Intermolecular radical addition reactions of α-iodo cycloalkenones and synthetic study of formal synthesis of enantiopure fawcettimine†

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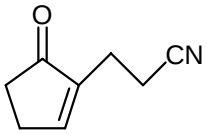
General:
Reactions were carried out in oven and flame-dried glassware under a positive pressure of Argon. Ether and THF was distilled over sodium/benzophenone. Dichloromethane and benzene was distilled over calcium hydride. All reagents were purchased commercially and used without further purification. TLC was performed on Merck 5735 DC-plastikfolien Kieselgel 60 F254 precoated plates. Flash column chromatography was performed with silica gel Merck 7736 Kieselgel 60H. 1H-NMR (7.24 ppm for $CDCl_3$ as internal standard) and ^{13}C-NMR (77.0 ppm for $CDCl_3$ as internal standard) spectra were recorded on Varian Unity-400 MHz instrument. Coupling Constants are measured in Hertz. IR spectra was recorded from Bomen MB-100FT spectrometer. Optical rotation was recorded from JASCO DIP-1000 polarimeter at 589 nm (sodium D-line). Melting point was recorded on Buchi 530 melting-point apparatus and not corrected. HRMS data was obtained from FOEL JMS-HX110 spectrometer. Single crystal X-ray analysis was performed on a Siemens Smart CCD diffractometer.

General procedure for the intermolecular addition reaction of α-carbonyl vinyl radical with electron-withdrawing olefin:

To a refluxing benzene solution (0.2M with respect to α-iodoenone) of α-iodoenone and olefin (10.0 eq.) under an atmosphere of argon was added a solution of AIBN (0.12 eq.) and Bu_3SnH (1.2 eq.) in benzene (0.5M with respect to Bu_3SnH) 8 times at an interval of 40 min. After the starting material was consumed completely by monitoring with TLC (2 h), the reaction mixture was cooled to room temperature and benzene was evaporated. Dilution with Et_2O followed by addition of saturated KF solution, the resulting mixture was stirred for another 2 h. Then moved the solid by filtration and the liquid was extracted with diethyl ether(x 5), the combined organic extracts were washed with brine, dried over $MgSO_4$. After filtration and concentration, purification by flash column chromatography afforded product as an oil.

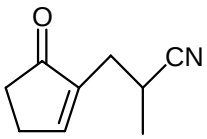
3-(5-oxocyclopent-1-enyl)propanenitrile (**1a**)



The reaction of α-iodocyclopent-2-enone with acrylonitrile gave the product **1a** in 42% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.53 (m, 1H), 2.66-2.61 (m, 2H), 2.60-2.61 (m, 4H), 2.44-2.40 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.7 (C), 160.0 (C), 142.0 (C), 118.9 (C), 34.3 (CH_2), 26.6 (CH_2), 21.3 (CH_2), 15.7 (CH_2); **IR** (neat) 2928, 2247, 1695, 1634, 1441, 1359 cm^{-1}; **MS** (EI) *m/z* 135(M^+, 5), 74 (49), 62 (100), 61 (53); **HRMS** (EI) *m/z* calcd for C_8H_9NO 135.0684, found 135.0685.

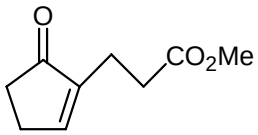
2-methyl-3-(5-oxocyclopent-1-enyl)propanenitrile (**1b**)



The reaction of α-iodocyclopent-2-enone with methacrylonitrile gave the product **1b** in 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.56 (m, 1H), 2.96-2.86 (m, 1H), 2.66-2.61 (m, 2H), 2.46-2.39 (m, 4H), 1.31 (d, *J* = 7.2Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.9 (C), 160.9 (CH), 141.4 (C), 122.2 (C), 34.2 (CH_2), 29.4 (CH_2), 26.6 (CH_2), 24.4 (CH), 17.8 (CH_3); **IR** (neat) 2925, 2240, 1698, 1633, 1440, 1355 cm^{-1}; **MS** (EI) *m/z* 149 (M^+, 94), 122 (38), 95 (60), 67 (100); **HRMS** (EI) *m/z* calcd for $C_9H_{11}NO$ 149.0841, found 149.0850.

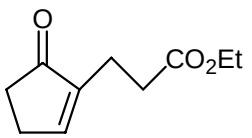
methyl 3-(5-oxocyclopent-1-enyl)propanoate (**1c**)



The reaction of α-iodocyclopent-2-enone with methyl acrylate gave the product **1c** in 31 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 1H), 3.65 (s, 3H), 2.57-2.52 (m, 2H), 2.52-2.49 (m, 4H), 2.40-2.36 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.2 (C), 173.0 (C), 158.2 (CH), 144.3 (C), 51.4 (CH_3), 34.3 (CH_2), 31.7 (CH_2), 26.4 (CH_2), 20.2 (CH_2); **IR** (neat) 2954, 2925, 1738, 1699, 1634, 1439, 1249, 1201, 1165 cm^{-1}; **MS** (EI) *m/z* 168 (M^+, 32), 136 (86), 108 (100), 79 (85); **HRMS** (EI) *m/z* calcd for $C_9H_{12}O_3$ 168.0786, found 168.0789.

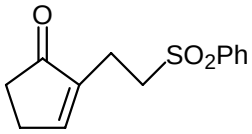
ethyl 3-(5-oxocyclopent-1-enyl)propanoate (**1d**)



The reaction of α-iodocyclopent-2-enone with ethyl acrylate gave the product **1d** in 38% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.57-2.52 (m, 2H), 2.51-2.48 (brs, 4H), 2.39 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.2 (C), 172.6 (C), 158.1 (CH), 144.5 (C), 60.3 (CH_2), 34.4 (CH_2), 32.1 (CH_2), 26.4 (CH_2), 20.3 (CH_2), 14.1 (CH_3); **IR** (neat) 2982, 2929, 1740, 1698, 1634, 1444, 1246, 1162 cm^{-1}; **MS** (EI) *m/z* 182 (M^+, 21), 137 (52), 108 (100), 79 (42); **HRMS** (EI) *m/z* calcd for $C_{10}H_{14}O_3$ 182.0943, found 182.0945.

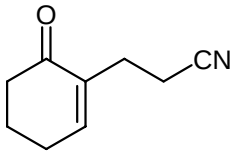
2-(2-(phenylsulfonyl)ethyl)cyclopent-2-enone (**1e**)



The reaction of α-iodocyclopent-2-enone with phenyl vinyl sulfone gave the product **1e** in 37% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.54 (dd, *J* = 7.4, 7.2 Hz, 2H), 7.38-7.35 (brs, 1H), 3.33 (t, *J*= 7.2 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.54-2.49 (m, 2H), 2.31-2.27 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.7 (C), 159.6 (CH), 141.8 (C), 139.0 (C), 133.7 (CH), 129.3 (CH), 128.1 (CH), 53.4 (CH_2), 34.3 (CH_2), 26.6 (CH_2), 19.4 (CH_2); **IR** (neat) 3065, 2923, 1697, 1634, 1306, 1151 cm^{-1}; **MS** (EI) *m/z* 250 (M^+, 6), 109 (100), 79 (24), 64 (16); **HRMS** (EI) *m/z* calcd for $C_{13}H_{14}O_3S$ 250.0664, found 250.0664.

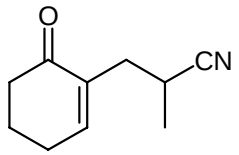
3-(6-oxocyclohex-1-enyl)propanenitrile (**2a**)



The reaction of α-iodocyclohex-2-enone with acrylonitrile gave the product **2a** in 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (dd, *J* = 4.0, 4.0 Hz, 1H), 2.54-2.36 (m, 8H), 2.03-1.95 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.8 (C), 148.6 (CH), 136.0 (C), 119.2 (C), 38.2 (CH_2), 26.6 (CH_2), 26.0 (CH_2), 22.8 (CH_2), 16.9 (CH_2); **IR** (neat) 2930, 2246, 1671, 1430, 1380 cm^{-1}; **MS** (EI) *m/z* 149 (M^+, 3), 88 (15), 73 (24), 70 (42), 61 (100); **HRMS** (EI) *m/z* calcd for $C_9H_{11}NO$ 149.0841, found 149.0835

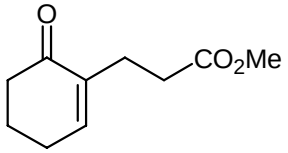
2-methyl-3-(6-oxocyclohex-1-enyl)propanenitrile (**2b**)



The reaction of α-iodocyclohex-2-enone with methacrylonitrile gave the product **2b** in 58 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 4.0, 4.0 Hz, 1H), 2.94-2.84 (m, 1H), 2.60-2.54 (m, 1H), 2.52-2.40 (m, 4H), 2.28-2.20 (m, 1H), 2.06-1.97 (m, 8H), 1.30 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.9 (C), 149.3 (CH), 135.4 (C), 122.6 (C), 38.2 (CH_2), 35.0 (CH_2), 26.1 (CH_2), 25.3 (CH), 22.9 (CH_2), 18.0 (CH_3); **IR** (neat) 2938, 2239, 1672, 1456, 1431, 1379 cm^{-1}; **MS** (EI) *m/z* 163 (M^+, 87), 136 (40), 107 (32), 81 (100); **HRMS** (EI) *m/z* calcd for $C_{10}H_{13}NO$ 163.0997, found 163.0999.

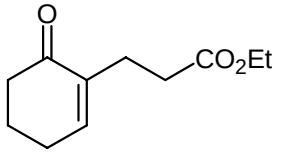
methyl 3-(6-oxocyclohex-1-enyl)propanoate (**2c**)



The reaction of α-iodocyclohex-2-enone with methyl acrylate gave the product **2c** in 48 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (dd, *J* = 4.4, 4.4 Hz, 1H), 3.63 (s, 3H), 2.52-2.37 (m, 6H), 2.36-2.29 (m, 2H), 1.99-1.91 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.3 (C), 172.8 (C), 145.8 (CH), 137.5 (C), 50.8 (CH_3), 37.9 (CH_2), 32.4 (CH_2), 25.5 (CH_2), 25.0 (CH_2), 22.5 (CH_2); **IR** (neat) 2951, 1738, 1672, 1436, 1253, 1198, 1166 cm^{-1}; **MS** (EI) *m/z* 182 (M^+, 10), 150 (50), 122 (100), 95 (63), 67 (72); **HRMS** (EI) *m/z* calcd for $C_{10}H_{14}O_3$ 182.0943, found 182.0935.

ethyl 3-(6-oxocyclohex-1-enyl)propanoate (**2d**)

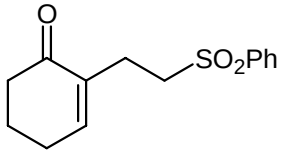


The reaction of α-iodocyclohex-2-enone with ethyl acrylate gave the product **2d** in 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (dd, *J* = 4.4, 4.4 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.50-2.44 (m, 2H), 2.43-2.36 (m, 4H), 2.34-2.28 (m, 2H), 1.98-1.90 (m, 2H), 1.21 (t, *J* =

7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.0 (C), 173.1 (C), 146.2 (CH), 138.1 (C), 60.2 (CH_2), 38.4 (CH_2), 33.2 (CH_2), 26.0 (CH_2), 25.5 (CH_2), 23.0 (CH_2), 14.2 (CH_3); **IR** (neat) 2931, 1735, 1673, 1451, 1253, 1196, 1163 cm^{-1}; **MS** (EI) *m/z* 196 (M^+, 11), 151 (34), 122(100), 94 (17); **HRMS** (EI) *m/z* calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1108.

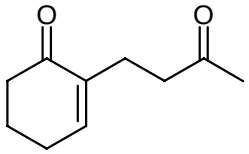
2-(2-(phenylsulfonyl)ethyl)cyclohex-2-enone (**2e**)



The reaction of α-iodocyclohex-2-enone with phenyl vinyl sulfone gave the product **2e** in 62%yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53 (dd, *J* = 7.6, 7.4 Hz, 2H), 6.79 (dd, *J* = 4.0, 4.0 Hz, 1H), 3.26 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.32-2.25 (m, 4H), 1.92-1.83 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.6 (C), 147.9 (CH), 139.2 (C), 135.5 (C), 133.5 (C), 129.1 (CH), 127.9 (CH), 54.4 (CH_2), 38.0 (CH_2), 25.9 (CH_2), 24.4 (CH_2), 22.6 (CH_2); **IR** (neat) 3065, 2931, 1669, 1585, 1306, 1143 cm^{-1}; **MS** (EI) *m/z* (M^+, 20), 123(100), 91 (21), 77 (25); **HRMS** (EI) *m/z* calcd for $C_{14}H_{16}O_3S$ 264.0820, found 264.0812.

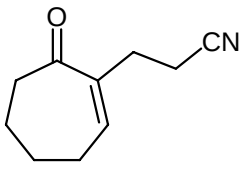
2-(3-oxobutyl)cyclohex-2-enone (**2f**)



The reaction of α-iodocyclohex-2-enone with 3-buten-2-one gave the product **2f** in 9% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 4.4, 4.4 Hz, 1H), 2.54 (t, *J* = 7.4 Hz, 2H), 2.43-2.35 (m, 4H), 2.34-2.26 (m, 2H), 2.08 (s, 3H), 1.97-1.89 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.2 (C), 199.3 (C), 146.5 (CH), 138.4 (C), 42.5 (CH_2), 38.4 (CH_2), 29.8 (CH_3), 26.0 (CH_2), 24.5 (CH_2), 23.0 (CH_2); **IR** (neat) 1671, 1715, 1430, 1167 cm^{-1}; **MS** (EI) *m/z* 166 (M^+, 36), 123 (65), 99(49), 67(100), 40(51); **HRMS** (EI) *m/z* calcd for $C_{10}H_{14}O_2$ 166.0994, found 166.0996.

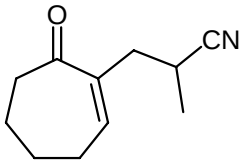
3-((Z)-7-oxocyclohept-1-enyl)propanenitrile (**3a**)



The reaction of α-iodocyclohept-2-enone with acrylonitrile gave the product **3a** in 45% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 6.6, 6.6 Hz, 1H), 2.58-2.54 (m, 2H), 2.49-2.46 (m, 4H), 2.45-2.38 (m, 2H), 1.78-1.70 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.7 (C), 146.4 (CH), 139.5 (C), 119.2 (C), 42.5 (CH_2), 29.6 (CH_2), 27.6 (CH_2), 24.9 (CH_2), 21.1 (CH_2), 17.3 (CH_2); **IR** (neat) 2939, 2246, 1661, 1454, 1428, 1390 cm^{-1}; **MS** (EI) *m/z* 163 (M^+, 57), 121 (32), 95 (100), 79 (49); **HRMS** (EI) *m/z* calcd for $C_{10}H_{13}NO$ 163.0997, found 163.0996.

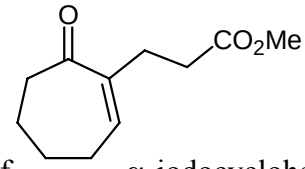
2-methyl-3-((Z)-7-oxocyclohept-1-enyl)propanenitrile (**3b**)



The reaction of α-iodocyclohept-2-enone with methacrylonitrile gave the product **3b** in 42%yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (dd, *J* = 6.6, 6.6 Hz, 1H), 2.92-2.81 (m, 1H), 2.61-2.53 (m, 3H), 2.47-2.40 (m, 2H), 2.29-2.20 (m, 1H), 1.80-1.70 (m, 4H), 1.27 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.9 (C), 146.8 (CH), 139.1 (C), 122.6 (C), 42.5 (CH_2), 38.2 (CH_2), 27.7 (CH_2), 25.7 (CH), 24.9 (CH_2), 21.2 (CH_2), 18.0 (CH_3); **IR** (neat) 2940, 2238, 1668, 1455, 1386 cm^{-1}; **MS** (EI) *m/z* 177 (M^+, 21), 150 (44), 123 (50), 95 (100), 67 (42); **HRMS** (EI) *m/z* calcd for $C_{11}H_{15}NO$ 177.1154, found 177.1153.

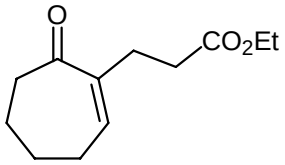
methyl 3-((Z)-7-oxocyclohept-1-enyl)propanoate (**3c**)



The reaction of α-iodocyclohept-2-enone with methyl acrylate gave the product **3c** in 35%yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (dd, *J* = 6.4, 6.4 Hz, 1H), 3.62 (s, 3H), 2.58-2.49 (m, 4H), 2.43-2.32 (m, 4H), 1.78-1.65 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.4 (C), 173.5(C), 143.1 (CH), 141.9 (C), 51.4 (CH_3), 42.5 (CH_2), 33.6 (CH_2), 28.8 (CH_2), 27.5 (CH_2), 24.9 (CH_2), 21.3 (CH_2); **IR** (neat) 2947, 1738, 1666, 1436, 1254, 1164 cm^{-1}; **MS** (EI) *m/z* 196 (M^+, 20), 164 (60), 136 (63), 95 (42), 70 (62), 61 (100); **HRMS** (EI) *m/z* calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1102.

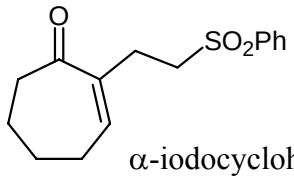
ethyl 3-((Z)-7-oxocyclohept-1-enyl)propanoate (**3d**)



The reaction of α-iodocyclohept-2-enone with ethyl acrylate gave the product **3d** in 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (dd, *J* = 6.4, 6.4 Hz, 1H), 4.07 (q, *J* = 7.4 Hz, 2H), 2.57-2.49 (m, 4H), 2.41-2.31 (m, 4H), 1.78-1.64 (m, 4H), 1.21 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.4 (C), 173.0 (C), 142.9 (CH), 142.0 (C), 60.1 (CH_2), 42.5 (CH_2), 33.8 (CH_2), 28.8 (CH_2), 27.4 (CH_2), 24.9 (CH_2), 21.3 (CH_2), 14.2 (CH_3); **IR** (neat) 2938, 1733, 1665, 1446, 1251, 1181, 1161 cm^{-1}; **MS** (EI) *m/z* 210 (M^+, 16), 164 (94), 136 (100), 108 (63); **HRMS** (EI) *m/z* calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1265.

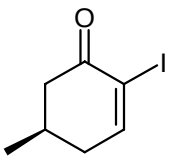
(Z)-2-(2-(phenylsulfonyl)ethyl)cyclohept-2-enone (**3e**)



The reaction of α-iodocyclohept-2-enone with phenyl vinyl sulfone gave the product **3e** in 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.64 (t, *J* = 6.2 Hz, 1H), 3.26 (t, *J* = 8.0 Hz, 2H), 2.56 (t, *J* = 8.0 Hz, 2H), 2.47 (dd, *J* = 6.0, 6.0 Hz, 2H), 2.37-2.31 (m, 2H), 1.73-1.64 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.5 (C), 145.4 (CH), 139.3 (C), 133.5 (CH), 129.1 (CH), 127.9 (CH), 55.0 (CH_2), 42.4 (CH_2), 27.6 (CH_2), 27.4 (CH_2), 24.9 (CH_2), 21.1 (CH_2); **IR** (neat) 3064, 2938, 1660, 1585, 1306, 1148 cm^{-1}; **MS** (EI) *m/z* 278 (M^+, 37), 137 (90), 125 (37), 104 (31), 93 (32), 77 (100); **HRMS** (EI) *m/z* calcd for $C_{15}H_{18}O_3S$ 278.0977, found 278.0978.

(*R*)-2-iodo-5-methylcyclohex-2-enone (**5**)

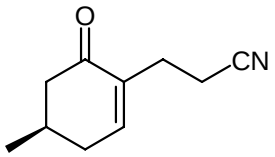


To a solution of I_2 (4.95 g, 19.5 mmol) and pyridine (12.6 mL, 156 mmol) in CH_2Cl_2 (12 mL) at 0 ^{o}C was added enone **4** (1.43g , 13.0 mmol) and the mixture was stirred at 0^{o}C for 30 min and then room temperature for 8 h. The reaction was quenched with HCl (10%,

3 mL) and extracted with CH_2Cl_2 (20 mL x 5). The combined organic extracts were washed with saturated $Na_2S_2O_3$ solution (20 mL x 3), brine (20mL) and dried over $MgSO_4$. After filtration and concentration, purification by flash column chromatography (ethyl acetate/hexane 1:8) afforded **5** (2.91 g, 95%) as a solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 5.8, 3.0 Hz, 1H), 2.78-2.69 (m, 1H), 2.48-2.40 (m, 1H), 2.32-2.23 (m, 2H), 2.18-2.10 (m, 1H), 1.05 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.9 (C), 158.4 (CH), 103.1 (C), 44.7 (CH_2), 37.5 (CH_2), 30.0 (CH), 20.3 (CH_3); **IR** (neat) 3025, 1683, 1590, 739 cm^{-1}; **MS** (EI) *m/z* 236 (M^+, 100), 194 (89), 109 (27); **HRMS** (EI) *m/z* calcd for C_7H_9IO 235.9700, found 235.9707.
$[\alpha]_D$ = -75.8° (c = 1.2, $CHCl_3$)

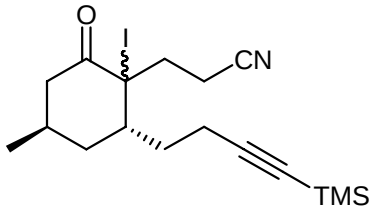
3-((*R*)-4-methyl-6-oxocyclohex-1-enyl)propanenitrile (**6**)



To a refluxing benzene solution (1.1 mL) of **5** (52 mg, 0.22 mmol) and acrylonitrile (0.15 mL, 2.20 mmol) under an atmosphere of argon was added a solution of AIBN (4.3 mg, 0.026 mmol) and Bu_3SnH (71 uL, 0.264 mmol) in benzene (0.53 mL) 8 times at an interval of 40 min. After the starting material was consumed completely by montoring with TLC (2 h), the reaction mixture was cooled to room temperature and benzene was evaporated. After dilution with Et_2O (5 mL) followed by addition of saturated KF solution (5 mL), the resulting mixture was stirred for another 2 h. Then moved the solid by filtration and the liquid was extracted with diethyl ether (5 mL x 3), the combined organic extracts were washed with brine (5 mL) and dried over $MgSO_4$. After filtration and concentration, purification by flash chromatography (ethyl acetate/hexane 1:5) afforded compound **6** (25.1 mg, 70 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (dd, *J* = 5.4, 2.6 Hz, 1H), 2.53-2.42 (m, 6H), 2.27-2.14 (m, 1H), 2.12-2.04 (m, 2H), 1.05 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 98.6 (C), 147.5 (CH), 135.3(C), 119.0 (C), 46.0 (CH_2), 33.9 (CH_2), 30.1 (CH), 26.0 (CH_2), 20.7 (CH_3), 16.5 (CH_2); **IR** (neat) 3025, 2246, 1670, 1590, 739 cm^{-1}; **MS** (EI) *m/z* 163 (M^+, 44), 148 (72), 121 (45), 81 (100); **HRMS** (EI) *m/z* calcd for $C_{10}H_{13}NO$ 163.1997, found 163.1998.

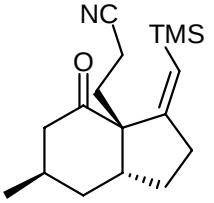
3-((2*R*,4*R*)-1-iodo-4-methyl-2-(4-(trimethylsilyl)but-3-ynyl)-6-oxocyclohexyl)propanenitrile (**7**)



To a suspension of magnesium powder (1.48 g, 60.75 mmol) in THF (15 mL) was added a solution of 4-chloro-1-trimethylsilyl-1-butyne (4.88 g, 30.38 mmol) and 1,2-dibromobutane (0.51 mL, 5.92 mmol) in THF (15 mL) with a syringe pump (0.1mL/min). After addition, the mixture was heated to reflux for 2 h and then cooled to -78^{o}C. CuI (6.08 g, 31.90 mmol) and hexamethylphosphoramide (0.32 mL, 1.82 mmol) were added. The reaction mixture was stirred for 30 min. To this mixture was added a solution of compound **6** (1.98 g, 12.15 mmol) and chlorotrimethylsilane (3.86 mL, 30.38 mmol) in THF (3 mL) with a syringe pump followed by addition of triethyl amine (4.23 mL, 30.38 mmol). The reaction mixture was warmed to rt and stirred for 15 h. Hexane was added and the mixture was filtered and washed with saturated $NaHCO_3$ solution (5 mL), brine (10 mL), and then dried ($MgSO_4$). Filtration through Florisol and concentration gave crude product (3.84 g, 84 %). The crude product was used for next step without further purification.
To a solution of NaI (4.87 g, 32.77 mmol) and the crude product (3.84 g, 10.63 mmol) in THF (60 mL) was added a solution of *m*-CPBA (85 %, 5.60 g, 32.47 mmol) in THF (83 mL) dropwise at 0^{o}C. The reaction mixture was stirred for 2 h at 0^{o}C and then Et_2O (8 mL) was added. The organic layer was washed with K_2CO_3 solution (10 mL x 3), $Na_2S_2O_3$ solution (10 mL x 3) and brine (10 mL x 3), and dried ($MgSO_4$). After filtration and concentration, purification by flash chromatography (ethyl acetate/hexane 1:45) afforded compound **7** (3.42 g, 78 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (dd, *J* = 14.6, 6.6 Hz, 1H), 2.97-2.87 (m, 1H), 2.79-2.70 (m, 1H), 2.67-2.51 (m, 6H), 2.22-2.13 (m, 1H), 1.80-1.72 (m, 3H), 1.48-1.38 (m, 1H), 0.90 (d, *J* = 7.2 Hz, 3H), 0.11 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.1 (C), 118.4 (C), 105.6 (C), 86.5 (C), 42.3 (CH_2), 37.5 (CH), 34.8 (CH_2), 33.6 (CH_2), 32.9 (CH_2), 28.6 (CH), 19.3 (CH_3), 16.9 (CH_2), 15.5 (CH_2), -0.1 (CH_3); **IR** (neat) 2246, 2187, 1712, 1263, 562 cm^{-1}; **MS** (EI) *m/z* 415(M^+, 40), 288 (100), 262 (60), 189 (65), 127 (78) ; **HRMS** (EI) *m/z* calcd for $C_{17}H_{26}INOSi$ 415.0828, found 415.0830.

