Enantioselective Total Synthesis of (-)-α-Kainic Acid

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Supporting Information

Commonly used abbreviations:

b	Branched
Boc	*tert*-Butoxycarbonyl
COD	1,5-Cyclooctadiene
DMF	*N,N*-Dimethylformamide
dr	Diastereomeric Ratio
ESI	Electrospray Ionization
FAB	Fast Atom Bombardment
HR	High Resolution
l	Linear
mmu	Millimass
NMO	*N*-Methylmorpholine *N*-Oxide
R_f	Retention Factor in Chromatography
TBD	5,7-Triazabicyclo[4.4.0]dec-5-ene
TBDMS	*tert*-Butyldimethylsilyl
TFA	Trifluoroacetic Acid
TLC	Thin Layer Chromatography
TPAP	tetra-*n*-Propylammonium Perruthenate
t_R	Retention Time

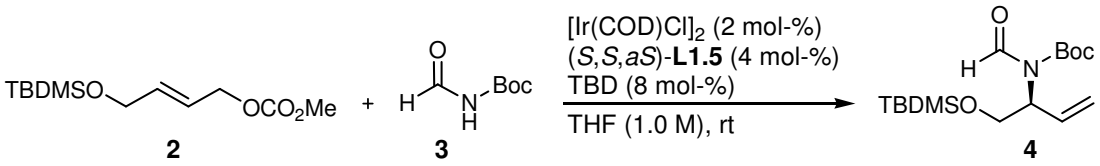
General: All reactions were carried out under an atmosphere of argon with dry solvents. TLC: Macherey & Nagel Polygram Sil G/UV precoated sheets, visualization of spots by treatment with aqueous $KMnO_4$ or ninhydrine solution. Column chromatography: Fluka silica gel, grade 60 (0.032-0.062 mm). ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 200, DRX 300 or a DRX 500 instrument. Chemical shifts are relative to residual non-deuterated solvent peaks [^1H NMR: $CDCl_3$ δ = 7.26, toluene-d_8 δ = 2.09, D_2O δ = 4.80; ^{13}C NMR: $CDCl_3$ δ = 77.16, toluene-d_8 δ = 20.40]. HR-MS: JEOL JMS-700 (FAB+) or FT-ICR-MS (ESI+). GC/MS: HP 5890 Series II Plus model, coupled with a HP 5972 Mass Selective Detector and a HP 1 Crosslinked Methyl Silicone Column (25 m x 0.2 mm,

0.33 µm) [temperature program: 50°C 1 min, heating rate 20°C/min (10 min), 250°C 14 min; injection temperature 250°C]. HPLC: Hewlett Packard HP 1090 or HP 1100 with chiral a DAICEL column [Chiralpak AS-H (25 cm x 0.46 cm) with precolumn AS-H (5 cm x 0.46 cm)]. Elemental analysis: Microanalytical Laboratory of the Organisch-Chemisches Institut, Universität Heidelberg.

General Procedure 1: **Iridium-Catalyzed Allylic Amination.**

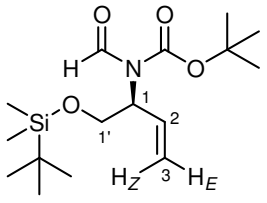
Success with the following procedure requires dry THF (< 35 µg of H_2O/mL, Karl Fischer titration). Under argon, in a heatgun dried Schlenk-tube a solution of $[Ir(COD)Cl]_2$ (13.4 mg, 20.0 µmol), **L*** (40.0 µmol) and TBD (11.1 mg, 80.0 µmol, stored in a desiccator over KOH) in dry THF (0.5-1.0 mL) was stirred for 5-10 min at room temperature until a white precipitate was formed at the glass wall above the solution. The allylic carbonate (1.0 mmol) and after further 5 min the nucleophile (1.2 mmol) were added. The mixture was stirred until TLC or GC/MS indicated complete conversion. The solvent was removed under reduced pressure and the residue analyzed with respect to content of branched and linear product by ^{1}H NMR. The pure reaction products were obtained by column chromatography on silica gel (petroleum ether/ethyl acetate).

***tert*-Butyl [(1*S*)-1-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)prop-2-en-1-yl}formylcarbamate (4)**



2 **3** **4**

According to *GP1*, a mixture of $[Ir(COD)Cl]_2$ (13.4 mg, 20 µmol), (*S*,*S*,*aS*)-**L2** (22.9 mg, 40 µmol), TBD (11.1 mg, 80 µmol), TBDMS-carbonate **2** (260 mg, 1.00 mmol), Boc-amide **3** (174 mg, 1.20 mmol) and dry THF (1 mL) was stirred for 5 h at room temperature until TLC monitoring (R_f(**2**) = 0.46, R_f(**4**) = 0.56, petroleum ether/ethyl acetate 4:1, $KMnO_4$) showed full consumption of the starting material. The solvent was removed *in vacuo*, and the ratio **b**:**l** was determined by ^{1}H NMR of the crude product (**b**:**l** = 92:08). After column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) the branched allylamine derivative **4** (287 mg, 0.87 mmol, 87 %) was obtained as colourless oil.



4

Optical Rotation (97.5 %ee (*S*), determined by chiral HPLC)

$[\alpha]_D^{20}$ = +2.0

(*c* = 0.75, $CHCl_3$).

HPLC

(Daicel Chiralpak AS-H 4.6 x 250 mm with precolumn AS-H 10 x 4 mm, *n*-hexane/*i*-PrOH 99.7:0.3, flow = 0.4 mL/min, λ = 215 nm).

t_R[(+)-(*S*)-**4**] = 10.8 min

t_R[(-)-(*R*)-**4**] = 11.6 min.

^{1}H NMR ($CDCl_3$, 500.13 MHz), **H,H-COSY** (d090909ghaf.648A)

δ = 0.01, 0.02 (2 s, 6 H, Si<u>Me$_2$</u>*t*-Bu), 0.84 (s, 9 H, SiMe$_2$<u>*t*-Bu</u>), 1.52 (s, 9 H, *t*-Bu), 3.76 (dd, *J* = 9.9 Hz, *J* = 6.3 Hz, 1 H, 1'-H_a), 4.00 (dd, *J* = 9.5 Hz, *J* = 9.5 Hz, 1 H, 1-H_b), 5.04 (dd, *J* = 15.5 Hz, *J* = 6.7 Hz, 1 H, 1-H), 5.13 (d, *J* = 10.3 Hz, 1 H, 3-H_E), 5.20 (d, *J* = 17.0 Hz, 1 H, 3-H_Z), 5.98 (ddd, *J* = 17.3 Hz, *J* = 10.4 Hz, *J* = 6.8 Hz, 1 H, 2-H), 9.21 (s, 1 H, CHO).

^{13}C NMR ($CDCl_3$, 125.76 MHz), **DEPT**, **HSQC** (d090909ghaf.648A)

δ = -5.35, -5.26 (2 q, Si(<u>C</u>H$_3$)$_2$*t*-Bu), 18.23 (s, Si<u>C</u>(CH$_3$)$_3$Me$_2$), 25.89 (q, SiC(<u>C</u>H$_3$)$_3$Me$_2$), 28.22 (q, OC(<u>C</u>H$_3$)$_3$), 56.46 (d, C-1), 62.44 (t, C-1'), 84.09 (s, O<u>C</u>(CH$_3$)$_3$), 118.33 (t, C-3), 133.56 (d, C-2), 152.48 (s, <u>C</u>O$_2$*t*-Bu), 163.52 (d, CHO).

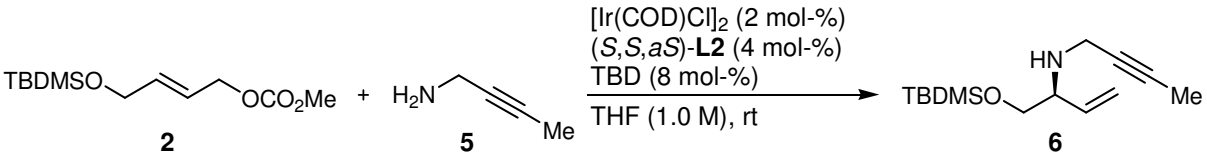
HR-MS (ESI+)

$C_{16}H_{31}NO_4SiK$	Calcd.	368.1654	
$[M+K]^+$	Found	368.1657	Diff.: -0.3 mmu.

Elemental Analysis

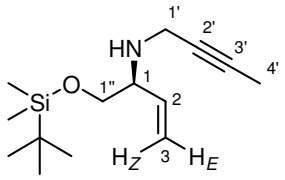
$C_{16}H_{31}NO_4Si$	Calcd.	C 58.32	H 9.48	N 4.25
(329.51)	Found	C 58.38	H 9.46	N 4.47.

(2*S*)-1-{[*tert*-Butyl(dimethyl)silyl]oxy}-*N*-but-1-yn-1-ylbut-3-en-2-amine (6)



2 **5** **6**

According to *GP1*, a mixture of $[Ir(COD)Cl]_2$ (13.8 mg, 20 µmol), (*S*,*S*,*aS*)-**L2** (24.6 mg, 41 µmol), TBD (13.1 mg, 94 µmol), TBDMS-carbonate **2** (279 mg, 1.0 mmol), but-2-yn-1-amine **5** (85.0 mg, 1.20 mmol) and dry THF (1 mL) was stirred for 24 h at rt until TLC monitoring (petroleum ether/ethyl acetate 4:1, R_f(**2**) = 0.43, R_f(**6**) = 0.25, $KMnO_4$) showed full consumption of the starting material. The ratio **b**:**l** was determined by ^{1}H NMR of the crude product (**b**:**l** = 94:06). After column chromatography on silica gel (petroleum ether/diethyl ether 9:1) the branched allylamine **6** (165 mg, 0.65 mmol, 65 %) was obtained as yellowish oil.



6

Optical Rotation (98.5 %ee (*R*), determined by chiral HPLC)

$[\alpha]_D^{20}$ = -47.2, $[\alpha]_{578}^{20}$ = -49.2, $[\alpha]_{546}^{20}$ = -55.5, $[\alpha]_{436}^{20}$ = -93.0, $[\alpha]_{365}^{20}$ = -145.4

(*c* = 1.00, $CHCl_3$).

HPLC

(Daicel Chiralpak AS-H 4.6 x 250 mm with precolumn AS-H 10 x 4 mm, *n*-hexane/*i*-PrOH 99.7:0.3, flow = 0.4 mL/min, λ = 210 nm).

t_R[(+)-(*S*)-**6**] = 12.1 min

t_R[(-)-(*R*)-**6**] = 13.9 min.

^{1}H NMR ($CDCl_3$, 300.13 MHz), **H,H-COSY** (b091120ghot.1098B)

δ = 0.05 (s, 6 H, $SiMe_2$*t*-Bu), 0.89 (s, 9 H, $SiMe_2$*t*-Bu), 1.79 (t, *J* = 2.4 Hz, 3 H, 4'-H), 1.92 (bs, 1 H, NH), 3.20 (dq, *J* = 16.6 Hz, *J* = 2.3 Hz, 1 H, 1'-H_a), 3.30-3.50 (m, 3 H, 1'-H_b, 1-H, 1''-H_a), 3.59 (dd, *J* = 9.8 Hz, *J* = 4.1 Hz, 1 H, 1''-H_b), 5.16 (dd, *J* = 10.2 Hz, *J* = 1.9 Hz, 1 H, 3-H_E), 5.22-5.28 (m, 1 H, 3-H_Z), 5.54 (ddd, *J* = 17.5 Hz, *J* = 10.1 Hz, *J* = 7.9 Hz, 1 H, 2-H).

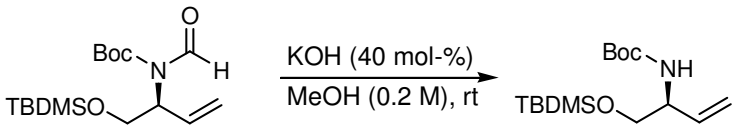
^{13}C NMR ($CDCl_3$, 75.48 MHz), **DEPT**, **HSQC** (b091120ghot.1098B)

δ = -5.26, -5.20 (2 q, $Si(\underline{C}H_3)_2$*t*-Bu), 3.62 (q, C-4'), 18.40 (s, $Si\underline{C}(CH_3)_3Me_2$), 25.99 (q, $SiC(\underline{C}H_3)_3Me_2$), 36.08 (t, C-1'), 62.10 (d, C-1), 66.20 (t, C-1''), 77.50 (s, C-3'), 78.79 (s, C-2'), 118.39 (t, C-3), 137.13 (d, C-2).

HR-MS (ESI+)

$C_{14}H_{28}NOSi$	Calcd. 254.1935	
$[M+H]^+$	Found 254.1932	Diff.: +0.2 mmu.

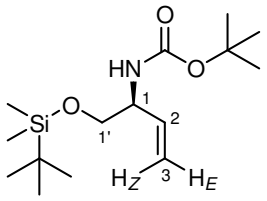
***tert*-Butyl [(1*S*)-1-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)prop-2-en-1-yl}carbamate (4a)**



4 **4a**

KOH (675 mg, 12.0 mmol) was added to a solution of amide **4** (9.90 g, 30.1 mmol) in MeOH (150 mL). The mixture was stirred for 1.5 h at room temperature until GC/MS monitoring (t_R(**4**) = 10.3 min, t_R(**4a**) = 9.6 min) showed full conversion of the starting material. The mixture was neutralized with Amberlite IR-120(H^+), and the exchange resign was filtered off. The solvent was removed under reduced

pressure, and the residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 9:1, R_f(**4a**) = 0.58 in petroleum ether/ethyl acetate 4:1, $KMnO_4$) yielding **4a** (8.58 g, 28.5 mmol, 95 %) as colourless oil.



4a

Optical Rotation (97.5 %ee (*S*), according to the starting material)

$[\alpha]_D^{20}$ = -35.0

(*c* = 1.05, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 500.13 MHz), **H,H-COSY** (d090914ghaf.654Am)

δ = 0.03, 0.04 (2 s, 6 H, Si<u>Me$_2$</u>*t*-Bu), 0.87 (s, 9 H, SiMe$_2$<u>*t*-Bu</u>), 1.44 (s, 9 H, *t*-Bu), 3.61 (dd, *J* = 10.0 Hz, *J* = 4.1 Hz, 1 H, 1'-H_a), 3.67 (dd, *J* = 10.0 Hz, *J* = 4.4 Hz, 1 H, 1'-H_b), 4.15 (bs, 1 H, 1-H), 4.82 (bs, 1 H, NH), 5.13 (d, *J* = 10.4 Hz, 1 H, 3-H_E), 5.20 (d, *J* = 17.3 Hz, 1 H, 3-H_Z), 5.82 (ddd, *J* = 17.1 Hz, *J* = 10.4 Hz, *J* = 5.6 Hz, 1 H, 2-H).

^{13}C NMR ($CDCl_3$, 125.77 MHz), **HSQC** (d090914ghaf.654Am)

δ = -5.31, -5.29 (2 q, Si(<u>C</u>H$_3$)$_3$*t*-Bu), 18.44 (s, Si<u>C</u>(CH$_3$)$_3$Me$_2$), 25.98 (q, SiC(<u>C</u>H$_3$)$_3$Me$_2$), 28.54 (q, OC(<u>C</u>H$_3$)$_3$), 54.38 (d, C-1), 65.43 (t, C-1'), 79.44 (s, O<u>C</u>(CH$_3$)$_3$), 115.65 (t, C-3), 136.73 (d, C-2), 155.58 (s, <u>C</u>O$_2$*t*-Bu).

GC/MS

t_R(**4a**) = 9.6 min, m/z = 245 $[M-C_4H_8]^+$.

HR-MS (ESI+)

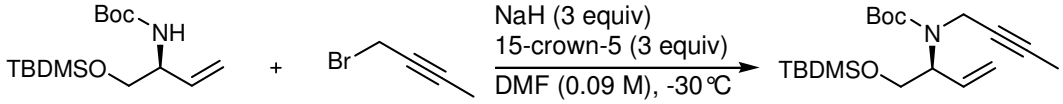
$C_{15}H_{32}NO_3Si$	Calcd.	302.2146	
$[M+H]^+$	Found	302.2140	Diff.: -0.3 mmu
$C_{15}H_{31}NO_3SiNa$	Calcd.	324.1965	
$[M+Na]^+$	Found	324.1969	Diff.: -0.4 mmu
$C_{15}H_{31}NO_3SiK$	Calcd.	340.1705	
$[M+K]^+$	Found	340.1708	Diff.: -0.3 mmu.

Elemental Analysis

$C_{15}H_{31}NO_3Si$	Calcd.	C 59.76	H 10.36	N 4.65
(301.50)	Found	C 59.57	H 10.51	N 4.65.

***tert*-Butyl [(1*S*)-1-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)prop-2-en-1-yl]but-2-yn-1-ylcarbamate (8)**

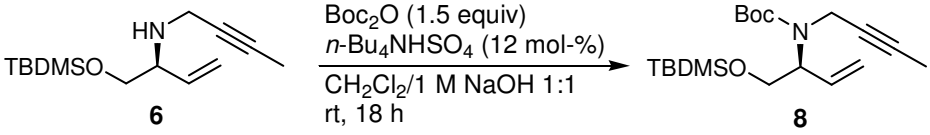
Method A:



4a **7** **8**

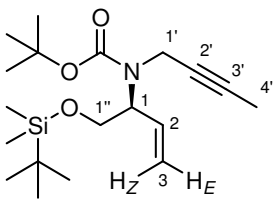
A solution of carbamate **4a** (8.20 g, 27.2 mmol) in dry DMF (300 mL) was cooled to -30 °C. Propargyl bromide (**7**) (18.1 g, 136 mmol) and 15-crown-5 (18.0 g, 81.5 mmol) were added, and the mixture was allowed to stir for 10 min. NaH (1.98 g, 81.5 mmol) was added in two portions in 0.5 h intervals, and the mixture was stirred for 3.5 h at -30 °C until TLC monitoring (petroleum ether/ethyl acetate 4:1, R_f(**4a**) = 0.51, R_f(**8**) = 0.58, $KMnO_4$) showed full consumption of the starting material. Saturated NH_4Cl solution (150 mL) was added, and the cooling bath was removed. The mixture was allowed to warm up to room temperature, and the aqueous phase was extracted with Et_2O (3 x 250 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 30:1 → 20:1) to afford enyne **8** (9.43 g, 26.7 mmol, 98 %) as yellowish oil.

Method B:



6 **8**

Boc_2O (193 mg, 0.88 mmol) was added to a biphasic mixture of enyne **6** (150 mg, 0.59 mmol) and *n*-Bu_4NHSO_4 (24.0 mg, 71 µmol) in CH_2Cl_2 (0.5 mL) and 1 M NaOH (0.5 mL). The mixture was vigorously stirred at room temperature for 18 h when TLC monitoring (petroleum ether/ethyl acetate, R_f(**6**) = 0.35, R_f(**8**) = 0.58, $KMnO_4$) indicated full consumption of the starting material. Water was added and the mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was subjected to column chromatography on silica gel (petroleum ether/diethyl ether 95:5) to yield **8** (193 mg, 0.55 mmol, 93 %) as colourless oil.



