An Atom-Economic and Selective Ruthenium-Catalyzed Redox Isomerization of Propargylic Alcohols. An Efficient Strategy for the Synthesis of Leukotrienes

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Supplemental Experimental Procedures & Spectra

Triethylammonium hexafluorophosphate. Hexafluorophosphoric acid (75% in water, 5.26 mL, 50 mmol) was dissolved in ether (50 mL) and the solution was cooled in an ice bath. Triethylamine (7.67 mL, 5.57 g, 55 mmol) was added dropwise and the ether was removed under vacuum. The yellowish syrup was suspended in toluene (100 mL) and heated at reflux for 24 h in a Dean-Stark apparatus. The toluene was removed under vacuum and the residue was placed in the freezer overnight. The resulting semicrystalline material was recrystallized in isopropanol (40 mL) and washed with isopropanol (3x5 mL) and pentane (5 mL) to give 6.54 g fine white powder (53% yield). All spectral data compared favorably with those reported in the literature.[1] The melting point was considerably higher than the reported value, but stands in better accordance with other trialkylammonium hexafluorophosphates (trimethyl mp > 250 °C and tri-*n*-propyl mp 238 °C). mp 215 °C dec (lit. 87-88 °C); IR (KBr): 3448, 2976, 2940, 2740, 2679, 2492, 1476, 1399, 1174, 1037, 831, 738 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 3.50 (br), 3.02 (q, J = 7.2 Hz, 6H), 1.15 (t, J = 7.3 Hz, 9H).

6-Phenyl-2-hexyn-1-ol (3a). Lithium (0.93 g, 134 mmol) was added in small portions to liquid ammonia (200 mL) containing catalytic iron (III) nitrate. After the blue color dissipated and the white lithium amide was visible, propargyl alcohol (2.88 mL, 2.77 g, 49.4 mmol) in THF (5 mL) was added. After 1 h, 1-bromo-3-phenylpropane (8.36 mL, 10.79 g, 54.2 mmol) in THF (10 mL) was added by syringe over 10 min. The solution was stirred overnight during which time the ammonia was allowed to evaporate. The residue was partitioned between 10% aqueous ammonium chloride (100 mL) and ether (200 mL) and the aqueous layer was extracted with ether (2x100 mL). The combined extracts were dried over sodium sulfate and the solvent

was removed under vacuum. Vacuum distillation yielded 5.53 g of clear oil (64% yield). All spectral data compared favorably with those reported in the literature.[2] IR (film): 3332, 3026, 2938, 2861, 2224, 1603, 1496, 1455, 1133, 1012; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.17 (m, 5H), 4.28 (dt, J = 6.0, 2.2 Hz, 2H), 2.72 (t, J = 7.6 Hz, 2H), 2.24 (tt, J = 7.1, 2.1 Hz, 2H), 1.84 (quint, J = 7.2 Hz, 2H), 1.50-1.46 (m, 1H).

1,1-Dibromo-2-cyclohexylethene. To triphenylphosphine (20.98 g, 80.0 mmol) in methylene chloride (100 mL) was added carbon tetrabromide (13.3 g, 40 mmol) at room temperature and stirring was continued for 1 h. Cyclohexanecarboxaldehyde (2.42 mL, 2.24 g, 20 mmol) was added and stirring was continued for 4 h. The solvent was removed under vacuum and the product was filtered through silica with hexanes to give 4.45 g of the nearly pure dibromide (83% yield). All spectral data compared favorably with those reported in the literature.[3] IR (film): 2927, 2852, 1610, 1448, 1274, 1218, 1140, 966, 894, 815, 766; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.23 (d, J = 9.1 Hz, 1H), 2.34-2.21 (m, 1H), 1.74-1.63 (m, 5H), 1.37-1.05 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8, 87.0, 42.3, 31.1 (2), 25.6, 25.4 (2).

3-Cyclohexyl-2-propyn-1-ol (3b). To 1,1-dibromo-2-cyclohexylethene (1.34 g, 5.00 mmol) in THF (15 mL) at -78 °C was added *n*-butyllithium (6.56 mL, 1.6M, 10.5 mmol) and stirring was continued 1 h at this temperature. The mixture was warmed to room temperature and paraformaldehyde (300 mg, 10 mmol) was added. After stirring overnight the mixture was worked up with 1M aqueous sulfuric acid (50 mL) and extracted with ether (4x50 mL) and the combined extracts were dried over magnesium sulfate. Removal of the solvent and purification by flash chromatography (5:1 hexanes:ethyl acetate) gave 635 mg clear oil (92% yield). IR (film): 3342, 2931, 2854, 2229, 1449, 1361, 1149, 1078, 1026, 986 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.27 (d, J = 3.6 Hz, 2H), 2.42-2.35 (m, 1H), 2.08 (br, 1H), 1.82-1.65 (m, 4H), 1.57-1.25 (m, 6H)**;** ^{13}C NMR (75 MHz, $CDCl_3$): δ 90.5, 78.1, 51.2, 32.5 (2), 28.9, 25.6, 24.7 (2); HRMS Calcd for $C_9H_{14}O$ (M^+): 138.1045. Found 138.1041.

(*E*)-3-Cyclohexyl-2-propenal (4b). 3-Cyclohexyl-2-propyn-1-ol (138 mg, 1.00 mmol) was subjected to the standard indium trichloride isomerization conditions. The reaction was complete in 90 min and the product was purified by flash

chromatography on silica (10:1 hexanes:ethyl acetate) to give 124 mg of clear oil (90% yield). All spectral data compared favorably with those reported in the literature.[4] IR (film): 2928, 2854, 2729, 1693, 1633, 1450, 1122, 1099, 977 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.50 (d, J = 7.9 Hz, 1H), 6.78 (dd, J = 15.7, 6.6 Hz, 1H), 6.07 (ddd, J = 15.7, 7.9, 1.4 Hz, 1H), 2.30-2.25 (m, 1H), 1.85-1.67 (m, 5H), 1.40-1.13 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.8, 164.0, 130.6, 40.8, 31.4 (2), 25.7, 25.5 (2).

1-Tetrahydropyranyloxy-6-chloro-2-hexyne. In a flame-dried 50-mL flask, 1-tetrahydropyranyloxy-2-propyne (4.20 g, 30.0 mmol) was dissolved in dry THF (15 mL). The solution was cooled to -78 °C and *n*-butyllithium (1.6 M in hexane, 20.6 mL, 33.0 mmol) was added slowly. After 15 min 1-bromo-3-chloropropane (5.21 g, 33.1 mmol) was added and the solution was brought to gentle reflux for 24 h. The yellow mixture was quenched with saturated sodium bicarbonate (20 mL) and extracted with ether (3x25 mL). The combined extracts were washed with water (50 mL) and brine (50 mL) and dried over magnesium sulfate. Removal of the solvent under vacuum gave the crude product as a yellow oil (5.22 g) which was taken directly to the next step. All spectral data compared favorably with those reported in the literature.[5] IR (film): 2944, 2870, 2223, 1442, 1346, 1202, 1118, 1024, 903, 872, 817, 655 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.80 (t, J = 3.2 Hz, 1H), 4.25 (qt, J = 15.3, 2.2 Hz, 2H), 3.88-3.80 (m, 1H), 3.65 (t, J = 6.5 Hz, 2H), 3.57-3.50 (m, 1H), 2.43 (tt, J = 6.8, 2.2 Hz), 1.97 (quint, J = 6.6 Hz, 2H), 1.86-1.51 (m, 6H).

