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Supporting Information
for

Silanol: A bifunctional group for peptide synthesis and late-stage functionalization

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1. General Information

Commercially available materials and solvents purchased from Alfa Aesar, Sigma-Aldrich, *J&K* Chemical, or 3A Chemical and were used as received. No attempts were made to optimize yields for substrate synthesis.

Protected Fmoc-amino acids and coupling reagents were purchased from Bidepharm. DCM, DCE, DMF, and TFA were purchased from J&K Chemical and were used without further purification.

Flash chromatography was performed using Silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical. 2-Cl-Trt resin (0.98 mmol/g) were purchased from Tianjin Nankai HECHENG.

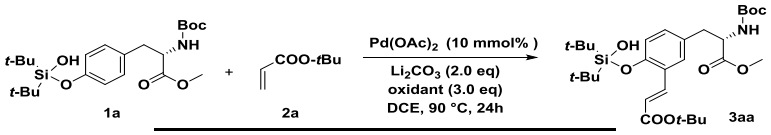
Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (400 or 500 MHz) spectrometer. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl3 or MeOD solution. ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker [(400 MHz) (100 MHz) or (500 MHz) (125 MHz)] spectrometer.

High resolution mass spectral analysis (HRMS) was performed on Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation).

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) or neutral alumina column (200-300 mesh) with solvents distilled prior to use.

2. Optimization of reaction conditions

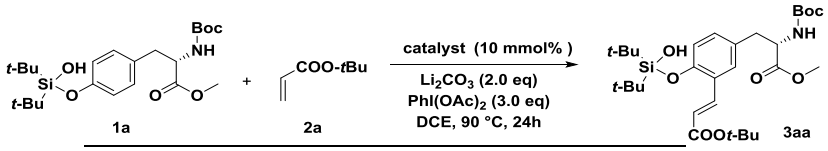
Table S1. Optimization of oxidant for olefination of **1a** with **2a**



Entry	Oxidant	Solvent	Yield[%]
1	AgOAc	DCE	< 5%
2	$Cu(OAc)_2$	DCE	< 5%
3	$Cu(OTf)_2$	DCE	n.d
4	BQ	DCE	n.d
5	AgOTf	DCE	n.d
6	$K2_S2O_8$	DCE	n.d
7	$PhI(OAc)_2$	DCE	47%
8	Oxygen	DCE	< 5%
9	Ag_2CO_3	DCE	12%

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.4 mmol, 4.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 0.1 equiv), oxidant (0.3 mmol, 3.0 equiv), Li_2CO_3 (0.2 mmol, 2.0 equiv) in DCE (1.0 mL) under 90 °C for 24 h .

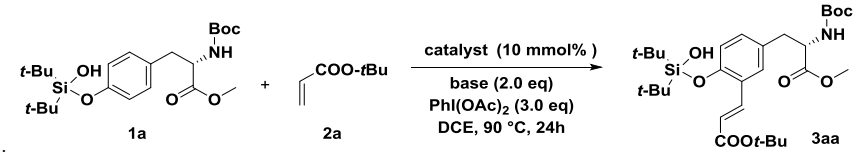
Table S2. Optimization of catalyst for olefination of **1a** with **2a**.



Entry	catalyst	Yield[%]
1	$Pd(TFA)_2$	26%
2	$NiCl_2$	n.d
3	$Pd(OH)_2/C$	20%
4	$Pd(PPh_3)_4$	21%
5	$Pd(dba)_2$	18%
6	$Pd(Ph_3P)_2Cl_2$	27%
7	$PdCl_2$	25%
8	$Pd(OAc)_2$	47%

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.4 mmol, 4.0 equiv), catalyst (0.01 mmol, 0.1equiv), $PhI(OAc)_2$ (0.3 mmol, 3.0 equiv), Li_2CO_3 (0.2 mmol, 2.0 equiv) in DCE (1.0 mL) under 90 °C for 24 h.

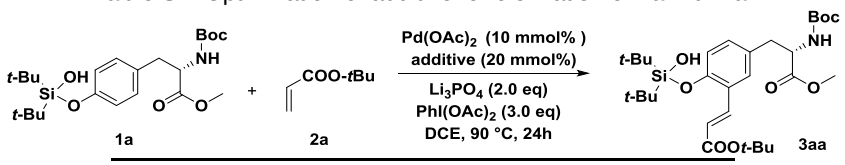
Table S3. Optimization of base for olefination of **1a** with **2a**



Entry	base	Yield[%]
1	Cs_2CO_3	n.d
2	K_2CO_3	n.d
3	K_3PO_4	n.d
4	K_2HPO_4	n.d
5	KH_2PO_4	31%
6	PivOK	n.d
7	Na_2CO_3	< 5%
8	$NaHCO_3$	22%
9	Na_2HPO_4	26%
10	NaOAc	16%
11	Li_3PO_4	58%
12	LiH_2PO_4	38%
13	LiOAc	< 5%
14	DBU	n.d

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.4 mmol, 4.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 0.1equiv), $PhI(OAc)_2$ (0.3 mmol, 3.0 equiv), Base (0.2 mmol, 2.0 equiv) in DCE (1.0 mL) under 90 °C for 24 h.

Table S4. Optimization of additive for olefination of **1a** with **2a**.



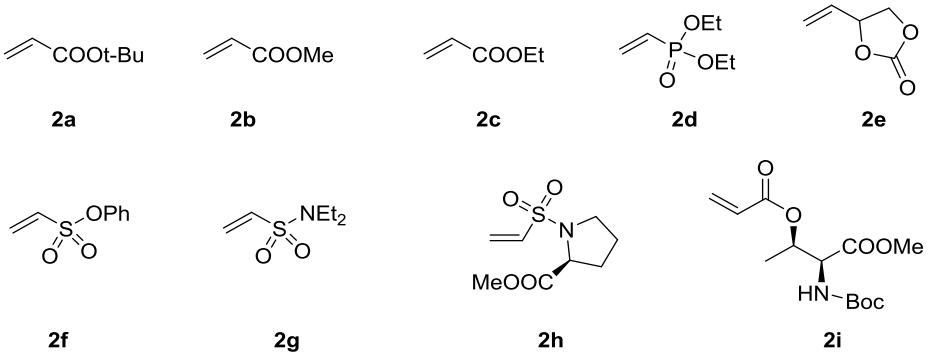
Entry	additive	Yield[%]
1	BQ	75%
2	Ac-G-OH	36%
3	(+)-Menthyl(O_2C)-Leu-OH	45%
4	Boc-Ile-OH	26%
5	(t-Bu)$_3$P	< 5%
6	6-methylpyridin-2-ol	48%
7	PivOH	33%
8	AcOH	28%
9	Ac_2O	46%

[a] Reaction conditions: 1a (0.1 mmol, 1.0 equiv), 2a (0.4 mmol, 4.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 0.1 equiv), additive (0.02 mmol, 0.2 equiv), $PhI(OAc)_2$ (0.3 mmol, 3.0 equiv), Li_3PO_4 (0.2 mmol, 2.0 equiv) in DCE (1.0 mL) under 90 °C for 24 h.

3. Synthesis of coupling partners 2f-2i

Coupling partners **2a-2e** were commercially available, **2f**-**2h** were synthesized according to the reported procedure[1], **2i** was synthesized according to the reported procedure[2].

Table. S5 Coupling partners.



2a **2b** **2c** **2d** **2e**

2f **2g** **2h** **2i**

4. Removal of silanol group

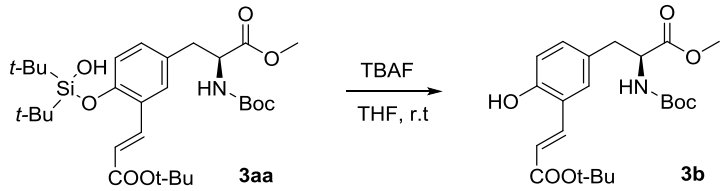
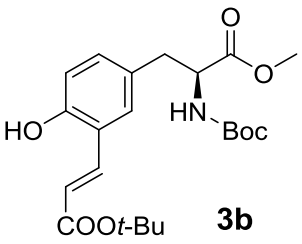


Figure S1. Removal of silanol from 3aa by treating with TBAF under r.t for 30 min.



To a solution of **3b** (85 mg, 0.15 mmol)in THF was added the solution of TBAF in THF, kept stirring at r.t for 30 min then evaporated and purified via Purified via flash column chromatography on silica gel (eluent: PE/EA = 5/1) to afford the compound **8a** as white solid, (77mg, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 16.2 Hz, 1H), 7.60 (s, 1H), 7.19 (d, *J* = 2.0 Hz, 1H), 6.95 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.76 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.50 (d, *J* = 16.2 Hz, 1H), 5.08 (d, *J* = 8.2 Hz, 1H), 4.53 (d, *J* = 6.8 Hz, 1H), 3.72 (s, 3H), 3.04 (dd, *J* = 13.8, 5.4 Hz, 1H), 2.93 (dd, *J* = 13.8, 6.8 Hz, 1H), 1.54 (s, 9H), 1.42 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.51, 167.69, 155.26, 154.95, 139.51, 131.83, 130.34, 129.59, 127.48, 121.79, 120.17, 116.63, 80.68, 80.30, 54.58, 52.35, 37.60, 28.30, 28.25; **HRMS** (ESI) calcd. for $C_{22}H_{31}NO_7$ $[M+Na]^+$: 444.1993, found: 444.1975.

5. Synthesis of building blocks 1a-1f

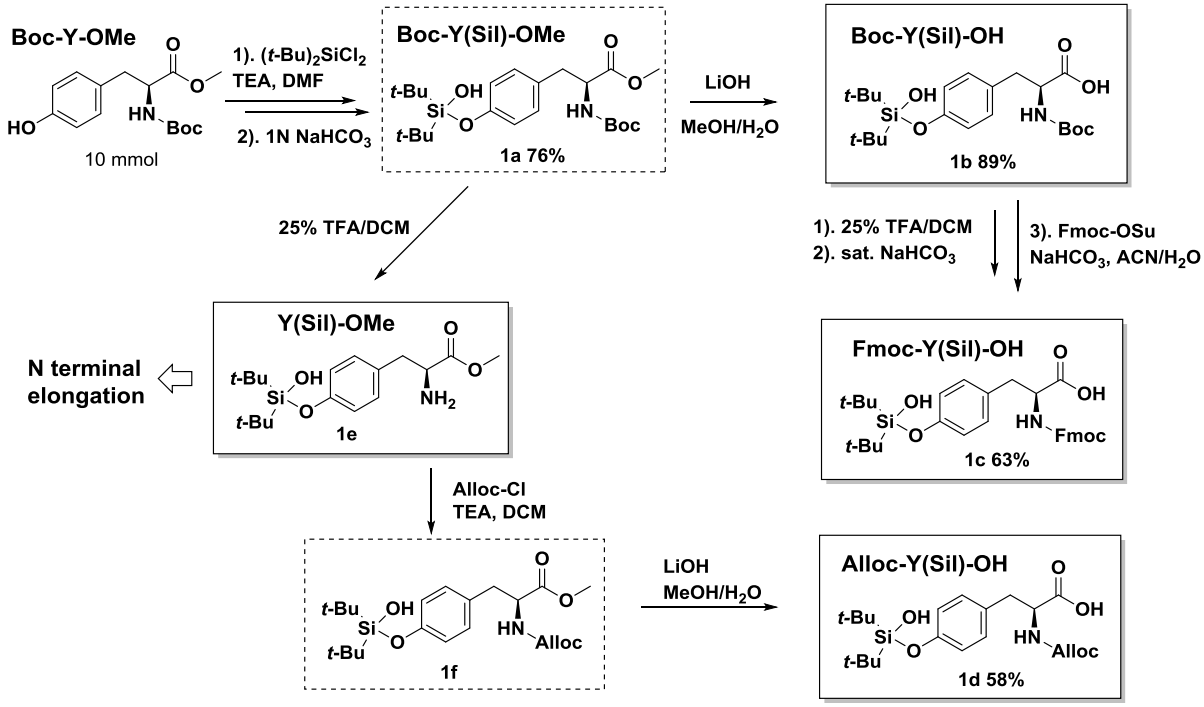
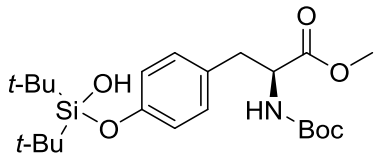


Figure S2. Synthesis of building blocks.

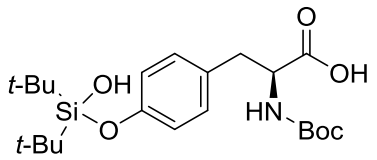
Synthesis of **1a**: Silanol was loaded according to the amended literature procedure[3]. To a solution of TEA (3.64 g , 36 mmol) in dry DMF (10 mL), ^{t}Bu_2SiCl_2 (2.56 g, 12 mmol) was added at 0 °C under Argon atmosphere via a syringe. After 15 min agitated, the solution of Boc-Tyr-OMe (2.95 g, 10 mmol) in dry DMF (10 mL) was added very slowly via drop funnel standing for 30 min, then the reaction mixture was warmed to r.t and kept stirring for another 2 h. Cold 1N $NaHCO_3$ (20 mL) was then added and the reaction mixture was stirred for 1 h. The reaction mixture was diluted by EA (100 mL), the organic layer was collected and washed by water (100 mL x 3). brine, dried over Na_2SO_4 and evaporated. The residue was purified via flash column chromatography on silica gel (eluent: PE / EA = 20/1) to afford the compound **1a**.



1a

Compound **1a,** white solid, (3.42g, 76%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93 (q, *J* = 8.6 Hz, 4H), 5.04 (d, *J* = 8.2 Hz, 1H), 4.52 (dd, *J* = 13.8, 6.2 Hz, 1H), 3.66 (s, 3H), 3.22 (s, 1H), 3.05 - 2.90 (m, 2H), 1.40 (s, 9H), 1.05 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.64, 155.20, 154.93, 130.16, 128.36, 119.90, 79.98, 54.57, 52.17, 37.61, 29.70, 28.31, 27.53, 27.47, 27.45, 27.38, 27.30, 27.28, 27.22, 25.96, 20.63; **HRMS** (ESI) calcd. for $C_{23}H_{39}NO_6Si$ $[M+Na]^+$: 476.2439, found: 476.2419.

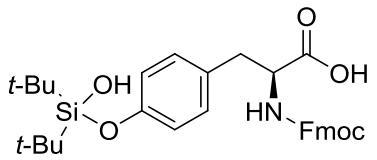
Synthesis of **1b**: To a solution of compound **1a** (2.27 g, 5 mmol) in MeOH/H_2O (30 mL, 1/1), LiOH (240 mg, 10 mmol) was added under r.t and the reaction mixturee was stirred for 30 min. After the removal of MeOH under vaccum, the aqueous layer was adjusted to pH 2~3 by 1N HCl (a.q) and extracted with DCM (20 mL x3), the combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified via flash column chromatography on silica gel (eluent: DCM / MeOH = 50 / 1) to afford compound **1b**.



1b

Compound **1b**, white solid, (1.97 g, 89%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.04 (d, *J* = 7.6 Hz, 1H), 4.57 (d, *J* = 5.6 Hz, 1H), 3.11 (dd, *J* = 13.6, 4.6 Hz, 1H), 3.02 (dd, *J* = 13.6, 5.6 Hz, 1H), 1.43 (s, 9H), 1.08 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.71, 155.48, 154.85, 130.34, 128.37, 119.92, 80.31, 54.38, 37.12, 28.31, 27.36, 27.20, 20.62, 20.58, 19.81; **HRMS** (ESI) calcd. for $C_{22}H_{37}NO_6Si$ $[M+Na]^+$: 462.2282, found: 462.2275.

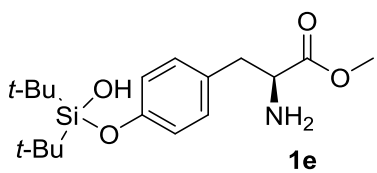
Synthesis of **1c**: Compound **1b** (880 mg, 2 mmol) was added to a solution of 25% TFA/DCM, kept stirring at r.t for 1 h then evaporated. sat.$NaHCO_3$ (a.q, 10 mL) and ACN (10 mL) was added to the resulting mixture and kept stirring under r.t for 30 min, followed by the addition of Fmoc-OSu (745 mg, 2.2 mmol) and kept stirring for another 3 h. After the removal of ACN, the aqueous layer was adjusted to pH 2~3 with 1N HCl (a.q) and extracted with DCM (20 mL x3), the combined organic layer was dried over Na_2SO_4 and evaporated. Purified via Purified via flash column chromatography on silica gel (eluent: DCM / MeOH = 100 / 1) to afford compound **1c**.



1c

Compound **1c**, white solid, (708 mg, 63%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 6.6 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.26 (d, *J* = 8.2 Hz, 1H), 4.65 (dd, *J* = 13.4, 5.6 Hz, 1H), 4.43 (dd, *J* = 10.2, 7.4 Hz, 1H), 4.33 (dd, *J* = 10.4, 7.2 Hz, 1H), 4.19 (t, *J* = 7.0 Hz, 1H), 3.11 (dd, *J* = 14.0, 5.4 Hz, 1H), 3.03 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.04 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.73, 155.85, 155.00, 143.78, 143.66, 141.34, 130.35, 127.95, 127.77, 127.11, 125.13, 125.08, 120.02, 67.15, 54.67, 47.12, 37.03, 27.35, 20.59; **HRMS** (ESI) calcd. for $C_{32}H_{39}NO_6Si$ $[M+H]^+$: 562.2619, found: 562.2629.

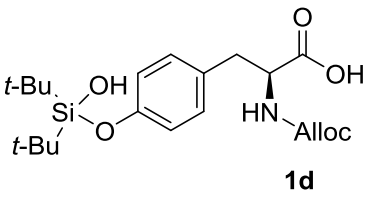
Synthesis of **1e**: Compound **1a** (680 mg, 1.5 mmol) was added to a solution of 25% TFA/DCM, and the reaction mixture was stirred at r.t for 1 h then evaporated. Diluted by sat.$NaHCO_3$ (a.q, 15 mL), the aqueous layer was extracted by DCM (15 mL x 3). The combined organic layer was dried over Na_2SO_4 and evaporated to afford the crude compound **1e**. Compound **1e** was used directly in the next step without purification.



1e

Compound **1e**， white solid, (crude porduct); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.70 (s, 3H), 3.70 - 3.65 (m, 1H), 3.01 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.81 (dd, *J* = 13.6, 7.8 Hz, 1H), 1.31 (d, *J* = 19.2 Hz, 1H), 1.26 (s, 1H), 1.07 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.72, 130.20, 129.47, 119.93, 55.82, 52.00, 40.17, 27.37, 27.25, 20.61, 19.79; **HRMS** (ESI) calcd. for $C_{18}H_{31}NO_4Si$ $[M+H]^+$: 354.2076, found: 354.2065.

Synthesis of **1d**: Compound **1e** was added to a solution of TEA (303 mg, 3 mmol) in DCM (6 mL), followed by the addition of Alloc-Cl (271 mg, 2.25mmol) dropwise via syringe under 0 °C, kept stirring for 1 h. Diluted by DCM (15 mL), the organic layer was washed by water (20 mL x 2), brine, dried over Na_2SO_4 and evaporated to afford crude compound **1f**. To a solution of crude compound **1f** (601 mg) in MeOH/H_2O (10 mL, 1:1), LiOH (72 mg, 3 mmol) was added under r.t and kept stirring for 30 min. The reaction mixture was concentrated under vaccum and the aqueous layer was adjusted to pH 2~3 by 1N HCl (a.q) and extracted with DCM (10 mL x3), the combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified via flash column chromatography on silica gel (eluent: DCM / MeOH = 100 / 1) to afford compound **1d**.



1d

Compound **1d**, white solid, (369 mg, 58% in 3 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.85 (m, 1H), 5.36 (d, *J* = 8.4 Hz, 1H), 5.26 (d, *J* = 16.8 Hz, 1H), 5.19 (d, *J* = 10.6 Hz, 1H), 4.61 (dd, *J* = 13.6, 5.8 Hz, 1H), 4.52 (d, *J* = 5.6 Hz, 2H), 3.08 (dd, *J* = 14.0, 5.4 Hz, 1H), 3.01 (dd, *J* = 14.0, 6.2 Hz, 1H), 1.05 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.59, 155.97, 154.95, 132.40, 130.30, 128.07, 120.01, 118.06, 66.09, 54.71, 37.08, 27.37, 20.62, 20.60; **HRMS** (ESI) calcd. for $C_{21}H_{33}NO_6Si$ $[M+H]^+$: 424.2150, found: 424.2161.

6. Synthesis of dipeptide substrates 4b-4o

General procedure for dipeptide synthesis :

Typically, to a solution of *N*-Boc protected amino acid (1.5 mmol) in DCM (10 mL) was added 1-ethyl-3-(3-(dimethylamino)propyl) carbodiimide hydrochloride (EDCI, 2.0 mmol) in one portion, followed by the addition of the relevant methyl amino acid ester (1.0 mmol) in DCM (5 mL) dropwise. After stirring under r.t for 3 h, the reaction mixture was partitioned between DCM and water, the aqueous layer was extracted with DCM, and the combined organic phase was wash by brine and dried over Na_2SO_4 then evaporated. The residue was purified via flash column to afford pure dipeptide as white solid.

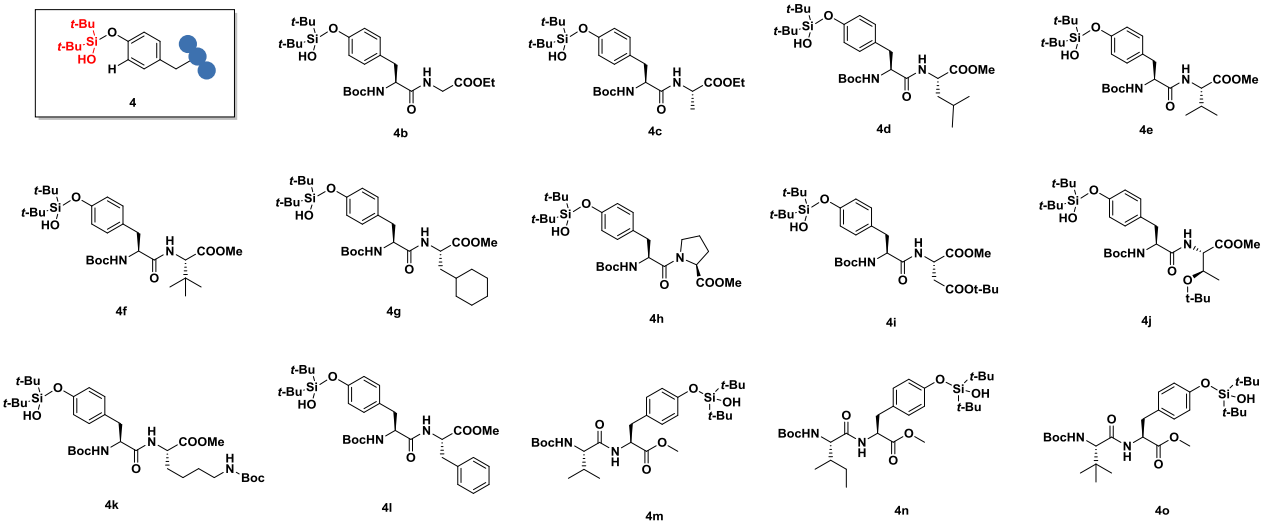
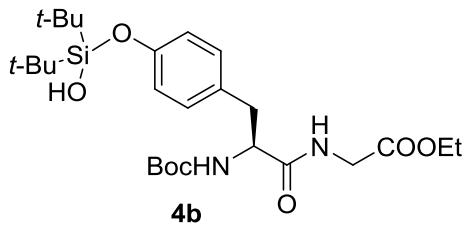
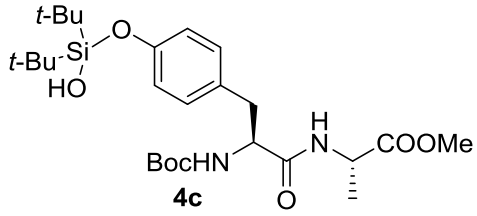


Figure S3. Dipeptides substrates bearing Tyr residue.



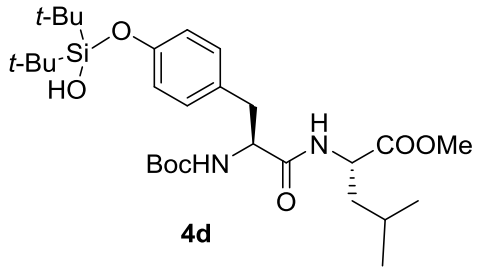
4b

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 15/1) to yield compound **4b** as white solid, (393 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.61 (s, 1H), 5.23 (s, 1H), 4.35 (s, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 4.00 - 3.79 (m, 3H), 2.96 (t, *J* = 8.6 Hz, 2H), 1.39 (s, 9H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.06 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.94, 169.49, 155.55, 154.82, 130.13, 128.94, 120.06, 80.18, 61.52, 55.79, 41.29, 37.74, 28.26, 27.39, 20.66, 20.60, 14.10; **HRMS** (ESI) calcd. for $C_{26}H_{44}N_2O_7Si$ [M+Na]$^+$: 547.2810, found: 547.2788.



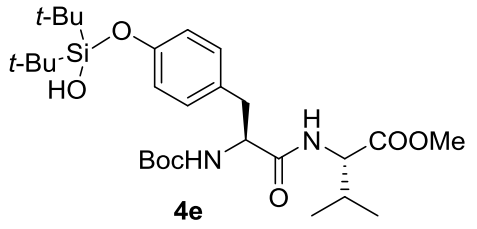
4c

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 15/1) to yield compound **4c** as white solid, (373 mg, 71%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.53 (d, *J* = 5.8 Hz, 1H), 5.21 (s, 1H), 4.60 - 4.44 (m, 1H), 4.31 (s, 1H), 3.70 (s, 3H), 2.96 (td, *J* = 13.8, 6.8 Hz, 2H), 1.41 (s, 9H), 1.32 (d, *J* = 7.2 Hz, 3H), 1.07 (d, *J* = 1.4 Hz, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.89, 171.10, 155.42, 154.85, 130.18, 128.85, 120.08, 80.16, 55.84, 52.45, 48.04, 37.71, 28.26, 27.39, 20.68, 20.57, 18.24; **HRMS** (ESI) calcd. for $C_{26}H_{44}N_2O7Si$ [M+Na]$^+$: 547.2810, found: 547.2807.



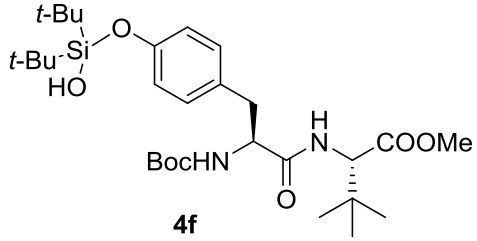
4d

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 15/1) to yield compound **4d** as white solid, (460 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.26 (d, *J* = 7.8 Hz, 1H), 5.14 (s, 1H), 4.57 (td, *J* = 8.6, 5.0 Hz, 1H), 4.27 (d, *J* = 7.0 Hz, 1H), 3.69 (s, 3H), 3.54 (s, 1H), 2.96 (qd, *J* = 14.0, 7.0 Hz, 2H), 1.62 - 1.52 (m, 2H), 1.49 - 1.45 (m, 1H), 1.41 (s, 9H), 1.07 (d, *J* = 1.8 Hz, 18H), 0.88 (t, *J* = 5.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.90, 171.18, 155.47, 154.75, 130.21, 128.95, 120.12, 80.21, 55.97, 52.34, 50.62, 41.56, 37.40, 28.25, 27.38, 24.61, 22.75, 21.85, 20.71, 20.53; **HRMS** (ESI) calcd. for $C_{29}H_{50}N_2O_7Si$ [M+Na]$^+$: 589.3280, found: 589.3302.



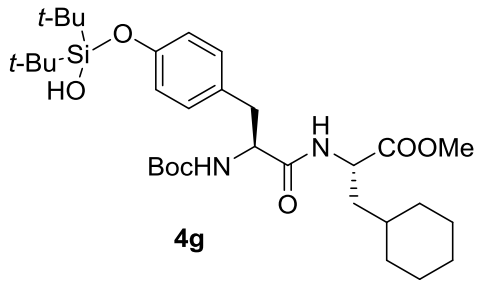
4e

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 12/1) to yield compound **4e** as white solid, (345 mg, 66%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.33 (d, *J* = 8.6 Hz, 1H), 5.14 (s, 1H), 4.44 (dd, *J* = 8.6, 5.2 Hz, 1H), 4.26 (d, *J* = 6.2 Hz, 1H), 3.68 (s, 3H), 2.95 (qd, *J* = 13.8, 7.2 Hz, 2H), 2.11 - 2.00 (m, 1H), 1.40 (s, 9H), 1.05 (d, *J* = 2.4 Hz, 18H), 0.83 (dd, *J* = 11.8, 7.0 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.86, 171.43, 155.51, 154.79, 130.14, 128.96, 120.14, 80.16, 59.88, 57.18, 52.17, 37.36, 31.33, 28.26, 27.39, 20.70, 20.54, 18.81, 17.75; **HRMS** (ESI) calcd. for $C_{28}H_{48}N_2O_7Si$ [M+Na]$^+$: 575.3123, found: 575.3114.



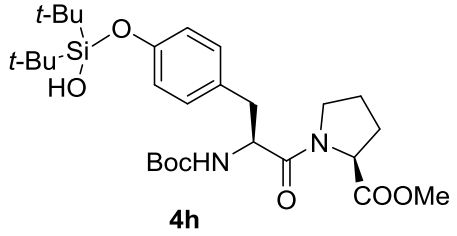
4f

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 16/1) to yield compound **4f** as white solid, (464 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.31 (d, *J* = 9.2 Hz, 1H), 5.16 (s, 1H), 4.38 (d, *J* = 9.2 Hz, 1H), 4.25 (d, *J* = 6.8 Hz, 1H), 3.68 (s, 3H), 3.40 (s, 1H), 2.95 (qd, *J* = 13.8, 7.4 Hz, 2H), 1.42 (s, 9H), 1.07 (d, *J* = 3.8 Hz, 18H), 0.89 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.39, 171.21, 155.51, 154.72, 130.11, 129.06, 120.20, 80.21, 60.01, 56.37, 51.88, 37.36, 34.80, 28.27, 27.38, 26.39, 20.72, 20.51; **HRMS** (ESI) calcd. for $C_{29}H_{50}N_2O_7Si$ [M+H]$^+$: 567.3460, found: 567.3460.



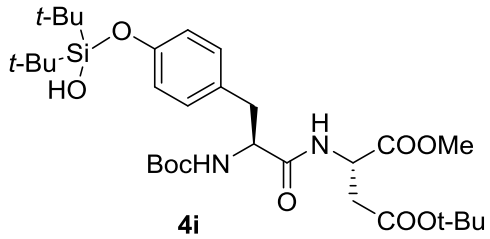
4g

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 18/1) to yield compound **4g** as white solid, (515 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 5.2 Hz, 1H), 5.28 (d, *J* = 9.6 Hz, 1H), 4.58 (td, *J* = 8.6, 5.4 Hz, 1H), 4.28 (s, 2H), 3.67 (s, 3H), 2.94 (d, *J* = 7.0 Hz, 2H), 1.74 (d, *J* = 12.2 Hz, 1H), 1.60 (ddd, *J* = 14.6, 13.6, 9.8 Hz, 5H), 1.47 (dd, *J* = 9.0, 5.6 Hz, 1H), 1.41 (s, 9H), 1.27 - 1.12 (m, 5H), 1.07 (s, 18H), 0.94 - 0.82 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.95, 171.41, 155.54, 154.82, 130.17, 128.83, 120.07, 80.15, 55.90, 52.26, 50.07, 40.01, 37.41, 33.84, 33.34, 32.39, 28.26, 27.40, 26.32, 26.04, 25.92, 20.69, 20.56; **HRMS** (ESI) calcd. for $C_{32}H_{54}N_2O_7Si$ $[M+Na]^+$: 629.3593, found: 629.3563.



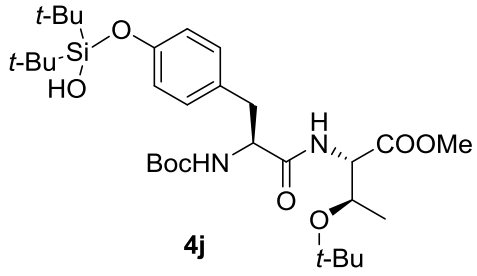
4h

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 15/1) to yield compound **4h** as white solid, (dr : 4/1, 375 mg, 68%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.54 (dd, *J* = 16.6, 8.8 Hz, 1H), 4.62 (dd, *J* = 15.8, 7.4 Hz, 1H), 4.46 (d, *J* = 6.8 Hz, 1H), 3.70 (s, 3H), 3.65 - 3.51 (m, 1H), 3.31 - 3.09 (m, 1H), 2.97 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.83 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.23 - 2.07 (m, 1H), 1.88 (s, 2H), 1.37 (s, 9H), 1.06 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.28, 171.22, 155.32, 154.87, 130.48, 128.58, 119.79, 79.63, 58.91, 53.38, 52.18, 46.87, 38.41, 28.31, 27.42, 24.76, 20.72, 20.63; **HRMS** (ESI) calcd. for $C_{28}H_{46}N_2O_7Si$ $[M+HOOC]^-$: 595.3056, found: 595.3049.



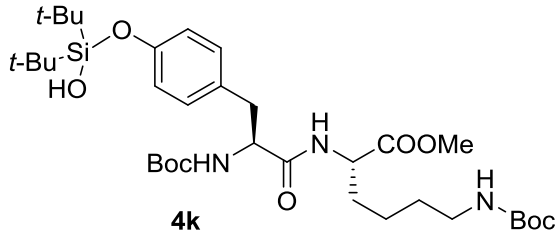
4i

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 10/1) to yield compound **4i** as white solid, (482 mg, 77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.03 (s, 1H), 4.80 - 4.70 (m, 1H), 4.31 (s, 1H), 3.72 (s, 3H), 2.98 (ddd, *J* = 20.6, 13.8, 7.0 Hz, 2H), 2.86 (dd, *J* = 16.8, 4.6 Hz, 1H), 2.67 (dt, *J* = 11.2, 4.6 Hz, 1H), 1.41 (s, 9H), 1.40 (s, 9H), 1.07 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.26, 170.90, 169.69, 155.21, 154.83, 130.14, 128.64, 120.12, 81.82, 80.06, 55.77, 52.60, 48.67, 37.62, 37.51, 28.24, 27.95, 27.39, 20.63, 20.58; **HRMS** (ESI) calcd. for $C_{31}H_{52}N_2O_9Si$ $[M+H]^+$: 625.3515, found: 625.3510.



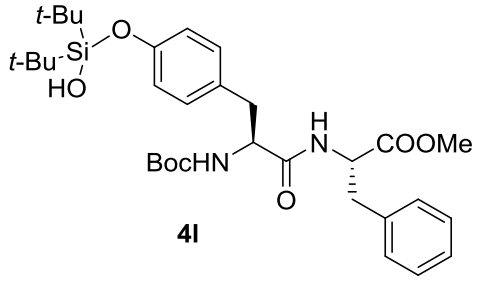
4j

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 10/1) to yield compound **4j** as white solid, (482 mg, 77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 1H), 5.15 (s, 1H), 4.48 (dd, *J* = 9.2, 1.8 Hz, 1H), 4.38 (d, *J* = 5.8 Hz, 1H), 4.18 (dt, *J* = 6.4, 4.6 Hz, 1H), 3.69 (s, 3H), 3.01 (d, *J* = 6.8 Hz, 2H), 1.43 (s, 9H), 1.13 (d, *J* = 12.0 Hz, 3H), 1.09 (s, 9H), 1.07 (d, *J* = 3.4 Hz, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.89, 170.90, 155.25, 154.67, 130.29, 129.04, 120.06, 79.91, 74.14, 67.42, 57.76, 55.93, 52.24, 37.69, 28.27, 27.39, 20.70, 20.54; **HRMS** (ESI) calcd. for $C_{31}H_{54}N_2O_8Si$ $[M+Na]^+$: 633.3542, found: 633.3567.



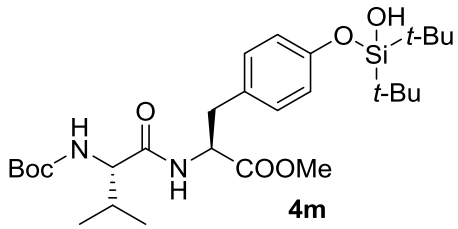
4k

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 10/1) to yield compound **4k** as white solid, (462 mg, 67%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 8.0 Hz, 1H), 5.01 (s, 1H), 4.66 (s, 1H), 4.55 (dd, *J* = 12.6, 7.6 Hz, 1H), 4.34 (d, *J* = 4.8 Hz, 1H), 3.99 (s, 1H), 3.71 (s, 3H), 3.27 - 3.16 (m, 1H), 3.07 (dd, *J* = 13.0, 6.4 Hz, 2H), 2.85 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.81 (ddd, *J* = 15.6, 10.4, 5.4 Hz, 1H), 1.69 (s, 2H), 1.63 - 1.55 (m, 1H), 1.44 (s, 18H), 1.23 - 1.14 (m, 2H), 1.07 (s, 9H), 1.05 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.29, 171.17, 156.20, 155.16, 154.61, 133.38, 130.34, 120.20, 80.32, 79.53, 55.73, 52.45, 52.04, 40.37, 37.12, 32.08, 29.61, 28.44, 28.29, 27.45, 27.37, 22.27, 20.76, 20.55; **HRMS** (ESI) calcd. for $C_{34}H_{59}N_3O_9Si$ $[M+H]^+$: 682.4093, found: 682.4060.



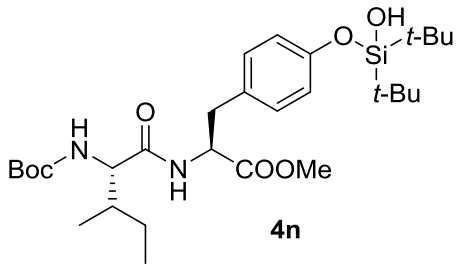
4l

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 18/1) to yield compound **4l** as white solid, (455 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (q, *J* = 6.4 Hz, 3H), 7.08 - 7.00 (m, 4H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.34 (d, *J* = 7.8 Hz, 1H), 5.10 (d, *J* = 3.2 Hz, 1H), 4.79 (dd, *J* = 12.4, 5.8 Hz, 1H), 4.39 - 4.19 (m, 1H), 3.68 (s, 3H), 3.05 (tt, *J* = 13.8, 6.9 Hz, 2H), 2.93 (d, *J* = 6.8 Hz, 2H), 1.42 (s, 9H), 1.08 (d, *J* = 2.4 Hz, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.50, 170.74, 155.31, 154.90, 136.51, 130.12, 129.42, 128.67, 126.98, 119.98, 80.26, 77.36, 77.04, 76.72, 55.66, 53.46, 52.26, 38.29, 37.19, 28.24, 27.39, 20.63, 20.59; **HRMS** (ESI) calcd. for $C_{32}H_{48}N_2O_7Si$ $[M+Na]^+$: 623.3123, found: 623.3100.



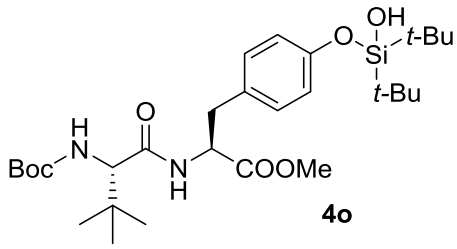
4m

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 12/1) to yield compound **4l** as white solid, (411 mg, 74%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 - 6.87 (m, 4H), 6.56 (d, *J* = 7.0 Hz, 1H), 5.18 (d, *J* = 8.8 Hz, 1H), 4.79 (dd, *J* = 13.4, 6.2 Hz, 1H), 4.05 - 3.91 (m, 1H), 3.66 (s, 3H), 2.99 (d, *J* = 5.8 Hz, 2H), 2.06 (dd, *J* = 12.0, 5.8 Hz, 1H), 1.43 (s, 9H), 1.07 (s, 18H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.84, 171.55, 155.85, 155.03, 130.09, 128.03, 119.99, 79.92, 59.75, 53.35, 52.23, 37.13, 31.01, 28.30, 27.40, 20.64, 19.13, 17.76; **HRMS** (ESI) calcd. for $C_{28}H_{48}N_2O_7Si$ $[M+Na]^+$: 575.3123, found: 575.3114.



4n

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 18/1) to yield compound **4n** as white solid, (455 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.92 (q, *J* = 8.6 Hz, 4H), 6.55 (d, *J* = 7.0 Hz, 1H), 5.17 (d, *J* = 8.6 Hz, 1H), 4.78 (dd, *J* = 13.2, 6.2 Hz, 1H), 4.04 - 3.90 (m, 1H), 3.66 (s, 3H), 3.14 (s, 1H), 2.99 (d, *J* = 5.6 Hz, 2H), 1.81 (d, *J* = 4.0 Hz, 1H), 1.43 (s, 9H), 1.07 (s, 18H), 0.87 (dd, *J* = 10.4, 4.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.80, 171.52, 155.79, 154.99, 130.10, 128.10, 120.01, 79.97, 59.10, 53.34, 52.23, 37.25, 37.13, 28.31, 27.40, 24.66, 20.62, 15.37, 11.34; **HRMS** (ESI) calcd. for $C_{29}H_{50}N_2O_7Si$ $[M+Na]^+$: 589.3280, found: 589.3280.

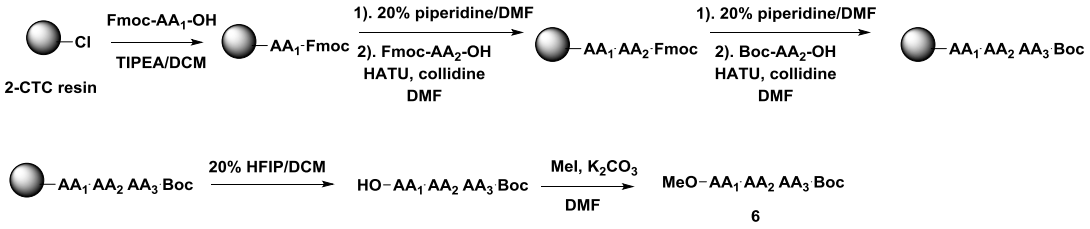


4o

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 18/1) to yield compound **4o** as white solid, (465 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.91-6.97 (m, 4H), 6.16 (d, *J* = 7.2 Hz, 1H), 5.29 (d, *J* = 9.0 Hz, 1H), 4.80 (dd, *J* = 13.0, 6.0 Hz, 1H), 3.85 (d, *J* = 9.6 Hz, 1H), 3.71 (s, 3H), 3.04 (d, *J* = 5.2 Hz, 2H), 1.47 (s, 9H), 1.08 (s, 18H), 0.97 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.73, 170.62, 155.77, 155.01, 130.12, 128.01, 120.06, 79.76, 62.34, 53.23, 52.21, 36.95, 34.57, 28.34, 27.38, 26.42, 20.60; **HRMS** (ESI) calcd. for $C_{29}H_{50}N_2O_7Si$ $[M+Na]^+$: 589.3280, found: 589.3262.

7. Synthesis of polypeptides 6a-6n

SPPS synthesis route :



General procedure :

2-CTC resin (510 mg, 0.50 mmol) was swelled in dry DCM (3 mL) for 10 min, and then drained. A mixture of Fmoc-AA_1-OH (1.5 mmol) and DIEA (1.60 mmol) in of DCM (3 mL) was added to the resin, the reaction mixture was stirred at room temperature for 2 h. The resin was drained, washed with capping solution DCM/MeOH/DIEA (4 mL, 17:2:1, v/v), DCM (4 mL), DMF (4 mL), and DCM (4 mL) 3 times each. Then, 10% piperidine in DMF (4 mL) was added to the resin and the reaction mixture was agitated for 2 min then drained, and washed with DMF (4 mL) three times. This procedure was repeated once. After that, a mixture of Fmoc-AA_2-OH (1.5 mmol), HATU (2.0 mmol) and collidine (2.0 mmol) in DMF (4 mL) was added to the resin and the reaction was agitated for 2 h. The resin was drained and washed with DMF (4 mL) three times. 10% piperidine (4 mL) in DMF was added to the resin and the reaction mixture was agitated for 2 min, the resin was drained and washed with DMF (4 mL) three times. This procedure was repeated once. The peptide elongation procedure was ended with the coupling of *N*-Boc protected AAs. A mixture of Boc-AA_x-OH (1.5 mmol), HATU (2.0 mmol) and collidine (2.0 mmol) in DMF (4 mL) was added to the resin and the reaction mixture was agitated at room temperature for 2h. The resin was drained, washed with DMF (4 mL) three times, and 20% piperidine in DMF (4 mL) was added to the resin and the reaction mixture was agitated for 10 min, the resin was drained and washed with DMF (4 mL), MeOH (4 mL), and DCM (4 mL) for 3 times each. To the resin was added the solution of 25% HFIP in DCM (4 mL), the mixture was kept agitating for another 30 min, the solution was collected and the resin was washed by DCM (4 mL) for 3 times. The combined solution part was evaporated in *vacuo* to give the crude polypeptides as pale yellow solid.

To the mixture of MeI (1.0 mmol) and the crude polypeptide obtained above in DMF (5 mL) was added K_2CO_3 (1.5 mmol) in one portion. After 2 h stirring at r.t, the reaction mixture was partitioned between EA and water, the organic phase was wash by water 3 times, brine, and dried over Na_2SO_4 then evaporated. Purified via flash column to afford pure polypeptide as white solid.

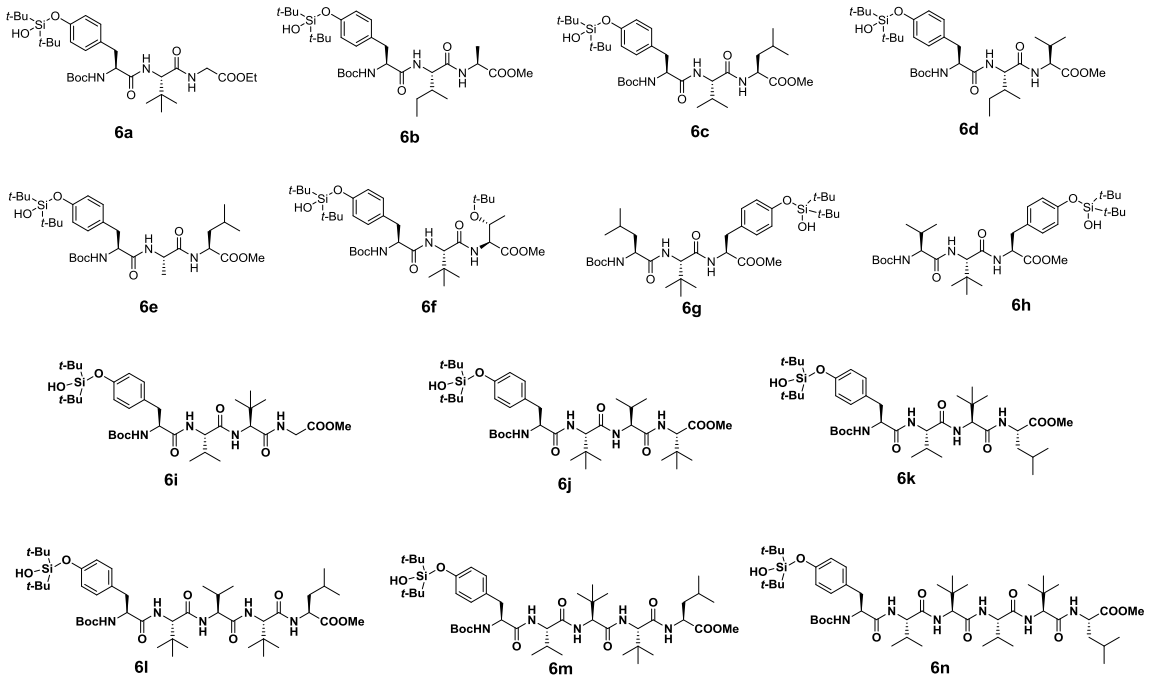
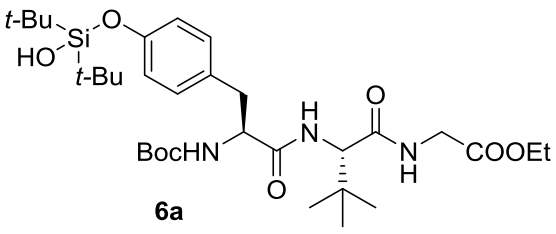
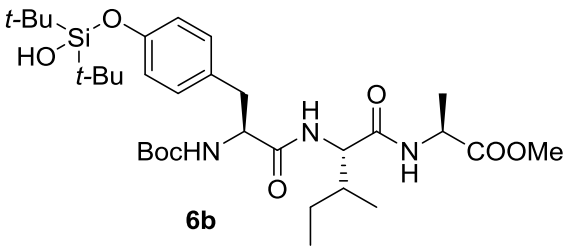


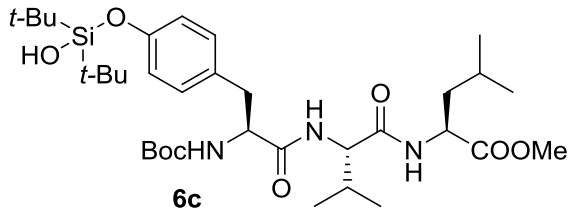
Figure S4. Polypeptide substrates.



To a solution of compound **6a** (453 mg, 0.8 mmol) in MeOH/H_2O (20 mL, v/v = 1/1), was added LiOH (38 mg, 1.6 mmol) under r.t and kept stirring for 30 min. After the removal of MeOH under vaccum, the aqueous layer was adjusted to pH 2~3 via 1N HCl (a.q) and extracted by DCM (20 mL x3), the combined organic layer was dried over Na_2SO_4 and evaporated. The resulting crude acid was obtained as white solid and used directly to the next step. The corresponding amine was added to the solution of crude acid and EDCI (191 mg, 1.0 mmol) in DCM and kept stirring at r.t for 2h, the reaction mixture was partitioned between DCM and water, the aqueous layer was extracted with DCM, and the combined organic phase was wash by brine and dried over Na_2SO_4 then evaporated. Purified by flash column chromatography on silica gel (eluent: PE/EA = 3/1) to yield compound **6a** as white solid, (465 mg, 36%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.71 (s, 1H), 6.18 (s, 1H), 5.36 (s, 1H), 4.28-4.19 (m, 4H), 4.08 (dd, *J* = 18.2, 5.2 Hz, 1H), 4.02 - 3.91 (m, 1H), 3.02 (dd, *J* = 13.6, 5.6 Hz, 1H), 2.86 (dd, *J* = 13.6, 8.6 Hz, 1H), 1.43 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.09 (s, 9H), 1.06 (s, 9H), 0.93 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.27, 170.02, 169.64, 155.47, 154.73, 129.95, 129.01, 120.53, 80.10, 61.58, 60.45, 56.69, 41.25, 38.01, 34.64, 28.31, 27.42, 27.37, 26.40, 20.91, 20.31, 14.13; **HRMS** (ESI) calcd. for $C_{32}H_{55}N_3O_8Si$ $[M+H]^+$: 638.3831, found: 638.3834.

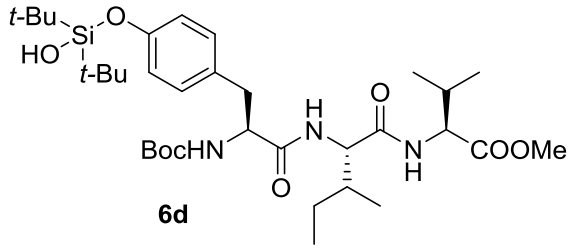


According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 3/1) to yield compound **6b** as white solid, (249 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.42 (s, 1H), 5.30 (s, 1H), 4.55 (p, *J* = 7.2 Hz, 1H), 4.30 (t, *J* = 7.8 Hz, 2H), 4.06 (d, *J* = 23.8 Hz, 1H), 3.73 (s, 3H), 2.95 (ddd, *J* = 30.2, 13.8, 7.2 Hz, 2H), 1.79 (d, *J* = 5.8 Hz, 1H), 1.47 (d, *J* = 3.8 Hz, 2H), 1.41 (s, 9H), 1.39 (d, *J* = 3.0 Hz, 3H), 1.08 (s, 9H), 1.06 (s, 9H), 0.85 (dd, *J* = 11.6, 7.0 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.03, 171.46, 170.31, 155.53, 154.80, 130.00, 128.87, 120.33, 80.14, 57.59, 56.25, 52.41, 47.96, 37.53, 37.00, 28.28, 27.41, 27.38, 24.69, 20.81, 20.43, 18.06, 15.19, 11.19; **HRMS** (ESI) calcd. for $C_{32}H_{55}N_3O_8Si$ $[M+H]^+$: 638.3831, found: 638.3805.



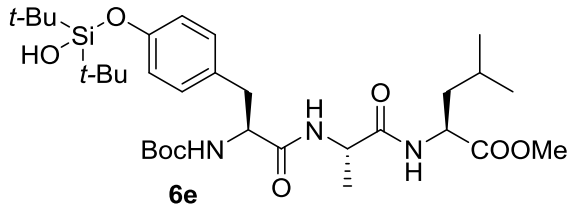
6c

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 4/1) to yield compound **6c** as white solid, (240 mg, 72%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 8.6 Hz, 1H), 5.22 (d, *J* = 6.4 Hz, 1H), 4.58 (td, *J* = 8.6, 5.2 Hz, 1H), 4.34 - 4.22 (m, 2H), 3.72 (s, 4H), 2.96 (ddd, *J* = 32.8, 13.9, 6.8 Hz, 2H), 2.11 - 2.00 (m, 1H), 1.93 (s, 1H), 1.72 - 1.56 (m, 3H), 1.41 (s, 9H), 1.08 (s, 9H), 1.06 (s, 9H), 0.94 (dd, *J* = 6.0, 2.6 Hz, 6H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.05, 171.48, 170.53, 155.53, 154.81, 130.02, 128.90, 120.39, 80.23, 58.44, 56.26, 52.26, 50.80, 41.12, 37.44, 30.80, 28.28, 27.39, 27.37, 24.86, 22.79, 21.93, 20.80, 20.43, 19.03, 17.94; **HRMS** (ESI) calcd. for $C_{34}H_{59}N_3O_8Si$ $[M+H]^+$: 666.4144, found: 666.4124.



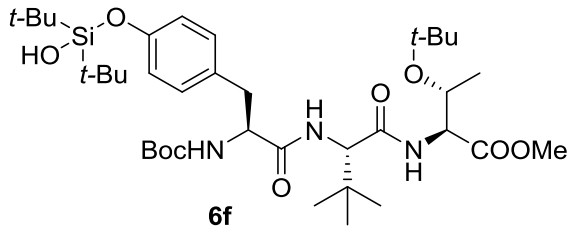
6d

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 4/1) to yield compound **6d** as white solid, (268 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.29 (d, *J* = 8.6 Hz, 1H), 5.34 (d, *J* = 5.8 Hz, 1H), 4.50 (dd, *J* = 8.8, 5.2 Hz, 1H), 4.32 (dd, *J* = 17.2, 8.8 Hz, 2H), 3.92 (s, 1H), 3.74 (s, 3H), 3.00 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.89 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.17 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.99 (s, 1H), 1.79 - 1.70 (m, 1H), 1.49 - 1.44 (m, 1H), 1.41 (s, 9H), 1.09 (s, 9H), 1.06 (s, 9H), 0.97 - 0.92 (m, 6H), 0.87 - 0.81 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.09, 171.41, 170.65, 155.46, 154.74, 129.98, 128.98, 120.45, 80.04, 57.77, 57.19, 56.23, 52.15, 37.58, 37.13, 31.10, 28.28, 27.41, 27.38, 24.82, 20.85, 20.39, 18.87, 18.01, 15.20, 11.21. **HRMS** (ESI) calcd. for $C_{34}H_{59}N_3O_8Si$ $[M+H]^+$: 666.4144, found: 666.4124.



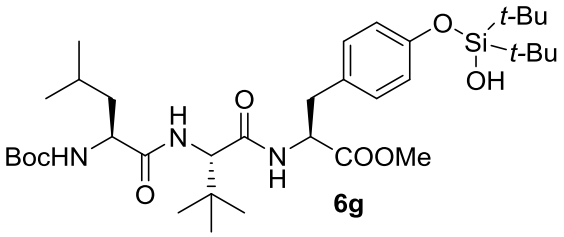
6e

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 4/1) to yield compound **6e** as white solid, (242 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 6.6 Hz, 1H), 5.24 (d, *J* = 7.8 Hz, 1H), 4.59 - 4.46 (m, 2H), 4.31 (d, *J* = 4.8 Hz, 1H), 3.89 (d, *J* = 4.8 Hz, 1H), 3.72 (s, 3H), 2.99 (dd, *J* = 13.4, 6.4 Hz, 1H), 2.90 (dd, *J* = 13.8, 7.0 Hz, 1H), 1.65 (td, *J* = 10.3, 4.0 Hz, 2H), 1.57 (d, *J* = 9.0 Hz, 1H), 1.40 (s, 9H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.08 (s, 9H), 1.06 (s, 9H), 0.94 (t, *J* = 5.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.17, 171.66, 171.33, 155.44, 154.87, 130.04, 128.73, 120.33, 80.23, 55.95, 52.31, 50.91, 48.75, 41.11, 37.83, 28.28, 27.40, 27.39, 24.84, 22.75, 21.95, 20.78, 20.46, 18.16; **HRMS** (ESI) calcd. for $C_{32}H_{55}N_3O_8Si$ $[M+H]^+$: 638.3831, found: 638.3830.



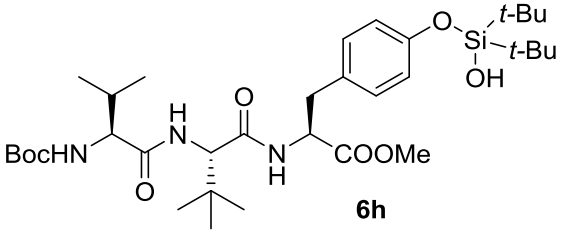
6f

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 4/1) to yield compound **6f** as white solid, (239 mg, 66%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 8.8 Hz, 1H), 6.25 (d, *J* = 9.0 Hz, 1H), 5.27 (d, *J* = 6.8 Hz, 1H), 4.45 (d, *J* = 8.2 Hz, 1H), 4.33 - 4.20 (m, 3H), 3.70 (s, 3H), 3.01 (dd, *J* = 12.6, 5.2 Hz, 1H), 2.88 (dd, *J* = 13.6, 8.2 Hz, 1H), 1.42 (s, 9H), 1.22 (d, *J* = 6.4 Hz, 3H), 1.12 (s, 9H), 1.09 (s, 9H), 1.05 (s, 9H), 0.97 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.98, 170.75, 170.16, 155.27, 154.66, 129.88, 129.13, 120.52, 79.91, 74.28, 67.00, 60.61, 58.03, 56.55, 52.08, 37.93, 35.20, 28.29, 27.40, 27.36, 26.33, 21.25, 20.89, 20.28. **HRMS** (ESI) calcd. for $C_{37}H_{65}N_3O_9Si$ $[M+H]^+$: 724.4563, found: 724.4533.



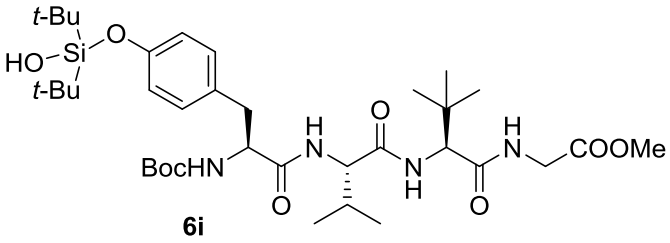
6g

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 4/1) to yield compound **6g** as white solid, (262 mg, 77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.96 - 6.87 (m, 4H), 6.70 (d, *J* = 8.8 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 5.31 (d, *J* = 8.6 Hz, 1H), 4.79 (dd, *J* = 13.6, 6.4 Hz, 1H), 4.28 (d, *J* = 9.2 Hz, 1H), 3.97 (d, *J* = 7.4 Hz, 1H), 3.83 (s, 1H), 3.68 (s, 3H), 3.07 - 2.95 (m, 2H), 2.20 (d, *J* = 7.6 Hz, 1H), 1.87 (dd, *J* = 8.0, 4.8 Hz, 1H), 1.52 (s, 1H), 1.07 (d, *J* = 0.6 Hz, 18H), 0.97 (s, 9H), 0.93 - 0.88 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.87, 169.93, 155.88, 155.01, 130.00, 127.96, 120.11, 79.84, 60.44, 59.56, 53.23, 52.23, 36.94, 36.79, 34.60, 28.31, 27.41, 26.51, 24.84, 20.67, 20.58, 15.61, 11.28; **HRMS** (ESI) calcd. for $C_{34}H_{59}N_3O_8Si$ $[M+H]^+$: 680.4234, found: 680.4260.



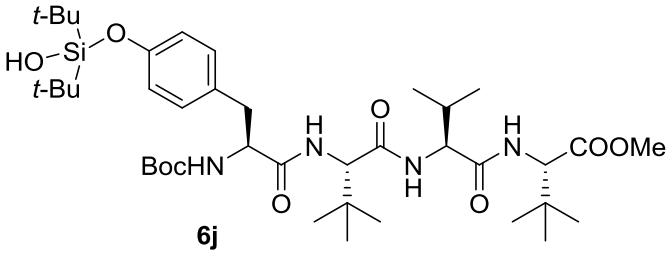
6h

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 4/1) to yield compound **6h** as white solid, (226 mg, 65%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.91 (q, *J* = 8.8 Hz, 4H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.36 (d, *J* = 9.0 Hz, 1H), 4.79 (dd, *J* = 13.8, 6.4 Hz, 1H), 4.31 (d, *J* = 9.2 Hz, 1H), 3.97 (s, 1H), 3.67 (s, 3H), 3.06 - 2.93 (m, 2H), 2.17 - 2.05 (m, 1H), 1.43 (s, 9H), 1.07 (d, *J* = 1.2 Hz, 18H), 0.97 (s, 9H), 0.92 (dd, *J* = 6.4, 4.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.92, 170.02, 155.99, 155.02, 129.99, 127.96, 120.08, 79.81, 60.43, 53.29, 52.21, 36.98, 34.59, 30.61, 28.31, 27.42, 26.51, 20.66, 20.60, 19.34, 18.06; **HRMS** (ESI) calcd. for $C_{34}H_{59}N_3O_8Si$ $[M+H]^+$: 666.4144, found: 666.4134.



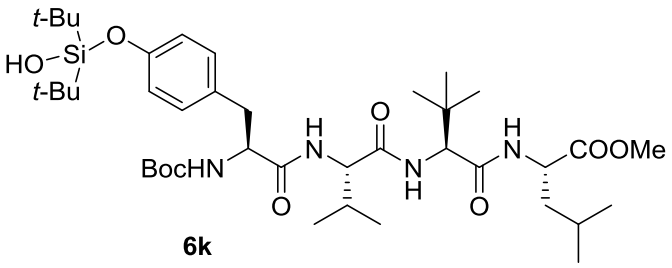
6i

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 2/1) to yield compound **6i** as white solid, (199 mg, 55%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.13 (d, *J* = 9.0 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.55 (s, 1H), 5.72 (d, *J* = 7.6 Hz, 1H), 4.48 (d, *J* = 5.6 Hz, 1H), 4.44 – 4.38 (m, 2H), 4.14 (dd, *J* = 18.0, 6.0 Hz, 1H), 3.86 (dd, *J* = 18.0, 5.1 Hz, 1H), 3.72 (s, 3H), 3.03 (dd, *J* = 13.6, 5.6 Hz, 1H), 2.87 (dd, *J* = 13.4, 8.4 Hz, 1H), 1.93 – 1.89 (m, 1H), 1.42 (s, 9H), 1.12 (s, 9H), 1.10 (s, 9H), 1.07 (s, 9H), 0.84 (dd, *J* = 6.6, 3.4 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.40, 171.21, 170.71, 169.94, 155.50, 154.47, 129.95, 129.28, 120.53, 79.74, 60.65, 58.30, 56.28, 52.12, 40.99, 38.58, 33.89, 31.47, 28.33, 27.34, 26.64, 21.03, 20.17, 18.91, 18.27; **HRMS** (ESI) calcd. for $C_{36}H_{62}N_4O_9Si$ $[M+H]^+$: 723.4359, found: 723.4377.



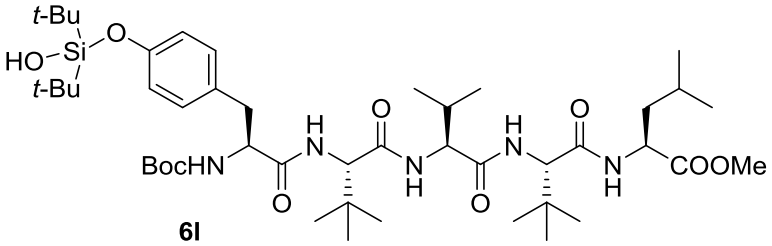
6j

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: PE/EA = 2/1) to yield compound **6j** as white solid, (203 mg, 52%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 9.4 Hz, 1H), 6.92 (dd, *J* = 16.2, 8.4 Hz, 2H), 6.81 (t, *J* = 9.4 Hz, 2H), 6.24 (d, *J* = 8.6 Hz, 1H), 5.37 (d, *J* = 8.6 Hz, 1H), 4.44 (d, *J* = 9.8 Hz, 1H), 4.40 (d, *J* = 9.6 Hz, 1H), 4.14 (d, *J* = 9.6 Hz, 1H), 3.64 (s, 3H), 3.01 (dd, *J* = 12.8, 4.2 Hz, 1H), 2.66 (t, *J* = 12.2 Hz, 1H), 2.15 (dd, *J* = 16.4, 6.6 Hz, 1H), 1.36 (s, 9H), 1.11 (s, 9H), 1.01 (s, 15H), 0.91 (s, 9H), 0.69 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.57, 171.18, 171.15, 169.94, 155.71, 154.57, 129.51, 129.40, 121.23, 79.43, 60.25, 59.43, 59.37, 57.58, 51.64, 39.09, 34.48, 34.17, 30.01, 28.35, 27.46, 27.31, 26.84, 26.05, 21.44, 19.77, 19.33, 19.22; **HRMS** (ESI) calcd. for $C_{40}H_{70}N_4O_9Si$ $[M+H]^+$: 779.4985, found: 779.5023.



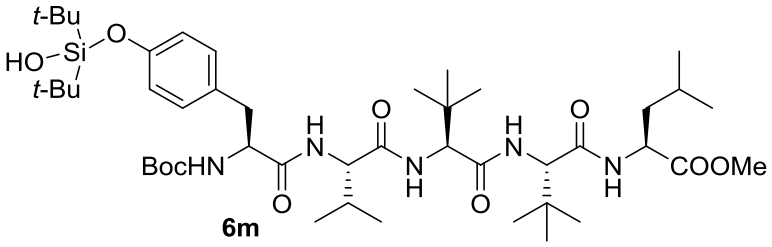
6k

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: DCM/MeOH = 25/1) to yield compound **6k** as white solid, (214 mg, 55%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 5.92 (s, 1H), 5.67 (d, *J* = 8.2 Hz, 1H), 4.65 – 4.55 (m, 1H), 4.32 – 4.21 (m, 3H), 3.63 (s, 3H), 2.96 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.70 (dd, *J* = 13.2, 9.8 Hz, 1H), 1.69 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.58 – 1.44 (m, 3H), 1.35 (s, 9H), 1.07 (s, 9H), 1.03 (s, 9H), 1.00 (s, 9H), 0.81 – 0.76 (m, 6H), 0.72 (dd, *J* = 10.4, 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.05, 171.17, 170.02, 155.40, 154.38, 129.81, 129.43, 120.84, 79.72, 60.57, 58.05, 56.74, 52.11, 50.26, 41.05, 38.89, 33.77, 31.59, 28.36, 27.37, 27.33, 26.62, 24.61, 22.94, 21.52, 21.14, 19.99, 18.69, 18.38; **HRMS** (ESI) calcd. for $C_{40}H_{70}N_4O_9Si$ $[M+H]^+$: 779.4985, found: 779.5016.



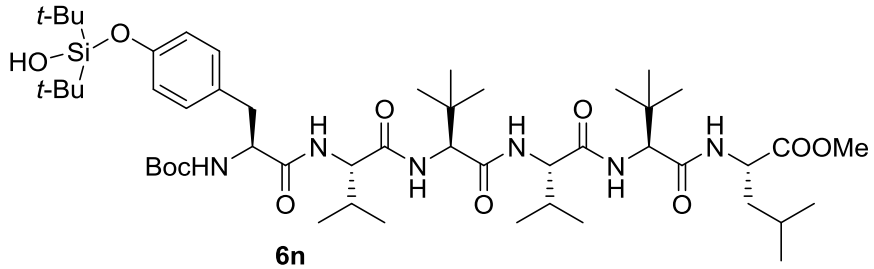
6l

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: DCM/MeOH = 25/1) to yield compound **6l** as white solid, (211 mg, 47%); **^{1}H NMR** (400 MHz, MeOD) δ 8.40 (d, *J* = 9.0 Hz, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 8.18 (d, *J* = 9.4 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.51 (d, *J* = 8.4 Hz, 1H), 4.58 – 4.38 (m, 5H), 3.61 (s, 3H), 2.90 (dd, *J* = 13.8, 3.8 Hz, 1H), 2.68 (dd, *J* = 13.6, 9.4 Hz, 1H), 1.96 – 1.87 (m, 1H), 1.55 (dd, *J* = 15.6, 6.8 Hz, 3H), 1.27 (s, 9H), 0.91 (t, *J* = 12.8 Hz, 36H), 0.84 – 0.80 (m, 6H), 0.77 (dd, *J* = 6.0, 4.4 Hz, 6H); **^{13}C NMR** (101 MHz, MeOD) δ 173.09, 172.69, 172.09, 171.16, 170.87, 156.22, 154.83, 129.92, 129.46, 119.28, 79.12, 78.06, 60.23, 60.07, 58.65, 55.76, 51.24, 50.68, 40.06, 37.19, 34.66, 34.09, 30.94, 27.47, 26.71, 26.11, 25.97, 24.51, 22.05, 20.62, 20.26, 20.22, 18.34; **HRMS** (ESI) calcd. for $C_{46}H_{80}N_5O_{10}Si$ $[M+H]^+$: 892.5825, found: 892.5862.



6m

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: DCM/MeOH = 20/1) to yield compound **6m** as white solid, (200 mg, 45%); **^{1}H NMR** (400 MHz, MeOD) δ 8.27 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 11.8 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 8.6 Hz, 1H), 4.59 (d, *J* = 9.2 Hz, 1H), 4.40 (dd, *J* = 14.6, 7.2 Hz, 3H), 4.33 (d, *J* = 9.2 Hz, 1H), 3.60 (s, 3H), 2.88 (dd, *J* = 13.6, 3.6 Hz, 1H), 2.67 (dd, *J* = 13.6, 9.8 Hz, 1H), 1.93 (dd, *J* = 13.8, 7.0 Hz, 1H), 1.59 (dd, *J* = 13.6, 6.6 Hz, 1H), 1.54 – 1.48 (m, 2H), 1.26 (s, 9H), 0.94 (s, 18H), 0.92 (s, 9H), 0.88 (s, 9H), 0.83 – 0.77 (m, 12H); **^{13}C NMR** (101 MHz, MeOD) δ 173.01, 172.77, 172.05, 171.97, 171.01, 156.16, 154.84, 129.87, 129.41, 119.27, 79.13, 78.06, 60.17, 58.35, 55.65, 51.18, 50.63, 39.90, 37.37, 34.32, 34.13, 31.16, 27.44, 26.70, 26.06, 25.91, 24.52, 22.01, 20.61, 20.26, 20.22, 18.60, 17.77; **HRMS** (ESI) calcd. for $C_{46}H_{80}N_5O_{10}Si$ $[M+H]^+$: 892.5825, found: 892.5858.



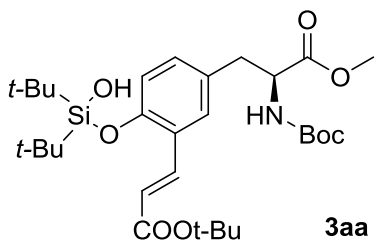
6n

According to the general procedure, the crude product was purified by flash column chromatography on silica gel (eluent: DCM/MeOH = 20/1) to yield compound **6n** as white solid, (198 mg, 40%); **^{1}H NMR** (400 MHz, MeOD) δ 8.64 (d, *J* = 9.0 Hz, 1H), 8.46 (d, *J* = 8.2 Hz, 1H), 8.32 (d, *J* = 6.8 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 4.66 (dd, *J* = 39.0, 18.4 Hz, 8H), 3.73 (s, 3H), 3.03 – 2.95 (m, 1H), 2.81 (dd, *J* = 13.4, 9.4 Hz, 1H), 2.04 (d, *J* = 6.8 Hz, 2H), 1.66 (d, *J* = 4.6 Hz, 3H), 1.37 (s, 9H), 1.04 (s, 27H), 0.98 (s, 9H), 0.90 (dd, *J* = 12.8, 4.4 Hz, 18H); **^{13}C NMR** (101 MHz, MeOD) δ 173.14, 172.71, 172.16, 172.06, 171.06, 170.47, 156.11, 154.78, 129.96, 129.45, 119.26, 79.02, 78.06, 59.80, 58.40, 57.99, 55.53, 51.30, 50.66, 40.08, 37.69, 34.35, 34.04, 31.31, 31.00, 27.54, 26.75, 26.38, 26.08, 24.57, 22.06, 20.83, 20.26, 18.66, 18.35, 18.20, 17.98; **HRMS** (ESI) calcd. for $C_{51}H_{90}N_6O_{11}Si$ $[M+H]^+$: 991.6510, found: 991.6528.

8. Pd-catalyzed olefination of substrates

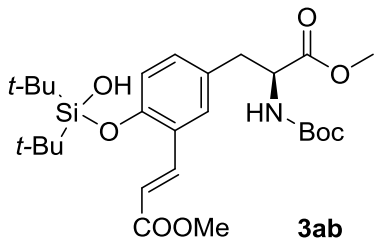
General procedure:

To a 15 ml sealed reaction tube, peptide substrate (0.20 mmol), olefination reagent (0.8 mmol), $Pd(OAc)_2$ (0.02 mmol), BQ (0.04 mmol), Li_3PO_4 (0.4 mmol), $PhI(OAc)_2$ (0.60 mmol) and DCE (2.0 ml) was added. The reaction mixture was stirred at 90 °C for 24 h, cooled to room temperature and diluted with EA (5.0 ml). The resulting solution was filtered through a Celite pad, concentrated under reduced pressure and further purified by column chromatography. The resulting products were typically obtained as colorless oil.



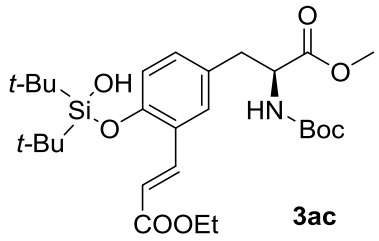
3aa

Compound **3aa**, (81 mg, 73%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 16.2 Hz, 1H), 7.24 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 5.04 (d, *J* = 8.2 Hz, 1H), 4.53 (dd, *J* = 13.2, 6.0 Hz, 1H), 3.67 (s, 3H), 3.35 (s, 1H), 3.02 (dd, *J* = 13.8, 5.6 Hz, 1H), 2.94 (dd, *J* = 13.8, 6.0 Hz, 1H), 1.50 (s, 9H), 1.40 (s, 9H), 1.06 (s, 18H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.35, 166.40, 155.08, 153.93, 138.48, 131.82, 128.72, 127.84, 124.99, 120.12, 119.96, 80.23, 80.08, 54.47, 52.25, 37.64, 28.30, 28.22, 27.40, 20.73; **HRMS** (ESI) calcd. for $C_{30}H_{49}NO_8Si$ $[M+Na]^+$: 602.3120, found: 602.3092.



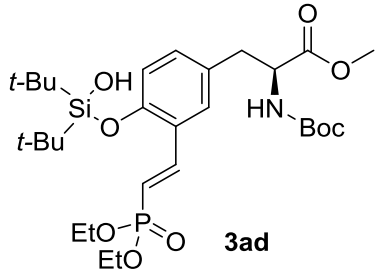
3ab

Compound **3ab**, (71 mg, 66%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 16.2 Hz, 1H), 7.27 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.99 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.38 (d, *J* = 16.2 Hz, 1H), 5.05 (d, *J* = 7.8 Hz, 1H), 4.55 (d, *J* = 6.6 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.05 (dd, *J* = 13.6, 5.4 Hz, 1H), 2.96 (dd, *J* = 13.6, 6.0 Hz, 1H), 1.41 (s, 9H), 1.08 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.34, 167.72, 155.08, 154.17, 140.15, 132.23, 128.82, 127.98, 124.69, 120.09, 117.35, 80.09, 54.44, 52.25, 51.61, 37.65, 28.28, 27.36, 20.72; **HRMS** (ESI) calcd. for $C_{27}H_{43}NO_8Si$ $[M+Na]^+$: 560.2650, found: 560.2630.



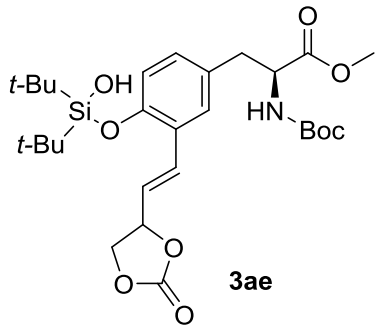
3ac

Compound **3ac**, (78 mg, 71%), colorless oil, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 16.5 Hz, 1H), 7.27 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 16.5 Hz, 1H), 5.04 (s, 1H), 4.55 (d, *J* = 5.5 Hz, 1H), 4.24 (q, *J* = 6.5 Hz, 2H), 3.70 (s, 3H), 3.05 (d, *J* = 13.0 Hz, 1H), 2.96 (d, *J* = 12.5 Hz, 1H), 1.42 (s, 9H), 1.31 (t, *J* = 6.5 Hz, 3H), 1.08 (s, 18H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.32, 167.20, 155.06, 154.05, 139.67, 132.16, 128.83, 127.83, 124.76, 120.04, 117.83, 80.08, 77.29, 77.04, 76.78, 60.34, 54.44, 52.26, 37.66, 28.30, 27.37, 20.73, 14.26; **HRMS** (ESI) calcd. for $C_{28}H_{45}NO_8Si$ $[M+Na]^+$: 574.2807, found: 574.2788.



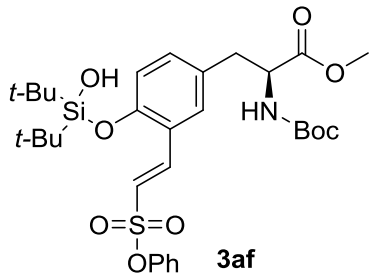
3ad

Compound **3ad**, (98mg, 80%), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 23.2, 17.8 Hz, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.97 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.17 (dd, *J* = 19.2, 17.8 Hz, 1H), 5.00 (d, *J* = 7.8 Hz, 1H), 4.53 (d, *J* = 6.2 Hz, 1H), 4.15 - 4.04 (m, 4H), 3.69 (s, 3H), 3.04 (dd, *J* = 13.8, 5.4 Hz, 1H), 2.94 (dd, *J* = 13.4, 6.4 Hz, 1H), 1.40 (s, 9H), 1.32 (t, *J* = 7.0 Hz, 6H), 1.05 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.34, 155.06, 153.88, 143.95, 132.07, 128.81, 127.65, 120.34, 114.44, 112.53, 80.04, 61.82, 61.77, 54.45, 52.26, 37.68, 28.30, 27.42, 20.72, 16.42, 16.36; **HRMS** (ESI) calcd. for $C_{29}H_{50}NO_9PSi$ $[M+Na]^+$: 638.2885, found: 638.2881.



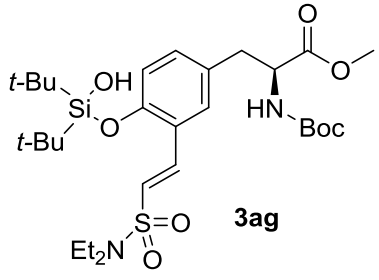
3ae

Compound **3ae**, (63mg, 55%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 7.17 (d, *J* = 4.6 Hz, 1H), 7.14 (d, *J* = 2.8 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.13 (dd, *J* = 16.0, 7.8 Hz, 1H), 5.29 (q, *J* = 7.8 Hz, 1H), 5.07 (d, *J* = 7.8 Hz, 1H), 4.64 (t, *J* = 8.4 Hz, 1H), 4.55 (d, *J* = 6.0 Hz, 1H), 4.23 (t, *J* = 8.0 Hz, 1H), 3.69 (s, 3H), 3.04 (dd, *J* = 12.6, 4.8 Hz, 1H), 2.99 - 2.89 (m, 1H), 2.16 - 2.03 (m, 1H), 1.40 (s, 9H), 1.05 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.48, 155.13, 154.94, 153.11, 132.22, 130.92, 128.77, 127.45, 125.08, 122.13, 119.90, 80.10, 78.37, 69.37, 54.50, 52.27, 37.73, 28.30, 27.38, 20.72, 20.69; **HRMS** (ESI) calcd. for $C_{28}H_{43}NO_9Si$ $[M+Na]^+$: 589.2610, found: 589.2617.



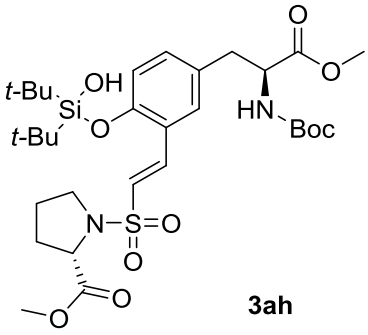
3af

Compound **3af**, (86mg, 68%), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 15.8 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.27 - 7.23 (m, 3H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.86 (d, *J* = 15.8 Hz, 1H), 5.06 (d, *J* = 7.8 Hz, 1H), 4.56 (d, *J* = 6.4 Hz, 1H), 3.70 (s, 3H), 3.07 (dd, *J* = 13.6, 5.0 Hz, 1H), 2.94 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.41 (s, 9H), 0.99 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.26, 155.10, 154.84, 149.64, 141.66, 133.85, 129.78, 129.22, 128.80, 127.06, 122.38, 121.94, 120.34, 120.07, 116.20, 80.28, 54.34, 52.38, 37.60, 28.30, 27.27, 20.62; **HRMS** (ESI) calcd. for $C_{31}H_{45}NO_9SSi$ $[M+Na]^+$: 658.2477, found: 658.2478.



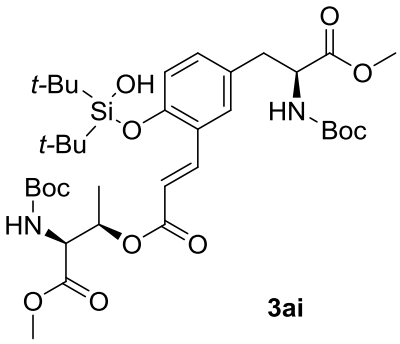
3ag

compound **3ag**, (79mg, 64%), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 15.6 Hz, 1H), 7.23 - 7.16 (m, 2H), 7.01 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 5.03 (d, *J* = 8.0 Hz, 1H), 4.61 - 4.50 (m, 1H), 3.70 (s, 3H), 3.25 (q, *J* = 7.0 Hz, 4H), 3.05 (dd, *J* = 13.8, 5.8 Hz, 1H), 2.95 (dd, *J* = 13.8, 6.4 Hz, 1H), 1.41 (s, 9H), 1.21 (t, *J* = 7.0 Hz, 6H), 1.07 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.32, 155.08, 154.18, 136.44, 132.48, 129.03, 128.41, 124.57, 123.21, 120.16, 80.12, 54.40, 52.31, 41.84, 37.66, 28.30, 27.35, 20.68, 14.56; **HRMS** (ESI) calcd. for $C_{29}H_{50}N_2O_8SSi$ $[M+Na]^+$: 637.2949, found: 637.2935.



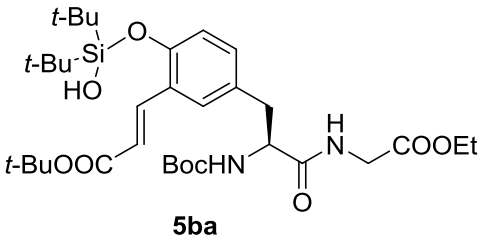
3ah

Compound **3ah**, (93mg, 69%), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 15.6 Hz, 1H), 7.22 (d, *J* = 1.0 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 15.6 Hz, 1H), 5.05 (d, *J* = 7.8 Hz, 1H), 4.56 (d, *J* = 6.8 Hz, 1H), 4.40 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.48 - 3.39 (m, 2H), 3.06 (dd, *J* = 13.8, 5.6 Hz, 1H), 2.97 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.30 - 2.20 (m, 1H), 2.08 - 1.93 (m, 3H), 1.41 (s, 9H), 1.08 (s, 9H), 1.07 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.13, 172.32, 155.11, 154.29, 137.82, 132.73, 129.05, 128.63, 123.09, 120.35, 80.12, 60.42, 54.41, 52.50, 52.34, 47.76, 37.60, 31.08, 28.29, 27.38, 27.23, 25.95, 24.84, 20.71, 20.69; **HRMS** (ESI) calcd. for $C_{31}H_{50}N_2O_{10}SSi$ $[M+Na]^+$: 693.2848, found: 693.2832.



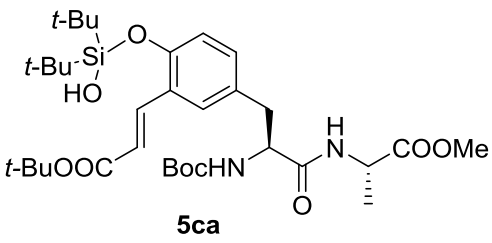
3ai

Compound **3ai**, (90mg, 61%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 16.2 Hz, 1H), 7.27 (d, *J* = 1.6 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.02 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.28 (d, *J* = 16.2 Hz, 1H), 5.61 (d, *J* = 9.8 Hz, 1H), 5.50 (qd, *J* = 6.2, 2.2 Hz, 1H), 5.06 (d, *J* = 8.2 Hz, 1H), 4.54 (dd, *J* = 9.8, 2.2 Hz, 2H), 4.06 (s, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.06 (dd, *J* = 13.8, 5.6 Hz, 1H), 2.96 (dd, *J* = 13.8, 6.2 Hz, 1H), 1.47 (s, 9H), 1.42 (s, 9H), 1.36 (d, *J* = 6.4 Hz, 3H), 1.10 (s, 9H), 1.06 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.27, 171.46, 165.57, 156.05, 155.03, 154.29, 140.59, 132.54, 129.05, 127.64, 124.55, 120.61, 116.95, 80.22, 80.06, 70.69, 57.36, 54.44, 52.74, 52.27, 37.65, 28.34, 28.30, 27.40, 27.36, 20.80, 20.68, 16.95; **HRMS** (ESI) calcd. for $C_{36}H_{58}N_2O_{12}Si$ $[M+Na]^+$: 761.3677, found: 761.3510.



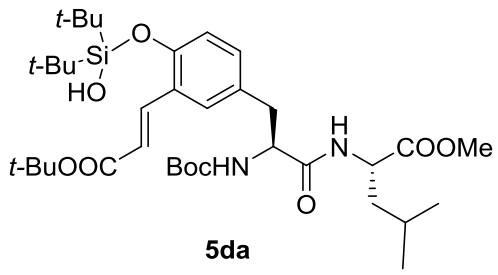
5ba

Compound **5ba**, (68mg, 52%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 16.2 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.61 (s, 1H), 6.30 (d, *J* = 16.2 Hz, 1H), 5.18 (d, *J* = 6.8 Hz, 1H), 4.38 (d, *J* = 5.8 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.02 - 3.88 (m, 2H), 2.99 (ddd, *J* = 20.4, 13.8, 7.2 Hz, 2H), 1.51 (s, 9H), 1.39 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 4H), 1.07 (d, *J* = 2.0 Hz, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.64, 169.45, 166.41, 155.49, 153.86, 138.40, 131.88, 129.23, 127.81, 125.11, 120.19, 120.11, 80.36, 80.17, 61.59, 55.65, 41.30, 37.67, 28.25, 28.23, 27.40, 20.77, 20.72, 14.11; **HRMS** (ESI) calcd. for $C_{33}H_{54}N_2O_9Si$ $[M+HOOC]^-$: 695.3581, found: 695.3557.



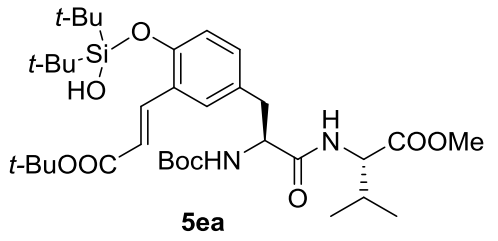
5ca

Compound **5ca**, (88mg, 66%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.62 (d, *J* = 5.6 Hz, 1H), 6.29 (d, *J* = 16.2 Hz, 1H), 5.21 (d, *J* = 6.0 Hz, 1H), 4.58 - 4.47 (m, 1H), 4.34 (d, *J* = 3.6 Hz, 1H), 3.71 (s, 3H), 2.98 (d, *J* = 6.4 Hz, 2H), 1.51 (s, 9H), 1.40 (s, 9H), 1.34 (d, *J* = 7.2 Hz, 3H), 1.07 (d, *J* = 1.8 Hz, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.91, 170.95, 166.43, 155.42, 153.92, 138.44, 131.97, 129.10, 127.83, 125.08, 120.11, 80.30, 80.17, 55.55, 52.53, 48.08, 37.67, 28.25, 28.23, 27.41, 20.78, 20.72, 18.27; **HRMS** (ESI) calcd. for C33H54N2O9Si $[M+Na]^+$: 673.3491, found: 673.3458.



