Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

A Stereoselecitve Construction of *E*- and *Z*-Δ-Ile from E-Dehydroamino Acid Ester: the Synthesis of Phomopsin A Tripeptide Side Chain

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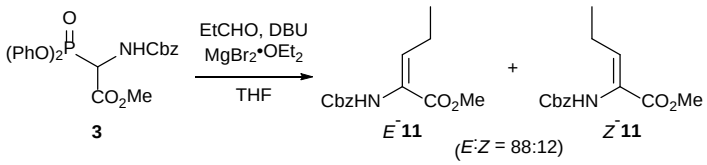
General.

All reagents and solvents were purchased from either Aldrich Chemical Company, Inc., Kanto Kagaku Co., Inc., Merck & Co., Inc., Nacalai Tesque Company, Ltd., Peptide Institute, Tokyo Kasei Kogyo Co., Ltd., or Wako Pure Chemical Industries, Ltd., and used without further purification unless otherwise indicated. Dichloromethane (CH_2Cl_2) was distilled from phosphoric pentaoxide (P_2O_5). Tetrahydrofuran (THF), chloroform ($CHCl_3$), and dimethylformamide (DMF) of anhydrous grade were used.

Optical rotations were taken on a JASCO P-1030 polarimeter with a sodium lamp (D line). Melting points were determined with a Yanaco MP-21 melting point apparatus and were uncorrected. FTIR spectra were measured on a JASCO FT/IR-6200 infrared spectrophotometer. ^{1}H NMR spectra were recorded on an either Bruker AVANCE 300 (300 MHz), JEOL JNM-LA 400 (400 MHz), or Bruker AVANCE 600 (600 MHz) spectrometer. Chemical shifts of ^{1}H NMR were reported in perts per million (ppm, δ) relative to $CHCl_3$ (δ = 7.26) in $CDCl_3$, CD_2HOD (δ = 3.31). ^{13}C NMR spectra were recorded on an either Bruker AVANCE 300 (75 MHz), JEOL JNM-LA 400 (100 MHz), or Bruker AVANCE 600 (150 MHz) spectrometer. Chemical shifts of ^{13}C NMR were reported in ppm (δ) relative to $CHCl_3$ (δ = 77.0) in $CDCl_3$. Low resolution mass spectra (LRMS) and high resolution mass spectra (HRMS) were obtained on an JEOL JMS-AX500 for fast atom bombardment ionization (FAB), chemical ionization (CI), or electron ionization (EI). All reactions were monitored by thin layer chromatography (TLC), which was performed with precoated plates (silica gel 60 F-254, 0.25 mm thickness, manufactured by Merck). TLC visualization was accompanied using UV lamp (254 nm) or a charring solution (ethanoic phosphomolybdic acid, aqueous potassium permanganate and butanoic ninhydrin). Daisogel IR-60 1002W (40/63 μm) was used for flash column chromatography on silica gel.

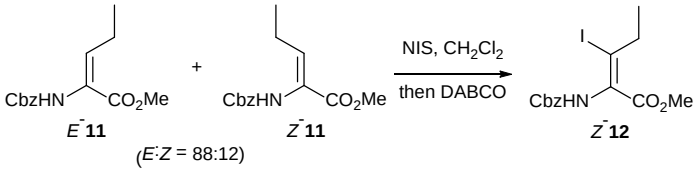
Compounds **7**, **9**, and **23** were obtained as an inseparable mixture. Amide rotamers are observed in compounds **7**~**9** and **18**~**23** under the NMR analysis conditions. These NMR signals are broaden and complicated. Therefore, NMR data assignments are not given for these compounds. Instead, actual spectra are provided.

Methyl 2-(((benzyloxy)carbonyl)amino)pent-2-enoate (11)



To a solution of **3**[1] (502 mg, 1.10 mmol) and $MgBr_2 \cdot OEt_2$ (258 mg, 1.00 mmol) in THF (10 mL) was added DBU (150 μL, 1.00 mmol) at 0 ℃ under argon. The mixture was stirred for 30 min at 0 ℃, then propionaldehyde (76 μL, 1.00 mmol, 95% purity) was added to the mixture. The mixture was stirred for 12 h at room temperature, quenched with sat. NH_4Cl (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine (30 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20 : 1 to 7 : 1) to give a *E*/*Z* mixture of **11** (229 mg, 87%, *E* : *Z* = 88 : 12) as a colorless oil. The *E*/*Z* ratio was determined by comparison of the chemical shift values of the olefinic (*E*: 6.79 ppm, *Z*: 6.63 ppm) and N-H (*E*: 6.79 ppm, *Z*: 6.15 ppm) protons.[2] NMR data of *E*/*Z* -**11** were identical to those of the reported data.[3]

(*Z*)-Methyl 2-(((benzyloxy)carbonyl)amino)-3-iodopent-2-enoate (*Z*-12)



To a solution of **11** (229 mg, 870 μmol, *E* : *Z* = 88 : 12) in CH_2Cl_2 (8.7 mL) was added NIS (234 mg, 1.04 mmol) at 0 ℃ under argon. The mixture was stirred at room temperature for 2 h. DABCO (195 mg, 1.74 mmol) was added to the mixture at 0 ℃. The mixture was stirred for 16 h at room temperature and quenched with 1*N* $NaHSO_4$ (10 mL). The organic layer was separated. The aqueous layer was extracted with EtOAc (10 mL × 2). The combined organic layers were washed with sat. Na_2SO_3 (30 mL) and brine (30 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 15 : 1) to give *Z*-**12** (292 mg, 86%).

White solid;

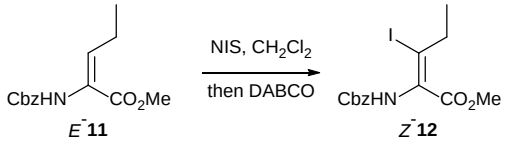
mp 75–77 ℃;

FTIR (neat) 3318, 2973, 2952, 1726, 1622, 1481, 1304, 1267, 1220, 1039 cm^{-1};

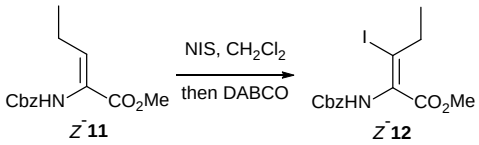
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5 H), 6.41 (brs, 1 H), 5.14 (s, 2 H), 3.82 (brs, 3 H), 2.76 (brq, *J* = 7.3 Hz, 2 H), 1.13 (t, *J* = 7.3 Hz, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 153.2, 135.4, 130.6, 128.5, 128.3, 128.2, 109.3, 67.7, 52.5, 33.8, 14.8;

HRMS (FAB) calcd for $C_{14}H_{17}INO_4$ *m*/*z* 390.0202 $[M+H]^+$, found 390.0201.

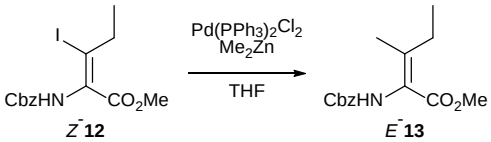


According to the same procedure, *E*-**11** (156 mg, 593 μmol) purified from the 88:12 *E*/*Z*-mixture of **11** by repeating silicagel column chromatography was subjected to the iodination reaction to give *Z*-**12** (191 mg, 83%). Spectroscopic data of the resulting *Z*-**12** was identical with those of *Z*-**12** described above.



According to the same procedure, *Z*-**11** (157 mg, 596 μmol) purified from the 88:12 mixture of *E*/*Z*-**11** by repeating silicagel column chromatography was subjected to the iodination reaction to give *Z*-**12** (172 mg, 74%). Spectroscopic data of the resulting *Z*-**12** was identical with those of *Z*-**12** described above.

(*E*)-Methyl 2-(((benzyloxy)carbonyl)amino)-3-methylpent-2-enoate (*E*-13)



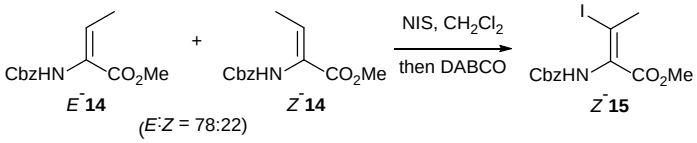
To a solution of *Z*-**12** (20.0 mg, 51.4 μmol) and $Pd(PPh_3)_2Cl_2$ (1.8 mg, 2.6 μmol) in THF (0.5 mL) was added Me_2Zn (100 μL, 102 μmol, 1.02 M solution in hexane) at 0 ℃ under argon. The mixture was stirred for 13 h at room temperature, quenched with sat. NH_4Cl (5 mL), and extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine (15 mL), dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 12 : 1 to 3 : 1) to give *E*-**13** (13.2 mg, 93%) as a 7 : 2 mixture of rotamers. Stereochemistry of *E*-**13** was determined by NOESY analysis shown in P13. ^{13}C NMR of *E*-**13** was identical with that of the reported data.[4]

White solid;

^1H NMR (600 MHz, $CDCl_3$) δ 7.37–7.33 (m, 5 H), 5.95 (brs, 7/9H), 5.64 (brs, 2/9H), 5.14 (s, 2 H), 3.74 (brs, 21/9H), 3.53 (brs, 6/9H), 2.52 (q, *J* = 7.2 Hz, 2 H), 1.86 (s, 3 H), 1.10 (brt, *J* = 7.2 Hz, 3 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 154.4, 149.7, 136.0, 128.1, 127.74, 127.68, 120.7, 66.6, 51.3, 27.2, 19.0, 12.3.

(*Z*)-Methyl 2-(((benzyloxy)carbonyl)amino)-3-iodobut-2-enoate (*Z*-15)



E-**14** (*E*:*Z* = 78:22) *Z*-**14** *Z*-**15**

According to the literature,[2] **14** (*E* : *Z* = 78 : 22) was prepared by condensation of **3** and acetaldehyde. To a solution of **14**[2] (10.0 mg, 40.1 μmol, *E* : *Z* = 78 : 22) in CH_2Cl_2 (2.0 mL) was added NIS (10.8 mg, 48.0 μmol) at 0 ℃ under argon. The mixture was stirred at room temperature for 2 h. DABCO (8.97 mg, 80.0 μmol) was added to the mixture at 0 ℃. The mixture was stirred for 7 h at room temperature. The reaction was quenched with 1*N* $NaHSO_4$ (5 mL) and extracted with EtOAc (5 mL × 3). The combined organic layers were washed with sat. Na_2SO_3 (15 mL) and brine (15 mL), dried over anhydrous $MgSO_4$, and filtered. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 15 : 1 to 3 : 1) to give *Z*-**15** (9.5 mg, 63%).

White solid;

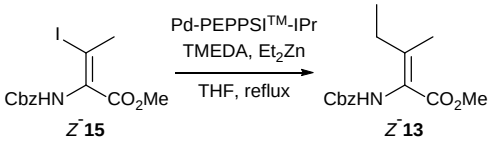
FTIR (neat) 3324, 2952, 1724, 1626, 1483, 1305, 1229, 1049 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 5 H), 6.35 (brs, 1 H), 5.14 (s, 2 H), 3.81 (brs, 3 H), 2.76 (s, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 153.4, 135.5, 131.2, 128.6, 128.4, 128.3, 101.1, 67.8, 52.6, 29.1;

HRMS (EI) calcd for $C_{13}H_{14}INO_4$ *m*/*z* 374.9968 $[M^{\cdot}]^+$, found 374.9977.

(*Z*)-Methyl 2-(((benzyloxy)carbonyl)amino)-3-methylpent-2-enoate (*Z*-13)



Z-**15** *Z*-**13**

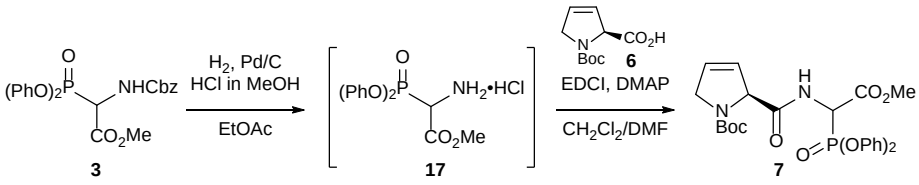
To a solution of *Z*-**15** (28.9 mg, 77.0 μmol), Pd-PEPPSI™-IPr (2.7 mg, 3.85 μmol, 98% purity) and TMEDA (46 μL, 308 μmol) in THF (770 μL) was added Et_2Zn (154 μL, 154 μmol, 1.0 M solution in hexane) at 0 ℃ under argon. The mixture was stirred for 20 min at reflux, quenched with sat. NH_4Cl (5 mL), and extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine (15 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10 : 1 to 6 : 1) to give *Z*-**13** (20.8 mg, 98%) as a 3 : 1 mixture of rotamers. Stereochemistry of *Z*-**13** was determined by NOESY analysis shown in P14. ^{13}C NMR of *Z*-**13** was identical with that of the reported data.[4]

White solid;

^1H NMR (600 MHz, $CDCl_3$) δ 7.37–7.33 (m, 5 H), 5.88 (brs, 3/4H), 5.65 (brs, 1/4H), 5.14 (s, 2 H), 3.74 (brs, 9/4H), 3.51 (brs, 3/4 H), 2.24 (q, *J* = 7.6 Hz, 2 H), 2.12 (s, 3 H), 1.04 (brt, *J* = 7.6 Hz, 3 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 154.9, 150.6, 136.2, 128.1, 127.7, 120.5, 66.7, 51.4, 28.1, 18.2, 11.2.

(2*S*)-*tert*-Butyl 2-((1-(diphenoxyphosphoryl)-2-methoxy-2-oxoethyl)carbamoyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (7)



To a solution of **3**[1] (1.00 g, 2.20 mmol) in EtOAc (20 mL) was added methanolic HCl prepared from methanol (7.3 mL) and AcCl (1.2 mL, 16.5 mmol) at 0 ℃. 10% Pd/C (100 mg, 10 wt%) was then added to the mixture. The mixture was stirred under hydrogen for 3.5 h at room temperature and filtrated through a thin Celite® pad. The filtrate was concentrated under reduced pressure to give crude ammonium salt **17** which was subjected to the next acylation without further purification. **6**[5] (422 mg, 1.98 mmol), DMAP (134 mg, 1.10 mmol), and EDCI (464 mg, 2.42 mmol) were added to a solution of the crude **17** in CH_2Cl_2/DMF (2 : 1, 21 mL) at 0 ℃ under argon. The mixture was stirred for 13 h at room temperature, quenched with sat. NH_4Cl (25 mL), and extracted with EtOAc (25 mL × 3). The combined organic layers were washed with brine (75 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1 to 1 : 1) to give **7** (618 mg, 55% over 2 steps) as a 1 : 1 inseparable mixture of diastereomers.

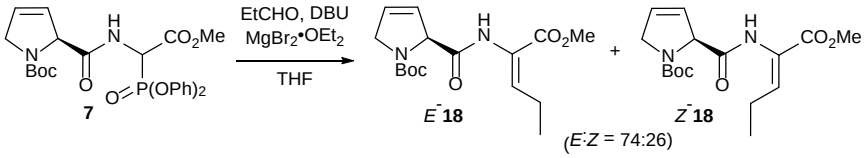
Colorless amorphous solid;

FTIR (neat) 3278, 3064, 2978, 2931, 2869, 1750, 1696, 1590, 1524, 1149, 1456, 1436, 1401, 1366, 1311, 1281, 1205, 1181, 1162, 1119, 1025, 1009 cm^{-1};

HRMS (FAB) calcd for $C_{25}H_{30}N_2O_8P$ *m*/*z* 517.1740 $[M+H]^+$, found 517.1746.

^1H and ^{13}C NMR spectra: see P15~16.

