

SUPPORTING INFORMATION

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Experimental part

All reactions were performed under nitrogen atmosphere with oven (80°C) or flame-dried glassware. All solvents were distilled prior to use; diethyl ether and tetrahydrofuran were dried by distilling over sodium benzophenone ketyl. Toluene, acetonitrile, dichloromethane and dimethylformamide were distilled over calcium hydride. Cesium carbonate and sodium iodide were flame-dried under reduced pressure before use. Materials were detected by visualization under ultraviolet lamp and/or by spraying with a solution of phosphomolybdic acid (10% in ethanol) or an aqueous solution of KMnO₄ (1% w/w) followed by heating on a hot plate. For the NMR spectra assignments, the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad. Chemical shifts are reported in δ values relative to the solvent used (CHCl₃: 7.26 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR) as internal standard. Where necessary COSY, NOESY and J-resolved correlation experiment were performed.

Alcohol 5.

To a solution of but-3-yn-1-ol (1 mL, 13.2 mmol) in CH₂Cl₂ (60 mL) at 0°C, was added *p*-toluenesulfonic acid (29.3 mg, 0.15 mmol) followed by 3,4-dihydro-2H-pyran (1.55 mL, 17 mmol). The solution was stirred overnight at room temperature. NaHCO₃ (32 mg) and sat. NaHCO₃ (25 mL) were introduced and the mixture was stirred for 15 min, followed by extraction with CH₂Cl₂ (3 x 60 mL). The organic layer was dried over MgSO₄, the solvent was evaporated *in vacuo*, and the residue was chromatographed on silica gel with 5% EtOAc in hexane to give **5** as an oil (1.75 g, 86%).

¹H NMR (300 MHz, CDCl₃, δ ppm): 4.65 (1H, t, J=3.5Hz, OCH₂O); 3.92-3.80 (2H, m, CH₂CH₂O); 3.60-3.45 (2H, m, CH₂CH₂O); 2.50 (2H, td, J=7Hz, 3Hz, OCH₂CH₂); 1.95 (1H, t, J=2.5Hz, HC C); 1.85-1.50 (6H, m, CH₂ THP). ¹³C NMR (75 MHz, CDCl₃, δ ppm): 98.57, 81.27, 69.17, 65.38, 61.99, 30.41, 25.32, 19.82, 19.26. IR (film, ν cm⁻¹): 3294, 2943, 2873, 2359, 2120, 1441, 1201. MS (MH)⁺: 153. HRMS calcd: 153.0915 (MH)⁺; found: 153.0918.

Chlorohydrine 6

A solution of allyl chloride (3 mL, 36.8 mmol) in CH₂Cl₂ (20 mL) at -78°C was treated with ozone. The mixture was quenched with dimethyl-sulfide (37 mL) at -78°C and was warmed to room temperature over 2 h. The chloroacetaldehyde was purified by distillation (bp. \approx 80°C).

To a solution of alkynol **5** (1.55 g, 10.09 mmol) in THF (25 mL) at -40°C, was added *n*-BuLi (8.53 mL, 11.09 mmol). After 10 min, the mixture was cooled to -60°C. Chloroacetaldehyde (1.11 g, 14.25 mmol) was added dropwise via a cannula at -60°C, and the mixture was warmed to room temperature and stirred for 2h. Sat. NH₄Cl (25 mL) was then added and the compound was extracted with Et₂O (3 x 25 mL). The organic layer was dried

over MgSO_4 and the residue was chromatographed on silica gel with 20% EtOAc in hexane to give **6** as an oil (1.4 g, 60%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 4.60 (1H, m, OCHO) ; 4.50-4.45 (1H, m, OCHC C) ; 3.85-3.75 (2H, m, CH_2O) ; 3.65-3.45 (4H, m, CH_2Cl , CH_2O) ; 3.30 (1H, d, $J=5.5\text{Hz}$, OH) ; 2.50 (2H, td, $J=7\text{Hz}$, 2Hz, C C CH_2) ; 1.80-1.45 (6H, m, CH_2 THP). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 98.68, 83.83, 78.72, 65.68, 62.42, 62.15, 48.98, 30.40, 25.28, 20.09, 19.23. IR (film, ν cm^{-1}): 3383, 2944, 2661, 2231, 1201. MS (M-H) $^+$: 231. HRMS calcd: 231.0788 (M-H) $^+$; found: 231.0792.

Alcohol 7

To a solution of chlorohydrin **6** (0.64 g, 2.77 mmol) in THF (28 mL) at 0°C , 2,6-lutidine (0.42 mL, 3.6 mmol) and triisopropylsilane triflate (0.9 mL, 3.33 mmol) were added. The mixture was stirred for 45 min at 0°C , quenched with sat. NH_4Cl (25 mL) then extracted with Et_2O (3 x 25 mL). The organic layer was dried over MgSO_4 and the residue was chromatographed on silica gel with 20% Et_2O in hexanes to give **7** (1.05 g, 98%) as an oil.

^1H NMR (300 MHz, CDCl_3 , δ ppm): 4.65-4.55 (2H, m, OCHO et OCHC C) ; 3.90-3.75 (2H, m, CH_2O) ; 3.65-3.45 (4H, m, CH_2Cl , CH_2O) ; 2.50 (2H, td, $J=7\text{Hz}$, 2Hz, C C CH_2) ; 1.85-1.50 (6H, m, CH_2 THP) ; 1.30-1.10 (21H, m, TIPS). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 98.26, 83.03, 79.63, 65.13, 63.82, 61.50, 48.66, 30.33, 25.35, 19.96, 19.06, 17.74, 12.17, 12.13, 12.08. IR (film, ν cm^{-1}): 2944, 2867, 2363, 2229, 1464, 1201. MS (M - C_3H_7) $^+$: 345. HRMS calcd: 345.1653 (M - C_3H_7) $^+$; found: 345.1657.

Alkene 8

To a solution of alkyne **7** (1.5 g, 3.87 mmol) in Et_2O (40 mL), Lindlar catalyst (250 mg) was added under H_2 . The mixture was stirred for 4 h at room temperature and filtered through Celite with Et_2O . The organic layer was dried over MgSO_4 and evaporated *in vacuo* to give the alkene **8** (1.48 g, 98%) as an oil.

^1H NMR (300 MHz, CDCl_3 , δ ppm): 5.60-5.40 (2H, m, $\text{HC}=\text{CH}$) ; 4.70 (1H, td, $J=6.5\text{Hz}$, 6Hz, CHOTIPS) ; 4.60-4.55 (1H, m, OCHO) ; 3.90-3.70 (2H, m, CH_2O) ; 3.55-3.35 (4H, m, CH_2Cl , CH_2O) ; 2.45-2.35 (2H, m, $\text{CH}_2\text{-CH=}$) ; 1.85-1.50 (6H, m, CH_2 THP) ; 1.12-0.91 (21H, m, TIPS). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 132.30, 128.45, 98.88, 69.24, 66.52, 62.23, 48.97, 30.58, 28.94, 25.41, 19.52, 17.94, 12.20. IR (film, ν cm^{-1}): 2944, 2867, 1654, 1464. MS (M - C_3H_7) $^+$: 347.

HRMS calcd: 347.1809 (M - C_3H_7) $^+$; found: 347.1818.

Alcohol 9

To a solution of alcohol **8** (1.5 g, 3.84 mmol) in MeOH (39 mL) was added *p*-Toluenesulfonic acid (73 mg, 0.38 mmol). The solution was stirred for 1 h at room temperature and was quenched with sat. NaHCO_3 (30 mL). The mixture was extracted with Et_2O (3 x 30 mL). The organic layer was dried over MgSO_4 , the solvent was evaporated *in vacuo*, and the residue was chromatographed on silica gel with 30% EtOAc in hexanes to give **9** (0.88 g, 75%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 5.60-5.50 (2H, m, $\text{CH}=\text{CH}$) ; 4.69 (1H, ABX, $J_{\text{AX}}=6.5\text{Hz}$, $J_{\text{BX}}=5.5\text{Hz}$, CHOTIPS) ; 3.70 (2H, td, $J=6.5\text{Hz}$, 1Hz, CH_2OH) ; 3.55 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{BX}}=5.5\text{Hz}$, CHHCl) ; 3.40 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{AX}}=6.5\text{Hz}$, CHHCl) ; 2.40 (2H, m, $\text{CH}_2\text{CH}=\text{CH}$) ; 1.10-0.85 (21H, m, TIPS). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 133.07, 128.22, 69.05, 61.83, 48.74, 31.60, 17.87, 12.20. IR (film, ν cm^{-1}): 3333, 2944, 2866, 1654, 1094. MS (M - C_3H_7) $^+$: 263. HRMS calcd: 263.1234 (M - C_3H_7) $^+$; found: 263.1239.

Mesylate 10

To a solution of alcohol **9** (1.74 g, 5.68 mmol) in CH_2Cl_2 (56 mL) at 0°C were added triethylamine (1.15 mL, 7.95 mmol), methanesulfonyl chloride (0.53 mL, 6.81 mmol) and 4-dimethylaminopyridine (69 mg, 0.57 mmol). After stirring for 30 min at 0°C , the mixture was quenched with sat NH_4Cl (50 mL), then extracted with CH_2Cl_2 (3 x 50 mL). The organic layer was dried over MgSO_4 and the solvent was evaporated *in vacuo*. The residue was chromatographed on silica gel with 20% EtOAc in hexanes to give **10** (2.13 g, 98%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 5.60-5.55 (2H, m, $\text{CH}=\text{CH}$) ; 4.65 (1H, ABX, $J_{\text{AX}}=7\text{Hz}$, $J_{\text{BX}}=5.5\text{Hz}$, CHOTIPS) ; 4.25 (2H, t, $J=6.5\text{Hz}$, CH_2OSO_2) ; 3.55 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{BX}}=5.5\text{Hz}$, CHHCl) ; 3.40 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{AX}}=7\text{Hz}$, CHHCl) ; 3.00 (3H, s, CH_3) ; 2.60-2.55 (2H, td, $J=6.5\text{Hz}$, 6Hz , $\text{CH}_2\text{CH}=\text{CH}$) ; 1.20-0.90 (21H, m, TIPS). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 134.13, 125.85, 68.90, 68.58, 48.53, 37.33, 28.30, 17.86, 12.24. IR (film, ν cm^{-1}): 2945, 2867, 1464, 1177. MS ($\text{M} - \text{C}_3\text{H}_7$) $^+$: 341. ($\text{M} - \text{CH}_2\text{Cl}$) $^+$: 335. HRMS calcd: 341.1009 ($\text{M} - \text{C}_3\text{H}_7$) $^+$; found: 341.1016.

Malonate 11

To a solution of sodium hydride in a mixture of THF and DMF (1/1, 76 mL) at 0°C , dimethyl-malonate was added dropwise. The resulting mixture was stirred at room temperature 20 min then the mesylate **10** (2.49 g, 7.63 mmol) and potassium iodide (2.53 g, 15.27 mmol) were added. The solution was stirred at 80°C for 3 h. The mixture was quenched at room temperature with sat NH_4Cl (70 mL) and extracted with a mixture of Et_2O and hexane (1/1, 3 x 70 mL). The organic layer was dried over MgSO_4 , the solvent was removed, and the residue was chromatographed on silica gel with 20% Et_2O in hexane yielded **11** (2.56 g, 80%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 5.50-5.25 (2H, m, $\text{CH}=\text{CH}$) ; 4.65 (1H, ABX, $J_{\text{BX}}=6\text{Hz}$, $J_{\text{AX}}=6.5\text{Hz}$, CHOTIPS) ; 3.75 (6H, s, CH_3O) ; 3.50 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{BX}}=6\text{Hz}$, CHHCl) ; 3.40 (1H, t, $J=7\text{Hz}$, CHCO_2Me) ; 3.35 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{AX}}=6.5\text{Hz}$, CHHCl) ; 2.15-2.05 (2H, m, $\text{CH}_2\text{-CH}=\text{CH}$) ; 2.00-1.95 (2H, m, CH_2CH) ; 1.10-0.85 (21H, m, TIPS). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 169.37, 131.96, 130.18, 68.95, 52.34, 50.83, 48.68, 28.38, 25.81, 17.84, 12.18. IR (film, ν cm^{-1}): 2946, 2807, 1755, 1738, 1469, 1434, 1249. MS ($\text{M} - \text{C}_3\text{H}_7$) $^+$: 377. ($\text{M} - \text{CH}_2\text{Cl}$) $^+$: 371. HRMS calcd: 377.1551 ($\text{M} - \text{C}_3\text{H}_7$) $^+$; found: 377.1556.

Ether 13

To a solution of the iodoalcohol **12** (1.32 g, 7.16 mmol) in CH_2Cl_2 (50 mL), were added *p*-toluenesulfonic acid (181 mg, 0.72 mmol) and 3,4-dihydro-2H-pyran (1 mL, 10.97 mmol) at room temperature. The solution was stirred overnight in the dark. The mixture was quenched with saturated aqueous NaHCO_3 (50 mL) and extracted with Et_2O (3 x 50 mL). The organic layer was dried over MgSO_4 , the solvent was removed, and the residue was chromatographed on silica gel with 20% Et_2O in hexanes to give **13** (1.82 g, 95%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 6.48 (1H, ddd, $J=8\text{Hz}$, 6Hz , 5Hz , $\text{CH}=\text{CH}$) ; 6.40 (1H, dt, $J=8\text{Hz}$, 1.5Hz , $\text{CH}=\text{CH}$) ; 4.65 (1H, m, OCHO) ; 4.28 (1H, complex system AB appearing as a ddd, $J_{\text{AB}}=13.5\text{Hz}$, $J=5\text{Hz}$, $J=1.5\text{Hz}$, CHHOTHP) ; 4.12 (1H, complex system AB appearing as a ddd, $J_{\text{AB}}=13.5\text{Hz}$, $J=6\text{Hz}$, $J=1.5\text{Hz}$, CHHOTHP) ; 3.90-3.85 (1H, m, CHHO THP) ; 3.55-3.50 (1H, m, CHHO THP) ; 1.85-1.5 (6H, m, CH_2THP). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 138.29, 98.42, 82.79, 69.99, 62.2, 30.49, 25.36, 19.34. IR (film, ν cm^{-1}): 2945, 2865, 1612, 1447. MS ($\text{M} - \text{OTHP}$) $^+$: 167 HRMS calcd: 166.9358 ($\text{M} - \text{OTHP}$) $^+$; found: 166.9363.

Ether 15

To the compound **14** (2.29 g, 6.17 mmol) in CH_2Cl_2 (40 mL), imidazole (1.05 g, 15.43 mmol) and *t*-butyldimethylsilyl chloride (1.12 g, 7.4 mmol) were added at 0°C. After stirring for 1 h at room temperature, water was added (40 mL), and the solution was extracted with CH_2Cl_2 (3 x 40 mL). The organic layer was dried over MgSO_4 , the solvent was removed and the residue was chromatographed on silica gel with 10% Et_2O in hexane yielding **15** as an oil (2.65 g, 93%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 6.17 (1H, ABX , $J_{\text{AB}}=19\text{Hz}$, $J_{\text{AX}}=1.5\text{Hz}$, $\text{CH}=\text{CHSn}$); 6.05 (1H, ABX , $J_{\text{AB}}=19\text{Hz}$, $J_{\text{BX}}=4\text{Hz}$, $\text{CH}=\text{CHSn}$); 4.20 (2H, ABX , $J_{\text{BX}}=4\text{Hz}$, $J_{\text{AX}}=1.5\text{Hz}$, CH_2OTBDMS); 1.60-1.43 (6H, m, CH_2Sn); 1.40-1.25 (6H, m, $\text{CH}_2\text{CH}_2\text{Sn}$); 1.00-0.75 (24H, m, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Sn}$, $\text{C}(\text{CH}_3)_3$); 0.05 (6H, s, CH_3Si). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 147.25, 126.77, 66.69, 28.94, 27.21, 25.92, 13.67, 9.36, -5.17. IR (film, ν cm^{-1}): 2928, 2855, 1463, 1361, 1253, 1093. MS ($\text{M} - \text{C}_4\text{H}_9$) $^+$: 405. HRMS calcd: 405.1636 ($\text{M} - \text{C}_4\text{H}_9$) $^+$; found: 405.1639.

Diene 18

To a solution of the alcohol **12** (0.82 g, 4.39 mmol) in *N,N*-dimethylformamide (45 mL), the compound **15** (2.79 g, 5.75 mmol) was added and the mixture was degassed. *Bis*-acetonitrile palladium-chloride (57 mg, 0.22 mmol) was added and the mixture was degassed again. The solution was stirred for 3 h at room temperature, quenched with saturated NH_4Cl (50 mL) and extracted with a mixture of Et_2O and hexane (1/1, 3 x 50 mL). The organic layer was dried over MgSO_4 , the solvent was removed and the residue was chromatographed on silica gel with 20% Et_2O in hexane to yield **18** as an oil (0.8 g, 80%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 6.55 (1H, dd, $J=15\text{Hz}$, 11Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.10 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.80 (1H, dt, $J=15\text{Hz}$, 5Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 5.58 (1H, m, $\text{CH}=\text{CHCH}=\text{CH}$); 4.30 (2H, td, $J=6\text{Hz}$, 1Hz , CH_2OH); 4.25 (2H, dd, $J=4.5\text{Hz}$, 1.5Hz , CH_2OTBDMS); 1.30-0.90 (9H, m, $(\text{CH}_3)_3\text{C}$); 0.05 (6H, s, CH_3Si). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 134.63, 129.85, 129.25, 124.08, 63.28, 58.61, 25.89, 18.37, -5.27. IR (film, ν cm^{-1}): 3345, 2929, 2857, 1656, 1613, 1471. MS ($\text{M} - \text{C}_4\text{H}_9$) $^+$: 171; ($\text{M} - \text{H}_2\text{O}$) $^+$: 210. HRMS calcd: 171.0841 ($\text{M} - \text{C}_4\text{H}_9$) $^+$; found: 171.0846; calcd: 210.1440 ($\text{M} - \text{H}_2\text{O}$) $^+$; found: 210.1447.

Diene 19

To a solution of alcohol **18** (0.50 g, 2.2 mmol) in *N,N*-dimethylformamide (20 mL) at 0°C were added 2,4,6-collidine (1.16 mL, 8.78 mmol) methanesulfonyl chloride (0.68 mL, 8.78 mmol) and dry lithium chloride (372 mg, 8.78 mmol). The solution was stirred at 0°C for 3 h and water (20 mL) was added. The mixture was extracted with hexane and ether (1/1, 3 x 30 mL). The organic layer was dried over MgSO_4 , the solvent was removed, and the residue was chromatographed on silica gel with 20% Et_2O in hexanes yielding **19** as an oil (0.43 g, 80%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 6.55 (1H, dd, $J=15\text{Hz}$, 11Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.10 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.90 (1H, dt, $J=15\text{Hz}$, 4.5Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 5.60 (1H, dt, $J=11\text{Hz}$, 8Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 4.30 (2H, dd, $J=4.5\text{Hz}$, 1Hz , CH_2OTBDMS); 4.21 (2H, d, $J=8\text{Hz}$, CH_2Cl); 1.30-0.90 (9H, m, $(\text{CH}_3)_3\text{C}$); 0.05 (6H, s, CH_3Si). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 136.47, 132.27, 124.96, 122.92, 63.15, 39.51, 25.89, 18.35, -5.27. IR (film, ν cm^{-1}): 2955, 2857, 1651, 1613, 1471. MS ($\text{M} - \text{C}_4\text{H}_9$) $^+$: 189; ($\text{M} - \text{Cl}$) $^+$: 211. HRMS calcd: 189.0502 ($\text{M} - \text{C}_4\text{H}_9$) $^+$; found: 189.0502.

triene 20

To a solution of sodium hydride (215 mg, 5.38 mmol) in N,N-dimethylformamide and tetrahydrofuran (1/1, 40 mL) at 0°C, the compound **11** (2.16 g, 5.13 mmol) was added dropwise via a cannula. The mixture was stirred at room temperature during 20 min, cooled at 0°C and the diene **17** (1.22 g, 5.65 mmol) in tetrahydrofuran (5 mL) was added dropwise via a cannula. The solution was stirred at room temperature for 17 h and quenched with sat. NH₄Cl (40 mL). The mixture was extracted with hexane and ether (1/1, 3 x 30 mL). The organic layer was dried over MgSO₄, the solvent was removed, and the residue was chromatographed on silica gel with toluene yielding **20** as an oil (2.68 g, 87%).

¹H NMR (300 MHz, CDCl₃, δ ppm): 6.40 (1H, dd, J=15Hz, 11Hz, CH=CHCH=CH); 6.05 (1H, t, J=11Hz, CH=CHCH=CH); 5.60-5.40 (4H, m, CH=CHCH=CH, CH=CH); 4.65-4.60 (2H, m, CHOTIPS, OCHO); 4.30 (1H, complex AB, J_{AB}=13Hz, J=6.5Hz, CHHOTHP); 4.20 (1H, complex AB, J_{AB}=13Hz, J=7Hz, CHHOTHP); 3.90-3.80 (1H, m, CHHO THP); 3.75 (6H, s, CH₃O); 3.55-3.50 (2H, m, CHHCl, CHHO THP); 3.35 (1H, ABX, J_{AB}=11Hz, J_{AX}=6.5Hz, CHHCl); 2.70 (2H, d, J=7.5Hz, CCH₂CH=CHCH=CH); 2.00-1.45 (10H, m, CH₂); 1.10-0.90 (21H, m, TIPS). ¹³C NMR (75 MHz, CDCl₃, δ ppm): 171.22, 131.45, 130.82, 130.60, 129.13, 126.61, 97.72, 69.09, 62.63, 62.10, 57.53, 53.41, 52.38, 48.72, 36.47, 32.45, 30.56, 25.41, 23.12, 19.39, 17.92, 12.22. IR (film, ν cm⁻¹): 2947, 2867, 1732, 1655, 1454, 1441. MS (M – C₃H₇)⁺: 557.

HRMS calcd: 557.2701 (M – C₃H₇)⁺; found: 557.2708.

Triene 21

The same method was applied from **11** (1.53 g, 3.62 mmol) and **19** (0.98 g, 3.99 mmol) and gave **21** as an oil (2.2 g, 96%).

¹H NMR (300 MHz, CDCl₃, δ ppm): 6.50 (1H, dd, J=15Hz, 11Hz, CH=CHCH=CH); 6.10 (1H, t, J=11Hz, CH=CHCH=CH); 5.80 (1H, dt, J=15Hz, 5Hz, CH=CHCH=CH); 5.50-5.30 (2H, m, CH=CHCH=CH, CH=CH); 5.20 (1H, dt, J=8Hz, 7.5Hz, CH=CH); 4.60 (1H, ABX, J_{AX}=6.5Hz, J_{BX}=6Hz, CHOTIPS); 4.20 (2H, d, J=5Hz, CH₂OTBDMS); 3.70 (3H, s, CH₃O); 3.68 (3H, s, CH₃O); 3.45 (1H, ABX, J_{AB}=11Hz, J_{BX}=6Hz, CHHCl); 3.35 (1H, ABX, J_{AB}=11Hz, J_{AX}=6.5Hz, CHHCl); 2.80 (2H, d, J=8Hz, CCH₂CH=CH); 2.00-1.90 (4H, m, CH₂CH₂); 1.10-0.90 (21H, m, TIPS); 0.9 (9H, s, (CH₃)₃C); 0.05 (6H, s, CH₃Si). ¹³C NMR (75 MHz, CDCl₃, δ ppm): 171.35, 134.45, 131.58, 131.49, 130.59, 124.25, 123.67, 69.08, 63.46, 57.33, 52.4, 52.34, 48.79, 32.25, 30.91, 25.86, 23.15, 17.90, 12.23, -5.28. IR (film, ν cm⁻¹): 2949, 2865, 1738, 1654, 1463, 1254. MS (M – C₃H₇)⁺: 587. HRMS calcd: 587.2991 (M – C₃H₇)⁺; found: 587.2980.

Alcohol 22

To a solution of THP ether **20** (2.68 g, 4.46 mmol) in methanol (50 mL), *para*-toluene-sulfonic acid (42 mg, 0.23 mmol) was added. The mixture was stirred for 2 h at room temperature, and quenched with NaHCO₃ sat (30 mL). The methanol was removed in vacuo and extracted with ether (3 x 45 mL). The organic layer was dried over MgSO₄, the solvent was removed, and the residue was chromatographed on silica gel with 20% Et₂O in hexanes yielding **22** as an oil (1.72 g, 75%).

¹H NMR (300 MHz, CDCl₃, δ ppm): 6.35 (1H, dd, J=14.5Hz, 11Hz, CH=CHCH=CH); 6.00 (1H, t, J=11Hz, CH=CHCH=CH); 5.60-5.30 (4H, m, CH=CHCH=CH, CH=CH); 4.60 (1H, ABX, J_{AX}=6.5Hz, J_{BX}=6Hz, CHOTIPS); 4.30 (2H, dd, J=7Hz, 1Hz, CH₂OH); 3.70 (6H, s, CH₃O); 3.50 (1H, ABX, J_{AB}=11Hz, J_{BX}=6Hz, CHHCl); 3.35 (1H, ABX, J_{AB}=11Hz, J_{AX}=6.5Hz, CHHCl); 2.70 (2H, d, J=7.5Hz, CCH₂CH=CH); 2.00-1.85 (4H, m, CH₂CH₂); 1.10-0.90 (21H, m, TIPS). ¹³C NMR (75 MHz, CDCl₃, δ ppm): 171.28, 131.51, 130.60, 130.12, 129.43, 129.06, 128.81,

69.12, 58.71, 52.46, 48.72, 36.43, 32.49, 23.13, 17.95, 17.90, 12.24. IR (film, ν cm^{-1}): 3367, 2947, 2866, 1731, 1654, 1454. MS ($M - \text{C}_3\text{H}_7$)⁺: 473. HRMS calcd: 473.2126 ($M - \text{C}_3\text{H}_7$)⁺; found: 473.2119.

Chloride 23

To a solution of alcohol **22** (1.73 g, 3.34 mmol) in tetrahydrofuran (59 mL) at -20°C were added triphenylphosphine (1.75 g, 6.64 mmol) and hexachloroacetone (0.76 mL, 5 mmol). After 5 min, the solution was quenched with sat. NH_4Cl (50 mL) and extracted with ether (3 x 40 mL). The organic layer was dried over MgSO_4 , the solvent was removed and the residue was chromatographed on silica gel with 20% Et_2O in hexane yielding **23** as an oil (1.78 g, 98%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 6.35 (1H, dd, $J=15\text{Hz}$, 11Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.10 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.65 (1H, dt, $J=15\text{Hz}$, 7.5Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 5.55 (1H, dt, $J=10.5\text{Hz}$, 8Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 5.50-5.30 (2H, m, $\text{CH}=\text{CH}$); 4.60 (1H, ABX, $J_{\text{AX}}=6.5\text{Hz}$, $J_{\text{BX}}=6\text{Hz}$, CHOTIPS); 4.15 (2H, d, $J=8\text{Hz}$, CH_2Cl); 3.70 (6H, s, CH_3O); 3.50 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{BX}}=6\text{Hz}$, CHCHHCl); 3.35 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{AX}}=6.5\text{Hz}$, CHCHHCl); 2.75 (2H, d, $J=7.5\text{Hz}$, $\text{CCH}_2\text{CH}=\text{CH}$); 2.00-1.85 (4H, m, CH_2CH_2); 1.10-0.90 (21H, m, TIPS). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 171.20, 132.29, 131.57, 131.21, 130.54, 127.87, 125.02, 69.13, 52.52, 48.72, 39.31, 36.56, 32.60, 23.15, 17.95, 17.90, 12.25. IR (film, ν cm^{-1}): 2949, 2867, 1785, 1731, 1651, 1453, 1201. MS ($M - \text{C}_3\text{H}_7$)⁺: 491. HRMS calcd: 491.1787 ($M - \text{C}_3\text{H}_7$)⁺; found: 491.1792.

Substituted malonate 24

To a solution of NaH (267 mg, 6.67 mmol) in N,N -dimethylformamide and tetrahydrofuran (1/1, 65 mL) at 0°C was added dropwise the dimethylmalonate (0.76 mL, 6.68 mmol). The mixture was stirred at room temperature during 20 min and a solution of the allyl chloride **23** (1.78 g, 3.34 mmol) and potassium iodide (1.1 g, 6.67 mmol) in tetrahydrofuran (5 mL) was added dropwise at 0°C . The mixture was stirred at room temperature for 2h, quenched with sat. NH_4Cl (50 mL) and extracted with ether and hexane (1/1, 3 x 50 mL). The organic layer was dried over MgSO_4 , the solvent was removed, and the residue was chromatographed on silica gel with 20% Et_2O in hexane yielding **24** as an oil (1.89 g, 90%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 6.35 (1H, dd, $J=15\text{Hz}$, 11Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.00 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.65-5.25 (4H, m, $\text{CH}=\text{CHCH}=\text{CH}$, $\text{CH}=\text{CH}$); 4.60 (1H, ABX, $J_{\text{AX}}=6.5\text{Hz}$, $J_{\text{BX}}=6\text{Hz}$, CHOTIPS); 3.72 (12H, s, CH_3O); 3.50 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{BX}}=6\text{Hz}$, CHHCl); 3.40 (1H, t, $J=7.5\text{Hz}$, $\text{CH}(\text{CO}_2\text{CH}_3)_2$); 3.35 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{AX}}=6.5\text{Hz}$, CHHCl); 2.70-2.60 (4H, m, $\text{CCH}_2\text{CH}=\text{CH}$); 2.00-1.80 (4H, m, CH_2CH_2); 1.10-0.90 (21H, m, TIPS). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 171.27, 169.13, 131.46, 130.80, 130.60, 128.87, 128.73, 125.55, 69.09, 57.59, 52.49, 52.43, 51.45, 48.76, 36.49, 32.47, 27.09, 23.14, 17.99, 12.23. IR (film, ν cm^{-1}): 2951, 2867, 1731, 1435. MS ($M - \text{C}_3\text{H}_7$)⁺: 587. HRMS calcd: 587.2443 ($M - \text{C}_3\text{H}_7$)⁺; found: 587.2446.

chlorohydrine 25

To a solution of silyl ether **24** (0.69 g, 1.1 mmol) in tetrahydrofuran (12 mL) at -20°C was added 1 M tetra-*n*-butylammonium fluoride (2.75 mL, 2.75 mmol). The solution was stirred at -20°C during 2 h. The solution was quenched with sat. NH_4Cl (20 mL) and extracted with ether (3 x 20 mL). The organic layer was dried over MgSO_4 , the solvent was removed and the residue was chromatographed on silica gel with 40% Et_2O in hexane yielding **25** as an oil (0.42 g, 80%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 6.39 (1H, dd, $J=15\text{Hz}$, 11Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.00 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.65-5.35 (3H, m, $\text{CH}=\text{CHCH}=\text{CH}$, $\text{CH}=\text{CH}$); 5.28 (1H, td, $J=7.5\text{Hz}$, 7Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 4.55 (1H, m, CHOH); 3.73 (12H, s, CH_3O); 3.50 (2H, m, CH_2Cl); 3.40 (1H, t, $J=7.5\text{Hz}$, $\text{CH}(\text{CO}_2\text{CH}_3)_2$); 2.80-2.70 (4H, m, $\text{CCH}_2\text{CH}=\text{CH}$); 2.20-1.90 (4H, m, CH_2CH_2). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 171.30, 169.22, 132.92, 130.71, 129.08, 128.99, 128.62, 125.59, 67.59, 57.32, 52.53, 51.47, 51.35, 49.02, 36.34, 32.22, 27.06, 22.82. IR (film, $\nu\text{ cm}^{-1}$): 2951, 2867, 1731, 1435. MS ($M - \text{OCH}_3$) $^+$: 443; ($M - \text{Cl}$) $^+$: 439. HRMS calcd: 443.1473 ($M - \text{OCH}_3$) $^+$; found: 443.1465.

Chloroketone 26

To a solution of chlorohydrine **25** (124 mg, 0.26 mmol) in dichloromethane (6 mL) was added diisopropylamine (37 μL , 0.26 mmol) and Dess-Martin reagent (382 mg, 0.78 mmol). The mixture was stirred at room temperature during 20 min. The solution was quenched with 10% $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL), extracted with dichloromethane (3 x 15 mL). The organic layer was dried over MgSO_4 , the solvent was removed, and the residue was chromatographed on Florisil (treated with Et_3N) with 40% Et_2O in hexane yielding **26** as an oil (104 mg, 85%).

^1H NMR (300 MHz, CD_2Cl_2 , δ ppm): 6.40 (1H, ddd, $J=15\text{Hz}$, 11Hz , 1Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.35-6.20 (2H, m, $\text{CH}=\text{CH}$); 6.00 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.55 (1H, dt, $J=15\text{Hz}$, 8Hz , $\text{CH}=\text{CH}-\text{CH}=\text{CH}$); 5.30 (1H, dt, $J=11\text{Hz}$, 8Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 4.15 (2H, s, CH_2Cl); 3.70 (6H, s, OCH_3); 3.68 (6H, s, OCH_3); 3.40 (1H, t, $J=7.5\text{Hz}$, $\text{CH}(\text{CO}_2\text{CH}_3)_2$); 2.75-2.70 (4H, m, $\text{CH}=\text{CHCH}=\text{CHCH}_2$); 2.60-2.55 (2H, m, $\text{CH}=\text{CHCH}_2$); 2.00-1.95 (2H, m, $\text{CH}=\text{CHCH}_2\text{CH}_2$). ^{13}C NMR (75 MHz, CD_2Cl_2 , δ ppm): 191.63, 171.09, 169.08, 150.02, 130.59, 129.11, 128.75, 125.73, 123.17, 57.44, 52.32, 51.42, 49.29, 35.92, 31.36, 27.02, 24.43. IR (film, $\nu\text{ cm}^{-1}$): 3008, 2956, 2848, 1730, 1695, 1621, 1435. MS (M) $^+$: 472; ($M - \text{HCl}$) $^+$: 436. HRMS calcd: 472.1500 (M) $^+$; found: 472.1507; calcd: 436.1733 ($M - \text{HCl}$) $^+$; found: 436.1739.

Alcohol 27

The same method as that used to prepare **22** was applied from **21** (2.2 g, 3.49 mmol) to give **27** as an oil (1.71 g, 95%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 6.50 (1H, dd, $J=15\text{Hz}$, 11Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.10 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.85 (1H, dt, $J=15\text{Hz}$, 6Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 5.45-5.20 (3H, m, $\text{CH}=\text{CHCH}=\text{CH}$, $\text{CH}=\text{CH}$); 4.60 (1H, ABX, $J_{AX}=6.5\text{Hz}$, $J_{BX}=6\text{Hz}$, CHOTIPS); 4.20 (2H, td, $J=5\text{Hz}$, 1Hz , CH_2OH); 3.70 (6H, s, CH_3O); 3.50 (1H, ABX, $J_{AB}=11\text{Hz}$, $J_{BX}=6\text{Hz}$, CHHCl); 3.35 (1H, ABX, $J_{AB}=11\text{Hz}$, $J_{AX}=6.5\text{Hz}$, CHHCl); 2.80 (2H, d, $J=7\text{Hz}$, $\text{CCH}_2\text{CH}=\text{CH}$); 2.00-1.85 (4H, m, CH_2CH_2); 1.10-0.90 (21H, m, TIPS). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 171.38, 133.91, 131.52, 131.35, 130.60, 125.45, 124.54, 69.10, 63.19, 57.3, 52.5, 48.78, 32.18, 30.90, 23.14, 17.94, 12.24. IR (film, $\nu\text{ cm}^{-1}$): 3444, 2950, 2867, 1738, 1667, 1455. MS ($M - \text{C}_3\text{H}_7$) $^+$: 473. HRMS calcd: 473.2126 ($M - \text{C}_3\text{H}_7$) $^+$; found: 473.2135.