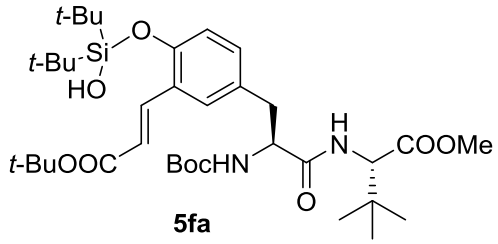
5da

Compound **5da**, (75mg, 54%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.40 - 6.22 (m, 2H), 5.11 (d, *J* = 3.6 Hz, 1H), 4.58 (td, *J* = 8.6, 5.0 Hz, 1H), 4.30 (d, *J* = 6.8 Hz, 1H), 3.70 (s, 3H), 2.99 (d, *J* = 6.8 Hz, 2H), 1.58 (dd, *J* = 10.8, 5.4 Hz, 2H), 1.51 (s, 9H), 1.42 (s, 9H), 1.25 (s, 1H), 1.08 (d, *J* = 2.0 Hz, 18H), 0.89 (dd, *J* = 6.0, 4.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.90, 170.93, 166.34, 155.37, 153.81, 138.35, 131.95, 129.22, 127.88, 125.20, 120.29, 120.09, 80.34, 80.12, 55.69, 52.33, 50.71, 41.62, 37.33, 28.25, 28.23, 27.39, 24.69, 22.73, 21.88, 20.76, 20.68; **HRMS** (ESI) calcd. for $C_{36}H_{60}N_2O_9Si$ $[M+Na]^+$: 715.3960, found: 715.3990.



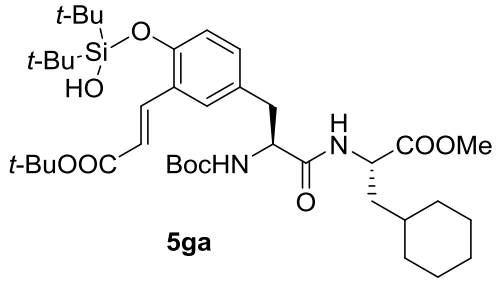
5ea

Compound **5ea**, (62mg, 46%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 16.2 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 16.2 Hz, 1H), 5.11 (s, 1H), 4.48 (dd, *J* = 8.6, 5.0 Hz, 1H), 4.30 (d, *J* = 6.6 Hz, 1H), 3.70 (s, 3H), 3.33 (s, 1H), 2.99 (d, *J* = 6.8 Hz, 2H), 2.15 - 2.05 (m, 1H), 1.51 (s, 9H), 1.42 (s, 9H), 1.08 (d, *J* = 1.8 Hz, 18H), 0.85 (dd, *J* = 11.4, 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.86, 171.13, 166.33, 155.43, 153.81, 138.29, 131.93, 129.25, 127.79, 125.20, 120.25, 120.13, 80.34, 80.12, 57.15, 55.87, 52.21, 37.26, 31.31, 28.28, 28.24, 27.40, 27.39, 20.77, 20.70, 18.81, 17.72; **HRMS** (ESI) calcd. for $C_{35}H_{58}N_2O_9Si$ $[M+Na]^+$: 710.3804, found: 710.3811.



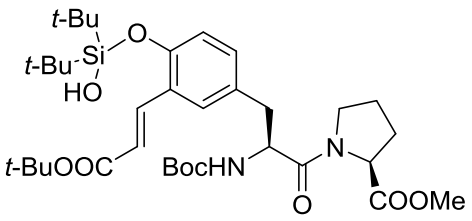
5fa

Compound **5fa**, (87mg, 63%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.58 (d, *J* = 7.2 Hz, 1H), 6.29 (d, *J* = 16.2 Hz, 1H), 5.25 (s, 1H), 4.39 (d, *J* = 9.4 Hz, 1H), 4.29 (d, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 3.06 - 2.90 (m, 2H), 1.51 (s, 9H), 1.41 (s, 9H), 1.08 (s, 18H), 0.91 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.30, 171.27, 166.41, 155.59, 153.95, 138.43, 131.88, 130.07, 129.14, 127.65, 125.09, 120.16, 120.12, 80.34, 80.11, 60.09, 56.11, 51.85, 37.01, 34.81, 28.25, 28.23, 27.44, 27.42, 26.44, 20.78, 20.75; **HRMS** (ESI) calcd. for $C_{36}H_{60}N_2O_9Si$ $[M+HOOC]^-$: 737.4050, found: 737.4019.



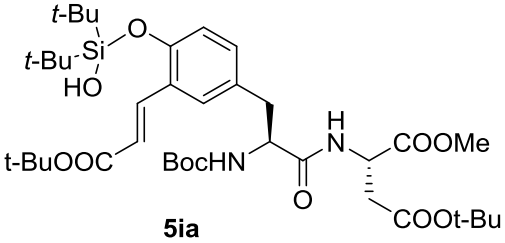
5ga

Compound **5ga**, (69mg, 47%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.30 (d, *J* = 16.2 Hz, 2H), 5.16 (s, 1H), 4.58 (td, *J* = 8.6, 5.6 Hz, 1H), 4.30 (d, *J* = 6.4 Hz, 1H), 3.69 (s, 3H), 2.97 (dd, *J* = 13.6, 7.0 Hz, 3H), 1.77 - 1.55 (m, 7H), 1.51 (s, 9H), 1.41 (s, 9H), 1.20 - 1.11 (m, 3H), 1.07 (d, *J* = 2.4 Hz, 18H), 0.95 - 0.79 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.01, 171.05, 166.39, 155.42, 153.86, 138.40, 131.97, 129.19, 127.85, 125.12, 120.19, 120.12, 80.28, 80.13, 55.68, 52.36, 50.13, 40.06, 37.43, 33.92, 33.34, 32.45, 28.28, 28.23, 27.41, 27.40, 26.31, 26.06, 25.93, 20.79, 20.70; **HRMS** (ESI) calcd. for $C_{39}H_{64}N_2O_9Si$ $[M+Na]^+$: 755.4273, found: 755.4254.



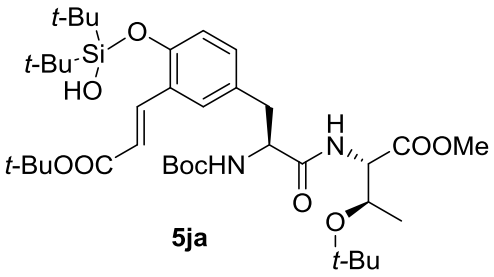
5ha

Compound **5ha**, (57mg, 42%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 16.2 Hz, 1H), 7.45 (d, *J* = 1.6 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.39 (d, *J* = 16.2 Hz, 1H), 5.38 (d, *J* = 9.0 Hz, 1H), 4.64 (dd, *J* = 15.2, 6.8 Hz, 1H), 4.50 (dd, *J* = 8.2, 4.0 Hz, 1H), 3.74 (s, 3H), 3.68 - 3.61 (m, 1H), 3.27 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.02 (dd, *J* = 13.8, 7.1 Hz, 1H), 2.87 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.17 (ddd, *J* = 16.0, 8.2, 3.0 Hz, 1H), 1.92 (d, *J* = 3.6 Hz, 3H), 1.51 (s, 9H), 1.44 (d, *J* = 3.0 Hz, 1H), 1.39 (s, 9H), 1.08 (d, *J* = 2.0 Hz, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.25, 170.73, 166.52, 155.21, 153.84, 138.56, 132.56, 128.85, 128.21, 124.95, 120.14, 119.82, 79.95, 79.72, 58.81, 53.03, 52.33, 46.93, 38.13, 28.97, 28.31, 28.23, 27.42, 27.41, 24.81, 20.79, 20.73; **HRMS** (ESI) calcd. for $C_{35}H_{56}N_2O_9Si$ $[M+H]^+$: 677.3828, found: 677.3807.



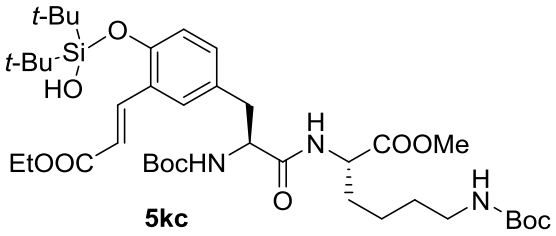
5ia

Compound **5ia**, (79mg, 53%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.30 (d, *J* = 16.2 Hz, 1H), 5.07 (d, *J* = 5.6 Hz, 1H), 4.77 (dt, *J* = 8.6, 4.4 Hz, 1H), 4.35 (s, 1H), 3.73 (s, 3H), 3.07 - 2.94 (m, 2H), 2.89 (dd, *J* = 17.0, 4.4 Hz, 1H), 2.66 (dd, *J* = 17.0, 4.8 Hz, 1H), 1.51 (s, 9H), 1.40 (d, *J* = 4.4 Hz, 18H), 1.08 (d, *J* = 2.2 Hz, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.92, 169.83, 166.36, 155.14, 153.81, 138.40, 131.98, 128.97, 127.85, 125.12, 120.15, 81.97, 80.20, 80.11, 55.50, 52.73, 48.59, 37.66, 37.49, 28.26, 28.24, 27.98, 27.41, 20.75, 20.71; **HRMS** (ESI) calcd. for $C_{38}H_{62}N_2O_{11}Si$ $[M+HOOC]^-$: 795.4105, found: 795.4079.



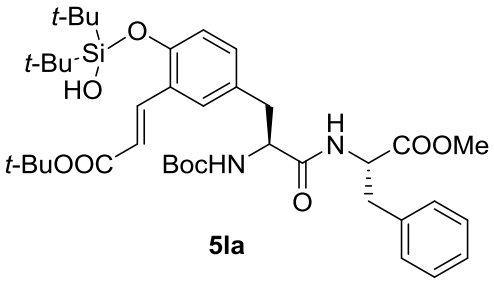
5ja

Compound **5ja**, (83mg, 56%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.40 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.49 (d, *J* = 9.0 Hz, 1H), 6.32 (d, *J* = 16.2 Hz, 1H), 5.16 (d, *J* = 7.4 Hz, 1H), 4.47 (dd, *J* = 9.0, 1.7 Hz, 1H), 4.41 (d, *J* = 6.2 Hz, 1H), 4.19 (qd, *J* = 6.2, 1.6 Hz, 1H), 3.70 (s, 3H), 3.24 (s, 1H), 3.03 (qd, *J* = 14.0, 6.4 Hz, 2H), 1.51 (s, 10H), 1.42 (s, 10H), 1.10 (d, *J* = 6.4 Hz, 3H), 1.07 (s, 18H), 1.07 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.55, 170.88, 166.40, 155.17, 153.75, 138.46, 132.20, 129.28, 127.99, 125.03, 120.12, 120.00, 80.01, 74.13, 67.27, 57.79, 55.54, 52.31, 37.73, 28.28, 28.24, 27.41, 20.82, 20.77, 20.69; **HRMS** (ESI) calcd. for $C_{38}H_{64}N_2O_{10}Si$ $[M+HOOC]^-$: 781.4312, found: 731.4285.



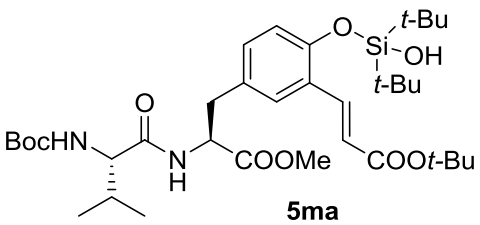
5kc

Compound **5kc**, (76mg, 48%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 16.2 Hz, 1H), 7.34 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.71 (s, 1H), 6.38 (d, *J* = 16.2 Hz, 1H), 5.14 (s, 1H), 4.80 (s, 1H), 4.55 (dd, *J* = 12.6, 7.8 Hz, 1H), 4.40 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.69 (s, 3H), 3.09 (dd, *J* = 23.4, 9.8 Hz, 3H), 2.94 (dd, *J* = 13.8, 6.2 Hz, 1H), 1.85 - 1.76 (m, 1H), 1.63 - 1.56 (m, 1H), 1.43 (s, 9H), 1.41 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.27 - 1.18 (m, 4H), 1.08 (s, 9H), 1.06 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.26, 171.30, 167.19, 156.23, 155.44, 154.35, 139.65, 132.22, 130.23, 128.02, 124.74, 120.29, 117.81, 80.38, 79.41, 60.25, 55.40, 52.40, 52.08, 40.30, 37.10, 31.97, 29.51, 28.43, 28.26, 27.44, 27.38, 22.42, 20.81, 20.72, 14.24; **HRMS** (ESI) calcd. for $C_{41}H_{69}N_3O_{11}Si$ $[M+HOOC]^-$: 836.4734, found: 836.4715.



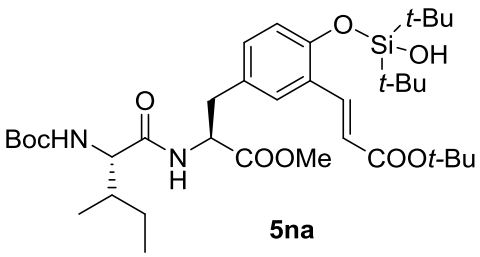
5la

Compound **5la**, (52mg, 36%), pale yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 16.2 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.23 (t, *J* = 6.2 Hz, 3H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.04 (s, 1H), 7.00 (dd, *J* = 7.6, 1.8 Hz, 2H), 6.29 (d, *J* = 16.2 Hz, 1H), 6.23 (d, *J* = 7.2 Hz, 1H), 5.35 (t, *J* = 4.6 Hz, 1H), 5.01 (d, *J* = 5.8 Hz, 1H), 4.79 (dd, *J* = 13.4, 6.2 Hz, 1H), 4.27 (d, *J* = 6.6 Hz, 1H), 3.68 (s, 3H), 3.03 (dd, *J* = 13.8, 7.4 Hz, 2H), 2.95 (d, *J* = 6.6 Hz, 2H), 1.51 (s, 9H), 1.41 (s, 9H), 1.07 (s, 9H), 1.06 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.43, 170.71, 166.32, 153.81, 151.89, 138.27, 135.56, 131.96, 129.20, 128.59, 127.82, 127.17, 120.27, 120.13, 80.15, 55.69, 53.22, 52.39, 37.97, 37.59, 28.27, 28.24, 27.39, 27.32, 20.76, 20.68; **HRMS** (ESI) calcd. for $C_{41}H_{69}N_3O_{11}Si$ $[M+HOOC]^-$: 771.3894, found: 771.3857.



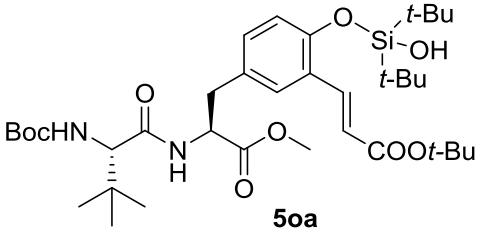
5ma

Compound **5ma**, (73mg, 54%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 16.2 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.66 (d, *J* = 6.8Hz, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 5.11 (d, *J* = 8.4 Hz, 1H), 4.83 (dd, *J* = 13.8, 6.1 Hz, 1H), 4.02 (s, 1H), 3.67 (s, 3H), 3.00 (s, 2H), 2.09 (dd, *J* = 13.1, 6.6 Hz, 1H), 1.51 (s, 9H), 1.41 (s, 9H), 1.08 (d, *J* = 3.8 Hz, 18H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.68, 171.08, 166.38, 155.88, 154.08, 138.38, 131.86, 128.37, 127.65, 125.07, 120.12, 120.00, 80.20, 80.00, 59.74, 53.24, 52.32, 37.25, 30.96, 28.27, 28.22, 27.42, 20.79, 20.72, 19.18, 17.66; **HRMS** (ESI) calcd. for $C_{35}H_{58}N_2O_9Si$ $[M+Na]^+$: 701.3804, found: 701.3825.



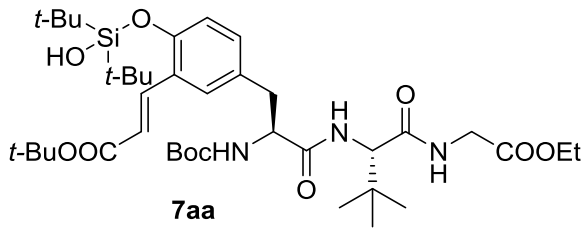
5na

Compound **5na**, (66mg, 48%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 16.2 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.64 (d, *J* = 6.8 Hz, 1H), 6.27 (d, *J* = 16.2 Hz, 1H), 5.10 (d, *J* = 8.0 Hz, 1H), 4.83 (dd, *J* = 13.8, 6.2 Hz, 1H), 4.01 (s, 1H), 3.85 (s, 1H), 3.67 (s, 3H), 3.01 (s, 2H), 1.83 (tdd, *J* = 13.2, 8.4, 5.0 Hz, 1H), 1.51 (s, 9H), 1.43 (d, *J* = 6.4 Hz, 2H), 1.42 (s, 9H), 1.08 (d, *J* = 2.8 Hz, 18H), 0.90 - 0.84 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.67, 166.40, 155.80, 154.07, 138.41, 131.86, 128.41, 127.62, 125.07, 120.10, 120.04, 80.21, 80.05, 59.23, 53.23, 52.32, 37.22, 28.28, 28.22, 27.42, 24.62, 20.78, 20.72, 15.43, 11.42; **HRMS** (ESI) calcd. for $C_{36}H_{60}N_2O_9Si$ $[M+Na]^+$: 715.3960, found: 715.3945.



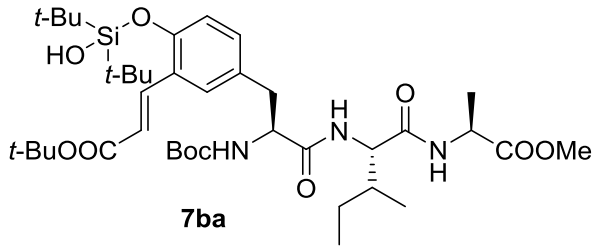
5oa

Compound **5oa**, (79mg, 57%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 16.2 Hz, 1H), 7.24 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.92 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.43 (d, *J* = 7.2 Hz, 1H), 6.25 (d, *J* = 16.2 Hz, 1H), 5.29 (d, *J* = 9.4 Hz, 1H), 4.80 (dd, *J* = 13.8, 6.2 Hz, 1H), 3.89 (d, *J* = 9.4 Hz, 1H), 3.65 (s, 3H), 3.08 - 2.90 (m, 2H), 1.49 (s, 9H), 1.40 (s, 9H), 1.06 (d, *J* = 4.0 Hz, 18H), 0.95 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.66, 170.91, 166.42, 155.82, 154.12, 138.41, 131.87, 128.32, 127.60, 125.12, 120.13, 120.04, 80.20, 79.85, 62.25, 53.24, 52.28, 37.07, 34.56, 28.32, 28.22, 27.42, 26.46, 20.77, 20.73; **HRMS** (ESI) calcd. for $C_{36}H_{60}N_2O_9Si$ $[M+HOOC]^-$: 737.4039, found: 737.4050.



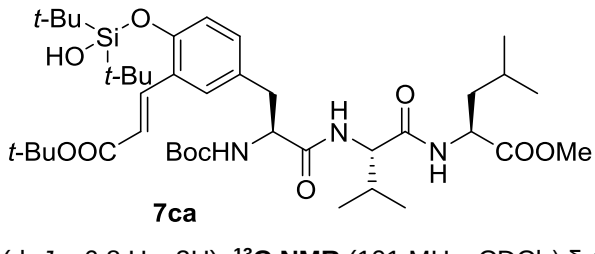
7aa

Compound **7aa**, (69mg, 45%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.33 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.82 (s, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 6.29 (d, *J* = 16.2 Hz, 1H), 5.36 (d, *J* = 7.8 Hz, 1H), 4.33 (d, *J* = 8.4 Hz, 2H), 4.20 (dd, *J* = 14.2, 7.0 Hz, 2H), 4.10 (dd, *J* = 18.1, 5.6 Hz, 1H), 3.87 (dd, *J* = 18.2, 4.6 Hz, 1H), 3.04 - 2.90 (m, 2H), 1.51 (s, 9H), 1.42 (s, 9H), 1.27 (t, *J* = 7.0 Hz, 4H), 1.07 (d, *J* = 14.2 Hz, 18H), 0.94 (d, *J* = 11.4 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.19, 170.18, 169.62, 166.37, 155.50, 153.82, 138.45, 131.88, 129.22, 127.65, 125.22, 120.34, 120.14, 80.16, 61.54, 60.53, 56.28, 41.27, 37.55, 34.76, 28.30, 28.23, 27.44, 27.41, 26.48, 20.88, 20.60, 14.12; **HRMS** (ESI) calcd. for $C_{39}H_{65}N_3O_{10}Si$ $[M+HOOC]^-$: 808.4421, found: 808.4415.



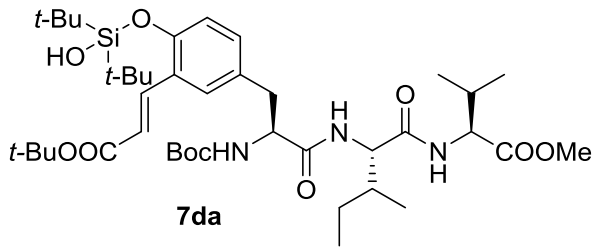
7ba

Compound **7ba**, (62mg, 41%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.00 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.53 (d, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 16.2 Hz, 1H), 5.11 (d, *J* = 6.6 Hz, 1H), 4.53 (p, *J* = 7.2 Hz, 1H), 4.35 - 4.20 (m, 2H), 3.74 (s, 3H), 3.55 (s, 1H), 3.05 - 2.93 (m, 2H), 1.75 (s, 2H), 1.51 (s, 9H), 1.42 (s, 9H), 1.39 (d, *J* = 7.2 Hz, 3H), 1.08 (d, *J* = 8.6 Hz, 18H), 0.86 (t, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.01, 171.15, 170.18, 166.35, 155.49, 153.87, 138.36, 131.76, 129.13, 127.69, 125.27, 120.29, 120.26, 80.44, 80.21, 57.66, 56.02, 52.47, 48.08, 37.33, 37.09, 28.27, 28.23, 27.41, 27.38, 24.72, 20.84, 20.63, 18.06, 15.20, 11.29; **HRMS** (ESI) calcd. for $C_{39}H_{65}N_3O_{10}Si$ $[M+HOOC]^-$: 808.4421, found: 808.4486.



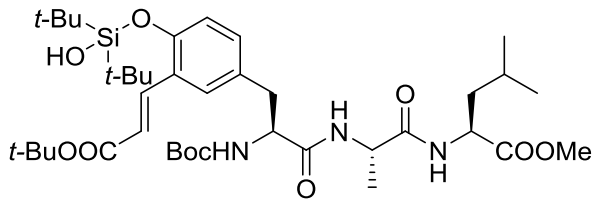
7ca

Compound **7ca**, (77mg, 49%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.36 (s, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.99 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.56 (d, *J* = 6.8 Hz, 2H), 6.31 (d, *J* = 16.2 Hz, 1H), 5.14 (d, *J* = 7.0 Hz, 1H), 4.63 - 4.54 (m, 1H), 4.35 - 4.24 (m, 2H), 3.72 (s, 3H), 2.99 (d, *J* = 6.6 Hz, 2H), 2.25 - 1.95 (m, 2H), 1.68 - 1.61 (m, 2H), 1.51 (s, 9H), 1.40 (s, 10H), 1.07 (d, *J* = 6.8 Hz, 19H), 0.93 (dd, *J* = 5.6, 3.8 Hz, 6H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.08, 171.42, 170.58, 166.36, 155.55, 153.88, 138.36, 131.80, 129.16, 127.70, 125.25, 120.40, 120.27, 80.42, 80.18, 58.48, 56.02, 52.29, 50.83, 41.12, 37.14, 28.24, 27.41, 27.37, 24.85, 22.77, 21.89, 20.83, 20.64, 19.01, 17.91; **HRMS** (ESI) calcd. for $C_{41}H_{69}N_3O_{11}Si$ $[M+HOOC]^-$: 836.4734, found: 836.4715.



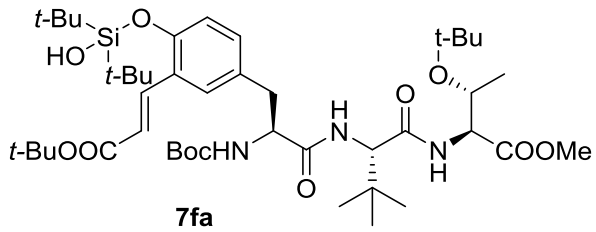
7da

Compound **7da**, (79mg, 50%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 16.2 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.98 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.79 (d, *J* = 5.4 Hz, 1H), 6.63 (s, 1H), 6.31 (d, *J* = 16.2 Hz, 1H), 5.30 (d, *J* = 6.0 Hz, 1H), 4.51 (dd, *J* = 8.6, 5.2 Hz, 1H), 4.36 (dd, *J* = 15.8, 7.8 Hz, 2H), 3.74 (s, 3H), 2.98 (d, *J* = 6.8 Hz, 2H), 2.21 - 2.12 (m, 1H), 1.80 (d, *J* = 6.4 Hz, 1H), 1.52 (s, 9H), 1.49 - 1.43 (m, 2H), 1.40 (s, 9H), 1.09 (s, 9H), 1.07 (s, 9H), 0.93 (t, *J* = 6.8 Hz, 6H), 0.89 - 0.84 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.13, 171.45, 170.83, 166.38, 155.48, 153.85, 138.48, 131.81, 129.21, 127.68, 125.16, 120.26, 120.15, 80.20, 80.12, 57.89, 57.22, 55.88, 52.15, 37.13, 31.08, 28.23, 27.41, 27.38, 24.87, 20.85, 20.63, 18.90, 17.95, 15.19, 11.26; **HRMS** (ESI) calcd. for $C_{41}H_{69}N_3O_{10}Si$ $[M+HOOC]^-$: 836.4734, found: 836.4704.



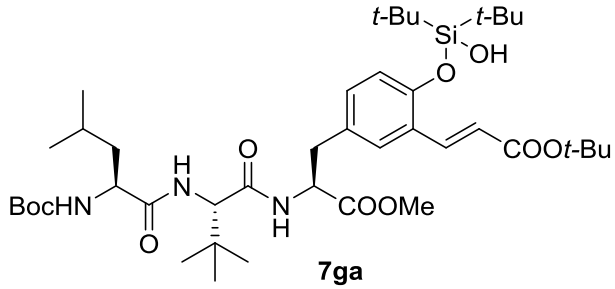
7ea

Compound **7ea**, (59mg, 39%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.99 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 6.8 Hz, 1H), 6.30 (d, *J* = 16.2 Hz, 1H), 5.14 (d, *J* = 8.0 Hz, 1H), 4.55 (dt, *J* = 8.2, 4.2 Hz, 1H), 4.50 - 4.44 (m, 1H), 4.31 (s, 1H), 3.72 (s, 3H), 2.97 (d, *J* = 6.6 Hz, 2H), 1.65 (dd, *J* = 9.8, 4.2 Hz, 2H), 1.56 (dd, *J* = 9.6, 2.0 Hz, 1H), 1.51 (s, 9H), 1.39 (s, 9H), 1.30 (d, *J* = 7.0 Hz, 3H), 1.07 (d, *J* = 5.8 Hz, 18H), 0.93 (dd, *J* = 6.0, 4.4 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.11, 171.55, 171.20, 166.33, 155.47, 153.91, 138.33, 131.83, 129.05, 127.66, 125.26, 120.29, 120.27, 80.45, 80.22, 55.78, 52.35, 50.93, 48.85, 41.21, 37.55, 28.24, 27.40, 27.37, 24.85, 22.74, 21.94, 20.83, 20.63, 18.07; **HRMS** (ESI) calcd. for $C_{39}H_{65}N_3O_{10}Si$ [M+HOOC]$^-$: 808.4421, found: 808.4416.



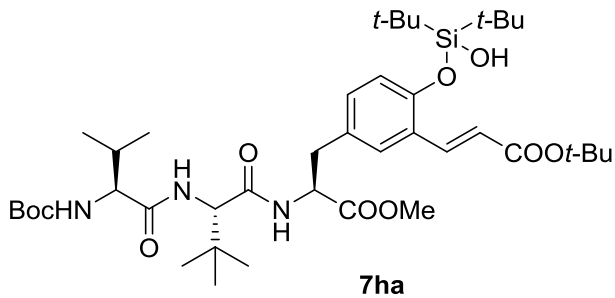
7fa

Compound **7fa**, (84mg, 49%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.2 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.96 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.43 (d, *J* = 9.2 Hz, 1H), 6.37 (d, *J* = 8.6 Hz, 1H), 6.32 (d, *J* = 16.2 Hz, 1H), 5.35 (t, *J* = 4.6 Hz, 1H), 5.12 (d, *J* = 6.4 Hz, 1H), 4.43 (d, *J* = 8.6 Hz, 1H), 4.33 - 4.21 (m, 3H), 3.70 (s, 3H), 3.03 - 2.92 (m, 2H), 1.51 (s, 9H), 1.42 (s, 9H), 1.19 (d, *J* = 6.4 Hz, 3H), 1.10 (d, *J* = 9.6 Hz, 18H), 1.05 (s, 9H), 0.98 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.82, 170.79, 170.23, 166.32, 155.27, 153.71, 138.39, 131.74, 129.93, 127.65, 125.40, 120.41, 120.28, 80.15, 80.08, 74.32, 67.00, 60.63, 58.06, 52.15, 35.24, 29.33, 28.30, 28.24, 27.40, 27.34, 27.22, 26.36, 21.28, 20.90, 20.51; **HRMS** (ESI) calcd. for $C_{44}H_{75}N_3O_{11}Si$ [M-H]$^-$: 848.5098. Found: 848.5095.



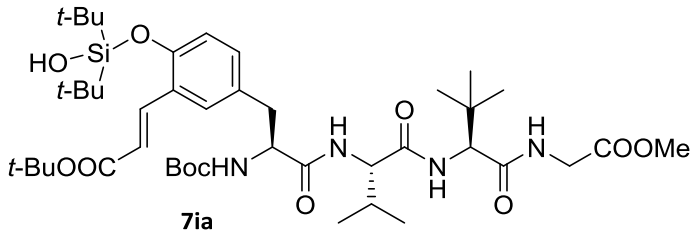
7ga

Compound **7ga**, (72mg, 45%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 16.2 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.94 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.66 (d, *J* = 8.6 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 6.32 (d, *J* = 16.2 Hz, 1H), 5.24 (d, *J* = 8.0 Hz, 1H), 4.82 (dd, *J* = 13.2, 6.0 Hz, 1H), 4.22 (d, *J* = 9.0 Hz, 1H), 4.02 - 3.96 (m, 1H), 3.72 (s, 3H), 3.04 (qd, *J* = 14.2, 6.2 Hz, 2H), 2.03 (dd, *J* = 13.0, 7.2 Hz, 1H), 1.92 (ddd, *J* = 15.6, 6.4, 3.6 Hz, 1H), 1.73 - 1.57 (m, 1H), 1.53 (s, 9H), 1.45 (s, 9H), 1.09 (s, 18H), 0.98 (s, 9H), 0.93 - 0.90 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.00, 171.68, 169.96, 166.46, 155.93, 154.10, 138.38, 131.89, 128.26, 127.55, 125.11, 120.15, 120.12, 80.18, 80.02, 60.64, 59.62, 53.13, 52.37, 36.94, 34.48, 29.33, 28.31, 28.22, 27.42, 26.53, 20.78, 20.70, 15.66, 11.29; **HRMS** (ESI) calcd. for $C_{42}H_{71}N_3O_{10}Si$ [M+HOOC]$^-$: 850.4955, found: 850.4977.



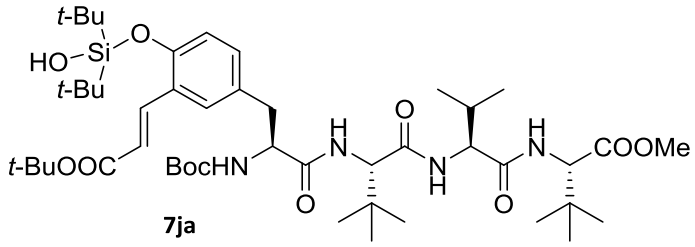
7ha

Compound **7ha**, (68mg, 43%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 16.2 Hz, 1H), 7.38 (s, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 6.8 Hz, 1H), 6.30 (d, *J* = 16.2 Hz, 1H), 6.13 (d, *J* = 8.4 Hz, 1H), 5.25 (d, *J* = 8.4 Hz, 1H), 4.59 (d, *J* = 5.4 Hz, 1H), 4.43 (s, 1H), 3.85 (d, *J* = 8.8 Hz, 1H), 3.69 (s, 3H), 3.03 (d, *J* = 11.2 Hz, 1H), 2.97 - 2.90 (m, 1H), 2.04 (s, 1H), 1.51 (s, 9H), 1.43 (s, 9H), 1.07 (d, *J* = 2.4 Hz, 18H), 0.95 (s, 9H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.73, 170.84, 170.33, 166.38, 155.74, 153.91, 138.25, 131.91, 130.13, 128.89, 127.76, 120.36, 120.24, 80.12, 79.91, 77.35, 77.03, 76.71, 62.55, 57.27, 54.64, 52.28, 34.51, 31.14, 29.33, 28.34, 28.23, 27.39, 26.54, 18.83, 17.75; **HRMS** (ESI) calcd. for $C_{41}H_{69}N_3O_{10}Si$ [M+HOOC]$^-$: 836.4734, found: 836.4718.



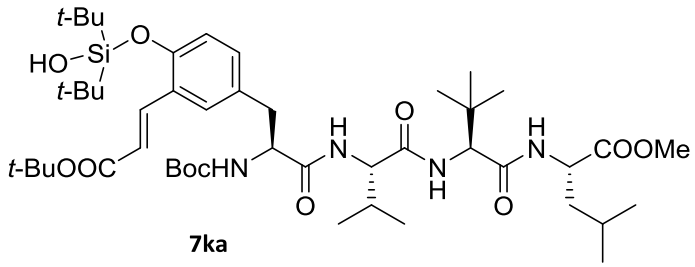
7ia

Compound **7ia**, (42mg, 33%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 16.4 Hz, 1H), 7.37 (s, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.92 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.80 (d, *J* = 9.2 Hz, 1H), 6.33 (d, *J* = 16.4 Hz, 1H), 5.44 (d, *J* = 7.8 Hz, 1H), 4.44 (s, 1H), 4.38 – 4.29 (m, 2H), 4.12 (dd, *J* = 18.0, 6.0 Hz, 1H), 3.87 (dd, *J* = 18.0, 5.0 Hz, 1H), 3.71 (s, 3H), 3.00 – 2.90 (m, 2H), 2.03 – 1.98 (m, 1H), 1.51 (s, 9H), 1.41 (s, 9H), 1.10 (s, 9H), 1.05 (s, 18H), 0.85 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.37, 171.10, 170.62, 169.94, 166.43, 155.46, 153.66, 138.54, 131.84, 129.88, 129.28, 127.74, 125.35, 120.29, 80.21, 80.12, 60.84, 60.72, 58.71, 52.18, 41.06, 33.92, 31.12, 29.32, 28.30, 28.24, 27.41, 27.30, 26.61, 20.96, 20.50, 19.04, 18.11; **HRMS** (ESI) calcd. for $C_{43}H_{72}N_4O_{11}Si$ $[M-H]^-$: 847.4894, found: 847.4859.



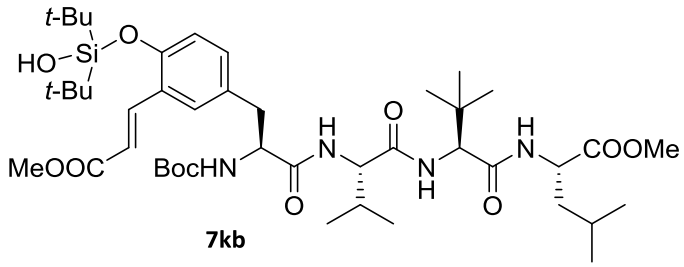
7ja

Compound **7ja**, (38mg, 28%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 16.2 Hz, 1H), 7.45 (s, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.38 (d, *J* = 16.2 Hz, 1H), 5.99 (d, *J* = 7.4 Hz, 1H), 5.92 (d, *J* = 11.4 Hz, 1H), 4.47 (t, *J* = 8.6 Hz, 2H), 4.30 (t, *J* = 9.2 Hz, 1H), 3.74 (s, 3H), 3.04 (dd, *J* = 13.2, 4.7 Hz, 1H), 2.87 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.21 – 2.14 (m, 1H), 2.07 (s, 1H), 1.54 (s, 9H), 1.45 (s, 9H), 1.18 (s, 9H), 1.08 (d, *J* = 6.8 Hz, 15H), 1.00 (s, 9H), 0.84 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.30, 171.05, 170.06, 169.32, 166.31, 155.49, 153.61, 138.55, 131.41, 129.39, 127.33, 125.89, 121.11, 120.40, 80.17, 79.69, 60.25, 60.03, 59.30, 57.07, 51.71, 38.67, 34.52, 34.32, 30.40, 28.35, 28.24, 27.41, 27.26, 26.74, 26.25, 21.28, 20.89, 20.24, 19.13; **HRMS** (ESI) calcd. for $C_{47}H_{80}N_4O_{11}Si$ $[M+H]^+$: 905.5666, found: 905.5696.



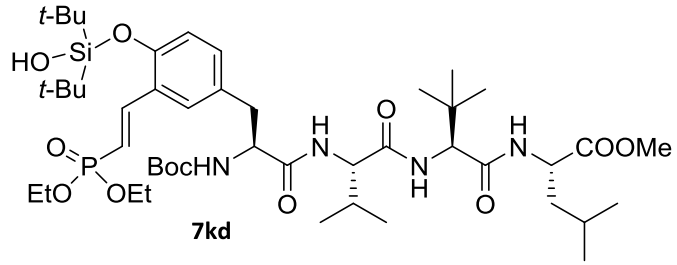
7ka

Compound **7ka**, (43mg, 32%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 16.2 Hz, 1H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.19 (d, *J* = 6.2 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 13.8 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.67 (s, 1H), 6.34 (d, *J* = 16.2 Hz, 1H), 5.59 (d, *J* = 7.4 Hz, 1H), 4.68 – 4.61 (m, 1H), 4.49 – 4.29 (m, 3H), 3.71 (s, 3H), 2.93 (qd, *J* = 13.6, 6.8 Hz, 2H), 1.89 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.67 – 1.54 (m, 3H), 1.51 (s, 9H), 1.40 (s, 9H), 1.11 (s, 9H), 1.06 (s, 18H), 0.88 – 0.82 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.16, 171.26, 170.10, 169.98, 166.47, 155.42, 153.58, 138.63, 131.84, 129.37, 127.72, 125.37, 120.80, 120.25, 80.21, 79.91, 60.59, 58.47, 55.98, 52.15, 50.47, 41.09, 38.43, 33.97, 31.41, 28.34, 28.23, 27.42, 27.30, 26.57, 24.71, 22.87, 21.62, 20.98, 20.46, 18.88, 18.34; **HRMS** (ESI) calcd. for $C_{47}H_{80}N_4O_{11}Si$ $[M+H]^+$: 905.5666, found: 905.5702.



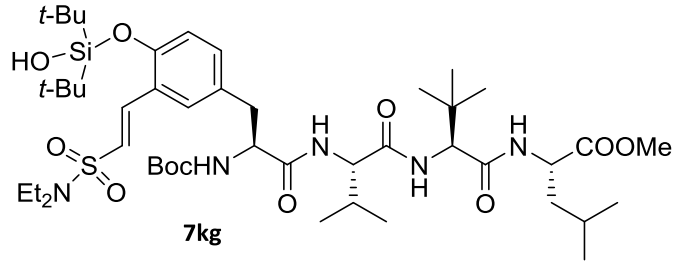
7kb

Compound **7kb**, (36mg, 28%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 16.2 Hz, 1H), 7.39 (s, 1H), 7.19 (d, *J* = 6.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.42 (d, *J* = 16.2 Hz, 1H), 5.67 (d, *J* = 7.2 Hz, 1H), 4.68 – 4.63 (m, 1H), 4.39 (dd, *J* = 40.2, 9.2 Hz, 3H), 3.78 (s, 3H), 3.71 (s, 3H), 3.00 – 2.86 (m, 2H), 2.03 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.91 (dt, *J* = 13.8, 6.8 Hz, 1H), 1.58 (dd, *J* = 10.8, 4.4 Hz, 2H), 1.39 (s, 9H), 1.11 (s, 9H), 1.05 (s, 18H), 0.88 – 0.84 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.16, 171.32, 170.10, 169.98, 167.74, 155.45, 153.82, 140.29, 132.22, 129.50, 127.87, 124.96, 120.40, 117.40, 79.85, 60.54, 58.39, 55.96, 52.15, 51.56, 50.46, 41.08, 38.41, 34.01, 31.47, 28.32, 27.39, 27.24, 26.57, 24.72, 22.87, 21.65, 20.96, 20.46, 18.87, 18.36; **HRMS** (ESI) calcd. for $C_{44}H_{74}N_4O_{11}Si$ $[M+H]^+$: 863.5196, found: 863.5228



7kd

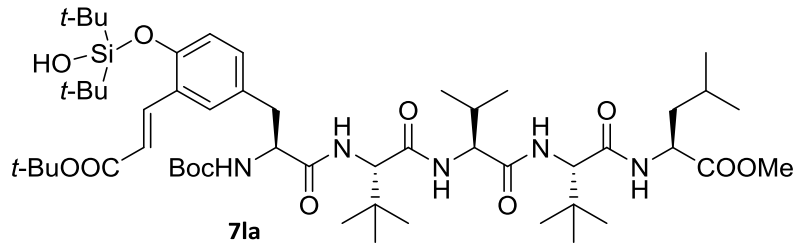
Compound **7kd**, (36mg, 26%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 23.2, 17.8 Hz, 1H), 7.37 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.27 (t, *J* = 18.4 Hz, 1H), 5.59 (s, 1H), 4.67 – 4.60 (m, 1H), 4.43 (d, *J* = 8.4 Hz, 1H), 4.35 (s, 2H), 4.15 – 4.07 (m, 4H), 3.73 (s, 3H), 2.94 (d, *J* = 6.4 Hz, 2H), 1.94 (dd, *J* = 13.8, 7.0 Hz, 1H), 1.66 – 1.56 (m, 3H), 1.40 (s, 9H), 1.35 (t, *J* = 7.0 Hz, 6H), 1.11 (s, 9H), 1.06 (s, 18H), 0.87 (dd, *J* = 11.8, 5.8 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.16, 171.32, 171.16, 170.14, 155.40, 153.59, 143.70, 143.61, 132.09, 129.40, 127.59, 125.58, 125.36, 120.52, 114.54, 112.62, 79.91, 61.78, 61.73, 61.70, 60.50, 58.58, 55.95, 52.15, 50.52, 41.05, 38.27, 34.04, 31.36, 28.33, 28.27, 27.43, 27.33, 26.56, 24.71, 22.86, 21.63, 20.94, 20.48, 18.91, 18.33, 16.42, 16.36; **HRMS** (ESI) calcd. for $C_{46}H_{81}N_4O_{12}PSi$ $[M+H]^+$: 941.5431, found: 941.5454.



7kg

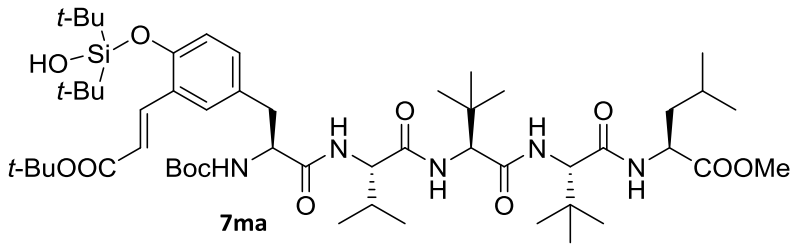
Compound **7kg**, (32mg, 23%), colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 15.4 Hz, 1H), 7.36 (s, 1H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.97 (t, *J* = 9.4 Hz, 2H), 6.79 (d, *J* = 15.4 Hz, 1H), 6.33 – 6.22 (m, 1H), 5.53 (d, *J* = 7.4 Hz, 1H), 4.63 (dd, *J* = 8.6, 4.8 Hz, 1H), 4.39 – 4.25 (m, 3H), 3.73 (s, 3H), 3.28 (q, *J* = 7.2 Hz, 4H), 3.04 – 2.89 (m, 2H), 1.72 – 1.50 (m, 4H), 1.44 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 6H), 1.14 (s, 9H), 1.07 (d, *J* = 5.8 Hz, 18H), 0.91 – 0.84 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.01, 171.05, 171.00, 170.05, 155.37, 153.92, 136.26, 132.47, 129.51, 128.16, 124.57, 123.54, 120.61, 80.07, 60.61, 58.66, 56.17, 52.18, 50.50, 41.97, 41.13, 34.00, 31.22, 29.32, 28.34, 27.39, 27.25, 26.51, 24.68, 22.87, 21.57, 20.98, 20.41, 18.89, 18.22, 14.65; **HRMS** (ESI) calcd. for $C_{46}H_{81}N_5O_{11}SSi$ $[M-H]^-$: 938.5350, found: 938.5389.

+



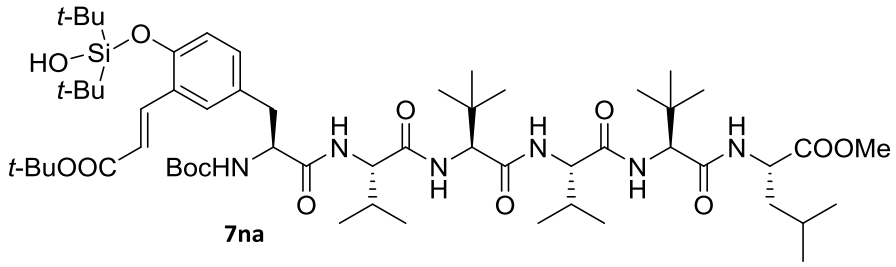
7la

Compound **7la**, (33mg, 22%), colorless oil, **^{1}H NMR** (400 MHz, MeOD) δ 8.05 (d, *J* = 16.2 Hz, 1H), 7.47 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.38 (d, *J* = 16.2 Hz, 1H), 4.59 (s, 1H), 4.53 (dd, *J* = 9.6, 4.8 Hz, 4H), 4.44 – 4.40 (m, 1H), 3.72 (s, 3H), 3.05 (dd, *J* = 13.8, 4.2 Hz, 1H), 2.78 (dd, *J* = 13.6, 10.2 Hz, 1H), 2.02 (dd, *J* = 14.6, 5.4 Hz, 1H), 1.65 (dd, *J* = 14.6, 7.4 Hz, 3H), 1.53 (s, 9H), 1.37 (s, 9H), 1.08 (s, 9H), 1.06 (s, 9H), 1.04 (s, 9H), 1.00 (s, 9H), 0.93 (dd, *J* = 6.4, 2.4 Hz, 6H), 0.89 (dd, *J* = 6.4, 2.6 Hz, 6H); **^{13}C NMR** (101 MHz, MeOD) δ 173.02, 172.52, 171.88, 171.04, 170.83, 166.91, 156.29, 154.00, 139.18, 132.06, 130.02, 127.66, 124.16, 119.48, 118.93, 80.03, 79.23, 60.25, 60.01, 58.62, 55.66, 51.21, 50.50, 40.01, 36.81, 34.50, 34.09, 30.91, 27.40, 27.19, 26.70, 26.66, 25.98, 25.86, 24.47, 22.00, 20.47, 20.38, 20.34, 18.26, 18.21; **HRMS** (ESI) calcd. for $C_{53}H_{91}N_5O_{12}Si$ $[M+H]^+$: 1018.6506, found: 1018.6498.



7ma

Compound **7ma**, (28mg, 23%), colorless oil, **^{1}H NMR** (400 MHz, MeOD) δ 8.05 (d, *J* = 16.2 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.14 – 7.07 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 4.60 (d, *J* = 17.8 Hz, 2H), 4.53 – 4.42 (m, 4H), 3.72 (s, 3H), 3.03 (d, *J* = 9.6 Hz, 1H), 2.82 – 2.72 (m, 1H), 2.10 – 2.02 (m, 1H), 1.75 – 1.66 (m, 1H), 1.66 – 1.61 (m, 2H), 1.53 (s, 9H), 1.36 (s, 9H), 1.06 (dd, *J* = 8.2, 4.0 Hz, 18H), 1.03 (s, 9H), 0.99 (s, 9H), 0.94 (d, *J* = 6.2 Hz, 6H), 0.89 (d, *J* = 6.4 Hz, 6H); **^{13}C NMR** (101 MHz, MeOD) δ 173.00, 172.70, 171.99, 171.00, 170.90, 166.94, 156.22, 154.03, 139.18, 132.11, 129.85, 127.65, 124.18, 119.49, 118.97, 80.05, 79.23, 60.16, 58.54, 55.51, 51.17, 50.56, 39.93, 37.12, 34.33, 34.12, 30.98, 27.39, 27.19, 26.71, 26.67, 26.00, 25.85, 24.48, 21.99, 20.39, 20.35, 20.24, 20.21, 18.52, 17.69; **HRMS** (ESI) calcd. for $C_{53}H_{91}N_5O_{12}Si$ $[M+H]^+$: 1018.6506, found: 1018.6524.



7na

Compound **7na**, (35mg, 21%), colorless oil, **^{1}H NMR** (500 MHz, MeOD) δ 8.01 (d, *J* = 16.0 Hz, 1H), 7.42 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.94 – 6.81 (m, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.34 (t, *J* = 4.5 Hz, 1H), 4.63 – 4.50 (m, 8H), 3.70 (s, 3H), 2.96 (d, *J* = 12.5 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.02 – 1.94 (m, 2H), 1.62 (dd, *J* = 13.5, 6.8 Hz, 3H), 1.50 (s, 9H), 1.33 (s, 9H), 1.03 (d, *J* = 10.5 Hz, 18H), 1.01 (s, 9H), 0.96 (s, 9H), 0.88 (dd, *J* = 20.5, 5.5 Hz, 18H); **^{13}C NMR** (101 MHz, MeOD) δ 177.98, 173.13, 172.11, 171.06, 170.55, 166.90, 156.21, 154.00, 139.25, 132.23, 129.96, 127.72, 124.12, 119.46, 118.93, 80.00, 79.14, 70.11, 60.80, 59.95, 58.47, 58.10, 55.46, 51.27, 50.69, 39.98, 37.40, 35.15, 31.68, 29.44, 29.36, 29.08, 28.93, 27.49, 27.21, 26.73, 26.71, 24.54, 20.70, 20.39, 20.36, 20.23, 18.54, 18.34, 18.15, 17.90; **HRMS** (ESI) calcd. for $C_{58}H_{100}N_6O_{13}Si$ $[M+H]^+$: 1117.7190, found: 1117.7197.

9. NMR analysis and structural confirmation

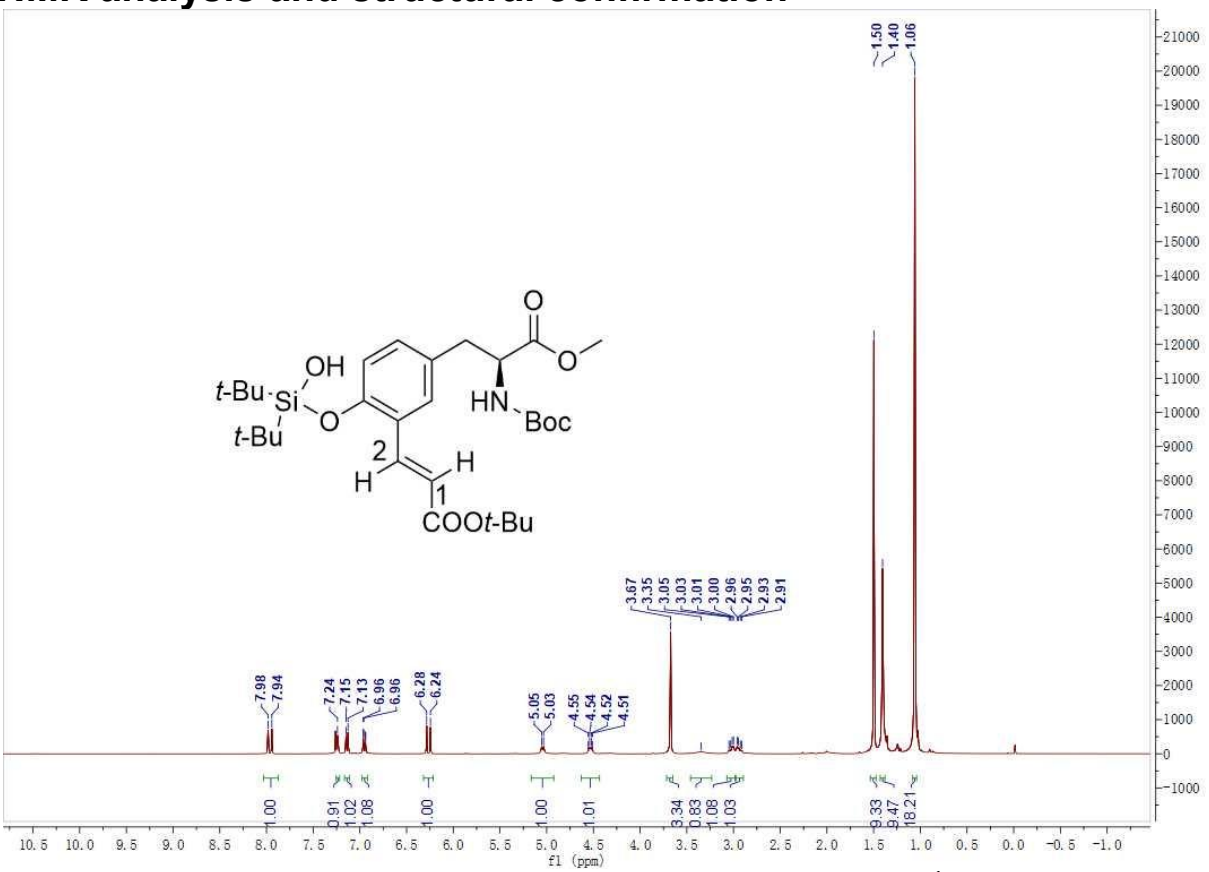


Figure S5. Determination of the configuration of exocyclic double bond in product **3aa** by ^{1}H NMR (400 MHz, $CDCl_3$). The coupRling constant was $J_{H1,H2}$=16.0 Hz, and therefore the double bond is in *E*-configuration.

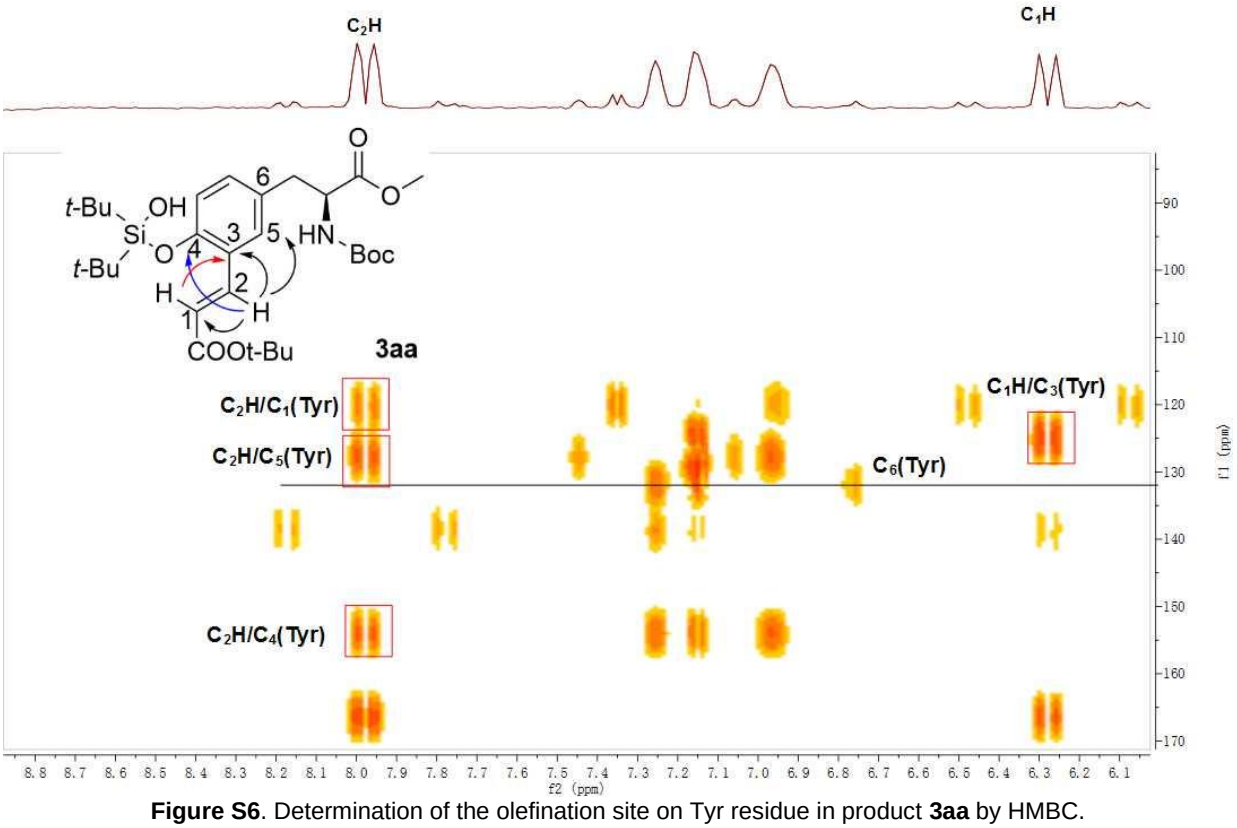


Figure S6. Determination of the olefination site on Tyr residue in product **3aa** by HMBC.

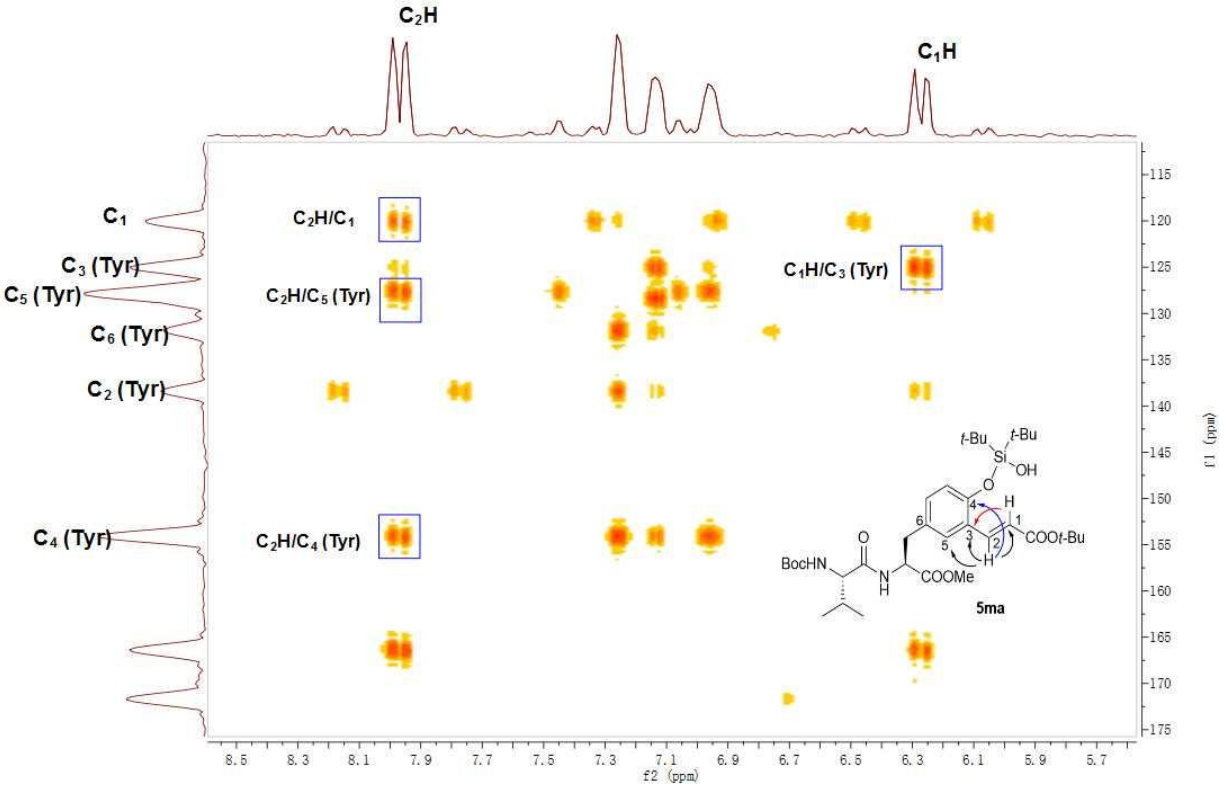


Figure S7. Determination of the olefination site on Tyr residue in product **5ma** by HMBC.

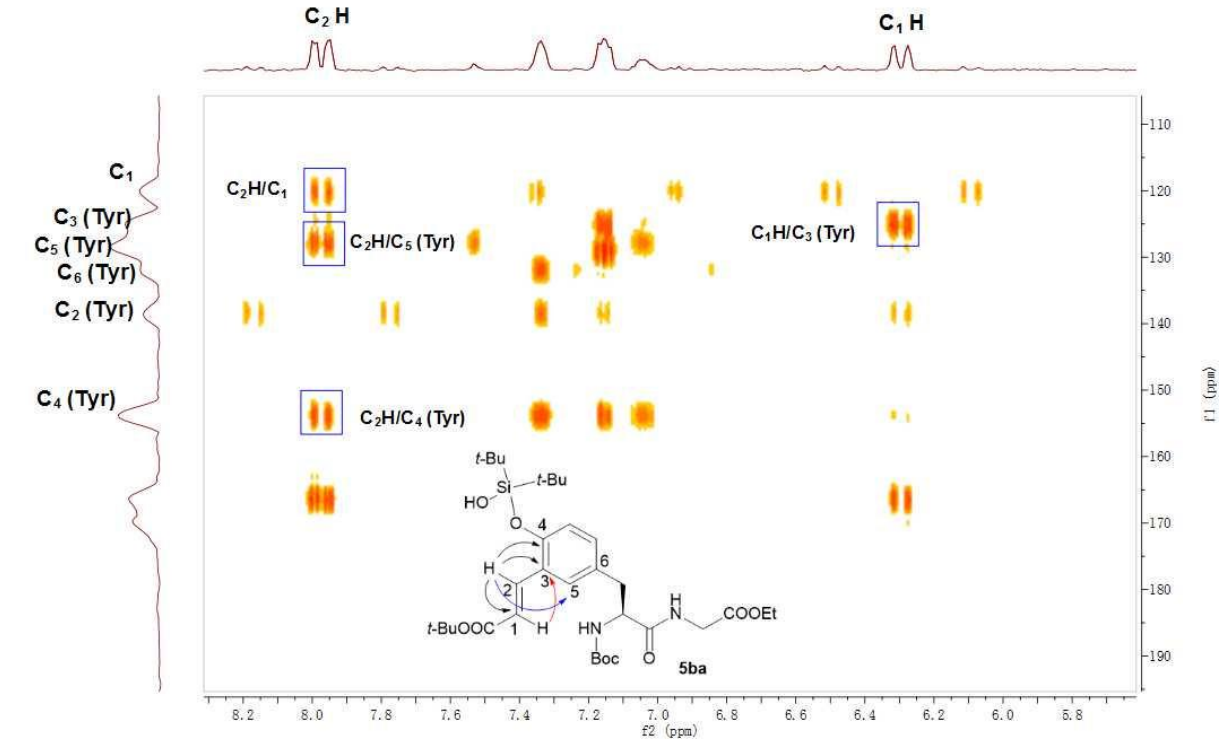
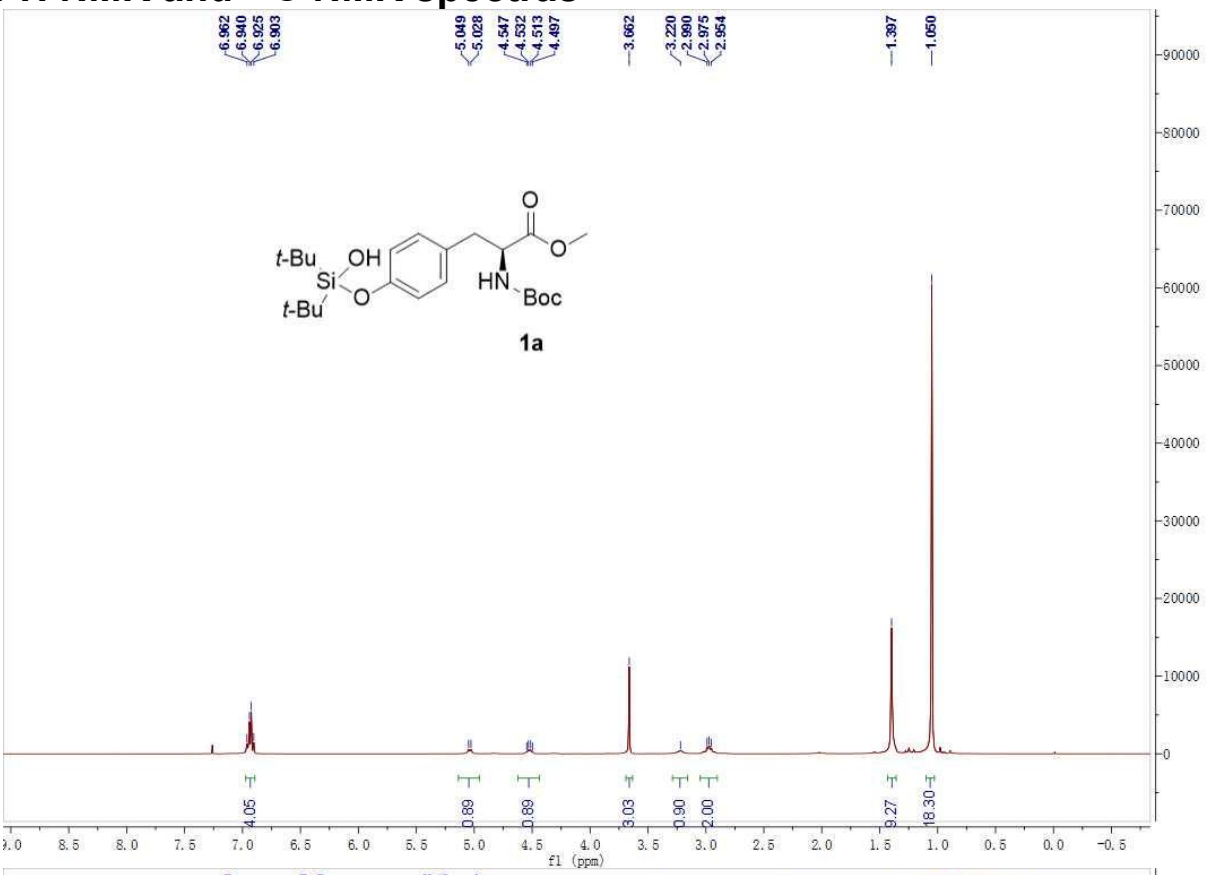
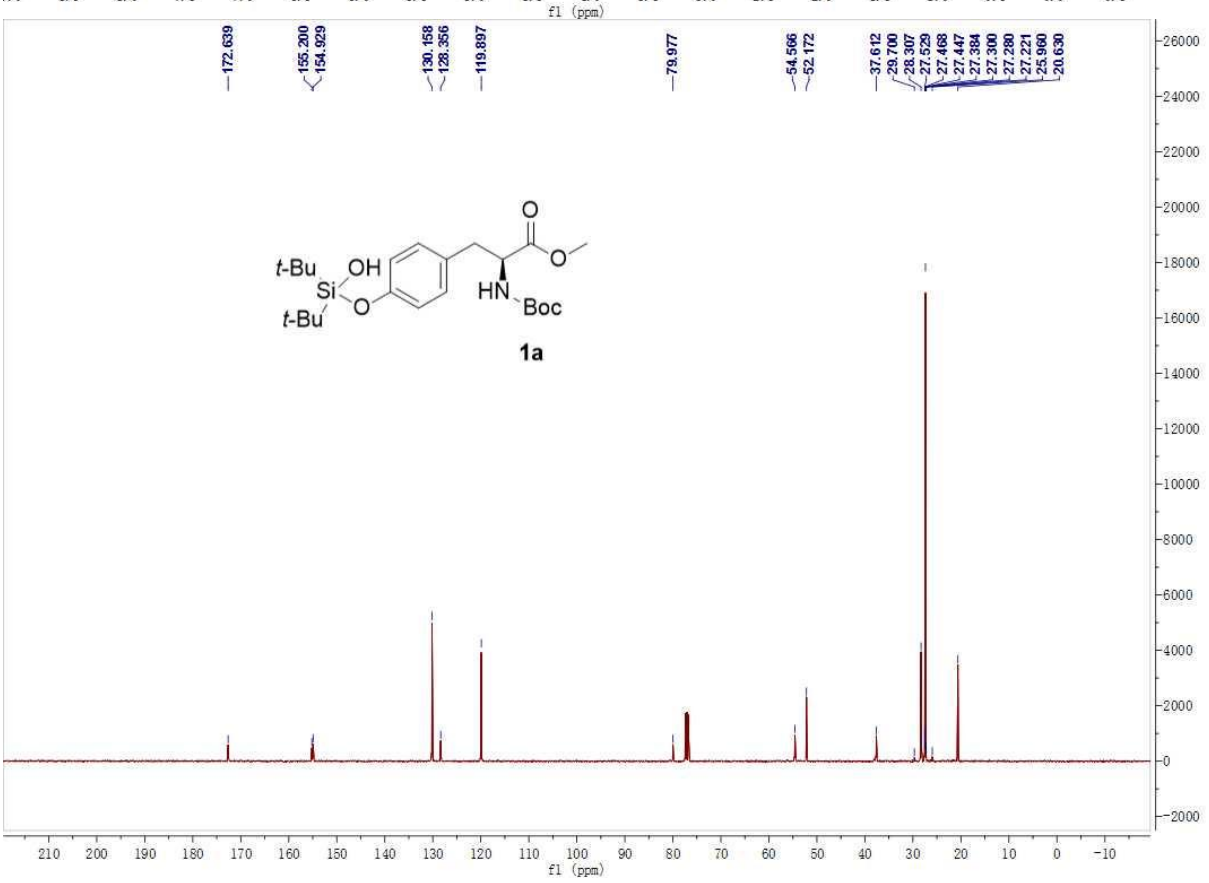
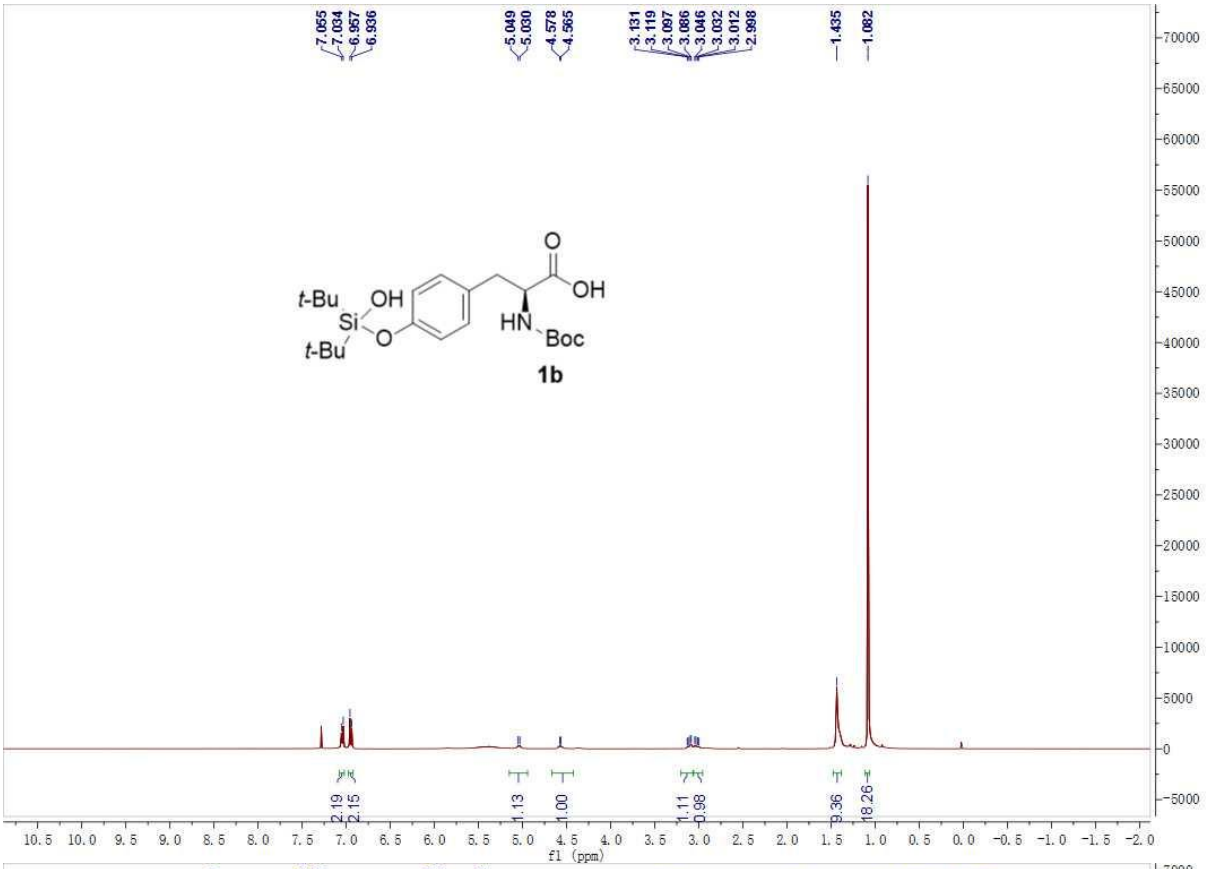


Figure S8. Determination of the olefination site on Tyr residue in product **5ba** by HMBC**.**

