Synthesis of Amino Acid-Derived Enaminones via Wolff Rearrangement Using Vinylogous Amides as Carbon Nucleophiles

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1. General methods

Unless specified, all reactions were performed under a nitrogen atmosphere in oven-dried glassware. Dry THF and CH_2Cl_2 were dried before use over an activated alumina column. All reagents were used as received. The methods for analysis are as following.

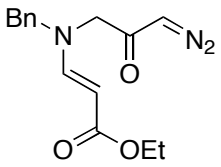
1) TLC analysis was conducted on silica gel 250 μm plates). All diazo ketones and enaminone products were UV-active. Diazoketones and enaminones were also detectible with ninhydrine and $KMnO_4$, respectively.
2) NMR data were recorded using a 400 MHz spectrometer. Chemical shifts are shown as ppm values relative to internal $CHCl_3$ (δ 7.26 for ^1H, δ 77.0 for ^{13}C).
3) Melting points are uncorrected.
4) Optical rotation was measured at 22 °C.

2. General procedure for the preparation of diazoketones

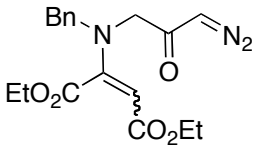
Preparation of substrates was carried out employing 2.0 mmol of amino acids.[1] Generally diazoketones were synthesized from amino acids in one-flask.[2]

> **Warning:** Diazomethane was used for the following transformation. Even in a small scale, proper care should be taken when handling this highly explosive reagent. All glassware used was free of cracks, scratches or ground-glass joints and a blast shield was used.

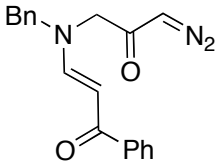
Procedure to synthesize diazoketones:
To a solution of the amino acid and NaOMe (1.0 equiv.) in MeOH (0.33 M), alkyne (1.0 equiv.) was added at 0 °C.[3] The consumption of alkyne was confirmed generally within 20 min. The solvent was evaporated under reduced pressure, affording the acid salt as a slightly yellow solid. The acid salt was re-dissolved in THF (0.2 M) at 0 °C, and ClCOO*i*-Bu (1.0 equiv.) was added. After 30 min, freshly distilled diazomethane (3 equiv), prepared from DIAZALD and KOH in Et_2O was carefully transferred into the solution at once. The reaction mixture was allowed to warm to room temperature, stirred overnight in the dark. The reaction was quenched with aq. AcOH (10 wt%, 1 mL) at 0 °C, followed by addition of water and EtOAc. The partitioned organic layer was washed with aq. 10 wt% H_3PO_4, sat. aq. $NaHCO_3$ and brine, and dried over $MgSO_4$. The filtered organic phase was concentrated *in vacuo*, and subjected to silica gel column chromatography (EtOAc/hexanes), furnishing the diazoketone.



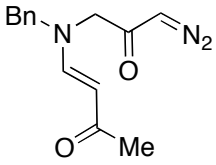
(*E*)-Ethyl 3-(Benzyl(3-diazo-2-oxopropyl)amino)acrylate (1): yellow solid (55% yield); mp: 113.5-113.9 °C; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 1.25 (t, *J* = 7.2 Hz, 3H), 3.75 (s, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.42 (s, 2H), 4.72 (d, *J* = 13.1 Hz, 1H), 5.31 (s, 1H), 7.17-7.22 (m, 2H), 7.28-7.38 (m, 3H), 7.63 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*: 14.5, 53.8, 56.1 (determined by HMQC), 59.3, 59.5 (determined by HMQC), 87.8, 127.8, 128.3, 129.0, 135.3, 151.7, 169.1, 190.1; IR (neat, cm^{-1}): 1144, 1370, 1612, 1685, 2109; HRMS (ESI) calcd for $C_{15}H_{18}N_3O_3$ $(M + H)^+$ 288.1348, found 288.1353.



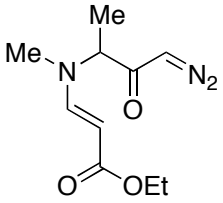
Diethyl 2-(Benzyl(3-diazo-2-oxopropyl)amino)but-2-enedioate (3): yellow solid (53% yield); mp: 78.1-79.9 °C; single isomer by NMR, stereochemistry not determined. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.24 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 3.75 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 4.37-4.44 (m, 4H), 4.75 (s, 1H), 5.49 (s, 1H), 7.23-7.28 (m, 2H), 7.28-7.39 (m, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*: 13.8, 14.3, 54.0, 55.3, 56.1, 59.7, 62.5, 88.0, 127.8, 128.3, 129.0, 134.7, 153.9, 165.3, 167.0, 190.0; IR (neat, cm^{-1}): 1148, 1376, 1579, 1646, 1694, 1735, 2110; HRMS (ESI) calcd for $C_{18}H_{22}N_3O_5$ $(M + H)^+$ 360.1559, found 360.1566.



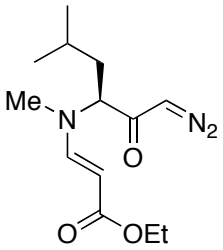
(*E*)-3-(Benzyl(3-diazo-2-oxopropyl)amino)-1-phenylprop-2-en-1-one (5): yellow oil (46% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 3.89 (s, 2H), 4.55 (s, 2H), 5.34 (s, 1H), 5.70-6.20 (bs, 1H), 7.21-7.27 (m, 2H), 7.31-7.51 (m, 6H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.91-8.12 (bs, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*:54.0, 55.2, 61.1, 94.4, 127.6, 127.9, 128.2, 128.4, 129.0, 131.4, 134.9, 139.7, 153.2, 189.2, 189.5; IR (neat, cm^{-1}): 1200, 1368, 1548, 1581, 1644, 2109; HRMS (ESI) calcd for $C_{19}H_{18}N_3O_2$ $(M + H)^+$ 320.1399, found 320.1393.



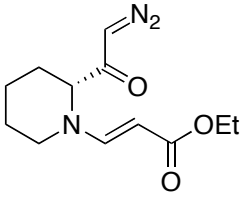
(*E*)-4-(Benzyl(3-diazo-2-oxopropyl)amino)but-3-en-2-one (7): yellow oil (33% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 2.10 (s, 3H), 3.77 (s, 2H), 4.44 (s, 2H), 5.20 (bs, 1H), 5.30 (s, 1H), 7.16-7.21 (d, *J* = 7.2 Hz, 2H), 7.27-7.38 (m, 3H), 7.63 (d, *J* = 12.1 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*:28.5, 53.8, 54.9, 60.6, 98.9, 127.8, 128.3, 129.0, 135.0, 151.5, 189.4, 195.9; IR (neat, cm^{-1}): 1265, 1363, 1563, 1607, 1652, 2108; HRMS (ESI) calcd for $C_{14}H_{16}N_3O_2$ $(M + H)^+$ 258.1243, found 258.1240.



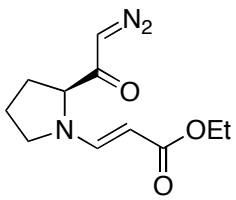
(*E*)-Ethyl 3-((4-Diazo-3-oxobutan-2-yl)(methyl)amino)acrylate (9): yellow oil (31% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.23 (t, J = 7.1 Hz, 3H), 1.38 (d, J = 7.1 Hz, 3H), 2.70 (s, 3H), 3.90 (bd, J = 6.7 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 4.67 (d, J = 13.0 Hz, 1H), 5.35 (s, 1H), 7.46 (d, J = 13.0 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 14,4, 14.5, 33.5, 53.8, 59.1, 66.7, 87.2, 151.0, 169.1, 192.8; IR (neat, cm^{-1}): 1052, 1095, 1155, 1224, 1349, 1610, 1686, 2109, 2981; HRMS (ESI) calcd for $C_{10}H_{16}N_3O_3$ $(M + H)^+$ 226.1192, found 226.1182.



(*S*,*E*)-Ethyl 3-((1-Diazo-5-methyl-2-oxohexan-3-yl)(methyl)amino)acrylate (11): yellow oil (45% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (d, J = 6.5 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 1.43-1.57 (m, 1H), 1.61-1.77 (m, 2H), 2.70 (s, 3H), 3.79 (bs, 1H), 4.12 (q, J = 7.1 Hz, 2H), 4.68 (d, J = 13.0 Hz, 1H), 5.32 (s, 1H), 7.47 (d, J = 13.0 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 14.5, 21.4, 23.1, 24.4, 32.9, 36.8, 54.1, 59.1, 70.2, 86.9, 151.6, 169.2, 192.6; IR (neat, cm^{-1}): 1130, 1156, 1222, 1344, 1609, 1686, 2107, 2958; $[\alpha]_D$= −377 (c = 0.981 in $CHCl_3$); HRMS (ESI) calcd for $C_{13}H_{22}N_3O_3$ $(M + H)^+$ 268.1661, found 268.1662.

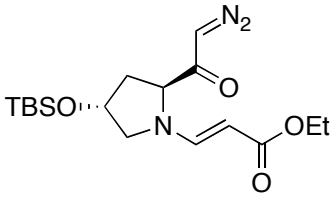


(*R*,*E*)-Ethyl 3-(2-(2-Diazoacetyl)piperidin-1-yl)acrylate (13): yellow oil (42% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.25 (t, J = 7.1 Hz, 3H), 1.34-1.75 (m, 5H), 2.33-2.36 (bd, J = 13.4 Hz,1H), 3.18 (bs, 1H), 3.39-3.42 (d, J = 12.9 Hz, 1H), 3.99 (d, J = 4.4 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 4.72 (d, J = 13.2 Hz, 1H), 5.42 (s, 1H) 7.43 (d, J = 13.2 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 14.5, 20.1, 24.6, 25.6, 48.0, 54.1, 59.2, 64.3, 86.0, 152.2, 169.4, 192.9; IR (neat, cm^{-1}): 1144, 1369, 1607, 1686, 2106; $[\alpha]_D$= −402 (c = 1.02 in $CHCl_3$); HRMS (ESI) calcd for $C_{12}H_{18}N_3O_3$ $(M + H)^+$ 252.1348, found 252.1350.

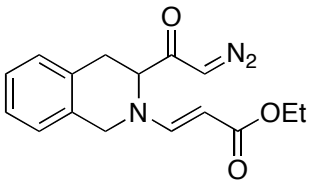


(*S*,*E*)-Ethyl 3-(2-(2-Diazoacetyl)pyrrolidin-1-yl)acrylate (15): yellow oil (52% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.25 (t, J = 7.1 Hz, 3H), 1.90-2.01 (m, 2H), 2.08-2.28 (m, 2H), 3.15-3.60 (bm, 2H), 4.03 (bs, 1H), 4.08-4.17 (m, 2H), 4.63 (d, J = 13.1 Hz , 1H), 5.37 (s, 1H), 7.56 (d, J = 13.1 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 14.5, 23.7, 30.9, 49.2, 53.6, 59.1, 68.1, 88.5, 147.8, 168.9, 194.6; IR (neat, cm^{-1}):

1143, 1364, 1609, 1686, 2107; $[\alpha]_D$= −302 (*c* = 0.990 in $CHCl_3$); HRMS (ESI) calcd for $C_{11}H_{16}N_3O_3$ $(M + H)^+$ 238.1192, found 238.1186.



(*E*)-Ethyl 3-((2*S*,4*R*)-4-(*tert*-Butyldimethylsilyloxy)-2-(2-diazoacetyl)pyrrolidin-1-yl)acrylate (17): yellow oil (40% yield); ^1H NMR (400 MHz, $CDCl_3$) *δ*: 0.05 (d, *J* = 3.0 Hz, 6H), 0.85 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 3H), 2.06-2.16 (m, 1H), 2.17-2.29 (m, 1H), 3.18 (d, *J* = 10.2 Hz, 1H), 3.57 (bd, *J* = 6.4 Hz, 1H), 4.07-4.20 (m, 3H), 4.40-4.48 (m, 1H), 4.61 (d, *J* = 13.2 Hz, 1H), 5.38 (s, 1H), 7.50 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*: −4.9, −4.8, 14.5, 18.0, 25.7, 40.2, 53.5, 58.9, 59.2, 66.2, 70.0, 88.8, 148.4, 168.9, 194.0; IR (neat, cm^{-1}): 777, 838, 1145, 1252, 1363, 1616, 1685, 2108, 2857, 2930, 2955; $[\alpha]_D$= −134 (*c* = 1.02 in $CHCl_3$); HRMS(ESI) calcd for $C_{17}H_{30}N_3O_4Si$ $(M + H)^+$ 368.2006, found 368.2003.

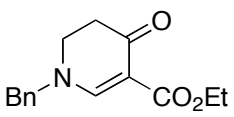


(*E*)-Ethyl 3-(3-(2-Diazoacetyl)-3,4-dihydroisoquinolin-2(1*H*)-yl)acrylate (19): yellow syrup (48% yield)); ^1H NMR (400 MHz, $CDCl_3$) *δ*: 1.28 (t, *J* = 7.1 Hz, 3H), 3.09-3.18 (dd, *J* = 6.0, 15.5 Hz, 1H), 3.30-3.40 (bd, *J* = 15.5 Hz, 1H), 4.10-4.25 (m, 3H), 4.38 (s, 2H), 4.84 (d, *J* = 13.2 Hz, 1H), 5.20 (s, 1H), 7.09-7.25 (m, 4H), 7.60 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*: 14.5, 31.1, 48.0, 54.3, 59.3, 64.8, 88.1, 126.0, 127.1, 127.5, 128.5, 131.2, 131.9, 150.9, 168.8, 193.2; IR (neat, cm^{-1}): 752, 795, 1048, 1152, 1352, 1609, 1683, 2109, 2980; HRMS (ESI) calcd for $C_{16}H_{18}N_3O_3$ $(M + H)^+$ 300.1348, found 300.1341.

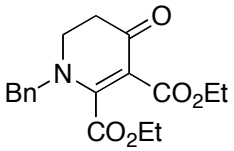
3. General procedure for cyclization via Wolff rearrangement

To a solution of the diazoketone (0.1 mmol) in CH_2Cl_2 (0.5 mL), $PhCO_2Ag$ (0.01 mmol) was added. Under air, the flask was sealed with a septum. The reaction was stirred for 24 h in the dark. Then the crude mixture was directly subjected to silica gel column chromatography (20% acetone/CH_2Cl_2 to 1-3%MeOH/CH_2Cl_2), affording the enaminone.

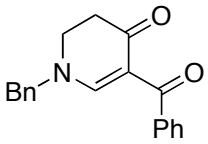
To synthesize enaminone **16**, Ag_2O and $C_2H_4Cl_2$ were used as catalyst and solvent respectively. For the synthesis of enaminone **8**, 20 mol% of $PhCO_2Ag$ was employed.



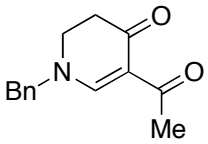
Ethyl 1-Benzyl-4-oxo-1,4,5,6-tetrahydropyridine-3-carboxylate (2): clear oil (99% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.32 (t, J = 7.1 Hz, 3H), 2.50 (dd, J = 7.6, 7.8 Hz, 2H), 3.45 (dd, J = 7.6, 7.8 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 4.55 (s, 2H), 7.25-7.29 (m, 2H), 7.35-7.44 (m, 3H), 8.32 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 14.5, 35.9, 46.0, 59.9, 61.0, 100.7, 127.7, 128.9, 129.3, 134.0, 159.4, 165.4, 186.4; IR (neat, cm^{-1}): 1053, 1152, 1600, 1659, 1716; HRMS (ESI) calcd for $C_{15}H_{18}NO_3$ $(M + H)^+$ 260.1287, found 260.1290.



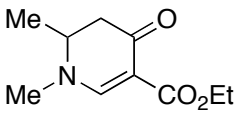
Diethyl 1-Benzyl-4-oxo-1,4,5,6-tetrahydropyridine-2,3-dicarboxylate (4): clear oil (80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.27-1.36 (m, 6H), 2.46 (t, J = 7.6 Hz, 2H), 3.50 (t, J = 7.4 Hz , 2H), 4.26 (q, J = 7.1 Hz, 2H), 4.40 (q, J = 7.2 Hz, 2H), 4.48 (s, 2H), 7.31-7.43 (m, 5H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 13.8, 14.4, 35.5, 47.0, 57.2, 60.5, 62.8, 100.6, 127.9, 128.8, 129.2, 134.0, 160.2, 163.6, 165.3, 186.8; IR (neat, cm^{-1}): 1154, 1256, 1377, 1452, 1550, 1669, 1739, 2981; HRMS (ESI) calcd for $C_{18}H_{22}NO_5$ $(M + H)^+$ 332.1498, found 332.1494.



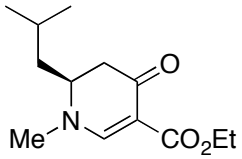
5-Benzoyl-1-benzyl-2,3-dihydropyridin-4(1*H*)-one (6): white solid (88% yield); mp: 81.7-83.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.54 (t, J = 7.6 Hz, 2H), 3.45 (t, J = 7.6 Hz, 2H), 4.59 (s, 2H), 7.27-7.32 (d, J = 6.4 Hz, 2H), 7.34-7.49 (m, 6H), 7.65 (d, J = 7.0 Hz, 2H), 8.26 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 35.6, 46.2, 61.1, 110.2, 127.6, 127.8, 128.9, 129.0, 129.3, 131.2, 133.9, 140.1, 159.6, 186.7, 192.5; IR (neat, cm^{-1}): 1188, 1337, 1583, 1623, 1652; HRMS (ESI) calcd for $C_{19}H_{18}NO_2$ $(M + H)^+$ 292.1338, found 292.1332.



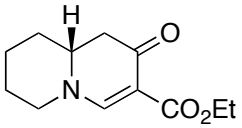
5-Acetyl-1-benzyl-2,3-dihydropyridin-4(1*H*)-one (8): clear oil (93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.49 (m, 5H), 3.46 (dd, J = 7.6, 7.8 Hz , 2H), 4.57 (s, 2H), 7.24-7.28 (m, 2H), 7.35-7.45 (m, 3H), 8.44 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 30.5, 35.7, 46.2, 61.3, 110.0, 127.8, 129.0, 129.3, 133.8, 159.2, 188.0, 195.3; IR (neat, cm^{-1}): 1045, 1325, 1361, 1387, 1577, 1636, 2922; HRMS (ESI) calcd for $C_{14}H_{16}NO_2$ $(M + H)^+$ 230.1181, found 230.1183.



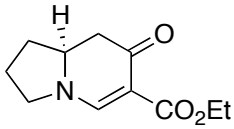
(*S*)-Ethyl 1,6-Dimethyl-4-oxo-1,4,5,6-tetrahydropyridine-3-carboxylate (10): clear oil (93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.27 (m, 6H), 2.27 (dd, *J* = 3.7, 15.9 Hz , 1H), 2.79 (dd, *J* = 6.7, 15.9 Hz, 1H), 3.22 (s, 3H), 3.65 (m, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 8.02 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*: 14.5, 15.5, 42.1, 42.7, 54.7, 59.8, 99.6, 158.5, 165.4, 185.9; IR (neat, cm^{-1}): 1055, 1173, 1279, 1303, 1332, 1383, 1426, 1606,1652, 1714, 2975; HRMS (ESI) calcd for $C_{10}H_{16}NO_3$ $(M + H)^+$ 198.1130, found 198.1128.



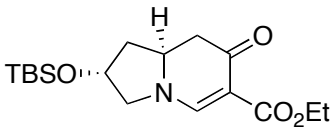
(*S*)-Ethyl 6-Isobutyl-1-methyl-4-oxo-1,4,5,6-tetrahydropyridine-3-carboxylate (12): clear oil (76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.86 (d, *J* = 6.4 Hz, 3H), 0.92 (d, *J* = 6.3 Hz , 3H), 1.26-1.42 (m, 4H), 1.59-1.72 (m, 2H), 2.36 (dd, *J* = 2.2, 15.9 Hz, 1H), 2.78 (dd, *J* = 6.7, 15.9 Hz, 1H), 3.23 (s, 3H), 3.46-3.55 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 8.03 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*: 14.5, 21.1, 23.4, 24.1, 37.1, 39.5, 42.6, 57.4, 59.8, 99.4, 158.6, 165.3, 185.7; IR (neat, cm^{-1}): 1047, 1061, 1174, 1296, 1330, 1396, 1603, 1655, 1716, 2957; $[\alpha]_D$= −38 (*c* = 0.95 in $CHCl_3$); HRMS (ESI) calcd for $C_{13}H_{22}NO_3$ $(M + H)^+$ 240.1600, found 240.1605.



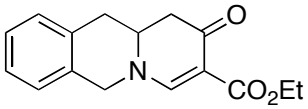
(*R*)-Ethyl 2-Oxo-2,6,7,8,9,9a-hexahydro-1*H*-quinolizine-3-carboxylate (14): white solid (93% yield); mp: 55.8-57.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.30 (t, *J* = 7.1 Hz, 3H), 1.40-1.79 (m, 3H), 1.79-1.95 (m, 3H), 2.41 (dd, *J* = 10.8, 16.2 Hz, 1H), 2.64 (dd, *J* = 6.2, 16.2 Hz, 1H), 3.27 (dt, *J* = 2.9, 12.8 Hz, 1H), 3.46-3.57 (m, 1H), 3.59-3.67 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 8.02 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*:14.5, 22.9, 25.9, 31.8, 43.3, 54.4, 56.8, 59.8, 100.5, 159.1, 165.3, 186.7; IR (neat, cm^{-1}): 1153, 1306, 1595, 1663, 1719, 2937; $[\alpha]_D$= −16 (*c* = 0.96 in $CHCl_3$); HRMS (ESI) calcd for $C_{12}H_{18}NO_3$ $(M + H)^+$ 224.1287, found 224.1282.



(***S*)-Ethyl 7-Oxo-1,2,3,7,8,8a-hexahydroindolizine-6-carboxylate (16):** yellow oil (86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.30 (t, *J* = 7.1 Hz, 3H), 1.64-1.78 (m, 1H), 1.91-2.06 (m, 1H), 2.12-2.22 (m, 1H), 2.30-2.42 (m, 2H), 2.56 (dd, *J* = 4.6, 15.6 Hz, 1H), 3.57-3.68 (m, 1H), 3.70-3.85 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 8.30 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*: 14.5, 24.1, 32.6, 41.9, 50.5, 58.1, 59.6, 100.0, 155.7, 165.4, 187.2; IR (neat, cm^{-1}): 1056, 1145, 1190, 1288, 1599, 1651, 1716, 2977; $[\alpha]_D$= −574 (*c* = 1.01 in $CHCl_3$); HRMS (ESI) calcd for $C_{11}H_{16}NO_3$ $(M + H)^+$ 210.1130, found 210.1127.