Chloride 28

The same method as that used to prepare **23** was applied from **27** (1.66 g, 3.21 mmol) to give **28** as an oil (1.68 g, 98%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 6.55 (1H, dd, $J=15\text{Hz}$, 11Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.10 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.85 (1H, dt, $J=15\text{Hz}$, 7Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 5.50-5.30 (3H, m, $\text{CH}=\text{CHCH}=\text{CH}$, $\text{CH}=\text{CH}$); 4.60 (1H, ABX, $J_{AX}=6.5\text{Hz}$, $J_{BX}=6\text{Hz}$, CHOTIPS); 4.10 (2H, d, $J=7\text{Hz}$, $\text{CH}=\text{CHCH}_2\text{Cl}$); 3.70 (6H, s, CH_3O); 3.50 (1H, ABX, $J_{AB}=11\text{Hz}$, $J_{BX}=6\text{Hz}$, CHHCl); 3.35 (1H, ABX, $J_{AB}=11\text{Hz}$, $J_{AX}=6.5\text{Hz}$, CHHCl); 2.80 (2H, d, $J=8\text{Hz}$, $\text{CCH}_2\text{CH}=\text{CH}$); 2.00-1.80 (4H, m, CH_2CH_2); 1.10-0.90 (21H, m, TIPS). ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 171.23, 131.57,

130.64, 130.50, 129.90, 128.64, 126.44, 69.09, 57.33, 52.53, 48.73, 44.89, 32.2, 30.94, 23.14, 17.92, 12.24. IR (film, ν cm^{-1}): 2951, 2867, 1794, 1654, 1458, 1201. MS ($M - \text{C}_3\text{H}_7$)⁺: 491. HRMS calcd: 491.1787 ($M - \text{C}_3\text{H}_7$)⁺; found: 491.1778.

Substituted malonate 29

The same method as that used to prepare **24** was applied from **28** (1.68 g, 3.15 mmol) to give **29** as an oil (1.41 g, 71%).

¹H NMR (300 MHz, CDCl_3 , δ ppm): 6.35 (1H, dd, $J=15\text{Hz}$, 11Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.05 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.65 (1H, dt, $J=15\text{Hz}$, 7Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 5.50-5.30 (2H, m, $\text{CH}=\text{CH}$); 5.20 (1H, br q, $J=7.5\text{Hz}$, $\text{CH}=\text{CH}-\text{CH}=\text{CH}$); 4.60 (1H, ABX, $J_{\text{AX}}=6.5\text{Hz}$, $J_{\text{BX}}=6\text{Hz}$, CHOTIPS); 3.75 (6H, s, CH_3O); 3.70 (6H, s, CH_3O); 3.50 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{BX}}=6\text{Hz}$, CHHCl); 3.45 (1H, t, $J=7.5\text{Hz}$, $\text{CH}(\text{CO}_2\text{CH}_3)_2$); 3.35 (1H, ABX, $J_{\text{AB}}=11\text{Hz}$, $J_{\text{AX}}=6.5\text{Hz}$, CHHCl); 2.80 (2H, d, $J=8\text{Hz}$, $\text{CCH}_2\text{CH}=\text{CH}$); 2.70 (2H, t, $J=7.5\text{Hz}$, $\text{CH}_2\text{CH}(\text{CO}_2\text{Me})_2$); 2.00-1.90 (4H, m, CH_2CH_2); 1.05 (21H, m, TIPS). ¹³C NMR (75 MHz, CDCl_3 , δ ppm): 171.34, 169.10, 131.53, 130.74, 130.58, 130.20, 127.76, 123.65, 69.09, 57.32, 52.54, 52.46, 51.58, 48.79, 32.22, 32.04, 30.95, 23.15, 17.9, 12.24. IR (film, ν cm^{-1}): 2948, 2867, 1737, 1440, 1202. MS ($M - \text{C}_3\text{H}_7$)⁺: 587. HRMS calcd: 587.2443 ($M - \text{C}_3\text{H}_7$)⁺; found: 587.2446.

Chlorohydrine 30

The same method as that used to prepare **25** was applied from **29** (0.69 g, 1.1 mmol) to give **27** as an oil (0.44 g, 84%).

¹H NMR (300 MHz, CDCl_3 , δ ppm): 6.35 (1H, dd, $J=15\text{Hz}$, 11Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.05 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.65 (1H, dt, $J=15\text{Hz}$, 7Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 5.50 (1H, m, $\text{CH}=\text{CHCH}=\text{CH}$); 5.45 (1H, dd, $J=11\text{Hz}$, 8Hz , $\text{CH}=\text{CH}$); 5.15 (1H, dt, $J=11\text{Hz}$, 7.5Hz , $\text{CH}=\text{CH}$); 4.55 (1H, m, CHOH); 3.70 (6H, s, OCH_3); 3.68 (6H, s, OCH_3); 3.50 (2H, m, CH_2Cl); 3.45 (1H, t, $J=7.5\text{Hz}$, $\text{CH}(\text{CO}_2\text{Me})_2$); 2.80 (2H, d, $J=7.5\text{Hz}$, $\text{CCH}_2\text{CH}=\text{CH}$); 2.70 (2H, t, $J=7\text{Hz}$, $\text{CH}_2\text{CH}(\text{CO}_2\text{Me})_2$); 2.11-1.90 (4H, m, CH_2CH_2). ¹³C NMR (75 MHz, CDCl_3 , δ ppm): 171.40, 169.13, 133.07, 131.57, 130.93, 129.02, 127.65, 123.67, 67.55, 57.14, 52.53, 52.54, 51.5, 49.16, 32.15, 31.98, 30.94, 22.93. IR (film, ν cm^{-1}): 3522, 3011, 2954, 2846, 1733, 1435. MS ($M - \text{OCH}_3$)⁺: 443; ($M - \text{Cl}$)⁺: 439. HRMS calcd: 443.1473 ($M - \text{OCH}_3$)⁺; found: 443.1465.

Chloroketone 31

The same method as that used to prepare **26** was applied from **30** (122.5 mg, 0.26 mmol) to give **31** as an oil (105 mg, 85%).

¹H NMR (300 MHz, CD_2Cl_2 , δ ppm): 6.40 (1H, ddd, $J=15\text{Hz}$, 11Hz , 1Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 6.35-6.20 (2H, m, $\text{CH}=\text{CHCH}=\text{CH}$, $\text{COCH}=\text{CH}$); 6.05 (1H, t, $J=11\text{Hz}$, $\text{CH}=\text{CHCH}=\text{CH}$); 5.65 (1H, dt, $J=15\text{Hz}$, 7.5Hz , $\text{CH}=\text{CHCH}=\text{CH}$); 5.25 (1H, br q, $J=9\text{Hz}$, $\text{COCH}=\text{CH}$); 4.25 (2H, s, CH_2Cl); 3.71 (6H, s, OCH_3); 3.70 (6H, s, OCH_3); 3.45 (1H, t, $J=7.5\text{Hz}$, $\text{CH}(\text{CO}_2\text{CH}_3)_2$); 2.80 (2H, d, $J=8\text{Hz}$, $\text{CCH}_2\text{CH}=\text{CH}$); 2.75 (2H, t, $J=7.5\text{Hz}$, $\text{CH}_2\text{CH}(\text{CO}_2\text{Me})_2$); 2.58 (2H, m, $\text{COCH}=\text{CHCH}_2$); 2.00-1.95 (2H, m, $\text{COCH}=\text{CHCH}_2\text{CH}_2$). ¹³C NMR (75 MHz, CD_2Cl_2 , δ ppm): 191.58, 171.15, 169.07, 150.07, 131.53, 130.81, 127.75, 123.76, 123.16, 57.25, 52.32, 51.50, 49.36, 41.13, 31.95, 31.28, 30.55, 24.55. IR (film, ν cm^{-1}): 3008, 2956, 2848, 1730, 1695, 1621, 1435. MS (M)⁺: 472; ($M - \text{HCl}$)⁺: 436. HRMS calcd: 472.1500 (M)⁺; found: 472.1507; calcd: 436.1733 ($M - \text{HCl}$)⁺; found: 436.1739.

Macrocycle 2

To a solution of cesium carbonate (581.8 mg, 1.50 mmol) and cesium iodide (392 mg, 1.50 mmol) in acetonitrile (67 mL) was added the chloroketone **26** (95.1 mg, 0.2 mmol) in

acetonitrile (1 mL). The solution was stirred at room temperature for 48 h in the dark. The mixture was filtered, the solvent was removed and the residue was chromatographed on silica gel with 40% Et₂O in hexane yielding **26** as an oil (26 mg, 30%).

¹H NMR (300 MHz, C₆D₆, 375K, δ ppm): 6.40 (1H, dd, J=15Hz, 11Hz, CH=CHCH=CH); 5.98 (1H, t, J=11Hz, CH=CHCH=CH); 5.72 (1H, d, J=11.5Hz, 7Hz, COCH=CH); 5.50-5.40 (2H, m, CH=CHCH=CH); 5.22 (1H, td, J=11.5Hz, 9Hz, COCH=CH); 3.40 (6H, s, OCH₃); 3.35 (6H, s, OCH₃); 3.17 (2H, s, COCH₂); 2.80 (2H, d, J=8Hz, CH=CHCH=CHCH₂); 2.40 (2H, br q, J=8.5Hz, CH₂CH=CHCH=CH); 1.90-1.80 (4H, m, CH₂-CH₂). ¹³C NMR (75 MHz, CDCl₃, δ ppm): 199.69, 170.60, 142.845, 132.5, 130.75, 130.10, 127.98, 125, 56.16, 54.5, 52.72, 44.38, 35.44, 31.66, 30.29, 29.68, 27.11, 22.1. IR ((CH₂Cl₂), ν cm⁻¹): 3003, 2955, 1734, 1695, 1628, 1444, 1266, 1221. MS (M)⁺: 436. HRMS calcd: 436.1733 (M)⁺; found: 436.1739. mp: 160-162°C.

Macrocycle 3

To a solution of cesium carbonate (45 mg, 0.12 mmol) and cesium iodide (30 mg, 0.12 mmol) in acetonitrile (15 mL), the compound **31** (11 mg, 0.02 mmol) in acetonitrile (1 mL) was slowly added via a syringe pump over 10 h at 40°C. The solution was stirred at 40°C for an additional 12 h period. The mixture was filtered and the solvent was removed. The residue was chromatographed on silica gel with 40% Et₂O in hexane to yield **3** as an oil (1.8 mg, 17%).

¹H NMR (300 MHz, CDCl₃, δ ppm): 6.35 (1H, dd, J=15Hz, 11.5Hz, CH=CHCH=CH); 6.15-6.05 (2H, m, CH=CHCH=CH, COCH=CH); 5.75 (1H, dt, J=11.5Hz, 7Hz, CH=CHCH=CH); 5.65 (1H, dt, J=15Hz, 7Hz, CH=CH-CH=CH); 4.95 (1H, br q, J=9Hz, CH₂CH=CHCO); 3.80 (6H, s, OCH₃); 3.78 (6H, s, OCH₃); 3.15-1.8 (10H, br m, CH₂). ¹³C NMR (75 MHz, CDCl₃, δ ppm): 200.75, 172.13, 172.04, 141.93, 132.69, 131.10, 130.20, 129.47, 125.55, 57.94, 53.99, 53.72, 45.63, 36.77, 31.75, 30.69, 30.44, 24.5. IR (film, ν cm⁻¹): 2955, 1732, 1698, 1633, 1436, 1270, 1223. MS (M)⁺: 436. HRMS calcd: 436.1733. found: 436.1739.

Diels-Alder adduct 33 and its epimer 34

The macrocycle **2** (10 mg, 23 μmol) in toluene (2 mL) in a quartz tube was sealed *in vacuo* and heated in an oven for 2h at 220°C. The solvent was removed and the residue was chromatographed on silica gel with 40% AcOEt in hexane. It was impossible to separate both compounds **33** and **34** at that stage, their relative population was evaluated by integration of the NMR signal corresponding to the alkene (1:1).

The mixture of the two tricycles was then treated with *para*-toluenesulfonic acid (catalytic) in toluene (3 mL) at reflux for 5h. The residue was purified on silica gel with 40% AcOEt in hexane to afford the tricycle **34** (9mg, 87%).

TAT tricycle **34**: ¹H NMR (300 MHz, CDCl₃, δ ppm): 5.45 (2H, s, CH=CH); 3.75 (6H, s, OCH₃); 3.74 (3H, s, OCH₃); 3.69 (3H, s, OCH₃); 2.90 (1H, dd, J=13Hz, 3Hz, CHHCO); 2.72 (1H, d, J=13Hz, CHHCO); 2.60-2.50 (2H, m, CH); 2.45-2.30 (3H, m, COCHCHCH=CH, CH); 2.15 (1H, t, J=11Hz, CHCO, this coupling proves the TAT ring junction); 1.95-1.80 (2H, m, CH); 1.75 (1H, dt, J=14Hz, 4Hz, CH); 1.60-1.40 (3H, m, CH); 1.11-0.90 (2H, m, CH). ¹³C NMR (75 MHz, CDCl₃, δ ppm): 206.68, 172.41, 171.62, 170.60, 170.41, 131.72, 128.51, 57.73, 55.63, 55.35, 53.21, 53.11, 52.7, 52.55, 46.25, 40.32, 38.55, 38.16, 37.89, 37.52, 36.93, 31.29, 29.69, 25.7, 22.68. IR (film, ν cm⁻¹): 2956, 2854, 1731, 1450, 1436, 1258. MS (M)⁺: 436. HRMS calcd: 436.1733 (M)⁺; found: 436.1730.

CST tricycle **33**: Only a few ¹H NMR signals could be attributed for this compound which could not be separated from its epimer **34**: ¹H NMR (300 MHz, CDCl₃, δ ppm): 5.66 (1H,

complex AB system appearing as a doublet of doublet, $J_{AB}=10\text{Hz}$, $J=3.5\text{Hz}$, $\text{CH}=\text{CH}$); 5.57 (1H, complex AB system appearing as a doublet of doublet, $J_{AB}=10\text{Hz}$, $J=4\text{Hz}$, $\text{CH}=\text{CH}$); 3.72 (3H, s, OCH_3).

Diels-Alder adduct **35** and its epimer **36**

The macrocycle **3** (1.6 mg, 3.6 μmol) in toluene (2 mL) in a quartz tube was sealed *in vacuo* and heated in an oven for 2h at 160°C. The solvent was removed and the residue was chromatographed on silica gel with 40% AcOEt in hexane. It was impossible to separate both compounds **35** and **36** at that stage, their relative population was evaluated by integration of the NMR signal corresponding to the alkene (1:1).

The mixture of the two tricycles was then treated with *para*-toluenesulfonic acid (catalytic) in toluene (3 mL) at reflux for 5h. The final mixture still contained both compounds but with a different **36/35** ratio of 3:1 and with no significant total weight loss.

In a separate experiment a solution of 1M SnCl_4 (7.6 μL) was added to a solution of the macrocycle **3** (1.6 mg, 3.6 μL) in dichloromethane (1 mL) at 30°C. The solution was stirred at 30°C for 3.5 h and quenched with sat. NaHCO_3 (1 mL). The mixture was extracted with dichloromethane (3 x 5mL) and dried. Pure tricycle **35** was obtained after purification on silica gel with 40% AcOEt in hexane. (1.5 mg, 94%). Since the conditions had been sufficiently mild to avoid epimerization, **35** could be crystallized from pentane and ether and its structure proven crystal X-ray diffraction analysis.

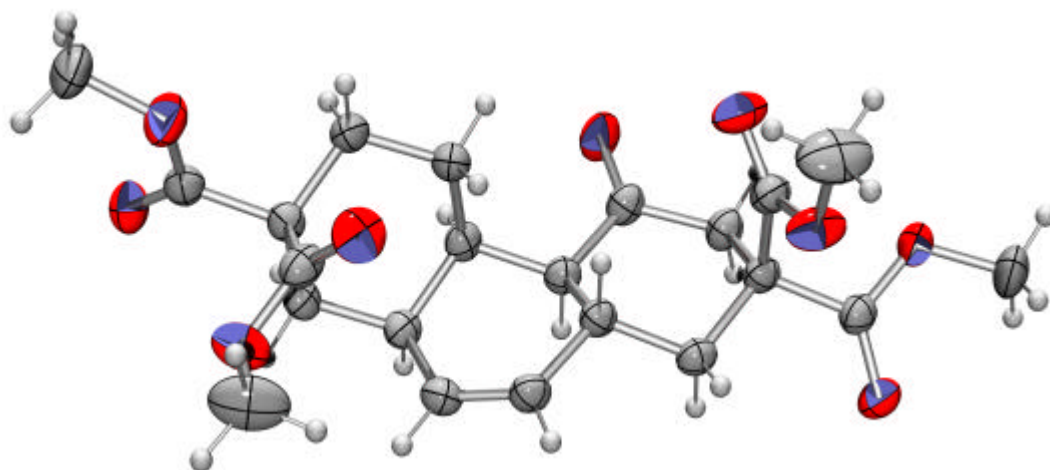
Finally, pure tricycle **35** was treated with *para*-toluenesulfonic acid (catalytic) in toluene (3 mL) at reflux for 5h. The solvent was removed and the residue was chromatographed on silica gel with 40% AcOEt in hexane. A 3:1 mixture of compounds **36** and **35** was obtained as previously observed.

CST tricycle **35**: ^1H NMR (300 MHz, CDCl_3 , δ ppm) : 5.45 (2H, s, $\text{CH}=\text{CH}$) ; 3.76 (3H, s, OCH_3) ; 3.75 (3H, s, OCH_3) ; 3.69 (3H, s, OCH_3) ; 3.67 (3H, s, OCH_3) ; 3.05 (1H, dd, $J=15\text{Hz}$, 2.5Hz, COCH) ; 2.60-1.95 (9H, m, CH) ; 1.70-1.30 (4H, m, CH).

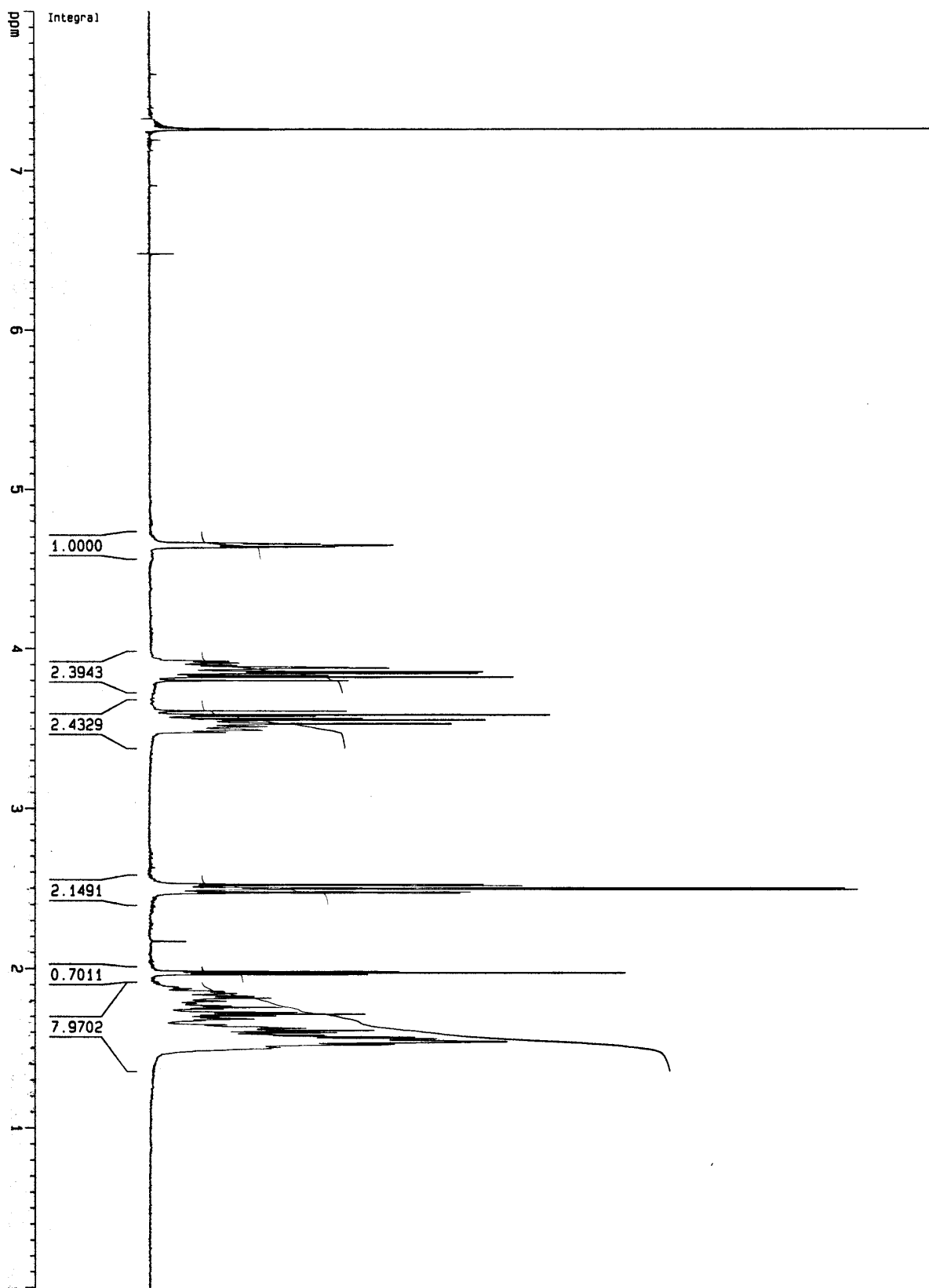
IR (film, ν cm^{-1}) : 2922, 1734, 1437, 1257. SM (M) $^+$: 436. HRMS calcd: 436.1733 (M) $^+$; found: 436.1730. mp : 153-155°C

CAC tricycle **36**: Only a few ^1H NMR signals could be attributed for this compound which could not be separated from its epimer **35**: ^1H NMR (300 MHz, CDCl_3 , δ ppm): 5.66 (1H, complex AB system appearing as a doublet of doublet, $J_{AB}=9\text{Hz}$, $J=4\text{Hz}$, $\text{CH}=\text{CH}$); 5.56 (1H, complex AB system appearing as a doublet of doublet, $J_{AB}=9\text{Hz}$, $J=3.5\text{Hz}$, $\text{CH}=\text{CH}$); 3.74 (6H, s, OCH_3); 3.72 (3H, s, OCH_3); 3.68 (3H, s, OCH_3).

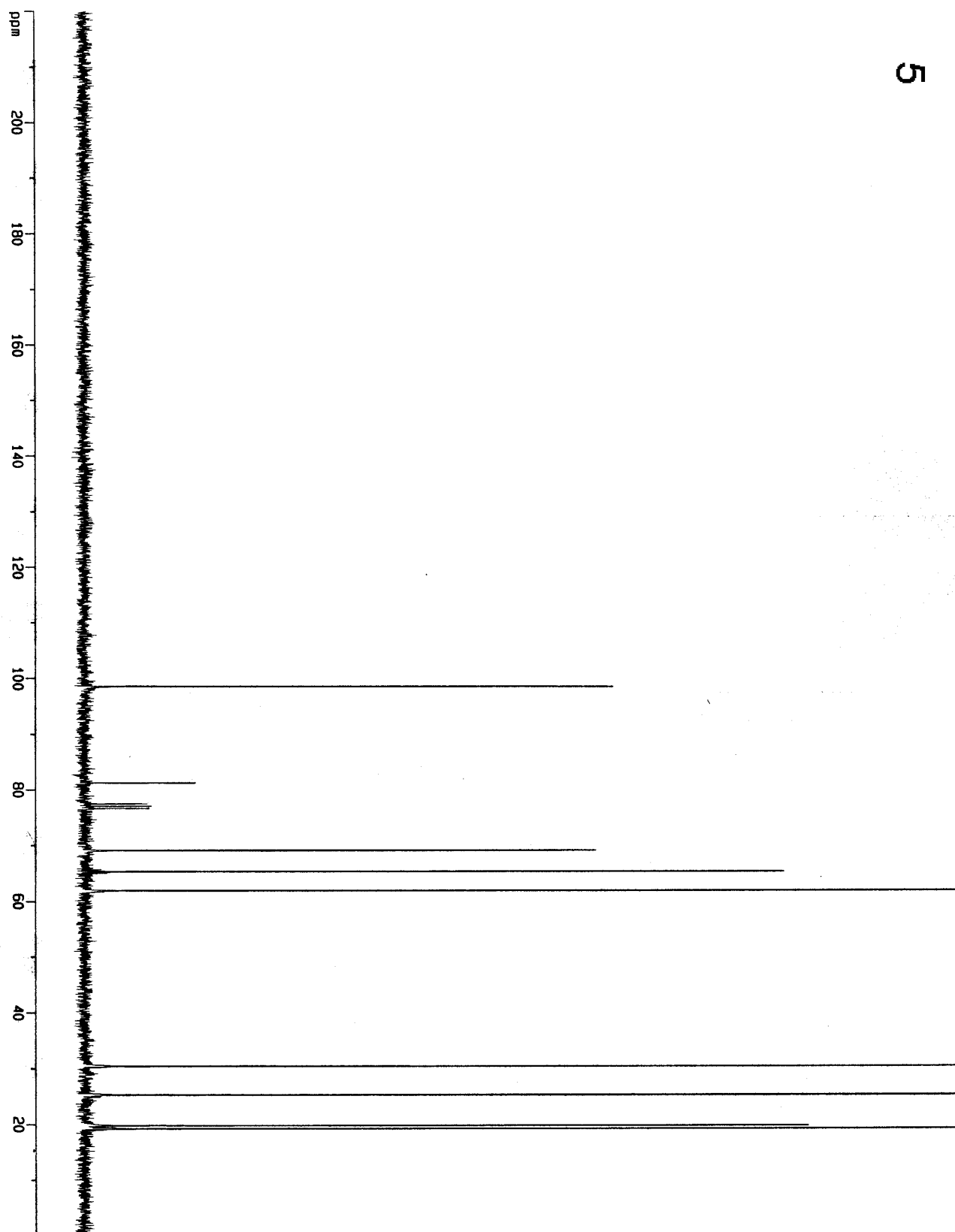
ORTEP
representation
of **35**



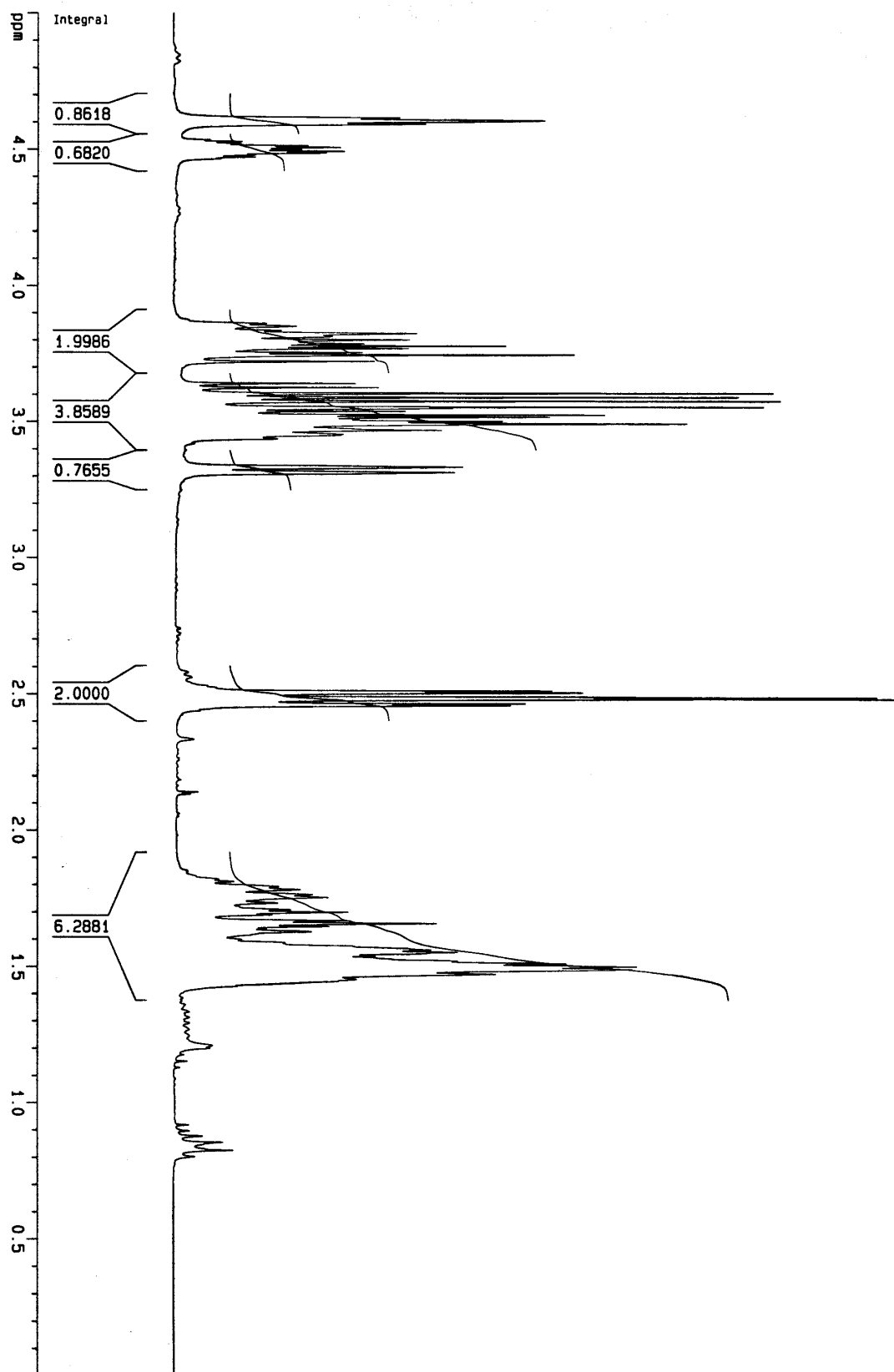
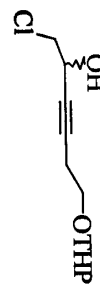
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5

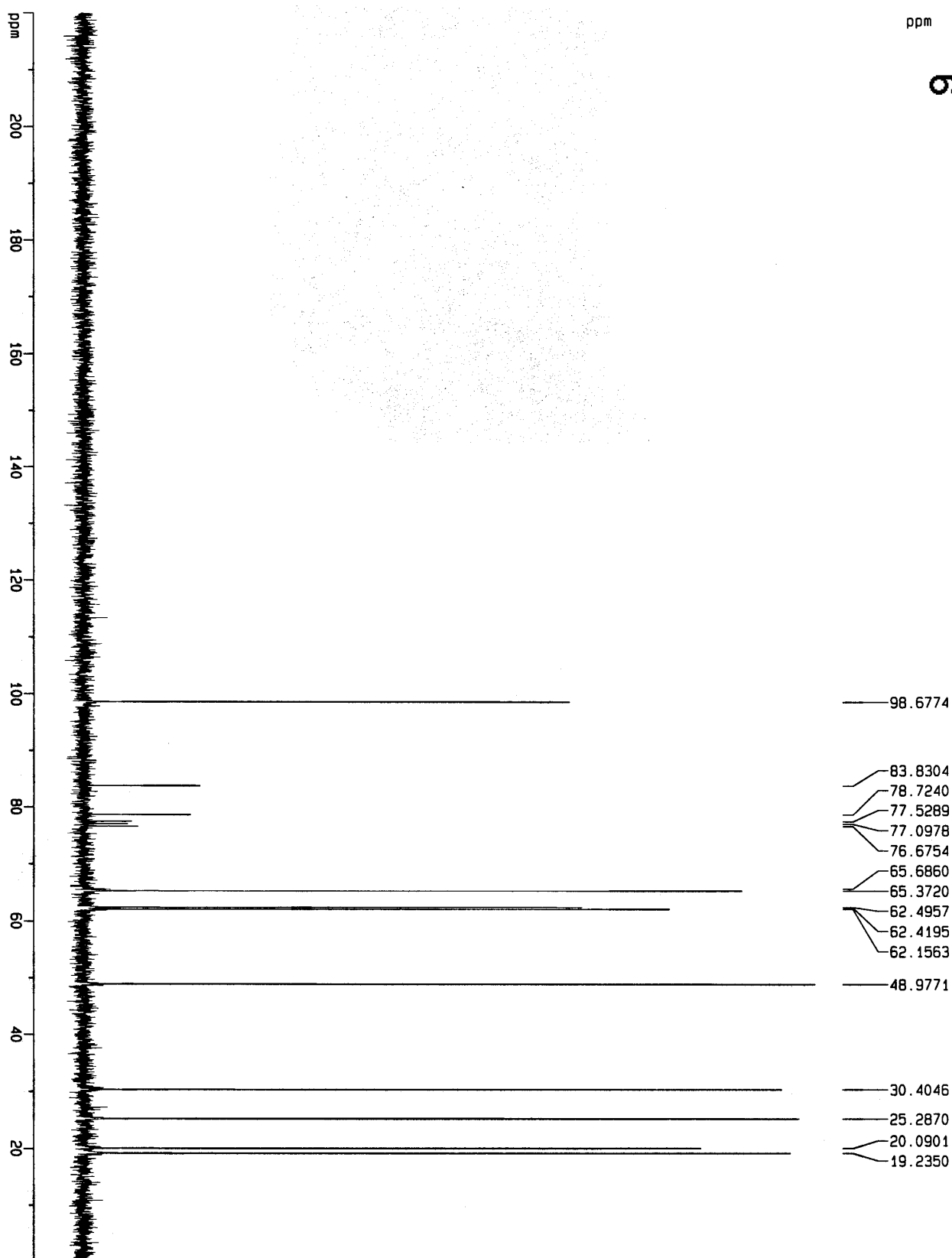


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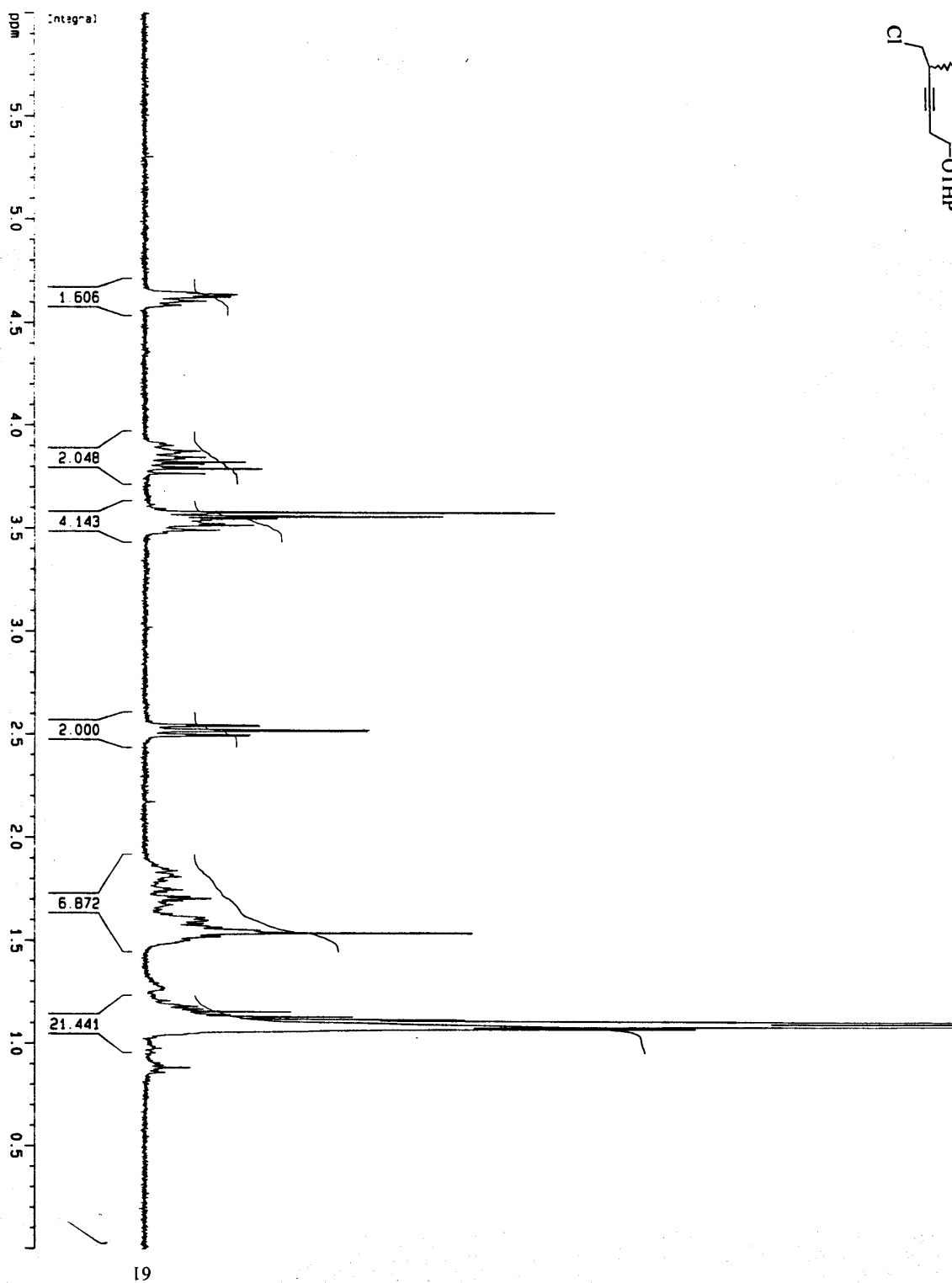
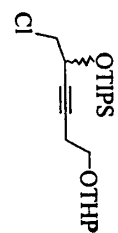


