

Total Synthesis of (\pm)-Paeonilide

Chenyang Wang,^{a,b} Jikai Liu,^a Yanhua Ji,^b Jingfeng Zhao,^b Liang Li,^b and
Hongbin Zhang^{b*}

^aState Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, Yunnan 650204, and ^bKey Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Research School of Pharmacy, Yunnan University, Kunming, Yunnan 650091, P. R. China Fax: 86-871-5035538.

E-mail: zhanghb@ynu.edu.

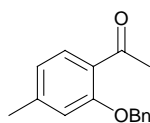
Supporting information

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Section A: General Experimental

General Experimental: Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz. Carbon-13 nuclear magnetic resonance ($^{13}\text{C-NMR}$) was recorded on Bruker Avance 300 spectrometer at 75 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. Low-resolution Mass spectra were recorded on a VG Auto Spec-3000 magnetic sector MS spectrometer. High Resolution Mass spectra were taken on AB QSTAR Pulsar mass spectrometer. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, Fluka and were used without purification, unless otherwise indicated.

Section B: Synthesis of Compounds



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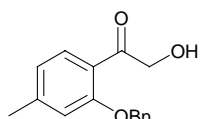
1-(2-Benzyloxy-4-methyl-phenyl)-ethanone

To a solution of 2-hydroxy-4-methylacetophenone (750 mg, 5 mmol) and benzyl chloride (700 mg, 5.5 mmol, 1.1 eq) in acetonitrile (15 ml) was added Potassium iodide (166 mg, 1 mmol) and Potassium carbonate (1.38 g, 10 mmol, 2.0 eq). The resulting mixture was then stirred at 70 °C overnight. After filtration through Celite, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 1:30) to afford the product (1.2g, 95%), after recrystallization from ethyl acetate, as colorless needles.

m.p. : 56-58°C

IR ν_{max} (KBr) cm^{-1} : 1662 ν_s , 1606 s , 1495 s , 1453 m , 1409 m , 1380 m , 1356 m , 1288 s , 1254 s , 1240 s , 1170 s , 1137 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 7.72 (1H, d , $J = 7.8\text{Hz}$), 7.47-7.35 (5H, m), 6.85 (1H, s), 6.82 (1H, d , $J = 7.8\text{Hz}$), 5.15 (2H, s), 2.59

(3H, *s*), 2.38 (3H, *s*). ^{13}C -NMR (75MHz, CDCl_3), $\delta(\text{ppm})$: 199.2 (*s*), 158.4 (*s*), 144.8 (*s*), 136.3 (*s*), 130.7 (*d*), 128.7 (*d*), 128.2 (*d*), 127.7 (*d*), 126.0 (*s*), 121.8 (*d*), 113.5 (*d*), 70.7 (*t*), 32.2 (*q*), 21.9 (*q*). EIMS m/z (%): 240 (M^+ , 15%), 225 (7), 149 (15), 135 (8), 91 (100). HRMS m/z Found: 263.1051, Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Na}$ ($\text{M}+23$) $^+$: 263.1047.



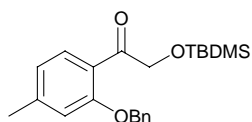
10 1-(2-Benzyloxy-4-methylphenyl)-2-hydroxy-ethanone

To a solution of 2-Benzyloxy-4-methylacetophenone (120 mg, 0.5 mmol) in anhydrous THF (5 ml) was added LDA (1.6M, 0.4 ml, 0.64 mmol, 1.3 eq) at $-78\text{ }^\circ\text{C}$ under nitrogen atmosphere. The resulting mixture was stirred for 30 minutes, and trimethylsilyl chloride (TMSCl, 0.14 ml, 0.75 mmol, 1.5 eq) was then added *via* syringe over 5 minutes. The reaction was stirred for another 30 minutes at $-78\text{ }^\circ\text{C}$, then stirred at room temperature for 2 hours. After removal of the solvent under reduced pressure, the residue was redissolved in dichloromethane (2 ml) and anhydrous NaHCO_3 (168 mg 2 mmol, 4.0 eq) was added at $10\text{ }^\circ\text{C}$. The resulting mixture was treated with pre-dried *m*-chloroperbenzoic acid in dichloromethane (0.1M, 7.5ml, 0.75 mmol, 1.5 eq) for 3 hours at room temperature. Water (5 ml) was added to the reaction mixture and the organic phase was separated. The aqueous phase was extracted with dichloromethane (2X5 ml). The organic phases were combined, washed with aqueous Na_2SO_3 (2X5 ml), saturated aqueous NaHCO_3 (2X5 ml), and dried over anhydrous MgSO_4 . The solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane (5 ml) and treated with 1.5 M aqueous HCl (0.5 ml). After stir at room temperature for 3 hours, the organic phase was separated and the aqueous phase was extracted with dichloromethane (2X5 ml). The combined organic phases were washed with saturated aqueous NaHCO_3 (2X5 ml), brine (3X5 ml) and dried over MgSO_4 . After removal of the solvent, the residue was chromatographed on silica gel (Petroleum ether $60\text{-}90\text{ }^\circ\text{C}$: ethyl acetate = 10:1) to afford the product (83mg, 65%), after recrystallization from ethyl acetate and

petroleum (2:1), as colorless crystals.

m.p. : 90-92 °C

IR ν_{\max} (KBr) cm^{-1} : 3458 s , 2923 m , 1649 vs , 1605 s , 1419 s , 1390 s , 1254 s , 1254 s , 1176 s , 1137 s , 1076 s , 977 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 7.99 (1H, d , $J = 8.1\text{Hz}$), 7.44-7.37 (5H, m), 6.90 (1H, d , $J = 8.1\text{Hz}$), 5.16 (2H, s), 4.69 (2H, d , $J = 4.8\text{Hz}$), 3.76 (1H, t , $J = 4.8\text{Hz}$), 2.41 (3H, s). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 198.9 (s), 156.0 (s), 147.2 (s), 135.9 (s), 131.6 (d), 129.3 (d), 129.0 (d), 128.4 (d), 122.6 (s), 121.2 (d), 113.7 (d), 71.3 (t), 70.5 (q), 22.5 (q). EIMS m/z (%): 256 (M^+ , 6%), 225 (27), 149 (55), 91 (99), 57 (100). HRMS m/z Found: 279.0999, Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{Na}$ ($\text{M}+23$) $^+$: 279.0997.

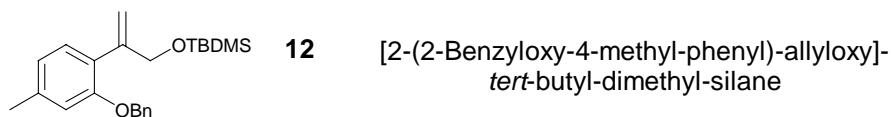


11 1-(2-Benzyloxy-4-methyl-phenyl)-2-(*tert*-butyl-dimethyl-silyloxy)-ethanone

To a solution of α -hydroxyketone (256 mg, 1 mmol) in DMF (5 ml) was added imidazole (136mg, 2mmol, 2.0 eq) and *tert*-butyldimethylsilyl chloride (TBDMSCl, 225 mg, 1.5 mmol, 1.5 eq). The resulting mixture was stirred for 3 hours at room temperature. The solvent was removed under high vacuum to afford the crude product. After chromatography on silica gel (Petroleum ether 60-90 °C) the product (370 mg, 100%) was obtained as colorless oil.

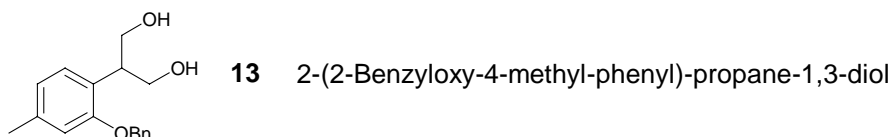
IR ν_{\max} (KBr) cm^{-1} : 2928 s , 2855 s , 1662 vs , 1683 s , 1607 s , 1457 s , 1286 s , 1254 s , 1137 s , 982 s , 839 s , 770 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 7.84 (1H, d , $J = 8.4\text{Hz}$), 7.41-7.37 (5H, m), 6.84 (1H, s), 6.82 (1H, d , $J = 8.4\text{Hz}$), 5.07 (2H, s), 4.78 (2H, s), 2.36 (3H, s), 0.85 (9H, s), 0.0 (6H, s). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 198.0 (s), 158.4 (s), 145.1 (s), 135.8 (s), 130.9 (d), 128.8 (d), 128.5 (d), 128.1 (d), 123.0 (s), 122.1 (d), 113.0 (d), 71.3 (t), 70.8 (t), 25.9 (q), 21.9 (q), 18.5 (s), -5.5 (q). EIMS m/z (%): 313 (45), 295 (7), 267 (15), 225 (30), 193 (10), 91(100). ESIA m/z

371 (M+1)⁺ HRMS *m/z* Found: 393.1867, Calcd. for C₂₂H₃₀O₃NaSi (M+23)⁺: 393.1861.



To a solution of Ph₃PMeI (336mg, 1.2 mmol, 1.2 eq) in anhydrous THF (8 ml) was added *n*-BuLi (1.6M, 0.8 ml, 1.28 mmol, 1.28 eq) at nitrogen atmosphere at room temperature. The resulting mixture was then stirred under nitrogen for 1 hour at room temperature. A solution of ether (370 mg, 1 mmol) in anhydrous THF (2 ml) was added followed by stirring at room temperature for 5 hours. The solvent was removed and the crude products were chromatographed on silica gel (Petroleum ether 60-90 °C) to provide the product (350 mg, 95%) as colorless oil.

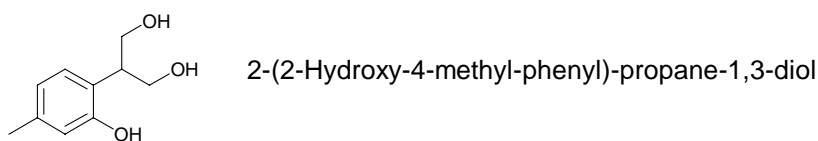
IR ν_{\max} (KBr) cm⁻¹: 2954_s, 2928_s, 2856_s, 1610_{vs}, 1504_s, 1470_s, 1255_s, 1069_s, 837_s, 777_s. ¹H-NMR (300MHz, CDCl₃), δ (ppm): 7.44-7.33 (5H, *m*), 7.13 (1H, *d*, *J* = 8.1Hz), 6.80 (1H, *d*, *J* = 8.1Hz), 6.78 (1H, *s*), 5.48 (1H, *d*, *J* = 2.1Hz), 5.18 (1H, *d*, *J* = 2.1Hz), 5.05 (2H, *s*), 4.48 (2H, *m*), 2.36 (3H, *s*), 0.91 (9H, *s*), 0.02 (6H, *s*). ¹³C-NMR (75MHz, CDCl₃), δ (ppm): 156.0 (*s*), 147.8 (*s*), 138.9 (*s*), 137.2 (*s*), 130.5 (*d*), 128.6 (*d*), 127.9 (*d*), 127.6 (*d*), 127.4 (*s*), 121.7 (*d*), 113.2 (*d*), 112.3 (*t*), 70.5 (*t*), 65.2 (*t*), 26.1 (*q*), 21.6 (*q*), 18.5 (*s*), -5.3 (*q*). EIMS *m/z* (%): 311 (20), 293 (62), 291 (43), 219 (16), 195 (13), 175 (12), 145 (10), 129 (10), 91 (100). HRMS *m/z* Found: 391.2062, Calcd. for C₂₃H₃₂O₂NaSi (M+23)⁺: 391.2069.



To a solution of olefin (368 mg, 1 mmol) in anhydrous THF (5 ml) was added BH₃-Me₂S (1M in DCM, 0.5 ml, 0.5 mmol, 0.5 eq) under nitrogen. The reaction

mixture was then stirred at room temperature overnight. Aqueous sodium hydroxide solution (1M, 2ml, 2 mmol, 2.0 eq) was added followed by 30% H₂O₂ (1 ml, 8.8 mmol, 8.8 eq). After stirring for 1 hour at room temperature, the reaction mixture was extracted with ethyl acetate (3X10 ml). The organic phases were combined, washed with aqueous Na₂SO₃ (3X10 ml), brine (3X10 ml) and dried over MgSO₄. The solvent was removed under reduced pressure, and the oily residue was dissolved in THF (5 ml). To this solution was added *n*-Bu₄NF (1.0M in THF, 2 ml, 2.0 mmol, 2.0 eq). The mixture was stirred at room temperature for 1 hour. After removal of the solvent, the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 5:1) to afford the product (245 mg, 90%) as a colorless oil.

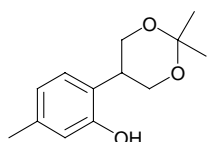
IR ν_{\max} (KBr) cm^{-1} : 3383_s, 2925_s, 2880_s, 1612_s, 1578_m, 1506_s, 1454_s, 1415_s, 1259_s, 1028_s, 812_s, 736_s, 697_s. ¹H-NMR (300MHz, CDCl₃), δ (ppm): 7.33-7.19 (5H, *m*), 6.95 (1H, *d*, *J* = 7.8Hz), 6.67 (1H, *s*), 6.64 (1H, *d*, *J* = 7.8Hz), 4.90 (2H, *s*), 3.86-3.74 (4H, *m*), 3.69 (1H, *brs*), 3.46 (1H, *m*), 2.22 (3H, *s*). ¹³C-NMR (75MHz, CDCl₃), δ (ppm): 156.2 (*s*), 137.5 (*s*), 137.0 (*s*), 128.4 (*d*), 128.1 (*d*), 127.7 (*d*), 127.1 (*d*), 125.1 (*s*), 121.4 (*d*), 112.8 (*d*), 70.0 (*t*), 64.5 (*t*), 42.4 (*d*), 21.3 (*q*). EIMS *m/z* (%) : 272 (M⁺, 25), 254 (10), 164 (25), 151 (16), 133 (55), 121 (18), 105 (17), 91 (100). HRMS *m/z* Found: 295.1314, Calcd. for C₁₇H₂₀O₃Na (M+23)⁺: 295.1310.



To a solution of benzyl ether (2.72 g, 10 mmol) in absolute ethanol (100 ml) was added palladium on carbon (5% Pd/C, 136 mg). The resulting mixture was degassed and purged with hydrogen (3 times). The reaction was then stirred at room temperature under hydrogen (H₂) overnight. After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel

(ethyl acetate) to afford the product (1.82g, 100%) as colorless syrup.

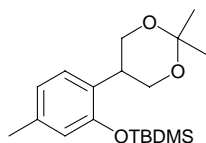
IR ν_{\max} (KBr) cm^{-1} : 3329 s , 2954 s , 2918 s , 1617 s , 1585 m , 1526 m , 1425 s , 1293 s , 1215 s , 1190 s , 1089 s , 1059 s , 955 s , 810 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 6.88 (1H, d , $J = 7.8\text{Hz}$), 6.64 (1H, s), 6.61 (1H, d , $J = 7.8\text{Hz}$), 3.92 (4H, m), 3.07 (1H, m), 2.22 (3H, s). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 155.2 (s), 138.8 (s), 130.3 (d), 123.7 (s), 121.4 (d), 118.0 (d), 63.6 (t), 46.9 (d), 21.3 (q). EIMS m/z (%): 182 (M^+ , 48), 164 (43), 151 (43), 133 (100), 121 (18), 105 (69), 91 (18), 77 (18). HRMS m/z Found: 205.0840, Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}_3\text{Na}$ ($\text{M}+23$) $^+$: 205.0840.



14 2-(2,2-Dimethyl-[1,3]dioxan-5-yl)-5-methyl-phenol

To a solution of triol (1.82 g, 10 mmol) in dichloromethane (20 ml) was added 2,2-dimethoxypropane (DMP, 2.5 ml, 20 mmol, 2.0eq). The resulting mixture was stirred at 40 °C under nitrogen overnight. After removal of the solvent, the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 10:1) to afford the product (2.1 g, 94.5%) as colorless oil.

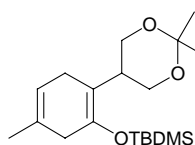
IR ν_{\max} (KBr) cm^{-1} : 3278 s , 2998 w , 1615 s , 1582 m , 1518 m , 1458 w , 1423 s , 1374 s , 1261 s , 1198 s , 1125 s , 1054 s , 959 s , 809 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 7.21 (1H, s), 6.95 (1H, d , $J = 7.8\text{Hz}$), 6.68 (1H, s), 6.66 (1H, d , $J = 7.8\text{Hz}$), 4.12 (2H, dd , $J = 5.1, 12\text{Hz}$), 4.02 (2H, dd , $J = 6.9, 12\text{Hz}$), 3.24 (1H, m), 2.28 (3H, s), 1.56 (3H, s), 1.51 (3H, s). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 154.5 (s), 138.6 (s), 129.9 (d), 122.9 (s), 121.2 (d), 117.5 (d), 99.4 (s), 63.5 (t), 38.3 (d), 24.8 (q), 23.1 (q), 21.0 (q). EIMS m/z (%): 222 (M^+ , 7), 207 (5), 164 (43), 147 (17), 133 (100), 119 (10), 105 (24), 91 (18). HRMS m/z Found: 245.1155, Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{Na}$ ($\text{M}+23$) $^+$: 245.1153.



15b *tert*-Butyl-[2-(2,2-dimethyl-[1,3]dioxan-5-yl)-5-methyl-phenoxy]-dimethyl-silane

To a solution of ketal (224 mg, 1 mmol) in dichloromethane (5 ml) and triethylamine (5 ml) was added *tert*-butyldimethylsilyl chloride (TBDMSCl, 300 mg, 2 mmol, 2.0eq) and dimethylaminopyridine (DMAP, 10 mg). The resulting mixture was stirred at room temperature under nitrogen for 6 days. After removal of the solvent, the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 50:1) to afford the product (336 mg, 100%) as colorless oil.

IR ν_{\max} (KBr) cm^{-1} : 2956 s , 2931 s , 2859 s , 1612 m , 1574 m , 1506 s , 1255 s , 1196 s , 1067 s , 838 s , 780 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 7.14 (1H, d , $J = 7.8\text{Hz}$), 6.75 (1H, d , $J = 7.8\text{Hz}$), 6.63 (1H, s), 3.96 (2H, d , $J = 7.2\text{Hz}$), 3.46 (1H, m), 2.27 (3H, s), 1.53 (3H, s), 1.47 (3H, s), 1.02 (9H, s), 0.25 (6H, s). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 154.0 (s), 137.9 (s), 127.8 (d), 127.0 (s), 122.3 (d), 119.8 (d), 98.1 (s), 64.7 (t), 34.0 (d), 27.9 (q), 26.2 (q), 21.6 (q), 21.2 (q), 18.7 (s), -3.7 (q). EIMS m/z (%): 336 (M^+ , 5), 261 (18), 249 (13), 235 (21), 221 (41), 191 (100). HRMS m/z Found: 359.2029, Calcd. for $\text{C}_{19}\text{H}_{32}\text{O}_3\text{NaSi}$ ($\text{M}+23$) $^+$: 359.2018.

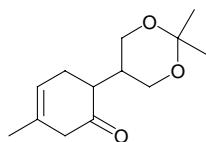


16 *tert*-Butyl-[2-(2,2-dimethyl-[1,3]dioxan-5-yl)-5-methyl-cyclohexa-1,4-dienyloxy]-dimethyl-silane

The ketal (200 mg, 0.6 mmol) was dissolved in THF and ethanol (3 ml, 2:1). Liquid ammonia (200 ml) was distilled into this solution (Birch condenser, acetone-dry ice). Lithium metal (ca. 600 mg) was added in small pieces until the dark blue color persisted for 15 minutes. The reaction mixture was allowed to evaporate in fume hood.