10.^{1}H NMR and ^{13}C NMR spectras



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4.565
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3.046
3.032
3.012
2.998
1.435
1.082
t-Bu
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Si
O
t-Bu
O
OH
HN
Boc
1b
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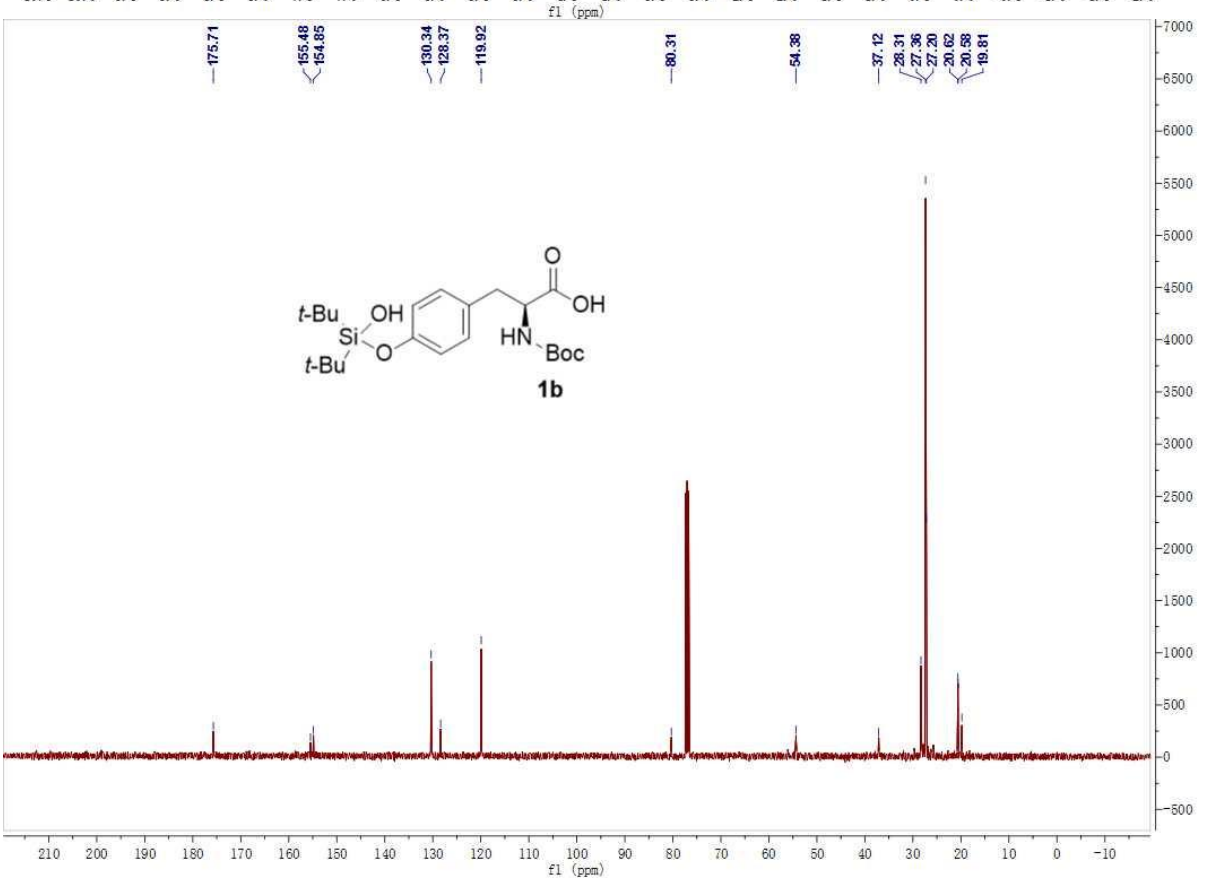
18.26
f1 (ppm)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Si
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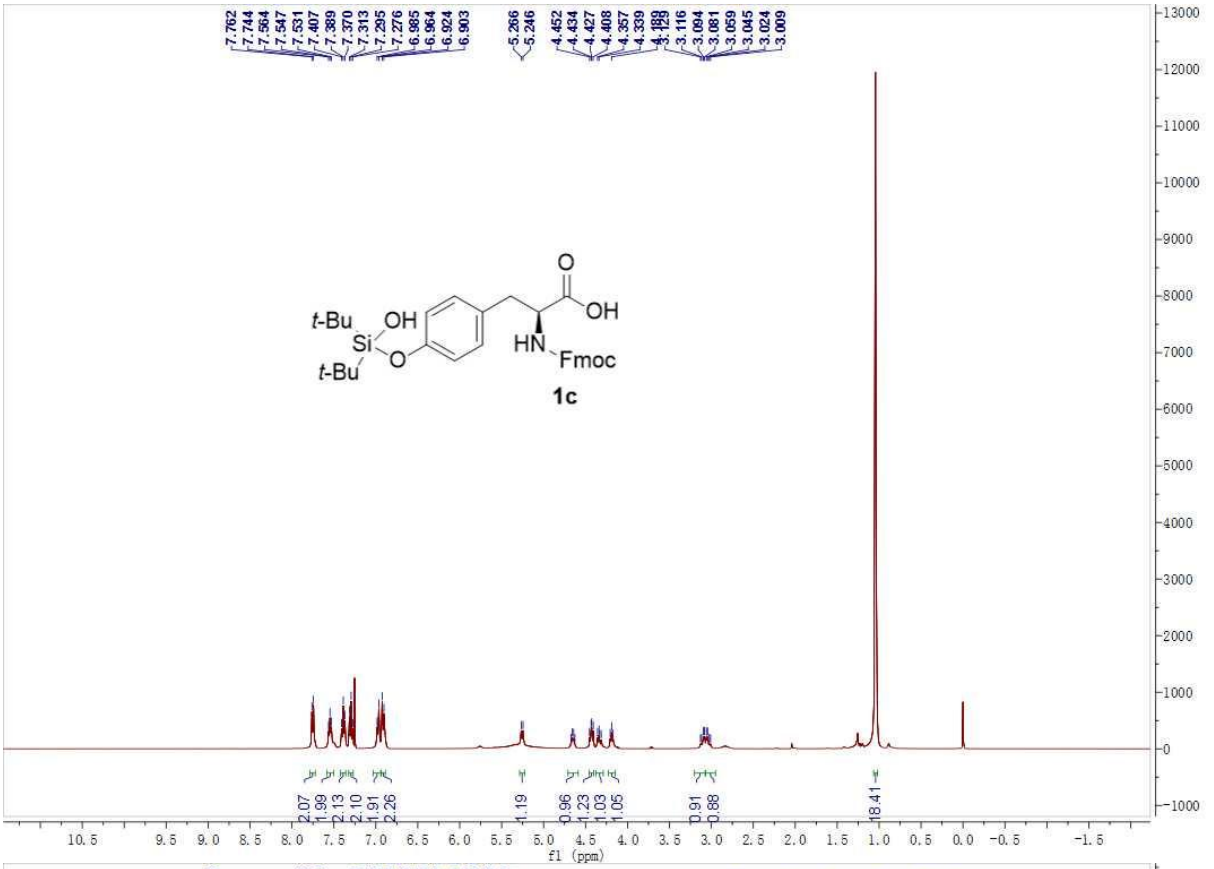
t-Bu
O
OH
HN
Boc
1b
f1 (ppm)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4.339
3.116
3.094
3.081
3.059
3.045
3.024
3.009
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Si
O
t-Bu
O
OH
HN
Fmoc
1c
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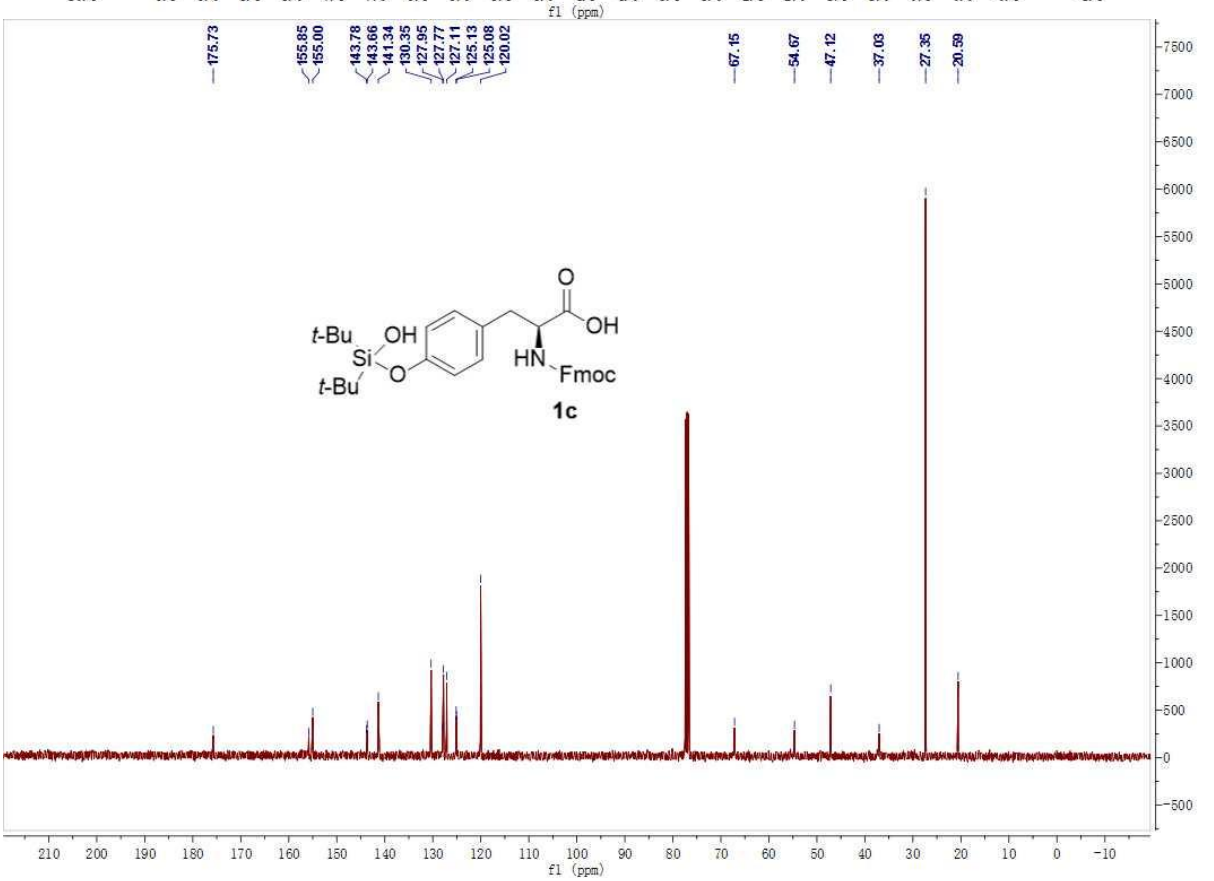
f1 (ppm)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127.77
127.11
125.13
125.08
120.02
67.15
54.67
47.12
37.03
27.35
20.59
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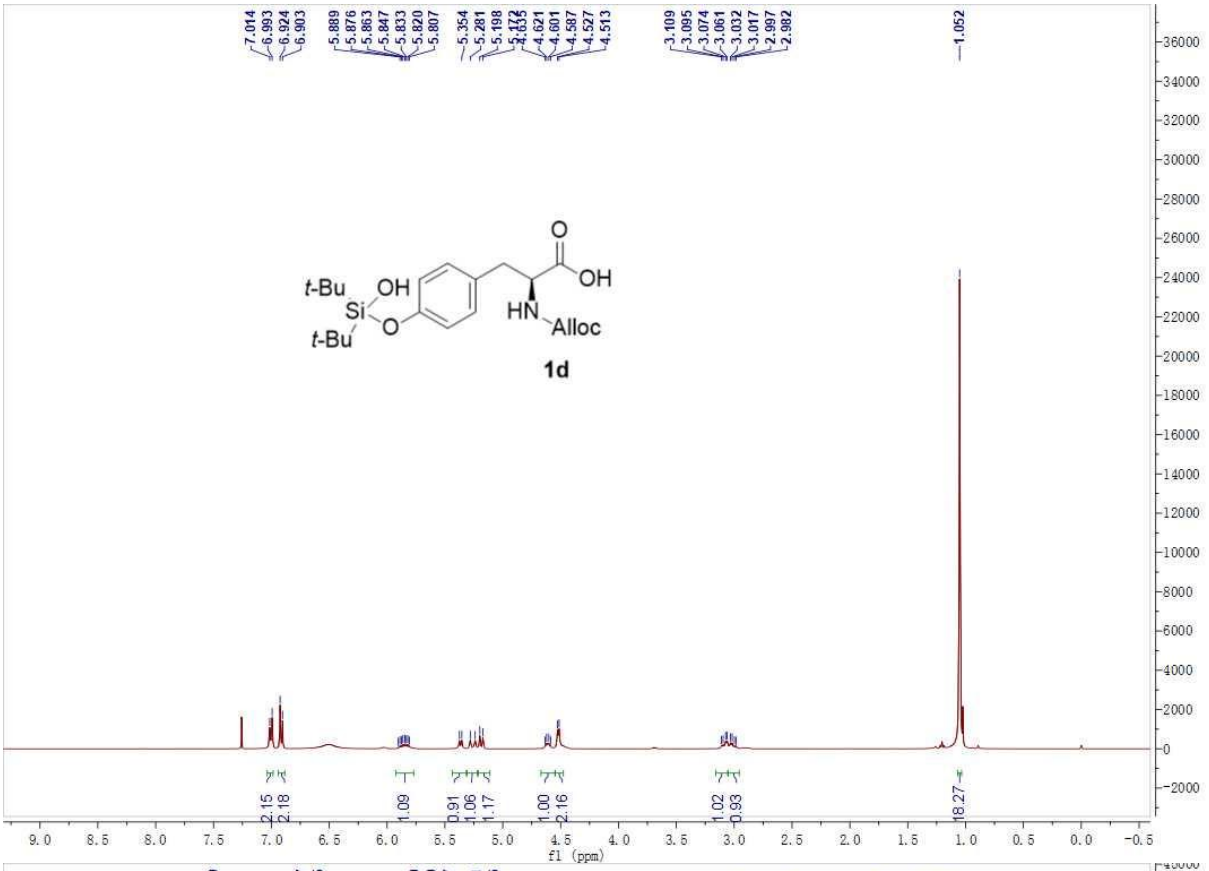
Si
O
t-Bu
O
OH
HN
Fmoc
1c
f1 (ppm)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4.621
4.601
4.587
4.527
4.513
3.109
3.095
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3.017
2.997
2.982
1.052
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Si
O
t-Bu
O
OH
HN
Alloc
1d
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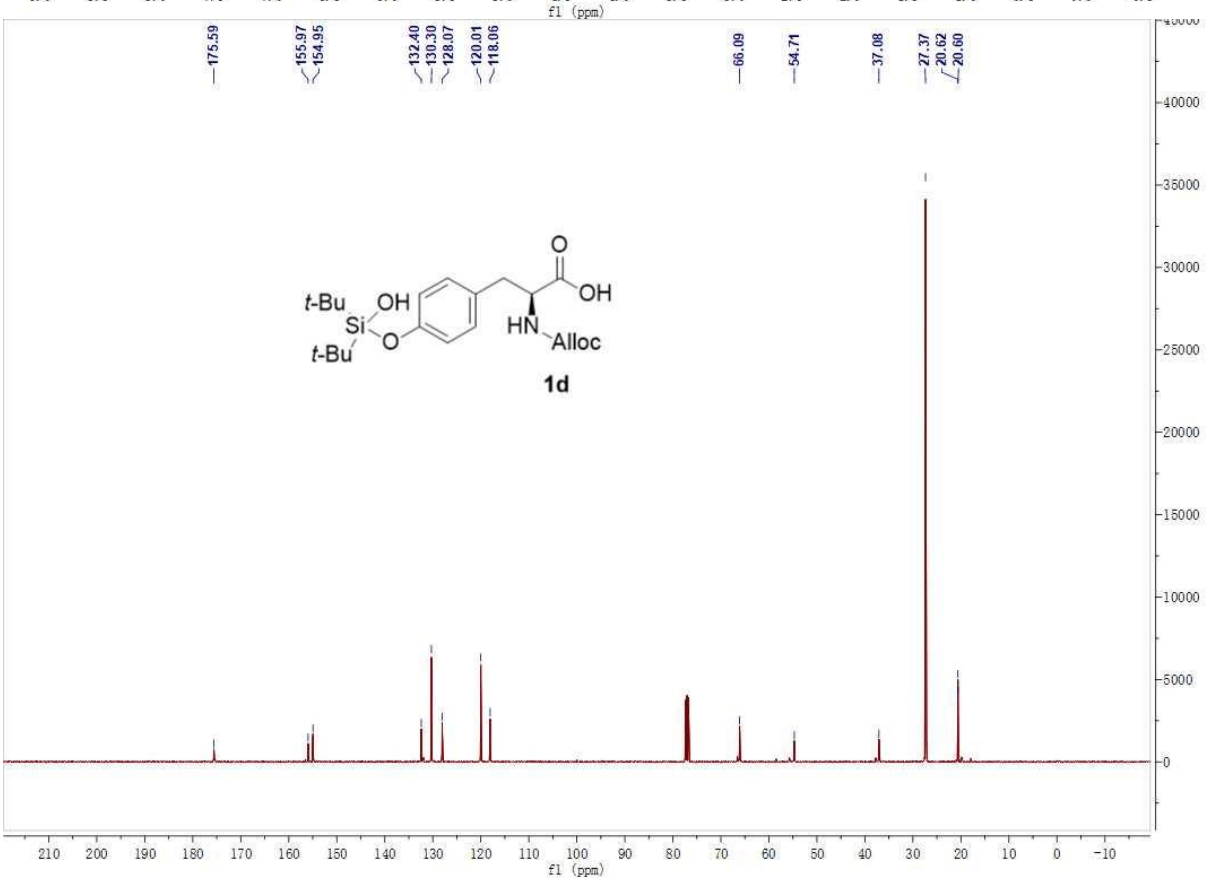
f1 (ppm)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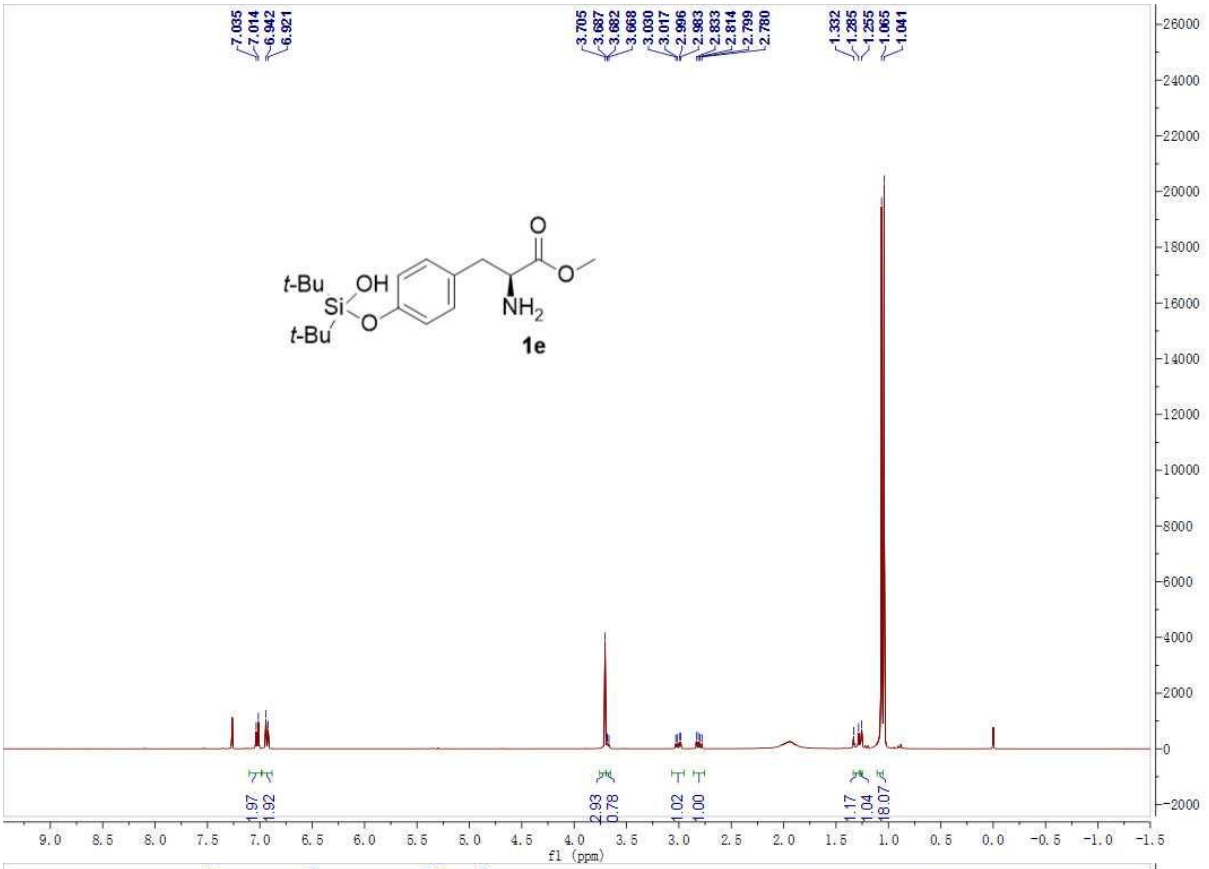
Alloc
1d
f1 (ppm)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t-Bu
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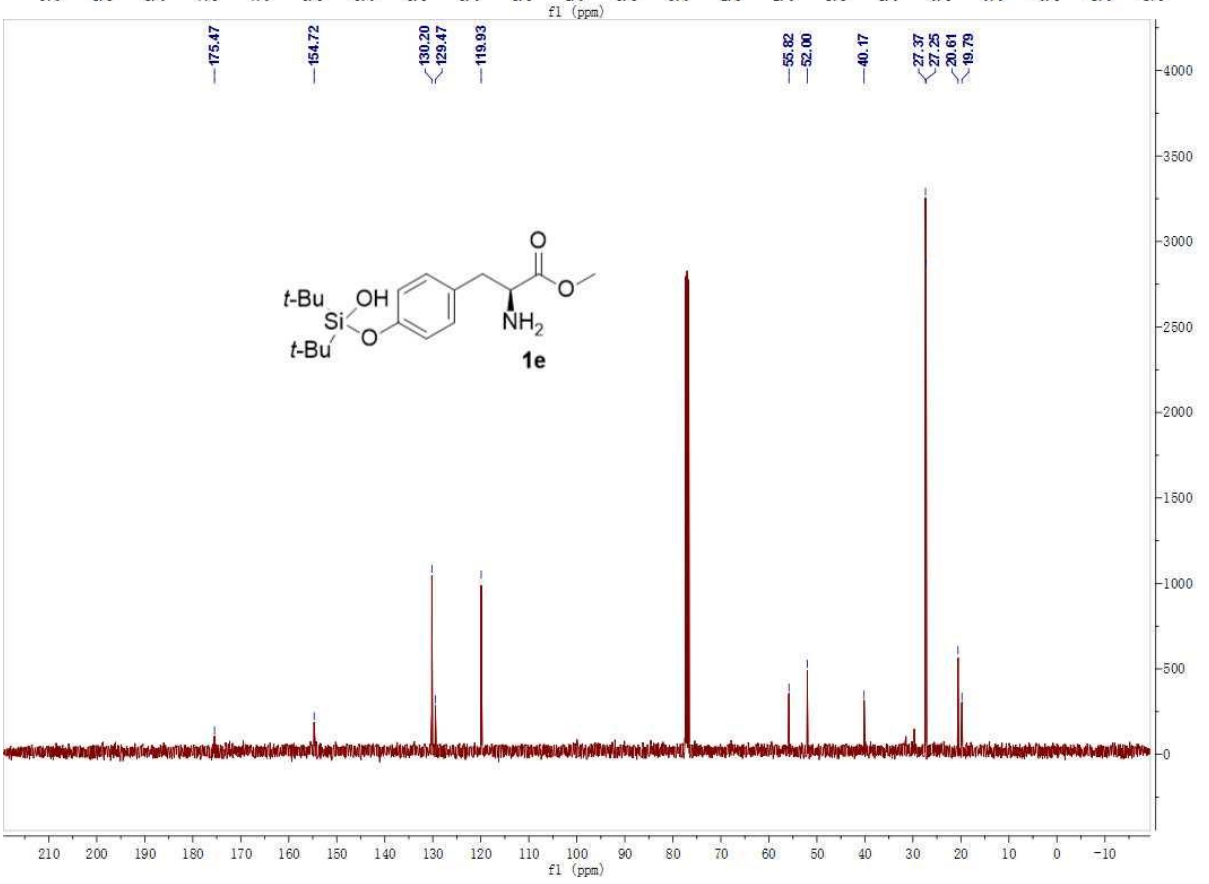
18.07
f1 (ppm)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t-Bu
O
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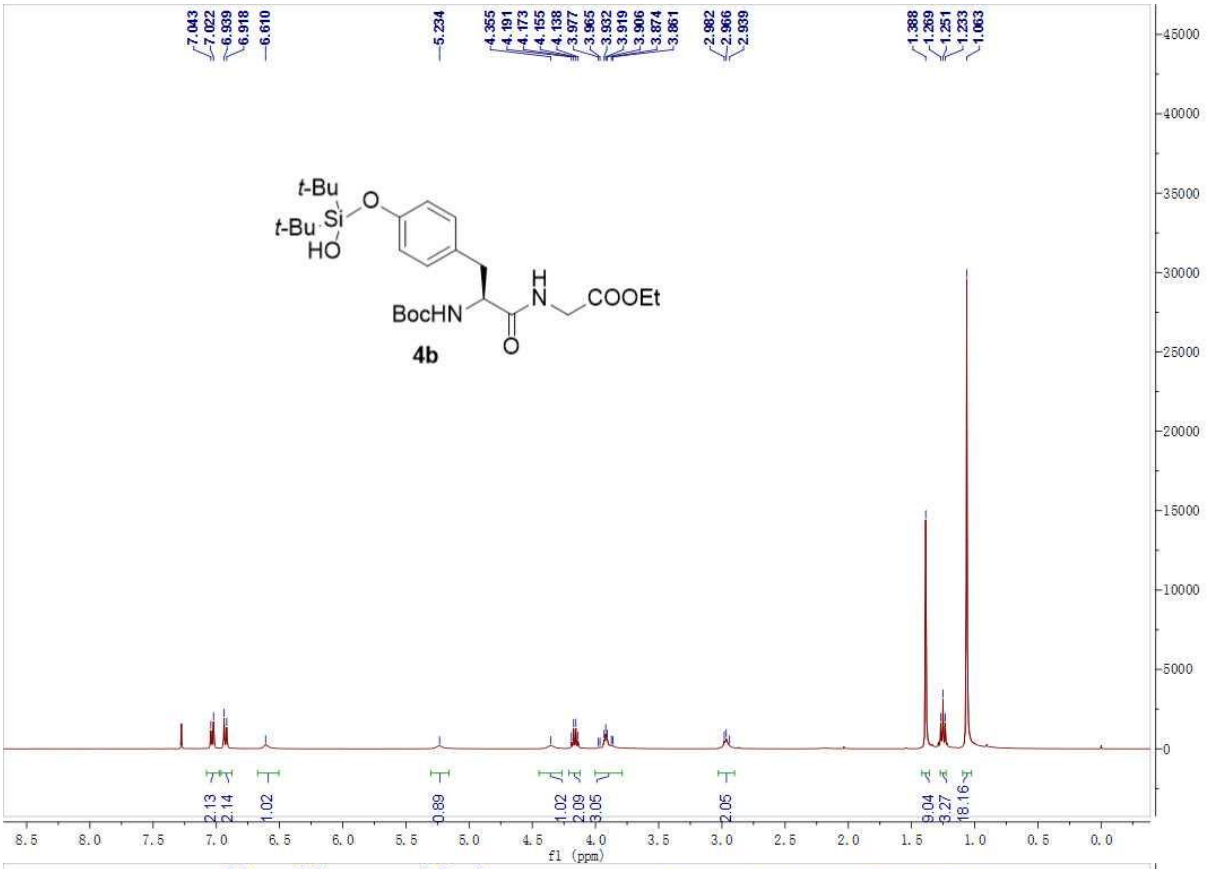
NH2
1e
f1 (ppm)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t-Bu
Si
HO
O
BocHN
H
N
COOEt
O
4b
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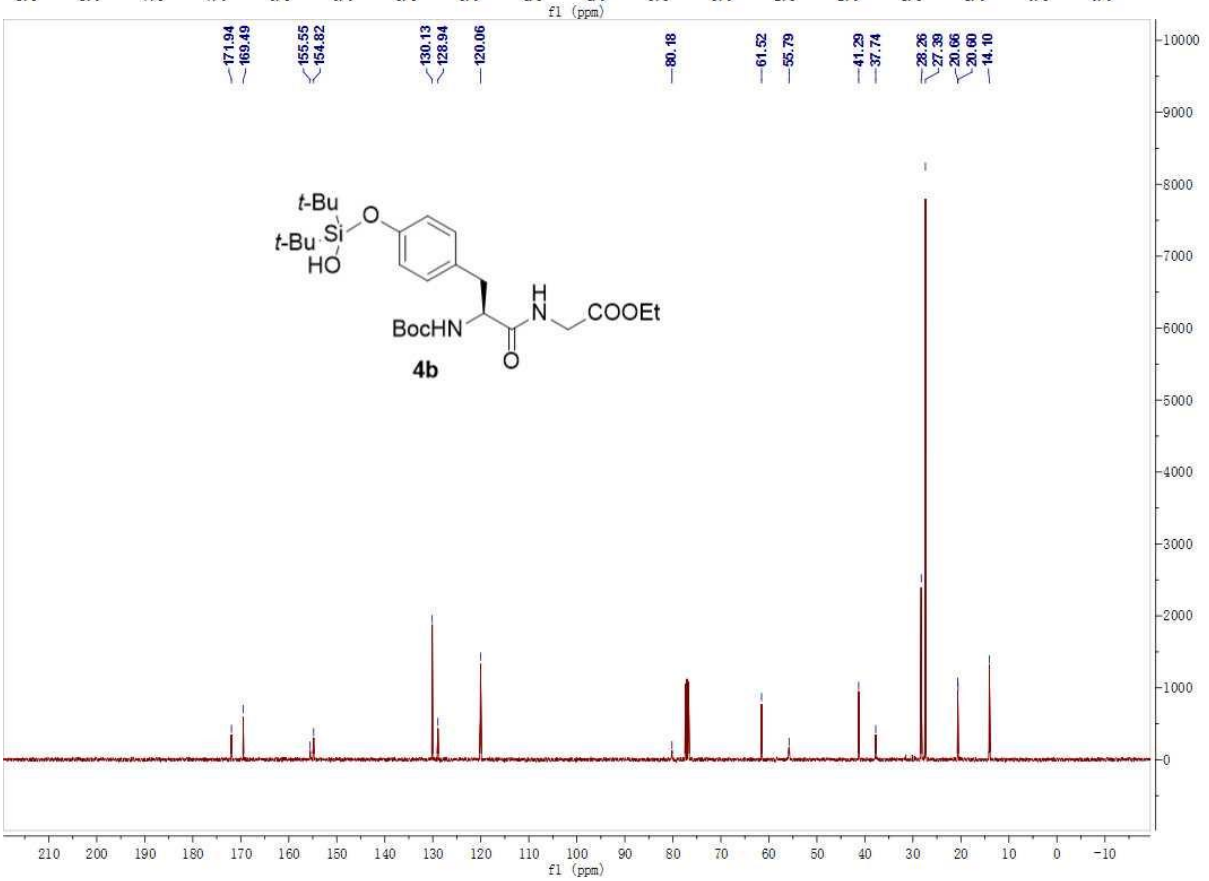
18.16
f1 (ppm)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27.39
20.66
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H
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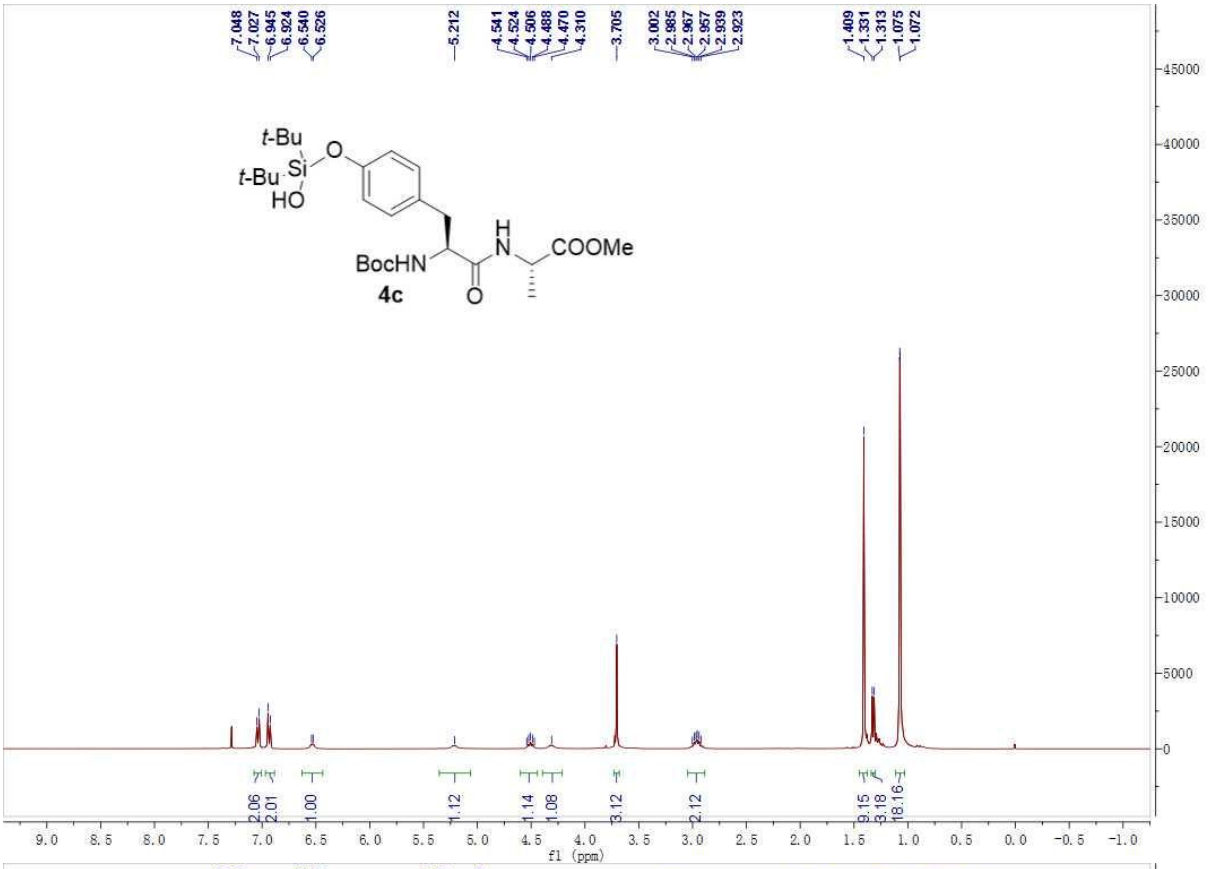
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2.957
2.939
2.923
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1.313
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t-Bu
t-Bu
Si
HO
O
BocHN
H
N
COOMe
O
4c
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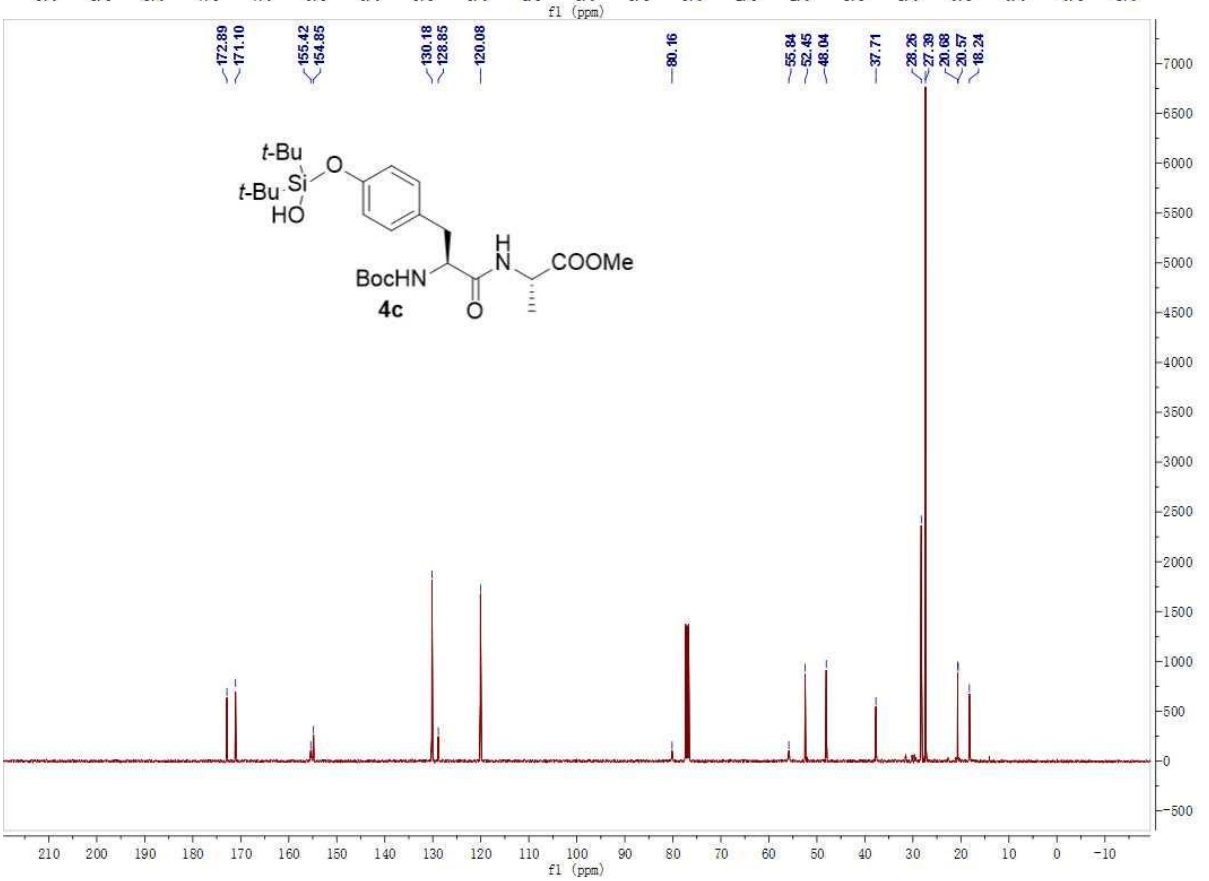
f1 (ppm)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t-Bu
Si
HO
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BocHN
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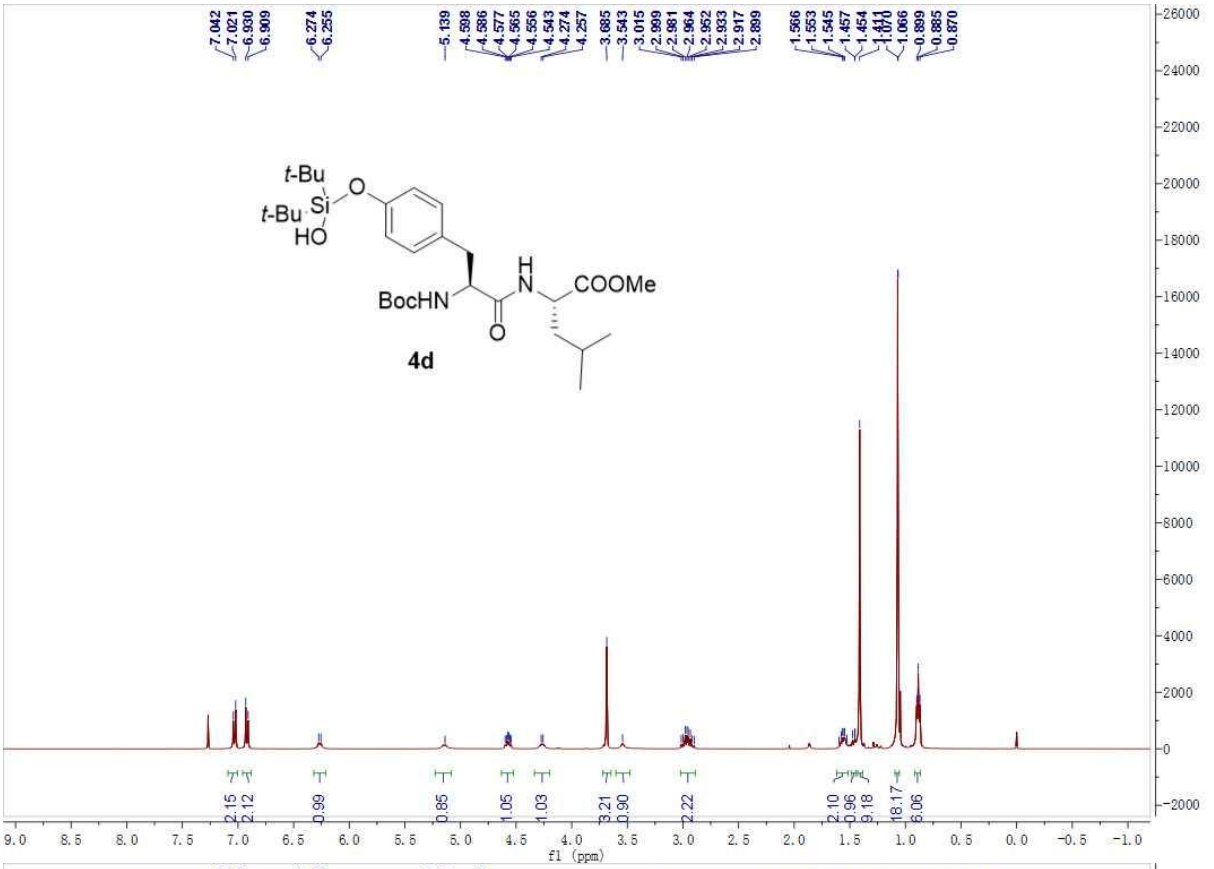
N
COOMe
O
4c
f1 (ppm)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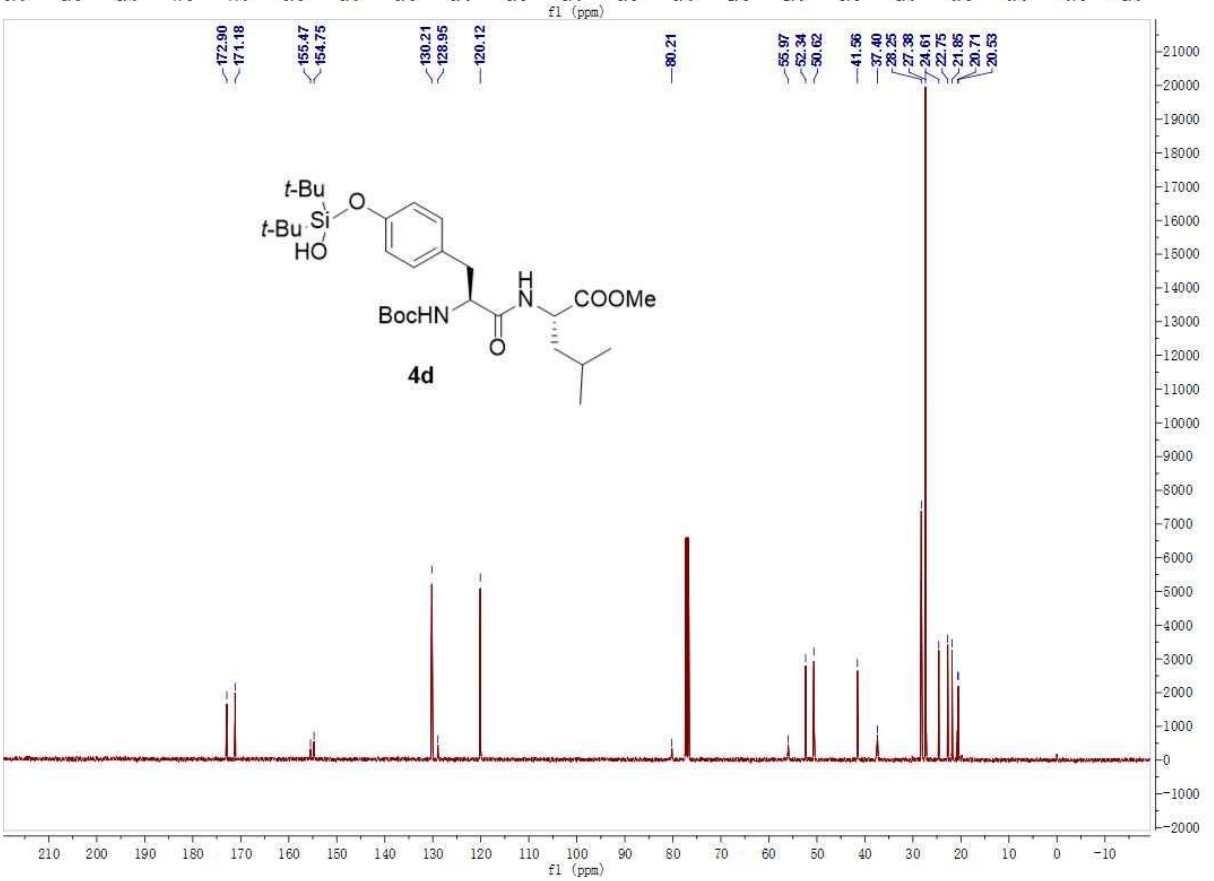
7.021
6.930
6.909
6.274
6.255
5.139
4.598
4.586
4.577
4.565
4.556
4.543
4.274
4.257
3.685
3.543
3.015
2.999
2.981
2.964
2.952
2.933
2.917
2.899
1.566
1.553
1.545
1.457
1.454
1.066
0.899
0.885
0.870
t-Bu
t-Bu
Si
HO
O
BocHN
H
N
COOMe
O
4d
2.15
2.12
0.99
0.85
1.05
1.03
3.21
0.90
2.22
2.10
0.96
9.18
18.17
6.06
f1 (ppm)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120.12
80.21
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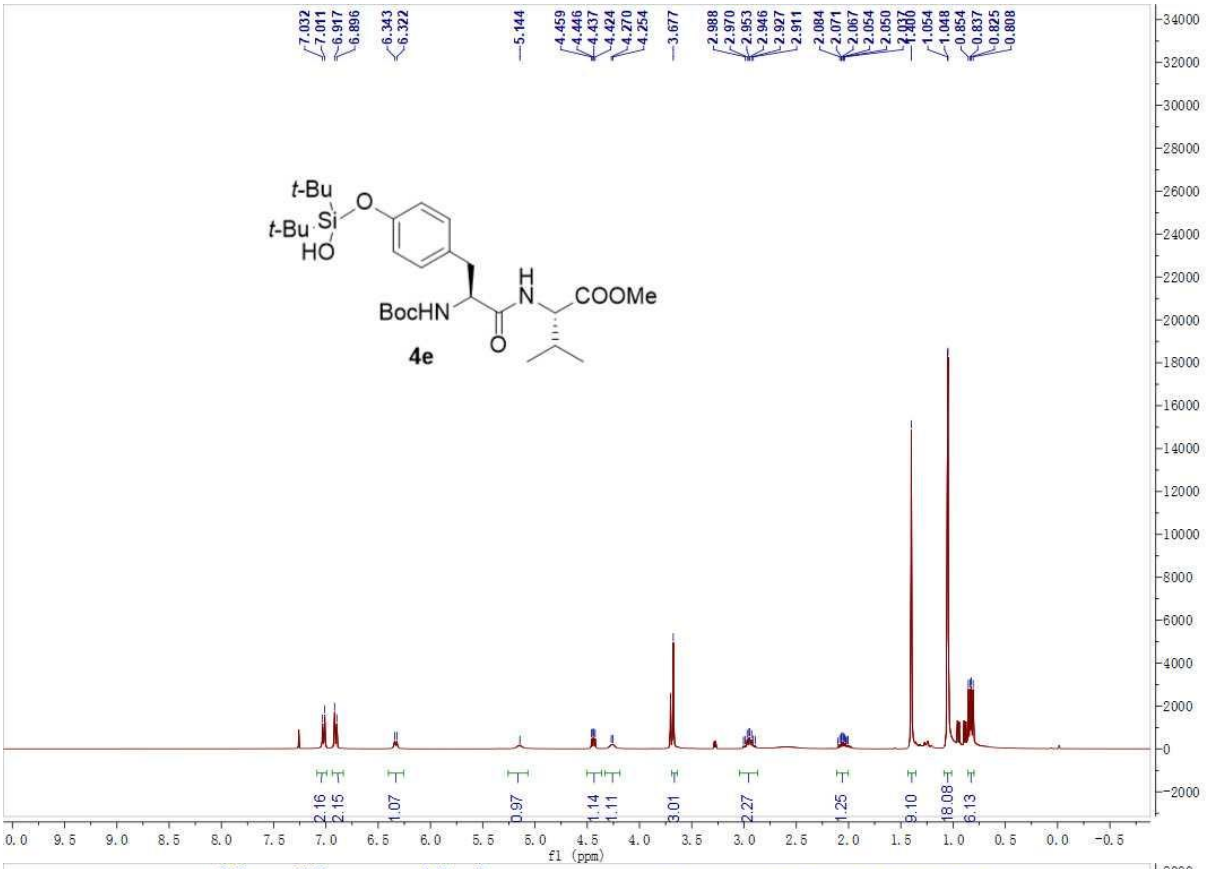
52.34
50.62
41.56
37.40
28.25
27.38
24.61
22.75
21.85
20.71
20.53
t-Bu
t-Bu
Si
HO
O
BocHN
H
N
COOMe
O
4d
f1 (ppm)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4.459
4.446
4.437
4.424
4.270
4.254
3.677
2.988
2.970
2.953
2.946
2.927
2.911
2.084
2.071
2.067
2.054
2.050
2.037
2.030
1.054
1.048
0.854
0.837
0.825
0.808
t-Bu
t-Bu
Si
O
HO
BocHN
H
N
COOMe
O
4e
2.16
2.15
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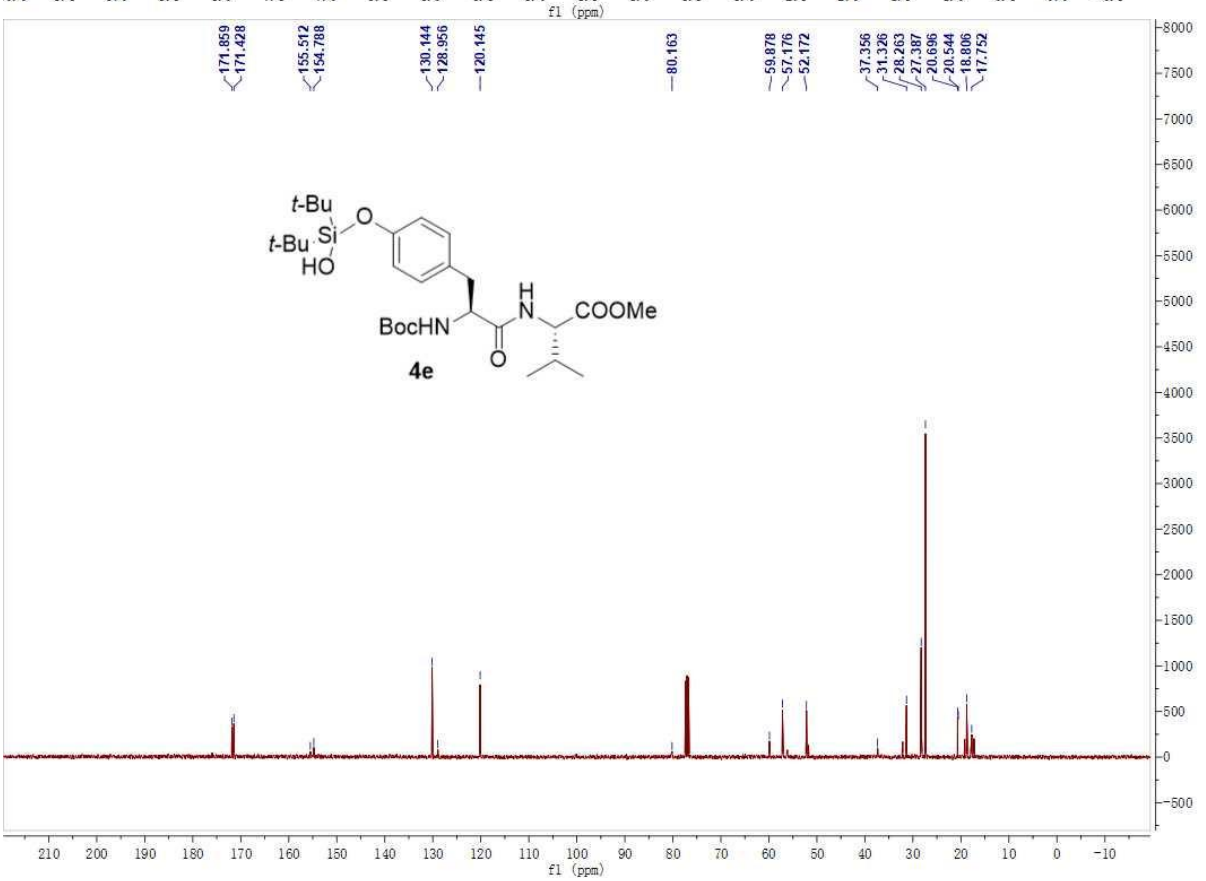
1.14
1.11
3.01
2.27
1.25
9.10
18.08
6.13
f1 (ppm)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128.956
120.145
80.163
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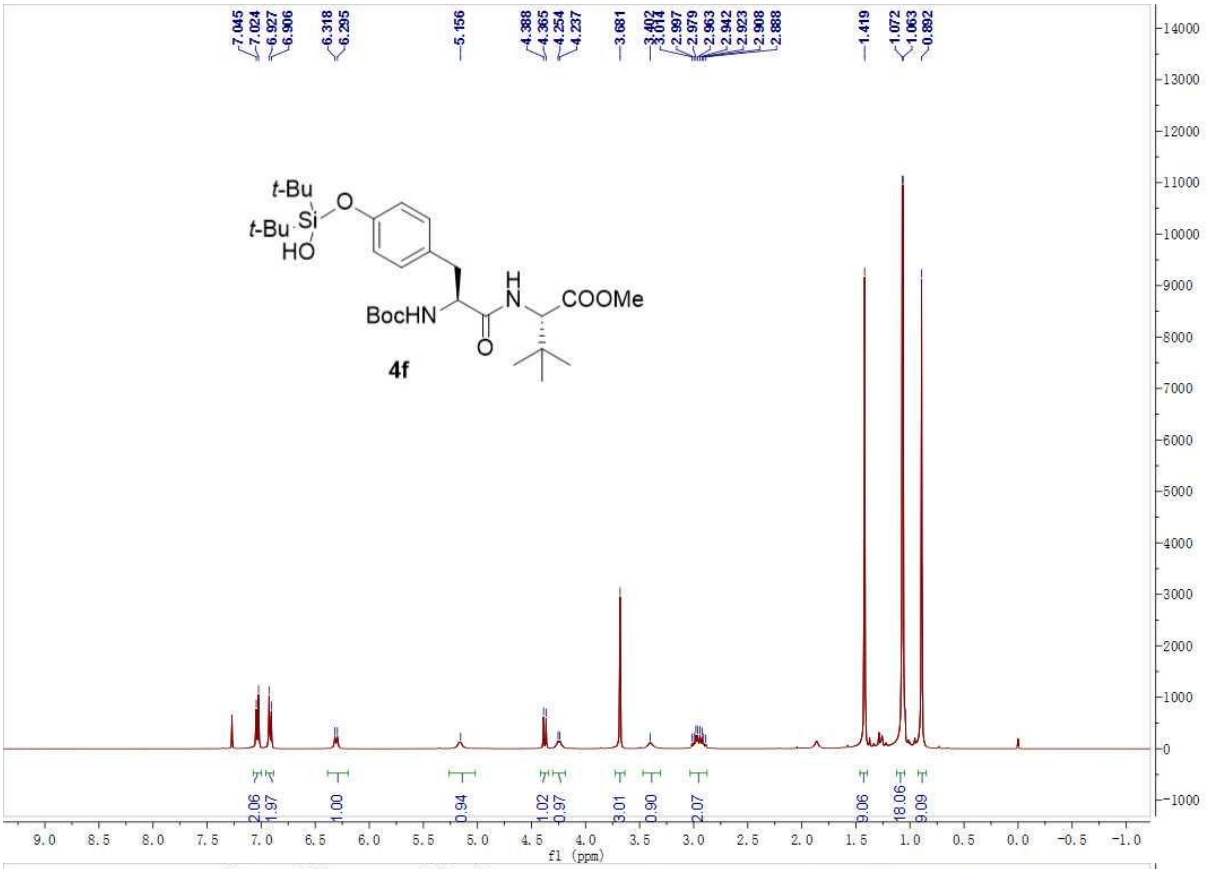
57.176
52.172
37.356
31.326
28.263
27.387
20.696
20.544
18.806
17.752
t-Bu
t-Bu
Si
O
HO
BocHN
H
N
COOMe
O
4e
f1 (ppm)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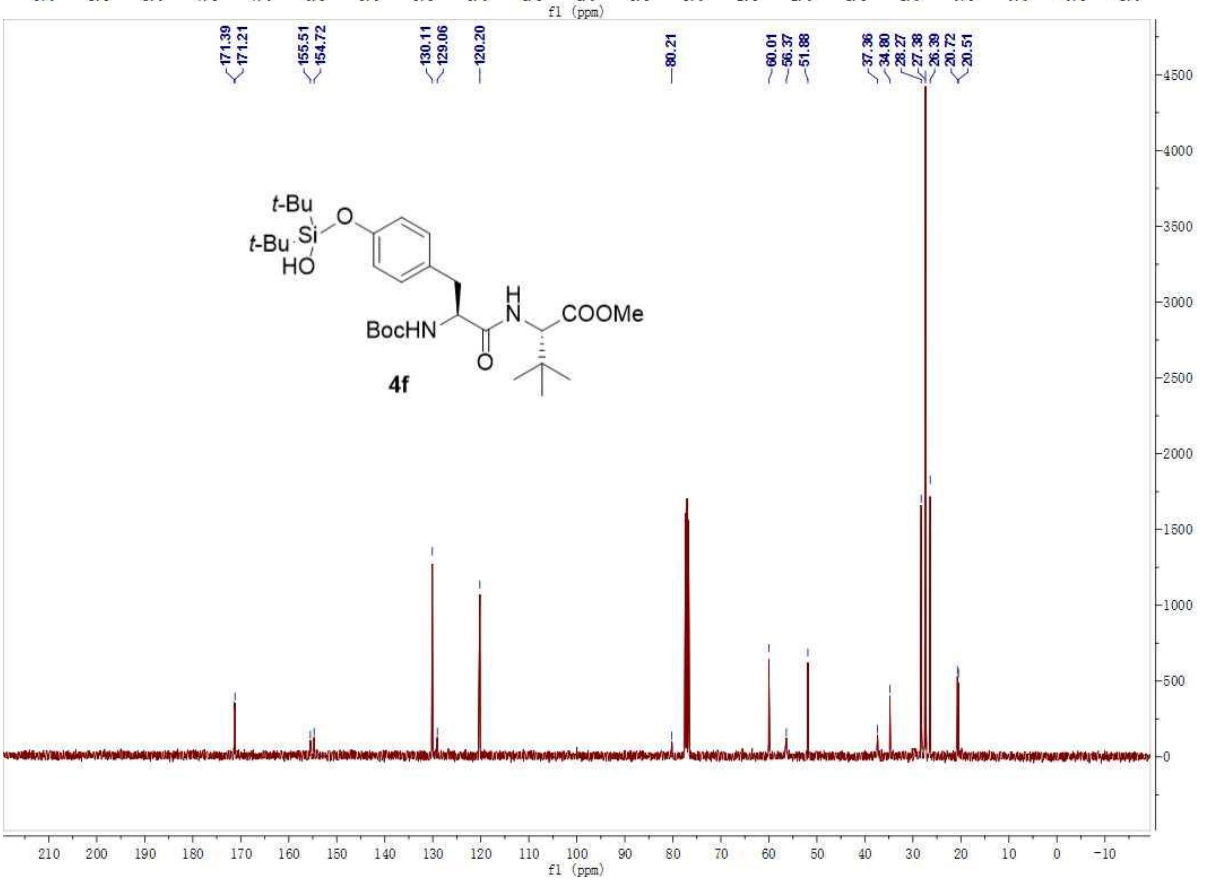
6.927
6.906
6.318
6.295
5.156
4.388
4.365
4.254
4.237
3.681
3.402
3.014
2.997
2.979
2.963
2.942
2.923
2.908
2.888
1.419
1.072
1.063
0.892
t-Bu
t-Bu
Si
O
HO
BocHN
H
N
COOMe
O
4f
2.06
1.97
1.00
0.94
1.02
0.97
3.01
0.90
2.07
9.06
18.06
9.09
f1 (ppm)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155.51
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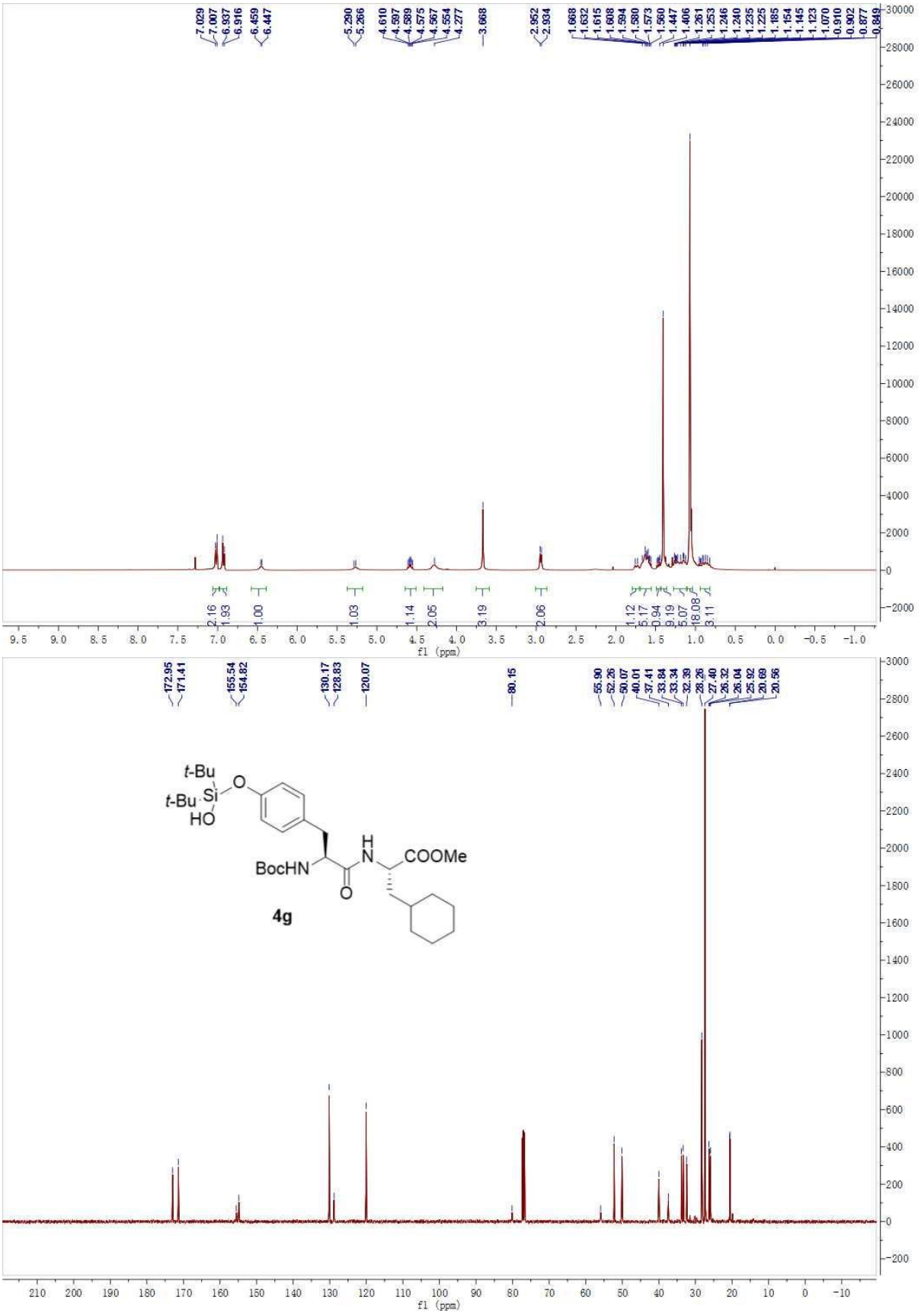
129.06
120.20
80.21
60.01
56.37
51.88
37.36
34.80
28.27
27.38
26.39
20.72
20.51
t-Bu
t-Bu
Si
O
HO
BocHN
H
N
COOMe
O
4f
f1 (ppm)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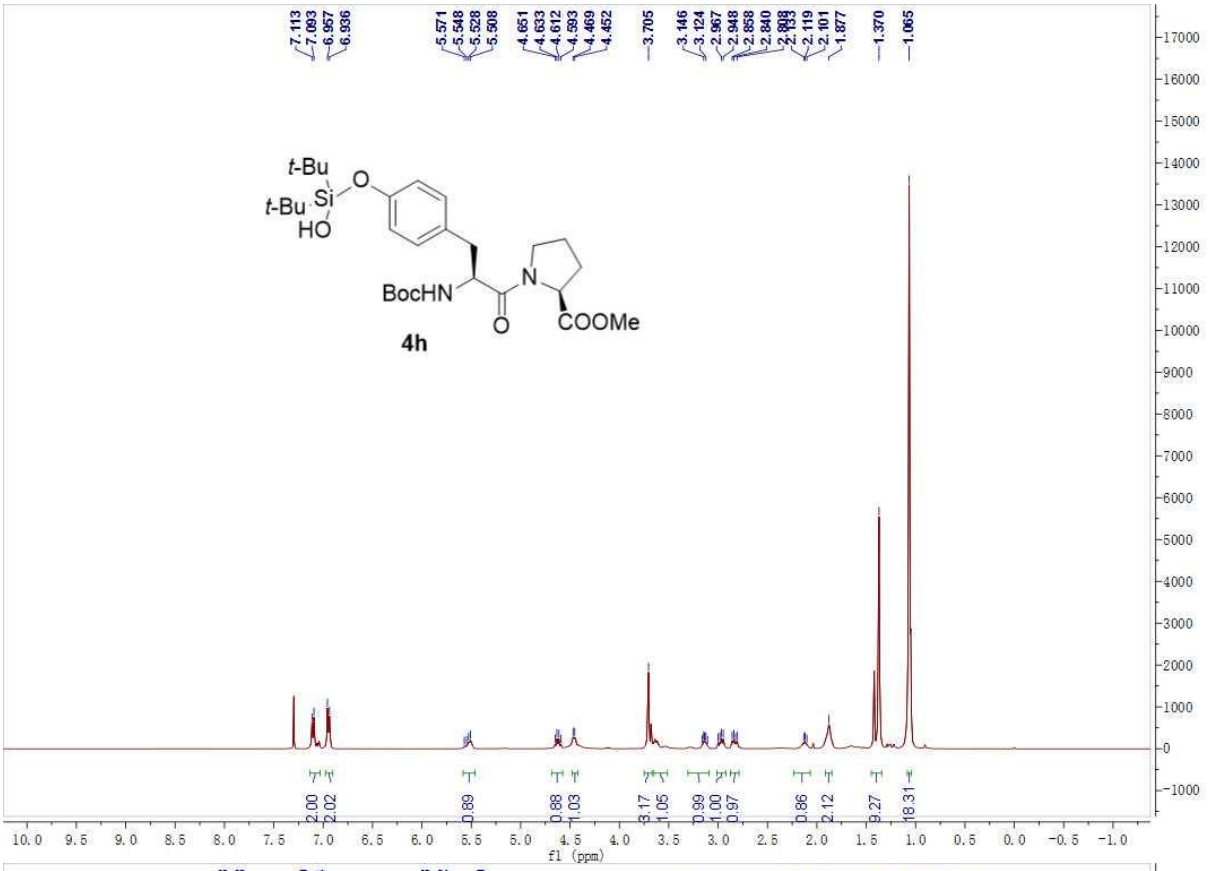
6.447
5.290
5.266
4.610
4.597
4.589
4.575
4.567
4.554
4.277
3.668
2.952
2.934
1.668
1.632
1.615
1.608
1.594
1.580
1.573
1.560
1.447
1.406
1.261
1.253
1.246
1.240
1.235
1.225
1.185
1.154
1.145
1.123
1.070
0.910
0.902
0.877
0.849
2.16
1.93
1.00
1.03
1.14
2.05
3.19
2.06
1.12
5.17
0.94
9.19
5.07
18.08
3.11
f1 (ppm)
172.95
171.41
155.54
154.82
130.17
128.83
120.07
80.15
55.90
52.26
50.07
40.01
37.41
33.84
33.34
32.39
28.26
27.40
26.32
26.04
25.92
20.69
20.56
t-Bu
t-Bu
Si
O
HO
BocHN
H
N
O
COOMe
4g
f1 (ppm)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6.957
6.936
5.571
5.548
5.528
5.508
4.651
4.633
4.612
4.593
4.469
4.452
3.705
3.146
3.124
2.967
2.948
2.858
2.840
2.119
2.101
1.877
1.370
1.065
t-Bu
t-Bu
Si
HO
O
BocHN
N
O
COOMe
4h
2.00
2.02
0.89
0.88
1.03
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1.05
0.99
1.00
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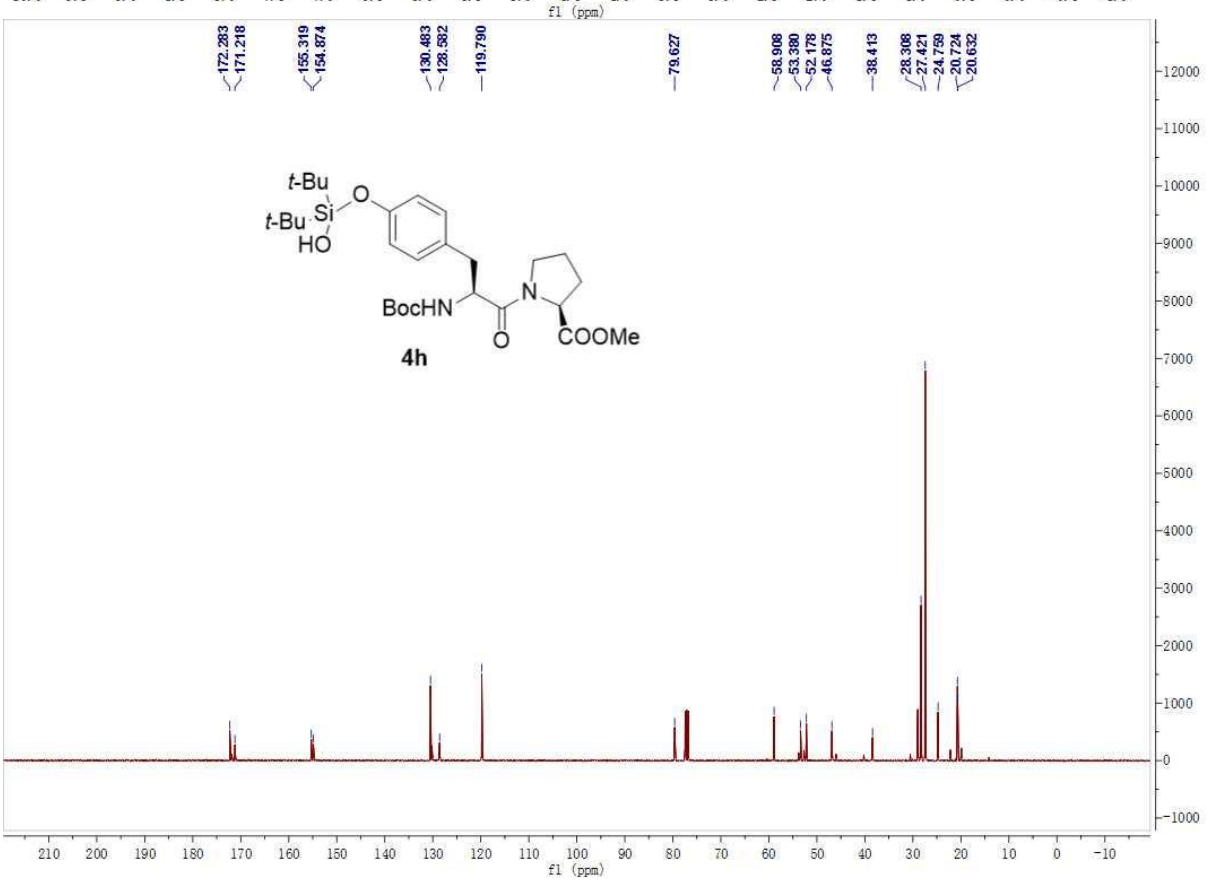
0.86
2.12
9.27
18.31
f1 (ppm)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79.627
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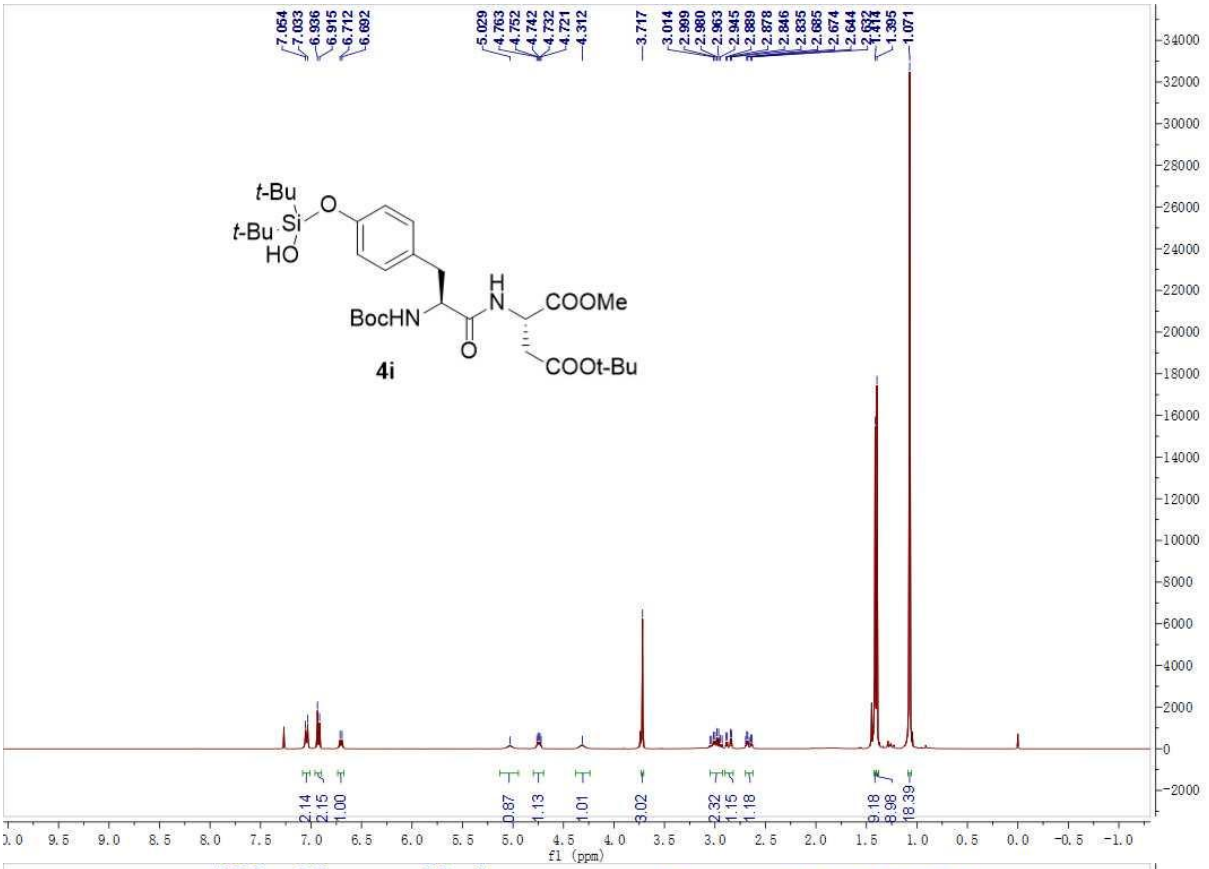
52.178
46.875
38.413
28.308
27.421
24.759
20.724
20.632
t-Bu
t-Bu
Si
HO
O
BocHN
N
O
COOMe
4h
f1 (ppm)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6.712
6.692
5.029
4.763
4.752
4.742
4.732
4.721
4.312
3.717
3.014
2.999
2.980
2.963
2.945
2.889
2.878
2.846
2.835
2.685
2.674
2.644
1.395
1.071
t-Bu
t-Bu
Si
HO
O
BocHN
H
N
O
COOMe
COOt-Bu
4i
2.14
2.15
1.00
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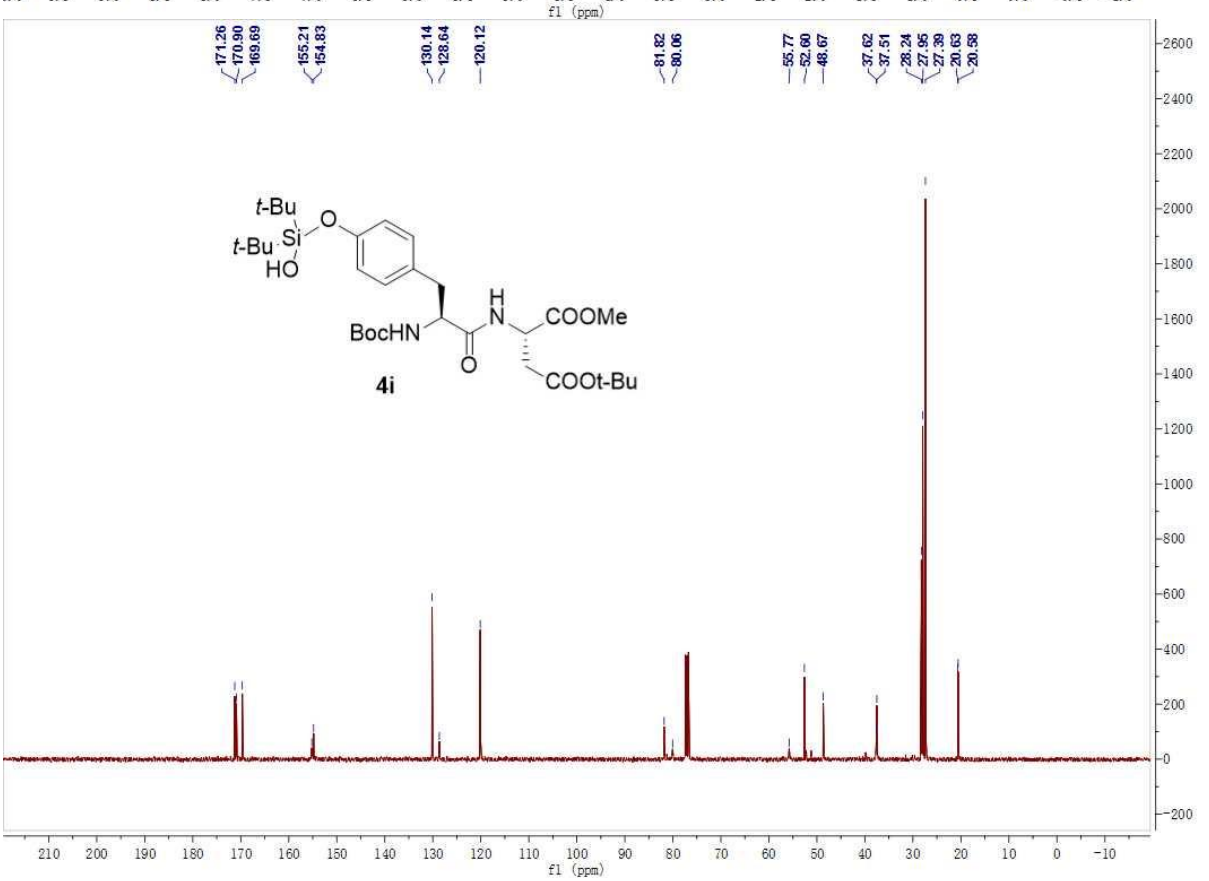
1.01
3.02
2.32
1.15
1.18
9.18
8.98
18.39
f1 (ppm)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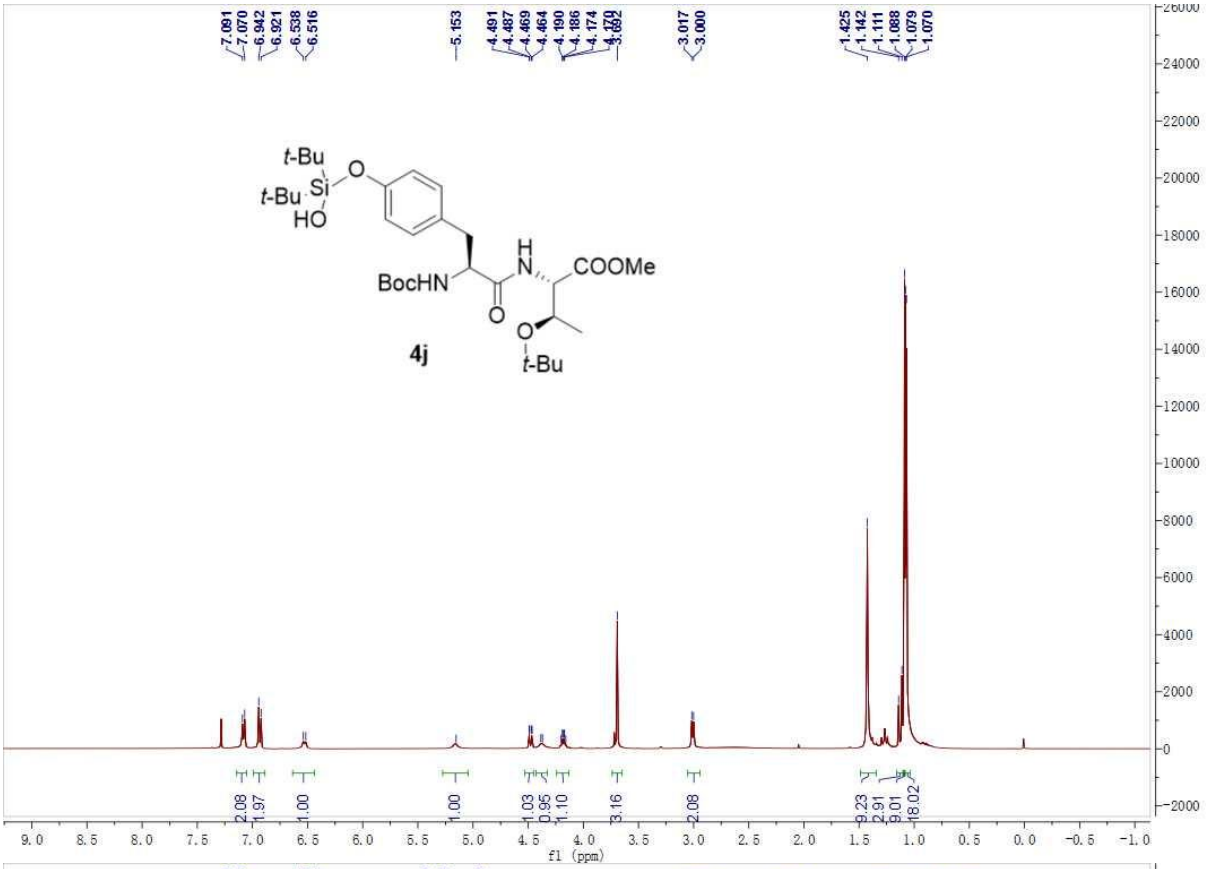
169.69
155.21
154.83
130.14
128.64
120.12
81.82
80.06
55.77
52.60
48.67
37.62
37.51
28.24
27.95
27.39
20.63
20.58
t-Bu
t-Bu
Si
HO
O
BocHN
H
N
O
COOMe
COOt-Bu
4i
f1 (ppm)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6.921
