## *Supporting Information*

# THE SYNTHESIS OF SIMPLIFIED ANALOGUES OF CRAMBESCIN B CARBOXYLIC ACID AND THEIR INHIBITORY ACTIVITY OF VOLTAGE-GATED SODIUM CHANNELS: NEW ASPECTS OF STRUCTURE–ACTIVITY RELATIONSHIPS

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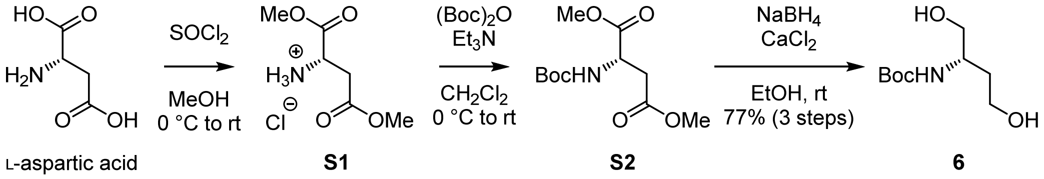
## General Experimental

Melting points (mp) were recorded on a Yanaco MP-S3 melting point apparatus and are not corrected. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. Infrared spectra (IR) were recorded on a JASCO FT/IR-4100 spectrophotometer and are reported in wave number ($cm^{-1}$). Proton nuclear magnetic resonance ($^1H$ NMR) spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts of all compounds are reported in ppm relative to the residual undeuterated solvent (chloroform-*d* as $\delta = 7.26$, methanol-$d_4$ as $\delta = 3.31$). Data were reported as follows: Chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broadened), coupling constant, and assignment. Carbon nuclear magnetic resonance ($^{13}C$ NMR) spectra were recorded on a Bruker Avance-400 (100 MHz) spectrometer. Chemical shifts of all compounds are reported in ppm relative to the solvent (chloroform-*d* as $\delta = 77.16$, methanol-$d_4$ as $\delta = 49.00$, acetone-$d_6$ as $\delta = 29.84$). All NMR were measured at 300 K. High-resolution mass spectra (HRMS) were recorded on an Applied Biosystems Mariner ESI-TOF for ESI-MS, an Agilent technologies 6220 LC/TOF-MS spectrometer for ESI-MS, or a JEOL JMS-700 MStation spectrometer for FAB-MS, and are reported in *m/z*.

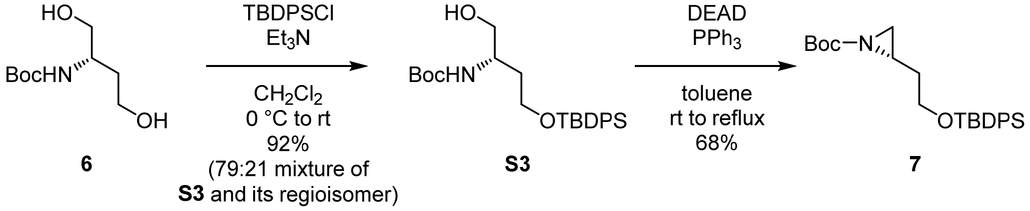
Reactions were monitored by thin layer chromatography (TLC) on 0.25 mm silica gel coated glass plates $60F_{254}$ (Merck, #1.05715.0001). Visualization was achieved by using UV light (254 nm) and appropriate reagent (7% ethanolic phosphomolybdic acid, *p*-anisaldehyde solution in $H_2SO_4$/AcOH/EtOH, or ninhydrin solution in *n*-BuOH/$H_2O$/AcOH), followed by heating. Silica gel 60 (particle size 0.063-0.200 mm, Merck, #1.07734.9025) was used for silica gel open column chromatography. Silica gel 60 (spherical, particle size 0.04-0.05 mm, Kanto, #37562-84) was used for silica gel flash column chromatography. Silica gel 60N (spherical, neutral, particle size 0.04-0.05 mm, Kanto, #37563-79) was used for neutral silica gel flash column chromatography. Chromatorex®-DIOL (particle size MB100-40/75, Fuji Silysia Chemical Ltd. HU50710) was used for Chromatorex DIOL silica gel open column chromatography. Dry THF and $CH_2Cl_2$ were purchased from Kanto Chemical Co., Inc. $BF_3 \cdot OEt_2$ was distilled from

$CaH_2$. Celite® (Hyflo Super-Cel Celite®) was purchased from Nacalai Tesque Co., Inc. All other commercially available reagents were as received.



**Diol 6:** This compound was synthesized according to the modified procedure reported by Bolm, C. *et al.*[1] To a solution of L-aspartic acid (18.8 g, 141 mmol) in MeOH (350 mL) was added $SOCl_2$ (23.0 mL, 317 mmol) at 0 °C. After being stirred at room temperature for 5 days, the reaction mixture was concentrated under reduced pressure to provide crude dimethyl ester-HCl salt **S1**, which was used for the next reaction without further purification. To a solution of crude dimethyl ester-HCl salt **S1** in dry $CH_2Cl_2$ (255 mL) were added $Et_3N$ (40.0 mL, 287 mmol) and $(Boc)_2O$ (32.5 mL, 141 mmol) at 0 °C. After being stirred at room temperature for 23 h, the reaction was quenched with a saturated aqueous solution of $Na_2CO_3$ (100 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with $CH_2Cl_2$ (60 mL x 2). The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure to provide crude Boc-dimethyl ester **S2**, which was used for the next reaction without further purification. To a suspension of $NaBH_4$ (20.6 g, 545 mmol) and $CaCl_2$ (61.7 g, 556 mmol) in EtOH (405 mL) was added a solution of crude Boc-dimethyl ester **S2** in EtOH (50 mL) at room temperature. After being stirred at room temperature for 22 h, the reaction was quenched with 10% aqueous solution of citric acid. The resulting mixture was filtered through a pad of Celite® (eluted with EtOH) to remove the insoluble deposition. The filtrate was extracted with $CHCl_3$/2-PrOH (3/1, 150 mL x 2). The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. Three times recrystallization from hexane/2-PrOH (9/1), hexane, and hexane/2-PrOH (19/1) afforded diol **6** (21.8 g, 77% in 3 steps) as a white solid. The $^1$H NMR was identical to that reported previously for this compound.[1]

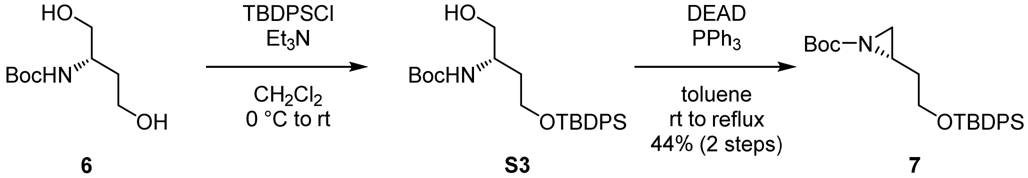
mp: 67-70 °C; lit.[1]: 62 °C. $[\alpha]_D^{22}$ −9.76 (*c* 1.69, $CHCl_3$); lit.[1]: $[\alpha]_D^{22}$ −9.9 (*c* 1.67, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3336, 2977, 2936, 2880, 1685, 1523, 1366, 1265, 1171, 1054. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 1.42 (9H, s, -O$^t$Bu), 1.59 (1H, m, -C$H_a$H$_b$CH$_2$OH), 1.77 (1H, dddd, *J* = 18, 4 Hz, -CH$_a$$H_b$CH$_2$OH), 3.55-3.95 (7H, m, -C$H_2$O*H*, -C*H*NH-, -CH$_2$C$H_2$O*H*), 5.23 (1H, d, *J* = 8 Hz, -CHN*H*-). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 28.4, 34.8, 49.5, 58.8, 65.1, 80.0, 157.1. HRMS (ESI, positive): calcd. For $C_9H_{19}NO_4Na$ $[M+Na]^+$, 228.1206; found, 228.1204.



**Aziridine 7:** To a solution of diol **6** (16.6 g, 80.9 mmol) and $Et_3N$ (32.7 mL, 235 mmol) in dry $CH_2Cl_2$ (800 mL) was added TBDPSCl (50.5 mL, 194 mmol) at 0 °C. After being stirred at room temperature for 16 h, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (800 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with $H_2O$ (800 mL), dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel open column chromatography (hexane/EtOAc = 5/1 to EtOAc) to afford monosilyl ethers (32.9 g, 92%) as a 79:21 mixture of **S3** and its regioisomer as a colorless oil, which was used for the next reaction without further purification.

To a solution of the silyl ethers (7.70 g, 17.4 mmol) in dry toluene (150 mL) were added $PPh_3$ (9.10 g, 34.8 mmol) and DEAD (2.2 M solution in toluene, 16.0 mL, 34.8 mmol) at room temperature under Ar atmosphere. After being stirred at reflux for 20 min, the reaction mixture was cooled to room temperature, and then concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 14/1 to 5/1) to afford aziridine **7** (4.00 g, 68%) as a colorless oil.

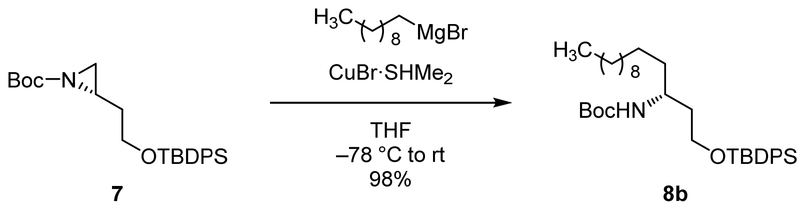
$[\alpha]_D^{23}$ +22.6 (*c* 1.04, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 2931, 2858, 1719, 1308, 1162, 1112. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 1.12 (9H, s, -Si$^t$Bu), 1.48 (9H, s, -O$^t$Bu), 1.68 (1H, m, -C*H*$_a$H$_b$CH$_2$OTBDPS), 1.88 (1H, m, -CH$_a$*H*$_b$CH$_2$OTBDPS), 1.99 (1H, d, *J* = 4 Hz, -C*H*$_a$H$_b$N-), 2.31 (1H, d, *J* = 6 Hz, -CH$_a$*H*$_b$N-), 2.58 (1H, m, -C*H*NBoc), 3.85-3.96 (2H, m, -CH$_2$C*H*$_2$OTBDPS), 7.38-7.47 (6H, m, -Si-Ph), 7.70-7.77 (4H, m, -Si-Ph). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 19.2, 26.8, 27.9, 31.6, 35.4, 35.7, 61.6, 80.7, 127.7, 129.7, 133.7, 135.49, 135.52, 162.5. HRMS (ESI, positive): calcd. For $C_{25}H_{35}NO_3NaSi$ $[M+Na]^+$, 448.2278; found, 448.2274.



**6** **S3** **7**

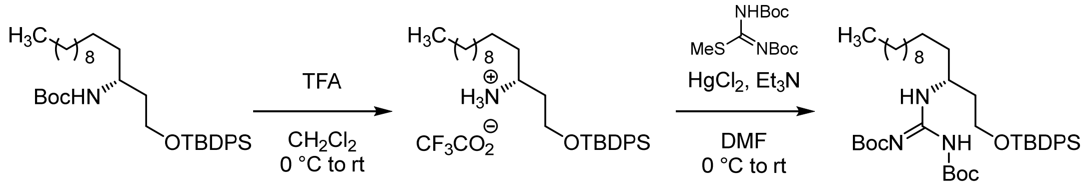
**Small scale synthesis of aziridine 7:** To a solution of diol **6** (100 mg, 0.487 mmol) and $Et_3N$ (0.20 mL, 1.4 mmol) in dry $CH_2Cl_2$ (4.8 mL) was added TBDPSCl (0.30 mL, 1.2 mmol) at 0 °C. After being stirred at room temperature for 5 h, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (4.8 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with $CH_2Cl_2$ (4.8 mL). The combined organic layer was washed with $H_2O$ (9.6 mL), dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel open column chromatography (hexane/EtOAc = 3/1) to afford monosilyl ethers (188 mg, 92%) as a 79:21 mixture of **S3** and its regioisomer as a colorless oil, which was used for the next reaction without further purification.

To a solution of the silyl ethers in dry toluene (4.2 mL) were added $PPh_3$ (222 mg, 0.848 mmol) and DEAD (2.2 M solution in toluene, 0.39 mL, 0.85 mmol) at room temperature under Ar atmosphere. After being stirred at reflux for 20 min, the reaction mixture was cooled to room temperature, and then concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 14/1 to 5/1) to afford aziridine **7** (92.1 mg, 44% in 2 steps) as a colorless oil.



**Amide 8b:** To a suspension of freshly prepared CuBr·$SMe_2$ (1.7 g, 8.2 mmol) in dry THF (131 mL) were added $C_{10}H_{21}MgBr$ (0.65 M solution in THF, 108 mL, 70.5 mmol) and a solution of aziridine **7** (10.0 g, 23.5 mmol) in dry THF (140 mL) at −78 °C under Ar atmosphere. And then the reaction mixture was allowed to warm to room temperature slowly. After being stirred for 14 h, the reaction was quenched with a saturated aqueous solution of $NH_4Cl$ (300 mL). The resulting mixture was filtered through a pad of Celite® (eluted with EtOAc). The filtrate was partitioned, and the aqueous layer was extracted with EtOAc. The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane to hexane/EtOAc = 19/1) to afford amide **8b** (13.1 g, 98%) as a colorless oil.

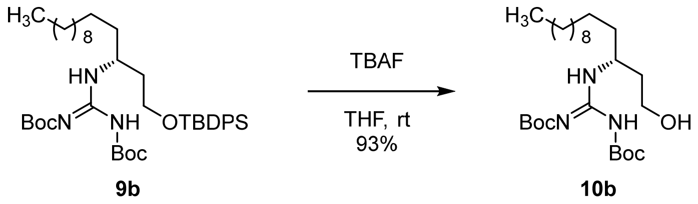
$[\alpha]_D^{27}$ −2.60 (*c* 1.50, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3424, 3361, 2927, 2856, 1703, 1503, 1364, 1174, 1112. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.88 (3H, t, $J$ = 7 Hz, -$(CH_2)_9CH_3$), 1.06 (9H, s, -Si-$^t$Bu), 1.20-1.35 (18H, m, -$(CH_2)_9CH_3$), 1.38-1.50 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.43 (9H, s, -O$^t$Bu), 1.56 (1H, m, -$CH_aH_bCH_2$OTBDPS), 1.82 (1H, m, -$CH_aH_bCH_2$OTBDPS), 3.64-3.75 (2H, m, -$CH_2CH_2$OTBDPS), 3.79 (1H, m, -CHNH-), 4.97 (1H, d, $J$ = 8 Hz, -CHNH-), 7.36-7.46 (6H, m, -Si-Ph), 7.65-7.70 (4H, m, -Si-Ph). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 14.3, 19.2, 22.8, 26.1, 27.0, 28.6, 29.5, 29.76, 29.78, 29.81, 32.1, 35.2, 36.6, 49.2, 61.5, 78.7, 127.8, 129.8, 133.6, 135.7, 155.7. HRMS (ESI, positive): calcd. For $C_{35}H_{57}NO_3NaSi$ $[M+Na]^+$, 590.4000; found, 590.4021.



**8b** **S4** **9b**

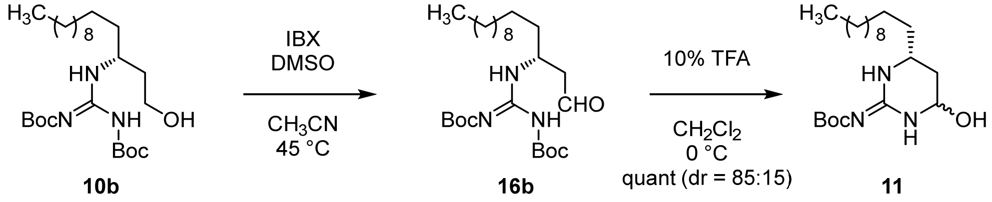
**Guanidine 9b:** To a solution of amide **8b** (13.1 g, 23.1 mmol) in $CH_2Cl_2$ (115 mL) was added TFA (115 mL) at 0 °C. After being stirred at room temperature for 30 min, the reaction mixture was diluted with toluene, and then concentrated under reduced pressure to provide crude ammonium-TFA salt **S4** as a yellow oil. This crude residue was used for the next reaction without further purification. To a solution of crude ammonium-TFA salt **S4**, diBoc-methylisothiourea (7.40 g, 25.4 mmol), and $Et_3N$ (9.6 mL, 69 mmol) in DMF (231 mL) was added $HgCl_2$ (6.90 g, 25.4 mmol) at 0 °C. After being stirred at room temperature for 20 min, the reaction mixture was diluted with EtOAc, and then filtered through a pad of Celite® (eluted with EtOAc). The filtrate was washed with $H_2O$ and brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 34/1) to afford guanidine **9b** (12.5 g, 76% in 2 steps) as a colorless oil.

$[\alpha]_D^{28}$ −3.81 (*c* 1.05, $CHCl_3$). IR (film): $\nu_{max}$ (cm$^{-1}$) 3325, 2928, 2856, 1719, 1637, 1613, 1334, 1158, 1116. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.88 (3H, t, $J$ = 7 Hz, -$(CH_2)_9CH_3$), 1.04 (9H, s, -Si$^t$Bu), 1.17-1.35 (18H, m, -$(CH_2)_9CH_3$), 1.36-1.65 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.47 (9H, s, -O$^t$Bu), 1.48 (9H, s, -O$^t$Bu), 1.71 (1H, m, -$CH_aH_bCH_2$OTBDPS), 1.82 (1H, m, -$CH_aH_bCH_2$OTBDPS), 3.71 (2H, t, $J$ = 6 Hz, -$CH_2CH_2$OTBDPS), 4.29 (1H, m, -CHNH-), 7.33-7.45 (6H, m, -Si-Ph), 7.60-7.67 (4H, m, -Si-Ph), 8.17 (1H, d, $J$ = 8 Hz, -CHNH-), 11.5 (1H, s, -NHBoc). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 14.3, 19.3, 22.8, 25.5, 27.0, 28.3, 28.5, 29.5, 29.7, 29.77, 29.80, 29.81, 32.1, 34.9, 37.2, 48.2, 61.2, 78.9, 82.9, 127.7, 127.8, 129.7, 133.9, 134.0, 135.7, 135.8, 153.4, 155.9, 164.1. HRMS (ESI, positive): calcd. For $C_{41}H_{68}N_3O_5Si$ $[M+H]^+$, 710.4923; found, 710.4930.



**Alcohol 10b:** To a solution of guanidine **9b** (12.5 g, 17.6 mmol) in dry THF (213 mL) was added TBAF (1.0 M solution in THF, 19.4 mL, 19.4 mmol) at room temperature. After being stirred at room temperature for 30 min, the reaction mixture was diluted with $CH_2Cl_2$ (200 mL), and then washed with $H_2O$ (300 mL). The aqueous layer was extracted with $CH_2Cl_2$ (300 mL). The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 9/1) to afford alcohol **10b** (7.70 g, 93%) as a colorless oil.

$[\alpha]_D^{30}$ +1.53 (*c* 0.85, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3320, 2925, 2855, 1721, 1651, 1415, 1367, 1132, 1057. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.87 (3H, t, *J* = 7 Hz, -(CH$_2$)$_9$C*H*$_3$), 1.20-1.40 (19H, m, -C*H*$_a$CH$_b$(C*H*$_2$)$_9$CH$_3$), 1.40-1.60 (2H, m, -CH$_a$C*H*$_b$(CH$_2$)$_9$CH$_3$, -C*H*$_a$H$_b$CH$_2$OH), 1.46 (9H, s, -O$^t$Bu), 1.50 (9H, s, -O$^t$Bu), 1.86 (1H, m, -CH$_a$*H*$_b$CH$_2$OH), 3.46-3.62 (2H, m, -CH$_2$C*H*$_2$OH), 4.15 (1H, m, -C*H*NH-), 5.26 (1H, br s, -CH$_2$CH$_2$O*H*), 8.16 (1H, d, *J* = 8 Hz, -CHN*H*-), 11.4 (1H, s, -N*H*Boc). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 14.3, 22.8, 26.3, 28.2, 28.3, 29.5, 29.55, 29.57, 29.62, 29.8, 32.0, 35.9, 39.4, 48.1, 58.0, 79.6, 83.6, 153.4, 156.9, 163.0. HRMS (ESI, positive): calcd. For $C_{25}H_{50}N_3O_5$ $[M+H]^+$, 472.3745; found, 472.3748.

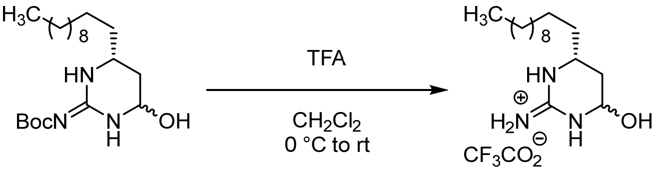


**Boc-Hemiaminal 11:** To a solution of alcohol **10b** (2.19 g, 4.64 mmol) and DMSO (0.66 mL, 9.3 mmol) in $CH_3CN$ (87.6 mL) was added IBX (1.95 g, 6.96 mmol) at 45 °C. after being stirred at 45 °C for 1.5 h, the reaction mixture was cooled to room temperature, and then filtered through a pad of Celite® (eluted with $CH_3CN$). The filtrate was concentrated under reduced pressure to provide crude aldehyde **16b** as a colorless oil. This crude residue was used for the next reaction without further purification.

**16b:** $[\alpha]_D^{27}$ +20.2 (*c* 0.50, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3322, 3132, 2926, 2855, 1721, 1643, 1616, 1568, 1417, 1366, 1330, 1157, 1129, 1056. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.87 (3H, t, $J$ = 7 Hz, $-(CH_2)_9CH_3$), 1.20-1.40 (18H, m, $-(CH_2)_9CH_3$), 1.48 (9H, s, -O$^t$Bu), 1.49 (9H, s, -O$^t$Bu), 1.54-1.66 (2H, m, $-CH_2(CH_2)_9CH_3$), 2.55-2.70 (2H, m, $-CH_2CHO$), 4.55 (1H, m, -C*H*NH-), 8.41 (1H, d, $J$ = 8 Hz, -CHN*H*-), 9.79 (1H, s, $-CH_2CHO$), 11.5 (1H, s, -N*H*Boc). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 14.2, 22.8, 25.9, 28.2, 28.4, 29.45, 29.47, 29.53, 29.6, 29.7, 32.0, 34.7, 46.4, 48.8, 79.3, 83.3, 153.3, 155.8, 163.6, 201.0. HRMS (ESI, positive): calcd. For $C_{26}H_{52}N_3O_6$ $[M+H+MeOH]^+$, 502.3851; found, 502.3849.

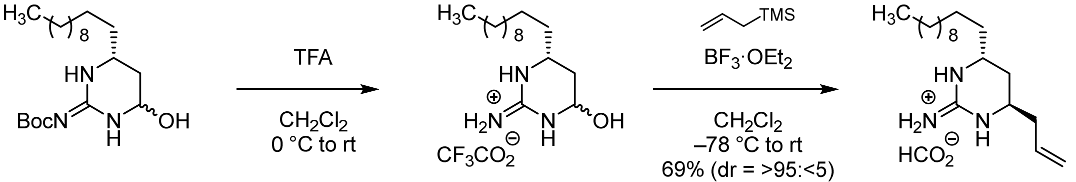
To a solution of crude aldehyde **16b** in $CH_2Cl_2$ (40 mL) was added $CH_2Cl_2$/TFA (1/1, 10 mL) at 0 °C. After being stirred at 0 °C for 2 h, the reaction mixture was diluted with toluene (30 mL), and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 2/1 to $CH_2Cl_2$/MeOH = 9/1) to afford Boc-hemiaminal **11** (1.71 g, quant. in 2 steps, dr = 85:15) as a yellow oil.

**11:** $[\alpha]_D^{30}$ +85.2 (*c* 1.45, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3283, 2927, 2856, 1734, 1685, 1256, 1203, 1152. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.90 (3H, t, $J$ = 7 Hz, $-(CH_2)_9CH_3$), 1.20-1.50 (18H, m, $-(CH_2)_9CH_3$), 1.54 (9H, s, -O$^t$Bu), 1.59-1.85 (3H, m, $-CH_2(CH_2)_9CH_3$, $-CH_aH_bCHOH$), 2.10 (0.85H, ddd, $J$ = 14, 4, 2 Hz, $-CH_aH_bCHOH$), 2.23 (0.15H, dt, $J$ = 14, 5 Hz, $-CH_aH_bCHOH$), 3.66 (0.15H, m, -C*H*NH-), 3.75 (0.85H, m, -C*H*NH-), 5.18 (0.85H, t, $J$ = 2 Hz, $-CH_2CHOH$), 5.20 (0.15H, m, $-CH_2CHOH$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 14.4, 23.7, 26.1, 28.1, 30.4, 30.45, 30.52, 30.6, 30.7, 33.1, 33.5, 35.0, 46.8, 72.1, 86.0, 152.1, 153.5. HRMS (ESI, positive): calcd. For $C_{16}H_{32}N_3O_3$ $[M+H-{}^tBu]^+$, 314.2438; found, 314.2464.


**11** **4**

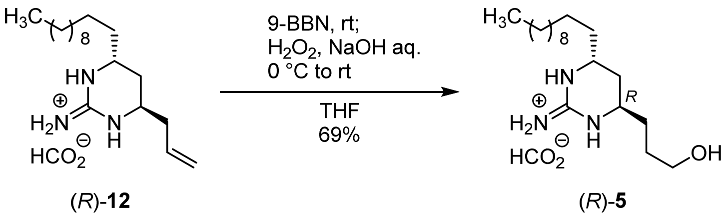
**Hemiaminal analogue 4:** To a solution of Boc-hemiaminal **11** (356 mg, 0.963 mmol) in $CH_2Cl_2$ (12 mL) was added TFA (12 mL) at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was diluted with toluene (18 mL), and then concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (EtOAc to $CH_2Cl_2$/Acetone/TFA/$H_2O$ = 13/7/0.3/0.3) to afford hemiaminal analogue **4** (144 mg, 39%) as a yellow oil.

$[\alpha]_D^{23}$ +73.0 (*c* 1.15, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3326, 2926, 2856, 1683, 1617, 1204, 1140. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.90 (3H, t, $J$ = 7 Hz, -$(CH_2)_9CH_3$), 1.25-1.45 (18H, m, -$(CH_2)_9CH_3$), 1.52-1.70 (3H, m, -$CH_2(CH_2)_9CH_3$, -$CH_aH_bCHOH$), 2.11 (1H, dt, $J$ = 14, 2 Hz, -$CH_aH_bCHOH$), 3.59 (1H, m, -CHNH-), 5.10 (1H, t, $J$ = 2 Hz, -$CH_2CHOH$). $^{13}C$ NMR (100 MHz, acetone-$d_6$): $\delta$ (ppm) 14.4, 23.3, 25.5, 30.1, 30.2, 30.27, 30.32, 30.4, 30.6, 32.2, 32.6, 35.1, 46.3, 74.2, 155.0. HRMS (ESI, positive): calcd. For $C_{15}H_{32}N_3O$ $[M]^+$, 270.2540; found, 270.2529.


**11** **4** (*R*)-**12**

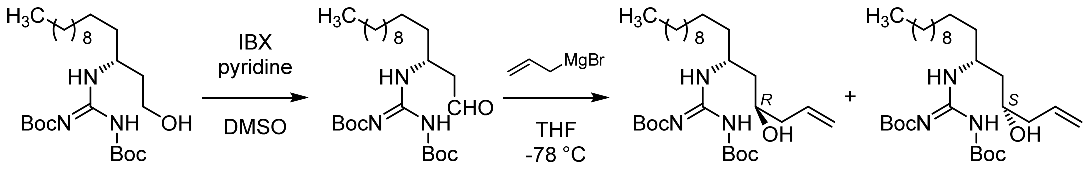
**Allyl analogue (*R*)-12:** To a solution of Boc-hemiaminal **11** (60.0 mg, 0.162 mmol) in $CH_2Cl_2$ (9 mL) was added TFA (9 mL) at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was diluted with toluene, and then concentrated under reduced pressure to provide crude hemiaminal analogue **4** as a yellow oil. This crude residue was used for the next reaction without further purification. To a solution of crude hemiaminal analogue **4** in dry $CH_2Cl_2$ (4 mL) were added allyltrimethylsilane (0.39 mL, 2.4 mmol) and dry $BF_3\cdot OEt_2$ (0.15 mL, 1.2 mmol) at −78 °C. And then the reaction mixture was allowed to warm to room temperature slowly. After being stirred for 16.5 h, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$. The resulting mixture was partitioned, and the aqueous layer was extracted with $CHCl_3$/2-PrOH (3/1). The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography ($CH_2Cl_2$/MeOH/$HCO_2H$ = 95/5/1 to 90/10/1) to afford (*R*)-allyl analogue (*R*)-**12** (38.0 mg, 69% in 2 steps, dr = >95:<5) as a yellow oil. Relative stereochemistry of the newly generated stereogenic center was determined by NOESY analysis.

$[\alpha]_D^{28}$ +44.3 (*c* 1.00, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3358, 3224, 3080, 2925, 2855, 1673, 1625, 1577, 1350, 1054. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.90 (3H, t, *J* = 7 Hz, $-(CH_2)_9CH_3$), 1.25-1.44 (18H, m, $-(CH_2)_9CH_3$), 1.44-1.65 (2H, m, $-CH_2(CH_2)_9CH_3$), 1.74-1.87 (2H, m, $-CH_2CHCH_2CH=CH_2$), 2.26-2.40 (2H, m, $-CH_2CH=CH_2$), 3.49 (1H, quintd, *J* = 7, 6.5 Hz, -C*H*NH-), 3.56 (1H, quintd, *J* = 7, 6 Hz, $-CH_2CHCH_2CH=CH_2$), 5.15-5.25 (2H, m, $-CH_2CH=CH_2$), 5.82 (1H, m, $-CH_2CH=CH_2$). $^{13}C$ NMR (100 MHz, $CD_3OD$): $\delta$ (ppm) 14.4, 23.7, 26.4, 30.45, 30.49, 30.6, 30.66, 30.72, 30.74, 30.8, 33.1, 36.5, 40.8, 47.7, 48.3, 119.4, 134.4, 155.2. HRMS (ESI, positive): calcd. For $C_{18}H_{36}N_3$ $[M]^+$, 294.2904; found, 294.2892.



**Hydroxypropyl analogue (*R*)-5:** To a solution of (*R*)-allyl analogue (*R*)-**12** (20 mg, 0.059 mmol) in dry THF (3 mL) was added 9-BBN (0.5 M solution in THF, 3.0 mL, 1.5 mmol) at room temperature. After being stirred at room temperature for 40 min, to the reaction mixture were added NaOH (2 N solution in $H_2O$, 4.8 mL, 9.6 mmol) and $H_2O_2$ (35% solution in $H_2O$, 4.8 mL, 69 mmol) at 0 °C. After being stirred at room temperature for 20 min, the reaction was quenched with a saturated aqueous solution of $NH_4Cl$. The resulting mixture was partitioned, and the aqueous layer was extracted with $CHCl_3$/2-PrOH (3/1). The combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (EtOAc to $CH_2Cl_2$/MeOH = 9/1 to $CH_2Cl_2$/MeOH/$HCO_2H$/$H_2O$ = 88/12/1/1 to 80/20/2/1) to afford (*R*)-hydroxypropyl analogue (*R*)-**5** (14.5 mg, 69%) as a yellow oil.

$[\alpha]_D^{28}$ +54.5 (*c* 0.20, MeOH). IR (film): $\nu_{max}$ (cm$^{-1}$) 3366, 2925, 2854, 1666, 1626. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.90 (3H, t, *J* = 7 Hz, $-(CH_2)_9CH_3$), 1,25-1.48 (18H, m, $-(CH_2)_9CH_3$), 1.48-1.70 (6H, m, $-CH_2(CH_2)_9CH_3$, $-(CH_2)_2CH_2OH$), 1.81 (2H, t, *J* = 5 Hz, $-CH_2CH(CH_2)_3OH$), 3.45-3.55 (2H, m, -NHC*H*-, $-CH_2CH(CH_2)_3OH$), 3.60 (2H, t, *J* = 6 Hz, $-(CH_2)_2CH_2OH$). $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ (ppm) 14.4, 23.7, 26.5, 29.4, 30.46, 30.54, 30.6, 30.68, 30.73, 30.8, 31.4, 33.1, 33.2, 36.6, 62.4, 155.1 (two sp$^3$ carbons are missing due to overlap with $CD_3OD$). HRMS (ESI, positive): calcd. For $C_{18}H_{38}N_3O$ $[M]^+$, 312.3009; found, 312.3028.



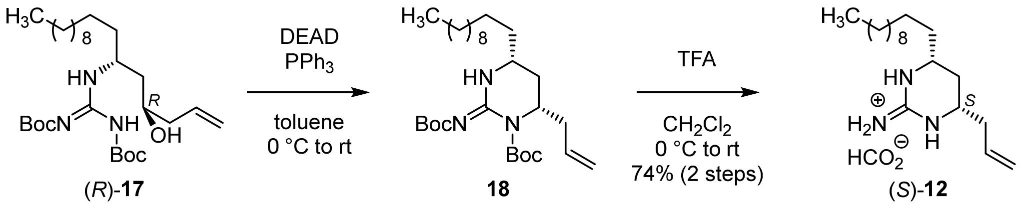
**10b** **16b** (*R*)-**17** 22% (dr = >95:<5) (2 steps) (*S*)-**17** 24% (dr = >95:<5) (2 steps)

**Allylation of aldehyde 16b:** To a solution of alcohol **10b** (100 mg, 0.212.mmol) in DMSO (3.1 mL) were added pyridine (31 µL, 0.38 mmol) and IBX (107 mg, 0.382 mmol) at room temperature. After being stirred at room temperature for 1 h, the reaction was quenched with cooled $H_2O$. The resulting mixture was filtered through a cotton pad (eluted with EtOAc). The filtrate was partitioned, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with $H_2O$ and brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. High polar compounds were removed by neutral silica gel flash column chromatography (hexane/EtOAc = 3/1) to afford aldehyde **16b** as a colorless oil, which was used for the next reaction without further purification. To a solution of aldehyde **16b** in dry THF (17.3 mL) was added CH$_2$=CHCH$_2$MgBr (0.56 M solution in Et$_2$O, 1.5 mL, 0.84 mmol) at −78 °C. After being stirred at −78 °C for 16 min, the reaction was quenched with a saturated aqueous solution of NH$_4$Cl (17 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine (20 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 8/1) to afford (*R*)-**17** (24.3 mg, 22% in 2 steps, dr = >95:<5) as a colorless oil and (*S*)-**17** (25.7 mg, 24% in 2 steps, dr = >95:<5) as a colorless oil. Relative stereochemistry of the newly generated stereogenic center in (*R*)-**17** was determined by NOESY analysis of **18**.

**(*R*)-17:** $[\alpha]_D^{29}$ +8.40 (*c* 1.00, CHCl$_3$). IR (film): $\nu_{max}$ (cm$^{-1}$) 3320, 2927, 1721, 1650, 1614, 1415, 1367, 1335, 1157, 1132. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 0.87 (3H, t, *J* = 7 Hz, -(CH$_2$)$_9$C*H*$_3$), 1.20-1.60 (22H, m, -C*H*$_2$(C*H*$_2$)$_9$CH$_3$, -C*H*$_2$CHCH$_2$CH=CH$_2$), 1.46 (9H, s, -O$^t$Bu), 1.50 (9H, s, -O$^t$Bu), 2.17 (1H, m, -C*H*$_a$H$_b$CH=CH$_2$), 2.32 (1H, m, -CH$_a$*H*$_b$CH=CH$_2$), 3.57 (1H, m, -CH$_2$C*H*CH$_2$CH=CH$_2$), 4.20 (1H, m, -C*H*NH-), 4.99-5.10 (2H, m, -CH$_2$CH=C*H*$_2$), 5.53 (1H, s, -CHO*H*), 5.87 (1H, m, -CH$_2$C*H*=CH$_2$), 8.14 (1H, d, *J* = 9 Hz, -CHN*H*-), 11.5 (1H, s, -N*H*Boc). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 14.3, 22.8, 26.2, 28.2, 28.3, 29.47, 29.54, 29.58, 29.62, 29.8, 32.0, 36.0, 41.3, 44.2, 48.5, 66.3, 79.5, 83.6, 116.4, 135.9, 153.3, 156.9, 163.1. HRMS (ESI, positive): calcd. For $C_{28}H_{54}N_3O_5$ [M+H]$^+$, 512.4058; found, 512.4041.

**(*S*)-17:** $[\alpha]_D^{30}$ +16.2 (*c* 1.30, CHCl$_3$). IR (film): $\nu_{max}$ (cm$^{-1}$) 3324, 2926, 2855, 1720, 1644, 1416, 1367, 1334, 1126. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 0.87 (3H, t, *J* = 7 Hz, -(CH$_2$)$_9$C*H*$_3$), 1.20-1.42 (19H, m, -C*H*$_a$H$_b$(C*H*$_2$)$_9$CH$_3$), 1.42-1.75 (3H, m, -CH$_a$*H*$_b$(CH$_2$)$_9$CH$_3$, -C*H*$_2$CHCH$_2$CH=CH$_2$), 1.47 (9H, s, -O$^t$Bu), 1.49 (9H, s, -O$^t$Bu), 2.24 (2H, t, *J* = 6 Hz, -C*H*$_2$CH=CH$_2$), 3.71 (1H, m, -CH$_2$C*H*CH$_2$CH=CH$_2$), 3.99 (1H, m, -C*H*NH-), 5.02-5.10 (2H, m, -CH$_2$CH=C*H*$_2$), 5.83 (1H, m, -CH$_2$C*H*=CH$_2$), 8.35 (1H, d, *J* = 8 Hz, -CHN*H*-), 11.4 (1H, s, -N*H*Boc). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 14.3, 22.8, 26.0, 28.2, 28.4, 29.5, 29.56, 29.58, 29.64, 29.8, 32.0, 35.9, 42.4, 43.8, 49.4, 69.6, 79.4, 83.4, 117.2, 135.4, 153.3, 155.6, 163.1. HRMS (ESI, positive): calcd. For

$C_{28}H_{54}N_3O_5$ [M+H]$^+$, 512.4058; found, 512.4082.

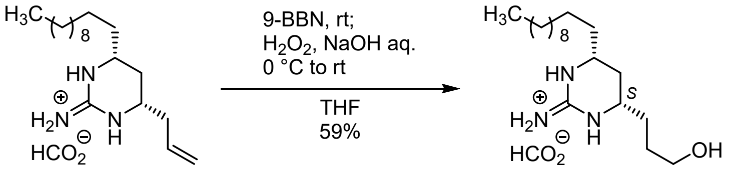


**Allyl analogue (*S*)-12:** To a solution of (*R*)-**17** (31.5 mg, 0.0616 mmol) and PPh$_3$ (65.0 mg, 0.248 mmol) in dry toluene (1.5 mL) was added DEAD (2.2 M solution in toluene, 0.11 mL, 0.24 mmol) at 0 °C under Ar atmosphere. After being stirred at room temperature for 3 h, the reaction mixture was concentrated under reduced pressure. High polar compounds were removed by neutral silica gel column chromatography (hexane/EtOAc = 5/1) to afford cyclic compound **18** as a colorless oil, which was used for the next reaction without further purification. Relative stereochemistry of the newly generated stereogenic center was determined by NOESY analysis.

**18:** $[\alpha]_D^{21}$ +127.3 (*c* 0.33, CHCl$_3$). IR (film): $\nu_{max}$ (cm$^{-1}$) 2926, 2854, 1737, 1644, 1367, 1308, 1241, 1160. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 0.88 (3H, t, *J* = 7 Hz, -(CH$_2$)$_9$C*H*$_3$), 1.20-1.45 (20H, m, -C*H*$_2$(C*H*$_2$)$_9$CH$_3$), 1.47 (9H, s, -O$^t$Bu), 1.50 (9H, s, -O$^t$Bu), 1.59 (1H, m, -C*H*$_a$H$_b$CHCH$_2$CH=CH$_2$), 2.16-2.28 (2H, m, -CH$_a$*H*$_b$CHC*H*$_a$H$_b$CH=CH$_2$), 2.65 (1H, m, -CH$_a$*H*$_b$CH=CH$_2$), 3.20 (1H, m, -C*H*NH-), 4.13 (1H, qd, *J* = 9, 4 Hz, -CH$_2$C*H*CH$_2$CH=CH$_2$), 5.04-5.14 (2H, m, -CH$_2$CH=C*H*$_2$), 5.72 (1H, m, -CH$_2$C*H*=CH$_2$). $^{13}$C NMR (100 MHz, CD$_3$OD): $\delta$ (ppm) 14.5, 23.8, 27.0, 28.3, 28.6, 30.5, 30.57, 30.60, 30.7, 30.8, 33.1, 35.3, 38.6, 41.6, 55.5, 80.6, 83.7, 118.7, 135.0, 153.6. HRMS (ESI, positive): calcd. For $C_{28}H_{52}N_3O_4$ [M+H]$^+$, 494.3952; found, 494.3946.

To a solution of cyclic compound **18** in CH$_2$Cl$_2$ (1.5 mL) was added TFA (1.5 mL) at 0 °C. After being stirred at room temperature for 50 min, the reaction mixture was diluted with toluene (5 mL), and then concentrated under reduced pressure. The residue was purified by neutral silica gel column chromatography (CH$_2$Cl$_2$/MeOH/HCO$_2$H/H$_2$O = 90/10/1/1 to 88/12/1/1 to 80/20/1/2) to afford (*S*)-allyl analogue (*S*)-**12** (15.6 mg, 74% in 2 steps) as a yellow oil.

**(*S*)-12:** $[\alpha]_D^{29}$ +5.33 (*c* 0.75, MeOH). IR (film): $\nu_{max}$ ($cm^{-1}$) 3338, 3251, 3080, 2926, 2855, 1676, 1622, 1348, 1203, 1180, 1136. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.90 (3H, t, *J* = 7 Hz, $-(CH_2)_9C\mathit{H}_3$), 1.20-1.45 (18H, m, $-(C\mathit{H}_2)_9CH_3$), 1.48-1.65 (3H, m, $-C\mathit{H}_2(CH_2)_9CH_3$, $-C\mathit{H}_aH_bCHCH_2CH{=}CH_2$), 2.12 (1H, dt, *J* = 14, 3 Hz, $-CH_a\mathit{H}_bCHCH_2CH{=}CH_2$), 2.25-2.44 (2H, m, $-C\mathit{H}_2CH{=}CH_2$), 3.40-3.57 (2H, m, $-C\mathit{H}NH-$, $-CH_2C\mathit{H}CH_2CH{=}CH_2$), 5.16-5.27 (2H, m, $-CH_2CH{=}C\mathit{H}_2$), 5.82 (1H, m, $-CH_2C\mathit{H}{=}CH_2$). $^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ (ppm) 14.4, 23.7, 26.0, 30.5, 30.58, 30.61, 30.67, 30.73, 30.8, 33.1, 33.9, 36.2, 40.3, 50.4, 51.1, 119.8, 133.9, 155.9. HRMS (ESI, positive): calcd. For $C_{18}H_{36}N_3$ $[M]^+$, 294.2904; found, 294.2930.

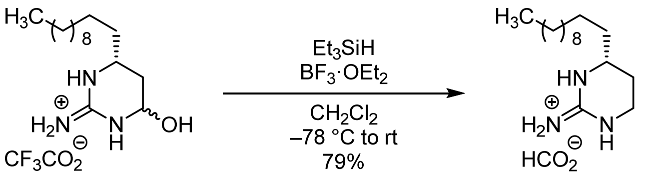


(*S*)-**12** (*S*)-**5**

**Hydroxypropyl analogue (*S*)-5:** To a solution of (*S*)-allyl analogue (*S*)-**12** (16 mg, 0.055 mmol) in dry THF (2.4 mL) was added 9-BBN (0.5 M solution in THF, 2.4 mL, 1.2 mmol) at room temperature. After being stirred at room temperature for 40 min, to the reaction mixture were added NaOH (2 N solution in $H_2O$, 3.8 mL, 7.6 mmol) and $H_2O_2$ (35% solution in $H_2O$, 3.8 mL, 55 mmol) at 0 °C. After being stirred at room temperature for 20 min, the reaction was quenched with a saturated aqueous solution of $NH_4Cl$ (8 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with $CHCl_3$/2-PrOH (3/1, 10 mL x 3). The combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (EtOAc to $CH_2Cl_2$/MeOH/$HCO_2H$/$H_2O$ = 90/10/0/0 to 88/12/1/1 to 80/20/2/1) to afford hydroxypropyl analogue (*S*)-**5** (10 mg, 59%) as a yellow oil.