8

Optical Rotation (97.5 %ee (*S*), according to the starting material)

$[\alpha]_D^{20}$ = -4.4 (*c* = 0.91, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300.13 MHz, 50°C), **H,H-COSY** (b090916ghaf.656Am)

δ = 0.06 (s, 6 H, $SiMe_2$*t*-Bu), 0.90 (s, 9 H, $SiMe_2$*t*-Bu), 1.47 (s, 9 H, *t*-Bu), 1.78 (t, *J* = 2.3 Hz, 3 H, 4'-H), 3.81 (dd, *J* = 10.2 Hz, *J* = 6.4 Hz, 1 H, 1''-H_a), 3.88 (dd, *J* = 10.2 Hz, *J* = 6.7 Hz, 1 H, 1''-H_b), 3.89-4.05 (m, 2 H, 1'-H), 4.41 (bs, 1 H, 1-H), 5.18 (ddd, *J* = 10.6 Hz, *J* = 1.6 Hz, *J* = 1.6 Hz, 1 H, 3-H_E), 5.21 (ddd, *J* = 17.5 Hz, *J* = 1.7 Hz, *J* = 1.7 Hz, 1 H, 3-H_Z), 5.95 (ddd, *J* = 17.4 Hz, *J* = 10.6 Hz, *J* = 5.8 Hz, 1 H, 2-H)

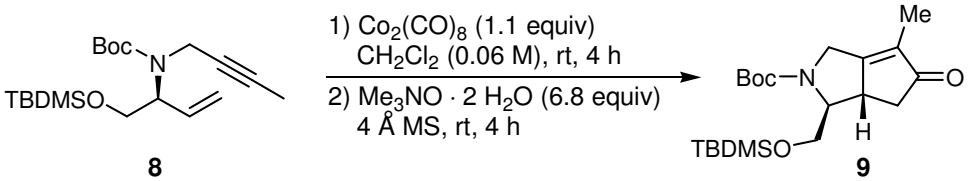
^{13}C NMR ($CDCl_3$, 75.47 MHz, 50°C), **DEPT**, **HSQC** (b090916ghaf.656Am)

δ = -5.26 (q, $Si(CH_3)_2$*t*-Bu), 3.54 (q, C-4'), 18.38 (s, $SiC(CH_3)_3Me_2$), 26.03 (q, $SiC(CH_3)_3Me_2$), 28.67 (q, $OC(CH_3)_3$), 35.55 (t, C-1'), 60.75 (d, C-1), 64.02 (t, C-1''), 76.59 (s, C-3'), 78.11 (s, C-2'), 80.12 (s, $OC(CH_3)_3$), 116.94 (t, C-3), 135.28 (d, C-2), 155.19 (s, CO_2*t*-Bu).

HR-MS (ESI+)

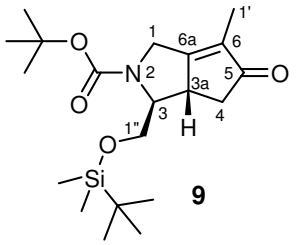
$C_{19}H_{36}NO_3Si$	Calcd. 354.2459	
$[M+H]^+$	Found 354.2463	Diff.: -0.4 mmu.

***tert*-Butyl (3*S*,3a*S*)-3-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)-6-methyl-5-oxo-3,3a,4,5-tetrahydrocyclopenta[*c*]pyrrole-2(1*H*)-carboxylate (9)**



8 **9**

$Co_2(CO)_8$ (7.34 g, 21.5 mmol) was added to a solution of enyne **8** (6.90 g, 19.5 mmol) in dry CH_2Cl_2 (325 mL). The mixture was stirred for 4 h at room temperature until TLC monitoring (petroleum ether/ethyl acetate 9:1, R_f(**8**) = 0.51, R_f(**8-$Co_2(CO)_6$**) = 0.65, $KMnO_4$) showed full consumption of the starting material. Then $Me_3NO \cdot 2\ H_2O$ (70.0 mg, 0.63 mmol) and 4 Å MS (25 g) were added. After stirring at room temperature for 4 h TLC monitoring (petroleum ether/ethyl acetate 4:1, R_f(**8-$Co_2(CO)_6$**) = 0.67, R_f(**9**) = 0.28, $KMnO_4$) indicated complete conversion of the cobalt-alkyne-complex. The solvent was removed *in vacuo*, and the crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) to afford cyclopentenone **9** (4.22 g, 11.1 mmol, 57 %) as colourless oil.



9

Optical Rotation (97.5 %ee (3*S*), according to the starting material)

$[\alpha]_D^{20}$ = -94.9, $[\alpha]_{578}^{20}$ = -98.6, $[\alpha]_{546}^{20}$ = -110.2, $[\alpha]_{436}^{20}$ = -152.6, $[\alpha]_{365}^{20}$ = +74.5

(*c* = 0.65, $CHCl_3$).

^{1}H NMR (Toluene-d_8, 300.13 MHz, 90°C), **H,H-COSY** (b091013ghaf.657Am)

δ = 0.03, 0.04 (2 s, 6 H, Si$\underline{Me_2}$*t*-Bu), 0.90 (s, 9 H, $SiMe_2$*t*-$\underline{Bu}$), 1.43 (s, 9 H, *t*-Bu), 1.51 (bs, 3 H, 1'-H), 1.87 (dd, *J* = 17.6 Hz, *J* = 3.5 Hz, 1 H, 4-H_a), 2.41 (dd, *J* = 17.6 Hz, *J* = 6.6 Hz, 1 H, 4-H_b), 2.90 (bs, 1 H, 3a-H), 3.10 (ddd, *J* = 8.3 Hz, *J* = 6.1 Hz, *J* = 2.8 Hz, 1 H, 3-H), 3.80 (d, *J* = 15.5 Hz, 1 H, 1''-H_a), 3.86 (d, *J* = 6.3 Hz, 1 H, 1-H_a), 4.05 (dd, *J* = 9.8 Hz, *J* = 3.0 Hz, 1 H, 1-H_b), 4.22 (d, *J* = 15.5 Hz, 1 H, 1''-H_b).

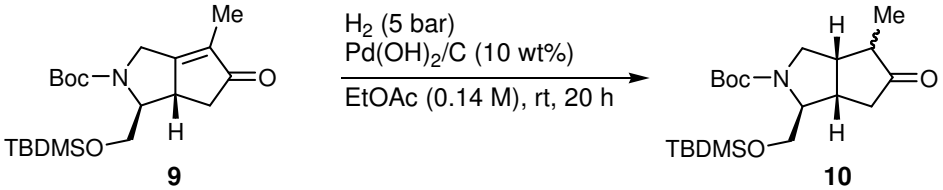
^{13}C NMR (Toluene-d_8, 75.48 MHz, 90°C), **DEPT**, **HSQC** (b091013ghaf.657Am)

δ = -5.07 (q, Si($\underline{C}H_3$)$_2$*t*-Bu), 8.38 (q, C-1'), 18.65 (s, Si$\underline{C}(CH_3)_3Me_2$), 26.29 (q, SiC($\underline{C}H_3$)$_3Me_2$), 28.82 (q, OC($\underline{C}H_3$)$_3$), 41.21 (t, C-4), 46.01 (d, C-3a), 47.61 (t, C-1), 64.70 (t, C-1''), 65.19 (d, C-3), 79.92 (s, O$\underline{C}(CH_3)_3$), 132.88 (s, C-6), 154.72 (s, $\underline{C}O_2$*t*-Bu), 168.80 (s, C-6a), 205.96 (s, C-5).

HR-MS (ESI+)

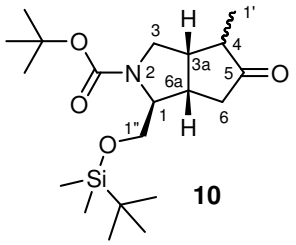
$C_{20}H_{34}NO_4Si$	Calcd. 380.2252	
$[M-H]^+$	Found 380.2254	Diff.: -0.2 mmu.

***tert*-Butyl (1*S*,3a*S*,6a*S*)-1-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)-4-methyl-5-oxo-hexahydrocyclopenta[*c*]pyrrole-2(1*H*)-carboxylate (10)**



9 **10**

$Pd(OH)_2$/C (408 mg, 10 wt%) was added to a solution of cyclopentenone **9** (4.08 g, 10.7 mmol) in EtOAc (76 mL). The black suspension was placed in an autoclave and stirred for 18 h under H_2 (5 bar). The mixture was filtered through a pad of silica (EtOAc) and concentrated *in vacuo* to give **10** (3.98 g, 10.4 mmol, 97 %) as colourless oil (dr = 60:40).



10

Optical Rotation (97.5 %ee (1*S*), according to the starting material)

$[\alpha]_D^{20}$ = +5.8, $[\alpha]_{578}^{20}$ = +6.2, $[\alpha]_{546}^{20}$ = +7.9, $[\alpha]_{436}^{20}$ = +27.4, $[\alpha]_{365}^{20}$ = +103.2

(*c* = 0.82, $CHCl_3$).

Mixture of stereoisomers at C-4, ratio 60:40

^{1}H NMR (Toluene-d_8, 300.13 MHz, 90°C), **H,H-COSY** (b090923ghaf.659A)

δ = 0.03 (s, 6 H, $Si(CH_3)_{2\_min}$), 0.05 (s, 6 H, $Si(CH_3)_{2\_maj}$), 0.84-0.90 (m, 6 H, 1'-$H_{maj+min}$), 0.90 (s, 9 H, Si*t*-Bu_{min}), 0.92 (s, 9 H, Si*t*-Bu_{maj}), 1.41 (s, 9 H, *t*-Bu_{maj}), 1.42 (s, 9 H, *t*-Bu_{min}), 1.56-1.70 (m, 2 H, 4-H_{min}, 6-H_{a_maj}), 1.92-1.99 (m, 2 H, 4-H_{maj}, 6-H_{a_min}), 2.08-2.09 (m, 1 H, 6-H_{b_min}), 2.13-2.24 (m, 2 H, 6a-H_{min}, 6-H_{b_maj}), 2.50 (dd, *J* = 16.4 Hz, *J* = 8.4 Hz, 1 H, 6a-H_{maj}), 2.61-2.79 (m, 2 H, 3a-$H_{maj+min}$), 2.95 (dd, *J* = 10.8 Hz, *J* = 9.8 Hz, 1 H, 3-H_{a_maj}), 3.34-3.39 (m, 3 H, 3-H_{min}, 3-H_{b_maj}), 3.47 (dd, *J* = 8.5 Hz, *J* = 4.4 Hz, 1 H, 1-H_{min}), 3.60-3.79 (m, 5 H, 1'-H_{maj}, 1''-$H_{maj+min}$).

^{13}C NMR (Toluene-d_8, 75.47 MHz, 90°C), **DEPT**, **HSQC** (b090923ghaf.659A)

δ = -5.10 (q, $Si(\underline{C}H_3)_{2\_min}$), -5.04 (q, $Si(\underline{C}H_3)_{2\_maj}$), 10.59 (q, C-1'$_{maj}$), 14.22 (q, C-1'$_{min}$), 18.62 (s, $Si\underline{C}(CH_3)_{3\_min}$), 18.65 (s, $Si\underline{C}(CH_3)_{3\_maj}$), 26.31 (2 q, $SiC(\underline{C}H_3)_{3\_maj+min}$), 28.83 (2 q, $OC(\underline{C}H_3)_{3\_maj+min}$), 40.61 (d, C-6a$_{maj}$), 40.96 (d, C-3a$_{min}$), 41.31 (t, C-6$_{maj}$), 41.73 (d, C-6a$_{min}$), 42.26 (t, C-6$_{min}$), 43.27 (d, C-3a$_{maj}$), 46.98 (d, C-4$_{maj}$), 47.26 (d, C-4$_{min}$), 47.85 (t, C-3$_{maj}$), 51.94 (t, C-3$_{min}$), 64.32 (t, C-1''$_{min}$), 64.49 (t, C-1''$_{maj}$), 65.59 (d, C-1$_{maj}$), 65.65 (d, C-1$_{min}$), 79.35 (s, $O\underline{C}(CH_3)_{3\_min}$), 79.40 (s, $O\underline{C}(CH_3)_{3\_maj}$), 154.45 (s, $\underline{C}O_2$*t*-Bu_{maj}), 154.53 (s, $\underline{C}O_2$*t*-Bu_{min}), 214.82 (s, C-5$_{maj}$), 215.90 (s, C-5$_{min}$).

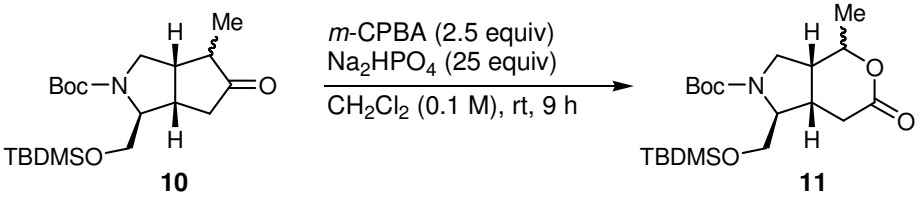
HR-MS (ESI+)

$C_{20}H_{38}NO_4Si$	Calcd. 384.2565	
$[M+H]^+$	Found 384.2566	Diff.: -0.1 mmu.

Elemental Analysis

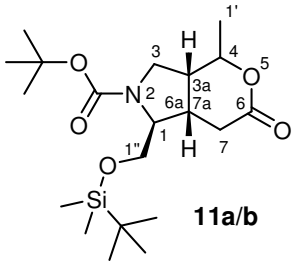
$C_{20}H_{37}NO_4Si$	Calcd.	C 62.62	H 9.72	N 3.65
(383.60)	Found	C 62.55	H 9.90	N 3.72.

***tert*-Butyl (1*S*,3a*R*,7a*S*)-1-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)-4-methyl-6-oxo-hexahydropyrano[3,4-*c*]pyrrole-2(3*H*)-carboxylate (11)**



10 **11**

Under an atmosphere of argon cyclopentanone **10** (3.30 g, 8.62 mmol) was dissolved in dry CH_2Cl_2 (86 mL). Na_2HPO_4 (30.6 g, 215 mmol) and *m*-CPBA (3.72 g, 21.6 mmol) were added, and the suspension was stirred at room temperature for 9 h until GC/MS monitoring (t_R(**10**) = 13.6 min and 13.7 min, t_R(**11**) = 15.7 min and 15.9 min) indicated full consumption of the starting material. Saturated Na_2SO_3 solution (100 mL) was added and the mixture was stirred at room temperature for 20 min. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 250 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1 → 2:1, R_f(**11a**) = 0.39, R_f(**11b**) = 0.27 in petroleum ether/ethyl acetate 2:1, $KMnO_4$) furnished lactone **11** as a mixture of diastereoisomers (dr = 60:40) (2.95 g, 7.37 mmol, 86 % combined yield). Analytically pure samples of each diastereoisomer could be obtained by partial separation upon a second column chromatography on silica gel (petroleum ether/ethyl acetate 4:1). **11a** is a colourless oil and **11b** crystallized on standing as colourless needles, mp 78-80 °C.



11a/b

Analytical data for 11a:

Optical Rotation (97.5 %ee (1*S*), according to the starting material)

$[\alpha]_D^{20}$ = -3.7, $[\alpha]_{578}^{20}$ = -3.6, $[\alpha]_{546}^{20}$ = -3.2, $[\alpha]_{436}^{20}$ = -0.4, $[\alpha]_{365}^{20}$ = +11.7

(*c* = 0.53, $CHCl_3$).

^{1}H NMR (Toluene-d_8, 300.13 MHz, 90 °C), **H,H-COSY** (b090924ghaf.660A)

δ = 0.00 (s, 6 H, Si<u>Me$_2$*t*-Bu</u>), 0.87 (s, 9 H, SiMe$_2$<u>*t*-Bu</u>), 0.98 (d, *J* = 6.1 Hz, 3 H, 1'-H), 1.43 (s, 9 H, *t*-Bu), 1.92 (dd, *J* = 14.4 Hz, *J* = 10.9 Hz, 1 H, 7-H_a), 1.94-2.00 (m, 1 H, 3a-H), 2.28-2.44 (m, 2 H, 7a-H, 7-H_b), 3.20 (dd, *J* = 11.5 Hz, *J* = 4.0 Hz, 1 H, 3-H_a), 3.31 (dd, *J* = 11.5 Hz, *J* = 8.4 Hz, 1 H, 3-H_b), 3.45 (dd, *J* = 5.2 Hz, *J* = 2.6 Hz, 1 H, 1-H), 3.50-3.59 (m, 3 H, 1-H, 1''-H_a, 4-H), 3.65 (dd, *J* = 9.8 Hz, *J* = 5.4 Hz, 1 H, 1''-H_b).

^{13}C NMR (Toluene-d_8, 75.47 MHz, 90°C), **DEPT**, **HSQC** (b090924ghaf.660A)

δ = -5.18 (q, Si(<u>C</u>H$_3$)$_2$*t*-Bu), 18.57 (s, Si<u>C</u>(CH$_3$)$_3$Me$_2$), 20.12 (q, 1'-H), 26.23 (q, SiC(<u>C</u>H$_3$)$_3$Me$_2$), 28.82 (q, OC(<u>C</u>H$_3$)$_3$), 33.99 (t, C-7), 38.73 (d, C-7a), 43.54 (d, C-3a), 49.82 (t, C-3), 64.59 (t, C-1''), 66.10 (d, C-1), 75.98 (d, C-4), 79.69 (s, O<u>C</u>(CH$_3$)$_3$), 154.07 (s, <u>C</u>O$_2$*t*-Bu), 169.80 (s, C-6).

HR-MS (ESI+)

$C_{20}H_{38}NO_5Si$	Calcd. 400.2514	
$[M+H]^+$	Found 400.2513	Diff.: +0.1 mmu
$C_{19}H_{37}NO_5SiNa$	Calcd. 422.2333	
$[M+Na]^+$	Found 422.2332	Diff.: +0.2 mmu.

Elemental Analysis

$C_{20}H_{37}NO_5Si$	Calcd.	C 60.11	H 9.33	N 3.51
(399.60)	Found	C 59.97	H 9.46	N 3.47.

Analytical data for 11b:

Optical Rotation (97.5 %ee (1*S*), according to the starting material)

$[\alpha]_D^{20}$ = -54.7, $[\alpha]_{578}^{20}$ = -56.7, $[\alpha]_{546}^{20}$ = -62.9, $[\alpha]_{436}^{20}$ = -104.5, $[\alpha]_{365}^{20}$ = -162.0

(*c* = 0.25, $CHCl_3$).

^{1}H NMR (Toluene-d_8, 300.13 MHz, 90°C), **H,H-COSY** (b090924ghaf.660B)

δ = 0.03 (s, 6 H, Si<u>Me$_2$</u>*t*-Bu), 0.90 (s, 9 H, SiMe$_2$<u>*t*-Bu</u>), 0.95 (d, *J* = 6.4 Hz, 3 H, 1'-H), 1.40 (s, 9 H, *t*-Bu), 2.03-2.24 (m, 3 H, 3a-H, 7-H), 2.40-2.47 (m, 1 H, 7a-H), 3.25 (dd, *J* = 10.8 Hz, *J* = 9.7 Hz, 1 H, 3-H$_a$), 3.53-3.65 (m, 4 H, 1-H, 1''-H, 3-H$_b$), 3.78-3.84 (m, 1 H, 4-H).

^{13}C NMR (Toluene-d_8, 75.47 MHz, 90°C), **DEPT**, **HSQC** (b090924ghaf.660B)

δ = -5.12 (q, Si(<u>C</u>H$_3$)$_2$*t*-Bu), 18.60 (s, Si<u>C</u>(CH$_3$)$_3$Me$_2$), 18.76 (q, 1'-H), 26.27 (q, SiC(<u>C</u>H$_3$)$_3$Me$_2$), 28.79 (q, OC(<u>C</u>H$_3$)$_3$), 33.77 (t, C-7), 38.39 (d, C-7a), 40.54 (d, C-3a), 45.38 (t, C-3), 64.70 (t, C-1''), 67.37 (d, C-1), 73.46 (d, C-4), 79.74 (s, O<u>C</u>(CH$_3$)$_3$), 154.14 (s, <u>C</u>O$_2$*t*-Bu), 169.13 (s, C-6).

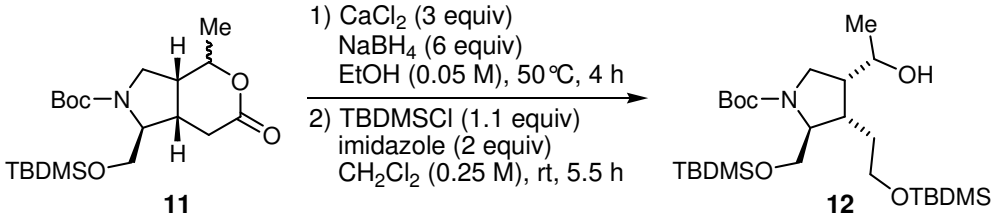
HR-MS (ESI+)

$C_{20}H_{38}NO_5Si$	Calcd. 400.2514	
$[M+H]^+$	Found 400.2515	Diff.: -0.1 mmu
$C_{19}H_{37}NO_5SiNa$	Calcd. 422.2333	
$[M+Na]^+$	Found 422.2335	Diff.: -0.1 mmu.