1-Tetrahydropyranyloxy-6-iodo-2-hexyne. The crude 1-tetrahydropyranyloxy-6-chloro-2-hexyne above was suspended in 30 mL acetone in a 100-mL flask fitted with a reflux condenser. Sodium iodide (13.50 g, 90 mmol) was added and the mixture was refluxed under nitrogen overnight. The mixture was quenched with water (25 mL) and the orange mixture was extracted with ether (3x25 mL). The combined extracts were washed with water (25 mL) and brine (25 mL) and dried over magnesium sulfate. Evaporation of the solvent under vacuum and purification by flash chromatography on silica (10:1 pentane:ether) gave 6.75 g clear oil (73% yield over two steps). IR (film): 2941, 2869, 2228, 1441, 1346, 1222, 1201, 1118, 1023, 903, 872, 816, 728 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.80 (t, J = 3.2 Hz, 1H), 4.33-4.17 (m, 2H), 3.89-

3.81 (m, 1H), 3.57-3.52 (m, 1H), 3.30 (t, J = 6.7 Hz, 2H), 2.38 (tt, J = 6.7, 2.1 Hz, 2H), 2.00 (quint, J = 6.7 Hz, 2H), 1.85-1.52 (m, 6H); ^{13}C NMR (75 MHz, C_6D_6): δ 96.5, 84.0, 78.0, 61.5, 54.4, 32.2, 30.6, 25.7, 19.8, 19.2, 5.1; HRMS Calcd for $C_{11}H_{17}IO_2$ (M^+): 308.0274. Found 308.0262.

1-Tetrahydropyranyoxy-7-phenyl-2-heptyn-7-ol. 1-Tetrahydropyranyloxy-6-iodo-2-hexyne (1.33 g, 4.32 mmol) was dissolved in freshly distilled ether (40 mL) in a 250-mL flask. The solution was cooled to -78 °C and *t*-butyllithium (1.7 M in pentane, 5.60 mL, 9.52 mmol) was added via syringe. The white mixture was stirred at -78 °C for 30 min and freshly distilled benzaldehyde (0.88 mL, 0.92 g, 0.87 mmol) was added via syringe. The mixture was allowed to warm to room temperature and was quenched with acetic acid (1.2 equivalents) followed by water (25 mL). The aqueous layer was extracted with ether (3x25 mL) and the combined extracts washed with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. Removal of the solvent under vacuum and purification by flash chromatography on silica (3:1 hexanes:ethyl acetate) yielded 1.21 g clear oil (97% yield). IR (film): 3432, 2940, 2867, 2225, 1455, 1346, 1202, 1117, 1022, 903, 871, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.26 (m, 5H), 4.79 (t, J = 3.2 Hz, 1H), 4.70 (t, J = 6.6 Hz, 1H), 4.23 (qt, J = 15.0, 2.2 Hz, 2H), 3.86-3.79 (m, 1H), 3.54-3.47 (m, 1H), 2.26 (tt, J = 6.9, 2.1 Hz, 2H), 1.97 (br, 1H), 1.94-1.47 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.6, 128.5 (2), 127.6, 125.8 (2), 96.6, 86.2, 76.2, 74.1, 62.0, 54.6, 38.1, 30.3, 25.3, 24.8, 19.1, 18.7; Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found C, 74.75; H, 8.29.

1-Tetrahydropyranyloxy-7-oxo-7-phenyl-2-heptyne. 1-Tetrahydropyranyoxy-7-phenyl-2-heptyn-7-ol (1.44 g, 5.00 mmol) was added to a suspension of pyridinium dichromate (4.14 g, 11.0 mmol) in methylene chloride (50 mL). After stirring for 3 h, celite (5 g) was added. After stirring an additional 10 min the mixture was filtered through a plug of florisil and the solvent was removed under vacuum. Flash chromatography on silica gel (5:1 hexanes:ethyl acetate) and removal of the solvent under vacuum gave 1.33 g of clear oil (93% yield). IR (film): 2942, 2870, 2235, 1686, 1598, 1449, 1231, 1201, 1117, 1023, 903, 871, 754 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99-7.97 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.44 (m, 2H), 4.80 (t, J = 3.3 Hz, 1H), 4.25 (qt, J = 15.4, 2.1 Hz, 2H), 3.87-3.81 (m, 1H), 3.55-3.48 (m, 1H), 3.12

(t, J = 7.2 Hz, 2H), 2.38 (tt, J = 6.8, 2.1 Hz, 2H), 1.97 (quint, J = 7.1 Hz, 2H), 1.85-1.49 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.6, 136.9, 133.0, 128.5 (2), 128.0 (2), 96.7, 85.7, 76.7, 62.0, 54.6, 37.2, 30.2, 25.3, 22.9, 19.1, 18.3.

7-Oxo-7-phenyl-2-heptyn-1-ol (3c). 1-Tetrahydropyranyloxy-7-oxo-7-phenyl-2-heptyne (1.30 g, 4.55 mmol) and catalytic *p*-toluenesulfonic acid were dissolved in methanol (25 mL) and stirred for 3 h at room temperature. The methanol was removed under vacuum and the residue was purified by flash chromatography on silica (3:1 hexanes:ethyl acetate) to give 773 mg of slightly tan solid (84% yield). mp 39.5-40.0; IR (film): 3423, 2938, 2224, 1683, 1598, 1449, 1232, 1014, 753, 691 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00-7.97 (m, 2H), 7.60-7.54 (m, 1H), 7.50-7.44 (m, 2H), 4.25 (s, 2H), 3.12 (t, J = 7.2 Hz, 2H), 2.37 (tt, J = 6.9, 2.2 Hz, 2H), 1.97 (quint, J = 7.0 Hz, 2H), 1.72 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.7, 136.9, 133.1, 128.6 (2), 128.0 (2), 85.6, 79.3, 51.3, 37.1, 22.9, 18.3; Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found C, 77.39; H, 6.97.

(*E*)-7-Oxo-7-phenyl-2-heptenal (4c). 7-Oxo-7-phenyl-2-heptyn-1-ol (202 mg, 1.00 mmol) was subjected to the standard indium trichloride isomerization conditions. The reaction was complete in 90 min and the product was purified by flash chromatography on silica (5:1 hexanes:ethyl acetate) to give 161 mg of light yellow crystals (80% yield). mp 31.0-31.5; IR (film): 3061, 2938, 2818, 2738, 1689, 1638, 1598, 1449, 1224, 1125, 974, 754 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.52 (d, J = 7.9 Hz, 1H), 7.97-7.94 (m, 2H), 7.61-7.55 (m, 1H), 7.50-7.44 (m, 2H), 6.88 (dt, J = 15.6, 6.8 Hz, 1H), 6.16 (ddt, J = 15.6, 7.9, 1.4 Hz, 1H), 3.04 (t, J = 7.1 Hz, 2H), 2.46 (qd, J = 7.3, 1.4 Hz, 2H), 1.99 (quint, J = 7.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.2, 193.9, 157.6, 136.7, 133.4, 133.2, 128.8 (2), 127.9 (2), 37.4, 32.0, 22.1; Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found C, 77.11; H, 6.87.

1-Tetrahydropyranyloxy-7-acetoxy-7-phenyl-2-heptyne. 1-Tetrahydropyranyoxy-7-phenyl-2-heptyn-7-ol (1.44 g, 5.00 mmol) was dissolved in freshly distilled pyridine (5 mL) containing catalytic DMAP and the solution was cooled in an ice bath. Acetic anhydride (1.4 mL, 1.53 g, 15.0 mmol) was added and the mixture was warmed to room temperature. After 2 h the reaction mixture was

poured into water (25 mL) and extracted with ether (3x10 mL). The combined extracts were washed with water (3x25 mL) and the solvent was removed under vacuum. Flash chromatography on silica gel (5:1 hexanes:ethyl acetate) gave 1.44 g clear oil (92% yield). IR (film): 2943, 2869, 2235, 1735, 1455, 1372, 1238, 1117, 1023, 903, 761, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.25 (m, 5H), 5.75 (dd, J = 7.8, 6.1 Hz, 1H), 4.79 (t, J = 3.2 Hz, 1H), 4.23 (qt, J = 15.3, 2.1 Hz, 2H), 3.87-3.80 (m, 1H), 3.55-3.48 (m, 1H), 2.24 (tt, J = 7.1, 2.1 Hz, 2H), 2.07 (s, 3H), 2.11-1.41 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 140.4, 128.4 (2), 127.9, 126.4 (2), 96.7, 85.7, 76.4, 75.5, 62.0, 54.6, 35.4, 30.2, 25.3, 24.5, 21.2, 19.1, 18.6.

