Dipolar Cylcloadditions of Trimethylsilyldiazomethane Revisited: Steric Demand of the Dipolarophile and the Influence on Product Distribution.

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Supporting Information

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Compound Data

1-benzyl 5-methyl 3-(trimethylsilyl)-1H-pyrazole-1,5(4H,5H)-dicarboxylate (5b)

Light yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ 7.39-7.28 (m, 5H), 5.34 (d, 1H, J= 12.4Hz), 5.21 (br. s, 1H), 4.63 (dd, 1H, J=6.0, 12.4Hz), 3.64 (br. s, 3H), 3.22 (dd, 1H, J=12.4, 18.1Hz), 2.95 (dd, 1H, J=6.4, 18.1Hz), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 173.6 (s), 164.2 (s), 154.7 (s), 138.4(s), 130.7, 130.5, 130.4, 70.0, 59.1, 54.8, 45.7, 0.0. **HR-MS (EI$^+$)** calcd for $C_{16}H_{23}N_2O_4Si$ (MH^+): 335.1427; found 335.1422.

1-benzyl 5-methyl 1H-pyrazole-1,5(4H,5H)-dicarboxylate (5c)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ 7.31-7.20 (m, 5H), 6.77 (s, 1H), 5.24 (d, 1H, J= 12.4Hz), 5.13 (d, 1H, J= 11.6Hz), 4.66 (dd, 1H, J=5.8, 12.4Hz), 3.61 (s, 3H), 3.17 (dd, 1H, J=12.4, 18.4Hz), 2.89 (dd, 1H, J=6.0, 18.4Hz) ^{13}C NMR ($CDCl_3$, 100M Hz) δ 169.2 (s), 151.2 (s), 143.2, 134.5 (s), 127.2, 126.97, 126.95, 66.7, 55.6, 51.3, 37.8. **HR-MS (EI$^+$)** calcd for $C_{13}H_{15}O_4N_2$ (MH^+): 263.1032, found 263.1027.

1-benzyl 5-ethyl 3-(trimethylsilyl)-1H-pyrazole-1,5(4H,5H)-dicarboxylate (6b)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.50-7.25 (m, 5H), 5.30-5.15 (m, 2H), 4.61 (dd, 1H, J=6.0, 12.4Hz), 4.10 (bs, 2H), 3.20 (dd 1H, J=18Hz, 12.3Hz), 2.95 (dd, 1H, J=18.1Hz, 6.1Hz), 1.22 (bs, 3H), 0.25 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 171.1 (s), 162.2 (s), 152.7(s), 136.5(s), 128.8, 128.5, 68.0, 61.9, 57.3, 43.8, 14.4, -1.9; **HR-MS (EI+)**: calcd for $C_{17}H_{24}O_4N_2Si$ (M+): 348.1505, found: 348.1496

1-benzyl 5-ethyl 1H-pyrazole-1,5(4H,5H)-dicarboxylate (6c)

Yellow oil; 90% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.50-7.25 (m, 5H), 6.85 (s, 1H), 5.35-5.15 (m, 2H), 4.70 (dd, 1H, J=12.6, 5.9 Hz), 4.35-3.59 (bs, 2H), 3.25 (dd, 1H, J=18.4, 12.6 Hz), 2.95 (dd 1H, J=18.5, 5.2 Hz), 1.40-1.10 (bs, 3H); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 170.5 (s), 152.8 (s), 145.5, 136.2(s), 128.8, 128.6, 128.5, 71.0, 68.1, 62.1, 57.3, 39.4, 14.3; **HR-MS (EI+)**: calcd for $C_{14}H_{16}O_4N_2$ (M+): 276.111007, found: 276.111427

1-benzyl 5-*tert*-butyl 3-(trimethylsilyl)-1H-pyrazole-1,5(4H,5H)-dicarboxylate (7b) Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz), δ 7.20-7.00 (m, 5H), 5.00 (bs, 2H), 4.25 (dd, 1H, J=12.2, 5.8 Hz), 2.95 (dd, 1H,

J=17.9, 12.3 Hz), 2.65 (dd, 1H, J=17.9, 5.8 Hz), 1.15 (s, 9H), 0.03 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.1, 164.1, 154.7, 138.5, 131.0, 130.9, 130.8, 130.7, 130.68, 84.3, 69.8, 59.9, 45.9, 30.1, 0.0; **HR-MS (EI$^+$)**: calcd for $C_{19}H_{28}O_4N_2Si$ (M^+): 376.1818, found: 376.1831

1-benzyl 5-*tert*-butyl 1H-pyrazole-1,5(4H,5H)-dicarboxylate (7c)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.38-7.24 (m, 5H), 6.80 (s, 1H), 5.25 (d, 1H, J= 12.8Hz), 5.21 (d, 1H, J= 12.3Hz), 4.57 (dd, 1H, J=5.6, 12.5Hz), 3.19 (dd, 1H, J=12.6, 18.4Hz), 2.88 (dd, 1H, J=5.6, 18.6Hz), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 169.5 (s), 152.9 (s), 144.9 (d), 136.3 (s), 128.8 (d), 128.7 (d), 128.6 (d), 82.8 (s), 68.1 (t), 58.0 (d), 39.5 (t), 28.1 (q). **HR-MS (EI$^+$)**: calcd for $C_{16}H_{21}N_2O_4$ (MH^+): 305.1501; found 305.1492

1-benzyl 5-(2-isopropyl-5-methylcyclohexyl) 3-(trimethylsilyl)-1H-pyrazole-1,5(4H,5H)-dicarboxylate (8b) Yellow oil; **^{1}H NMR** Both diastereoisomers: ($CDCl_3$, 400MHz), δ 7.20-7.00 (m, 5H), 5.10-4.90 (m, 2H), 4.50-4.30 (m, 2H), 3.05-2.90 (m, 1H), 2.75-2.60 (m, 1H), 1.75-1.45 (m, 2H), 1.40 (m, 2H), 1.30-1.00 (m, 2H), 0.85-0.50 (m, 9H), 0.45 (m, 3H), 0.00 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100MHz) Major diastereoisomer: δ 172.6, 164.1, 154.7, 138.4, 130.9, 130.8, 130.6, 130.4, 130.3, 77.9, 69.9, 59.5, 49.1, 48.9, 46.8, 42.5, 36.4, 33.7, 28.4, 25.6, 24.3, 23.1, 18.6, 0.3; Minor isomer: 164.0, 130.8, 77.9, 69.8, 59.6, 49.1, 42.8, 36.4, 33.6, 28.4, 25.7, 23.0, 18.5; **HR-MS (EI$^+$)**: calcd for $C_{25}H_{38}O_4N_2Si$ (MH^+): 459.2679, found: 459.2687

1-benzyl 5-(2-isopropyl-5-methylcyclohexyl) 1H-pyrazole-1,5(4H,5H)-dicarboxylate (8c)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz), δ 7.45-7.25 (m, 5H), 6.83 (s, 1H), 5.35-5.10 (m, 2H), 4.73-4.65 (m, 2H), 3.30-3.15 (m, 1H), 2.85 (d, 1H Major isomer J=5.7 Hz, d, 1H, Minor isomer J=5.6 Hz), 2.00-1.75 (m, 2H), 1.70-1.60 (d, 2H, J=13.2 Hz), 1.50-1.30 (m, 2H), 1.00 (q, 1H, J=11.0 Hz), 0.95-0.80 (m, 9H), 0.75-0.65 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) Major diastereoisomer: δ 169.6, 152.4, 144.6, 135.9, 128.5, 128.2, 128.1, 127.2, 75.8, 67.8, 57.2, 46.7, 40.4, 39.2, 34.0, 31.3, 26.2, 23.3, 20.8, 18.8 ; Minor diastereoisomer: 169.5, 144.6, 135.7, 128.3, 128.2, 126.8, 75.8, 67.7, 57.1, 46.7, 40.2, 31.2, 26.0, 23.1; **HR-MS (EI$^+$)**: calcd for $C_{22}H_{30}O_4N_2$ (MH^+): 387.2284, found: 387.2294

1-benzyl 3-ethyl 4-methyl-5-(trimethylsilyl)-1H-pyrazole-1,3(4H,5H)-dicarboxylate (9a)

Yellow oil; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 7.35 (m, 2H), 7.30-7.20 (m, 3H), 5.25 (d, 1H, J= 12.2 Hz), 5.18 (d, 1H, J= 12.2 Hz), 4.25 (q, 2H, J=7.1 Hz), 3.40 (d, 1H, J=7.7 Hz), 3.25 (m, 1H), 1.30 (t, 3H, J= 7.1 Hz), 1.22 (d, 3H, J= 6.9Hz), 0.06 (s, 9H); **^{13}C NMR ($CDCl_3$, 100MHz)** δ 161.8 (s), 152.9 (s), 151.0 (s), 135.8 (s), 128.6 (d), 128.5 (d), 128.3 (d), 68.1 (t), 61.7 (t), 58.9 (d), 42.6 (d), 20.1 (q), 14.18 (q), -2.99 (q). **HRMS (EI$^+$)** calcd for $C_{18}H_{27}N_2O_4Si$ (MH^+) 363.1740; found 363.1748; Elemental analysis: calculated: C 59.64 %, H 7.23 %, N 7.73 %; found: C 59.69 %, H 7.26 %, N 7.74 %;

1-benzyl 5-ethyl 4-methyl-3-(trimethylsilyl)-1H-pyrazole-1,5(4H,5H)-dicarboxylate (9b)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz), δ 7.20-6.95 (m, 5H), 5.05-4.90 (m, 2H), 3.93 (d, 1H, J=5.3 Hz), 3.84 (bs, 2H), 3.05-2.95 (quintet, 1H J= 6.0 Hz), 1.00 (d, 3H, J= 7.3 Hz), 0.90 (bs, 3H), 0.00 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 171.9 (s), 167.3 (s), 154.0 (s), 137.6 (s), 129.9, 129.8, 129.6, 69.1, 66.5, 63.0, 53.8, 20.0, 15.6, 0.0; **HR-MS (EI$^+$)** calcd for $C_{18}H_{27}N_2O_4Si$ (M^+): 362.1662, found: 362.1656

1-benzyl 5-ethyl 4-methyl-1H-pyrazole-1,5(4H,5H)-dicarboxylate (9c)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) ($CDCl_3$, 400MHz), δ 7.30-7.26 (m, 5H), 6.75 (s, 1H), 5.30-5.10 (m, 2H), 4.28 (d, 1H, J=5.6 Hz), 4.12 (bs, 2H), 3.30-3.15 (m, 1H), 1.25 (d, 3H, J=7.3 Hz), 1.10 (bs, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.9, 152.6, 149.5, 135.9, 128.4, 128.2, 128.2, 68.0, 64.8, 61.7, 47.3, 17.5, 14.1; **HR-MS (EI$^+$)** calcd for $C_{15}H_{18}N_2O_4$ (M^+): 290.1267, found: 290.1268; Elemental analysis: calculated: C 62.06 %, H 6.25 %, N 9.65 %; found: C 61.75 %, H 6.23 %, N 9.58 %;

1-benzyl 5-*tert*-butyl 4-methyl-3-(trimethylsilyl)-1H-pyrazole-1,5(4H,5H)-dicarboxylate (10b)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400MHz), δ 7.20-6.98 (m, 5H), 5.00 (s, 2H), 3.81 (d, 1H, J=4.9 Hz), 2.95 (dq, 1H, J=7.2Hz, 5.1 Hz), 1.15 (s, 9H), 0.98 (d, 3H, J= 7.3 Hz), 0.00 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 170.9, 167.2, 154.2, 137.7, 130.3, 130.1, 130.0, 129.7, 129.6, 83.4, 69.0, 67.4, 53.7, 29.4, 20.0, 0.0; **HR-MS**: **(EI$^+$)** calcd for $C_{20}H_{30}O_4N_2Si$ (M^+): 390.1975, found: 390.1977

1-benzyl 5-tert**-butyl 4-methyl-1H-pyrazole-1,5(4H,5H)-dicarboxylate (10c)**

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400MHz), δ 7.40-7.20 (m, 5H), 6.70 (s, 1H), 5.25 (s, 1H, J=12.2Hz), 5.21 (s, 1H, J=12.2Hz), 4.13 (d, 1H, J=5.5Hz), 3.15 (d,quint, 1H, J=7.1 Hz, 1 Hz), 1.35 (s, 9H), 1.20 (d, 3H, J=7.3Hz); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 168.8, 152.7, 148.9, 135.9, 128.9, 128.5, 128.3, 128.2, 128.0, 82.4, 67.8, 65.4, 47.3, 27.8, 17.6; **HR-MS (EI$^+$)** calcd for $C_{17}H_{22}O_4N_2$ (M^+): 319.1658, found: 319.1667

1-benzyl 5-(2-isopropyl-5-methylcyclohexyl) 4-methyl-3-(trimethylsilyl)-1H-pyrazole-1,5(4H,5H)-dicarboxylate (11b) Yellow oil; **^{1}H NMR** ($CDCl_3$, 400MHz), δ 7.45-7.25 (m, 5H), 5.40-5.10 (m, 2H), 4.70-4.60 (m, 1H), 4.20 (d, 1H major isomer J= 4.3 Hz, minor isomer J= 4.9 Hz), 3.20 (m, 1H), 2.00-1.75 (m, 1H), 1.75-1.55 (m, 3H), 1.50-1.30 (m, 2H), 1.25 (d, 3H, J= 9.1 Hz), 1.10-0.95 (m, 1H), 0.95-0.75 (m, 9H), 0.70 (m, 3H), 0.25 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100MHz) Major diastereoisomer: δ 171.6, 167.4, 154.2, 137.5, 130.2, 130.1, 130.0, 129.9, 77.1, 69.0, 66.7, 48.1, 42.0, 35.7, 32.9, 27.7, 24.8, 23.6, 22.2, 20.3, 17.7, 0.0; Minor diastereoisomer: 171.5, 130.1, 130.0, 130.0, 129.9, 129.8, 77.0, 69.2, 66.8, 48.3, 42.0, 35.6, 32.8, 27.6, 24.6, 22.4, 19.9, 17.5, 0.2; **HR-MS (EI$^+$)** calcd for $C_{26}H_{40}O_4N_2Si$ (MH^+): 473.2836, found: 473.2823

1-benzyl 5-(2-isopropyl-5-methylcyclohexyl) 4-methyl-1H-pyrazole-1,5(4H,5H)-dicarboxylate (11c) Yellow oil; **^{1}H NMR** ($CDCl_3$, 400MHz), δ 7.40-7.20 (m, 5H), 6.70 (s, 1H), 5.30-5.00 (m, 2H), 4.70-4.55 (m, 1H), 4.2 (d, 1H major isomer J=5.2 Hz, minor isomer 5.7 Hz), 3.2-3.05 (m, 1H), 1.90-1.65 (m, 2H) 1.65-1.55 (m, 2H), 1.45-1.25 (m, 2H), 1.23 (d, 3H, major diastereoisomer J= 7.3Hz, minor diastereoisomer J=7.3 Hz), 1.00-0.85 (m, 1H), 0.85-0.70 (m, 9H), 0.60 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) Major diastereoisomer: δ 169.4, 152.5, 135.8, 128.4, 128.2, 128.1, 127.1, 103.9, 77.7, 77.1, 75.6, 67.8, 65.7, 47.5, 40.5, 34.0, 34.0, 31.2, 26.28, 23.4, 22.6, 20.8, 18.2, Minor diastereoisomer: 169.3, 149.0, 135.7, 128.1, 126.7, 103.5, 77.4, 75.9, 67.7, 23.1; **HR-MS (EI$^+$)** calcd for: $C_{23}H_{32}O_4N_2$ (MH^+): 401.2440, found: 401.2445

1-benzyl 3-ethyl 4-phenyl-5-(trimethylsilyl)-1H-pyrazole-1,3(4H,5H)-dicarboxylate (12a)

White crystalline solid, mp: 76-78 ^{o}C, **^{1}H NMR** ($CDCl_3$, 600MHz) δ 7.35 (d, 2H, J=1.6Hz), 7.39-7.10 (m, 6H), 7.00 (d, 1H, J=6.9 Hz), 5.25 (d, 1H, J=12.2 Hz), 5.15 (d, 1H, J=12.2 Hz) 4.25 (d, 1H, J=6.8 Hz), 4.1

(m, 2H), 3.83 (d, 1H, J=6.7 Hz), 1.1 (t, 3H, J=7.1 Hz), 0.00 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 161.3, 152.6, 149.0, 141.2, 135.8, 129.1, 128.5, 128.4, 127.7, 127.1, 68.3, 61.7, 61.1, 53.1, 14.0, -2.9; **HR-MS (EI$^+$)** calcd for $C_{23}H_{28}O_4N_2Si$ (MH^+): 425.1897, found: 425.1884

1-benzyl 5-ethyl 4-phenyl-3-(trimethylsilyl)-1H-pyrazole-1,5(4H,5H)-dicarboxylate (12b)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.43-7.25 (m, 8H), 7.10 (d, 2H 7.6 Hz), 5.35-5.10 (m, 2H), 4.5 (d, 1H, J= 4.8 Hz), 4.20 (d, 1H, J= 5.0 Hz), 4.1 (bs, 2H), 1.17 (bs, 3H), 0.00 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 171.8, 165.4, 154.0, 140.1, 137.7, 131.0, 130.8, 130.8, 130.2, 130.0, 129.9, 129.8, 129.4, 69.5, 68.0, 64.7, 63.4, 15.8, 0.0.