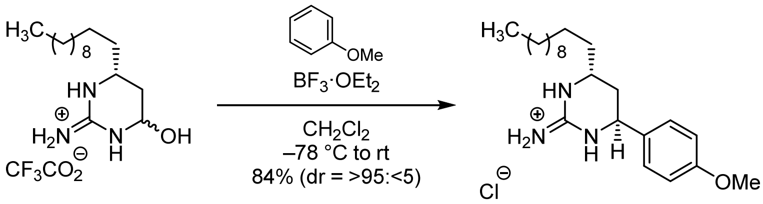
$[\alpha]_D^{28}$ +3.20 (*c* 0.25, MeOH). IR (film): $\nu_{max}$ ($cm^{-1}$) 3418, 2925, 2853, 1662, 1624, 1350. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.90 (3H, t, *J* = 7 Hz, $-(CH_2)_9C\mathit{H}_3$), 1,20-1.50 (19H, m, $-C\mathit{H}_aH_b(C\mathit{H}_2)_9CH_3$), 1.50-1.70 (6H, m, $-CH_a\mathit{H}_b(CH_2)_9CH_3$, -

$\mathrm{C\mathit{H}_aH_bCH(C\mathit{H}_2)_2CH_2OH}$), 2.15 (1H, dt, $J$ = 13, 3 Hz, -$\mathrm{CH_a\mathit{H}_bCH(CH_2)_3OH}$), 3.40-3.53 (2H, m, -$\mathrm{C\mathit{H}NH}$-, -$\mathrm{CH_2C\mathit{H}(CH_2)_3OH}$), 3.53-3.69 (2H, m, -$\mathrm{(CH_2)_2C\mathit{H}_2OH}$). $^{13}$C NMR (100 MHz, $\mathrm{CD_3OD}$): $\delta$ (ppm) 14.4, 23.7, 26.1, 29.0, 30.5, 30.60, 30.62, 30.67, 30.73, 30.8, 32.8, 33.1, 34.2, 36.2, 51.1, 51.2, 62.4, 155.8. HRMS (ESI, positive): calcd. For $\mathrm{C_{18}H_{38}N_3O}$ $[\mathrm{M}]^+$, 312.3009; found, 312.3034.



**4** **3**

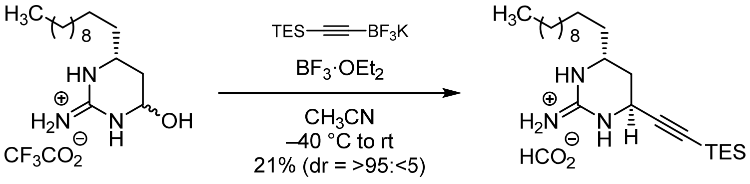
**Methylene analogue 3:** To a solution of hemiaminal analogue **4** (44.0 mg, 0.115 mmol) in dry $\mathrm{CH_2Cl_2}$ (4 mL) were added $\mathrm{Et_3SiH}$ (0.13 mL, 0.82 mmol) and dry $\mathrm{BF_3{\cdot}OEt_2}$ (82 μL, 0.65 mmol) at −78 °C. And then the reaction mixture was allowed to warm to room temperature slowly. After being stirred for 21 h, the reaction was quenched with a saturated aqueous solution of $\mathrm{NaHCO_3}$ (4 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with $\mathrm{CHCl_3}$/2-PrOH (3/1, 8 mL x 2). The combined organic layer was dried over anhydrous $\mathrm{Na_2SO_4}$ and concentrated under reduced pressure. The residue was purified by neutral silica gel column chromatography ($\mathrm{CH_2Cl_2/MeOH/HCO_2H/H_2O}$ = 88/12/1/1) to afford methylene analogue **3** (27.0 mg, 79%) as a white solid.mp: 97-108 °C. $[\alpha]_D^{28}$ +13.4 ($c$ 0.95, $\mathrm{CHCl_3}$). IR (film): $\nu_{\mathrm{max}}$ ($\mathrm{cm^{-1}}$) 3358, 3249, 3194, 3095, 2922, 2852, 1685, 1625, 1206, 1180, 1133. $^1$H NMR (400 MHz, $\mathrm{CD_3OD}$): $\delta$ (ppm) 0.90 (3H, t, $J$ = 7 Hz, -$\mathrm{(CH_2)_9C\mathit{H}_3}$), 1.20-1.47 (18H, m, -$\mathrm{(C\mathit{H}_2)_9CH_3}$), 1.47-1.70 (3H, m, -$\mathrm{C\mathit{H}_2(CH_2)_9CH_3}$, -$\mathrm{C\mathit{H}_aH_bCH_2NH}$-), 2.03 (1H, m, -$\mathrm{CH_a\mathit{H}_bCH_2NH}$-), 3.25-3.46 (3H, m, -$\mathrm{C\mathit{H}NH}$-, -$\mathrm{CH_2C\mathit{H}_2NH}$-). $^{13}$C NMR (100 MHz, $\mathrm{CD_3OD}$): $\delta$ (ppm) 14.4, 23.7, 26.3, 26.7, 30.5, 30.55, 30.62, 30.67, 30.73, 30.8, 33.1, 36.3, 38.3, 50.6, 155.6. HRMS (ESI, positive): calcd. For $\mathrm{C_{15}H_{32}N_3}$ $[\mathrm{M}]^+$, 254.2591; found, 254.2578.



**4** **13**

**4-Anysyl-analogue 13:** To a solution of hemiaminal analogue **4** (30 mg, 0.078 mmol) in dry $CH_2Cl_2$ (1.6 mL) were added anisole (51 μL, 0.47 mmol) and dry $BF_3{\cdot}OEt_2$ (1.3 M solution in $CH_2Cl_2$, 0.35 mL, 0.46 mmol) at −78 °C. And then the reaction mixture was allowed to warm to room temperature slowly. After being stirred for 24 h, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (2 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with $CHCl_3$/2-PrOH (3/1, 8 mL x 2). The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by neutral silica gel column chromatography ($CH_2Cl_2$/MeOH/$HCO_2H$/$H_2O$ = 95/5/1/0 to 88/12/1/1). The product was then dissolved in MeOH (2 mL), and then ion exchange resin (Amberlite® IRA-410J Cl, 92 mg) was added to the solution. After being stirred at room temperature for 30 min, the reaction mixture was filtered through a cotton pad (eluted with MeOH). The filtrate was concentrated under reduced pressure to afford 4-anysyl analogue **13** (26 mg, 84%, dr = >95:<5) as a yellow oil. Relative stereochemistry of the newly generated stereogenic center was determined by NOESY analysis.

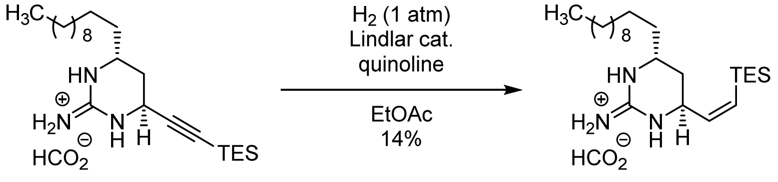
$[\alpha]_D^{24}$ +26.6 (*c* 1.37, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3246, 2926, 2854, 1665, 1624, 1514, 1252, 1179. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.90 (3H, t, *J* = 7 Hz, -$(CH_2)_9CH_3$), 1.25-1.35 (18H, m, -$(CH_2)_9CH_3$), 1.50-1.70 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.90-2.10 (2H, m, -$CH_2$CHAr), 3.29 (1H, m, -CHNH-), 3.79 (3H, s, -$OCH_3$), 4.70 (1H, t, *J* = 5 Hz, -$CH_2$CHAr), 6.93-6.98 (2H, m, Ar), 7.20-7.25 (2H, m, Ar). $^{13}C$ NMR (100 MHz, $CD_3OD$): $\delta$ (ppm) 14.4, 23.7, 26.3, 30.5, 30.6, 30.66, 30.72, 33.1, 34.7, 36.1, 47.9, 51.7, 55.8, 115.3, 128.3, 134.3, 155.5, 161.0. HRMS (ESI, positive): calcd. For $C_{22}H_{38}N_3O$ $[M]^+$, 360.3009; found, 360.3008.



4 14

**TES-Alkynyl analogue 14:** To a solution of hemiaminal analogue **4** (108 mg, 0.282 mmol) in dry $CH_3CN$ (7 mL) were added TES-alkynyl-trifluoroborate-potassium salt[2] (1.0 g, 4.1 mmol) and dry $BF_3{\cdot}OEt_2$ (0.35 mL, 2.8 mmol) at −40 °C. And then the reaction mixture was allowed to warm to room temperature slowly. After being stirred for 6 h, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (7 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with $CHCl_3$/2-PrOH (3/1, 24 mL x 3). The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by neutral silica gel column chromatography ($CH_2Cl_2$/MeOH/$HCO_2H$ = 95/5/1) to afford TES-alkynyl analogue **14** (26.5 mg, 21%, dr = >95:<5) as a brown oil. Relative stereochemistry of the newly generated stereogenic center was determined by NOESY analysis of its derivative **15**.

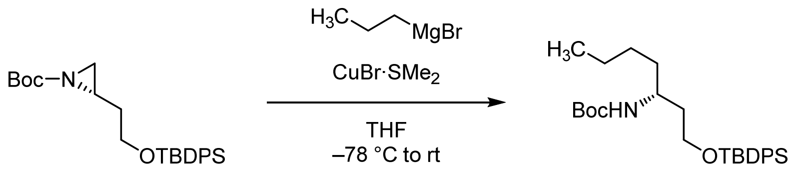
$[\alpha]_D^{24}$ +48.8 (*c* 0.38, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3344, 2925, 2170, 1668, 1458, 1349, 1018. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.62 (6H, q, $J$ = 8 Hz, -$Si(CH_2CH_3)_3$), 0.90 (3H, t, $J$ = 7 Hz, -$(CH_2)_9CH_3$), 1.01 (9H, t, $J$ = 8 Hz, -$Si(CH_2CH_3)_3$), 1.25-1.40 (18H, m, -$(CH_2)_9CH_3$), 1.53-1.71 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.79 (1H, ddd, $J$ = 14, 10, 5 Hz, -$CH_aH_bCHC{\equiv}CTES$), 2.14 (1H, dt, $J$ = 14, 3 Hz, -$CH_aH_bCHC{\equiv}CTES$), 3.70 (1H, m, -CHNH-), 4.48 (1H, dd, $J$ = 5, 3 Hz, -$CH_2CHC{\equiv}CTES$). $^{13}C$ NMR (100 MHz, $CD_3OD$): $\delta$ (ppm) 5.1, 7.8, 14.4, 23.7, 26.1, 30.3, 30.5, 30.6, 30.70, 30.73, 30.74, 33.0, 33.1, 35.4, 41.6, 48.2, 87.6, 106.3, 155.0. HRMS (ESI, positive): calcd. For $C_{23}H_{46}N_3Si$ $[M]^+$, 392.3456; found, 392.3460.



**14** **15**

**TES-vinyl analogue 15:** To a solution of TES-alkynyl analogue **14** (4.9 mg, 0.011 mmol) in EtOAc (1 mL) were added quinoline (13 μL, 0.11 mmol) and Lindlar catalyst (5% Pd/$CaCO_3$/Lead-poisoned, 23 mg, 0.011 mmol) at room temperature. After being stirred at room temperature for 21 h under $H_2$ atmosphere (1 atm), the reaction mixture was filtered through a pad of Celite® (eluted with MeOH). The filtrate was concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography ($CH_2Cl_2$/MeOH/$HCO_2H$/$H_2O$ = 95/5/1/0 to 88/12/1/1). The product was then dissolved in EtOAc (1 mL), and then quinoline (5 μL, 4 μmol) and Lindlar catalyst (5% Pd/$CaCO_3$/Lead-poisoned, 3.9 mg, 1.8 μmol) were added to the solution. After being stirred at room temperature for 26 h under $H_2$ atmosphere (1 atm), the reaction mixture was filtered through a cotton pad (eluted with $CH_2Cl_2$/MeOH = 9/1). The filtrate was concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography ($CH_2Cl_2$/MeOH/$HCO_2H$ = 95/5/1) to afford TES-vinyl analogue **15** (0.7 mg, 14% in 2 steps) as a colorless oil. Relative stereochemistry of the newly generated stereogenic center was determined by NOESY analysis.

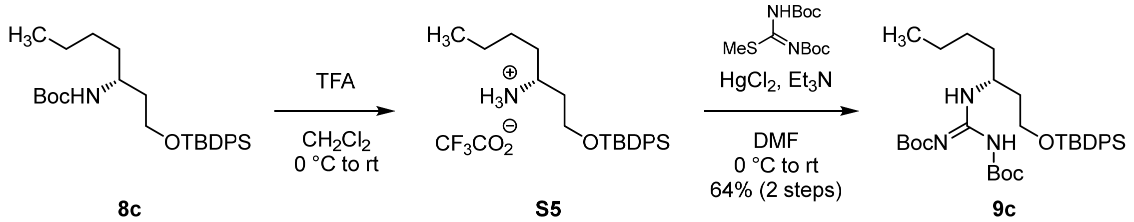
$[\alpha]_D^{21}$ +31.4 (*c* 0.035, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 2954, 2925, 2872, 2853, 1675, 1618. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.70 (6H, q, $J$ = 8 Hz, -Si(C$H_2$$CH_3$)$_3$), 0.90 (3H, t, $J$ = 7 Hz, -($CH_2$)$_9$C$H_3$), 1.01 (9H, t, $J$ = 8 Hz, -Si($CH_2$C$H_3$)$_3$), 1.25-1.45 (18H, m, -(C$H_2$)$_9$$CH_3$), 1.47-1.67 (2H, m, -C$H_2$($CH_2$)$_9$$CH_3$), 1.78-1.91 (2H, m, -C$H_2$CHCH=CHTES), 3.54 (1H, m, -C*H*NH-), 4.07 (1H, m, -$CH_2$C*H*CH=CHTES), 5.79 (1H, d, $J$ = 14 Hz, -CH=C*H*TES), 6.31 (1H, dd, $J$ = 14, 9 Hz, -C*H*=CHTES). HRMS (ESI, positive): calcd. For $C_{23}H_{48}N_3Si$ $[M]^+$, 394.3612; found, 394.3600.



**7** **8c**

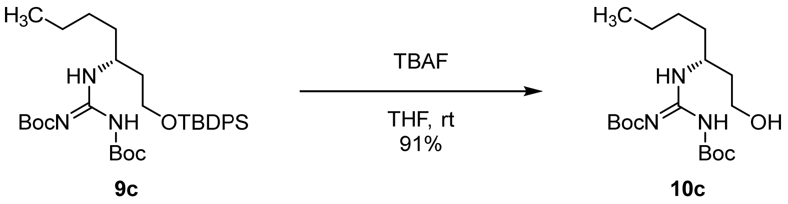
**C$_4$-amide 8c:** To a suspension of freshly prepared CuBr·SMe$_2$ (415 mg, 2.02 mmol) in dry THF (34 mL) were added C$_3$H$_7$MgBr (0.69 M solution in Et$_2$O, 25.0 mL, 17.3 mmol) and a solution of aziridine **7** (2.45 g, 5.76 mmol) in dry THF (34 mL) at −78 °C under Ar atmosphere. And then the reaction mixture was allowed to warm to room temperature slowly. After being stirred for 6 h, the reaction was quenched with a saturated aqueous solution of NH$_4$Cl (68 mL). The reaction mixture was filtered through a pad of Celite® (eluted with EtOAc). The filtrate was partitioned, and the aqueous layer was extracted with EtOAc. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 7/1) to afford C$_4$-amide **8c** (2.50 g, 92%) as a colorless oil.

$[\alpha]_D^{22}$ −4.66 (*c* 1.18, CHCl$_3$). IR (film): $\nu_{max}$ (cm$^{-1}$) 2957, 2931, 2858, 1716, 1700, 1507, 1174, 1111. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 0.88 (3H, t, *J* = 7 Hz, -(CH$_2$)$_2$C*H*$_3$), 1.06 (9H, s, -Si$^t$Bu), 1.20-1.36 (4H, m, -(C*H*$_2$)$_2$CH$_3$), 1.38-1.50 (2H, m, -C*H*$_2$(CH$_2$)$_2$CH$_3$), 1.42 (9H, s, -O$^t$Bu), 1.58 (1H, m, -C*H*$_a$H$_b$CH$_2$OTBDPS), 1.83 (1H, m, -CH$_a$*H*$_b$CH$_2$OTBDPS), 3.64-3.75 (2H, m, -CH$_2$C*H*$_2$OTBDPS), 3.79 (1H, m, -C*H*NH-), 4.97 (1H, d, *J* = 8 Hz, -CHN*H*-), 7.35-7.46 (6H, m, -Si-Ph), 7.65-7.70 (4H, m, -Si-Ph). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 14.2, 19.2, 22.8, 27.0, 28.3, 28.6, 34.9, 36.6, 49.1, 61.5, 78.7, 127.8, 129.8, 133.6, 135.7, 155.8. HRMS (ESI, positive): calcd. For C$_{28}$H$_{43}$NO$_3$NaSi [M+Na]$^+$, 492.2904; found, 492.2900.



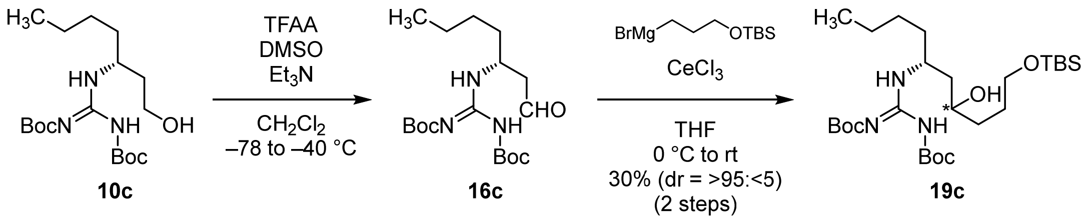
**$C_4$-guanidine 9c:** To a solution of $C_4$-amide **8c** (420 mg, 0.894 mmol) in $CH_2Cl_2$ (4.5 mL) was added TFA (4.5 mL) at 0 °C. After being stirred at room temperature for 30 min, the reaction mixture was diluted with toluene, and then concentrated under reduced pressure to provide crude $C_4$-ammonium-TFA salt **S5** as a yellow oil. This crude residue was used for the next reaction without further purification. To a solution of crude $C_4$-ammonium-TFA salt **S5**, diBoc-methylisothiourea (285 mg, 0.983 mmol), and $Et_3N$ (0.37 mL, 2.7 mmol) in DMF (8.9 mL) was added $HgCl_2$ (267 mg, 0.983 mmol) at 0 °C. After being stirred at room temperature for 17 min, the reaction mixture was diluted with EtOAc, and then filtered through a pad of Celite® (eluted with EtOAc). The filtrate was washed with $H_2O$ and brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 34/1) to afford $C_4$-guanidine **9c** (348 mg, 64% in 2 steps) as a colorless oil.

$[\alpha]_D^{22}$ −7.26 (*c* 1.01, $CHCl_3$). IR (film): $\nu_{max}$ (cm$^{-1}$) 3325, 2959, 2931, 2858, 1718, 1636, 1615, 1335, 1157, 1115. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.87 (3H, t, *J* = 7 Hz, -$(CH_2)_2CH_3$), 1.04 (9H, s, -Si$^t$Bu), 1.20-1.35 (4H, m, -$(CH_2)_2CH_3$), 1.40-1.65 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.47 (18H, s, -O$^t$Bu), 1.72 (1H, m, -$CH_aH_bCH_2$OTBDPS), 1.82 (1H, m, -$CH_aH_bCH_2$OTBDPS), 3.71 (2H, t, *J* = 7 Hz, -$CH_2CH_2$OTBDPS), 4.30 (1H, m, -C*H*NH-), 7.34-7.44 (6H, m, -Si-Ph), 7.64-7.69 (4H, m, -Si-Ph), 8.18 (1H, d, *J* = 8 Hz, -CHN*H*-), 11.5 (1H, s, -N*H*Boc). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 14.1, 19.2, 22.8, 27.0, 27.7, 28.3, 28.5, 34.7, 37.2, 48.1, 61.2, 78.9, 82.9, 127.7, 127.8, 129.7, 133.9, 134.0, 135.7, 135.8, 153.4, 155.9, 164.1. HRMS (ESI, positive): calcd. For $C_{34}H_{53}N_3O_5NaSi$ $[M+Na]^+$, 634.3647; found, 634.3637.



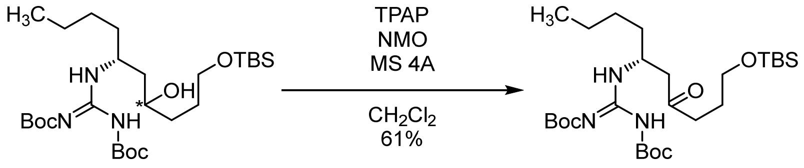
**$C_4$-alcohol 10:** To a solution of $C_4$-guanidine **9c** (338 mg, 0.552 mmol) in dry THF (6.6 mL) was added TBAF (1.0 M solution in THF, 0.60 mL, 0.60 mmol) at room temperature. After being stirred at room temperature for 50 min, the reaction mixture was diluted with $CH_2Cl_2$, and then washed with brine. The aqueous layer was extracted with $CH_2Cl_2$ and $CHCl_3$/2-PrOH (3/1). The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 9/1 to 2/1) to afford $C_4$-alcohol **10** (187 mg, 91%) as a colorless oil.

$[\alpha]_D^{22}$ +5.26 (*c* 1.05, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3318, 2959, 2934, 1720, 1647, 1614, 1576, 1416, 1367, 1333, 1159, 1133, 1058. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.81 (3H, t, $J$ = 7 Hz, $-(CH_2)_2CH_3$), 1.15-1.60 (7H, m, $-CH_2(CH_2)_2CH_3$, $-CH_aH_bCH_2OH$), 1.38 (9H, s, $-O^tBu$), 1.42 (9H, s, $-O^tBu$), 1.79 (1H, m, $-CH_aH_bCH_2OH$), 3.39-3.55 (2H, m, $-CH_2CH_2OH$), 4.08 (1H, m, -C*H*NH-), 5.17 (1H, br s, $-CH_2CH_2OH$), 8.09 (1H, d, $J$ = 8 Hz, -CHN*H*-), 11.4 (1H, s, -N*H*Boc). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 13.9, 22.5, 28.0, 28.1, 28.3, 35.4, 39.2, 47.8, 57.8, 79.3, 83.4, 153.2, 156.7, 162.8. HRMS (ESI, positive): calcd. For $C_{18}H_{35}N_3O_5Na$ $[M+Na]^+$, 396.2469; found, 396.2460.



**$C_4$-alcohol 19c:** To a solution of DMSO (0.22 mL, 3.1 mmol) in dry $CH_2Cl_2$ (2 mL) was added a solution of TFAA (0.22 mL, 1.6 mmol) in dry $CH_2Cl_2$ (2 mL) at −78 °C. After being stirred at −78 °C for 10 min, to the reaction mixture was added a solution of $C_4$-alcohol **10c** (83.0 mg, 0.222 mmol) in dry $CH_2Cl_2$ (2 mL). After being stirred at −78 °C for 30 min, to the reaction mixture was added $Et_3N$ (0.65 mL, 4.7 mmol). After being stirred at −78 °C for 25 min, the reaction mixture was allowed to warm to −40 °C slowly. After being stirred at for 1 h, the reaction was quenched with $H_2O$ (6 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure to provide crude $C_4$-aldehyde **16c** as a colorless oil, which was used for the next reaction without further purification. To a suspension of dry $CeCl_3$ (438 mg, 1.78 mmol) in dry THF (3 mL) were added $TBSOC_3H_6MgBr$ (0.23 M solution in THF, 7.7 mL, 1.8 mmol) and a solution of crude $C_4$-aldehyde **16c** in dry THF (3 mL) at 0 °C. And then the reaction mixture was allowed to warm to room temperature slowly. After being stirred for 14 h, the reaction was quenched with a saturated aqueous solution of $NH_4Cl$ (13 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 9/1) to afford $C_4$-alcohol **19c** (36.6 mg, 30% in 2 steps, dr = >95:<5) as a colorless oil.

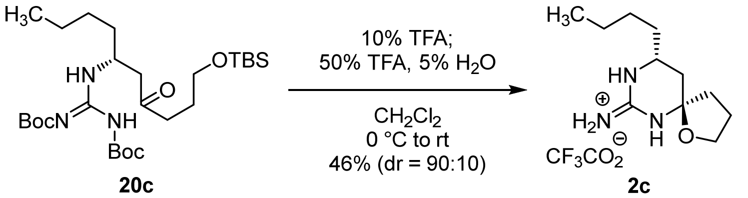
$[\alpha]_D^{22}$ +2.01 (*c* 0.85, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3320, 2931, 2858, 1720, 1649, 1615, 1417, 1367, 1335, 1140. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.03 (6H, s, -Si(C*H*$_3$)$_2$), 0.86-0.91 (3H, m, -(CH$_2$)$_2$C*H*$_3$), 0.88 (9H, s, -Si$^t$Bu), 1.20-1.74 (12H, m, -C*H*$_2$(C*H*$_2$)$_2$CH$_3$, -C*H*$_2$CH(C*H*$_2$)$_2$CH$_2$OTBS), 1.46 (9H, s, -O$^t$Bu), 1.50 (9H, s, -O$^t$Bu), 3.50 (1H, m, -CH$_2$C*H*(CH$_2$)$_3$OTBS), 3.55-3.67 (2H, m, -(CH$_2$)$_2$C*H*$_2$OTBS), 4.21 (1H, m, -C*H*NH-), 5.42 (1H, d, *J* = 3 Hz, -CHO*H*), 8.15 (1H, d, *J* = 8 Hz, -CHN*H*-), 11.5 (1H, s, -N*H*Boc). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) −5.2, −5.1, 14.1, 18.5, 22.7, 26.1, 28.2, 28.3, 28.4, 29.5, 33.1, 35.7, 44.9, 48.5, 63.5, 66.4, 79.5, 83.5, 153.3, 156.8, 163.1. HRMS (ESI, positive): calcd. For $C_{27}H_{55}N_3O_6NaSi$ $[M+Na]^+$, 568.3752; found, 568.3760.



**19c** **20c**

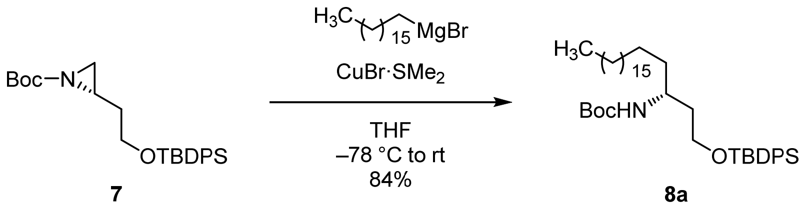
**C$_4$-ketone 20c:** To a solution of C$_4$-alcohol **19c** (22.0 mg, 40.3 μmol) in dry $CH_2Cl_2$ (0.8 mL) were added MS 4A (20 mg), NMO (7.1 mg, 61 μmol), and TPAP (24 mM solution in $CH_2Cl_2$, 0.40 mL, 9.6 μmol) at room temperature. To the reaction mixture was added additional TPAP until starting material was consumed on TLC. After being stirred at room temperature for 15.5 h, the reaction mixture was diluted with $CH_2Cl_2$, and then filtered through a cotton pad (eluted with $CH_2Cl_2$). The filtrate was washed with brine. The aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by neutral silica gel column chromatography (toluene/EtOAc = 19/1) to afford C$_4$-ketone **20c** (13.5 mg, 61%) as a colorless oil.

$[\alpha]_D^{22}$ +6.67 (*c* 0.20, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3325, 2956, 2930, 2859, 1718, 1637, 1366, 1337, 1158, 1124. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.03 (6H, s, -Si(C$H_3$)$_2$), 0.86-0.90 (3H, m, -(CH$_2$)$_2$C$H_3$), 0.88 (9H, s, -Si$^t$Bu), 1.20-1.40 (4H, m, -(C$H_2$)$_2$CH$_3$), 1.48 (9H, s, -O$^t$Bu), 1.49 (9H, s, -O$^t$Bu), 1.53-1.67 (2H, m, -C$H_2$(CH$_2$)$_2$CH$_3$), 1.73-1.82 (2H, m, -C$H_2$CH$_2$OTBS), 2.44-2.73 (4H, m, -C$H_2$C(=O)C$H_2$(CH$_2$)$_2$OTBS), 3.57-3.63 (2H, t, *J* = 6 Hz, -CH$_2$C$H_2$OTBS), 4.44 (1H, m, -C$H$NH-), 8.55 (1H, d, *J* = 8 Hz, -CHN$H$-), 11.4 (1H, s, -N$H$Boc). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) −5.2, 14.1, 18.5, 22.7, 26.1, 26.8, 28.25, 28.32, 28.5, 33.9, 39.8, 46.7, 47.3, 62.3, 79.1, 83.1, 153.2, 155.8, 163.9, 209.5. HRMS (ESI, positive): calcd. For $C_{27}H_{53}N_3O_6NaSi$ $[M+Na]^+$, 566.3596; found, 566.3602.



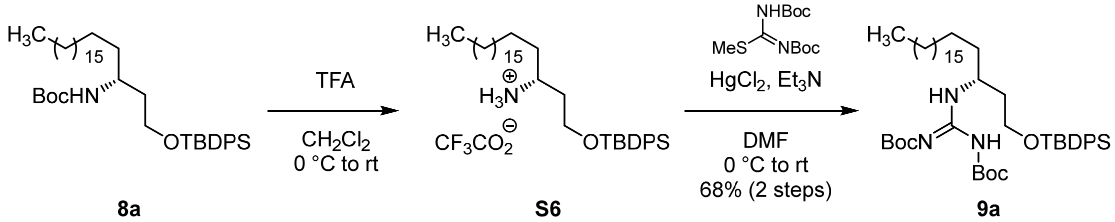
**$C_4$-decarboxylate analogue 2c:** To a solution of $C_4$-ketone **20c** (4.7 mg, 8.6 μmol) in $CH_2Cl_2$ (2.7 mL) was added TFA (0.3 mL) at 0 °C. After being stirred at room temperature for 40 min, to the reaction mixture was added TFA/$H_2O$ (9/1, 3.0 mL). After being stirred at room temperature for 12 h, the reaction mixture was diluted with toluene, and then concentrated under reduced pressure. The residue was purified by Chromatorex DIOL silica gel open column chromatography ($CH_2Cl_2$/MeOH/$HCO_2H$ = 97/3/1). The product was further purified by HPLC on Nomura Chemical ODS-HG-5 monitored by UV detector (4.6 x 250 mm, MeOH/$H_2O$ = 95/5, 0.5 mL/min, 220 nm). The product was further purified by HPLC on Nomura Chemical ODS-HG-5 monitored by UV detector (4.6 x 250 mm, MeOH/$H_2O$/TFA = 85/15/0.1, 0.5 mL/min, 220 nm) to afford $C_4$-decarboxylate analogue **2c** (1.3 mg, 46%) as a colorless oil.

$[\alpha]_D^{22}$ +72.7 (*c* 0.11, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3244, 2931, 1684, 1616, 1202. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.96 (3H, t, $J$ = 7 Hz, $-(CH_2)_2CH_3$), 1.35-1.45 (4H, m, $-(CH_2)_2CH_3$), 1.53-1.65 (2H, m, $-CH_2(CH_2)_2CH_3$), 1.70 (1H, t, $J$ = 13 Hz, $-CH_aH_bCO-$), 2.02-2.16 (5H, m, $-CH_aH_bCO-$, $-(CH_2)_2CH_2O-$), 3.62 (1H, m, $-CHNH-$), 3.91 (1H, m, $-(CH_2)_2CH_aH_bO-$), 3.97 (1H, m, $-(CH_2)_2CH_aH_bO-$). $^{13}C$ NMR (100 MHz, $CD_3OD$): $\delta$ (ppm) 14.2, 23.6, 25.7, 28.1, 35.3, 37.7, 38.1, 68.7, 89.6, 155.3 (one $sp^3$ carbon is missing due to overlap with $CD_3OD$). HRMS (ESI, positive): calcd. For $C_{11}H_{22}N_3O$ $[M]^+$, 212.1757; found, 212.1757.



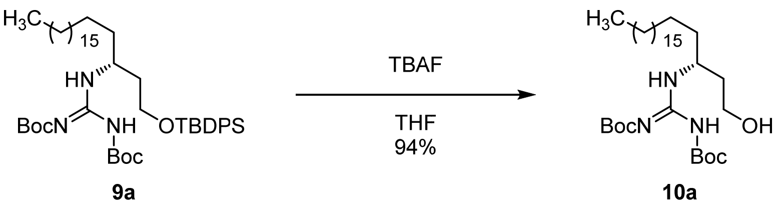
**$C_{18}$-amide 8a:** To a suspension of freshly prepared CuBr·SMe$_2$ (73.0 mg, 0.357 mmol) in dry THF (8 mL) were added $C_{17}H_{35}MgBr$ (0.66 M solution in THF, 4.6 mL, 3.0 mmol) and a solution of aziridine **7** (434 mg, 1.02 mmol) in dry THF (8 mL) at −78 °C under Ar atmosphere. And then the reaction mixture was allowed to warm to room temperature slowly. After being stirred for 18 h, the reaction was quenched with a saturated aqueous solution of $NH_4Cl$ (16 mL). The resulting mixture was filtered through a pad of Celite® (eluted with EtOAc). The filtrate was partitioned, and the aqueous layer was extracted with EtOAc. The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane to hexane/EtOAc = 19/1) to afford $C_{18}$-amide **8a** (572 mg, 84%) as a colorless oil.

$[\alpha]_D^{25}$ −1.96 (*c* 1.12, $CHCl_3$). IR (film): $\nu_{max}$ (cm$^{-1}$) 3437, 2925, 2854, 1702, 1505, 1364, 1173, 1112. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.88 (3H, t, *J* = 7 Hz, -$(CH_2)_{16}CH_3$), 1.06 (9H, s, -Si$^t$Bu), 1.20-1.35 (32H, m, -$(CH_2)_{16}CH_3$), 1.38-1.51 (2H, m, -$CH_2(CH_2)_{16}CH_3$), 1.42 (9H, s, -O$^t$Bu), 1.56 (1H, m, -$CH_aH_bCH_2$OTBDPS), 1.82 (1H, m, -$CH_aH_bCH_2$OTBDPS), 3.63-3.74 (2H, m, -$CH_2CH_2$OTBDPS), 3.78 (1H, m, -CHNH-), 4.96 (1H, d, *J* = 8 Hz, -CHNH-), 7.36-7.46 (6H, m, -Si-Ph), 7.65-7.70 (4H, m, -Si-Ph). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 14.3, 19.2, 22.8, 26.1, 27.0, 28.6, 29.5, 29.77, 29.81, 29.83, 29.9, 32.1, 35.2, 36.5, 49.2, 61.5, 78.7, 127.8, 129.8, 133.6, 135.7, 155.7. HRMS (FAB, positive): calcd. For $C_{42}H_{71}NO_3NaSi$ $[M+Na]^+$, 688.5101; found, 688.5124.



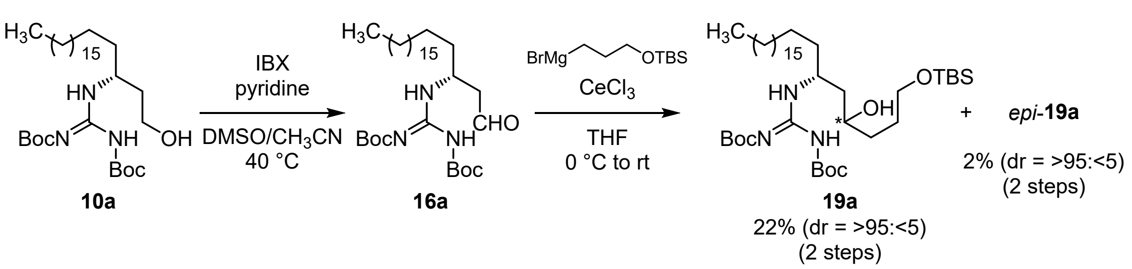
**$C_{18}$-guanidine 9a:** To a solution of $C_{18}$-amide **8a** (646 mg, 0.970 mmol) in $CH_2Cl_2$ (4.8 mL) was added TFA (4.8 mL) at 0 °C. After being stirred at room temperature for 30 min, the reaction mixture was diluted with toluene (10 mL), and then concentrated under reduced pressure to provide crude $C_{18}$-ammonium-TFA salt **S6** as a yellow oil, which was used for the next reaction without further purification. To a solution of crude C18-ammonium-TFA salt **S6**, diBoc-methylisothiourea (311 mg, 1.07 mmol), and $Et_3N$ (0.40 mL, 2.9 mmol) in DMF (9.7 mL) was added $HgCl_2$ (290 mg, 1.07 mmol) at 0 °C. After being stirred at room temperature for 10 min, the reaction mixture was diluted with EtOAc, and then filtered through a pad of Celite® (eluted with EtOAc). The filtrate was washed with $H_2O$ and brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 34/1) to afford $C_{18}$-guanidine **9a** (537 mg, 68% in 2 steps) as a colorless oil.

$[\alpha]_D^{25}$ −4.66 (*c* 1.16, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3327, 2925, 2854, 1718, 1637, 1335, 1157, 1115. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.88 (3H, t, $J$ = 7 Hz, $-(CH_2)_{16}CH_3$), 1.04 (9H, s, -Si$^t$Bu), 1.17-1.36 (32H, m, $-(CH_2)_{16}CH_3$), 1.36-1.57 (2H, m, $-CH_2(CH_2)_{16}CH_3$), 1.47 (18H, s, -O$^t$Bu), 1.72 (1H, m, $-CH_aH_bCH_2$OTBDPS), 1.82 (1H, m, $-CH_aH_bCH_2$OTBDPS), 3.71 (2H, t, $J$ = 7 Hz, $-CH_2CH_2$OTBDPS), 4.29 (1H, m, -C*H*NH-), 7.34-7.45 (6H, m, -Si-Ph), 7.64-7.69 (4H, m, -Si-Ph), 8.18 (1H, d, $J$ = 8 Hz, -CHN*H*-), 11.5 (1H, s, -N*H*Boc). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 14.3, 19.3, 22.8, 25.5, 27.0, 28.3, 28.5, 29.5, 29.7, 29.78, 29.81, 29.9, 32.1, 35.0, 37.2, 48.2, 61.2, 78.9, 82.9, 127.7, 127.8, 129.7, 133.9, 134.0, 135.7, 135.8, 153.4, 155.9, 164.1. HRMS (FAB, positive): calcd. For $C_{48}H_{82}N_3O_5Si$ $[M+H]^+$, 808.6024; found, 808.6043.



**$C_{18}$-alcohol 10a:** To a solution of $C_{18}$-guanidine **9a** (397 mg, 0.491 mmol) in dry THF (5.9 mL) was added TBAF (1.0 M solution in THF, 0.54 mL, 0.54 mmol) at room temperature. After being stirred at room temperature for 2.5 h, the reaction mixture was diluted with $CH_2Cl_2$ (5.9 mL), and then washed with $H_2O$ (12.8 mL). The aqueous layer was extracted with $CH_2Cl_2$ (12.8 mL). The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 12/1) to afford $C_{18}$-alchol **10a** (265 mg, 94%) as a white solid.

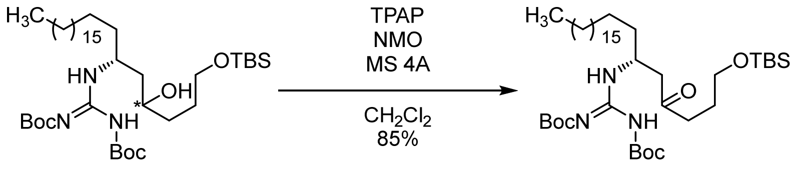
mp: 42-45 °C. $[\alpha]_D^{22}$ +1.01 (*c* 1.09, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3317, 2925, 2854, 1720, 1649, 1615, 1416, 1367, 1332, 1158, 1132. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.87 (3H, t, *J* = 7 Hz, $-(CH_2)_{16}CH_3$), 1.17-1.43 (33H, m, $-CH_aH_b(CH_2)_{16}CH_3$), 1.43-1.60 (2H, m, $-CH_aH_b(CH_2)_{16}CH_3$, $-CH_aH_bCH_2OH$), 1.46 (9H, s, $-O^tBu$), 1.50 (9H, s, $-O^tBu$), 1.86 (1H, m, $-CH_aH_bCH_2OH$), 3.47-3.63 (2H, m, $-CH_2CH_2OH$), 4.15 (1H, m, -C*H*NH-), 5.26 (1H, br s, $-CH_2CH_2OH$), 8.16 (1H, d, *J* = 8 Hz, -CHN*H*-), 11.4 (1H, s, -N*H*Boc). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 14.3, 22.8, 26.3, 28.2, 28.3, 29.5, 29.56, 29.58, 29.64, 29.77, 29.80, 29.84, 32.1, 35.9, 39.4, 48.1, 58.0, 79.6, 83.6, 153.4, 156.9, 163.0. HRMS (ESI, positive): calcd. For $C_{32}H_{63}N_3O_5Na$ $[M+Na]^+$, 592.4660; found, 592.4663.



**$C_{18}$-alcohol 19a:** To a solution of $C_{18}$-alcohol **10a** (151 mg, 0.265 mmol) and pyridine (38 μL, 0.48 mmol) in DMSO/$CH_3CN$ (2.6/1, 5.4 mL) was added IBX (134 mg, 0.477

mmol) at 40 °C. After being stirred at 40 °C for 30 min, the reaction was quenched with cooled H$_2$O (4 mL). The reaction mixture was filtered through a pad of Celite$^{®}$ (eluted with EtOAc). The filtrate was partitioned, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with H$_2$O and brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. High polar compounds were removed by neutral silica gel flash column chromatography (hexane/EtOAc = 3/1) to afford C$_{18}$-aldehyde **16a** as a colorless oil, which was used for the next reaction without further purification. To a suspension of dry CeCl$_3$ (211 mg, 0.856 mmol) in dry THF (3 mL) were added TBSOC$_3$H$_6$MgBr (0.34 M solution in THF, 2.50 mL, 0.856 mmol) and a solution of C$_{18}$-aldehyde **16a** in dry THF (3 mL) was added at 0 °C. And then the reaction mixture was allowed to warm to room temperature slowly. After being stirred for 5 h, the reaction was quenched with a saturated aqueous solution of NH$_4$Cl (10 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 10/1) to afford C$_{18}$-alcohol **19a** (44.0 mg, 22% in 2 steps, dr = >95:<5) as a colorless oil and *epi*-C$_{18}$-alcohol *epi*-**19a** (4.0 mg, 2% in 2 steps, dr = >95:<5) as a colorless oil.

