Supporting Information

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

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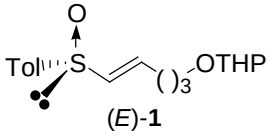
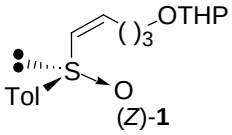
General Methods. Optical rotations were measured using a JASCO DIP-360 digital polarimeter. ^{1}H-NMR spectra were recorded in a $CDCl_3$ solution using a JEOL JNM-LA-500 (500 MHz) spectrometer. ^{13}C-NMR spectra were recorded in a $CDCl_3$ solution using a JEOL JNM-EX270 (68 MHz) spectrometer, a JEOL 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.



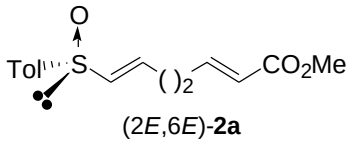
(*E*)-**1**



(*Z*)-**1**

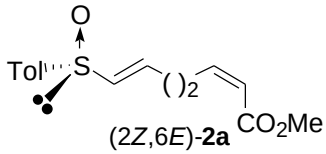
(*R*)-[(*E*)-5-(Tetrahydro-2*H*-pyran-2-yloxy)-1-pentenyl] *p*-Tolyl Sulfoxide [(*E*)-1] and (*R*)-[(*Z*)-5-(Tetrahydro-2*H*-pyran-2-yloxy)-1-pentenyl] *p*-Tolyl Sulfoxide [(*Z*)-1] (*E*)-**1:** $[\alpha]^{26}_{D}$ +93.0 (*c* 0.85, $CHCl_3$). ^{1}H NMR δ: 1.48–1.83 (8H, m), 2.30–2.36 (2H, m), 2.40 (3H, 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 $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84; S, 10.39. Found: C, 66.39; H, 7.77; S, 10.25. (*Z*)-**1:** $[\alpha]^{26}_{D}$ –231.0 (*c* 0.84, $CHCl_3$). ^{1}H 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.



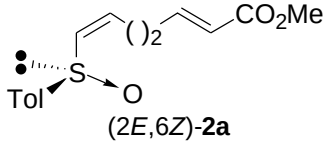
(2*E*,6*E*)-**2a**

Methyl (2*E*,6*E*)-7-[(*R*)-(*p*-Tolylsulfinyl)]-2,6-heptadienoate [(2*E*,6*E*)-2a] $[\alpha]^{26}_D$ +115.1 (*c* 0.85, $CHCl_3$). ^1H NMR δ: 2.36–2.43 (7H, m, Ar-C<u>H</u>$_3$), 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 H), 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.



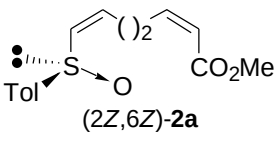
(2*Z*,6*E*)-**2a**

Methyl (2*Z*,6*E*)-7-[(*R*)-(*p*-Tolylsulfinyl)]-2,6-heptadienoate [(2*Z*,6*E*)-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.



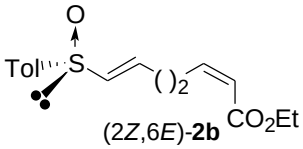
(2*E*,6*Z*)-**2a**

Methyl (2*E*,6*Z*)-7-[(*R*)-(*p*-Tolylsulfinyl)]-2,6-heptadienoate [(2*E*,6*Z*)-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.



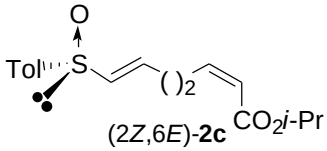
(2*Z*,6*Z*)-**2a**

Methyl (2*Z*,6*Z*)-7-[(*R*)-(*p*-Tolylsulfinyl)]-2,6-heptadienoate [(2*Z*,6*Z*)-2a] $[\alpha]^{26}_{D}$ –221.1 (*c* 0.49, $CHCl_3$). ^{1}H 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 $C_{15}H_{18}O_3S$ (M^+): 278.0976. Found: 278.0950.



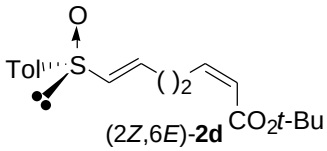
(2*Z*,6*E*)-**2b**

Ethyl (2*Z*,6*E*)-7-[(*R*)-(*p*-Tolylsulfinyl)]-2,6-heptadienoate [(2*Z*,6*E*)-2b] $[\alpha]^{25}_{D}$ +70.4 (*c* 3.15, $CHCl_3$). ^{1}H 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 $C_{16}H_{21}O_3S$ (MH^+): 293.1212. Found: 293.1212.



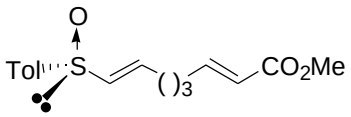
(2*Z*,6*E*)-**2c**

Isopropyl (2*Z*,6*E*)-7-[(*R*)-(*p*-Tolylsulfinyl)]-2,6-heptadienoate [(2*Z*,6*E*)-2c] $[\alpha]^{26}_{D}$ +34.4 (*c* 0.52, $CHCl_3$). ^{1}H 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 $C_{17}H_{23}O_3S$ (MH^+): 307.1368. Found: 307.1355.



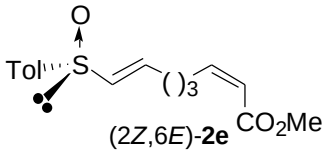
(2*Z*,6*E*)-**2d**

***tert*-Butyl (2*Z*,6*E*)-7-[(*R*)-(*p*-Tolylsulfinyl)]-2,6-heptadienoate [(2*Z*,6*E*)-2d]** $[\alpha]^{24}_{D}$ +37.3 (*c* 0.66, $CHCl_3$). ^{1}H 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 $C_{18}H_{25}O_3S$ (MH^+): 321.1524. Found: 321.1518.



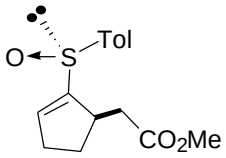
(2*E*,6*E*)-**2e**

Methyl (2*E*,7*E*)-8-[(*R*)-(*p*-Tolylsulfinyl)]-2,7-octadienoate [(2*E*,7*E*)-2e] $[\alpha]^{26}_{D}$ +106.0 (*c* 0.85, $CHCl_3$). ^{1}H 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 $C_{16}H_{20}O_3S$ (M^+): 292.1133. Found: 292.1131.

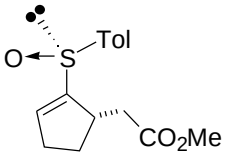


(2*Z*,6*E*)-**2e**

Methyl (2*Z*,7*E*)-8-[(*R*)-(*p*-Tolylsulfinyl)]-2,7-octadienoate [(2*Z*,7*E*)-2e] $[\alpha]^{26}_{D}$ +82.4 (*c* 0.90, $CHCl_3$). ^{1}H 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 H), 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 $C_{16}H_{20}O_3S$ (M^+): 292.1133. Found: 292.1135.



3a

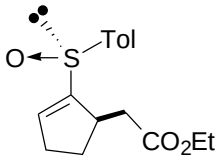


3b

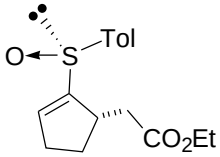
General Procudure of Intramolecular Michael Addition

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 (2*E*,6*E*)-**2** (47 mg, 0.17 mmol) in dry THF (1 mL) was added to a solution of LDA [prepared from *i*-Pr_2NH (38 μL, 0.27 mmol) and 1.60 M *n*-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**: $[\alpha]^{27}_{D}$ +94.7 (*c* 0.50, $CHCl_3$). ^{1}H 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 $C_{15}H_{19}O_3S$ (MH^+): 279.1055. Found: 279.1081. **3b**: $[\alpha]^{27}_{D}$ +90.8 (*c* 0.60, $CHCl_3$). ^{1}H 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 $C_{15}H_{19}O_3S$ (MH^+): 279.1055. Found: 279.1049.

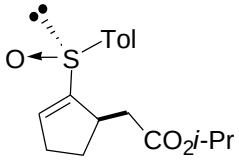


4a

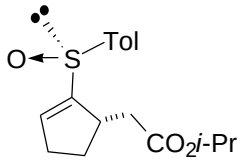


4b

Ethyl [(1*R*)-2-[(*R*)-(*p*-Tolylsulfinyl)]-2-cyclopentenyl]acetate (4a) and Ethyl [(1*S*)-2-[(*R*)-(*p*-Tolylsulfinyl)]-2-cyclopentenyl]acetate (4b) 4a: $[\alpha]^{27}_D$ +86.2 (*c* 0.66, $CHCl_3$). ^{1}H 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 $C_{16}H_{21}O_3S$ (MH^+): 293.1211. Found: 293.1252. **4b**: $[\alpha]^{26}_D$ +72.8 (*c* 0.51, $CHCl_3$). ^{1}H 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 $C_{16}H_{21}O_3S$ $(MH)^+$: 293.1211. Found: 293.1217.



