

Supporting Information

Doyle-Kirmse Reaction of Allylic Sulfides with Diazoalkane-Free (2-Furyl)carbenoid Transfer

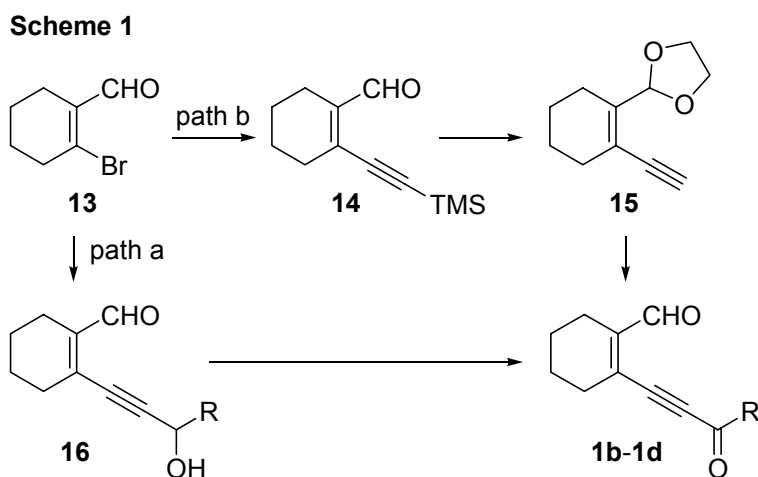
Yumiko Kato, Koji Miki, Fumiaki Nishino, Kouichi Ohe*, and Sakae Uemura*

*Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*

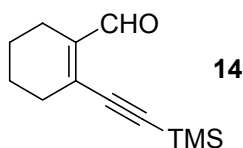
General Procedures. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. NMR spectra were measured for solutions in CDCl₃ with Me₄Si as an internal standard or CD₂Cl₂ (¹H and ¹³C): the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. IR spectra were recorded with an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL JMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. All new compounds prepared were fully characterized. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon, and other solvents were dried by the usual methods and distilled before use.

Synthesis of Substrates.

The substrates were prepared by following procedures (Scheme 1). 2-Bromo-1-cyclohexenecarboxaldehyde (**13**)^{1,2} and the substrate **1a**^{2b} were prepared by reported method.

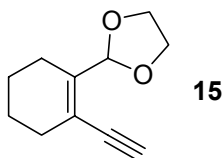


Ene-yne-carbonyl compound **14**



To a solution of trimethylsilylacetylene (2.4 mL, 18 mmol), **13** (2.8 g, 15 mmol), and triethylamine (10 mL, 75 mmol) in benzene (15 mL) were added CuI (0.21 g, 7.5 mol%) and Pd(PPh₃)₄ (0.43 g, 2.5 mol%) at 0 °C under N₂. After stirring at room temperature for 10 min, the resulting black solution was washed with saturated aqueous NH₄Cl solution (30 mL) and the aqueous phase was extracted with AcOEt (10 mL x 3). The organic phase was dried over MgSO₄. The organic solvents were removed under reduced pressure, and the residue was subjected to column chromatography on SiO₂ with hexane/AcOEt (v/v = 20/1) as an eluent to afford ene-yne-carbonyl compound **14** (3.0 g, 15 mmol, 98% yield) as a pale yellow oil; IR (neat) 675, 760, 844, 878, 894, 1146, 1226, 1250, 1363, 1599, 1677 (C=O), 2140 (C≡C), 2834, 2862, 2939 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 0.19 (s, 9H), 1.60–1.63 (m, 4H), 2.22–2.24 (m, 2H), 2.35–2.38 (m, 2H), 10.2 (s, 1H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 0.4, 21.7, 22.4, 22.6, 32.9, 102.1, 105.3, 140.4, 144.3, 193.7. HRMS (FAB): calcd for C₁₂H₁₉OSi (M+H⁺), 207.1205; found, 207.1207.

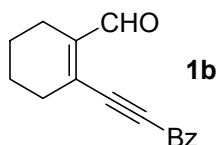
Ene-yne compound **15**.



To a solution of **14** (3.0 g, 15 mmol) and ethyleneglycol (2.5 mL, 45 mmol) in benzene (10 mL) was added *p*-toluenesulfonic acid mono hydrate (43 mg, 5 mol%) at room temperature. After stirring for 2 h at reflux temperature using Dean-Stark apparatus, the solution was washed with saturated aqueous NaHCO₃ solution and the aqueous phase was extracted with Et₂O (10 mL x 3). The combined organic phase was dried over MgSO₄. The organic solvent was removed under reduced pressure. To a solution of the residue in DMSO (20 mL) was added KF (1.28 g, 22 mmol) at room temperature. After stirring for 1 h, the resulting brown solution was poured into water/Et₂O mixture (50 mL, v/v = 1/1). The aqueous phase was extracted with

Et₂O (10 mL x 3) and the combined organic phase was dried over MgSO₄. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO₂ with hexane/AcOEt (v/v = 15/1) to afford ene-yne compound **15** (1.8 g, 10 mmol, 67% yield for 2 steps) as a white solid (gradually decomposed at room temperature); mp. 32.0–32.3 °C; IR (KBr) 659, 949, 987, 1070, 1075, 1101, 1142, 1227, 1387, 2080 (C≡C), 2892, 2935, 3258 (≡C-H) cm⁻¹; ¹H NMR (270 MHz, CDCl₃, 25 °C) δ 1.58–1.65 (m, 4H), 2.08–2.18 (m, 2H), 2.18–2.26 (m, 2H), 3.12 (s, 1H), 3.90–4.05 (m, 4H), 5.88 (s, 1H); ¹³C NMR (67.5 MHz, CDCl₃, 25 °C) δ 21.6, 21.9, 22.1, 30.5, 65.6, 81.2, 82.0, 102.8, 121.0, 142.3. HRMS (FAB): calcd for C₁₁H₁₅O₂ (M+H⁺), 179.1072; found, 179.1074.

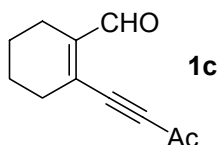
Ene-yne-carbonyl compound 1b (path a).



To a solution of 1-phenyl-2-propyn-1-ol (2.5 mL, 10 mmol), **13** (2.5 g, 13 mmol), and triethylamine (7.0 mL, 50 mmol) in benzene (10 mL) were added CuI (0.15 g, 7.5 mol%) and Pd(PPh₃)₄ (0.29 g, 2.5 mol%) at 0 °C under N₂. After stirring at room temperature for 1 h, the resulting black solution was washed with saturated aqueous NH₄Cl solution (20 mL) and the aqueous phase was extracted with AcOEt (20 mL x 3). The organic phase was dried over MgSO₄. The organic solvents were removed under reduced pressure, and the residue was subjected to short column chromatography on SiO₂ with hexane/AcOEt (v/v = 40/1) as an eluent to afford crude propargylic alcohol as a pale brown oil. This crude alcohol was oxidized by Swern method to give ene-yne-carbonyl compound **1b** (0.8 g, 3.4 mmol, 34% yield for 2 steps) as a colorless solid; mp. 82.8–84.6 °C; IR (KBr) 638, 707, 993, 1003, 1159, 1219, 1265, 1283, 1311, 1448, 1578, 1595, 1639 (C=O), 1675 (C=O), 2184 (C≡C), 2859, 2913, 2936, 2958 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 1.70–1.79 (m, 4H), 2.33–2.39 (m, 2H), 2.54–2.60 (m, 2H), 7.52 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.65 (dd, *J* = 7.2, 7.2 Hz, 1H), 8.12 (d, *J* = 7.2 Hz, 2H), 10.29 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ 20.7, 21.7, 22.4, 31.6, 88.2, 94.1, 128.7, 129.3, 134.4, 136.3, 136.4,

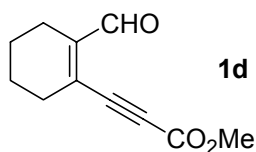
147.3, 177.1, 191.2. Anal. Calcd for C₁₆H₁₄O₂: C, 80.65; H, 5.92. Found: C, 80.36; H, 5.92.

Ene-yne-carbonyl compound 1c (path a).



Ene-yne-carbonyl compound **1c** was obtained by the same procedure for the synthesis of **1b**; A yellow oil (34% yield for 2 steps); IR (neat) 608, 706, 1214, 1246, 1364, 1428, 1680 (C=O), 2183 (C≡C), 2860, 2934 cm⁻¹; ¹H NMR (270 MHz, CDCl₃, 25 °C) δ 1.65–1.71 (m, 4H), 2.28–2.35 (m, 2H), 2.42 (s, 3H), 2.45–2.50 (m, 2H), 10.2 (s, 1H); ¹³C NMR (67.5 MHz, CDCl₃, 25 °C) δ 20.7, 21.9, 22.4, 31.5, 32.8, 85.6, 95.2, 136.0, 147.2, 183.5, 191.3. HRMS (FAB): calcd for C₁₁H₁₃O₂ (M+H⁺), 177.0916; found, 177.0916.

Ene-yne-carbonyl compound 1d (path b).



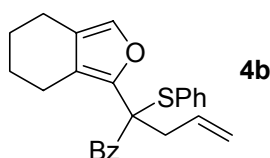
To a solution of *i*-Pr₂NH (0.64 mL, 4.5 mmol) in THF (50 mL) was slowly added *n*-BuLi (2.8 mL, 4.5 mmol, 1.6 M in hexane) at -78 °C under N₂. After stirring at -78 °C for 10 min, to this pale yellow solution was added dropwise **15** (0.53 g, 3.0 mmol) in THF (5 mL) at -78 °C. After stirring for 30 min at -78 °C, to this pale yellow solution was added dropwise chloroformate (0.70 mL, 9.0 mmol) at -78 °C, and then the resulting solution was gradually warmed up to room temperature. After an additional stirring for 30 min, the solution was washed with saturated aqueous NH₄Cl solution (50 mL), and the aqueous phase was extracted with AcOEt (20 mL x 3). The combined organic phase was dried over MgSO₄. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO₂ with hexane/AcOEt (v/v = 10/1) as an eluent to afford ene-yne-carbonyl compound **1d** (0.41 g, 2.1 mmol, 71% yield) as a colorless oil; IR (neat) 733, 747, 1147, 1221, 1261, 1281, 1433, 1681 (C=O), 1716 (C=O), 2210

(C≡C), 2863, 2943 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 1.63–1.75 (m, 4H), 2.29–2.33 (m, 2H), 2.42–2.48 (m, 2H), 3.83 (s, 3H), 10.1 (s, 1H); ^{13}C NMR (67.5 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 20.7, 21.7, 22.4, 31.3, 53.0, 82.2, 87.9, 135.5, 147.7, 153.6, 191.3. HRMS (FAB): calcd for $\text{C}_{11}\text{H}_{13}\text{O}_3$ ($\text{M}+\text{H}^+$), 193.0865; found, 193.0865.

Typical Procedure for Catalytic Carbene Transfer Reaction with **1**.

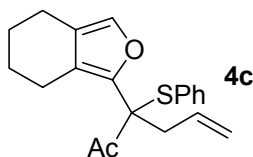
To a solution of **1** (0.25 mmol) and sulfide (10 equiv) placed in the flame dried Schlenk flask and dissolved in dry and deoxygenated CH_2Cl_2 or $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1.0 mL) was added $[\text{Rh}(\text{OAc})_2]_2$ (2.7 mg, 0.006 mmol) at room temperature. After the reaction was complete, the organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/ AcOEt ($v/v = 20/1$) as an eluent to afford the corresponding product **4**, **7**, **9**, **10**, and **12**.

Sulfide **4b**.



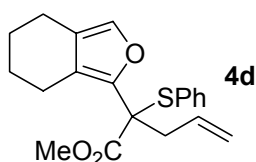
A colorless oil (98% yield); IR (neat) 693, 749, 919, 1123, 1182, 1213, 1229, 1255, 1439, 1446, 1473, 1579, 1595, 1679 ($\text{C}=\text{O}$), 2855, 2931, 3073 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 1.49–1.60 (m, 4H), 1.80–1.89 (m, 1H), 2.34–2.43 (m, 1H), 2.45–2.53 (m, 2H), 2.90 (d, $J = 6.8$ Hz, 2H), 4.78 (d, $J = 17.2$ Hz, 1H), 5.03 (d, $J = 10.0$ Hz, 1H), 5.94 (tdd, $J = 6.8, 10.0, 17.2$ Hz, 1H), 7.09 (s, 1H), 7.13 (d, $J = 7.2$ Hz, 2H), 7.22 (dd, $J = 7.2, 7.2$ Hz, 2H), 7.28–7.36 (m, 3H), 7.45 (dd, $J = 7.2, 7.2$ Hz, 1H), 7.58 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 20.4, 21.1, 22.9, 23.0, 38.6, 67.0, 118.7, 120.4, 123.3, 128.1, 128.3, 129.1, 129.1, 130.7, 132.2, 132.3, 135.5, 136.1, 137.5, 143.7, 194.7. HRMS (FAB): calcd for $\text{C}_{25}\text{H}_{25}\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$), 389.1575; found, 389.1570.

Sulfide **4c**.



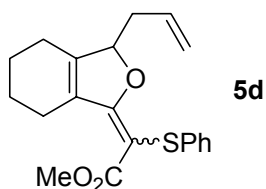
A colorless oil (94% yield); IR (neat) 693, 748, 917, 1180, 1350, 1440, 1715 (C=O), 2935 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 1.58–1.65 (m, 4H), 1.99–2.08 (m, 1H), 2.17 (s, 3H), 2.40–2.48 (m, 1H), 2.48–2.56 (m, 2H), 2.74 (d, J = 6.9 Hz, 2H), 5.09 (d, J = 17.1 Hz, 1H), 5.13 (d, J = 9.6 Hz, 1H), 5.93 (tdd, J = 6.9, 9.6, 17.1 Hz, 1H), 7.08 (s, 1H), 7.15 (d, J = 7.8 Hz, 2H), 7.23 (dd, J = 7.8, 7.8 Hz, 2H), 7.33 (dd, J = 7.8, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 20.3, 21.4, 22.7, 23.1, 26.4, 37.0, 68.1, 118.5, 120.8, 123.0, 128.5, 129.2, 130.5, 132.8, 136.5, 137.1, 143.5, 202.3. HRMS (FAB): calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$), 327.1419; found, 327.1418.

Sulfide 4d.



A colorless oil (83% yield); IR (neat) 692, 730, 953, 990, 1053, 1216, 1315, 1437, 1612, 1705 (C=O), 2941, 3431 cm^{-1} ; ^1H NMR (300 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 1.40–1.63 (m, 4H), 1.78 (td, J = 6.6, 16.2 Hz, 1H), 2.20 (td, J = 6.6, 16.2 Hz, 1H), 2.45–2.47 (m, 2H), 2.83–2.92 (m, 2H), 3.72, (s, 3H), 5.15 (d, J = 16.8 Hz, 1H), 5.16 (d, J = 10.2 Hz, 1H), 5.98 (tdd, J = 6.6, 10.2, 16.8 Hz, 1H), 7.04 (s, 1H), 7.12 (d, J = 7.2 Hz, 2H), 7.22 (dd, J = 7.2, 7.2 Hz, 2H), 7.34 (dd, J = 7.2, 7.2 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 20.6, 21.3, 23.0, 23.4, 39.7, 53.1, 63.0, 119.1, 120.8, 123.2, 128.7, 129.6, 131.1, 133.3, 136.1, 137.9, 144.5, 170.6. HRMS (FAB): calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{S}$ (M^+), 342.1290; found, 342.1288.

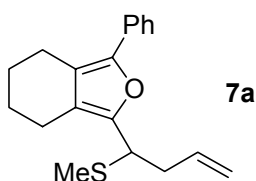
Sulfide 5d.



A colorless oil (85% yield); IR (neat) 690, 739, 1024, 1024, 1255, 1438, 1478, 1741 (C=O), 2934 cm^{-1} ; ^1H NMR (270 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 1.52–1.68 (m, 4H), 2.30–2.47 (m, 4H), 2.49–2.73 (m, 2H), 3.57, (s, 3H), 3.67 (t, J = 6.8 Hz, 1H), 4.90 (d, J = 10.0 Hz, 1H), 4.96 (d, J = 17.0 Hz, 1H), 5.62 (tdd, J = 6.8, 10.0, 17.0 Hz, 1H), 6.95 (d,

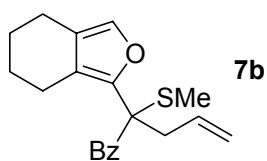
$J = 7.3$ Hz, 2H), 7.04 (dd, $J = 7.3$, 7.3 Hz, 1H), 7.14 (dd, $J = 7.3$, 7.3 Hz, 2H); ^{13}C NMR (67.5 MHz, CD_2Cl_2 , 25 °C) δ 20.7, 21.6, 23.1, 23.3, 34.4, 44.4, 52.4, 117.1, 121.0, 125.9, 126.6, 126.7, 129.1, 132.2, 135.1, 137.5, 148.8, 171.3. HRMS (FAB): calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{S}$ (M^+), 342.1290; found, 342.1292.

Sulfide 7a.

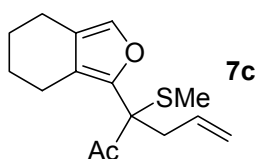


A yellow oil [purified by column chromatography on SiO_2 with hexane/AcOEt (v/v = 300/1), 60% yield]; IR (neat) 691, 763, 912, 1067, 1440, 1495, 1596, 2935, 3403 cm^{-1} ; ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C) δ 1.66–1.73 (m, 4H), 1.99 (s, 3H), 2.48–2.50 (m, 2H), 2.60–2.85 (m, 4H), 3.87 (dd, $J = 6.8$, 8.6 Hz, 1H), 4.98 (d, $J = 10.3$ Hz, 1H), 5.07 (d, $J = 17.0$ Hz, 1H), 5.78 (tdd, $J = 6.8$, 10.3, 17.0 Hz, 1H), 7.16 (dd, $J = 7.6$, 7.6 Hz, 1H), 7.34 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.56 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) δ 14.2, 21.1, 23.2, 23.3, 23.8, 37.7, 42.5, 116.8, 119.5, 121.0, 124.4, 126.4, 128.9, 132.4, 136.0, 145.7, 146.8. HRMS (FAB): calcd for $\text{C}_{19}\text{H}_{22}\text{OS}$ (M^+), 298.1391; found, 298.1389.

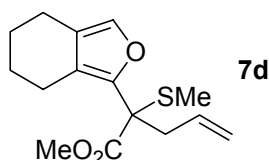
Sulfide 7b.



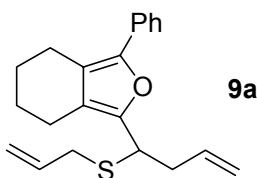
A colorless oil (77% yield); IR (neat) 695, 915, 1231, 1446, 1595, 1681 ($\text{C}=\text{O}$), 1769, 2937, 3071, 3470 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 1.45–1.56 (m, 4H), 1.86 (s, 3H), 2.30–2.35 (m, 2H), 2.35–2.48 (m, 2H), 2.98 (d, $J = 6.6$ Hz, 2H), 4.96 (d, $J = 17.3$ Hz, 1H), 5.02 (d, $J = 10.0$ Hz, 1H), 5.76 (tdd, $J = 6.6$, 10.0, 17.3 Hz, 1H), 7.12 (s, 1H), 7.26 (dd, $J = 7.2$, 7.2 Hz, 2H), 7.42 (dd, $J = 7.2$, 7.2 Hz, 1H), 7.64 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (67.5 MHz, CD_2Cl_2 , 25 °C) δ 11.4, 20.6, 21.7, 23.3, 23.5, 37.9, 61.1, 118.0, 119.7, 123.7, 128.1, 129.3, 132.3, 133.0, 135.8, 136.3, 144.3, 194.1. HRMS (FAB): calcd for $\text{C}_{20}\text{H}_{23}\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$), 327.1419; found, 327.1418.

Sulfide 7c.

A colorless oil (72% yield); IR (neat) 914, 1129, 1352, 1437, 1597, 1702 (C=O), 1769, 2937, 3380 cm^{-1} ; ^1H NMR (270 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 1.63–1.69 (m, 4H), 1.80 (s, 3H), 2.06 (s, 3H), 2.45–2.52 (m, 4H), 2.78 (d, J = 7.0 Hz, 2H), 5.04 (d, J = 17.0 Hz, 1H), 5.06 (d, J = 10.0 Hz, 1H), 5.68 (tdd, J = 7.0, 10.0, 17.0 Hz, 1H), 7.10 (s, 1H); ^{13}C NMR (67.5 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 11.4, 20.7, 22.1, 23.3, 23.7, 25.7, 36.2, 62.6, 117.7, 120.1, 123.3, 133.5, 136.6, 143.9, 201.1. HRMS (FAB): calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$), 265.1262; found, 265.1263.

Sulfide 7d.

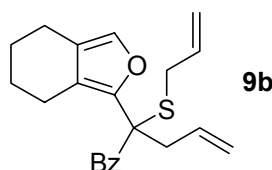
A colorless oil (91% yield); IR (neat) 609, 755, 917, 1128, 1211, 1435, 1737 (C=O), 2930, 3450 cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 1.49–1.58 (m, 4H), 1.81 (s, 3H), 2.27–2.31 (m, 1H), 2.40–2.43 (m, 3H), 2.86 (d, J = 7.2 Hz, 2H), 3.65 (s, 3H), 4.97 (d, J = 10.0 Hz, 1H), 5.01 (d, J = 16.8 Hz, 1H), 5.69 (tdd, J = 7.2, 10.0, 16.8 Hz, 1H), 7.00 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 12.9, 20.6, 21.7, 23.2, 23.6, 39.9, 52.9, 57.4, 118.5, 119.4, 123.1, 133.2, 136.1, 144.6, 170.8. HRMS (FAB): calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{S}$ (M^+), 280.1133; found, 280.1136.

Sulfide 9a.

A yellow oil [purified by column chromatography on SiO_2 with hexane/AcOEt (v/v = 300/1), 43% yield]; IR (neat) 692, 762, 916, 989, 1070, 1438, 1492, 1600, 2360, 2925, 3077 cm^{-1} ; ^1H NMR (400 MHz, d_8 -THF, 25 $^\circ\text{C}$) δ 1.66–1.75 (m, 4H), 2.47 (dd, J =

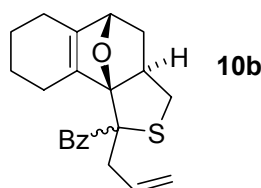
6.0, 6.0 Hz, 2H), 2.54–2.59 (m, 1H), 2.72–2.76 (m, 3H), 3.06 (dd, $J = 6.0, 6.0$ Hz, 2H), 3.93 (dd, $J = 6.8, 9.2$ Hz, 1H), 4.96–5.10 (m, 4H), 5.72–5.81 (m, 2H), 7.10 (dd, $J = 7.6, 7.6$ Hz, 1H), 7.28 (dd, $J = 7.6, 7.6$ Hz, 2H), 7.53 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, d_8 -THF, 25 °C) δ 20.9, 20.9, 22.9, 23.5, 33.9, 37.9, 40.4, 115.8, 116.0, 118.8, 120.2, 123.8, 125.7, 128.2, 132.1, 135.0, 135.4, 145.4, 146.6. HRMS (FAB): calcd for $\text{C}_{21}\text{H}_{25}\text{OS}$ ($\text{M}+\text{H}^+$), 325.1626; found, 325.1629.

Sulfide 9b.



A colorless oil [purified by column chromatography on SiO_2 with hexane/AcOEt ($v/v = 30/1$ to $20/1$), 32% yield]; IR (neat) 696, 919, 1020, 1230, 1260, 1446, 1673 ($\text{C}=\text{O}$), 1769, 2934, 3075, 3435 cm^{-1} ; ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C) δ 1.31–1.67 (m, 4H), 2.29–2.48 (m, 4H), 2.97 (d, $J = 6.9$ Hz, 2H), 3.04 (d, $J = 6.9$ Hz, 2H), 4.88–5.13 (m, 4H), 5.62–5.83 (m, 2H), 7.14 (s, 1H), 7.29 (dd, $J = 7.5, 7.5$ Hz, 2H), 7.45 (dd, $J = 7.5, 7.5$ Hz, 1H), 7.60 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) δ 20.5, 21.7, 23.2, 23.4, 31.9, 39.2, 62.5, 117.8, 118.4, 120.1, 123.9, 128.3, 129.4, 132.5, 133.1, 133.9, 135.9, 136.4, 144.4, 194.8. HRMS (FAB): calcd for $\text{C}_{22}\text{H}_{24}\text{O}_2\text{S}$ (M^+), 352.1497; found, 352.1495.

Sulfide 10b.



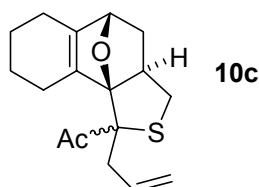
After the reaction of **1b** at 80 °C was complete, **10b** was obtained as a mixture of diastereoisomers (92% yield, d.r. = 79:21). These isomers could be separated by column chromatography on SiO_2 with hexane/AcOEt ($v/v = 20/1$ to $4/1$) as an eluent.

10b (major); a colorless oil; IR (neat) 646, 697, 767, 923, 1000, 1294, 1443, 1669 ($\text{C}=\text{O}$), 2359, 2932, 3507 cm^{-1} ; ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C) δ 1.30–1.49 (m, 2H), 1.58–1.69 (m, 2H), 1.71–2.12 (m, 5H), 2.21–2.28 (m, 1H), 2.68 (dd, $J = 5.4$,

10.8 Hz, 1H), 2.84–3.02 (m, 3H), 3.14 (dd, $J = 9.5, 10.8$ Hz, 1H), 4.36 (d, $J = 17.0$ Hz, 1H), 4.73 (s, 1H), 4.75 (d, $J = 10.3$ Hz, 1H), 5.55 (tdd, $J = 7.6, 10.3, 17.0$ Hz, 1H), 7.40 (dd, $J = 7.5, 7.5$ Hz, 2H), 7.50 (dd, $J = 7.5, 7.5$ Hz, 1H), 7.82 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) δ 22.5, 22.8, 23.2, 25.3, 36.2, 38.3, 38.9, 49.7, 64.1, 78.8, 103.7, 118.5, 128.2, 128.9, 131.5, 133.1, 138.6, 139.8, 143.4, 198.3. HRMS (FAB): calcd for $\text{C}_{22}\text{H}_{25}\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$), 353.1575; found, 353.1575.

10b (minor); a yellow oil; IR (neat) 639, 696, 921, 1003, 1230, 1445, 1597, 1667 ($\text{C}=\text{O}$), 2923, 3422 cm^{-1} ; ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C) δ 1.48–1.64 (m, 4H), 1.74–1.77 (m, 2H), 1.87–2.00 (m, 1H), 2.17–2.31 (m, 2H), 2.48–2.55 (m, 2H), 2.66–2.76 (m, 2H), 3.14 (dd, $J = 8.4, 10.8$ Hz, 1H), 3.45 (dd, $J = 7.2, 13.2$ Hz, 1H), 4.69 (d, $J = 3.9$ Hz, 1H), 5.03 (d, $J = 17.1$ Hz, 1H), 5.07 (d, $J = 10.2$ Hz, 1H), 5.76 (tdd, $J = 6.9, 10.2, 17.1$ Hz, 1H), 7.34 (dd, $J = 7.2, 7.2$ Hz, 2H), 7.43 (dd, $J = 7.2, 7.2$ Hz, 1H), 7.66 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) δ 22.3, 22.9, 23.6, 24.4, 36.2, 37.7, 43.2, 49.6, 71.8, 80.8, 104.6, 119.3, 127.7, 128.6, 131.1, 133.8, 138.5, 140.1, 144.5, 201.7. HRMS (FAB): calcd for $\text{C}_{22}\text{H}_{25}\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$), 353.1575; found, 353.1573.