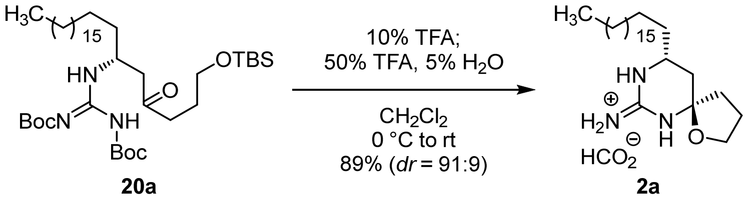
**19a:** $[\alpha]_D^{22}$ −2.11 (*c* 2.14, CHCl$_3$). IR (film): $\nu_{\mathrm{max}}$ (cm$^{-1}$) 3318, 2926, 2854, 1721, 1649, 1615, 1417, 1367, 1334, 1157, 1126. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 0.03 (6H, s, -Si(C$H_3$)$_2$), 0.86-0.90 (3H, m, -(CH$_2$)$_{16}$C$H_3$), 0.87 (9H, s, -Si$^t$Bu), 1.20-1.40 (34H, m, -C$H_2$(C$H_2$)$_{16}$CH$_3$), 1.40-1.73 (6H, m, , -C$H_2$CH(C$H_2$)$_2$CH$_2$OTBS), 1.45 (9H, s, -O$^t$Bu), 1.50 (9H, s, -O$^t$Bu), 3.49 (1H, m, -CH$_2$C$H$(CH$_2$)$_3$OTBS), 3.54-3.67 (2H, m, -(CH$_2$)$_2$C$H_2$OTBS), 4.20 (1H, m, -C$H$NH-), 5.42 (1H, d, $J$ = 3 Hz, -CHO$H$), 8.15 (1H, d, $J$ = 9 Hz, -CHN$H$-), 11.4 (1H, s, -N$H$Boc). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) −5.2, 14.3, 18.5, 22.8, 26.1, 26.2, 28.2, 28.3, 29.5, 29.56, 29.61, 29.64, 29.77, 29.79, 29.83, 32.1, 33.1, 36.0, 44.8, 48.6, 63.5, 66.4, 79.4, 83.5, 153.3, 156.8, 163.1. HRMS (FAB, positive): calcd. For C$_{41}$H$_{84}$N$_3$O$_6$Si [M+H]$^+$, 742.6129; found, 742.6119.



**19a** **20a**

**C18-ketone 20a:** To a solution of C18-alcohol **19a** (40 mg, 0.054 mmol) in dry $CH_2Cl_2$ (1.2 mL) were added MS 4A (27 mg), NMO (9.5 mg, 0.081 mmol), and TPAP (4.6 mg, 0.013 mmol) at room temperature. After being stirred at room temperature for 1.5 h, the reaction mixture was diluted with $CH_2Cl_2$, and then filtered through a cotton pad (eluted with $CH_2Cl_2$). The filtrate was washed with brine. The aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (toluene/EtOAc = 5/1) to afford C18-ketone **20a** (34 mg, 85%) as a colorless oil.

$[\alpha]_D^{22}$ +8.23 (*c* 0.71, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3327, 2925, 2854, 1717, 1637, 1559, 1457, 1418, 1364, 1254, 1157, 1123. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 0.02 (6H, s, -Si(C*H*$_3$)$_2$), 0.85-0.90 (3H, m, -(CH$_2$)$_{16}$C*H*$_3$), 0.87 (9H, s, -Si$^t$Bu), 1.20-1.40 (32H, m, -(C*H*$_2$)$_{16}$CH$_3$), 1.48 (9H, s, -O$^t$Bu), 1.49 (9H, s, -O$^t$Bu), 1.52-1.60 (2H, m, -C*H*$_2$(CH$_2$)$_{16}$CH$_3$), 1.72-1.82 (2H, m, -C*H*$_2$CH$_2$OTBS), 2.43-2.72 (4H, m, -C*H*$_2$C(=O)C*H*$_2$(CH$_2$)$_2$OTBS), 3.60 (2H, t, *J* = 6 Hz, -CH$_2$C*H*$_2$OTBS), 4.43 (1H, m, -C*H*NH-), 8.55 (1H, d, *J* = 8 Hz, -CHN*H*-), 11.5 (1H, s, -N*H*Boc). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) −5.2, 14.3, 18.4, 22.8, 26.1, 26.2, 26.8, 28.2, 28.5, 29.5, 29.59, 29.64, 29.7, 29.8, 29.9, 32.1, 34.2, 39.8, 46.7, 47.4, 62.3, 79.1, 83.0, 153.2, 155.8, 163.9, 209.4. HRMS (FAB, positive): calcd. For $C_{41}H_{82}N_3O_6Si$ $[M+H]^+$, 740.5973; found, 740.5988.



**$C_{18}$-decarboxylate analogue 2a:** To a solution of $C_{18}$-ketone **20a** (15.4 mg, 20.8 μmol) in $CH_2Cl_2$ (8.1 mL) was added TFA (0.9 mL) at 0 °C. After being stirred at room temperature for 2.5 h, TFA/$H_2O$ (9/1, 1 mL) was added. After being stirred at room temperature for 45 min, the reaction mixture was diluted with toluene, and then concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography ($CH_2Cl_2$/MeOH/$HCO_2H$/$H_2O$ = 95/5/1/0 to 88/12/1/1) to afford $C_{18}$-decarboxylate analogue **2a** (8.9 mg, 89%) as a white solid.

mp: 71-73 °C. $[\alpha]_D^{22}$ +44.3 (*c* 0.12, $CHCl_3$). IR (film): $\nu_{max}$ ($cm^{-1}$) 3247, 2918, 2850, 1684, 1616, 1263, 1203, 1135, 1022. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ (ppm) 0.90 (3H, t, $J$ = 7 Hz, $-(CH_2)_{16}CH_3$), 1.23-1.50 (32H, m, $-(CH_2)_{16}CH_3$), 1.51-1.65 (2H, m, $-CH_2(CH_2)_{16}CH_3$), 1.69 (1H, t, $J$ = 13 Hz, $-CH_aH_bCO-$), 2.01-2.15 (5H, m, $-CH_aH_bCO-$, $-(CH_2)_2CH_2O-$), 3.62 (1H, m, $-CHNH-$), 3.91 (1H, m, $-(CH_2)_2CH_aH_bO-$), 3.97 (1H, m, $-(CH_2)_2CH_aH_bO-$). $^{13}C$ NMR (100 MHz, $CD_3OD$): $\delta$ (ppm) 14.4, 23.7, 25.7, 26.0, 30.5, 30.56, 30.60, 30.7, 30.8, 33.1, 35.6, 37.6, 38.1, 68.7, 89.6, 155.3. HRMS (ESI, positive): calcd. For $C_{25}H_{50}N_3O$ $[M]^+$, 408.3948; found, 408.3948.

## References

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1 Jörres, M.; Schiffers, I.; Atodiresei, I.; Bolm, C. *Org. Lett.* **2012**, *14*, 4518-4521.
2 Darses, S.; Michaud, G.; Genêt, J. P. *Eur. J. Org. Chem.* **1999**, 1875-1883.

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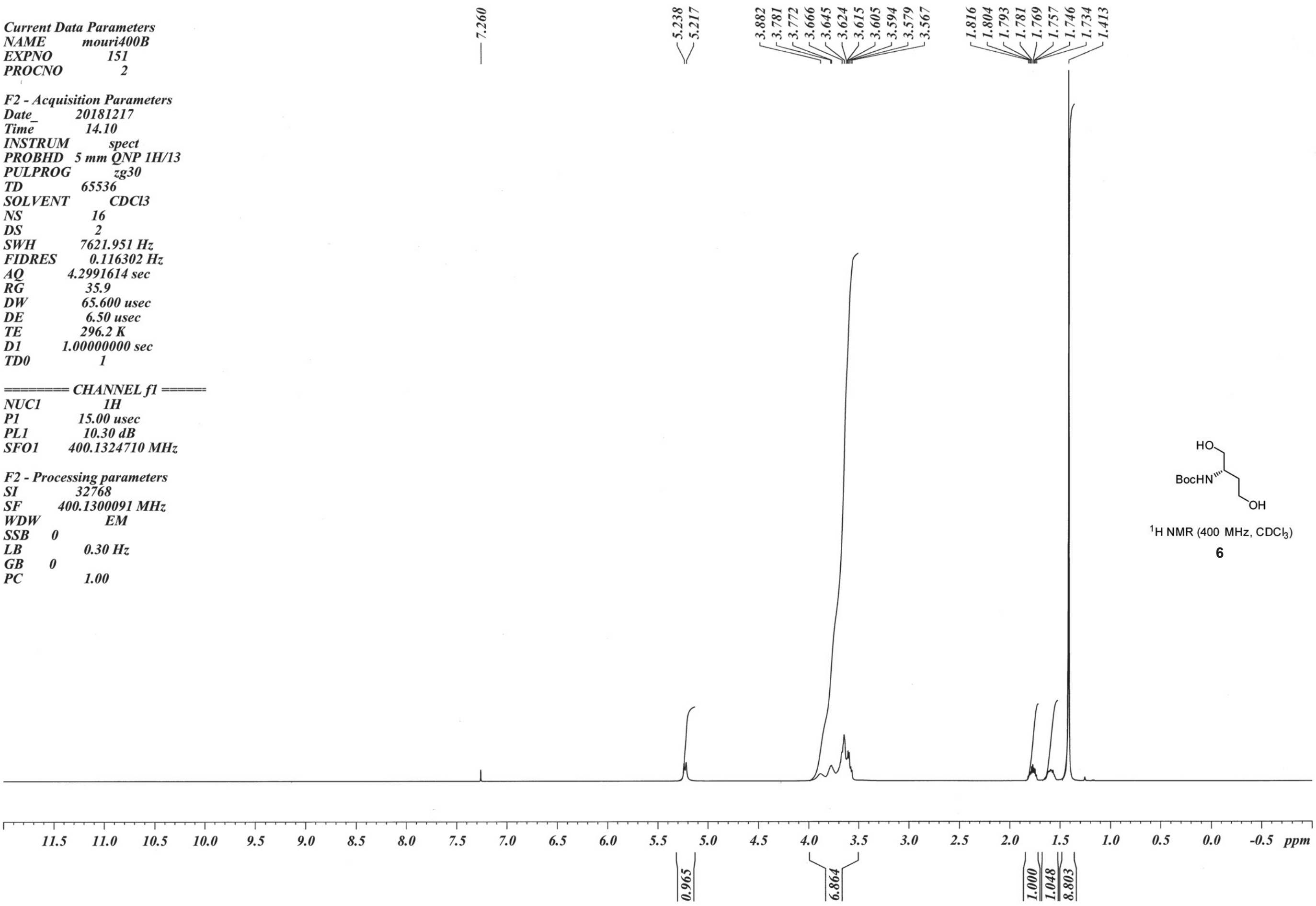

$^1$H NMR (400 MHz, CDCl$_3$)

**6**

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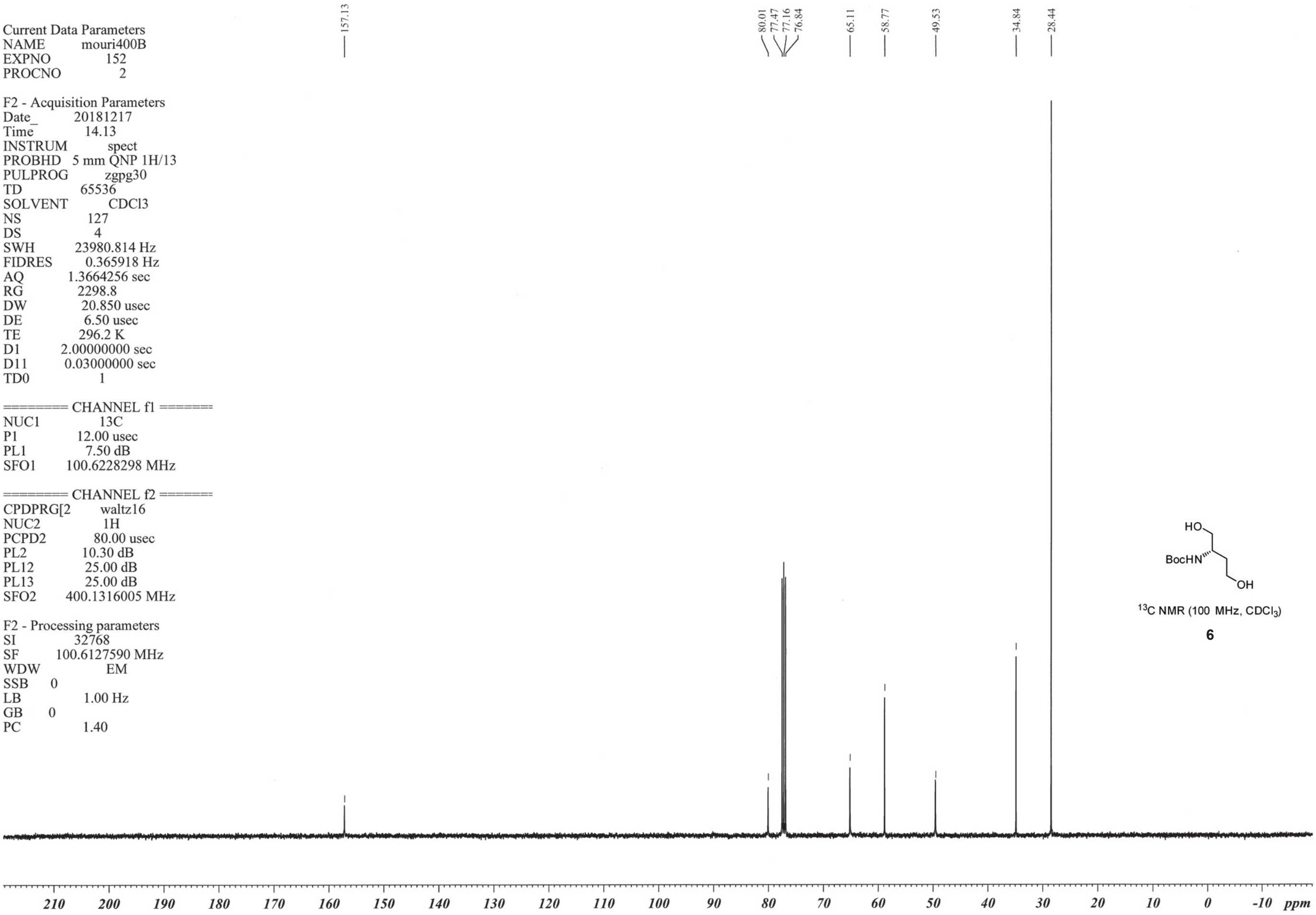

$^{13}$C NMR (100 MHz, CDCl$_3$)

**6**

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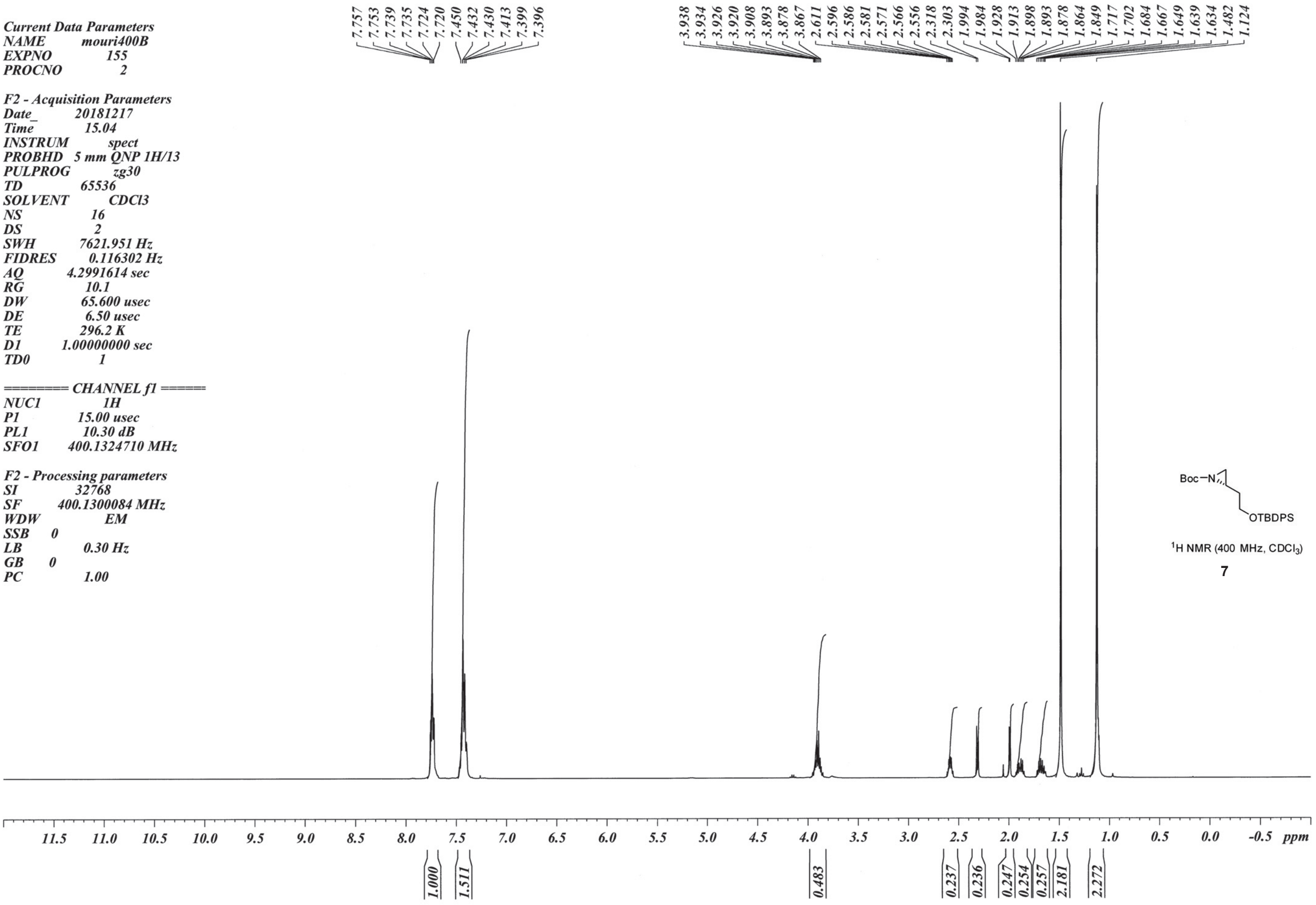

$^1$H NMR (400 MHz, CDCl$_3$)

**7**

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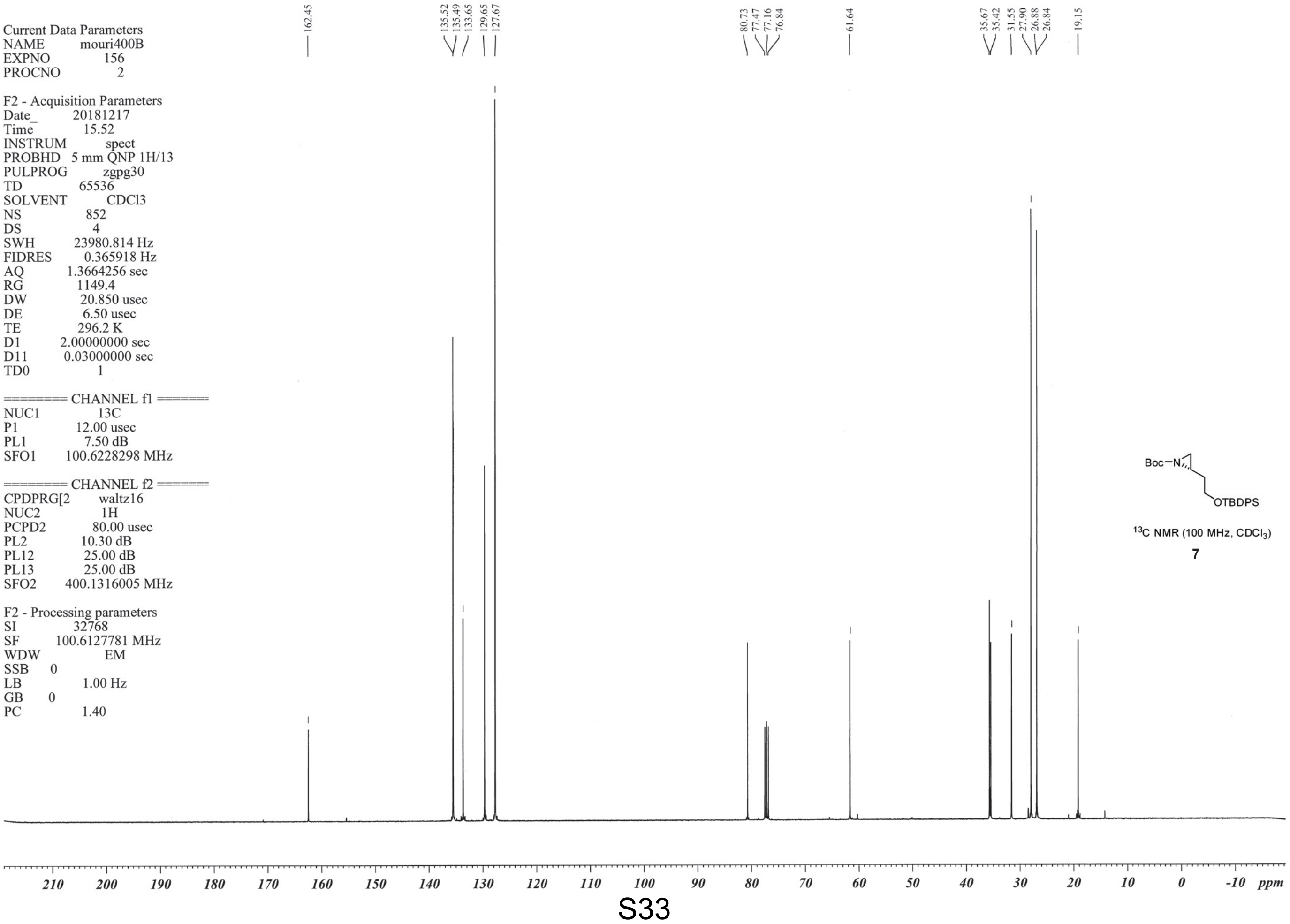
PC 1.40



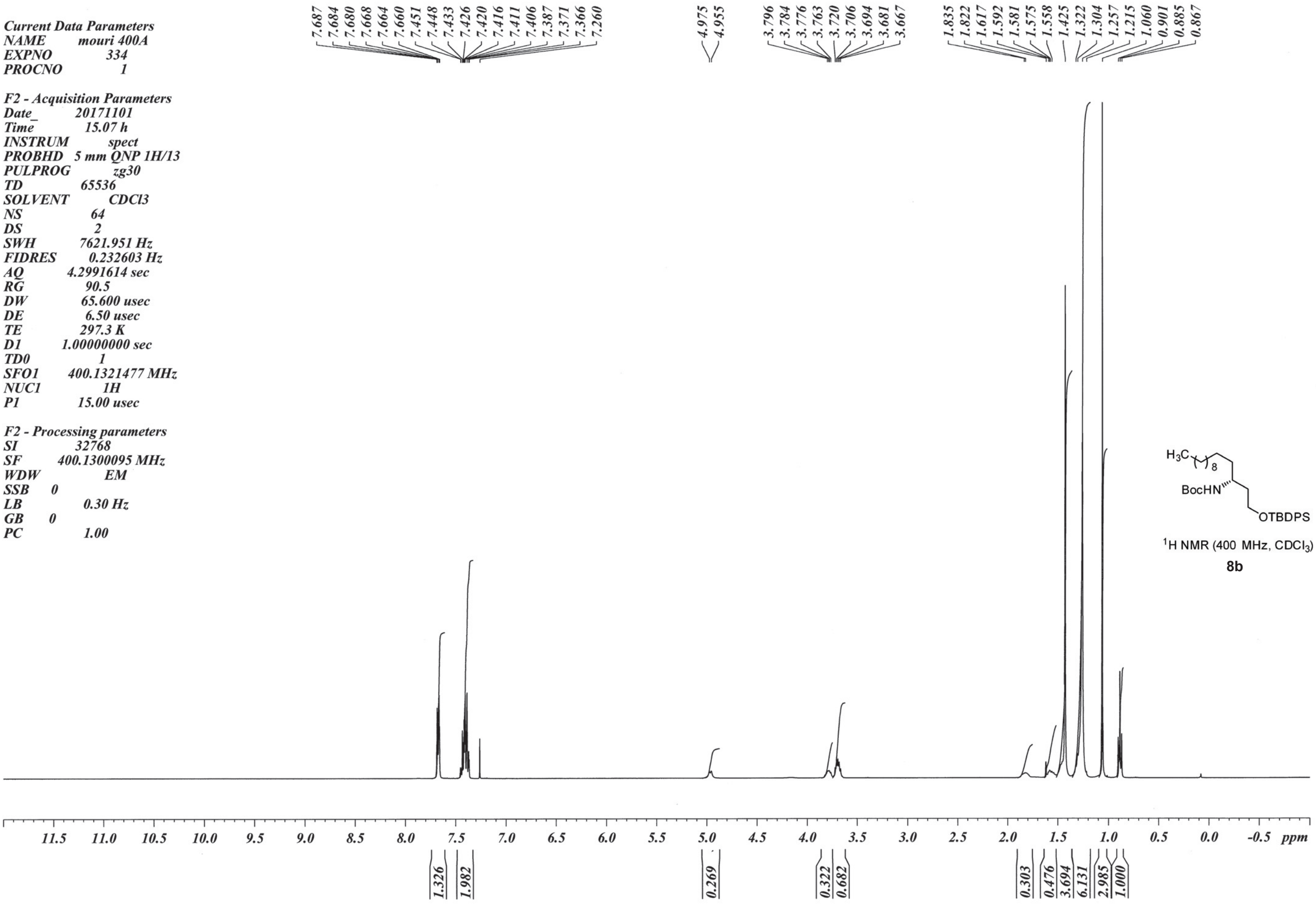
$^{13}$C NMR (100 MHz, CDCl$_3$)

**7**

***Current Data Parameters***
***NAME mouri 400A***
***EXPNO 334***
***PROCNO 1***

***F2 - Acquisition Parameters***
***Date_ 20171101***
***Time 15.07 h***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT CDCl3***
***NS 64***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.232603 Hz***
***AQ 4.2991614 sec***
***RG 90.5***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 297.3 K***
***D1 1.00000000 sec***
***TD0 1***
***SFO1 400.1321477 MHz***
***NUC1 1H***
***P1 15.00 usec***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300095 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***



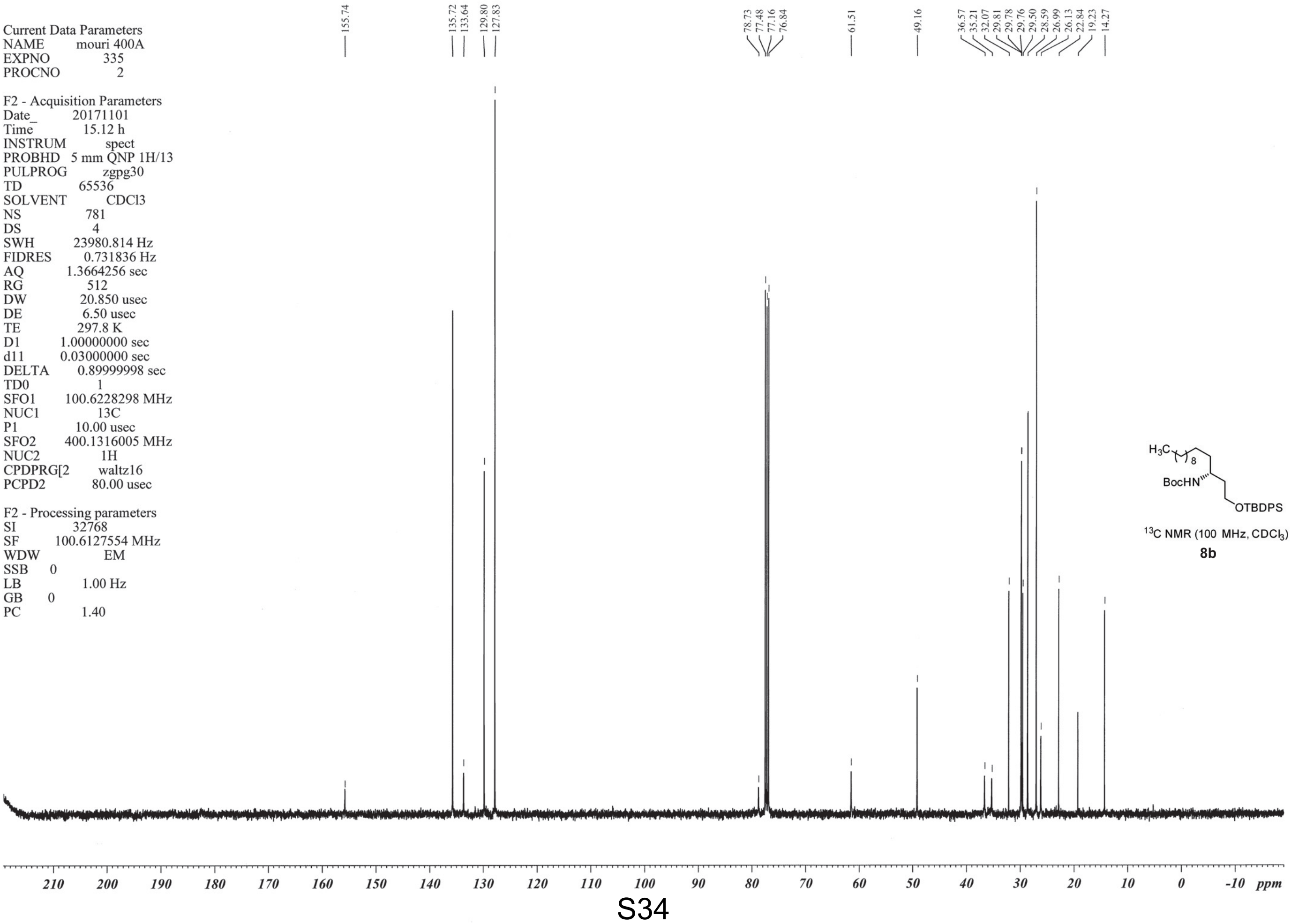
$^1$H NMR (400 MHz, CDCl$_3$)

**8b**

Current Data Parameters
NAME mouri 400A
EXPNO 335
PROCNO 2

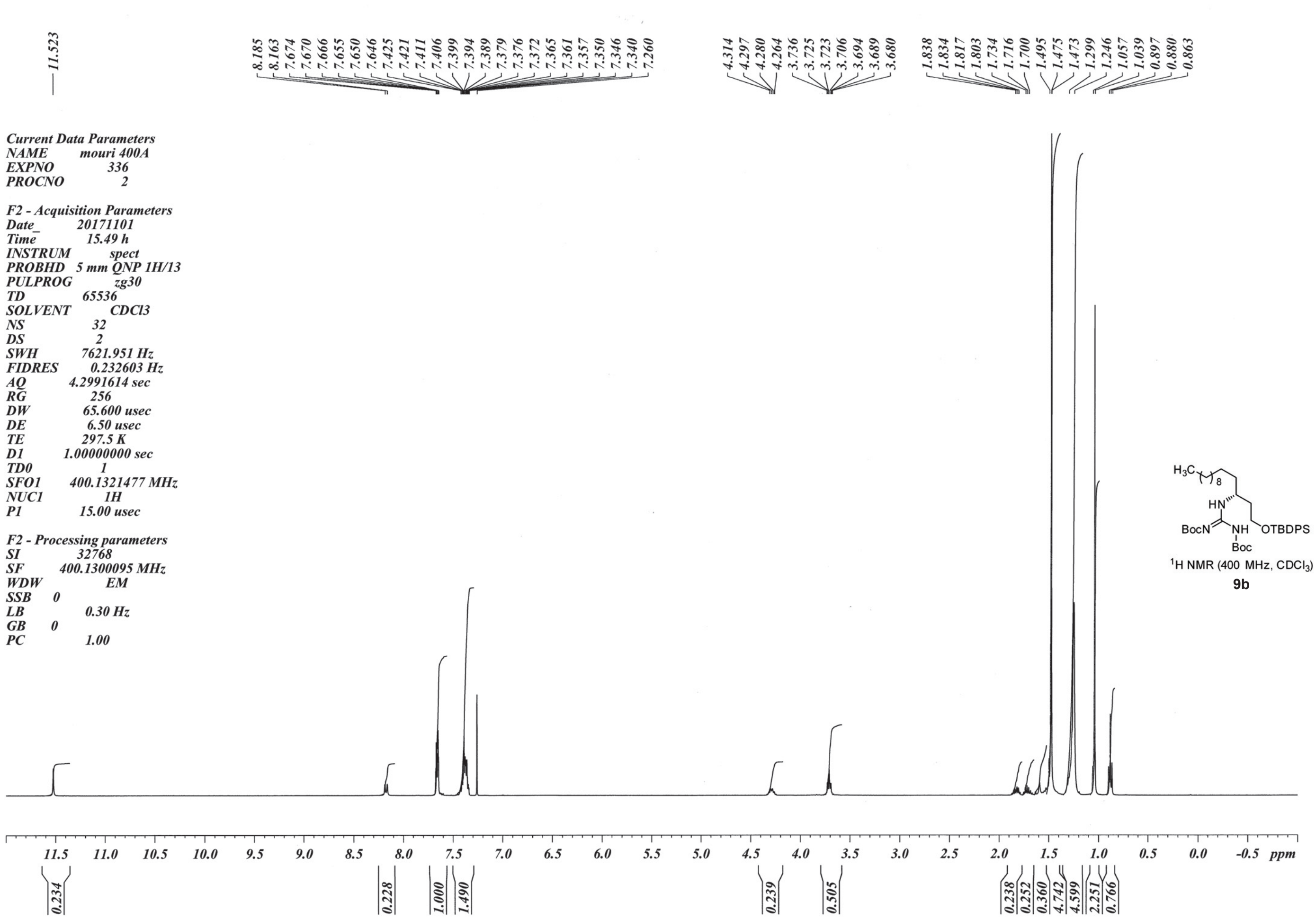
F2 - Acquisition Parameters
Date_ 20171101
Time 15.12 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 781
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 512
DW 20.850 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6127554 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



$^{13}$C NMR (100 MHz, CDCl$_3$)

**8b**

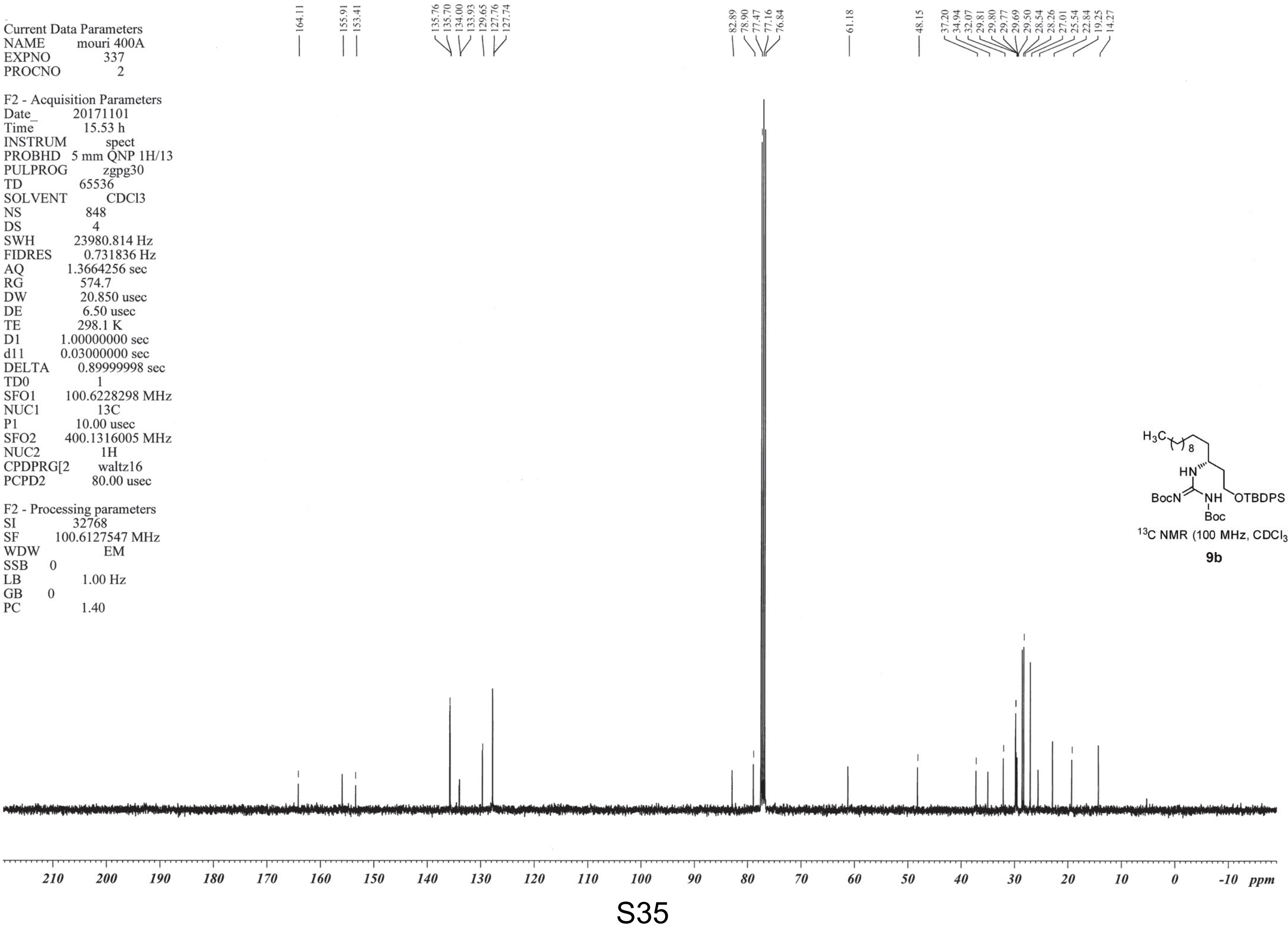


*Current Data Parameters*
*NAME mouri 400A*
*EXPNO 336*
*PROCNO 2*

*F2 - Acquisition Parameters*
*Date_ 20171101*
*Time 15.49 h*
*INSTRUM spect*
*PROBHD 5 mm QNP 1H/13*
*PULPROG zg30*
*TD 65536*
*SOLVENT CDCl3*
*NS 32*
*DS 2*
*SWH 7621.951 Hz*
*FIDRES 0.232603 Hz*
*AQ 4.2991614 sec*
*RG 256*
*DW 65.600 usec*
*DE 6.50 usec*
*TE 297.5 K*
*D1 1.00000000 sec*
*TD0 1*
*SFO1 400.1321477 MHz*
*NUC1 1H*
*P1 15.00 usec*

*F2 - Processing parameters*
*SI 32768*
*SF 400.1300095 MHz*
*WDW EM*
*SSB 0*
*LB 0.30 Hz*
*GB 0*
*PC 1.00*

$^1$H NMR (400 MHz, CDCl$_3$)
**9b**

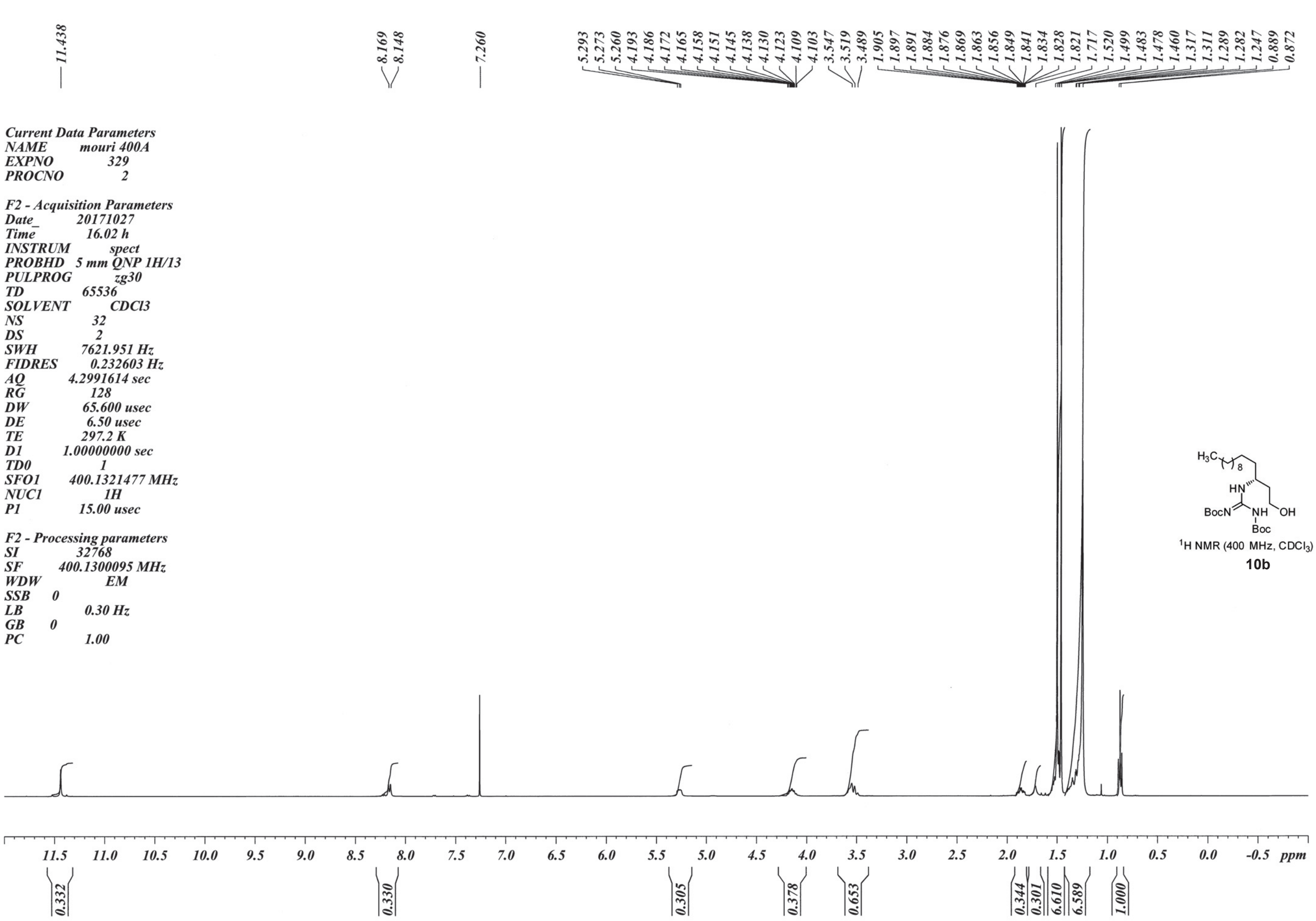


Current Data Parameters
NAME mouri 400A
EXPNO 337
PROCNO 2

F2 - Acquisition Parameters
Date_ 20171101
Time 15.53 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 848
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 574.7
DW 20.850 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6127547 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