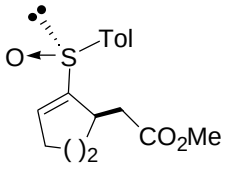
5a



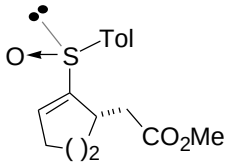
5b

Isopropyl [(1*R*)-2-[(*R*)-(*p*-Tolylsulfinyl)]-2-cyclopentenyl]acetate (5a) and Isopropyl [(1*S*)-2-[(*R*)-(*p*-Tolylsulfinyl)]-2-cyclopentenyl]acetate (5b) 5a: $[\alpha]^{27}_D$ +45.5 (*c* 0.43, $CHCl_3$). ^{1}H 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 $C_{17}H_{23}O_3S$ (MH^+): 307.1368. Found: 308.1357. **5b**: $[\alpha]^{26}_D$ +71.3 (*c* 0.41, $CHCl_3$). ^{1}H 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 $C_{17}H_{23}O_3S$ (MH^+): 307.1368.

Found: 307.1362.

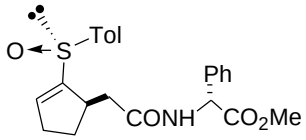


7a



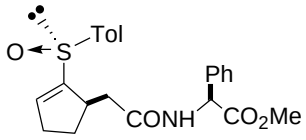
7b

Methyl [(1*R*)-2-[(*R*)-(*p*-Tolylsulfinyl)]-2-cyclohexenyl]acetate (7a) and Methyl [(1*S*)-2-[(*R*)-(*p*-Tolylsulfinyl)]-2-cyclohexenyl]acetate (7b) 7a: $[\alpha]^{26}_{D}$ +110.4 (*c* 1.91, $CHCl_3$). ^{1}H 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 $C_{16}H_{21}O_3S$ (MH^+): 293.1212. Found: 293.1198. **7b**: $[\alpha]_D^{23}$ –0.4 (*c* 2.11, $CHCl_3$). ^{1}H 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 $C_{16}H_{21}O_3S$ (MH^+): 293.1212. Found: 293.1216.



8: (*R*)-PGME amide

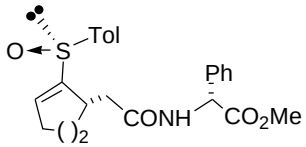
***N*-[(1*R*)-2-[(*R*)-(*p*-Tolylsulfinyl)]-2-cyclopentenyl]acetyl-D-2-phenylglycine Methyl Ester [(*R*)-PGME amide 8]** $[\alpha]^{27}_{D}$ –120.7 (*c* 0.74, $CHCl_3$). ^{1}H NMR δ: 1.93–2.01 (2H, m), 2.15–2.23 (1H, m), 2.29 (1H, dd, *J*=12.8, 3.7 Hz), 2.41 (3H, s), 2.78 (1H, dd, *J*=12.8, 5.5 Hz), 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 $C_{23}H_{26}NO_4S$ (MH^+): 412.1583. Found: 293.1577.



8: (*S*)-PGME amide

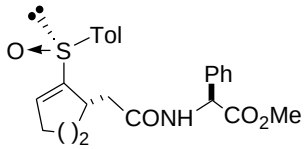
***N*-[(1*R*)-2-[(*R*)-(*p*-Tolylsulfinyl)]-2-cyclopentenyl]acetyl-L-2-phenylglycine Methyl Ester [(*S*)-PGME amide 8]** $[\alpha]^{27}_{D}$ +121.7 (*c* 0.49, $CHCl_3$). ^{1}H NMR δ: 2.10 (2H, dt, *J*=7.9, 7.3 Hz), 2.33 (1H, dd, *J*=13.0, 4.3 Hz), 2.35–2.46 (1H, m), 2.41 (3H, s), 2.62–2.71 (1H, m), 2.78 (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 $C_{23}H_{26}NO_4S$ (MH^+): 412.1583. Found: 412.1582.



9: (*R*)-PGME amide

***N*-[(1*R*)-2-[(*R*)-(*p*-Tolylsulfinyl)]-2-cyclohexenyl]acetyl-D-2-phenylglycine Methyl Ester [(*R*)-PGME amide 9]** $[\alpha]^{27}_D$ –33.9 (*c* 0.89, $CHCl_3$). ^{1}H 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 $C_{24}H_{28}NO_4S$ (MH^+): 426.1739. Found: 426.1734.



9: (*S*)-PGME amide

***N*-[(1*R*)-2-[(*R*)-(*p*-Tolylsulfinyl)]-2-cyclohexenyl]acetyl-L-2-phenylglycine Methyl Ester [(*S*)-PGME amide 9]** $[\alpha]^{26}_D$ +142.6 (*c* 1.69, $CHCl_3$). ^{1}H 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 $C_{24}H_{28}NO_4S$ (MH^+): 426.1739. Found: 426.1759.

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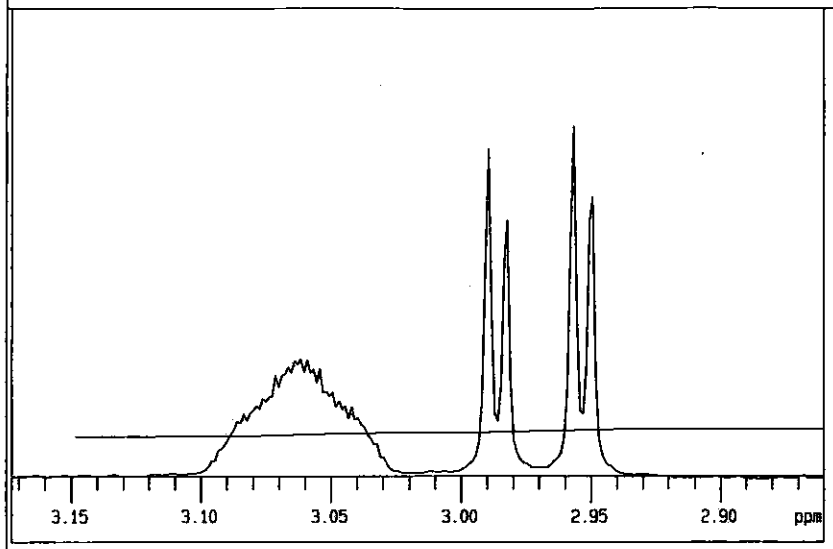