Elemental Analysis

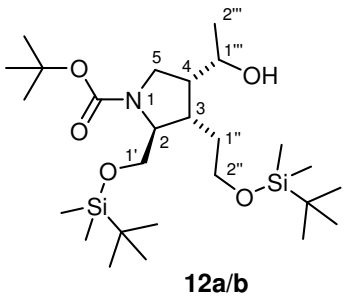
$C_{20}H_{37}NO_5Si$	Calcd.	C 60.11	H 9.33	N 3.51
(399.60)	Found	C 59.96	H 9.37	N 3.49.

***tert*-Butyl (2*S*,3*S*,4*R*)-3-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl)-2-({[*tert*-butyl(dimethyl)-silyl]oxy}methyl)-4-(1-hydroxyethyl)pyrrolidine-1-carboxylate (12)**



Freshly powdered $CaCl_2$ (2.19 g, 19.8 mmol) and $NaBH_4$ (1.49 g, 39.5 mmol) were added to a solution of lactone **11** (2.63 g, 6.58 mmol) in EtOH (132 mL). The white suspension was heated at 50 °C. After stirring for 4 h TLC monitoring (petroleum ether/ethyl acetate 1:1, R_f(**11**) = 0.60 and 0.54, R_f(**dialcohol**) = 0.27 and 0.19, $KMnO_4$) indicated full conversion. Water (32 mL) and MeOH (16 mL) were added to give a cloudy precipitation. 2 M HCl was added dropwise until the suspension became clear. Stirring was continued for further 10 min, and the aqueous phase was extracted with $CHCl_3$ (3 x 250 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (50 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a colourless, sticky foam.

Under an atmosphere of argon the residue was dissolved in dry CH_2Cl_2 (13 mL) and imidazole (896 mg, 13.2 mmol) was added. After stirring for 5 min at room temperature a solution of TBDMSCl (1.09 g, 7.24 mmol) in CH_2Cl_2 (13 mL) was added dropwise. Stirring was continued for 5.5 h when TLC monitoring (petroleum ether/ethyl acetate 1:1, R_f(**dialcohol**) = 0.27 and 0.19, R_f(**12**) = 0.73 and 0.64, $KMnO_4$) indicated full consumption of the starting material. Saturated $NaHSO_4$ solution (25 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1, R_f(**12a**) = 0.47, R_f(**12b**) = 0.29 in petroleum ether/ethyl acetate 4:1, $KMnO_4$) yielded alcohol **12** (3.12 g, 6.03 mmol, 92 % combined yield) as a mixture of diastereoisomers (dr = 60:40). Analytically pure samples of each diastereoisomer could be obtained by partial separation upon a second column chromatography on silica gel (petroleum ether/ethyl acetate 4:1). **12a** and **12b** are both a colourless, viscous oils.



12a/b

Analytical data for 12a:

Optical Rotation (97.5 %ee (2*S*), according to the starting material)

$[\alpha]_D^{20}$ = -22.9, $[\alpha]_{578}^{20}$ = -23.6, $[\alpha]_{546}^{20}$ = -26.0, $[\alpha]_{436}^{20}$ = -43.1, $[\alpha]_{365}^{20}$ = -64.9

(*c* = 0.55, $CHCl_3$).

^{1}H NMR (Toluene-d_8, 300.13 MHz, 90°C), **H,H-COSY** (b091008ghaf.675A)

δ = 0.06, 0.07 (2 s, 12 H, 2 Si$\underline{Me_2}$*t*-Bu), 0.93-0.95 (m, 21 H, 2 SiMe_2*t*-$\underline{Bu}$, 2'''-H), 1.23-1.35 (m, 2 H, 1''-H_a, OH), 1.44 (s, 9 H, *t*-Bu), 1.77-1.88 (m, 1 H, 1''-H_b), 2.22-2.33 (m, 1 H, 4-H), 2.41-2.47 (m, 1 H, 3-H), 2.98 (dd, *J* = 10.5 Hz, *J* = 10.5 Hz, 1 H, 5-H_a), 3.26 (dd, *J* = 10.3 Hz, *J* = 8.2 Hz, 5-H_b), 3.50-3.57 (m, 1 H, 1'''-H), 3.60-3.77 (m, 5 H, 1'-H, 2-H, 2''-H).

^{13}C NMR (Toluene-d_8, 75.47 MHz, 90°C), **DEPT**, **HSQC** (b091008ghaf.675A)

δ = -5.01 (q, 2 Si($\underline{C}H_3$)$_2$*t*-Bu), 18.67, 18.71 (2 s, 2 Si$\underline{C}(CH_3)_3Me_2$), 22.94 (q, C-2'''), 26.38 (q, 2 SiC($\underline{C}H_3$)$_3Me_2$), 28.92 (q, OC($\underline{C}H_3$)$_3$), 31.95 (t, C-1''), 39.45 (d, C-3), 48.31 (t, C-5), 48.49 (d, C-4), 63.00, 64.32 (2 t, C-1', C-2''), 65.90 (d, C-2), 66.62 (d, C-1'''), 79.01 (s, O$\underline{C}(CH_3)_3$), 154.68 (s, $\underline{C}O_2$*t*-Bu).

HR-MS (ESI+)

$C_{26}H_{56}NO_5Si_2$	Calcd. 518.3692	
$[M+H]^+$	Found 518.3694	Diff.: -0.3 mmu.

Elemental Analysis

$C_{26}H_{55}NO_5Si_2$	Calcd.	C 60.30	H 10.70	N 2.70
(517.89)	Found	C 60.26	H 10.76	N 2.70.

Analytical data for 12b:

Optical Rotation (97.5 %ee (2*S*), according to the starting material)

$[\alpha]_D^{20}$ = -26.5, $[\alpha]_{578}^{20}$ = -27.6, $[\alpha]_{546}^{20}$ = -31.3, $[\alpha]_{436}^{20}$ = -52.3, $[\alpha]_{365}^{20}$ = -80.2

(*c* = 1.19, $CHCl_3$).

^{1}H NMR (Toluene-d_8, 300.13 MHz, 90°C), **H,H-COSY** (b091008ghaf.676A)

δ = 0.04, 0.07 (2 s, 12 H, 2 Si$\underline{Me_2}$*t*-Bu), 0.93, 0.94 (2 s, 18 H, 2 SiMe_2*t*-$\underline{Bu}$), 1.03 (d, *J* = 6.1 Hz, 3 H, 2'''-H), 1.24-1.39 (m, 1 H, 1''-H_a), 1.46 (s, 9 H, *t*-Bu), 1.53-1.64 (m, 1 H, 1''-H_b), 2.15-2.27 (m, 2 H, 3-H, 4-H), 3.33 (dd, *J* = 10.0 Hz, *J* = 10.0 Hz, 1 H, 5-H_a), 3.54-3.71 (m, 5 H, 1'-H_a, 1'''-H, 2''-H, 5-H_b), 3.78-3.80 (m, 2 H, 1'-H_b, 2-H).

^{13}C NMR (Toluene-d_8, 75.47 MHz, 90°C), **DEPT**, **HSQC** (b091008ghaf.676A)

δ = -5.01 (q, 2 Si($\underline{C}H_3$)$_2$*t*-Bu), 18.69 (s, 2 Si$\underline{C}$(CH_3)$_3$$Me_2$), 22.88 (q, C-2'''), 26.39 (q, 2 SiC($\underline{C}H_3$)$_3$$Me_2$), 28.95 (q, OC($\underline{C}H_3$)$_3$), 31.68 (t, C-1''), 39.76 (d, C-3), 47.92 (d, C-4), 49.25 (t, C-5), 62.51 (t, C-2''), 64.30 (t, C-1'), 65.38 (d, C-2), 67.94 (d, C-1'''), 78.94 (s, O$\underline{C}$(CH_3)$_3$), 154.91 (s, $\underline{C}O_2$*t*-Bu).

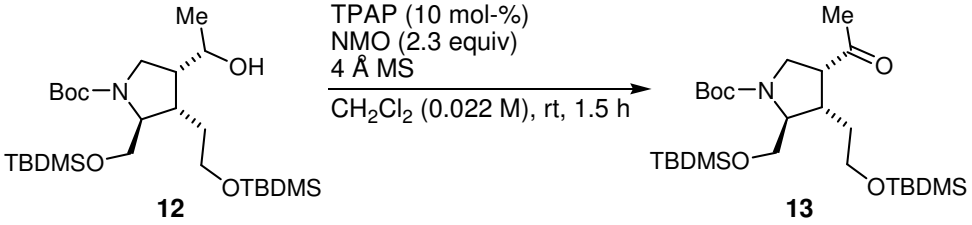
HR-MS (ESI+)

$C_{26}H_{56}NO_5Si_2$	Calcd.	518.3692	
$[M+H]^+$	Found	518.3694	Diff.: -0.2 mmu
$C_{26}H_{55}NO_5Si_2K$	Calcd.	556.3250	
$[M+K]^+$	Found	556.3259	Diff.: -0.8 mmu.

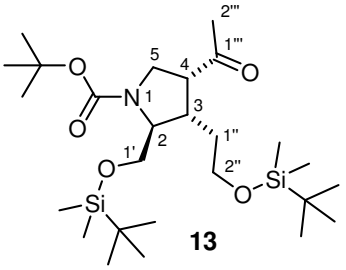
Elemental Analysis

$C_{26}H_{55}NO_5Si_2$	Calcd.	C 60.30	H 10.70	N 2.70
(517.89)	Found	C 60.39	H 10.72	N 2.70.

***tert*-Butyl (2*S*,3*S*,4*R*)-4-Acetyl-3-(2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl)-2-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)pyrrolidine-1-carboxylate (13)**



Under an atmosphere of argon at room temperature, TPAP (208 mg, 0.59 mmol) was added to a solution of alcohol **12** (3.06 g, 5.91 mmol), NMO (1.59 g, 13.6 mmol) and powdered 4 Å MS (6.1 g) in dry CH_2Cl_2 (268 mL). The suspension was stirred for 1.5 h until TLC monitoring (petroleum ether/ethyl acetate 4:1, R_f(**12**) = 0.32 and 0.20, R_f(**13**) = 0.48, $KMnO_4$) indicated full conversion of the substrate. Celite (14 g) was added, and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) to yield **13** (2.75 g, 5.33 mmol, 90 %) as colourless oil.



13

Optical Rotation (97.5 %ee (2*S*), according to the starting material)

$[\alpha]_D^{20}$ = -19.9, $[\alpha]_{578}^{20}$ = -20.5, $[\alpha]_{546}^{20}$ = -22.3, $[\alpha]_{436}^{20}$ = -27.1, $[\alpha]_{365}^{20}$ = -1.4

(*c* = 0.99, $CHCl_3$).

^{1}H NMR (Toluene-d_8, 300.13 MHz, 90°C), **H,H-COSY** (b091002ghaf.664Am)

δ = 0.00, 0.06 (2 s, 12 H, 2 Si$\underline{Me_2}$*t*-Bu), 0.90, 0.92 (2 s, 18 H, 2 SiMe_2*t*-$\underline{Bu}$), 1.32-1.47 (m, 2 H, 1''-H), 1.43 (s, 9 H, *t*-Bu), 1.85 (s, 3 H, 2'''-H), 2.62-2.69 (m, 1 H, 3-H), 3.15-3.22 (m, 1 H, 4-H), 3.34 (dd, *J* = 11.1 Hz, *J* = 7.6 Hz, 1 H, 5-H_a), 3.52 (dd, *J* = 6.0 Hz, *J* = 6.0 Hz, 2 H, 2''-H), 3.70-3.81 (m, 4 H, 1'-H, 2-H, 5-H_b).

^{13}C NMR (Toluene-d_8, 75.47 MHz, 90°C), **DEPT**, **HSQC** (b091002ghaf.664Am)

δ = -5.07 (q, 2 Si($\underline{C}H_3$)$_2$*t*-Bu), 18.66, 18.69 (2 s, 2 Si$\underline{C}$(CH_3)$_3$$Me_2$), 26.36 (q, 2 SiC($\underline{C}H_3$)$_3$$Me_2$), 28.87 (q, OC($\underline{C}H_3$)$_3$), 29.16 (q, C-2'''), 33.09 (t, C-1''), 40.58 (d, C-3), 47.35 (t, C-5), 53.61 (d, C-4), 61.93 (t, C-2''), 64.28 (t, C-1'), 64.89 (d, C-2), 79.26 (s, O$\underline{C}$(CH_3)$_3$), 154.74 (s, $\underline{C}O_2$*t*-Bu), 204.81 (s, C-1''').

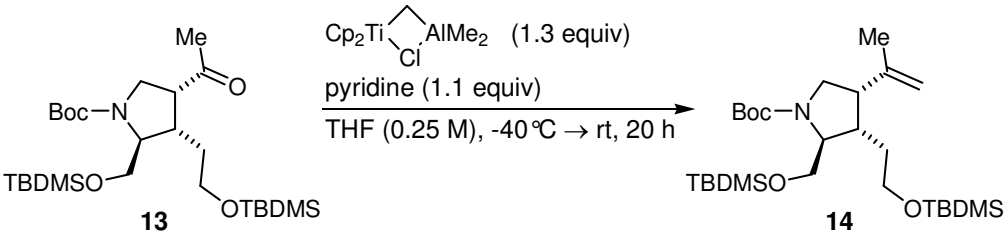
HR-MS (ESI+)

$C_{26}H_{54}NO_5Si_2$	Calcd.	516.3535	
$[M+H]^+$	Found	516.3534	Diff.: +0.1 mmu.

Elemental Analysis

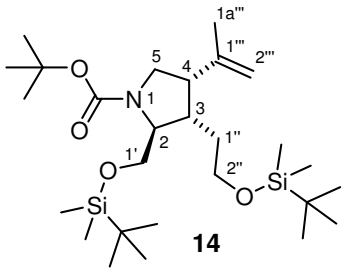
$C_{26}H_{53}NO_5Si_2$	Calcd.	C 60.53	H 10.36	N 2.72
(515.87)	Found	C 60.66	H 10.66	N 2.74.

***tert*-Butyl (2*S*,3*S*,4*S*)-3-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl)-2-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)-4-isopropenylpyrrolidine-1-carboxylate (14)**



Under an atmosphere of argon a solution of ketone **13** (2.53 g, 4.90 mmol) in dry THF (19.6 mL) was stirred and cooled to -40°C. Pyridine (435 µL, 5.39 mmol) was added, and stirring was continued for 10 min. A solution of Tebbe reagent (0.5 M in toluene, 12.8 mL, 6.38 mmol) was added dropwise, and the resulting deep red mixture was allowed to warm up to room temperature over 20 h until GC/MS monitoring (t_R(**13**) = 18.4 min, t_R(**14**) = 16.9 min) indicated full conversion of the substrate. The solution was diluted with Et_2O (100 mL), and 3 M NaOH was added dropwise until gas evolution ceases. The mixture was dried over Na_2SO_4, filtered through a pad of celite (EtOAc) and concentrated *in vacuo*. The crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 20:1, R_f(**14**) = 0.26, $KMnO_4$) to yield **14** (1.72 g, 3.35 mmol, 68 %) as colourless oil. The

synthesis of the **14** has been described in the literature via a different route and without complete analytical data.[1]



14

Optical Rotation (97.5 %ee (2*S*), according to the starting material)

$[\alpha]_D^{20}$ = -27.8, $[\alpha]_{578}^{20}$ = -29.0, $[\alpha]_{546}^{20}$ = -32.7, $[\alpha]_{436}^{20}$ = -53.3, $[\alpha]_{365}^{20}$ = -78.1

(*c* = 0.65, $CHCl_3$).

(lit.[1] $[\alpha]_D$ = -27.8; *c* = 1.0, $CHCl_3$)

^{1}H NMR (Toluene-d_8, 300.13 MHz, 90°C), **H,H-COSY** (b090930ghaf.665Am)

δ = 0.03, 0.07 (2 s, 12 H, 2 Si$\underline{Me_2}$*t*-Bu), 0.92, 0.93 (2 s, 18 H, 2 SiMe$_2$*t*-$\underline{Bu}$), 1.24-1.35 (m, 1 H, 1''-H_a), 1.45 (s, 9 H, *t*-Bu), 1.49-1.59 (m, 1 H, 1''-H_b), 1.64 (s, 3 H, 1a'''-H), 2.43-2.50 (m, 1 H, 3-H), 2.90 (dd, *J* = 14.6 Hz, *J* = 7.2 Hz, 1 H, 4-H), 3.40-3.52 (m, 2 H, 5-H), 3.55-3.67 (m, 2 H, 2''-H), 3.76-3.80 (m, 3 H, 1'-H, 2-H), 4.60, 4.78 (2 s, 2 H, 2'''-H).

^{13}C NMR (Toluene-d_8, 75.47 MHz, 90°C), **DEPT**, **HSQC** (b090930ghaf.665Am)

δ = -5.04 (q, 2 Si($\underline{C}H_3$)$_2$*t*-Bu), 18.69, 18.70 (2 s, 2 Si$\underline{C}$(CH$_3$)$_3$Me$_2$), 22.48 (q, C-1a'''), 26.38 (q, 2 SiC($\underline{C}H_3$)$_3$Me$_2$), 28.92 (q, OC($\underline{C}H_3$)$_3$), 32.38 (t, C-1''), 40.12 (d, C-3), 46.93 (d, C-4), 49.32 (t, C-5), 62.38 (t, C-2''), 64.33 (t, C-1'), 65.07 (d, C-2), 78.99 (s, O$\underline{C}$(CH$_3$)$_3$), 111.95 (t, C-2'''), 143.86 (s, C-1'''), 154.76 (s, $\underline{C}O_2$*t*-Bu).

HR-MS (ESI+)

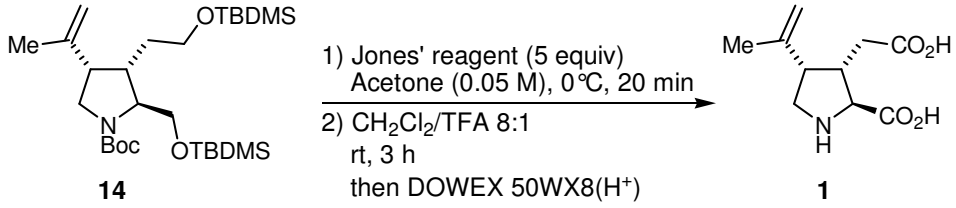
$C_{27}H_{56}NO_4Si_2$	Calcd.	514.3742	
$[M+H]^+$	Found	514.3741	Diff.: +0.1 mmu
$C_{27}H_{55}NO_4Si_2Na$	Calcd.	536.3562	
$[M+Na]^+$	Found	536.3561	Diff.: +0.1 mmu
$C_{27}H_{55}NO_4Si_2K$	Calcd.	552.3301	
$[M+K]^+$	Found	552.3305	Diff.: -0.4 mmu.

1 ^{1}H NMR ($CDCl_3$): Konno, K.; Hashimoto, K.; Ohfune, Y.; Shirahama, H.; Matsumoto, T. *J. Am. Chem. Soc.* **1988**, *110*, 4807-4815.

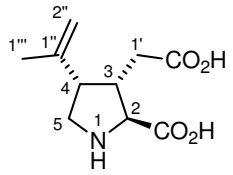
Elemental Analysis

$C_{27}H_{55}NO_4Si_2$	Calcd.	C 63.10	H 10.79	N 2.73
(513.90)	Found	C 63.18	H 11.03	N 2.76.

(-)-α-Kainic Acid / (3*S*,4*S*)-3-(Carboxymethyl)-4-isopropenyl-L-proline (1)



Precooled Jones' reagent (2.5 M, 420 µL, 1.05 mmol) was added dropwise over 5 min to a stirred ice-cooled (0 °C) solution of **14** (108 mg, 0.21 mmol) in acetone (4.2 mL), and stirring was continued for 20 min at 0 °C. The excess of Jones' reagent was quenched by addition of *i*-propanol (420 µL). The green suspension was stirred for 5 min at 0 °C and 10 min at room temperature. The clear greenish supernatant was decanted, and the remaining green residue was extracted with EtOAc (5 x 15 mL). The combined organic layers were washed with brine (3 x 4 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. A solution of the residue in Et_2O was filtered through a plug of see sand to remove further precipitated chromium salts. The solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (800 µL). The solution was treated with TFA (100 µL). After stirring at room temperature for 3 h TLC monitoring (petroleum ether/ethyl acetate 1:1 + AcOH, R_f(*N*-Boc-kainic acid) = 0.32, R_f(**1**) = 0.01, $KMnO_4$) indicated full consumption of the starting material. After removal of the solvent under reduced pressure the residue was dissolved in water (1 mL) and added to a column (1 x 1 cm) containing DOWEX 50WX8(H^+) (50-100 mesh). Elution with 1 M NH_4OH and evaporation of the collected fractions (ninhydrine) under reduced pressure yielded an orange oil, which was subjected to a second column (1 x 1 cm) containing Amberlite CG-50 (50-100 mesh) and eluted with water. The solvent was removed under reduced pressure to afford (-)-α-kainic acid **1** (34.0 mg, 0.16 mmol, 76 %) as light yellow needles (mp 238-240 °C dec., lit.[2] 237-243 °C dec.).