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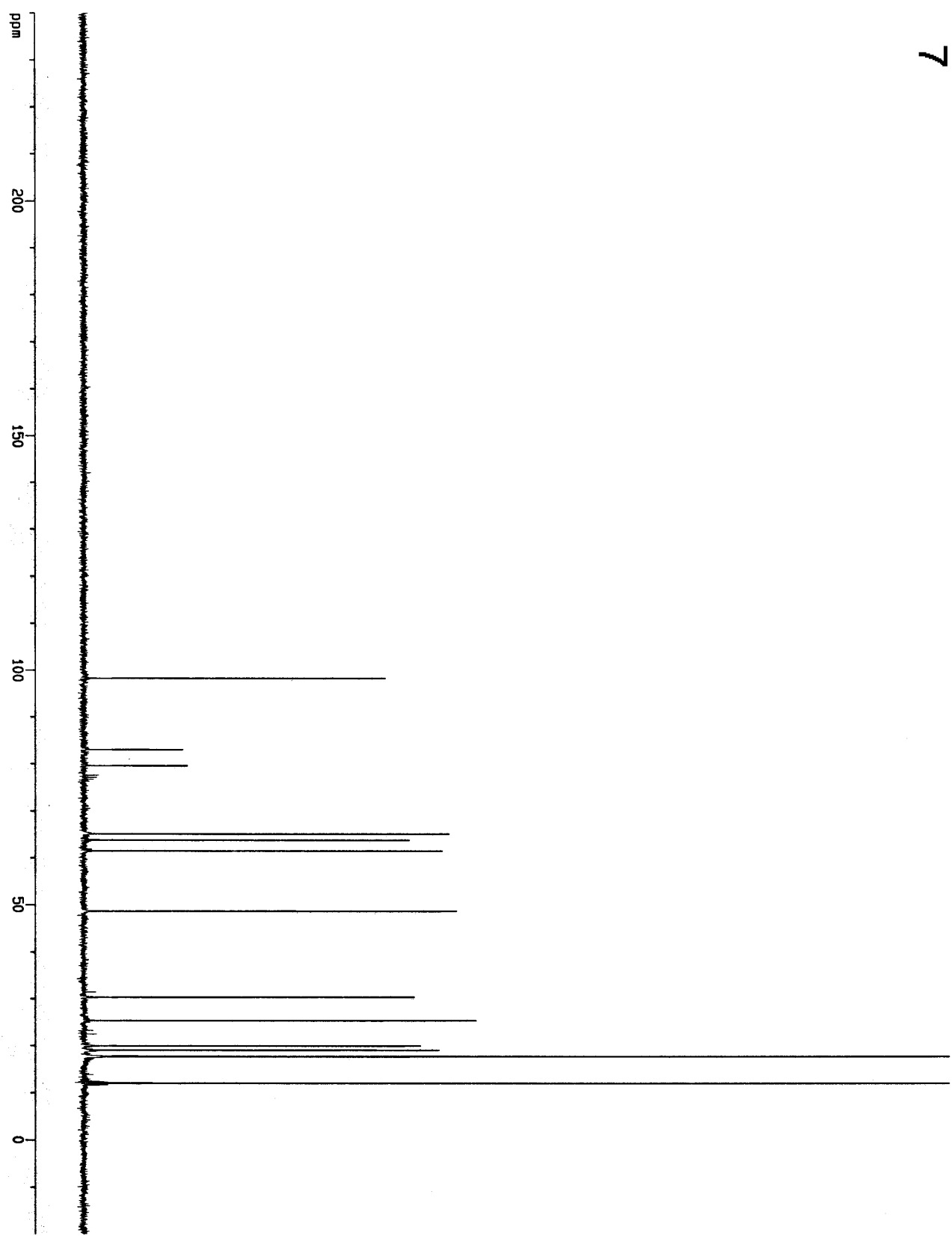
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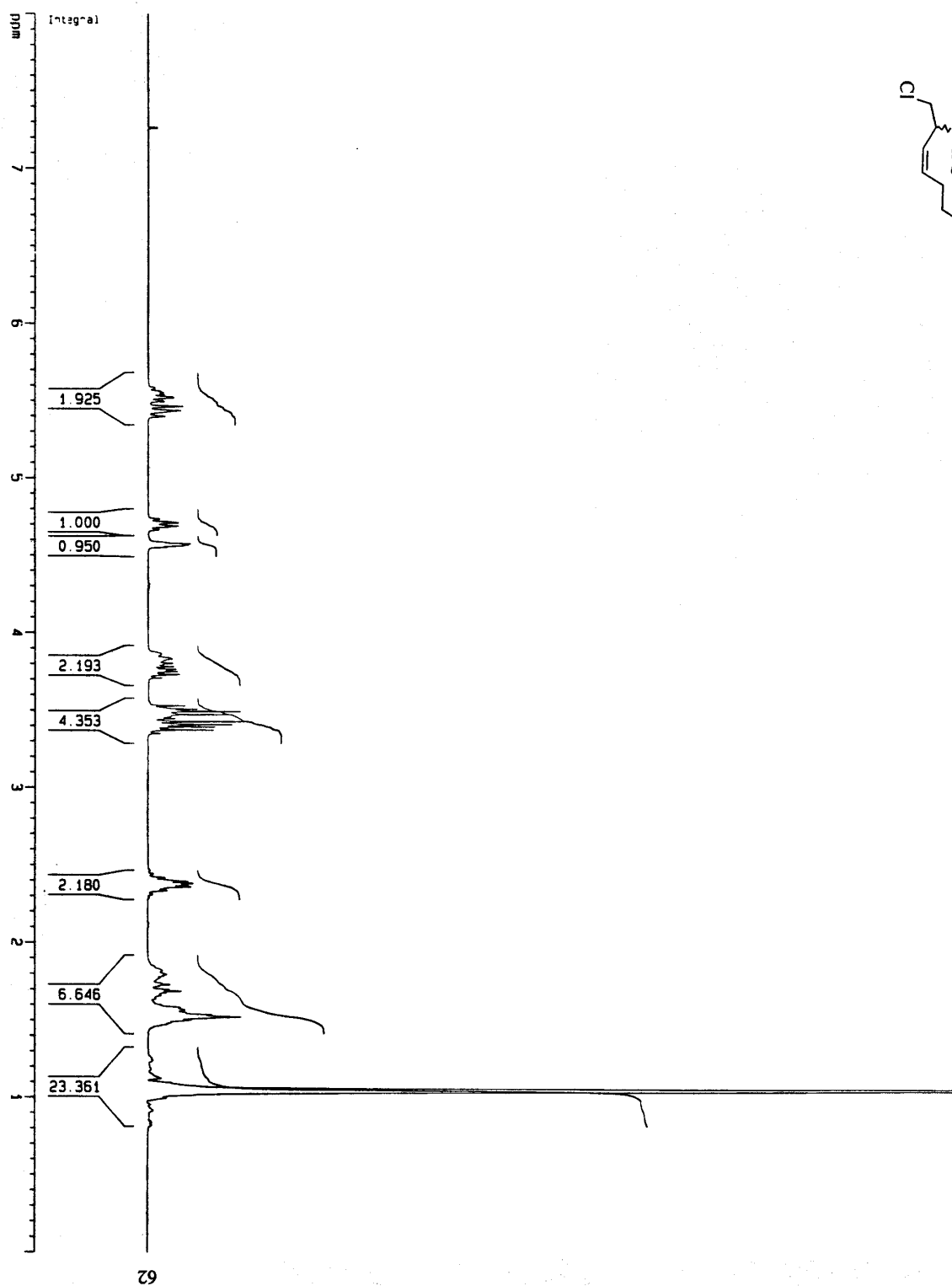


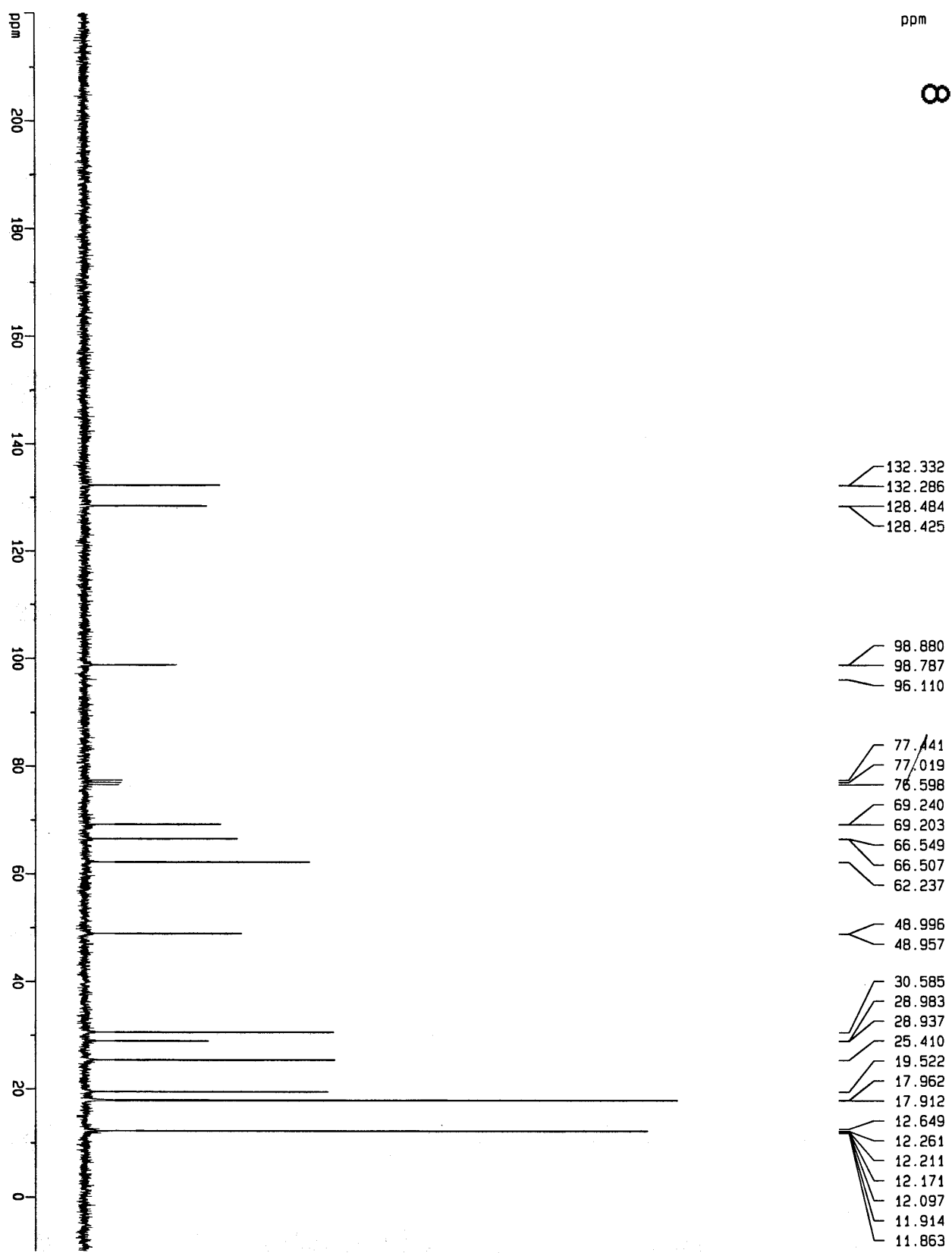
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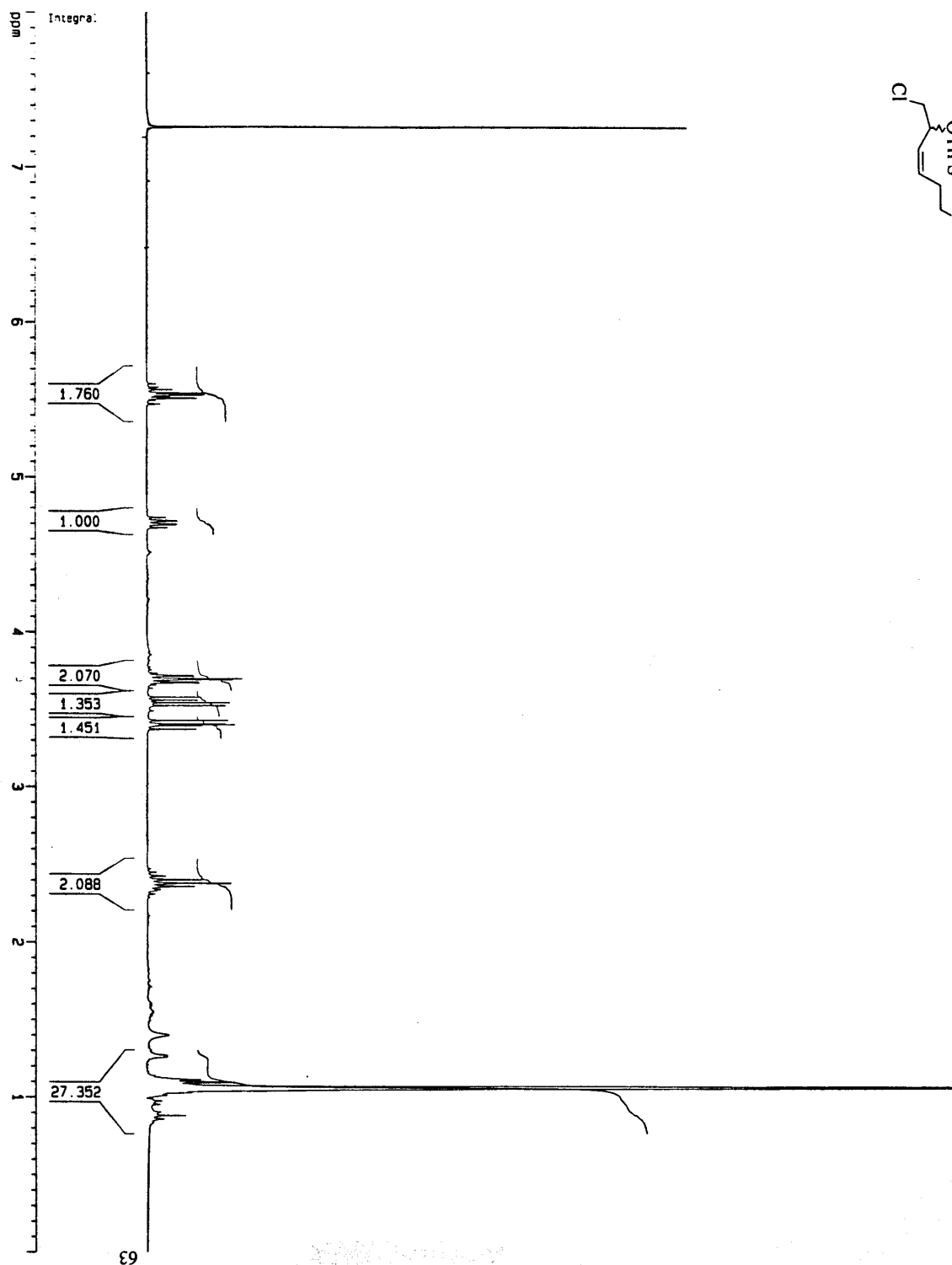
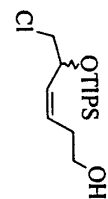
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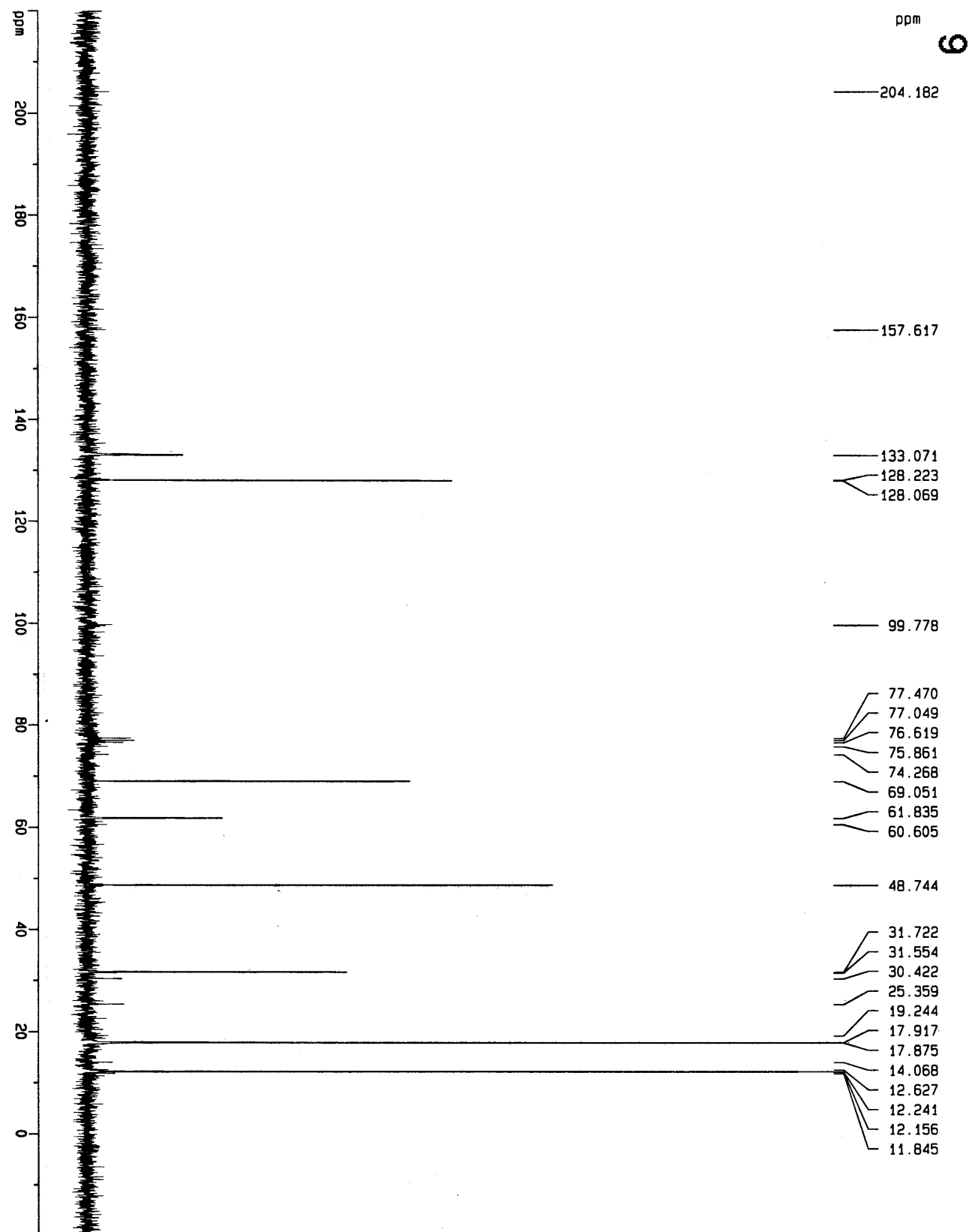


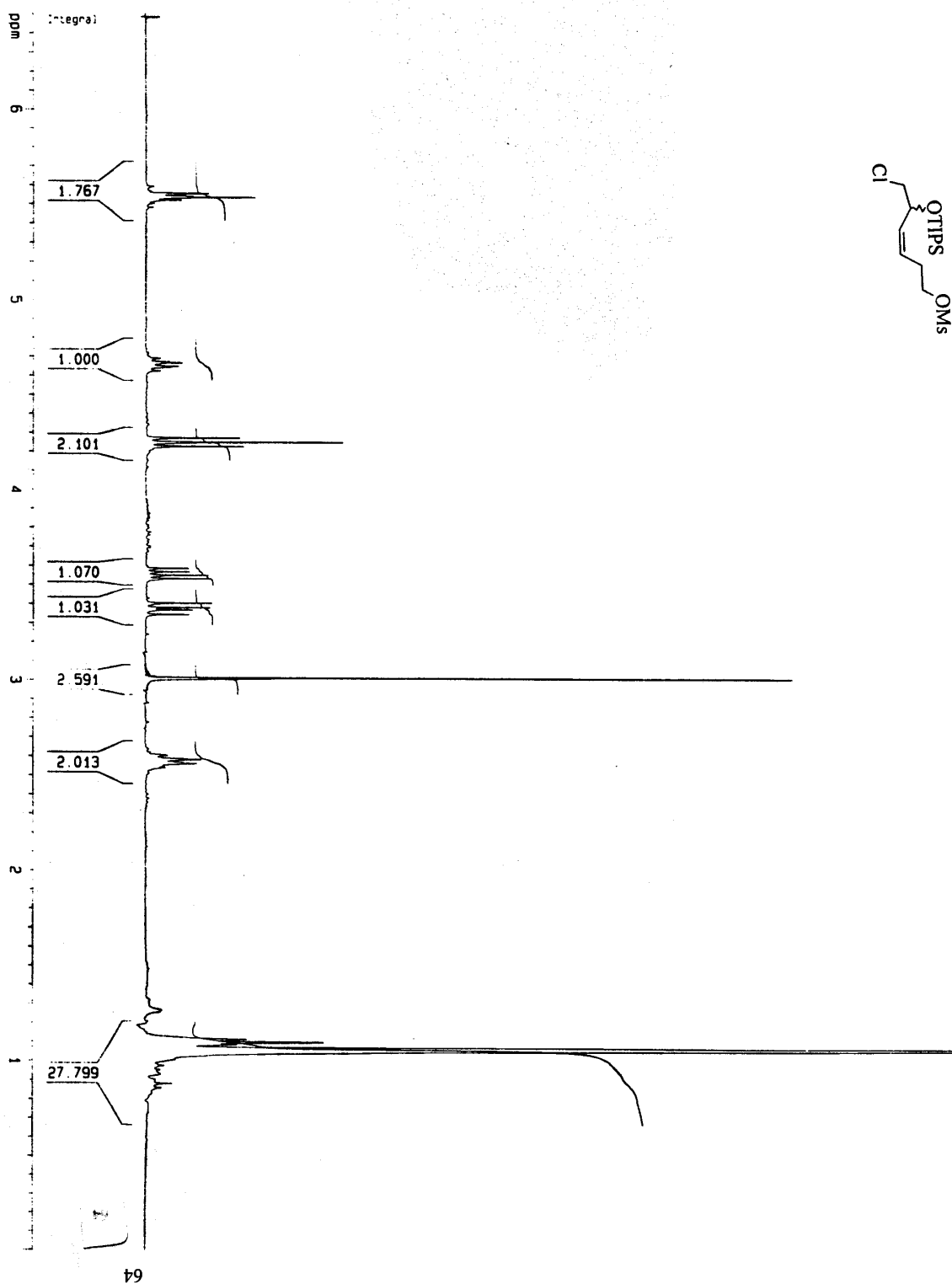
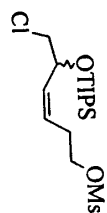




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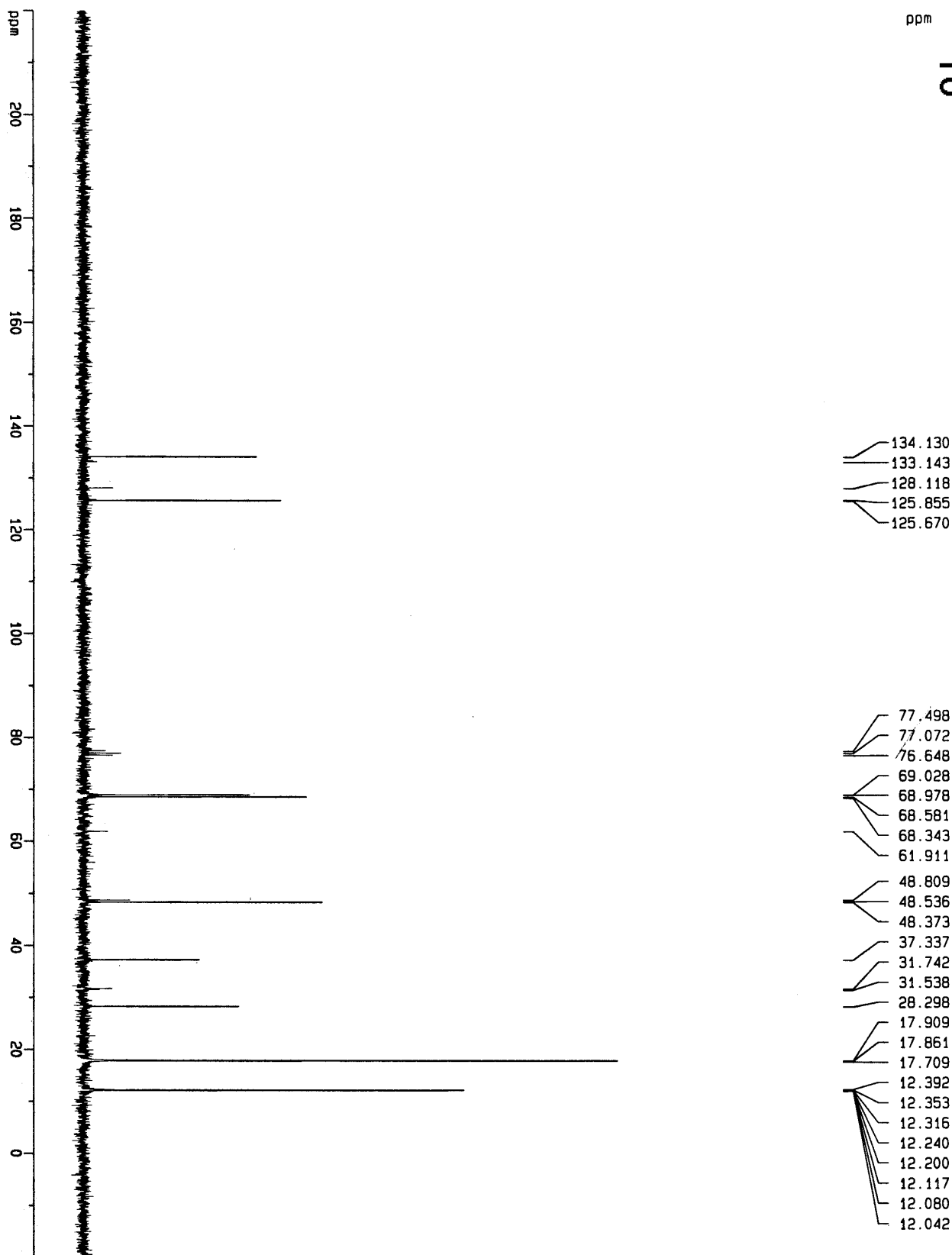


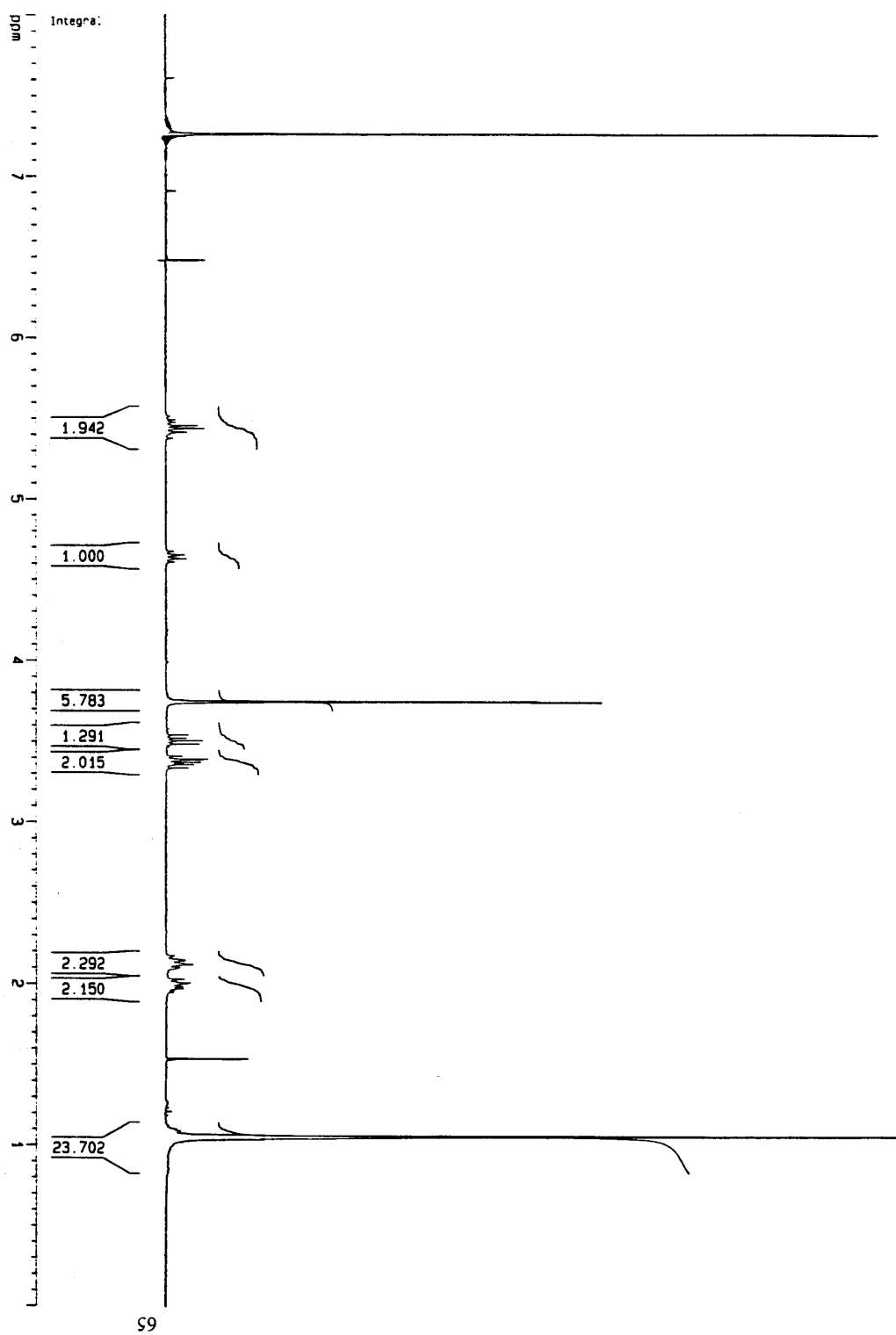
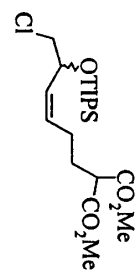