(*S*,*E*)-*tert*-Butyl 2-((1-methoxy-1-oxopent-2-en-2-yl)carbamoyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (*E*-18) and (*S*,*Z*)-*tert*-Butyl 2-((1-methoxy-1-oxopent-2-en-2-yl)carbamoyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (*Z*-18)



To a solution of **7** (618 mg, 1.20 mmol) and $MgBr_2 \cdot OEt_2$ (340 mg, 1.32 mmol) in THF (13 mL) was added DBU (181 μL, 1.32 mmol) at 0 ℃ under argon. The mixture was stirred for 30 min at 0 ℃. Propionaldehyde (100 μL, 1.32 mmol, 95% purity) was added to the mixture. The mixture was stirred for 13 h at room temperature, quenched with sat. NH_4Cl (20 mL), and extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine (45 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography

on silica gel (hexane/EtOAc = 7 : 1 to 1 : 1) to give **18** (354 mg, 91%, *E* : *Z* = 74 : 26). The *E*/*Z* ratio was determined by comparison of the chemical shift values of olefinic proton (*E*: 7.12 ppm, *Z*: 6.68 ppm).[2] *E*- and *Z*-**18** was partly separated by flash column chromatography on silica gel repeatedly (hexane/EtOAc = 7 : 1 to 1 : 1);

E-**18**:

Colorless sticky oil, as a 4 : 3 mixture of rotamers;

$[\alpha]_D^{20}$ = –111.7 (*c* 2.36, $CHCl_3$);

FTIR (neat) 3351, 2976, 2034, 2873, 1681, 1521, 1436, 1392, 1366, 1317, 1245, 1220, 1164, 1125 cm^{-1};

^1H NMR spectrum: see P17.

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 164.2, 154.7, 153.8, 134.7, 127.6, 126.1, 123.7, 80.7, 69.4, 68.4, 53.7, 52.0, 28.0, 21.5, 13.8;

HRMS (FAB) calcd for $C_{16}H_{25}N_2O_5$ *m*/*z* 325.1763 $[M+H]^+$, found 325.1752.

Z-**18**:

White solid, as a 2 : 1 mixture of rotamers;

mp 44–45 ℃;

$[\alpha]_D^{21}$ = –205.2 (*c* 1.03, $CHCl_3$);

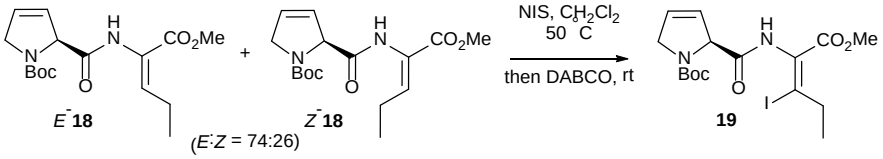
FTIR (neat) 3279, 2974, 2935, 2874, 1682, 1504, 1437, 1394, 1366, 1312, 1275, 1249, 1173, 1126, 1085 cm^{-1};

^1H NMR spectrum: see P19.

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 164.6, 154.9, 154.1, 140.4, 139.8, 127.7, 126.3, 126.0, 124.2, 123.4, 80.9, 69.0, 67.7, 53.9, 52.1, 28.0, 22.2, 21.9, 12.5;

HRMS (FAB) calcd for $C_{16}H_{25}N_2O_5$ *m*/*z* 325.1763 $[M+H]^+$, found 325.1758.

(*S*,*Z*)-*tert*-Butyl 2-((3-iodo-1-methoxy-1-oxopent-2-en-2-yl)carbamoyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (19)



To a solution of **18** (638 mg, 2.78 mmol, *E* : *Z* = 74 : 26) in $CHCl_3$ (11 mL) was added NIS (490 mg, 2.18 mmol) at 0 ℃ under argon. The mixture was stirred at 50 ℃ for 3 h. DABCO (611 mg, 5.45 mmol) was added to the mixture at room temperature. The mixture was stirred for 11 h and quenched with 1*N* $NaHSO_4$ (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (15 mL × 2). The combined organic layers were washed with sat. Na_2SO_3 (45 mL) and brine (45 mL), dried over

anhydrous $MgSO_4$, and filtered. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5 : 1 to 3 : 1) to give **19** (364 mg, 74%) as a 2 : 1 mixture of rotamers.

Colorless amorphous solid;

$[\alpha]_D^{17}$ = –117.3 (*c* 1.47, $CHCl_3$);

FTIR (neat) 3278, 2976, 2933, 2871, 1730, 1697, 1621, 1480, 1433, 1395, 1366, 1293, 1258, 1220, 1166, 1124, 1082 cm^{-1};

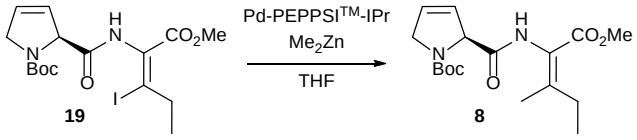
^1H NMR spectrum: see P21.

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 161.4, 155.4, 154.0, 130.8, 130.0, 128.1, 127.6, 125.9, 109.7, 81.4, 68.8, 67.2, 54.0, 52.5, 33.5, 28.2, 14.8;

HRMS (FAB) calcd for $C_{16}H_{24}IN_2O_5$ *m*/*z* 451.0730 $[M+H]^+$, found 451.0729.

According to the same procedure, *E*-**18** (32.0 mg, 98.7 μmol) and *Z*-**18** (29.5 mg, 90.9 μmol) were converted to **19**, respectively [35.0 mg, 79% from *E*-**18**; 21.0 mg, 51% from *Z*-**18**].

(*S*,*E*)-*tert*-Butyl 2-((1-methoxy-3-methyl-1-oxopent-2-en-2-yl)carbamoyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (8)



To a solution of **19** (840 mg, 1.87 mmol) and Pd-PEPPSI^{TM}-IPr (38.8 mg, 56.0 μmol, 98% purity) in THF (19 mL) was added Me_2Zn (3.8 mL, 3.73 mmol, 0.99 M solution in hexane) at 0 ℃ under argon. The mixture was stirred for 1 h at room temperature, quenched with sat. NH_4Cl (30 mL), and extracted with EtOAc (20 mL × 3). The combined organic layers were wash with brine (60 mL), dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5 : 1 to 1 : 1) to give **8** (597 mg, 94%) as a 5 : 4 mixture of rotamers;

Colorless sticky oil;

$[\alpha]_D^{18}$ = –188.0 (*c* 1.0, $CHCl_3$);

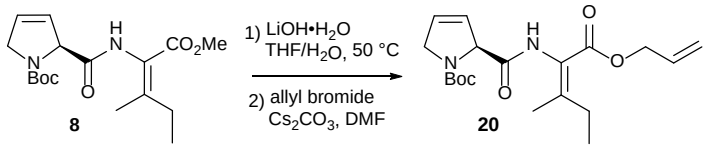
FTIR (neat) 3277, 2978, 2874, 1675, 1508, 1433, 1396, 1367, 1306, 1268, 1218, 1173, 1125, 1106 cm^{-1};

^1H NMR spectrum: see P23.

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 164.6, 155.2, 154.4, 151.3, 147.7, 127.3, 126.7, 126.1, 120.7, 119.9, 81.1, 69.1, 67.3, 54.1, 51.6, 28.2, 27.5, 19.7, 19.1, 12.6;

HRMS (FAB) calcd for $C_{17}H_{27}N_2O_5$ *m*/*z* 339.1920 $[M+H]^+$, found 339.1917.

(*S*,*E*)-*tert*-Butyl 2-((1-(allyloxy)-3-methyl-1-oxopent-2-en-2-yl)carbamoyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (20)



To a solution of **8** (169 mg, 499 μmol) in THF/H_2O (1 : 1, 5.0 mL) was added LiOH·H_2O (105 mg, 2.50 mmol). The mixture was stirred for 14 h at 50 ℃, quenched with 1*N* HCl (10 mL). The pH of the solution was adjusted to acidity (pH 1–2). The aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The resulting carboxylic acid was subjected to the next esterification without further purification. To a solution of crude carboxylic acid in DMF (5.0 mL) were added Cs_2CO_3 (163 mg, 501 μmol) and allyl bromide (51 μL, 601 μmol) at 0 ℃. The mixture was stirred for 3.5 h at room temperature, quenched with H_2O (10 mL), and extracted with hexane/EtOAc (1 : 1, 10 mL × 3). The combined organic layers were washed with brine (30 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 7 : 1 to 3 : 1) to give **20** (156 mg, 86% over 2 steps) as a 5 : 4 mixture of rotamers.

White solid;

mp 111–113 ℃;

$[\alpha]_D^{21}$ = –2.7 (*c* 1.15, $CHCl_3$);

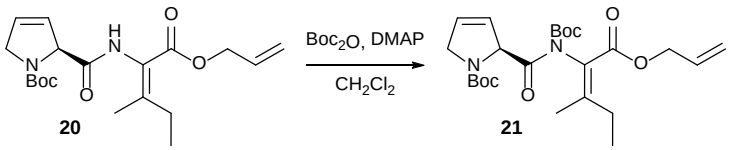
FTIR (neat) 3289, 2978, 2935, 2874, 1700, 1508, 1456, 1398, 1366, 1303, 1261, 1201, 1173, 1125, 1107 cm^{-1};

^{1}H NMR spectrum: see P25.

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 163.8, 155.1, 154.4, 151.5, 148.1, 132.0, 127.3, 126.6, 126.1, 120.8, 119.9, 118.3, 117.9, 81.1, 69.0, 67.3, 65.3, 54.0, 28.2, 27.5, 19.8, 19.1, 12.6;

HRMS (FAB) calcd for $C_{19}H_{29}N_2O_5$ *m*/*z* 365.2076 $[M+H]^+$, found 365.2069.

(*S*,*E*)-*tert*-Butyl 2-((1-(allyloxy)-3-methyl-1-oxopent-2-en-2-yl) (*tert*-butoxycarbonyl)carbamoyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (21)



To a solution of **20** (156 mg, 428 μmol) in CH_2Cl_2 (2.1 mL) were added Boc_2O (200 μL, 858 μmol) and DMAP (52.4 mg, 429 μmol) at 0 ℃. The mixture was stirred for 3 h at room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20 : 1 to 10 : 1) to give **21** (201 mg, quant.) as a colorless sticky oil;

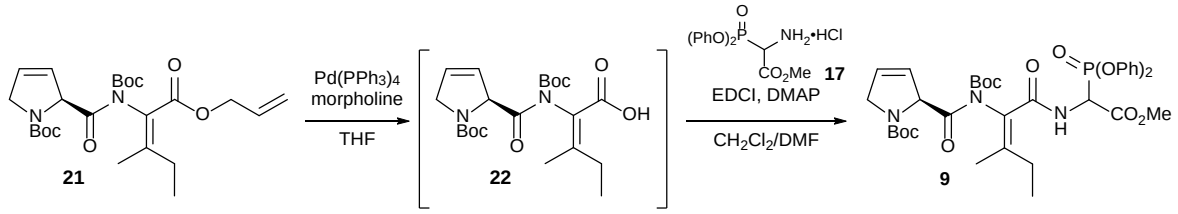
$[\alpha]_D^{21}$ = –1.7 (*c* 1.09, $CHCl_3$);

FTIR (neat) 3419, 3087, 2978, 2935, 2871, 1722, 1701, 1648, 1458, 1402, 1368, 1294, 1257, 1225, 1203, 1154, 1129, 1107, 1058 cm^{-1};

HRMS (FAB) calcd for $C_{24}H_{37}N_2O_7$ *m*/*z* 465.2601 $[M+H]^+$, found 465.2586.

NMR spectra: see P27~28.

(2*S*)-*tert*-Butyl 2-((*tert*-butoxycarbonyl)((*E*)-1-((1-(diphenoxyphosphoryl)-2-methoxy-2-oxoethyl) amino)-3-methyl-1-oxopent-2-en-2-yl)carbamoyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (9)



To a solution of **21** (162 mg, 349 μmol) in THF (3.5 mL) were added $Pd(PPh_3)_4$ (40.3 mg, 34.9 μmol) and morpholine (300 μL, 3.49 mmol) at 0 ℃. The mixture was stirred for 2 h at room temperature, quenched with 1*N* HCl (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to give carboxylic acid **22** which was subjected to the next reaction without further purification. The crude **22** in CH_2Cl_2 (2.4 mL), EDCI (110 mg, 575 μmol), and DMAP (32.0 mg, 262 μmol) were subsequently added to a solution of α-(diphenylphosphono)glycine ammonium salt **17** in DMF (1.2 mL) prepared form **3**[1] (238 mg, 523 μmol), 10% Pd/C (23.8 mg, 10 wt%), AcCl (280 μL, 3.92 mmol), and MeOH (1.2 mL) in EtOAc (3.5 mL) at 0 ℃ under argon. The mixture was stirred for 15 h at room temperature, quenched with sat. NH_4Cl (5 mL), and extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine (15 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10 : 1 to 1 : 1) to give **9** (143 mg, 56% over 2 steps) as a 1 : 1 mixture of diastereomers;

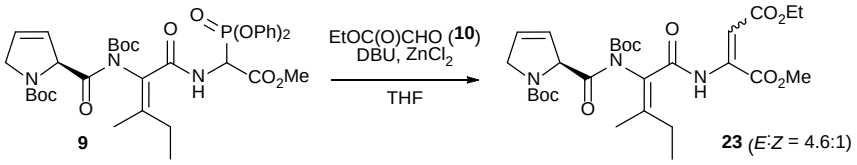
Colorless sticky oil.

FTIR (neat) 3320, 3009, 2979, 2934, 2871, 1739, 1681, 1591, 1489, 1405, 1369, 1288, 1256, 1209, 1181, 1153, 1059, 1026, 1009 cm^{-1};

HRMS (FAB) calcd for $C_{36}H_{47}N_3O_{11}P$ *m*/*z* 728.2948 $[M+H]^+$, found 728.2944.

NMR spectra: see P29~30.

4-Ethyl 1-methyl 2-((*E*)-2-((*S*)-*N*,1-bis(*tert*-butoxycarbonyl)-2,5-dihydro-1*H*-pyrrole-2-carboxamido)-3-methylpent-2-enamido)but-2-enedioate (23)



To a solution of **9** (140 mg, 192 μmol) and $ZnCl_2$ (384 μL, 384 μmol, 1.0 M solution in Et_2O) in THF (1.9 mL) was added DBU (29 μL, 192 μmol) at 0 ℃ under argon. The mixture was stirred for 30 min at 0 ℃. Ethyl glyoxalate polymer form (**10**) (41 μL, 192 μmol, 47% solution in toluene) was added to the mixture. The mixture was stirred for 15 h at room temperature, quenched with sat. NH_4Cl (5 mL), and extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine (15 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 9 : 1 to 5 : 1) to give **23** (88.5 mg, 80%, *E* : *Z* = 4.6 : 1) as a mixture of *E*-**23** and *Z*-**23**.

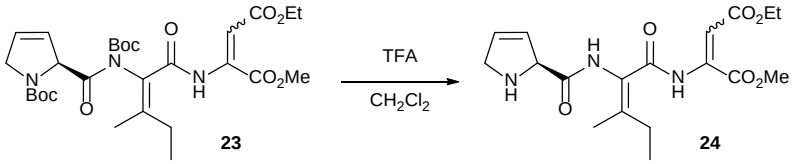
Colorless amorphous solid;

FTIR (neat) 3294, 3018, 2980, 2936, 2873, 1739, 1716, 1671, 1623, 1520, 1420, 1370, 1288, 1258, 1218, 1143, 1098, 1063, 1038 cm^{-1};

HRMS (CI) calcd for $C_{28}H_{42}N_3O_{10}$ *m/z* 580.2870 $[M+H]^+$, found 580.2878.

NMR spectra: see P31~32.