Sulfide **10c**.



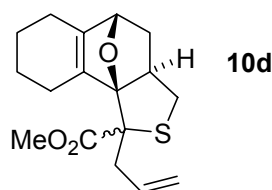
After the reaction of **1c** at 80 °C was complete, **10c** was obtained as a mixture of diastereoisomers (80% yield, d.r. = 67:33). These isomers could be separated by column chromatography on SiO_2 with hexane/ AcOEt ($v/v = 20/1$ to $4/1$) as an eluent.

10c (major); A yellow oil; IR (neat) 843, 920, 1185, 1360, 1440, 1675, 1690 ($\text{C}=\text{O}$), 2856, 2925, 3414 cm^{-1} ; ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C) δ 1.33–1.48 (m, 2H), 1.62–1.70 (m, 2H), 1.73–1.78 (m, 2H), 1.81–1.88 (m, 2H), 1.93–1.98 (m, 1H), 2.15–2.28 (m, 1H), 2.32 (s, 3H), 2.64–2.72 (m, 2H), 2.78 (tdd, $J = 5.4, 6.9, 9.3$ Hz, 1H), 2.93 (dd, $J = 5.4, 14.4$ Hz, 1H), 3.11 (dd, $J = 9.3, 10.2$ Hz, 1H), 4.67 (d, $J = 4.5$ Hz, 1H), 5.06 (d, $J = 10.2$ Hz, 1H), 5.16 (d, $J = 17.1$ Hz, 1H), 5.78 (tdd, $J = 7.2, 10.2, 17.1$ Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) δ 22.4, 22.8, 23.1, 25.1, 25.8, 35.8,

37.3, 39.1, 49.5, 65.8, 78.7, 102.4, 118.4, 134.3, 139.3, 143.8, 202.0. HRMS (FAB): calcd for C₁₇H₂₂O₂S (M⁺), 290.1341; found, 290.1339.

10c (minor); A white solid; mp. 87.2-89.0 °C; IR (KBr) 649, 668, 678, 871, 924, 1071, 1123, 1450, 1535, 1635 (C=O), 2341, 2360, 2929, 3443 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂, 25 °C) δ 1.41–1.62 (m, 4H), 1.71–1.76 (m, 3H), 1.86–1.90 (m, 1H), 2.11–2.16 (m, 1H), 2.23 (s, 3H), 2.42–2.55 (m, 3H), 2.70 (dd, *J* = 7.5, 10.8 Hz, 1H), 3.16 (dd, *J* = 8.4, 10.8 Hz, 1H), 3.29 (dd, *J* = 6.9, 13.5 Hz, 1H), 4.66 (d, *J* = 3.6 Hz, 1H), 5.09 (d, *J* = 10.5 Hz, 1H), 5.13 (d, *J* = 17.1 Hz, 1H), 5.75 (tdd, *J* = 6.9, 10.5, 17.1 Hz, 1H); ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C) δ 22.2, 22.8, 23.5, 24.4, 29.7, 35.6, 38.1, 41.7, 48.6, 72.0, 80.4, 104.0, 118.8, 134.0, 137.6, 145.4, 206.0. HRMS (FAB): calcd for C₁₇H₂₂O₂S (M⁺), 290.1341; found, 290.1340.

Sulfide **10d**.



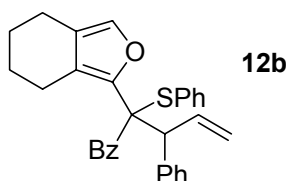
After the reaction of **1d** at reflux temperature of CH₂Cl₂ was complete, **10d** was obtained as a mixture of diastereoisomers (90% yield, d.r. = 73:27). These isomers could be separated by column chromatography on SiO₂ with hexane/AcOEt (v/v = 10/1 to 4/1) as an eluent.

10d(major); a colorless oil; IR (neat) 698, 917, 976, 1003, 1130, 1219, 1436, 1731 (C=O), 2938, 3443 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂, 25 °C) δ 1.37–1.53 (m, 2H), 1.59–1.99 (m, 7H), 2.17–2.28 (m, 1H), 2.70–2.75 (m, 3H), 2.83–2.91 (m, 1H), 3.31 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.73 (s, 3H), 4.71 (d, *J* = 4.5 Hz, 1H), 5.00 (d, *J* = 10.2 Hz, 1H), 5.12 (d, *J* = 17.1 Hz, 1H), 5.87 (tdd, *J* = 7.2, 10.2, 17.1 Hz, 1H); ¹³C NMR (100 MHz, CD₂Cl₂, 25 °C) δ 22.3, 22.6, 22.9, 23.1, 36.6, 37.4, 38.7, 50.0, 52.3, 59.7, 79.4, 102.6, 118.2, 134.8, 138.3, 144.3, 173.2. HRMS (FAB): calcd for C₁₇H₂₂O₃S (M⁺), 306.1290; found, 306.1290.

10d(minor); a yellow oil; IR (neat) 917, 992, 1126, 1226, 1267, 1433, 1731 (C=O), 2934, 3478 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂, 25 °C) δ 1.43–1.77 (m, 7H), 2.03–2.16 (m, 1H), 2.18–2.29 (m, 1H), 2.37–2.48 (m, 1H), 2.52 (dd, *J* = 6.3, 13.2 Hz, 2H),

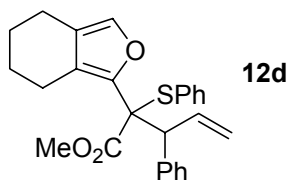
2.66 (dd, $J = 6.3, 11.1$ Hz, 1H), 3.15 (dd, $J = 9.0, 11.1$ Hz, 1H), 3.23 (dd, $J = 7.5, 13.2$ Hz, 1H), 3.65 (s, 3H), 4.65 (d, $J = 4.2$ Hz, 1H), 5.12 (d, $J = 10.2$ Hz, 1H), 5.15 (d, $J = 17.1$ Hz, 1H), 5.87 (tdd, $J = 6.3, 10.2, 17.1$ Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) δ 22.3, 22.7, 23.4, 24.1, 34.7, 38.8, 41.9, 47.7, 52.7, 67.2, 80.0, 103.6, 118.8, 133.9, 138.1, 144.4, 171.1. HRMS (FAB): calcd for $\text{C}_{17}\text{H}_{22}\text{O}_3\text{S}$ (M^+), 306.1290; found, 306.1293.

Sulfide 12b.



A colorless oil [purified by column chromatography on SiO_2 with hexane/ AcOEt ($v/v = 30/1$), 99% yield]; IR (neat) 700, 747, 918, 971, 1024, 1182, 1226, 1446, 1595, 1673 ($\text{C}=\text{O}$), 2853, 2934, 3052 cm^{-1} ; ^1H NMR (300 MHz, d_8 -THF, 25 °C) δ 1.14–1.23 (m, 1H), 1.38–1.51 (m, 3H), 1.76–1.83 (m, 1H), 2.24–2.33 (m, 1H), 2.45–2.53 (m, 2H), 4.47 (d, $J = 7.2$ Hz, 1H), 4.80 (d, $J = 16.8$ Hz, 1H), 4.92 (d, $J = 10.2$ Hz, 1H), 6.16 (ddd, $J = 7.2, 10.2, 16.8$ Hz, 1H), 6.97 (s, 1H), 7.16–7.38 (m, 13H), 7.72 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (75 MHz, d_8 -THF, 25 °C) δ 19.3, 21.8, 22.1, 22.3, 55.1, 64.6, 115.5, 120.9, 122.3, 125.7, 126.5, 126.7, 127.6, 128.4, 128.8, 130.1, 130.3, 130.8, 135.7, 135.9, 136.5, 138.8, 139.3, 142.7, 190.7. HRMS (FAB): calcd for $\text{C}_{31}\text{H}_{29}\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$), 465.1888; found, 465.1887.

Sulfide 12d.



A colorless oil [purified by column chromatography on SiO_2 with hexane/ AcOEt ($v/v = 25/1$), 93% yield]; IR (neat) 700, 753, 919, 1025, 1065, 1233, 1437, 1600, 1731 ($\text{C}=\text{O}$), 2926, 3076 cm^{-1} ; ^1H NMR (270 MHz, CD_2Cl_2 , 25 °C) δ 1.19–1.38 (m, 2H), 1.40–1.49 (m, 2H), 1.56–1.67 (m, 1H), 1.86–1.94 (m, 1H), 2.38–2.42 (m, 2H), 3.36 (s, 3H), 4.35 (d, $J = 8.9$ Hz, 1H), 5.07 (d, $J = 18.1$ Hz, 1H), 5.09 (d, $J = 10.0$ Hz, 1H),

6.35 (ddd, $J = 8.9, 10.0, 18.1$ Hz, 1H), 6.90 (s, 1H), 7.07–7.23 (m, 10H); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) δ 20.7, 22.7, 23.1, 23.6, 52.2, 57.9, 65.5, 118.0, 122.6, 123.2, 127.2, 127.8, 128.5, 129.2, 130.0, 132.1, 135.7, 136.5, 137.9, 139.8, 143.1, 169.1. HRMS (FAB): calcd for $\text{C}_{26}\text{H}_{27}\text{O}_3\text{S}$ ($\text{M}+\text{H}^+$), 419.1681; found, 419.1676.

References

- Pajamannar, T.; Balasubramanian, K. K. *Tetrahedron Lett.* **1988**, 29, 5789.
- (a) Ohe, K.; Miki, K.; Yokoi, T.; Nishino, F.; Uemura, S. *Organometallics* **2000**, 19, 5525. (b) Miki, K.; Yokoi, T.; Nishino, F.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **2002**, 645, 228. Also see: (c) Herndon, J. W.; Wang, H. *J. Org. Chem.* **1998**, 63, 4564.

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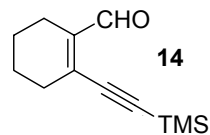
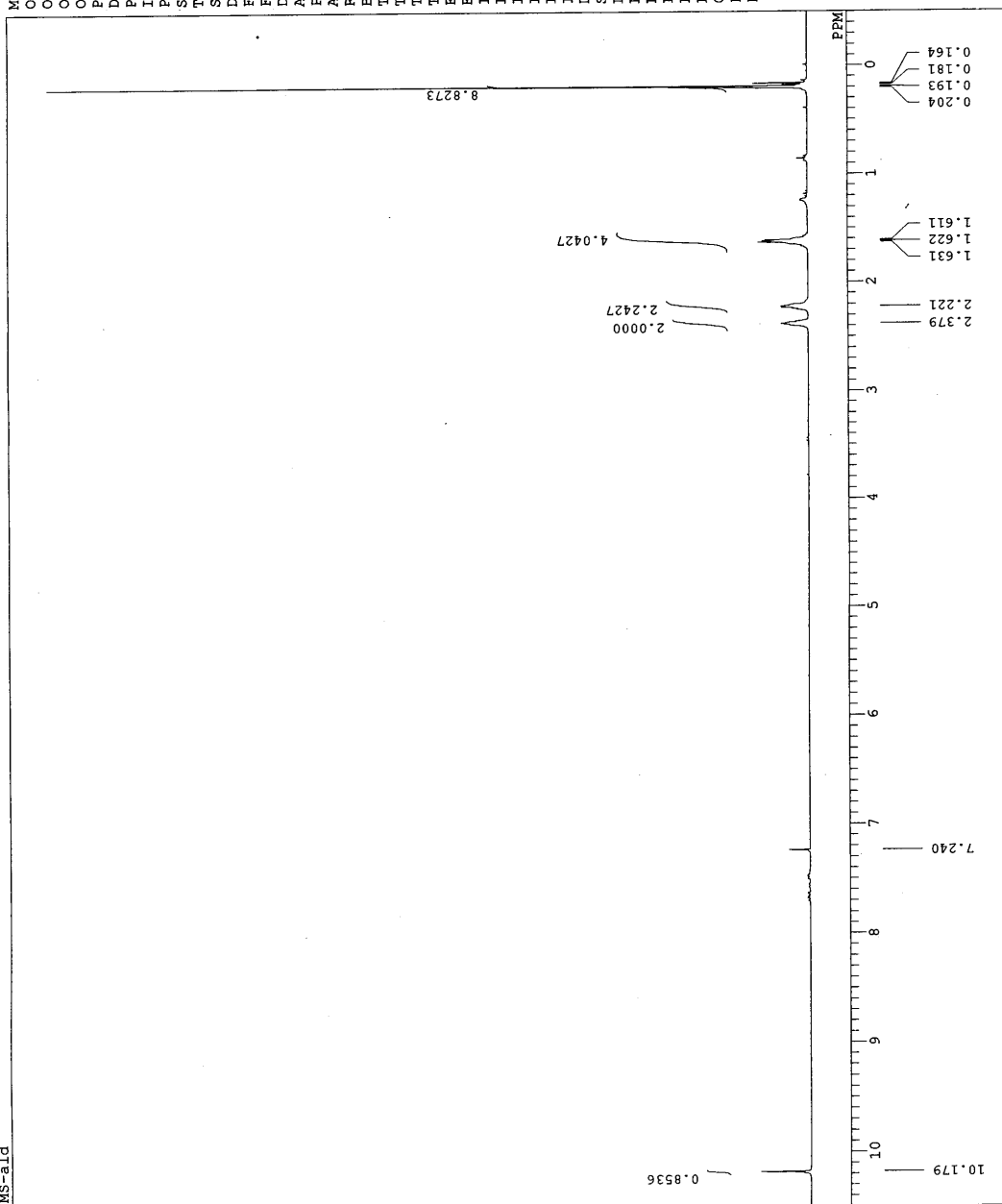
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TMS-ald

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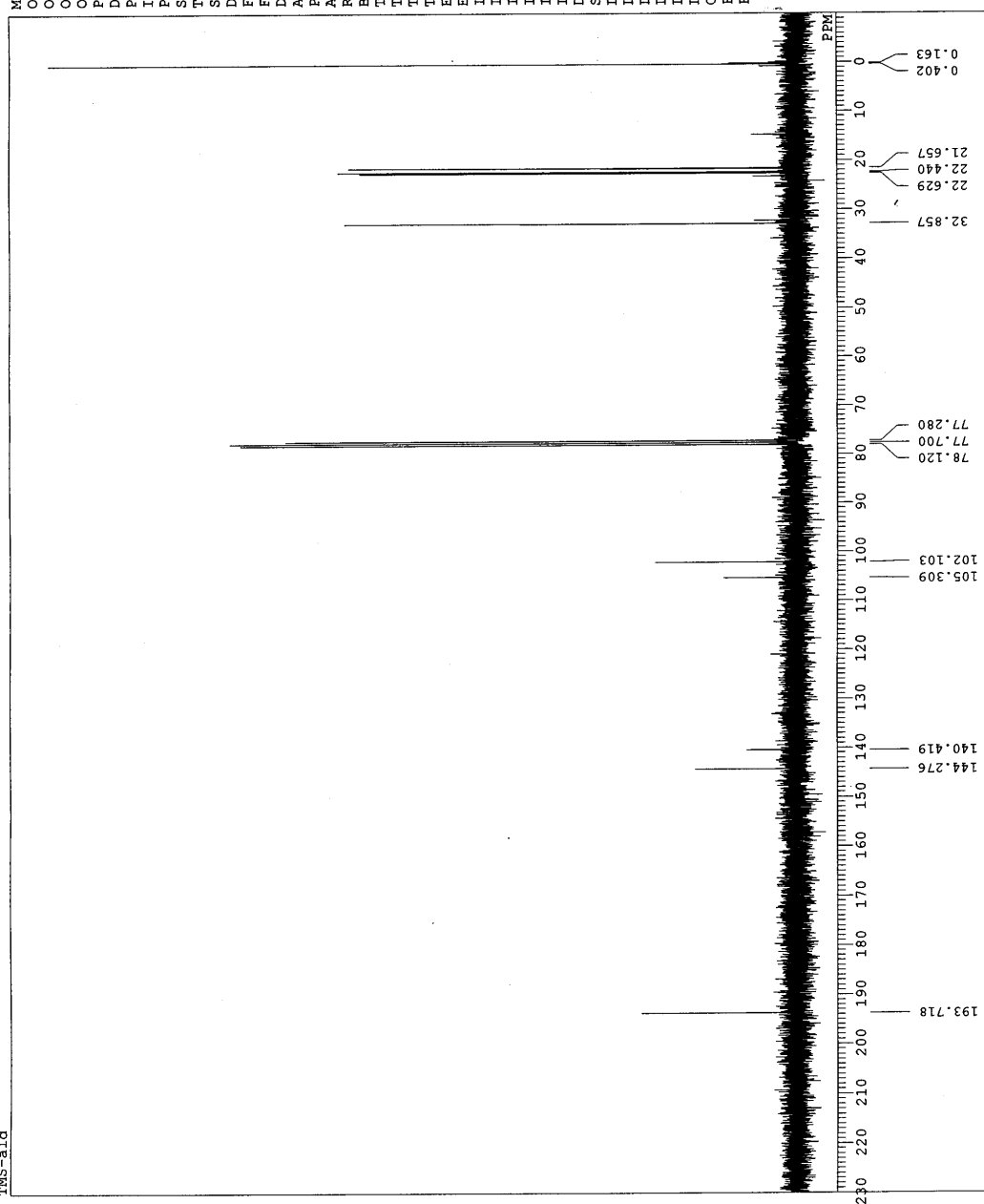
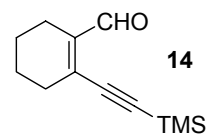
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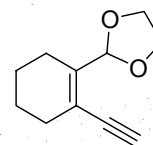
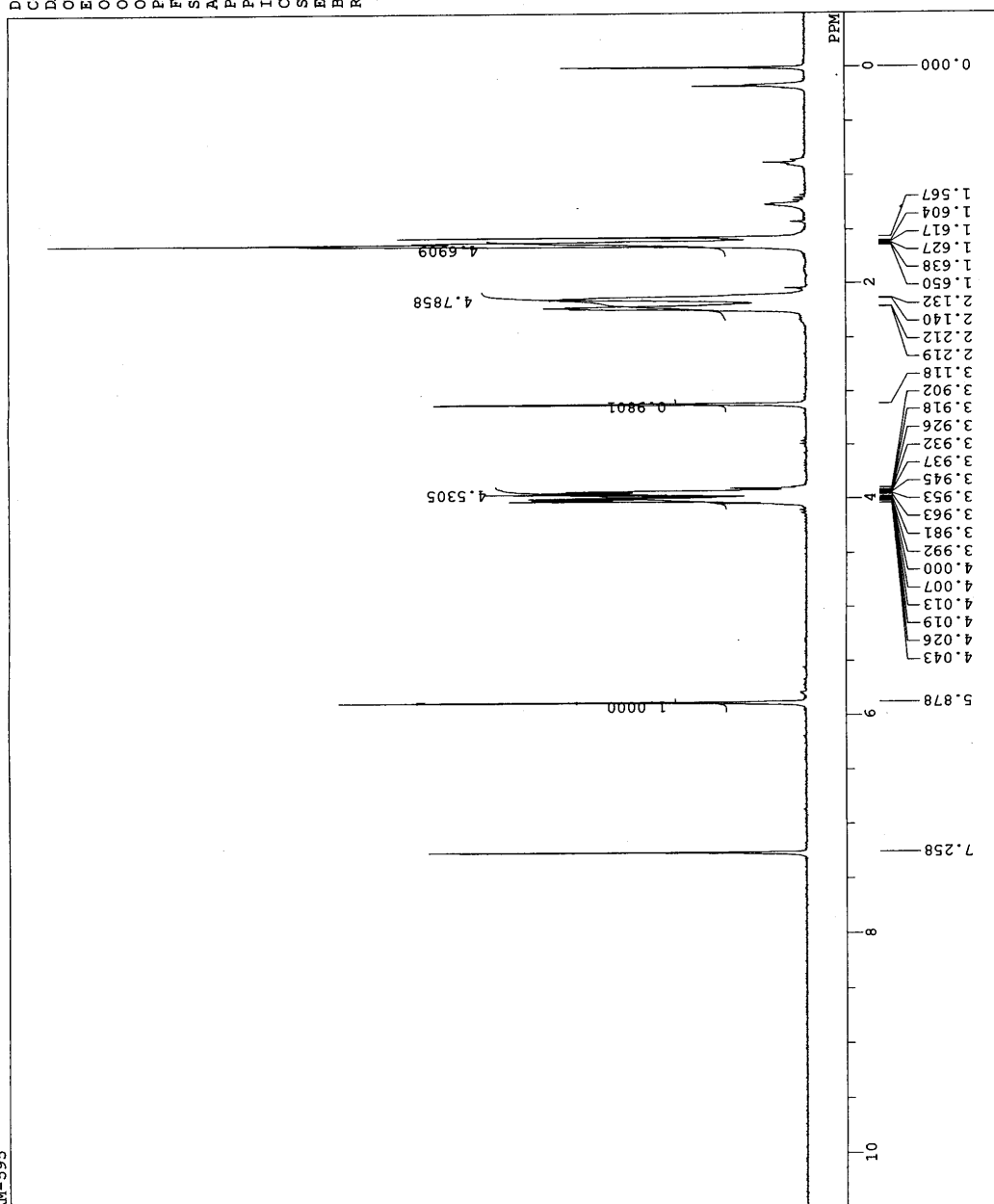


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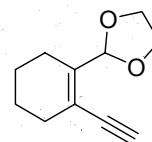
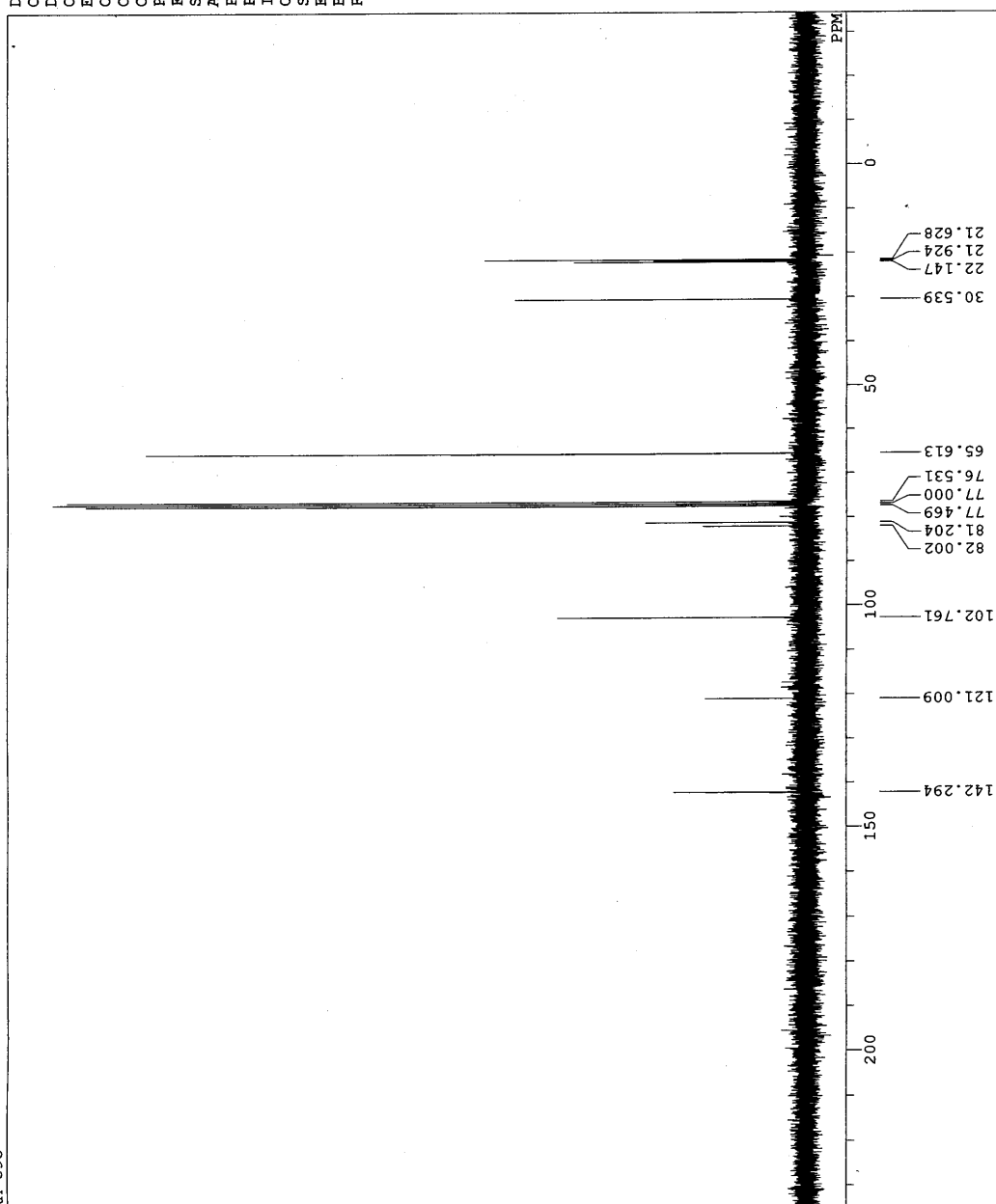
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15