The residue was diluted with ice-cool water (20 ml) and extracted with ethyl acetate (4X30 ml). The organic phases were combined and dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure and the crude product was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 50:1) to afford the product (182 mg, 90%) as colorless oil.

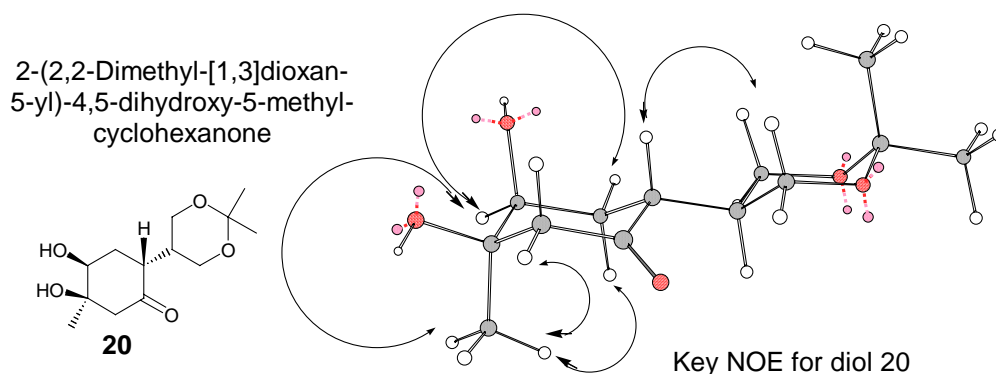
IR ν_{\max} (KBr) cm^{-1} : 2958 s , 2931 s , 2858 s , 1669 w , 1471 m , 1383 m , 1368 m , 1254 s , 1193 s , 1084 m , 932 m , 835 s , 778 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 5.35 (1H, brs), 3.76 (2H, t , $J = 10.8\text{Hz}$), 3.73 (2H, dd , $J = 5.1, 11.7\text{Hz}$), 3.30 (1H, m), 2.72 (2H, m), 2.59 (2H, t , $J = 7.5\text{Hz}$), 1.66 (3H, s), 1.45 (3H, s), 1.40 (3H, s), 0.96 (9H, s), 0.16 (6H, s). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 143.8, 130.7, 118.8, 109.2, 97.8, 62.8, 36.6, 34.0, 28.4, 28.0, 26.2, 23.1, 20.7, 18.7, -3.1. EIMS m/z (%): 339 ($\text{M}+1$, $^+$ 3), 293 (20), 275 (7), 261 (10), 249 (12), 235 (22), 221 (23), 191 (24), 167 (23), 149 (100). HRMS m/z Found: 361.2185, Calcd. for $\text{C}_{19}\text{H}_{34}\text{O}_3\text{NaSi}$ ($\text{M}+23$) $^+$: 361.2174.



7 6-(2,2-Dimethyl-[1,3]dioxan-5-yl)-3-methyl-cyclohex-3-enone

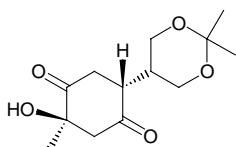
To a mixture of tetrabutylammonium fluoride (TBAF, 1M in THF, 1.1 ml, 1.1 mmol, 2.0eq), water (1.3 ml) and boric acid (32.9 mg, 0.53 mmol, 1.0eq) was added a solution of diene (180 mg, 0.53 mmol) in THF (7.5 ml). The resulting mixture was stirred at 10 °C under nitrogen. The reaction progress was monitored by thin layer chromatography. The reaction mixture was diluted with water (50 ml) and extracted with chloroform (6X40 ml). The organic phases were combined and washed with water (80 ml) and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 10:1) to afford the product (103 mg, 86.7%) as colorless oil.

IR ν_{\max} (KBr) cm^{-1} : 3430 s , 2926 s , 1714 m , 1658 s , 1440 m , 1380 s , 1075 s , 1034 s , 939 m , 874 m , 834 m . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 5.51 (1H, m), 3.97 (1H, dd , $J = 3.9, 11.7\text{Hz}$), 3.91 (1H, dd , $J = 4.0, 11.7\text{Hz}$), 3.70 (1H, dd , $J = 6.6, 12\text{Hz}$), 3.65 (1H, dd , $J = 6.3, 12\text{Hz}$), 2.94 (1H, brd , $J = 20\text{Hz}$), 2.79-2.51 (3H, m), 2.18-2.02 (2H, m), 1.70 (3H, s), 1.40 (3H, s), 1.37 (3H, s). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 210.6 (s), 133.1 (s), 120.5 (d), 98.4 (s), 63.6 (t), 62.0 (t), 46.6 (d), 46.1 (t), 33.2 (d), 29.8 (t), 24.4 (q), 24.3 (q), 22.8 (q). EIMS m/z (%): 192 (30), 95 (100). HRMS m/z Found: 247.1317, Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_3\text{Na}$ ($\text{M}+23$) $^+$: 247.1310.



To a mixture of nonconjugated ketone (60 mg, 0.27 mmol) in THF-*t*-BuOH- H_2O (5.7 ml, 10:8:1) was added *N*-methylmorpholine *N*-oxide (94.7 mg, 0.81 mmol, 3.0 eq) followed by osmium tetroxide (14.4 mg, 0.057 mmol, 0.21 eq). The resulting mixture was stirred at room temperature. The reaction progress was monitored by thin layer chromatography. Aqueous saturated sodium sulfite (5 ml) was added. The reaction mixture was diluted with water (5 ml) and extracted with ethyl acetate (4X15 ml). The organic phases were combined and washed with brine (10 ml) and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was chromatographed on silica gel (Petroleum ether 60-90 $^\circ\text{C}$: ethyl acetate = 1:1) to afford the product (63.5 mg, 92%) as colorless oil.

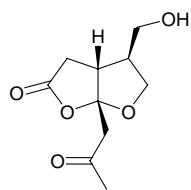
IR ν_{\max} (KBr) cm^{-1} : 3433 s , 2990 s , 2938 s , 2874 s , 1709 s , 1374 s , 1258 s , 1198 s , 1154 s , 1061 s , 831 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 3.99 (1H, *dd*, $J = 4.2, 11.7\text{Hz}$), 3.88 (1H, *dd*, $J = 4.2, 11.7\text{Hz}$), 3.84 (1H, *brs*), 3.72 (1H, *dd*, $J = 6.6, 11.7\text{Hz}$), 3.65 (1H, *dd*, $J = 6.6, 11.7\text{Hz}$), 3.33 (1H, *brs*, OH), 3.01 (1H, *brs*, OH), 2.90 (1H, *d*, $J = 12.3\text{Hz}$), 2.89 (1H, *m*), 2.34 (1H, *d*, $J = 12.3\text{Hz}$), 2.24 (1H, *m*), 2.02 (1H, *m*), 1.57 (1H, *ddd*, $J = 2.5, 14.5, 14.6\text{Hz}$), 1.40 (3H, *s*), 1.38 (3H, *s*), 1.16 (3H, *s*). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 209.4 (*s*), 98.5 (*s*), 76.0 (*s*), 72.7 (*d*), 63.5 (*t*), 61.9 (*t*), 51.8 (*t*), 43.1 (*d*), 32.9 (*d*), 31.8 (*t*), 25.6 (*q*), 24.6 (*q*), 24.0 (*q*). EIMS m/z (%) : 259 ($\text{M}+1, ^+$ 1), 243 (68), 225 (29), 200 (7), 183 (32), 169 (44), 165 (100), 126 (72). HRMS m/z Found: 281.1361, Calcd. for $\text{C}_{13}\text{H}_{22}\text{O}_5\text{Na}$ ($\text{M}+23$) $^+$: 281.1364.



21 5-(2,2-Dimethyl-[1,3]dioxan-5-yl)-2-hydroxy-2-methyl-cyclohexane-1,4-dione

To a solution of *cis*-diol (60 mg, 0.23 mmol) in ethyl acetate (5 ml) was added IBX (195 mg, 0.70 mmol, 3.0 eq). The resulting mixture was stirred at reflux for 3-4 hours. After filtration and washed with ethyl acetate, the filtrate was combined. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 1:1) to afford the product (56 mg, 94%) as colorless syrup.

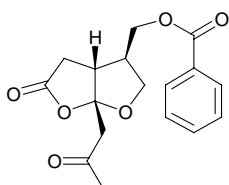
IR ν_{\max} (KBr) cm^{-1} : 3403 s , 2993 s , 2977 s , 1718 s , 1454 m , 1434 m , 1376 s , 1261 s , 1200 s , 1147 s , 1116 s , 1065 s , 828 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 4.10 (1H, *dd*, $J = 3.9, 12.0\text{Hz}$), 4.00 (1H, *dd*, $J = 3.6, 12.0\text{Hz}$), 3.73-3.58 (2H, *m*), 3.21-3.04 (2H, *m*), 2.95-2.81 (2H, *m*), 2.70 (1H, *t*, $J = 13.8\text{Hz}$); 2.09 (1H, *m*), 1.42 (3H, *s*), 1.36 (3H, *s*), 1.35 (3H, *s*). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 209.6 (*s*), 205.4 (*s*), 98.7 (*s*), 76.4 (*s*), 63.3 (*t*), 61.2 (*t*), 54.8 (*t*), 48.7 (*d*), 38.3 (*t*), 33.3 (*d*), 26.7 (*q*), 26.5 (*q*), 21.7 (*q*). EIMS m/z (%) : 239 (70), 181 (100), 163 (83). HRMS m/z Found: 279.1203, Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_5\text{Na}$ ($\text{M}+23$) $^+$: 279,1208.



5 4-Hydroxymethyl-6a-(2-oxo-propyl)-tetrahydro-furo[2,3-*b*]furan-2-one

To a solution of diketone (25.6 mg, 0.1 mmol) in ethyl acetate (5 ml) was added periodic acid ($\text{HIO}_4 \cdot 2\text{H}_2\text{O}$, 22.8 mg, 0.1 mmol, 1.0 eq). The resulting mixture was stirred at room temperature for 3-4 hours. The reaction progress was monitored by thin layer chromatography. Aqueous saturated sodium sulfite (3 ml) was added. The reaction mixture was diluted with water (3 ml) and extracted with ethyl acetate (6X10 ml). The organic phases were combined and washed with brine (10 ml) and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 1:3) to afford the desired alcohol as the sole isolated product (colorless oil, 9 mg, 42%).

IR ν_{max} (KBr) cm^{-1} : 3430 s , 2924 m , 1767 s , 1717 s , 1410 m , 1372 s , 1280 s , 1174 s , 1038 s , 950 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 4.00 (1H, *dd*, $J = 5.4, 9.9\text{Hz}$), 3.95 (1H, *dd*, $J = 1.8, 9.9\text{Hz}$), 3.58 (2H, *d*, $J = 6.9\text{Hz}$), 3.32 (1H, *d*, $J = 17.4\text{Hz}$), 3.29 (1H, *dd*, $J = 10.5, 18.5\text{Hz}$), 2.97 (1H, *m*), 2.96 (1H, *d*, $J = 17.4\text{Hz}$), 2.51 (1H, *dd*, $J = 2.7, 18.5\text{Hz}$), 2.24 (1H, *m*), 2.20 (3H, *s*). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 204.9 (*s*), 175.1 (*s*), 115.8 (*s*), 68.8 (*t*), 64.3 (*t*), 50.0 (*d*), 49.7 (*t*), 44.5 (*d*), 37.2 (*t*), 31.4 (*q*). EIMS m/z (%): 196 ($\text{M}^+ - 18$, 3), 183 (10), 166 (8), 157 (17), 152 (17), 139 (68), 97 (100). HRMS m/z Found: 237.0742, Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}_5\text{Na}$ ($\text{M} + 23$) $^+$: 237,0738.



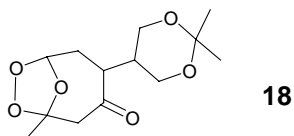
4 Paeonilide

To a solution of diketone (56 mg, 0.219 mmol) in ethyl acetate (5 ml) was added periodic acid ($\text{HIO}_4 \cdot 2\text{H}_2\text{O}$, 50 mg, 0.219 mmol, 1.0 eq). The resulting mixture was

stirred at room temperature for 3-4 hours. The reaction progress was monitored by thin layer chromatography. Aqueous saturated sodium sulfite (3 ml) was added. The reaction mixture was diluted with water (3 ml) and extracted with ethyl acetate (6X10 ml). The organic phases were combined and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane (3 ml) and treated with benzoyl chloride (0.05 ml, 0.43 mmol, 2.0 eq) and pyridine (0.2 ml). The resulting mixture was stirred at room temperature for 2 hours. The solvent was removed and the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 2:1) to afford the product (32 mg, 46%) as colorless needles.

m.p. : 168-170 °C

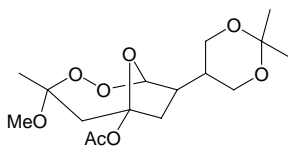
IR ν_{\max} (KBr) cm^{-1} : 1763 s , 1708 s , 1451 w , 1410 w , 1371 s , 1281 s , 1255 m , 1208 w , 1178 m , 1119 s , 1070 w , 1041 s , 1025 w , 974 m , 948 s , 921 s , 902 w , 717 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 8.01 (2H, d , $J = 7.8\text{Hz}$), 7.59 (1H, t , $J = 7.6\text{Hz}$), 7.46 (2H, dd , $J = 7.6, 7.8\text{Hz}$), 4.29 (1H, dd , $J = 7.3, 11.0\text{Hz}$), 4.18 (1H, dd , $J = 8.1, 11.0\text{Hz}$), 4.05 (2H, m), 3.40 (1H, d , $J = 17.7\text{Hz}$), 3.34 (1H, dd , $J = 10.5, 18.5\text{Hz}$), 3.00 (1H, m), 2.96 (1H, d , $J = 17.7\text{Hz}$), 2.54 (1H, dd , $J = 2.7, 18.5\text{Hz}$), 2.53 (1H, m), 2.19 (3H, s). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 204.5 (s), 174.7 (s), 166.5 (s), 133.6 (d), 129.7 (d), 129.6 (s), 128.7 (d), 115.1 (s), 68.1 (t), 65.0 (t), 49.7 (t), 46.8 (d), 44.5 (d), 36.7 (t), 31.1 (q). EIMS m/z (%): 318 (M^+ , 0.2), 196 (21), 178 (10), 152 (64), 105 (100), 94 (53), 77 (37). HRMS m/z Found: 341.1009, Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_6\text{Na}$ ($\text{M}+23$) $^+$: 341.1001.



To a solution of ozone saturated (blue color) dichloromethane (4 ml) was added a solution of nonconjugated ketone (20 mg, 0.089 mmol) in dichloromethane (3 ml) at

-78 °C. The reaction progress was monitored by thin layer chromatography. After removal of the solvent, the residue (20 mg) was directly used for NMR analysis without further purification.

IR ν_{\max} (KBr) cm^{-1} : 3440 s , 2938 s , 1711 s , 1631 s . $^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 5.63 (1H, d , $J = 3.1\text{Hz}$), 3.96 (2H, td , $J = 3.6, 12.5\text{Hz}$), 3.80 (1H, t , $J = 5.7\text{Hz}$), 3.68 (1H, dd , $J = 4.5, 12.1\text{Hz}$), 3.48-3.30 (2H, m), 2.80 (1H, d , $J = 20.6\text{Hz}$), 2.73 (1H, d , $J = 20.6\text{Hz}$), 2.27-2.23 (2H, m), 1.59 (3H, s), 1.40 (3H, s), 1.36 (3H, s). $^{13}\text{C-NMR}$ (75MHz, CDCl_3), δ (ppm): 205.9 (s), 107.3 (s), 103.0 (d), 98.7 (s), 63.4 (t), 61.7 (t), 56.3 (t), 43.2 (d), 34.3 (d), 32.6 (t), 26.4 (q), 22.2 (q), 20.1 (q). EIMS m/z (%) : 257 (8), 239 (12), 196 (22), 181 (64), 157 (42), 139 (59), 111 (41), 97 (100), 85 (95), 69 (64). HRMS m/z Found: 295.1154, Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_6\text{Na}$ ($\text{M}+23$) $^+$: 295.1157.

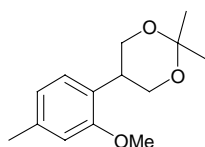


19

To a solution of ozone saturated (blue color) dichloromethane and methanol (10 ml, 4:1) was added a solution of nonconjugated ketone (22.4 mg, 0.1 mmol) in dichloromethane (3 ml) at -78 °C. The reaction progress was monitored by thin layer chromatography. After removal of the solvent, the residue was treated with acetic anhydride (0.05 ml) and pyridine (0.1 ml) in dichloromethane (4 ml) for 4 hours at room temperature. After removal of the solvent, the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 8:1) to afford the product (27 mg, 78%) as colorless oil.

$^1\text{H-NMR}$ (300MHz, CDCl_3), δ (ppm): 6.25 (1H, dd , $J = 4.5, 6.4\text{Hz}$), 4.09 (2H, d , $J = 4.2\text{Hz}$), 3.96 (1H, dd , $J = 3.7, 11.8\text{Hz}$), 3.62 (1H, dd , $J = 5.1, 11.8\text{Hz}$), 3.25 (3H, s), 2.90 (1H, d , $J = 13.9\text{Hz}$), 2.77 (1H, d , $J = 13.9\text{Hz}$), 2.72-2.52 (2H, m), 2.06 (3H, s),

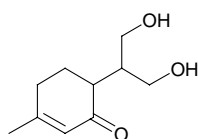
1.93-1.80 (2H, *m*), 1.48 (3H, *s*), 1.41 (3H, *s*), 1.37 (3H, *s*). ¹³C-NMR (75MHz, CDCl₃), δ (ppm): 171.0 (*s*), 115.7 (*s*), 108.0 (*s*), 98.5 (*s*), 97.0 (*d*), 63.8 (*t*), 62.4 (*t*), 56.1 (*t*), 49.8 (*q*), 41.8 (*d*), 36.5 (*t*), 35.4 (*d*), 25.4 (*q*), 23.2 (*q*), 21.8 (*q*), 18.1 (*q*). EIMS *m/z* (%): 346 (M⁺, 0.04), 331 (8), 313 (59), 255 (41), 241 (15), 229 (32), 213 (100), 195 (47), 155 (42), 141 (82), 111 (46), 95 (80). HRMS *m/z*. Found: 369.1518, Calcd. for C₁₆H₂₆O₈Na (M+23)⁺: 369.1525.



15a 5-(2-Methoxy-4-methyl-phenyl)-2,2-dimethyl-[1,3]dioxane

To a solution of phenol (222 mg, 1 mmol) in acetone (10 ml) was added potassium carbonate (552 mg, 4 mmol, 4.0 eq) and dimethylsulfate (132 mg, 1.05 mmol). The resulting mixture was stirred at room temperature overnight. After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 10:1) to afford the product (228 mg, 97%) as colorless oil.

¹H-NMR (300MHz, CDCl₃), δ (ppm): 7.11 (1H, *d*, *J* = 7.8Hz), 6.75 (1H, *d*, *J* = 7.8Hz), 6.70 (1H, *s*), 4.10 (2H, *t*, *J* = 10.5Hz), 3.94 (2H, *dd*, *J* = 4.8, 10.5Hz), 3.81 (3H, *s*), 3.54-3.45 (1H, *m*), 2.34 (3H, *s*), 1.56 (3H, *s*), 1.48 (3H, *s*). ¹³C-NMR (75MHz, CDCl₃), δ (ppm): 157.9 (*s*), 138.4 (*s*), 128.2 (*d*), 124.5 (*s*), 121.6 (*d*), 112.0 (*d*), 98.1 (*s*), 64.3 (*t*), 55.7 (*q*), 35.3 (*d*), 28.6 (*q*), 21.9 (*q*), 20.6 (*q*).