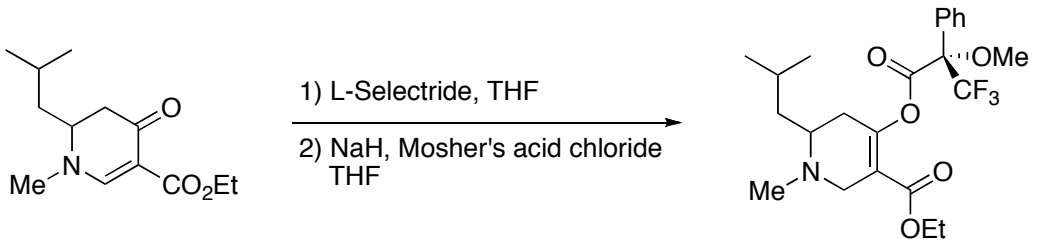


(**2*R*,8a*S*)-Ethyl 2-(*tert*-Butyldimethylsilyloxy)-7-oxo-1,2,3,7,8,8a-hexahydroindolizine-6-carboxylate (18):** yellow oil (79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*:0.07 (d, *J* = 1.0 Hz, 6H), 0.86 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.72-1.82 (m, 1H), 2.22 (dd, *J* = 5.4, 12.7 Hz, 1H), 2.35 (t, *J* = 15.7 Hz, 1H), 2.56 (dd, *J* = 4.6, 15.6 Hz, 1H), 3.56 (d, *J* = 12.2 Hz, 1H), 3.78 (dd, *J* = 4.1, 12.1 Hz, 1H), 4.07-4.20 (m, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.56 (t, *J* = 3.8 Hz, 1H), 8.26 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*: −4.9, −4.8, 14.5, 17.9, 25.7, 29.7, 41.7, 42.2, 56.0, 59.7, 70.3, 100.4, 155.9, 165.4, 187.2; IR (neat, cm^{-1}): 1069, 1191, 1290, 1325, 1374, 1594, 1717, 2857, 2931, 2954; $[\alpha]_D$= −8.9 (*c* = 0.99 in $CHCl_3$); HRMS (ESI) calcd for $C_{17}H_{30}NO_4Si$ $(M + H)^+$ 340.1944, found 340.1933.



Ethyl 2-Oxo-2,6,11,11a-tetrahydro-1*H*-pyrido[1,2-*b*]isoquinoline-3-carboxylate (20): clear oil (81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.30 (t, *J* = 7.1, 3H), 2.57 (dd, *J* = 7.8, 16.3 Hz, 1H), 2.80-2.85 (m, 2H), 3.08-3.15 (dd, *J* = 12.1, 15.8 Hz, 1H), 3.89-3.93 (m, 1H), 4.24 (q, *J* = 7.1, 2H), 4.67 (d, *J* = 15.8, 1H), 4.78 (d, *J* = 15.8, 1H), 7.12-7.19 (m, 2H), 7.25-7.27 (m, 2H), 8.24 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*: 14.5, 33.2, 41.5, 54.3, 55.2, 59.9, 100.5, 125.7, 127.2, 127.9, 128.7, 131.8, 133.3, 158.2, 165.2, 186.0; IR (neat, cm^{-1}): 1052, 1152, 1189, 1304, 1348, 1393, 1456, 1595, 1657, 1715, 2979; HRMS (ESI) calcd for $C_{16}H_{18}NO_3$ $(M + H)^+$ 272.1287, found 272.1287.

4. Determination of *ee* by derivatization using Mosher's acid chloride

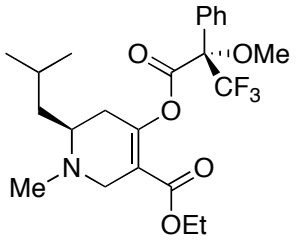


12 (chiral)
12' (racemic)

21 (single diastereomer)
21' (diastereomeric mixture)

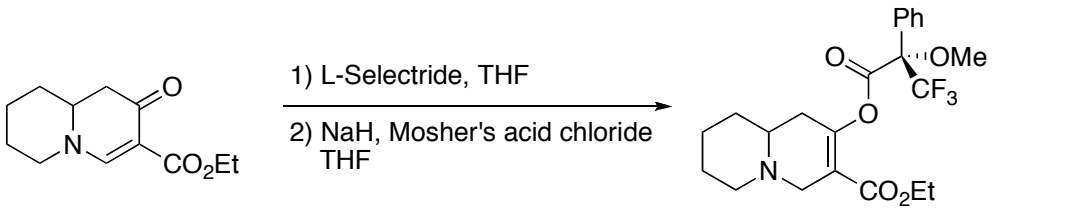
First, racemic enaminone **12'** was prepared. Racemic and enantiopure enaminones were derivatized by the following procedure.

The enaminone (0.1 mmol) was dissolved in THF (1 mL) at − 78 °C. L-Selectride (1.0 M in THF, 1.1 equiv.) was added, and stirring was continued for 3 h at − 78 °C. Acetone (0.5 mL) was added and the solution was warmed to room temperature and evaporated under reduced pressure. The crude mixture was purified by preparative TLC, affording the corresponding enol. The enol was dissolved in THF (0.7 mL) and the solution was cooled to 0 °C. NaH (2 equiv.) was added to the solution, which was stirred for another 10 min. (*R*)-Mosher's acid chloride in THF (0.3 mL) was then added to the reaction mixture. The reaction was warmed to room temperature and left for 2 h with stirring. Water and EtOAc were added to the reaction mixture, and the partitioned organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The crude mixture was purified by preparative TLC, affording the desired Mosher's ester derivative. The diastereomeric mixture **21'** (3.3 mg) was dissolved in $CDCl_3$ (1.2 mL) and the ^{19}F NMR was taken. Slightly overlapping ^{19}F peaks were separated using Gaussian deconvolution. The ^{19}F NMR of compound **21** was also recorded at a similar concentration, and a single ^{19}F peak was observed.



(*S*)-Ethyl 6-Isobutyl-1-methyl-4-((*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyloxy)-1,2,5,6-tetrahydropyridine-3-carboxylate (21): clear oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.87-0.94 (d, J = 6.6 Hz, 6H), 1.19 (t, J = 7.1 Hz, 3H), 1.21-1.27 (m, 1H), 1.40-1.50 (m, 1H), 1.57-1.71 (m, 1H), 2.00-2.11 (m, 1H), 2.22-2.32 (m, 1H), 2.35 (s, 3H), 2.78-2.89 (m, 1H), 3.42-3.57 (dt, J = 2.1, 17.2 Hz, 2H), 3.65 (s, 3H), 4.10 (q, J = 7.1 Hz, 2H), 7.40-7.47 (m, 3H), 7.63-7.69 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 14.1, 22.4, 23.0, 24.7, 29.8, 38.5, 40.3, 51.7, 55.3, 55.7, 60.7, 84.5, 84.8, 117.1, 121.6, 124.5, 127.7, 128.4, 129.8, 131.4, 151.2, 163.9, 164.0; IR (neat, cm^{-1}): 703, 1004, 1045, 1123, 1174, 1236, 1732, 1763, 2930, 2958; $[\alpha]_D$= −0.600 (c = 1.33 in $CHCl_3$); HRMS (ESI) calcd for $C_{23}H_{31}F_3NO_5$ $(M + H)^+$ 458.2154, found 458.2156.

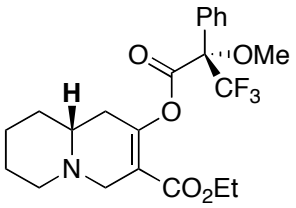
Enaminones **14**, **16** were derivatized similarly.



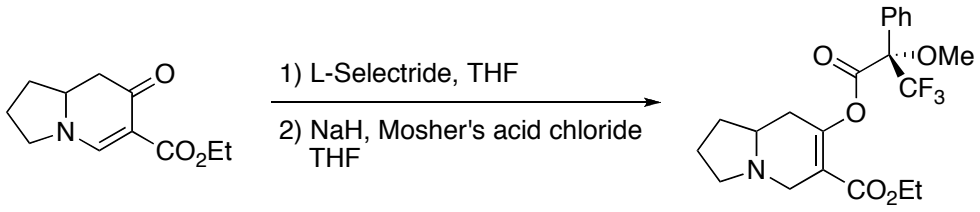
14 (chiral)
14' (racemic)

22 (single diastereomer)
22' (diastereomeric mixture)

The enantiopurity of compound **22** was confirmed by HPLC analysis. The ^{19}FNMR of the compound **22** showed a single ^{19}F peak.



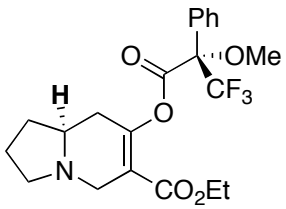
(*R*)-Ethyl 2-((*S*)-3,3,3-Trifluoro-2-methoxy-2-phenylpropanoyloxy)-4,6,7,8,9,9a-hexahydro-1*H*-quinolizine-3-carboxylate (22): clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (t, J = 7.1 Hz, 3H), 1.52-1.81 (m, 6H), 2.04-2.17 (m, 1H), 2.17-2.32 (m, 3H), 2.94-3.07 (m, 2H), 3.63 (s, 3H), 3.68 (d, J = 16.3 Hz, 1H), 4.03-4.16 (m, 2H), 7.41-7.46 (m, 3H), 7.60-7.66 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ:14.1, 23.5, 25.5, 32.7, 35.6, 54.0, 54.8, 55.6, 56.2, 60.8, 84.6, 84.9, 117.2, 121.6, 124.5, 127.8, 128.4, 129.8, 131.3, 151.2, 163.3, 163.7; IR (neat, cm^{-1}): 1048, 1107, 1183, 1239, 1725, 1763, 2937; $[\alpha]_D$= −47 (c = 0.39 in $CHCl_3$); HRMS (ESI) calcd for $C_{22}H_{27}F_3NO_5$ $(M + H)^+$ 442.1841, found 442.1836.; HPLC analysis (Daicel CHIRACEL OD column) solvent system: Heptane/*i*-PrOH, 100/0 to 85/15 over 15 min; retention times: 10.5 min (**22**), 8.1 min (the other diastereomer).



16 (chiral)
16' (racemic)

23 (single diastereomer)
23' (diastereomeric mixture)

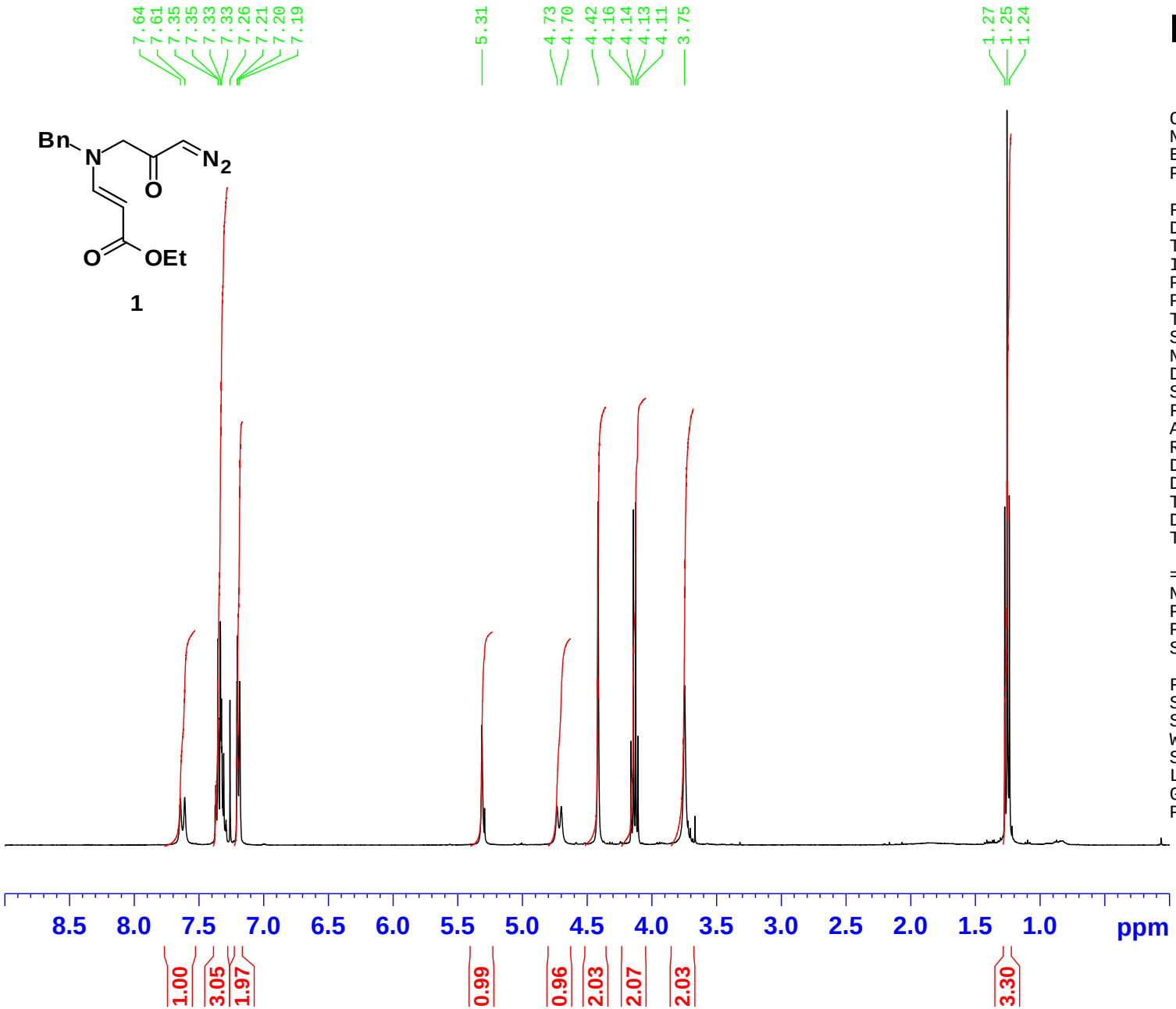
Enantiopurity of compound **23** was confirmed by HPLC analysis. A ^{19}FNMR of compound **23** showed a single ^{19}F peak.



(*S*)-Ethyl 7-((*S*)-3,3,3-Trifluoro-2-methoxy-2-phenylpropanoyloxy)-1,2,3,5,8,8a-hexahydroindolizine-6-carboxylate (23): clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.17 (t, *J* = 7.1 Hz, 3H), 1.41-1.55 (m, 1H), 1.72-2.07 (m, 3H), 2.26 (q, *J* = 9.0 Hz, 1H), 2.30-2.42 (m, 3H), 3.01 (dt, *J* = 3.5, 16.1 Hz, 1H), 3.22 (dt, *J* = 2.2, 8.7 Hz, 1H), 3.63 (s, 3H), 3.91 (d, *J* = 16.1 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 7.41-7.47(m, 3H), 7.62-7.68 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) *δ*: 14.1, 22.0, 30.5, 35.2, 50.9, 53.6, 55.8, 59.3, 60.9, 84.4, 84.7, 118.3, 121.6, 124.4, 127.7, 128.5, 129.9, 131.2, 153.1, 163.5, 164.0; IR (neat, cm^{-1}): 1002, 1056, 1108, 1172, 1234, 1733, 1767; $[\alpha]_D$= −46 (*c* = 0.76 in $CHCl_3$); HRMS (ESI) calcd for $C_{21}H_{25}F_3NO_5$ $(M + H)^+$ 428.1685, found 428.1688.; HPLC analysis (Daicel CHIRACEL OD column) solvent system: Hexanes/*i*-PrOH, 100/0 to 85/15 over 15 min; retention times: 5.3 min (**23**), 9.6 min (the other diastereomer).

5. References and notes

1. Diazoketone **17** was prepared on 1.0 mmol scale in EtOH. TBS protected hydroxyproline was obtained using a reported method. See: Zhang, D.; Yuan, C. *Tetrahedron Lett*. **2008**, *64*, 2480-2488.
2. For substrates from *N*-Bn glycine hydrochloride, NaCl was removed by filtration before diazotization.
3. The alkyne (1-phenylprop-2-yn-1-one) for substrate **5** was obtained using a reported method. See: Chassaing, S.; Kueny-Stotz, M.; Isorez, G.; Brouillard, R. *Eur. J. Org. Chem.* **2007**, 2438-2448.

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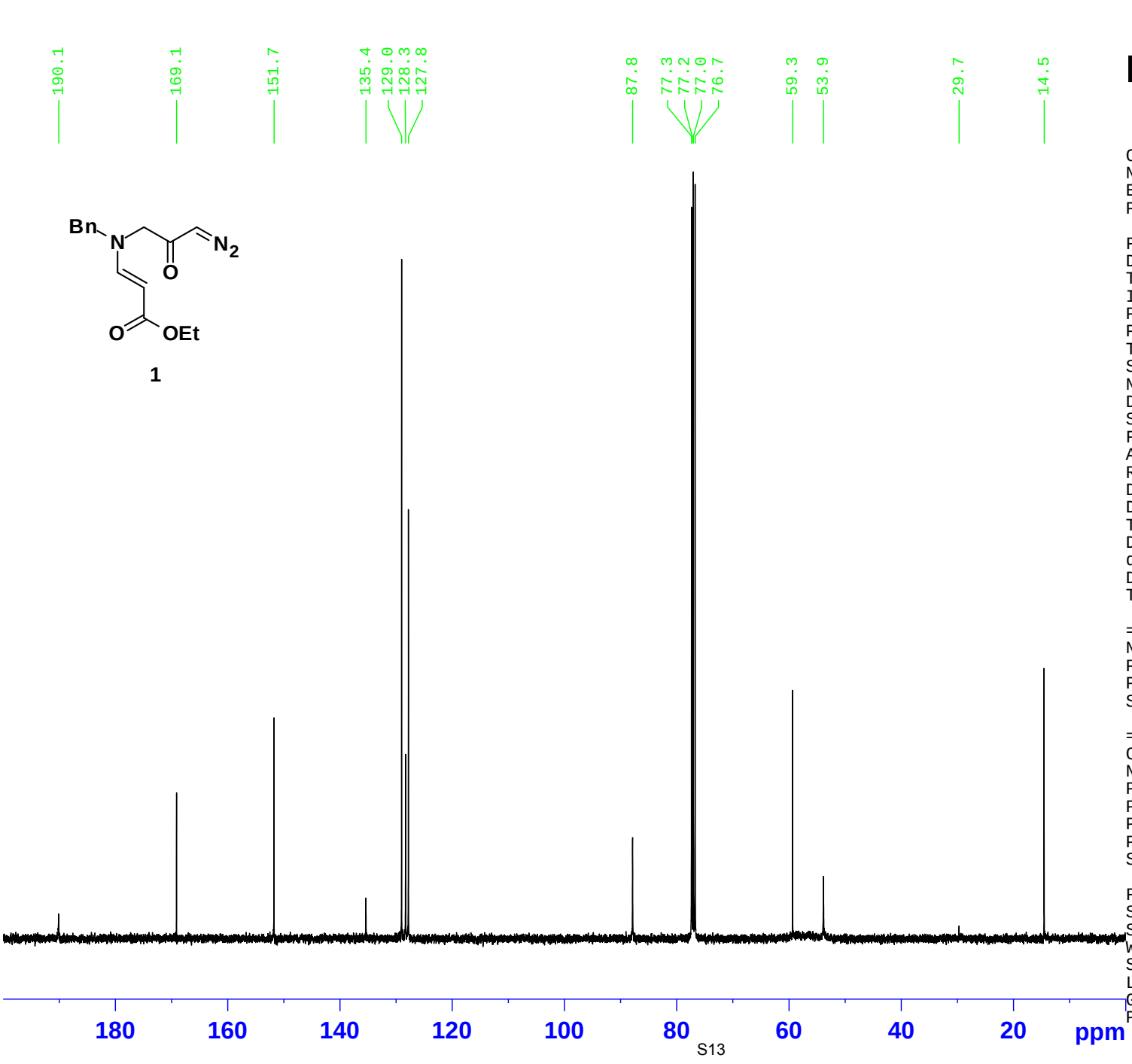

BRUKER

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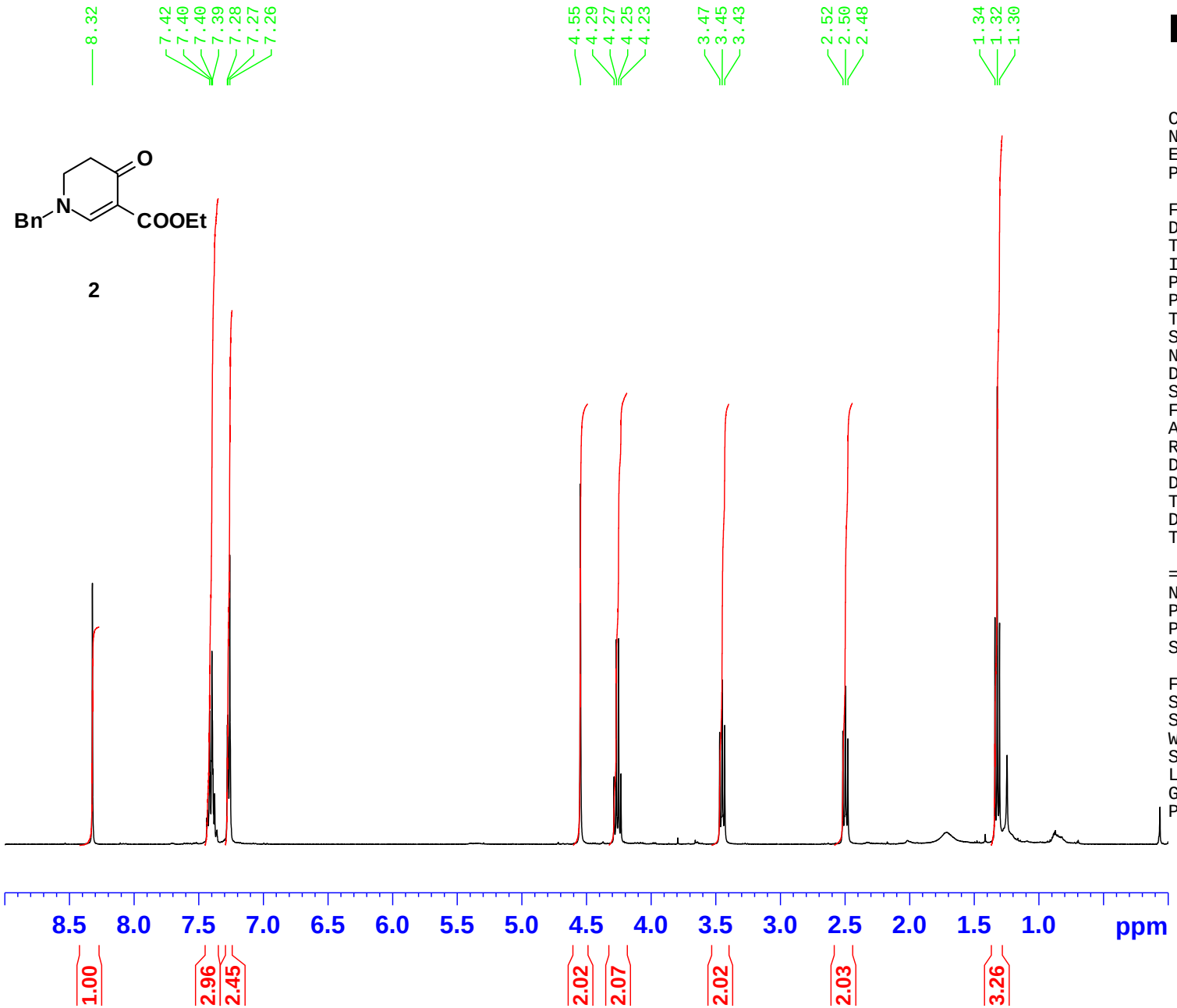