7-Acetoxy-7-phenyl-2-heptyn-1-ol (3e). 1-Tetrahydropyranyloxy-7-acetoxy-7-phenyl-2-heptyne (1.40 mg, 4.46 mmol) and catalytic *p*-toluenesulfonic acid were dissolved in methanol (25 mL) and stirred for 3 h at room temperature. The methanol was removed under vacuum and the residue was purified by flash chromatography on silica (3:1 hexanes:ethyl acetate) to give 1.02 g clear oil (93% yield). IR (film): 3428, 3034, 2938, 2868, 2224, 1729, 1496, 1373, 1238, 1134, 1021, 761 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$): δ 7.35-7.26 (m, 5H), 5.78 (dd, J = 7.7, 6.2 Hz, 1H), 4.21 (s, 2H), 2.28 (br s, 1H), 2.23 (tt, J = 7.0, 2.1 Hz, 2H), 2.07 (s, 3H), 2.10-1.84 (m, 2H), 1.58-1.43 (m, 2H)**;** ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 140.2, 128.4 (2), 127.9, 126.4 (2), 85.3, 79.0, 75.5, 51.1, 35.3, 24.3, 21.2, 18.4**;** HRMS Calcd for $C_{15}H_{16}O_2$ (M^+ - H_2O): 228.1150. Found 228.1154.

(*E*)-7-Acetoxy-7-phenyl-2-heptenal (4e). 7-Acetoxy-7-phenyl-2-heptyn-1-ol (246 mg, 1.0 mmol) was subjected to the standard indium trichloride isomerization conditions. After 90 min the product was recovered by standard workup and purified by flash chromatography on silica (5:1 hexanes:ethyl acetate) to give 213 mg of clear oil (87% yield). IR (film): 3034, 2944, 2866, 2738, 1734, 1690, 1638, 1373, 1239, 1132, 1023, 976 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.49 (d, J = 7.8 Hz, 1H), 7.38-7.27 (m, 5H), 6.79 (dt, J = 15.6, 6.7 Hz, 1H), 6.08 (dd, J = 15.6, 7.9 Hz, 1H), 5.75 (dd, J = 7.7, 6.3 Hz, 1H), 2.34 (quart, J = 7.2 Hz, 2H), 2.08 (s, 3H), 2.00-1.77 (m, 2H), 1.60-1.43 (m, 2H)**;** ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.8, 170.2, 157.6, 140.1, 133.2, 128.4 (2), 128.0, 126.3 (2), 75.4, 35.6, 32.1, 23.7, 21.1**;** HRMS Calcd for $C_{13}H_{15}O_2$ (M^+ - CH_3CO): 203.1072. Found 203.1065.

(*E*)-1-Phenyl-4-pentadecen-3-one (4h). 1-Phenyl-4-pentadecyn-3-ol [6] (300 mg, 1.00 mmol) was subjected to the standard indium trichloride isomerization conditions except that 10 mol % triethylammonium hexafluorophosphate and no ammonium hexafluorophosphate was used. After 24 h standard workup and purification of the product by flash chromatography on silica gel (20:1 hexanes:ethyl acetate) gave 259 mg of clear oil (86% yield). IR (film): 3028, 2926, 2855, 1698, 1674, 1631, 1455, 1366, 1186, 979, 747, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.16 (m, 5H), 6.82, (dt, J = 15.9, 6.9 Hz, 1H), 6.09 (dt, J = 15.9, 1.5 Hz, 1H), 2.97-2.83 (m, 4H), 2.20 (q, J = 6.7 Hz, 2H), 1.42 (br, 2H), 1.26 (br s, 14H), 0.89 (t, J = 6.6 Hz, 3H)**;** ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.5, 147.8, 141.3, 130.2, 128.4 (2), 128.3 (2), 126.0, 41.6, 32.5, 31.9, 30.1, 29.6, 29.5, 29.4, 29.3, 29.2, 28.1, 22.7, 14.1**;** HRMS Calcd for $C_{21}H_{32}O$ (M^+): 300.2453. Found 300.2458.

5-Methyl-4-hexen-2-yn-1-ol (3g). To tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol) and 1-bromo-2-methylpropene (270 mg, 2.00 mmol) in pyrrolidine (2 mL) at 0 °C was added copper iodide (57 mg, 0.30 mmol) followed by propargyl alcohol (233 μL, 224 mg, 4.00 mmol). The pale yellow solution was stirred for 4 h at room temperature and the catalyst was removed by filtration through silica with ether. The combined extracts were dried over magnesium sulfate and the solvent removed under vacuum. Flash chromatography gave 138 mg of pale yellow oil (63% yield). IR (film): 3333, 2912, 2867, 2210, 1634, 1445, 1380, 1335, 1203, 1171, 1010, 820 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.29 (s, 1H), 4.42 (s, 2H), 1.90 (s, 3H), 1.81 (s, 3H), 1.62 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.4, 104.5, 89.1, 83.8, 51.7, 24.8, 21.0; HRMS Calcd for $C_7H_{10}O$ (M^+): 110.0732. Found 110.0730.

(*E*)-5-Methyl-2,4-hexadienal (4g). 5-Methyl-4-hexen-2-yn-1-ol (110 mg, 1.00 mmol) was subjected to the standard indium trichloride isomerization conditions. After 90 min standard workup and purification by flash chromatography on silica (10:1 pentane:ether) to give 74 mg of clear oil (67% yield). All spectral data compared favorably with those reported in the literature.[7] IR (film): 2978, 2913, 2813, 2717, 1682, 1639, 1593, 1443, 1180, 1128, 982, 877 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.57 (d, J = 8.1 Hz, 1H), 7.39 (dd, J = 15.1, 11.5 Hz, 1H), 6.15 (d, J = 11.5

Hz, 1H), 6.06 (dd, J = 15.1, 8.2 Hz, 1H), 1.95 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.0, 149.4, 148.5, 129.6, 124.2, 26.8, 19.1.

1-Tetrahydropyranyloxy-9-chloro-2-nonyne. In a flame-dried 50-mL flask, 1-tetrahydropyranyloxy-2-propyne (2.10 mL, 2.10 g, 15.0 mmol) was dissolved in dry THF (10 mL). The solution was cooled to -78 °C and *n*-butyllithium (1.6 M in hexane, 10.3 mL, 16.5 mmol) was added slowly. After 15 min, 1-bromo-6-chlorohexane (2.65 mL, 3.29 g, 16.5 mmol) was added and the solution was brought to gentle reflux for 24 hours. The yellow mixture was quenched with saturated sodium bicarbonate (10 mL) and extracted with ether (3x10 mL). The combined extracts were washed with water (25 mL) and brine (25 mL) and dried over magnesium sulfate. Removal of the solvent under vacuum and purification by flash chromatography (10:1 hexanes:ethyl acetate) on silica gave 3.22 g of clear oil (83% yield). IR (film): 2939, 2861, 2222, 1442, 1346, 1201, 1117, 1023, 903, 872, 816 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.81 (t, J = 3.2 Hz, 1H), 4.25 (qt, J = 15.9, 2.2 Hz, 2H), 3.88-3.81 (m, 1H), 3.57-3.41 (m, 3H), 2.23 (tt, J = 6.9, 2.1 Hz, 2H), 1.90-1.34 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 96.6, 86.3, 75.9, 61.9, 54.6, 45.0, 32.4, 30.2, 28.3, 28.0, 26.3, 25.3, 19.1, 18.7; HRMS Calcd for $C_{14}H_{23}ClO_2$ (M^+): 258.1387. Found 258.1384.

