Supporting Information

Asymmetric Synthesis of Crambescin A-C Carboxylic Acids and Their Inhibitory Activity on Voltage-Gated Sodium Channels

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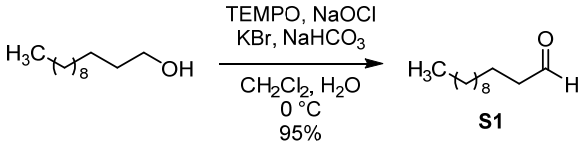
General Experimental

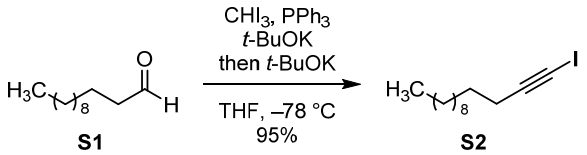
Infrared spectra (IR) were recorded on a JASCO FT/IR-8300 spectrophotometer and are reported in wave number (cm^{-1}). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Varian Gemini-2000 (300 MHz), a Bruker Avance-400 (400 MHz), or a Bruker Avance-600 (600 MHz) spectrometer. Chemical shifts of all compounds are reported in ppm relative to the residual undeuterated solvent (chloroform-*d* as δ = 7.26, methanol-d_4 as δ = 3.31). Data were reported as follows: Chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, 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 δ = 77.0, methanol-d_4 as δ = 49.0). All NMR were measured at 300 K. High-resolution mass spectra (HRMS) were recorded on an Applied Biosystems Mariner ESI-TOF spectrometer for ESI-MS or a JEOL JMS-700 MStation for EI-MS, and reported in *m*/*z*. Elemental analyses were performed by the Analytical Laboratory of Graduate School of Bioagricultural Sciences, Nagoya University.

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 (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 60N (spherical, neutral, particle size 0.04-0.05 mm, Kanto, #37563-79) was used for neutral silica gel flash column chromatography. Silica gel 60 (spherical, particle size 0.04-0.05 mm, Kanto, #37562-84) was used for silica gel flash column chromatography. Chromatorex®-DNH (particle size MB100-75/200, Fuji Silysia Chemical Ltd. HU20792) was used for Chromatorex DNH silica gel column chromatography. Chromatorex® C8 (particle size MB100-75/200, Fuji Silysia Chemical Ltd. KU11202) was used for Chromatorex C8 silica gel column chromatography. Preparative TLC separations were carried out on 0.5 mm silica gel plates 60F254 (Merck). Dry THF, Et_2O, and CH_2Cl_2 were purchased from Kanto Chemical Co., Inc. Dry HMPA, DMF, toluene, Et_3N, and pyridine were distilled from CaH_2. Dry MeOH was distilled from $Mg(OMe)_2$. Celite® (Hyflo Super-Cel Celite®) was purchased from Nacalai tesque Co., Inc. Florisil® was purchased from Kanto chemical Co., Inc. InI (anhydrous, powder, 99.999%) and CuI (powder and chunks, 99.999%) were purchased from sigma-Aldrich. All other commercially available reagents were as received.

^1H-NMR, ^{13}C-NMR, and IR data for compounds **5**, **6**, **9** to **16**, and **2** were identical to those reported previously for the corresponding compounds (Nishikawa, T. *et al. Org. Biomol. Chem.* **2014**, *12*, 53).



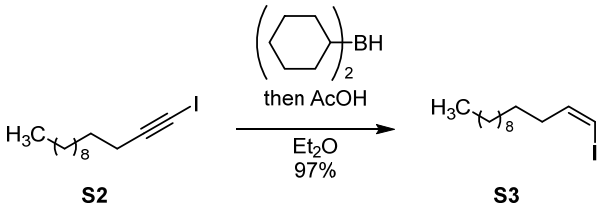
dodecanal S1: This compound was synthesized according to the modified procedure of Anelli *et al*.[1] To a mixture of 1-dodecanol (12.5 g, 66.9 mmol) in CH_2Cl_2 (200 mL) and sat. $NaHCO_3$ solution (200 mL) were added TEMPO (106 mg, 0.678 mmol) and KBr (797 mg, 6.69 mmol) at 0 °C under N_2 atmosphere. To a vigorously stirred mixture was added dropwise ca. 6% aqueous solution of NaOCl (ca. 50 mL) until the color of reaction mixture became brown and the temperature was maintained below 0 °C. After completion of the reaction, the solution was filtered through a pad of Celite® (eluted with CH_2Cl_2). The resulting mixture was partitioned, and the aqueous layer was extracted with CH_2Cl_2 (300 mL x 2). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/Et_2O = 19/1 to 9/1) to afford dodecanal **S1** (11.7 g, 95%) as a colorless oil.
IR (film): ν_{max} (cm^{-1}) 2925, 2854, 1728, 1466. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.87 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.20-1.36 (16H, m, -$CH_2(CH_2)_8CH_3$), 1.57-1.67 (2H, m, -CH_2CH_2CHO), 2.41 (2H, td, J = 7.5, 2.0 Hz, -CH_2CHO), 9.76 (1H, t, J = 2.0 Hz, -CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 22.1, 22.7, 29.2, 29.30, 29.34, 29.4, 29.6, 31.9, 43.9, 202.9. HRMS (EI, positive): calcd. For $C_{12}H_{24}O$, 184.1827; found, 184.1852.



iodoalkyne S2: This compound was synthesized according to the modified procedure of Rassat *et al*.[2] To a solution of CHI_3 (65.4 g, 0.166 mol) in anhydrous THF (600 mL) were added PPh_3 (43.5 g, 166 mmol) and then *t*-BuOK (18.6 g, 166 mmol) at room temperature under N_2 atmosphere. After being stirred for 15 min, to the reaction mixture was added a solution of dodecanal **S1** (20.4 g, 111 mmol) in THF (140 mL). After being stirred for 30 min, the reaction temperature was cooled to –78 °C, and then another portion of *t*-BuOK (62.0 g, 553 mmol) was added. The reaction temperature was warmed until the reaction was completed (ca. –60 °C) and then the reaction was quenched with brine (500 mL). The reaction mixture was filtered through a pad of Celite® (eluted with Et_2O), and the resulting mixture was extracted with Et_2O (500 mL x 2). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by

silica gel column chromatography (hexane) to afford iodoalkyne **S2** (32.2 g, 95%) as a yellow oil.

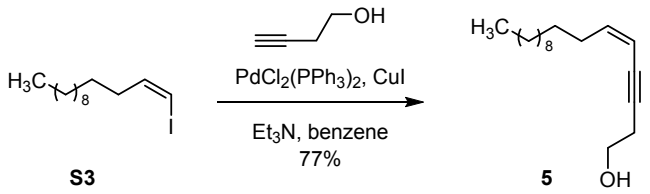
IR (film): ν_{max} (cm^{-1}) 2925, 2853, 1465. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, J = 6.5 Hz, -CH_2CH_3), 1.20-1.42 (16H, m, -$CH_2(CH_2)_8CH_3$), 1.47-1.55 (2H, m, I-C≡CCH_2CH_2-), 2.35 (2H, t, J = 7.0 Hz, I-C≡CCH_2CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) -7.75, 14.1, 20.8, 22.7, 28.5, 28.8, 29.1, 29.3, 29.5, 29.6, 31.9, 94.9. HRMS (EI, positive): calcd. For $C_{13}H_{23}I$, 306.0844; found, 306.0834.



S2 **S3**

***cis*-iodoalkene S3:** This compound was synthesized according to the modified procedure of Denmark *et al*.[3] A solution of $BH_3 \cdot SMe_2$ (2.0 M in toluene, 54.7 mL, 109 mmol) in anhydrous and degassed Et_2O (80 mL) was cooled to 5 °C. To the solution was added dropwise distilled cyclohexene (22.4 mL, 221 mmol) under N_2 atmosphere and the temperature was maintained below 15 °C. After being stirred at 5 °C for 15 min, the solution was allowed to warm to room temperature and stirred for 1 h. The resulting white suspension was cooled to 2-3 °C and a solution of iodoalkyne (30.4 g, 99.4 mmol) in Et_2O (30 mL) was added dropwise. After being stirred at 2-3 °C for 30 min, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The reaction mixture was cooled to 2-3 °C and acetic acid (50 mL, 873 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. After completion of the reaction, the reaction mixture was washed with H_2O (100 mL x 4). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane) to afford *cis*-iodoalkene **S3** (29.6 g, 97%) as a pale pink oil.

IR (film): ν_{max} (cm^{-1}) 2921, 2854, 1608, 1465, 1377, 1284. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.22-1.36 (16H, m, -$CH_2(CH_2)_8CH_3$), 1.36-1.48 (2H, m, ICH=$CHCH_2CH_2$-), 2.08-2.18 (2H, m, ICH=$CHCH_2$-), 6.12-6.21 (2H, m, ICH=$CHCH_2$-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 22.7, 28.0, 29.1, 29.3, 29.4, 29.55, 29.62, 31.9, 34.7, 82.1, 141.5. HRMS (EI, positive): calcd. For $C_{13}H_{25}I$, 308.1001; found, 308.0981.



S3 5

enyne 5: A solution of *cis*-iodoalkene **S3** (10.0 g, 32.4 mmol) in benzene (231 mL) was cooled to 0 °C. To the solution were added 3-butyn-1-ol (7.3 mL, 97.3 mmol), CuI (1.24 g, 6.49 mmol), $PdCl_2(PPh_3)_2$ (0.683 g, 0.973 mmol) and Et_3N (36 mL, 260 mmol) at 0 °C under Ar atmosphere. The resulting mixture was degassed by three freezed-thraw cycles, and the flask was filled with Ar. After being stirred at room temperature for 16 h, the reaction was quenched with sat. NH_4Cl solution (200 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with Et_2O (200 mL x 2). The combined organic layer was washed with H_2O (200 mL x 2) and brine (200 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (flash silica gel and Florisil®, hexane/Et_2O = 4/1) to afford enyne **5** (6.27 g, 77%) as a yellow oil.

IR (film): ν_{max} (cm^{-1}) 3350, 2925, 2854, 1466, 1044. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.20-1.35 (16H, m, -$CH_2(CH_2)_8CH_3$), 1.35-1.45 (2H, m, -CH_2CH_2CH=CH-), 1.74 (1H, br s, -O*H*), 2.28 (2H, qd, J = 7.5, 1.0 Hz, -CH_2CH=CH-), 2.62 (2H, td, J = 6.0, 2.0 Hz, -CH_2CH_2OH), 3.75 (2H, t, J = 6.0 Hz, -CH_2OH), 5.43 (1H, m, -CH_2CH=C*H*C≡C-), 5.86 (1H, dt, J = 10.5, 7.5 Hz, -CH_2CH=CHC≡C-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 22.7, 24.0, 28.8, 29.2, 29.3, 29.5, 29.59, 29.63, 29.7, 30.2, 31.9, 61.3, 79.4, 90.2, 108.7, 143.7. HRMS (EI, positive): calcd. For $C_{17}H_{30}O$, 250.2297; found, 250.2301.

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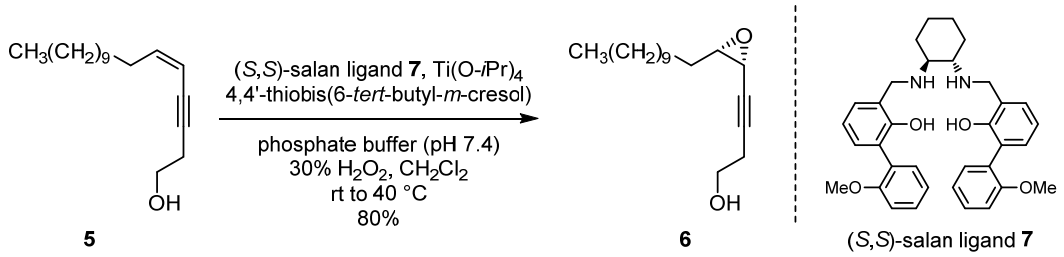
[1] Anelli, P. L.; Biffi, C.; Montanari, F.; Quici, S. *J. Org. Chem.* **1987**, *52*, 2559.

[2] Michel, P.; Rassat, A. *Tetrahedron Lett.* **1999**, *40*, 8579.

[3] Denmark, S. E.; Wang, Z. *Org. Synth.* **2005**, *81*, 42.



5 **6** (*S*,*S*)-salan ligand **7**

(–)-epoxide 6: This compound was synthesized according to the modified procedure of Katsuki *et al*.[4] To a solution of (*S*,*S*)-salan ligand **7** (1.18 g, 2.20 mmol) in dry CH_2Cl_2 (30 mL) was added freshly distilled Ti(O-*i*Pr)$_4$ (0.60 mL, 2.00 mmol) at room temperature under N_2 atmosphere. After being stirred at room temperature for 1 h, to the reaction mixture were added 4,4'-thiobis(6-*tert*-butyl-*m*-cresol) (470 mg, 1.30 mmol),[5] pH 7.4 phosphate buffer (2.5 mL), enyne **5** (5.00 g, 20.0 mmol) in dry CH_2Cl_2 (20 mL), and 30% H_2O_2 (4.5 mL, 40.0 mmol) under N_2 atmosphere. After being stirred at 40 °C for 7 h, the reaction mixture was allowed to cool to room temperature and to the reaction mixture was added solid NH_4Cl (7.5 g). The resulting mixture was filtered through a pad of Celite® (eluted with hexane), and the filtrate was washed with sat. NH_4Cl solution (50 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 flash column chromatography (hexane/Et_2O = 2/1) to afford (–)-epoxide **6** (4.25 g, 80%, 95% ee) as a yellow solid. Recrystallization from hexane afforded (–)-epoxide **6** (3.14 g, 74% yield, >99% ee) as a pale yellow solid. Enantiomeric excess was determined by chiral HPLC analysis of the corresponding *p*-nitrobenzoate derived from (–)-epoxide **6**. Chiral HPLC analysis (CHIRALPAK AS-H column, hexane/2-propanol = 9/1, flow rate = 0.50 mL/min, detection 270-nm light, 30 °C) t_R = 16.5 min (major isomer), 18.3 min (minor isomer). The absolute configuration was determined by the modified Mosher method of MTPA esters **S6a** and **S6b** (*vide infra*).

mp: 48 °C. $[\alpha]_D^{23}$ –9.27 (*c* 1.07, $CHCl_3$) for >99% ee. IR (film): ν_{max} (cm^{-1}) 3272, 2919, 2848, 1465, 1046, 879, 855. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 6.5 Hz, -CH_2CH_3), 1.20-1.42 (16H, m, -$CH_2(CH_2)_8CH_3$), 1.42-1.56 (2H, m, -$CH_2(CH_2)_8CH_3$), 1.63-1.72 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.77 (1H, t, *J* = 6.0 Hz, -O*H*), 2.51 (2H, td, *J* = 6.0, 1.5 Hz, -CHC≡CCH_2-), 3.01 (1H, td, *J* = 6.0, 4.0 Hz, -C*H*CHC≡C-), 3.42 (1H, dt, *J* = 4.0, 1.5 Hz, -CHC*H*C≡C-), 3.73 (2H, q, *J* = 6.0 Hz, -CH_2OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 22.7, 23.2, 25.9, 29.31, 29.33, 29.4, 29.53, 29.55, 29.62, 29.63, 31.9, 45.3, 58.1, 60.9, 77.2, 82.8. Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.38; H, 11.24.

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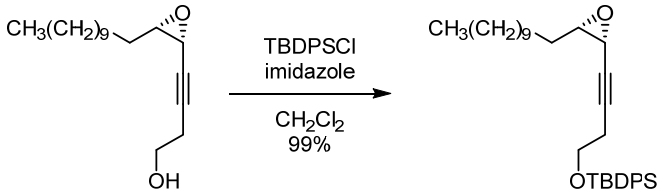
[4] Shimada, Y.; Kondo, S.; Ohara, Y.; Matsumoto, K.; Katsuki, T. *Synlett* **2007**, 2445.

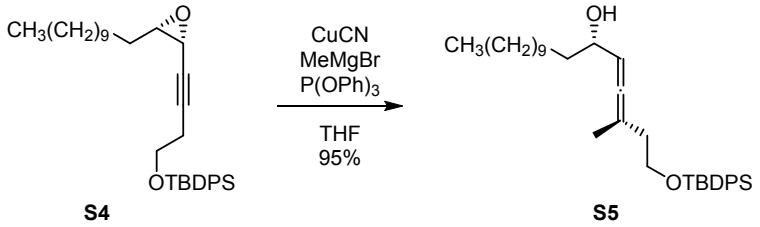
[5] Jackson, K. L.; Li, W.; Chen, C.-L.; Kishi, Y. *Tetrahedron* **2010**, *66*, 2263.



6 S4

silyl ether S4: To a solution of epoxide **6** (97.0 mg, 0.364 mmol) in dry CH_2Cl_2 (3 mL) were added imidazole (56.9 mg, 0.836 mmol) and TBDPSCl (0.10 mL, 0.38 mmol) at 0 °C. After being stirred for 1 h at room temperature, to the reaction mixture were added imidazole (57.0 mg, 0.837 mmol) and TBDPSCl (0.10 mL, 0.38 mmol) at room temperature. After being stirred for 5 min at room temperature, the reaction was quenched with sat. NH_4Cl solution (5 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (5 mL x 2). The combined organic layer was washed with water (10 mL) and brine (10 mL), 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 (–)-silyl ether **S4** (182 mg, 99%) as a colorless oil.

$[\alpha]_D^{24}$ –7.47 (*c* 0.25, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 2926, 2855, 1465, 1428, 1112. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 7.0 Hz, -CH_2CH_3), 1.05 (9H, s, -Si-^{t}Bu), 1.22-1.38 (16H, m, -$CH_2(CH_2)_8CH_3$), 1.40-1.52 (2H, m, -$CH_2(CH_2)_8CH_3$), 1.61-1.68 (2H, m, -$CH_2(CH_2)_9CH_3$), 2.48 (2H, td, *J* = 7.0, 1.5 Hz, -CHC≡CCH_2-), 2.97 (1H, td, *J* = 6.0, 4.0 Hz, -C*H*CHC≡C-), 3.38 (1H, dt, *J* = 4.0, 1.5 Hz, -CHC*H*C≡C-), 3.76 (2H, t, *J* = 7.0 Hz, -CH_2OTBDPS), 7.36-7.46 (6H, m, Ph), 7.65-7.70 (4H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 14.1, 19.2, 22.7, 23.0, 26.0, 26.8, 29.26, 29.34, 29.4, 29.5, 29.56, 29.63, 31.9, 45.4, 58.1, 62.3, 76.3, 83.4, 127.7, 129.7, 133.5, 135.5. HRMS (ESI, positive): calcd. For $C_{33}H_{48}O_2NaSi$ $[M+Na]^+$, 527.3316; found, 527.3323.



S4 **S5**

allene S5: This compound was synthesized according to the modified procedure of Fürstner *et al*.[6] CuCN (38.1 mg, 0.425 mmol) was dried azeotropically with dry toluene (0.2 mL x3). To the residue were added dry THF (8 mL) and $P(OPh)_3$ (0.11 mL, 0.421 mmol) at room temperature under Ar atmosphere. After being stirred for 20 min at room temperature, to the reaction mixture was added a solution of MeMgBr (0.3 mL, 0.3 mmol, 3.0 M in Et_2O) at –40 °C under Ar atmosphere. After being stirred for 30 min at –40 °C, to the reaction mixture was added a solution of silyl ether **S4** (177 mg, 0.350 mmol) in dry THF (4 mL). After being stirred for 3.5 h at –40 °C, the reaction mixture was warmed to 10 °C. After being stirred for 1 h at 10 °C, the reaction was quenched with sat. NH_4Cl solution (10 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (10 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 flash column chromatography (hexane/EtOAc = 14/1 to 9/1) to afford (+)-allene **S5** (174 mg, 95%, dr = >95:<5 determined by ^{1}H NMR analysis) as a colorless oil.

$[\alpha]_D^{24}$ +26.4 (*c* 1.43, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 3342, 2926, 2855, 1966, 1470, 1428, 1112. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.89 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.06 (9H, s, -Si-^{t}Bu), 1.23-1.41 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.45-1.55 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.71 (3H, d, J = 2.5 Hz, -C=C=CCH_3), 2.23 (2H, td, J = 6.5, 2.5 Hz, -CH_2CH_2OTBDPS), 3.76 (2H, t, J = 6.5 Hz, -CH_2OTBDPS), 4.03 (1H, q, J = 6.0 Hz, -CHOH), 5.12 (1H, td, J = 6.0, 2.5 Hz, -CH=C=C-), 7.36-7.46 (6H, m, Ph), 7.66-7.70 (4H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 19.1, 19.4, 22.7, 25.4, 26.8, 29.3, 29.57, 29.60, 29.63, 29.7, 31.9, 37.0, 37.5, 62.5, 70.0, 95.2, 99.9, 127.6, 129.6, 133.8, 135.6, 199.7. HRMS (ESI, positive): calcd. For $C_{34}H_{52}O_2NaSi$ $[M+Na]^+$, 543.3629; found, 543.3629.

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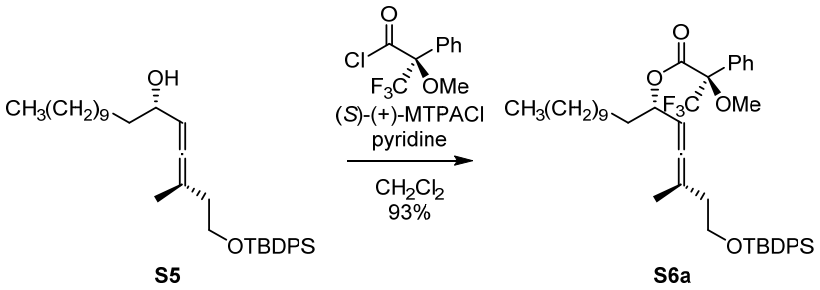
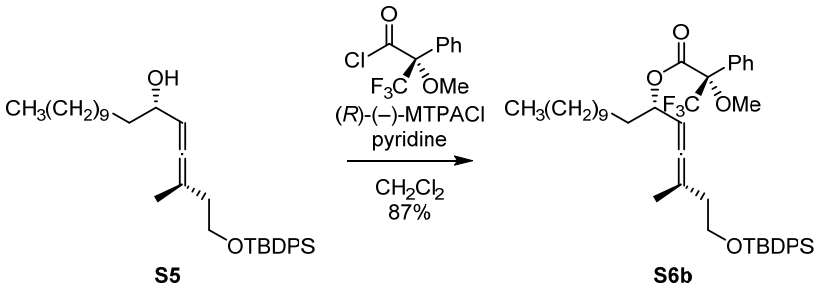
[6] Larivée, A.; Unger, J. B.; Thomas, M.; Wirtz, C.; Dubost, C.; Handa, S.; Fürstner, A. *Angew. Chem. Int. Ed.* **2011**, *50*, 304.



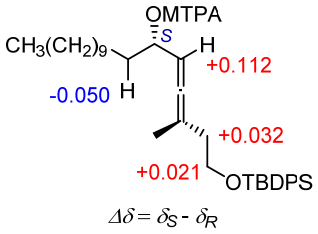
MTPA ester S6a: To dry pyridine (0.1 mL, 1.24 mmol) were added (+)-MTPACl (ca. 25 μL, 0.13 mmol) and a solution of allene **S5** (20.1 mg, 0.0386 mmol) in CH_2Cl_2 (0.5 mL) at room temperature. After being stirred for 1 h, to the reaction mixture was added (+)-MTPACl (ca. 10 μL, 0.053 mmol) at room temperature. After being stirred for 3 h at room temperature, the reaction was quenched with 3-dimethyl-amino-1-propylamine (20 μL). After being stirred for 5 min at room temperature, the resulting mixture was diluted with EtOAc (5 mL) and then washed with cold 1 M HCl (5 mL), cold sat. Na_2CO_3 solution (5 mL) and brine (5 mL). 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 (hexane/EtOAc = 20/1) to afford MTAP ester **S6a** (26.3 mg, 93%) as a colorless oil.

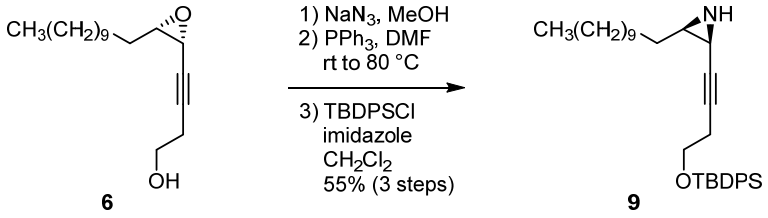
$[\alpha]_D^{26}$ +35.4 (*c* 1.30, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 2927, 1969, 1746, 1466, 1428, 1258, 1170, 1112, 1017. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 0.89 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.04 (9H, s, -Si-^{t}Bu), 1.20-1.33 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.58 (1H, m, -$CH_aH_b(CH_2)_9CH_3$), 1.66 (3H, d, J = 2.5 Hz, -C=C=CCH_3), 1.68 (1H, m, -$CH_aH_b(CH_2)_9CH_3$), 2.13-2.26 (2H, m, -CH_2CH_2OTBDPS), 3.54 (3H, s, -OMe), 3.71 (2H, t, J = 7.0 Hz, -CH_2OTBDPS), 4.97 (1H, m, -C*H*=C=C-), 5.34 (1H, q, J = 7.0 Hz, -CH_2C*H*-), 7.35-7.44 (9H, m, Ph), 7.50-7.54 (2H, m, Ph), 7.64-7.68 (4H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 18.9, 19.2, 22.7, 25.2, 26.8, 29.2, 29.3, 29.46, 29.54, 29.6, 31.9, 34.0, 36.7, 55.4, 62.3, 76.4, 89.2, 99.1, 127.5, 127.6, 128.3, 129.4, 129.6, 132.5, 133.9, 135.5, 165.8, 203.0 (CF_3 carbon peak is missing due to its very low intensity). HRMS (ESI, positive): calcd. For $C_{44}H_{59}O_4F_3NaSi$ $[M+Na]^+$, 759.4027; found, 759.4029.



MTPA ester S6b: To dry pyridine (0.1 mL, 1.24 mmol) were added (+)-MTPACl (ca. 25 μL, 0.13 mmol) and a solution of allene **S5** (20.1 mg, 0.0386 mmol) in CH_2Cl_2 (0.5 mL) at room temperature. After being stirred for 1 h, to the reaction mixture was added (+)-MTPACl (ca. 10 μL, 0.053 mmol) at room temperature. After being stirred for 3 h at room temperature, the reaction was quenched with 3-dimethyl-amino-1-propylamine (20 μL). After being stirred for 5 min at room temperature, the resulting mixture was diluted with EtOAc (5 mL) and then washed with cold 1 M HCl (5 mL), cold sat. Na_2CO_3 solution (5 mL) and brine (5 mL). 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 (hexane/EtOAc = 20/1) to afford MTPA ester **S6b** (17.6 mg, 87%) as a colorless oil.

$[\alpha]_D^{25}$ –19.4 (*c* 0.88, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 2927, 1747, 1472, 1270, 1186, 1111, 1019. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 0.89 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.04 (9H, s, -Si-^{t}Bu), 1.12-1.34 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.53 (1H, dt, J = 14.5, 6.0 Hz, -$CH_aH_b(CH_2)_9CH_3$), 1.61 (1H, dt, J = 14.5, 7.5 Hz, -$CH_aH_b(CH_2)_9CH_3$), 1.66 (3H, d, J = 2.5 Hz, -C=C=CCH_3), 2.16-2.30 (2H, m, -CH_2CH_2OTBDPS), 2.26 (1H, dtd, J = 14.5, 7.0, 2.5 Hz, -$CH_aH_bCH_2$OTBDPS), 3.55 (3H, s, -OMe), 3.73 (2H, t, J = 6.5 Hz, -CH_2OTBDPS), 5.08 (1H, m, -C*H*=C=C-), 5.36 (1H, q, J = 6.5 Hz, -CH_2C*H*-), 7.35-7.44 (9H, m, Ph), 7.52-7.56 (2H, m, Ph), 7.65-7.68 (4H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 18.9, 19.2, 22.7, 25.0, 26.8, 29.1, 29.3, 29.4, 29.5, 29.6, 31.9, 33.9, 36.7, 55.4, 62.3, 76.1, 89.4, 99.3, 127.3, 127.6, 128.3, 129.4, 129.6, 132.7, 133.82, 133.84, 135.5, 165.8, 203.0 (CF_3 carbon peak is missing due to its very low intensity). HRMS (ESI, positive): calcd. For $C_{44}H_{59}O_4F_3NaSi$ $[M+Na]^+$, 759.4027; found, 759.4029.

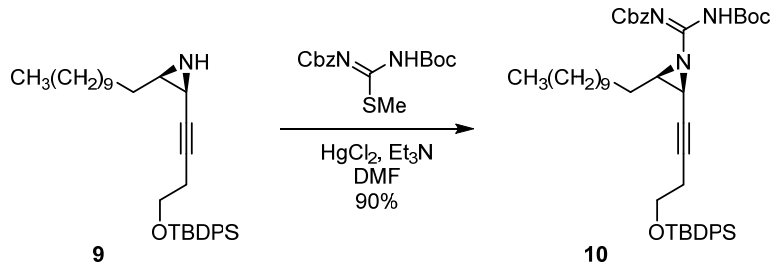




6 **9**

(–)-aziridine 9: To a solution of epoxide **6** (2.0 g, 7.5 mmol) in dry MeOH (90 mL) was added NaN_3 (4.0 g, 62 mmol) at room temperature. After being stirred vigorously for 37.5 h at room temperature, to the reaction mixture was added water (90 mL). The resulting mixture was extracted with EtOAc (100 mL x 3). The combined organic layer was washed with brine (200 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to provide crude azide. The crude azide was dried azeotropically with toluene (20 mL x 2), and dissolved in dry DMF (110 mL), and then PPh_3 (4.0 g, 15 mmol) was added to the solution. After being stirred for 5 h at 80 °C, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in dry CH_2Cl_2 (60 mL), and then to the solution were added imidazole (1.1 g, 16 mmol) and TBDPSCl (2.2 mL, 12 mmol) at 0 °C. After being stirred for 20 min at room temperature, the reaction was quenched with sat. NH_4Cl solution (60 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (60 mL x 2). The combined organic layer was washed with water (120 mL) and brine (120 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc/CH_2Cl_2 = 30/1/1 with 1% *i*-Pr_2NH to 20/1/1 with 1% *i*-Pr_2NH) to afford (–)-aziridine **9** (2.07 g, 55% in 3 steps) as a colorless oil.

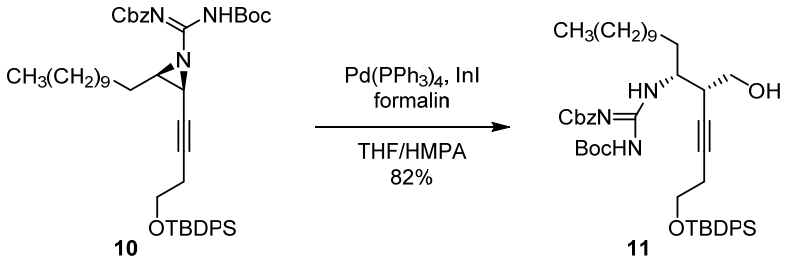
$[\alpha]_D^{29}$ –6.10 (*c* 1.03, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 2926, 2855, 1465, 1428, 1112. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 6.5 Hz, -CH_2CH_3), 1.05 (9H, s, -Si-^{t}Bu), 1.21-1.35 (16H, m, -$CH_2(CH_2)_8CH_3$), 1.40-1.49 (2H, m, -$CH_2(CH_2)_8CH_3$), 1.49-1.57 (2H, m, -$CH_2(CH_2)_9CH_3$), 2.01 (1H, br, -CHCHC≡C-), 2.40-2.48 (3H, m -CHC≡CCH_2-, -CHCHC≡C-), 3.75 (2H, t, *J* = 7 Hz, -CH_2OTBDPS), 7.35-7.45 (6H, m, -Si-Ph), 7.64-7.70 (4H, m, -Si-Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 19.2, 22.7, 23.0, 24.4, 26.8, 27.4, 29.3, 29.4, 29.57, 29.60, 29.63, 29.7, 30.6, 31.9, 37.0, 62.6, 77.2, 78.8, 127.6, 129.6, 133.6, 135.5. HRMS (ESI, positive): calcd. For $C_{33}H_{50}NOSi$ $[M+H]^+$, 504.3656; found, 504.3646.



9 **10**

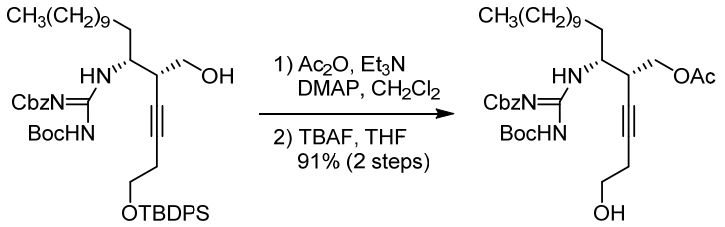
(+)-guanidino-aziridine 10: To a solution of aziridine **9** (2.07 g, 4.17 mmol), Boc,Cbz-methylisothiourea (1.5 g, 4.6 mmol), and dry Et_3N (5.8 mL, 42 mmol) in dry DMF (42 mL) was added $HgCl_2$ (1.2 g, 4.6 mmol) at room temperature. After being stirred for 1h at room temperature, the reaction mixture was diluted with EtOAc (40 mL), and then filtered through a pad of Celite® (eluted with EtOAc). The filtrate was washed with water (40 mL x 3), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was diluted with EtOAc (20 mL) filtered through a pad of Celite® (eluted with EtOAc) and concentrated under reduced pressure. The filtrate was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 19/1 with 1% *i*-Pr_2NH) and concentrated under reduced pressure. The residue was diluted with hexane/Et_2O = 1/1 (20 mL) and then filtered through a pad of Celite® (eluted with hexane/Et_2O = 1/1) to afford (+)-guanidino-aziridine **10** (2.88 g, 90%) as a yellow oil.

$[\alpha]_D^{30}$ +43.4 (*c* 1.00, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 2926, 2855, 1766, 1651, 1596, 1111. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 7.0 Hz, -CH_2CH_3), 1.04 (9H, s, -Si-^{t}Bu), 1.20-1.34 (16H, m, -$CH_2(CH_2)_8CH_3$), 1.35-1.55 (3H, m, -$CH_aH_bCH_2(CH_2)_8CH_3$), 1.47 (9H, s, -O-^{t}Bu), 2.10 (1H, m, -$CH_aH_b(CH_2)_9CH_3$), 2.48 (2H, td, *J* = 7.5, 1.5 Hz, -CHC≡CCH_2-), 2.69 (1H, ddd, *J* = 8.5, 6.0, 4.0 Hz, -CHCHC≡CCH_2-), 3.22 (1H, dt, *J* = 6.0, 1.5 Hz, -CHC≡CCH_2-), 3.76 (2H, t, *J* = 7.5 Hz, -CH_2OTBDPS), 5.15 (2H, s, -CH_2Ph), 7.27-7.44 (11H, m, -Si-Ph, -CH_2Ph), 7.63-7.69 (4H, m, -Si-Ph), 10.94 (1H, br, -NHBoc). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 19.2, 22.7, 23.0, 26.1, 26.8, 28.0, 28.7, 29.3, 29.4, 29.51, 29.54, 29.6, 29.7, 31.9, 34.7, 46.8, 62.4, 67.6, 75.5, 81.4, 82.5, 127.7, 128.2, 128.5, 129.7, 133.5, 135.5, 136.2, 148.5, 163.7. Anal. Calcd for $C_{47}H_{65}N_3O_5Si$: C, 72.36; H, 8.40; N, 5.39. Found: C, 72.19; H, 8.47; N, 5.58.



(–)-alcohol 11: To a mixture of guanidino-aziridine **10** (2.88 g, 3.69 mmol), $Pd(PPh_3)_4$ (213 mg, 0.185 mmol), and InI (1.33 g, 5.50 mmol) were added a degassed solution of dry THF (25 mL), dry HMPA (6.3 mL), and formalin (0.48 mL, 6.4 mmol, 37% solution) at room temperature under the argon atmosphere. After being stirred for 1 h at room temperature, the solution was passed through a short pad of neutral flash silica gel (eluted with EtOAc with 1% *i*-Pr_2NH), and the resulting solution was washed with water (100 mL x 3) and brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/Et_2O = 4/1 with 1% *i*-Pr_2NH to hexane/Et_2O = 1/1 with 1% *i*-Pr_2NH) to afford (–)-alcohol **11** (2.45 g, 82%, dr = >95:<5 determined by ^1H NMR analysis of diol **13**) as a yellow oil.

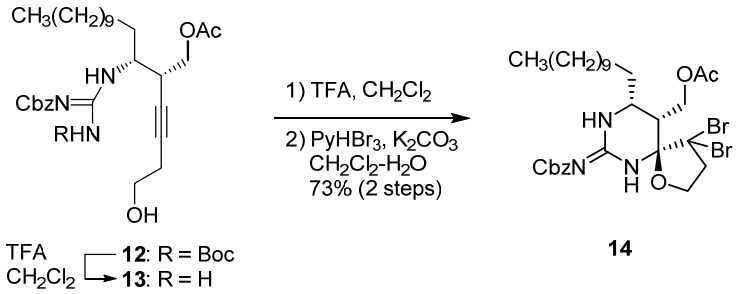
$[\alpha]_D^{29}$ –4.25 (*c* 1.08, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 3319, 2927, 2855, 1723, 1646, 1618, 1132, 1057. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 7.0 Hz, -CH_2CH_3), 1.05 (9H, s, -Si-^{t}Bu), 1.20-1.33 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.49 (9H, s, -O-^{t}Bu), 1.49-1.61 (1H, m, -$CH_aCH_b(CH_2)_9CH_3$), 2.02 (1H, m, -$CH_aCH_b(CH_2)_9CH_3$), 2.36 (1H, m, -$CHCH_2OH$), 2.49 (2H, td, *J* = 7.0, 2.0 Hz, -CH_2CH_2OTBDPS), 3.55-3.66 (2H, m, -CH_2OH), 3.76 (2H, t, *J* = 7.0 Hz, -CH_2OTBDPS), 4.12 (1H, qd, *J* = 9.0, 2.5 Hz, -NHC*H*-), 5.07 (1H, d, *J* = 12.5 Hz, -CH_aH_bPh), 5.13 (1H, d, *J* = 12.5 Hz, -CH_aH_bPh), 7.27-7.44 (11H, m, -Si-Ph, -CH_2Ph), 7.64-7.70 (4H, m, -Si-Ph), 8.32 (1H, d, *J* = 8.5 Hz, -N*H*(=NCbz)NHBoc), 11.33 (1H, br s, -N*H*Boc). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 19.2, 22.7, 23.1, 25.7, 26.8, 28.0, 28.1, 29.2, 29.3, 29.4, 29.5, 29.62, 29.64, 31.9, 33.0, 41.1, 51.3, 61.9, 62.7, 67.0, 79.7, 80.9, 83.9, 127.7, 127.8, 128.4, 129.6, 133.7, 135.5, 136.5, 153.0, 157.3, 163.1. Anal. Calcd for $C_{48}H_{69}N_3O_6Si$: C, 70.99; H, 8.56; N, 5.17. Found: C, 71.17; H, 8.51; N, 5.27.



11 **12**

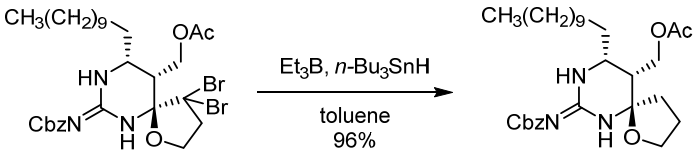
(+)-alcohol 12: To a solution of alcohol **11** (2.45 g, 3.02 mmol) in dry CH_2Cl_2 (75 mL) were added Et_3N (6.8 mL), Ac_2O (6.8 mL), and DMAP (37 mg, 0.303 mmol) at room temperature. After being stirred for 1 h at room temperature, the reaction mixture was concentrated under reduced pressure with toluene/MeOH (2/1, 20 mL), and then dried azeotropically with toluene/MeOH (2/1, 20 mL x3) to provide crude acetate. The residue of the acetate was dissolved in dry THF (75 mL), and then TBAF (9.0 mL, 9.0 mmol, 1.0 M solution in THF) was added at room temperature. After being stirred for 13 h at room temperature, to the reaction mixture was added TBAF (2.0 mL, 2.0 mmol). After being stirred for 4.5 h at room temperature, to the reaction mixture was added TBAF (1.0 mL, 1.0 mmol). After being stirred for 3 h at room temperature, the reaction was quenched with brine (70 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (70 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 flash column chromatography (hexane/EtOAc = 3/1 with 1% *i*-Pr_2NH) and then repurified by neutral silica gel flash column chromatography (hexane/EtOAc = 6/1 with 1% *i*-Pr_2NH) to afford (+)-alcohol **12** (1.70 g, 91% in 2 steps) as a pale yellow oil.

$[\alpha]_D^{29}$ +35.4 (*c* 1.08, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 3319, 2925, 2854, 1724, 1640, 1619, 1250, 1056. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 7.0 Hz, -CH_2CH_3), 1.17-1.45 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.50 (9H, s, -O-^{t}Bu), 1.53-1.63 (2H, m, -$CH_2(CH_2)_9CH_3$), 2.06 (3H, s, -CO-CH_3), 2.44 (2H, td, *J* = 5.5, 2.5 Hz, -CH_2CH_2OH), 3.04 (1H, m, -$CH$$CH_2OAc$), 3.69 (2H, t, *J* = 5.5 Hz, -CH_2OH), 4.04 (1H, dd, *J* = 10.5, 6.5 Hz, -CH_aH_bOAc), 4.23 (1H, dd, *J* = 10.5, 6.5 Hz, -CH_aH_bOAc), 4.42 (1H, ddd, *J* = 14, 9.5, 5.5 Hz, -NHC*H*-), 5.11 (1H, d, *J* = 12.5 Hz, -CH_aH_bPh), 5.15 (1H, d, *J* = 12.5 Hz, -CH_aH_bPh), 7.26-7.41 (5H, m, Ph), 8.57 (1H, d, *J* = 9.5 Hz, -N*H*(=NCbz)NHBoc), 11.44 (1H, br s, -N*H*Boc). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 20.8, 22.7, 23.4, 25.6, 28.0, 28.2, 29.3, 29.49, 29.52, 29.56, 29.61, 30.5, 31.9, 36.6, 50.2, 61.1, 63.8, 67.0, 78.1, 82.0, 83.7, 127.8, 127.9, 128.4, 136.9, 153.2, 156.2, 163.7, 170.9. HRMS (ESI, positive): calcd. For $C_{34}H_{53}N_3O_7Na$ $[M+Na]^+$, 638.3776; found, 638.3778.



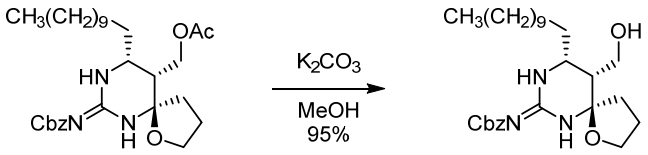
(+)-*spiro*-hemiaminal 14: A solution of guanidino-alcohol **12** (1.70 g, 2.76 mmol) in dry CH_2Cl_2 (50 mL) and TFA (5 mL) was stirred for 2.5 h at room temperature and then the reaction mixture was concentrated under reduced pressure with toluene/MeOH (2/1, 40 mL). The residue was dried azeotropically with toluene/MeOH (2/1, 20 mL x3) to provide crude alcohol **13**. The residue was dissolved in dry CH_2Cl_2/H_2O (330 mL, 1/1), and then K_2CO_3 (2.29 g, 16.6 mmol) was added. To a vigorously stirred mixture was added $PyHBr_3$ (2.64 g, 8.25 mmol). After being stirred for 30 min at room temperature, the reaction was quenched with sat. Na_2SO_3 solution (150 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (200 mL x 2). The combined organic layer was washed with water (400 mL) and brine (400 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 5/1 with 1% *i*-Pr_2NH) to afford (+)-*spiro*-hemiaminal **14** (1.35 g, 73%, dr = >95:<5 determined by ^1H NMR analysis) as a pale yellow oil.

$[\alpha]_D^{29}$ +115 (*c* 1.04, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 2925, 2853, 1744, 1635, 1241, 1030. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 7.0 Hz, -CH_2CH_3), 1.19-1.48 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.54-1.72 (2H, m, -$CH_2(CH_2)_9CH_3$), 2.02 (3H, s, -CO-CH_3), 2.67 (1H, dt, *J* = 5.5, 3.5 Hz, -$CHCH_2OAc$), 3.17 (1H, ddd, *J* = 14.5, 7.0, 2.0 Hz, -$CH_aH_bCBr_2$-), 3.27 (1H, m, -$CH_aH_bCBr_2$-), 3.93-4.01 (2H, m, -$OCH_aH_bCH_2$-, -NHC*H*-), 4.06 (1H, m, -$OCH_aH_bCH_2$-), 4.33 (1H, dd, *J* = 12.5, 5.5 Hz, -CH_aH_bOAc), 4.54 (1H, dd, *J* = 12.5, 3.5 Hz, -CH_aH_bOAc), 5.10 (2H, s, -CH_2Ph), 7.26-7.40 (5H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 20.9, 22.7, 25.9, 29.3, 29.4, 29.5, 29.6, 31.4, 31.9, 41.3, 49.0, 50.6, 58.5, 62.2, 63.4, 66.5, 93.2, 127.75, 127.82, 128.3, 136.8, 157.0, 163.1, 170.5. Anal. Calcd for $C_{29}H_{43}N_3O_5Br_2$: C, 51.72; H, 6.44; N, 6.24. Found: C, 52.01; H, 6.59; N, 6.33.



14 **15**

(+)-*spiro*-hemiaminal 15: To a solution of *spiro*-hemiaminal **14** (1.35 g, 2.00 mmol) and *n*-Bu_3SnH (2.7 mL, 10 mmol) in dry toluene (22 mL) were added Et_3B (1.0 mL, 1.0 mmol, 1.0 M solution in hexane) and air (1 mL) at room temperature. After being stirred for 2.5 h at room temperature, the solution was passed through a short pad of neutral flash silica gel (eluted with EtOAc) and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 5/1 with 1% *i*-Pr_2NH to 1/1 with 1% *i*-Pr_2NH) to afford (+)-*spiro*-hemiaminal **15** (990 mg, 96%) as a pale yellow oil. $[\alpha]_D^{31}$ +81.9 (*c* 1.00, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 2925, 2854, 1744, 1628, 1228. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 7.0 Hz, -CH_2CH_3), 1.20-1.45 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.53-1.66 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.96-2.24 (5H, m, -$OCH_2CH_2CH_2$-, -$CHCH_2OAc$), 2.03 (3H, s, -CO-CH_3), 3.85 (1H, m, -$OCH_aH_bCH_2$-), 3.91-4.01 (2H, m, -$OCH_aH_bCH_2$-, -NHC*H*-), 4.05 (1H, dd, *J* = 12, 4.5 Hz, -CH_aH_bOAc), 4.12 (1H, dd, *J* = 12, 5.5 Hz, -CH_aH_bOAc), 5.05 (1H, d, *J* = 12.5 Hz, -CH_aH_bPh), 5.09 (1H, d, *J* = 12.5 Hz, -CH_aH_bPh), 7.23-7.40 (5H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 20.9, 22.7, 24.7, 25.8, 29.3, 29.40, 29.43, 29.5, 29.6, 31.6, 31.9, 35.2, 42.1, 49.7, 60.7, 66.2, 66.5, 90.3, 127.6, 127.7, 128.3, 137.3, 157.9, 163.9, 170.6. HRMS (ESI, positive): calcd. For $C_{29}H_{46}N_3O_5$ $[M+H]^+$, 516.3432; found, 516.3450.



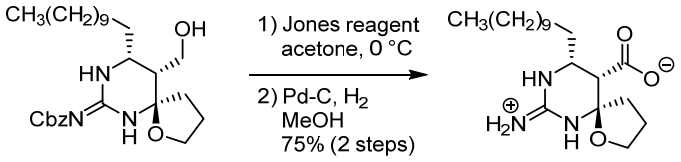
15 **16**

(+)-common intermediate 16: To a solution of *spiro*-hemiaminal **15** (990 mg, 1.91 mmol) in MeOH (50 mL) was added K_2CO_3 (265 mg, 1.92 mmol) at room temperature. After being stirred for 1 h at room temperature, the reaction was quenched with sat. NH_4Cl solution (50 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (50 mL x 2). The combined organic layer was washed with water (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (EtOAc with 1% *i*-Pr_2NH to CH_2Cl_2/MeOH = 20/1 with 1% *i*-Pr_2NH) to afford (+)-common intermediate **16**

(866 mg, 95%) as a pale yellow oil.

$[\alpha]_D^{30}$ +83.4 (*c* 1.02, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 3262, 2925, 2854, 1619, 1541, 1456, 1392, 1326, 1257, 1101, 1050. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 7.0 Hz, -CH_2CH_3), 1.20-1.46 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.53-1.70 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.90 (1H, td, *J* = 5.0, 4.0 Hz, -$CHCH_2OH$) 1.93-2.20 (4H, m, -$OCH_2CH_2CH_2$-), 3.52 (1H, dd, *J* = 11.5, 5.0 Hz, -CH_aH_bOH), 3.72 (1H, dd, *J* = 11.5, 5.0 Hz, -CH_aH_bOH), 3.78-3.96 (3H, m, -OCH_2CH_2-, -NHC*H*-), 5.02 (1H, d, *J* = 12.5 Hz, -CH_aH_bPh), 5.08 (1H, d, *J* = 12.5 Hz, -CH_aH_bPh), 7.23-7.39 (5H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 22.7, 24.7, 26.0, 29.3, 29.4, 29.5, 29.6, 31.6, 31.9, 35.0, 44.9, 49.9, 59.0, 66.2, 66.3, 90.7, 127.6, 127.9, 128.3, 137.2, 158.0, 163.7.

Anal. Calcd for $C_{27}H_{43}N_3O_4$: C, 68.47; H, 9.15; N, 8.87. Found: C, 68.26; H, 9.12; N, 8.78.

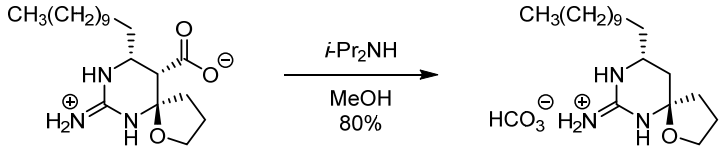


16 (+)-crambescin B carboxylic acid (**2**)

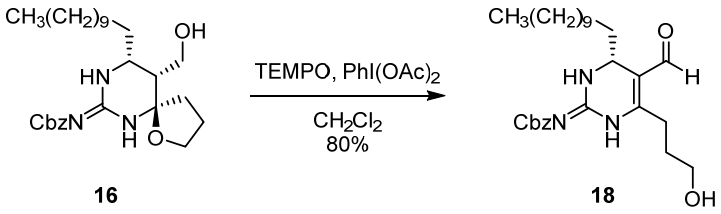
(+)-crambescin B carboxylic acid (2): To a solution of common intermediate **16** (30.2 mg, 0.0638 mmol) in acetone (3 mL) was added 2.5 M Jones reagent (100 μL) at 0 °C. After being stirred for 15 min at 0 °C, the reaction was quenched with 2-propanol (0.5 mL) and H_2O (3 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (5 mL x 2). The combined organic layer was washed with brine (10 mL), 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 = 20/1 with 1% *i*-Pr_2NH) to afford carboxylic acid (41.2 mg) as a white solid. Carboxylic acid (41.2 mg), 10% Pd-C (10.0 mg), and MeOH (5 mL) were placed in a recovery flask (20 mL) connected to an inlet adaptor with three way-stopcock. The atmosphere of the reaction vessel was replaced by hydrogen (1.0 atm). After being stirred for 20 min at room temperature, the catalyst was filtered off through a pad of Celite® (eluted with MeOH), and then the filtrate was concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (CH_2Cl_2/MeOH = 1/1 with 1% *i*-Pr_2NH) to afford (+)-crambescin B carboxylic acid (**2**) (16.8 mg, 75% in 2 steps) as a colorless oil.

$[\alpha]_D^{30}$ +89.9 (*c* 0.64, MeOH). IR (film): ν_{max} (cm^{-1}) 3247, 2924, 2853, 1683, 1616, 1568, 1403, 1040. ^1H-NMR and ^{13}C-NMR spectra were recorded as trifluoroacetic acid salts. ^1H NMR (400 MHz, CD_3OD): δ (ppm) 0.90 (3H, t, *J* = 7.0 Hz, -CH_2CH_3), 1.23-1.42 (16H, m, -$CH_2(CH_2)_8CH_3$), 1.42-1.53 (2H, m, -$CH_2(CH_2)_8CH_3$) 1.57-1.71 (2H, m, -$CH_2(CH_2)_9CH_3$),

2.01-2.23 (4H, m, -OCH$_2$C*H$_2$*C*H$_2$*-), 2.89 (1H, d, *J* = 4.0 Hz, -C*H*CO$_2$H), 3.84 (1H, td, *J* = 7.0, 4.0 Hz, -NHC*H*-), 3.93 (1H, m, -OC*H$_a$*H$_b$CH$_2$-), 4.02 (1H, m, -OCH$_a$*H$_b$*CH$_2$-). ^{13}C NMR (100 MHz, CD$_3$OD): δ (ppm) 14.4, 23.7, 25.7, 26.5, 30.4, 30.5, 30.6, 30.7, 32.8, 33.1, 36.2, 49.6, 49.9, 68.8, 90.0, 155.2, 171.4. HRMS (ESI, positive): calcd. For $C_{19}H_{36}N_3O_3$ $[M+H]^+$, 354.2751; found, 354.2750.

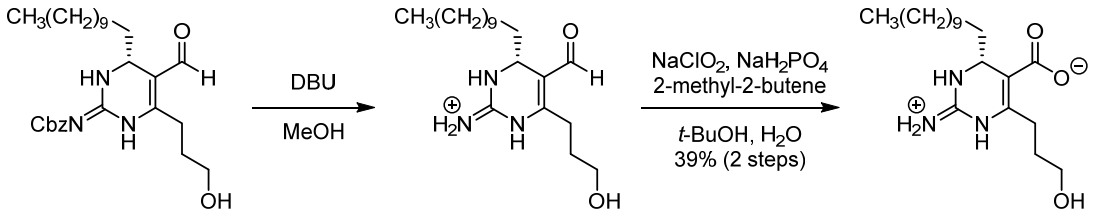


(+)-crambescin B decarboxylate (17): A solution of crambescin B carboxylic acid (**2**) (21.2 mg, 0.0600 mmol) in MeOH (10 mL) was stirred for 24 h at room temperature and then to the reaction mixture was added *i*-Pr$_2$NH (1 mL). After being stirred for 24 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by Chromatorex DNH silica gel column chromatography (EtOAc to CH_2Cl_2/MeOH = 9/1 to MeOH) to afford (+)-crambescin B decarboxylate (**17**) (17.8 mg, 80 %) as a colorless oil. The relative stereochemistry of **17** could not be determined by NOESY analysis.
$[\alpha]_D^{25}$ +70.9 (*c* 0.40, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 3234, 2925, 2854, 1682, 1613, 1465, 1399, 1350, 1195, 1028. ^{1}H-NMR and ^{13}C-NMR spectra were recorded as carbonic acid salts. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.87 (3H, t, *J* = 7.0 Hz, -CH$_2$C*H$_3$*), 1.20-1.54 (19H, m, -C*H$_a$*H$_b$(C*H$_2$*)$_9$CH$_3$), 1.54-1.68 (2H, m, -CH$_a$*H$_b$*(CH$_2$)$_9$CH$_3$, -CHC*H$_a$*H$_b$CO-, -C*H$_2$*-), 1.84-2.04 (3H, m, -CHCH$_a$*H$_b$*CO-, -C*H$_2$*-), 2.07-2.28 (2H, m), 3.59 (1H, m, -NHC*H*-), 3.85 (1H, m, -OC*H$_a$*H$_b$CH$_2$-), 3.97 (1H, m, -OCH$_a$*H$_b$*CH$_2$-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 22.7, 24.7, 25.1, 29.3, 29.45, 29.50, 29.56, 29.62, 31.9, 34.8, 36.8, 37.5, 47.2, 67.3, 88.0, 154.2, 179.3. HRMS (ESI, positive): calcd. For $C_{18}H_{36}N_3O$ $[M+H]^+$, 310.2853; found, 310.2856.



16 18

(–)-enal 18: To a solution of common intermediate **16** (303 mg, 0.640 mmol) and TEMPO (20 mg, 0.13 mmol) in dry CH_2Cl_2 (40 mL) was added $PhI(OAc)_2$ (517 mg, 1.61 mmol) at room temperature. After being stirred for 6.5 h at room temperature, the reaction was quenched with sat. $Na_2S_2O_3$ solution (40 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (40 mL x 3). The combined organic layer was washed with water (120 mL) and brine (120 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 2/1 with 1% *i*-Pr_2NH to 1/1 with 1% *i*-Pr_2NH to EtOAc with 1% *i*-Pr_2NH) to afford (–)-enal **18** (240 mg, 80%) as a brown oil.
$[\alpha]_D^{28}$ –17.8 (*c* 0.97, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 3283, 2925, 2854, 1747, 1652, 1457, 1255, 1067. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 7.0 Hz, -CH_2CH_3), 1.19-1.37 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.44-1.52 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.68-1.78 (2H, m, -CH_2CH_2OH), 2.58 (1H, dt, *J* = 14.5, 6.5 Hz, -$CH_aCH_bCH_2CH_2OH$), 2.69 (1H, dt, *J* = 14.5, 7.0 Hz, -$CH_aCH_bCH_2CH_2OH$), 3.58 (2H, t, *J* = 5.5 Hz, -CH_2OH), 4.44 (1H, t, *J* = 5.5 Hz, -NHC*H*-), 5.04 (1H, d, *J* = 12 Hz, -CH_aH_bPh), 5.15 (1H, d, *J* = 12 Hz, -CH_aH_bPh), 7.27-7.38 (5H, m, Ph), 9.69 (1H, s, -CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 22.6, 24.1, 24.4, 29.25, 29.29, 29.5, 29.57, 29.64, 30.6, 31.9, 36.2, 48.2, 60.2, 67.0, 113.4, 128.2, 128.3, 128.5, 136.2, 154.2, 156.0, 163.0, 185.3. HRMS (ESI, positive): calcd. For $C_{27}H_{42}N_3O_4$ $[M+H]^+$, 472.3170; found, 472.3190.



18 19 (+)-crambescin C carboxylic acid (**3**)

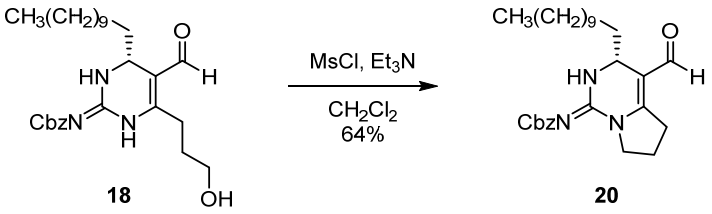
(+)-guanidine 19: To a solution of enal **18** (29.2 mg, 0.0619 mmol) in MeOH (6 mL) was added distilled DBU (ca. 20 μL, 0.134 mmol) at room temperature. After being stirred for 12 h, the reaction was quenched with 1 M HCl (10 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (5 mL x 3). The combined

organic layer was washed with brine (10 mL), 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 = 1/1) to afford (+)-guanidine **19** (20.0 mg) as a yellow oil.

$[\alpha]_D^{27}$ +27.2 (*c* 1.69, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 3295, 2925, 2853, 1694, 1661, 1548, 1460, 1366, 1258, 1063. ^1H NMR (400 MHz, CD_3OD): δ (ppm) 0.90 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.25-1.42 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.45-1.62 (2H, m, -$CH_2(CH_2)_9CH_3$) 1.88 (2H, m, -CH_2CH_2OH), 2.86 (2H, t, J = 7.5 Hz, -$CH_2CH_2CH_2OH$), 3.64 (2H, t, J = 6.0 Hz, -CH_2OH), 4.44 (1H, dd, J = 6.5, 4.5 Hz, -NHC*H*-), 9.86 (1H, s, -CHO). ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 14.4, 23.7, 25.0, 25.4, 30.3, 30.5, 30.58, 30.64, 30.73, 30.74, 32.2, 33.1, 36.9, 49.3, 61.8, 115.7, 153.4, 153.9, 188.0. HRMS (ESI, positive): calcd. For $C_{19}H_{36}N_3O_2$ $[M+H]^+$, 338.2802; found, 338.2800.