BRUKER

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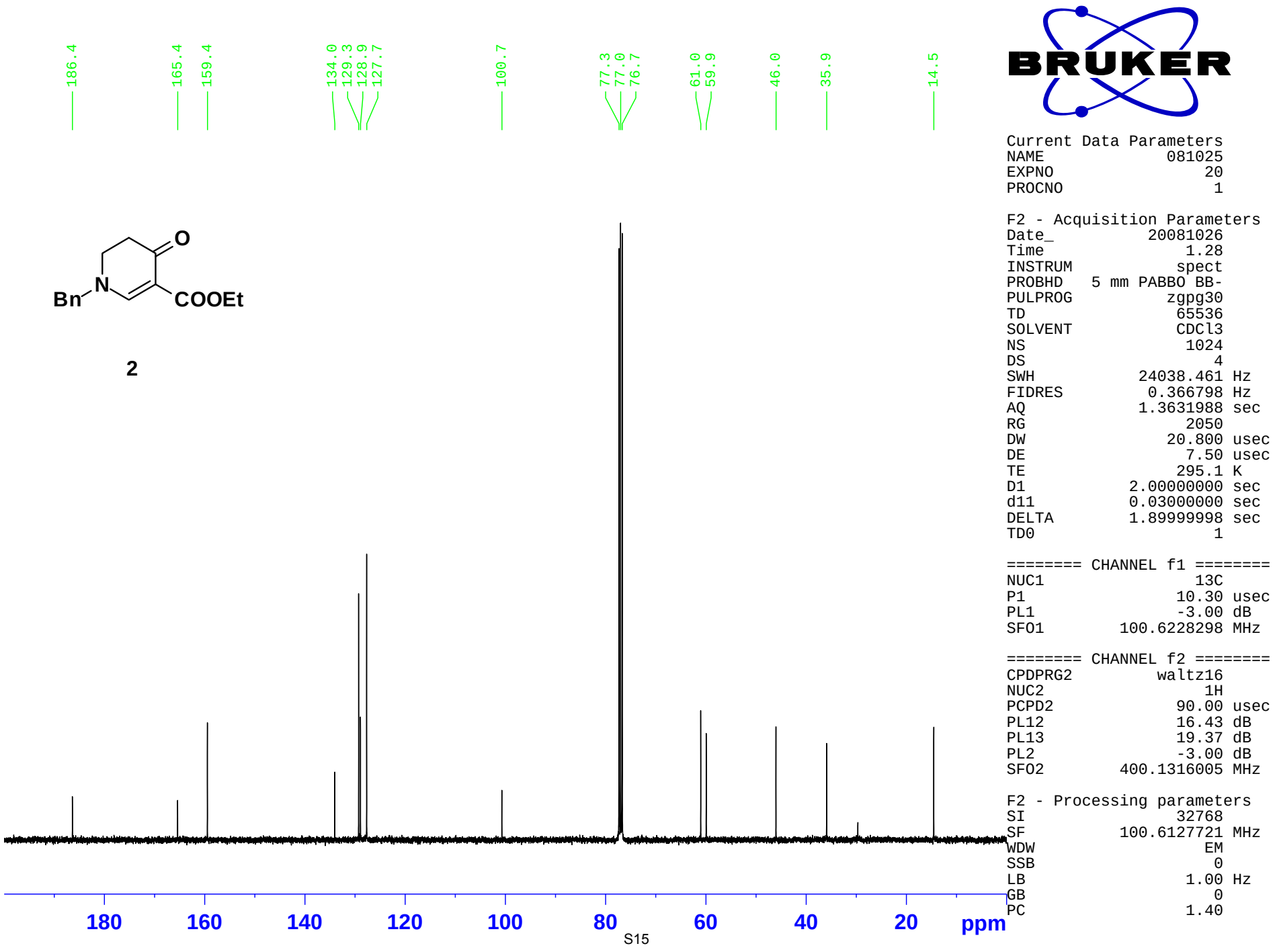
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```



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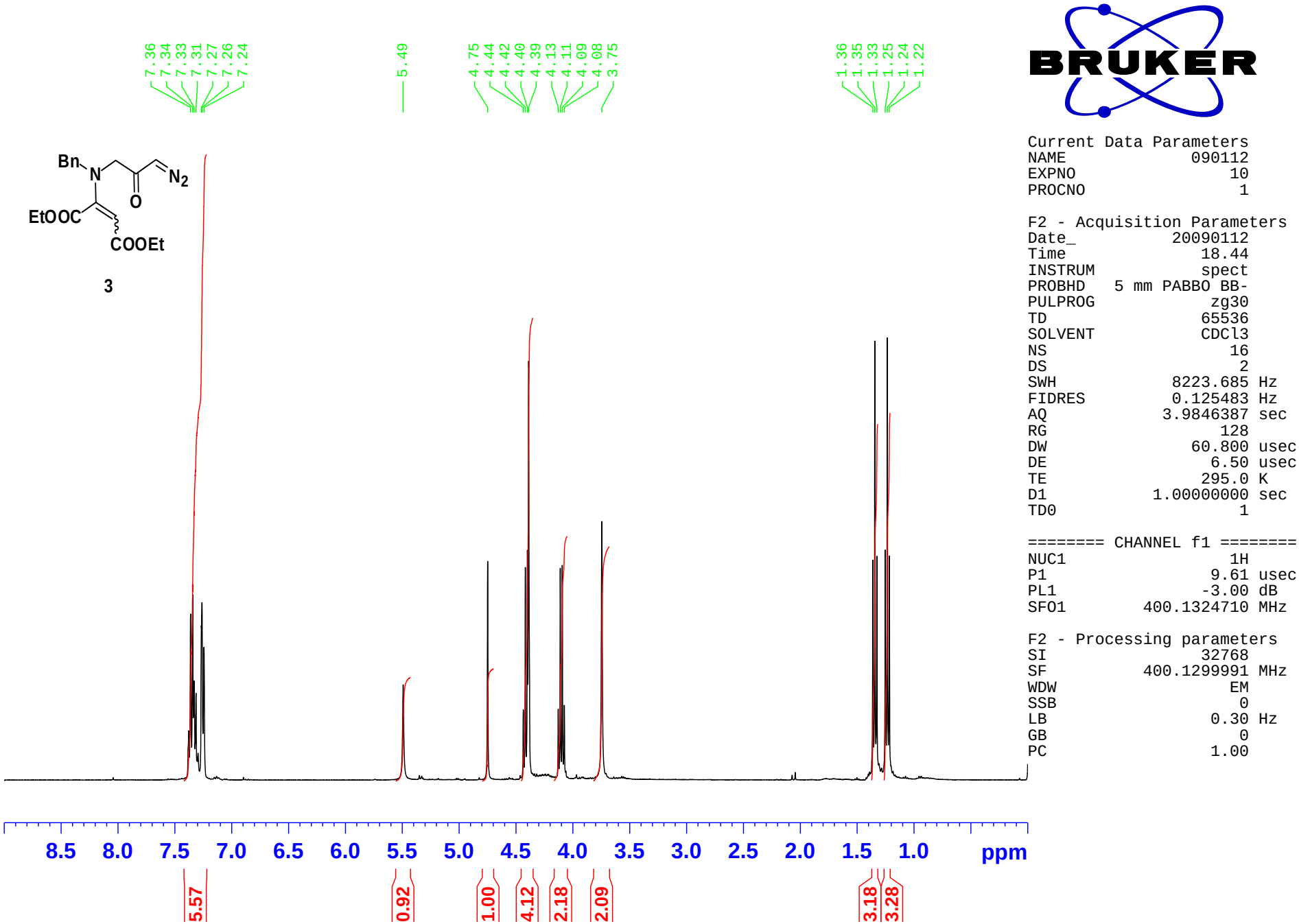
```
Current Data Parameters
NAME                  081025
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081026
Time                   1.28
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     2050
DW                20.800 usec
DE                 7.50 usec
TE                 295.1 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                   10.30 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                     1H
PCPD2                90.00 usec
PL12                 16.43 dB
PL13                 19.37 dB
PL2                  -3.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF             100.6127721 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.40
```

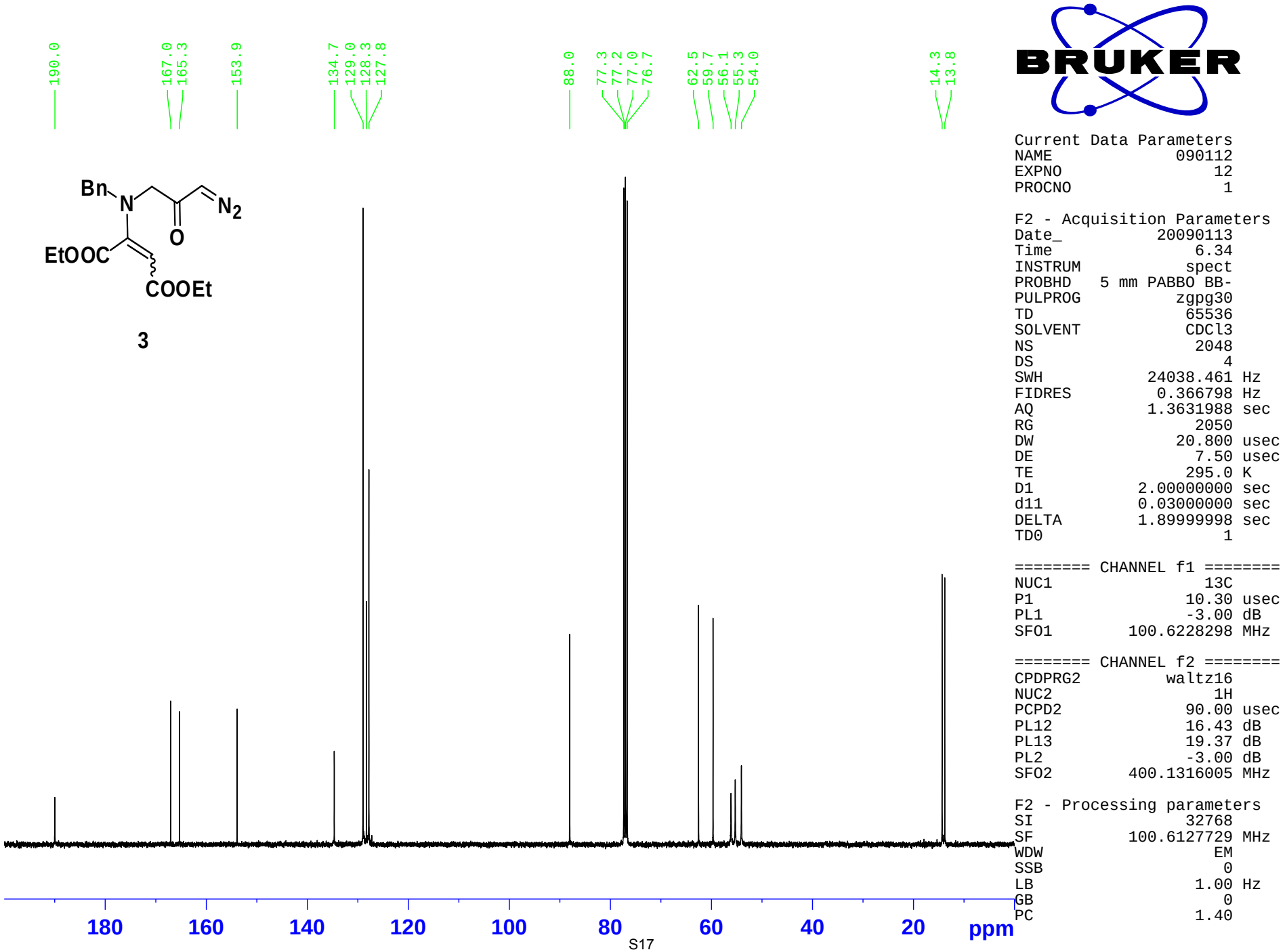



```
Current Data Parameters
NAME                  090112
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090112
Time                  18.44
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      128
DW                   60.800 usec
DE                    6.50 usec
TE                   295.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.61 usec
PL1                   -3.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF             400.1299991 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```




```
Current Data Parameters
NAME                 090112
EXPNO                    12
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090113
Time                   6.34
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                     2050
DW                20.800 usec
DE                 7.50 usec
TE                 295.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                  10.30 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                    1H
PCPD2               90.00 usec
PL12                16.43 dB
PL13                19.37 dB
PL2                 -3.00 dB
SFO2          400.1316005 MHz

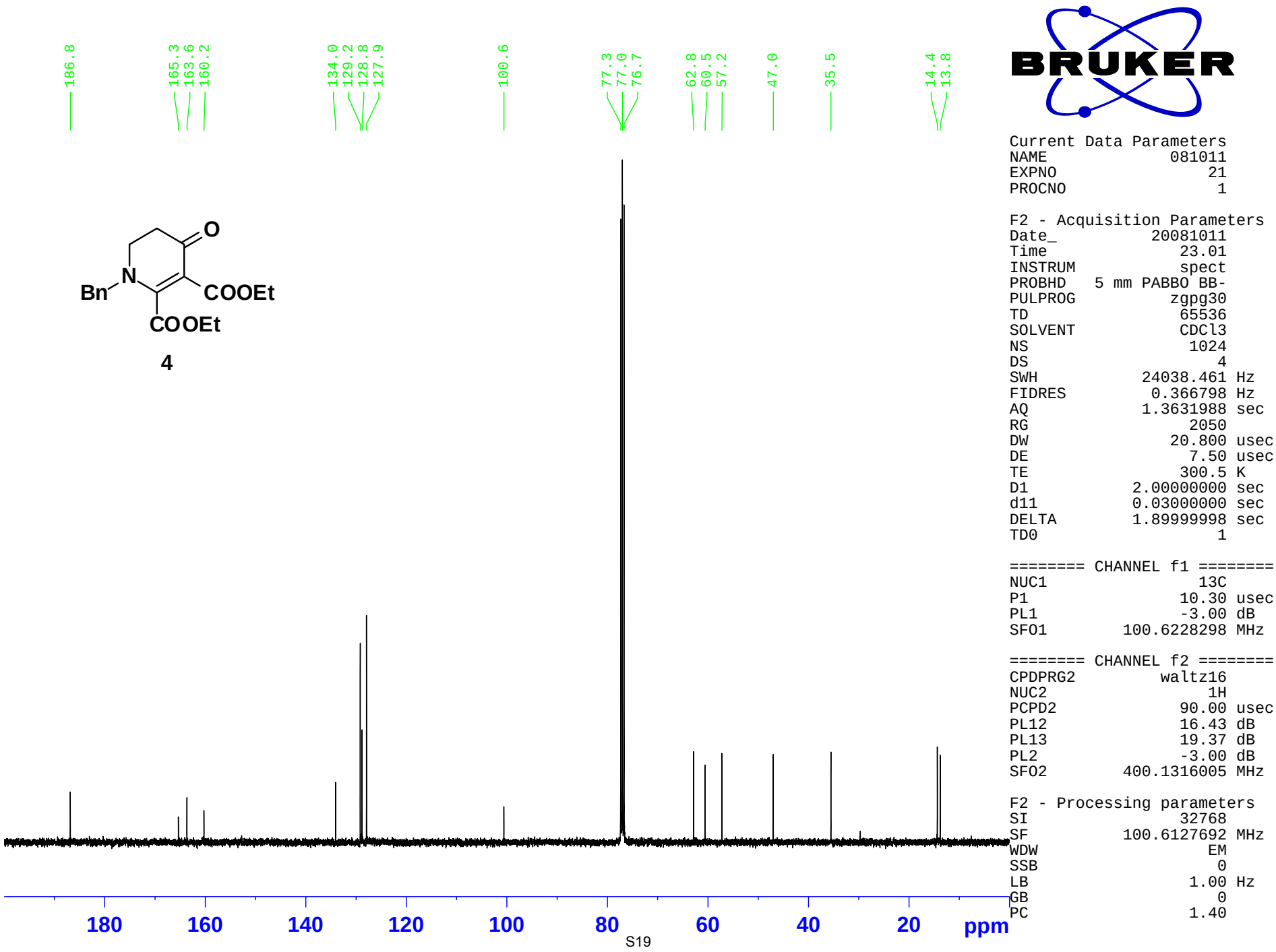
F2 - Processing parameters
SI                    32768
SF            100.6127729 MHz
WDW                      EM
SSB                       0
LB                  1.00 Hz
GB                        0
PC                  1.40
```

```
Current Data Parameters
NAME                  081011
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081011
Time                  14.18
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      322
DW                 60.800 usec
DE                  6.50 usec
TE                  298.6 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   9.61 usec
PL1                 -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300028 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                    1.00
```



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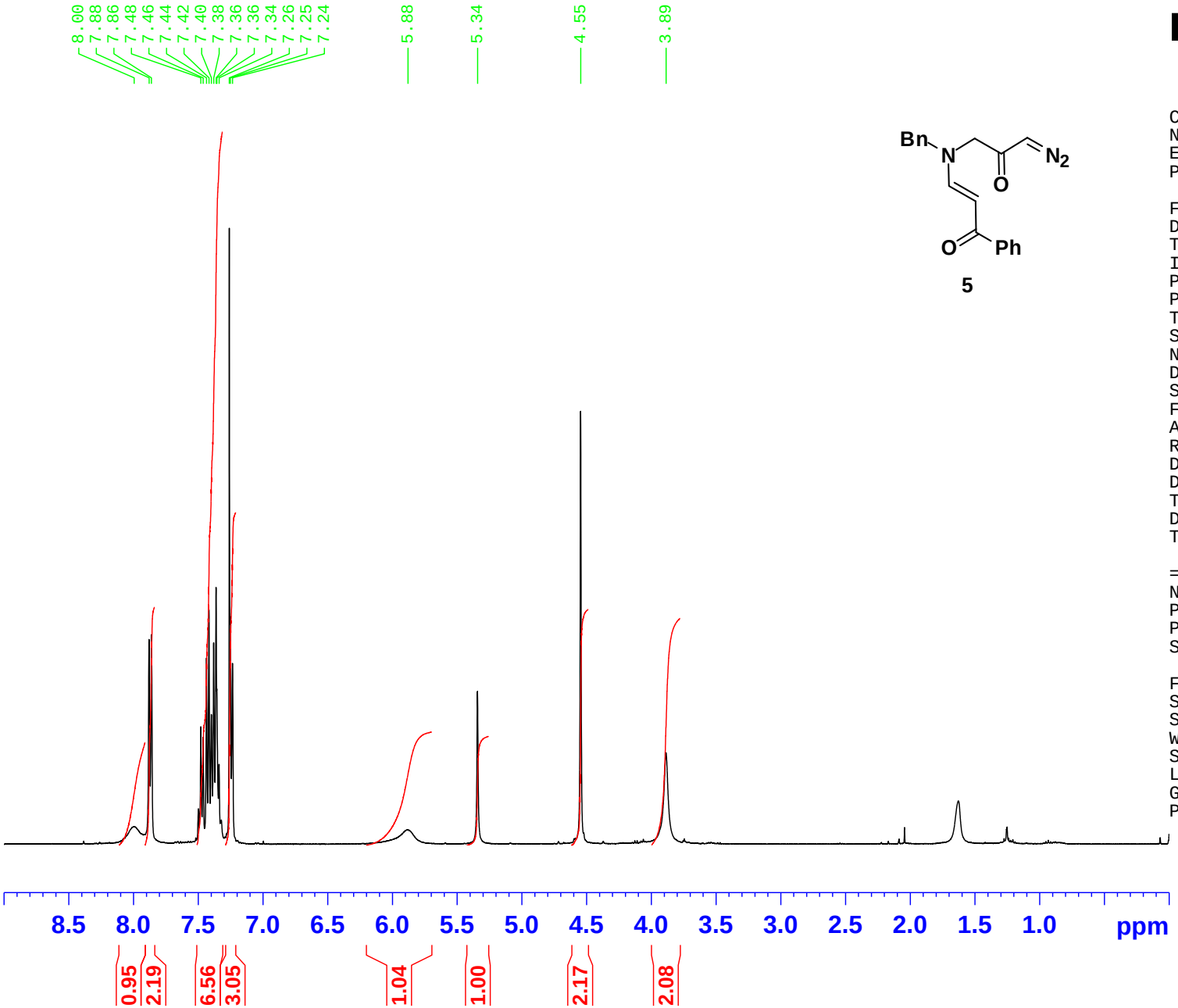
```
Current Data Parameters
NAME                  081011
EXPNO                     21
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081011
Time                  23.01
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     2050
DW                  20.800 usec
DE                   7.50 usec
TE                   300.5 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                   10.30 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                     1H
PCPD2                90.00 usec
PL12                 16.43 dB
PL13                 19.37 dB
PL2                  -3.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF             100.6127692 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.40
```



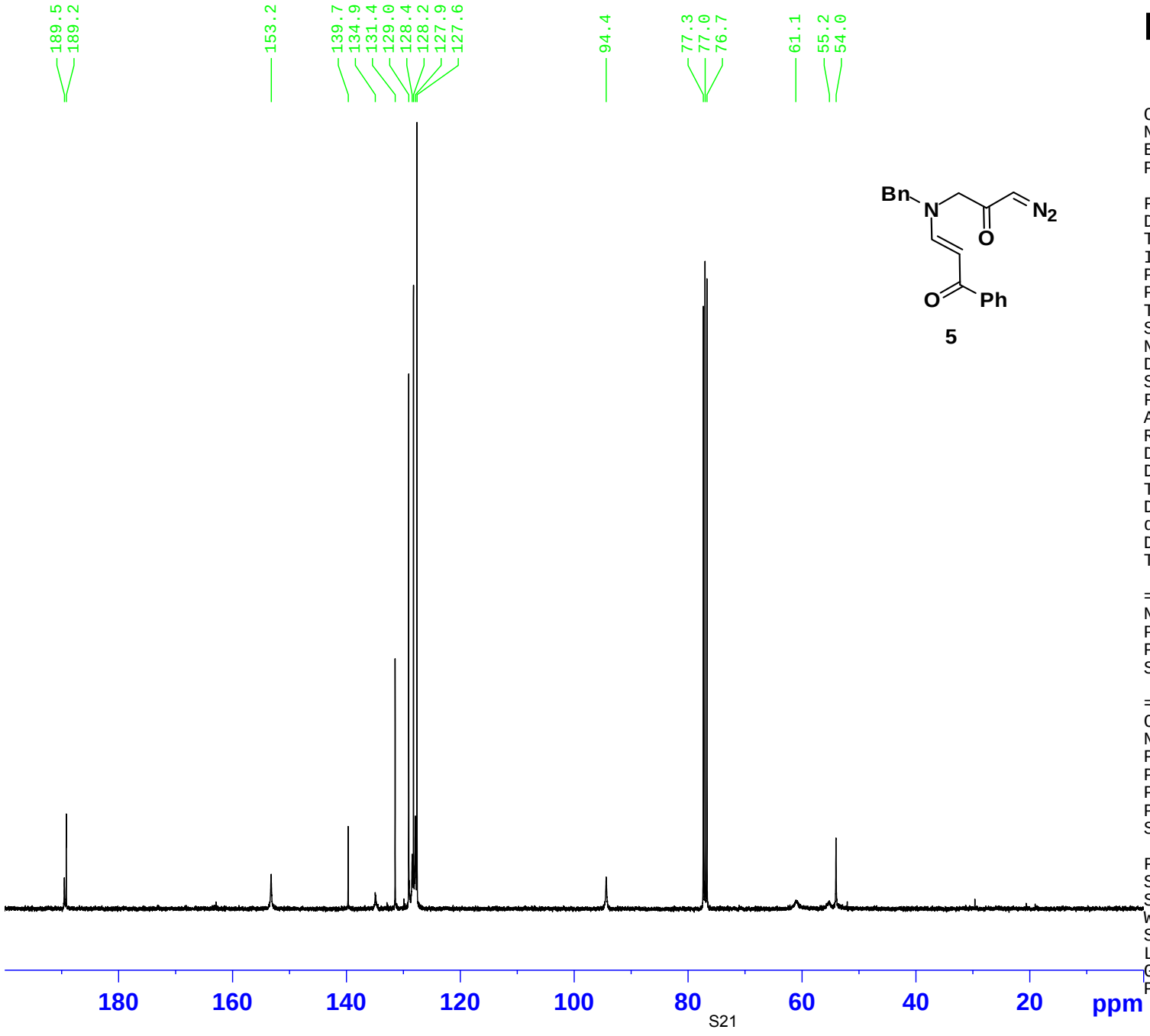
5