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6.516
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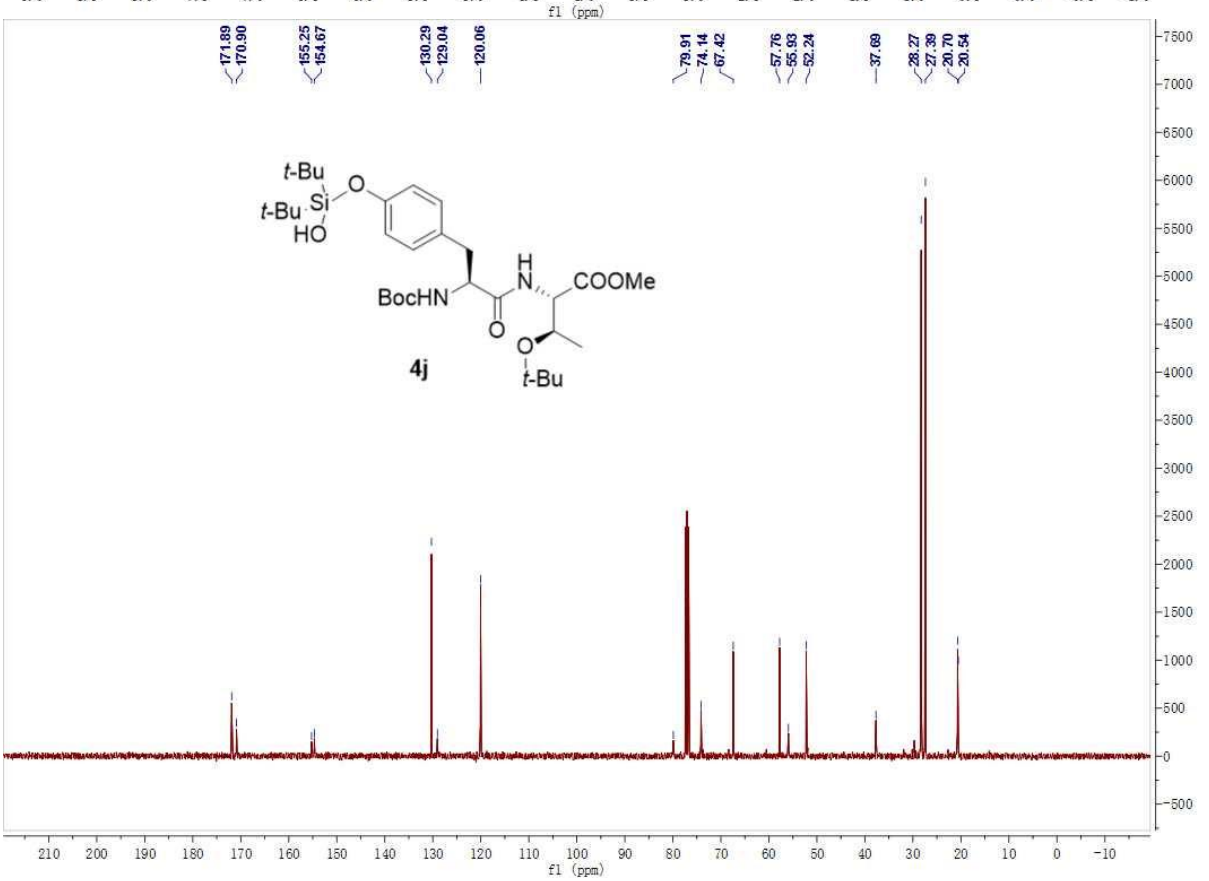
4.491
4.487
4.469
4.464
4.190
4.186
4.174
3.017
3.000
1.425
1.142
1.111
1.088
1.079
1.070
t-Bu
t-Bu
Si
HO
O
BocHN
H
N
COOMe
O
O
t-Bu
4j
2.08
1.97
1.00
1.00
1.03
0.95
1.10
3.16
2.08
9.23
2.91
9.01
18.02
f1 (ppm)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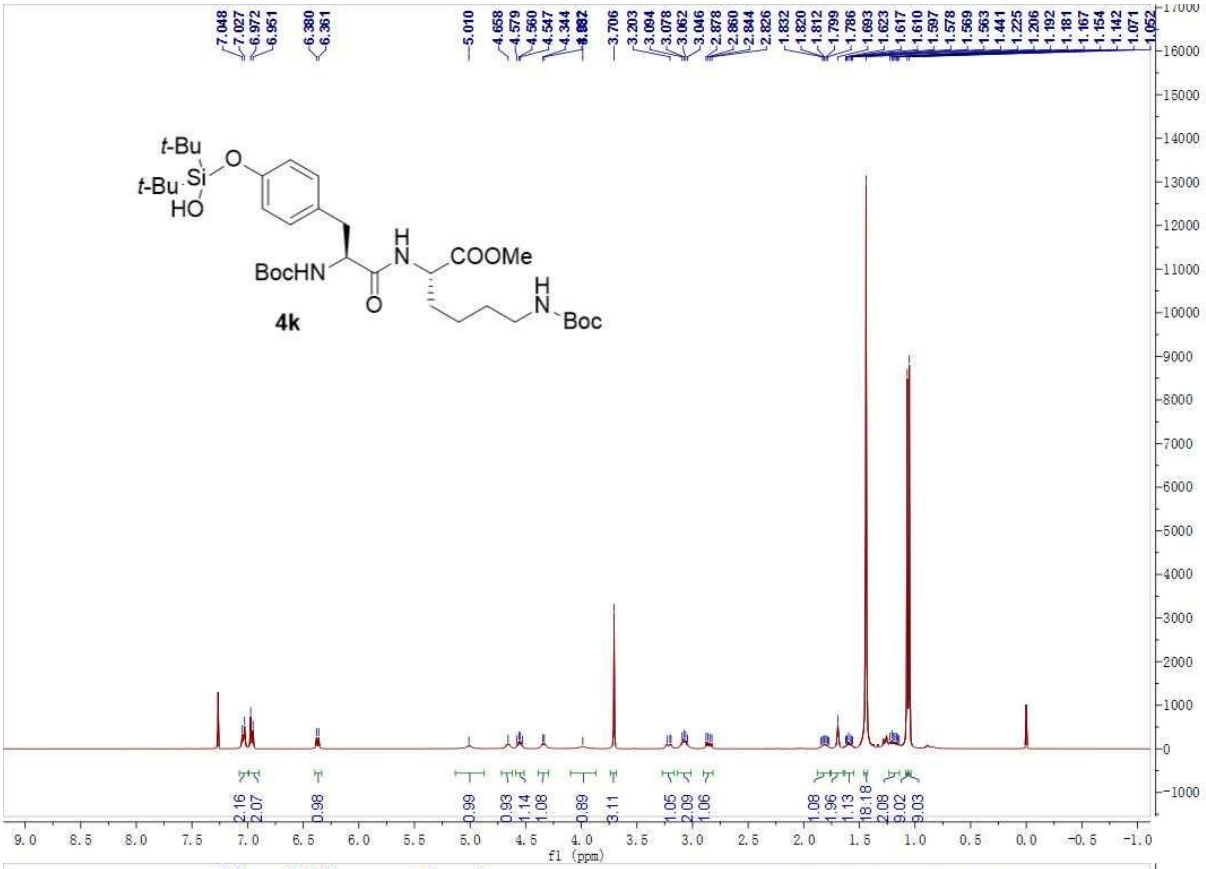
79.91
74.14
67.42
57.76
55.93
52.24
37.69
28.27
27.39
20.70
20.54
t-Bu
t-Bu
Si
HO
O
BocHN
H
N
COOMe
O
O
t-Bu
4j
f1 (ppm)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3.706
3.203
3.094
3.078
3.062
3.046
2.878
2.860
2.844
2.826
1.832
1.820
1.812
1.799
1.786
1.693
1.623
1.617
1.610
1.597
1.578
1.569
1.563
1.441
1.225
1.206
1.192
1.181
1.167
1.154
1.142
1.071
1.052
t-Bu
t-Bu
Si
O
HO
BocHN
H
N
COOMe
O
H
N
Boc
4k
2.16
2.07
0.98
0.99
0.93
1.14
1.08
0.89
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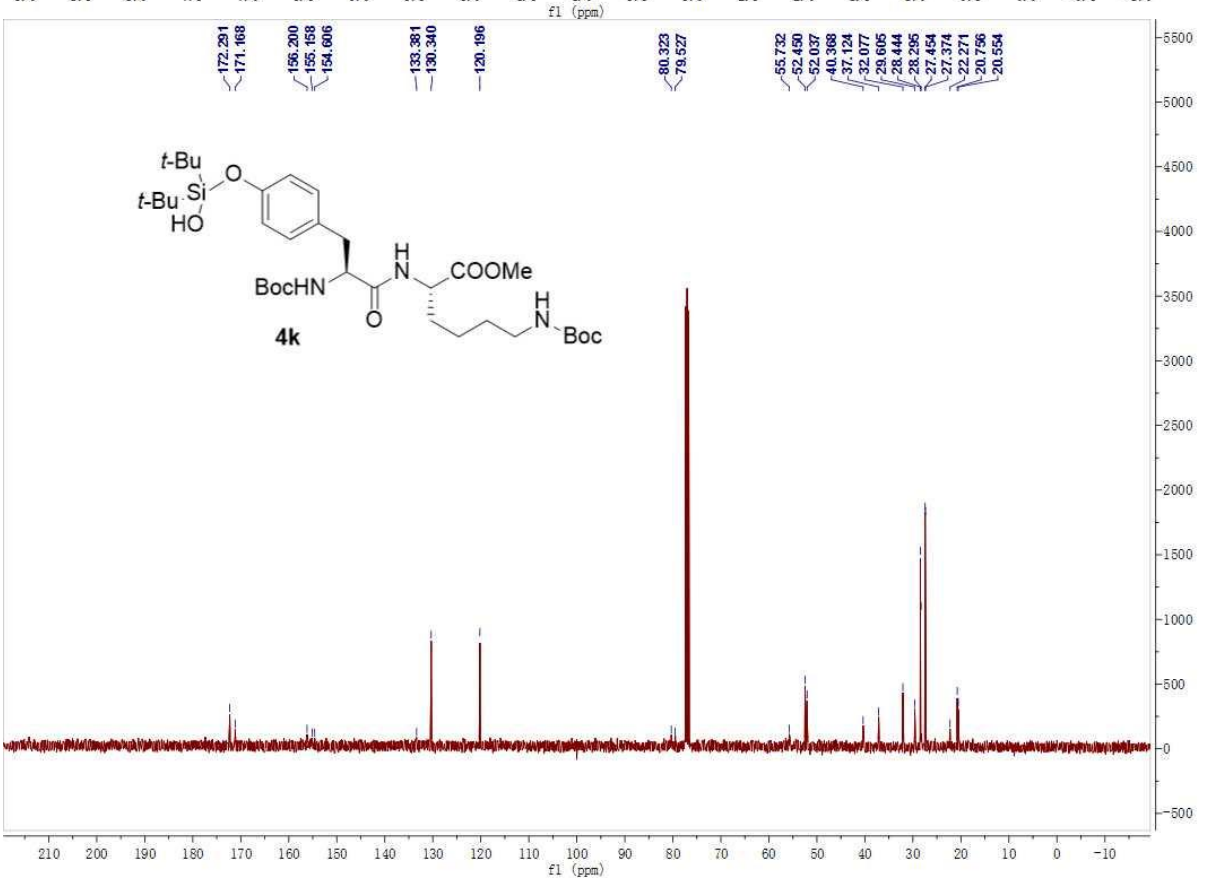
2.09
1.06
1.08
1.96
1.13
18.18
2.08
9.02
9.03
f1 (ppm)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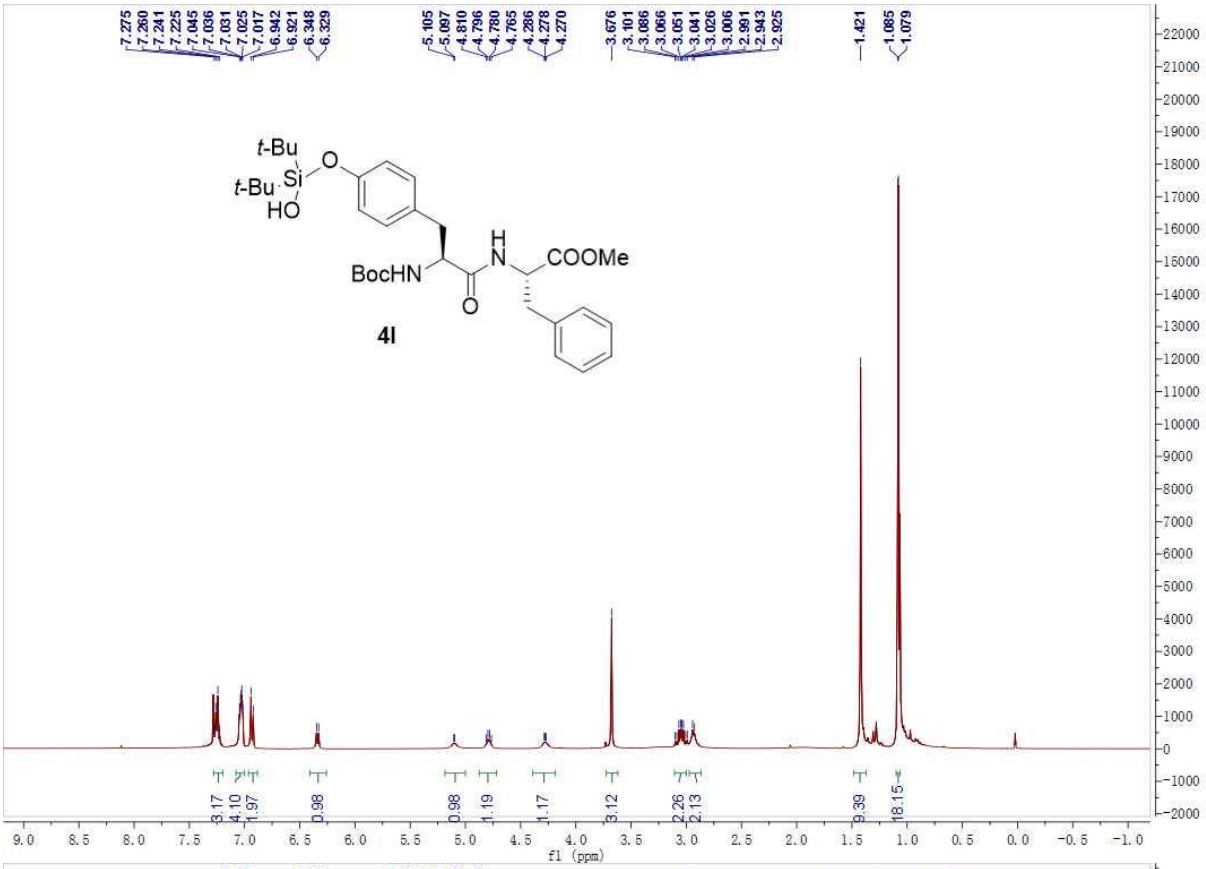
120.196
80.323
79.527
55.732
52.450
52.037
40.368
37.124
32.077
29.605
28.444
28.295
27.454
27.374
22.271
20.756
20.554
t-Bu
t-Bu
Si
O
HO
BocHN
H
N
COOMe
O
H
N
Boc
4k
f1 (ppm)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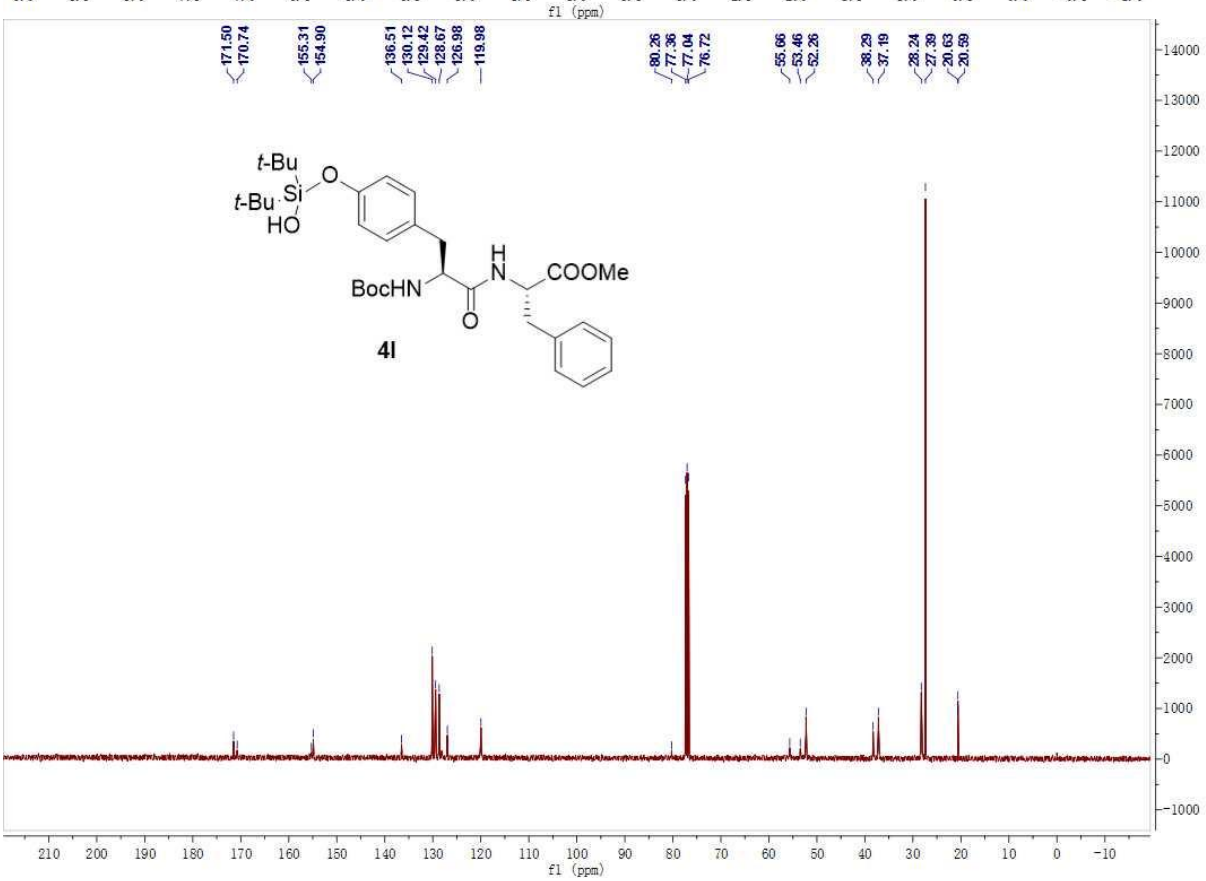
7.025
7.017
6.942
6.921
6.348
6.329
5.105
5.097
4.810
4.796
4.780
4.765
4.286
4.278
4.270
3.676
3.101
3.086
3.066
3.051
3.041
3.026
3.006
2.991
2.943
2.925
1.421
1.085
1.079
t-Bu
t-Bu
Si
HO
O
BocHN
H
N
O
COOMe
4l
3.17
4.10
1.97
0.98
0.98
1.19
1.17
3.12
2.26
2.13
9.39
18.15
f1 (ppm)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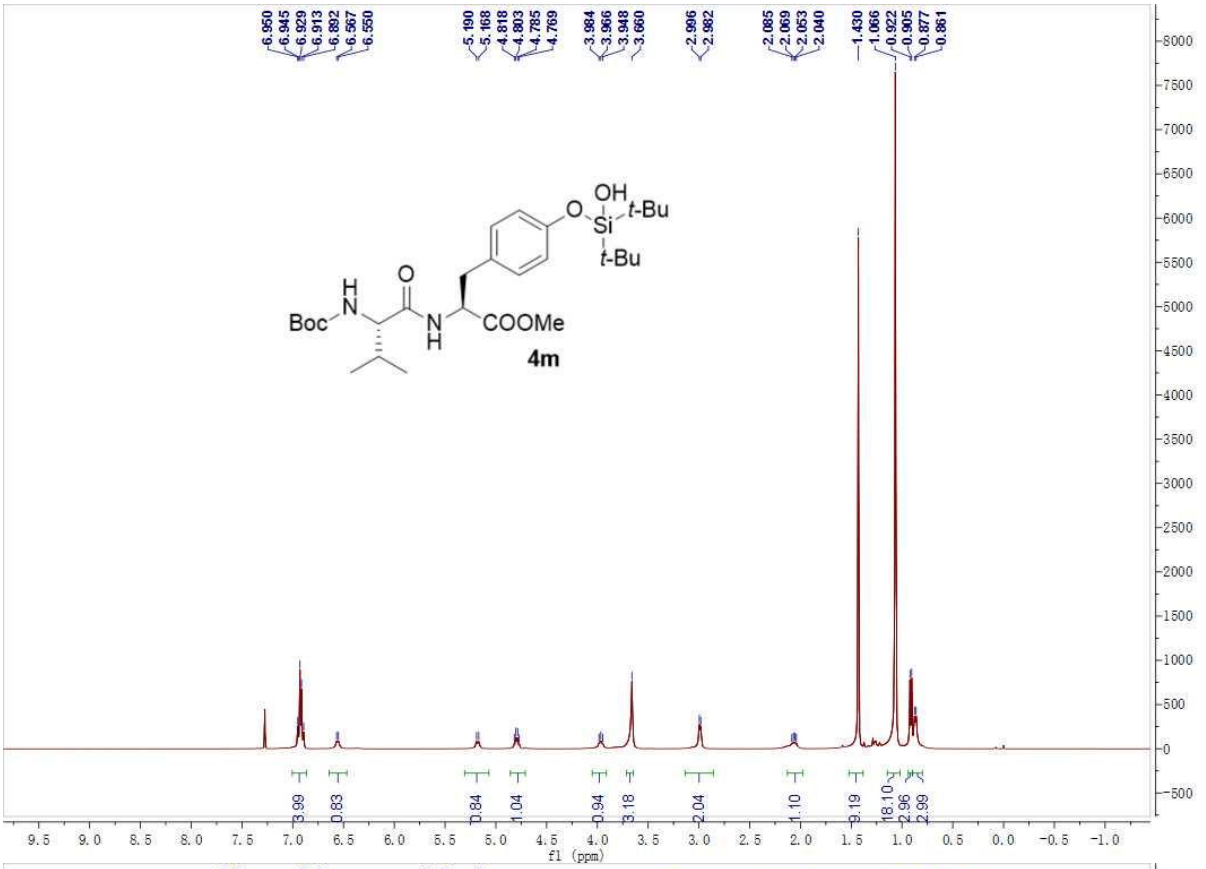
128.67
126.98
119.98
80.26
77.36
77.04
76.72
55.66
53.46
52.26
38.29
37.19
28.24
27.39
20.63
20.59
t-Bu
t-Bu
Si
HO
O
BocHN
H
N
O
COOMe
4l
f1 (ppm)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4.803
4.785
4.769
3.984
3.966
3.948
3.660
2.896
2.862
2.085
2.069
2.053
2.040
1.430
1.066
0.922
0.905
0.877
0.861
OH
t-Bu
O
Si
t-Bu
H
N
O
Boc
N
H
COOMe
4m
3.99
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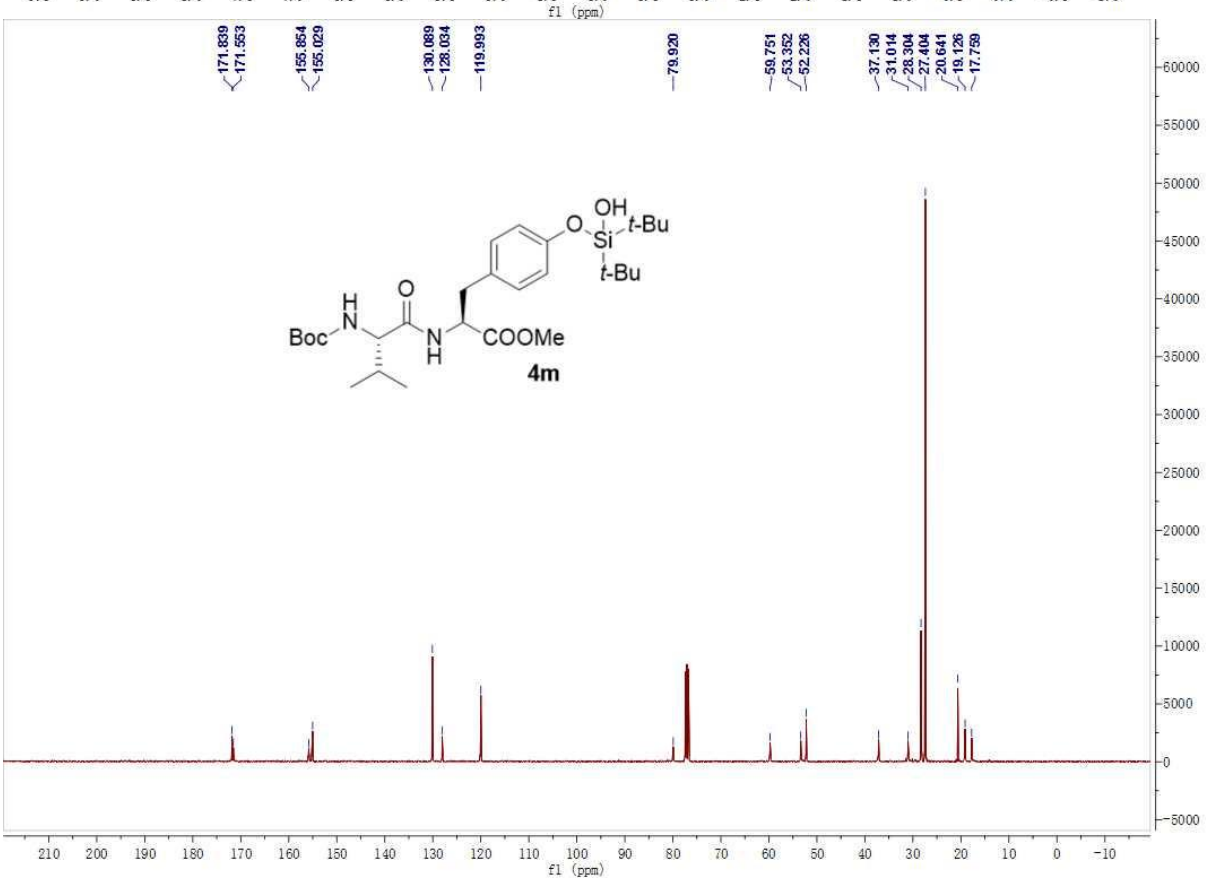
2.04
1.10
9.19
18.10
2.96
2.99
f1 (ppm)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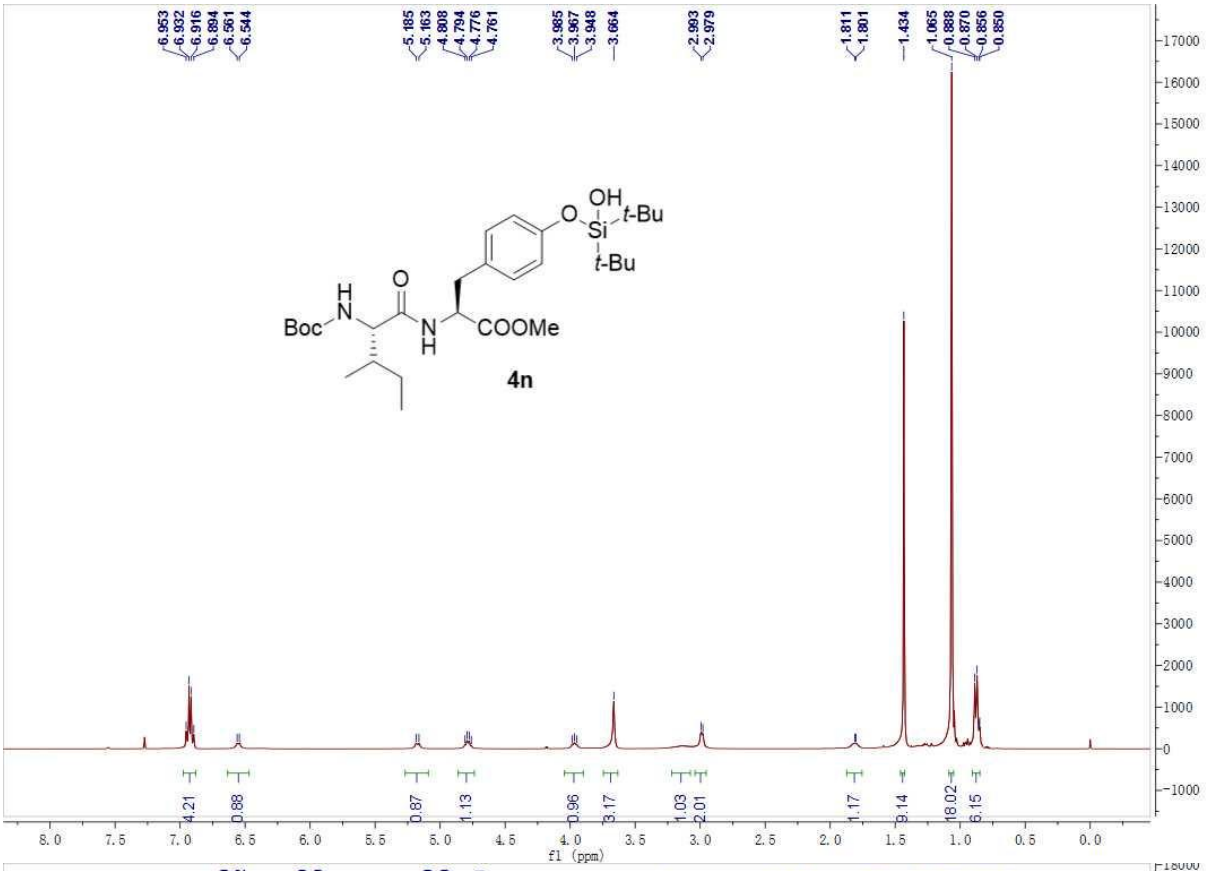
52.226
37.130
31.014
28.304
27.404
20.641
19.126
17.759
OH
t-Bu
O
Si
t-Bu
H
N
O
Boc
N
H
COOMe
4m
f1 (ppm)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5.163
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4.776
4.761
3.985
3.967
3.948
3.664
2.993
2.979
1.811
1.801
1.434
1.065
0.888
0.870
0.856
0.850
OH
t-Bu
O
Si
t-Bu
H
N
O
Boc
N
H
COOMe
4n
4.21
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0.87
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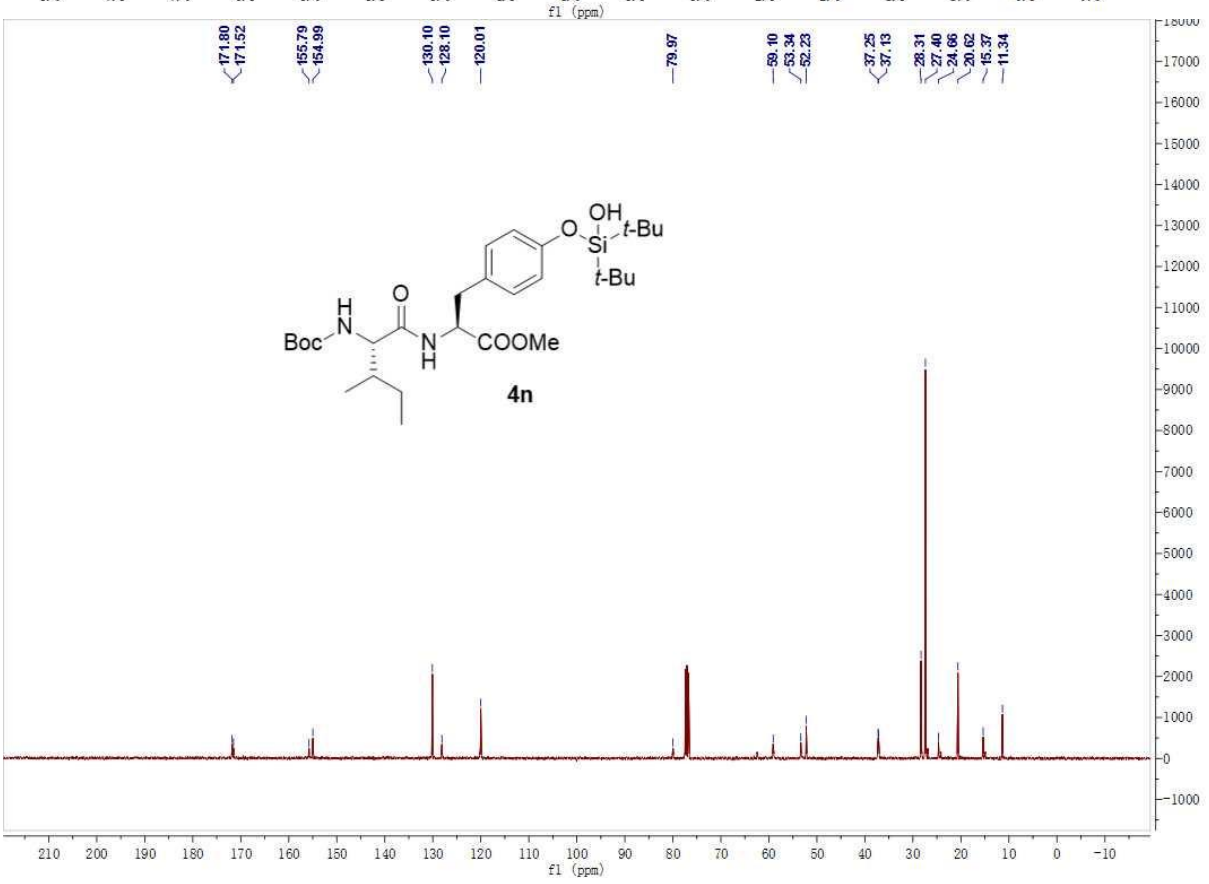
0.96
3.17
1.03
2.01
1.17
9.14
18.02
6.15
f1 (ppm)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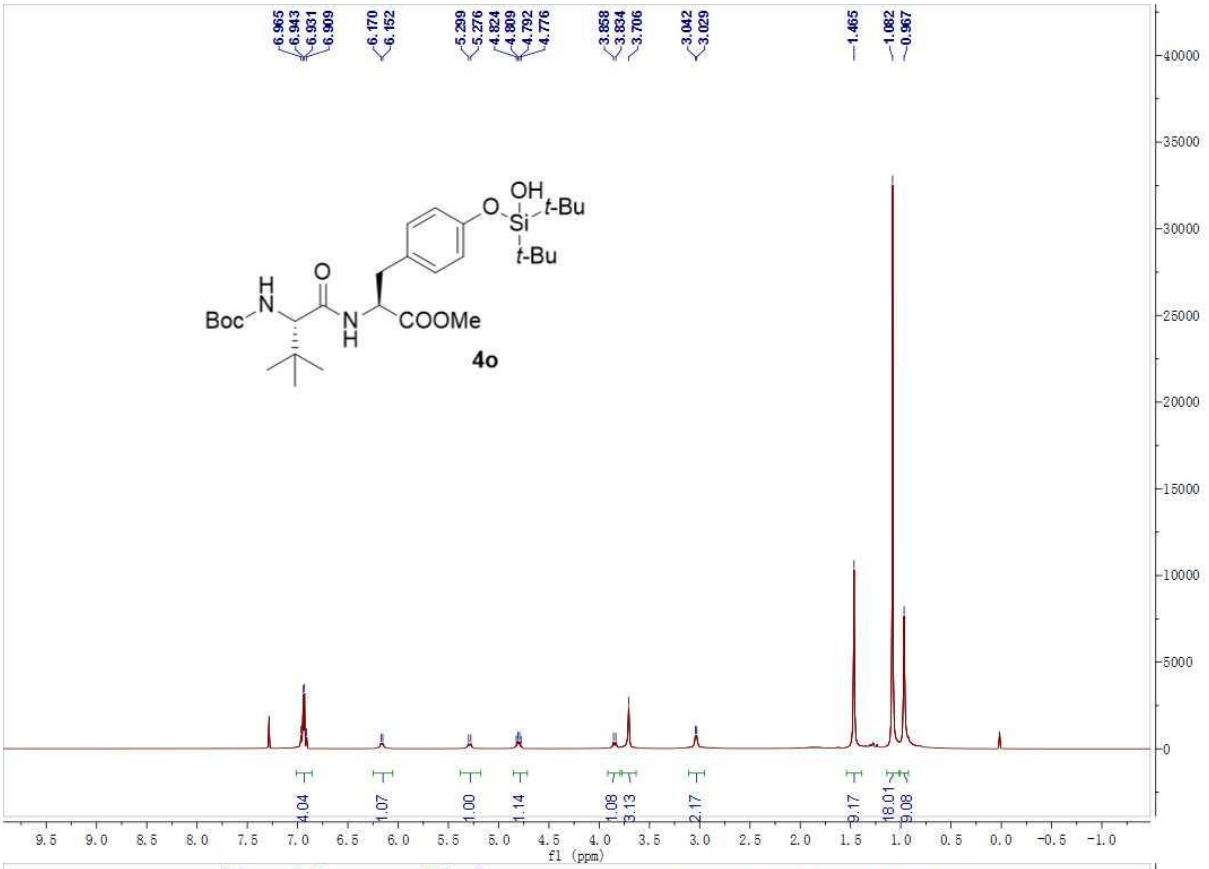
128.10
120.01
79.97
59.10
53.34
52.23
37.25
37.13
28.31
27.40
24.66
20.62
15.37
11.34
OH
t-Bu
O
Si
t-Bu
H
N
O
Boc
N
H
COOMe
4n
f1 (ppm)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5.276
4.824
4.809
4.792
4.776
3.858
3.834
3.706
3.042
3.029
1.465
1.082
0.967
OH
t-Bu
O
Si
t-Bu
H
N
O
Boc
N
H
COOMe
4o
4.04
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1.00
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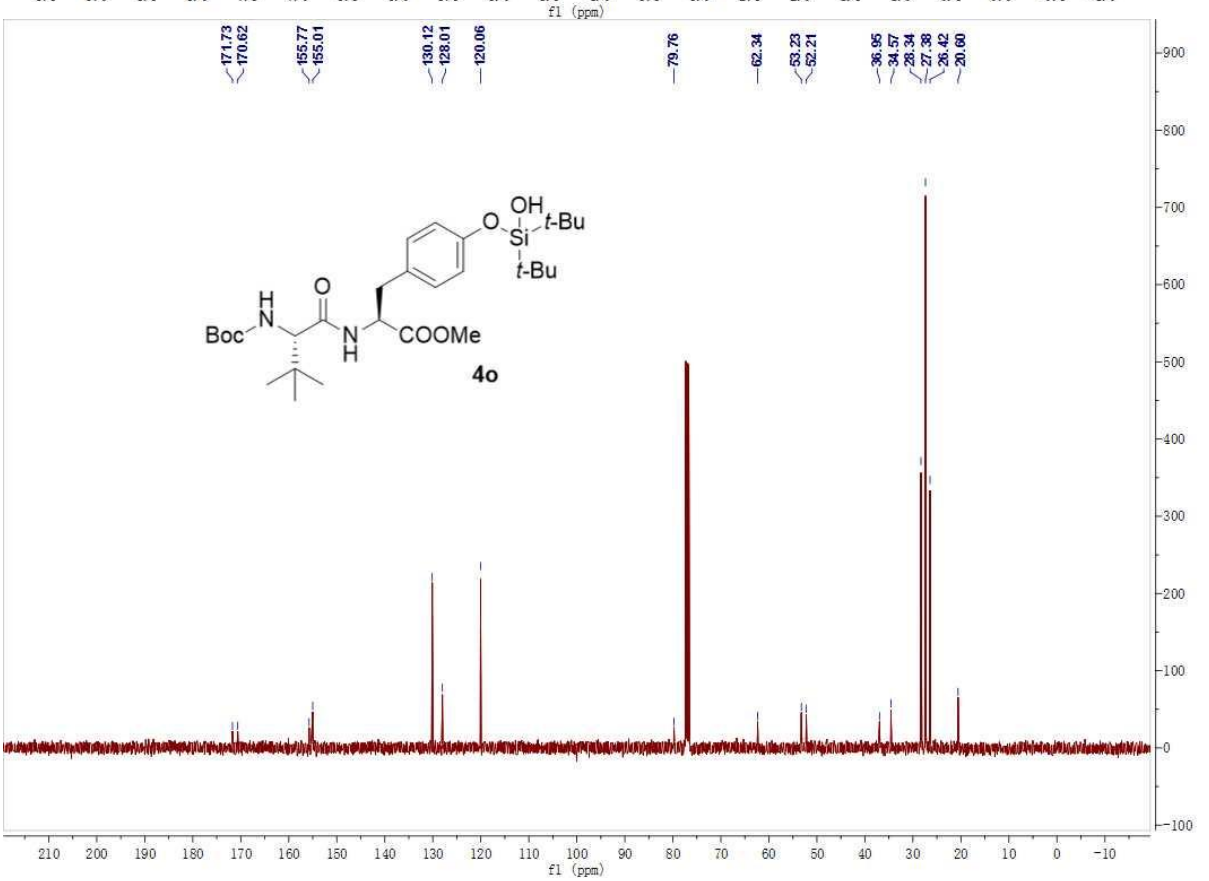
2.17
9.17
18.01
9.08
f1 (ppm)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128.01
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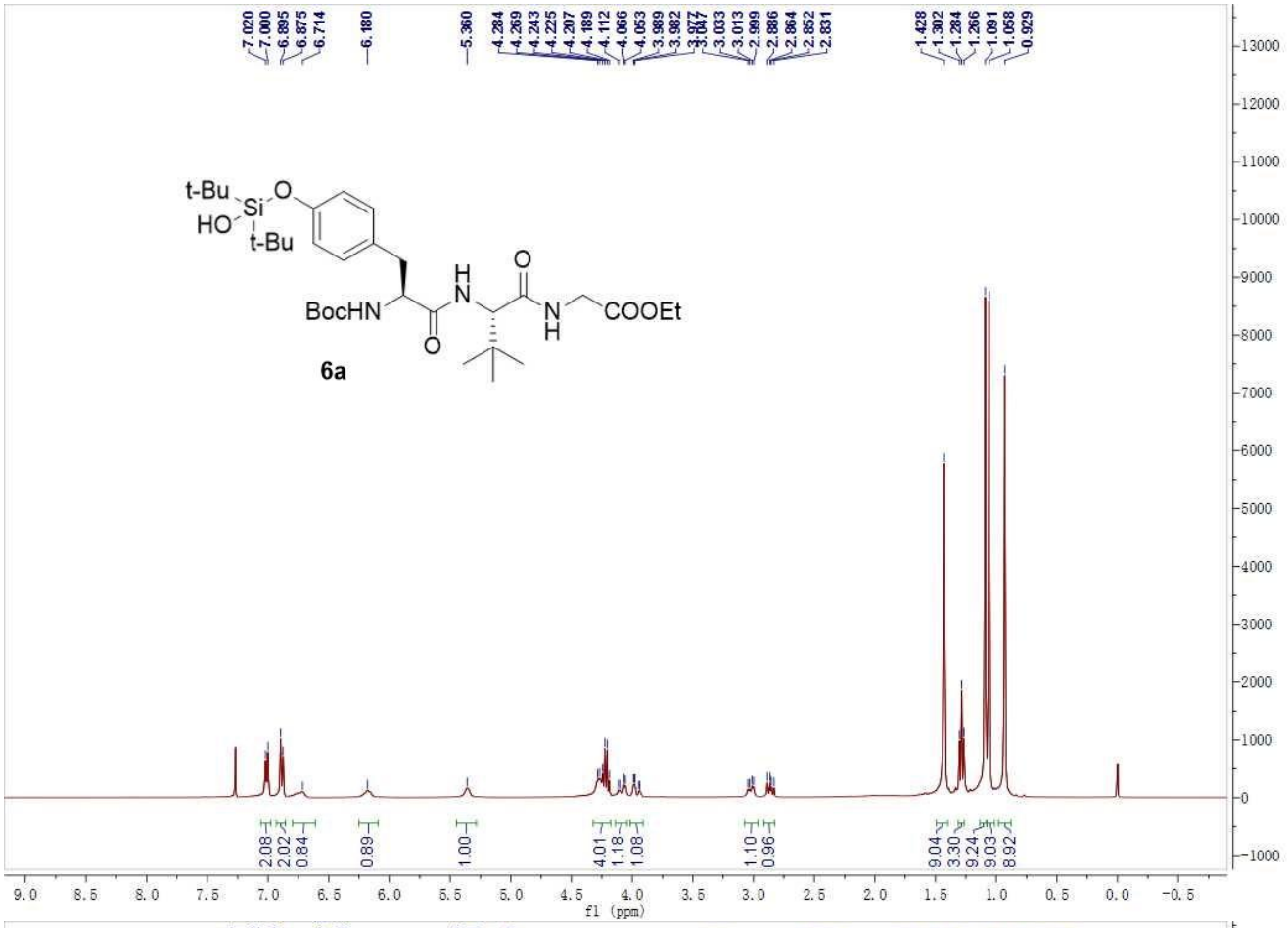
53.23
52.21
36.95
34.57
28.34
27.38
26.42
20.60
OH
t-Bu
O
Si
t-Bu
H
N
O
Boc
N
H
COOMe
4o
f1 (ppm)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6.875
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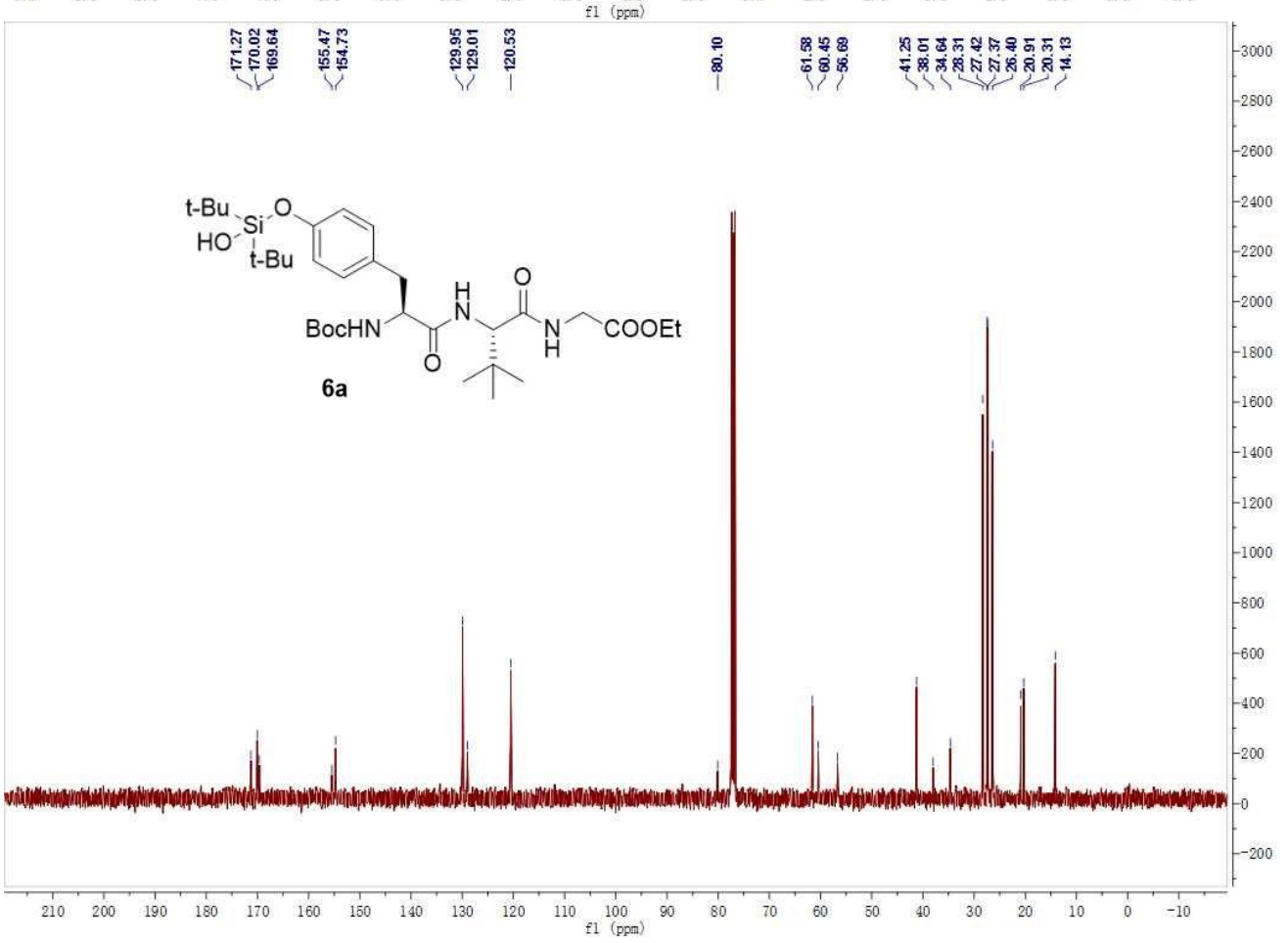
6.180
5.360
4.284
4.269
4.243
4.225
4.207
4.189
4.112
4.066
4.053
3.989
3.982
3.033
3.013
2.999
2.886
2.864
2.852
2.831
1.428
1.302
1.284
1.266
1.091
1.058
0.929
t-Bu
Si
O
HO
t-Bu
BocHN
H
N
O
N
H
COOEt
6a
2.08
2.02
0.84
0.89
1.00
4.01
1.18
1.08
1.10
0.96
9.04
3.30
9.24
9.03
8.92
f1 (ppm)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61.58
60.45
56.69
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38.01
34.64
28.31
27.42
27.37
26.40
20.91
20.31
14.13
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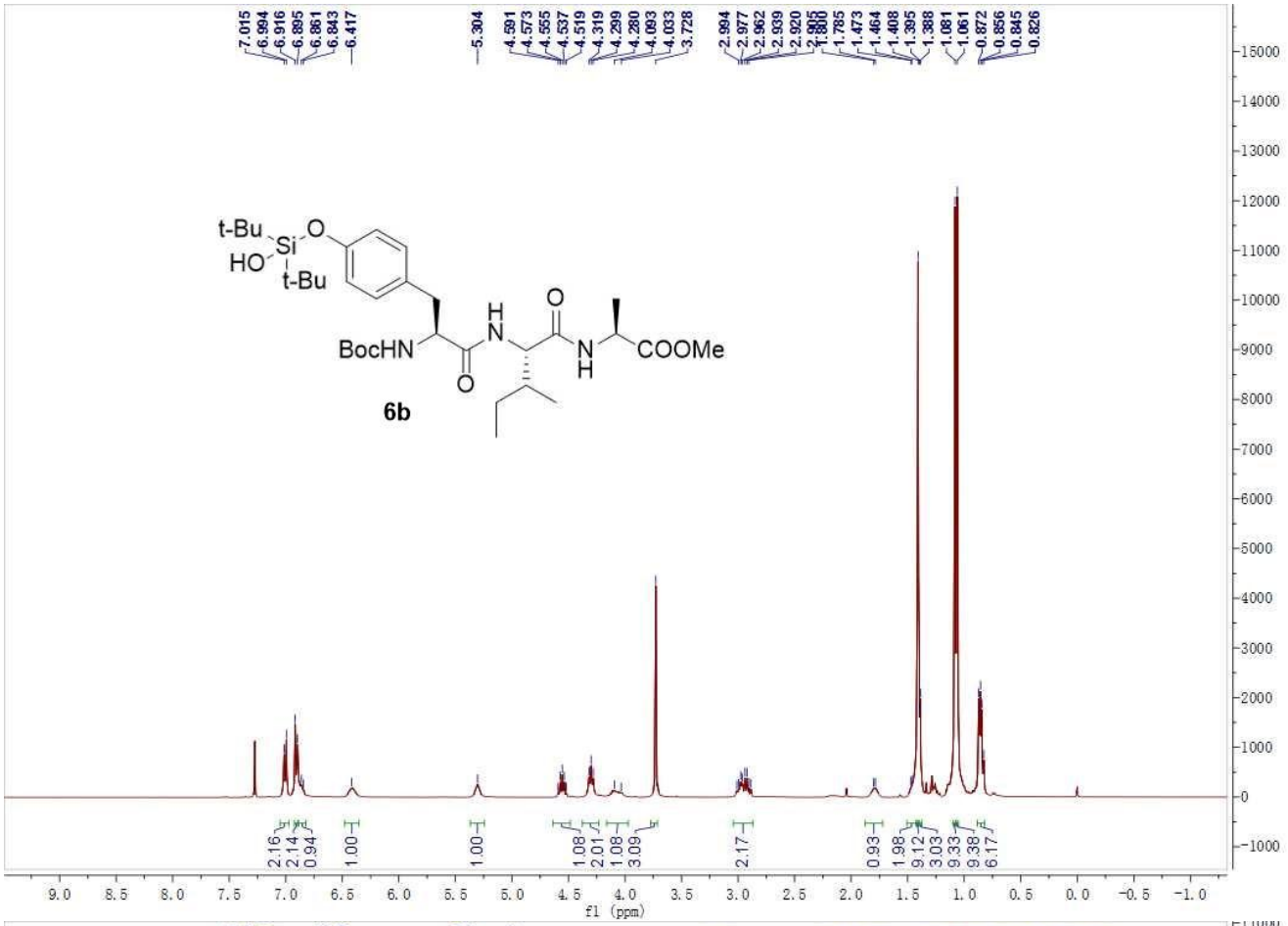
Si
O
HO
t-Bu
BocHN
H
N
O
N
H
COOEt
6a
f1 (ppm)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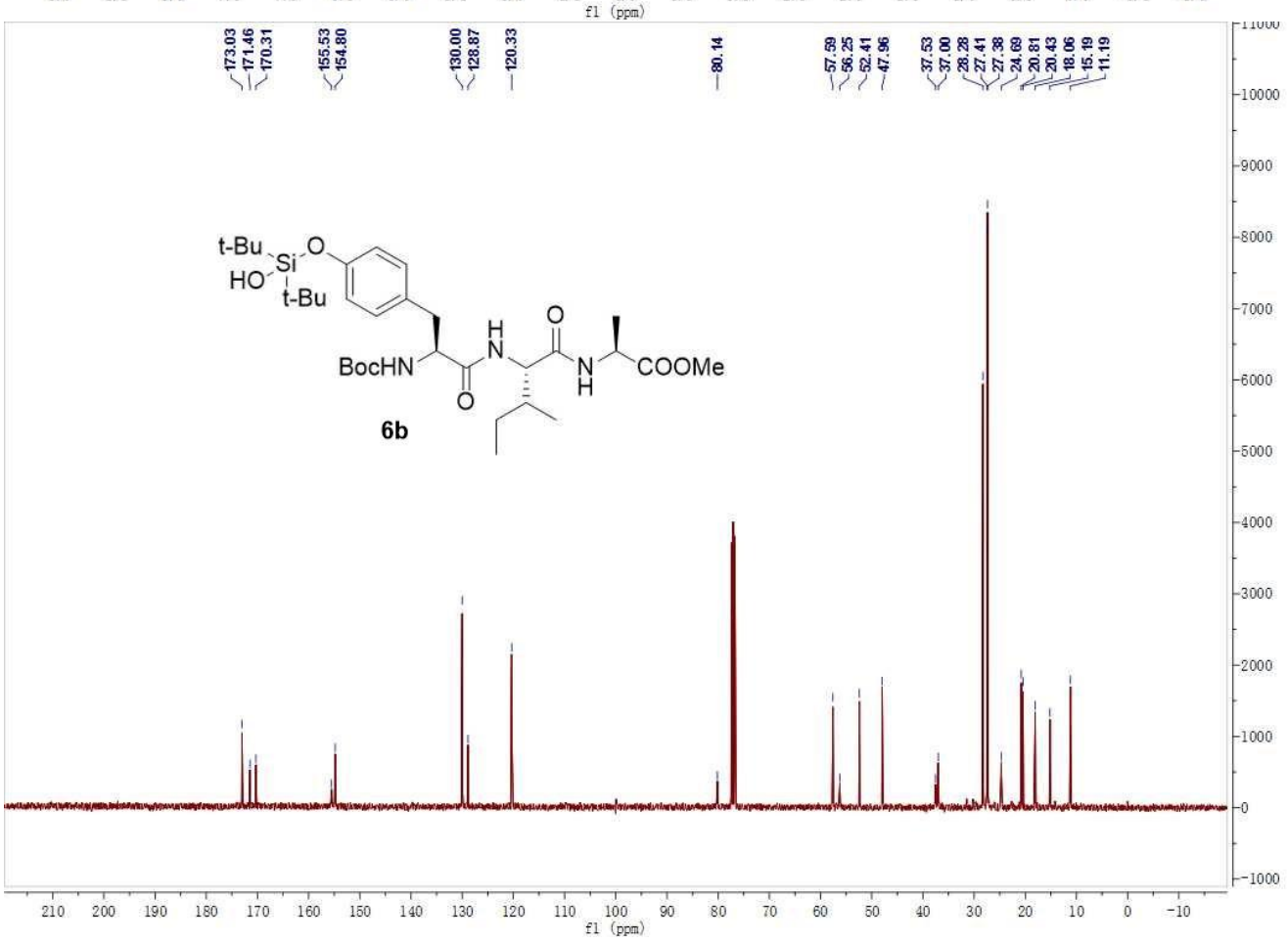
4.519
4.319
4.299
4.280
4.093
4.033
3.728
2.994
2.977
2.962
2.939
2.920
1.785
1.473
1.464
1.408
1.395
1.388
1.081
1.061
0.872
0.856
0.845
0.826
t-Bu
Si
O
HO
t-Bu
BocHN
H
N
O
N
H
COOMe
6b
2.16
2.14
0.94
1.00
1.00
1.08
2.01
1.08
3.09
2.17
0.93
1.98
9.12
3.03
9.38
6.17
f1 (ppm)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120.33
80.14
57.59
56.25
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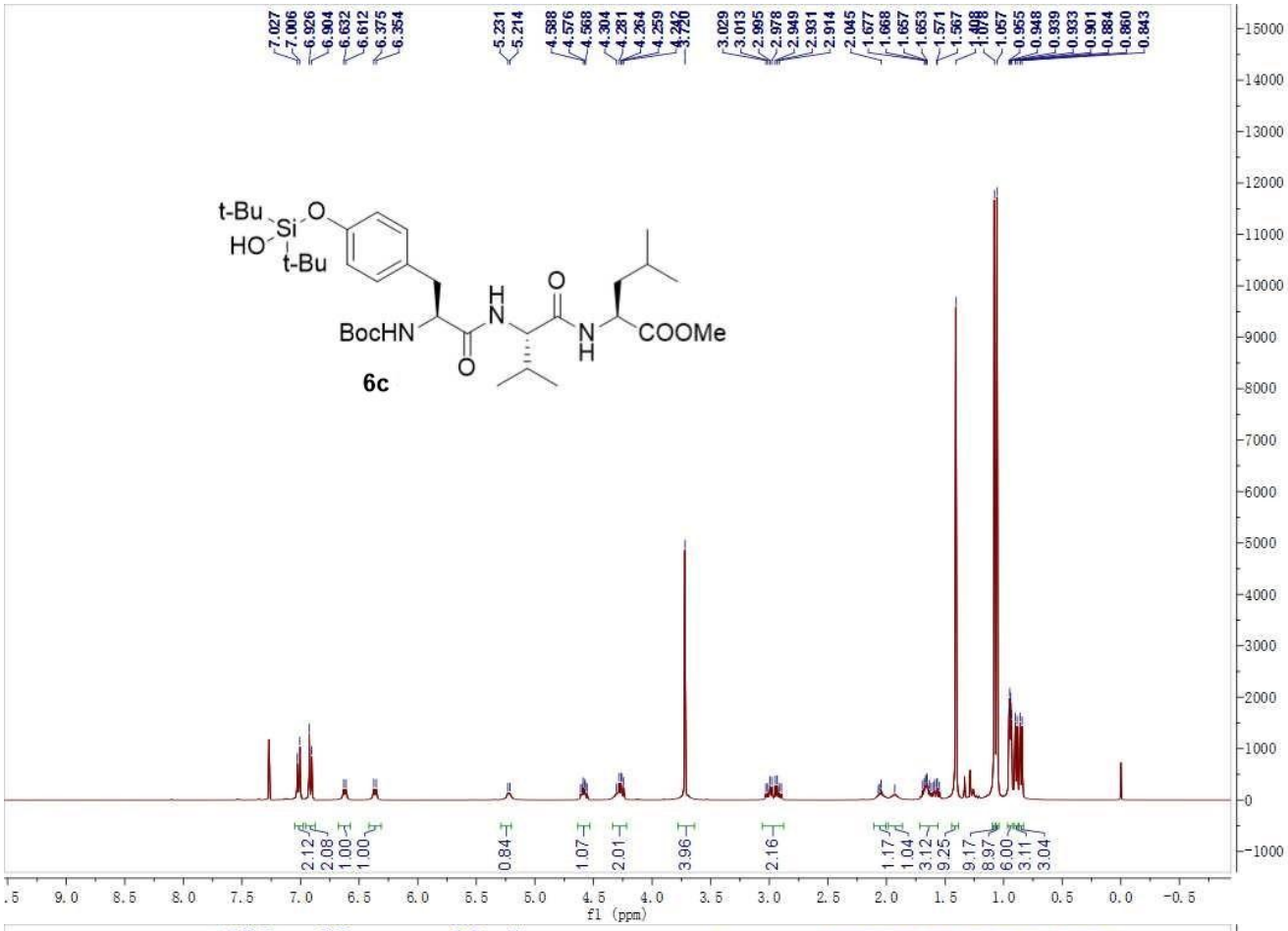
47.96
37.53
37.00
28.28
27.41
27.38
24.69
20.81
20.43
18.06
15.19
11.19
t-Bu
Si
O
HO
t-Bu
BocHN
H
N
O
N
H
COOMe
6b
f1 (ppm)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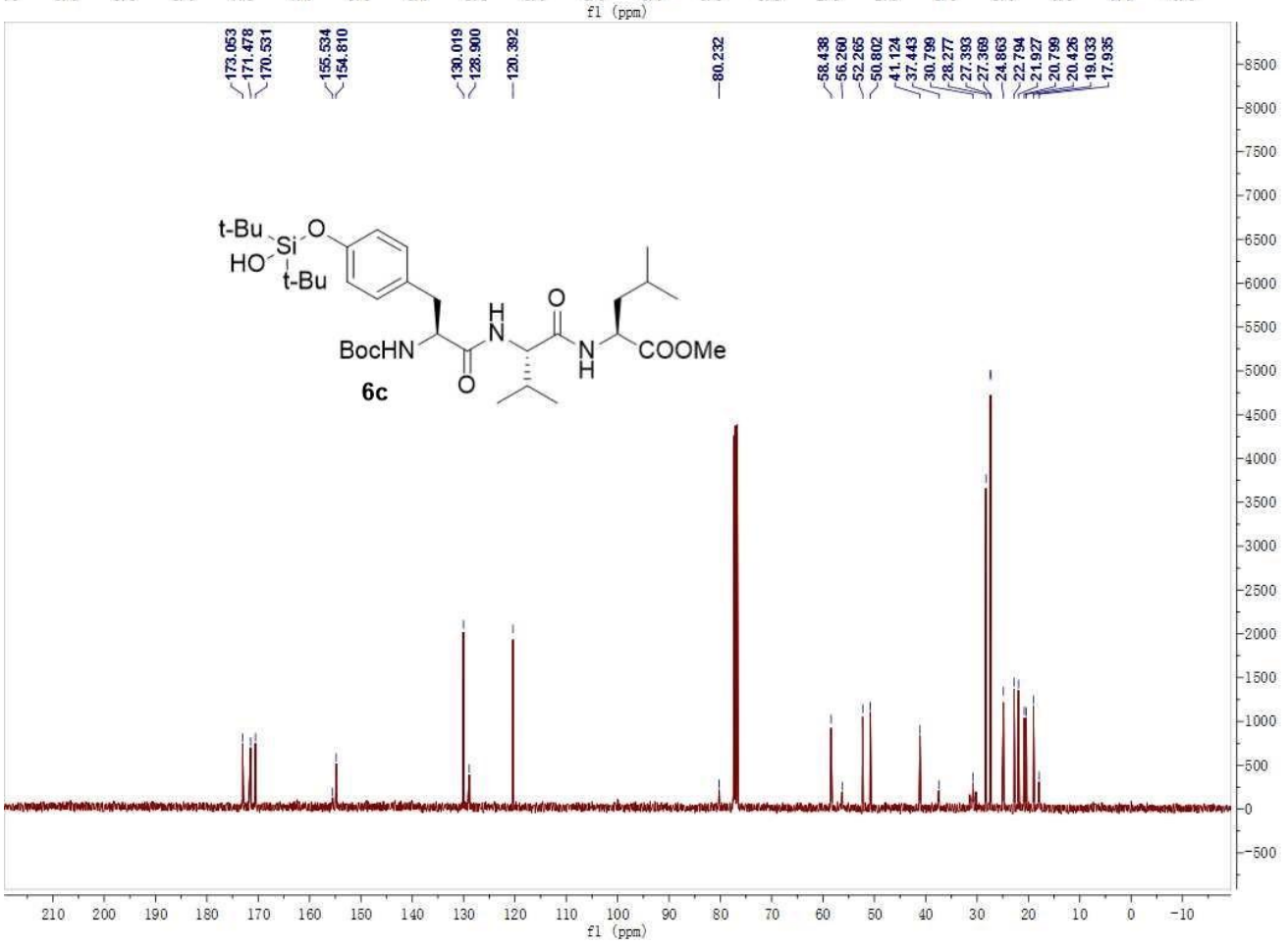
4.576
4.568
4.304
4.281
4.264
4.259
4.242
3.720
3.029
3.013
2.995
2.978
2.949
2.931
2.914
2.045
1.677
1.668
1.657
1.653
1.571
1.567
1.057
0.955
0.948
0.939
0.933
0.901
0.884
0.860
0.843
t-Bu
Si
O
HO
t-Bu
BocHN
H
N
O
O
H
N
COOMe
6c
2.12
2.08
1.00
1.00
0.84
1.07
2.01
3.96
2.16
1.17
1.04
3.12
9.25
9.17
8.97
6.00
3.11
3.04
f1 (ppm)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120.392
80.232
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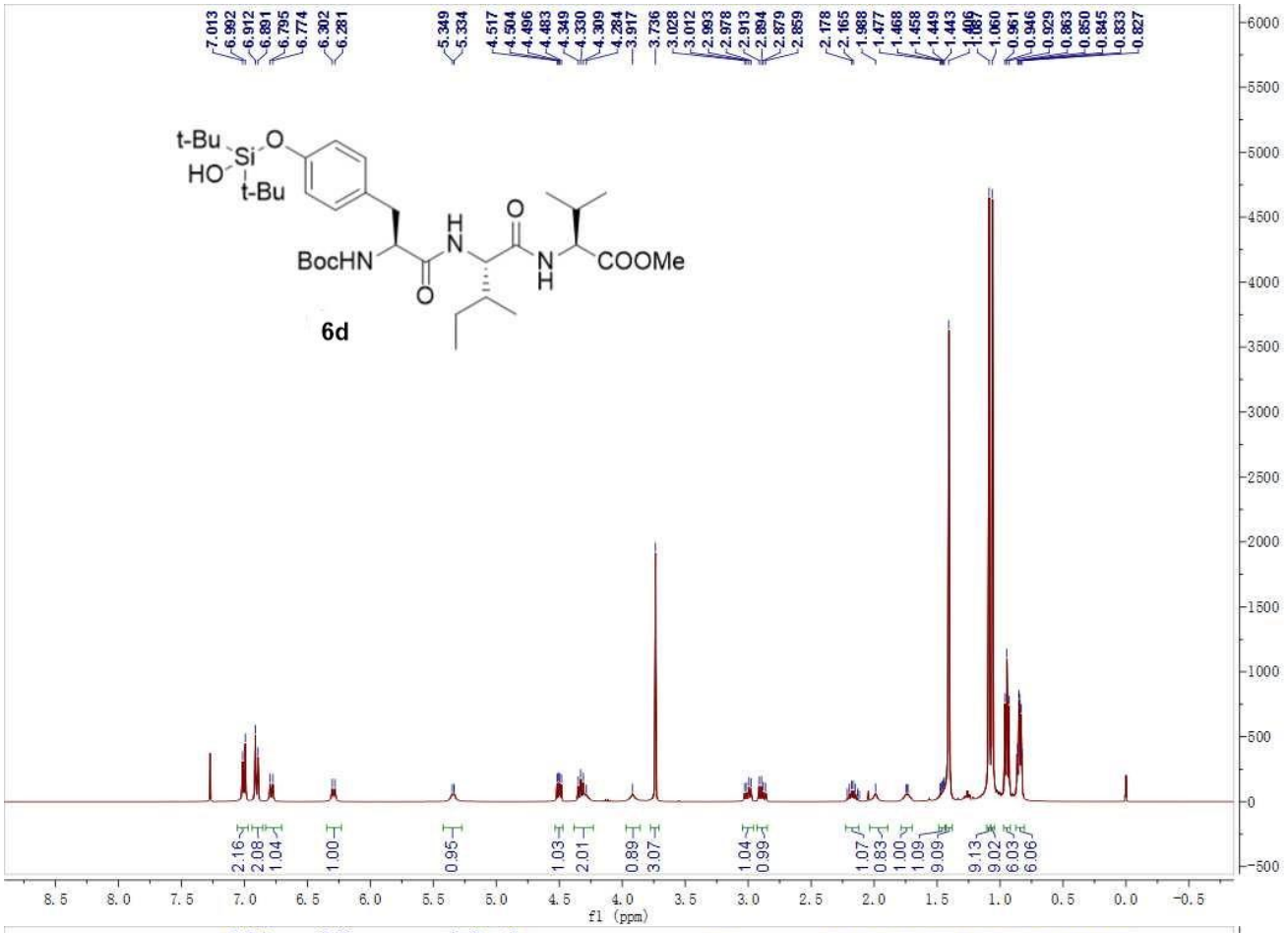
56.260
52.265
50.802
41.124
37.443
30.799
28.277
27.393
27.369
24.863
22.794
21.927
20.799
20.426
19.033
17.935
t-Bu
Si
O
HO
t-Bu
BocHN
H
N
O
O
H
N
COOMe
6c
f1 (ppm)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6.302
6.281
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5.334
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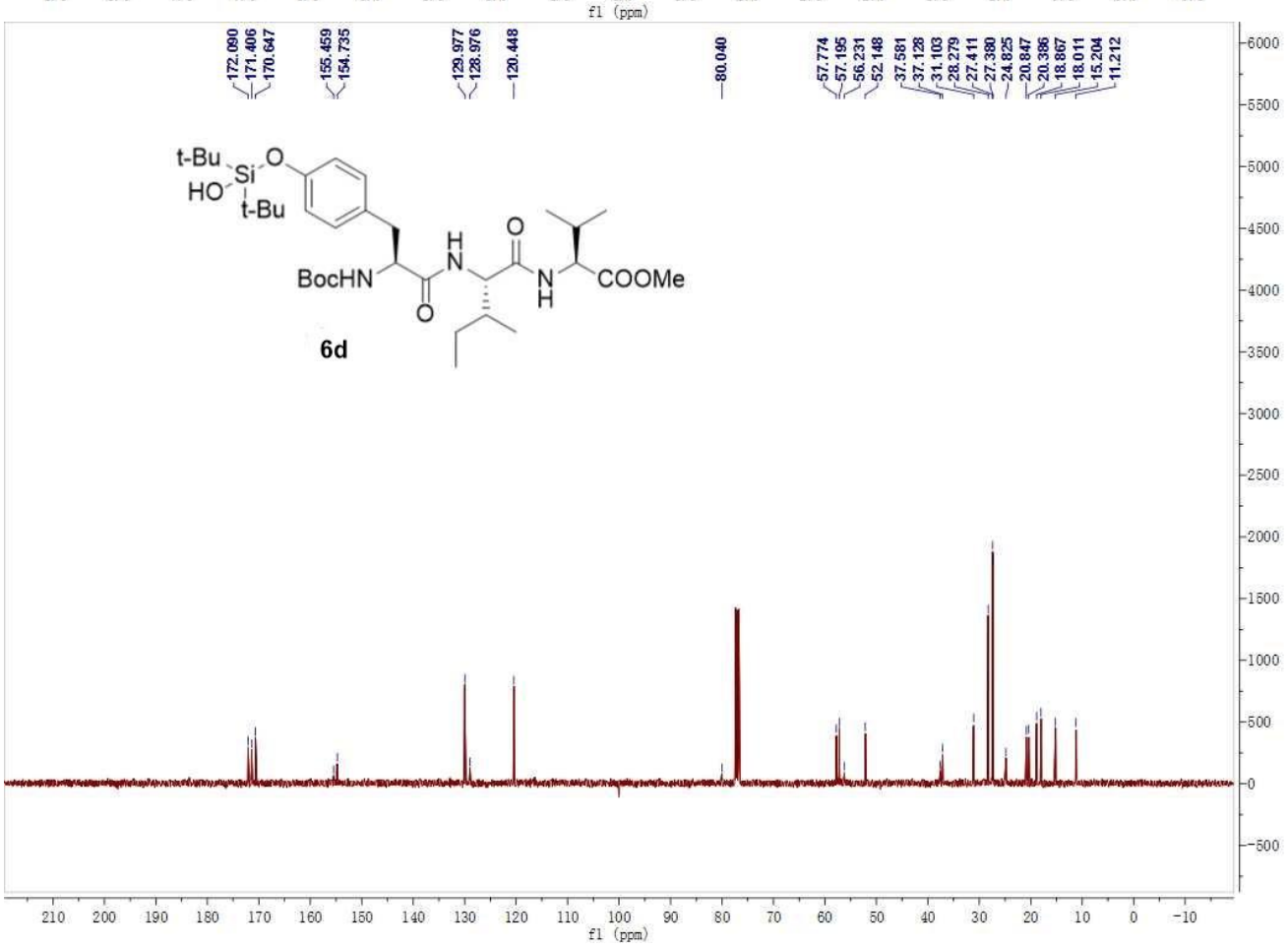
4.504
4.496
4.483
4.349
4.330
4.309
4.284
3.917
3.736
3.028
3.012
2.993
2.978
2.913
2.894
2.879
2.859
2.178
2.165
1.988
1.477
1.468
1.458
1.449
1.443
1.060
0.961
0.946
0.929
0.863
0.850
0.845
0.833
0.827
t-Bu
Si
O
HO
t-Bu
BocHN
H
N
O
O
H
N
COOMe
6d
2.16
2.08
1.04
1.00
0.95
1.03
2.01
0.89
3.07
1.04
0.99
1.07
0.83
1.00
1.09
9.09
9.13
9.02
6.03
6.06
f1 (ppm)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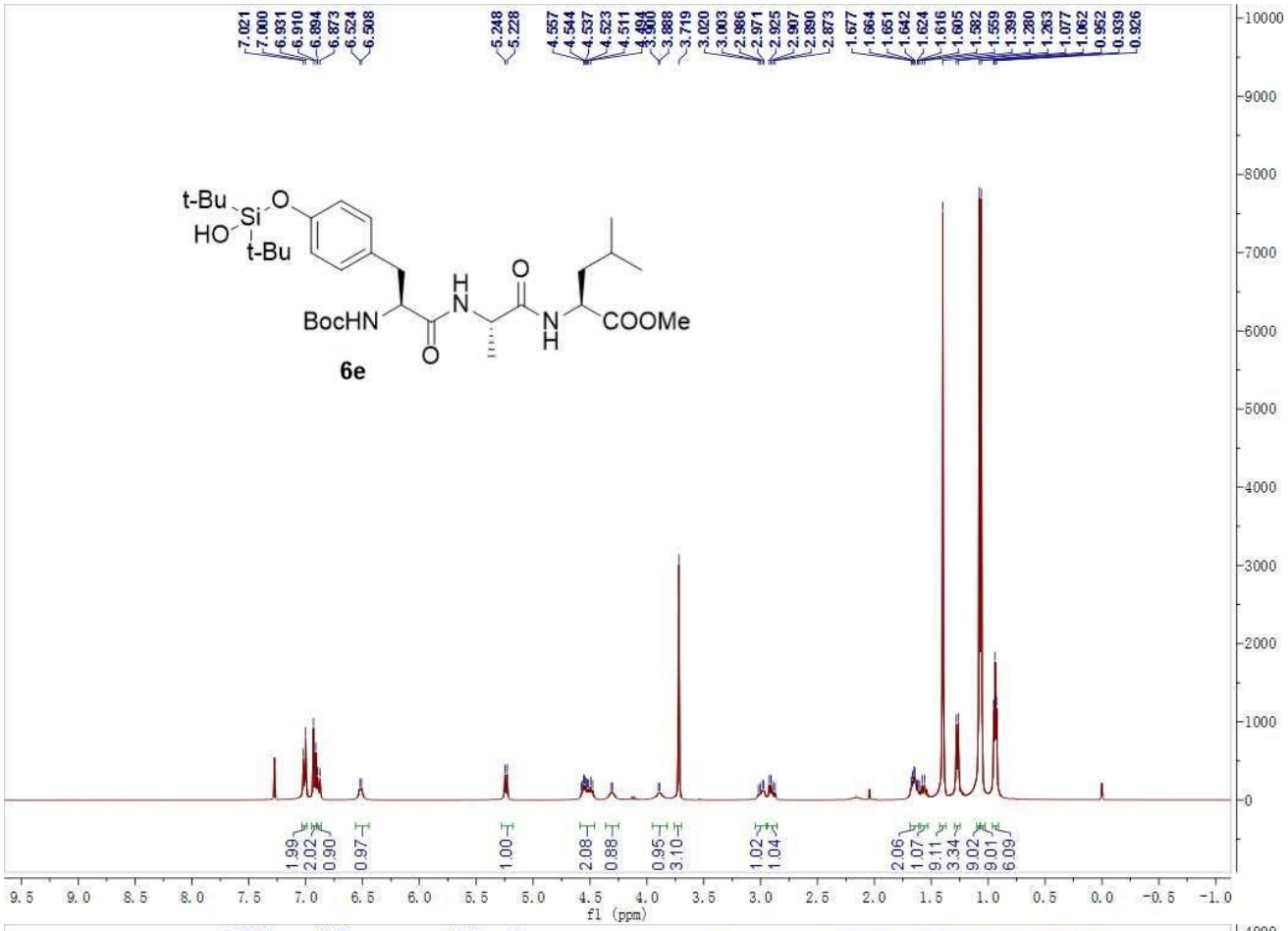
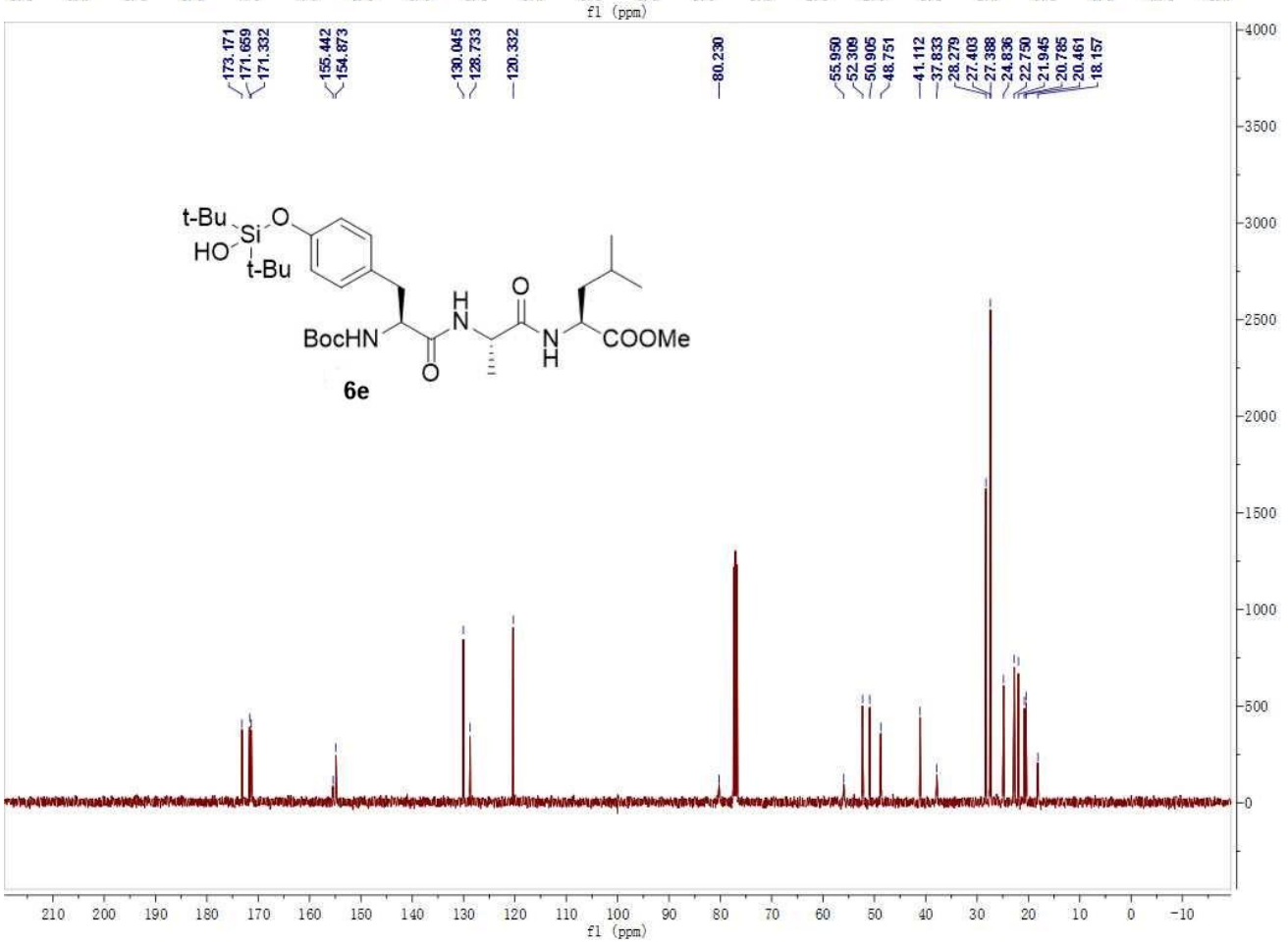
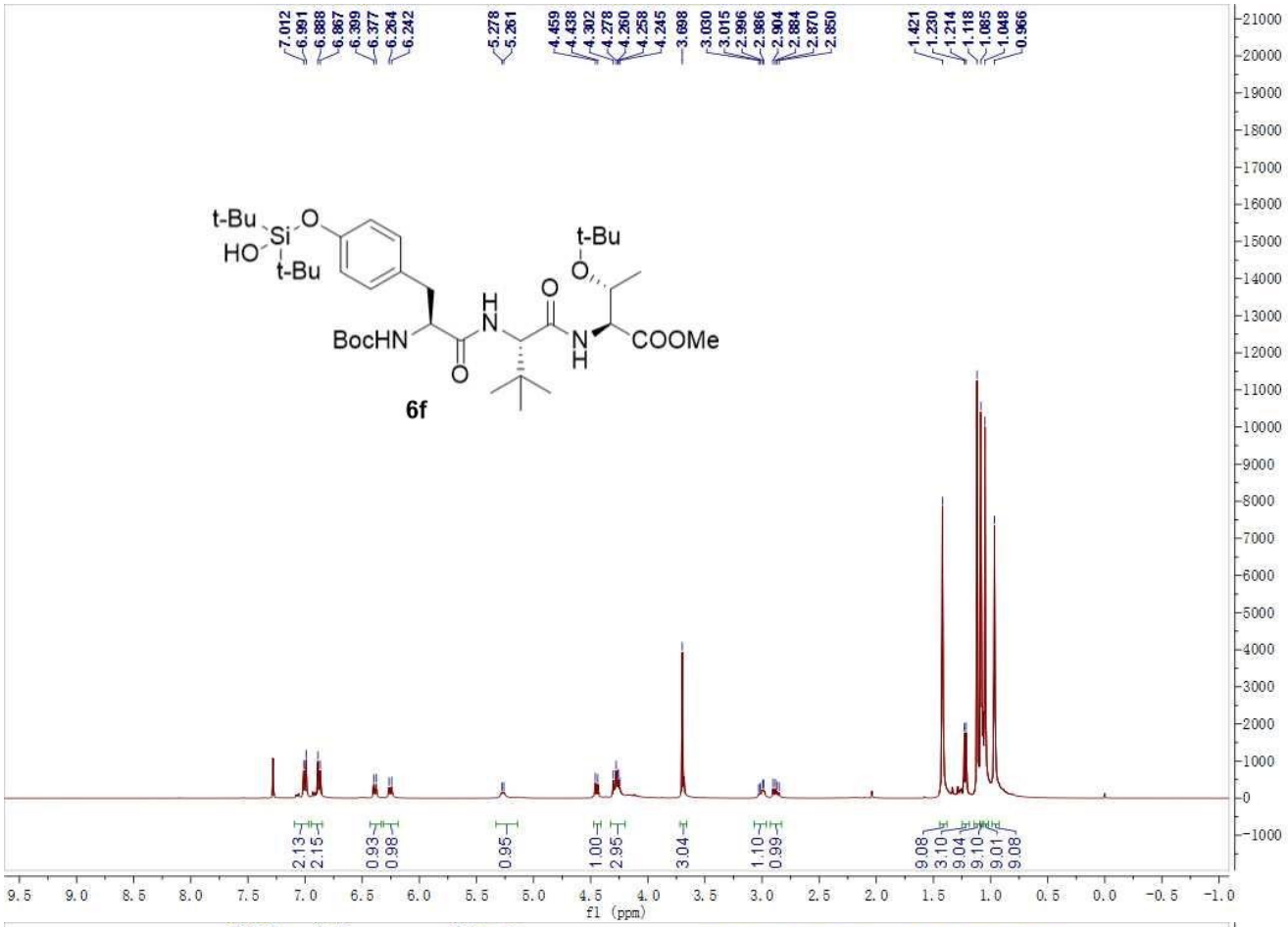
56.231
52.148
37.581
37.128
31.103
28.279
27.411
27.380
24.825
20.847
20.386
18.867
18.011
15.204
11.212
t-Bu
Si
O
HO
t-Bu
BocHN
H
N
O
O
H
N
COOMe
6d
f1 (ppm)


