

Supporting Information

Highly Stereoselective Intramolecular Michael Addition Using α -Sulfinyl Vinylolithium as an Unprecedented Michael Donor

Naoyoshi Maezaki, Sachiko Yuyama, Hiroaki Sawamoto, Tomoko Suzuki, Mayuko Izumi, and Tetsuaki Tanaka*

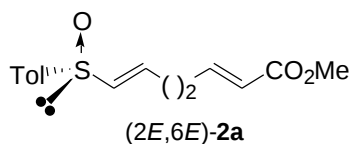
Graduate School of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565-0871, Japan

General Methods. Optical rotations were measured using a JASCO DIP-360 digital polarimeter. ^1H -NMR spectra were recorded in a CDCl_3 solution using a JEOL JNM-LA-500 (500 MHz) spectrometer. ^{13}C -NMR spectra were recorded in a CDCl_3 solution using a JEOL JNM-EX270 (68 MHz) spectrometer, a JEOL JNM-AL300 (75 MHz) spectrometer, or a JEOL JNM-LA-500 (125 MHz). IR absorption spectra (FT: diffuse reflectance spectroscopy) were recorded with KBr powder using a Horiba FT-210 IR spectrometer, and only noteworthy absorptions (cm^{-1}) are listed. Mass spectra were taken with a Shimadzu QP-1000 mass spectrometer and a JEOL JMS-D300 mass spectrometer. High resolution mass spectra were measured by a JEOL JMS-D300 or a JEOL JMS-600. Column chromatography was carried out using Merck silica gel 60 (70–230 mesh). All air- or moisture-sensitive reactions were carried out in flame-dried glassware under an atmosphere of Ar or N_2 . All solvents were dried and distilled according to standard procedures. All organic extracts were dried over anhydrous MgSO_4 , filtered, and concentrated with a rotary evaporator under reduced pressure.

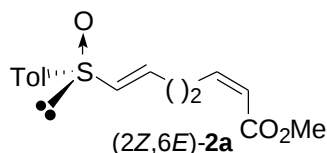


(R)-[(E)-5-(Tetrahydro-2H-pyran-2-yloxy)-1-pentenyl] p-Tolyl Sulfoxide [(E)-1] and (R)-[(Z)-5-(Tetrahydro-2H-pyran-2-yloxy)-1-pentenyl] p-Tolyl Sulfoxide [(Z)-1] (E)-1: $[\alpha]^{26}_{\text{D}} +93.0$ (c 0.85, CHCl_3). ^1H NMR δ : 1.48–1.83 (8H, m), 2.30–2.36 (2H, m), 2.40 (3H, s), 3.37–3.41 (1H, m), 3.45–3.49 (1H, m), 3.72–3.77 (1H, dt, $J=9.8, 6.7$ Hz), 3.79–3.84 (1H, m), 4.52–4.54 (1H, m), 6.24 (1H, d, $J=15.3$ Hz), 6.24 (1H, dt, $J=15.3, 6.7$ Hz), 7.30 (2H, d, $J=7.9$ Hz), 7.50 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 19.5, 21.3, 25.3, 28.1, 28.7 (1/2C), 28.7 (1/2C), 30.5, 62.2, 66.2 (1/2C), 66.2 (1/2C), 98.8, 124.4, 129.9 (2C), 135.3 (2C), 139.9 (1/2C), 139.9 (1/2C), 140.8, 141.2. IR 1082, 1036. MS (EI) m/z (%): 292 (M^+ , 8.4), 207 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{S}$: C, 66.20; H, 7.84; S, 10.39. Found: C, 66.39; H, 7.77; S, 10.25. (Z)-1: $[\alpha]^{26}_{\text{D}} -231.0$ (c 0.84, CHCl_3). ^1H NMR δ : 1.52–1.86 (8H, m), 2.40 (3H, s), 2.61–2.80 (2H, m), 3.43–3.52 (2H, m), 3.79–3.89 (2H, m), 4.59–4.60 (1H, m), 6.17–6.24 (2H, m), 7.30 (2H, d, $J=7.9$ Hz), 7.51 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 19.4 (1/2C), 19.5 (1/2C), 21.1,

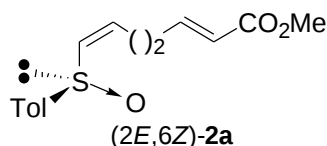
25.2, 26.0 (1/2C), 26.1 (1/2C), 28.8 (1/2C), 29.0 (1/2C), 30.4 (1/2C), 30.5 (1/2C), 62.1 (1/2C), 62.3 (1/2C), 66.0 (1/2C), 66.2 (1/2C), 98.7 (1/2C), 98.8 (1/2C), 123.8 (2C), 129.7 (2C), 137.1 (1/2C), 137.2 (1/2C), 140.9, 141.0, 141.2. IR 1082, 1036. MS (EI) m/z (%): 292 (M^+ , 8.4), 207 (100). Anal. Calcd for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84; S, 10.39. Found: C, 66.41; H, 7.83; S, 10.28.



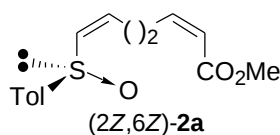
Methyl (2E,6E)-7-[(R)-(p-Tolylsulfinyl)]-2,6-heptadienoate [(2E,6E)-2a] $[\alpha]^{26}_D +115.1$ (c 0.85, $CHCl_3$). 1H NMR δ : 2.36–2.43 (7H, m, Ar-CH₃), 3.72 (3H, s), 5.84 (1H, d, $J=15.3$ Hz), 6.25 (1H, d, $J=15.3$ Hz), 6.56 (1H, dt, $J=15.3$, 6.7 Hz), 6.90 (1H, dt, $J=15.3$, 6.7 Hz), 7.31 (2H, d, $J=7.9$ Hz), 7.49 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 21.3, 30.0, 30.4, 51.4, 122.0, 124.5, 129.9 (2C), 136.0 (2C), 137.6, 140.5, 141.5, 146.8, 166.5. IR 1720, 1084, 1043. MS (EI) m/z (%): 278 (M^+ , 8.8), 230 (100). HRMS (EI) Calcd $C_{15}H_{18}O_3S$ (M^+): 278.0976. Found: 278.0971.



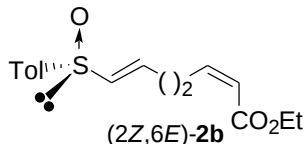
Methyl (2Z,6E)-7-[(R)-(p-Tolylsulfinyl)]-2,6-heptadienoate [(2Z,6E)-2a] $[\alpha]^{26}_D +83.9$ (c 0.81, $CHCl_3$). 1H NMR δ : 2.37–2.41 (5H, m), 2.84 (2H, dt, $J=6.7$, 1.8 Hz), 3.70 (3H, s), 5.81 (1H, dt, $J=11.6$, 1.8 Hz), 6.17 (1H, dt, $J=11.6$, 1.8 Hz), 6.27 (1H, dt, $J=15.3$, 1.8 Hz), 6.59 (1H, dt, $J=15.3$, 6.7 Hz), 7.31 (2H, d, $J=7.9$ Hz), 7.49 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 21.3, 27.2, 31.0, 51.1, 120.5, 124.5 (2C), 129.9 (2C), 135.8, 138.6, 140.7, 141.1, 148.0, 166.4. IR 1720, 1045. MS (EI) m/z (%): 278 (M^+ , 10), 230 (100). Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52; S, 11.52. Found: C, 64.74; H, 6.55; S, 11.32.



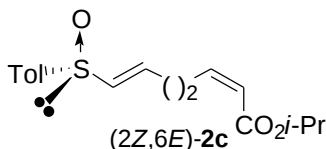
Methyl (2E,6Z)-7-[(R)-(p-Tolylsulfinyl)]-2,6-heptadienoate [(2E,6Z)-2a] $[\alpha]^{26}_D -224.2$ (c 0.55, $CHCl_3$). 1H NMR δ : 2.32 (3H, m), 2.30–2.40 (2H, m), 2.60–2.66 (1H, m), 2.70–2.76 (1H, m), 3.66 (3H, s), 5.82 (1H, dt, $J=15.9$, 1.8 Hz), 6.06 (1H, dt, $J=9.8$, 7.9 Hz), 6.19 (1H, dt, $J=9.8$, 1.2 Hz), 6.90 (1H, dt, $J=15.9$, 6.7 Hz), 7.23 (2H, d, $J=7.9$ Hz), 7.41 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 21.3, 27.6, 31.3, 51.4, 122.3, 124.0 (2C), 130.0 (2C), 135.8, 138.6, 140.7, 141.3, 146.6, 166.5. IR 1720, 1038. MS (EI) m/z (%): 278 (M^+ , 2.0), 261 (100). Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52; S, 11.52. Found: C, 64.67; H, 6.55; S, 11.43.



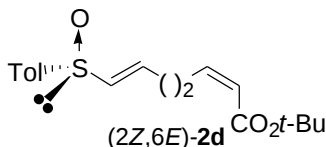
Methyl (2Z,6Z)-7-[(R)-(p-Tolylsulfinyl)]-2,6-heptadienoate [(2Z,6Z)-2a] $[\alpha]^{26}_D -221.1$ (c 0.49, CHCl_3). ^1H NMR δ : 2.41 (3H, s), 2.69–2.94 (4H, m), 3.72 (3H, s), 5.88 (1H, dt, $J=11.0, 1.8$ Hz), 6.16–6.28 (3H, m), 7.32 (2H, d, $J=7.9$ Hz), 7.51 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 21.3, 27.9, 28.6, 51.1, 120.8, 124.1 (2C), 130.0 (2C), 137.7, 140.2, 141.0, 141.2, 147.6, 166.4. IR 1720, 1039. MS (EI) m/z (%): 278 (M^+ , 2.3), 201 (100). HRMS (EI) Calcd $\text{C}_{15}\text{H}_{18}\text{O}_3\text{S}$ (M^+): 278.0976. Found: 278.0950.



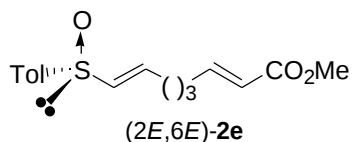
Ethyl (2Z,6E)-7-[(R)-(p-Tolylsulfinyl)]-2,6-heptadienoate [(2Z,6E)-2b] $[\alpha]^{25}_D +70.4$ (c 3.15, CHCl_3). ^1H NMR δ : 1.28 (3H, t, $J=7.3$ Hz), 2.37–2.41 (5H, m), 2.84 (2H, dq, $J=7.3, 1.8$ Hz), 4.16 (2H, q, $J=7.3$ Hz), 5.80 (1H, dt, $J=11.6, 1.2$ Hz), 6.15 (1H, dt, $J=11.6, 7.3$ Hz), 6.26 (1H, dt, $J=15.3, 1.2$ Hz), 6.59 (1H, dt, $J=15.3, 6.7$ Hz), 7.30 (2H, d, $J=7.9$ Hz), 7.49 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 14.2, 21.3, 27.2, 31.0, 59.9, 121.0, 124.5 (2C), 130.0 (2C), 135.9, 138.6, 140.8, 141.4, 147.6, 166.1. IR 1716, 1043. MS (FAB) m/z : 293 (MH^+). HRMS (FAB) Calcd $\text{C}_{16}\text{H}_{21}\text{O}_3\text{S}$ (MH^+): 293.1212. Found: 293.1212.