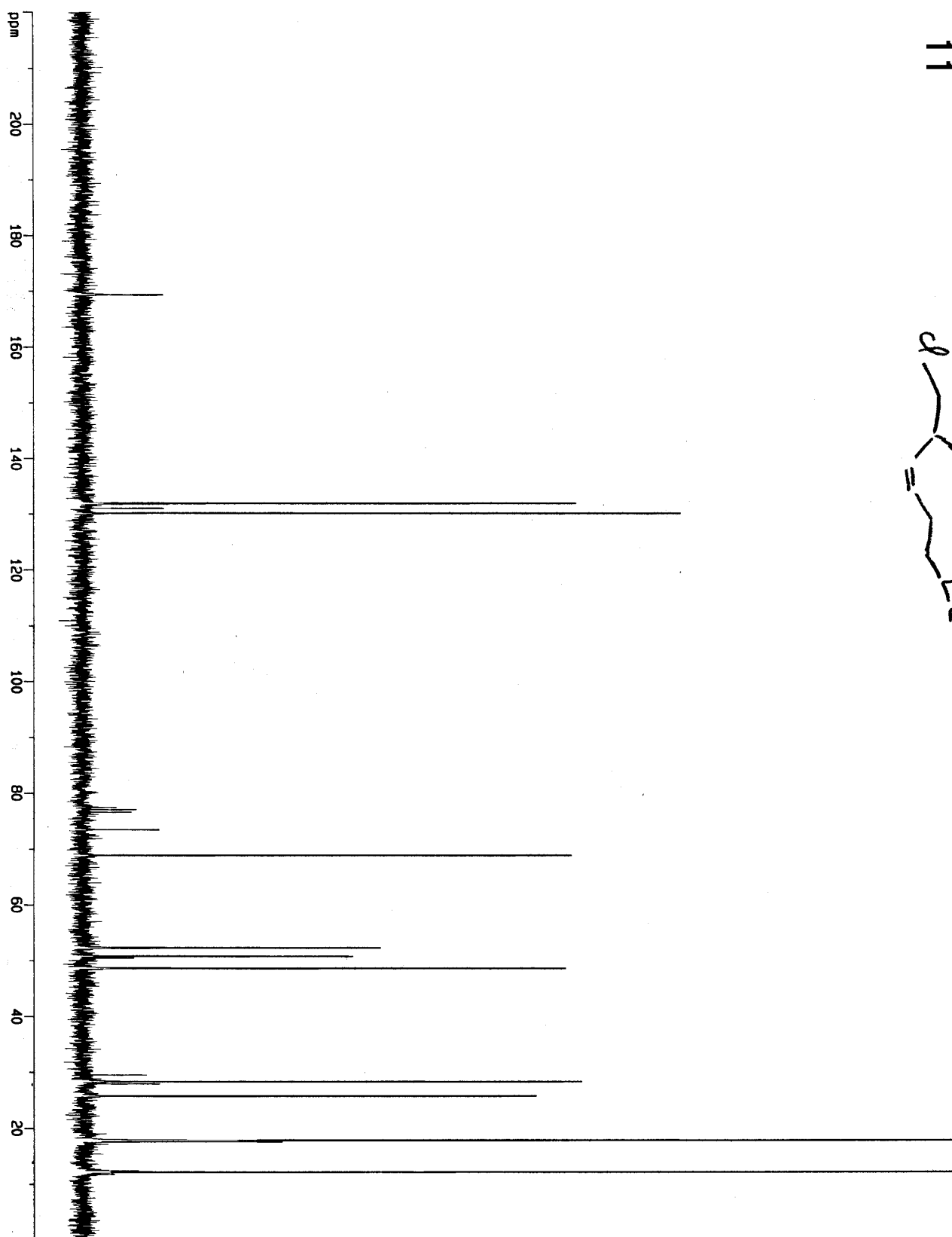
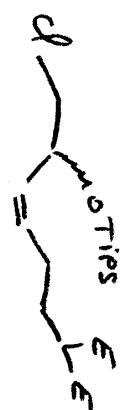
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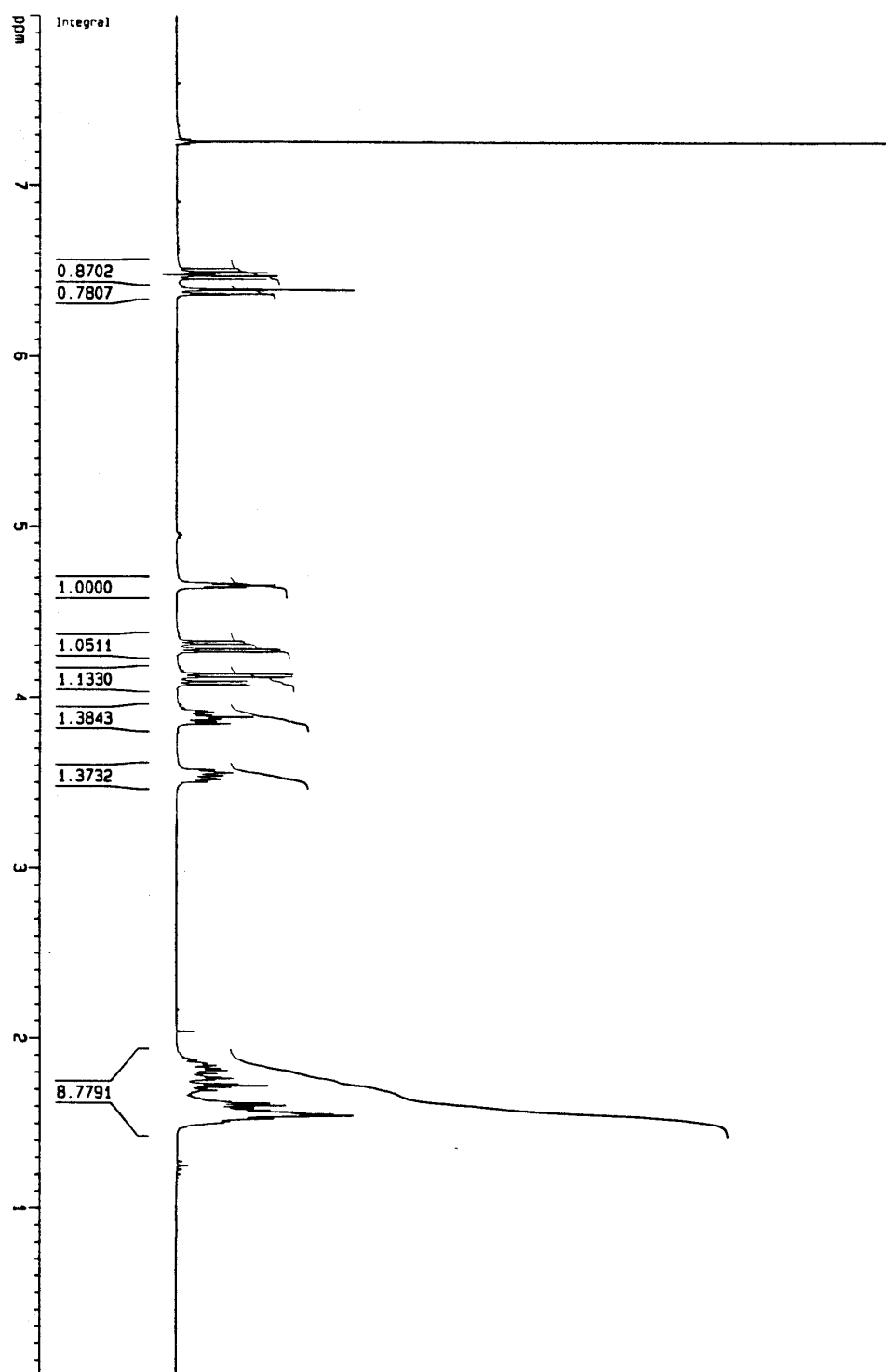




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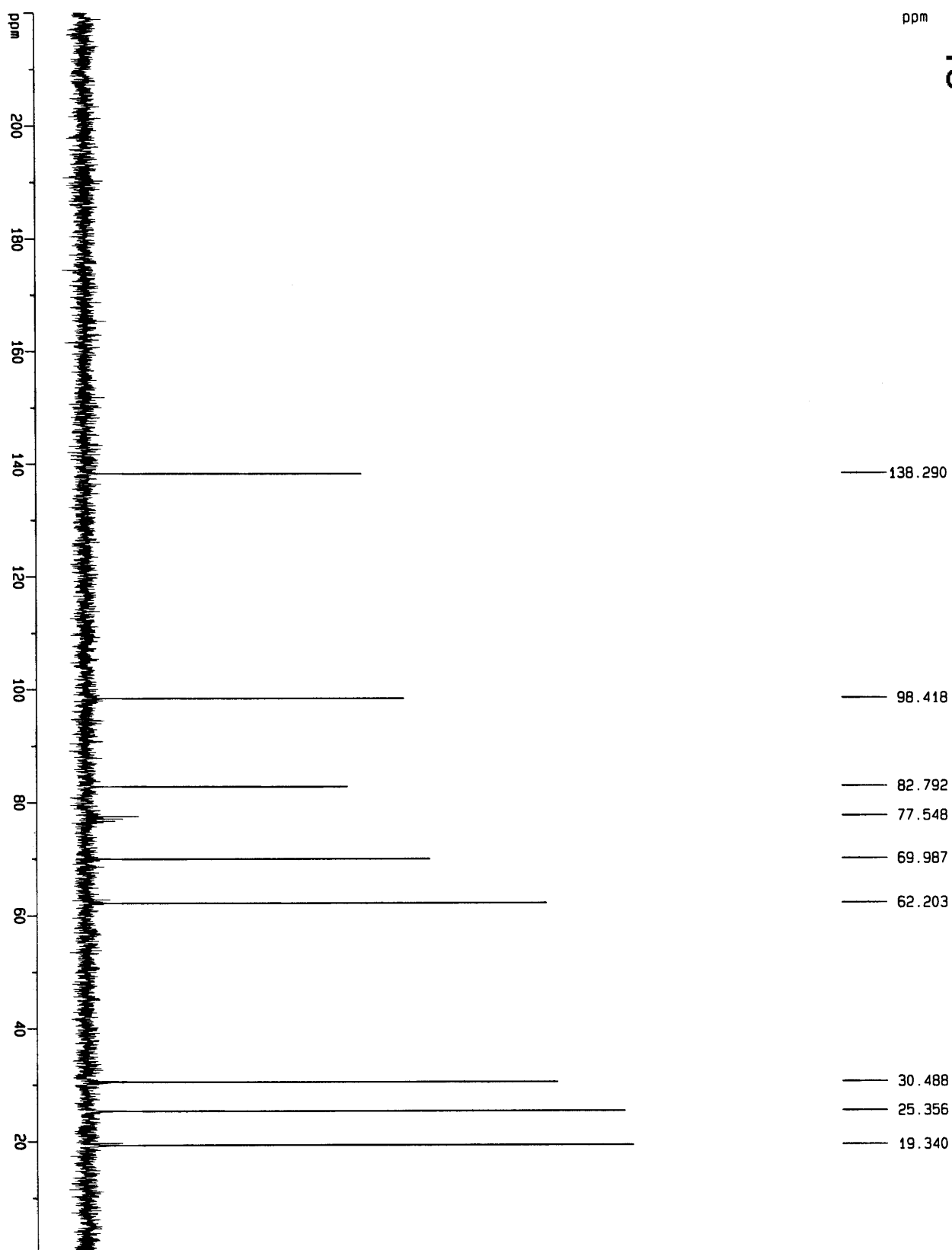
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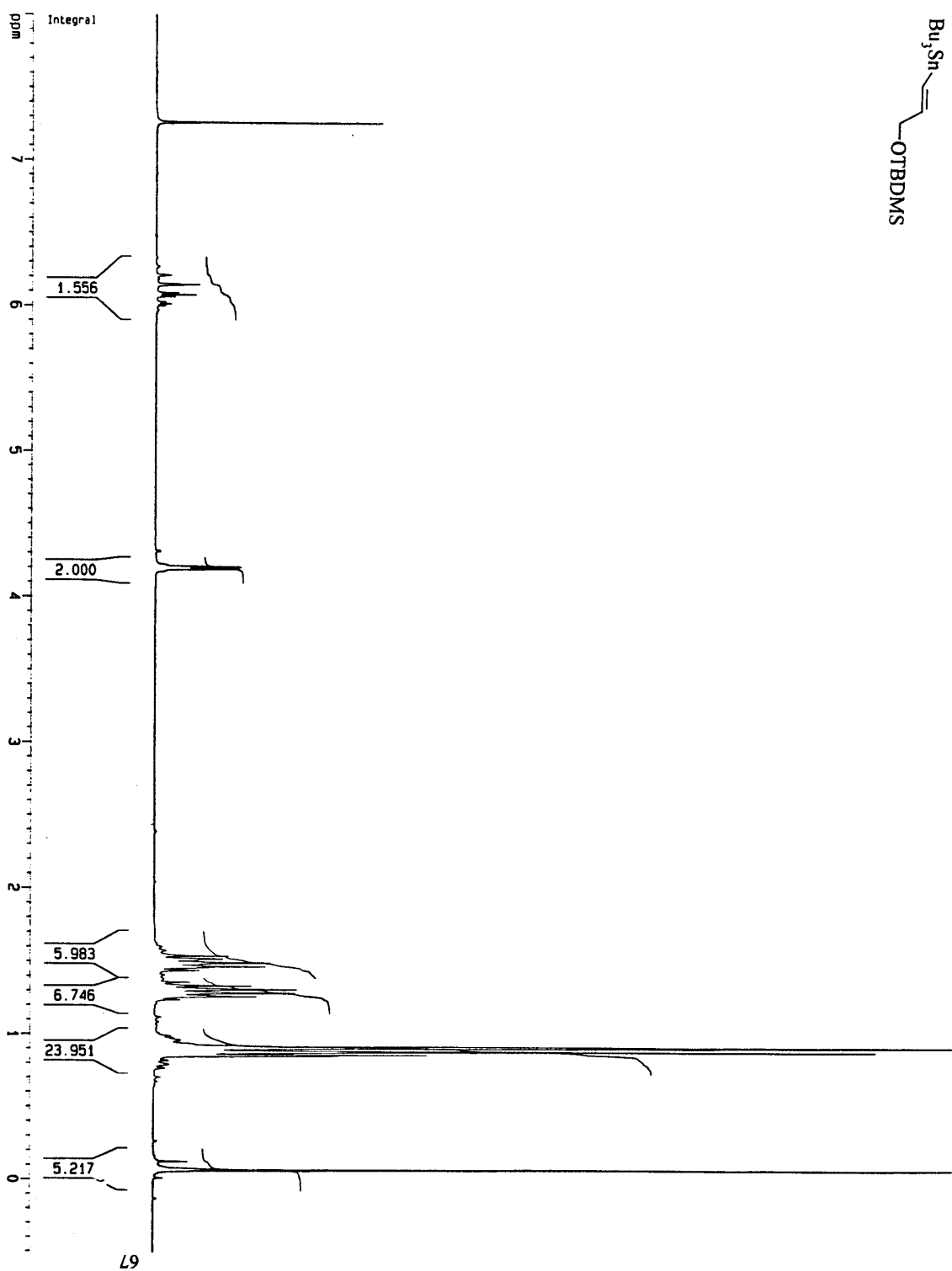
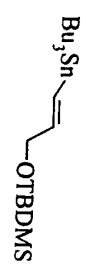


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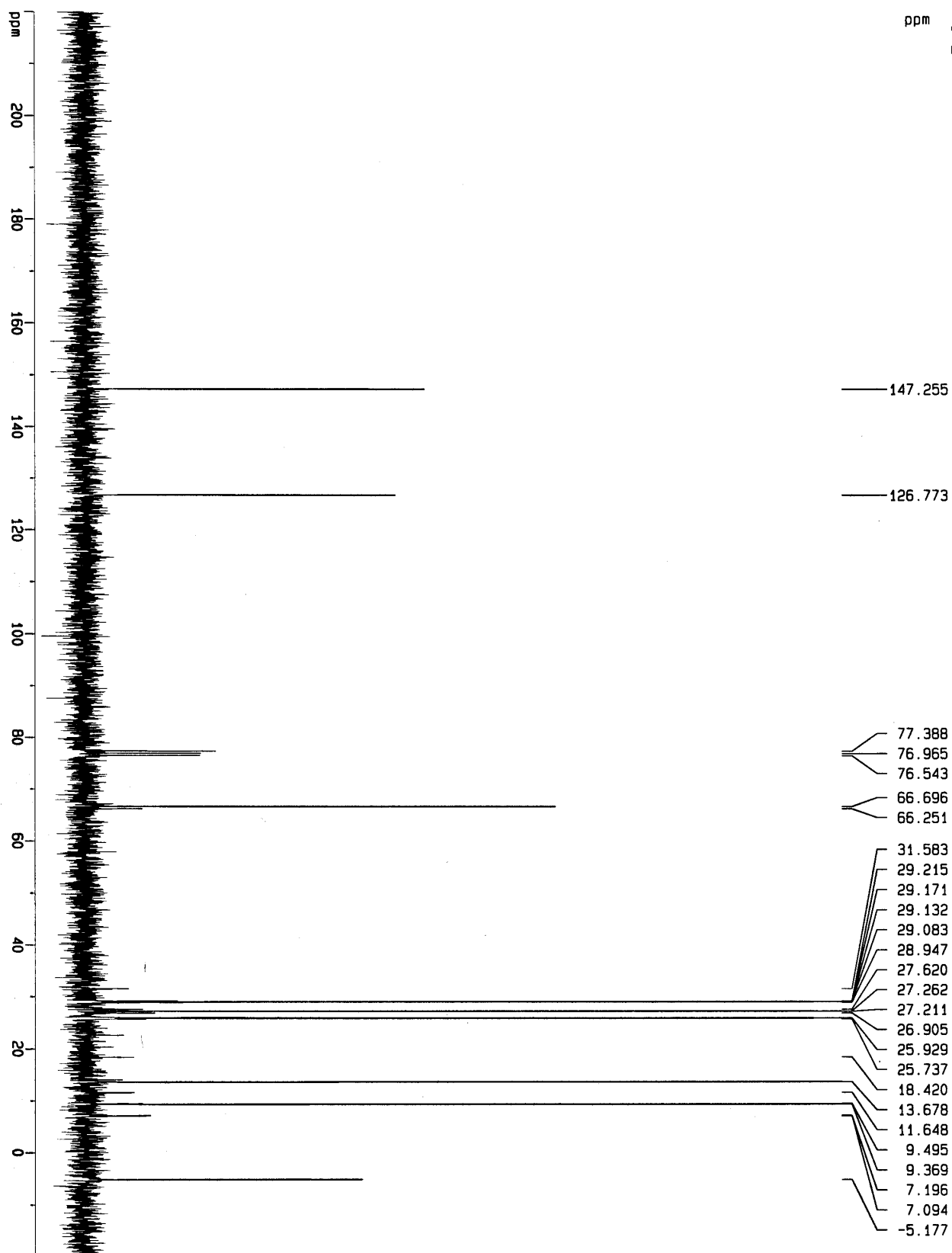
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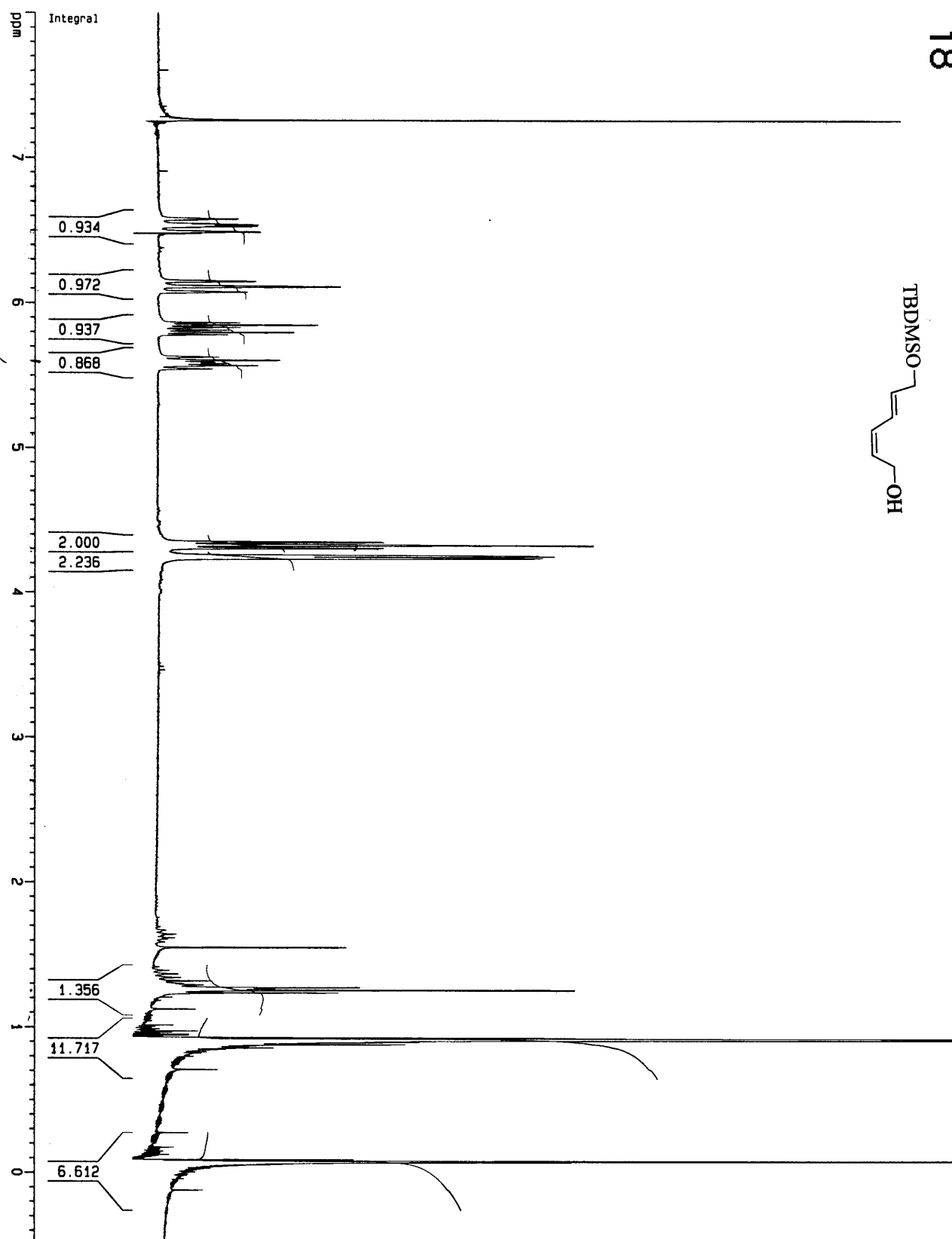
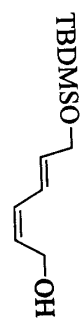


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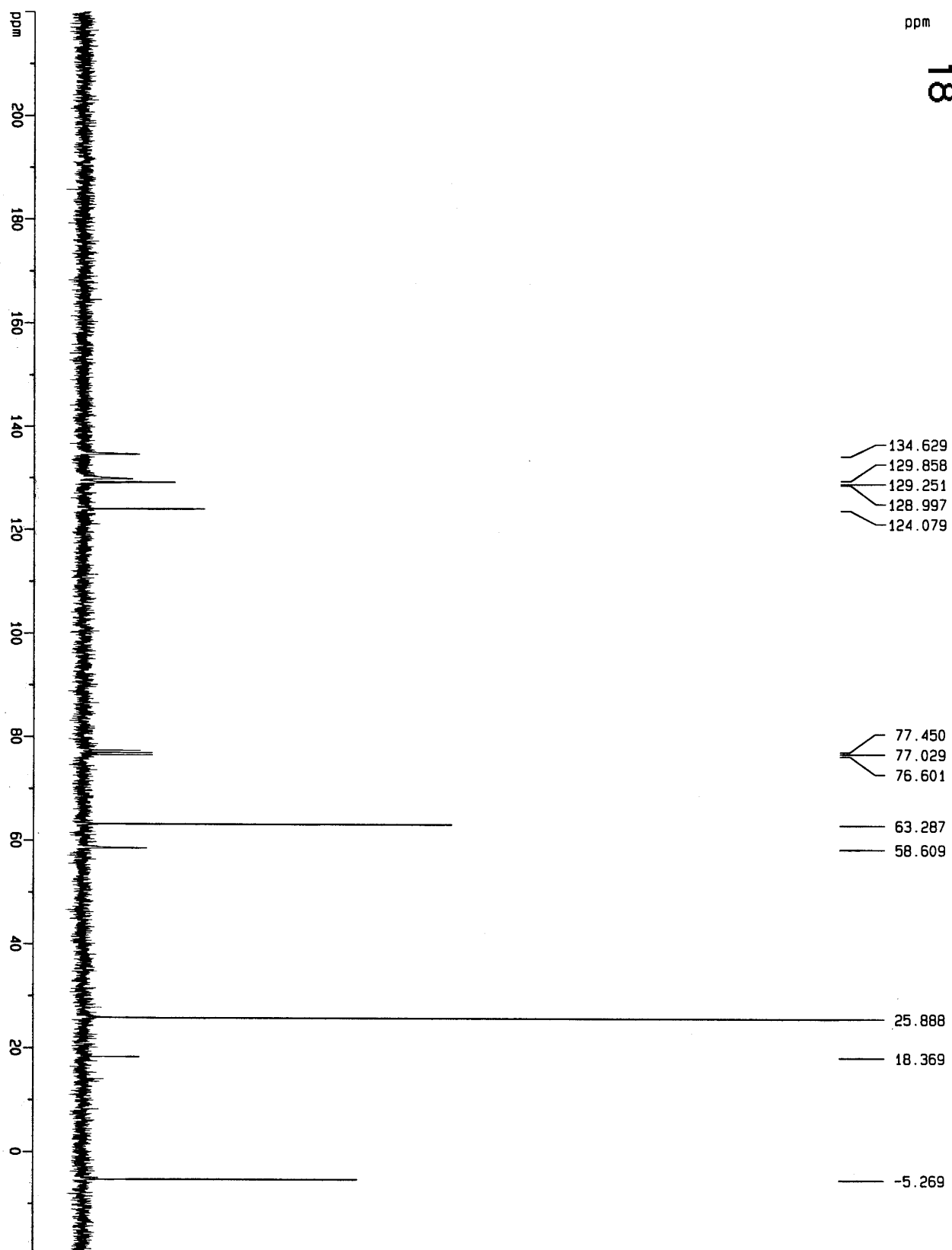


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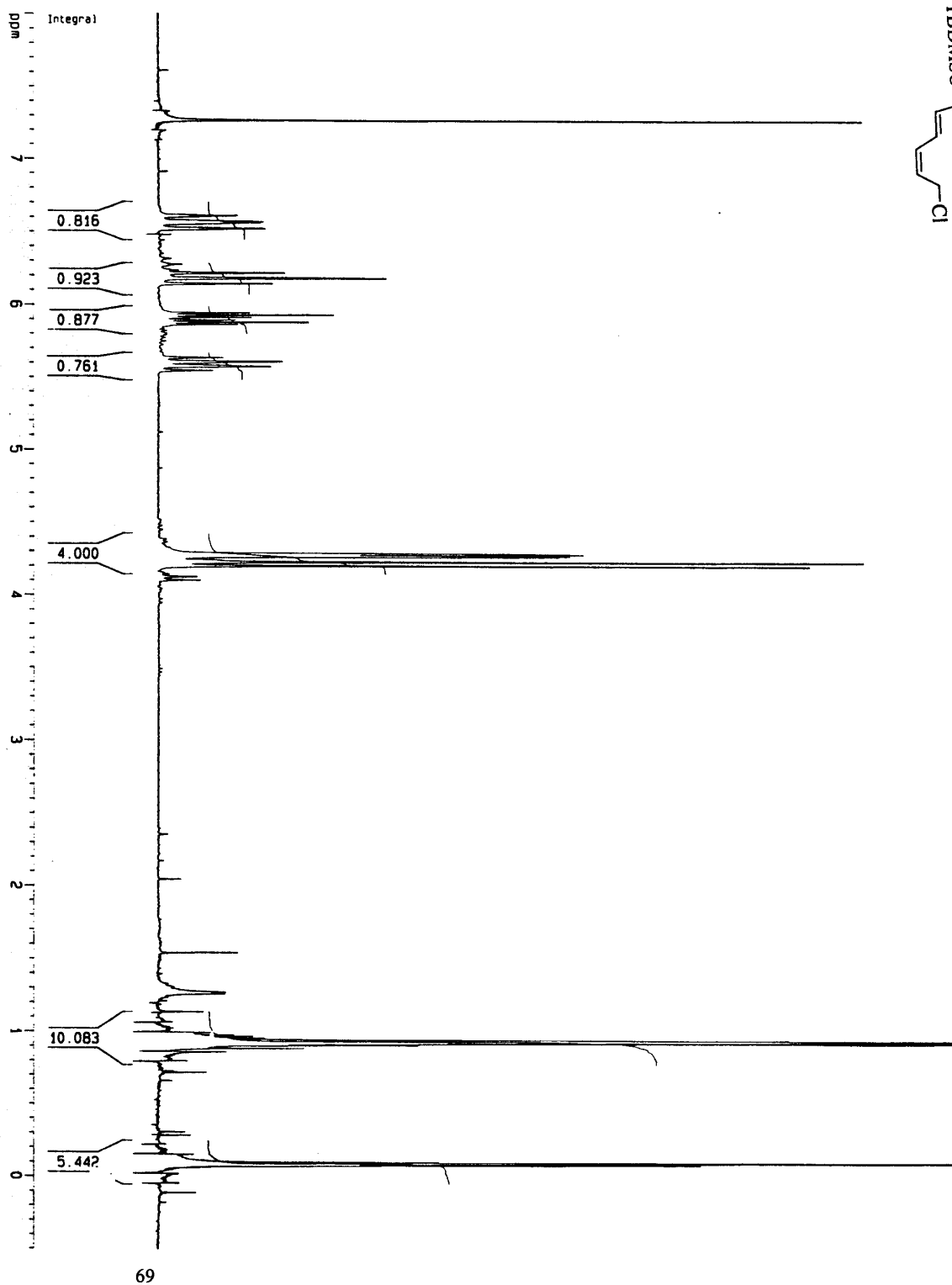


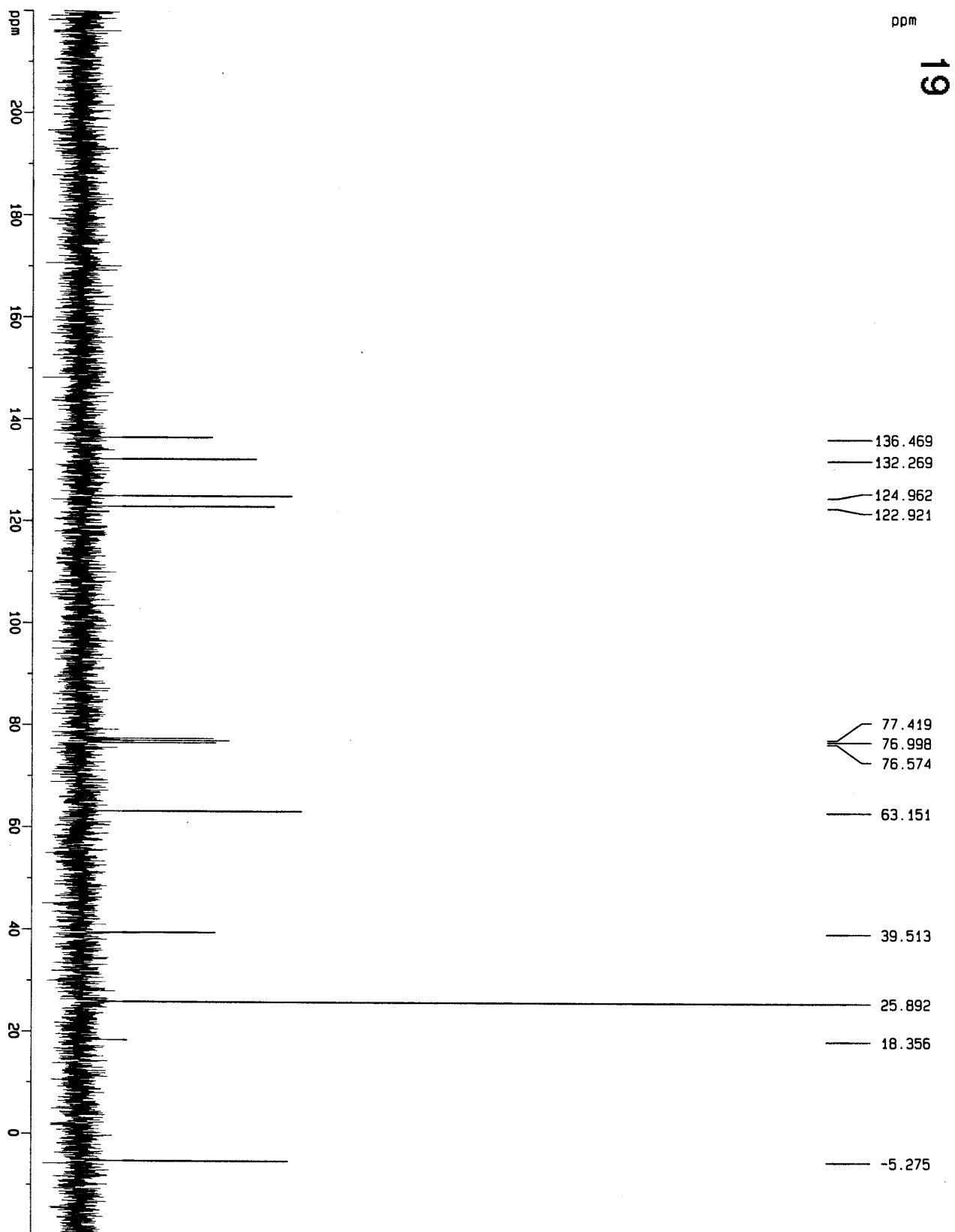
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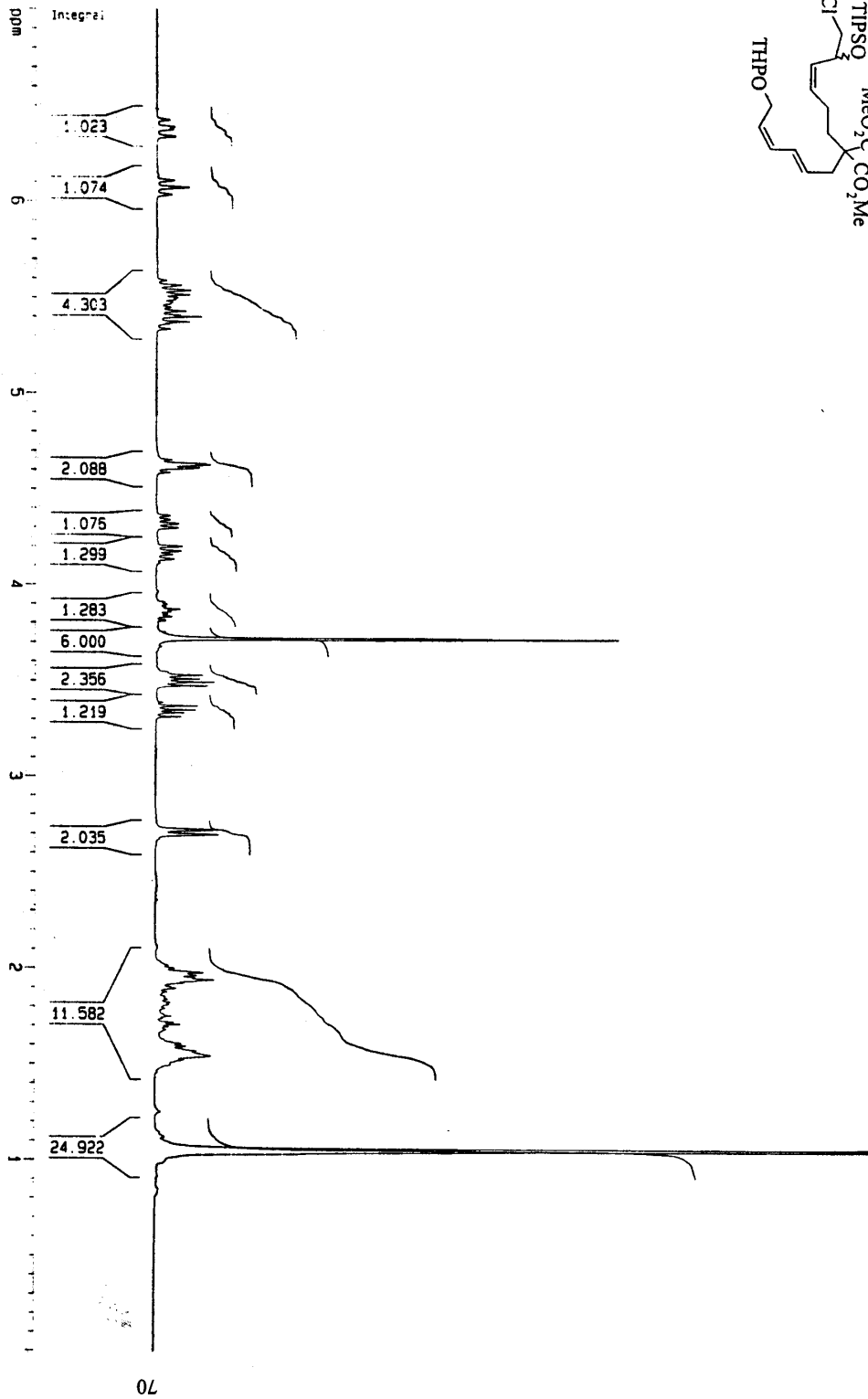
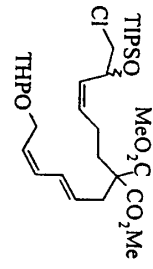
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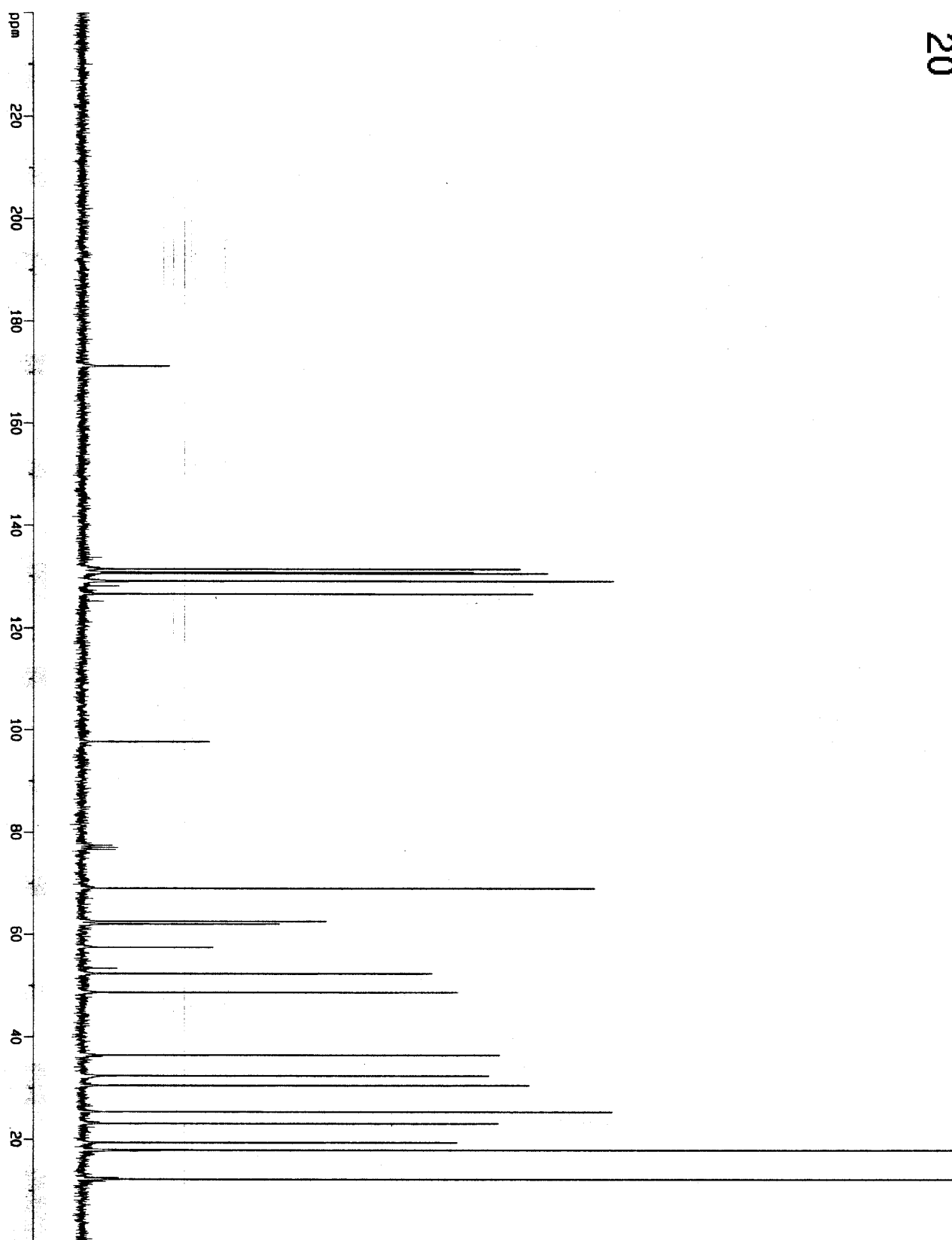