t-Bu
Si
O
HO
t-Bu
BocHN
H
N
O
N
H
COOMe
O
6e
f1 (ppm)


t-Bu
Si
O
HO
t-Bu
BocHN
H
N
O
N
H
COOMe
O
6e
f1 (ppm)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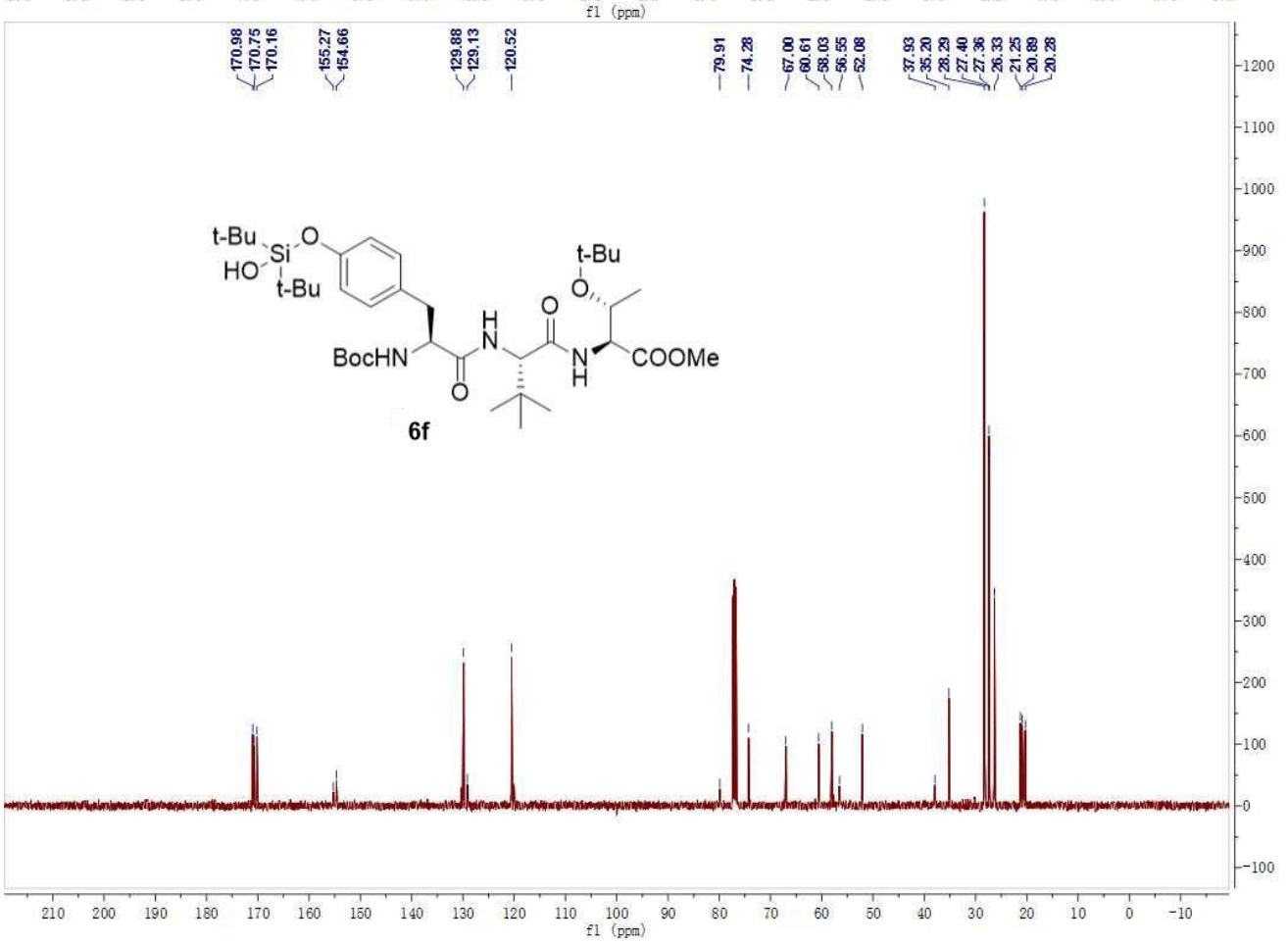
4.438
4.302
4.278
4.260
4.258
4.245
3.698
3.030
3.015
2.996
2.986
2.904
2.884
2.870
2.850
1.421
1.230
1.214
1.118
1.085
1.048
0.966
t-Bu
HO
Si
O
t-Bu
BocHN
H
N
O
O
t-Bu
O
H
N
COOMe
6f
2.13
2.15
0.93
0.98
0.95
1.00
2.95
3.04
1.10
0.99
9.08
3.10
9.04
9.10
9.01
9.08
f1 (ppm)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120.52
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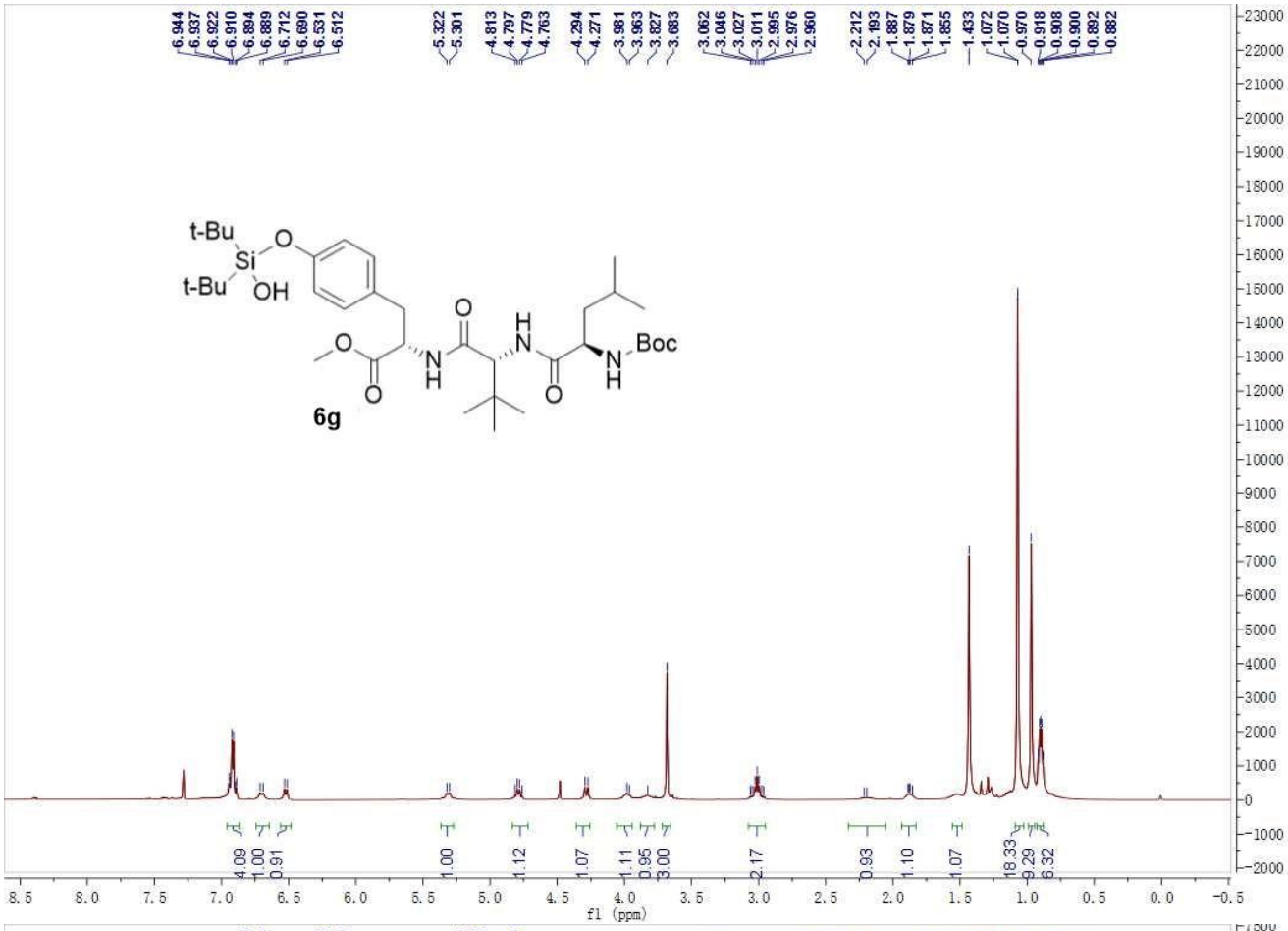
74.28
67.00
60.61
58.03
56.55
52.08
37.93
35.20
28.29
27.40
27.36
26.33
21.25
20.89
20.28
t-Bu
HO
Si
O
t-Bu
BocHN
H
N
O
O
t-Bu
O
H
N
COOMe
6f
f1 (ppm)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6.712
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6.512
5.322
5.301
4.813
4.797
4.779
4.763
4.294
4.271
3.981
3.963
3.827
3.683
3.062
3.046
3.027
3.011
2.995
2.976
2.960
2.212
2.193
1.887
1.879
1.871
1.855
1.433
1.072
1.070
0.970
0.918
0.908
0.900
0.892
0.882
t-Bu
Si
O
t-Bu
OH
O
O
N
H
O
N
H
O
N
H
Boc
6g
4.09
1.00
0.91
1.00
1.12
1.07
1.11
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3.00
2.17
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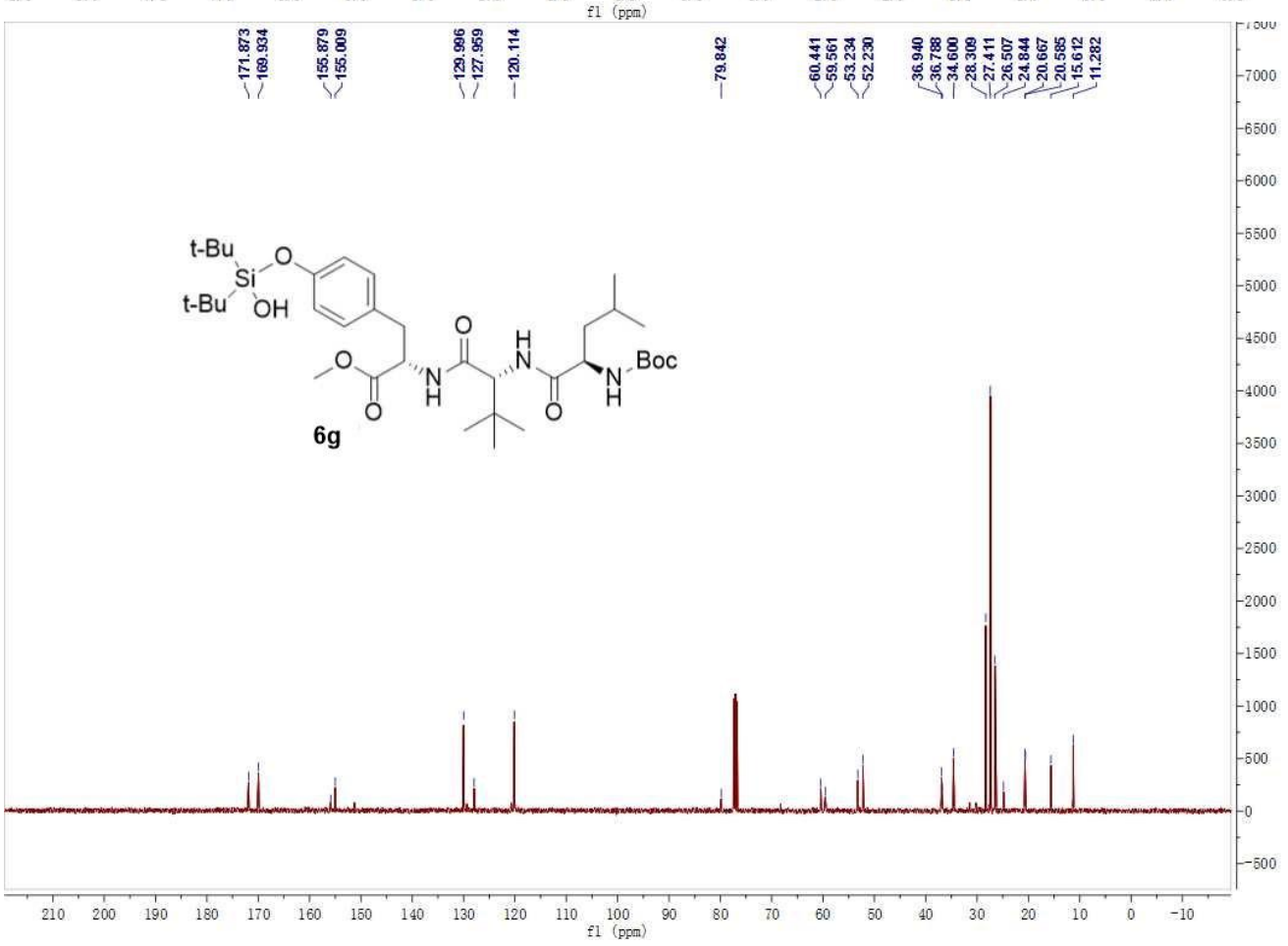
1.10
1.07
18.33
9.29
6.32
f1 (ppm)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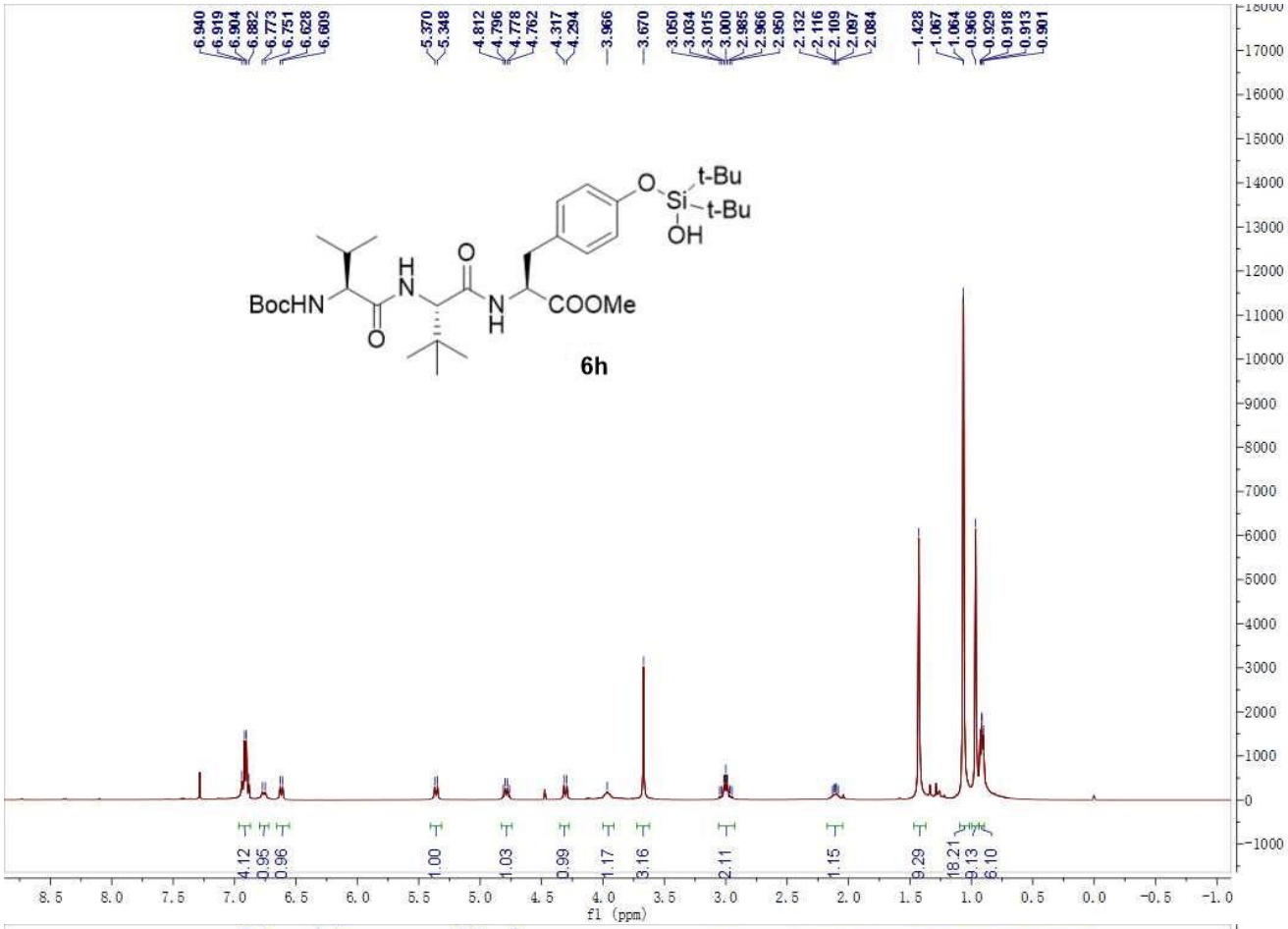
52.230
36.940
36.788
34.600
28.309
27.411
26.507
24.844
20.667
20.585
15.612
11.282
t-Bu
Si
O
t-Bu
OH
O
O
N
H
O
N
H
O
N
H
Boc
6g
f1 (ppm)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4.796
4.778
4.762
4.317
4.294
3.966
3.670
3.050
3.034
3.015
3.000
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2.966
2.950
2.132
2.116
2.109
2.097
2.084
1.428
1.067
1.064
0.966
0.929
0.918
0.913
0.901
t-Bu
t-Bu
Si
O
OH
BocHN
H
N
O
N
H
O
COOMe
6h
4.12
0.95
0.96
1.00
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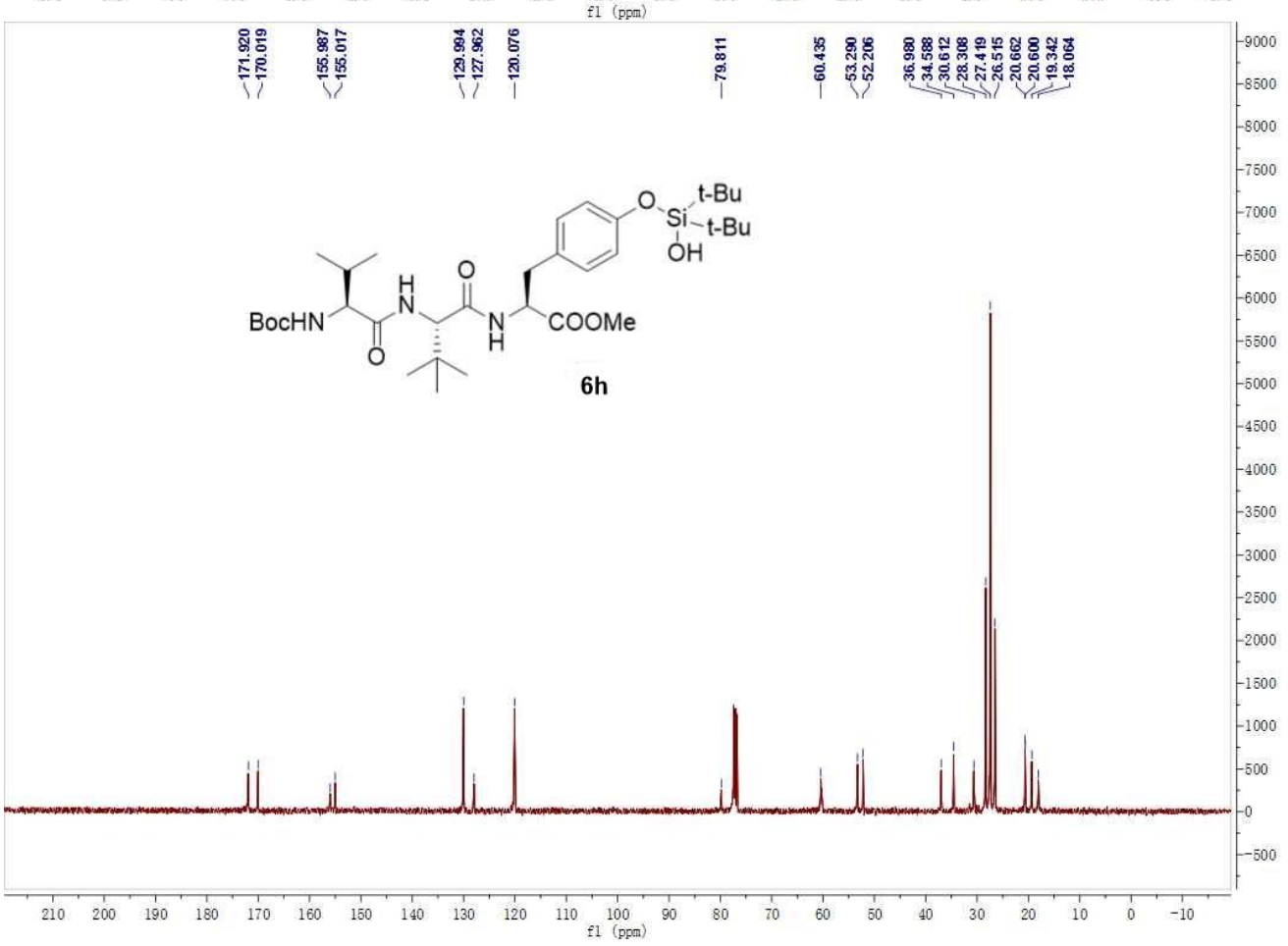
0.99
1.17
3.16
2.11
1.15
9.29
18.21
9.13
6.10
f1 (ppm)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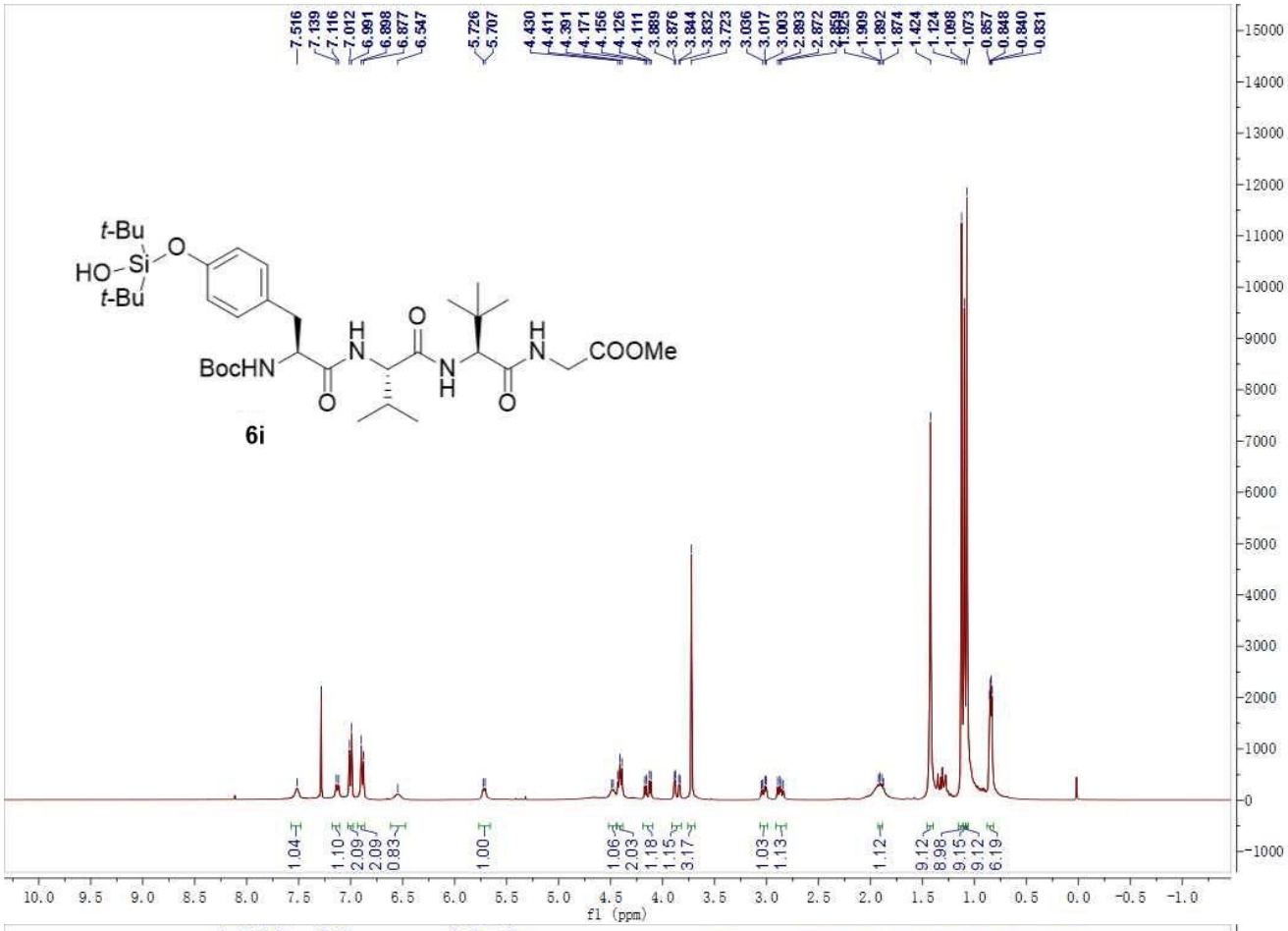
30.612
28.308
27.419
26.515
20.662
20.600
19.342
18.064
t-Bu
t-Bu
Si
O
OH
BocHN
H
N
O
N
H
O
COOMe
6h
f1 (ppm)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4.391
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4.156
4.126
4.111
3.889
3.876
3.844
3.832
3.723
3.036
3.017
3.003
2.893
2.872
1.909
1.892
1.874
1.424
1.124
1.098
1.073
0.857
0.848
0.840
0.831
t-Bu
HO
Si
t-Bu
O
BocHN
H
N
O
O
H
N
O
O
H
N
COOMe
6i
1.04
1.10
2.09
2.09
0.83
1.00
1.06
2.03
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1.03
1.13
1.12
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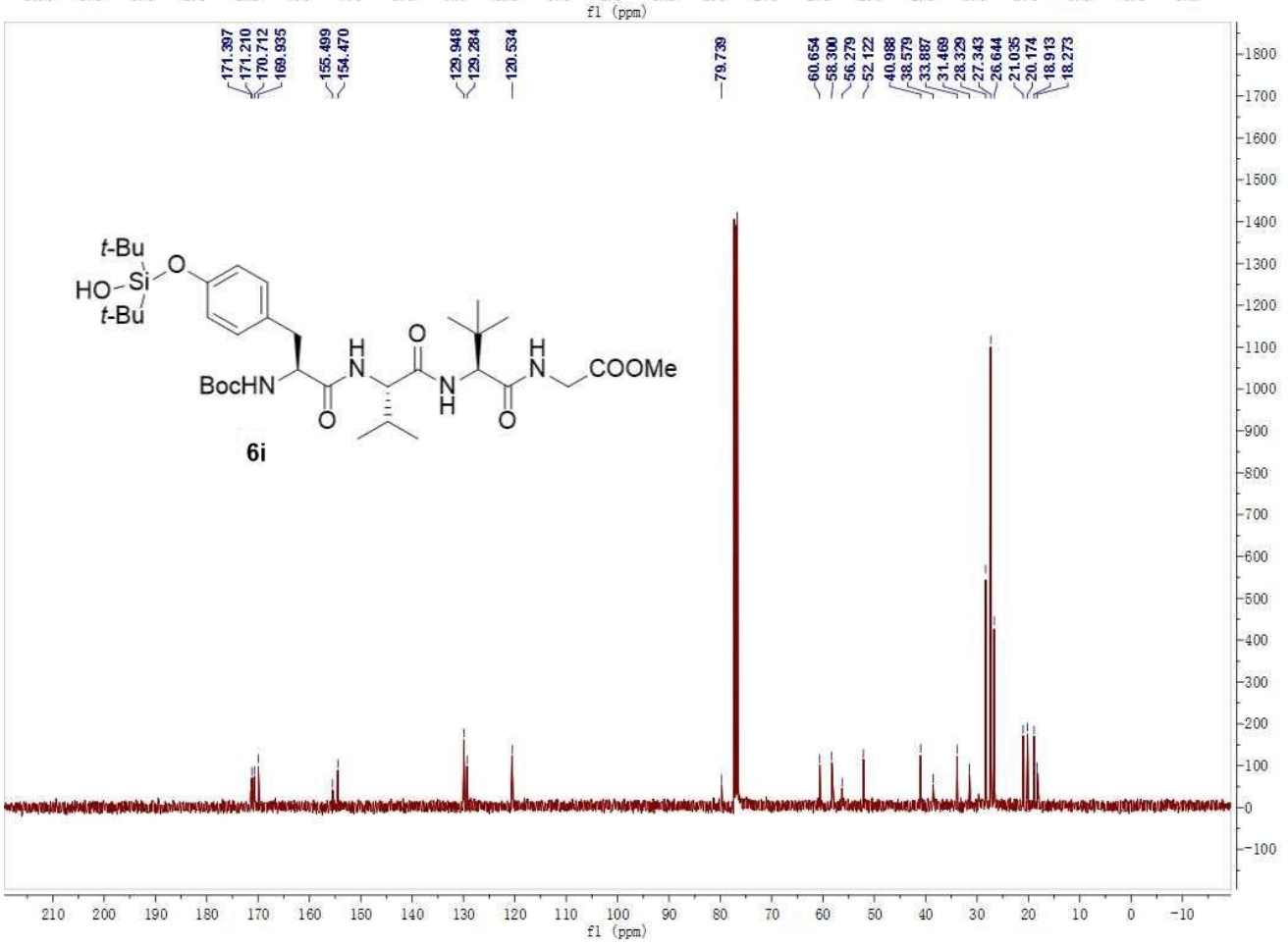
9.15
9.12
6.19
f1 (ppm)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40.988
38.579
33.887
31.469
28.329
27.343
26.644
21.035
20.174
18.913
18.273
t-Bu
HO
Si
t-Bu
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BocHN
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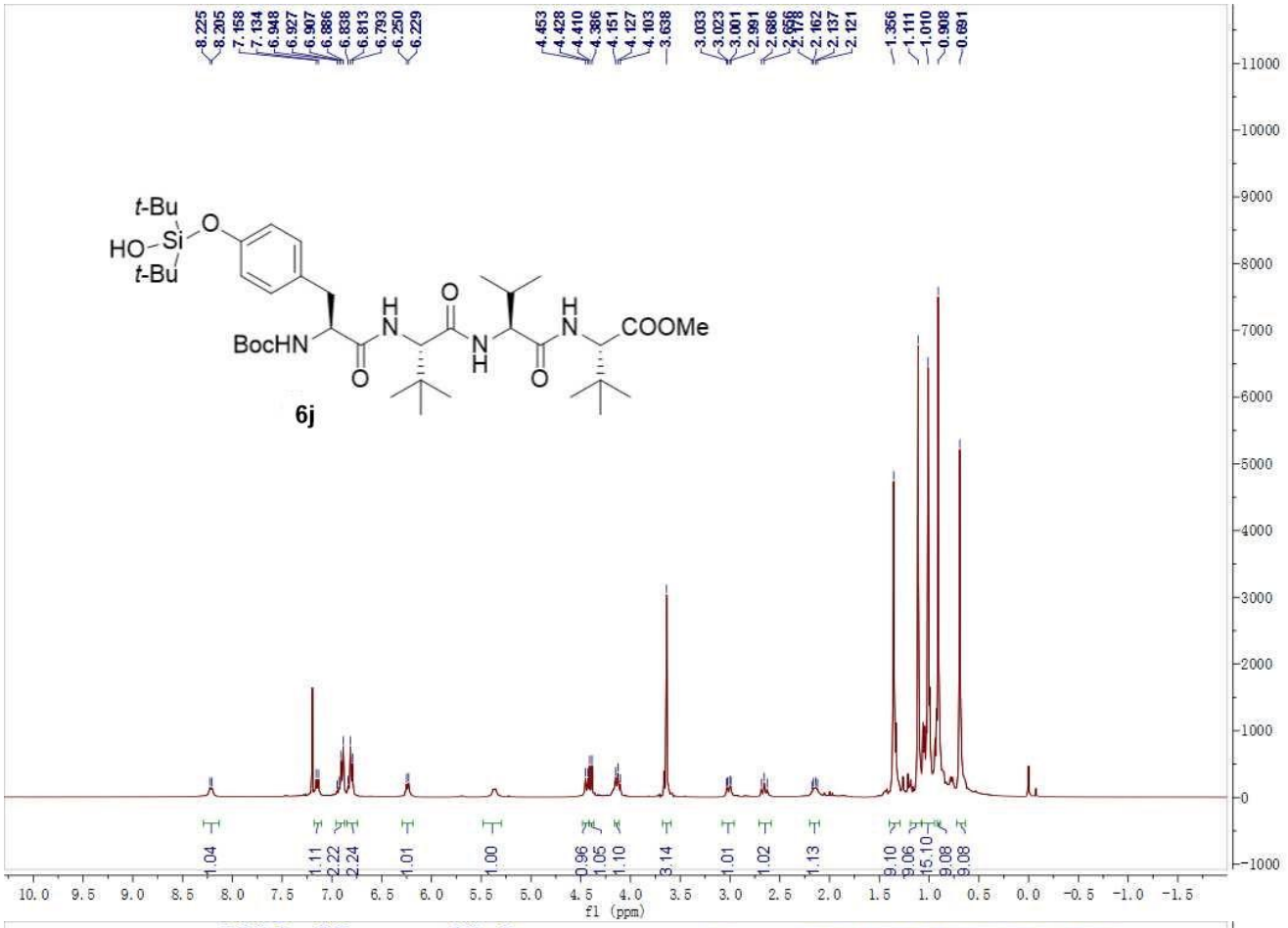
N
O
O
H
N
O
O
H
N
COOMe
6i
f1 (ppm)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6.793
6.250
6.229
4.453
4.428
4.410
4.386
4.151
4.127
4.103
3.638
3.033
3.023
3.001
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2.686
2.162
2.137
2.121
1.356
1.111
1.010
0.908
0.691
t-Bu
HO
Si
O
t-Bu
BocHN
H
N
O
N
H
O
H
N
COOMe
6j
1.04
1.11
2.22
2.24
1.01
1.00
0.96
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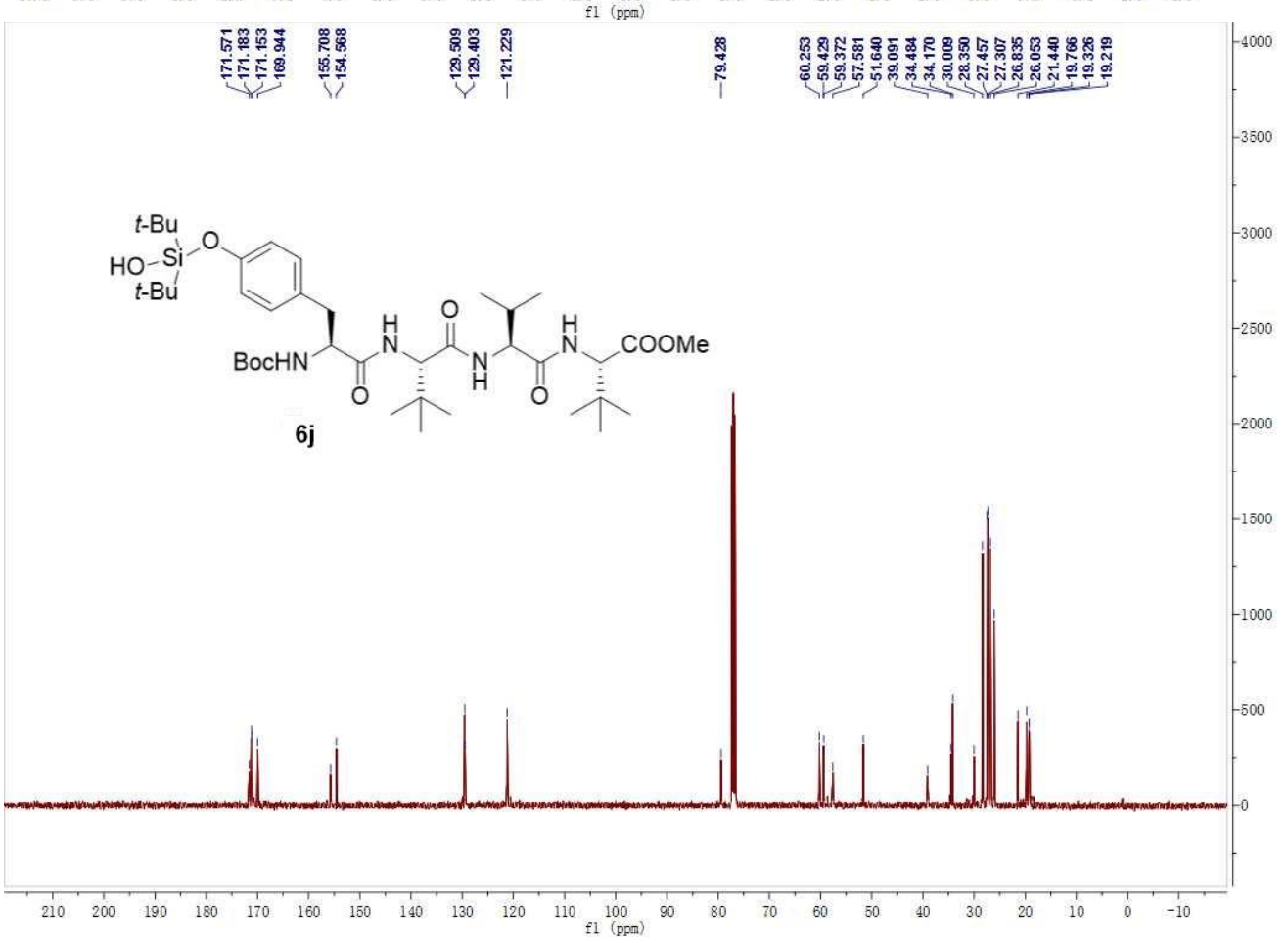
1.01
1.02
1.13
9.10
9.06
15.10
9.08
9.08
f1 (ppm)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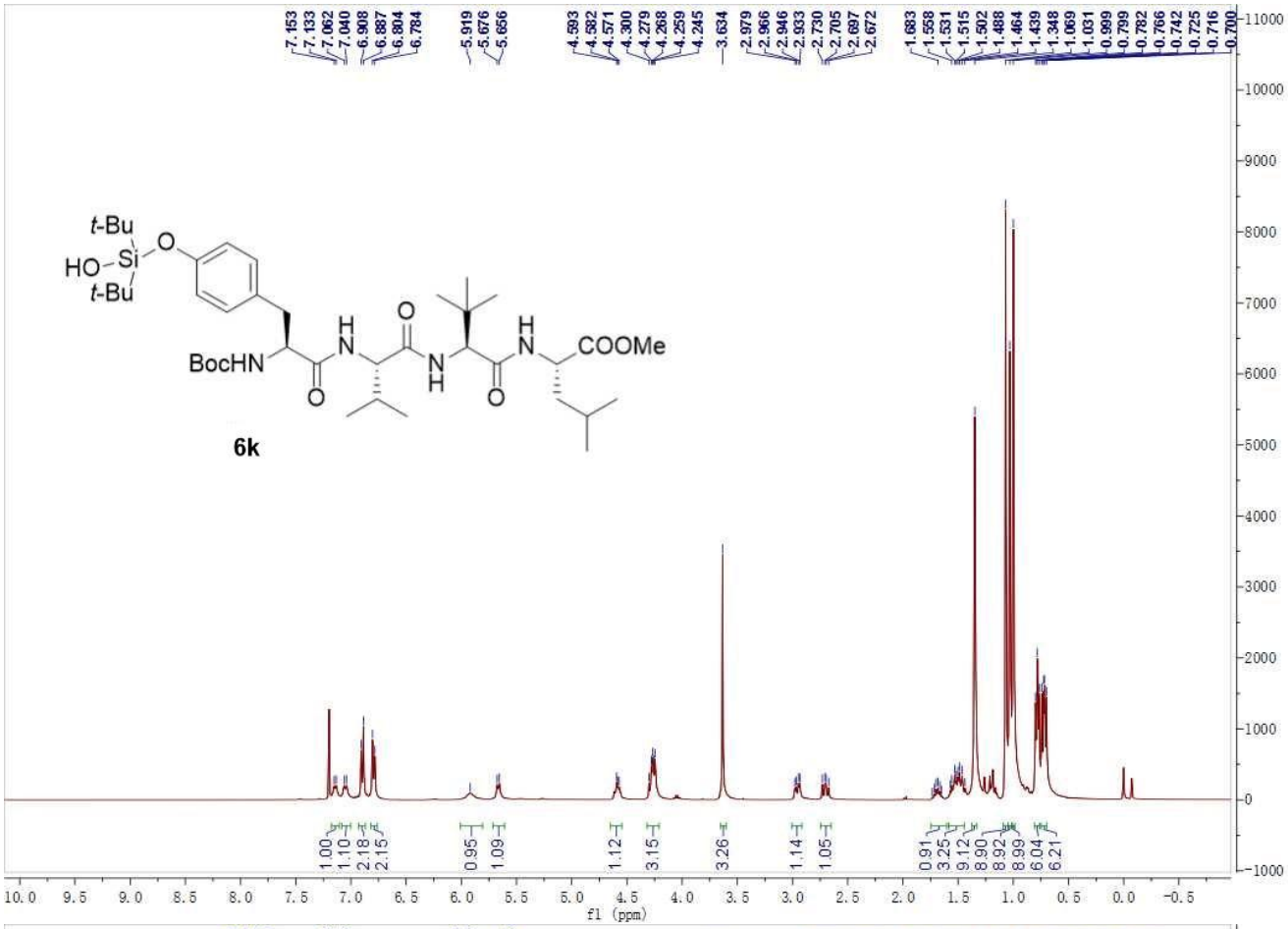
51.640
39.091
34.484
34.170
30.009
28.350
27.457
27.307
26.835
26.053
21.440
19.766
19.326
19.219
t-Bu
HO
Si
O
t-Bu
BocHN
H
N
O
N
H
O
H
N
COOMe
6j
f1 (ppm)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4.582
4.571
4.300
4.279
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4.259
4.245
3.634
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2.966
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2.933
2.730
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1.531
1.515
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1.488
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1.439
1.348
1.069
1.031
0.999
0.799
0.782
0.766
0.742
0.725
0.716
0.700
t-Bu
HO
Si
t-Bu
O
BocHN
N
H
O
N
H
O
N
H
COOMe
6k
1.00
1.10
2.18
2.15
0.95
1.09
1.12
3.15
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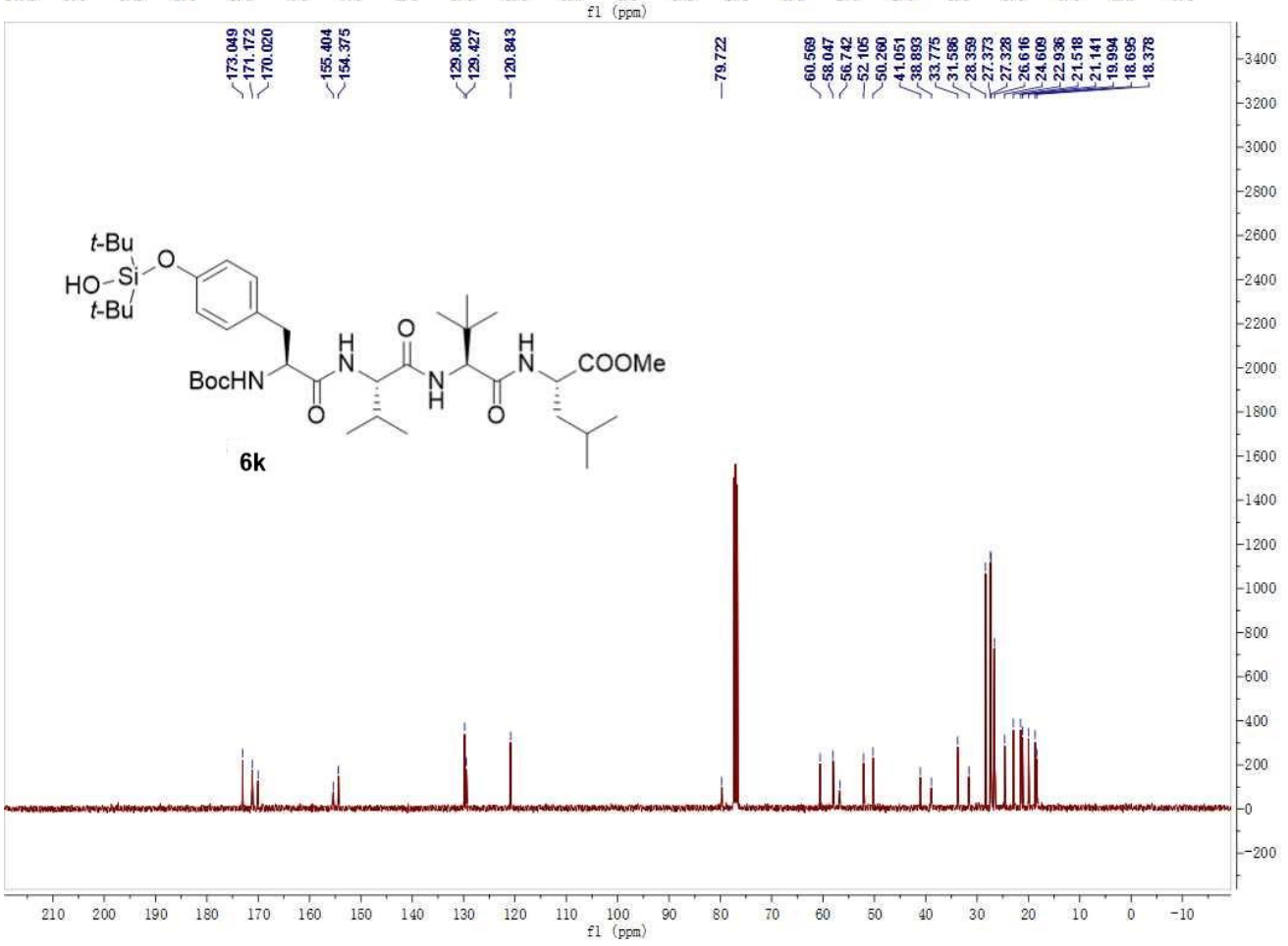
8.99
6.04
6.21
f1 (ppm)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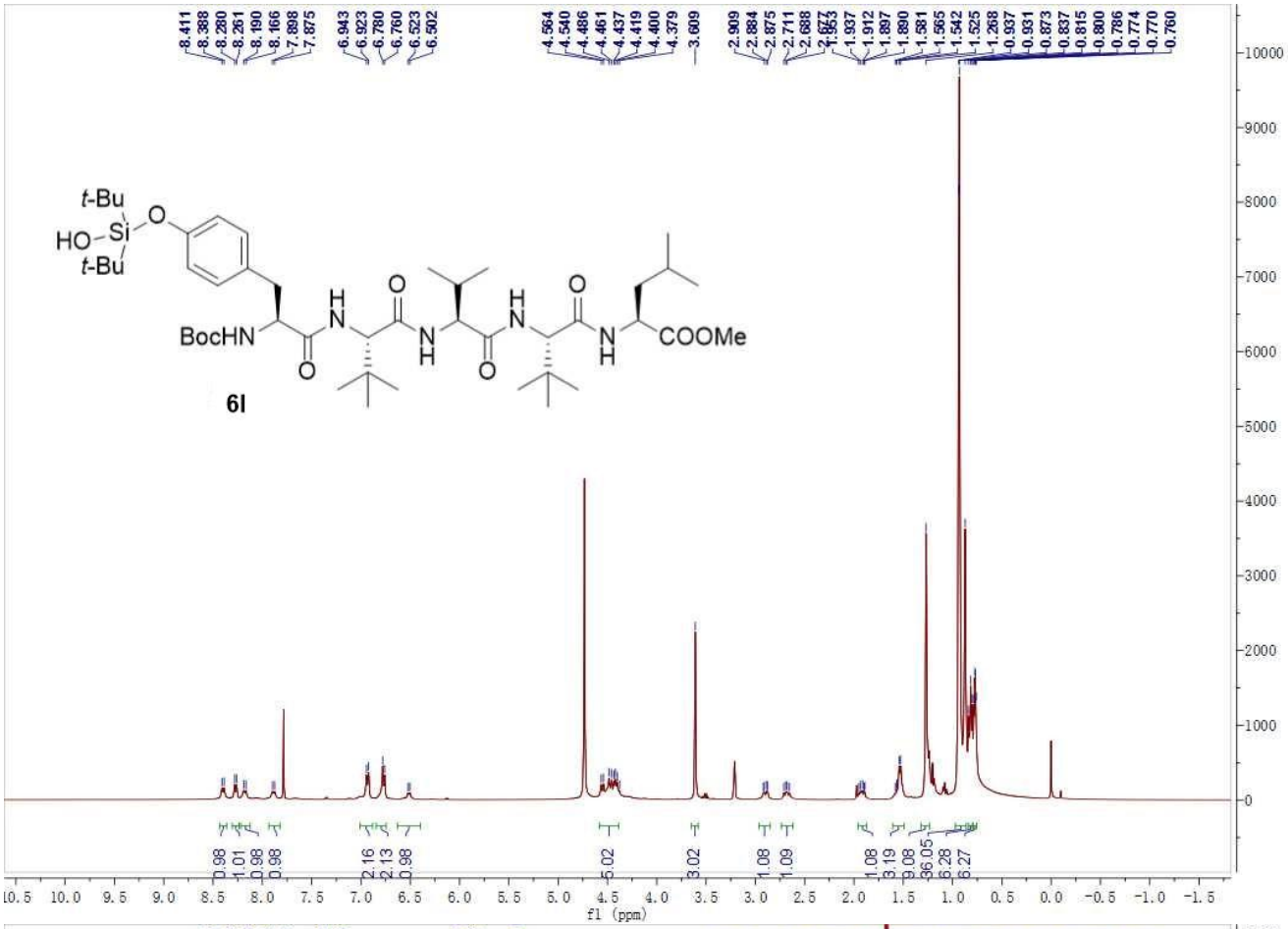
170.020
155.404
154.375
129.806
129.427
120.843
79.722
60.569
58.047
56.742
52.105
50.260
41.051
38.893
33.775
31.586
28.359
27.373
27.328
26.616
24.609
22.936
21.518
21.141
19.994
18.695
18.378
t-Bu
HO
Si
t-Bu
O
BocHN
N
H
O
N
H
O
N
H
COOMe
6k
f1 (ppm)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8.166
7.898
7.875
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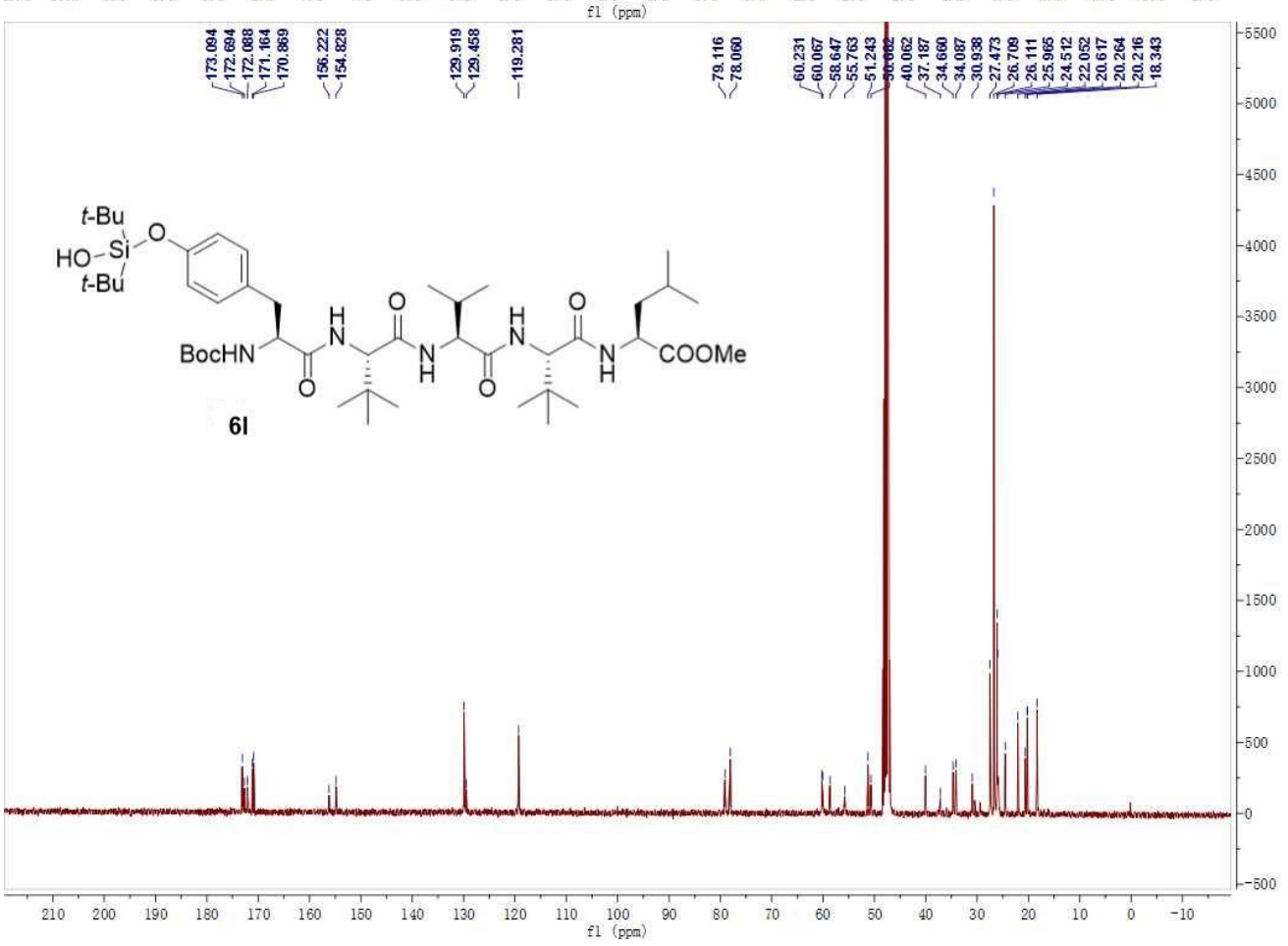
6.923
6.780
6.760
6.523
6.502
4.564
4.540
4.486
4.461
4.437
4.419
4.400
4.379
3.609
2.909
2.884
2.875
2.711
2.688
1.953
1.937
1.912
1.897
1.890
1.581
1.565
1.542
1.525
1.268
0.937
0.931
0.873
0.837
0.815
0.800
0.786
0.774
0.770
0.760
t-Bu
HO-Si-O
t-Bu
BocHN
COOMe
6l
f1 (ppm)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129.919
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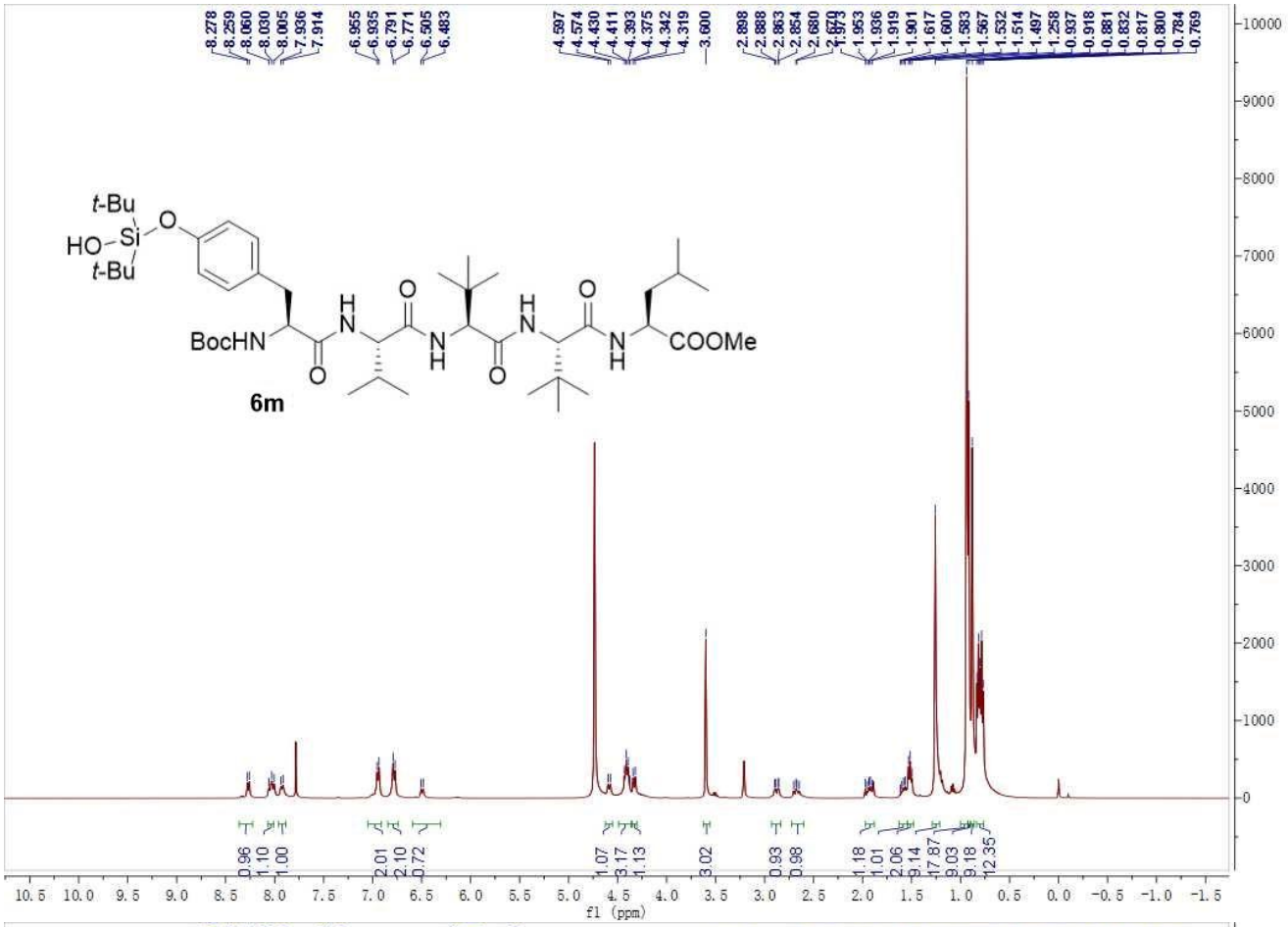
119.281
79.116
78.060
60.231
60.067
58.647
55.763
51.243
40.062
37.187
34.660
34.087
30.938
27.473
26.709
26.111
25.965
24.512
22.052
20.617
20.264
20.216
18.343
t-Bu
HO-Si-O
t-Bu
BocHN
COOMe
6l
f1 (ppm)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8.259
8.060
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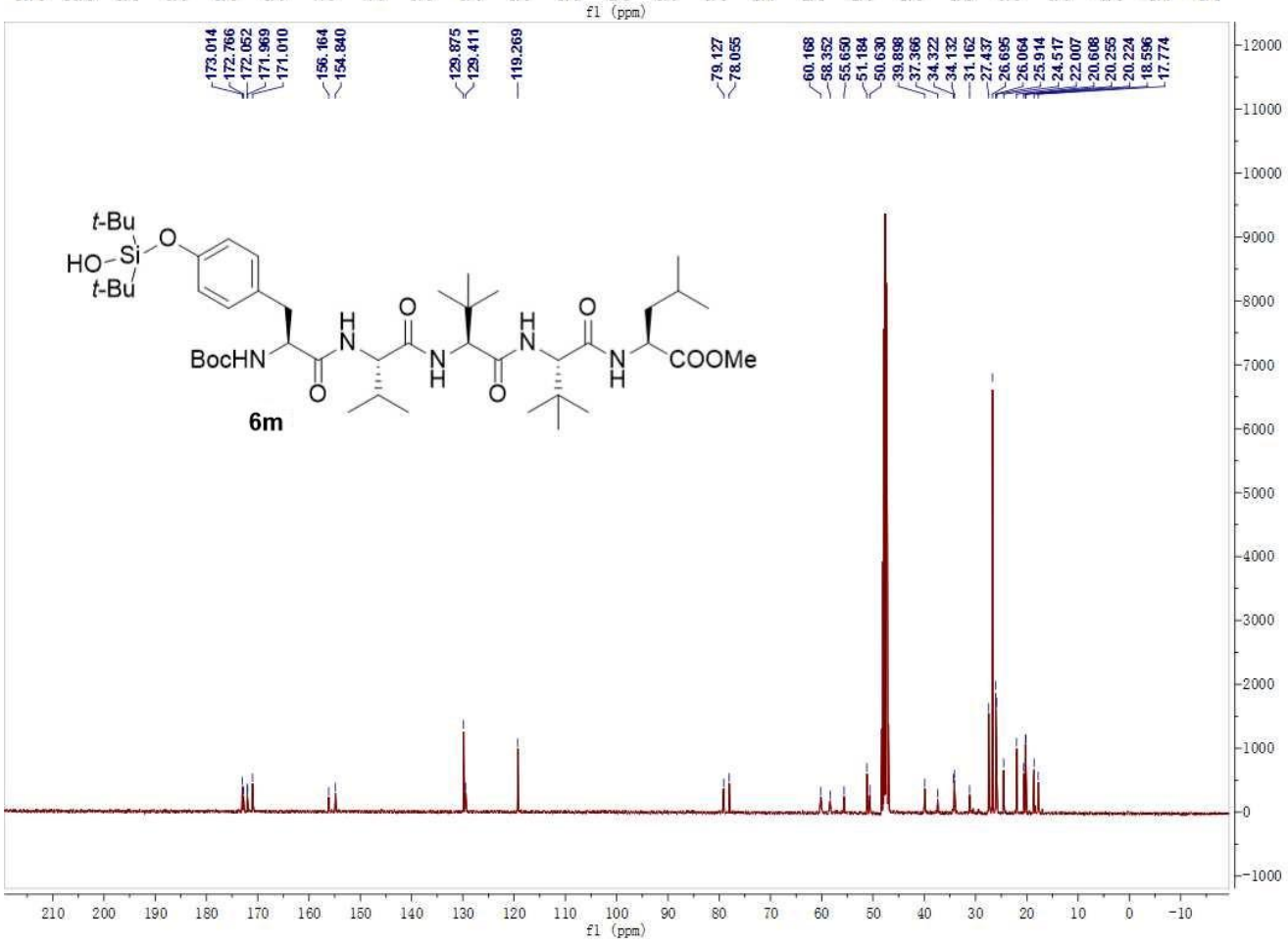
8.005
7.936
7.914
6.955
6.935
6.791
6.771
6.505
6.483
4.597
4.574
4.430
4.411
4.393
4.375
4.342
4.319
3.600
2.898
2.888
2.863
2.854
2.680
1.953
1.936
1.919
1.901
1.617
1.600
1.583
1.567
1.532
1.514
1.497
1.258
0.937
0.918
0.881
0.832
0.817
0.800
0.784
0.769
t-Bu
HO
Si
t-Bu
O
BocHN
H
N
O
COOMe
6m
0.96
1.10
1.00
2.01
2.10
0.72
1.07
3.17
1.13
3.02
0.93
0.98
1.18
1.01
2.06
9.14
17.87
9.03
9.18
12.35
f1 (ppm)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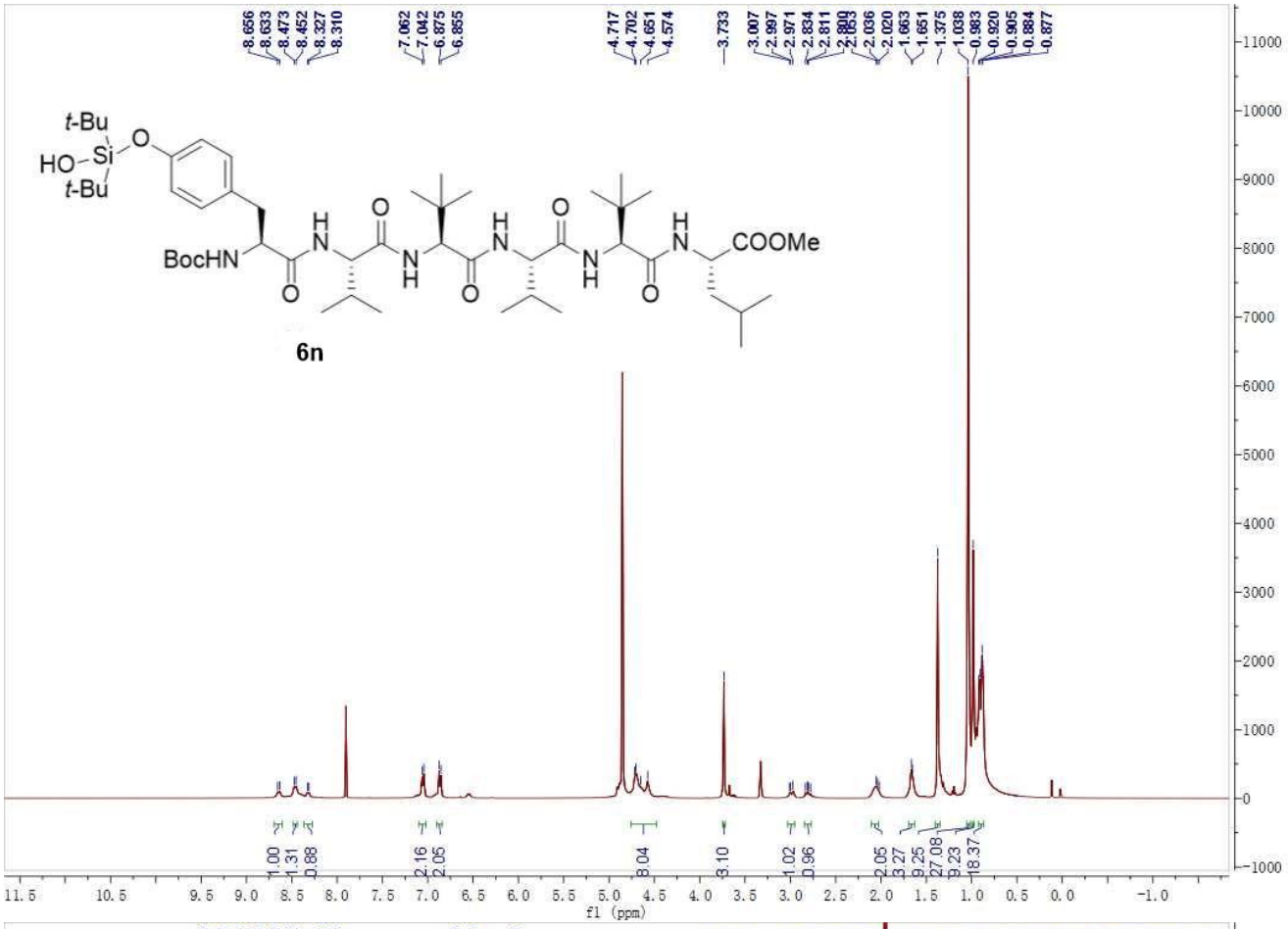
154.840
129.875
129.411
119.269
79.127
78.055
60.168
58.352
55.650
51.184
50.630
39.898
37.366
34.322
34.132
31.162
27.437
26.695
26.064
25.914
24.517
22.007
20.608
20.255
20.224
18.596
17.774
t-Bu
HO
Si
t-Bu
O
BocHN
H
N
O
COOMe
6m
f1 (ppm)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8.452
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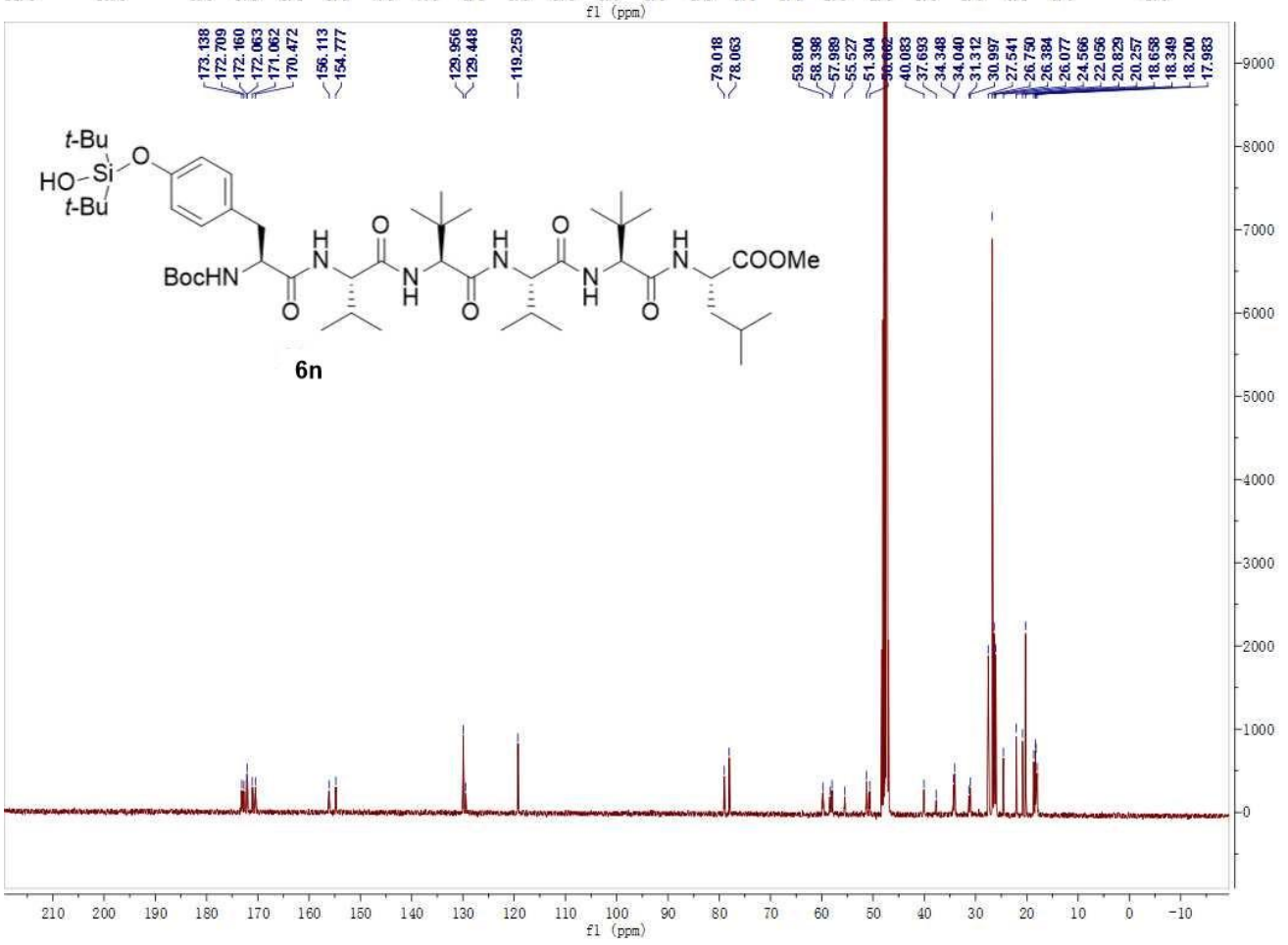
8.310
7.062
7.042
6.875
6.855
4.717
4.702
4.651
4.574
3.733
3.007
2.997
2.971
2.834
2.811
2.800
2.036
2.020
1.663
1.651
1.375
1.038
0.983
0.920
0.905
0.884
0.877
t-Bu
HO
Si
t-Bu
O
BocHN
H
N
O
COOMe
6n
1.00
1.31
0.88
2.16
2.05
8.04
3.10
1.02
0.96
2.05
3.27
9.25
27.08
9.23
18.37
f1 (ppm)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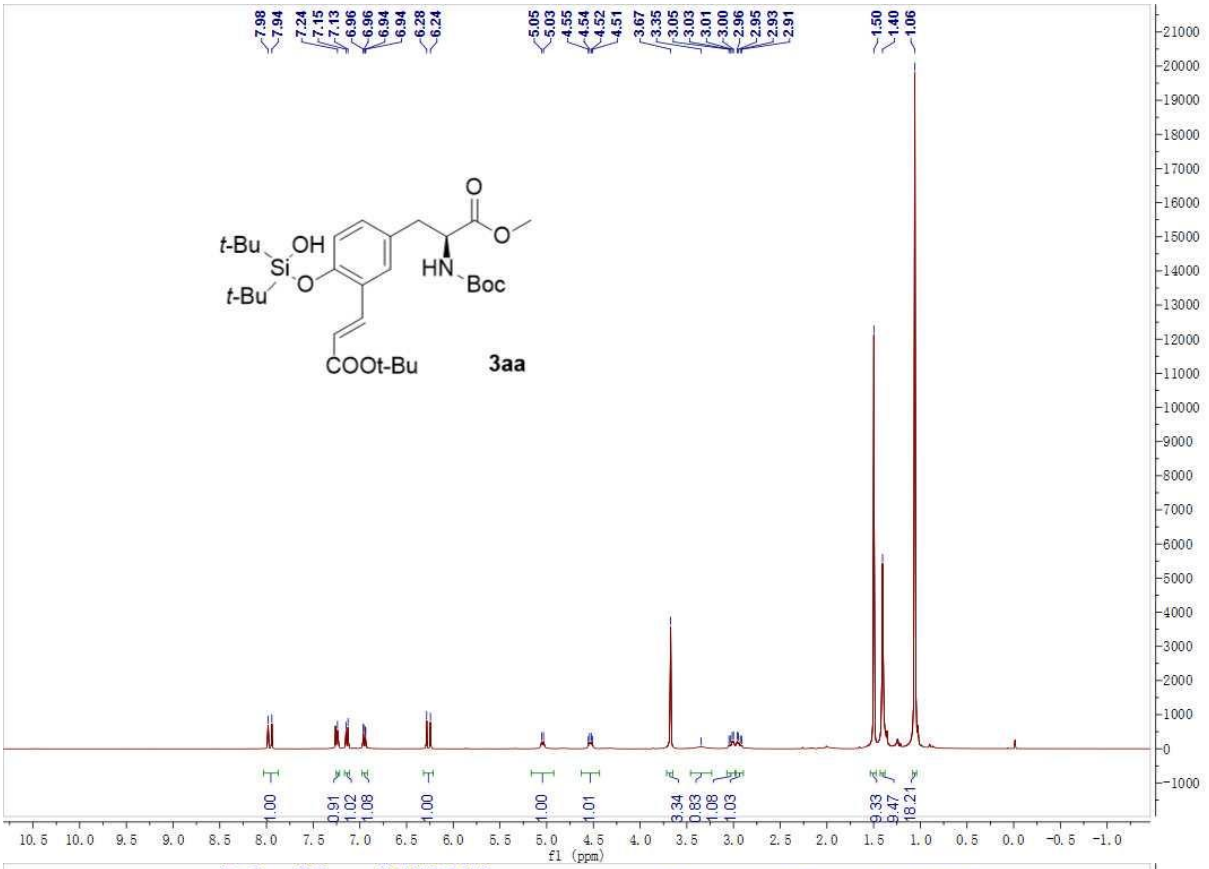
172.063
171.062
170.472
156.113
154.777
129.956
129.448
119.259
79.018
78.063
59.800
58.398
57.989
55.527
51.304
40.083
37.693
34.348
34.040
31.312
30.997
27.541
26.750
26.384
26.077
24.566
22.056
20.829
20.257
18.658
18.349
18.200
17.983
t-Bu
HO
Si
t-Bu
O
BocHN
H
N
O
COOMe
6n
f1 (ppm)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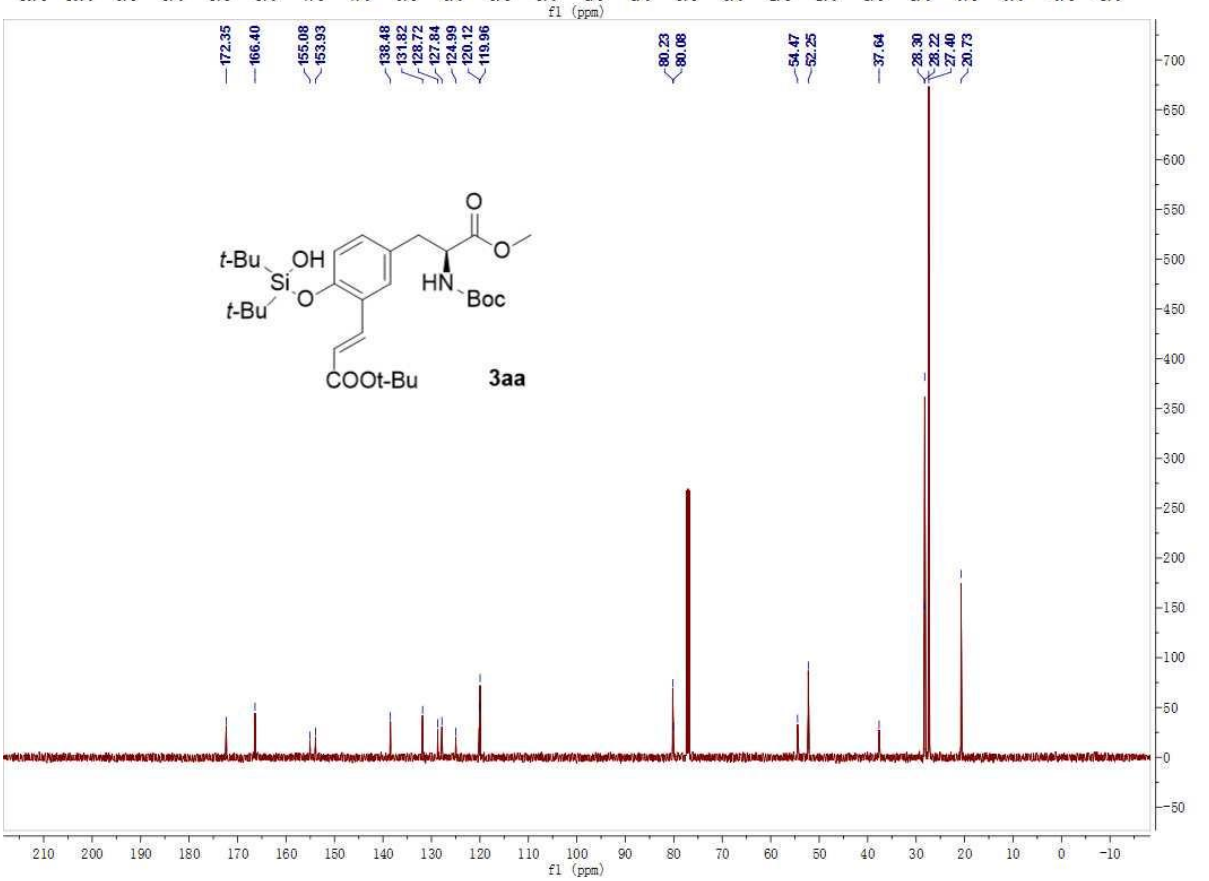
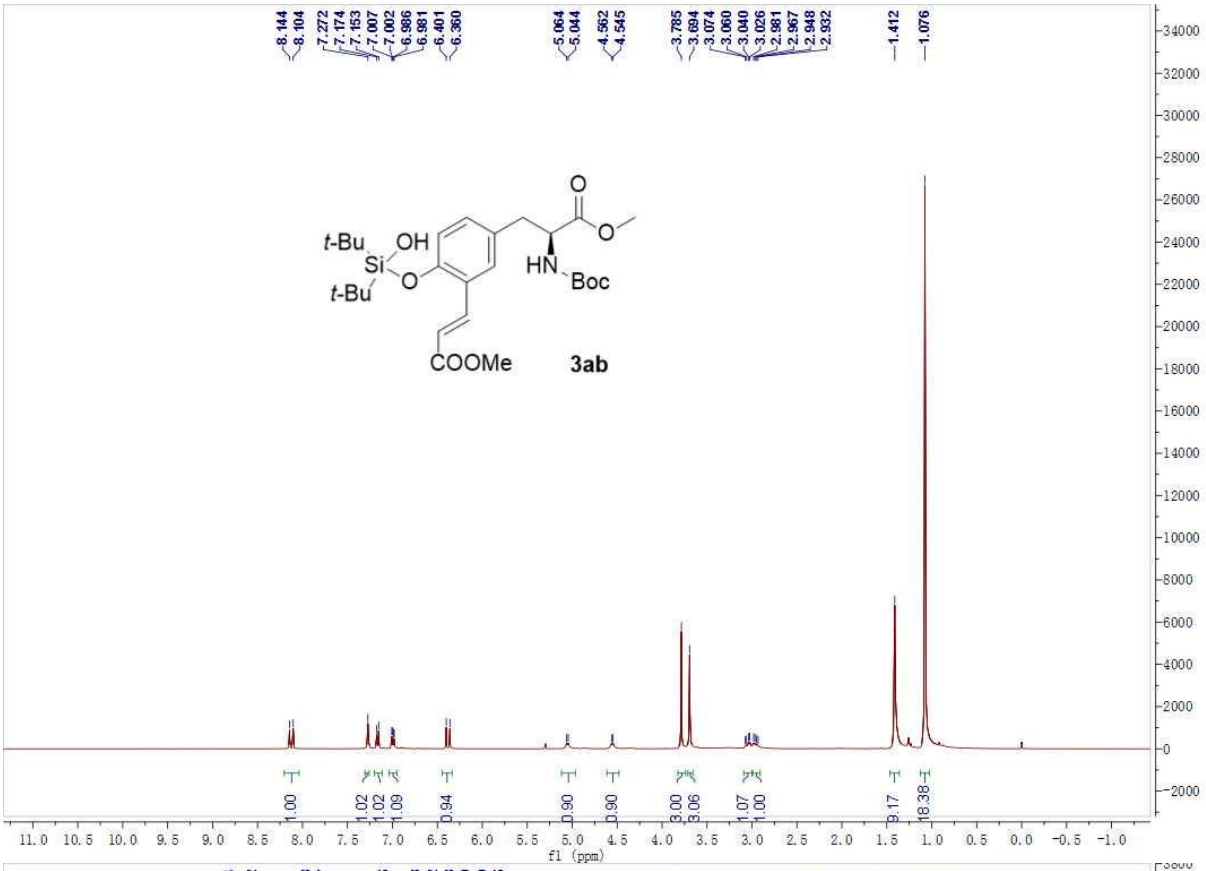
7.94
7.24
7.15
7.13
6.96
6.96
6.94
6.94
6.28
6.24
5.05
5.03
4.55
4.54
4.52
4.51
3.67
3.35
3.05
3.03
3.01
3.00
2.96
2.95
2.93
2.91
1.50
1.40
1.06
t-Bu
OH
Si
O
t-Bu
O
O
HN
Boc
COOt-Bu
3aa
1.00
0.91
1.02
1.08
1.00
1.00
1.01
3.34
0.83
1.08
1.03
9.33
9.47
18.21
f1 (ppm)