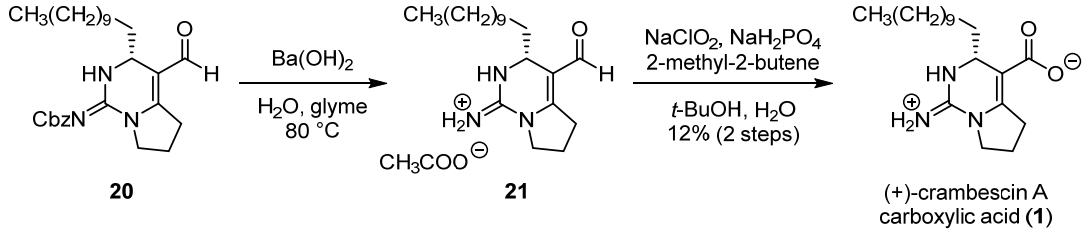
(+)-crambescin C carboxylic acid (3): To a solution of guanidine **19** (20.0 mg) in *t*-BuOH (6 mL) and 2-methyl-2-butene (0.40 mL, 3.76 mmol) was added a solution of $NaClO_2$ (54.0 mg, 0.597 mmol) and NaH_2PO_4 (138 mg, 1.15 mmol) in H_2O (2 mL) at room temperature. After being stirred for 22.5 h, the reaction was quenched with sat. $NaHSO_3$ (10 mL) and brine (10 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (30 mL x 2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by HPLC on Nomura Chemical ODS-HG-5 monitored by UV detector (4.6 x 250 mm, 0.013M TFA/MeCN, 1.0 mL/min, 220 nm) to afford (+)-crambescin C carboxylic acid (**3**) (8.6 mg, 39% in 2 steps) as a colorless oil.

$[\alpha]_D^{26}$ +46.3 (*c* 0.43, MeOH). IR (film): ν_{max} (cm^{-1}) 3735, 3191, 2924, 2853, 1687, 1557, 1247, 1059. ^1H- and ^{13}C-NMR spectra were recorded as trifluoroacetic acid salts. ^1H NMR (400 MHz, CD_3OD): δ (ppm) 0.90 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.23-1.50 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.53-1.64 (2H, m, -$CH_2(CH_2)_9CH_3$) 1.80 (2H, m, -CH_2CH_2OH), 2.75-2.92 (2H, m, -$CH_2CH_2CH_2OH$), 3.60 (2H, t, J = 6.0 Hz, -CH_2OH), 4.44 (1H, t, J = 5.0 Hz, -NHC*H*-). ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 14.4, 23.7, 25.1, 28.5, 30.3, 30.5, 30.60, 30.64, 30.7, 30.8, 31.9, 33.1, 36.9, 51.4, 62.0, 106.8, 148.1, 153.5, 168.0. HRMS (ESI, positive): calcd. For $C_{19}H_{36}N_3O_3$ $[M+H]^+$, 354.2751; found, 354.2740.



(+)-pyrrolidine 20: To a solution of enal **18** (49.5 mg, 0.105 mmol) and Et_3N (Ca. 30 μL, 0.22 mmol) in CH_2Cl_2 (5 mL) was added MsCl (ca. 15 μL, 0.19 mmol) at room temperature. After being stirred for 10 min at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 2/1 to EtOAc) and then repurified by neutral silica gel flash column chromatography (hexane/EtOAc = 3/1 to 2/1) to afford (+)-pyrrolidine **20** (30.3 mg, 64%) as a colorless oil.

$[\alpha]_D^{28}$ +13.2 (*c* 1.52, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 2925, 2853, 1653, 1602, 1243. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, *J* = 6.5 Hz, -CH_2CH_3), 1.20-1.40 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.44-1.61 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.99-2.21 (2H, m, -$NCH_2CH_2CH_2$-), 3.04 (1H, dt, *J* = 17, 9.0 Hz, -$NCH_2CH_2CH_aH_b$-), 3.16 (1H, ddd, *J* = 17, 8.5, 4.0 Hz, -$NCH_2CH_2CH_aH_b$-), 3.80-3.94 (2H, m, -NCH_2CH_2-), 4.48 (1H, m, -NHC*H*-), 5.11 (1H, d, *J* = 12 Hz, -CH_aH_bPh), 5.17 (1H, d, *J* = 12 Hz, -CH_aH_bPh), 7.26-7.43 (5H, m, Ph), 9.51 (1H, br, -N*H*-), 9.55 (1H, s, -CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 21.4, 22.7, 24.5, 28.0, 29.25, 29.31, 29.5, 29.6, 31.9, 36.8, 48.1, 49.3, 67.1, 110.2, 127.9, 128.2, 128.4, 136.7, 155.2, 157.1, 163.8, 185.2. HRMS (ESI, positive): calcd. For $C_{27}H_{40}N_3O_3$ $[M+H]^+$, 454.3064; found, 454.3085.

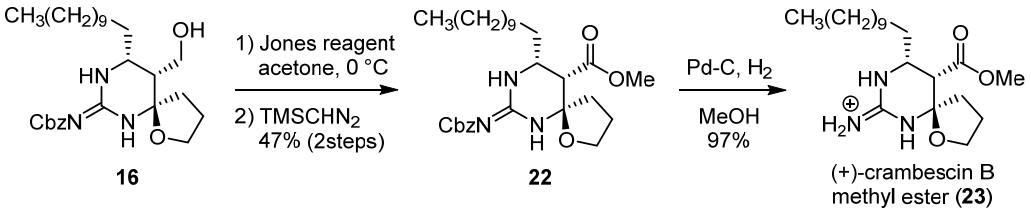


(+)-guanidine 21: To a solution of pyrrolidine **20** (30.3 mg, 0.0668 mmol) in glyme (3.6 mL) and H_2O (2.4 mL) was added to $Ba(OH)_2 \cdot 8H_2O$ (276 mg, 0.875 mmol) at room temperature. After being stirred for 8.5 h at 80 °C, the reaction mixture was added H_2O (5 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (10 mL x 2). The combined organic layer was washed with brine (20 mL), 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 = 5/1 to MeOH to MeOH with 1% CH_3COOH) to afford (+)-guanidine **21** (11.3 mg) as a pale yellow oil.

$[\alpha]_D^{28}$ +50.0 (*c* 0.56, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 3152, 2925, 2854, 1692, 1655, 1520, 1458, 1401, 1269, 1190. ^{1}H- and ^{13}C-NMR spectra were recorded as acetic acid salts. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 0.90 (3H, t, *J* = 6.5 Hz, -CH_2CH_3), 1.22-1.43 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.46-1.61 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.90 (3H, s, CH_3COO, overlap with residual acetic acid), 2.18 (1H, m, -$NCH_2CH_aH_bCH_2$-), 2.31 (1H, m, -$NCH_2CH_aH_bCH_2$-), 3.09 (1H, dt, *J* = 17, 9.0 Hz, -$NCH_2CH_2CH_aH_b$-), 3.31 (1H, m, -$NCH_2CH_2CH_aH_b$-), 3.72 (1H, td, *J* = 9.0, 7.5 Hz, -$NCH_aH_bCH_2$-), 3.87 (1H, td, *J* = 9.0, 3.0 Hz, -$NCH_aH_bCH_2$-), 4.43 (1H, t, *J* = 5.5 Hz, -NHC*H*-), 9.61 (1H, s, -CHO). ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 14.4, 23.1, 23.7, 24.0, 25.1, 28.1, 30.4, 30.5, 30.6, 30.66, 30.74, 30.8, 33.1, 37.3, 49.5, 49.7, 112.8, 153.3, 158.6, 180.9, 188.2. HRMS (ESI, positive): calcd. For $C_{19}H_{34}N_3O$ $[M+H]^+$, 320.2696; found, 320.2692.

(+)-crambescin A carboxylic acid (1): To a solution of guanidine **21** (11.3 mg) in *t*-BuOH (2.7 mL) and 2-methyl-2-butene (ca. 225 μL, 2.12 mmol) was added a solution of $NaClO_2$ (32.0 mg, 0.354 mmol) and NaH_2PO_4 (85 mg, 0.71 mmol) in H_2O (0.9 mL) at room temperature. After being stirred for 29.5 h, the reaction was quenched with sat. $NaHSO_3$ (2 mL) and brine (2 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (5 mL x 2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by HPLC on Nomura Chemical ODS-HG-5 monitored by UV detector (4.6 x 250 mm, 0.013 M TFA/MeCN, 1.0 mL/min, 220 nm) to afford (+)-crambescin A carboxylic acid (**1**) (2.8 mg, 12% in 2 steps) as a colorless oil.

$[\alpha]_D^{27}$ +51.9 (*c* 0.14, MeOH). IR (film): ν_{max} (cm^{-1}) 3393, 2925, 2853, 1684, 1543, 1433, 1264, 1187, 1139, 1033. ^{1}H-NMR and ^{13}C-NMR spectra were recorded as trifluoroacetic acid salts. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 0.90 (3H, t, *J* = 7.0 Hz, -CH_2CH_3), 1.25-1.48 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.59 (2H, q, *J* = 6.0 Hz,-$CH_2(CH_2)_9CH_3$), 2.10 (1H, m, -$NCH_2CH_aH_bCH_2$-), 2.23 (1H, m, -$NCH_2CH_aH_bCH_2$-), 2.97 (1H, dt, *J* = 18, 9.0 Hz, -$NCH_2CH_2CH_aH_b$-), 3.35 (1H, ddd, *J* = 18, 9.5, 3.0 Hz,-$NCH_2CH_2CH_aH_b$-), 3.66 (1H, td, *J* = 9.5, 7.5 Hz, -$NCH_aH_bCH_2$-), 3.81 (1H, td, *J* = 9.5, 2.5 Hz, -$NCH_aH_bCH_2$-), 4.38 (1H, t, *J* = 6.0 Hz, -NHC*H*-). ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 14.4, 23.0, 23.7, 25.2, 30.3, 30.5, 30.6, 30.66, 30.74, 30.8, 31.8, 33.1, 37.3, 49.5, 51.5, 103.9, 152.3, 153.1, 167.8. HRMS (ESI, positive): calcd. For $C_{19}H_{34}N_3O_2$ $[M+H]^+$, 336.2646; found, 336.2642.

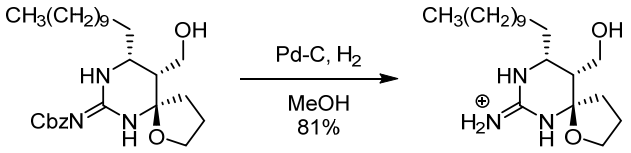


(+)-methyl ester 22: To a solution of common intermediate **16** (37.1 mg, 0.0783 mmol) in acetone (3.0 mL) was added 2.5 M Jones reagent (100 μL) at 0 °C. After being stirred for 15 min at 0 °C, the reaction was quenched with 2-propanol (0.3 mL) and H_2O (3 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (5 mL x 2). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to provide crude carboxylic acid. The residue of the carboxylic acid was dissolved in MeOH (6.0 mL), and then $TMSCHN_2$ (0.6 M in Hex, 0.6 mL, 0.4 mmol) was added at 0 °C. After being stirred for 10 min at 0 °C, to the reaction mixture were added $TMSCHN_2$ (0.6 mL, 0.4 mmol). After being stirred for 20 min at 0 °C, to the reaction mixture were added $TMSCHN_2$ (0.3 mL, 0.2 mmol). After being stirred for 40 min at 0 °C, the reaction was quenched with AcOH (0.3 mL). The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (Hexane/EtOAc = 1/1) to afford (+)-methyl ester **22** (18.4 mg, 47% in 2 steps) as a colorless oil.

$[\alpha]_D^{28}$ +79.9 (*c* 0.92, $CHCl_3$). IR (film): ν_{max} (cm^{-1}) 2925, 1744, 1631, 1546, 1457, 1391, 1243, 1098, 1029. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, J = 6.5 Hz, -CH_2CH_3), 1.21-1.45 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.48-1.56 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.95-2.16 (4H, m, -$OCH_2CH_2CH_2$-), 2.81 (1H, d, J = 4.0 Hz, -$CHCO_2CH_3$), 3.67 (3H, s, -CO_2CH_3), 3.81-3.90 (2H, m, -$OCH_aH_bCH_2$-, -NHC*H*-), 3.97 (1H, m, -$OCH_aH_bCH_2$-), 5.06 (1H, d, J = 12.5 Hz, -CH_aH_bPh), 5.10 (1H, d, J = 12.5 Hz, -CH_aH_bPh), 7.23-7.40 (5H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 22.6, 24.7, 25.6, 29.2, 29.3, 29.4, 29.6, 31.9, 32.1, 35.6, 48.5, 49.3, 51.9, 66.2, 67.0, 88.5, 127.5, 127.7, 128.2, 137.2, 157.6, 163.5, 168.8. HRMS (ESI, positive): calcd. For $C_{28}H_{44}N_3O_5$ $[M+H]^+$, 502.3276; found, 502.3282.

(+)-crambescin B methyl ester (23): Methyl ester **22** (4.3 mg, 8.57 μmol), 10% Pd-C (7.0 mg), and MeOH (2 mL) were placed in a recovery flask (10 mL) connected to an inlet adaptor with three way-stopcock. The atmosphere of the reaction vessel was replaced by hydrogen (1.0 atm). After being stirred for 10 min at room temperature, the resulting mixture was added TFA (25 μL). The catalyst was filtered off through a pad of Celite® (eluted with MeOH), and then the filtrate was concentrated under reduced pressure. The residue was purified by Chromatorex C8 silica gel column chromatography (MeOH/H_2O = 1/2 with 0.1% TFA to MeOH with 0.1% TFA) to afford (+)-crambescin B methyl ester (**23**) (4.0 mg, 97%) as a colorless oil.

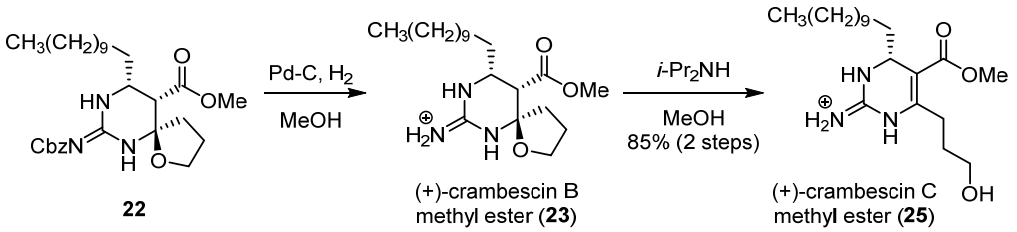
$[\alpha]_D^{28}$ +74.7 (*c* 0.22, MeOH). IR (film): ν_{max} (cm^{-1}) 3411, 2925, 2855, 1675, 1203, 1136. ^1H NMR (400 MHz, CD_3OD): δ (ppm) 0.90 (3H, t, J = 6.5 Hz, -CH_2CH_3), 1.23-1.41 (16H, m, -$CH_2(CH_2)_8CH_3$), 1.41-1.51 (2H, m, -$CH_2(CH_2)_8CH_3$), 1.51-1.62 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.98-2.20 (4H, m, -$OCH_2CH_2CH_2$-), 3.01 (1H, d, J = 4.0 Hz, -$CHCO_2CH_3$), 3.73 (3H, s, -CO_2CH_3), 3.86 (1H, td, J = 7.0, 4.0 Hz, -NHC*H*-), 3.93 (1H, m, -$OCH_aH_bCH_2$-), 4.02 (1H, m, -$OCH_aH_bCH_2$-). ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 14.4, 23.7, 25.7, 26.4, 30.4, 30.5, 30.6, 30.7, 32.7, 33.1, 36.1, 50.1, 52.5, 68.9, 89.9, 155.2, 170.3. HRMS (ESI, positive): calcd. For $C_{20}H_{38}N_3O_3$ $[M+H]^+$, 368.2908; found, 368.2922.



16 (+)-crambescin B alcohol (**24**)

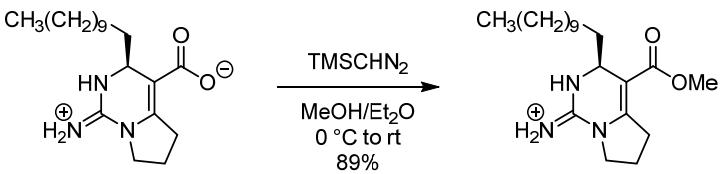
(+)-crambescin B alcohol (24): Common intermediate **16** (13.7 mg, 0.0289 mmol), 10% Pd-C (5.0 mg), and MeOH (2 mL) were placed in a recovery flask (10 mL) connected to an inlet adaptor with three way-stopcock. The atmosphere of the reaction vessel was replaced by hydrogen (1.0 atm). After being stirred for 20 min at room temperature, the catalyst was filtered off through a pad of Celite® (eluted with MeOH), and then the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC ($MeOH/H_2O$ = 9/1 with 0.1% AcOH) and then the residue was purified by Chromatorex DNH silica gel column chromatography (EtOAc to CH_2Cl_2/MeOH = 9/1 to MeOH) to afford (+)-crambescin B alcohol (**26**) (7.9 mg, 81%) as a colorless oil.

$[\alpha]_D^{30}$ +53.4 (*c* 0.40, MeOH). IR (film): ν_{max} (cm^{-1}) 3328, 2853, 2360, 1674, 1607, 1559, 1407, 1033. ^1H- and ^{13}C-NMR spectra were recorded as acetic acid salts. ^1H NMR (400 MHz, CD_3OD): δ (ppm) 0.90 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.25-1.50 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.57-1.81 (2H, m, -$CH_2(CH_2)_9CH_3$), 1.90 (3H, s, CH_3COO), 1.93 (1H, m, -$CHCH_2OH$), 1.95-2.22 (3H, m), 2.24-2.38 (1H, m), 3.52 (1H, dd, J = 11.5, 4.5 Hz, -CH_aH_bOH), 3.67 (1H, dd, J = 11.5, 5.0 Hz, -CH_aH_bOH), 3.81-3.93 (2H, m), 3.98 (1H, m). ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 14.4, 23.7, 24.2, 25.7, 26.8, 30.4, 30.5, 30.6, 30.66, 30.71, 30.73, 32.0, 33.1, 35.6, 45.7, 49.5, 51.3, 58.8, 68.1, 92.1, 155.3, 180.4. HRMS (ESI, positive): calcd. For $C_{19}H_{38}N_3O_2$ $[M+H]^+$, 340.2959; found, 340.2961.



(+)-crambescin C methyl ester (25): Methyl ester **22** (10.9 mg, 0.0217 mmol), 10% Pd-C (3.6 mg), and MeOH (2 mL) were placed in a recovery flask (20 mL) connected to an inlet adaptor with three way-stopcock. The atmosphere of the reaction vessel was replaced by hydrogen (1.0 atm). After being stirred for 20 min at room temperature, the catalyst was filtered off through a pad of Celite® (eluted with MeOH), and then the filtrate was concentrated under reduced pressure. The residue was purified by Chromatorex DNH silica gel column chromatography (EtOAc to MeOH) to afford (+)-crambescin B methyl ester (**23**) (8.8 mg) as a colorless oil. To a solution of crambescin B methyl ester (**23**) (8.8 mg) in MeOH (4 mL) was added *i*-Pr_2NH (0.5 mL) at room temperature. After being stirred for 41 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by Chromatorex C8 silica gel column chromatography (MeOH/H_2O = 1/2 to MeOH) to afford (+)-crambescin C methyl ester (**25**) (6.5 mg, 85% in 2 steps) as a colorless oil.

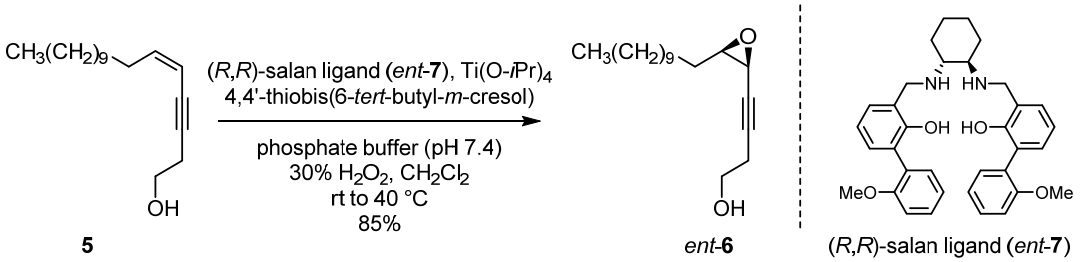
$[\alpha]_D^{29}$ +106 (*c* 0.33, MeOH). IR (film): ν_{max} (cm^{-1}) 3341, 2925, 2854, 1697, 1434, 1241, 1203, 1186, 1140, 1088. ^1H NMR (400 MHz, CD_3OD): δ (ppm) 0.90 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.23-1.65 (20H, m, -$(CH_2)_{10}CH_3$), 1.79 (2H, m, -CH_2CH_2OH), 2.71 (1H, dt, J = 12.5, 7.5 Hz, -$CH_aH_bCH_2CH_2OH$), 2.79 (1H, dt, J = 12.5, 7.5 Hz, -$CH_aH_bCH_2CH_2OH$), 3.59 (2H, t, J = 6.5 Hz, -CH_2OH), 3.71 (3H, s, -CO_2CH_3), 4.32 (1H, dd, J = 7.0, 3.5 Hz, -NHC*H*-). ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 14.4, 23.7, 25.1, 30.4, 30.5, 30.6, 30.7, 30.75, 30.77, 32.3, 33.1, 37.4, 51.0, 51.7, 62.5, 103.3, 155.4, 156.4, 167.8. HRMS (ESI, positive): calcd. For $C_{20}H_{38}N_3O_3$ $[M+H]^+$, 368.2908; found, 368.2904.



(–)-crambescin A carboxylic acid (*ent*-**1**) | (–)-crambescin A methyl ester (**1b**)

(–)-crambescin A methyl ester (1b): To a solution of (–)-crambescin A carboxylic acid (*ent*-**1**) (5.4 mg, 0.016 mmol) in MeOH (1 mL) and Et_2O (0.5 mL) was added $TMSCHN_2$ (0.6 M in Hex, 0.5 mL, 0.3 mmol) at 0 °C. After being stirred for 2 h at room temperature, the reaction was quenched with CH_3COOH (0.5 mL) and sat. $NaHCO_3$ solution (1 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (3 mL x2). The combined organic layer was washed with water (5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by preparative TLC ($MeOH/CH_2Cl_2/H_2O/HCOOH$ = 15/85/1/1) to afford (–)-crambescin A methyl ester (**1b**) (5.7 mg, 89%) as a colorless oil.

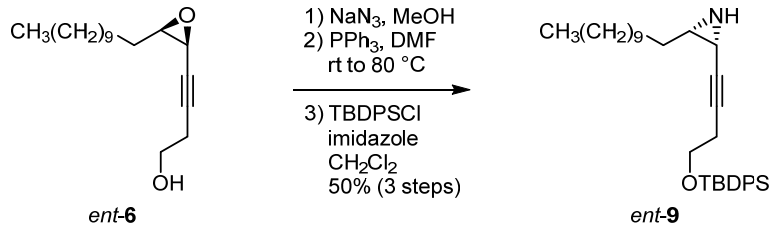
$[\alpha]_D^{25}$ –56.2 (*c* 0.28, MeOH). IR (film): ν_{max} (cm^{-1}) 3145, 2925, 2854, 1699, 1593, 1536, 1436, 1348, 1268, 1194, 1095. ^1H NMR (400 MHz, CD_3OD): δ (ppm) 0.90 (3H, t, J = 7.0 Hz, -CH_2CH_3), 1.25-1.48 (18H, m, -$CH_2(CH_2)_9CH_3$), 1.57 (2H, q, J = 6.0 Hz, -$CH_2(CH_2)_9CH_3$), 2.10 (1H, m, -$NCH_2CH_aH_bCH_2$-), 2.23 (1H, m, -$NCH_2CH_aH_bCH_2$-), 2.97 (1H, dt, J = 18, 9.0 Hz, -$NCH_2CH_2CH_aH_b$-), 3.32 (1H, ddd, J = 18, 8.5, 3.0 Hz, -$NCH_2CH_2CH_aH_b$-), 3.66 (1H, dt, J = 9.5, 7.5 Hz, -$NCH_aH_bCH_2$-), 3.76 (3H, s, -CO_2CH_3), 3.81 (1H, m, -$NCH_aH_bCH_2$-), 4.39 (1H, t, J = 5.5 Hz, -NHC*H*-), 8.53(1H, br s, -NH-). ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 14.4, 22.9, 23.7, 25.1, 30.3, 30.5, 30.6, 30.66, 30.74, 31.8, 33.1, 37.4, 48.9, 51.3, 52.1, 103.2, 152.7, 153.1, 166.6. HRMS (ESI, positive): calcd. For $C_{20}H_{36}N_3O_2$ $[M+H]^+$, 350.2802; found, 350.2809.



5 *ent*-**6** (*R*,*R*)-salan ligand (*ent*-**7**)

(+)-epoxide *ent*-6: This reaction was performed according to the reported procedure. To a solution of (*R*,*R*)-salan ligand (*ent*-**7**) (1.80 g, 3.34 mmol) in dry CH_2Cl_2 (45 mL) were added freshly distilled Ti(O-*i*Pr)$_4$ (0.90 mL, 3.0 mmol) at room temperature under N_2 atmosphere. After being stirred at room temperature for 1 h, to the reaction mixture was added 4,4'-thiobis(6-*tert*-butyl-*m*-cresol) (704 mg, 1.96 mmol), pH 7.4 phosphate buffer (3.8 mL), enyne **5** (7.61 g, 30.4 mmol) in dry CH_2Cl_2 (31 mL), and 30% H_2O_2 (7.0 mL, 61 mmol) under N_2 atmosphere. After being stirred at 40 °C for 5 h, the reaction mixture was allowed to cool to room temperature and to the reaction mixture was added solid NH_4Cl (11 g). The resulting mixture was filtered through a pad of Celite® (eluted with hexane), and the filtrate was washed with sat. NH_4Cl solution (50 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 flash column chromatography (hexane/Et_2O = 2/1) to afford (+)-epoxide *ent*-**6** (6.85 g, 85%, 95% ee) as a yellow solid. Recrystallization from hexane afforded (+)-epoxide *ent*-**6** (5.00 g, 73% yield, >99% ee) as a pale yellow solid. Enantiomeric excess was determined by chiral HPLC analysis of the corresponding *p*-nitrobenzoate derived from (+)-epoxide *ent*-**6**. Chiral HPLC analysis (CHIRALPAK AS-H column, hexane/2-propanol = 9/1, flow rate = 0.50 mL/min, detection 270-nm light, 30 °C) t_R = 16.5 min (minor isomer), 18.3 min (major isomer).

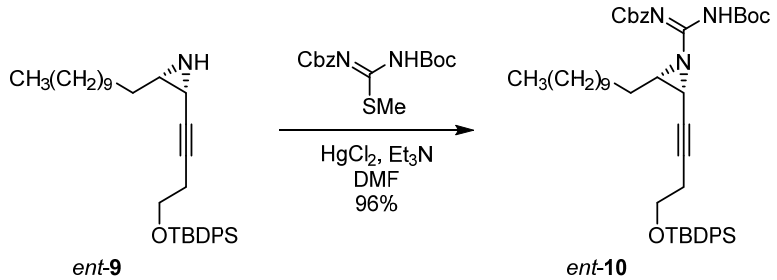
mp: 48 °C. $[\alpha]_D^{30}$ +8.96 (*c* 1.01, $CHCl_3$) for >99% ee. Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.61; H, 11.20. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (–)-epoxide **6**.



ent-**6** *ent*-**9**

(+)-aziridine *ent*-9: To a solution of epoxide *ent*-**6** (2.0 g, 7.5 mmol) in dry MeOH (80 mL) was added NaN_3 (4.0 g, 62 mmol) at room temperature. After being stirred vigorously for 44 h at room temperature, to the reaction mixture was added water (80 mL). The resulting mixture was extracted with EtOAc (100 mL x 3). The combined organic layer was washed with brine (200 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to provide crude azide. The crude azide was dried azeotropically with toluene (20 mL x 2), and dissolved in dry DMF (110 mL), and then PPh_3 (4.0 g, 15 mmol) was added to the solution. After being stirred for 5 h at 80 °C, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in dry CH_2Cl_2 (60 mL), and then to the solution were added imidazole (1.1 g, 16 mmol) and TBDPSCl (2.2 mL, 12 mmol) at 0 °C. After being stirred for 20 min at room temperature, the reaction was quenched with sat. NH_4Cl solution (60 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (60 mL x 2). The combined organic layer was washed with water (120 mL) and brine (120 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc/CH_2Cl_2 = 30/1/1 with 1% *i*-Pr_2NH to 20/1/1 with 1% *i*-Pr_2NH) to afford (+)-aziridine *ent*-**9** (1.89 g, 50% in 3 steps) as a colorless oil.

$[\alpha]_D^{31}$ +5.65 (*c* 1.26, $CHCl_3$). HRMS (ESI, positive): calcd. For $C_{33}H_{50}NOSi$ $[M+H]^+$, 504.3656; found, 504.3681. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (–)-aziridine **9**.

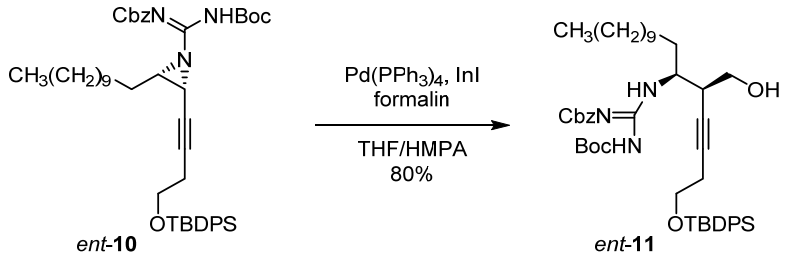


ent-**9** *ent*-**10**

(–)-guanidino-aziridine *ent*-10: To a solution of aziridine *ent*-**9** (1.89 g, 3.77 mmol), Boc,Cbz-methylisothiourea (1.3 g, 4.0 mmol), and dry Et_3N (5.3 mL, 38 mmol) in dry DMF (38 mL) was added $HgCl_2$ (1.1 g, 4.1 mmol) at room temperature. After being stirred for 3h at room temperature, the reaction mixture was diluted with EtOAc (40 mL), and then filtered

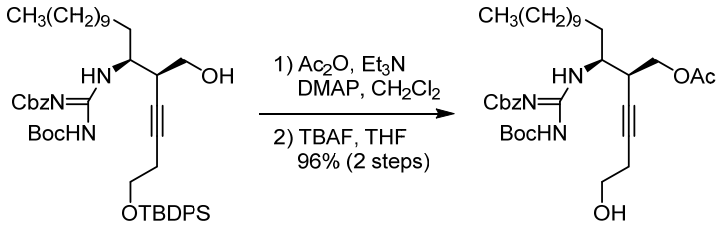
through a pad of Celite® (eluted with EtOAc). The filtrate was washed with water (40 mL x 3), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was diluted with EtOAc (20 mL) filtered through a pad of Celite® (eluted with EtOAc) and concentrated under reduced pressure. The filtrate was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 19/1 with 1% *i*-Pr_2NH) and concentrated under reduced pressure. The residue was diluted with hexane/Et_2O = 1/1 (20 mL) and then filtered through a pad of Celite® (eluted with hexane/Et_2O = 1/1) to afford (–)-guanidino-aziridine *ent*-**10** (2.80 g, 96%) as a yellow oil.

$[\alpha]_D^{30}$ –45.5 (*c* 1.27, $CHCl_3$). HRMS (ESI, positive): calcd. For $C_{47}H_{66}N_3O_5Si$ $[M+H]^+$, 780.4766; found, 780.4761. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-guanidino-aziridine **10**.



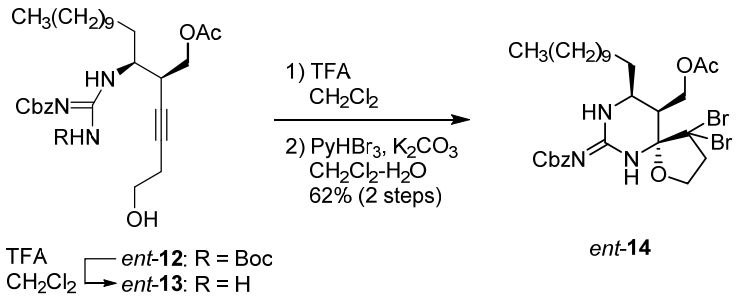
(+)-alcohol *ent*-11: To a mixture of guanidino-aziridine *ent*-**10** (2.80 g, 3.59 mmol), $Pd(PPh_3)_4$ (207 mg, 0.179 mmol), and InI (1.3 g, 5.4 mmol) were added a degassed solution of dry THF (25 mL), dry HMPA (6.3 mL), and formalin (0.48 mL, 6.4 mmol, 37% solution) at room temperature under the argon atmosphere. After being stirred for 1 h at room temperature, the solution was passed through a short pad of neutral flash silica gel (eluted with EtOAc with 1% *i*-Pr_2NH), and the resulting solution was washed with water (100 mL x 3) and brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified twice by neutral silica gel flash column chromatography (hexane/Et_2O = 4/1 with 1% *i*-Pr_2NH to hexane/Et_2O = 1/1 with 1% *i*-Pr_2NH) to afford (+)-alcohol *ent*-**11** (2.33 g, 80%, dr = >95:<5 determined by ^{1}H NMR analysis of diol *ent*-**13**) as a yellow oil.

$[\alpha]_D^{30}$ +5.21 (*c* 1.01, $CHCl_3$). HRMS (ESI, positive): calcd. For $C_{48}H_{69}N_3O_6SiNa$ $[M+Na]^+$, 834.4848; found, 834.4855. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (–)-alcohol **11**.



ent-**11** *ent*-**12**

(–)-alcohol *ent*-12: To a solution of alcohol *ent*-**11** (2.33 g, 2.87 mmol) in dry CH_2Cl_2 (75 mL) were added Et_3N (6.4 mL), Ac_2O (6.4 mL), and DMAP (35 mg, 0.286 mmol) at room temperature. After being stirred for 1 h at room temperature, the reaction mixture was concentrated under reduced pressure with toluene/MeOH (2/1, 20 mL), and then dried azeotropically with toluene/MeOH (2/1, 20 mL x2) to provide crude acetate. The residue of the acetate was dissolved in dry THF (75 mL), and then TBAF (8.6 mL, 8.6 mmol, 1.0 M solution in THF) was added at room temperature. After being stirred for 13 h at room temperature, to the reaction mixture was added TBAF (1.0 mL, 1.0 mmol). After being stirred for 4.5 h at room temperature, to the reaction mixture was added TBAF (1.0 mL, 1.0 mmol). After being stirred for 15 min at room temperature, the reaction was quenched with brine (70 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (70 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 flash column chromatography (hexane/EtOAc = 3/1 with 1% *i*-Pr_2NH) and then repurified by neutral silica gel flash column chromatography (hexane/EtOAc = 6/1 with 1% *i*-Pr_2NH) to afford (–)-alcohol *ent*-**12** (1.61 g, 91% in 2 steps) as a pale yellow oil.
$[\alpha]_D^{31}$ –36.8 (*c* 1.04, $CHCl_3$). HRMS (ESI, positive): calcd. For $C_{34}H_{53}N_3O_7Na$ $[M+Na]^+$, 638.3776; found, 638.3767. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-alcohol **12**.

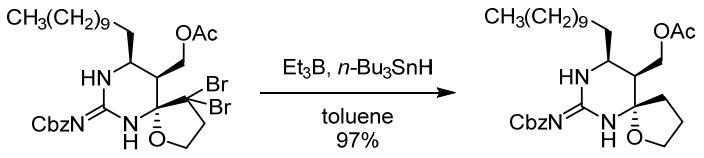


ent-**14**

(–)-*spiro*-hemiaminal *ent*-14: A solution of alcohol *ent*-**12** (1.69 g, 2.74 mmol) in dry CH_2Cl_2 (50 mL) and TFA (5 mL) was stirred for 2.5 h at room temperature and then the reaction mixture was concentrated under reduced pressure with toluene/MeOH (2/1, 40 mL).

The residue was dried azeotropically with toluene/MeOH (2/1, 20 mL x2) to provide crude alcohol *ent*-**13**. The residue was dissolved in dry CH_2Cl_2/H_2O (330 mL, 1/1), and then K_2CO_3 (2.24 g, 16.2 mmol) was added. To a vigorously stirred mixture was added $PyHBr_3$ (2.59 g, 8.09 mmol). After being stirred for 30 min at room temperature, the reaction was quenched with sat. Na_2SO_3 solution (150 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (200 mL x 2). The combined organic layer was washed with water (400 mL) and brine (400 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 5/1 with 1% *i*-Pr_2NH) to afford (–)-*spiro*-hemiaminal *ent*-**14** (1.12 g, 62%, dr = >95:<5 determined by ^{1}H NMR analysis) as a pale yellow oil.

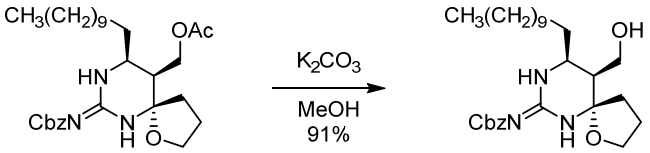
$[\alpha]_D^{31}$ –116 (*c* 1.06, $CHCl_3$). Anal. Calcd for $C_{29}H_{43}N_3O_5Br_2$: C, 51.72; H, 6.44; N, 6.24. Found: C, 52.01; H, 6.27; N, 6.31. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-*spiro*-hemiaminal **14**.



ent-**14** *ent*-**15**

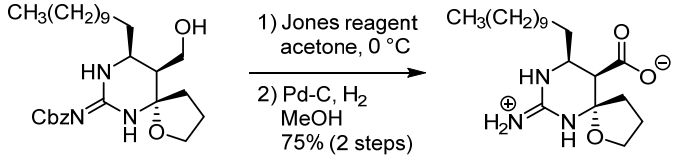
(–)-*spiro*-hemiaminal *ent*-15: To a solution of *spiro*-hemiaminal *ent*-**14** (1.12 g, 1.66 mmol) and *n*-Bu_3SnH (2.2 mL, 8.18 mmol) in dry toluene (18 mL) were added Et_3B (0.85 mL, 0.85 mmol, 1.0 M solution in hexane) and air (1 mL) at room temperature. After being stirred for 4.5 h at room temperature, the solution was passed through a short pad of neutral flash silica gel (eluted with EtOAc) and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 5/1 with 1% *i*-Pr_2NH to 1/1 with 1% *i*-Pr_2NH) to afford (–)-*spiro*-hemiaminal *ent*-**15** (830 mg, 97%) as a pale yellow oil.

$[\alpha]_D^{31}$ –79.7 (*c* 0.98, $CHCl_3$). Anal. Calcd for $C_{29}H_{45}N_3O_5$: C, 67.54; H, 8.80; N, 8.15. Found: C, 67.46; H, 8.70; N, 8.28. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-*spiro*-hemiaminal **15**.



ent-**15** *ent*-**16**

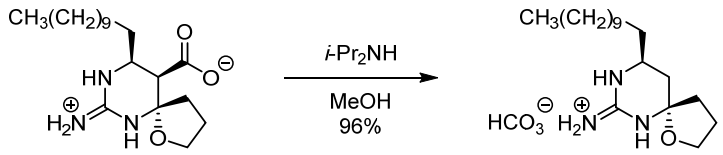
(–)-common intermediate *ent*-16: To a solution of *spiro*-hemiaminal *ent*-**15** (829 mg, 1.61 mmol) in MeOH (50 mL) was added K_2CO_3 (222 mg, 1.61 mmol) at room temperature. After being stirred for 1 h at room temperature, the reaction was quenched with sat. NH_4Cl solution (50 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (50 mL x 2). The combined organic layer was washed with water (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (EtOAc with 1% *i*-Pr_2NH to CH_2Cl_2/MeOH = 20/1 with 1% *i*-Pr_2NH) to afford (–)-common intermediate *ent*-**16** (692 mg, 91%) as a pale yellow oil.
$[\alpha]_D^{30}$ –82.6 (*c* 0.99, $CHCl_3$). Anal. Calcd for $C_{27}H_{43}N_3O_4$: C, 68.47; H, 9.15; N, 8.87. Found: C, 68.22; H, 9.21; N, 8.86. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-common intermediate **16**.



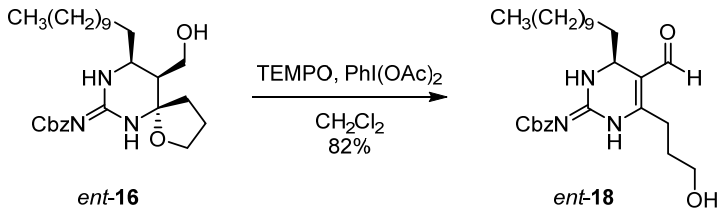
ent-**16** (–)-crambescin B carboxylic acid (*ent*-**2**)

(–)-crambescin B carboxylic acid (*ent*-2): To a solution of common intermediate *ent*-**16** (33.5 mg, 0.0707 mmol) in acetone (3 mL) was added 2.5 M Jones reagent (100 μL) at 0 °C. After being stirred for 15 min at 0 °C, the reaction was quenched with 2-propanol (0.5 mL) and H_2O (3 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (5 mL x 2). The combined organic layer was washed with brine (10 mL), 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 = 20/1 with 1% *i*-Pr_2NH) to afford carboxylic acid (45.3 mg) as a white solid. Carboxylic acid (45.3 mg), 10% Pd-C (19.2 mg), and MeOH (6 mL) were placed in a recovery flask (20 mL) connected to an inlet adaptor with three way-stopcock. The atmosphere of the reaction vessel was replaced by hydrogen (1.0 atm). After being stirred for 15 min at room temperature, the catalyst was filtered off through a pad of Celite® (eluted with MeOH), and then the filtrate was concentrated under reduced pressure. The residue was purified by neutral silica gel flash

column chromatography (CH_2Cl_2/MeOH = 1/1 with 1% *i*-Pr_2NH) to afford (–)-crambescin B carboxylic acid (*ent*-**2**) (23.6 mg, 94% in 2 steps) as a colorless oil.
$[\alpha]_D^{30}$ –75.9 (*c* 1.06, MeOH). HRMS (ESI, positive): calcd. For $C_{19}H_{36}N_3O_3$ $[M+H]^+$, 354.2751; found, 354.2738. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-crambescin B carboxylic acid (**2**).

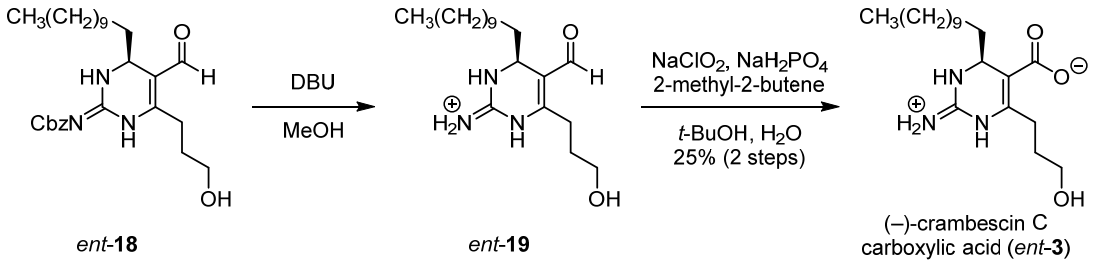


(–)-crambescin B decarboxylate (*ent*-17): A solution of crambescin B carboxylic acid (*ent*-**2**) (7.1 mg, 0.020 mmol) in MeOH (4 mL) was stirred for 24 h at room temperature and then to the reaction mixture was added *i*-Pr_2NH (0.5 mL). After being stirred for 24 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by Chromatorex DNH silica gel column chromatography (EtOAc to CH_2Cl_2/MeOH = 9/1 to MeOH) to afford (–)-crambescin B decarboxylate (*ent*-**17**) (7.2 mg, 96 %) as a colorless oil.
$[\alpha]_D^{26}$ –76.1 (*c* 0.11, $CHCl_3$). HRMS (ESI, positive): calcd. For $C_{18}H_{36}N_3O$ $[M+H]^+$, 310.2853; found, 310.2856. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-crambescin B decarboxylate (**17**).



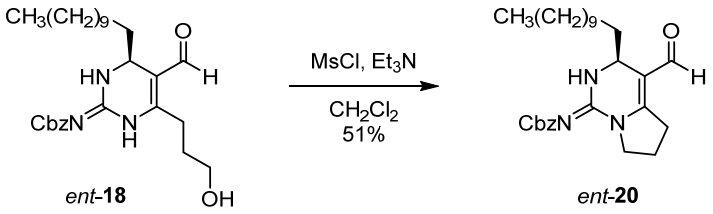
(+)-enal *ent*-18: To a solution of common intermediate *ent*-**16** (295 mg, 0.623 mmol) and TEMPO (20 mg, 0.13 mmol) in dry CH_2Cl_2 (40 mL) was added $PhI(OAc)_2$ (501 mg, 1.56 mmol) at room temperature. After being stirred for 7 h at room temperature, the reaction was quenched with sat. $Na_2S_2O_3$ solution (40 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (40 mL x 3). The combined organic layer was washed with water (120 mL) and brine (120 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral silica gel flash

column chromatography (hexane/EtOAc = 2/1 with 1% *i*-Pr_2NH to 1/1 with 1% *i*-Pr_2NH to EtOAc with 1% *i*-Pr_2NH) to afford (+)-enal *ent*-**18** (242 mg, 82%) as a brown oil.
$[\alpha]_D^{29}$ +19.9 (*c* 1.00, $CHCl_3$). HRMS (ESI, positive): calcd. For $C_{27}H_{42}N_3O_4$ $[M+H]^+$, 472.3170; found, 472.3186. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (–)-enal **18** (242 mg, 82%).



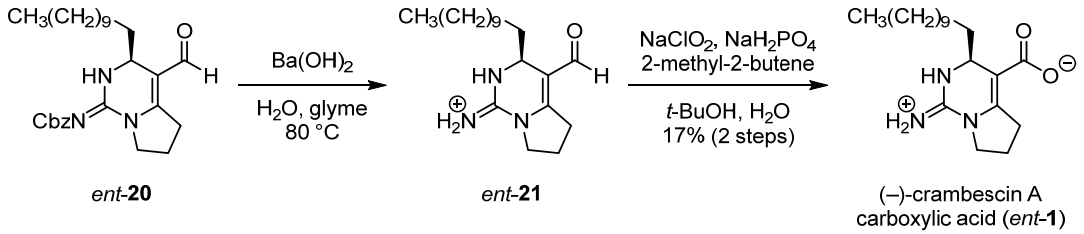
ent-**18** *ent*-**19**

(–)-guanidine *ent*-19: To a solution of enal *ent*-**18** (50.6 mg, 0.107 mmol) in MeOH (10 mL) was added distilled DBU (ca. 30 μL, 0.20 mmol) at room temperature. After being stirred for 18 h, the reaction was quenched with 1 M HCl (10 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (5 mL x 2). The combined organic layer was washed with brine (10 mL), 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 = 1/1) to afford (–)-guanidine *ent*-**19** (34.1 mg) as a yellow oil.
$[\alpha]_D^{28}$ –24.7 (*c* 1.71, $CHCl_3$). HRMS (ESI, positive): calcd. For $C_{19}H_{36}N_3O_2$ $[M+H]^+$, 338.2802; found, 338.2808. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-guanidine **19**.
(–)-crambescin C carboxylic acid (*ent*-3): To a solution of guanidine *ent*-**19** (34.1 mg) in *t*-BuOH (9 mL) and 2-methyl-2-butene (0.65 mL, 6.12 mmol) was added a solution of $NaClO_2$ (91.4 mg, 1.01 mmol) and NaH_2PO_4 (242 mg, 2.02 mmol) in H_2O (3 mL) at room temperature. After being stirred for 12 h, the reaction was quenched with sat. $NaHSO_3$ (10 mL) and brine (10 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (30 mL x 2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by HPLC on Nomura Chemical ODS-HG-5 monitored by UV detector (4.6 x 250 mm, 0.013 M TFA/MeCN, 1.0 mL/min, 220 nm) to afford (–)-crambescin C carboxylic acid (*ent*-**3**) (9.5 mg, 25% in 2 steps) as a colorless oil.
$[\alpha]_D^{26}$ –46.3 (*c* 0.48, MeOH). HRMS (ESI, positive): calcd. For $C_{19}H_{36}N_3O_3$ $[M+H]^+$, 354.2751; found, 354.2757. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-crambescin C carboxylic acid (**3**).



(–)-pyrrolidine *ent*-20: To a solution of enal *ent*-**18** (157 mg, 0.333 mmol) and Et_3N (100 μL, 0.717 mmol) in CH_2Cl_2 (16 mL) was added MsCl (50 μL, 0.65 mmol) at room temperature. After being stirred for 10 min at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by neutral silica gel flash column chromatography (hexane/EtOAc = 2/1) to afford (–)-pyrrolidine *ent*-**20** (77.7 mg, 51%) as a colorless oil.

$[\alpha]_D^{28}$ –12.7 (*c* 0.86, $CHCl_3$). HRMS (ESI, positive): calcd. For $C_{27}H_{40}N_3O_3$ $[M+H]^+$, 454.3064; found, 454.3071. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-pyrrolidine **20**.



(–)-guanidine *ent*-21: To a solution of pyrrolidine *ent*-**20** (17.2 mg, 0.0379 mmol) in glyme (2 mL) and H_2O (1.3 mL) was added to $Ba(OH)_2 \cdot 8H_2O$ (157 mg, 0.498 mmol) at room temperature. After being stirred for 7.5 h at 80 °C, the reaction mixture was added H_2O (5 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (10 mL x 2). The combined organic layer was washed with brine (20 mL), 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 = 5/1 to MeOH to MeOH with 1% CH_3COOH) to afford (–)-guanidine *ent*-**21** (7.0 mg) as a pale yellow oil.

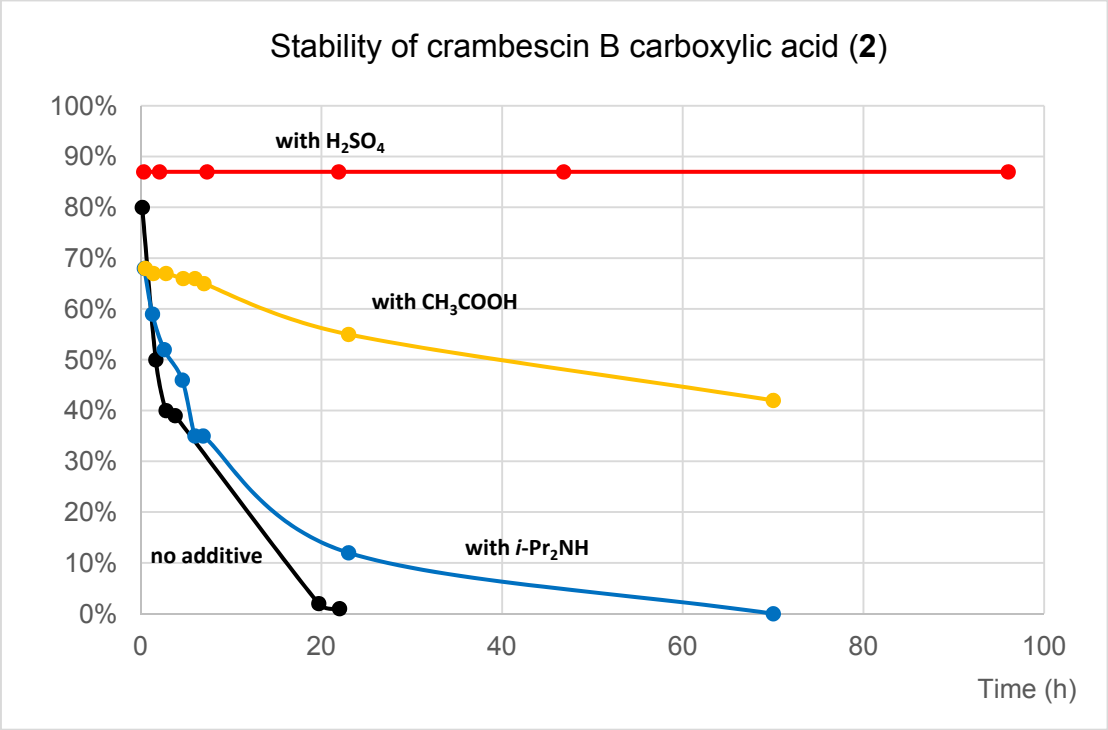
$[\alpha]_D^{27}$ –50.6 (*c* 0.33, $CHCl_3$). HRMS (ESI, positive): calcd. For $C_{19}H_{34}N_3O$ $[M+H]^+$, 320.2696; found, 320.2708. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-guanidine **21**.

(–)-crambescin A carboxylic acid (*ent*-1): To a solution of guanidine *ent*-**21** (7.0 mg) in *t*-BuOH (1.5 mL) and 2-methyl-2-butene (130 μL, 1.22 mmol) was added a solution of $NaClO_2$ (18.4 mg, 0.203 mmol) and NaH_2PO_4 (48.4 mg, 0.403 mmol) in H_2O (0.5 mL) at

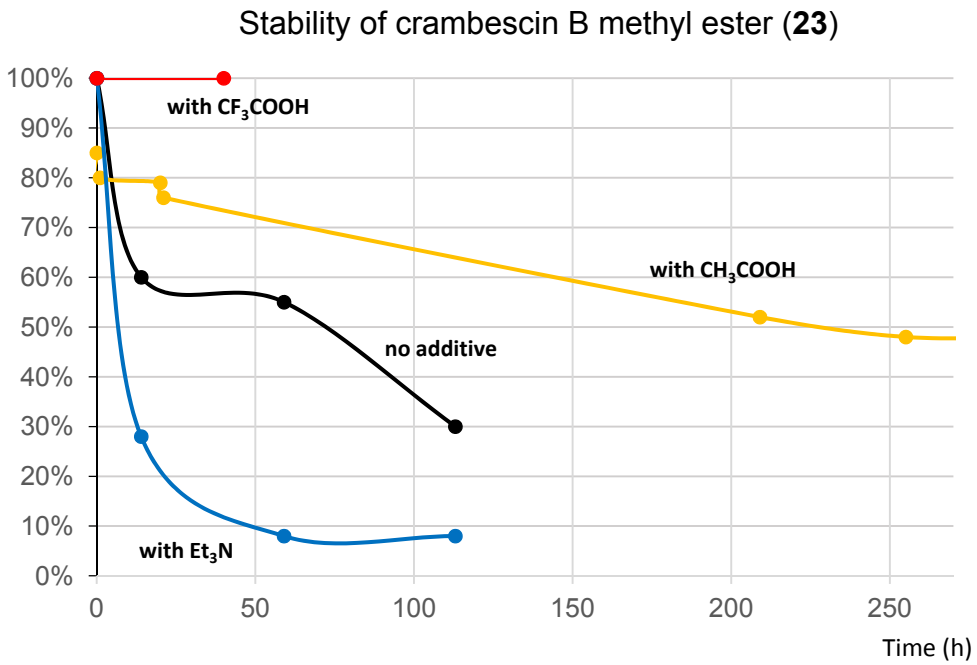
room temperature. After being stirred for 12 h, the reaction was quenched with sat. $NaHSO_3$ (2 mL) and brine (2 mL). The resulting mixture was partitioned, and the aqueous layer was extracted with EtOAc (5 mL x 2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by HPLC on Nomura Chemical ODS-HG-5 monitored by UV detector (4.6 x 250 mm, 0.013 M TFA/MeCN, 1.0 mL/min, 220 nm) to afford (–)-crambescin A carboxylic acid (*ent*-**1**) (2.2 mg, 17% in 2 steps) as a colorless oil.

$[\alpha]_D^{28}$ –53.9 (*c* 0.11, MeOH). HRMS (ESI, positive): calcd. For $C_{19}H_{34}N_3O_2$ $[M+H]^+$, 336.2646; found, 336.2654. IR, ^{1}H-NMR, and ^{13}C-NMR data were in agreement with those of (+)-crambescin A carboxylic acid (**1**).

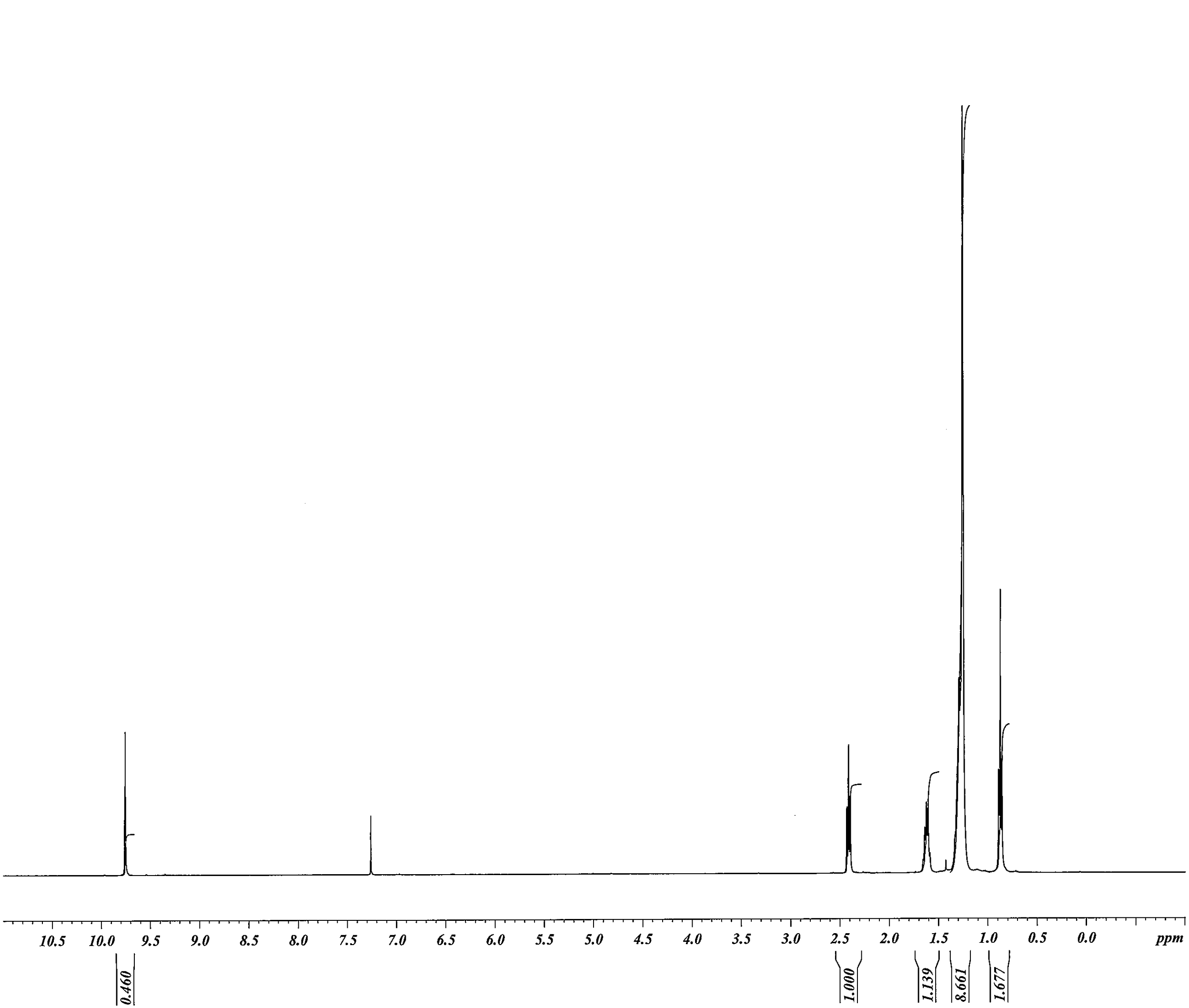
Stability of crambescin B carboxylic acid (2) and its methyl ester (23)



Decarboxylation of **2** (ca. 5 mg) into crambescin B decarboxylate **17** was monitored by ^{1}H NMR analysis at room temperature in CD_3OD (0.75 mL) in the presence of 6-10% of H_2SO_4, CH_3COOH, or *i*-Pr_2NH.



Transformation of **23** (ca. 5 mg) into crambescin C methyl ester **25** was monitored by ^{1}H NMR analysis at room temperature in CD_3OD (0.75 mL) in the presence of 6-10% of CF_3COOH, CH_3COOH, or Et_3N.