Synthesis of the tripeptide side chain 24



To a solution of **23** (10.1 mg, 17.4 μmol) was added TFA (0.5 mL) in CH_2Cl_2 (0.5 mL) at 0 ℃ under argon. The mixture was stirred for 30 min at room temperature and concentrated under reduce pressure to give a crude 4.3:1 mixture of *E*-**24** and *Z*-**24**. The residue was purified by PLC (silica gel 60 F-254, 0.5 mm thickness, manufactured by Merck) ($CHCl_3$/MeOH = 10 : 1) to give *E*-**24** (2.3 mg, 35%) and a 1 : 1.6 mixture of *E*-**24** and *Z*-**24** (1.2 mg, 18%). The stereochemistry was determined by comparison of the chemical shift values of olefinic proton (*E*: 6.05 ppm, *Z*: 5.46 ppm).[2];

E-**24**:

^{1}H NMR (300 MHz, CD_3OD) δ 6.05 (s, 1 H), 6.00 (m, 1 H), 5.87 (m, 1 H), 4.59 (m, 1 H), 4.13 (q, *J* = 7.2 Hz, 2 H), 3.88 (m, 2 H), 3.81 (s, 3 H), 2.36 (q, *J* = 7.5 Hz, 2 H), 1.77 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.09 (t, *J* = 7.5 Hz, 3 H).

Z-**24**:

^{1}H NMR (300 MHz, CD_3OD) δ 6.00 (m, 1 H), 5.93 (m, 1 H), 5.46 (s, 1 H), 4.58 (m, 1 H), 4.22 (q, *J* = 7.2 Hz,

2 H), 3.90 (m, 2 H), 3.83 (s, 3 H), 2.56 (q, *J* = 7.5 Hz, 2 H), 1.80 (s, 3 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.11 (t, *J* = 7.5 Hz, 3 H).

References

1) Hamada, M.; Shinada, T.; Ohfune, Y. *Org. Lett*. **2009**, *11*, 4664–4667.

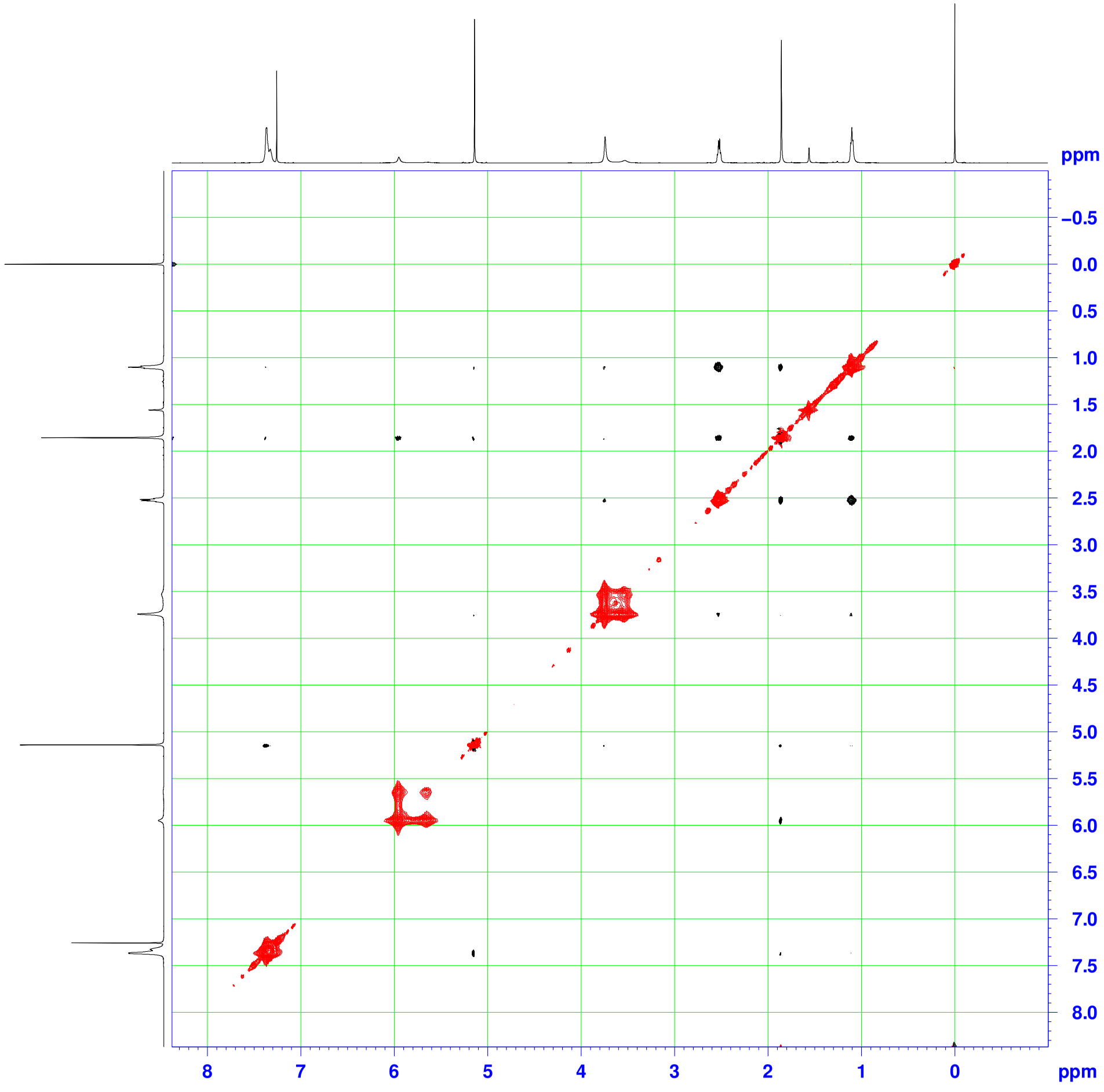
2) Yasuno, Y.; Hamada, M.; Yamada, T.; Shinada, T.; Ohune, Y. *Eur. J. Org. Chem*. **2013**, 1884–1888.

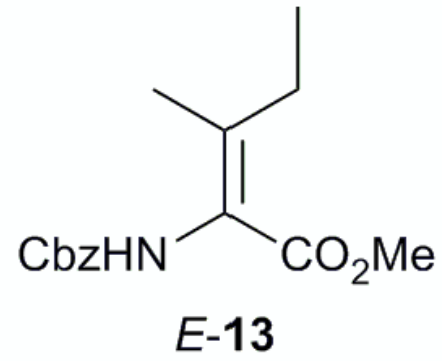
3) Mazurkiewicz, R.; Kuźnic, A. *Tetrahedron Lett*. **2006**, *47*, 3439–3442.

4) Schmidt, U.; Griesser, H.; Leitenberger, V.; Lieberknecht, A. Mangold, R.; Meyer, R.; Riedl, B. *Synthesis*, **1992**, 487–490.

5) (a) Shangguan, N.; Joullié, M. *Tetrahedron. Lett*. **2009**, *50*, 6748–6750. (b) Schumacher, K. K.; Jiang, J.; Joullié, M. M. *Tetrahedron: Asymmetry* **1998**, *9*, 47–53.

Et–Me (E)_noesy_CDCl3_temp25





E-13

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PROCNO                   1

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PULPROG          noesytp
TD                  2048
SOLVENT             CDCl3
NS                    24
DS                    48
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FIDRES           2.749331 Hz
AQ              0.1820012 sec
RG                   256
DW                88.800 usec
DE                 6.00 usec
TE                298.0 K
d0             0.00000300 sec
D1             1.50000000 sec
D8             0.80000001 sec
IN0            0.00008880 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.20 usec
PL1                3.50 dB
SFO1         600.1322205 MHz

F1 - Acquisition parameters
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TD                  512
SFO1            600.1322 MHz
FIDRES         10.997326 Hz
SW                 9.382 ppm
FnMODE         undefined

F2 - Processing parameters
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SF           600.1300044 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
SI                   512
MC2                 TPPI
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WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
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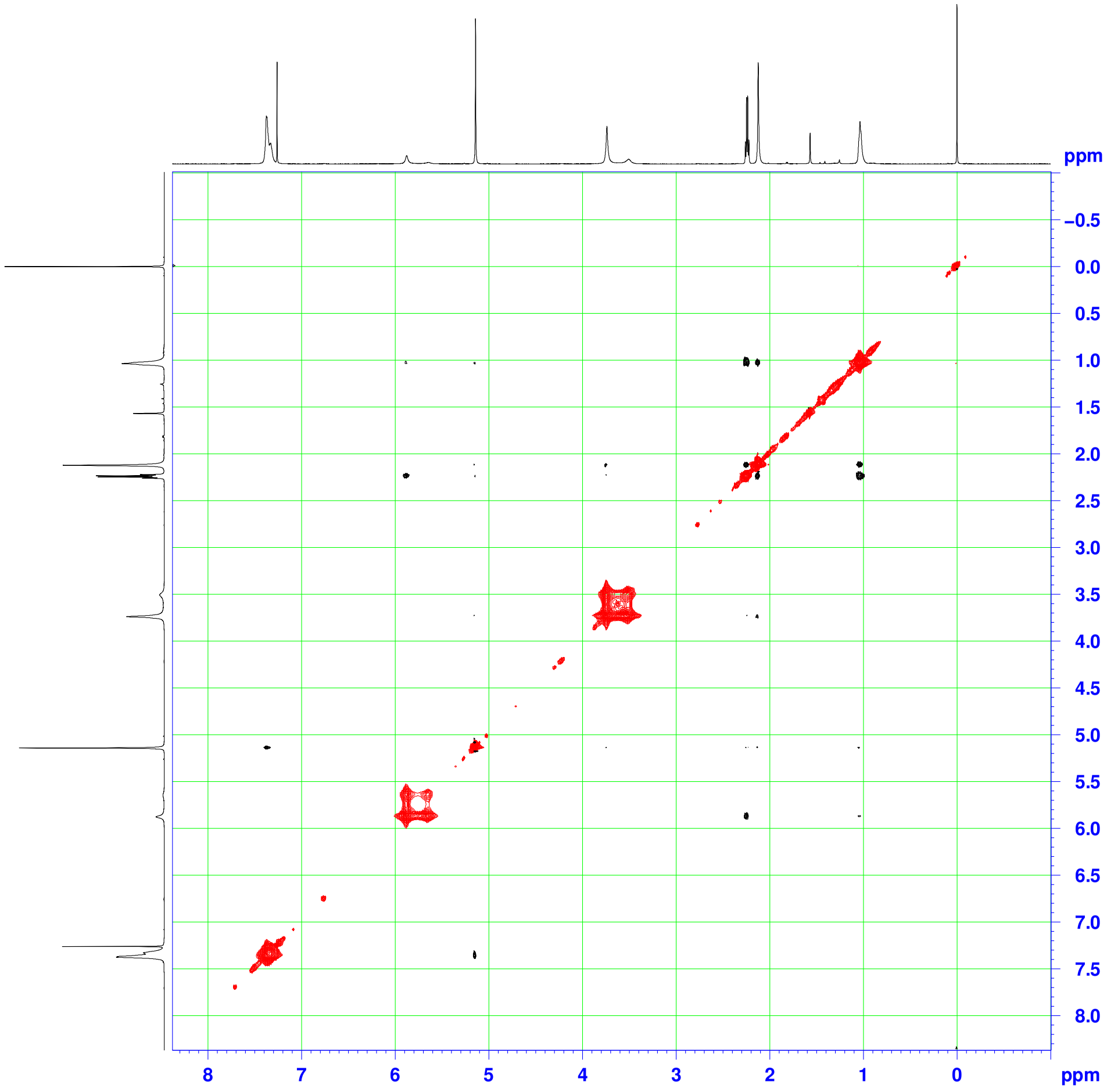
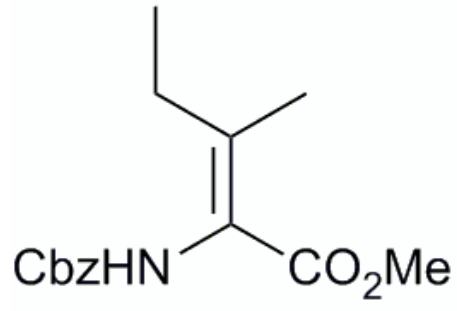
Et–Me (Z)_noesy_CDCl3_temp25





Z-13

BRUKER

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NAME                  md5
EXPNO                 357
PROCNO                  1

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PULPROG          noesytp
TD                  2048
SOLVENT             CDCl3
NS                    24
DS                    48
SWH              5630.631 Hz
FIDRES           2.749331 Hz
AQ               0.1820012 sec
RG                   256
DW                88.800 usec
DE                 6.00 usec
TE                298.0 K
d0            0.00000300 sec
D1            1.50000000 sec
D8            0.80000001 sec
IN0           0.00008880 sec

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P1                 10.20 usec
PL1                3.50 dB
SFO1         600.1322205 MHz

F1 - Acquisition parameters
ND0                   2
TD                  512
SFO1            600.1322 MHz
FIDRES         10.997326 Hz
SW                9.382 ppm
FnMODE        undefined

F2 - Processing parameters
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SF           600.1300073 MHz
WDW                 QSINE
SSB                     2
LB                 0.00 Hz
GB                      0
PC                 1.00

F1 - Processing parameters
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MC2                 TPPI
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WDW                 QSINE
SSB                     2
LB                 0.00 Hz
GB                      0
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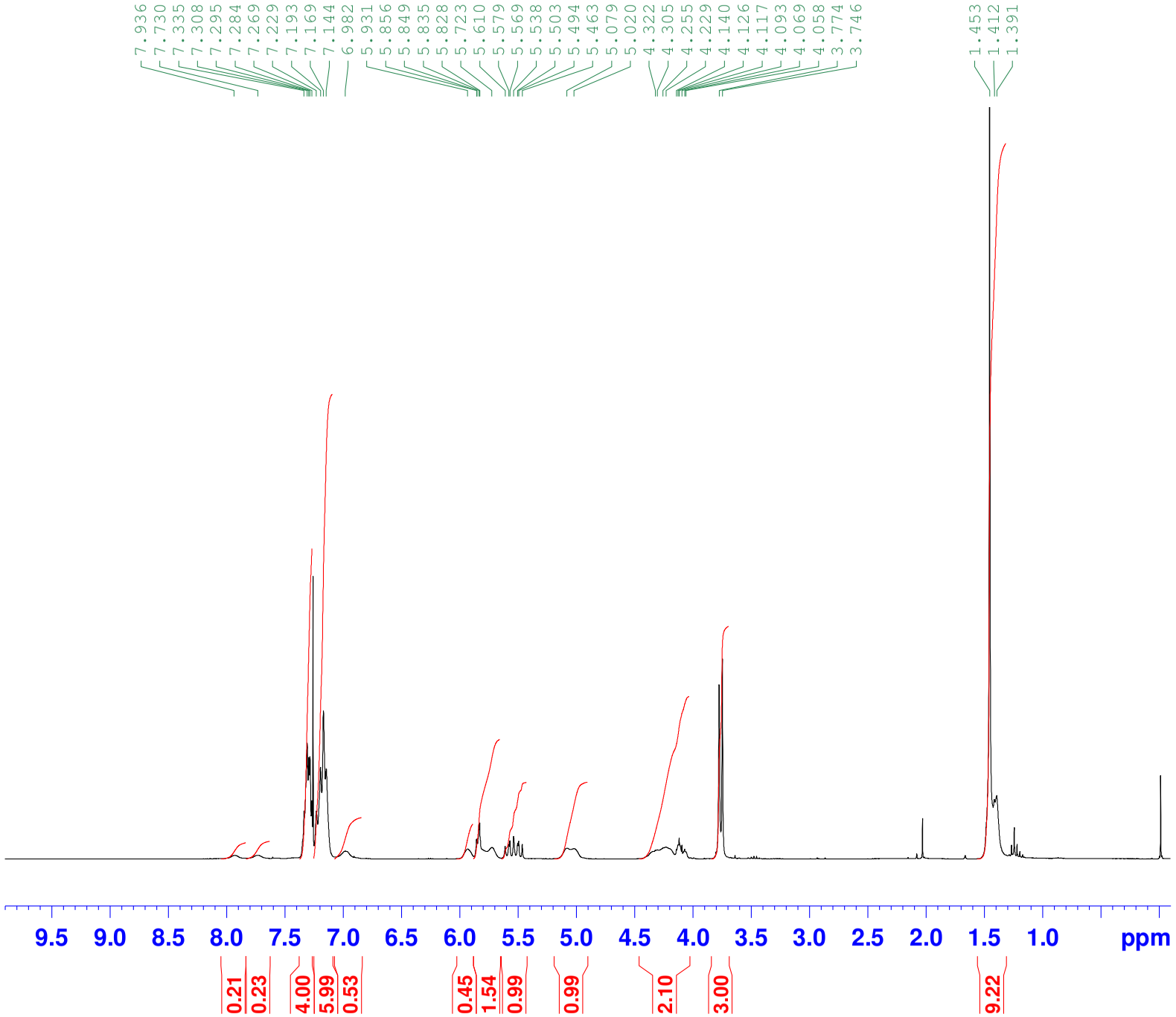