```
Current Data Parameters
NAME                  081014
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081015
Time                  10.41
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      228
DW                   60.800 usec
DE                    6.50 usec
TE                   294.8 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.61 usec
PL1                   -3.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                     32768
SF             400.1300033 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                     1.00
```



5

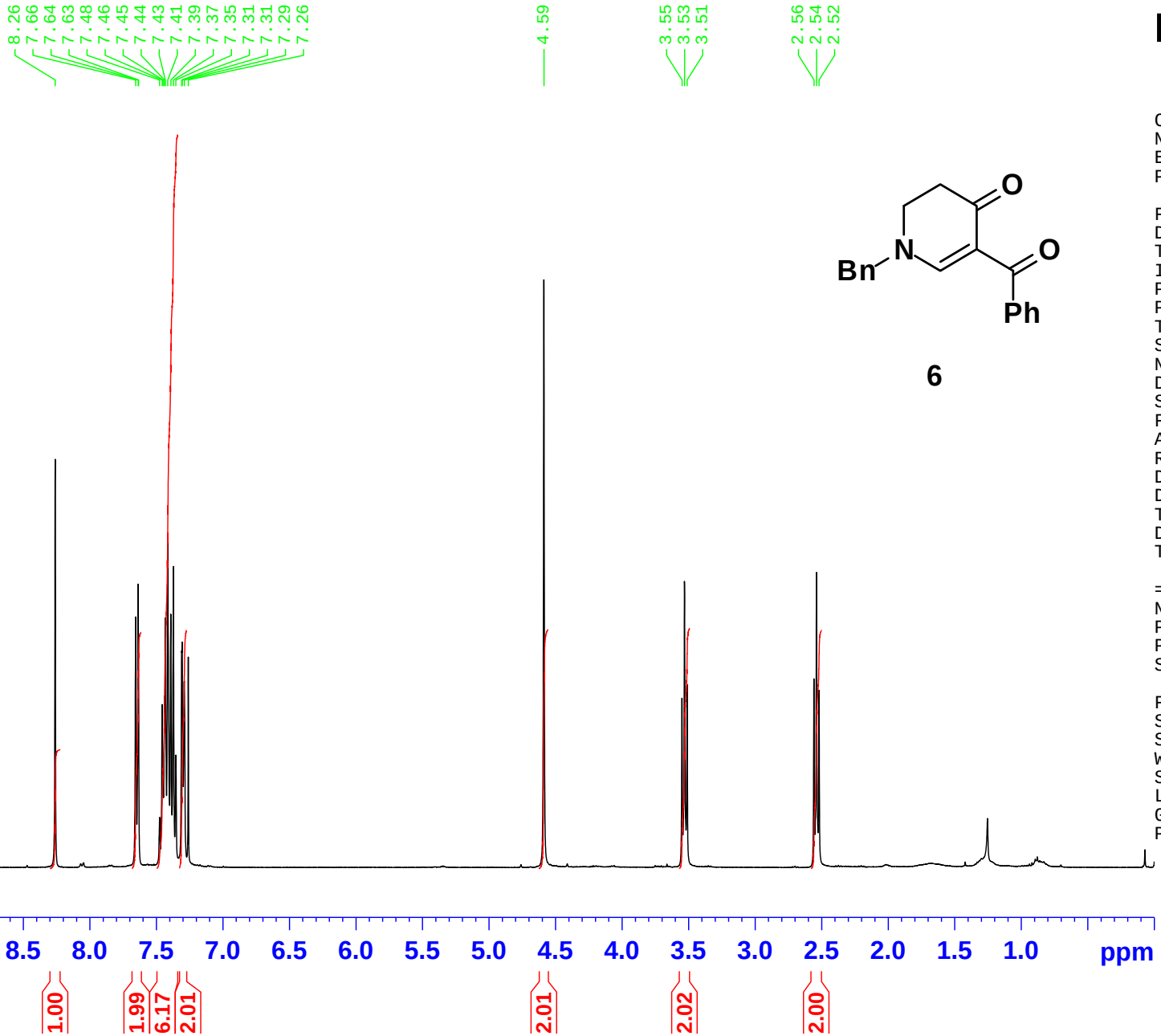
```
Current Data Parameters
NAME                  090121
EXPNO                     21
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090123
Time                   1.05
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                     1620
DW                   20.800 usec
DE                    7.50 usec
TE                   298.0 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     10.30 usec
PL1                    -3.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 90.00 usec
PL12                  16.43 dB
PL13                  19.37 dB
PL2                   -3.00 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF              100.6127751 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.40
```

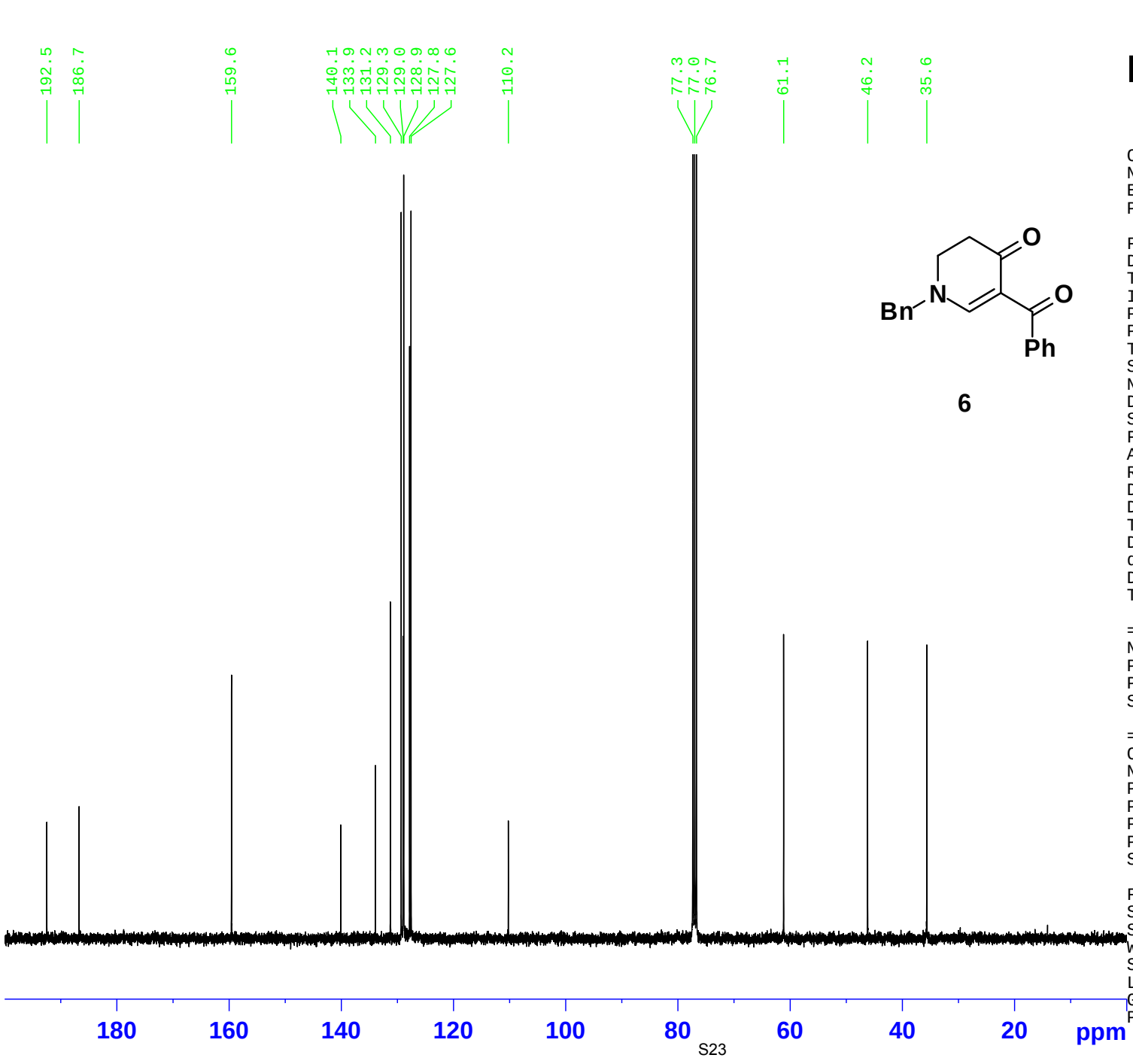



```
Current Data Parameters
NAME                  081202
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081202
Time                  13.38
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      181
DW                   60.800 usec
DE                    6.50 usec
TE                   295.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.61 usec
PL1                   -3.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF             400.1300028 MHz
WDW                        EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                     1.00
```



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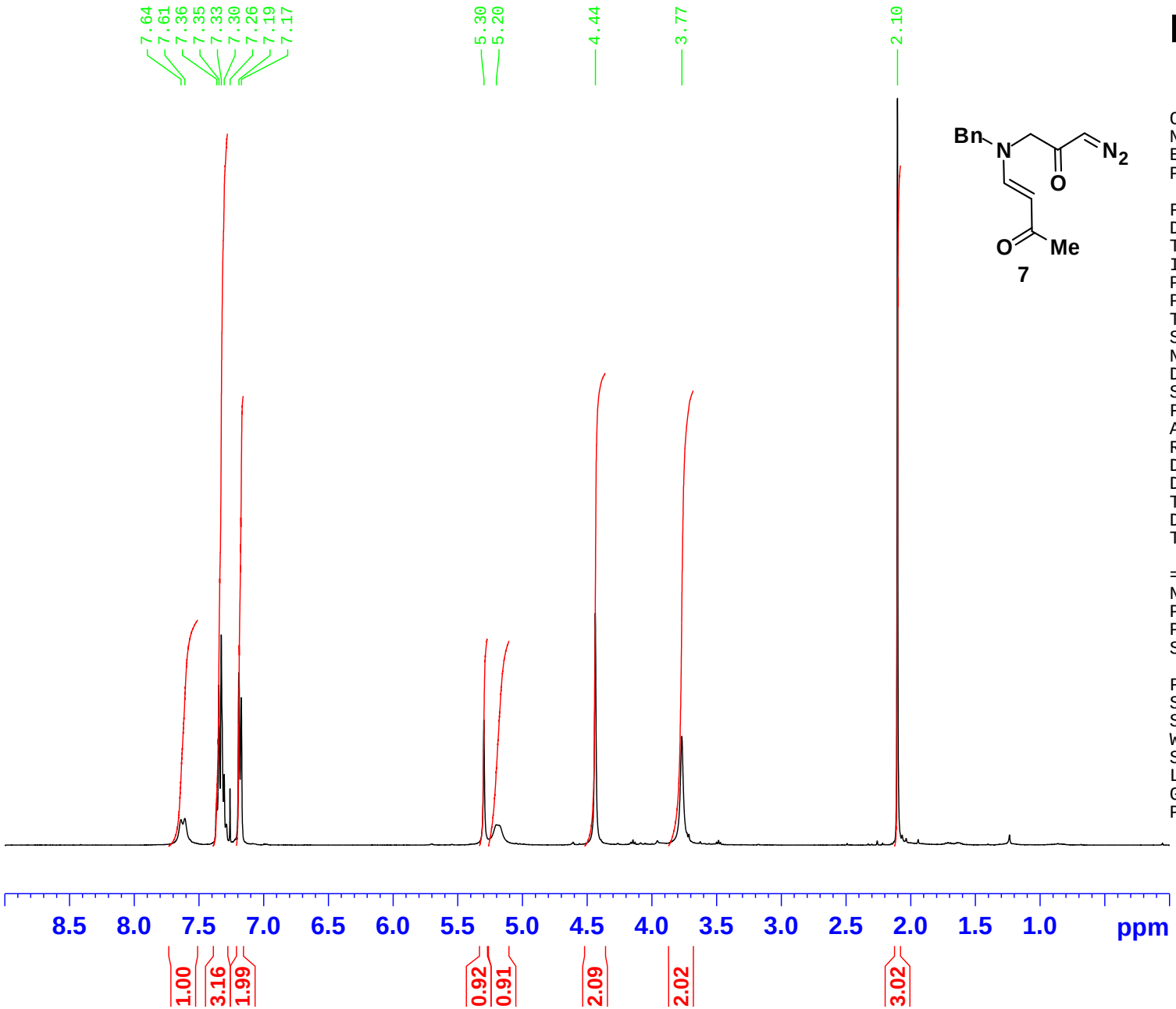
```
Current Data Parameters
NAME                  081202
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081202
Time                  23.59
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                     2050
DW                   20.800 usec
DE                    7.50 usec
TE                   295.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     10.30 usec
PL1                    -3.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                90.00 usec
PL12                 16.43 dB
PL13                 19.37 dB
PL2                  -3.00 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                    1.40
```



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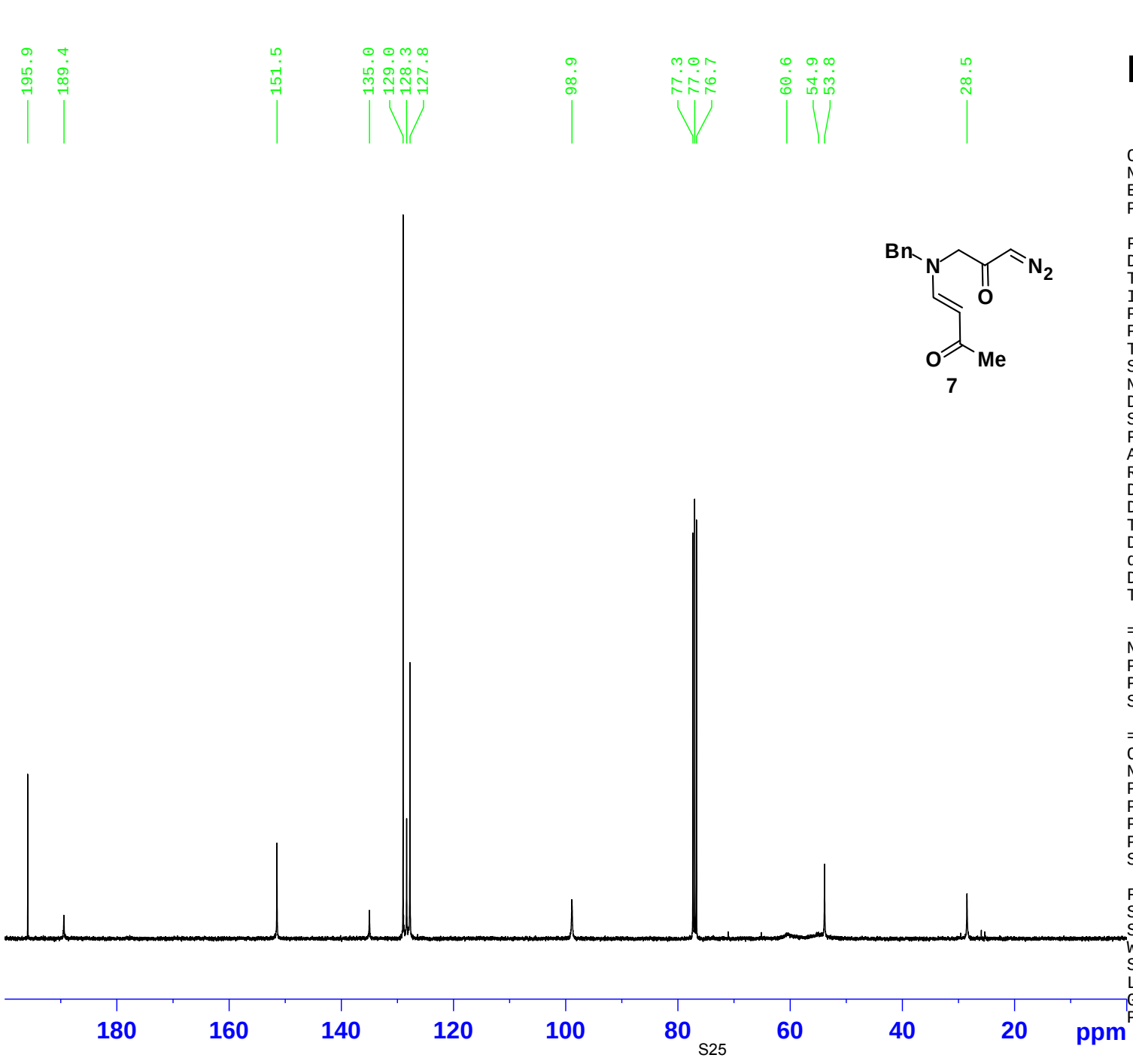
```
Current Data Parameters
NAME                  090121
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090122
Time                  13.26
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      101
DW                   60.800 usec
DE                    6.50 usec
TE                   297.9 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.61 usec
PL1                   -3.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF             400.1300026 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



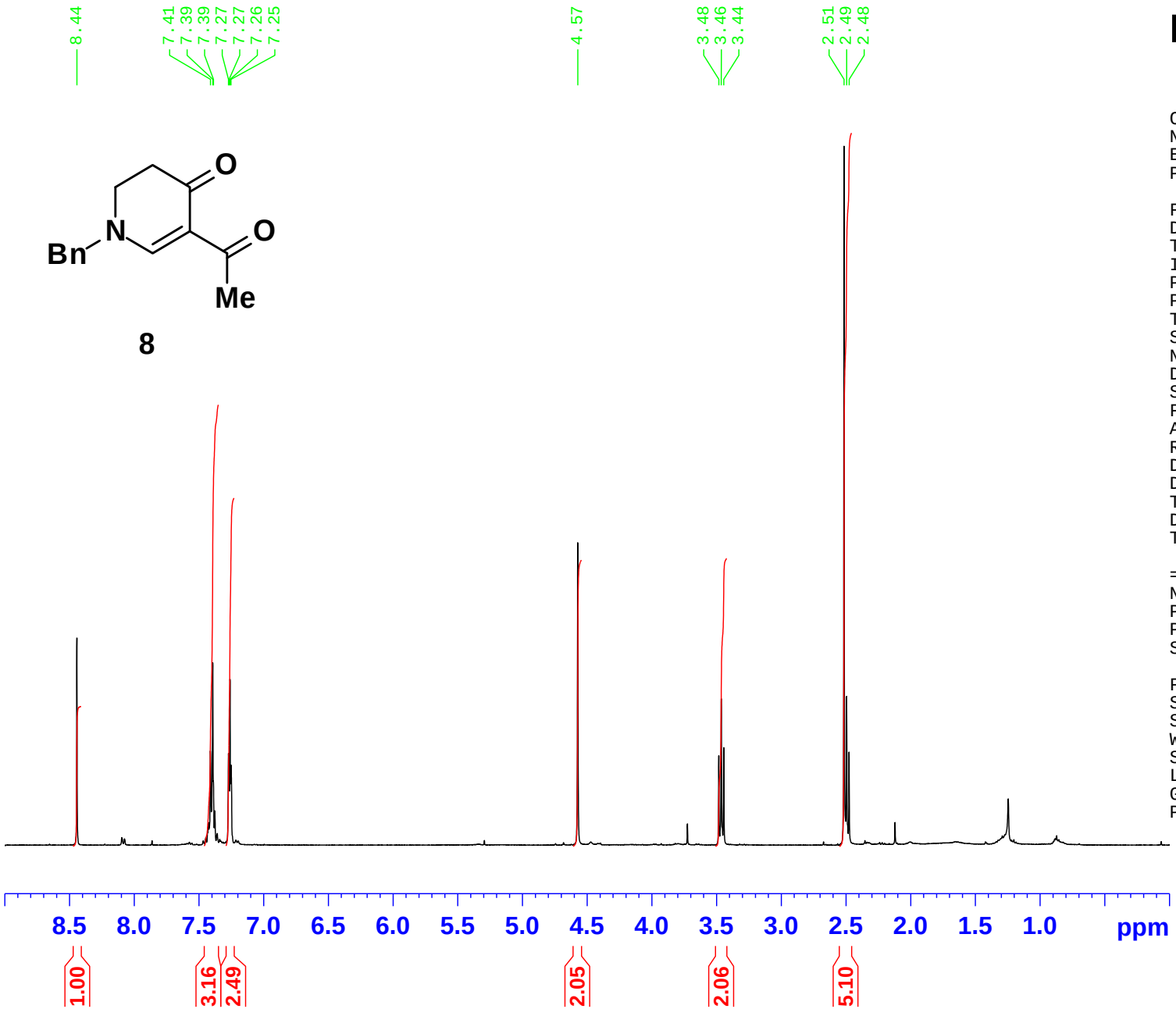
Current Data Parameters
NAME 090121
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090123
Time 3.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1030
DW 20.800 usec
DE 7.50 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL12 16.43 dB
PL13 19.37 dB
PL2 -3.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127758 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

