Strategies for the Generation of Molecularly Imprinted Polymeric Nitroxide Catalysts

Christopher D. Anderson, Kenneth J. Shea* and Scott D. Rychnovsky*

Department of Chemistry, 516 Rowland Hall, University of California, Irvine, CA 92697-2025

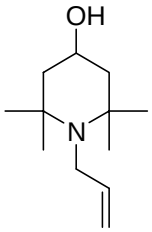
srychnov@uci.edu

Table of Contents

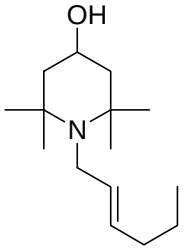
A. General Experimental Details: IR spectra were recorded on a MIDAC Prospect FT-IR spectrometer. ^{1}H NMR were recorded at 500 and 400 MHz and ^{13}C spectra were recorded at 125 and 100 MHz on Bruker instruments. ^{1}H NMR and ^{13}C chemical shifts are reported as δ values in ppm relative to TMS. ^{1}H NMR coupling constants are reported in hertz and refer to apparent multiplicities and not true coupling constants. Muliplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), etc. EPR spectra were obtained using Bruker instruments at ambient temperature. Optical rotations were determined on a JASCO DIP-370 digital polarimeter; concentration *c* is reported as g/100 mL. Combustion analyses were performed by M-H-W laboratories, Phoenix, AZ. Mass spectra were determined on an Fisions autospec spectrometer or a Micromass LCT electrospray mass spectrometer. Tetrahydrofuran (THF), Et_2O and CH_2Cl_2 were dried by filtration through alumina according to the procedure described by Grubbs.[1] Pyridine and triethyl amine were distilled from KOH. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on Sorbent Technologies silica gel (230-450 mesh).[2] Moisture sensitive reactions were carried out under an atmosphere of argon using oven or flame dried glassware and standard syringe/septa techniques.

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
[2] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

B. Template Synthesis

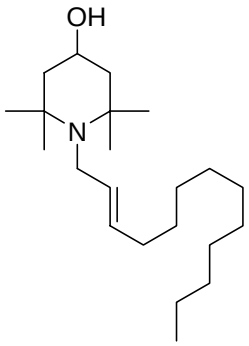


4-Hydroxy-1-(2-propenyl)-2,2,6,6-tetramethylpiperidine (S1). To a mixture of 4-hydroxy-2,2,6,6-tetramethylpiperidine (5.0 g, 39 mmol) and toluene (13 mL) in a heavy-walled tube was added allyl bromide (1.59 mL, 19.6 mmol). The tube was sealed and placed in a 130 °C oil bath for 46 h. The resultant mixture was cooled to ambient temperature, diluted with hexanes (10 mL) and was purified by flash chromatography (SiO_2, 20:80 ethyl acetate:hexanes) to yield 2.8 g (73% yield) of **S1** as a white solid. m.p. 89–90 °C; 1H NMR (500 MHz, CDCl3) 5.79–5.88 (m, 1 H), 5.12–5.16 (m, 1 H), 4.91–4.95 (m, 1 H), 3.94–4.00 (m, 1 H), 3.13–3.14 (m, 2 H), 1.82 (dd, *J* = 4.1, 12.1, 2 H), 1.36 (t, *J* = 11.5, 2 H), 1.08 (s, 6 H), 1.04 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) 143,3, 113.2, 64.5, 56.6, 50.6, 46.4, 34.4, 22.7; IR (film) 3290 (br), 2932, 1458, 1036 cm^{-1}; HRMS (CI/NH_3) Calcd for $C_{12}H_{23}NO$ (M^+) 197.1775, Found: 197.1780; Anal. Calcd for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.10. Found: C, 73.20; H, 11.76; N, 7.29.

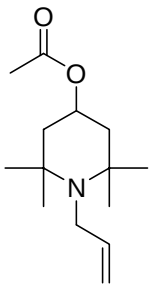


4-Hydroxy-1-(*E*-2-hexenyl)-2,2,6,6-tetramethylpiperidine (7). To a mixture of 4-hydroxy-2,2,6,6-tetramethylpiperidine (3.5 g, 22 mmol) and toluene (5 mL) in a heavy-walled tube was added *E*-1-bromo-2-hexene (1.8 g, 11 mmol). The tube was sealed and the reaction mixture heated at 150 °C for 45 h. The black reaction mixture was then cooled to ambient temperature and purified by flash chromatography (SiO_2, 20:80 ethyl acetate:hexanes → 30:70 ethyl

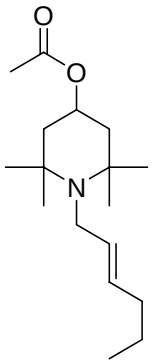
acetate:hexanes) to yield 1.7 g (53% yield) of **7** as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) 5.36–5.48 (m, 2 H), 3.95 (tdt, J = 4.2, 5.5, 11.5, 1 H), 3.07 (d, J = 4.5, 1 H), 1.94 (dt, J = 6.4, 6.8, 2 H), 1.77–1.82 (m, 2 H), 1.31–1.41 (m, 5 H), 1.08 (s, 6 H), 1.02 (s, 6 H), 0.86 (t, J = 7.4, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 134.4, 128.8, 64.0, 56.1, 50.1, 45.3, 34.4, 34.1, 22.6, 22.2, 13.7; IR (film) 3337 (br), 2963, 1462 cm^{-1}; HRMS (CI/NH_3) calcd for $C_{15}H_{29}NO$ (M^+) 239.2249, found: 239.2251.



4-Hydroxy-1-(*E*-2-tridecenyl)-2,2,6,6-tetramethylpiperidine (S2). To a solution of *E*-1-bromo-2-tridecene (4.2 g, 16 mmol) in toluene (125 mL) was added 4-hydroxy-2,2,6,6-tetramethylpiperidine (5.5 g, 35 mmol). The mixture was heated at reflux for 8 d. The reaction mixture was cooled to ambient temperature, diluted with saturated aqueous $NaHCO_3$ (50 mL) and then extracted with ethyl acetate (3 × 25 mL). The combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, 15:85 ethyl acetate:hexanes) to yield 2.8 g (51%) **S2** as an off-white solid. mp 45–47 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 5.34–5.46 (m, 2 H), 3.89–3.97 (m, 1 H), 3.05 (d, J = 4.7, 2 H), 1.91–1.97 (m, 2 H), 1.78 (dd, J = 4.0, 12.1, 2 H), 1.20–1.37 (m, 19 H), 1.07 (s, 6 H), 1.01 (s, 6 H), 0.86 (t, J = 6.9, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 134.1, 129.0, 63.8, 56.0, 50.0, 45.2, 34.1, 32.3, 31.9, 29.59, 29.56, 29.50, 29.46, 29.3, 29.1, 22.6, 22.1, 14.1; IR (film) 3336 (br), 2925, 1462 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{44}NO$ (M + H^+) 338.3423, found: 338.2430.

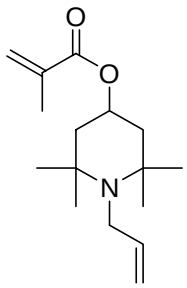


4-Acetoxy-1-(2-propenyl)-2,2,6,6-tetramethylpiperidine (3a). To a solution of amine **S1** (555 mg, 2.81 mmol) and pyridine (455 μL, 5.62 mmol) in CH_2Cl_2 (5 mL) was added Ac_2O (530 μL, 5.6 mmol). The resultant solution was maintained at ambient temperature for 15 h. After this period, the excess reagents were quenched by the addition of saturated aqueous $NaHCO_3$ (5 mL). The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. The resultant oil was purified by flash chromatography (SiO_2, 10:90 ethyl acetate:hexane) to provide 350 mg (52%) of **3a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) 5.83 (tdd, *J* = 5.0, 10.1, 17.1, 1 H), 5.11–5.17 (m, 1 H), 5.07 (tt, *J* = 4.1, 11.6, 1 H), 4.91–4.95 (m, 1 H), 3.12–3.15 (m, 2 H), 3.02 (s, 3 H), 1.79–1.84 (m, 2 H), 1.47 (t, *J* = 11.6, 2 H), 1.079 (s, 6 H), 1.076 (s, 6 H); ^{13}C (125 MHz, $CDCl_3$) 142.7, 112.9, 67.7, 56.0, 45.90, 45.85, 33.7, 22.3, 21.5; IR (film) 2968, 1738, 1244 cm^{-1}; HRMS (ESI), calcd for $C_{14}H_{26}NO_2$ ($M + H^+$) 240.1964, found: 240.1960.



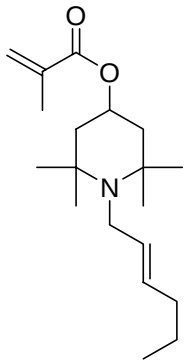
4-Hydroxy-1-(2-hexenyl)-2,2,6,6-tetramethylpiperidine (3b). To a solution of amine **7** (103 mg, 0.430 mmol), DMAP (1 mg) and pyridine (70 μL, 0.9 mmol) in CH_2Cl_2 (2 mL) was added Ac_2O (80 μL, 0.9 mmol). The resultant solution was maintained at ambient temperature for 24 h and then the excess reagents were quenched by addition of saturated aqueous $NaHCO_3$ (3 mL).

The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organics were dried over Na_2SO_4. The organic solution was concentrated under reduced pressure and the residue was purified by flash chromatography (SiO_2, 5:95 ethyl acetate:hexanes → 60:40 ethyl acetate:hexanes) to yield 99 mg (82%) of **3b** as a slightly yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) 5.35–5.55 (m, 2 H), 5.06 (tt, *J* = 4.1, 11.6, 1 H), 3.08 (d, *J* = 4.4, 2 H), 2.02 (s, 3 H), 1.95 (dd, *J* = 6.7, 13.4, 2 H), 1.76–1.83 (m, 2 H), 1.46 (t, *J* = 11.7, 2 H), 1.30–1.41 (m, 2 H), 1.09 (s, 6 H), 1.07 (s, 6 H), 0.87 (t, *J* = 7.4, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 170.7, 134.3, 128.9, 67.8, 56.0, 45.9, 45.2, 34.4, 33.8, 22.6, 22.3, 21.4, 13.6; IR (film) 2965, 1738, 1244 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{32}NO_2$ ($M + H^+$): 282.2433, Found: 282.2436.

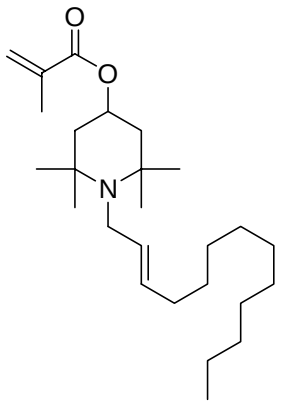


4-Methacryloyloxy-1-(2-propenyl)-2,2,6,6-tetramethylpiperidine (4a). To a chilled solution (0 °C) of hydroxylamine **S1** (501 mg, 2.53 mmol), DMAP (1 mg), pyridine (225 μL, 2.78 mmol) in CH_2Cl_2 (8 mL) was added methacroyl chloride (260 μL, 2.66 mmol). The solution was allowed to warm to ambient temperature over 17 h. After this period, the excess reagents were quenched by the addition of saturated aqueous $NaHCO_3$ (5 mL). The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. The resultant oil was purified by flash chromatography (SiO_2, 10:90 ethyl acetate:hexane) to provide 440 mg (66%) of **4a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) 6.07–6.08 (m, 1 H), 5.84 (tdd, *J* = 5.0, 10.1, 17.1, 1 H), 5.52–5.54 (m, 1 H), 5.11–5.18 (m, 2 H), 4.92–4.96 (m, 1 H), 3.15 (td, *J* = 1.8,4.8, 2 H), 1.82–1.94 (m, 5 H), 1.54 (t, *J* = 11.8, 2H), 1.10 (s, 6 H), 1.09 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.1, 142.7, 136.8, 125.0, 112.9, 68.1, 56.0,

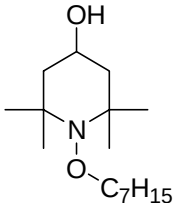
45.9, 45.8, 33.5, 22.5, 18.3; IR (film) 2968, 1715, 1165 cm^{-1}; HRMS (ESI), calcd for $C_{16}H_{28}NO_2$ ($M + H^+$): 266.2120, found: 266.2117.



4-Methacryloyloxy-1-(*E*-2-hexenyl)-2,2,6,6-tetramethylpiperidine (4b). To a 0 °C solution of alcohol **7** (224 mg, 0.936 mmol), NEt_3 (391 μL, 2.81 mmol) and DMAP (9 mg) in CH_2Cl_2 (3 mL) was added methacrylic acid anhydride (279 μL, 1.87 mmol). The solution was allowed to warm to ambient temperature over 14 h. The excess anhydride was quenched by the addition of saturated aqueous $NaHCO_3$ (5 mL). The mixture was extracted with CH_2Cl_2 (3 × 5 mL) and the combined organics were dried over Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, 20:80 ethyl acetate:hexanes) to provide 188 mg (66%) of **4b** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) 6.01 (s, 1 H), 5.53 (t, J = 1.53, 1 H), 5.36–5.50 (m, 2 H), 5.13 (tt, J = 4.2, 11.5, 1 H) 3.08 (d, J = 4.8 Hz, 2 H), 1.95 (dd, J = 6.9, 13.1, 2 H), 1.92 (s, 3 H), 1.84 (dd, J = 4.1, 12.2, 2 H), 1.53 (t, J = 11.6, 2 H), 1.31–1.40 (m, 2 H), 1.10 (s, 6 H), 1.09 (s, 6 H), 0.87 (t, J = 7.3, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.1, 136.8, 134.2, 129.0, 125.0, 68.1, 56.0, 45.8, 45.2, 34.4, 33.7, 22.7, 22.4, 18.3, 13.7; IR (film) 2966, 1716, 1164 cm^{-1}; HRMS (ESI), calcd for $C_{19}H_{34}NO_2$ ($M + H^+$) 308.2589, found: 308.2591.

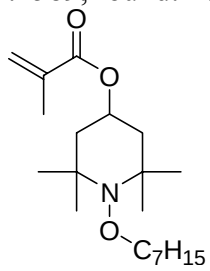


4-Methacryloyloxy-1-(*E*-2-tridecenyl)-2,2,6,6-tetramethylpiperidine (4c). To a solution of alcohol **S2** (212 mg, 0.63 mmol), methacrylic acid (67 mg, 0.78 mmol) and DMAP (1 mg) in CH_2Cl_2 (5 mL) was added DCC (157 mg, 0.76 mmol). The solution was maintained at ambient temperature for 3 h. The mixture was then concentrated under reduced pressure and the alcohol was dissolved in a solution of 20 % ethyl acetate in hexanes (5 mL) and purified by flash chromatography (SiO_2, 20:80 ethyl acetate:hexanes) to provide 204 mg (78%) of **4c** as a slightly yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) 6.07 (s, 1 H), 5.51–5.54 (m, 1 H), 5.36–5.50 (m, 2 H), 5.14 (tt, *J* = 4.1, 11.5, 1 H), 3.09 (d, *J* = 4.4, 1 H), 1.94–1.99 (m, 2 H), 1.93 (s, 3 H), 1.82–1.88 (m, 2 H), 1.53 (t, *J* = 11.6, 2 H), 1.20–1.36 (m, 17 H), 1.10 (s, 6 H), 1.09 (s, 6 H), 0.88 (t, *J* = 6.9, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.1, 136.8, 134.0, 129.2, 125.0, 68.2, 56.0, 45.8, 45.2, 33.7, 32.3, 31.9, 29.63, 29.60, 29.53, 29.50, 29.3, 29.2, 22.7, 22.5, 18.3, 14.1; IR (film) 2925, 1717, 1164 cm^{-1}; HRMS (ESI), calcd for $C_{26}H_{48}NO_2$ ($M + H^+$) 406.3685, found: 406.3684.

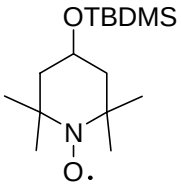


4-Hydroxy-1-(1-heptoxy)-2,2,6,6-tetramethylpiperidine (S3). 4-Hydroxy-2,2,6,6-tetramethylpiperinyloxy (720 mg, 4.2 mmol), 1-iodoheptane (690 mL, 4.2 mmol) and tributyl tin hydride (1.1 mL, 4.2 mmol) were dissolved in C_6H_6 (50 mL) in a quartz flask. The solution was degassed by three freeze-pump-thaw cycles. The solution was irradiated with a Hanovia UV

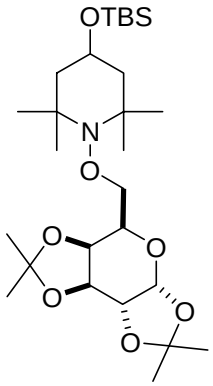
utility lamp (low pressure Hg) for 5 h. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (SiO_2, 15:85 ethyl acetate:hexanes) to yield 540 mg (48%) **S3** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) 3.90–3.98 (m, 1 H), 3.71 (t, J = 6.3 Hz, 2 H), 1.79 (d, J = 9.5 Hz, 2 H), 1.40–1.55 (m, 4 H), 1.25–1.39 (m, 9 H), 1.18 (s, 6 H), 1.14 (s, 6 H), 0.88 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, C_6D_6) 77.7, 63.2, 60.4, 49.0, 33.8, 32.6, 30.2, 29.6, 27.2, 23.4, 21.5, 14.7 ; IR (film) 3359 (br), 2930, 1373, 1047 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{34}O_2N$ ($M + H^+$) 272.2589, found: 272.2586.



4-Methacryloyloxy-1-(1-heptoxy)-2,2,6,6-tetramethylpiperidine (9b). To a solution of alcohol **S3** (245 mg, 0.903 mmol) and DMAP (25 mg) in pyridine (2 mL) was added methacrylic acid anhydride (150 μL, 1.0 mmol). The resultant solution was maintained at ambient temperature for 22 h. The excess reagents were quenched by addition of saturated aqueous $NaHCO_3$ (3 mL). The mixture was extracted with EtOAc (2 × 5 mL) and the combined organics were washed with 1 M $NaHSO_4$ (3 × 10 mL). The combined organics were then dried over $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (SiO_2, 5:95 ethyl acetate:hexanes) to yield 69 mg (22%) **9b** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) 6.05 (s, 1 H), 5.52 (s, 1 H), 5.06 (tt, J = 4.3, 11.3, 1 H), 3.72 (t, J = 6.7, 2 H), 1.91 (s, 3 H), 1.82–1.88 (m, 2 H), 1.58 (t, J = 11.9, 2 H), 1.51 (td, J = 6.7, 14.3, 2H), 1.24–1.38 (m, 8 H), 1.19 (s, 12 H), 0.88 (t, J = 6.9, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.0, 136.7, 125.1, 77.0, 67.1, 59.9, 44.1, 33.1, 31.8, 29.4, 28.7, 26.4, 22.6, 20.9, 18.2, 14.1; IR (film) 2930, 1718, 1164 cm^{-1}; HRMS (ESI), calcd for $C_{20}H_{38}NO_3$ ($M + H^+$): 340.2852, found: 340.2857.

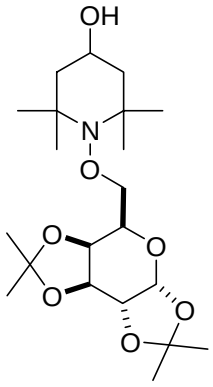


4-(*tert*-butyldimethylsilyloxy)-2,2,6,6-tetramethylpiperidinyloxy (14). To a solution of 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (8.1 g, 47 mmol) and NEt_3 (6.5 mL, 71 mmol) in CH_2Cl_2 (100 mL) was added TBDMSCl (8.5 g, 56 mmol). The resultant solution was maintained at ambient temperature for 17h. The reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ (50 mL). The mixture was partitioned and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. The resultant oil was purified by flash chromatography (SiO_2: 20:80 ethyl acetate:hexanes → 65:35 ethyl acetate:hexanes) to yield 5.3 g (65% yield) of 4-hydroxy-2,2,6,6-tetramethylpiperdinyloxy as an orange solid and 4.5 g (33% yield, 97% yield brsm) of nitroxide **14** as a red solid. mp 32–34 °C, IR (film) 2933, 1463, 1254, 1089, 836 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{32}NO_2SiNa$ ($M + Na^+$) 309.2100, Found: 309.2104; Anal. Calcd for $C_{15}H_{32}NO_2Si$: C, 62.88; H, 11.26, N, 4.89. Found: C, 63.00; H, 11.07; N, 4.64.



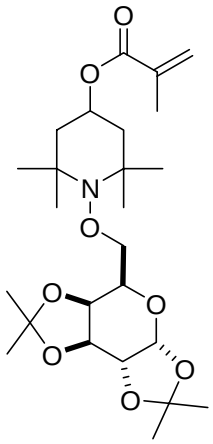
***O*-Diisopropylidene-galactose silyloxyhydroxylamine 15.** A solution of 4-(*tert*-butyldimethylsilyloxy)-2,2,6,6-tetramethylpiperidinyloxy (**14**) (1.56 g, 5.42 mmol), tributyltin hydride (870 μL, 4.2 mmol), 5-iodo-diisopropylidene galactose (1.00 g, 2.70 mmol) and benzene (50 mL) in a quartz flask was degassed by four freeze-pump-thaw cycles. The degassed mixture was irradiated by a Hanovia UV utility lamp (low pressure Hg) for 22 h. The reaction mixture

was concentrated under reduced pressure and the residue was purified by flash chromatography (SiO_2, 4:96 ethyl acetate:hexane) to provide 1.02 g (71%) of **15** as a colorless oil. $[\alpha]^{D}_{23} = -42.02$ (*c* 1.04, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) 5.52 (d, *J* = 4.9, 1 H), 4.58 (dd, *J* =2.1, 7.9, 1 H), 4.28 (dd, *J* = 2.2, 4.9, 1 H), 4.24 (d, *J* = 7.9, 1 H), 3.84–4.00 (m, 4 H), 1.60–1.67 (m, 2 H), 1.54 (s, 3 H), 1.44–1.54 (m, 2 H), 1.43 (s, 3 H), 1.33 (s, 3 H), 1.32 (s, 3 H), 1.20 (s, 3 H), 1.19 (s, 3 H), 1.13 (s, 3 H), 1.12 (s, 3 H), 0.88 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) 109.1, 108.4, 96.3, 75.6, 71.5, 70.8, 70.6, 66.3, 63.9, 60.2, 60.0, 48.5, 33.1, 33.0, 26.1, 26.0, 25.9, 25.0, 24.4, 20.9, 18.2, –4.7 IR (film) 2934, 1378, 1074 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{51}NO_7SiNa$ ($M + Na^+$) 552.3333, Found: 552.3344.