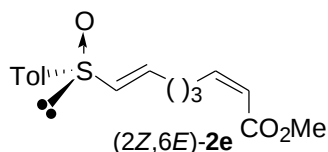
Isopropyl (2Z,6E)-7-[(R)-(p-Tolylsulfinyl)]-2,6-heptadienoate [(2Z,6E)-2c] $[\alpha]^{26}_D +34.4$ (c 0.52, CHCl_3). ^1H NMR δ : 1.25 (6H, t, $J=6.1$ Hz), 2.37–2.41 (5H, m), 2.83 (2H, dq, $J=7.3, 1.8$ Hz), 5.03 (1H, quint, $J=6.1$ Hz), 5.77 (1H, dt, $J=11.6, 1.8$ Hz), 6.12 (1H, dt, $J=11.6, 7.3$ Hz), 6.26 (1H, dt, $J=15.3, 1.8$ Hz), 6.59 (1H, dt, $J=15.3, 6.7$ Hz), 7.30 (2H, d, $J=7.9$ Hz), 7.80 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 21.4, 21.9 (2C), 30.2, 30.6, 67.6, 123.0, 124.7 (2C), 130.1 (2C), 136.1, 138.0, 140.7, 141.6, 146.3, 165.8. IR 1713, 1047. MS (FAB) m/z : 307 (MH^+). HRMS (FAB) Calcd $\text{C}_{17}\text{H}_{23}\text{O}_3\text{S}$ (MH^+): 307.1368. Found: 307.1355.



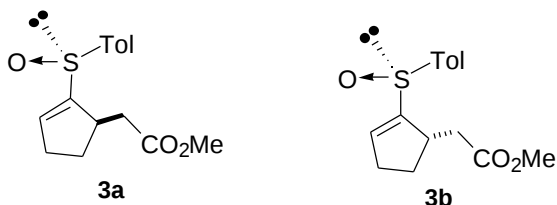
tert-Butyl (2Z,6E)-7-[(R)-(p-Tolylsulfinyl)]-2,6-heptadienoate [(2Z,6E)-2d] $[\alpha]^{24}_D +37.3$ (c 0.66, CHCl_3). ^1H NMR δ : 1.40 (9H, s), 2.31 (2H, q, $J=7.3$ Hz), 2.33 (3H, s), 2.73 (2H, dq, $J=7.3, 1.8$ Hz), 5.64 (1H, dt, $J=11.6, 1.8$ Hz), 5.98 (1H, dt, $J=11.6, 7.3$ Hz), 6.20 (1H, dt, $J=15.3, 1.2$ Hz), 6.52 (1H, dt, $J=15.3, 6.7$ Hz), 7.23 (2H, d, $J=8.5$ Hz), 7.42 (2H, d, $J=8.5$ Hz). ^{13}C NMR δ : 21.2, 26.9, 28.0 (3C), 31.0, 80.1, 121.7, 124.4 (2C), 129.8 (2C), 135.7, 138.8, 140.7, 141.2, 146.0, 165.4. IR 1713, 1045. MS (FAB) m/z : 321 (MH^+). HRMS (FAB) Calcd $\text{C}_{18}\text{H}_{25}\text{O}_3\text{S}$ (MH^+): 321.1524. Found: 321.1518.



Methyl (2E,7E)-8-[(R)-(p-Tolylsulfinyl)]-2,7-octadienoate [(2E,7E)-2e] $[\alpha]_D^{26} +106.0$ (c 0.85, CHCl_3). ^1H NMR δ : 1.64 (2H, quint, $J=7.3$ Hz), 2.20–2.28 (4H, m), 2.41 (3H, s), 3.72 (3H, s), 5.80 (1H, dt, $J=15.3, 1.2$ Hz), 6.23 (1H, dt, $J=15.3, 1.2$ Hz), 6.56 (1H, dt, $J=15.3, 6.7$ Hz), 6.91 (1H, dt, $J=15.3, 6.7$ Hz), 7.31 (2H, d, $J=8.5$ Hz), 7.50 (2H, d, $J=8.5$ Hz). ^{13}C NMR δ : 21.2, 26.2, 31.0, 31.2, 51.3, 121.4, 124.4 (2C), 129.9 (2C), 135.6, 138.8, 140.7, 141.3, 148.0, 166.7. IR 1720, 1045. MS (EI) m/z (%): 292 (M^+ , 6.6), 208 (100). HRMS (EI) Calcd $\text{C}_{16}\text{H}_{20}\text{O}_3\text{S}$ (M^+): 292.1133. Found: 292.1131.



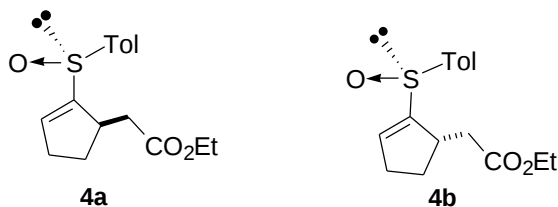
Methyl (2Z,7E)-8-[(R)-(p-Tolylsulfinyl)]-2,7-octadienoate [(2Z,7E)-2e] $[\alpha]_D^{26} +82.4$ (c 0.90, CHCl_3). ^1H NMR δ : 1.62 (2H, quint, $J=7.3$ Hz), 2.27 (2H, q, $J=6.7$ Hz), 2.40 (3H, s), 2.68 (2H, dq, $J=7.3, 1.8$ Hz), 3.70 (3H, s), 5.80 (1H, dt, $J=11.6, 1.8$ Hz), 6.19 (1H, dt, $J=11.6, 7.3$ Hz), 6.24 (1H, dt, $J=15.3, 1.2$ Hz), 6.59 (1H, dt, $J=15.3, 6.7$ Hz), 7.31 (2H, d, $J=7.9$ Hz), 7.50 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 21.2, 27.2, 28.1, 31.4, 50.9, 119.8, 124.4 (2C), 129.8 (2C), 135.3, 139.6, 140.7, 141.2, 149.1, 166.4. IR 1720, 1045. MS (EI) m/z (%): 292 (M^+ , 20.8), 100 (100). HRMS (EI) Calcd $\text{C}_{16}\text{H}_{20}\text{O}_3\text{S}$ (M^+): 292.1133. Found: 292.1135.



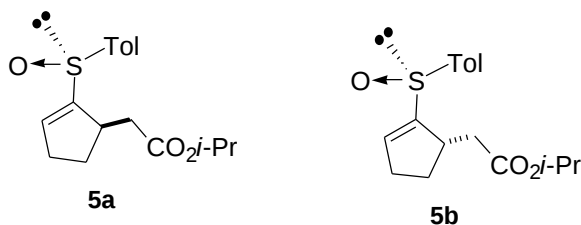
General Procedure of Intramolecular Michael Addition

Methyl [(R)-2-[(R)-(p-Tolylsulfinyl)]-2-cyclopentenyl]acetate (3a) and Methyl [(S)-2-[(R)-(p-Tolylsulfinyl)]-2-cyclopentenyl]acetate (3b) A solution of the enoate (2E,6E)-2 (47 mg, 0.17 mmol) in dry THF (1 mL) was added to a solution of LDA [prepared from $i\text{-Pr}_2\text{NH}$ (38 mL, 0.27 mmol) and 1.60 M $n\text{-BuLi}$ in hexane (0.16 mL, 0.18 mmol) in THF (1 mL) at -78°C for 30 min]. After 30 min, the reaction was quenched with saturated NH_4Cl and the resulting mixture was extracted with AcOEt . The extracts were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane– AcOEt (1:1) to give (*R*)-3 (20 mg, 44%) and (*S*)-3 (19 mg, 40%) each as a yellow oil. **3a**: $[\alpha]_D^{27} +94.7$ (c 0.50, CHCl_3). ^1H NMR δ : 1.66 (1H, m), 2.14 (1H, m), 2.31 (1H, dd, $J=16.5, 11.0$ Hz), 2.34–2.40 (4H, m), 2.51–2.58 (1H, m), 2.97 (1H, dd, $J=16.5, 3.7$ Hz), 3.06 (1H, m), 3.59 (3H, s), 6.52 (1H, q, $J=2.0$ Hz), 7.28 (2H, d, $J=7.9$ Hz), 7.44 (2H, d, $J=7.9$ Hz, Ar-H). ^{13}C NMR δ : 21.3, 31.1, 31.1, 38.5, 40.4, 51.4, 124.5 (2C), 129.9 (2C), 139.0, 141.1, 141.5, 148.6, 172.6. IR 1736, 1045. MS (FAB) m/z : 279 (MH^+). HRMS (FAB) Calcd $\text{C}_{15}\text{H}_{19}\text{O}_3\text{S}$ (MH^+): 279.1055. Found: 279.1081. **3b**: $[\alpha]_D^{27} +90.8$ (c 0.60, CHCl_3). ^1H NMR δ : 1.68 (1H, ddd,

$J=17.2, 8.5, 4.3$ Hz), 2.10 (1H, dd, $J=16.0, 9.8$ Hz), 2.14–2.22 (1H, m), 2.34 (3H, s), 2.35–2.41 (1H, m), 2.45 (1H, dd, $J=16.0, 4.9$ Hz), 2.48–2.54 (1H, m), 2.93 (1H, m), 3.56 (3H, s), 6.49 (1H, q, $J=1.2$ Hz), 7.23 (2H, d, $J=7.9$ Hz), 7.47 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 21.4, 30.8, 31.2, 38.0, 40.5, 51.5, 125.3 (2C), 130.0 (2C), 136.3, 139.4, 141.8, 149.7, 172.2. IR 1736, 1047. MS (FAB) m/z : 279 (MH^+). HRMS (FAB) Calcd $\text{C}_{15}\text{H}_{19}\text{O}_3\text{S}$ (MH^+): 279.1055. Found: 279.1049.

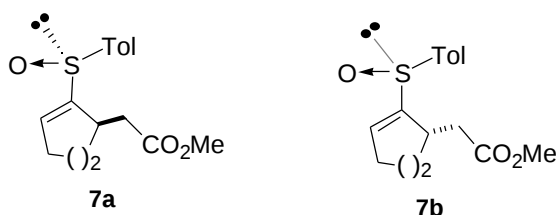


Ethyl [(1R)-2-[(R)-(p-Tolylsulfinyl)]-2-cyclopentenyl]acetate (4a) and Ethyl [(1S)-2-[(R)-(p-Tolylsulfinyl)]-2-cyclopentenyl]acetate (4b) **4a**: $[\alpha]^{27}_{\text{D}} +86.2$ (c 0.66, CHCl_3). ^1H NMR δ : 1.22 (3H, t, $J=7.3$ Hz), 1.68–1.74 (1H, m), 2.14–2.21 (1H, m), 2.32 (1H, dd, $J=16.5, 11.0$ Hz), 2.36–2.42 (4H, m), 2.55–2.60 (1H, m), 2.99 (1H, dd, $J=16.5, 3.7$ Hz), 3.10 (1H, m), 4.08 (2H, q, $J=7.3$ Hz), 6.53 (1H, q, $J=1.8$ Hz), 7.31 (2H, d, $J=7.9$ Hz), 7.48 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 14.2, 21.4, 31.0, 31.2, 38.8, 40.5, 60.2, 124.6 (2C), 129.9 (2C), 139.1, 141.1, 141.4, 148.7, 172.2. IR: 1732, 1084, 1045. MS (FAB) m/z : 293 (MH^+). HRMS (FAB) Calcd $\text{C}_{16}\text{H}_{21}\text{O}_3\text{S}$ (MH^+): 293.1211. Found: 293.1252. **4b**: $[\alpha]^{26}_{\text{D}} +72.8$ (c 0.51, CHCl_3). ^1H NMR δ : 1.16 (3H, t, $J=7.3$ Hz), 1.66–1.72 (1H, m), 2.10 (1H, dd, $J=15.9, 7.3$ Hz), 2.14–2.25 (1H, m), 2.34 (3H, s), 2.37–2.40 (1H, m), 2.44 (1H, dd, $J=14.9, 4.3$ Hz), 2.48–2.52 (1H, m), 2.92 (1H, m), 4.01–4.05 (2H, m), 6.50 (1H, s), 7.24 (2H, d, $J=7.9$ Hz), 7.48 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 14.2, 21.5, 30.9, 31.3, 38.3, 40.6, 60.5, 125.3 (2C), 130.1 (2C), 136.3, 139.4, 141.9, 149.7, 171.9. IR 1732, 1084, 1045. MS (FAB) m/z : 293 (MH^+). HRMS (FAB) Calcd $\text{C}_{16}\text{H}_{21}\text{O}_3\text{S}$ (MH^+): 293.1211. Found: 293.1217.