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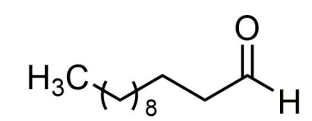

aldehyde **S1**

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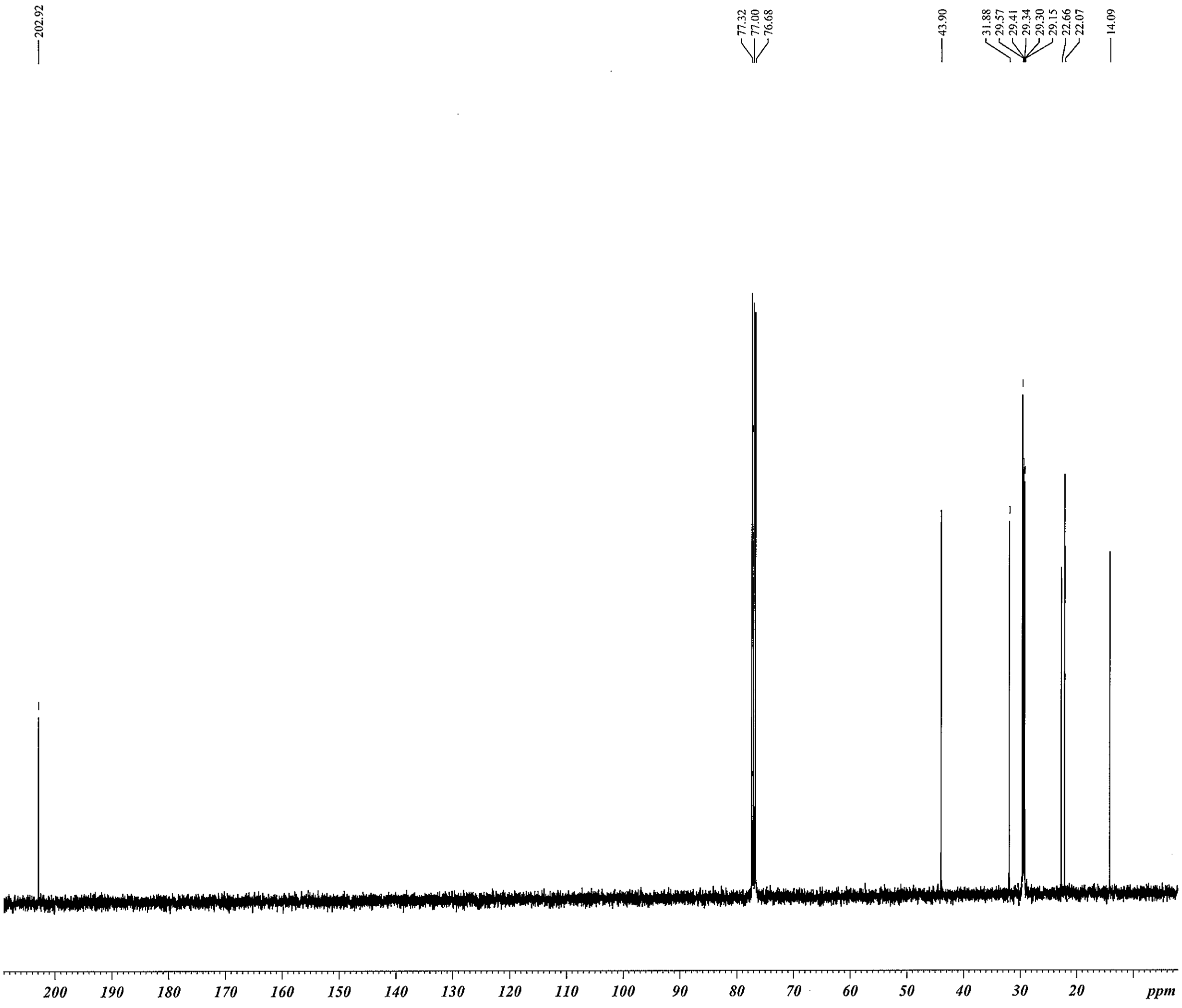

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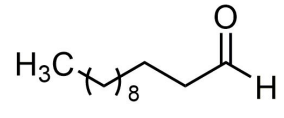
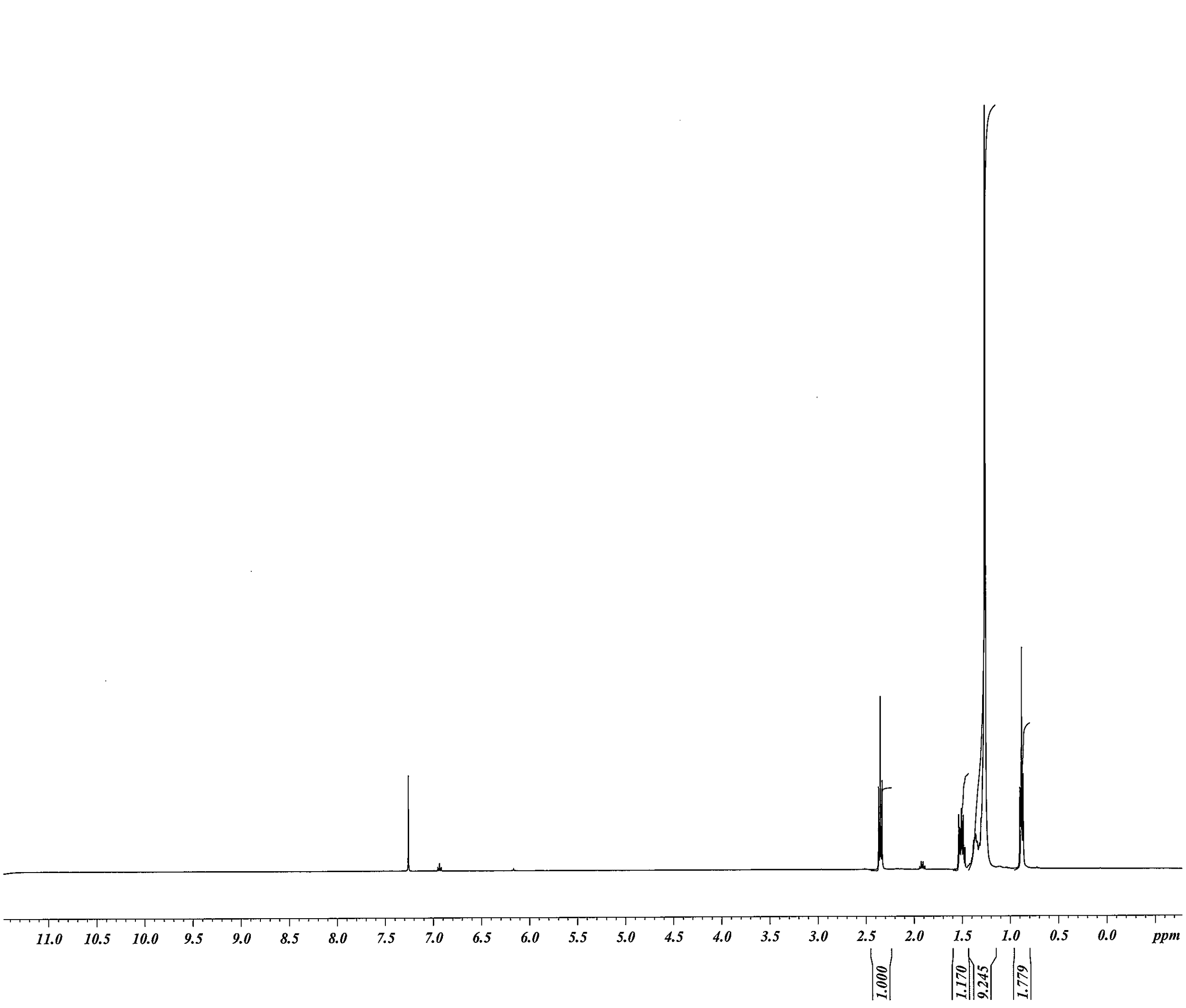
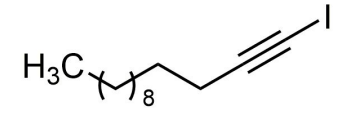


aldehyde **S1**

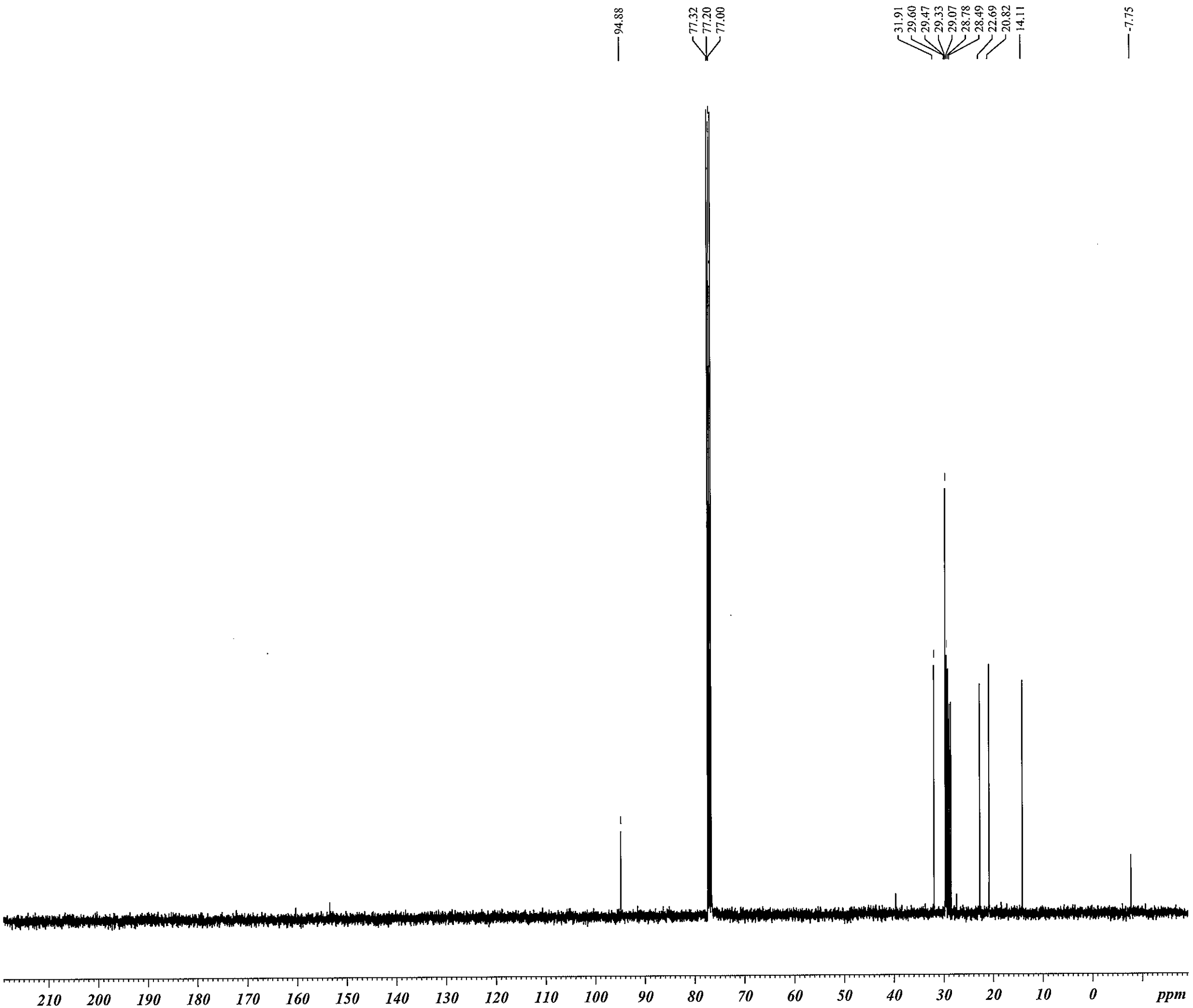
^{13}C NMR (100 MHz, $CDCl_3$)





iodoalkyne **S2**

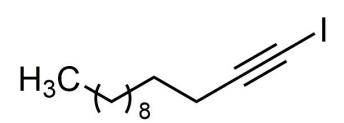
^{1}H NMR (400 MHz, $CDCl_3$)



Current Data Parameters
NAME nakane-A400
EXPNO 95
PROCNO 2

F2 - Acquisition Parameters
Date_ 20160329
Time 22.35
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 20642.5
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
PLW1 -1.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

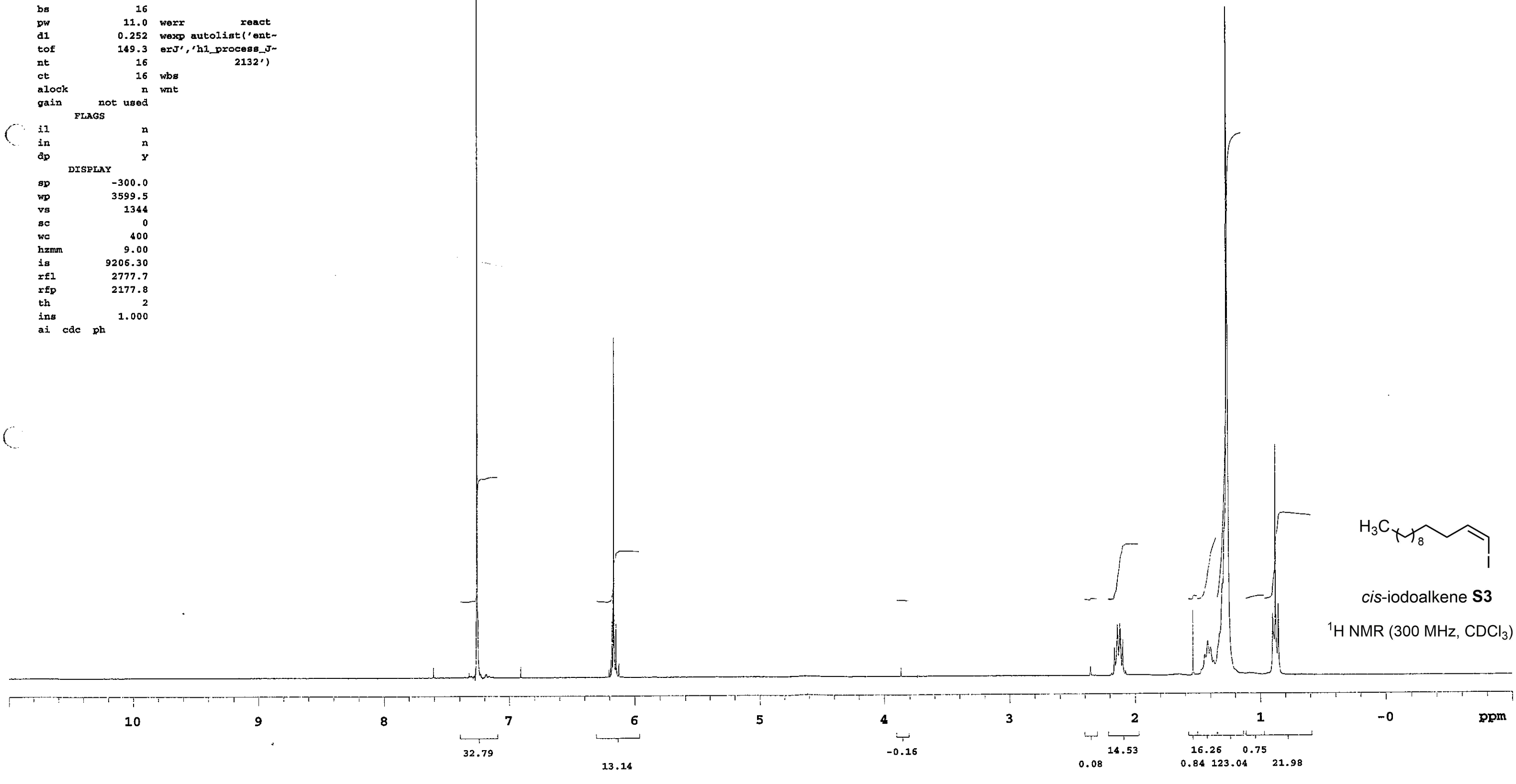
F2 - Processing parameters
SI 32768
SF 100.6127697 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



iodoalkyne **S2**

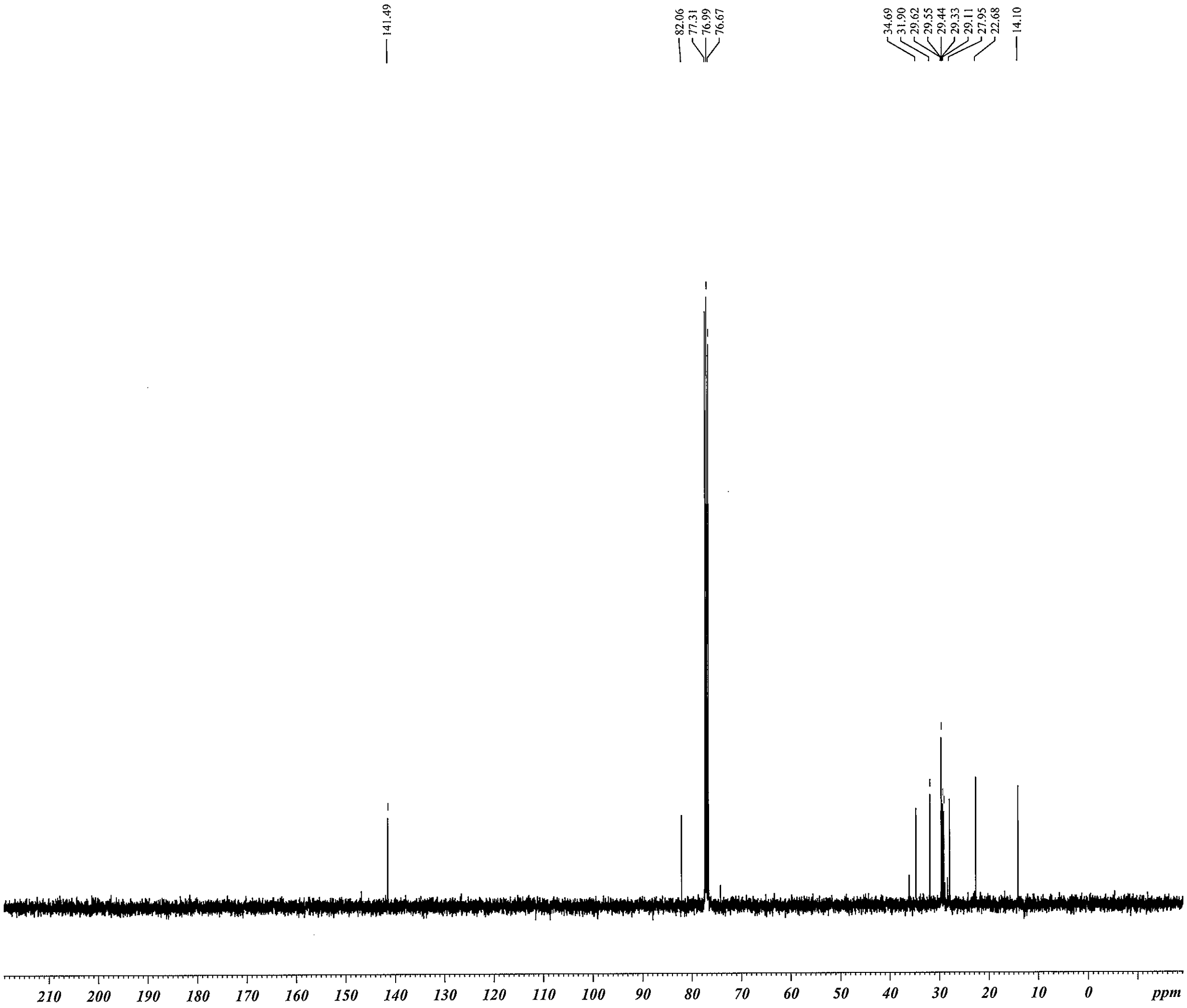
^{13}C NMR (100 MHz, $CDCl_3$)

```
exp9  std1h

      SAMPLE
date      Jan 31 14
solvent       CDCl3
file             exp
   ACQUISITION
sfrq        299.967
tn               H1
at             3.748
np             33728
sw            4499.5
fb              2250
bs                16
pw              11.0
d1             0.252
tof            149.3
nt                16
ct                16
alock              n
gain       not used
      FLAGS
il                 n
in                 n
dp                 Y
     DISPLAY
sp            -300.0
wp            3599.5
vs              1344
sc                 0
wc               400
hzmm            9.00
is           9206.30
rfl          2777.7
rfp          2177.8
th                 2
ins            1.000
ai  cdc  ph

      DEC. & VT
dfrq         299.957
dn                H1
dof         -10000.0
dm                nnn
dmm                 c
dmf               200
     PROCESSING
wtfile
proc               ft
fn          not used

werr           react
wexp autolist('ent~
erJ',’h1_process_J~
                2132')
wbs
wnt
```



cis-iodoalkene **S3**

^{1}H NMR (300 MHz, $CDCl_3$)



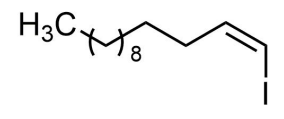
Current Data Parameters
NAME nakane-B400
EXPNO 163
PROCNO 2

F2 - Acquisition Parameters
Date_ 20160406
Time 17.39
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

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

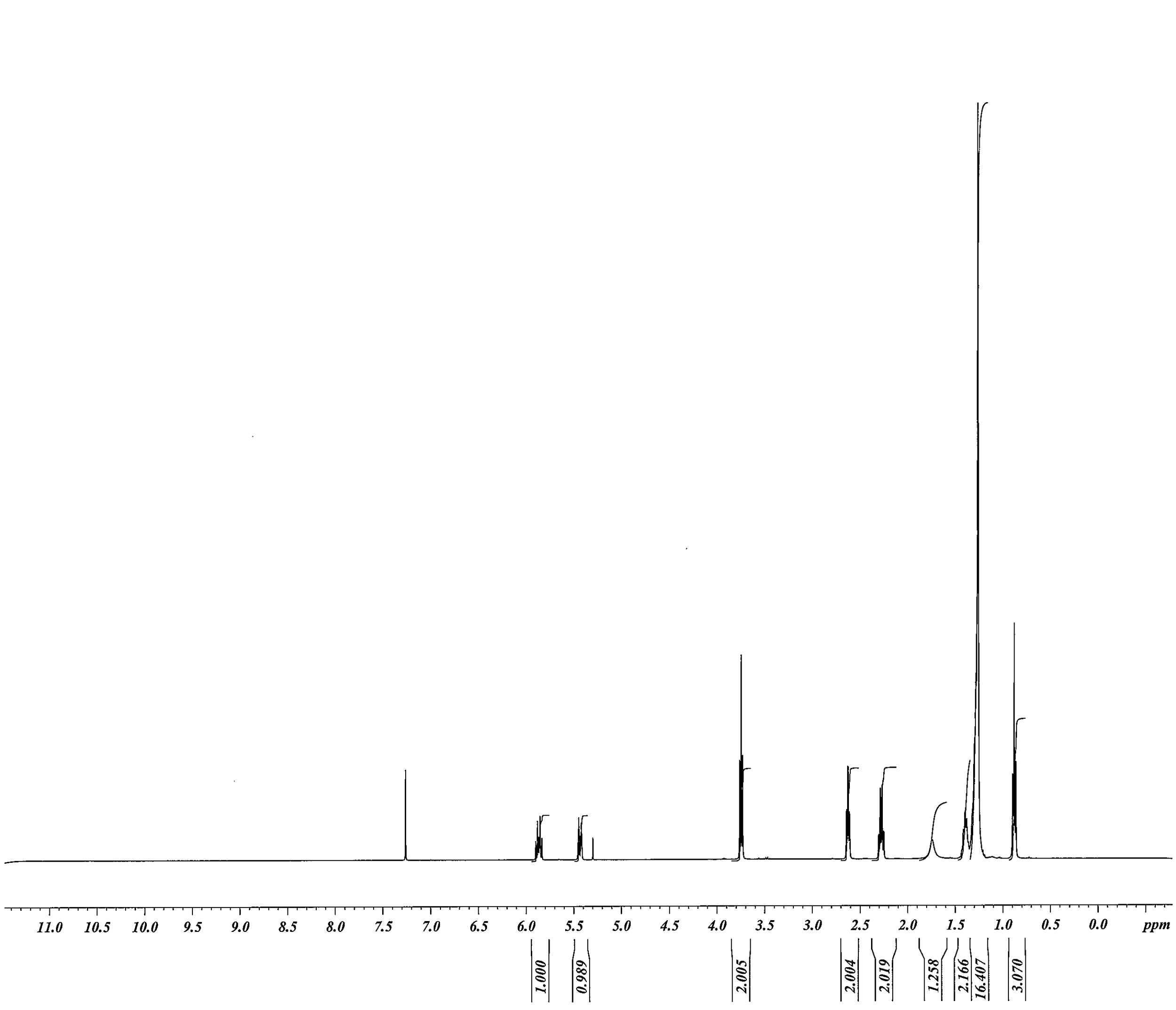
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

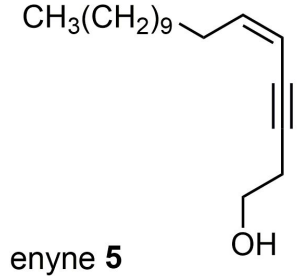
F2 - Processing parameters
SI 32768
SF 100.6127706 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



cis-iodoalkene **S3**

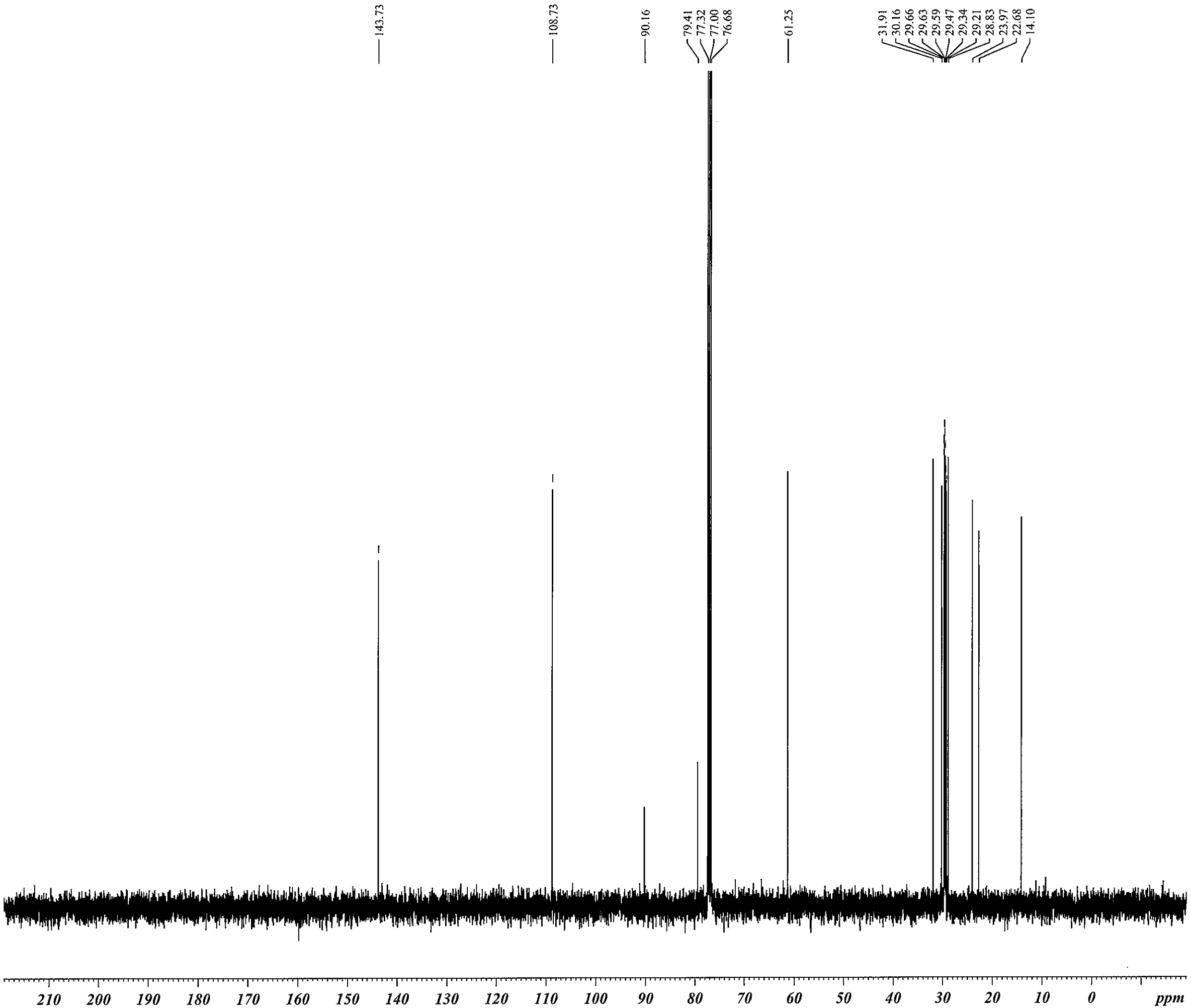
^{13}C NMR (100 MHz, $CDCl_3$)





enyne **5**

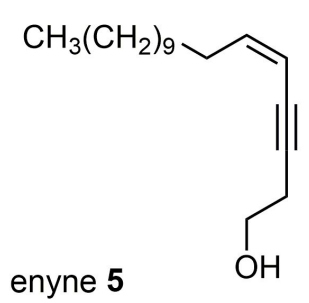
^{1}H NMR (400 MHz, $CDCl_3$)



Current Data Parameters
NAME nakane-A400
EXPNO 106
PROCNO 2

F2 - Acquisition Parameters
Date_ 20160407
Time 11.08
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 16384
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
PLW1 -1.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 100.6127704 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



enyne **5**

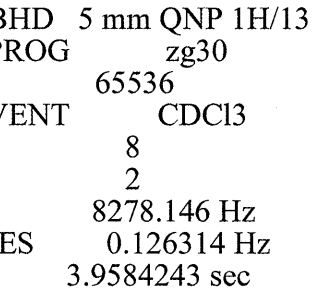
^{13}C NMR (100 MHz, $CDCl_3$)

Current Data Parameters
NAME nakane-n400
EXPNO 209
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150206
Time 16.52
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 203.2
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

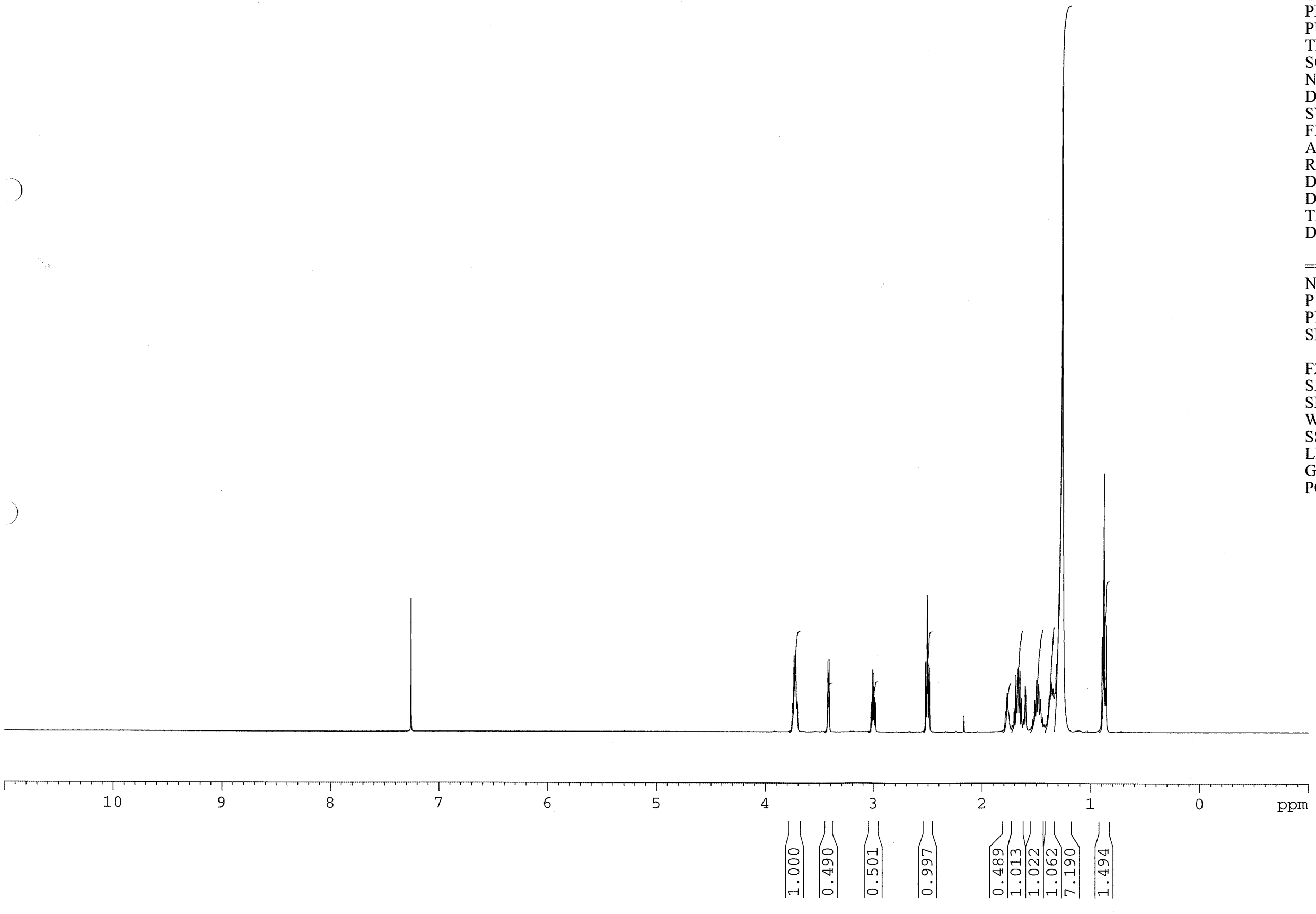
======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

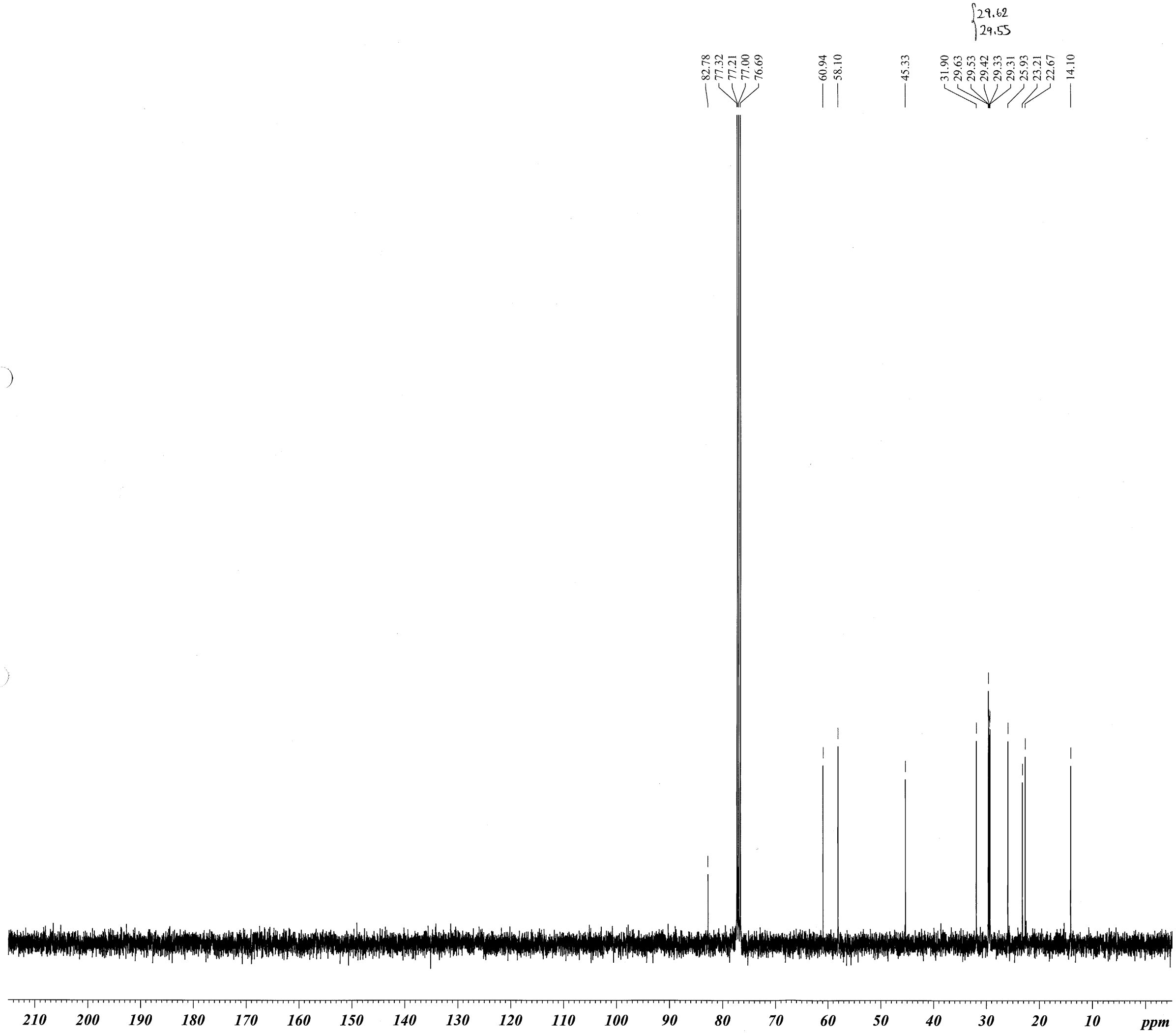
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



(–)-epoxide **6**

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





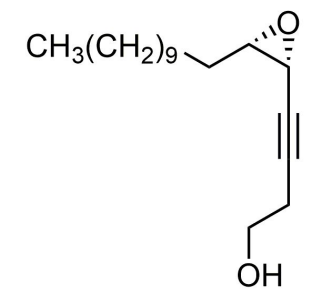
Current Data Parameters
NAME nakane-n400
EXPNO 210
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150206
Time 16.56
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 262
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(–)-epoxide **6**

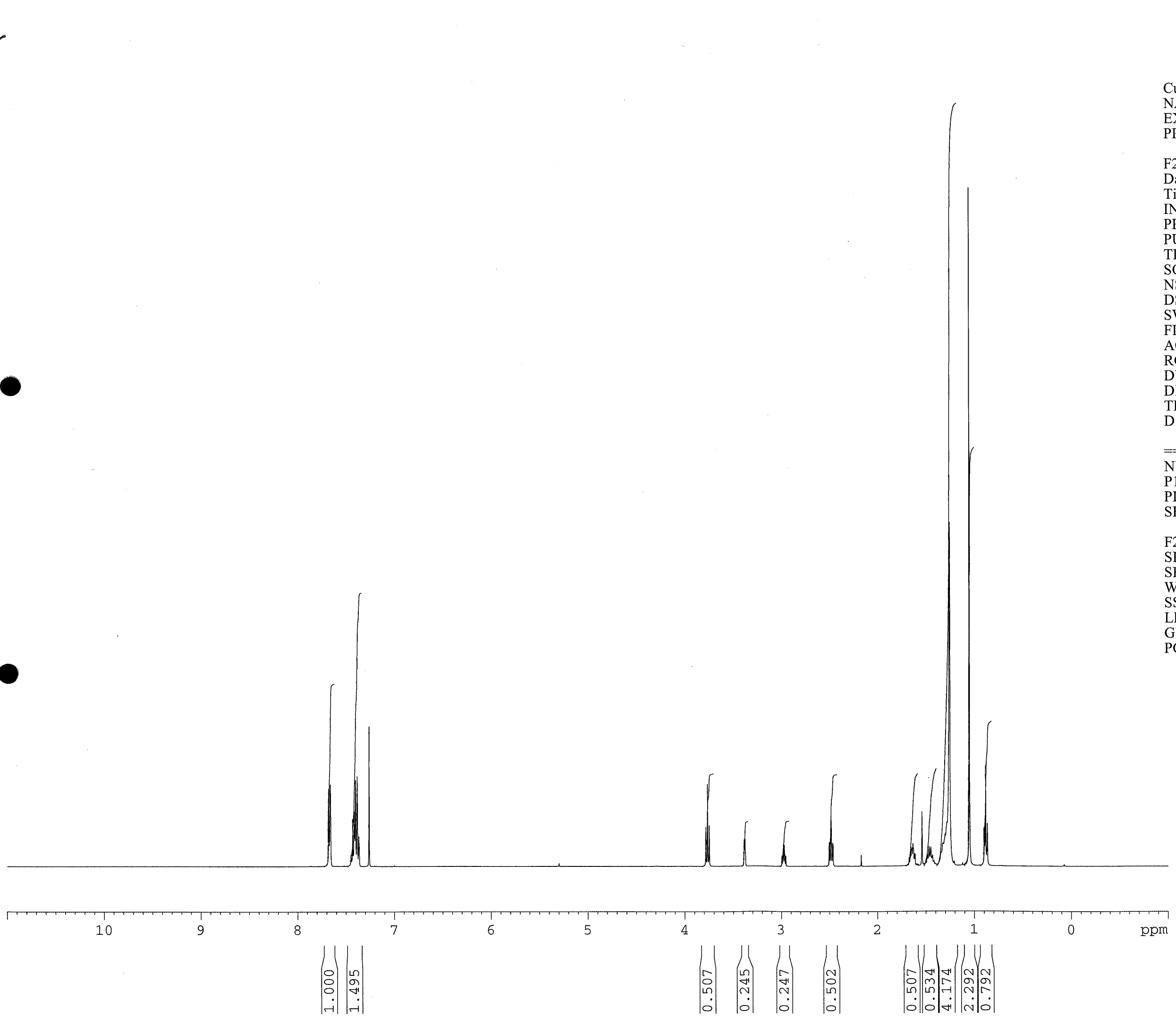
^{13}C NMR (100 MHz, $CDCl_3$)

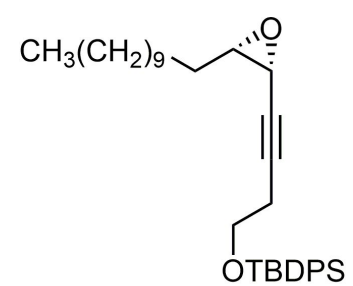
Current Data Parameters
NAME nakane-n400
EXPNO 241
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150210
Time 9.27
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 256
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

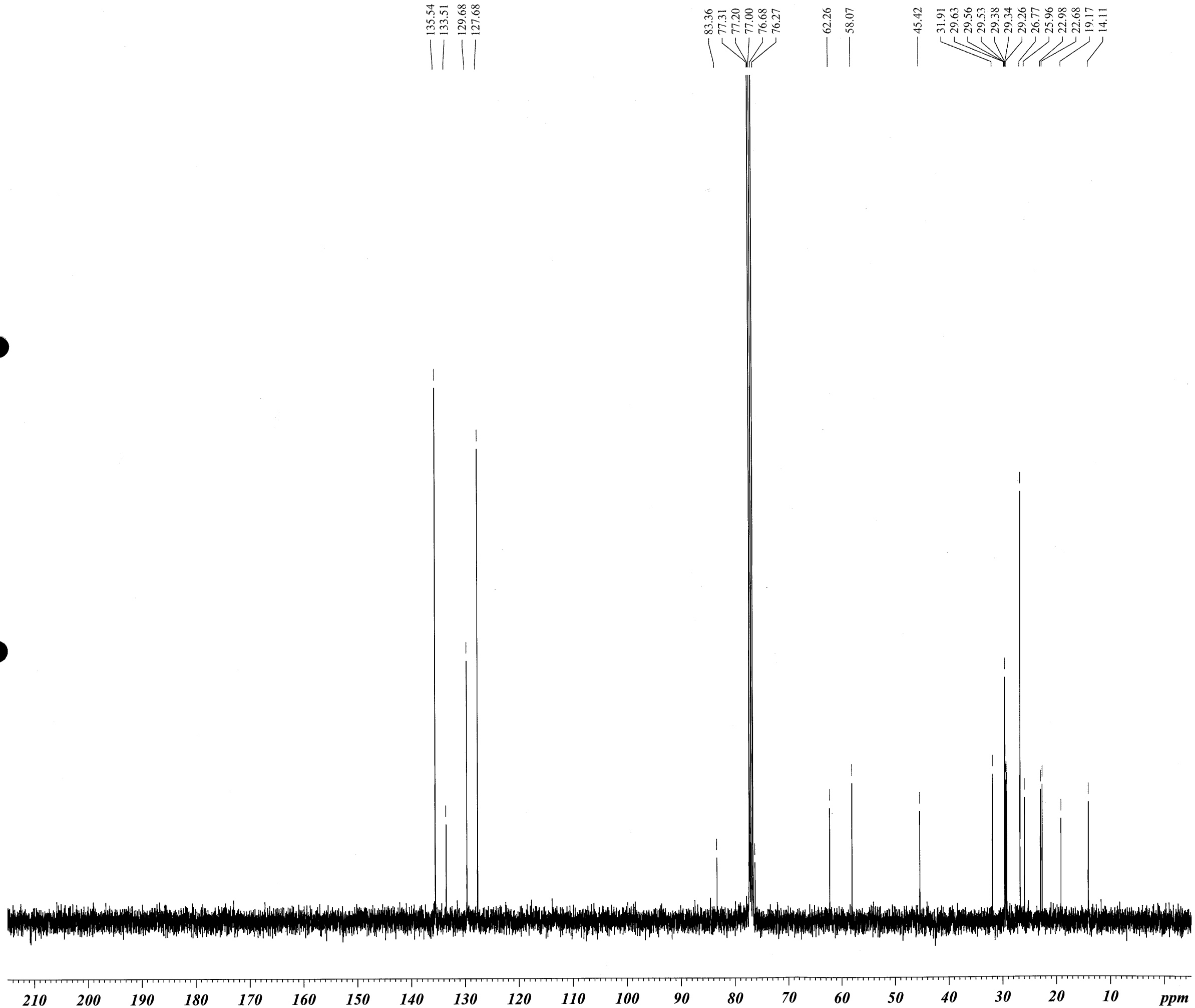
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(–)-epoxide **S4**

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



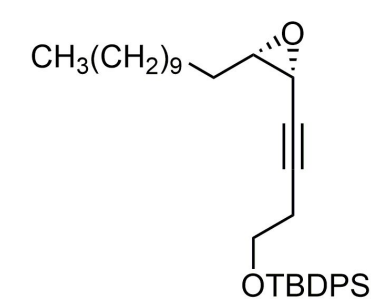
Current Data Parameters
NAME nakane-n400
EXPNO 242
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150210
Time 9.53
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 760
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(–)-epoxide **S4**

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

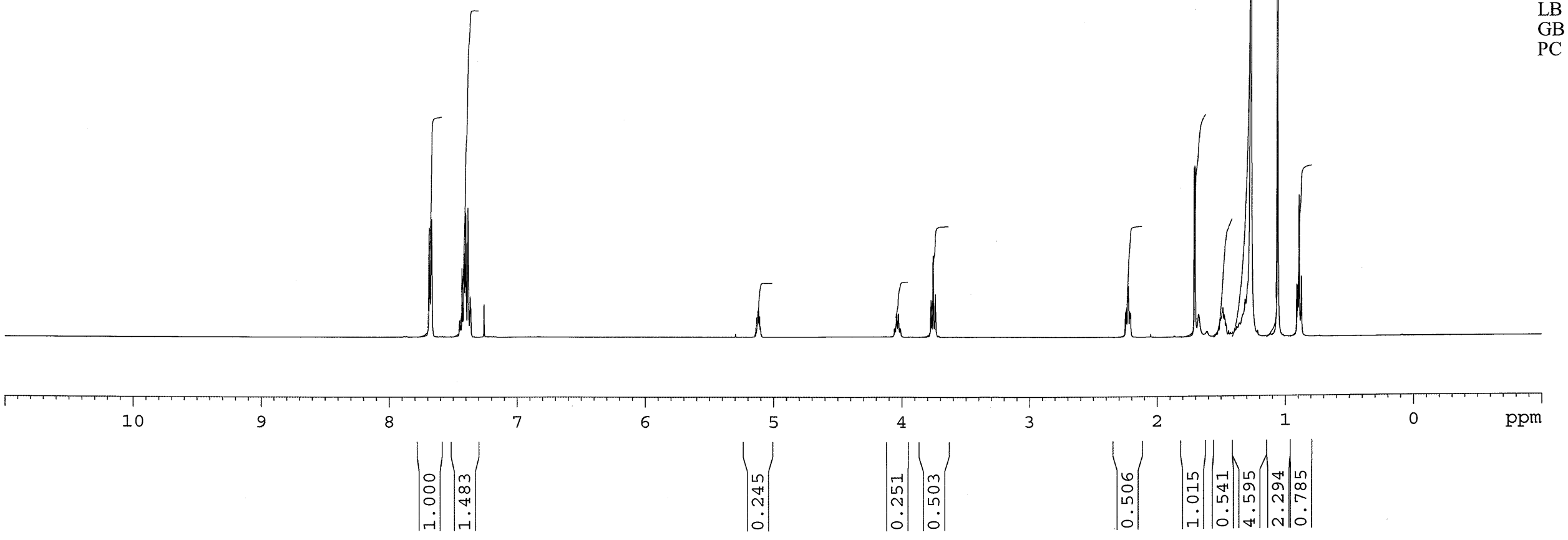
S50

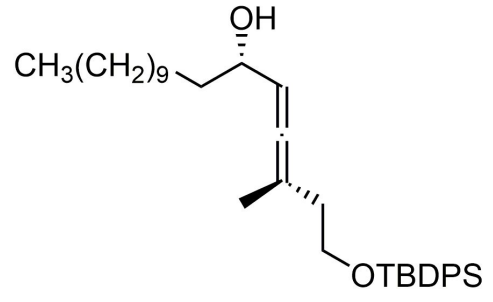
Current Data Parameters
NAME nakane-n400
EXPNO 174
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150113
Time 21.23
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 80.6
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

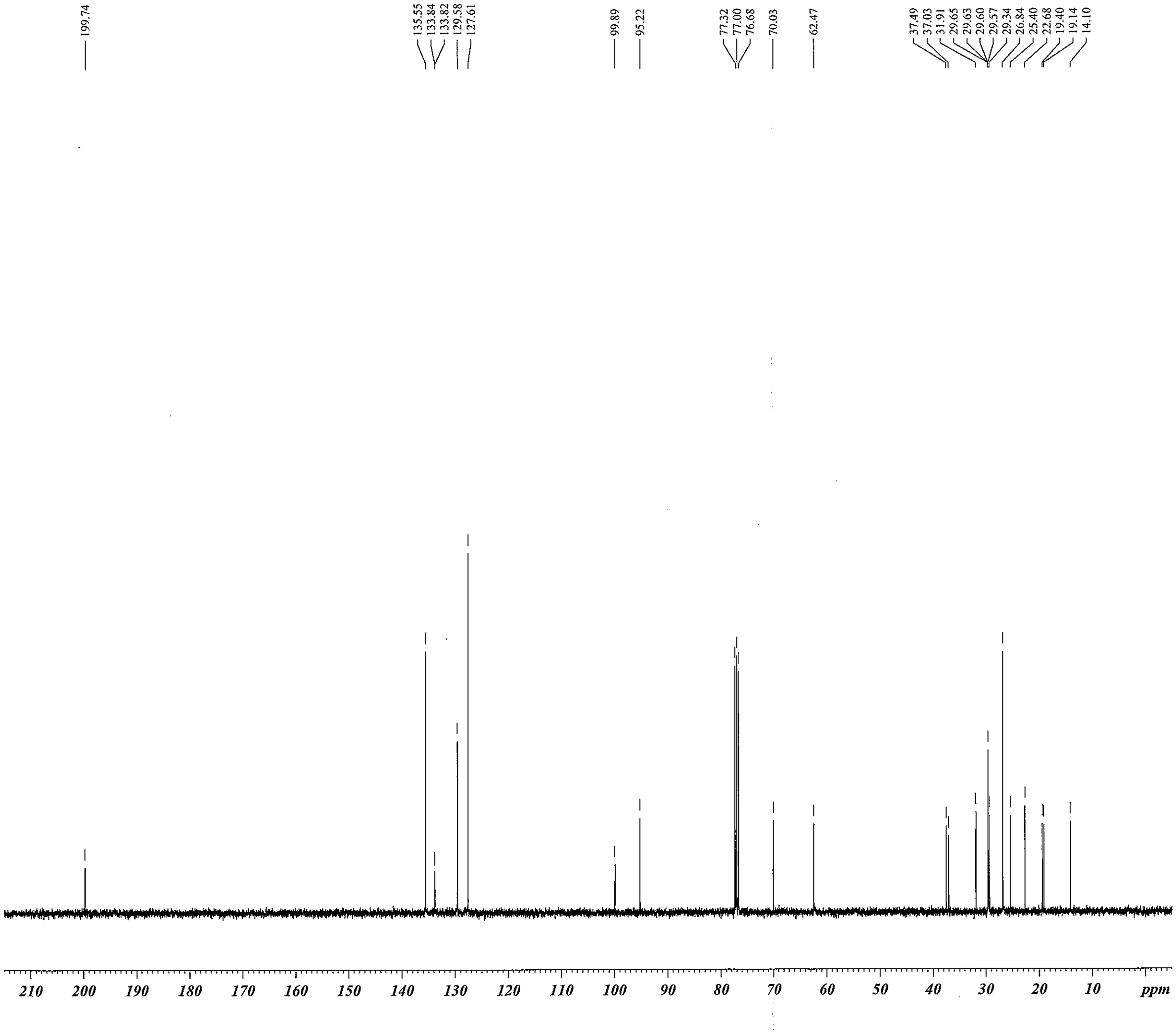
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(+)-allene **S5**

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



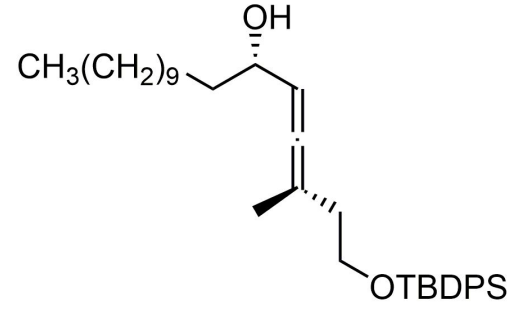
Current Data Parameters
NAME nakane-n400
EXPNO 175
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150113
Time 21.26
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 125
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

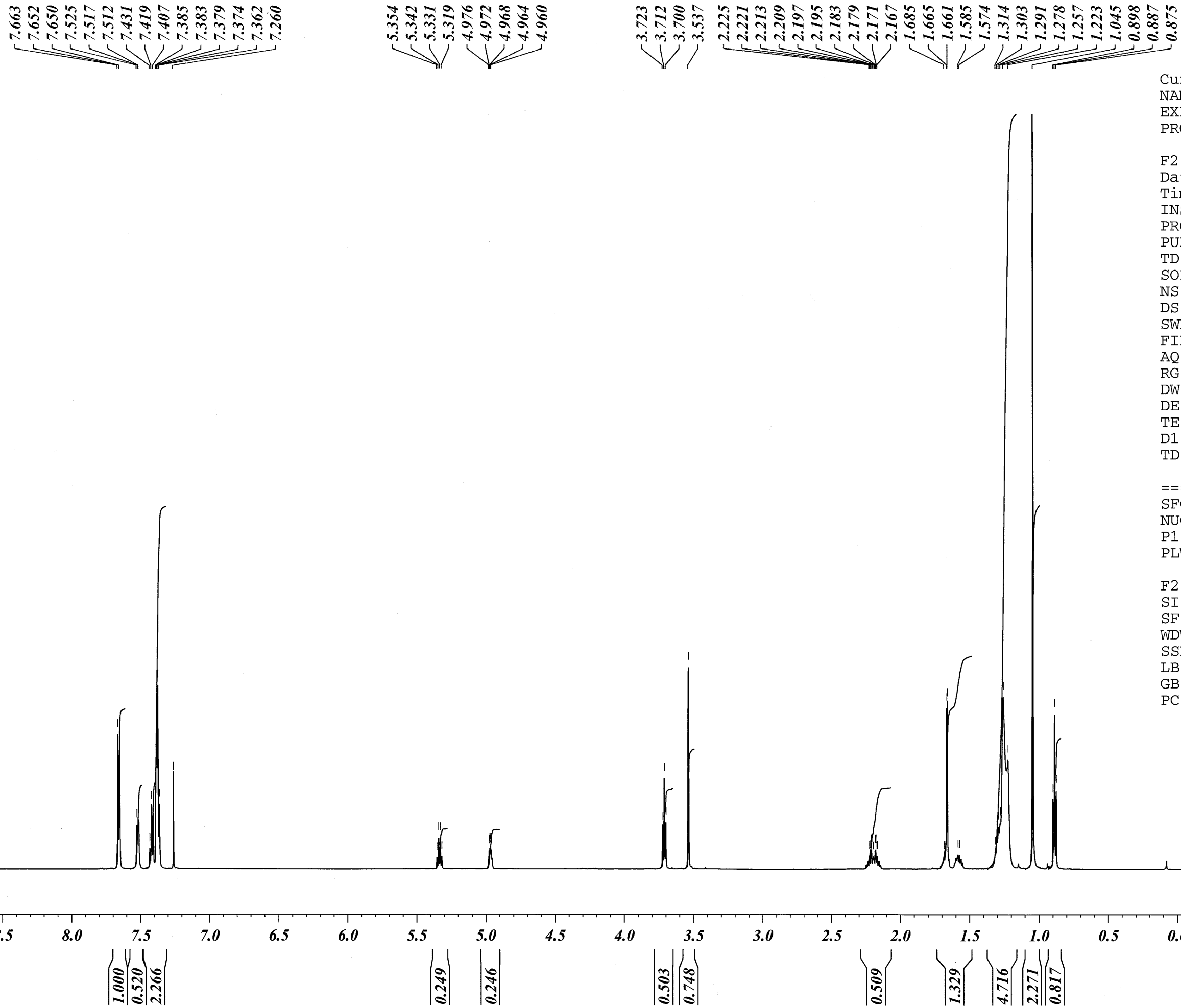
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127722 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