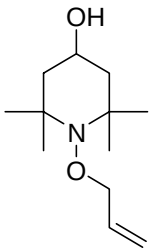


***O*-Diisopropylidene-galactose hydroxylamine (S4).** To a chilled (0 °C) solution of hydroxylamine **15** (507 mg, 0.958 mmol) in THF (10 mL) was added a 1.0 M solution of TBAF (1.9 mL, 1.9 mmol) in THF. The solution was allowed to warm to ambient temperature over 3 h. After 3.3 h, the reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. The resultant oil was purified by flash chromatography (SiO_2, 40:60 ethyl acetate:hexane) to provide 355 mg (89%) of **S4** as a white solid. mp 114–116 °C; $[\alpha]^{D}_{23} = -61.58$ (*c* 1.01, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) 5.51 (d, *J* = 5.0, 1 H), 4.49 (dd, *J* = 2.2, 7.9, 1 H), 4.22–4.28 (m, 2 H), 4.18–4.22 (m, 1 H), 4.16 (dd, *J* = 2.3, 5.0, 1 H), 4.07 (dd, *J* = 1.5, 7.9, 1 H), 3.69–3.79 (m, 1 H), 1.60–1.71 (m, 2 H), 1.40–1.54 (m, 8 H), 1.28–1.32 (m, 7 H), 1.15–1.20 (m, 9 H), 1.06 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) 109.6, 108.8, 97.2, 76.9, 72.5, 71.6, 71.5, 67.3, 63.2, 60.8, 60.6, 49.1, 33.8, 33.5, 26.6, 25.4, 24.9, 21.5;

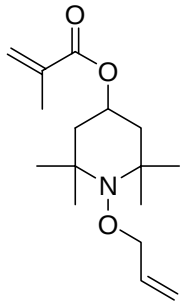
IR (film) 3394 (br), 2978, 1378 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{37}NO_7Na$ ($M + Na^+$) 438.2468, Found: 438.2467.



***O*-Diisopropylidene-galactose metacryloyloxyhydroxylamine 16.** To a solution of hydroxylamine **S4** (1.17 g, 2.82 mmol), NEt_3 (786 μL, 5.64 mmol) and DMAP (1 mg) in CH_2Cl_2 (10 mL) was added methacroyl chloride (386 μL, 3.95 mmol). The resultant solution was maintained for 14 h at ambient temperature and then the excess reagents were quenched by addition of saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. The resultant oil was purified by flash chromatography (SiO_2, 10:90 ethyl acetate:hexane) to provide 1.08 g (79%) of **16** as a white solid. mp 83–85 °C; $[\alpha]^D_{23} = -54.87$ (*c* 0.90, $CHCl_3$); ^1H NMR (500 MHz,C_6D_6) 6.16 (s, 1 H), 5.51 (d, *J* = 5.0, 1 H), 5.22–5.25 (m, 1 H), 5.20 (td, *J* = 4.3, 11.7, 1 H), 4.49 (dd, *J* = 2.3, 7.9, 1 H), 4.22–4.25 (m, 2 H), 4.17–4.20 (m, 1 H), 4.17 (dd, *J* = 2.3, 7.9, 1 H), 4.05 (dd, *J* = 1.3, 7.9, 1 H), 1.88 (s, 3 H), 1.82 (td, *J* = 3.6, 12.2, 1 H), 1.78 (td, *J* = 3.6, 12.2, 1 H), 1.53–1.62 (m, 2 H), 1.47 (s, 3 H), 1.45 (s, 3 H), 1.25–1.27 (m, 6 H), 1.22 (s, 3 H), 1.21 (s, 3 H), 1.16 (s, 3 H), 1.06 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 166.9, 137.7, 125.2, 109.6, 108.8, 97.2, 76.9, 72.4, 71.6, 71.5, 67.4, 67.1, 60.8, 60.6, 44.9, 44.8, 33.7, 33.4, 26.6, 25.3, 24.8, 21.3, 21.2, 18.8; IR (film) 2979, 1716, 1379, 1168 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{42}NO_8$ ($M + H^+$) 484.2910, Found: 484.2913.

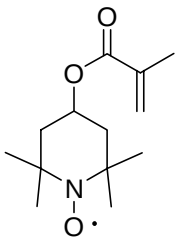


4-Hydroxy-1-(2-propenoxy)-2,2,6,6-tetramethylpiperidine (S5). A solution of 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (1.00 g, 5.80 mmol), tributyltin hydride (1.56 mL, 5.80 mmol) and allyl bromide (505 μL, 5.80 mmol) and benzene (50 mL) in a quartz flask was degassed by three freeze-pump-thaw cycles. The degassed mixture was irradiated by a Hanovia UV utility lamp (low pressure Hg) for 15 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (SiO_2, 6:94 ethyl acetate:hexanes → 15:85 ethyl acetate:hexane) to provide 472 mg (38%) of **S5** as a white solid. mp 58–60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 5.89 (tdd, *J* = 5.4, 10.7, 17.6, 1 H), 5.24–5.30 (m, 1 H), 5.11–5.15 (m, 1 H), 4.27–4.30 (m, 2 H), 3.92–4.00 (m, 1 H), 1.78–1.84 (m, 2 H), 1.58 (br s, 1 H), 1.45 (t, *J* = 11.7, 2 H), 1.20 (s, 6 H), 1.16 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) 133.9, 116.2, 78.4, 63.4, 60.0, 48.3, 33.0, 21.0; IR (film) 3267 (br), 2927, 1055 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{24}NO_2$ ($M + H^+$) 214.1807, found: 214.1802.

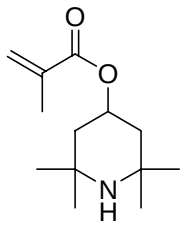


4-Methacryloyloxy-1-(2-propenoxy)-2,2,6,6-tetramethylpiperidine (17). To a solution of hydroxylamine **S5** (55 mg, 0.26 mmol), DMAP (1 mg), NEt_3 (73 μL, 0.52 mmol) in CH_2Cl_2 (1 mL) was added methacrylic acid anhydride (78 μL, 52 mmol). The solution was maintained at ambient temperature for 9 h. After this period, additional NEt_3 (73 μL, 0.52 mmol) and methacrylic acid anhydride (78 μL, 52 mmol) was added. The resultant solution was maintained

for 4.5 h and then the excess reagents were quenched by the addition of saturated aqueous $NaHCO_3$ (5 mL). The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organics were dried over sodium sulfate and concentrated under reduced pressure. The resultant oil was purified by flash chromatography (SiO_2, 5:95 ethyl acetate:hexane) to provide 55 mg (76%) of **17** as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) 6.06 (s, 1 H), 5.89 (tdd, *J* = 5.5, 10.7, 17.2, 1 H), 5.53 (s, 1 H), 5.28–5.24 (m, 1 H), 5.11–5.15 (m, 1 H), 5.08 (tt, *J* = 4.4, 11.3, 1 H), 4.27–4.31 (m, 2 H), 1.92 (s, 3 H), 1.85–1.90 (m, 2 H), 1.59 (t, *J* = 11.9, 2 H), 1.22 (s, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.0, 136.6, 133.8, 125.2, 116.2, 78.4, 67.0, 60.0, 44.1, 33.0, 20.9, 18.2; IR (film) 2977, 1718, 1165 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{28}NO_3$ (M + H$^+$) 282.2069, found: 282.2064.



4-Methacroyl-2,2,6,6-tetramethylpiperidinyloxy (12b). To a solution of 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (100 mg, 0.58 mmol), NEt_3 (170 μL, 1.16 mmol) and DMAP (1 mg) in CH_2Cl_2 (2 mL) was added methacrylic acid anhydride (172 mL, 1.16 mmol). The resulting solution was maintained at ambient temperature for 9 h. After this period, additional NEt_3 (170 μL, 0.52 mmol) and methacrylic acid anhydride (172 μL, 1.16 mmol) was added. The resulting solution was maintained at ambient temperature for 4.5 h and then the excess reagents were quenched by addition of saturated aqueous $NaHCO_3$ (5 mL). The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. The resultant oil was purified by flash chromatography (SiO_2, 5:95 ethyl acetate:hexane) to provide 125 mg (90%) of **12b** as a pink solid. mp 86–87 °C, HRMS (ESI) Calcd for $C_{13}H_{22}NO_3Na$ (M + Na$^+$) 263.1497, Found: 263.1492; Anal. Calcd for $C_{13}H_{22}NO_3$: C, 64.97; H, 9.23; N, 5.83. Found: C, 64.79; H, 9.01; N, 5.62.



4-Methacryloyloxy-2,2,6,6-tetramethylpiperidine (S6). To a solution of 4-hydroxy-2,2,6,6-tetramethylpiperidine (2.14 g, 13.6 mmol), DMAP (166 mg, 1.36 mmol) and pyridine (1.43 mL, 17.7 mmol) in CH_2Cl_2 (30 mL) was added methacrylic acid anhydride (2.43 mL, 16.3 mmol). The solution was maintained at ambient temperature for 12 h and then the excess reagents were quenched by the addition of saturated aqueous $NaHCO_3$ (15 mL). The mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. The resultant oil was purified by flash chromatography (SiO_2, 20:80 ethyl acetate:hexane) to provide 1.32 mg (43 %) of **S6** as white solid. mp 60–62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 6.08 (s, 1 H), 5.53–5.55 (m, 1 H), 5.25 (tt, J = 4.2, 11.3, 1 H), 1.92–1.98 (m, 5 H), 1.25 (s, 6 H), 1.20 (t, J = 11.9, 2 H), 1.16 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.0, 136.8, 125.0, 69.1, 51.4, 43.8, 34.8, 29.1, 18.3; IR (film) 3312 (br), 2969, 1702, 1633, 1165 cm^{-1}; Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.50; H, 10.21; N, 6.09.

C. Polymerizations

General Procedure for Polymerization. Preparation of hexenylamine template copolymer S7. Ethylene glycol dimethacrylate (1.84 mL, 9.76 mmol, 0.8 equiv), methyl methacrylate (182 μL, 1.71 mmol, 0.14 equiv), amine **4b** (188 mg, 0.61 mmol, 0.05 equiv), AIBN (20 mg, 0.1 mmol, 0.01 equiv) and CH_3CN (2.25 mL) were combined in a 20 mL vial. The solution was degassed for 5 min with argon and then sealed and placed in an 80 °C oil bath for 40 h. After cooling to ambient temperature, the solid was crushed and placed in a Soxholet extractor and extracted with MeOH for 24 h. The solid was then dried under vacuum to provide 3.73 g of polymer **S7**.

Blank Polymer **S8**: Following the general experimental amine **S6** (225 mg, 1.00 mmol) was processed to provide 3.16 g of amino polymer **S8**.

Allyl Polymer **S9**: Following the general experimental amine **4a** (265 mg, 1.00 mmol) was processed to provide 3.73 g of amino polymer **S9**.

Tridecenyl Polymer **S10**: Following the general experimental amine **4c** (406 mg, 1.00 mmol) was processed to provide 3.81 g of amino polymer **S10**.

Diisopropylidene Galactose Polymer **S11**: Following the general experimental amine **16** (200 mg, 0.41 mmol) was processed to provide 1.63 g of amino polymer **S11**.

O-Heptyl Polymer **S12**: Following the general experimental amine **9b** (118 mg, 0.35 mmol) was processed to provide 1.32 g of amino polymer **S12**.

O-Allyl Polymer **S13**: Following the general experimental amine **17** (272 mg, 0.98 mmol) was processed to provide 2.78 g of amino polymer **S13**.

General Procedure for the Generation of Nitroxide Containing Polymers. Preparation of hexenylamine templated nitroxide polymer S14. To a suspension of polymer **S7** (2.03 g) in CH_2Cl_2 (10 mL) was added *m*-CPBA (0.986 g, 5.71 mmol). The mixture was allowed to stand for 18 h and then filtered and washed with CH_2Cl_2 (3 × 10 mL). The resulting pink solid was placed in a Soxholet extractor and extracted with MeOH for 24 h. The solid was dried under vacuum to provide 2.53 g of templated nitroxide polymer **S14** as a pink solid.

Blank Nitroxide Polymer **S15**: Following the general experimental, polymer **S8** (2.93 g) was converted to polymer **S15** (3.12 g).

Allyl Templated Polymer **S16**: Following the general experimental, polymer **S9** (3.54 g) was converted to polymer **S16** (3.12 g).

Tridecenyl Templated Polymer **S17**: Following the general experimental, polymer **S10** (3.64 g) was converted to polymer **S17** (4.35 g).

Galactose Templated Polymer **S18**: Following the general experimental, polymer **S11** (1.55 g) was converted to polymer **S18** (1.50 g)

O-Heptyl Templated Polymer **S19**: Following the general experimental, polymer **S12** (1.00 g) was converted to polymer **S19** (1.00 g).

O-Allyl Templated Polymer **S20**: Following the general experimental, polymer **S13** (0.96 g) was converted to polymer **S20** (0.99 g)

D. Oxidation Chemistry

Table 1, Entry 1: Benzaldehyde. Following the general experimental (see text, Ref. 21), benzyl alcohol (66 mg) was converted to benzaldehyde (52 mg, 80 % yield).Data are in agreement with literature values.[3]

Table 1, Entry 2: Phenyl Ethyl Ketone. Following the general experimental (see text, Ref. 21), 1-phenylpropan-1-ol (83 mg) was converted to phenyl ethyl ketone (62 mg, 76 % yield). Data are in agreement with literature values.[4]

Table 1, Entry 3: Decanal. Following the general experimental (see text, Ref. 21), 1-decanol (100 mg) was converted to Decanal (79 mg, 80 % yield). Data are in agreement with literature values.[5]

Table 1, Entry 4: 5-Phenyl Pentanal. See References 21–22 in the text.

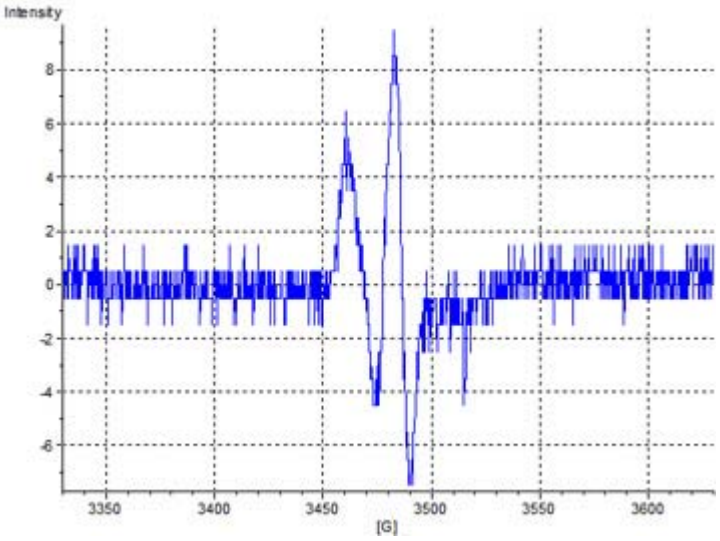
Table 1, Entry 5: 2-Methyl-Dodecanal. Following the general experimental (see text, Ref. 21), 2-methyl-1-dodecanol (50 mg) was converted to 2-methyl-dodecanal (33 mg, 68 % yield). Data are in agreement with literature values.[6]

---

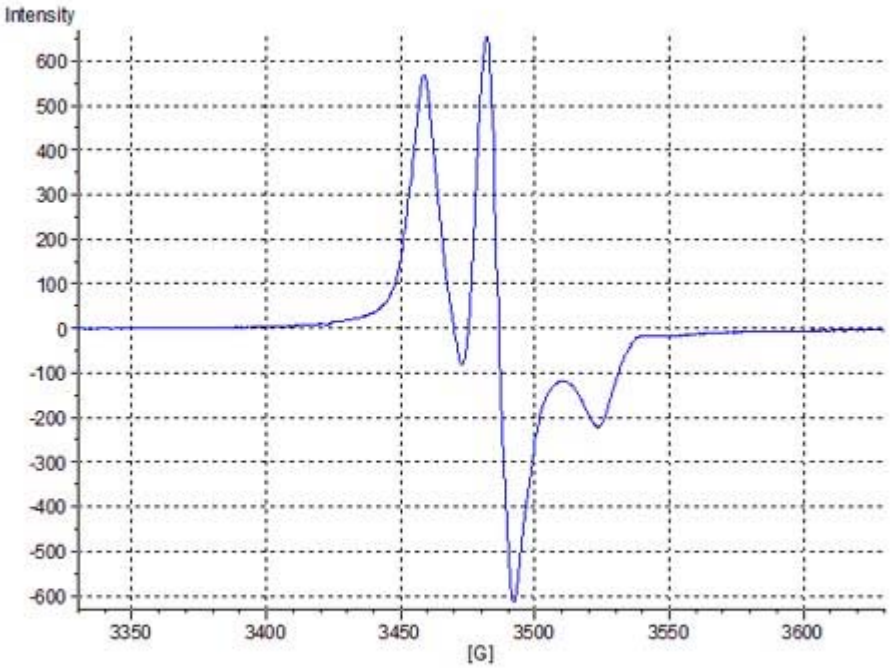
[3] Abraham, R. J.; Chadwick, D. J.; Sancassan, F. *Tetrahedron* **1982,** *38,* 1485–1492.
[4] Wang, D.; Zhang, Z. *Org. Lett.* **2003,** *5,* 4645–4648.
[5] Velusamy, S.; Punniyamurthy, T. *Org. Lett.* **2004,** *6,* 217–220.
[6] Fischli, A. *Helv. Chim. Acta* **1978,** *61,* 2560–2578.