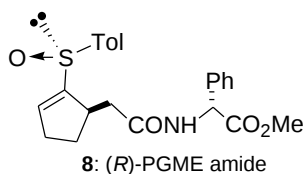


Isopropyl [(1R)-2-[(R)-(p-Tolylsulfinyl)]-2-cyclopentenyl]acetate (5a) and Isopropyl [(1S)-2-[(R)-(p-Tolylsulfinyl)]-2-cyclopentenyl]acetate (5b) **5a**: $[\alpha]^{27}_{\text{D}} +45.5$ (c 0.43, CHCl_3). ^1H NMR δ : 1.19 (3H, d, $J=6.1$ Hz), 1.20 (3H, d, $J=6.1$ Hz), 1.67–1.74 (1H, m), 2.13–2.20 (1H, m), 2.27 (1H, dd, $J=16.5, 11.0$ Hz), 2.38–2.42 (4H, m), 2.54–2.61 (1H, m), 2.96 (1H, dd, $J=16.5, 3.7$ Hz), 3.10 (1H, m), 4.95 (1H, quint, $J=6.1$ Hz), 6.52 (1H, q, $J=2.1$ Hz), 7.31 (2H, d, $J=7.9$ Hz), 7.48 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 21.4, 21.77, 21.84, 30.9, 31.2, 39.2, 40.6, 67.6, 124.6 (2C), 129.9 (2C), 139.0, 141.1, 141.2, 148.7, 171.7. IR 1728, 1045. MS (FAB) m/z : 329 (MNa^+). HRMS (FAB) Calcd $\text{C}_{17}\text{H}_{23}\text{O}_3\text{S}$ (MH^+): 307.1368. Found: 308.1357. **5b**: $[\alpha]^{26}_{\text{D}} +71.3$ (c 0.41, CHCl_3). ^1H NMR δ : 1.20 (3H, d, $J=6.1$ Hz), 1.22 (3H, d, $J=6.1$ Hz), 1.73–1.80 (1H, m), 2.13 (1H, dd, $J=15.3, 9.8$ Hz), 2.20–2.27 (1H, m), 2.41 (3H, s), 2.35–2.52 (1H, m), 2.49 (1H, dd, $J=15.3, 4.3$ Hz), 2.54–2.60 (1H, m), 2.98 (1H, m), 4.96 (1H, quint, $J=6.1$ Hz), 6.56 (1H, q, $J=1.8$ Hz), 7.30 (2H, d, $J=7.9$ Hz), 7.55 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 21.4, 21.7, 21.8, 30.9, 31.2, 38.7, 40.7, 67.9, 125.3 (2C), 130.0 (2C), 136.1, 139.5, 141.8, 149.9, 171.3. IR 1728, 1047. MS (FAB) m/z : 307 (MH^+). HRMS (FAB) Calcd $\text{C}_{17}\text{H}_{23}\text{O}_3\text{S}$ (MH^+): 307.1368.

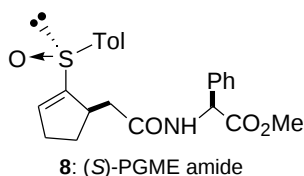
Found: 307.1362.



Methyl [(1R)-2-[(R)-(p-Tolylsulfinyl)]-2-cyclohexenyl]acetate (7a) and Methyl [(1S)-2-[(R)-(p-Tolylsulfinyl)]-2-cyclohexenyl]acetate (7b) **7a**: $[\alpha]_D^{26} +110.4$ (c 1.91, CHCl_3). ^1H NMR δ : 1.56–1.67 (4H, m), 2.15–2.19 (1H, m), 2.33–2.41 (5H, m), 2.71 (1H, m, 1-H), 3.13 (1H, dd, $J=16.5, 3.1$ Hz), 3.62 (3H, s), 6.73 (1H, t, $J=3.7$ Hz), 7.31 (2H, d, $J=7.9$ Hz), 7.45 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 17.3, 21.4, 26.1, 27.7, 29.1, 38.1, 51.4, 124.4 (2C), 129.7 (2C), 137.9, 139.1, 140.7, 145.4, 172.2. IR 1736, 1045. MS (FAB) m/z : 293 (MH^+). HRMS (FAB) Calcd $\text{C}_{16}\text{H}_{21}\text{O}_3\text{S}$ (MH^+): 293.1212. Found: 293.1198. **7b**: $[\alpha]_D^{23} -0.4$ (c 2.11, CHCl_3). ^1H NMR δ : 1.55–1.66 (4H, m), 1.78–2.40 (6H, m), 2.48–2.56 (2H, m), 3.66 (3H, s), 6.77 (1H, t, $J=3.7$ Hz), 7.29 (2H, d, $J=7.9$ Hz), 7.53 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 17.8, 21.4, 25.5, 27.6, 29.3, 37.8, 51.6, 125.6 (2C), 130.0 (2C), 130.2, 139.9, 141.9, 144.4, 172.1. IR 1736, 1053. MS (FAB) m/z : 293 (MH^+). HRMS (FAB) Calcd $\text{C}_{16}\text{H}_{21}\text{O}_3\text{S}$ (MH^+): 293.1212. Found: 293.1216.

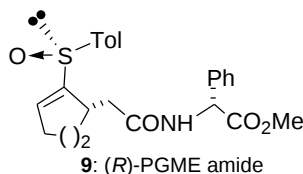


N-[(1R)-2-[(R)-(p-Tolylsulfinyl)]-2-cyclopentenyl]acetyl-D-2-phenylglycine Methyl Ester [(R)-PGME amide 8] $[\alpha]_D^{27} -120.7$ (c 0.74, CHCl_3). ^1H NMR δ : 1.93–2.01 (2H, m), 2.15–2.23 (1H, m), 2.29 (1H, dd, $J=12.8, 3.7$ Hz), 2.41 (3H, s), 2.78 (1H, dd, $J=12.8, 5.5$ Hz), 2.77–2.84 (1H, m), 3.72 (3H, s), 5.60 (1H, d, $J=7.9$ Hz), 6.31 (1H, t, $J=1.8$ Hz), 7.32 (2H, d, $J=7.9$ Hz), 7.30–7.35 (1H, m), 7.37 (2H, t, $J=6.7$ Hz), 7.44 (2H, d, $J=6.7$ Hz), 7.45 (2H, d, $J=7.9$ Hz), 8.41 (2H, d, $J=7.3$ Hz). ^{13}C NMR δ : 21.3, 28.6, 31.7, 39.6, 41.5, 52.5, 56.5, 124.1 (2C), 127.7 (2C), 128.1, 128.6 (2C), 130.0 (2C), 137.3, 137.7, 141.0, 145.3, 145.5, 170.6, 171.1. IR 1747, 1668, 1032. MS (FAB) m/z : 412 (MH^+). HRMS (FAB) Calcd $\text{C}_{23}\text{H}_{26}\text{NO}_4\text{S}$ (MH^+): 412.1583. Found: 293.1577.

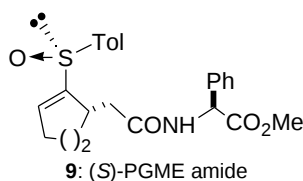


N-[(1R)-2-[(R)-(p-Tolylsulfinyl)]-2-cyclopentenyl]acetyl-L-2-phenylglycine Methyl Ester [(S)-PGME amide 8] $[\alpha]_D^{27} +121.7$ (c 0.49, CHCl_3). ^1H NMR δ : 2.10 (2H, dt, $J=7.9, 7.3$ Hz), 2.33 (1H, dd, $J=13.0, 4.3$ Hz), 2.35–2.46 (1H, m), 2.41 (3H, s), 2.62–2.71 (1H, m), 2.78 (1H, dd, $J=13.0, 4.9$ Hz), 2.85–2.92 (1H, br s),

3.69 (3H, s), 5.45 (1H, d, $J=6.7$ Hz), 6.88 (1H, d, $J=1.8$ Hz), 7.31 (2H, d, $J=7.9$ Hz), 7.32 (1H, t, $J=7.3$ Hz), 7.37 (2H, t, $J=7.6$ Hz), 7.43 (2H, t, $J=7.9$ Hz), 7.45 (2H, d, $J=7.9$ Hz), 8.28 (1H, d, $J=7.3$ Hz). ^{13}C NMR δ : 21.3, 28.8, 31.9, 39.8, 41.3, 52.3, 56.8, 124.1 (2C), 127.6 (2C), 128.3, 128.8 (2C), 129.9 (2C), 136.0, 137.8, 140.9, 145.3, 146.1, 170.9, 171.3. IR 1747, 1670, 1030. MS (FAB) m/z : 412 (MH^+). HRMS (FAB) Calcd $\text{C}_{23}\text{H}_{26}\text{NO}_4\text{S}$ (MH^+): 412.1583. Found: 412.1582.



***N*-[(1*R*)-2-[(*R*)-(p-Tolylsulfinyl)]-2-cyclohexenyl]acetyl-D-2-phenylglycine Methyl Ester [(*R*)-PGME amide 9]** $[\alpha]_{\text{D}}^{27} -33.9$ (c 0.89, CHCl_3). ^1H NMR δ : 1.46–1.71 (4H, m), 2.16 (1H, dd, $J=14.6$, 9.8 Hz), 2.15–2.26 (1H, m), 2.33 (1H, dd, $J=20.1$, 4.3 Hz), 2.38 (3H, s), 2.45 (1H, dd, $J=14.6$, 3.7 Hz), 2.53–2.61 (1H, br s), 3.72 (3H, s), 5.52 (1H, d, $J=6.7$ Hz), 6.58 (1H, d, $J=7.3$ Hz), 6.71 (1H, t, $J=3.7$ Hz), 7.24 (2H, d, $J=7.9$ Hz), 7.31–7.41 (5H, m), 7.48 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 18.1, 21.4, 25.6, 27.7, 29.8, 40.0, 52.8, 56.6, 125.6 (2C), 127.4 (2C), 128.7, 129.0 (2C), 130.0 (2C), 130.2, 136.1, 139.8, 141.9, 144.8, 170.3, 171.3. IR 1747, 1672, 1041. MS (FAB) m/z : 426 (MH^+). HRMS (FAB) Calcd $\text{C}_{24}\text{H}_{28}\text{NO}_4\text{S}$ (MH^+): 426.1739. Found: 426.1734.



***N*-[(1*R*)-2-[(*R*)-(p-Tolylsulfinyl)]-2-cyclohexenyl]acetyl-L-2-phenylglycine Methyl Ester [(*S*)-PGME amide 9]** $[\alpha]_{\text{D}}^{26} +142.6$ (c 1.69, CHCl_3). ^1H NMR δ : 1.46–1.57 (2H, m), 1.49–1.67 (2H, m), 2.15 (1H, dd, $J=14.6$, 9.8 Hz), 2.15–2.23 (1H, m), 2.29 (1H, dd, $J=18.9$, 4.3 Hz), 2.38 (3H, s), 2.48 (1H, dd, $J=14.3$, 4.3 Hz), 2.55–2.63 (1H, m), 3.73 (3H, s), 5.53 (1H, d, $J=7.3$ Hz), 6.69 (1H, t, $J=3.7$ Hz), 6.75 (1H, d, $J=6.7$ Hz), 7.26 (2H, d, $J=7.9$ Hz), 7.29–7.40 (5H, m), 7.52 (2H, d, $J=7.9$ Hz). ^{13}C NMR δ : 18.0, 21.4, 25.6, 27.6, 30.0, 40.0, 52.7, 56.5, 125.6 (2C), 127.2 (2C), 128.5, 128.9 (2C), 130.0 (2C), 130.3, 136.5, 140.0, 141.9, 144.9, 170.3, 171.2. IR 1747, 1672, 1043. MS (FAB) m/z : 426 (MH^+). HRMS (FAB) Calcd $\text{C}_{24}\text{H}_{28}\text{NO}_4\text{S}$ (MH^+): 426.1739. Found: 426.1759.