172.35
166.40
155.08
153.93
138.48
131.82
128.72
127.84
124.99
120.12
119.96
80.23
80.08
54.47
52.25
37.64
28.30
28.22
27.40
20.73
t-Bu
OH
Si
O
t-Bu
O
O
HN
Boc
COOt-Bu
3aa
f1 (ppm)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7.272
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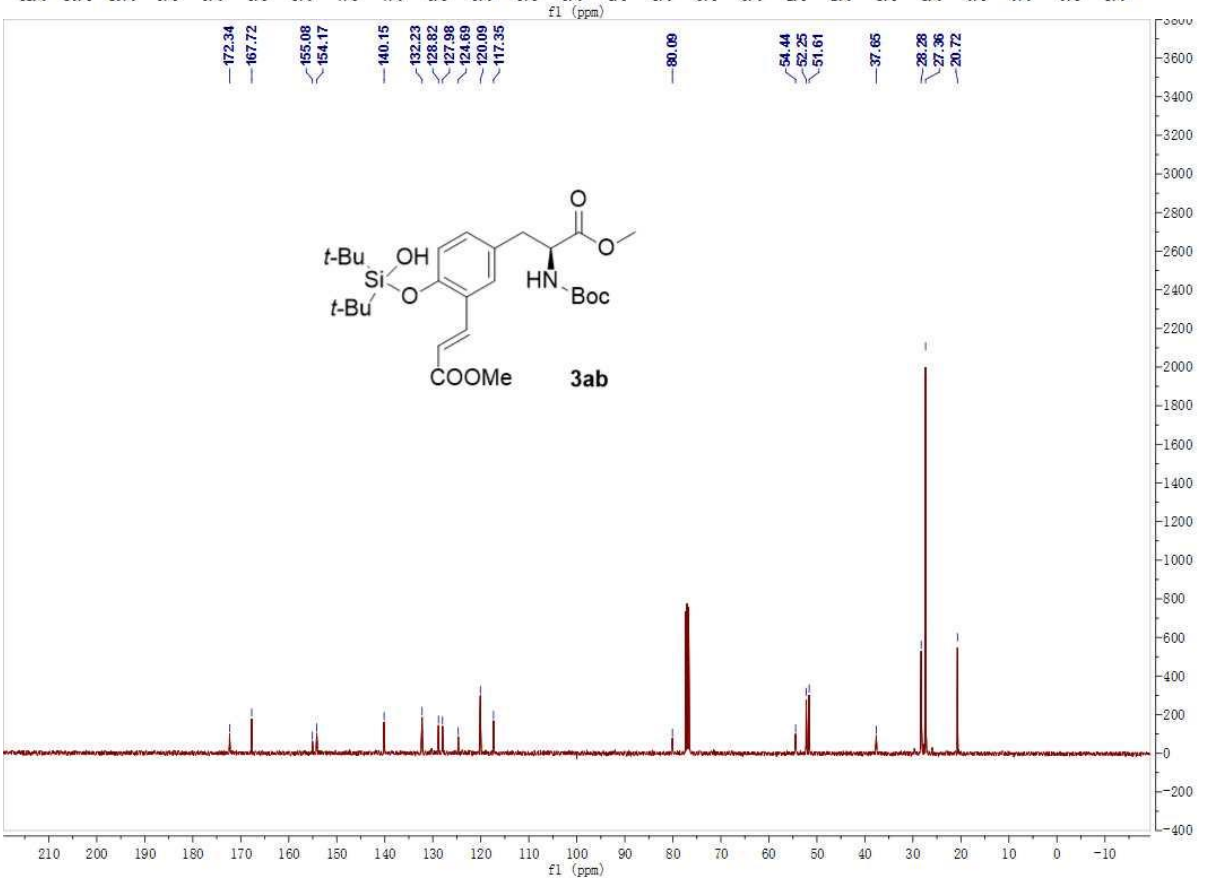
7.153
7.007
7.002
6.986
6.981
6.401
6.360
5.064
5.044
4.562
4.545
3.785
3.694
3.074
3.060
3.040
3.026
2.981
2.967
2.948
2.932
1.412
1.076
t-Bu
OH
Si
O
t-Bu
HN
Boc
O
O
COOMe
3ab
1.00
1.02
1.02
1.09
0.94
0.90
0.90
3.00
3.06
1.07
1.00
9.17
18.38
f1 (ppm)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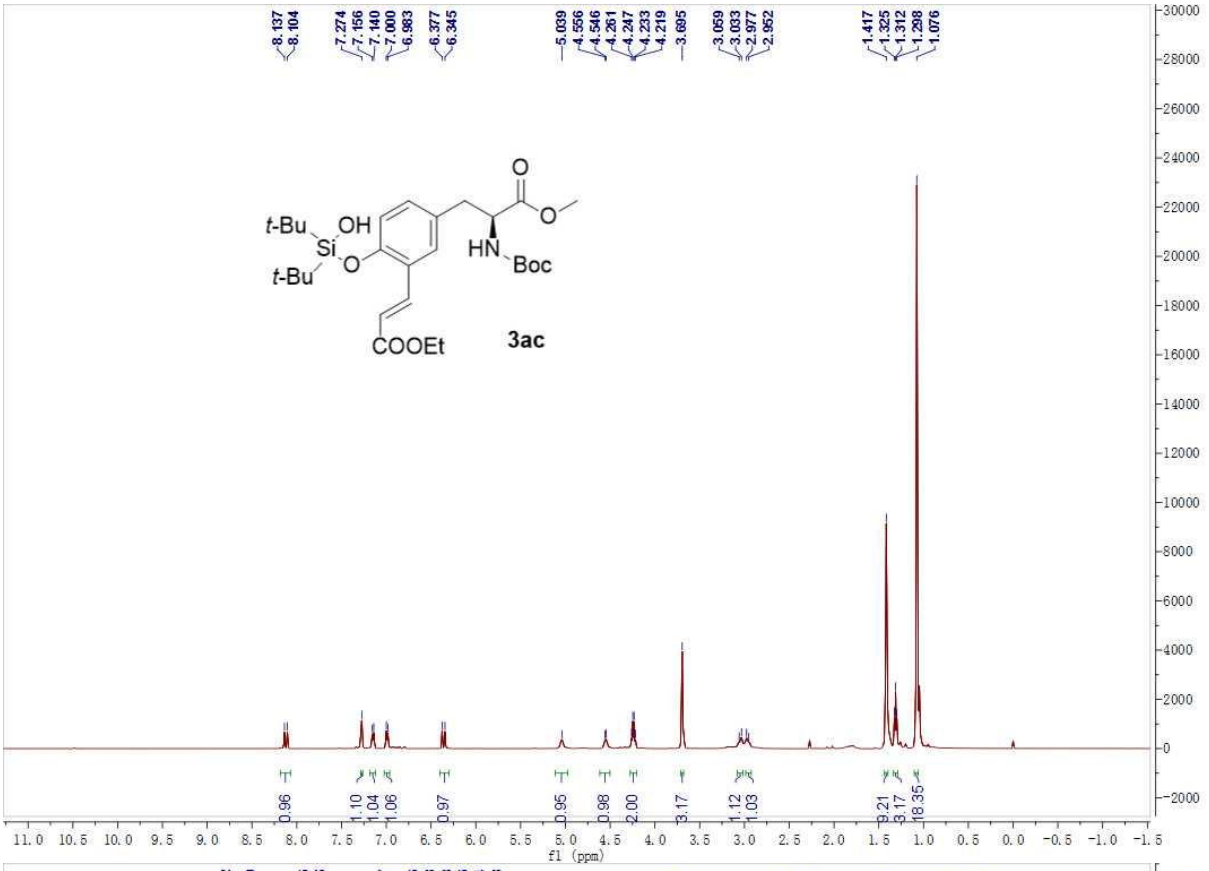
167.72
155.08
154.17
140.15
132.23
128.82
127.98
124.69
120.09
117.35
80.09
54.44
52.25
51.61
37.65
28.28
27.36
20.72
t-Bu
OH
Si
O
t-Bu
HN
Boc
O
O
COOMe
3ab
f1 (ppm)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7.156
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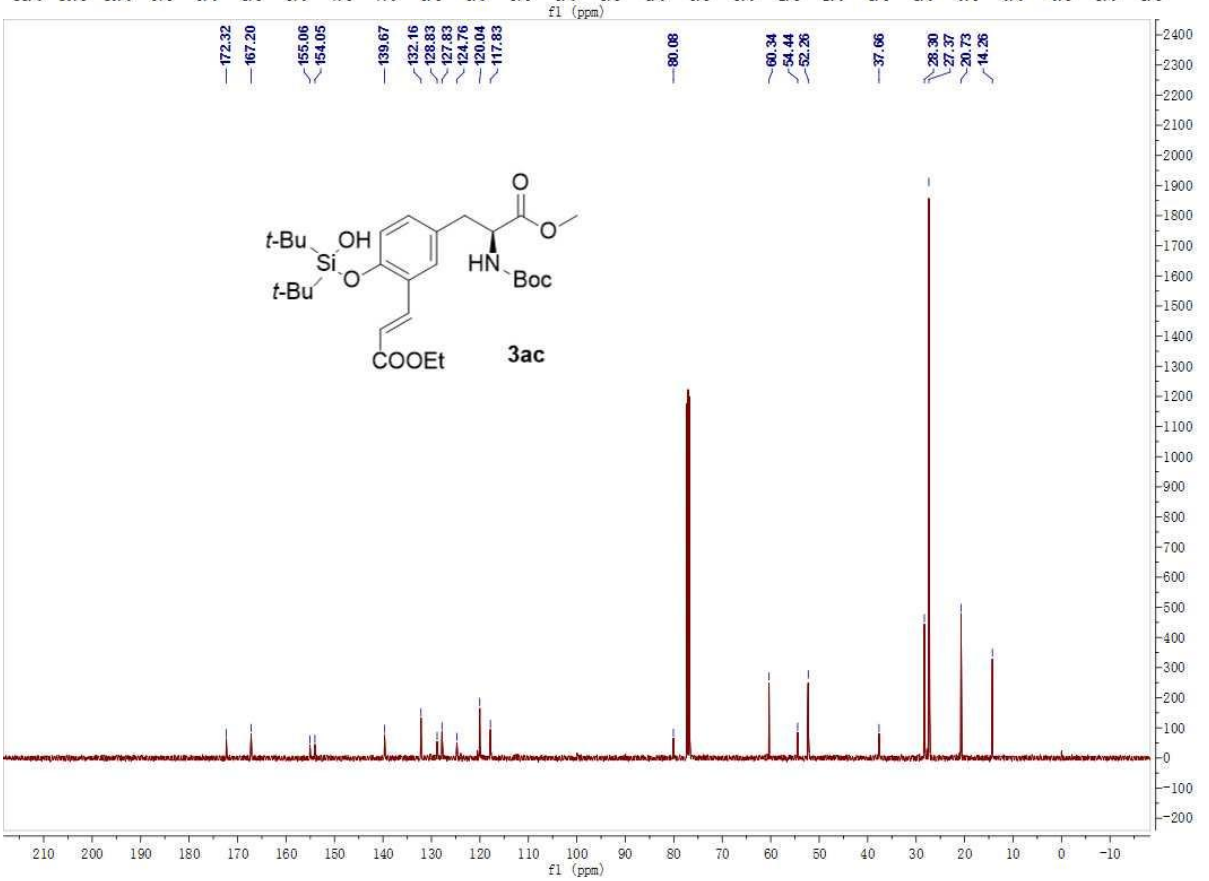
7.000
6.983
6.377
6.345
5.039
4.556
4.546
4.261
4.247
4.233
4.219
3.695
3.059
3.033
2.977
2.952
1.417
1.325
1.312
1.298
1.076
t-Bu
OH
Si
O
t-Bu
HN
Boc
COOEt
3ac
0.96
1.10
1.04
1.06
0.97
0.95
0.98
2.00
3.17
1.12
1.03
9.21
3.17
18.35
f1 (ppm)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154.05
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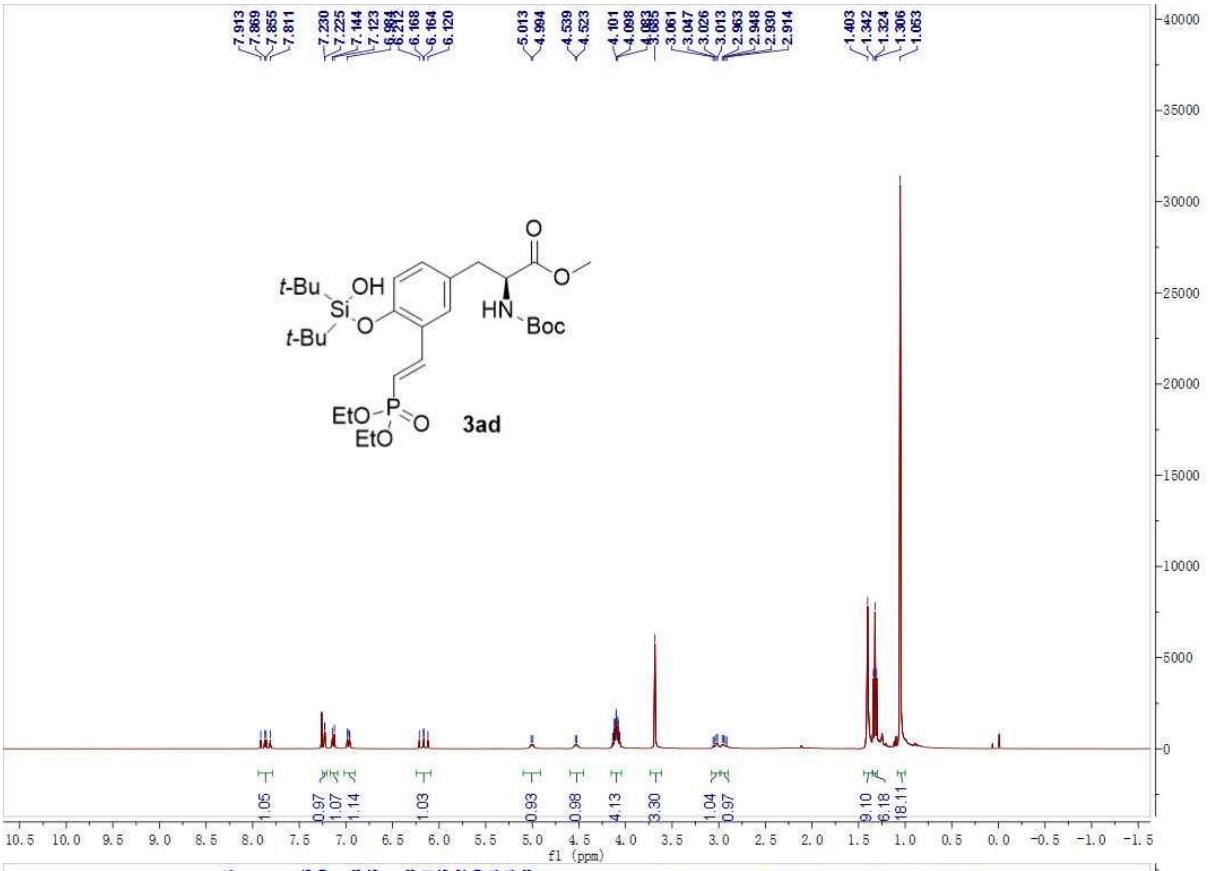
132.16
128.83
127.83
124.76
120.04
117.83
80.08
60.34
54.44
52.26
37.66
28.30
27.37
20.73
14.26
t-Bu
OH
Si
O
t-Bu
HN
Boc
COOEt
3ac
f1 (ppm)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7.123
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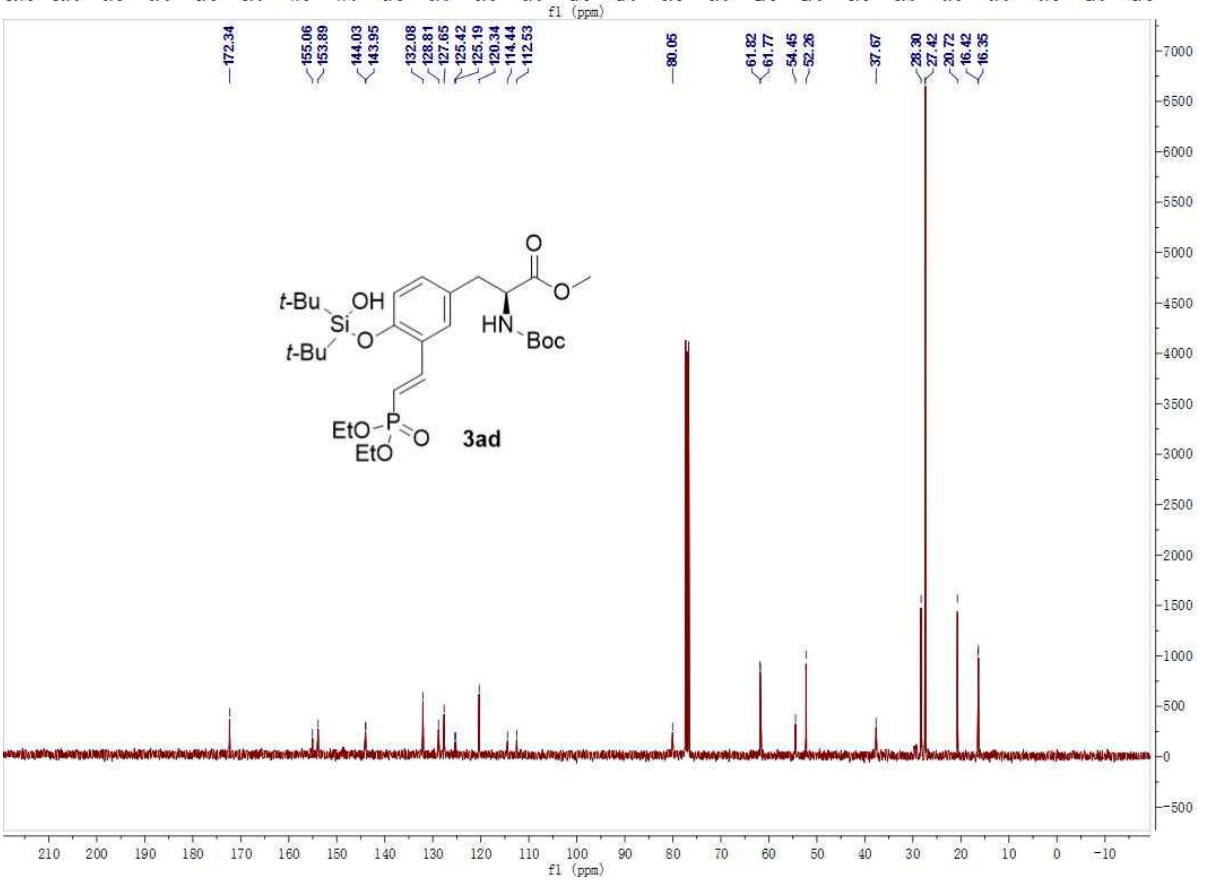
6.164
6.120
5.013
4.994
4.539
4.523
4.101
4.088
3.061
3.047
3.026
3.013
2.963
2.948
2.930
2.914
1.403
1.342
1.324
1.306
1.053
t-Bu
OH
Si
O
t-Bu
HN
Boc
O
O
EtO
P
O
EtO
3ad
1.05
0.97
1.07
1.14
1.03
0.93
0.98
4.13
3.30
1.04
0.97
9.10
6.18
18.11
f1 (ppm)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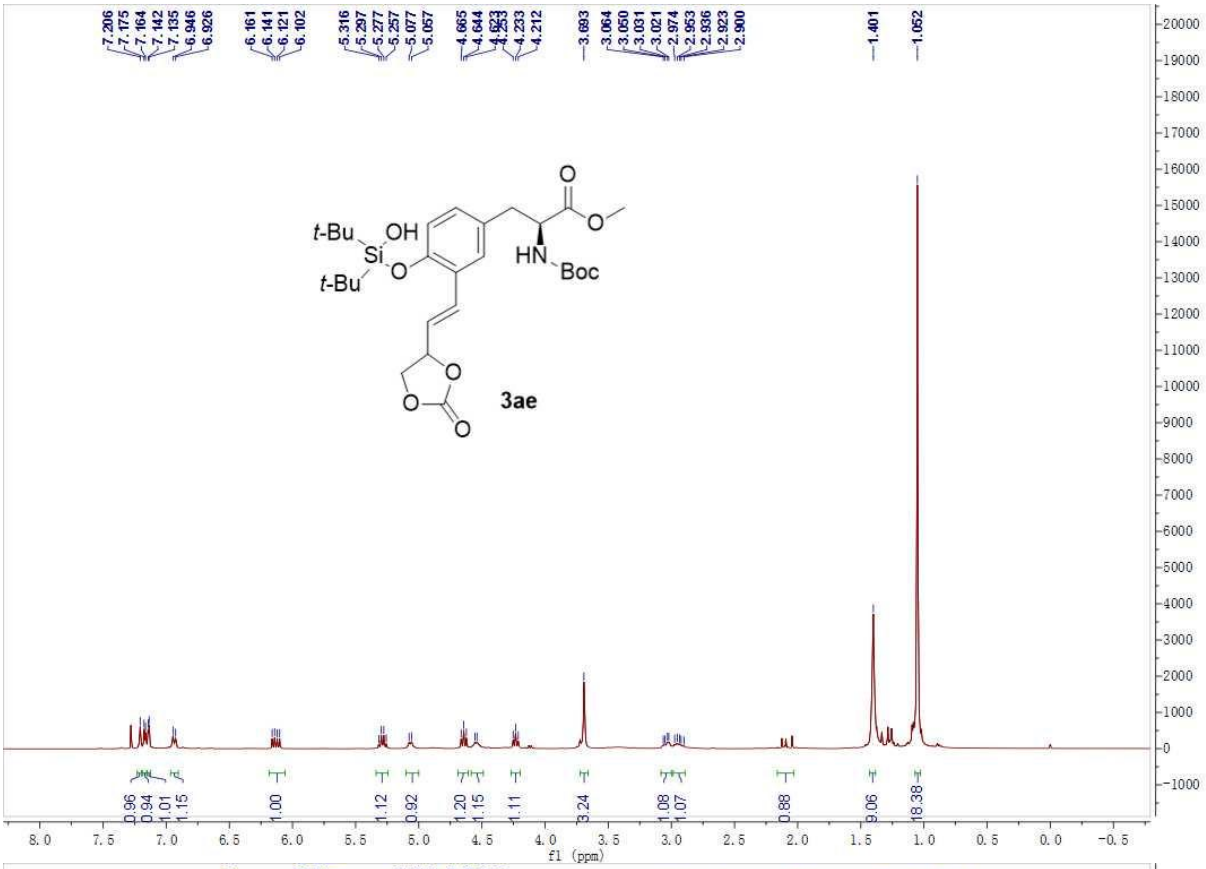
127.65
125.42
125.19
120.34
114.44
112.53
80.05
61.82
61.77
54.45
52.26
37.67
28.30
27.42
20.72
16.42
16.35
t-Bu
OH
Si
O
t-Bu
HN
Boc
O
O
EtO
P
O
EtO
3ad
f1 (ppm)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6.141
6.121
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5.297
5.277
5.257
5.077
5.057
4.665
4.644
4.623
4.253
4.233
4.212
3.693
3.064
3.050
3.031
3.021
2.974
2.953
2.936
2.923
2.900
1.401
1.052
t-Bu
OH
Si
O
t-Bu
HN
Boc
O
O
O
O
O
3ae
0.96
0.94
1.01
1.15
1.00
1.12
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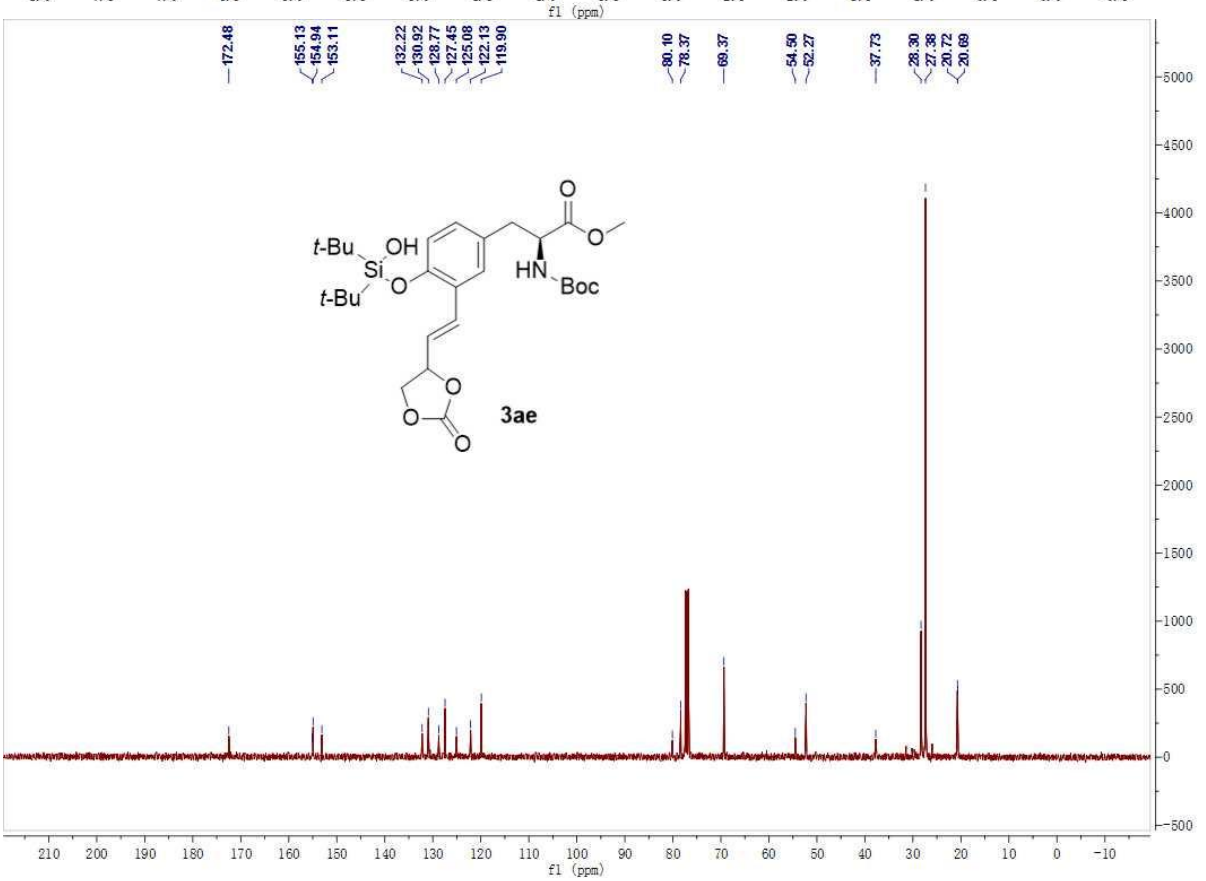
1.20
1.15
1.11
3.24
1.08
1.07
0.88
9.06
18.38
f1 (ppm)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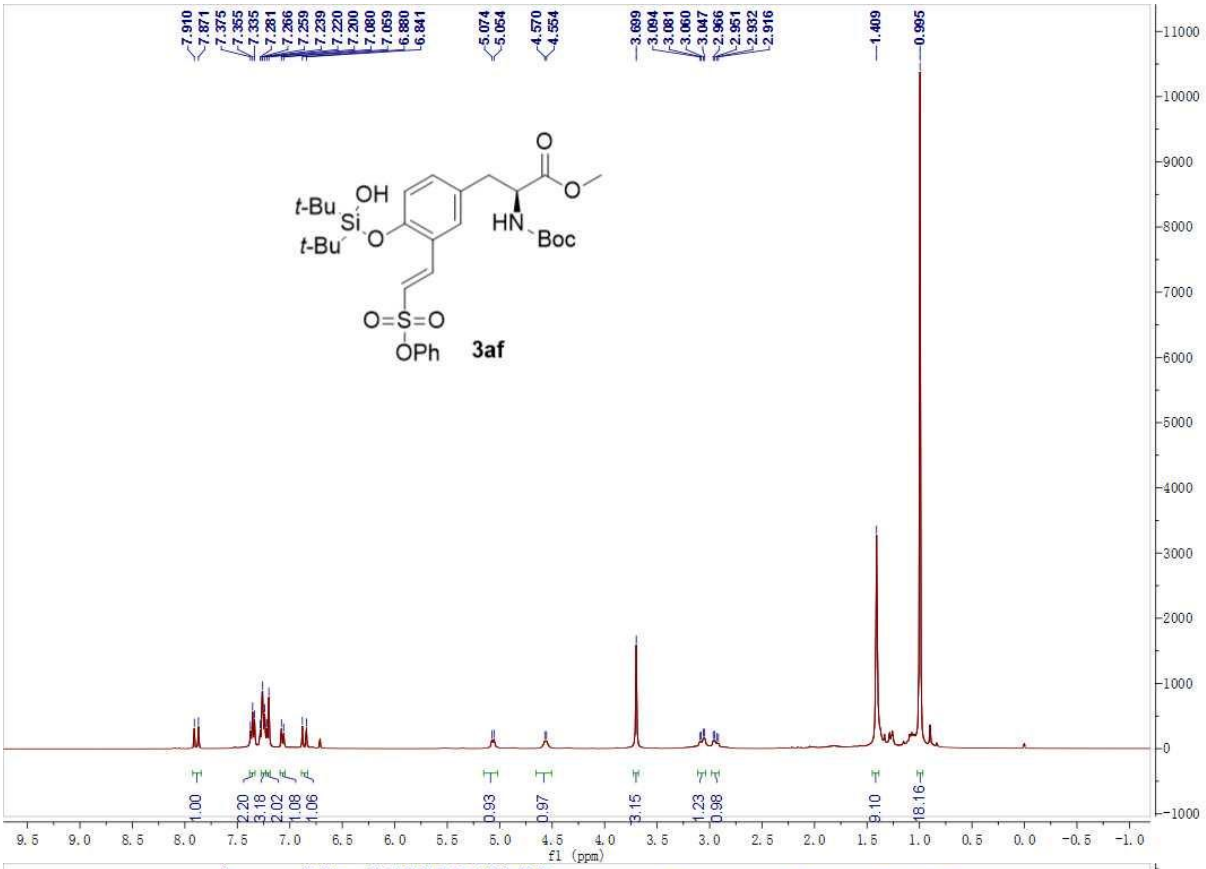
127.45
125.08
122.13
119.90
80.10
78.37
69.37
54.50
52.27
37.73
28.30
27.38
20.72
20.69
t-Bu
OH
Si
O
t-Bu
HN
Boc
O
O
O
O
O
3ae
f1 (ppm)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7.259
7.239
7.220
7.200
7.080
7.059
6.880
6.841
5.074
5.054
4.570
4.554
3.699
3.694
3.681
3.660
3.647
2.966
2.951
2.932
2.916
1.409
0.995
t-Bu
OH
Si
O
t-Bu
O
O
O
HN
Boc
O=S=O
OPh
3af
1.00
2.20
3.18
2.02
1.08
1.06
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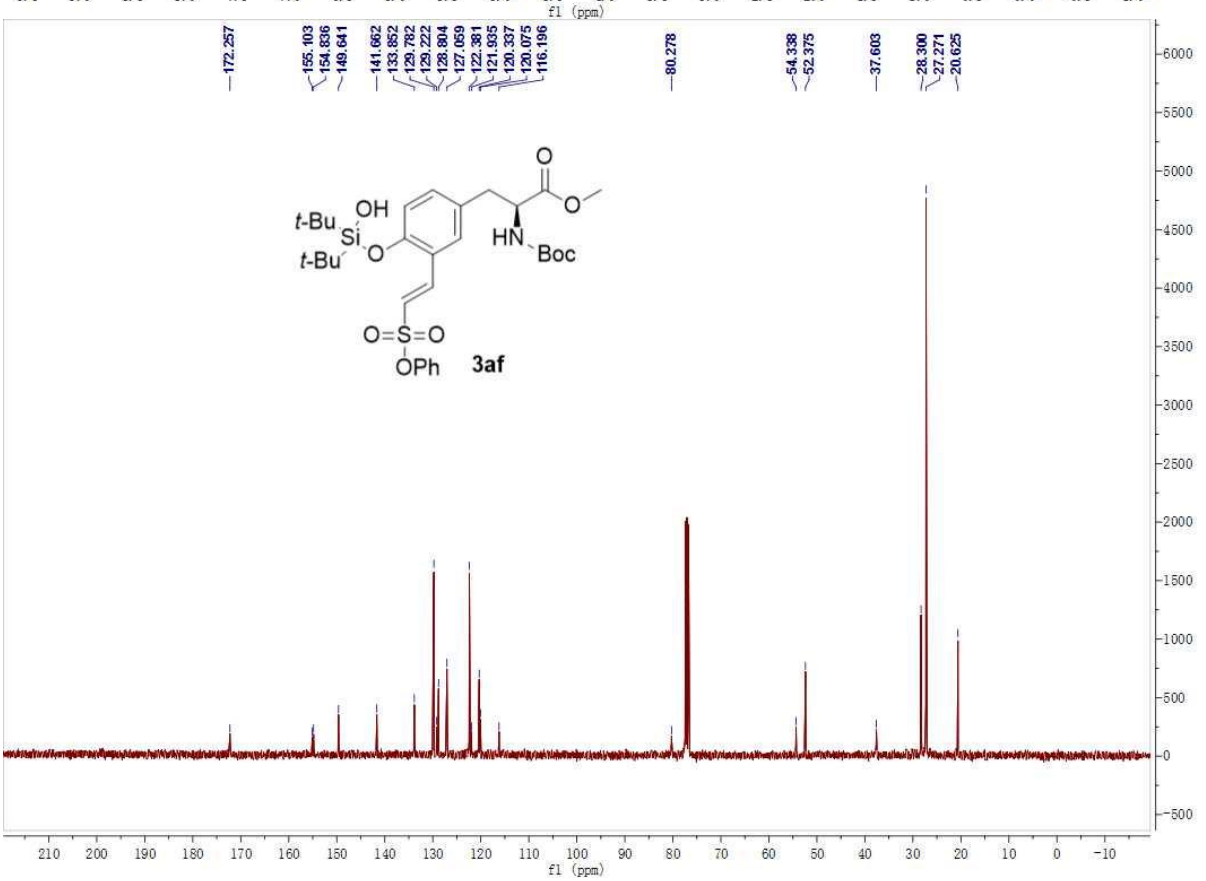
0.97
3.15
1.23
0.98
9.10
18.16
f1 (ppm)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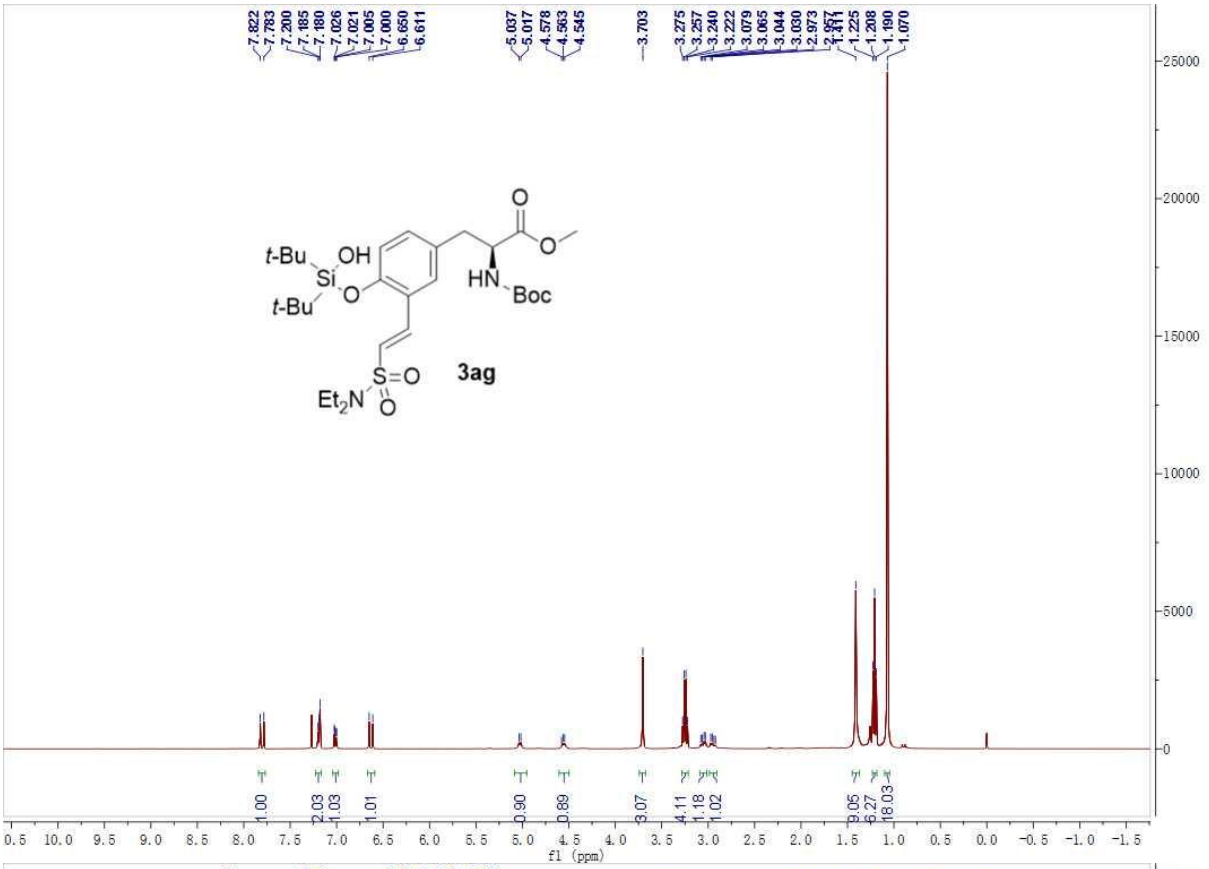
122.381
121.935
120.337
120.075
116.196
80.278
54.338
52.375
37.603
28.300
27.271
20.625
t-Bu
OH
Si
O
t-Bu
O
O
O
HN
Boc
O=S=O
OPh
3af
f1 (ppm)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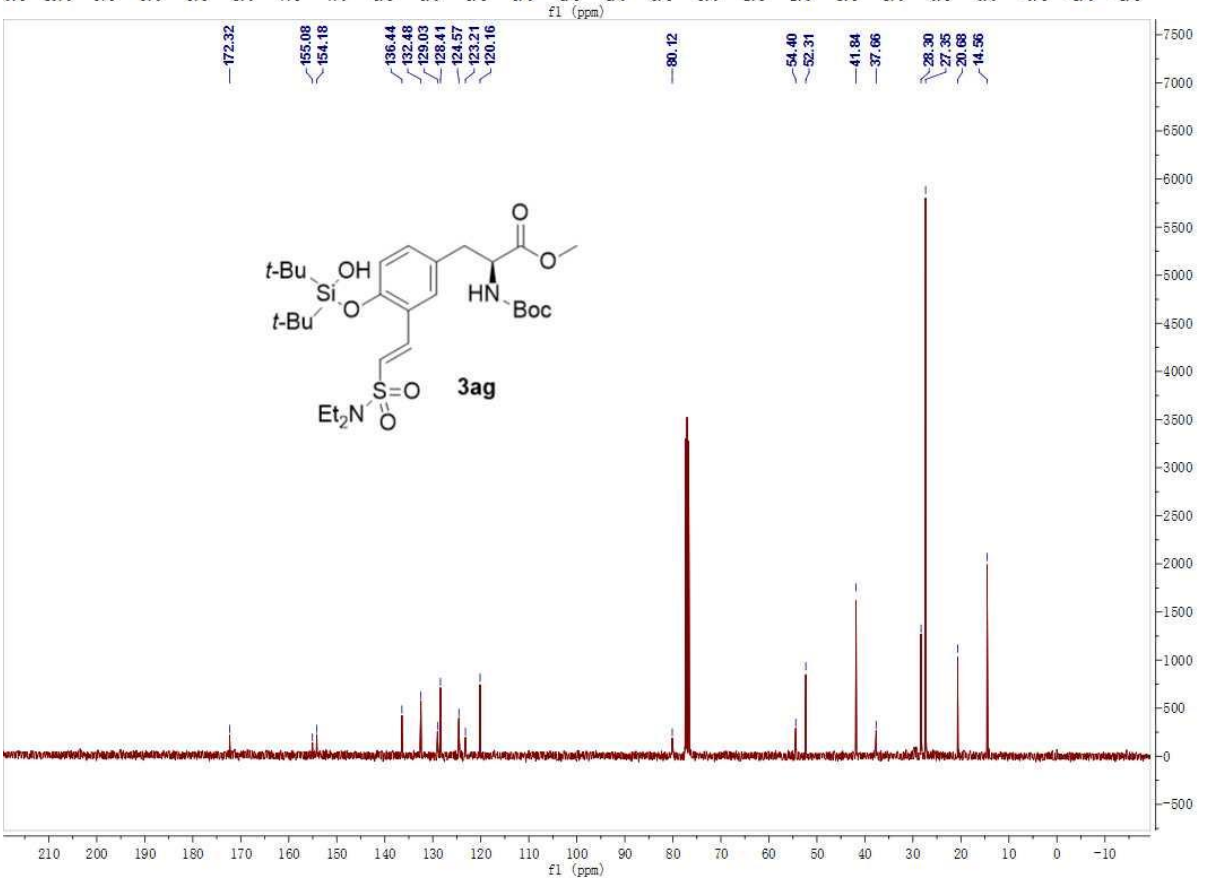
7.185
7.180
7.026
7.021
7.005
7.000
6.650
6.611
5.037
5.017
4.578
4.563
4.545
3.703
3.275
3.257
3.240
3.222
3.079
3.065
3.044
3.030
2.973
2.957
1.311
1.225
1.208
1.190
1.070
t-Bu
OH
Si
O
t-Bu
HN
Boc
O
O
S=O
Et2N
O
3ag
1.00
2.03
1.03
1.01
0.90
0.89
3.07
4.11
1.18
1.02
9.05
6.27
16.03
f1 (ppm)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154.18
136.44
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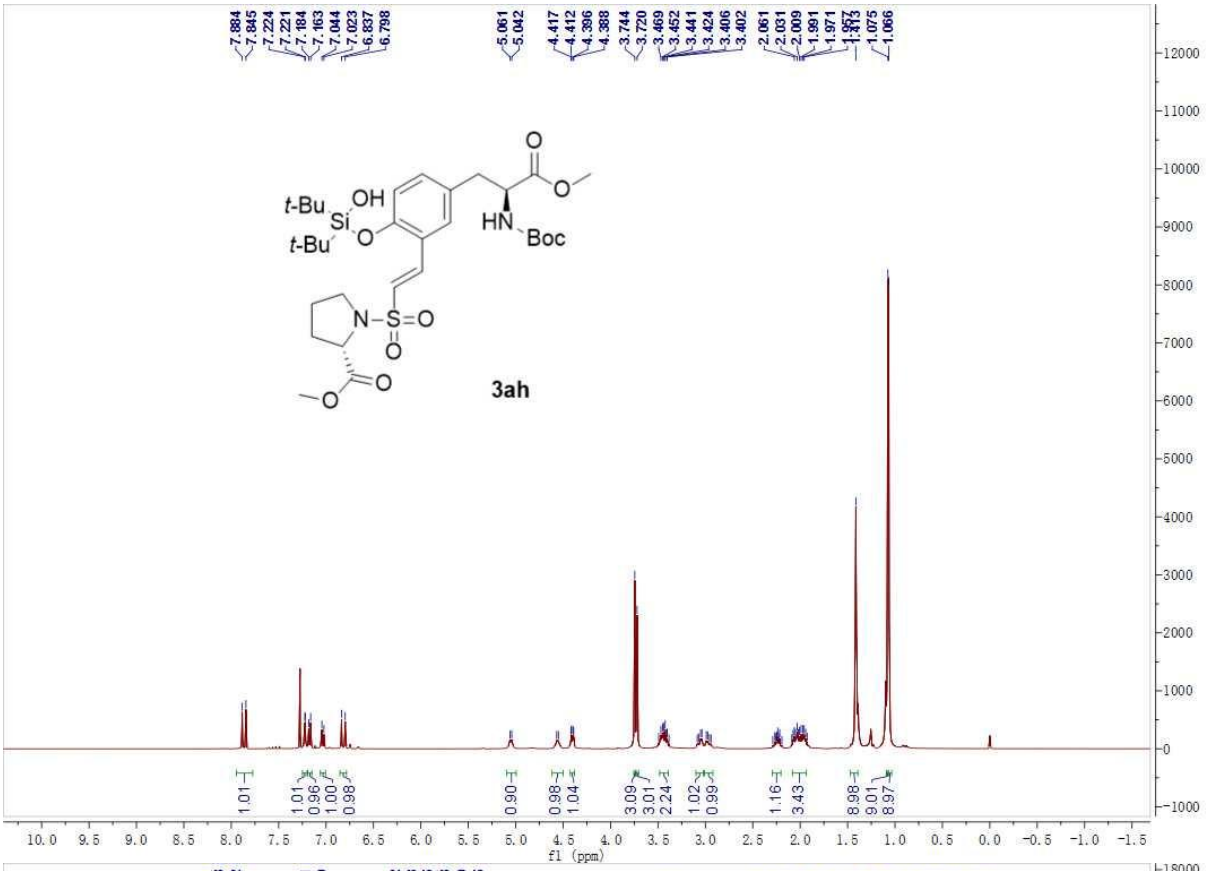
128.41
124.57
123.21
120.16
80.12
54.40
52.31
41.84
37.66
28.30
27.35
20.68
14.56
t-Bu
OH
Si
O
t-Bu
HN
Boc
O
O
S=O
Et2N
O
3ag
f1 (ppm)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6.798
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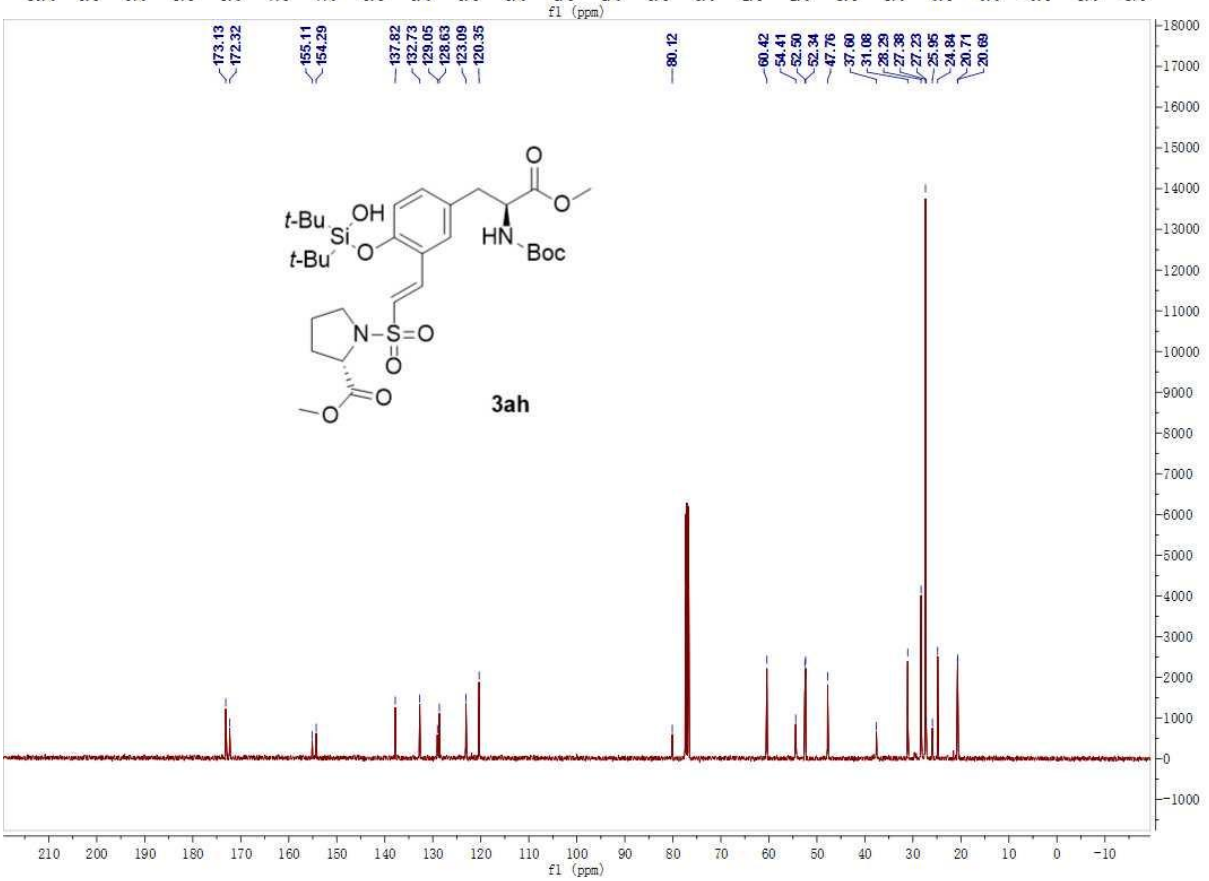
5.042
4.417
4.412
4.396
4.388
3.744
3.720
3.469
3.452
3.441
3.424
3.406
3.402
2.061
2.031
2.009
1.991
1.971
1.075
1.066
t-Bu
OH
Si
O
t-Bu
HN
Boc
N–S=O
O
3ah
1.01
1.01
0.96
1.00
0.98
0.90
0.98
1.04
3.09
3.01
2.24
1.02
0.99
1.16
3.43
8.98
9.01
8.97
f1 (ppm)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128.63
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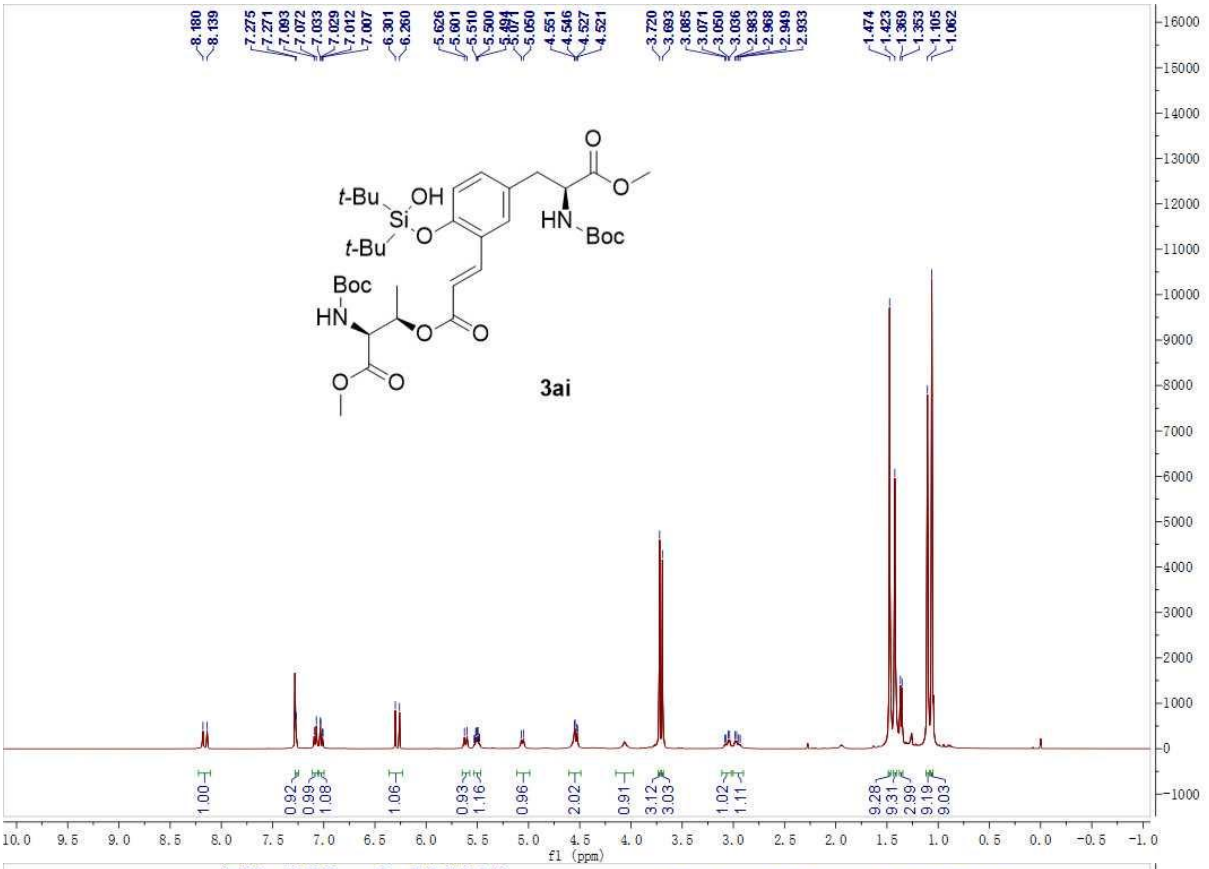
52.50
52.34
47.76
37.60
31.08
28.29
27.38
27.23
25.95
24.84
20.71
20.69
t-Bu
OH
Si
O
t-Bu
HN
Boc
N–S=O
O
3ah
f1 (ppm)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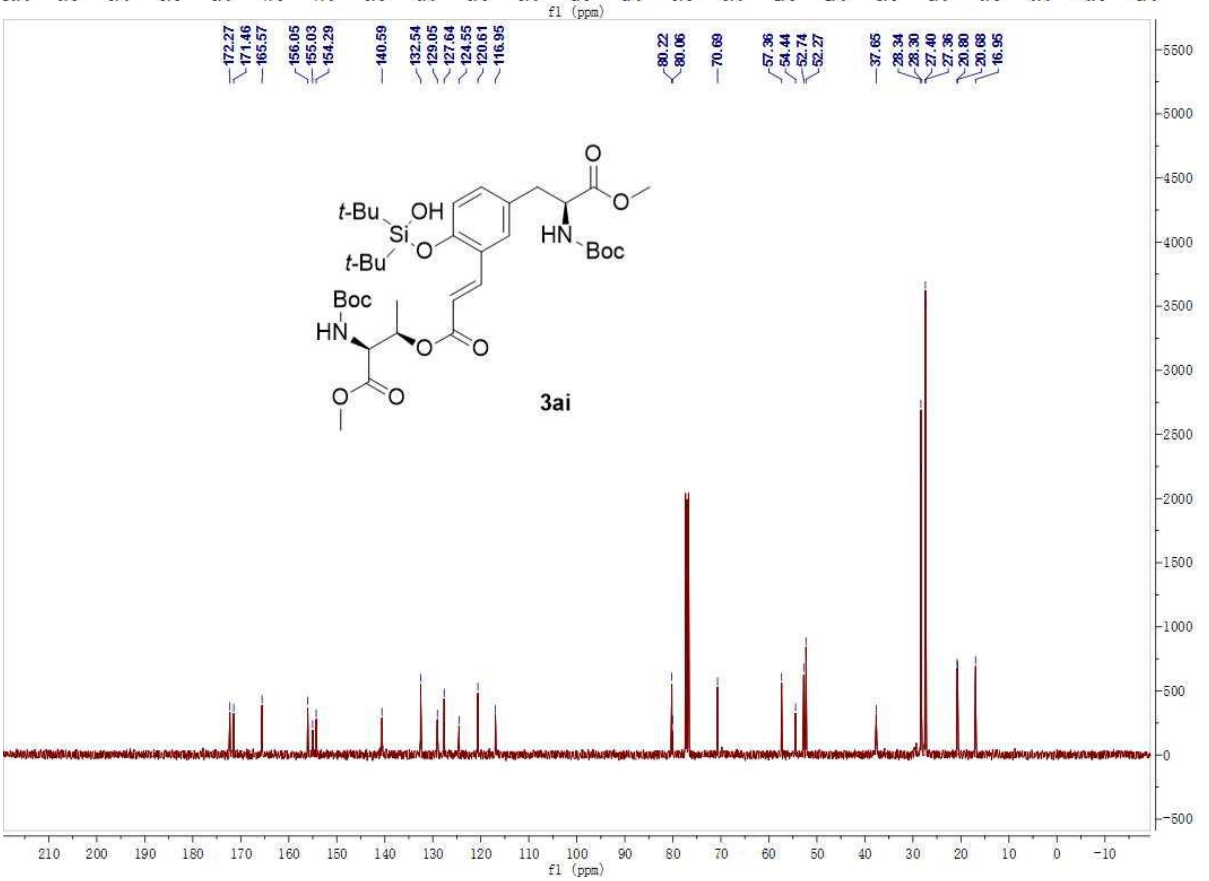
7.275
7.271
7.093
7.072
7.033
7.029
7.012
7.007
6.301
6.280
5.626
5.601
5.510
5.500
5.494
5.471
5.050
4.551
4.546
4.527
4.521
3.720
3.693
3.685
3.071
3.050
3.036
2.983
2.968
2.949
2.933
1.474
1.423
1.369
1.353
1.105
1.062
t-Bu
OH
Si
O
t-Bu
HN
Boc
Boc
HN
O
O
O
O
O
3ai
1.00
0.92
0.99
1.08
1.06
0.93
1.16
0.96
2.02
0.91
3.12
3.03
1.02
1.11
9.28
9.31
2.99
9.19
9.03
f1 (ppm)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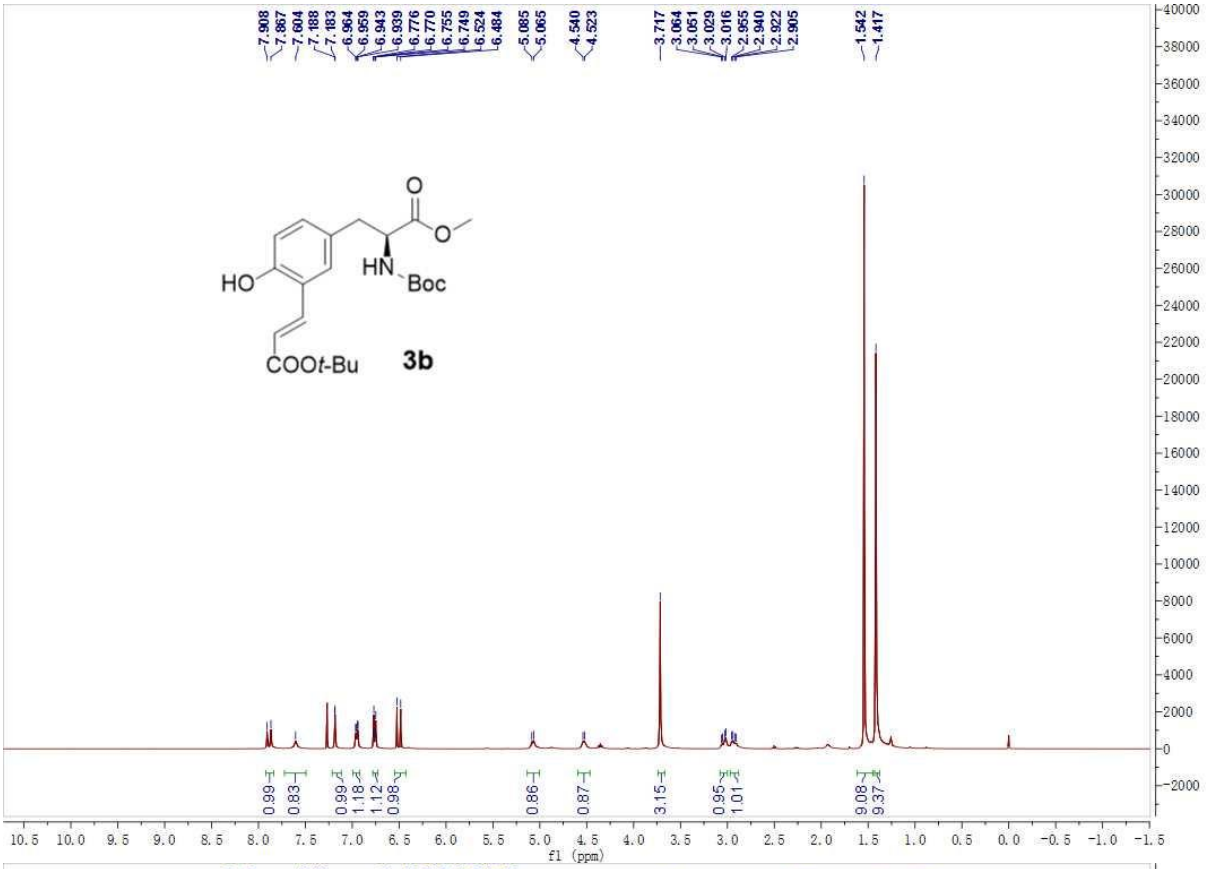
155.03
154.29
140.59
132.54
129.05
127.64
124.55
120.61
116.95
80.22
80.06
70.69
57.36
54.44
52.74
52.27
37.65
28.34
28.30
27.40
27.36
20.80
20.68
16.95
t-Bu
OH
Si
O
t-Bu
HN
Boc
Boc
HN
O
O
O
O
O
3ai
f1 (ppm)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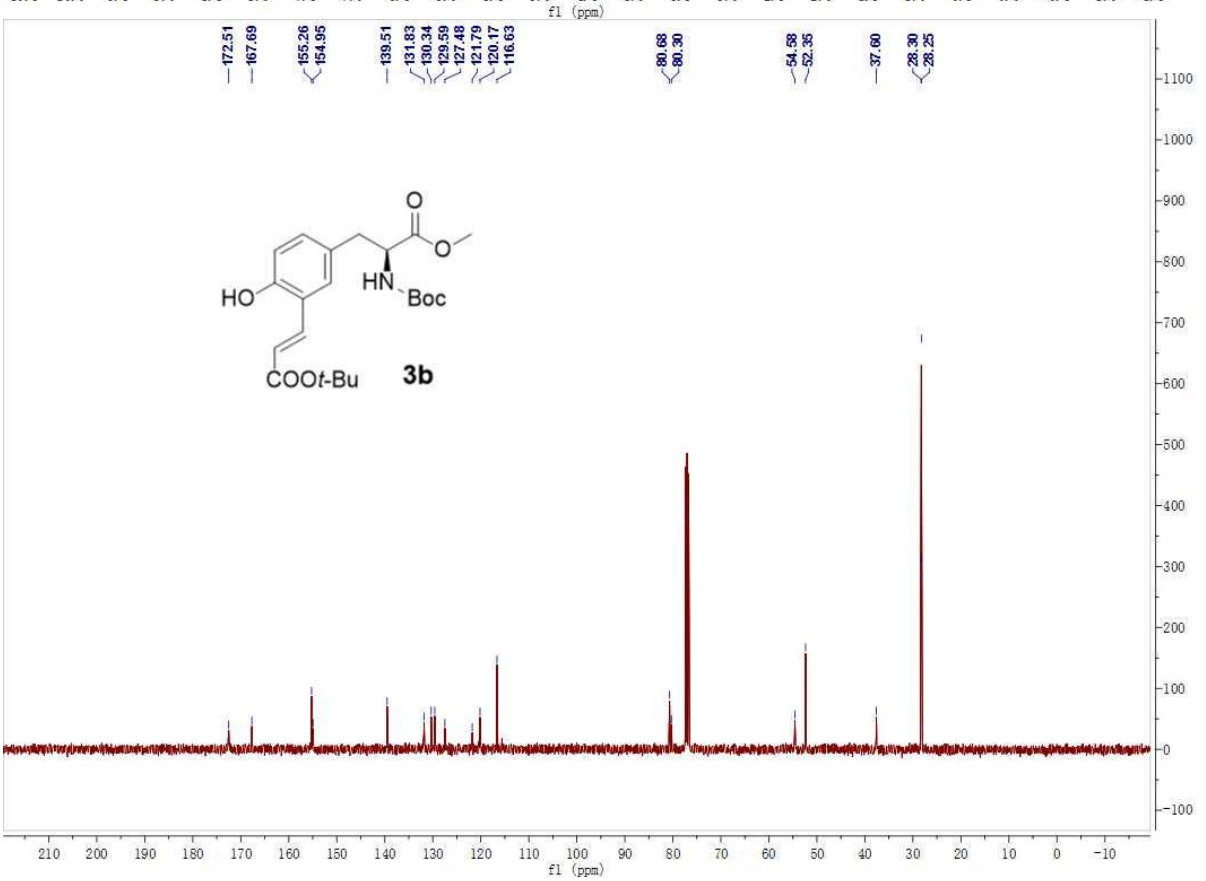
6.959
6.943
6.939
6.776
6.770
6.755
6.749
6.524
6.484
5.085
5.065
4.540
4.523
3.717
3.064
3.051
3.029
3.016
2.955
2.940
2.922
2.905
1.542
1.417
HO
HN
Boc
O
O
COOt-Bu
3b
0.99
0.83
0.99
1.18
1.12
0.98
0.86
0.87
3.15
0.95
1.01
9.08
9.37
f1 (ppm)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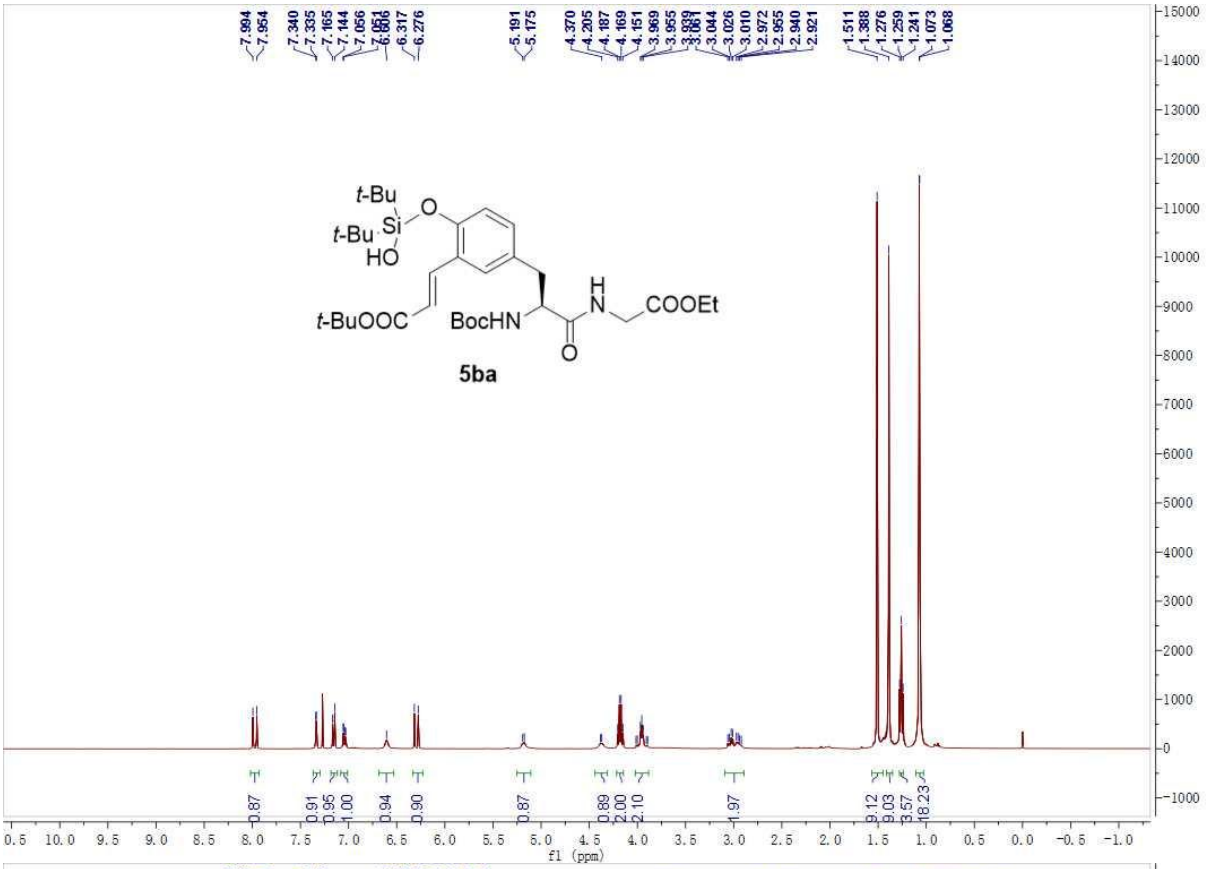
167.69
155.26
154.95
139.51
131.83
130.34
129.59
127.48
121.79
120.17
116.63
80.68
80.30
54.58
52.35
37.60
28.30
28.25
HO
HN
Boc
O
O
COOt-Bu
3b
f1 (ppm)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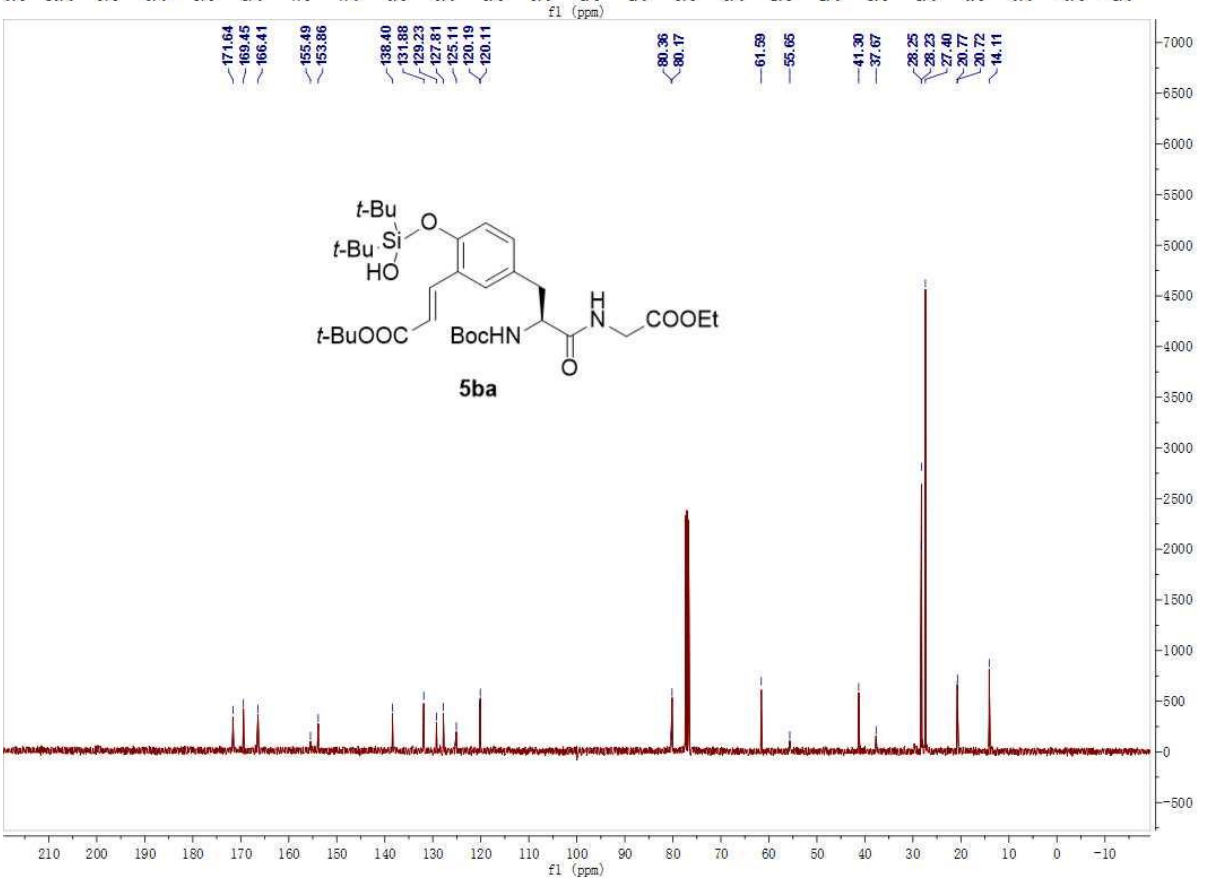
7.340
7.335
7.165
7.144
7.056
6.317
6.276
5.191
5.175
4.370
4.205
4.187
4.169
4.151
3.969
3.955
3.044
3.026
3.010
2.972
2.955
2.940
2.921
1.511
1.388
1.276
1.259
1.241
1.073
1.068
t-Bu
t-Bu
Si
O
HO
t-BuOOC
BocHN
H
N
COOEt
O
5ba
0.87
0.91
0.95
1.00
0.94
0.90
0.87
0.89
2.00
2.10
1.97
9.12
9.03
3.57
18.23
f1 (ppm)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166.41
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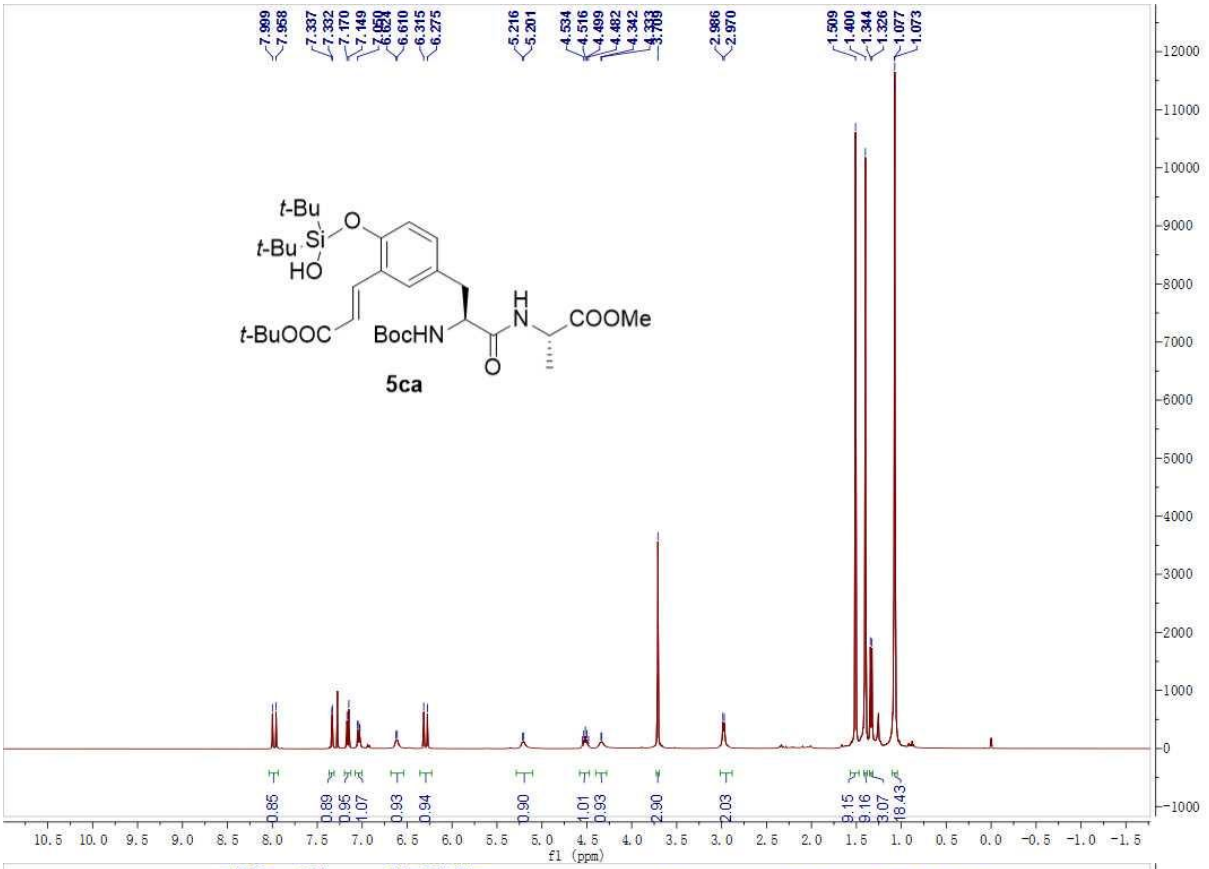
131.88
129.23
127.81
125.11
120.19
120.11
80.36
80.17
61.59
55.65
41.30
37.67
28.25
28.23
27.40
20.77
20.72
14.11
t-Bu
t-Bu
Si
O
HO
t-BuOOC
BocHN
H
N
COOEt
O
5ba
f1 (ppm)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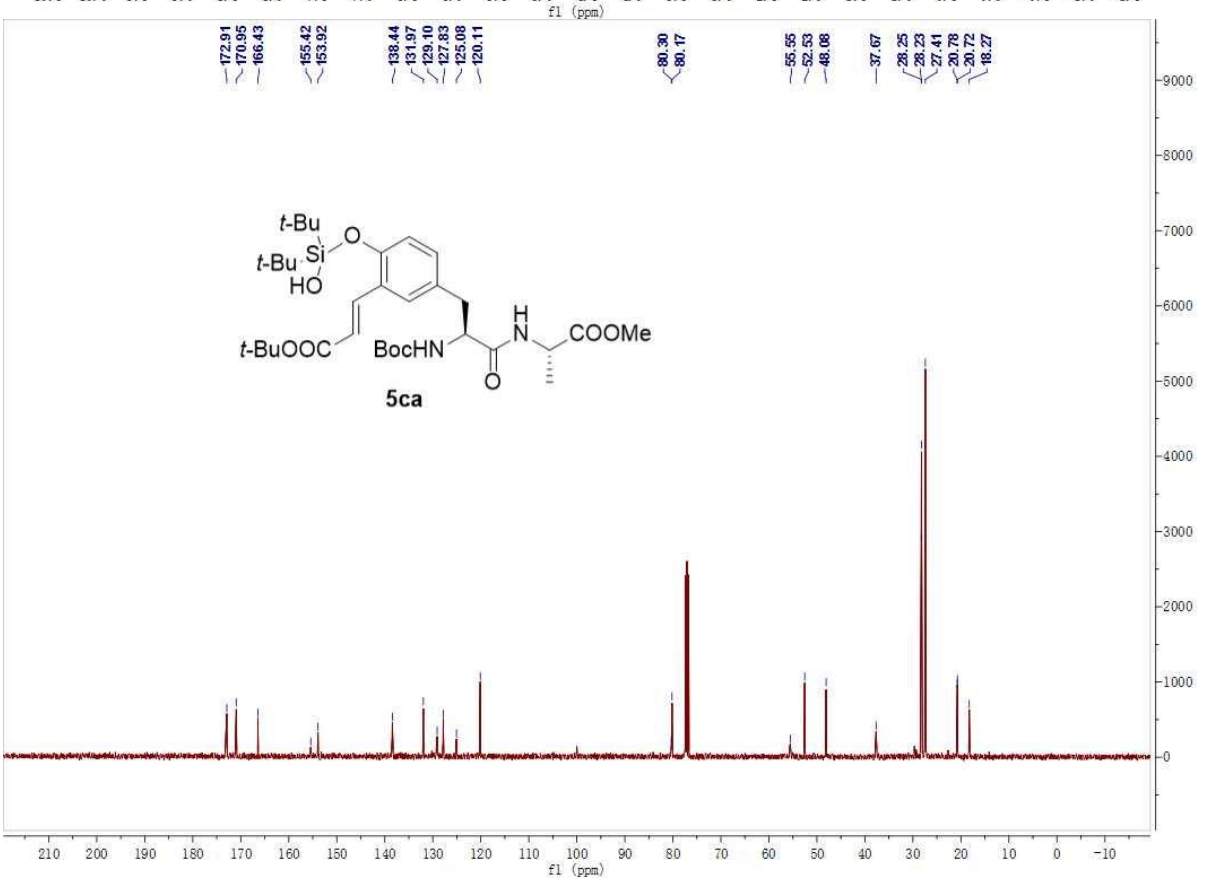
7.337
7.332
7.170
7.149
6.624
6.610
6.315
6.275
5.216
5.201
4.534
4.516
4.499
4.482
4.342
4.333
3.708
2.986
2.970
1.509
1.400
1.344
1.326
1.077
1.073
0.85
0.89
0.95
1.07
0.93
0.94
0.90
1.01
0.93
2.90
2.03
9.15
9.16
3.07
18.43
f1 (ppm)
t-Bu
t-Bu
Si
O
HO
t-BuOOC
BocHN
H
N
O
COOMe
5ca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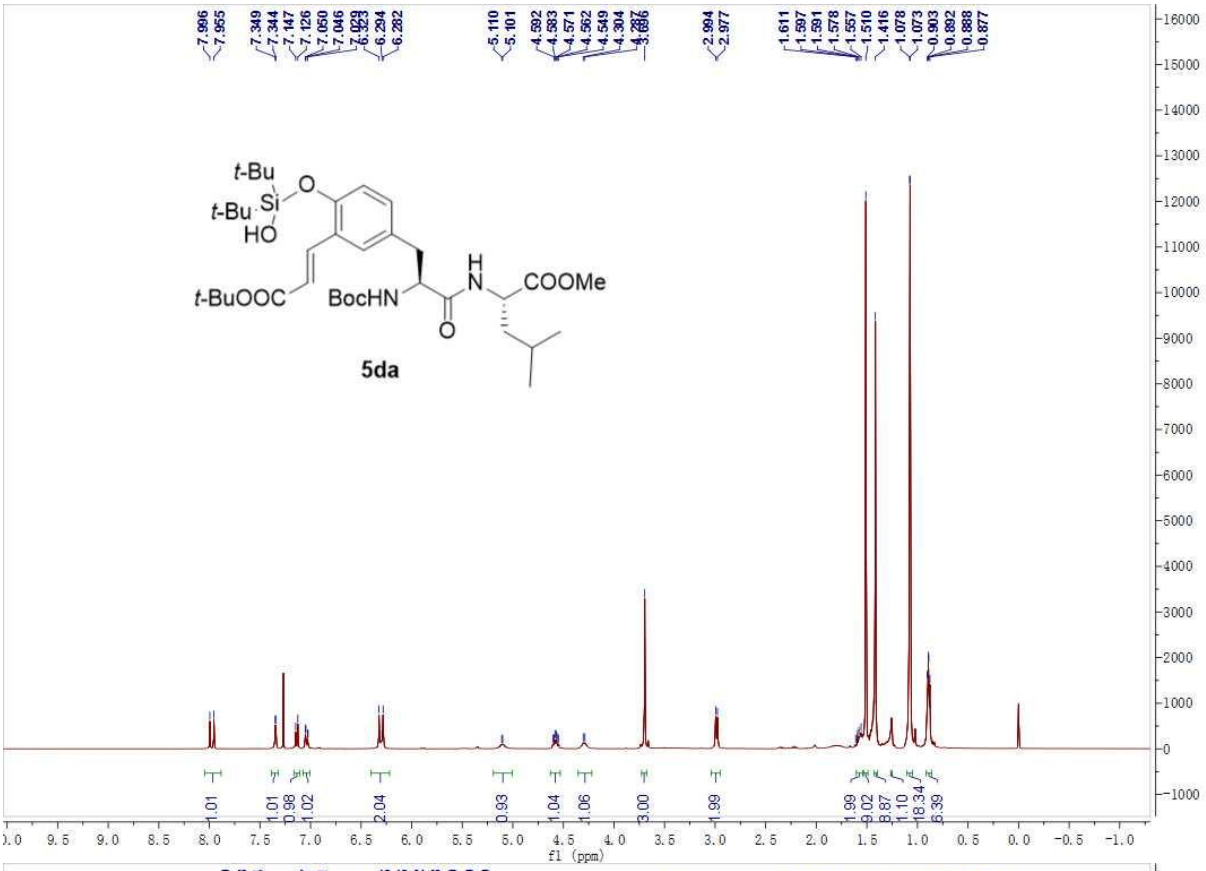
170.95
166.43
155.42
153.92
138.44
131.97
129.10
127.83
125.08
120.11
80.30
80.17
55.55
52.53
48.08
37.67
28.25
28.23
27.41
20.78
20.72
18.27
f1 (ppm)
t-Bu
t-Bu
Si
O
HO
t-BuOOC
BocHN
H
N
O
COOMe
5ca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7.349
7.344
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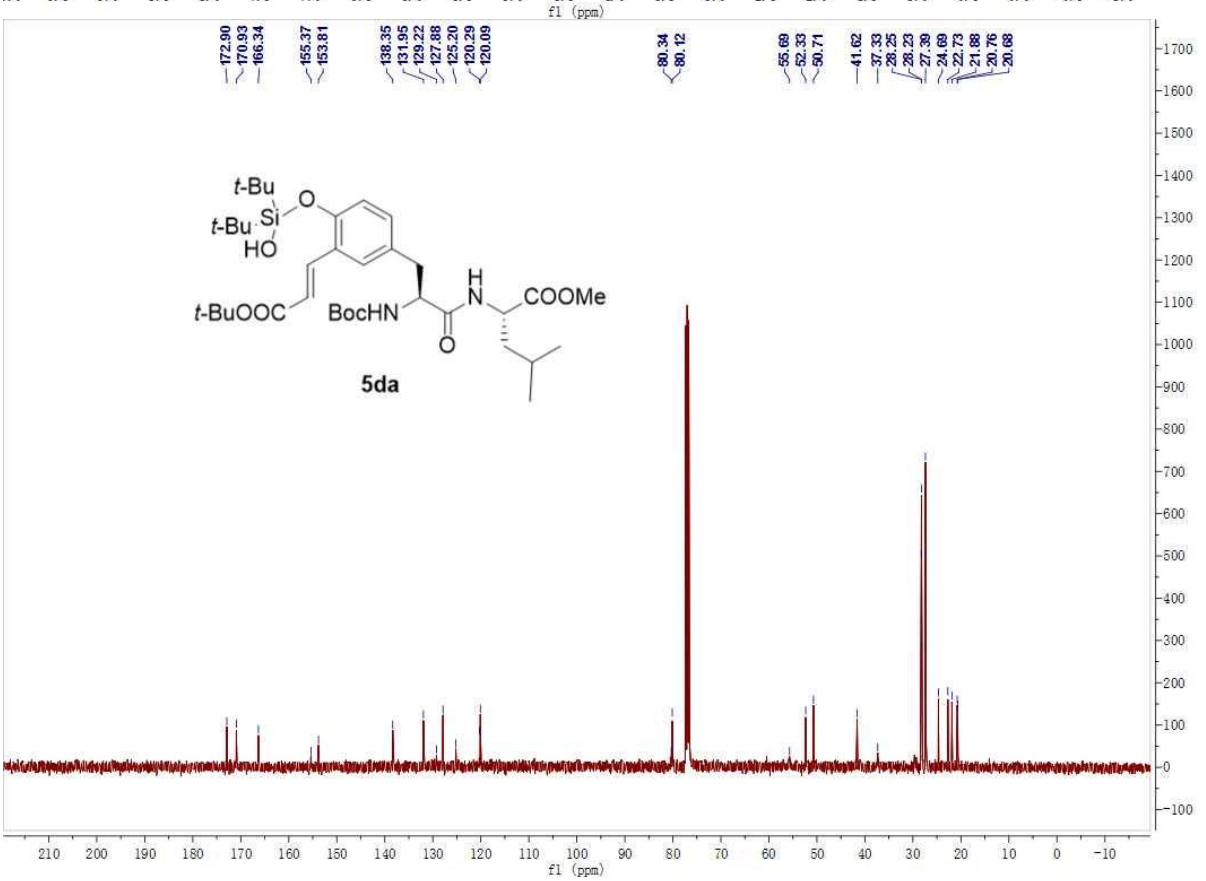
7.126
7.050
7.046
6.294
6.282
5.110
5.101
4.592
4.583
4.571
4.562
4.549
4.304
2.994
2.977
1.611
1.597
1.591
1.578
1.557
1.510
1.416
1.078
1.073
0.903
0.892
0.888
0.877
t-Bu
t-Bu
Si
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
5da
1.01
1.01
0.98
1.02
2.04
0.93
1.04
1.06
3.00
1.99
1.99
9.02
8.87
1.10
18.34
6.39
f1 (ppm)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166.34
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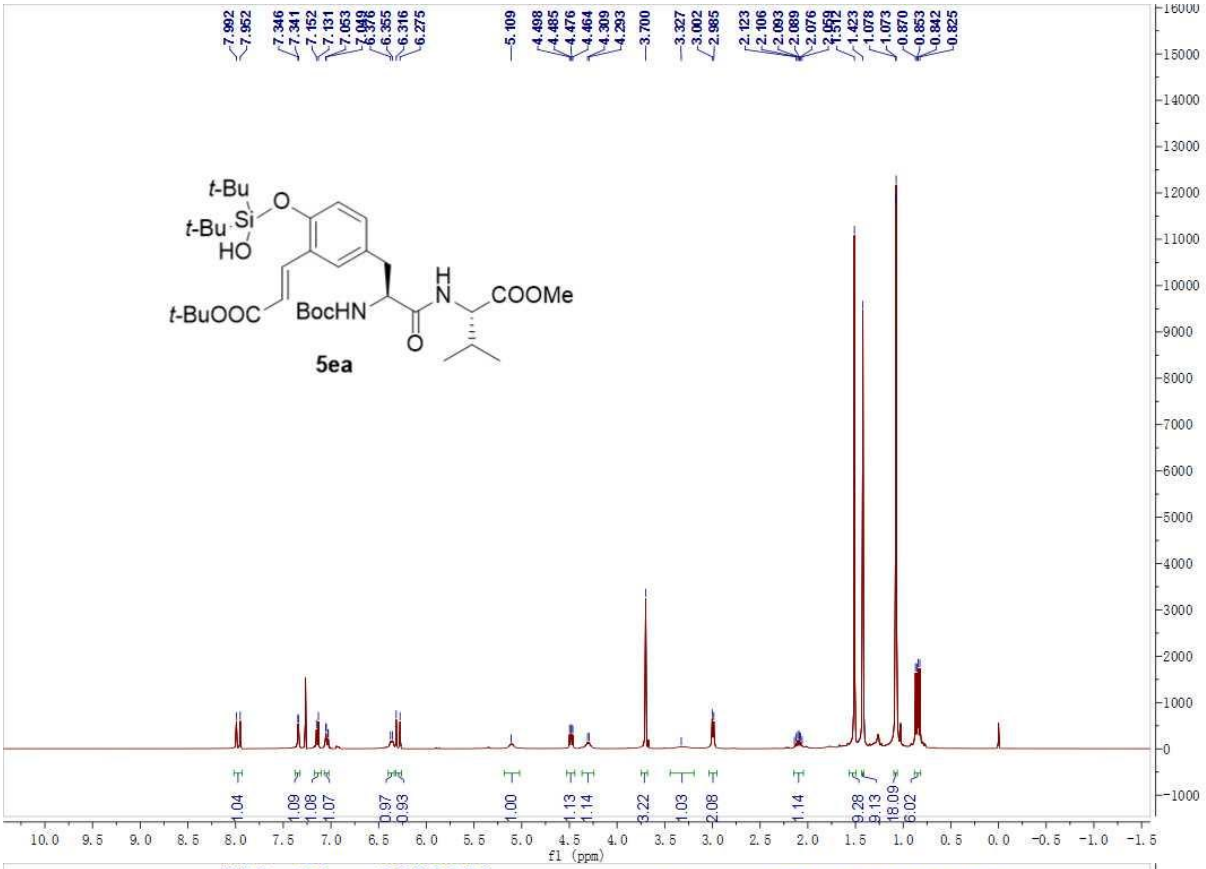
153.81
138.35
131.95
129.22
127.88
125.20
120.29
120.09
80.34
80.12
55.69
52.33
50.71
41.62
37.33
28.25
28.23
27.39
24.69
22.73
21.88
20.76
20.68
t-Bu
t-Bu
Si
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
5da
f1 (ppm)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7.341
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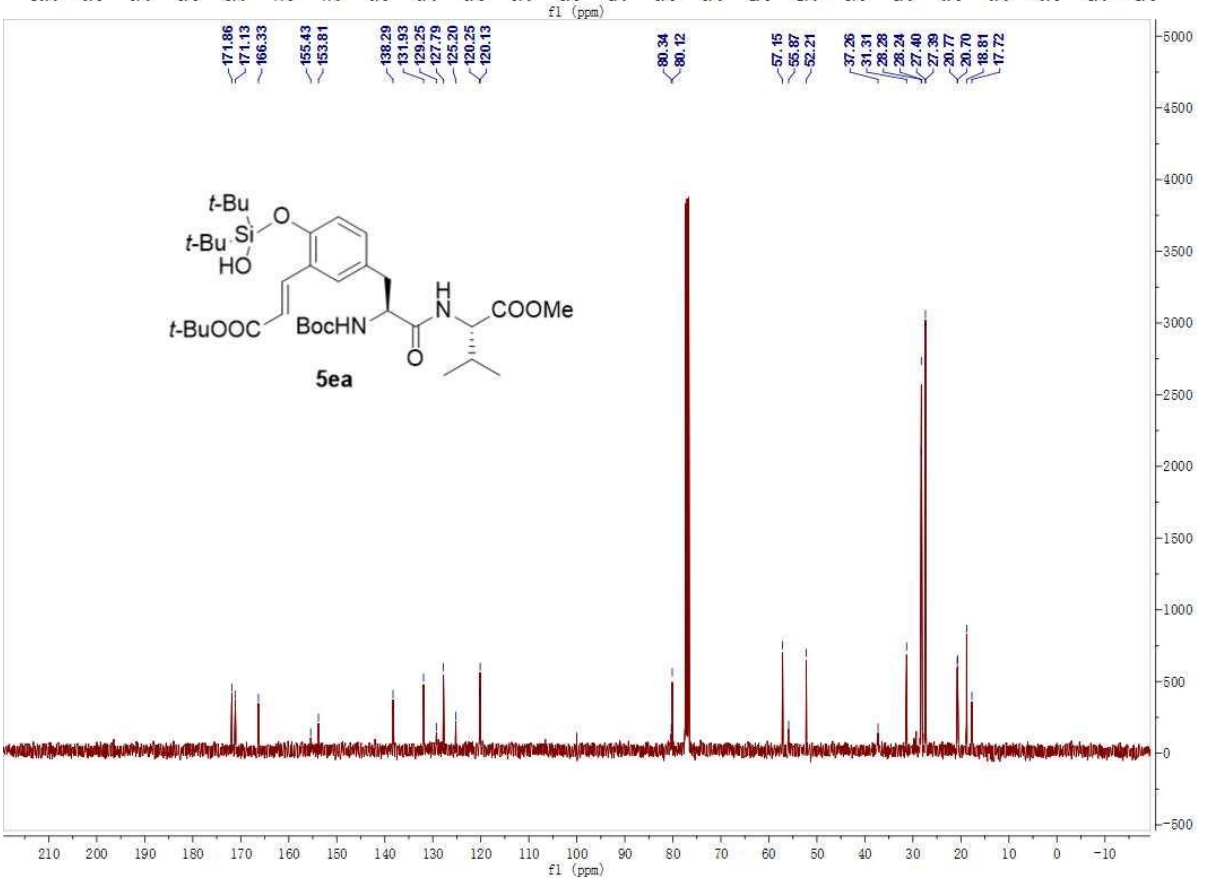
7.131
7.053
6.355
6.316
6.275
5.109
4.498
4.485
4.476
4.464
4.309
4.293
3.700
3.327
3.002
2.885
2.123
2.106
2.093
2.089
2.076
2.059
1.512
1.423
1.078
1.073
0.870
0.853
0.842
0.825
t-Bu
t-Bu
Si
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
5ea
1.04
1.09
1.08
1.07
0.97
0.93
1.00
1.13
1.14
3.22
1.03
2.08
1.14
9.28
9.13
18.09
6.02
f1 (ppm)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166.33
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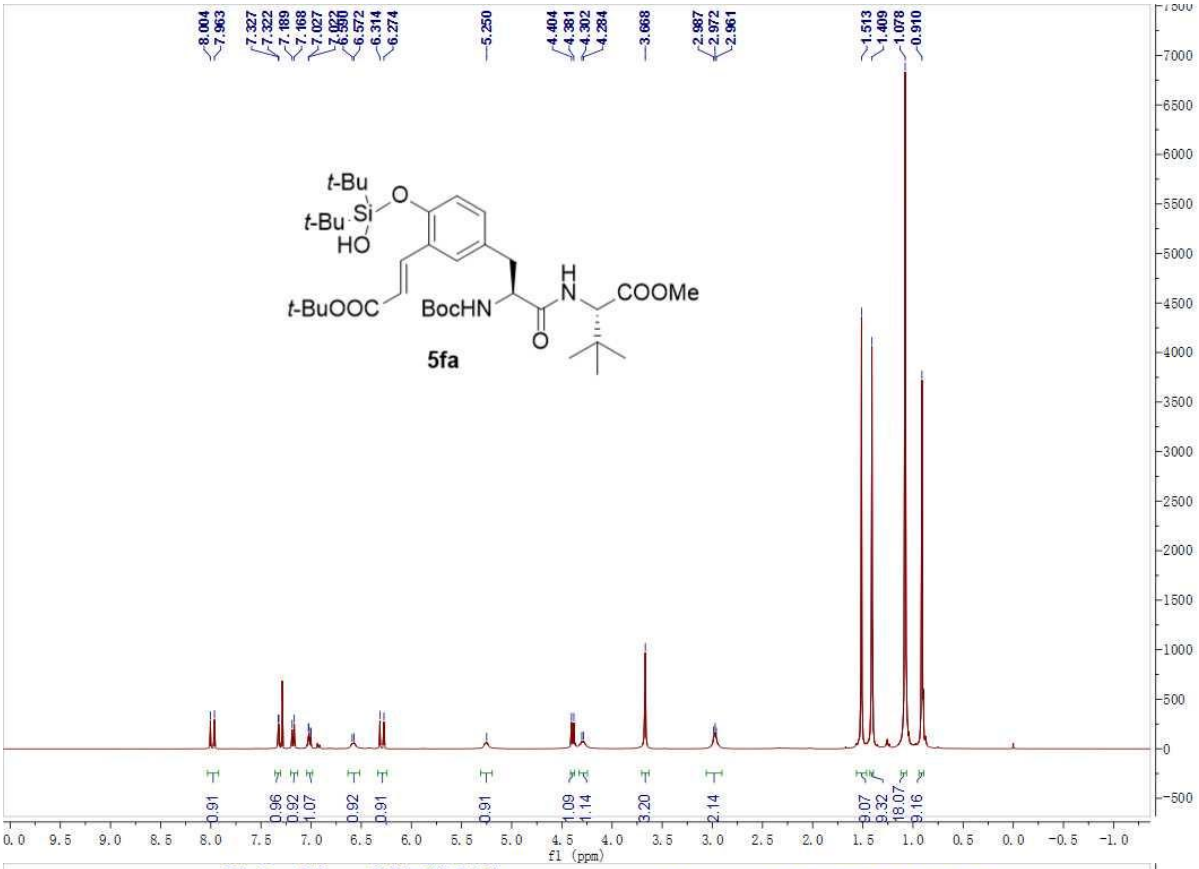
153.81
138.29
131.93
129.25
127.79
125.20
120.25
120.13
80.34
80.12
57.15
55.87
52.21
37.26
31.31
28.28
28.24
27.40
27.39
20.77
20.70
18.81
17.72
t-Bu
t-Bu
Si
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
5ea
f1 (ppm)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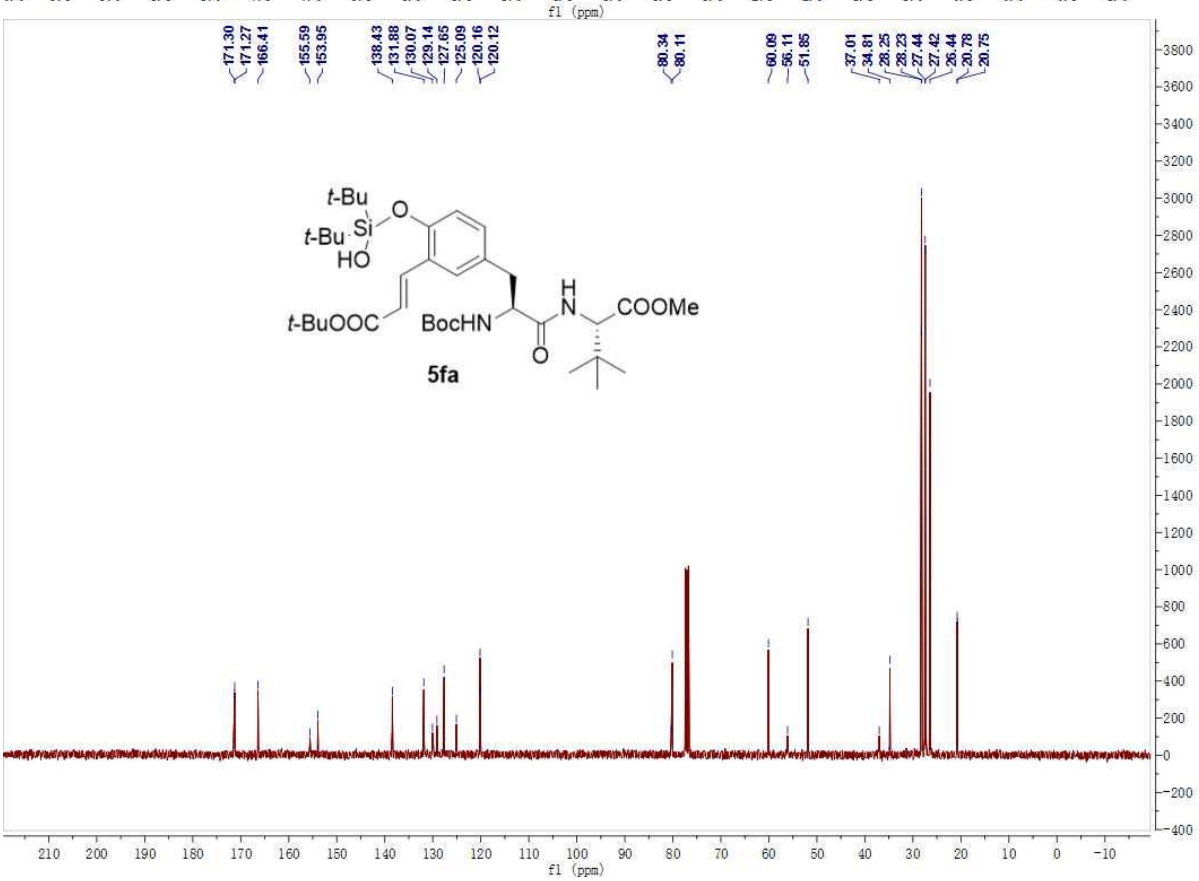
6.314
6.274
5.250
4.404
4.381
4.302
4.284
3.668
2.987
2.972
2.961
1.513
1.409
1.078
0.910
t-Bu
t-Bu
Si
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
5fa
0.91
0.96
0.92
1.07
0.92
0.91
0.91
1.09
1.14
3.20
2.14
9.07
9.32
18.07
9.16
f1 (ppm)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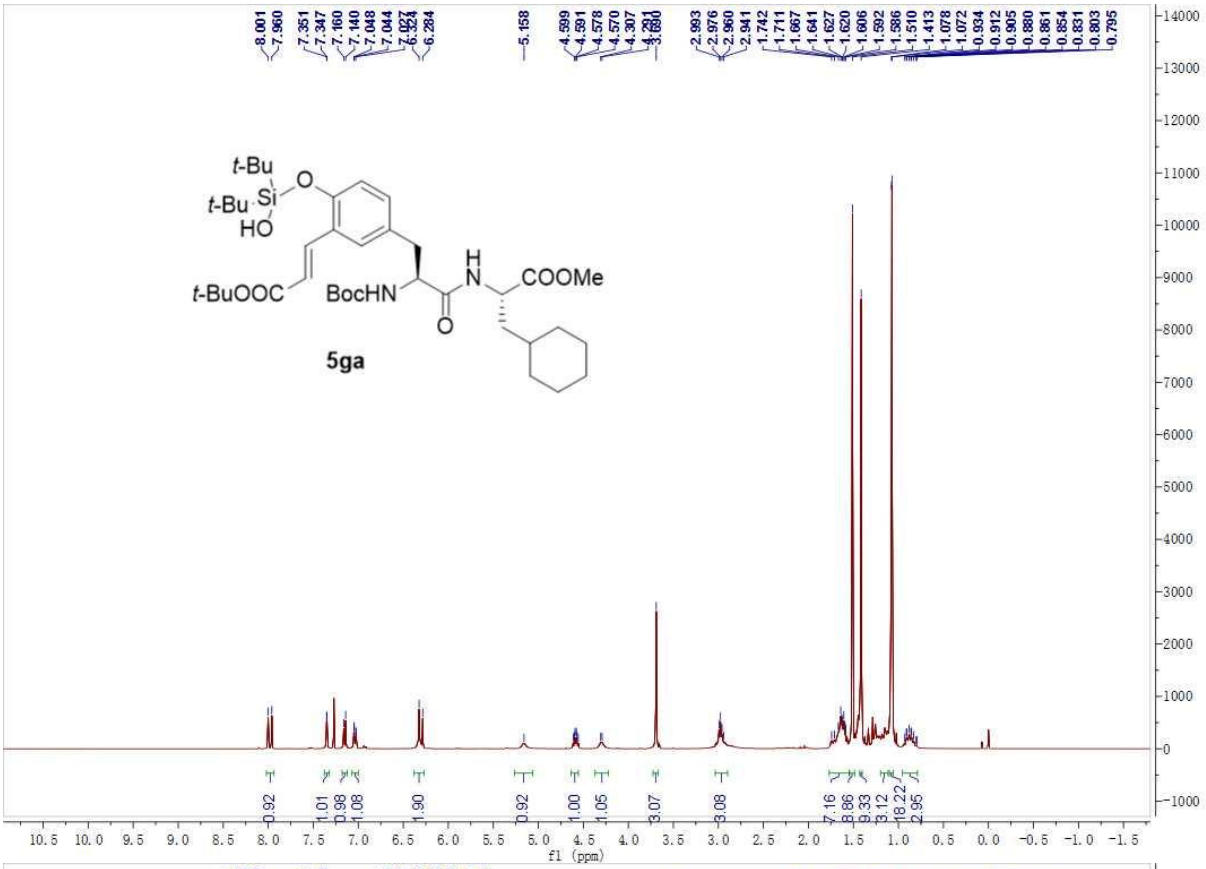
130.07
129.14
127.65
125.09
120.16
120.12
80.34
80.11
60.09
56.11
51.85
37.01
34.81
28.25
28.23
27.44
27.42
26.44
20.78
20.75
t-Bu
t-Bu
Si
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
5fa
f1 (ppm)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7.140
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7.044
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6.284
5.158
4.599
4.591
4.578
4.570
4.307
2.993
2.976
2.960
2.941
1.742
1.711
1.667
1.641
1.627
1.620
1.606
1.592
1.386
1.510
1.413
1.078
1.072
0.934
0.912
0.905
0.880
0.861
0.854
0.831
0.803
0.795
t-Bu
t-Bu
Si
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
5ga
0.92
1.01
0.98
1.08
1.90
0.92
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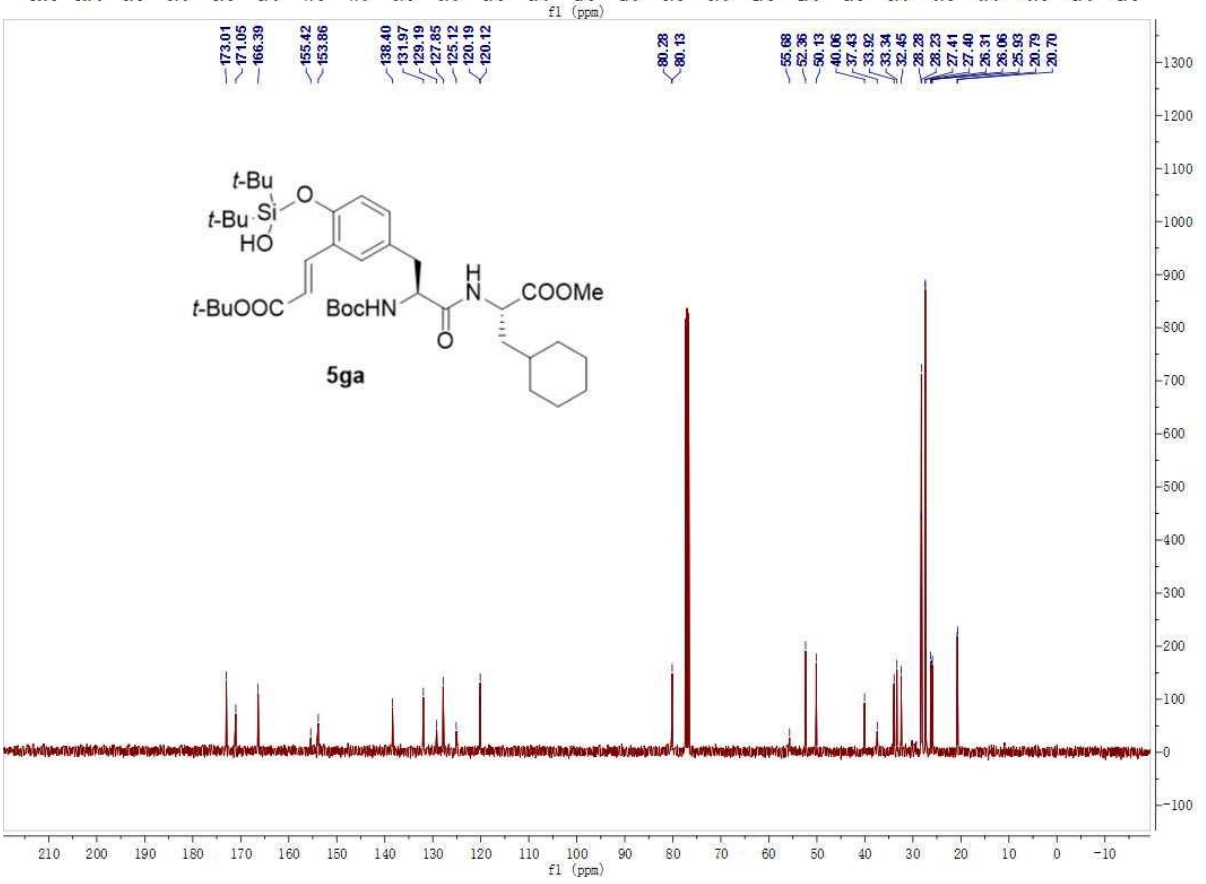
3.07
3.08
7.16
3.86
9.33
3.12
18.22
2.95
f1 (ppm)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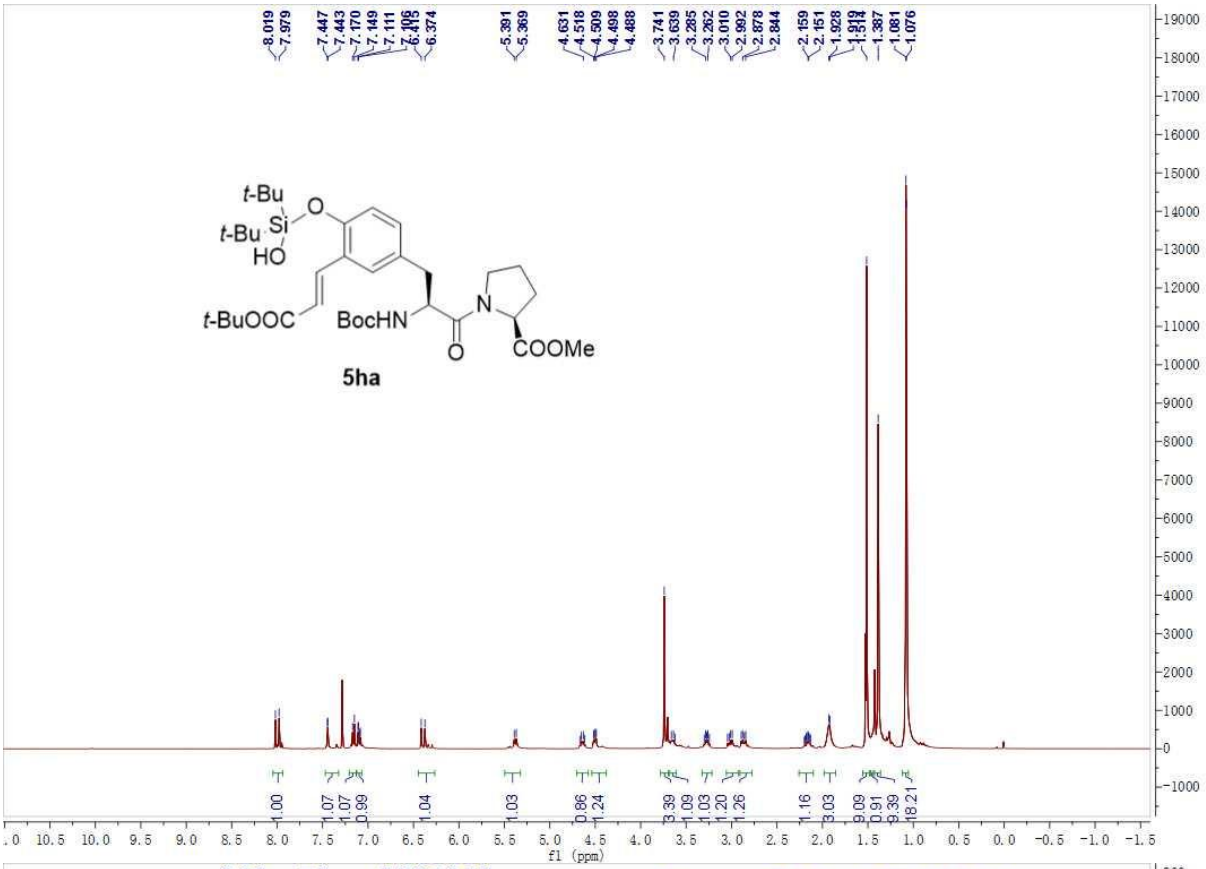
131.97
129.19
127.85
125.12
120.19
120.12
80.28
80.13
55.68
52.36
50.13
40.06
37.43
33.92
33.34
32.45
28.28
28.23
27.41
27.40
26.31
26.06
25.93
20.79
20.70
t-Bu
t-Bu
Si
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
5ga
f1 (ppm)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5.391
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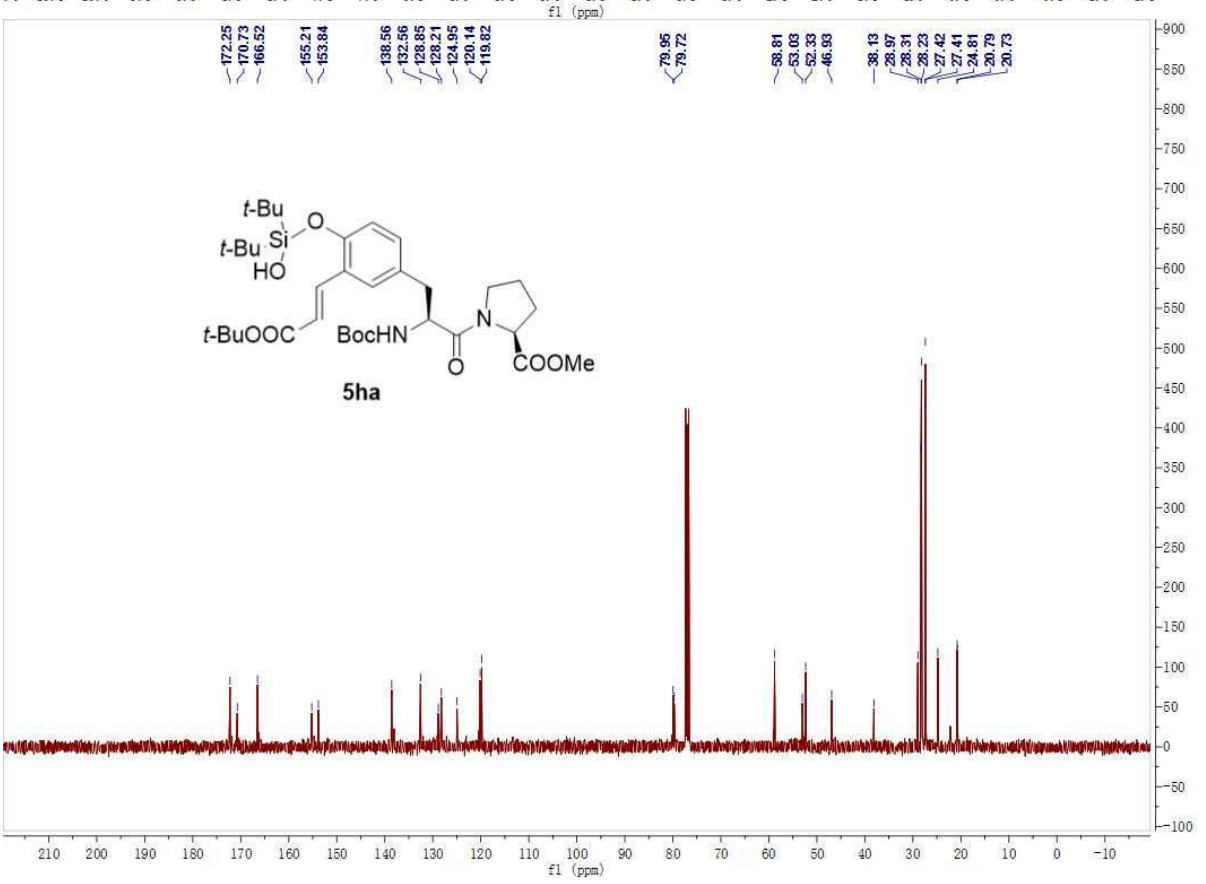
4.518
4.509
4.498
4.488
3.741
3.639
3.285
3.262
3.010
2.892
2.878
2.844
2.159
2.151
1.928
1.387
1.081
1.076
t-Bu
t-Bu
Si
O
HO
t-BuOOC
BocHN
N
O
COOMe
5ha
1.00
1.07
1.07
0.99
1.04
1.03
0.86
1.24
3.39
1.09
1.03
1.20
1.26
1.16
3.03
9.09
0.91
9.39
18.21
f1 (ppm)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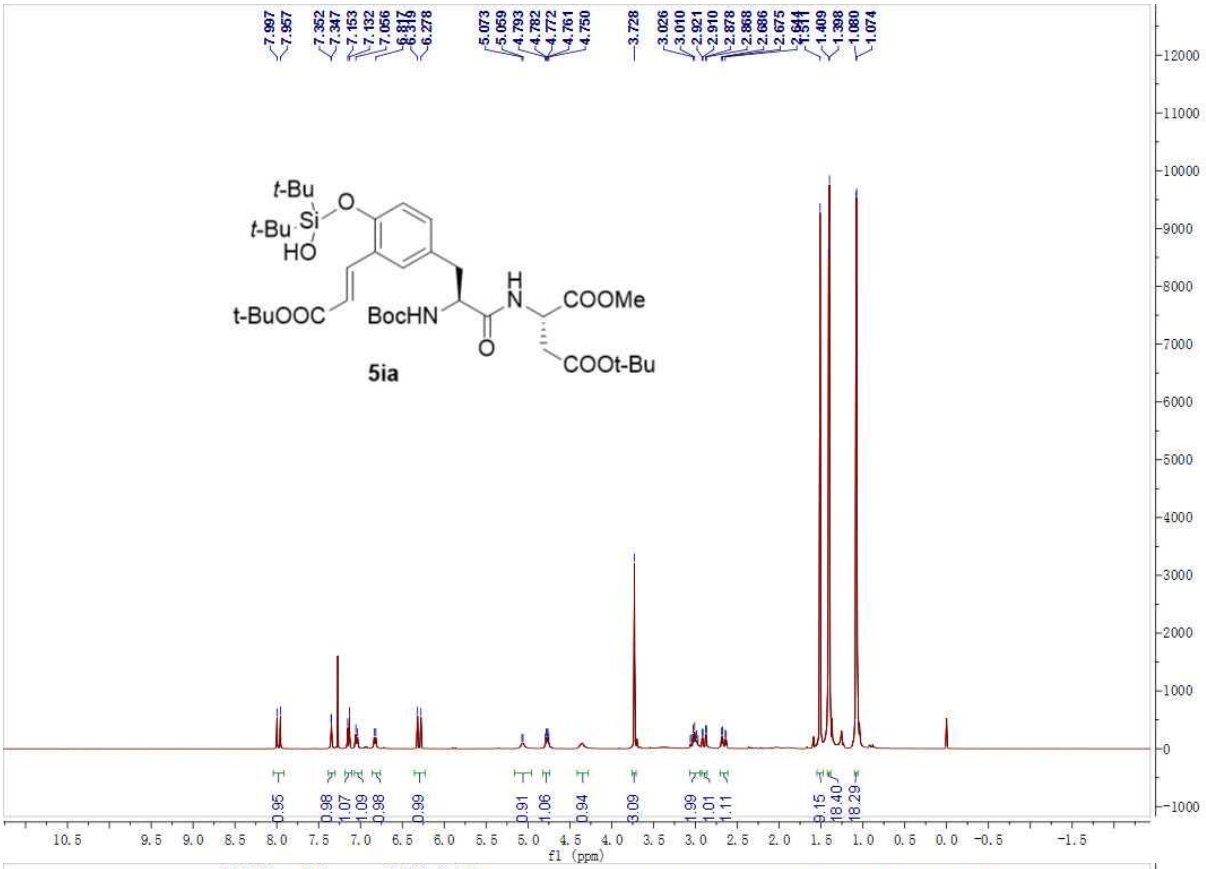
132.56
128.85
128.21
124.95
120.14
119.82
79.95
79.72
58.81
53.03
52.33
46.93
38.13
28.97
28.31
28.23
27.42
27.41
24.81
20.79
20.73
t-Bu
t-Bu
Si
O
HO
t-BuOOC
BocHN
N
O
COOMe
5ha
f1 (ppm)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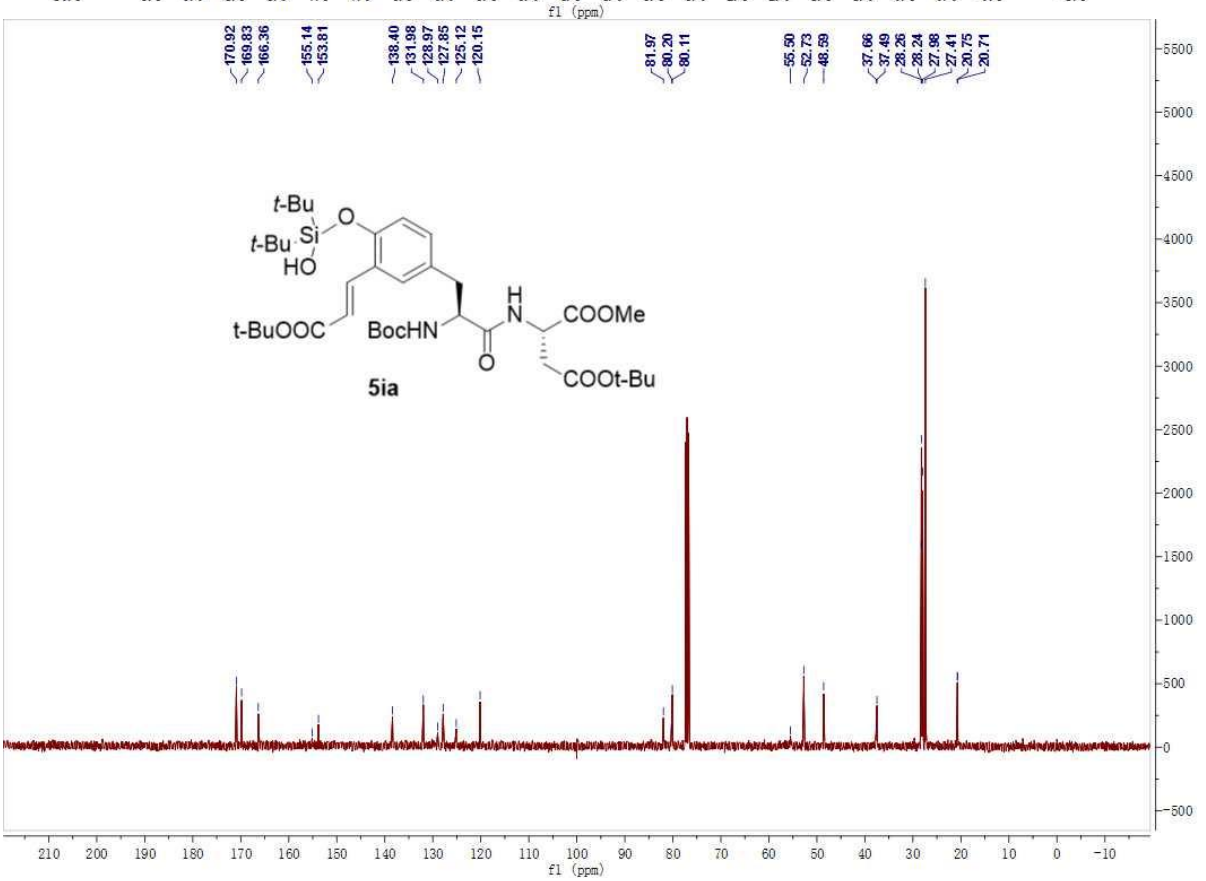
4.782
4.772
4.761
4.750
3.728
3.026
3.010
2.921
2.910
2.878
2.868
2.686
2.675
1.541
1.409
1.398
1.080
1.074
t-Bu
t-Bu
Si
O
HO
t-BuOOC
BocHN
H
N
COOMe
O
COOt-Bu
5ia
0.95
0.98
1.07
1.09
0.98
0.99
0.91
1.06
0.94
3.09
1.99
1.01
1.11
9.15
18.40
18.29
f1 (ppm)