1-benzyl 5-ethyl 4-phenyl-1H-pyrazole-1,5(4H,5H)-dicarboxylate (12c)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.45-7.25 (m 8H), 7.10 (d, 2H, J= 5.6 Hz), 6.90 (s, 1H), 5.30-5.10 (m, 2H), 4.65 (d, 1H, J=5.4 Hz), 4.33 (d, 1H, J=5.5), 4.19 (bs, 2H), 1.27 (bs, 3H); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 169.5 (s), 152.4 (s), 146.5, 137.1 (s), 135.7 (s), 129.4, 128.6, 128.5, 128.5, 128.3, 128.3, 128.0, 127.3, 68.1, 66.0, 62.0, 57.7, 14.1; **HR-MS (EI$^+$)** calcd for**:** $C_{20}H_{20}O_4N_2$ (MH^+): 352.1423, found: 352.1430

1-benzyl 3-tert-butyl 4-phenyl-5-(trimethylsilyl)-1H-pyrazole-1,3(4H,5H)-dicarboxylate (13a)

White crystalline solid, mp: 88-90 ^{o}C, **^{1}H NMR** ($CDCl_3$, 400MHz), δ 7.33 (d, 2H, J=5.7 Hz), 7.30-7.10 (m, 6H), 7.00 (d, 2H, J=7.0 Hz), 5.23 (d, 1H, J=12.3 Hz), 5.15 (d, 1H, J=12.7 Hz), 4.15 (d, 1H, J=7.4 Hz), 3.80 (d, 1H, J=7.4 Hz,), 1.20 (s, 9H), 0.20 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 160.1, 152.8, 150.3, 141.5, 135.8, 129.0, 128.5, 128.3, 127.5, 127.3, 82.8, 68.8, 60.9, 53.5, 27.8, -2.8; **HR-MS (EI$^+$)** calcd for: $C_{25}H_{32}O_4N_2Si$ (MH^+): 453.2210, found: 453.2206

1-benzyl 5-tert-butyl 4-phenyl-3-(trimethylsilyl)-1H-pyrazole-1,5(4H,5H)-dicarboxylate (13b)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400MHz), δ 7.40-7.20 (m, 8H), 7.05 (d, 2H, J= 6.4 Hz), 5.30-5.15 (m, 2H), 4.40 (d, 1H, J=4.7 Hz), 4.15 (d, 1H, J=4.7 Hz,), 1.35 (s, 9H), 0.00 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 170.8, 165.3, 154.2, 140.3, 137.7, 130.9, 130.2, 129.9, 129.9, 129.4, 84.0, 69.4, 68.7, 64.9, 29.6, 0.0; **HR-MS (EI$^+$)** calcd for: $C_{25}H_{32}O_4N_2Si$ (MH^+): 453.2210, found: 453.2223

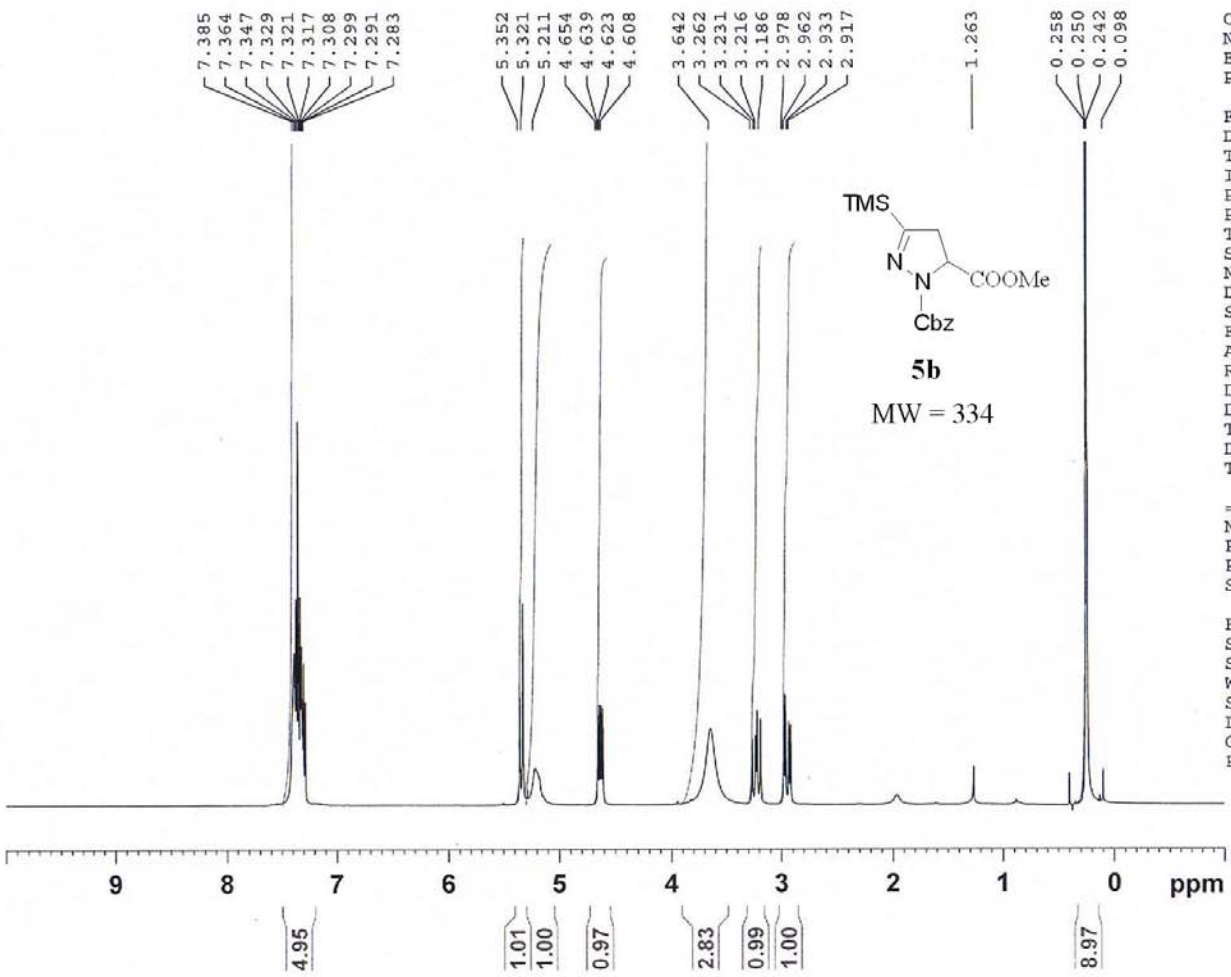
1-benzyl 5-tert-butyl 4-phenyl-1H-pyrazole-1,5(4H,5H)-dicarboxylate (13c)

White crystalline solid, mp: 97-100 ^{o}C, **^{1}H NMR** ($CDCl_3$, 400 MHz), δ 7.48-7.28 (m, 8H), 7.15 (m, 2H), 6.92 (s, 1H), 5.35-5.25 (m, 2H), 4.55 (d, 1H, J=5.4Hz), 4.30 (dd, 1H, J=5.4, 1.3 Hz,), 1.48 (s, 9H), **^{13}C NMR** ($CDCl_3$, 100MHz) δ 168.5, 152.5, 146.2, 137.4, 135.7, 129.4, 128.5, 128.4, 128.3, 127.3, 82.7, 68.0, 66.6, 57.9, 28.0; **HR-MS (EI^{+})** calcd for: $C_{22}H_{24}O_4N_2$ (M^{+}): 381.1814, found: 381.1817

1-benzyl 3-(2-isopropyl-5-methylcyclohexyl) 4-phenyl-5-(trimethylsilyl)-1H-pyrazole-1,3(4H,5H)-dicarboxylate (14a) White crystalline solid, mp: 140-142 ^{o}C, **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.35 (m, 2H), 7.30-7.10 (m, 6H), 7.00 (d, 2H, J= 6.8 Hz), 5.25 (d, 1H, J= 12.2 Hz), 5.15 (d, 1H, 12.2 Hz), 4.55 (m, 1H,), 4.20 (d, 1H, J=7.1 Hz), 3.80 (d, 1H, J=7.1 Hz), 1.70-1.55 (m, 2H), 1.50 (m, 5H), 1.30-1.10 (m, 3H), 0.95-0.80 (m, 1H), 0.70 (m, 7H), 0.50 (d, 3H, J= 6.9 Hz), 0.00 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ major diastereomer: 160.9, 152.8, 149.6, 141.1, 129.0, 128.5, 128.3, 127.6, 127.2, 76.0, 68.2, 60.6, 53.4, 46.7, 40.1, 34.0, 31.3, 26.5, 23.7, 21.9, 20.5, 16.5, -2.89; **HR-MS (FAB^{+})** calcd for $C_{31}H_{42}O_4N_2Si$ (MH^{+}): 535.2992, found: 535.2970, diastereomers ratio 63:37%.

1-benzyl 5-(2-isopropyl-5-methylcyclohexyl) 4-phenyl-1H-pyrazole-1,5(4H,5H)-dicarboxylate (14c) Yellow oil; **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.50-7.20 (m, 8H), 7.13 (t, 2H, J= 6.5 Hz), 6.90 (bs, 1H), 5.40-5.15 (m, 2H), 4.75 (m, 1H), 4.65 (m, 1H), 4.30 (d, 1H, major isomer J=4.7 Hz, minor isomer J= 5.8 Hz), 2.05-1.75 (m, 2H), 1.70 (m, 2H), 1.55-1.30 (m, 2H), 0.60-0.50 (m, 1H), 0.95-0.80 (m, 8H), 0.80-0.65 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100MHz) Major diastereoisomer: δ 169.3, 152.4, 146.3, 137.2, 135.8, 129.4, 128.6, 128.5, 128.3, 127.5, 127.3, 76.2, 68.2, 66.4, 58.0, 46.8, 40.4, 34.1, 31.4, 26.2, 23.4, 22.0, 20.8, 16.2; Minor diasteroisomer: 169.3, 146.2, 137.0, 135.6, 76.1, 68.0, 66.1, 46.7, 40.4, 26.0, 23.0, 22,0, 20.7, 16.0; **HR-MS (EI^{+})** calcd for: $C_{28}H_{34}O_4N_2$ (MH^{+}): 463.2597, found: 463.2586

Table 1, Cmpd. 5b

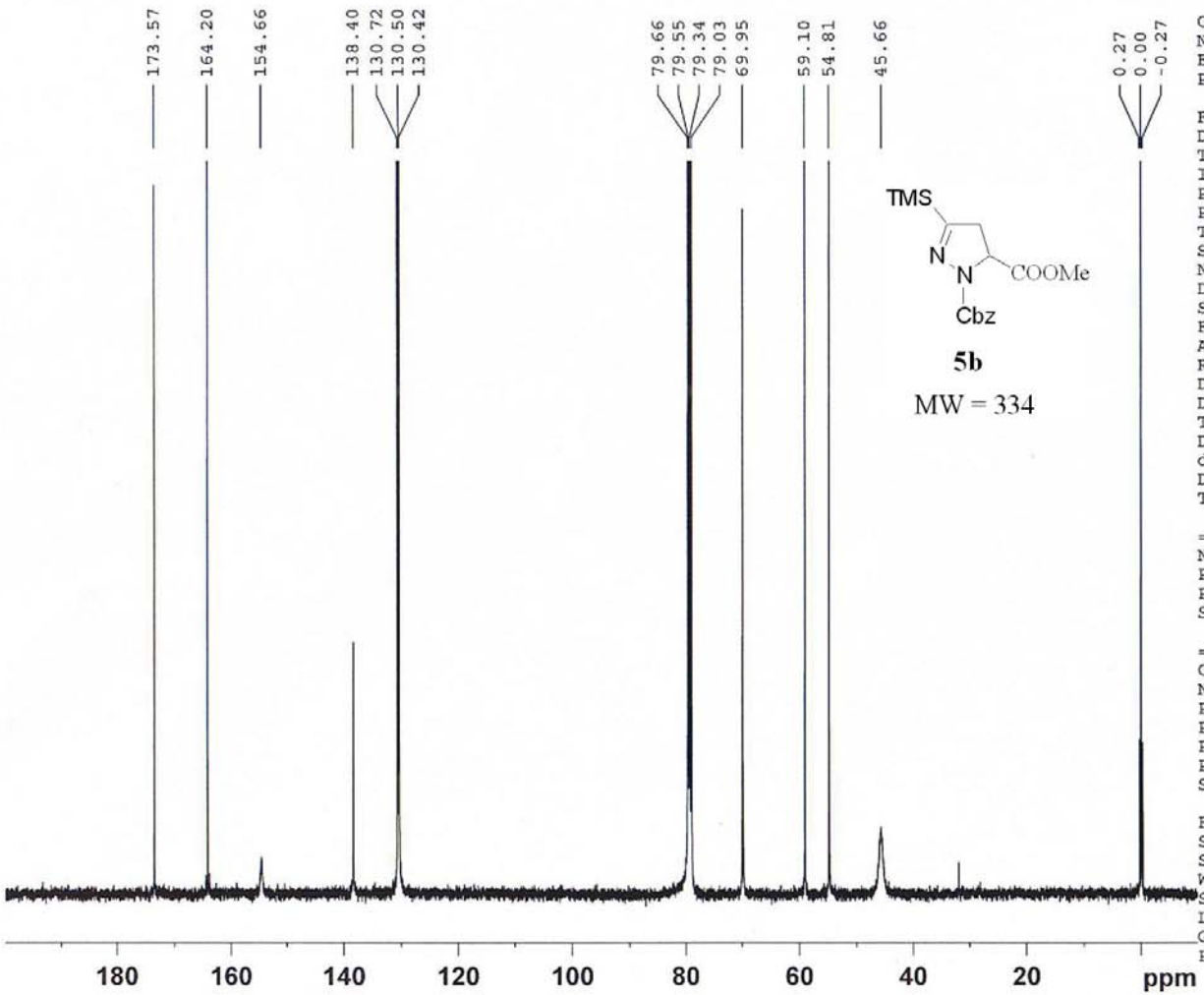


5b

MW = 334

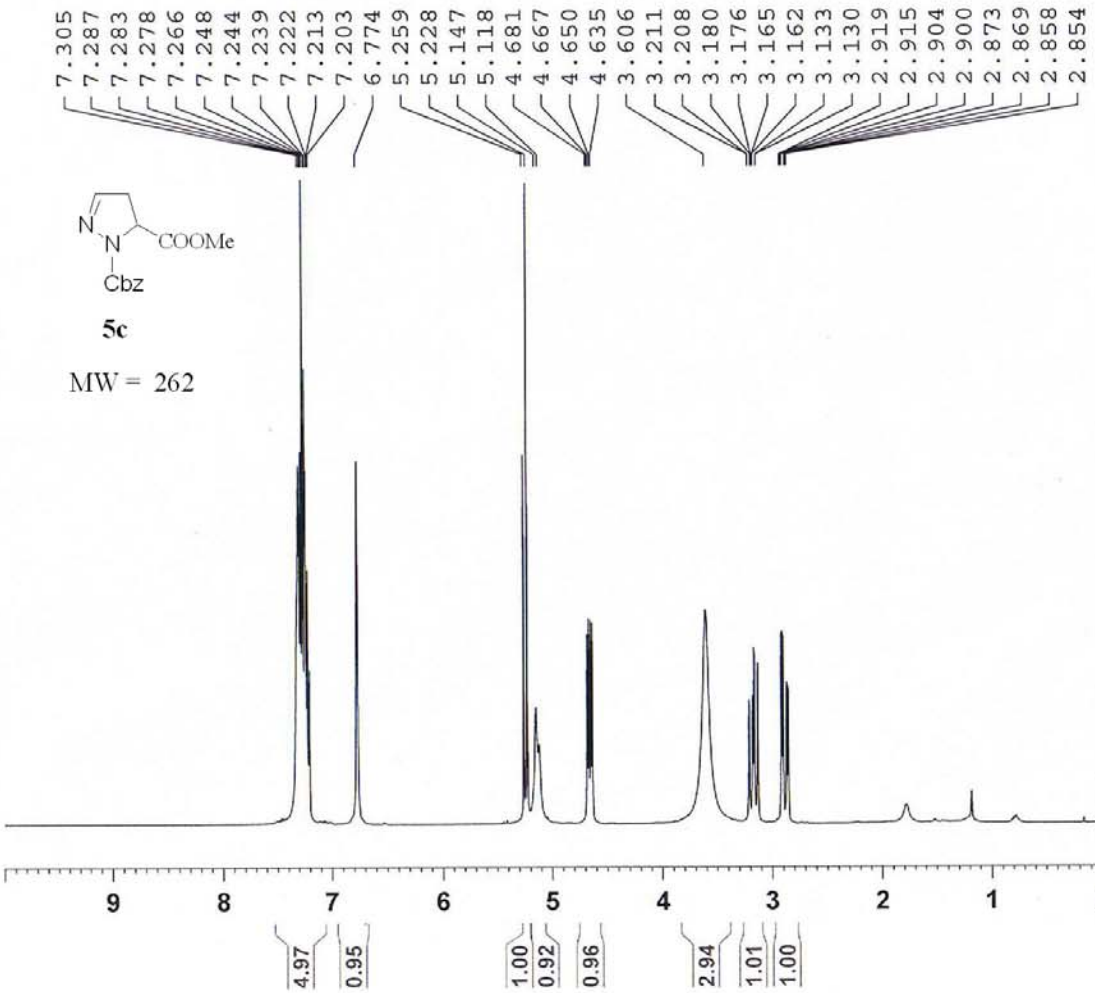
```
Current Data Parameters
NAME          400-08122006
EXPNO                   30
PROCNO                   1

F2 - Acquisition Parameters
Date_              20060812
Time                  22.37
INSTRUM               spect
PROBHD    5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                     45.3
DW                   60.400 usec
DE                    6.00 usec
TE                   296.2 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.25 usec
PL1                    0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF            400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

Table 1, Cmpd. 5b