15

BRUKER

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Current Data Parameters
NAME                  Pro-HWE
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20140101
Time                   16.15
INSTRUM                av300
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PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                        64
DW                   80.800 usec
DE                    6.50 usec
TE                   291.8 K
D1               1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                    15.00 usec
PLW1             7.50000000 W
SFO1           300.1318534 MHz

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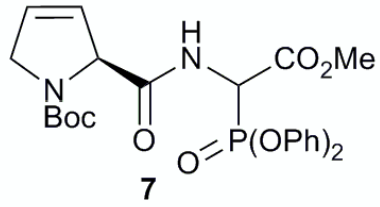
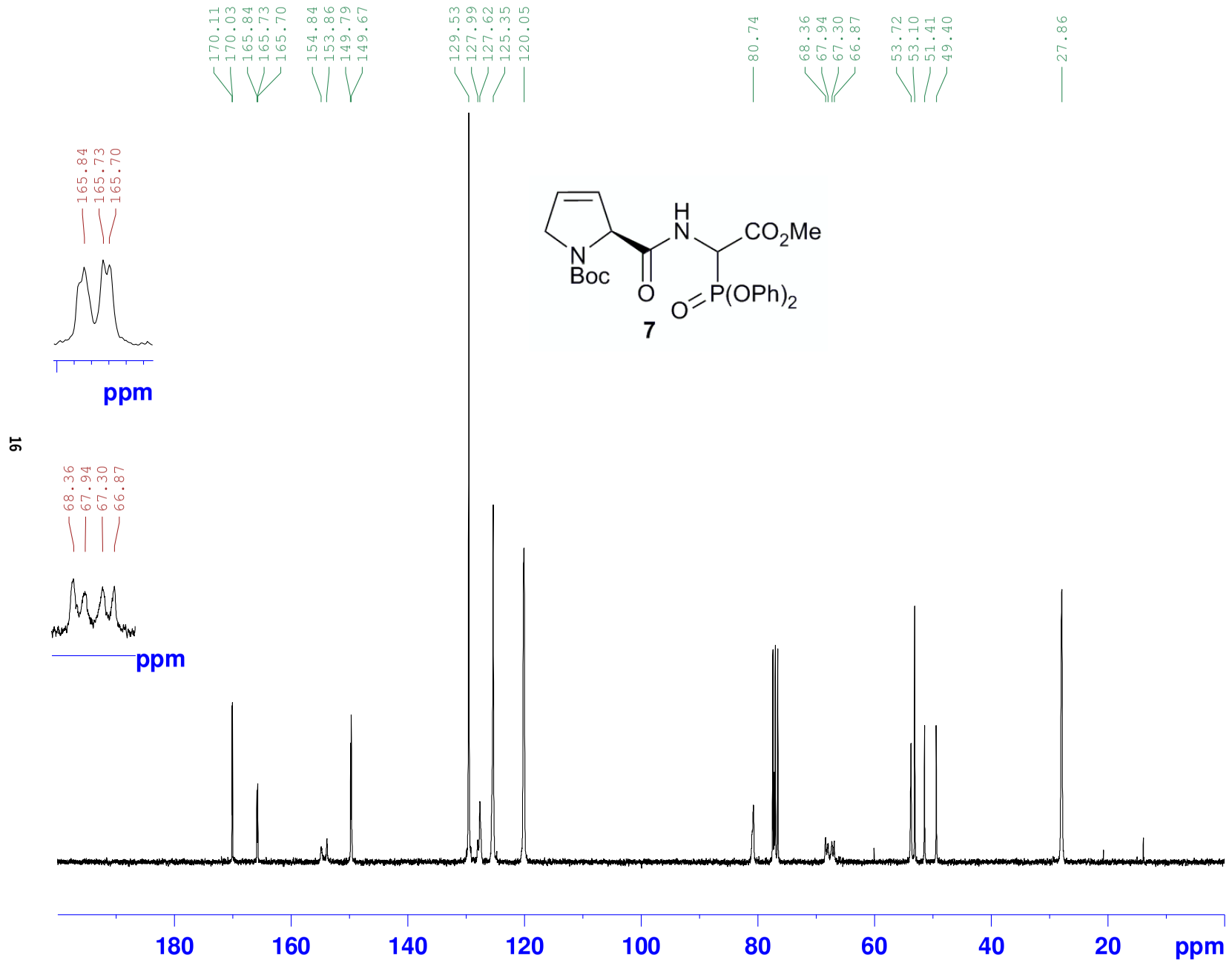


7



16

BRUKER

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PROCNO 1

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TD 65536
SOLVENT CDCl3
NS 1024
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 292.8 K
D1 2.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
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P1 10.00 usec
PLW1 38.05099869 W
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
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NUC2 1H
PCPD2 90.00 usec
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PLW12 0.20833001 W
PLW13 0.16875000 W
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F2 - Processing parameters
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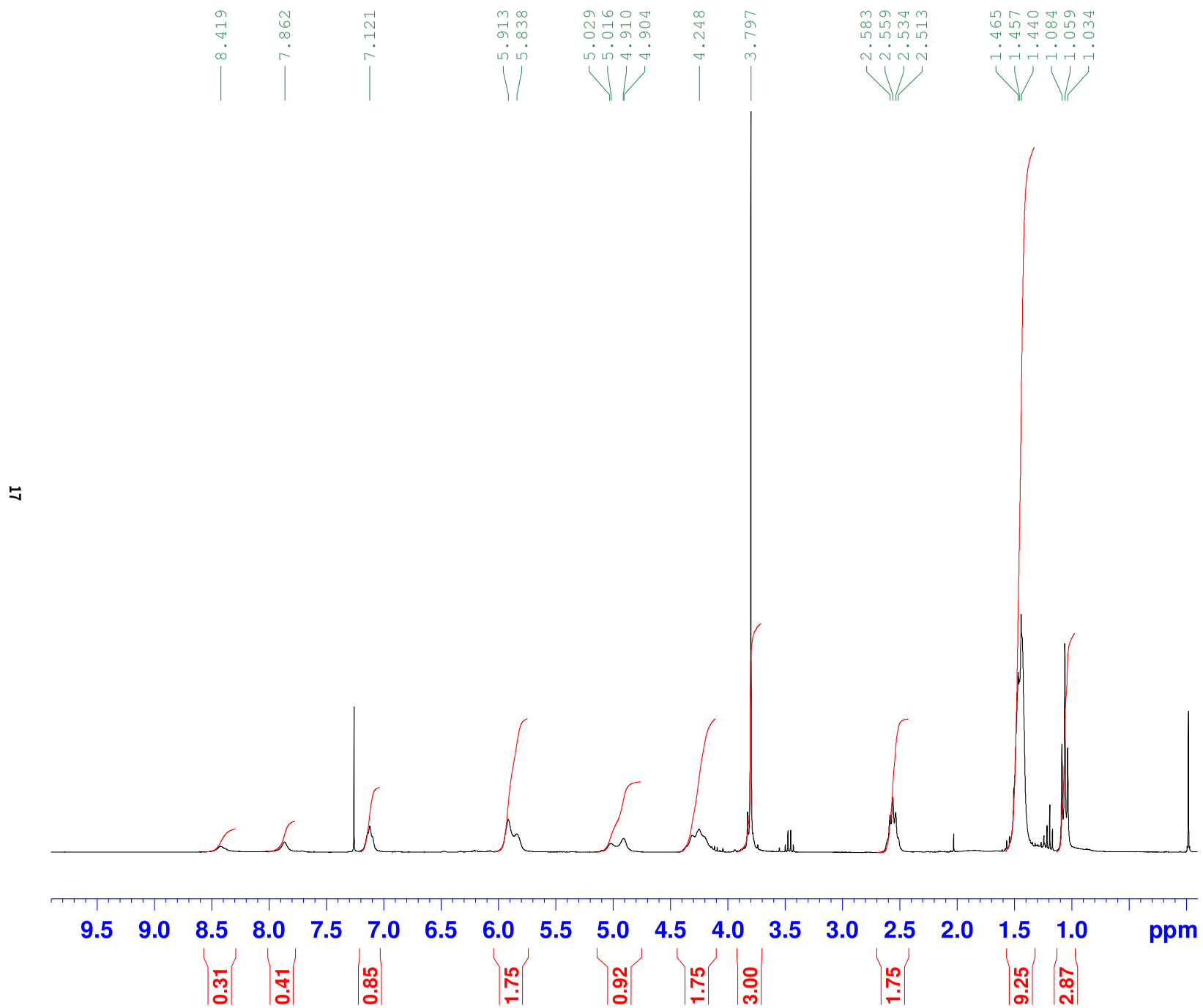

17

Current Data Parameters
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EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
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Time 22.07
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 80.6
DW 80.800 usec
DE 6.50 usec
TE 292.4 K
D1 1.00000000 sec

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P1 15.00 usec
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F2 - Processing parameters
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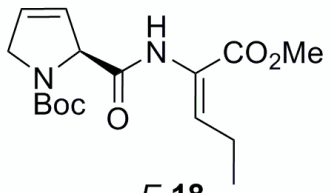
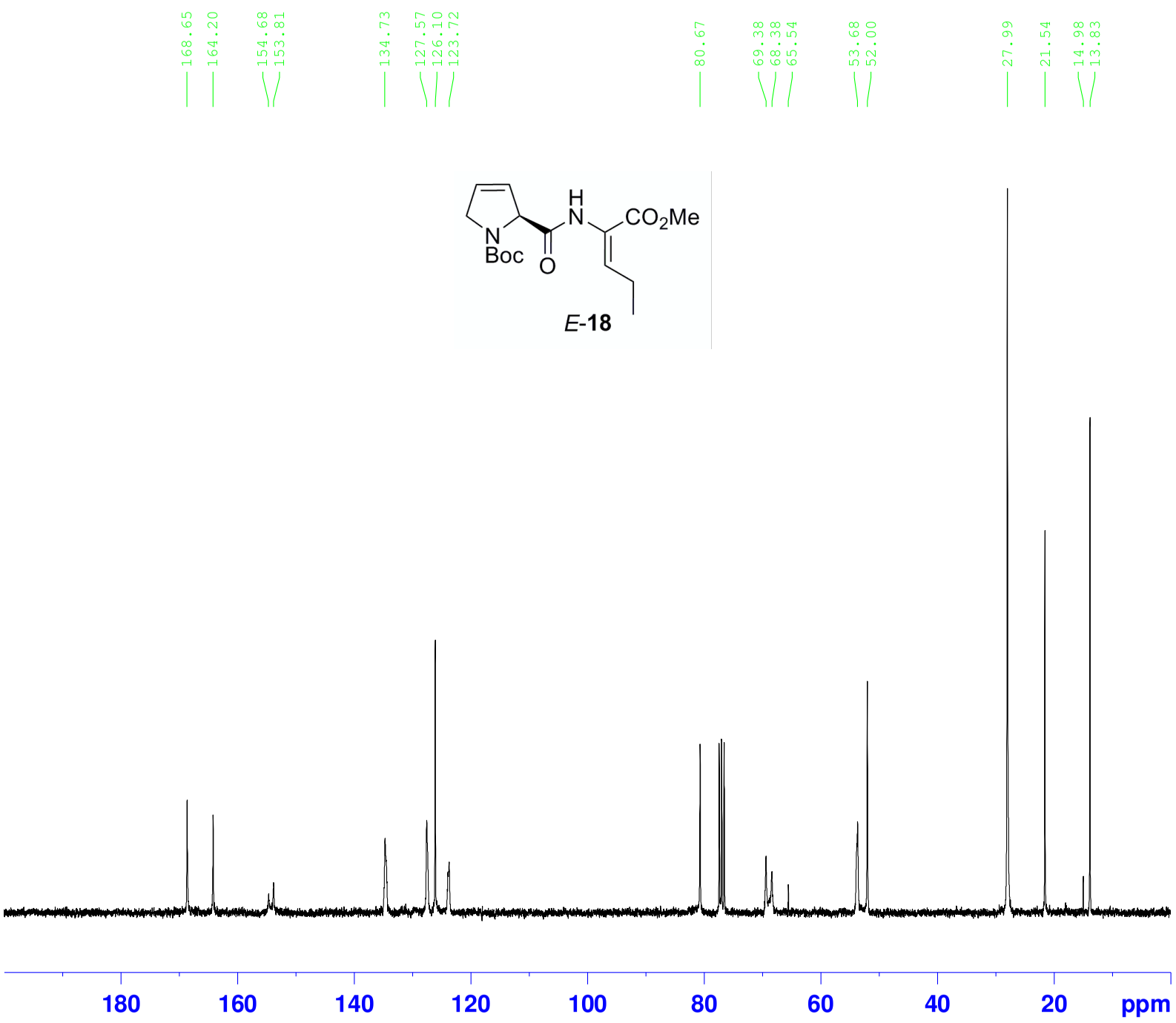
PC 1.00



E-18



Current Data Parameters
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PROCNO 1

