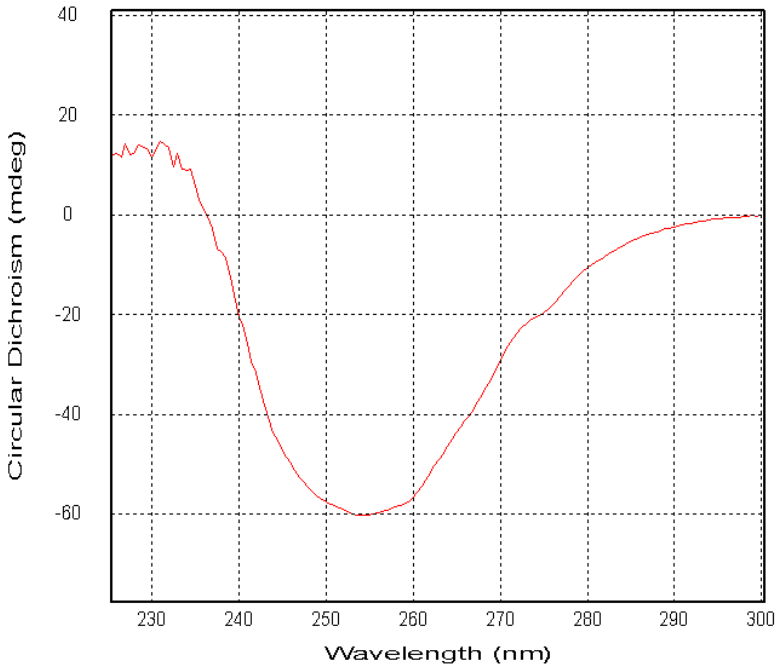
CD spectra for product 3i

3j



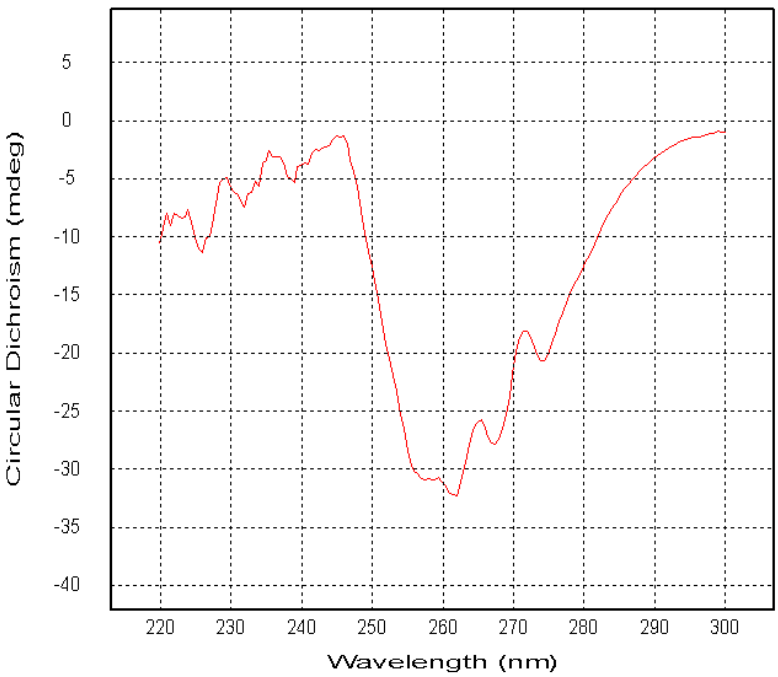
CD spectra for product 3j

3k



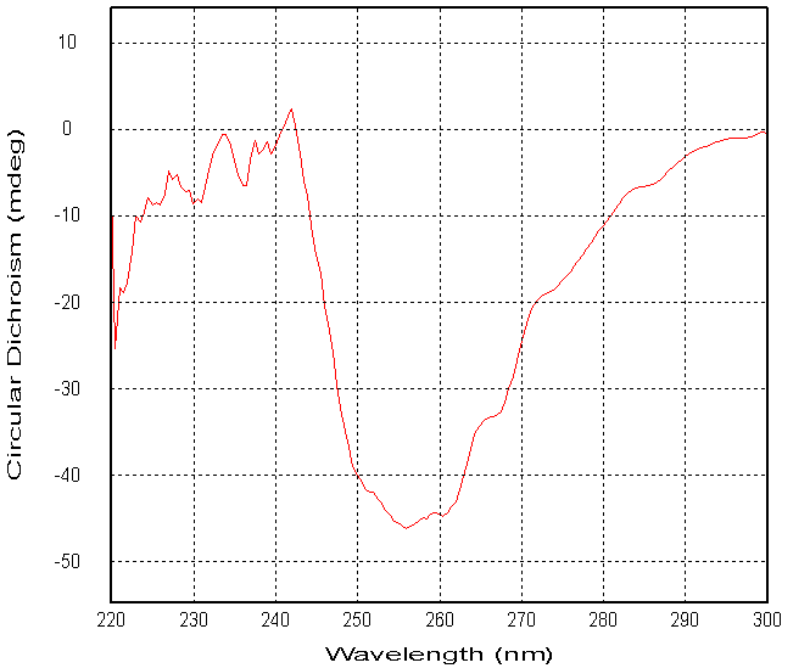
CD spectra for product 3k

3l



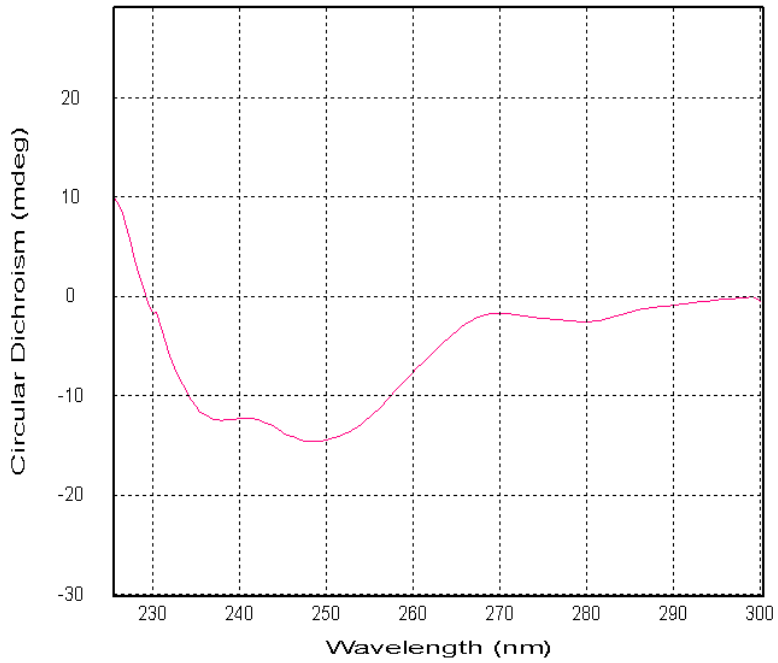
CD spectra for product 3l