```
Current Data Parameters
NAME          400-08132006
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_              20060814
Time                   8.43
INSTRUM               spect
PROBHD    5 mm QNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    23500
DS                        4
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                 1.3664756 sec
RG                    1290.2
DW                    20.850 usec
DE                     6.00 usec
TE                    296.2 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    12.50 usec
PL1                    0.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  16.30 dB
PL13                  16.30 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF             100.6125395 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                      1.40
```

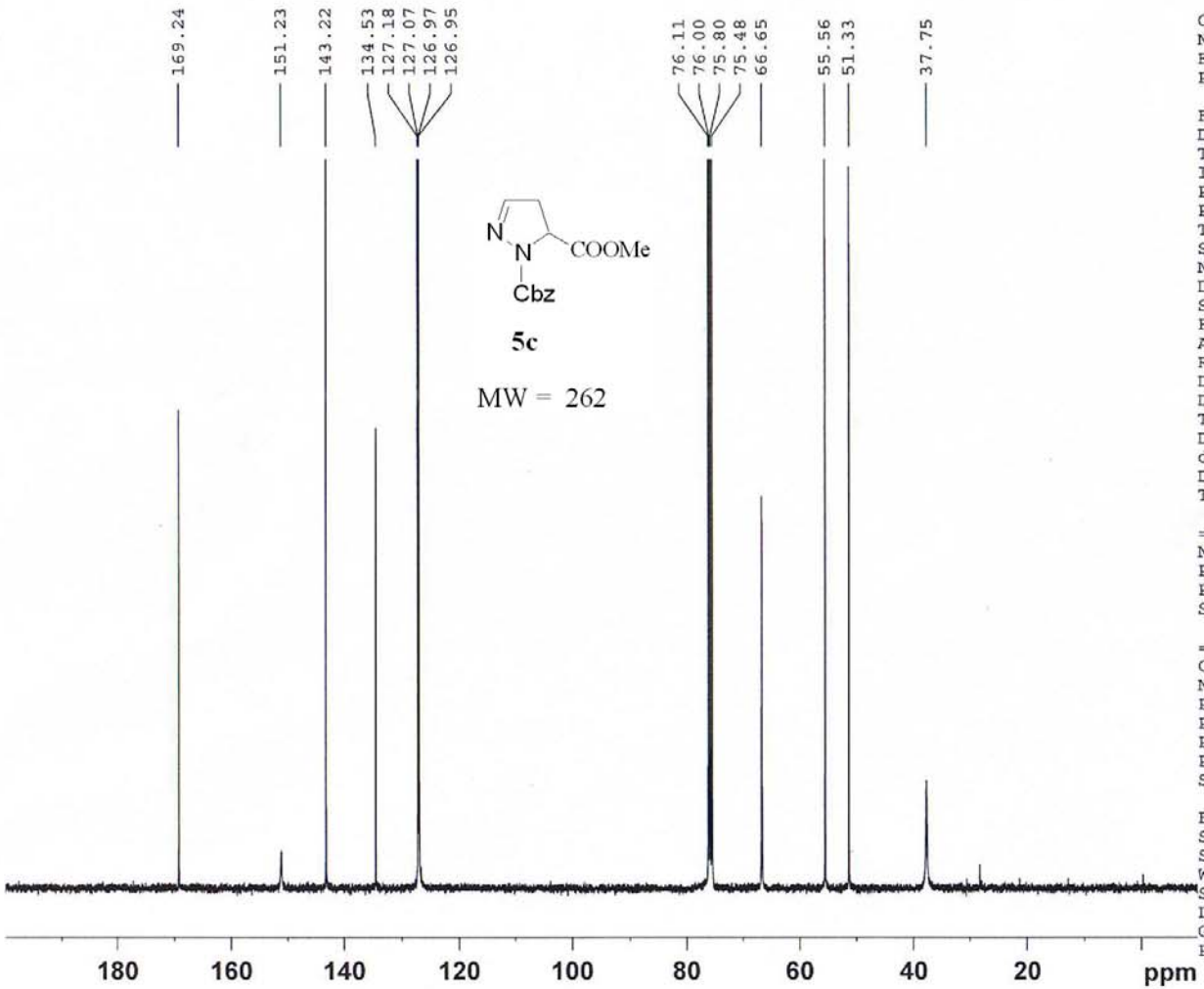
Table 1, Cmpd. 5c



BRUKER

```
Current Data Parameters
NAME      WM-400-Aug06-2005
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameters
Date_              20050806
Time                 15.51
INSTRUM              spect
PROBHD    5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                     64
DW                60.400 usec
DE                 6.00 usec
TE                298.2 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.25 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300320 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

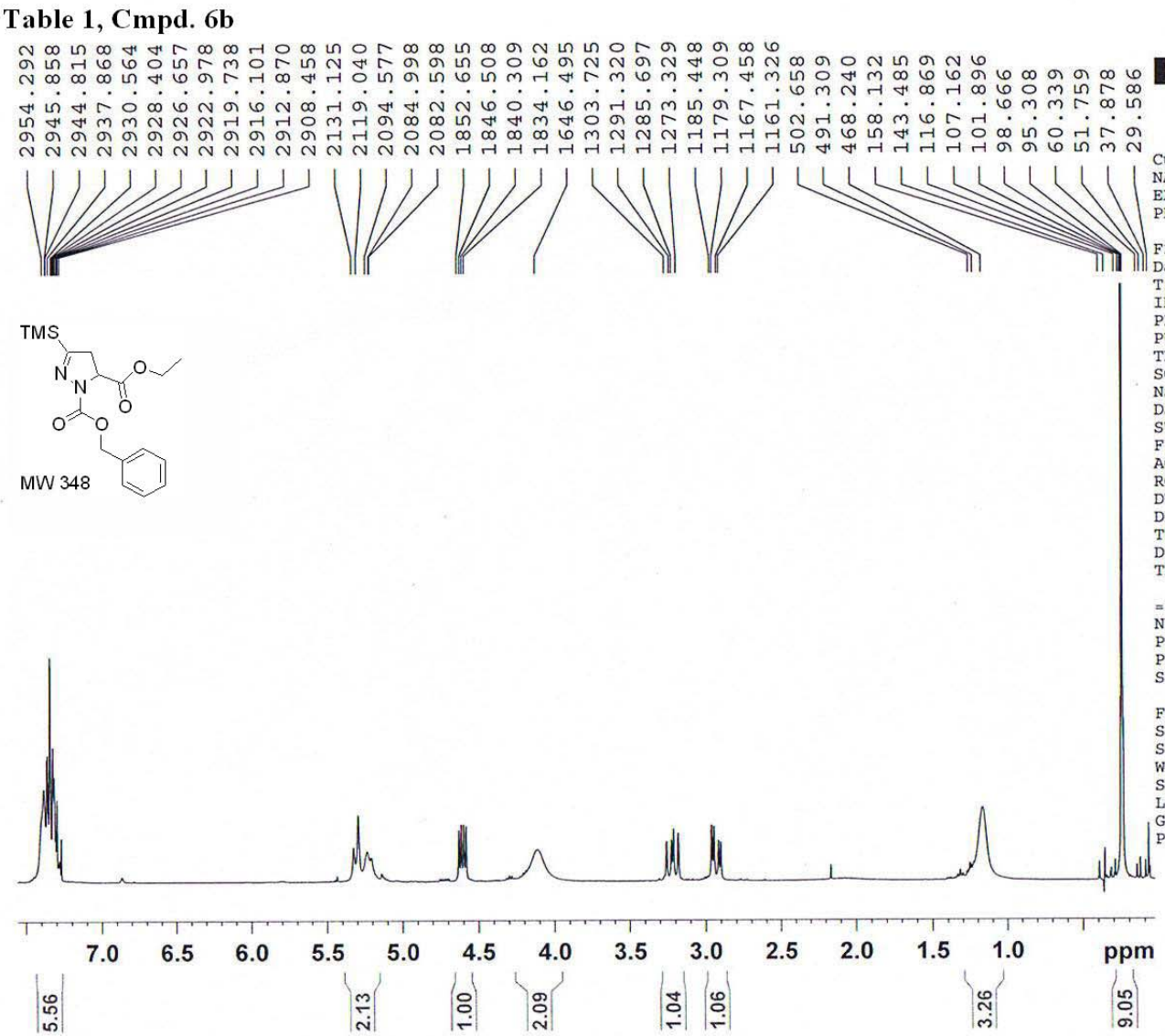
Table 1, Cmpd. 5c



BRUKER

```
Current Data Parameters
NAME      WM-400-Aug10-2005
EXPNO                   31
PROCNO                   1

F2 - Acquisition Parameters
Date_             20050811
Time                 1.21
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   4700
DS                      4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                   3251
DW                20.850 usec
DE                 6.00 usec
TE                302.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 12.50 usec
PL1                 0.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               16.30 dB
PL13               16.30 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF           100.6129016 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

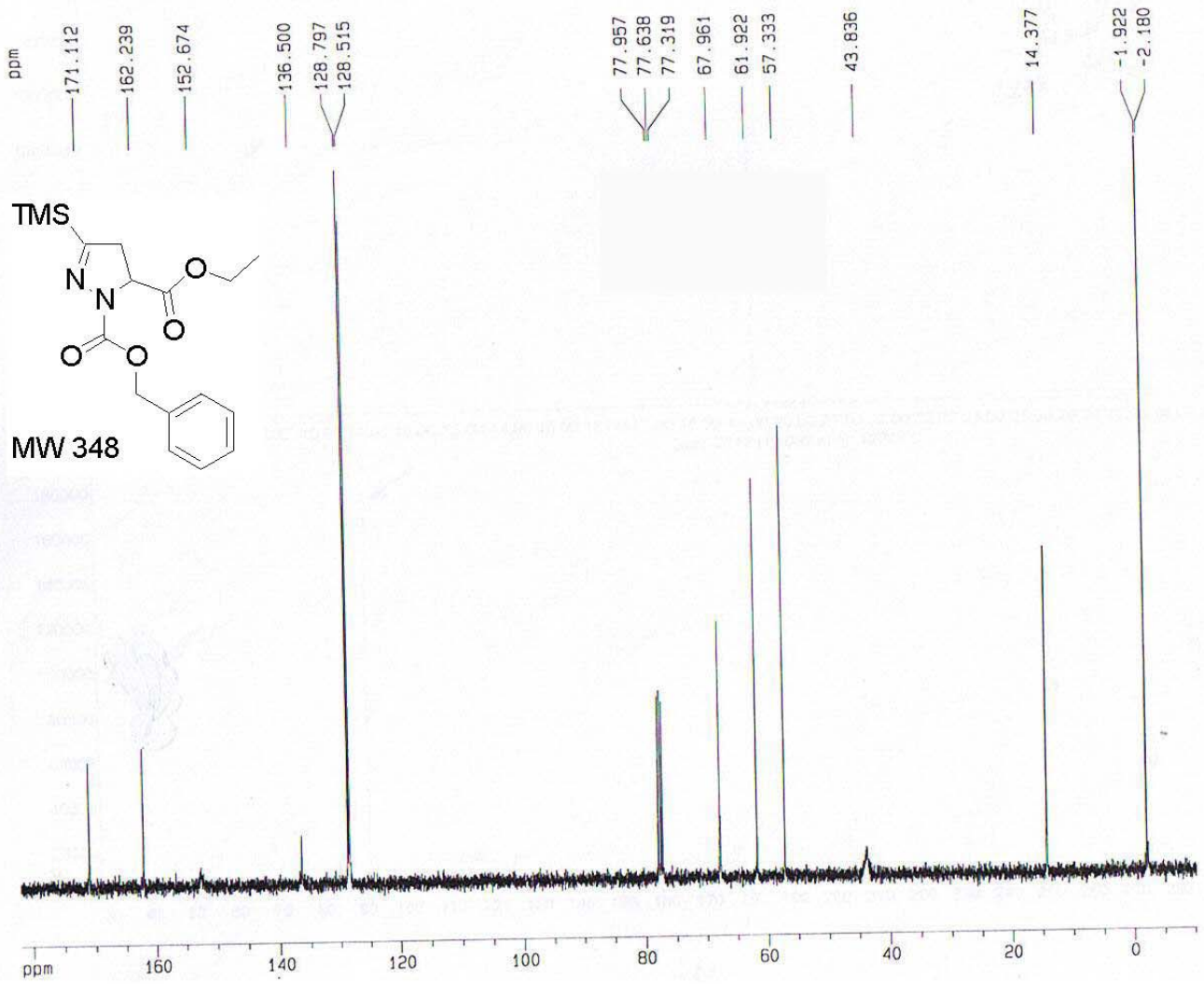
Table 1, Cmpd. 6b



BRUKER

```
Current Data Parameters
NAME      400-Aug03-2006
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060803
Time              15.31
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                 90.5
DW               60.400 usec
DE                6.00 usec
TE               296.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.25 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300059 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Table 1, Cmpd. 6b



Current Data Parameters

NAME	Dragan4
EXPNO	17
PROCNO	1

F2 - Acquisition Parameters

Date_	20050307
Time	13.24
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	70
DS	4
SWH	25125.629 Hz
FIDRES	0.383387 Hz
AQ	1.3042164 sec
RG	4096
DW	19.900 usec
DE	6.00 usec
TE	300.0 K
D1	0.50000000 sec
D11	0.03000000 sec
D12	0.00002000 sec

CHANNEL f1

NUC1	13C
P1	12.50 usec
PL1	0.00 dB
SFO1	100.6237959 MHz

CHANNEL f2

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	19.00 dB
SFO2	400.1316005 MHz

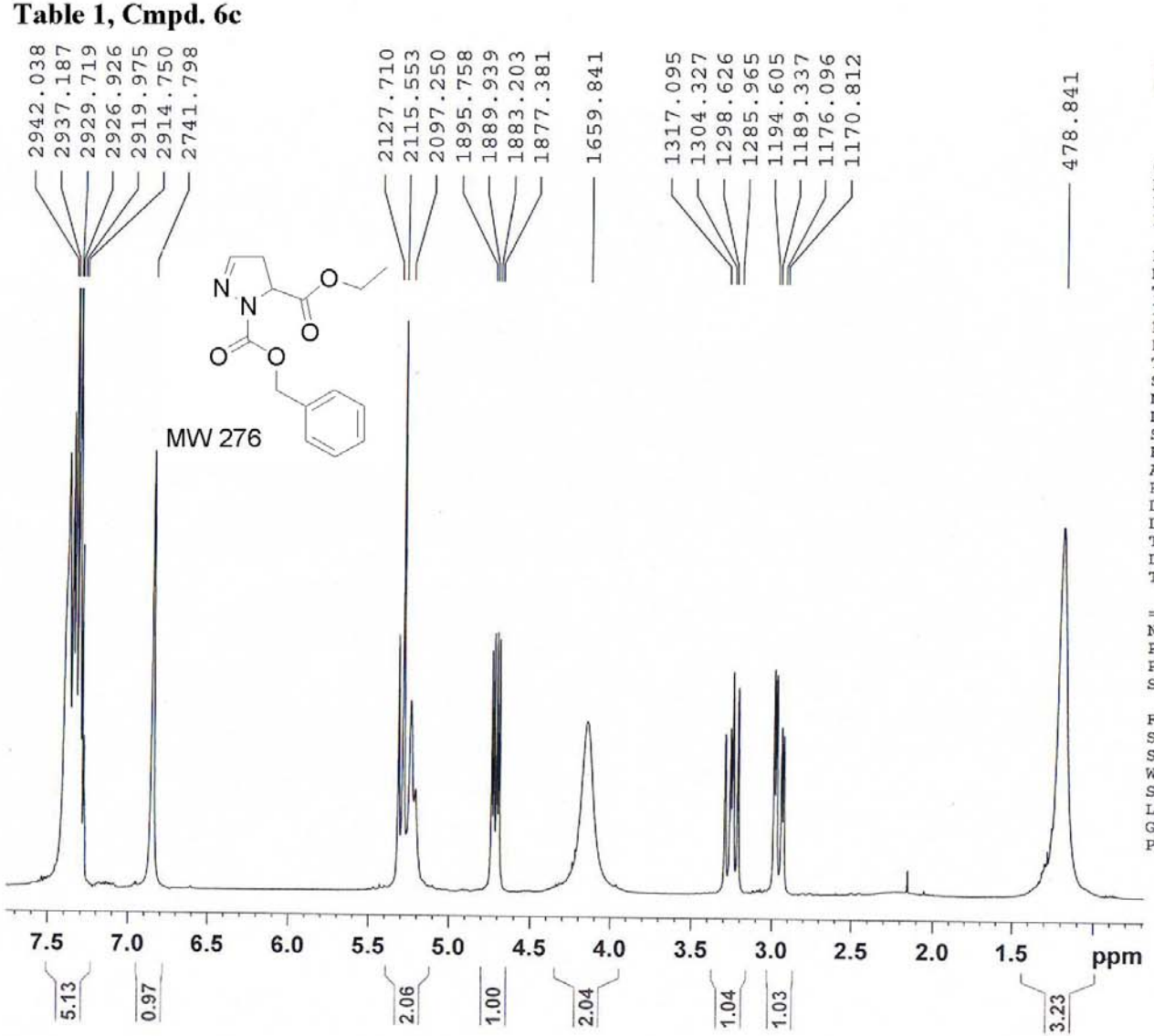
F2 - Processing parameters

SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	182.066 ppm
F1	18318.13 Hz
F2P	-10.123 ppm
F2	-1018.46 Hz
PPMCM	9.60941 ppm/cm
HZCM	966.82941 Hz/cm