$^{13}$C NMR (100 MHz, CDCl$_3$)
**9b**

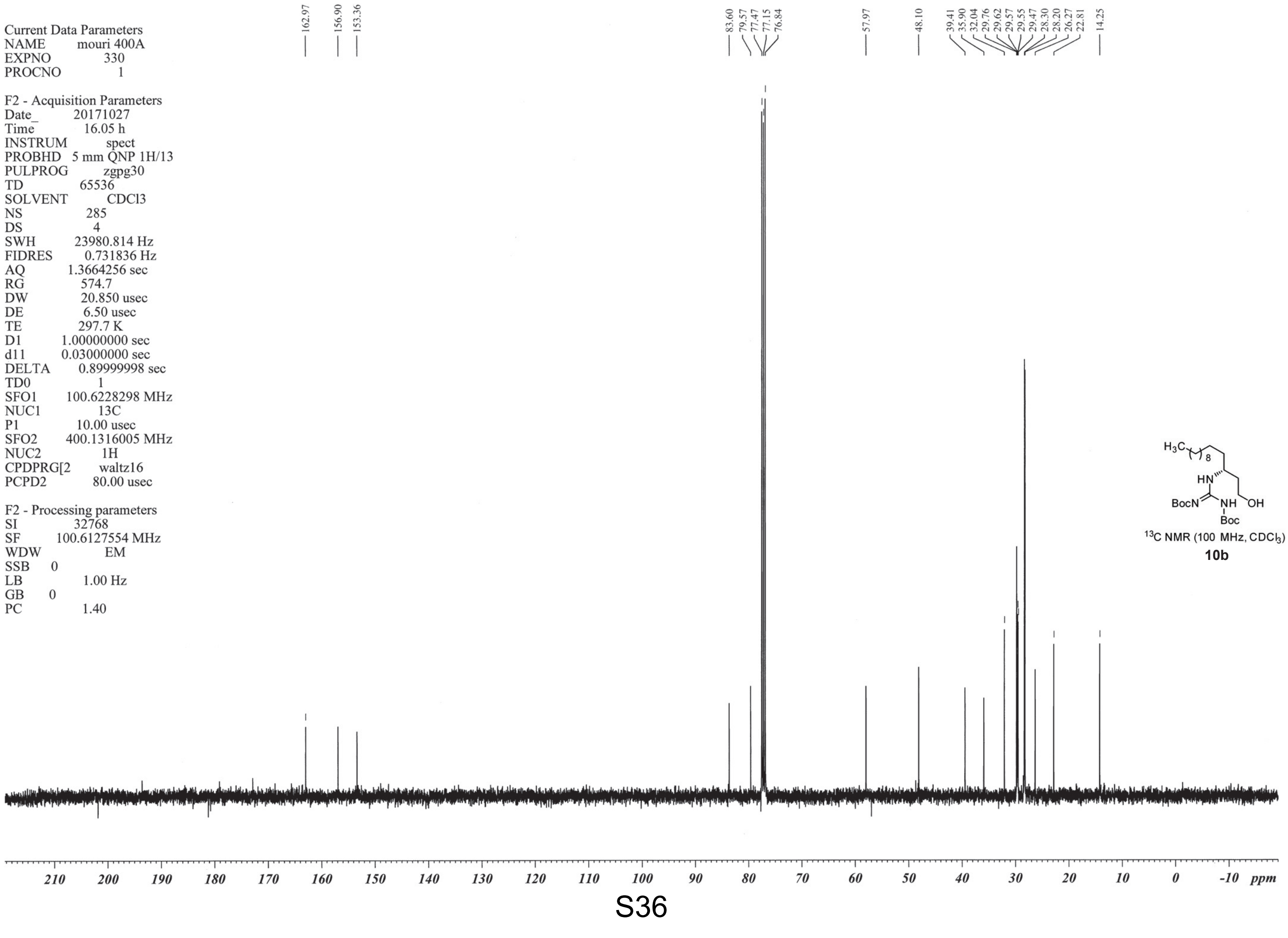


*Current Data Parameters*
*NAME mouri 400A*
*EXPNO 329*
*PROCNO 2*

*F2 - Acquisition Parameters*
*Date_ 20171027*
*Time 16.02 h*
*INSTRUM spect*
*PROBHD 5 mm QNP 1H/13*
*PULPROG zg30*
*TD 65536*
*SOLVENT CDCl3*
*NS 32*
*DS 2*
*SWH 7621.951 Hz*
*FIDRES 0.232603 Hz*
*AQ 4.2991614 sec*
*RG 128*
*DW 65.600 usec*
*DE 6.50 usec*
*TE 297.2 K*
*D1 1.00000000 sec*
*TD0 1*
*SFO1 400.1321477 MHz*
*NUC1 1H*
*P1 15.00 usec*

*F2 - Processing parameters*
*SI 32768*
*SF 400.1300095 MHz*
*WDW EM*
*SSB 0*
*LB 0.30 Hz*
*GB 0*
*PC 1.00*

$^1H$ NMR (400 MHz, $CDCl_3$)
**10b**

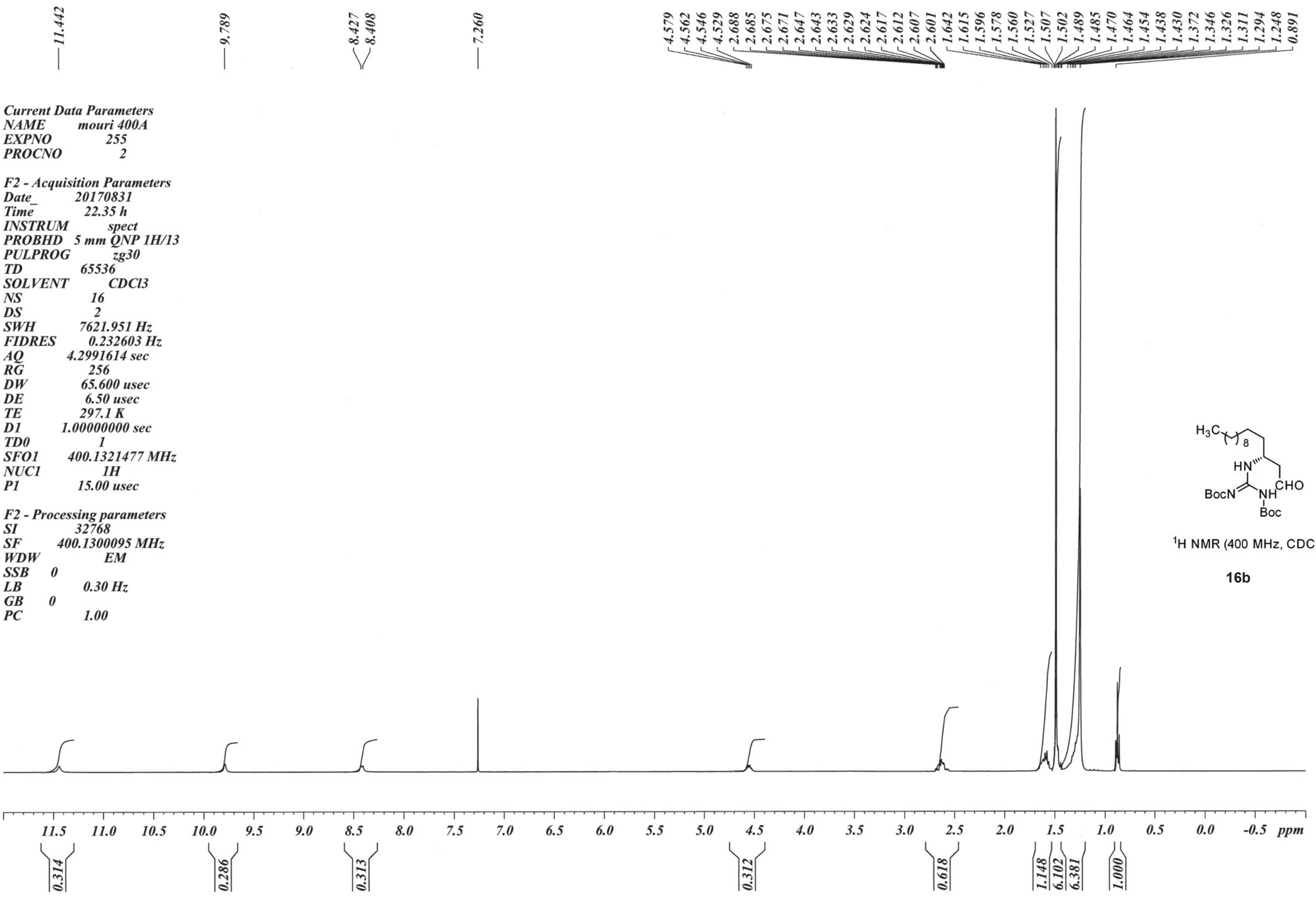


Current Data Parameters
NAME mouri 400A
EXPNO 330
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171027
Time 16.05 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 285
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 574.7
DW 20.850 usec
DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6127554 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

$^{13}C$ NMR (100 MHz, $CDCl_3$)
**10b**



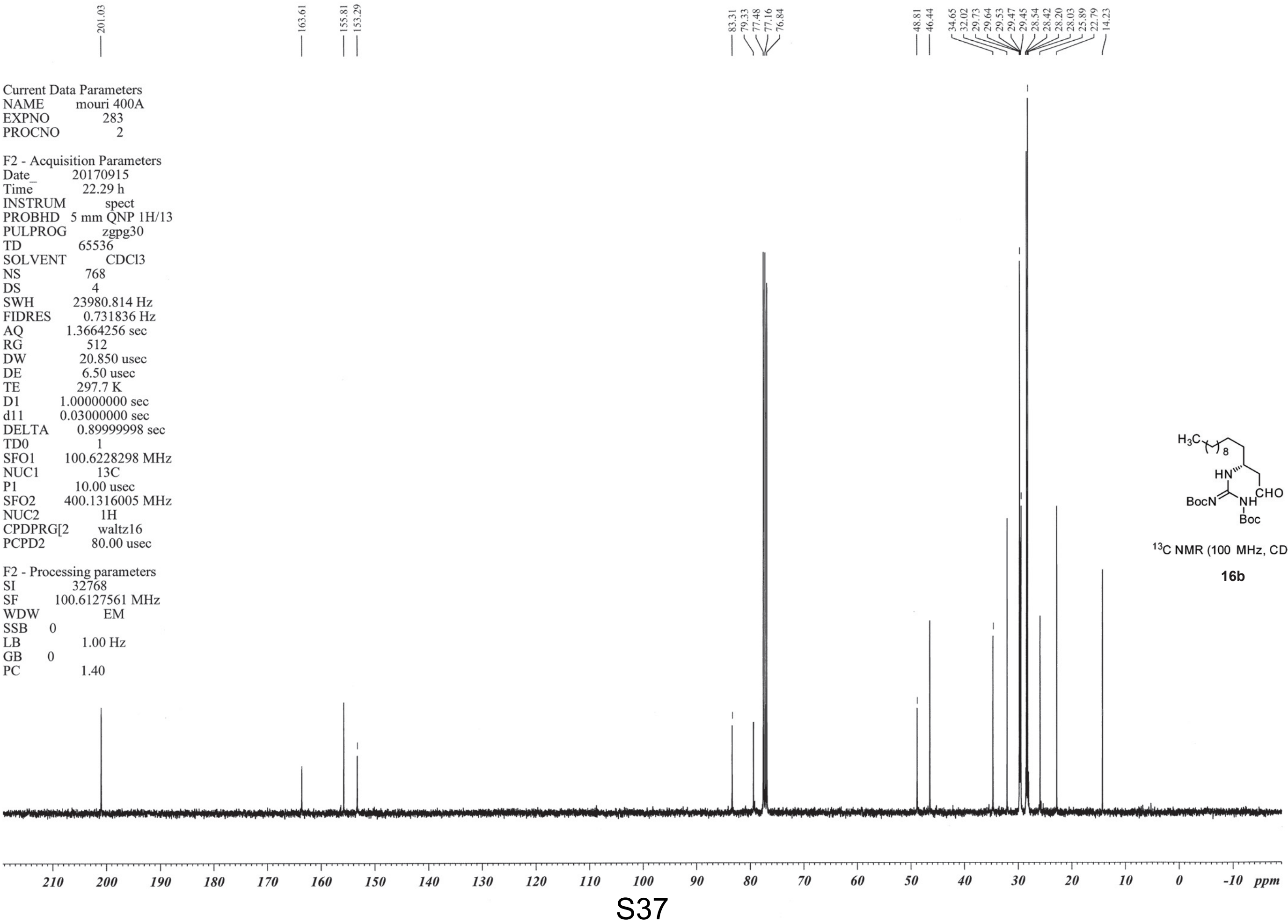
***Current Data Parameters***
*NAME mouri 400A*
*EXPNO 255*
*PROCNO 2*

***F2 - Acquisition Parameters***
*Date_ 20170831*
*Time 22.35 h*
*INSTRUM spect*
*PROBHD 5 mm QNP 1H/13*
*PULPROG zg30*
*TD 65536*
*SOLVENT CDCl3*
*NS 16*
*DS 2*
*SWH 7621.951 Hz*
*FIDRES 0.232603 Hz*
*AQ 4.2991614 sec*
*RG 256*
*DW 65.600 usec*
*DE 6.50 usec*
*TE 297.1 K*
*D1 1.00000000 sec*
*TD0 1*
*SFO1 400.1321477 MHz*
*NUC1 1H*
*P1 15.00 usec*

***F2 - Processing parameters***
*SI 32768*
*SF 400.1300095 MHz*
*WDW EM*
*SSB 0*
*LB 0.30 Hz*
*GB 0*
*PC 1.00*

$^1$H NMR (400 MHz, CDCl$_3$)

**16b**



Current Data Parameters
NAME mouri 400A
EXPNO 283
PROCNO 2

F2 - Acquisition Parameters
Date_ 20170915
Time 22.29 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 768
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 512
DW 20.850 usec
DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6127561 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

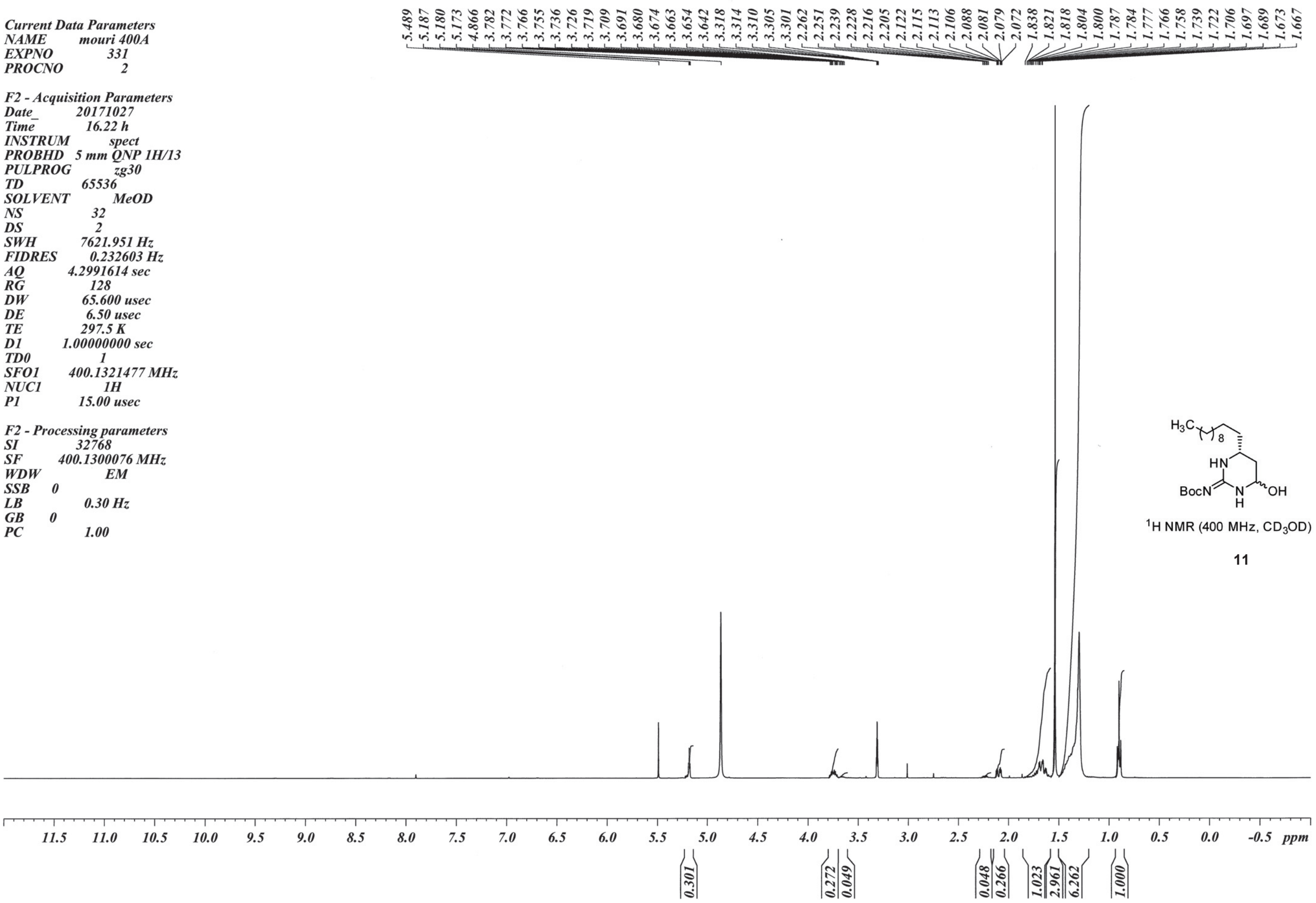
$^{13}$C NMR (100 MHz, CDCl$_3$)

**16b**

***Current Data Parameters***
***NAME mouri 400A***
***EXPNO 331***
***PROCNO 2***

***F2 - Acquisition Parameters***
***Date_ 20171027***
***Time 16.22 h***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT MeOD***
***NS 32***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.232603 Hz***
***AQ 4.2991614 sec***
***RG 128***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 297.5 K***
***D1 1.00000000 sec***
***TD0 1***
***SFO1 400.1321477 MHz***
***NUC1 1H***
***P1 15.00 usec***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300076 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***



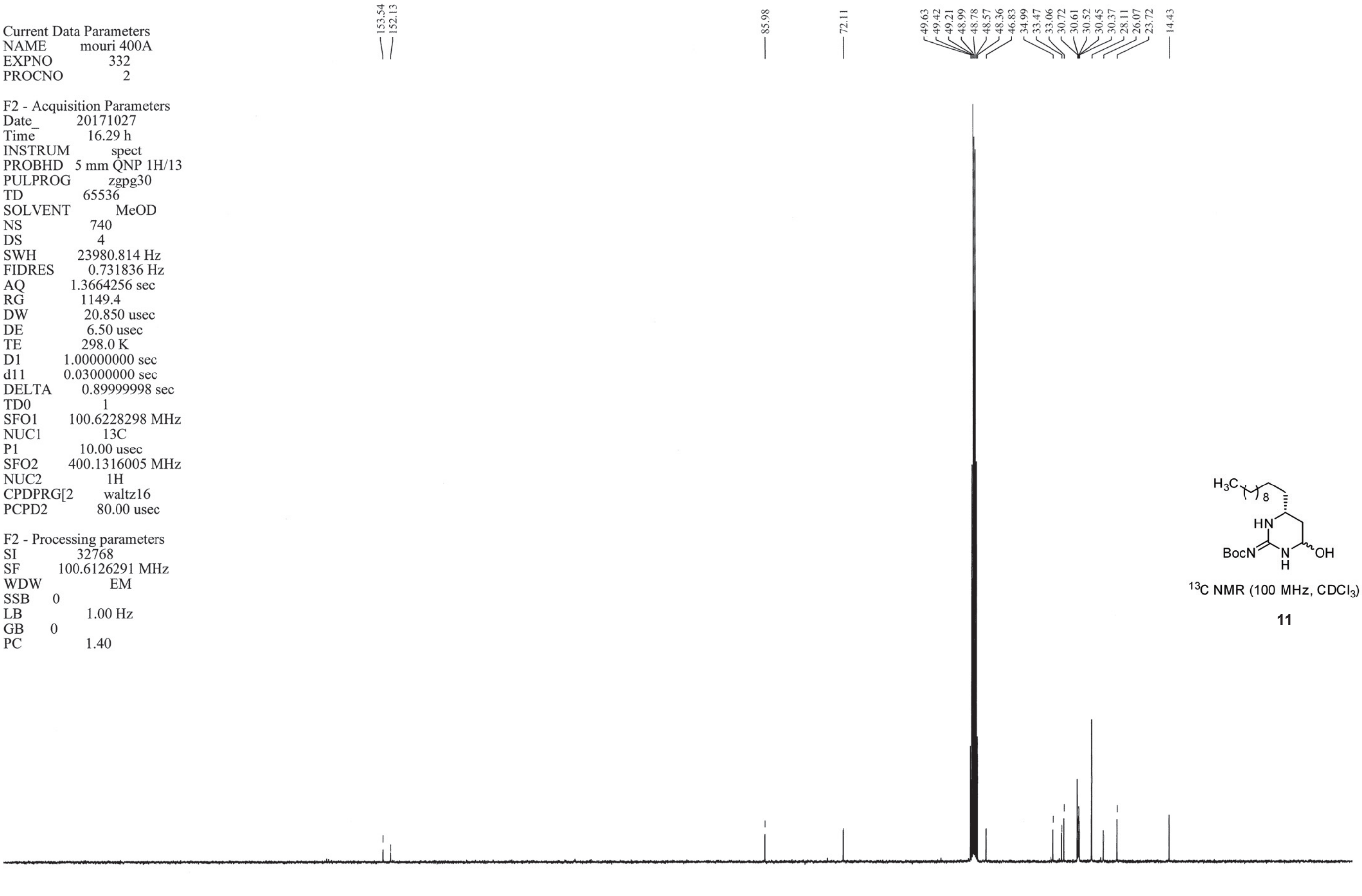
$^1$H NMR (400 MHz, CD$_3$OD)

**11**

Current Data Parameters
NAME mouri 400A
EXPNO 332
PROCNO 2

F2 - Acquisition Parameters
Date_ 20171027
Time 16.29 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 740
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 1149.4
DW 20.850 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6126291 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



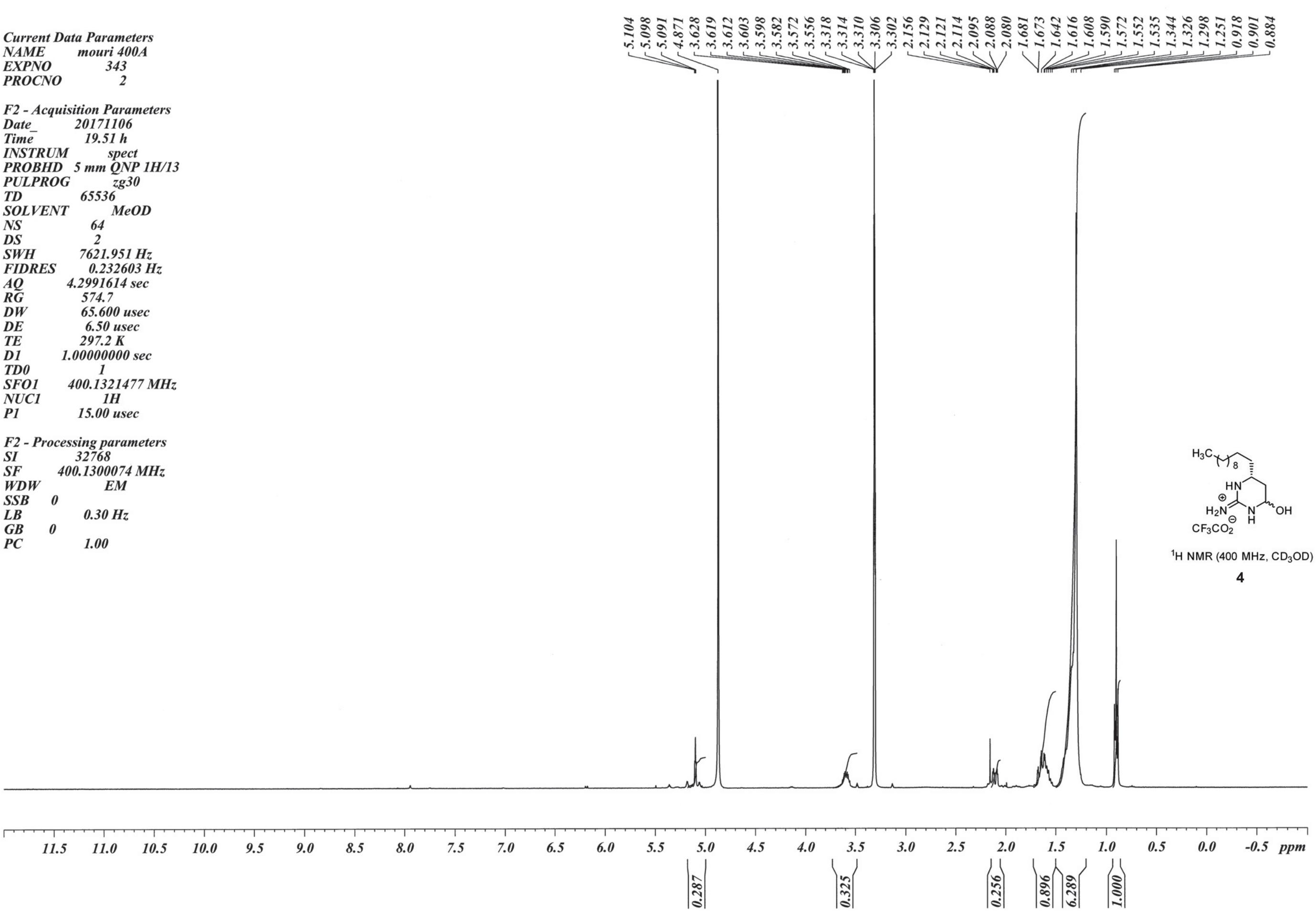
$^{13}$C NMR (100 MHz, CDCl$_3$)

**11**

***Current Data Parameters***
***NAME mouri 400A***
***EXPNO 343***
***PROCNO 2***

***F2 - Acquisition Parameters***
***Date_ 20171106***
***Time 19.51 h***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT MeOD***
***NS 64***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.232603 Hz***
***AQ 4.2991614 sec***
***RG 574.7***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 297.2 K***
***D1 1.00000000 sec***
***TD0 1***
***SFO1 400.1321477 MHz***
***NUC1 1H***
***P1 15.00 usec***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300074 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***



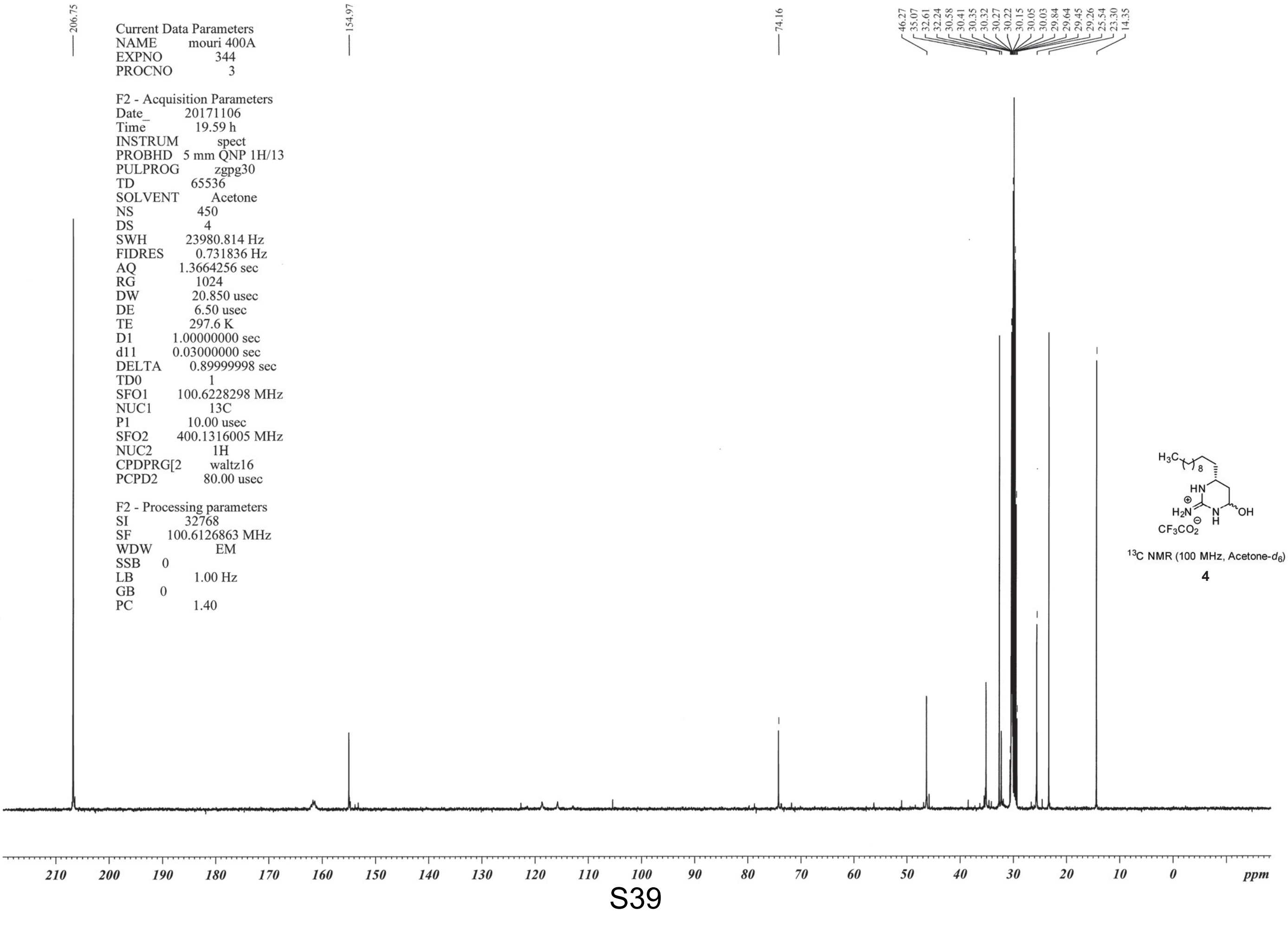
$^{1}$H NMR (400 MHz, CD$_3$OD)

**4**

Current Data Parameters
NAME mouri 400A
EXPNO 344
PROCNO 3

F2 - Acquisition Parameters
Date_ 20171106
Time 19.59 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 450
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 1024
DW 20.850 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

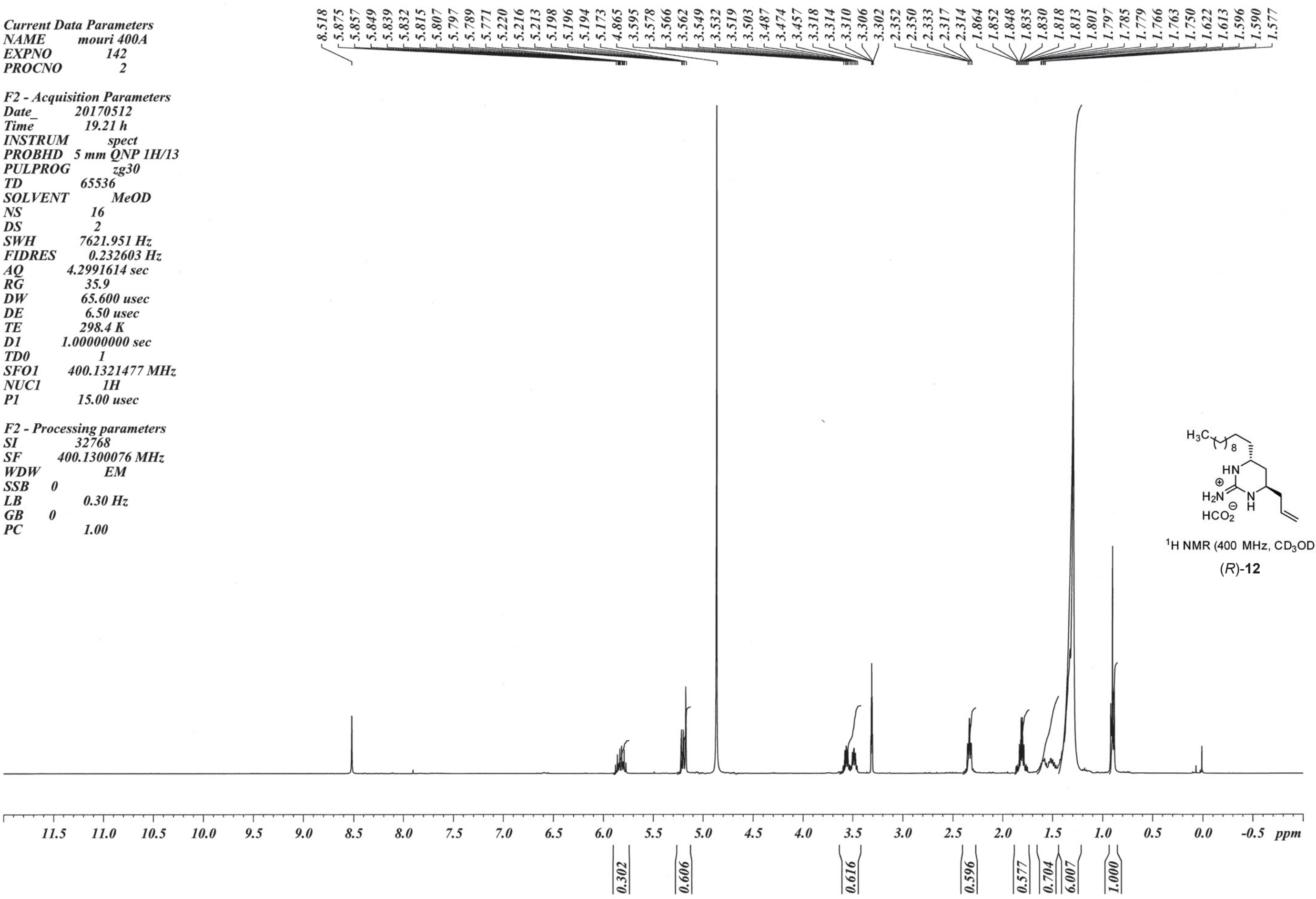
F2 - Processing parameters
SI 32768
SF 100.6126863 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



$^{13}$C NMR (100 MHz, Acetone-$d_6$)

**4**

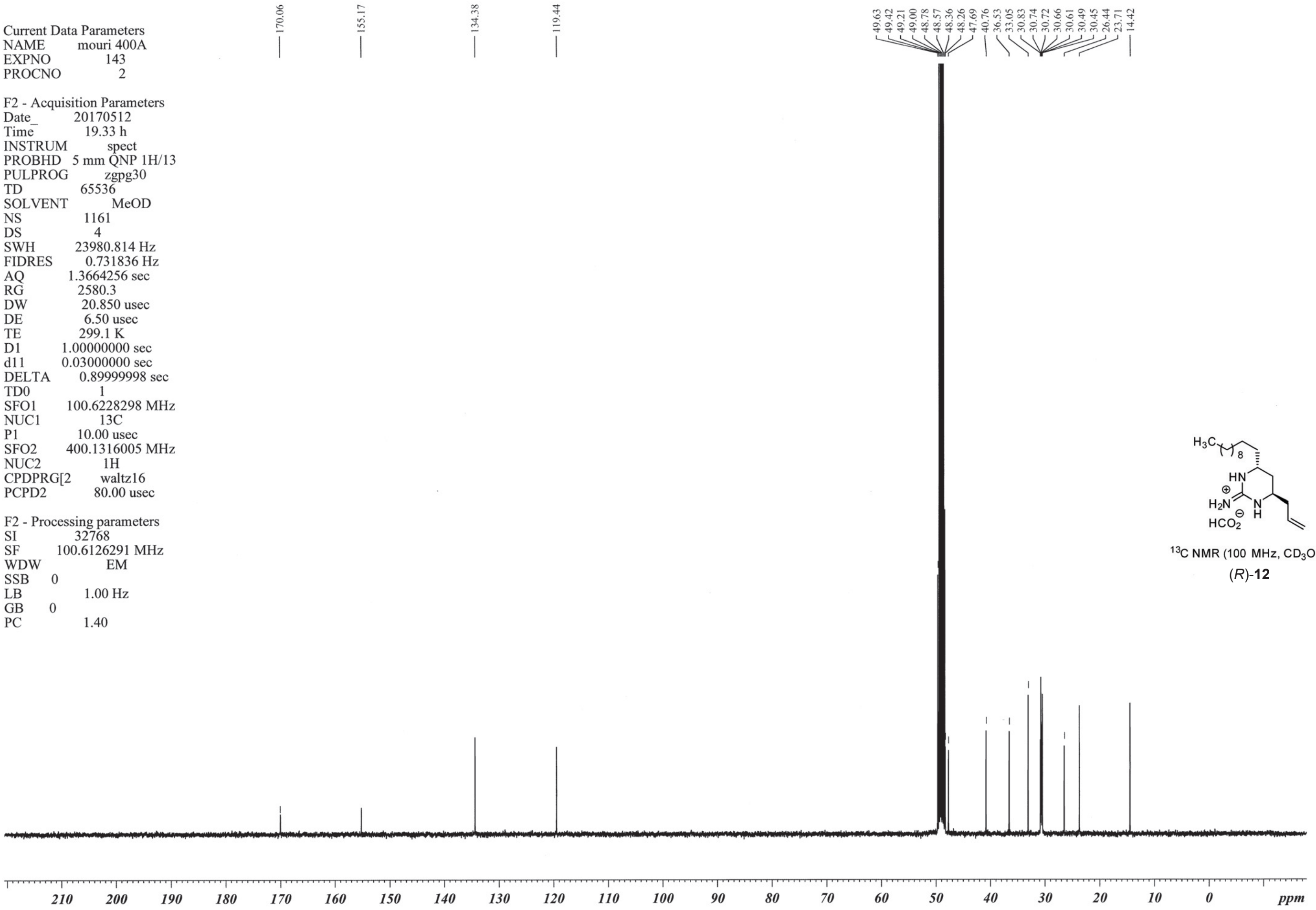
```
Current Data Parameters
NAME        mouri 400A
EXPNO              142
PROCNO               2

F2 - Acquisition Parameters
Date_        20170512
Time           19.21 h
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG           zg30
TD            65536
SOLVENT           MeOD
NS               16
DS                2
SWH         7621.951 Hz
FIDRES      0.232603 Hz
AQ        4.2991614 sec
RG             35.9
DW           65.600 usec
DE             6.50 usec
TE            298.4 K
D1       1.00000000 sec
TD0               1
SFO1     400.1321477 MHz
NUC1             1H
P1            15.00 usec

F2 - Processing parameters
SI            32768
SF       400.1300076 MHz
WDW              EM
SSB      0
LB             0.30 Hz
GB       0
PC             1.00
```



$^1$H NMR (400 MHz, $CD_3OD$)

(*R*)-**12**

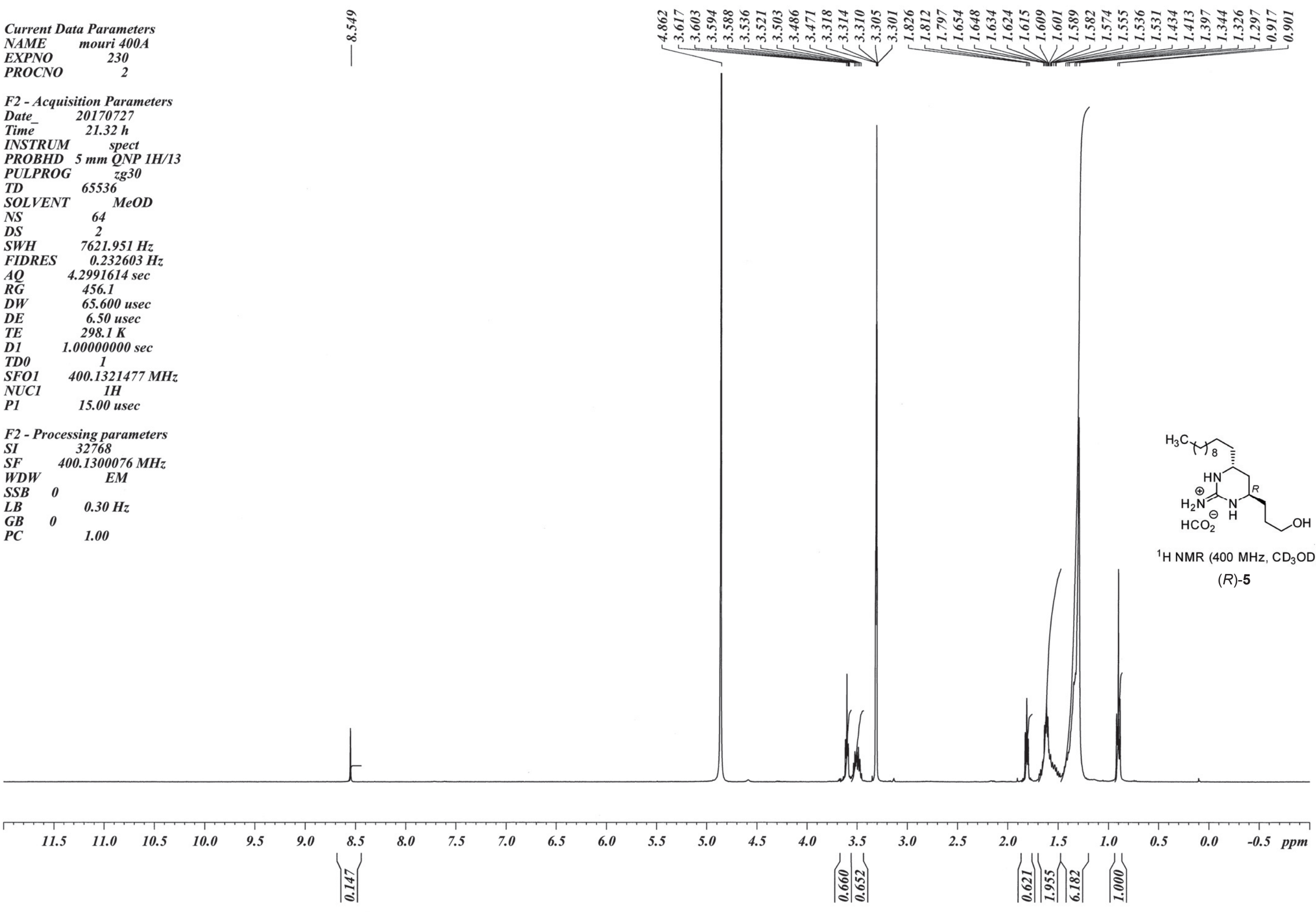
```
Current Data Parameters
NAME        mouri 400A
EXPNO              143
PROCNO               2

F2 - Acquisition Parameters
Date_        20170512
Time           19.33 h
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD            65536
SOLVENT           MeOD
NS             1161
DS                4
SWH        23980.814 Hz
FIDRES      0.731836 Hz
AQ        1.3664256 sec
RG           2580.3
DW           20.850 usec
DE             6.50 usec
TE            299.1 K
D1       1.00000000 sec
d11      0.03000000 sec
DELTA    0.89999998 sec
TD0               1
SFO1     100.6228298 MHz
NUC1            13C
P1            10.00 usec
SFO2     400.1316005 MHz
NUC2             1H
CPDPRG[2      waltz16
PCPD2         80.00 usec

F2 - Processing parameters
SI            32768
SF       100.6126291 MHz
WDW              EM
SSB      0
LB             1.00 Hz
GB       0
PC             1.40
```



$^{13}$C NMR (100 MHz, $CD_3OD$)

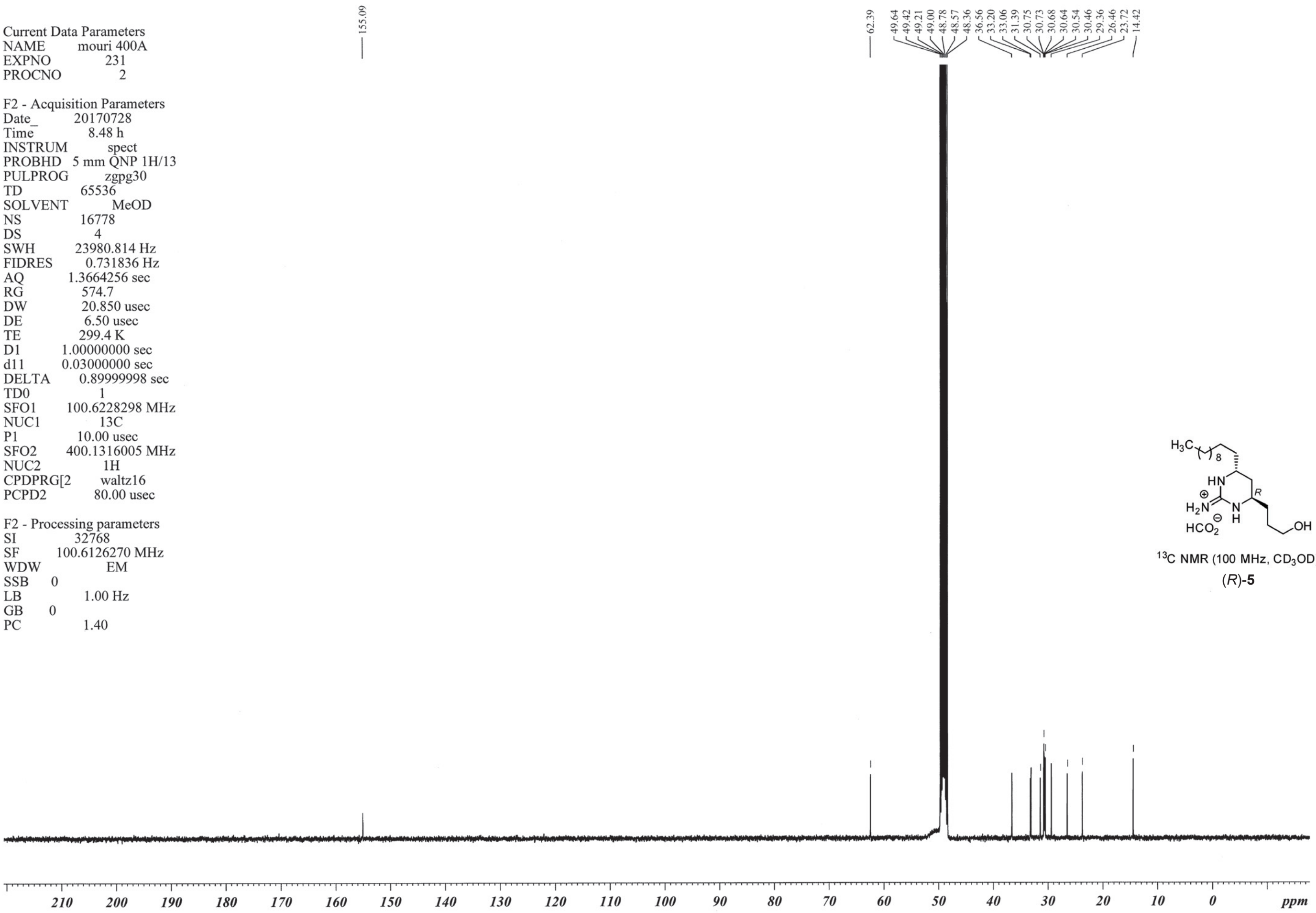
(*R*)-**12**

```
Current Data Parameters
NAME        mouri 400A
EXPNO            230
PROCNO             2

F2 - Acquisition Parameters
Date_         20170727
Time           21.32 h
INSTRUM          spect
PROBHD  5 mm QNP 1H/13
PULPROG           zg30
TD              65536
SOLVENT           MeOD
NS                 64
DS                  2
SWH         7621.951 Hz
FIDRES      0.232603 Hz
AQ        4.2991614 sec
RG              456.1
DW             65.600 usec
DE               6.50 usec
TE              298.1 K
D1         1.00000000 sec
TD0                 1
SFO1      400.1321477 MHz
NUC1               1H
P1              15.00 usec

F2 - Processing parameters
SI              32768
SF        400.1300076 MHz
WDW                EM
SSB    0
LB               0.30 Hz
GB     0
PC               1.00
```