3m



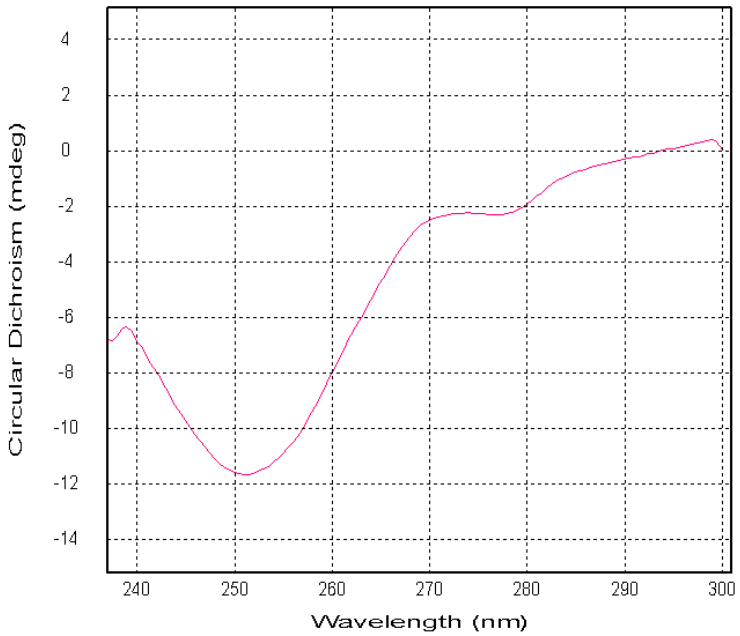
CD spectra for product 3m

3n



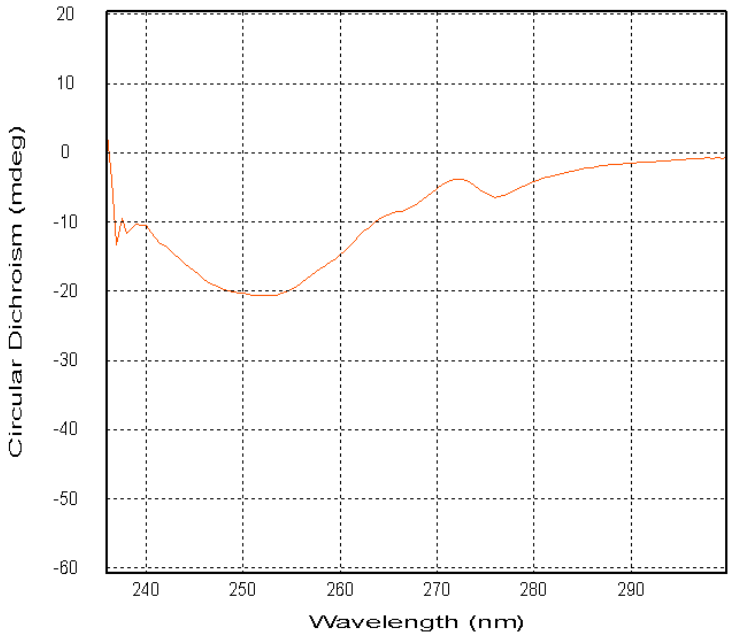
CD spectra for product 3n

3p



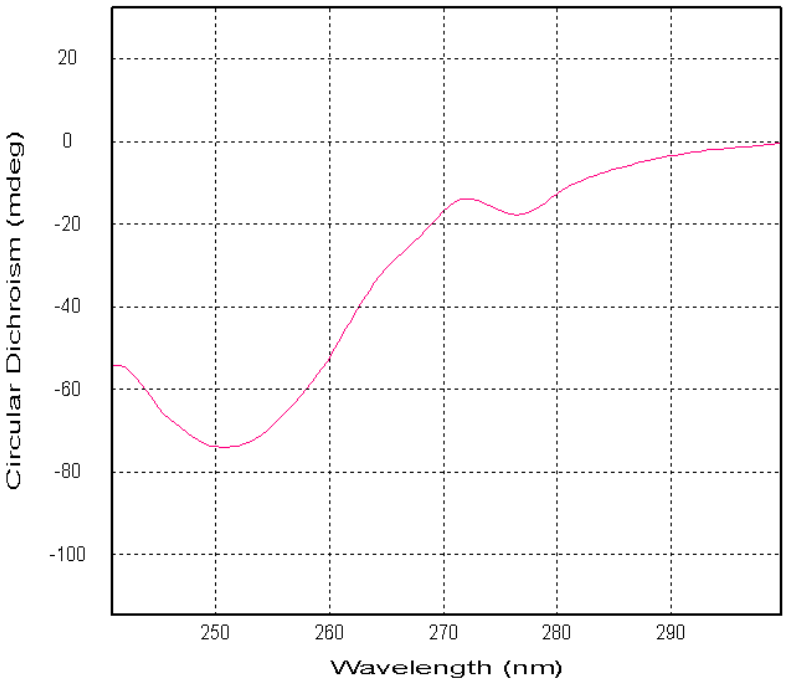
CD spectra for product 3p

3q



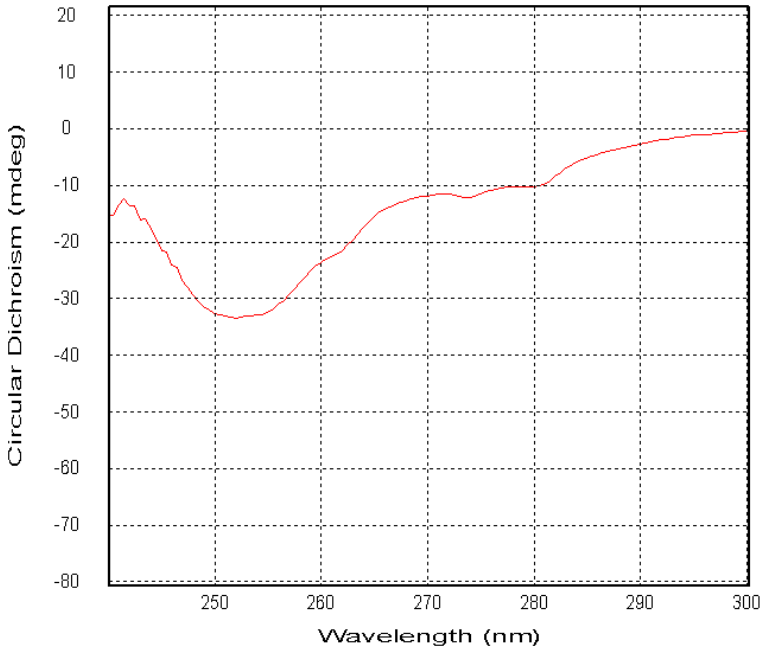