17 6-(2-Hydroxy-1-hydroxymethyl-ethyl)-3-methyl-cyclohex-2-enone

The ketal (200 mg, 0.6 mmol) was dissolved in THF and ethanol (3 ml, 2:1). Liquid ammonia (200 ml) was distilled into this solution (Birch condenser, acetone-dry ice).

Lithium metal (ca 600 mg) was added in small pieces until the dark blue color persisted for 15 minutes. The reaction mixture was allowed to evaporate in fume hood. The residue was diluted with ice-cool water (20 ml) and extracted with ethyl acetate (4X30 ml). The organic phases were combined and dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure and the crude product was treated with oxalic acid in methanol and water (10 ml, 4:1) for 30 minutes at room temperature. The solvent was removed under reduced pressure and the residue was diluted with aqueous saturated sodium bicarbonate solution (8 ml). The mixture was extracted with ethyl acetate (6X 10 ml). The organic phases were combined and dried over anhydrous sodium sulfate. After removal of solvent, the residue was chromatographed on silica gel (Petroleum ether 60-90 °C : ethyl acetate = 1:3) to afford the product (120 mg, 77%) as colorless oil.

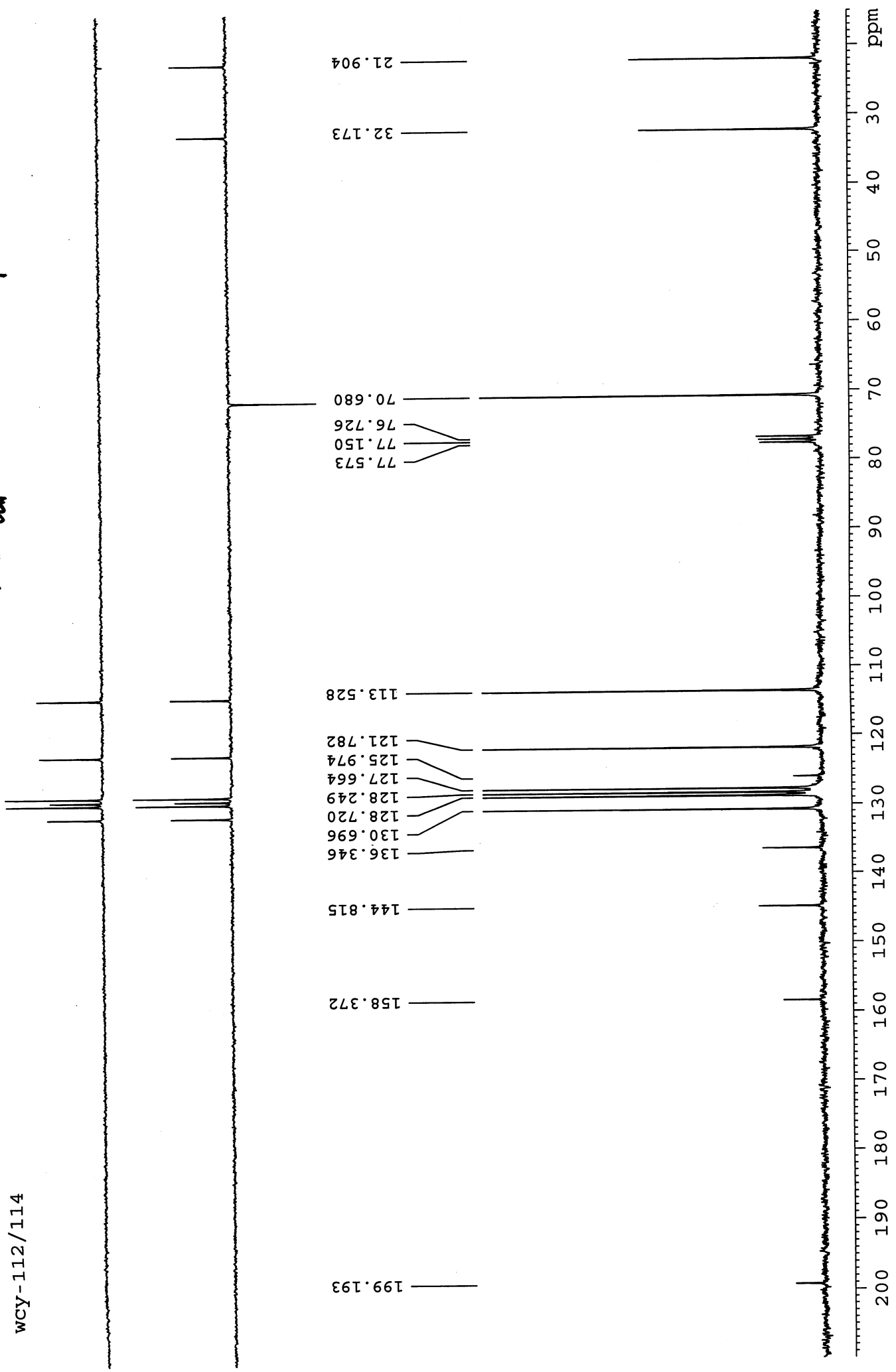
¹H-NMR (300MHz, CDCl₃), δ (ppm): 5.85 (1H, *d*, *J* = 1.2Hz), 3.77-3.61 (4H, *m*), 3.50 (1H, *brs*), 3.34 (1H, *brs*), 2.49 (1H, *m*, *J* = 5.4Hz), 2.31 (2H, *t*, *J* = 5.4Hz), 2.22 (1H, *dd*, *J* = 5.4, 10.8Hz), 2.07-1.70 (2H, *m*), 1.93 (3H, *s*). ¹³C-NMR (75MHz, CDCl₃), δ (ppm): 202.2 (*s*), 163.2 (*s*), 126.6 (*d*), 63.2 (*t*), 63.0 (*t*), 45.2 (*d*), 41.8 (*d*), 30.6 (*t*), 25.3 (*t*), 24.3 (*q*).

Section C: NMR Spectrum of Compounds



Compound 9

WCY-112/114





Compound 9

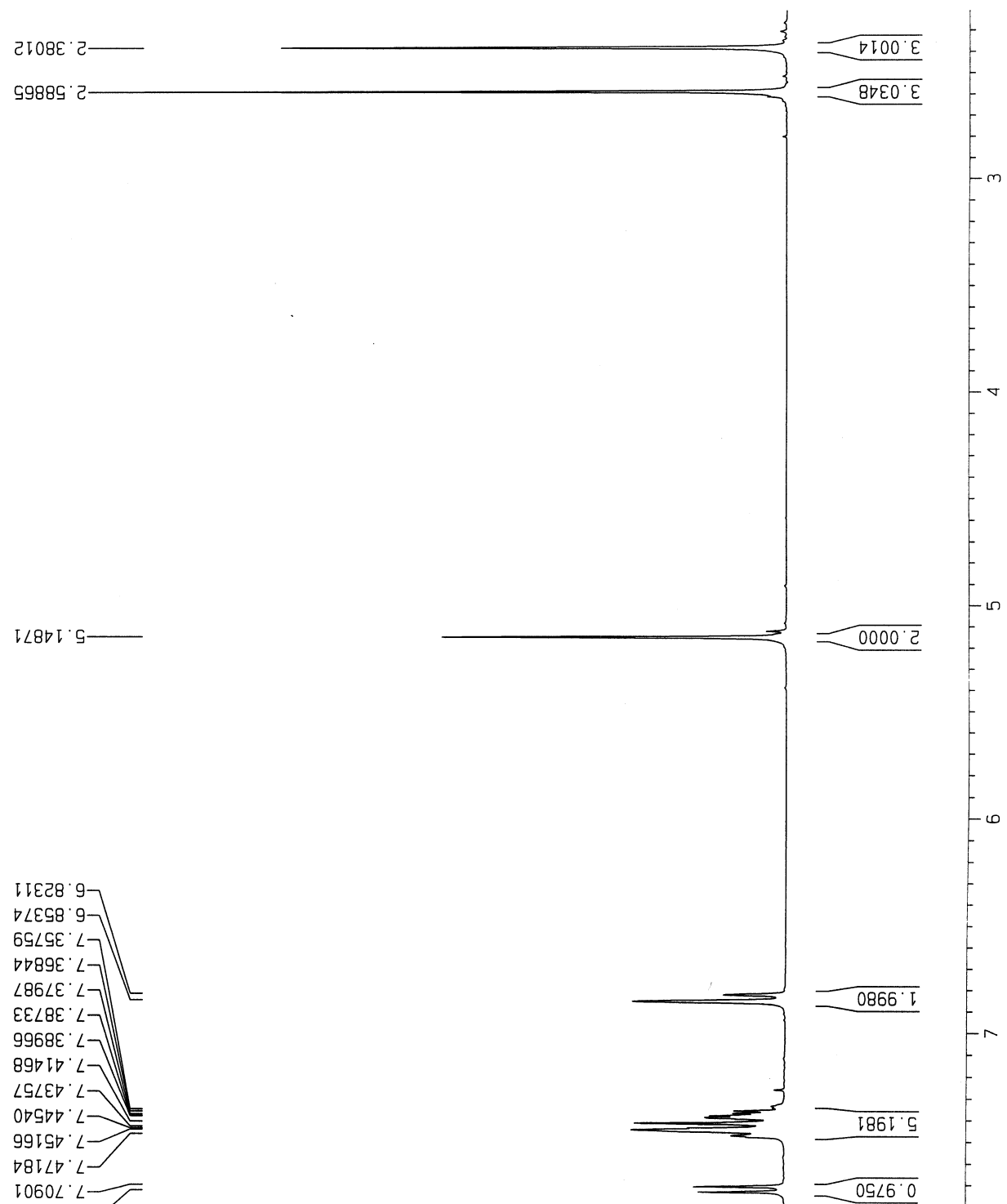
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 TD 65536
 SOLVENT CDCl3
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 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 71.8
 DW 81.000 usec
 DE 6.00 usec
 TE 294.7 K
 D1 1.0000000 sec
 MCREST 0.0000000 sec
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==== CHANNEL f1 =====
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 SF01 300.1318534 MHz

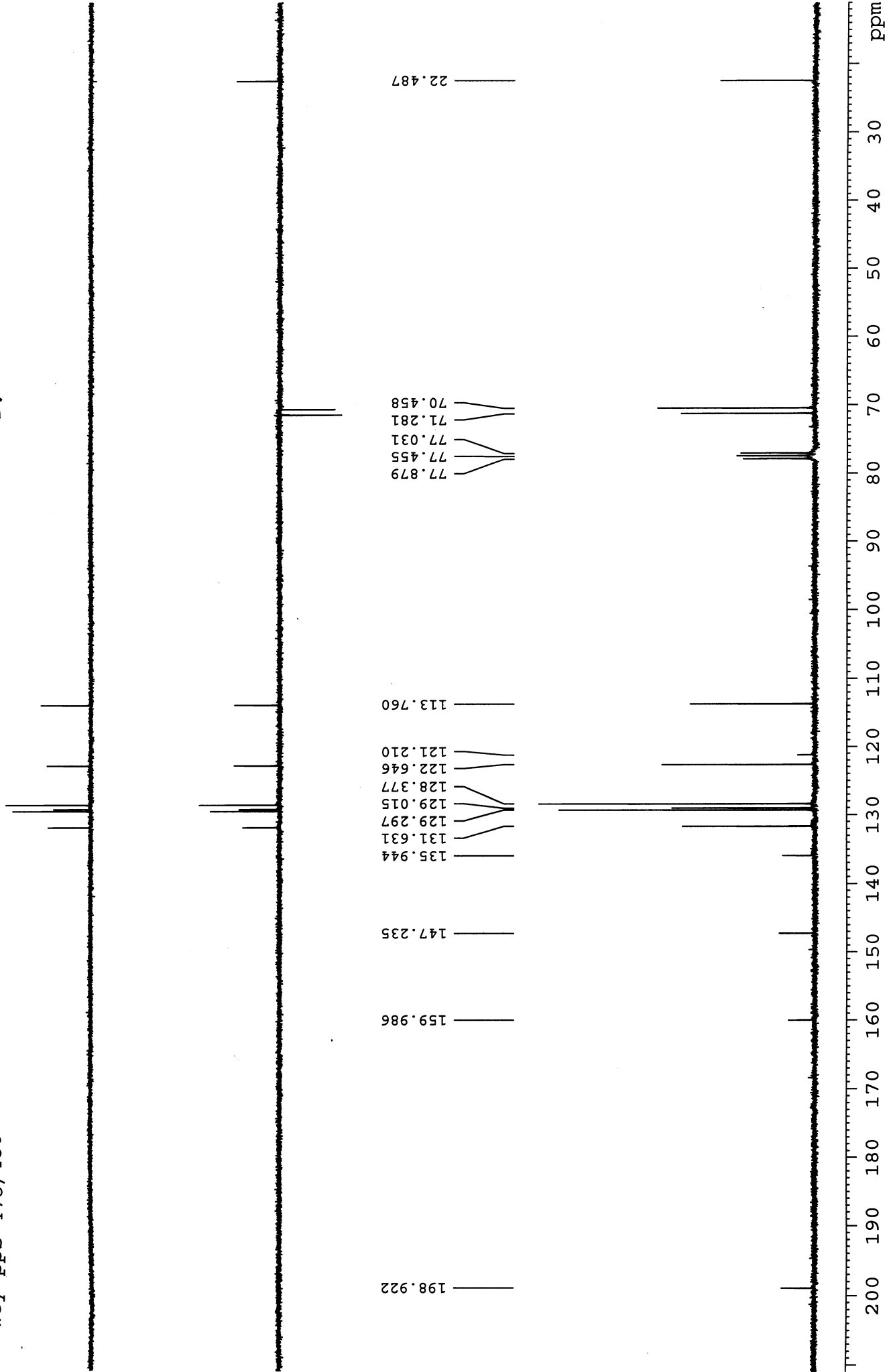
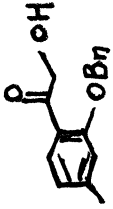
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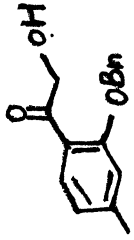
1D NMR plot parameters
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 CY 12.50 cm
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 F1 2412.36 Hz
 F2P 2.207 ppm
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 PPMCM 0.29155 ppm/cm
 HZCM 87.50188 Hz/cm



wcy-pps-478/480

Compound 10





Compound 10

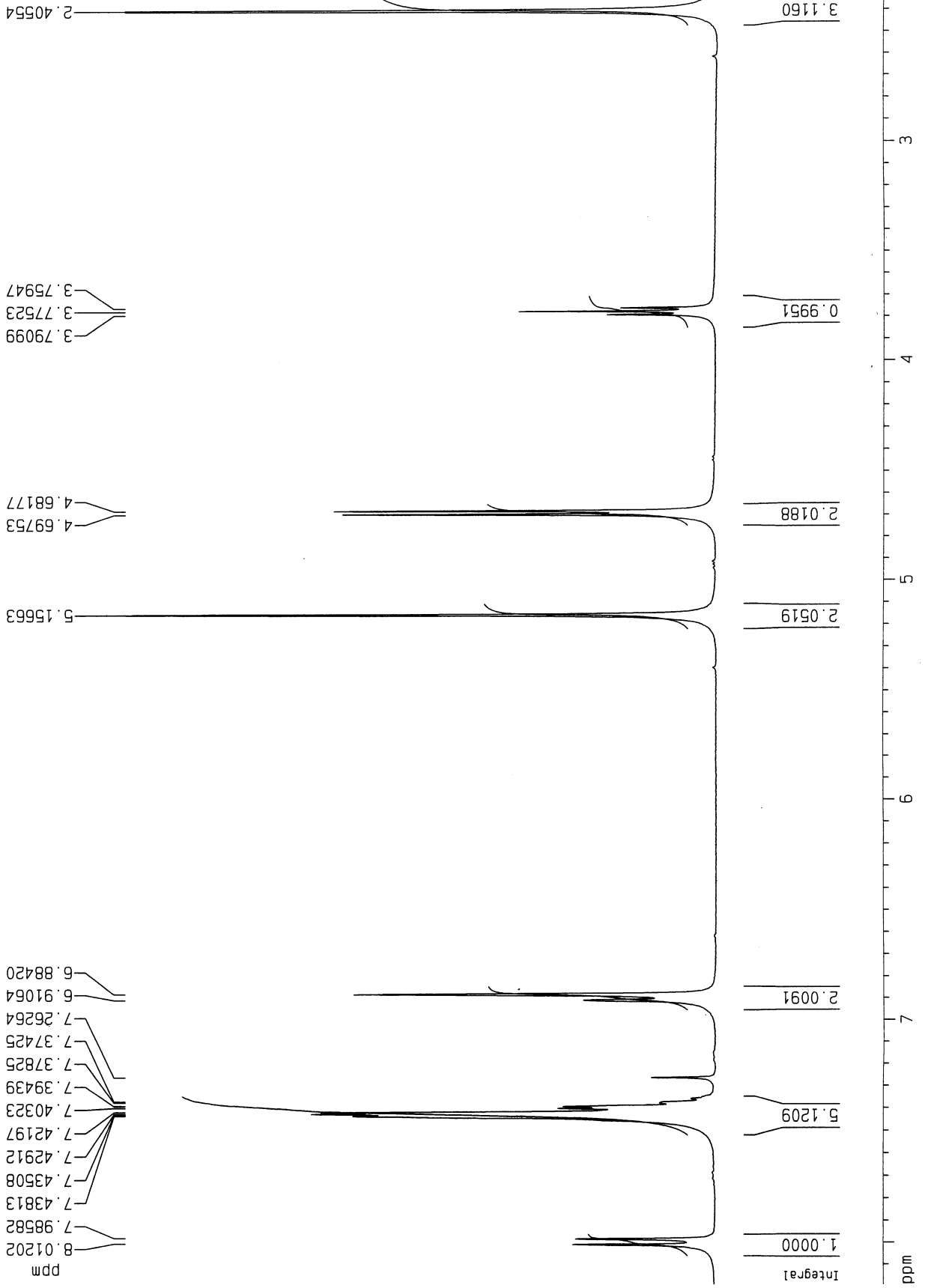
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 PROCNO 1

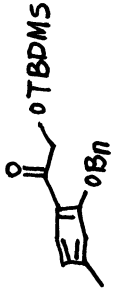
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 TD 65536
 SOLVENT CDCl3
 NS 6
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 256
 DW 81.000 usec
 DE 6.00 usec
 TE 294.8 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWK 0.01500000 sec

==== CHANNEL f1 =====
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 P1 8.60 usec
 PL1 -2.00 dB
 SF01 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300081 MHz
 MDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX *23.00 cm
 CY 15.00 cm
 F1P 8.193 ppm
 F1 2459.03 Hz
 F2P 2.217 ppm
 F2 665.27 Hz
 PPMCM 0.25985 ppm/c
 HZCM 77.98952 Hz/cr