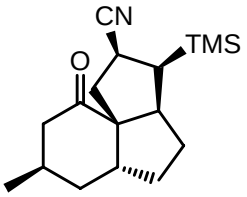
3-((*Z*,3a*R*,5*R*,7a*S*)-octahydro-5-methyl-1-((trimethylsilyl)methylene)-7-oxo-1*H*-inden-7a-yl)propanenitrile (**8**)

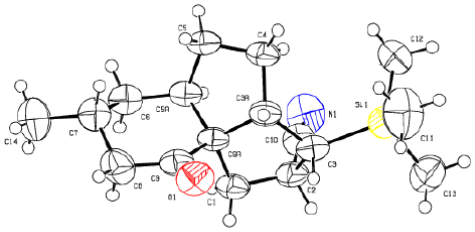


To a refluxing solution of compound **7** (1.83 g, 4.42 mmol) in benzene (267 mL) was added Bu_3SnH (1.43 mL, 5.30 mmol) and AIBN (87 mg, 0.53 mmol) in benzene (83 mL) with a syringe pump in a period of 6 h. After addition, the reaction mixture was heated at reflux for 2 h, and then cooled to rt. After concentration, Et_2O (25 mL) and saturated KF solution (25 mL) were added. The mixture was stirred at rt for 4 h. Solid precipitation was removed by filtration. The organic layer was separated and washed with saturated $NaHCO_3$ solution (20 mL) and brine (20 mL), and dried ($MgSO_4$). Silica gel chromatography (ethyl acetate/hexane 1:15) gave compound **8** as a yellow liquid (818 mg, 64 %) and trace compound **18** and **19** (89 mg totally, 7 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (dd, *J* = 2.4, 2.4 Hz, 1H), 2.66-2.21 (m, 7H), 2.06-1.74 (m, 5H), 1.63 (dd, *J* = 10.8, 3.6 Hz, 2H), 0.90 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.1 (C), 160.5 (C), 124.3 (CH), 120.3 (C), 65.2 (C), 45.3 (CH_2), 42.3 (CH), 34.6 (CH_2), 30.6 (CH_2), 29.9(CH), 29.4 (CH_2), 29.4 (CH_2), 18.9 (CH_3), 13.6 (CH_2), -0.7 (CH_3); **IR** (neat) 2956, 2246, 1703, 1630, 1249 cm^{-1}; **MS** (EI) *m/z* 289 (M^+, 32), 263 (78), 175 (100), 144 (45); **HRMS** (EI) *m/z* calcd for $C_{17}H_{27}NOSi$ 289.1862, found 289.1865.
$[\alpha]_D$ = -108.6° (c = 1.28, $CHCl_3$)

(2*S*,3*S*,3a*S*,5a*R*,7*R*,9a*S*)-decahydro-7-methyl-3-(trimethylsilyl)-9-oxo-1*H*-cyclopenta[*i*]indene-2-carbonitrile (**18**). 50% probability was chosen for the ellipsoids in these plots.





Identification code mr19m
Empirical formula C17 H27 N O Si
Formula weight 289.49
Temperature 296(2) K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group P2(1)/c
Unit cell dimensions a = 7.5791(14) Å = 90°.
b = 12.075(2) Å = 91.904(3)°.
c = 19.243(4) Å = 90°.
Volume 1760.1(6) Å3
Z 4
Density (calculated) 1.092 Mg/m3
Absorption coefficient 0.131 mm-1
F(000) 632
Crystal size 0.65 x 0.55 x 0.30 mm3
Theta range for data collection 1.99 to 28.31°.

Index ranges $-9 \leq h \leq 10$, $-14 \leq k \leq 15$, $-21 \leq l \leq 25$
Reflections collected 10942
Independent reflections 4155 [R(int) = 0.0240]
Completeness to theta = 28.31° 95.1 %
Absorption correction Empirical
Max. and min. transmission 0.9700 and 0.8862
Refinement method Full-matrix least-squares on F2
Data / restraints / parameters 4155 / 0 / 181
Goodness-of-fit on F2 1.025
Final R indices [I>2sigma(I)] R1 = 0.0524, wR2 = 0.1439
R indices (all data) R1 = 0.0805, wR2 = 0.1623
Largest diff. peak and hole 0.305 and -0.222 e.Å-3

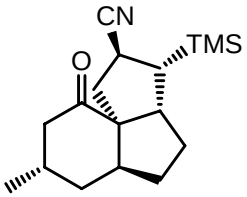
Bond length data (Å)

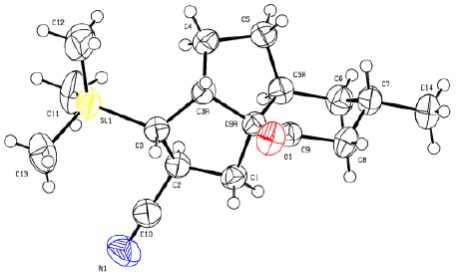
Si(1)-C(15)	1.845(3)
Si(1)-C(17)	1.852(2)
Si(1)-C(16)	1.862(2)
Si(1)-C(12)	1.890(2)
O(1)-C(4)	1.209(2)
N(1)-C(13)	1.139(3)
C(1)-C(13)	1.470(3)
C(1)-C(2)	1.537(3)
C(1)-C(12)	1.544(2)
C(2)-C(3)	1.550(2)
C(3)-C(4)	1.532(2)
C(3)-C(8)	1.550(2)
C(3)-C(11)	1.564(2)
C(4)-C(5)	1.497(3)
C(5)-C(6)	1.520(3)
C(6)-C(7)	1.516(3)
C(6)-C(14)	1.523(3)
C(7)-C(8)	1.518(3)
C(8)-C(9)	1.527(2)
C(9)-C(10)	1.509(3)
C(10)-C(11)	1.548(2)
C(11)-C(12)	1.543(2)

Bond angle data (°)

C(15)-Si(1)-C(17)	110.52(13)
C(15)-Si(1)-C(16)	108.32(14)
C(17)-Si(1)-C(16)	107.59(11)
C(15)-Si(1)-C(12)	107.04(12)
C(17)-Si(1)-C(12)	108.09(10)
C(16)-Si(1)-C(12)	115.28(9)
C(13)-C(1)-C(2)	112.76(16)
C(13)-C(1)-C(12)	113.53(15)
C(2)-C(1)-C(12)	103.52(15)
C(1)-C(2)-C(3)	105.40(14)
C(4)-C(3)-C(8)	112.30(14)
C(4)-C(3)-C(2)	107.88(13)
C(8)-C(3)-C(2)	113.20(13)
C(4)-C(3)-C(11)	111.97(14)
C(8)-C(3)-C(11)	105.57(12)
C(2)-C(3)-C(11)	105.79(14)
O(1)-C(4)-C(5)	121.25(17)
O(1)-C(4)-C(3)	121.13(17)
C(5)-C(4)-C(3)	117.59(15)
C(4)-C(5)-C(6)	113.28(17)
C(7)-C(6)-C(5)	107.96(16)
C(7)-C(6)-C(14)	111.56(17)
C(5)-C(6)-C(14)	112.16(19)
C(6)-C(7)-C(8)	114.41(15)
C(7)-C(8)-C(9)	116.36(15)
C(7)-C(8)-C(3)	115.94(14)
C(9)-C(8)-C(3)	102.73(13)
C(10)-C(9)-C(8)	102.02(14)
C(9)-C(10)-C(11)	104.60(14)
C(12)-C(11)-C(10)	118.08(15)
C(12)-C(11)-C(3)	106.31(13)
C(10)-C(11)-C(3)	104.21(13)
C(11)-C(12)-C(1)	104.44(14)
C(11)-C(12)-Si(1)	121.56(12)
C(1)-C(12)-Si(1)	117.69(13)
N(1)-C(13)-C(1)	177.9(2)

(2S,3R,3aR,5aS,7S,9aR)-decahydro-7-methyl-3-(trimethylsilyl)-9-oxo-1H-cyclopenta[i]indene-2-carbonitrile (**19**). 50% probability was chosen for the ellipsoids in these plots.





^{1}H NMR (400 MHz, $CDCl_3$) δ 3.04 (dd, *J* = 17.6, 8.8 Hz, 1H), 2.56 (ddd, *J* = 13.4, 11.2, 6.4 Hz, 1H), 2.47-2.37 (m, 1H), 2.14 (dd, *J* = 12.6, 5.8 Hz, 1H), 2.00-1.79 (m, 5H), 1.58-1.42 (m, 4H), 1.27-1.15 (m, 1H), 1.12-1.00 (m, 1H), 0.98 (d, *J* = 6.0 Hz, 3H), 0.14 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.6 (C), 121.4 (C), 63.9 (C), 50.4 (CH), 48.6 (CH_2), 47.7 (CH), 43.9 (CH_2), 37.7 (CH), 34.3 (CH_2), 31.7 (CH_2), 29.8 (CH), 29.7 (CH_2), 28.2 (CH), 21.8 (CH_3), -1.0 (CH_3); **IR** (neat) 2245, 1712, 564 cm^{-1}; **MS** (EI) *m/z* 289 (M^+, 79), 263 (100), 159 (49); **HRMS** (EI) *m/z* calcd for $C_{17}H_{27}NOSi$ 289.1862, found 289.1861.

Identification code jn20m
Empirical formula C17 H27 N O Si
Formula weight 289.49
Temperature 296(2) K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group P2(1)/c
Unit cell dimensions a = 11.6687(8) Å = 90°.
b = 12.3423(9) Å = 95.921(2)°.
c = 12.2850(9) Å = 90°.
Volume 1759.8(2) Å3
Z 4
Density (calculated) 1.093 Mg/m3
Absorption coefficient 0.131 mm-1
F(000) 632
Crystal size 0.7 x 0.5 x 0.4 mm3
Theta range for data collection 1.75 to 28.26°.
Index ranges $-14 \le h \le 10$, $-16 \le k \le 15$, $-13 \le l \le 15$
Reflections collected 10218
Independent reflections 3920 [R(int) = 0.0201]
Completeness to theta = 28.26° 89.8 %
Absorption correction Empirical
Max. and min. transmission 0.98096 and 0.88685
Refinement method Full-matrix least-squares on F2
Data / restraints / parameters 3920 / 0 / 181

Goodness-of-fit on F2 1.056
Final R indices [I>2sigma(I)] R1 = 0.0463, wR2 = 0.1348
R indices (all data) R1 = 0.0577, wR2 = 0.1435
Largest diff. peak and hole 0.278 and -0.181 e.Å-3

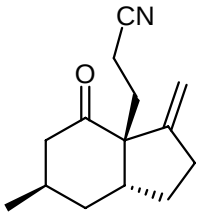
Bond length data (Å)

Si(1)-C(13)	1.842(2)
Si(1)-C(15)	1.854(2)
Si(1)-C(14)	1.863(2)
Si(1)-C(12)	1.9000(15)
O(1)-C(8)	1.2146(18)
N(1)-C(17)	1.135(2)
C(1)-C(2)	1.543(2)
C(1)-C(12)	1.548(2)
C(1)-C(9)	1.5713(19)
C(2)-C(3)	1.524(2)
C(3)-C(4)	1.527(2)
C(4)-C(5)	1.527(2)
C(4)-C(9)	1.549(2)
C(5)-C(6)	1.520(2)
C(6)-C(16)	1.527(2)
C(6)-C(7)	1.530(2)
C(7)-C(8)	1.491(2)
C(8)-C(9)	1.5295(18)
C(9)-C(10)	1.5508(19)
C(10)-C(11)	1.537(2)
C(11)-C(17)	1.468(2)
C(11)-C(12)	1.5513(19)

Bond angle data (°)

C(11)-C(12)	1.5513(19)
C(13)-Si(1)-C(15)	108.08(12)
C(13)-Si(1)-C(14)	111.40(15)
C(15)-Si(1)-C(14)	109.07(11)
C(13)-Si(1)-C(12)	110.53(9)
C(15)-Si(1)-C(12)	107.57(9)
C(14)-Si(1)-C(12)	110.09(8)
C(2)-C(1)-C(12)	117.72(12)
C(2)-C(1)-C(9)	104.86(12)
C(12)-C(1)-C(9)	106.14(11)
C(3)-C(2)-C(1)	104.24(12)
C(2)-C(3)-C(4)	102.57(12)
C(5)-C(4)-C(3)	117.36(13)
C(5)-C(4)-C(9)	115.22(12)
C(3)-C(4)-C(9)	102.92(12)
C(6)-C(5)-C(4)	113.78(13)
C(5)-C(6)-C(16)	111.78(15)
C(5)-C(6)-C(7)	108.39(13)
C(16)-C(6)-C(7)	109.81(14)
C(8)-C(7)-C(6)	113.28(12)
O(1)-C(8)-C(7)	121.42(13)
O(1)-C(8)-C(9)	120.74(13)
C(7)-C(8)-C(9)	117.78(12)
C(8)-C(9)-C(4)	113.25(11)
C(8)-C(9)-C(10)	108.41(11)
C(4)-C(9)-C(10)	111.98(11)
C(8)-C(9)-C(1)	111.83(11)
C(4)-C(9)-C(1)	105.44(11)
C(10)-C(9)-C(1)	105.69(11)
C(11)-C(10)-C(9)	103.41(11)
C(17)-C(11)-C(10)	112.13(13)
C(17)-C(11)-C(12)	114.07(12)
C(10)-C(11)-C(12)	103.38(11)
C(1)-C(12)-C(11)	101.80(11)
C(1)-C(12)-Si(1)	120.72(10)
C(11)-C(12)-Si(1)	116.43(9)
N(1)-C(17)-C(11)	179.3(2)

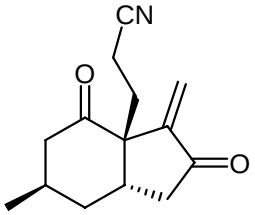
3-((3a*R*,5*R*,7a*S*)-octahydro-5-methyl-1-methylene-7-oxo-1*H*-inden-7a-yl)propanenitrile (**9**)



To a solution of compound **8** (847 mg, 2.93 mmol) in CH_2Cl_2 (20 mL) was added dropwise CF_3COOH (1.74 mL, 23.44 mmol). The reaction mixture was stirred for 3 h and then neutralized with 2N NaOH. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (20 mL x 3). The combined organic layer was dried over $MgSO_4$. Concentration and silica gel column chromatography (ethyl acetate/hexane 1:15) gave compound **9** as a yellow liquid (496 mg, 78 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (dd, *J* = 2.4, 2.4 Hz, 1H), 4.67 (dd, *J* = 2.4, 2.4 Hz, 1H), 2.64-2.54 (m, 2H), 2.52-2.20 (m, 5H), 2.04-1.80 (m, 4H), 1.72-1.63 (m, 1H), 1.62-1.50 (m, 2H), 0.91 (d, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.7 (C), 152.1 (C), 120.0 (C), 109.9 (CH_2), 62.3 (C), 45.2 (CH_2), 43.1 (C), 34.3 (CH_2), 30.4 (CH_2), 29.5 (C), 28.8 (CH_2), 19.1 (CH_3), 13.4 (CH_2); **IR** (neat) 3075, 2954, 2246, 1698, 1647 cm^{-1}; **MS** (EI) *m/z* 217 (M^+, 32), 191 (50), 160 (100), 26 (40); **HRMS** (EI) *m/z* calcd for $C_{14}H_{19}NO$ 217.1467 , found 217.1465.
$[\alpha]_D = -37.9^\circ$ (c = 7.23, $CHCl_3$)

3-((3a*S*,5*R*,7a*S*)-octahydro-5-methyl-1-methylene-2,7-dioxo-1*H*-inden-7a-yl)propanenitrile (**10**)

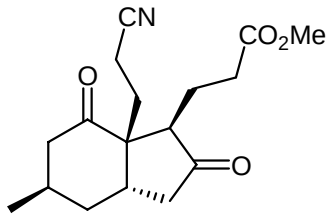


To a CH_2Cl_2 (2 mL) solution of SeO_2 (190 mg, 1.71 mmol) was added ^{t}BuOOH (1.5 mL) and compound **9** (62 mg, 0.29 mmol) dropwise at 0 ^{o}C. After 10 min, the reaction mixture was warmed to rt and stirred for 2 days. Saturated Na_2CO_3 was added to quench the reaction. The mixture was extracted with Et_2O (10 mL x 3) and the combined organic layers were washed with brine (10 mL x 3) and dried ($MgSO_4$). After filtration and concentration, a pale yellow oil was obtained. Then Jones oxidation was carried out. To a solution of crude product in acetone (8 mL) was added Jones reagent (1.5 mL) at 0 ^{o}C and stirred for 2 h. Isopropyl alcohol (3 mL) was added, and the mixture was washed with brine (10 mL x 3) and then dried ($MgSO_4$). After filtration and concentration,

purification by flash chromatography (ethyl acetate/hexane 1:2) afforded compound **10** (35 mg, 52 %) as a yellow oil.

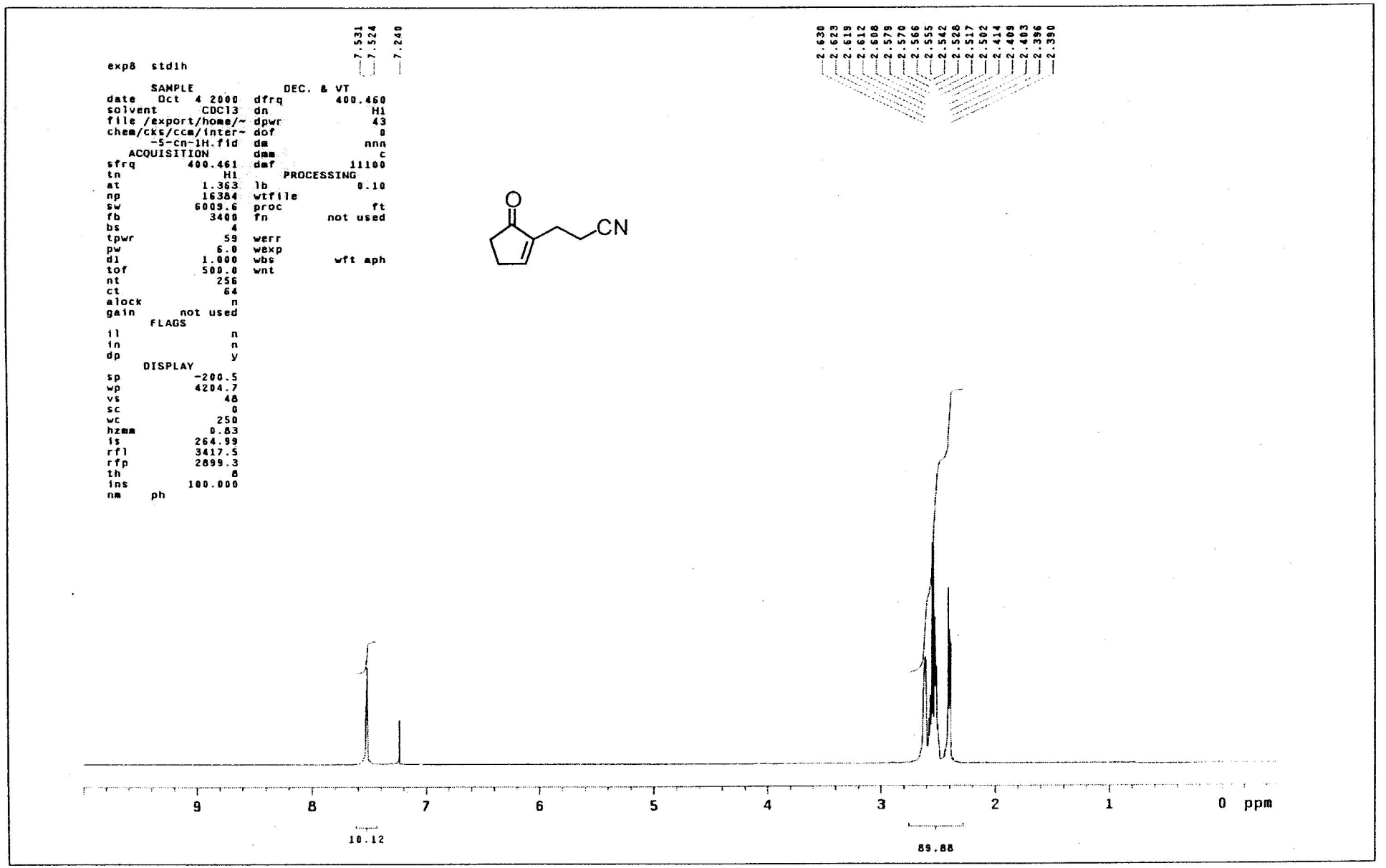
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (s, 1H), 5.19 (s, 1H), 2.72-2.44 (m, 4H), 2.39-1.92 (m, 6H), 1.76-1.69 (m, 1H), 1.65-1.55 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.2 (C), 202.4 (C), 145.2 (C), 121.3 (CH_2), 119.1(C), 58.7 (C), 44.8 (CH_2), 41.9 (CH_2), 35.8 (CH), 35.3 (CH_2), 30.2 (CH_2), 28.0 (CH), 19.4 (CH_3), 13.0 (CH_2); **IR** (neat) 2956, 2246, 1727, 1703, 1637, 1457 cm^{-1}; **MS** (EI) *m/z* 231 (M^+, 17), 205 (67), 173 (100), 158 (39); **HRMS** (EI) *m/z* calcd for $C_{14}H_{17}NO_2$ 231.1259, found 231.1255. $[\alpha]_D$ = -229.6° (c = 0.49, $CHCl_3$)