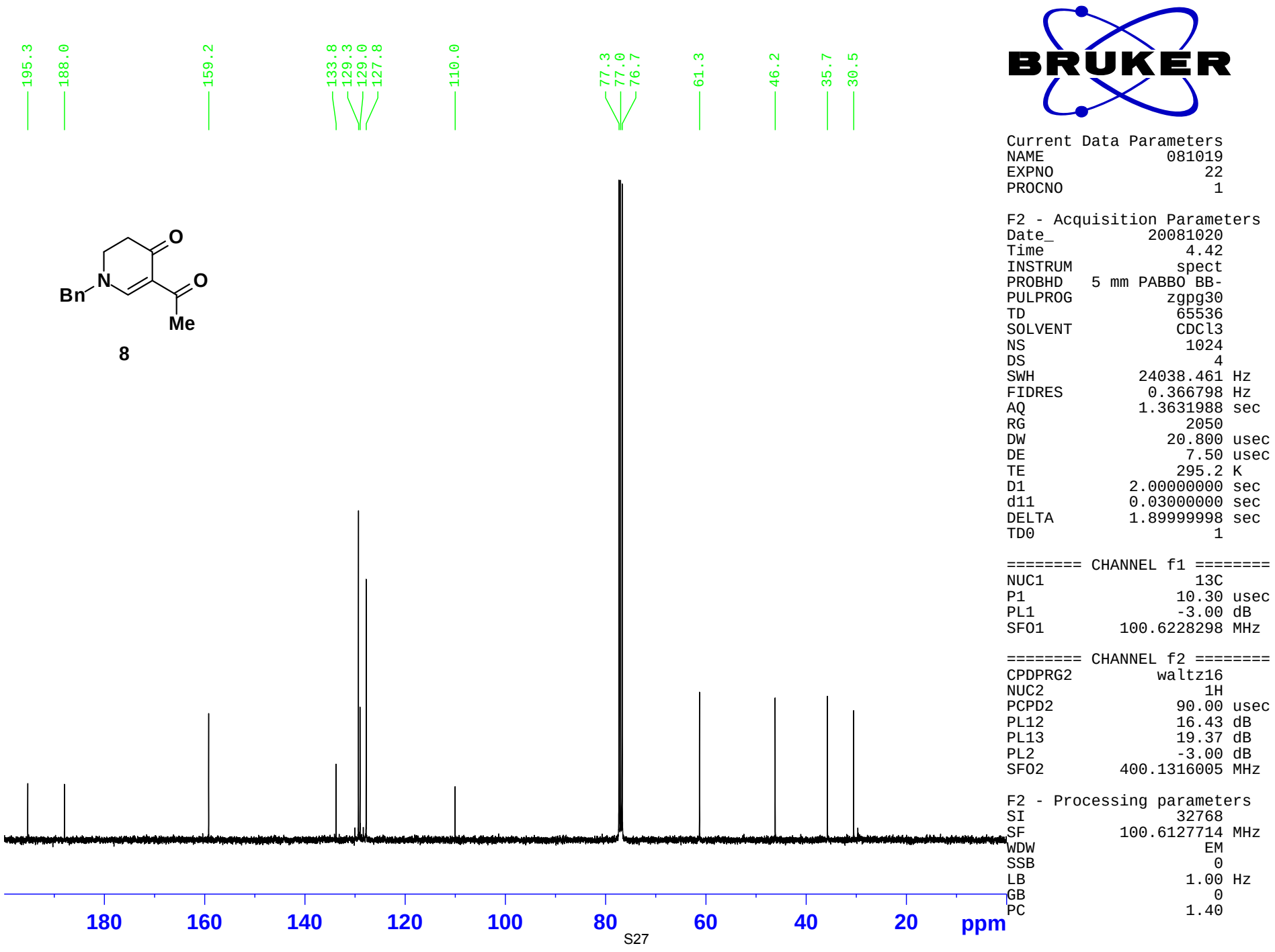



```
Current Data Parameters
NAME                 081019
EXPNO                    21
PROCNO                    1

F2 - Acquisition Parameters
Date_              20081020
Time                   3.42
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      203
DW                 60.800 usec
DE                  6.50 usec
TE                  294.7 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.61 usec
PL1                  -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300035 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                    1.00
```



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```
Current Data Parameters
NAME                  081019
EXPNO                     22
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081020
Time                   4.42
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                     2050
DW                   20.800 usec
DE                    7.50 usec
TE                   295.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     10.30 usec
PL1                    -3.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                90.00 usec
PL12                 16.43 dB
PL13                 19.37 dB
PL2                  -3.00 dB
SFO2            400.1316005 MHz

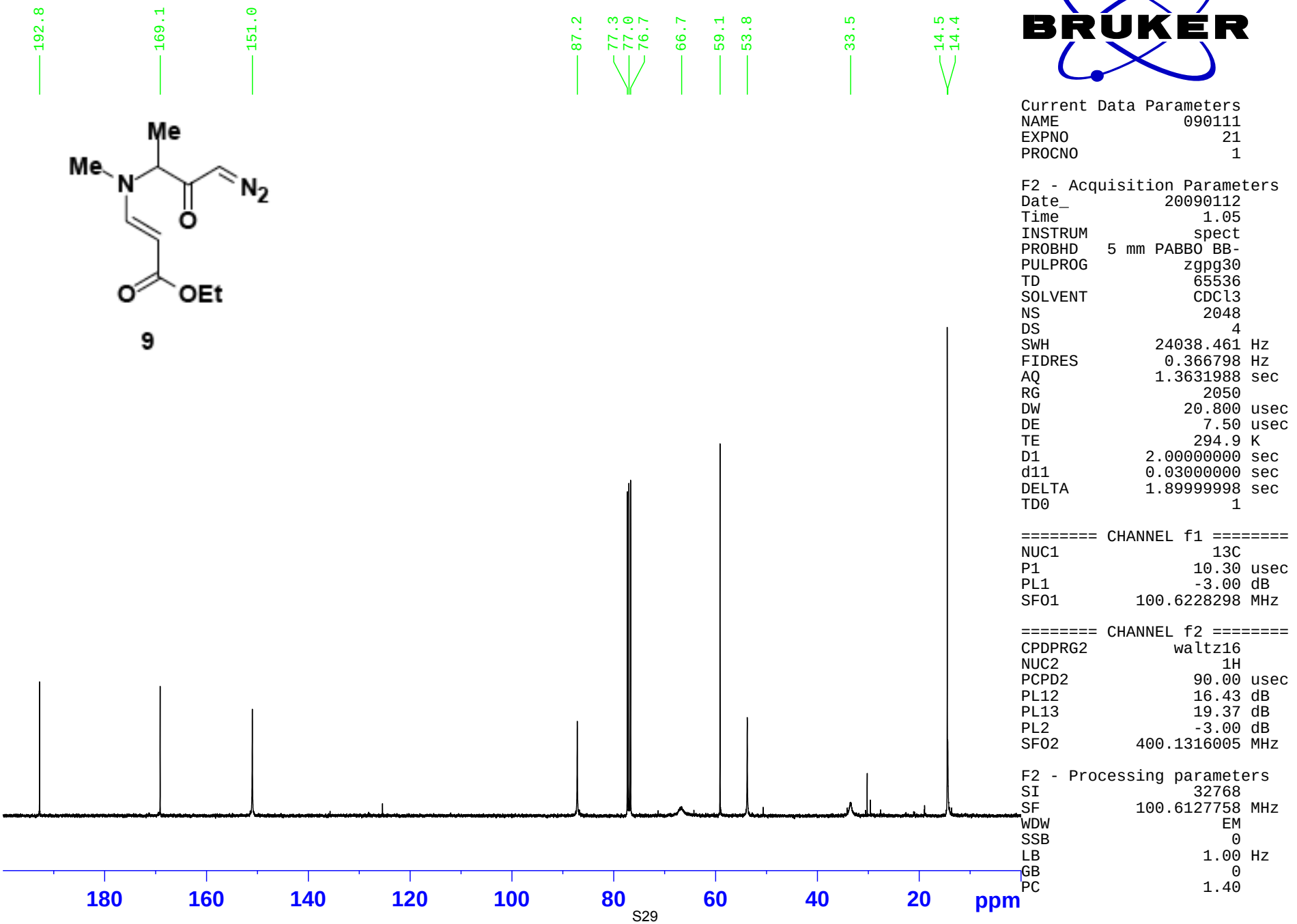
F2 - Processing parameters
SI                       32768
SF              100.6127714 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.40
```

```
Current Data Parameters
NAME                 090111
EXPNO                    20
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090111
Time                 14.57
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                   71.8
DW                  60.800 usec
DE                   6.50 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.61 usec
PL1                 -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300023 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



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```
Current Data Parameters
NAME                  090111
EXPNO                     21
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090112
Time                   1.05
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     2050
DW                  20.800 usec
DE                   7.50 usec
TE                  294.9 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                   10.30 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                     1H
PCPD2                90.00 usec
PL12                 16.43 dB
PL13                 19.37 dB
PL2                  -3.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF             100.6127758 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.40
```

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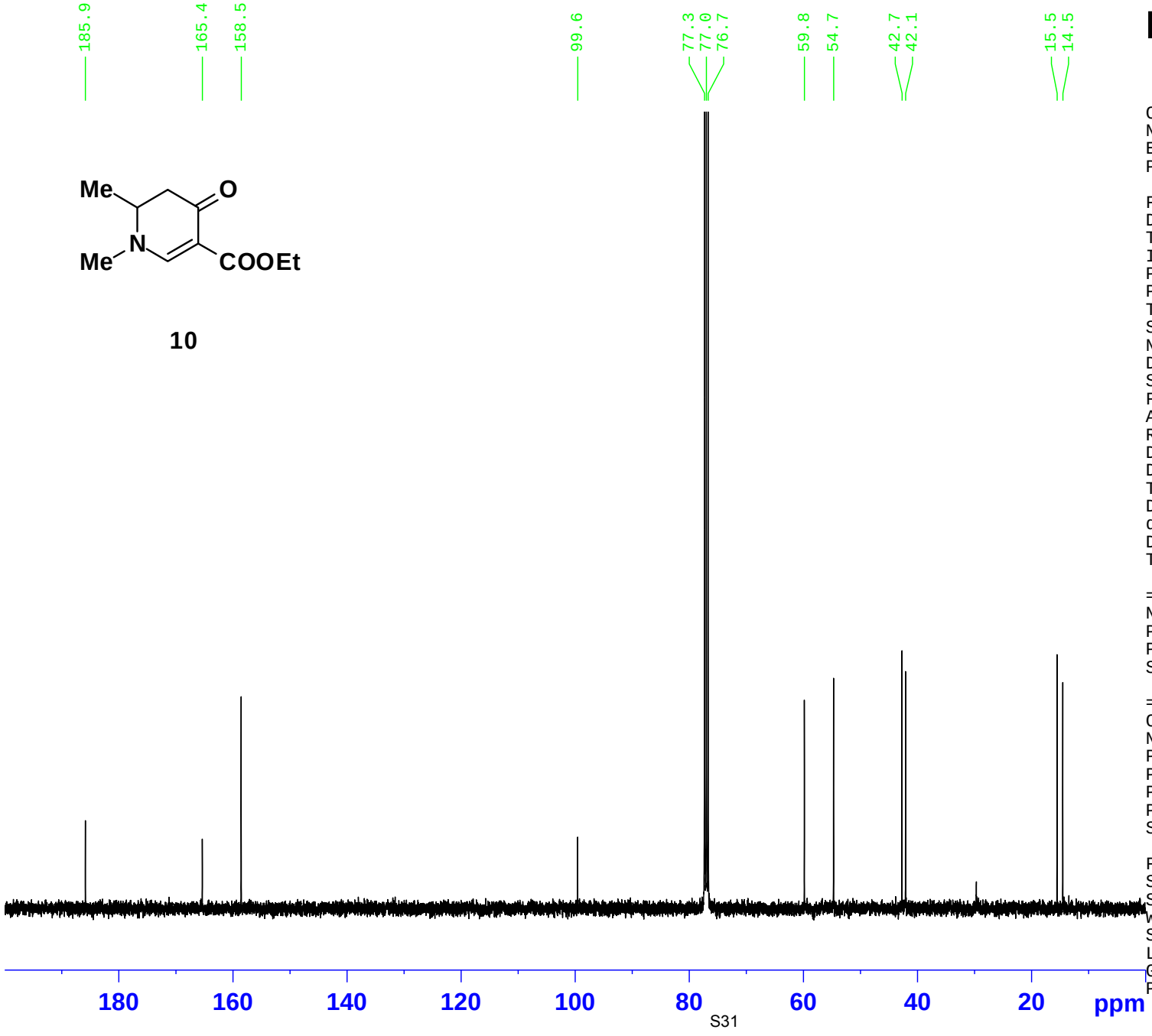
```
Current Data Parameters
NAME                 090111
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090111
Time                 13.49
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     128
DW                  60.800 usec
DE                   6.50 usec
TE                  294.9 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   9.61 usec
PL1                 -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300028 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



Current Data Parameters
NAME 090108
EXPNO 22
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090109
Time 0.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 7.50 usec
TE 295.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL12 16.43 dB
PL13 19.37 dB
PL2 -3.00 dB
SFO2 400.1316005 MHz

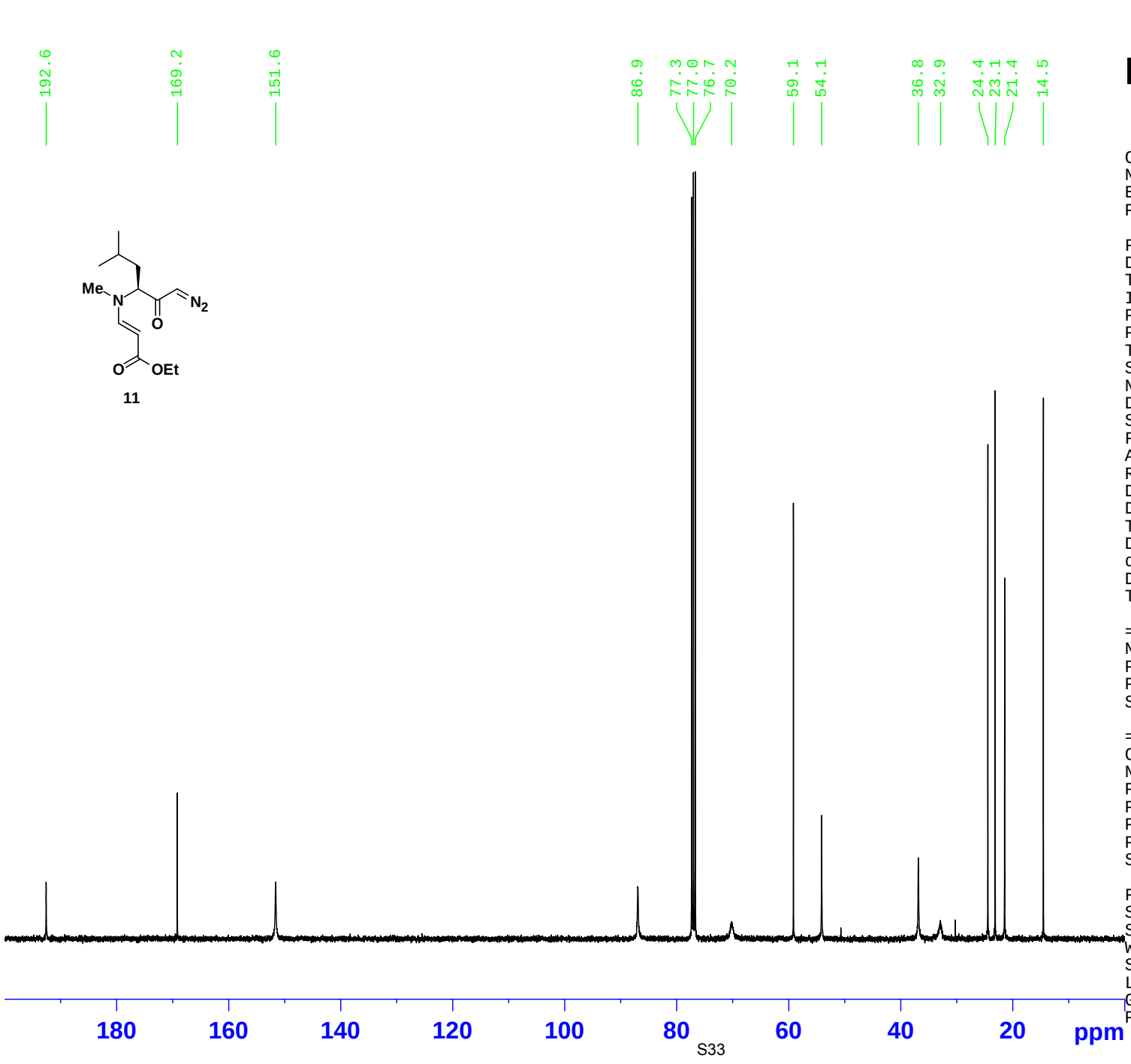
F2 - Processing parameters
SI 32768
SF 100.6127714 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

```
Current Data Parameters
NAME                  090113
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090113
Time                  17.16
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      80.6
DW                    60.800 usec
DE                     6.50 usec
TE                    294.8 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.61 usec
PL1                   -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300033 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



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```
Current Data Parameters
NAME                  090113
EXPNO                     12
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090114
Time                   5.54
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     2050
DW                20.800 usec
DE                 7.50 usec
TE                 295.4 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                    13C
P1                  10.30 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                    1H
PCPD2               90.00 usec
PL12                16.43 dB
PL13                19.37 dB
PL2                 -3.00 dB
SFO2          400.1316005 MHz

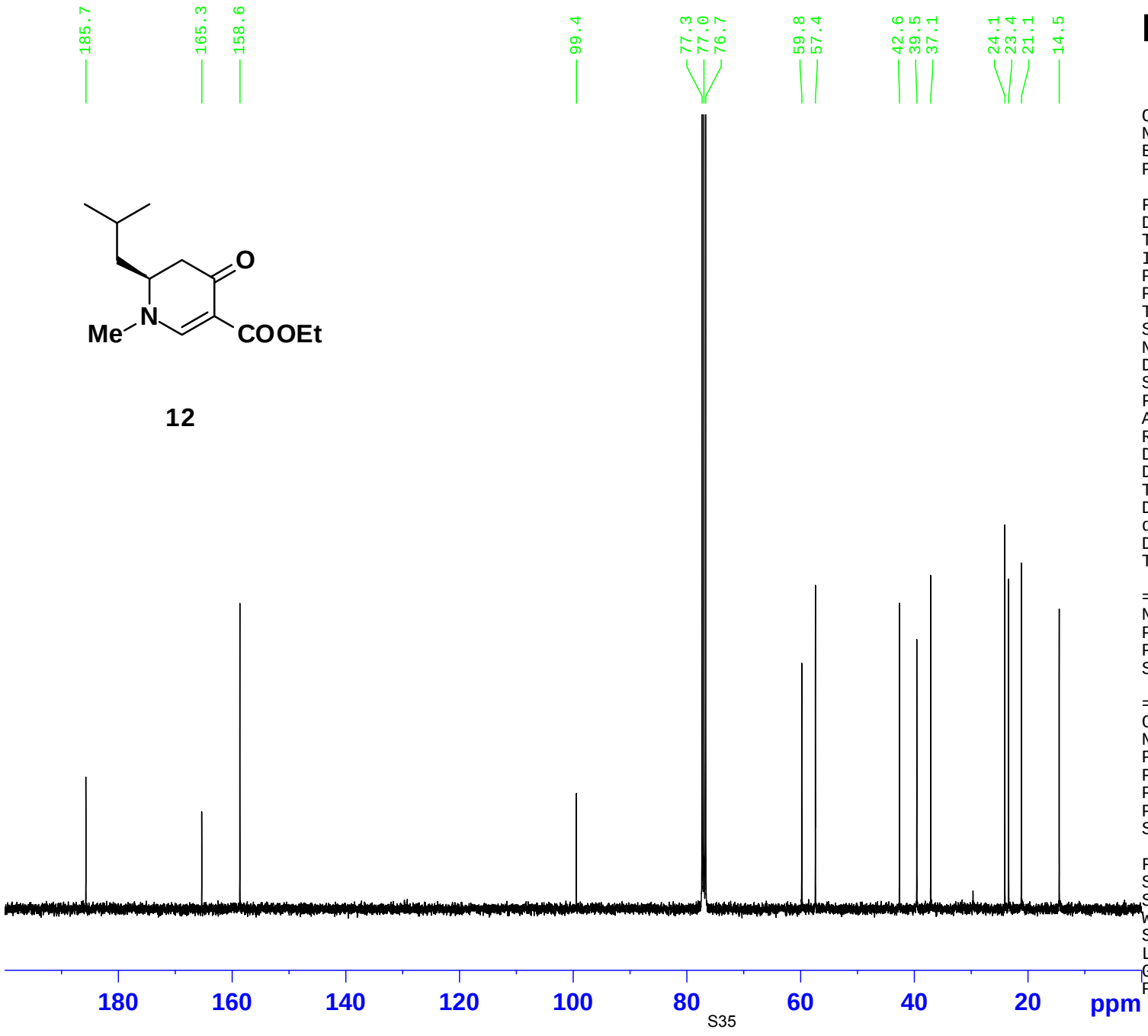
F2 - Processing parameters
SI                     32768
SF            100.6127736 MHz
WDW                       EM
SSB                        0
LB                   1.00 Hz
GB                         0
PC                    1.40
```

```
Current Data Parameters
NAME                 090108
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090108
Time                 20.48
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                    161
DW                  60.800 usec
DE                   6.50 usec
TE                  295.1 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.61 usec
PL1                 -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300028 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME                 090108
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090108
Time                 23.02
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                    2050
DW                 20.800 usec
DE                  7.50 usec
TE                 295.4 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  10.30 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL12                16.43 dB
PL13                19.37 dB
PL2                 -3.00 dB
SFO2          400.1316005 MHz

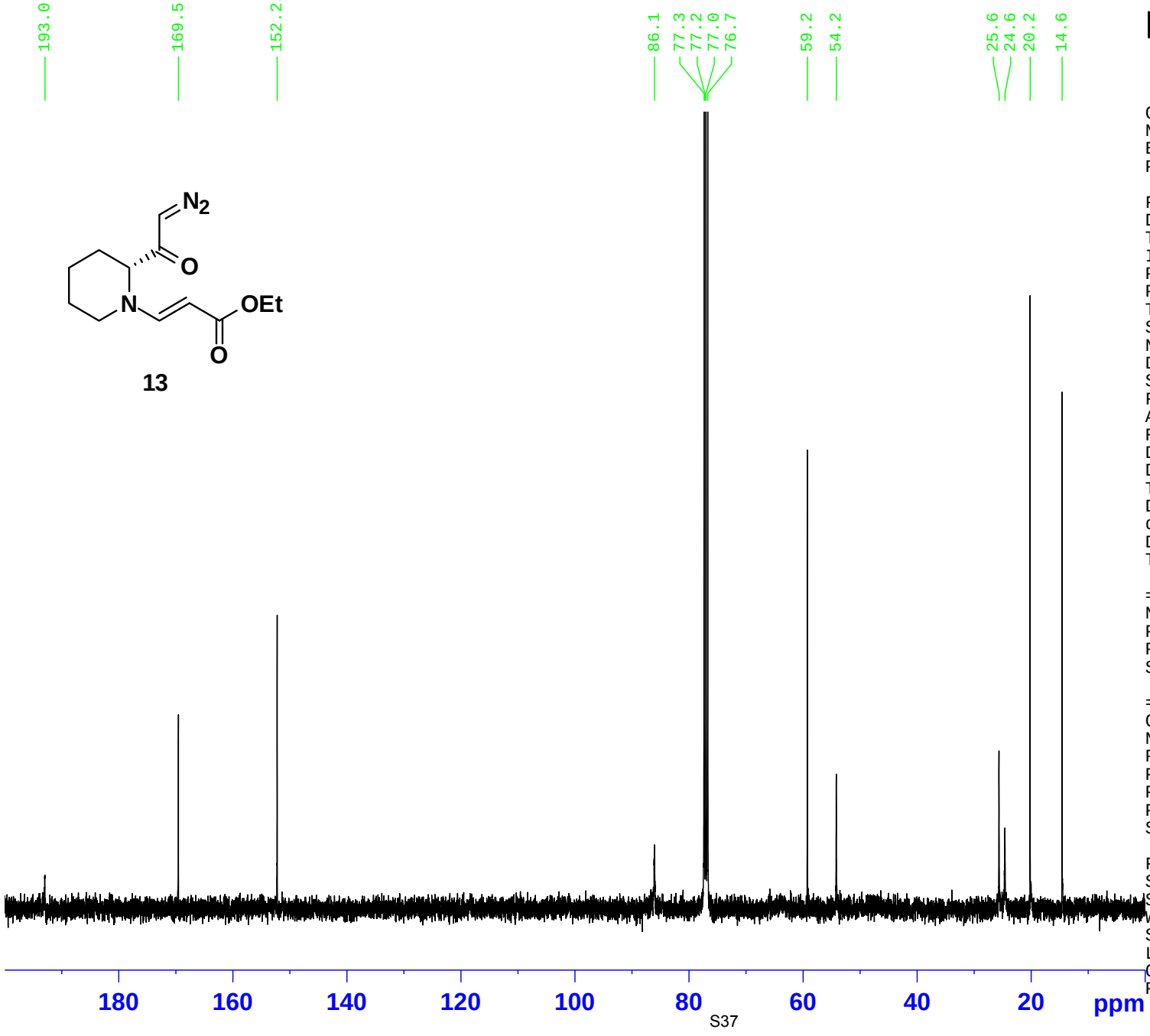
F2 - Processing parameters
SI                    32768
SF            100.6127721 MHz
WDW                      EM
SSB                       0
LB                   1.00 Hz
GB                        0
PC                    1.40
```

```
Current Data Parameters
NAME                  081024
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081024
Time                  14.11
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      203
DW                   60.800 usec
DE                    6.50 usec
TE                   294.9 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.61 usec
PL1                  -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300036 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



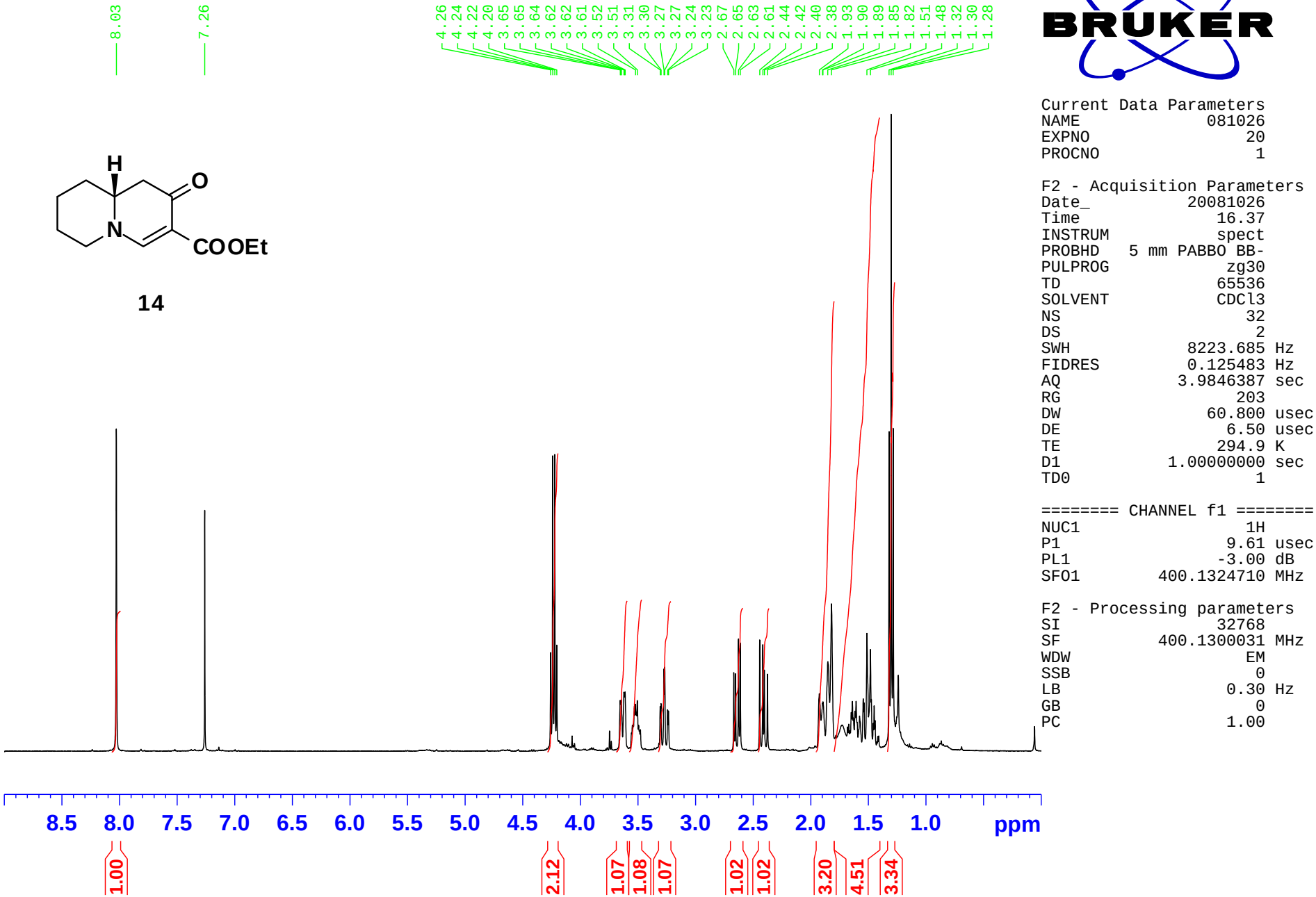