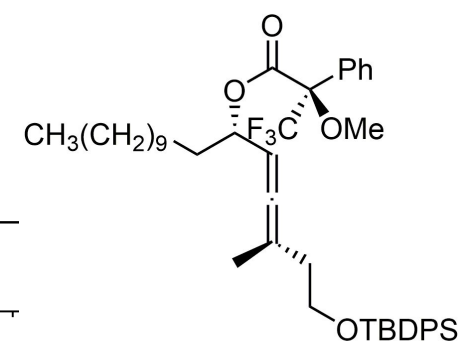
(+)-allene **S5**

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



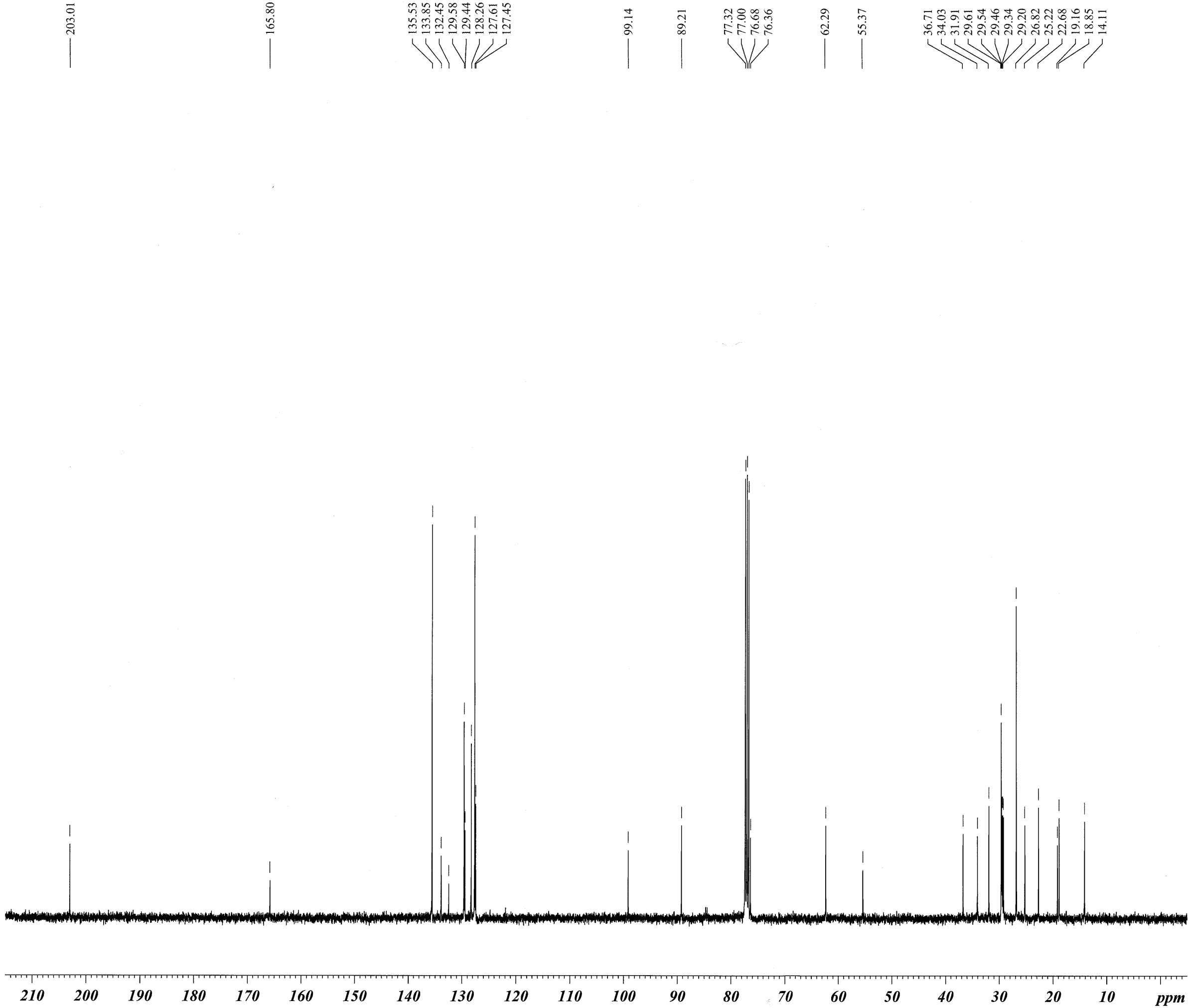
[2102] 1H r

```
Current Data Parameters
NAME          nakane600-1
EXPNO                  10
PROCNO                  2

F2 - Acquisition Parameters
Date_           20150210
Time               10.28
INSTRUM            spect
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             5699.088 Hz
FIDRES          0.086961 Hz
AQ              5.7496920 sec
RG                  6.64
DW                 87.733 usec
DE                 10.00 usec
TE                 295.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1325529 MHz
NUC1                   1H
P1                 10.00 usec
PLW1          4.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300153 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



(+)-MTPA ester **S6a**

^{1}H NMR (600 MHz, $CDCl_3$)



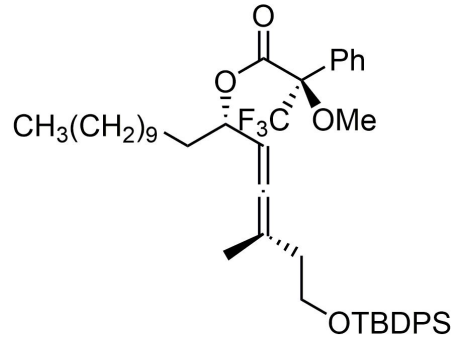
Current Data Parameters
NAME nakane-n400
EXPNO 181
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150115
Time 13.13
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 703
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

========== CHANNEL f1 ==========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127715 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

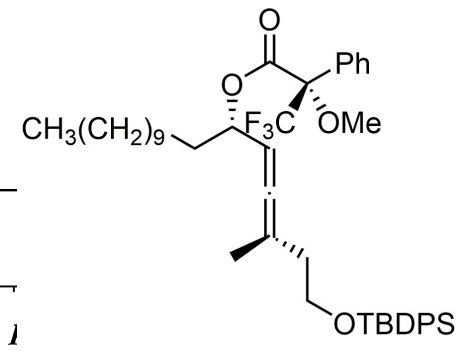


(+)-MTPA ester **S6a**

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

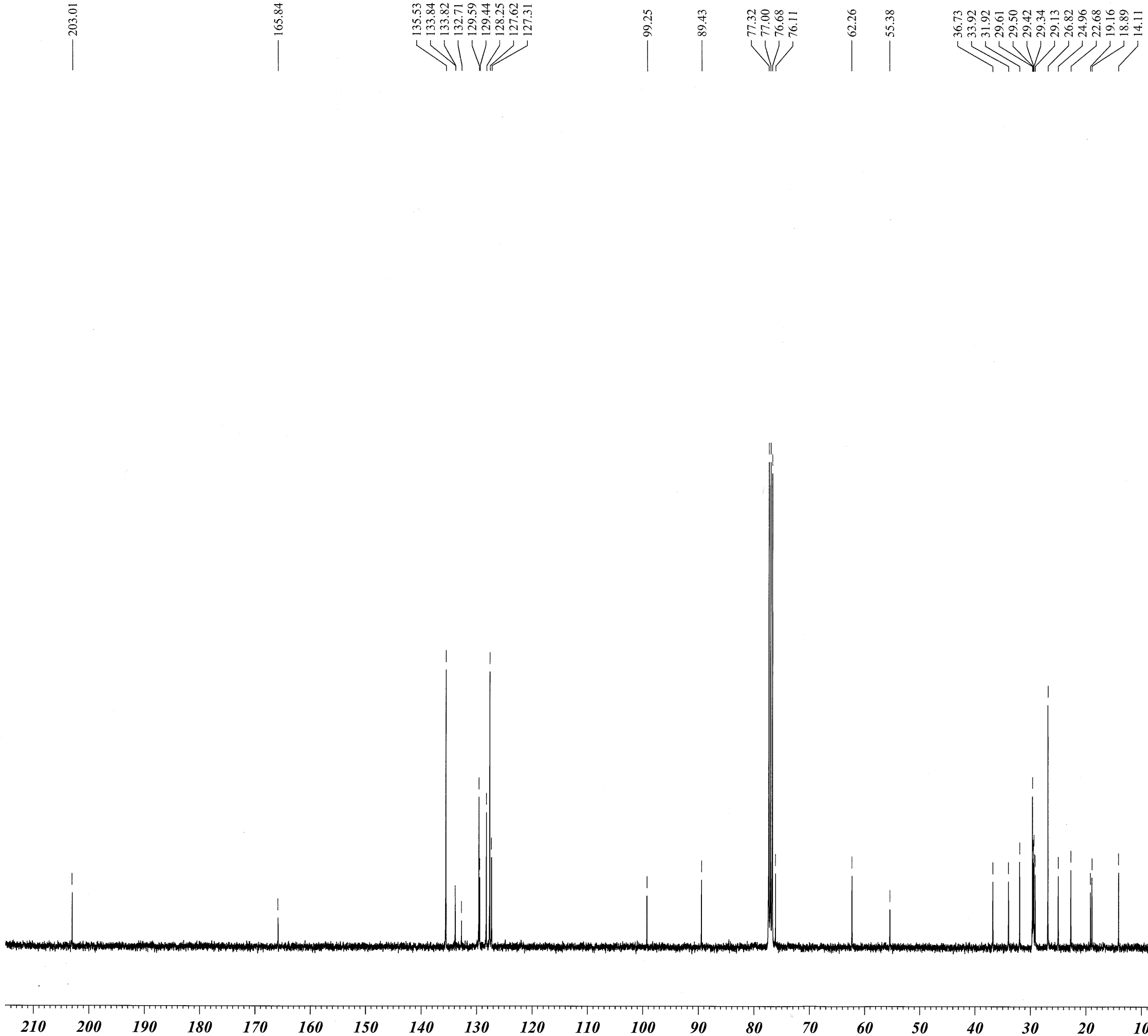
[2101] 1H r

```
Current Data Parameters
NAME          nakane600-1
EXPNO                   9
PROCNO                  2

F2 - Acquisition Parameters
Date_            20150210
Time                10.15
INSTRUM             spect
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              5699.088 Hz
FIDRES           0.086961 Hz
AQ               5.7496920 sec
RG                   6.64
DW                 87.733 usec
DE                 10.00 usec
TE                 295.0 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1325529 MHz
NUC1                   1H
P1                 10.00 usec
PLW1          4.00000000 W

F2 - Processing parameters
SI                  65536
SF           600.1300143 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



(+)-MTPA ester **S6b**

^{1}H NMR (600 MHz, $CDCl_3$)



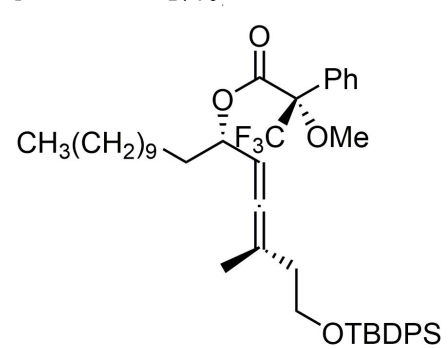
Current Data Parameters
NAME nakane-n400
EXPNO 178
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150115
Time 11.37
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1220
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(+)-MTPA ester **S6b**

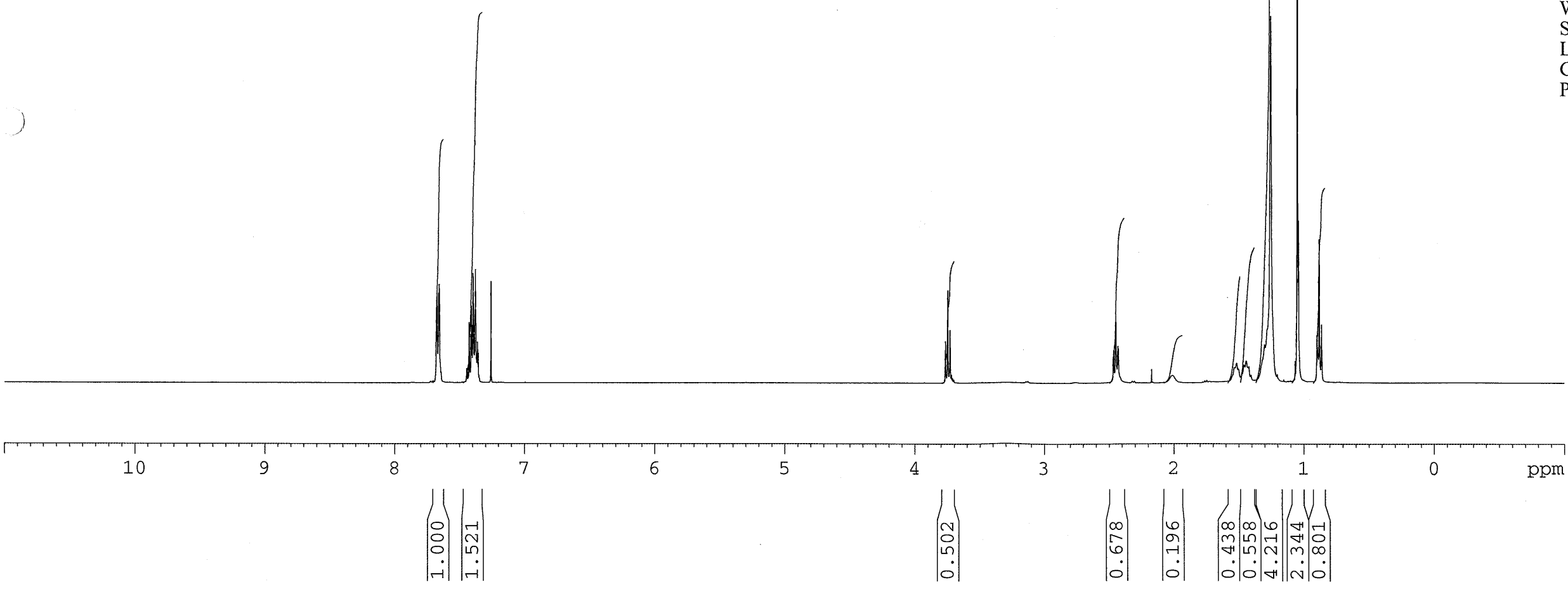
^{13}C NMR (100 MHz, $CDCl_3$)

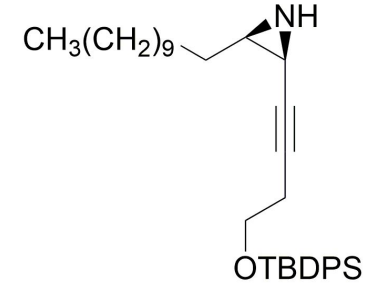
Current Data Parameters
NAME nakane-n400
EXPNO 215
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150206
Time 20.09
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 161.3
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 =======
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

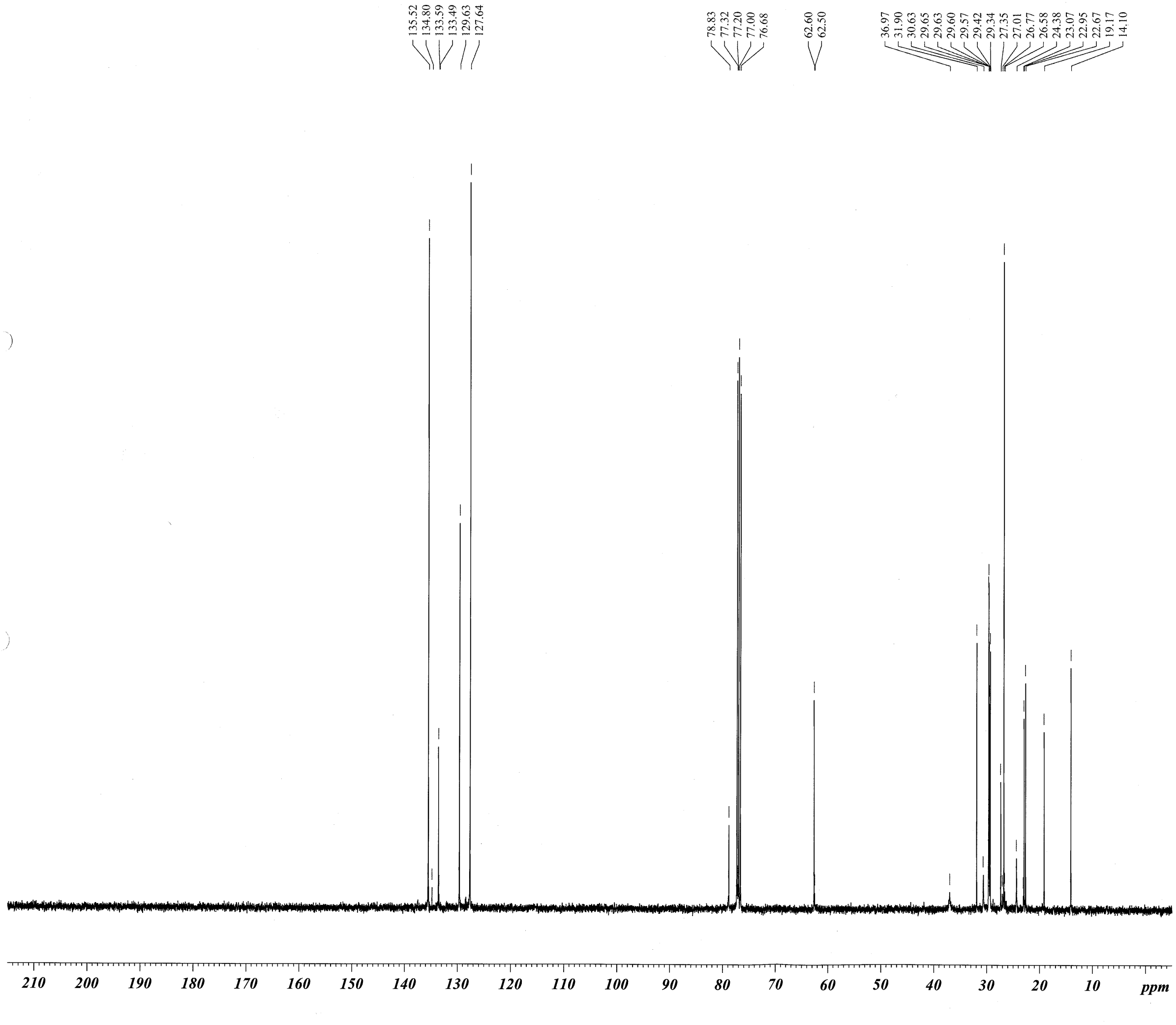
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(–)-aziridine **9**

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



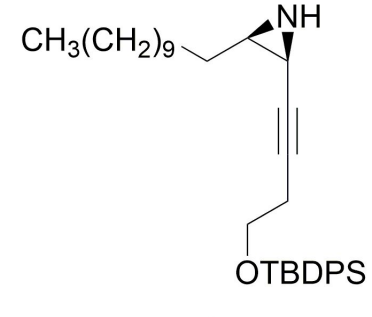
Current Data Parameters
NAME nakane-n400
EXPNO 216
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 20.04
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1076
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127729 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.70



(–)-aziridine **9**

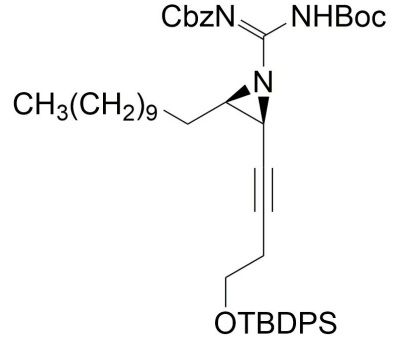
^{13}C NMR (100 MHz, $CDCl_3$)

Current Data Parameters
NAME nakane-n400
EXPNO 217
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150206
Time 22.11
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

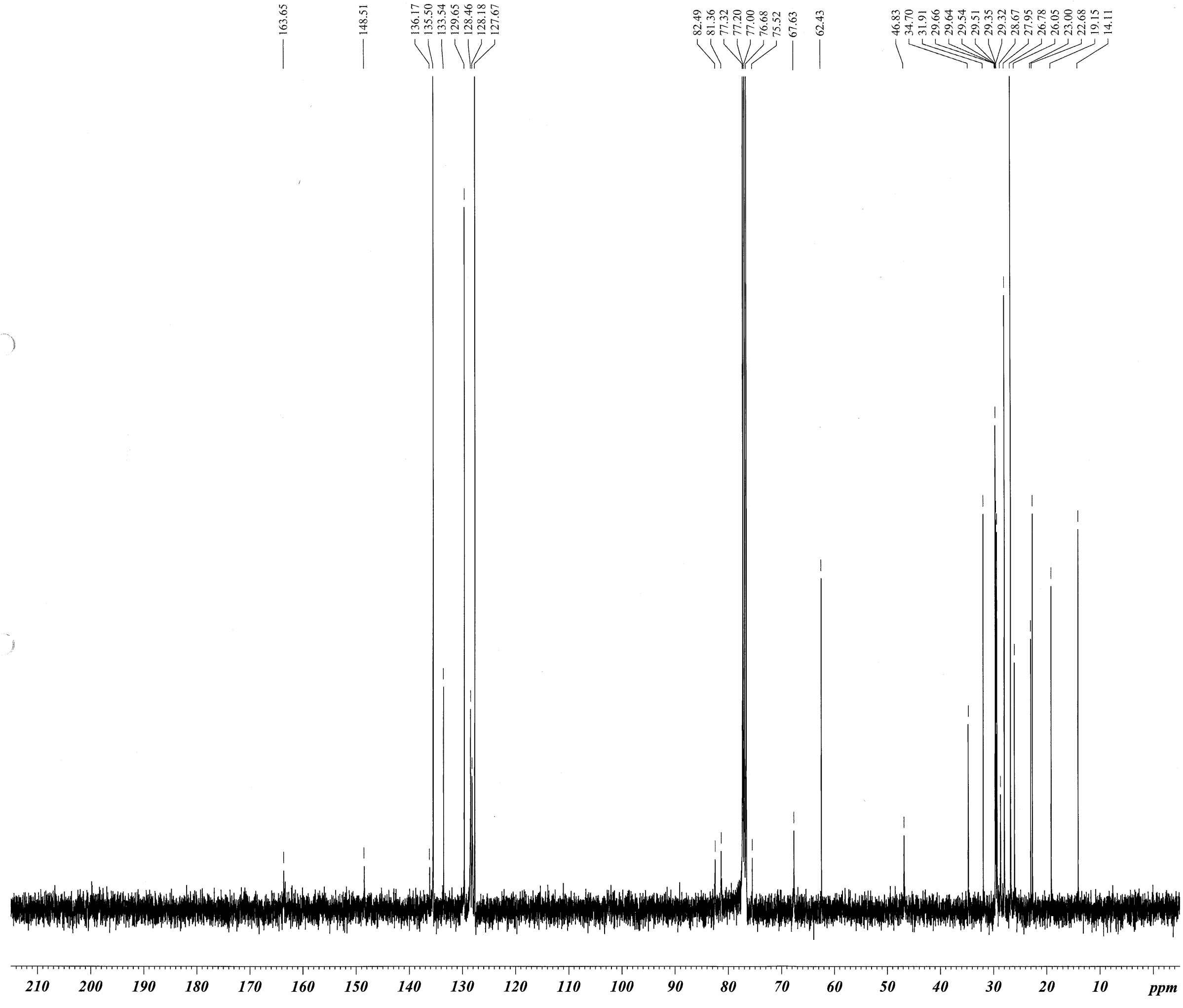
======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



(+)-guanidino-aziridine **10**

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



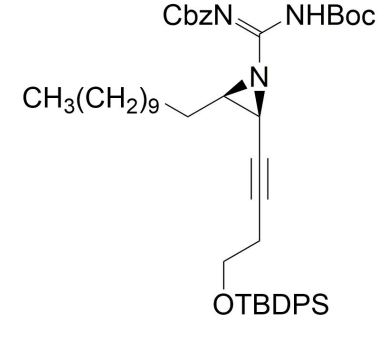
Current Data Parameters
NAME nakane-n400
EXPNO 218
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150206
Time 23.13
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2400
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127715 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(+)-guanidino-aziridine **10**

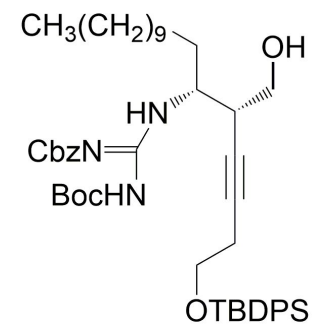
^{13}C NMR (100 MHz, $CDCl_3$)

Current Data Parameters
NAME nakane-n400
EXPNO 223
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150210
Time 21.11
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 512
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

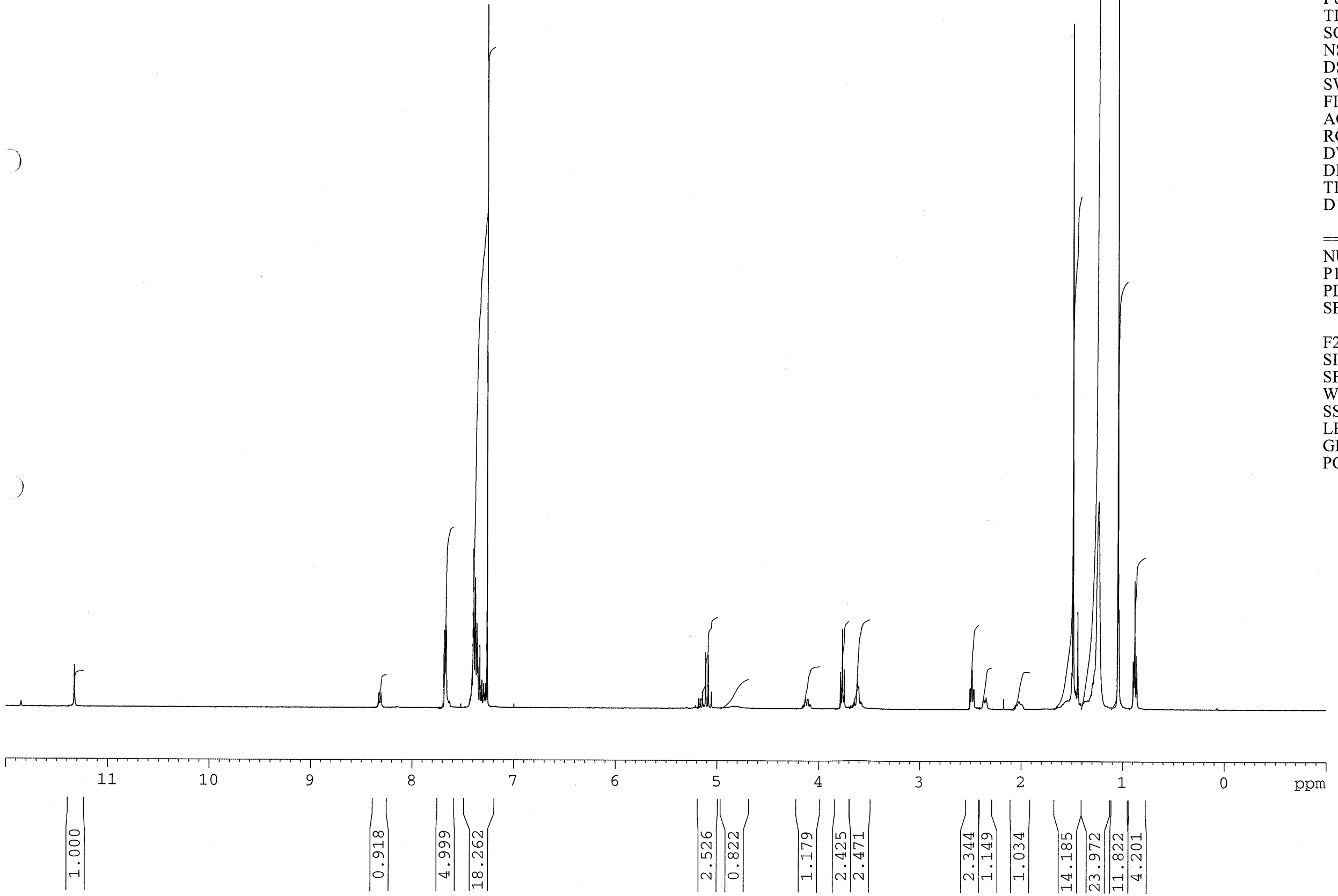
========== CHANNEL f1 ==========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

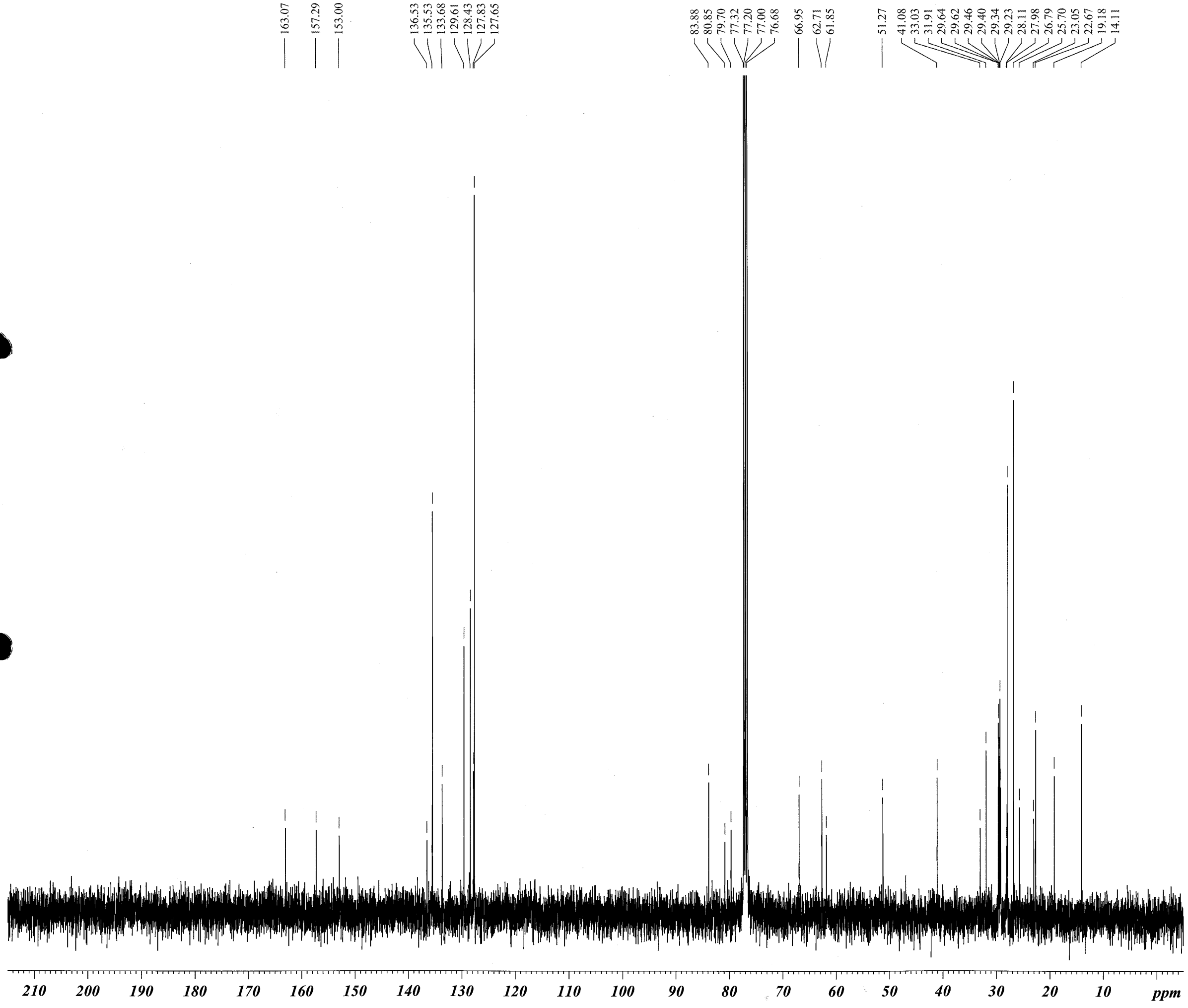
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



(–)-alcohol **11**

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





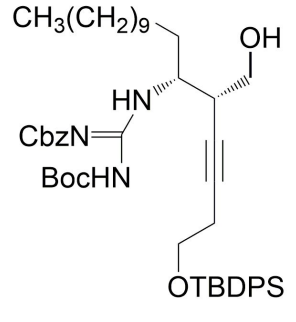
Current Data Parameters
NAME nakane-n400
EXPNO 224
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150207
Time 10.58
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1300
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

========== CHANNEL f1 ==========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(–)-alcohol **11**

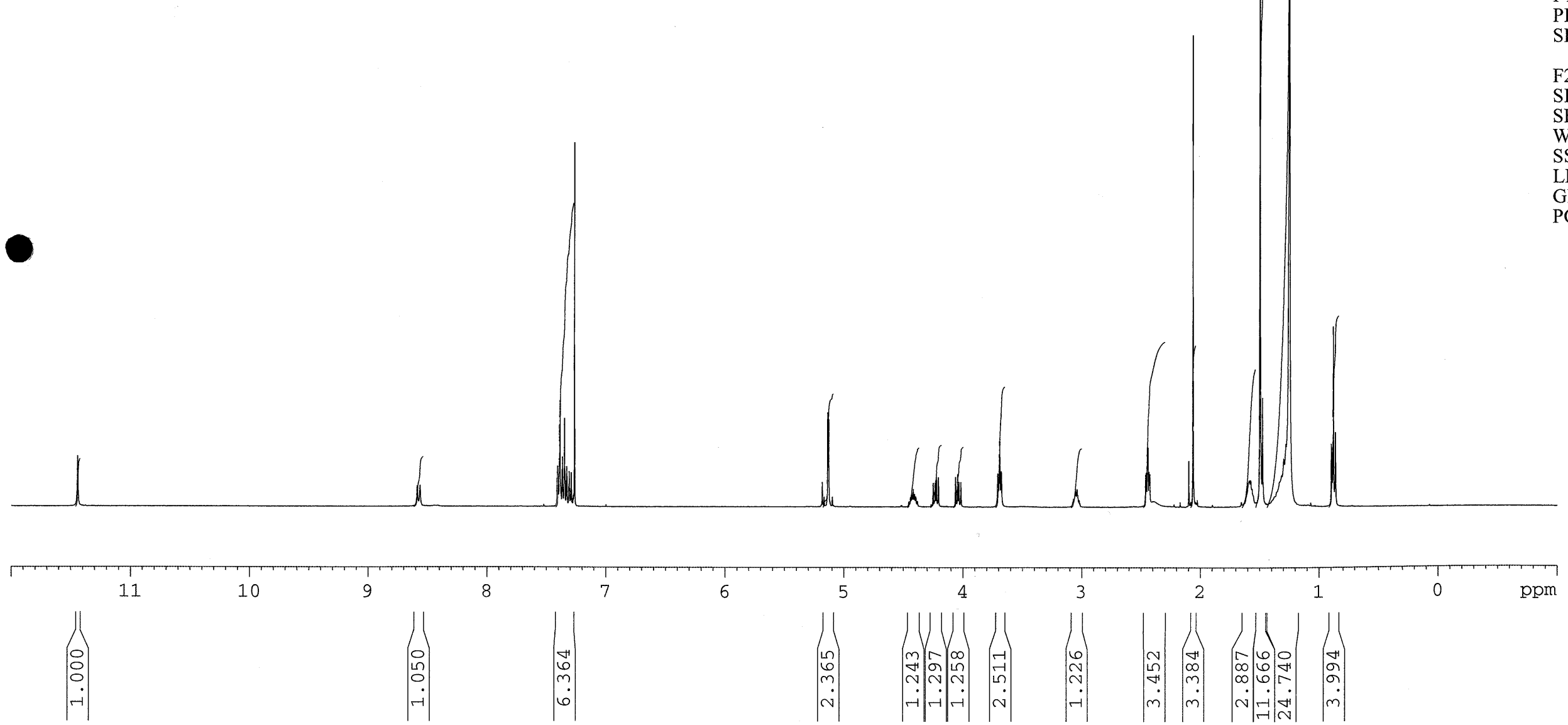
^{13}C NMR (100 MHz, $CDCl_3$)

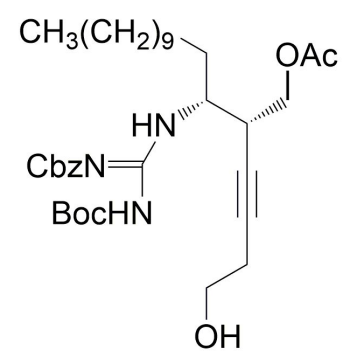
Current Data Parameters
NAME nakane-n400
EXPNO 227
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150212
Time 17.14
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

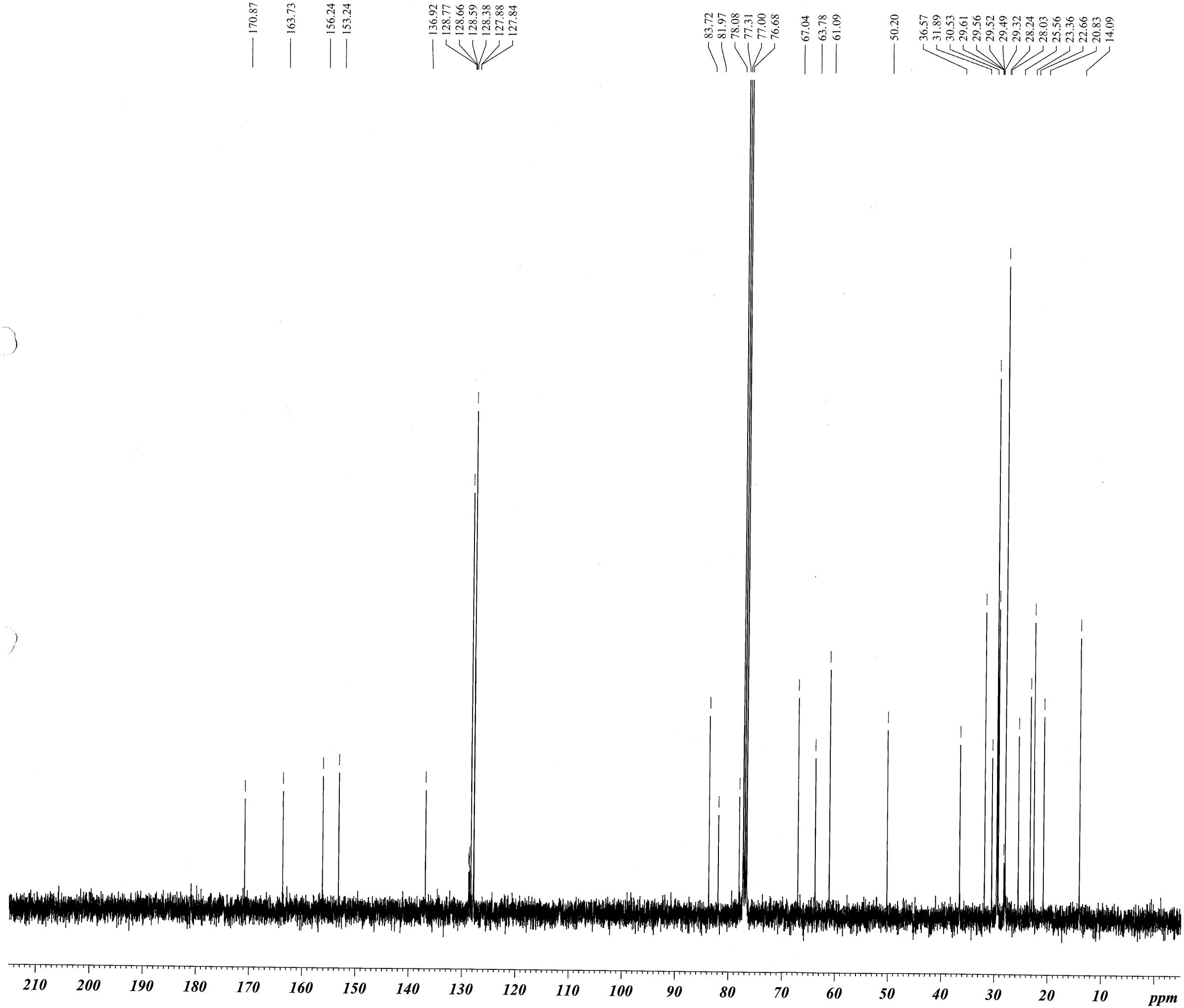
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(+)-alcohol **12**

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



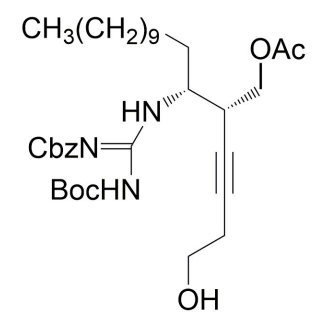
Current Data Parameters
NAME nakane-n400
EXPNO 228
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150207
Time 14.19
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127722 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(+)-alcohol **12**

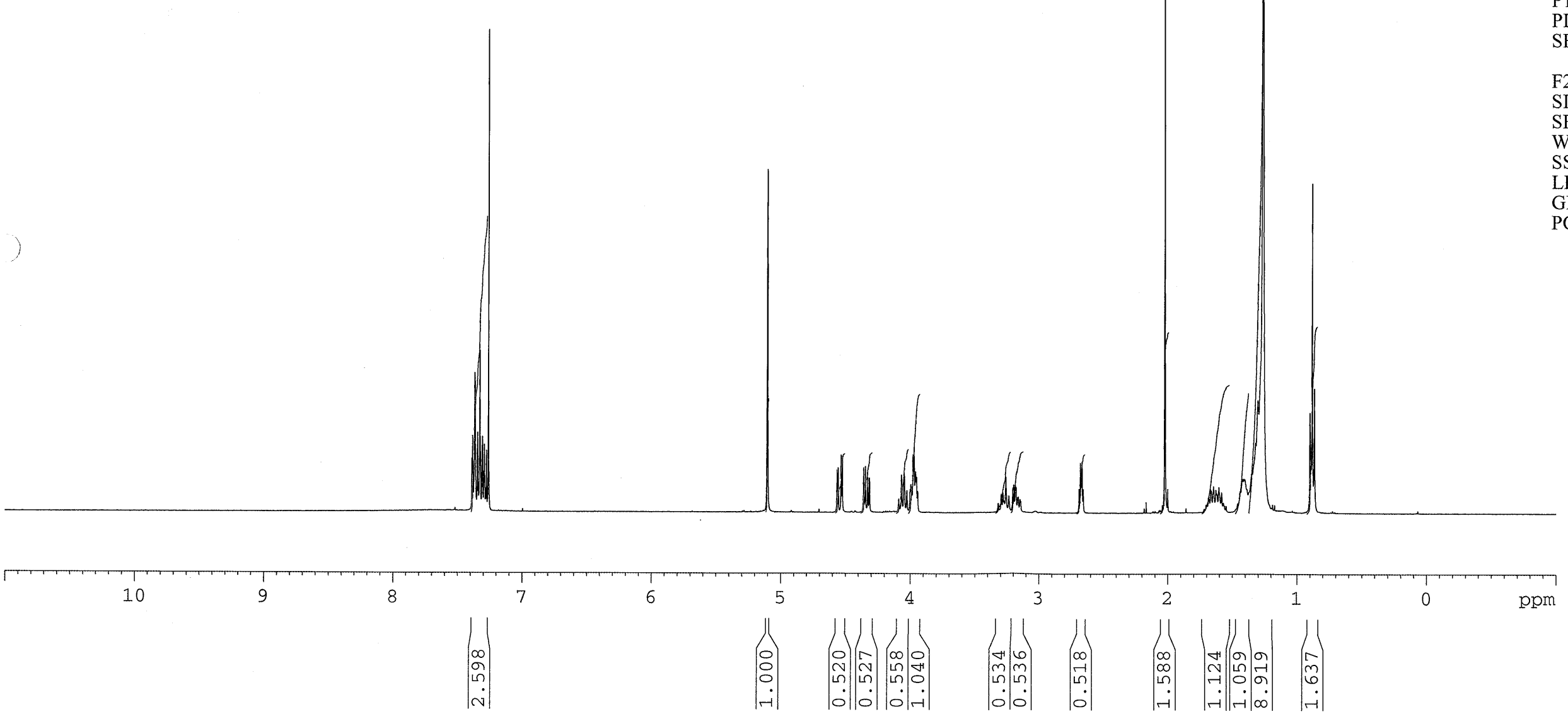
^{13}C NMR (100 MHz, $CDCl_3$)

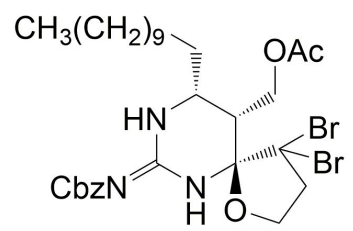
Current Data Parameters
NAME nakane-n400
EXPNO 231
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150210
Time 21.17
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

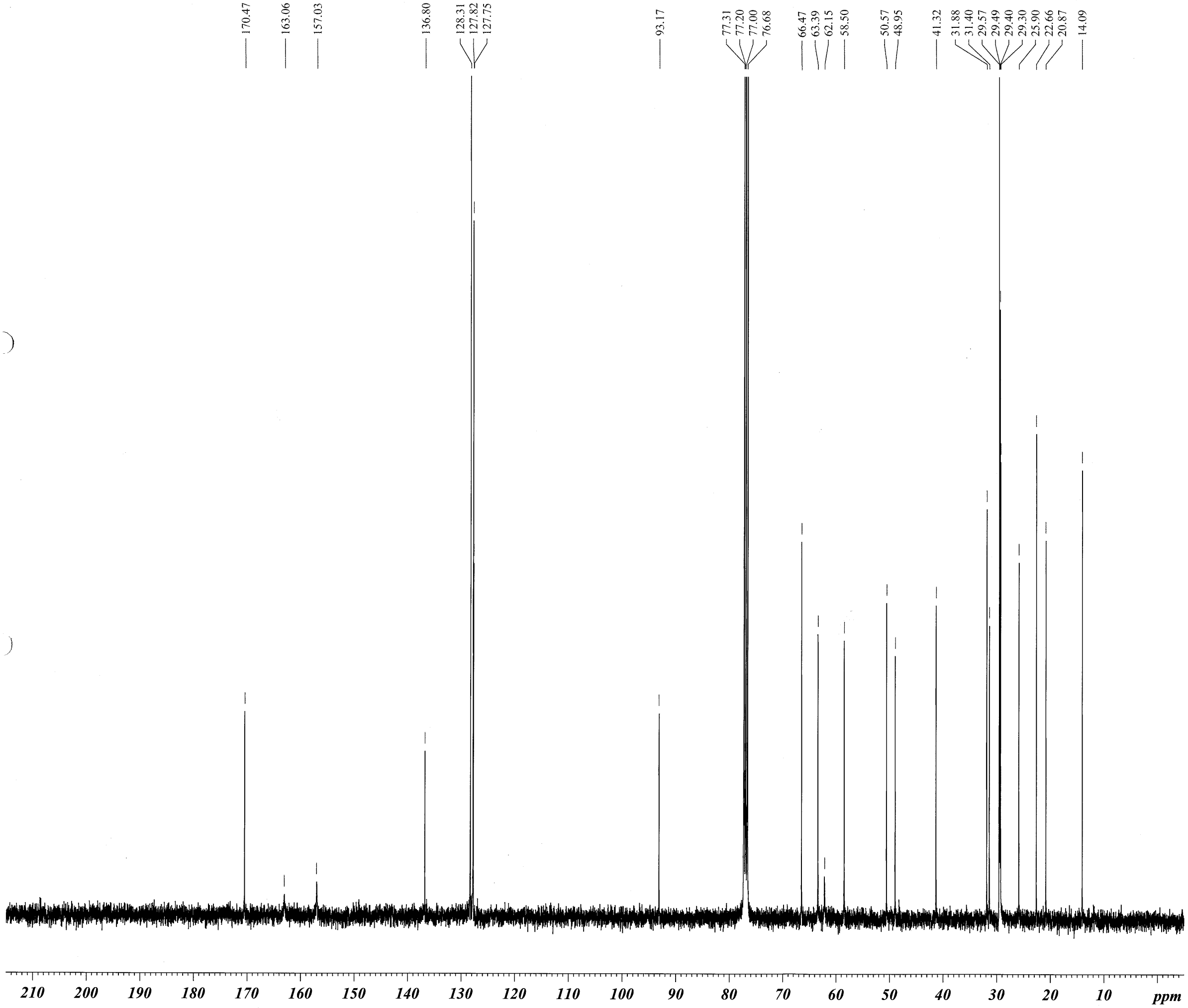
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(+)-*spiro*-aminal **14**

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



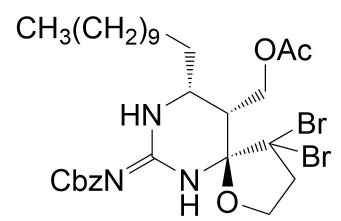
Current Data Parameters
NAME nakane-n400
EXPNO 232
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150207
Time 20.16
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4000
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127722 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(+)-*spiro*-aminal **14**

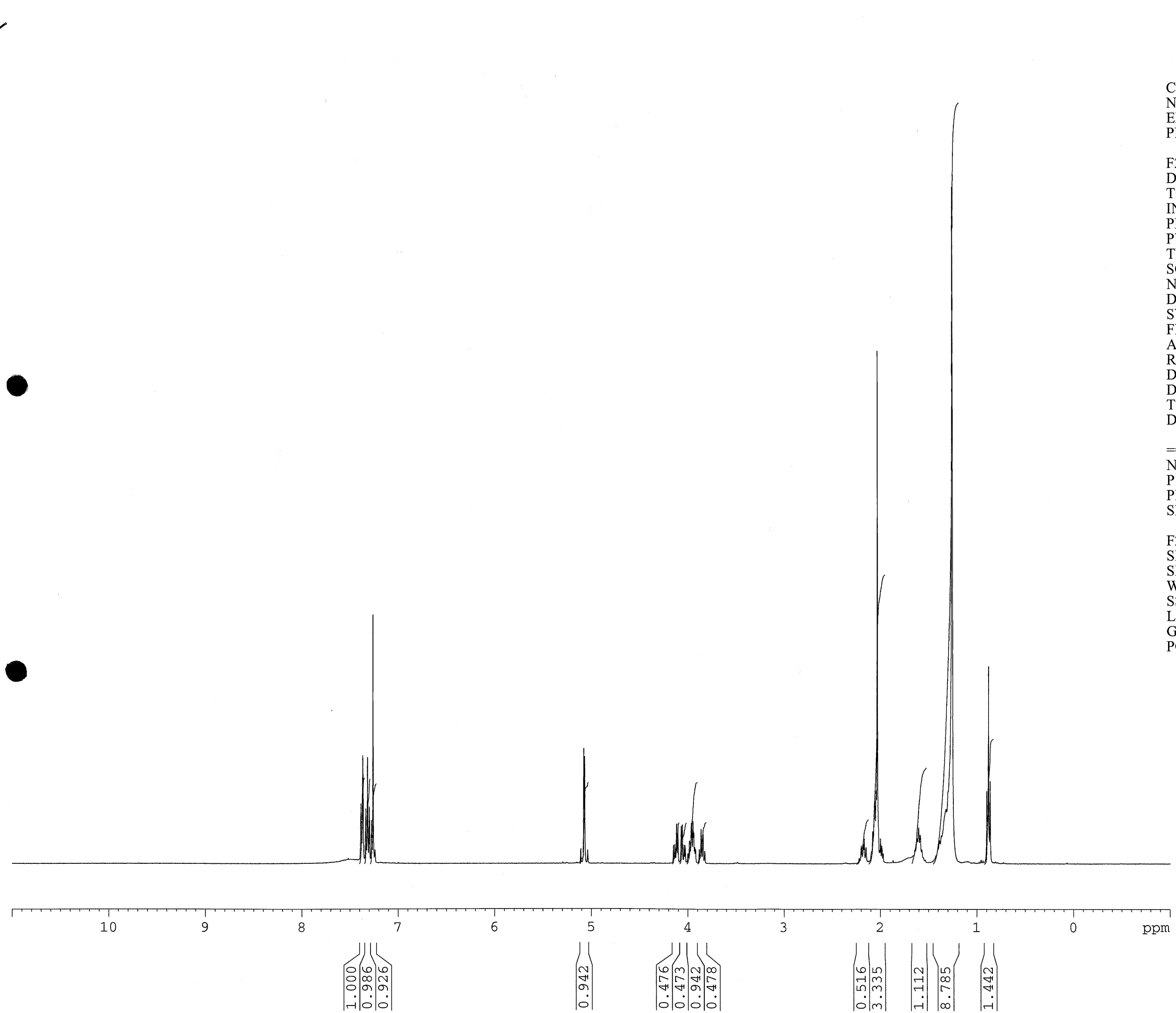
^{13}C NMR (100 MHz, $CDCl_3$)

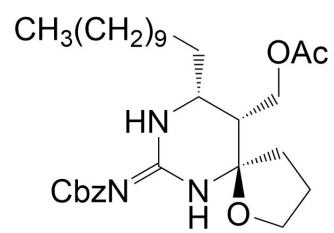
Current Data Parameters
NAME nakane-n400
EXPNO 235
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 11.53
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 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 1.40

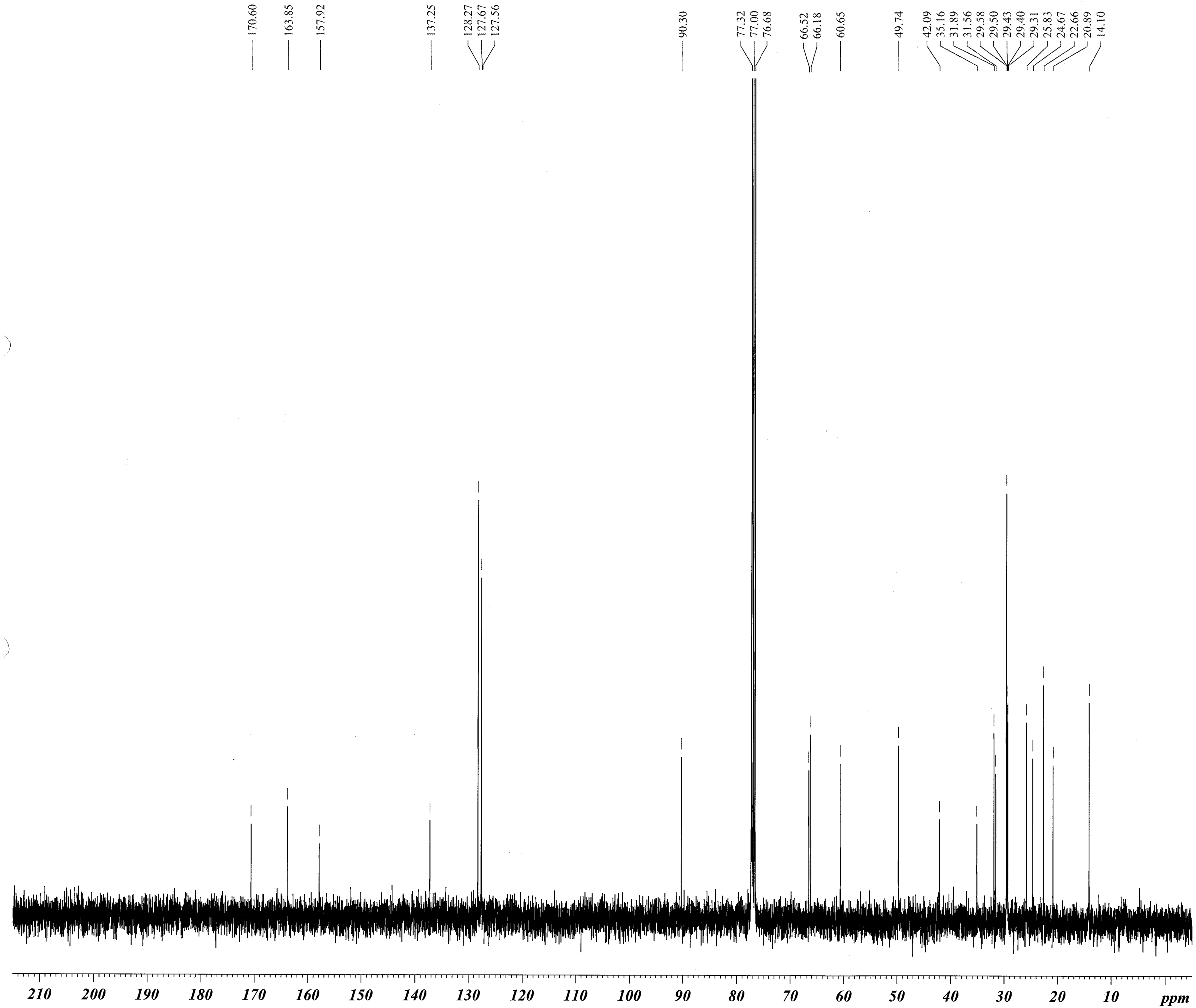




(+)-*spiro*-aminal **15**

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

S66



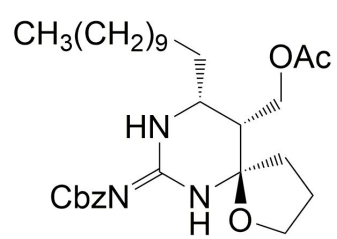
Current Data Parameters
NAME nakane-n400
EXPNO 236
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 12.26
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 700
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127715 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(+)-*spiro*-aminal **15**

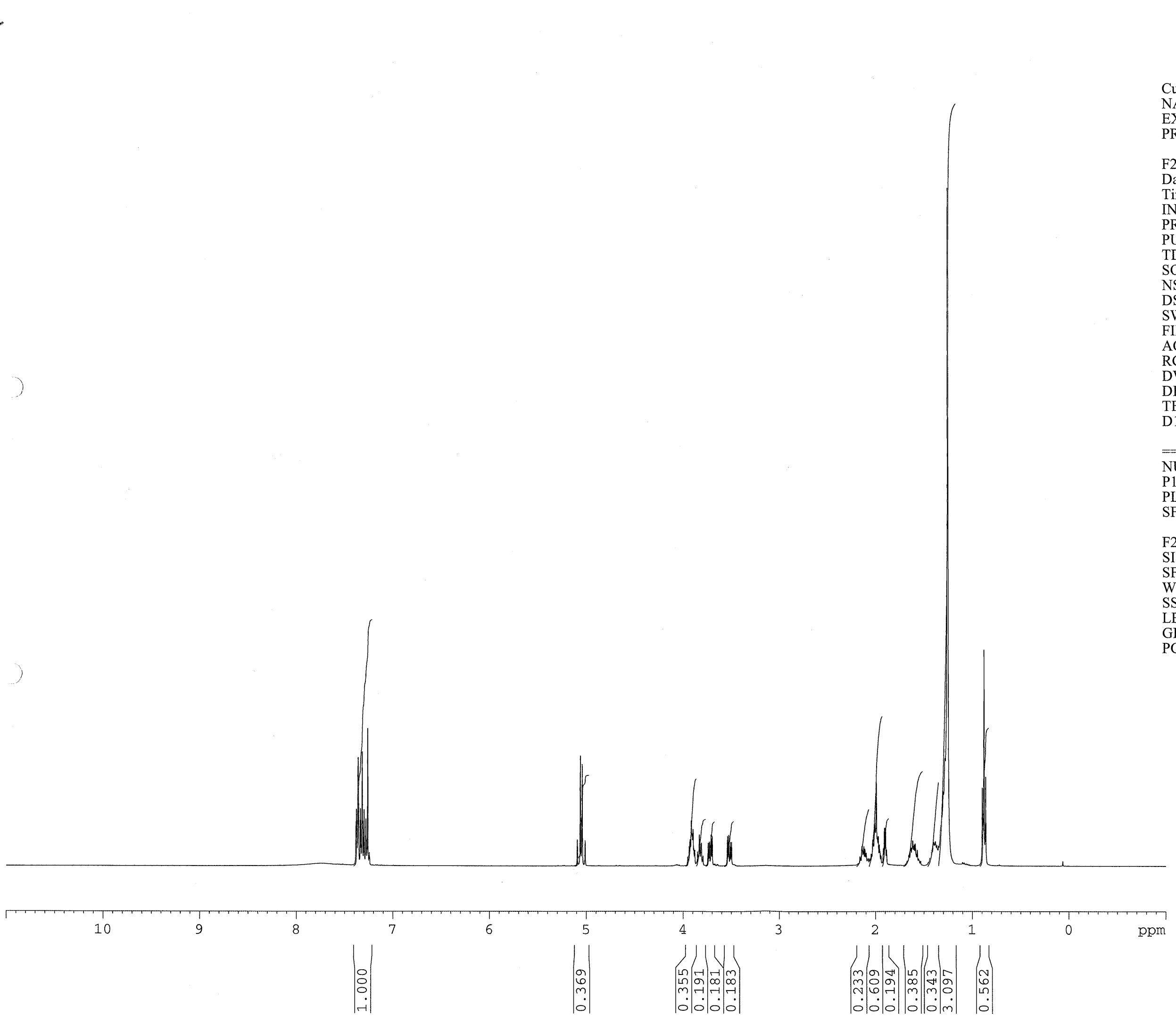
^{13}C NMR (100 MHz, $CDCl_3$)

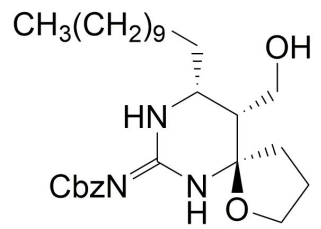
Current Data Parameters
NAME nakane-n400
EXPNO 239
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 12.58
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 143.7
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

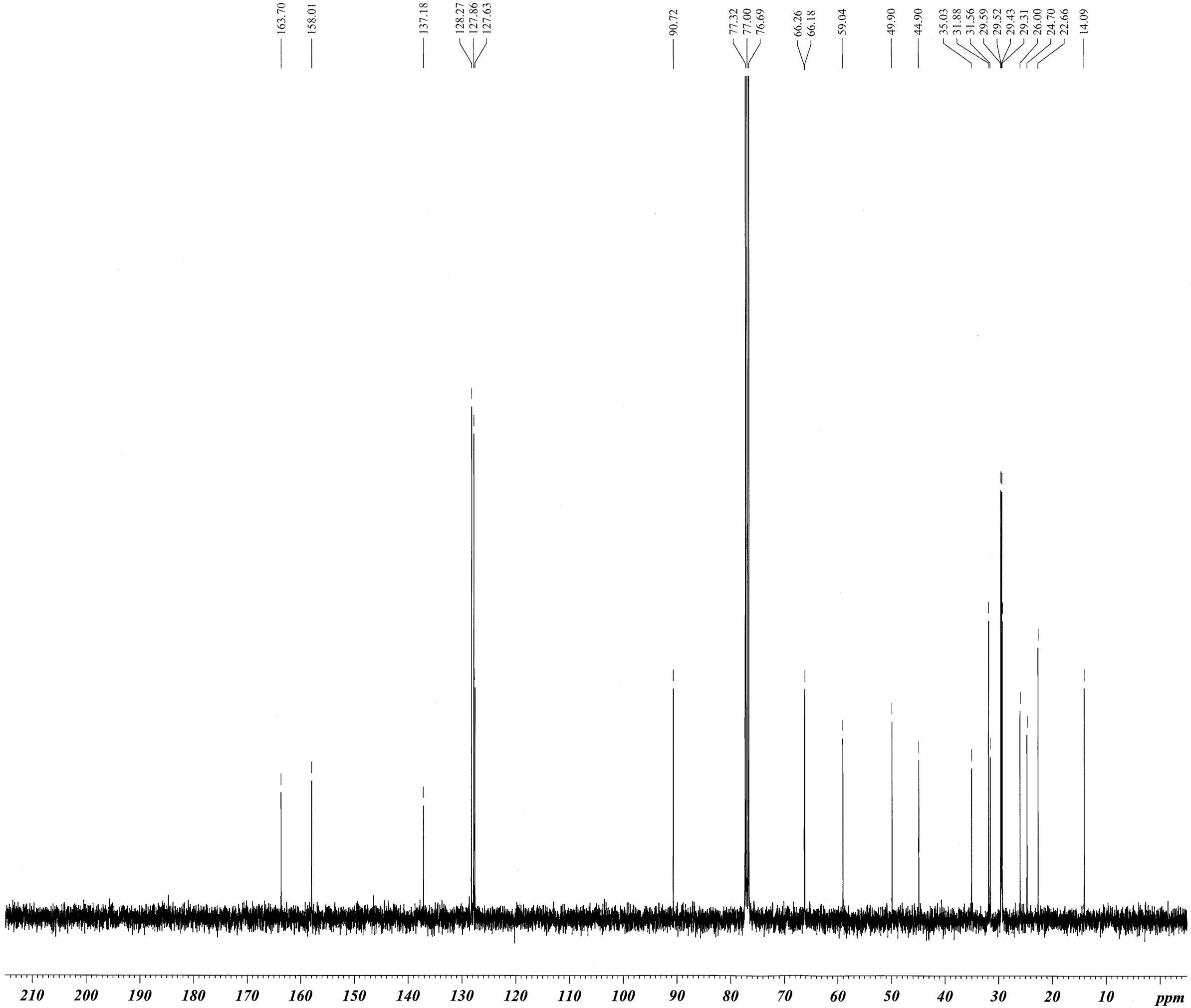
F2 - Processing parameters
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(+)-common intermediate **16**