$^1$H NMR (400 MHz, CD$_3$OD)
(*R*)-**5**

```
Current Data Parameters
NAME        mouri 400A
EXPNO            231
PROCNO             2

F2 - Acquisition Parameters
Date_         20170728
Time            8.48 h
INSTRUM          spect
PROBHD  5 mm QNP 1H/13
PULPROG         zgpg30
TD              65536
SOLVENT           MeOD
NS              16778
DS                  4
SWH         23980.814 Hz
FIDRES       0.731836 Hz
AQ         1.3664256 sec
RG              574.7
DW             20.850 usec
DE               6.50 usec
TE              299.4 K
D1         1.00000000 sec
d11        0.03000000 sec
DELTA      0.89999998 sec
TD0                 1
SFO1      100.6228298 MHz
NUC1              13C
P1              10.00 usec
SFO2      400.1316005 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           80.00 usec

F2 - Processing parameters
SI              32768
SF        100.6126270 MHz
WDW                EM
SSB    0
LB               1.00 Hz
GB     0
PC               1.40
```

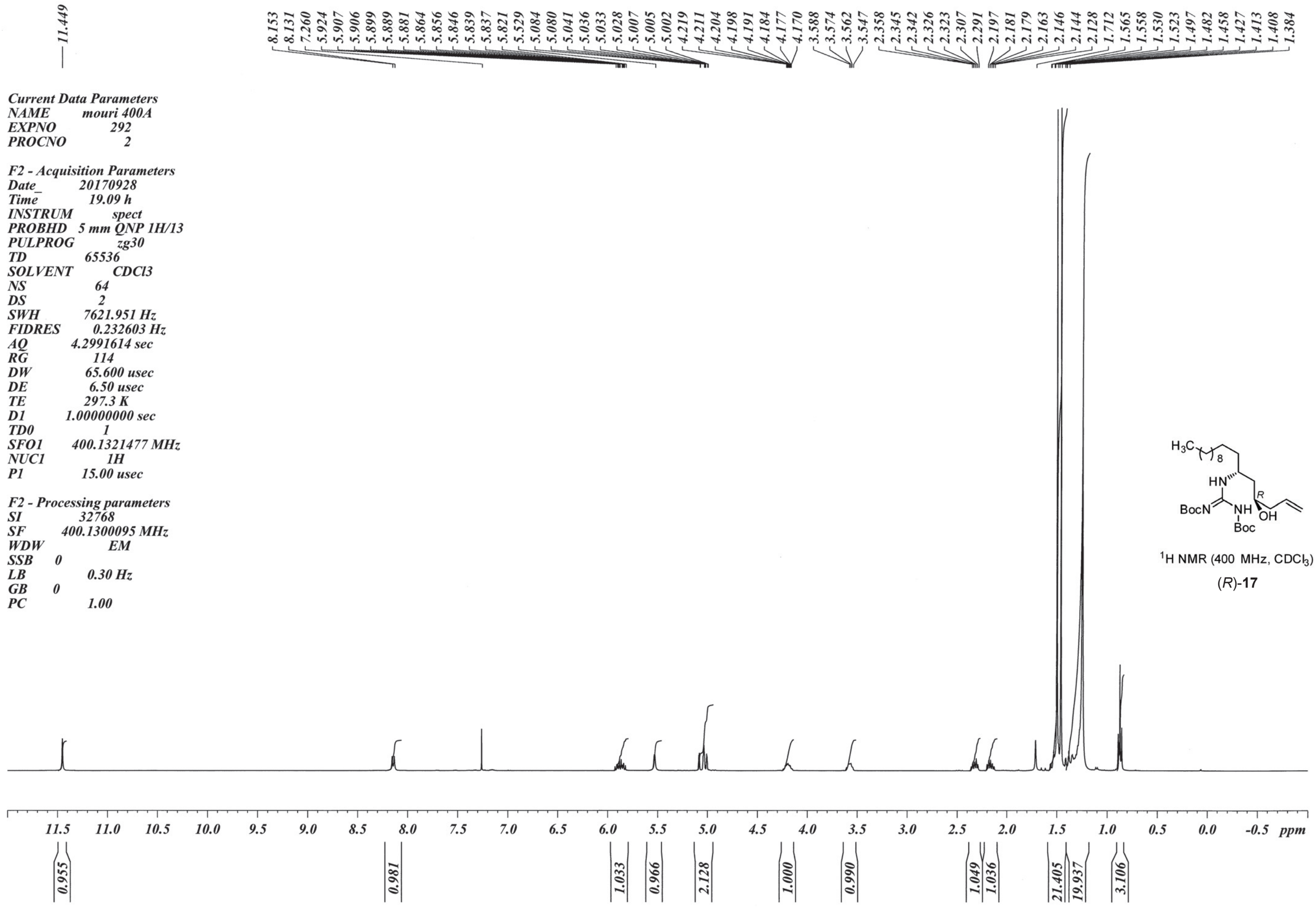


$^{13}$C NMR (100 MHz, CD$_3$OD)
(*R*)-**5**

***Current Data Parameters***
***NAME mouri 400A***
***EXPNO 292***
***PROCNO 2***

***F2 - Acquisition Parameters***
***Date_ 20170928***
***Time 19.09 h***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT CDCl3***
***NS 64***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.232603 Hz***
***AQ 4.2991614 sec***
***RG 114***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 297.3 K***
***D1 1.00000000 sec***
***TD0 1***
***SFO1 400.1321477 MHz***
***NUC1 1H***
***P1 15.00 usec***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300095 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***

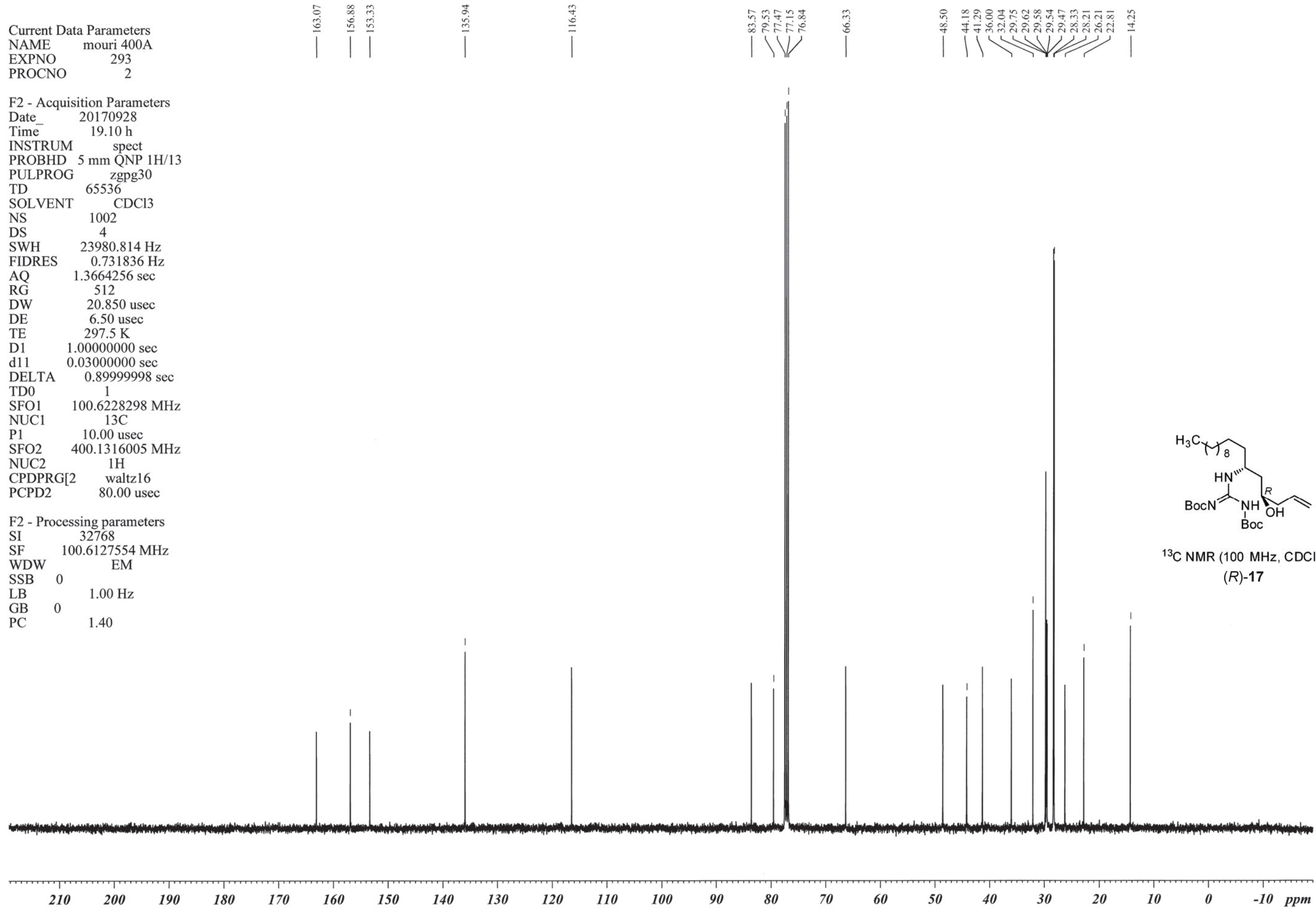


$^1$H NMR (400 MHz, CDCl$_3$)
(*R*)-**17**

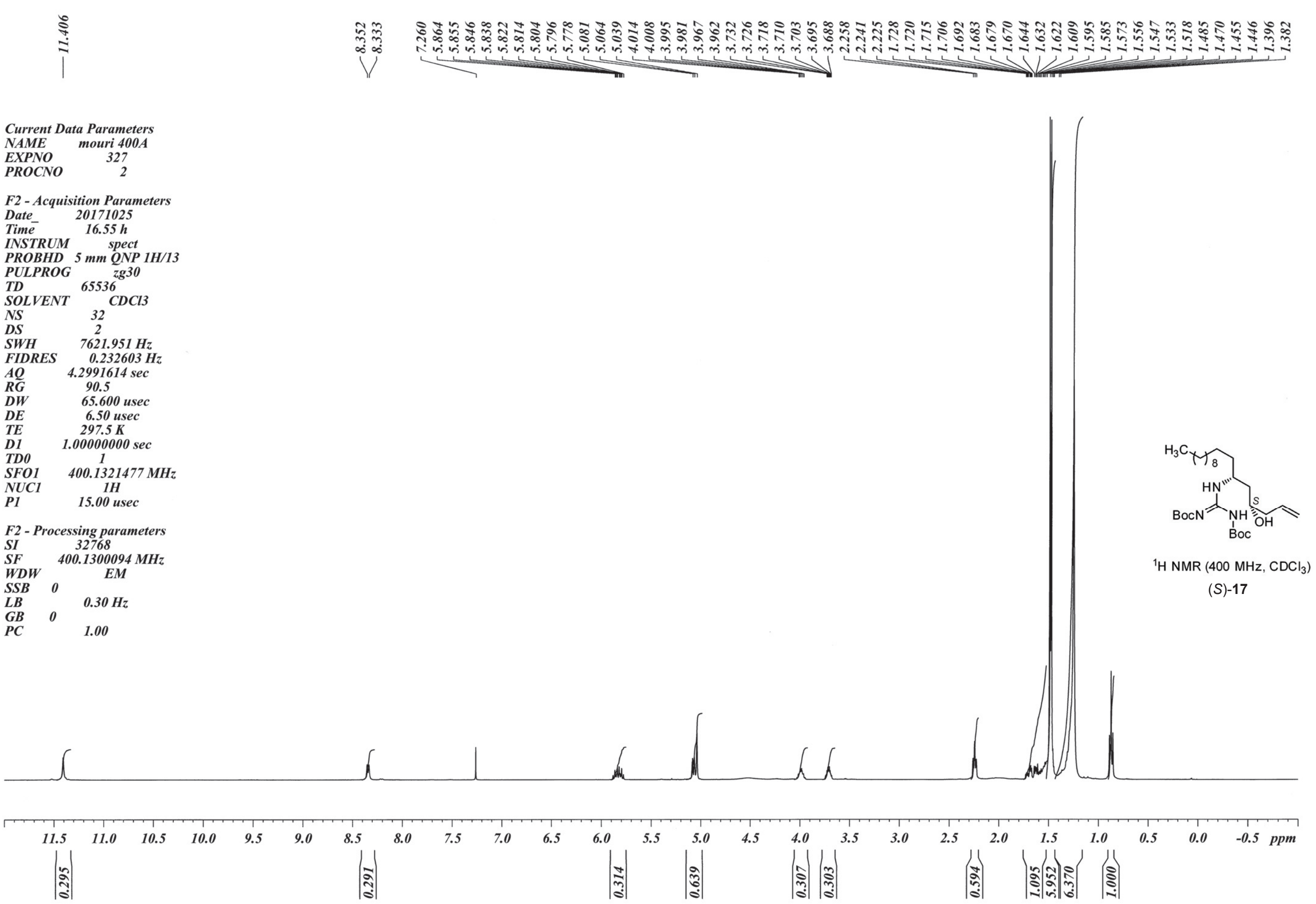
Current Data Parameters
NAME mouri 400A
EXPNO 293
PROCNO 2

F2 - Acquisition Parameters
Date_ 20170928
Time 19.10 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1002
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 512
DW 20.850 usec
DE 6.50 usec
TE 297.5 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6127554 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



$^{13}$C NMR (100 MHz, CDCl$_3$)
(*R*)-**17**

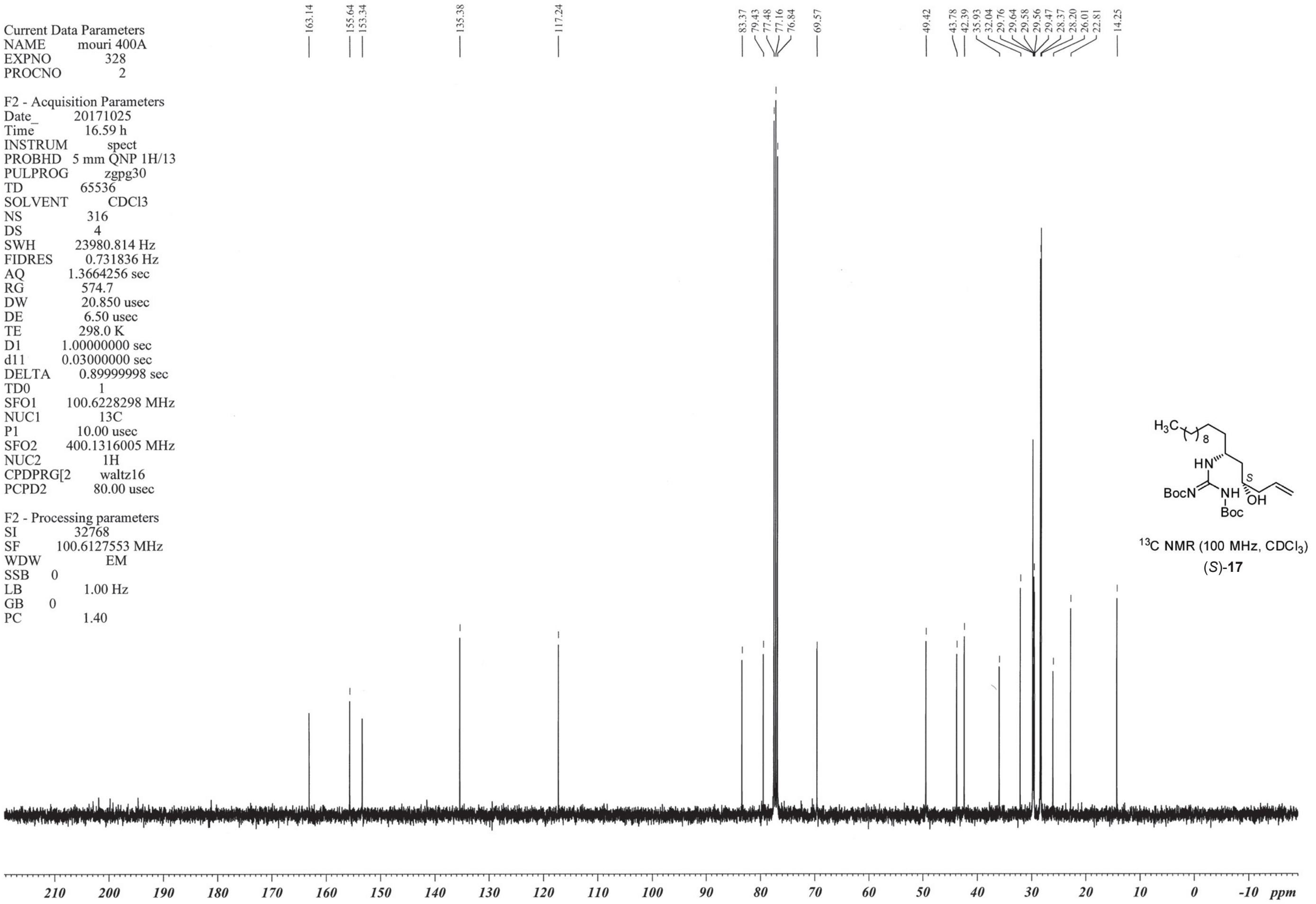


***Current Data Parameters***
*NAME mouri 400A*
*EXPNO 327*
*PROCNO 2*

***F2 - Acquisition Parameters***
*Date_ 20171025*
*Time 16.55 h*
*INSTRUM spect*
*PROBHD 5 mm QNP 1H/13*
*PULPROG zg30*
*TD 65536*
*SOLVENT CDCl3*
*NS 32*
*DS 2*
*SWH 7621.951 Hz*
*FIDRES 0.232603 Hz*
*AQ 4.2991614 sec*
*RG 90.5*
*DW 65.600 usec*
*DE 6.50 usec*
*TE 297.5 K*
*D1 1.00000000 sec*
*TD0 1*
*SFO1 400.1321477 MHz*
*NUC1 1H*
*P1 15.00 usec*

***F2 - Processing parameters***
*SI 32768*
*SF 400.1300094 MHz*
*WDW EM*
*SSB 0*
*LB 0.30 Hz*
*GB 0*
*PC 1.00*

$^1$H NMR (400 MHz, CDCl$_3$)
(*S*)-**17**



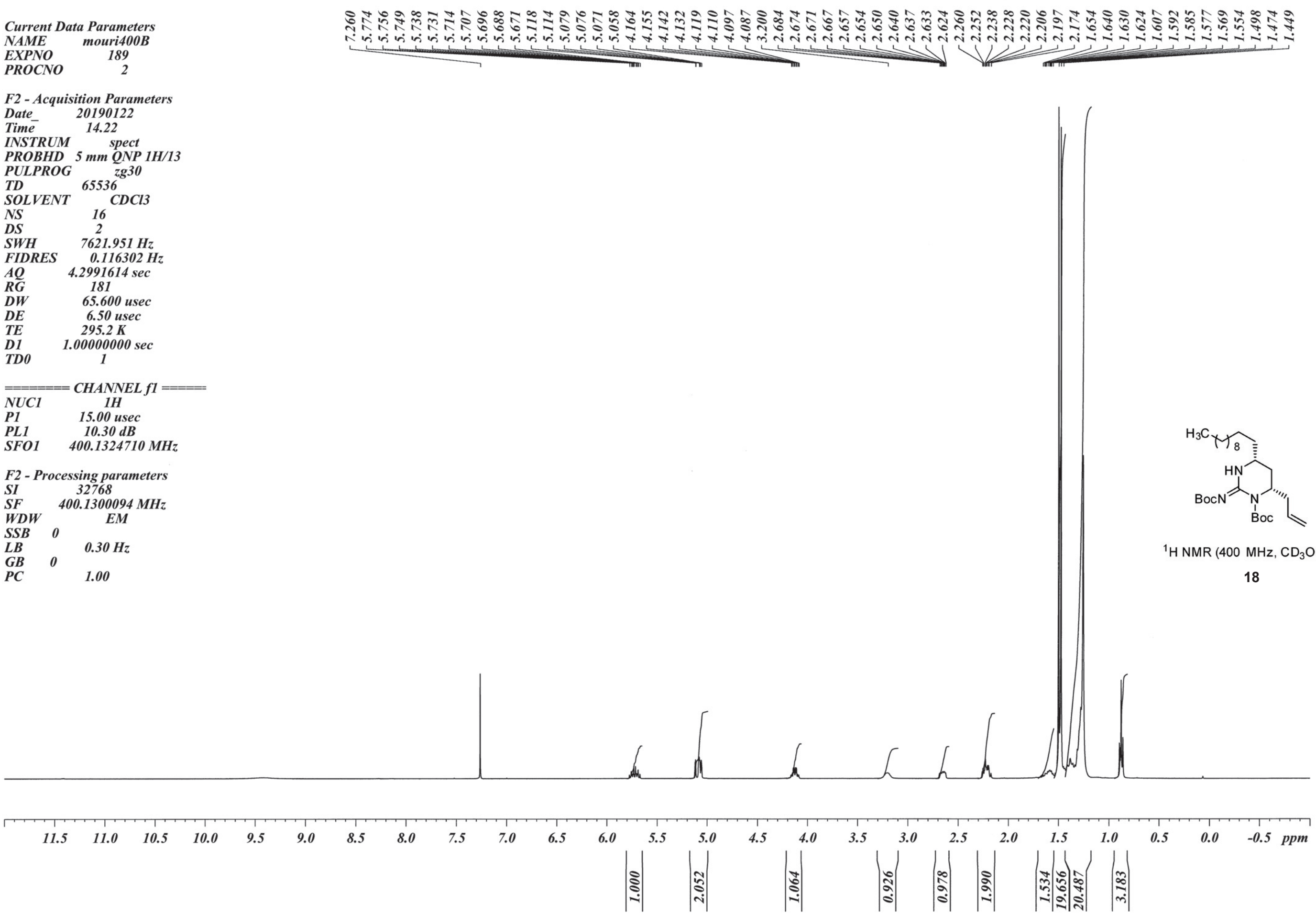
Current Data Parameters
NAME mouri 400A
EXPNO 328
PROCNO 2

F2 - Acquisition Parameters
Date_ 20171025
Time 16.59 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 316
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 574.7
DW 20.850 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6127553 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

$^{13}$C NMR (100 MHz, CDCl$_3$)
(*S*)-**17**

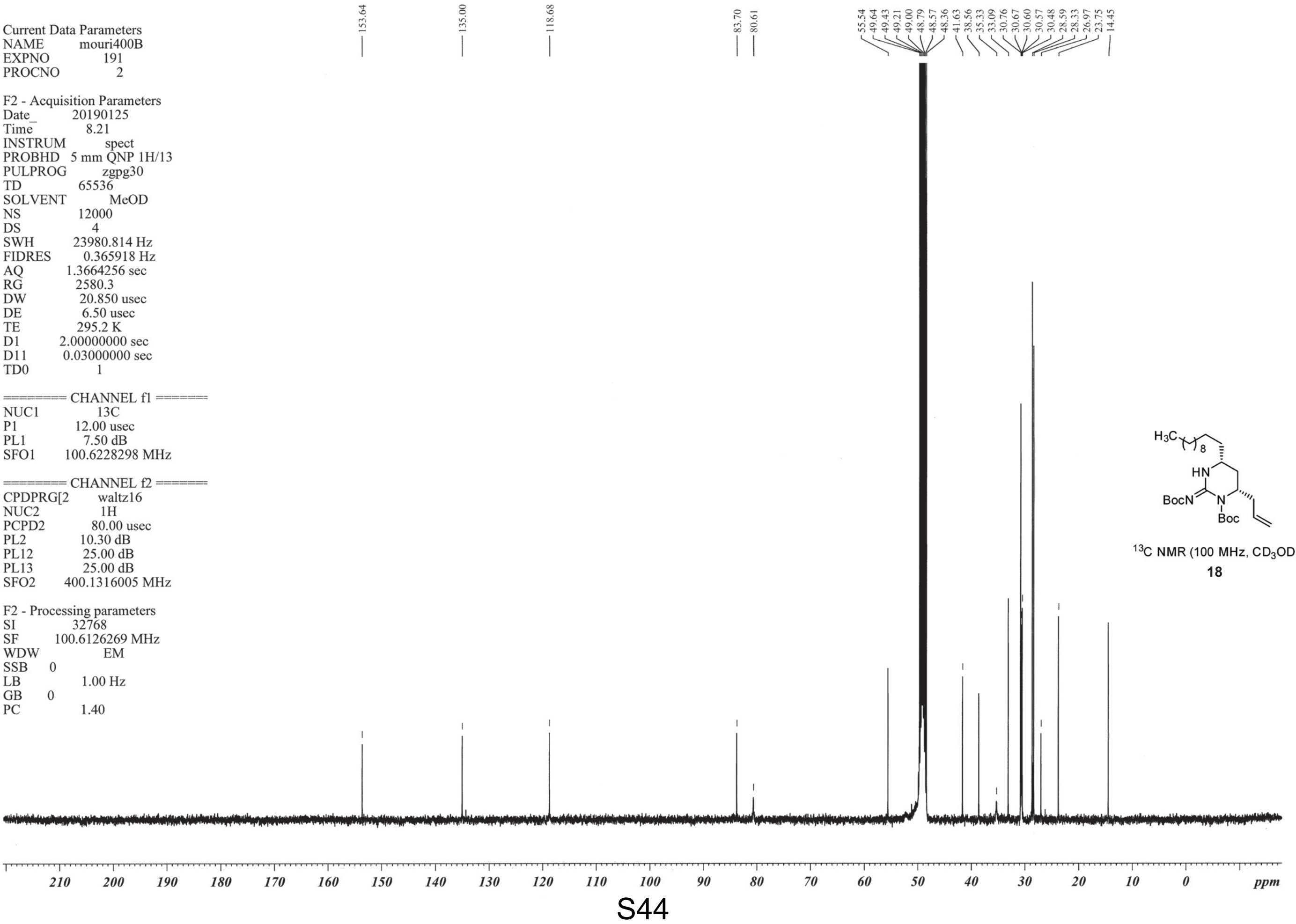
```
Current Data Parameters
NAME          mouri400B
EXPNO              189
PROCNO               2

F2 - Acquisition Parameters
Date_         20190122
Time             14.22
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH        7621.951 Hz
FIDRES     0.116302 Hz
AQ       4.2991614 sec
RG                 181
DW         65.600 usec
DE           6.50 usec
TE             295.2 K
D1      1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1          15.00 usec
PL1           10.30 dB
SFO1    400.1324710 MHz

F2 - Processing parameters
SI               32768
SF      400.1300094 MHz
WDW                 EM
SSB     0
LB             0.30 Hz
GB      0
PC                1.00
```



$^1$H NMR (400 MHz, CD$_3$OD)

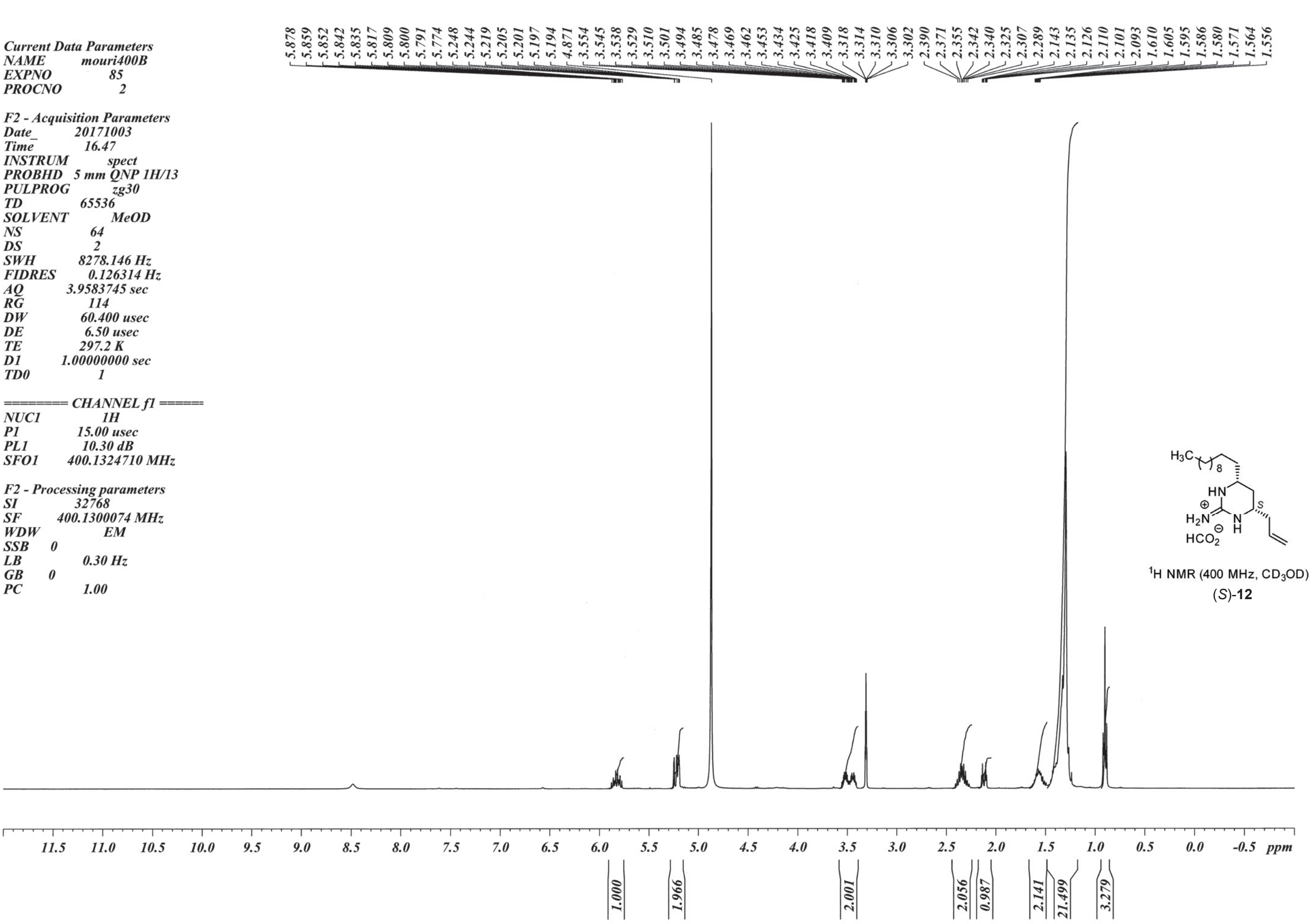
**18**

```
Current Data Parameters
NAME          mouri400B
EXPNO              191
PROCNO               2

F2 - Acquisition Parameters
Date_         20190125
Time              8.21
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD               65536
SOLVENT           MeOD
NS               12000
DS                   4
SWH       23980.814 Hz
FIDRES     0.365918 Hz
AQ       1.3664256 sec
RG              2580.3
DW         20.850 usec
DE           6.50 usec
TE             295.2 K
D1      2.00000000 sec
D11     0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1          12.00 usec
PL1            7.50 dB
SFO1    100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2       waltz16
NUC2                1H
PCPD2       80.00 usec
PL2           10.30 dB
PL12          25.00 dB
PL13          25.00 dB
SFO2    400.1316005 MHz

F2 - Processing parameters
SI               32768
SF      100.6126269 MHz
WDW                 EM
SSB     0
LB             1.00 Hz
GB      0
PC                1.40
```



$^{13}$C NMR (100 MHz, CD$_3$OD)

**18**



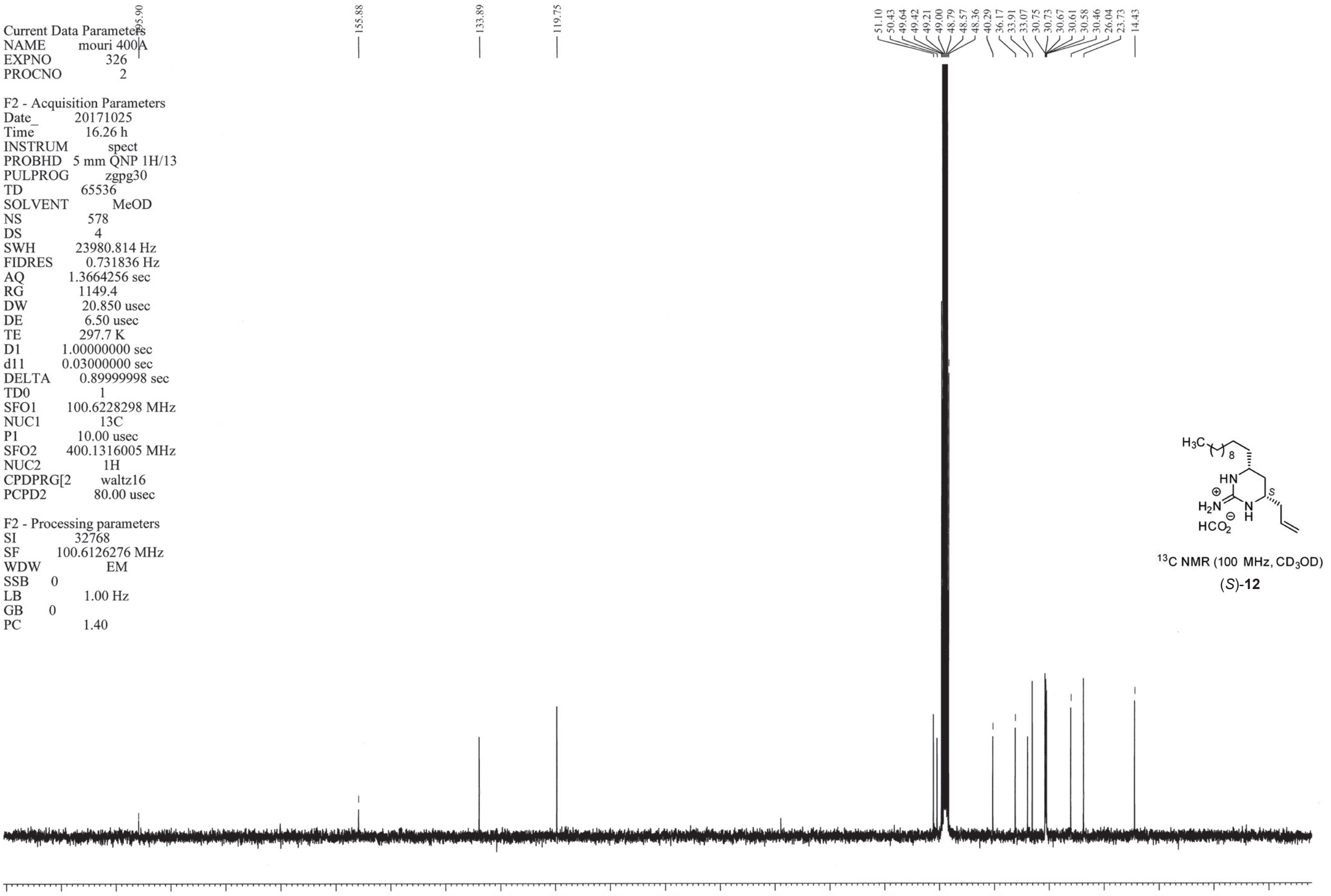
***Current Data Parameters***
***NAME mouri400B***
***EXPNO 85***
***PROCNO 2***

***F2 - Acquisition Parameters***
***Date_ 20171003***
***Time 16.47***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT MeOD***
***NS 64***
***DS 2***
***SWH 8278.146 Hz***
***FIDRES 0.126314 Hz***
***AQ 3.9583745 sec***
***RG 114***
***DW 60.400 usec***
***DE 6.50 usec***
***TE 297.2 K***
***D1 1.00000000 sec***
***TD0 1***

***======== CHANNEL f1 ========***
***NUC1 1H***
***P1 15.00 usec***
***PL1 10.30 dB***
***SFO1 400.1324710 MHz***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300074 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***

$^1$H NMR (400 MHz, $CD_3OD$)
(*S*)-**12**



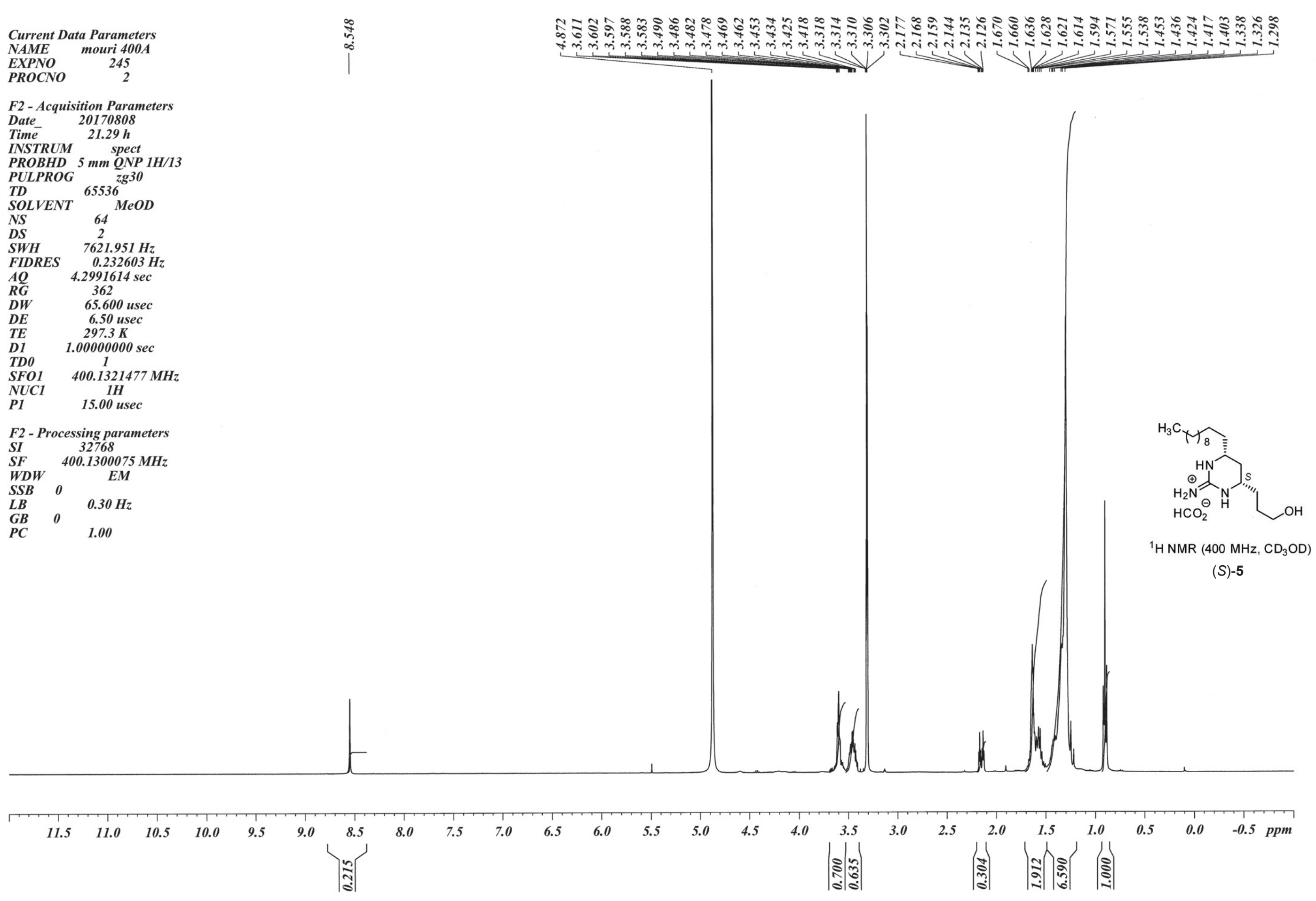
Current Data Parameters
NAME mouri 400A
EXPNO 326
PROCNO 2

F2 - Acquisition Parameters
Date_ 20171025
Time 16.26 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 578
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 1149.4
DW 20.850 usec
DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6126276 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

$^{13}$C NMR (100 MHz, $CD_3OD$)
(*S*)-**12**

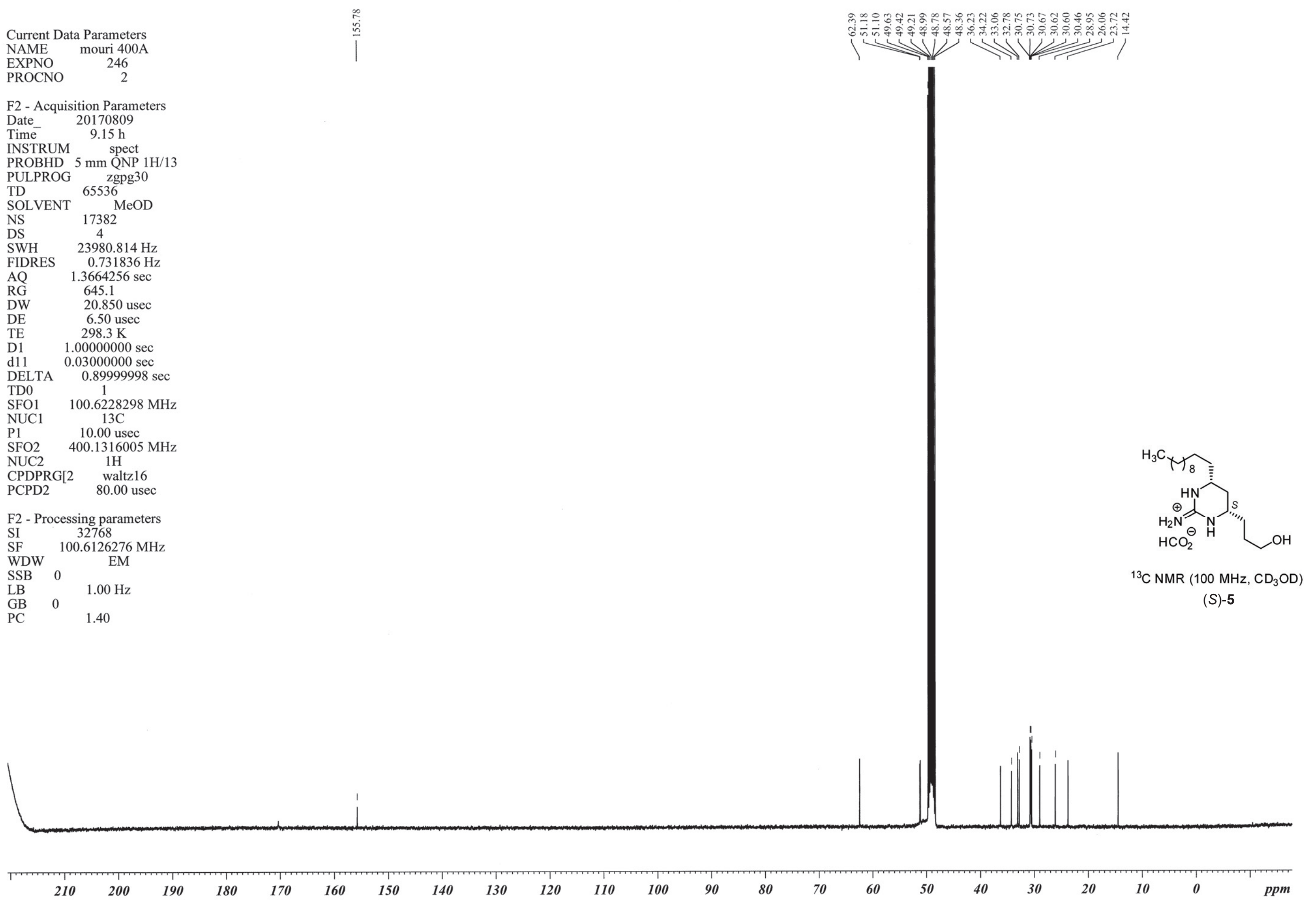
```
Current Data Parameters
NAME        mouri 400A
EXPNO             245
PROCNO              2

F2 - Acquisition Parameters
Date_         20170808
Time             21.29 h
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD              65536
SOLVENT            MeOD
NS                 64
DS                  2
SWH          7621.951 Hz
FIDRES       0.232603 Hz
AQ          4.2991614 sec
RG                362
DW             65.600 usec
DE               6.50 usec
TE              297.3 K
D1         1.00000000 sec
TD0                 1
SFO1      400.1321477 MHz
NUC1               1H
P1              15.00 usec

F2 - Processing parameters
SI              32768
SF        400.1300075 MHz
WDW                EM
SSB    0
LB               0.30 Hz
GB     0
PC               1.00
```