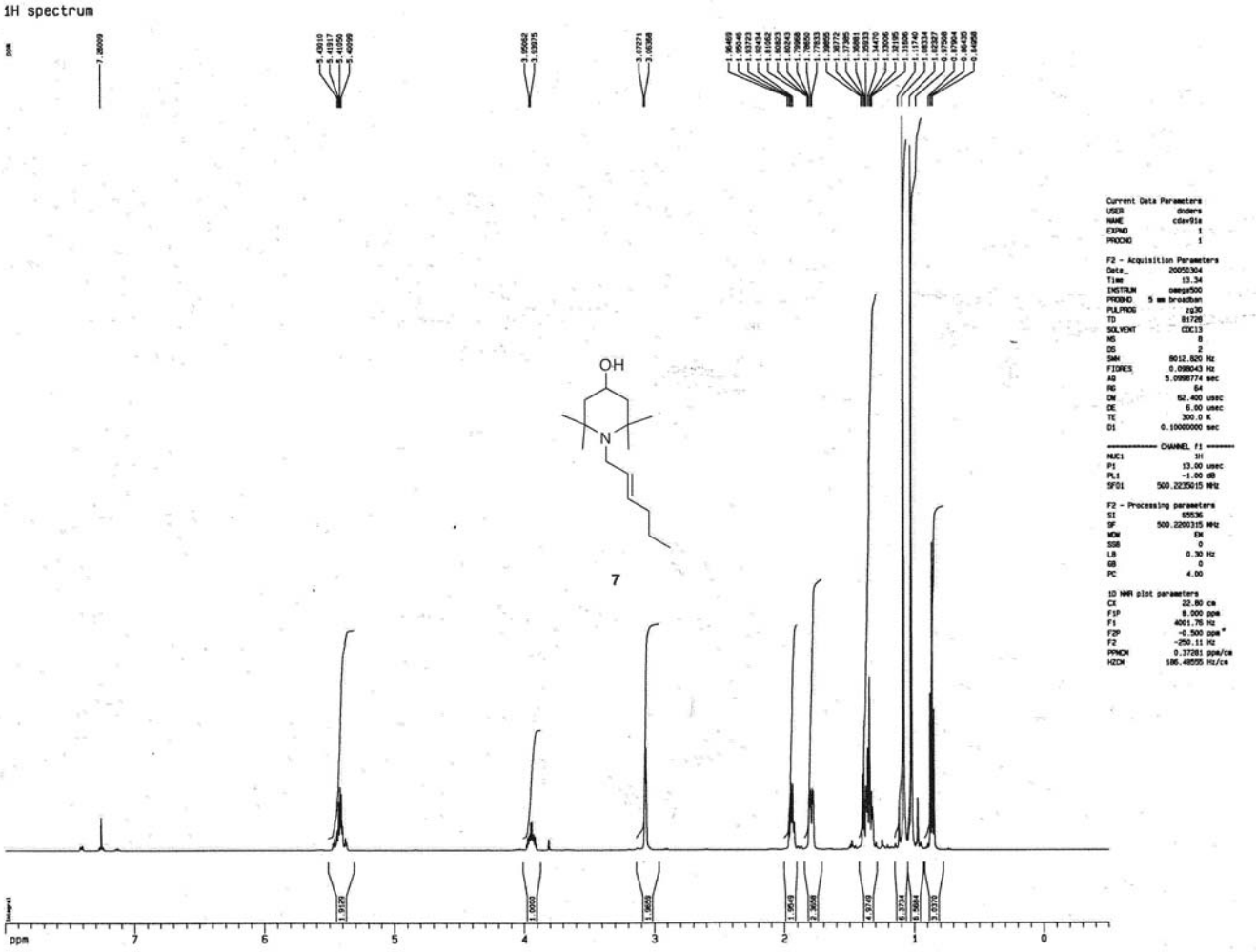
E. Representative EPR Spectra

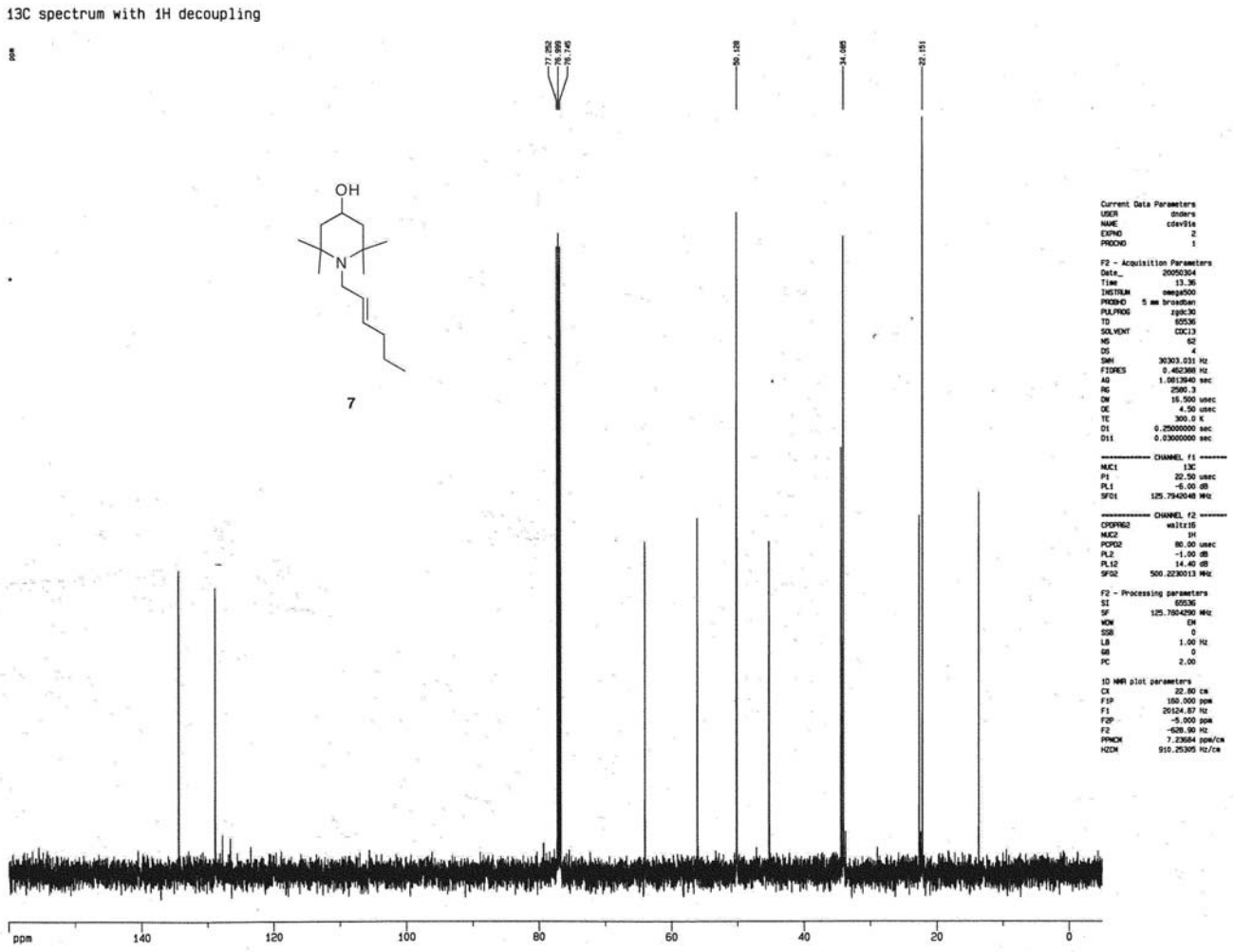
Polymer **S11** (prior to oxidation)

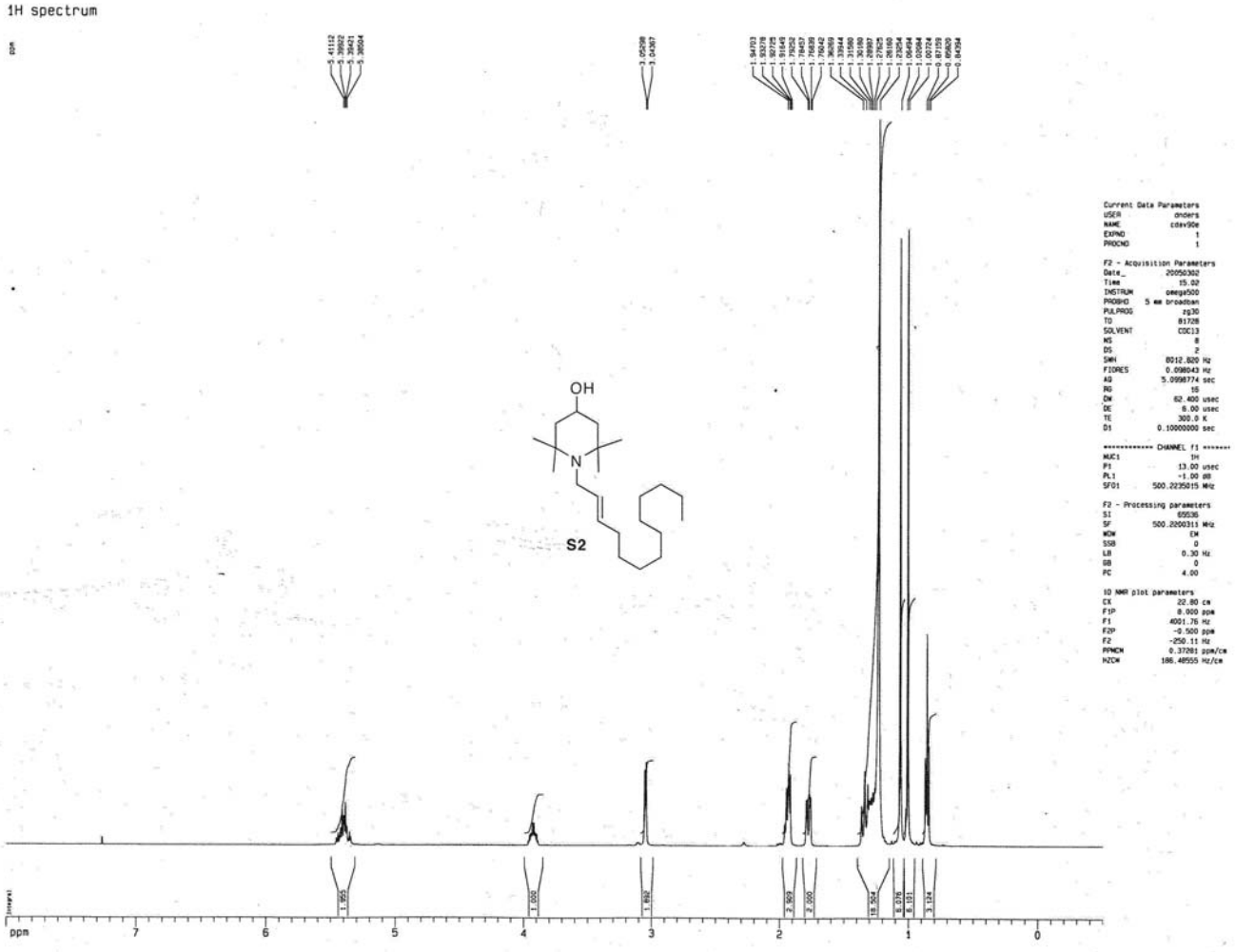


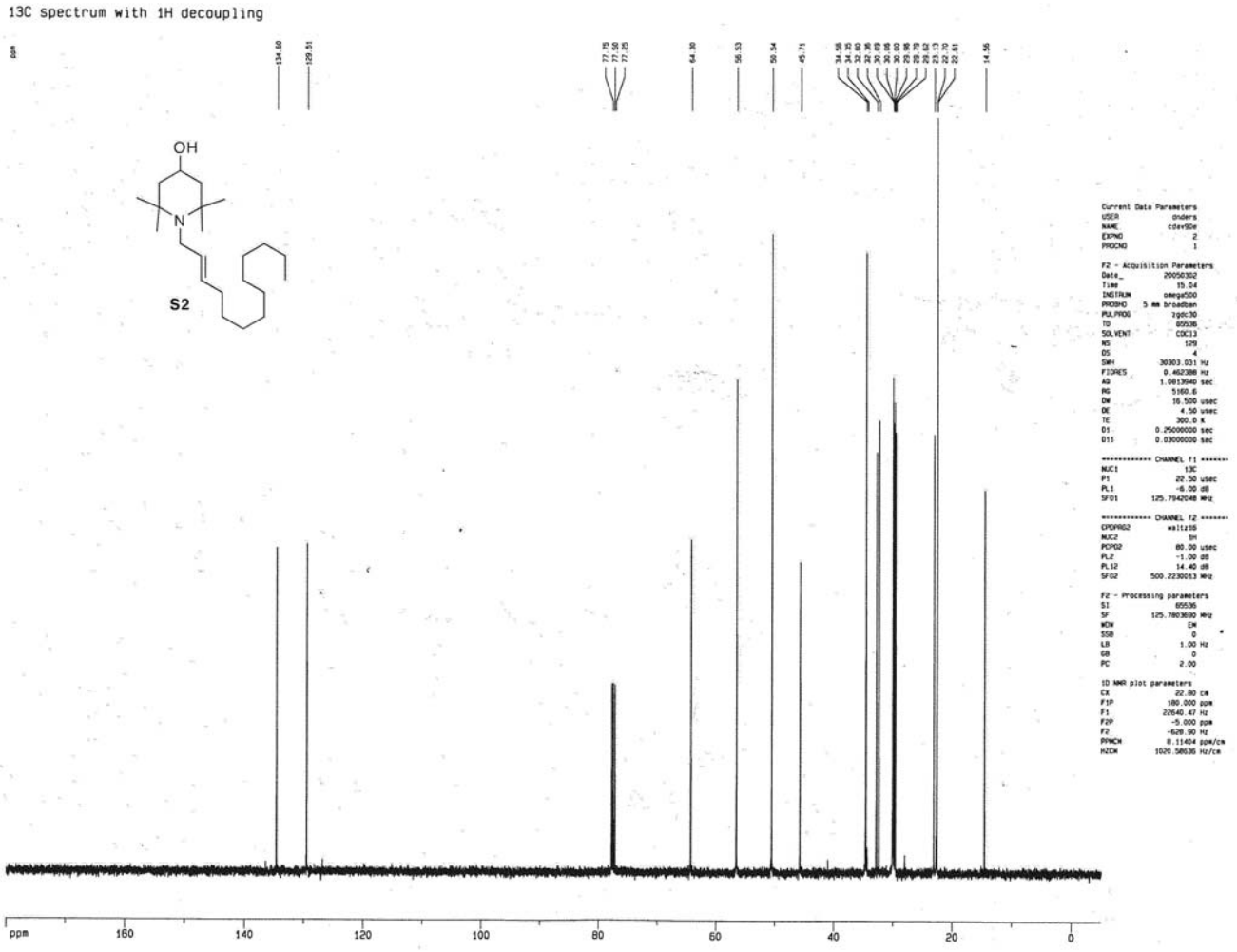
Polymer **S18**

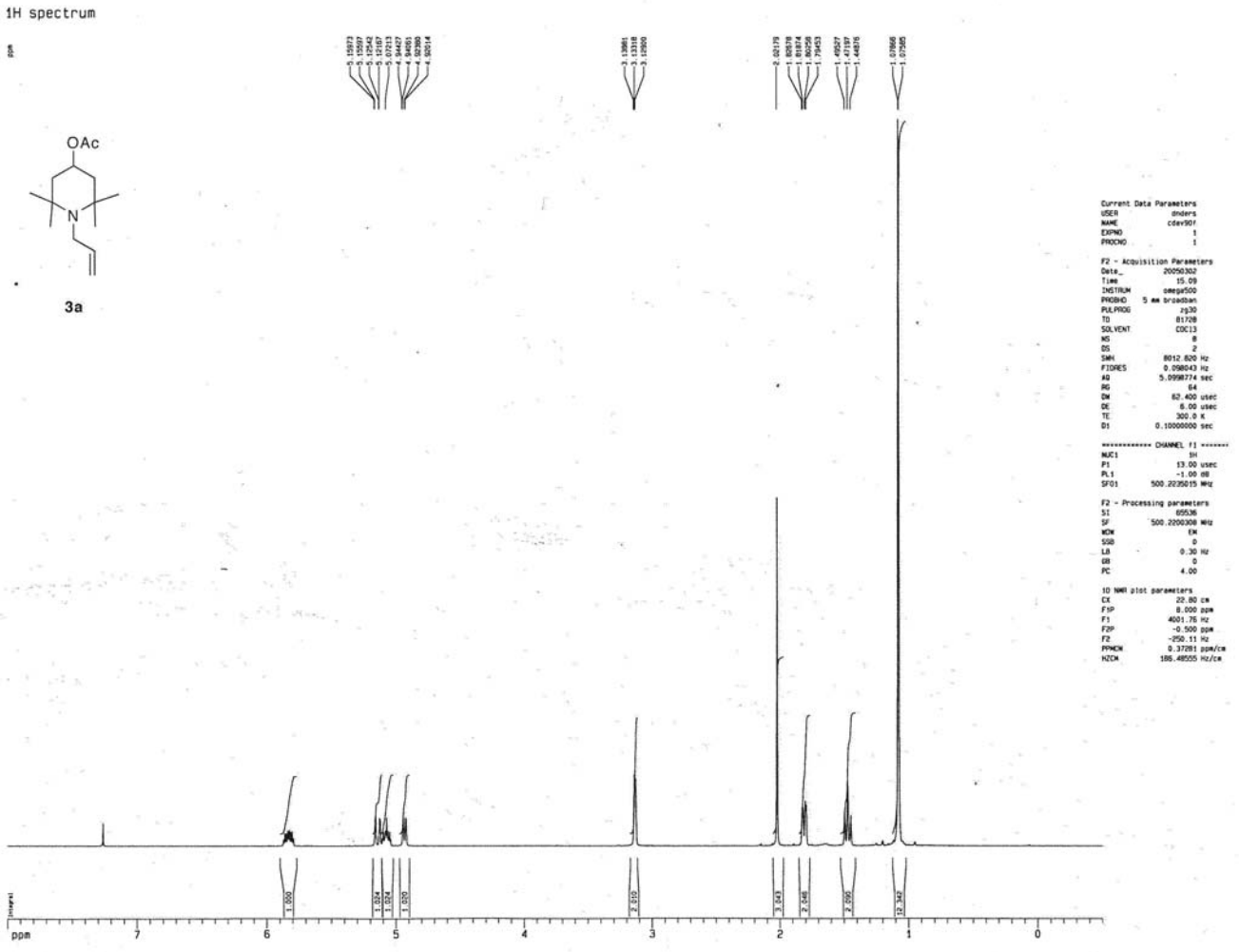


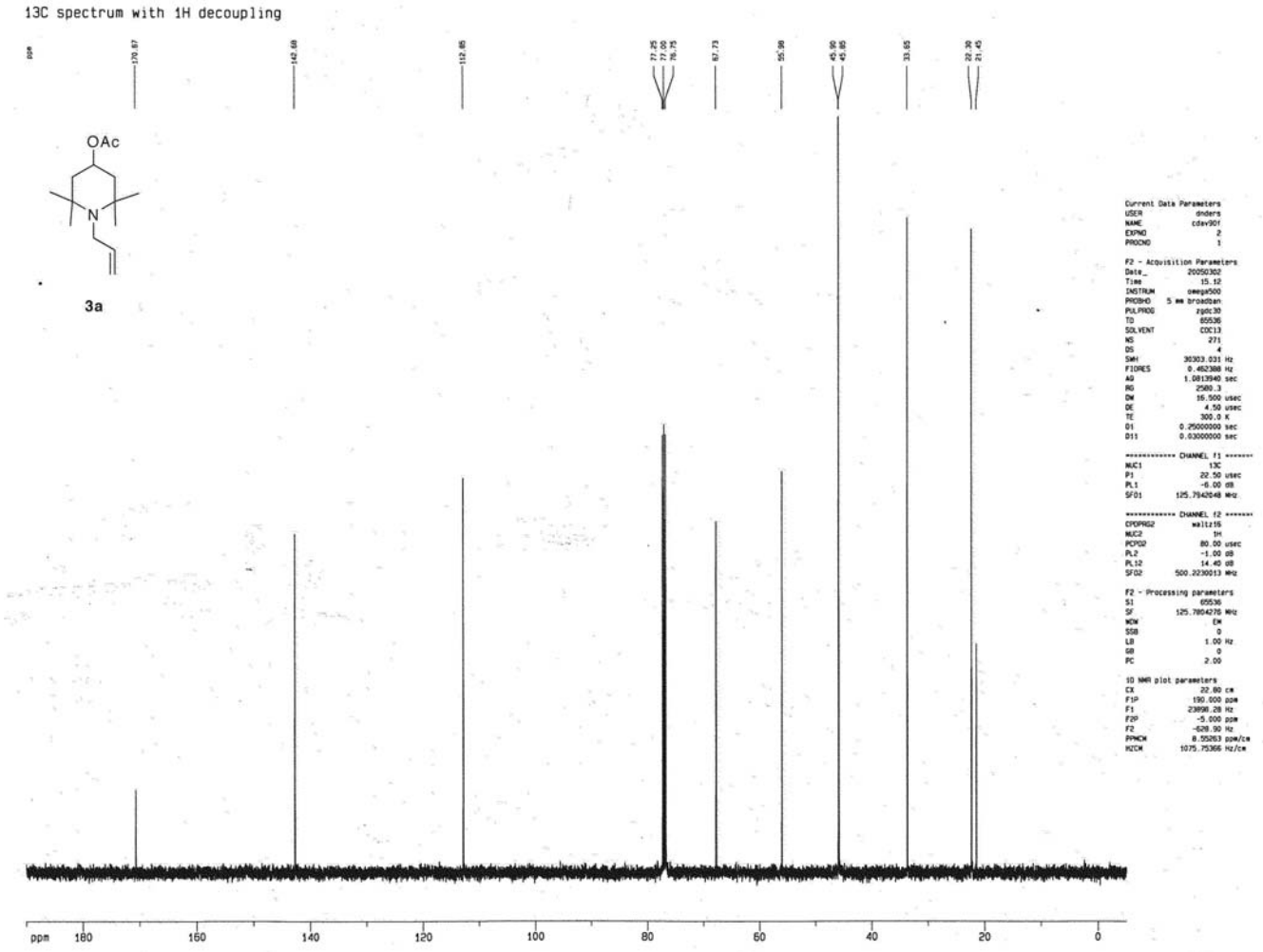

1H spectrum
OH
N
7
ppm
7
6
5
4
3
2
1
0

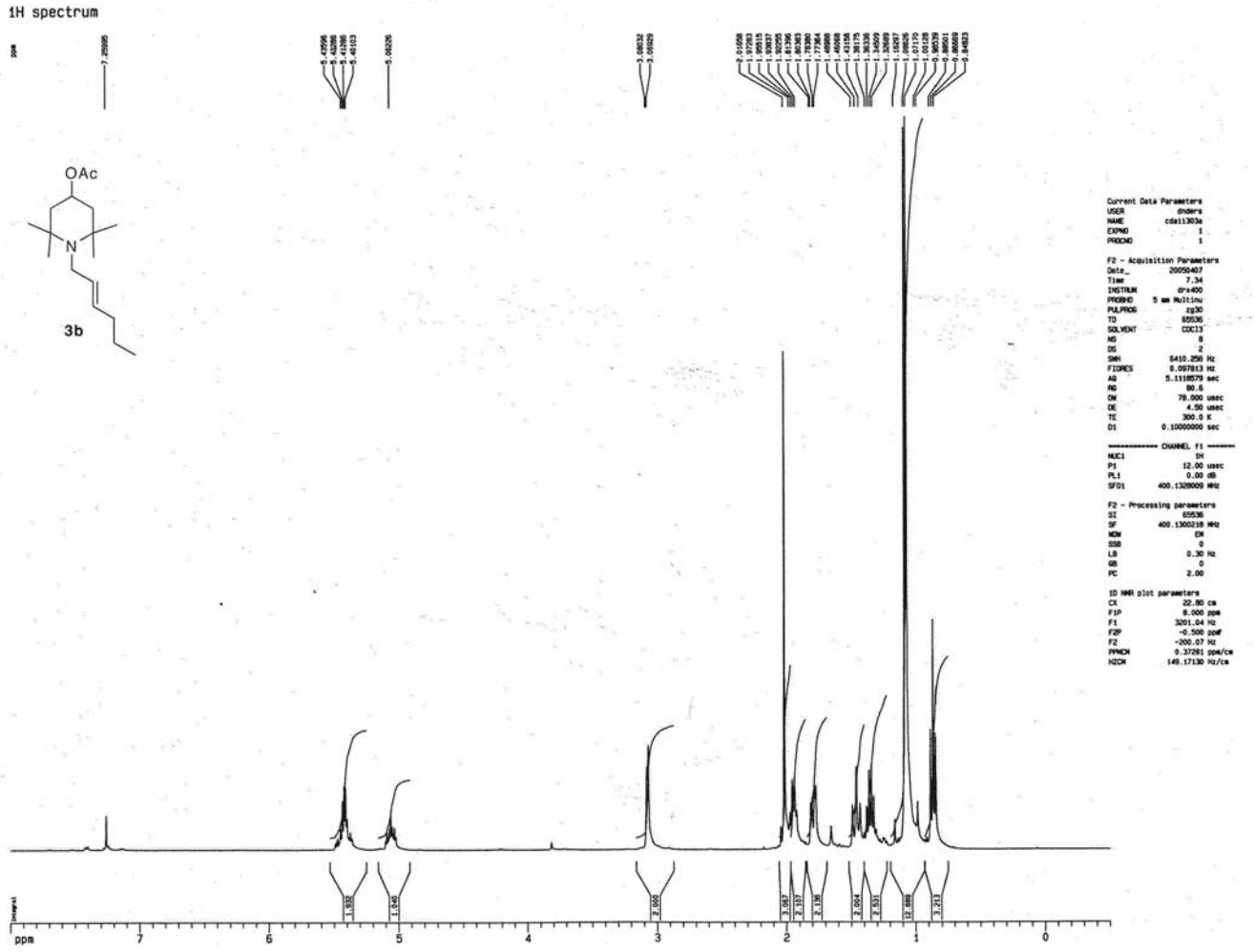

13C spectrum with 1H decoupling
ppm
77.252
76.999
76.745
50.128
34.685
22.151
OH
N
7
Current Data Parameters
USER dnders
NAME cdev91a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050304
Time 13.36
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zgpc30
TD 65536
SOLVENT CDCl3
NS 62
DS 4
SWH 30303.031 Hz
FIDRES 0.462308 Hz
AQ 1.0812640 sec
RG 2580.3
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 22.50 usec
PL1 -6.00 dB
SFO1 125.7942048 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz
F2 - Processing parameters
SI 65536
SF 125.7804290 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.00 cm
F1P 160.000 ppm
F1 20124.87 Hz
F2P -5.000 ppm
F2 -628.90 Hz
PPMCM 7.23684 ppm/cm
HZCM 910.25305 Hz/cm
ppm
140
120
100
80
60
40
20
0