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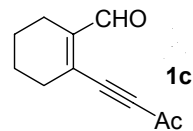
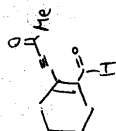
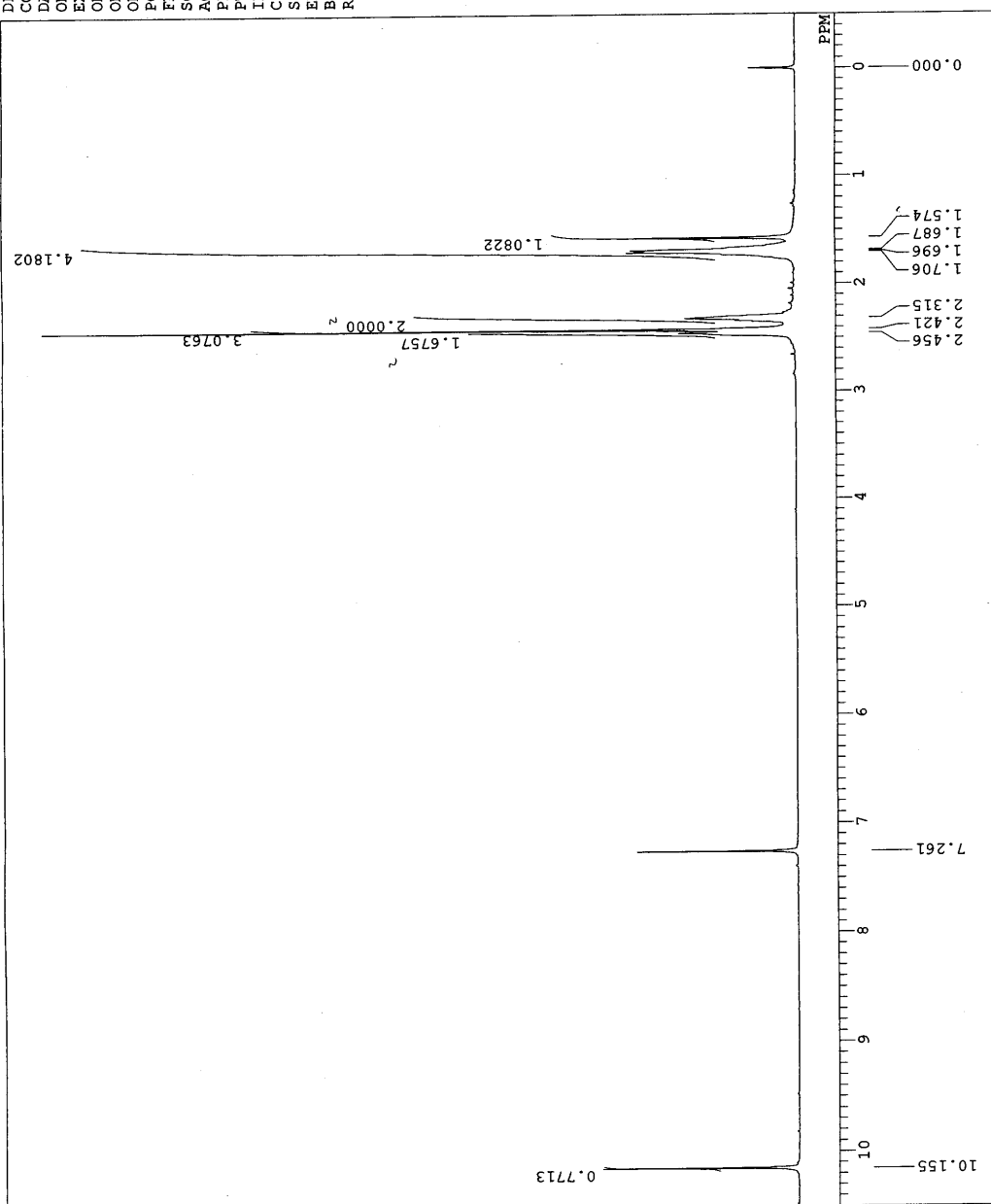
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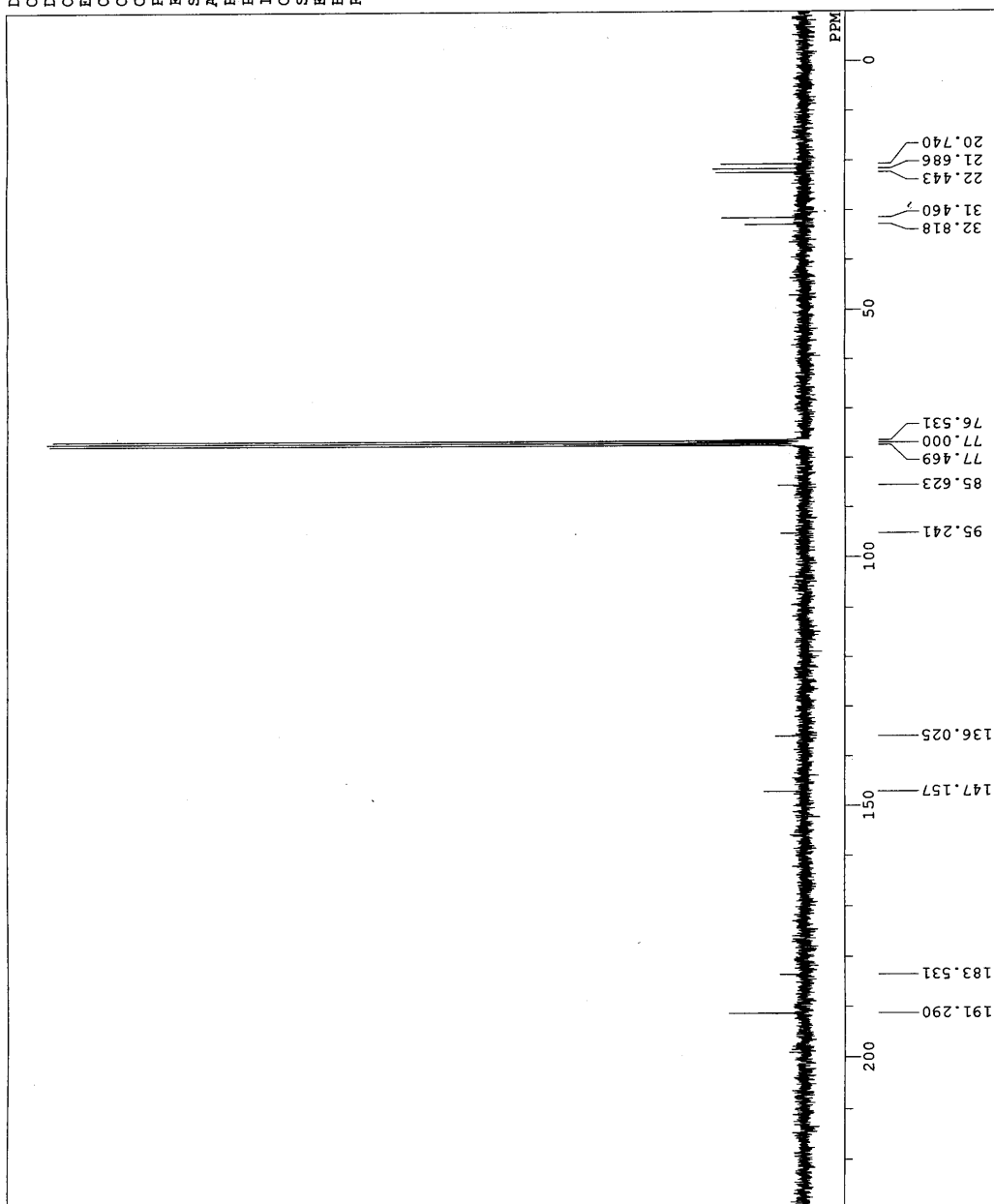
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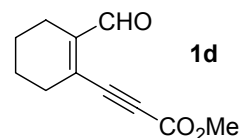
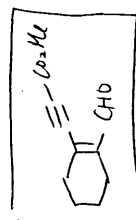
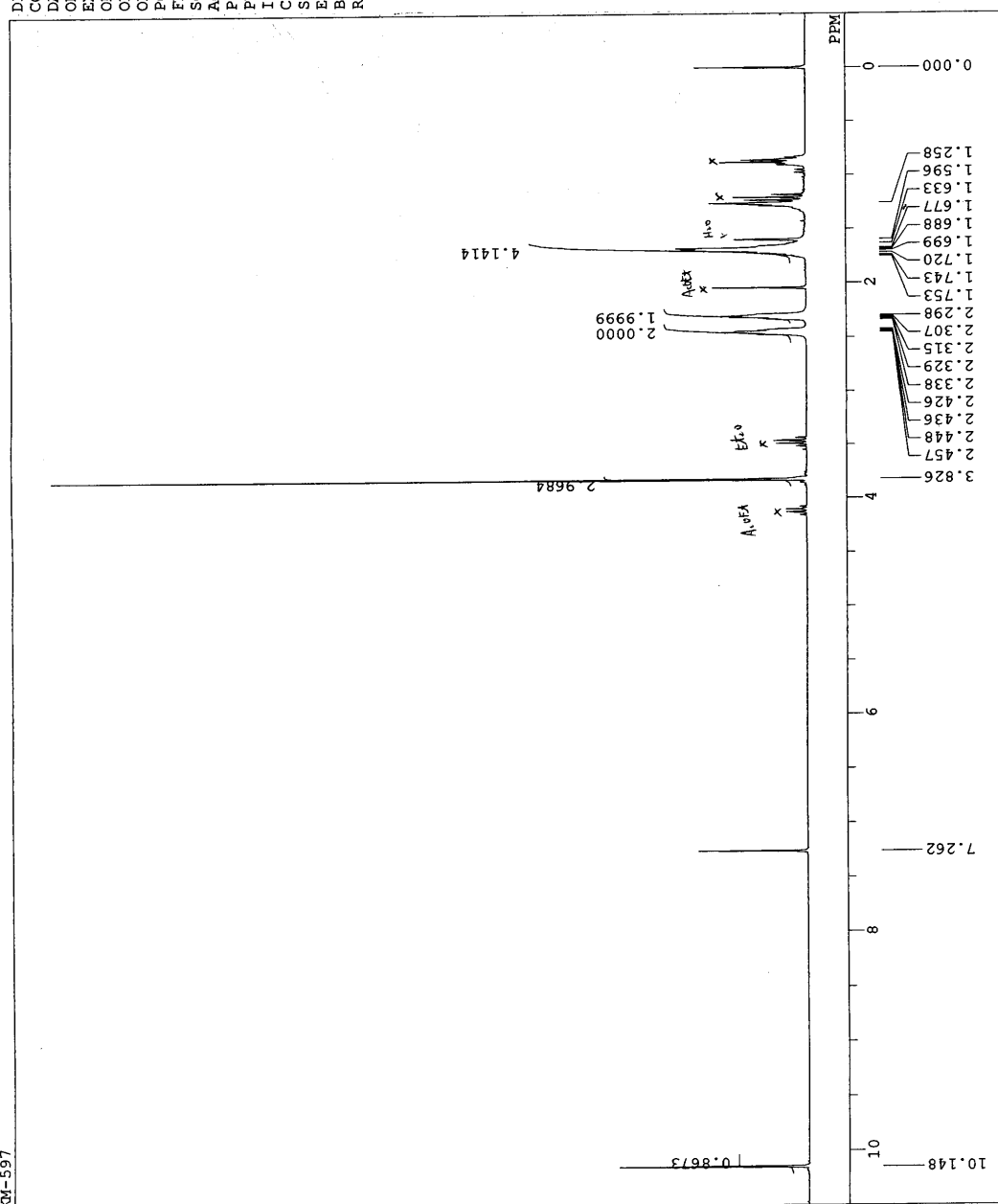


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KM-597

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PWL 1H
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20



C:\WINNMR98\COMMON_DEFAULT.ALS
KM-597

D:\FILE C:\WINNMR98\COMMON_DEFAULT.ALS

COMET KM-597
DATIM Wed Jan 15 01:59:02 2003

ORNUC 13C
EXMOD BCM

OBFRQ 67.80 MHz
OBSET 135.00 KHz

OBFIN 5200.0 Hz
POINT 32768

FREQ 18315.0 Hz
SCANS 1015

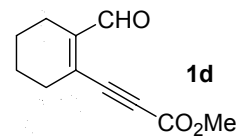
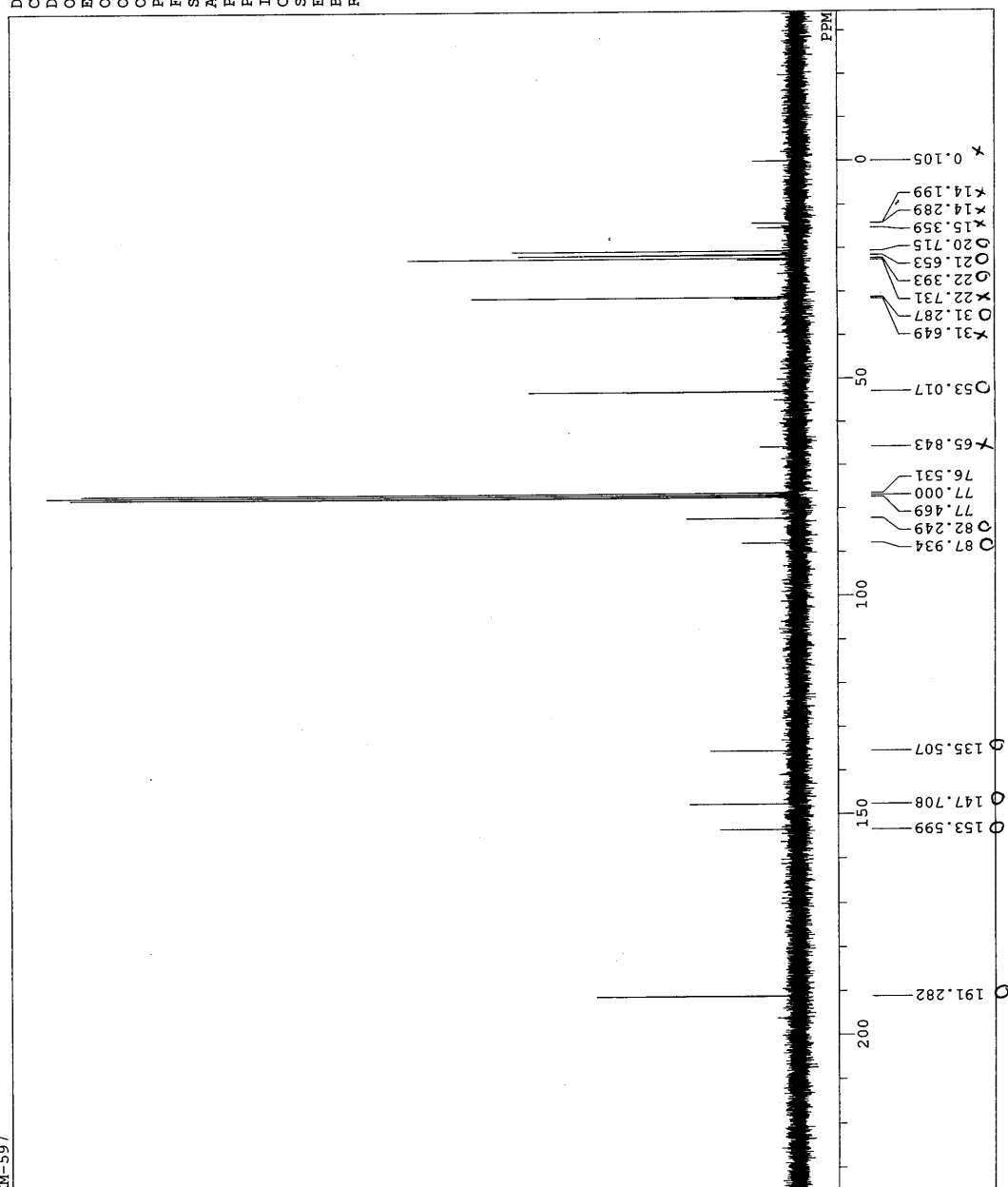
ACQTM 1.789 sec
PD 1.211 sec

PW1 4.2 us
IRNUC 1H

CTEMP 25.2 C
SLVNT CDCL3

EXREF 77.00 ppm
BF 0.12 Hz

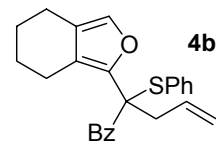
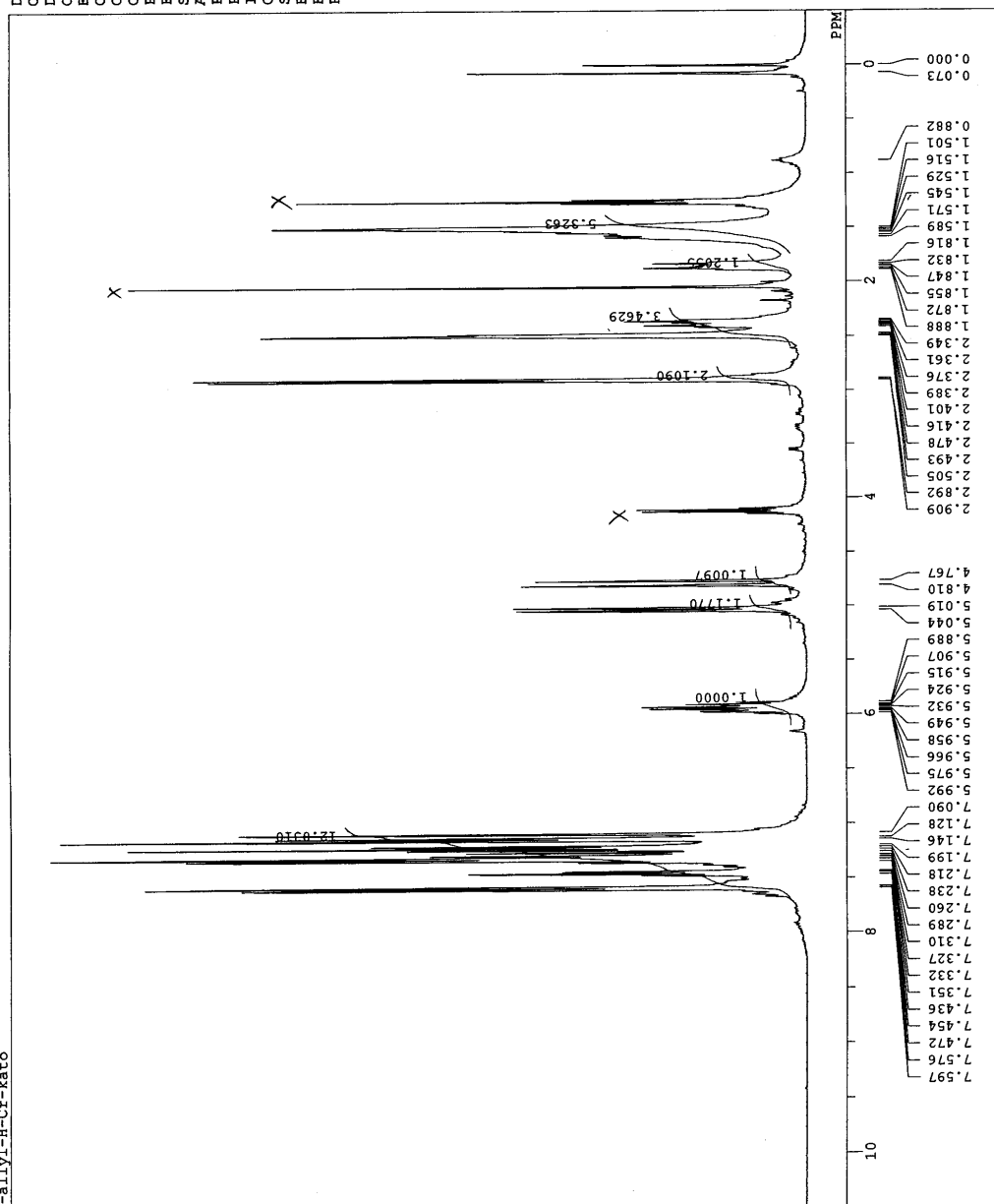
RGAIN 28



C:\WINNR98\COMMON_DEFAULT.ALS
S-allyl-H-Cr-kato

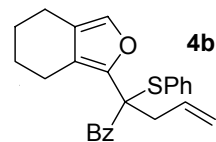
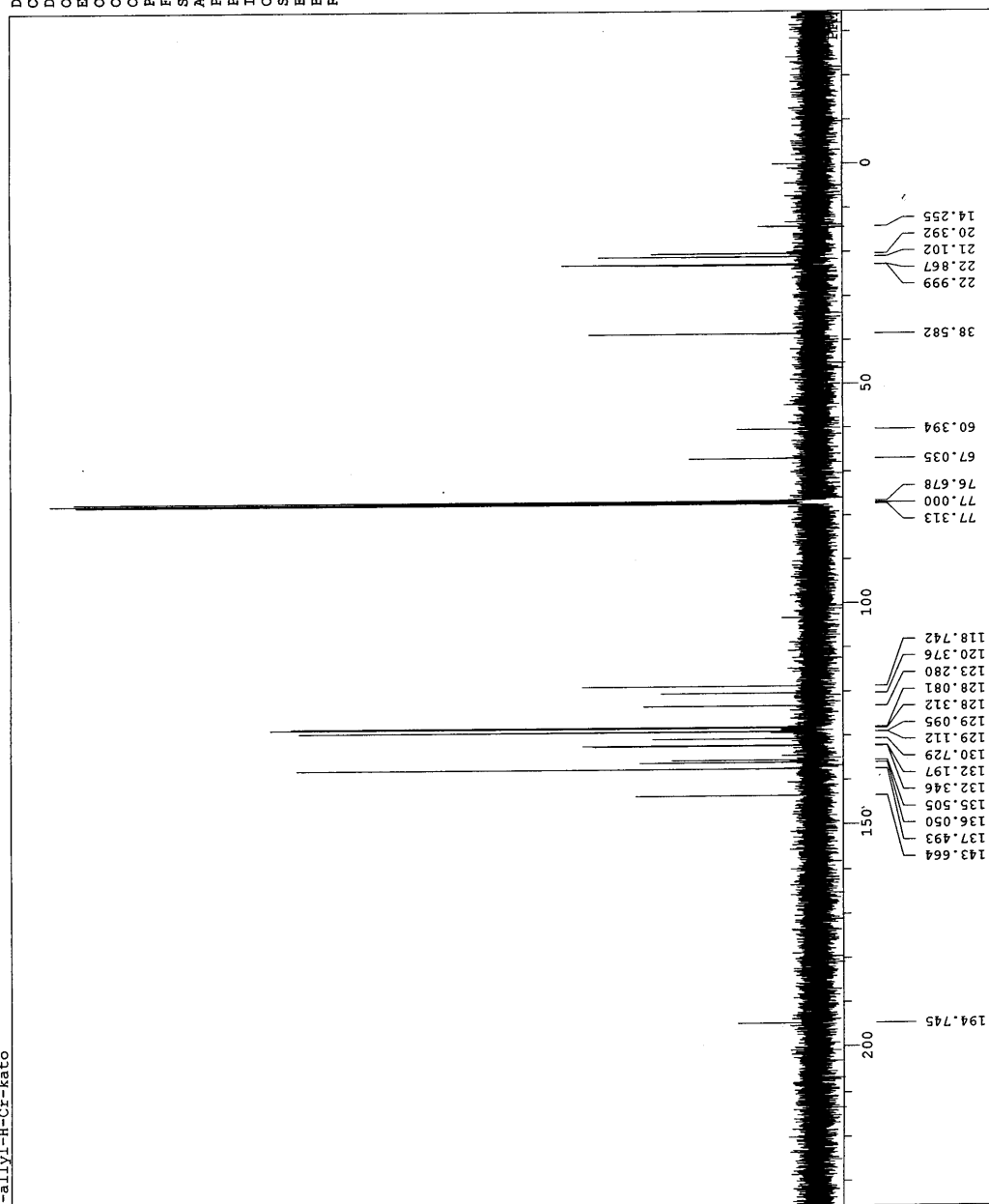
C:\WINNR98\COMMON_DEFAULT.ALS

DEFILE
COMPT S-allyl-H-Cr-kato
DATIM Wed Dec 19 01:02:26 2001
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 8
ACQTM 2.048 sec
PD 2.952 sec
PWL 8.5 us
IRNUC 1H
CTEMP 25.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17



C:\WINMR98\COMMON_DEFAULT.ALS
S-allyl-H-Cr-kato

DFILE C:\WINMR98\COMMON_DEFAULT.ALS
 COMNT S-allyl-H-Cr-kato
 DATIM Wed Dec 19 01:30:37 2001
 ORNUC 13C
 EXMOD ECM
 OBSFQ 100.40 MHz
 OBSST 125.00 KHz
 OBSIN 10500.0 Hz
 POINT 32768
 FREQU 27173.9 Hz
 SCANS 447
 ACQTM 1.206 sec
 PD 1.794 sec
 PW1 5.0 us
 IRNUC 1H
 CTEMP 25.3 c
 SLVNT CDCl3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 33

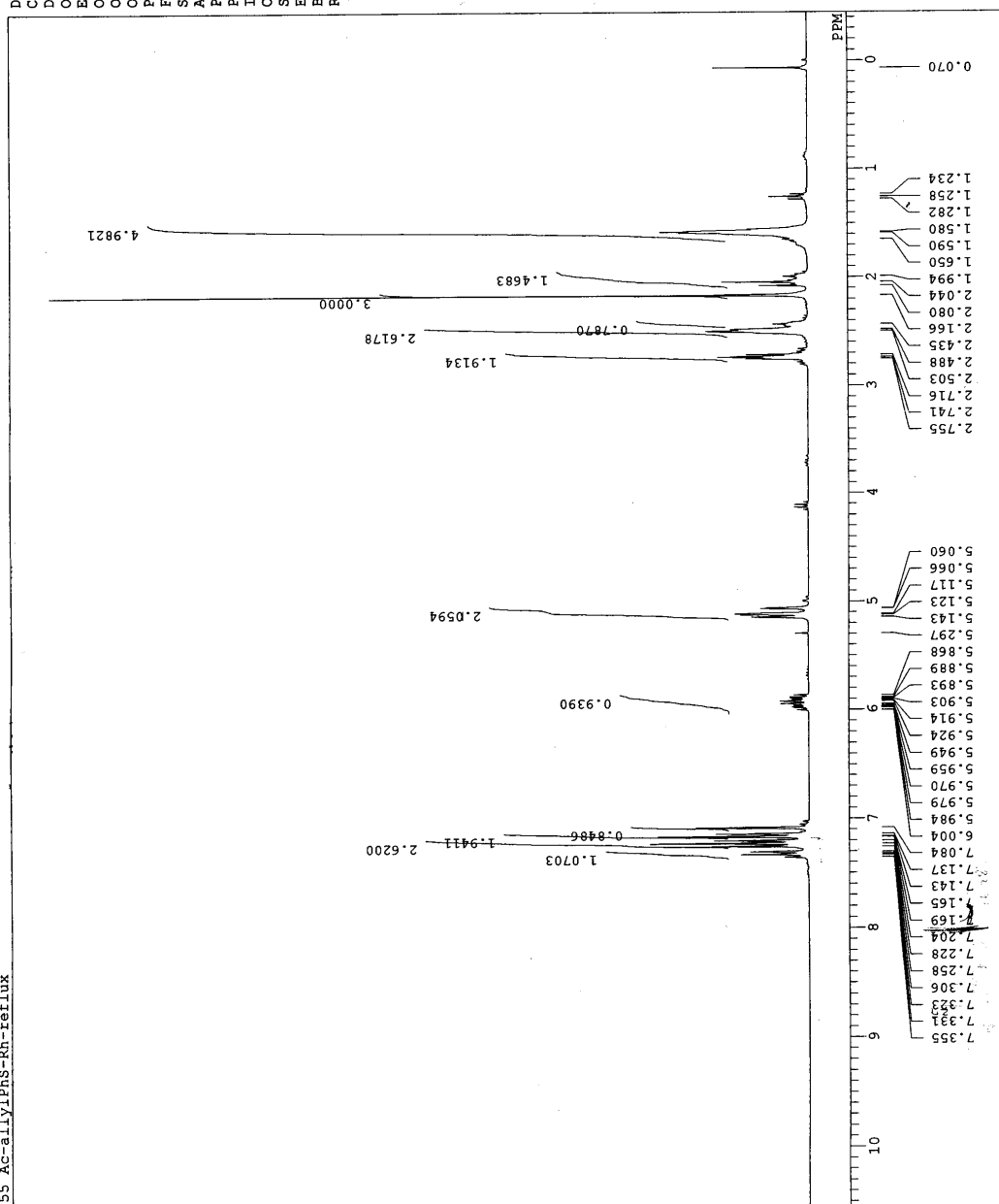
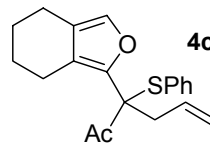


```

DFILE C:\WINMR98\COMMON\DEFAULT.ALS
COMMT 255 Ac-allylPhS-Rh-reflux
DATIM Mon Nov 25 19:55:45 2002