1-Tetrahydropyranyloxy-2,10-pentadecadiyne. In a 25-mL flask, freshly distilled hexyne (690 μL, 493 mg, 6.0 mmol) was dissolved in THF (5 mL). The solution was cooled to -78 °C and n-butyllithium (1.6 M in hexanes, 4.13 mL, 6.6 mmol) was added. After stirring 15 min 1-tetrahydropyranyoxy-9-chloro-2-nonyne (1.29 g, 5 mmol), hexamethylphosphoramide (1.74 mL, 1.79 g, 10 mmol), and catalytic sodium iodide (113 mg, 0.75 mmol) were added. The solution was heated to reflux and after 3 h the reaction was complete. The reaction mixture was quenched with water (50 mL) and extracted with ether (3x50 mL). The combined extracts were washed with water and dried over magnesium sulfate. The solvent was removed under vacuum and the residue purified by flash chromatography on silica (10:1 hexanes:ethyl acetate) to give 1.32 g of clear oil (87% yield). This intermediate was carried forward without complete characterization. IR (film): 2935, 2860, 1456, 1346, 1201, 1118, 1024, 903, 872, 816 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.81 (t, J

= 3.3 Hz, 1H), 4.30 (dt, J = 15.3, 2.2 Hz, 1H), 4.20 (dt, J = 15.2, 2.1 Hz, 1H), 3.89-3.81 (m, 1H), 3.56-3.49 (m, 1H), 2.22 (tt, J = 7.0, 2.1 Hz, 2H), 2.14 (t, J = 6.5 Hz, 4H), 1.86-1.33 (m, 18H), 0.91 (t, 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 96.6, 86.6, 80.3, 80.0, 75.8, 62.0, 54.6, 31.2, 30.3, 29.0, 28.5, 28.4, 28.3, 25.4, 21.9, 19.1, 18.8, 18.7, 18.4, 13.6.

2,10-Pentadecadiyn-1-ol (3f). 1-Tetrahydropyranyloxy-2,10-pentadecadiyne (1.30 g, 4.27 mmol) and a catalytic quantity of *p*-toluenesulfonic acid were dissolved in methanol (25 mL) and stirred for three hours at room temperature. The methanol was removed under vacuum and the residue was purified by flash chromatography on silica (5:1 hexanes:ethyl acetate) to give 0.91 g of clear oil (97% yield). IR (film): 3353, 2934, 2860, 2226, 1464, 1434, 1331, 1137, 1013, 726 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$): δ 4.25 (s, 2H), 2.22 (tt, J = 7.0, 2.2 Hz, 2H), 2.17-2.12 (m, 4H), 1.70 (s, 1H), 1.54-1.38 (m, 12H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 86.5, 80.3, 80.0, 78.3, 51.4, 31.2, 28.9, 28.4, 28.31, 28.25, 21.9, 18.7 (2), 18.4, 13.6; HRMS Calcd for $C_{14}H_{21}O$ (M^+ - CH_3): 205.1592. Found 205.1589.

(*E*)-2-Pentadecen-10-ynal (4f). 2,10-Pentadecadiyn-1-ol (220 mg, 1.0 mmol) was subjected to the standard indium trichloride isomerization conditions. After 90 min, the product was recovered and purified by flash chromatography on silica (20:1 hexanes:ethyl acetate) to give 182 mg of clear oil (83% yield). IR (film): 2933, 2859, 2733, 1694, 1638, 1465, 1434, 1157, 1124, 976 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.51 (d, J = 7.9 Hz, 1H), 6.86 (dt, J = 15.6, 6.8 Hz, 1H), 6.12 (ddt, J = 15.6, 7.9, 1.5 Hz, 1H), 2.35 (qd, J = 7.2, 1.5 Hz, 2H), 2.15 (t, J = 6.6 Hz, 4H), 1.58-1.31 (m, 12H), 0.91 (t, J = 7.1 Hz, 3H)**;** ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.1, 158.8, 132.9, 80.3, 79.8, 32.6, 31.2, 28.9, 28.6, 28.4, 27.7, 21.9, 18.6, 18.4, 13.6**;** HRMS Calcd for $C_{14}H_{23}$ (M^+ - CHO): 191.1436. Found 191.1429.

1-Tetrahydropyranyoxy-9-iodo-2-nonyne. 1-Tetrahydropyranyoxy-9-chloro-2-nonyne (2.38 g, 9.21 mmol) was dissolved in acetone (30 mL) in a 100-mL flask. Sodium iodide (4.50 g, 30 mmol) was added and the mixture was heated at reflux under nitrogen overnight. The mixture was quenched with water (25 mL) and the yellow mixture was extracted with ether (3x25 mL). The combined extracts were

washed with water (25 mL) and brine (25 mL) and dried over magnesium sulfate. Evaporation of the solvent under vacuum and purification by flash chromatography on silica (10:1 pentane:ether) gave 2.48 g of clear oil (77% yield). IR (film): 2936, 2857, 2223, 1455, 1441, 1346, 1201, 1118, 1023, 903, 872, 816 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.81 (t, J = 3.2 Hz, 1H), 4.24 (qt, J = 15.3, 2.1 Hz, 2H), 3.88-3.81 (m, 1H), 3.56-3.49 (m, 1H), 3.19 (t, J = 7.0, 2H), 2.23 (tt, J = 6.9, 2.1 Hz, 2H), 1.85-1.38 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 96.6, 86.3, 75.9, 61.9, 54.6, 33.3, 30.3, 29.9, 28.3, 27.7, 25.3, 19.1, 18.7, 7.0; HRMS Calcd for $C_{14}H_{23}IO_2$ (M^+): 350.0743. Found 350.0731.

1-Tetrahydropyranyloxy-10-phenyl-2-decyn-10-ol. 1-Tetrahydropyranyoxy-9-iodo-2-nonyne (1.75 g, 5.0 mmol) was dissolved in freshly distilled ether (50 mL) in a flame dried 250-mL flask. The solution was cooled to -78 °C and *t*-butyllithium (1.7 M in pentane, 6.50 mL, 11 mmol) was added via syringe. The white mixture was stirred at -78 °C for 30 min and freshly distilled benzaldehyde (1.02 mL, 1.06 g, 10.0 mmol) was added via syringe. The mixture was stirred for 30 min and then quenched with acetic acid (1.2 equivalents) followed by water (50 mL). The aqueous layer was extracted with ether (3x25 mL) and the combined extracts washed with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. Removal of the solvent under vacuum and purification by flash chromatography on silica yielded 1.23 g of clear oil (74% yield). IR (film): 3437, 2935, 2857, 2225, 1604, 1493, 1454, 1346, 1202, 1117, 1023, 903, 872 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.37-7.23 (m, 5H), 4.80 (t, J = 3.2 Hz, 1H), 4.64 (m, 1H), 4.27 (dt, J = 15.2, 2.2 Hz, 1H), 4.17 (dt, J = 15.3, 2.1 Hz, 1H), 3.86-3.78 (m, 1H), 3.54-3.47 (m, 1H), 2.19 (tt, J = 7.0, 2.1 Hz, 2H), 2.10 (s, 1H), 1.88-1.21 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.9, 128.3 (2), 127.4, 125.8 (2), 96.5, 86.6, 75.7, 74.5, 61.9, 54.6, 39.0, 30.2, 28.9, 28.6, 28.4, 25.6, 25.3, 19.0, 18.7.

10-Phenyl-2-decyn-1,10-diol (3d). 1-Tetrahydropyranyloxy-10-phenyl-2-decyn-10-ol (1.20 g, 3.63 mmol) and catalytic *p*-toluenesulfonic acid were dissolved in methanol (25 mL) and stirred for 3 h at room temperature. The methanol was removed under vacuum and the residue was purified by flash chromatography on silica (1:1 hexanes:ethyl acetate) to give 814 mg of clear oil (91% yield). IR (film):

3353, 2933, 2858, 2225, 1494, 1455, 1363, 1330, 1134, 1013, 761, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.25 (m, 5H), 4.66 (m, 1H), 4.22 (m, 2H), 2.19 (tt, J = 6.9, 2.2 Hz, 2H), 2.01 (s, 1H), 1.83-1.65 (m, 3H), 1.52-1.23 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.8, 128.4 (2), 127.4, 125.8 (2), 86.4, 78.4, 74.6, 51.2, 38.9, 28.8, 28.6, 28.3, 25.5, 18.6; Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found C, 78.19; H, 8.89.