CD spectra for product 3p

3s



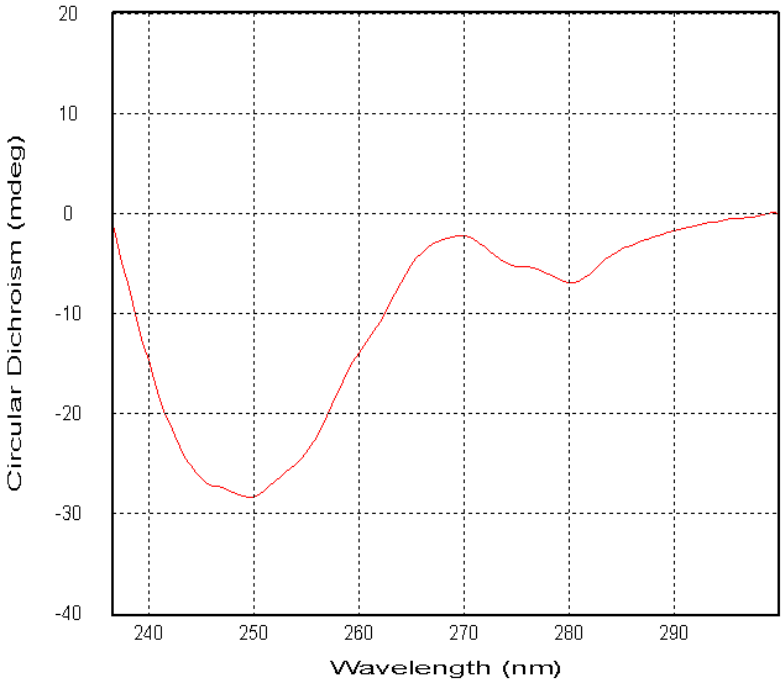
CD spectra for product 3s

3t



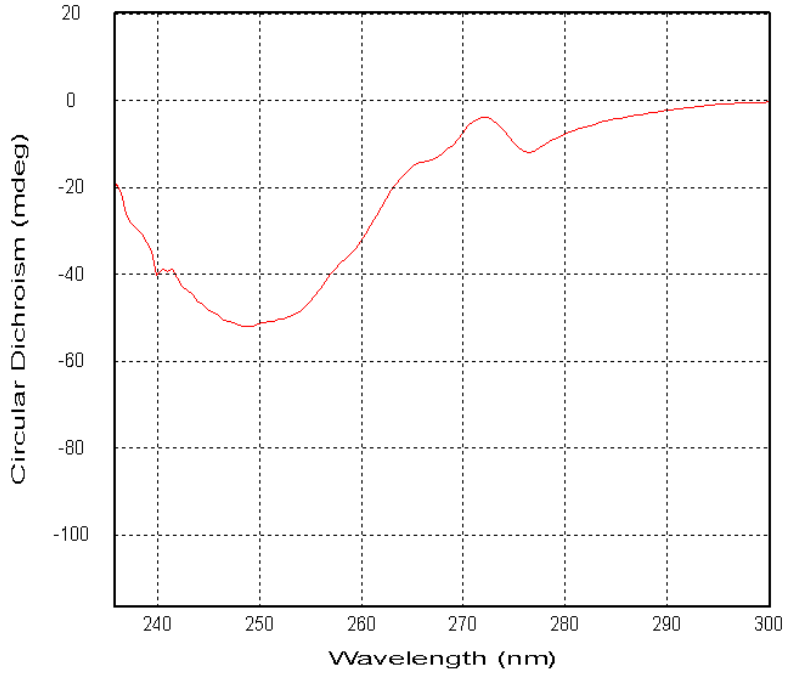
CD spectra for product 3t

3x



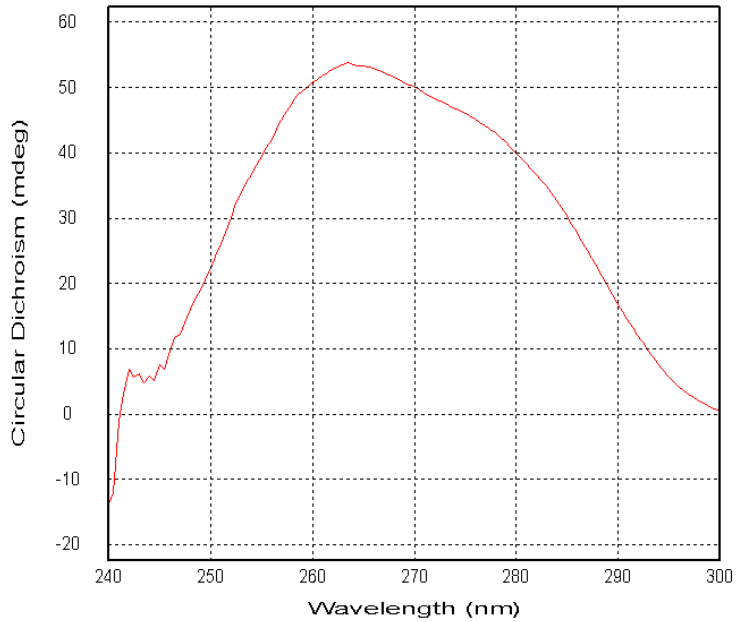
CD spectra for product 3x

3y



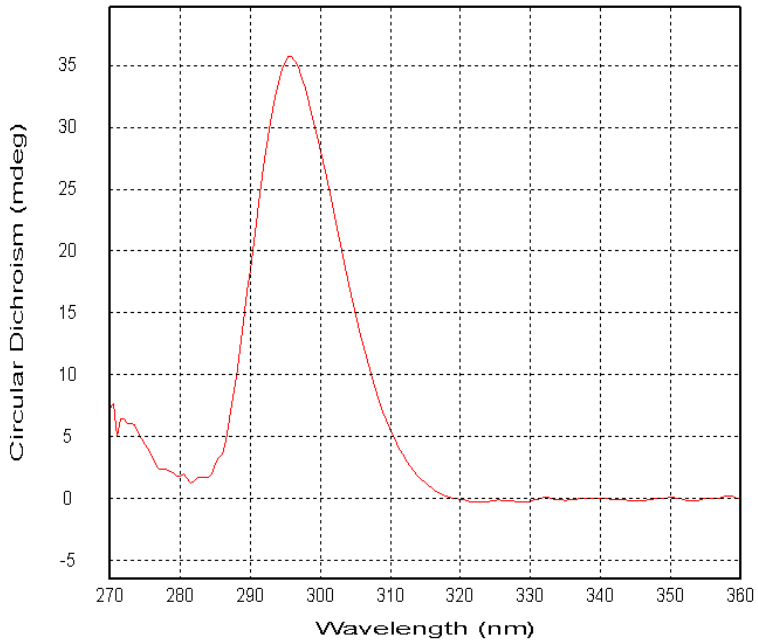