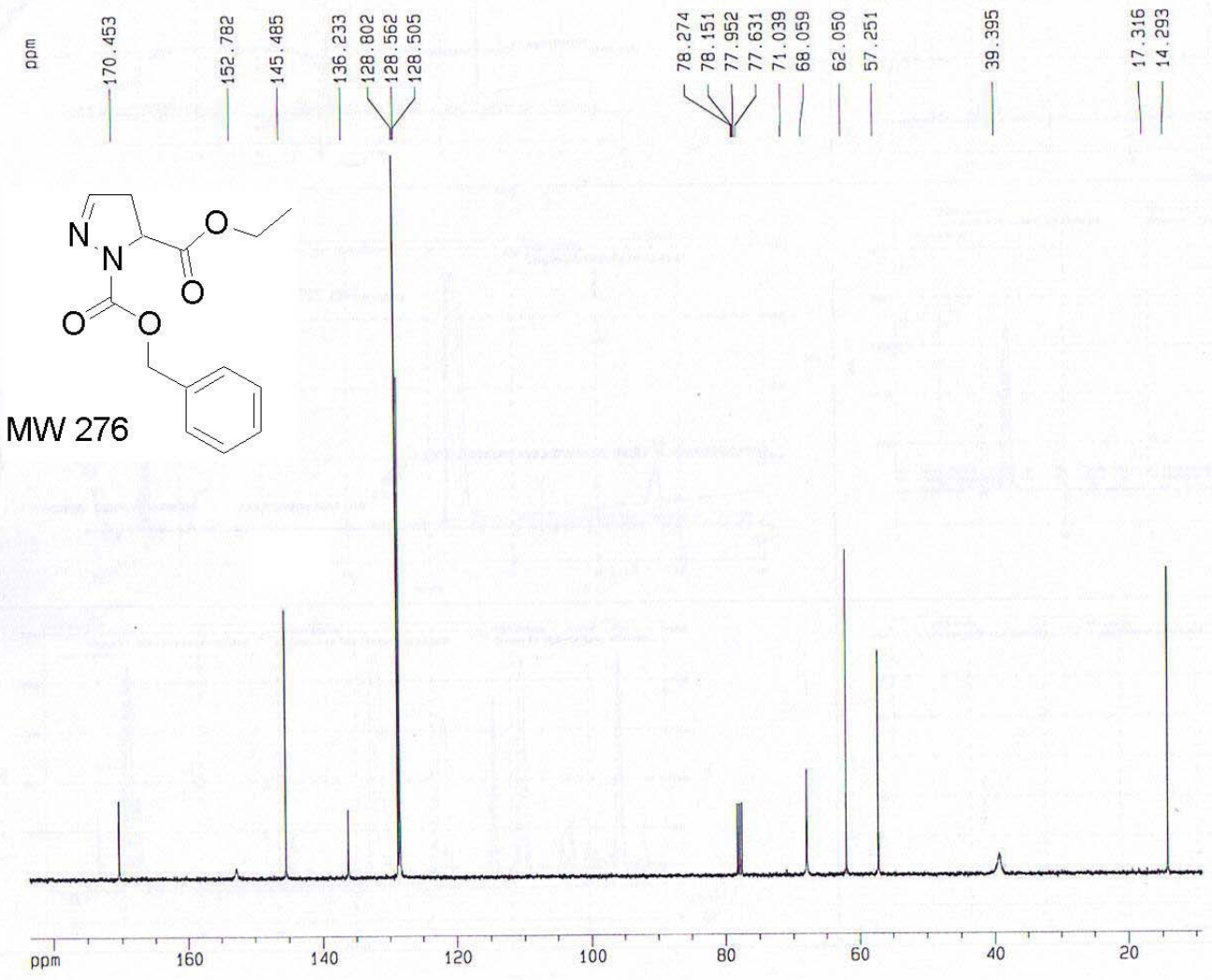
Table 1, Cmpd. 6c



BRUKER

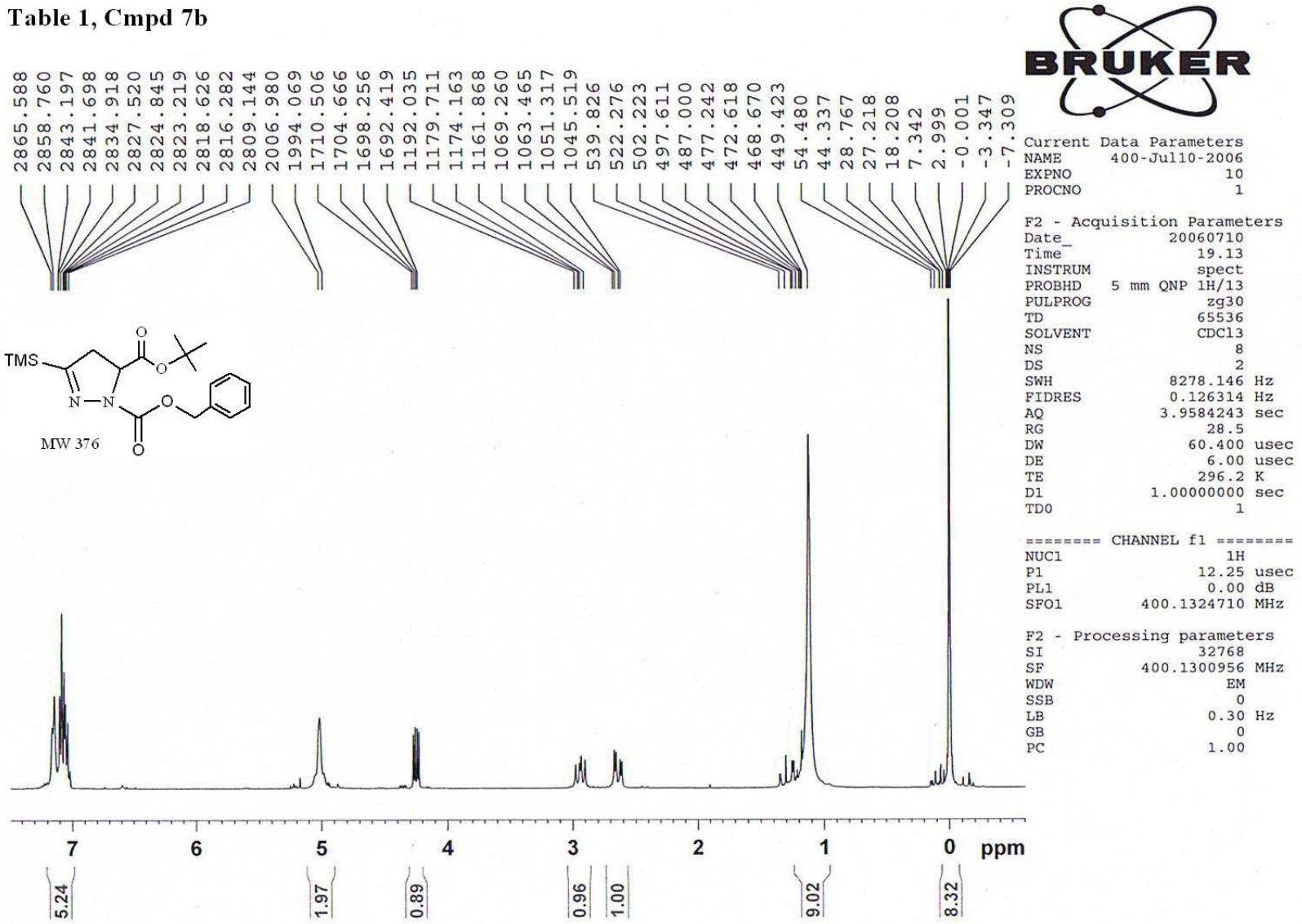
```
Current Data Parameters
NAME      400-Aug03-2006
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060803
Time_              15.38
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                    57
DW                60.400 usec
DE                 6.00 usec
TE                296.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.25 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1299994 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                  1.00
```

Table 1, Cmpd. 6c



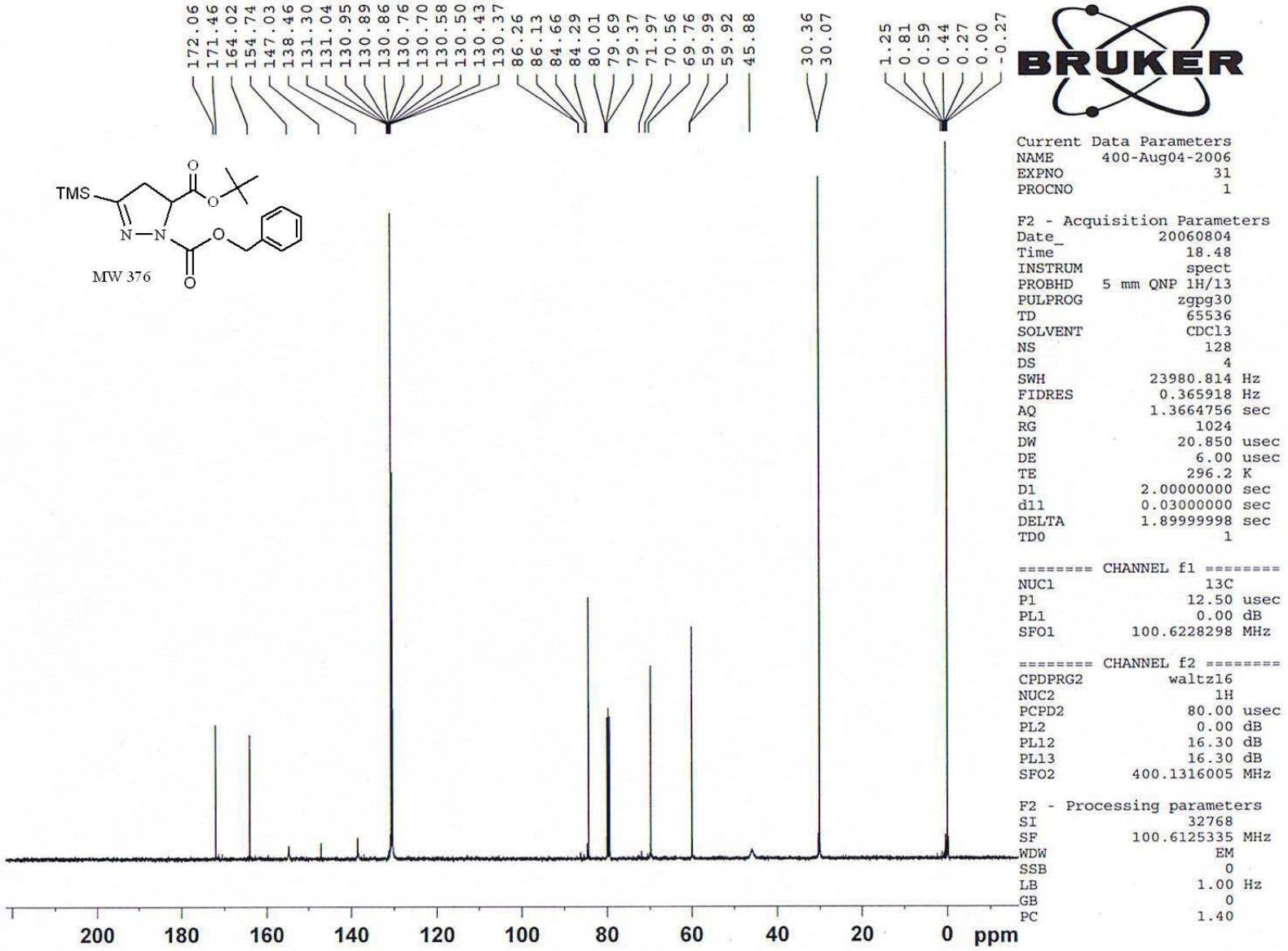

```
Current Data Parameters
NAME                 Dragan4
EXPNO                     14
PROCNO                     1

F2 - Acquisition Parameters
Date_               20050307
Time                   13.10
INSTRUM                spect
PROBHD     5 mm QNP  1H
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       100
DS                         4
SWH                25125.629 Hz
FIDRES             0.383387 Hz
AQ                 1.3042164 sec
RG                      4096
DW                   19.900 usec
DE                    6.00 usec
TE                   300.0 K
D1                 0.50000000 sec
D11                0.03000000 sec
D12                0.00002000 sec

========== CHANNEL f1 ==========
NUC1                      13C
P1                   12.50 usec
PL1                   0.00 dB
SFO1              100.6237959 MHz

========== CHANNEL f2 ==========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                100.00 usec
PL2                   0.00 dB
PL12                 19.00 dB
PL13                 19.00 dB
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                100.6127290 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                    20.00 cm
F1P                 183.549 ppm
F1                 18467.33 Hz
F2P                   9.156 ppm
F2                  921.17 Hz
PPMCM               8.71965 ppm/cm
HZCM              877.30817 Hz/cm
```

Table 1, Cmpd 7b




```
Current Data Parameters
NAME      400-Jul10-2006
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060710
Time               19.13
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  28.5
DW                60.400 usec
DE                 6.00 usec
TE                296.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.25 usec
PL1                0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300956 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```

Table 1, Cmpd 7b



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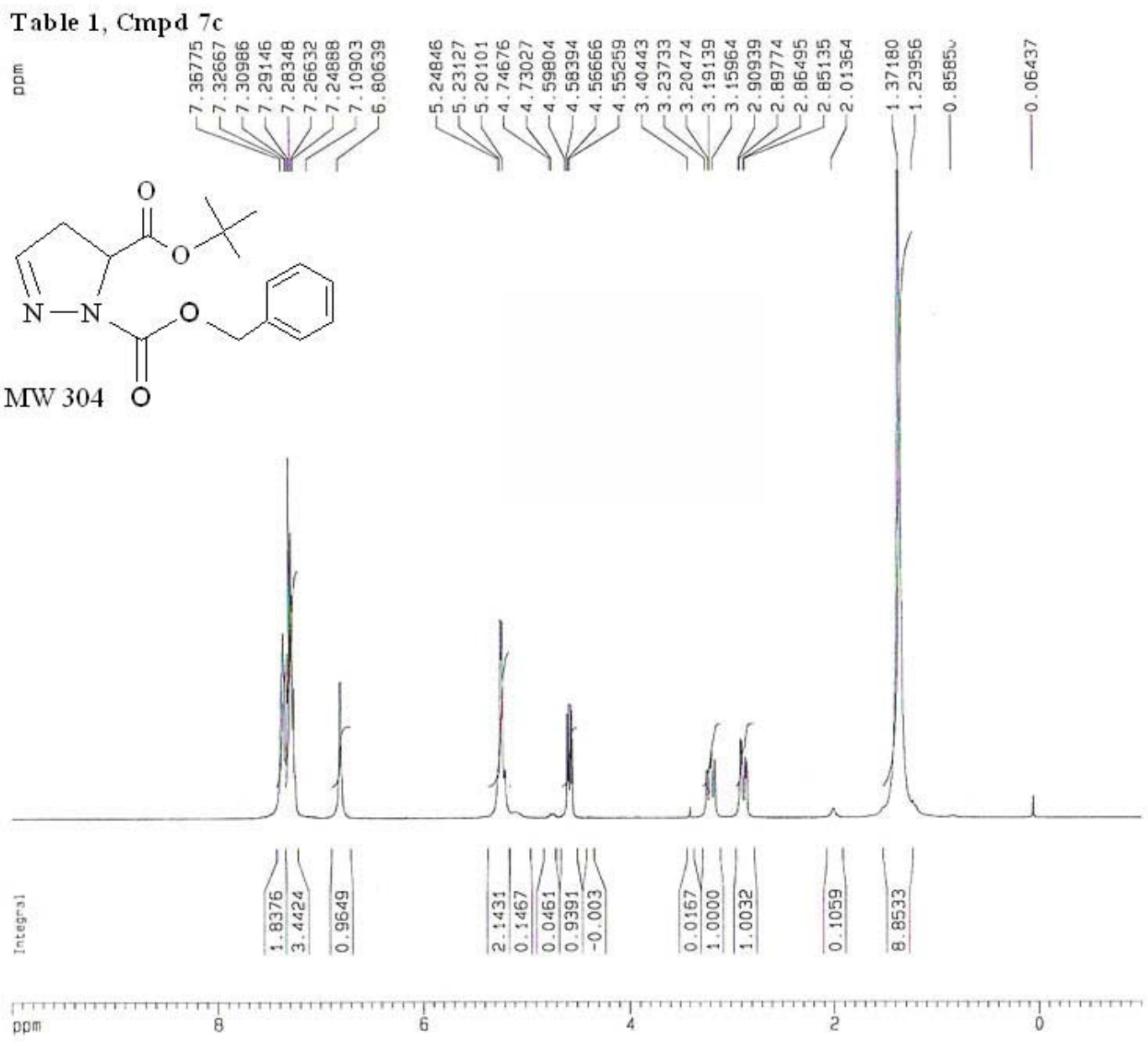
```
Current Data Parameters
NAME      400-Aug04-2006
EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060804
Time               18.48
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                 1024
DW               20.850 usec
DE                6.00 usec
TE               296.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                0.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              16.30 dB
PL13              16.30 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6125335 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

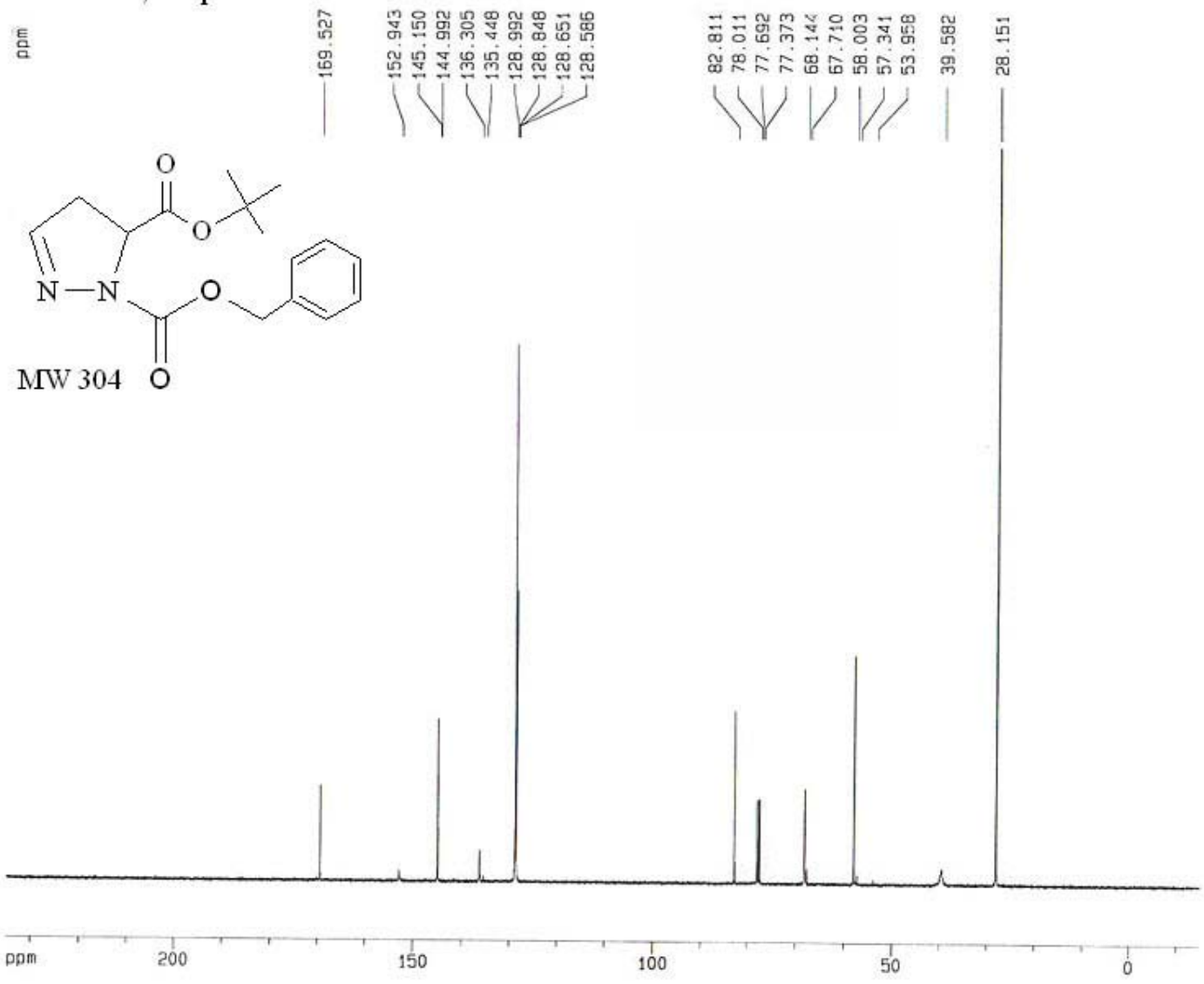
Table 1, Cmpd 7c



MW 304

```
Current Data Parameters
NAME            MM-P7-14-6
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20050513
Time                 18.51
INSTRUM              spect
PROBHD     5 mm GNP  1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                       8
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                      32
DW                 60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec

========== CHANNEL f1 ========
NUC1                    1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF              400.1300000 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                10.000 ppm
F1                 4001.30 Hz
F2P                -1.000 ppm
F2                 -400.13 Hz
PPMCM              0.55000 ppm/cm
HZCM             220.07150 Hz/cm
```