F2 - Acquisition Parameters
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TD 65536
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FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 293.1 K
D1 2.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 38.05099869 W
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 7.50000000 W
PLW12 0.20833001 W
PLW13 0.16875000 W
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LB 1.00 Hz
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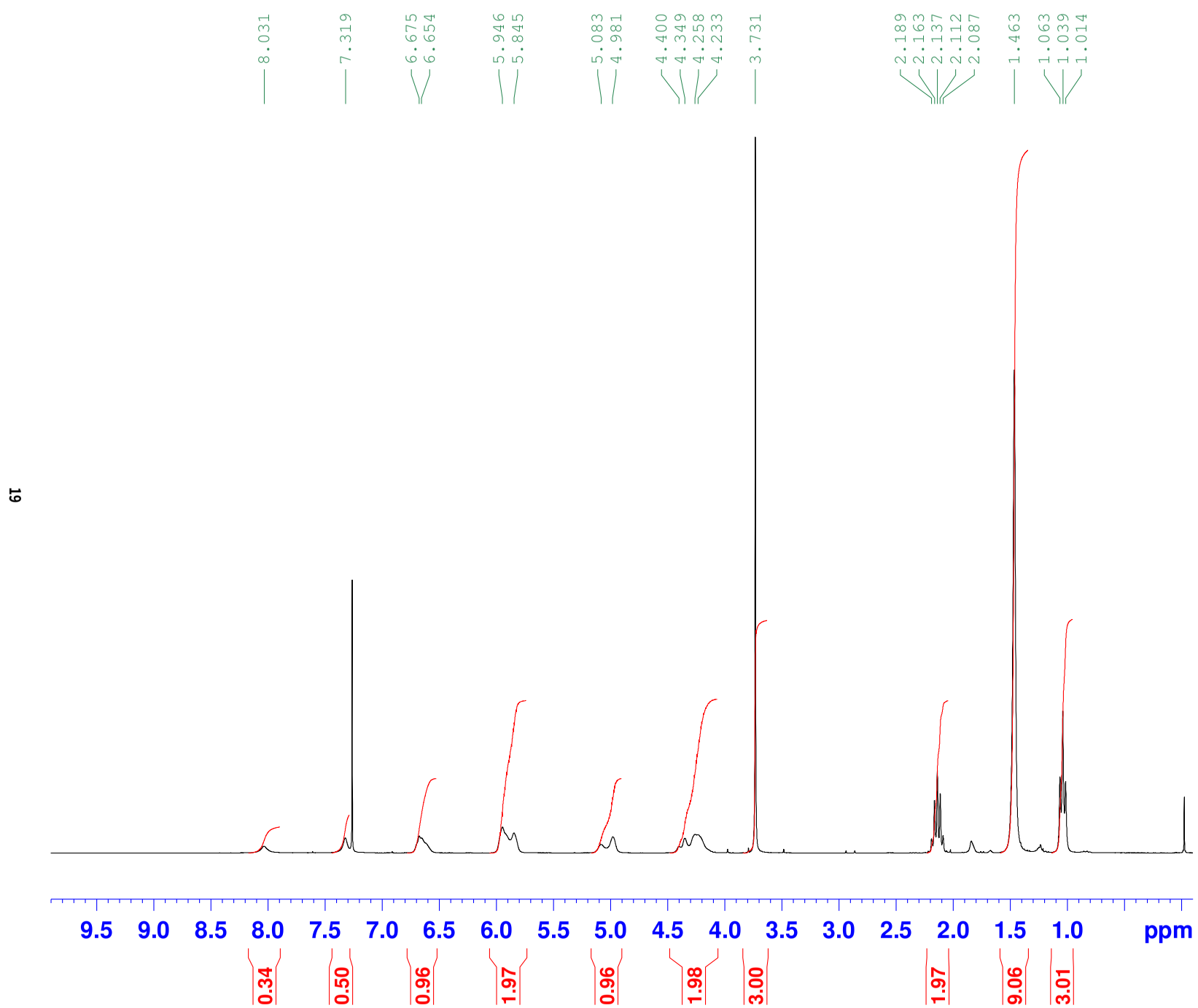
PC 1.40



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BRUKER

```
Current Data Parameters
NAME      phomo-Z-olefin
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140105
Time               12.37
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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953587 sec
RG                    64
DW                80.800 usec
DE                 6.50 usec
TE                290.5 K
D1             1.00000000 sec

======== CHANNEL f1 ========
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PLW1          7.50000000 W
SFO1         300.1318534 MHz

F2 - Processing parameters
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SF           300.1300061 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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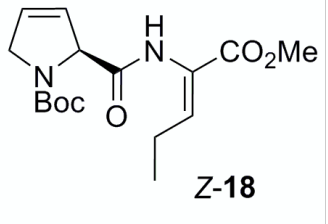
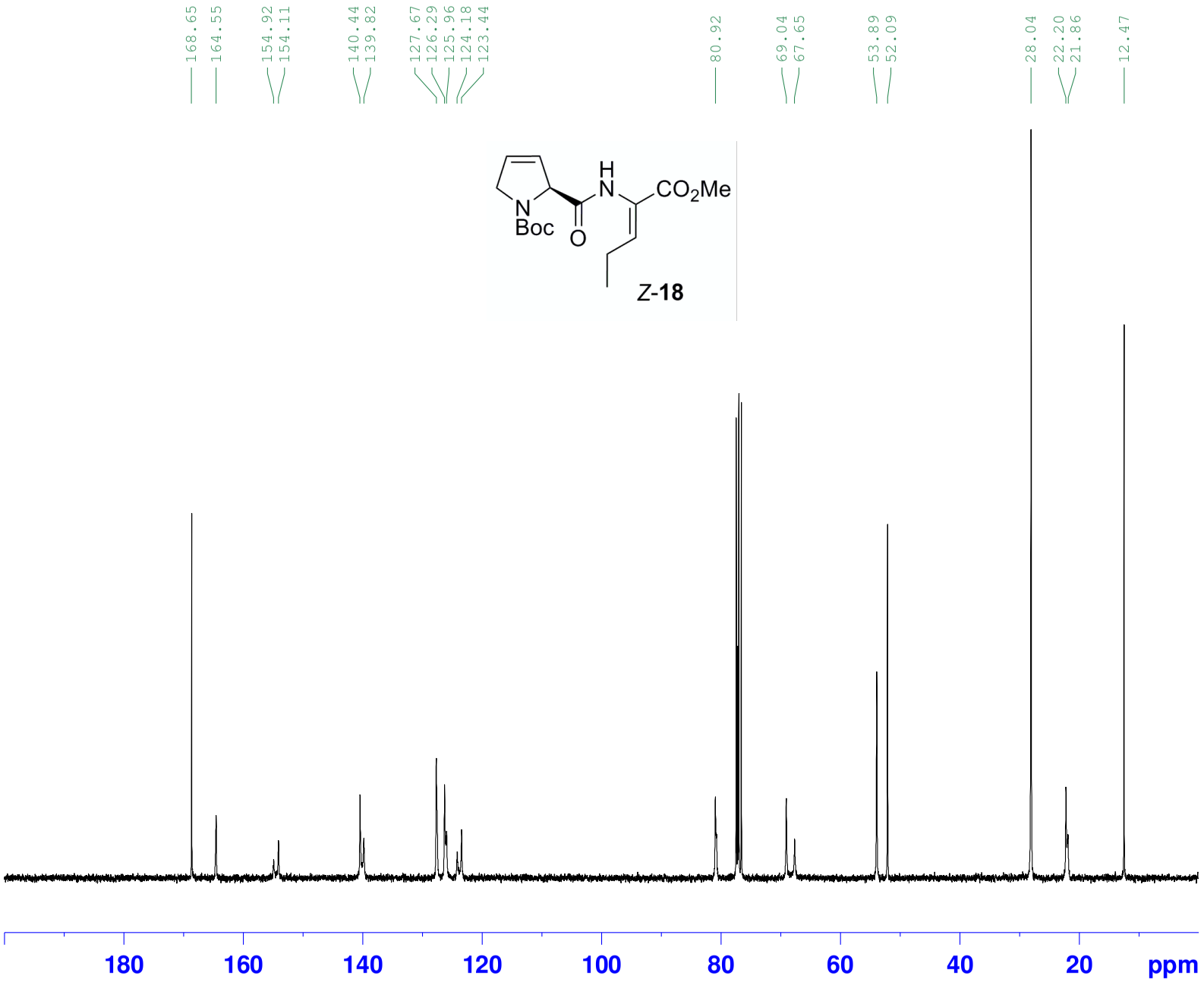


Z-18



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PROCNO 1

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SOLVENT CDCl3
NS 1024
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 291.7 K
D1 2.00000000 sec
D11 0.03000000 sec

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SFO1 75.4752953 MHz

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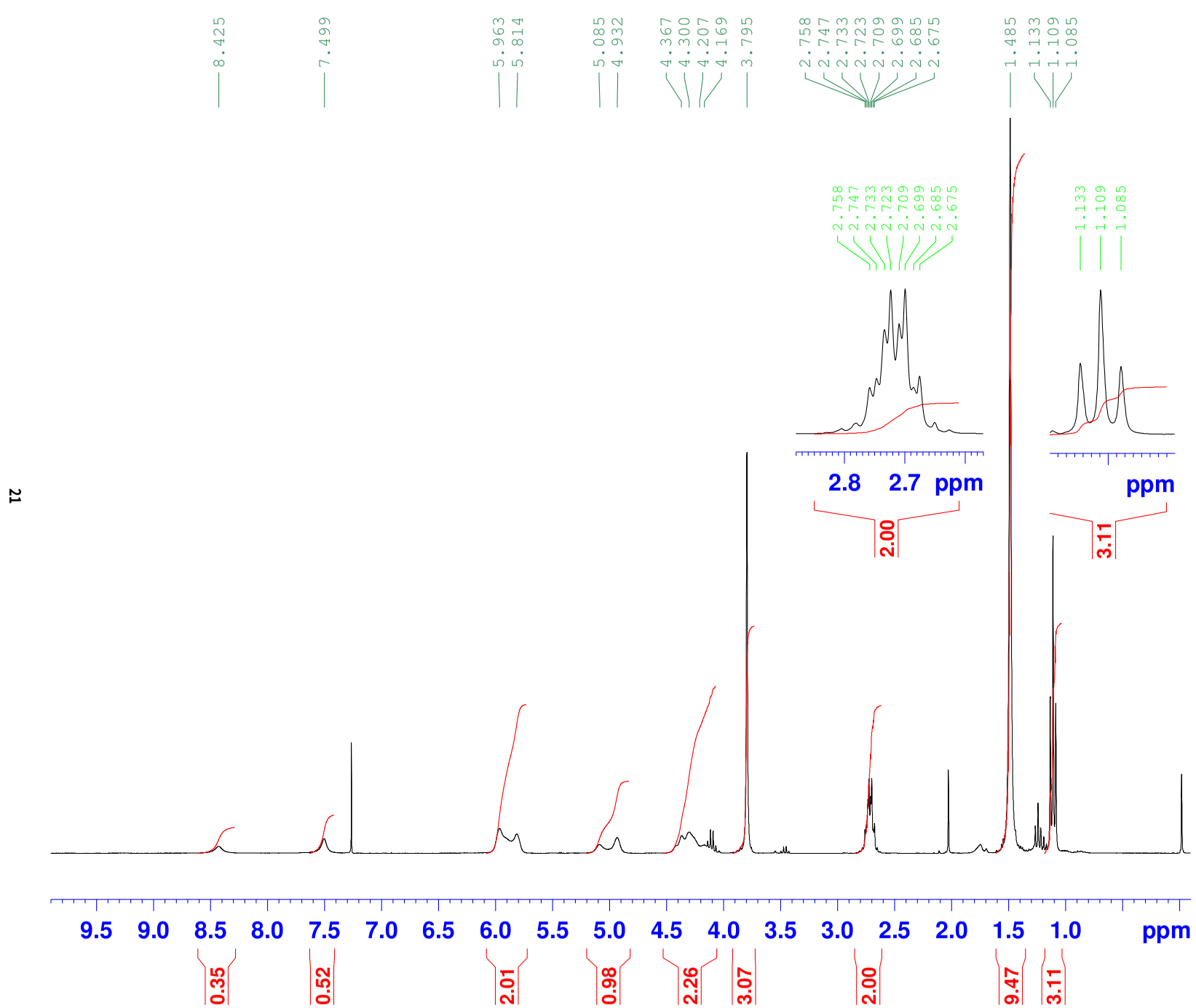

21

BRUKER

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PROCNO                 1

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TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
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TE                292.7 K
D1             1.00000000 sec

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SFO1         300.1318534 MHz

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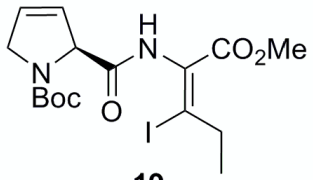

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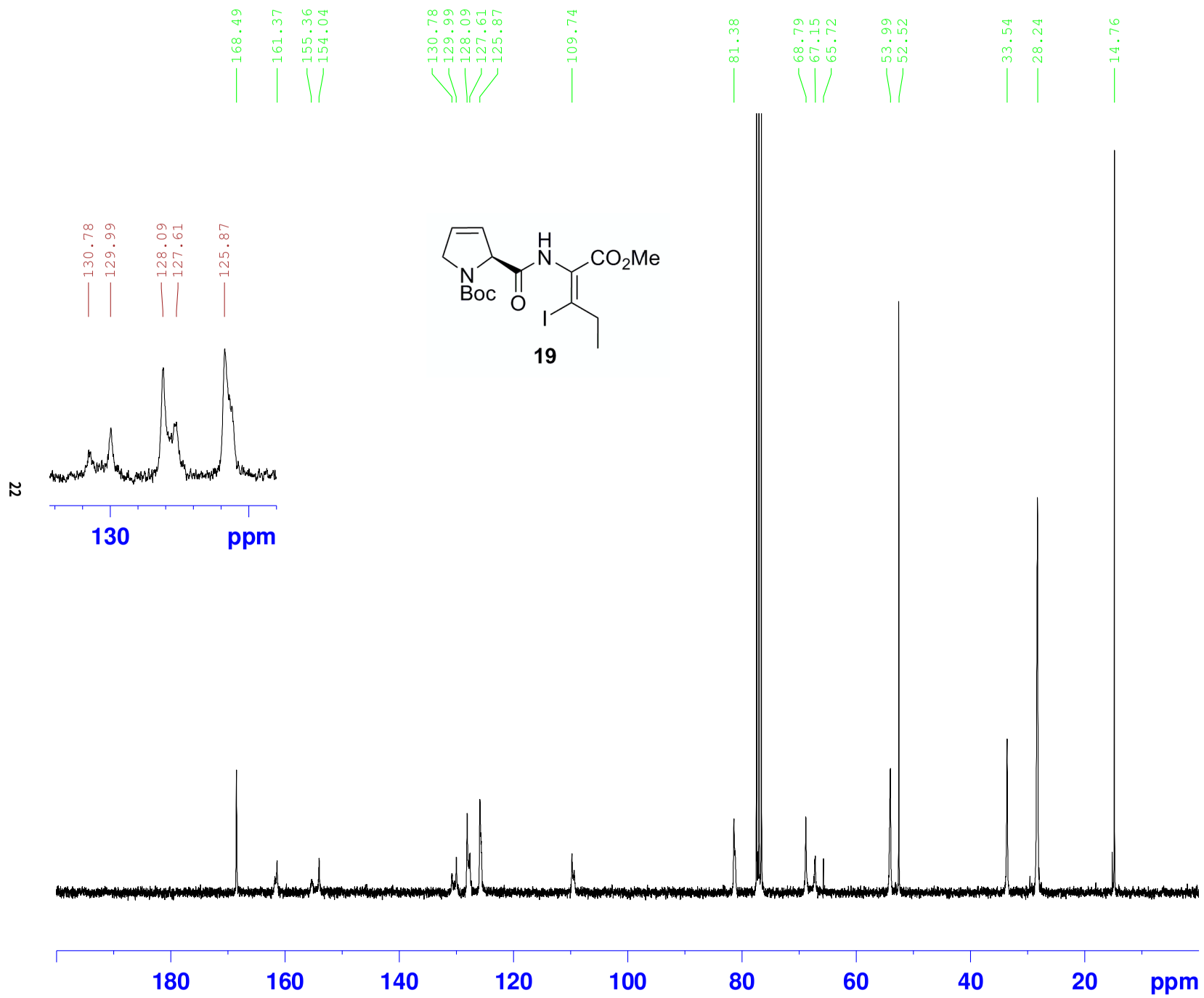

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BRUKER

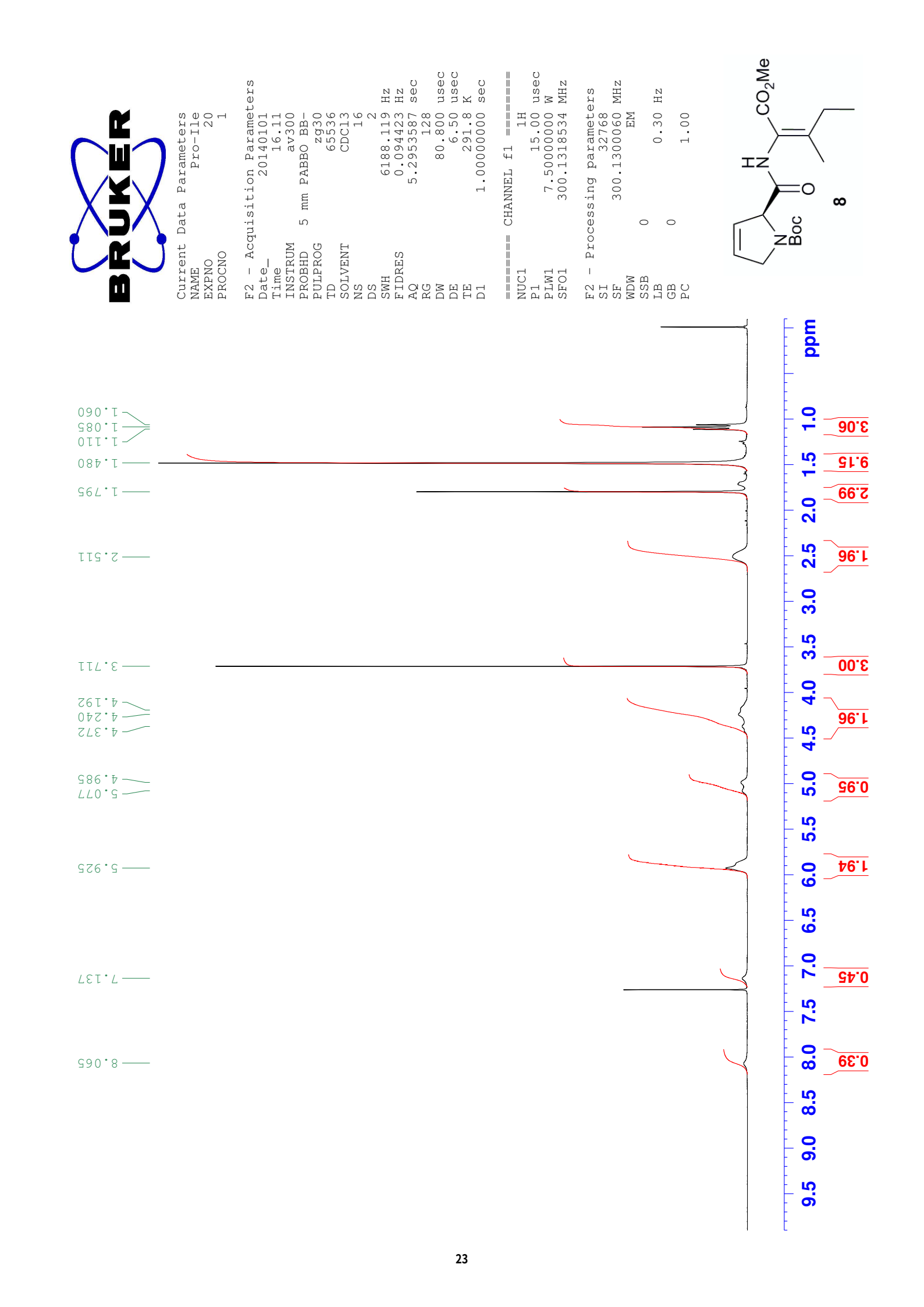
Current Data Parameters
NAME phomo-Z-iodo
EXPNO 20
PROCNO 1

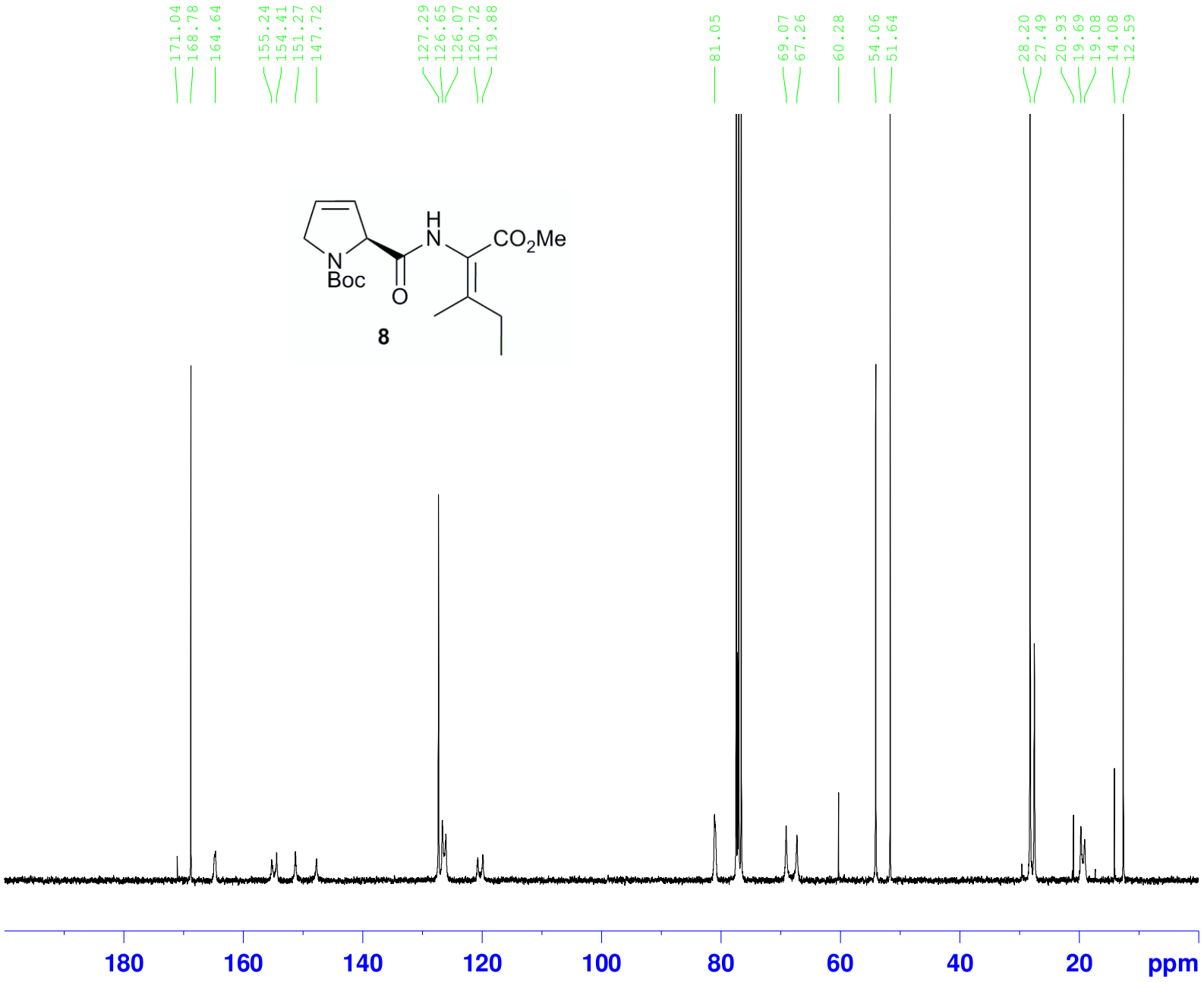
F2 - Acquisition Parameters
Date_ 20131114
Time 8.34
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1600
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 293.2 K
D1 2.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 38.05099869 W
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 7.50000000 W
PLW12 0.20833001 W
PLW13 0.16875000 W
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677564 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


Current Data Parameters
NAME Pro-Ile
EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140101
Time 16.11
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 128
DW 80.800 usec
DE 6.50 usec
TE 291.8 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PLW1 7.50000000 W
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
CO2Me
H
N
O
N
Boc
8
ppm
1.060
1.085
1.110
1.480
1.795
2.511
3.711
4.192
4.240
4.372
4.985
5.077
5.925
7.137
8.065
3.06
9.15
2.99
1.96
3.00
1.96
0.95
1.94
0.45
0.39



BRUKER

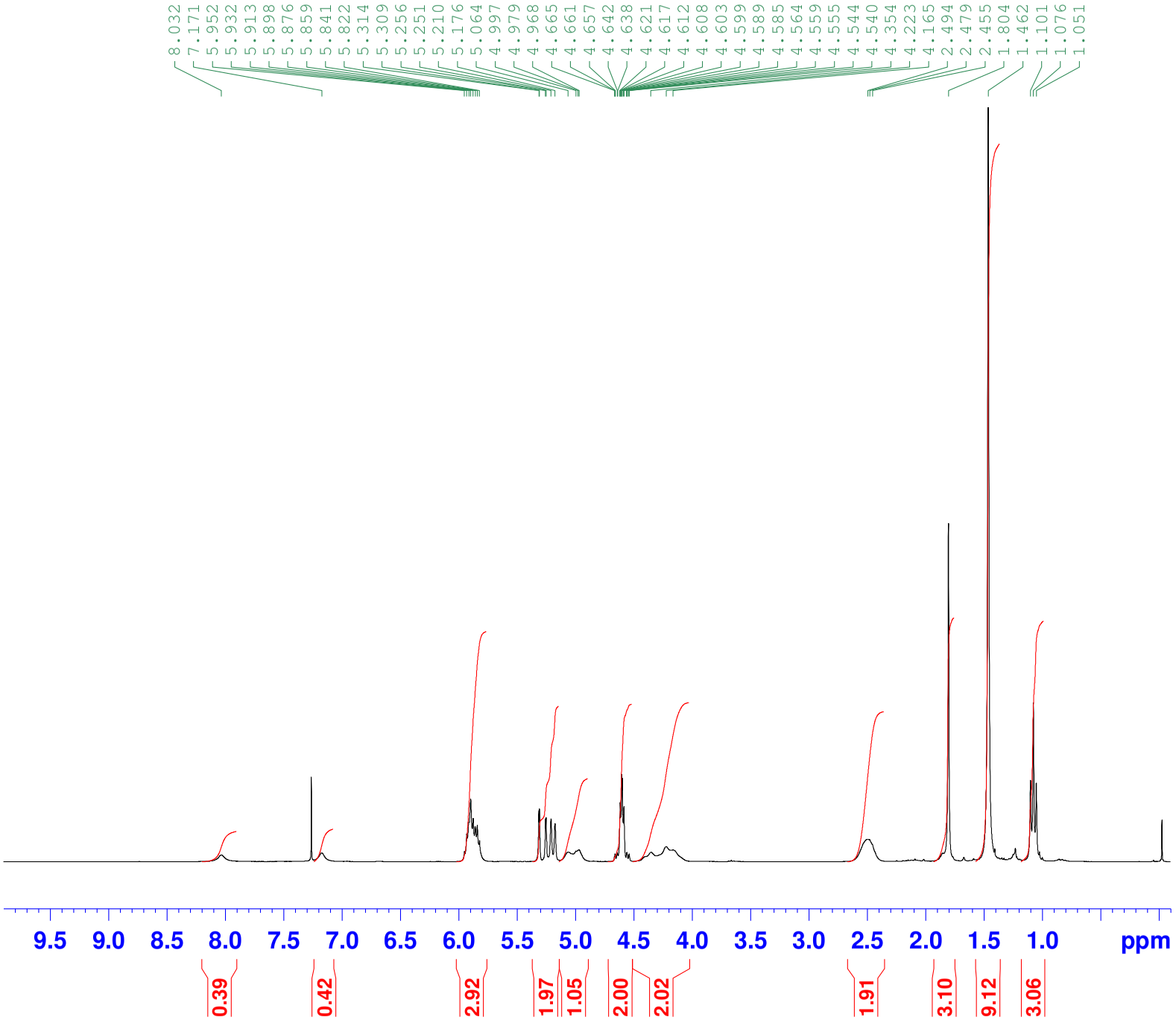
Current Data Parameters
NAME 15-60
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131119
Time 9.43
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 7452
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 293.6 K
D1 2.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 38.05099869 W
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 7.50000000 W
PLW12 0.20833001 W
PLW13 0.16875000 W
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677549 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



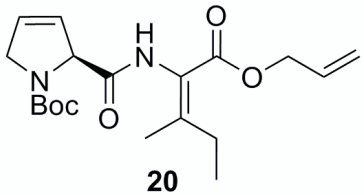
BRUKER