$^1H$ NMR (400 MHz, $CD_3OD$)

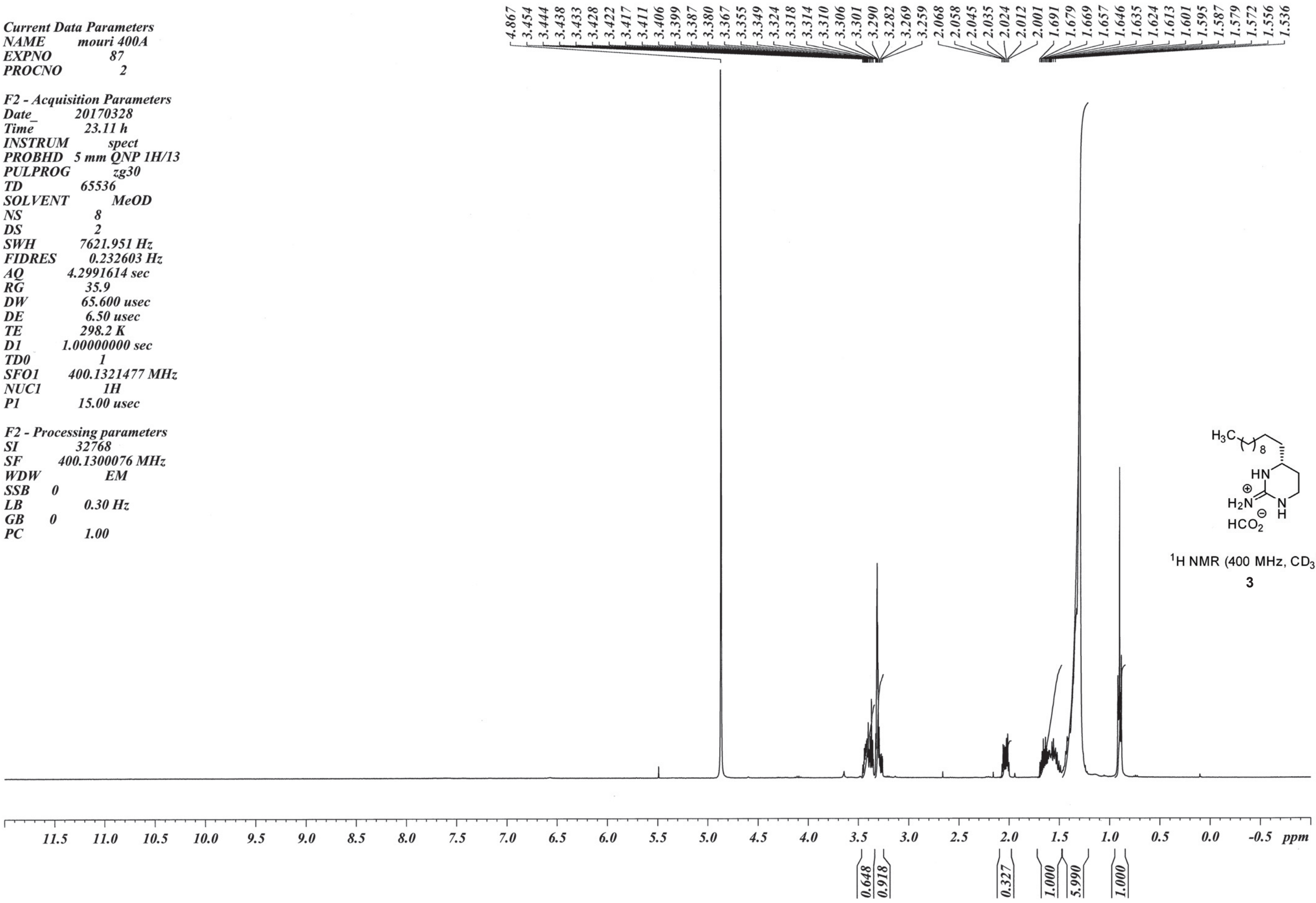
(*S*)-**5**

```
Current Data Parameters
NAME        mouri 400A
EXPNO             246
PROCNO              2

F2 - Acquisition Parameters
Date_         20170809
Time              9.15 h
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD              65536
SOLVENT            MeOD
NS              17382
DS                  4
SWH         23980.814 Hz
FIDRES       0.731836 Hz
AQ          1.3664256 sec
RG              645.1
DW             20.850 usec
DE               6.50 usec
TE              298.3 K
D1         1.00000000 sec
d11        0.03000000 sec
DELTA      0.89999998 sec
TD0                 1
SFO1      100.6228298 MHz
NUC1               13C
P1              10.00 usec
SFO2      400.1316005 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2           80.00 usec

F2 - Processing parameters
SI              32768
SF        100.6126276 MHz
WDW                EM
SSB    0
LB               1.00 Hz
GB     0
PC               1.40
```



$^{13}C$ NMR (100 MHz, $CD_3OD$)

(*S*)-**5**



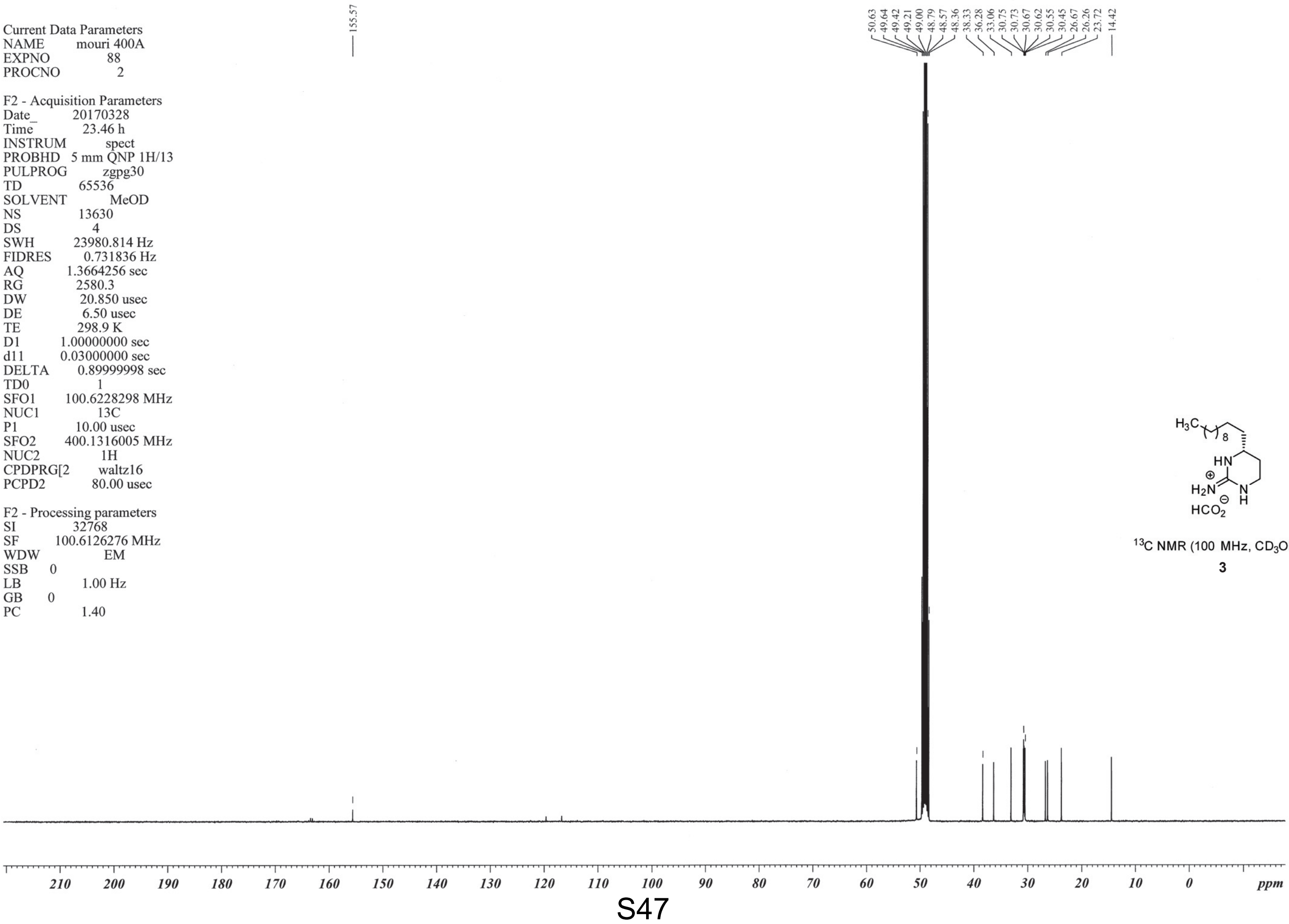
*Current Data Parameters*
*NAME mouri 400A*
*EXPNO 87*
*PROCNO 2*

*F2 - Acquisition Parameters*
*Date_ 20170328*
*Time 23.11 h*
*INSTRUM spect*
*PROBHD 5 mm QNP 1H/13*
*PULPROG zg30*
*TD 65536*
*SOLVENT MeOD*
*NS 8*
*DS 2*
*SWH 7621.951 Hz*
*FIDRES 0.232603 Hz*
*AQ 4.2991614 sec*
*RG 35.9*
*DW 65.600 usec*
*DE 6.50 usec*
*TE 298.2 K*
*D1 1.00000000 sec*
*TD0 1*
*SFO1 400.1321477 MHz*
*NUC1 1H*
*P1 15.00 usec*

*F2 - Processing parameters*
*SI 32768*
*SF 400.1300076 MHz*
*WDW EM*
*SSB 0*
*LB 0.30 Hz*
*GB 0*
*PC 1.00*

$^1$H NMR (400 MHz, CD$_3$OD)

**3**



Current Data Parameters
NAME mouri 400A
EXPNO 88
PROCNO 2

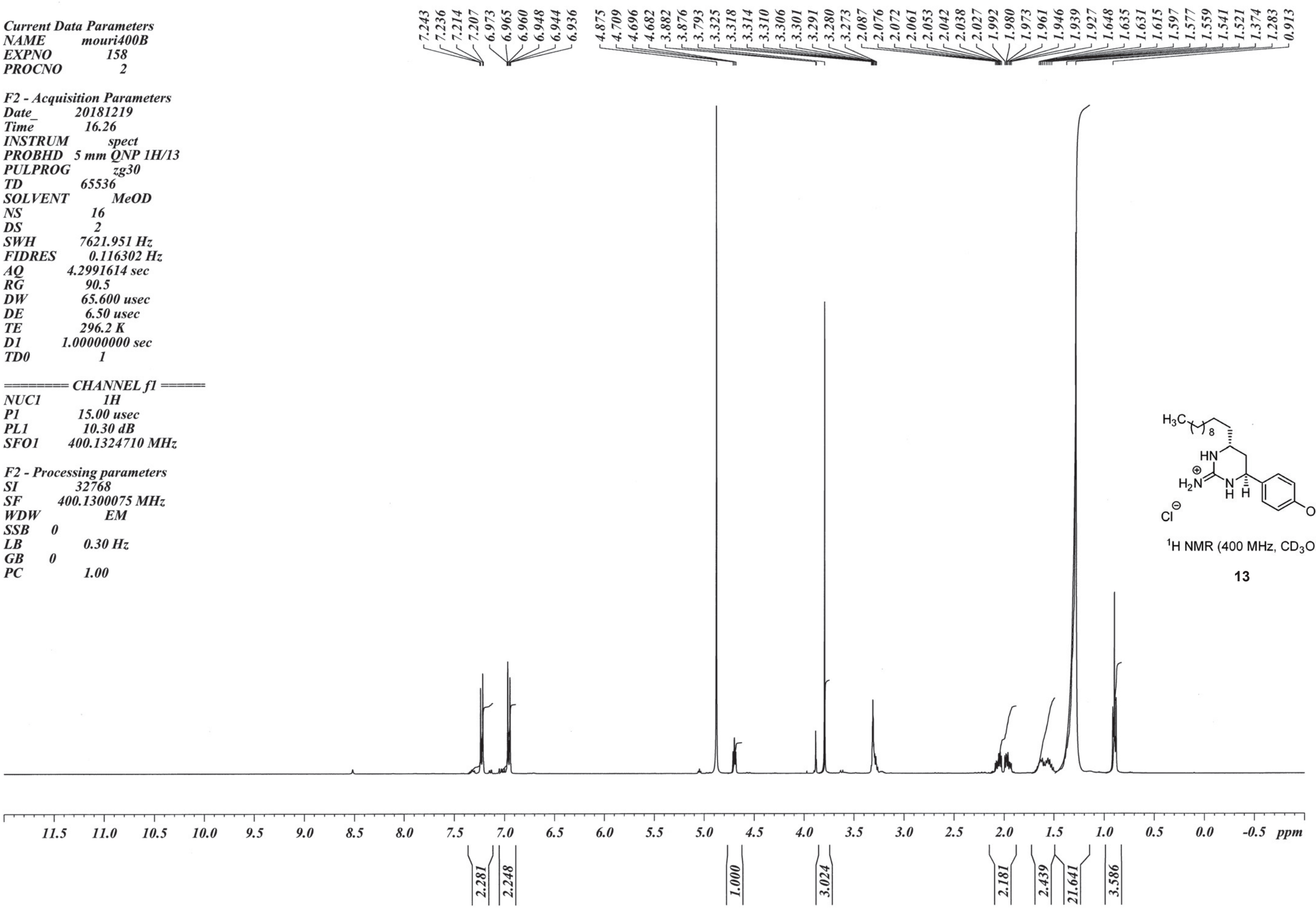
F2 - Acquisition Parameters
Date_ 20170328
Time 23.46 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 13630
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.50 usec
TE 298.9 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6126276 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

$^{13}$C NMR (100 MHz, CD$_3$OD)

**3**

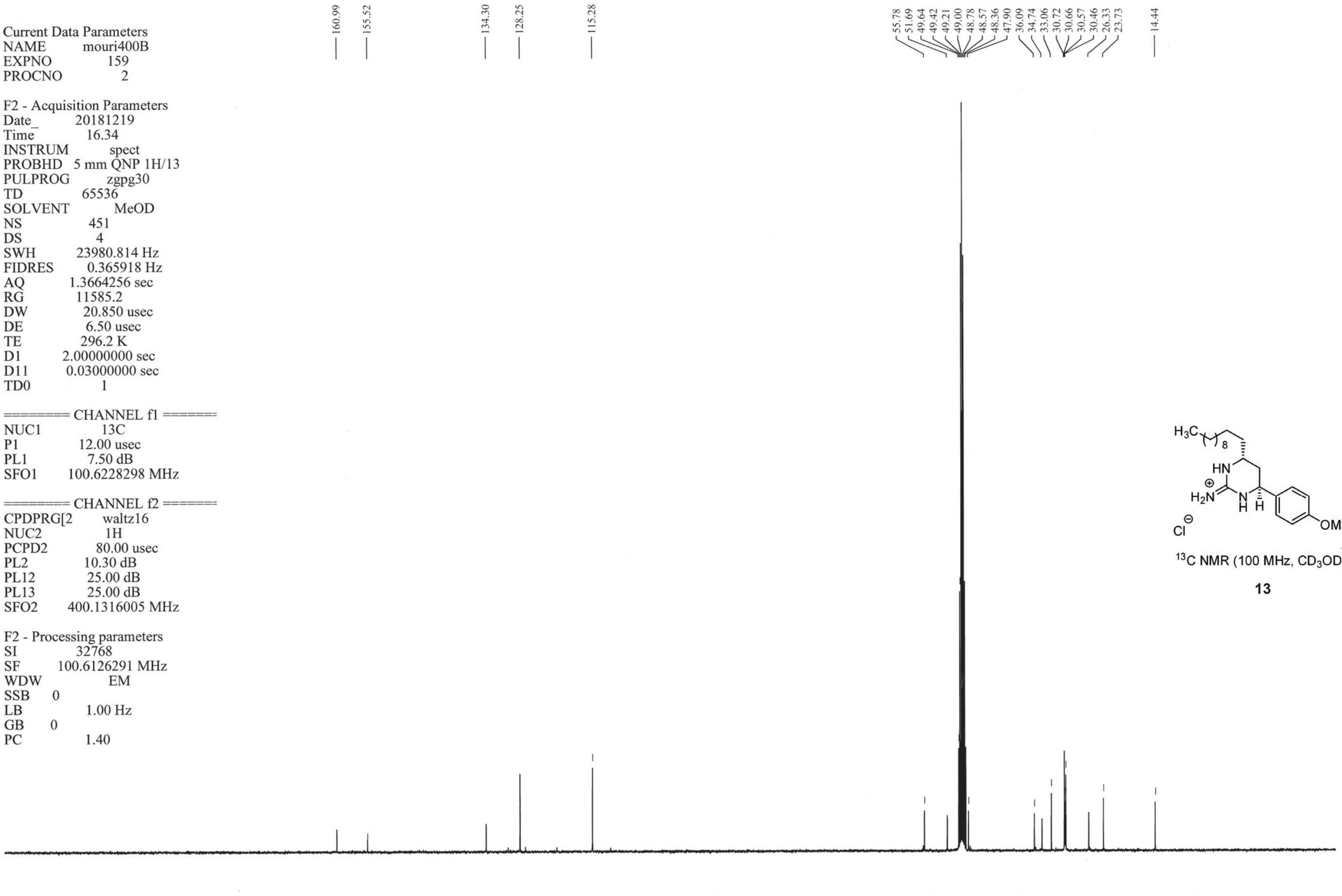
```
Current Data Parameters
NAME        mouri400B
EXPNO            158
PROCNO             2

F2 - Acquisition Parameters
Date_       20181219
Time           16.26
INSTRUM         spect
PROBHD  5 mm QNP 1H/13
PULPROG          zg30
TD             65536
SOLVENT          MeOD
NS                16
DS                 2
SWH         7621.951 Hz
FIDRES      0.116302 Hz
AQ         4.2991614 sec
RG              90.5
DW            65.600 usec
DE              6.50 usec
TE             296.2 K
D1        1.00000000 sec
TD0                1

======== CHANNEL f1 ======
NUC1              1H
P1             15.00 usec
PL1            10.30 dB
SFO1     400.1324710 MHz

F2 - Processing parameters
SI             32768
SF       400.1300075 MHz
WDW               EM
SSB    0
LB              0.30 Hz
GB     0
PC              1.00
```



$^1H$ NMR (400 MHz, $CD_3OD$)

13

```
Current Data Parameters
NAME        mouri400B
EXPNO            159
PROCNO             2

F2 - Acquisition Parameters
Date_       20181219
Time           16.34
INSTRUM         spect
PROBHD  5 mm QNP 1H/13
PULPROG        zgpg30
TD             65536
SOLVENT          MeOD
NS               451
DS                 4
SWH        23980.814 Hz
FIDRES      0.365918 Hz
AQ         1.3664256 sec
RG           11585.2
DW            20.850 usec
DE              6.50 usec
TE             296.2 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1

======== CHANNEL f1 ======
NUC1             13C
P1             12.00 usec
PL1             7.50 dB
SFO1     100.6228298 MHz

======== CHANNEL f2 ======
CPDPRG[2     waltz16
NUC2              1H
PCPD2          80.00 usec
PL2            10.30 dB
PL12           25.00 dB
PL13           25.00 dB
SFO2     400.1316005 MHz

F2 - Processing parameters
SI             32768
SF       100.6126291 MHz
WDW               EM
SSB    0
LB              1.00 Hz
GB     0
PC              1.40
```



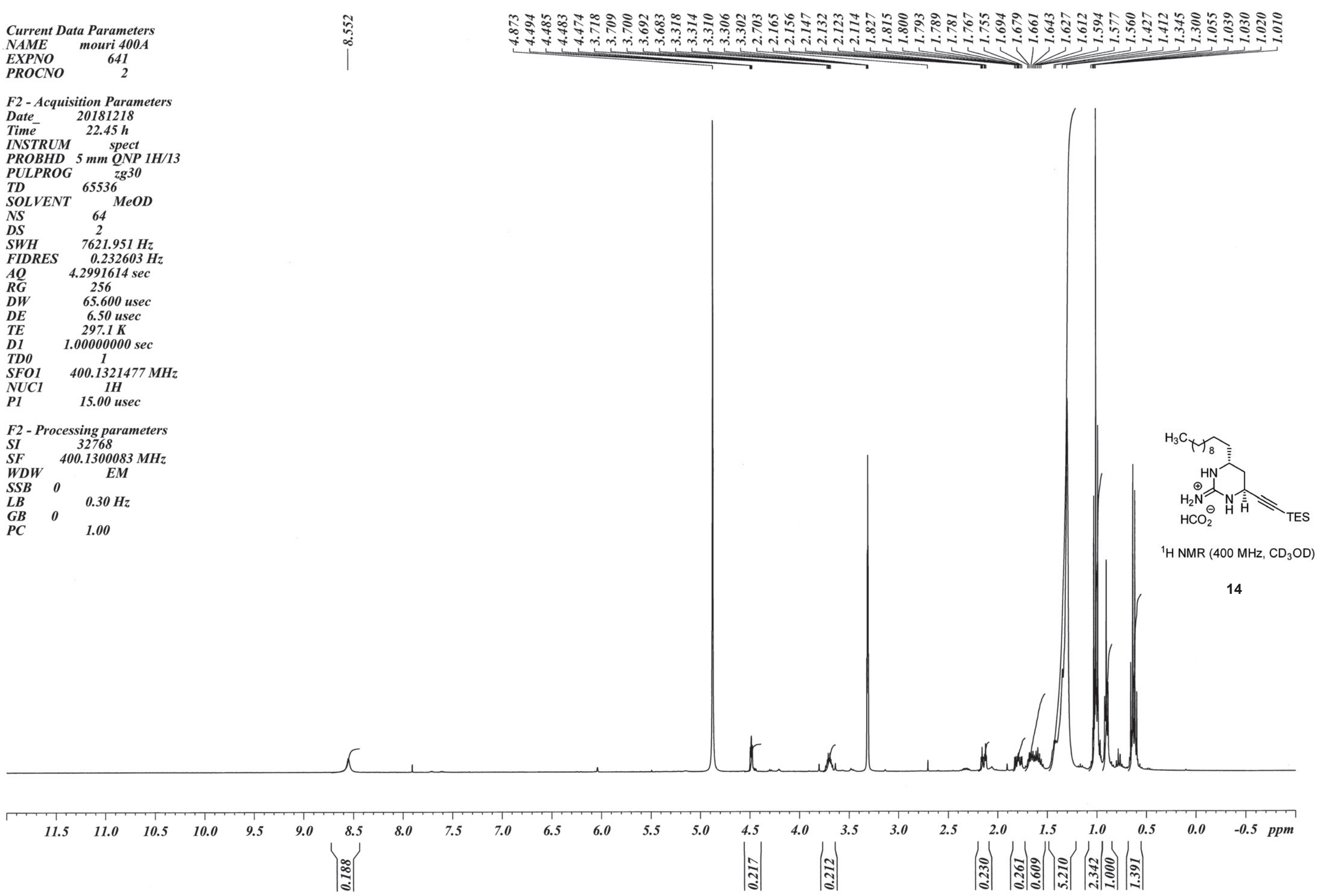
$^{13}C$ NMR (100 MHz, $CD_3OD$)

13

***Current Data Parameters***
***NAME mouri 400A***
***EXPNO 641***
***PROCNO 2***

***F2 - Acquisition Parameters***
***Date_ 20181218***
***Time 22.45 h***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT MeOD***
***NS 64***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.232603 Hz***
***AQ 4.2991614 sec***
***RG 256***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 297.1 K***
***D1 1.00000000 sec***
***TD0 1***
***SFO1 400.1321477 MHz***
***NUC1 1H***
***P1 15.00 usec***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300083 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***



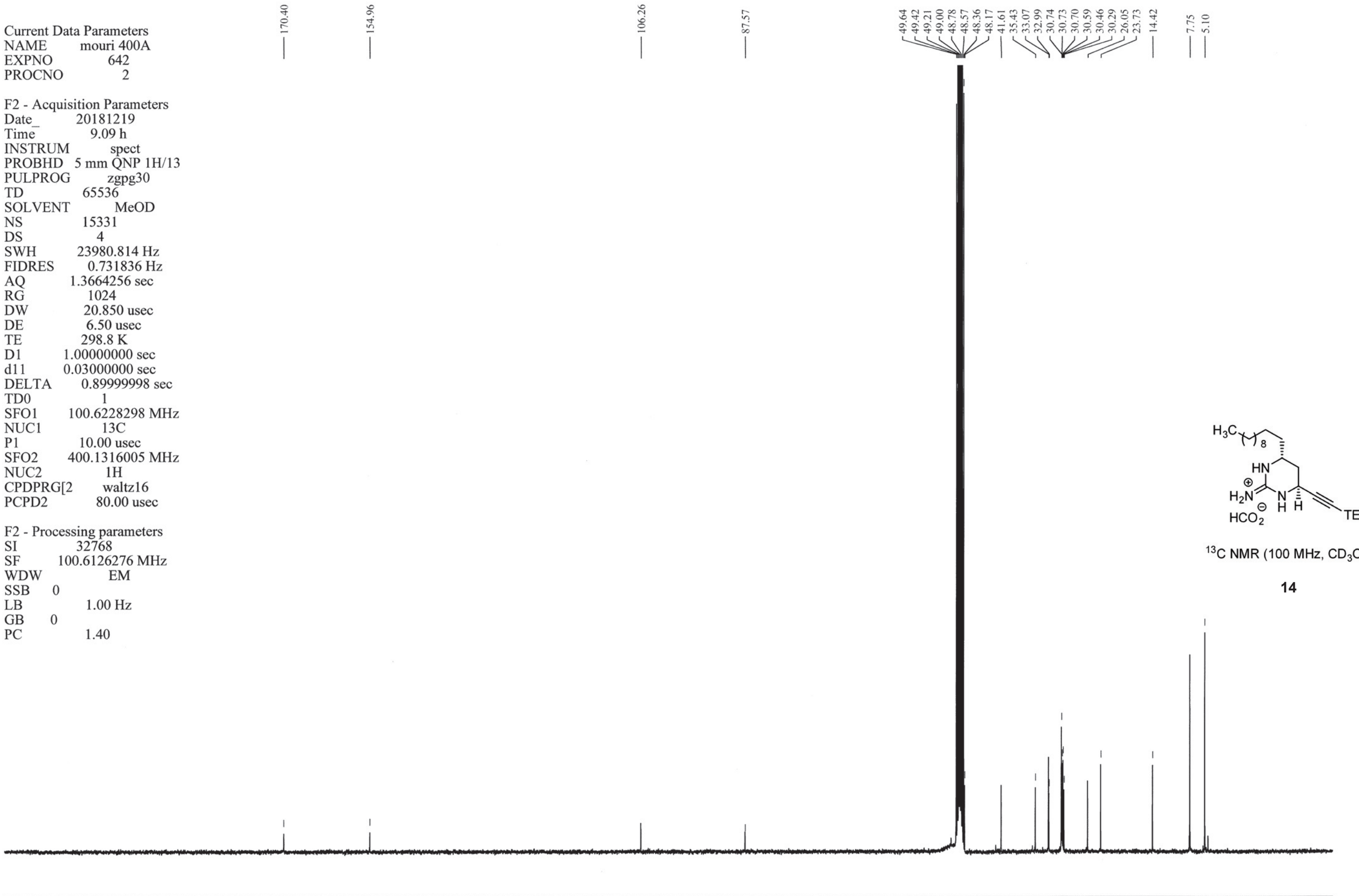
$^1$H NMR (400 MHz, $CD_3OD$)

**14**

Current Data Parameters
NAME mouri 400A
EXPNO 642
PROCNO 2

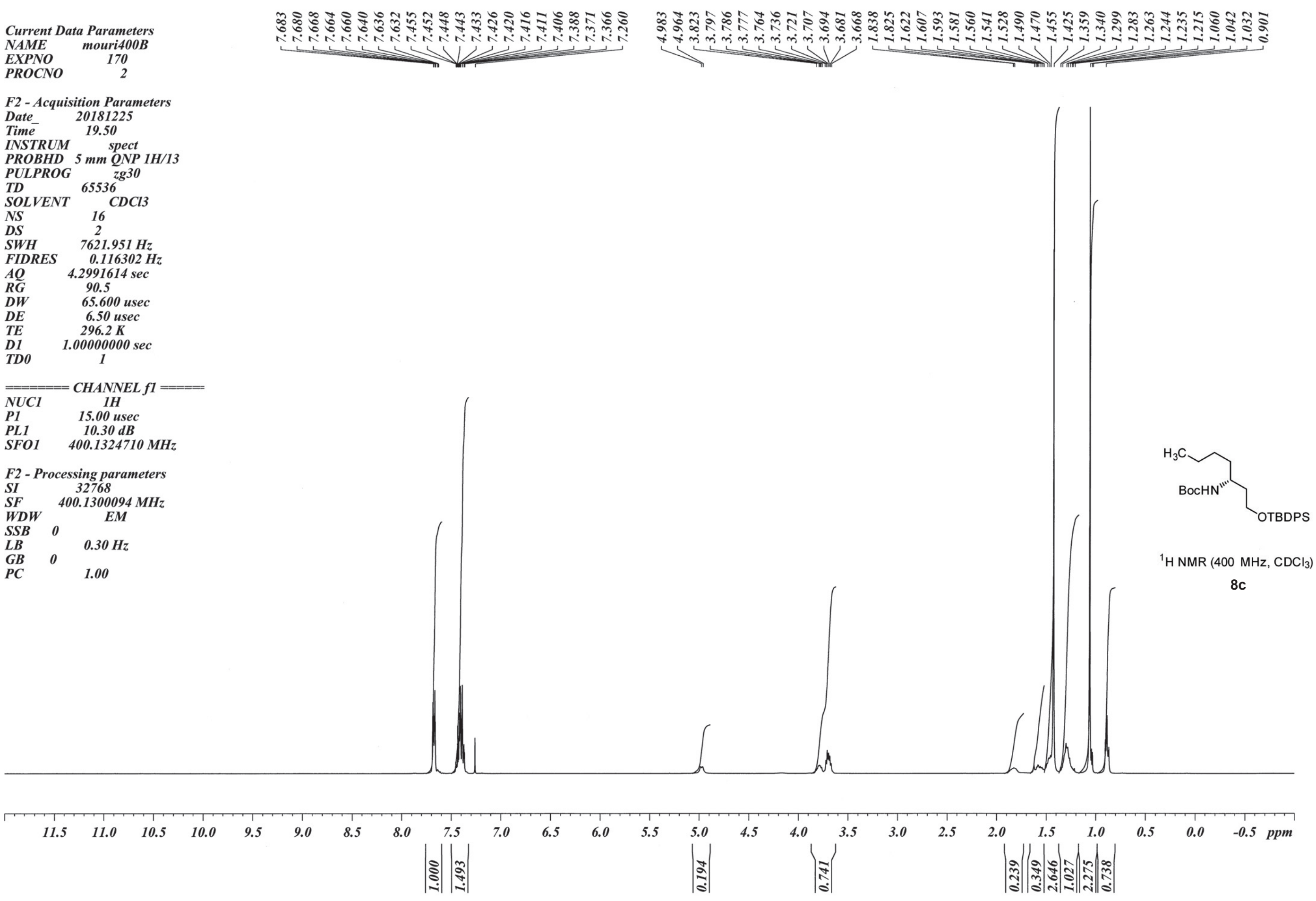
F2 - Acquisition Parameters
Date_ 20181219
Time 9.09 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 15331
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 1024
DW 20.850 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6126276 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



$^{13}$C NMR (100 MHz, $CD_3OD$)

**14**



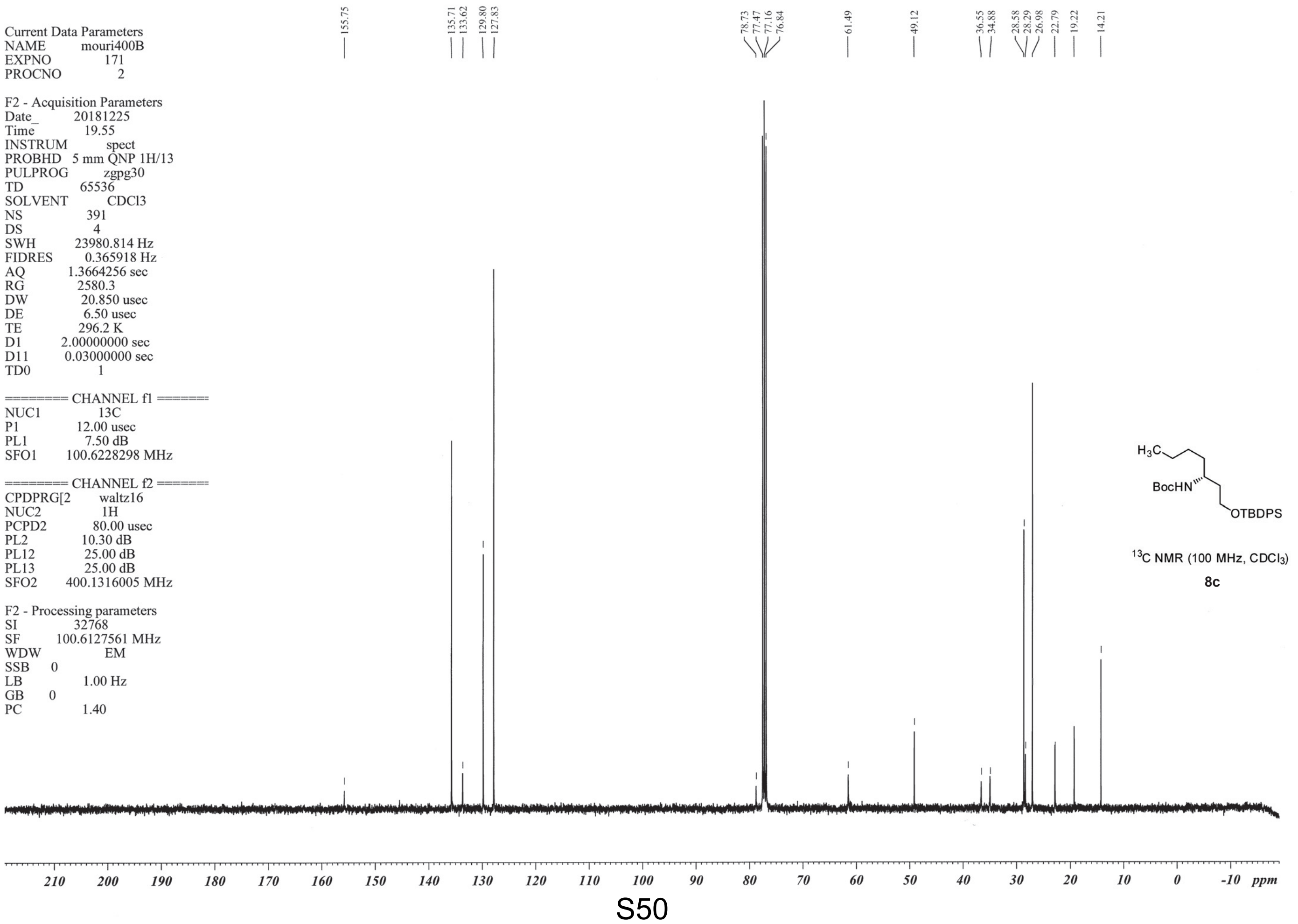
*Current Data Parameters*
*NAME mouri400B*
*EXPNO 170*
*PROCNO 2*

*F2 - Acquisition Parameters*
*Date_ 20181225*
*Time 19.50*
*INSTRUM spect*
*PROBHD 5 mm QNP 1H/13*
*PULPROG zg30*
*TD 65536*
*SOLVENT CDCl3*
*NS 16*
*DS 2*
*SWH 7621.951 Hz*
*FIDRES 0.116302 Hz*
*AQ 4.2991614 sec*
*RG 90.5*
*DW 65.600 usec*
*DE 6.50 usec*
*TE 296.2 K*
*D1 1.00000000 sec*
*TD0 1*

*======== CHANNEL f1 ========*
*NUC1 1H*
*P1 15.00 usec*
*PL1 10.30 dB*
*SFO1 400.1324710 MHz*

*F2 - Processing parameters*
*SI 32768*
*SF 400.1300094 MHz*
*WDW EM*
*SSB 0*
*LB 0.30 Hz*
*GB 0*
*PC 1.00*

$^1H$ NMR (400 MHz, $CDCl_3$)
**8c**



Current Data Parameters
NAME mouri400B
EXPNO 171
PROCNO 2

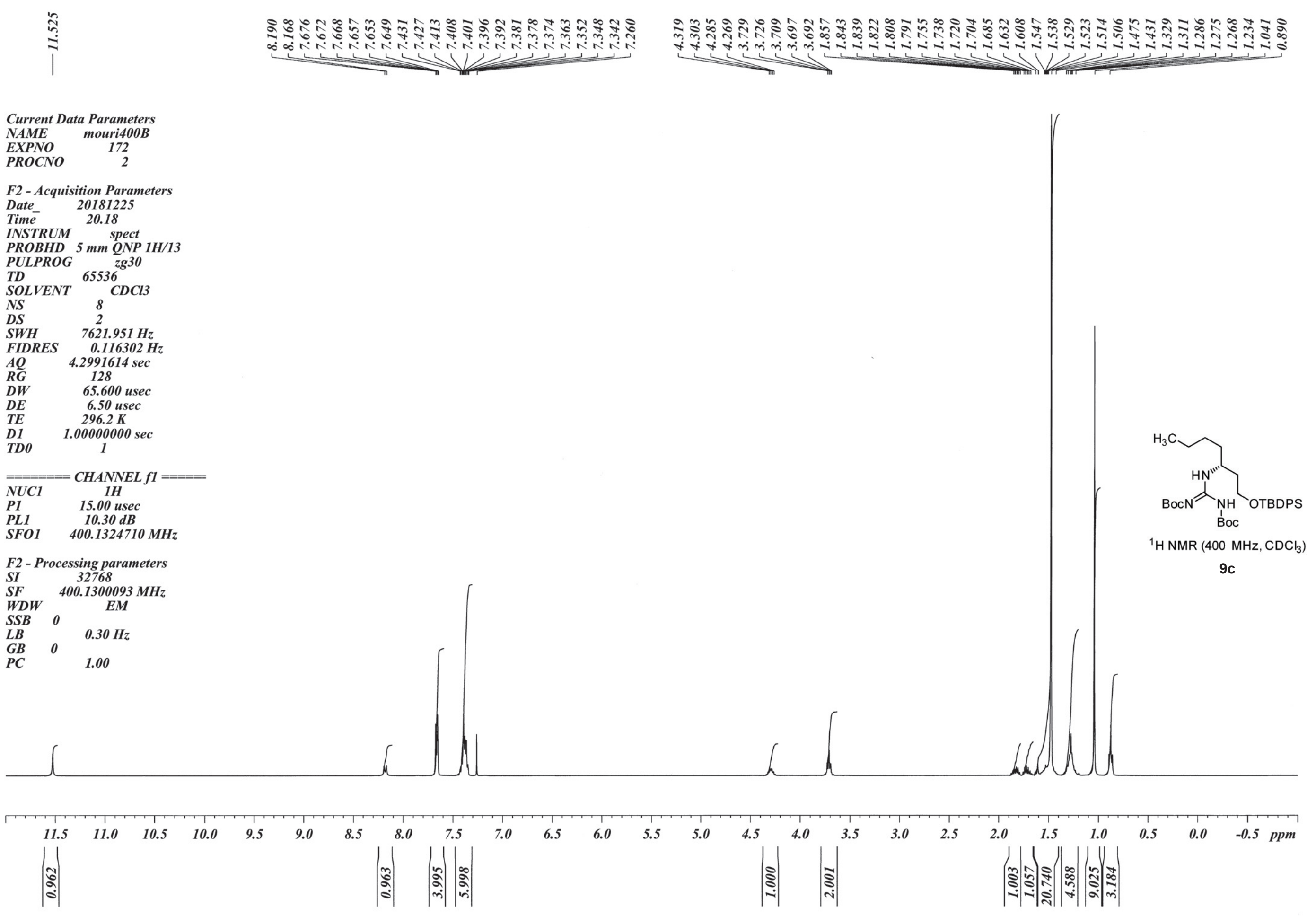
F2 - Acquisition Parameters
Date_ 20181225
Time 19.55
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 391
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127561 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