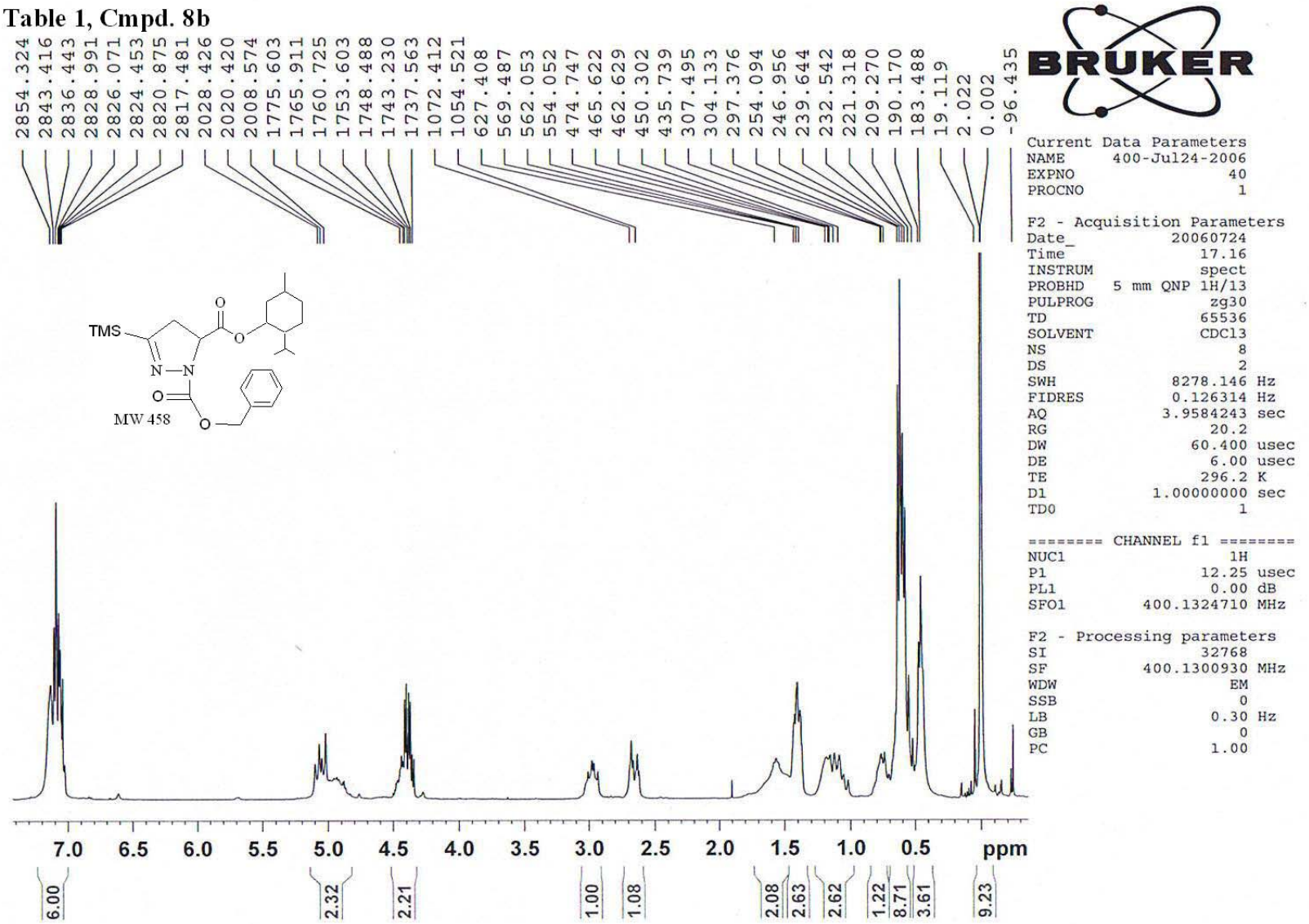
Table 1, Cmpd 7c



MW 304

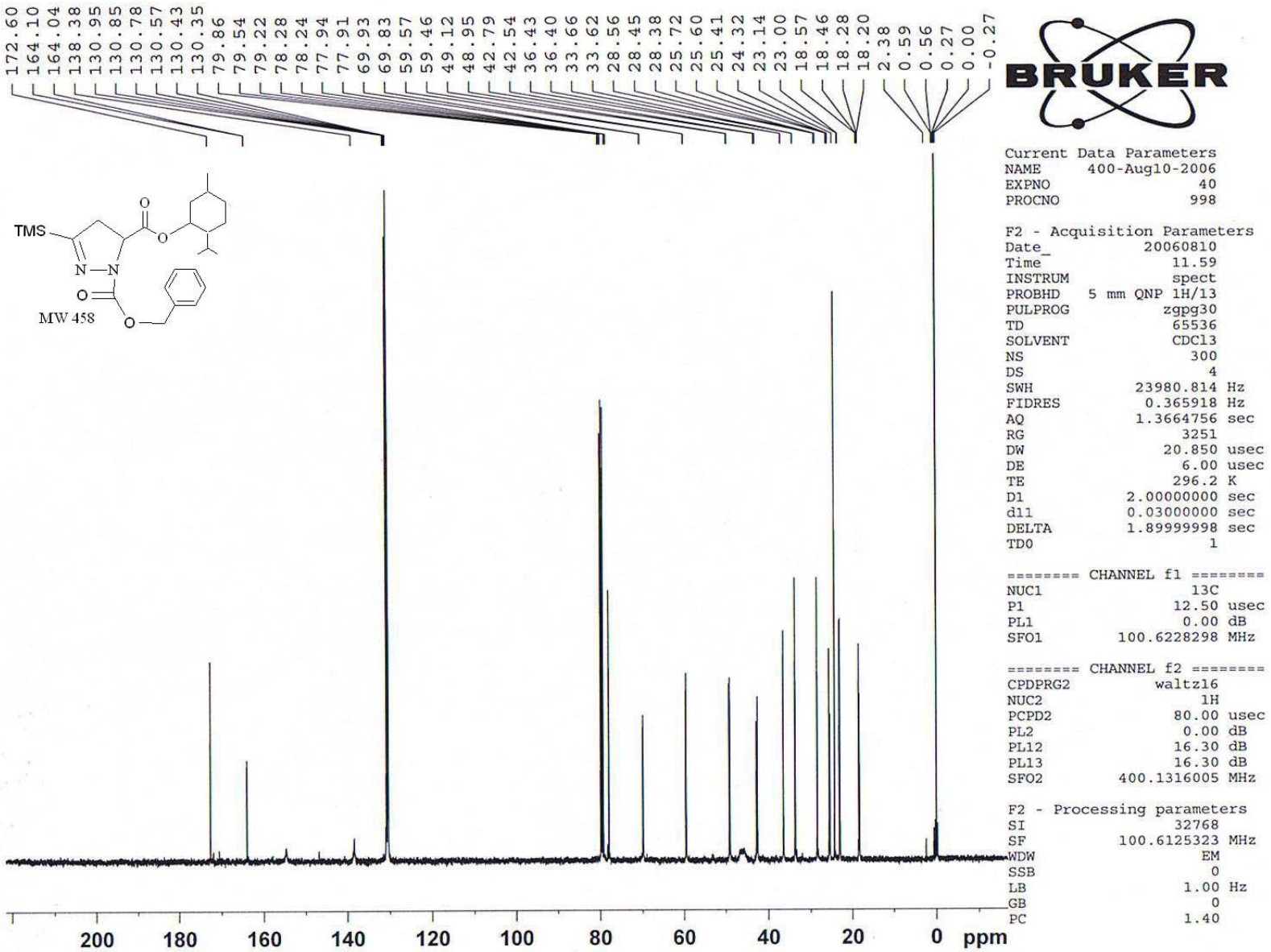
```
Current Dat Parameters
NAME                 AM-P7-14-6
EXPNO                         3
PROCNO                        1

F2 - Acquisition Parameters
Date_              20050517
Time                   12.07
INSTRUM                spect
PROBHD     5 mm QNP  1H
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      460
DS                        4
SWH                25.629 Hz
FIDRES          0.383387 Hz
AQ              1.3042164 sec
RG                    16384
DW                 19.900 usec
DE                  6.00 usec
TE                 300.0 K
D1              0.50000000 sec
D11             0.03000000 sec
D12             0.00002000 sec

========== CHANNEL f1 ==========
NUC1                  13C
P1                 12.50 usec
PL1                 0.00 dB
SFO1          100.6237959 MHz

========== CHANNEL f2 ==========
CPDPRG2            waltz16
NUC2                  1H
PCPD2              100.00 usec
PL2                 0.00 dB
PL12               19.00 dB
PL13               19.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127290 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              234.858 ppm
F1              23629.72 Hz
F2P              -14.868 ppm
F2              -1495.91 Hz
PPMCM           12.48631 ppm/cm
HZCM          1256.28149 Hz/cm
```

Table 1, Cmpd. 8b




```
Current Data Parameters
NAME      400-Jul24-2006
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060724
Time               17.16
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  20.2
DW                60.400 usec
DE                 6.00 usec
TE                296.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.25 usec
PL1                0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300930 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```

Table 1, Cmpd. 8b



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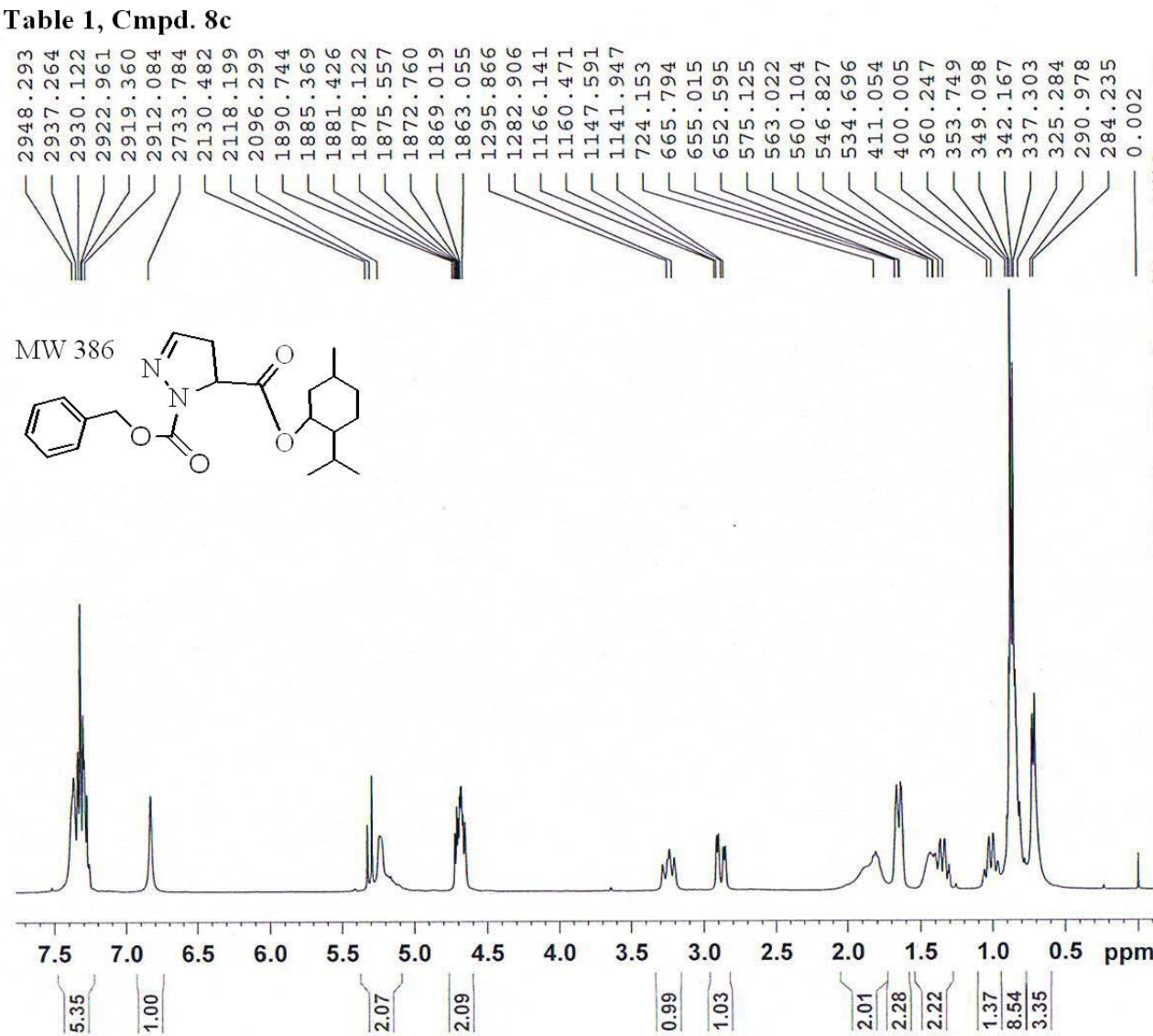
```
Current Data Parameters
NAME      400-Aug10-2006
EXPNO                 40
PROCNO               998

F2 - Acquisition Parameters
Date_           20060810
Time               11.59
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  300
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                 3251
DW               20.850 usec
DE                6.00 usec
TE               296.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                0.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              16.30 dB
PL13              16.30 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6125323 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

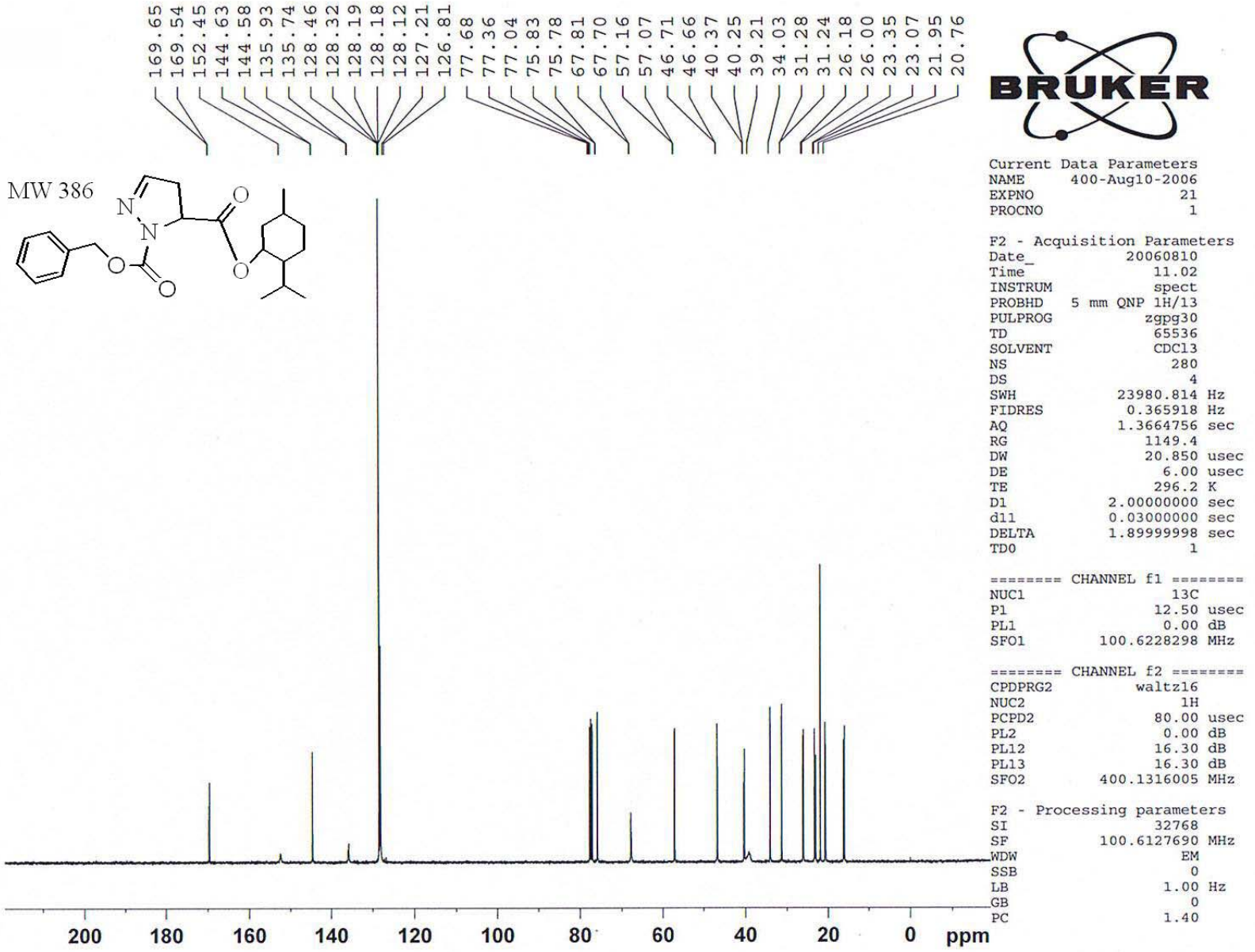
Table 1, Cmpd. 8c



BRUKER

```
Current Data Parameters
NAME      400-Aug10-2006
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060810
Time               10.56
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                    18
DW                60.400 usec
DE                 6.00 usec
TE                296.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.25 usec
PL1                 0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF            400.1299840 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

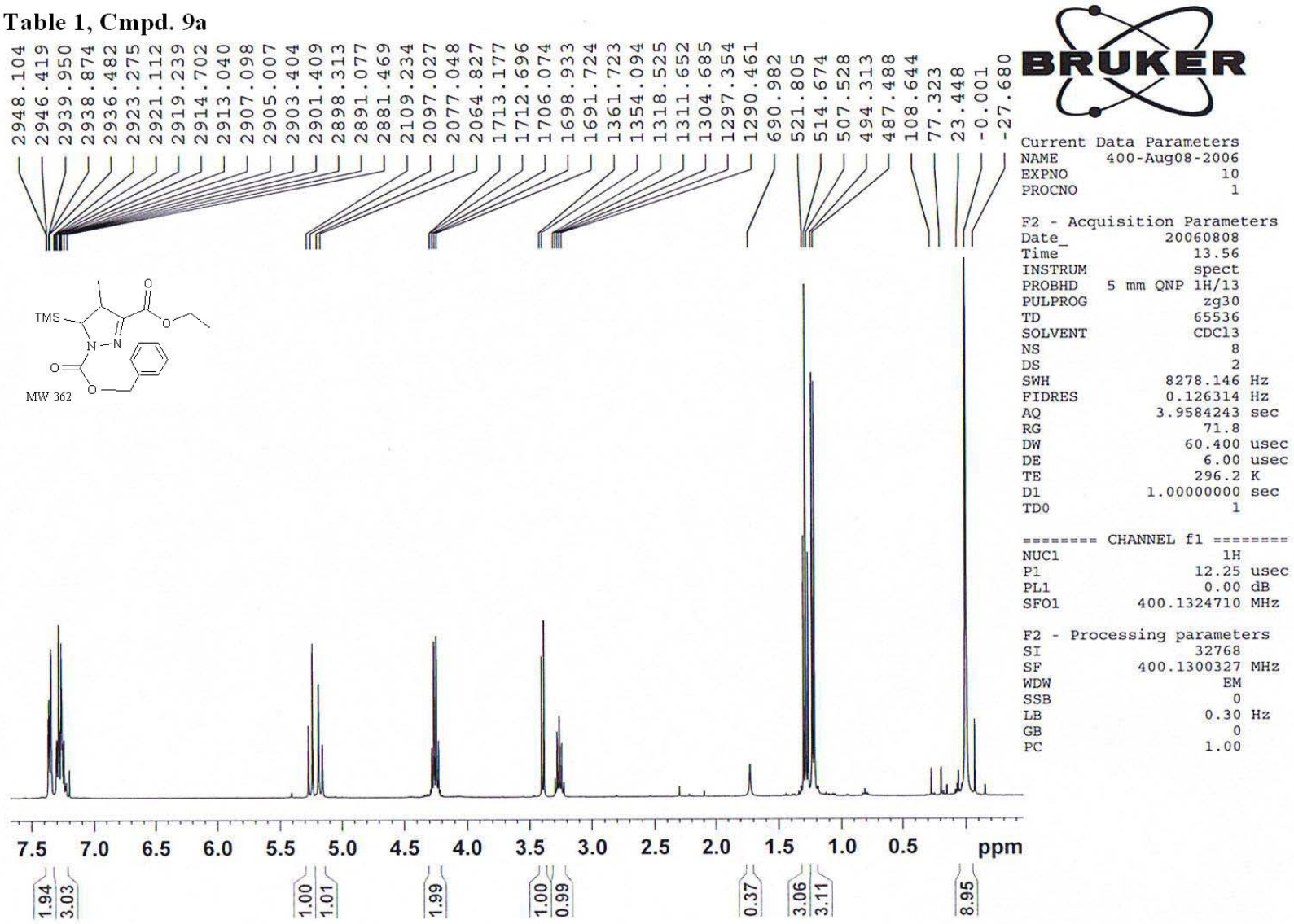
Table 1, Cmpd. 8c



BRUKER