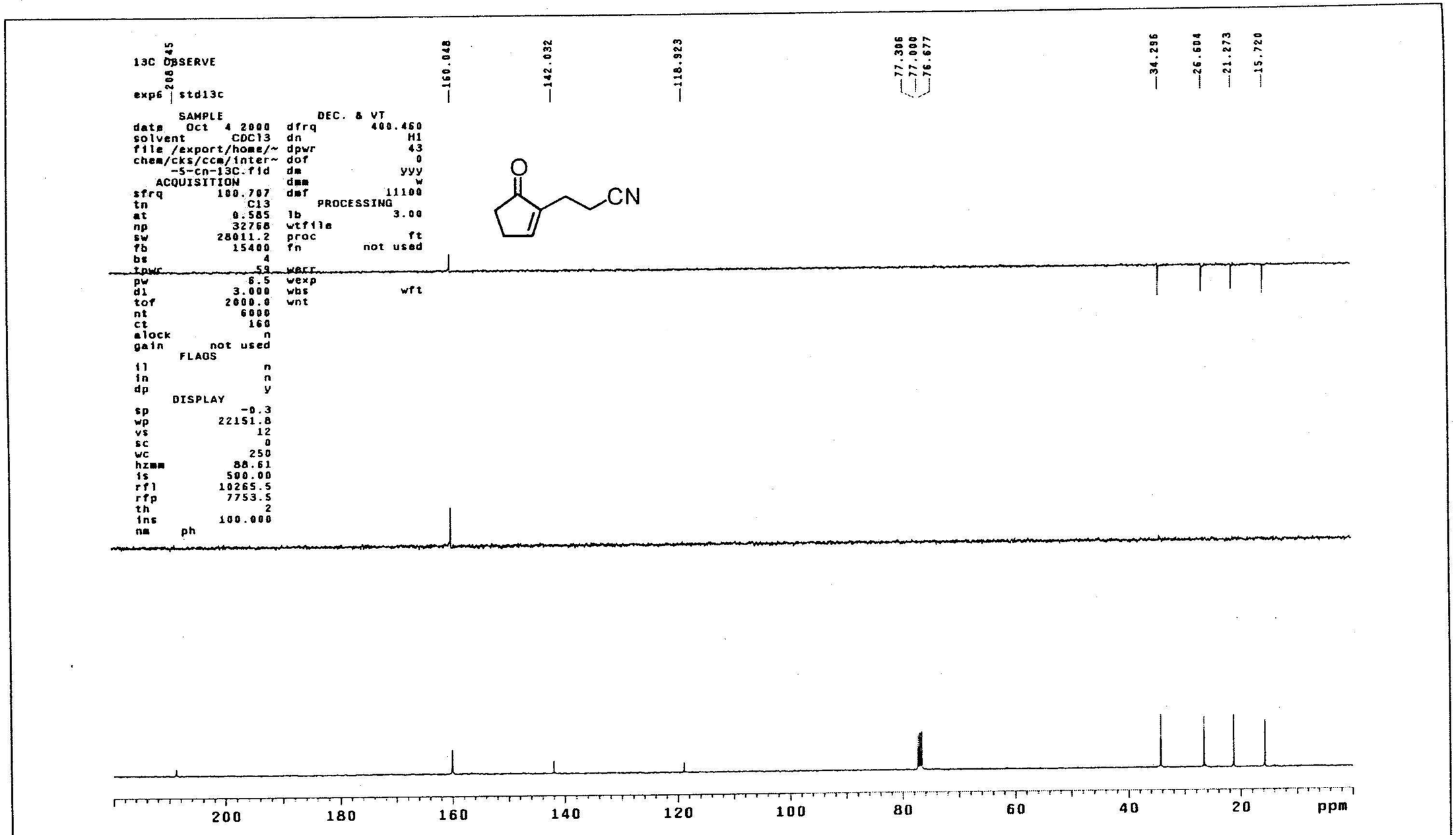
3-((1*R*,3a*S*,5*R*,7a*S*)-octahydro-5-methyl-2,7-dioxo-1-(methyl propionatyl)-1*H*-inden-7a-yl)propanenitrile (**11**)



To a solution of compound **10** (10.9 mg, 0.047 mmol) in Et_2O (5mL) was added $LiClO_4$ (125 mg, 1.175 mmol) and *tert*-butyldimethylsilyl methyl ketene acetal (9.4 mg, 0.05 mmol). The reaction mixture was stirrd for 8 h. THF (5 mL) and HOAc solution (10%, 5 mL) was added. The reaction mixture was stirred for 24 h at rt. 1N NaOH solution was added to neutralize the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ solution (5 mL) and brine (5 mL) and dried ($MgSO_4$). Concentration and silica gel chromatography (ethyl acetate/hexane 1:2) gave **11** as a pale yellow liquid (5.7 mg, 40 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 3H), 2.72 (dd, *J* = 12.0, 4.4 Hz, 1H), 2.69-2.62 (m, 1H), 2.50-2.47 (m, 1H), 2.39-2.33 (m, 1H), 2.30-1.96 (m, 7H), 1.86-1.43 (m, 4H), 1.34-1.20 (m, 2H), 0.98 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.5 (C), 211.2 (C), 173.2 (C), 119.3(C), 58.4 (C), 56.3 (CH), 51.6 (CH_3), 46.9 (CH_2), 40.4 (CH), 38.5 (CH_2), 33.4 (CH_2), 31.7 (CH_2), 30.5 (CH), 29.2 (CH_2), 24.9 (CH_2), 21.3 (CH_3), 12.7 (CH_2); **IR** (neat) 2247, 1742, 1713, 1699, 1645, 1251, 1197 cm^{-1}; **MS** (EI) *m/z* 305 (M^+, 43), 290 (66), 258 (100), 232 (44), 200 (39); **HRMS** (EI) *m/z* calcd for $C_{17}H_{23}NO_4$ 305.1627, found 305.1626. $[\alpha]_D$ = -198.6° (c = 0.62, $CHCl_3$)

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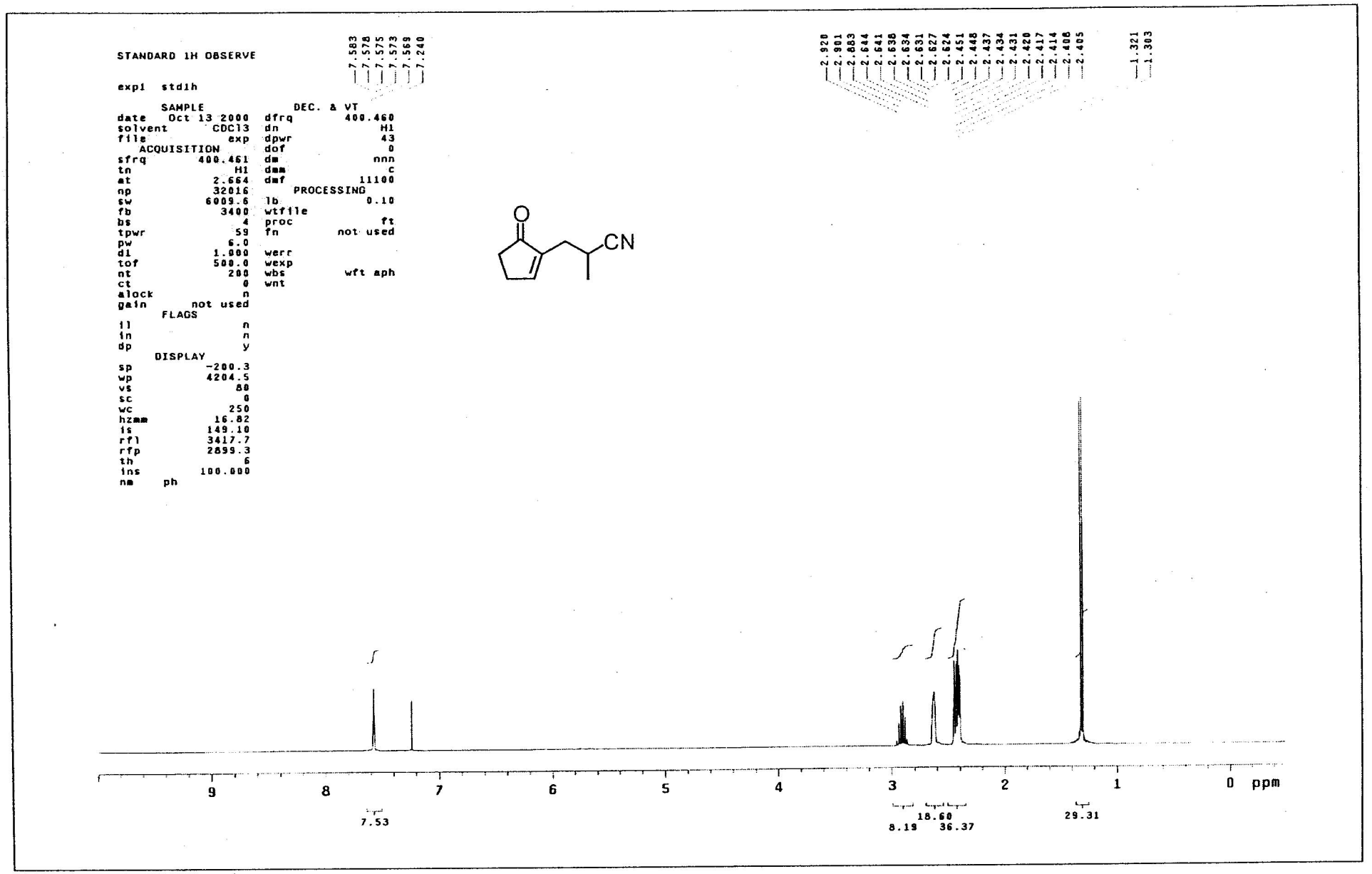