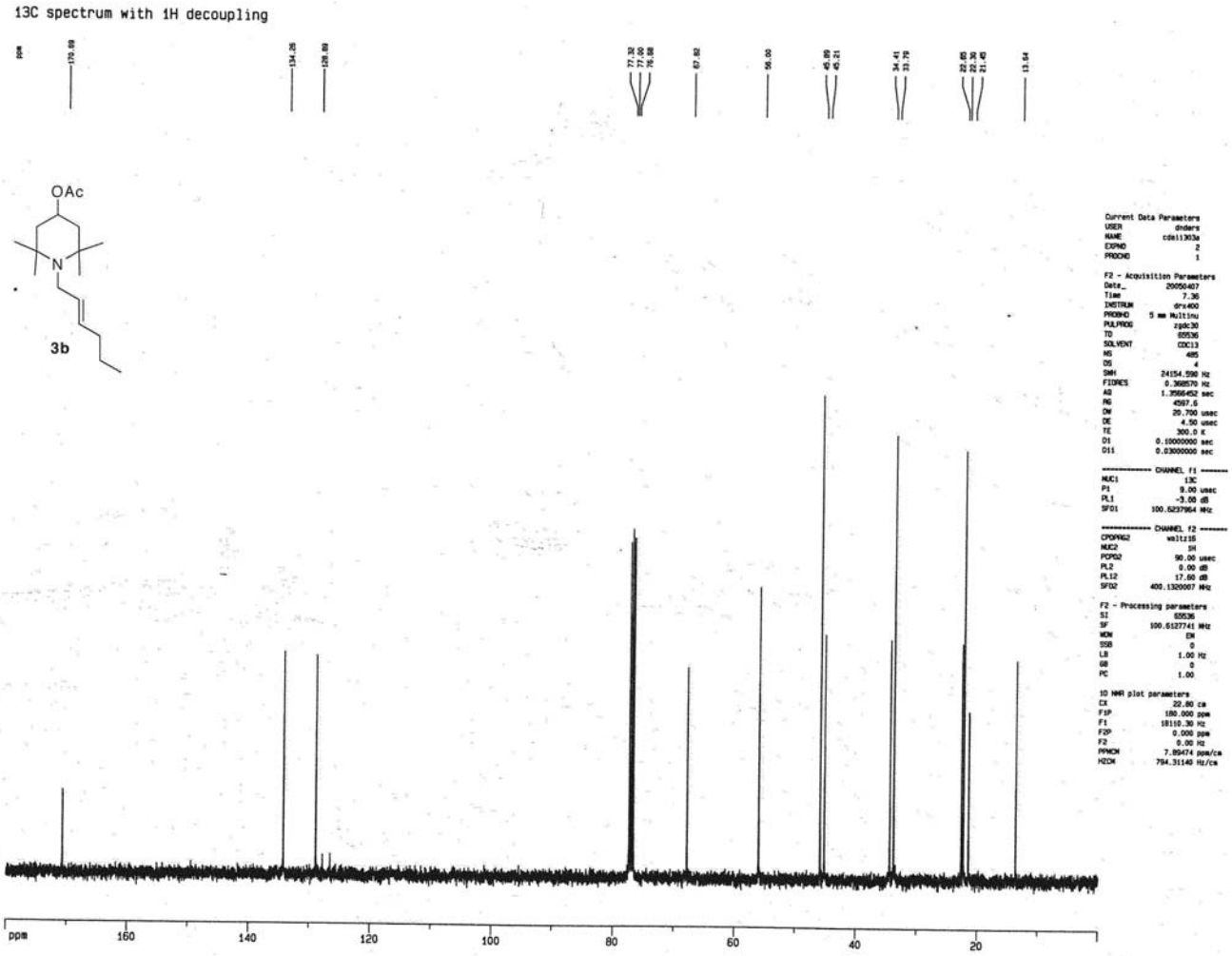

1H spectrum
ppm
OH
N
S2
ppm
7
6
5
4
3
2
1
0

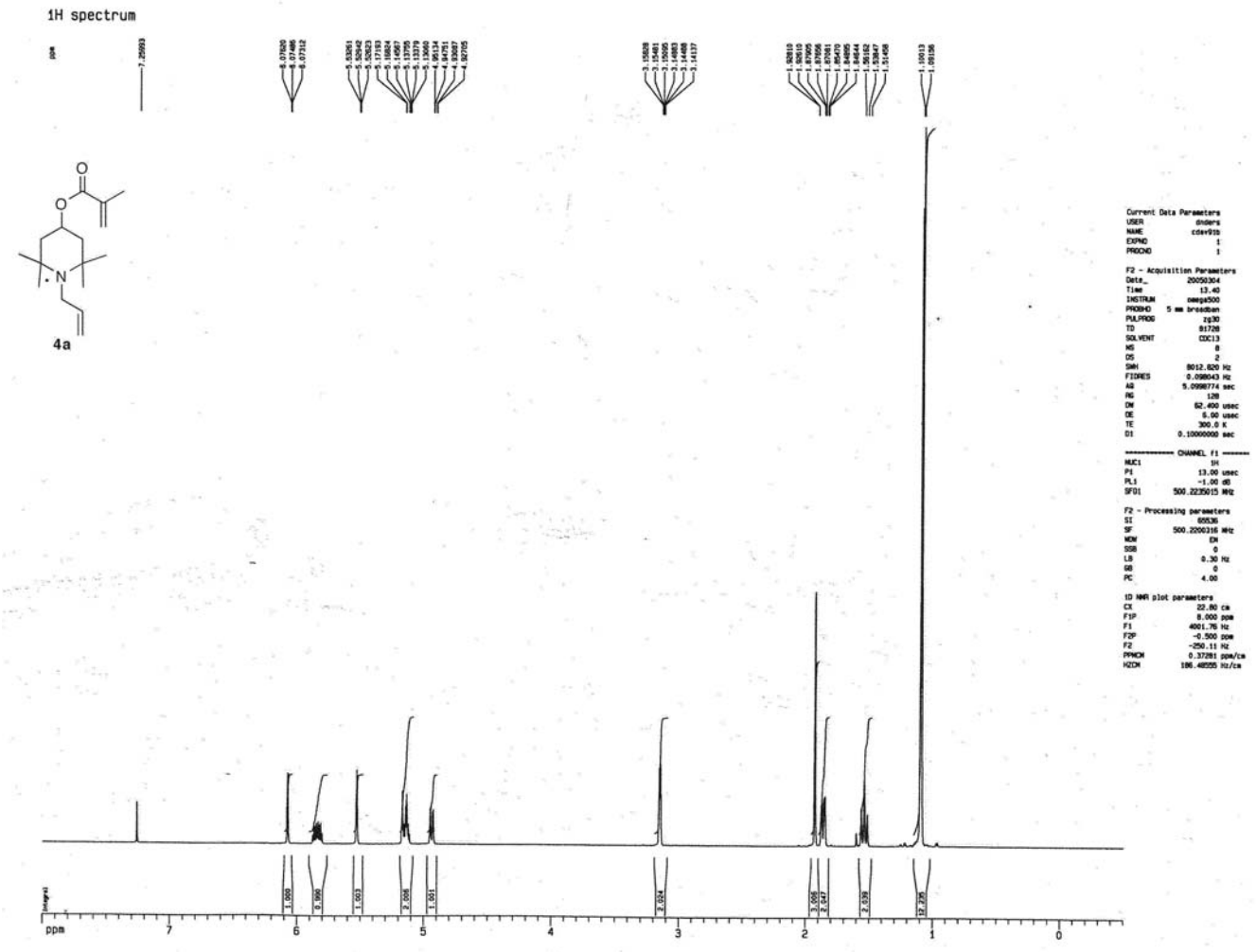

13C spectrum with 1H decoupling
OH
N
S2
ppm
160
140
120
100
80
60
40
20
0

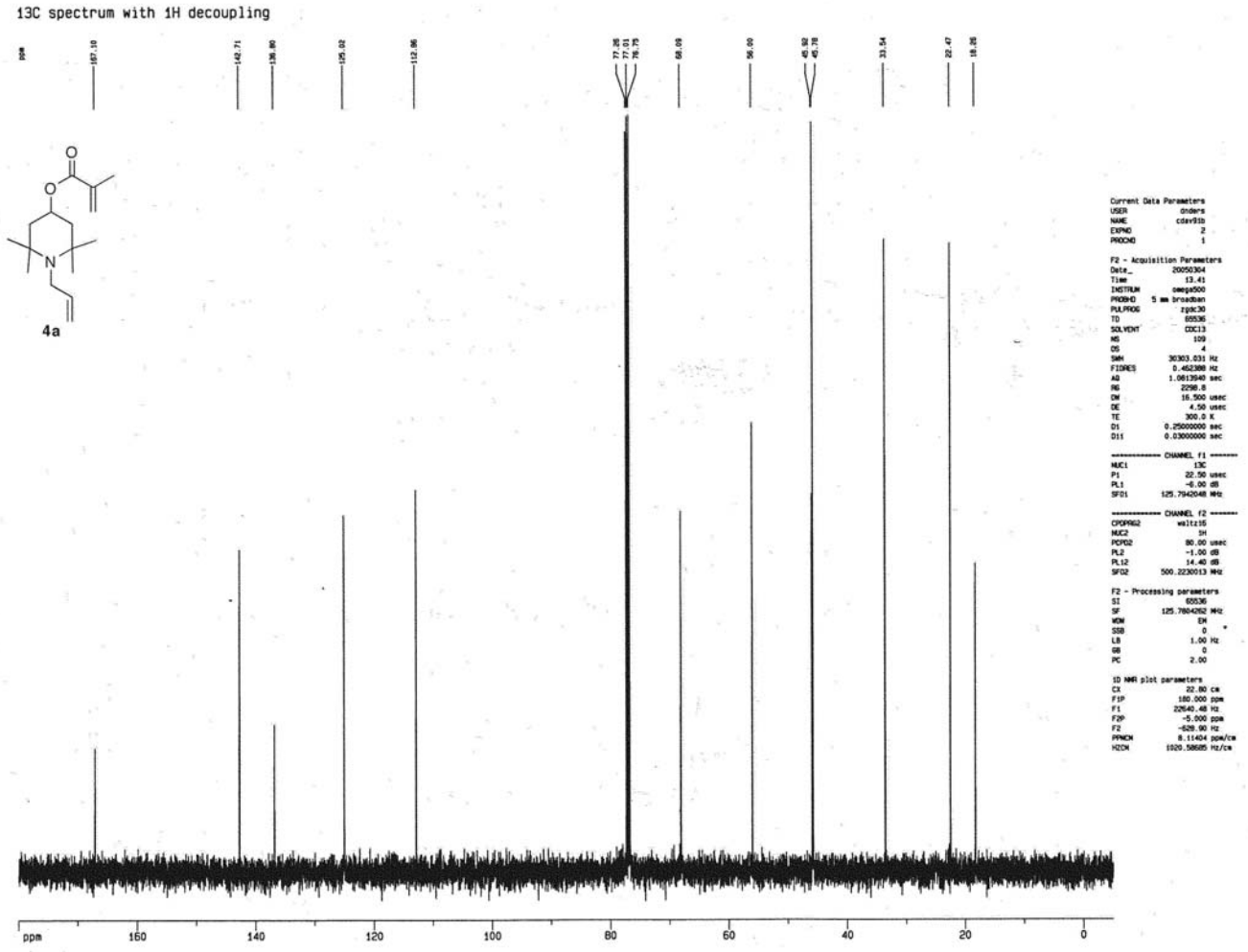

1H spectrum
OAc
N
3a
ppm
Integral
1.000
1.024
1.024
1.020
2.010
3.043
2.046
2.000
12.342
Current Data Parameters
USER onders
NAME cdev90f
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050302
Time 15.09
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 64
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
========== CHANNEL f1 =======
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200308 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
F1P 8.000 ppm
F1 4001.76 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.37281 ppm/cm
HZCM 186.48555 Hz/cm