(*E*)-10-Hydroxy-10-phenyl-2-decenal (4d). 10-Phenyl-2-decyn-1,10-diol (246 mg, 1.0 mmol) was subjected to the standard indium trichloride isomerization conditions. After 90 min, the product was recovered by flash chromatography on silica (3:1 hexanes:ethyl acetate) to give 211 mg of clear oil (86% yield). IR (film): 3438, 3029, 2931, 2857, 2738, 1689, 1636, 1494, 1454, 1157, 1129, 975 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.48 (d, J = 7.9 Hz, 1H), 7.38-7.25 (m, 5H), 6.83 (dt, J = 15.6, 6.8 Hz, 1H), 6.09 (ddt, J = 15.6, 7.9, 1.5 Hz, 1H), 4.65 (t, J = 6.6 Hz, 1H), 2.31 (qd, J = 7.2, 1.4 Hz, 2H), 2.03 (s, 1H), 1.83-1.67 (m, 2H), 1.51-1.24 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.1, 158.9,144.8, 132.9, 128.4 (2), 127.5, 125.8 (2), 74.5, 38.9, 32.6, 29.2, 29.0, 27.7, 25.6; Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found C, 78.16; H, 8.99.

2-Tridecyn-1-ol. To 1-dodecyne (4.28 mL, 3.33 g, 20.0 mmol) in THF (40 mL) at -78 °C was added *n*-butyllithium (13.1 mL, 1.6 M, 21.0 mmol). After stirring for 30 min, paraformaldehyde (1.20 g, 40.0 mmol) was added and the mixture was warmed to room temperature. After stirring overnight, the mixture was worked up with 1M aqueous sulfuric acid (50 mL) and extracted with ether (4x50 mL) and the combined extracts were dried over magnesium sulfate. Removal of the solvent under vacuum and purification by flash chromatography (5:1 hexanes:ethyl acetate) gave 3.78 g of waxy solid (96% yield). All spectral data compared favorably with those reported in the literature.[8] mp 29.5-30.0 °C**;** IR (film): 3332, 2924, 2855, 2289, 2226, 1466, 1378, 1130, 1228, 1013, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.26 (dt, J = 6.0, 2.2 Hz, 2H), 2.20 (tt, J = 7.1, 2.1 Hz, 2H), 1.57-1.26 (m, 17H), 0.88 (t, J = 6.5 Hz, 3H).

(*E*)-2-Tridecenal. 2-Tridecyn-1-ol (24.5 mg, 0.125 mmol) was subjected to the standard indium trichloride isomerization conditions. After 90 min, the product was

recovered by the standard isolation procedure and purified by flash chromatography on silica (10:1 hexanes:ethyl acetate) to give 20 mg of clear oil (82% yield). All spectral data compared favorably with those reported in the literature.[9] IR (film): 2926, 2855, 2723, 1697, 1652, 1466, 1421, 1285, 1160, 976, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.51 (d, J = 7.9 Hz, 1H), 6.86 (dt, J = 15.5, 6.8 Hz, 1H), 6.12 (dd, J = 15.6, 7.9 Hz, 1H), 2.34 (qd, J = 7.1, 1.4 Hz, 2H), 1.53-1.19 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H).

Methyl 2-tridecynoate. To dodecyne (1.07 mL, 0.83 g, 5.0 mmol) in freshly distilled THF (10 mL) at -78 °C was added *n*-butyllithium (3.44 mL, 1.6M, 5.5 mmol). After stirring 30 min, methyl chloroformate (0.47 mL, 0.57 mg, 6 mmol) was added and the mixture was warmed to room temperature. Workup with water (50 mL) and ether (3x50 mL) and purification by flash chromatography on silica gave 1.10 g clear oil (98% yield). IR (film): 2929, 2856, 2238, 1756, 1719, 1459, 1435, 1255, 1077, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 3H), 2.33 (t, J = 7.2 Hz, 2H), 1.60-1.26 (m, 16 H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.3, 90.0, 72.8, 52.5, 31.9, 29.5, 29.4, 29.3, 29.0, 28.8, 27.5, 22.7, 18.6, 14.1; HRMS Calcd for $C_{14}H_{25}O_2$ ($M + H^+$): 225.1855. Found 225.1858.

1,1-Dideutero-2-tridecyn-1-ol (5). To lithium aluminum deuteride (42 mg, 1.0 mmol) in dry THF (1 mL) at -78 °C was added methyl 2-tridecynoate (224 mg, 1.0 mmol). The mixture was slowly warmed to -30 °C and the reaction progress was monitored by TLC. The reaction was quenched with water (1 mL) and the mixture was extracted with ether (3x5 mL). The combined extracts were washed with brine (5 mL) and dried over magnesium sulfate. Evaporation of the solvent under vacuum and flash chromatography on silica (5:1 hexanes:ethyl acetate) gave 88 mg of waxy white solid (44% yield). mp 28.0-28.5 °C; IR (film): 3331, 2925, 2854, 2247, 2205, 2101, 1466, 1378, 1173, 1080, 1040, 965, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.21 (t, J = 7.0 Hz, 2H), 1.53-1.46 (m, 2H), 1.38-1.27 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H).

(*E*)-1,2-Dideutero-2-tridecenal (6). 1,1-Dideutero-2-tridecyn-1-ol (24.8 mg, 0.125 mmol) was subjected to the standard indium trichloride isomerization conditions. After 2 h the product was recovered by the standard isolation procedure and purified

by flash chromatography on silica (10:1 hexanes:ethyl acetate) to give 19.8 mg of clear oil (80% yield). IR (film): 2925, 2855, 2067, 1677, 1625, 1466, 1378, 1168, 934, 853 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.85 (dt, J = 6.8 Hz, 1H), 2.34 (q, J = 7.2 Hz, 2H), 1.53-1.19 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H).

(*E*)-3-Deutero-2-tridecenal (7). 2-Tridecyn-1-ol (24.5 mg, 0.125 mmol) was subjected to the standard indium trichloride isomerization conditions except that deuterium oxide (2.3 mL, 2.5 mg, 0.125 mmol) was added and the ammonium salts were omitted. After 3 h the product was recovered by the standard isolation procedure and purified by flash chromatography on silica (10:1 hexanes:ethyl acetate) to give 8 mg of the deutero and protio compounds (1:1 mixture by NMR). IR (film): 2926, 2855, 2717, 1695, 1621, 1466, 1152, 895, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.51 (dd, J = 8.0, 0.8 Hz, 1H), 6.12 (m, 0.5 H), 2.35 (m, 2H), 1.53-1.46 (m, 2H), 1.27 (s, 14H), 0.88 (t, J = 6.70 Hz, 3H).

1-Tetrahydropyranyloxy-2-decyn-4-ol. 1-Tetrahydropyranyloxy-2-propyne (1.40 g, 10.00 mmol) was dissolved in freshly distilled THF (10 mL) and *n*-butyllithium (1.6 M in hexanes, 6.88 mL, 11.0 mmol) was added dropwise at -78 °C. After 15 min, freshly distilled heptanal (1.54 mL, 1.26 g, 11.00 mmol) was added and the solution was stirred for 1 h at room temperature. The mixture was quenched with water (50 mL) and extracted with ether (4x50 mL). The solvent was removed under vacuum and the residue purified by flash chromatography on silica (5:1 hexanes:ethyl acetate) to give 2.41 g of clear oil (95% yield). IR (film): 3427, 2930, 2858, 2118, 1732, 1681, 1456, 1344, 1202, 1120, 1026, 903 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.81 (t, J = 3.1 Hz, 1H), 4.41 (br, 1H), 4.34 (dd, J = 15.6, 1.6 Hz, 1H), 4.26 (dd, J = 15.5, 1.4 Hz, 1H), 3.88-3.80 (m, 1H), 3.57-3.50 (m, 1H), 1.97 (br, 1H), 1.84-1.26 (m, 16H), 0.89 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 96.7, 87.2, 80.5, 62.3, 61.9, 54.2, 37.6, 31.6, 30.1, 28.8, 25.2, 24.9, 22.4, 18.8, 13.9.