$^{13}C$ NMR (100 MHz, $CDCl_3$)
**8c**



***Current Data Parameters***
***NAME mouri400B***
***EXPNO 172***
***PROCNO 2***

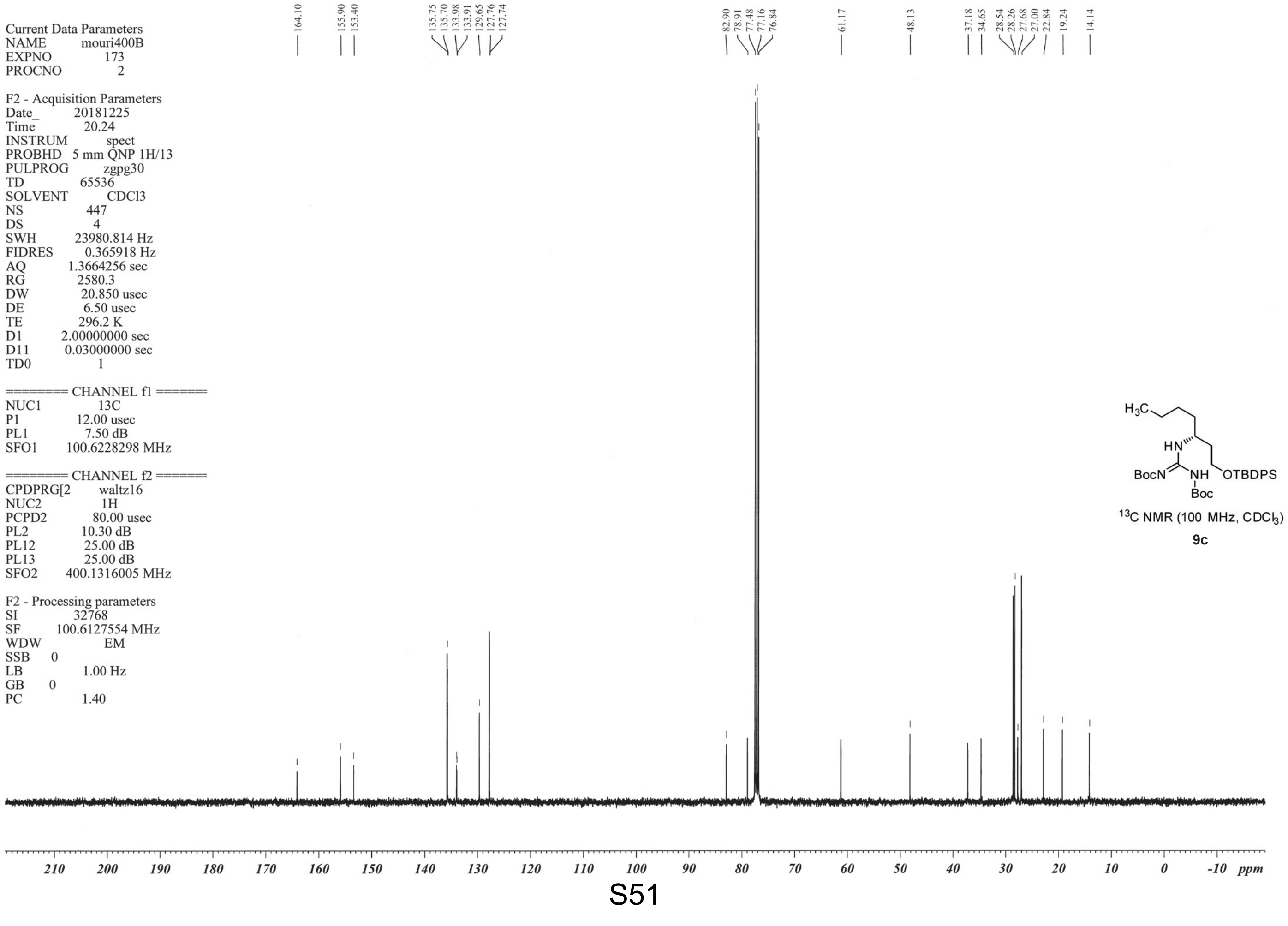
***F2 - Acquisition Parameters***
***Date_ 20181225***
***Time 20.18***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT CDCl3***
***NS 8***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.116302 Hz***
***AQ 4.2991614 sec***
***RG 128***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 296.2 K***
***D1 1.00000000 sec***
***TD0 1***

***======== CHANNEL f1 ========***
***NUC1 1H***
***P1 15.00 usec***
***PL1 10.30 dB***
***SFO1 400.1324710 MHz***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300093 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***

$^1$H NMR (400 MHz, CDCl$_3$)

**9c**



Current Data Parameters
NAME mouri400B
EXPNO 173
PROCNO 2

F2 - Acquisition Parameters
Date_ 20181225
Time 20.24
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 447
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

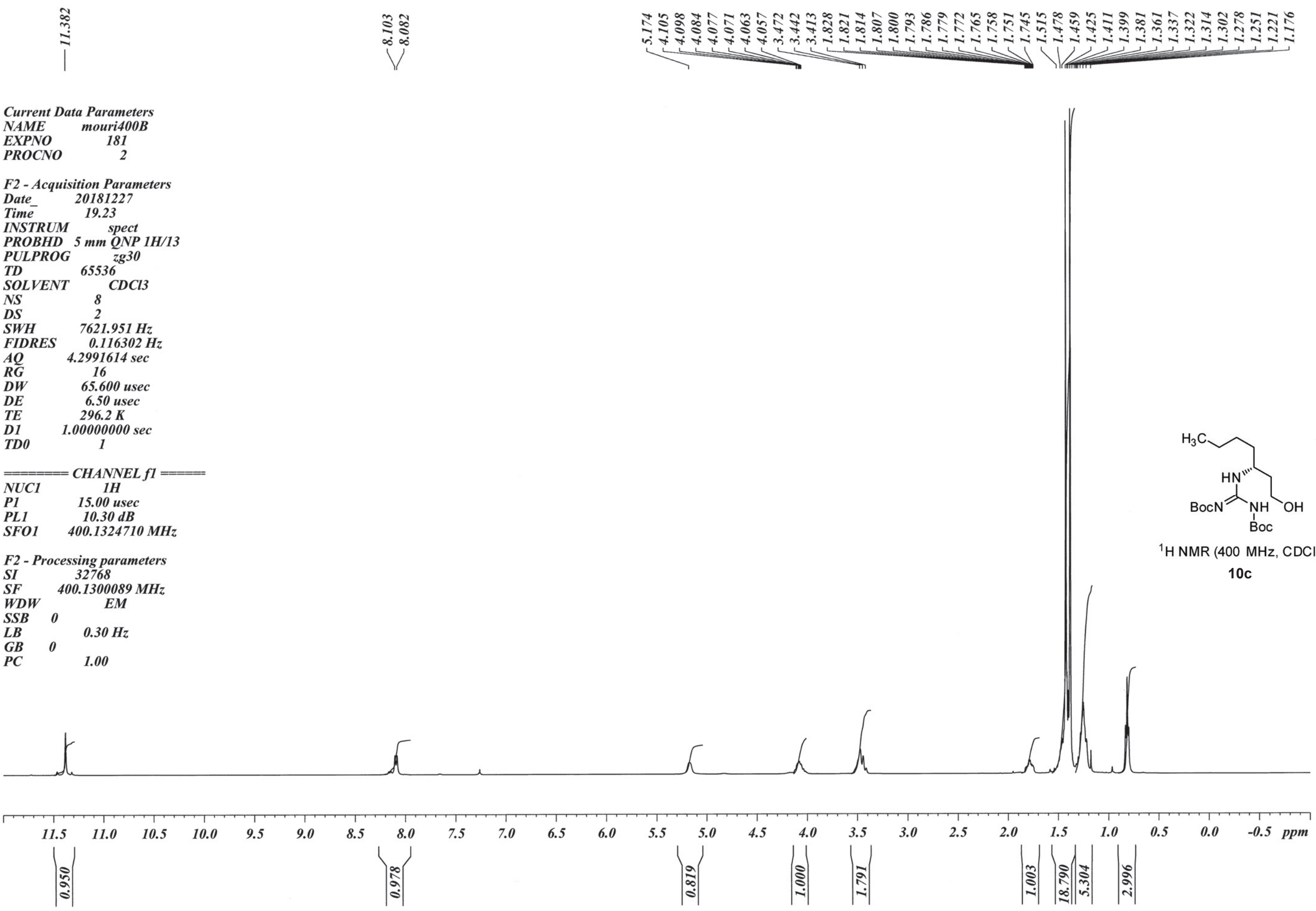
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127554 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

$^{13}$C NMR (100 MHz, CDCl$_3$)

**9c**



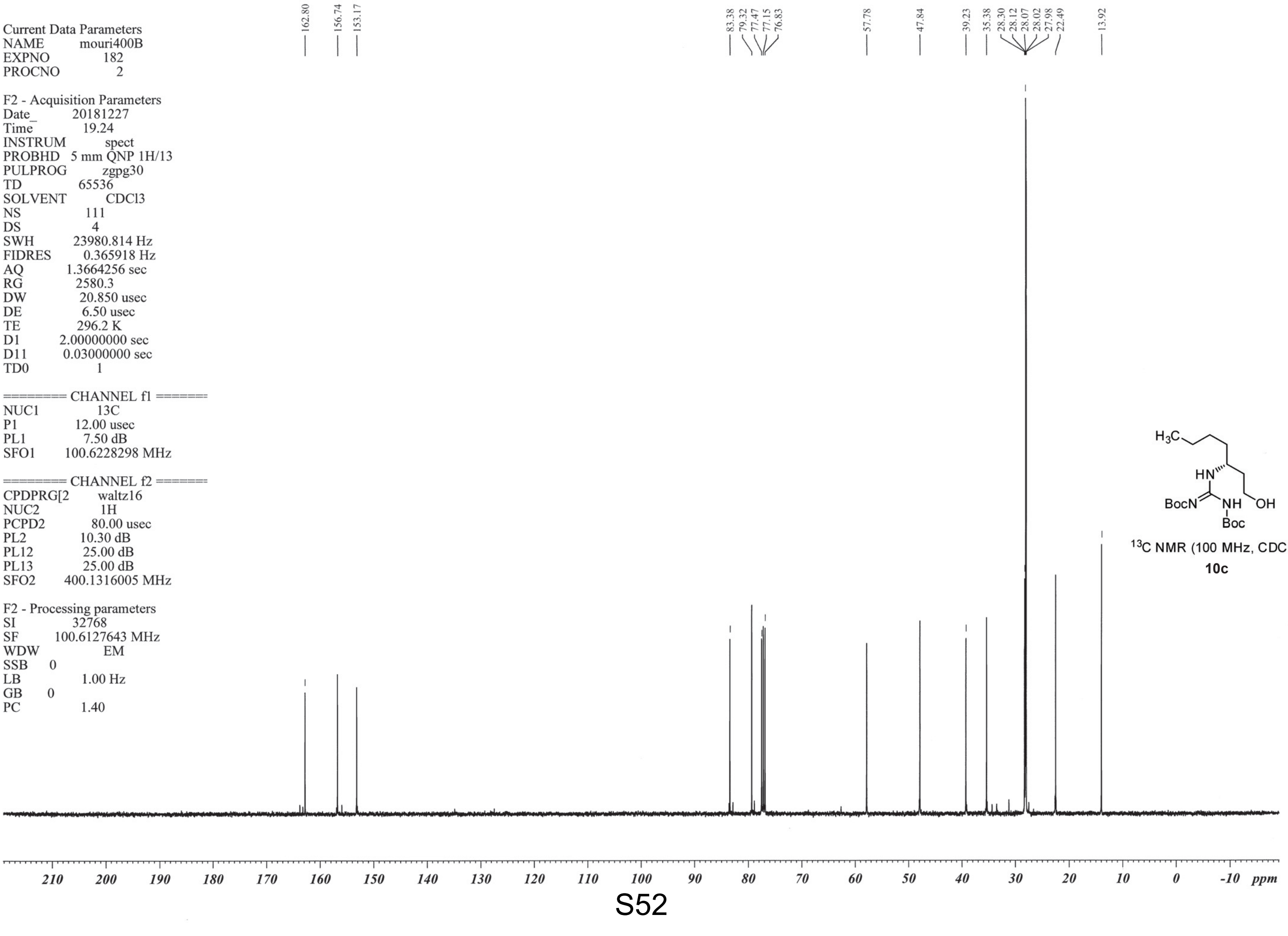
***Current Data Parameters***
***NAME mouri400B***
***EXPNO 181***
***PROCNO 2***

***F2 - Acquisition Parameters***
***Date_ 20181227***
***Time 19.23***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT CDCl3***
***NS 8***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.116302 Hz***
***AQ 4.2991614 sec***
***RG 16***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 296.2 K***
***D1 1.00000000 sec***
***TD0 1***

***======== CHANNEL f1 ========***
***NUC1 1H***
***P1 15.00 usec***
***PL1 10.30 dB***
***SFO1 400.1324710 MHz***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300089 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***

$^1$H NMR (400 MHz, CDCl$_3$)
**10c**



Current Data Parameters
NAME mouri400B
EXPNO 182
PROCNO 2

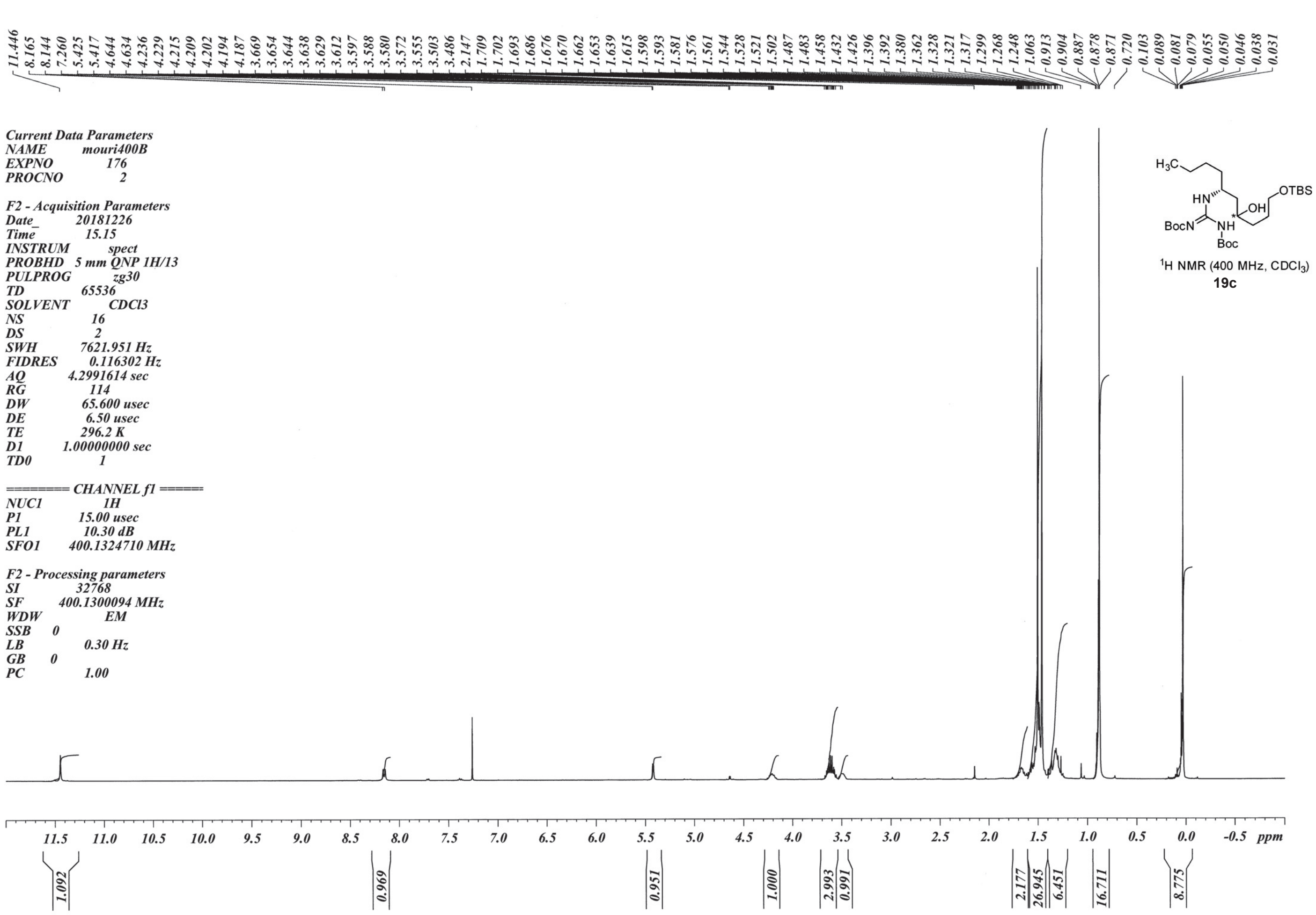
F2 - Acquisition Parameters
Date_ 20181227
Time 19.24
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 111
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

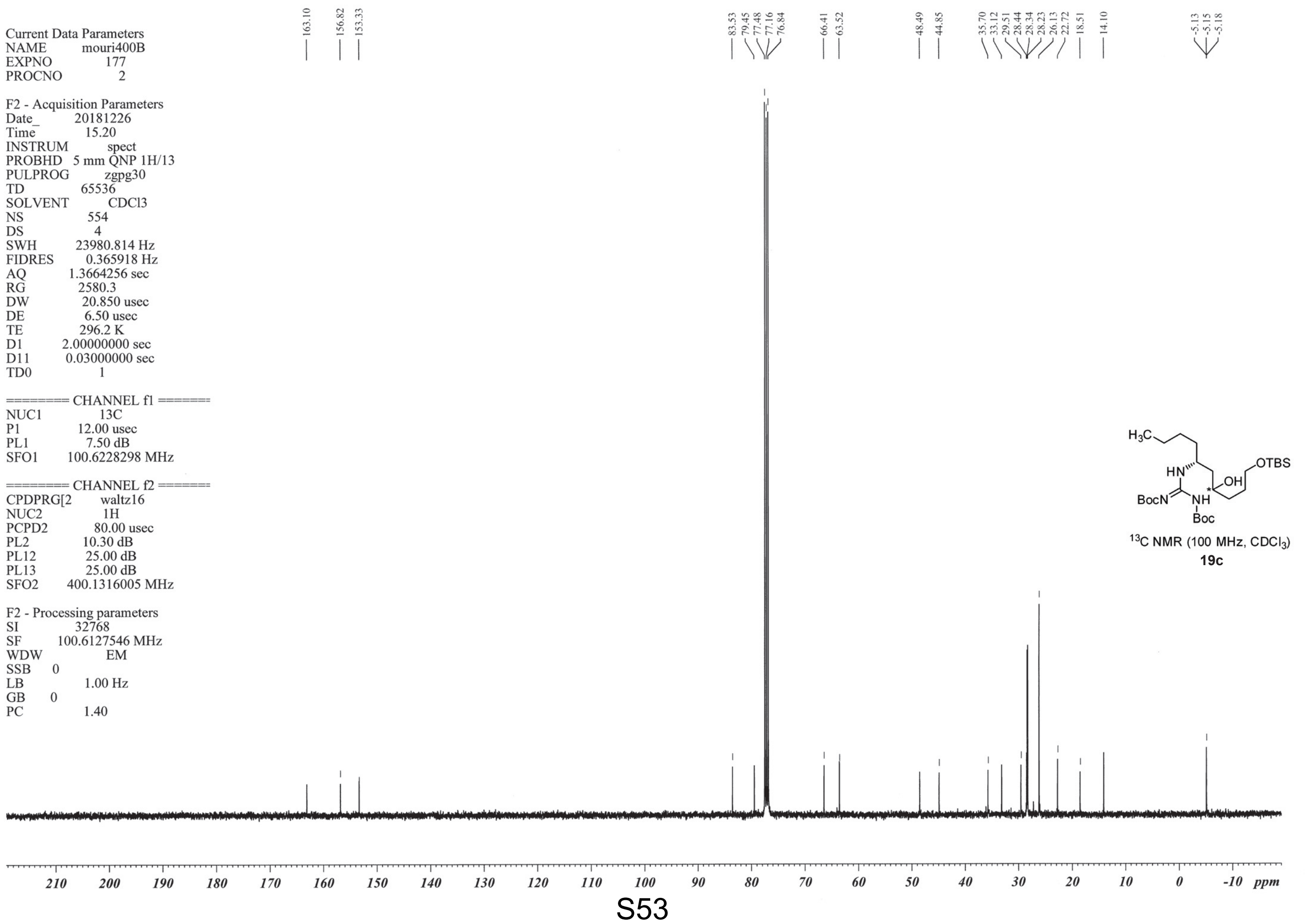
F2 - Processing parameters
SI 32768
SF 100.6127643 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

$^{13}$C NMR (100 MHz, CDCl$_3$)
**10c**



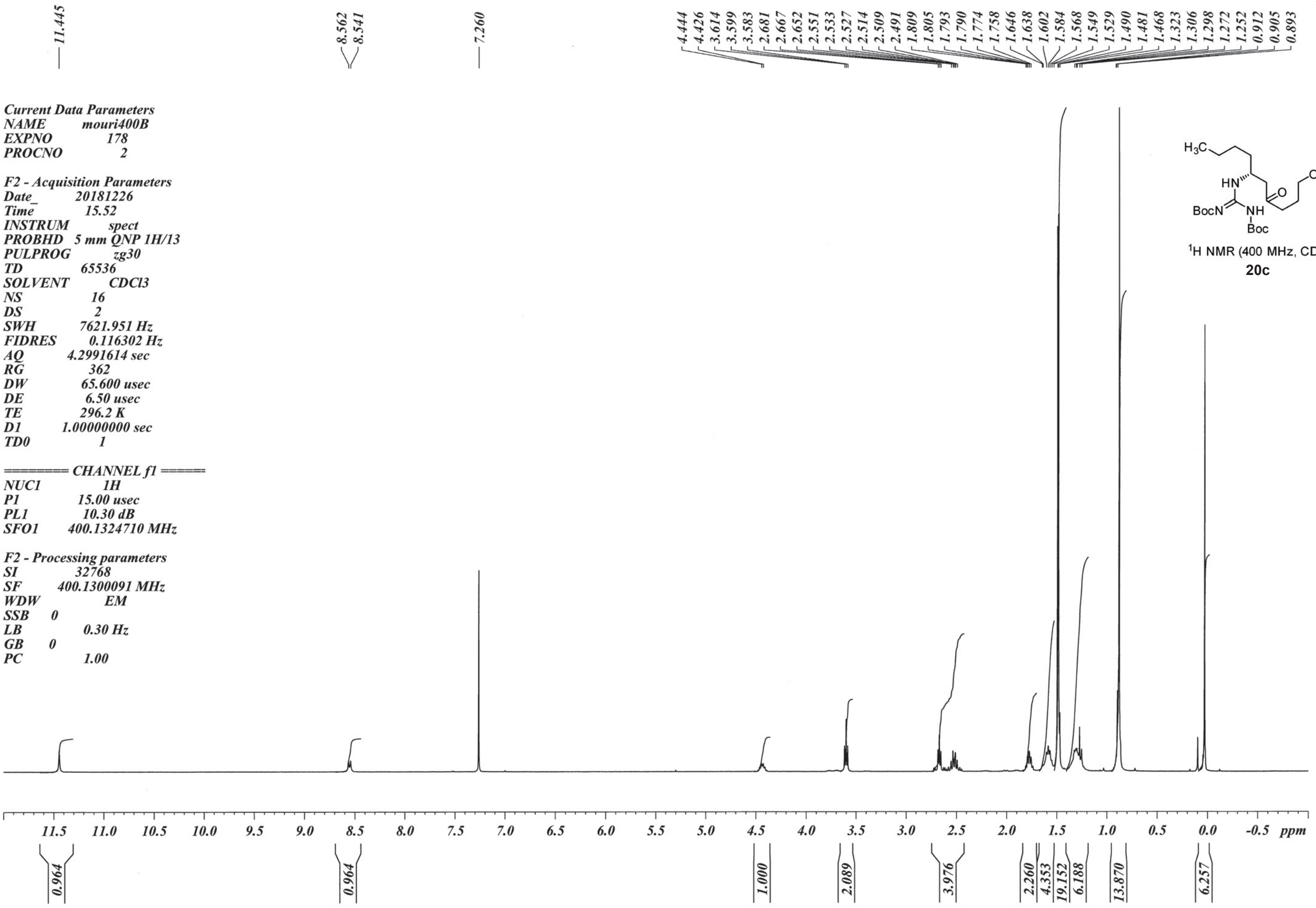
$^1$H NMR (400 MHz, CDCl$_3$)

**19c**



$^{13}$C NMR (100 MHz, CDCl$_3$)

**19c**



$^1$H NMR (400 MHz, CDCl$_3$)

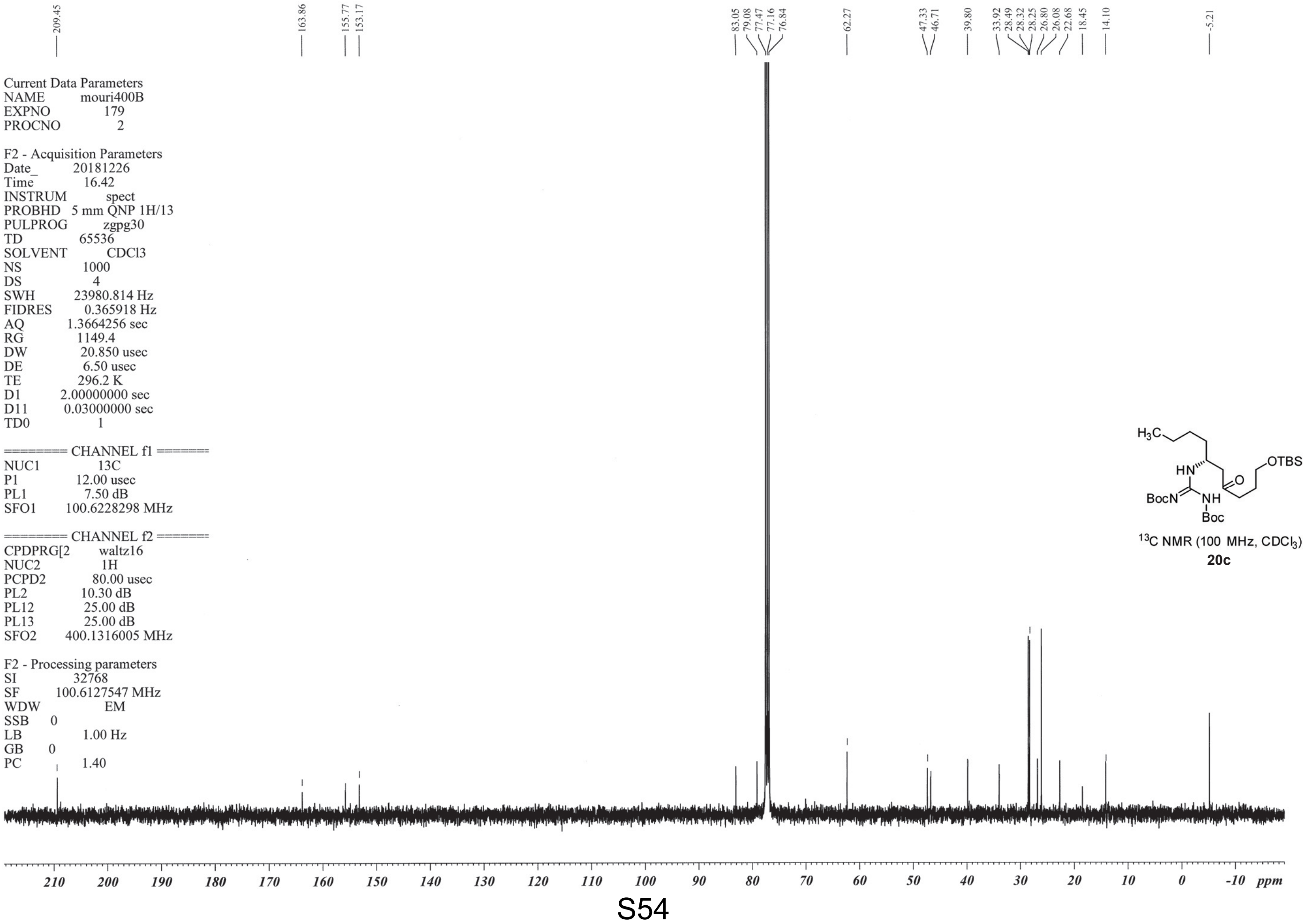
**20c**

***Current Data Parameters***
***NAME mouri400B***
***EXPNO 178***
***PROCNO 2***

***F2 - Acquisition Parameters***
***Date_ 20181226***
***Time 15.52***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT CDCl3***
***NS 16***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.116302 Hz***
***AQ 4.2991614 sec***
***RG 362***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 296.2 K***
***D1 1.00000000 sec***
***TD0 1***

***======== CHANNEL f1 ========***
***NUC1 1H***
***P1 15.00 usec***
***PL1 10.30 dB***
***SFO1 400.1324710 MHz***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300091 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***



$^{13}$C NMR (100 MHz, CDCl$_3$)

**20c**

Current Data Parameters
NAME mouri400B
EXPNO 179
PROCNO 2

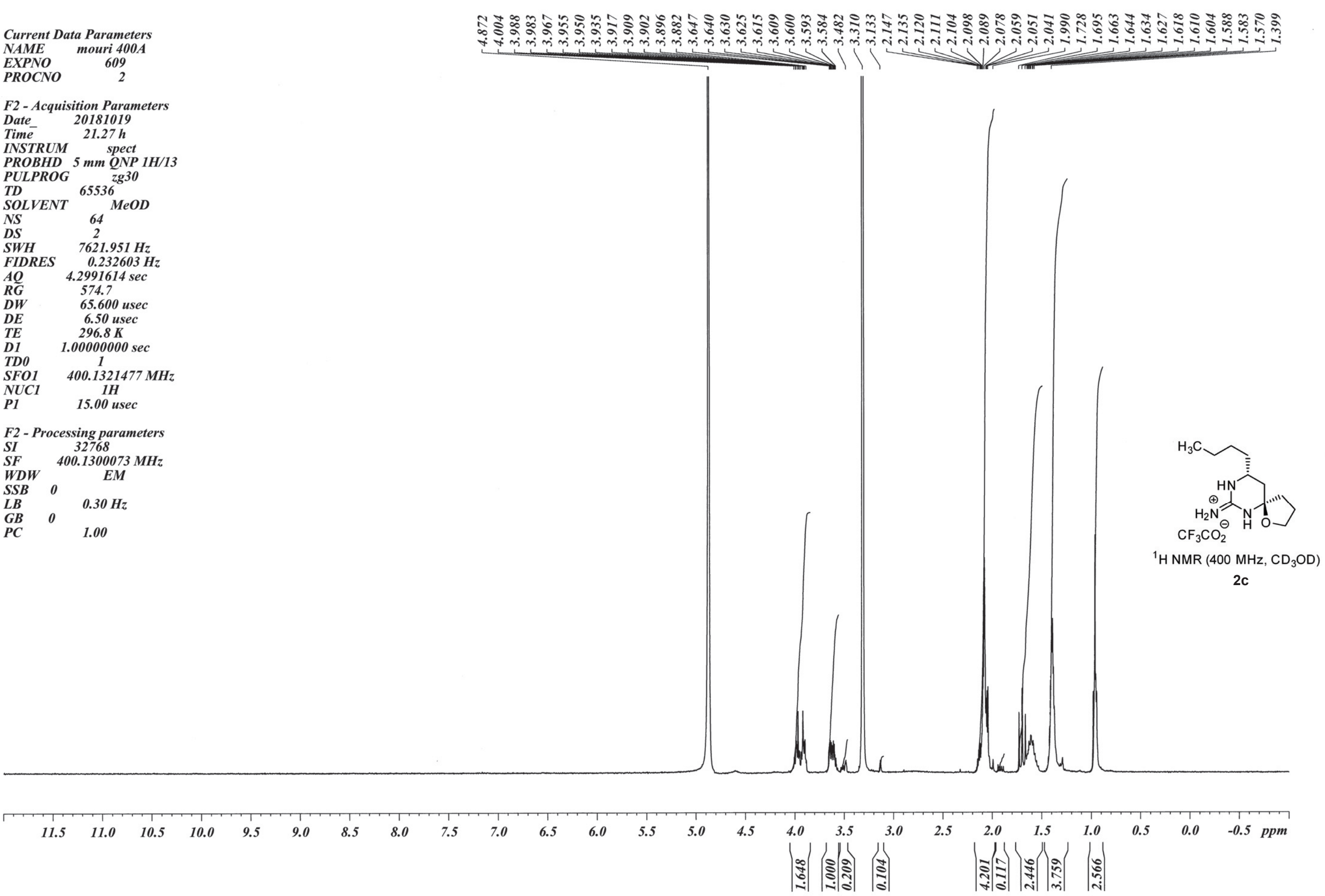
F2 - Acquisition Parameters
Date_ 20181226
Time 16.42
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 1149.4
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127547 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

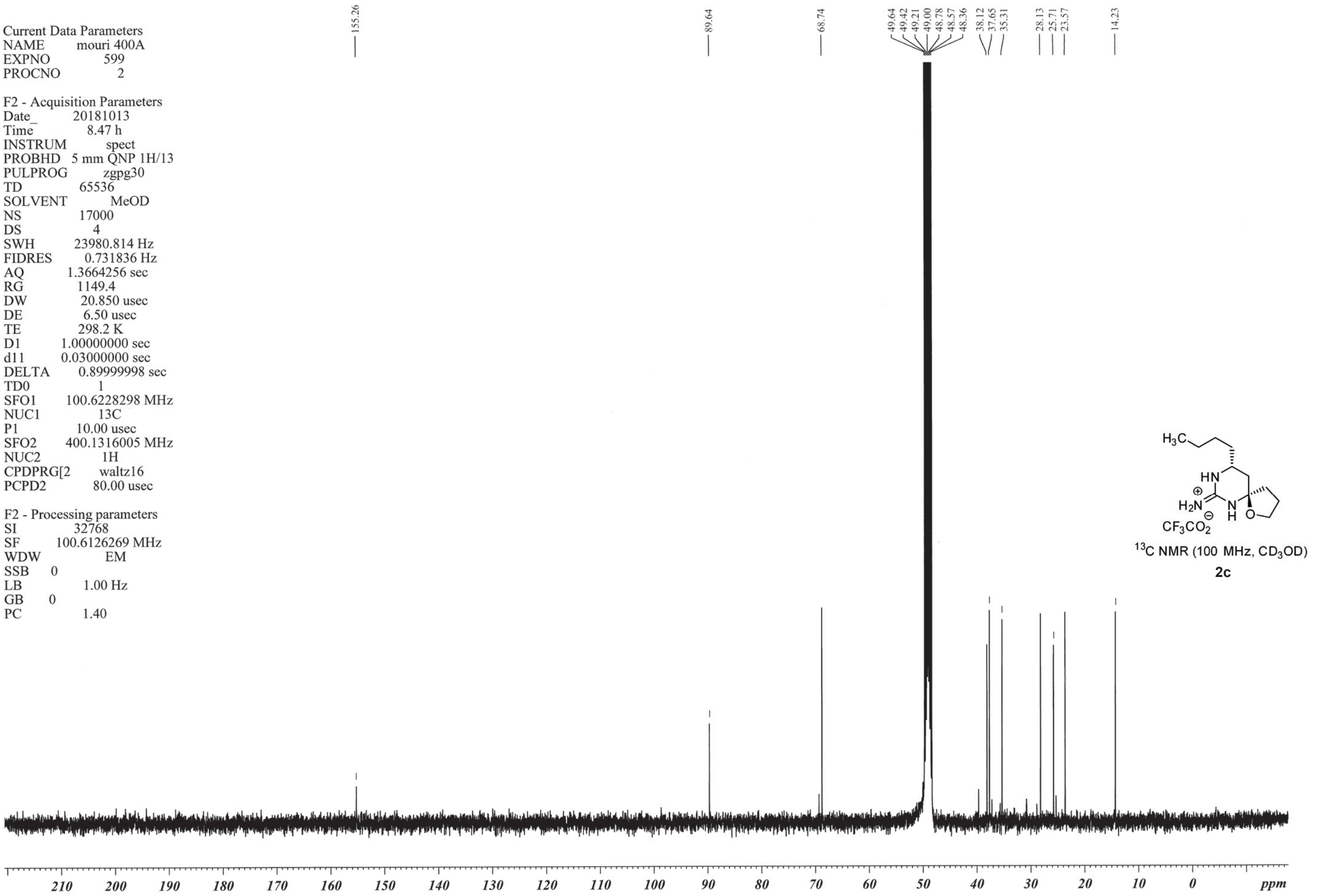
```
Current Data Parameters
NAME       mouri 400A
EXPNO           609
PROCNO            2

F2 - Acquisition Parameters
Date_       20181019
Time          21.27 h
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG          zg30
TD          65536
SOLVENT          MeOD
NS             64
DS              2
SWH         7621.951 Hz
FIDRES       0.232603 Hz
AQ         4.2991614 sec
RG            574.7
DW           65.600 usec
DE             6.50 usec
TE            296.8 K
D1       1.00000000 sec
TD0              1
SFO1     400.1321477 MHz
NUC1             1H
P1            15.00 usec

F2 - Processing parameters
SI          32768
SF       400.1300073 MHz
WDW              EM
SSB    0
LB             0.30 Hz
GB     0
PC             1.00
```



$^1$H NMR (400 MHz, $CD_3OD$)

**2c**

```
Current Data Parameters
NAME       mouri 400A
EXPNO           599
PROCNO            2

F2 - Acquisition Parameters
Date_       20181013
Time           8.47 h
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD          65536
SOLVENT          MeOD
NS          17000
DS              4
SWH        23980.814 Hz
FIDRES      0.731836 Hz
AQ         1.3664256 sec
RG            1149.4
DW            20.850 usec
DE              6.50 usec
TE             298.2 K
D1        1.00000000 sec
d11       0.03000000 sec
DELTA     0.89999998 sec
TD0              1
SFO1     100.6228298 MHz
NUC1            13C
P1            10.00 usec
SFO2     400.1316005 MHz
NUC2             1H
CPDPRG[2       waltz16
PCPD2          80.00 usec

F2 - Processing parameters
SI          32768
SF       100.6126269 MHz
WDW              EM
SSB    0
LB              1.00 Hz
GB     0
PC              1.40
```



$^{13}$C NMR (100 MHz, $CD_3OD$)

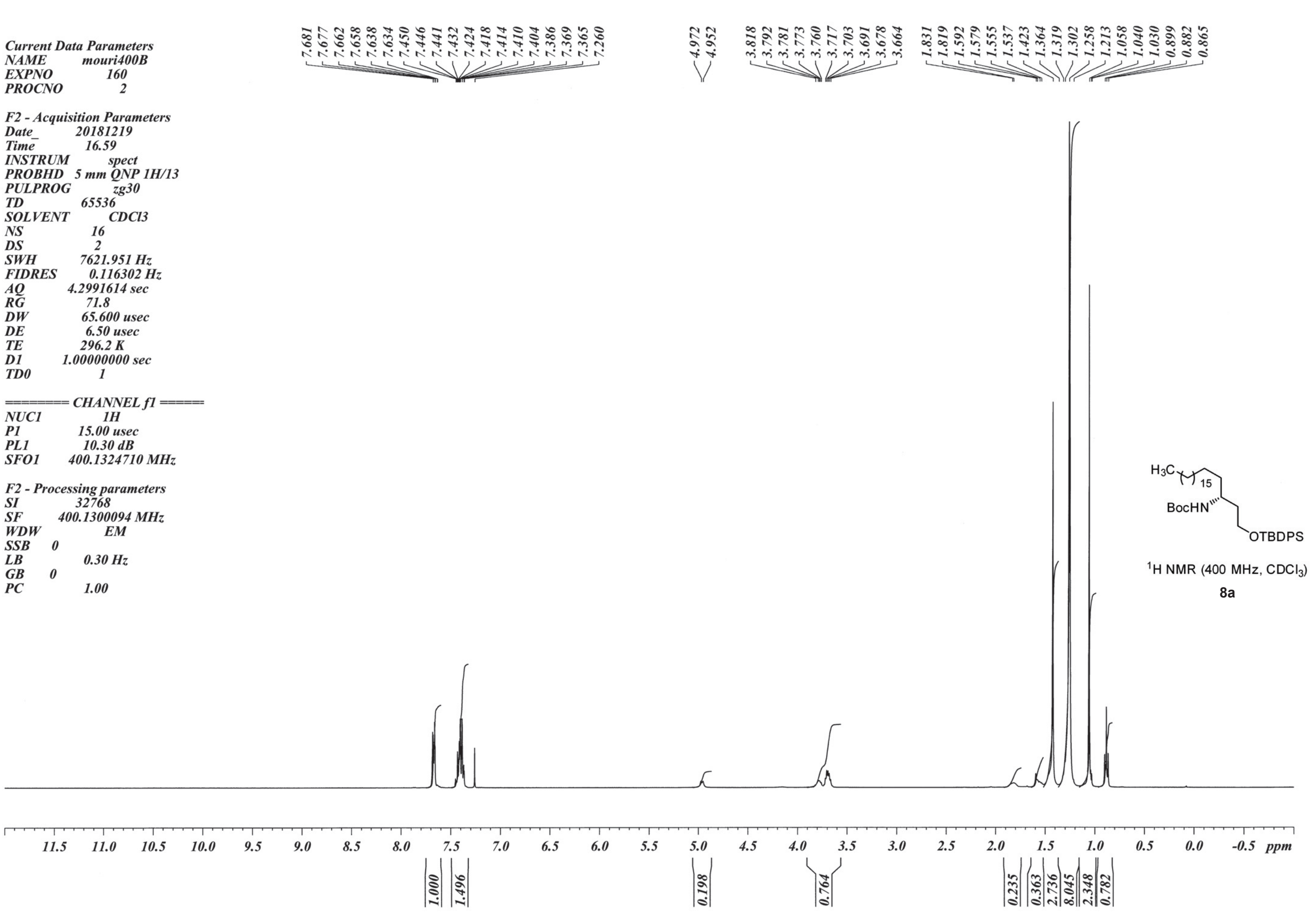
**2c**

***Current Data Parameters***
***NAME mouri400B***
***EXPNO 160***
***PROCNO 2***

***F2 - Acquisition Parameters***
***Date_ 20181219***
***Time 16.59***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT CDCl3***
***NS 16***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.116302 Hz***
***AQ 4.2991614 sec***
***RG 71.8***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 296.2 K***
***D1 1.00000000 sec***
***TD0 1***

***======== CHANNEL f1 ========***
***NUC1 1H***
***P1 15.00 usec***
***PL1 10.30 dB***
***SFO1 400.1324710 MHz***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300094 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***



$^1$H NMR (400 MHz, $CDCl_3$)

**8a**

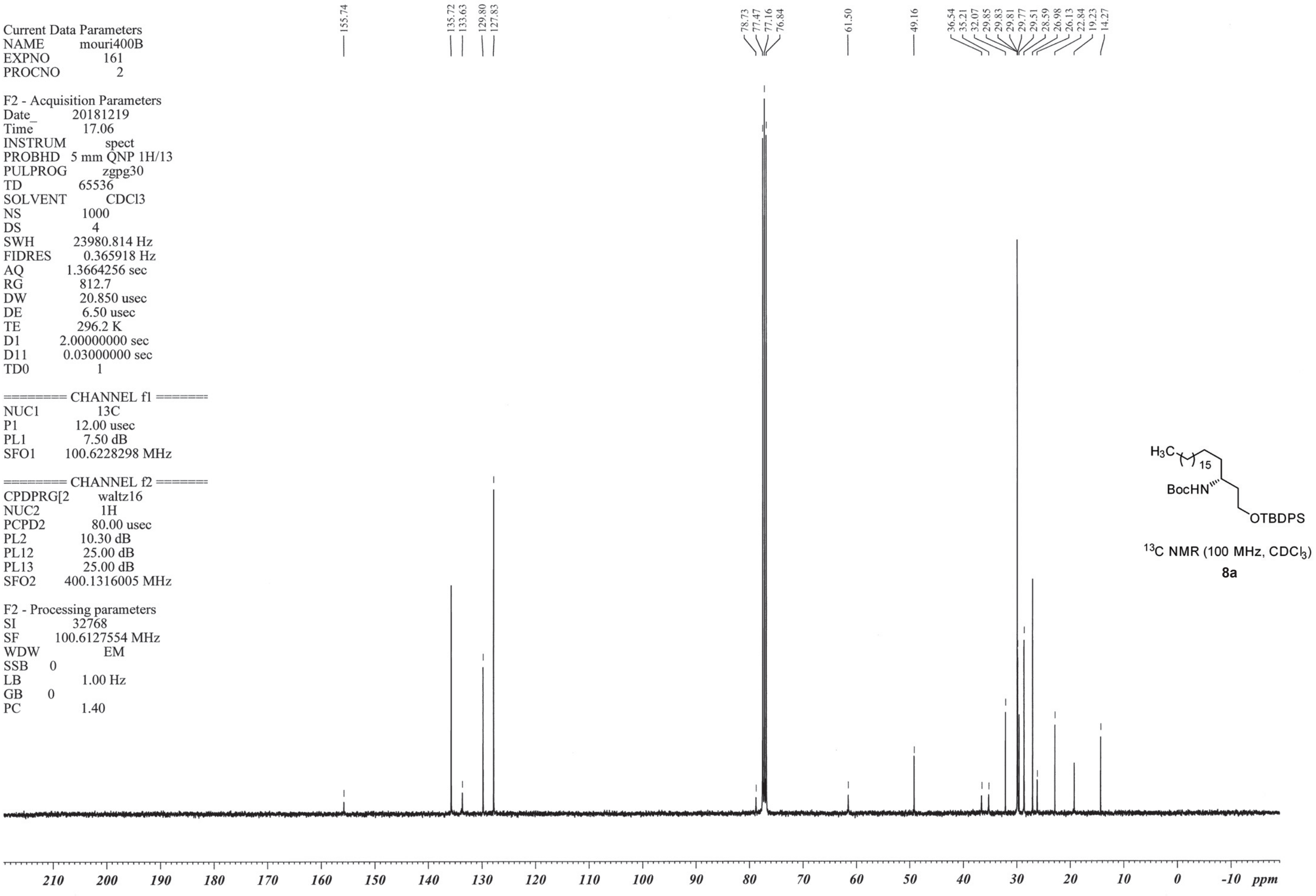
Current Data Parameters
NAME mouri400B
EXPNO 161
PROCNO 2