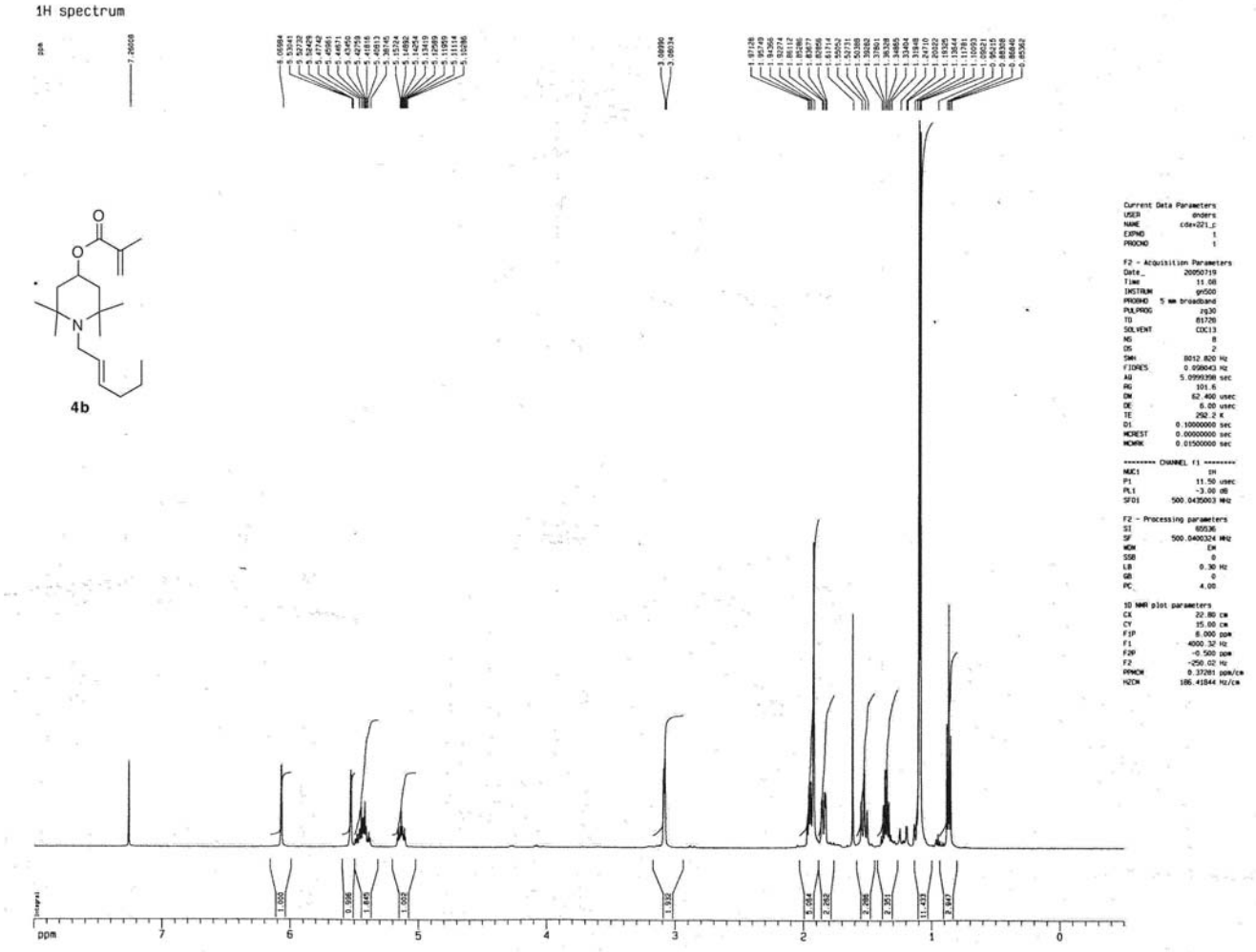

13C spectrum with 1H decoupling
OAc
N
3a
ppm
180
160
140
120
100
80
60
40
20
0

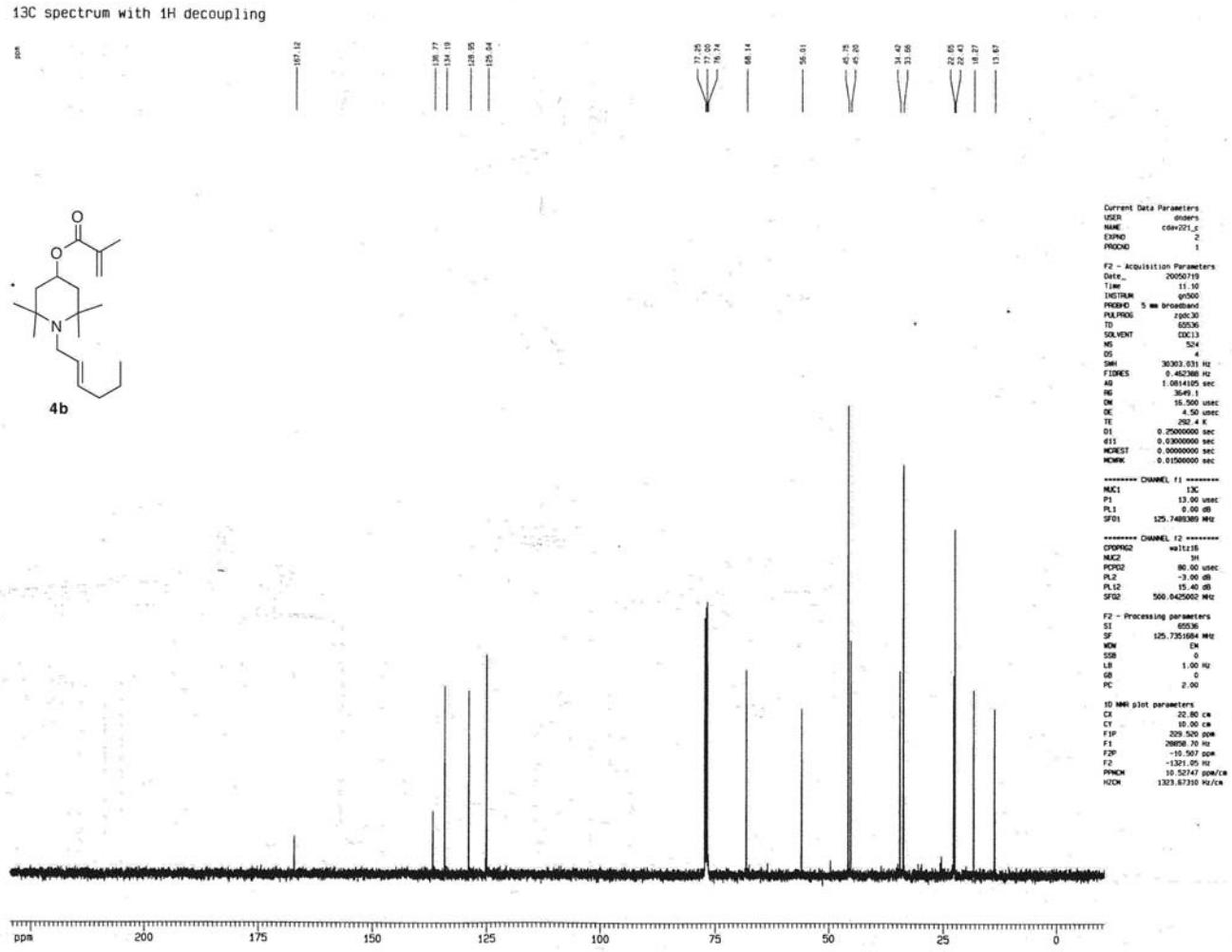

1H spectrum
OAc
N
3b
ppm
7
6
5
4
3
2
1
0

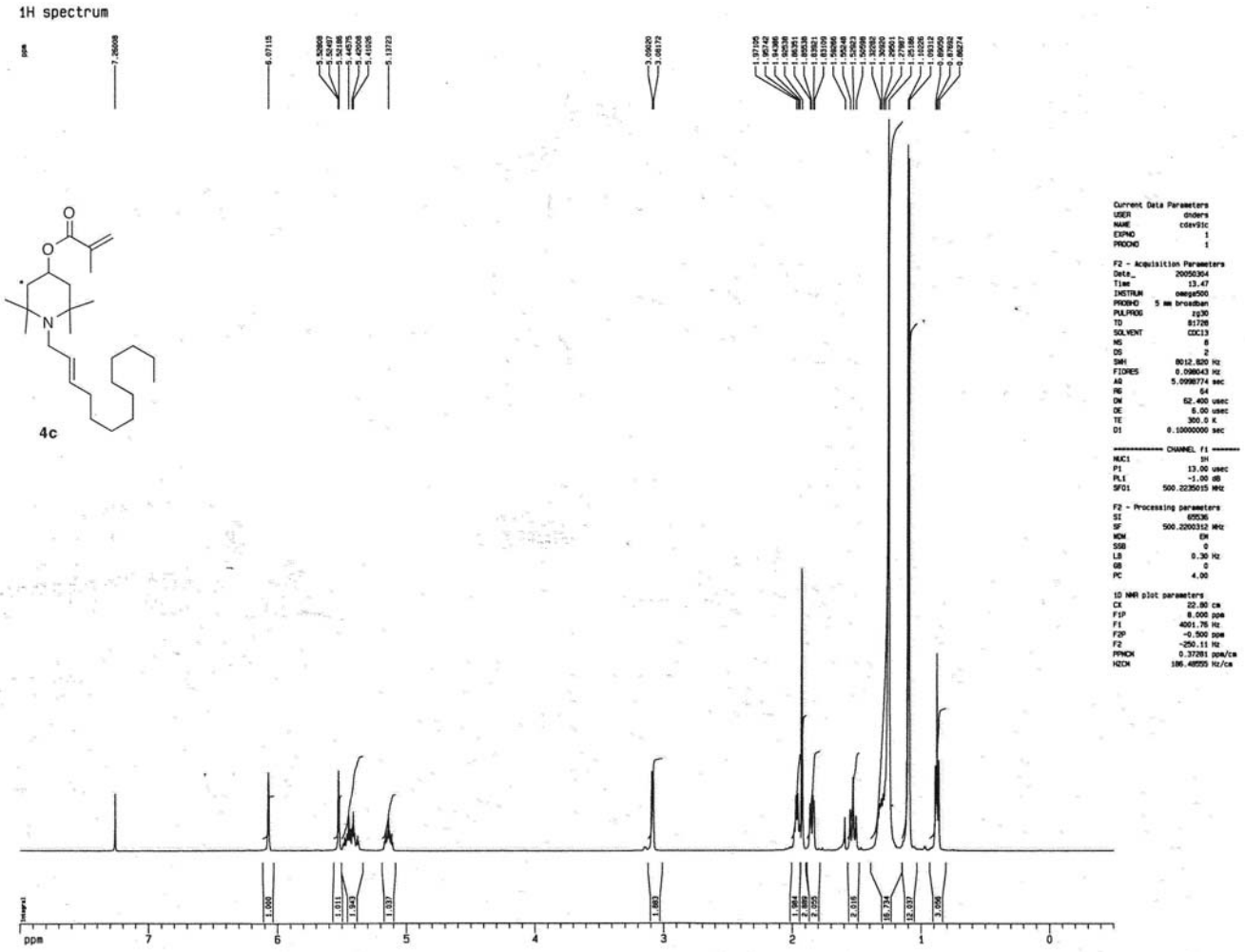

13C spectrum with 1H decoupling
ppm
170.89
134.26
126.89
77.32
77.00
76.68
67.82
56.00
45.89
45.21
34.41
33.79
22.85
22.30
21.45
13.64
OAc
N
3b
Current Data Parameters
USER dnders
NAME cdsl303a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050407
Time 7.36
INSTRUM drx400
PROBHD 5 mm Multinu
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 485
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 4587.6
DW 20.700 usec
DE 4.50 usec
TE 300.0 K
D1 0.10000000 sec
D11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.5237964 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 17.60 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 65536
SF 100.6127741 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
F1P 180.000 ppm
F1 18110.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 7.89474 ppm/cm
HZCM 794.31140 Hz/cm
ppm
160
140
120
100
80
60
40
20

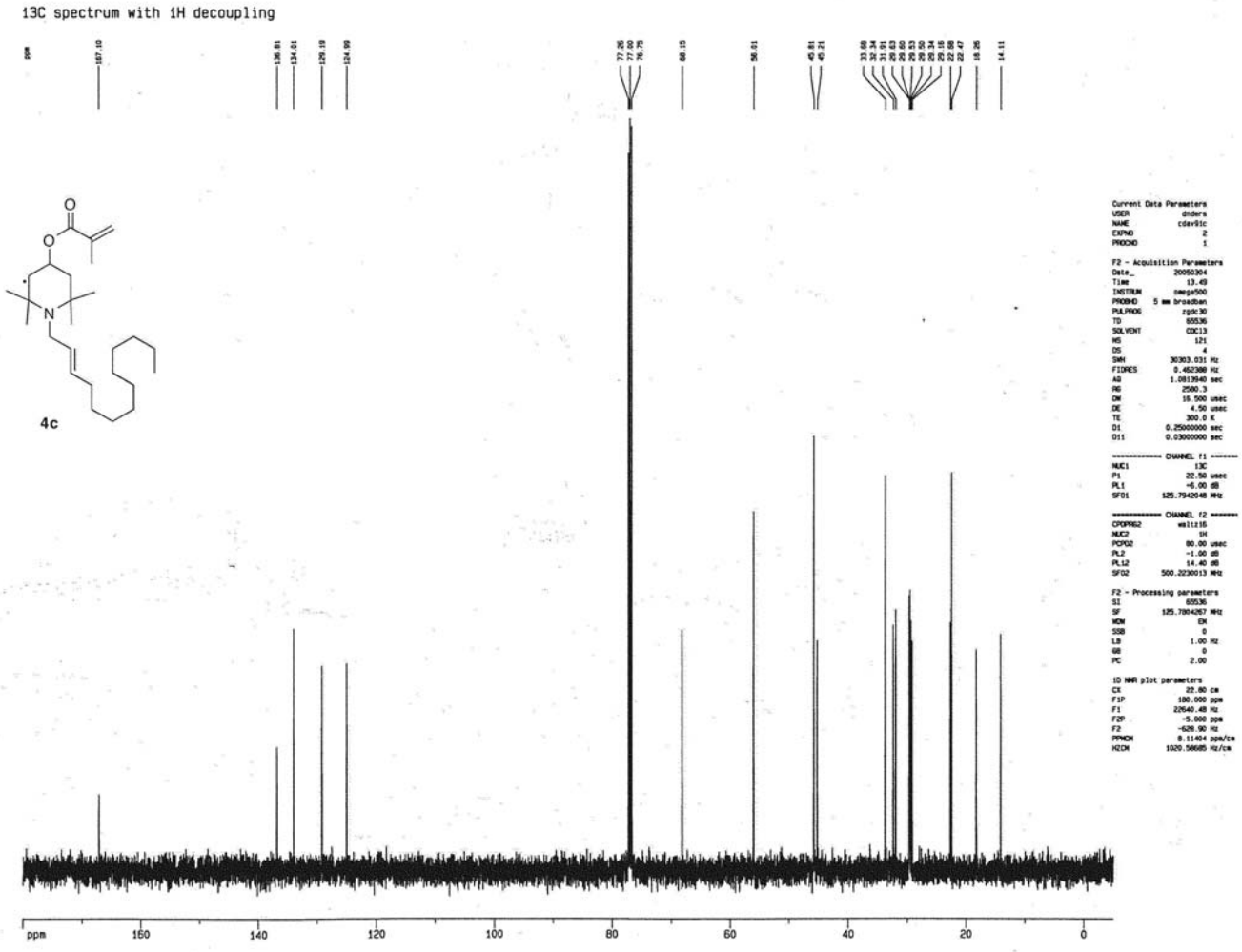

1H spectrum
4a
ppm
Integral

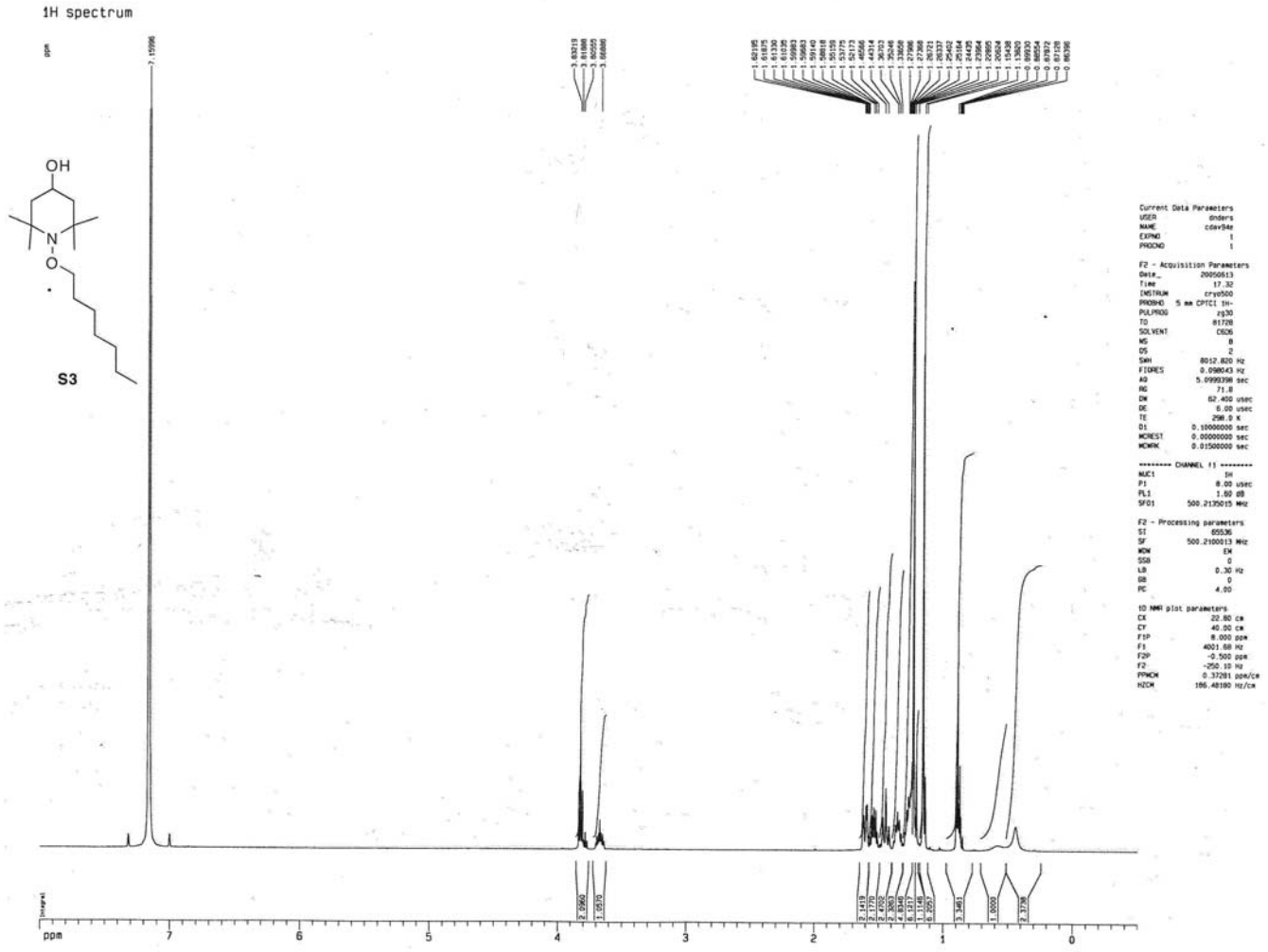

13C spectrum with 1H decoupling
ppm
167.10
142.71
136.80
125.02
112.86
77.26
77.01
76.75
68.09
56.00
45.92
45.76
33.54
22.47
18.26
4a
Current Data Parameters
USER anders
NAME cdav510
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050304
Time 13.41
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 109
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 2298.8
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 22.50 usec
PL1 -6.00 dB
SFO1 125.7942048 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz
F2 - Processing parameters
SI 65536
SF 125.7804262 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
F1P 180.000 ppm
F1 22640.48 Hz
F2P -5.000 ppm
F2 -629.90 Hz
PPMCM 8.11404 ppm/cm
HZCM 1020.58685 Hz/cm
ppm
160
140
120
100
80
60
40
20
0

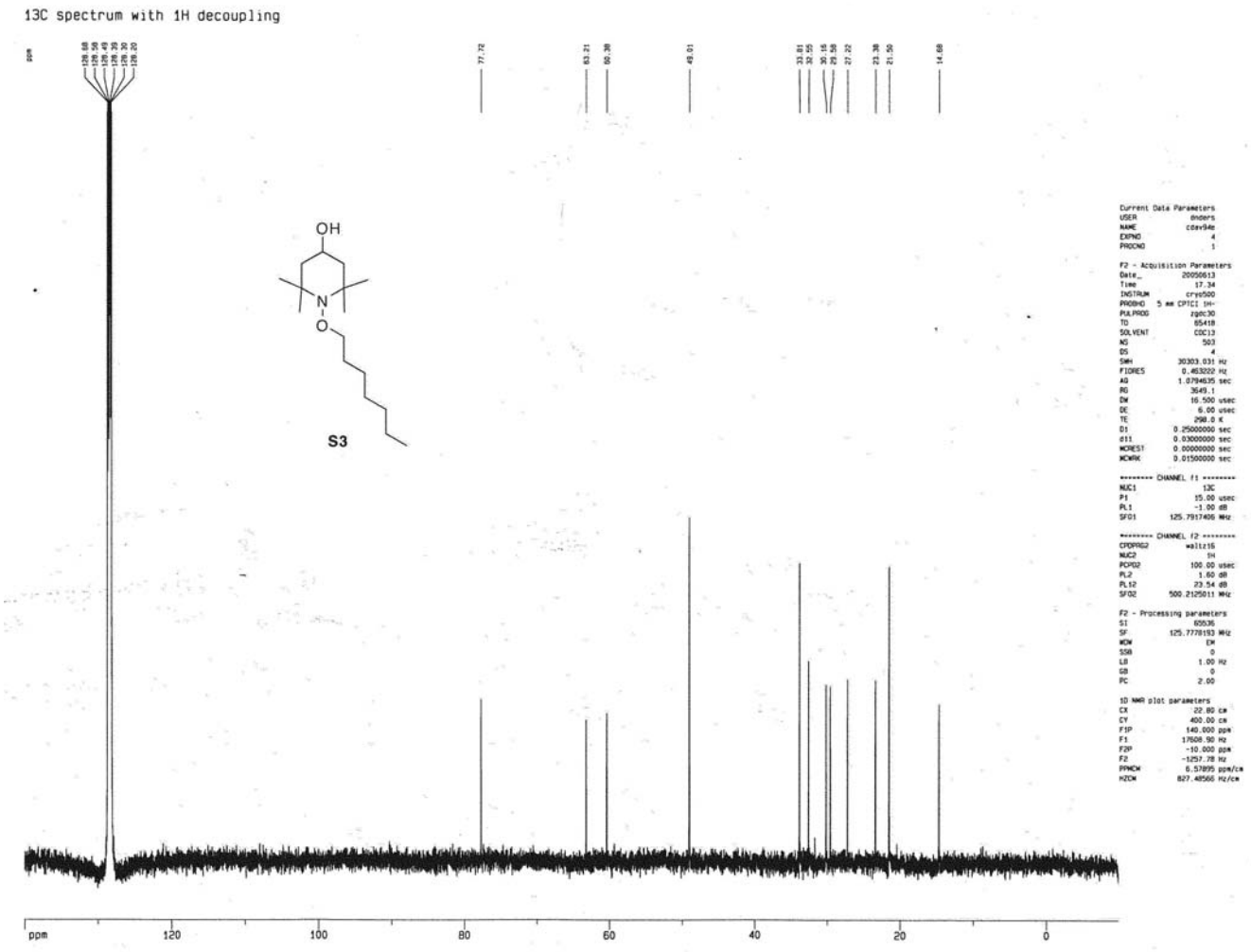

1H spectrum
4b
ppm

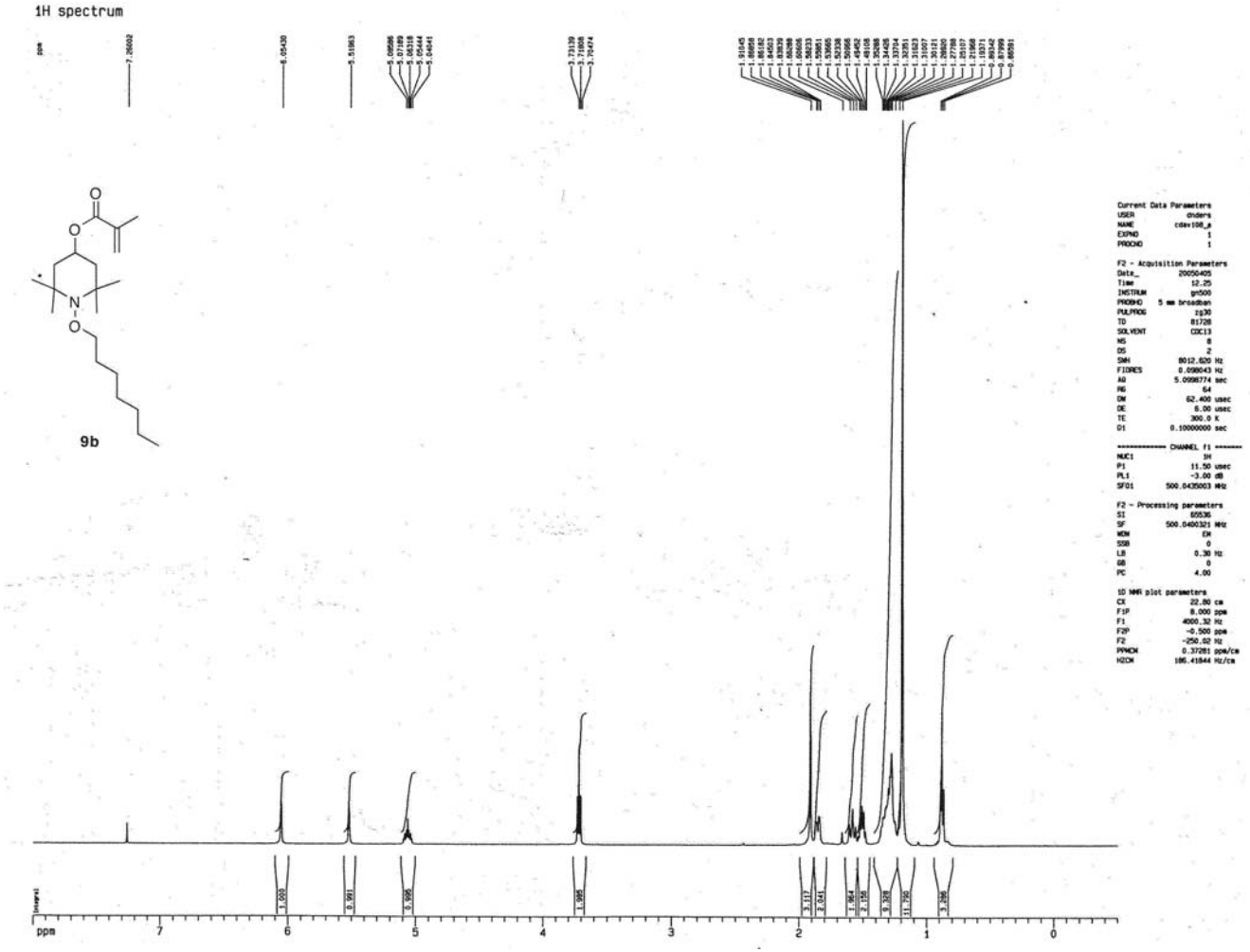

13C spectrum with 1H decoupling
ppm
167.12
136.77
134.19
126.95
125.54
77.25
77.00
76.74
68.14
56.01
45.75
45.20
34.42
33.86
22.85
22.43
18.27
13.87
4b
Current Data Parameters
USER dnders
NAME cdav221_c
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050719
Time 11.10
INSTRUM qn500
PROBHD 5 mm broadband
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 524
DS 4
SWH 30303.031 Hz
FIDRES 0.462368 Hz
AQ 1.0814105 sec
RG 3649.1
DW 16.500 usec
DE 4.50 usec
TE 292.4 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 13.00 usec
PL1 0.00 dB
SFO1 125.7489389 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 15.40 dB
SFO2 500.0425002 MHz
F2 - Processing parameters
SI 65536
SF 125.7351684 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 10.00 cm
F1P 229.520 ppm
F1 28858.70 Hz
F2P -10.507 ppm
F2 -1321.05 Hz
PPMCM 10.52747 ppm/cm
HZCM 1323.67310 Hz/cm
ppm
200
175
150
125
100
75
50
25
0