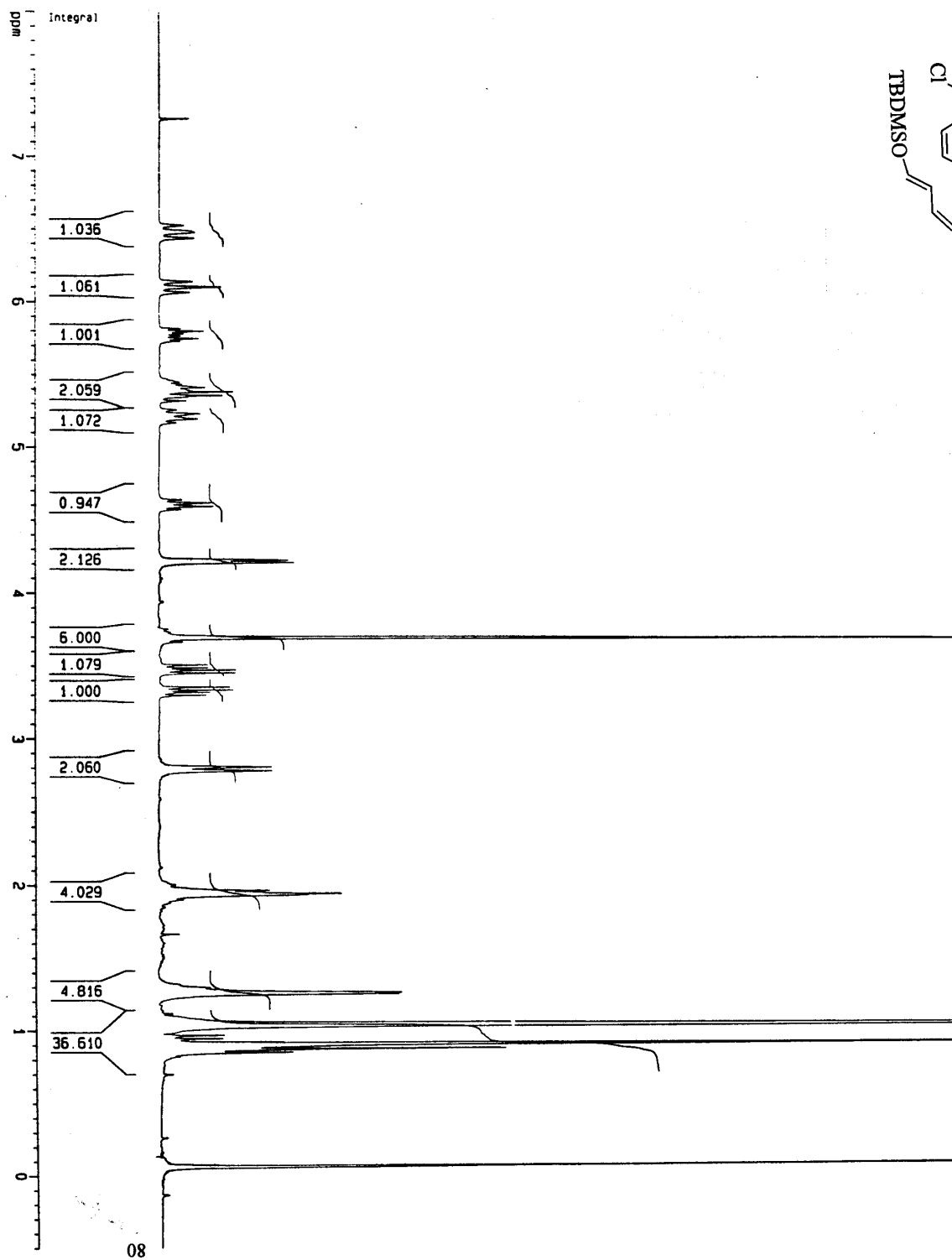
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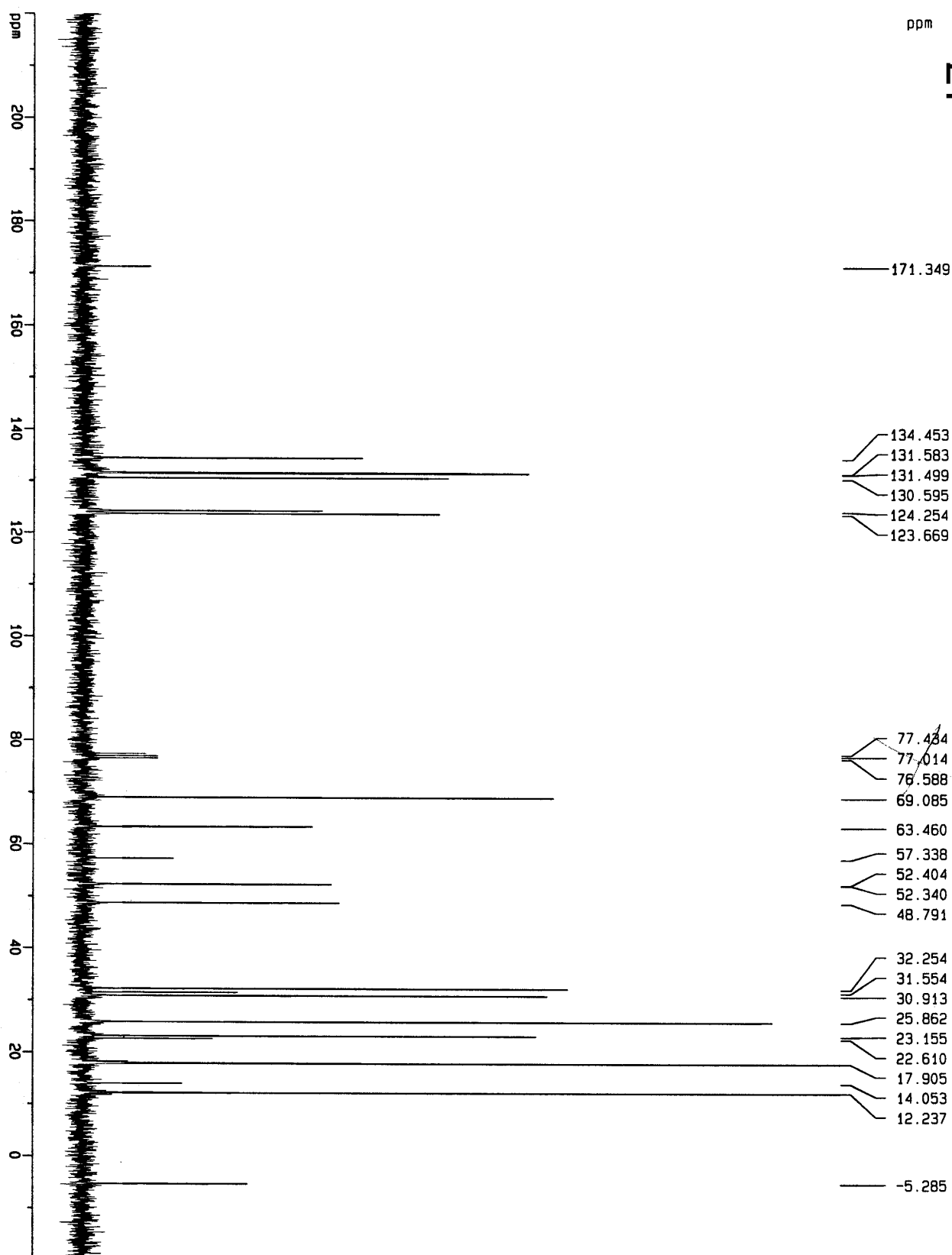




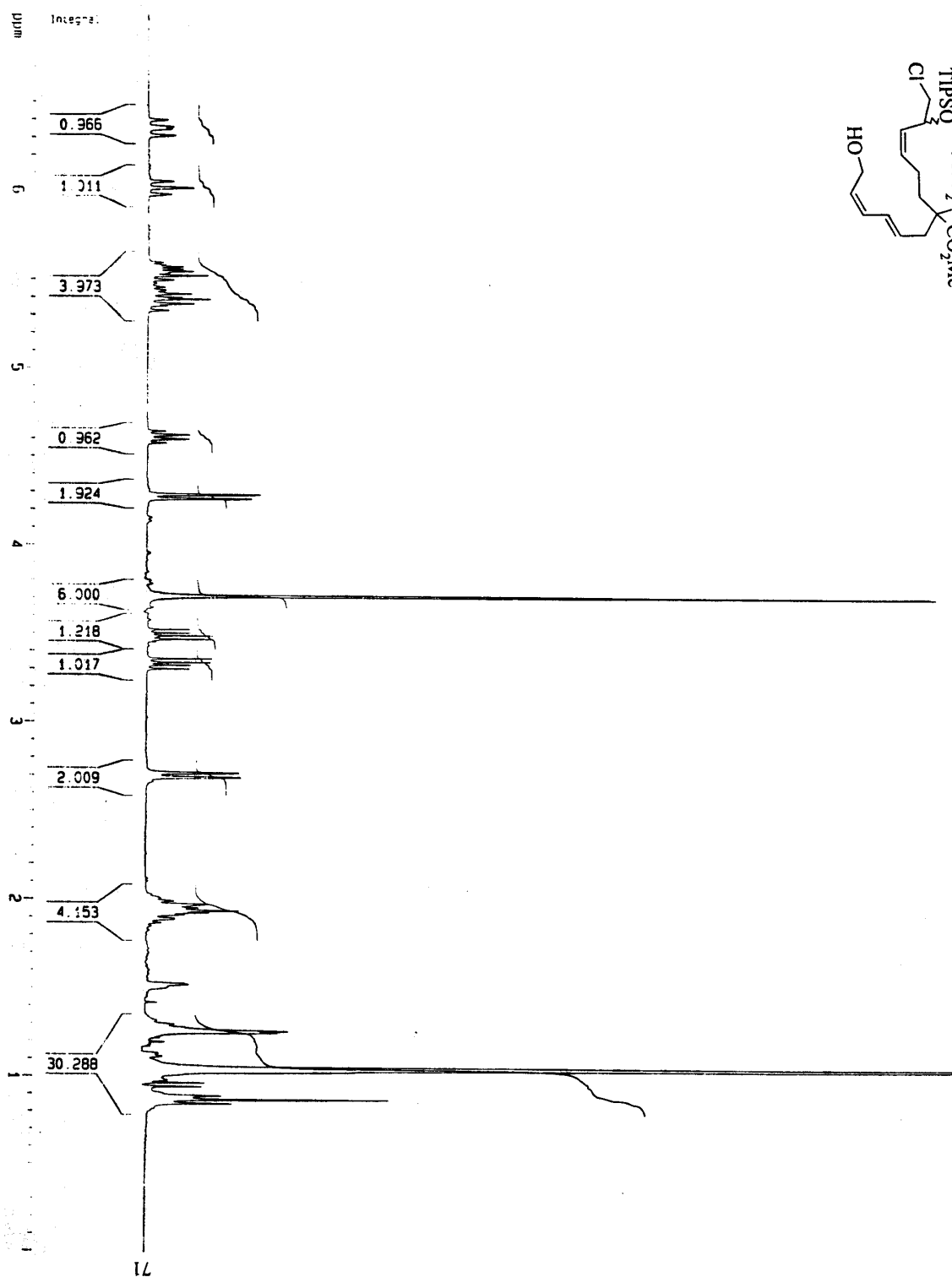
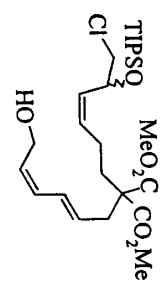


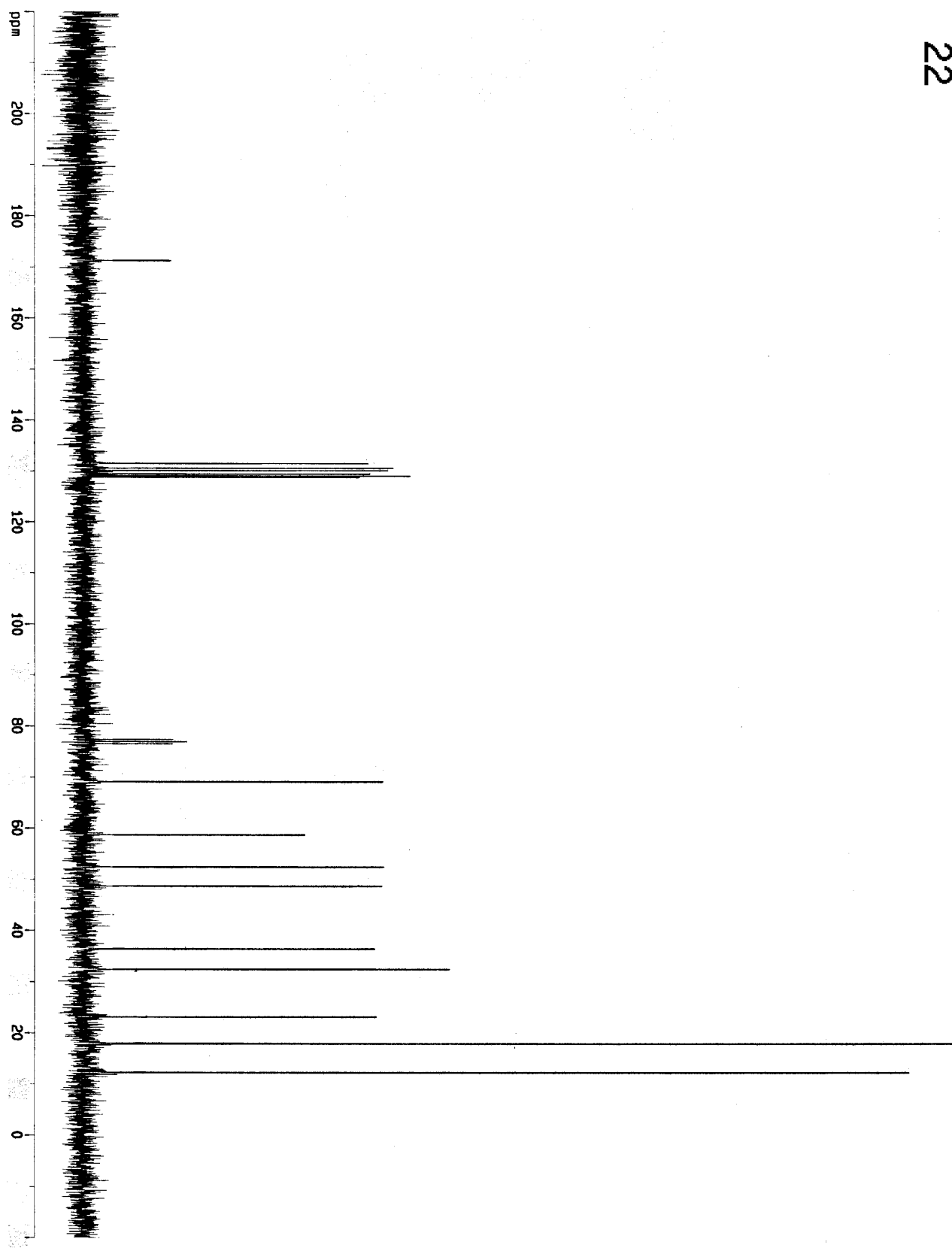
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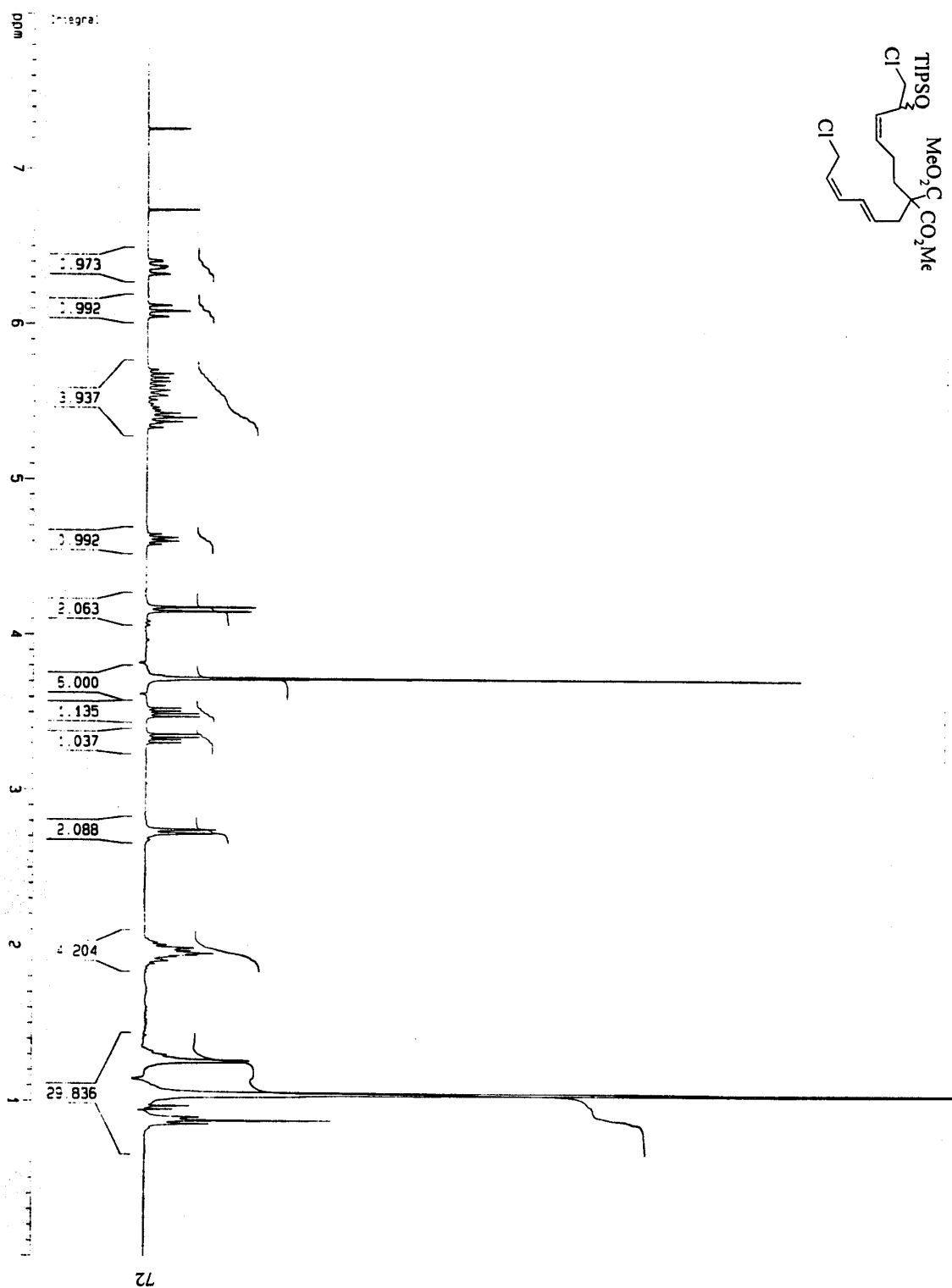
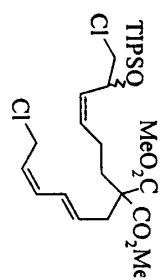
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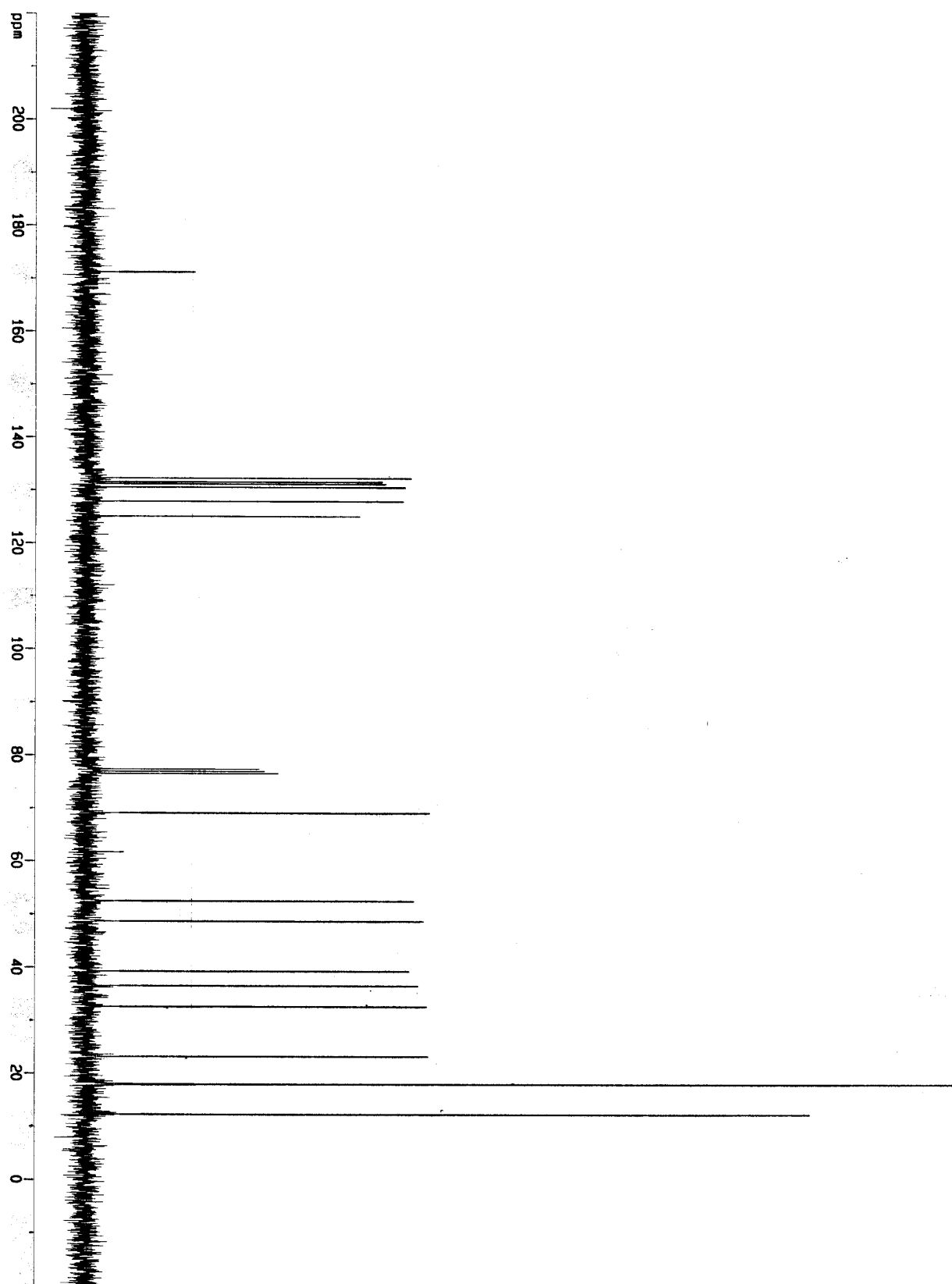


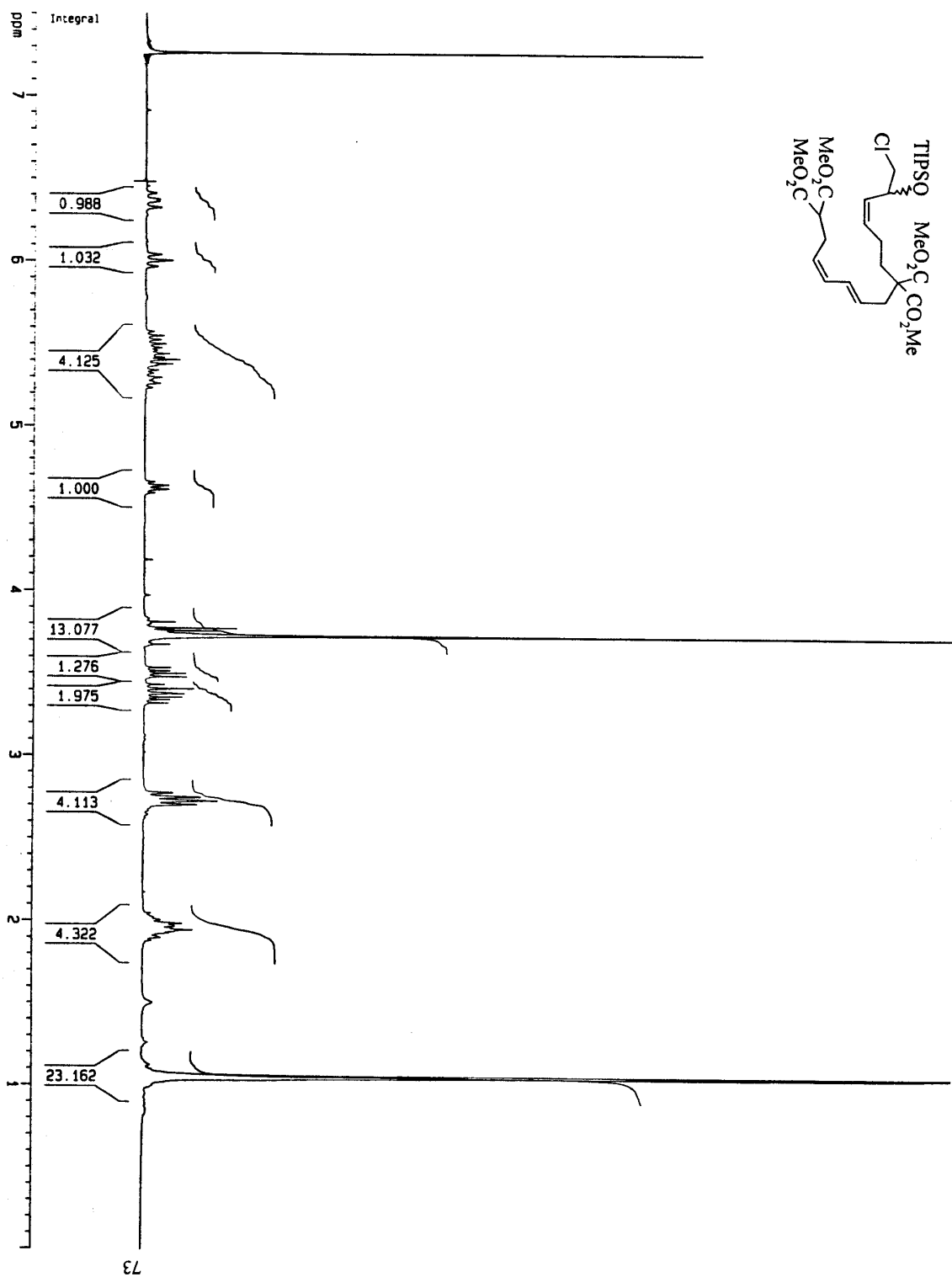
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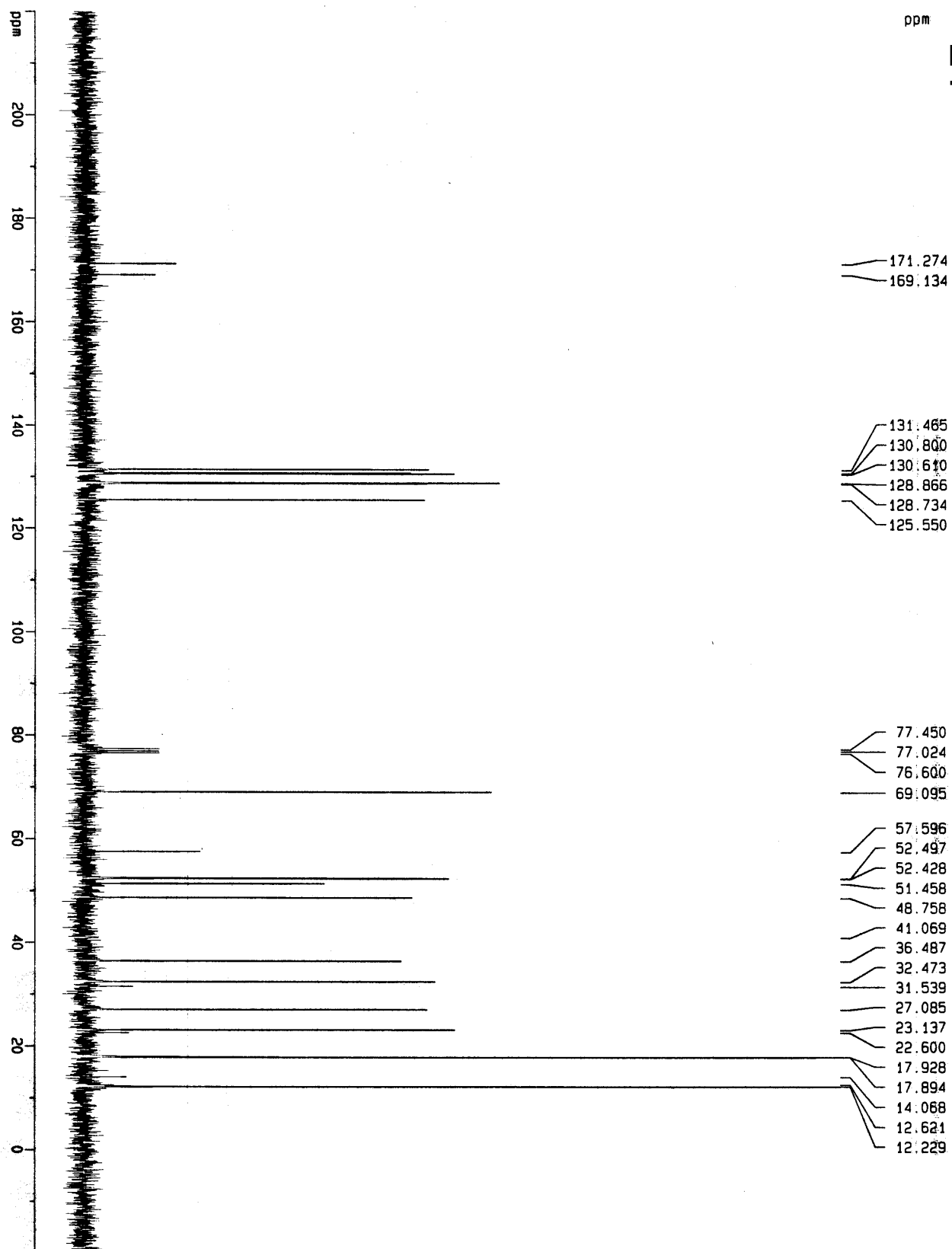