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



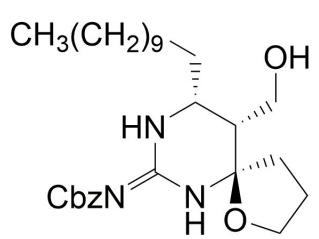
Current Data Parameters
NAME nakane-n400
EXPNO 240
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 12.59
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127722 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(+)-common intermediate **16**

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

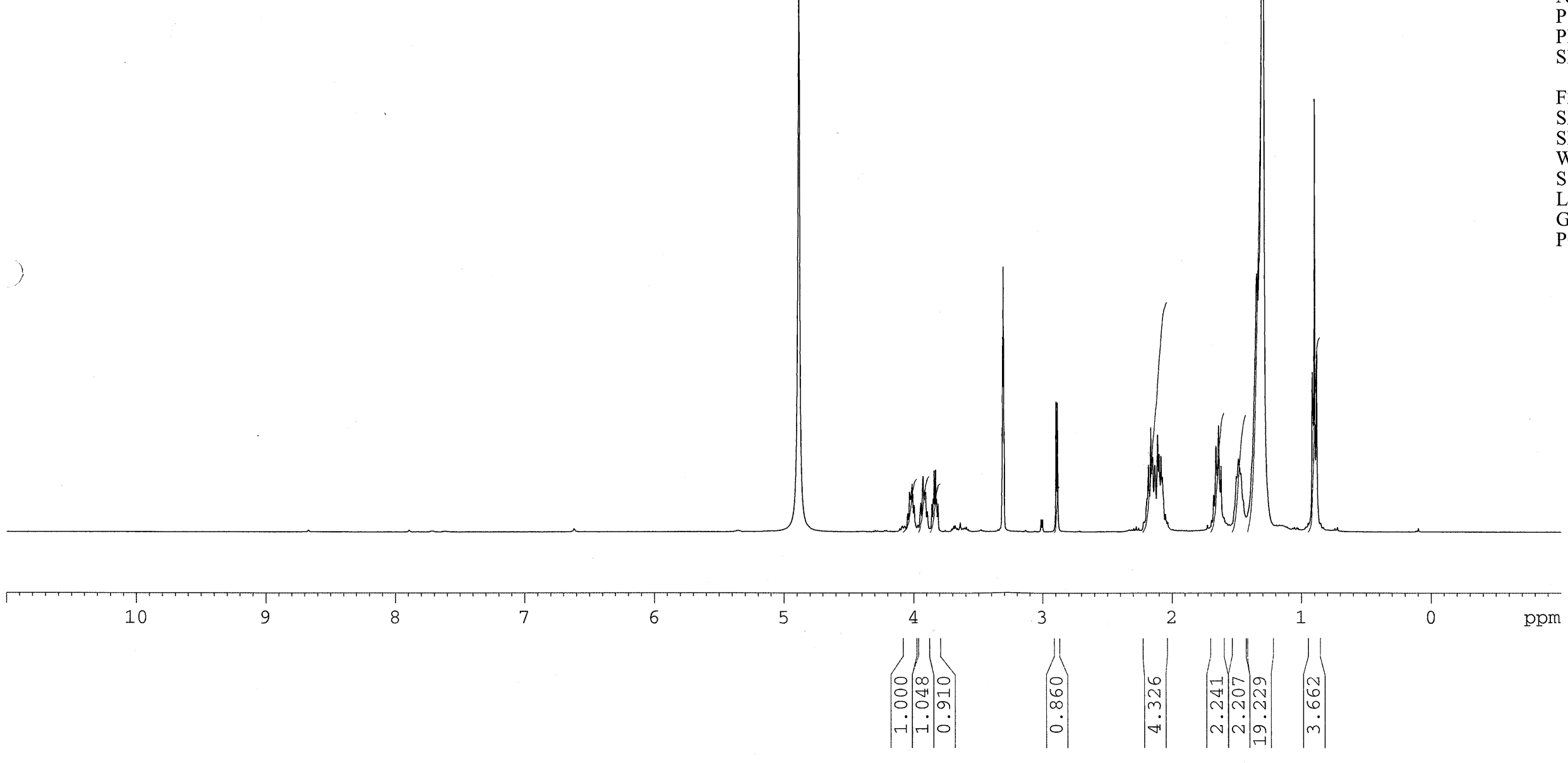
S70

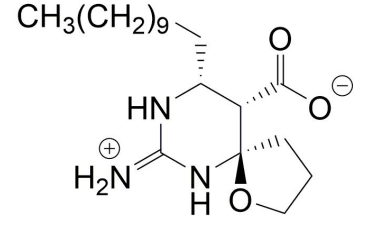
Current Data Parameters
NAME nakane-n400
EXPNO 251
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150221
Time 15.07
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 143.7
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

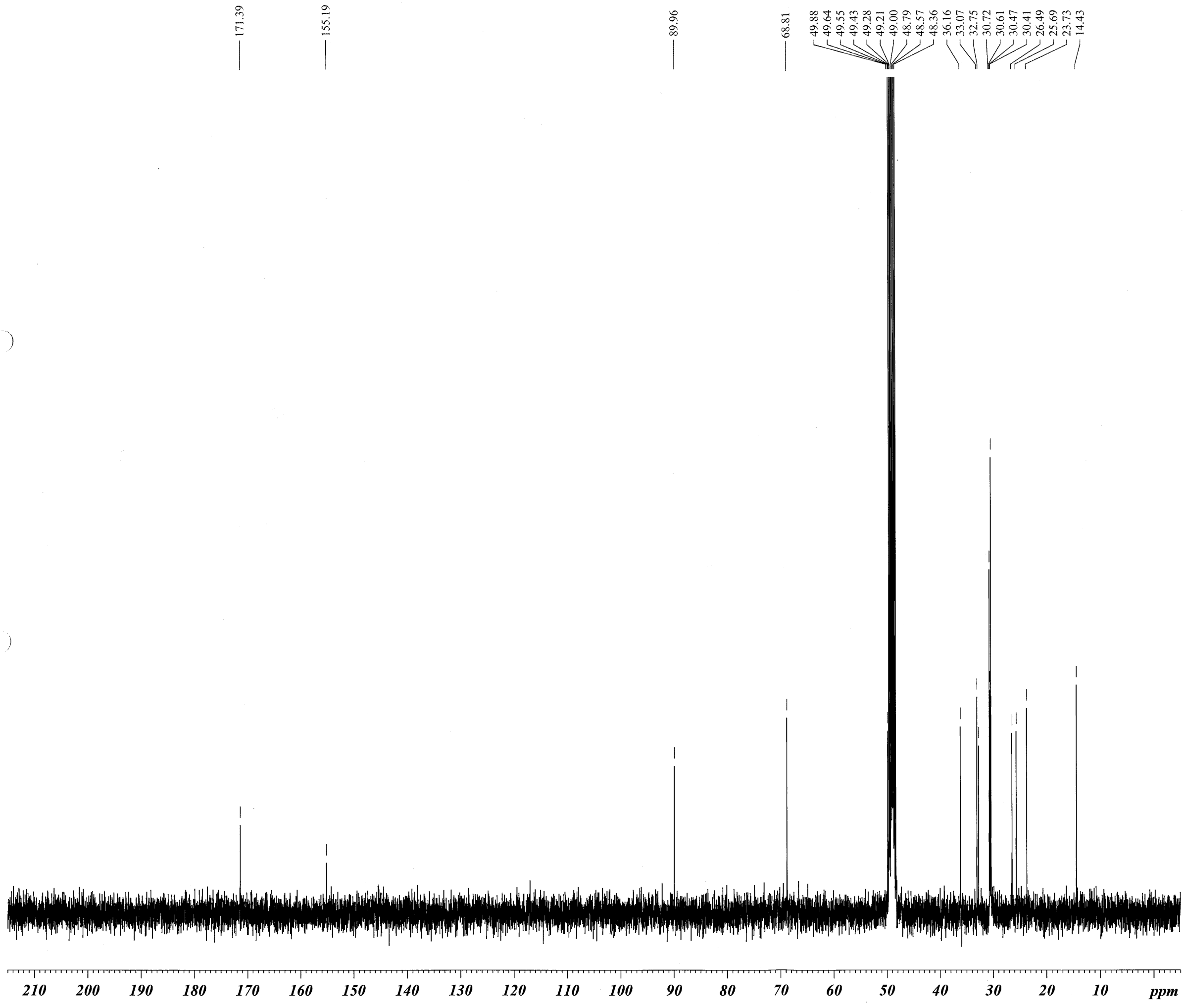
F2 - Processing parameters
SI 32768
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(+)-crambescin B carboxylic acid **2**

^{1}H NMR (400 MHz, CD_3OD)



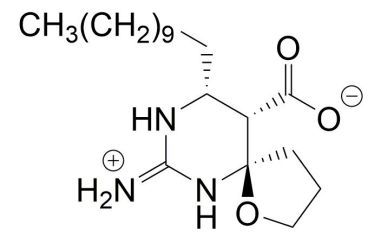
Current Data Parameters
NAME nakane-n400
EXPNO 252
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150220
Time 16.48
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 1000
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

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

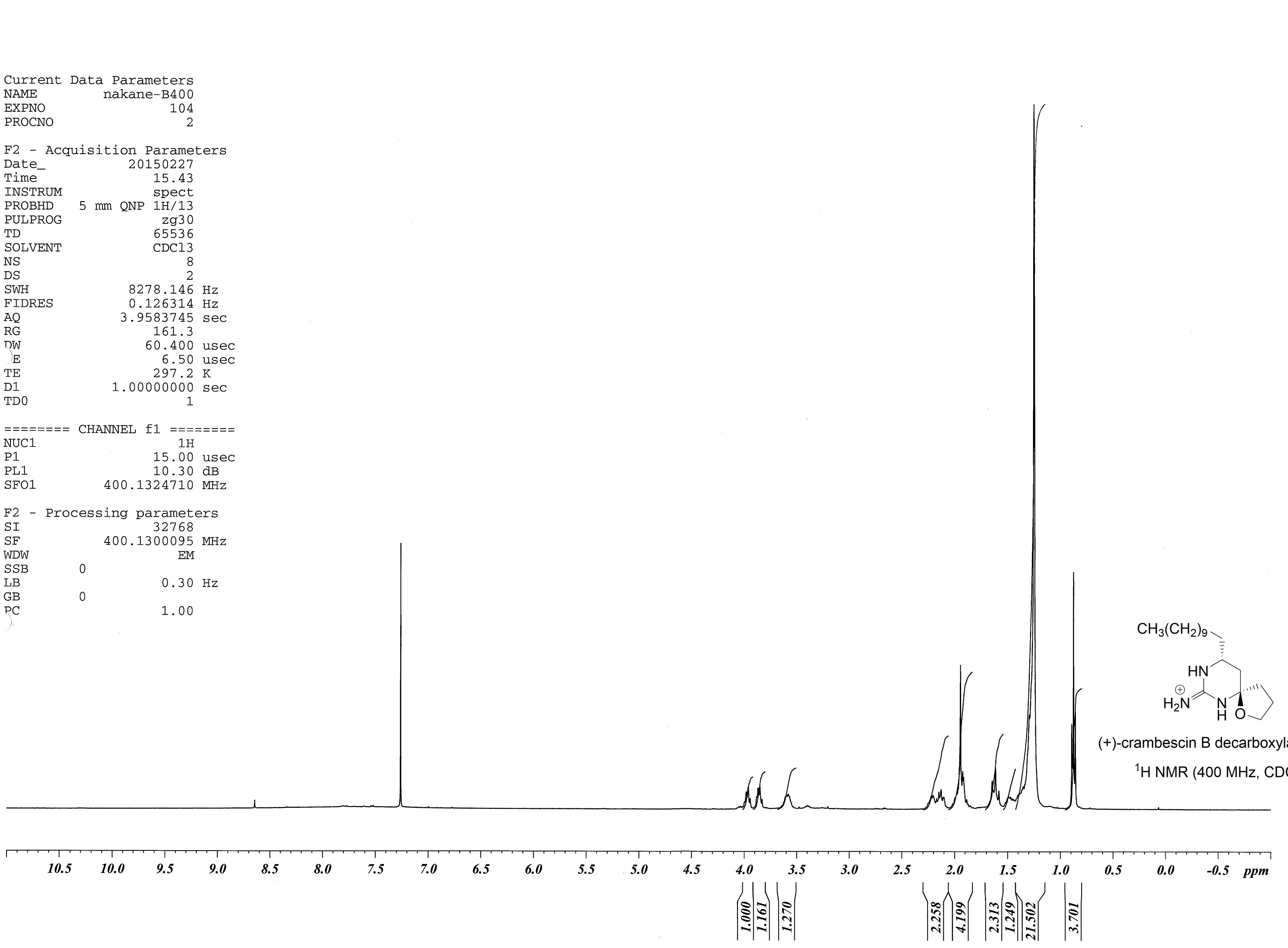


(+)-crambescin B carboxylic acid **2**

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

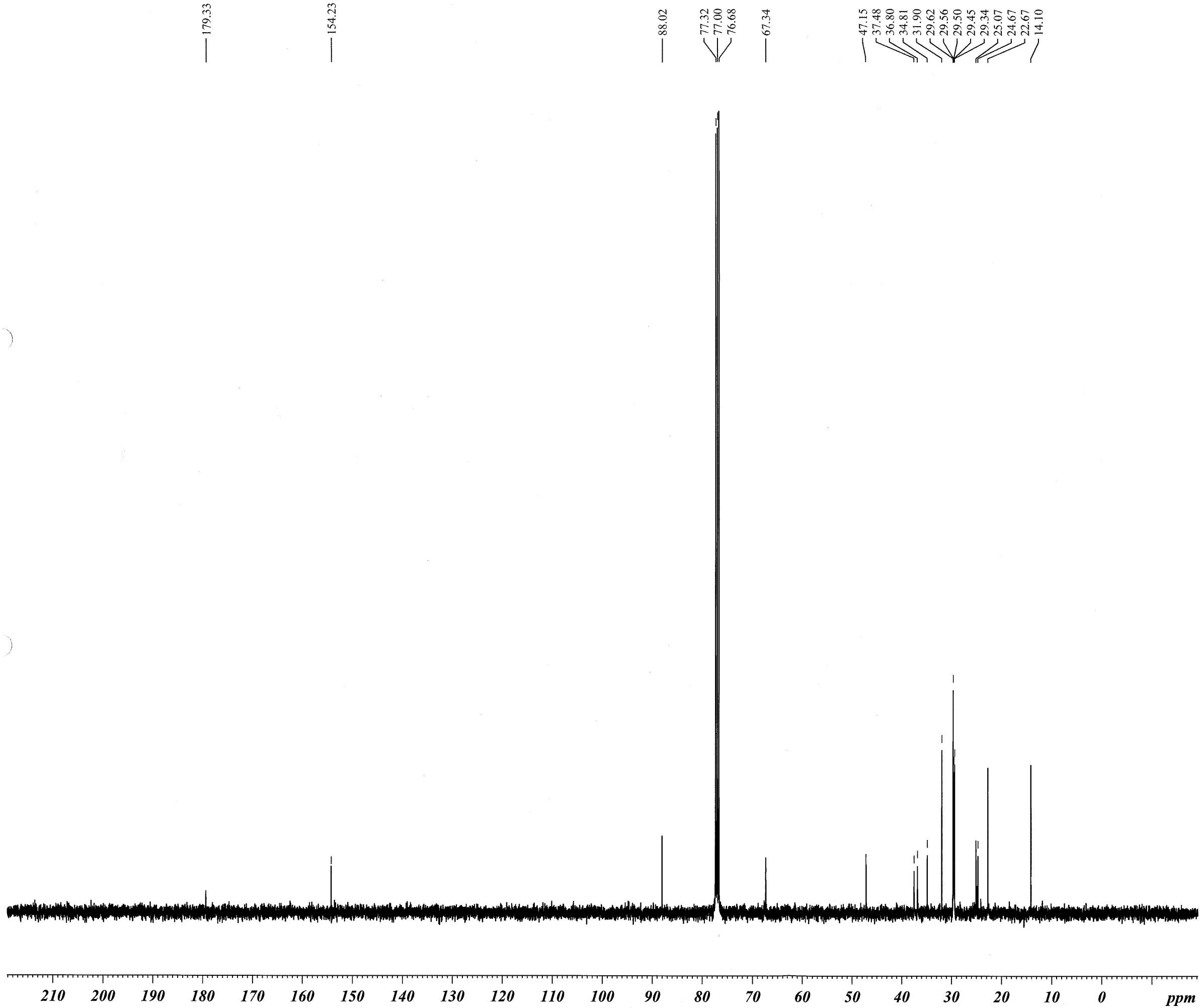
S72

```
Current Data Parameters
NAME        nakane-B400
EXPNO               104
PROCNO                2

F2 - Acquisition Parameters
Date_          20150227
Time              15.43
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9583745 sec
RG                161.3
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        400.1300095 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



(+)-crambescin B decarboxylate **17**

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



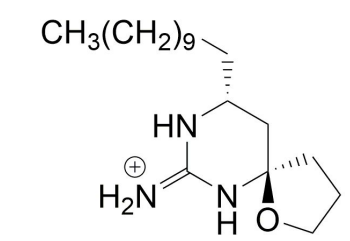
Current Data Parameters
NAME nakane-B400
EXPNO 105
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150227
Time 15.48
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 538
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 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 100.6127709 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(+)-crambescin B decarboxylate **17**

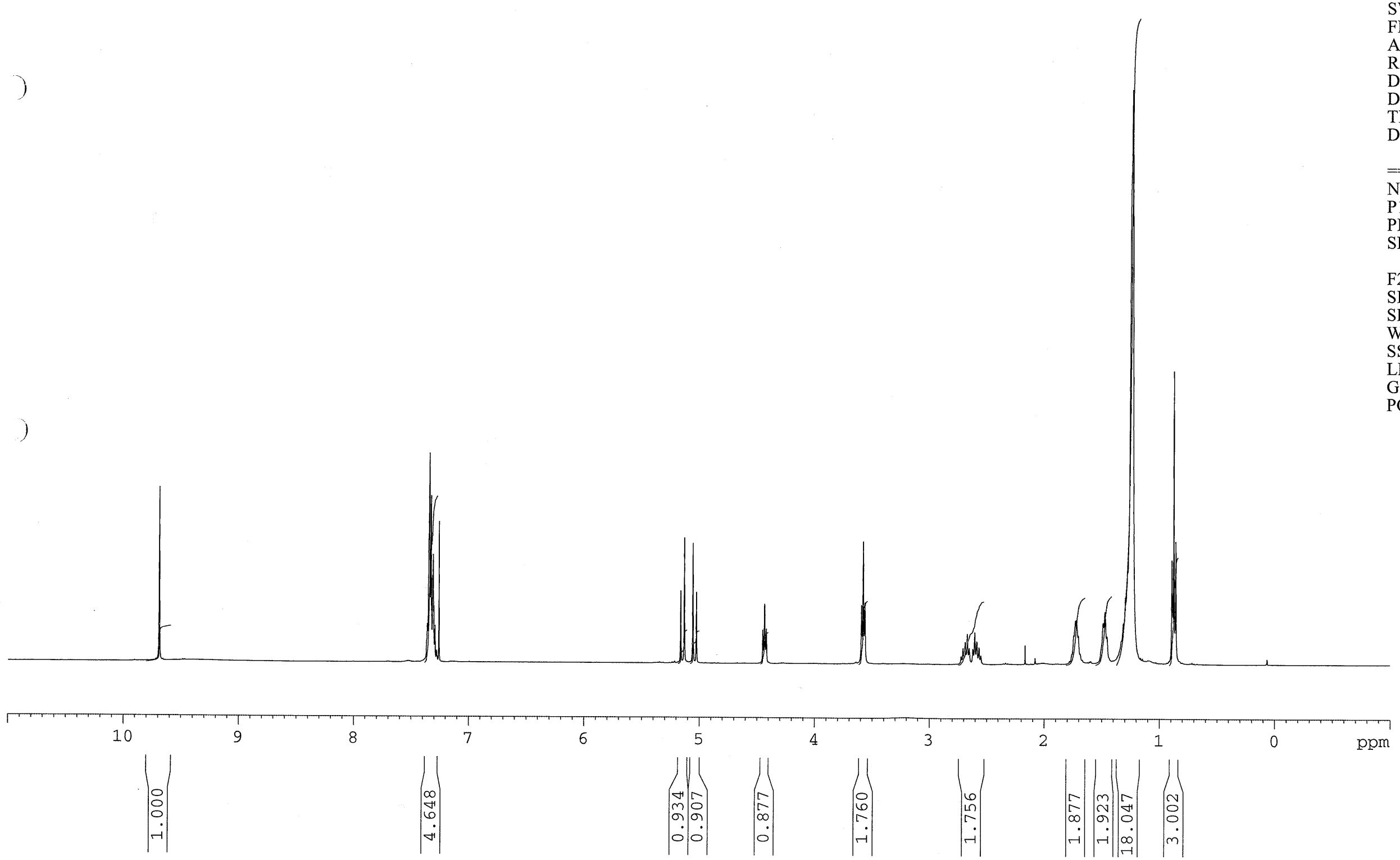
^{13}C NMR (100 MHz, $CDCl_3$)

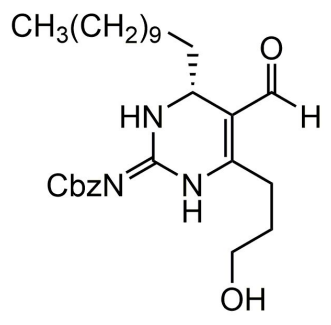
Current Data Parameters
NAME nakane-n400
EXPNO 243
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150213
Time 15.55
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 128
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

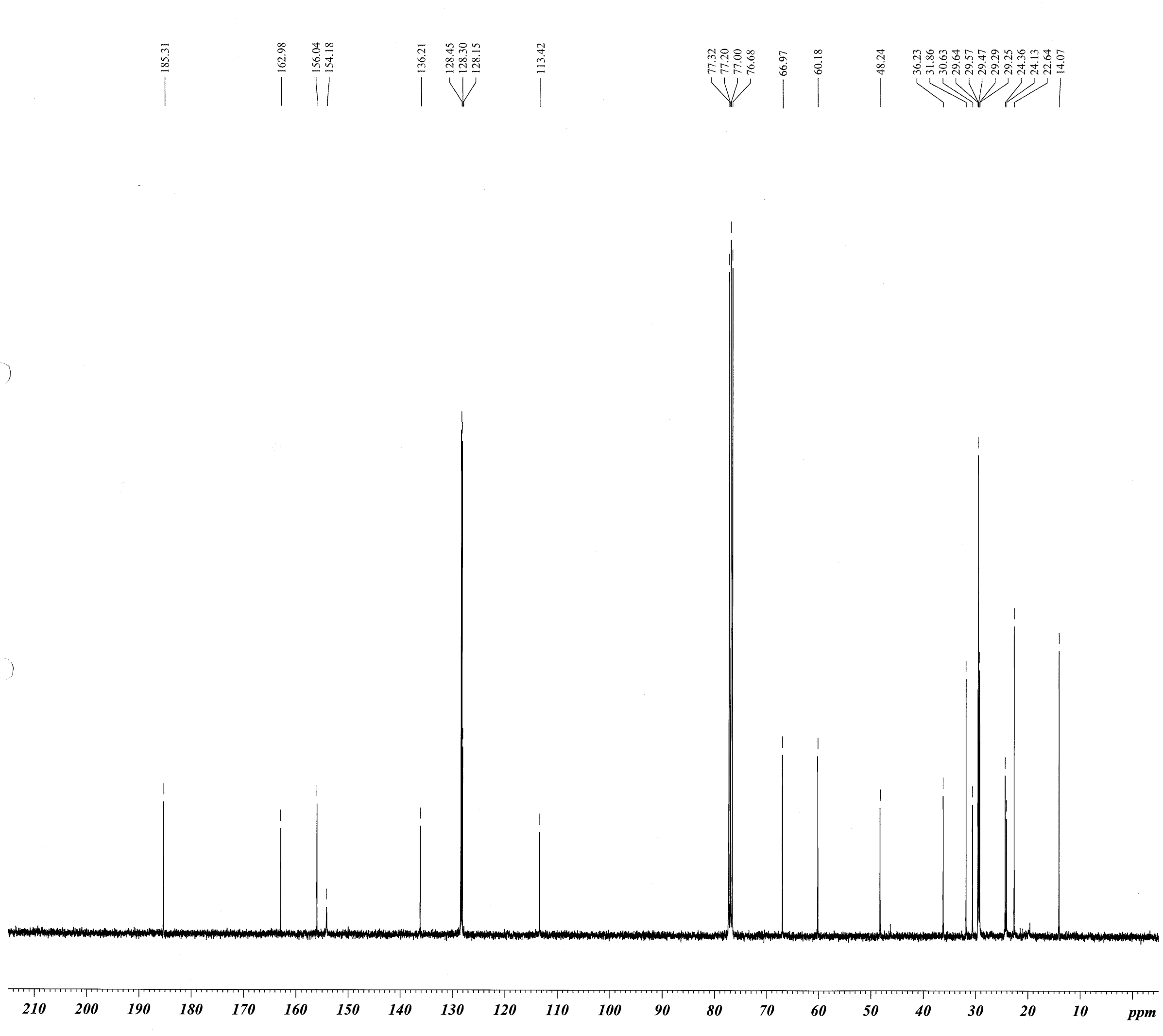
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(–)-enal **18**

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



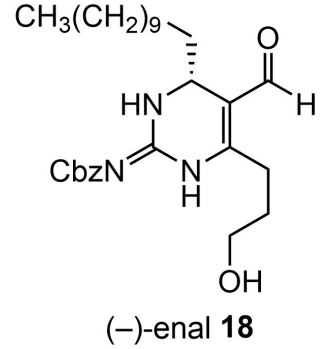
Current Data Parameters
NAME nakane-n400
EXPNO 244
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150212
Time 17.21
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1569
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127744 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(–)-enal **18**

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

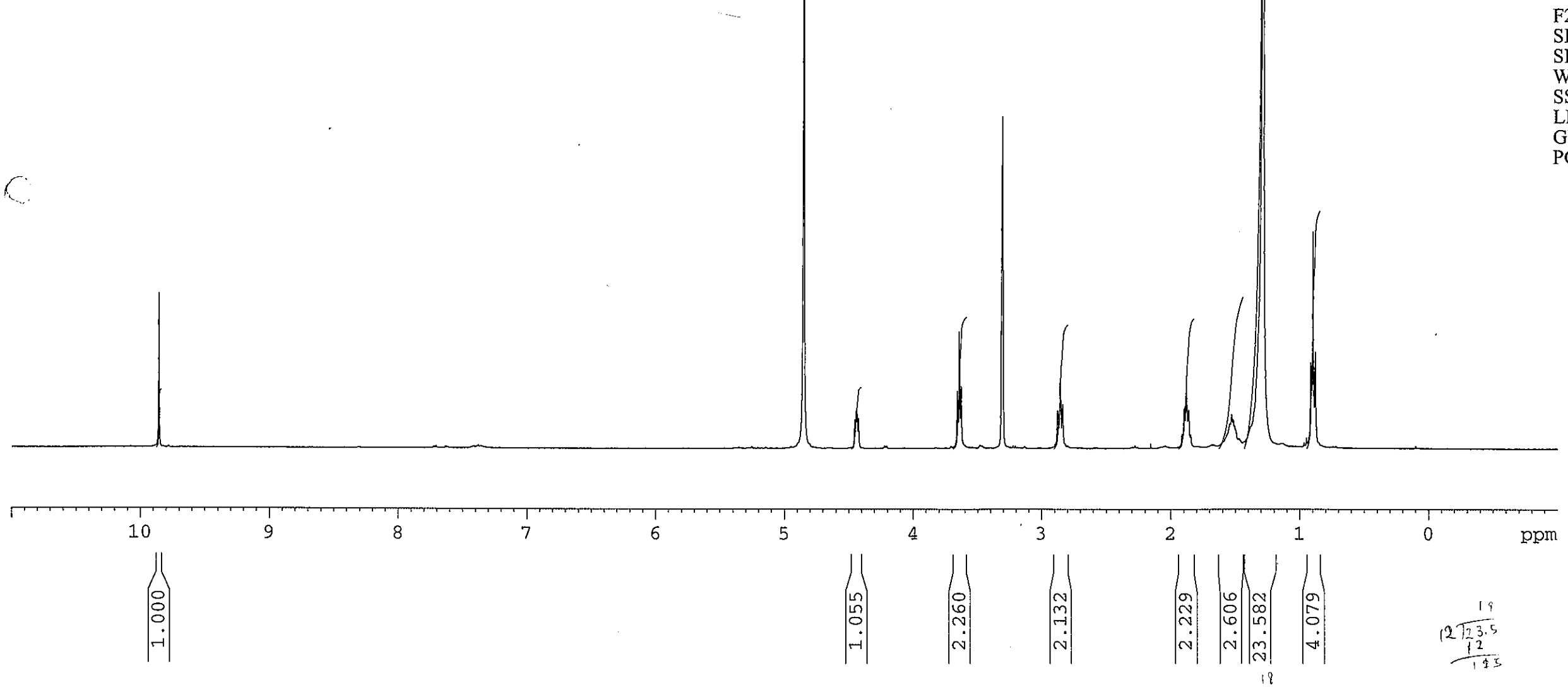
S76

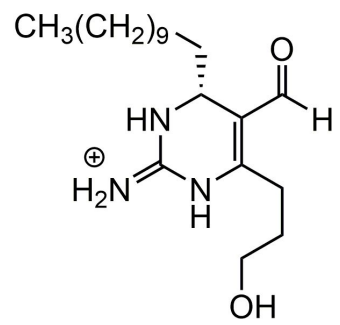
Current Data Parameters
NAME nakane-n400
EXPNO 245
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150216
Time 13.19
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 228.1
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

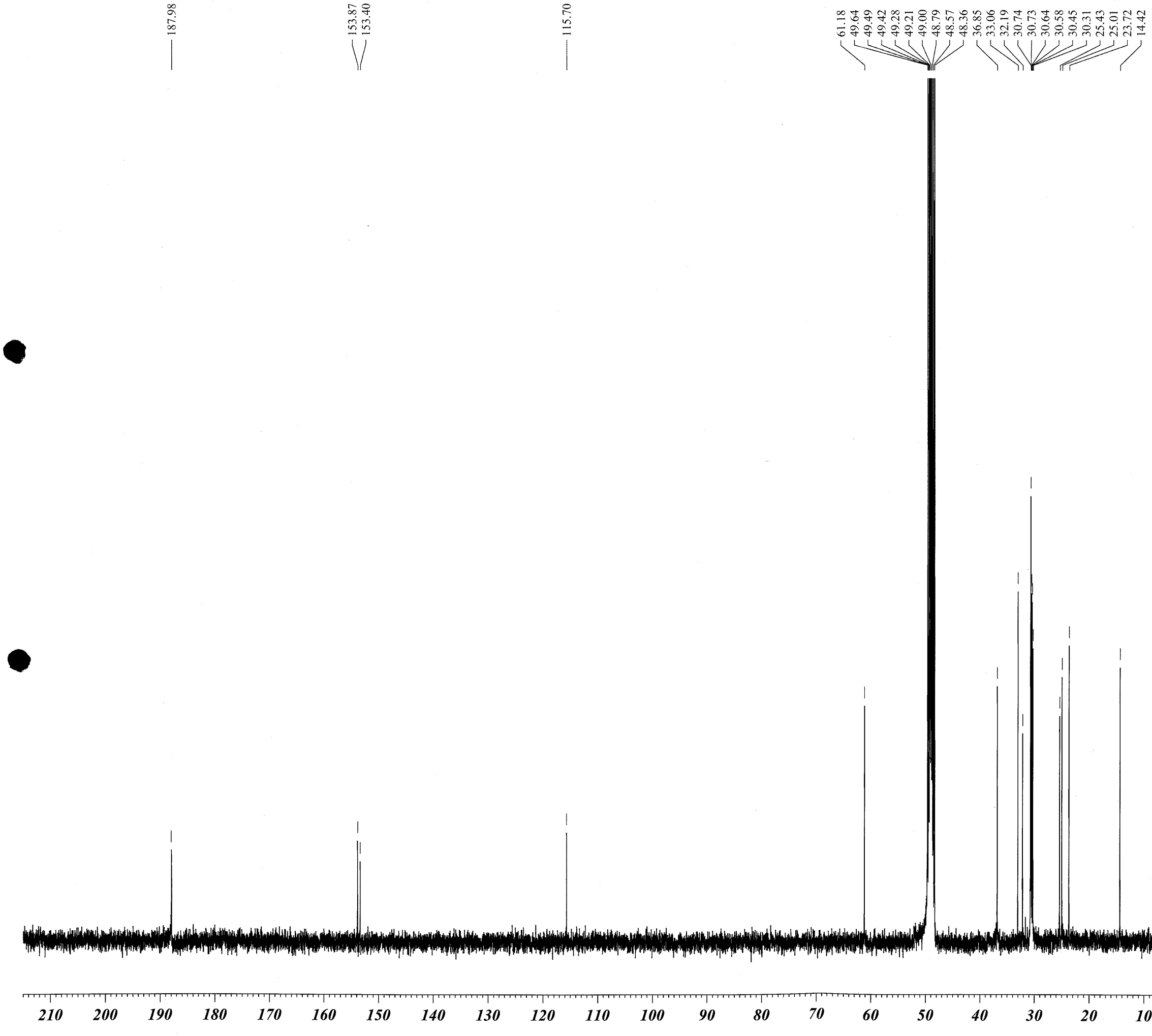
F2 - Processing parameters
SI 32768
SF 400.1315841 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(+)-guanidine **19**

^{1}H NMR (400 MHz, CD_3OD)



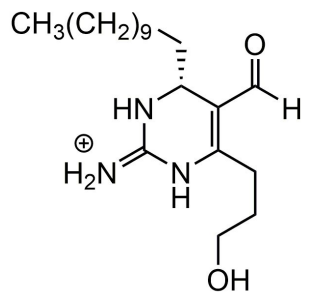
Current Data Parameters
NAME nakane-n400
EXPNO 246
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150216
Time 13.21
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 4480
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6130243 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(+)-guanidine **19**

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

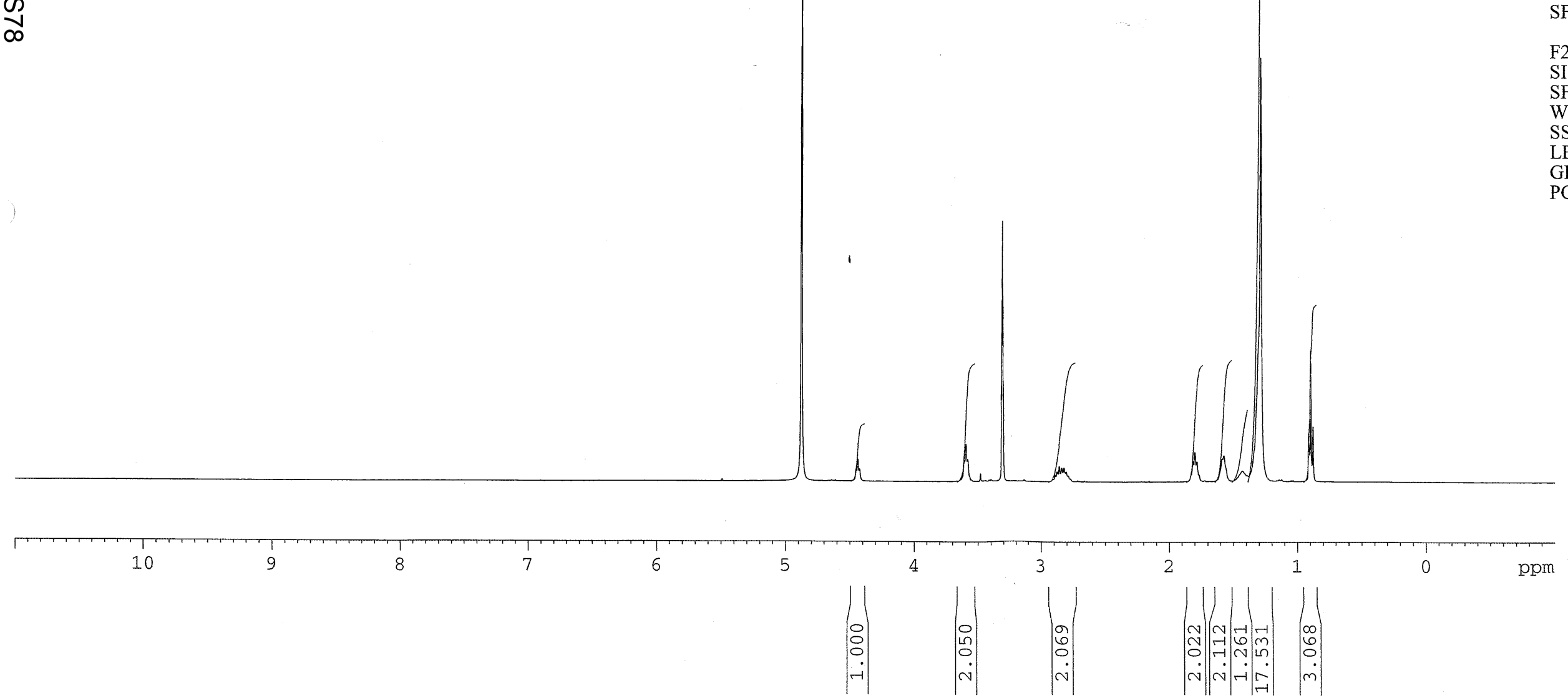
S78

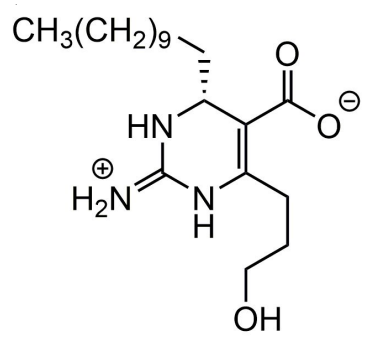
Current Data Parameters
NAME nakane-n400
EXPNO 161
PROCNO 1

F2 - Acquisition Parameters
Date_ 20141222
Time 15.57
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CD3OD
NS 32
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 256
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

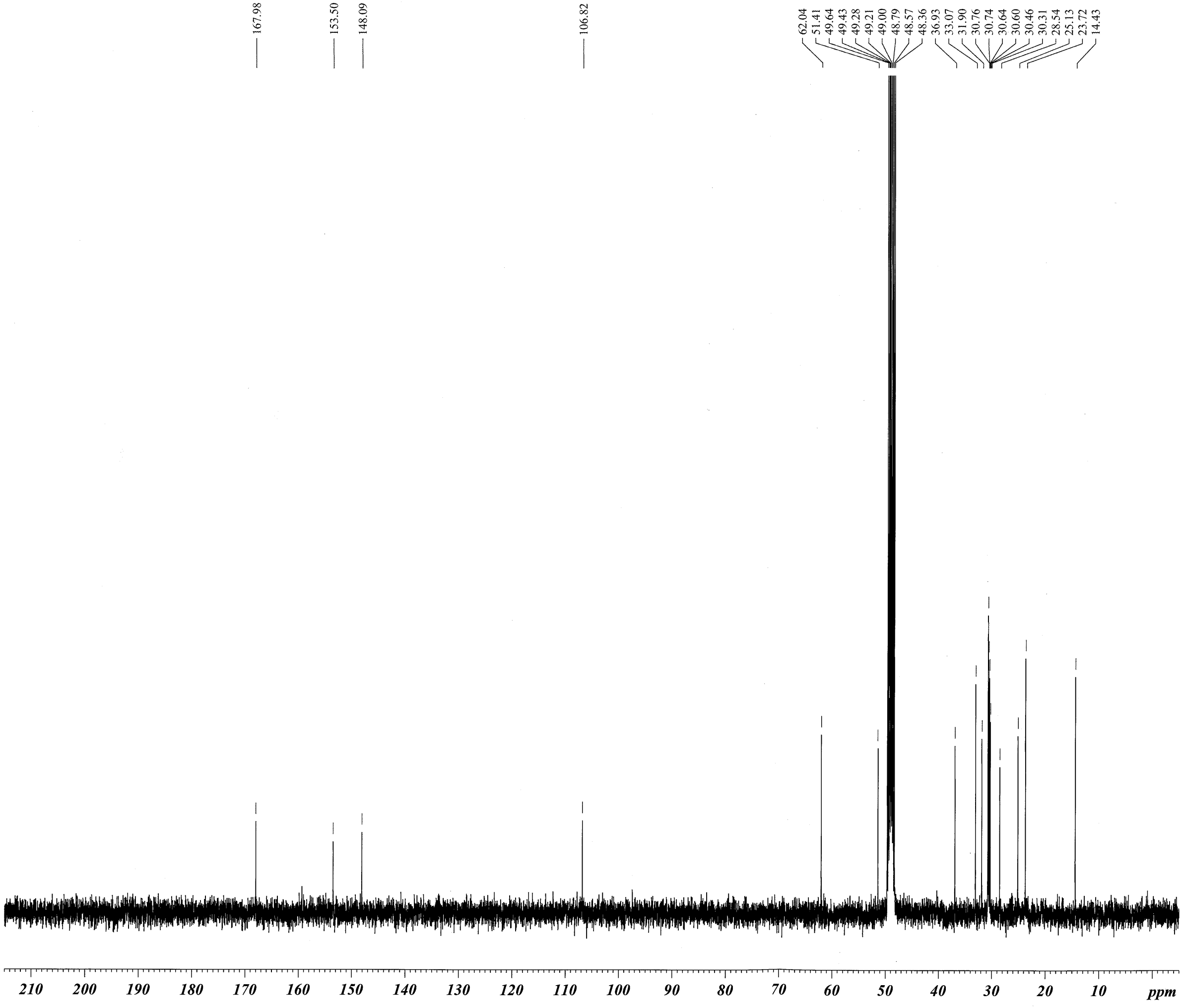
F2 - Processing parameters
SI 32768
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(+)-crambescin C carboxylic acid **3**

^{1}H NMR (400 MHz, CD_3OD)



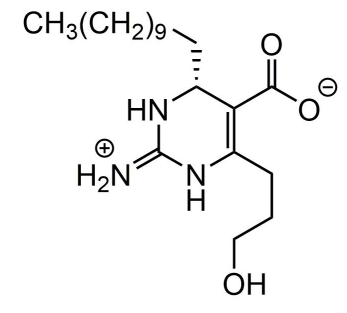
Current Data Parameters
NAME nakane-n400
EXPNO 203
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150131
Time 17.41
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 1293
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.20000005 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

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



(+)-crambescin C carboxylic acid **3**

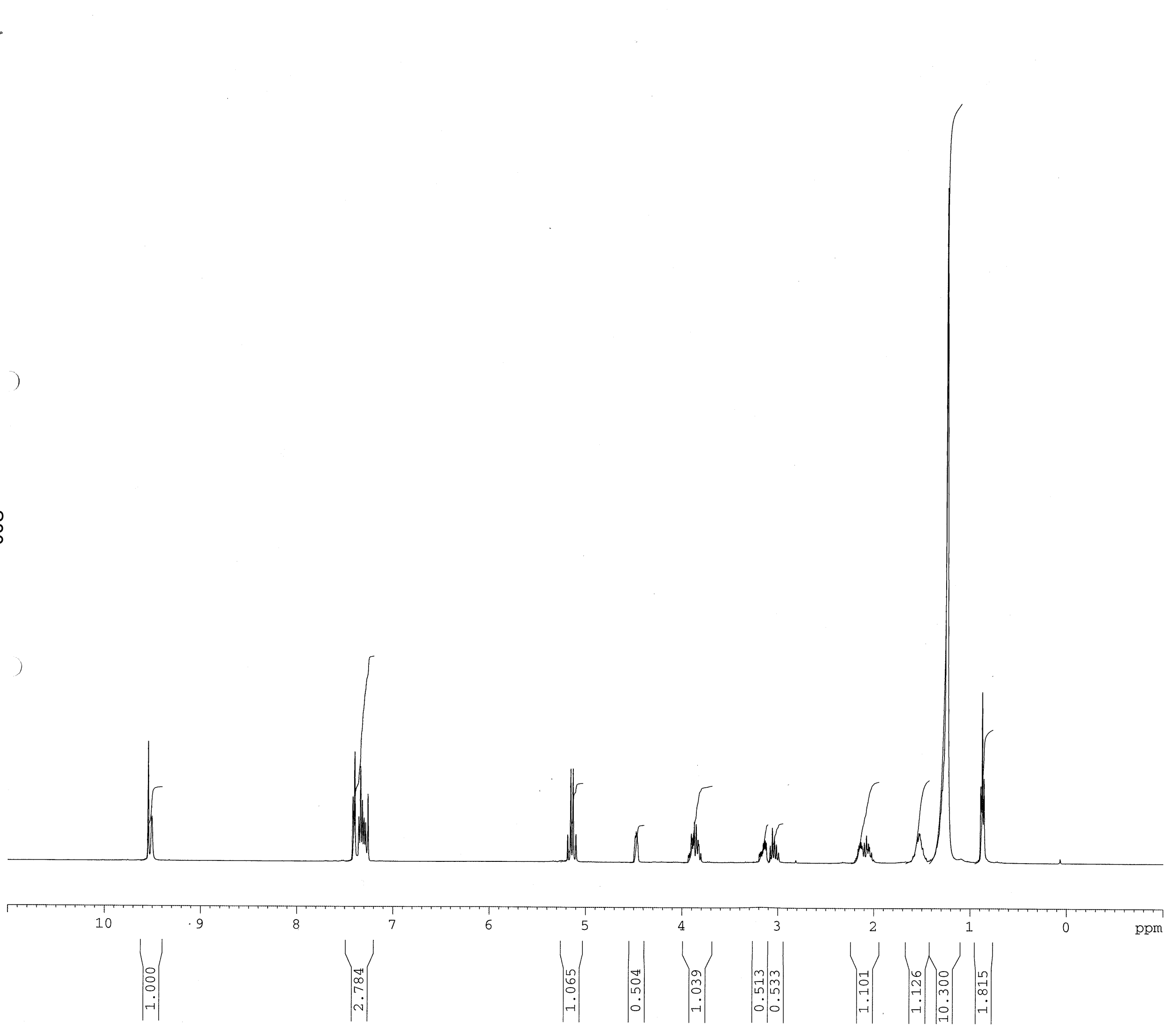
^{13}C NMR (100 MHz, CD_3OD)

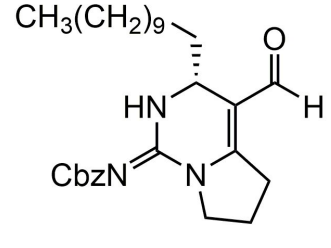
Current Data Parameters
NAME nakane-n400
EXPNO 247
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150216
Time 16.24
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 143.7
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

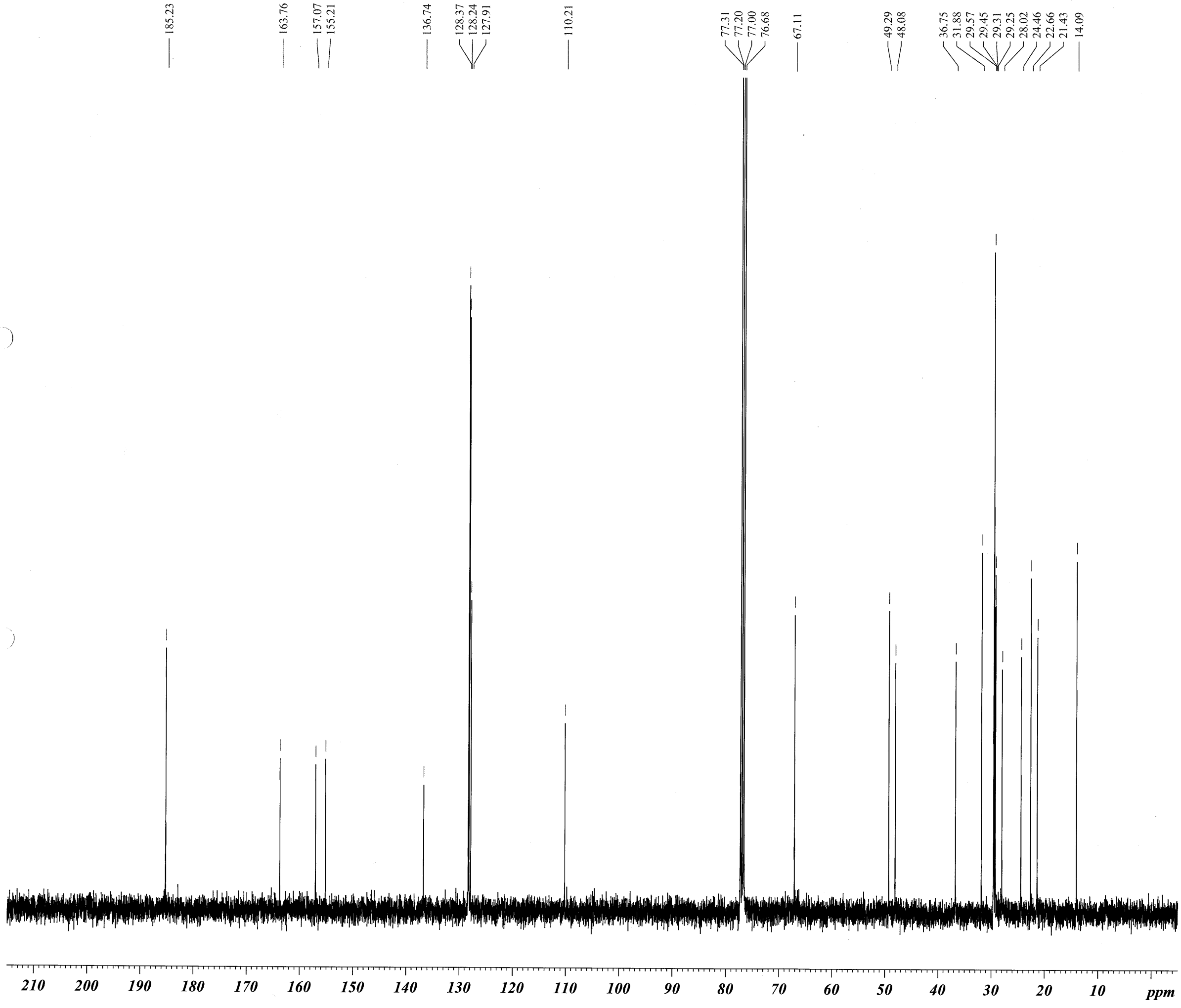
F2 - Processing parameters
SI 32768
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(+)-pyrrolidine **20**

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



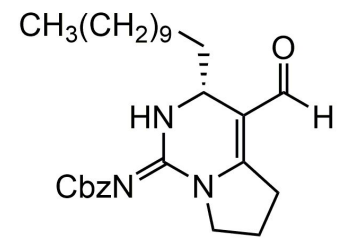
Current Data Parameters
NAME nakane-n400
EXPNO 248