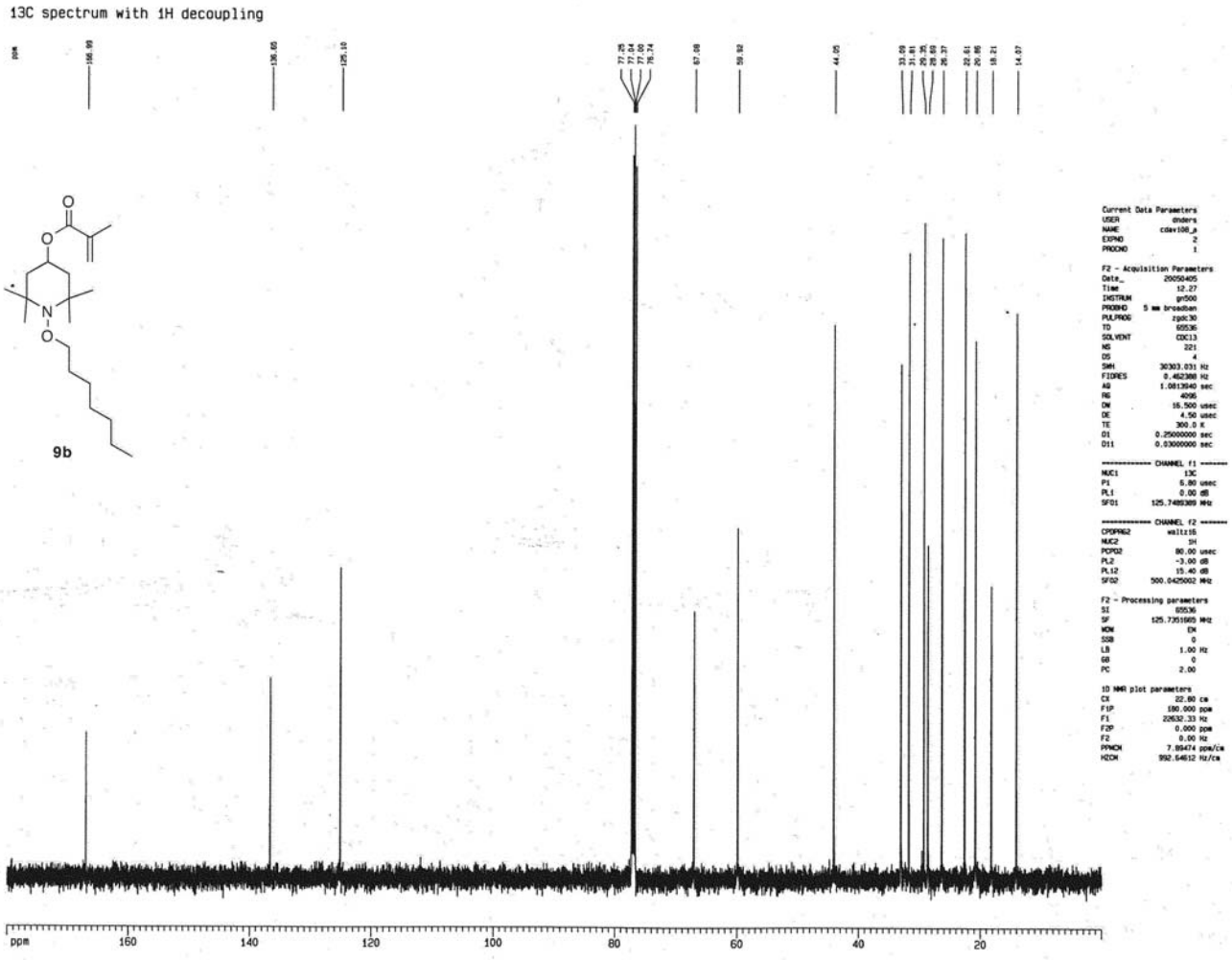

1H spectrum
4c
ppm

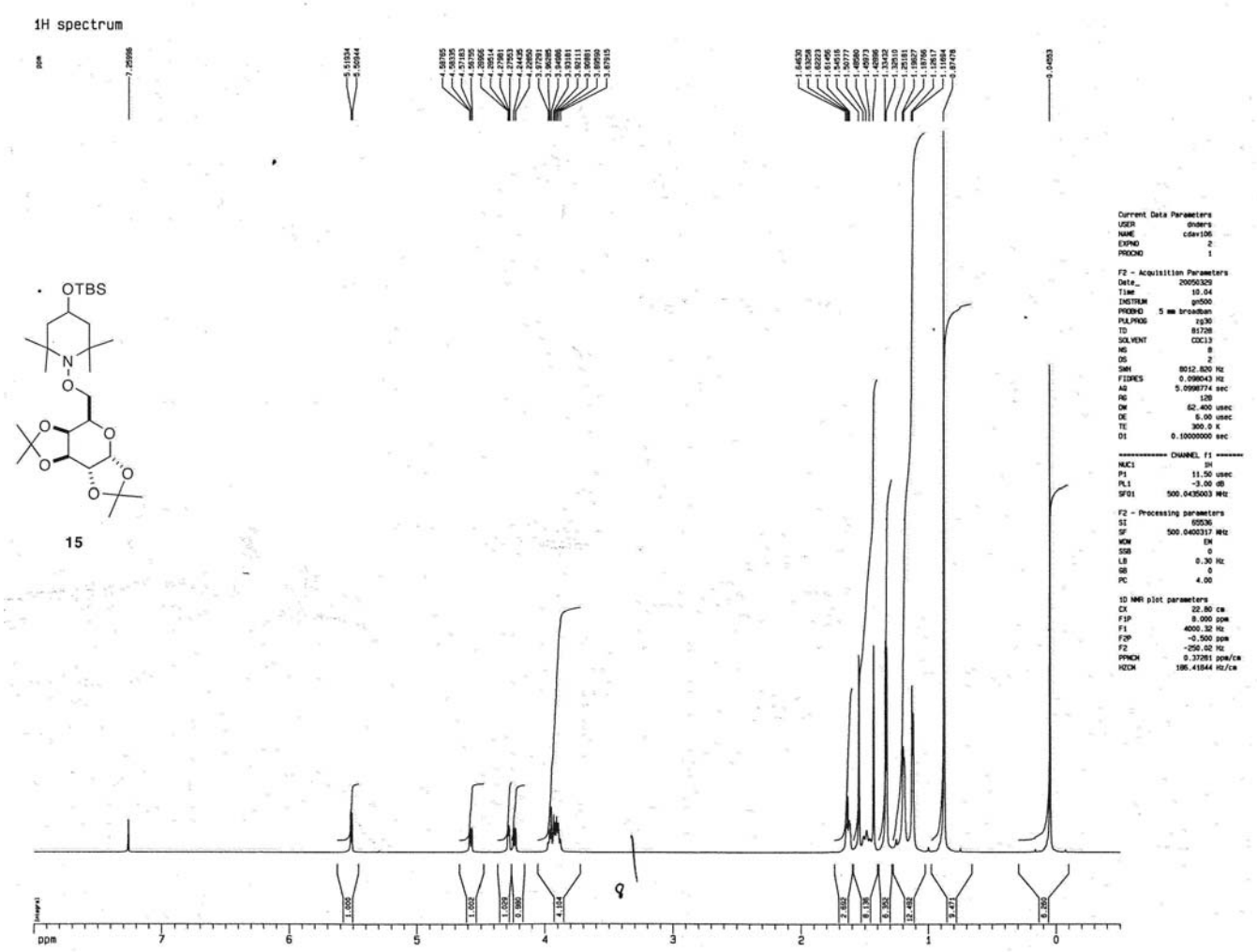

13C spectrum with 1H decoupling
ppm
167.10
136.01
134.01
125.19
124.99
77.26
77.00
76.75
66.15
56.01
45.61
45.21
33.68
32.34
31.91
29.63
29.60
29.53
29.50
29.34
29.15
22.68
22.47
18.25
14.11
4c
Current Data Parameters
USER dnders
NAME csevbic
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050304
Time 13.49
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 121
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 2580.3
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 22.50 usec
PL1 +6.00 dB
SF01 125.7942048 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.40 dB
SF02 500.2230013 MHz
F2 - Processing parameters
SI 65536
SF 125.7804267 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
F1P 180.000 ppm
F1 22640.48 Hz
F2P -5.000 ppm
F2 -628.90 Hz
PPMCM 8.11404 ppm/cm
HZCM 1020.58685 Hz/cm
ppm
160
140
120
100
80
60
40
20
0

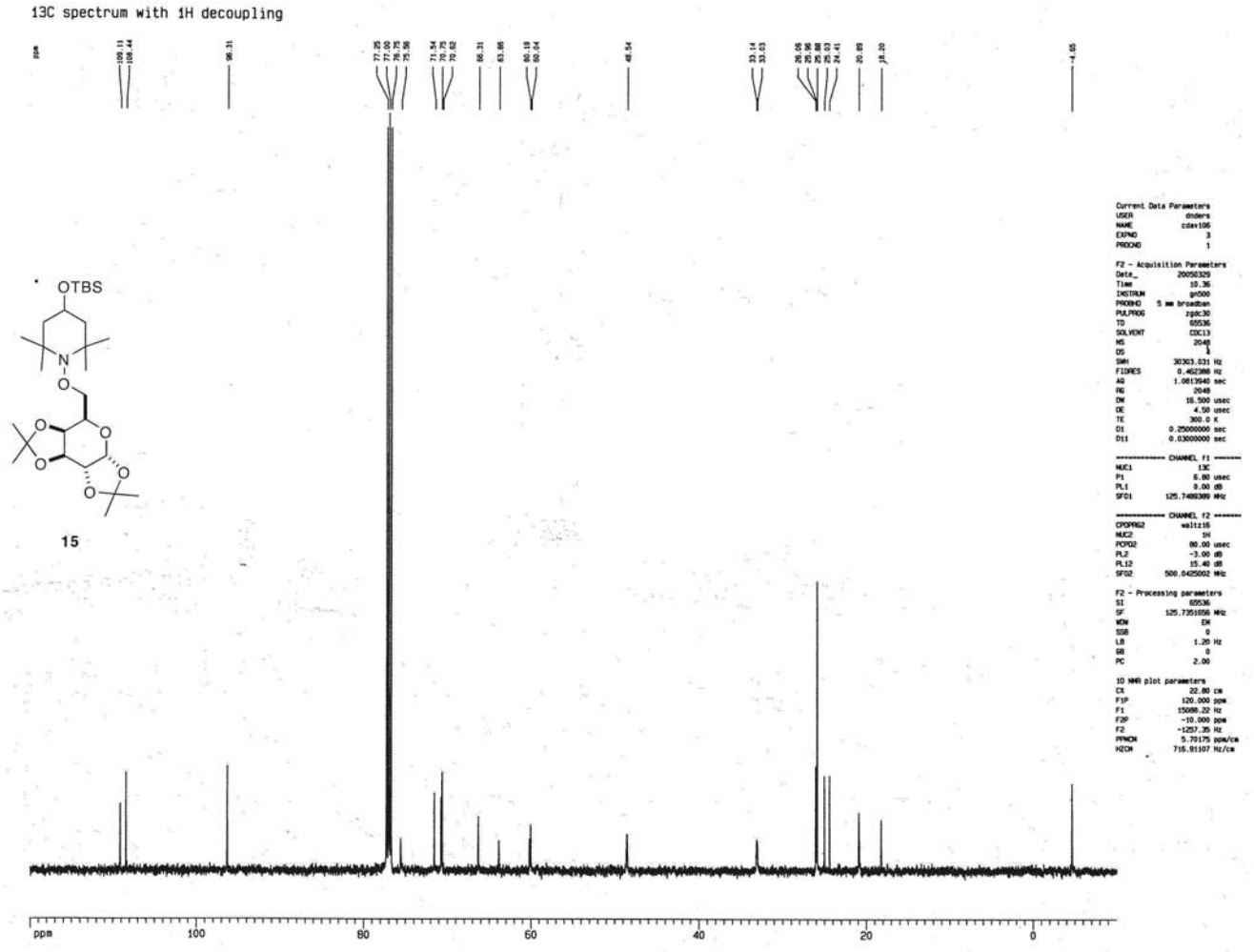

1H spectrum
OH
N
O
S3
ppm
7
6
5
4
3
2
1
0

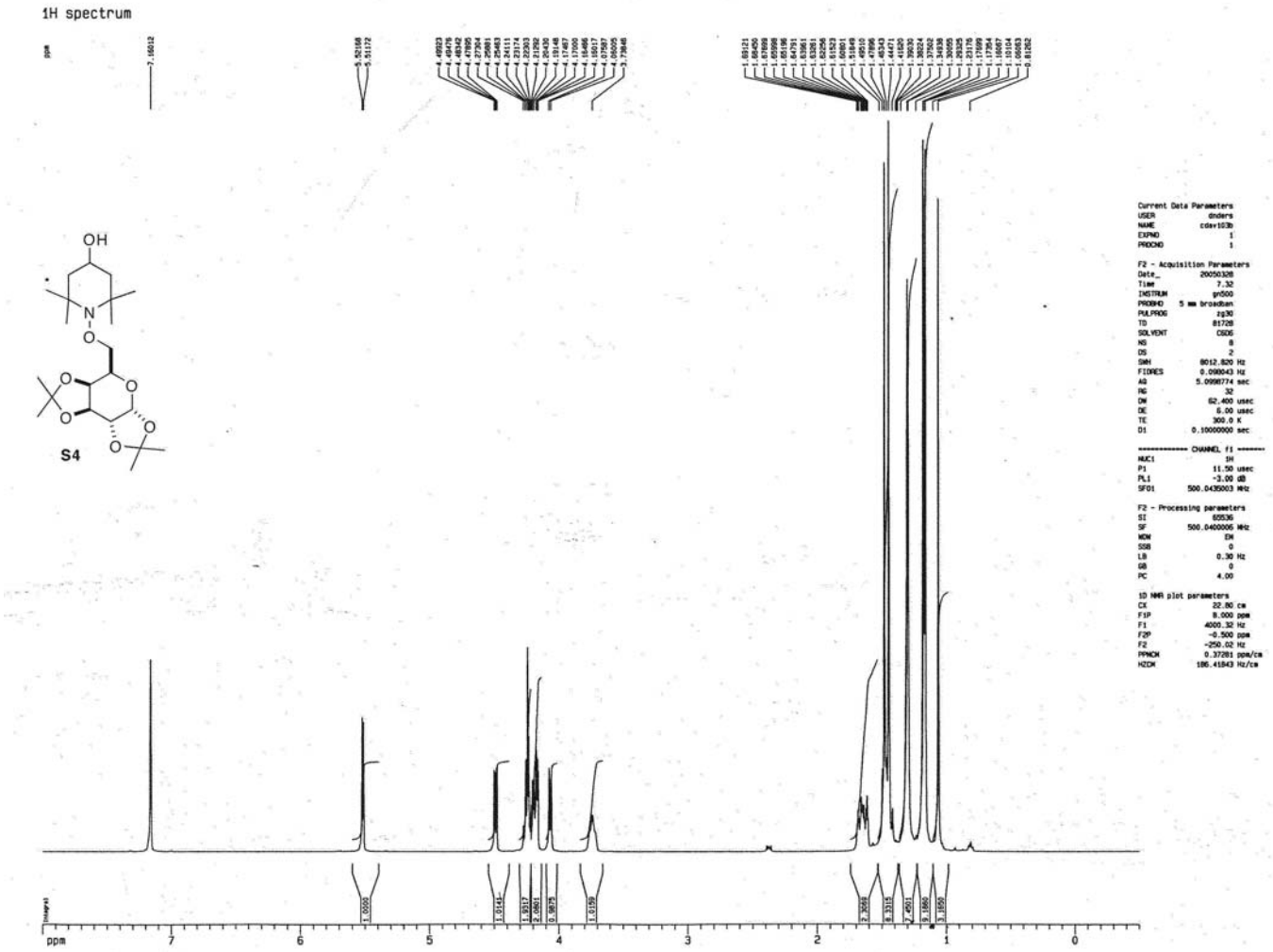

13C spectrum with 1H decoupling
OH
N
O
S3
ppm
120
100
80
60
40
20
0

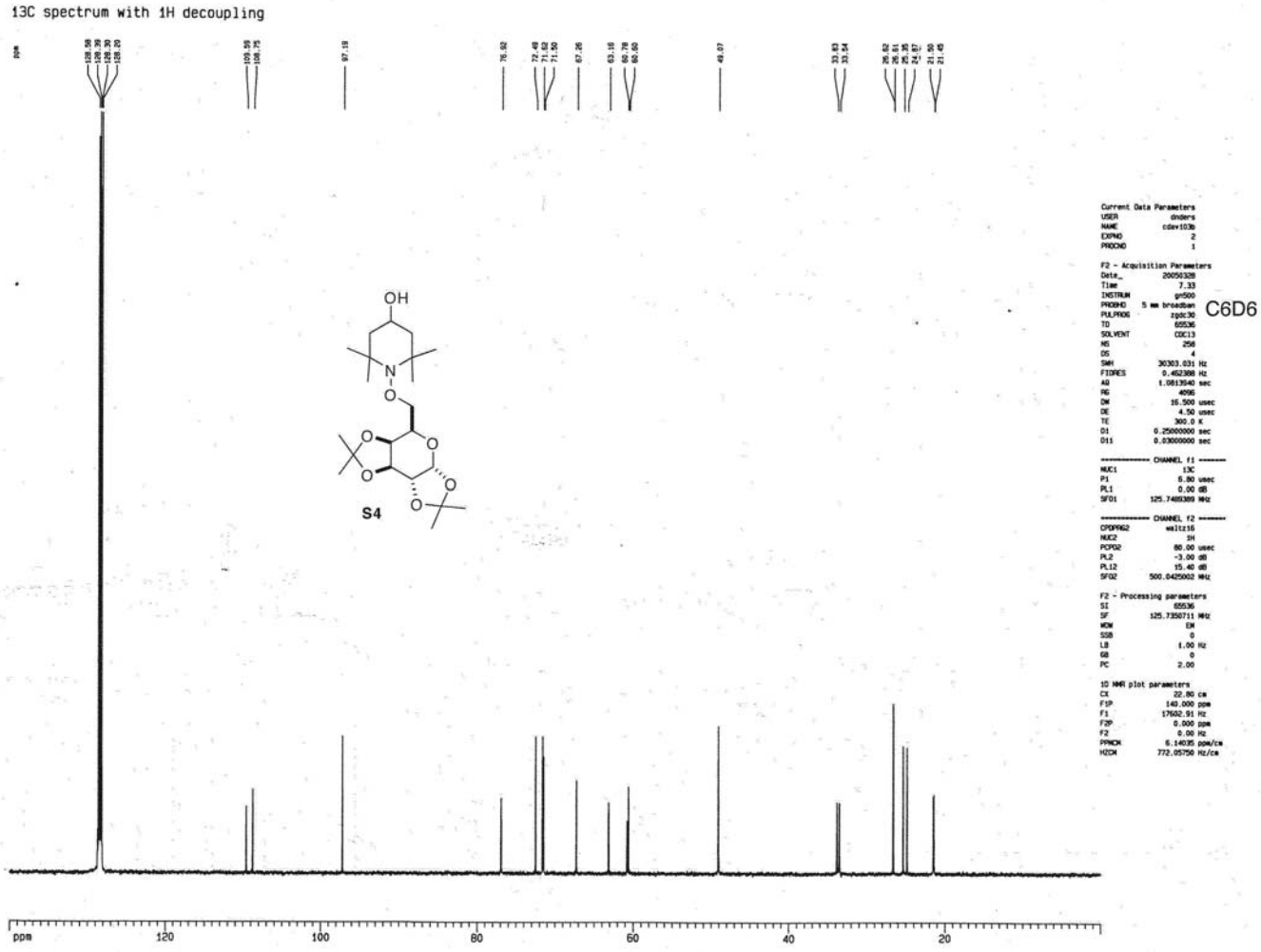

1H spectrum
9b
ppm
Integral

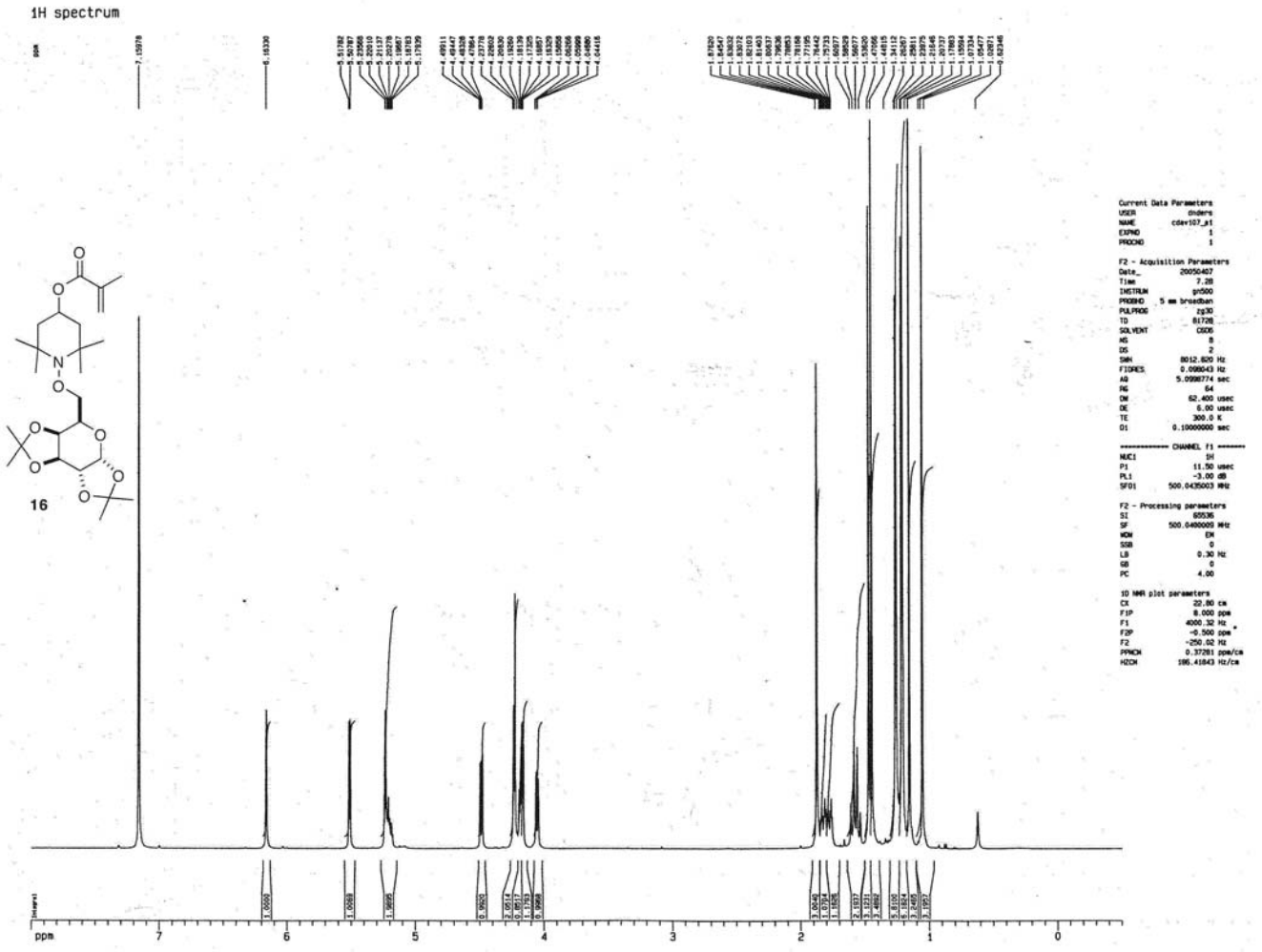

13C spectrum with 1H decoupling
ppm
166.69
136.65
125.10
77.25
77.04
76.99
76.74
67.08
59.92
44.05
33.69
31.81
29.25
28.65
26.37
22.61
20.86
18.21
14.07
9b
Current Data Parameters
USER dnders
NAME cdav108_a
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050405
Time 12.27
INSTRUM gn500
PROBHD 5 mm broadban
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 221
DS 4
SWH 30303.031 Hz
FIDRES 0.462308 Hz
AQ 1.0813040 sec
RG 4096
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 5.80 usec
PL1 0.00 dB
SFO1 125.7489389 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.40 dB
SFO2 500.0425002 MHz
F2 - Processing parameters
SI 65536
SF 125.7351605 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.00 cm
F1P 180.000 ppm
F1 22632.33 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 7.99474 ppm/cm
HZCM 992.64612 Hz/cm
ppm
160
140
120
100
80
60
40
20