170.92
169.83
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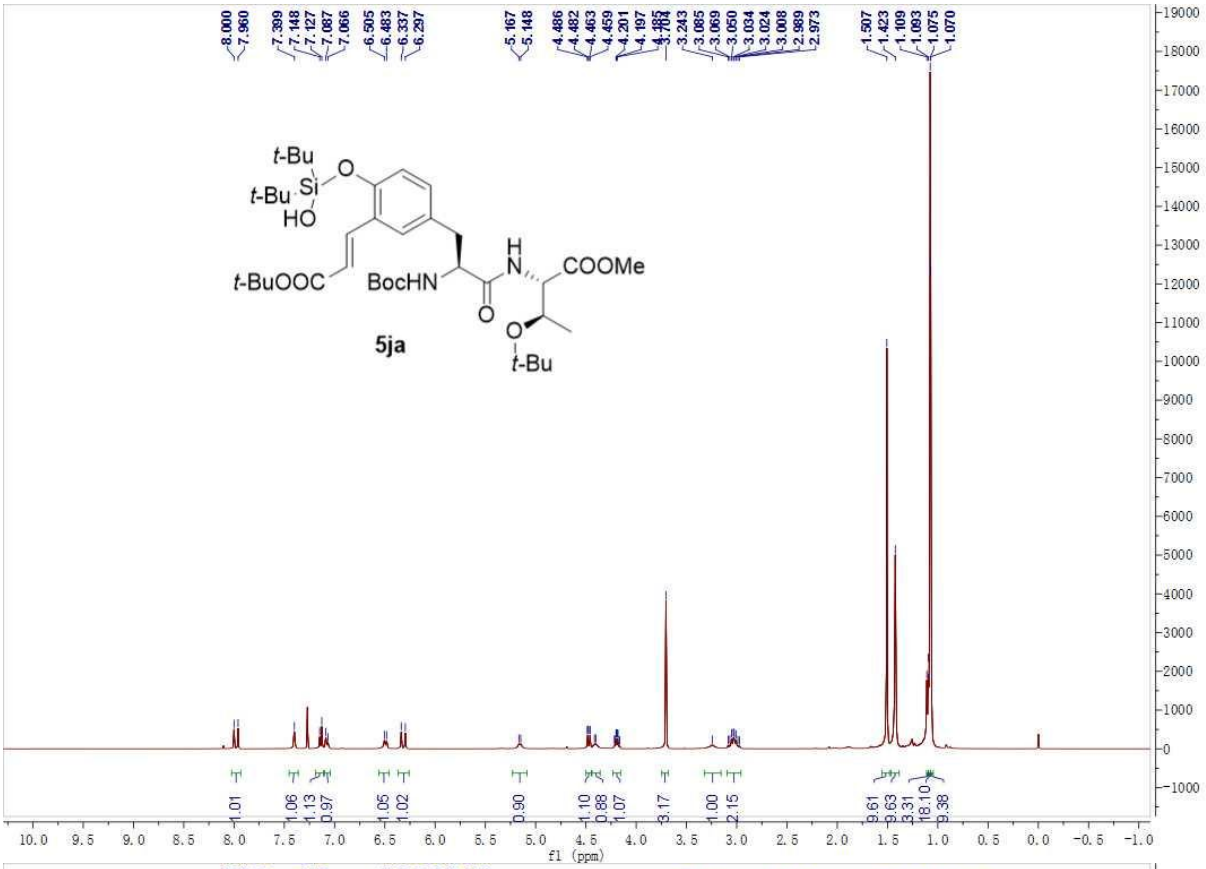
155.14
153.81
138.40
131.98
128.97
127.85
125.12
120.15
81.97
80.20
80.11
55.50
52.73
48.59
37.66
37.49
28.26
28.24
27.98
27.41
20.75
20.71
t-Bu
t-Bu
Si
O
HO
t-BuOOC
BocHN
H
N
COOMe
O
COOt-Bu
5ia
f1 (ppm)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6.337
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4.486
4.482
4.463
4.459
4.201
4.197
3.243
3.065
3.069
3.050
3.034
3.024
3.008
2.989
2.973
1.507
1.423
1.109
1.093
1.075
1.070
t-Bu
Si
t-Bu
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
O
t-Bu
5ja
1.01
1.06
1.13
0.97
1.05
1.02
0.90
1.10
0.88
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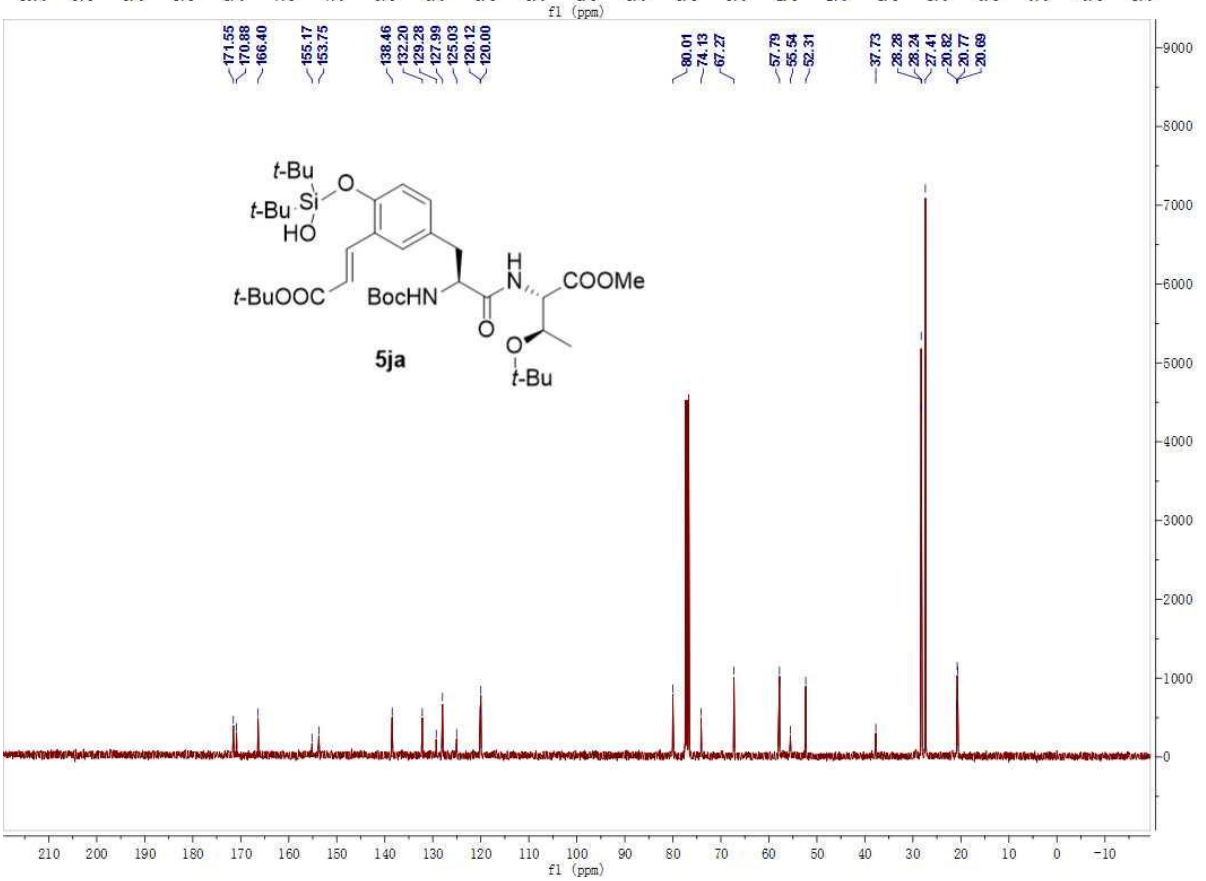
3.17
1.00
2.15
9.61
9.63
3.31
18.10
9.38
f1 (ppm)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153.75
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129.28
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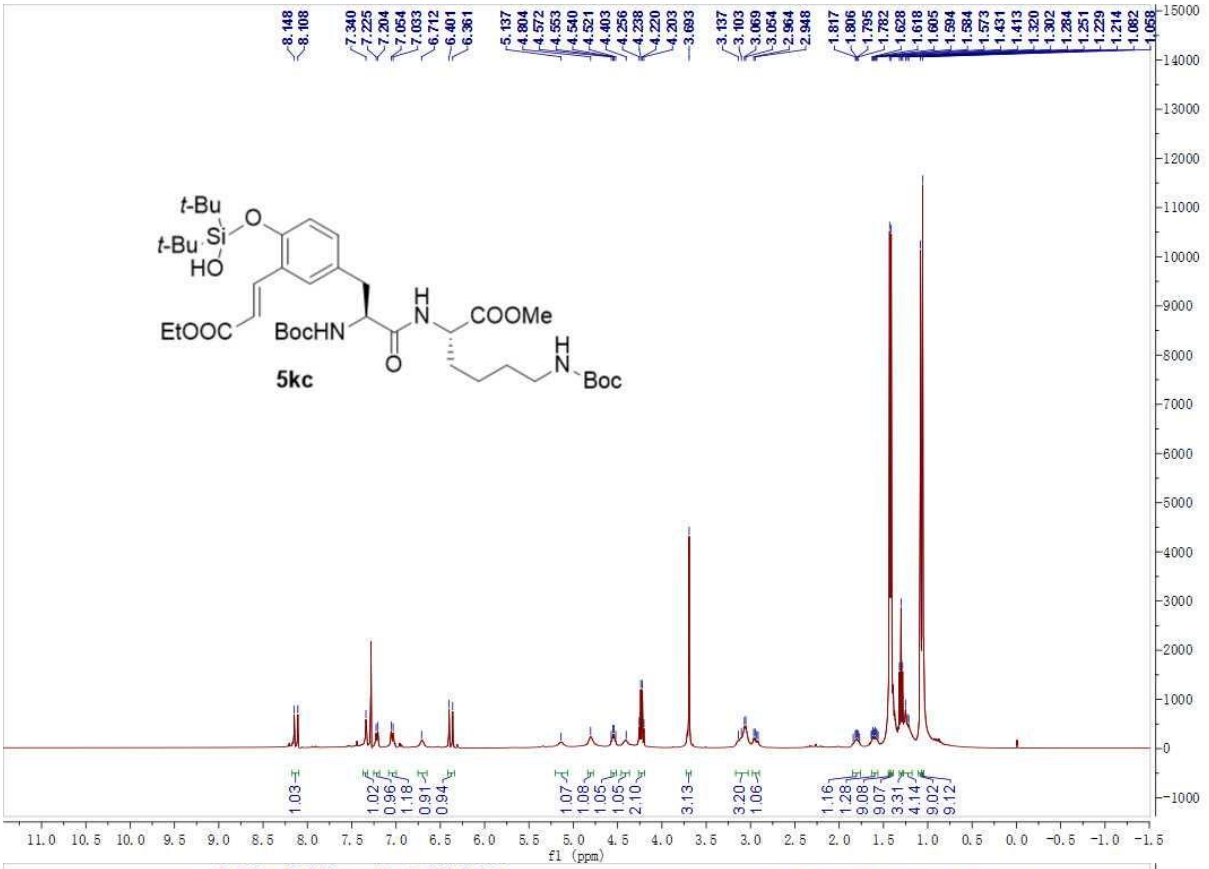
125.03
120.12
120.00
80.01
74.13
67.27
57.79
55.54
52.31
37.73
28.28
28.24
27.41
20.82
20.77
20.69
t-Bu
Si
t-Bu
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
O
t-Bu
5ja
f1 (ppm)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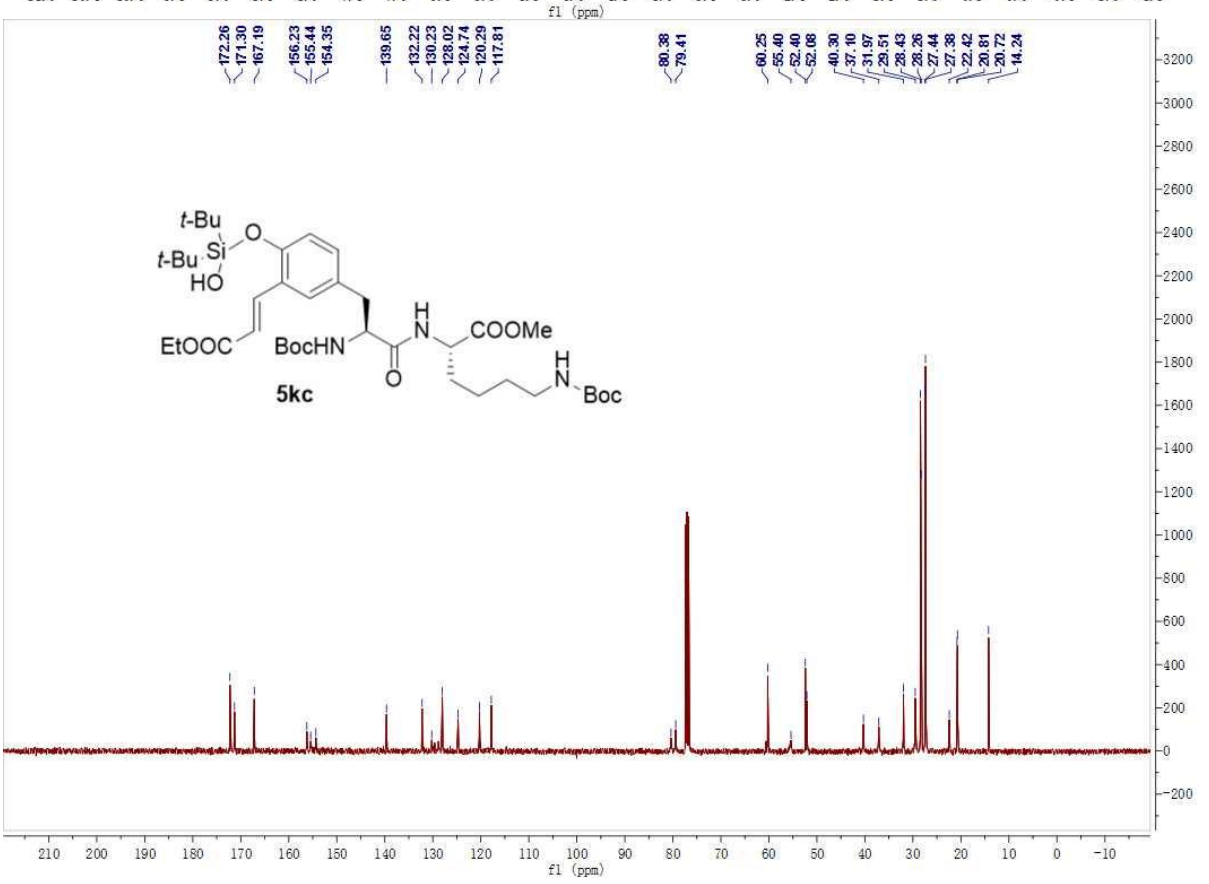
7.054
7.033
6.712
6.401
6.361
5.137
4.804
4.572
4.553
4.540
4.521
4.403
4.256
4.238
4.220
4.203
3.693
3.137
3.103
3.069
3.054
2.964
2.948
1.817
1.806
1.795
1.782
1.628
1.618
1.605
1.594
1.584
1.573
1.431
1.413
1.320
1.302
1.284
1.251
1.229
1.214
1.082
1.058
t-Bu
t-Bu
Si
O
HO
EtOOC
BocHN
H
N
O
COOMe
H
N
Boc
5kc
1.03
1.02
0.96
1.18
0.91
0.94
1.07
1.08
1.05
1.05
2.10
3.13
3.20
1.06
1.16
1.28
9.08
9.07
3.31
4.14
9.02
9.12
f1 (ppm)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139.65
132.22
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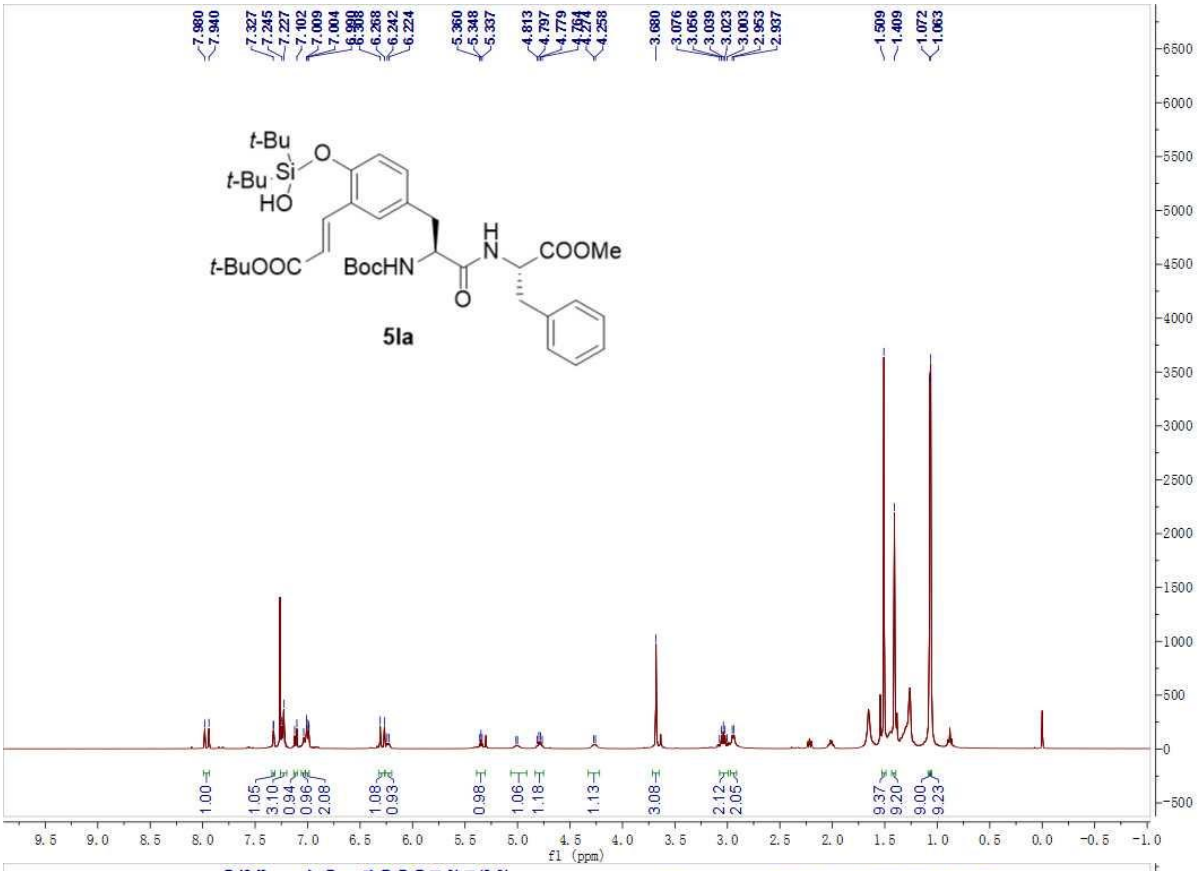
124.74
120.29
117.81
80.38
79.41
60.25
55.40
52.40
52.08
40.30
37.10
31.97
29.51
28.43
28.26
27.44
27.38
22.42
20.81
20.72
14.24
t-Bu
t-Bu
Si
O
HO
EtOOC
BocHN
H
N
O
COOMe
H
N
Boc
5kc
f1 (ppm)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7.327
7.245
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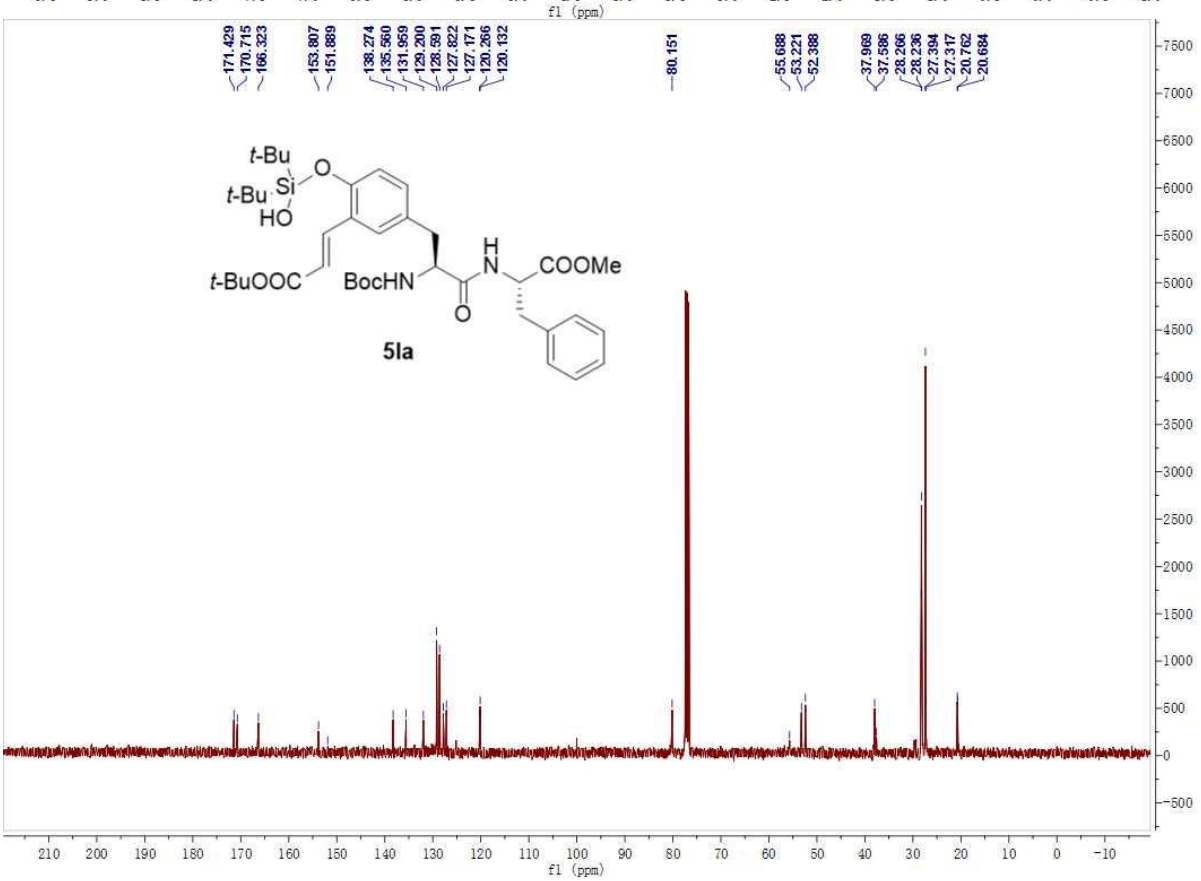
7.102
7.009
7.004
6.288
6.242
6.224
5.360
5.348
5.337
4.813
4.797
4.779
3.680
3.076
3.056
3.039
3.023
3.003
2.953
2.937
1.509
1.409
1.072
1.063
t-Bu
t-Bu
Si
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
5la
1.00
1.05
3.10
0.94
0.96
2.08
1.08
0.93
0.98
1.06
1.18
1.13
3.08
2.12
2.05
9.37
9.20
9.00
9.23
f1 (ppm)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166.323
153.807
151.889
138.274
135.560
131.959
129.200
128.591
127.822
127.171
120.266
120.132
80.151
55.688
53.221
52.388
37.969
37.586
28.266
28.236
27.394
27.317
20.762
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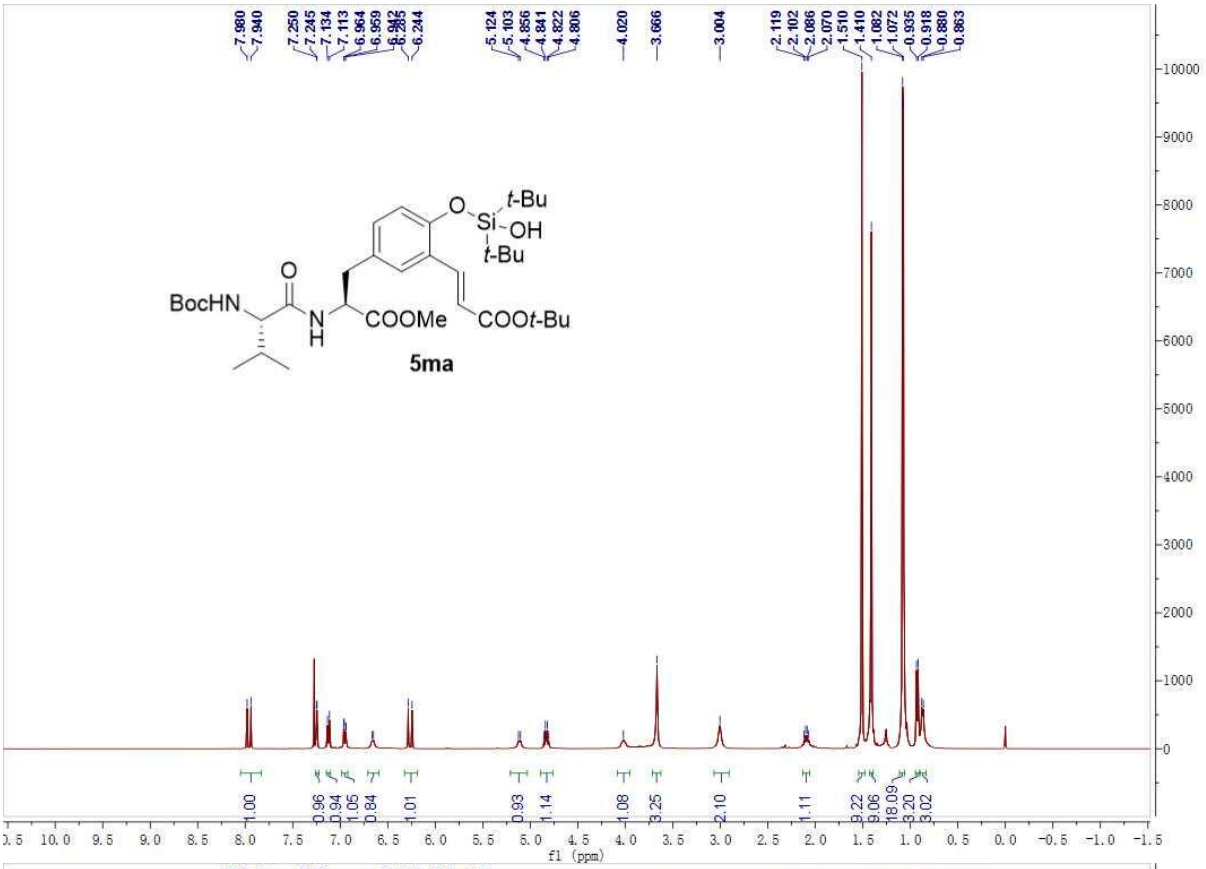
t-Bu
t-Bu
Si
HO
O
t-BuOOC
BocHN
H
N
COOMe
O
5la
f1 (ppm)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7.245
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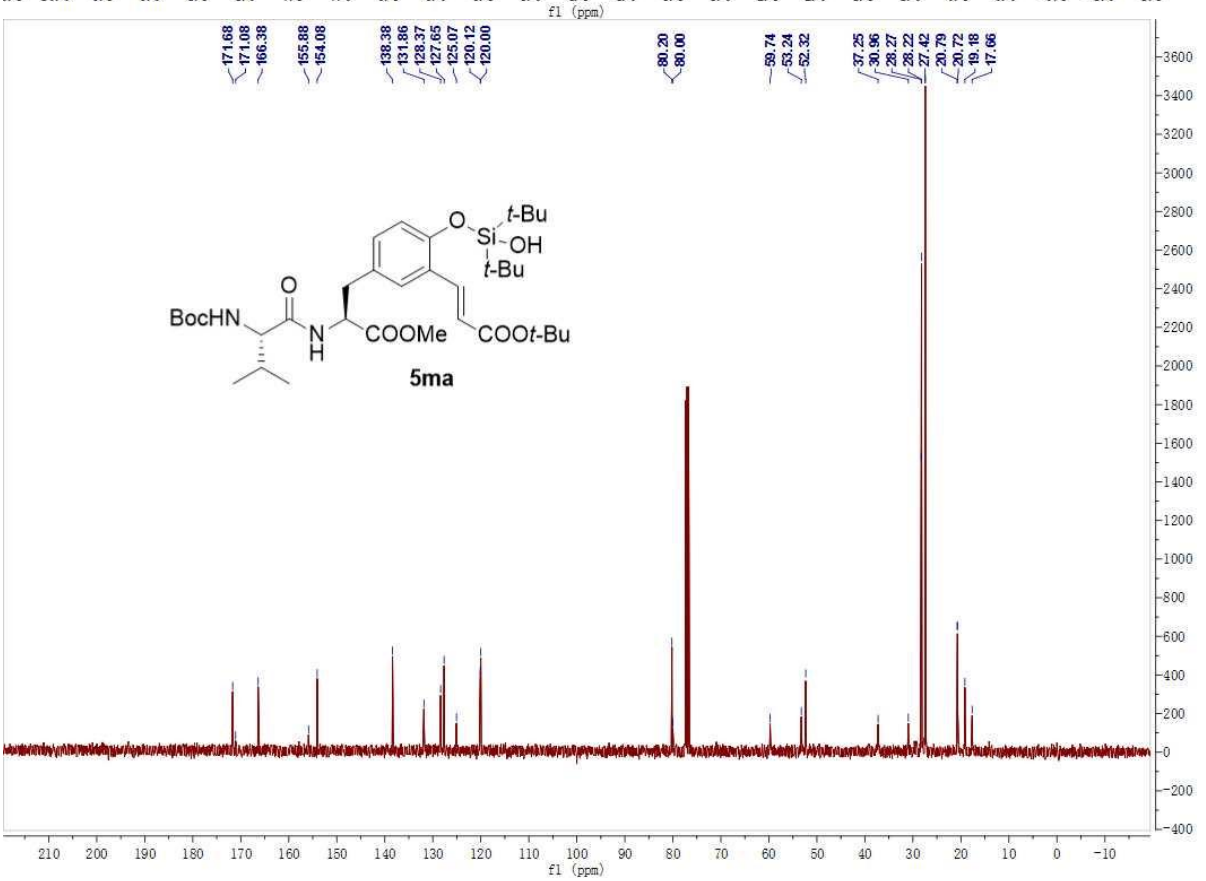
7.113
6.964
6.959
6.942
6.935
6.244
5.124
5.103
4.856
4.841
4.822
4.806
4.020
3.666
3.004
2.119
2.102
2.086
2.070
1.510
1.410
1.082
1.072
0.935
0.918
0.880
0.863
t-Bu
Si
OH
t-Bu
O
BocHN
N
H
COOMe
COOt-Bu
5ma
1.00
0.96
0.94
1.05
0.84
1.01
0.93
1.14
1.08
3.25
2.10
1.11
9.22
9.06
18.09
3.20
3.02
f1 (ppm)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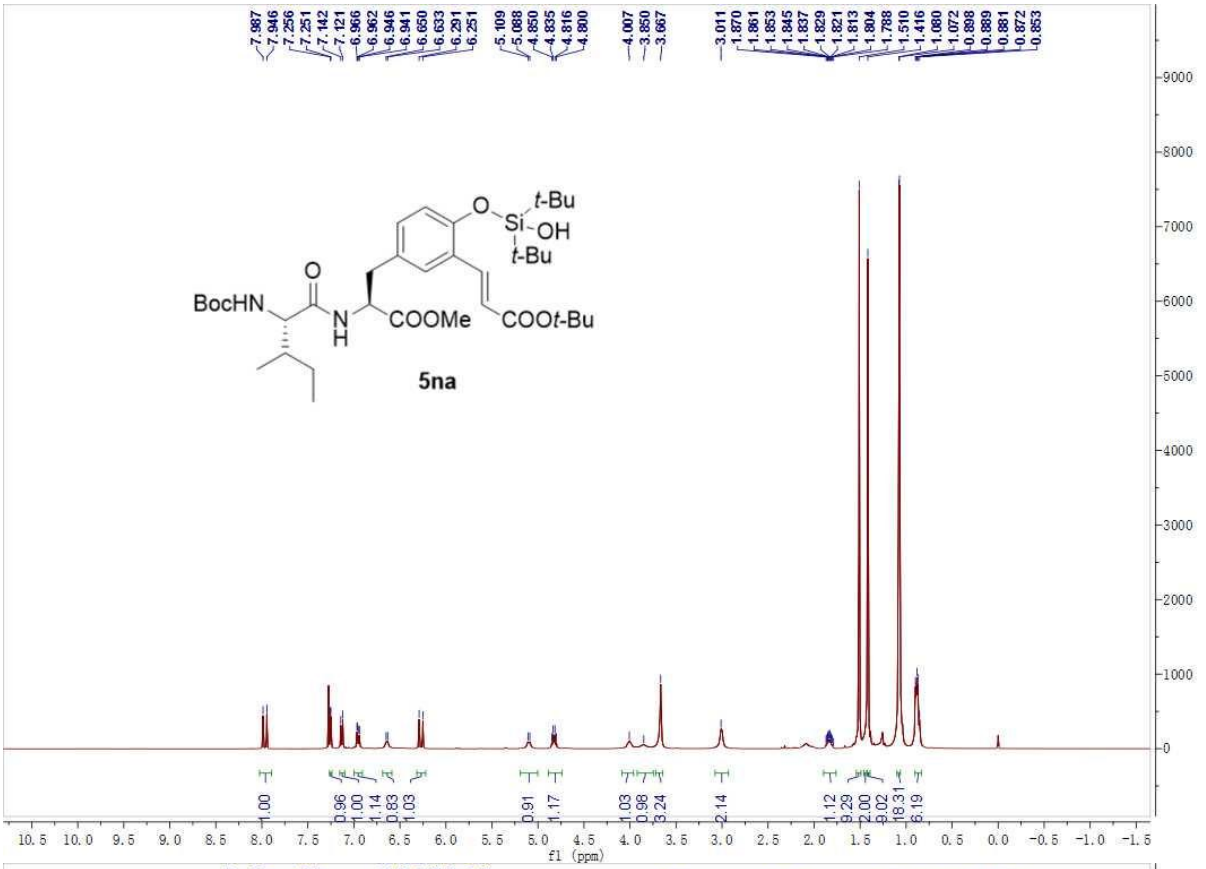
155.88
154.08
138.38
131.86
128.37
127.65
125.07
120.12
120.00
80.20
80.00
59.74
53.24
52.32
37.25
30.96
28.27
28.22
27.42
20.79
20.72
19.18
17.66
t-Bu
Si
OH
t-Bu
O
BocHN
N
H
COOMe
COOt-Bu
5ma
f1 (ppm)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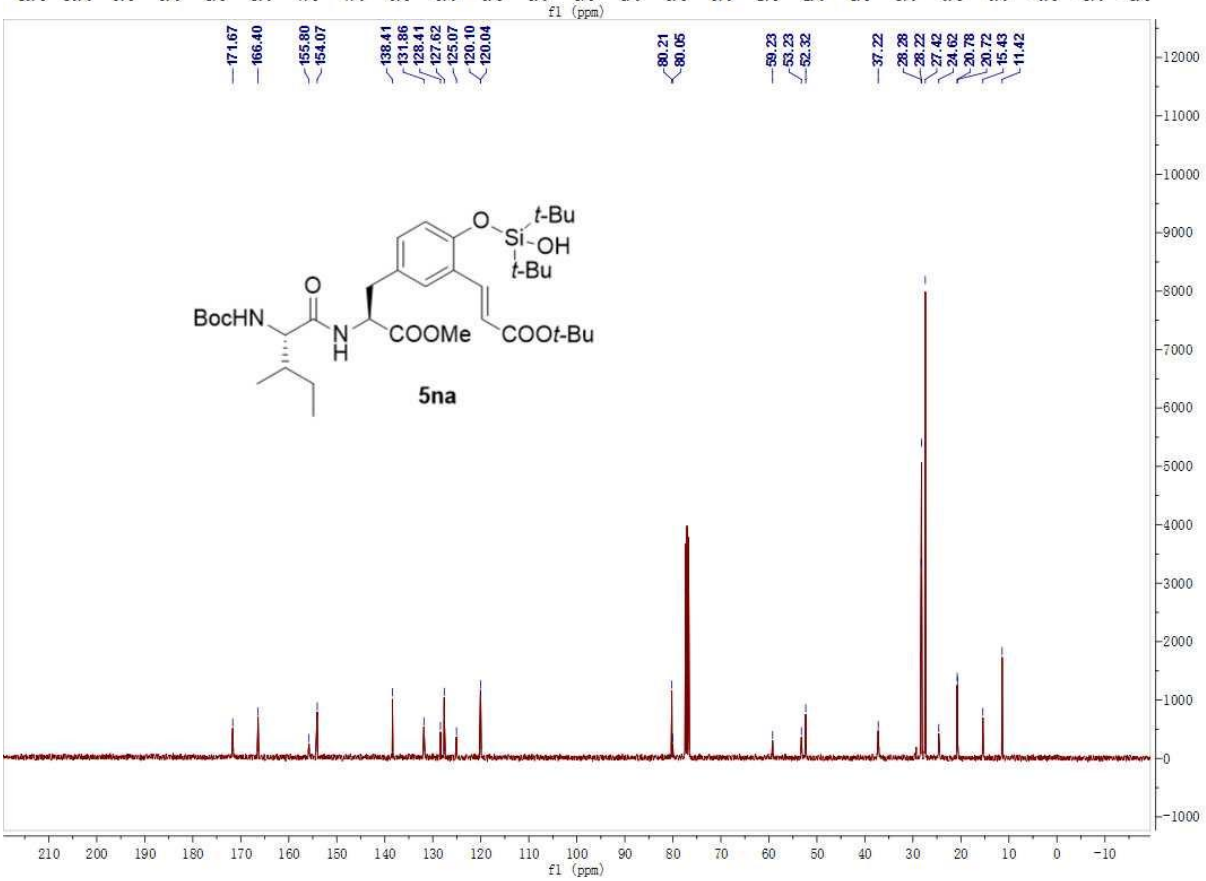
7.256
7.251
7.142
7.121
6.966
6.962
6.946
6.941
6.650
6.633
6.291
6.251
5.109
5.088
4.850
4.835
4.816
4.800
4.007
3.850
3.667
3.011
1.870
1.861
1.853
1.845
1.837
1.829
1.821
1.813
1.804
1.788
1.510
1.416
1.080
1.072
0.898
0.889
0.881
0.872
0.853
t-Bu
Si
OH
t-Bu
O
BocHN
N
H
COOMe
COOt-Bu
5na
1.00
0.96
1.00
1.14
0.83
1.03
0.91
1.17
1.03
0.98
3.24
2.14
1.12
9.29
2.00
9.02
18.31
6.19
f1 (ppm)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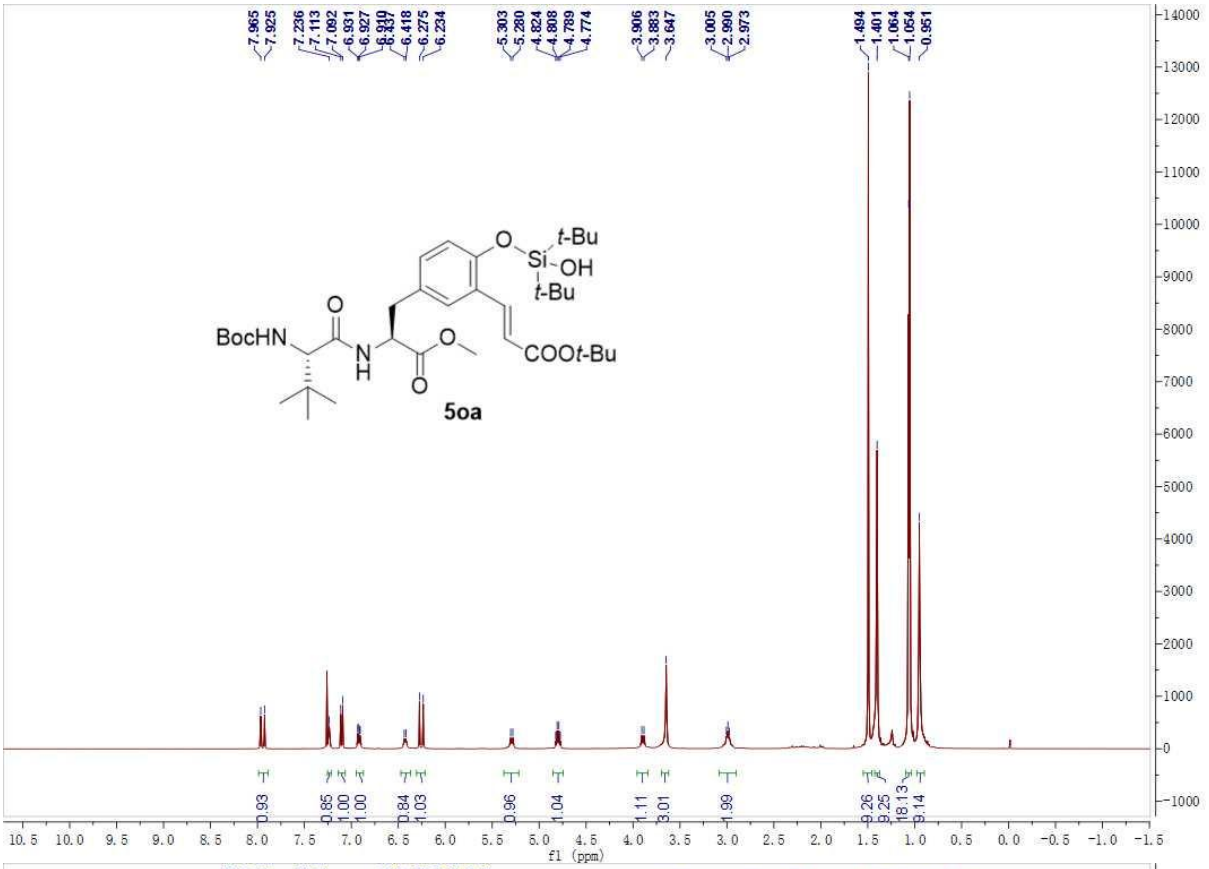
128.41
127.62
125.07
120.10
120.04
80.21
80.05
59.23
53.23
52.32
37.22
28.28
28.22
27.42
24.62
20.78
20.72
15.43
11.42
t-Bu
Si
OH
t-Bu
O
BocHN
N
H
COOMe
COOt-Bu
5na
f1 (ppm)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7.113
7.092
6.931
6.927
6.275
6.234
5.303
5.280
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4.808
4.789
4.774
3.906
3.883
3.647
3.005
2.990
2.973
1.494
1.401
1.064
1.054
0.951
t-Bu
Si
OH
t-Bu
BocHN
N
H
COOt-Bu
5oa
0.93
0.85
1.00
1.00
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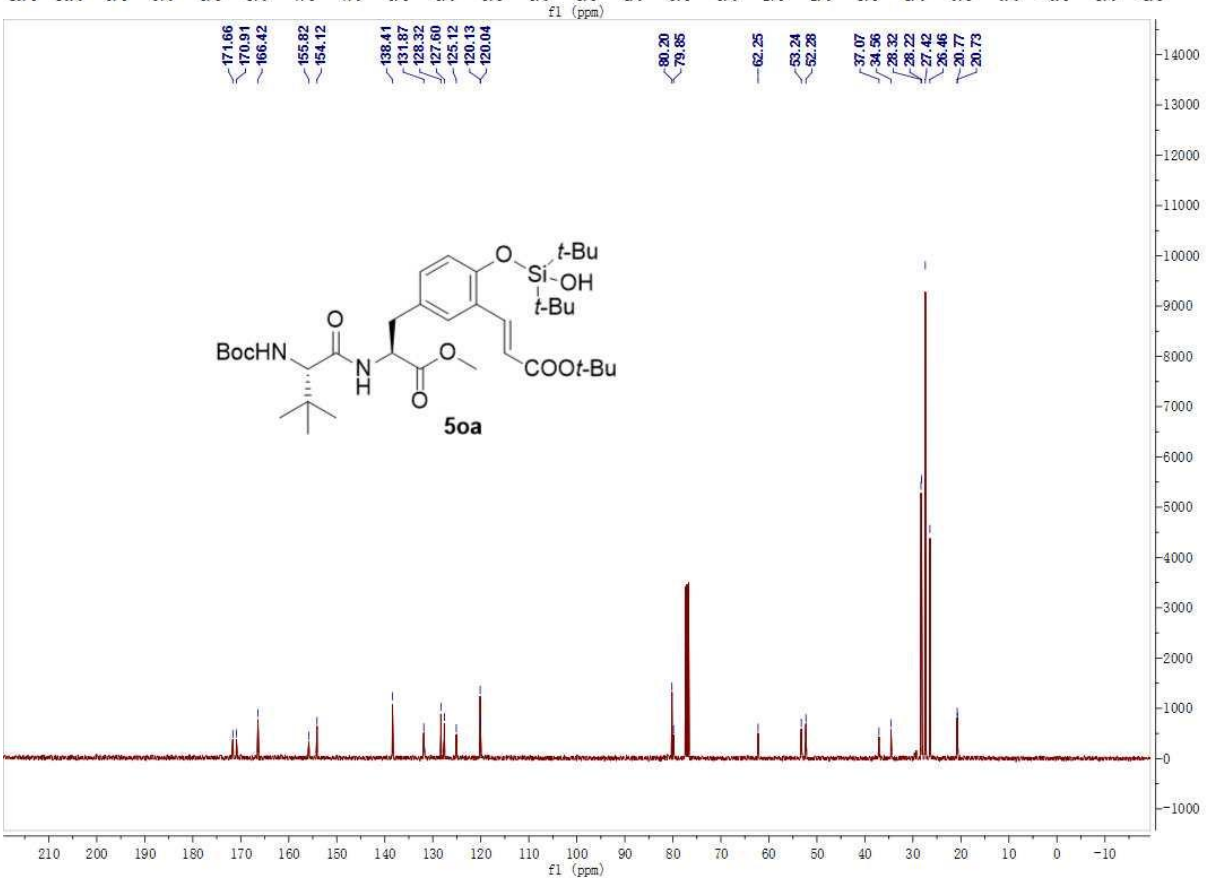
1.03
0.96
1.04
1.11
3.01
1.99
9.26
9.25
18.13
9.14
f1 (ppm)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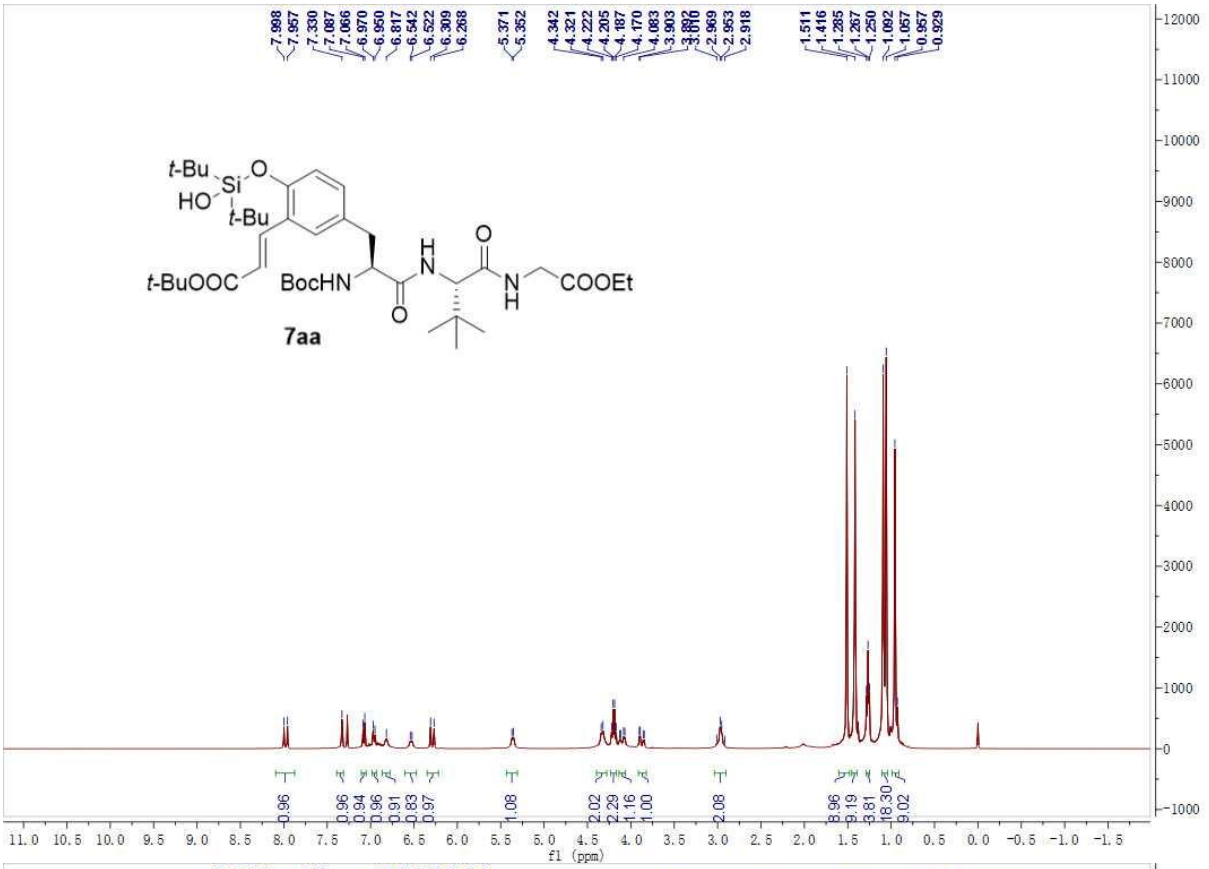
138.41
131.87
128.32
127.60
125.12
120.13
120.04
80.20
79.85
62.25
53.24
52.28
37.07
34.56
28.32
28.22
27.42
26.46
20.77
20.73
t-Bu
Si
OH
t-Bu
BocHN
N
H
COOt-Bu
5oa
f1 (ppm)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7.066
6.970
6.950
6.817
6.542
6.522
6.309
6.268
5.371
5.352
4.342
4.321
4.222
4.205
4.187
4.170
4.083
3.903
3.882
3.016
2.969
2.953
2.918
1.511
1.416
1.285
1.267
1.250
1.092
1.057
0.957
0.929
t-Bu
HO
Si
O
t-Bu
t-BuOOC
BocHN
H
N
O
O
N
H
COOEt
7aa
0.96
0.96
0.94
0.96
0.91
0.83
0.97
1.08
2.02
2.29
1.16
1.00
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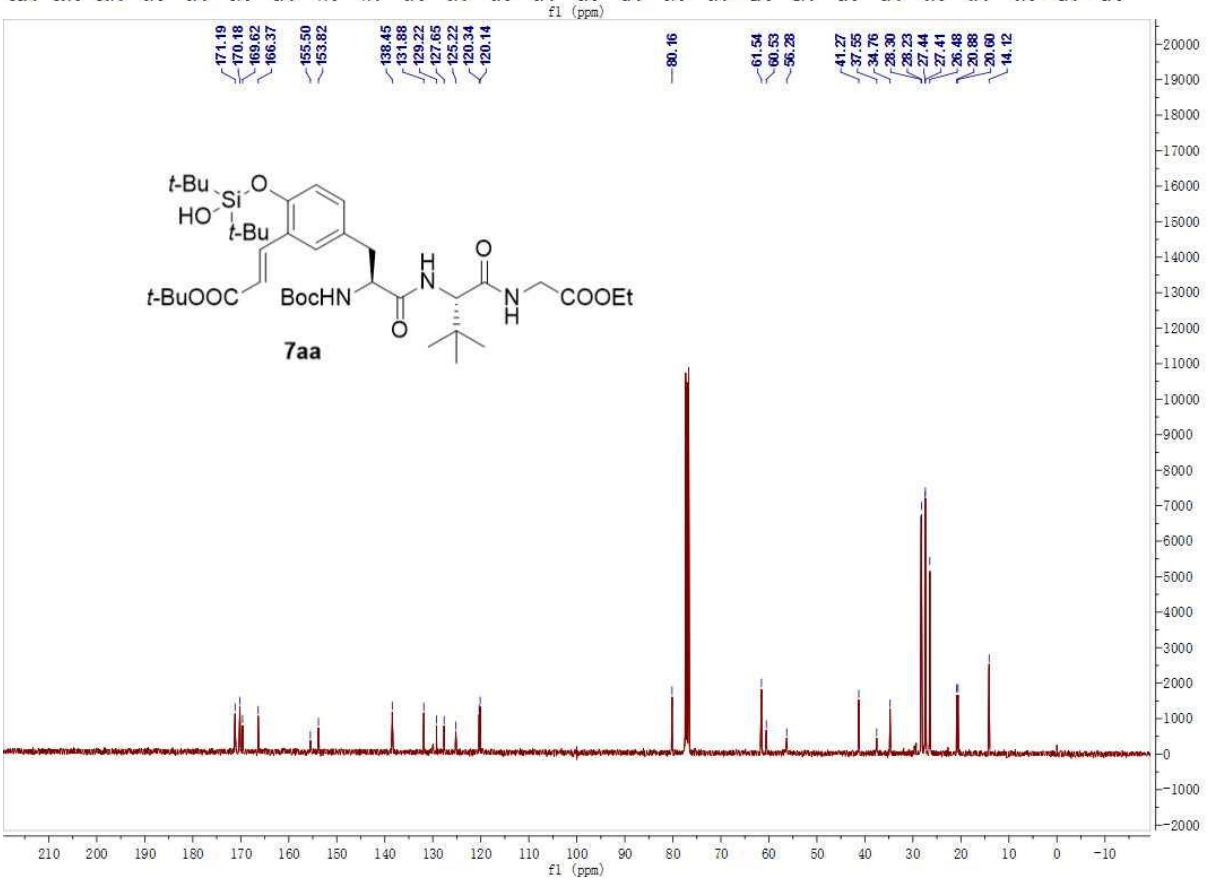
8.96
9.19
3.81
18.30
9.02
f1 (ppm)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170.18
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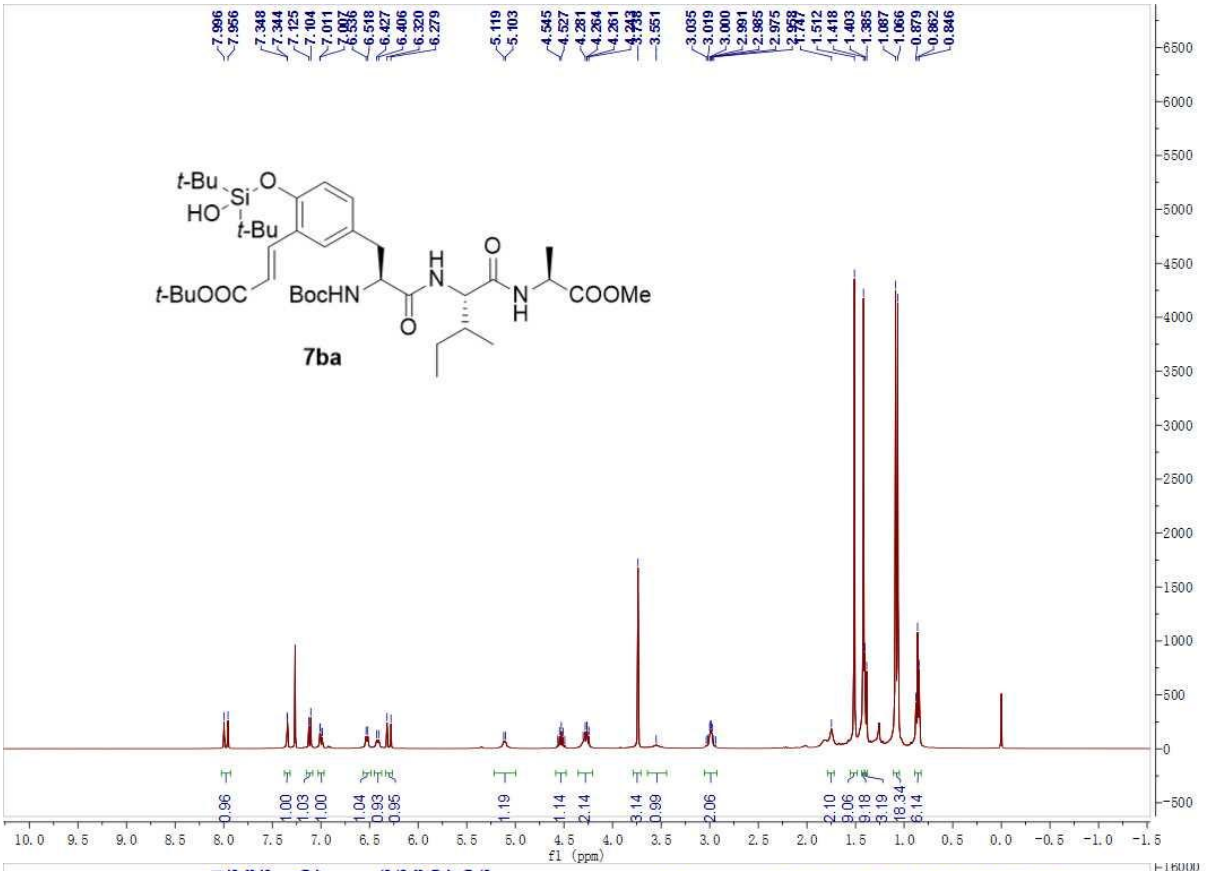
153.82
138.45
131.88
129.22
127.65
125.22
120.34
120.14
80.16
61.54
60.53
56.28
41.27
37.55
34.76
28.30
28.23
27.44
27.41
26.48
20.88
20.60
14.12
t-Bu
HO
Si
O
t-Bu
t-BuOOC
BocHN
H
N
O
O
N
H
COOEt
7aa
f1 (ppm)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7.344
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7.011
6.518
6.427
6.406
6.320
6.279
5.119
5.103
4.545
4.527
4.281
4.264
4.261
3.738
3.551
3.035
3.019
3.000
2.991
2.985
2.975
1.512
1.418
1.403
1.385
1.087
1.066
0.879
0.862
0.846
t-Bu
HO
Si
O
t-Bu
t-BuOOC
BocHN
H
N
O
N
H
COOMe
O
7ba
0.96
1.00
1.03
1.00
1.04
0.93
0.95
1.19
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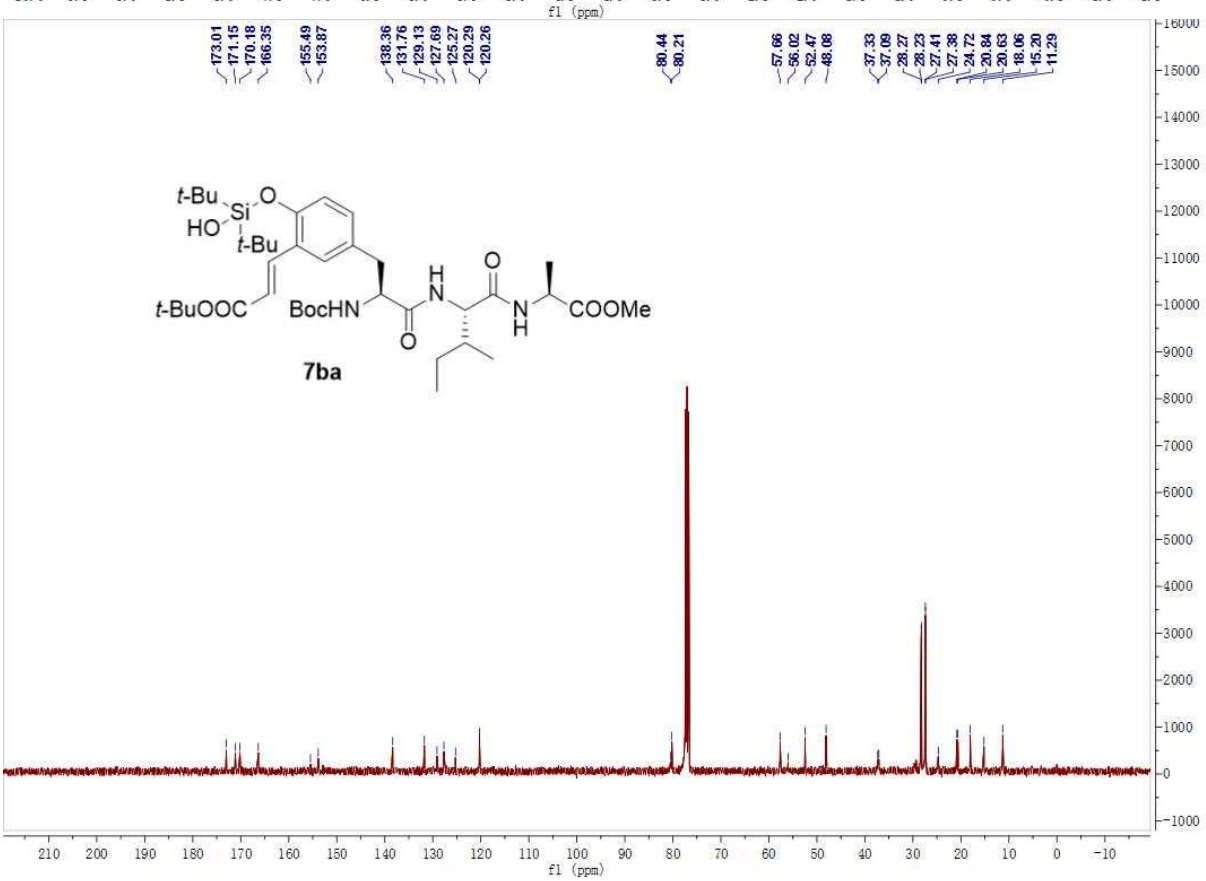
2.14
3.14
0.99
2.06
2.10
9.06
9.18
3.19
18.34
6.14
f1 (ppm)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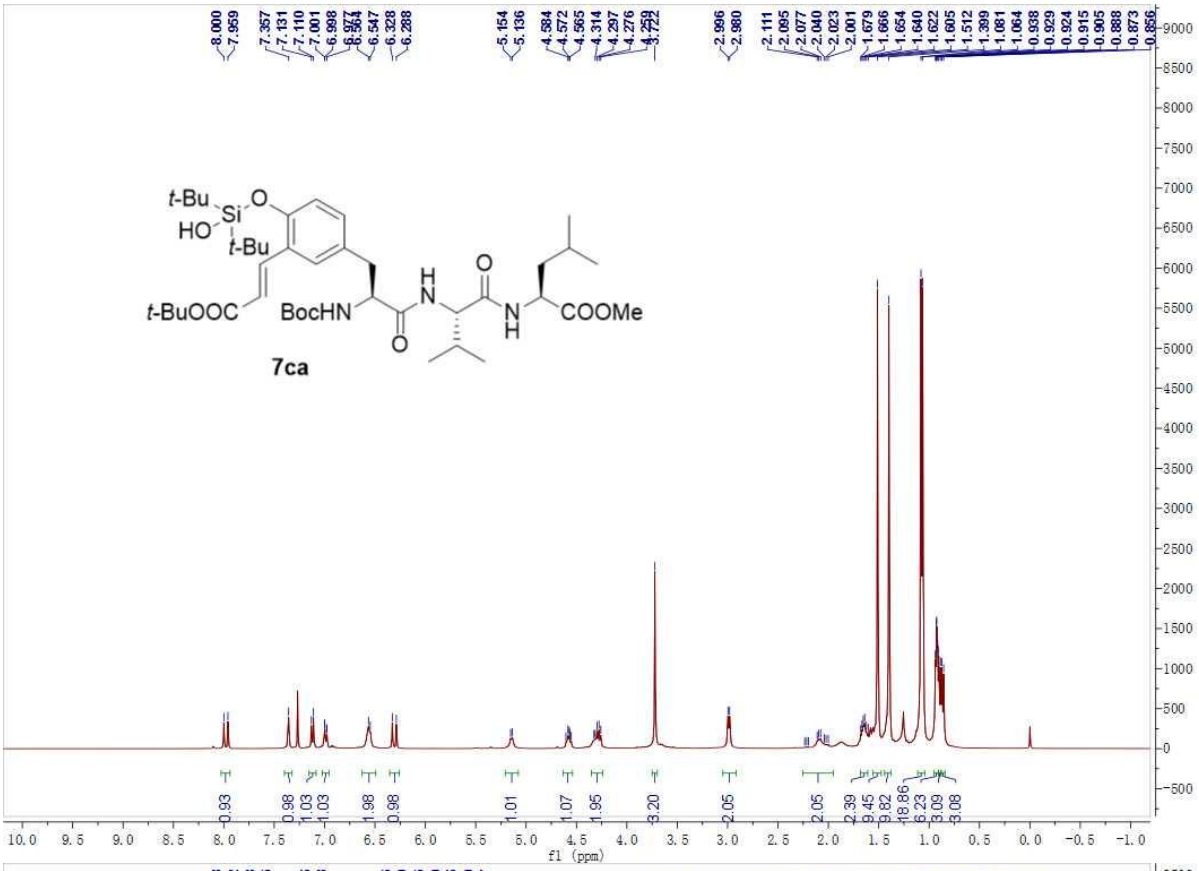
120.26
80.44
80.21
57.66
56.02
52.47
48.08
37.33
37.09
28.27
28.23
27.41
27.38
24.72
20.84
20.63
18.06
15.20
11.29
t-Bu
HO
Si
O
t-Bu
t-BuOOC
BocHN
H
N
O
N
H
COOMe
O
7ba
f1 (ppm)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6.288
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5.136
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4.565
4.314
4.297
4.276
3.722
2.996
2.980
2.111
2.095
2.077
2.040
2.023
2.001
1.679
1.666
1.654
1.640
1.622
1.605
1.512
1.399
1.081
1.064
0.938
0.929
0.924
0.915
0.905
0.888
0.873
0.856
t-Bu
HO
Si
O
t-Bu
t-BuOOC
BocHN
H
N
O
O
H
N
COOMe
7ca
0.93
0.98
1.03
1.03
1.98
0.98
1.01
1.07
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3.20
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2.05
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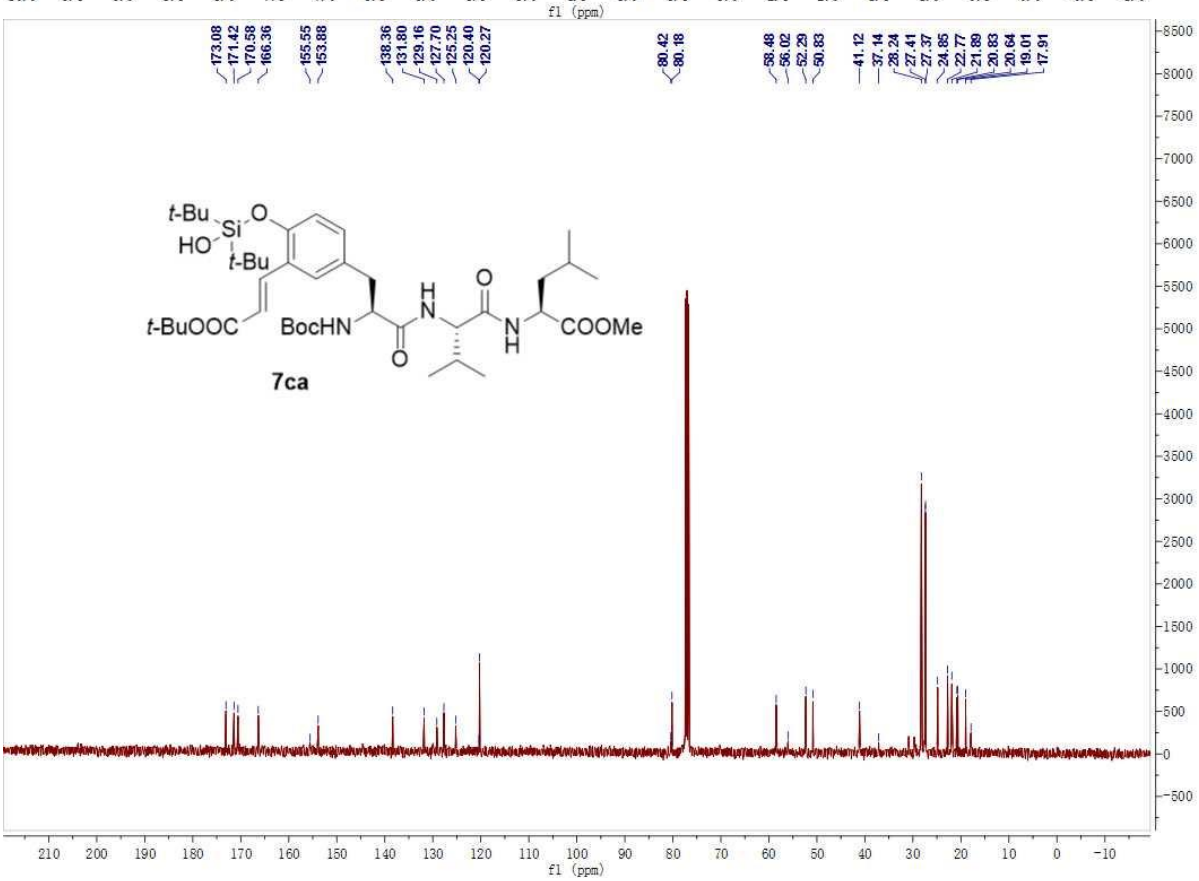
9.45
9.82
18.86
8.23
3.09
3.08
f1 (ppm)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120.27
80.42
80.18
58.48
56.02
52.29
50.83
41.12
37.14
28.24
27.41
27.37
24.85
22.77
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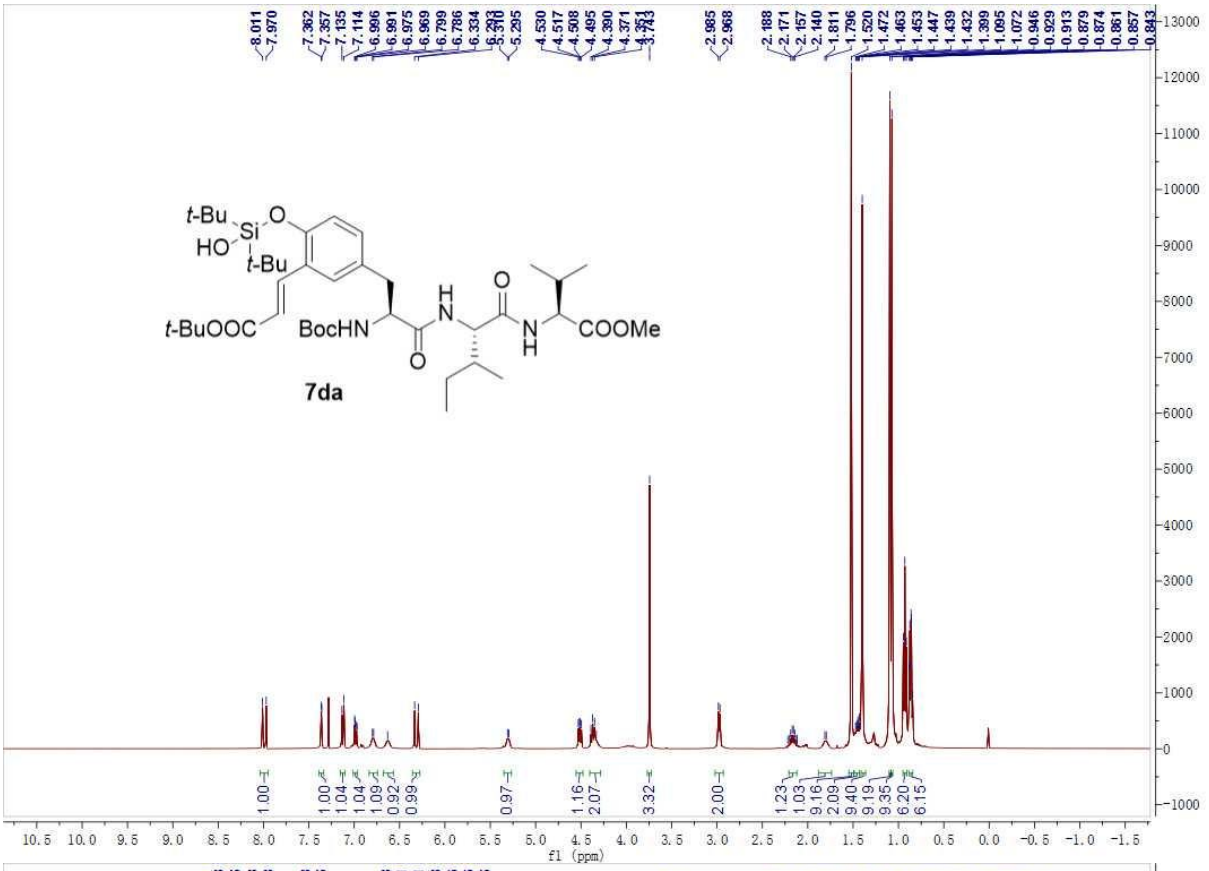
20.83
20.64
19.01
17.91
t-Bu
HO
Si
O
t-Bu
t-BuOOC
BocHN
H
N
O
O
H
N
COOMe
7ca
f1 (ppm)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HO
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BocHN
H
N
O
N
H
COOMe
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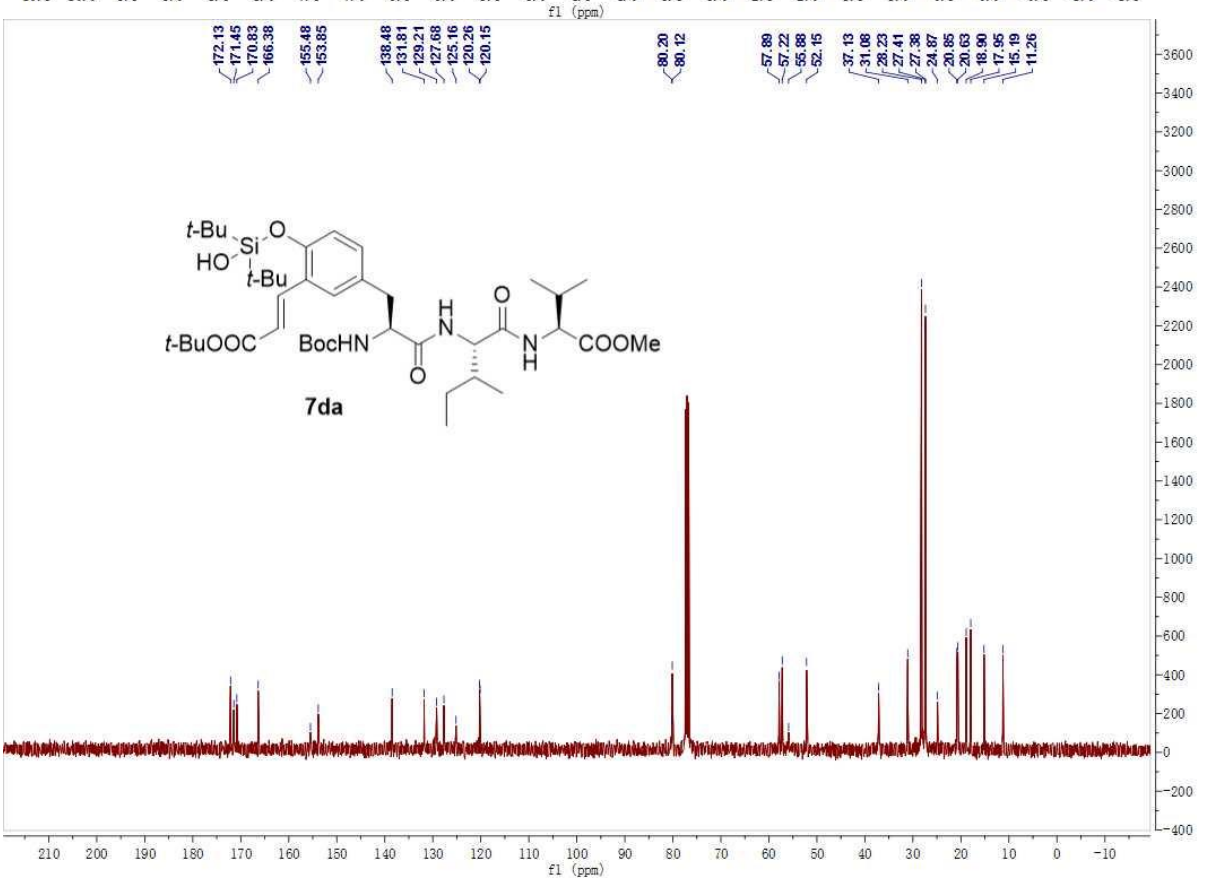
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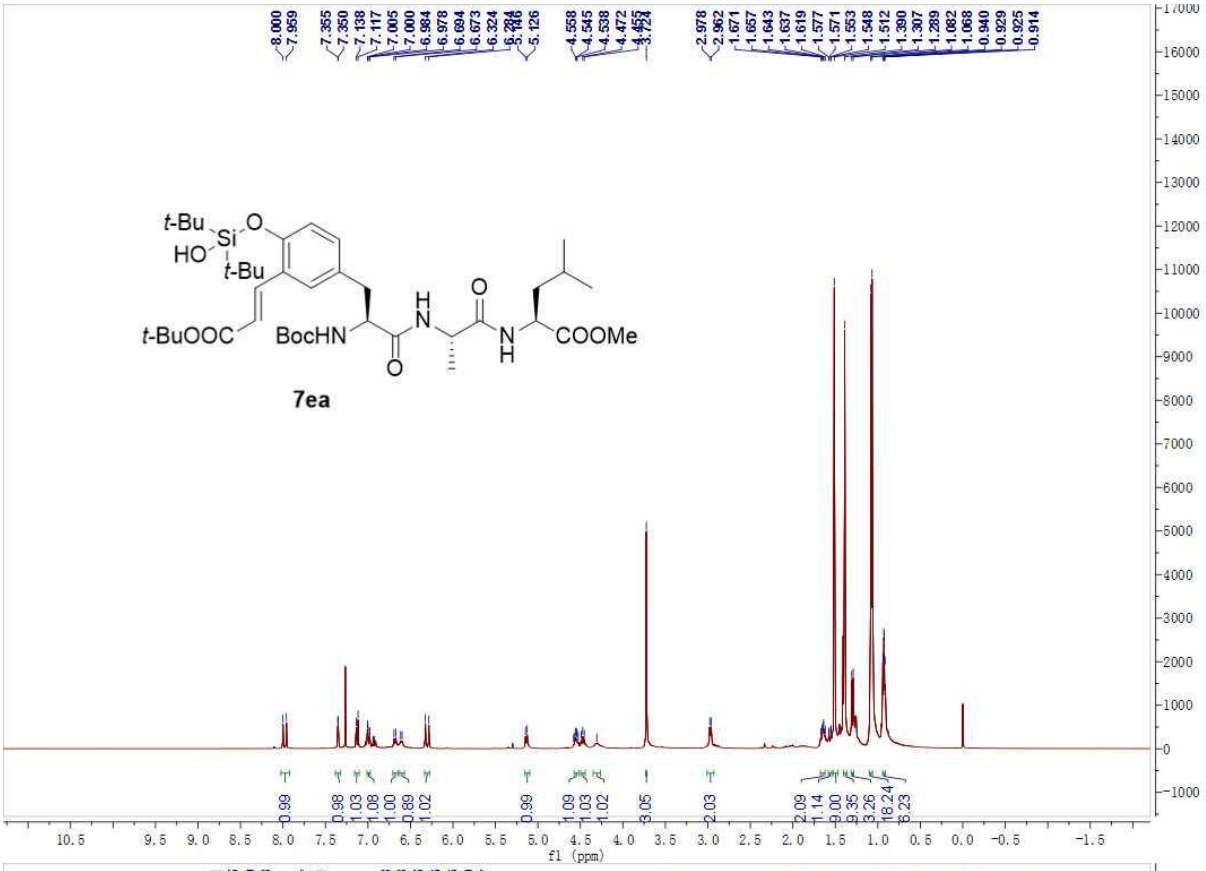
Si
O
HO
t-Bu
t-BuOOC
BocHN
H
N
O
N
H
COOMe
7da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5.126
4.558
4.545
4.538
4.472
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2.962
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1.637
1.619
1.577
1.571
1.553
1.548
1.512
1.390
1.307
1.289
1.082
1.068
0.940
0.929
0.925
0.914
t-Bu
HO
Si
O
t-Bu
t-BuOOC
BocHN
H
N
O
O
N
H
COOMe
7ea
0.99
0.98
1.03
1.08
1.00
0.89
1.02
0.99
1.09
1.03
1.02
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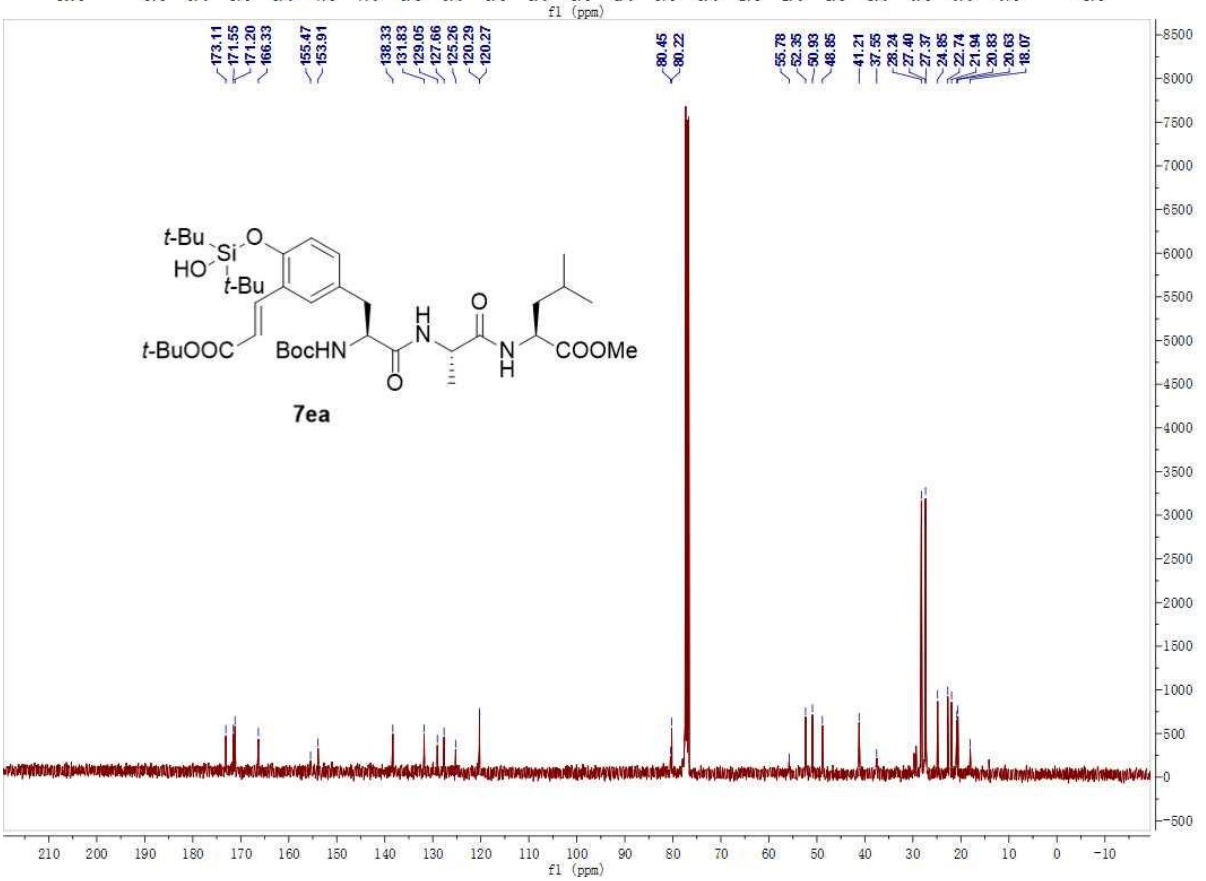
2.03
2.09
1.14
9.00
9.35
3.26
18.24
8.23
f1 (ppm)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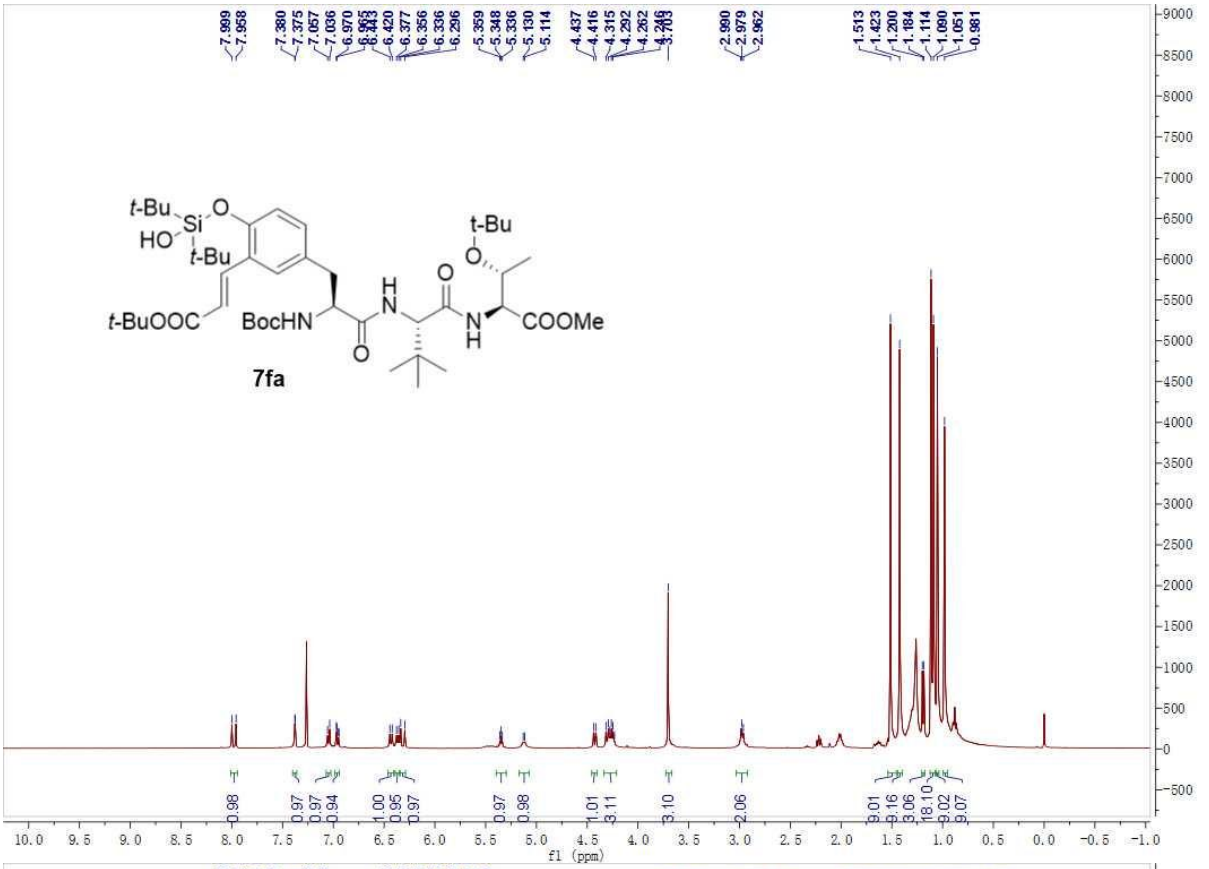
131.83
129.05
127.66
125.26
120.29
120.27
80.45
80.22
55.78
52.35
50.93
48.85
41.21
37.55
28.24
27.40
27.37
24.85
22.74
21.94
20.83
20.63
18.07
t-Bu
HO
Si
O
t-Bu
t-BuOOC
BocHN
H
N
O
O
N
H
COOMe
7ea
f1 (ppm)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5.114
4.437
4.416
4.315
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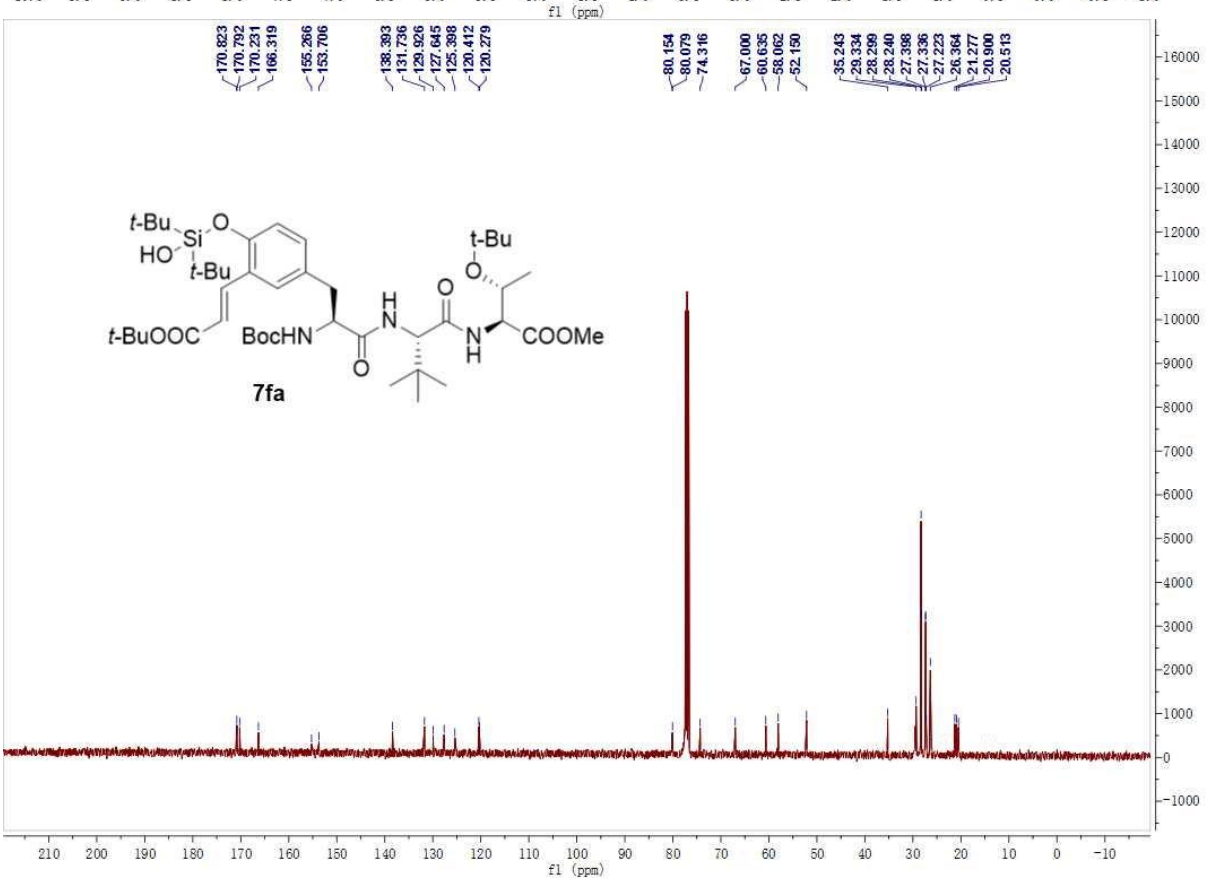
4.262
4.246
3.703
2.990
2.979
2.962
1.513
1.423
1.200
1.184
1.114
1.090
1.051
0.981
t-Bu
Si
O
HO
t-Bu
t-Bu
t-BuOOC
BocHN
H
N
O
O
t-Bu
O
N
H
COOMe
7fa
0.98
0.97
0.97
0.94
1.00
0.95
0.97
0.97
0.98
1.01
3.11
3.10
2.06
9.01
9.16
3.06
18.10
9.02
9.07
f1 (ppm)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170.231
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131.736
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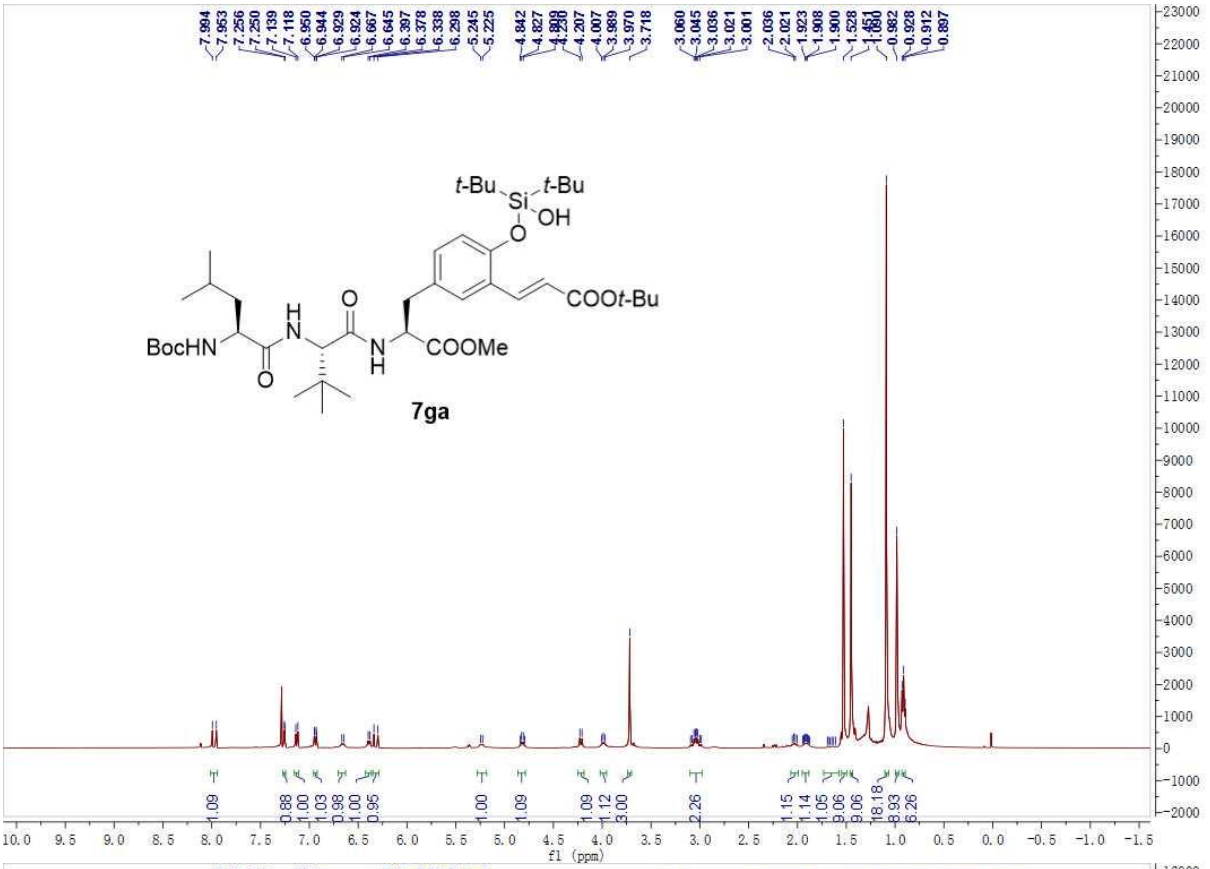
125.398
120.412
120.279
80.154
80.079
74.316
67.000
60.635
58.062
52.150
35.243
29.334
28.299
28.240
27.398
27.336
27.223
26.364
21.277
20.900
20.513
t-Bu
Si
O
HO
t-Bu
t-Bu
t-BuOOC
BocHN
H
N
O
O
t-Bu
O
N
H
COOMe
7fa
f1 (ppm)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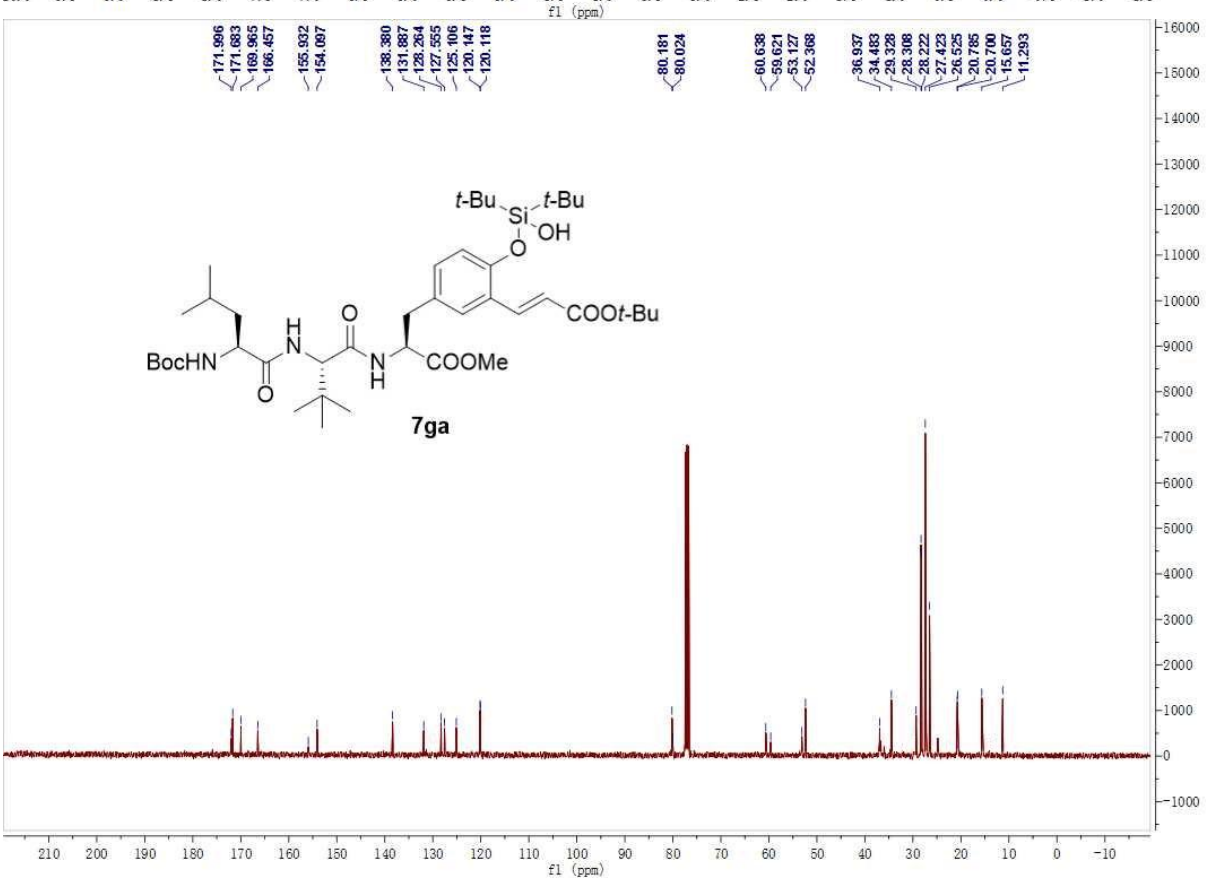
6.378
6.338
6.298
5.245
5.225
4.842
4.827
4.207
4.007
3.989
3.970
3.718
3.060
3.045
3.036
3.021
3.001
2.036
2.021
1.923
1.908
1.900
1.528
1.451
1.440
0.982
0.928
0.912
0.897
t-Bu
Si
t-Bu
OH
O
COOt-Bu
BocHN
H
N
O
N
H
COOMe
O
7ga
1.09
0.88
1.00
1.03
0.98
1.00
0.95
1.00
1.09
1.09
1.12
3.00
2.26
1.15
1.14
1.05
9.06
9.06
18.18
8.93
6.26
f1 (ppm)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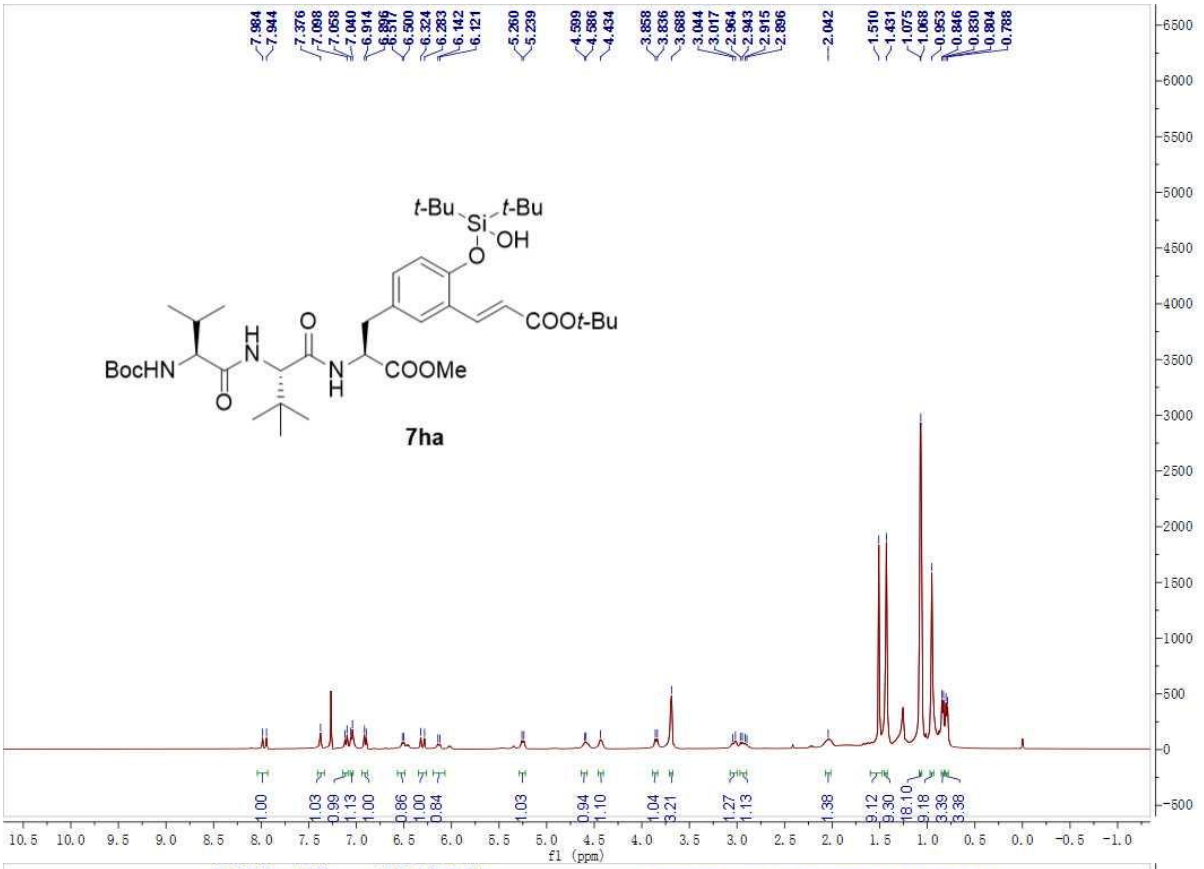
80.181
80.024
60.638
59.021
53.127
52.368
36.937
34.483
29.328
28.308
28.222
27.423
26.525
20.785
20.700
15.657
11.293
t-Bu
Si
t-Bu
OH
O
COOt-Bu
BocHN
H
N
O
N
H
COOMe
O
7ga
f1 (ppm)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7.058
7.040
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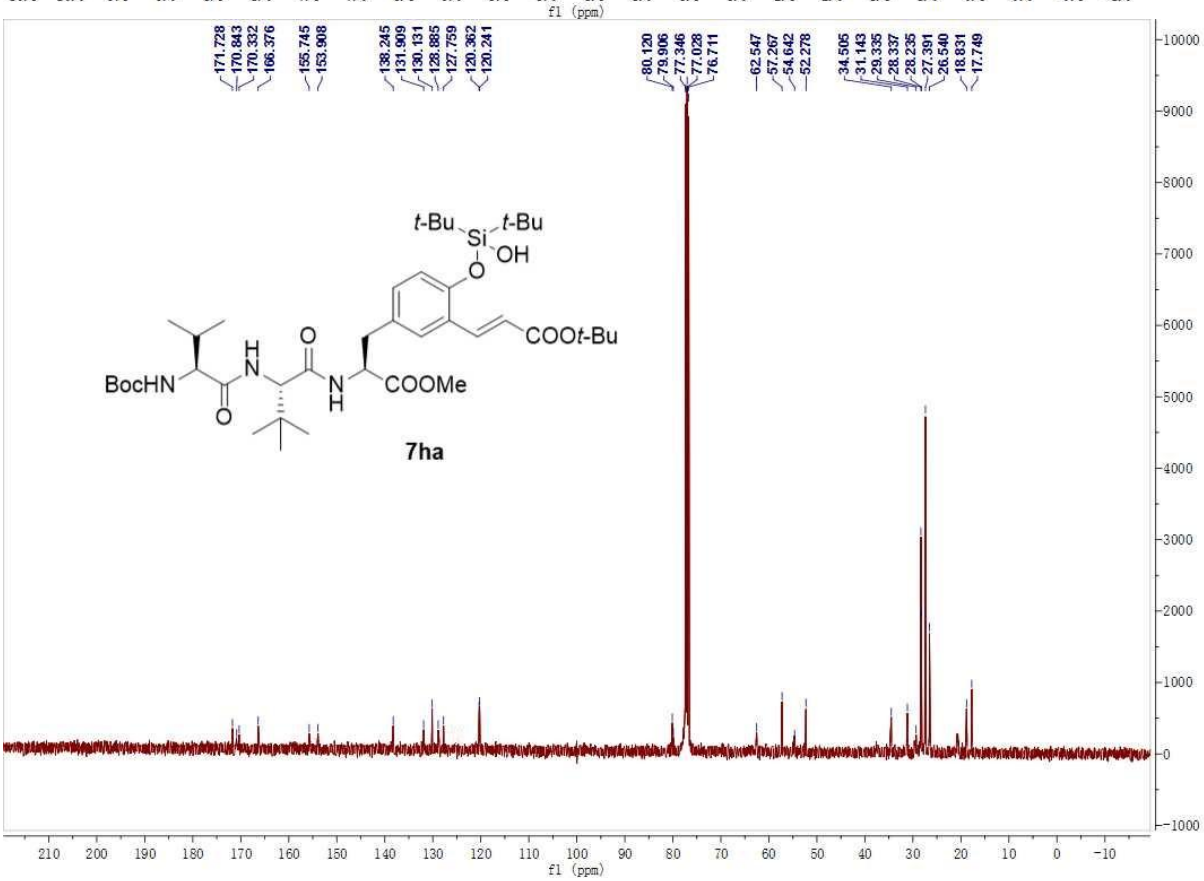
6.283
6.142
6.121
5.260
5.239
4.599
4.586
4.434
3.858
3.836
3.688
3.044
3.017
2.964
2.943
2.915
2.896
2.042
1.510
1.431
1.075
1.068
0.953
0.846
0.830
0.804
0.788
t-Bu
Si
t-Bu
OH
O
COOt-Bu
BocHN
H
N
O
N
H
COOMe
7ha
1.00
1.03
0.99
1.13
1.00
0.86
1.00
0.84
1.03
0.94
1.10
1.04
3.21
1.27
1.13
1.38
9.12
9.30
18.10
3.39
3.38
f1 (ppm)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80.120
79.906
77.346
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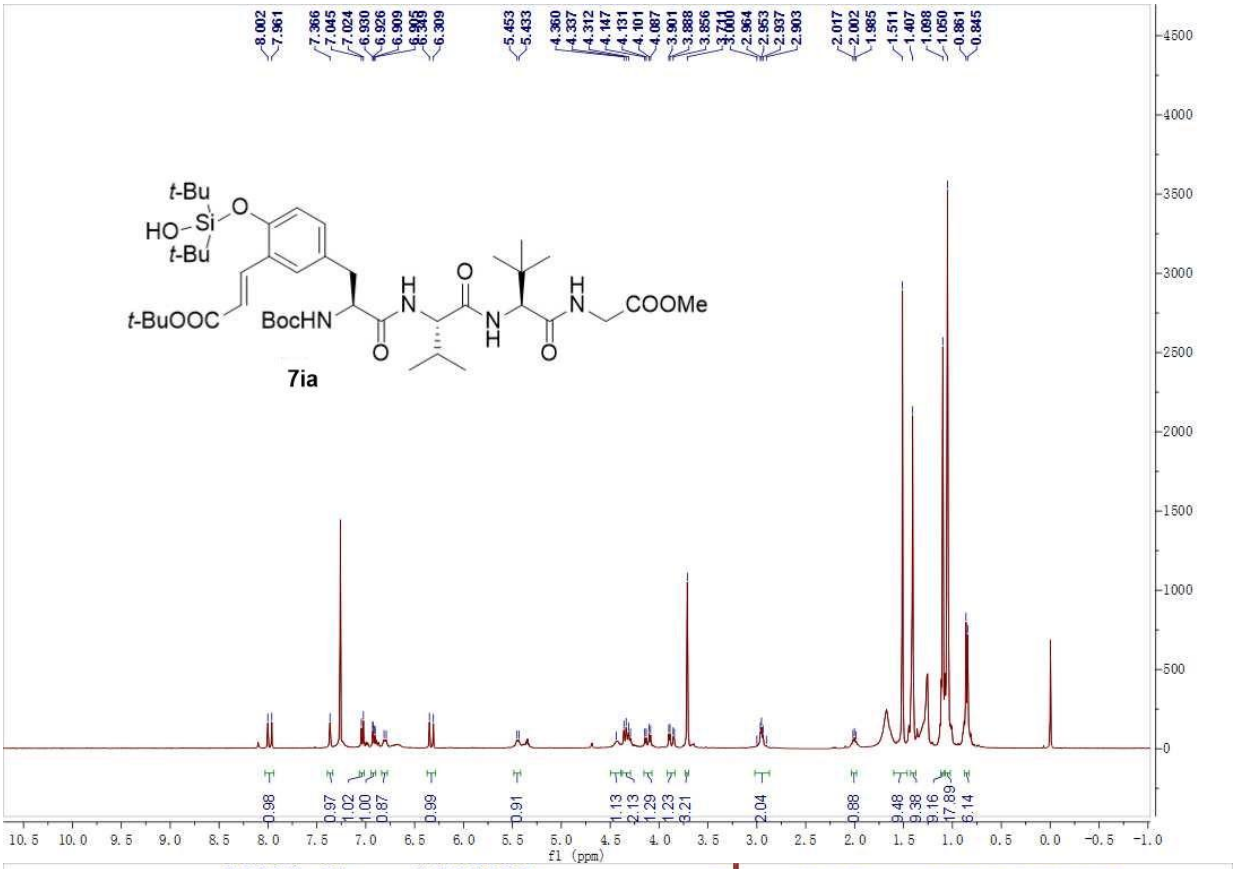
76.711
62.547
57.267
54.642
52.278
34.505
31.143
29.335
28.337
28.235
27.391
26.540
18.831
17.749
t-Bu
Si
t-Bu
OH
O
COOt-Bu
BocHN
H
N
O
N
H
COOMe
7ha
f1 (ppm)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6.309
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4.337
4.312
4.147
4.131
4.101
4.087
3.901
3.888
3.856
2.964
2.953
2.937
2.903
2.017
2.002
1.885
1.511
1.407
1.098
1.050
0.861
0.845
t-Bu
HO
Si
O
t-Bu
t-BuOOC
BocHN
H
N
O
H
N
O
H
N
COOMe
O
7ia
0.98
0.97
1.02
1.00
0.87
0.99
0.91
1.13
2.13
1.29
1.23
3.21
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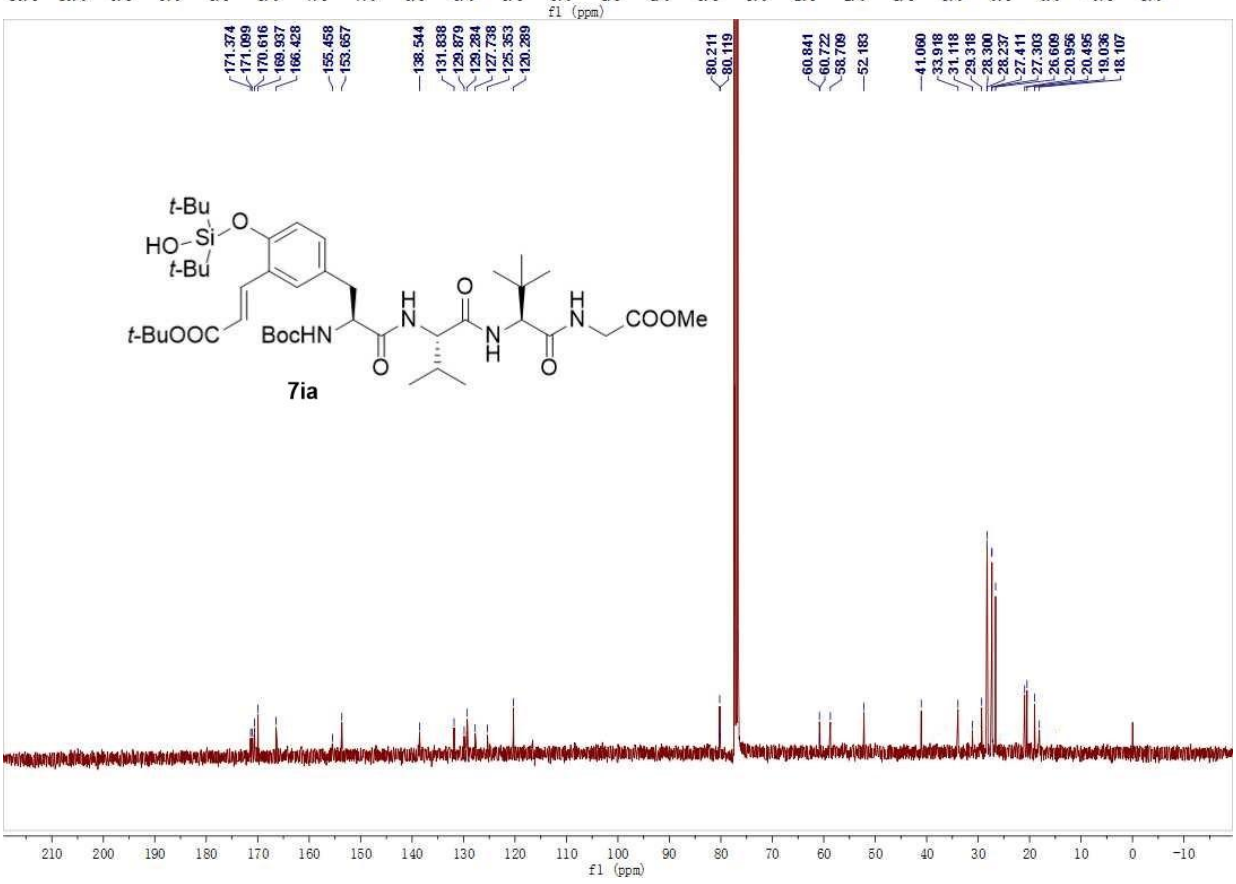
9.38
9.16
17.89
6.14
f1 (ppm)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125.353
120.289
80.211
80.119
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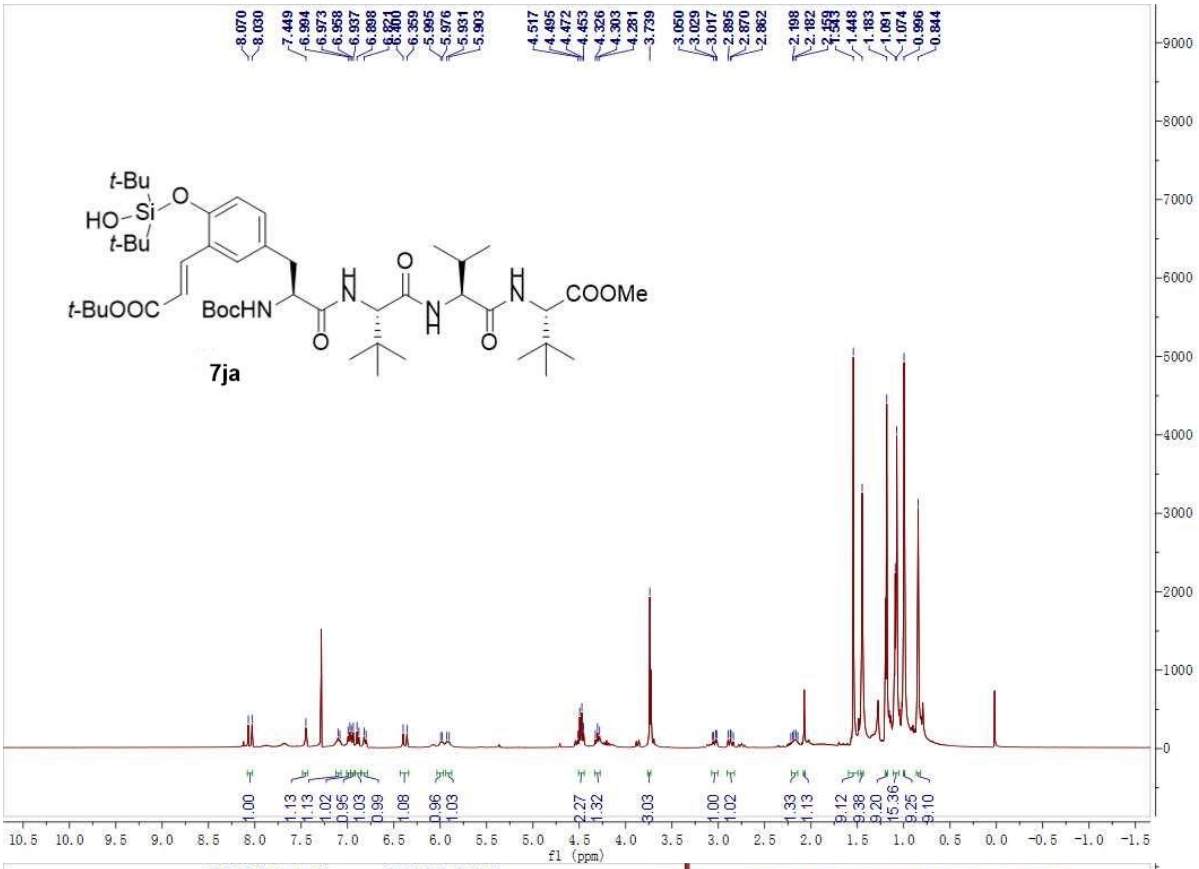
60.722
58.709
52.183
41.060
33.918
31.118
29.318
28.300
28.237
27.411
27.303
26.609
20.956
20.495
19.036
18.107
t-Bu
HO
Si
O
t-Bu
t-BuOOC
BocHN
H
N
O
H
N
O
H
N
COOMe
O
7ia
f1 (ppm)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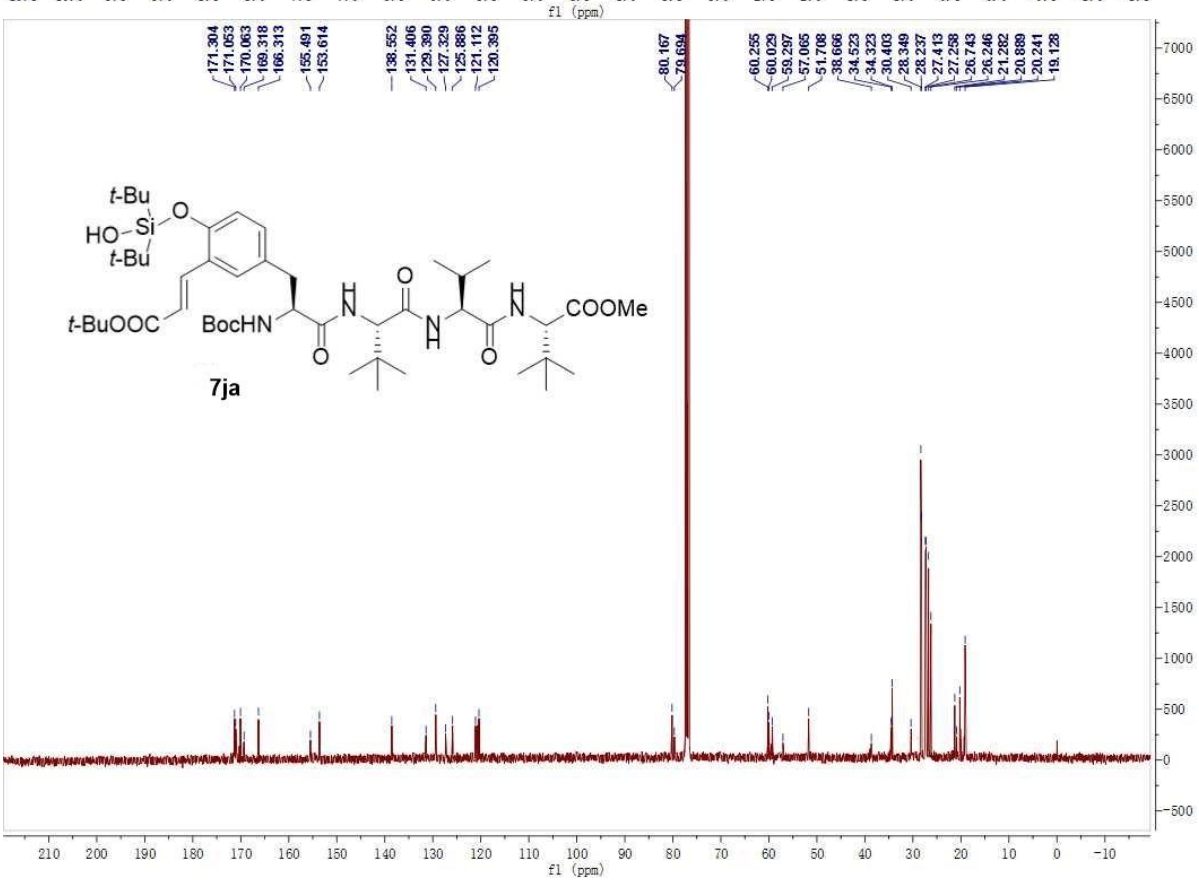
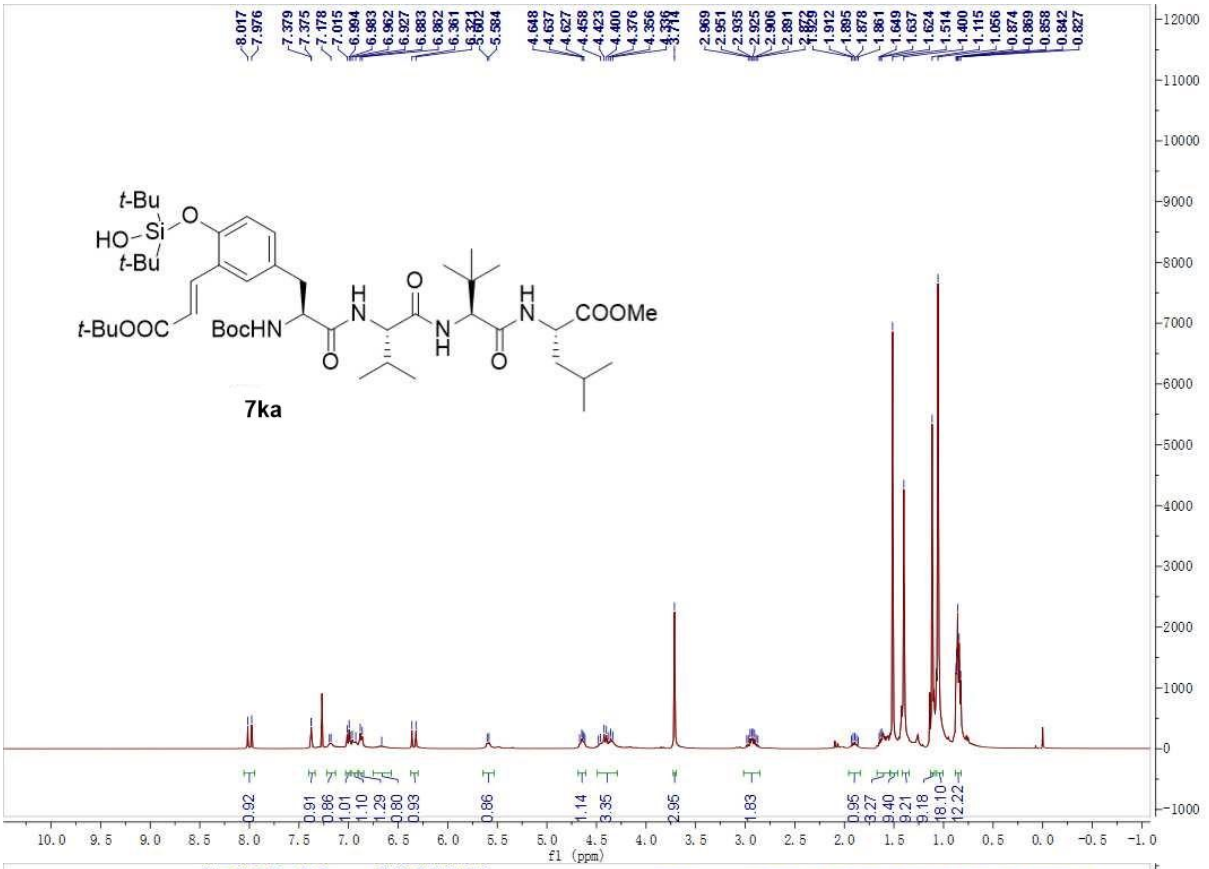
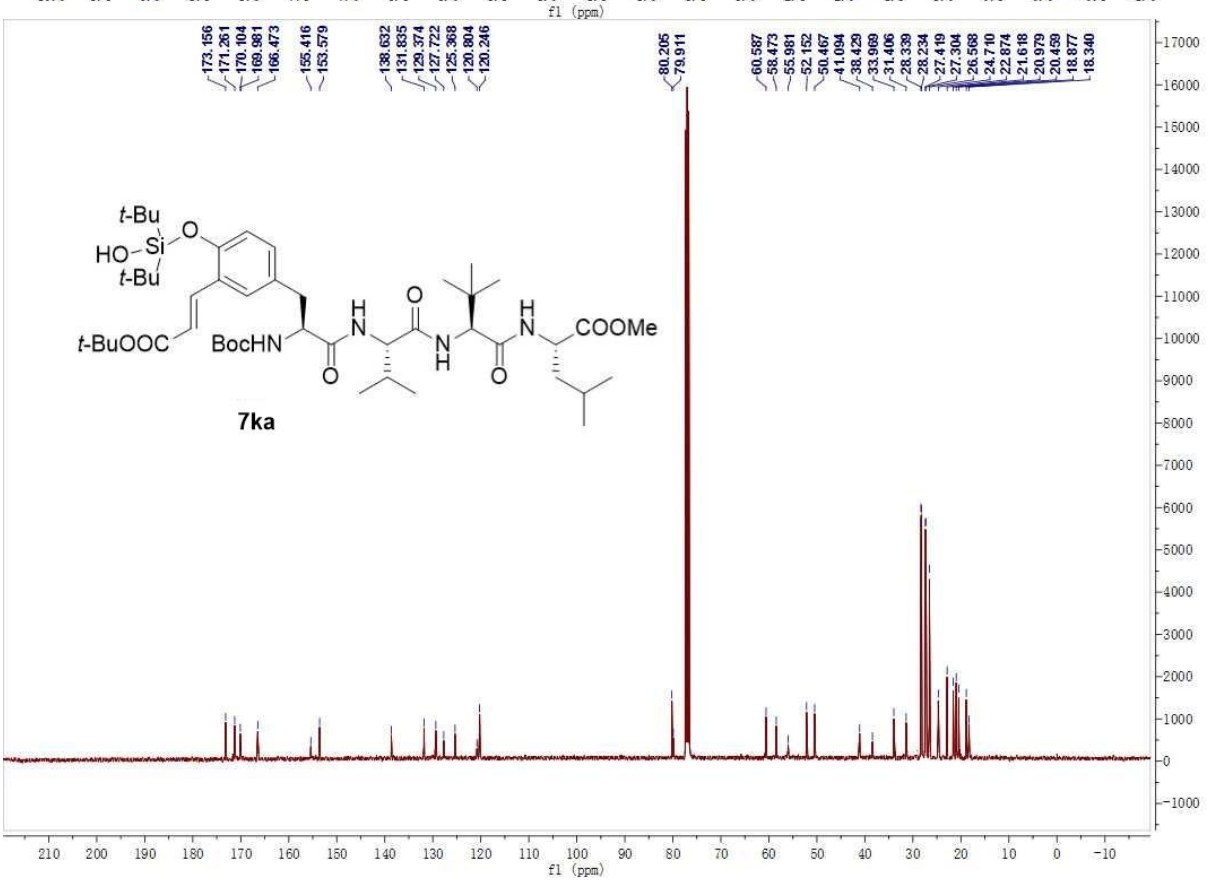
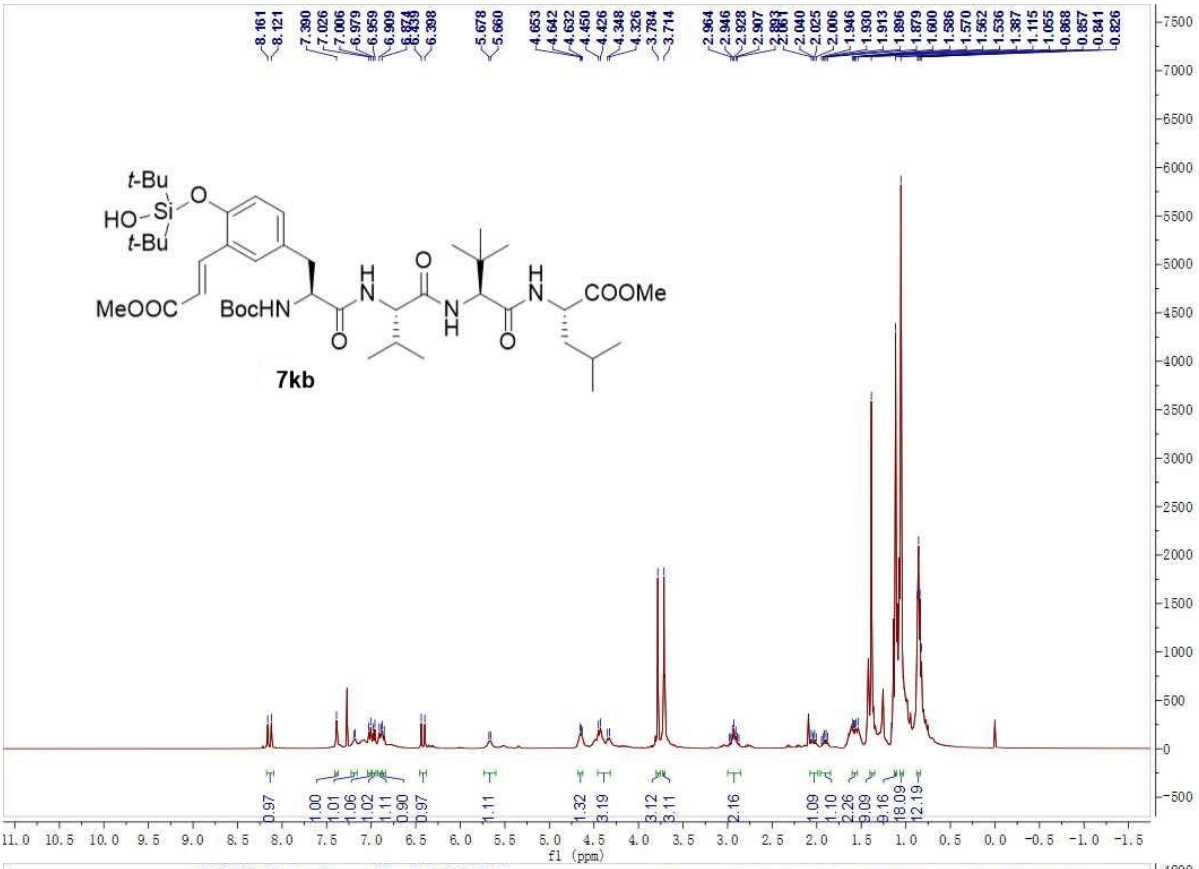
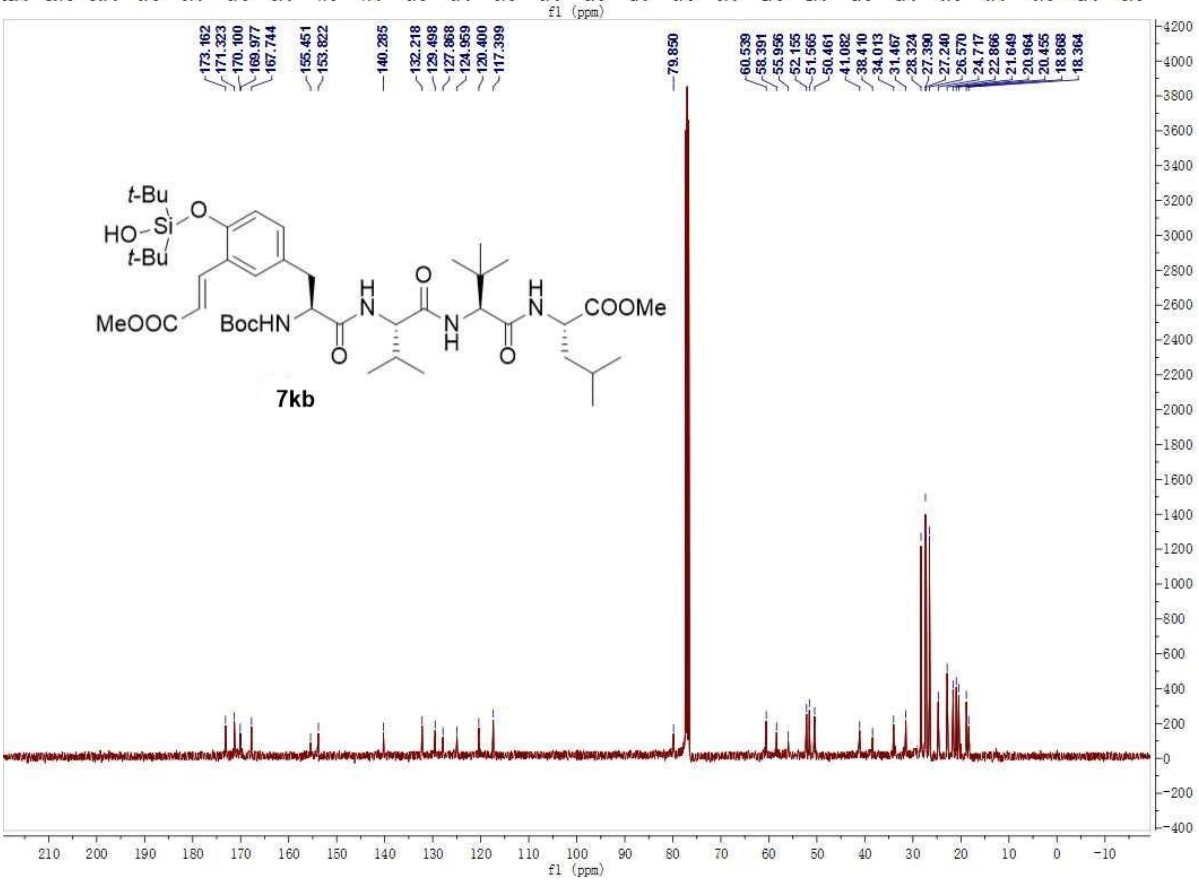
HO
Si
t-Bu
O
t-BuOOC
BocHN
COOMe
7ja