(-)-α-Kainic acid (1)

Optical Rotation (97.5 %ee (2*S*), according to the starting material)

$[\alpha]_D^{20}$ = -14.2

(*c* = 0.65, H_2O).

[2] Oppolzer, W.; Thirring, K. *J. Am. Chem. Soc.* **1982**, *104*, 4978-4979.

(lit.[3] $[\alpha]_D^{20}$ = -14.2; *c* = 0.23, H_2O)

^{1}H NMR (D_2O, 500.13 MHz), **H,H-COSY** (d091009ghaf.677A)

δ = 1.79 (s, 3 H, 1'''-H), 2.19 (dd, *J* = 15.6 Hz, *J* = 8.3 Hz, 1 H, 1'-H_a), 2.31 (dd, *J* = 15.6 Hz, *J* = 6.4 Hz, 1 H, 1'-H_b), 2.98-3.08 (m, 2 H, 3-H, 4-H), 3.45 (dd, *J* = 11.3 Hz, *J* = 11.3 Hz, 1 H, 5-H_a), 3.64 (dd, *J* = 11.9 Hz, *J* = 7.4 Hz, 1 H, 5-H_a), 4.08 (d, *J* = 3.0 Hz, 1 H, 2-H), 4.76, 5.04 (2 s, 2 H, 2''-H).

^{13}C NMR (D_2O, 125.77 MHz), **DEPT**, **HSQC** (d091009ghaf.677A)

δ = 22.17 (q, C-1'''), 35.68 (t, C-1'), 41.71 (d, C-3), 45.81 (d, C-4), 46.34 (t, C-5), 65.88 (d, C-2), 113.00 (t, C-2''), 140.21 (s, C-1''), 173.59, 179.24 (2 s, 2 $\underline{C}O_2H$).

HR-MS (ESI+)

$C_{10}H_{16}NO_4$	Calcd.	214.1074	
$[M+Na]^+$	Found	214.1072	Diff.: +0.2 mmu
$C_{10}H_{15}NO_4Na$	Calcd.	236.0893	
$[M+Na]^+$	Found	236.0892	Diff.: +0.1 mmu
$C_{20}H_{30}N_2O_8Na$	Calcd.	449.1894	
$[2M+Na]^+$	Found	449.1894	Diff.: 0.0 mmu.

[3] Takano, S.; Sugihara, T.; Satoh, S.; Ogasawara, K. *J. Am. Chem. Soc.* **1988**, *110*, 6467-6471.

HPLC diagrams

(+)-*tert*-Butyl [(1*S*)-1-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)prop-2-en-1-yl}formylcarbamate (4)

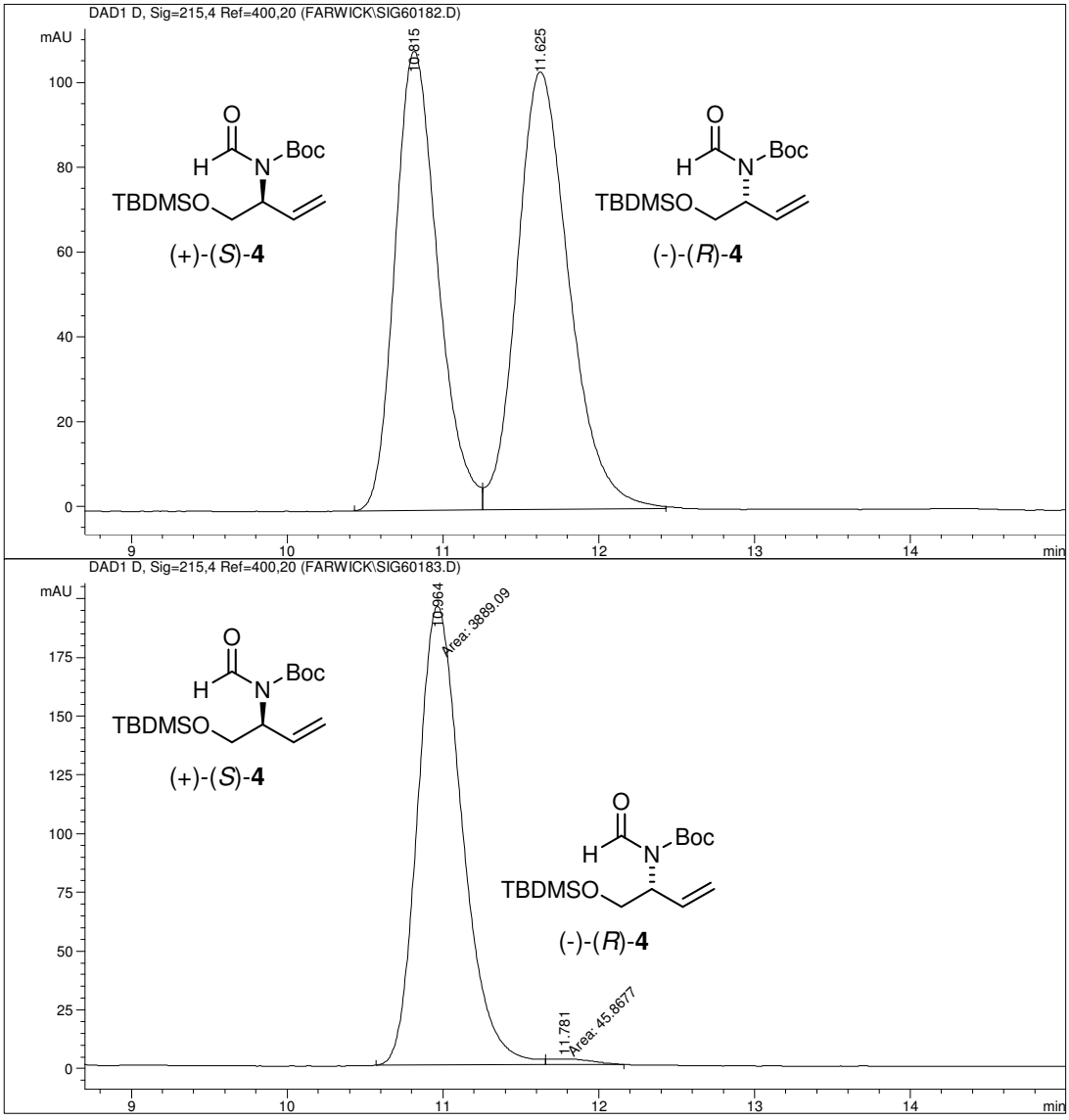


Figure 1: HPLC diagram of (±)-**4** (above) and the enantiomerically enriched product (+)-(*S*)-**4** (97.5 %ee, below).

Instrument:	HP1100 / HP 1090 Liquid Chromatograph
Column:	Daicel Chiralpak AS-H (250 x 4.6 mm, 5 µm) with guard cartridge AS-H (10 x 4 mm, 5 µm)
Conditions:	*n*-hexane/*i*-PrOH 99.7:0.3, flow 0.4 mL/min, λ = 215 nm, rt.
Retention time:	t_R[(+)-(*S*)-**4**] = 10.8 min
	t_R[(-)-(*R*)-**4**] = 11.8 min.

(+)-(2*S*)-1-{[*tert*-Butyl(dimethyl)silyl]oxy}-*N*-but-1-yn-1-ylbut-3-en-2-amine (6)

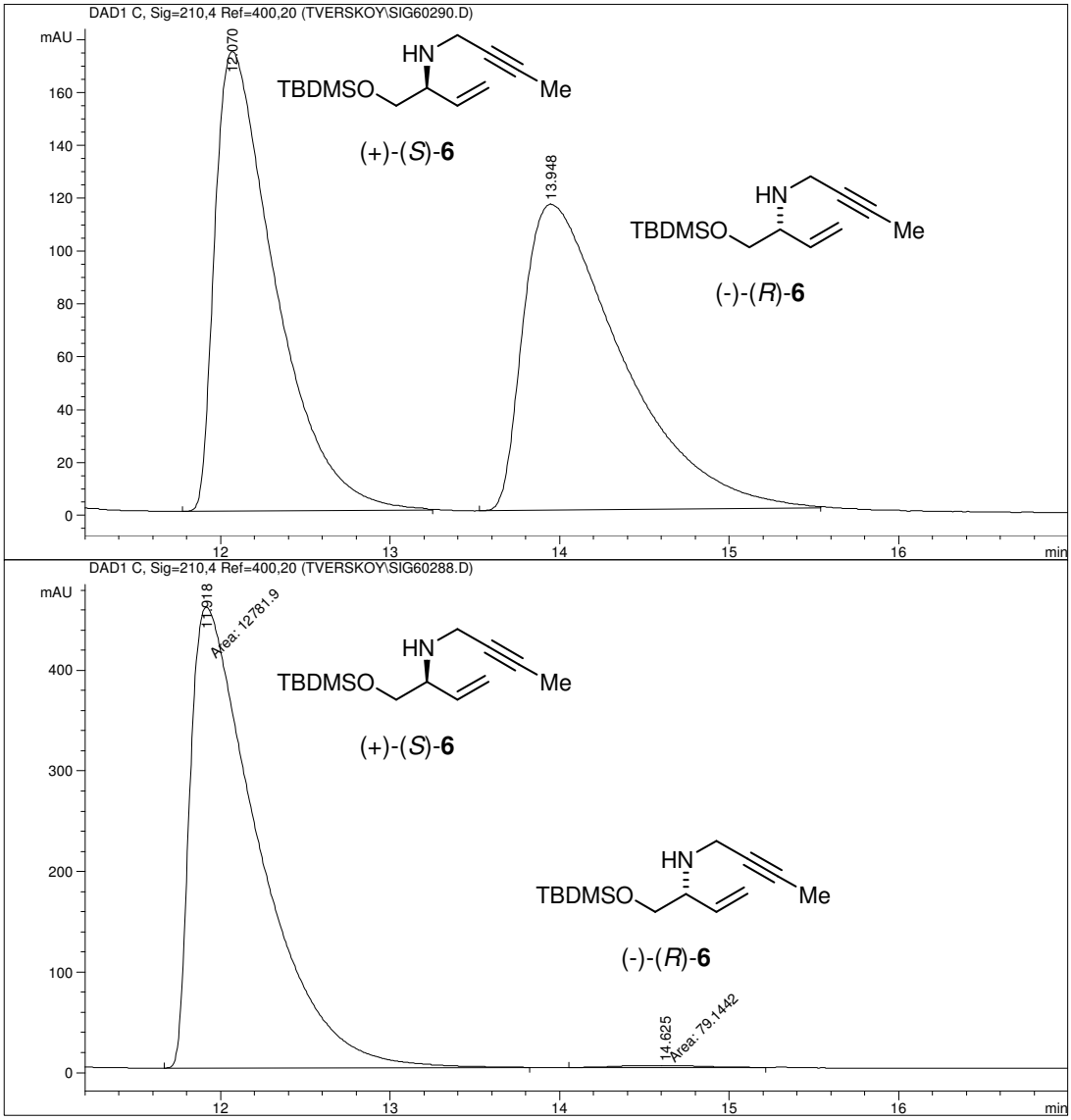
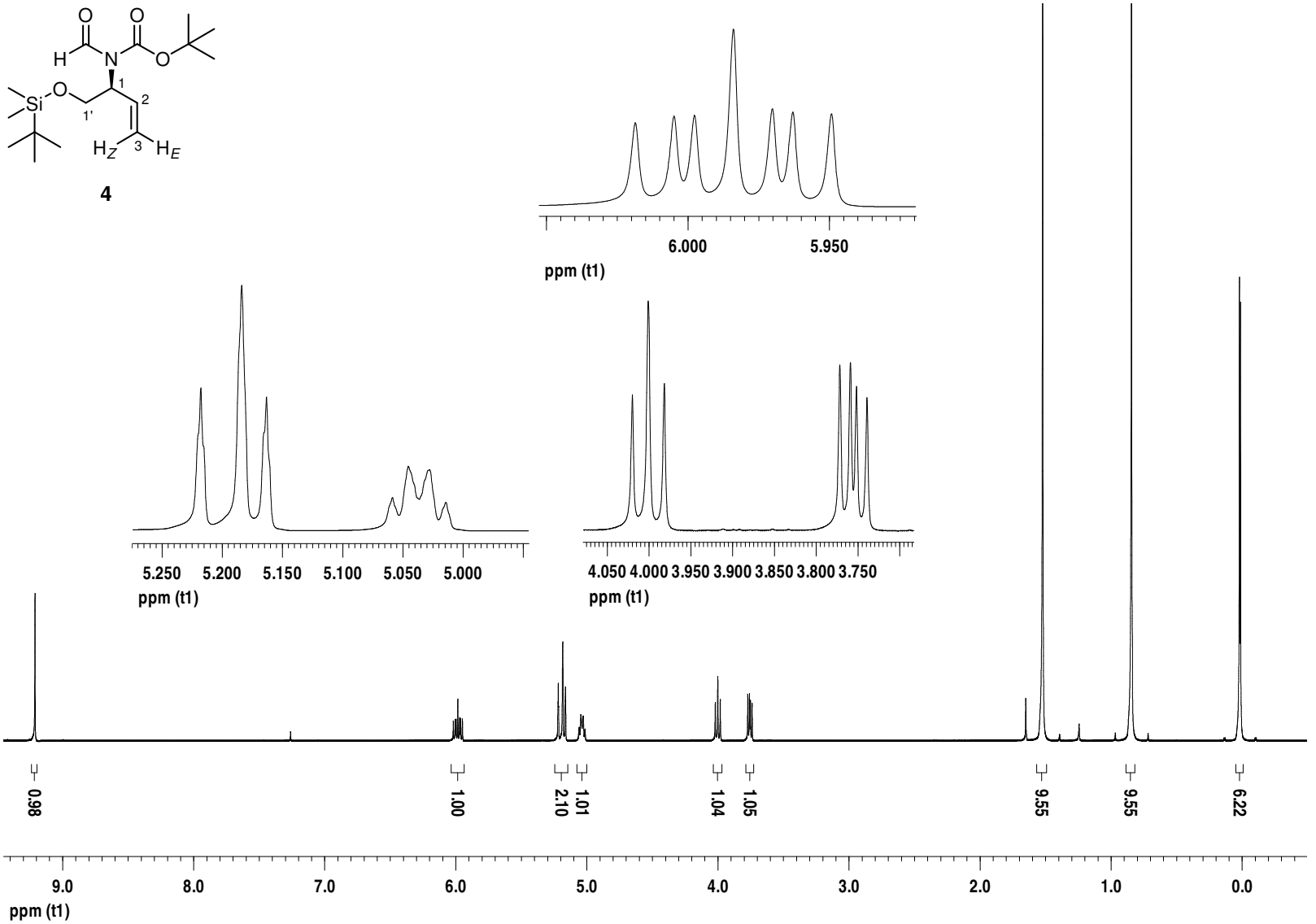


Figure 2: HPLC diagram of (±)-**6** (above) and the enantiomerically enriched product (+)-(*S*)-**6** (99 %ee, below).

Instrument:	HP1100 / HP 1090 Liquid Chromatograph
Column:	Daicel Chiralpak AS-H (250 x 4.6 mm, 5 µm) with guard cartridge AS-H (10 x 4 mm, 5 µm)
Conditions:	*n*-hexane/*i*-PrOH 99.7:0.3, flow 0.4 mL/min, λ = 210 nm, rt.
Retention time:	t_R[(+)-(*S*)-**6**] = 12.1 min
	t_R[(-)-(*R*)-**6**] = 13.9 min.

Selected NMR spectra

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PROCNO                   1

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TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                    32
DW                55.600 usec
DE                 6.00 usec
TE                298.1 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                 0.00 dB
SFO1         500.1325006 MHz

F2 - Processing parameters
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LB                 0.30 Hz
GB                     0
PC                  1.00
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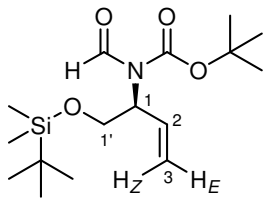

4


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Current Data Parameters
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EXPNO                   12
PROCNO                   1

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INSTRUM             spect
PROBHD   5 mm BBI 1H-BB
PULPROG           zgpg30
TD                163840
SOLVENT             CDCl3
NS                    640
DS                      4
SWH           31446.541 Hz
FIDRES         0.191934 Hz
AQ            2.6051061 sec
RG               9195.2
DW                15.900 usec
DE                20.00 usec
TE                298.1 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                   50

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.45 usec
PL1                -1.00 dB
SFO1        125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               18.00 dB
PL13               22.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                  65536
SF          125.7577890 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
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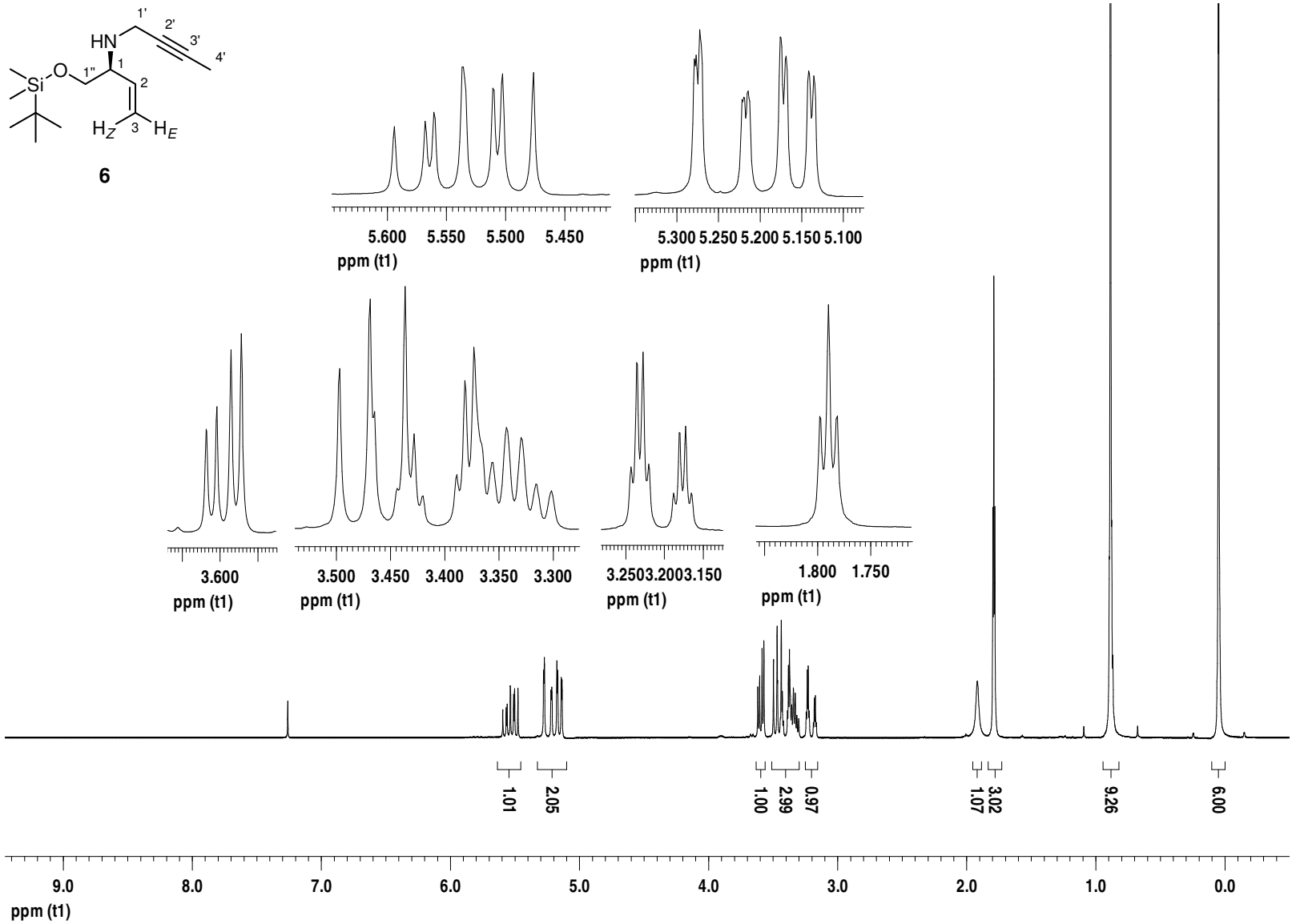