```

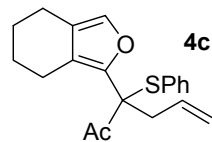
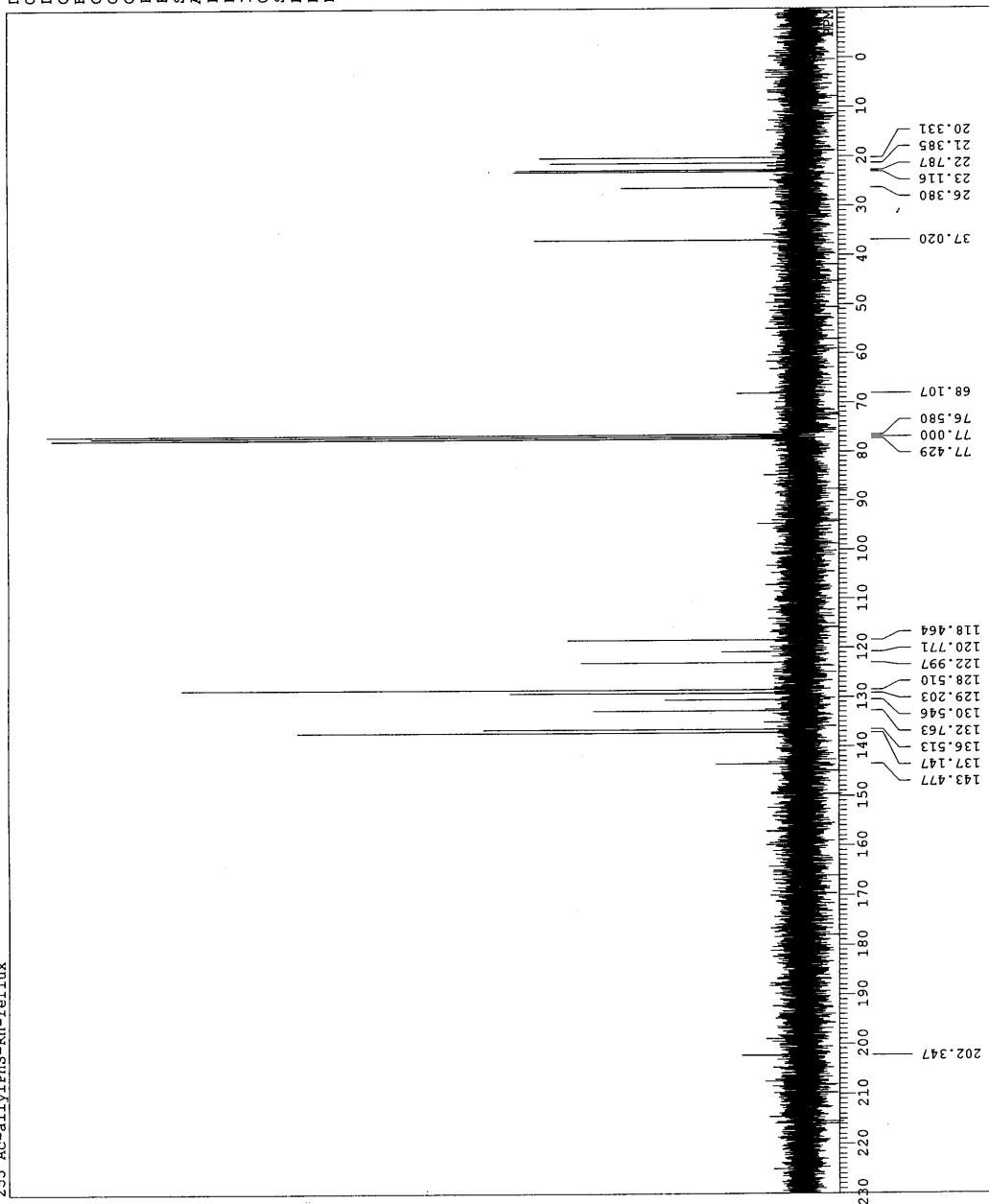
DFILE COMNT DATIM OBNUC EXMOD OBFRQ OBSET OBFIN POINT FREQU SCANS ACQTM PD PW1 IRNUC CTEMP SLVNT EXREF BF RGAIN

[illegible]

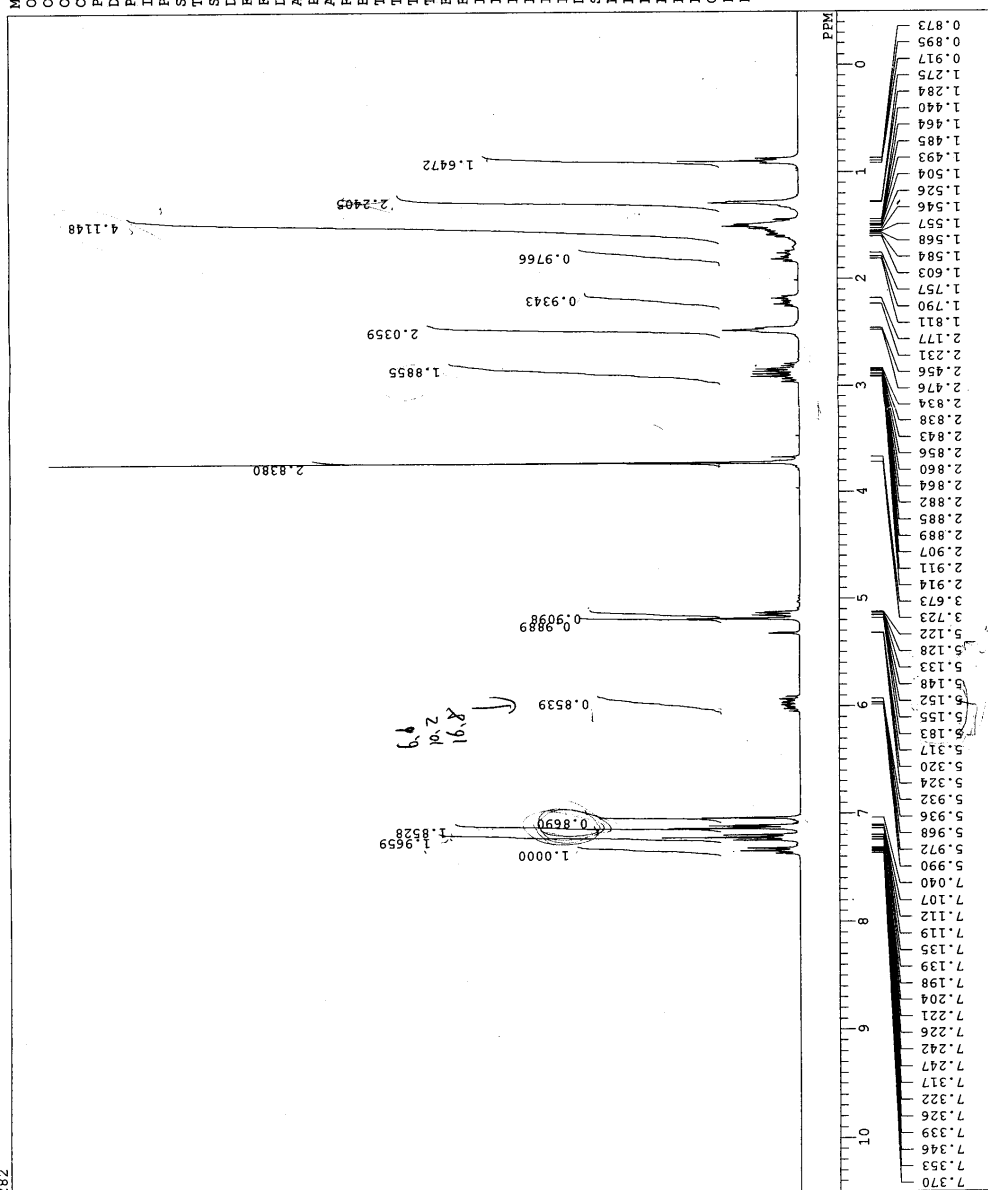
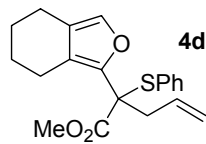
C:\WINNMR98\COMMON_DEFAULT.ALS
255 Ac-allylPhS-Rh-Reflux

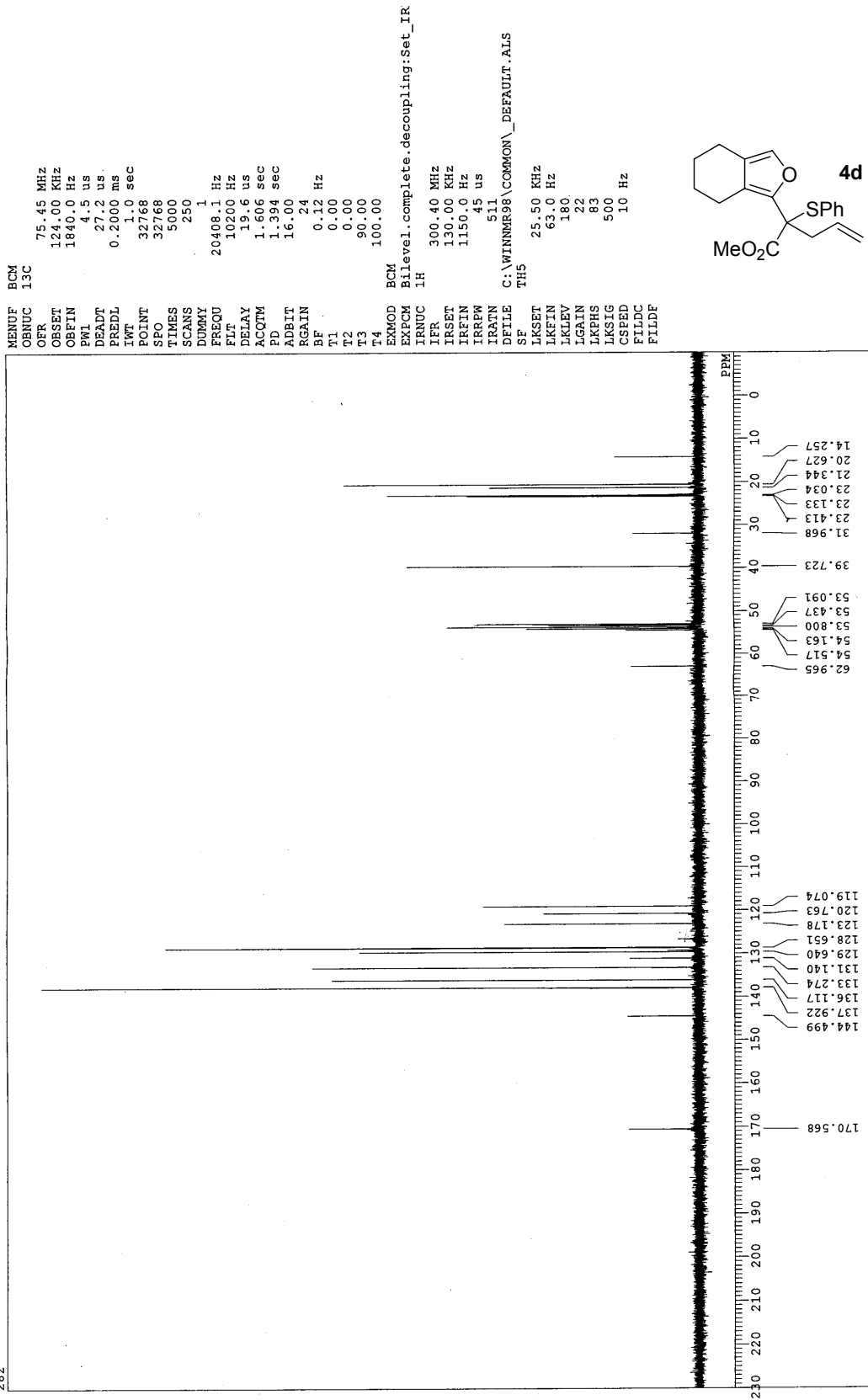
DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
COMNT 255 Ac-allylPhS-Rh-Reflux
DATIM Mon Nov 25 20:22:32 2002

OBNUC 13C
EXMOD BCM
OBSFQ 75.45 MHz
OBSRT 124.00 KHz
OBSFV 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 400
ACQTM 1.606 sec
PD 1.394 sec
PWL 4.4 us
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24



| | |
|------------|------------------------------------|
| 300.40 MHz | NON |
| 130.00 KHz | 1H |
| 1150.0 Hz | |
| 5.6 us | |
| 97.2 us | |
| 0.2000 ms | |
| 1.0 sec | |
| 32768 | |
| 32768 | |
| 16 | |
| 16 | |
| 1 | |
| 6013.2 Hz | |
| 3000 Hz | |
| 66.7 us | |
| 5.449 sec | |
| 1.551 sec | |
| 16.00 | |
| 13 | |
| 0.12 Hz | |
| 0.00 | |
| T1 | |
| 0.00 | |
| T2 | |
| 90.00 | |
| T3 | |
| 100.00 | |
| T4 | |
| EXMOD | NON |
| EXPCM | NON:Single,coupled:PWL_ACQTM_PD:1H |
| IRNUC | 1H |
| IFR | 300.40 MHz |
| IRSET | 130.00 KHz |
| IRFIN | 1150.0 Hz |
| IRPRP | 45 us |
| IRPN | 511 |
| DETL | C:\WINN98\COMMON_DEFAULT.ALS |
| SE | PHS |
| LSSET | 25.50 KHz |
| IRFIN | 63.0 Hz |
| LRLEV | 180 |
| LGAIN | 18 |
| LRPHS | 83 |
| LRSIG | 563 |
| CSFED | 8 Hz |
| FILDF | |

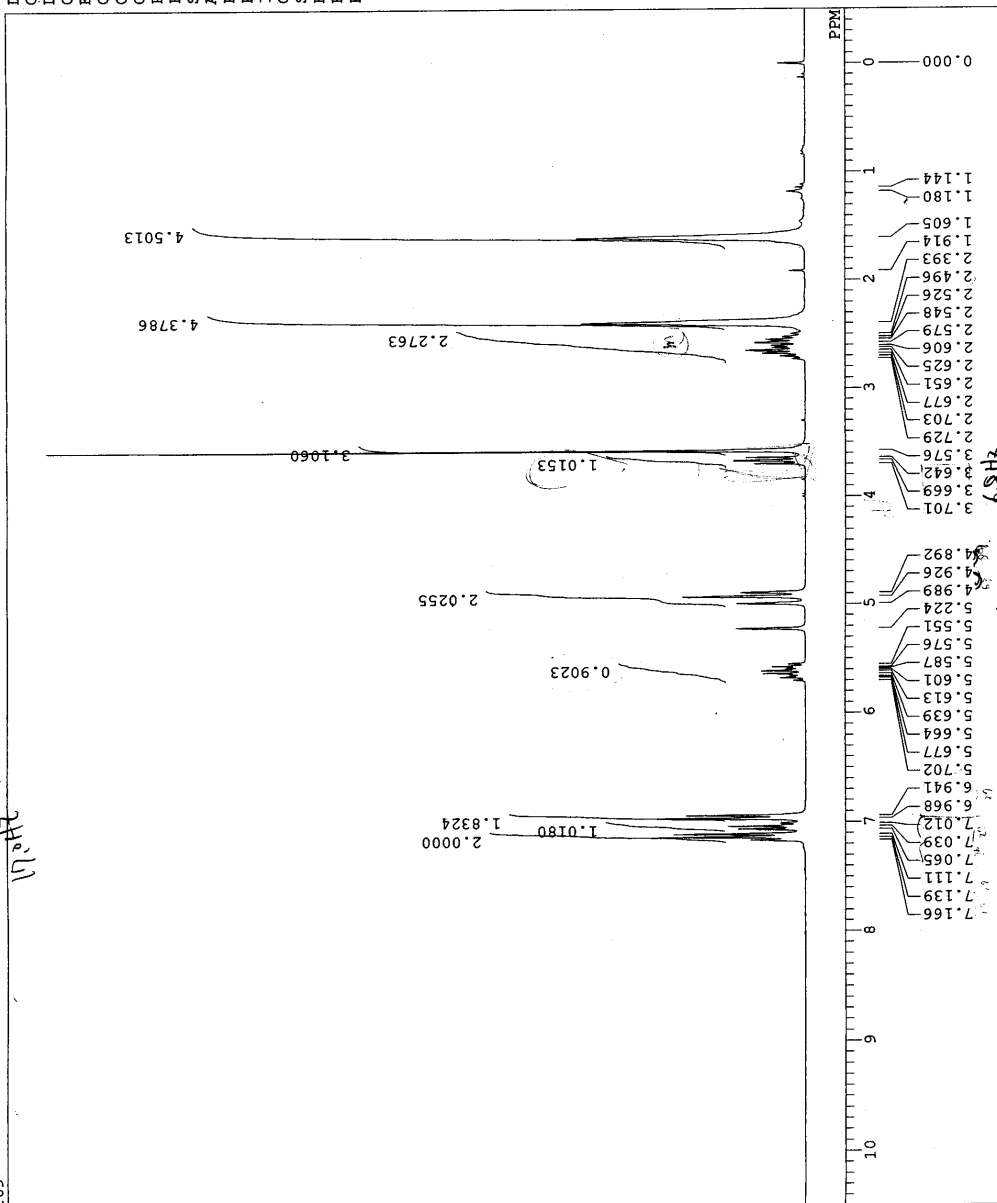




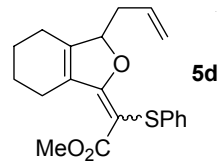
C:\WINNR98\COMMON_DEFAULT.ALS
269

113

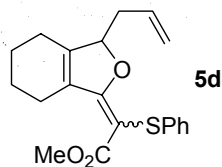
17.4 Hz



DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT 269
DATIM Tue Jan 21 22:10:31 2003
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 16384
FREQU 5402.4 Hz
SCANS 16
ACQTM 3.033 sec
PD 2.000 sec
PWI 5.6 us
IRNUC 1H
CTEMP 25.3 C
SLVNT CD2CL
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 19

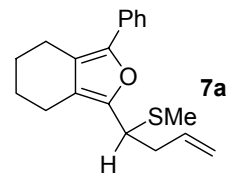
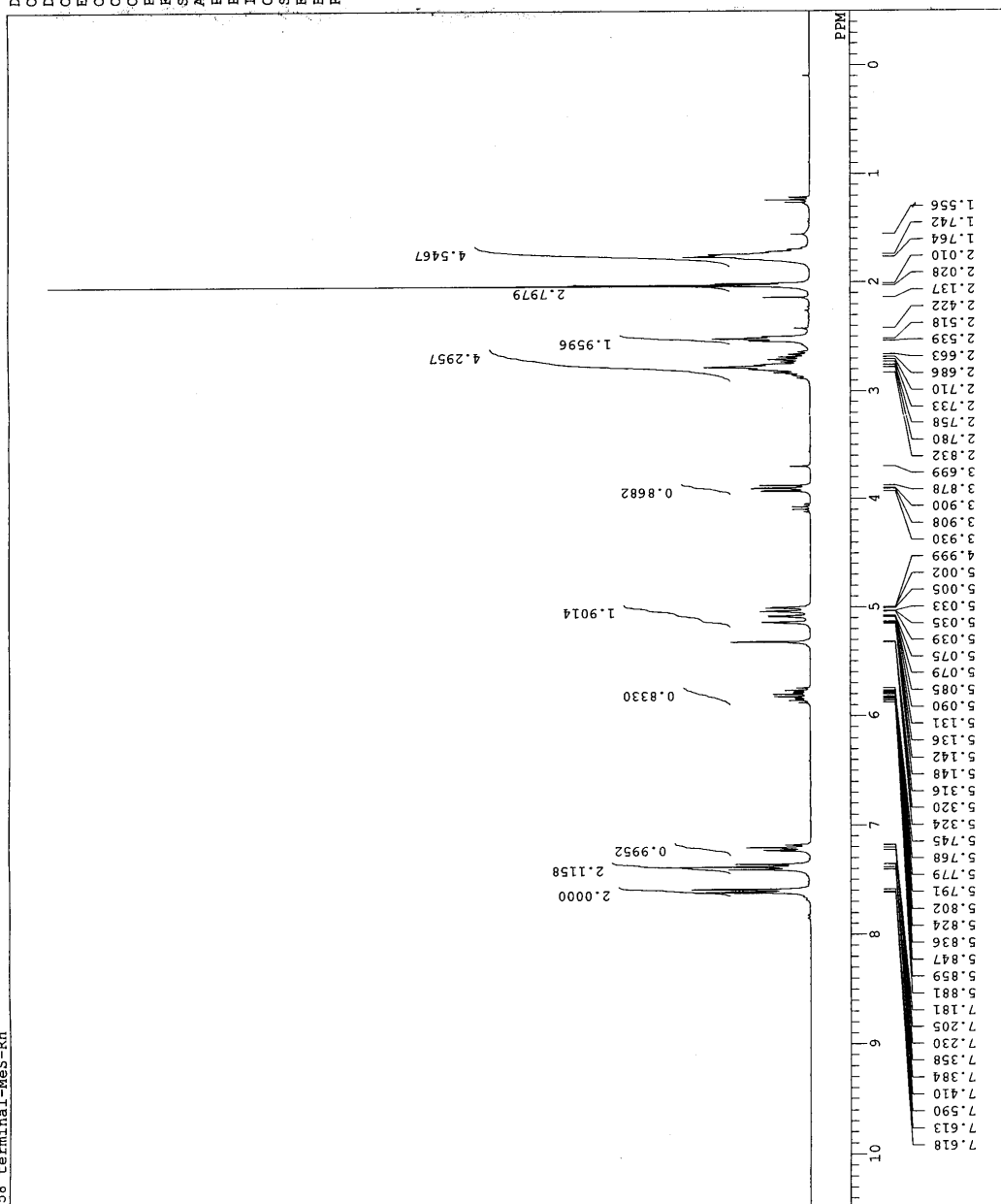


DFILE COMNT DATIM OBNUC EXMOD OBFRQ OBSET OBFIN POINT FREQU SCANS ACQTM PD PW1 IRNUC CTEMP SLVNT EXREF BF RGAIN



D:\258-terminal-MeS-Rh.als
258 terminal-MeS-Rh

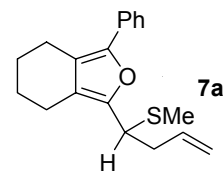
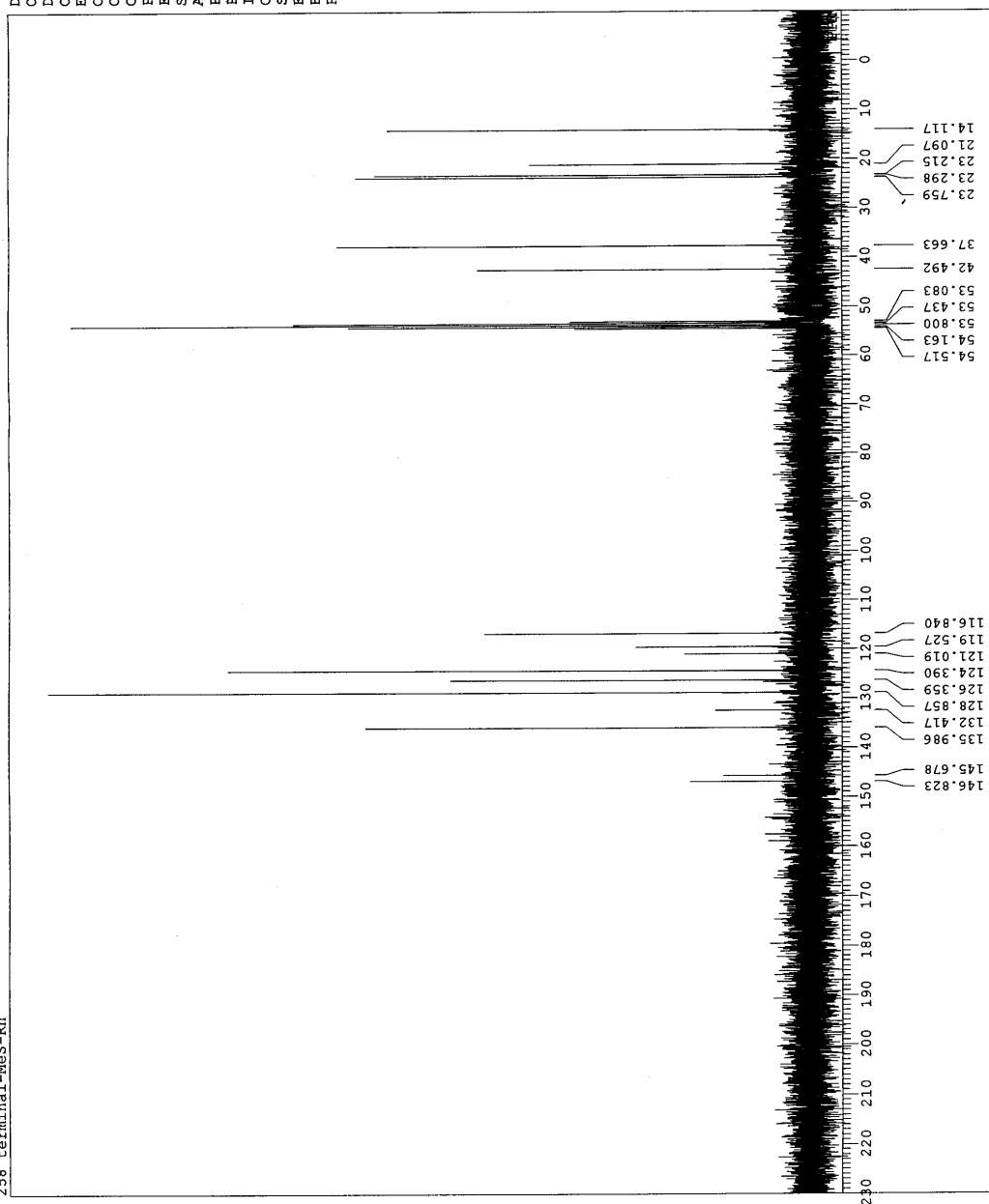
DETE D:\258-terminal-MeS-Rh.als
COMPT 258 terminal-MeS-Rh
DATE Sat Dec 14 22:38:01 2002
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQ 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
FWD 5.7 us
IRNUC 1H
CTEMP 23.1 c
SOLVT CD2CL2
EXREF 5.32 ppm
BF 0.12 Hz
RGAIN 15