Compound 11

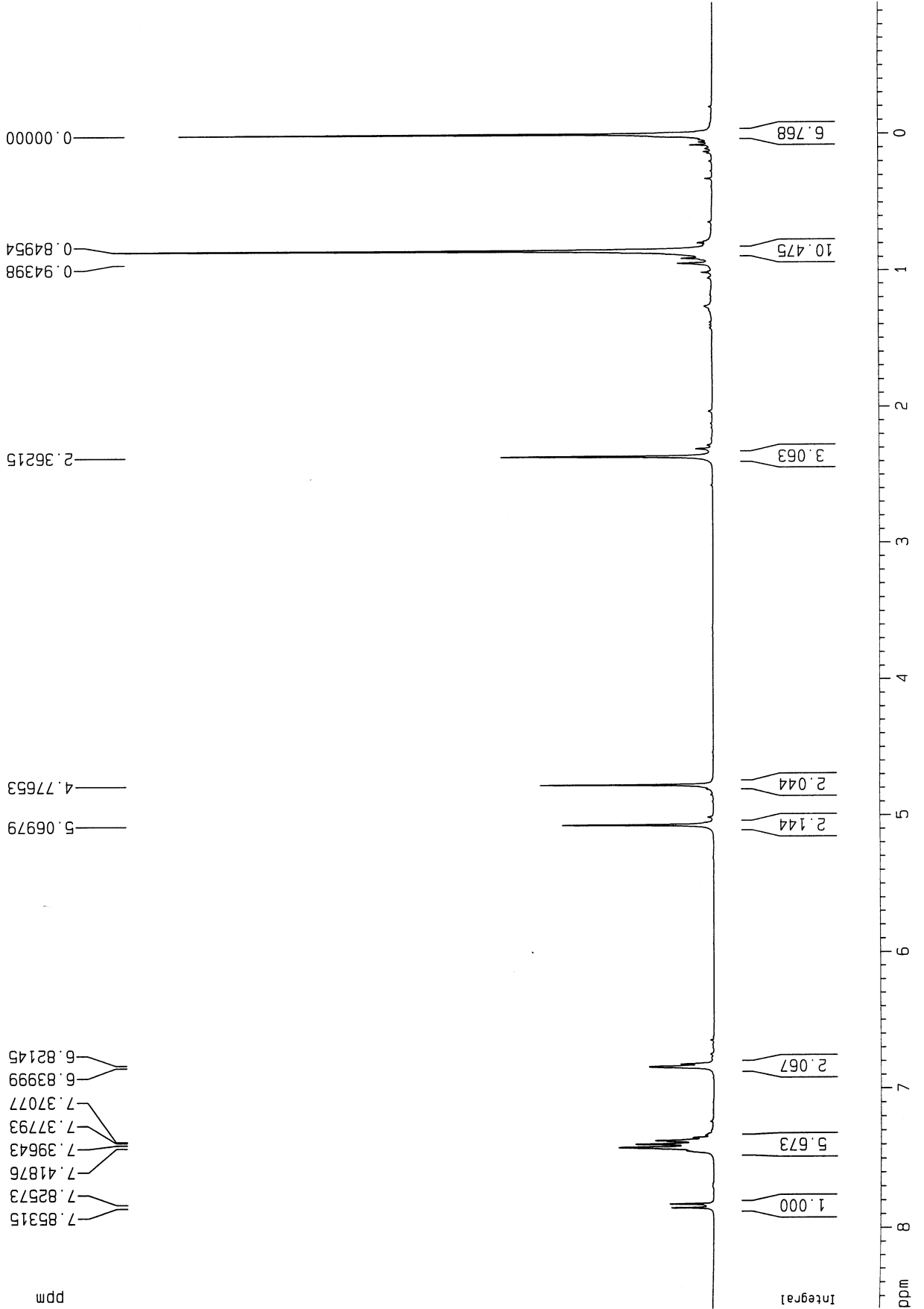
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 NS 16
 DS 2
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 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
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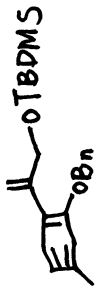
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F2 - Processing parameters
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1D NMR plot parameters
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 CY 12.50 cm
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 F1 2578.80 Hz
 F2P -0.965 ppm
 F2 -289.58 Hz
 PPMCM 0.41553 ppm/cm
 HZCM 124.71233 Hz/cm



Compound 12



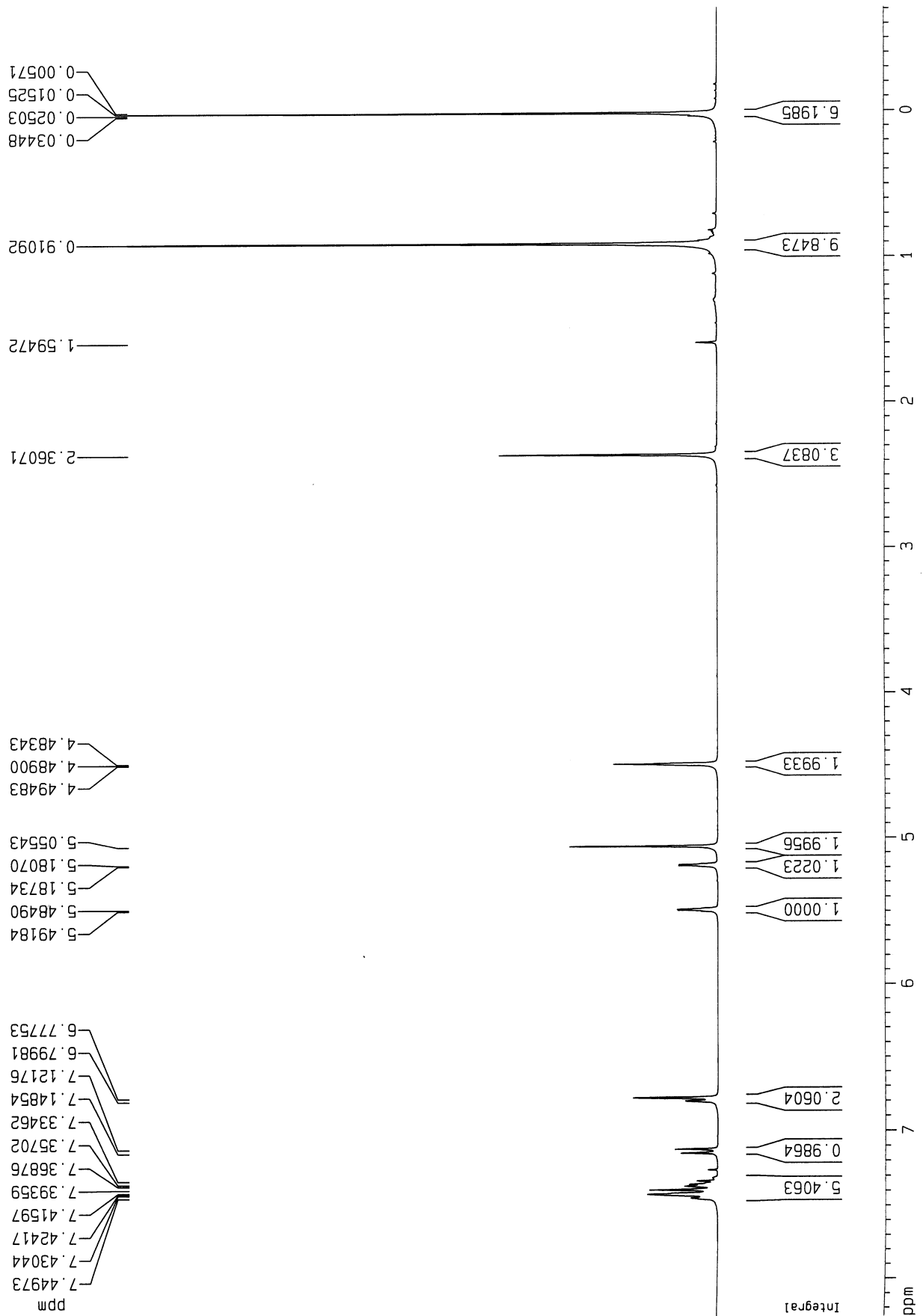
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 SOLVENT CDC13
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 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 64
 DW 81.000 usec
 DE 6.00 usec
 TE 292.2 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCMRK 0.01500000 sec

==== CHANNEL f1 =====
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 P1 8.60 usec
 PL1 -2.00 dB
 SF01 300.1318534 MHz

F2 - Processing parameters
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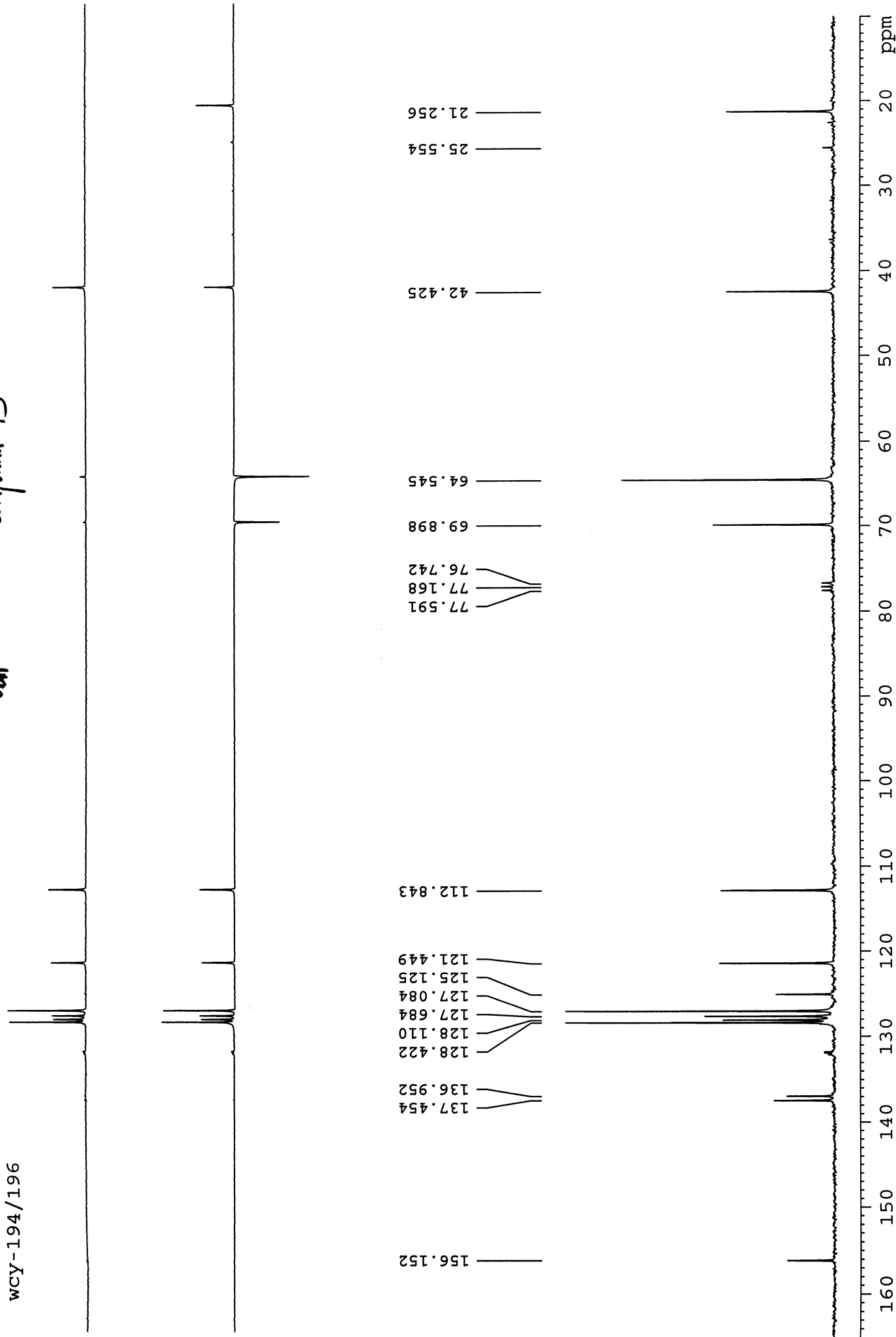
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 HZCM 117.12848 Hz/cm





Compound 13

WCY-194/196





Compound 13

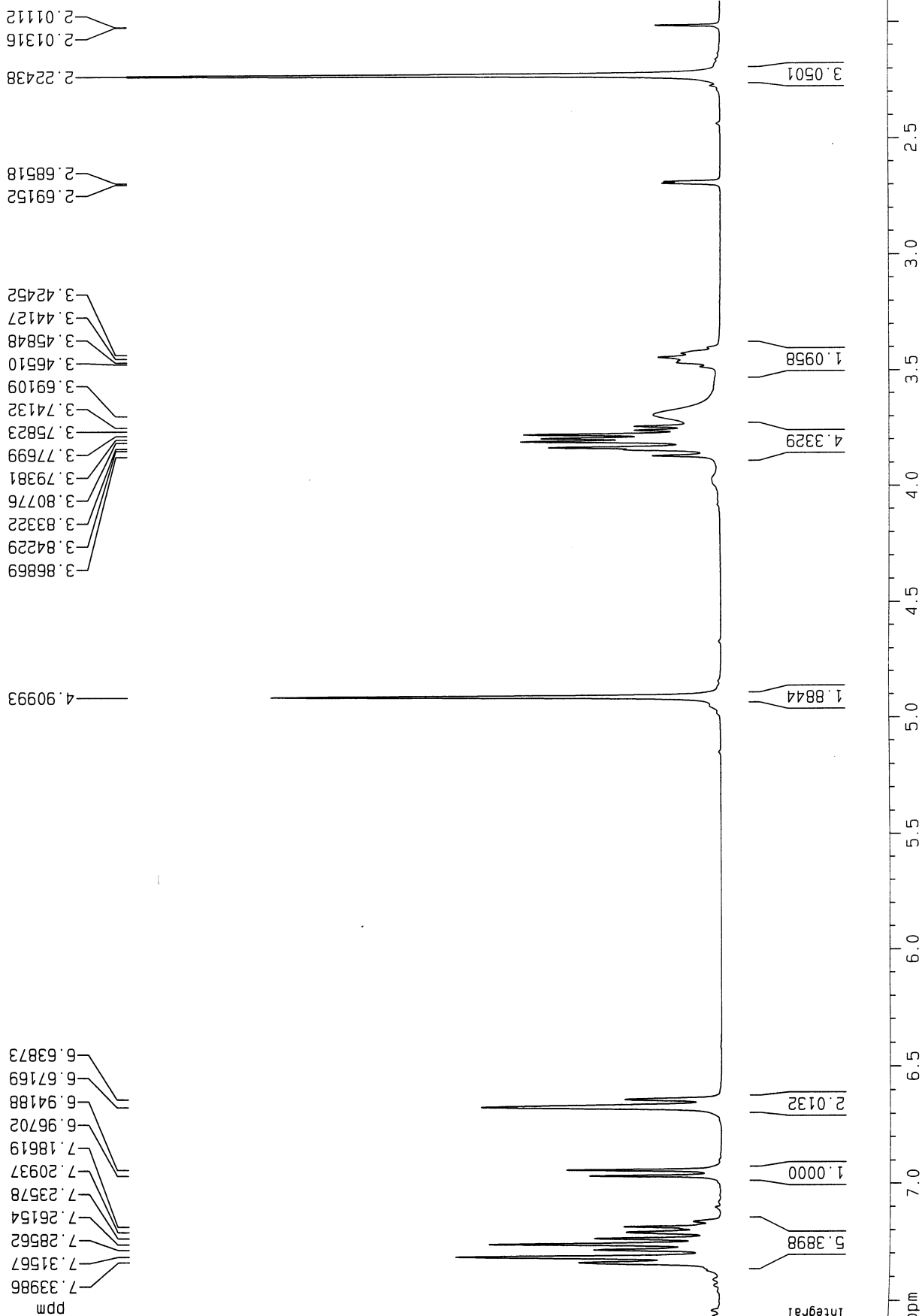
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 TD 65536
 SOLVENT CDC13
 NS 16
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 20.2
 DW 81.000 usec
 DE 6.00 usec
 TE 297.2 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

==== CHANNEL f1 =====
 NUC1 1H
 P1 8.60 usec
 PL1 -2.00 dB
 SF01 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300548 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 23.00 cm
 CY 12.50 cm
 F1P 7.591 ppm
 F1 2278.23 Hz
 F2P 1.907 ppm
 F2 572.40 Hz
 PPMCM 0.24711 ppm/cm
 HZCM 74.16652 Hz/cm





Compound 14

Current Data Parameters
 NAME wcy
 EXPNO 219
 PROCNO 1

F2 - Acquisition Parameters

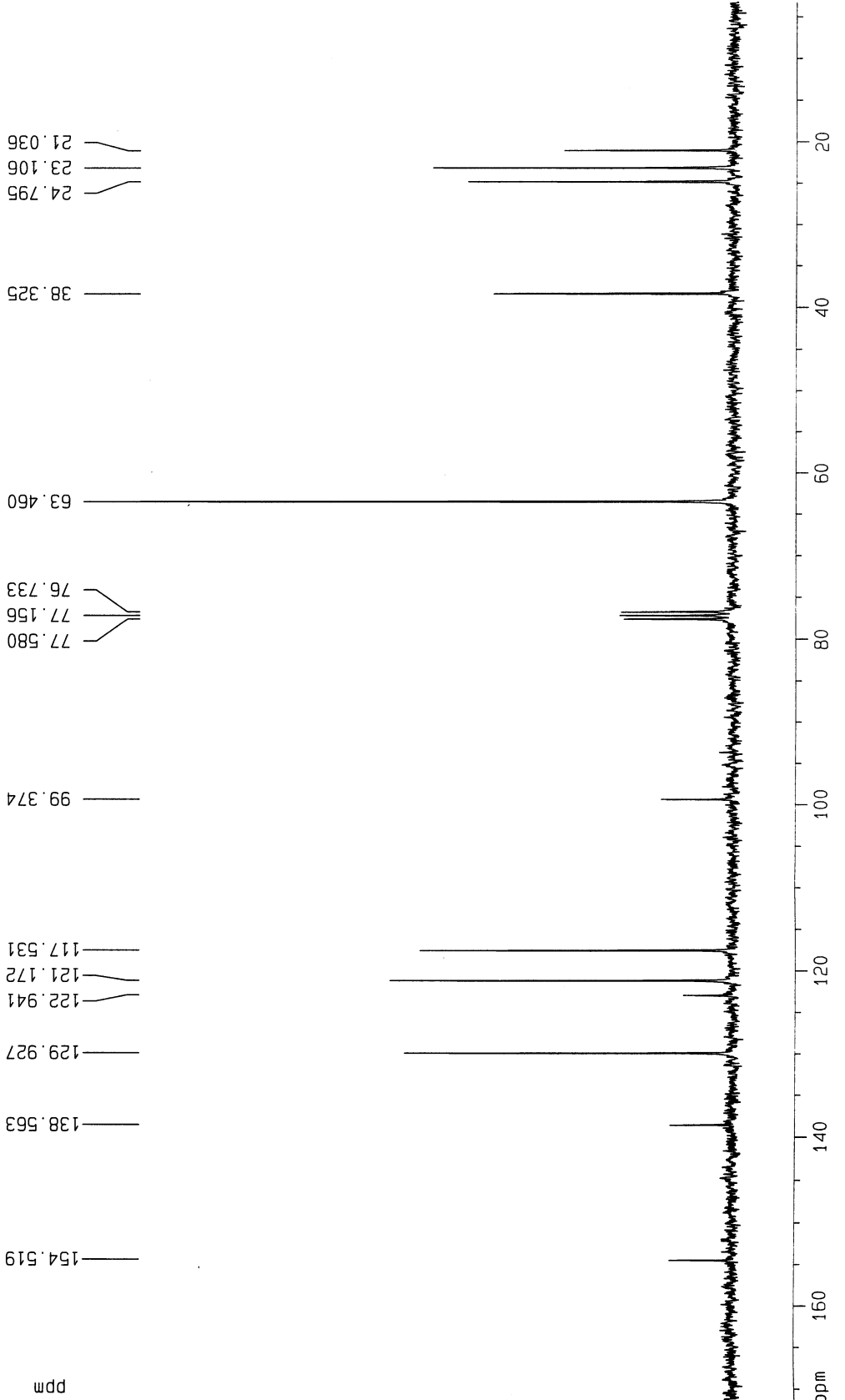
Date_ 20050205
 Time 16.25
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zgdc
 TD 32768
 SOLVENT CDC13
 NS 144
 DS 4
 SWH 21097.047 Hz
 FIDRES 0.643831 Hz
 AQ 0.7766516 sec
 RG 16384
 DM 23.700 usec
 DE 6.00 usec
 TE 298.0 K
 D1 2.0000000 sec
 d11 0.0300000 sec
 MCREST 0.0000000 sec
 MCWPK 0.0150000 sec