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Current Data Parameters
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EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20091120
Time                 11.45
INSTRUM              spect
PROBHD    5 mm TBI 1H/31
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               5112.475 Hz
FIDRES             0.312041 Hz
AQ                1.6024052 sec
RG                     45.3
DW                   97.800 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                   10.00 usec
PL1                   0.00 dB
SFO1          300.1321009 MHz

F2 - Processing parameters
SI                    32768
SF            300.1300204 MHz
WDW                     EM
SSB                      0
LB                    0.10 Hz
GB                       0
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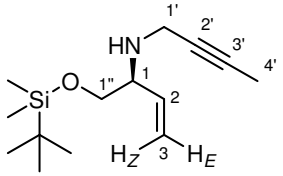

6


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Current Data Parameters
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EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
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INSTRUM            spect
PROBHD   5 mm TBI 1H/31
PULPROG             zgpg
TD                 32768
SOLVENT            CDCl3
NS                  1000
DS                     4
SWH           21097.047 Hz
FIDRES         0.643831 Hz
AQ            0.7766516 sec
RG               9195.2
DW                23.700 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                20.00 usec
PL1                0.00 dB
SFO1          75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                0.00 dB
PL12              20.00 dB
PL13             120.00 dB
SFO2         300.1316507 MHz

F2 - Processing parameters
SI                 65536
SF            75.4677190 MHz
WDW                   EM
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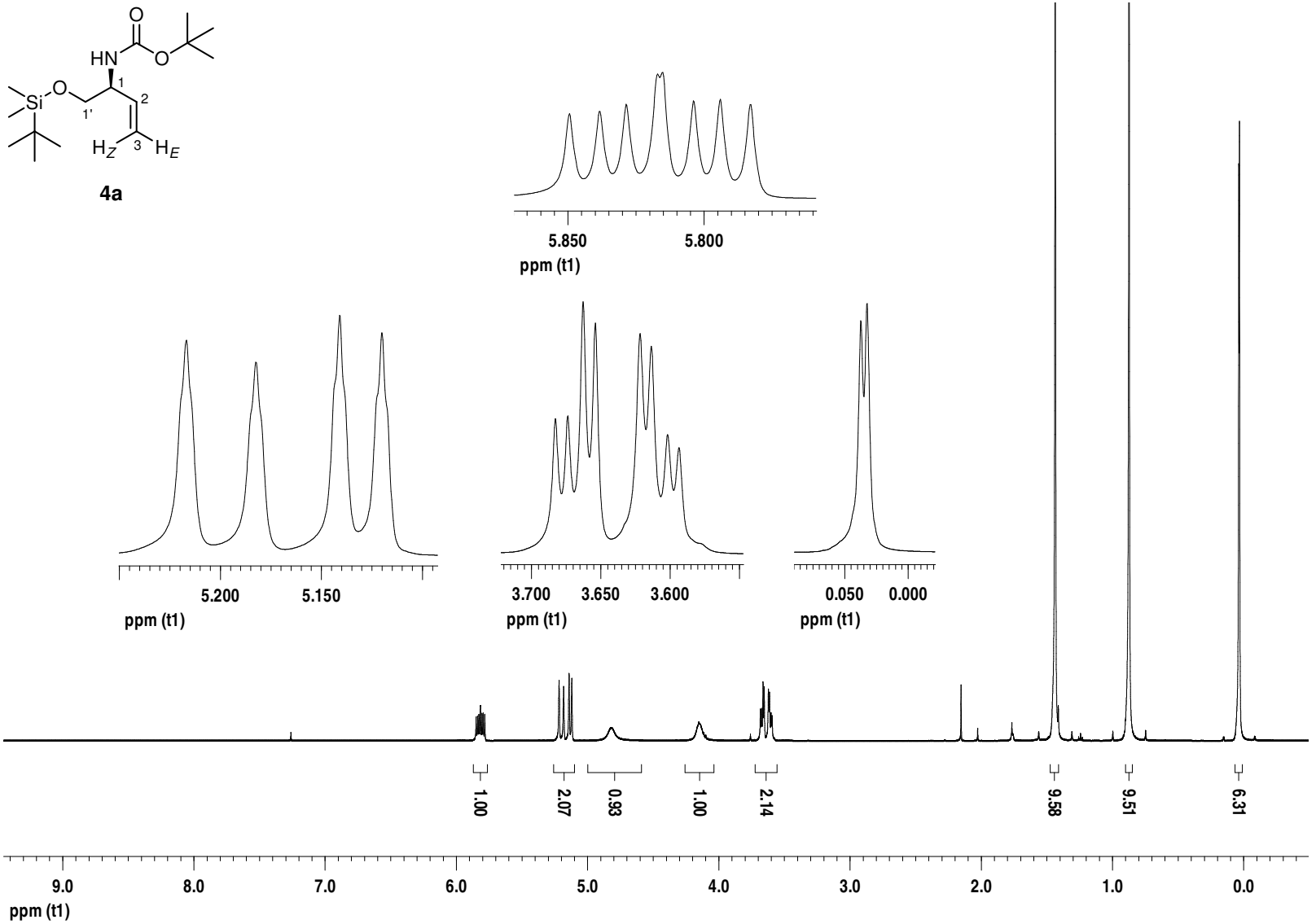


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EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
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Time                8.50
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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH              8992.806 Hz
FIDRES           0.137219 Hz
AQ             3.6438515 sec
RG                  28.5
DW                55.600 usec
DE                 6.00 usec
TE                298.0 K
D1             0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                 0.00 dB
SFO1         500.1325006 MHz

F2 - Processing parameters
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SF           500.1300299 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
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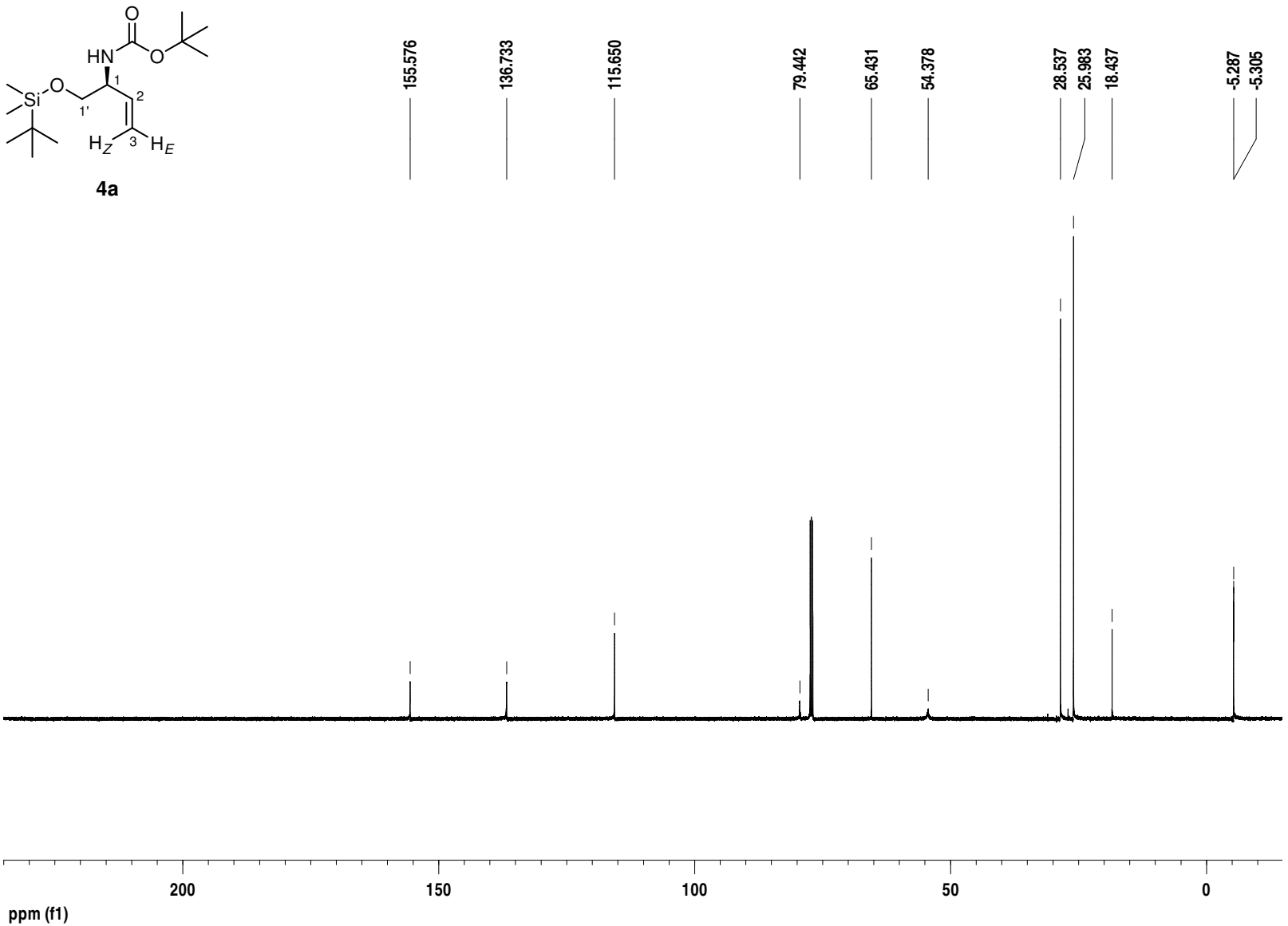

4a

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PROCNO                   1

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Time                9.26
INSTRUM            spect
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PULPROG           zgpg30
TD                163840
SOLVENT             CDCl3
NS                   1288
DS                      4
SWH           31446.541 Hz
FIDRES         0.191934 Hz
AQ            2.6051061 sec
RG                   8192
DW                15.900 usec
DE                20.00 usec
TE                297.9 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                    50

======== CHANNEL f1 ========
NUC1                  13C
P1                 16.45 usec
PL1                -1.00 dB
SFO1        125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               18.00 dB
PL13               22.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
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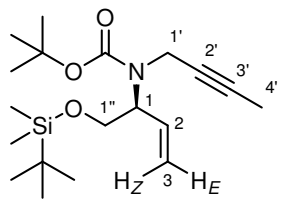

8


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Current Data Parameters
NAME      b090916ghaf.656Am
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20090916
Time                7.41
INSTRUM            spect
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PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5112.475 Hz
FIDRES          0.312041 Hz
AQ             1.6024052 sec
RG                   128
DW                97.800 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                10.00 usec
PL1                0.00 dB
SFO1         300.1321009 MHz

F2 - Processing parameters
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WDW                   EM
SSB                    0
LB                  0.10 Hz
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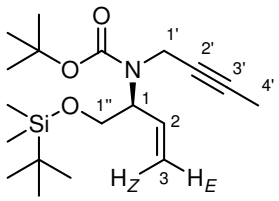

8


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Current Data Parameters
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PROCNO                   1

F2 - Acquisition Parameters
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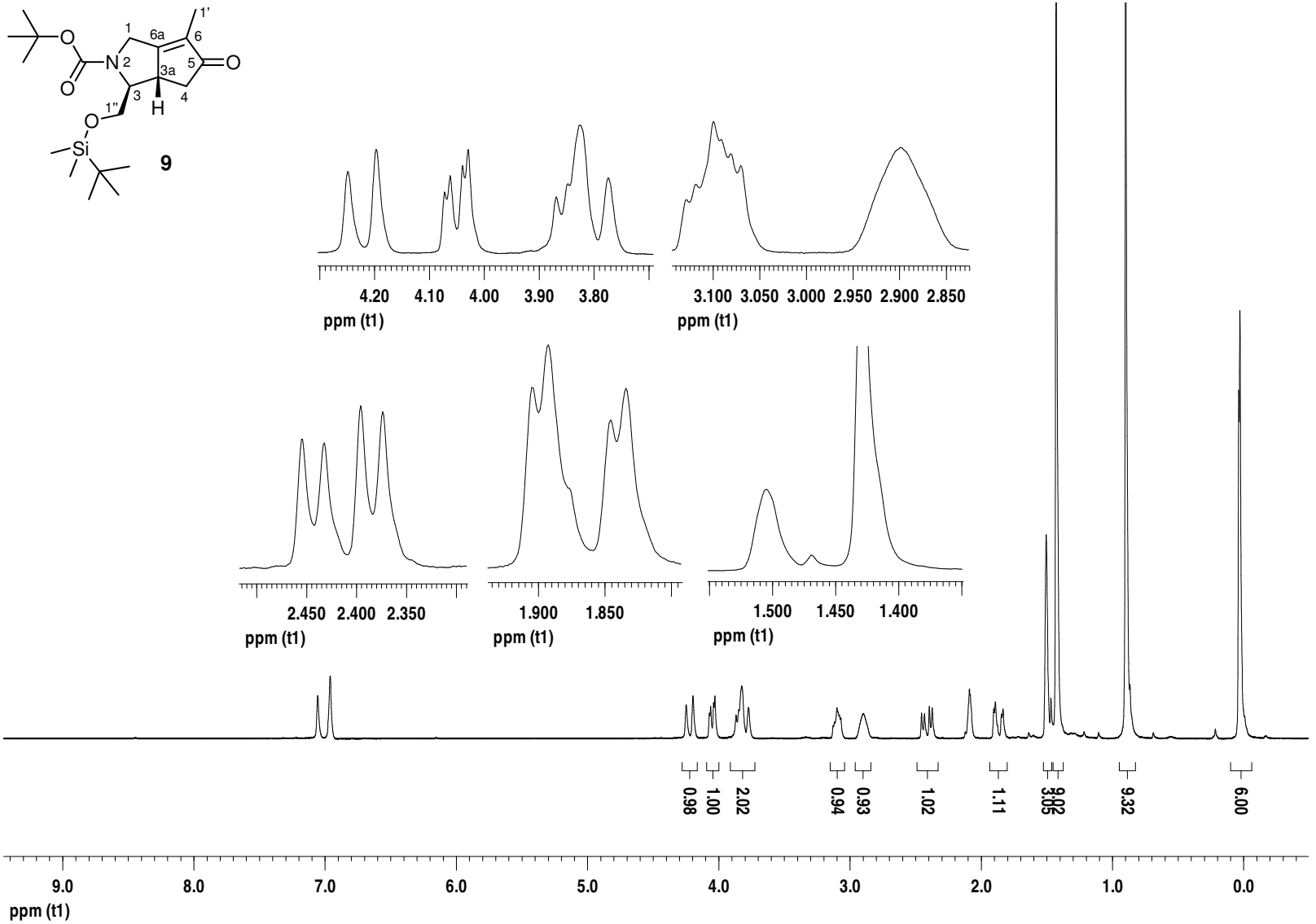
Time                8.28
INSTRUM            spect
PROBHD   5 mm TBI 1H/31
PULPROG             zgpg
TD                 32768
SOLVENT            CDCl3
NS                  4968
DS                     4
SWH            21097.047 Hz
FIDRES          0.643831 Hz
AQ             0.7766516 sec
RG                9195.2
DW                23.700 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                20.00 usec
PL1                0.00 dB
SFO1          75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             100.00 usec
PL2                0.00 dB
PL12              20.00 dB
PL13             120.00 dB
SFO2         300.1316507 MHz

F2 - Processing parameters
SI                 65536
SF            75.4677190 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  0.50
```

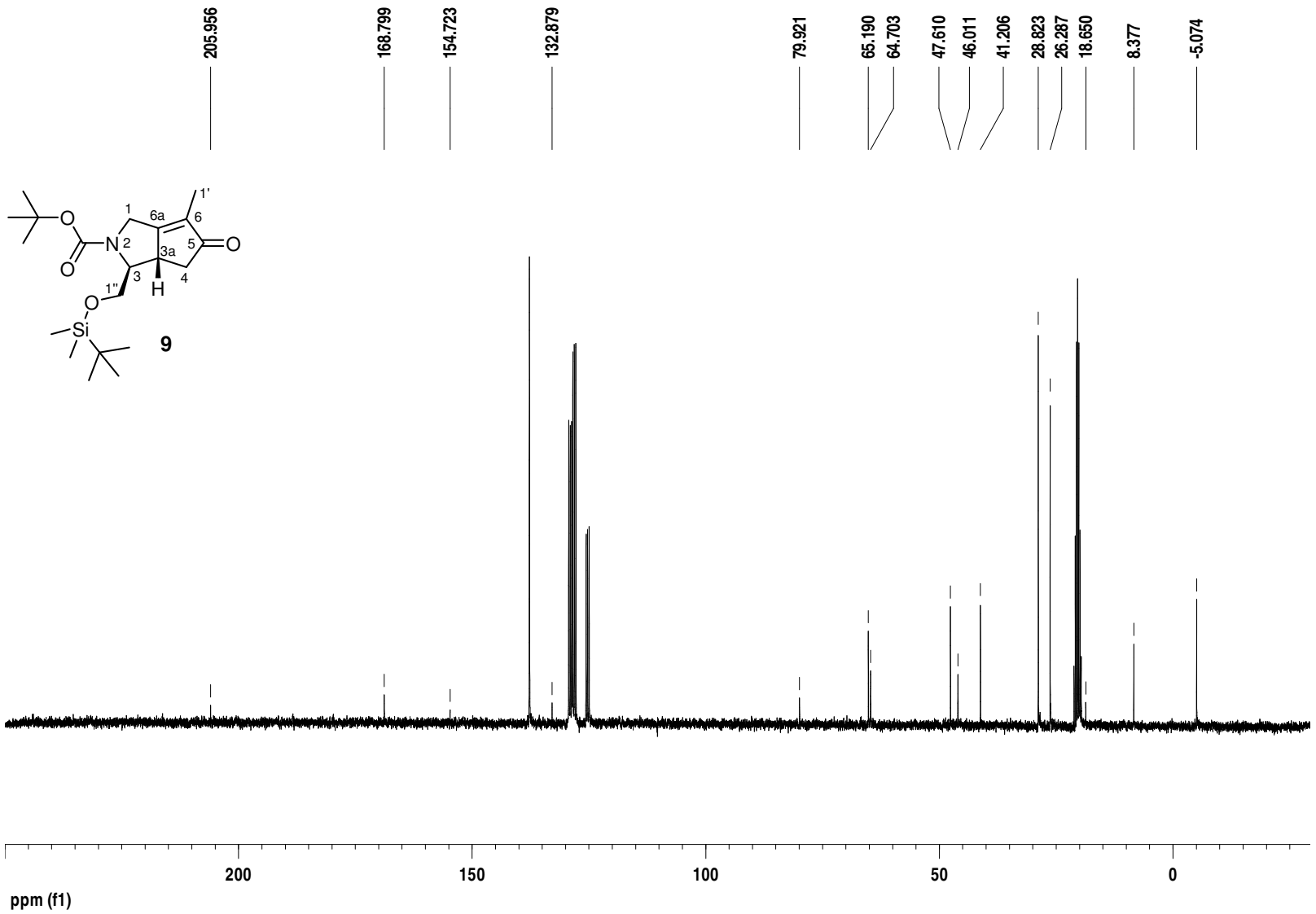



```
Current Data Parameters
NAME      b090924ghaf.657Am
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20090924
Time                8.36
INSTRUM            spect
PROBHD   5 mm TBI 1H/31
PULPROG             zg30
TD                 16384
SOLVENT              Tol
NS                    16
DS                     2
SWH             5112.475 Hz
FIDRES          0.312041 Hz
AQ             1.6024052 sec
RG                  40.3
DW                97.800 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                10.00 usec
PL1                0.00 dB
SFO1         300.1321009 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300149 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```