```
Current Data Parameters
NAME                 081023
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20081024
Time                   2.50
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     2050
DW                20.800 usec
DE                 7.50 usec
TE                 295.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                  10.30 usec
PL1                 -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               90.00 usec
PL12                16.43 dB
PL13                19.37 dB
PL2                 -3.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                      32768
SF             100.6127690 MHz
WDW                        EM
SSB                         0
LB                   1.00 Hz
GB                          0
PC                   1.40
```



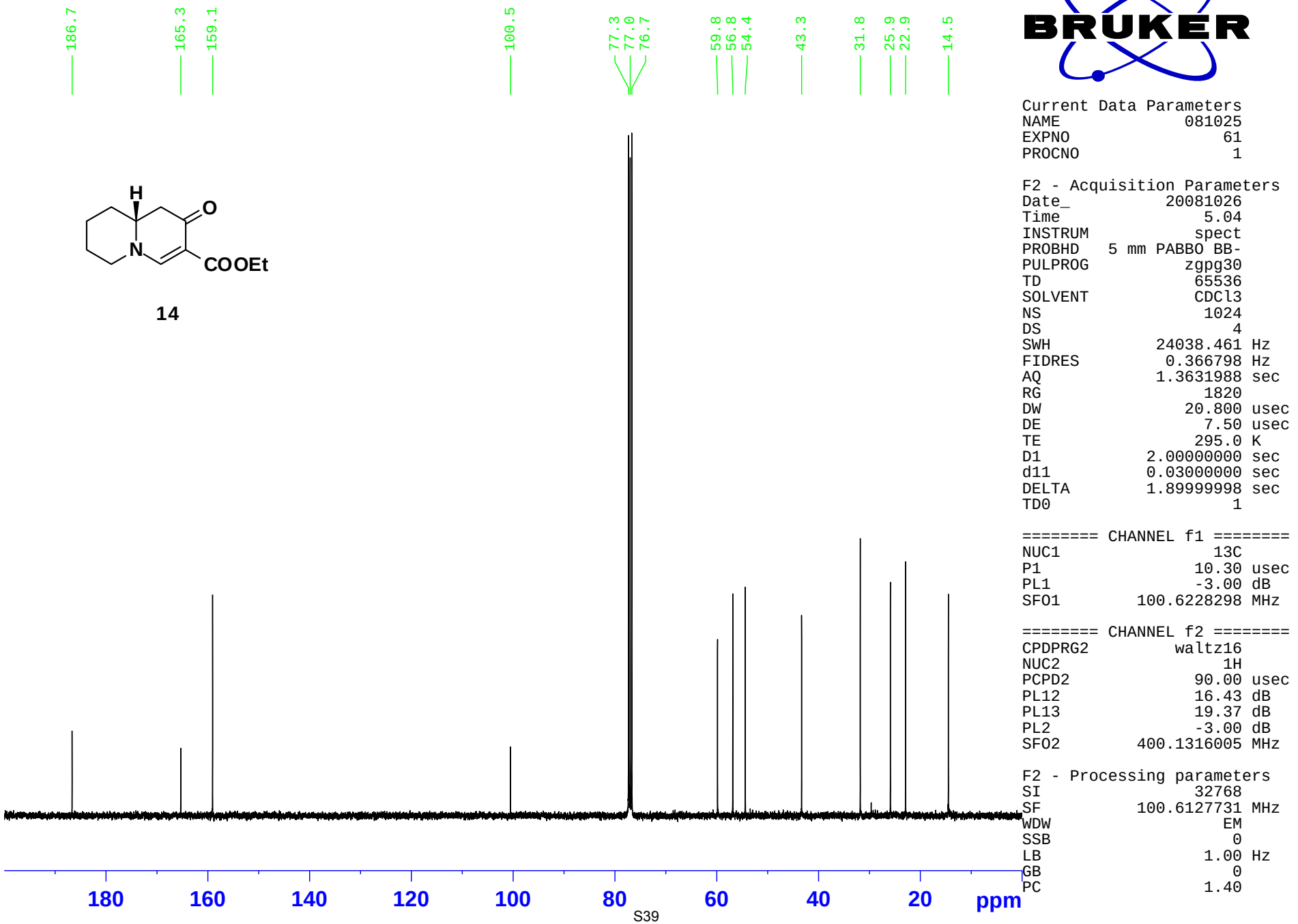
BRUKER

```
Current Data Parameters
NAME                 081026
EXPNO                    20
PROCNO                    1

F2 - Acquisition Parameters
Date_              20081026
Time                 16.37
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                    203
DW                  60.800 usec
DE                   6.50 usec
TE                  294.9 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.61 usec
PL1                 -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300031 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



BRUKER

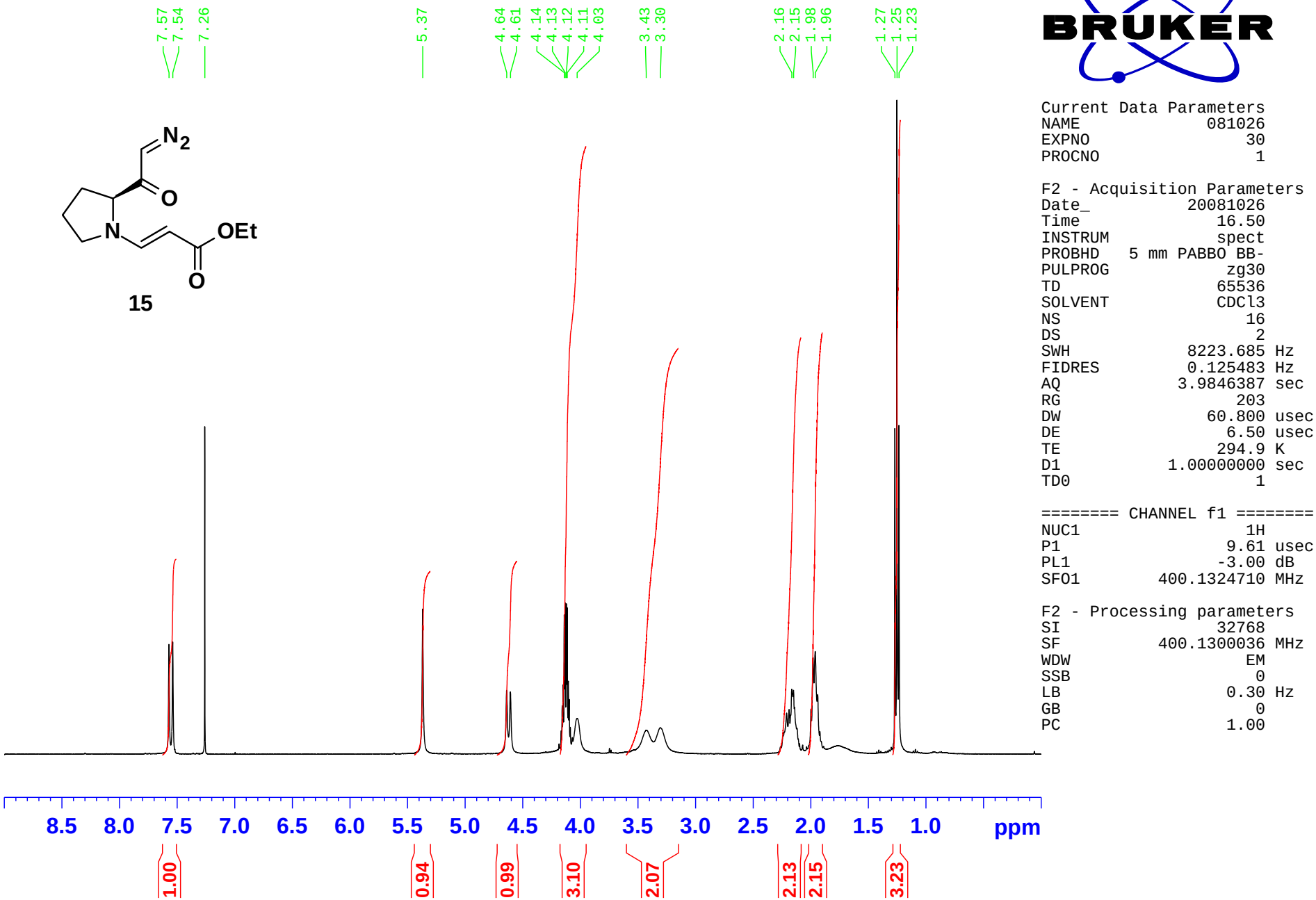
```
Current Data Parameters
NAME                  081025
EXPNO                     61
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081026
Time                   5.04
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                     1820
DW                20.800 usec
DE                 7.50 usec
TE                 295.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                   10.30 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                     1H
PCPD2                90.00 usec
PL12                 16.43 dB
PL13                 19.37 dB
PL2                  -3.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF             100.6127731 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.40
```

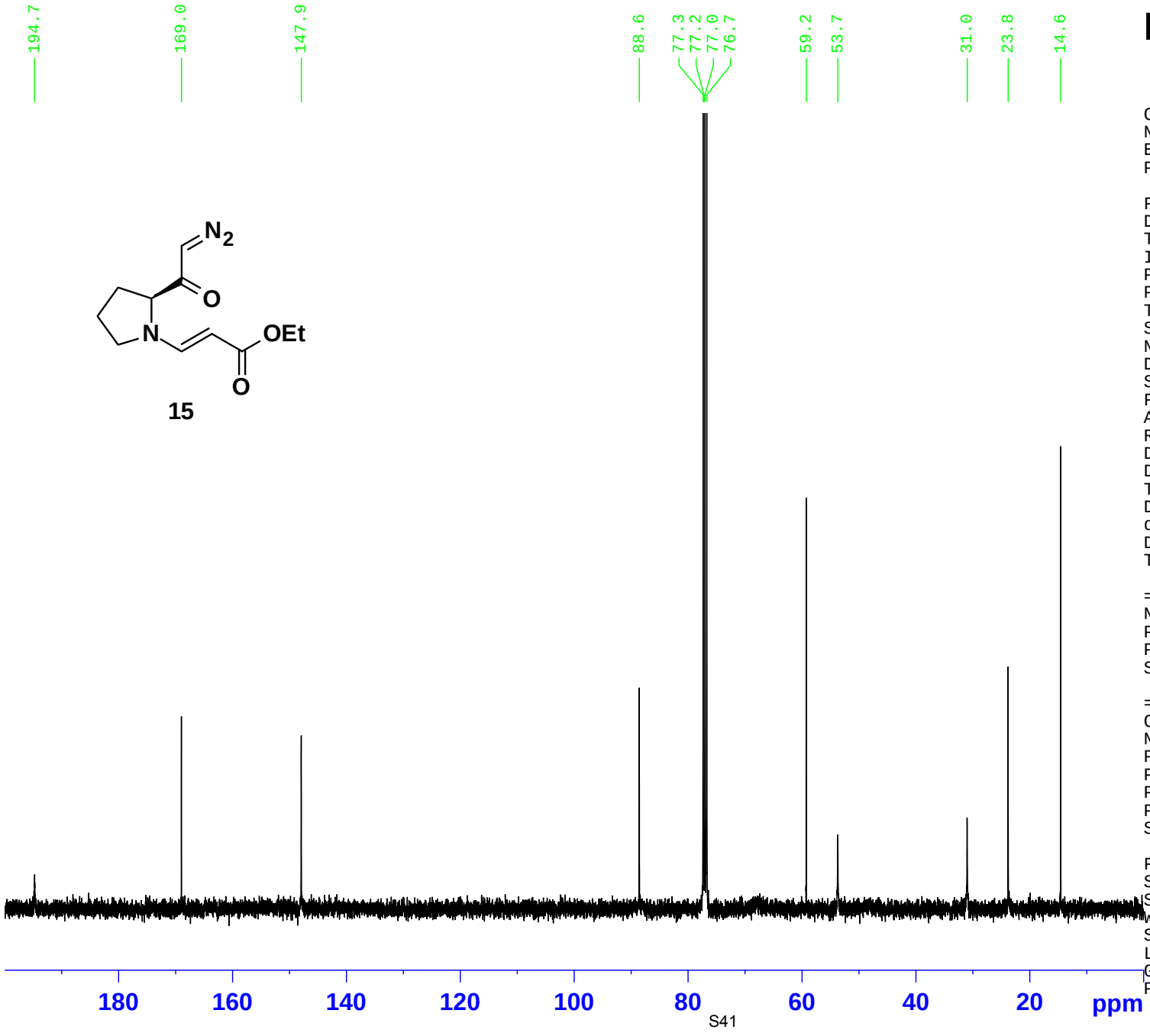



```
Current Data Parameters
NAME                  081026
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081026
Time                  16.50
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      203
DW                   60.800 usec
DE                    6.50 usec
TE                   294.9 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.61 usec
PL1                   -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300036 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



BRUKER

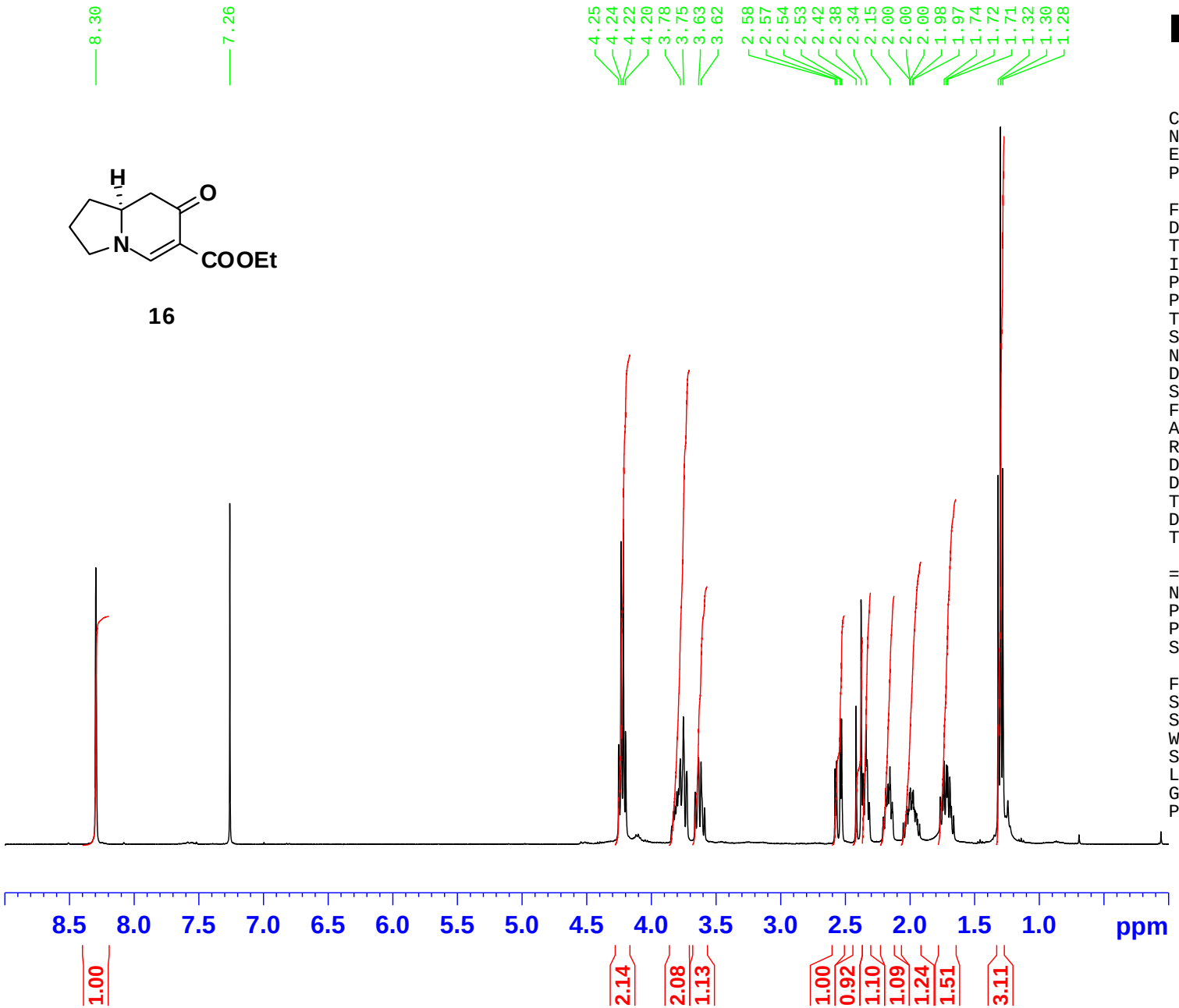
```
Current Data Parameters
NAME                 081026
EXPNO                    31
PROCNO                    1