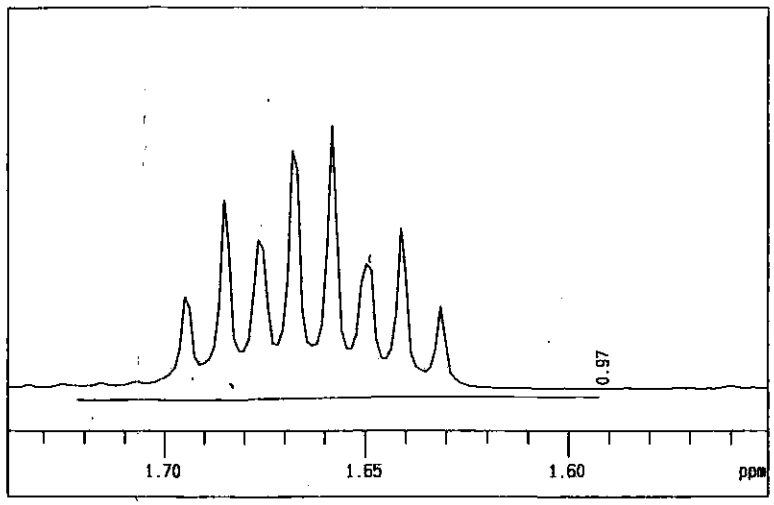

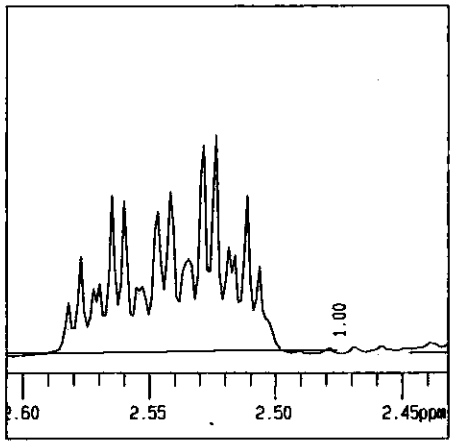

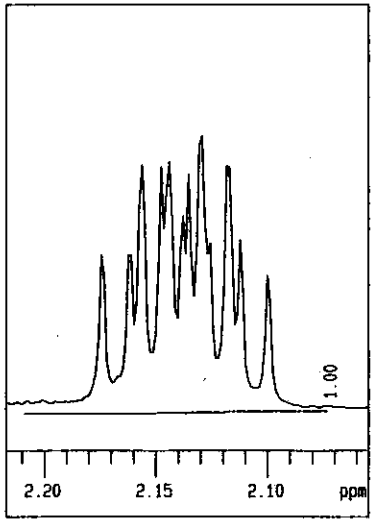

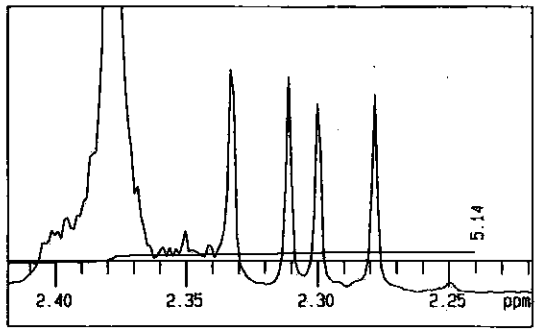

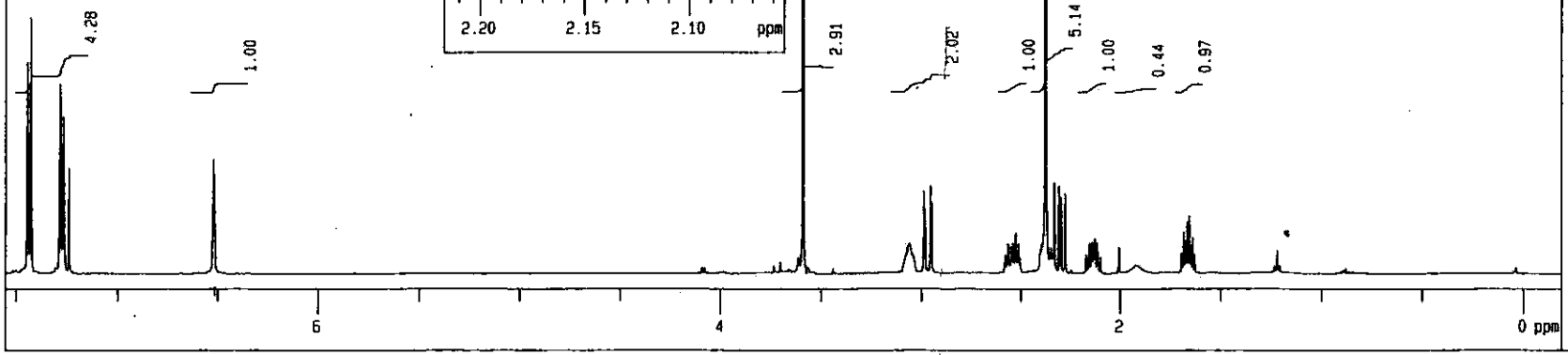

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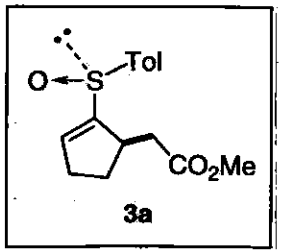

3a

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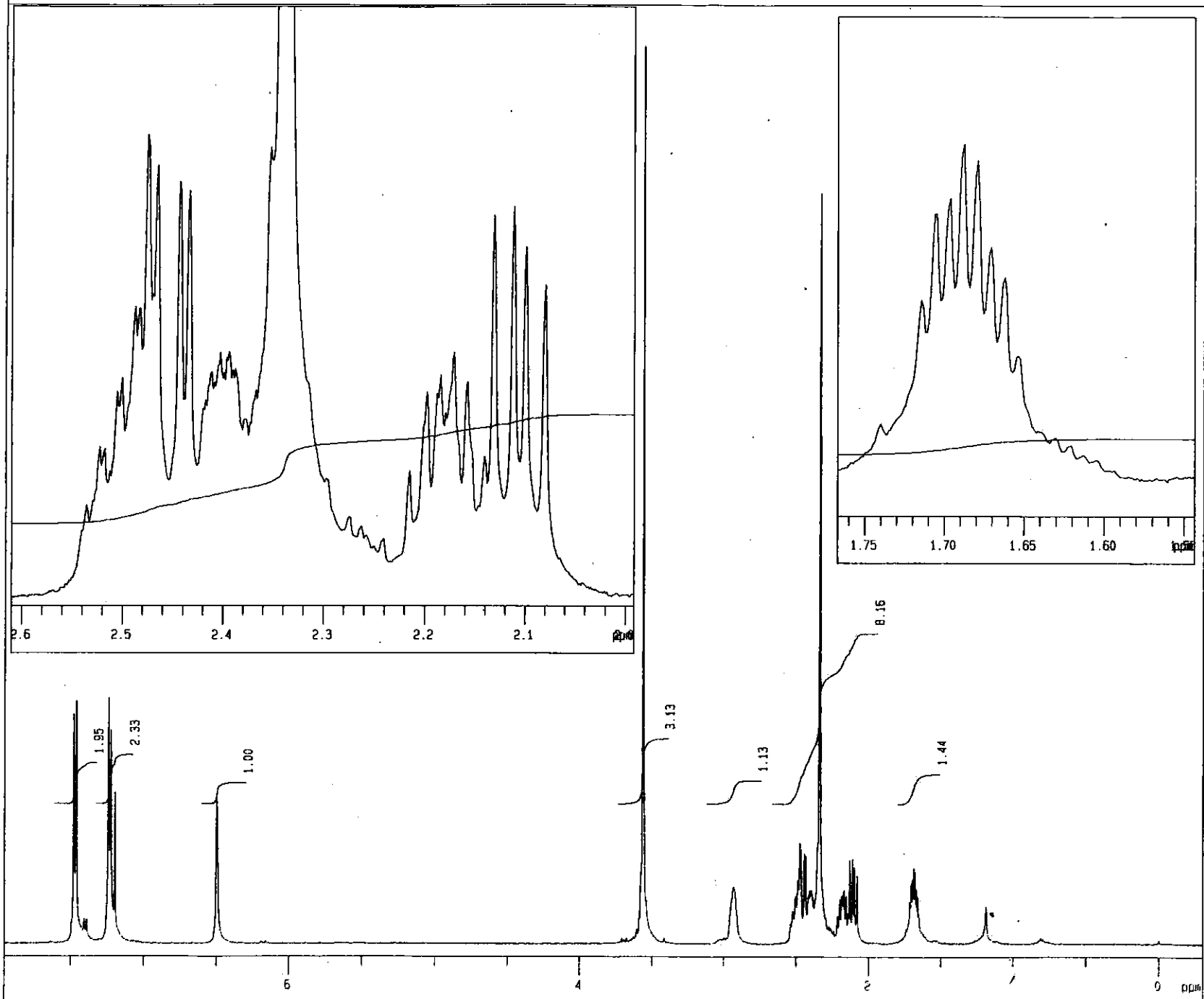

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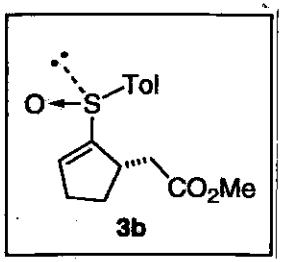

3b

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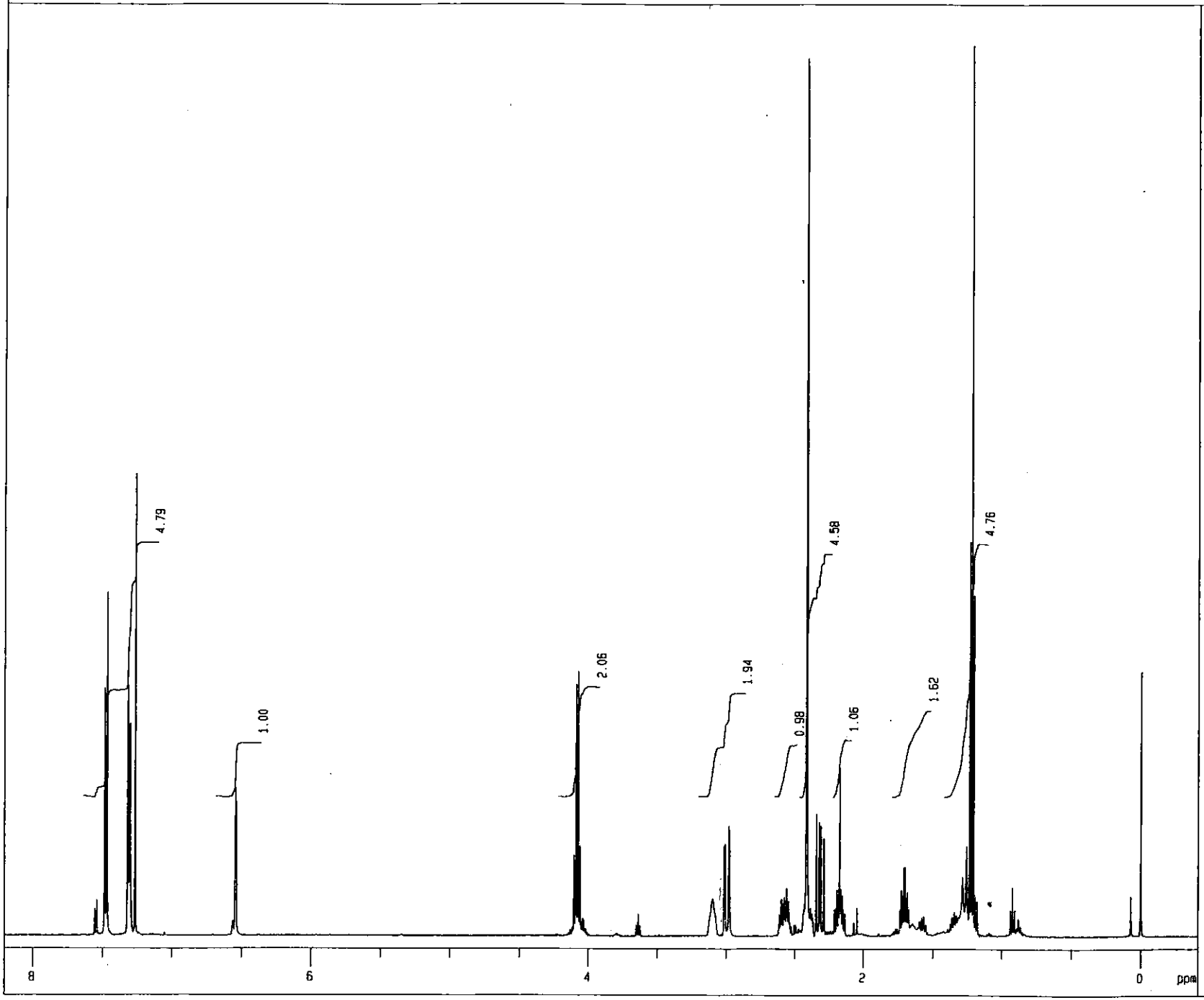