```
Current Data Parameters
NAME          allylester
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140105
Time               12.42
INSTRUM            av300
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES          0.094423 Hz
AQ              5.2953587 sec
RG                  50.8
DW                80.800 usec
DE                 6.50 usec
TE                290.7 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 15.00 usec
PLW1           7.50000000 W
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF            300.1300058 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



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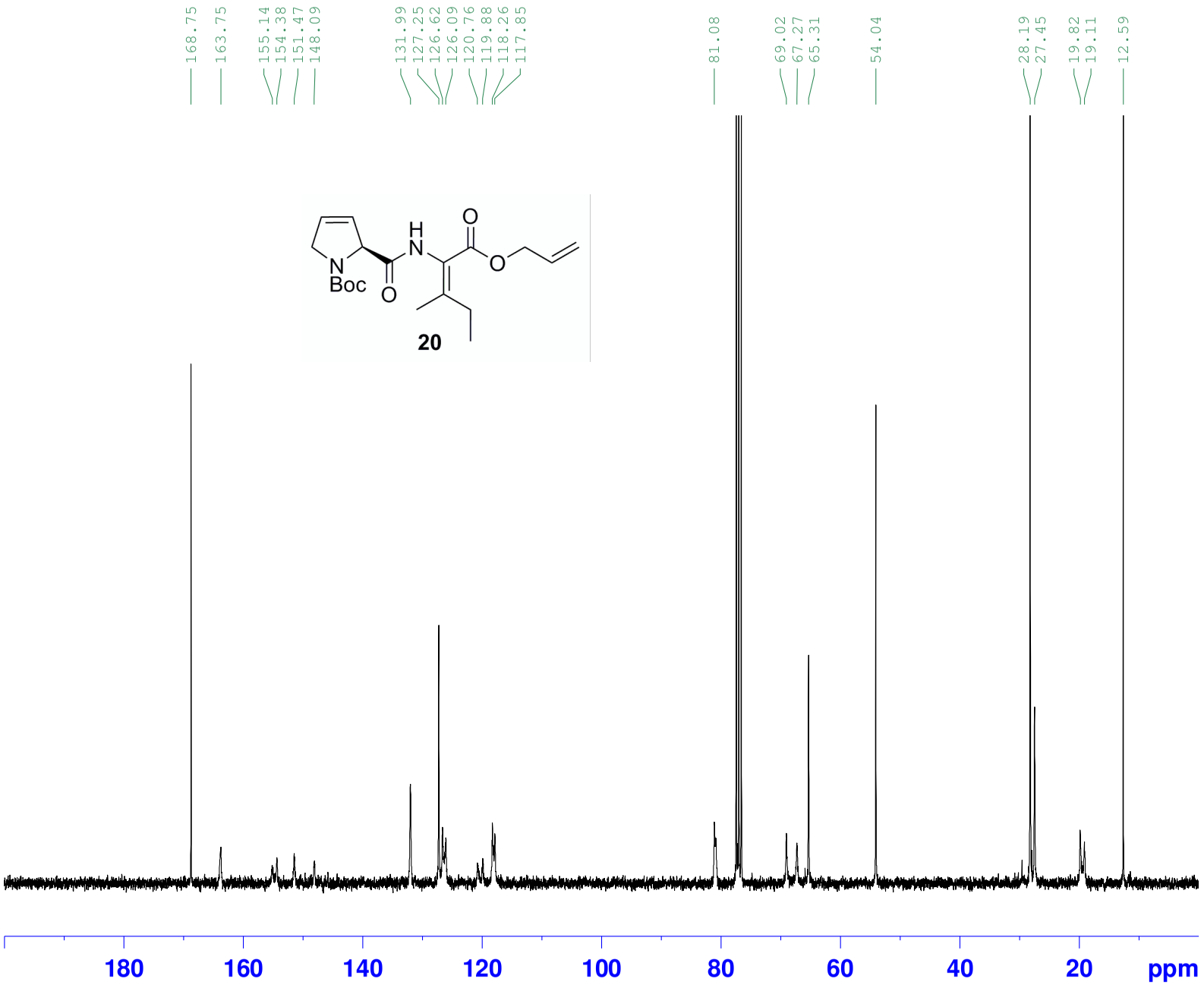