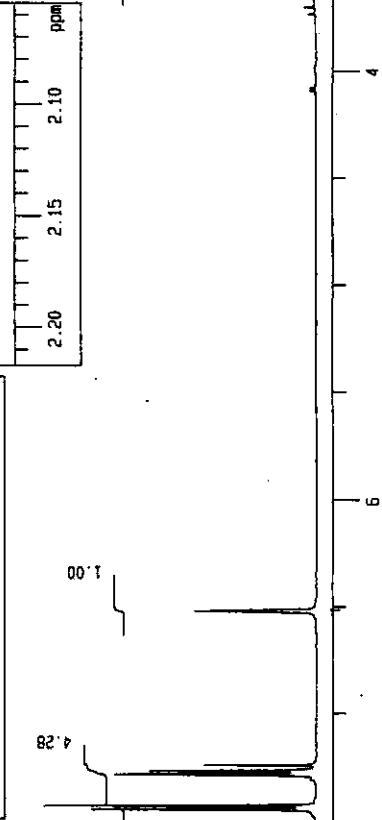
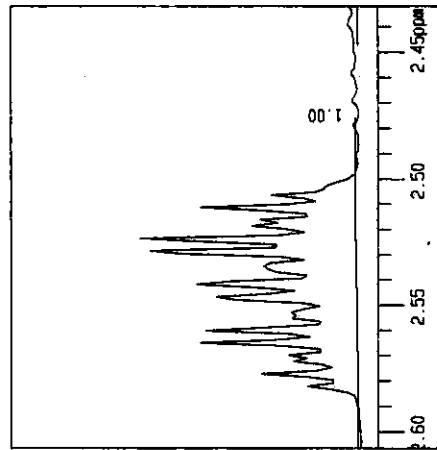
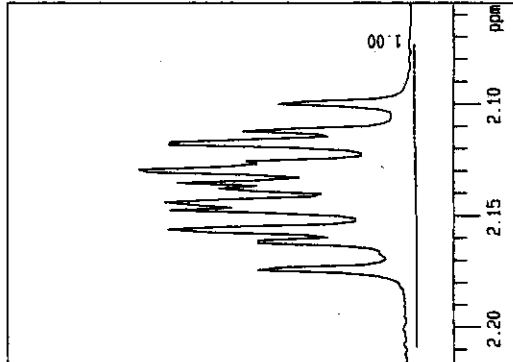
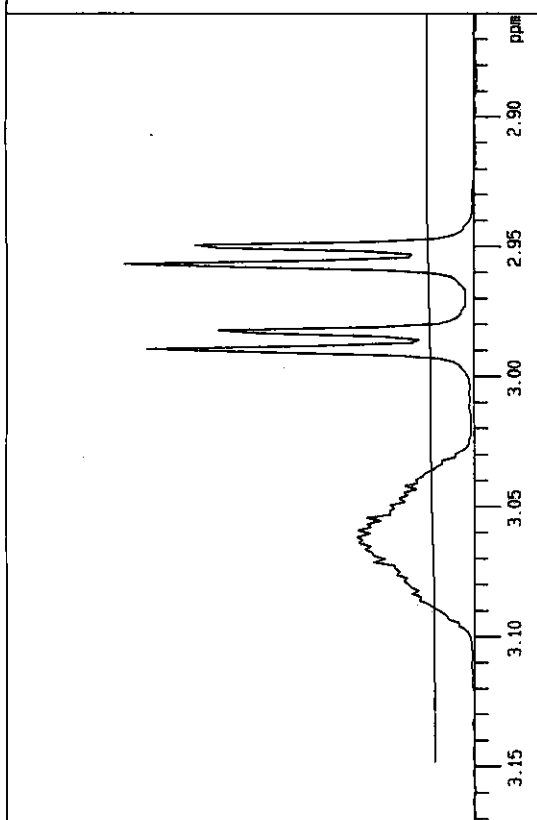
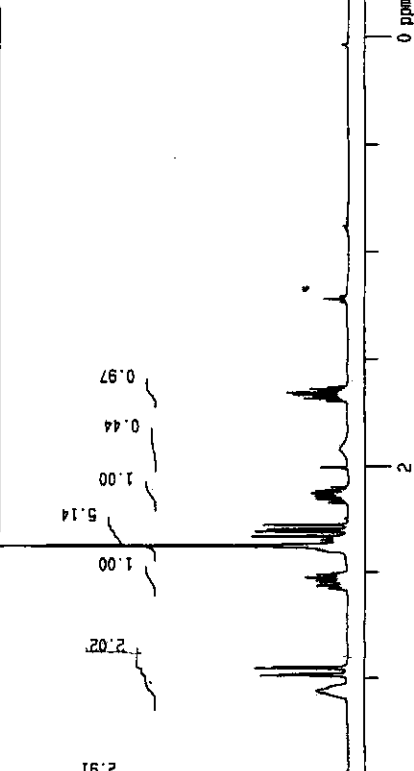
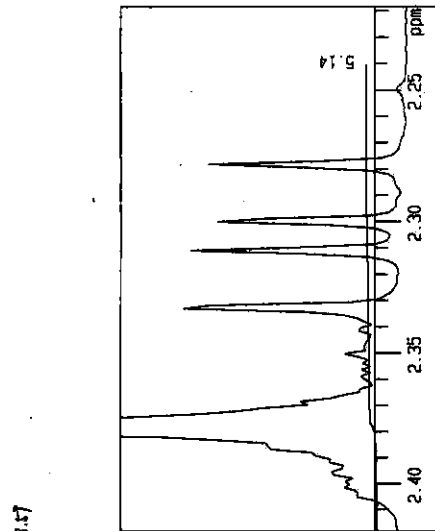
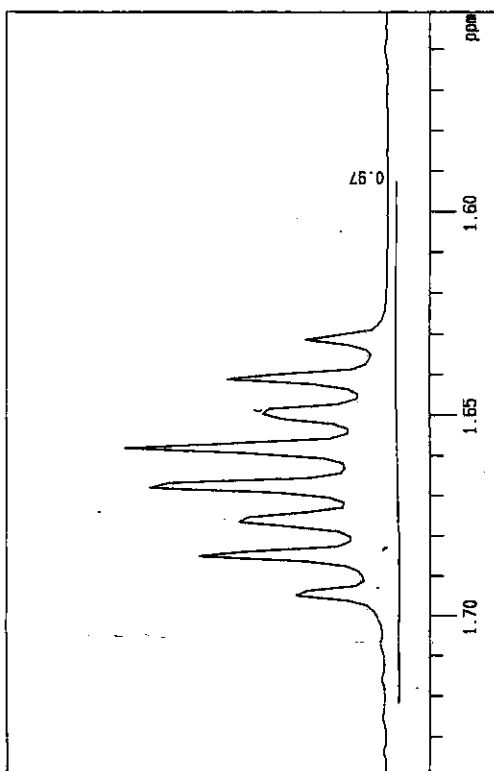
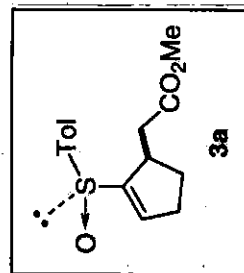
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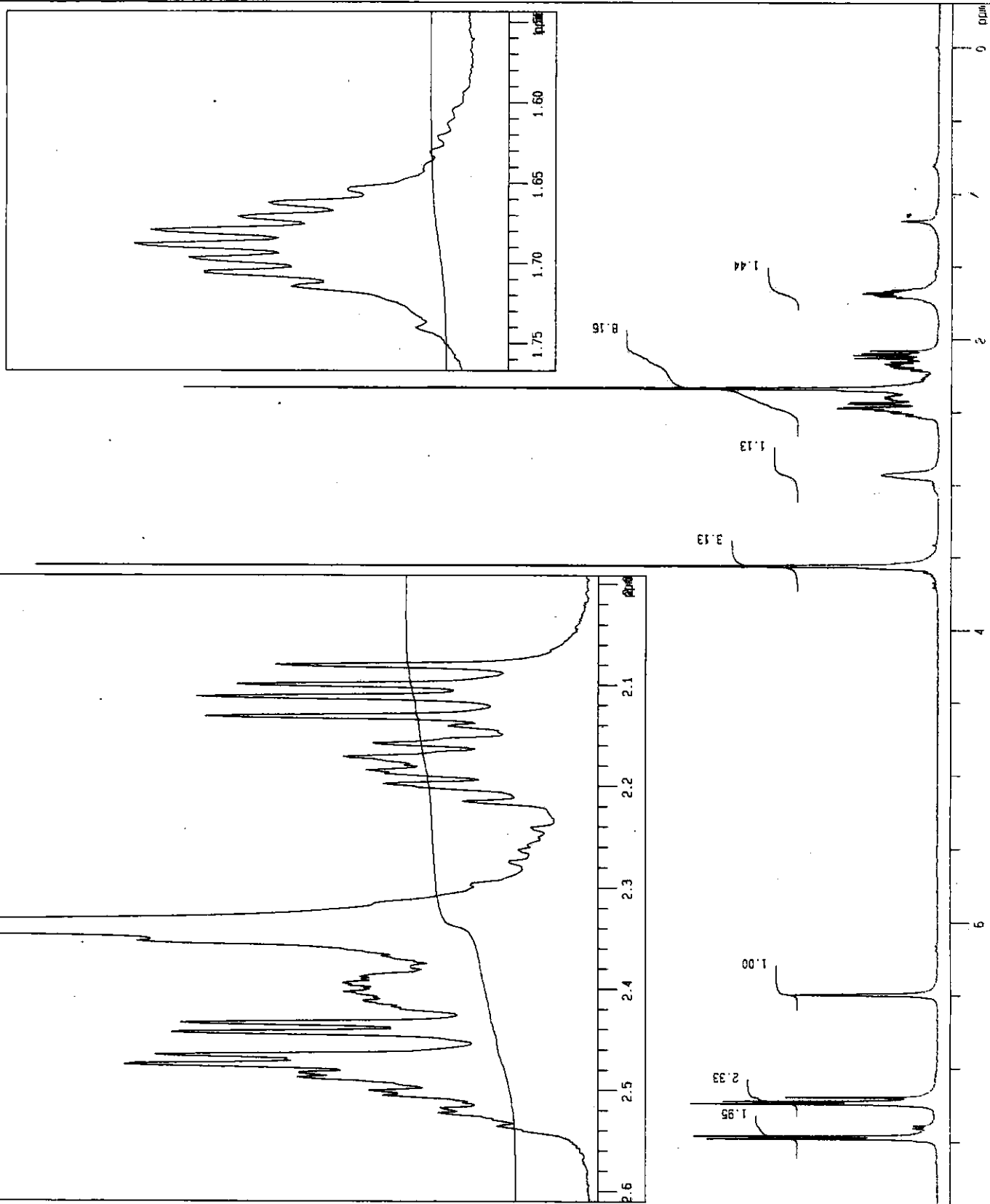
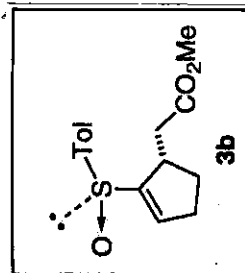