==== CHANNEL f1 =====
 NUC1 13C
 P1 8.20 usec
 PL1 -3.00 dB
 SF01 75.4767751 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 90.00 usec
 PL2 -2.00 dB
 PL12 18.00 dB
 SF02 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677406 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 3.00

1D NMR plot parameters
 CX 22.00 cm
 CY 12.50 cm
 F1P 171.718 ppm
 F1 12959.16 Hz
 F2P 3.198 ppm
 F2 241.32 Hz
 PPMCM 7.66001 ppm/cm
 HZCM 578.08380 Hz/cm





Compound 14

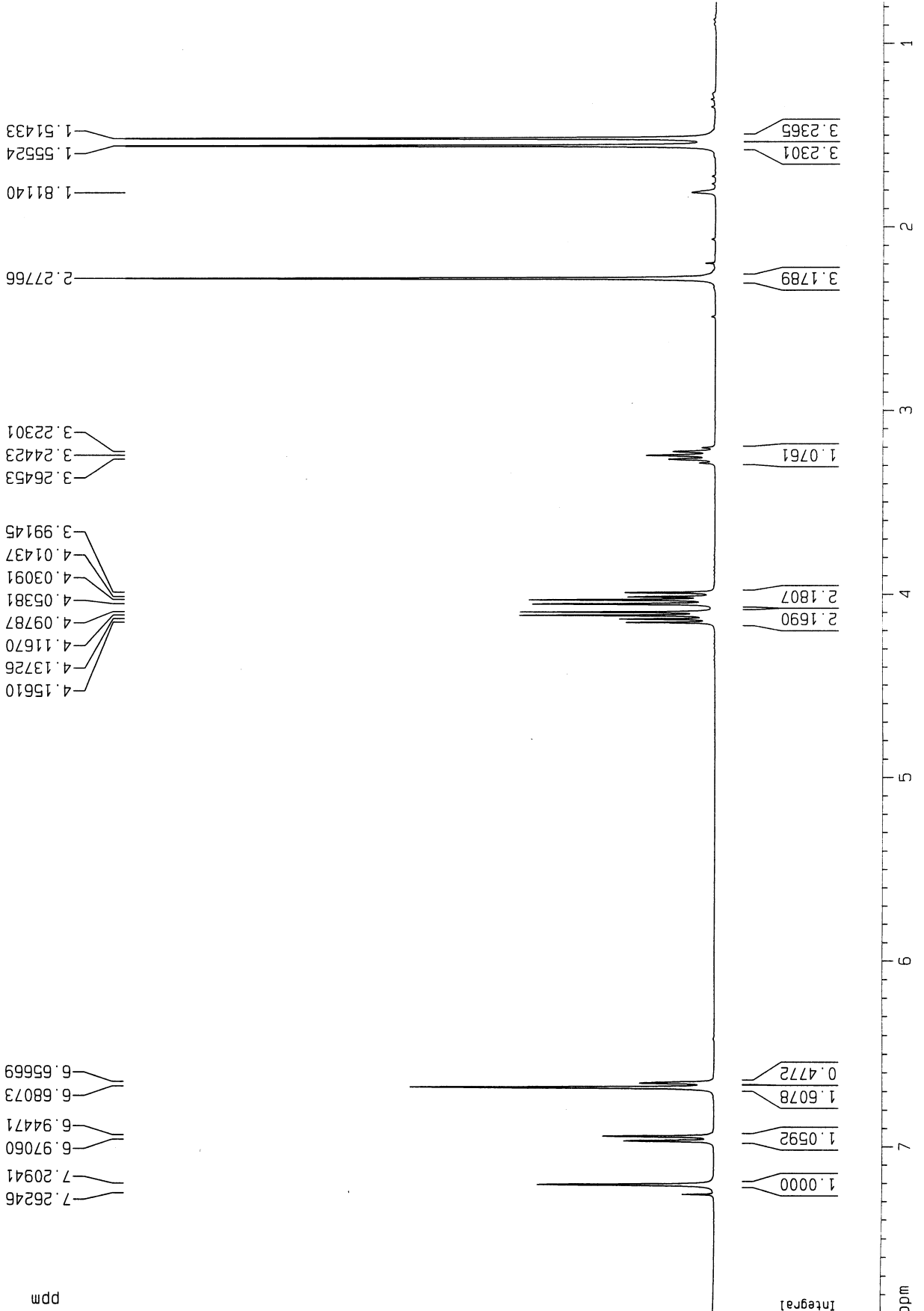
Current Data Parameters
 NAME wcy
 EXPNO 222
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050205
 Time 16.39
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SMH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 143.7
 DM 81.000 usec
 DE 6.00 usec
 TE 297.7 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCMRK 0.01500000 sec

==== CHANNEL f1 =====
 NUC1 1H
 P1 8.60 usec
 PL1 -2.00 dB
 SF01 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300083 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

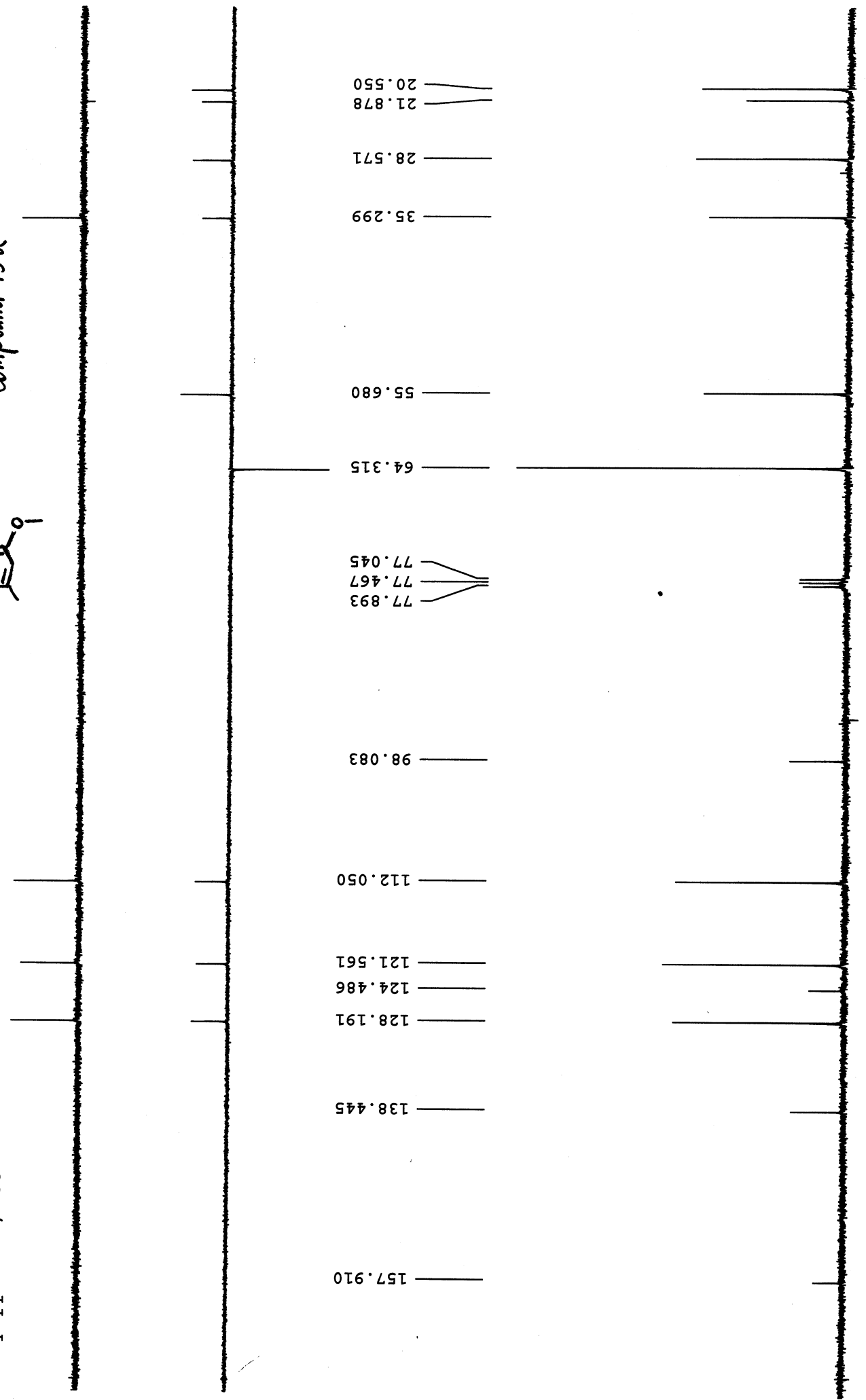
1D NMR plot parameters
 CX 23.00 cm
 CY 12.50 cm
 F1P 7.907 ppm
 F1 2373.27 Hz
 F2P 0.772 ppm
 F2 231.67 Hz
 PPMCM 0.31024 ppm/cm
 HZCM 93.11293 Hz/cm



wcy-pps-483/485



Compound 15a



157.910

138.445

128.191

124.486

121.561

112.050

98.083

77.893

77.467

77.045

64.315

55.680

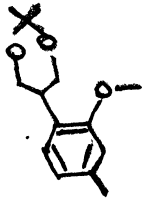
35.299

28.571

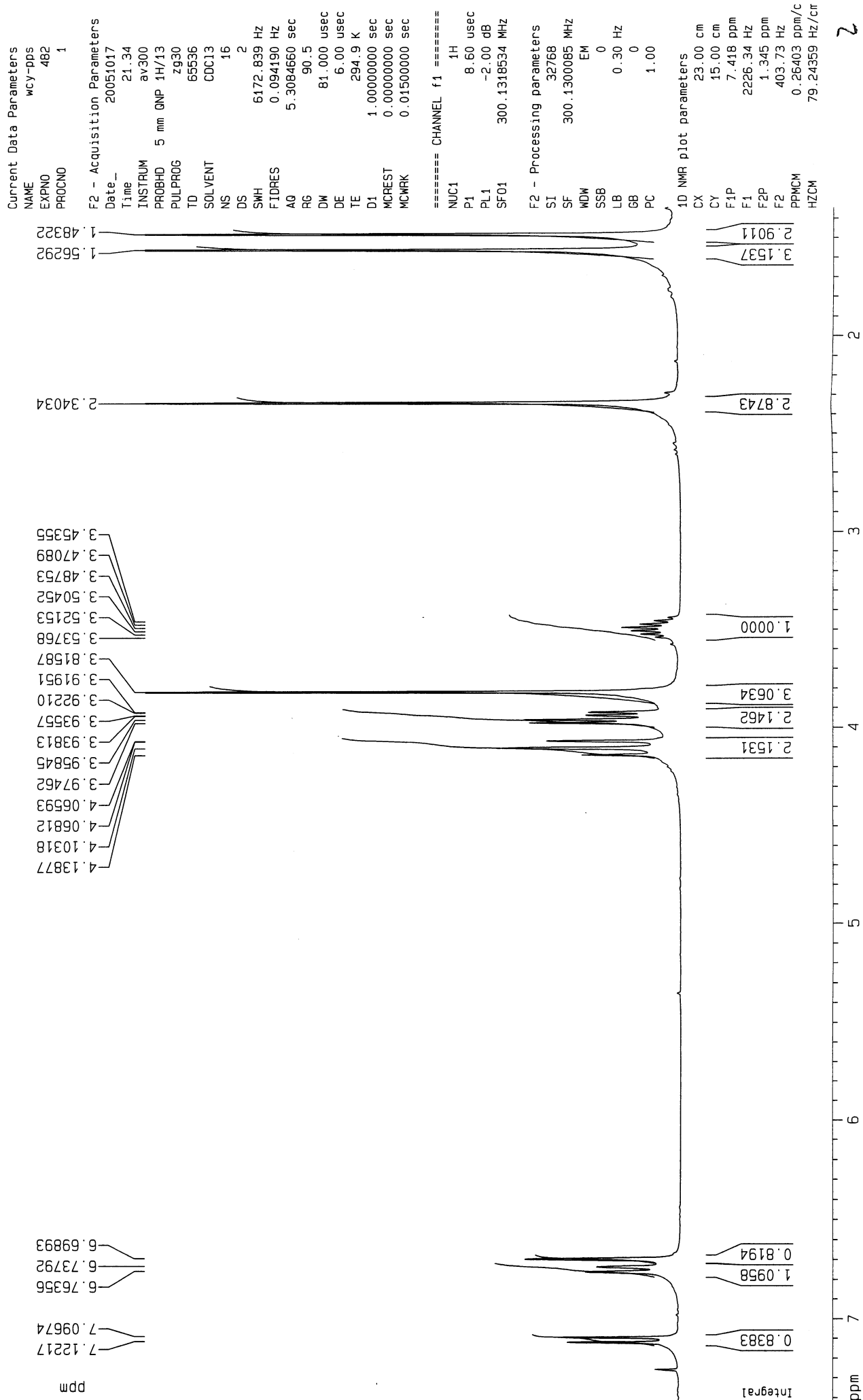
21.878

20.550

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

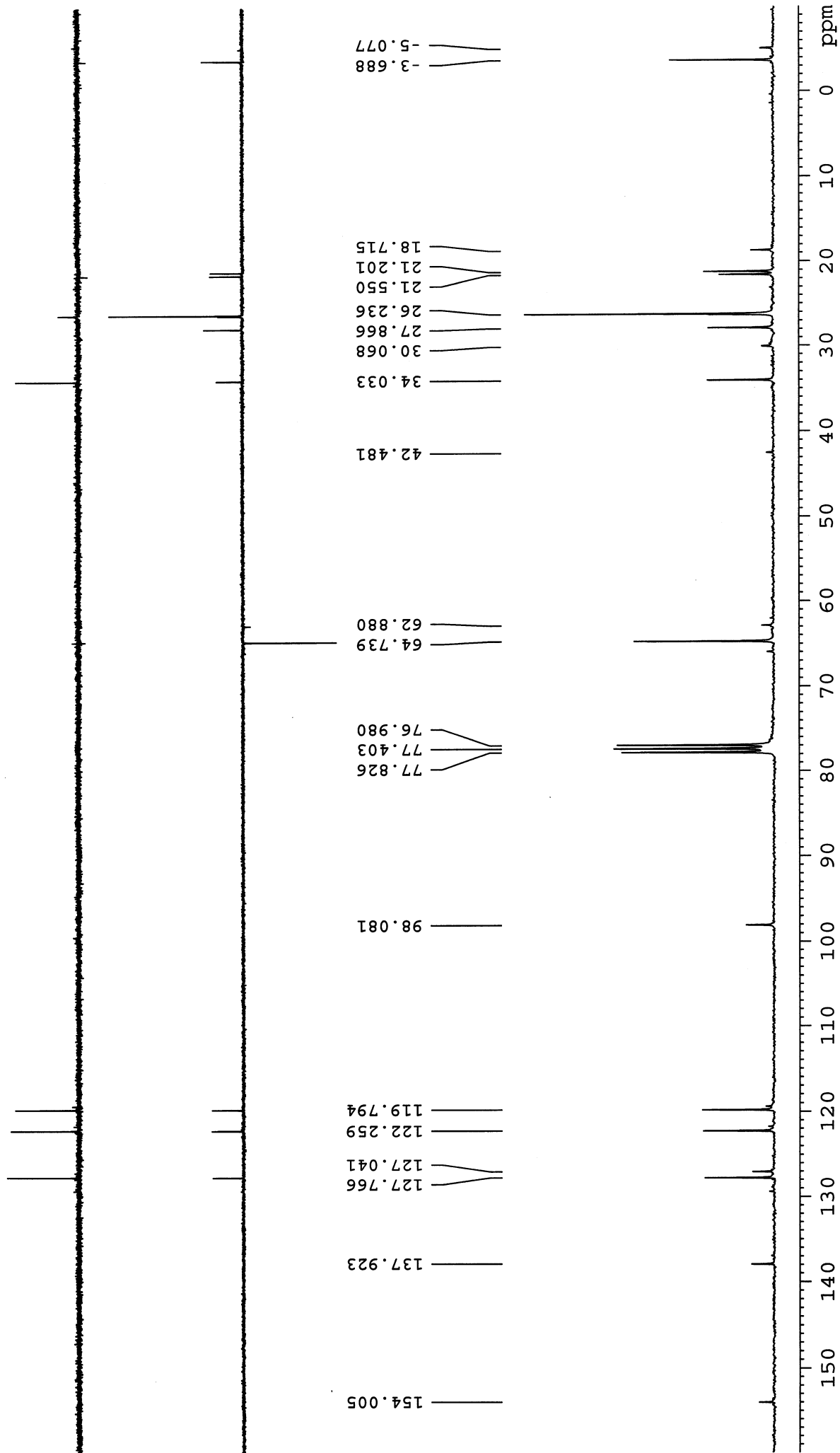


Compound 15a



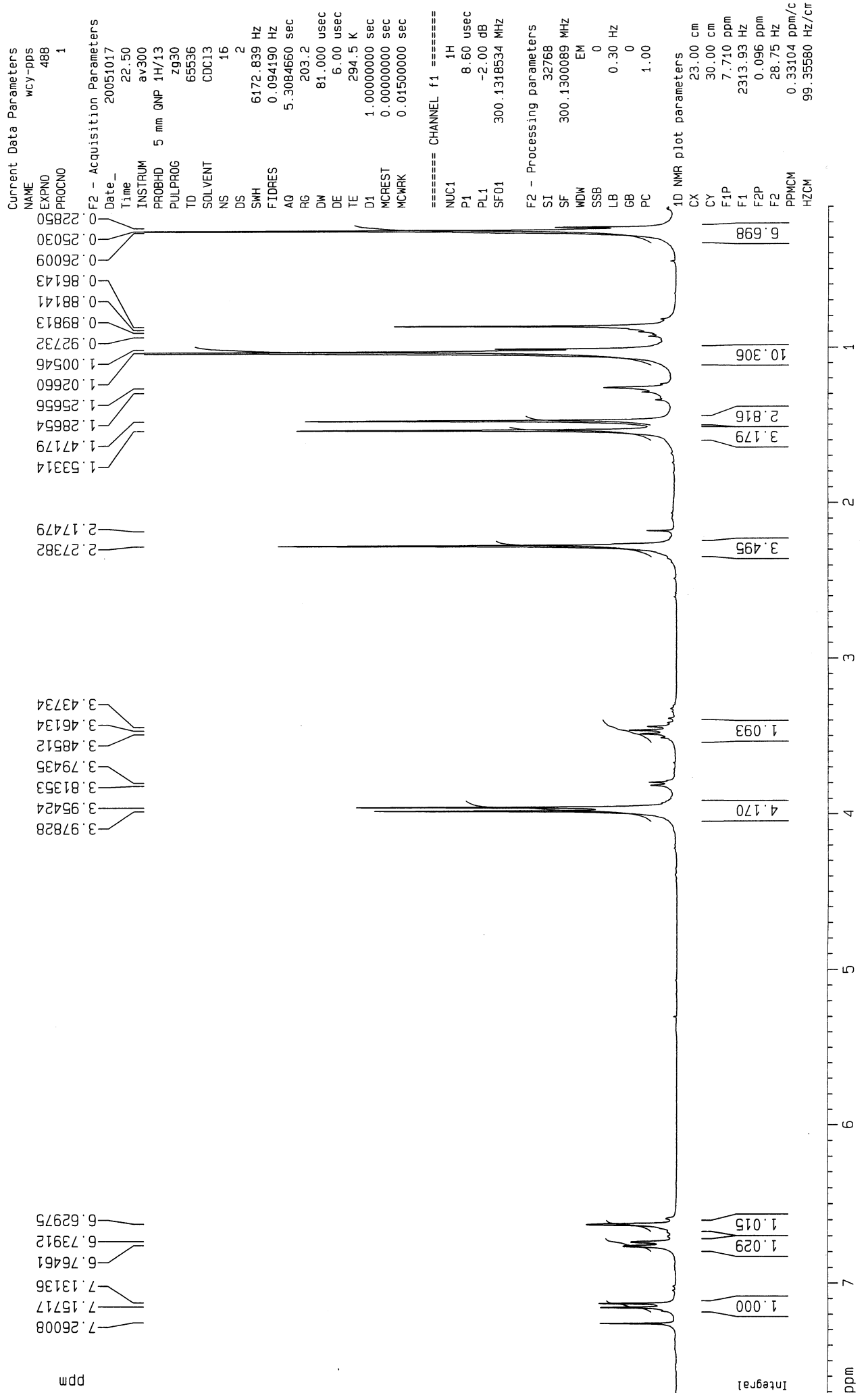
wcy-495/497

Compound 15b





Compound 156





Compound 16

Current Data Parameters
 NAME . wcy-pps
 EXPNO 468
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20051016
 Time 9.49