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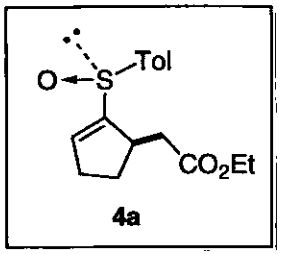

4a

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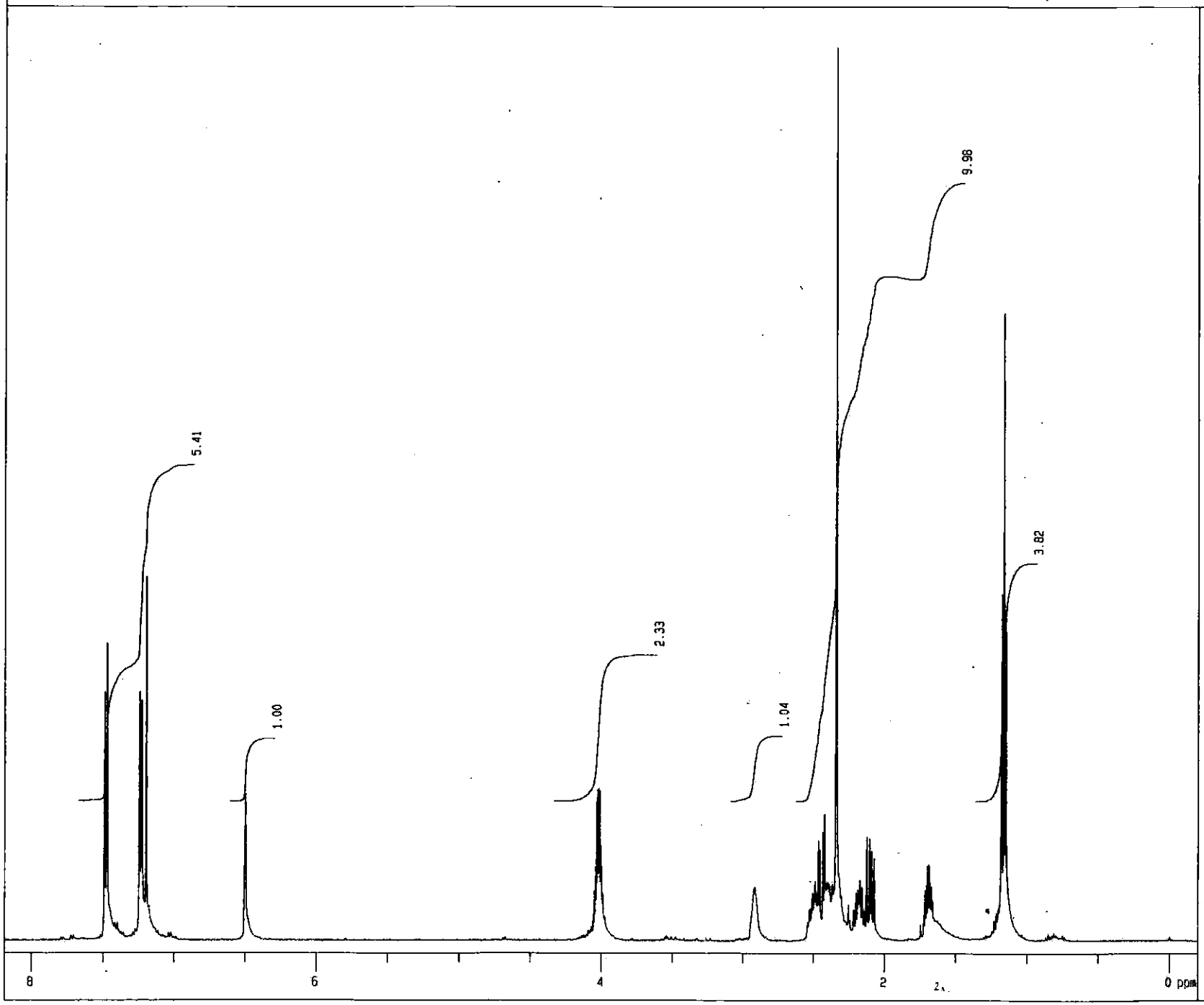

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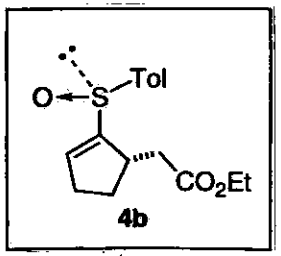
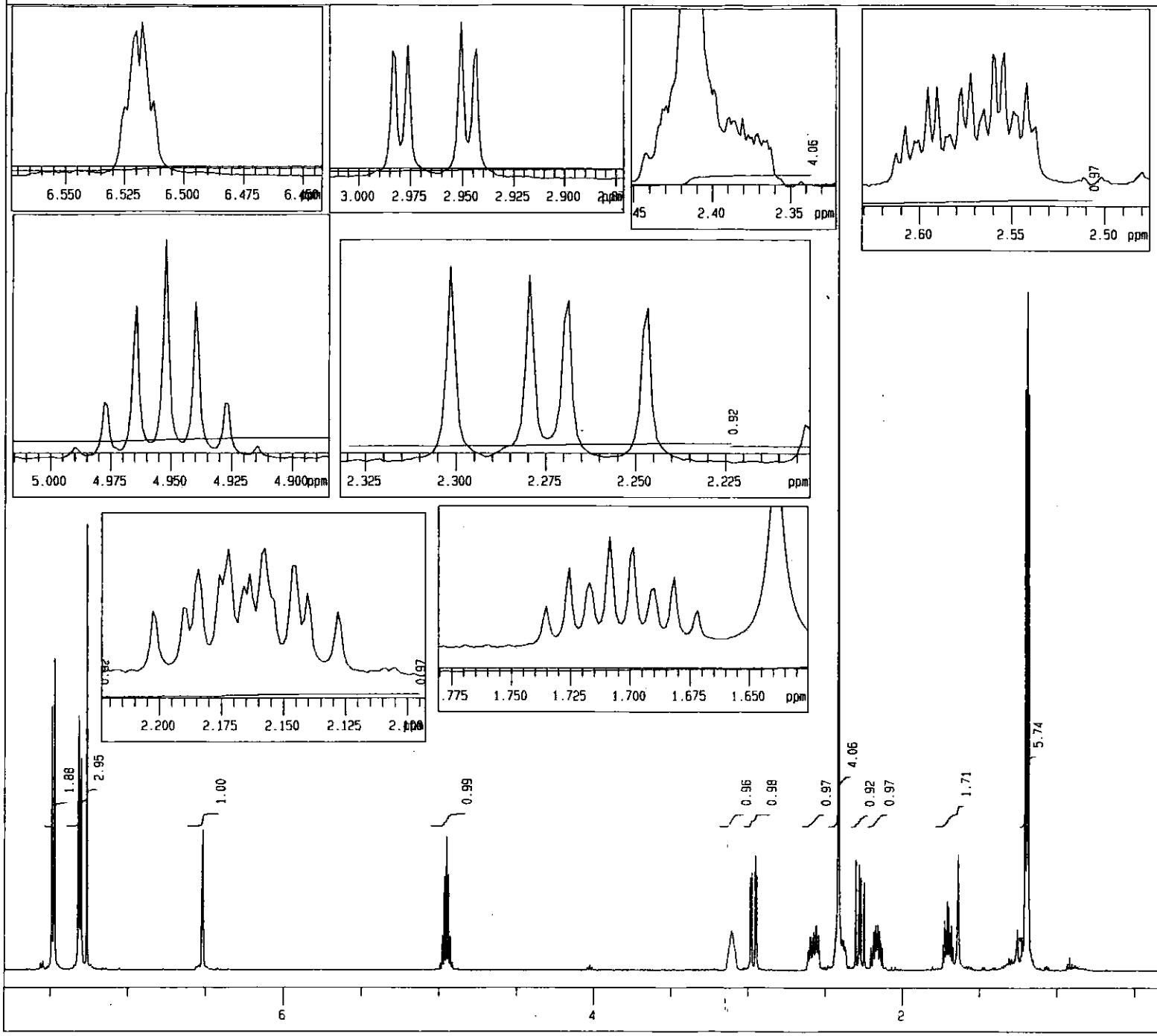
SCANS	:	16 times
SLVNT	:	CDCL3
SPINNING	:	12 Hz
TEMP	:	20.0 C