```
Current Data Parameters
NAME      400-Aug10-2006
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060810
Time               11.02
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  280
DS                    4
SWH           23980.814 Hz
FIDRES            0.365918 Hz
AQ             1.3664756 sec
RG                1149.4
DW                20.850 usec
DE                 6.00 usec
TE                296.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                0.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              16.30 dB
PL13              16.30 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
```

Table 1, Cmpd. 9a



BRUKER

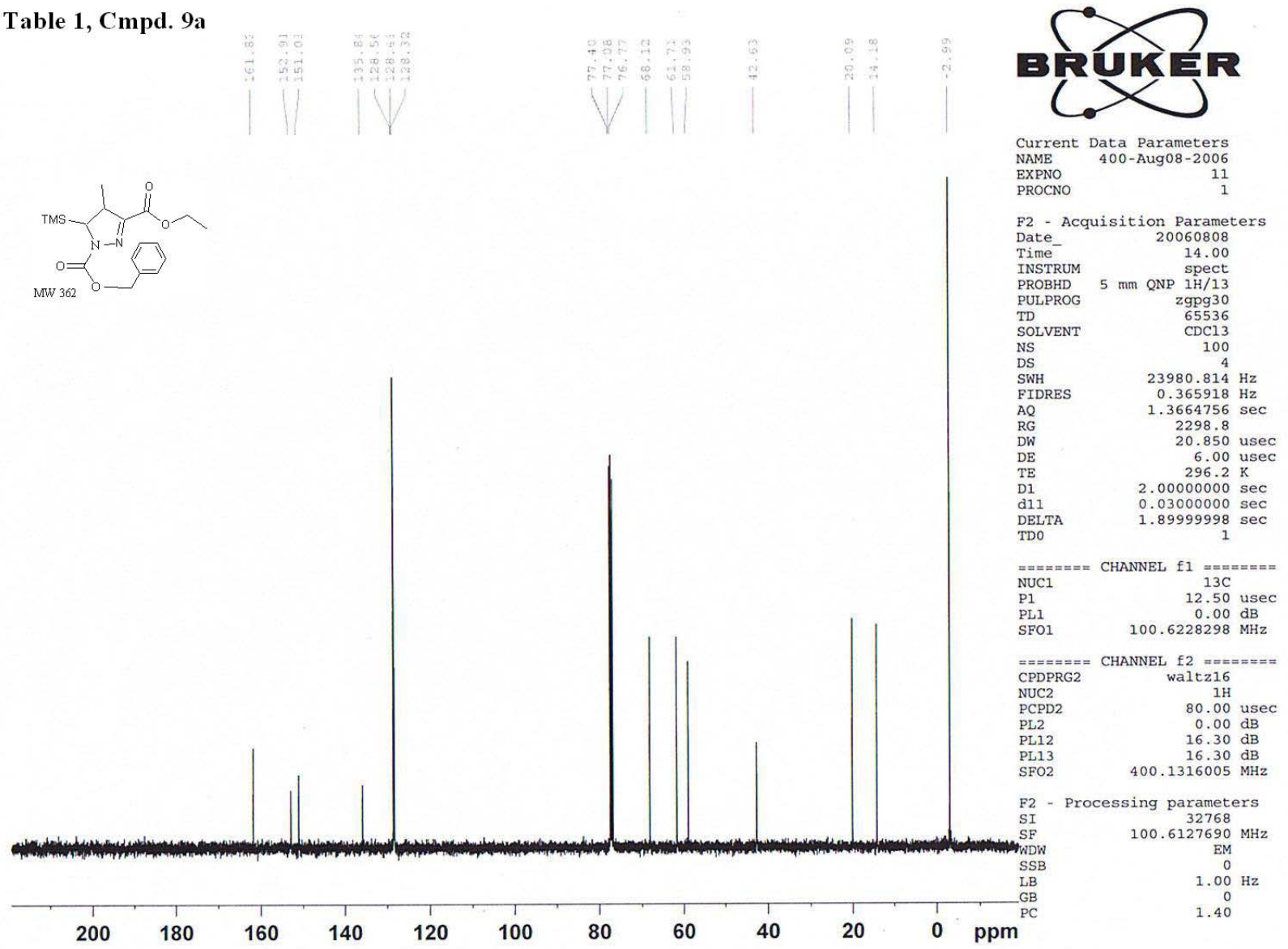
Current Data Parameters
NAME 400-Aug08-2006
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060808
Time 13.56
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 71.8
DW 60.400 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 12.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

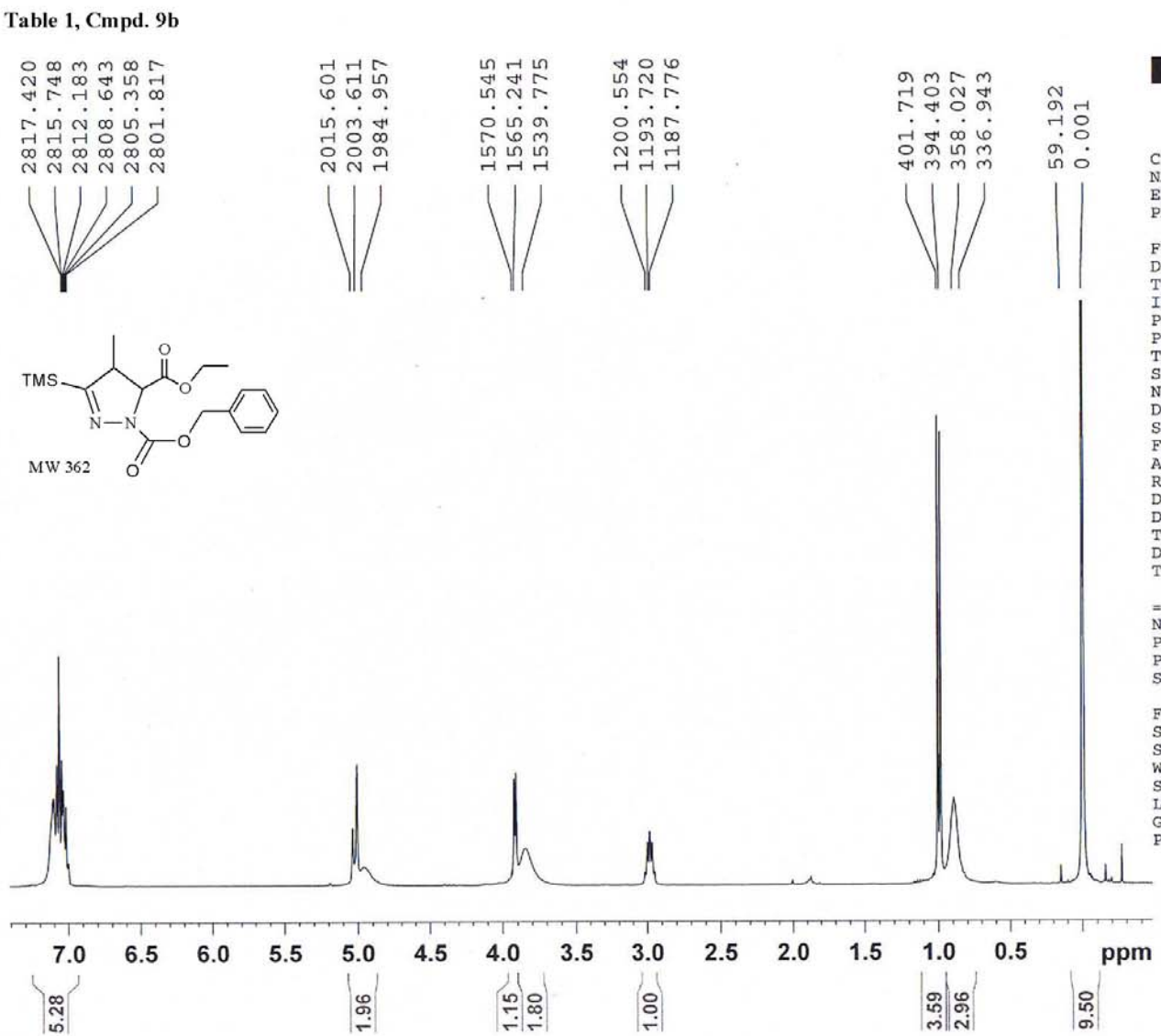
F2 - Processing parameters
SI 32768
SF 400.1300327 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Table 1, Cmpd. 9a




```
Current Data Parameters
NAME      400-Aug08-2006
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060808
Time               14.00
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  100
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                2298.8
DW                20.850 usec
DE                 6.00 usec
TE                296.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                0.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              16.30 dB
PL13              16.30 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
```

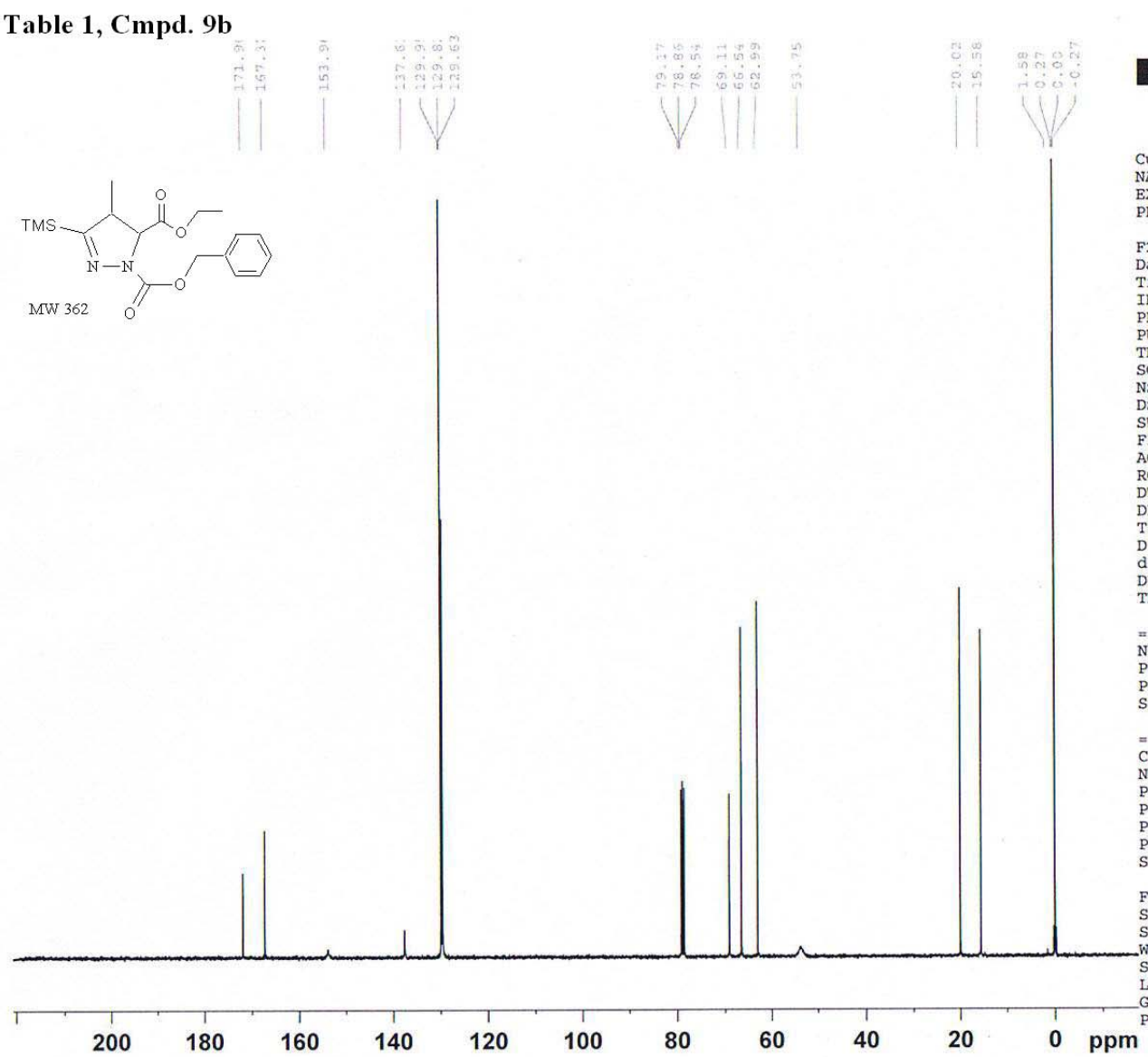
Table 1, Cmpd. 9b



BRUKER

```
Current Data Parameters
NAME      400-Aug14-2006
EXPNO                 50
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060814
Time               12.37
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  22.6
DW                60.400 usec
DE                 6.00 usec
TE                296.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.25 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300964 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