C:\WINNMR98\COMMON\DEFAULT.ALS
258 terminal-MeS-Rh

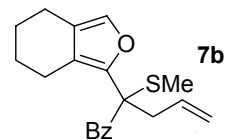
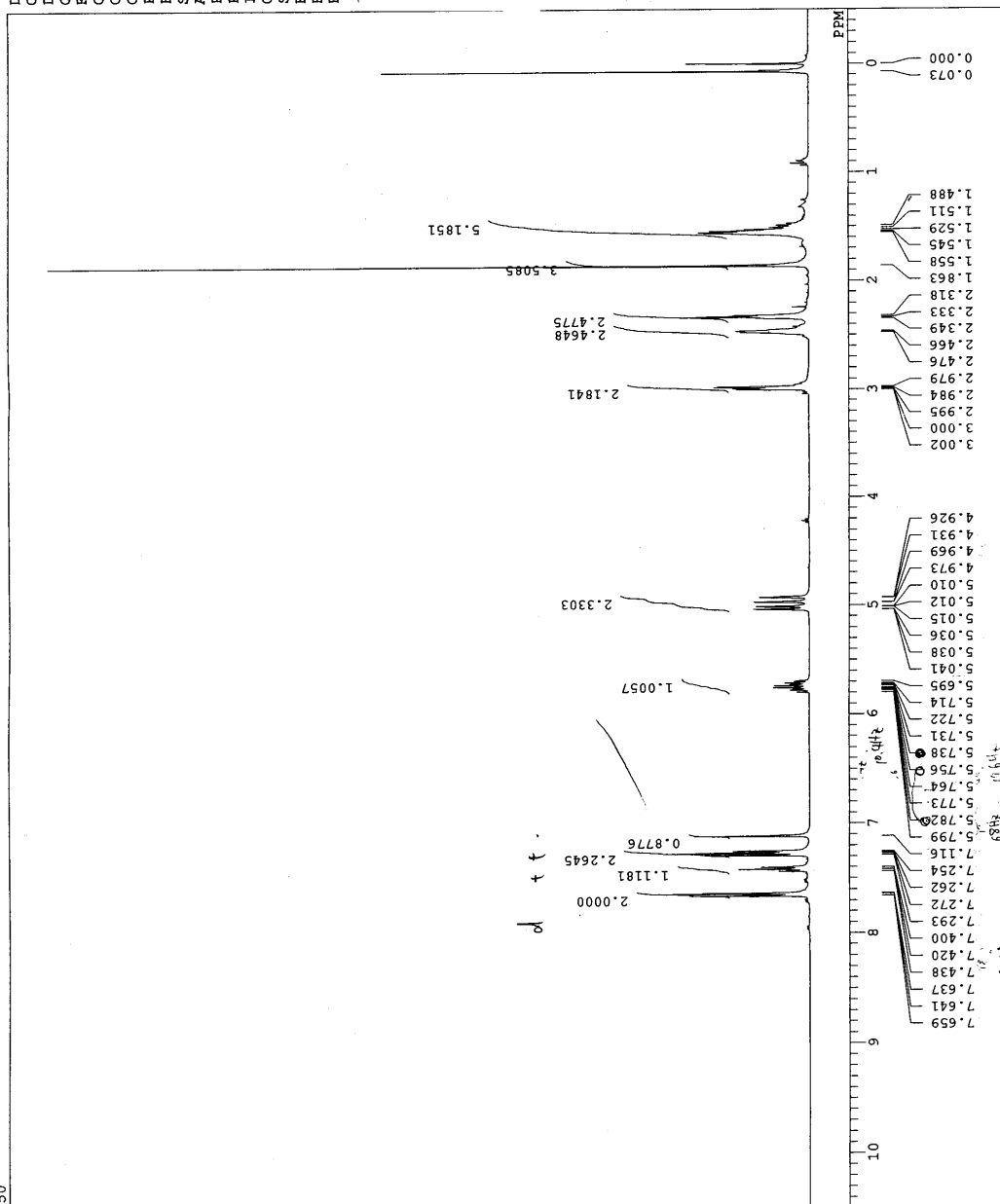
C:\WINNMR98\COMMON\DEFAULT.ALS
COMNT 258 terminal-MeS-Rh
DATIM Sat Dec 14 22:55:31 2002

ORNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 204081.1 Hz
SCANS 200
ACQTM 1.606 sec
PD 1.394 sec
PWL 4.4 us
IRNUC 1H
CTEMP 23.7 C
SLVNT CD2CL2
EXREF 53.80 ppm
BF 0.12 Hz
RGAIN 24



C:\WINNMR98\COMMON_DEFAULT.ALS
250

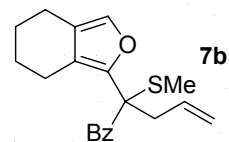
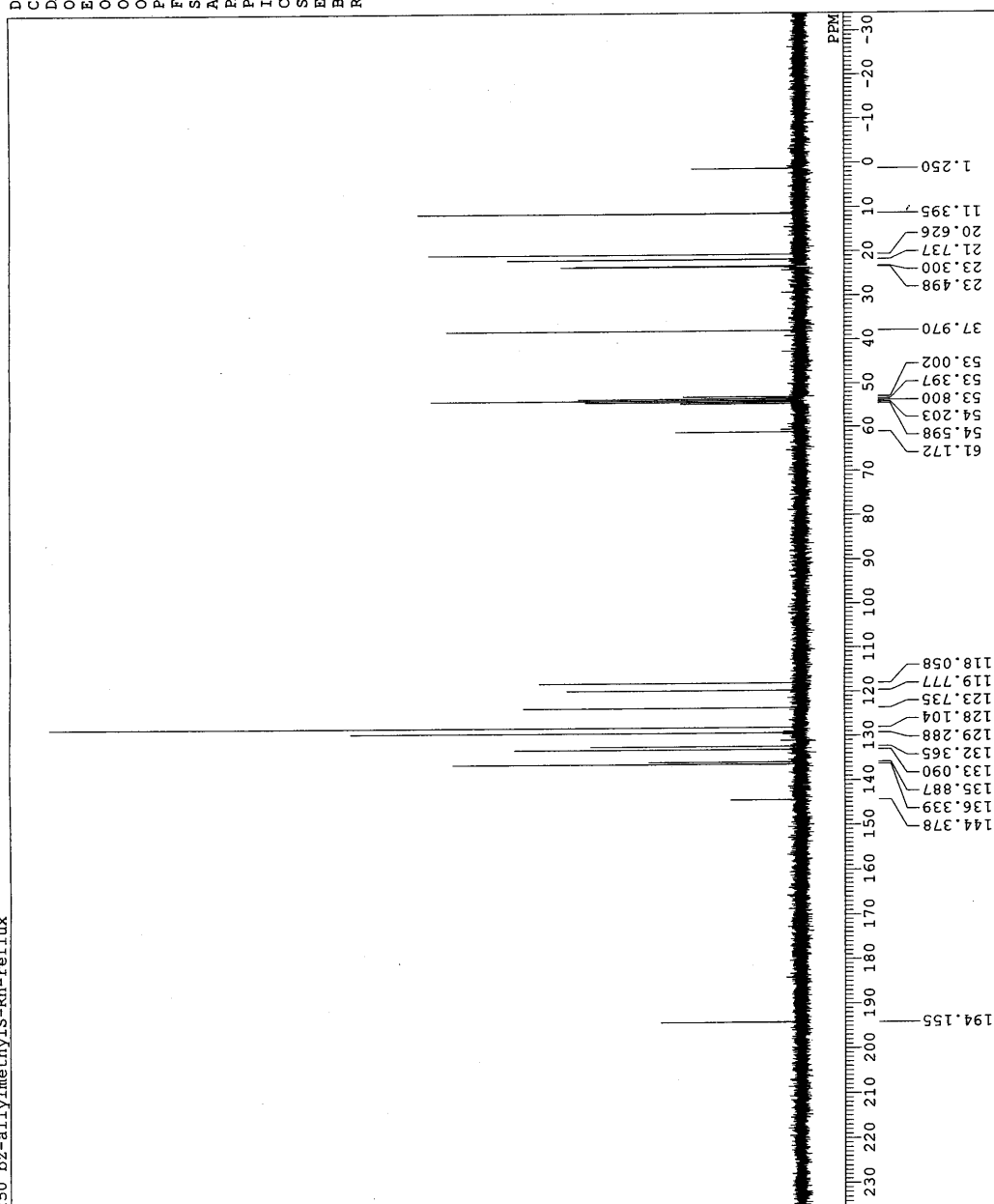
DFILE 250
COMNT Tue Nov 19 18:35:49 2002
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 8
ACQTM 2.048 sec
PD 2.952 sec
PWL 8.5 us
IRNUC 1H
CTEMP 25.8 c
SIVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 16



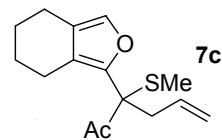
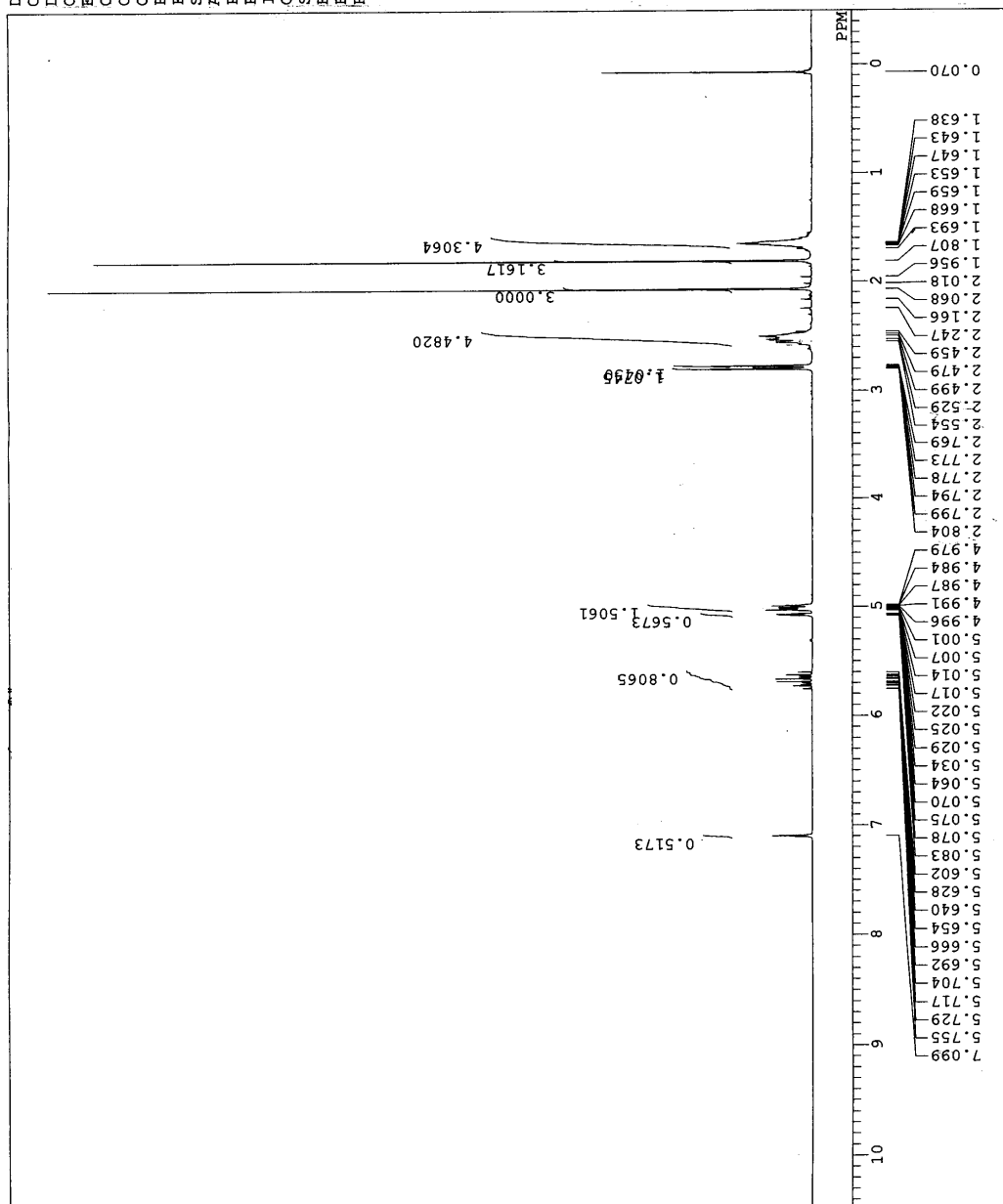
C:\WINNR98\COMMON_DEFAULT.ALS
250 bz-allylmethylS-Rh-reflux

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT 250 bz-allylmethylS-Rh-reflux
DATIM Mon Nov 18 23:01:10 2002

OBNUC 13C
EXMOD BCM
OBFREQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 251
ACQTM 1.789 sec
PD 1.211 sec
PW1 4.2 us
IRNUC 1H
CTEMP 24.4 C
SLVNT CD2CL
EXREF 53.80 ppm
BF 0.10 Hz
RGAIN 28



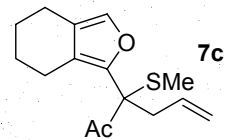
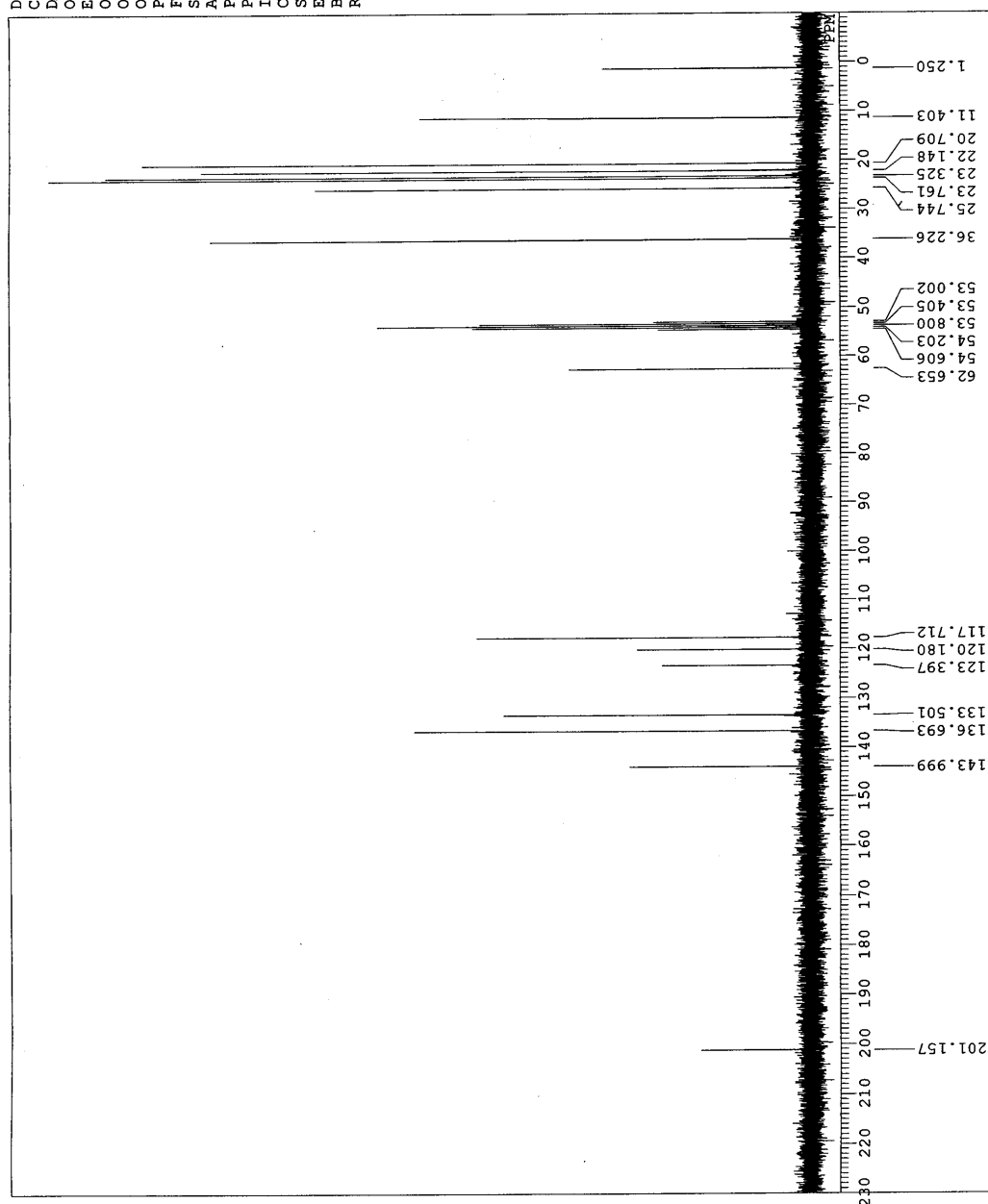
DFILE C:\WINMR98\COMMON\DEFAULT.AL
 CONNT Wed Jan 15 00:32:19 2003
 DATIM 1H
 EXMOD NON
 OBNUC 270.05 MHz
 OBFRQ 112.00 KHz
 OBSET 5800.0 Hz
 OBFIN 16384
 POINT 5402.4 Hz
 FREQU 16
 SCANS 3.033 sec
 ACQTM 2.000 sec
 PD 5.6 us
 PW1 25.4 C
 IRNUC 1H
 CTMP CD2CL
 SLVNT 0.07 ppm
 EXREF 0.12 Hz
 BF 16
 RGAIN



C:\WINMR98\COMMON_DEFAULT.ALS

DFILE C:\WINMR98\COMMON_DEFAULT.ALS

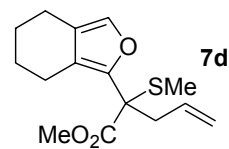
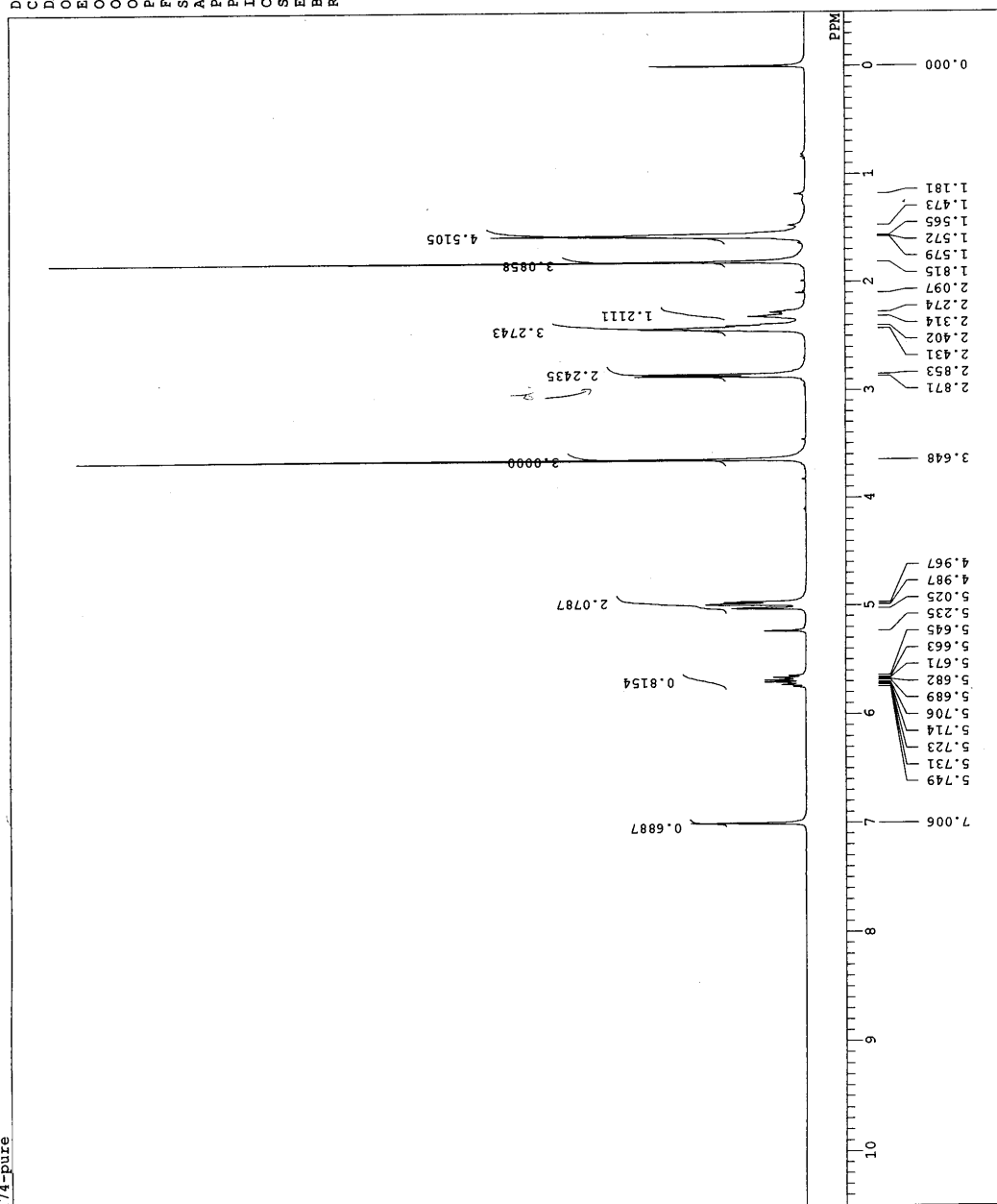
COMNT
DATIM Wed Jan 15 00:54:45 2003
OBNUC 13C
EXMOD BCM
OBFFQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 307
ACQTM 1.789 sec
PD 1.211 sec
PW1 4.2 us
IRNUC 1H
CTEMP 26.1 c
SLVNT CD2CL
EXREF 53.80 ppm
BF 0.12 Hz
RGAIN 28



C:\WINNR98\COMMON\DEFAULT.ALS
274-pure

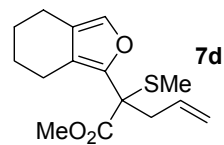
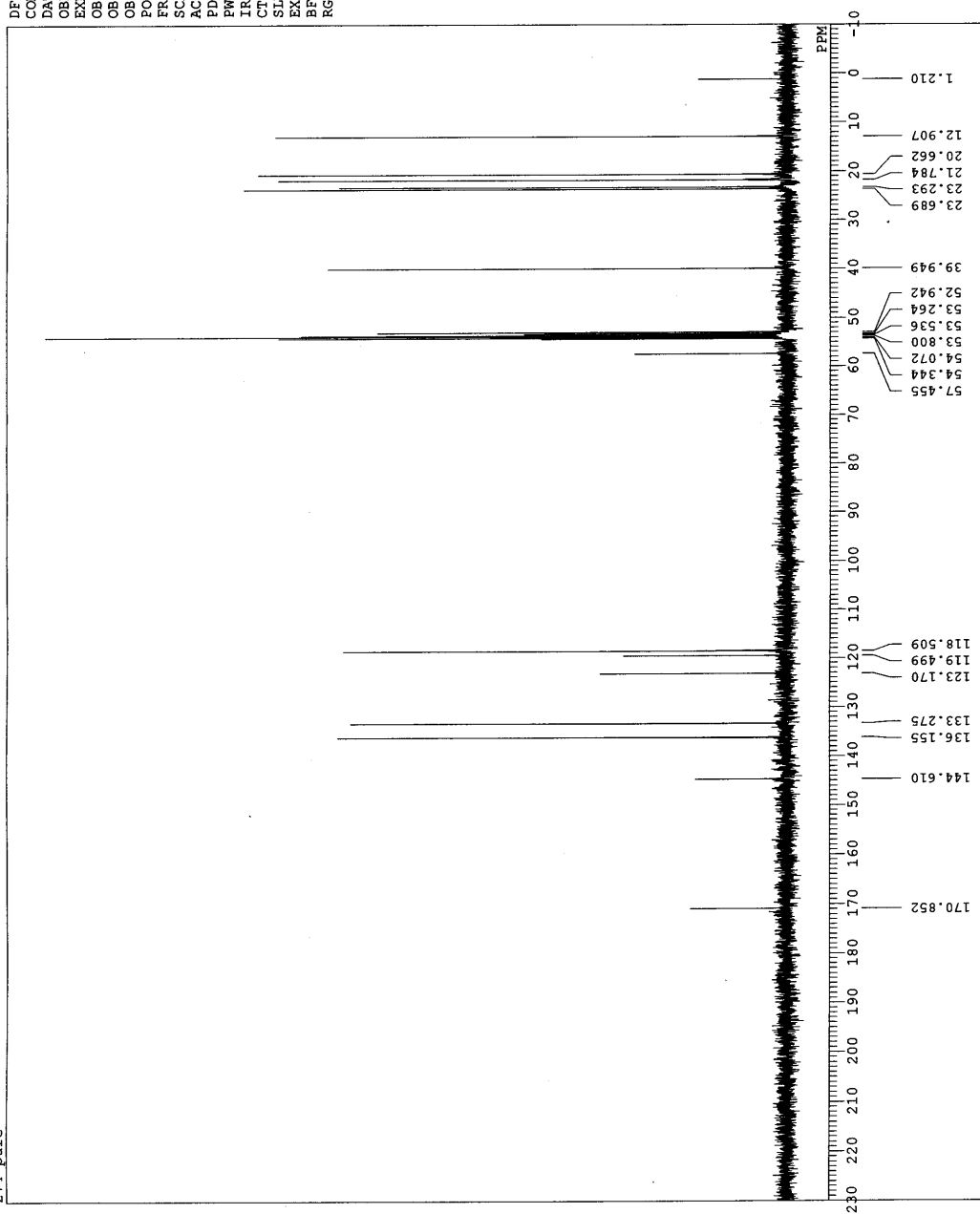
C:\WINNR98\COMMON\DEFAULT.ALS

DEFILE 274-pure
COMNT 274-pure
DATIM Mon Jan 27 23:29:41 2003
ORNUC 1H
EXMOD NON
OBFREQ 399.65 MHz
OBSEI 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 2.952 sec
PWL 8.5 us
IRNUC 1H
CTEMP 25.4 C
SIVNT CD2CL
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 13

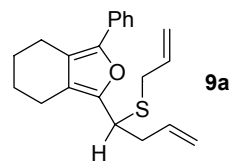
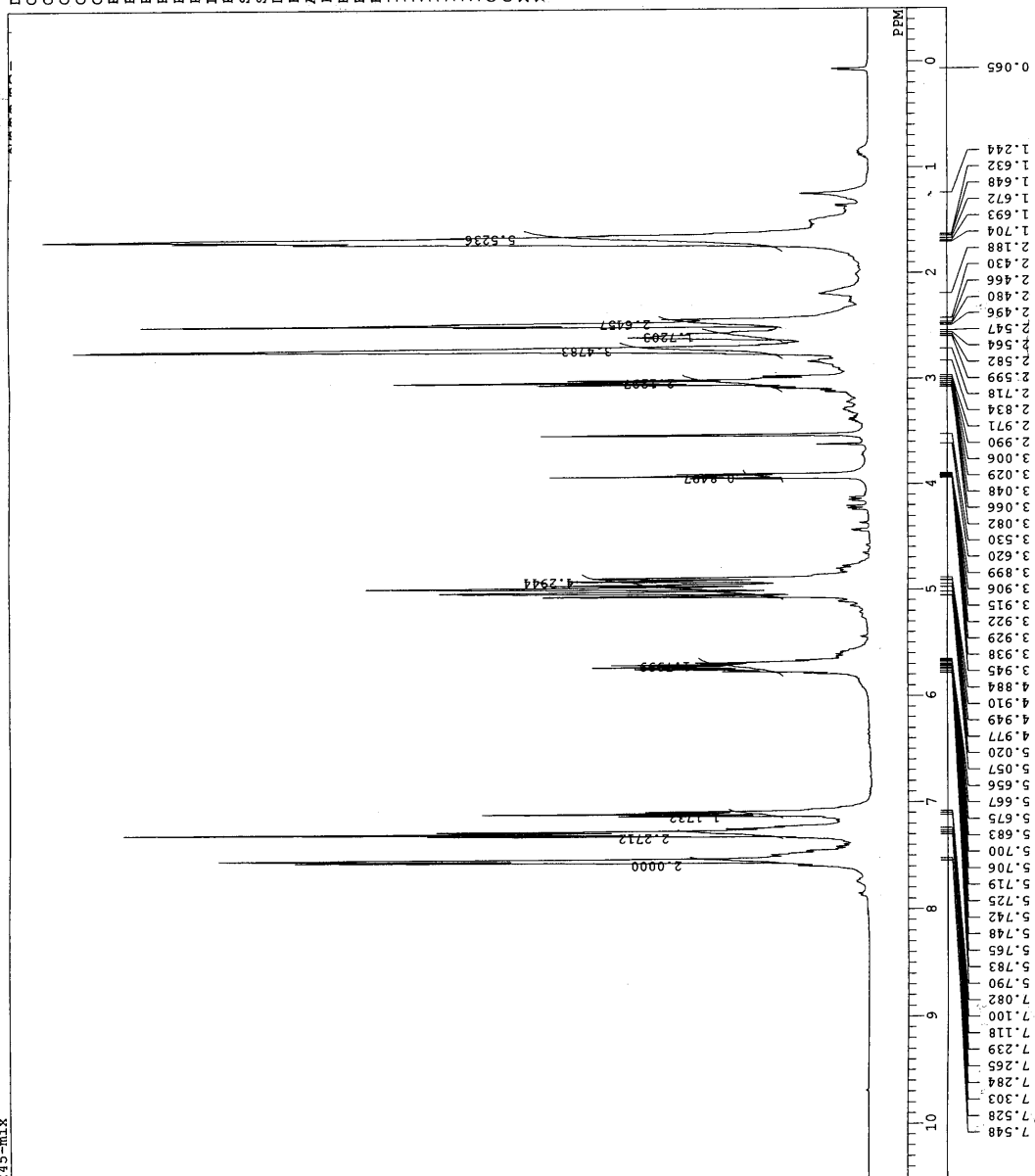