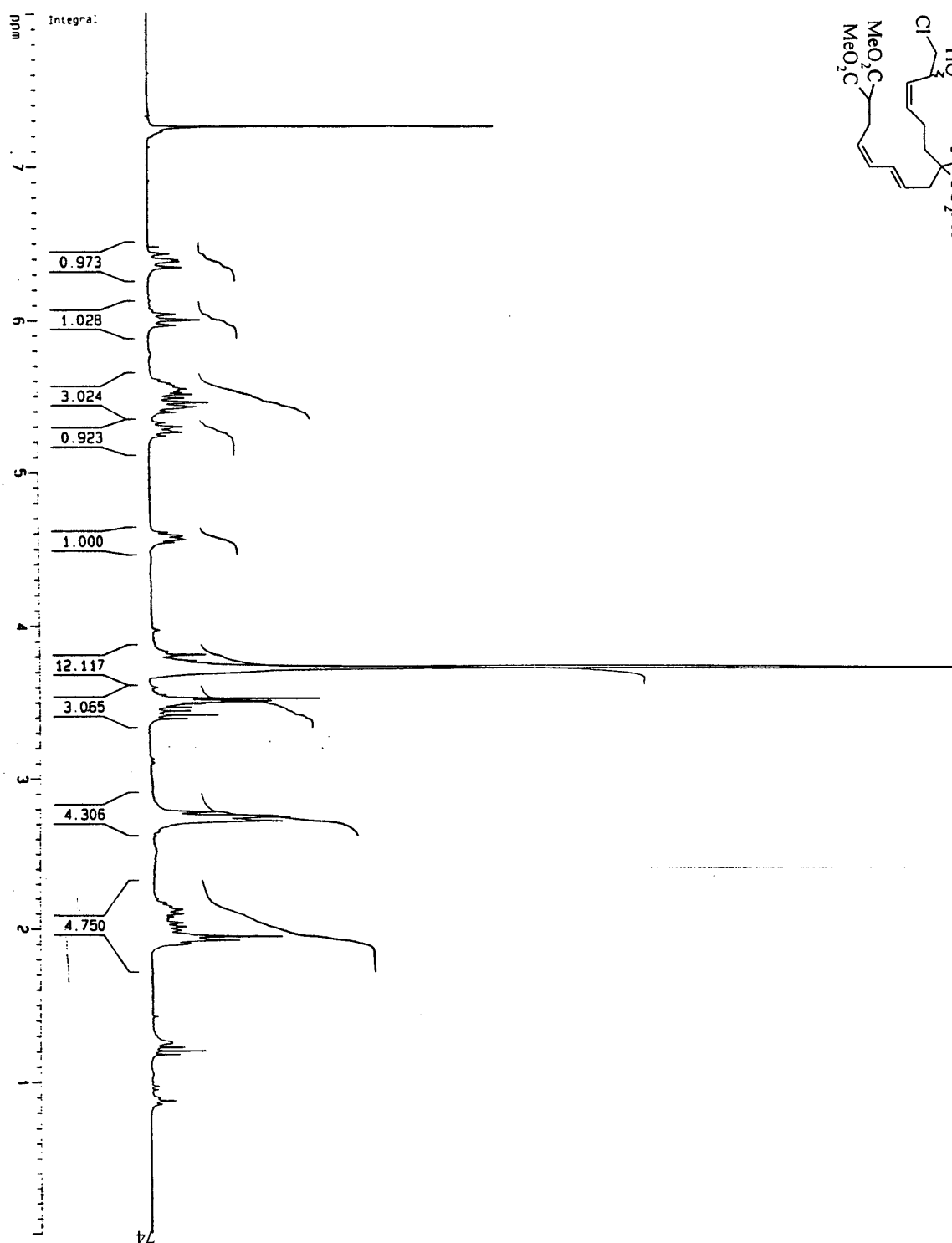
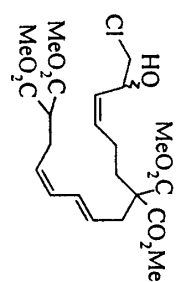


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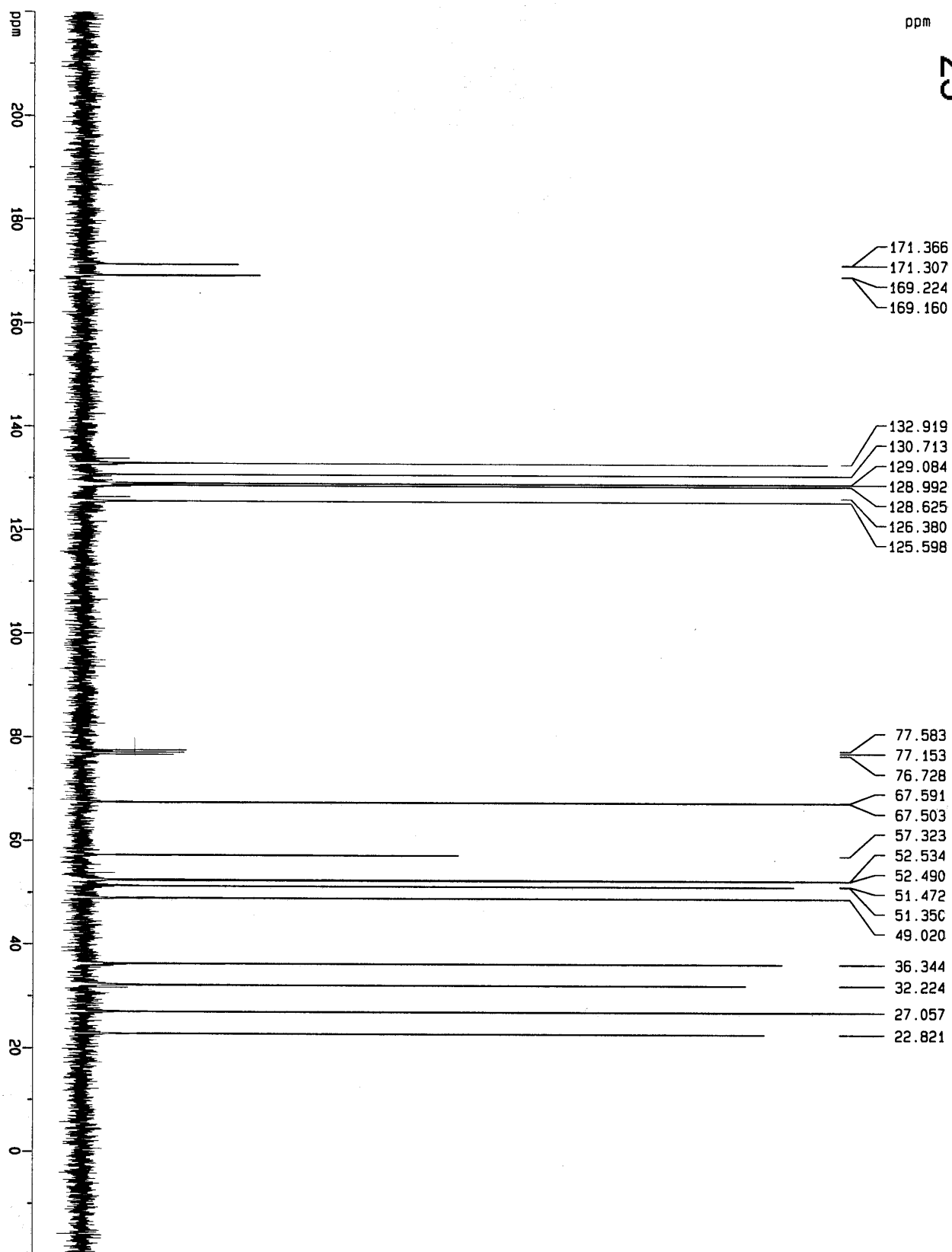


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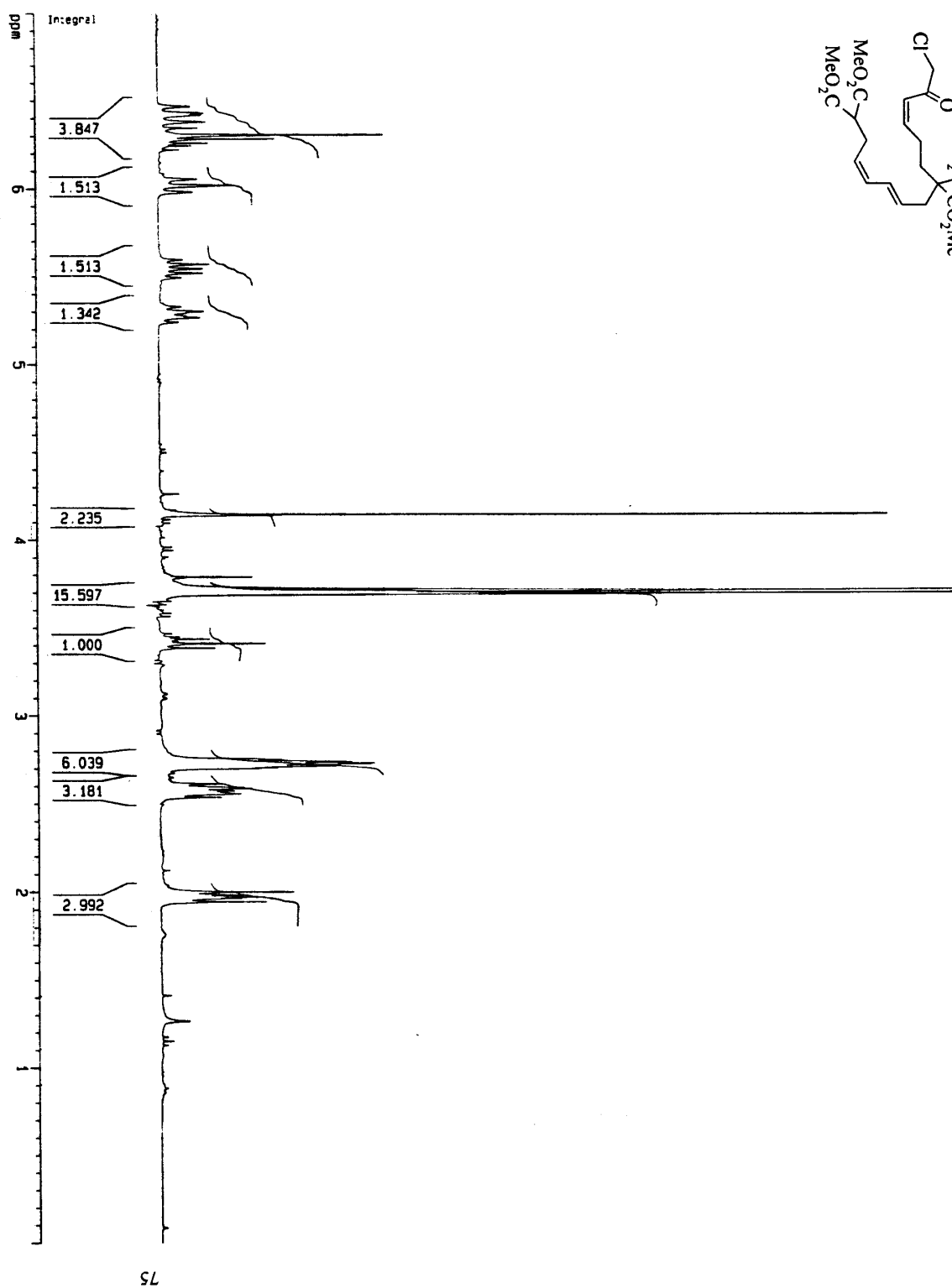
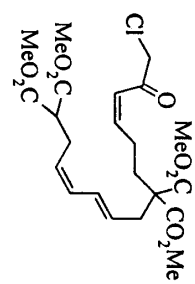


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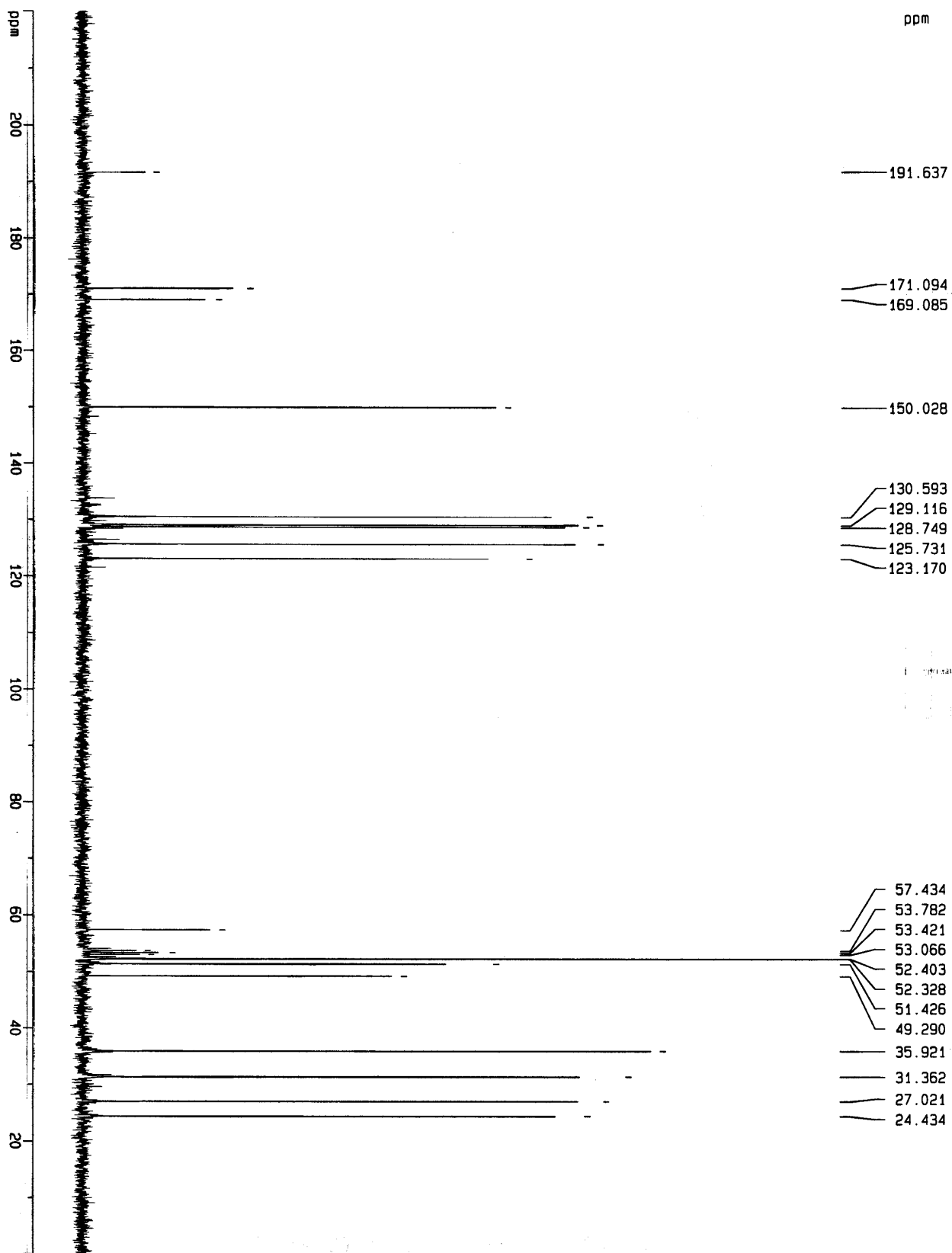
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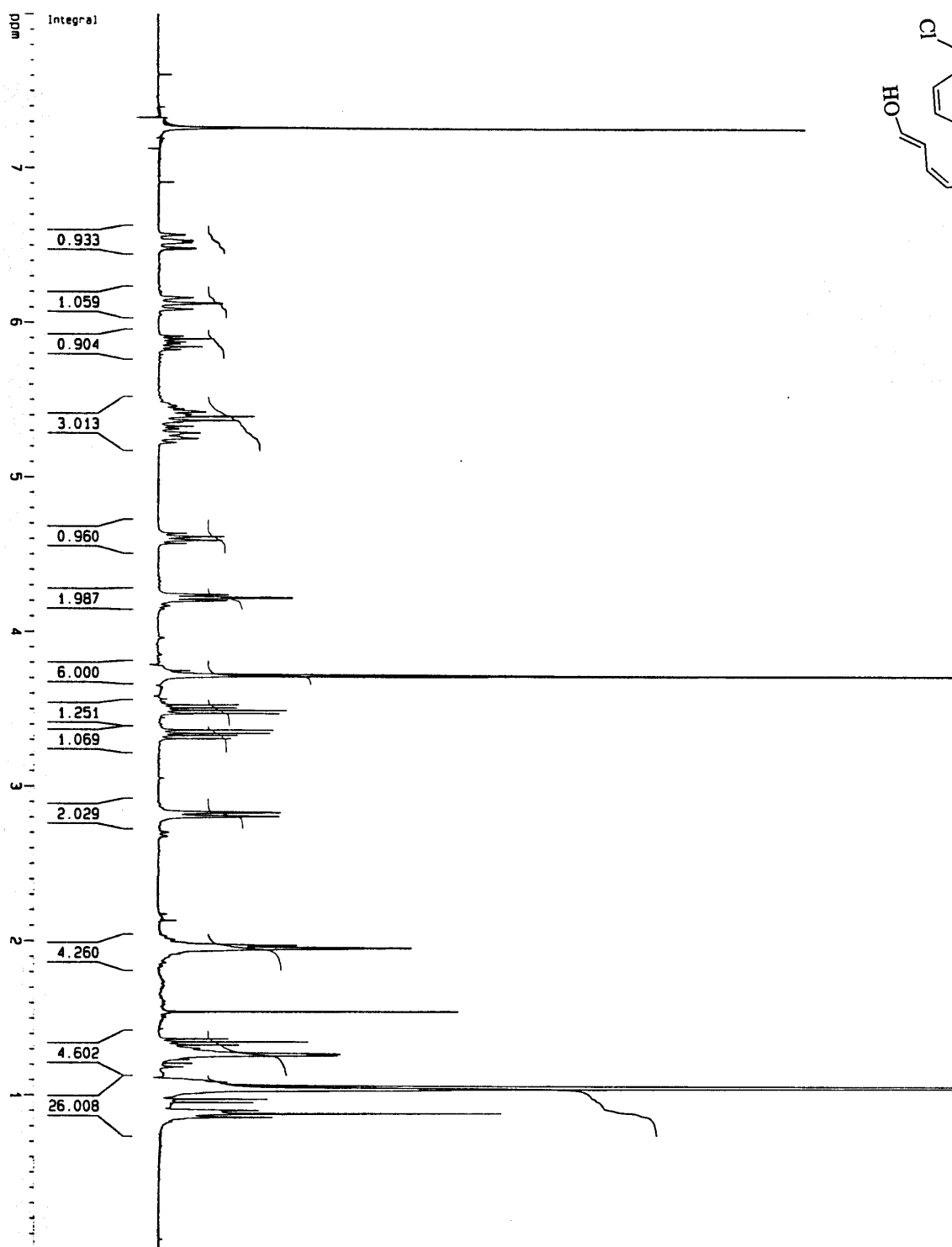
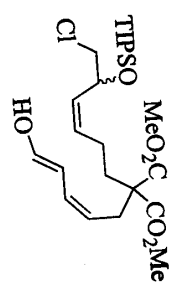
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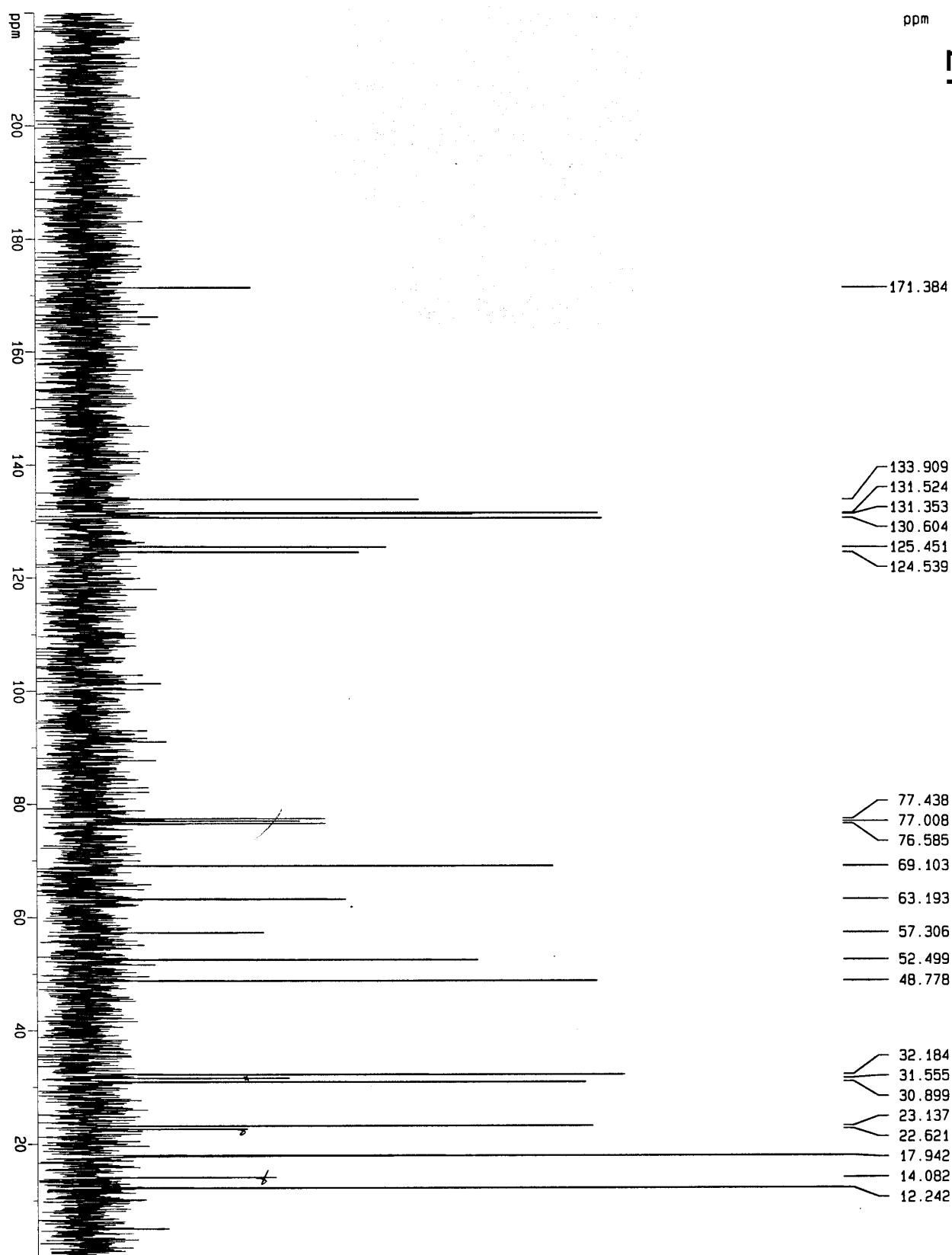
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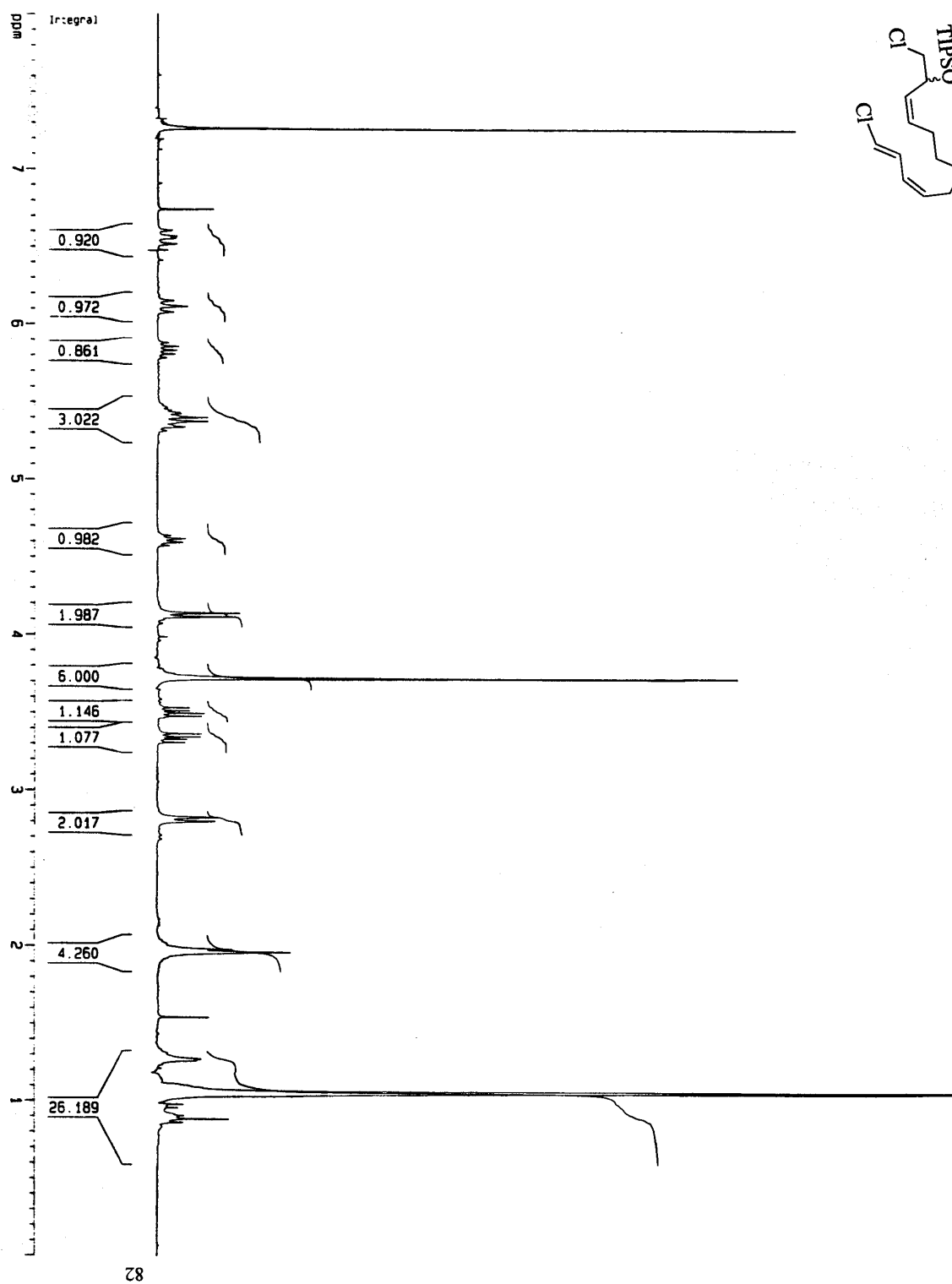
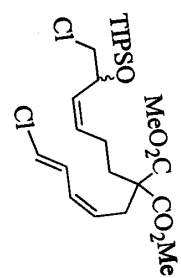


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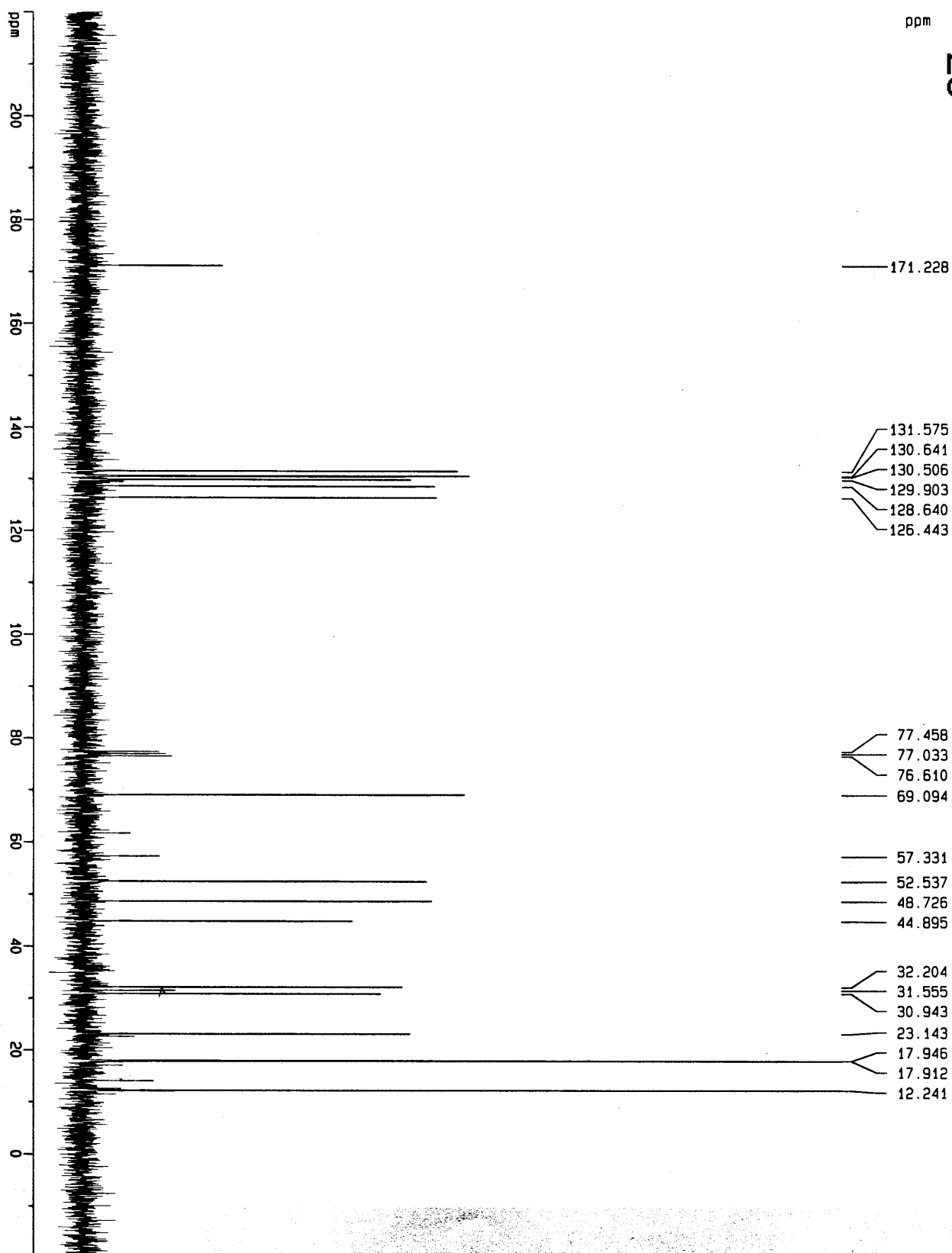
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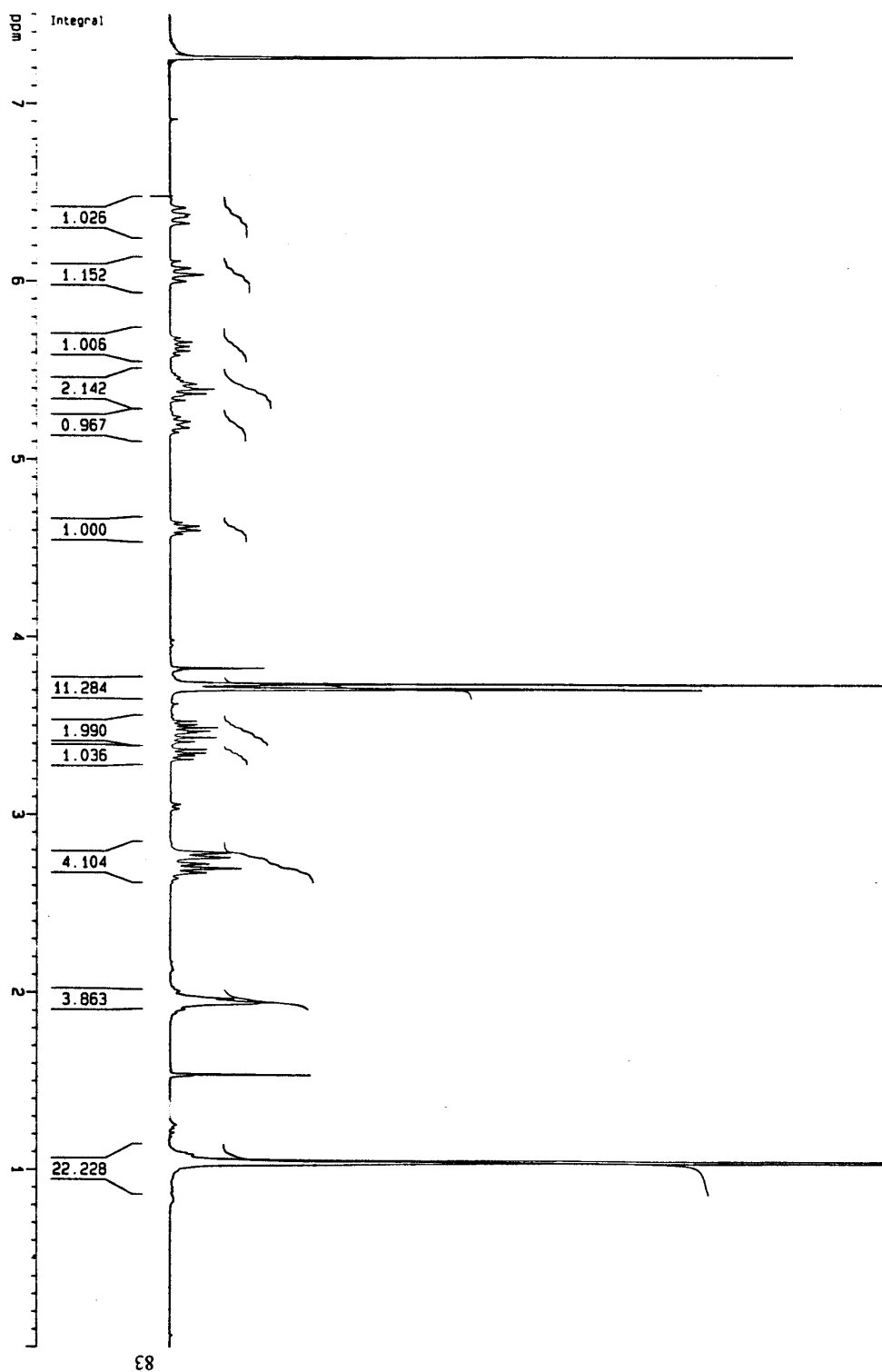
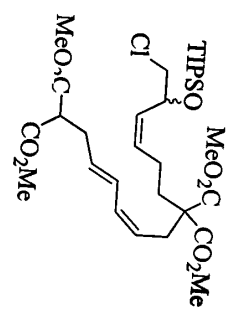