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150216
Time 16.27
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 565
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127729 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(+)-pyrrolidine **20**

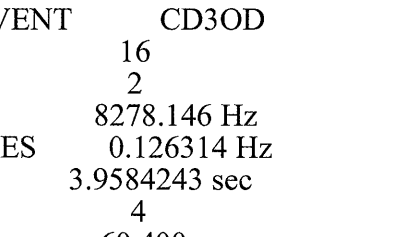
^{13}C NMR (100 MHz, $CDCl_3$)

Current Data Parameters
NAME nakane-n400
EXPNO 147
PROCNO 2

F2 - Acquisition Parameters
Date_ 20141023
Time 16.36
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CD3OD
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

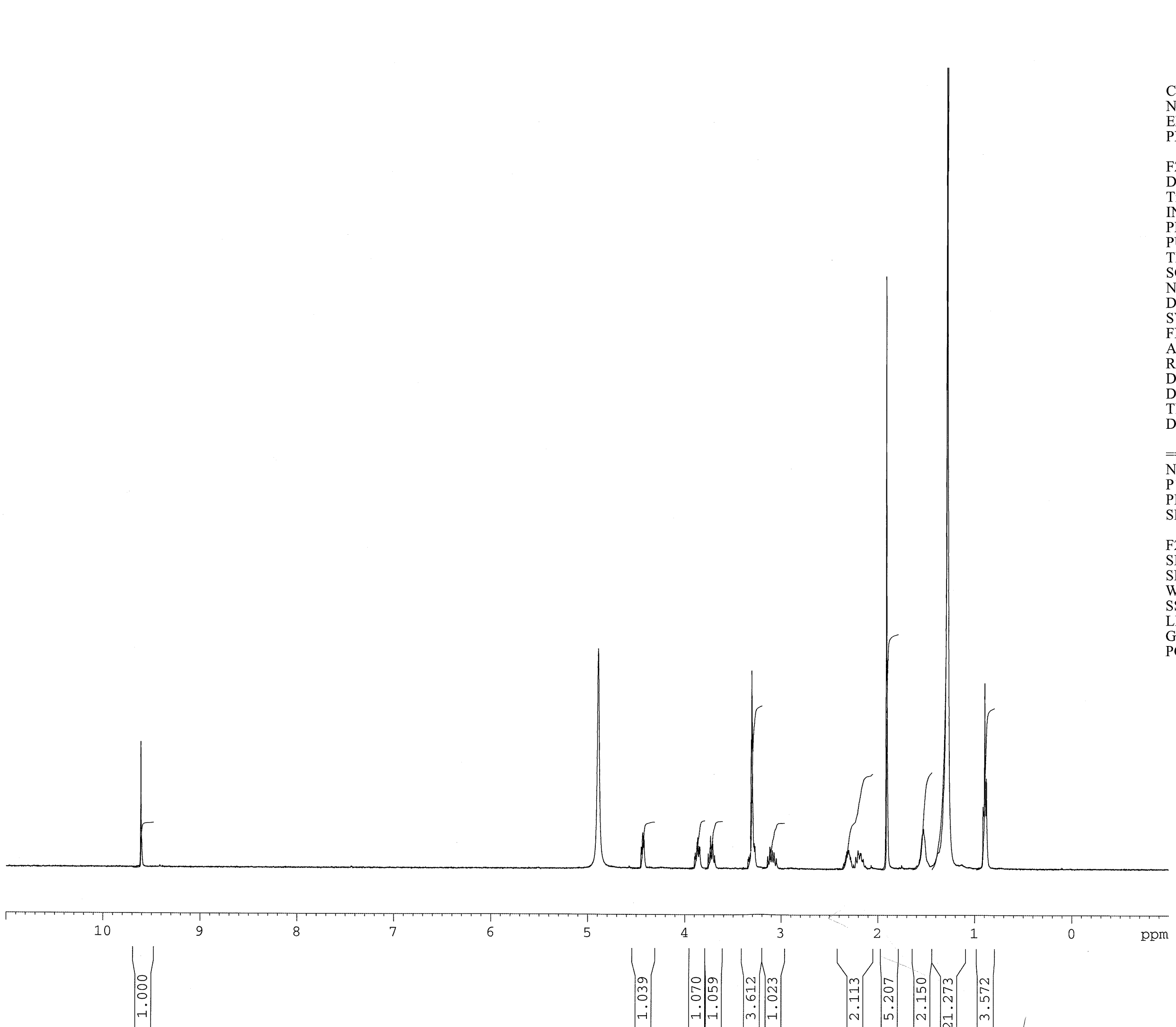
========== CHANNEL f1 ==========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

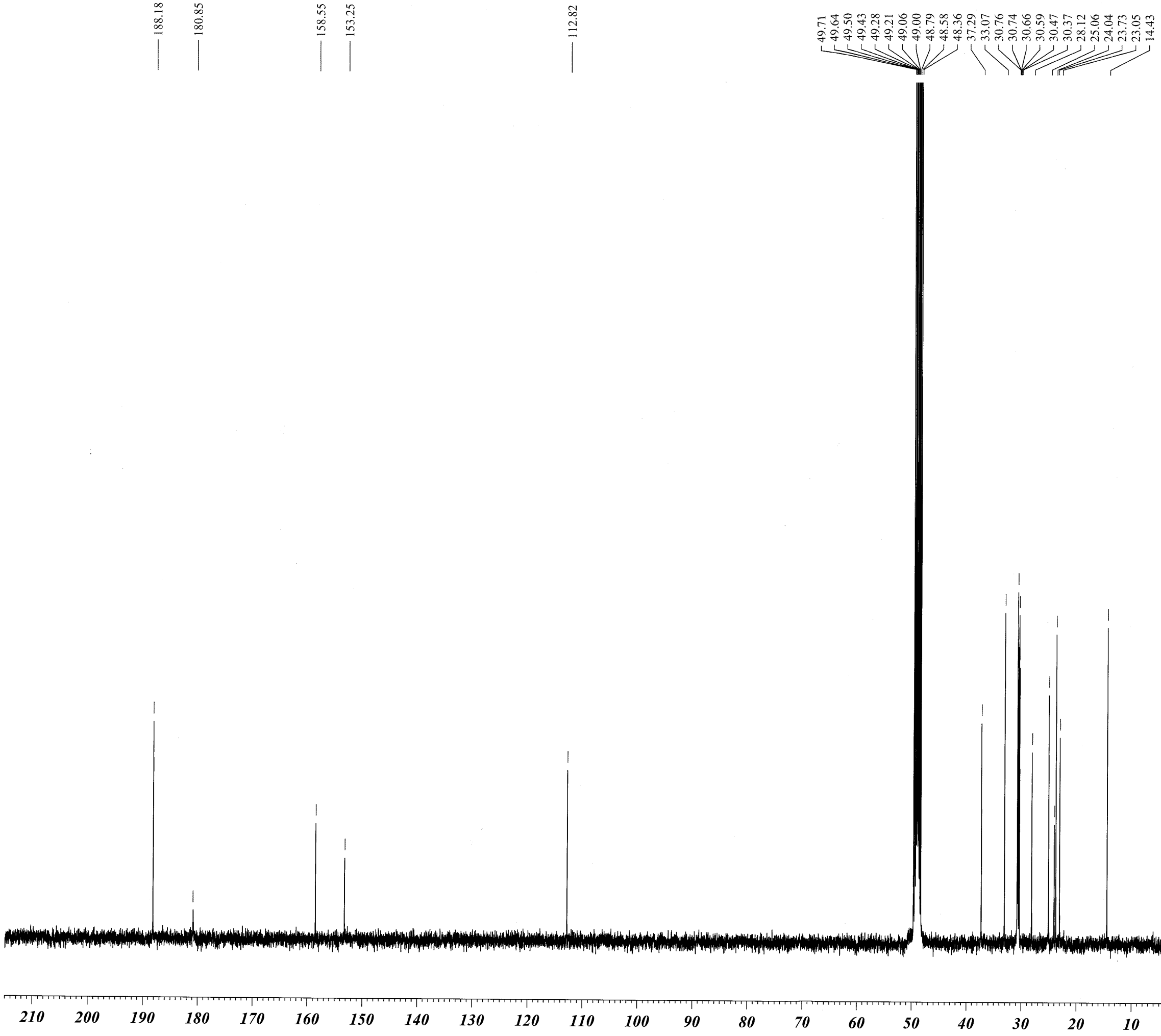
F2 - Processing parameters
SI 32768
SF 400.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



(+)-guanidine **21**

^{1}H NMR (400 MHz, CD_3OD)





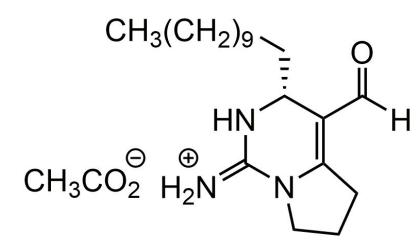
Current Data Parameters
NAME nakane-n400
EXPNO 148
PROCNO 2

F2 - Acquisition Parameters
Date_ 20141023
Time 16.51
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 2865
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

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



(+)-guanidine **21**

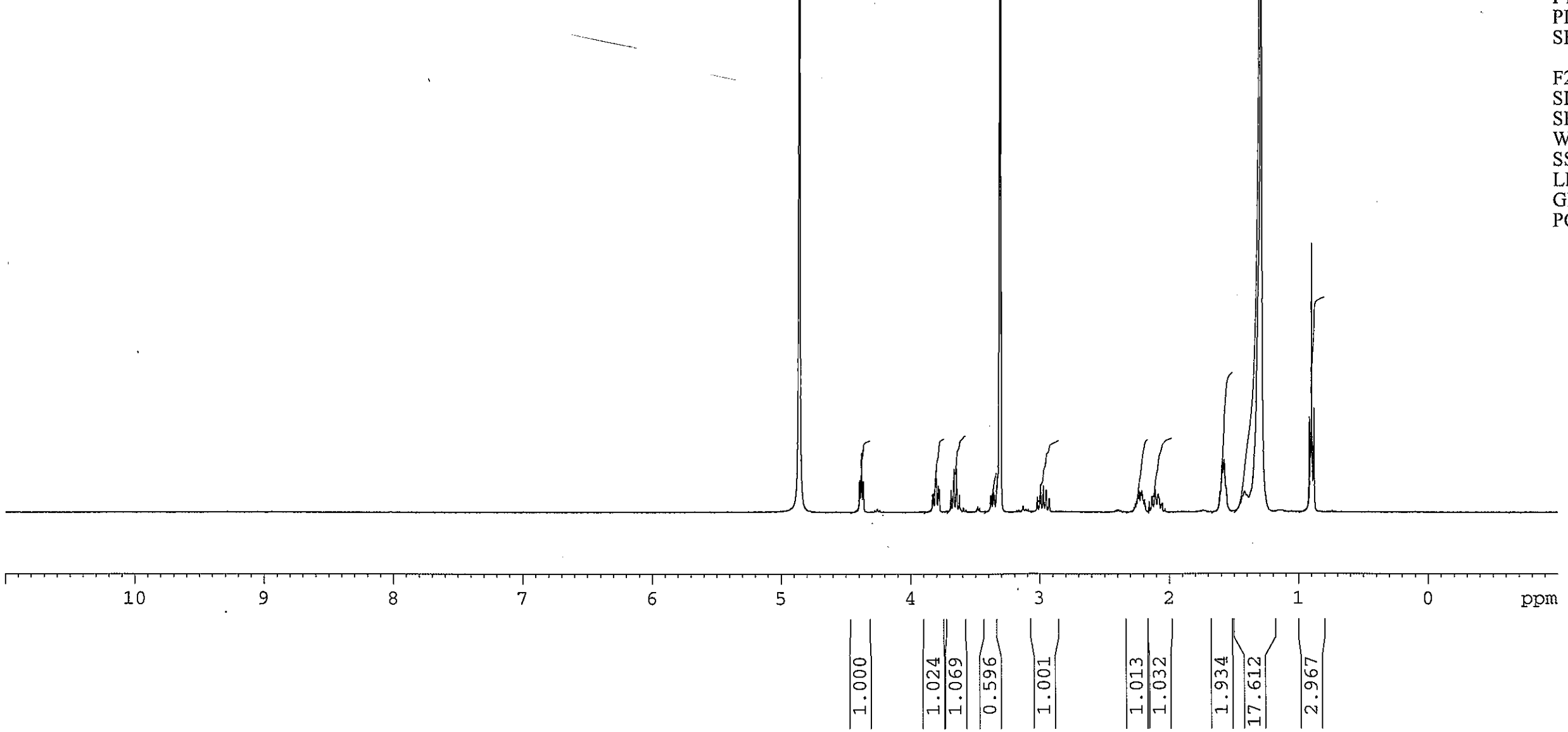
^{13}C NMR (100 MHz, CD_3OD)

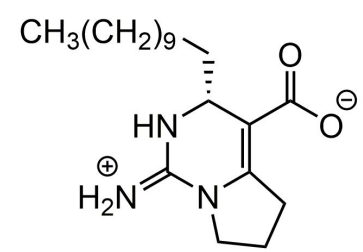
Current Data Parameters
NAME nakane-n400
EXPNO 167
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150105
Time 10.32
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 456.1
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

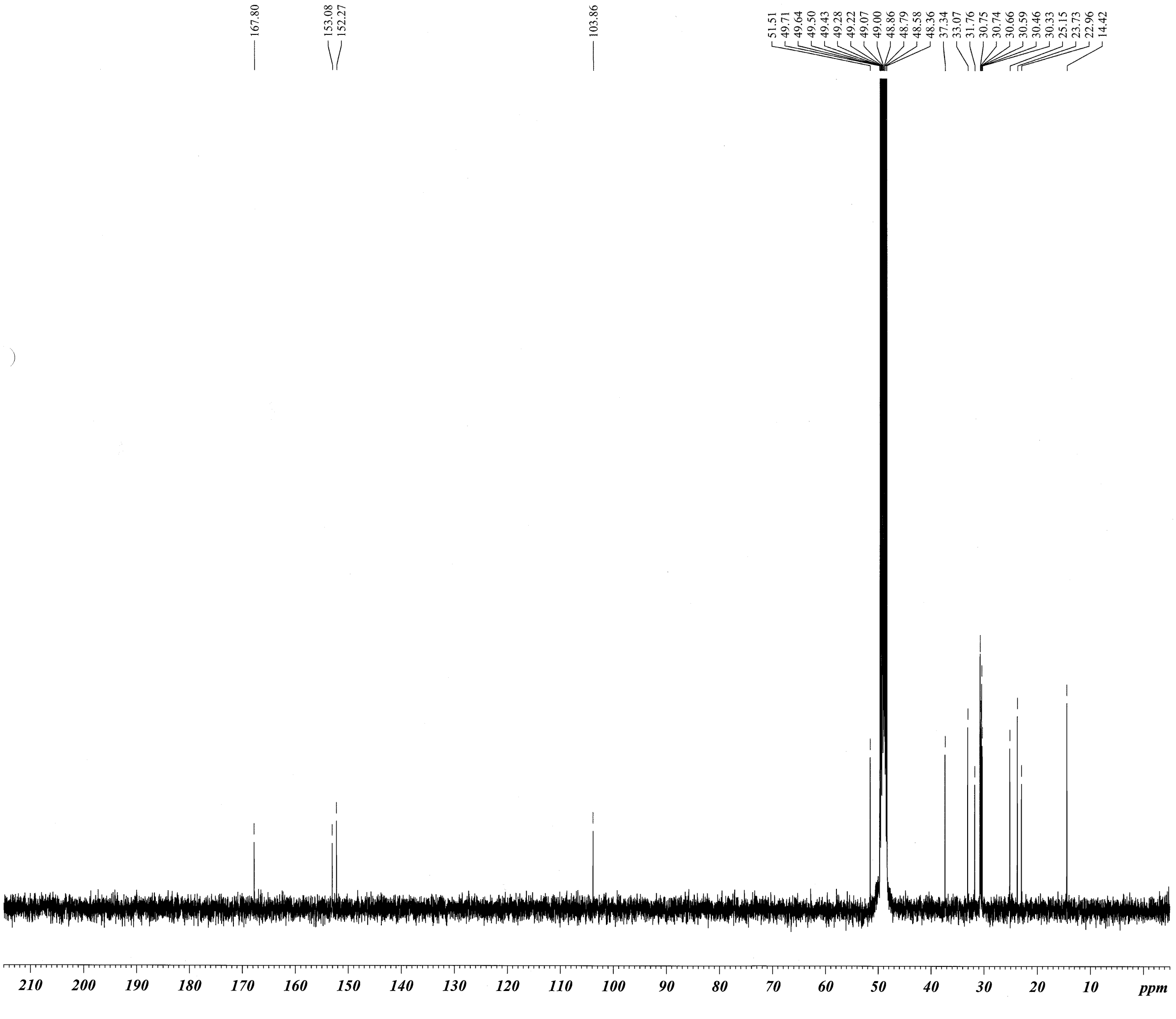
F2 - Processing parameters
SI 32768
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(+)-crambescin A carboxylic acid **1a**

^{1}H NMR (400 MHz, CD_3OD)



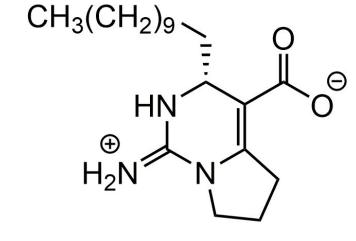
Current Data Parameters
NAME nakane-n400
EXPNO 170
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150105
Time 17.18
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 5282
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

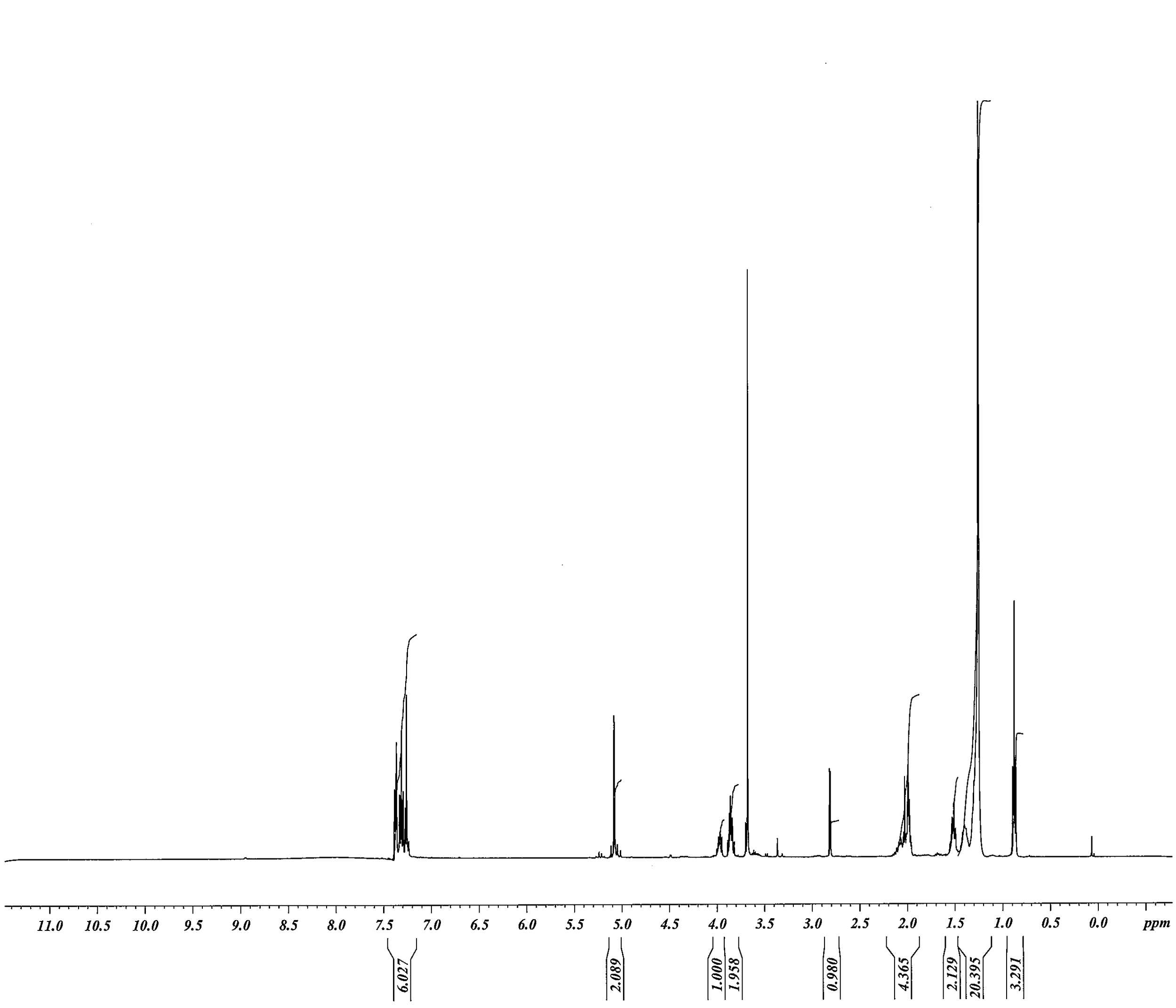
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

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



(+)-crambescin A carboxylic acid **1a**

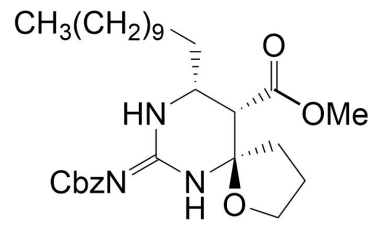
^{13}C NMR (100 MHz, CD_3OD)



Current Data Parameters
NAME nakane-A400
EXPNO 73
PROCNO 2

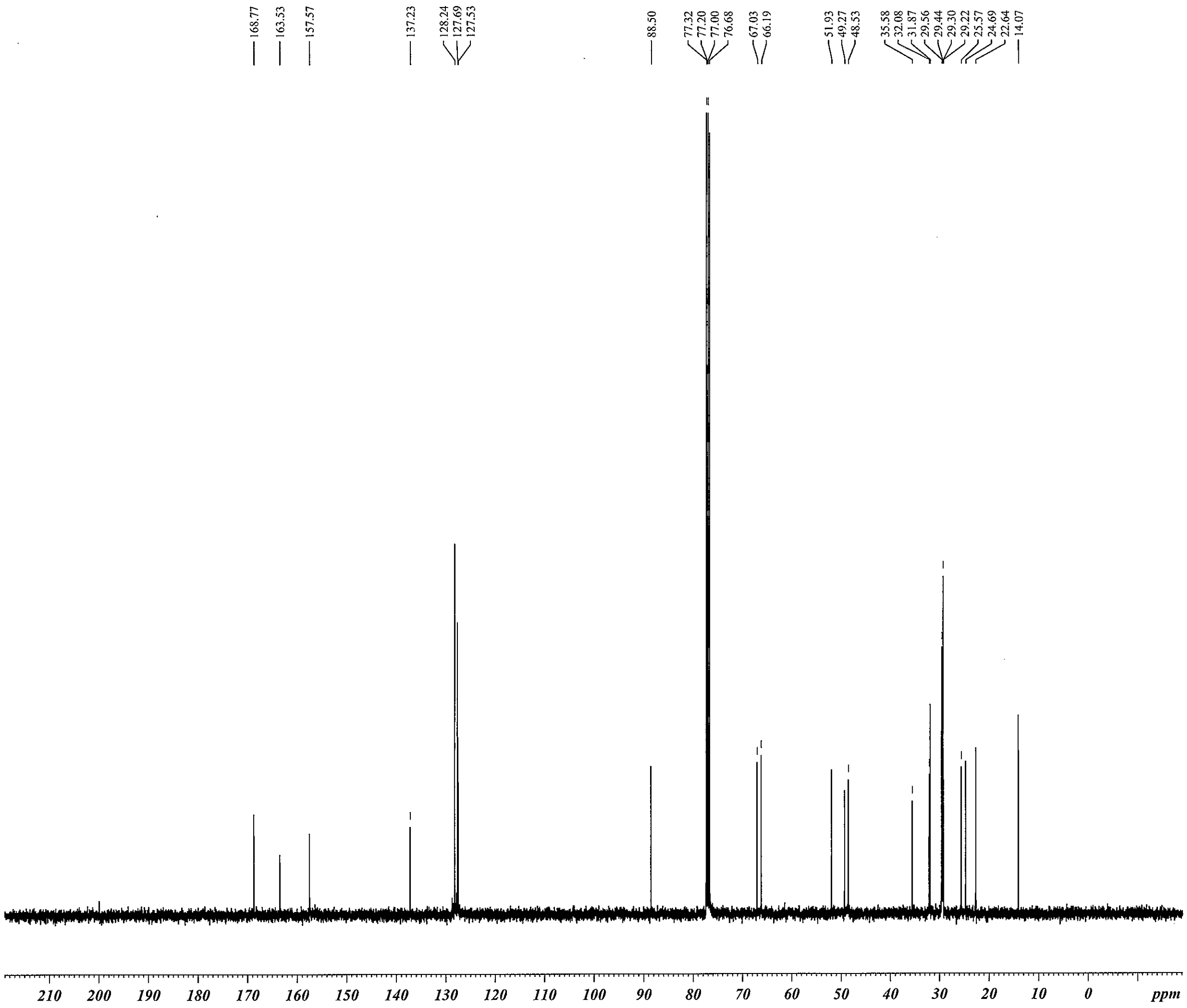
F2 - Acquisition Parameters
Date_ 20151016
Time 17.32
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 4901.961 Hz
FIDRES 0.074798 Hz
AQ 6.6846719 sec
RG 181
DW 102.000 usec
DE 6.50 usec
TE 298.5 K
D1 1.00000000 sec
TD0 1
SFO1 400.1321477 MHz
NUC1 1H
P1 15.00 usec
PLW1 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 400.1300093 MHz
WDW EM



(+)-methyl ester **22**

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

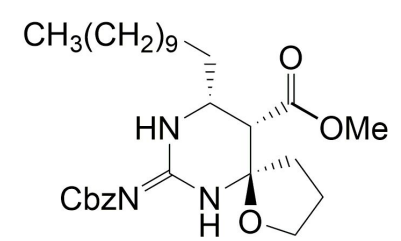


S87

Current Data Parameters
NAME nakane-A400
EXPNO 74
PROCNO 2

F2 - Acquisition Parameters
Date_ 20151016
Time 17.45
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1045
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 18390.4
DW 20.850 usec
DE 6.50 usec
TE 299.7 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
PLW1 -1.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

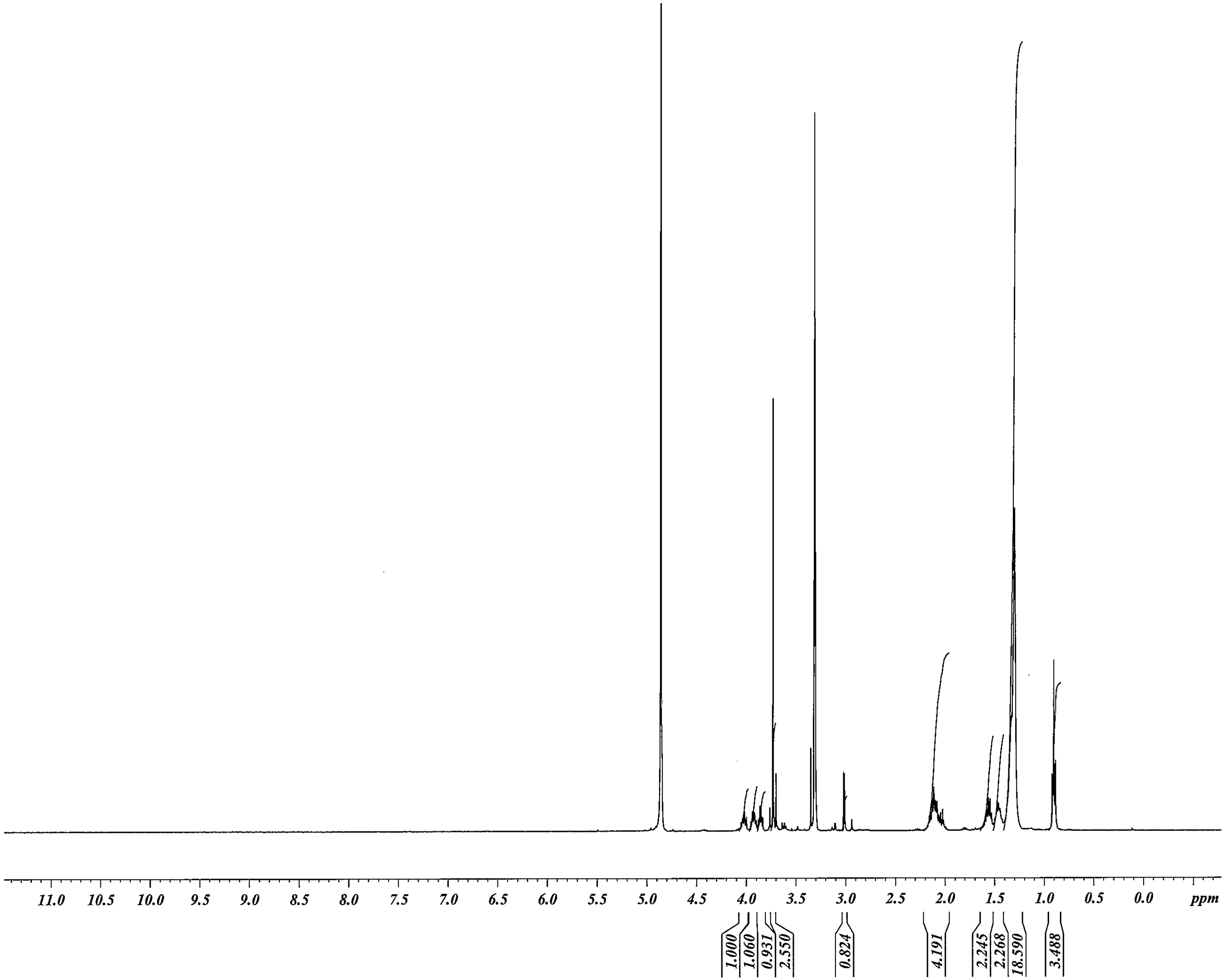
F2 - Processing parameters
SI 32768
SF 100.6127705 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(+)-methyl ester **22**

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

S88

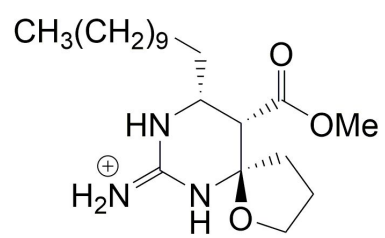


Current Data Parameters
NAME nakane-B400
EXPNO 145
PROCNO 2

F2 - Acquisition Parameters
Date_ 20151019
Time 21.00
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 362
DW 60.400 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1

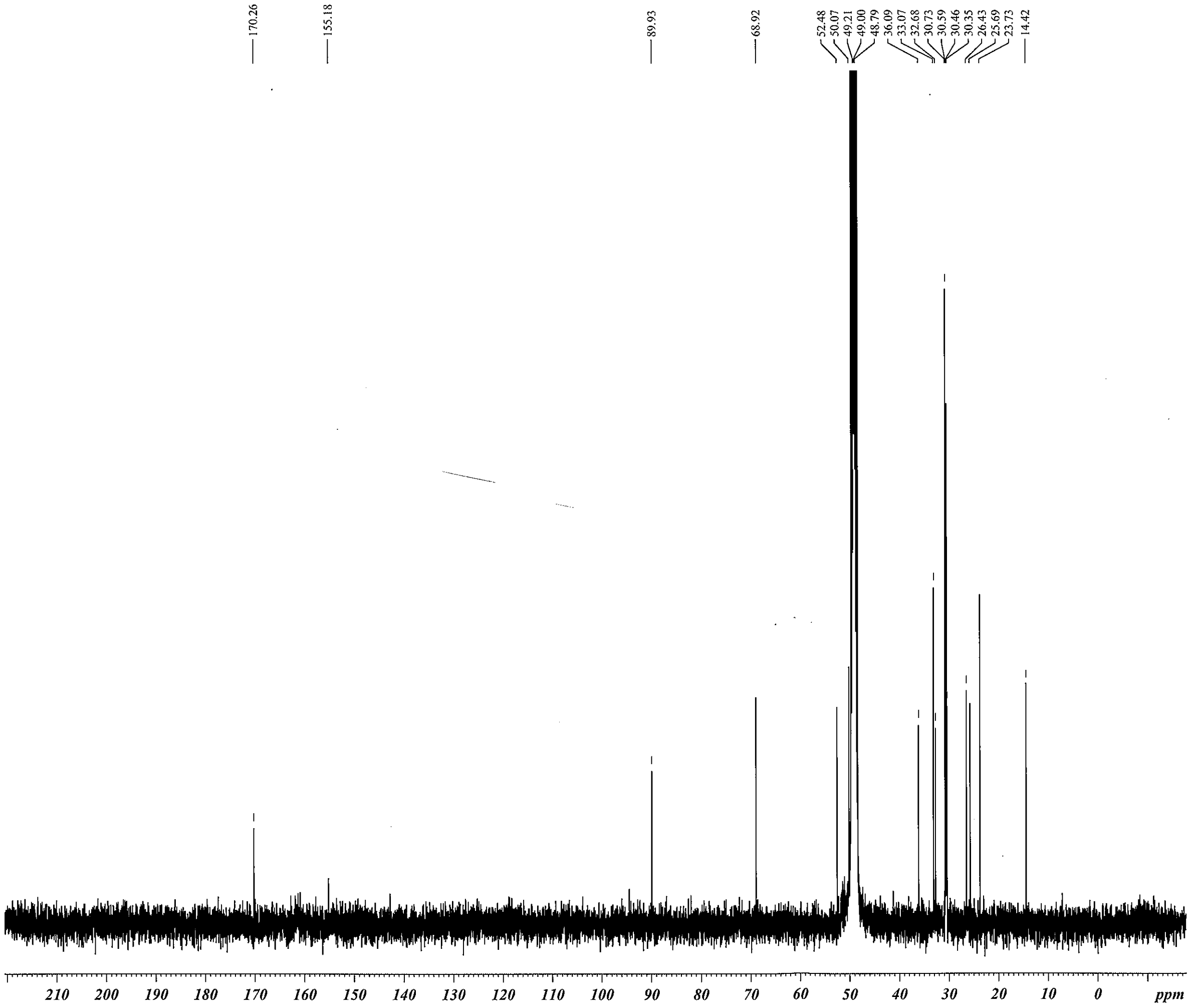
====== CHANNEL f1 ==
NUC1 1H
P1 15.00 usec
PL1 10.30 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768



(+)-crambescin B methyl ester **23**

^{1}H NMR (400 MHz, CD_3OD)



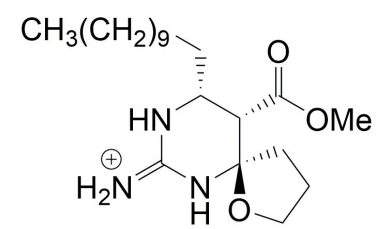
Current Data Parameters
NAME nakane-B400
EXPNO 143
PROCNO 2

F2 - Acquisition Parameters
Date_ 20151019
Time 16.26
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 8200
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 11585.2
DW 20.850 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

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

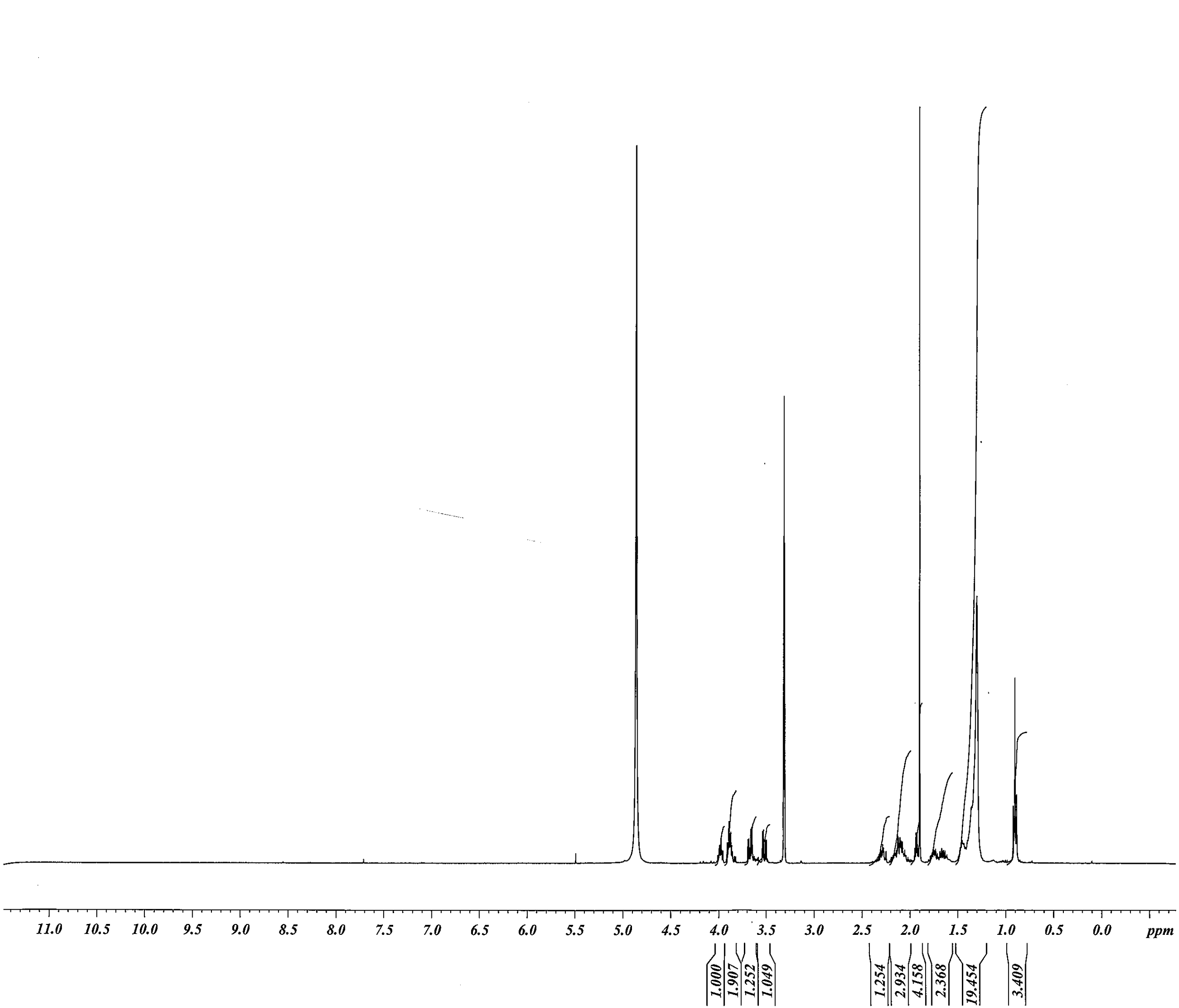
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6126265 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(+)-crambescin B methyl ester **23**

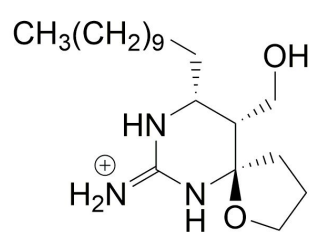
^{13}C NMR (100 MHz, CD_3OD)



Current Data Parameters
NAME nakane-A400
EXPNO 68
PROCNO 2

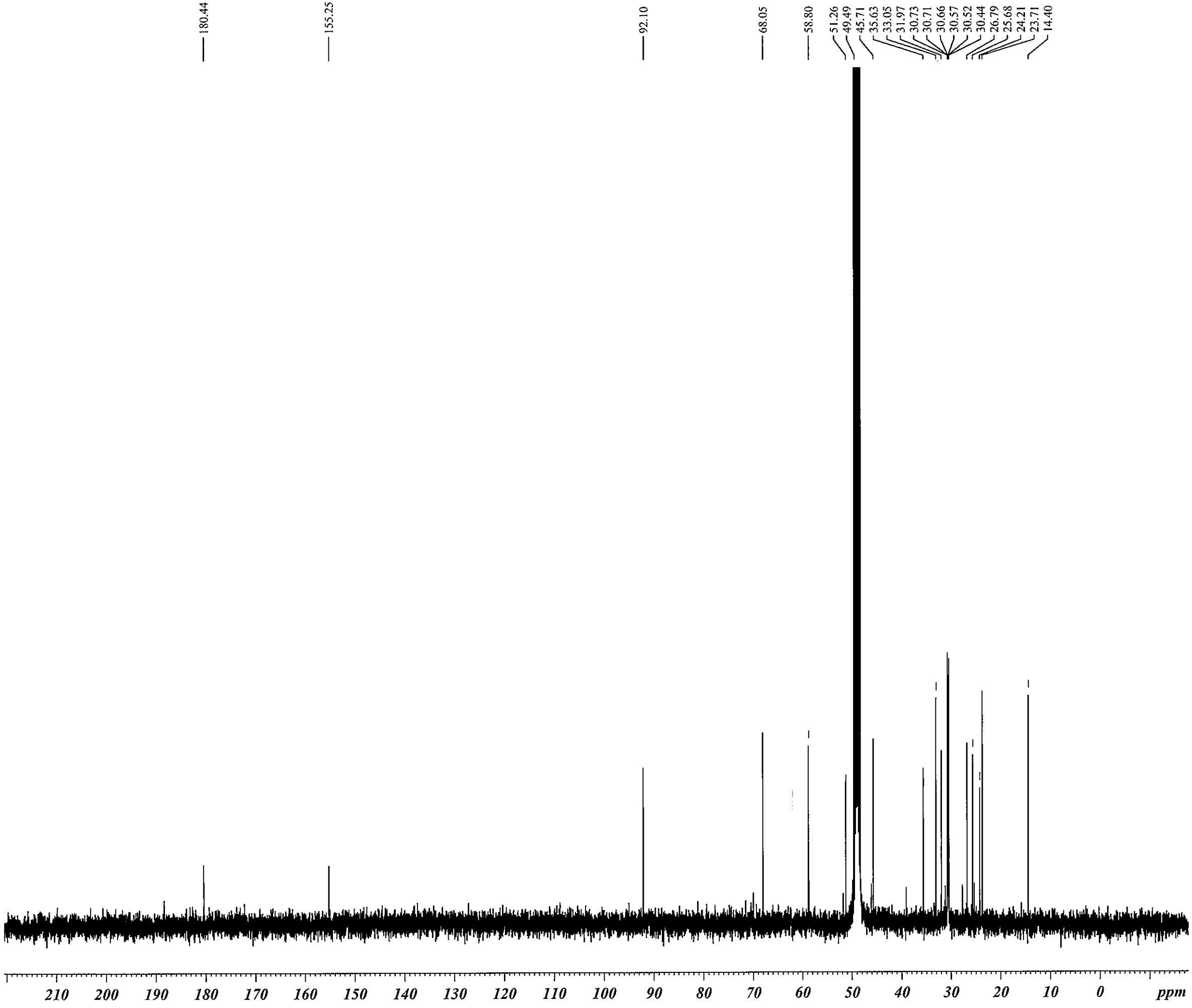
F2 - Acquisition Parameters
Date_ 20151002
Time 15.21
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 2
SWH 4901.961 Hz
FIDRES 0.074798 Hz
AQ 6.6846719 sec
RG 362
DW 102.000 usec
DE 6.50 usec
TE 298.7 K
D1 1.00000000 sec
TD0 1
SFO1 400.1321477 MHz
NUC1 1H
P1 15.00 usec
PLW1 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 400.1300074 MHz
WDW EM



(+)-crambescin B alcohol **24**

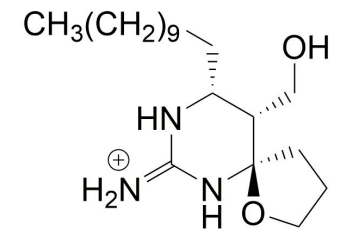
^{1}H NMR (400 MHz, CD_3OD)



Current Data Parameters
NAME nakane-A400
EXPNO 69
PROCNO 2

F2 - Acquisition Parameters
Date_ 20151002
Time 15.24
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 3500
DS 2
SWH 23980.816 Hz
FIDRES 0.365918 Hz
AQ 1.3664255 sec
RG 16384
DW 20.850 usec
DE 6.50 usec
TE 299.3 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
SFO1 100.6228328 MHz
NUC1 13C
P1 10.00 usec
PLW1 -1.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

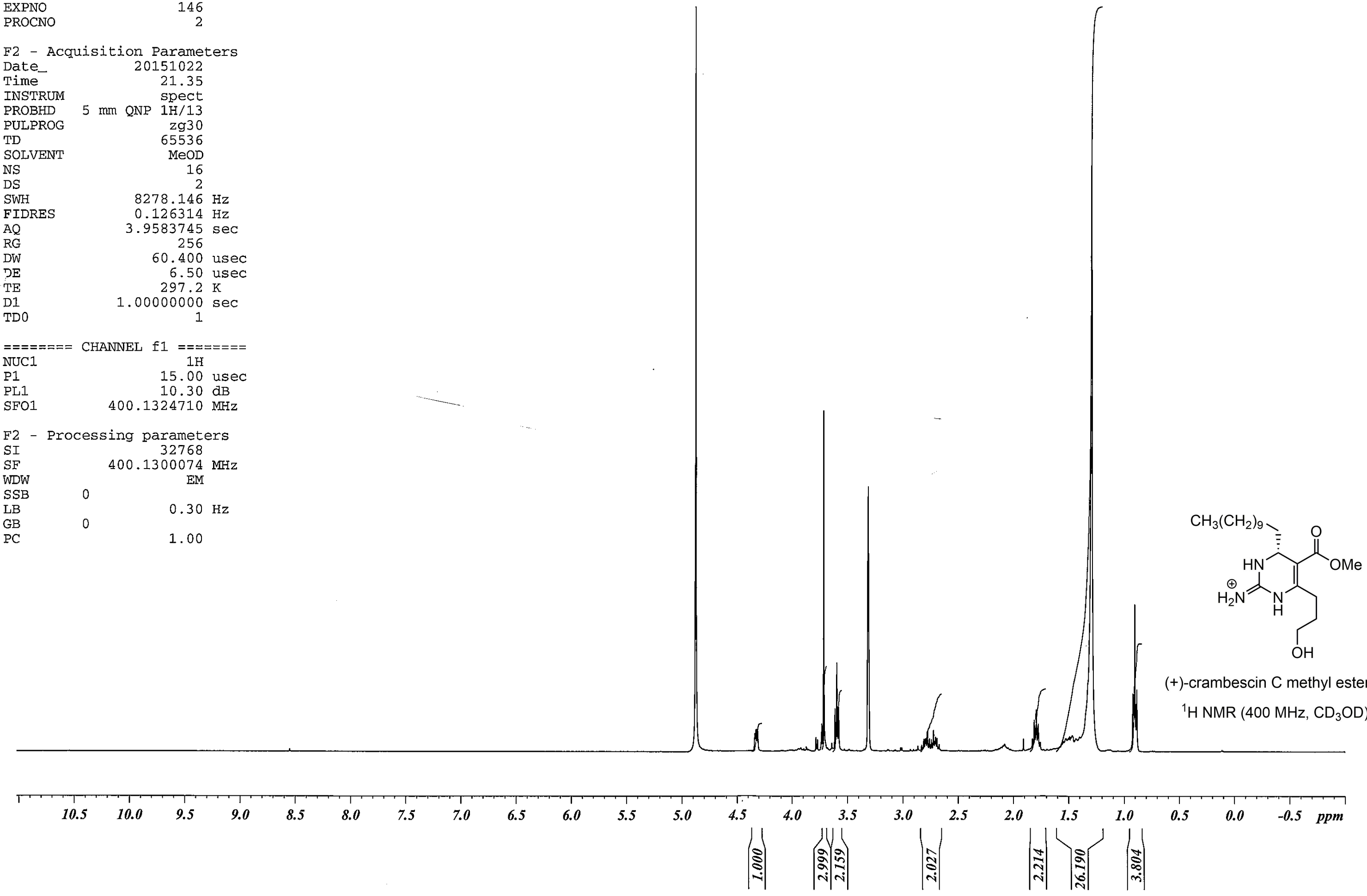
F2 - Processing parameters
SI 32768
SF 100.6126275 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(+)-crambescin B alcohol **24**

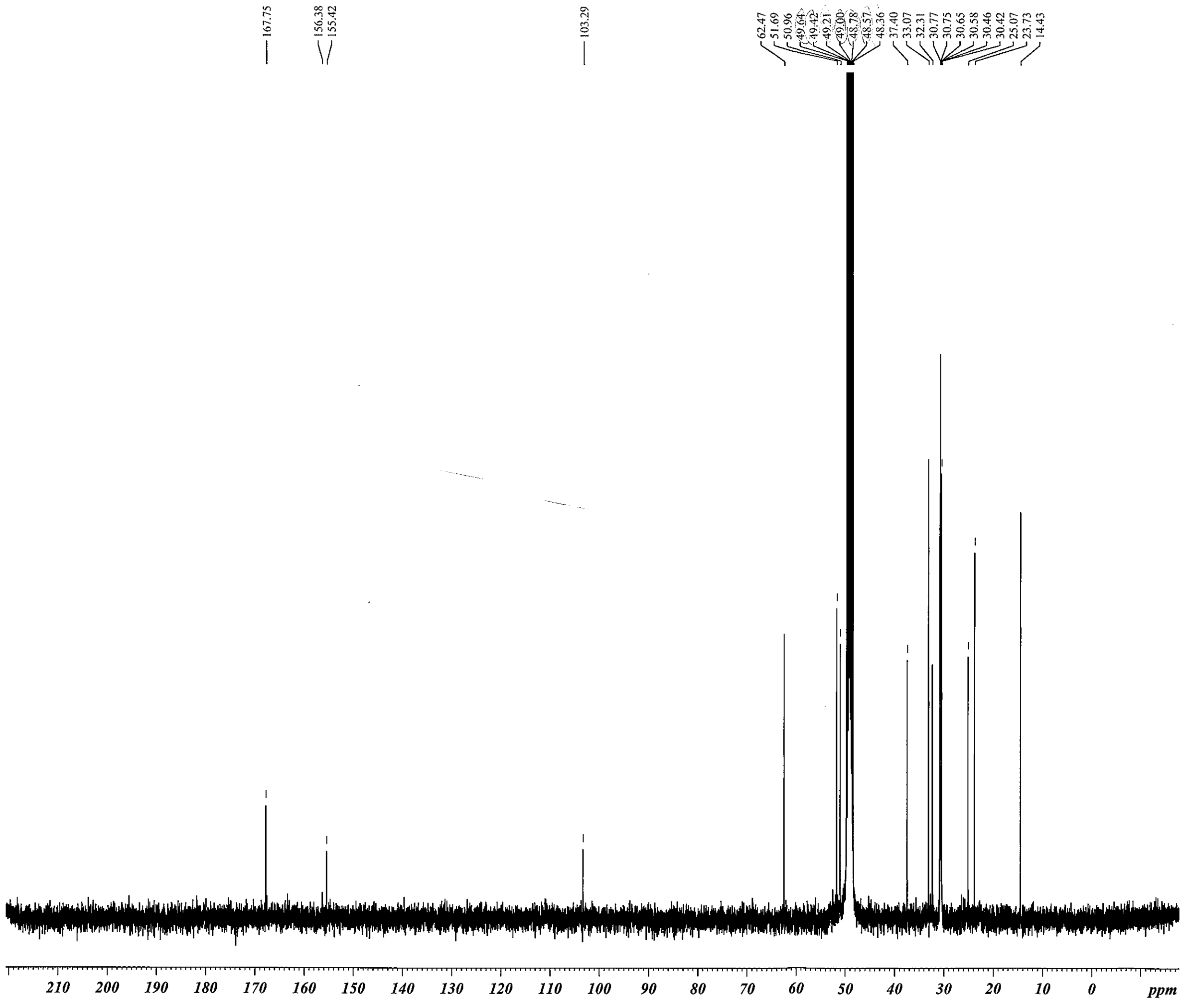
^{13}C NMR (100 MHz, CD_3OD)