C:\WINNR98\COMMON_DEFAULT.ALS
274-pure

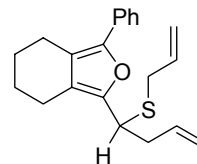
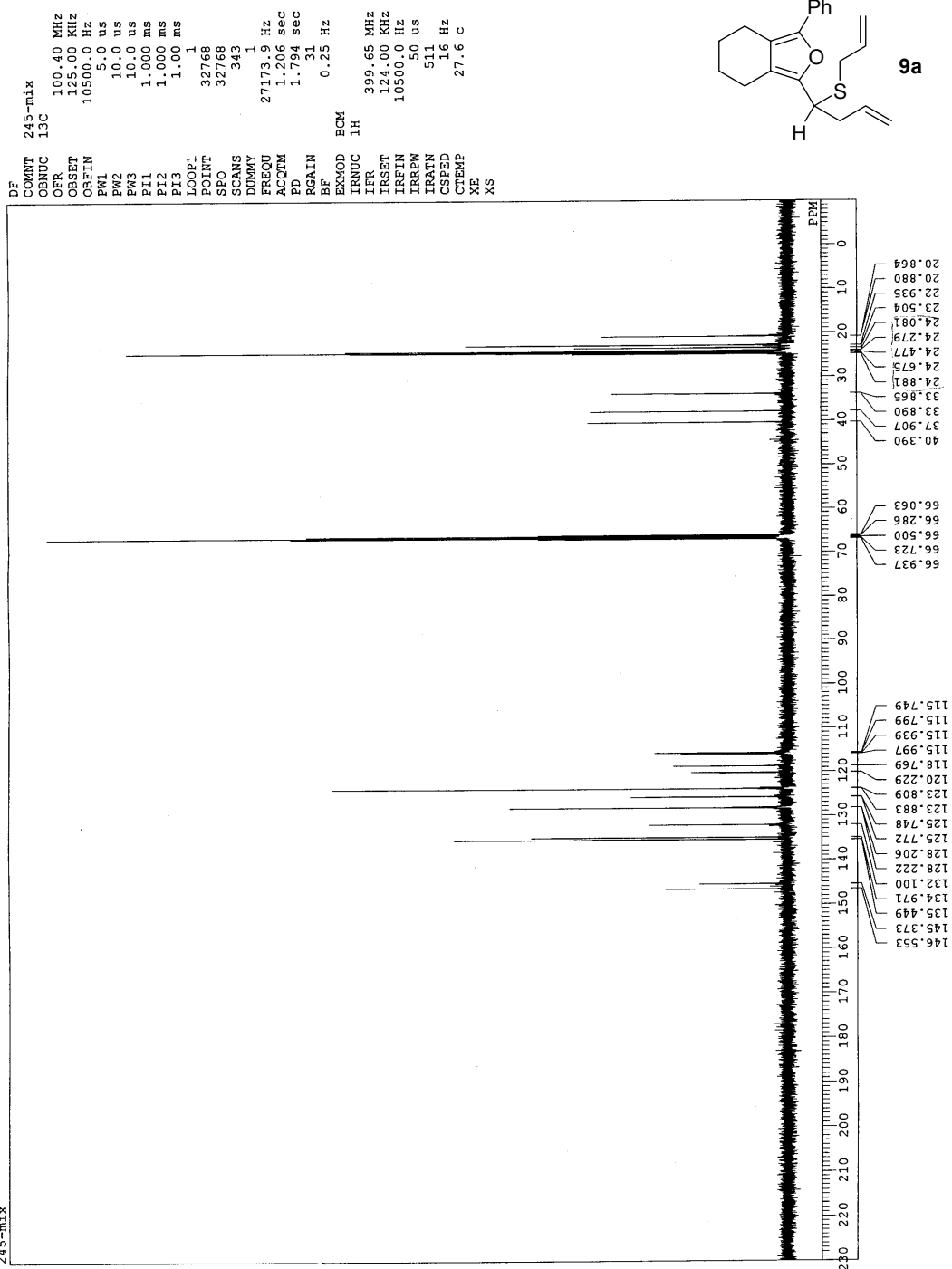
DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT 274-pure
DATIM Mon Jan 27 23:45:52 2003
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27173.9 Hz
SCANS 200
ACQTM 1.206 sec
PD 1.794 sec
PWL 5.0 us
IRNUC 1H
CTEMP 26.2 c
SIVNT CD2CL
EXREF 53.80 ppm
BF 1.20 Hz
RGAIN 32



| | | | |
|-------|-------|------------|--|
| DF | COMNT | 245-mix | |
| | CONUC | 1H | |
| OFR | | 399.65 MHz | |
| OSSET | | 124.00 KHz | |
| OSFIN | | 10500.0 Hz | |
| PFW1 | | 8.5 us | |
| PM2 | | 10.0 us | |
| PM3 | | 10.0 us | |
| PI1 | | 1.000 ms | |
| PI2 | | 1.000 ms | |
| PI3 | | 1.00 ms | |
| LOOP1 | | 1 | |
| POINT | | 16384 | |
| SFO | | 16384 | |
| SCANS | | 16 | |
| DDMMY | | 1 | |
| FREQU | | 8000.0 Hz | |
| AQCTM | | 2.048 sec | |
| PD | | 2.952 sec | |
| | RGAIN | 13 | |
| BF | | 0.25 Hz | |
| EXMOD | NON | | |
| IRNUC | 1H | | |
| IFR | | 399.65 MHz | |
| IRSET | | 124.00 KHz | |
| IRFZN | | 10500.0 Hz | |
| IRRPW | | 50 us | |
| IRATN | | 511 | |
| CSFED | | 16 Hz | |
| CTEMP | | 26.9 C | |
| XT | | | |
| XS | | | |



C:\WINMR98\COMMON_DEFAULT.ALS
245-mix



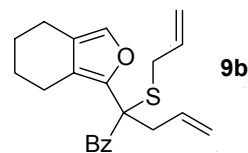
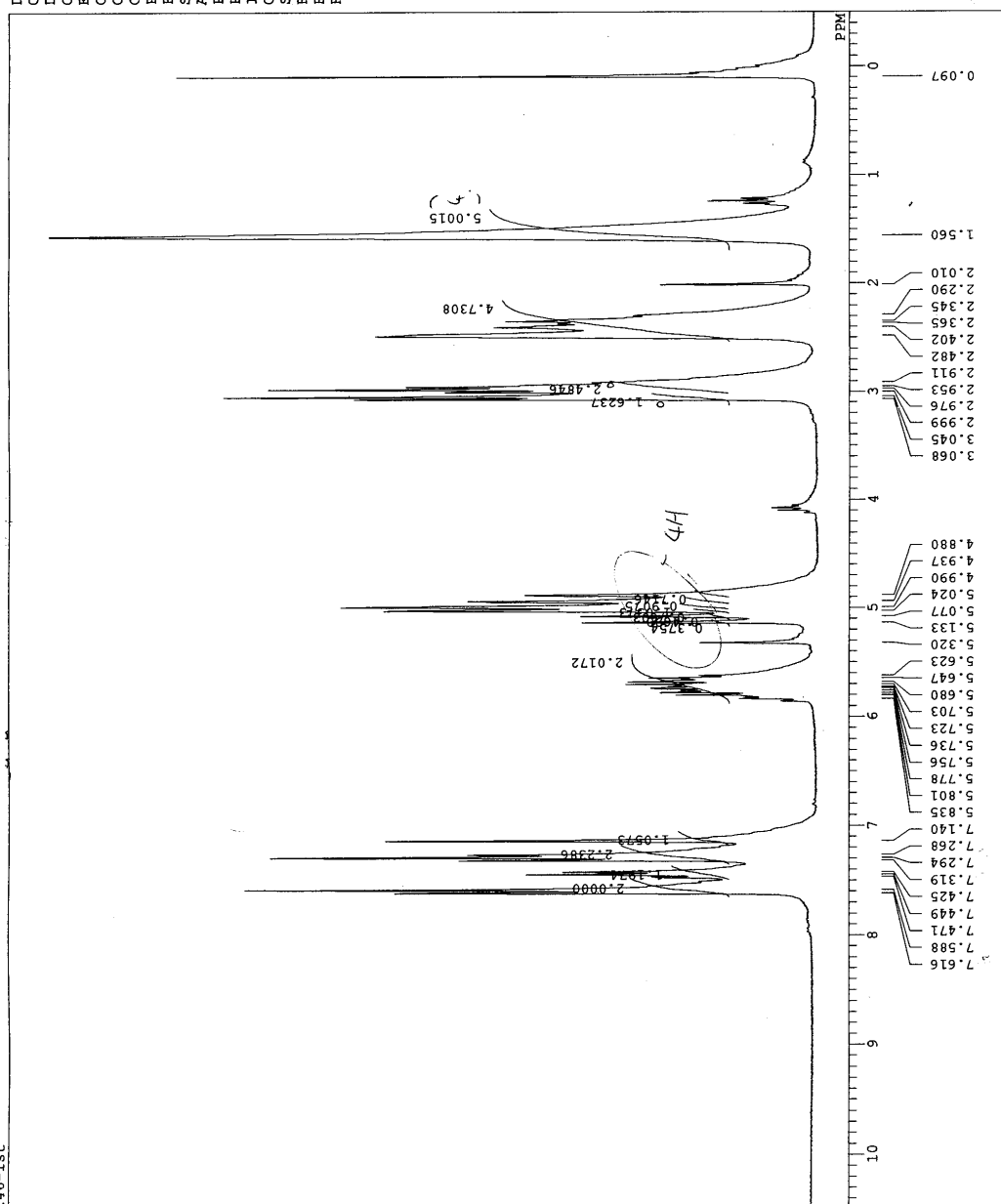
9a

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DFILE C:\WINMR98\COMMON\DEFAULT.ALS
COMMT 246-1st C6O2  $\Phi$   $\frac{13}{14}$ 
DATIM Thu Nov 07 16:45:14 2002

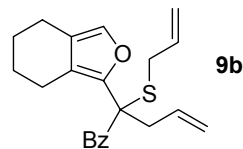
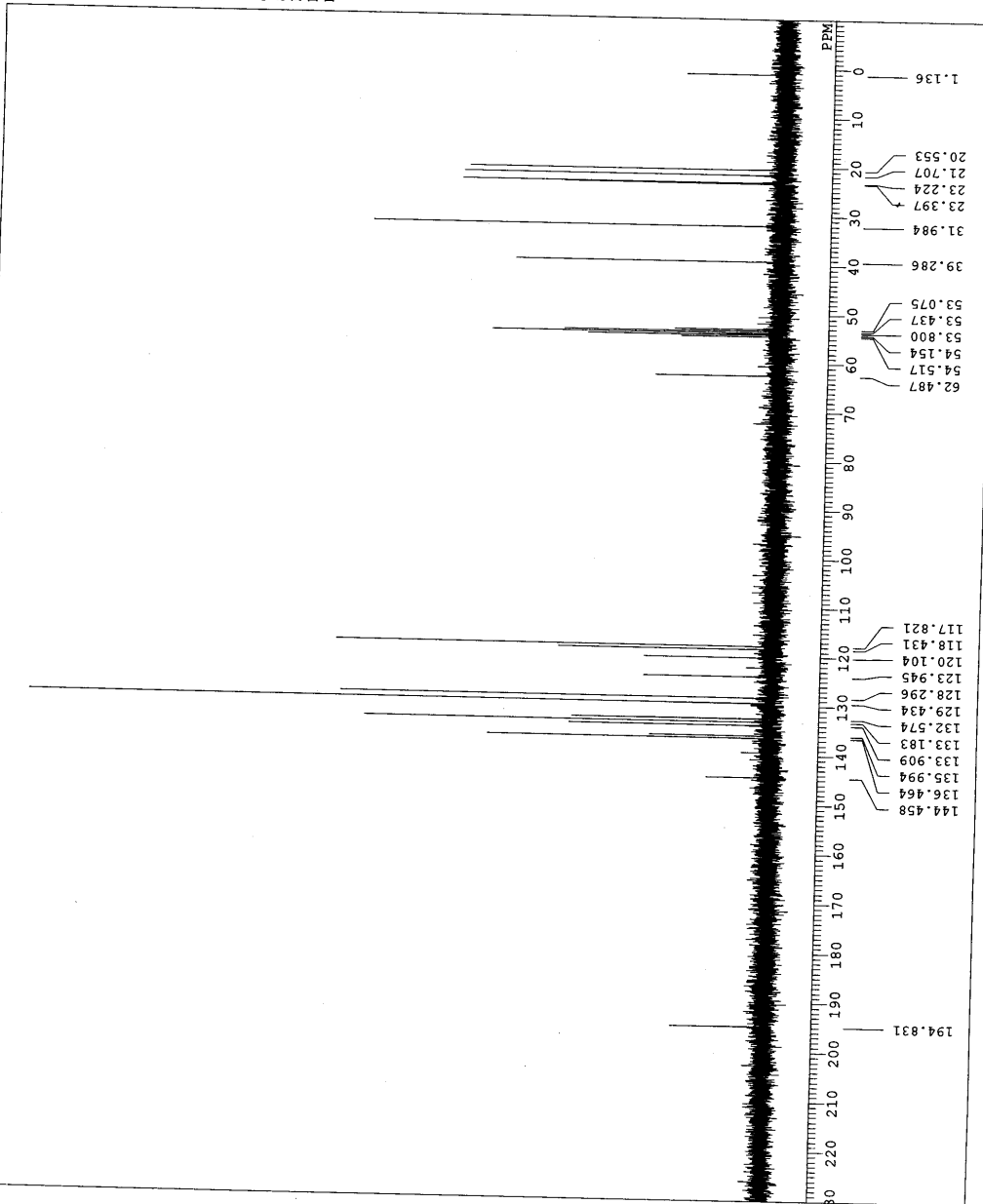
```

| OSNOC | IN | NON | 300.40 MHz |
|---------|----|--------|------------|
| OSBRQ | | | 130.00 KHz |
| OSBET | | | 1150.0 Hz |
| OSOFIN | | | 32768 |
| POPOINT | | | 6013.2 Hz |
| SCANS | | 16 | |
| ACQTM | | | 5.449 sec |
| PD | | | 1.551 sec |
| PR1 | 1H | | 5.7 us |
| IRNUC | | | 22.6 c |
| CTEMP | | CD2CL2 | |
| SIVNT | | | 5.32 ppm |
| EXREF | | | 0.10 Hz |
| BF | | | |
| RGAIN | | 13 | |



C:\WINNR98\COMMON_DEFAULT.ALS
246-1st

DEFILE C:\WINNR98\COMMON_DEFAULT.ALS
 COMNT 246-1st
 DATIM Thu Nov 07 17:26:40 2002
 OBNUC 13C
 EXMOD BCM
 OBFRQ 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQ 20408.1 Hz
 SCANS 104
 ACQTM 1.606 sec
 PD 1.394 sec
 PW 4.4 us
 IRNUC 1H
 CTEMP 23.0 C
 CD2CL2
 SLVNT
 EXREF 53.80 ppm
 BF 0.10 Hz
 RGAIN 24

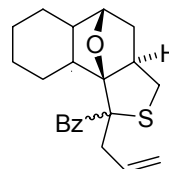
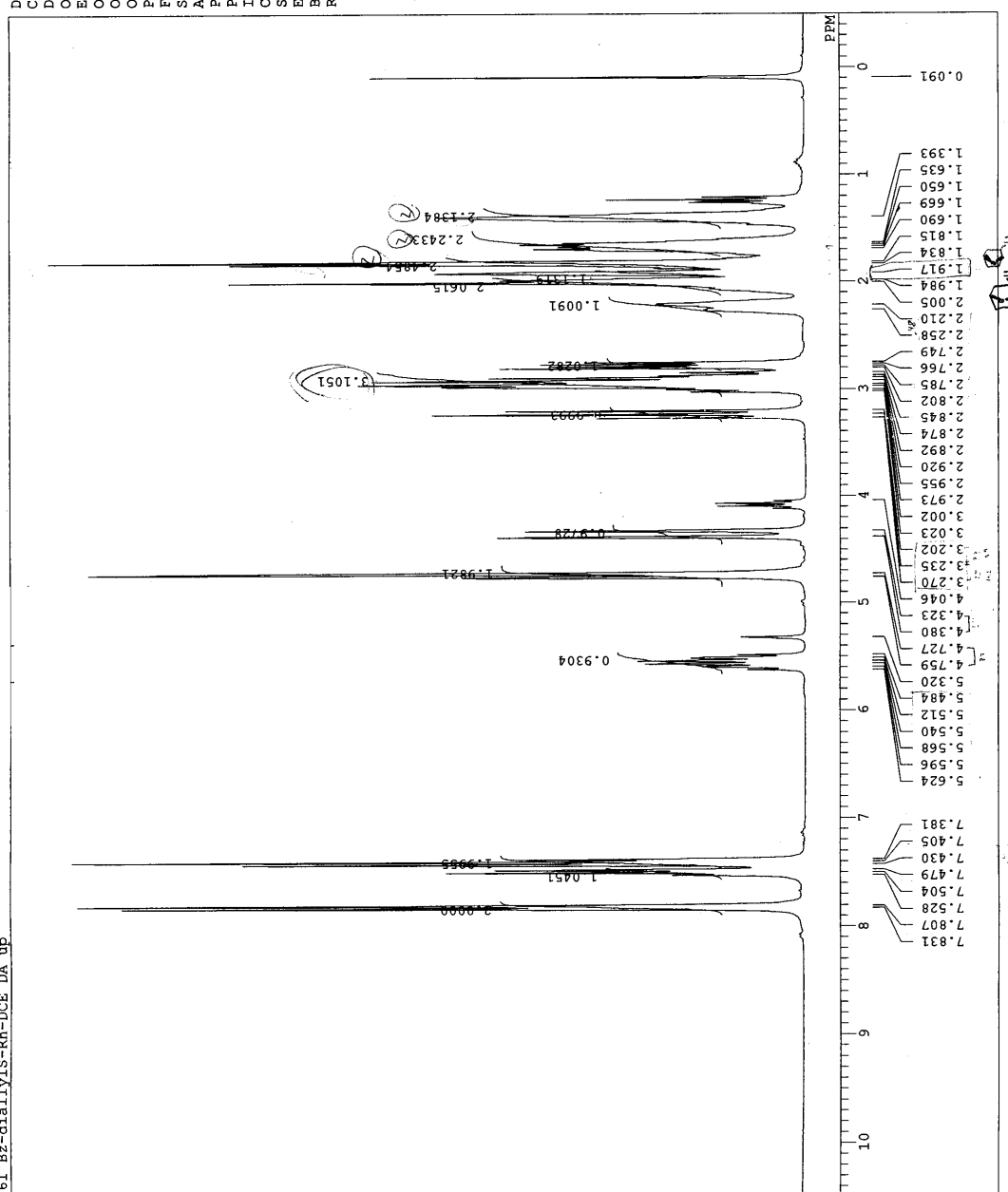