F2 - Acquisition Parameters
Date_ 20181219
Time 17.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 812.7
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127554 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



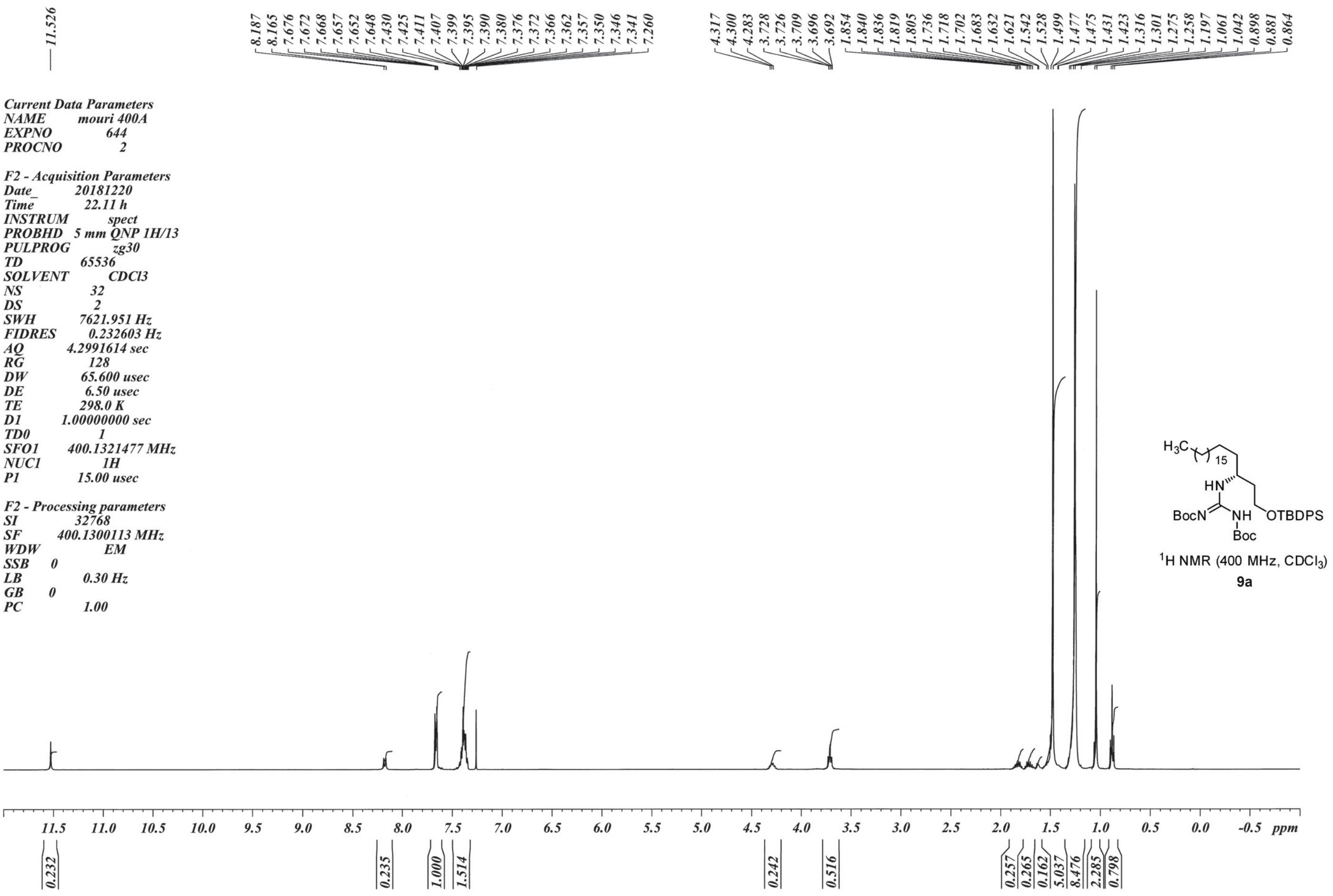
$^{13}$C NMR (100 MHz, $CDCl_3$)

**8a**

***Current Data Parameters***
***NAME mouri 400A***
***EXPNO 644***
***PROCNO 2***

***F2 - Acquisition Parameters***
***Date_ 20181220***
***Time 22.11 h***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT CDCl3***
***NS 32***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.232603 Hz***
***AQ 4.2991614 sec***
***RG 128***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 298.0 K***
***D1 1.00000000 sec***
***TD0 1***
***SFO1 400.1321477 MHz***
***NUC1 1H***
***P1 15.00 usec***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300113 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***



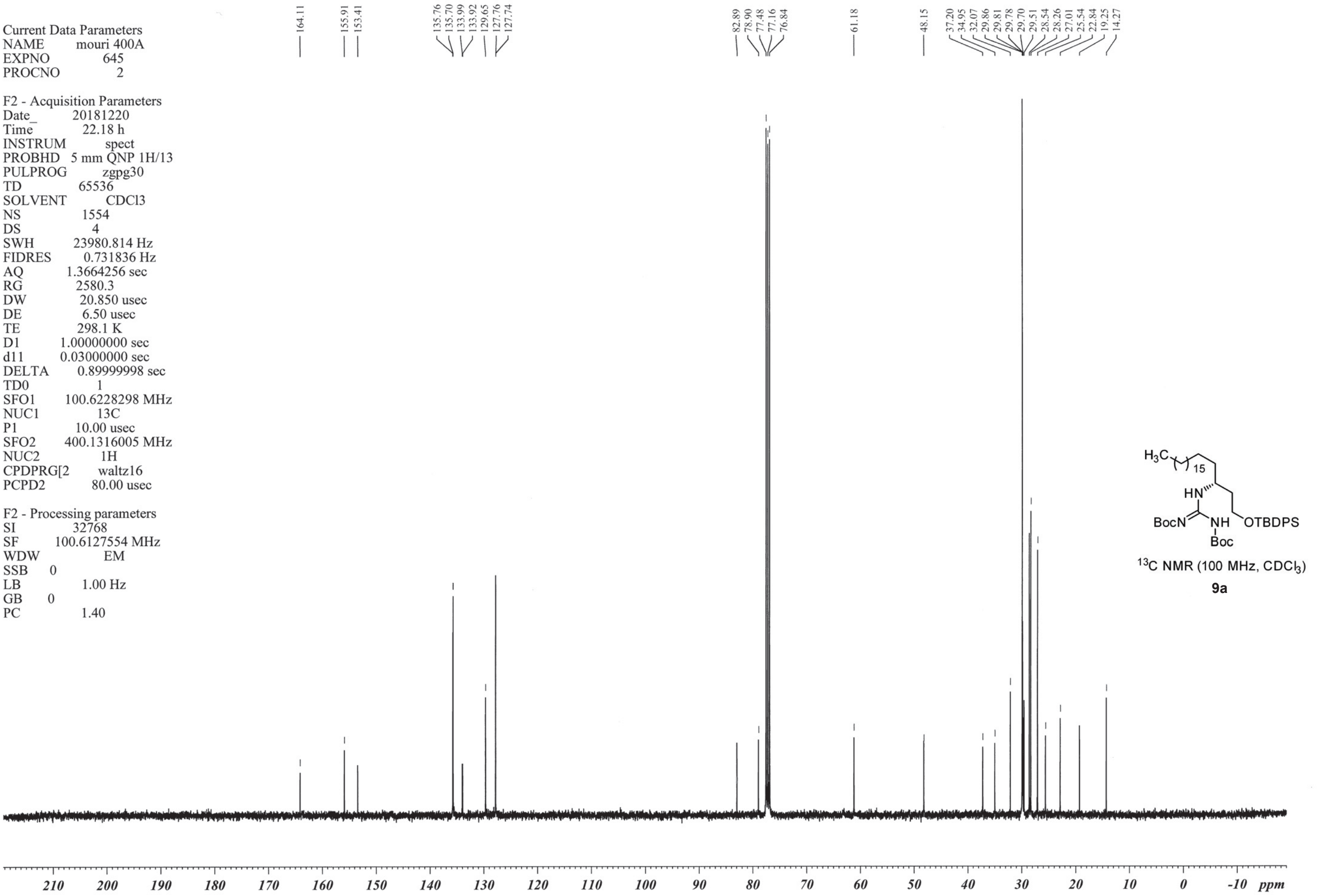
$^1$H NMR (400 MHz, CDCl$_3$)

**9a**

Current Data Parameters
NAME mouri 400A
EXPNO 645
PROCNO 2

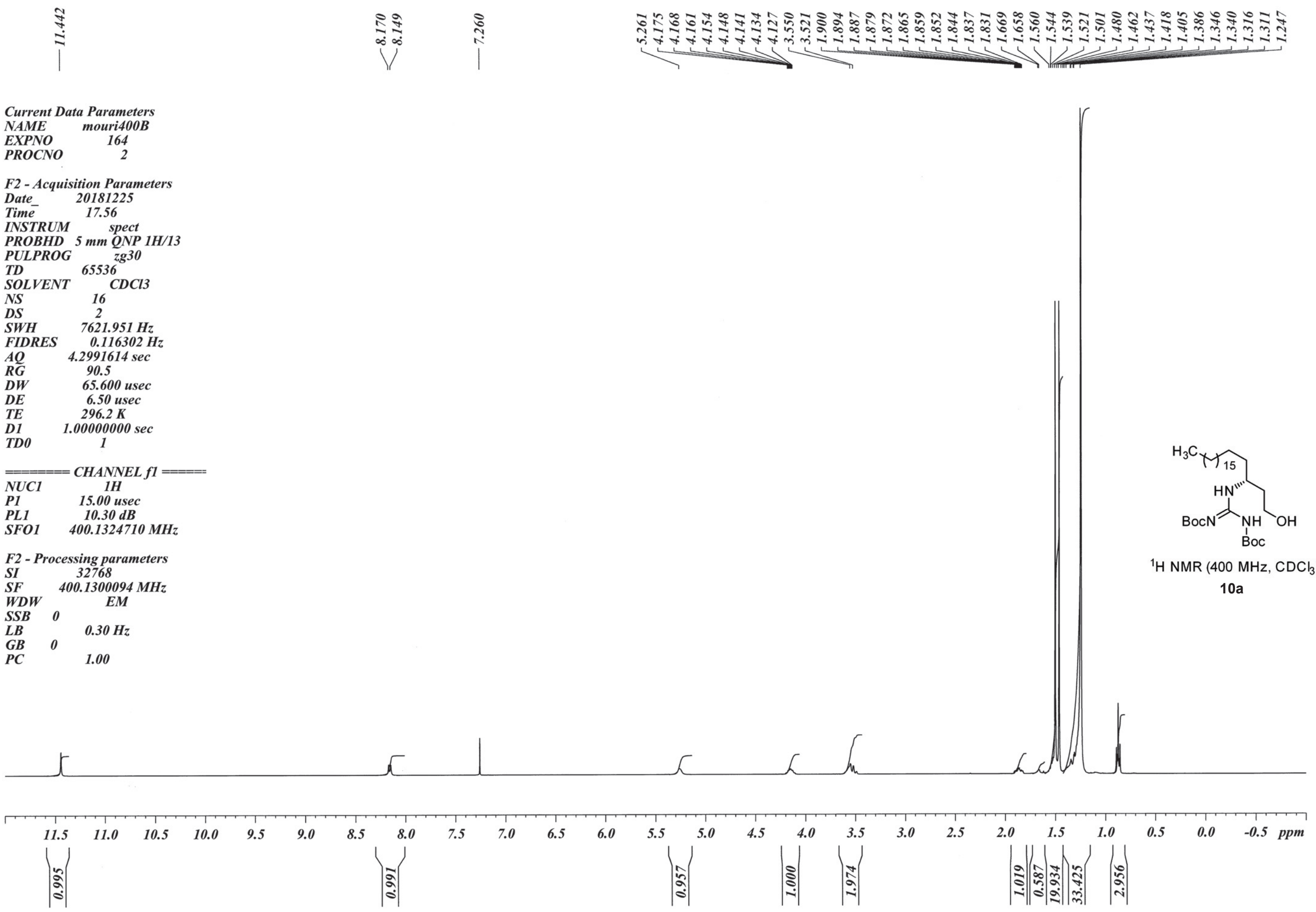
F2 - Acquisition Parameters
Date_ 20181220
Time 22.18 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1554
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6127554 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



$^{13}$C NMR (100 MHz, CDCl$_3$)

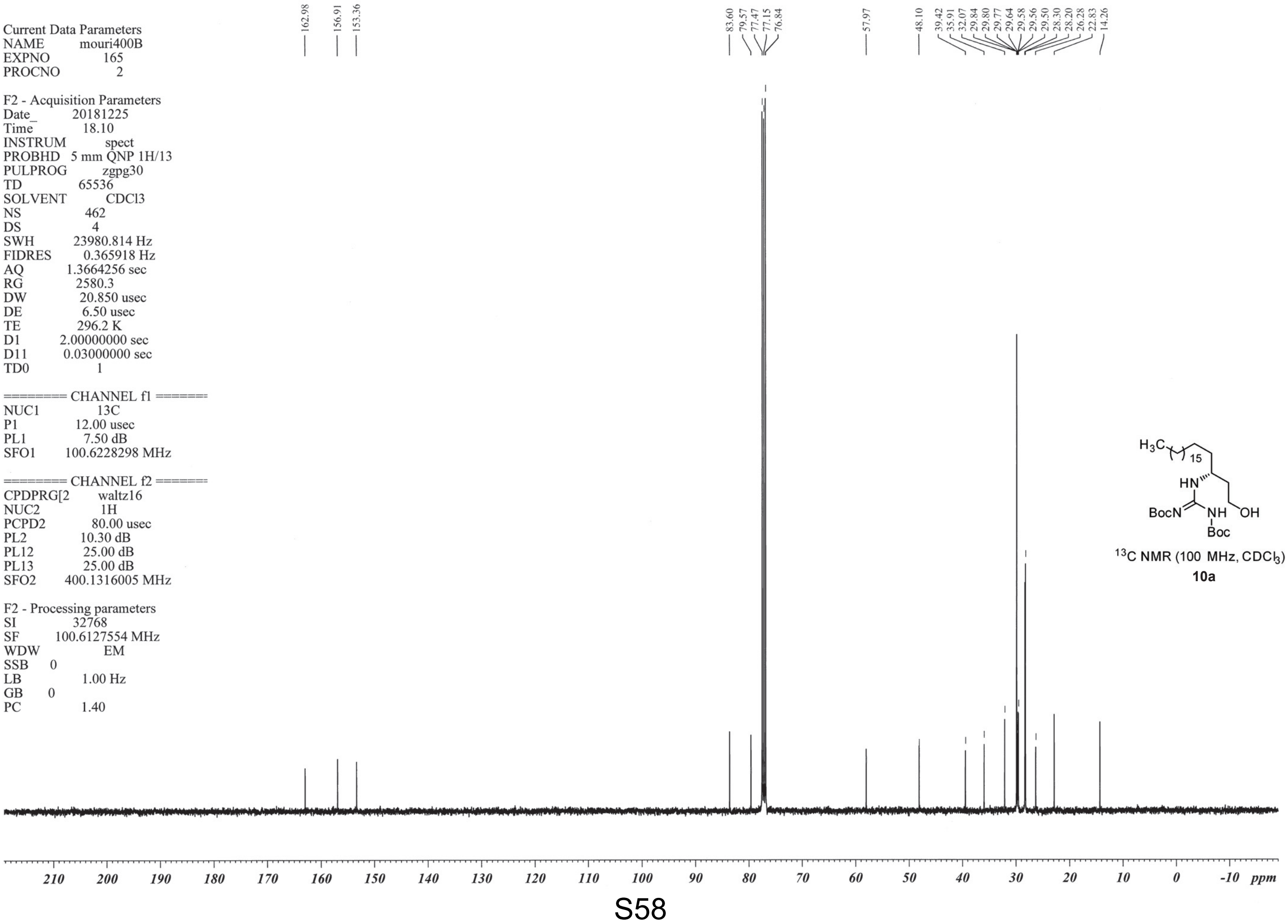
**9a**



```
Current Data Parameters
NAME        mouri400B
EXPNO             164
PROCNO              2

F2 - Acquisition Parameters
Date_       20181225
Time           17.56
INSTRUM         spect
PROBHD  5 mm QNP 1H/13
PULPROG          zg30
TD             65536
SOLVENT         CDCl3
NS                16
DS                 2
SWH        7621.951 Hz
FIDRES     0.116302 Hz
AQ        4.2991614 sec
RG              90.5
DW            65.600 usec
DE              6.50 usec
TE             296.2 K
D1        1.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              1H
P1             15.00 usec
PL1            10.30 dB
SFO1     400.1324710 MHz

F2 - Processing parameters
SI              32768
SF        400.1300094 MHz
WDW                EM
SSB     0
LB              0.30 Hz
GB      0
PC              1.00
```

$^1$H NMR (400 MHz, CDCl$_3$)

**10a**



```
Current Data Parameters
NAME        mouri400B
EXPNO             165
PROCNO              2

F2 - Acquisition Parameters
Date_       20181225
Time           18.10
INSTRUM         spect
PROBHD  5 mm QNP 1H/13
PULPROG        zgpg30
TD             65536
SOLVENT         CDCl3
NS               462
DS                 4
SWH       23980.814 Hz
FIDRES     0.365918 Hz
AQ        1.3664256 sec
RG            2580.3
DW            20.850 usec
DE              6.50 usec
TE             296.2 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1             13C
P1             12.00 usec
PL1             7.50 dB
SFO1     100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2       waltz16
NUC2              1H
PCPD2          80.00 usec
PL2            10.30 dB
PL12           25.00 dB
PL13           25.00 dB
SFO2     400.1316005 MHz

F2 - Processing parameters
SI              32768
SF        100.6127554 MHz
WDW                EM
SSB     0
LB              1.00 Hz
GB      0
PC              1.40
```

$^{13}$C NMR (100 MHz, CDCl$_3$)

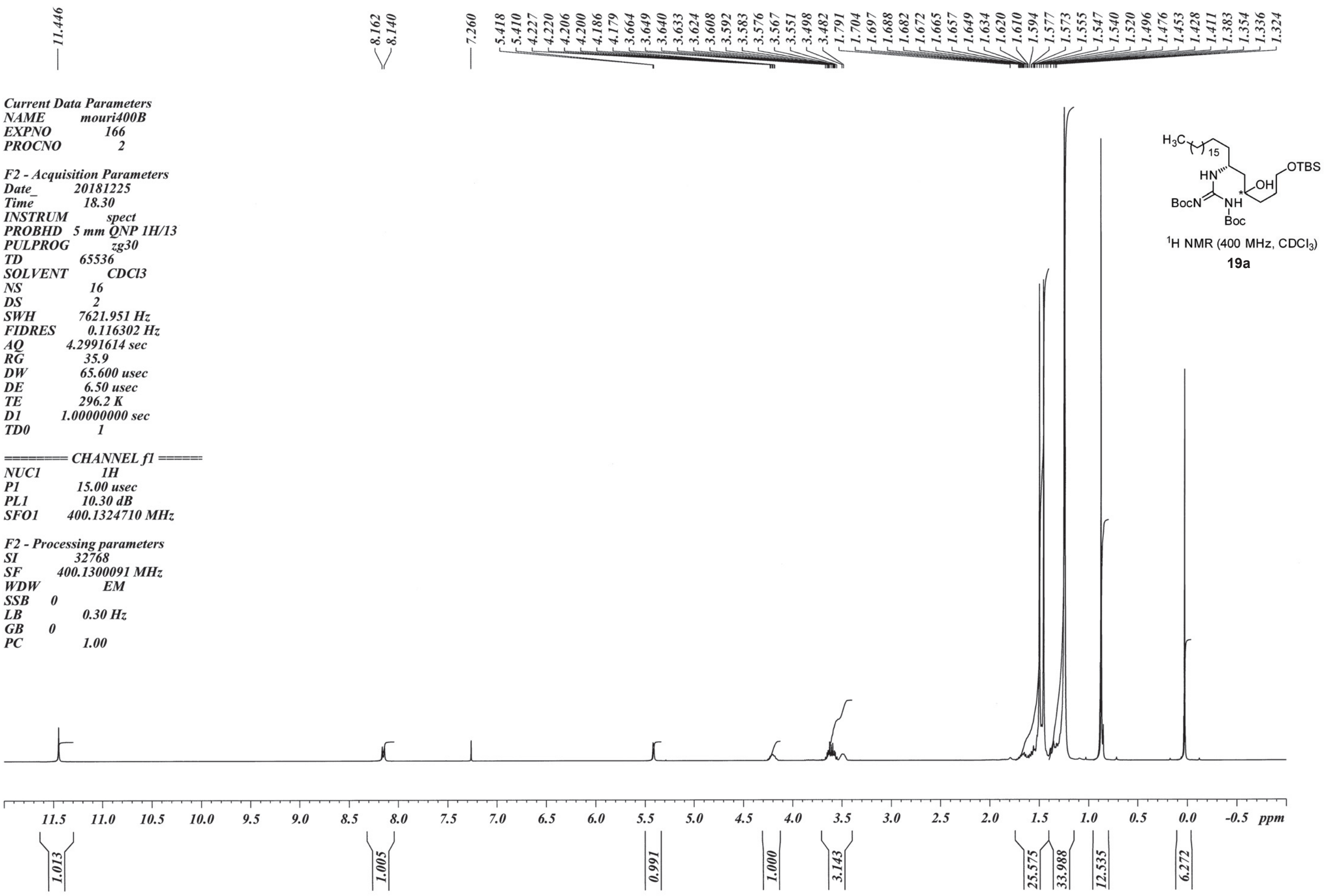
**10a**

***Current Data Parameters***
***NAME mouri400B***
***EXPNO 166***
***PROCNO 2***

***F2 - Acquisition Parameters***
***Date_ 20181225***
***Time 18.30***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT CDCl3***
***NS 16***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.116302 Hz***
***AQ 4.2991614 sec***
***RG 35.9***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 296.2 K***
***D1 1.00000000 sec***
***TD0 1***

***======== CHANNEL f1 ========***
***NUC1 1H***
***P1 15.00 usec***
***PL1 10.30 dB***
***SFO1 400.1324710 MHz***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300091 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***



$^1$H NMR (400 MHz, CDCl$_3$)
**19a**

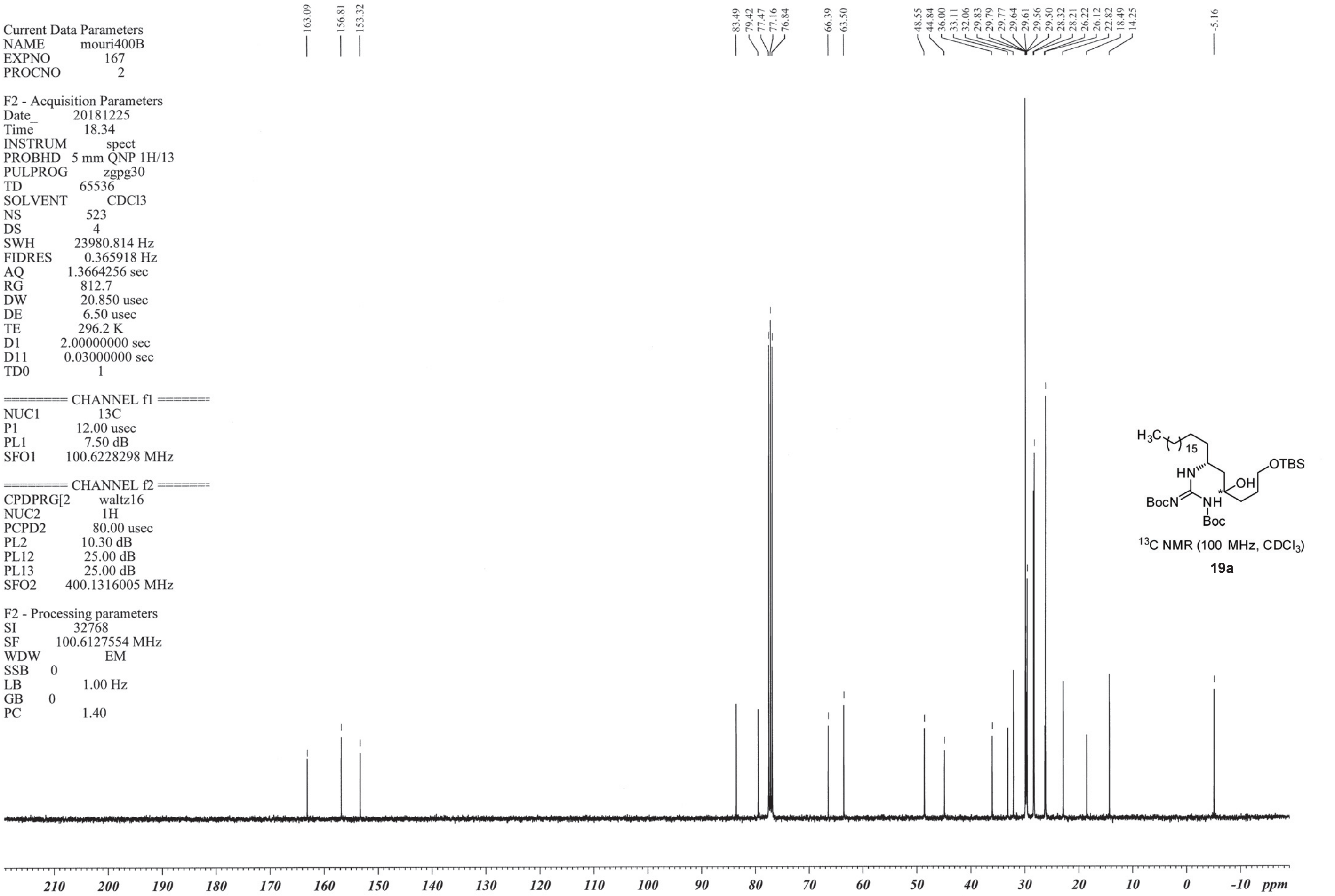
Current Data Parameters
NAME mouri400B
EXPNO 167
PROCNO 2

F2 - Acquisition Parameters
Date_ 20181225
Time 18.34
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 523
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 812.7
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

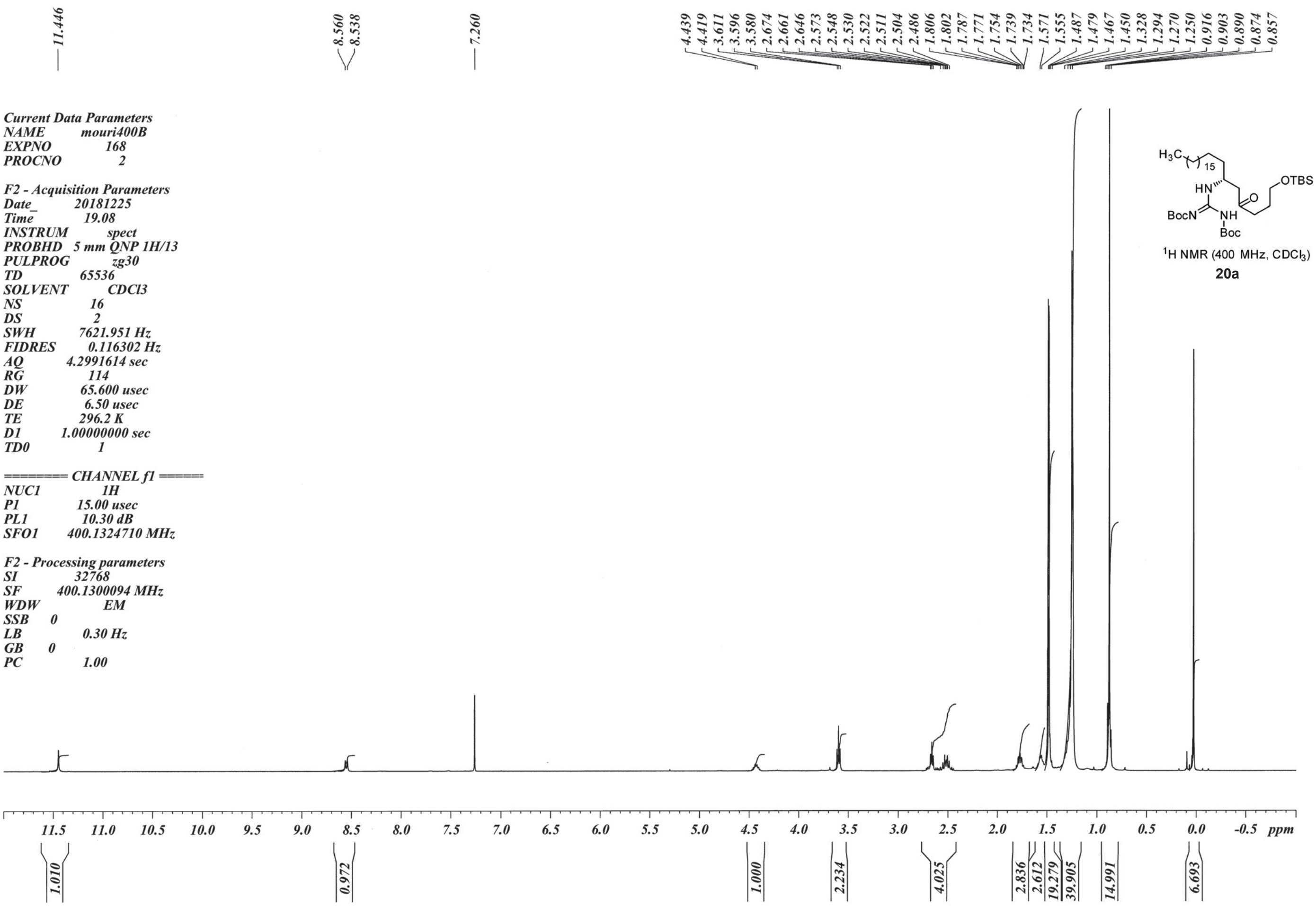
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127554 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



$^{13}$C NMR (100 MHz, CDCl$_3$)
**19a**



***Current Data Parameters***
***NAME mouri400B***
***EXPNO 168***
***PROCNO 2***

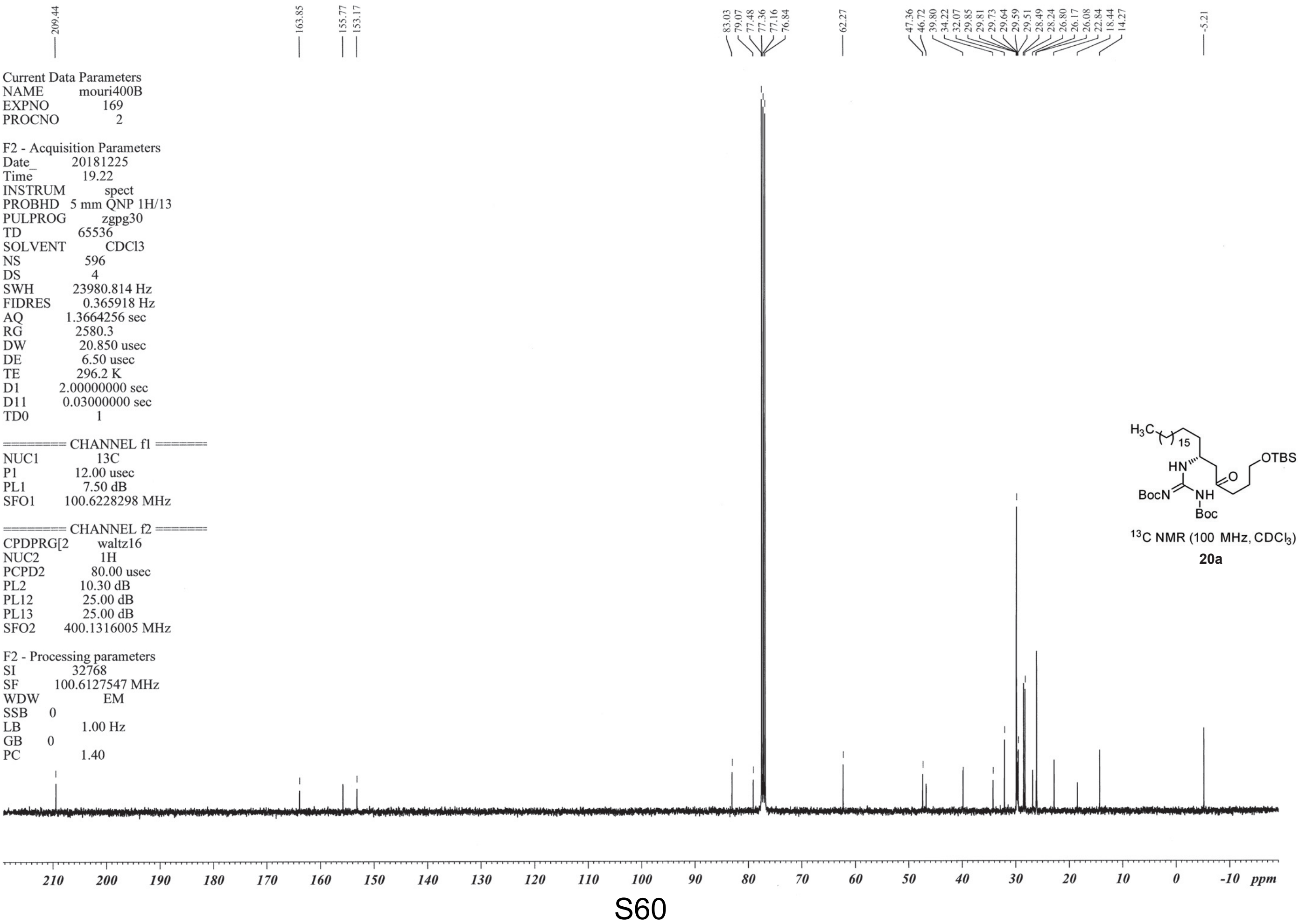
***F2 - Acquisition Parameters***
***Date_ 20181225***
***Time 19.08***
***INSTRUM spect***
***PROBHD 5 mm QNP 1H/13***
***PULPROG zg30***
***TD 65536***
***SOLVENT CDCl3***
***NS 16***
***DS 2***
***SWH 7621.951 Hz***
***FIDRES 0.116302 Hz***
***AQ 4.2991614 sec***
***RG 114***
***DW 65.600 usec***
***DE 6.50 usec***
***TE 296.2 K***
***D1 1.00000000 sec***
***TD0 1***

***======== CHANNEL f1 ========***
***NUC1 1H***
***P1 15.00 usec***
***PL1 10.30 dB***
***SFO1 400.1324710 MHz***

***F2 - Processing parameters***
***SI 32768***
***SF 400.1300094 MHz***
***WDW EM***
***SSB 0***
***LB 0.30 Hz***
***GB 0***
***PC 1.00***

$^1$H NMR (400 MHz, CDCl$_3$)

**20a**



Current Data Parameters
NAME mouri400B
EXPNO 169
PROCNO 2

F2 - Acquisition Parameters
Date_ 20181225
Time 19.22
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 596
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

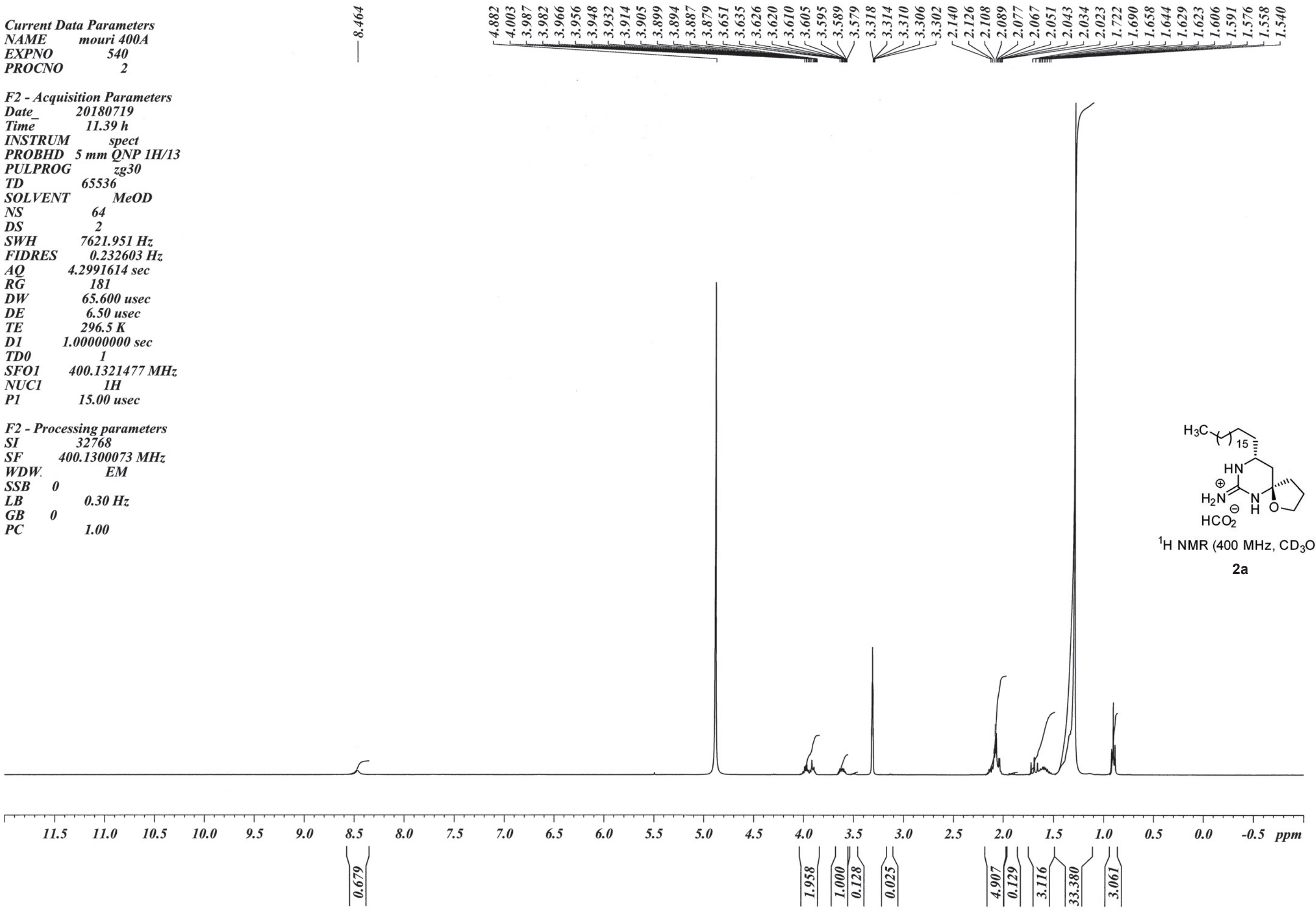
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127547 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

$^{13}$C NMR (100 MHz, CDCl$_3$)

**20a**



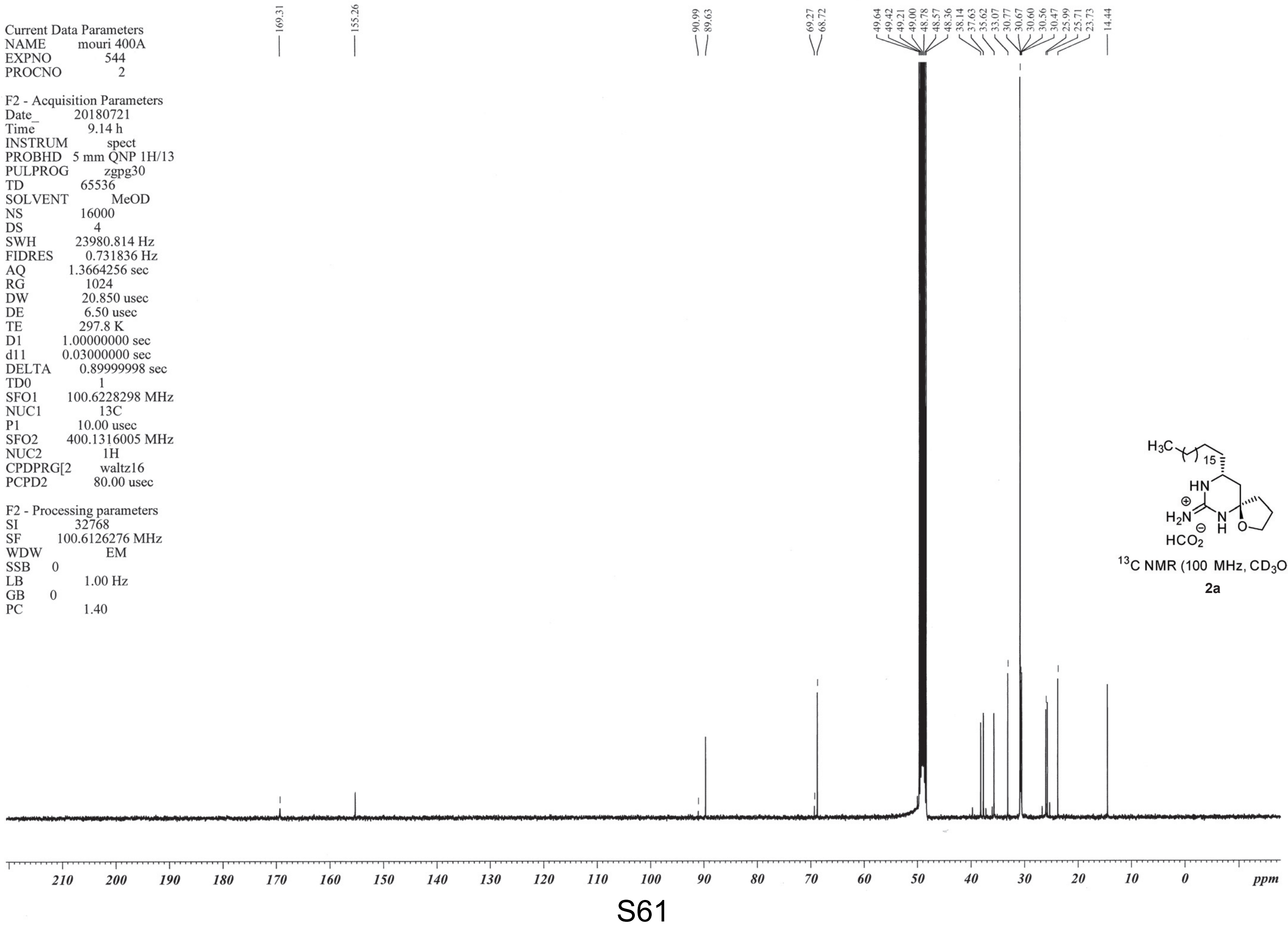
*Current Data Parameters*
*NAME mouri 400A*
*EXPNO 540*
*PROCNO 2*

*F2 - Acquisition Parameters*
*Date_ 20180719*
*Time 11.39 h*
*INSTRUM spect*
*PROBHD 5 mm QNP 1H/13*
*PULPROG zg30*
*TD 65536*
*SOLVENT MeOD*
*NS 64*
*DS 2*
*SWH 7621.951 Hz*
*FIDRES 0.232603 Hz*
*AQ 4.2991614 sec*
*RG 181*
*DW 65.600 usec*
*DE 6.50 usec*
*TE 296.5 K*
*D1 1.00000000 sec*
*TD0 1*
*SFO1 400.1321477 MHz*
*NUC1 1H*
*P1 15.00 usec*

*F2 - Processing parameters*
*SI 32768*
*SF 400.1300073 MHz*
*WDW EM*
*SSB 0*
*LB 0.30 Hz*
*GB 0*
*PC 1.00*

$^1$H NMR (400 MHz, CD$_3$OD)

**2a**



Current Data Parameters
NAME mouri 400A
EXPNO 544
PROCNO 2

F2 - Acquisition Parameters
Date_ 20180721
Time 9.14 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 16000
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 1024
DW 20.850 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

F2 - Processing parameters
SI 32768
SF 100.6126276 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

$^{13}$C NMR (100 MHz, CD$_3$OD)

**2a**