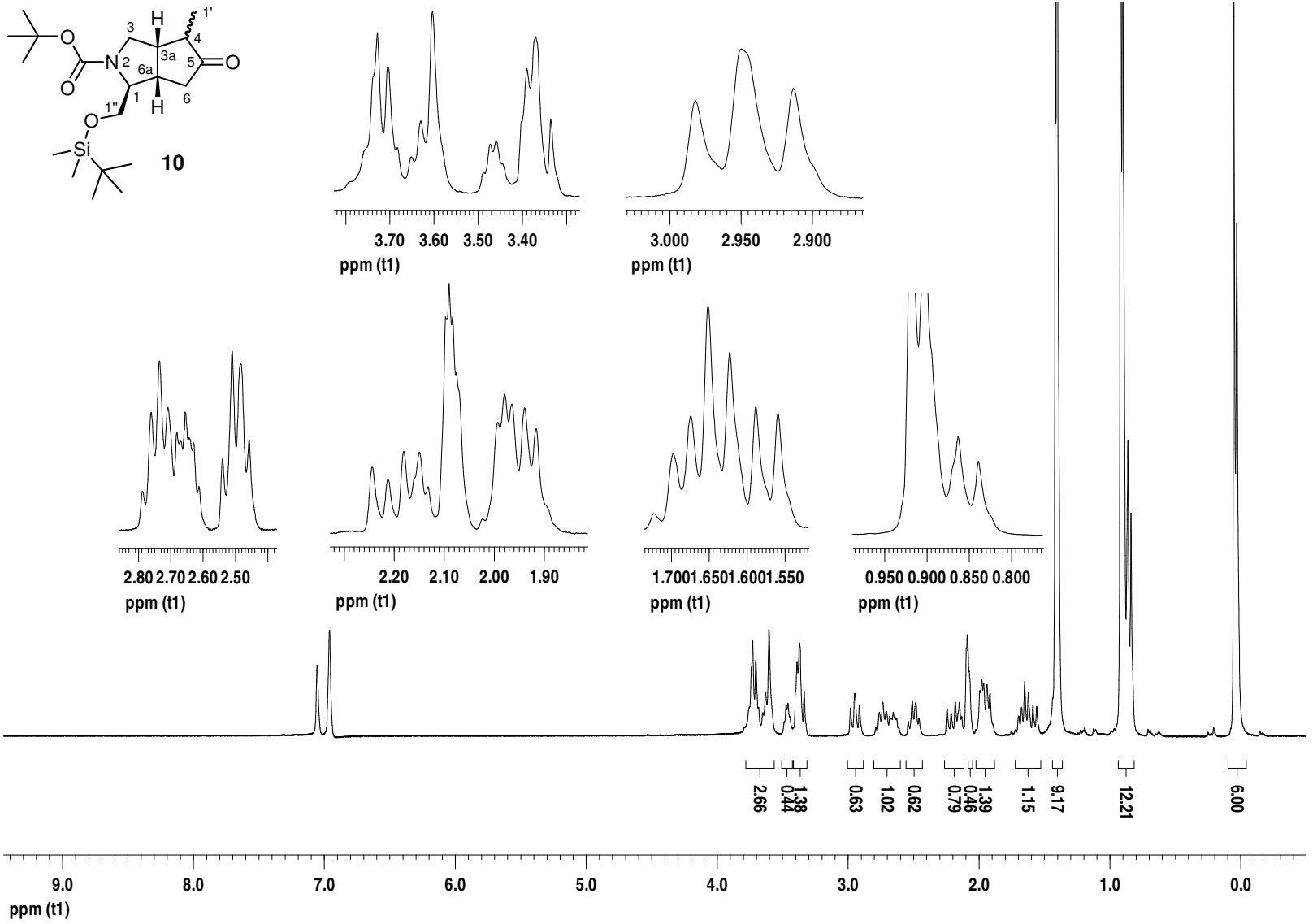

```
Current Data Parameters
NAME      b091013ghaf.657Am
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_            20091013
Time                 8.06
INSTRUM             spect
PROBHD   5 mm TBI 1H/31
PULPROG              zgpg
TD                  32768
SOLVENT               Tol
NS                   3368
DS                      4
SWH             21097.047 Hz
FIDRES           0.643831 Hz
AQ               0.7766516 sec
RG                  9195.2
DW                 23.700 usec
DE                  6.00 usec
TE                 300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 20.00 usec
PL1                 0.00 dB
SFO1           75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 0.00 dB
PL12               20.00 dB
PL13              120.00 dB
SFO2          300.1316507 MHz

F2 - Processing parameters
SI                  65536
SF             75.4676926 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   0.50
```

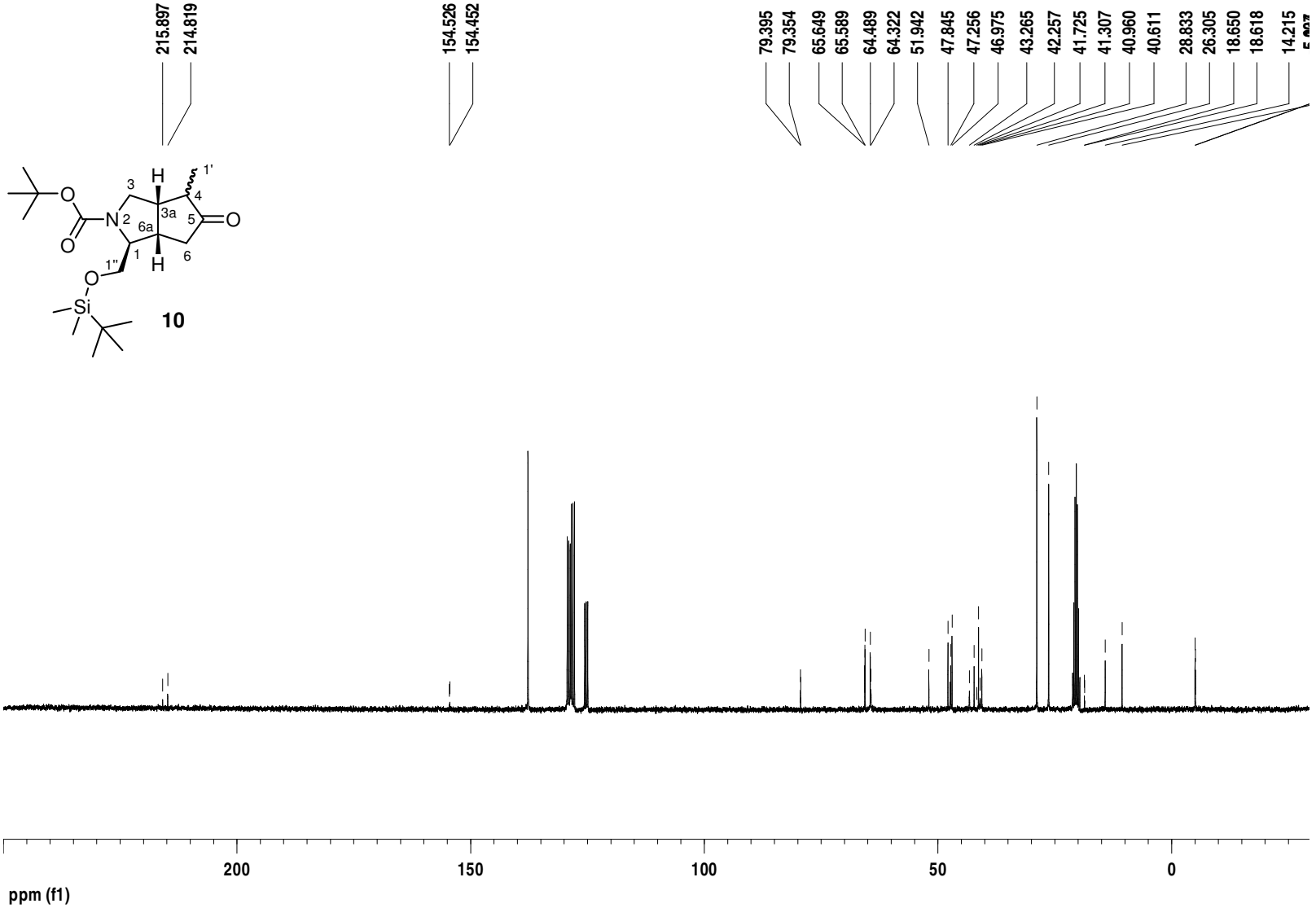



```
Current Data Parameters
NAME      b090923ghaf.659A
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20090923
Time                7.53
INSTRUM            spect
PROBHD   5 mm TBI 1H/31
PULPROG             zg30
TD                 16384
SOLVENT              Tol
NS                    16
DS                     2
SWH             5112.475 Hz
FIDRES          0.312041 Hz
AQ             1.6024052 sec
RG                    64
DW                97.800 usec
DE                 6.00 usec
TE                300.0 K
D1            2.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                10.00 usec
PL1                0.00 dB
SFO1         300.1321009 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300247 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```



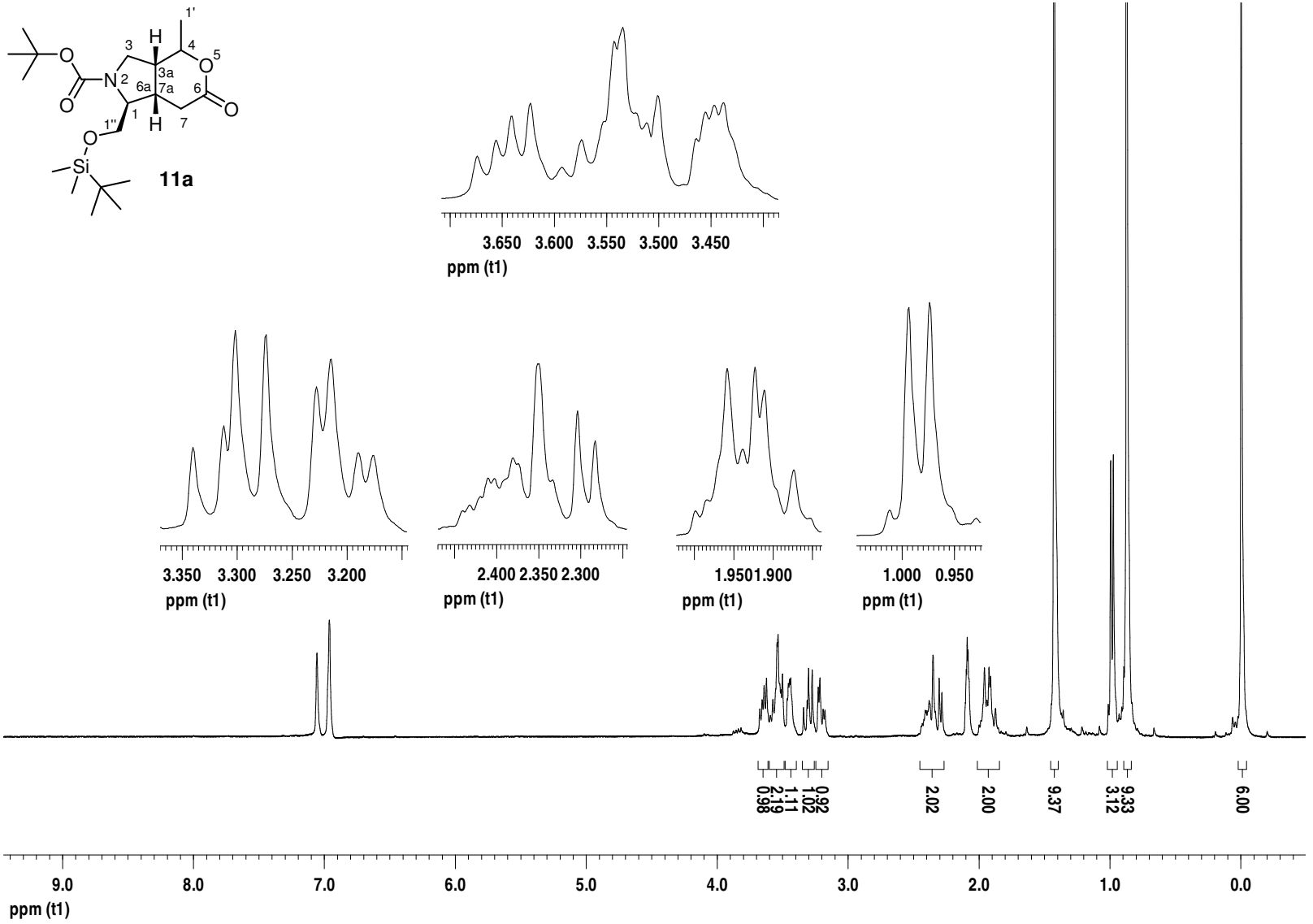

```
Current Data Parameters
NAME      b090923ghaf.659A
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090923
Time                  9.10
INSTRUM              spect
PROBHD   5 mm TBI 1H/31
PULPROG               zgpg
TD                   32768
SOLVENT                Tol
NS                    4688
DS                       4
SWH             21097.047 Hz
FIDRES           0.643831 Hz
AQ               0.7766516 sec
RG                  9195.2
DW                 23.700 usec
DE                  6.00 usec
TE                 300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                  20.00 usec
PL1                  0.00 dB
SFO1           75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  0.00 dB
PL12                20.00 dB
PL13               120.00 dB
SFO2          300.1316507 MHz

F2 - Processing parameters
SI                   65536
SF            75.4676926 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    0.50
```

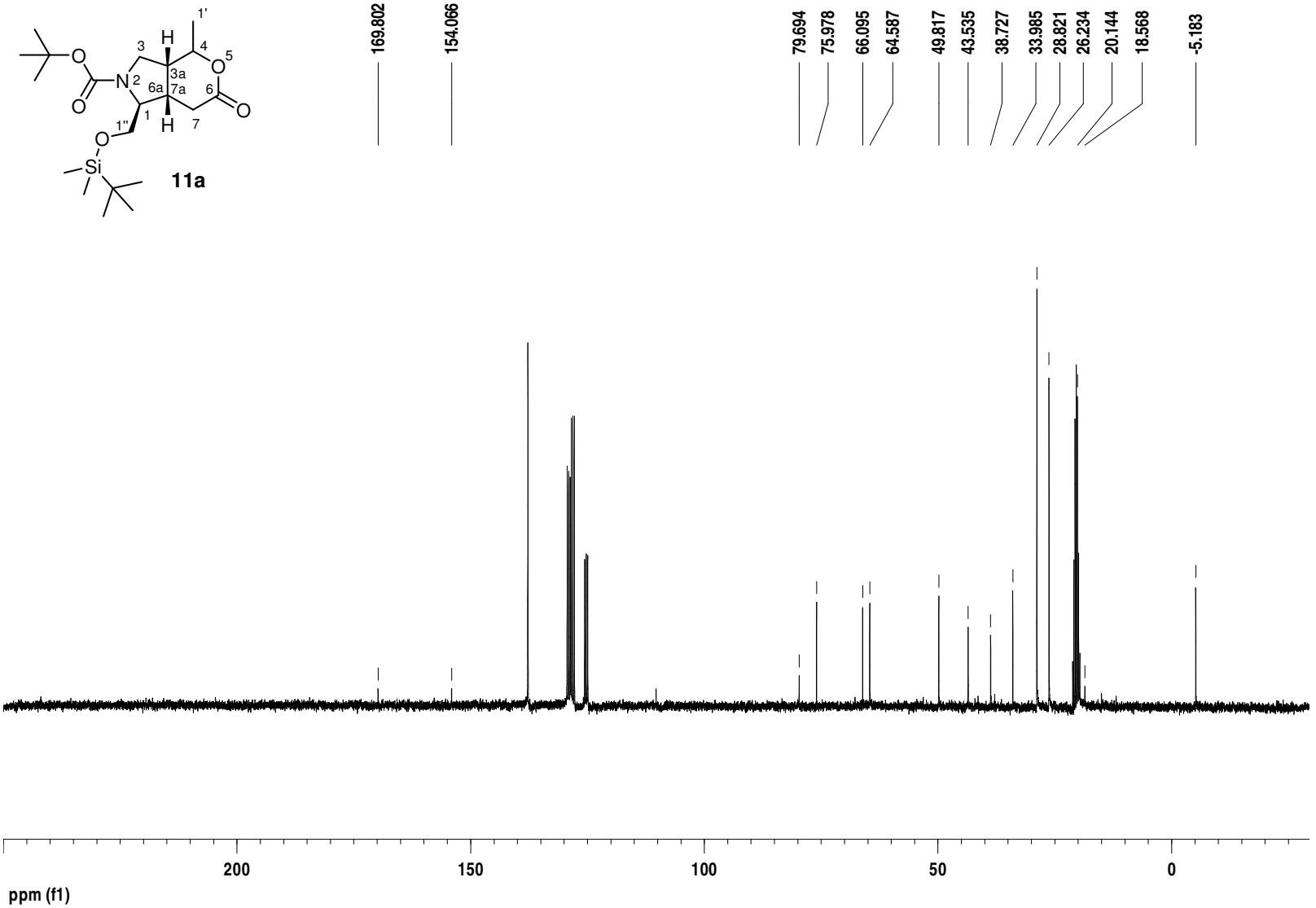



```
Current Data Parameters
NAME      b090924ghaf.660A
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20090924
Time                11.24
INSTRUM             spect
PROBHD   5 mm TBI 1H/31
PULPROG              zg30
TD                  16384
SOLVENT               Tol
NS                     16
DS                      2
SWH              5112.475 Hz
FIDRES           0.312041 Hz
AQ              1.6024052 sec
RG                    128
DW                 97.800 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.00 usec
PL1                 0.00 dB
SFO1         300.1321009 MHz

F2 - Processing parameters
SI                  32768
SF           300.1300078 MHz
WDW                    EM
SSB                     0
LB                 0.10 Hz
GB                      0
PC                   1.00
```



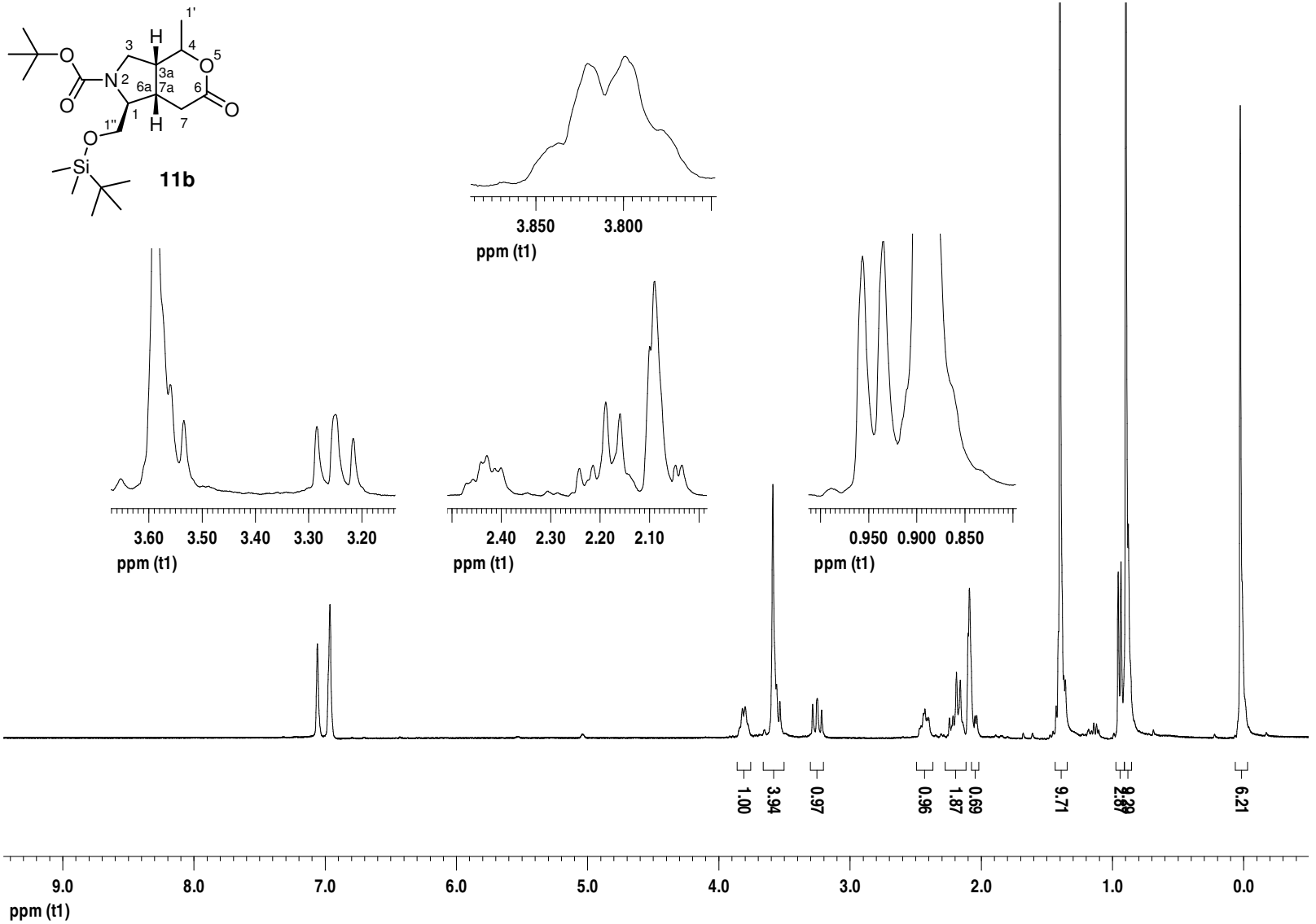