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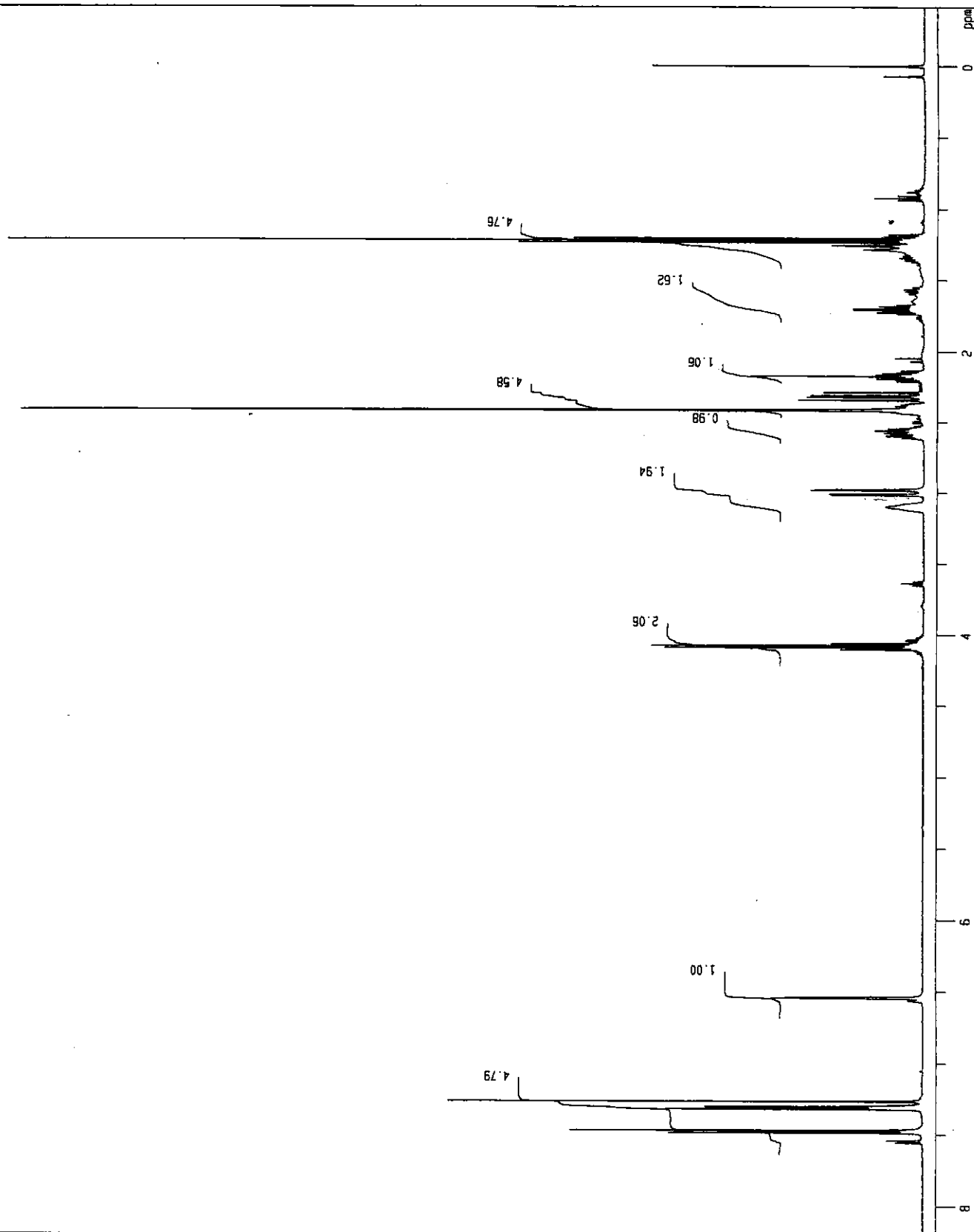
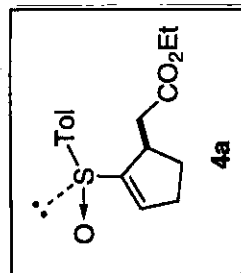
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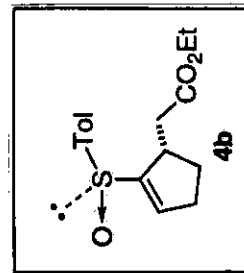
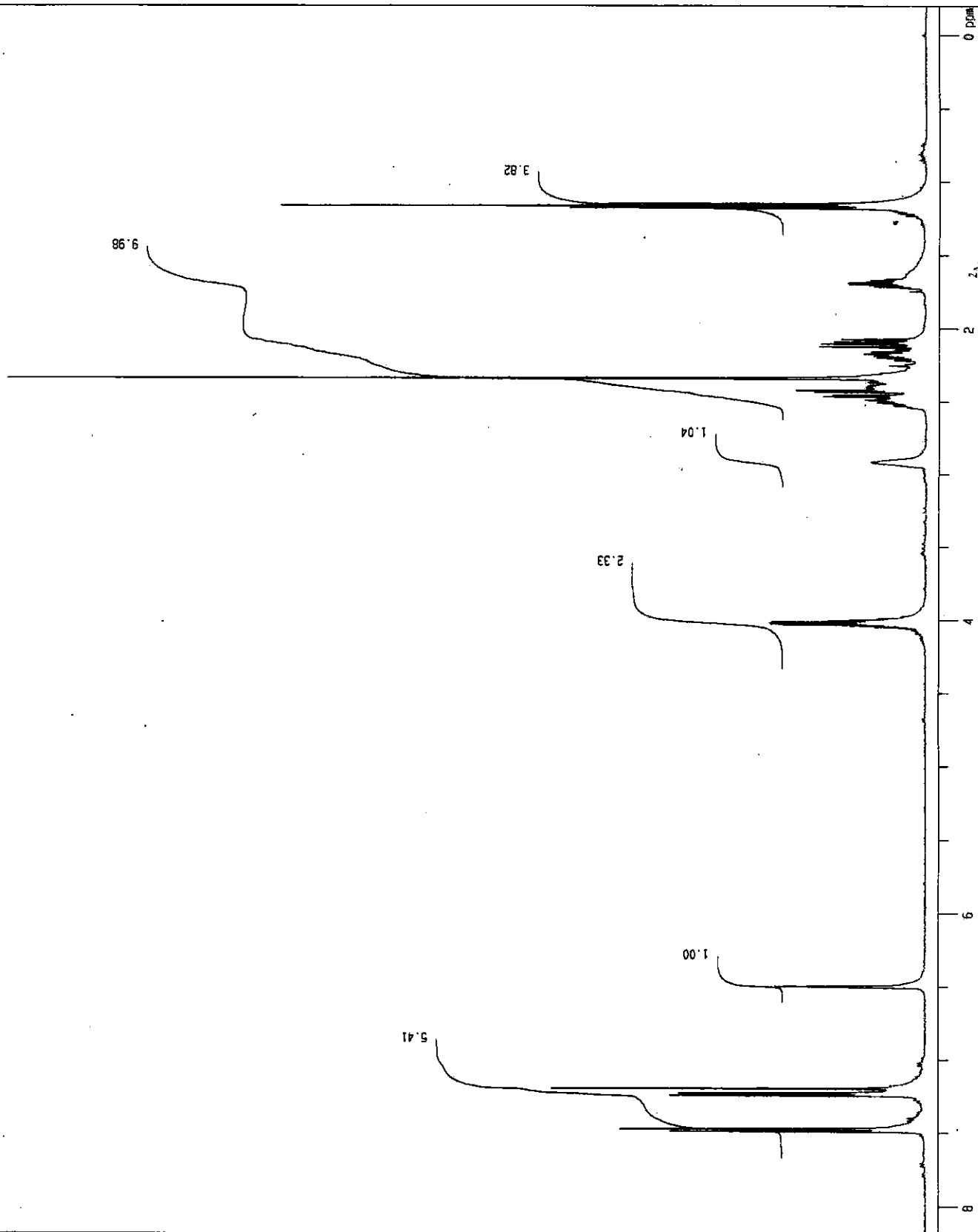
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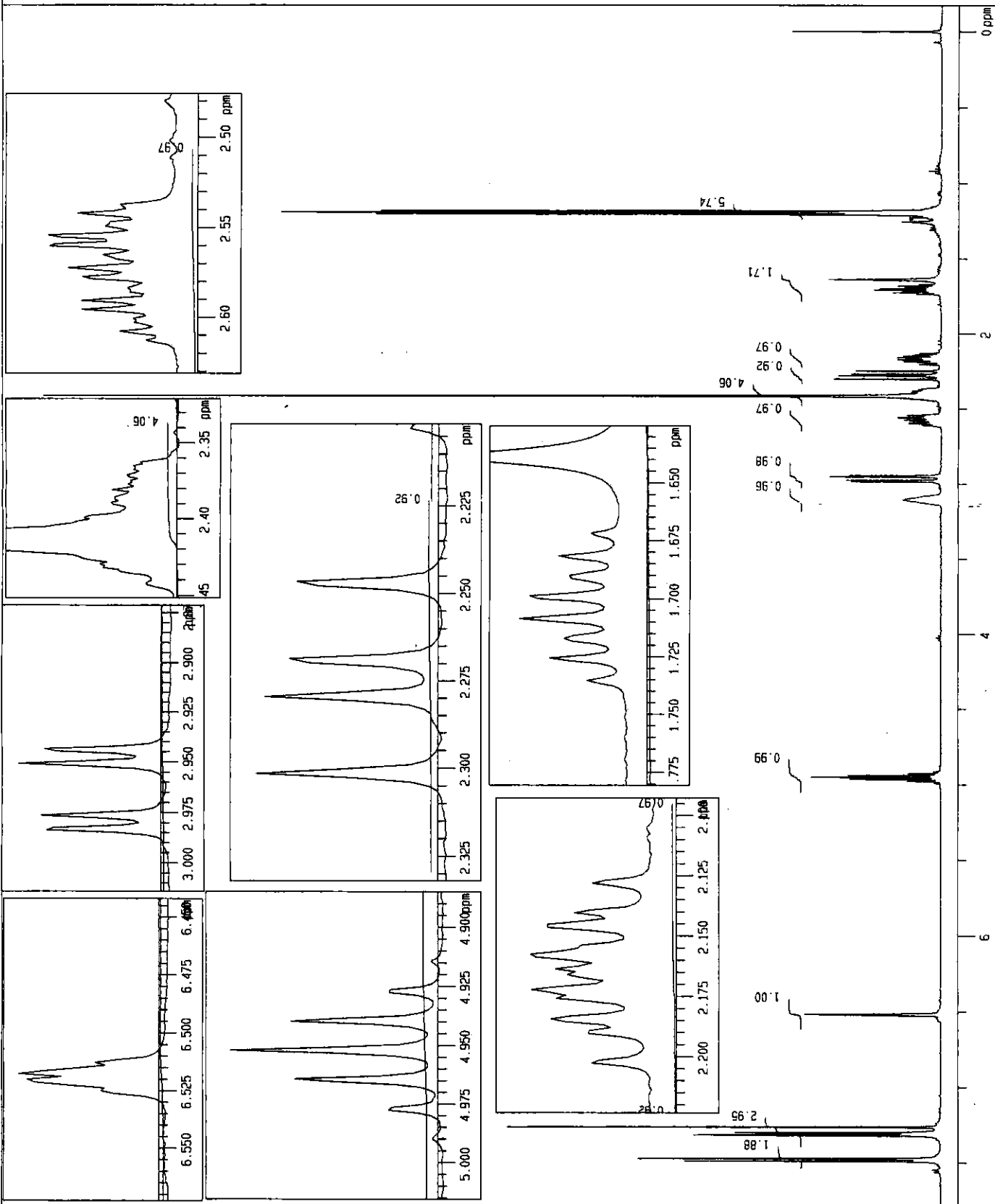
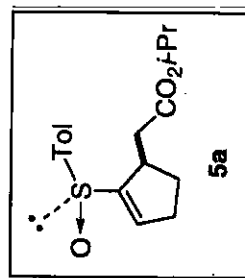
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1H Line

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 SPINNING : 13 Hz
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¹H NMR spectrum of compound 10a in CDCl₃. The spectrum shows peaks at 0.18, 7.44, 8.86, 8.89, 8.94, 6.31, 1.04, 1.00, 2.10, and 2.39 ppm. Integration values are provided for several peaks: 0.18, 0.27, 0.94, 8.86, 8.89, 8.94, 6.31, 1.04, 1.00, 2.10, and 2.39. Two insets show expanded regions: one from 2.0 to 3.0 ppm and another from 7.25 to 7.75 ppm.