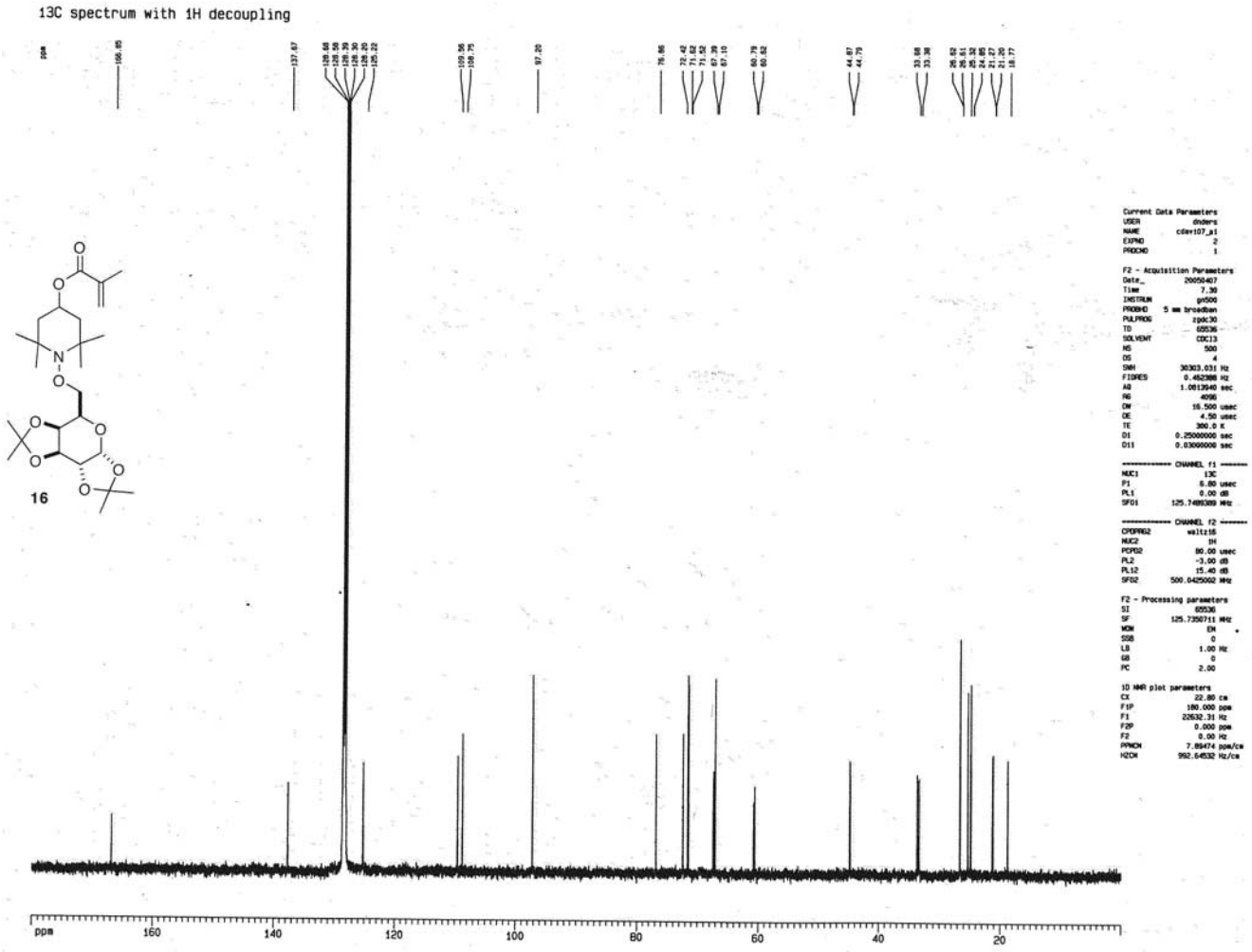

1H spectrum
OTBS
15
ppm

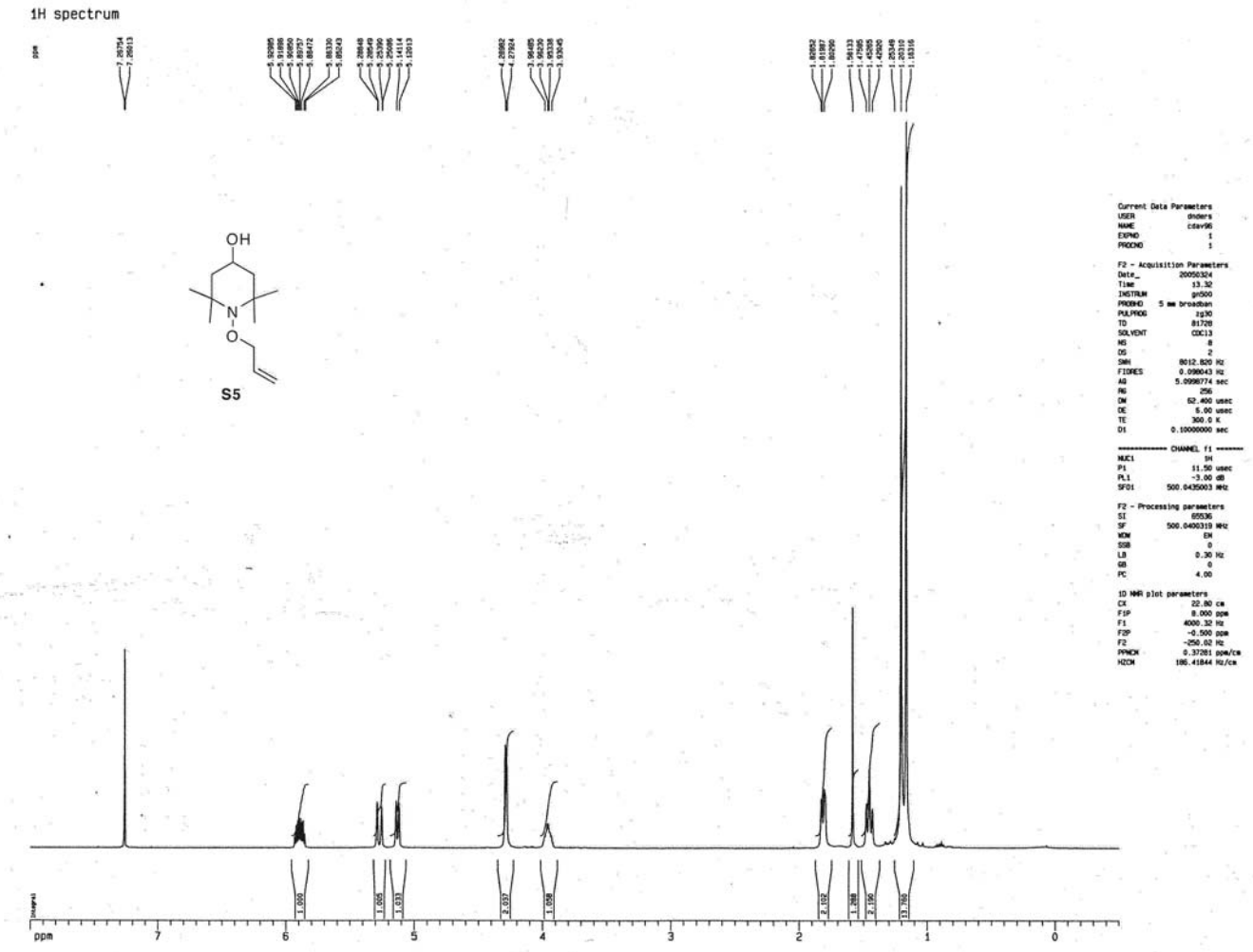

13C spectrum with 1H decoupling
OTBS
15
ppm
100
80
60
40
20
0

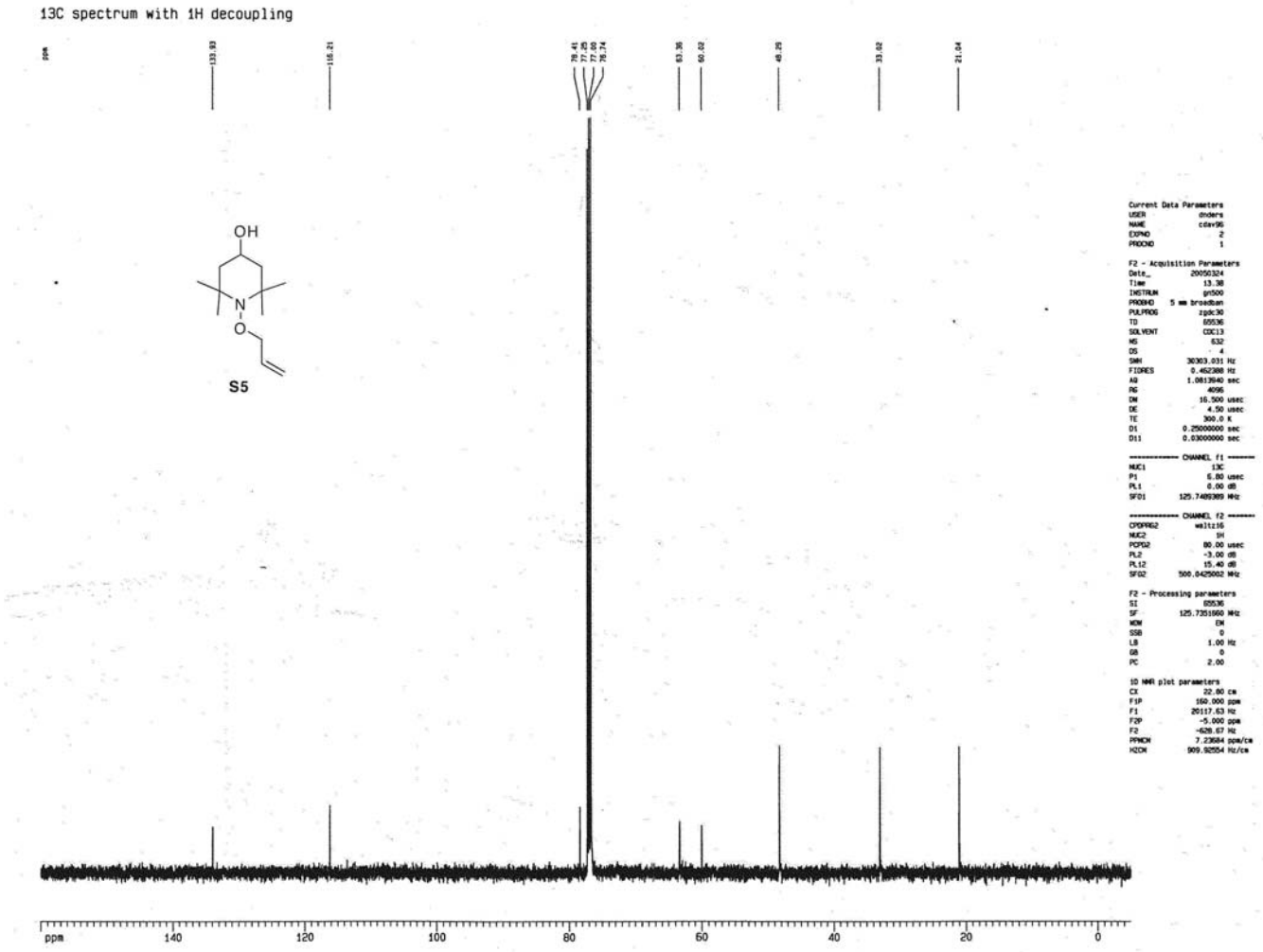

1H spectrum
OH
N
O
S4
ppm
7
6
5
4
3
2
1
0

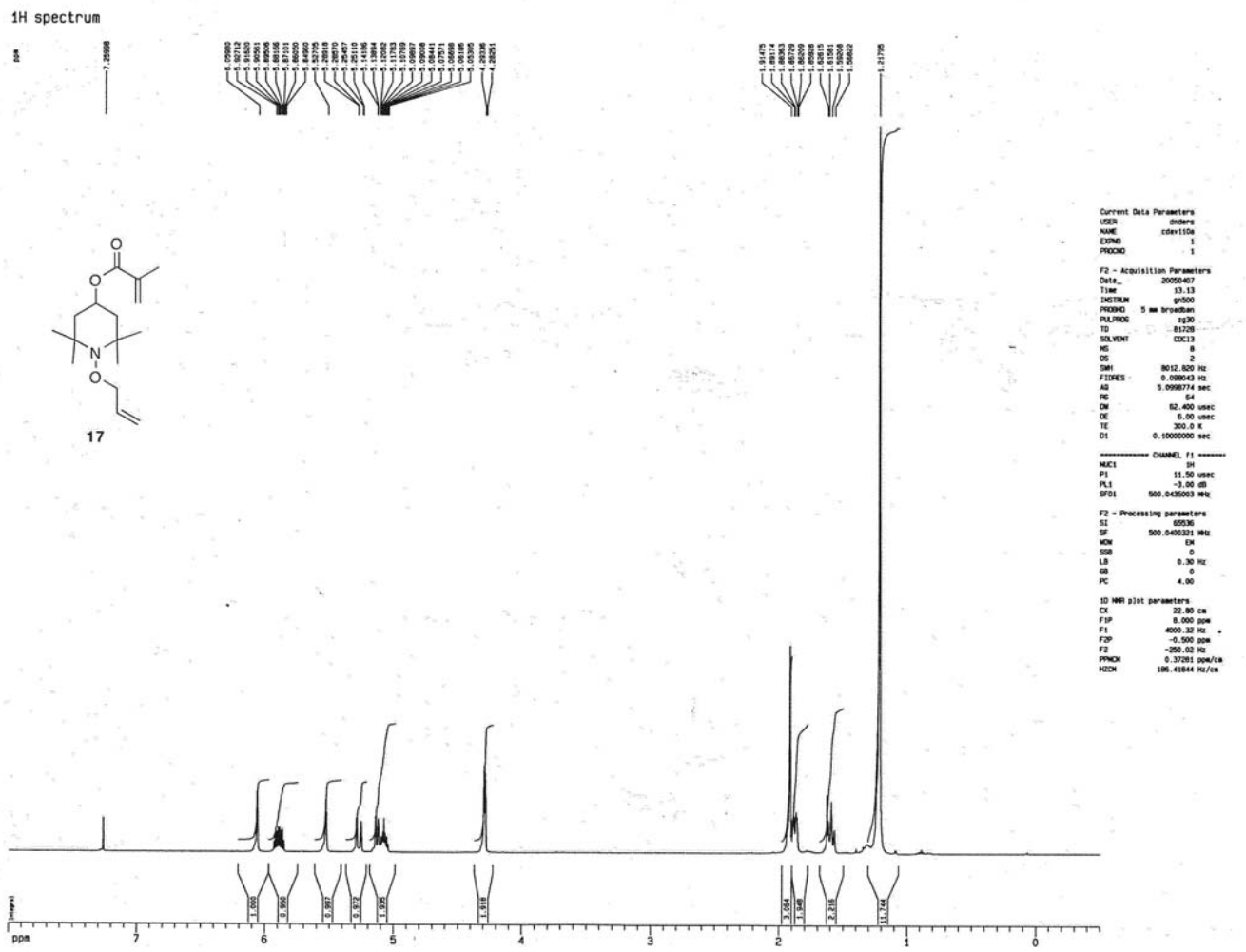

13C spectrum with 1H decoupling
OH
N
O
S4
C6D6
ppm
120
100
80
60
40
20

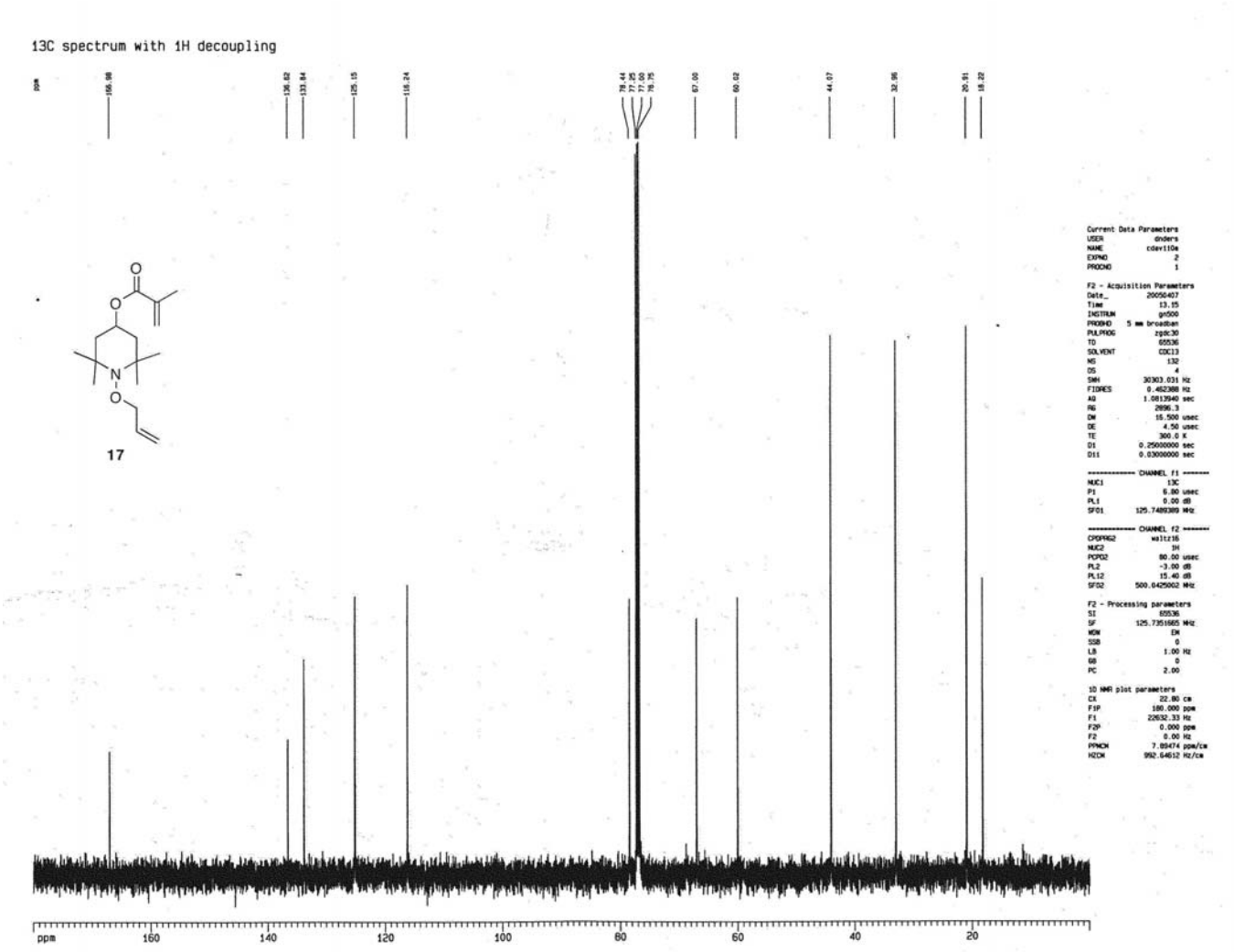

1H spectrum
16
ppm
7
6
5
4
3
2
1
0

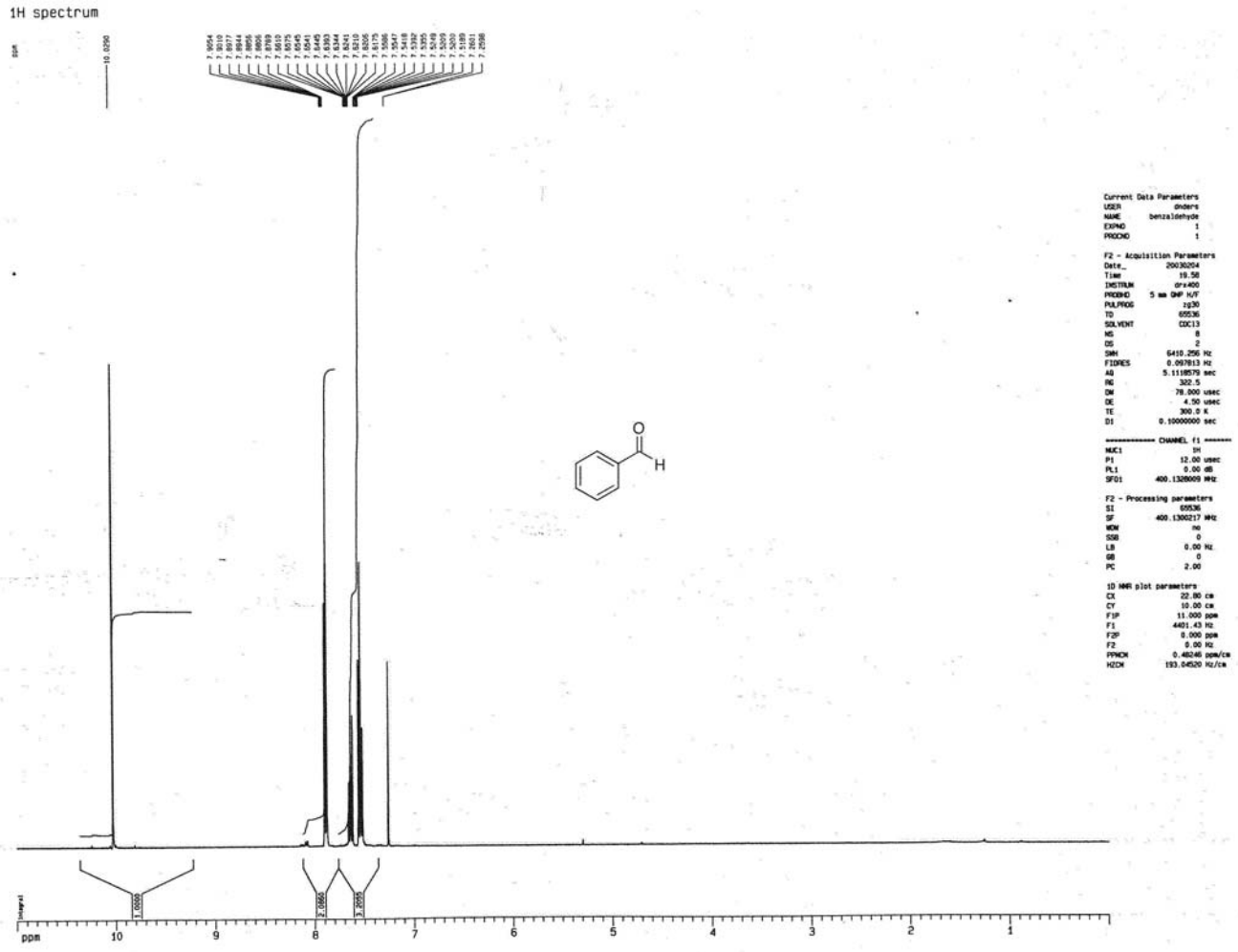

13C spectrum with 1H decoupling
16
ppm
160
140
120
100
80
60
40
20

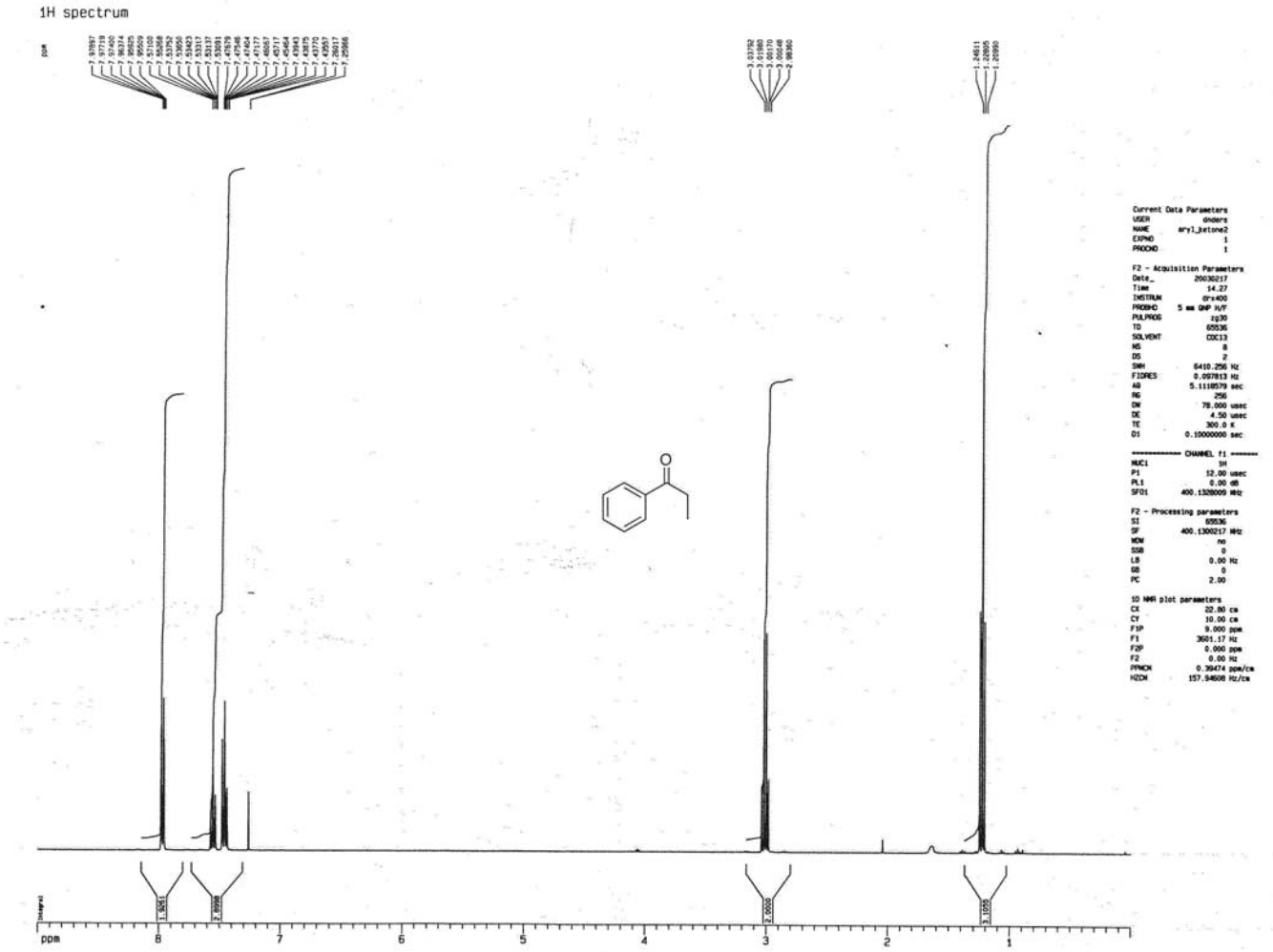

1H spectrum
OH
N
O
S5
ppm
7
6
5
4
3
2
1
0

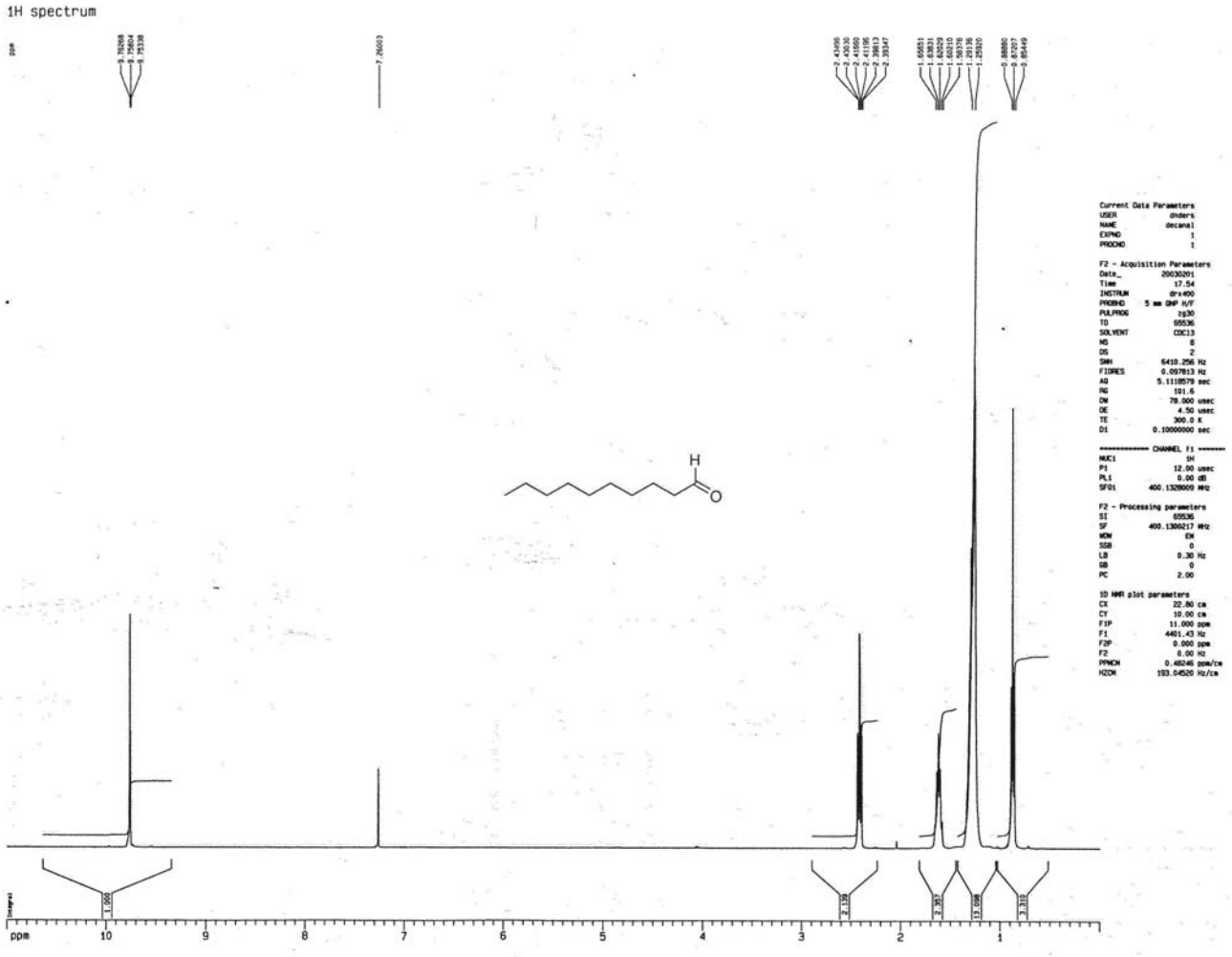

13C spectrum with 1H decoupling
ppm
133.93
116.21
78.41
77.25
77.00
76.74
63.36
60.02
49.29
33.02
21.04
OH
N
O
S5
Current Data Parameters
USER dnders
NAME cdcr96
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050324
Time 13.38
INSTRUM gn500
PROBHD 5 mm broadban
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 532
DS 4
SWH 30303.031 Hz
FIDRES 0.462308 Hz
AQ 1.0813940 sec
RG 4096
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 6.80 usec
PL1 0.00 dB
SFO1 125.7489369 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 15.40 dB