2-Decyne-1,4-diol (3m). 1-Tetrahydropyranyloxy-2-decyn-4-ol (508 mg, 2.00 mmol) and catalytic *p*-toluenesulfonic acid were dissolved in methanol (25 mL) and stirred for 3 h at room temperature. The methanol was removed under vacuum and the residue was purified by flash chromatography on silica (1:1 hexanes:ethyl acetate) to

give 258 mg of clear oil (76% yield). All spectral data compared favorably with those reported in the literature.[10] ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.40 (s, 1H), 4.31 (s, 2H), 3.28-2.70 (br, 2H), 1.74-1.66 (m, 2H), 1.46-1.29 (m, 8H), 0.89 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 86.9, 83.0, 62.4, 50.8, 37.5, 31.6, 28.8, 25.0, 22.5, 13.9.

4-Oxodecanal (4m). 2-Decyne-1,4-diol (170 mg, 1.00 mmol), indenyl catalyst **2** (23.3 mg, 0.03 mmol) and camphorsulfonic acid (11.6 mg, 0.05 mmol) were combined in THF (5 mL). After stirring under an inert atmosphere for several minutes, indium triflate (16.9 mg, 0.03 mmol) was added and the reaction was brought to reflux in a preheated oil bath. After 2 h, the mixture was diluted with ether and filtered through florisil with additional ether to remove the catalyst. Removal of the solvent under reduced pressure and flash chromatography on silica gel (10:1 pet ether:ethyl acetate) gave 136 mg of clear oil (80% yield). All spectral data compared favorably with those reported in the literature.[11] IR (film): 2931, 2859, 2726, 1715, 1467, 1411, 1129, 1089 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.81 (s, 1H), 2.78-2.63 (m, 4H), 2.45 (t, J = 7.5 Hz, 2H), 1.61-1.53 (m, 2H), 1.34-1.26 (m, 6H), 0.88 (t, J = 6.6 Hz, 3H).

1-Tetrahydropyranyloxy-4-(4-methoxybenzyl)oxy-2-decyne. 1-Tetrahydropyranyloxy-2-decyn-4-ol (5.5 mmol) was dissolved in dry DMF (10 mL) and the solution was cooled in an ice bath. Sodium hydride (240 mg, 60% suspension, 6.0 mmol) was added in several portions and the mixture was allowed to stir for 15 min. *p*-Methoxybenzyl chloride (814 μL, 940 mg, 6.0 mmol) was added and the mixture was allowed to stir for 3 h at room temperature. The reaction mixture was poured into water (25 mL) and extracted with ether (3x25 mL). The solvent was removed under vacuum and the residue purified by flash chromatography on silica gel (10:1 pet ether:ethyl acetate) to give 1.75 g of clear oil (85% yield). IR (film): 2933, 2858, 1613, 1514, 1249, 1121, 1079, 1026, 903, 818 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.26 (m, 2H), 6.90-6.85 (m, 2H), 4.85 (q, J = 2.9 Hz, 1H), 4.71 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.3 Hz, 1H), 4.34 (dd, J = 3.7, 1.0 Hz, 2H), 4.09 (t, 6.6 Hz, 1H), 3.90-3.81 (m, 1H), 3.80 (s, 3H), 3.58-3.47 (m, 1H), 1.88-1.19 (m, 16H), 0.87 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 130.2, 129.6 (2), 113.8 (2),

96.7, 85.2, 81.6, 70.0, 68.3, 62.0, 55.2, 54.2, 35.6, 31.6, 30.2, 28.8, 25.2, 25.1, 22.4, 19.0, 13.9.

4-(4-Methoxybenzyl)oxy-2-decyn-1-ol (3n). 1-Tetrahydropyranyloxy-4-(4-methoxybenzyl)oxy-2-decyne (1.75 g, 4.68 mmol) and catalytic *p*-toluenesulfonic acid were dissolved in methanol (25 mL) and stirred for 3 h at room temperature. The methanol was removed under vacuum and the residue was purified by flash chromatography on silica (3:1 pet ether:ethyl acetate) to give 1.25 of clear oil (93% yield). IR (film): 3410, 2930, 2859, 2217, 1613, 1515, 1465, 1249, 1174, 1073, 1036, 822 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, J = 8.7 Hz, 2H), 6.88 (dd, J = 6.7, 2.0 Hz, 2H), 4.71 (d, J = 11.3 Hz, 1H), 4.43 (d, 11.5 Hz, 1H), 4.34 (s, 2H), 4.08 (t, J = 6.6 Hz, 1H), 3.80 (s, 3H), 1.76-1.65 (m, 3H), 1.44-1.24 (m, 8H), 0.87 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 130.1, 129.7 (2), 113.8 (2), 85.1, 83.8, 70.2, 68.3, 55.2, 51.1, 35.6, 31.6, 28.8, 25.1, 22.5, 13.9; HRMS calcd for $C_{18}H_{26}O_3$ (M^+): 290.1882. Found 290.1882.

(*E*)-4-(4-Methoxybenzyl)oxy-2-decenal (4n). 4-(4-Methoxybenzyl)oxy-2-decyn-1-ol (288 mg, 1.00 mmol), indenyl catalyst **2** (38.8 mg, 0.05 mmol) and camphorsulfonic acid (11.6 mg, 0.05 mmol) were combined in THF (4 mL). After stirring under an inert atmosphere for several minutes, indium triflate (28.1 mg, 0.05 mmol) was added and the reaction was brought to reflux in a preheated oil bath. After 3 h, the mixture was diluted with ether and filtered through florisil with additional ether to remove the catalyst. Removal of the solvent under reduced pressure and flash chromatography on silica gel (10:1 pet ether:ethyl acetate) gave 179 mg of the desired aldehyde as clear oil (62% yield). IR (film): 2932, 2859, 2724, 1694, 1614, 1515, 1249, 1086, 1036, 979, 822 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.59 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.73 (dd, J = 15.8, 6.2 Hz, 1H), 6.27 (ddd, J = 15.8, 7.9, 1.1 Hz, 1H), 4.52 (d, J = 11.5 Hz, 1H), 4.34 (d, J = 11.5 Hz, 1H), 4.04 (q, J = 6.3 Hz, 1H), 3.80 (s, 3H), 1.69-1.53 (m, 2H), 1.41-1.26 (m, 8H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6, 159.5, 157.7, 132.3, 130.0, 129.5 (2), 113.9 (2), 77.6, 71.0, 55.2, 34.7, 31.6, 29.0, 24.9, 22.4, 13.9. HRMS Calcd for $C_{18}H_{26}O_3$ (M^+): 290.1882. Found 290.1879.

4-(*t*-Butyldiphenylsilyl)oxy-2-butyn-1-ol (3o). To 2-butyn-1,4-diol (1.72 g, 20.0 mmol) and imidazole (817 mg, 12.0 mmol) in methylene chloride (20 mL) at room temperature was added *t*-butyldiphenylsilyl chloride (2.60 ml, 2.75 g, 10.0 mmol). After stirring 3 h the mixture was worked up with water (50 mL) and methylene chloride (3x50 mL) and the combined extracts were dried over magnesium sulfate. Removal of the solvent under vacuum and flash chromatography on silica gel (10:1 pet ether:ethyl acetate) gave 2.60 g of the monoprotected material (80% yield). IR (film): 3361, 2932, 2859, 2243, 1715, 1428, 1135, 1113, 1075, 1009, 823, 740, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.72-7.70 (m, 4H), 7.44-7.37 (m, 6), 4.36 (s, 2H), 4.20 (d, J = 6.1 Hz, 2H), 1.31 (t, J = 6.2 Hz, 1H), 1.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.6 (4), 133.1 (2), 129.8 (2), 127.7 (4), 84.2, 83.4, 52.6, 51.1, 26.7, 19.1; Anal. Calcd for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.46. Found: C, 73.85; H, 7.33.