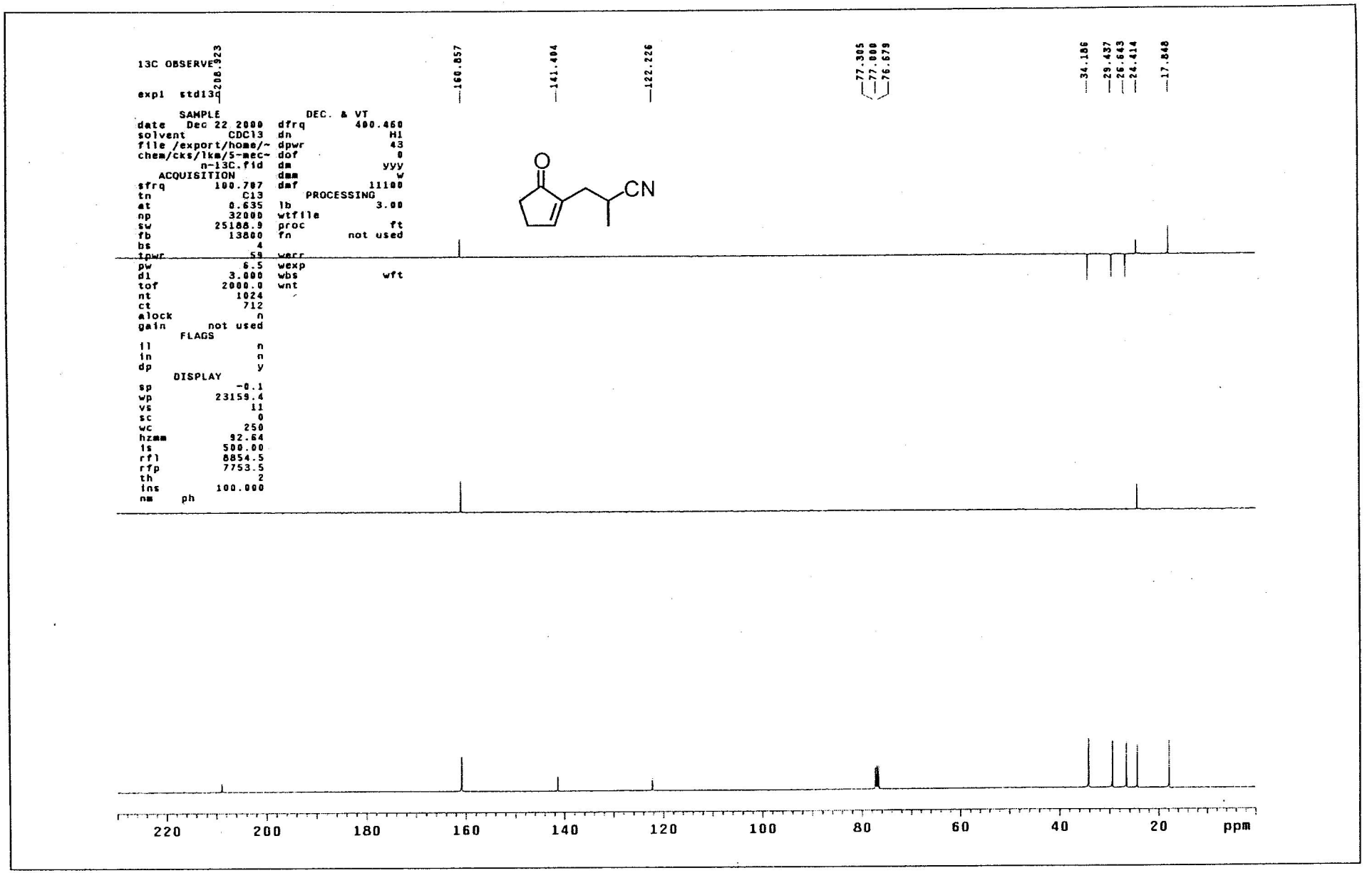

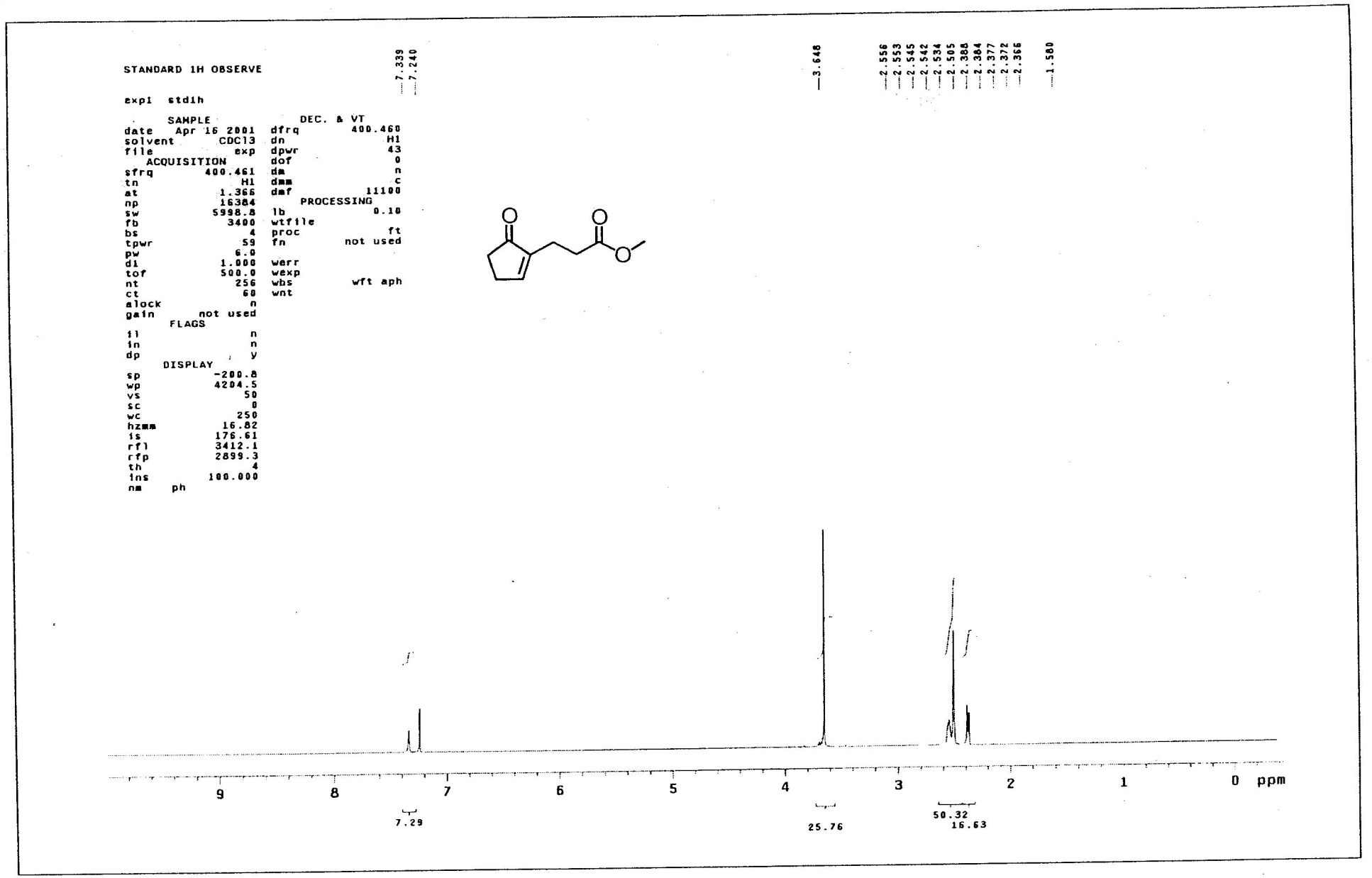

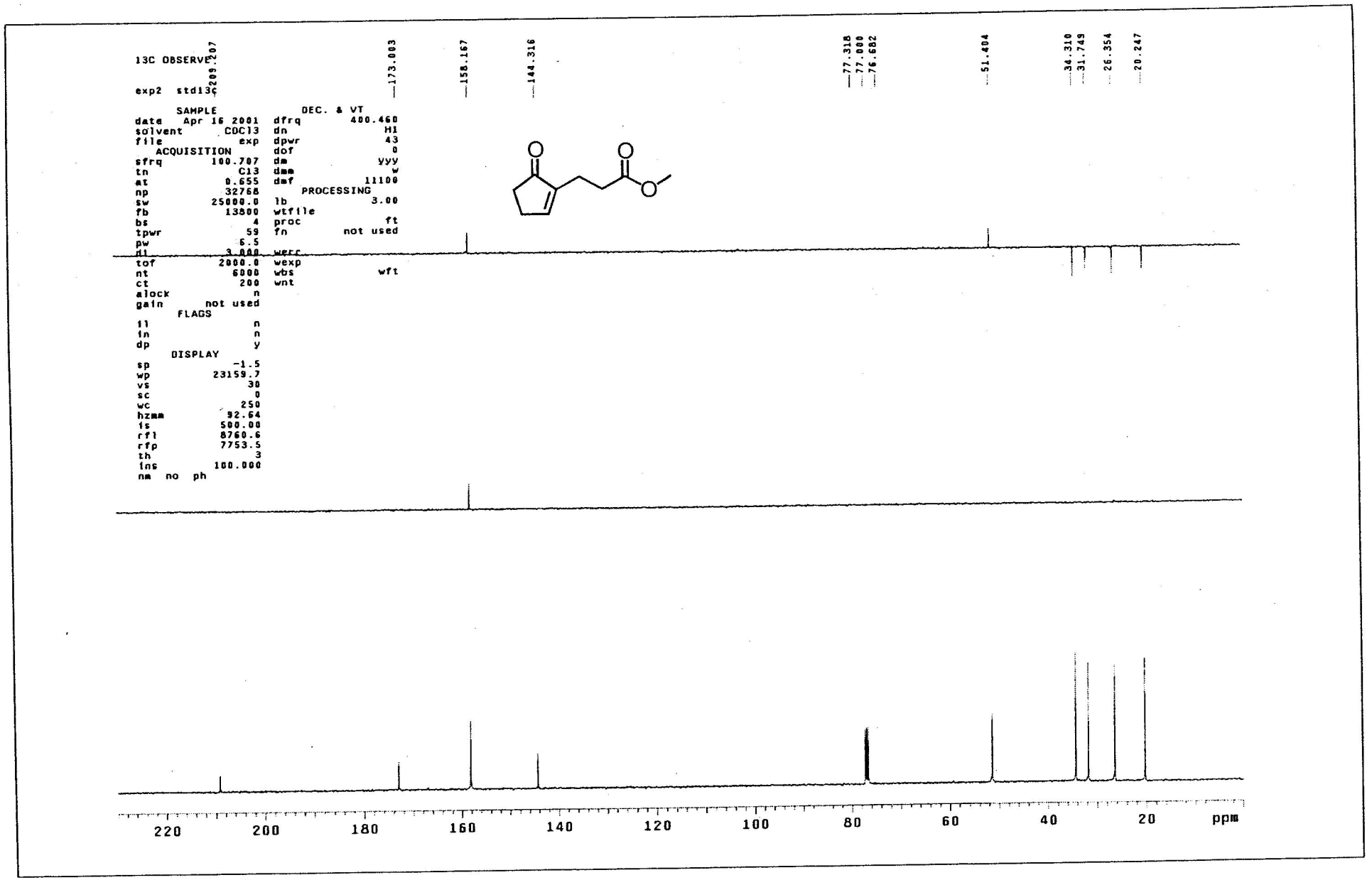

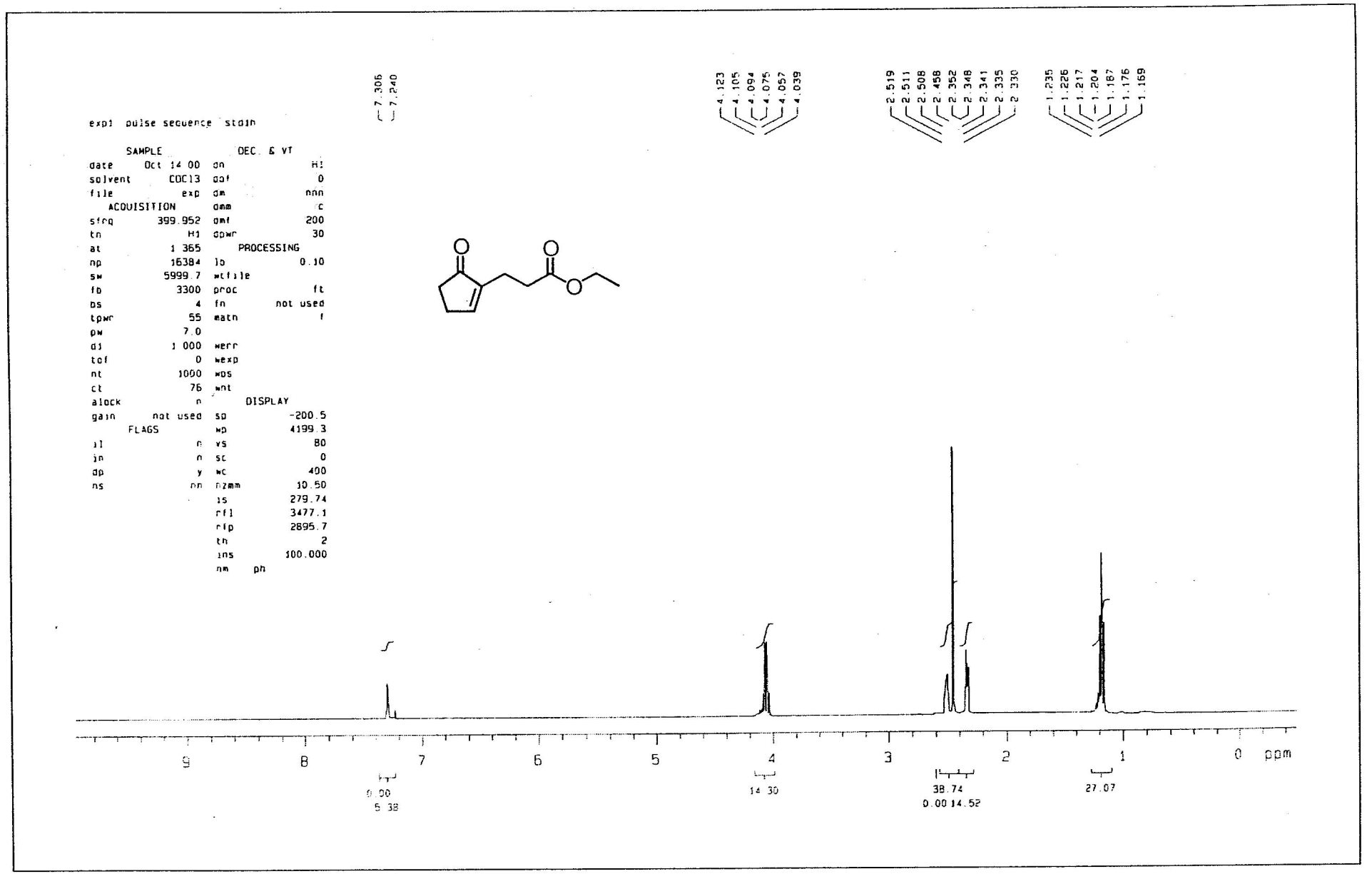

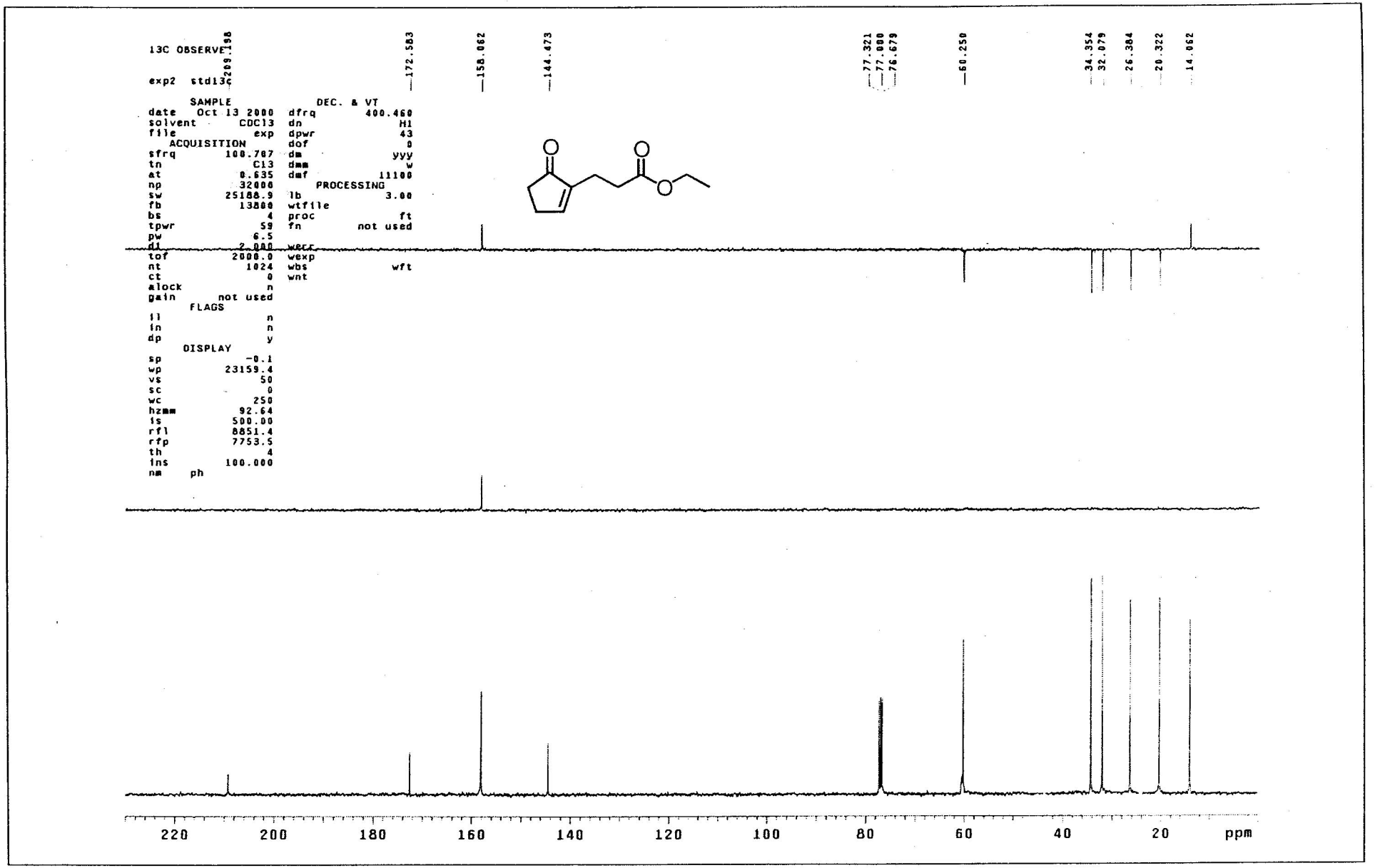

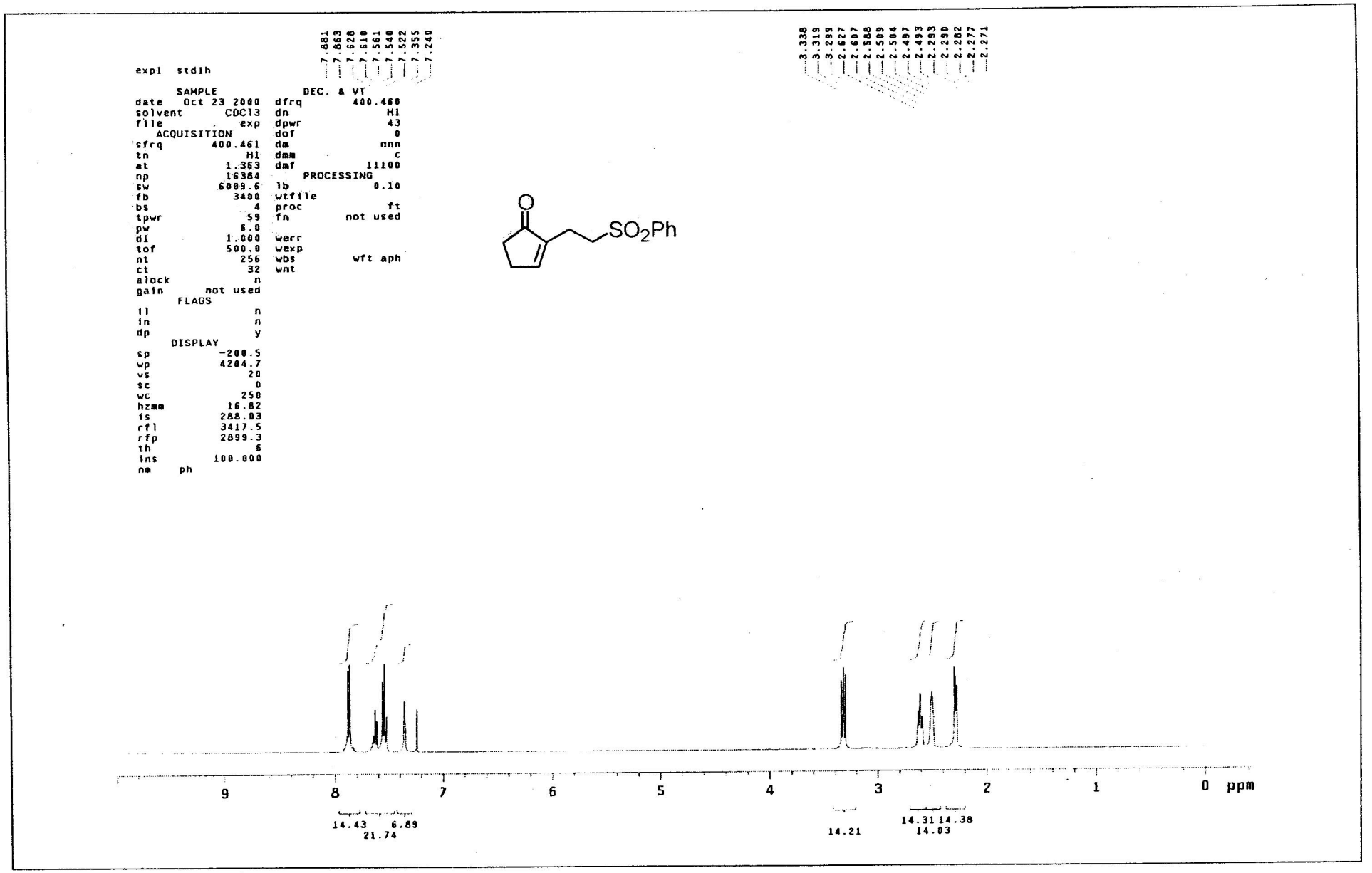

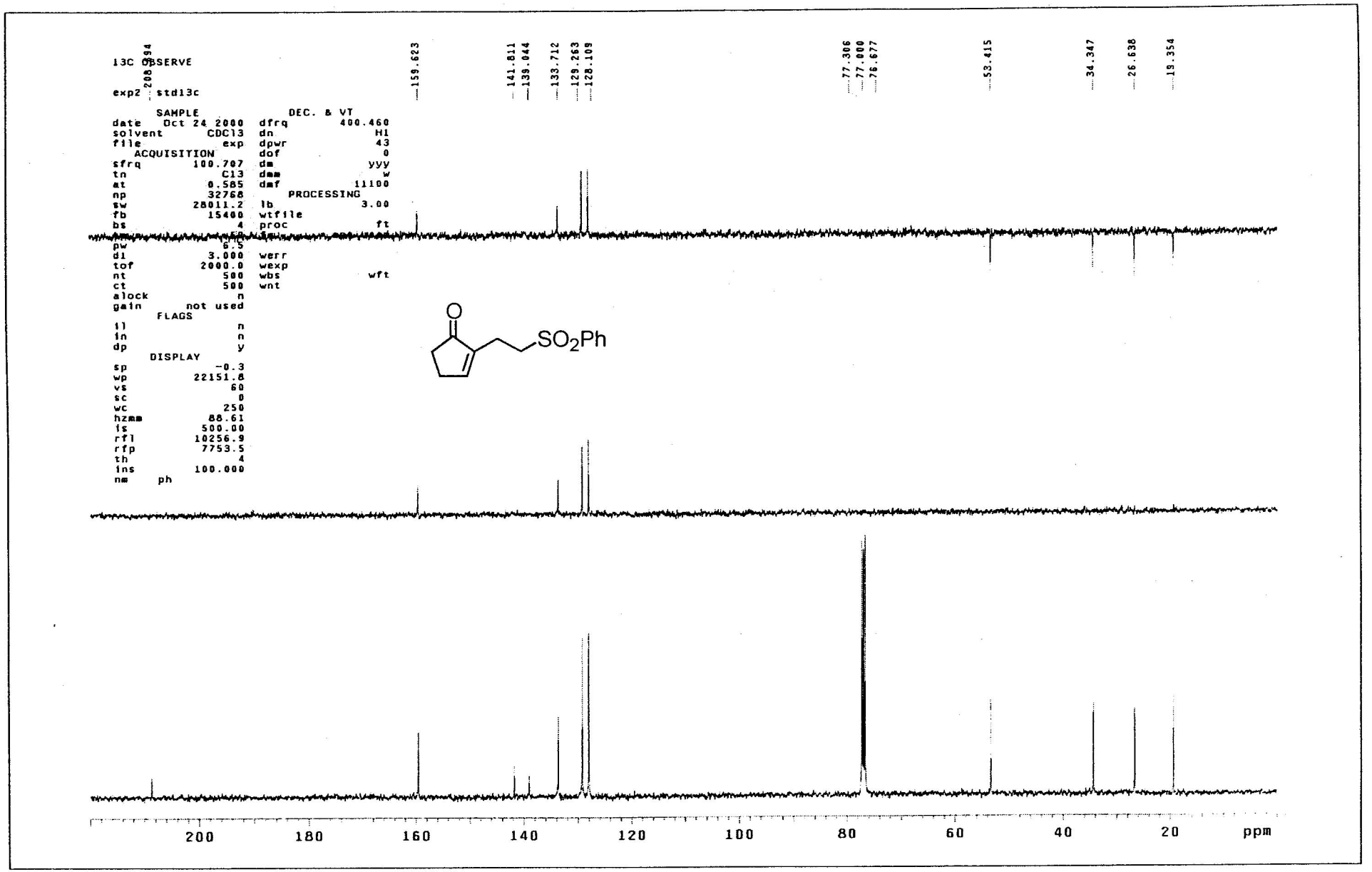

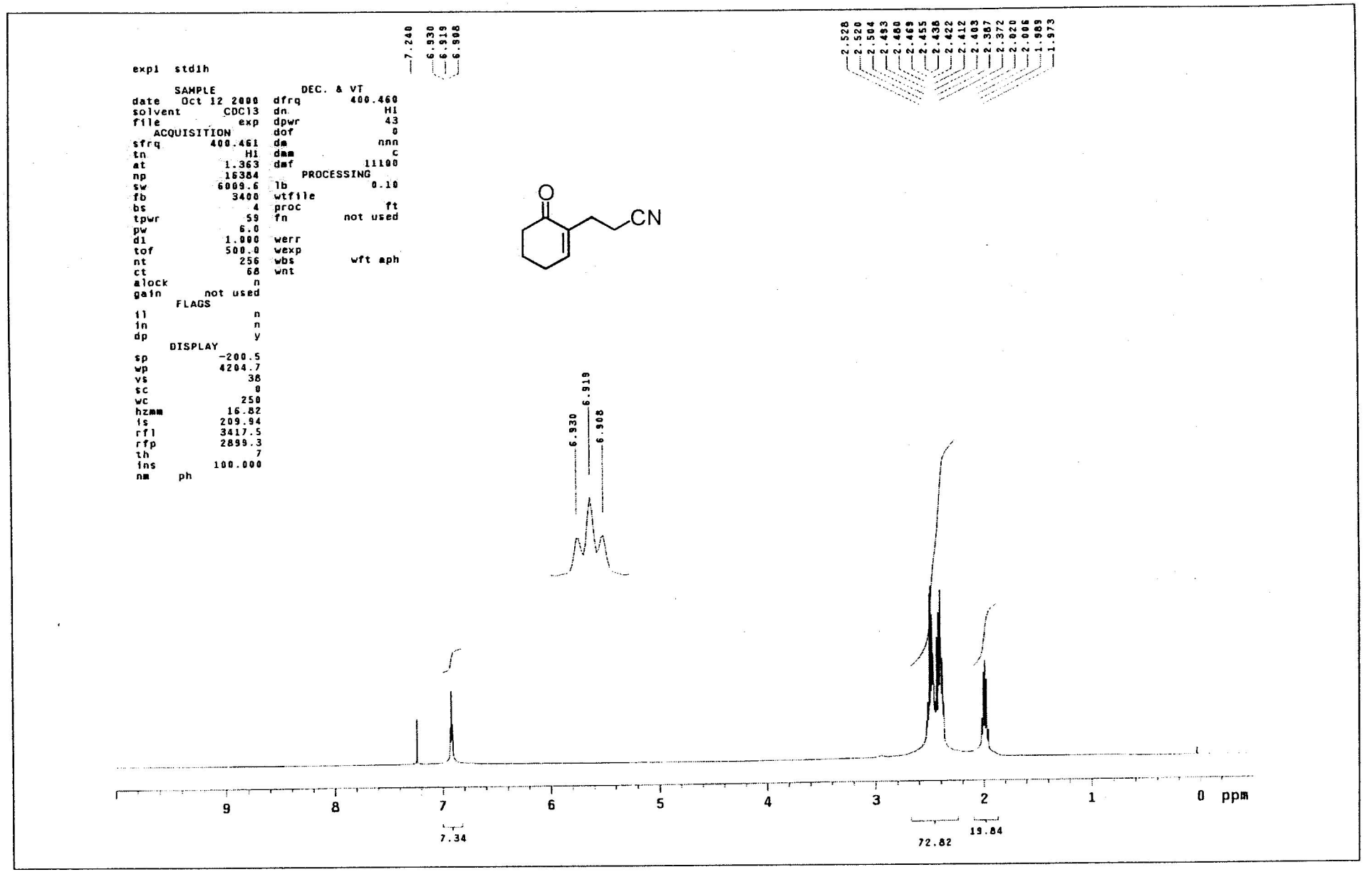

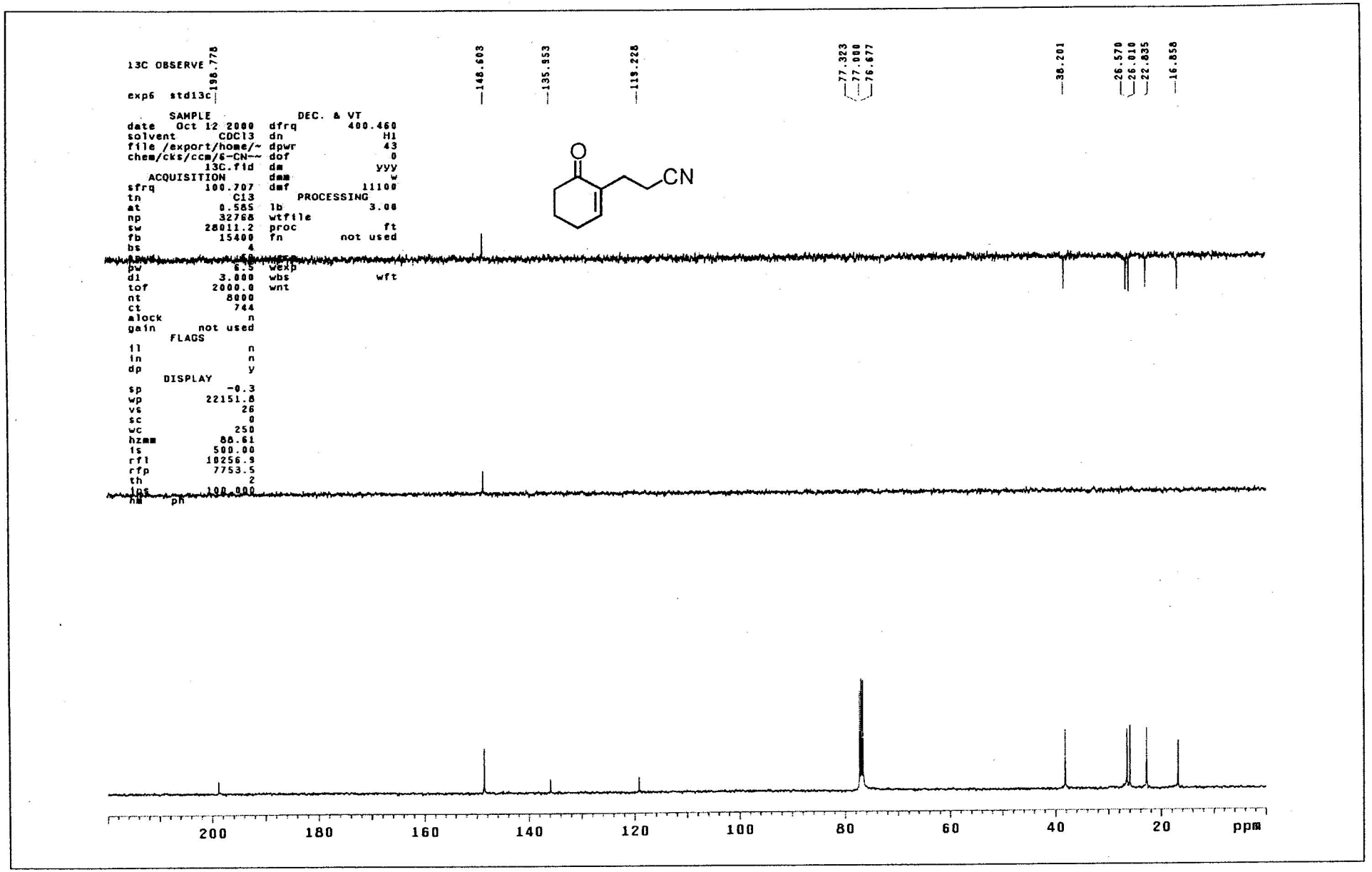

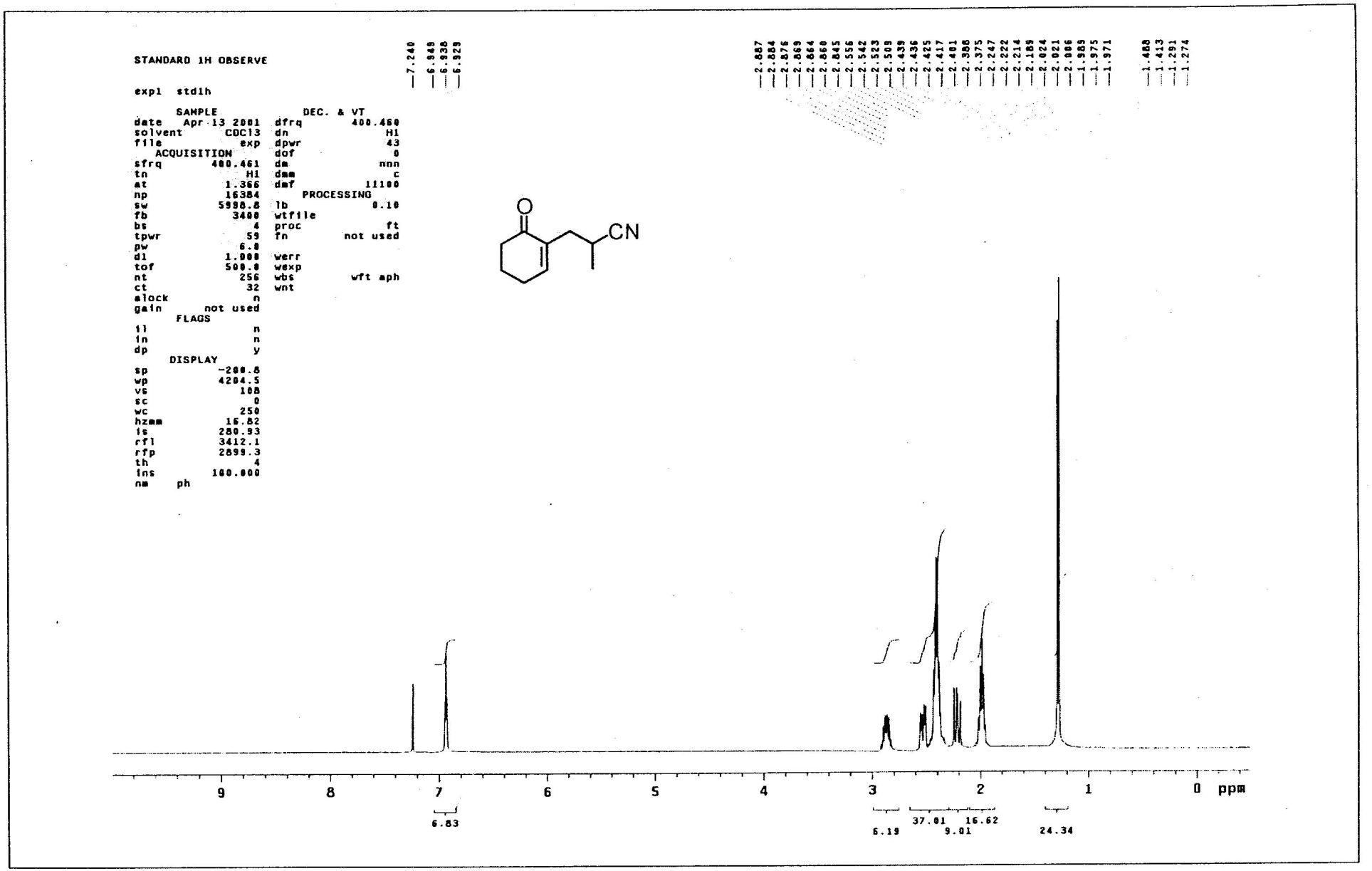

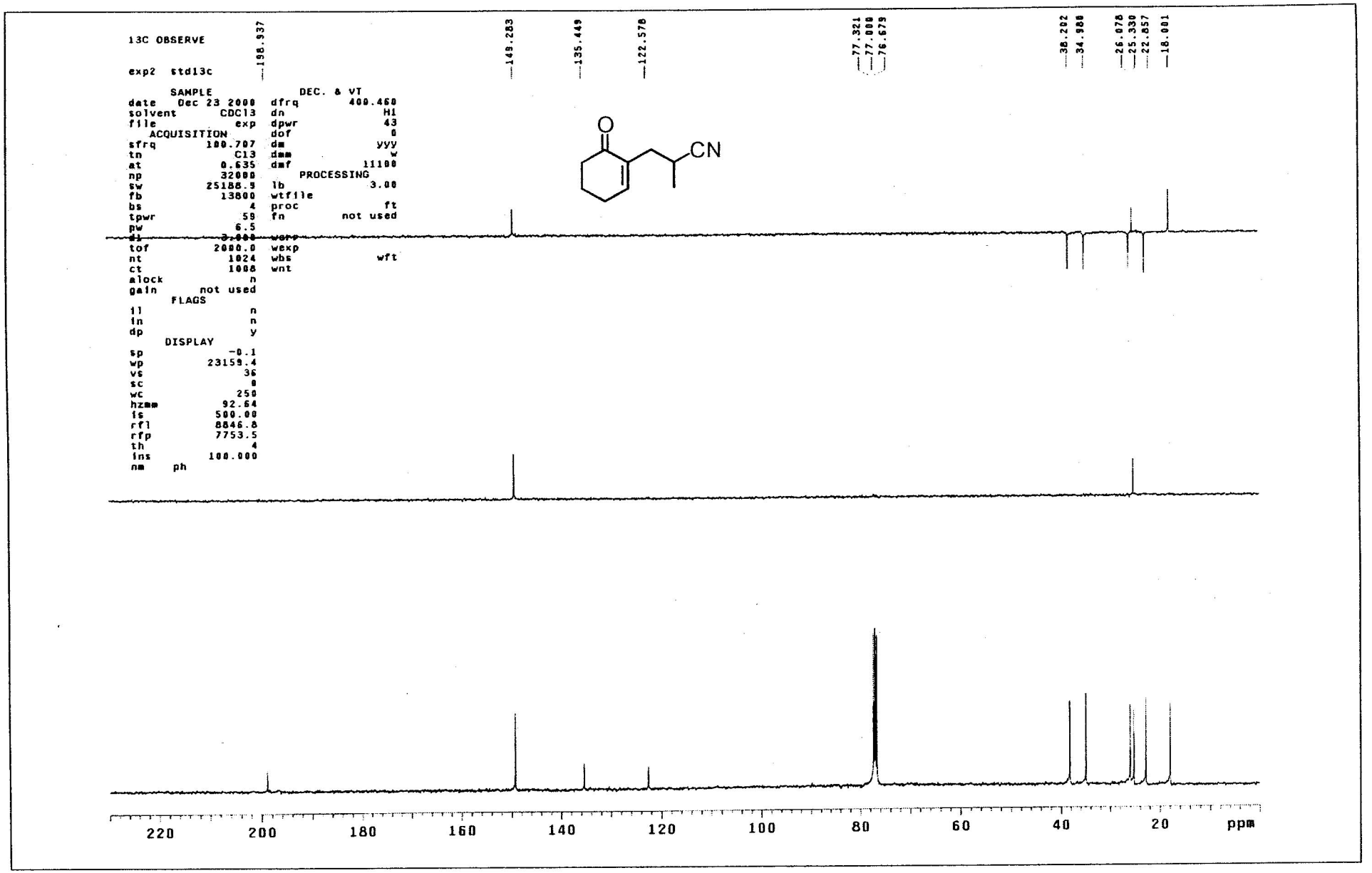