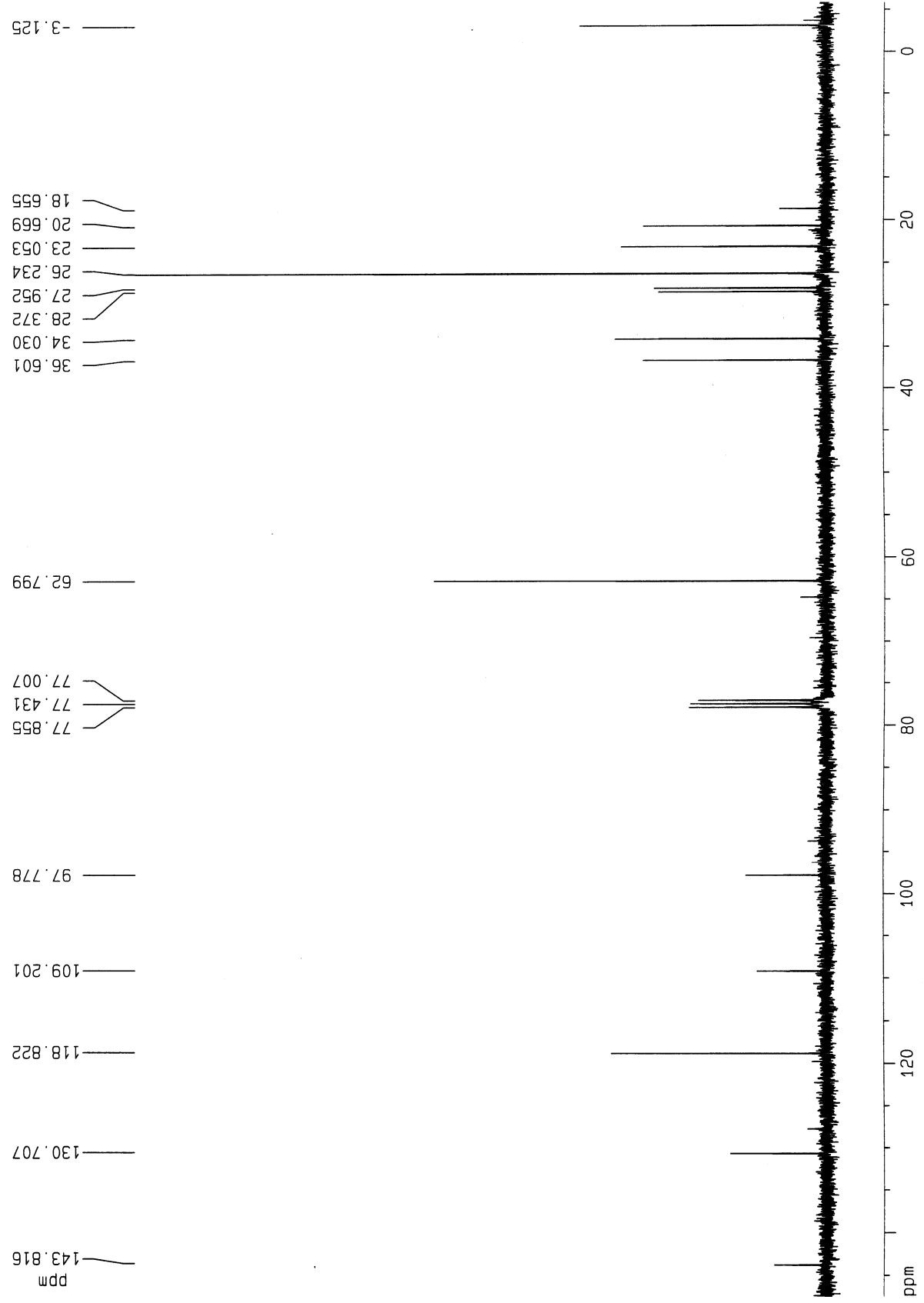
INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zgdc
 TD 32768
 SOLVENT CDC13
 NS 160
 DS 4
 SWH 21097.047 Hz
 FIDRES 0.643831 Hz
 AQ 0.7766516 sec
 RG 16384
 DW 23.700 usec
 DE 6.00 usec
 TE 295.3 K
 D1 6.00000000 sec
 d11 0.03000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

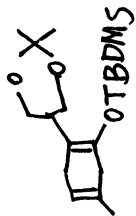
==== CHANNEL f1 =====
 NUC1 13C
 P1 8.20 usec
 PL1 -3.00 dB
 SF01 75.4767751 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 90.00 usec
 PL2 -2.00 dB
 PL12 18.00 dB
 SF02 300.1312005 MHz

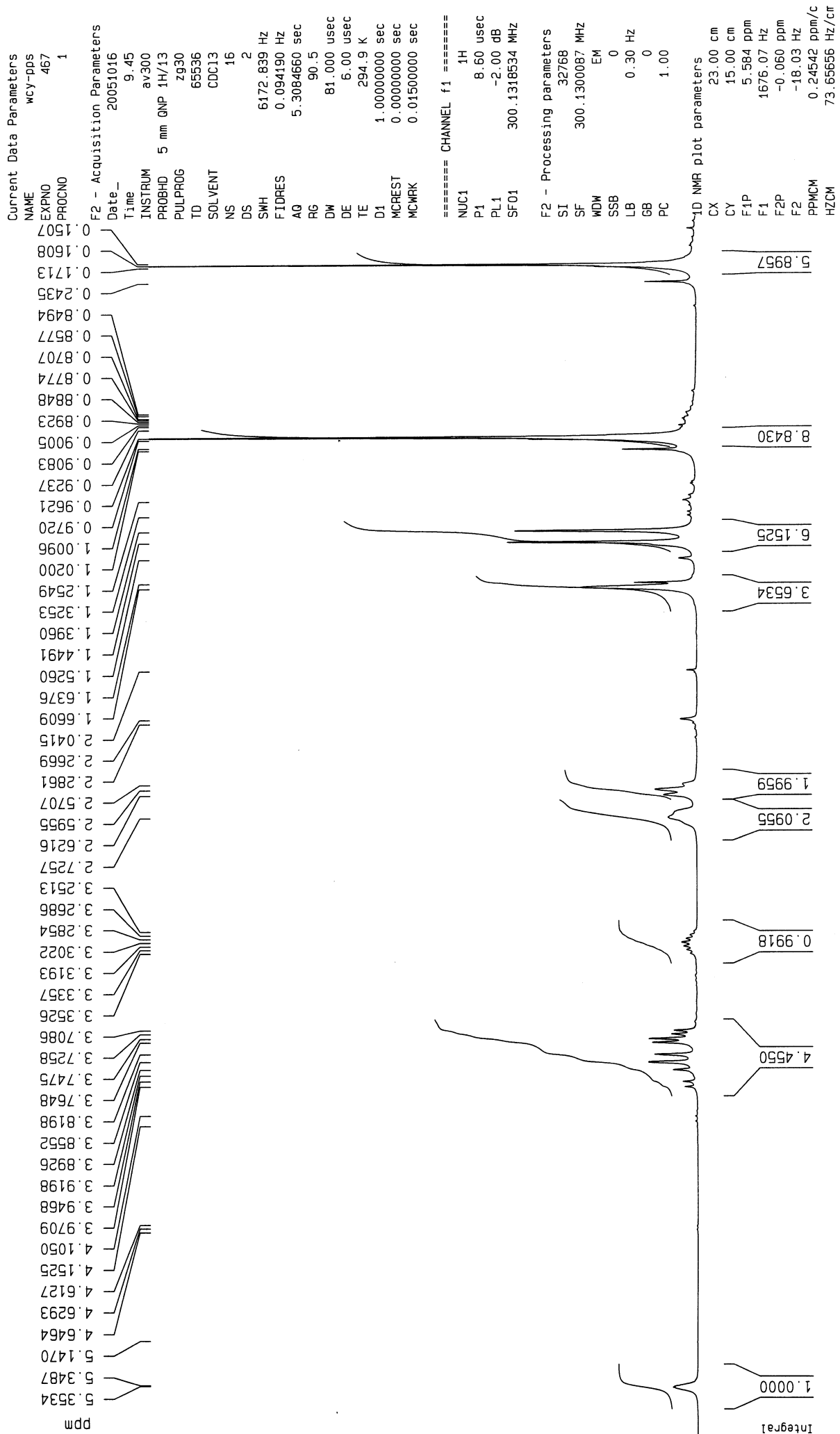
F2 - Processing parameters
 SI 32768
 SF 75.4677190 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 3.00

1D NMR plot parameters
 CX 22.00 cm
 CY 12.50 cm
 F1P 147.465 ppm
 F1 11128.84 Hz
 F2P -5.844 ppm
 F2 -441.00 Hz
 PPMCM 6.96857 ppm/cm
 HZCM 525.90192 Hz/cm

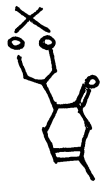




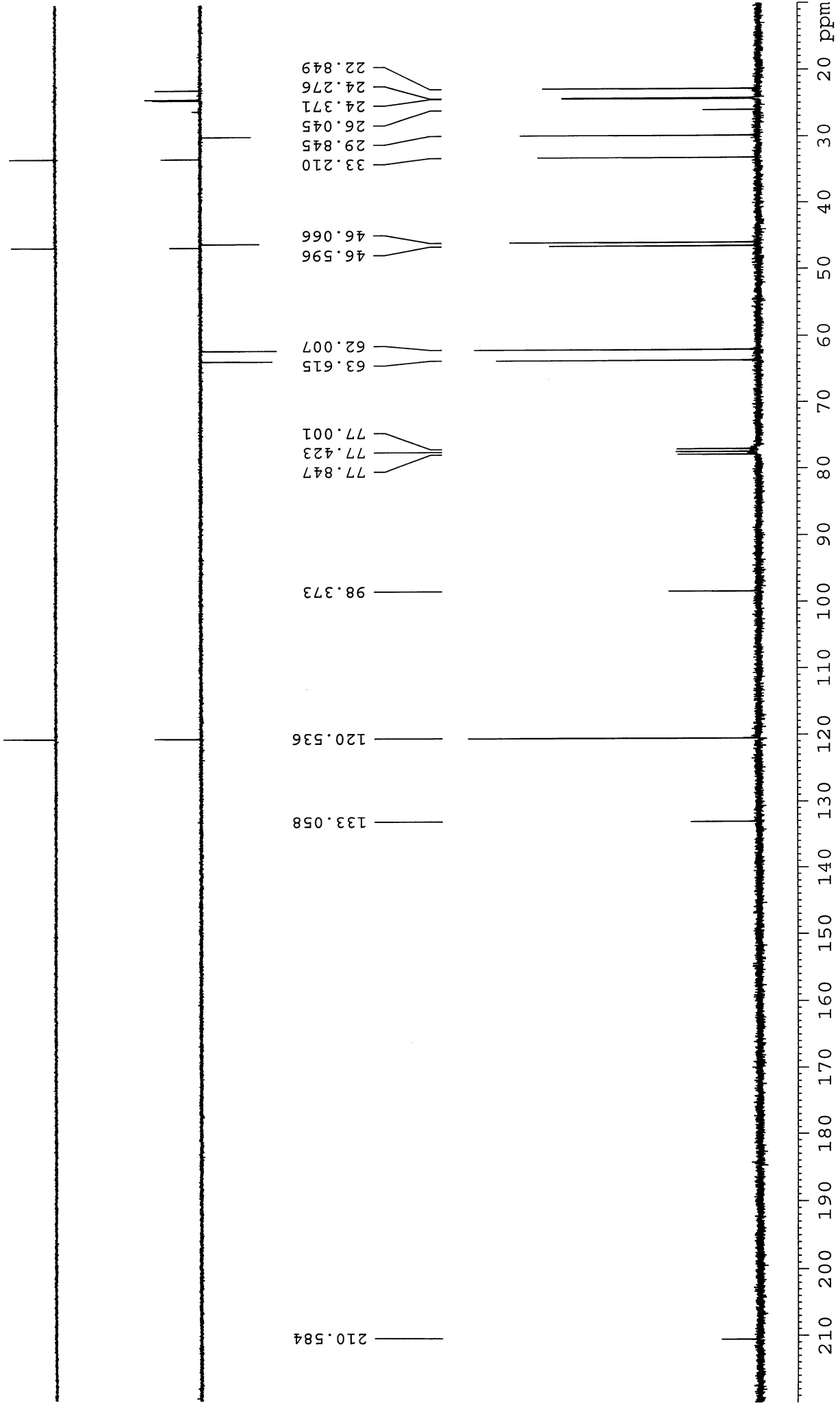
Compound 16

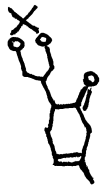


wcy-pps-222/224

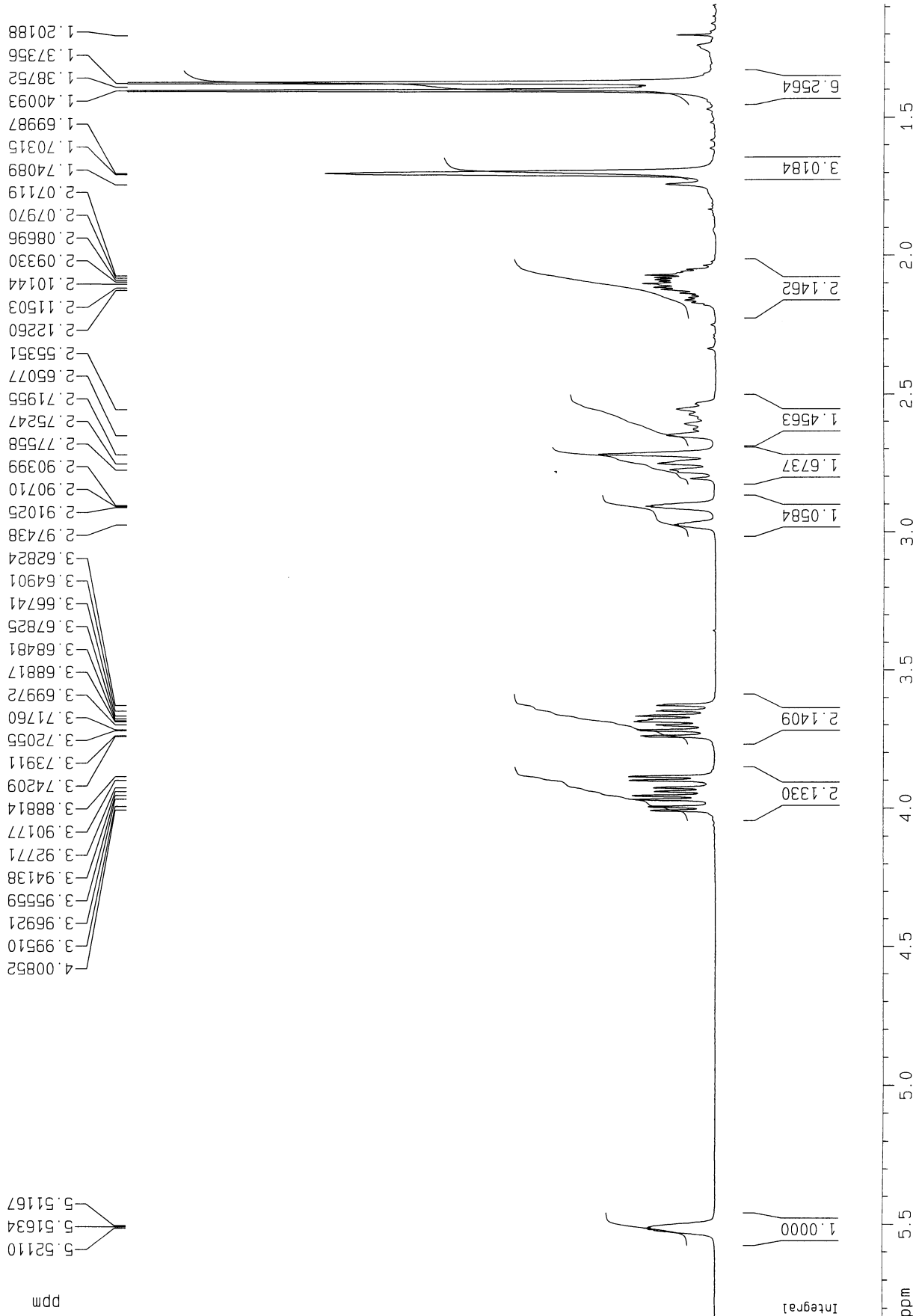


Compound 7





Compound 7



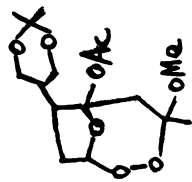
Current Data Parameter
 NAME wcy-pr
 EXPNO 225
 PROCNO

F2 - Acquisition Param
 Date_ 200508
 Time_ 9.2
 INSTRUM av3
 PROBHD 5 mm QNP 1H/1
 PULPROG zg
 TD 655
 SOLVENT CDC
 NS
 DS
 SMH 6172.8
 FIDRES 0.0941
 A0 5.308466
 RG 101
 DW 81.00
 DE 6.0
 TE 298
 D1 1.000000
 MCREST 0.000000
 MCWRK 0.015000