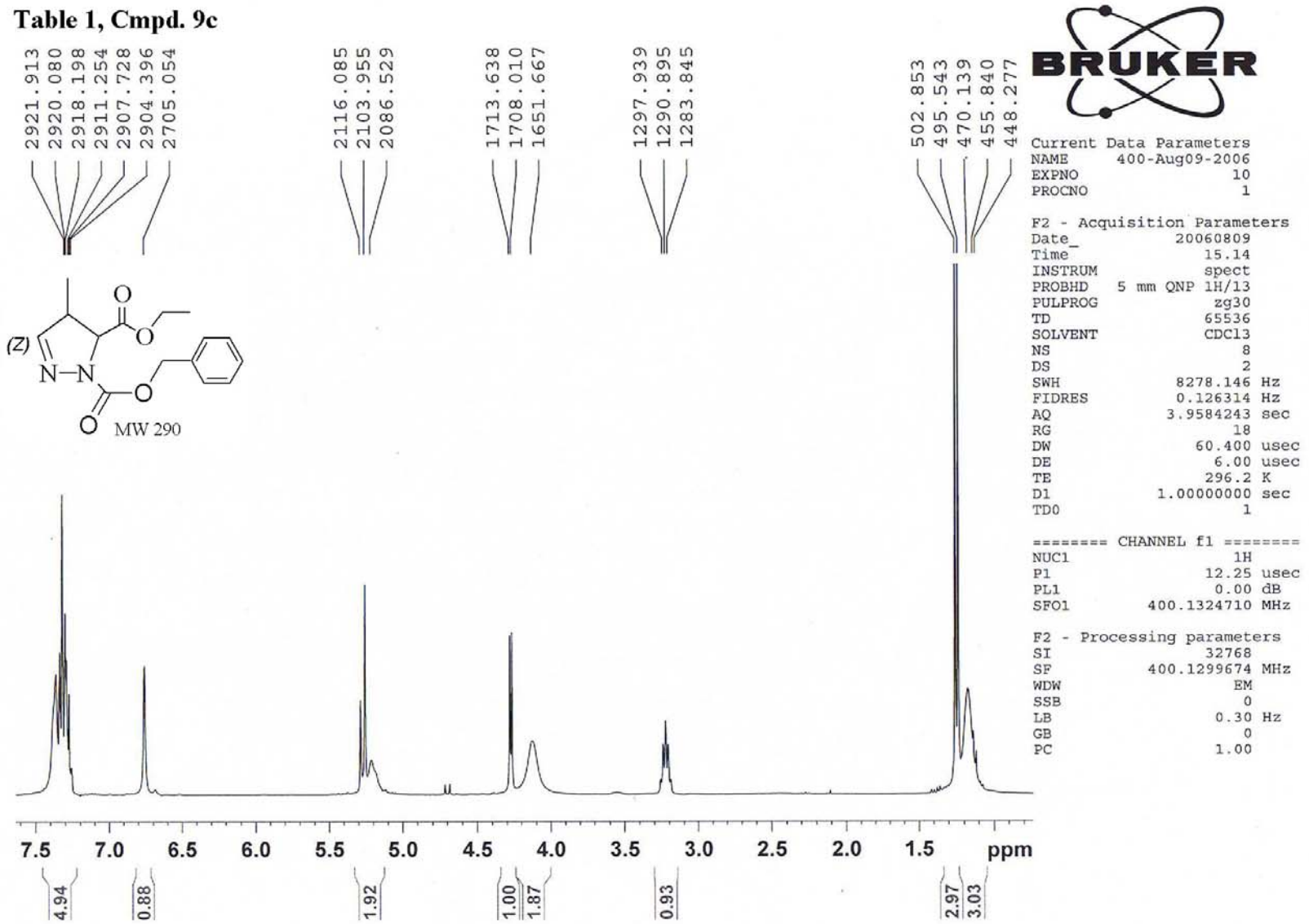
Table 1, Cmpd. 9b



BRUKER

```
Current Data Parameters
NAME      400-Aug14-2006
EXPNO                 52
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060814
Time               12.57
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG               4597.6
DW                20.850 usec
DE                 6.00 usec
TE                296.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL1                0.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2              80.00 usec
PL2                0.00 dB
PL12              16.30 dB
PL13              16.30 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6126119 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

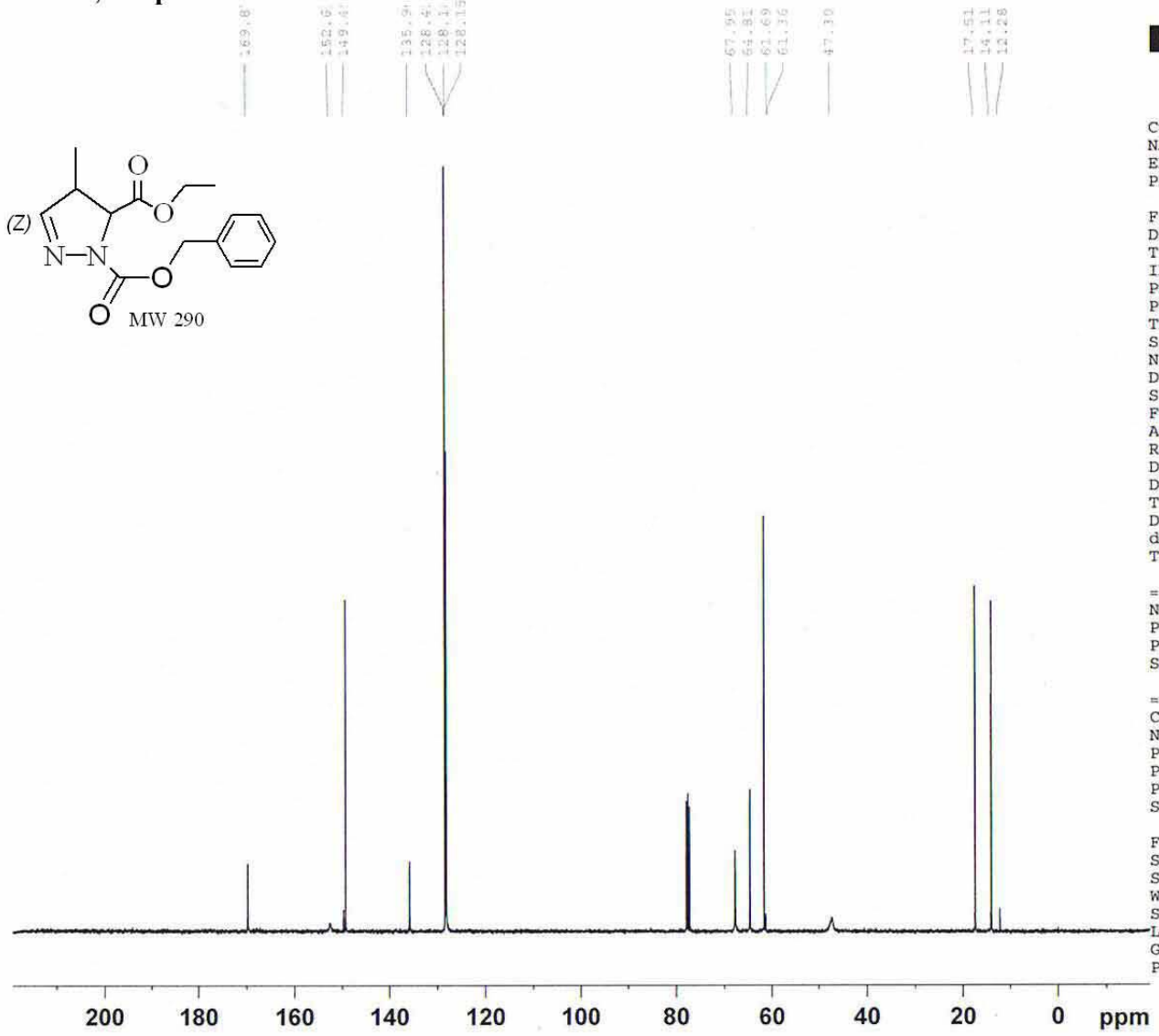
Table 1, Cmpd. 9c



BRUKER

```
Current Data Parameters
NAME      400-Aug09-2006
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060809
Time               15.14
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                    18
DW                60.400 usec
DE                 6.00 usec
TE                296.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.25 usec
PL1                 0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF            400.1299674 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

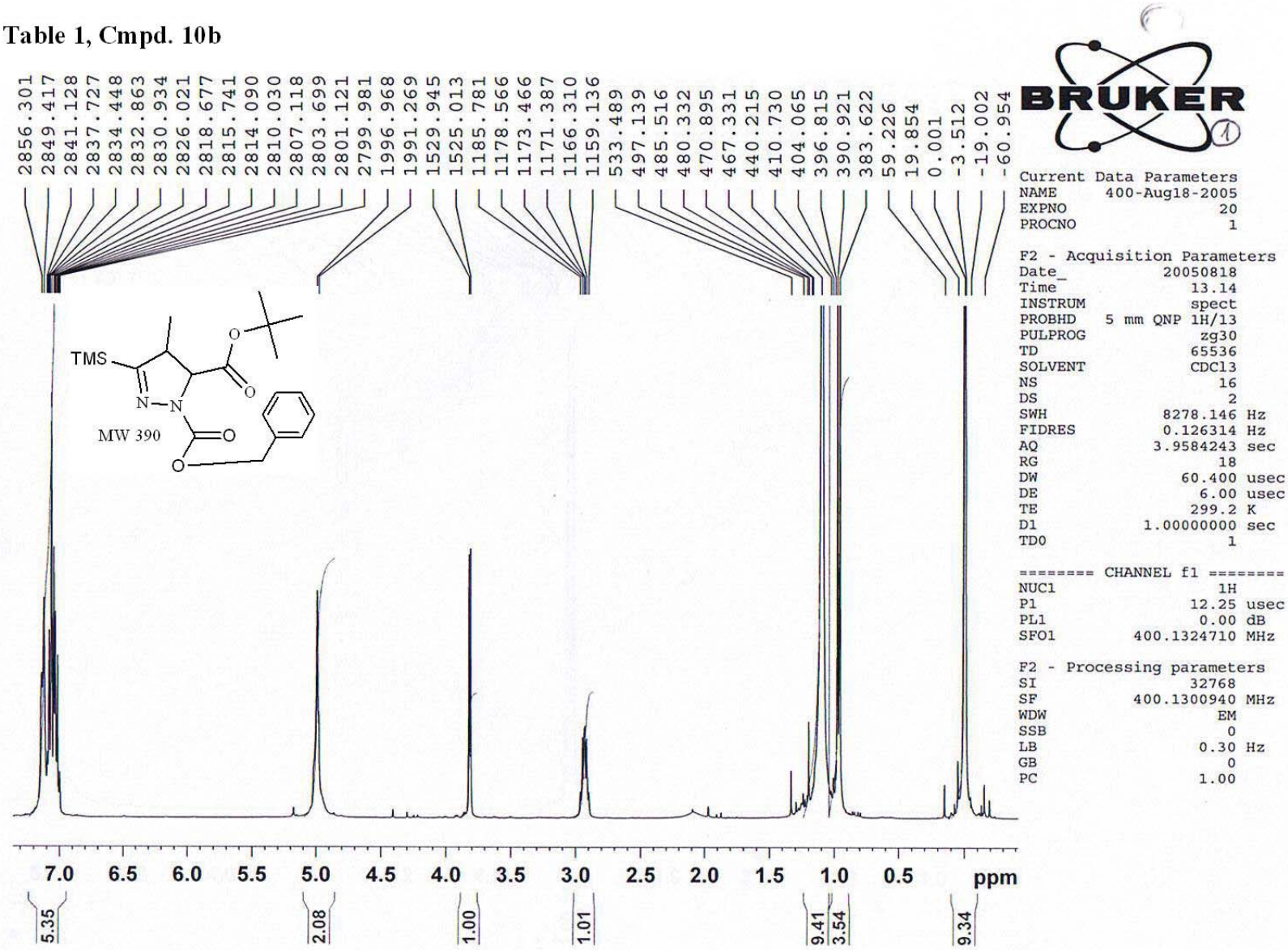
Table 1, Cmpd. 9c



BRUKER

```
Current Data Parameters
NAME      400-Aug09-2006
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060809
Time              15.17
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  101
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG               1290.2
DW               20.850 usec
DE                6.00 usec
TE               296.2 K
D1            2.00000000 sec
d11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                0.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              16.30 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
```

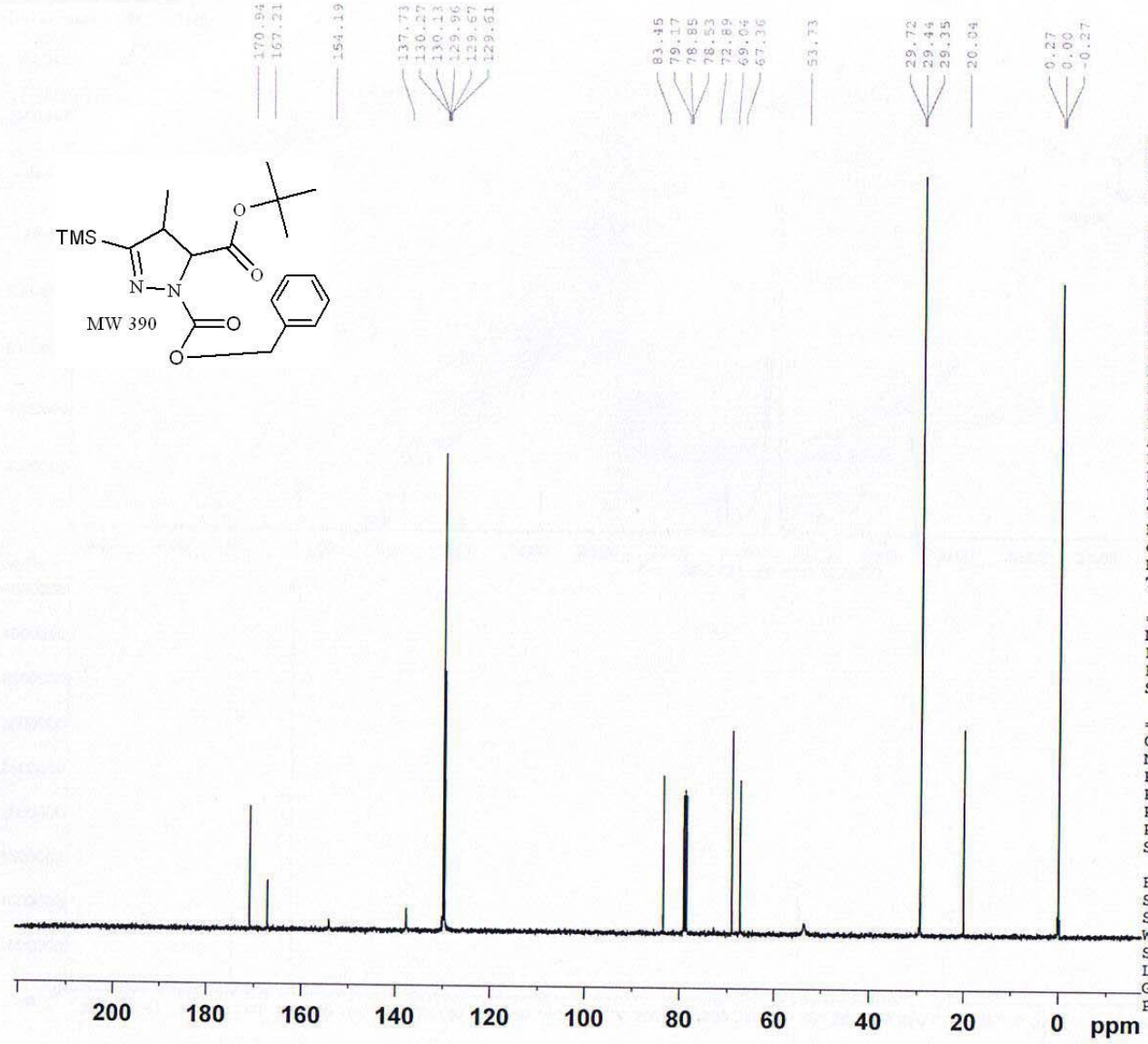
Table 1, Cmpd. 10b



BRUKER

```
Current Data Parameters
NAME      400-Aug18-2005
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050818
Time               13.14
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                    18
DW                60.400 usec
DE                 6.00 usec
TE                299.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.25 usec
PL1                0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300940 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```

Table 1, Cmpd. 10b



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Current Data Parameters
NAME 400-Aug18-2005
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters

Date_	20050818
Time	13.21
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	96
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	1625.5
DW	20.850 usec
DE	6.00 usec
TE	300.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	12.50 usec
PL1	0.00 dB
SFO1	100.6228298 MHz

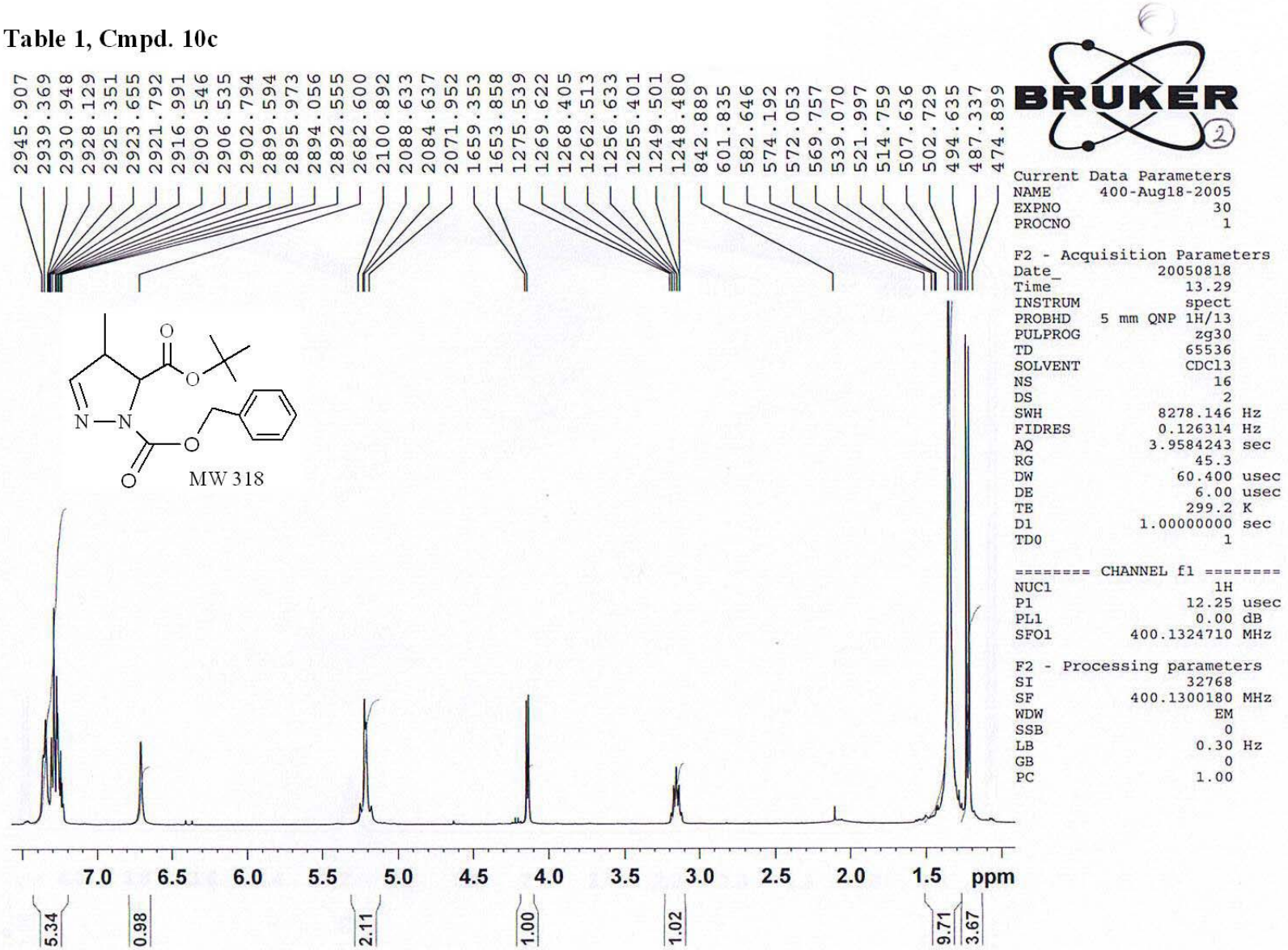
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	16.30 dB
PL13	16.30 dB
SFO2	400.1316005 MHz

F2 - Processing parameters

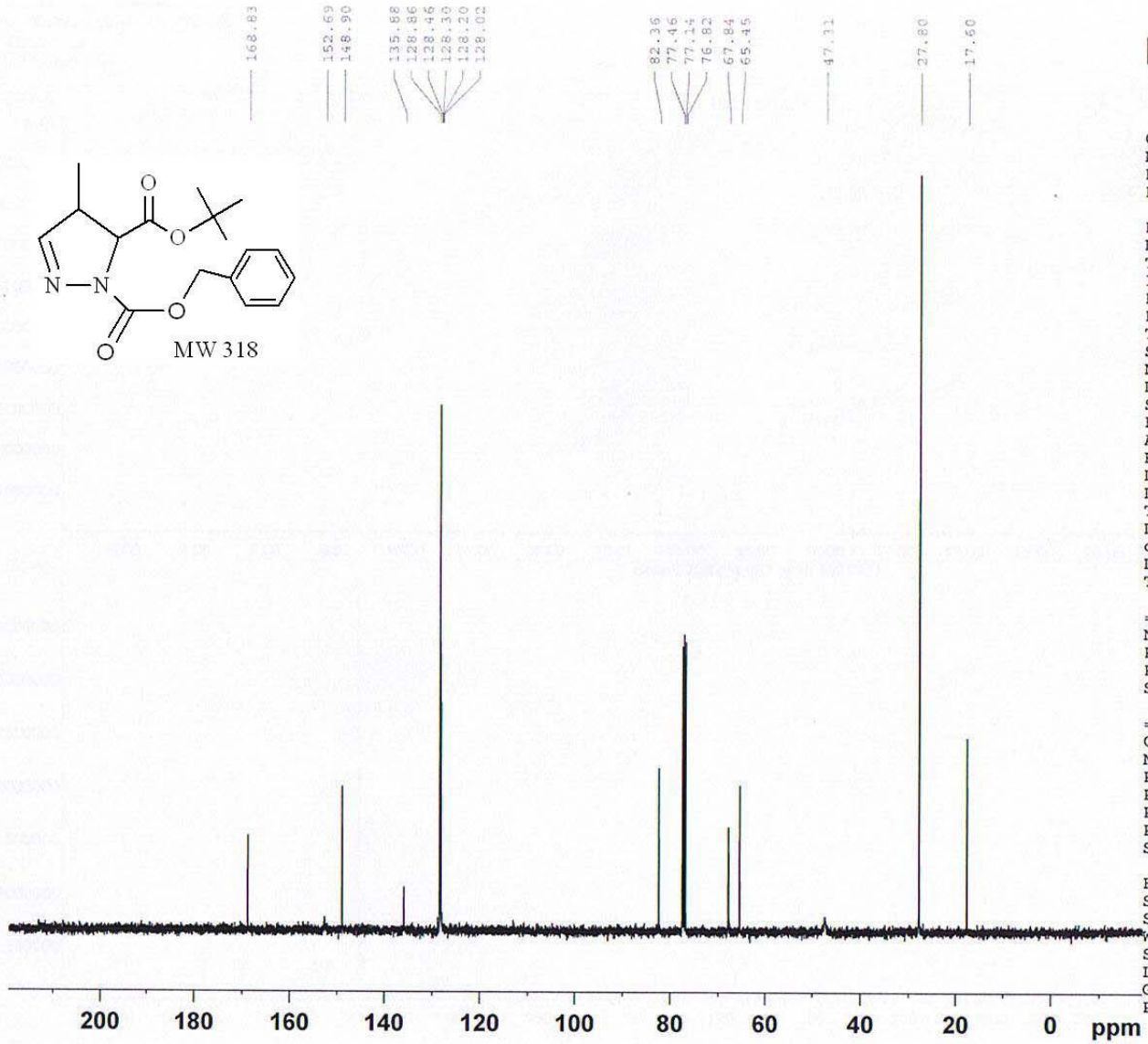
SI	32768
SF	100.6126087 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Table 1, Cmpd. 10c