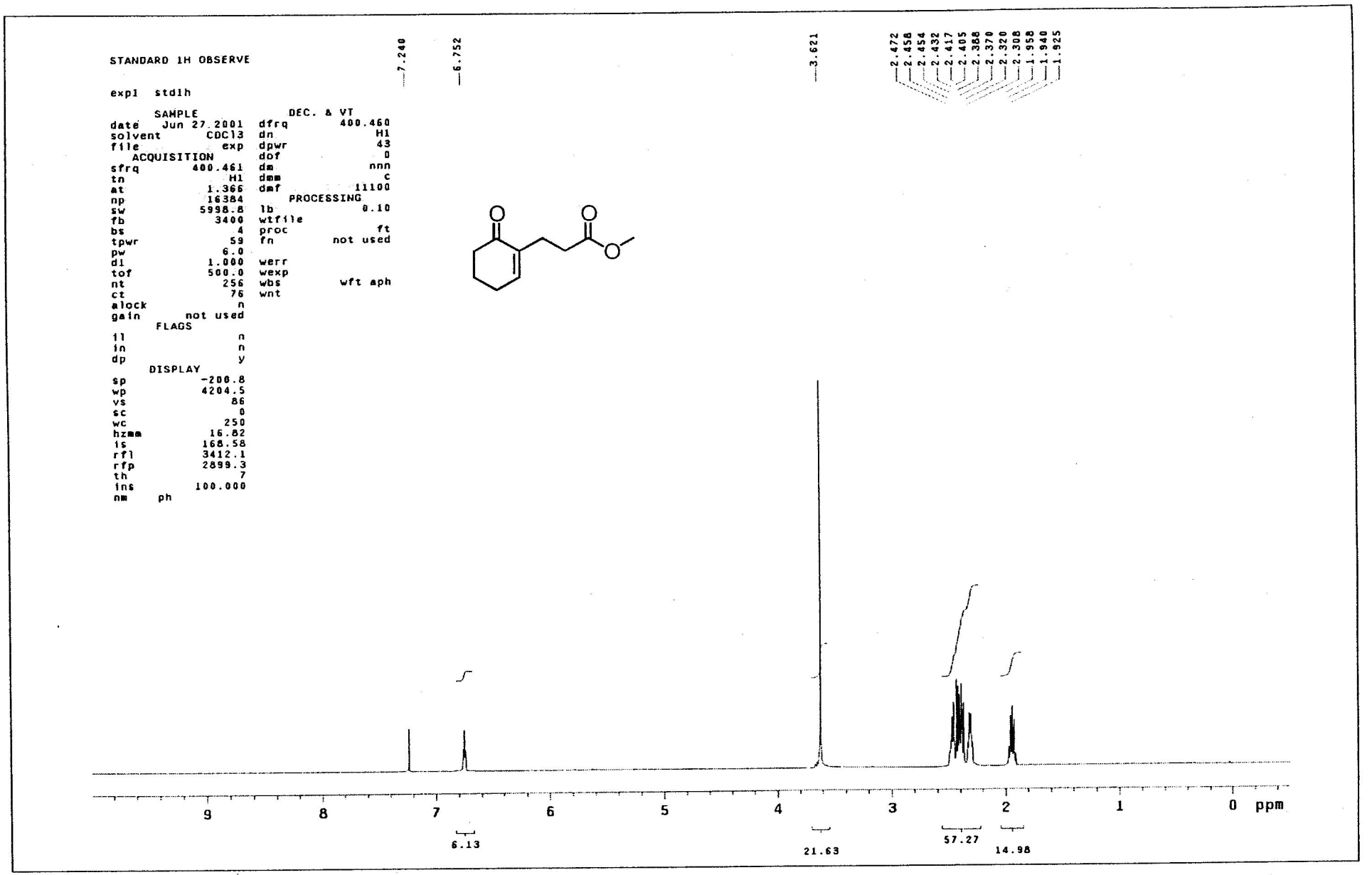

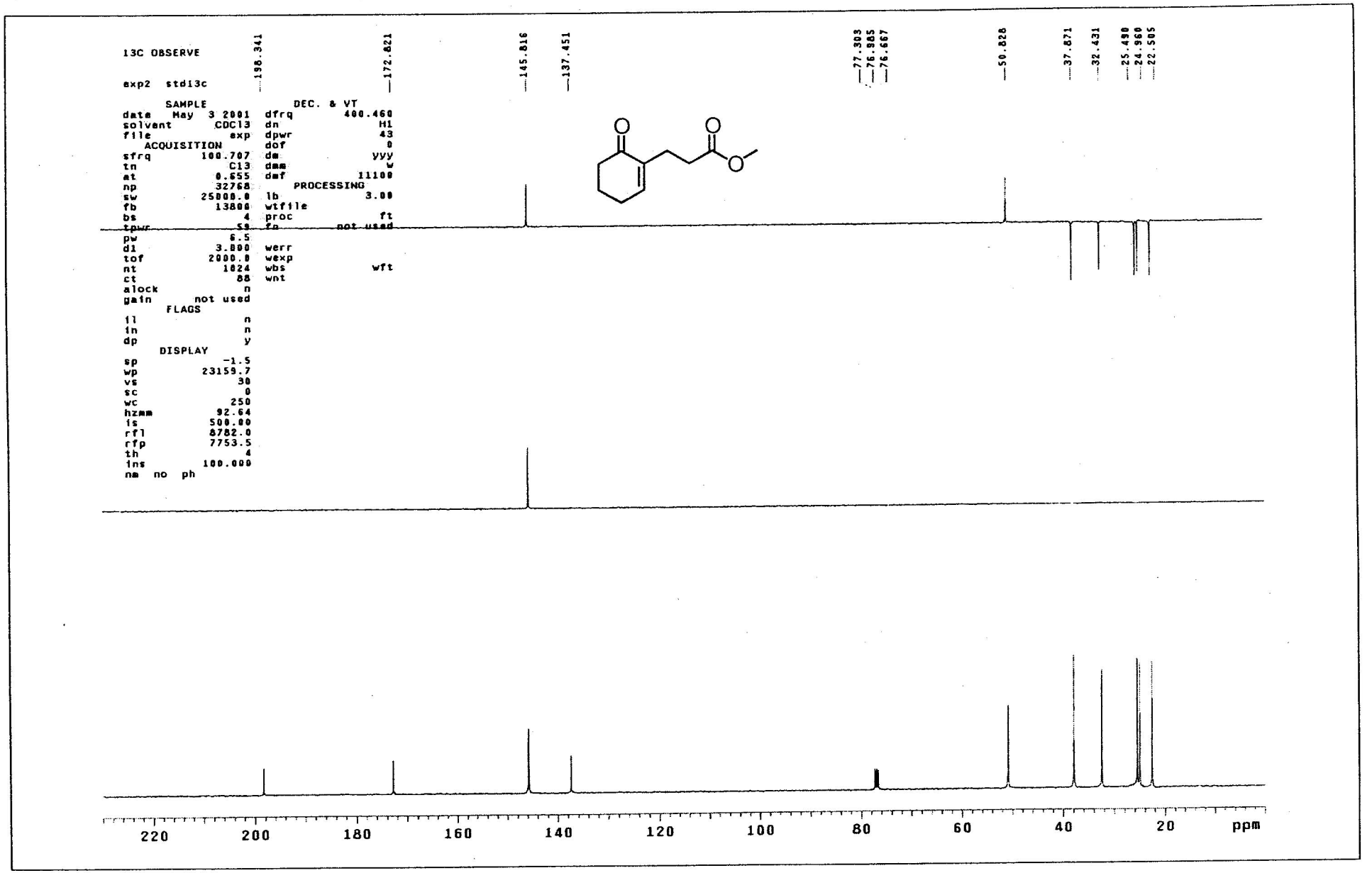

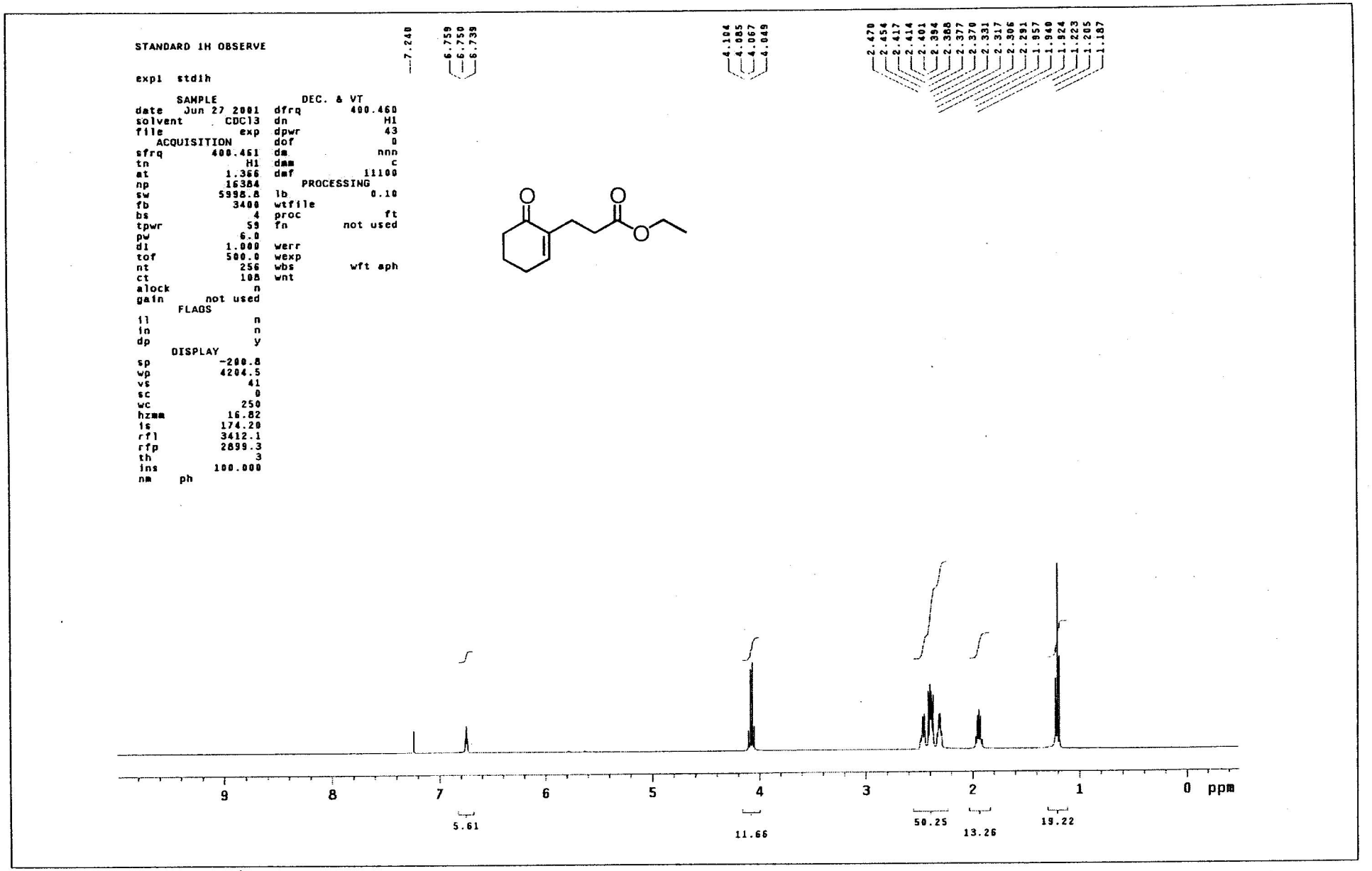

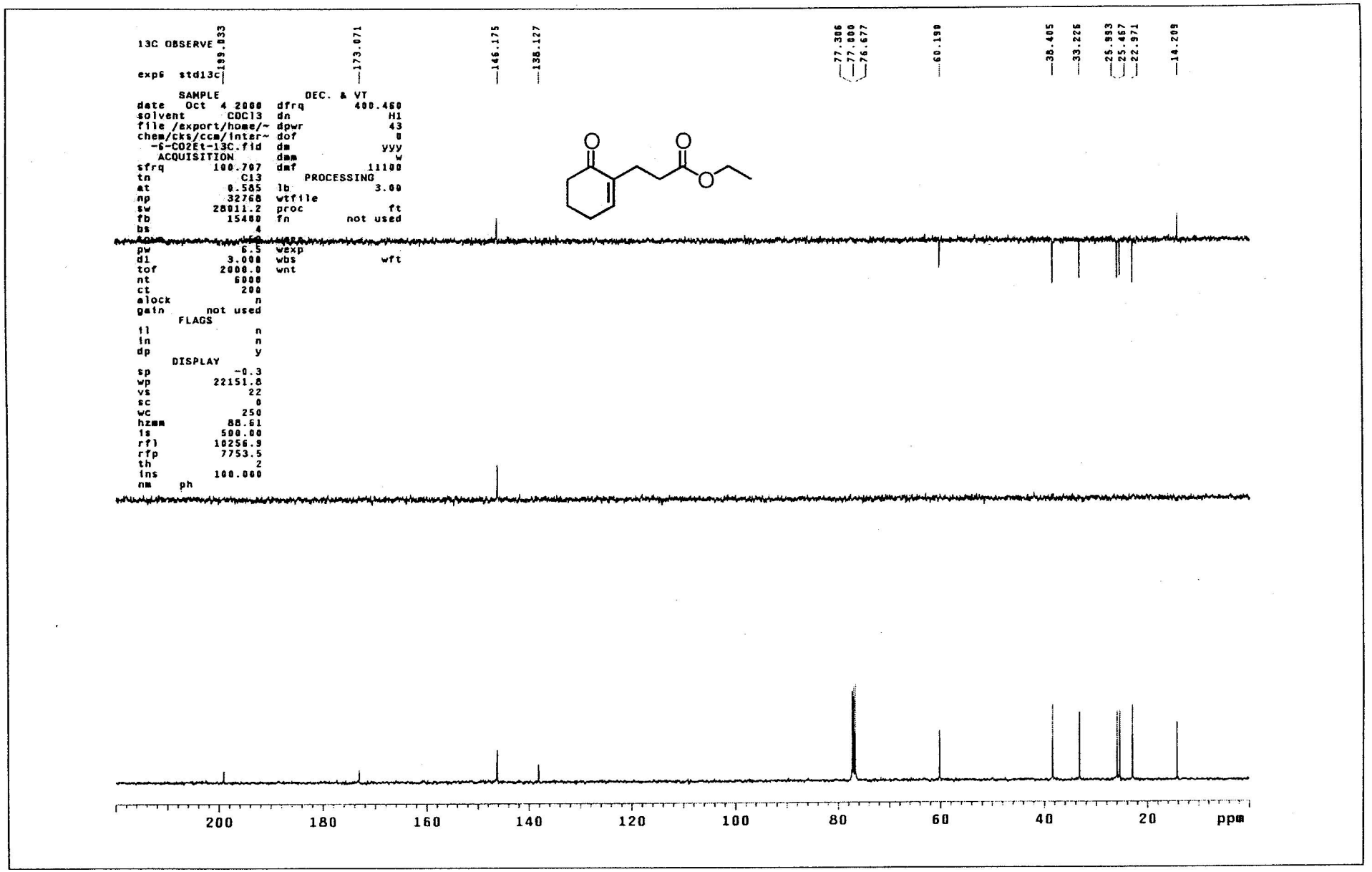

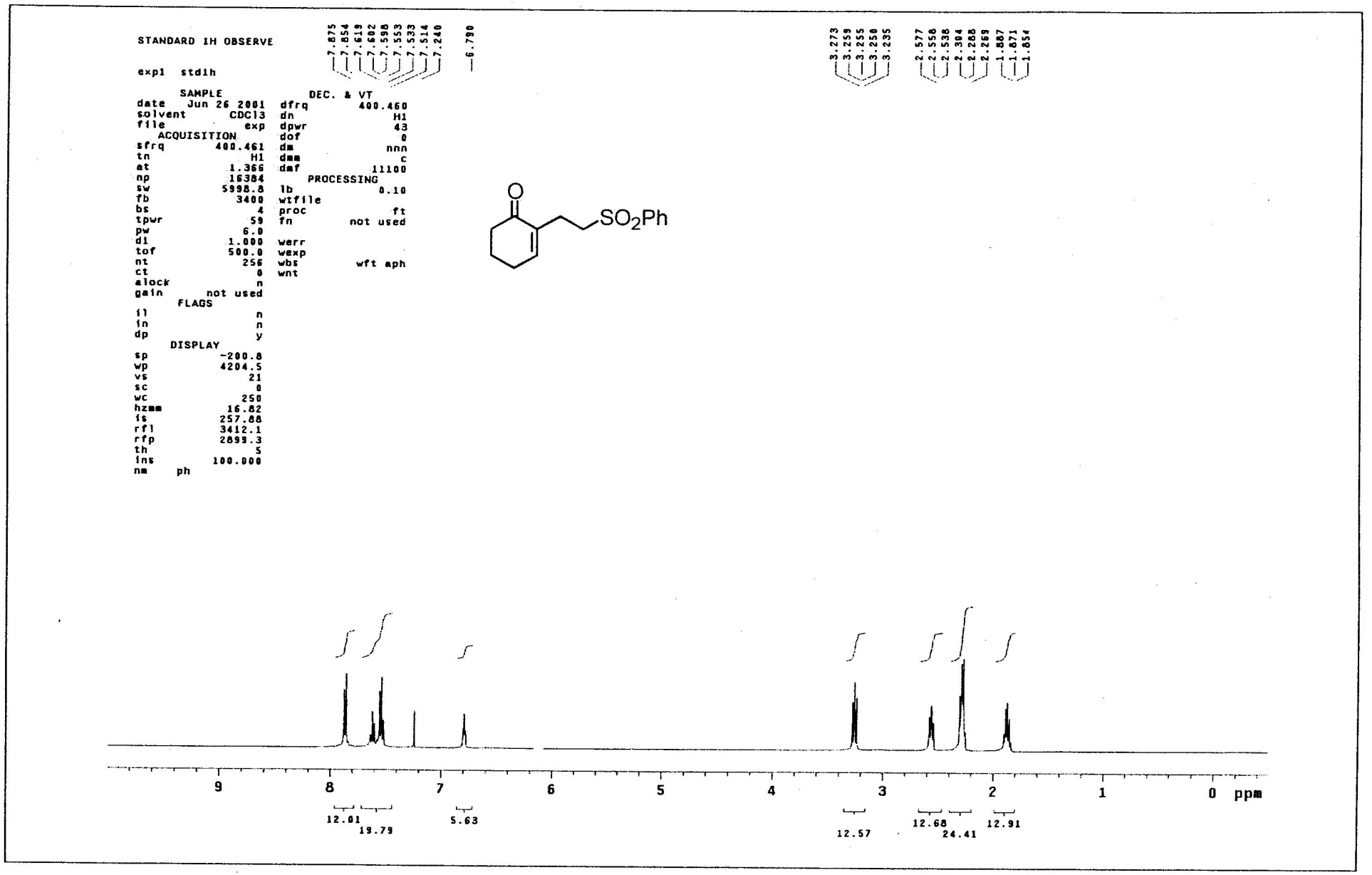

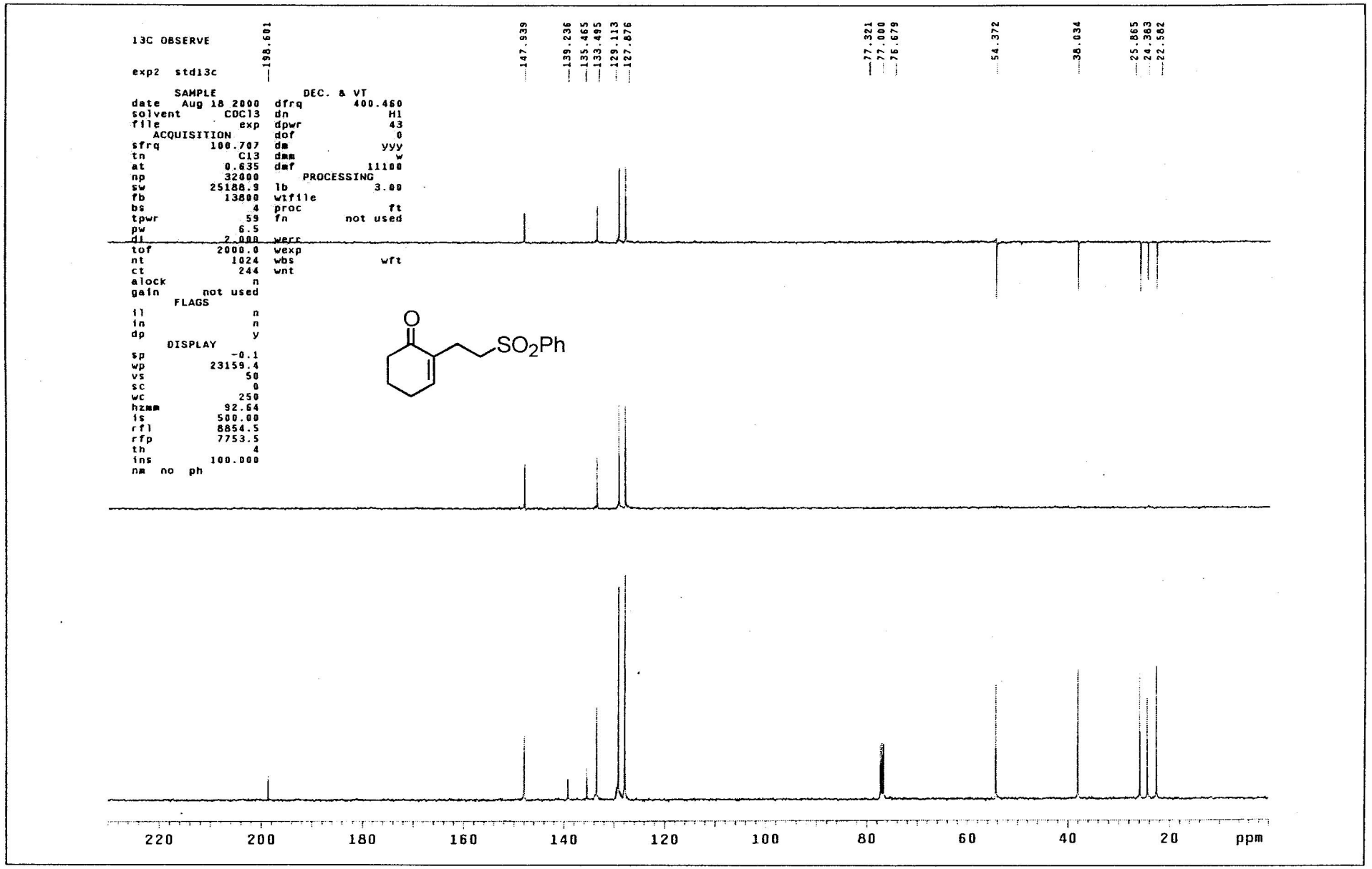

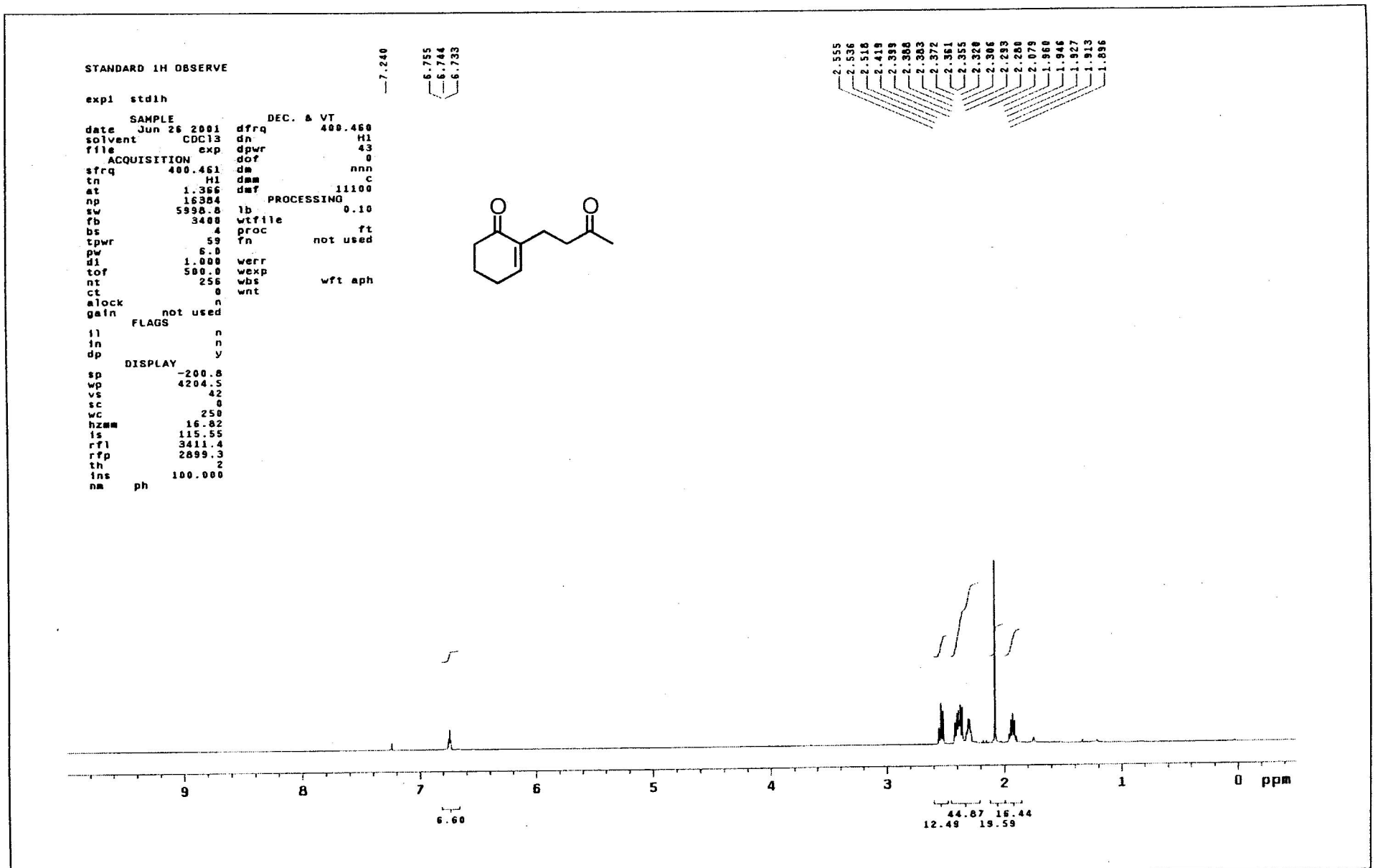

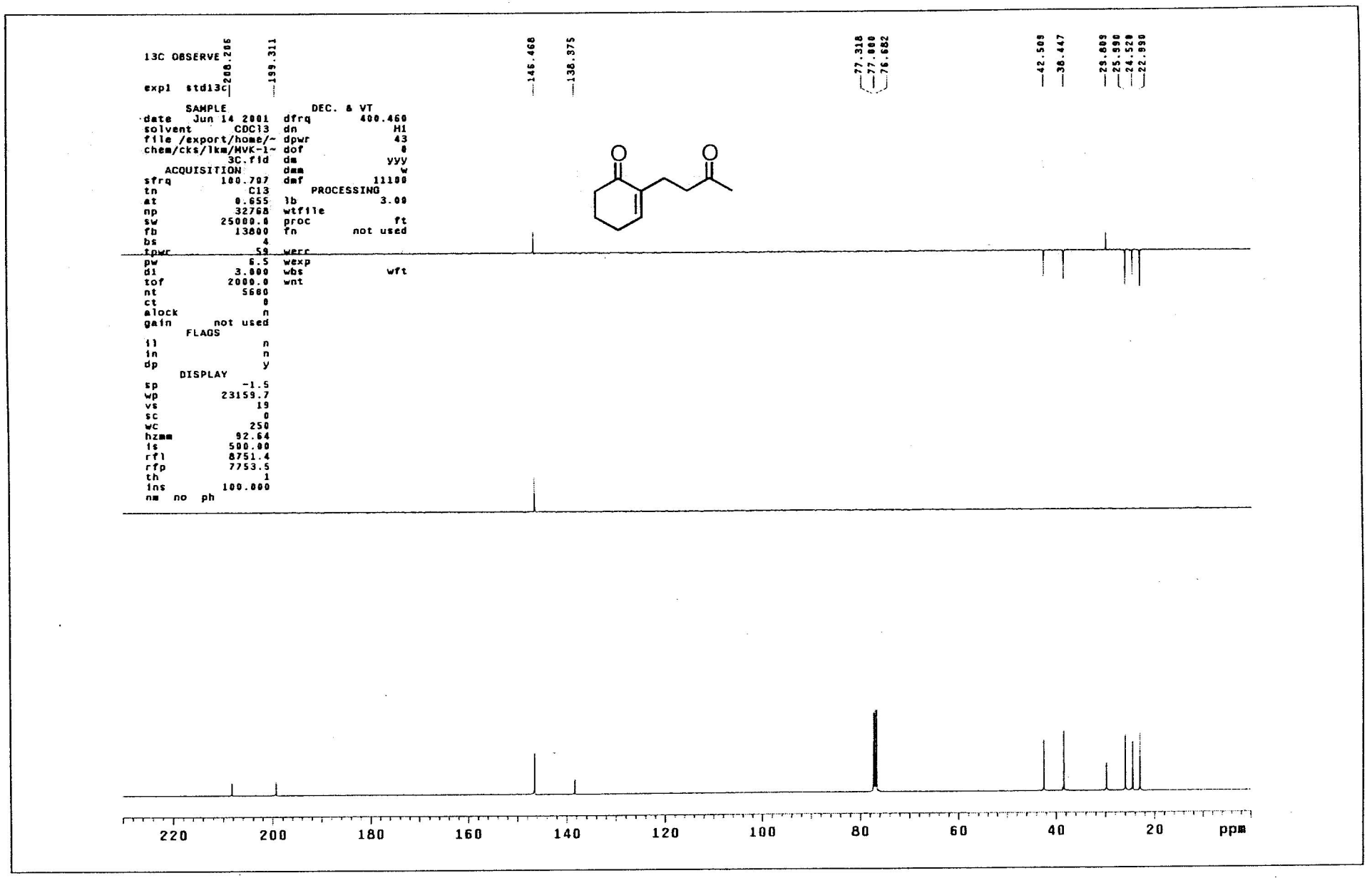

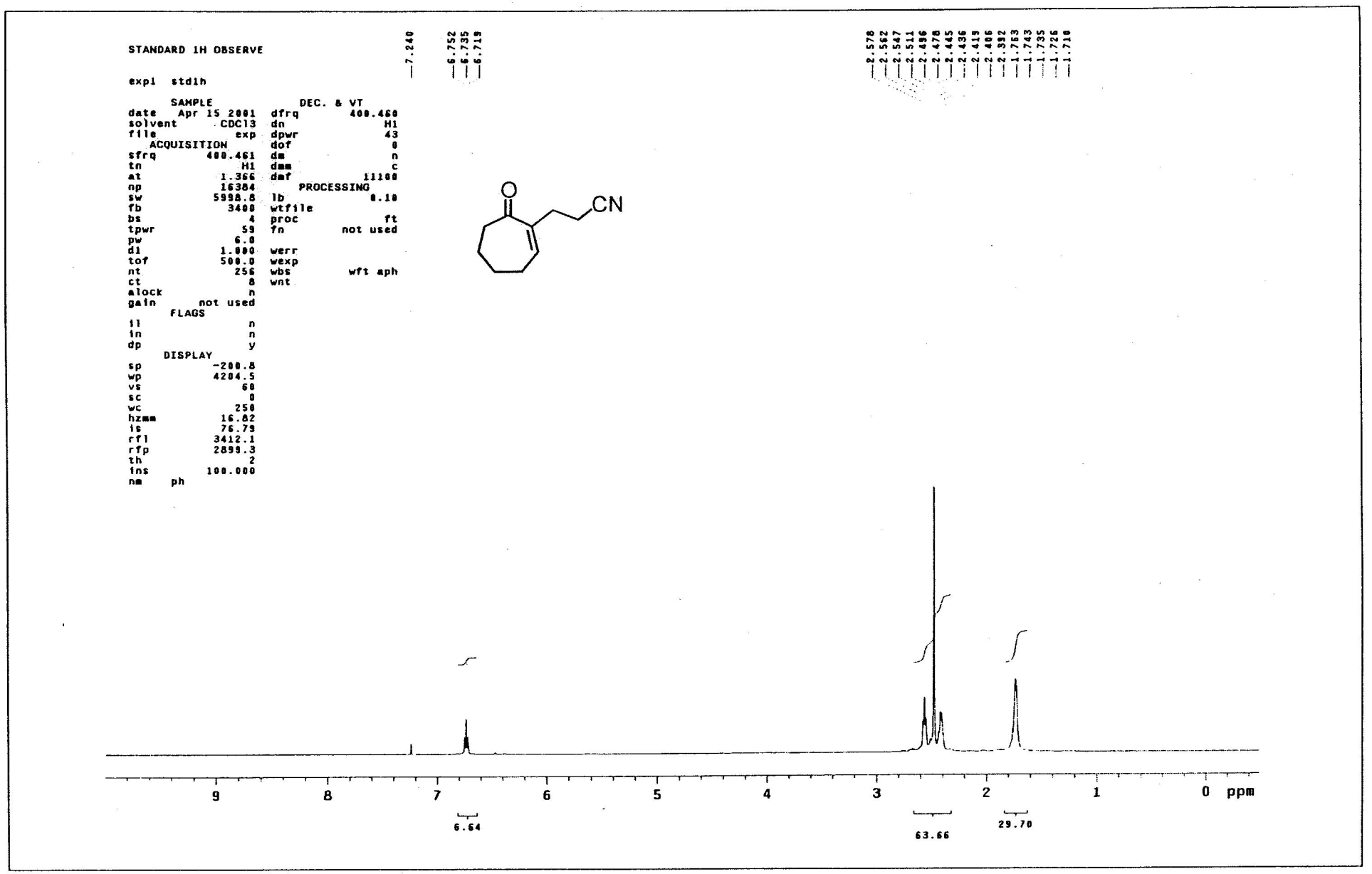

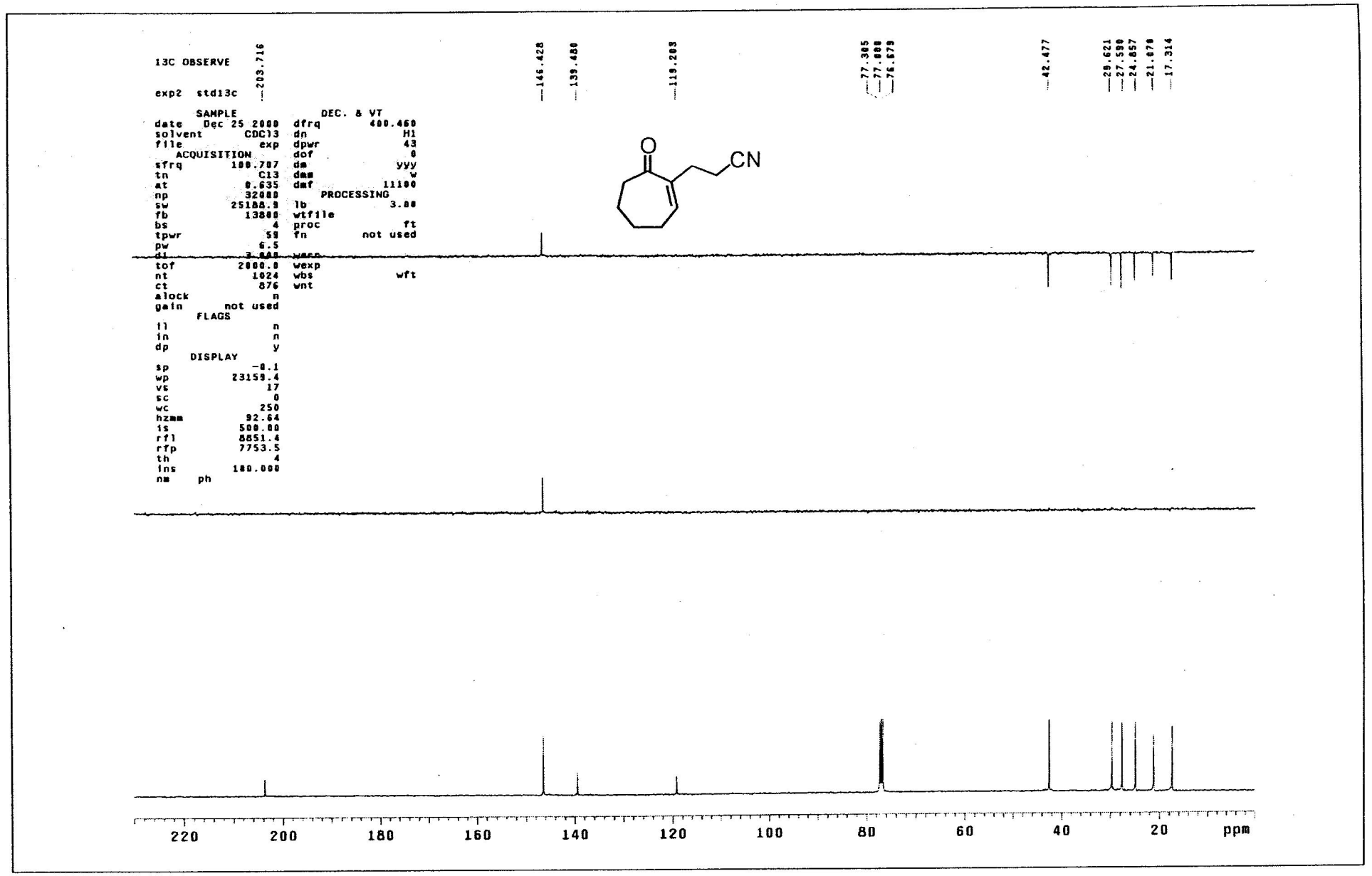

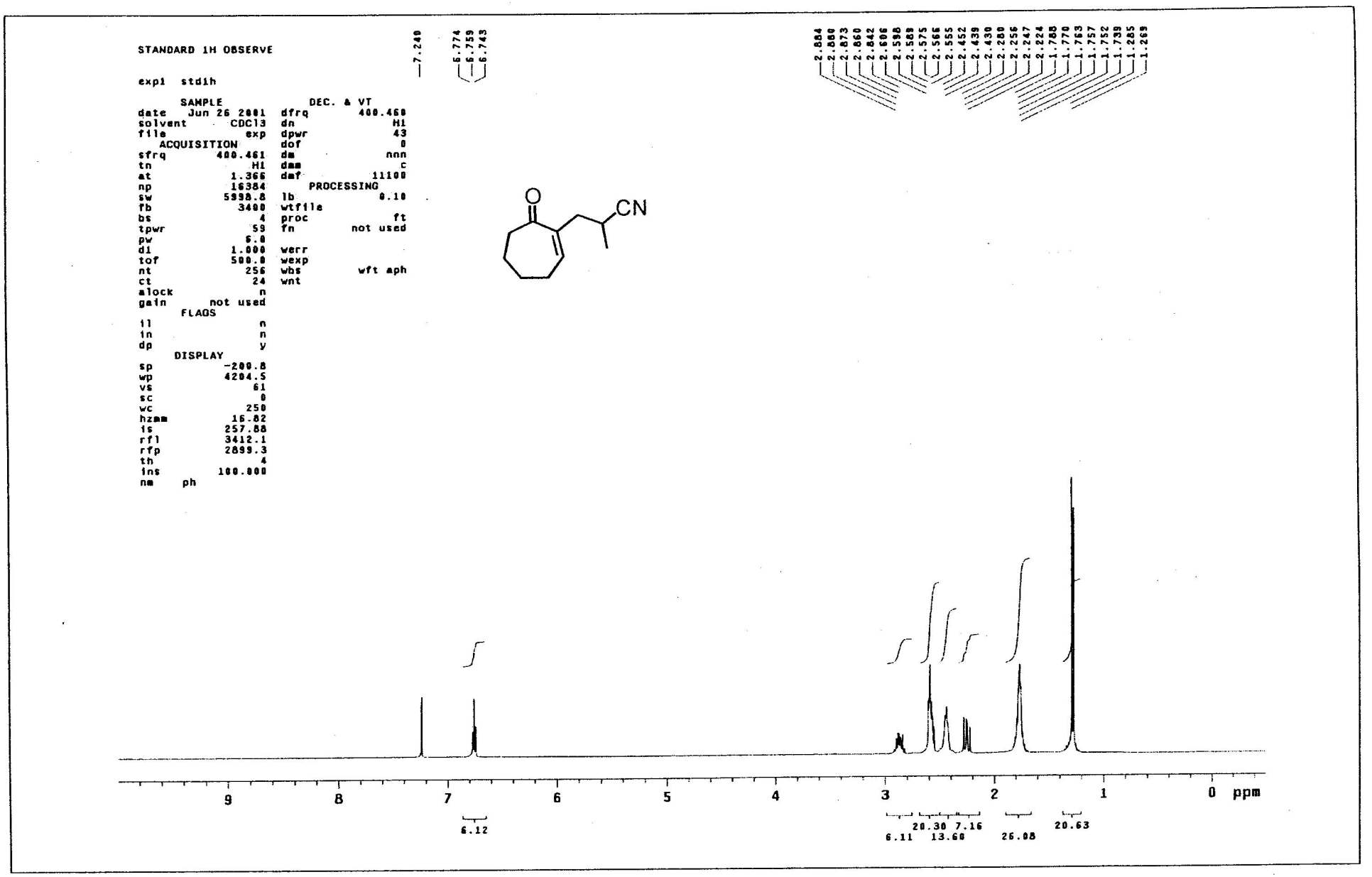

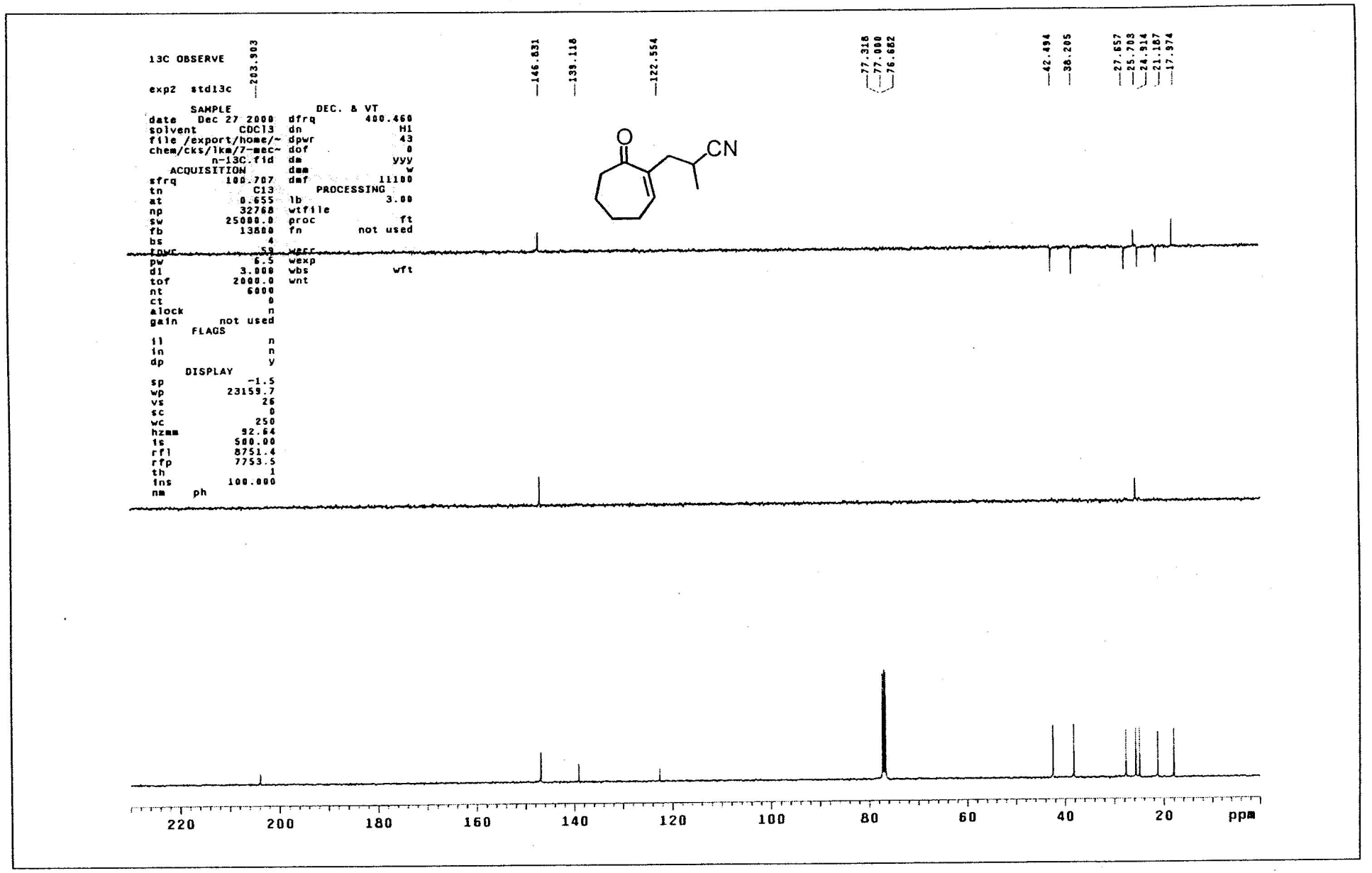