F2 - Acquisition Parameters
Date_              20081026
Time                 23.02
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     1030
DW                  20.800 usec
DE                   7.50 usec
TE                  295.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                   10.30 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL12                 16.43 dB
PL13                 19.37 dB
PL2                  -3.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                      32768
SF             100.6127690 MHz
WDW                        EM
SSB                         0
LB                   1.00 Hz
GB                          0
PC                   1.40
```



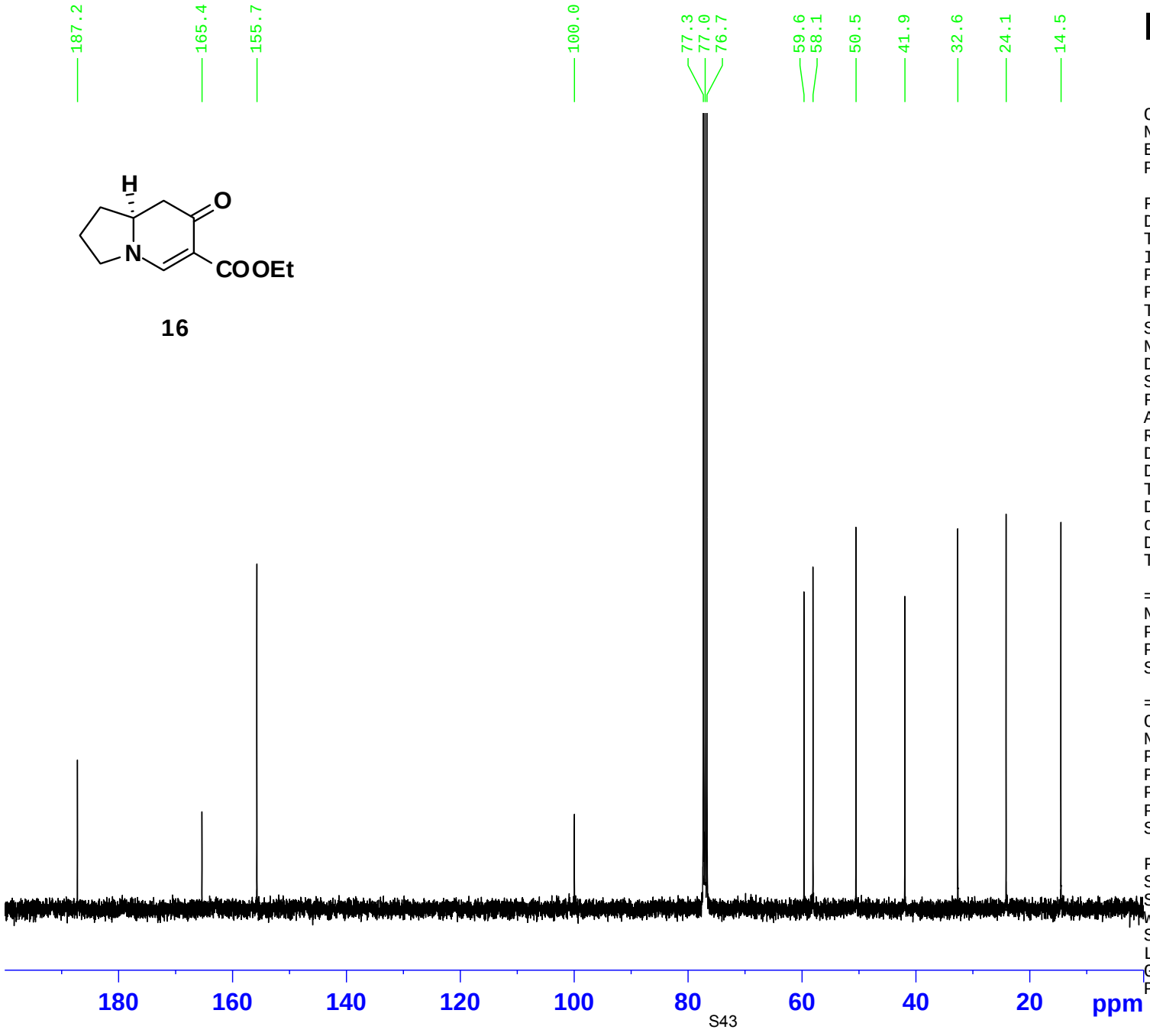
BRUKER

```
Current Data Parameters
NAME                 081012
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20081012
Time                 13.44
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                    181
DW                  60.800 usec
DE                   6.50 usec
TE                  296.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.61 usec
PL1                 -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300036 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



BRUKER

```
Current Data Parameters
NAME                  081012
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081013
Time                   3.22
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     2050
DW                20.800 usec
DE                 7.50 usec
TE                 295.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                   10.30 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                     1H
PCPD2                90.00 usec
PL12                 16.43 dB
PL13                 19.37 dB
PL2                  -3.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF             100.6127721 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.40
```

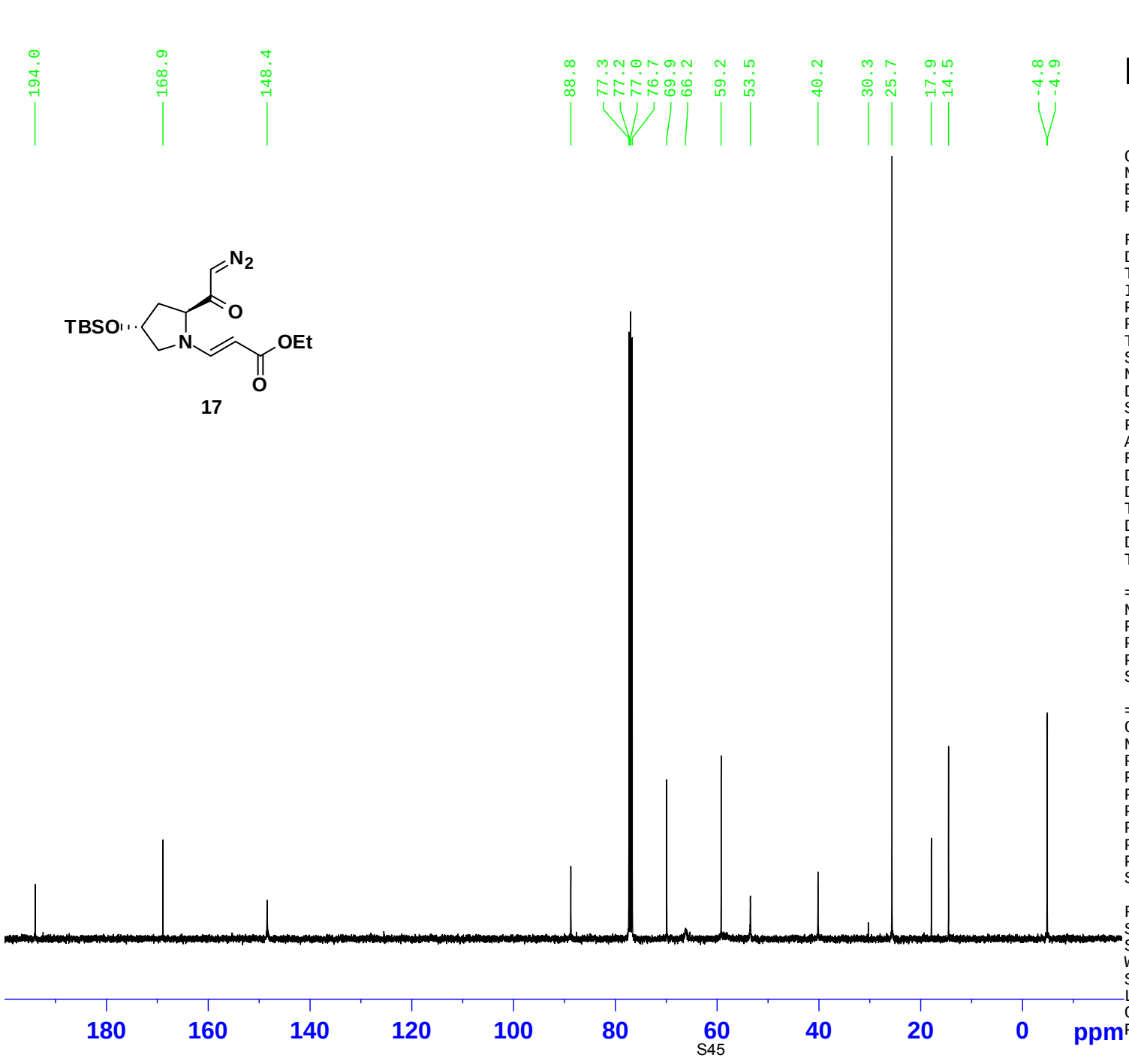
BRUKER

```
Current Data Parameters
NAME                  090512
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090512
Time                  15.34
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      101
DW                  60.800 usec
DE                   6.50 usec
TE                  298.0 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    11.06 usec
PL1                   -3.00 dB
PL1W          18.64416504 W
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                     32768
SF            400.1300053 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                     1.00
```




```
Current Data Parameters
NAME                  090512
EXPNO                     12
PROCNO                     1

F2 - Acquisition Parameters
Date_               20090513
Time                    6.24
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                       2050
DW                     20.800 usec
DE                      6.50 usec
TE                     298.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                     10.30 usec
PL1                    -3.00 dB
PL1W            71.16858673 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  90.00 usec
PL2                    -3.00 dB
PL12                   16.43 dB
PL13                   19.37 dB
PL2W            18.64416504 W
PL12W            0.21259004 W
PL13W            0.10802962 W
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
```

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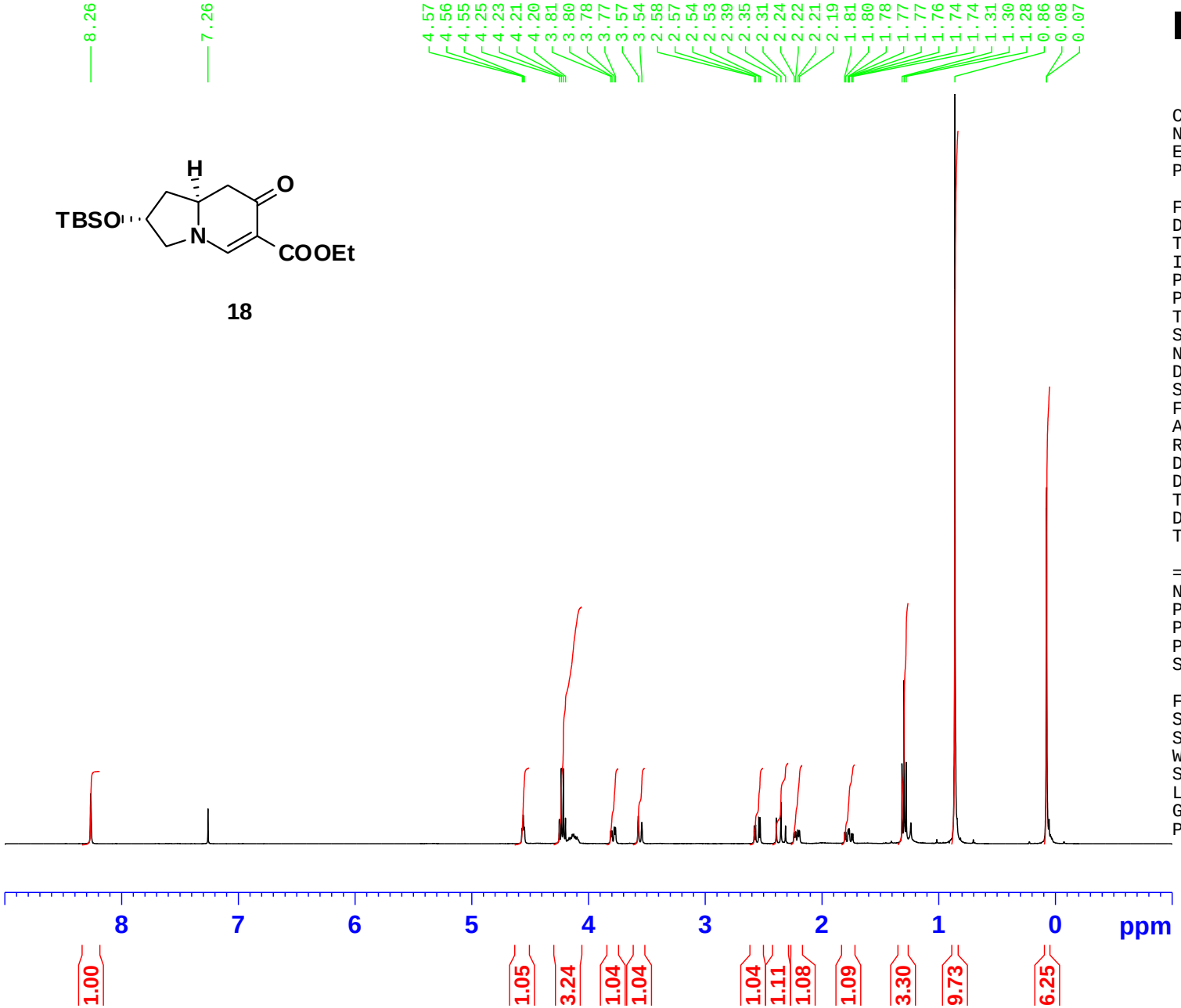
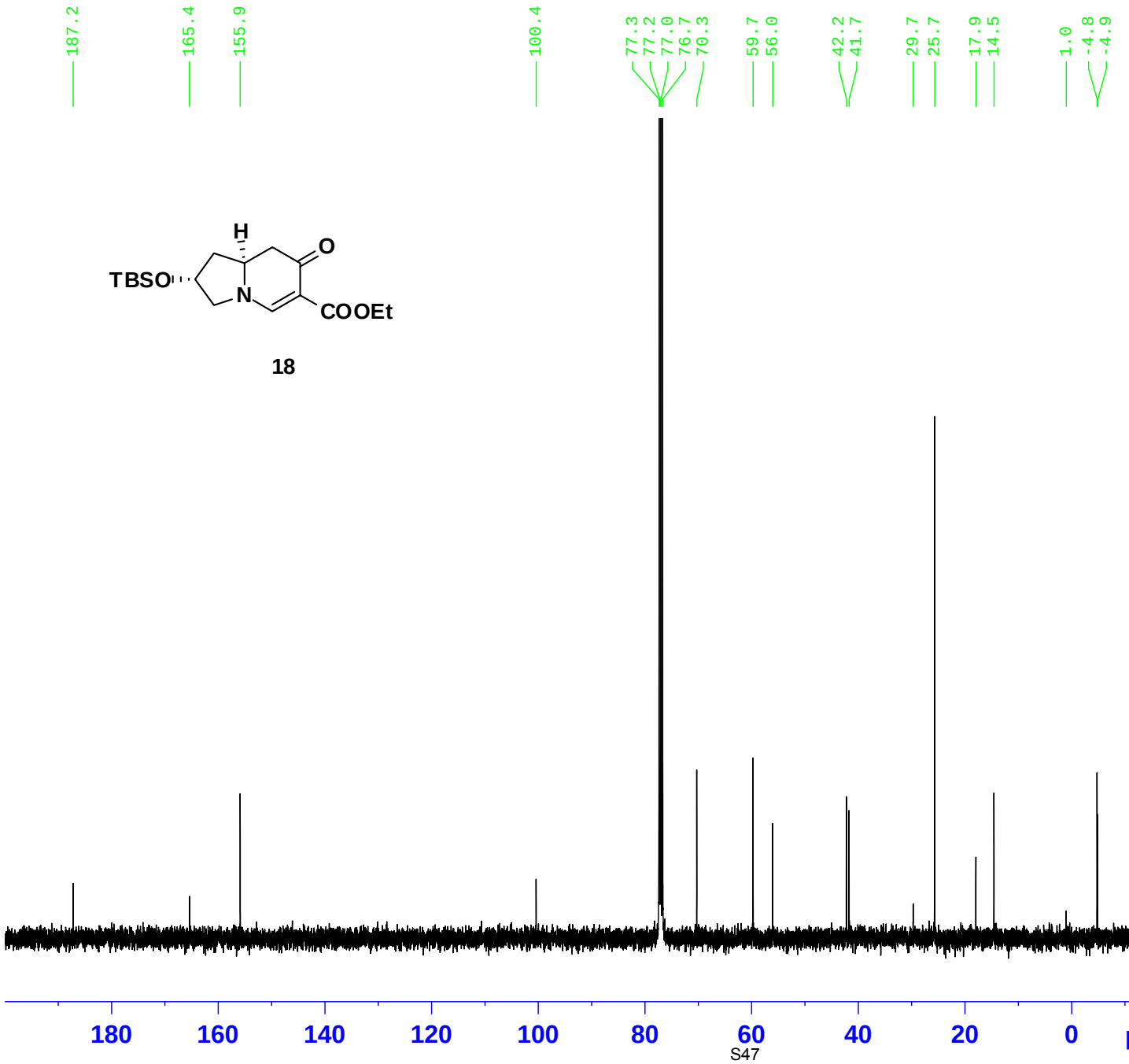



```
Current Data Parameters
NAME                  090513
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090513
Time                  18.37
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     90.5
DW                   60.800 usec
DE                    6.50 usec
TE                   298.1 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.06 usec
PL1                   -3.00 dB
PL1W          18.64416504 W
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300054 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                     1.00
```



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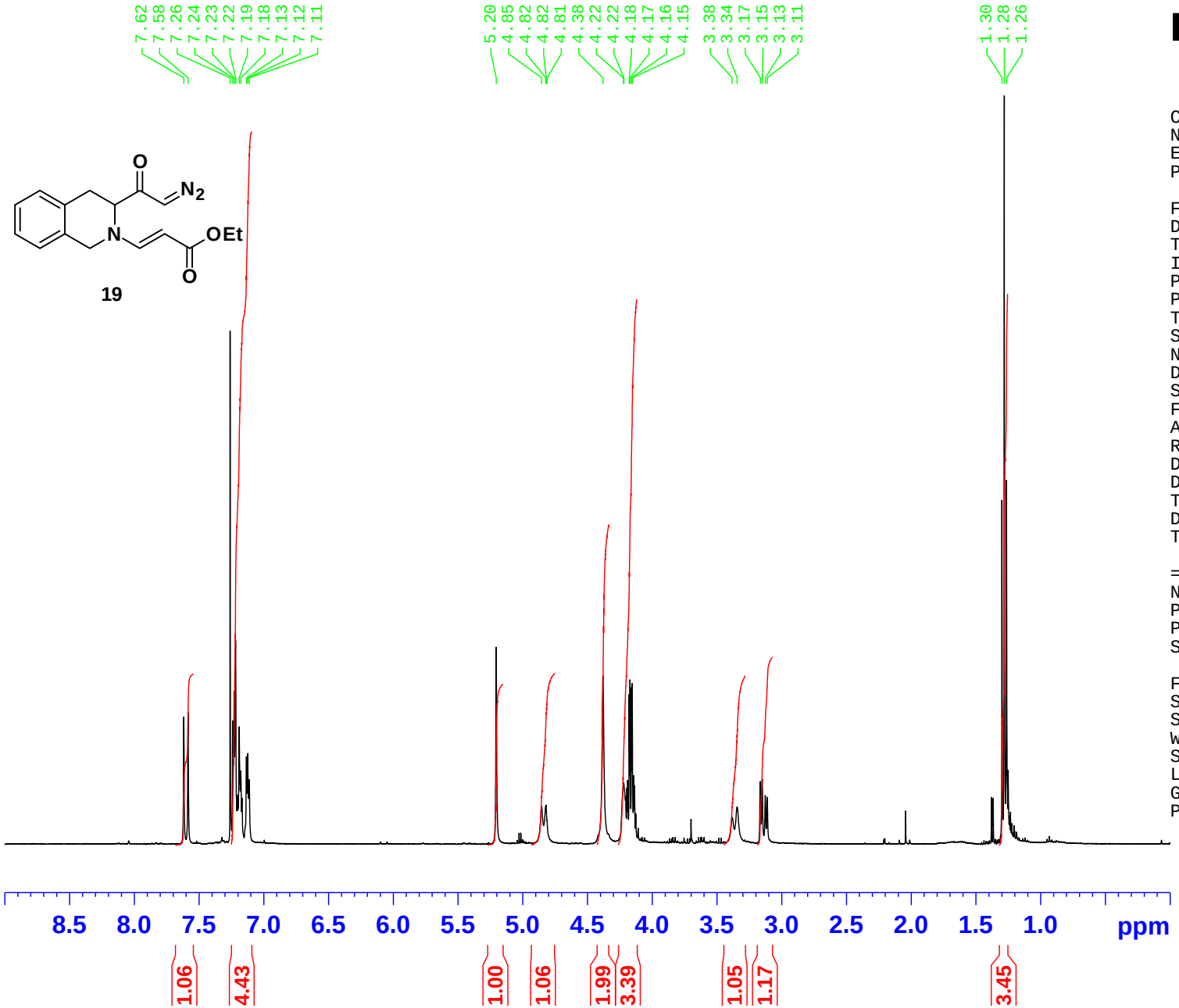
```
Current Data Parameters
NAME                 090728
EXPNO                    30
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090729
Time                   6.27
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                     2050
DW                   20.800 usec
DE                    6.50 usec
TE                   298.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.30 usec
PL1                   -3.00 dB
PL1W           71.16858673 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                   -3.00 dB
PL12                  16.43 dB
PL13                  19.37 dB
PL2W           18.64416504 W
PL12W           0.21259004 W
PL13W           0.10802962 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127690 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```



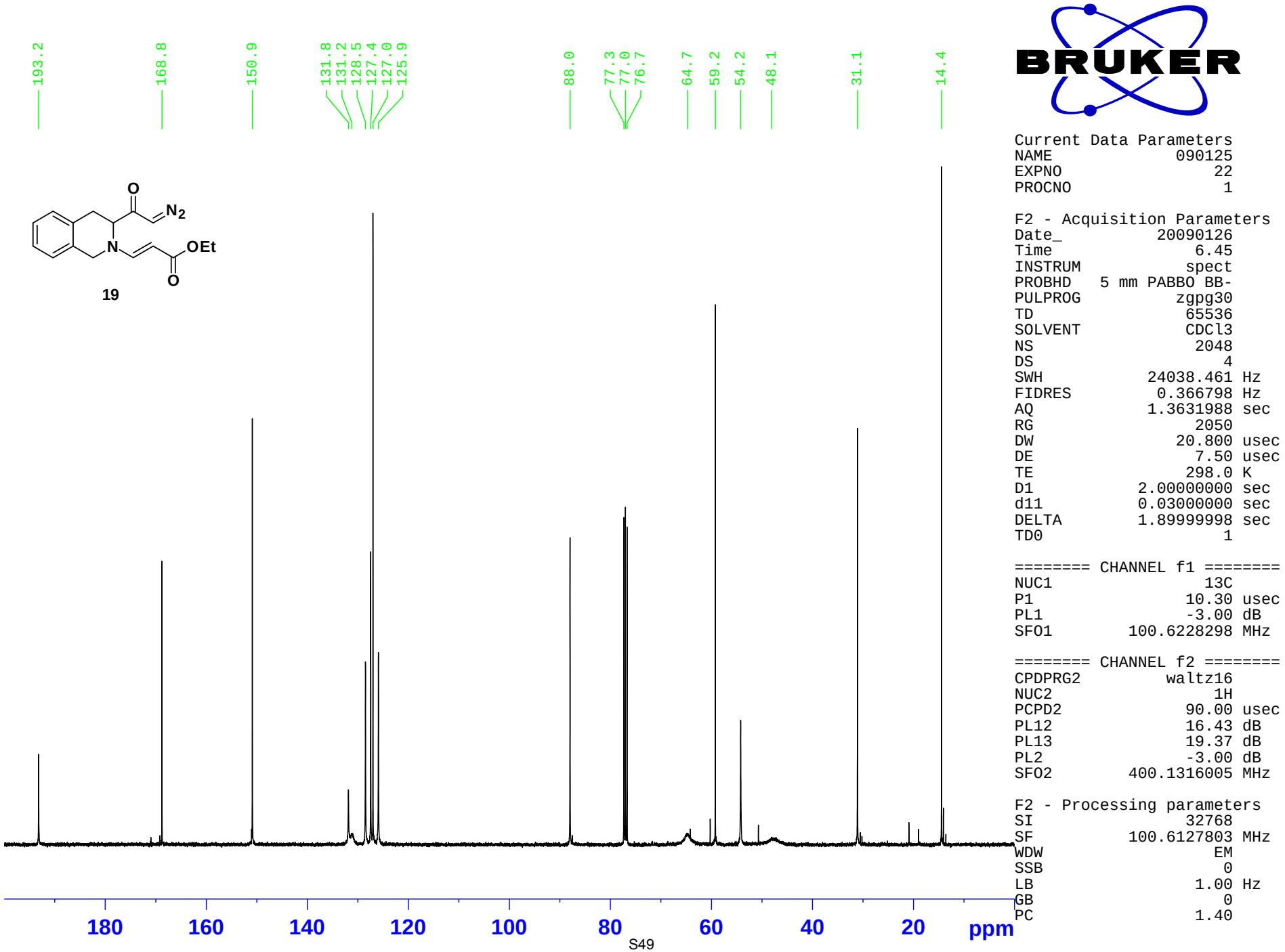
BRUKER