BRUKER

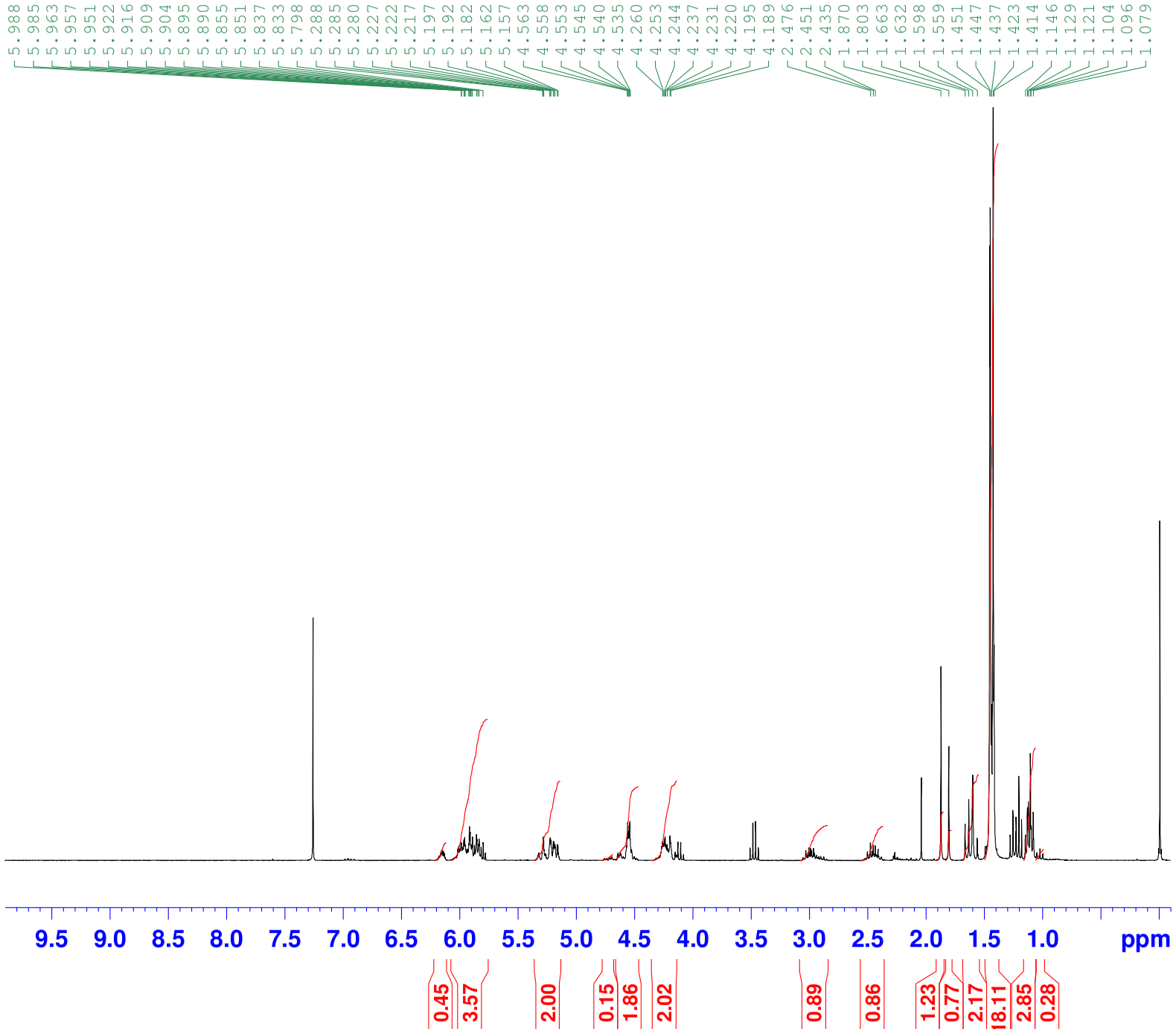
```
Current Data Parameters
NAME                   allylester
EXPNO                          20
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20140105
Time                        15.22
INSTRUM                    av300
PROBHD    5 mm PABBO BB-
PULPROG                   zgpg30
TD                         65536
SOLVENT                    CDCl3
NS                          1200
DS                             2
SWH                  18028.846 Hz
FIDRES                0.275098 Hz
AQ                    1.8175818 sec
RG                           203
DW                        27.733 usec
DE                         6.50 usec
TE                        292.0 K
D1                   2.00000000 sec
D11                  0.03000000 sec

======== CHANNEL f1 ========
NUC1                         13C
P1                        10.00 usec
PLW1                38.05099869 W
SFO1                 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     90.00 usec
PLW2                 7.50000000 W
PLW12                0.20833001 W
PLW13                0.16875000 W
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                   75.4677570 MHz
WDW                          EM
SSB             0
LB                        1.00 Hz
GB              0
PC                        1.40
```



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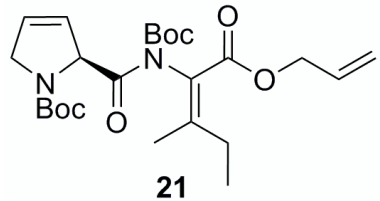
BRUKER

```
Current Data Parameters
NAME      phomo-Boc-Oallyl
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_              20131109
Time                 20.05
INSTRUM              av300
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6188.119 Hz
FIDRES           0.094423 Hz
AQ               5.2953587 sec
RG                     203
DW                80.800 usec
DE                 6.50 usec
TE                293.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 15.00 usec
PLW1          7.50000000 W
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF            300.1300068 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



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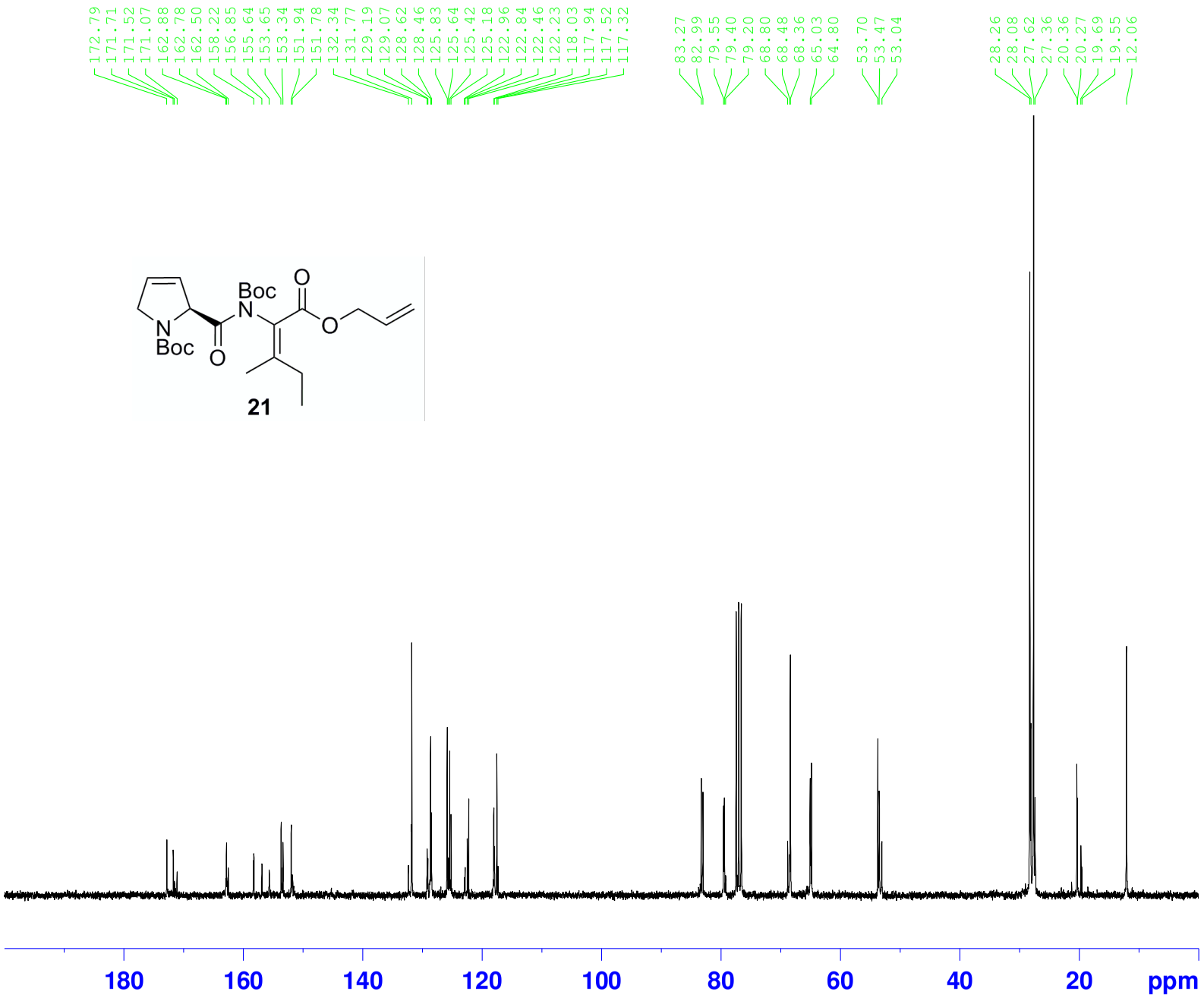

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BRUKER

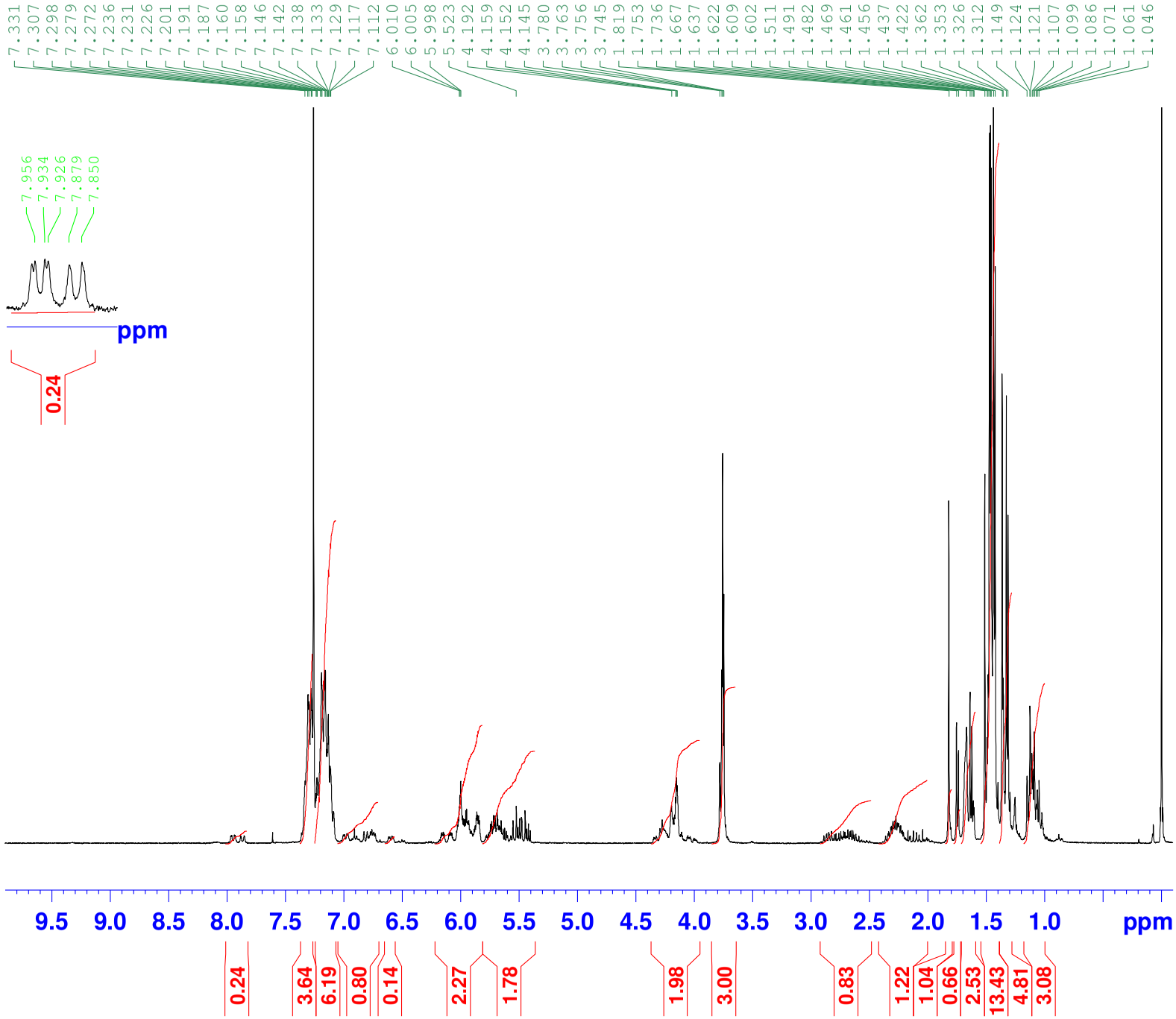
Current Data Parameters
NAME phomo-Boc-Oallyl
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131114
Time 10.57
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 901
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 293.3 K
D1 2.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 38.05099869 W
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 7.50000000 W
PLW12 0.20833001 W
PLW13 0.16875000 W
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677566 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



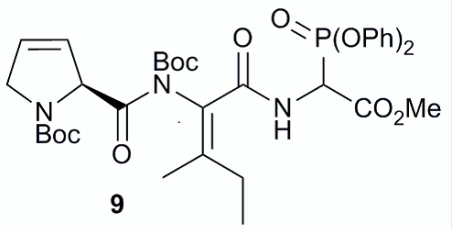
BRUKER

```
Current Data Parameters
NAME                  15-59
EXPNO                    20
PROCNO                    1