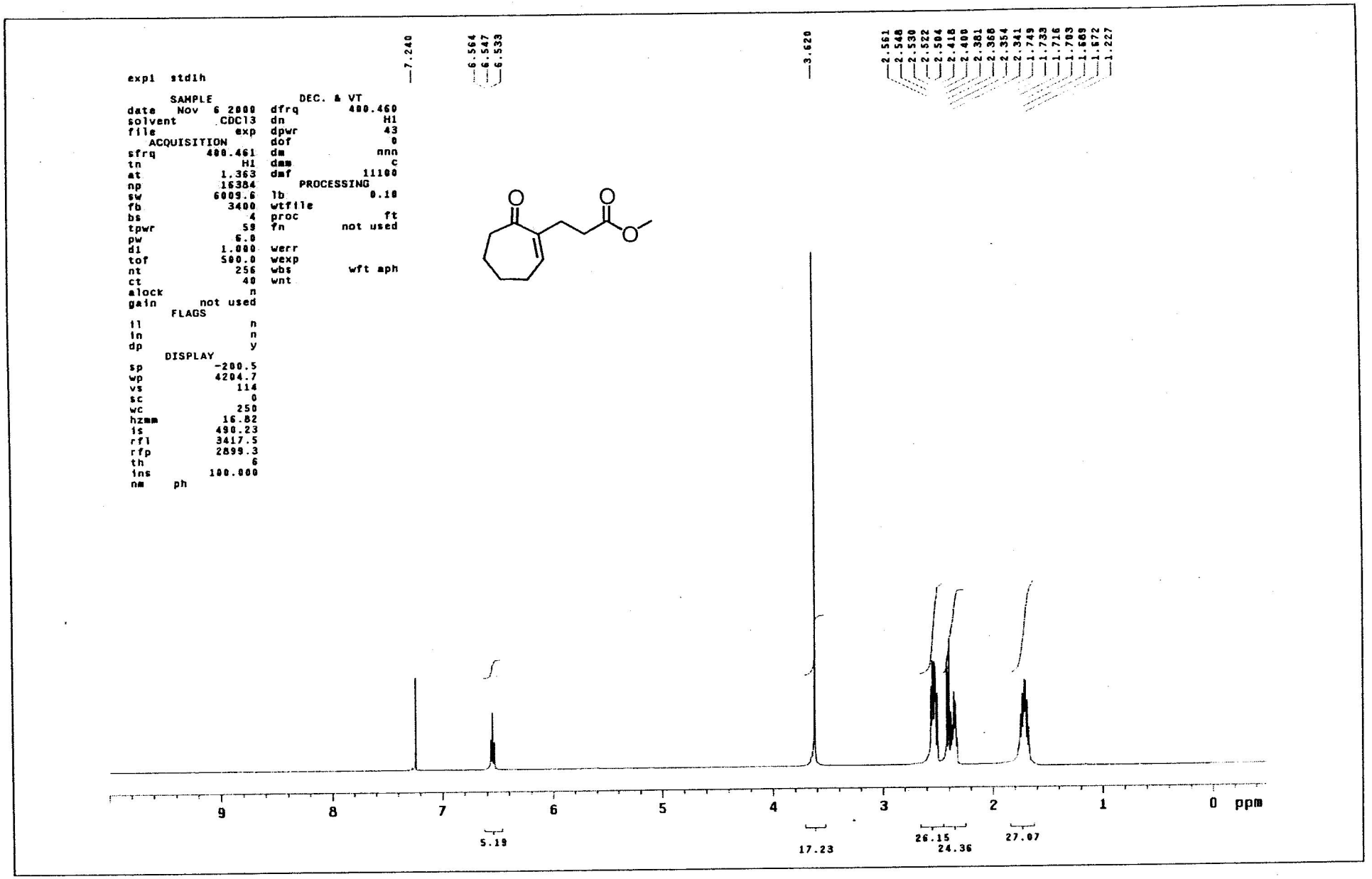

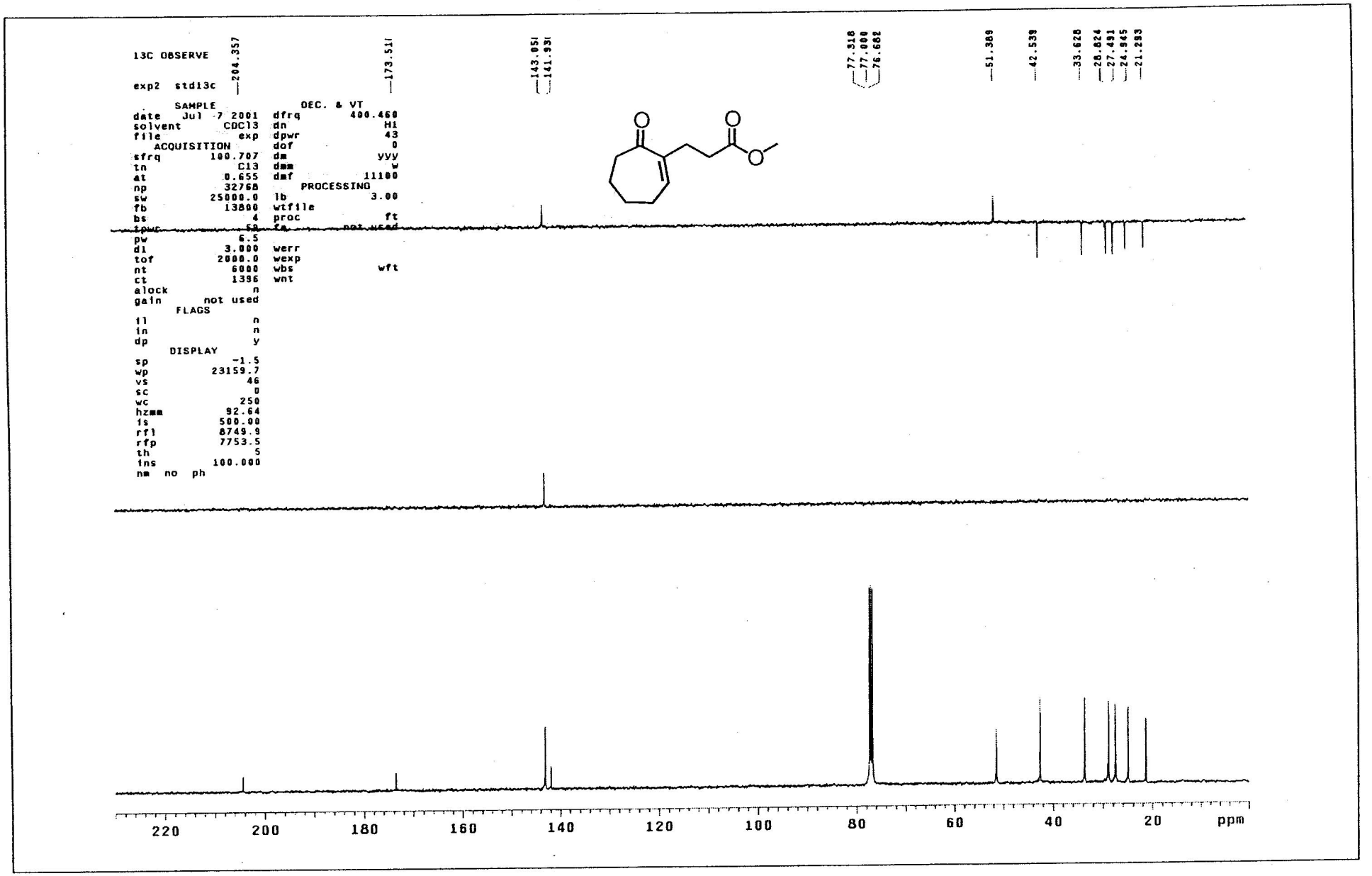

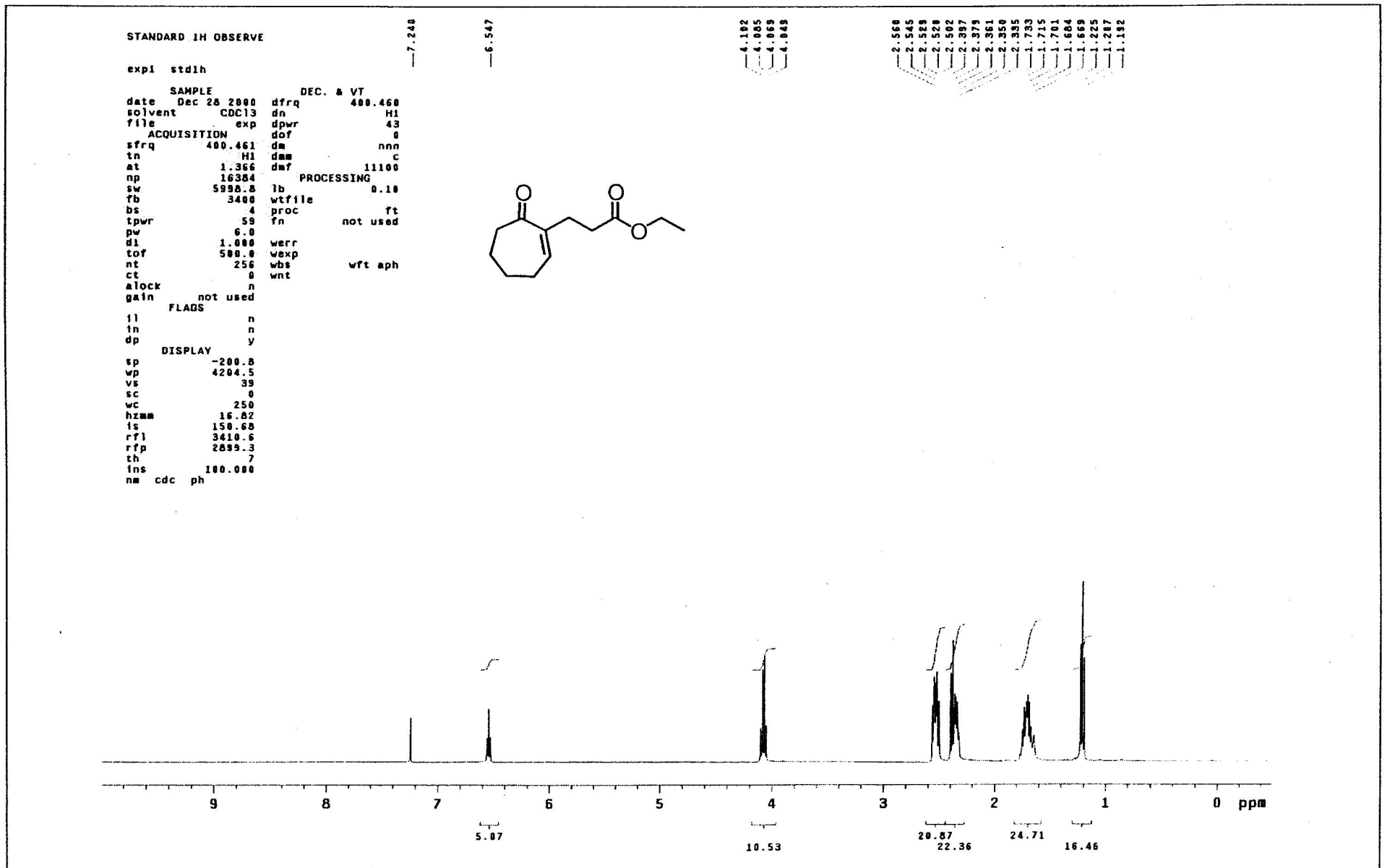

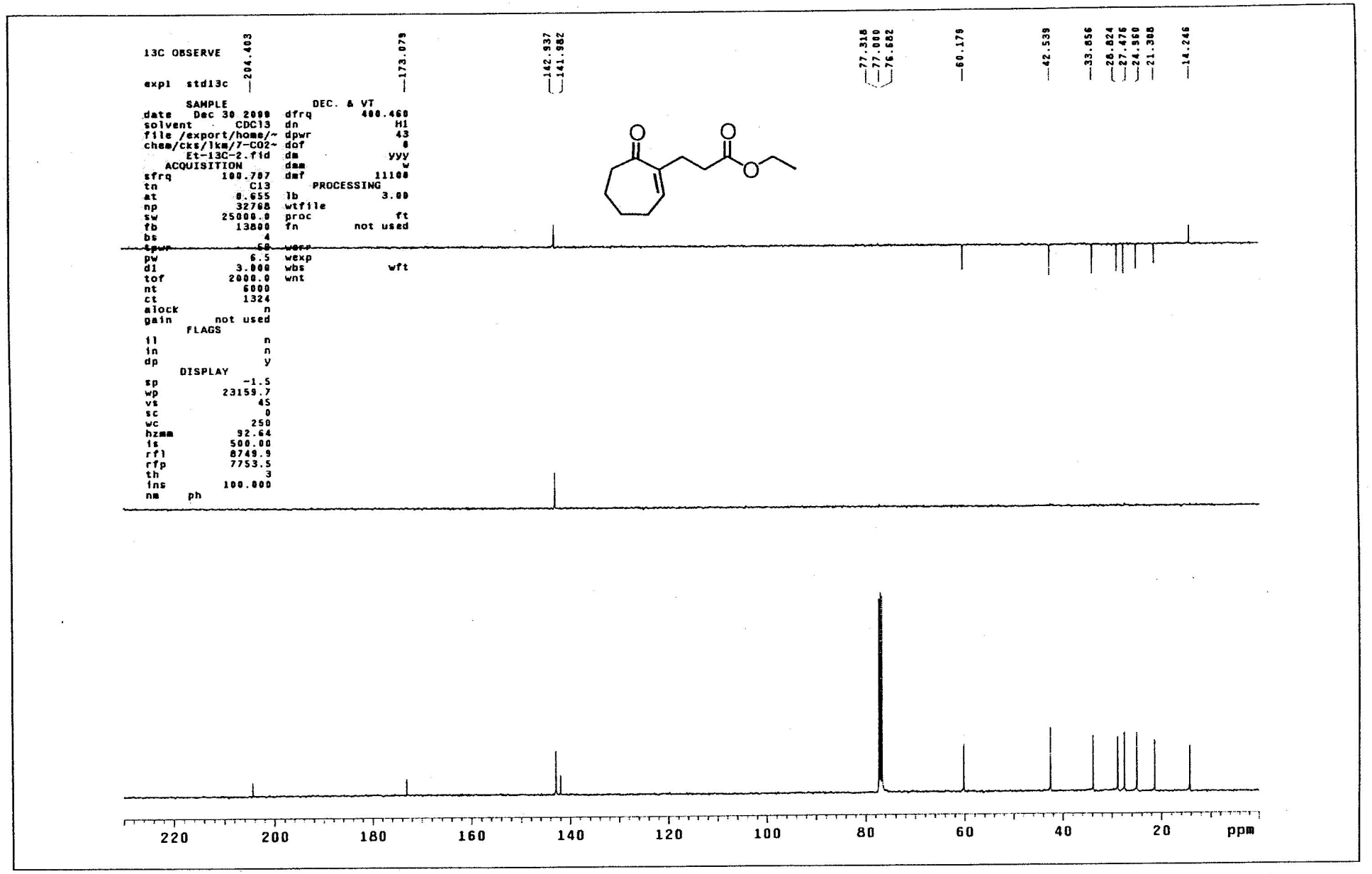

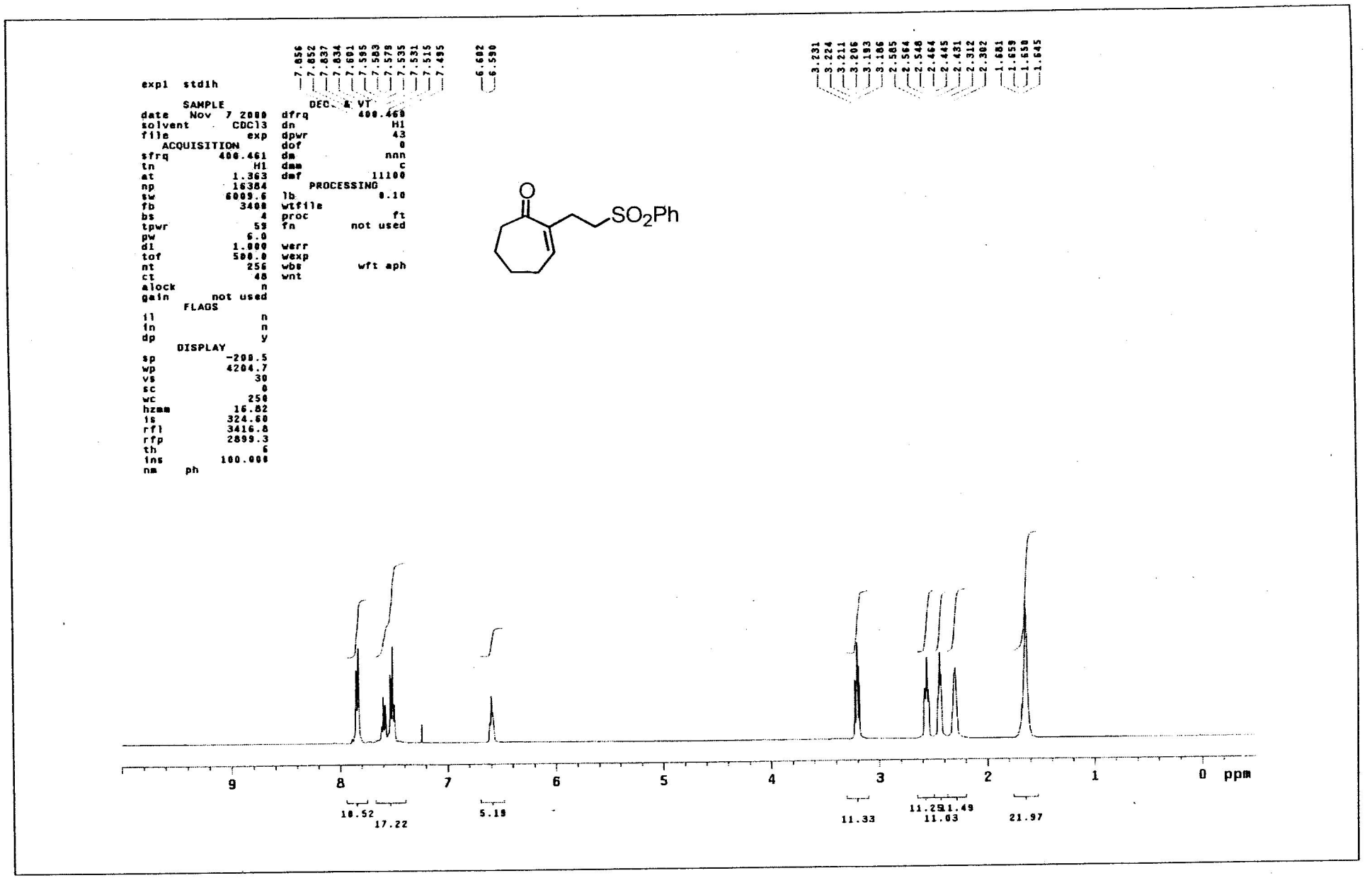

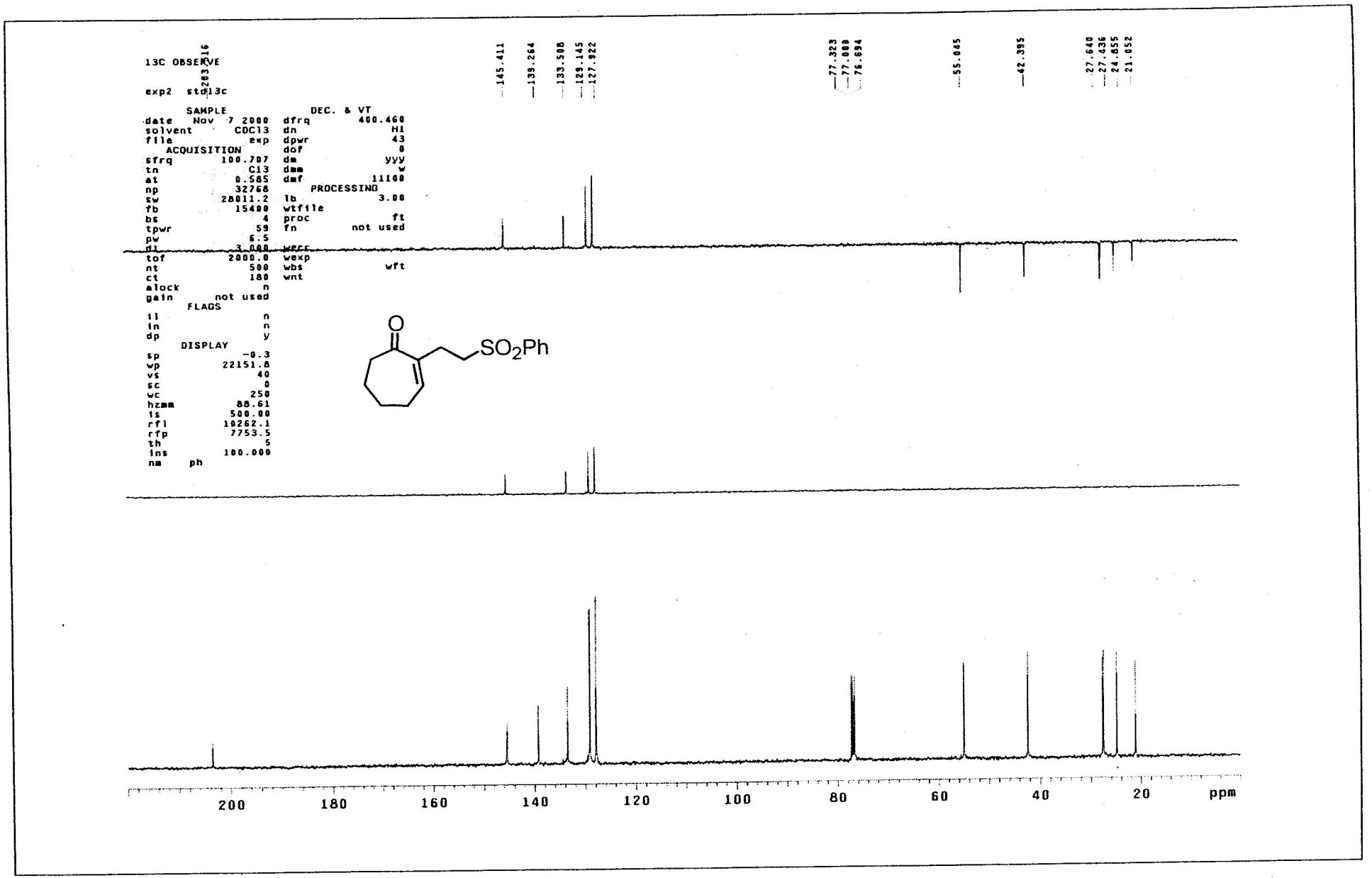

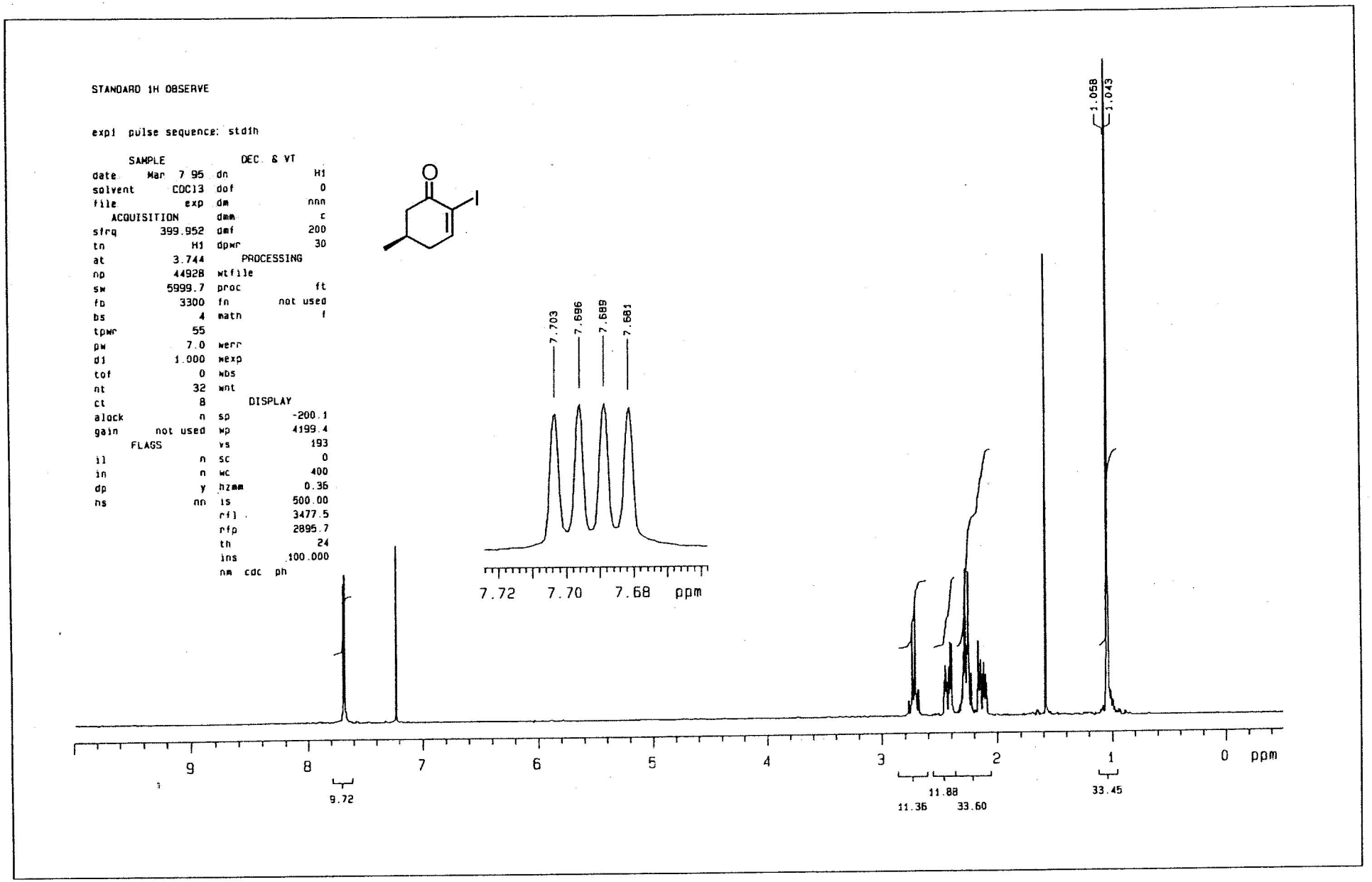

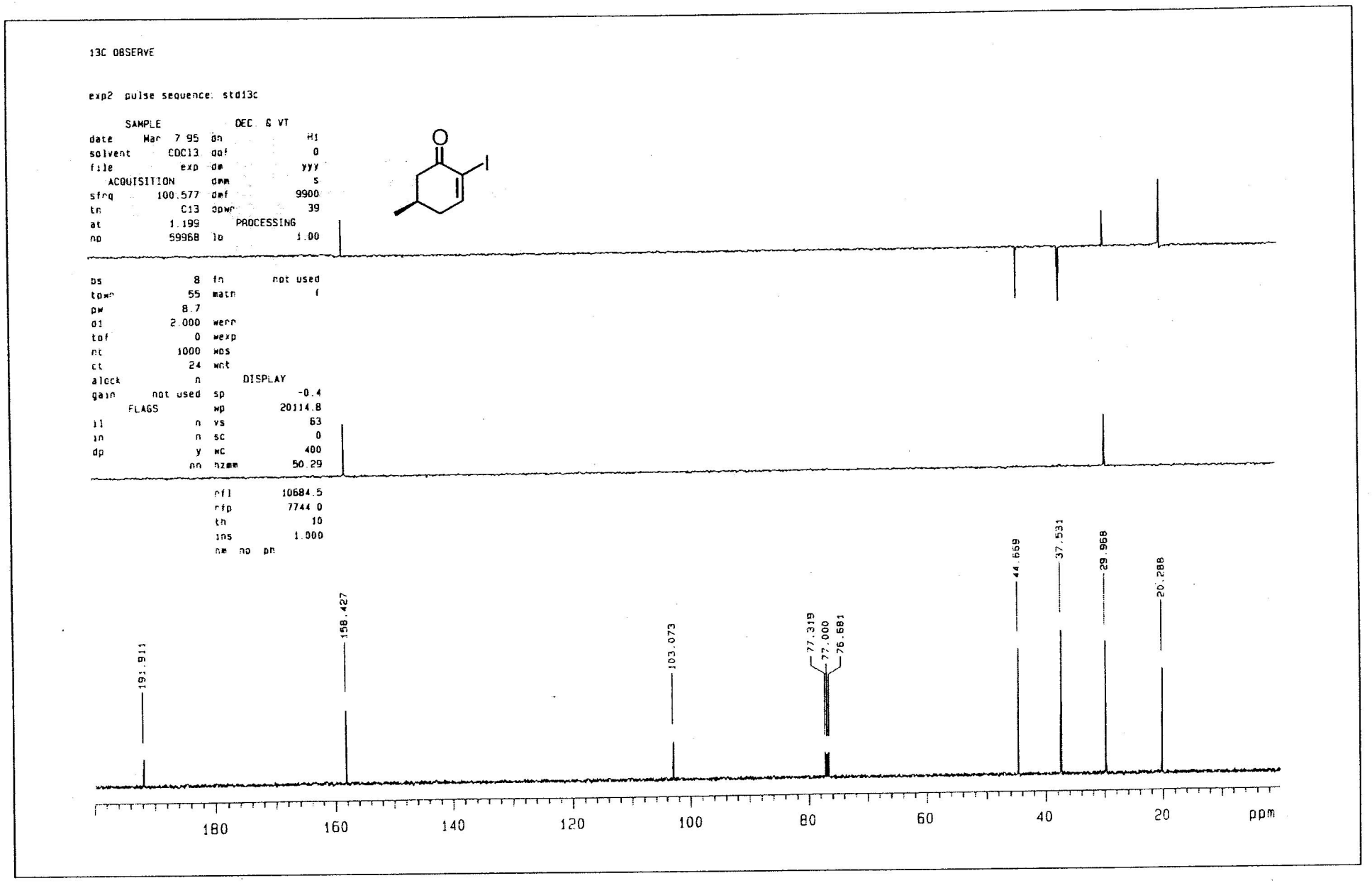
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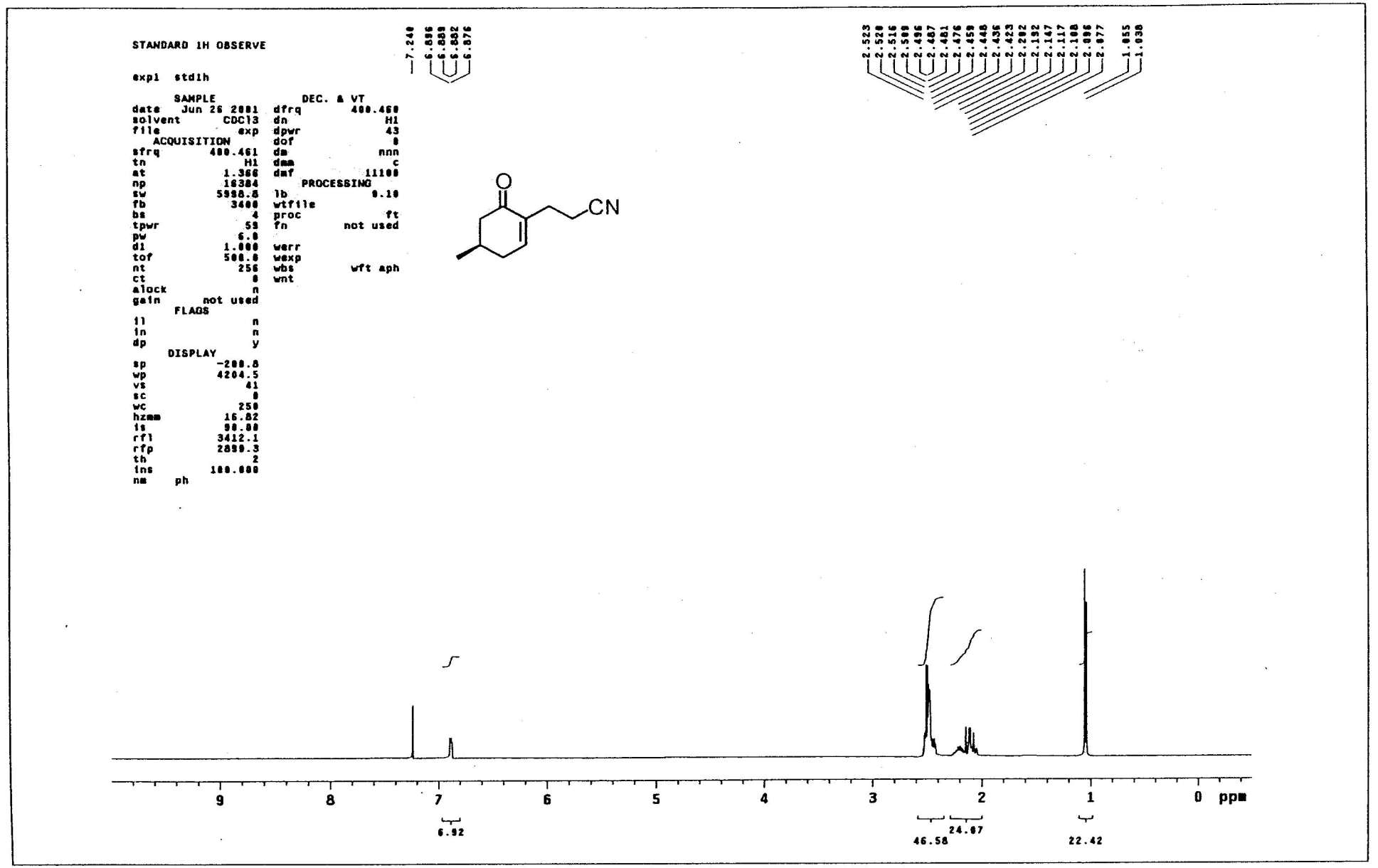