(*E*)-4-(*t*-Butyldiphenylsilyl)oxy-2-butenal (4o). 4-(*t*-Butyldiphenylsilyl)oxy-2-butyn-1-ol (324 mg, 1.00 mmol), indenyl catalyst **2** (38.8 mg, 0.05 mmol) and camphorsulfonic acid (11.6 mg, 0.05 mmol) were combined in THF (5 mL). After stirring under an inert atmosphere for several minutes, indium triflate (11.2 mg, 0.02 mmol) was added and the reaction was brought to reflux in a preheated oil bath. Thin layer and gas chromatography indicated that the reaction was complete within 45 min. The mixture was diluted with ether and filtered through florisil with additional ether to remove the catalyst. Removal of the solvent under reduced pressure and flash chromatography on silica gel (20:1 pet ether:ethyl acetate) gave the crystalline product contaminated with the hydrolyzed silanol. Washing with pentane gave 200 mg of the pure aldehyde (62% yield). All spectral data compared favorably with those reported in the literature.[12] IR (film): 3070, 2931, 2857, 2723, 1685, 1427, 1113, 969, 824, 743, 701, 630 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.61 (d, J = 8.1 Hz, 1H), 7.66-7.64 (m, 4H), 7.47-7.36 (m, 6), 6.85 (dt, J = 15.4, 3.2 Hz, 1H), 6.58 (dd, J = 15.4, 8.1 Hz, 1H), 4.46 (t, J = 2.6 Hz, 2H), 1.08 (s, 9H).

3-(1-Cyclohexenyl)-2-propyn-1-ol (3j). To 1-ethynylcyclohexene (1.18 mL, 1.06 g, 10.0 mmol) in THF (10 mL) at -78 °C was added *n*-butyllithium (6.56 mL, 1.6 M, 10.5 mL). After stirring 30 min, paraformaldehyde (600 mg, 20.0 mmol) was added and the mixture was warmed to room temperature. After stirring 4 h the mixture was

worked up with 1M aqueous sulfuric acid (50 mL) and extracted with ether (4x50 mL) and the combined extracts were dried over magnesium sulfate. Removal of the solvent under reduced pressure and vacuum distillation gave 1.13 g of clear oil (83% yield). All spectral data compared favorably with those reported in the literature.[13] IR (film): 3334, 3027, 2931, 2859, 2219, 1631, 1436, 1028, 1023, 978, 920, 845 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.08 (s, 1H), 4.35 (s, 2H), 2.08-2.06 (m, 4H), 1.83 (br, 1H), 1.62-1.54 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.4, 120.0, 87.5, 84.5, 51.6, 29.0, 25.6, 22.2, 21.4.

1-(1-Cyclohexenyl)-1-nonyn-3-ol (3k). To 1-ethynylcyclohexene (1.18 mL, 1.06 g, 10.0 mmol) in THF (20 mL) at -78 °C was added *n*-butyllithium (6.56 mL, 1.6 M, 10.5 mL). After stirring 30 min heptaldehyde (1.39 mL, 1.14 g, 10.0 mmol) was added and the mixture was warmed to room temperature. The mixture was worked up with water (50 mL) and extracted with ether (3x50 mL) and the combined extracts were dried over magnesium sulfate. Removal of the solvent under reduced pressure and vacuum distillation gave 1.70 g of clear oil (77% yield). IR (film): 3356, 2929, 2858, 2219, 1633, 1458, 1378, 1341, 1045, 918, 842 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.09 (s, 1H), 4.47 (t, J = 6.6 Hz, 1H), 2.11-2.09 (m, 4H), 1.99 (s, 1H), 1.75-1.29 (m, 14H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.0, 120.0, 87.5, 86.5, 62.8, 37.9, 31.7, 29.1, 28.9, 25.5, 25.1, 22.5, 22.2, 21.4, 14.0; Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.62; H, 10.76.

1-Phenyl-1-nonyn-3-ol (3l). To phenylacetylene (1.10 ml, 1.02 g, 10.0 mmol) in THF (20 mL) at -78 °C was added *n*-butyllithium (6.56 mL, 1.6 M, 10.5 mL). After stirring 30 min heptaldehyde (1.39 mL, 1.14 g, 10.0 mmol) was added and the mixture was warmed to room temperature. The mixture was worked up with water (50 mL) and extracted with ether (3x50 mL) and the combined extracts were dried over magnesium sulfate. Removal of the solvent under reduced pressure and vacuum distillation gave 1.80 g of clear oil (83% yield). IR (film): 3333, 2929, 2858, 2203, 1490, 1443, 1378, 1338, 1069, 1038, 756, 691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.31-7.29 (m, 3H), 4.59 (q, J = 6.2 Hz, 1H), 2.09 (s, 1H), 1.84-1.76 (m, 2H), 1.54-1.46 (m, 2H), 1.40-1.31 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.6, 128.3, 128.2, 122.7, 90.2, 84.7, 63.0, 37.9, 31.7,

28.9, 25.1, 14.0; Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.46; H, 9.15.

(*E*)-1-Phenyl-1-nonen-3-one (4l). 1-Phenyl-1-nonyn-3-ol (216 mg, 1.00 mmol), indenyl catalyst **2** (38.8 mg, 0.05 mmol), and camphorsulfonic acid (11.6 mg, 0.05 mmol) were combined in THF (1 mL). After stirring under an inert atmosphere for several minutes, indium triflate (28.1 mg, 0.05 mmol) was added and the reaction was brought to reflux in a preheated oil bath. After 90 min the mixture was diluted with ether and filtered through florisil with additional ether to remove the catalyst. Removal of the solvent under reduced pressure and flash chromatography on silica gel (20:1 pet ether:ethyl acetate) gave 129 mg of clear oil (60% yield). All spectral data compared favorably with those reported in the literature.[14] mp 31.5-32.0 °C; IR (film): 3028, 2929, 2857, 1691, 1670, 1612, 1450, 1331, 1176, 1071, 976, 747, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.58-7.52 (m, 3H), 7.40-7.38 (m, 3H), 6.74 (d, J = 16.4 Hz, 1H), 2.66 (t, J = 7.4 Hz, 2H), 1.72-1.65 (m, 2H), 1.38-1.32 (m, 6H), 0.89 (t, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7, 142.2, 134.6, 130.3, 128.9, 128.2, 126.2, 40.9, 31.6, 29.0, 24.3, 22.5, 14.0.

6-(*t*-Butyldimethylsilyl)oxy-2,4-hexadiyn-1-ol (Method A). To 95% sodium hydride (4.55 g, 180 mmol) in THF (200 mL) was added 2,4-hexadiyne-1,6-diol (19.8 g, 180 mmol) in THF (300 mL) at 0 °C. The mixture was stirred for 2 h at room temperature and *t*-butyldimethylsilyl chloride (18.09 g, 120 mmol) was added. After stirring 3 h at room temperature, methanol (20 mL) was added and the mixture was worked up with water (250 mL) and ether (4x250 mL). The combined extracts were dried over magnesium sulfate and the solvent was removed under vacuum. The residue was taken up in 5:1 pet ether:ethyl acetate (100 mL) and the excess diol was removed by filtration. The desired product was separated from the diprotected material by flash chromatography on silica (5:1 pet ether:ethyl acetate) to yield 16.73 g of pale yellow oil (62% yield). IR (film): 3354, 2956, 2930, 2858, 2254, 2184, 2132, 1472, 1363, 1257, 1090, 837 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.38 (s, 2H), 4.34 (d, J=5.6 Hz, 2H), 2.13 (br, 1H), 0.91 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 78.1, 76.9, 69.9, 68.8, 52.0, 51.4, 25.7 (3), 18.2, -5.2 (2); Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.23; H, 8.99. Found C, 64.03; H, 8.70.