CD spectra for product 3y

3aa



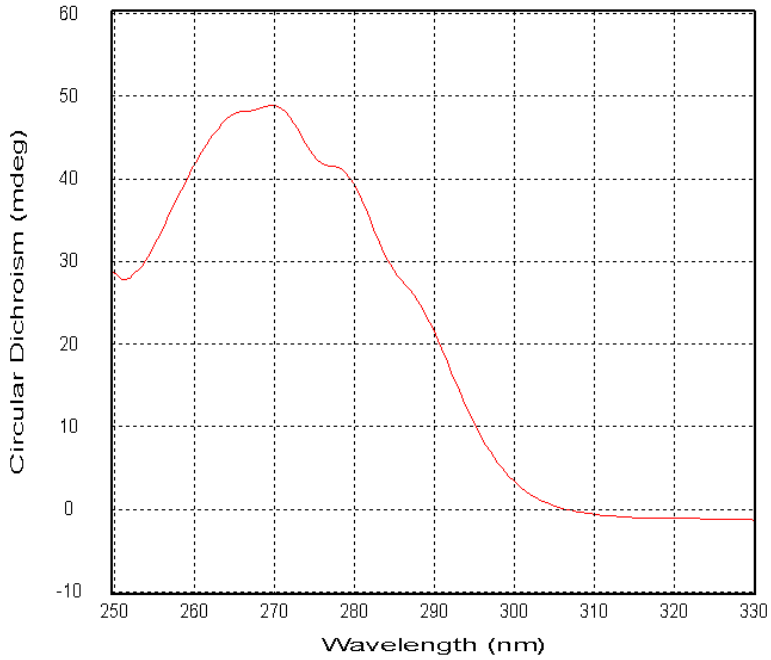
CD spectra for product 3aa

3ab



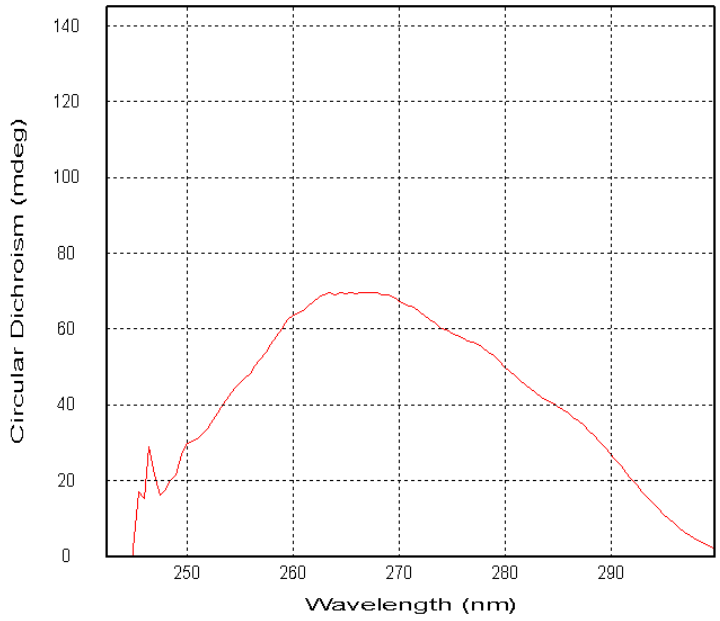
CD spectra for product 3ab

3ac



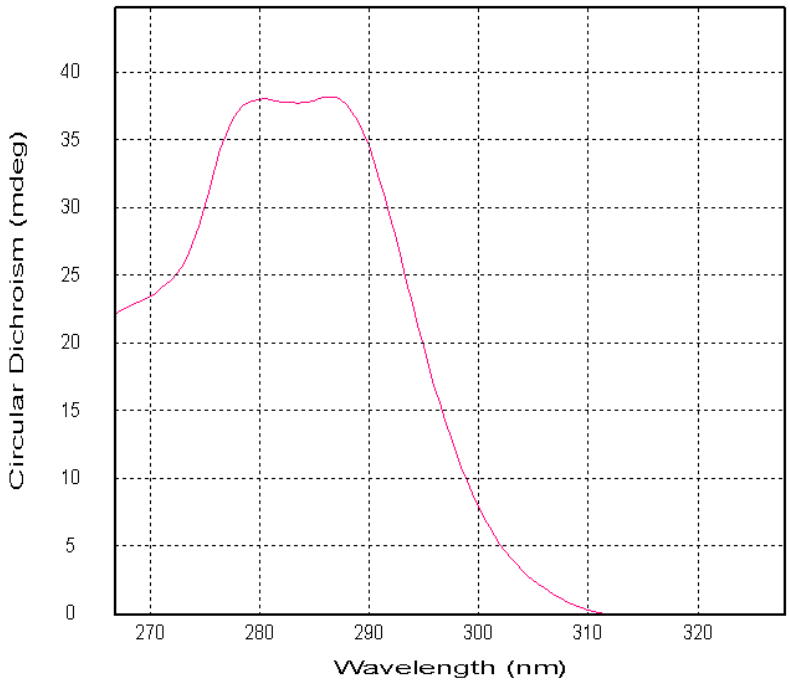
CD spectra for product 3ac

3ad



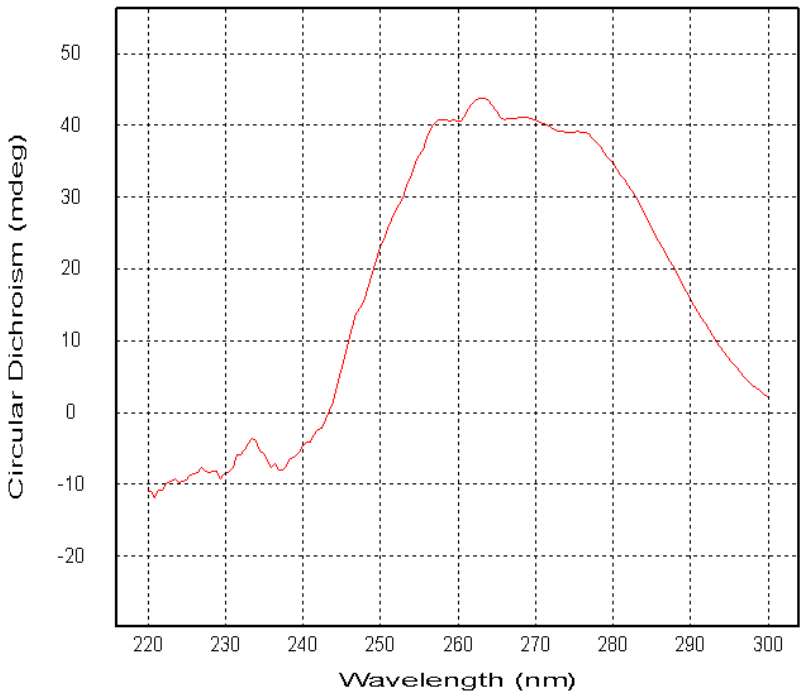