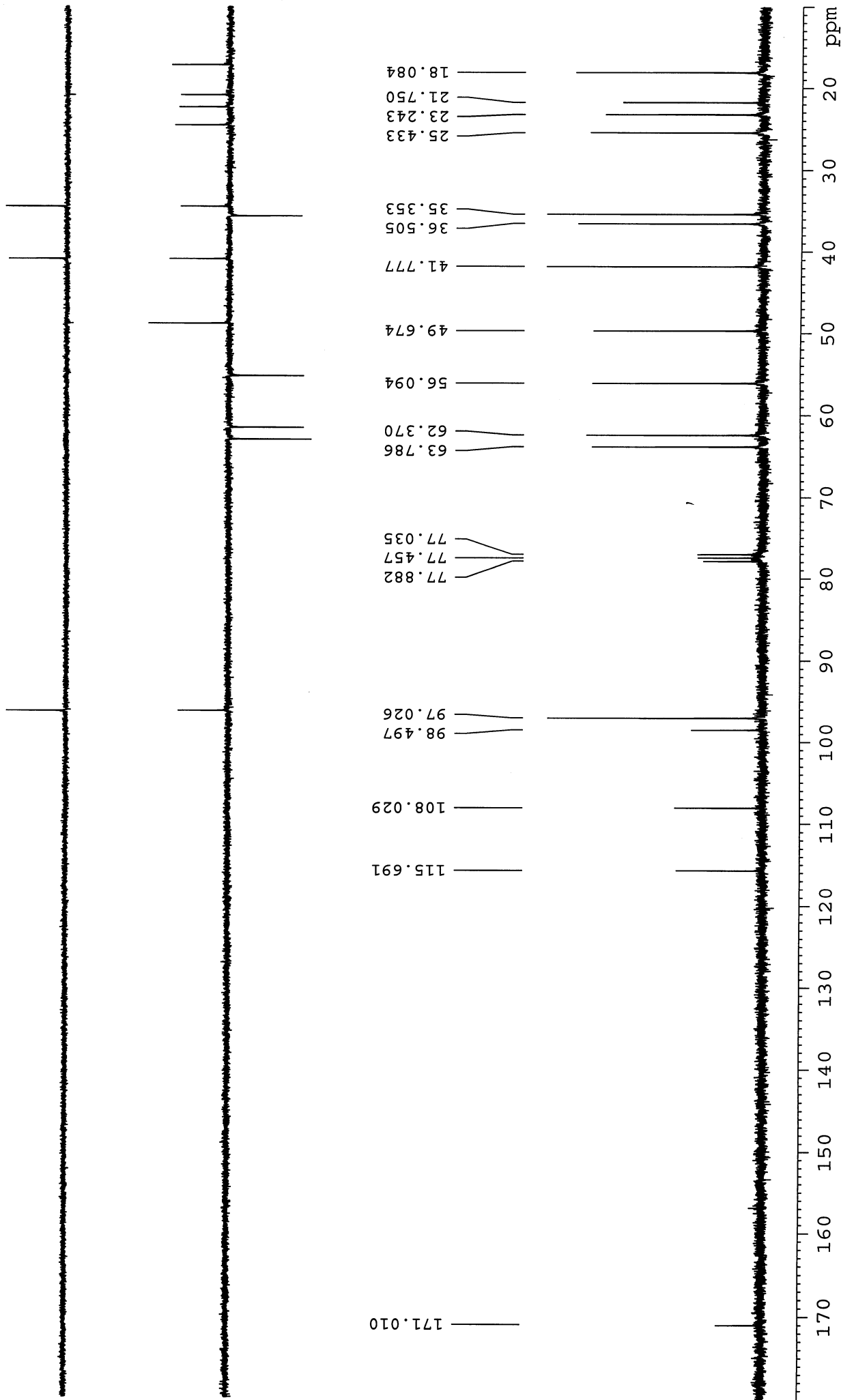
==== CHANNEL f1 ==
 NUC1
 P1 8.0
 PL1 -2.0
 SF01 300.13185
 F2 - Processing param
 SI 3278
 SF 300.130000
 WDM E
 SSB
 LB 0.3
 GB
 PC 1.0

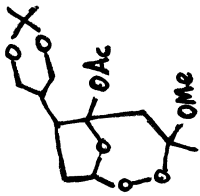
1D NMR plot parameters
 CX 23.0
 CY 15.0
 F1P 5.8
 F1 1750.8
 F2P 1.0
 F2 327.0
 PPMCM 0.206
 HZCM 61.904

wcy-pps-320/322

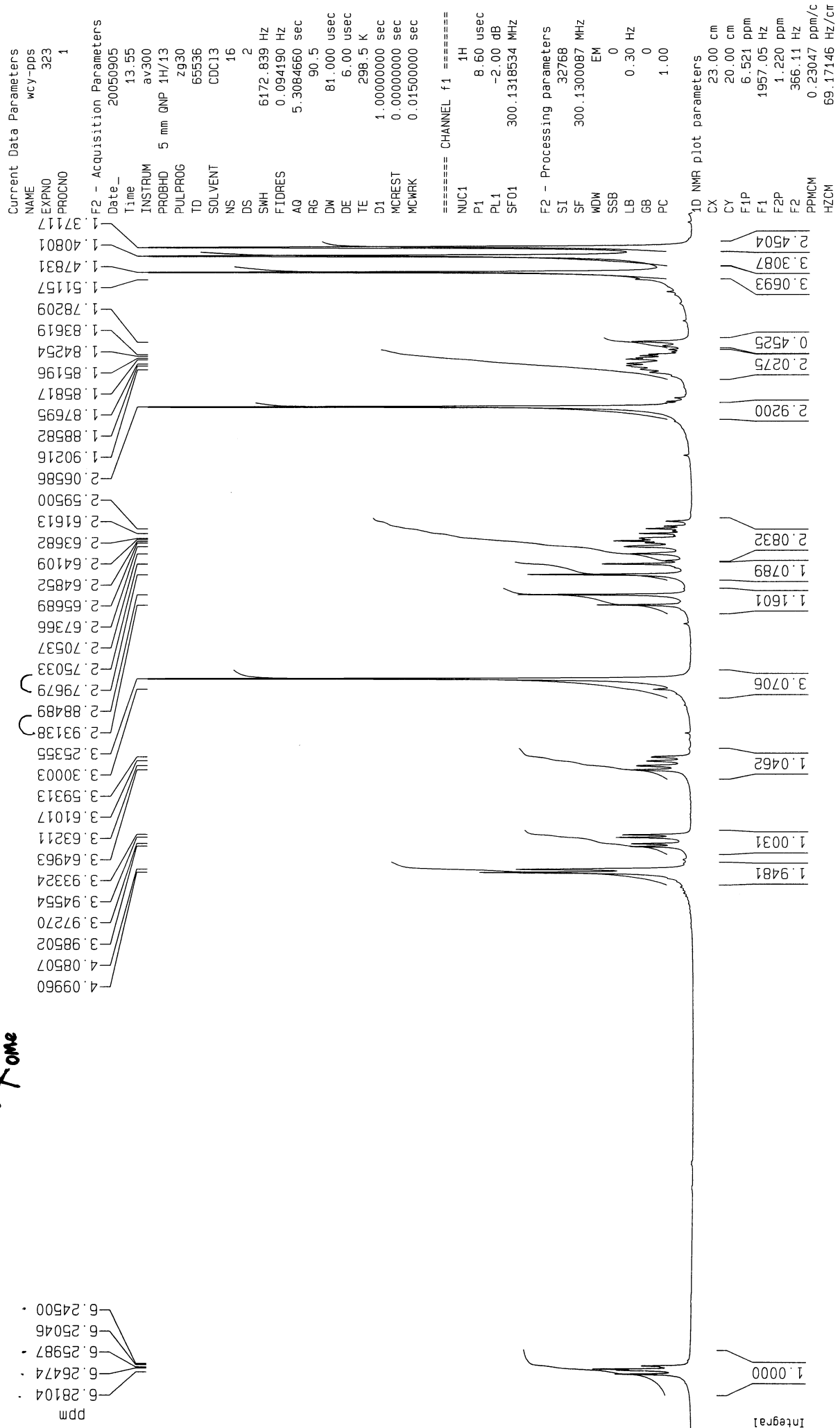


Compound 19





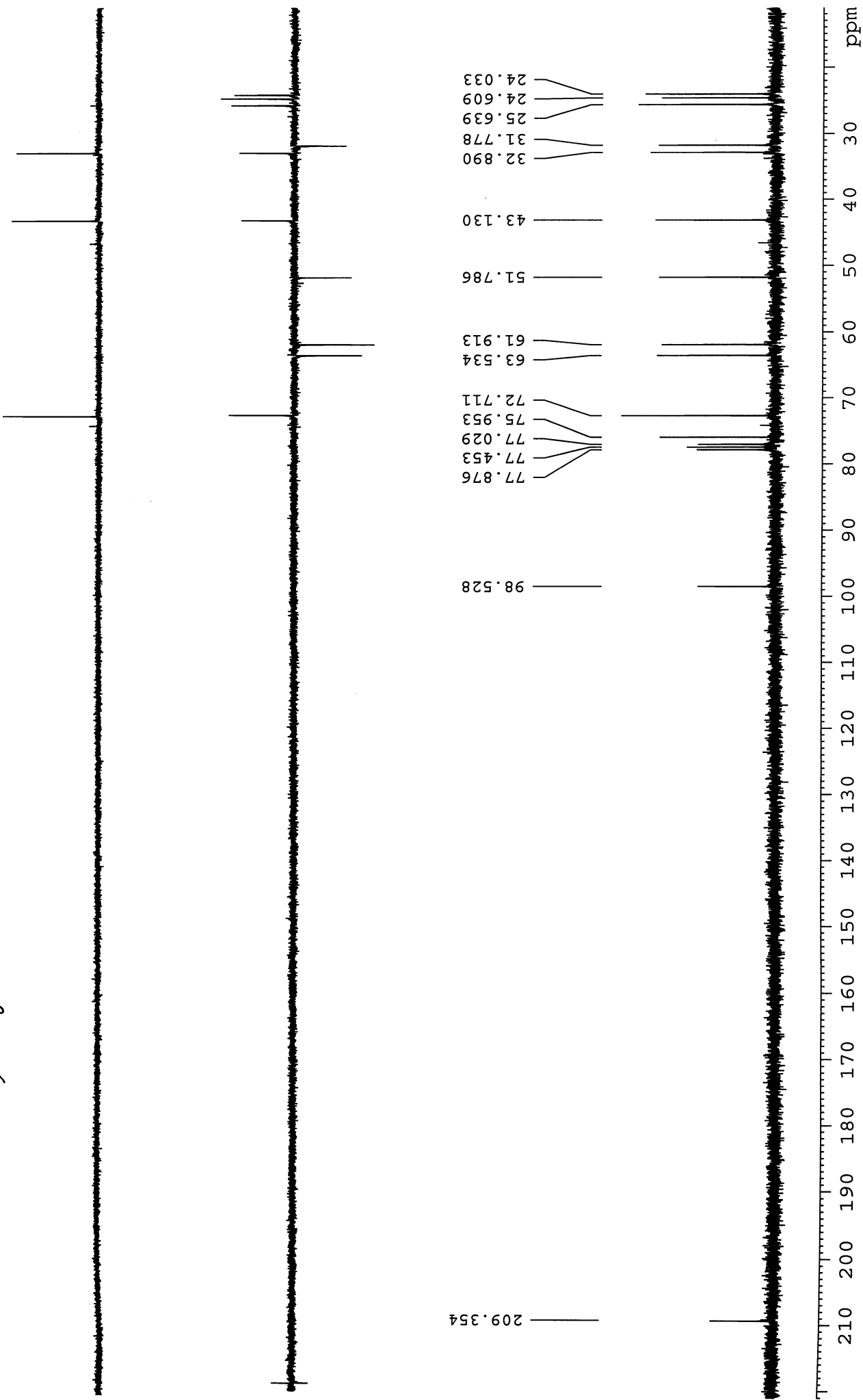
Compound 19



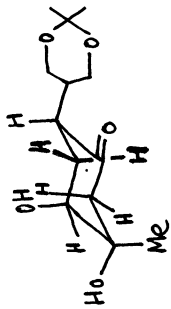
Compound 20



wcy-pps-377/379



Compound 20



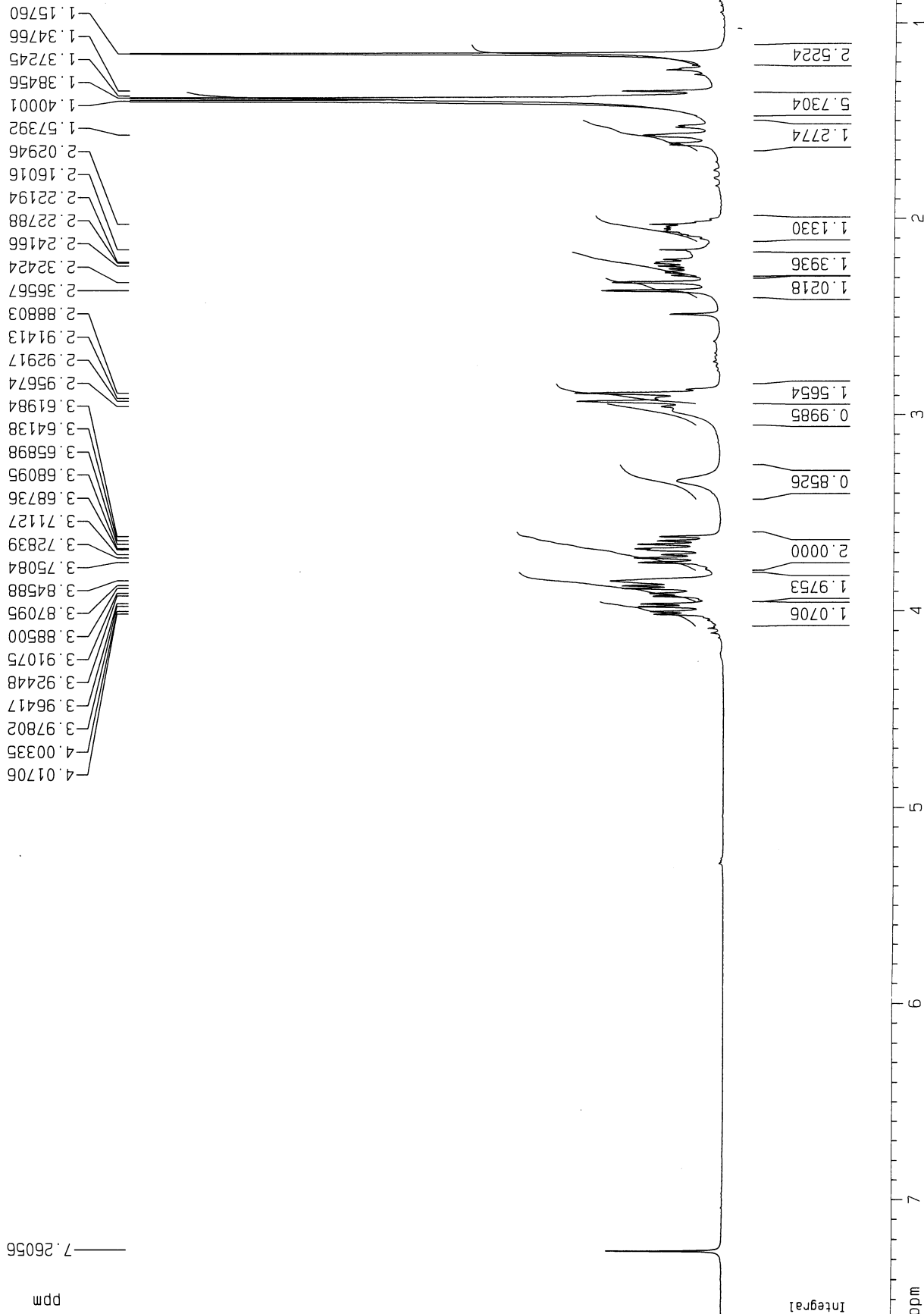
Current Data Parameters
 NAME wcy-pds
 EXPNO 380
 PROCNO 1

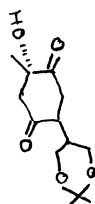
F2 - Acquisition Parameters
 Date_ 20050923
 Time 18.02
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 16
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 128
 DW 81.000 usec
 DE 6.00 usec
 TE 295.4 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 8.60 usec
 PL1 -2.00 dB
 SF01 300.1318534 MHz

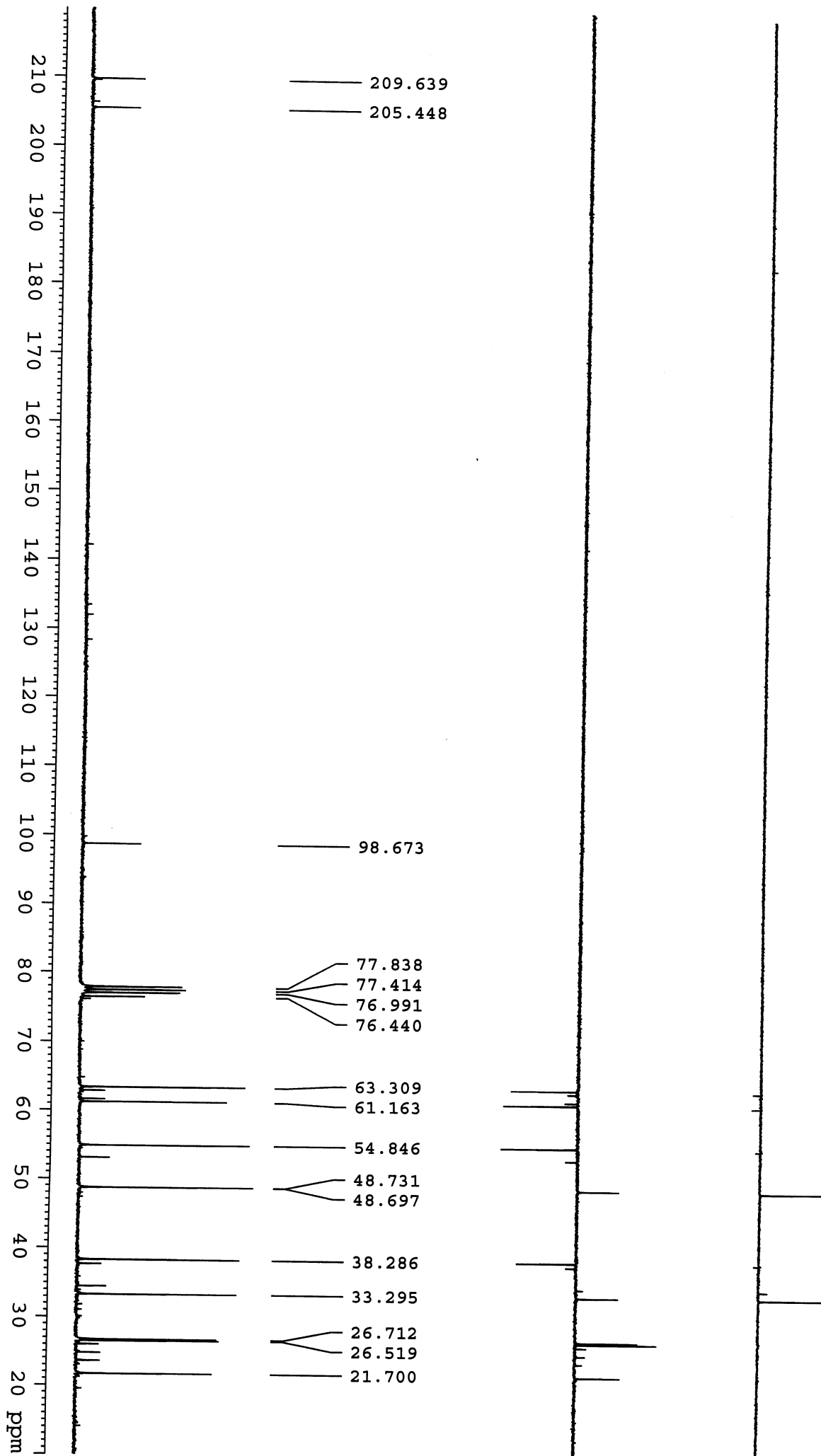
F2 - Processing parameters
 SI 32768
 SF 300.1300087 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