F2 - Acquisition Parameters
Date_              20131118
Time                  16.37
INSTRUM               av300
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                      203
DW                 80.800 usec
DE                  6.50 usec
TE                  292.7 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  15.00 usec
PLW1           7.50000000 W
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1300062 MHz
WDW                     EM
SSB       0
LB                   0.30 Hz
GB        0
PC                    1.00
```



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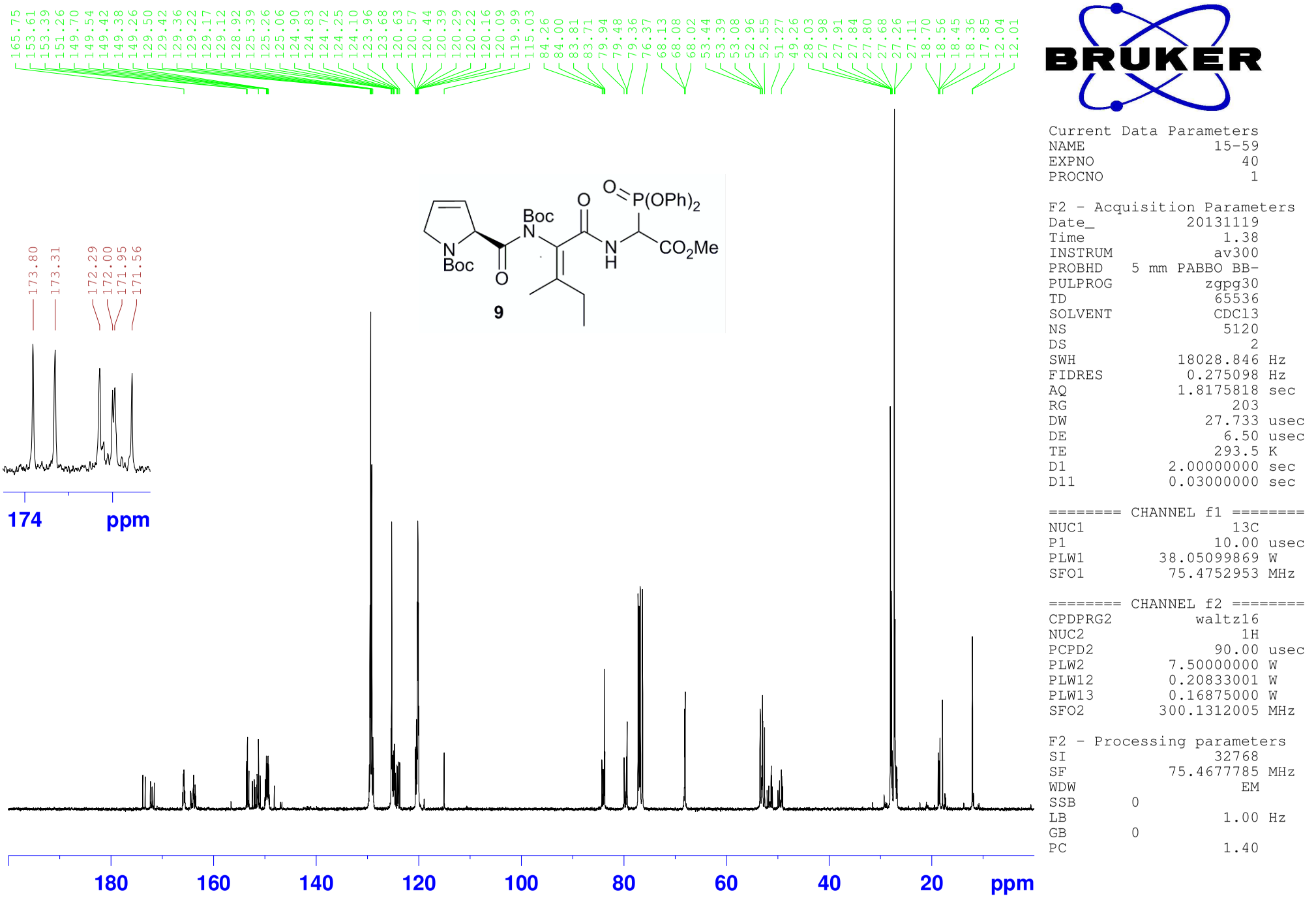


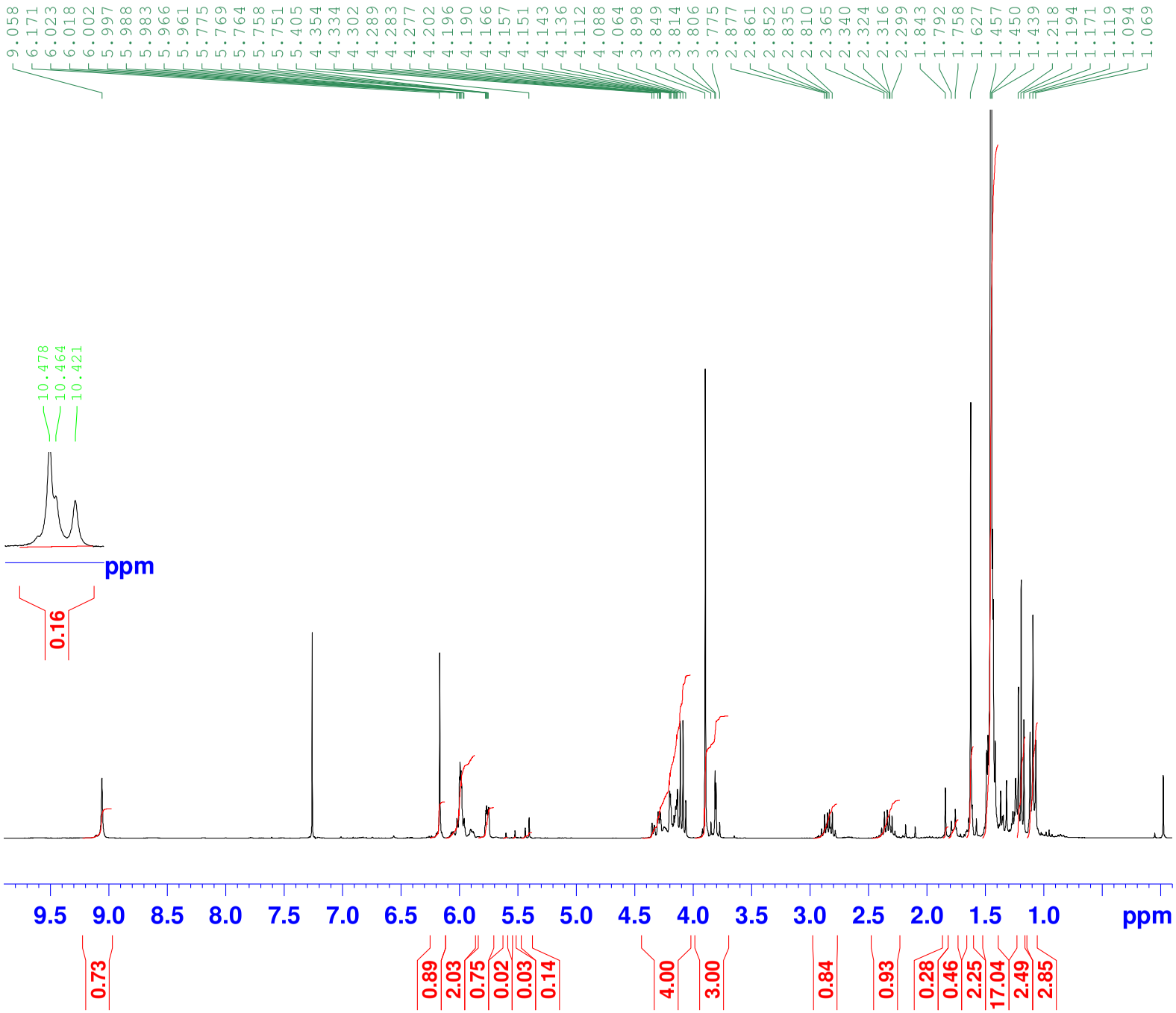
Current Data Parameters
NAME 15-59
EXPNO 40
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131119
Time 1.38
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5120
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 293.5 K
D1 2.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 38.05099869 W
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 7.50000000 W
PLW12 0.20833001 W
PLW13 0.16875000 W
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677785 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



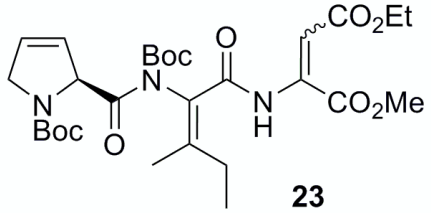
BRUKER

```
Current Data Parameters
NAME      phomo-tripeptide
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_              20131221
Time                 15.09
INSTRUM              av300
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH               6188.119 Hz
FIDRES            0.094423 Hz
AQ               5.2953587 sec
RG                      32
DW                 80.800 usec
DE                  6.50 usec
TE                 292.7 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  15.00 usec
PLW1           7.50000000 W
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF             300.1300062 MHz
WDW                     EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



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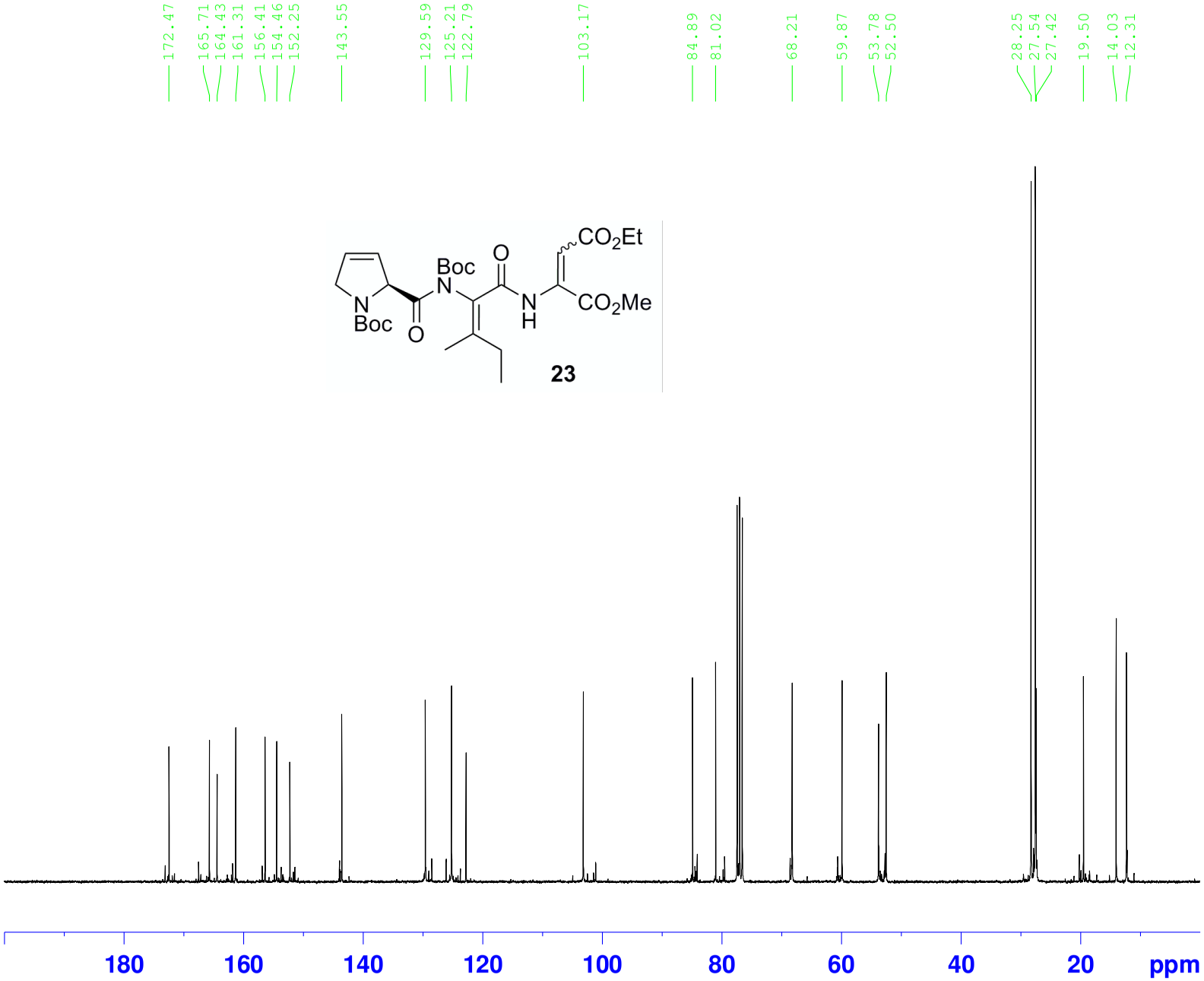


BRUKER

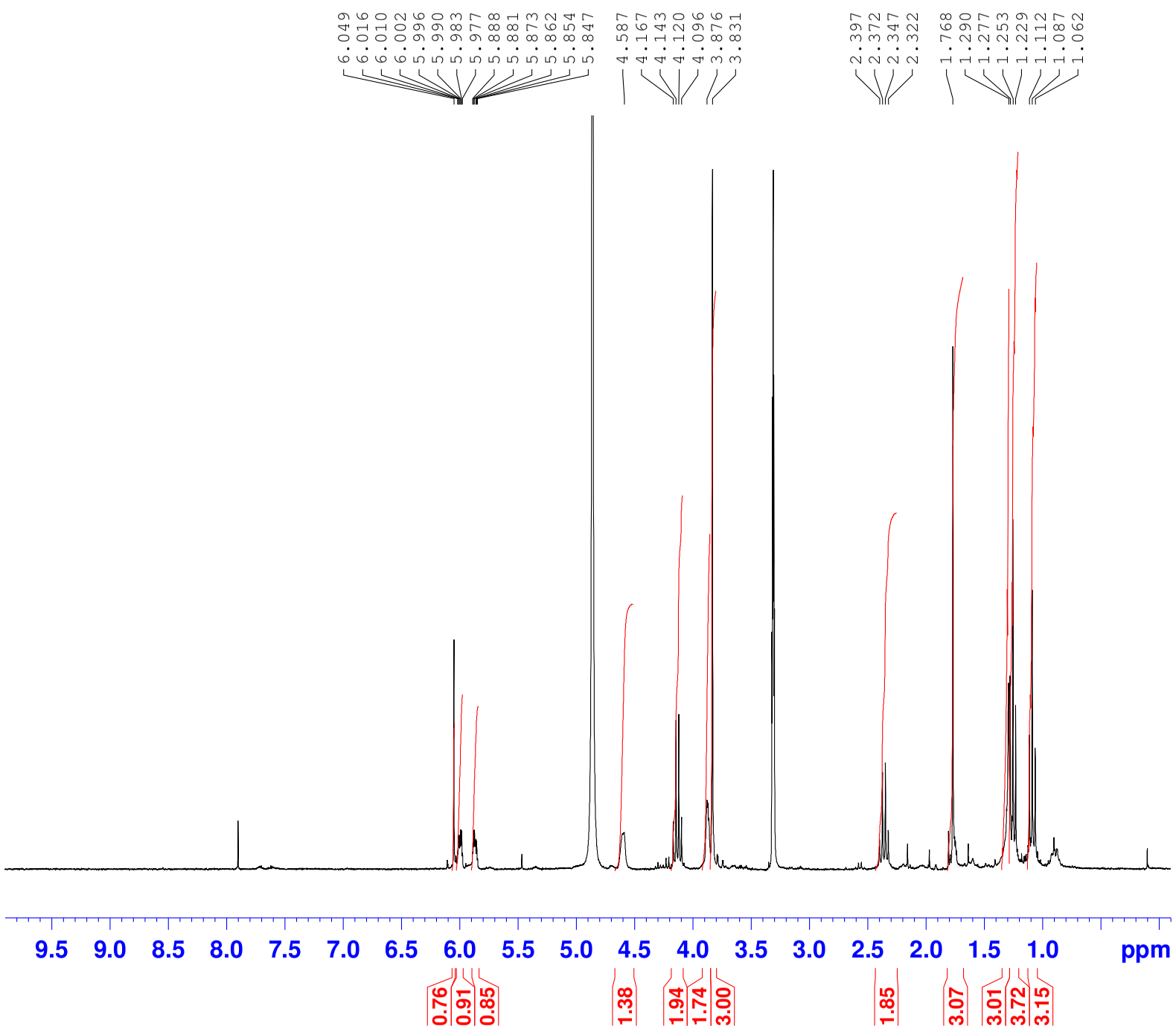
```
Current Data Parameters
NAME                  15-67
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20131128
Time                   8.12
INSTRUM               av300
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     5000
DS                        2
SWH             18028.846 Hz
FIDRES           0.275098 Hz
AQ               1.8175818 sec
RG                      203
DW                 27.733 usec
DE                  6.50 usec
TE                  293.3 K
D1              2.00000000 sec
D11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                  10.00 usec
PLW1          38.05099869 W
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2               90.00 usec
PLW2           7.50000000 W
PLW12          0.20833001 W
PLW13          0.16875000 W
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF             75.4677559 MHz
WDW                      EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

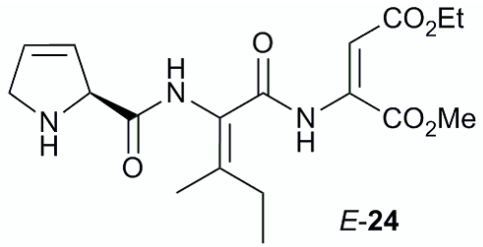


Current Data Parameters
NAME PLC-4
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151011
Time 13.56
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 203
DW 80.800 usec
DE 6.50 usec
TE 294.4 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PLW1 7.50000000 W
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300048 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



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