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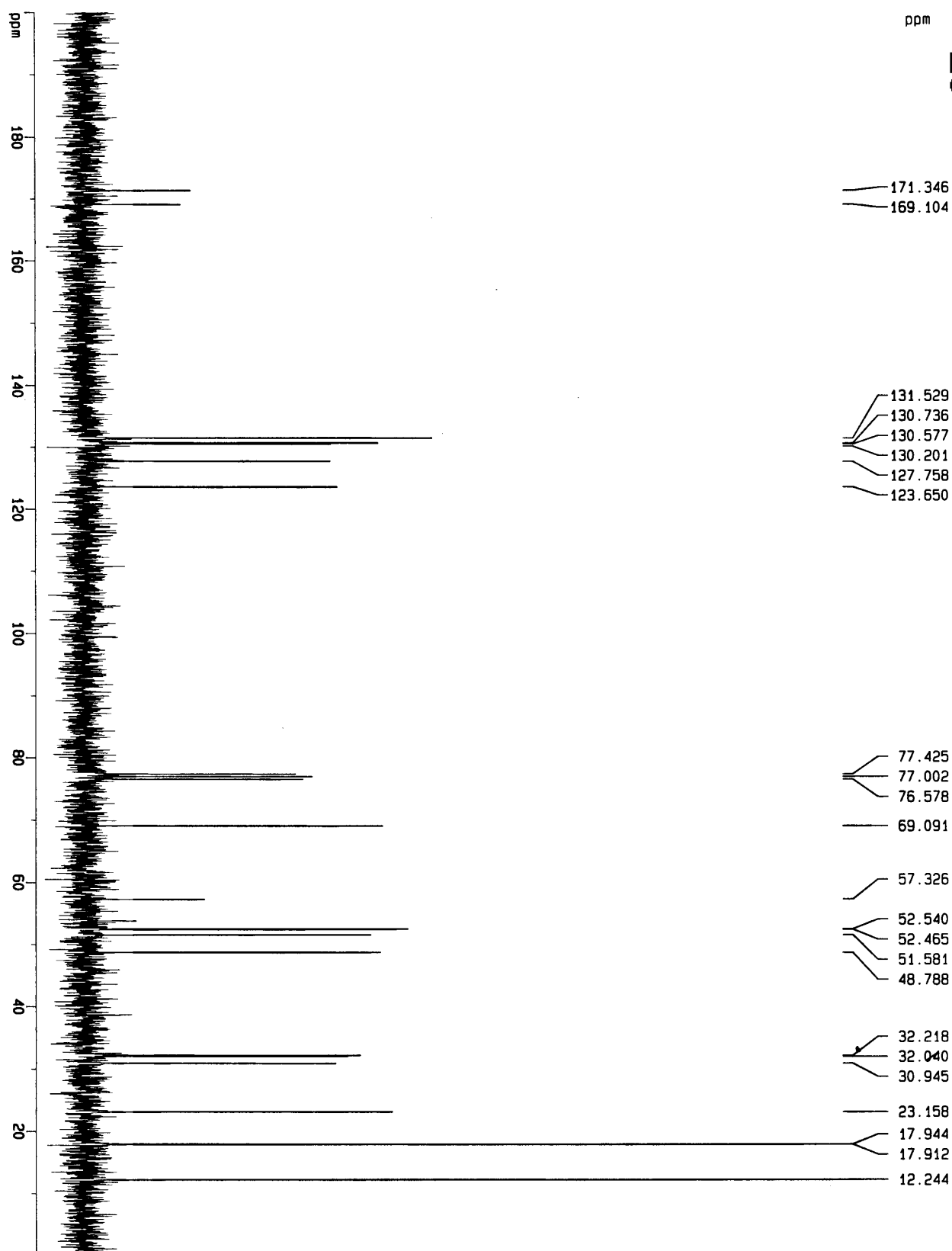
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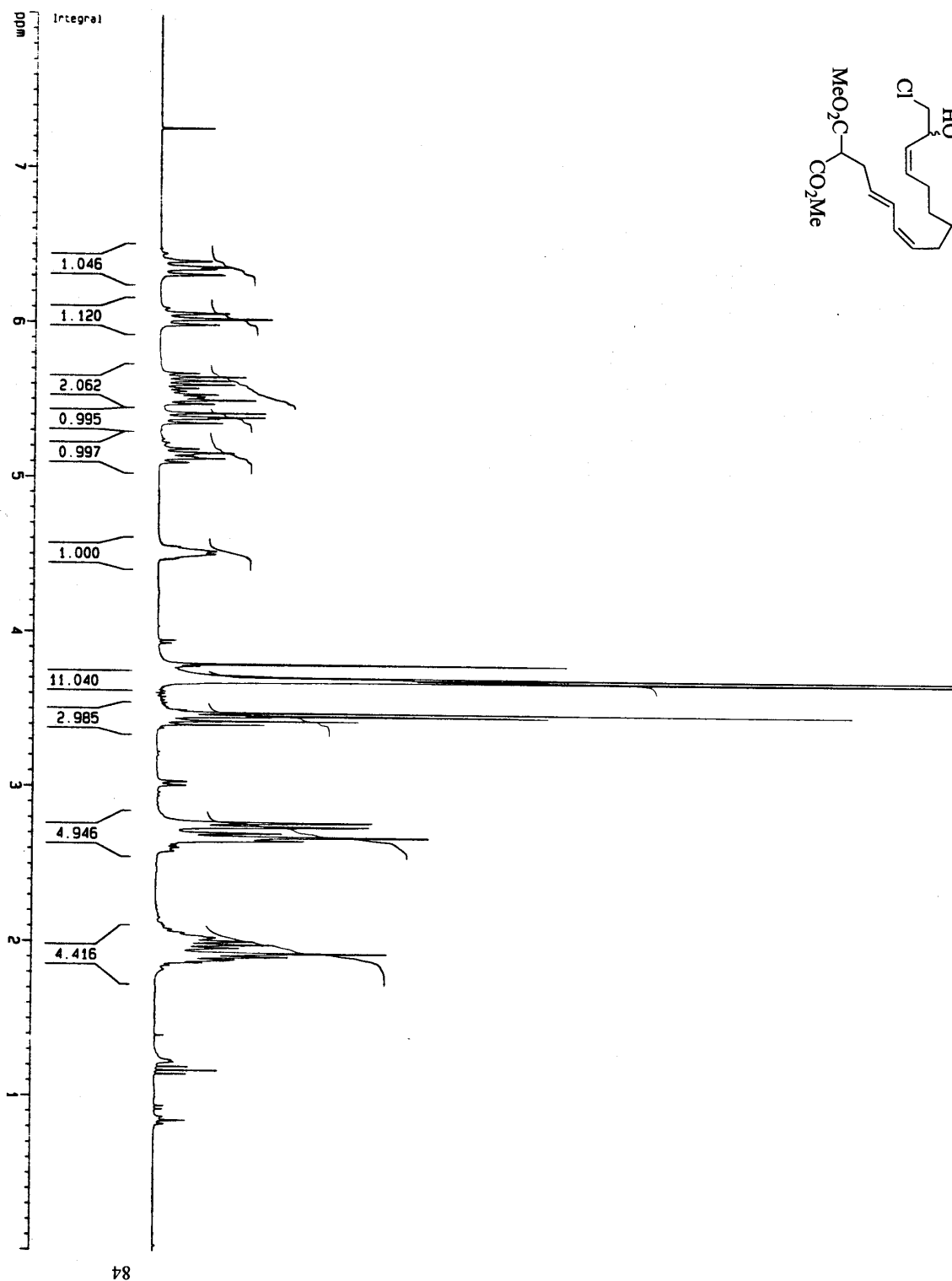
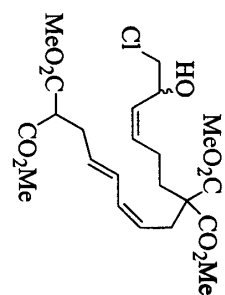


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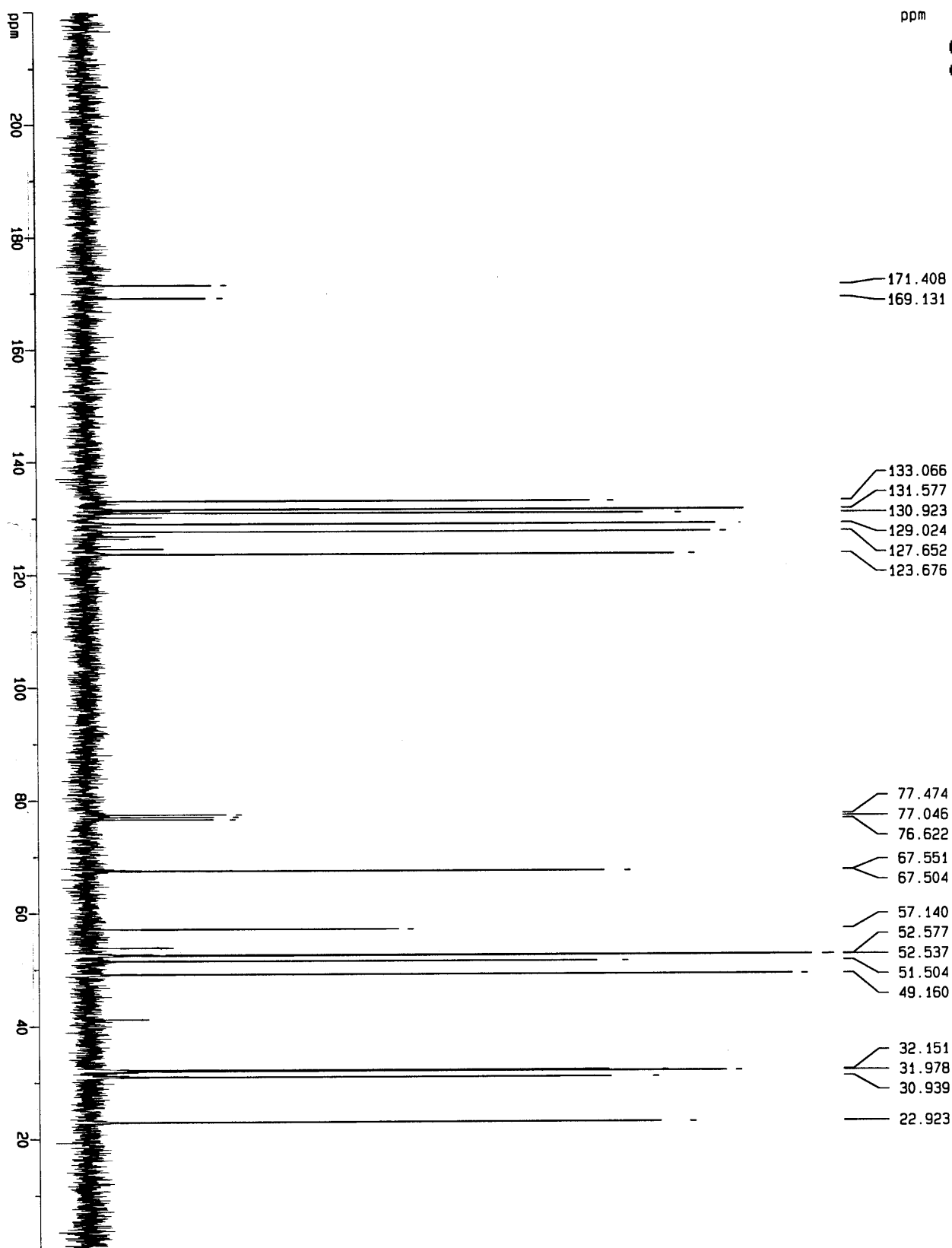
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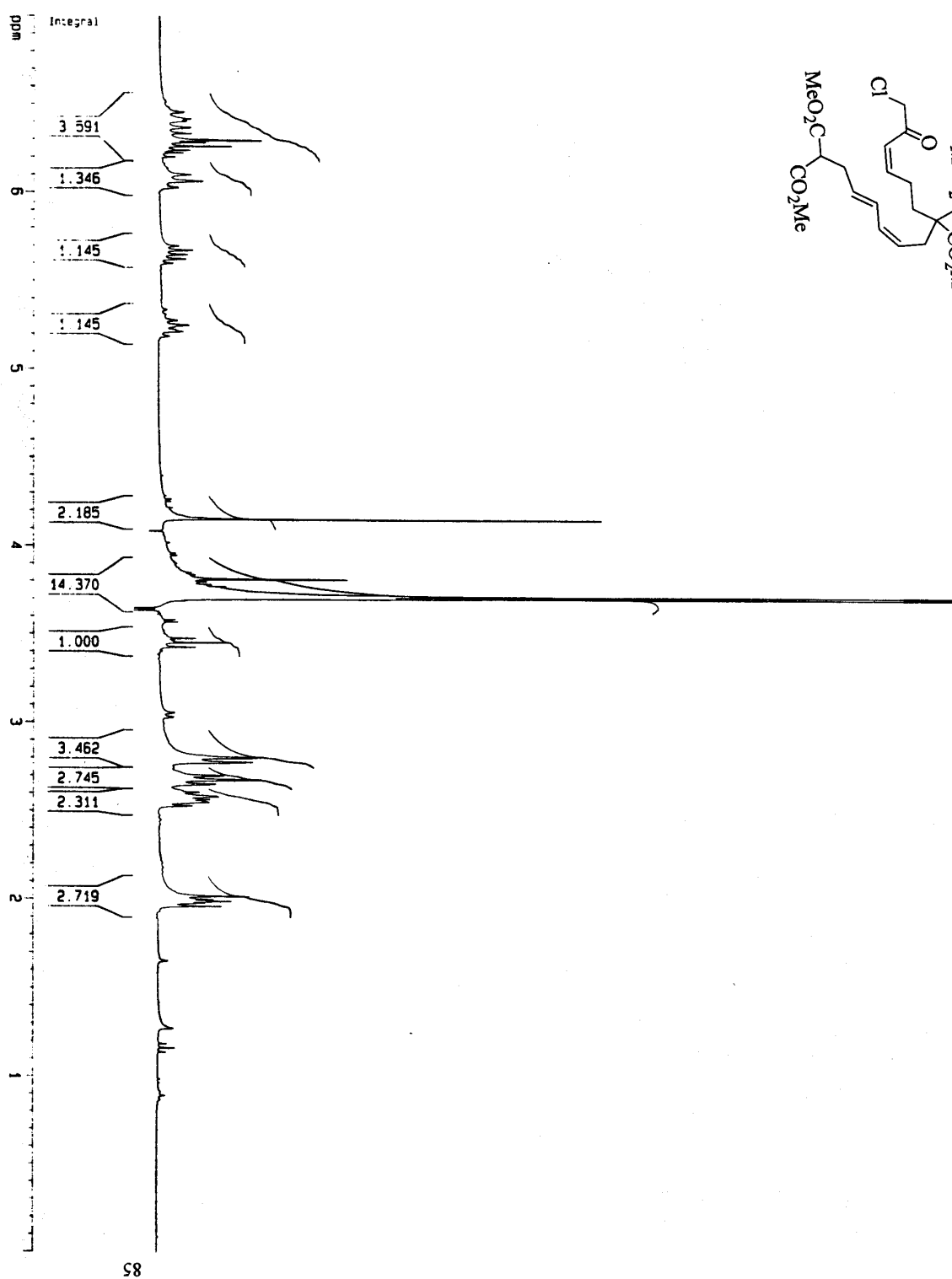
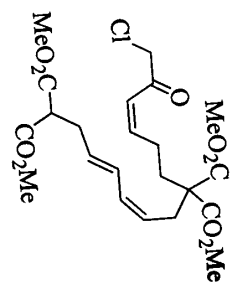
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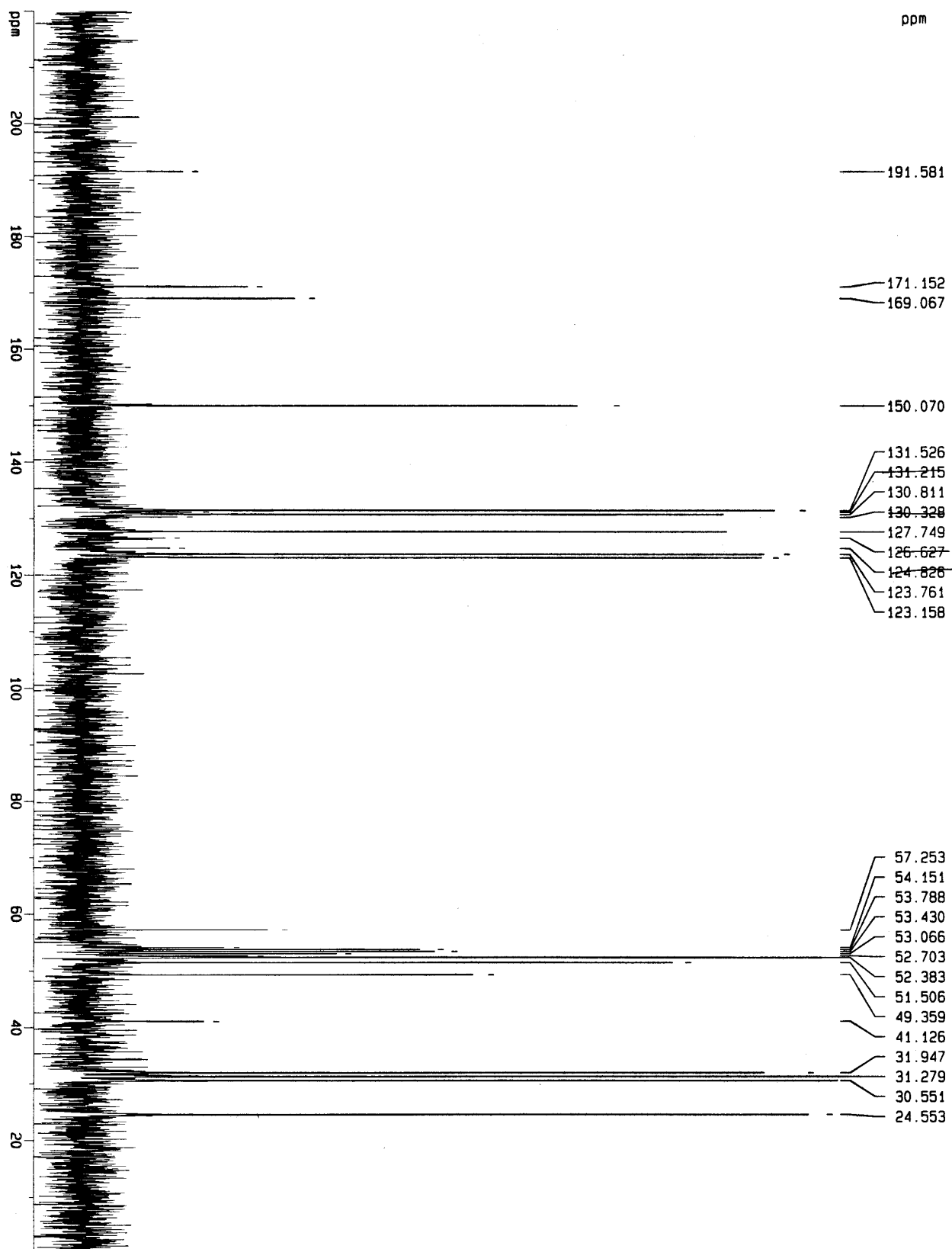


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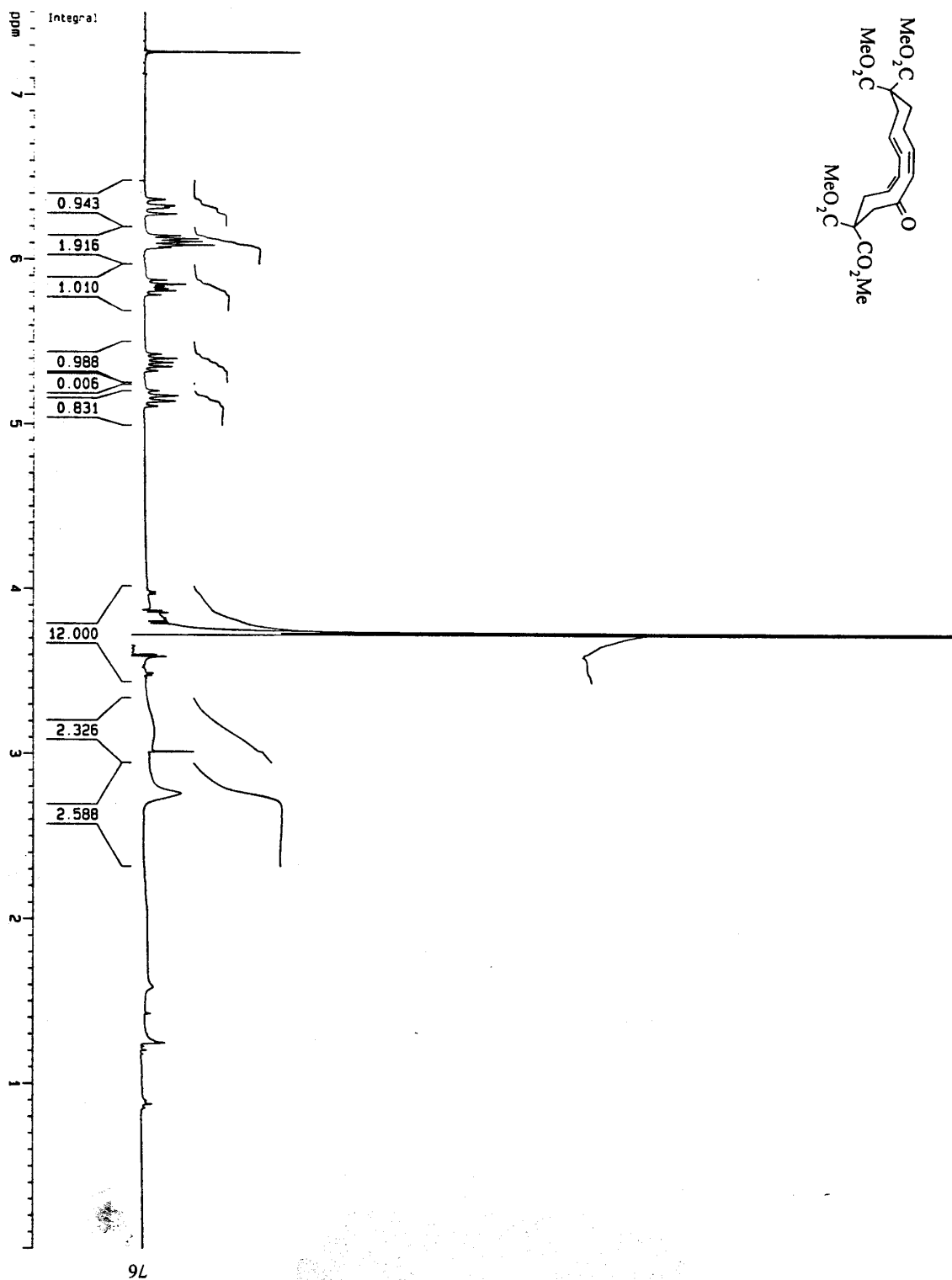
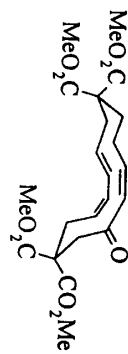


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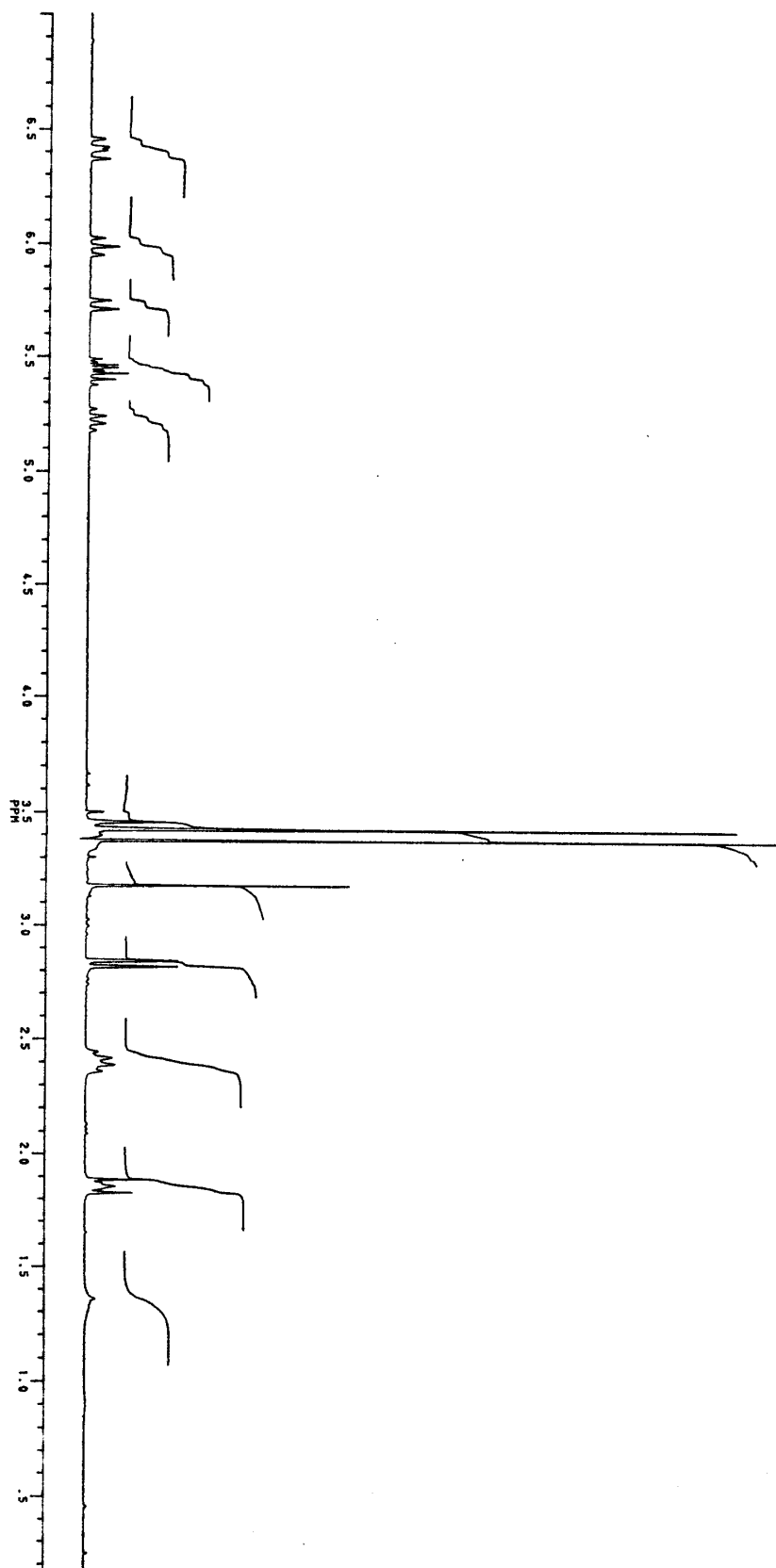


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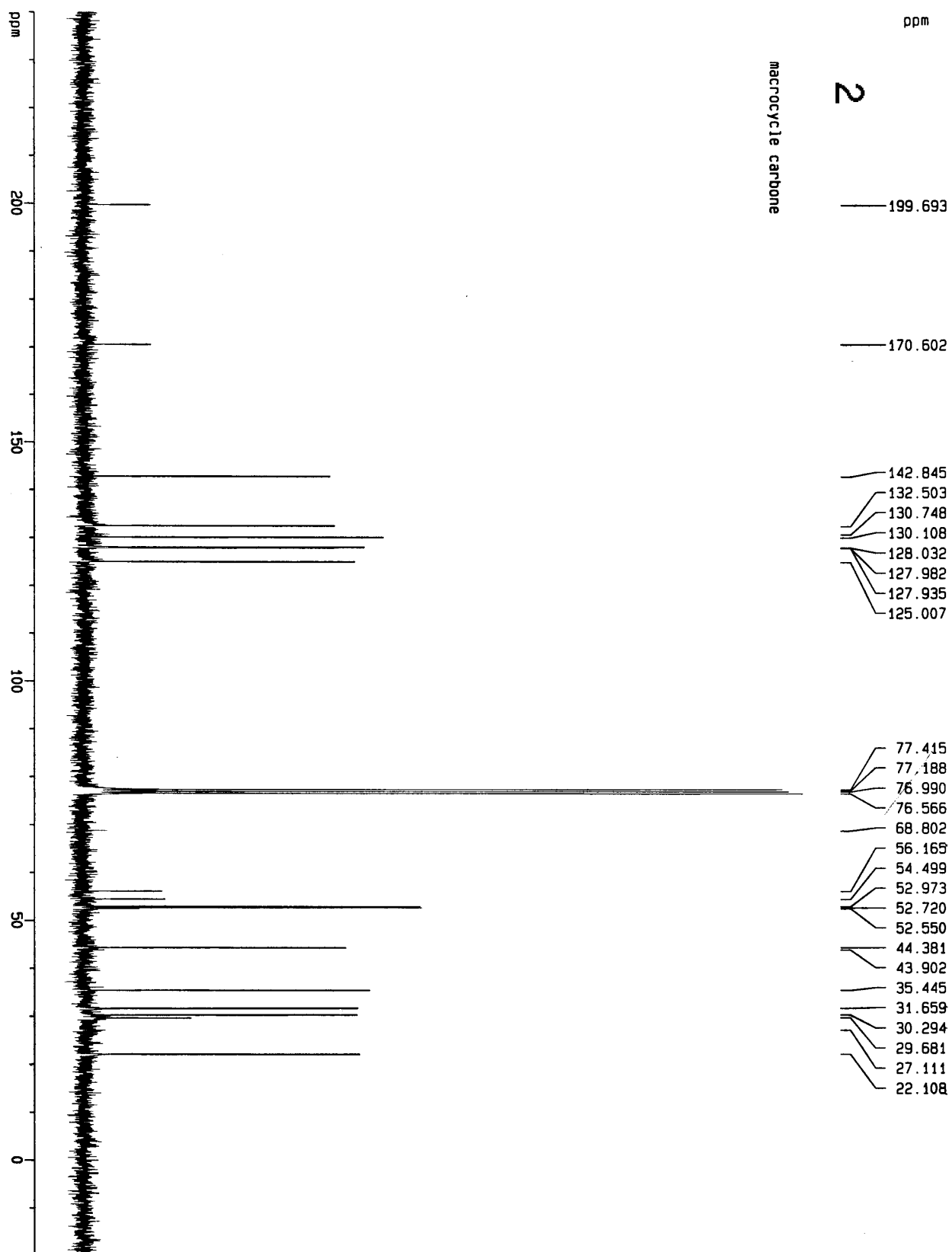


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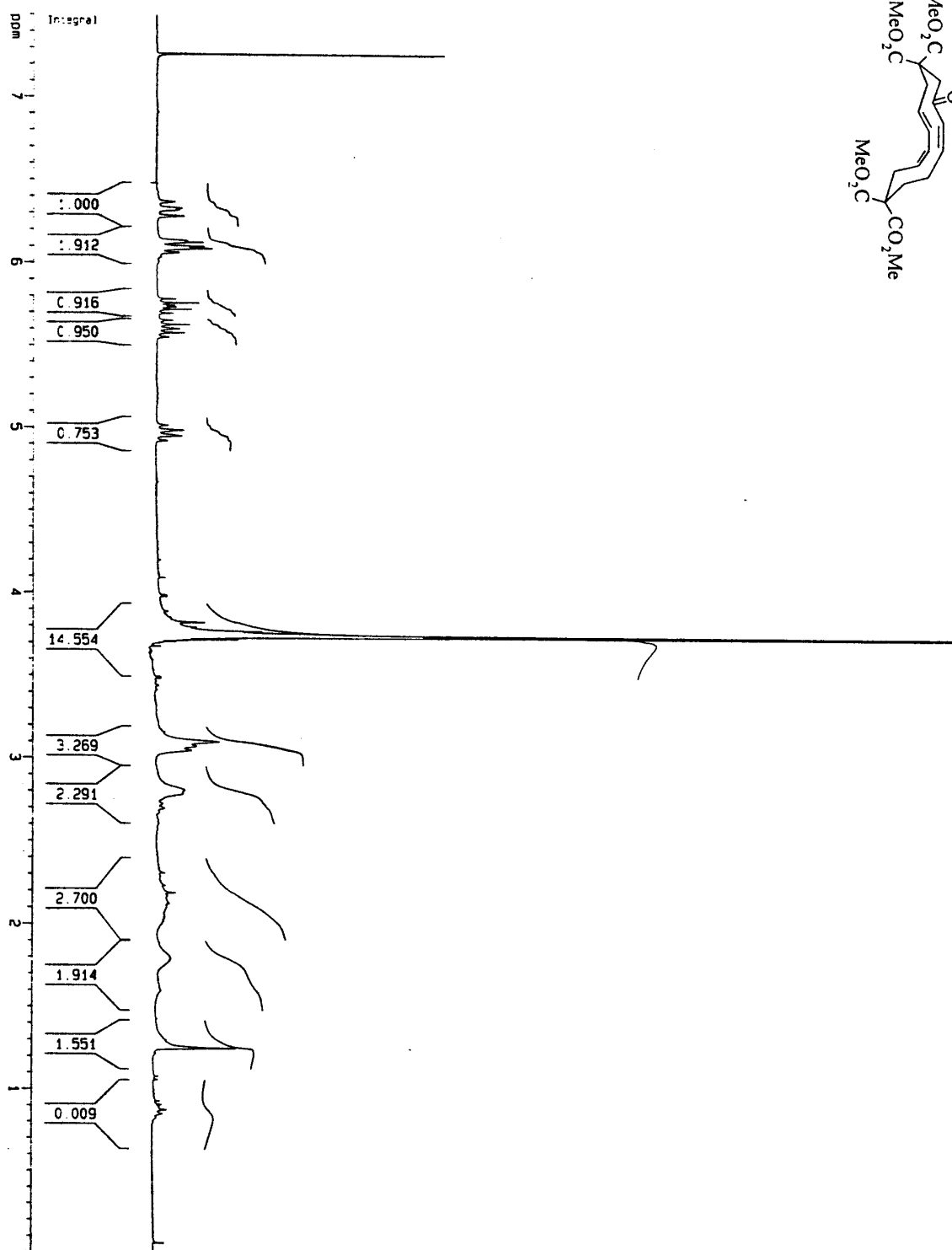
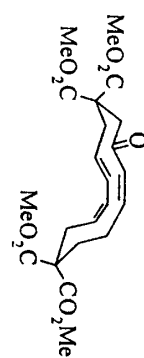
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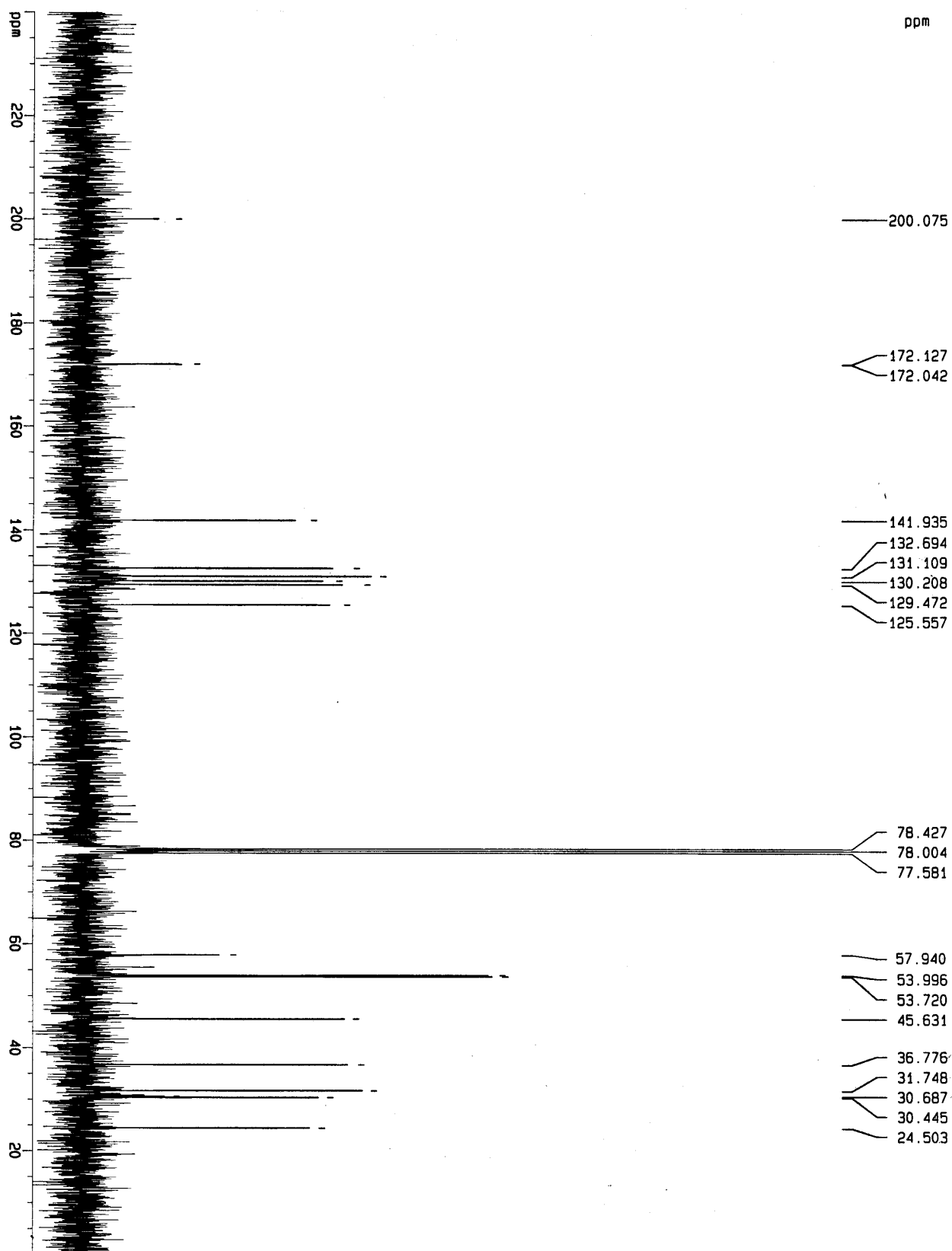