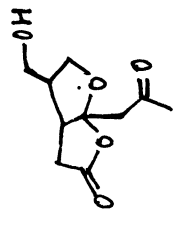
1D NMR plot parameters
 CX 23.00 cm
 CY 15.00 cm
 F1P 7.583 ppm
 F1 2275.98 Hz
 F2P 0.835 ppm
 F2 250.67 Hz
 PPMCM 0.29340 ppm/c
 HZCM 88.05703 Hz/cr





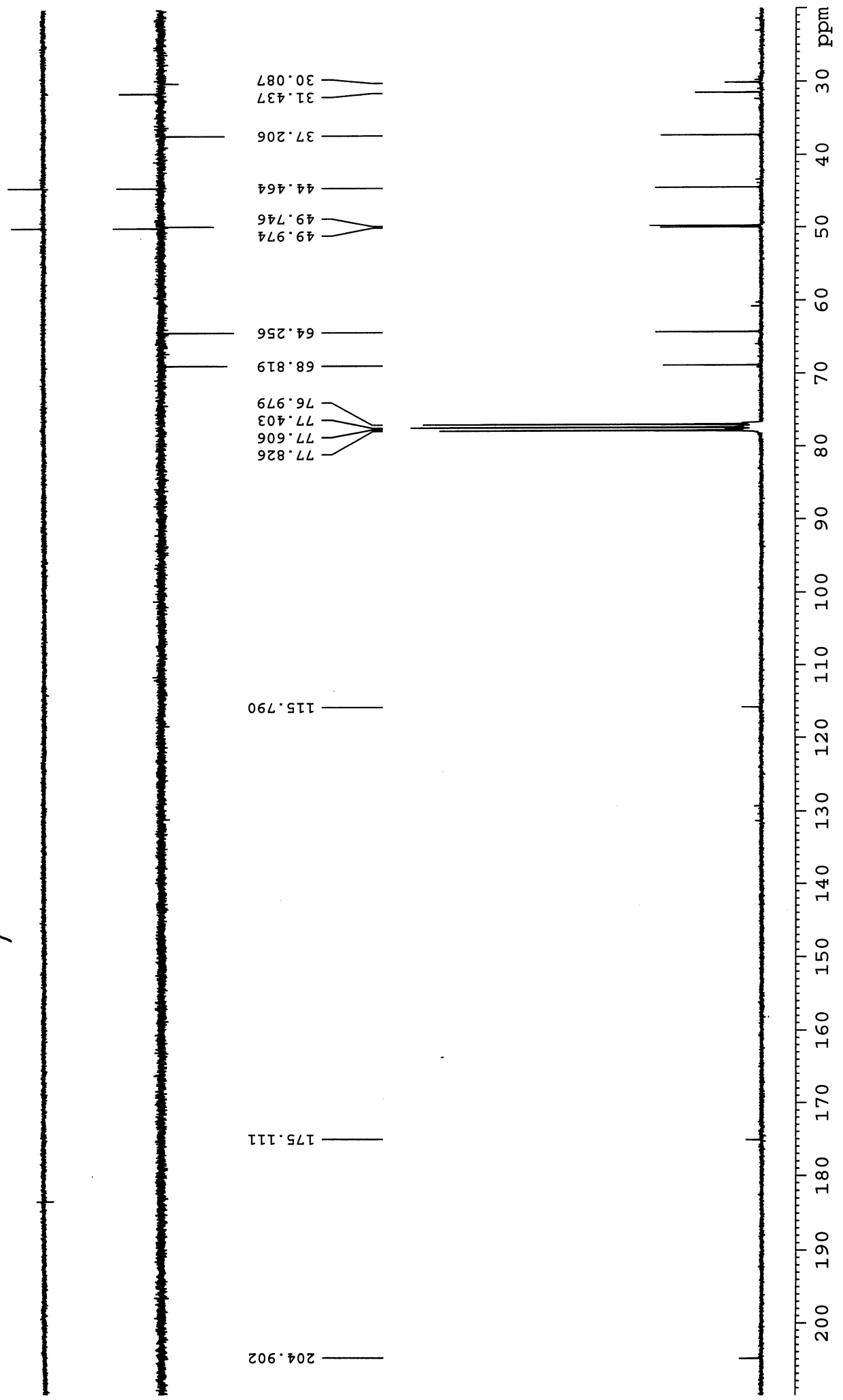
Compound 21

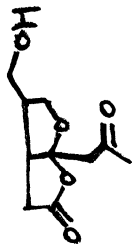




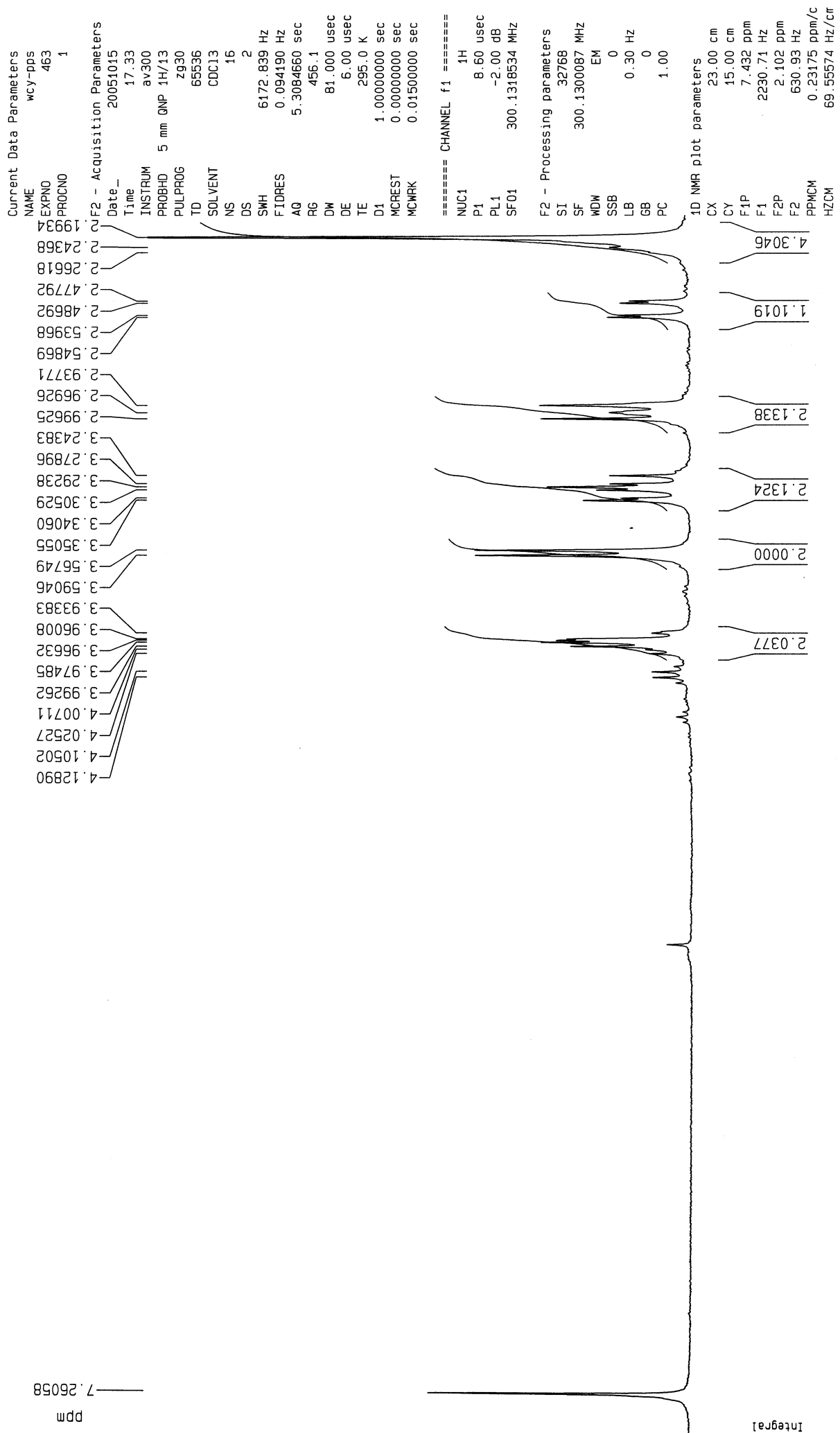
Compound 5

WCI-PPS-465/466-472



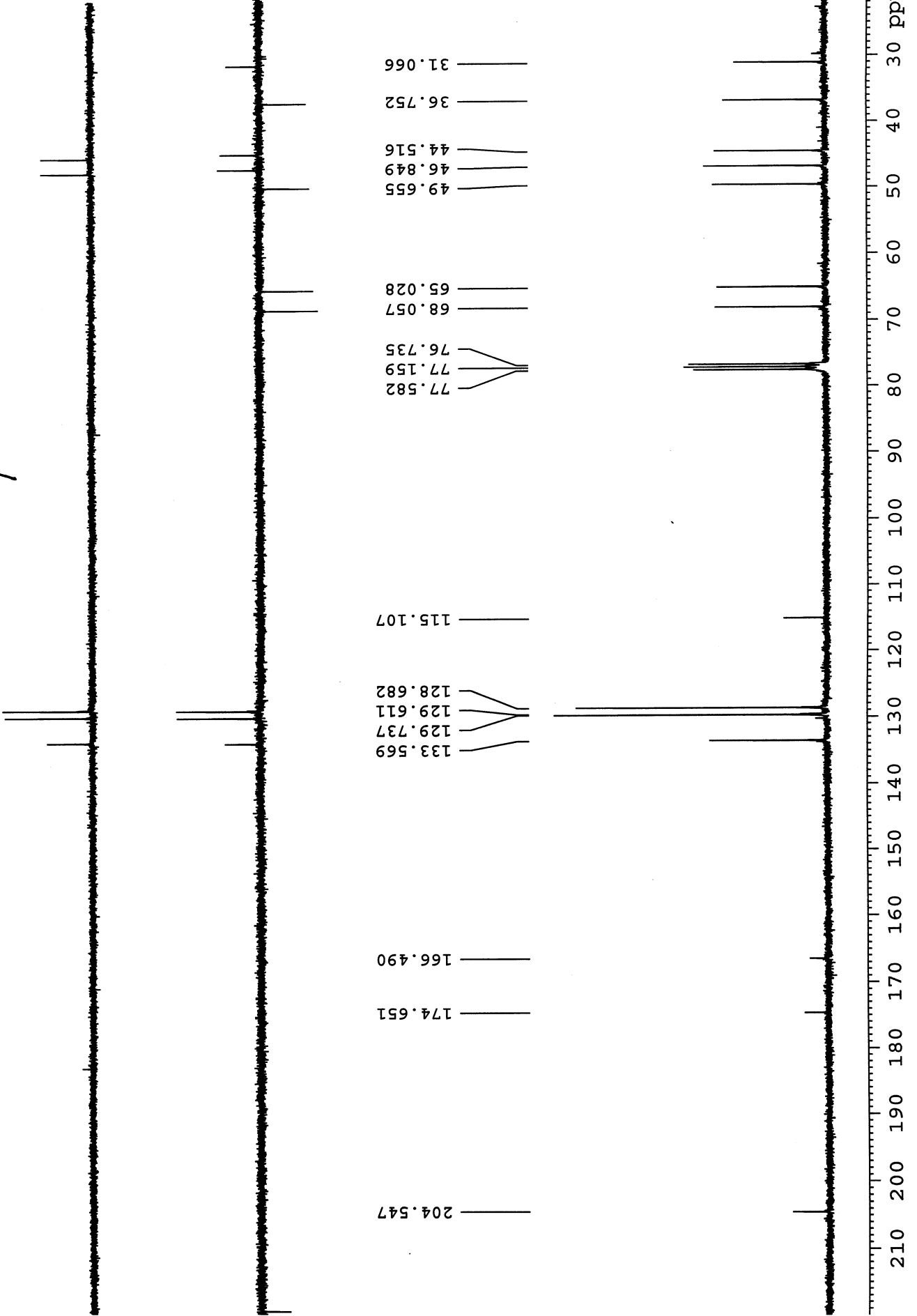
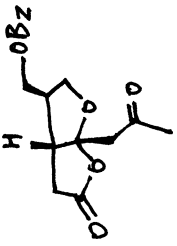


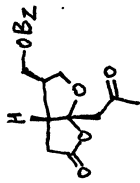
Compound 5



wcy-pps-438/440

Compound 4





Compound 4



1c12 roesy

Current Data Parameters
 NAME 1c12
 EXPNO 28
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20051116
 Time 14.13
 INSTRUM DPX500
 PROBHD 5 mm BBI 1H-BB
 PULPROG crossph
 TD 1024
 SOLVENT Acetone
 NS 8
 DS 16
 SWH 4006.410 Hz
 FIDRES 3.912510 Hz
 AQ 0.1278452 sec
 RG 64
 DW 124.600 USEC
 DE 6.00 USEC
 TE 300.0 K
 d0 0.00000000 sec
 d1 2.00000000 sec
 d12 0.00000000 sec
 d13 0.00004000 sec
 INO 0.00024894 sec
 MCREST 0.00000000 sec
 MCWRR 2.00000000 sec

***** CHANNEL f1 *****

NUC1 1H
 P1 8.90 USEC
 P15 1200000.00 USEC
 PL1 -1.00 DB
 PL11 22.20 DB
 SFO1 500.1318205 MHz

F1 - Acquisition parameters

NU0 1
 TO 136
 SFO1 500.1323 MHz
 FIDRES 29.419119 Hz
 SW 8.000 ppm
 F1MODE TPPI

F2 - Processing parameters

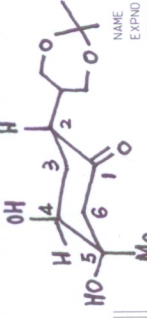
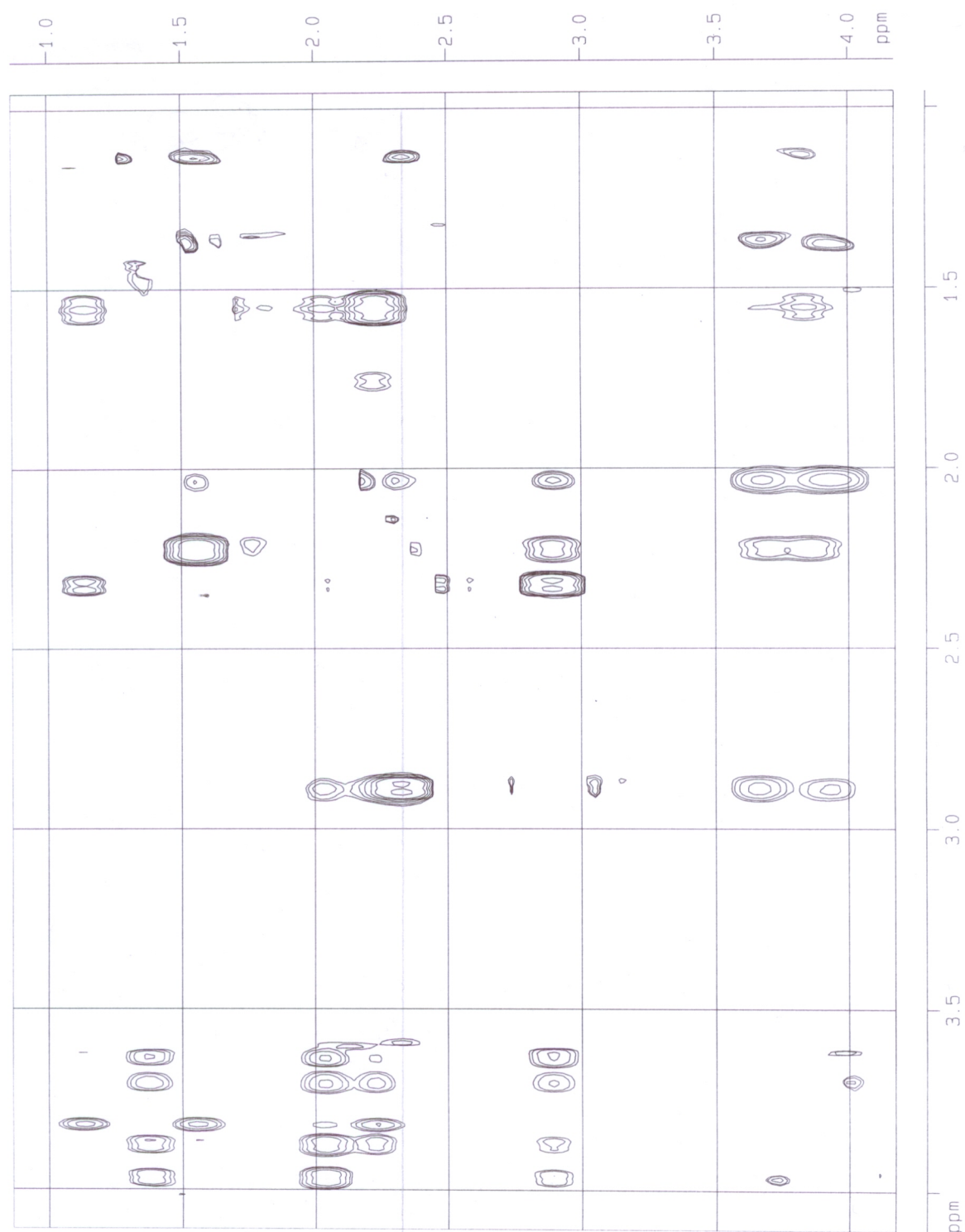
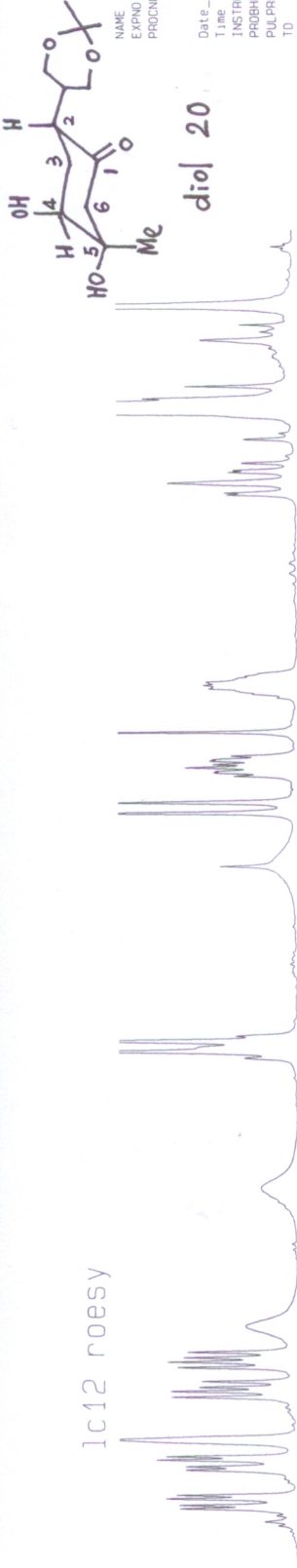
SF 1024
 SF 500.1300160 MHz
 WDW DSINE
 SSB 2
 LB 0.00 Hz
 GB 0
 PC 1.00

F1 - Processing parameters

SI 256
 MC2 TPPI
 SF 500.1304936 MHz
 WDW DSINE
 SSB 2
 LB 0.00 Hz
 GB 0

20 NMR pilot parameters

CX2 18.00 cm
 CX1 14.00 cm
 F2PLO 4.109 ppm
 F2LO 2054.67 Hz
 F2PHI 0.956 ppm
 F2HI 478.13 Hz
 F1PLO 4.176 ppm
 F1LO 2088.31 Hz
 F1PHI 0.863 ppm
 F1HI 431.65 Hz
 F2PRMCM 0.17515 ppm/cm
 F2RZCM 87.58675 Hz/cm
 F1PRMCM 0.23660 ppm/cm
 F1RZCM 118.33315 Hz/cm



diol 20