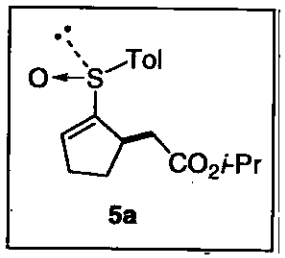
4b

1H Line



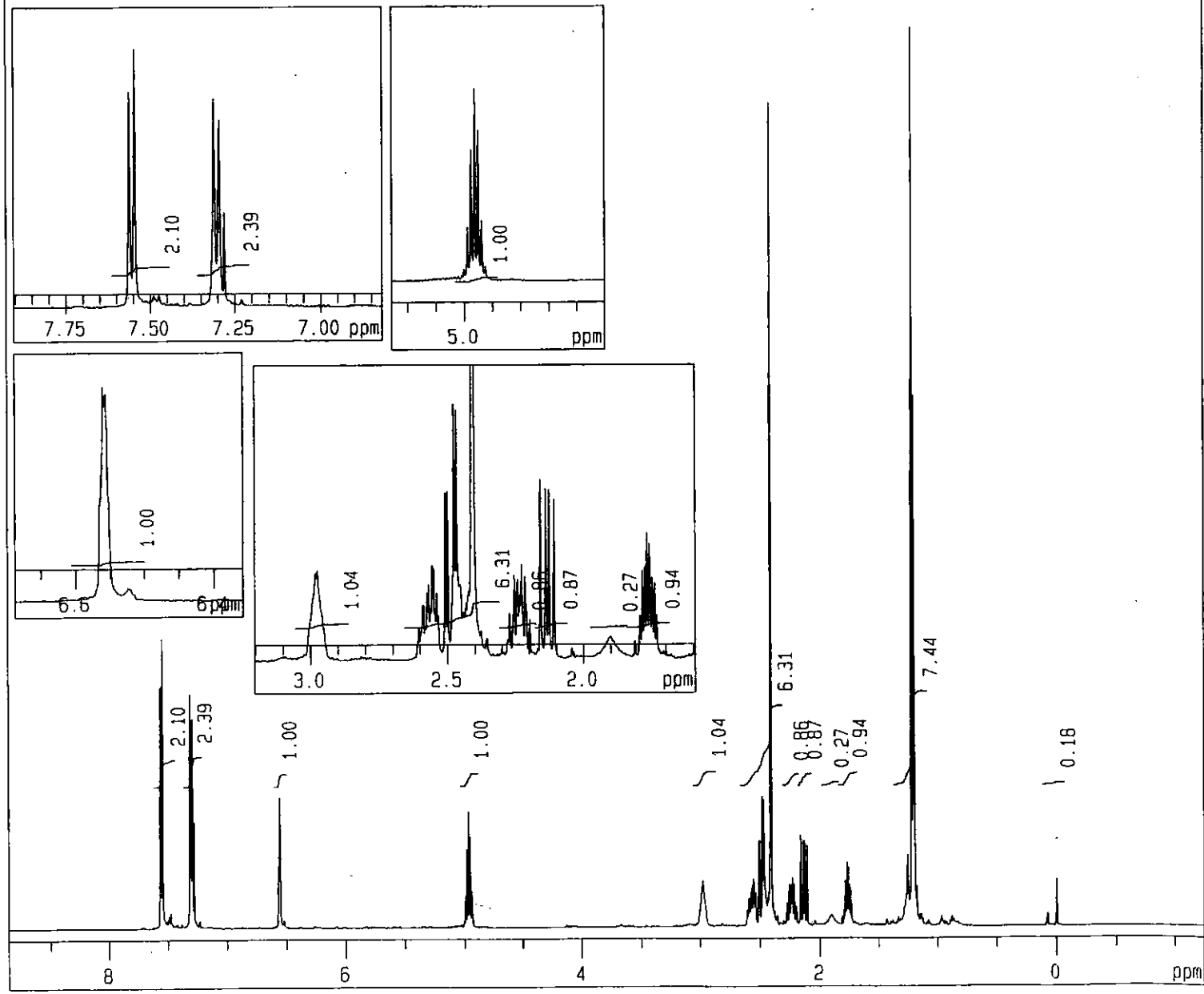
Date : Wed Jan 12 17:39:39 2000

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	non
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
ACQTM	:	1638.3999 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.61 Hz
PW1	:	2.63 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162167.63 Hz
RGAIN	:	22
SCANS	:	16 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	25.4 C



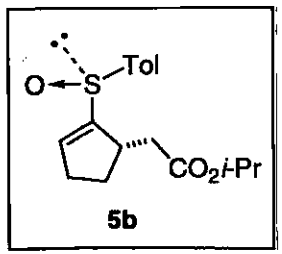
5a

1H Line

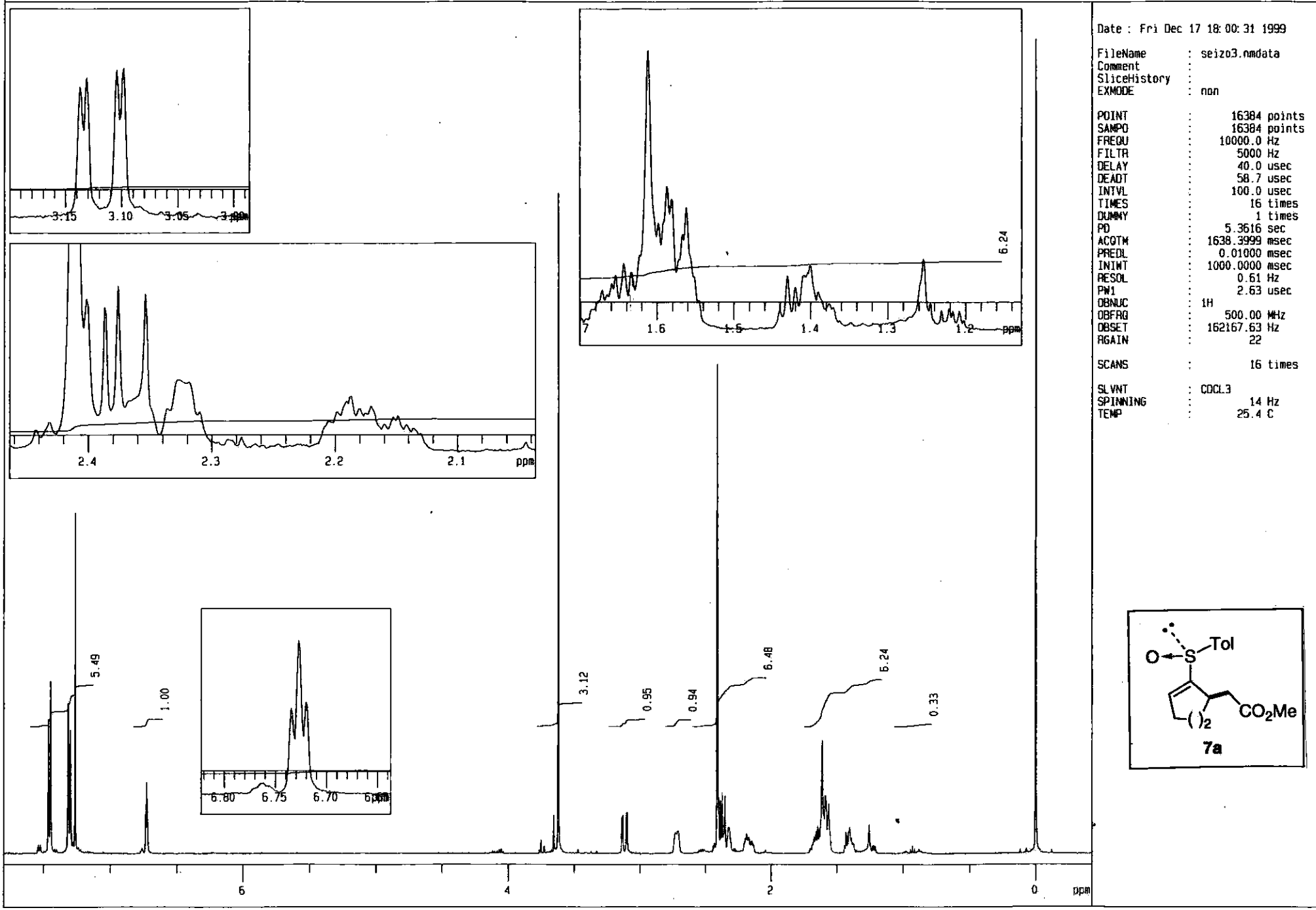


Date : Wed Sep 6 15:12:10 2000

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	non
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
ACQTM	:	1638.3999 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.61 Hz
PW1	:	2.63 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162167.63 Hz
RGAIN	:	19
SCANS	:	16 times
SLVNT	:	CDCL3
SPINNING	:	14 Hz
TEMP	:	23.0 C