```
Current Data Parameters
NAME         nakane-B400
EXPNO                146
PROCNO                 2

F2 - Acquisition Parameters
Date_           20151022
Time               21.35
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9583745 sec
RG                   256
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
```



(+)-crambescin C methyl ester **25**

^{1}H NMR (400 MHz, CD_3OD)



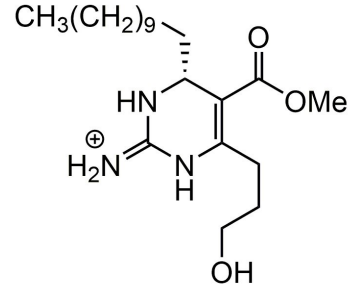
Current Data Parameters
NAME nakane-B400
EXPNO 147
PROCNO 2

F2 - Acquisition Parameters
Date_ 20151022
Time 21.49
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 4500
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 14596.5
DW 20.850 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 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 100.6126272 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(+)-crambescin C methyl ester **25**

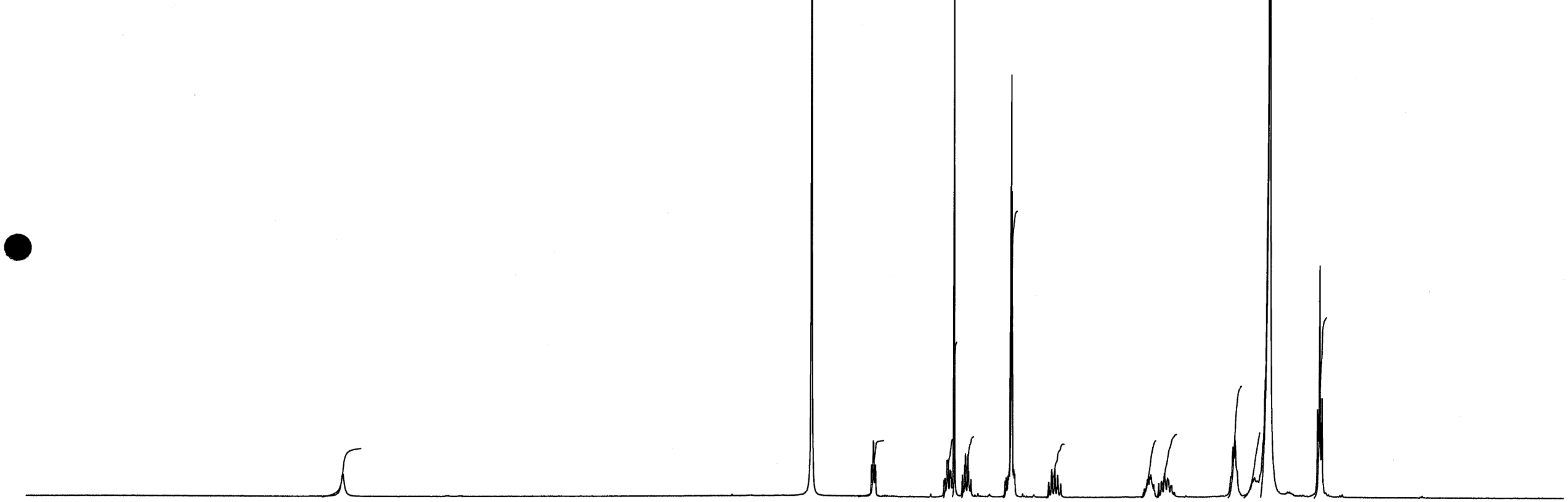
^{13}C NMR (100 MHz, CD_3OD)

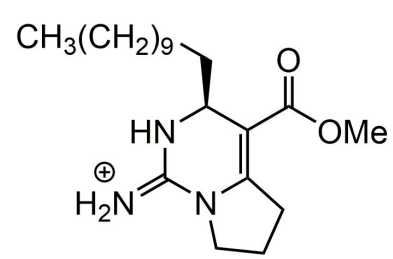
Current Data Parameters
NAME nakane-B400
EXPNO 100
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150205
Time 20.06
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 256
DW 60.400 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

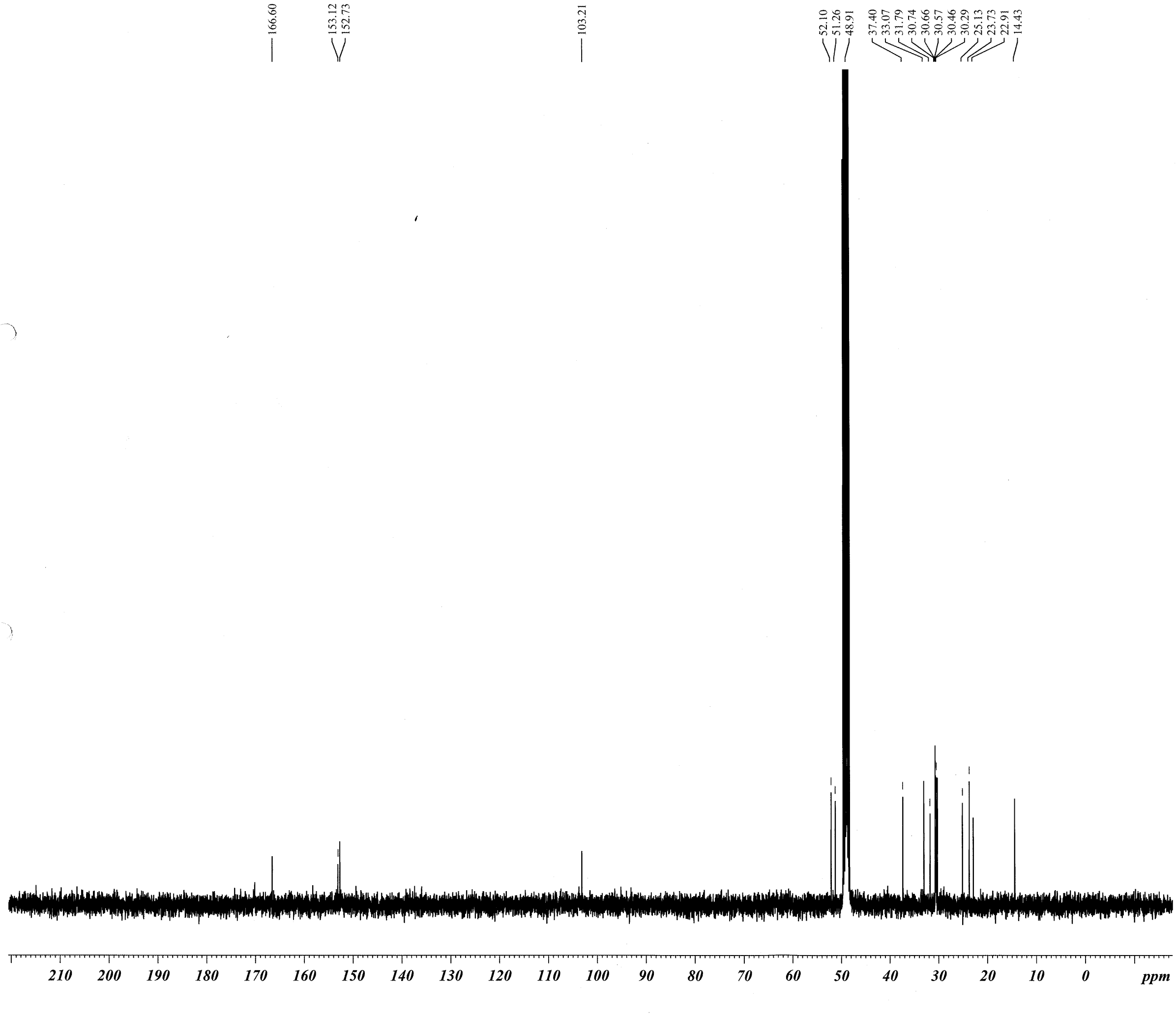
F2 - Processing parameters
SI 32768





(–)-crambescin A methyl ester **1b**

^{1}H NMR (400 MHz, CD_3OD)



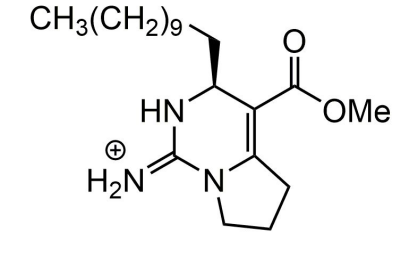
Current Data Parameters
NAME nakane-B400
EXPNO 101
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150205
Time 20.08
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 479
DS 2
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 1.00000000 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 100.6126273 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(–)-crambescin A methyl ester **1b**

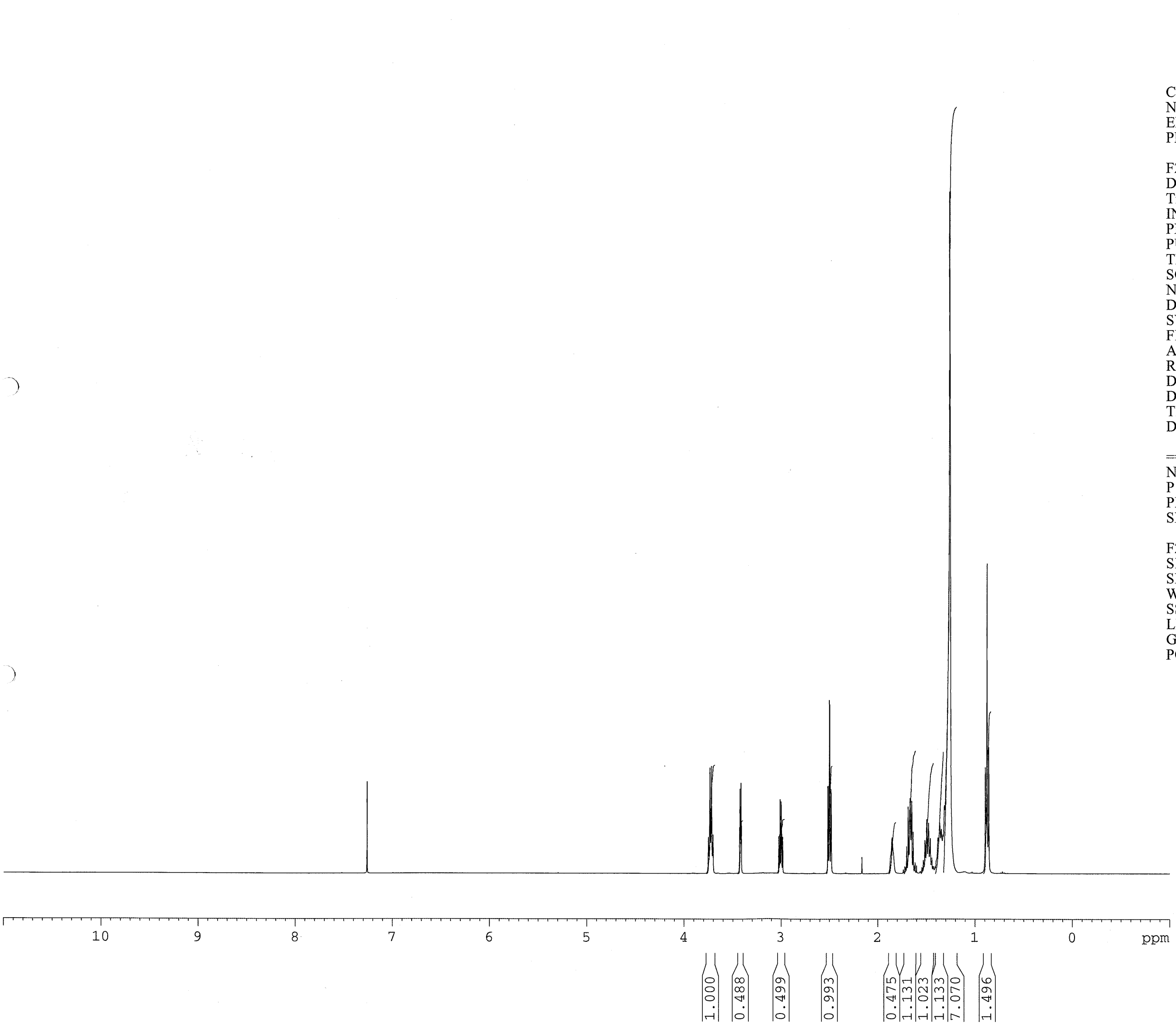
^{13}C NMR (100 MHz, CD_3OD)

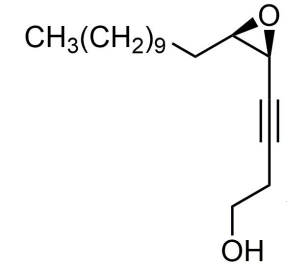
Current Data Parameters
NAME nakane-n400
EXPNO 211
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150206
Time 17.07
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 128
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

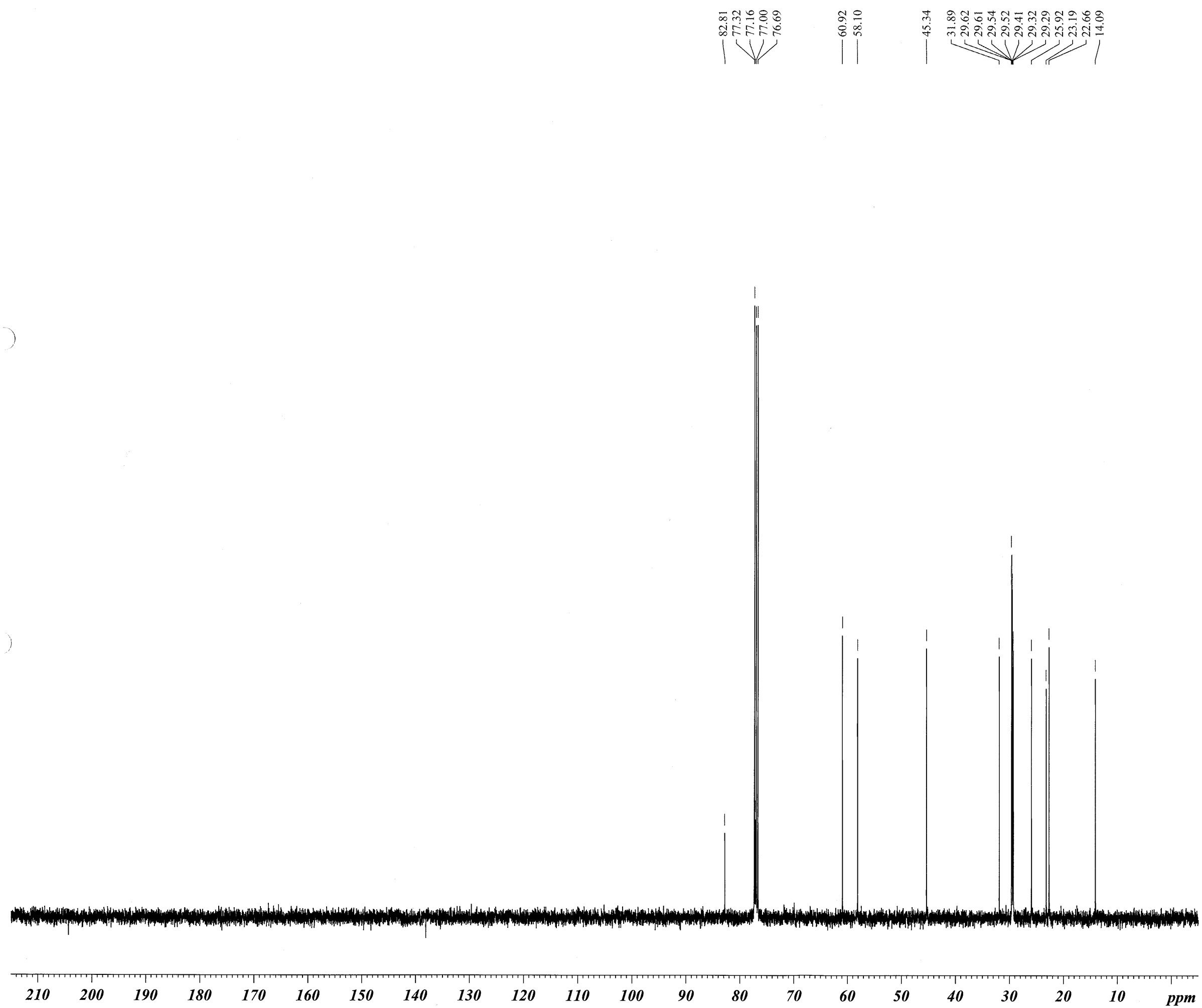
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(+)-epoxide *ent*-**6**

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



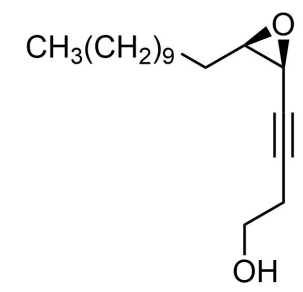
Current Data Parameters
NAME nakane-n400
EXPNO 212
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150206
Time 17.09
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127715 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(+)-epoxide *ent*-**6**

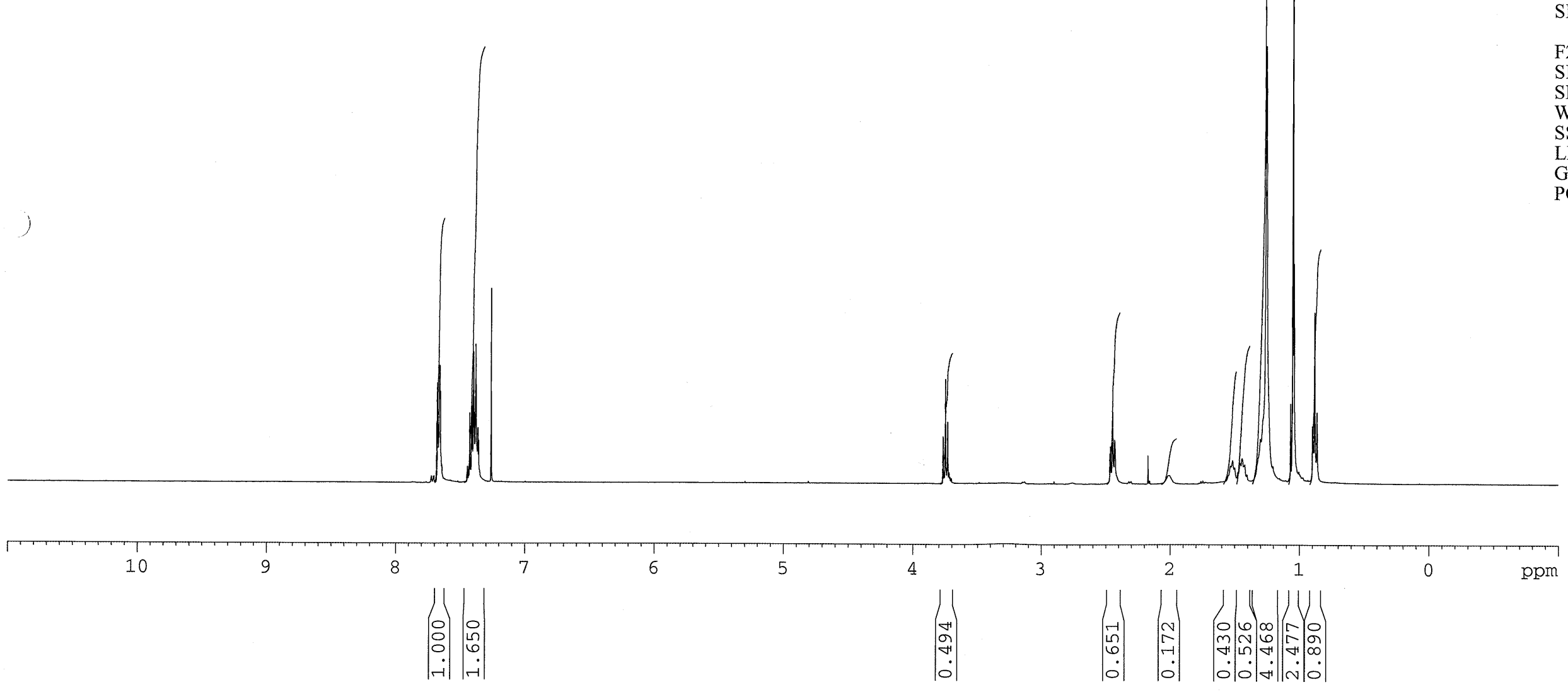
^{13}C NMR (100 MHz, $CDCl_3$)

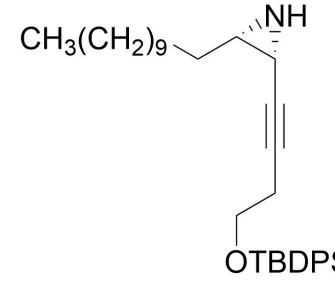
Current Data Parameters
NAME nakane-n400
EXPNO 213
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150206
Time 19.07
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 203.2
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

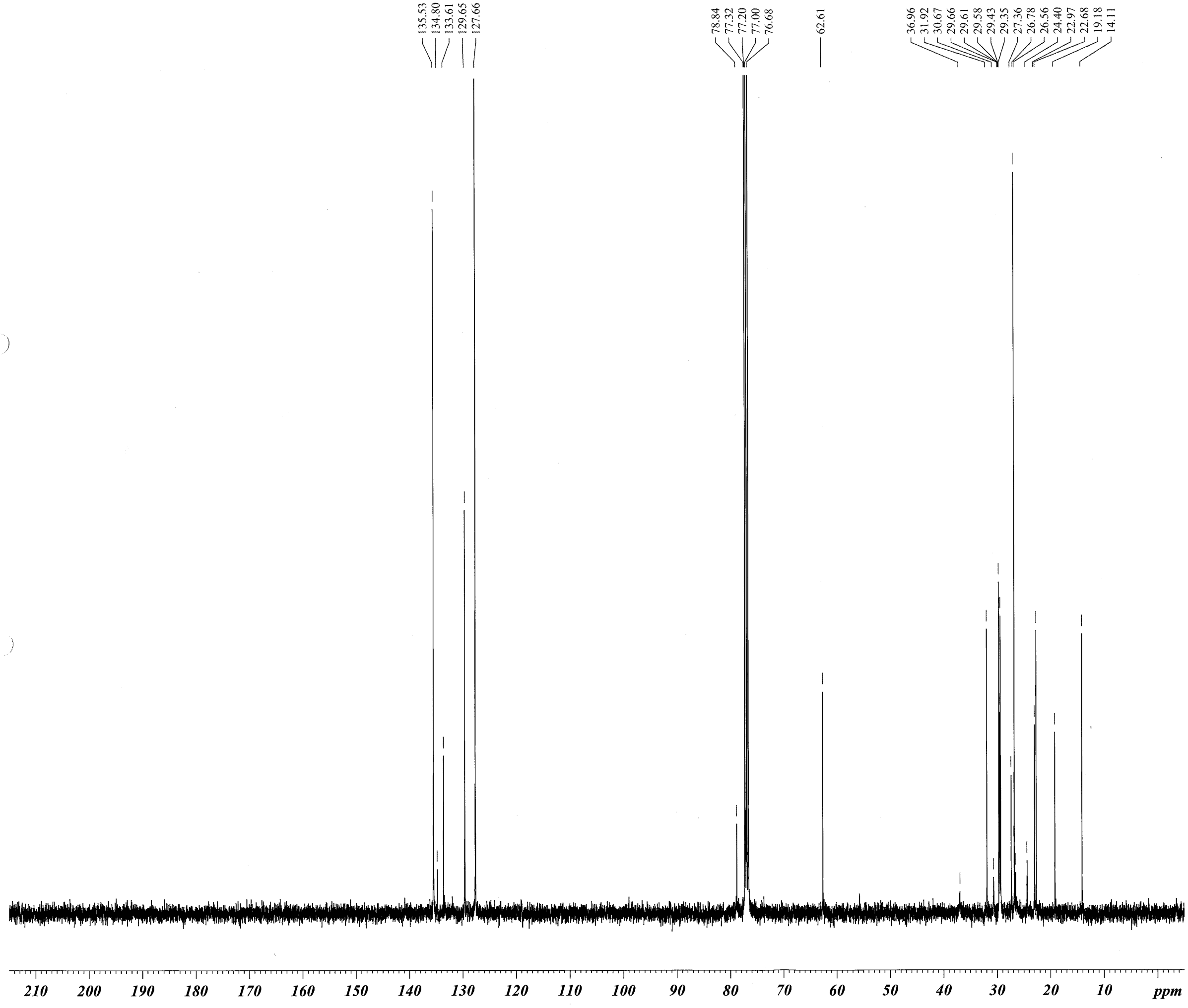
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(+)-aziridine *ent*-**9**

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



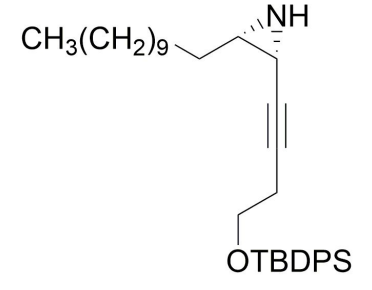
Current Data Parameters
NAME nakane-n400
EXPNO 214
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 19.40
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3000
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

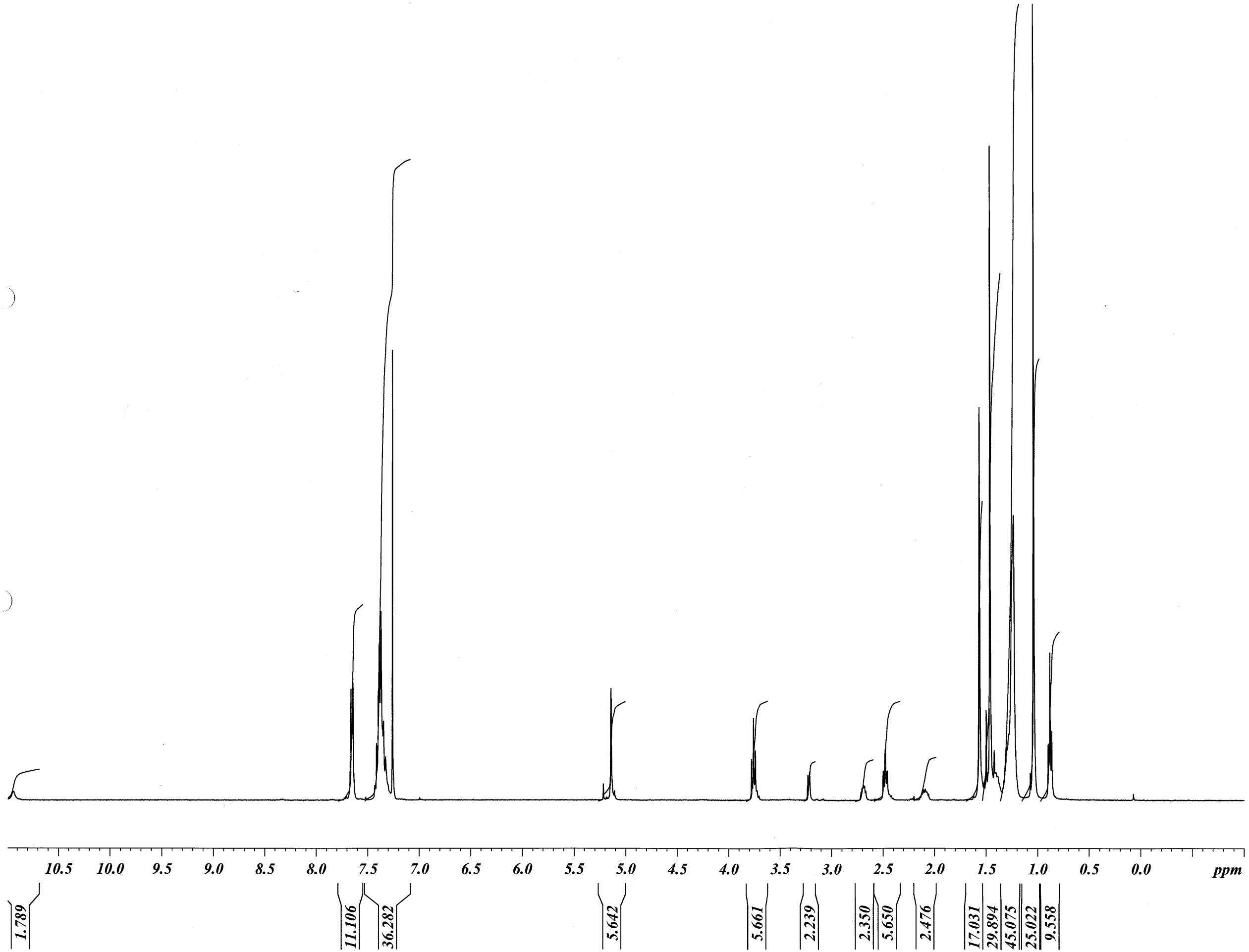
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.20



(+)-aziridine *ent*-**9**

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

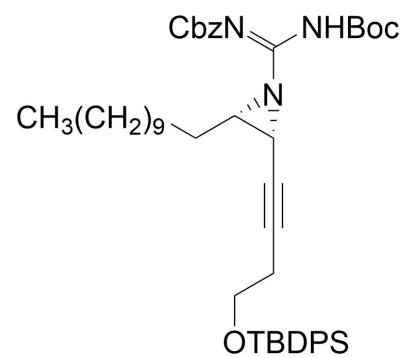


Current Data Parameters
NAME nakane-B400
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140617
Time 21.23
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 256
DW 60.400 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

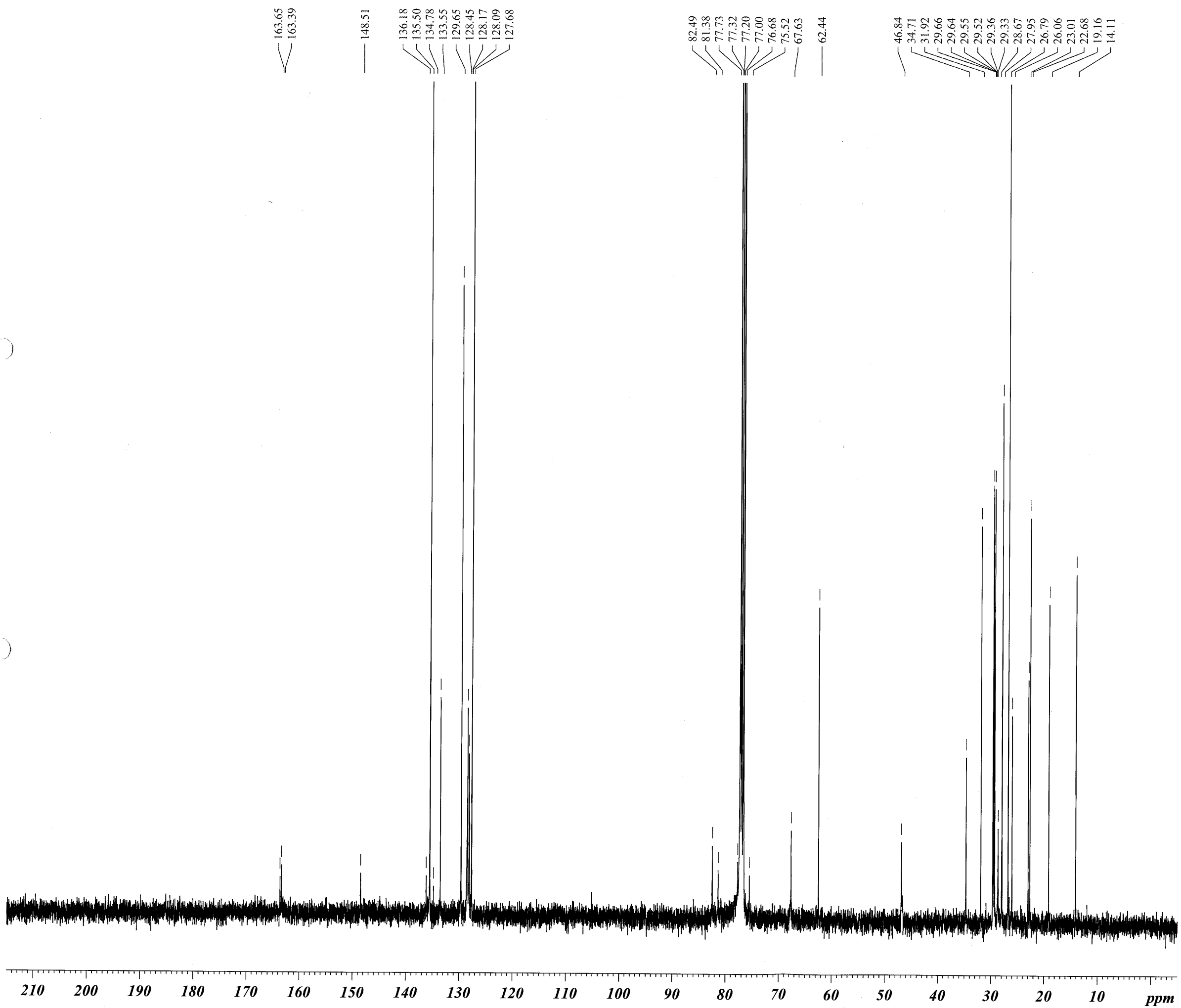
======== CHANNEL f1 ==
NUC1 1H
P1 15.00 usec
PL1 10.30 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768



(–)-guanidino-aziridine *ent*-**10**

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



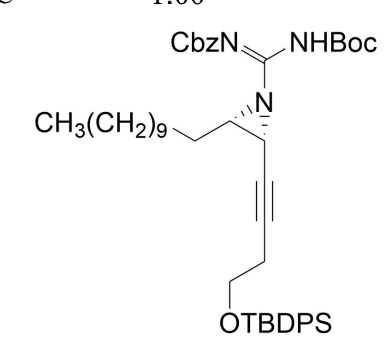
Current Data Parameters
NAME nakane-n400
EXPNO 220
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150206
Time 23.54
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 14300
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(–)-guanidino-aziridine *ent*-**10**

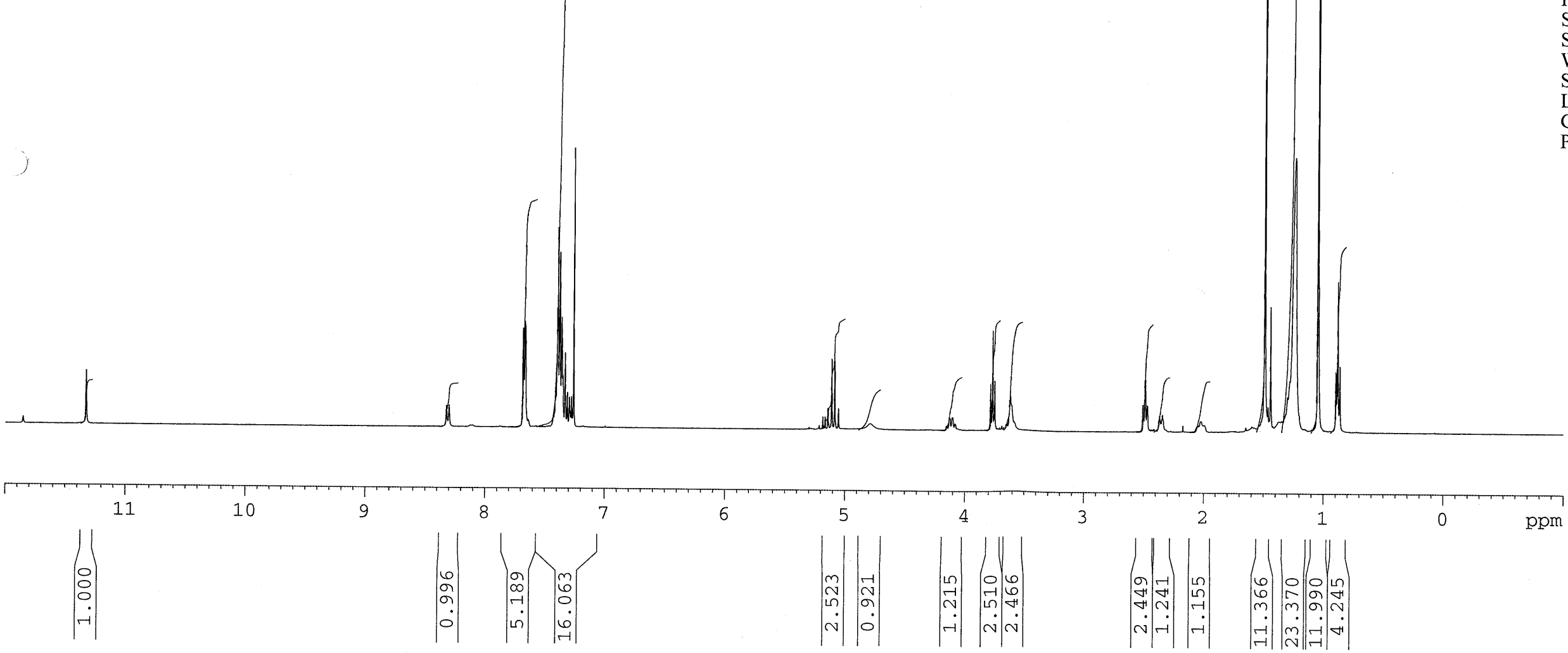
^{13}C NMR (100 MHz, $CDCl_3$)

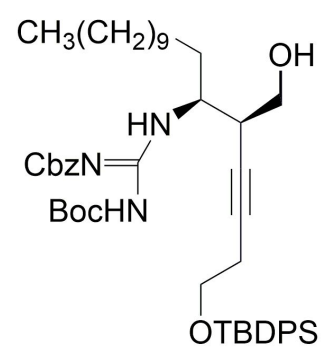
Current Data Parameters
NAME nakane-n400
EXPNO 221
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150210
Time 21.04
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 203.2
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

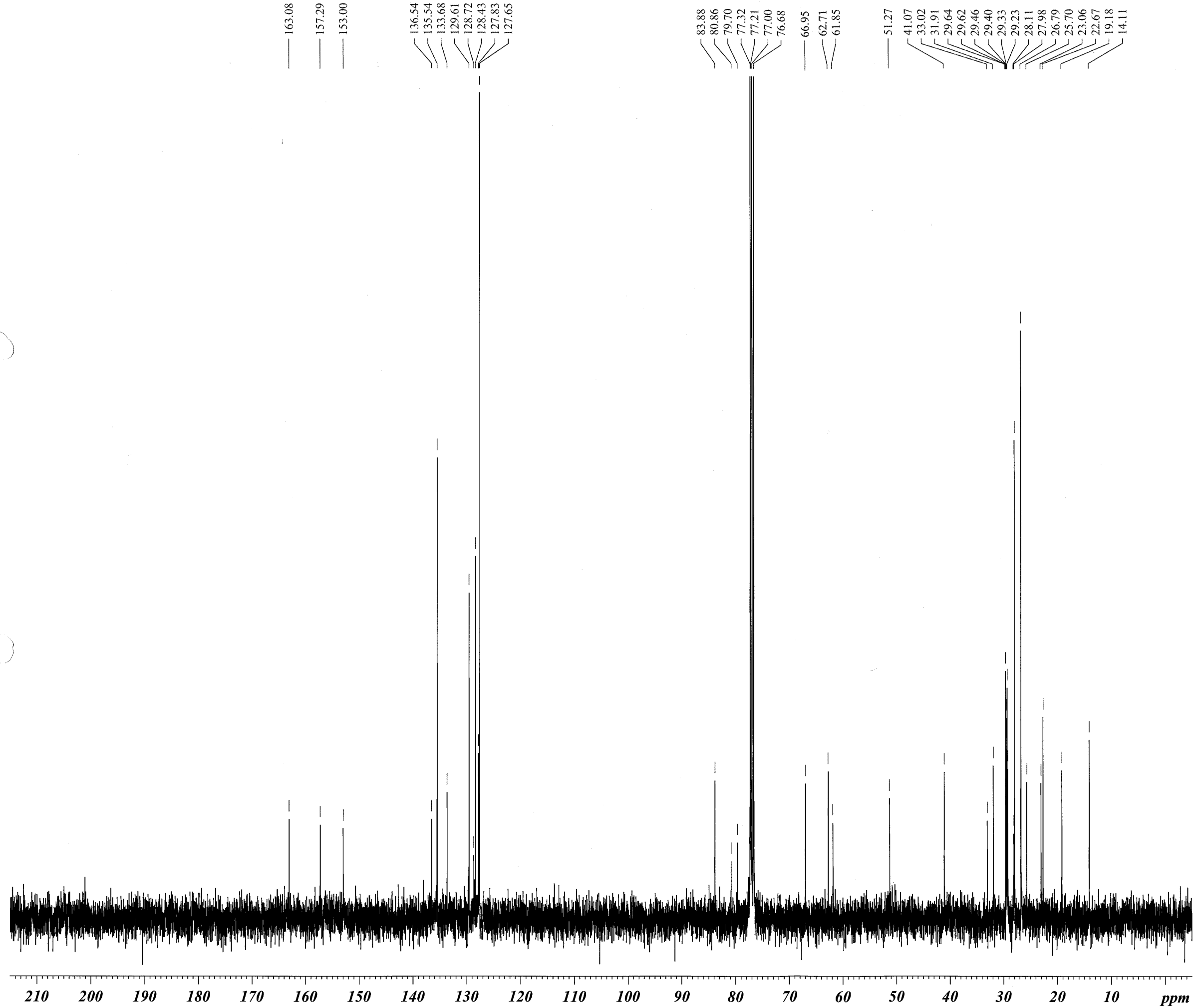
F2 - Processing parameters
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(+)-alcohol *ent*-**11**

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



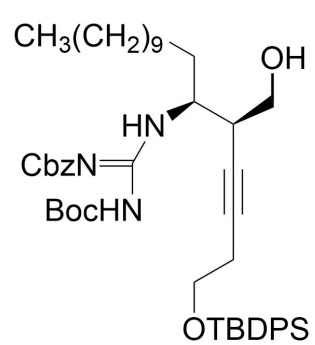
Current Data Parameters
NAME nakane-n400
EXPNO 222
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150207
Time 9.52
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 700
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(+)-alcohol *ent*-**11**

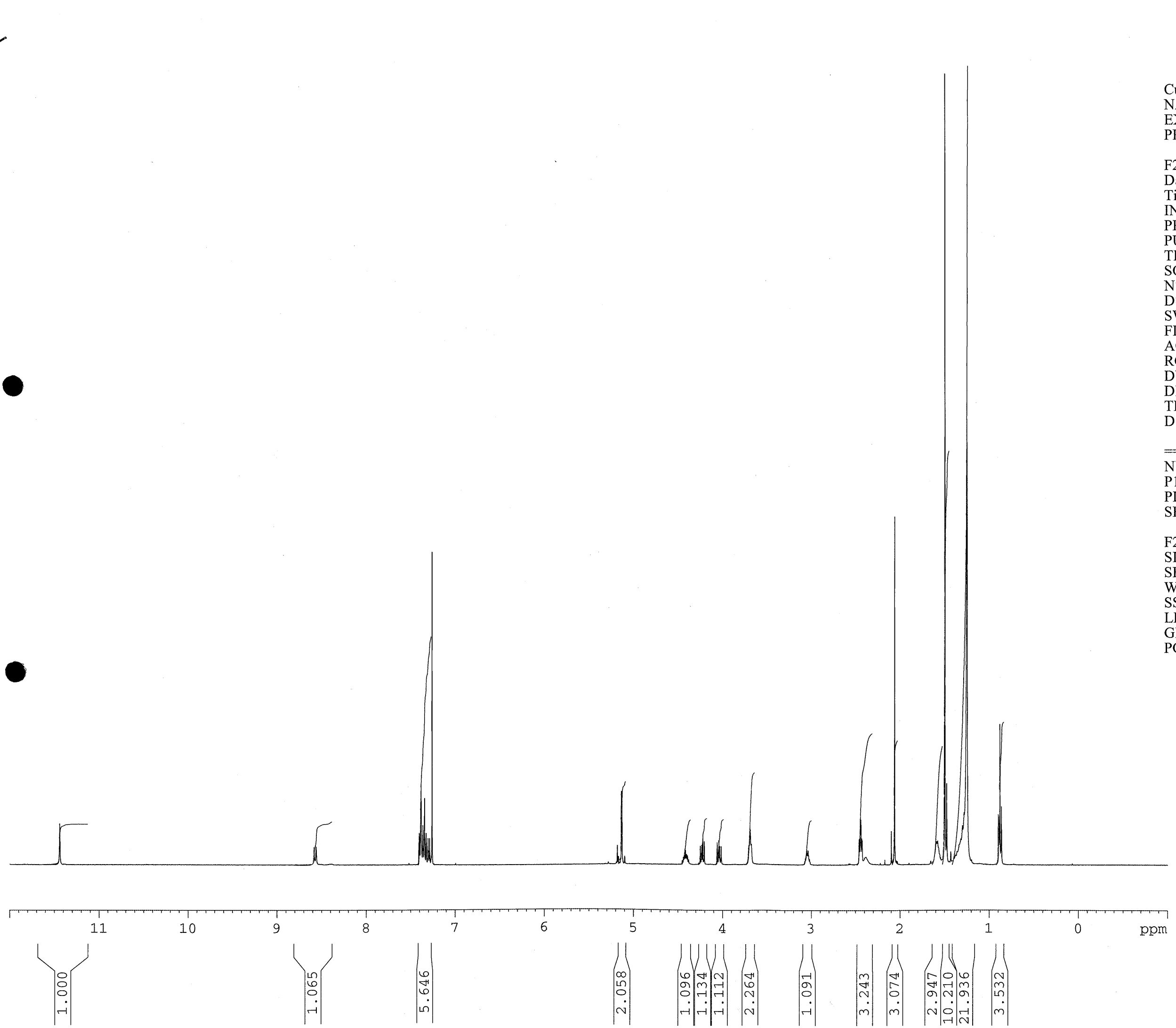
^{13}C NMR (100 MHz, $CDCl_3$)

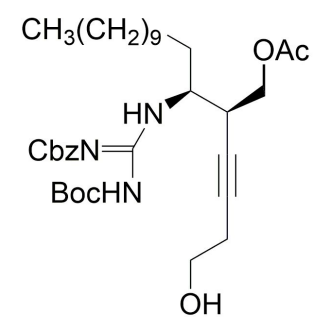
Current Data Parameters
NAME nakane-n400
EXPNO 225
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150212
Time 17.09
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 256
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

========== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

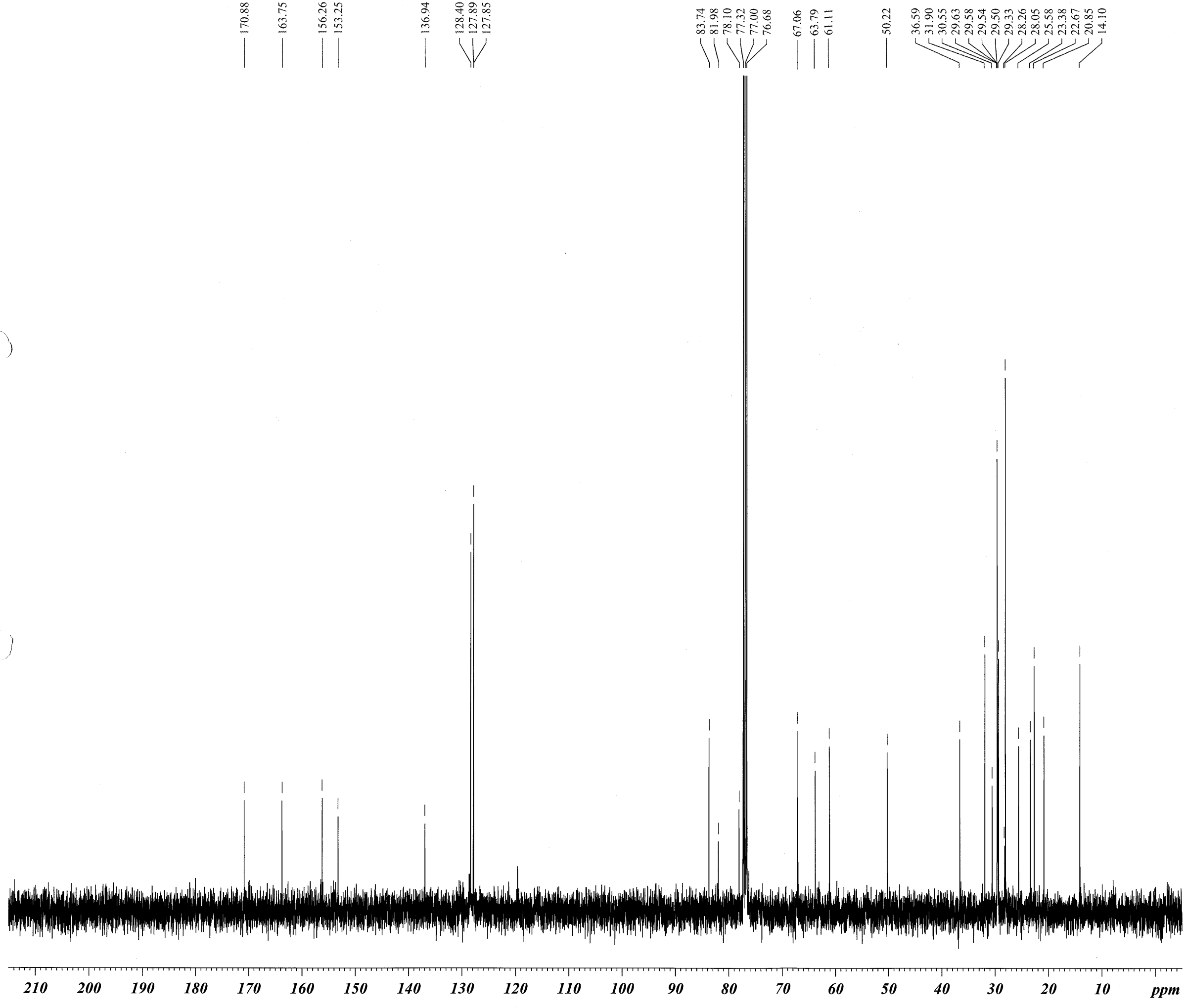
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(–)-alcohol *ent*-**12**

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



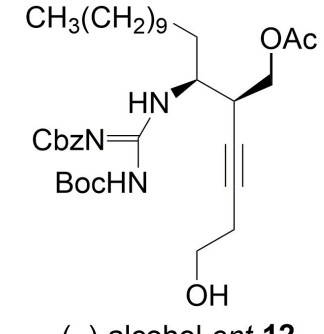
Current Data Parameters
NAME nakane-n400
EXPNO 226
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150207
Time 13.39
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(–)-alcohol *ent*-**12**

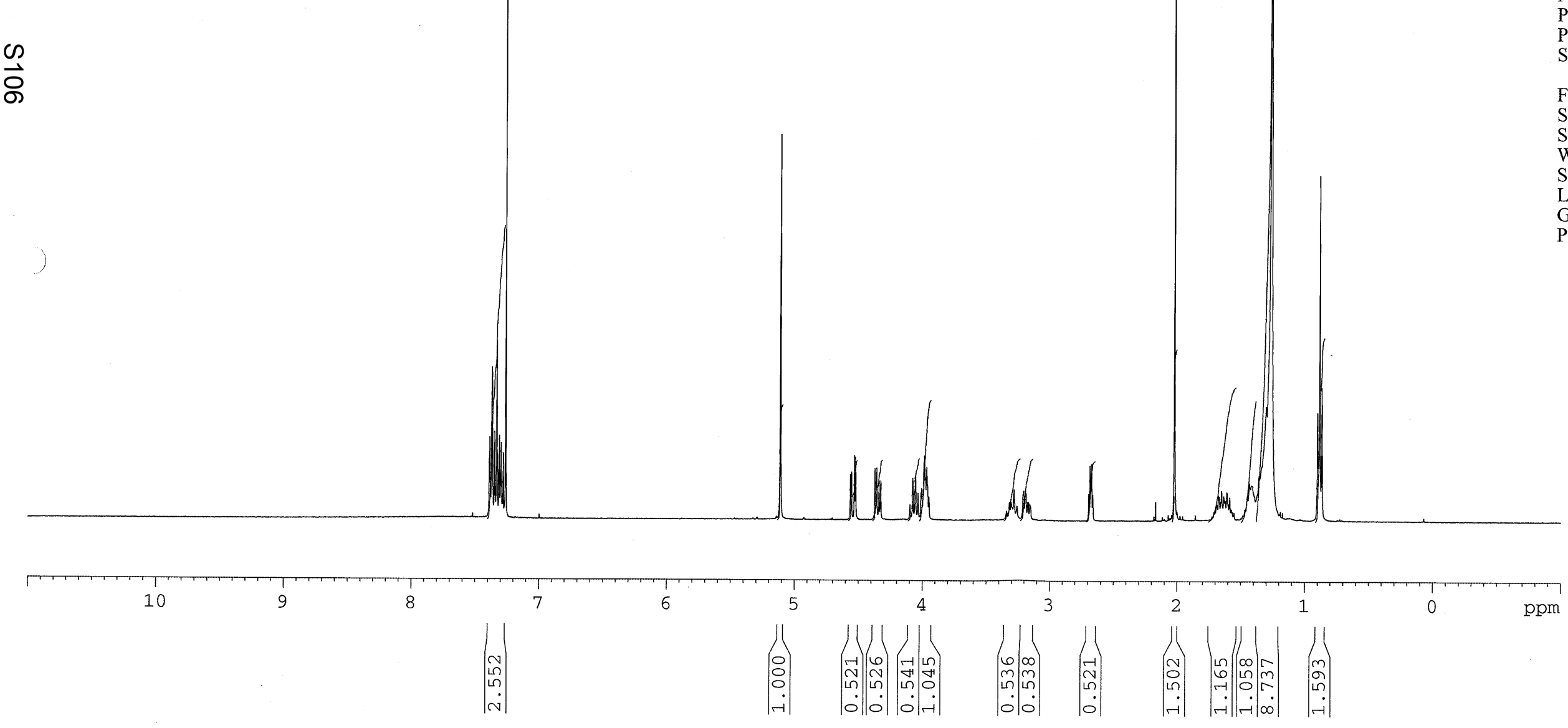
^{13}C NMR (100 MHz, $CDCl_3$)

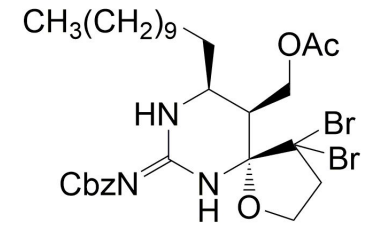
Current Data Parameters
NAME nakane-n400
EXPNO 229
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150210
Time 21.24
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 456.1
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

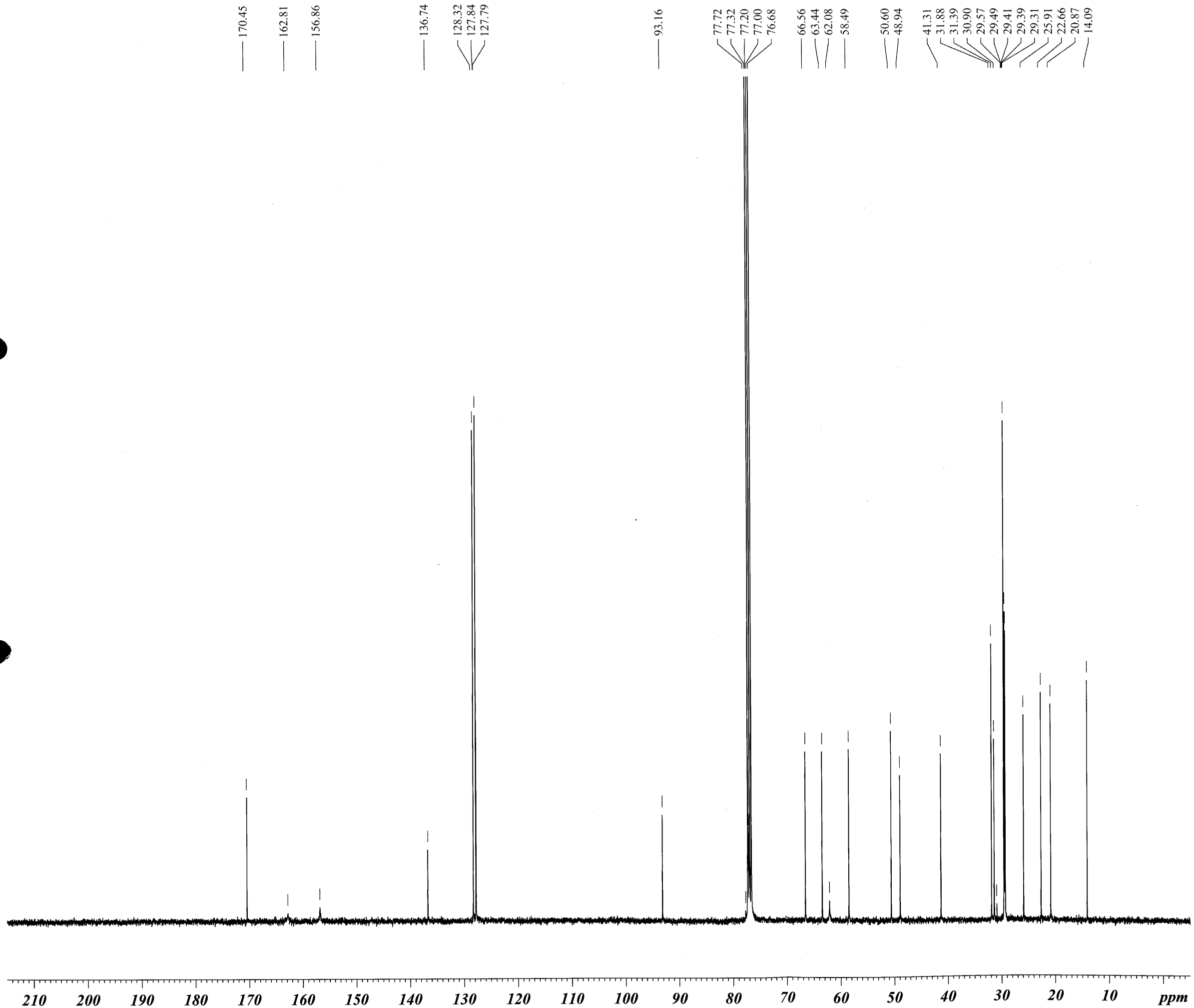
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(–)-*spiro*-aminal *ent*-**14**

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



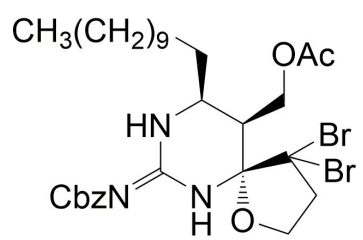
Current Data Parameters
NAME nakane-n400
EXPNO 230
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 21.35
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16500
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.20000005 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127715 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(–)-*spiro*-aminal *ent*-**14**

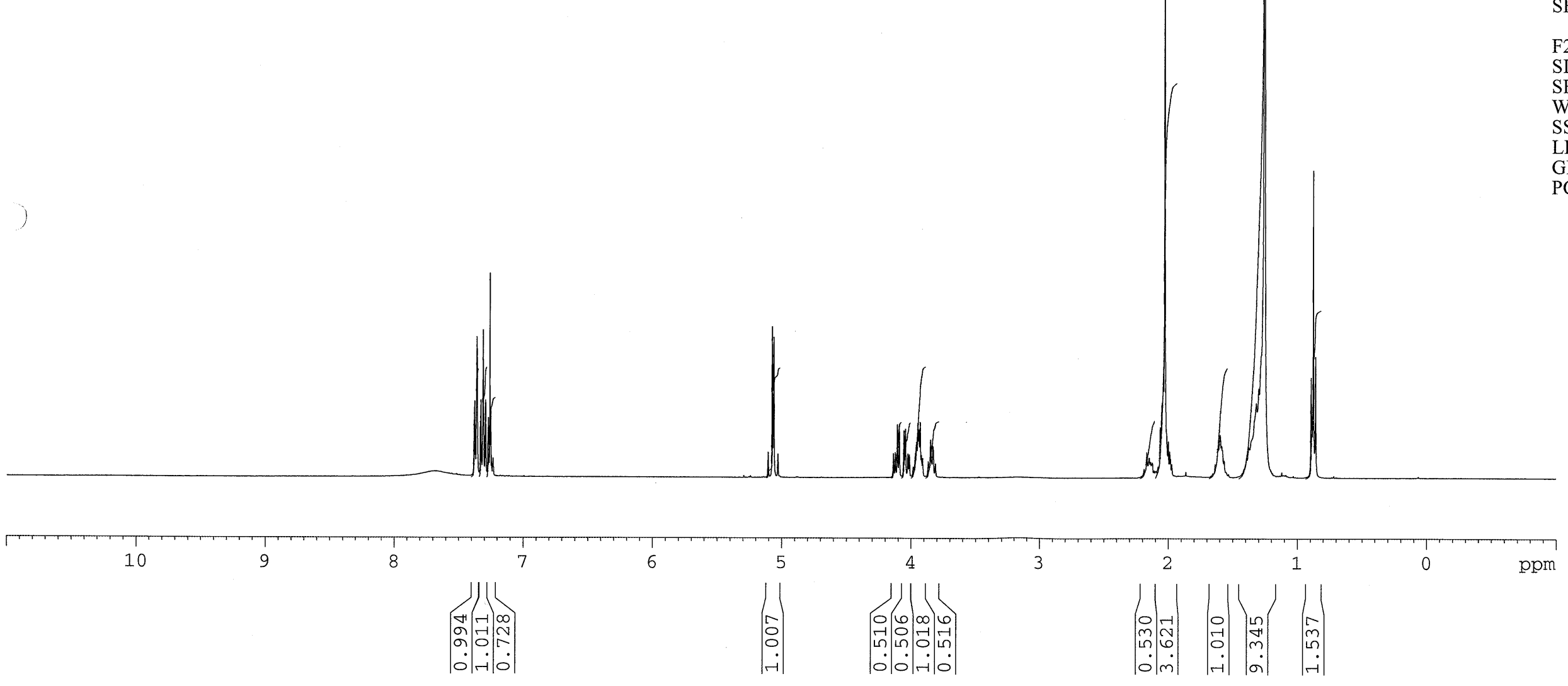
^{13}C NMR (100 MHz, $CDCl_3$)

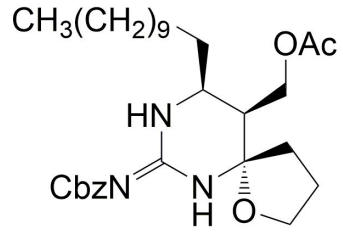
Current Data Parameters
NAME nakane-n400
EXPNO 233
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 11.28
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 161.3
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

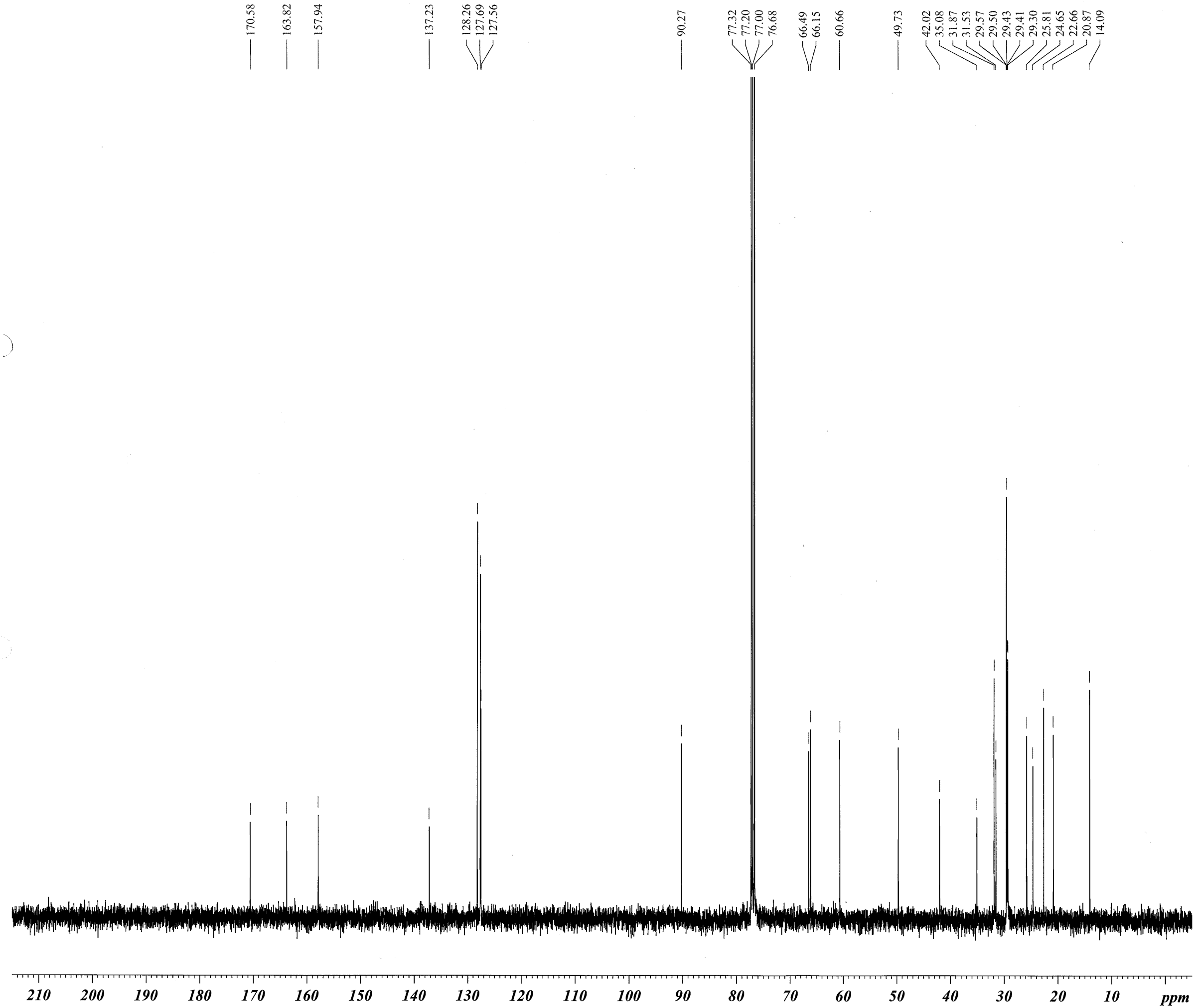
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(–)-*spiro*-aminal *ent*-**15**

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



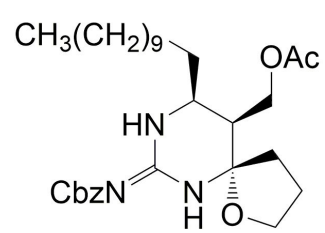
Current Data Parameters
NAME nakane-n400
EXPNO 234
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 11.31
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127722 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(–)-*spiro*-aminal *ent*-**15**

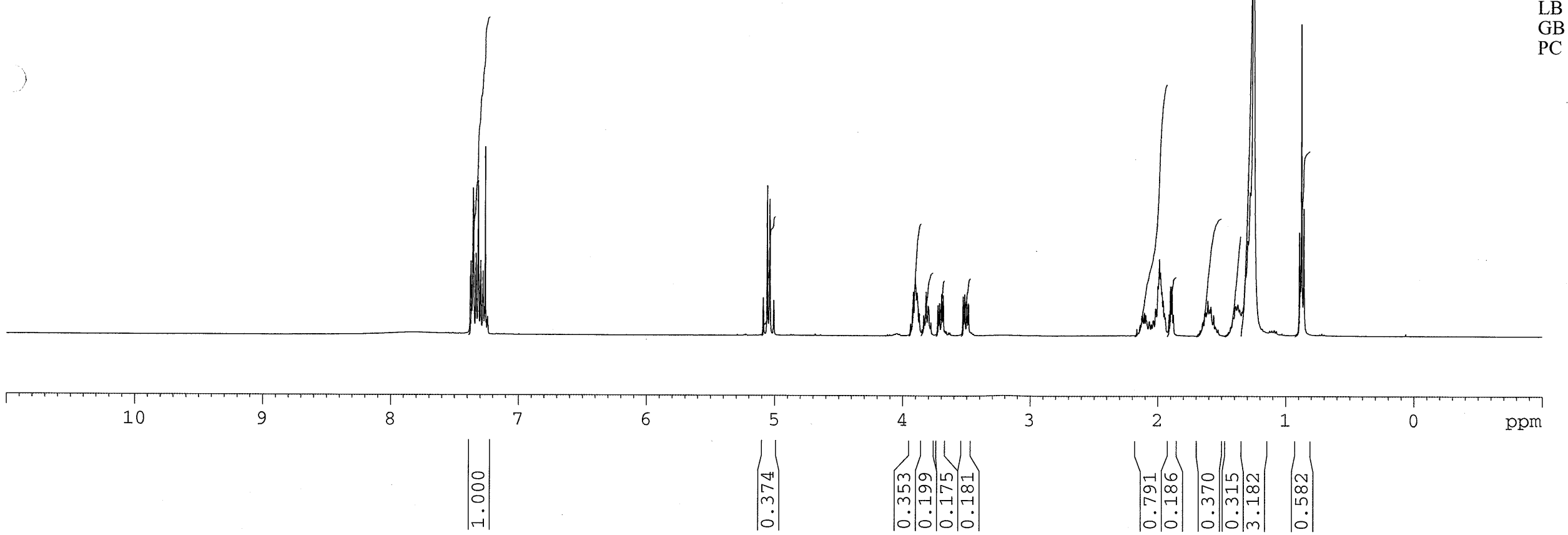
^{13}C NMR (100 MHz, $CDCl_3$)

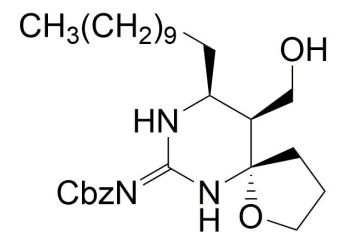
Current Data Parameters
NAME nakane-n400
EXPNO 237
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 12.37
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 114
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

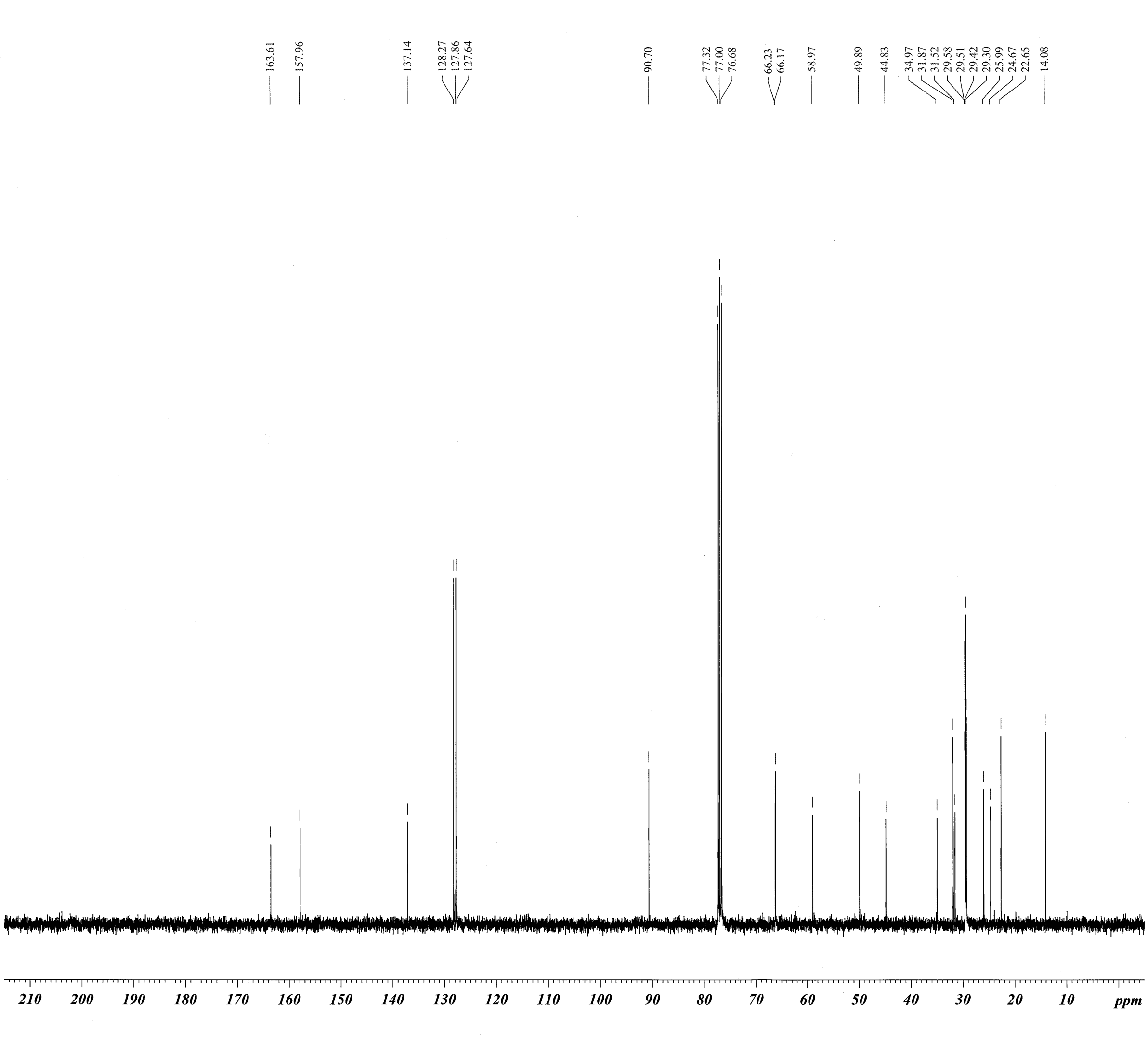
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(–)-common intermediate *ent*-**16**

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



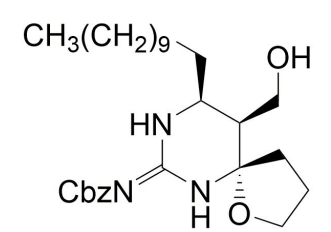
Current Data Parameters
NAME nakane-n400
EXPNO 238
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150209
Time 12.40
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 408
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127737 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(–)-common intermediate *ent*-**16**

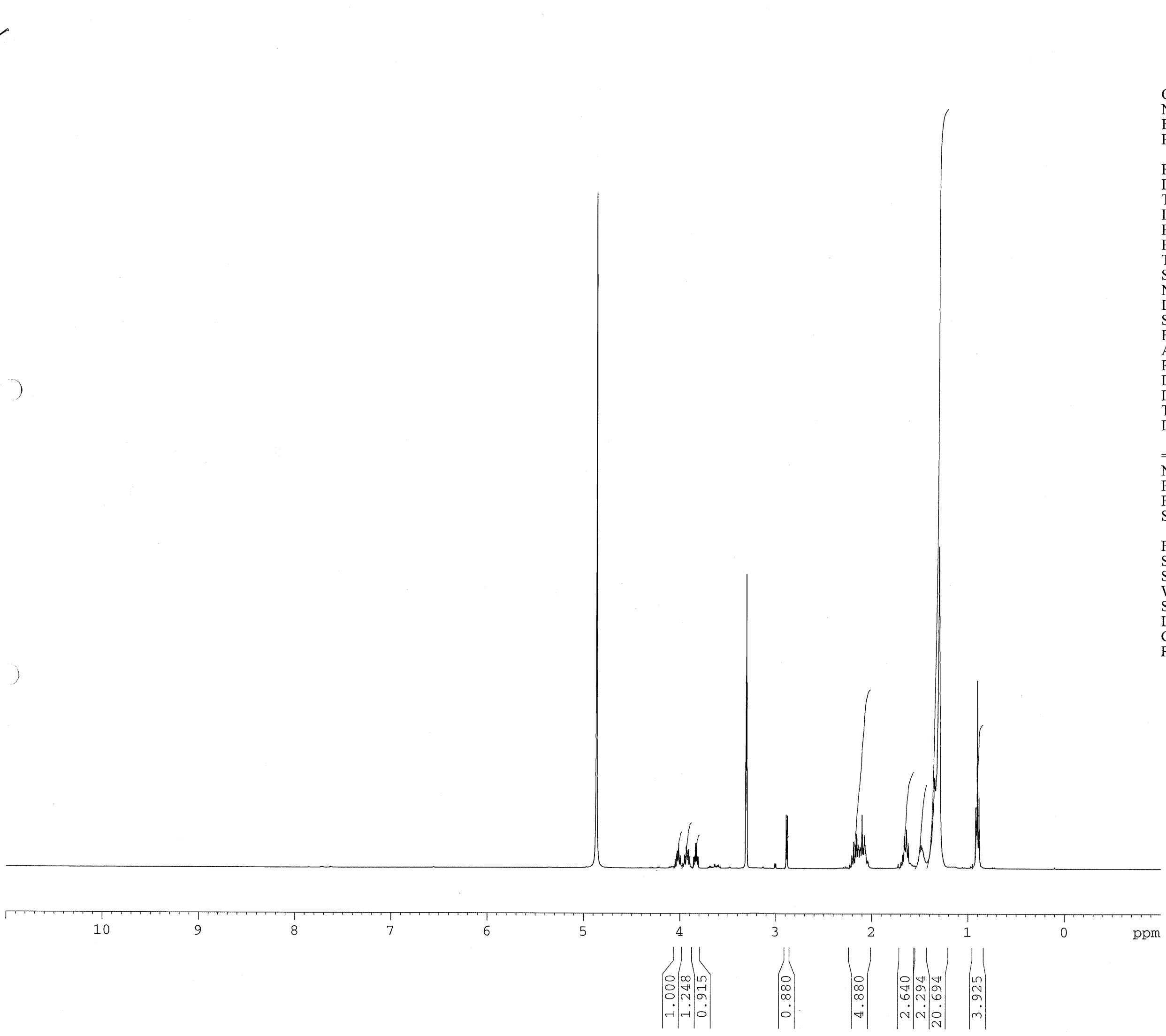
^{13}C NMR (100 MHz, $CDCl_3$)

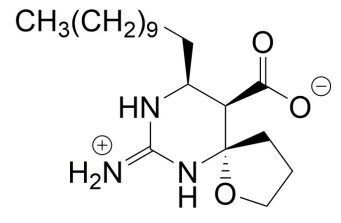
Current Data Parameters
NAME nakane-n400
EXPNO 249
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150221
Time 15.18
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CD3OD
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 228.1
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

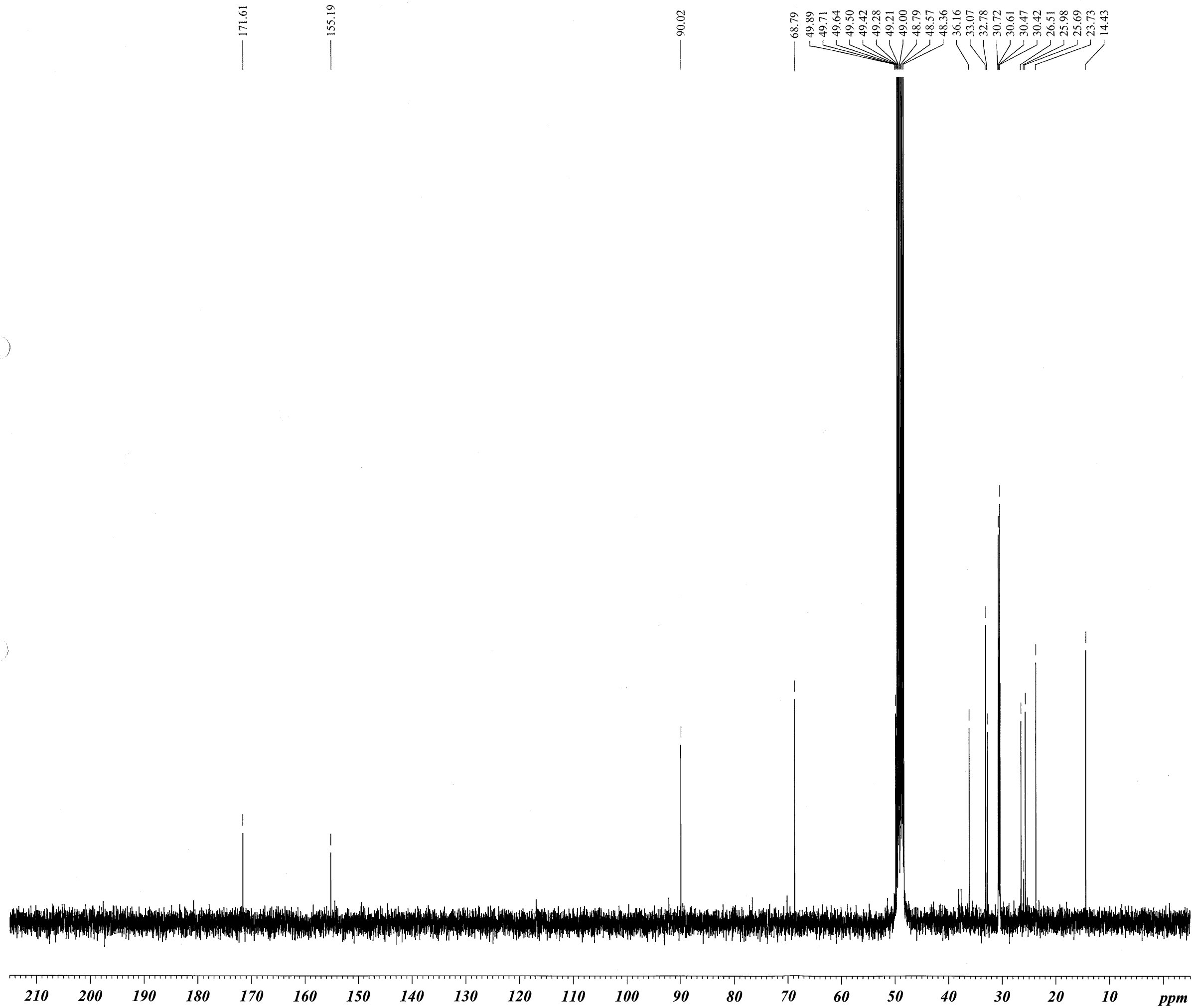
F2 - Processing parameters
SI 32768
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40





(–)-crambescin B carboxylic acid *ent*-**2**

^{1}H NMR (400 MHz, CD_3OD)



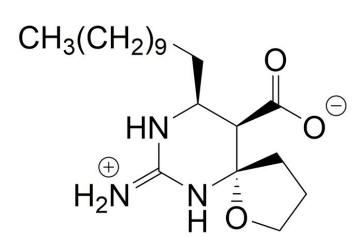
Current Data Parameters
NAME nakane-n400
EXPNO 250
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150221
Time 15.24
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2121
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

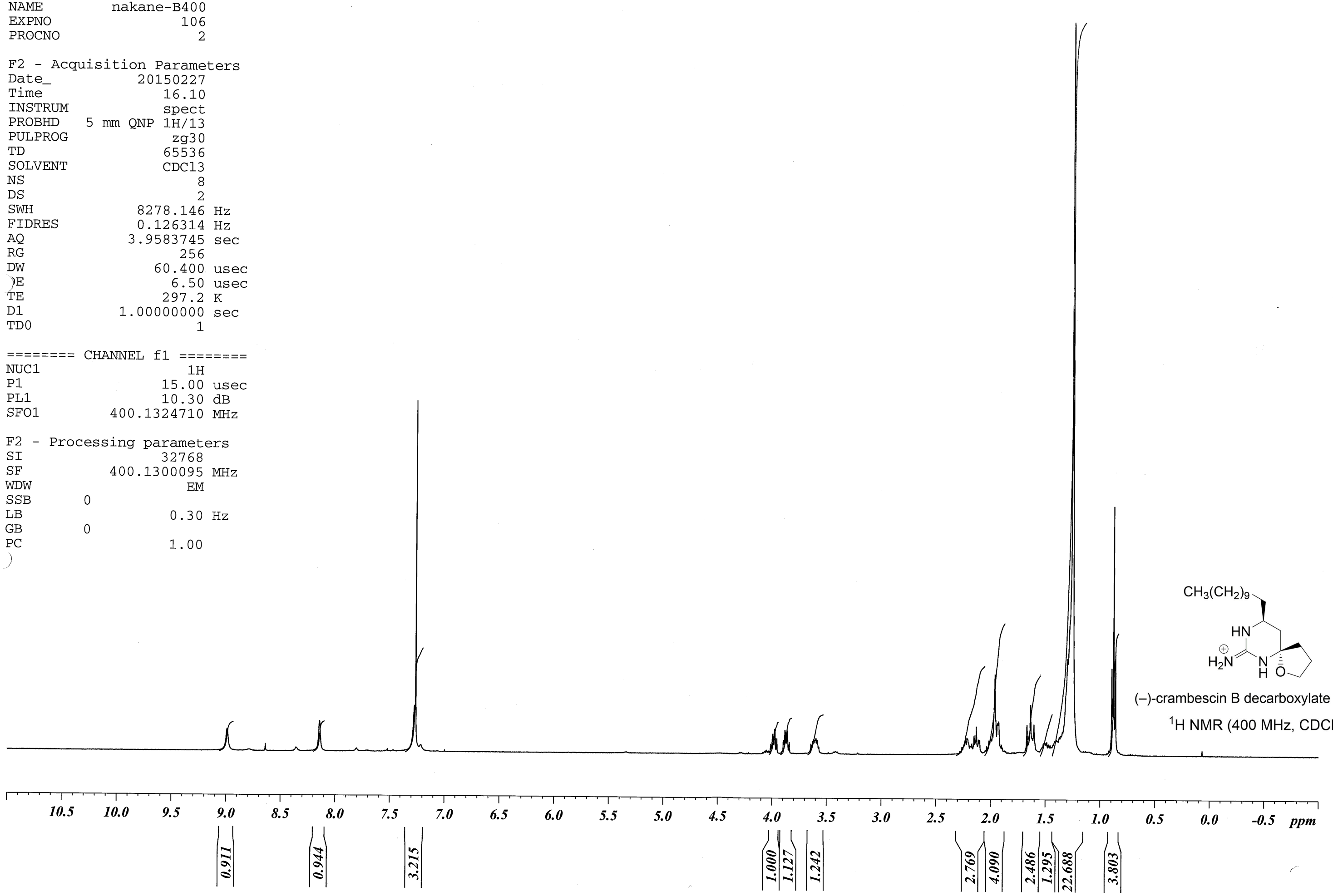
F2 - Processing parameters
SI 32768
SF 100.6126276 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(–)-crambescin B carboxylic acid *ent*-**2**

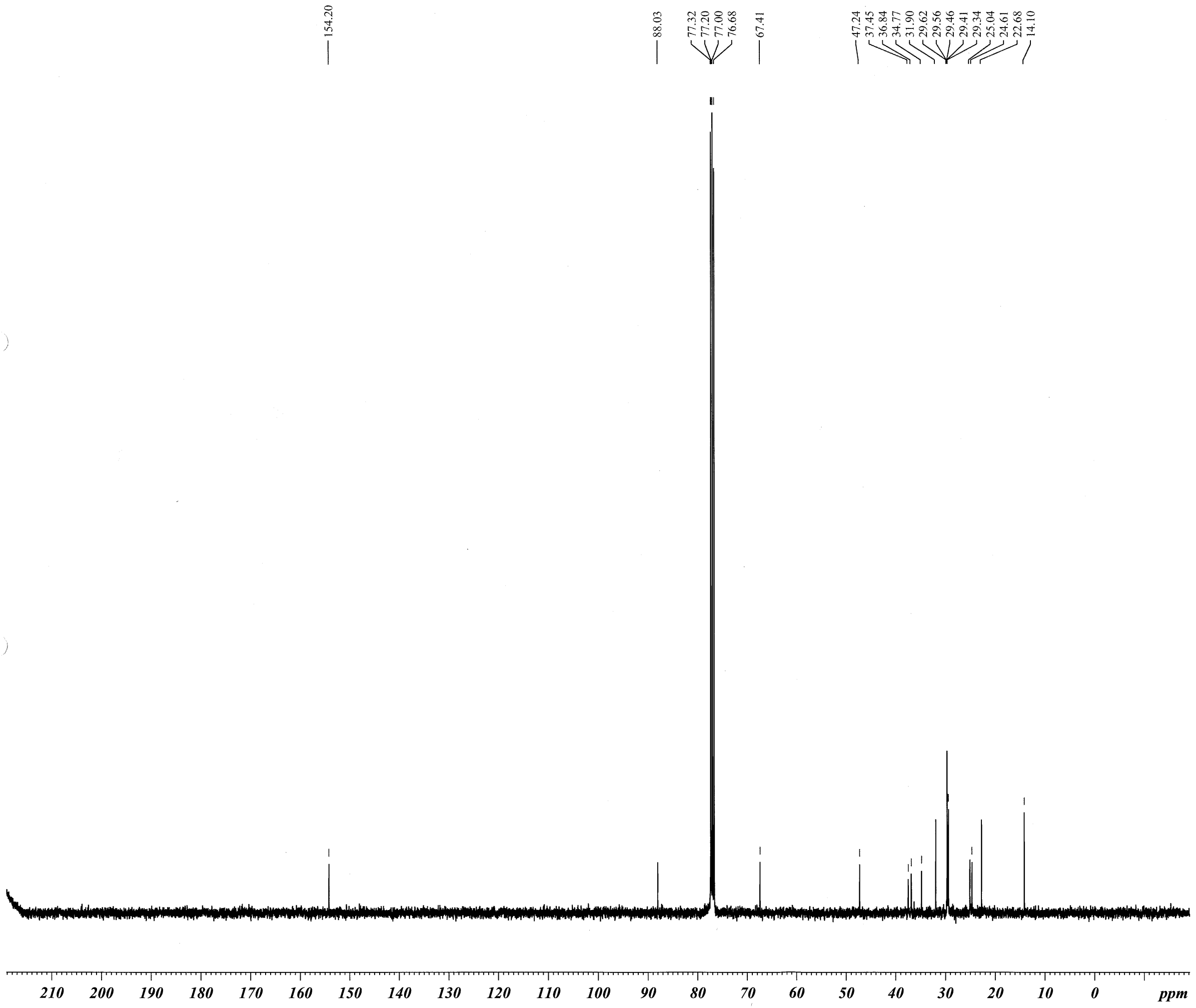
^{13}C NMR (100 MHz, CD_3OD)