CD spectra for product 3ad

3ae



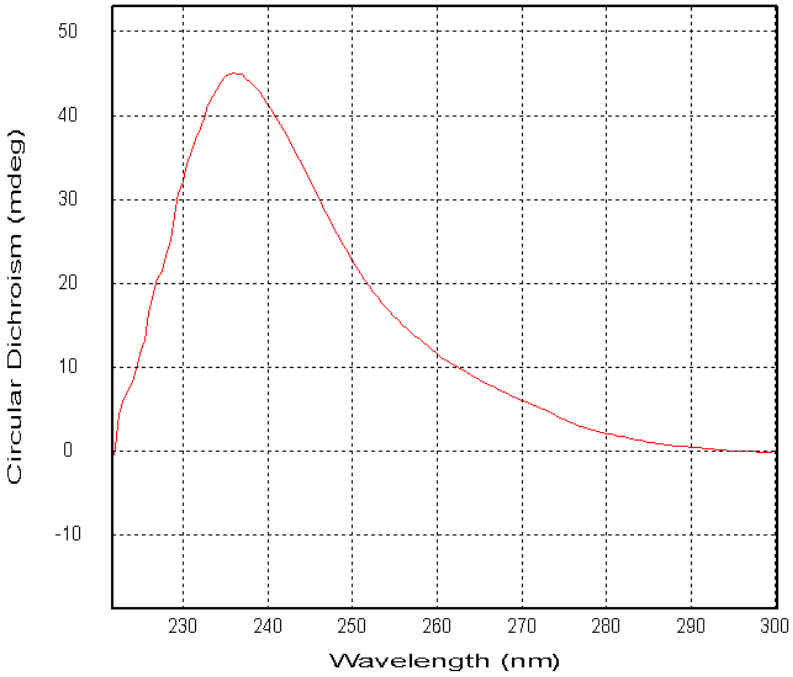
CD spectra for product 3ae

3af



CD spectra for product 3ae

3ah



CD spectra for product 3ah

12. References

1. (*a*) D. A. Nicewicz and J. S. Johnson, *J. Am. Chem. Soc.,* 2005, **127**, 