5b

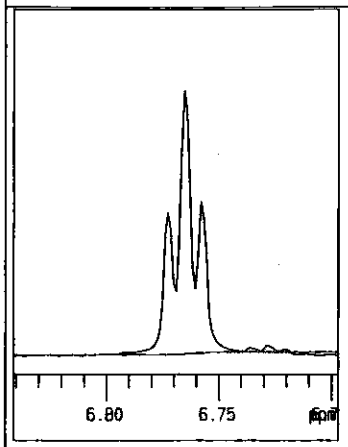


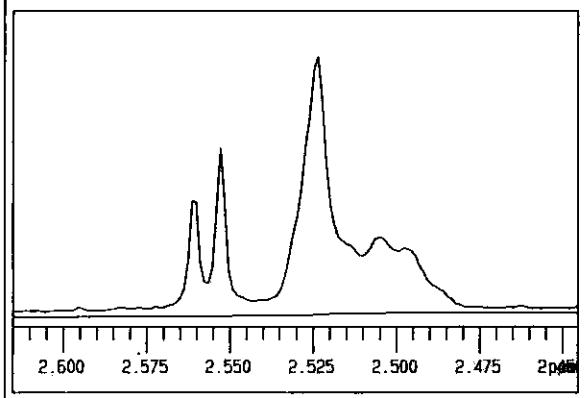
Date : Fri Dec 17 18:00:31 1999

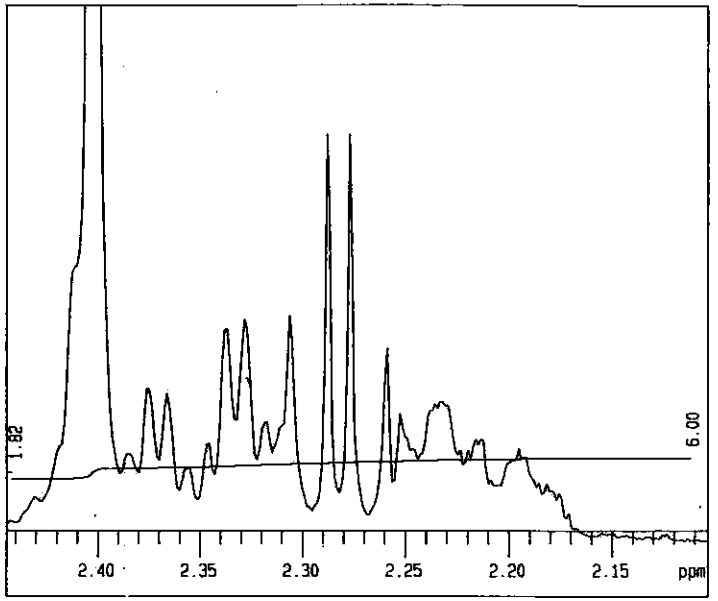
FileName	:	seizo3.nmdata
Comment	:	
SliceHistory	:	
EXMODE	:	non
POINT	:	16384 points
SAMPO	:	16384 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	58.7 usec
INTVL	:	100.0 usec
TIMES	:	16 times
DUMMY	:	1 times
PD	:	5.3616 sec
ACQTM	:	1638.3999 msec
PREDL	:	0.01000 msec
ININT	:	1000.0000 msec
RESOL	:	0.61 Hz
PW1	:	2.63 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162167.63 Hz
RGAIN	:	22
SCANS	:	16 times
SLVNT	:	CDCL3
SPINNING	:	14 Hz
TEMP	:	25.4 C

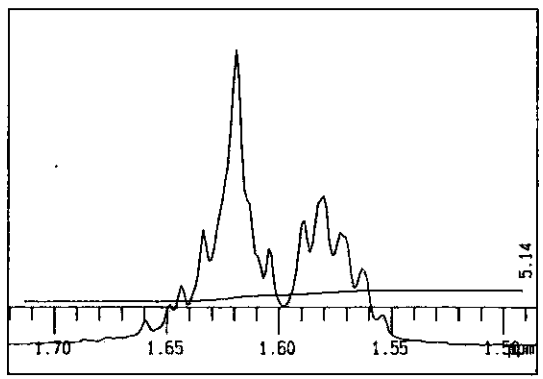
7a

1H Line



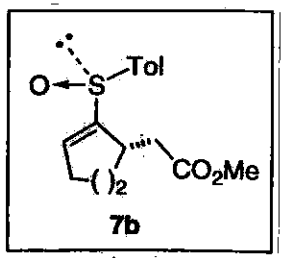






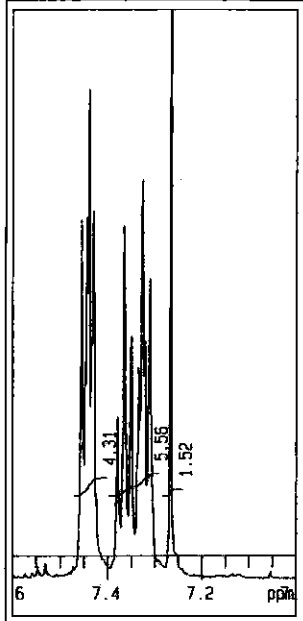
Date : Fri Dec 17 18:10:07 1999

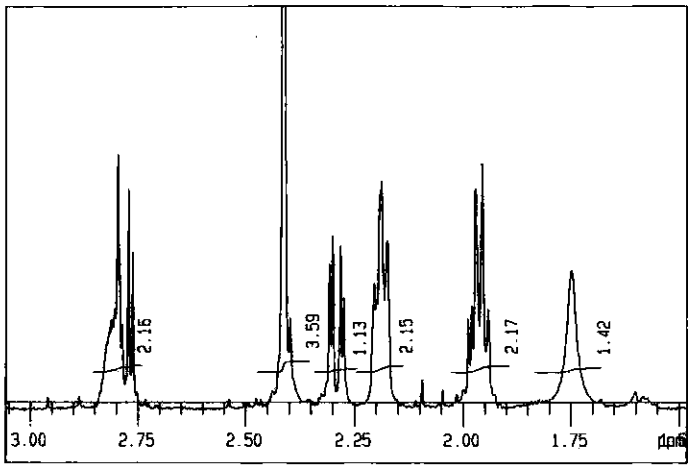
FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	non
POINT	:	16384 points
SAMPO	:	16384 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	58.7 usec
INTVL	:	100.0 usec
TIMES	:	16 times
DUMMY	:	1 times
PD	:	5.3616 sec
ACQTM	:	1638.3999 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.61 Hz
PW1	:	2.63 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162167.63 Hz
RGAIN	:	22
SCANS	:	16 times
SLVNT	:	CDCL3
SPINNING	:	14 Hz
TEMP	:	25.5 C