t-Bu
HO
Si
t-Bu
O
t-BuOOC
BocHN
COOMe
7ja


t-Bu
HO-Si-O
t-Bu
t-BuOOC
BocHN
COOMe
7ka


t-Bu
HO-Si-O
t-Bu
t-BuOOC
BocHN
COOMe
7ka


t-Bu
HO-Si
t-Bu
O
MeOOC
BocHN
H
N
O
H
N
O
H
N
COOMe
7kb


t-Bu
HO-Si
t-Bu
O
MeOOC
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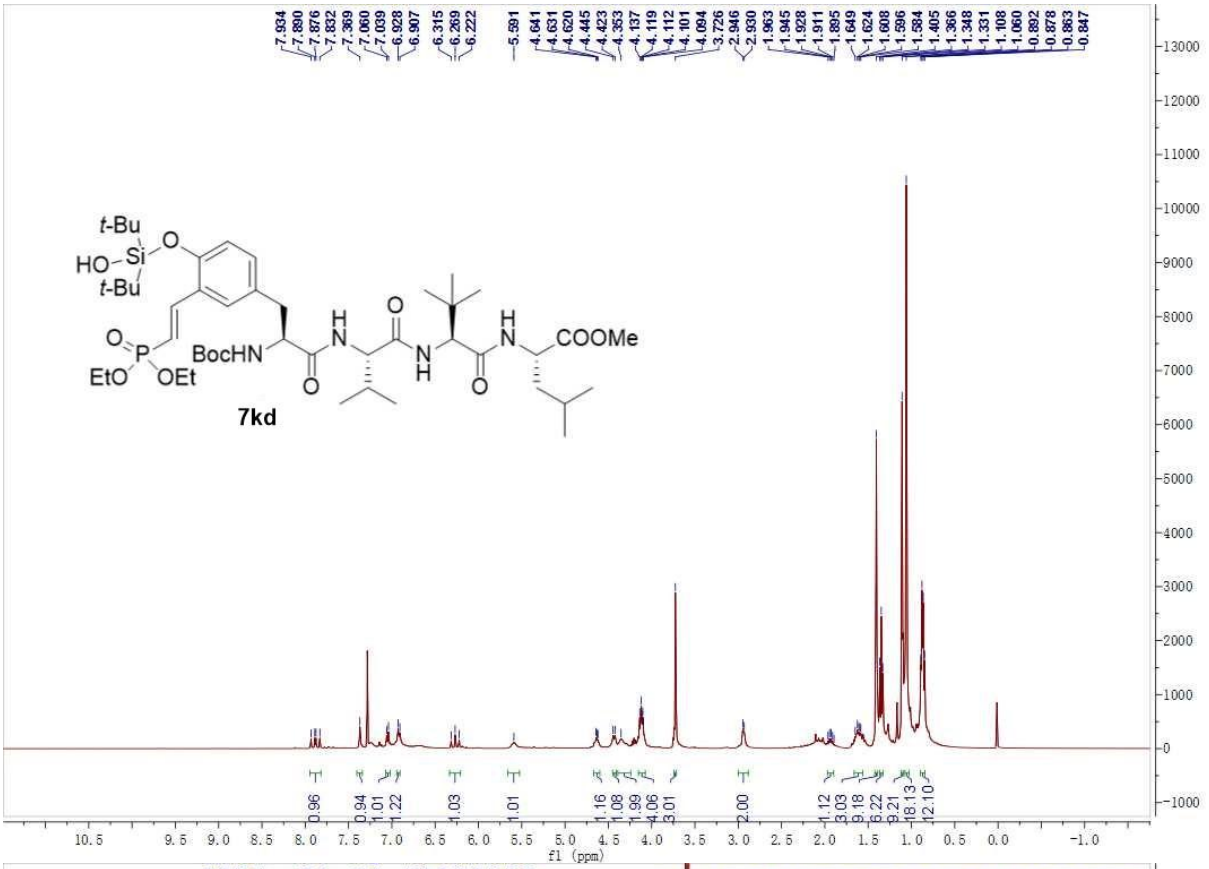
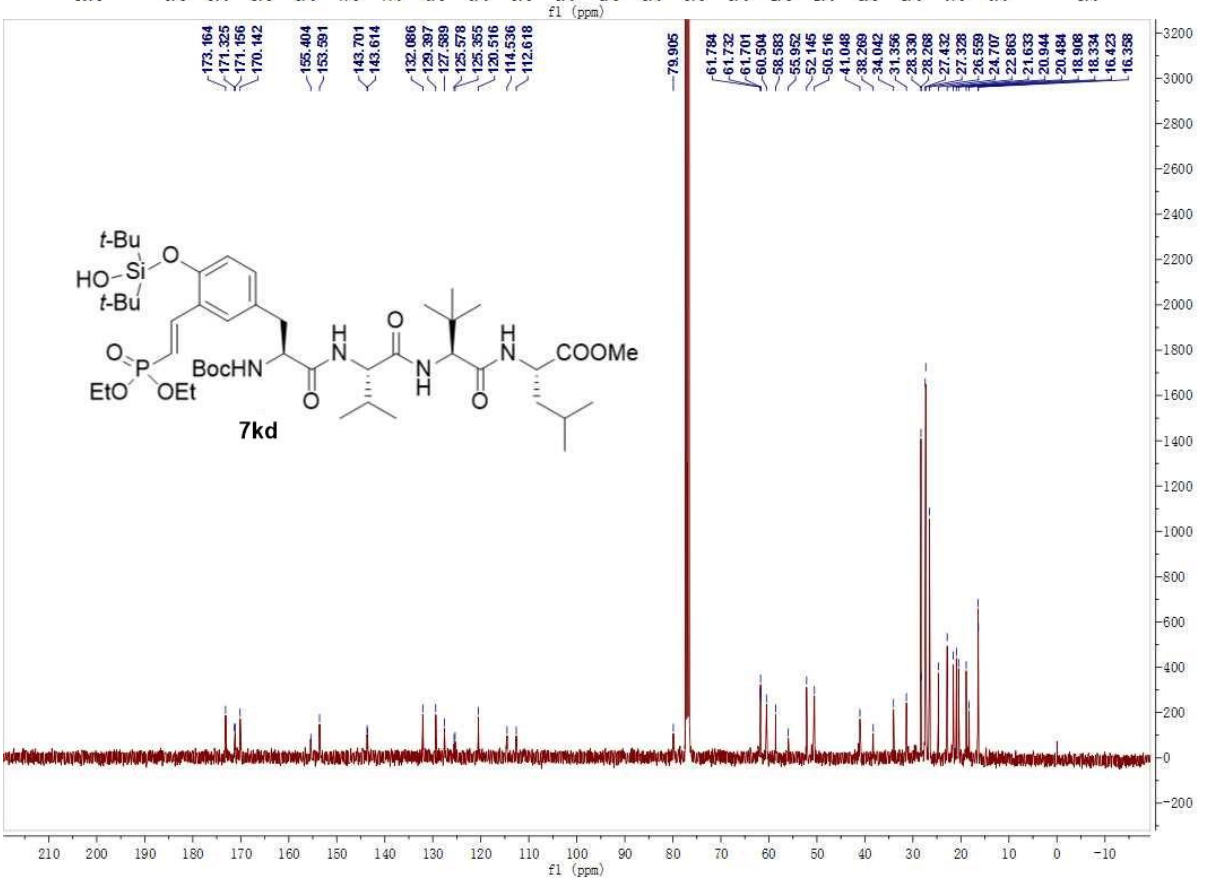
H
N
O
H
N
O
H
N
COOMe
7kb


7kd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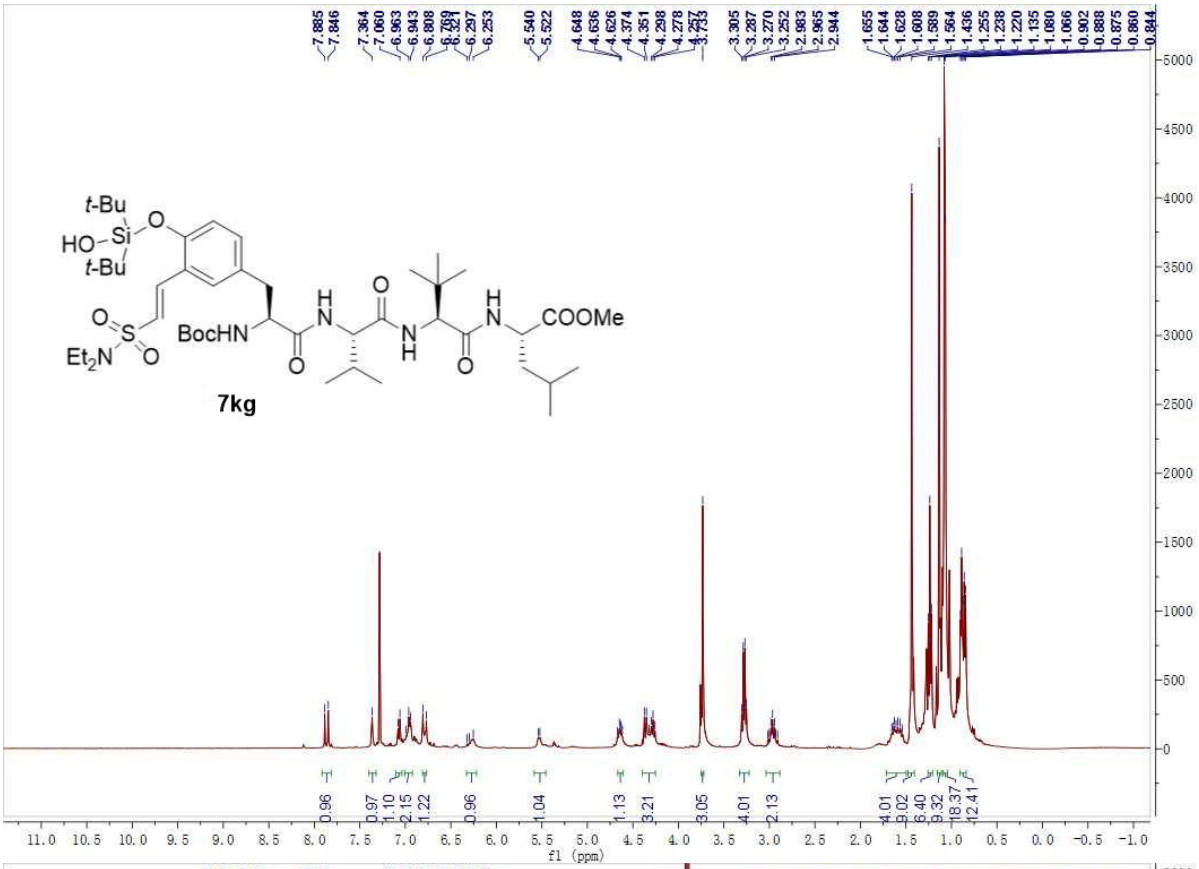
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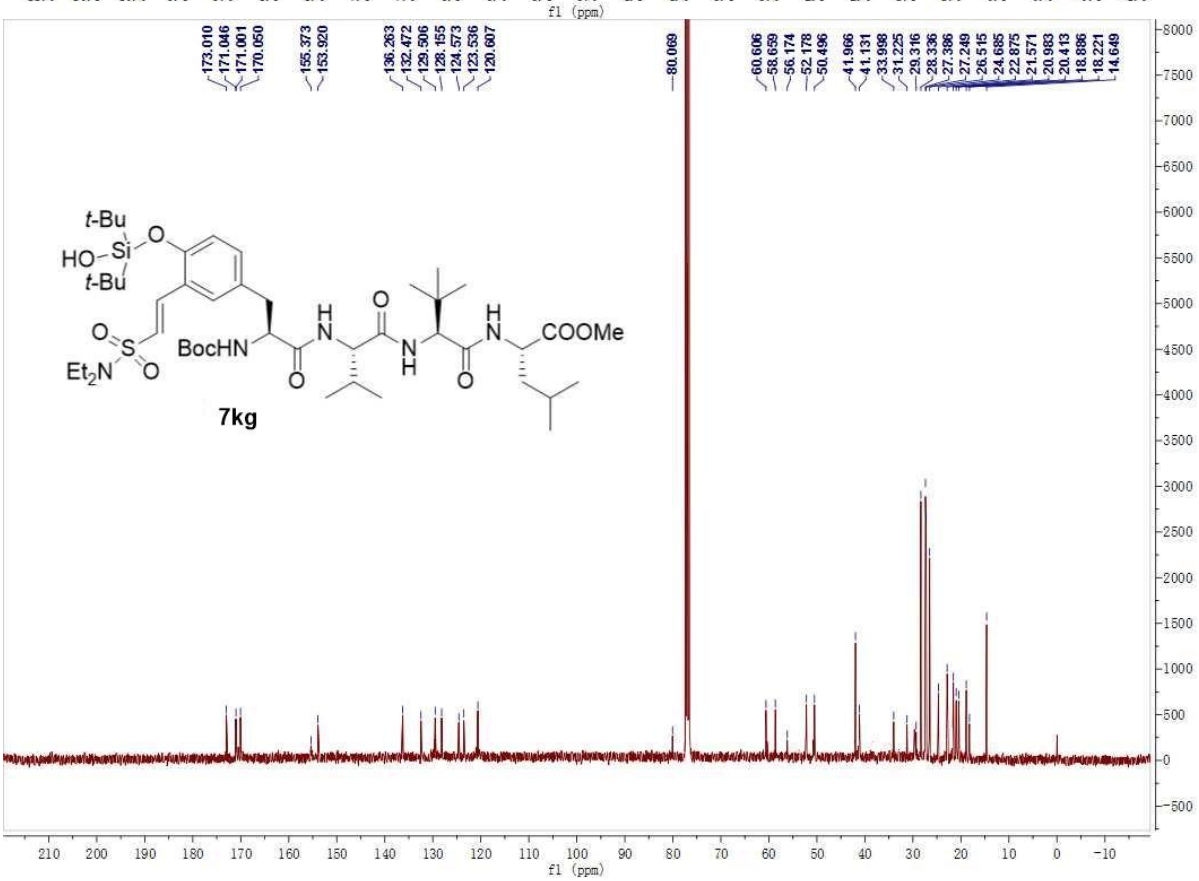
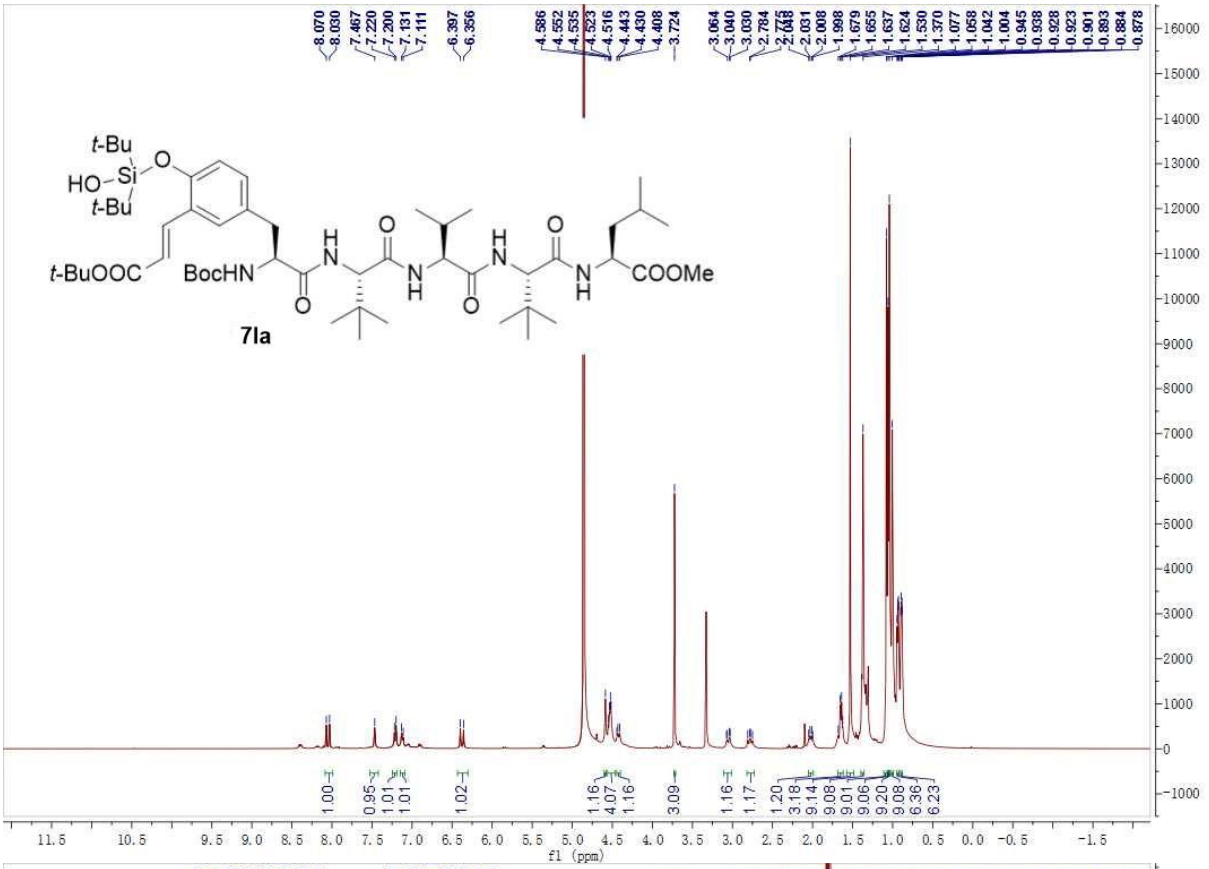

7kg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4.535
4.516
4.443
4.430
4.408
3.724
3.064
3.040
3.030
2.784
2.031
2.008
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1.679
1.655
1.637
1.624
1.530
1.370
1.077
1.058
1.042
1.004
0.945
0.938
0.928
0.923
0.901
0.893
0.884
0.878
t-Bu
HO-Si
t-Bu
O
t-BuOOC
BocHN
H
N
O
COOMe
7Ia
1.00
0.95
1.01
1.01
1.02
1.16
4.07
1.16
3.09
1.16
1.17
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9.14
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9.01
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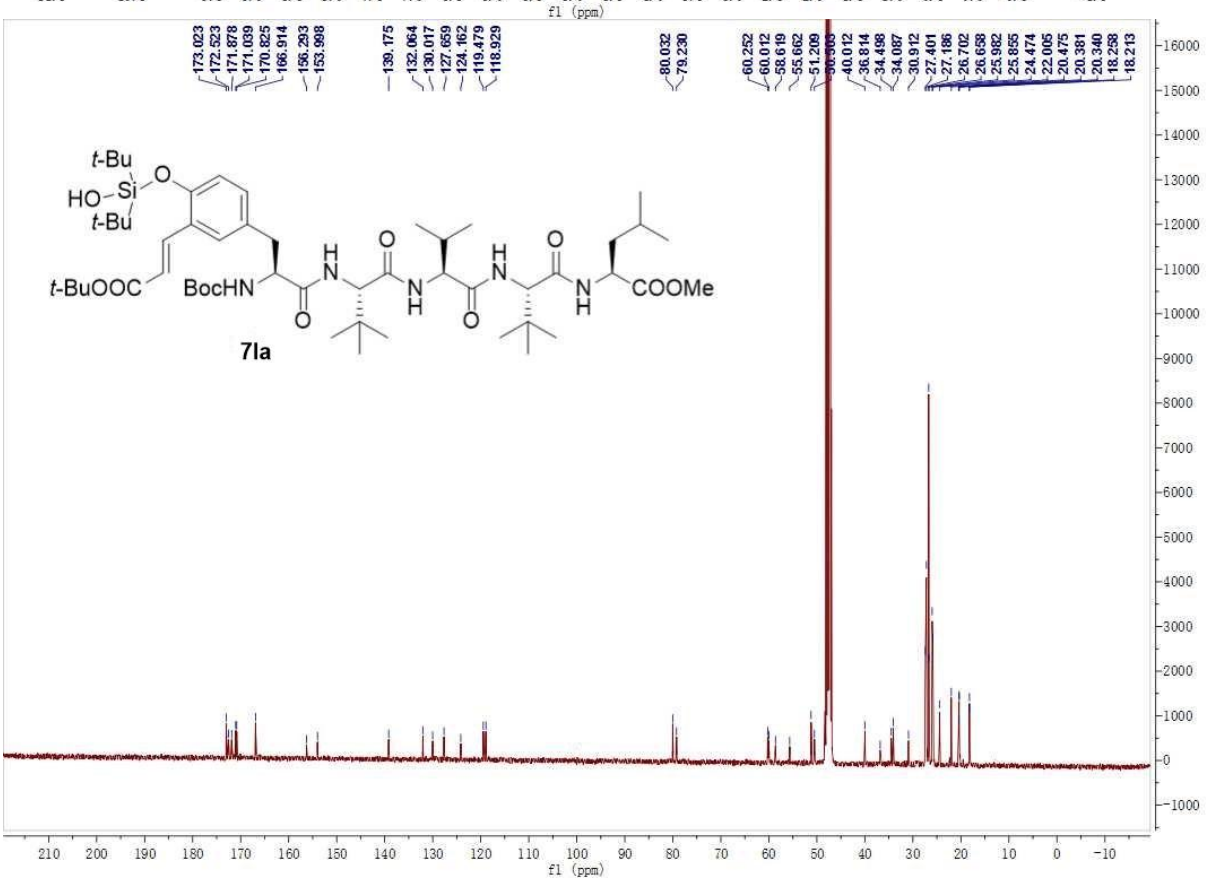
9.08
6.36
6.23
f1 (ppm)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119.479
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80.032
79.230
60.252
60.012
58.619
55.662
51.209
50.000
40.012
36.814
34.498
34.087
30.912
27.401
27.186
26.702
26.658
25.982
25.655
24.474
22.005
20.475
20.381
20.340
18.298
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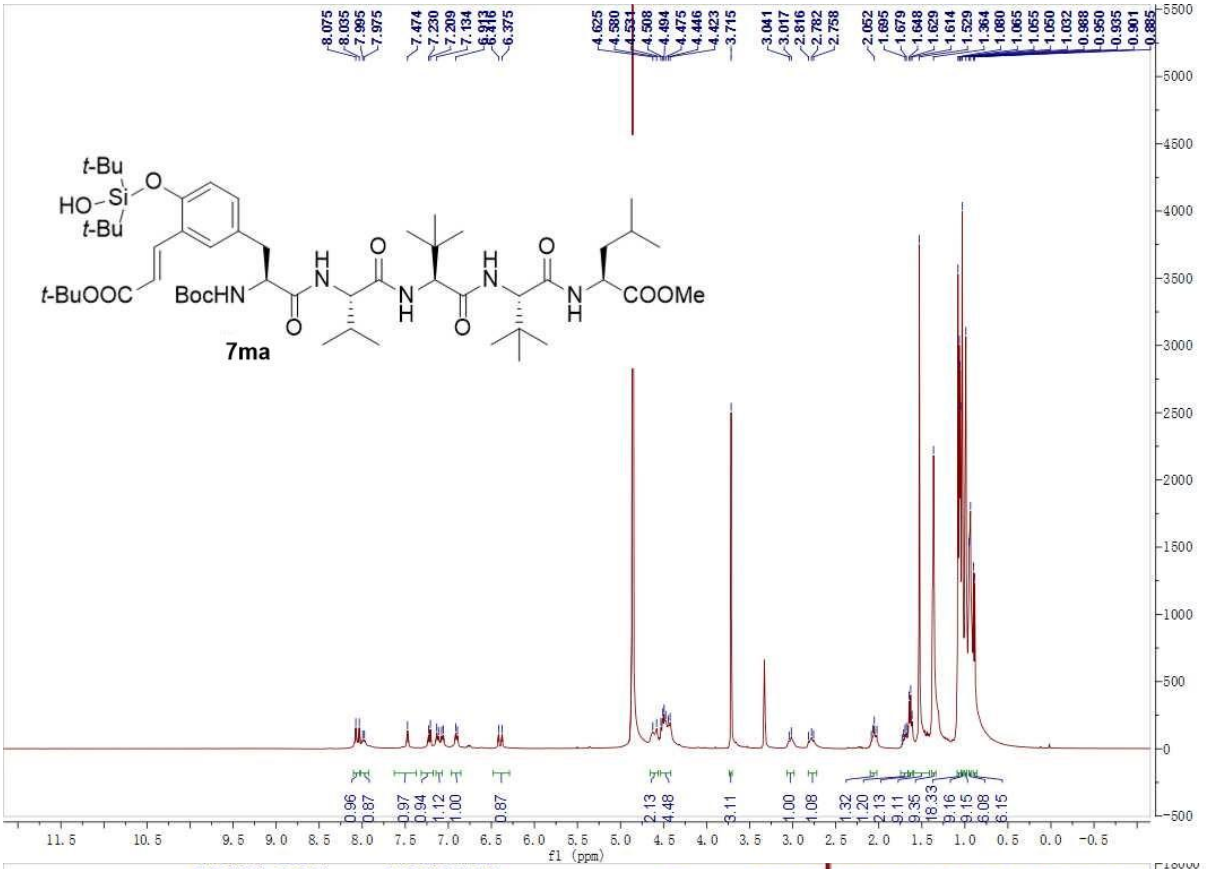
t-Bu
HO-Si
t-Bu
O
t-BuOOC
BocHN
H
N
O
COOMe
7Ia
f1 (ppm)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4.494
4.475
4.446
4.423
3.715
3.041
3.017
2.816
2.782
2.758
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1.695
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1.648
1.629
1.614
1.529
1.364
1.080
1.065
1.055
1.050
1.032
0.988
0.950
0.935
0.901
0.885
t-Bu
HO-Si
t-Bu
O
t-BuOOC
BocHN
H
N
O
N
H
O
H
N
O
N
H
COOMe
7ma
0.96
0.87
0.97
0.94
1.12
1.00
0.87
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4.48
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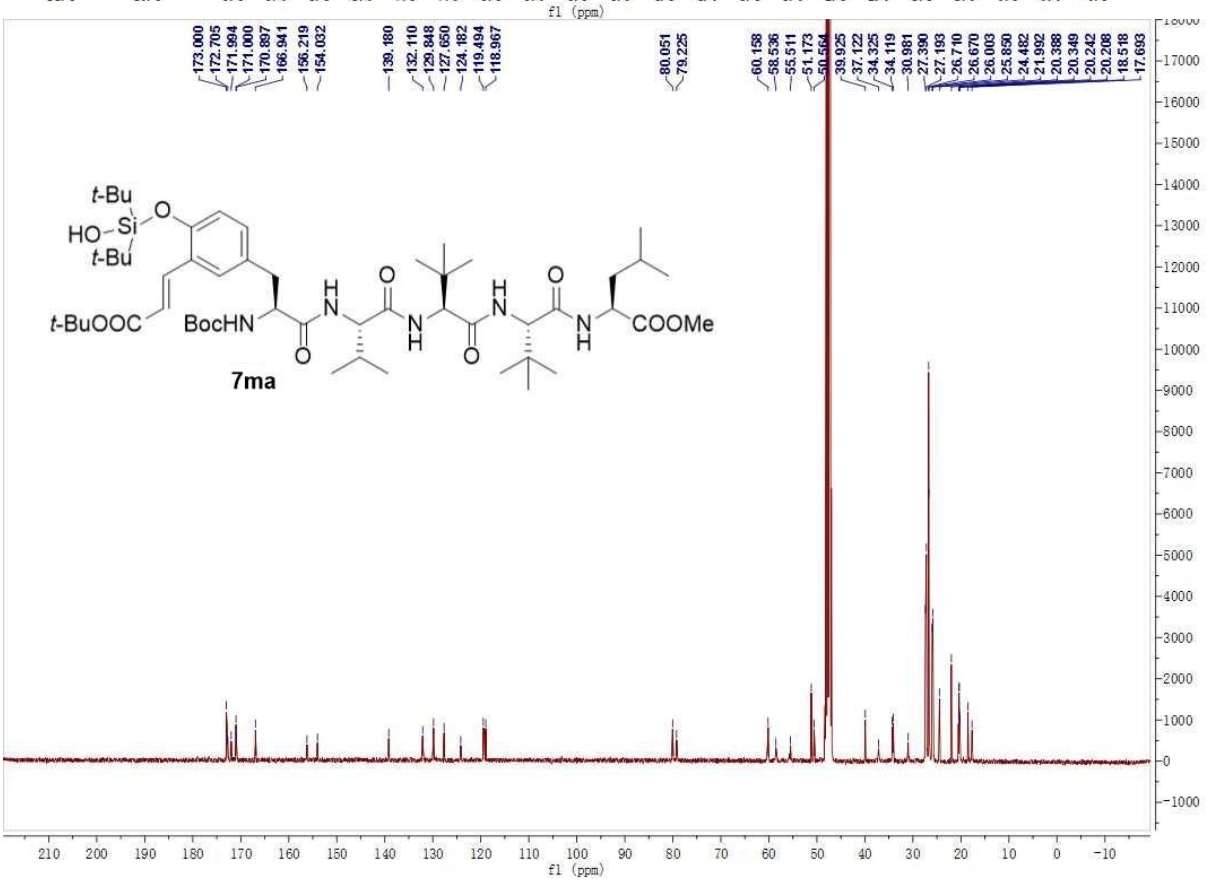
8.15
f1 (ppm)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127.650
124.182
119.494
118.967
80.051
79.225
60.158
58.536
55.511
51.173
50.564
39.925
37.122
34.325
34.119
30.981
27.390
27.193
26.710
26.670
26.003
25.850
24.482
21.992
20.388
20.349
20.242
20.208
18.518
17.693
t-Bu
HO-Si
t-Bu
O
t-BuOOC
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O
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H
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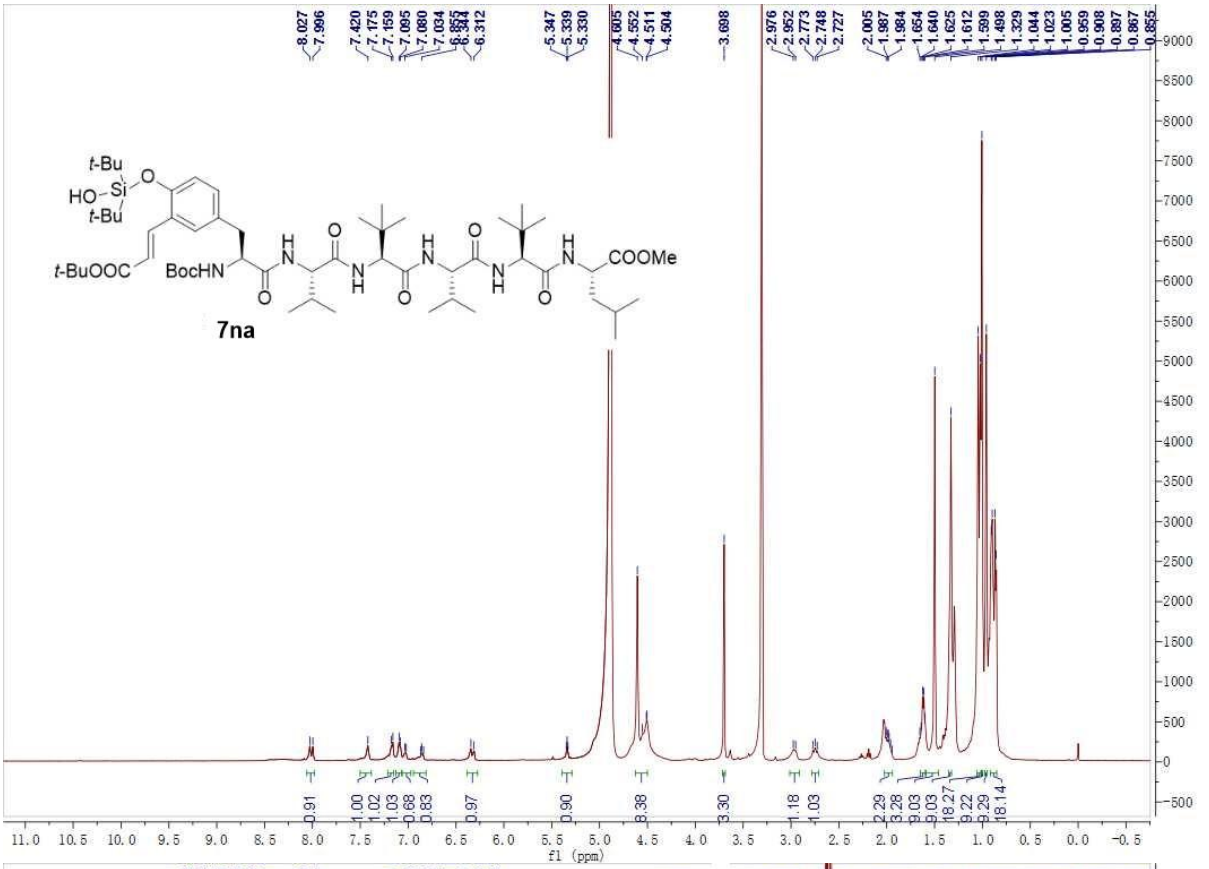
H
N
O
N
H
COOMe
7ma
f1 (ppm)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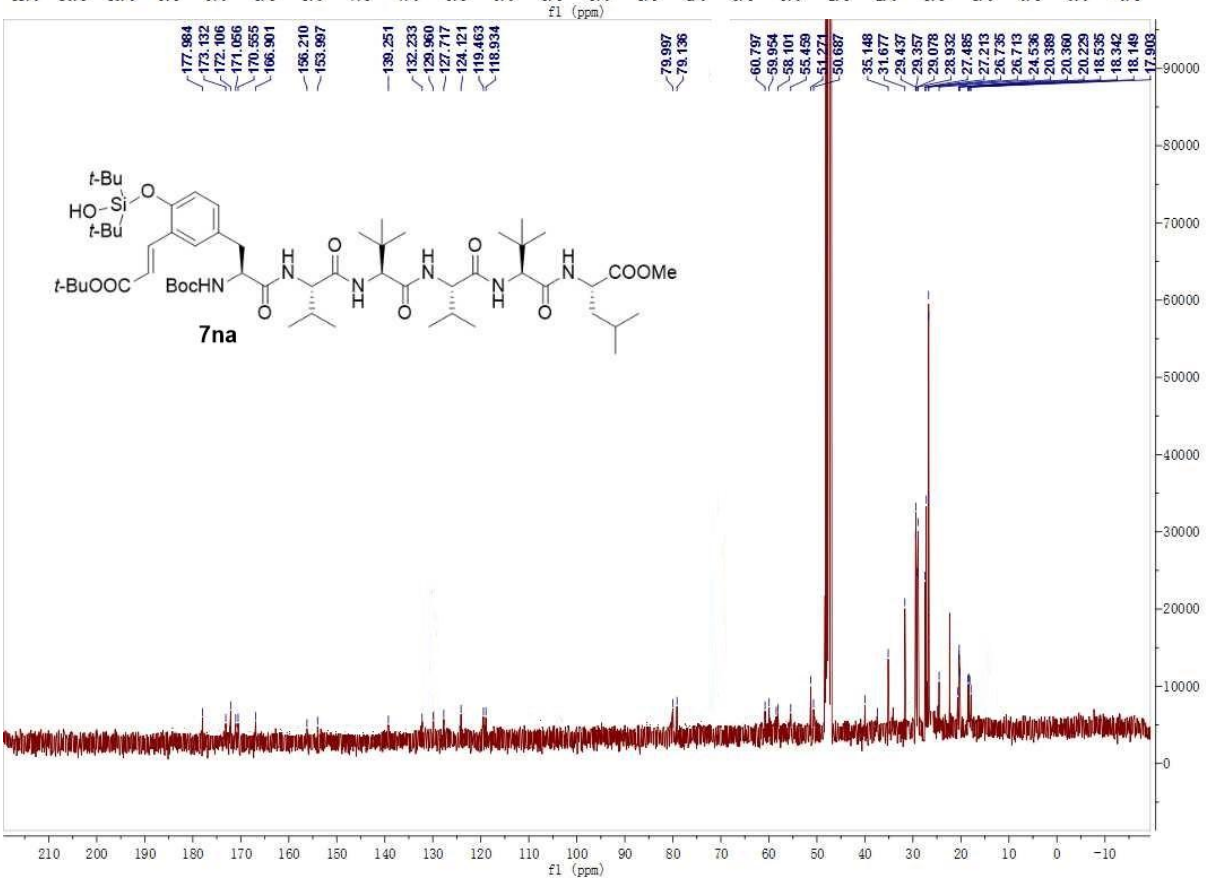
HO–Si
t-Bu
O
t-BuOOC
BocHN
COOMe
7na


t-Bu
HO–Si
t-Bu
O
t-BuOOC
BocHN
COOMe
7na

References

[1] T. Yamamoto, T. Iwasaki, T. Morita, Y. Yoshimi, *J. Org. Chem.* **2018**, *83*, 3702-3709.

[2] Z. Li, R. Yazaki, T. Ohshima, *Org. Lett.* **2016**, *18*, 3350-3353.

[3] Y. Wang, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2015**, *54*, 2255-2259；*Angew. Chem.* **2013**, *125*, 11000-11004.