6170; (*b*) C. Bolm, A. Kasyan, P. Heider, S. Saladin, K. Drauz, K. Günther and C. Wagner, *Org. Lett.,* 2002, **4**, 2265.
2. W. Uhlig, *J, Organomet. Chem.,* 1993, **452**, 29.
3. Y. H. Wen, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett*, 2005, 2445.
4. V. Gupta and S. K. Mandal, *Chem. Eur. J.,* 2020, **26**, 2658.
5. L. Zhang, Y. Xia, M. Li, D. Li and R. Hou, *Tetrahedron*, 2016, **72**, 7438.
6. T. Hoshi, T. Nakamura, T. Suzuki, M. Ando and H. Hagiwara, *Organometallics*, 2000, **19**, 4483.
7. S. K. Ray, M. M. Sadhu, R. G. Biswas, R. A. Unhale and V. K. Singh, *Org. Lett.,* 2019*,* **21**, 417.
8. M.-Y. Han, J. Lin, W. Li, W.-Y. Luan, P.-L. Mai and Y. Zhang, *Green Chem.,* 2018, **20**, 1228.
9. W. Li, J. Wang, X. L. Hu, K. Shen, W. T. Wang, Y. Y. Chu, L. L. Lin, X. H. Liu and X. M. Feng, *J. Am. Chem. Soc.,* 2010, **132**, 8532.