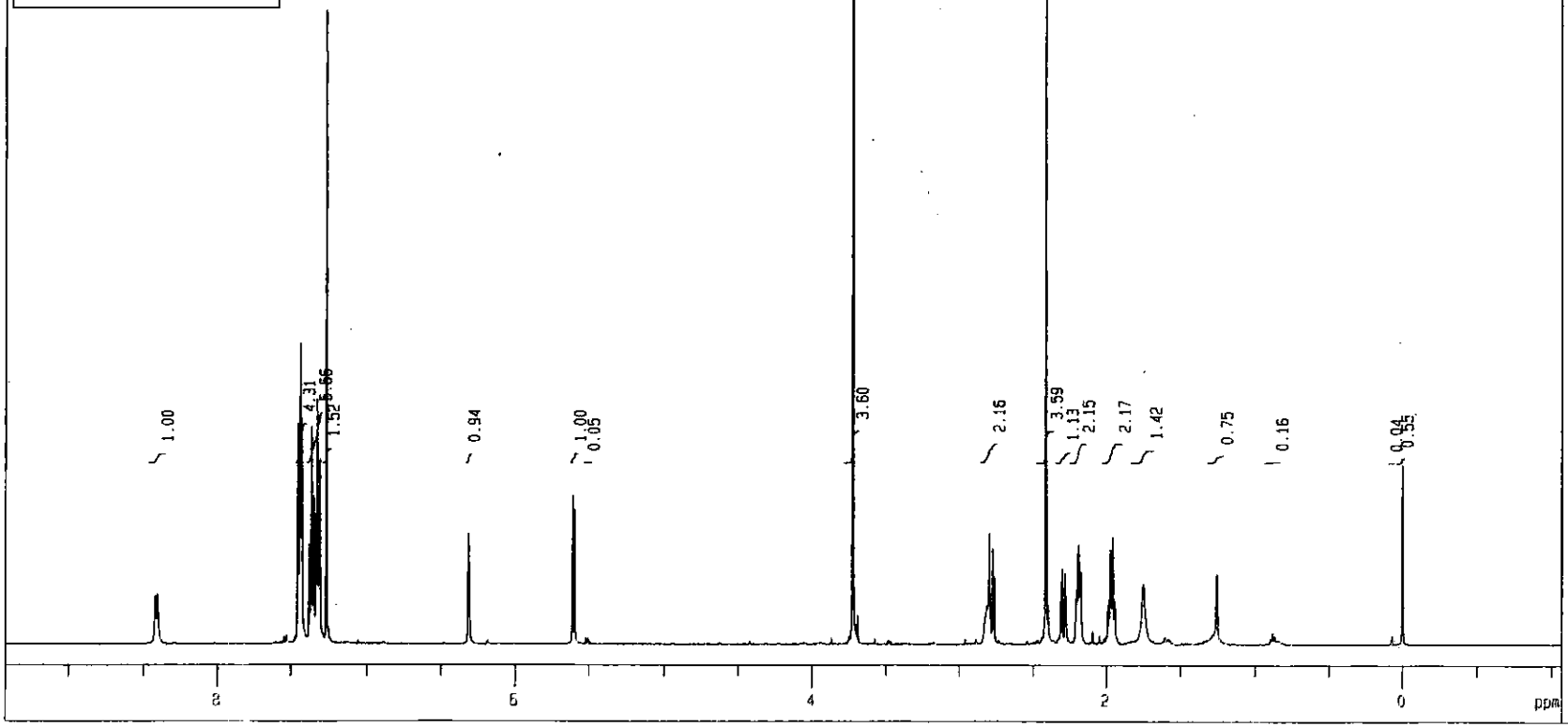


7b

1H Line

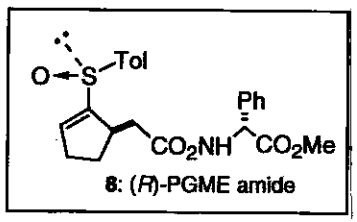






Date : Wed Sep 6 14:42:29 2000

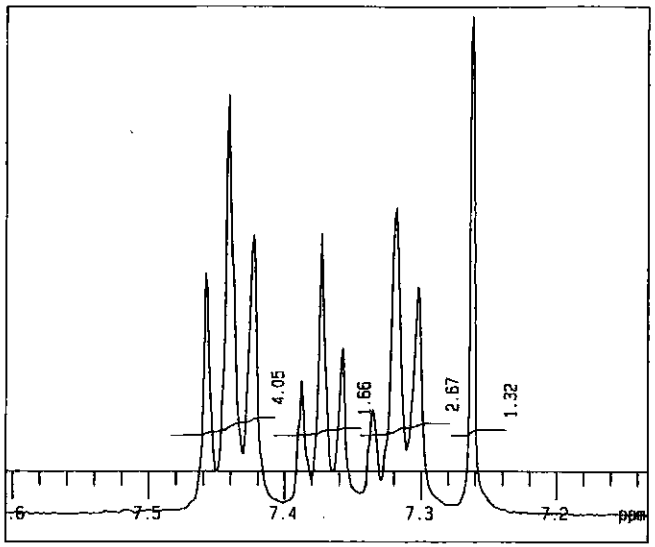
FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	non
POINT	:	16384 points
SAMPO	:	16384 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	58.7 usec
INTVL	:	100.0 usec
TIMES	:	16 times
DUMMY	:	1 times
PD	:	5.3616 sec
ACQTM	:	1638.3999 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.61 Hz
PW1	:	2.63 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162167.63 Hz
RGAIN	:	23
SCANS	:	16 times
SLVNT	:	CDCL3
SPINNING	:	11 Hz
TEMP	:	22.9 C

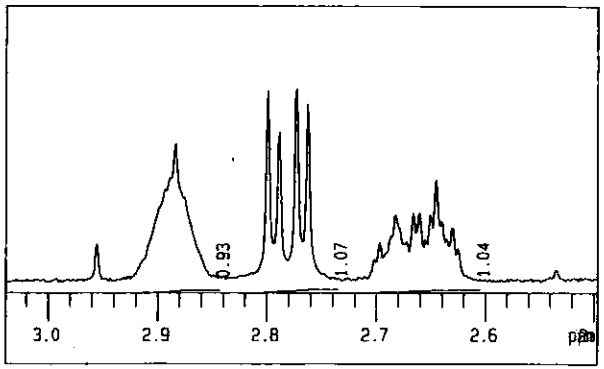


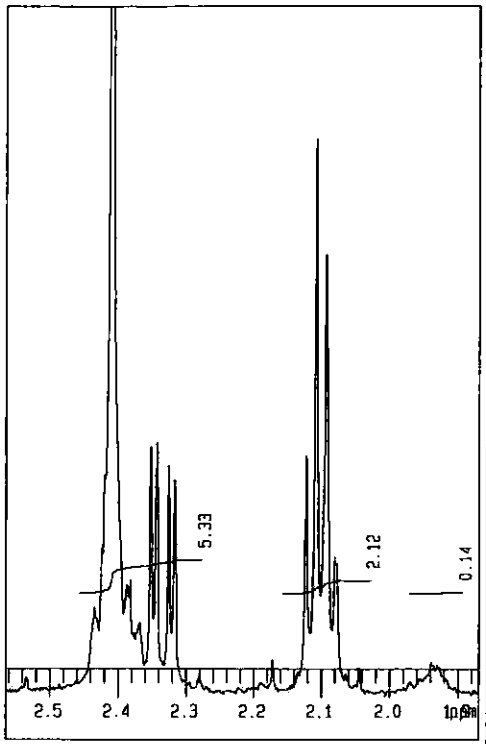
8: (*R*)-PGME amide

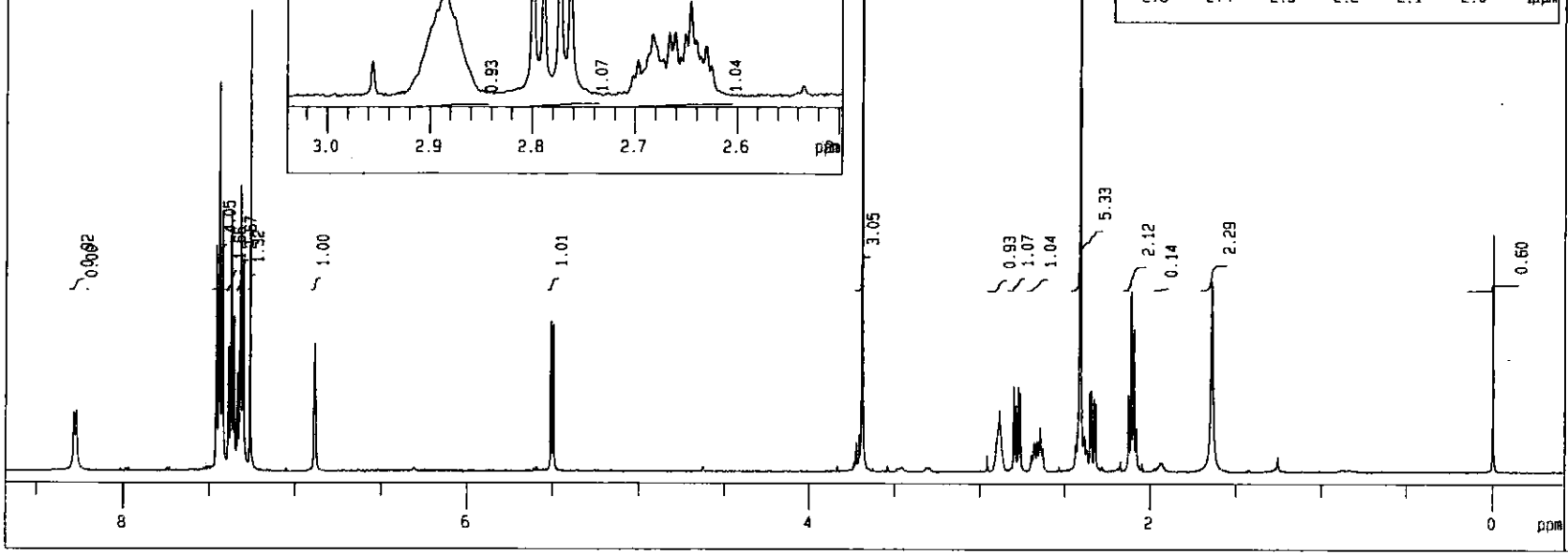
PGME 5 (S)