5b

Date : Fri Dec 17 18:00:31 1999

Filename

Comment

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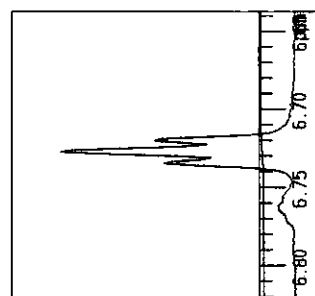
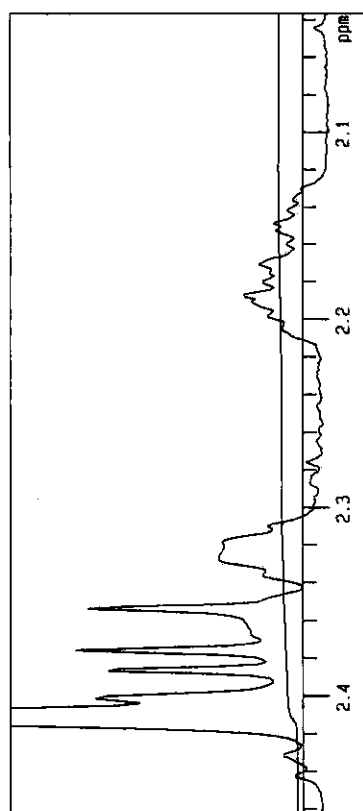
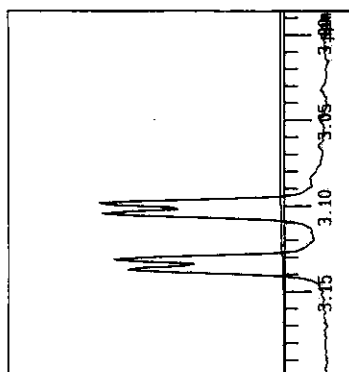
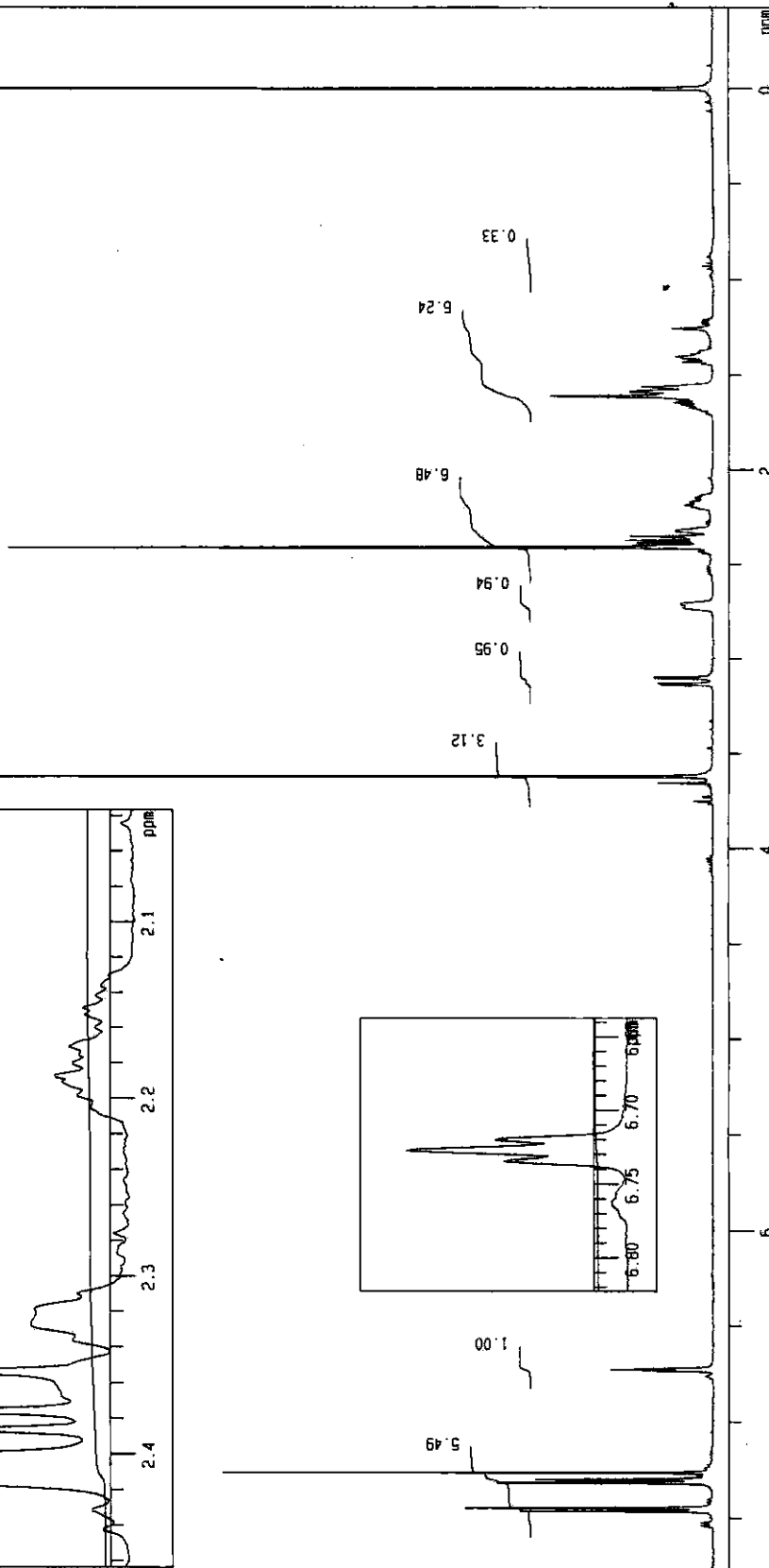
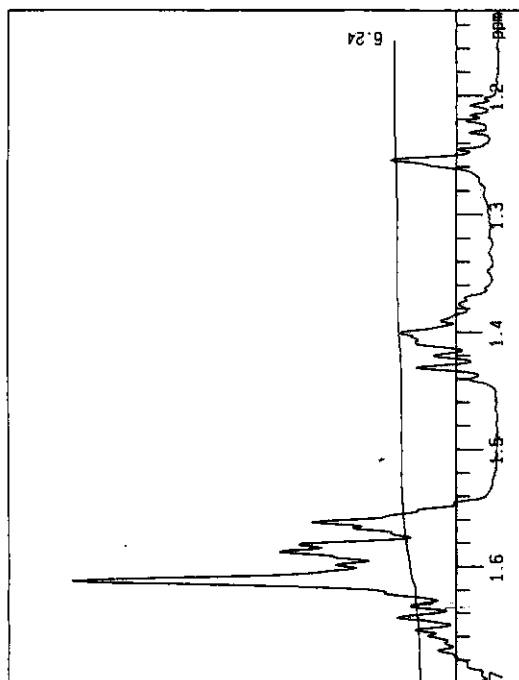
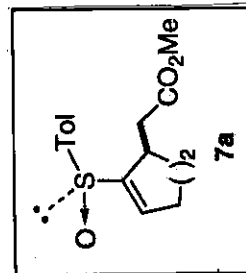
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SCANS 16 times

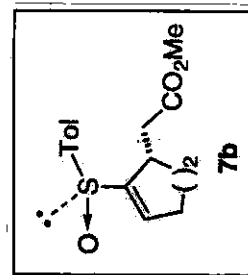
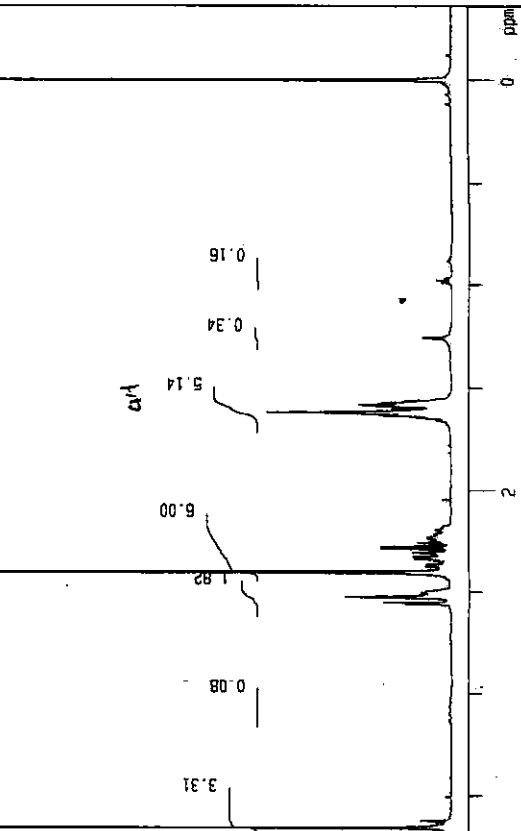
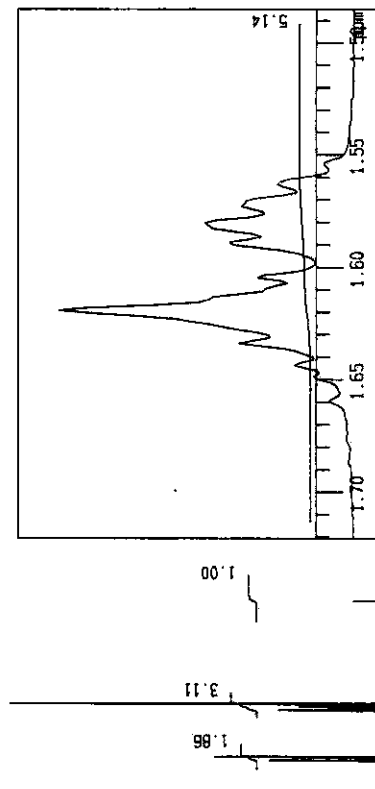
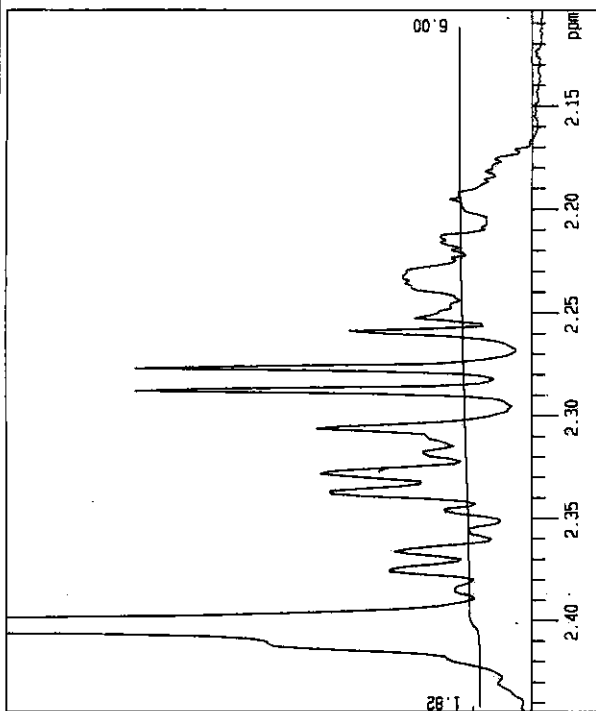
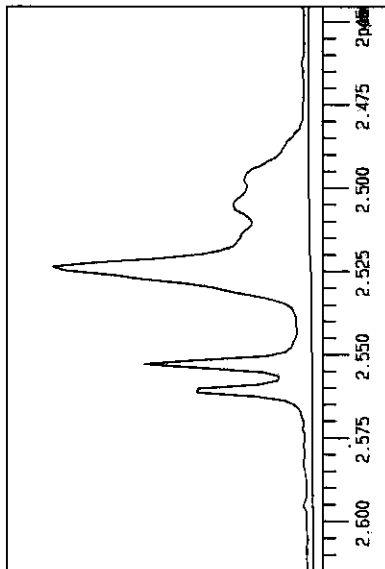
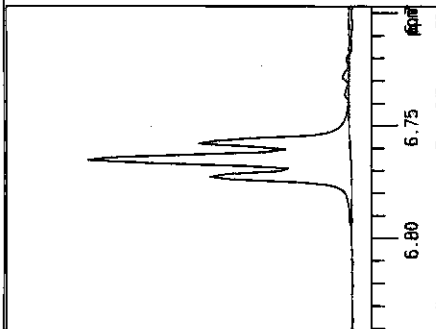
SLVNT CDCl3