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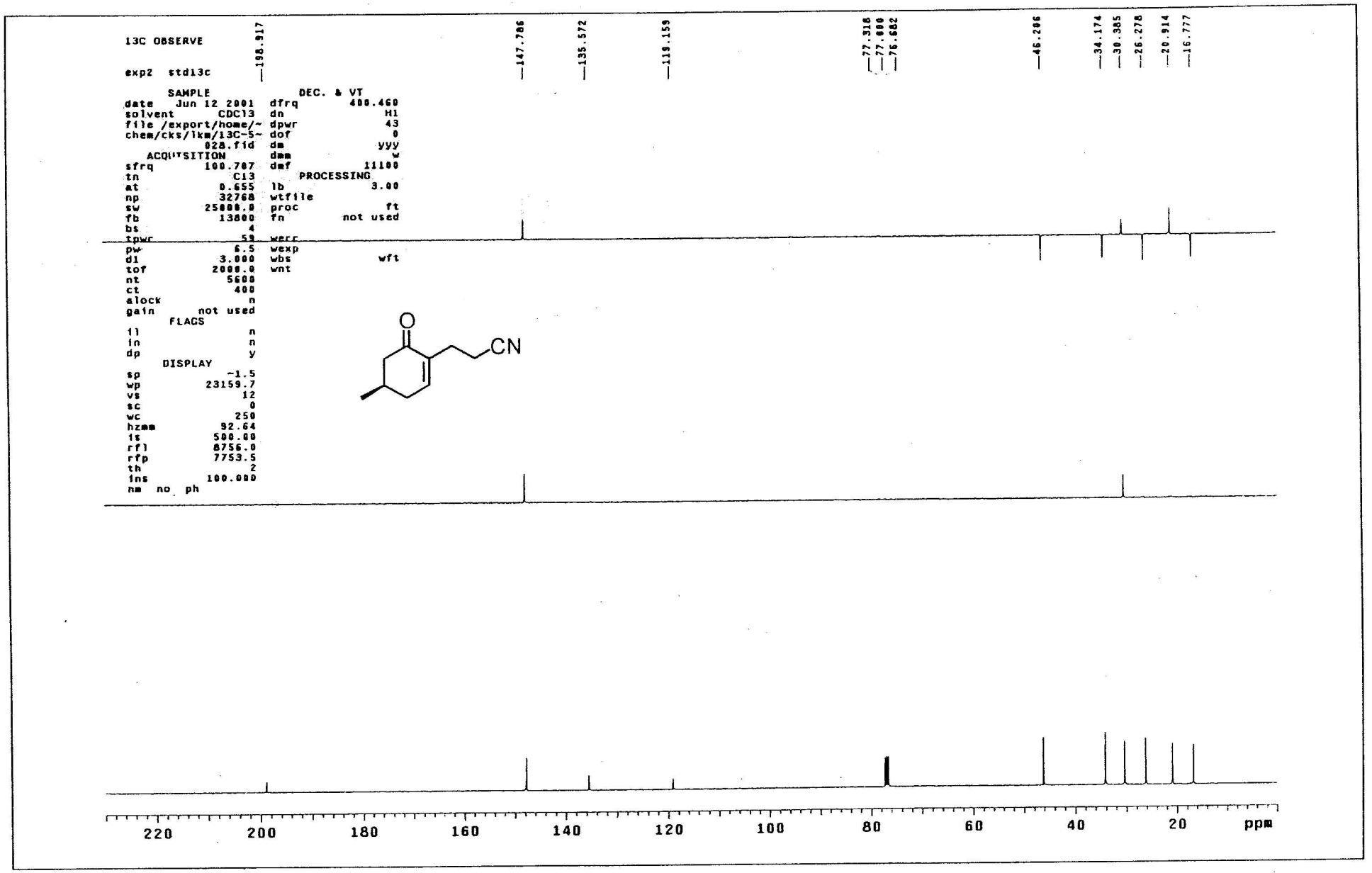

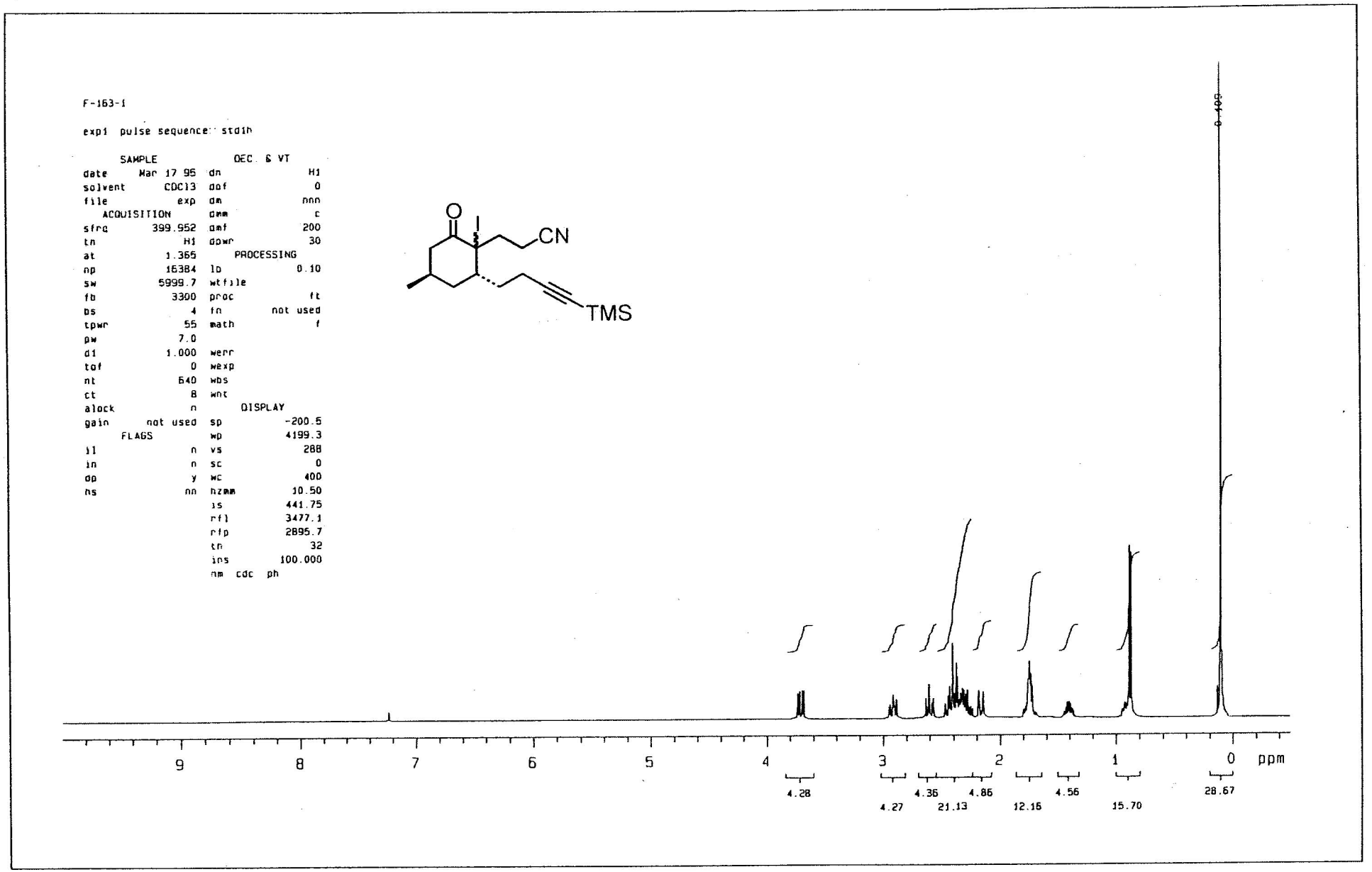

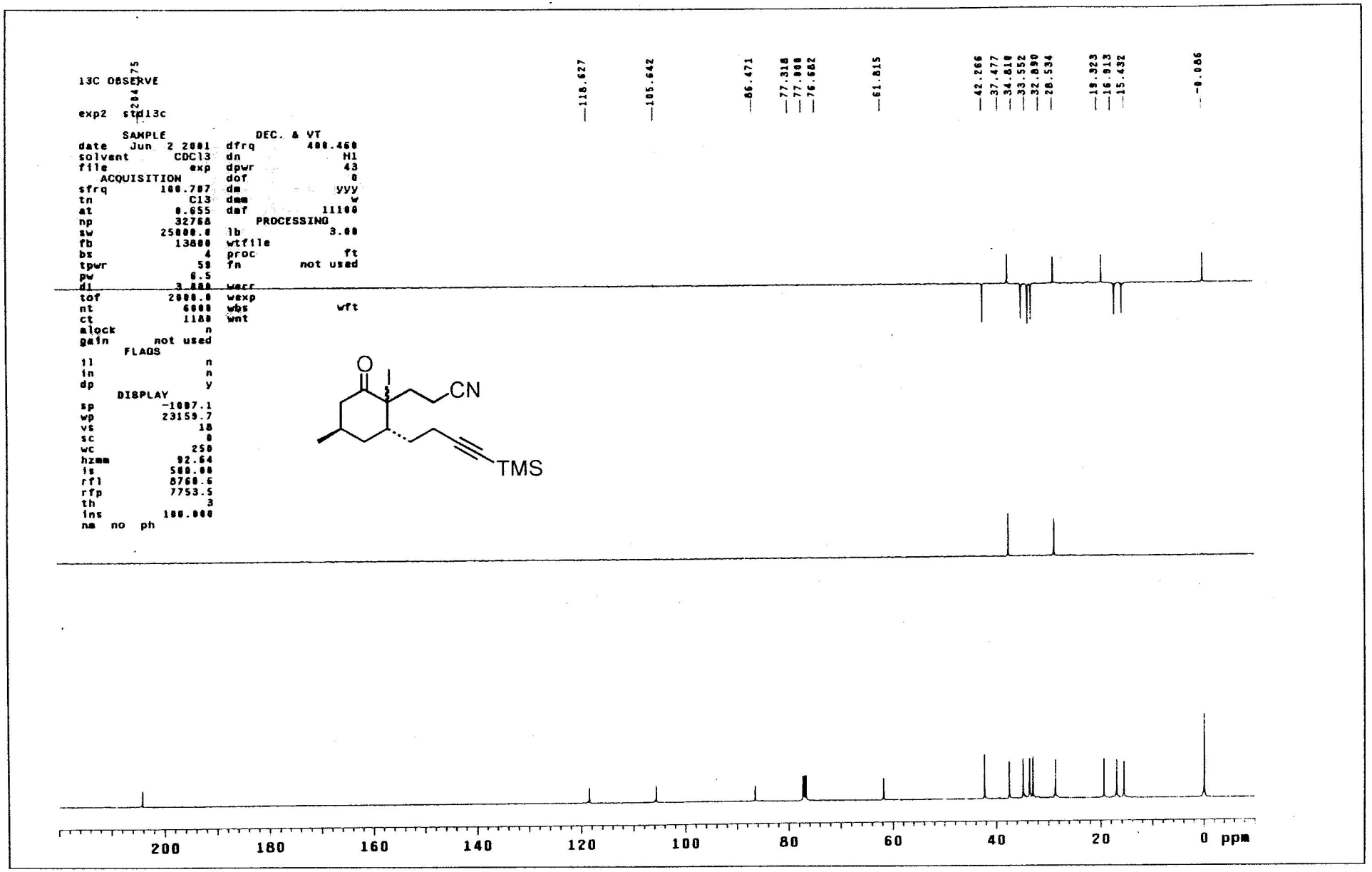

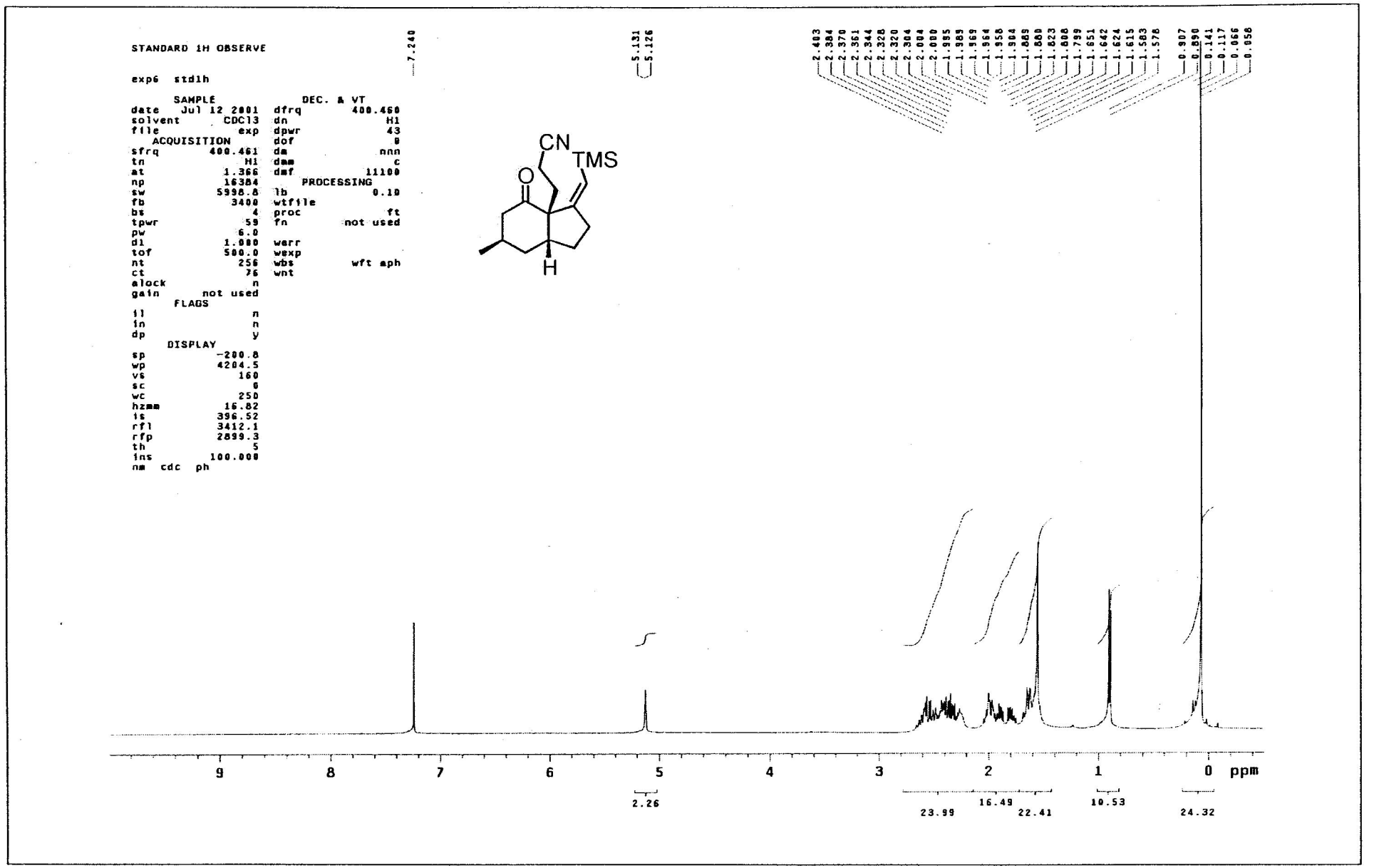

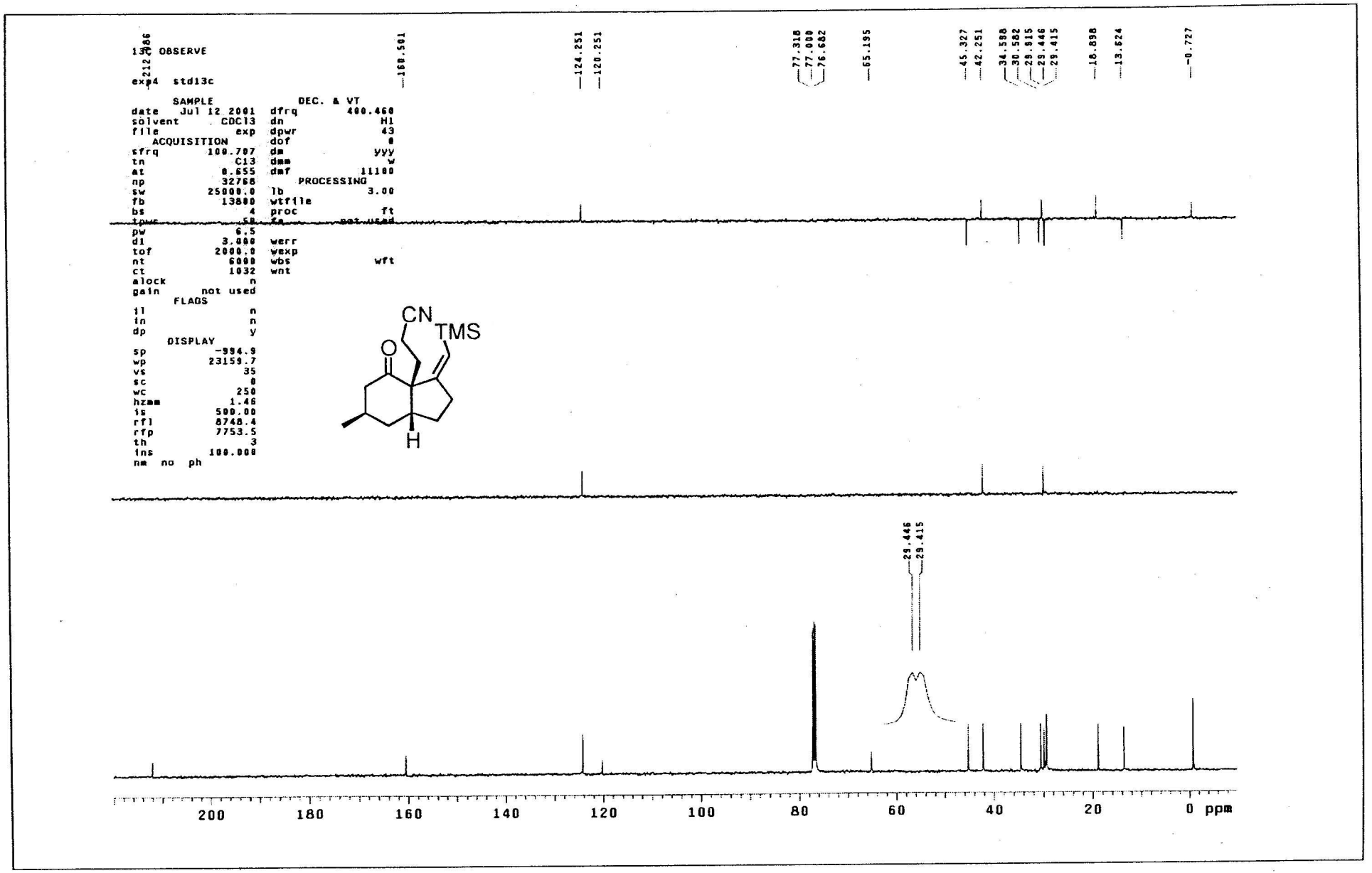
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SAMPLE
date Jul 12 2001
solvent CDCl3
file exp
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tn C13
at 0.655
np 32768
sw 25000.0
fb 13800
bs 4
pw 6.5
d1 3.000
tof 2000.0
nt 6000
ct 1032
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -994.9
wp 23159.7
vs 35
sc 0
wc 250
hzmm 1.46
is 500.00
rfl 8748.4
rfp 7753.5
th 3
ins 100.000
nm no ph
DEC. & VT
dfrq 400.460
dn H1
dpwr 43
dof 0
dm yyy
dmm w
dmf 11100
PROCESSING
lb 3.00
wtfile
proc ft
werr
wexp
wbs wft
wnt
CN
TMS
O
H
212.786
168.501
124.251
120.251
77.318
77.000
76.682
65.195
45.327
42.251
34.588
30.582
29.915
29.446
29.415
18.898
13.624
0.727
200
180
160
140
120
100
80
60
40
20
0 ppm