1H Line



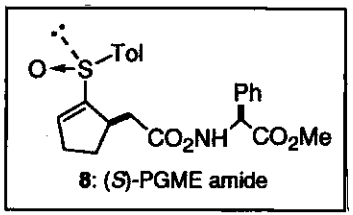






Date : Wed Sep 27 10:57:58 2000

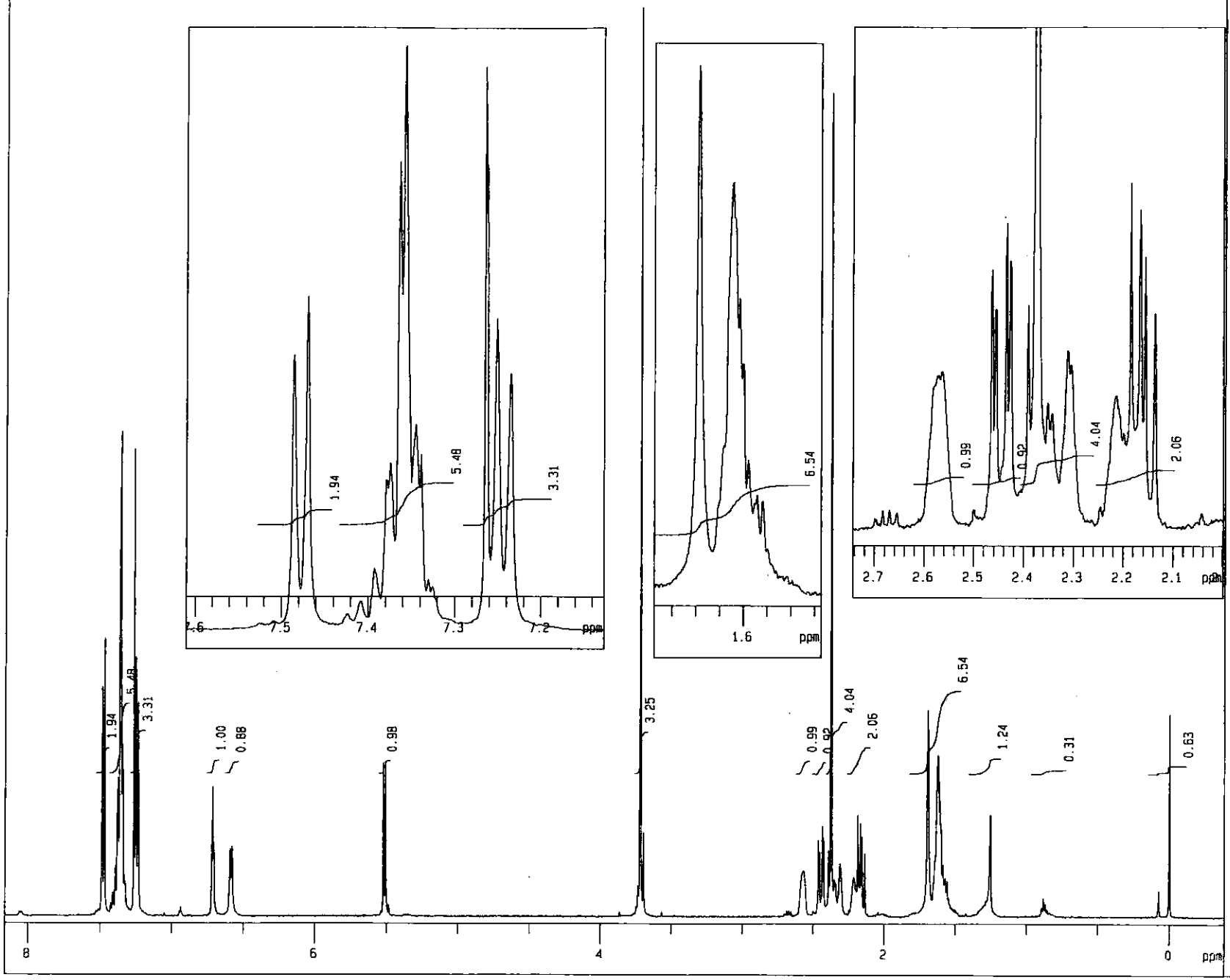
FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	non
POINT	:	16384 points
SAMPO	:	16384 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	58.7 usec
INTVL	:	100.0 usec
TIMES	:	16 times
DUMMY	:	1 times
PD	:	5.3616 sec
ACQTM	:	1638.3999 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.61 Hz
PW1	:	2.63 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162167.63 Hz
RGAIN	:	24
SCANS	:	16 times
SLVNT	:	CDCL3
SPINNING	:	11 Hz
TEMP	:	23.8 C



8: (*S*)-PGME amide

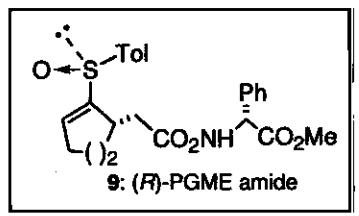
6 PGME (R)

1H Line



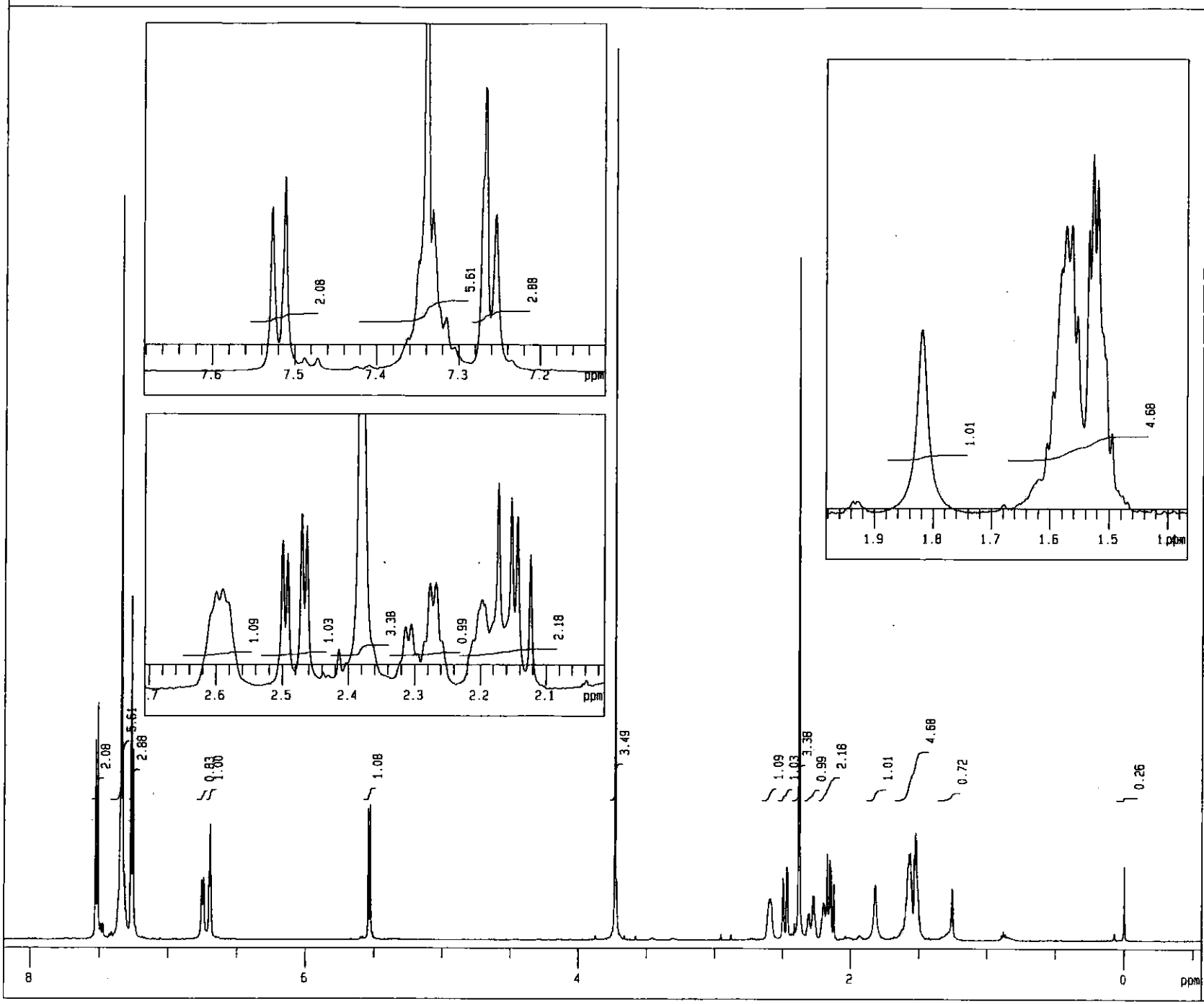
Date : Wed Sep 27 10:39:49 2000

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	non
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
ACQTM	:	1638.3999 msec
PREDL	:	0.01000 msec
ININT	:	1000.0000 msec
RESOL	:	0.61 Hz
PW1	:	2.63 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162167.63 Hz
RGAIN	:	22
SCANS	:	16 times
SLVNT	:	CDCL3
SPINNING	:	13 Hz
TEMP	:	23.7 C



9: (*R*)-PGME amide

1H Line



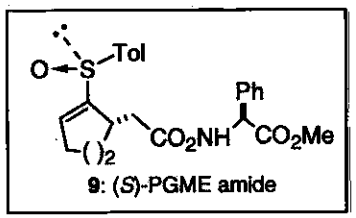

```
Date : Wed Sep 27 10:48:57 2000

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

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
ACQTM          :  1638.3999 msec
PREDL          :    0.01000 msec
INIWT          :  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
SPINNING       :         11 Hz
TEMP           :       23.8 C
```



9: (*S*)-PGME amide