SPINNT 14 Hz

TEMP 25.4 C

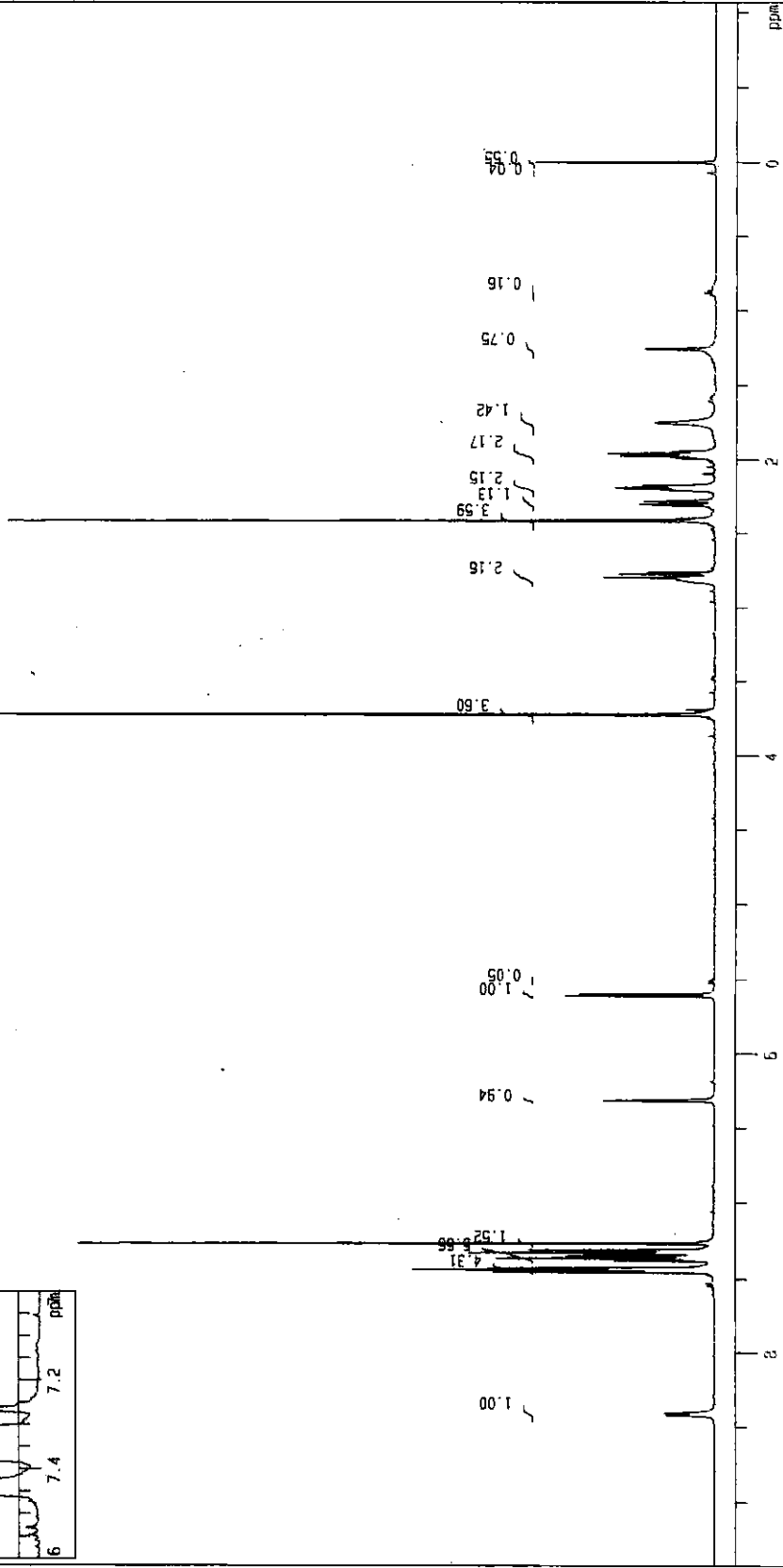
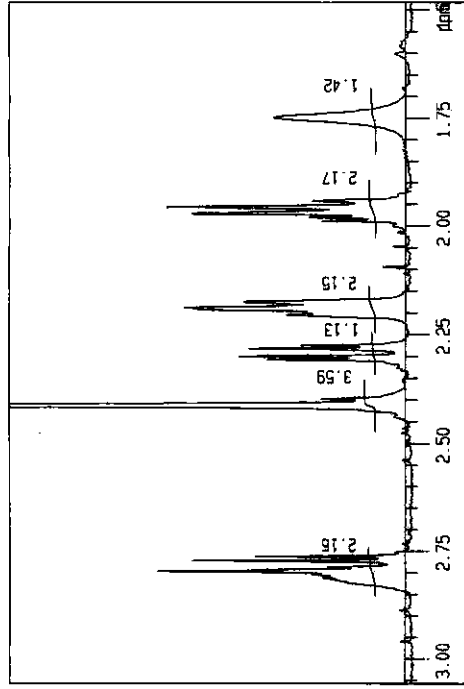
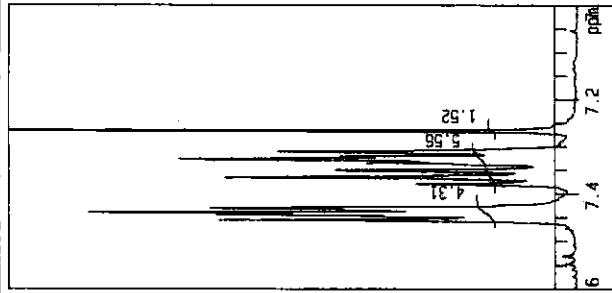


1H Line

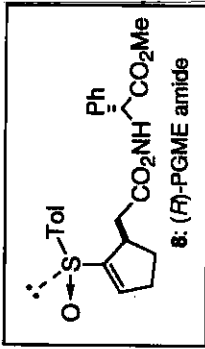


Date : Fri Dec 17 18:10:07 1999
 FileName : LoadingFID.mdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE :
 POINT : 16384 points
 SAMPO : 16384 points
 FREQ : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 58.7 usec
 INVL : 100.0 usec
 TIMES : 16 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PREDL : 0.01000 msec
 ININT : 1000.0000 msec
 RESOL : 0.61 Hz
 PW1 : 2.63 usec
 1H : 500.00 MHz
 DBFRQ : 162167.63 Hz
 DBSET : 22
 RGAIN :
 SCANS : 16 times
 SLWT :
 SPINNING : 14 Hz
 TEMP : 25.5 C

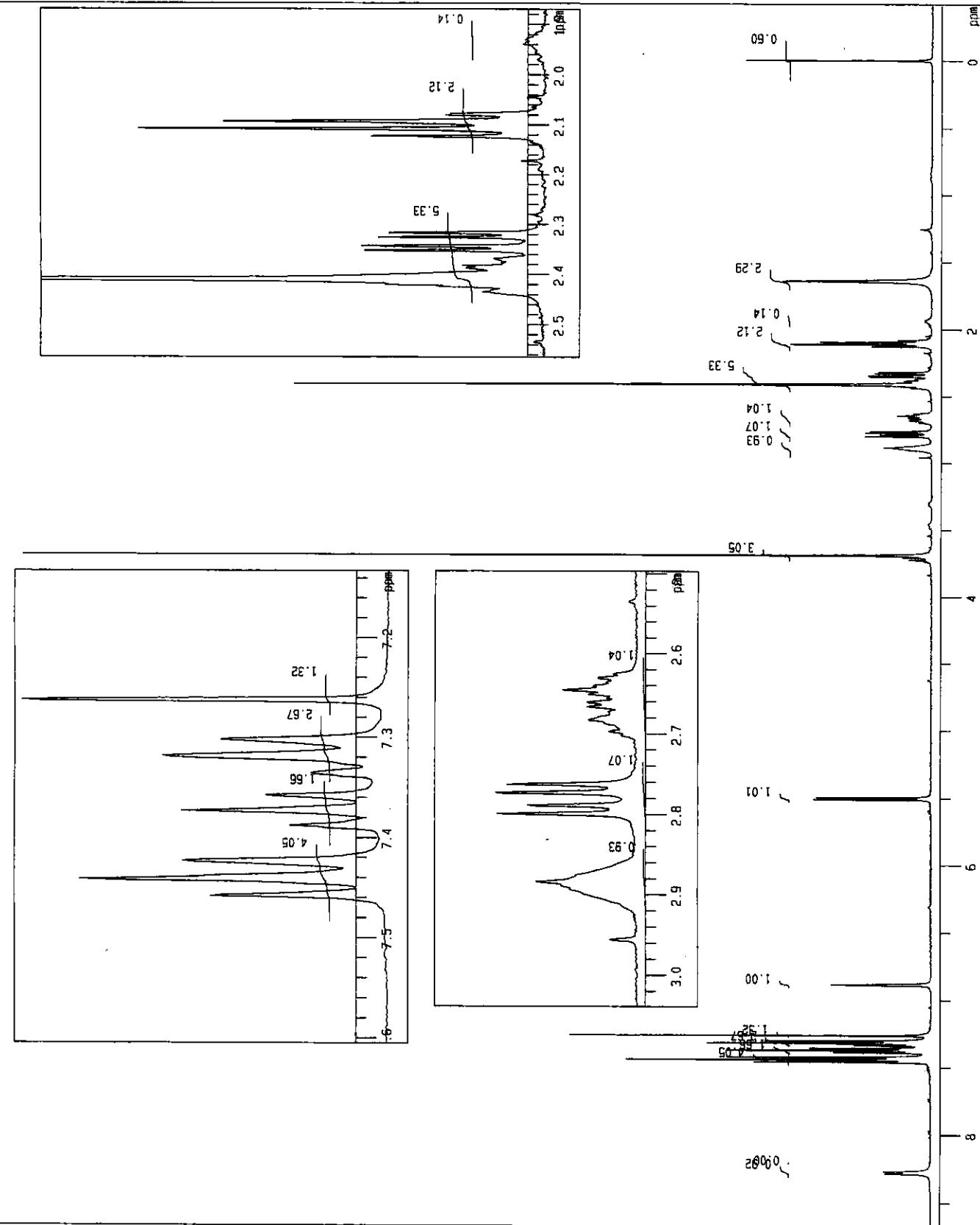
1H Line



Date : Wed Sep 6 14:42:29 2000
 FileName : .LoadingID.mdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE : non
 POINT : 16384 points
 SAMPD : 16384 points
 FREQ : 1000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 58.7 usec
 INTVL : 100.0 usec
 TIMES : 16 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PREDL : 0.01000 msec
 ININT : 1000.0000 msec
 RESOL : 0.61 Hz
 PWT : 2.63 usec
 OBNUC : 1H
 OBSFQ : 500.00 MHz
 OBSFQ : 162167.63 Hz
 RGAIN : 23
 SCANS : 16 times
 SLVNT : CDCl3
 SPINNTG : 11 Hz
 TEMP : 22.9 C