```
Current Data Parameters
NAME      400-Aug18-2005
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050818
Time               13.29
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  45.3
DW                 60.400 usec
DE                  6.00 usec
TE                 299.2 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.25 usec
PL1                 0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300180 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

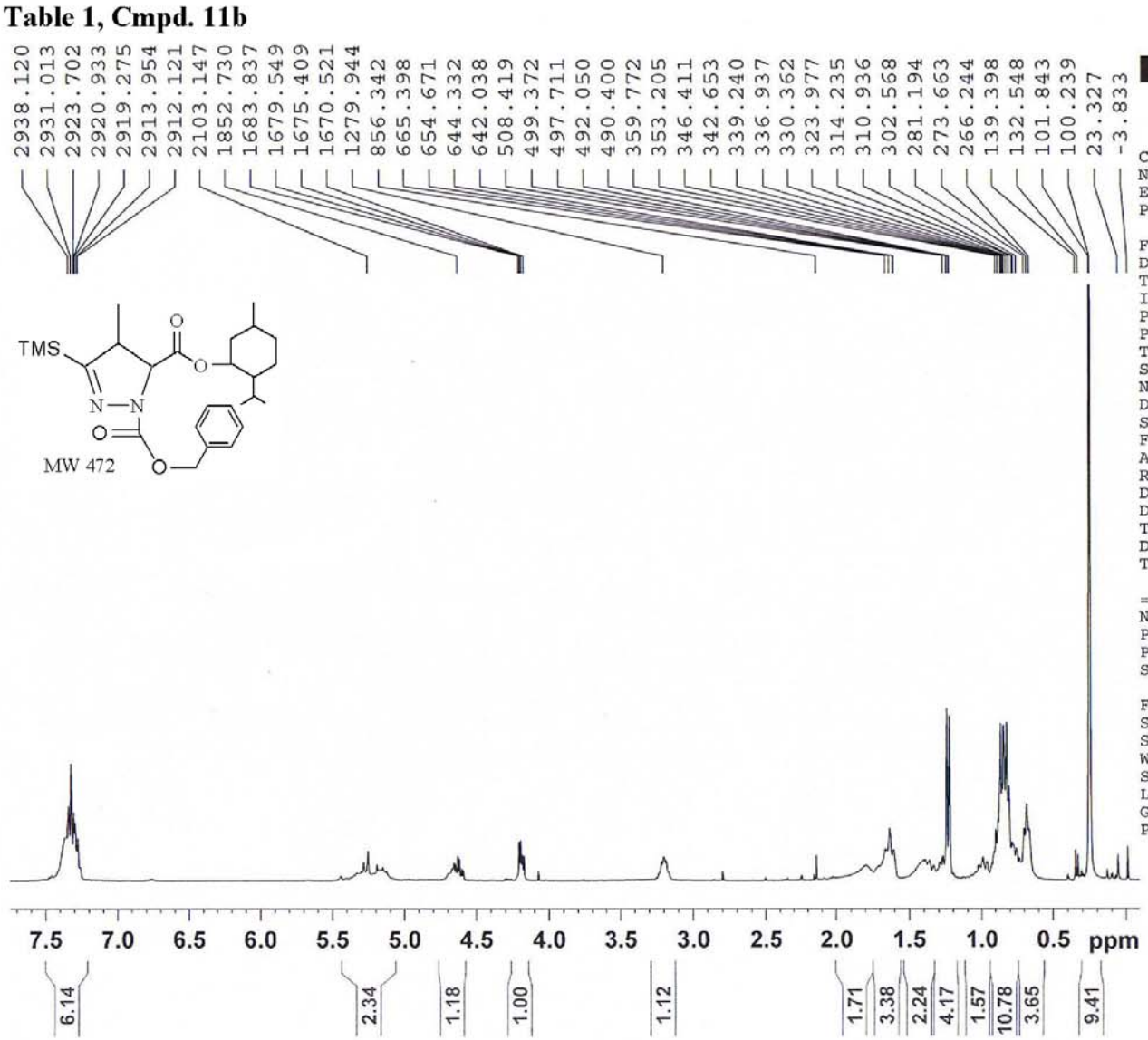
Table 1, Cmpd. 10c



BRUKER

```
Current Data Parameters
NAME      400-Aug18-2005
EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050818
Time               13.36
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   96
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                 1024
DW               20.850 usec
DE                6.00 usec
TE               300.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                0.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              16.30 dB
PL13              16.30 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
```

Table 1, Cmpd. 11b



BRUKER

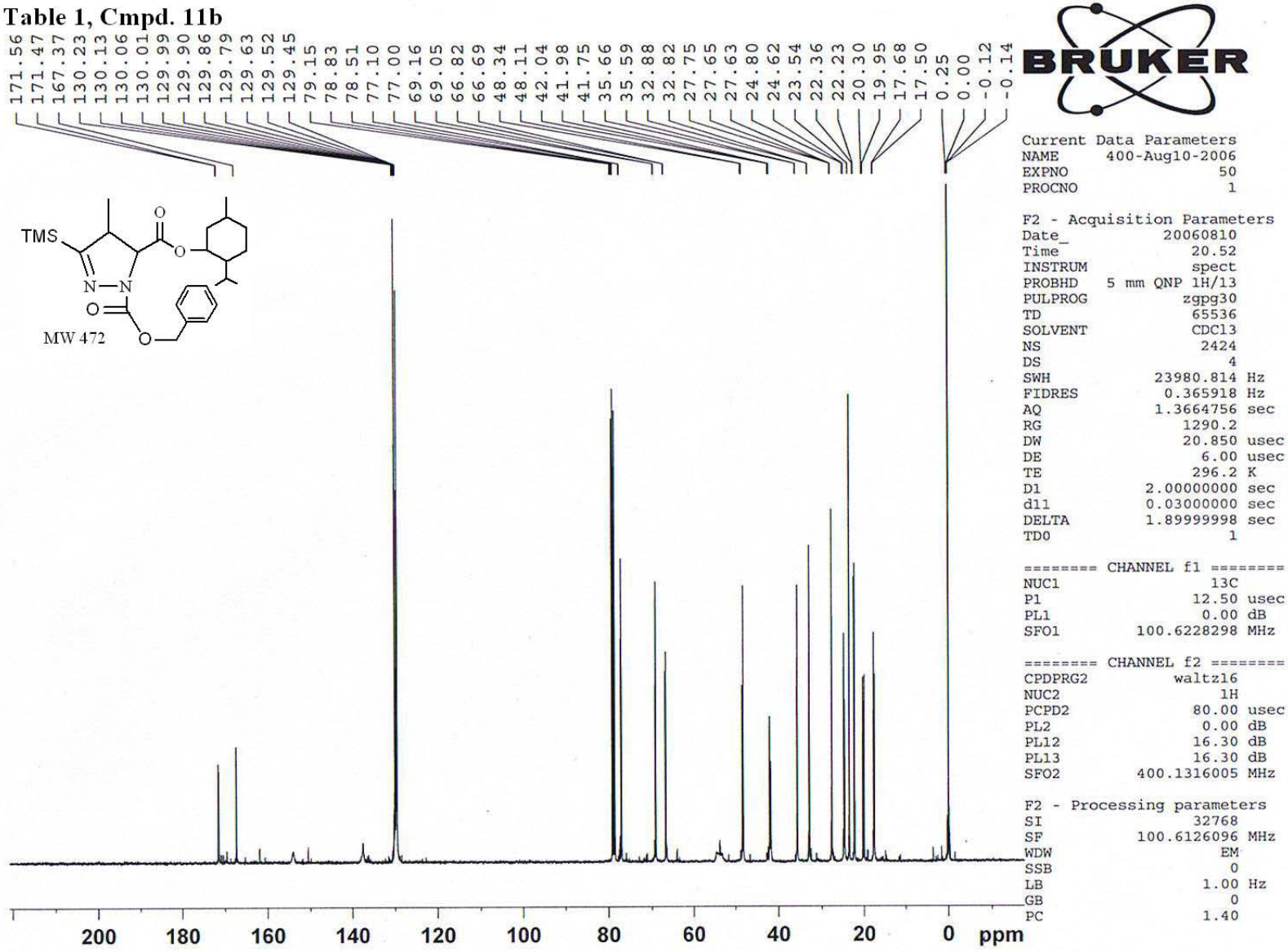
Current Data Parameters
NAME 400-Aug10-2006
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060810
Time 11.21
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 20.2
DW 60.400 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 12.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Table 1, Cmpd. 11b



BRUKER

Current Data Parameters
NAME 400-Aug10-2006
EXPNO 50
PROCNO 1

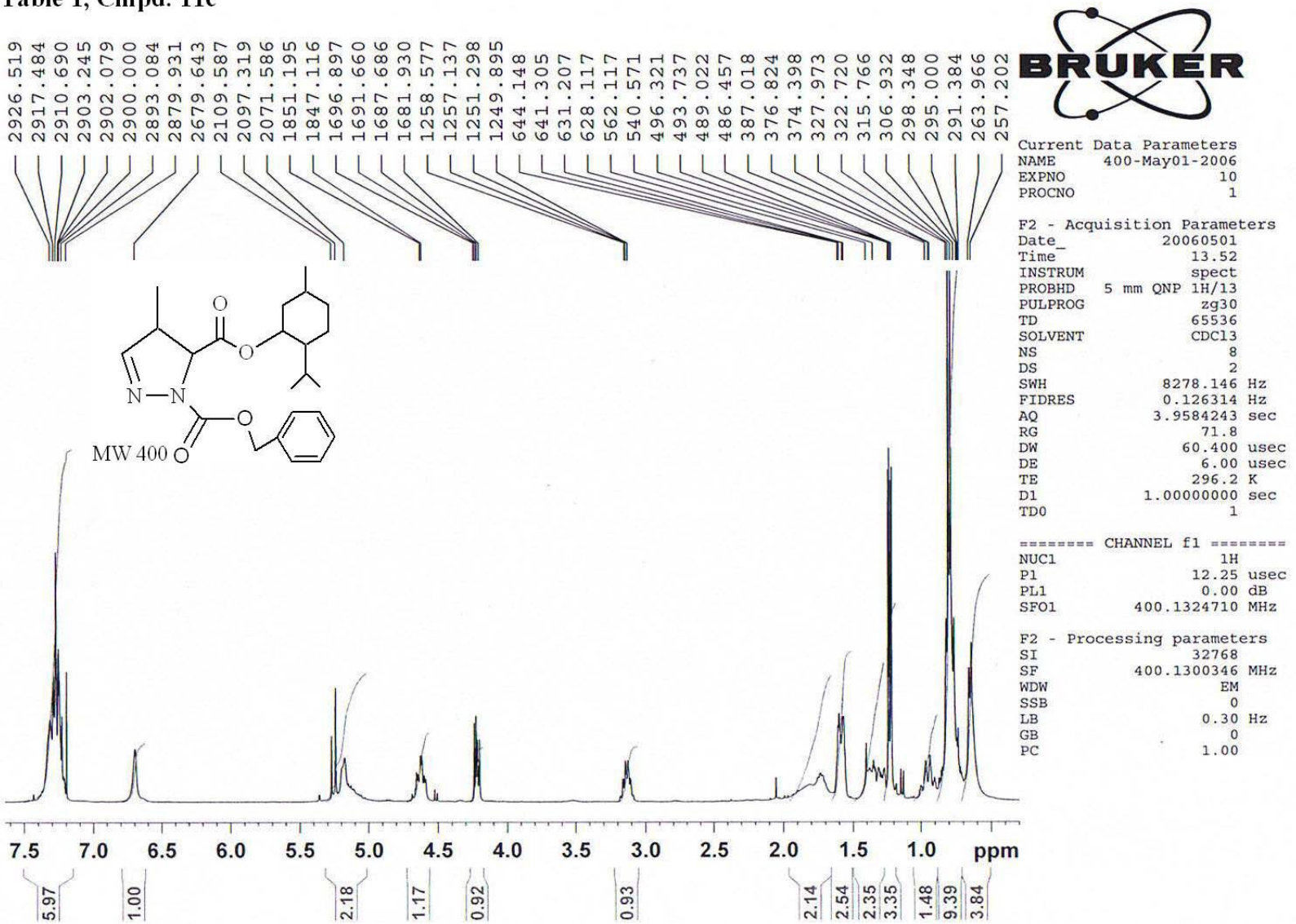
F2 - Acquisition Parameters
Date_ 20060810
Time 20.52
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2424
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 1290.2
DW 20.850 usec
DE 6.00 usec
TE 296.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.30 dB
PL13 16.30 dB
SFO2 400.1316005 MHz

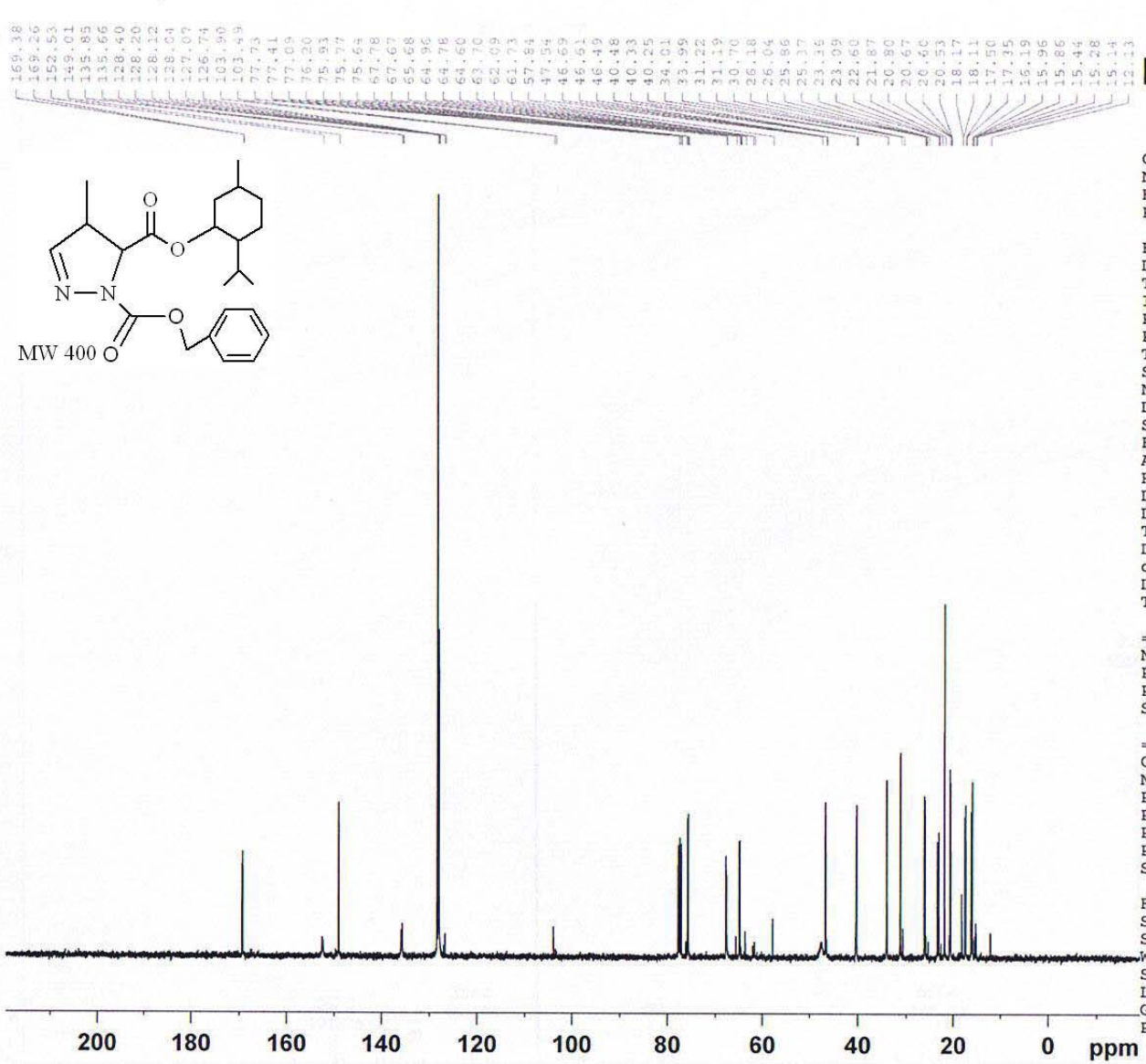
F2 - Processing parameters
SI 32768
SF 100.6126096 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Table 1, Cmpd. 11c




```
Current Data Parameters
NAME      400-May01-2006
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060501
Time               13.52
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  71.8
DW                60.400 usec
DE                 6.00 usec
TE                296.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.25 usec
PL1                0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300346 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```

Table 1, Cmpd. 11c




```
Current Data Parameters
NAME      400-Sep15-2005-Rein
EXPNO                     61
PROCNO                     1

F2 - Acquisition Parameters
Date_               20050915
Time                   14.35
INSTRUM                spect
PROBHD    5 mm QNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      128
DS                        4
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                 1.3664756 sec
RG                     4096
DW                   20.850 usec
DE                    6.00 usec
TE                   300.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                    13C
P1                    12.50 usec
PL1                    0.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  16.30 dB
PL13                  16.30 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
```