```

C:\WINMR98\COMMON\DEFAULT.ALS
261 Bz-diallyls-Rh-DCE DA up
DATIM Wed Dec 18 16:01:26 2002

```

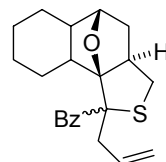
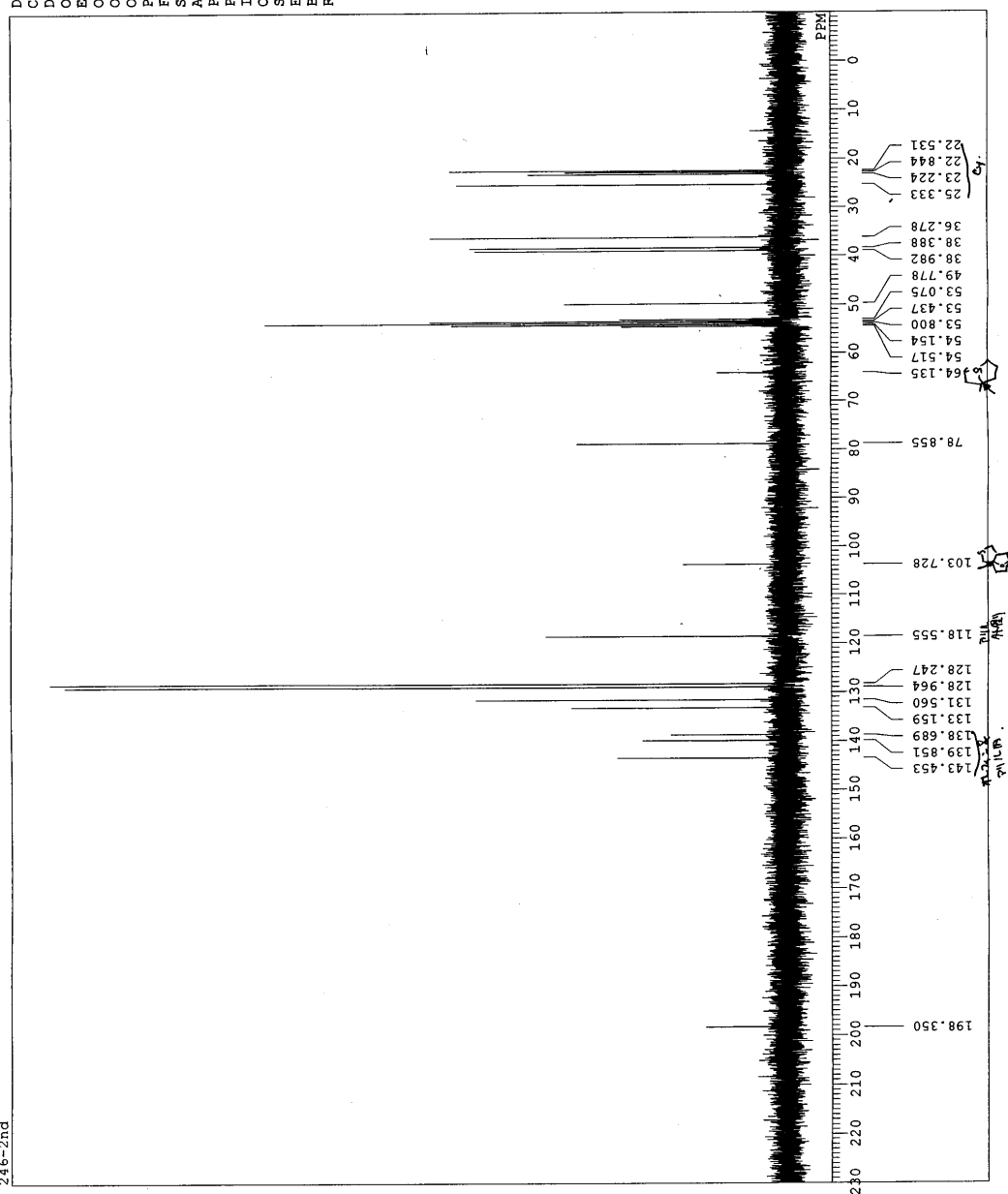
DFILE
 COMNT
 DATIM
 OBNUC
 EXMOD
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 SSCANS
 ACQTM
 PD
 PW1
 IRNUC
 CTEMP
 SLVNT
 EXREF
 BF
 RGAIN



10b-major

C:\WINNR98\COMMON_DEFAULT.ALS
246-2nd

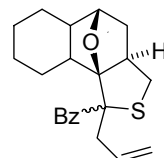
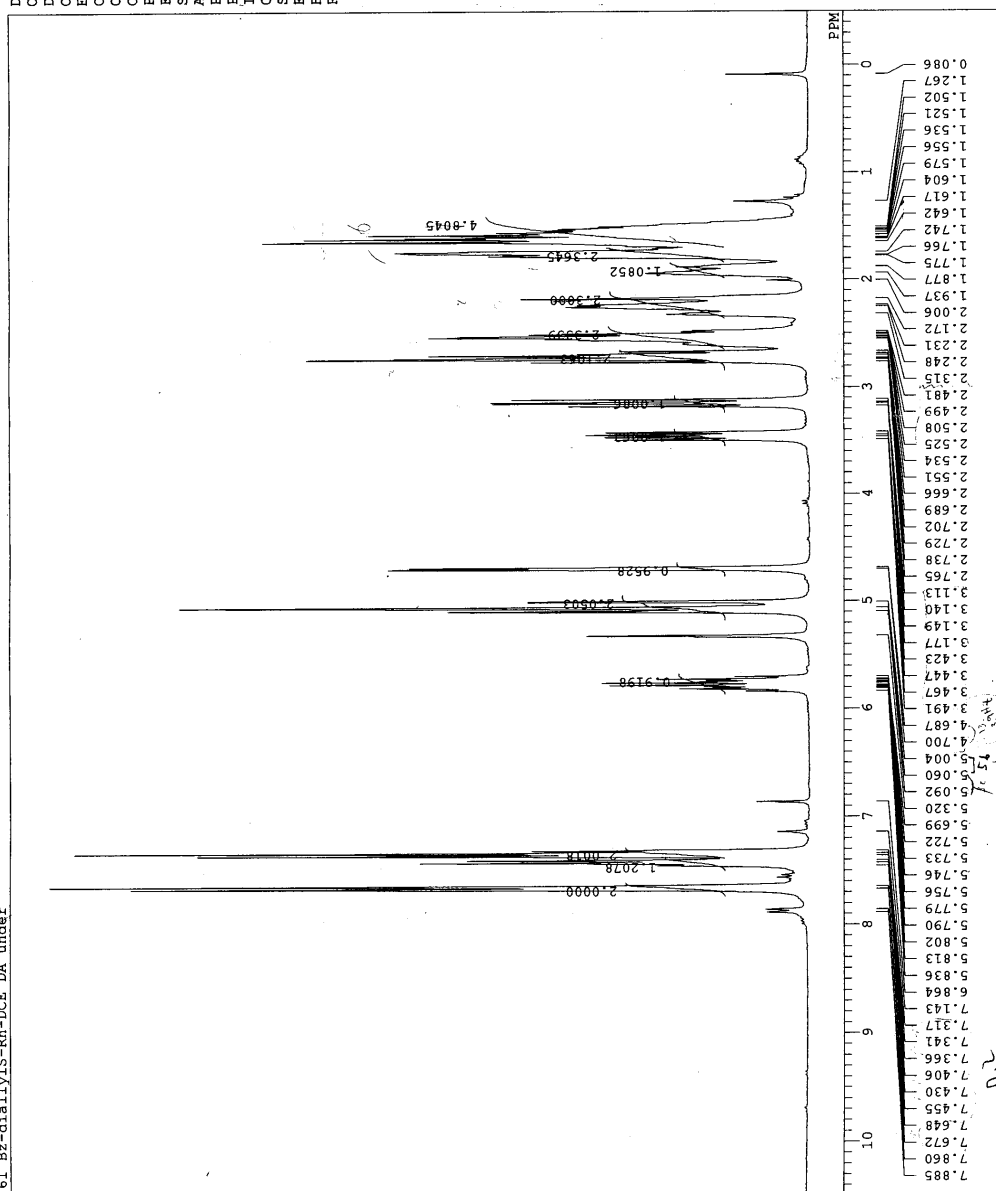
DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMMT 246-2nd
DATIM Thu Nov 07 17:16:06 2002
GENUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQ 20408.1 Hz
SCANS 231
ACQTM 1.606 sec
PD 1.394 sec
PW 4.4 us
IRNUC 1H
CTEMP 22.9 C
SIVNT CD2CL2
EXREF 53.80 ppm
BF 0.10 Hz
RGAIN 24



C:\WINNR98\COMMON\DEFAULT.ALS
261 Bz-diallyls-Rh-DCE DA under

C:\WINNR98\COMMON\DEFAULT.ALS
261 Bz-diallyls-Rh-DCE DA under
DATIM Wed Dec 18 16:11:08 2002

OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.7 us
IRNUC 1H
CTEMP 22.3 C
SOLNT CD2CL2
EXREF 5.32 ppm
BF 1.20 Hz
RGAIN 17

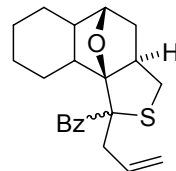
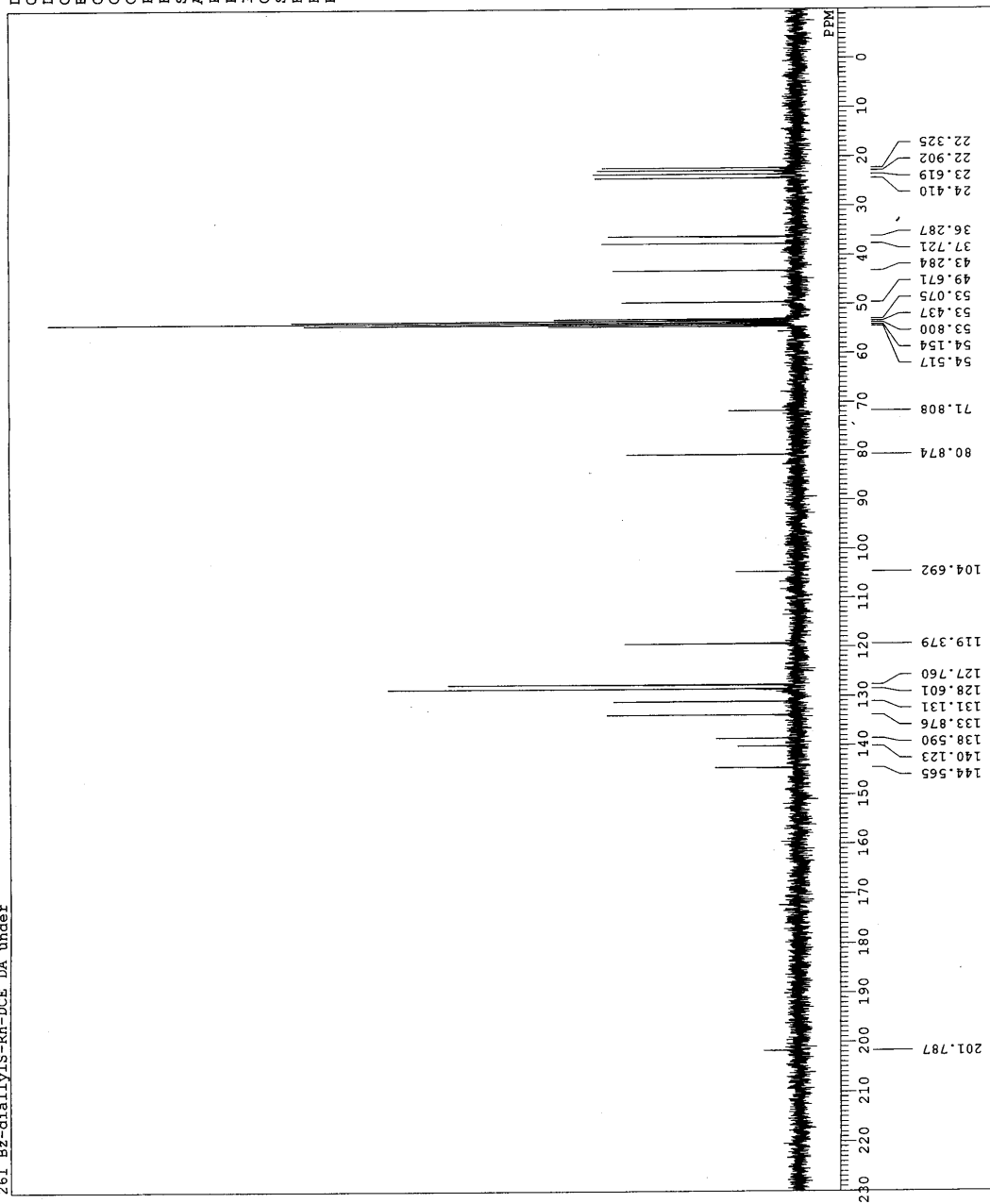


10b-minor

C:\WINNR98\COMMON\DEFAULT.ALS
261 Bz-diallyls-Rh-DCE DA under

DFILE C:\WINNR98\COMMON\DEFAULT.ALS
COMNT 261 Bz-diallyls-Rh-DCE DA under
DATIM Wed Dec 18 16:30:43 2002

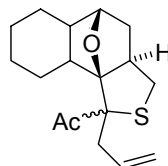
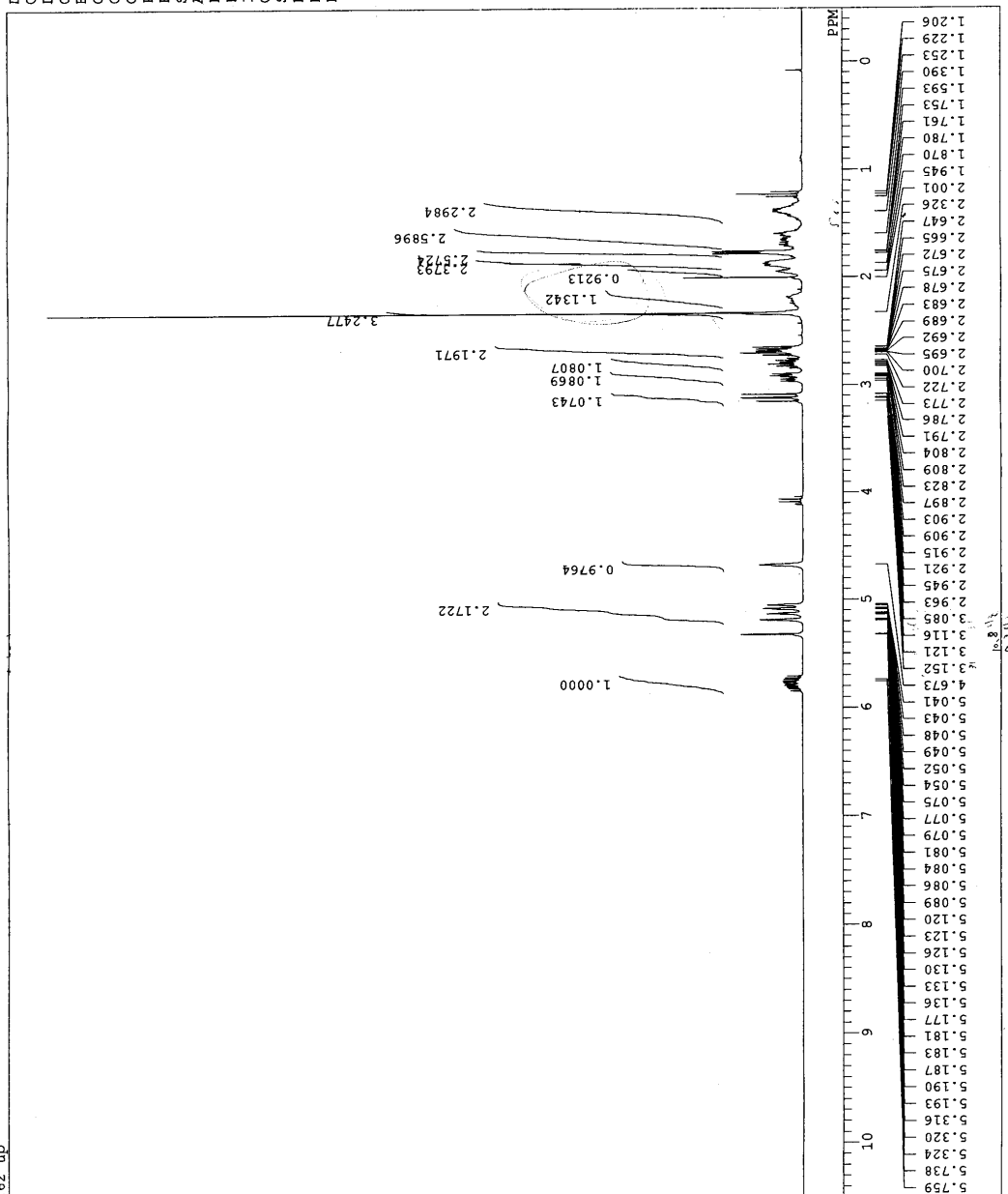
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQ 20408.1 Hz
SCANS 300
ACQTM 1.606 sec
PD 1.394 sec
F1 4.4 us
IRNUC 1H
CTEMP 23.3 C
SIVNT CD2CL2
EXREF 53.80 ppm
BF 1.20 Hz
RGAIN 24



10b-minor

C:\WINMR98\COMMON_DEFAULT.ALS
262 up

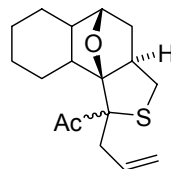
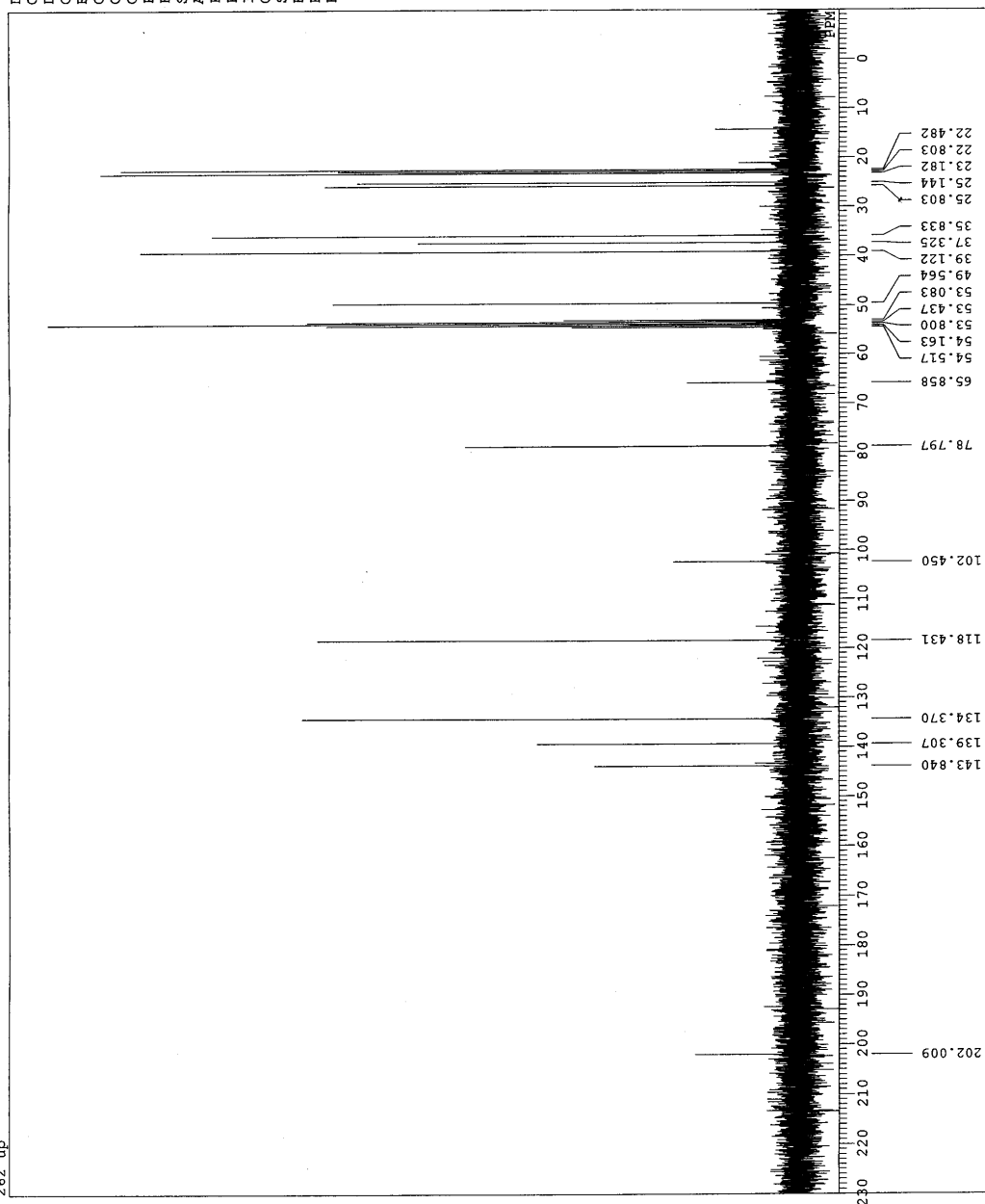
C:\WINMR98\COMMON_DEFAULT.ALS
262 up
DATIM Mon Dec 16 18:51:17 2002
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.7 us
IRNUC 1H
CTEMP 22.7 c
SIVNT CD2CL2
EXREF 5.32 ppm
BF 0.12 Hz
RGAIN 15



10c-major

C:\WINNMR98\COMMON_DEFAULT.ALS
262 up

DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
 COMMT 262 up
 DATIM Mon Dec 16 19:10:02 2002
 QBNUC 13C
 EXMOD BCM
 OBFRQ 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 200
 ACQTM 1.606 sec
 PD 1.394 sec
 PUL 4.4 us
 1H
 IRRUC 23.4 c
 CD2CL2
 SLVNT
 EXREF 53.80 ppm
 BF 0.12 Hz
 RGAIN 24

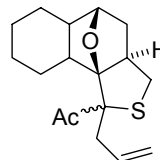


10c-major

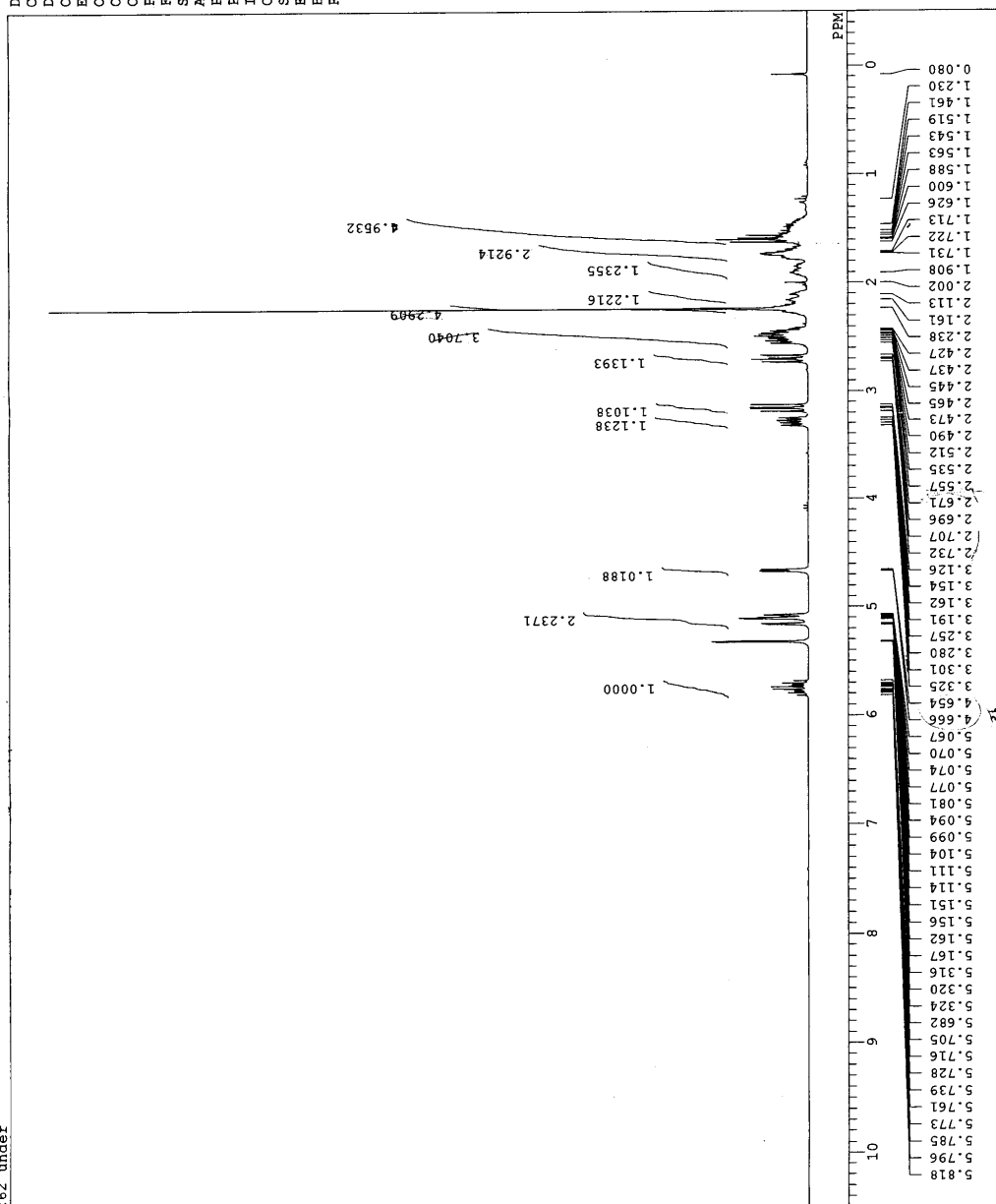
C:\WINNR98\COMMON\DEFAULT.ALS
262 under

DFILE C:\WINNR98\COMMON\DEFAULT.ALS
COMNT 262 under
DATIM Mon Dec 16 18:25:27 2002
EXMOD 1H
EXMOD NON

OSFRQ 300.40 MHz
OSSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
PWL 5.7 us
IRNUC 1H
CTEMP 22.2 C
SLVNT CD2CL2
EXREF 5.32 ppm
BF 0.12 Hz
RGAIN 15

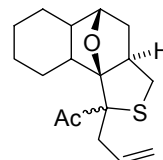
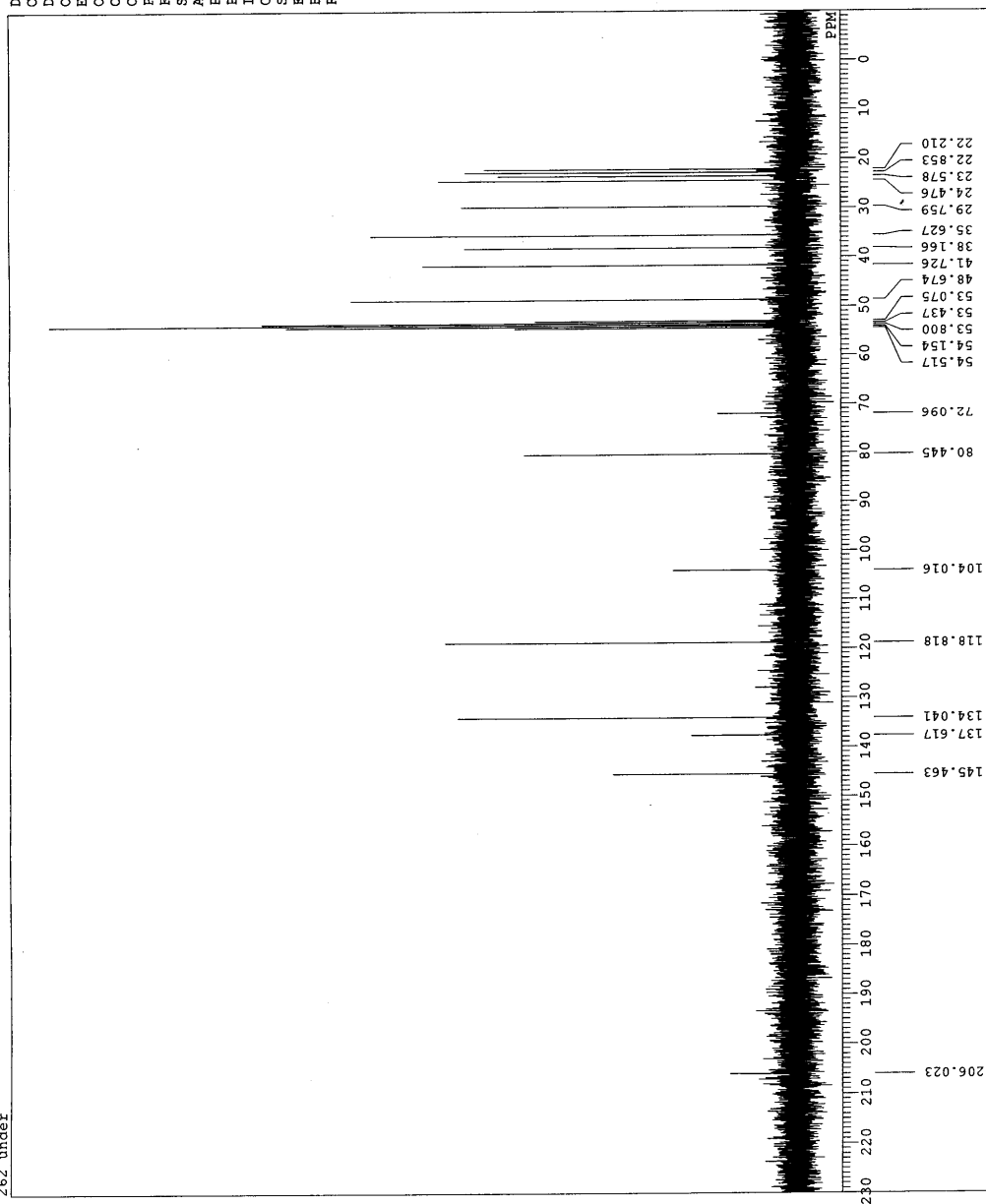


10c-minor



C:\WINNR98\COMMON_DEFAULT.ALS
262 under

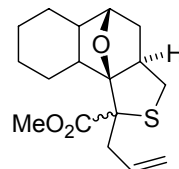
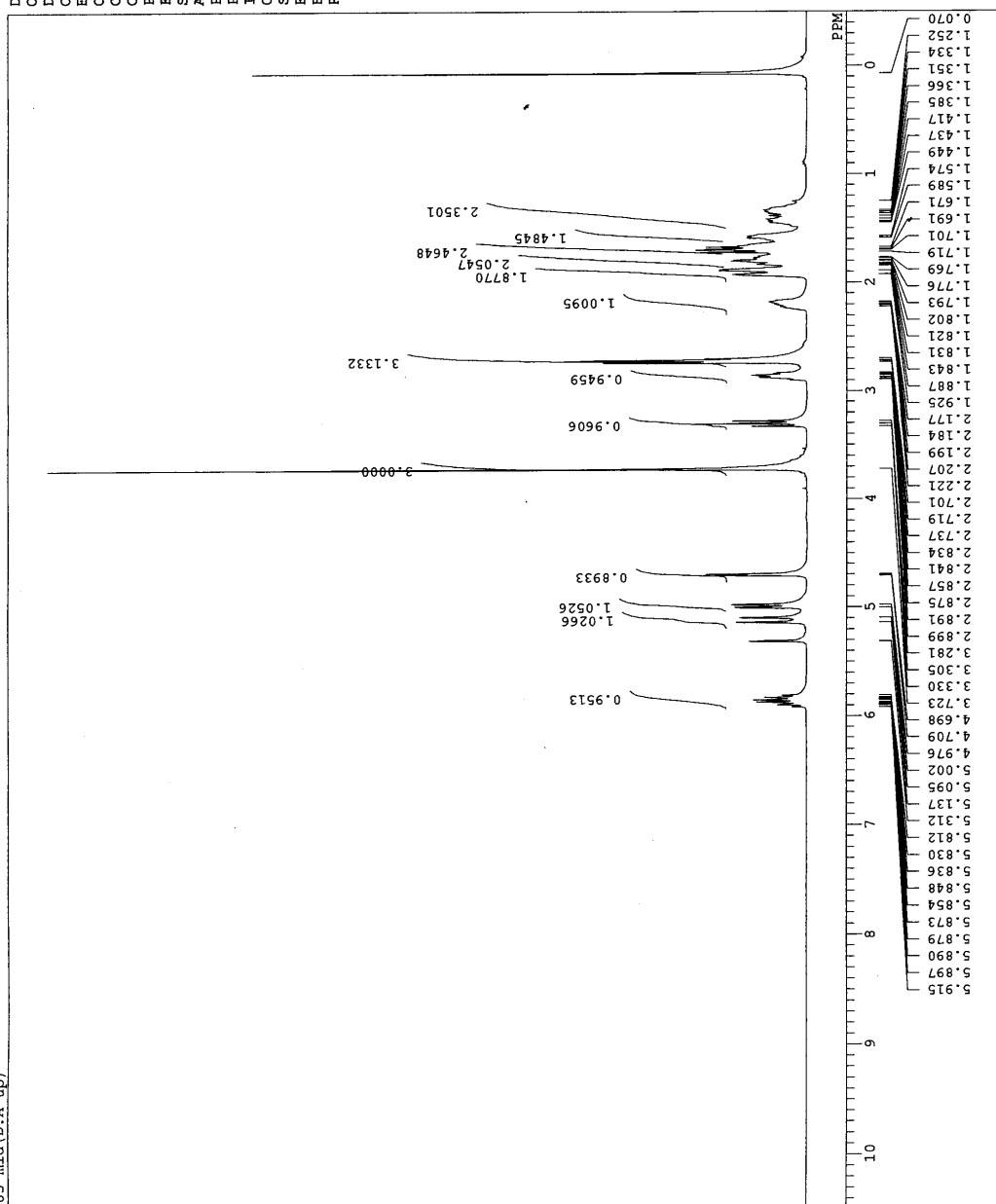
C:\WINNR98\COMMON_DEFAULT.ALS
COMNT 262 under
DATIM Mon Dec 16 18:43:39 2002
OBNUC 13C
EXMOD BCM
OBFREQ 75.45 MHz
OBSFQ 124.00 KHz
OBSFQ 1840.0 Hz
POINT 32768
FREQ 20408.1 Hz
SCANS 250
ACQTM 1.606 sec
PD 1.394 sec
FWD 4.4 us
IRNUC 1H
CTEMP 22.9 c
SLVNT CD2CL2
EXREF 53.80 ppm
BF 0.12 Hz
RGAIN 24



10c-minor

C:\WINNR98\COMMON_DEFAULT.ALS
283-mid(D.A up)

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT 283-mid(D.A up)
DATIM Mon Feb 17 11:45:52 2003
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 2.952 sec
PWL 5.4 us
IRNUC 1H
CTEMP 24.3 C
CD2CL
SIVNT 0.07 ppm
EXREF BF
RGAIN 14

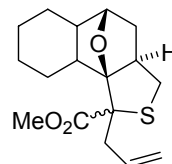
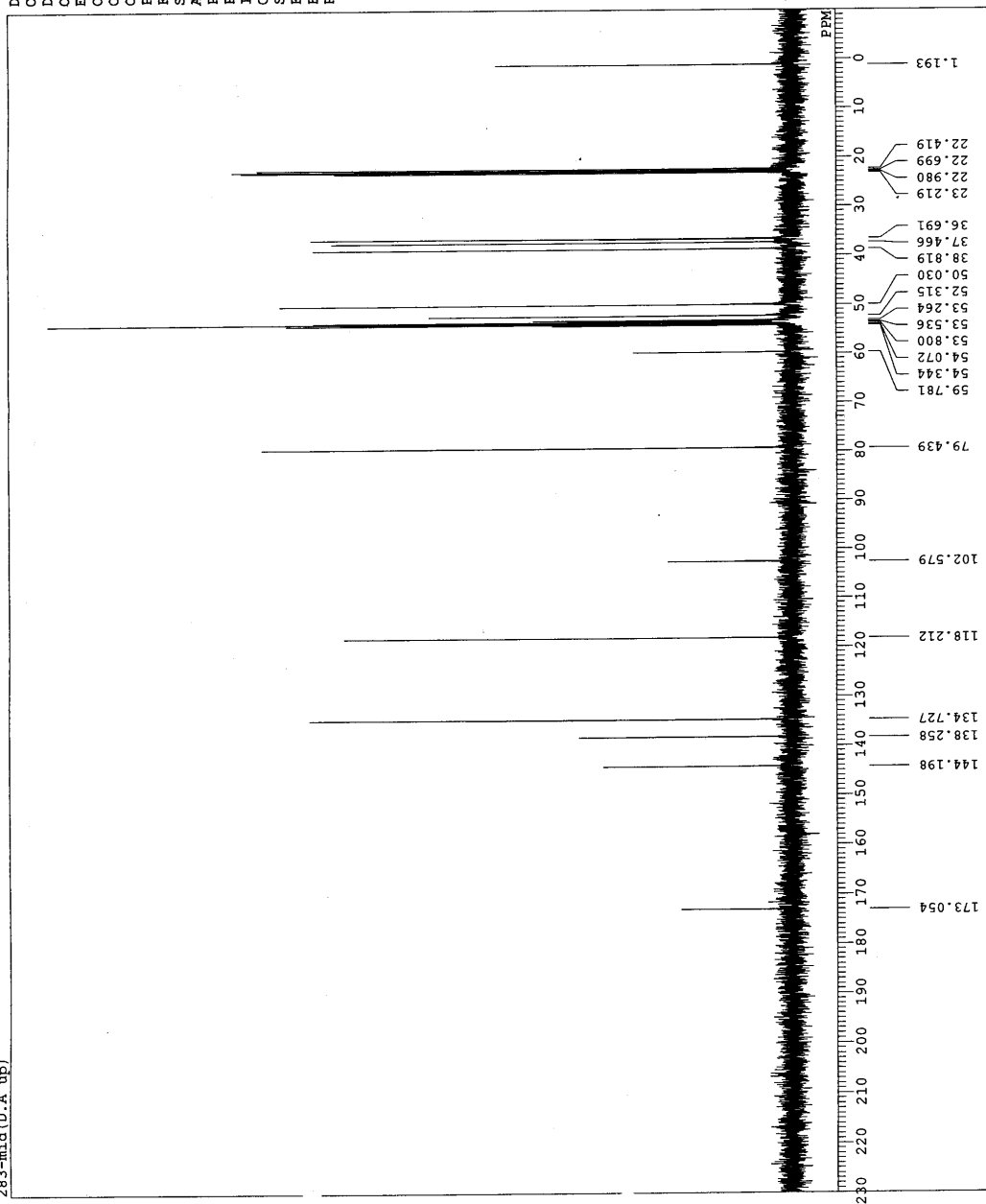


10d-major

C:\WINNR98\COMMON_DEFAULT.ALS
283-mid (D.A up)

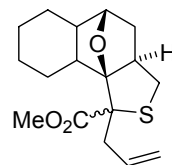
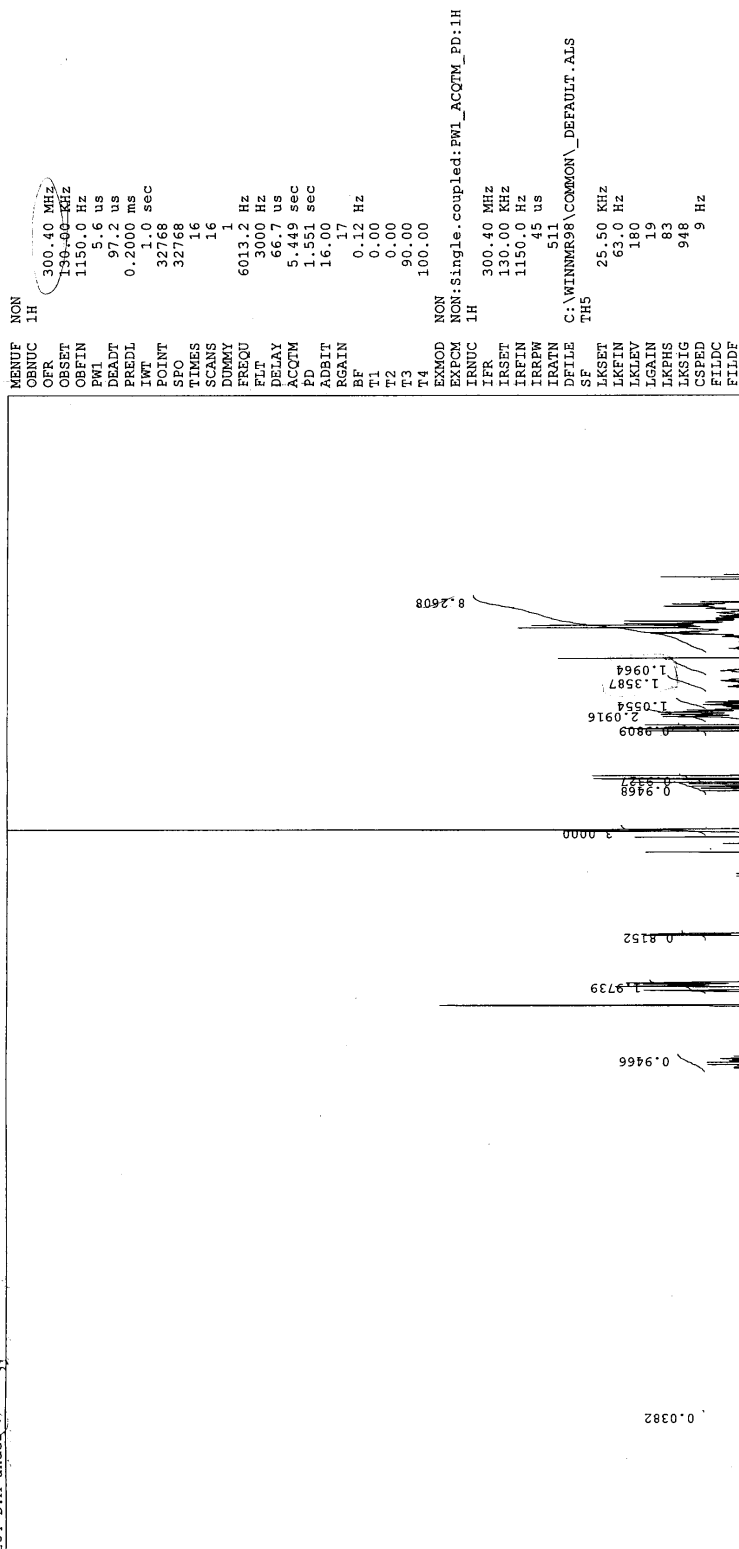
DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT 283-mid (D.A up)
DATIM Mon Feb 17 11:57:38 2003

OSNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQ 27173.9 Hz
SCANS 130
ACQTM 1.206 sec
PD 1.794 sec
F1 5.0 us
IRNUC 1H
CTEMP 25.1 c
SIVNT CD2CL
EXREF 53.80 dpm
BF 1.00 Hz
RGAIN 33



10d-major

C:\WINNR98\COMMON_DEFAULT.ALS
284-D.A under



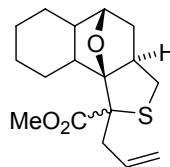
10d-minor

C:\WINNR98\COMMON_DEFAULT.ALS
284-D.A under

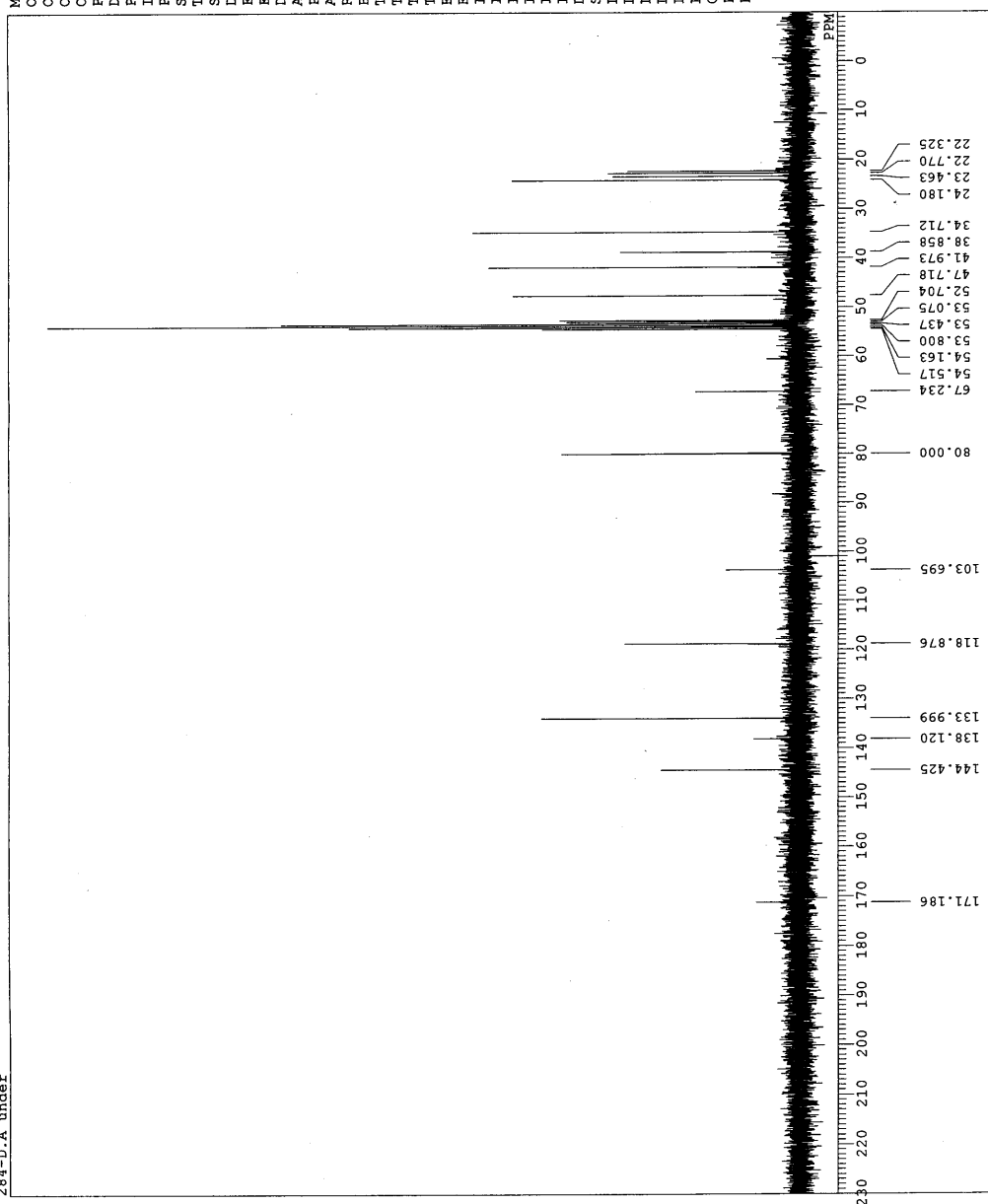
```