```
Current Data Parameters
NAME                  081121
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081121
Time                  10.58
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      322
DW                   60.800 usec
DE                    6.50 usec
TE                   294.8 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.61 usec
PL1                   -3.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF             400.1300036 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



BRUKER

```
Current Data Parameters
NAME                  090125
EXPNO                     22
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090126
Time                   6.45
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                     2050
DW                   20.800 usec
DE                    7.50 usec
TE                   298.0 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                   10.30 usec
PL1                  -3.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                     1H
PCPD2                90.00 usec
PL12                 16.43 dB
PL13                 19.37 dB
PL2                  -3.00 dB
SFO2            400.1316005 MHz

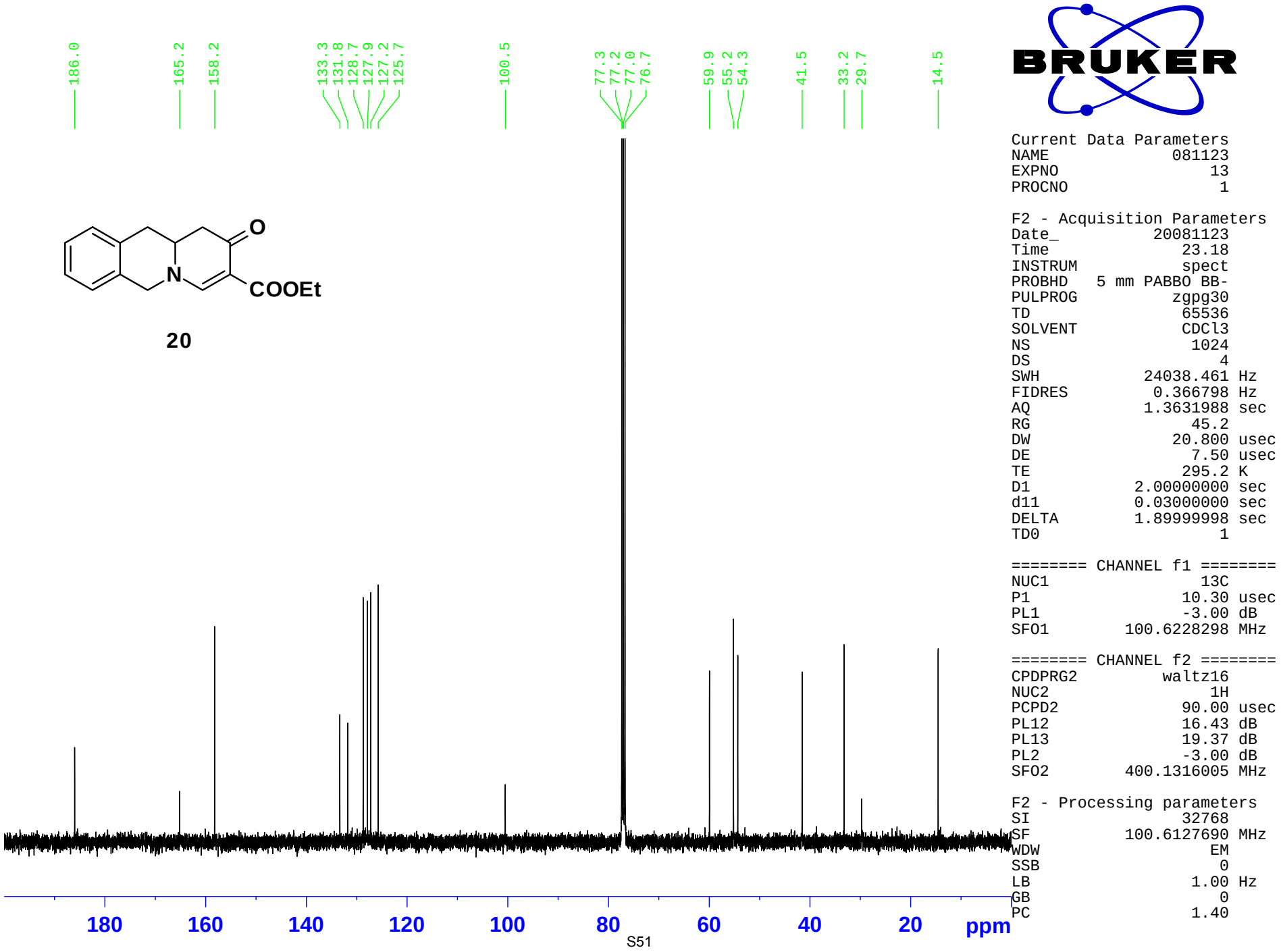
F2 - Processing parameters
SI                       32768
SF              100.6127803 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.40
```

```
Current Data Parameters
NAME                 081123
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20081123
Time                  15.06
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      287
DW                   60.800 usec
DE                    6.50 usec
TE                   295.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.61 usec
PL1                  -3.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF             400.1300031 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```



BRUKER

Current Data Parameters
NAME 081123
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20081123
Time 23.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 45.2
DW 20.800 usec
DE 7.50 usec
TE 295.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL12 16.43 dB
PL13 19.37 dB
PL2 -3.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

7.67
7.66
7.66
7.65
7.44
7.43
7.42
7.26
4.12
4.11
4.09
4.07
3.65
3.55
3.51
3.48
3.43
2.86
2.85
2.83
2.81
2.80
2.35
2.30
2.29
2.29
2.26
2.25
2.24
2.09
2.07
2.04
2.02
1.74
1.69
1.67
1.66
1.64
1.62
1.61
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1.49
1.47
1.45
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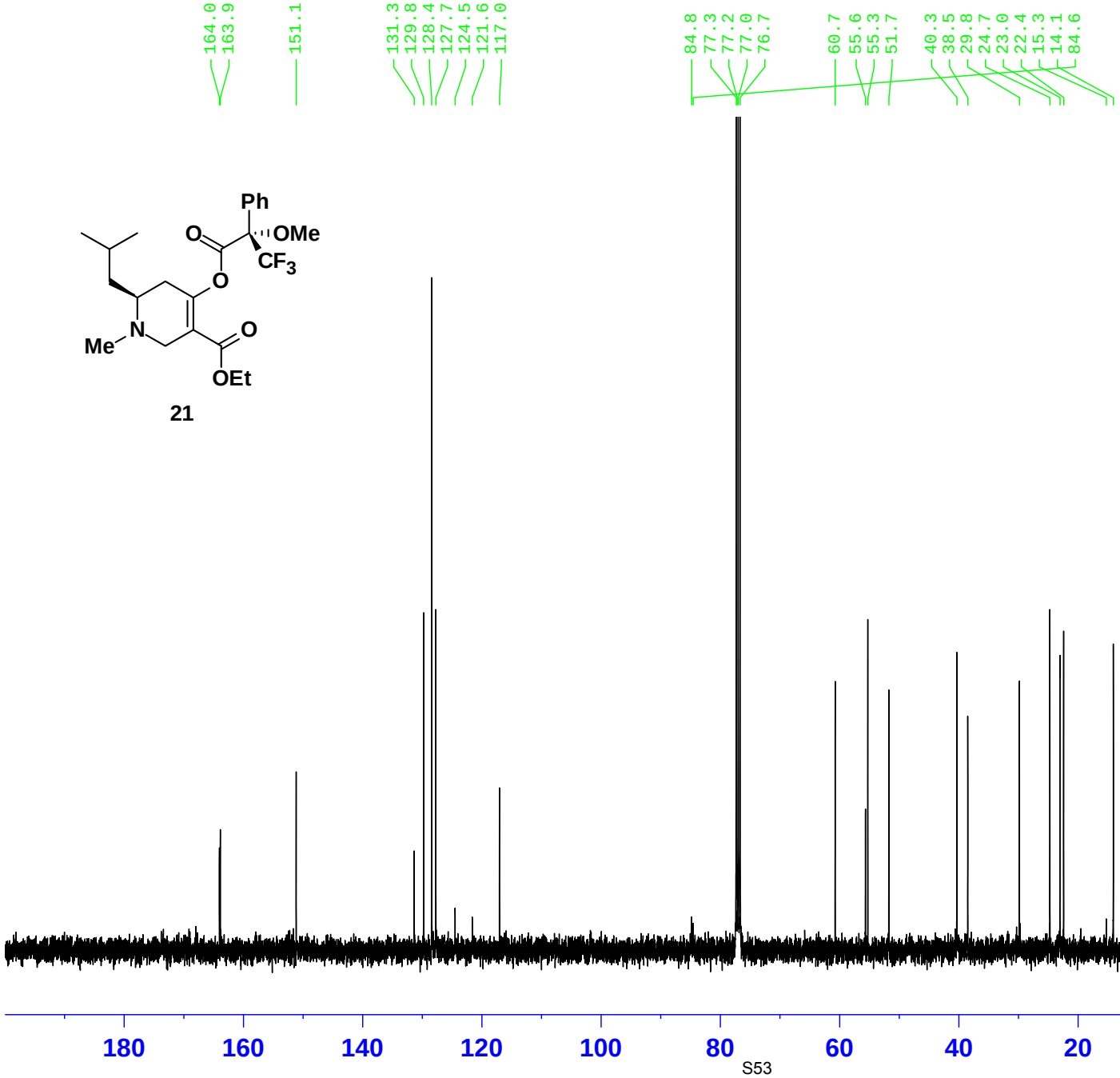
21
Current Data Parameters
NAME 090707
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090707
Time 21.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 181
DW 60.800 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.06 usec
PL1 -3.00 dB
PL1W 18.64416504 W
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300051 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
3.00
2.03
3.09
2.30
1.02
3.04
1.10
1.23
1.37
1.13
5.20
6.42



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```
Current Data Parameters
NAME                 090708
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090708
Time                   9.44
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                     2050
DW                   20.800 usec
DE                    6.50 usec
TE                   298.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.30 usec
PL1                   -3.00 dB
PL1W           71.16858673 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                   -3.00 dB
PL12                  16.43 dB
PL13                  19.37 dB
PL2W           18.64416504 W
PL12W           0.21259004 W
PL13W           0.10802962 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127690 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

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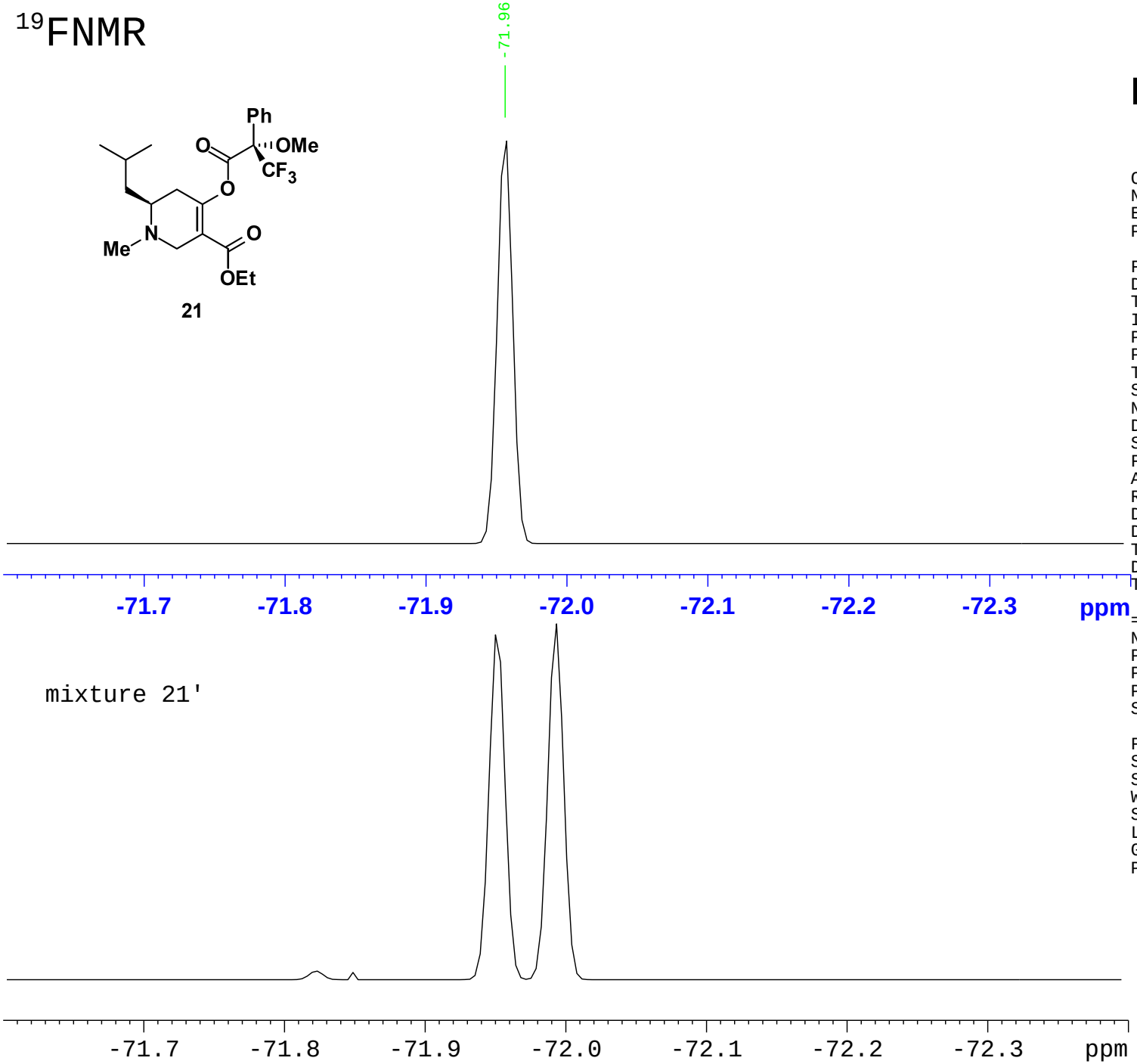



```
Current Data Parameters
NAME                 090708
EXPNO                    31
PROCNO                  999

F2 - Acquisition Parameters
Date_              20090708
Time                 14.06
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zgflqn
TD                   131072
SOLVENT              CDCl3
NS                      16
DS                       4
SWH              89285.711 Hz
FIDRES            0.681196 Hz
AQ               0.7340532 sec
RG                    1030
DW                  5.600 usec
DE                  6.50 usec
TE                  298.1 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   19F
P1                  11.00 usec
PL1                 -4.00 dB
PL1W          26.81568718 W
SFO1          376.4607164 MHz

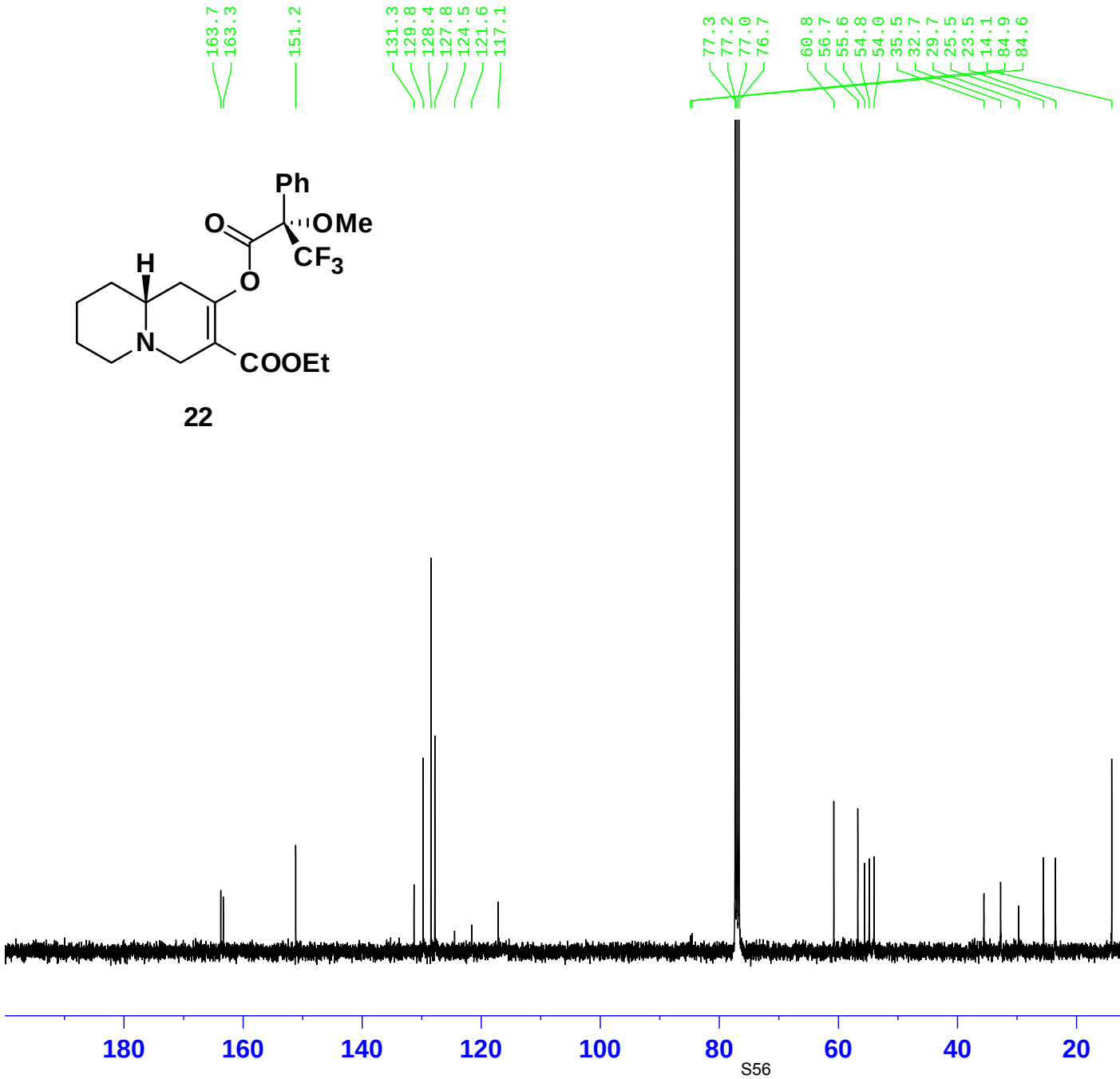
F2 - Processing parameters
SI                    65536
SF            376.4983660 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```

```
Current Data Parameters
NAME                  090614
EXPNO                     40
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090614
Time                  18.34
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      322
DW                   60.800 usec
DE                    6.50 usec
TE                   273.7 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.06 usec
PL1                    -3.00 dB
PL1W           18.64416504 W
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                     32768
SF             400.1300058 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                     1.00
```



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Current Data Parameters
NAME 090830
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090731
Time 1.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
PL1 -3.00 dB
PL1W 71.16858673 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 16.43 dB
PL13 19.37 dB
PL2W 18.64416504 W
PL12W 0.21259004 W
PL13W 0.10802962 W
SFO2 400.1316005 MHz

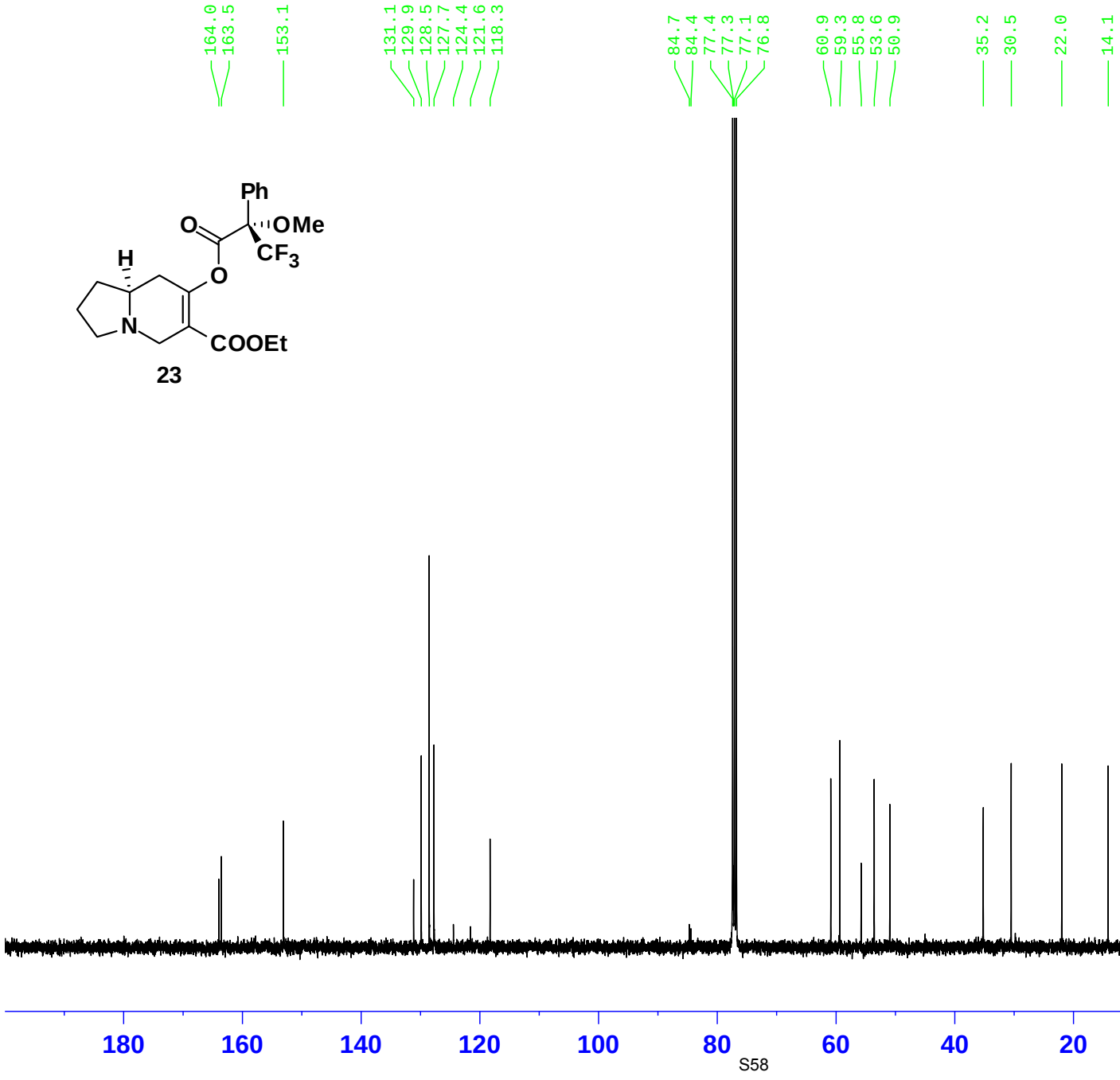
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

```
Current Data Parameters
NAME                 090612
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090612
Time                  11.47
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      256
DW                   60.800 usec
DE                    6.50 usec
TE                   273.2 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.06 usec
PL1                   -3.00 dB
PL1W           18.64416504 W
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF             400.1300058 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                     1.00
```



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```
Current Data Parameters
NAME                 090612
EXPNO                    13
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090612
Time                 23.02
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                   6.50 usec
TE                  274.8 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.30 usec
PL1                  -3.00 dB
PL1W          71.16858673 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2                90.00 usec
PL2                  -3.00 dB
PL12                 16.43 dB
PL13                 19.37 dB
PL2W          18.64416504 W
PL12W          0.21259004 W
PL13W          0.10802962 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF           100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```