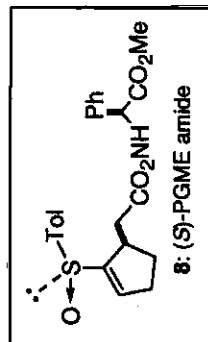


1H Line



Date : Wed Sep 27 10:57:58 2000
 FileName : .LoadingfID.nmdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE :

POINT : 16384 points
 SAMPD : 16384 points
 FREQD : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEATD : 58.7 usec
 INTR : 100.0 usec
 TIMES : 16 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PREDL : 0.01000 msec
 INTR : 1000.0000 msec
 RESOL : 0.61 Hz
 PW1 : 2.63 usec
 1H : 500.00 MHz
 162167.63 Hz
 SCANS : 16 times
 SLVNT : CDCl₃
 SPINNING : 11 Hz
 TEMP : 23.8 C

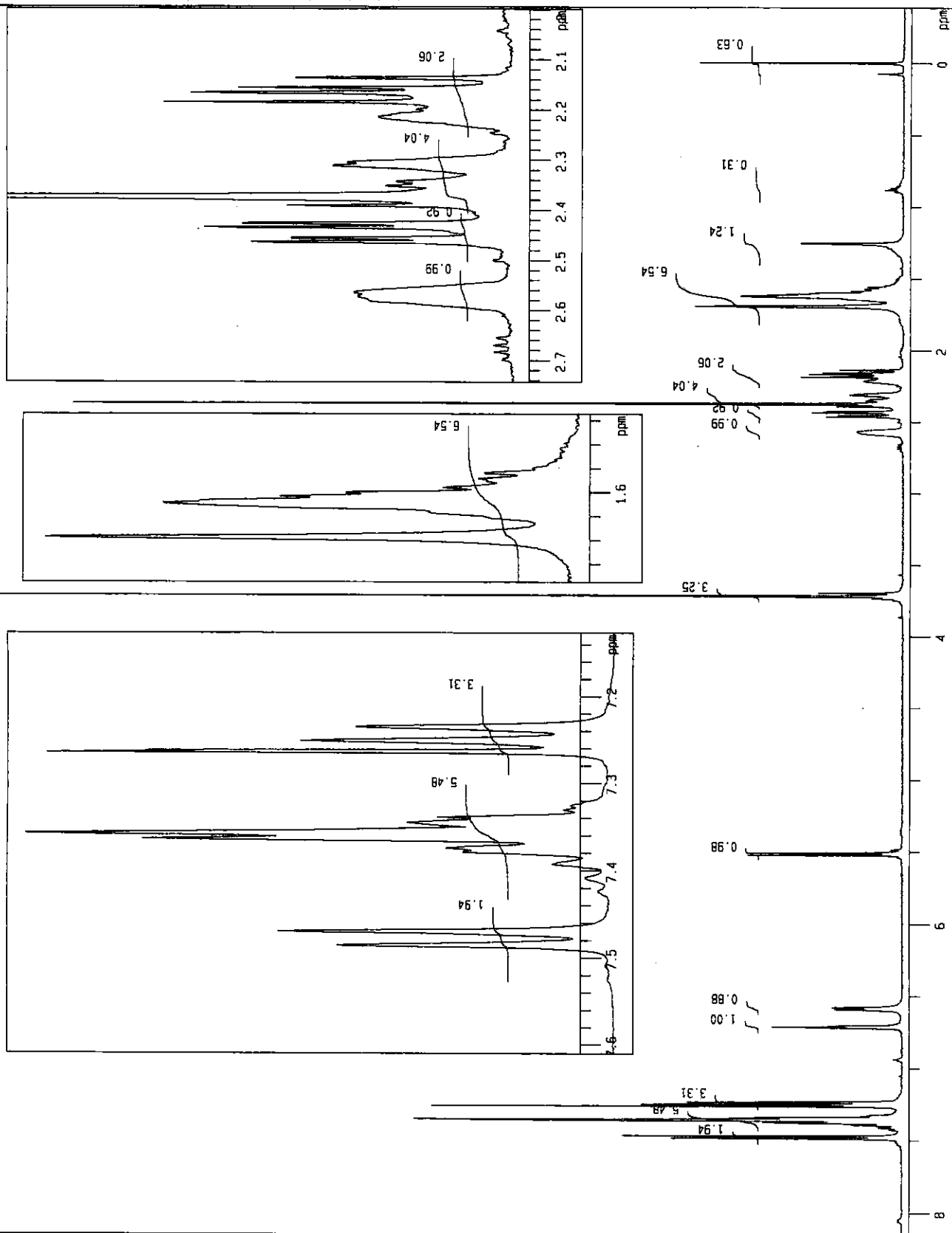
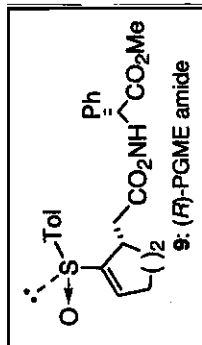


1H Line

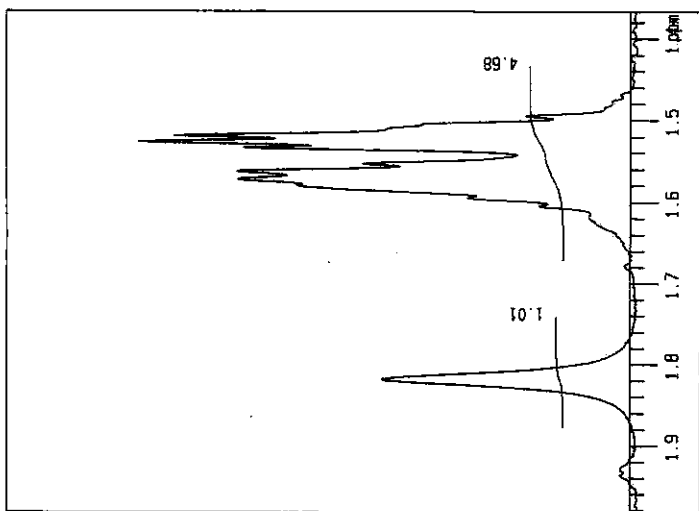
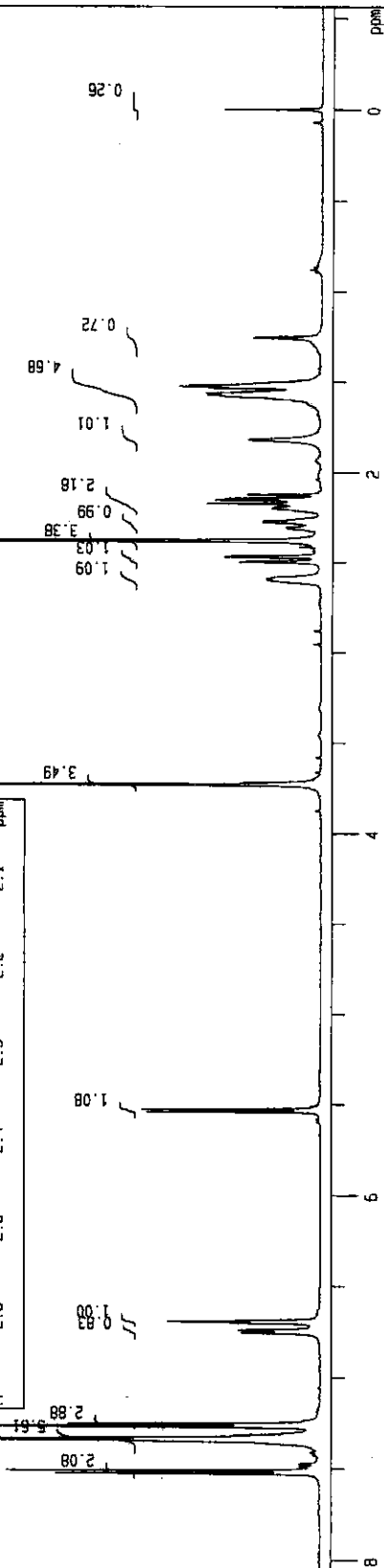
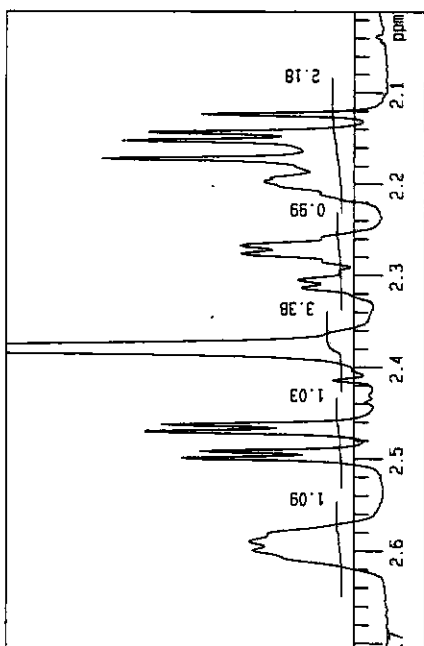
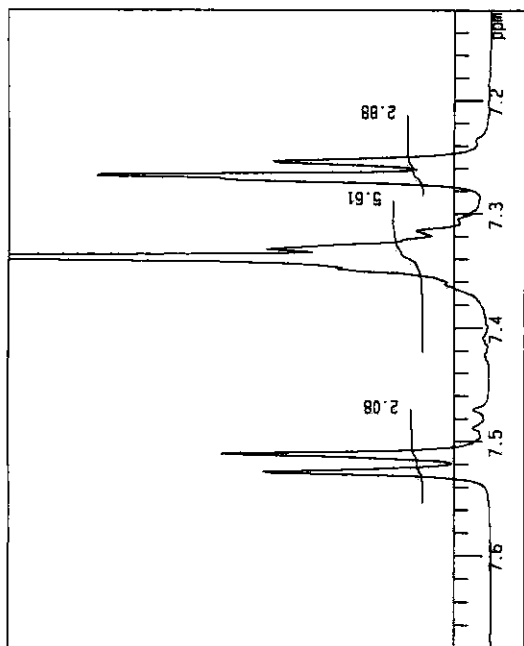
Date : Wed Sep 27 10:39:49 2000

Filename : .LoadingFID.nmdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE :

POINT 16384 points
 SAMPO 16384 points
 FREQU 10000.0 Hz
 FILTR 5000 Hz
 DELAY 40.0 usec
 DEADT 58.7 usec
 INTVL 100.0 usec
 TIMES 16 times
 DUMMY 1 times
 PD 5.3616 sec
 ACOTM 1638.3999 msec
 PREDL 0.01000 msec
 ININT 1000.0000 msec
 RESOL 0.61 Hz
 PH1 2.63 usec
 OBNUC 1H 500.00 MHz
 OBFRQ 162167.63 Hz
 OBSET 22
 RGAIN 16 times
 SCANS 16 times
 SLVNT CDCL3
 SPINNING 13 Hz
 TEMP 23.7 C



1H Line



Date : Wed Sep 27 10:48:57 2000
 FileName : .LoadingFID.nmdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE :
 POINT : 16384 points
 SAMPD : 16384 points
 FREQ : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEATH : 58.7 usec
 INTVL : 100.0 usec
 TIMES : 16 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PREDL : 0.01000 msec
 INTWT : 1000.0000 msec
 RESOL : 0.61 Hz
 PW1 : 2.63 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 162167.63 Hz
 RGAIN : 20
 SCANS : 16 times
 SLVNT : CDCL3
 SPINNT : 11 Hz
 TEMP : 23.8 C