MENUF BCM
OBNUC 13C
OPR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
PWL 4.5 us
DEADT 27.2 us
FREDL 0.2000 ms
IWT 1.0 sec
POINT 32768
SPO 32768
TIMES 5000
SCANS 350
DUMMY 1
FREQ 20408.1 Hz
FLT 10200 Hz
DELAY 19.6 us
ACQTM 1.606 sec
PD 1.394 sec
ADBIT 16.00
RGAIN 24
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD BCM
EXFCM Bilevel.complete.decoupling.set_ir
IRNUC 1H
IFR 300.40 MHz
IRSET 130.00 KHz
IRFIN 1150.0 Hz
IRREW 45 us
IRATN 511
DFILE C:\WINNR98\COMMON\_DEFAULT.ALS
SF TH5
LKSET 25.50 KHz
LKFIN 63.0 Hz
LKLEV 180
LGAIN 19
LKPHS 83
LKSIG 929
CSPED 8 Hz
FILDC
FILDF

```



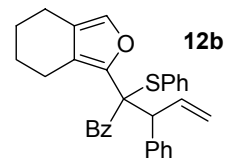
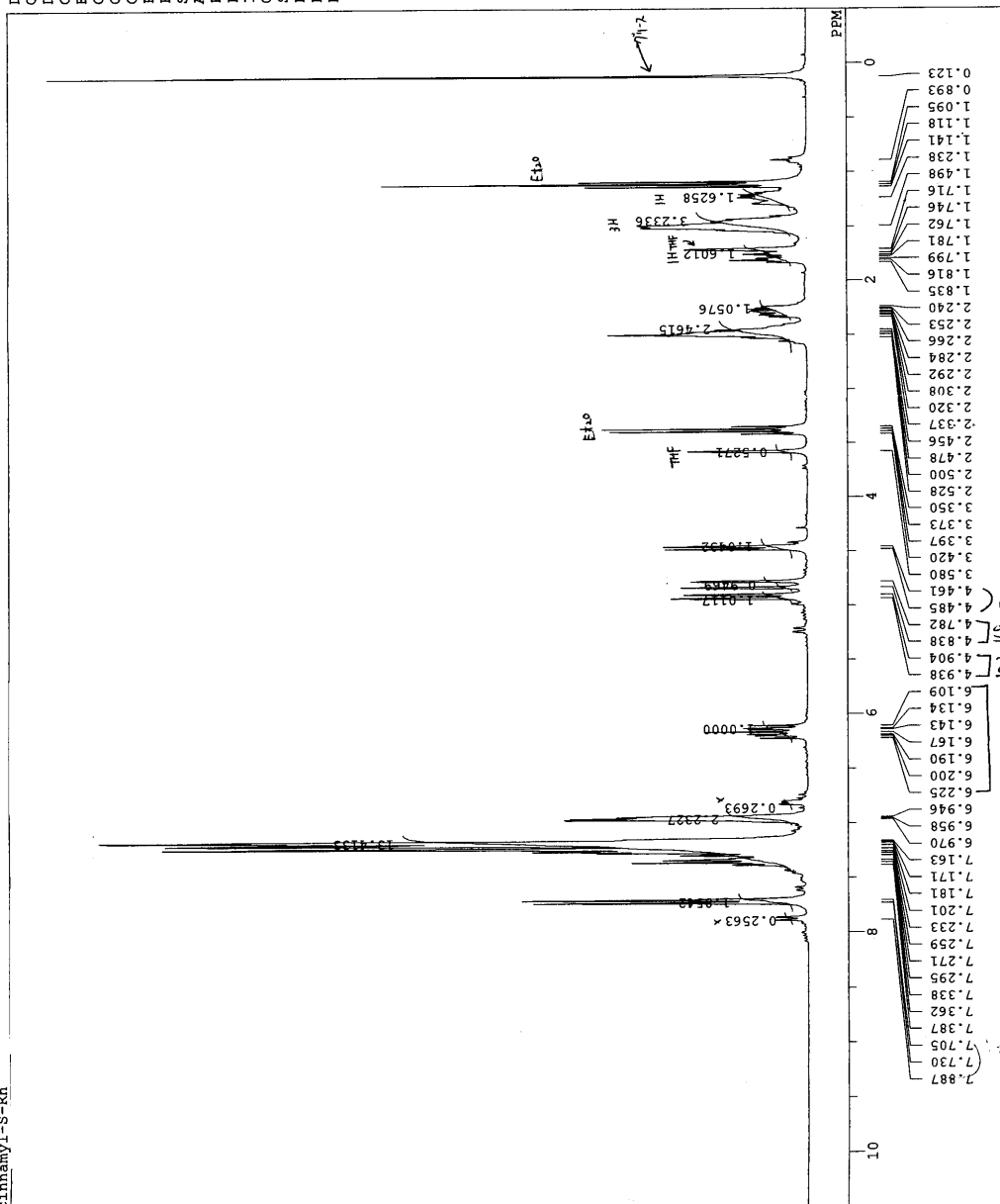
10d-minor



C:\WINNMR98\COMMON\DEFAULT.ALS
cinnamyl-S-Rh

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBPRO
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

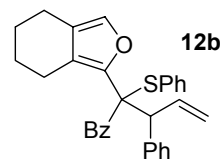
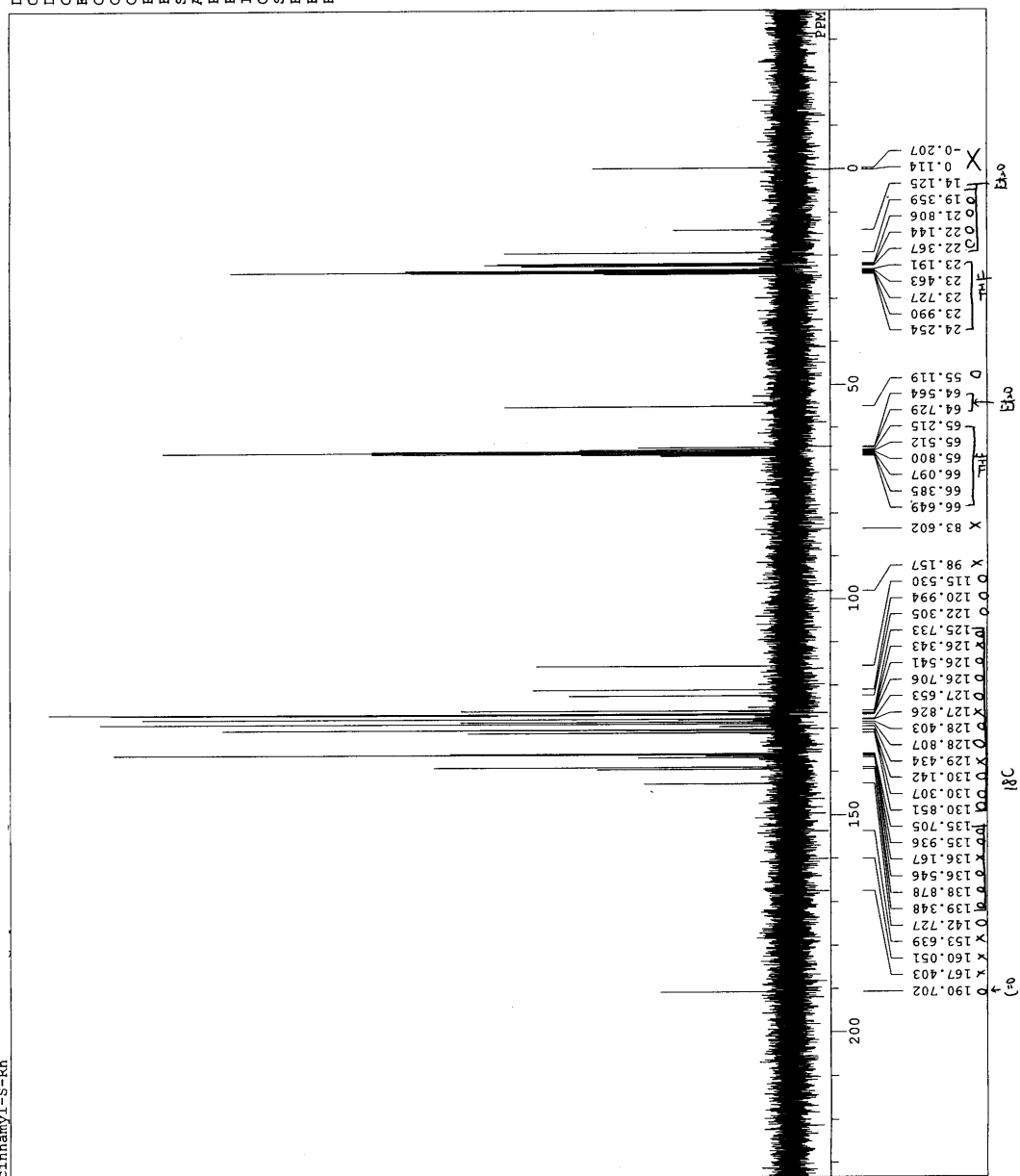
C:\WINNMR98\COMMON\DEFAULT.ALS
cinnamyl-S-Rh
Fri Mar 22 23:12:27 2002
1H
NON
300.40 MHz
130.00 KHz
1150.0 Hz
32768
6013.2 Hz
8
5.449 sec
1.551 sec
5.7 us
1H
23.3 c
C4D8O2
3.58 ppm
0.12 Hz
11



C:\WINNR98\COMMON_DEFAULT.ALS
cinnamyl-S-Rh

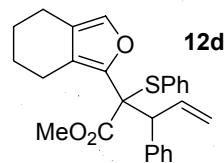
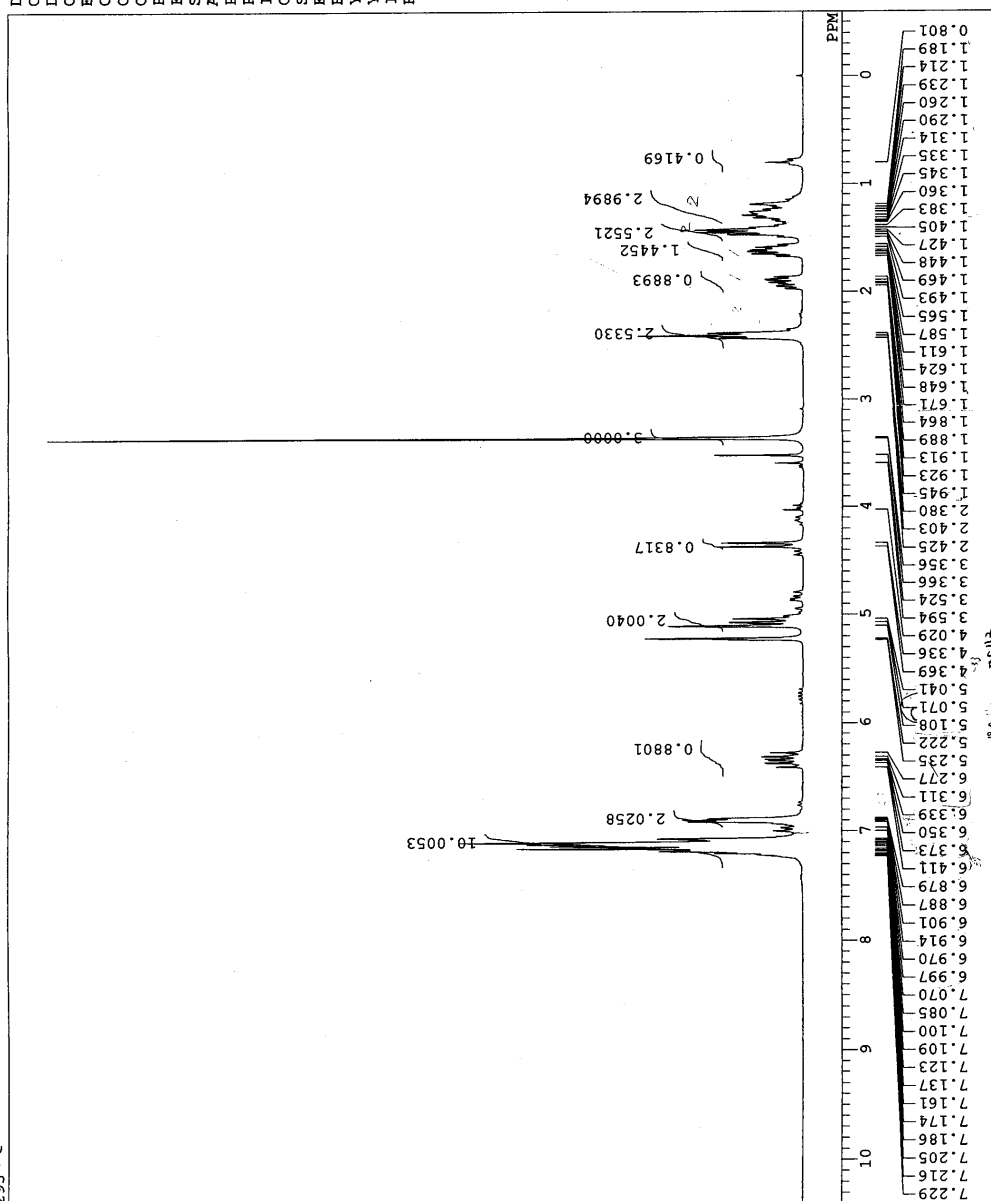
D:\FILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT cinnamyl-S-Rh
DATIM Fri Mar 22 23:07:18 2002
OBNUC 13C
EXMOD BCM

OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 56
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.3 us
IRNUC 1H
CTEMP 23.3 C
SIUNT C4D802
EXREF 65.80 ppm
BF 0.12 Hz
RGAIN 23



C:\WINMR98\COMMON_DEFAULT.ALS
293 -L

DFILE C:\WINMR98\COMMON_DEFAULT.AL
CONNT 293
DATIM Tue Mar 11 19:23:49 2003
OENUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 16384
FREQU 5402.4 Hz
SCANS 16
ACQTM 3.033 sec
PD 2.000 sec
PW1 5.6 us
IRNUC 1H
CTEMP 28.3 c
SLVNT CD2CL
EXREF 0.00 ppm
BF 1.00 Hz
YG
IG
RGAIN 20



C:\WINNMR98\COMMON_DEFAULT.ALS
293

DFILE C:\WINNMR98\COMMON_DEFAULT.ALS

COMNT 293
DATIM Tue Mar 11 19:51:30 2003

OBNUC 13C
EXMOD BCM

OBFRQ 67.80 MHz
OBSET 135.00 KHz

OBFIN 5200.0 Hz
POINT 32768

FREQU 18315.0 Hz
SCANS 499

ACQTM 1.789 sec
PD 1.211 sec

PW1 4.2 us
IRNUC 1H

CTEMP 29.4 c
SLVNT CD2CL

EXREF 53.80 ppm
BF 1.00 Hz

YG
IG

RGAIN 29