```
Current Data Parameters
NAME      b090924ghaf.660A
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090925
Time                  9.24
INSTRUM              spect
PROBHD   5 mm TBI 1H/31
PULPROG               zgpg
TD                   32768
SOLVENT                Tol
NS                    2424
DS                       4
SWH             21097.047 Hz
FIDRES           0.643831 Hz
AQ              0.7766516 sec
RG                 9195.2
DW                23.700 usec
DE                 6.00 usec
TE                300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 20.00 usec
PL1                 0.00 dB
SFO1          75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                  0.00 dB
PL12                20.00 dB
PL13               120.00 dB
SFO2         300.1316507 MHz

F2 - Processing parameters
SI                   65536
SF            75.4676926 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    0.50
```

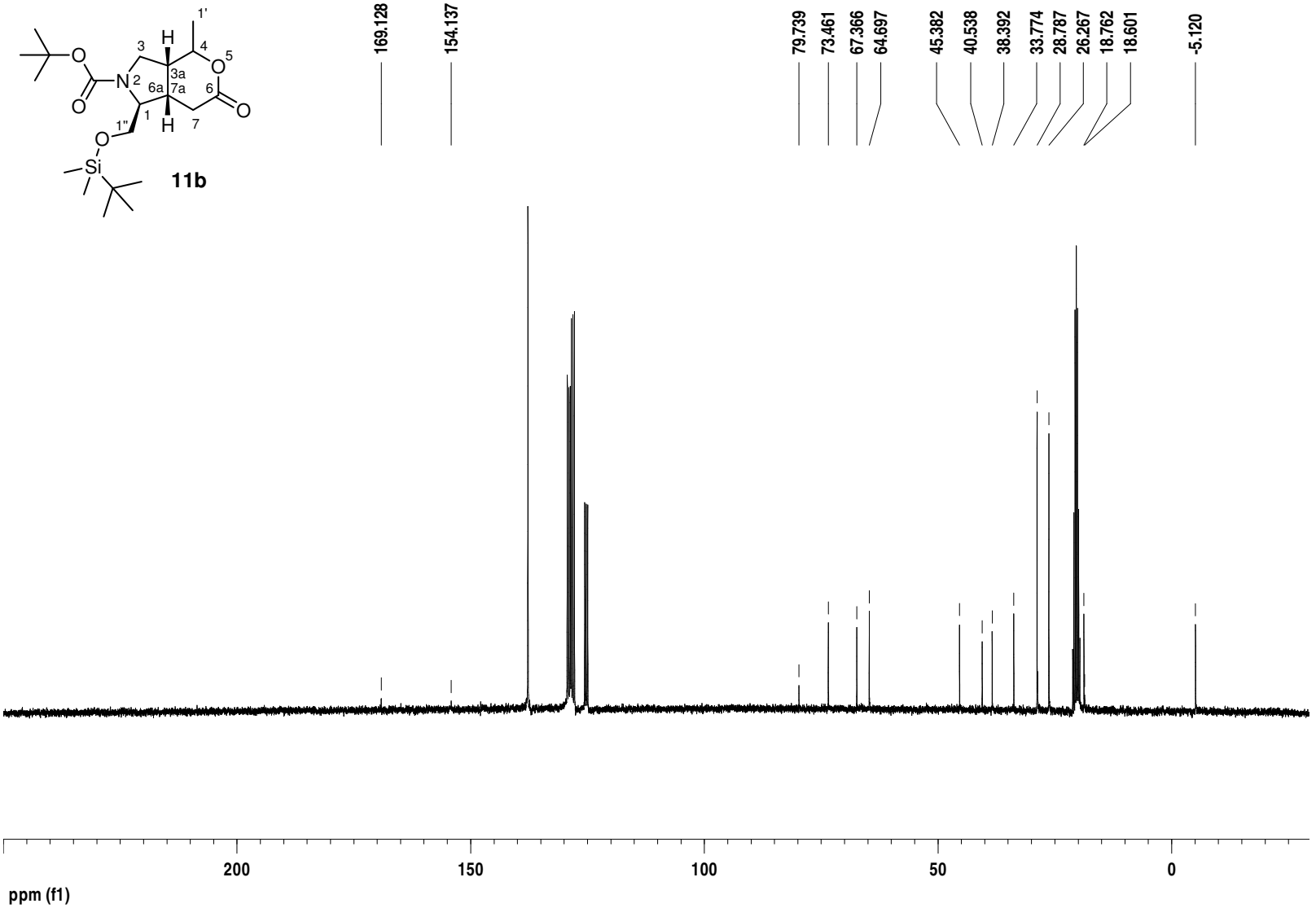



```
Current Data Parameters
NAME      b090924ghaf.660B
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20090924
Time                13.39
INSTRUM             spect
PROBHD   5 mm TBI 1H/31
PULPROG              zg30
TD                  16384
SOLVENT               Tol
NS                     16
DS                      2
SWH             5112.475 Hz
FIDRES          0.312041 Hz
AQ             1.6024052 sec
RG                    128
DW                 97.800 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.00 usec
PL1                 0.00 dB
SFO1         300.1321009 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300161 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```



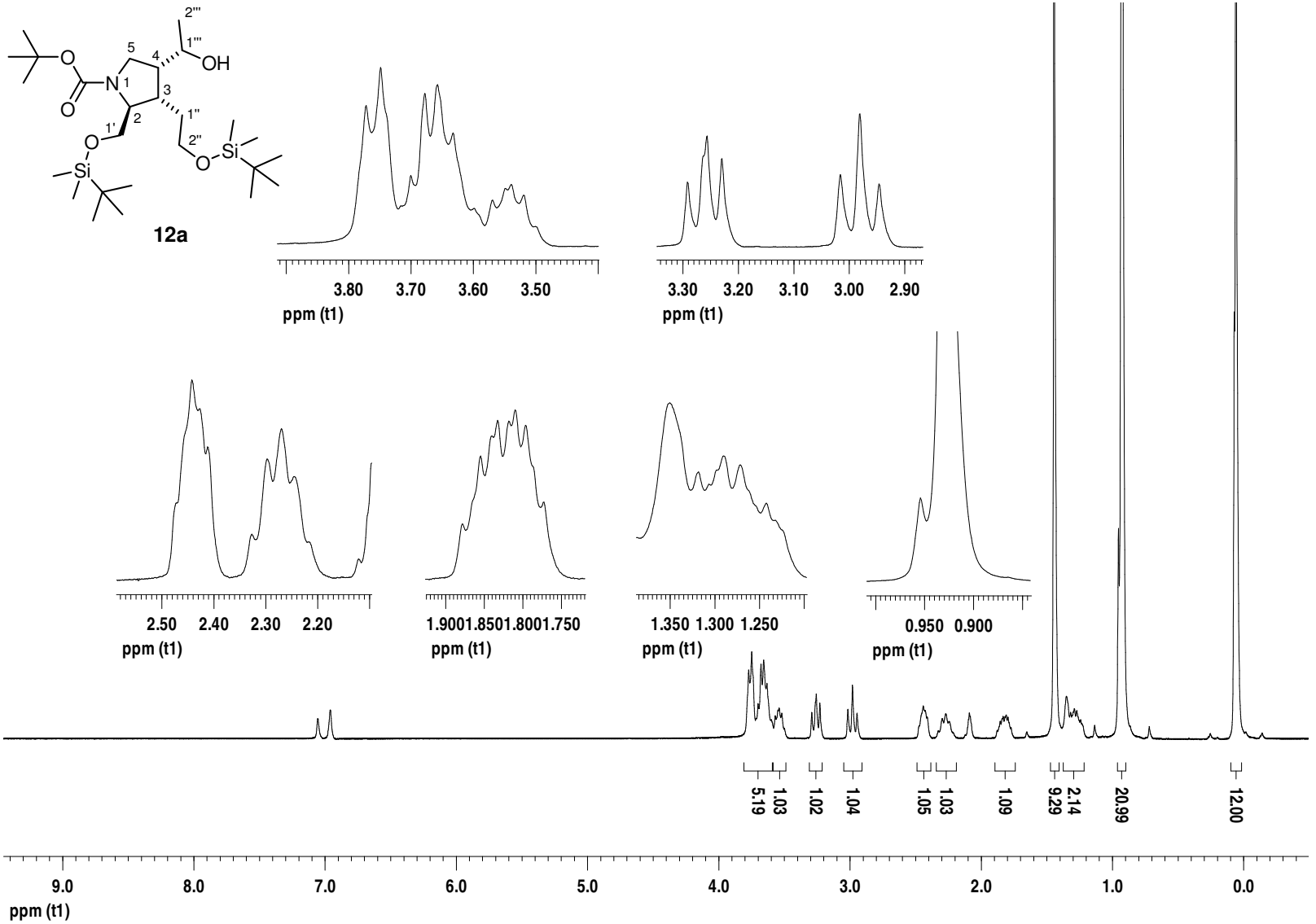

```
Current Data Parameters
NAME      b090924ghaf.660B
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_            20090928
Time                 8.01
INSTRUM             spect
PROBHD   5 mm TBI 1H/31
PULPROG              zgpg
TD                  32768
SOLVENT               Tol
NS                   8000
DS                      4
SWH            21097.047 Hz
FIDRES          0.643831 Hz
AQ             0.7766516 sec
RG                9195.2
DW                23.700 usec
DE                 6.00 usec
TE                300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                20.00 usec
PL1                0.00 dB
SFO1          75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                0.00 dB
PL12              20.00 dB
PL13             120.00 dB
SFO2         300.1316507 MHz

F2 - Processing parameters
SI                   65536
SF            75.4676926 MHz
WDW                     EM
SSB                      0
LB                1.00 Hz
GB                       0
PC                0.50
```

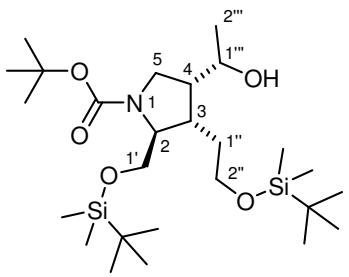



```
Current Data Parameters
NAME      b091008ghaf.675A
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20091008
Time                 12.30
INSTRUM              spect
PROBHD   5 mm TBI 1H/31
PULPROG               zg30
TD                   16384
SOLVENT                Tol
NS                      16
DS                       2
SWH               5112.475 Hz
FIDRES            0.312041 Hz
AQ               1.6024052 sec
RG                    45.3
DW                  97.800 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  10.00 usec
PL1                  0.00 dB
SFO1          300.1321009 MHz

F2 - Processing parameters
SI                   32768
SF            300.1300257 MHz
WDW                     EM
SSB                      0
LB                  0.10 Hz
GB                       0
PC                    1.00
```



12a

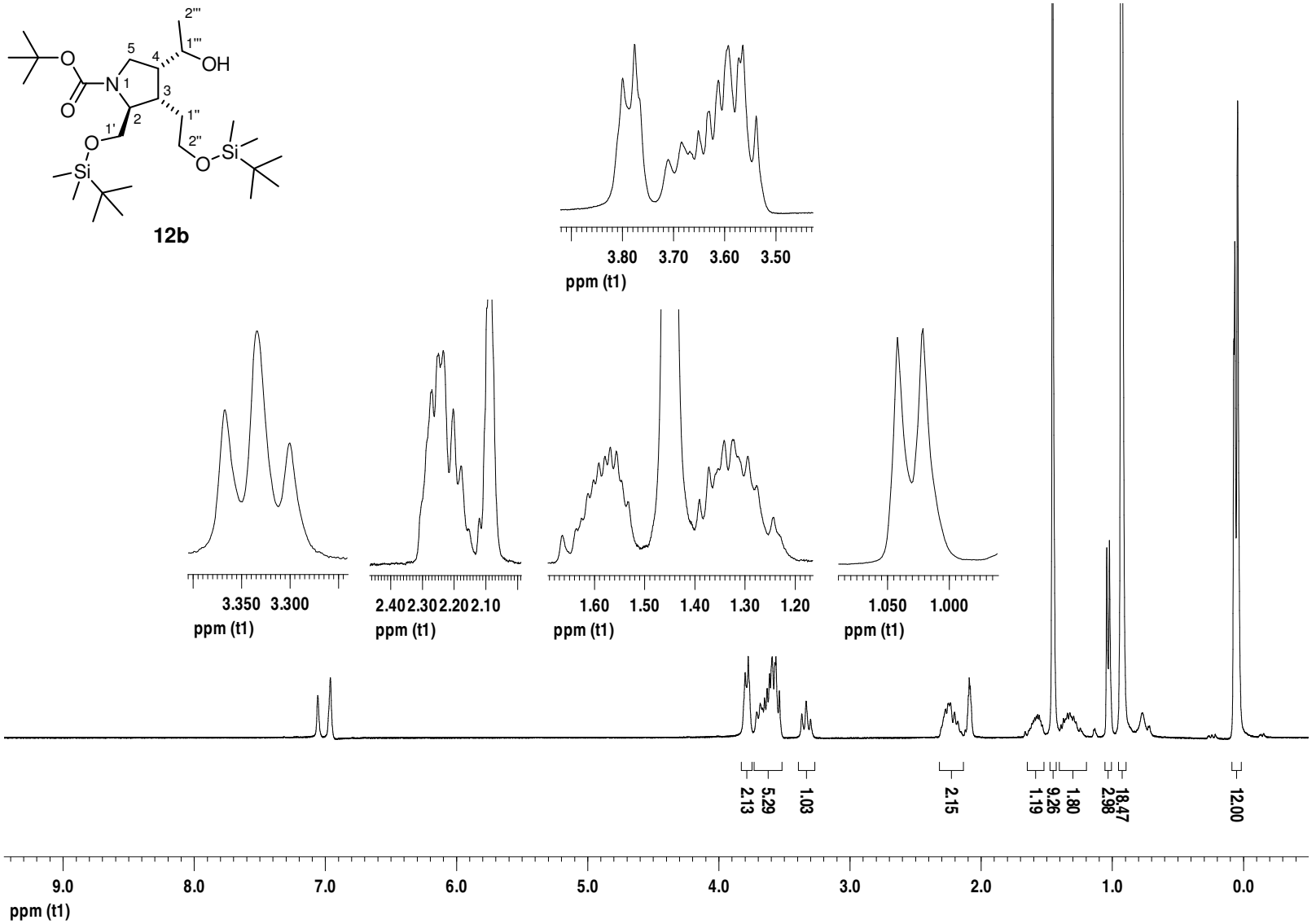

```
Current Data Parameters
NAME      b091008ghaf.675A
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20091008
Time                 12.10
INSTRUM              spect
PROBHD    5 mm TBI 1H/31
PULPROG              zgpg
TD                  32768
SOLVENT               Tol
NS                   1400
DS                      4
SWH             21097.047 Hz
FIDRES           0.643831 Hz
AQ               0.7766516 sec
RG                  9195.2
DW                 23.700 usec
DE                  6.00 usec
TE                 300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 20.00 usec
PL1                 0.00 dB
SFO1           75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 0.00 dB
PL12               20.00 dB
PL13              120.00 dB
SFO2          300.1316507 MHz

F2 - Processing parameters
SI                   65536
SF             75.4676926 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    0.50
```

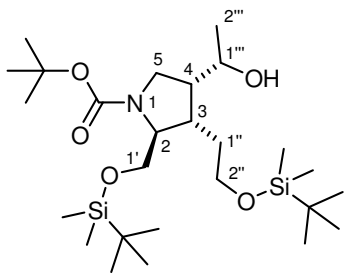



```
Current Data Parameters
NAME      b091008ghaf.676A
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_            20091008
Time                 9.32
INSTRUM             spect
PROBHD   5 mm TBI 1H/31
PULPROG              zg30
TD                  16384
SOLVENT               Tol
NS                     16
DS                      2
SWH             5112.475 Hz
FIDRES          0.312041 Hz
AQ             1.6024052 sec
RG                    128
DW                 97.800 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.00 usec
PL1                 0.00 dB
SFO1         300.1321009 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300218 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```



12b

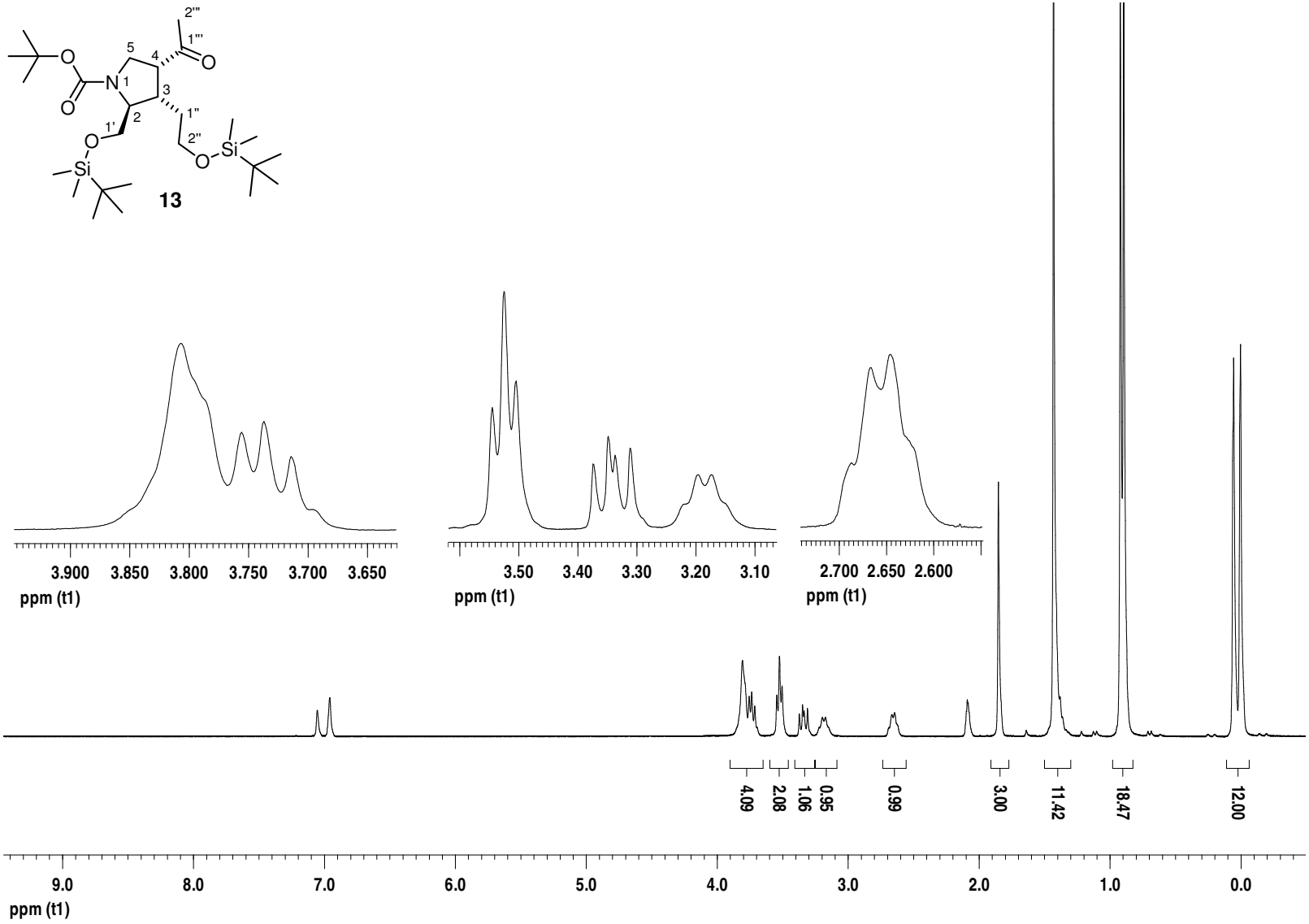