SFO2 500.0425002 MHz
F2 - Processing parameters
SI 65536
SF 125.7351660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
F1P 160.000 ppm
F1 20117.63 Hz
F2P -5.000 ppm
F2 -628.67 Hz
PPMCM 7.23684 ppm/cm
HZCM 909.92554 Hz/cm
ppm
140
120
100
80
60
40
20
0

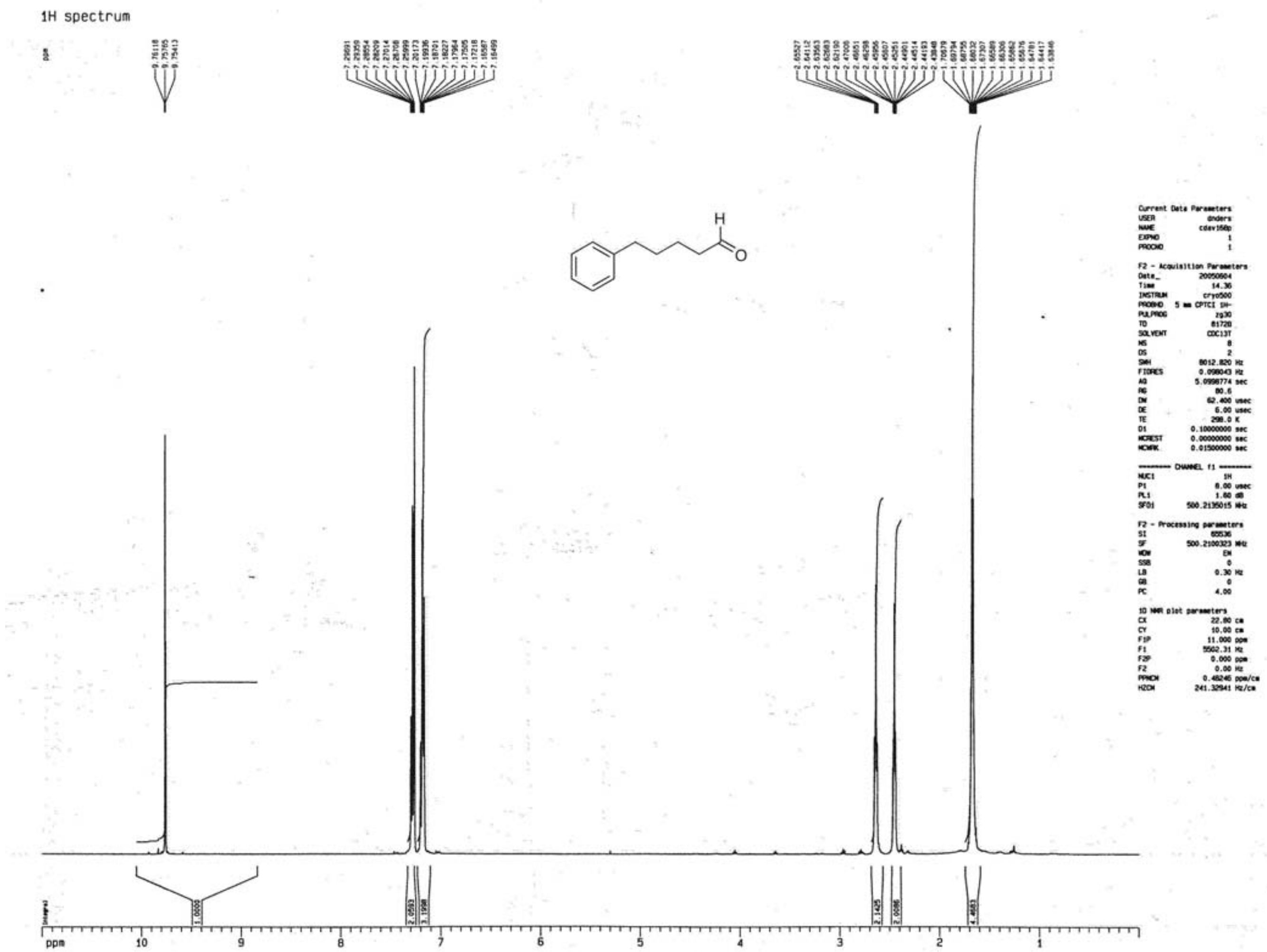

1H spectrum
17
ppm
7
6
5
4
3
2
1
0

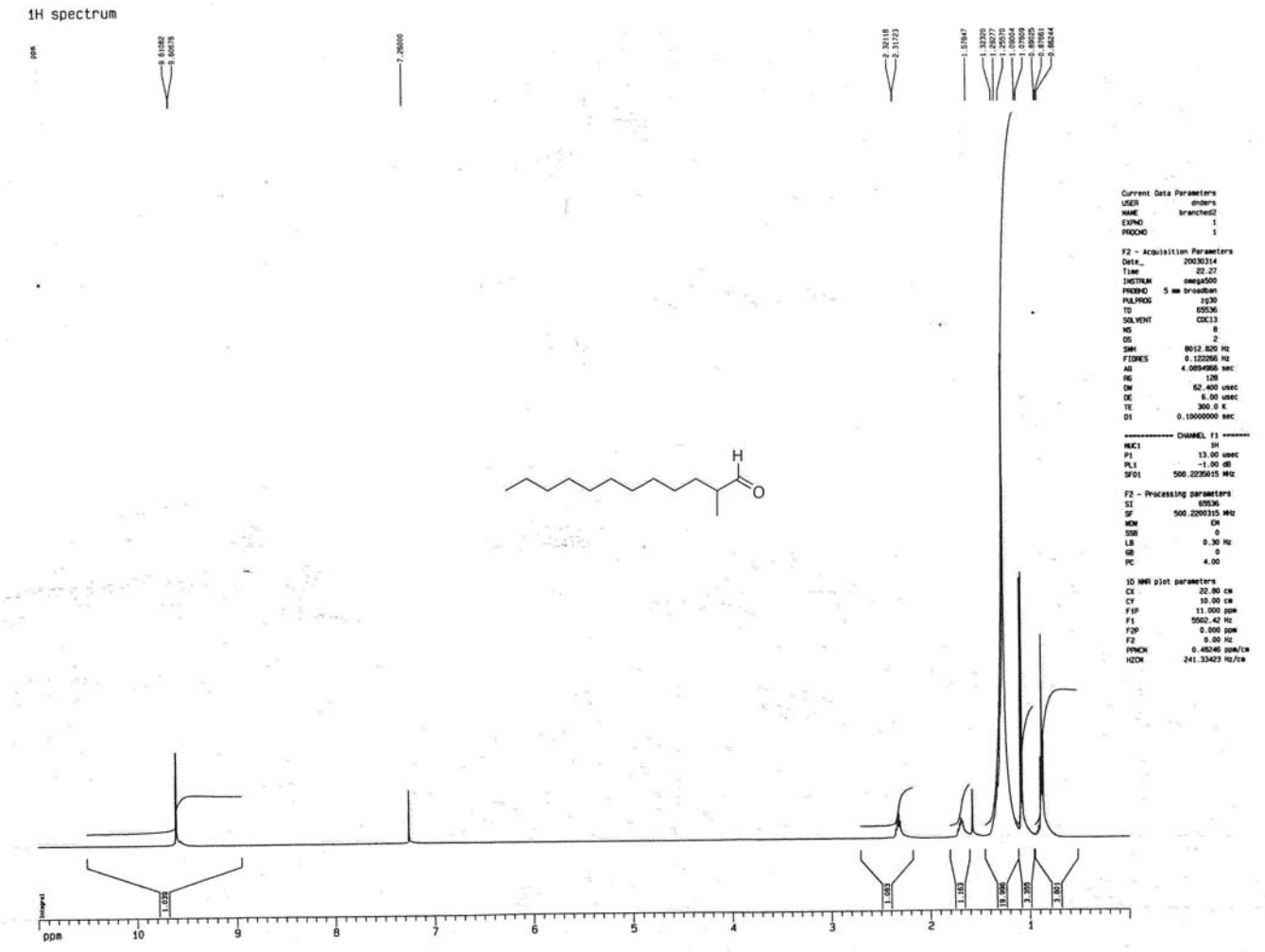

13C spectrum with 1H decoupling
17
ppm
160
140
120
100
80
60
40
20


1H spectrum
ppm
10
9
8
7
6
5
4
3
2
1
O
H


1H spectrum
ppm
1.3045
2.9998
2.0000
3.1595
8
7
6
5
4
3
2
1


1H spectrum
ppm
10
9
8
7
6
5
4
3
2
1
H
O


1H spectrum


1H spectrum
ppm
9.61082
9.60076
7.26000
2.32118
2.31703
1.57847
1.33330
1.28277
1.25053
1.23554
1.07959
0.89925
0.87994
0.86244
H
O
Current Data Parameters
USER anders
NAME branched2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20030314
Time 22.27
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894986 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200315 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 10.00 cm
F1P 11.000 ppm
F1 5502.42 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.48246 ppm/cm
HZCM 241.33423 Hz/cm
Integral
1.035
1.003
1.163
19.996
3.395
3.867
ppm
10
9
8
7
6
5
4
3
2
1