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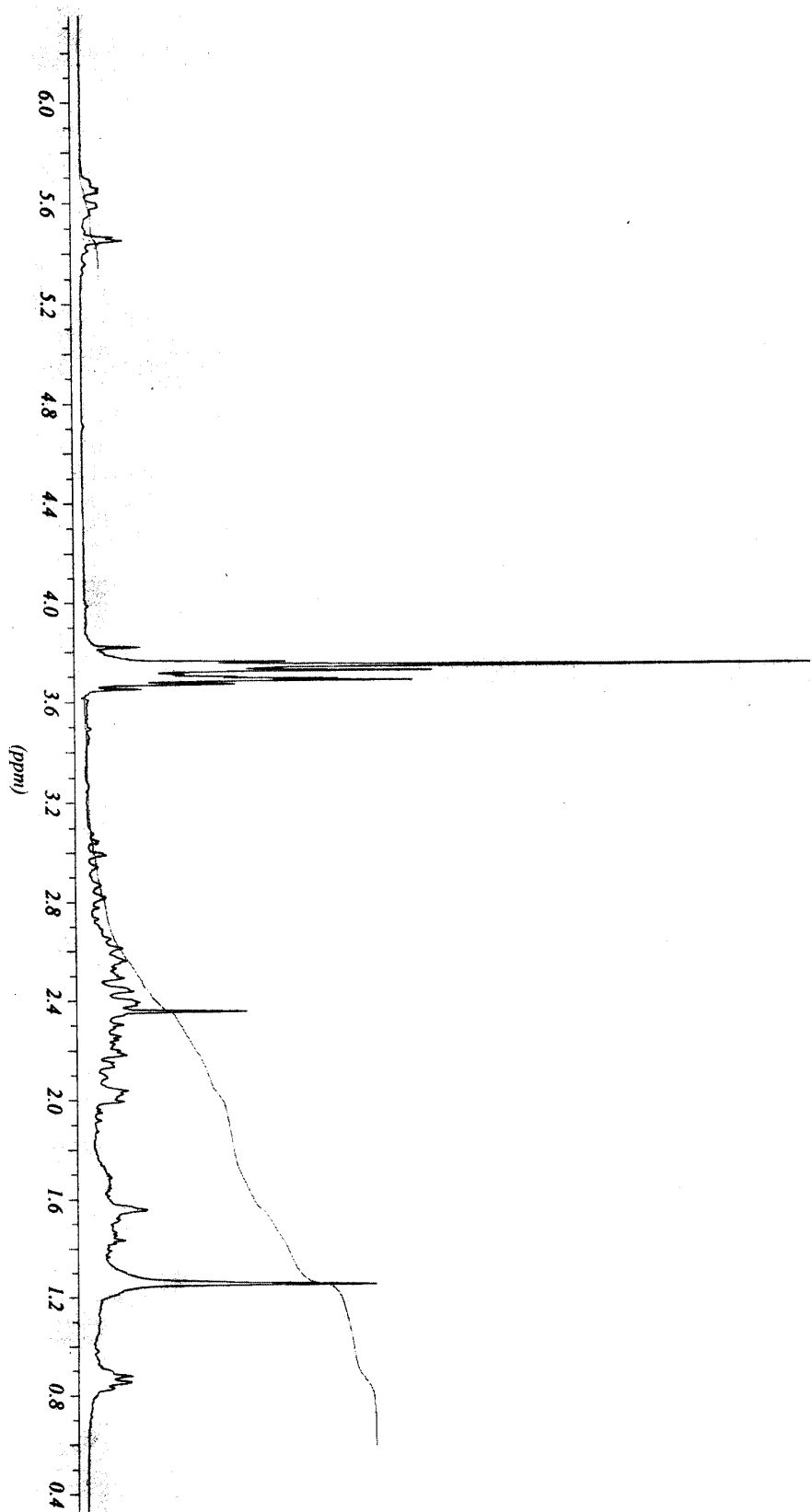


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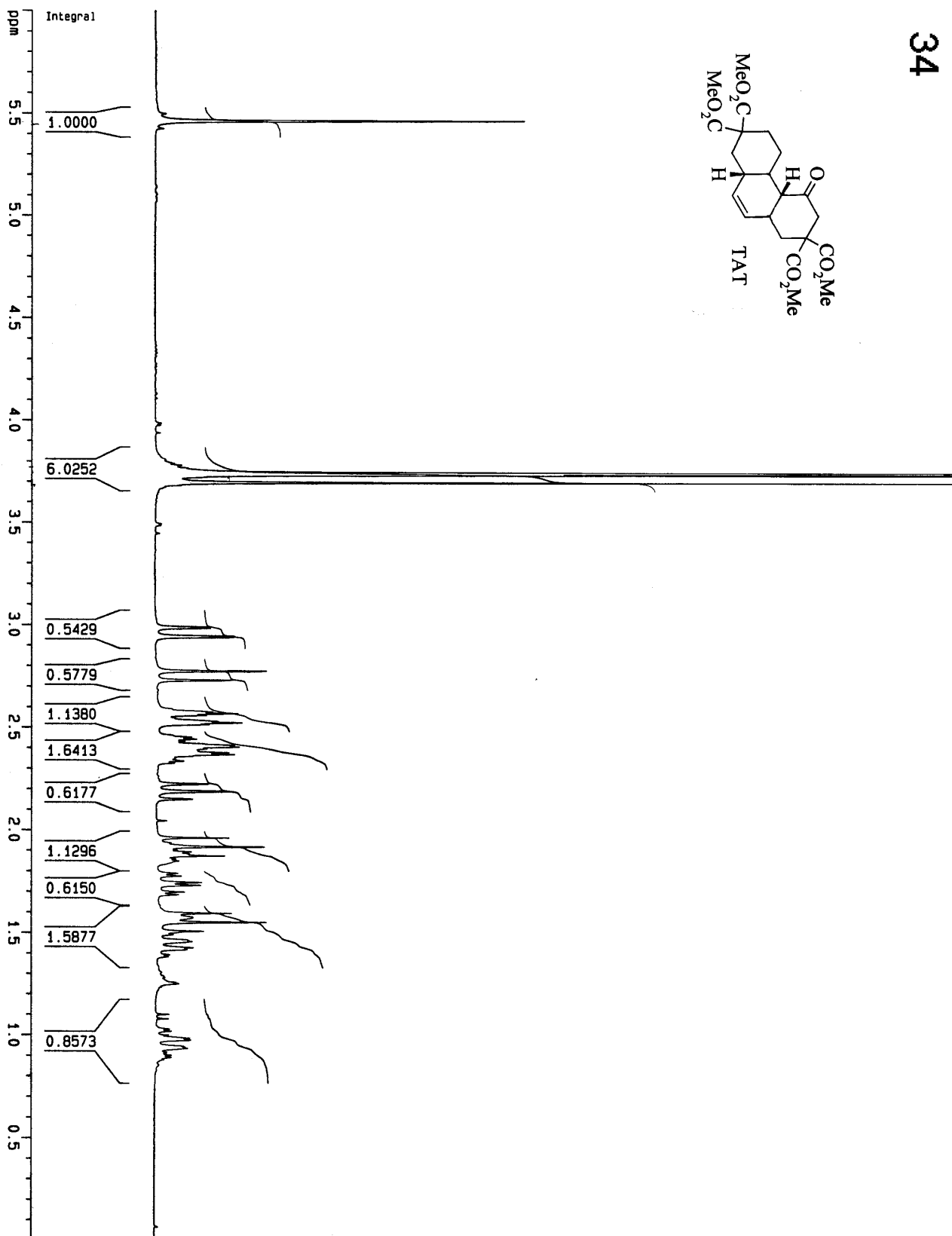
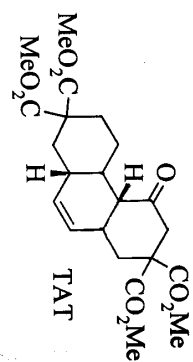
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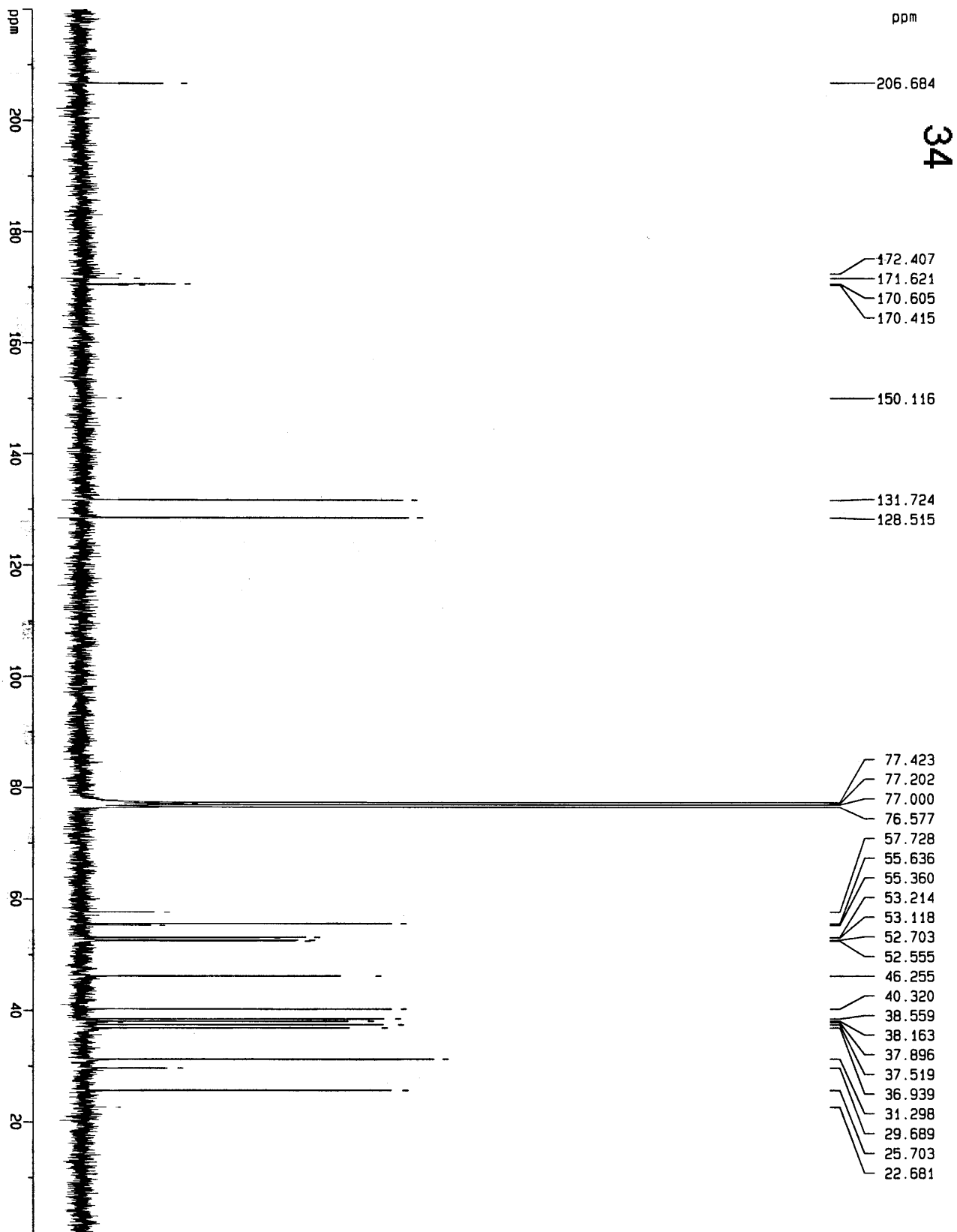


Mixture of 33 & 34

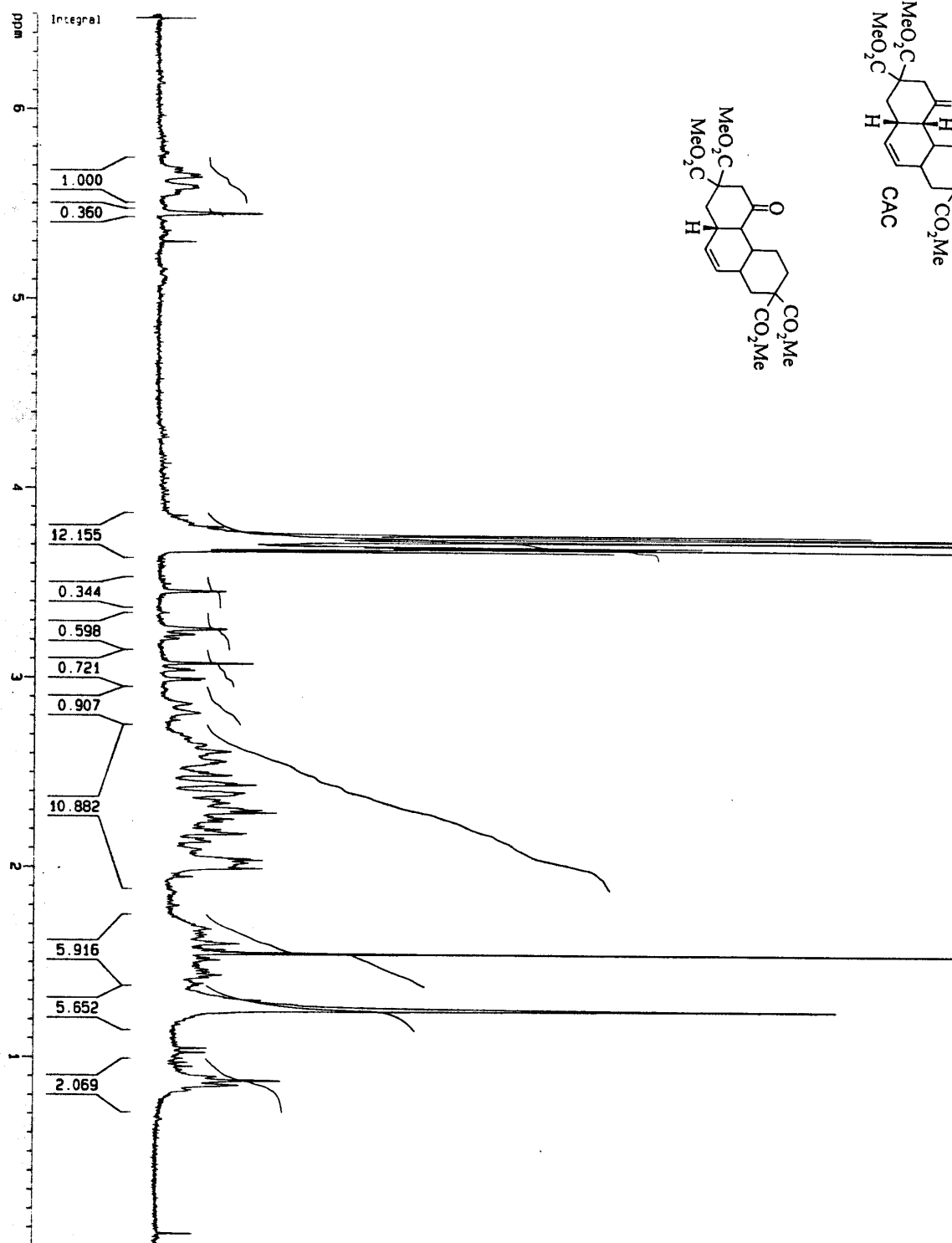
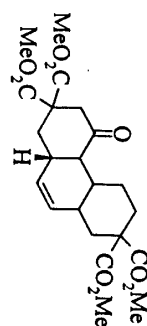
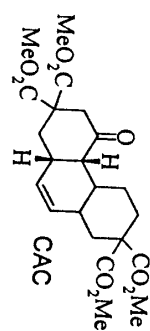


34

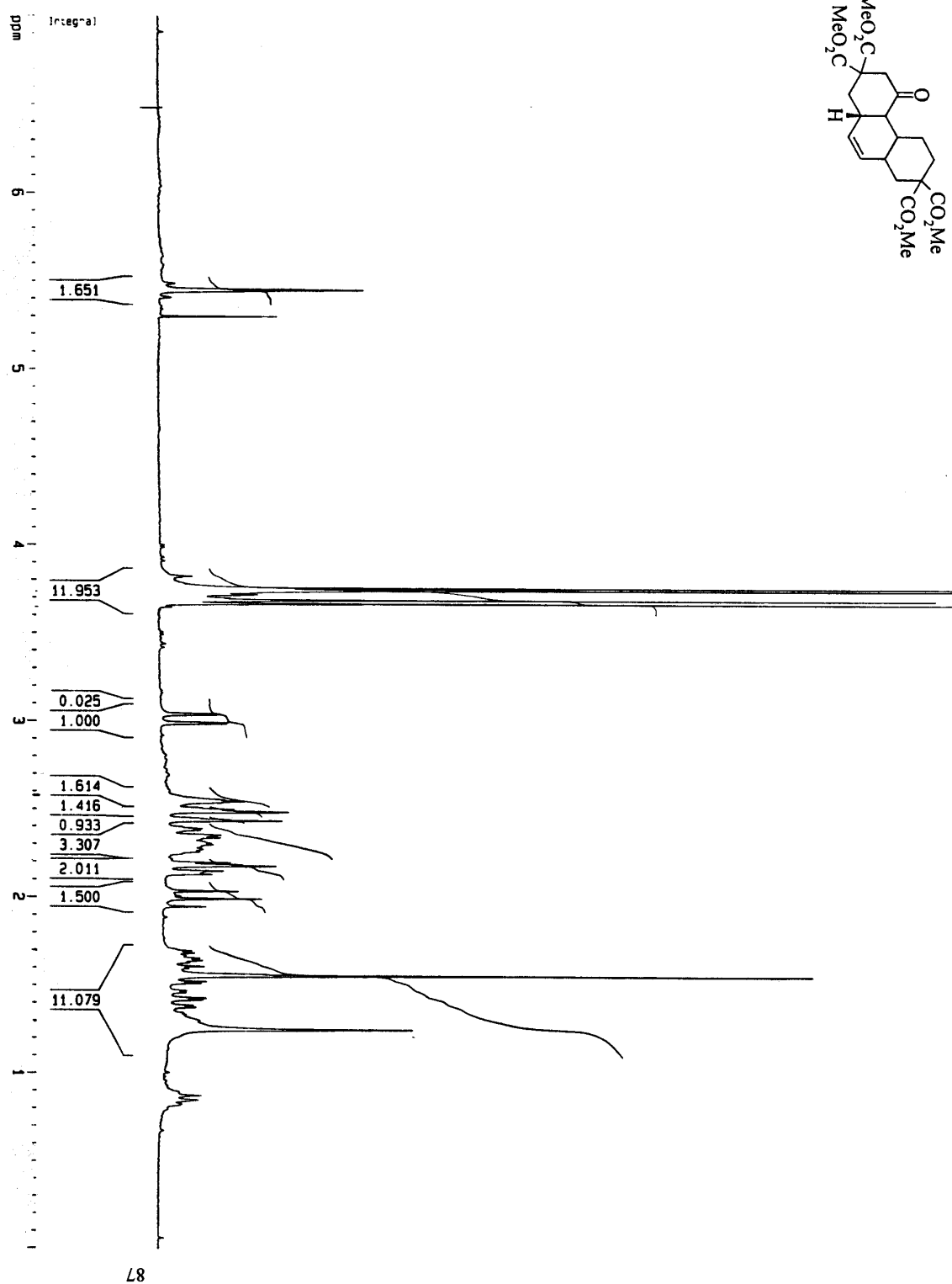
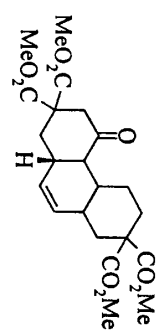




Mixture 35 & 36



35



36

```
mac M1 -539.9083443 au
C      2.502002   -1.685880   .660848
C      1.285935   -2.173190   -.084554
C      .040757    -1.891382   .260453
C     -1.137248   -2.288422   -.517118
C     -2.372984   -1.842348   -.349566
C     -2.860190    -.831744   .661430
C      3.325327    -.675054   -.182384
C      2.512115    .540904   -.669568
C      1.973562    1.431332   .476345
C      1.214982    2.613692   -.080914
C     -3.243866    .510608   -.016930
C     -2.037643    1.296258   -.571253
C     -1.161247    1.934307   .535899
C     -.088991     2.817698   -.060840
H      3.144585   -2.527073   .906719
H      2.202321   -1.229030   1.596475
H      1.477754   -2.748429   -.975648
H     -.129937    -1.313453   1.148837
H     -.950090    -2.991008   -1.310712
H     -3.136809   -2.206073   -1.015283
H     -3.745126   -1.231155   1.149734
H     -2.126513    -.655383   1.435069
H      3.727238   -1.194328   -1.047773
H      4.171117    -.334498   .407908
H      1.673670    .201718   -1.264327
H      3.142620    1.146959   -1.313858
H      1.342778    .845058   1.127318
H      2.812683    1.788077   1.068659
H      1.833316    3.345434   -.573717
H     -3.934602    .299088   -.827701
H     -3.774349    1.130605   .700094
H     -1.423283    .643753   -1.179333
H     -2.404607    2.089487   -1.216172
H     -.726315    1.161342   1.152060
H     -1.799330    2.539466   1.175442
H     -.467960     3.706602   -.537369
```

35

mac M2 -613.1917667 au

C	-2.641526	1.502524	.820158
C	-1.546995	2.077721	-.045785
C	-.260235	1.855371	.166602
C	.820687	2.326210	-.706147
C	2.108709	2.041361	-.567714
C	2.737970	1.212854	.527965
C	-3.530727	.490802	.047695
C	-2.732257	-.631769	-.643109
C	-1.984843	-1.570910	.340797
C	-1.103295	-2.503162	-.454380
C	3.304425	-.141559	.023703
C	2.290729	-1.025780	-.716559
C	1.106003	-1.483710	.114278
C	.212148	-2.442730	-.583565
O	.896285	-1.066564	1.240801
H	-3.279657	2.301273	1.188984
H	-2.202258	1.019907	1.684859
H	-1.865869	2.665804	-.891229
H	.021678	1.250280	1.004439
H	.515724	2.939847	-1.536535
H	2.797598	2.432776	-1.297014
H	3.565306	1.776211	.951780
H	2.041257	1.011165	1.321565
H	-4.090509	1.029668	-.711444
H	-4.253893	.061144	.734677
H	-2.005397	-.184873	-1.308884
H	-3.408801	-1.226020	-1.250771
H	-1.387533	-1.010158	1.036589
H	-2.711857	-2.149409	.903151
H	-1.631148	-3.231153	-1.047571
H	4.135616	.050465	-.647864
H	3.695119	-.683588	.877779
H	1.882782	-.488712	-1.568552
H	2.790955	-1.905716	-1.111671
H	.702889	-3.098892	-1.278296

35

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mac M3 -613.1894295 au
C      -2.131622    2.177379    .497735
C      -.852711    2.391678    -.275868
C      .306065    1.883899    .113136
C      1.572412    2.034824    -.608253
C      2.714505    1.431719    -.309545
C      2.974260    .456936    .815876
C      -3.153732    1.258769    -.229682
C      -2.551588    .003309    -.878313
C      -1.748958    -.898134    .040003
C      -1.249913    -2.131007    -.623348
C      3.347945    -.950012    .279400
C      2.199100    -1.630809    -.490299
C      1.059416    -2.143316    .429438
C      -.062434    -2.678276    -.426813
O      -1.498153    -.612892    1.197417
H      -2.613365    3.133806    .680097
H      -1.896421    1.732003    1.450435
H      -.916462    2.973687    -1.180970
H      .320151    1.301117    1.012506
H      1.549169    2.694404    -1.458702
H      3.571042    1.629037    -.931643
H      3.807228    .825896    1.408984
H      2.124372    .380519    1.478009
H      -3.650335    1.825152    -1.011504
H      -3.912902    .965989    .487297
H      -1.878698    .288800    -1.682374
H      -3.343419    -.587130    -1.331910
H      -1.914270    -2.559193    -1.351272
H      4.204883    -.850733    -.380217
H      3.654462    -1.578683    1.110194
H      1.787832    -.927287    -1.203357
H      2.594090    -2.471624    -1.053304
H      .691468    -1.363264    1.072747
H      1.445336    -2.942037    1.056313
H      .186508    -3.556069    -.999391

```

36

ts M1 cbc -539.8272233 au

C	.575180	-.516288	.996893
C	1.156946	1.150597	-.348439
C	-.777528	-.464622	1.282119
C	-1.748811	1.332068	.282624
C	-.790430	2.252999	.634850
C	.561638	2.198328	.305557
C	1.222128	-1.652633	.214006
C	2.745897	-1.479296	.059944
C	2.667489	1.042193	-.444727
C	3.133414	-.349493	-.910532
C	-1.766123	-1.569208	.902540
C	-2.151039	-1.707787	-.583330
C	-2.007735	.780167	-1.111088
C	-2.890987	-.477598	-1.119128
H	1.229703	-.069779	1.720217
H	.630376	.611071	-1.101574
H	-1.037031	.027257	2.197598
H	-2.665679	1.390572	.850072
H	-1.045582	2.923162	1.438517
H	1.208861	2.885400	.825297
H	.780447	-1.754229	-.769571
H	1.032266	-2.589000	.737317
H	3.186028	-1.286686	1.034361
H	3.168933	-2.411178	-.303162
H	3.033300	1.784693	-1.151446
H	3.114722	1.270965	.517950
H	4.212415	-.337191	-1.029961
H	2.706170	-.559260	-1.887756
H	-2.680844	-1.407440	1.464061
H	-1.361631	-2.521660	1.241081
H	-1.272253	-1.886654	-1.189848
H	-2.788794	-2.581539	-.684361
H	-2.528725	1.568393	-1.652883
H	-1.102328	.581066	-1.658199
H	-3.784669	-.301168	-.526203
H	-3.215157	-.670150	-2.137421

36

ts M1 bbc -539.8274153 au

C	.606252	-.628202	.905424
C	1.261816	1.101700	-.290965
C	-.772285	-.628924	1.068557
C	-1.650314	1.295301	.267228
C	-.688772	2.181019	.695568
C	.668474	2.116087	.420017
C	1.318492	-1.708914	.089335
C	2.846584	-1.526622	.029804
C	2.776226	1.002527	-.351991
C	3.273520	-.356599	-.870044
C	-1.646745	-1.670738	.371714
C	-3.079405	-1.193412	.074813
C	-1.866061	.715663	-1.122150
C	-3.103930	-.208842	-1.117177
H	1.188190	-.257280	1.727372
H	.752835	.657742	-1.117200
H	-1.156358	-.305905	2.016290
H	-2.583956	1.378786	.800440
H	-.972952	2.831776	1.504937
H	1.312228	2.753768	1.002652
H	.933190	-1.748831	-.923787
H	1.105951	-2.676674	.539777
H	3.232759	-1.373540	1.033631
H	3.291536	-2.442269	-.348045
H	3.151887	1.784995	-1.008594
H	3.192760	1.186022	.633725
H	4.356542	-.332117	-.940830
H	2.890231	-.521444	-1.873584
H	-1.690834	-2.546481	1.017644
H	-1.191894	-1.995283	-.555259
H	-3.710731	-2.046385	-.150984
H	-3.488978	-.724252	.962213
H	-2.030996	1.530330	-1.823266
H	-1.012697	.163194	-1.477388
H	-4.005911	.393575	-1.074257
H	-3.132075	-.767330	-2.047304

35

ts M2 cbc -613.1095926 au

C	-.576543	-.664950	-.782657
C	-1.573994	1.062030	.109284
C	.743978	-.368065	-1.081275
C	1.329708	1.689839	-.231447
C	.283650	2.347408	-.834537
C	-1.071762	2.082334	-.659625
C	-1.072721	-1.707637	.220311
C	-2.608742	-1.844421	.190033
C	-3.045152	.688901	.061895
C	-3.336638	-.631992	.798139
C	1.976222	-.970795	-.529889
C	2.127856	-1.106393	.966857
C	1.484691	1.348860	1.244398
C	2.550686	.273667	1.521409
O	2.910827	-1.239901	-1.266747
H	-1.242654	-.563444	-1.618371
H	-1.085301	.788579	1.015741
H	.922852	-.015303	-2.076872
H	2.290085	1.830123	-.703023
H	.533533	2.932028	-1.702966
H	-1.741787	2.542878	-1.366166
H	-.768515	-1.472973	1.231807
H	-.633871	-2.670019	-.029085
H	-2.935906	-1.989659	-.835295
H	-2.890089	-2.734321	.744306
H	-3.628981	1.481109	.525553
H	-3.373332	.612414	-.970139
H	-4.406200	-.815376	.785016
H	-3.042915	-.528596	1.839450
H	1.216314	-1.422515	1.444654
H	2.906471	-1.832235	1.159561
H	1.799786	2.271154	1.729415
H	.558239	1.059255	1.707609
H	3.492478	.559308	1.064979
H	2.713184	.197559	2.590656

35

ts M2 bbc -613.1128631 au

C	-.712980	-.508759	-1.015748
C	-1.317203	.942954	.336153
C	.687643	-.495737	-.996988
C	1.546675	1.705661	-.336420
C	.407847	2.358158	-.732079
C	-.892554	2.070650	-.349945
C	-1.484553	-1.722970	-.472118
C	-2.995715	-1.518950	-.309710
C	-2.815066	.829637	.604534
C	-3.307824	-.597030	.873724
C	1.455501	-1.100667	.070024
C	2.946127	-.842475	.028540
C	1.983201	1.298273	1.057206
C	3.196363	.336410	1.019070
O	.970510	-1.619516	1.075692
H	-1.159899	-.104985	-1.908111
H	-.697944	.476633	1.076256
H	1.225844	-.196194	-1.869255
H	2.397168	1.856948	-.984104
H	.507486	3.009167	-1.584456
H	-1.662436	2.650868	-.829642
H	-1.043169	-2.036874	.456610
H	-1.316448	-2.516996	-1.196817
H	-3.425054	-1.107499	-1.219864
H	-3.455832	-2.488501	-.146272
H	-3.050276	1.454999	1.463132
H	-3.359676	1.233452	-.243725
H	-4.377404	-.569216	1.056443
H	-2.833740	-.990489	1.767790
H	3.483431	-1.721086	.358889
H	3.271008	-.579497	-.967930
H	2.282766	2.209481	1.570985
H	1.191497	.853257	1.634012
H	4.089396	.876510	.726261
H	3.354047	-.062194	2.012173

35

ts M3 cbc -613.1191519 au

C	.516354	-.315728	1.053305
C	1.078810	1.393323	-.430449
C	-.853494	-.338926	1.296149
C	-1.818425	1.320159	.300942
C	-.919107	2.319012	.626183
C	.419910	2.378362	.257519
C	1.268480	-1.249766	.226691
C	2.774978	-1.051464	.256334
C	2.589934	1.379327	-.543970
C	3.159752	-.022163	-.836022
C	-1.798063	-1.496922	.932791
C	-2.210910	-1.681574	-.537683
C	-2.069107	.776028	-1.101407
C	-2.961243	-.472833	-1.100509
O	.782040	-2.101164	-.507699
H	1.118492	.225319	1.751586
H	.571747	.794735	-1.151743
H	-1.124001	.104380	2.235417
H	-2.734988	1.345101	.870888
H	-1.208023	2.978089	1.427151
H	1.024077	3.113626	.761169
H	3.111173	-.703681	1.224292
H	3.243257	-2.001019	.032814
H	2.883138	2.045246	-1.353674
H	3.029929	1.768502	.368178
H	4.239604	.039288	-.910398
H	2.784628	-.381332	-1.788539
H	-2.697401	-1.373757	1.527725
H	-1.317852	-2.413763	1.258909
H	-1.325277	-1.880417	-1.117619
H	-2.848268	-2.559790	-.591217
H	-2.569005	1.572187	-1.649252
H	-1.161474	.551228	-1.634063
H	-3.861309	-.281979	-.521464
H	-3.272265	-.683165	-2.119087

35

ts M3 bbc -613.1210002 au

C	.478747	-.299850	1.104325
C	1.083971	1.435600	-.373153
C	-.888369	-.281799	1.396440
C	-1.763350	1.365939	.430363
C	-.864915	2.384123	.711934
C	.469827	2.426233	.347887
C	1.134770	-1.140715	.117484
C	2.653601	-1.094170	.143047
C	2.591337	1.372716	-.523420
C	3.100536	-.034120	-.894500
C	-1.808796	-1.437283	.956202
C	-3.237864	-1.027254	.561834
C	-1.981497	.638950	-.896606
C	-3.242317	-.245573	-.773696
O	.570090	-1.761536	-.782666
H	1.139912	.152259	1.812560
H	.531040	.889438	-1.103995
H	-1.132589	.097210	2.372491
H	-2.688201	1.468557	.973017
H	-1.170276	3.086077	1.468496
H	1.093377	3.150978	.842542
H	3.032372	-.840718	1.123614
H	3.030986	-2.065085	-.150813
H	2.889207	2.066414	-1.307585
H	3.063978	1.702158	.395879
H	4.181861	-.020406	-.967507
H	2.703449	-.326242	-1.860152
H	-1.861528	-2.114302	1.805822
H	-1.344269	-1.965881	.142682
H	-3.846694	-1.919226	.461144
H	-3.681916	-.433723	1.353420
H	-2.116538	1.368078	-1.690349
H	-1.151700	.005572	-1.163140
H	-4.134175	.369712	-.837737
H	-3.263464	-.943931	-1.602661