```
Current Data Parameters
NAME      b091008ghaf.676A
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20091008
Time                  7.32
INSTRUM              spect
PROBHD   5 mm TBI 1H/31
PULPROG               zgpg
TD                   32768
SOLVENT                Tol
NS                    2824
DS                       4
SWH             21097.047 Hz
FIDRES           0.643831 Hz
AQ              0.7766516 sec
RG                    4096
DW                23.700 usec
DE                 6.00 usec
TE                 300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                20.00 usec
PL1                0.00 dB
SFO1          75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                0.00 dB
PL12              20.00 dB
PL13             120.00 dB
SFO2         300.1316507 MHz

F2 - Processing parameters
SI                   65536
SF            75.4676926 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 0.50
```

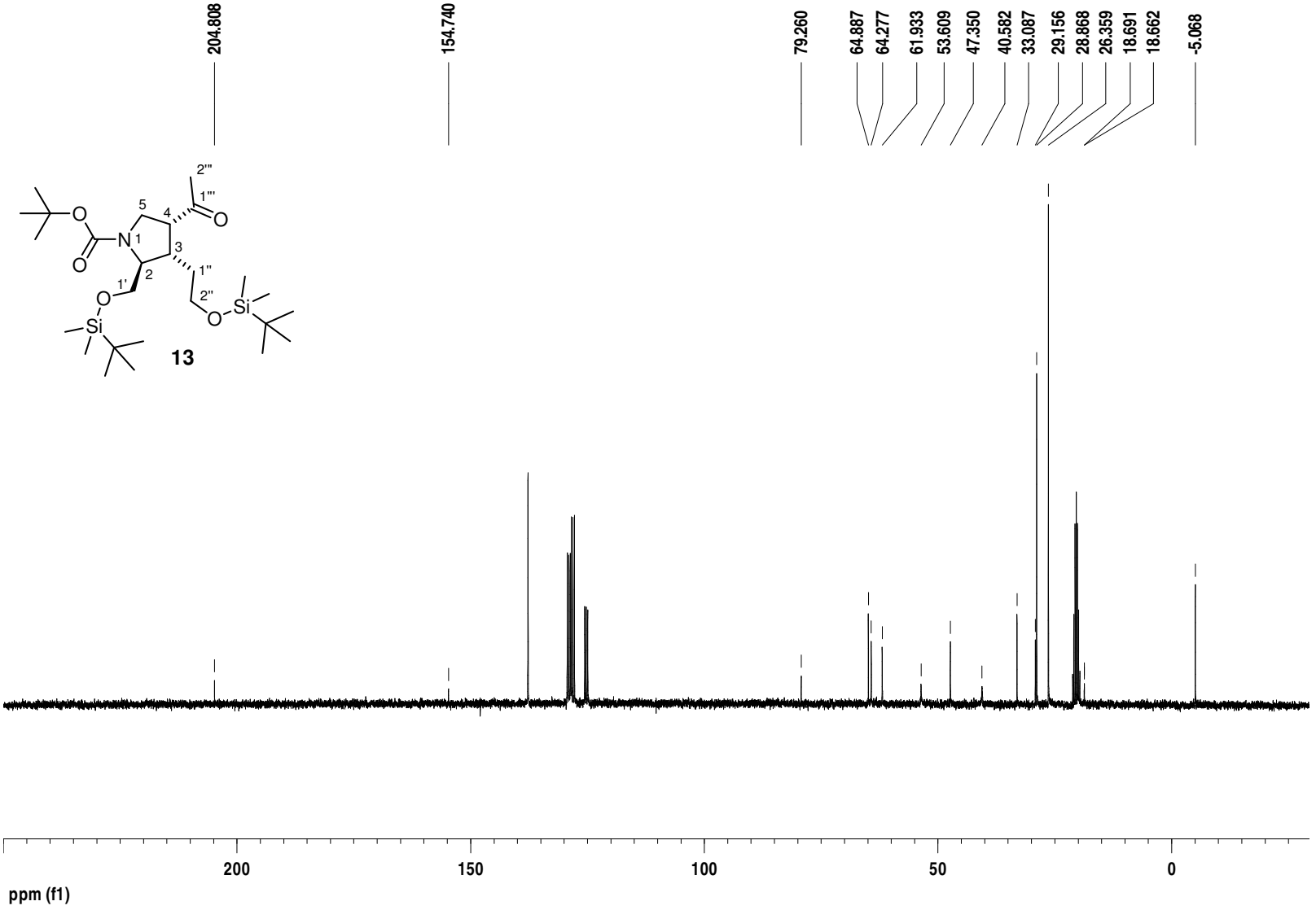



```
Current Data Parameters
NAME      b091002ghaf.664Am
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20091002
Time                7.59
INSTRUM            spect
PROBHD   5 mm TBI 1H/31
PULPROG             zg30
TD                 16384
SOLVENT              Tol
NS                    16
DS                     2
SWH             5112.475 Hz
FIDRES          0.312041 Hz
AQ             1.6024052 sec
RG                  50.8
DW                97.800 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                10.00 usec
PL1                0.00 dB
SFO1         300.1321009 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300100 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```



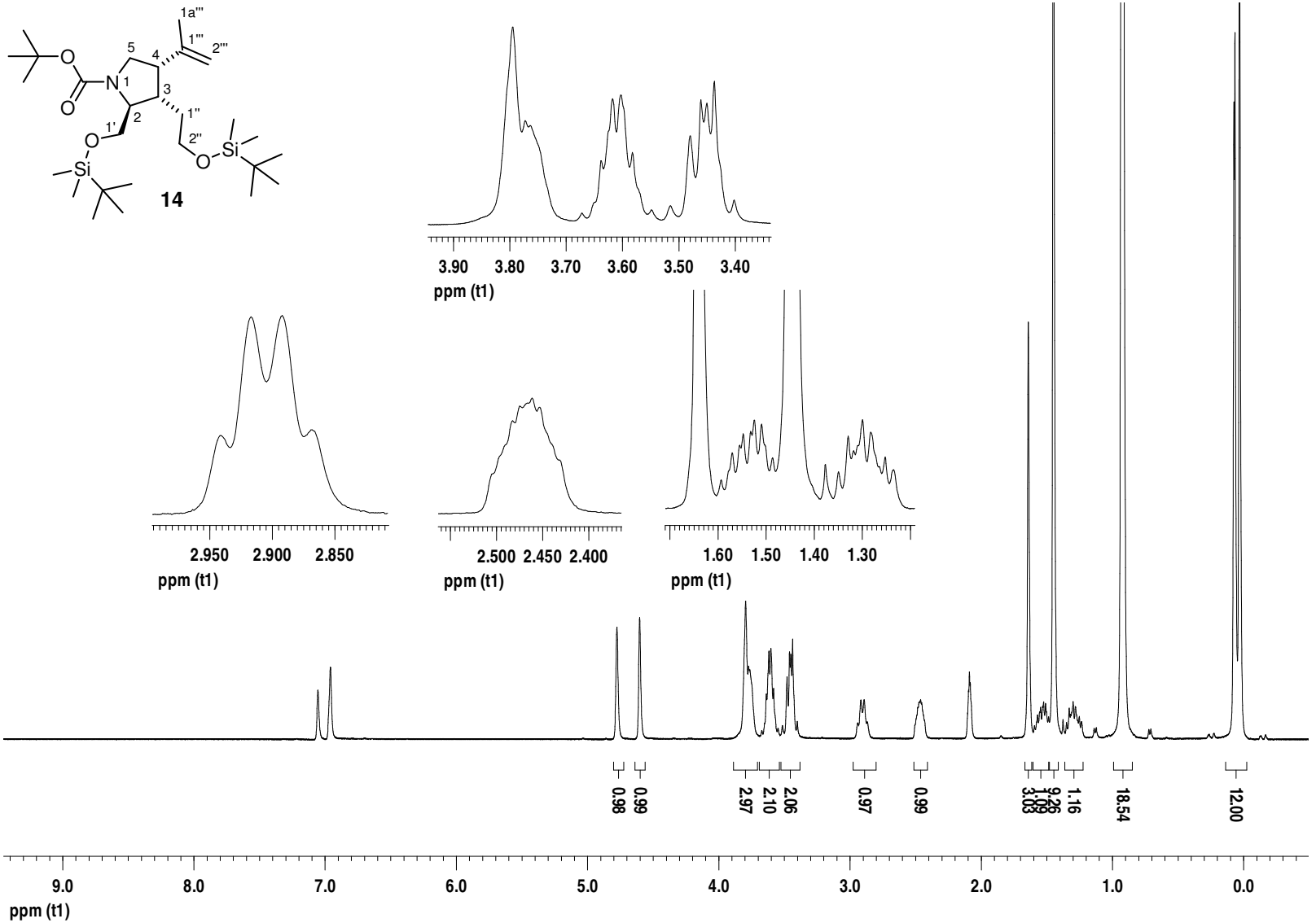

```
Current Data Parameters
NAME      b091002ghaf.664Am
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20091002
Time                  7.32
INSTRUM              spect
PROBHD   5 mm TBI 1H/31
PULPROG               zgpg
TD                   32768
SOLVENT                Tol
NS                    1256
DS                       4
SWH              21097.047 Hz
FIDRES            0.643831 Hz
AQ                0.7766516 sec
RG                   9195.2
DW                  23.700 usec
DE                   6.00 usec
TE                  300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                  20.00 usec
PL1                  0.00 dB
SFO1            75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2               100.00 usec
PL2                  0.00 dB
PL12                20.00 dB
PL13               120.00 dB
SFO2           300.1316507 MHz

F2 - Processing parameters
SI                    65536
SF              75.4676926 MHz
WDW                      EM
SSB                       0
LB                   1.00 Hz
GB                        0
PC                     0.50
```

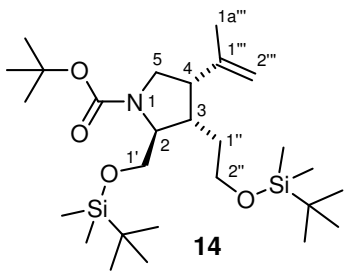



```
Current Data Parameters
NAME      b090930ghaf.665Am
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20090930
Time                11.58
INSTRUM             spect
PROBHD   5 mm TBI 1H/31
PULPROG              zg30
TD                  16384
SOLVENT               Tol
NS                     16
DS                      2
SWH              5112.475 Hz
FIDRES           0.312041 Hz
AQ              1.6024052 sec
RG                   50.8
DW                 97.800 usec
DE                  6.00 usec
TE                 300.0 K
D1             2.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  10.00 usec
PL1                  0.00 dB
SFO1          300.1321009 MHz

F2 - Processing parameters
SI                   32768
SF            300.1300178 MHz
WDW                     EM
SSB                      0
LB                    0.10 Hz
GB                       0
PC                    1.00
```



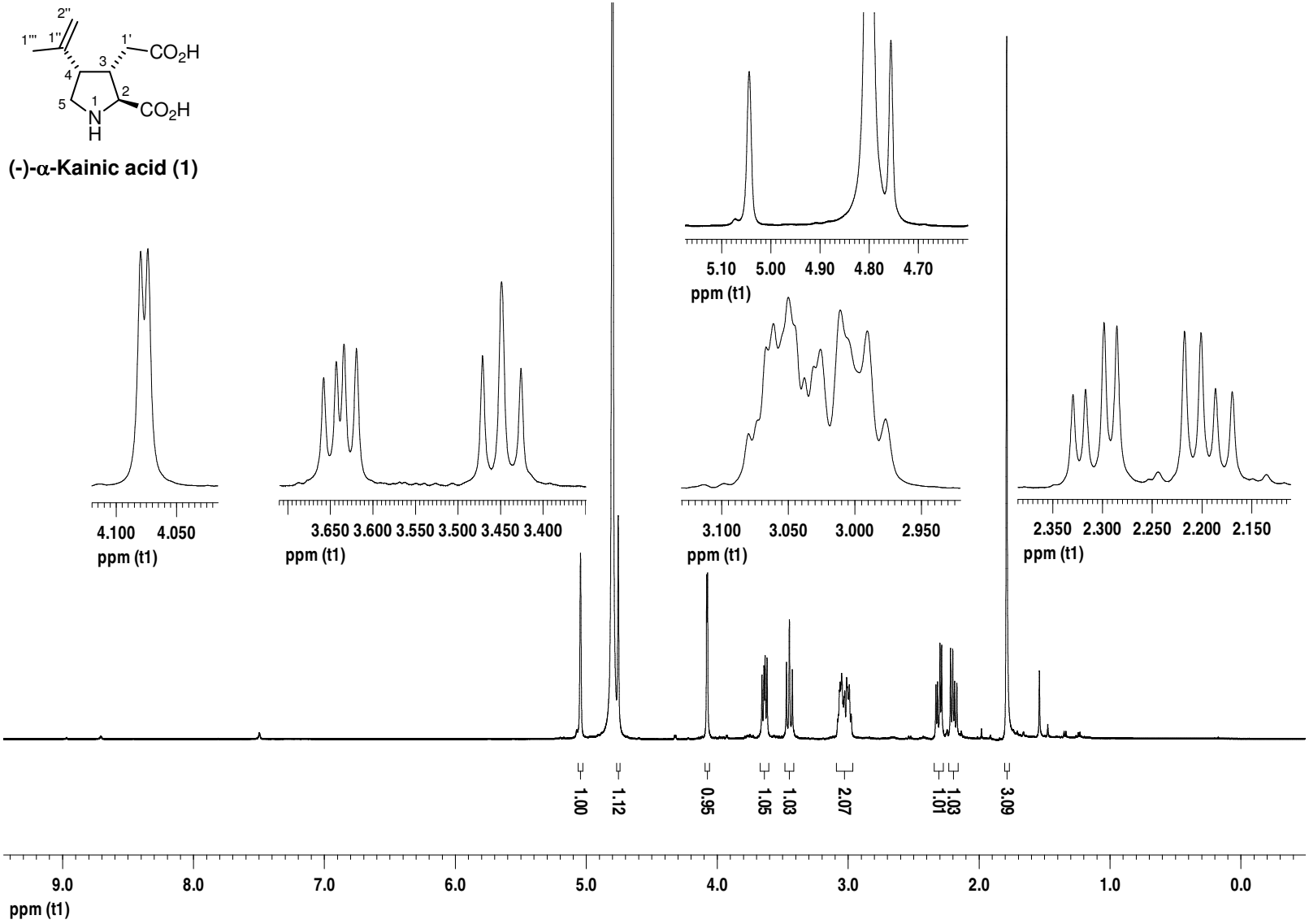

```
Current Data Parameters
NAME      b090930ghaf.665Am
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090930
Time                 10.25
INSTRUM              spect
PROBHD    5 mm TBI 1H/n31
PULPROG               zgpg
TD                   32768
SOLVENT                Tol
NS                    2384
DS                       4
SWH             21097.047 Hz
FIDRES           0.643831 Hz
AQ               0.7766516 sec
RG                  9195.2
DW                  23.700 usec
DE                   6.00 usec
TE                  300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                  20.00 usec
PL1                  0.00 dB
SFO1           75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  0.00 dB
PL12                20.00 dB
PL13               120.00 dB
SFO2          300.1316507 MHz

F2 - Processing parameters
SI                   65536
SF             75.4676926 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   0.50
```

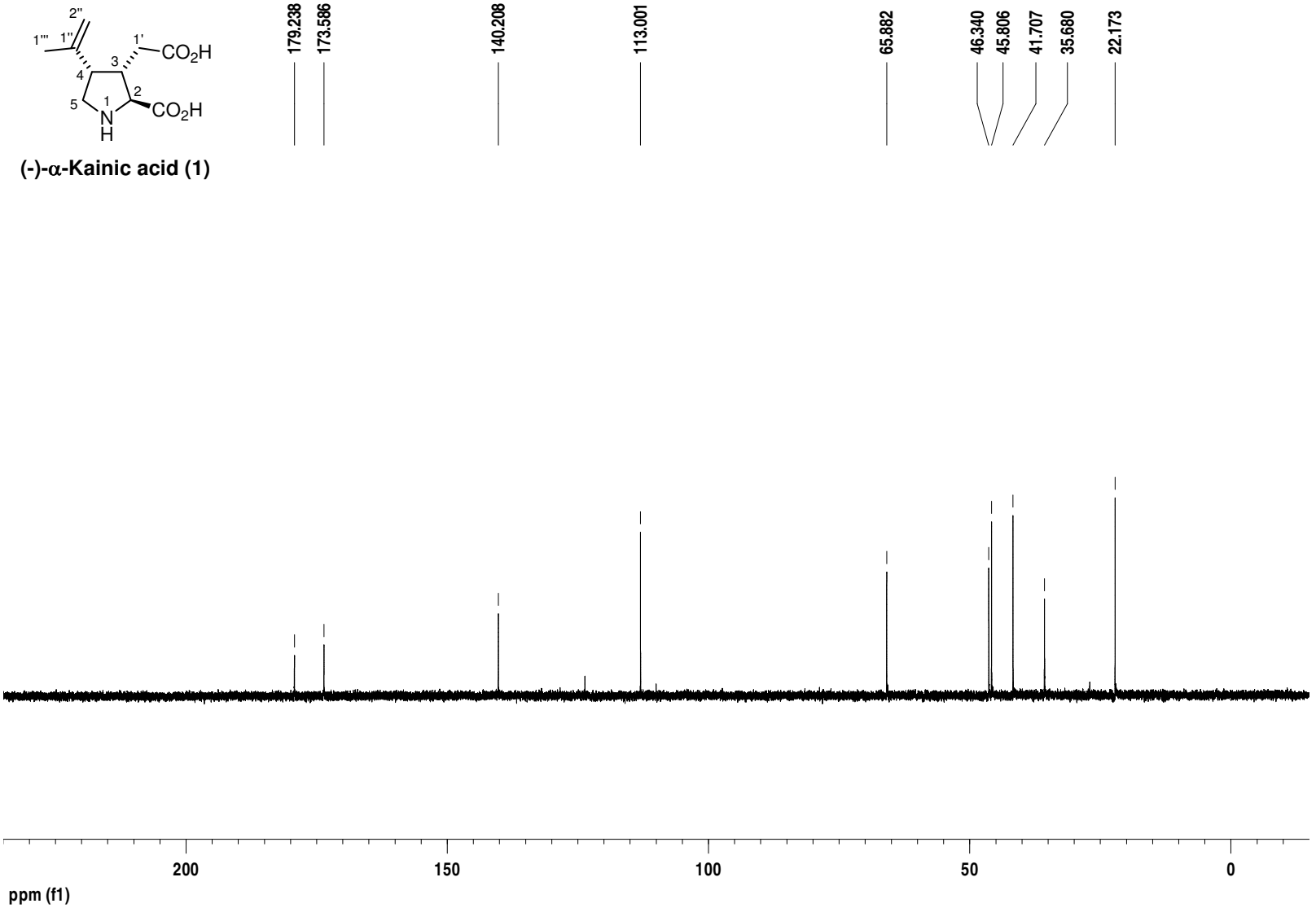



```
Current Data Parameters
NAME      d091009ghaf.677A
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_            20091009
Time                10.53
INSTRUM             spect
PROBHD   5 mm TBI 1H/13
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                       64
DS                        2
SWH              8992.806 Hz
FIDRES           0.137219 Hz
AQ             3.6438515 sec
RG                    80.6
DW                55.600 usec
DE                 6.00 usec
TE                298.0 K
D1            0.10000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                  12.00 usec
PL1                  0.00 dB
SFO1          500.1325006 MHz

F2 - Processing parameters
SI                   32768
SF            500.1300381 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```



(-)-α-Kainic acid (1)

```
Current Data Parameters
NAME      d091009ghaf.677A
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_           20091009
Time                8.14
INSTRUM            spect
PROBHD   5 mm TBI 1H/13
PULPROG           zgpg30
TD                163840
SOLVENT              D2O
NS                  2240
DS                     4
SWH           31446.541 Hz
FIDRES         0.191934 Hz
AQ            2.6051061 sec
RG                  8192
DW                15.900 usec
DE                20.00 usec
TE                298.1 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                  128

======== CHANNEL f1 ========
NUC1                13C
P1                11.48 usec
PL1               -1.00 dB
SFO1        125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              18.00 dB
PL13              21.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                  65536
SF          125.7577890 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```