```
Current Data Parameters
NAME         nakane-B400
EXPNO                106
PROCNO                 2

F2 - Acquisition Parameters
Date_           20150227
Time               16.10
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9583745 sec
RG                   256
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          400.1300095 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



(–)-crambescin B decarboxylate *ent*-**17**

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



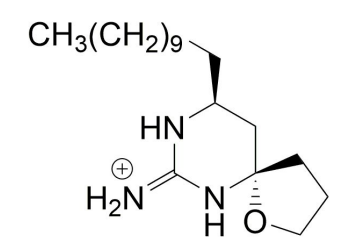
Current Data Parameters
NAME nakane-B400
EXPNO 107
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150227
Time 16.25
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1139
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 1290.2
DW 20.850 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 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 100.6127704 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(–)-crambescin B decarboxylate *ent*-**17**

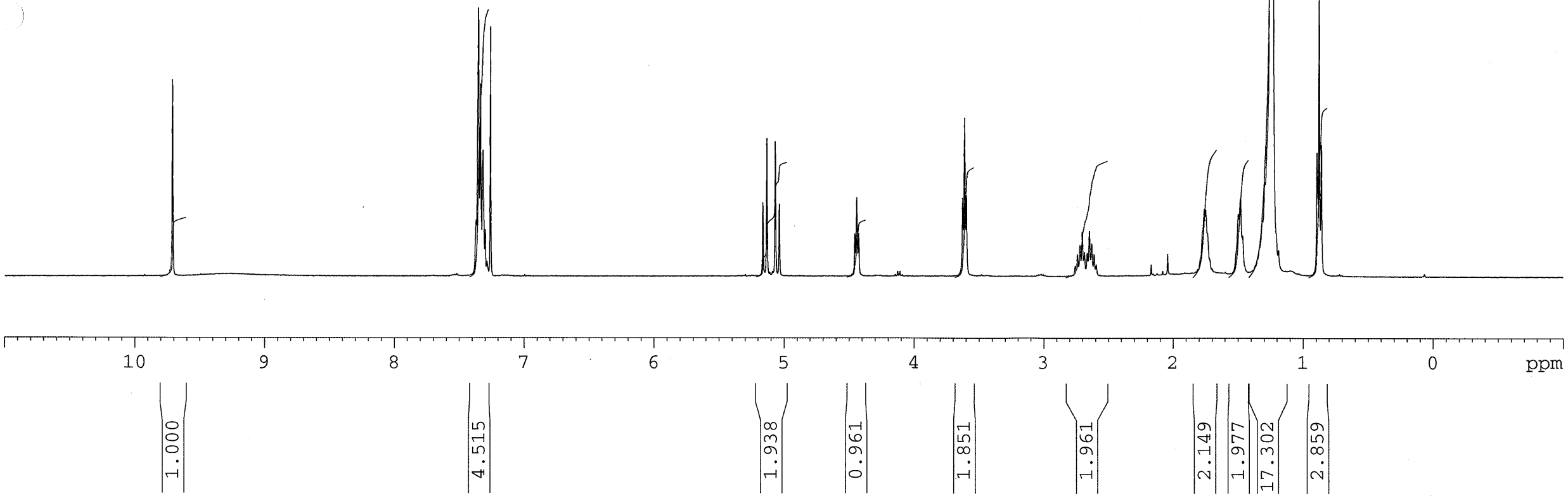
^{13}C NMR (100 MHz, $CDCl_3$)

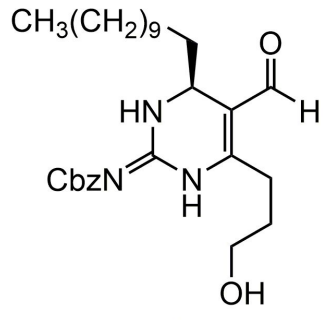
Current Data Parameters
NAME nakane-n400
EXPNO 190
PROCNO 3

F2 - Acquisition Parameters
Date_ 20150127
Time 10.24
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 =======
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

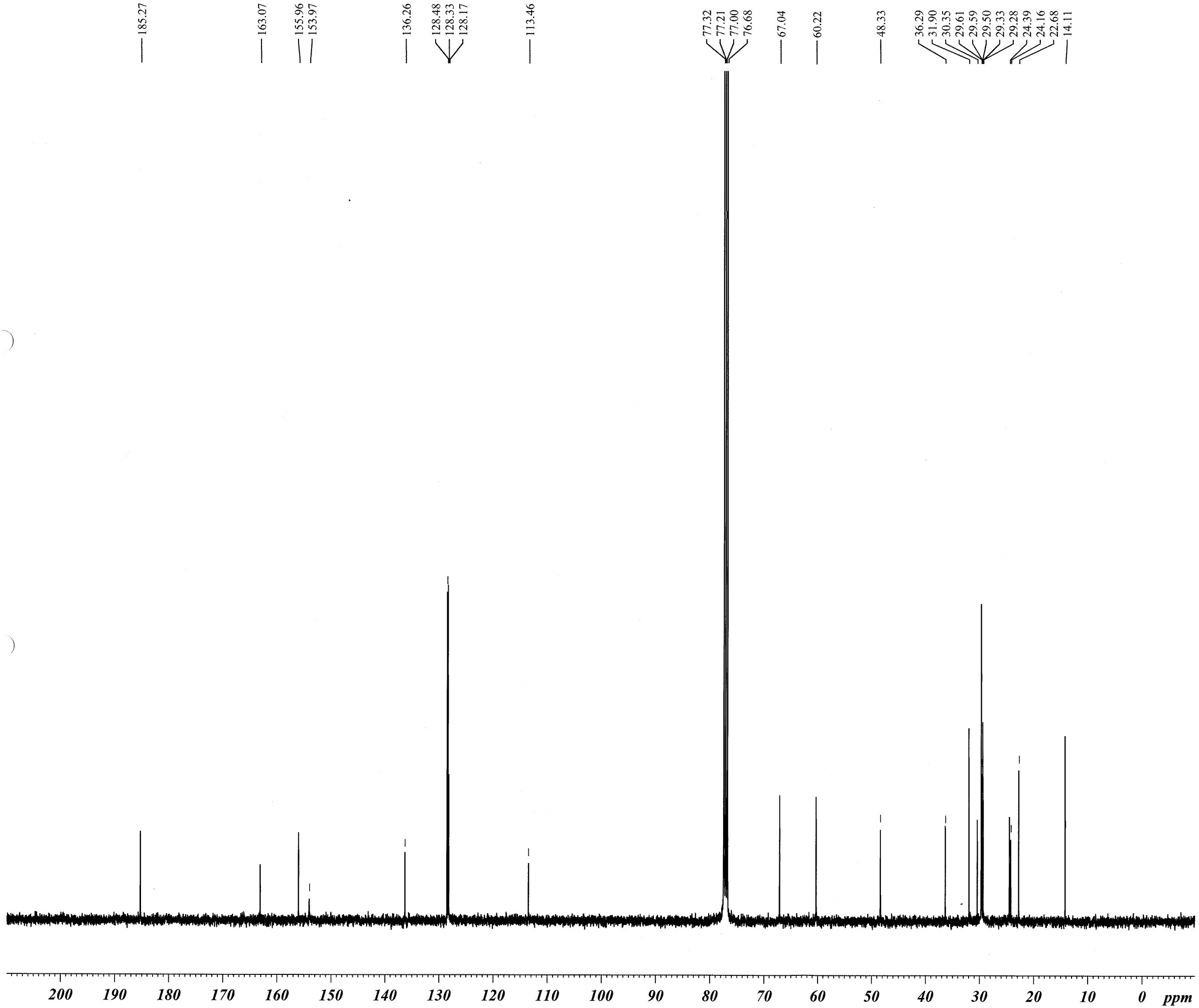
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(+)-enal *ent*-**18**

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



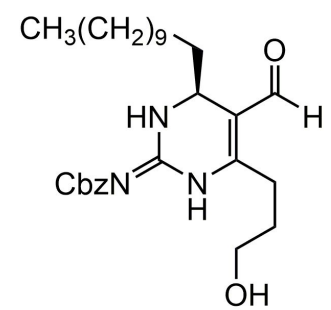
Current Data Parameters
NAME nakane-B400
EXPNO 98
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150131
Time 12.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2600
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 1024
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 1.20000005 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 100.6127711 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(+)-enal *ent*-**18**

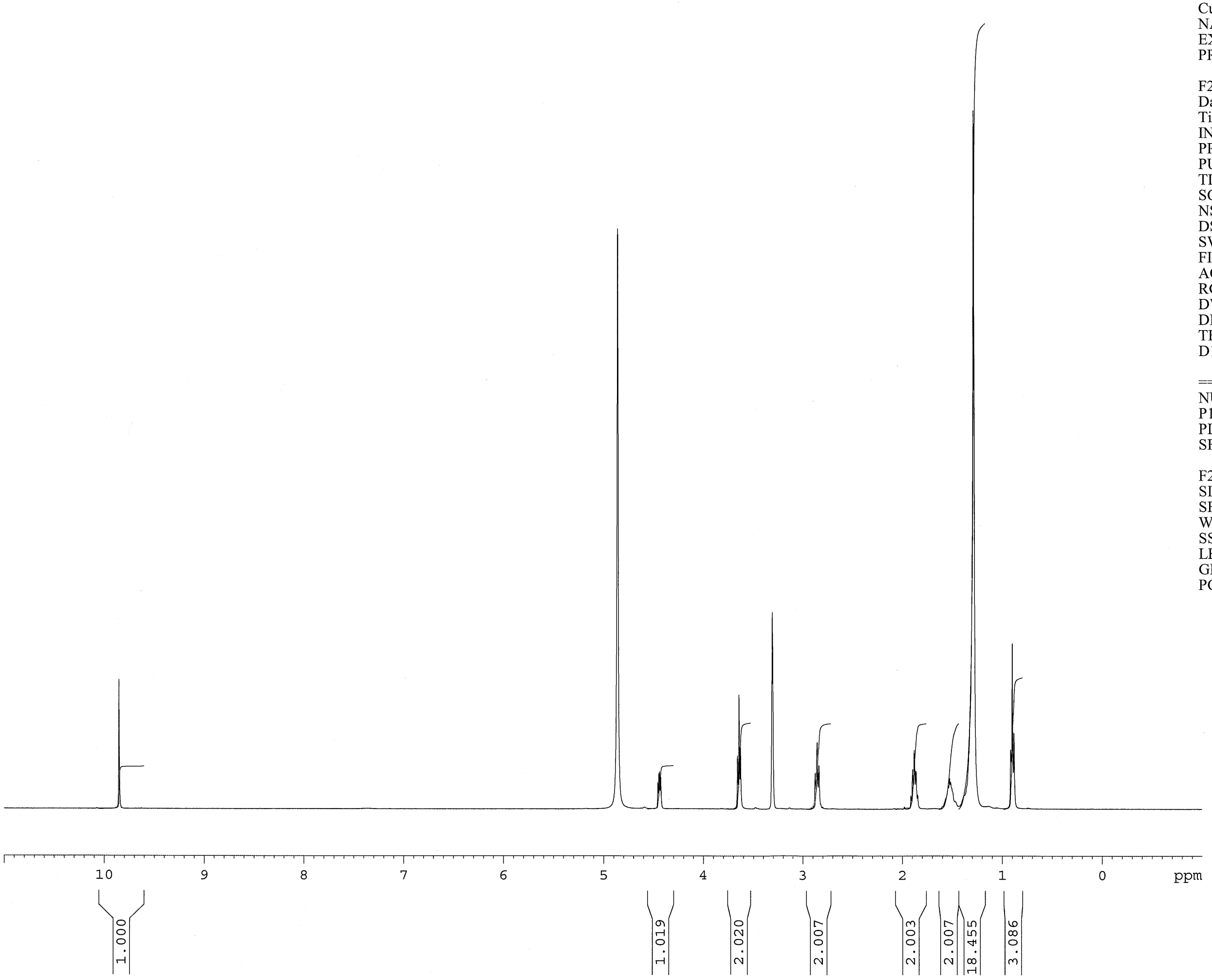
^{13}C NMR (100 MHz, $CDCl_3$)

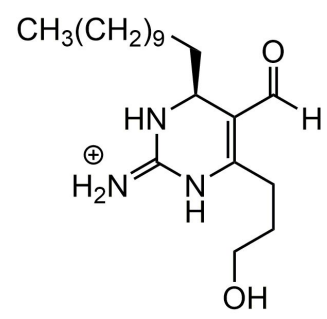
Current Data Parameters
NAME nakane-n400
EXPNO 140
PROCNO 2

F2 - Acquisition Parameters
Date_ 20141002
Time 20.40
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CD3OD
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 203.2
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

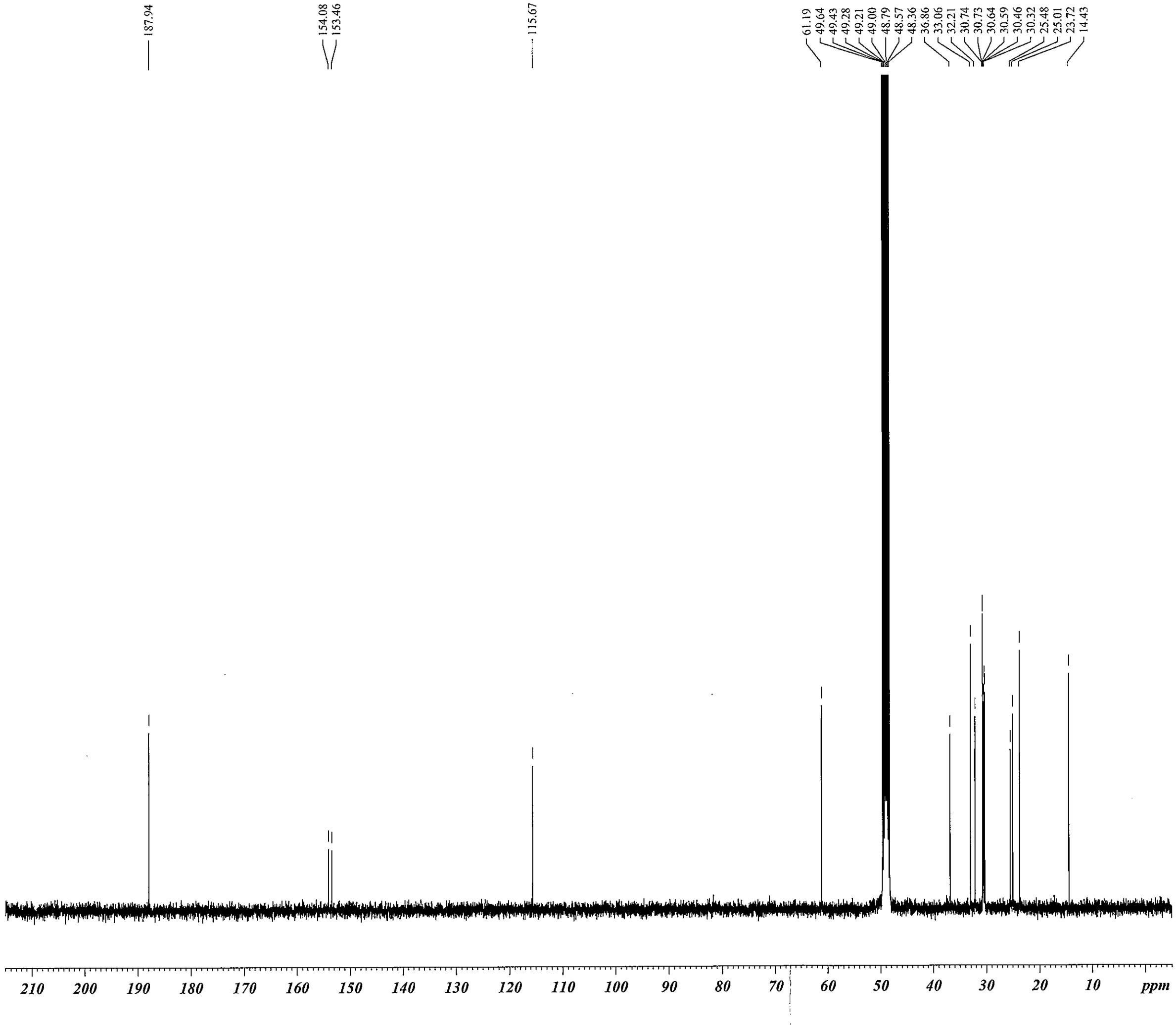
F2 - Processing parameters
SI 32768
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(–)-guanidine *ent*-**19**

^{1}H NMR (400 MHz, CD_3OD)



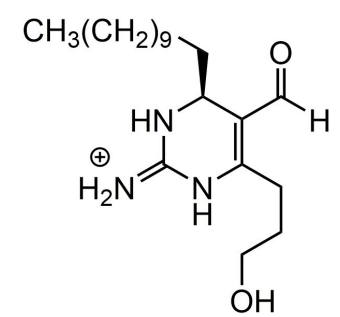
Current Data Parameters
NAME nakane-n400
EXPNO 142
PROCNO 2

F2 - Acquisition Parameters
Date_ 20141003
Time 10.22
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 3200
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

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



(–)-guanidine *ent*-**19**

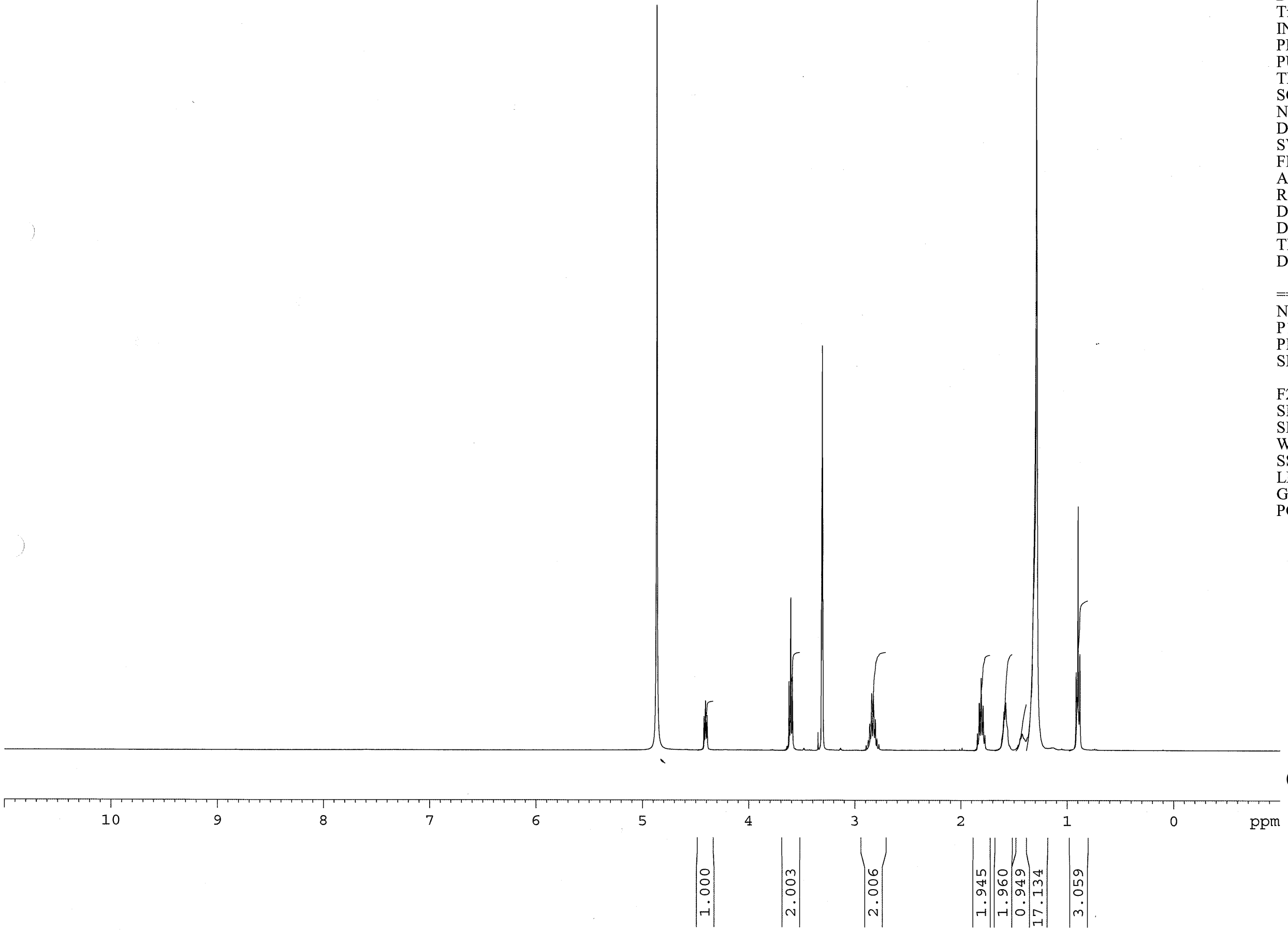
^{13}C NMR (100 MHz, CD_3OD)

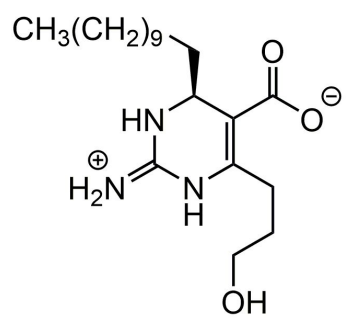
Current Data Parameters
NAME nakane-n400
EXPNO 171
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150113
Time 11.09
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CD3OD
NS 64
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 287.4
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

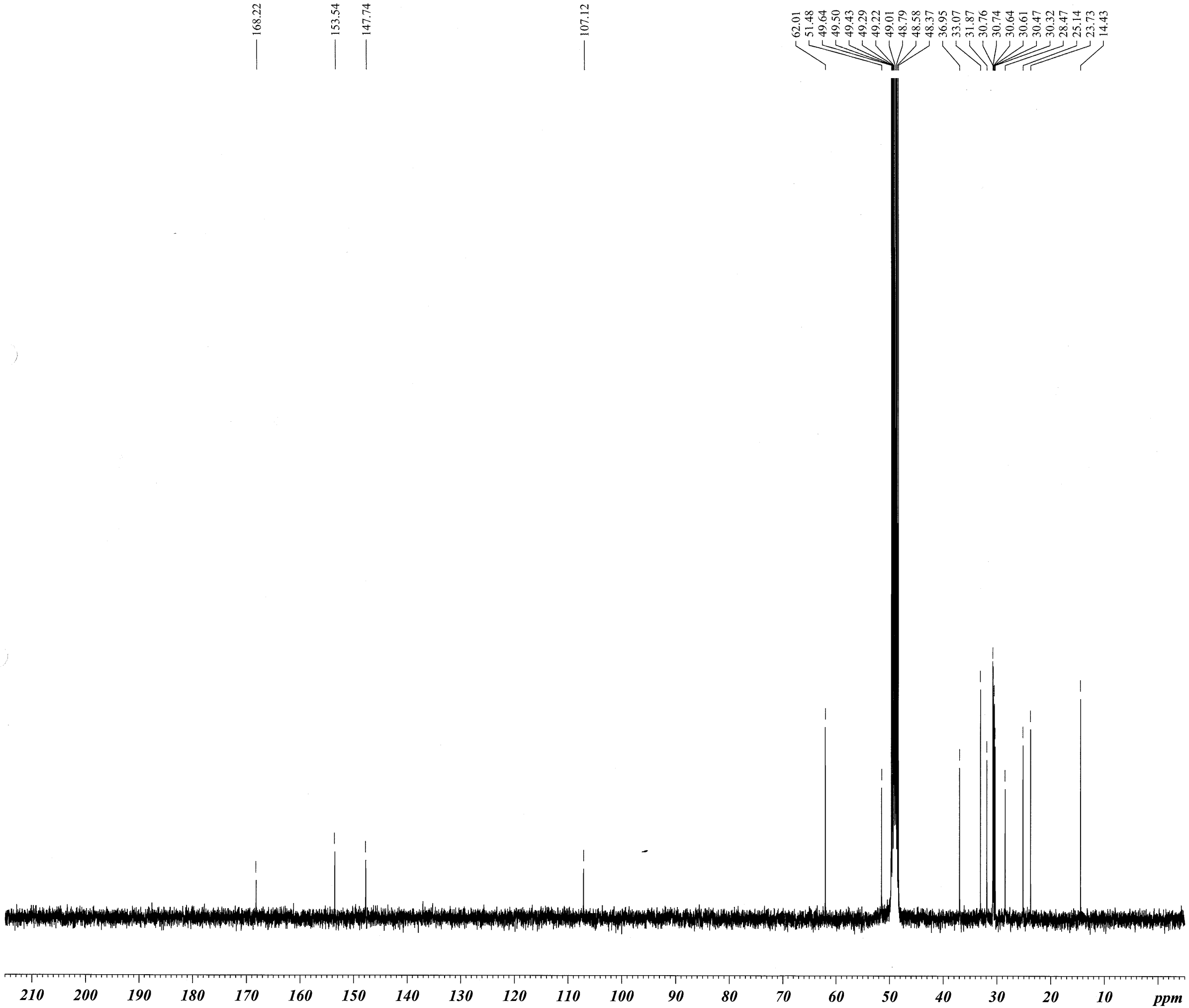
F2 - Processing parameters
SI 32768
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





(–)-crambescin C carboxylic acid *ent*-**3**

^{1}H NMR (400 MHz, CD_3OD)



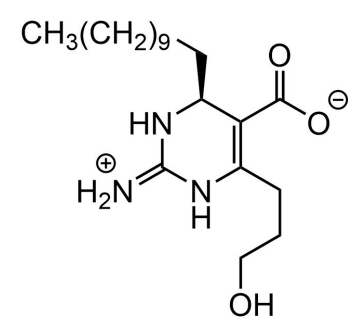
Current Data Parameters
NAME nakane-n400
EXPNO 172
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150113
Time 13.50
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 2800
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

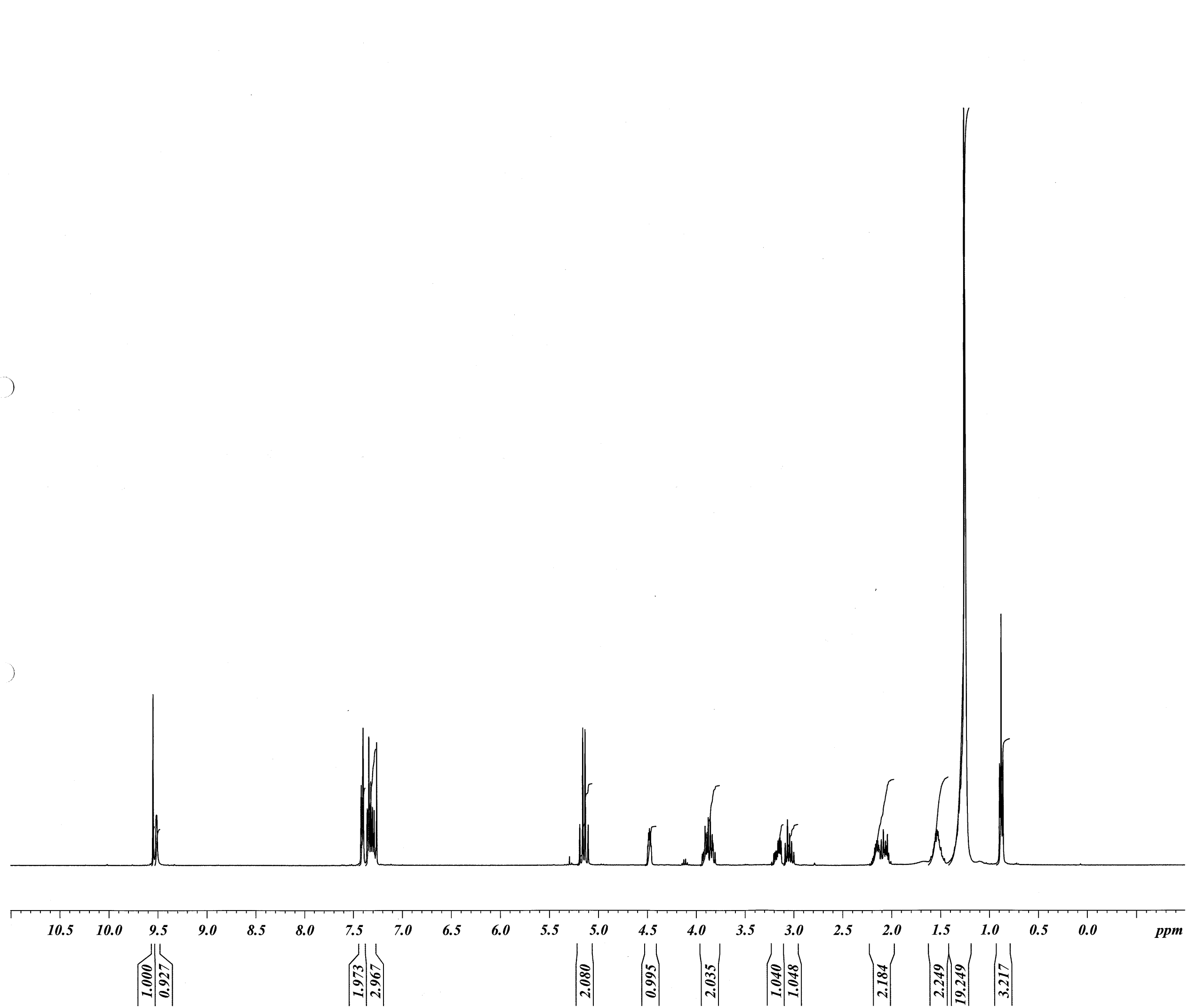
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

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



(–)-crambescin C carboxylic acid *ent*-**3**

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

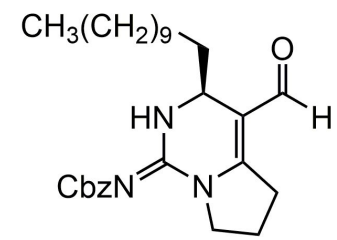


Current Data Parameters
NAME nakane-B400
EXPNO 93
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150129
Time 10.43
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 128
DW 60.400 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

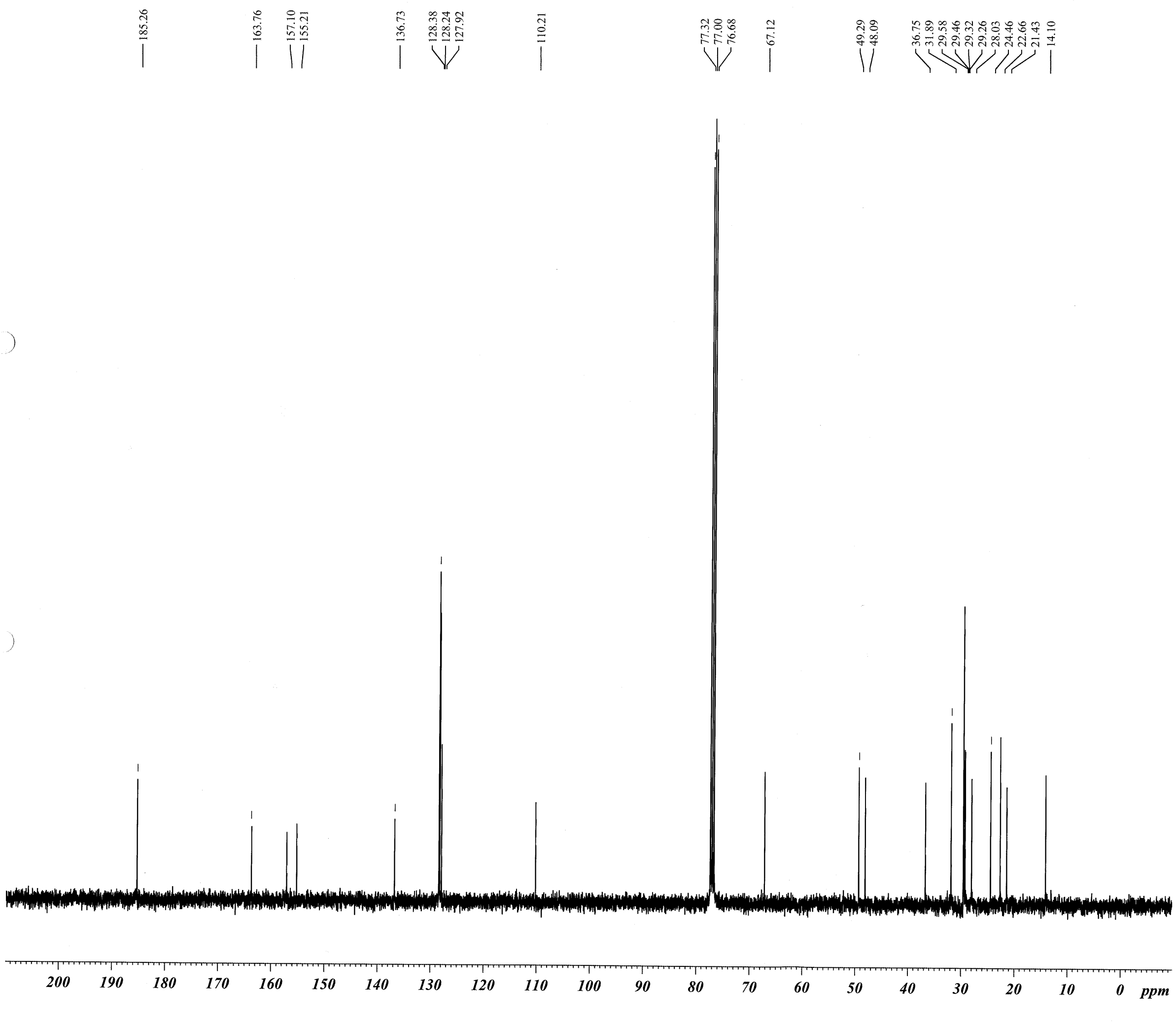
======== CHANNEL f1 ==
NUC1 1H
P1 15.00 usec
PL1 10.30 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768



(–)-pyrrolidine *ent*-**20**

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



S123

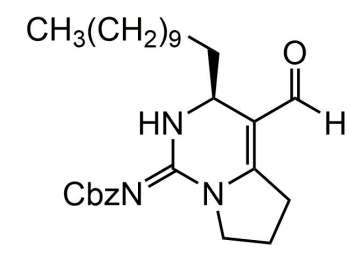
Current Data Parameters
NAME nakane-B400
EXPNO 94
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150129
Time 10.51
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 339
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2298.8
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 1.20000005 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 100.6127725 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



(–)-pyrrolidine *ent*-**20**

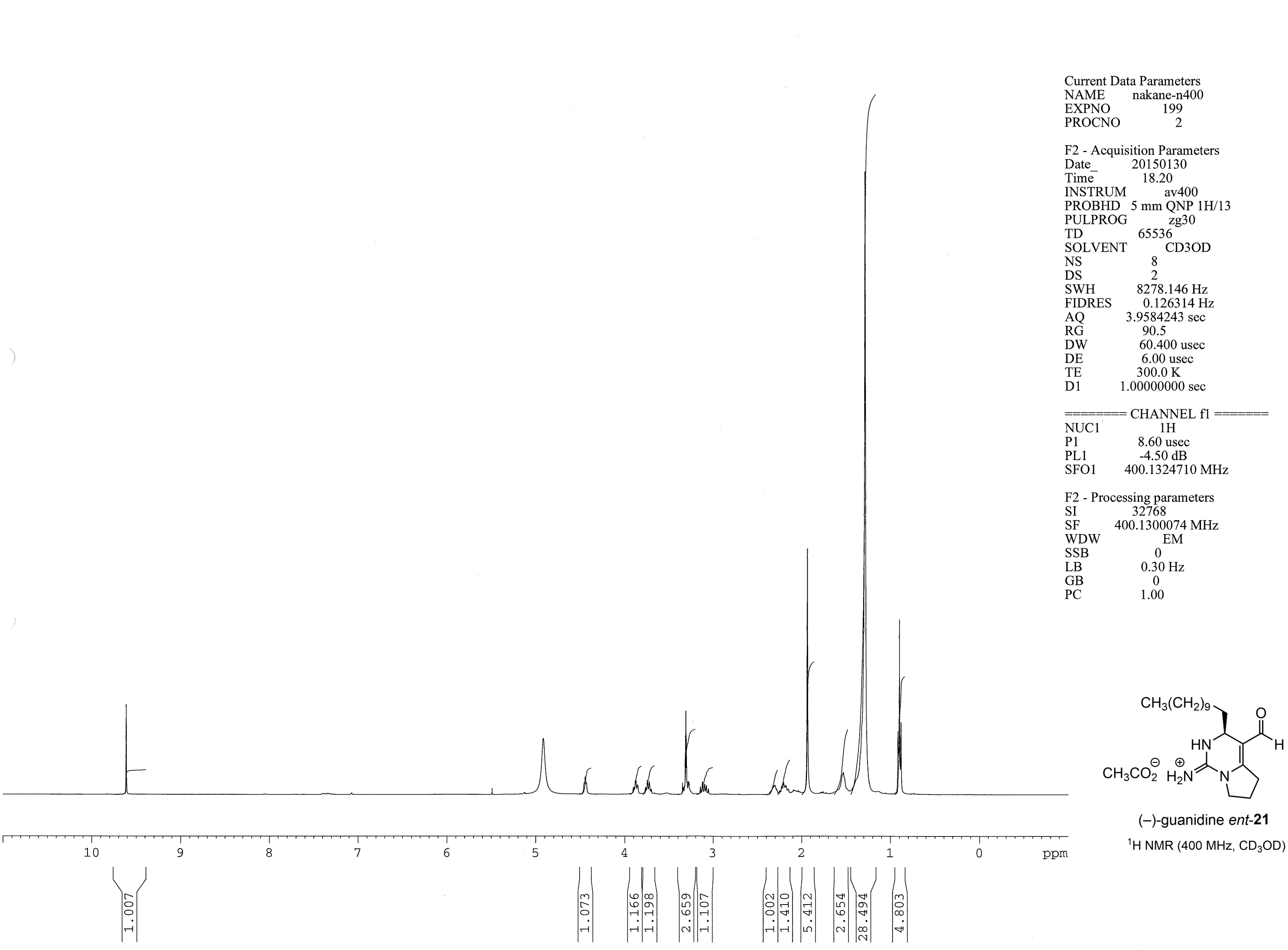
^{13}C NMR (100 MHz, $CDCl_3$)

Current Data Parameters
NAME nakane-n400
EXPNO 199
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150130
Time 18.20
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CD3OD
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 90.5
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

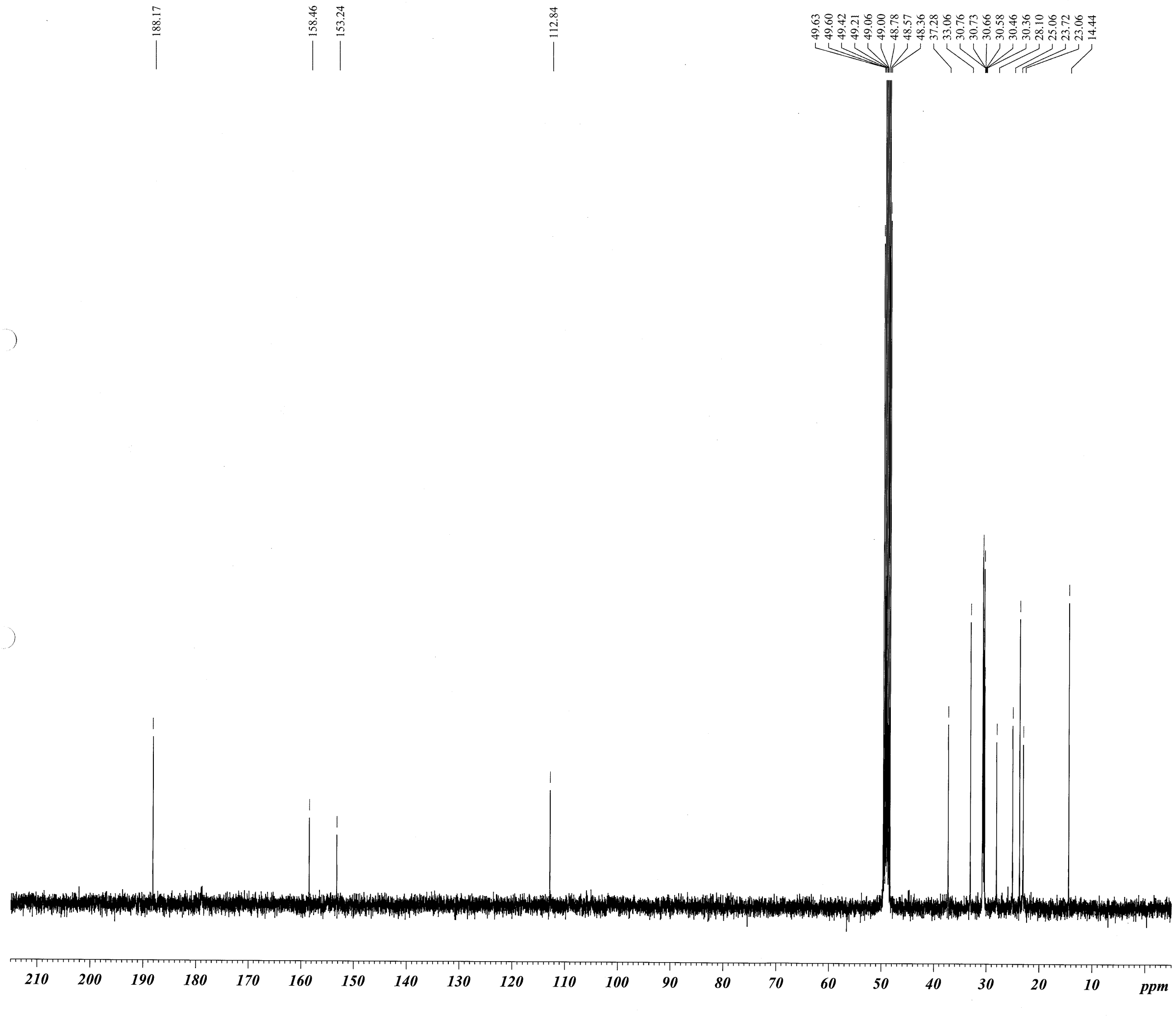
======== CHANNEL f1 ========
NUC1 1H
P1 8.60 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

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



(–)-guanidine *ent*-**21**

^{1}H NMR (400 MHz, CD_3OD)



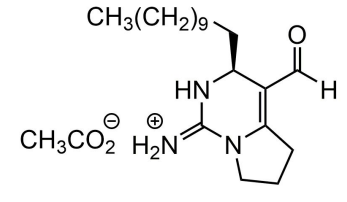
Current Data Parameters
NAME nakane-n400
EXPNO 200
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150130
Time 18.22
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 376
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.20000005 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

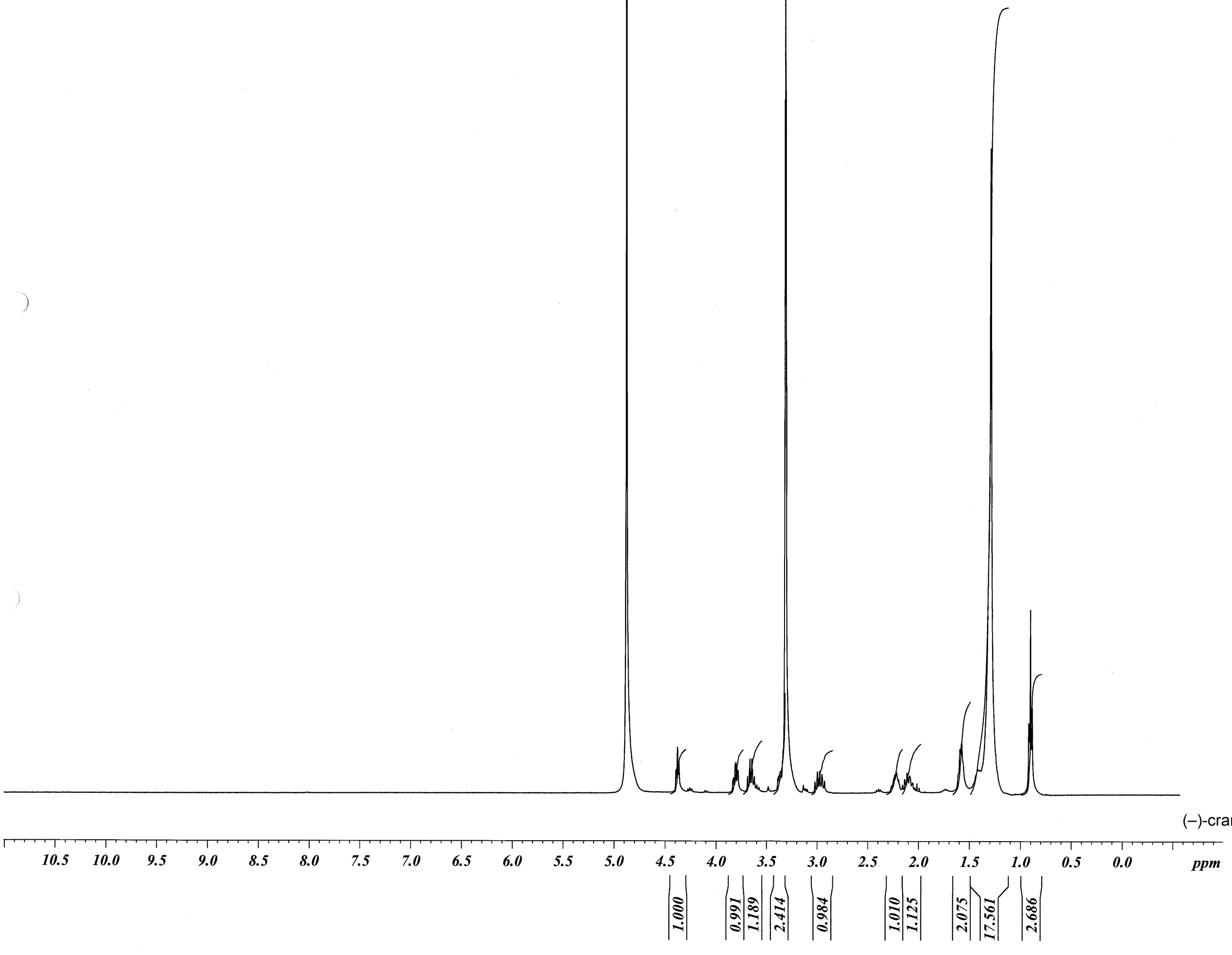
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6126298 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



(–)-guanidine *ent*-**21**

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

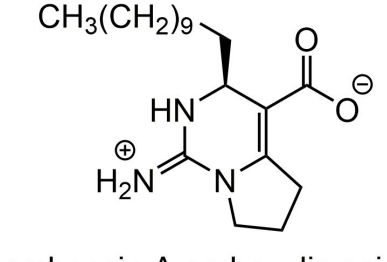


Current Data Parameters
NAME nakane-B400
EXPNO 88
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150110
Time 17.20
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 128
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 456.1
DW 60.400 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1

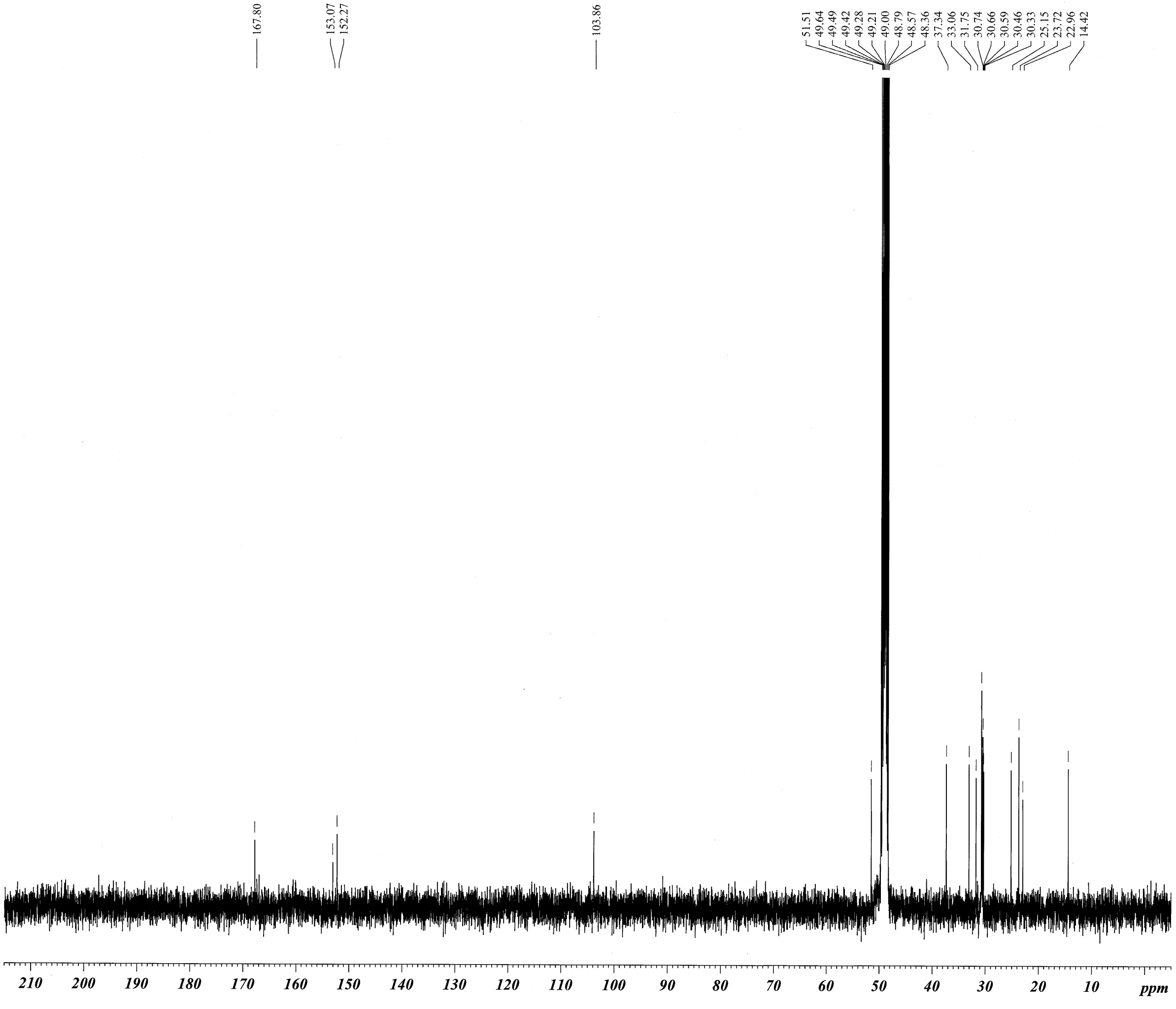
======== CHANNEL f1 ==
NUC1 1H
P1 15.00 usec
PL1 10.30 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768



(–)-crambescin A carboxylic acid *ent*-**1a**

^{1}H NMR (400 MHz, CD_3OD)



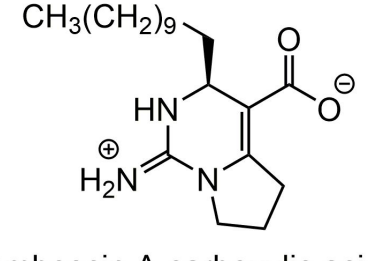
Current Data Parameters
NAME nakane-n400
EXPNO 208
PROCNO 2

F2 - Acquisition Parameters
Date_ 20150203
Time 18.00
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 4000
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 30.00 usec
TE 300.0 K
D1 1.20000005 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.50 dB
PL12 14.87 dB
PL13 14.80 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 1.00



(–)-crambescin A carboxylic acid *ent*-**1a**

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