6-(*t*-Butyldimethylsilyl)oxy-2,4-hexadiyn-1-ol (Method B). To 1-(*t*-butyldimethylsilyl)oxy-2-propyne (5.11 g, 30 mmol) in THF (30 mL) at -78 °C was added *n*-butyllithium (19.69 mL, 1.6 M, 31.5 mmol). After stirring at this temperature for 30 min, iodine (8.38 g, 31.5 mmol) in dry THF (20 mL) was added and the solution was warmed to room temperature. The mixture was worked up with saturated sodium thiosulfate (50 mL) and ether (3 x 100 mL). The combined extracts were dried over magnesium sulfate and the solvent removed under reduced pressure. The crude iodide was dissolved in THF (30 mL) and pyrrolidine (10 mL) and propargyl alcohol (3.49 mL, 3.36 g, 60 mmol) were added. Copper (I) iodide (571 mg, 3.00 mmol) was added in one portion at 0 °C and stirring was continued 2 h. Gas chromatography showed complete consumption of the iodide but significant reduction to the starting protected propargylic alcohol. The mixture was worked up with water (100 mL) and ether (4x100 mL) and the combined extracts were washed with 1M sulfuric acid (100 mL) and saturated sodium bicarbonate (100 mL). The combined extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. Purification by flash chromatography on silica (3:1 pet ether:ethyl acetate) gave 3.35 g of clear oil (50% yield over 2 steps).

(*E*)-6-(*t*-Butyldiphenylsilyl)oxy-4-tetradecen-2,8-diyn-1-ol (20). To alcohol **19** (3.34 g 10.0 mmol) in methylene chloride (50 mL) was added at 0 °C imidazole (1.02 g, 15.0 mmol), *t*-butyldiphenylsilyl chloride (3.12 mL, 3.30 g, 12.0 mmol) and catalytic DMAP. After stirring 2 h at room temperature, the reaction was worked up with water (100 mL) and ether (3x100 mL) The combined extracts were washed with 10% sodium bisulfate (50 mL) and dried over magnesium sulfate. Removal of the solvent under vacuum gave the crude diprotected material which was dissolved in methanol (100 mL). Camphorsulfonic acid (116 mg, 0.5 mmol) was added and deprotection was complete after stirring 20 min at room temperature. Solid sodium bicarbonate was added and the methanol was removed under vacuum. The material was dissolved in ether (200 mL) and washed with saturated aqueous sodium bicarbonate (50 mL) and water (100 mL). Drying over magnesium sulfate and removal of the solvent under vacuum followed by flash chromatography on silica (5:1 pet ether:ethyl acetate) gave 3.71 g of clear oil (81% yield over 2 steps). IR (film):

3348, 2958, 2932, 2859, 2218, 1472, 1428, 1362, 1112, 1071, 1009, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.70-7.61 (m, 4H), 7.45-7.33 (m, 6H), 6.26 (dd, J = 15.9, 5.4 Hz, 1H), 5.68 (dd, J = 15.9, 1.7 Hz, 1H), 4.38 (dd, J = 5.9, 1.7 Hz, 2H), 4.29 (q, 5.5 Hz, 1H), 2.29-2.24 (m, 2H), 2.09-2.04 (m, 2H), 1.57 (t, J = 6.1 Hz, 1H), 1.44-1.25 (m, 6H), 1.07 (s, 9H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.0, 135.8 (4), 133.7, 133.2, 129.7 (2), 127.6 (4), 109.1, 87.7, 84.0, 82.9, 75.5, 72.0, 51.6, 31.0, 29.5, 28.0, 26.9 (3), 22.2, 19.3, 18.7, 14.0; HRMS Calcd for $C_{26}H_{29}O_2Si$ (M^+ - C_4H_9): 401.1937. Found 401.1932.

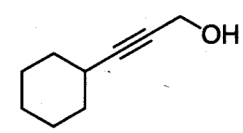
(3*E*,5*E*)-7-(*t*-Butyldiphenylsilyl)oxy-3,5-pentadecadien-1,9-diyne. To (bromomethyl)triphenylphosphonium bromide (938 mg, 2.15 mmol) in THF (5 mL) at -78 °C was added potassium *t*-butoxide (2.69 mL, 1M in THF, 2.69 mmol). After stirring 15 min, the aldehyde **21** (820 mg, 1.79 mmol) in THF (2 mL) was added. After warming to 0 °C additional potassium *t*-butoxide (3.58 mL, 1M in THF, 3.58 mmol) was added to the dark mixture. After 20 min no further conversion of the bromide to the alkyne could be detected and the mixture was worked up with 1M aqueous sodium bisulfate (25 mL) and ether (3x25 mL). The combined extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. Flash chromatography on silica (20:1 pet ether:ethyl acetate) gave 525 mg of yellow oil consisting of the desired diyne containing roughly 15% of the vinyl bromide (65% crude yield). The somewhat unstable material was taken promptly to the next step. ^1H NMR (300 MHz, $CDCl_3$): d 7.69-7.60 (m, 4H), 7.44-7.28 (m, 6H), 6.58 (dd, J = 15.6, 10.7 Hz, 1H), 6.02 (dd, J = 15.1, 10.7 Hz, 1H), 5.85 (dd, J = 15.1 Hz, 6.1 Hz, 1H), 5.43 (dd, J = 15.5, 2.1 Hz, 1H), 4.28 (q, J = 6.2 Hz, 1H), 3.00 (d, J = 2.2 HZ, 1H), 2.39-2.24 (m, 2H), 2.08-2.04 (m, 2H), 1.55-1.18 (m, 6H), 1.06 (s, 9H), 0.87 (t, J = 7.0 Hz, 3H).

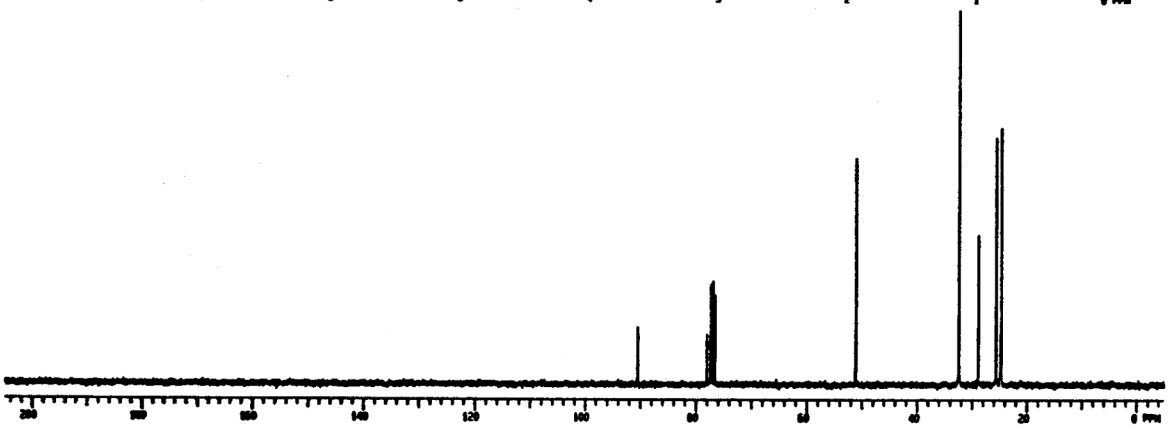
(8*E*,10*E*)-Methyl 5-hydroxy-12-(*t*-butyldiphenylsilyl)oxy-8,10-eicosadiene-6,14-diynoate (22). To (3*E*,5*E*)-7-(*t*-butyldiphenylsilyl)oxy-3,5-pentadecadien-1,9-diyne (525 mg, 1.16 mmol) in THF (5 mL) at -78 °C was added *n*-butyllithium (1.45 mL, 1.6M, 2.32 mmol). After stirring 5 min, methyl 5-oxopentanoate (302 mg, 2.32 mmol) was added via syringe and the mixture was warmed to room temperature. After 30 min the mixture was worked up with water (25 mL) and ether (3x25 mL) and the

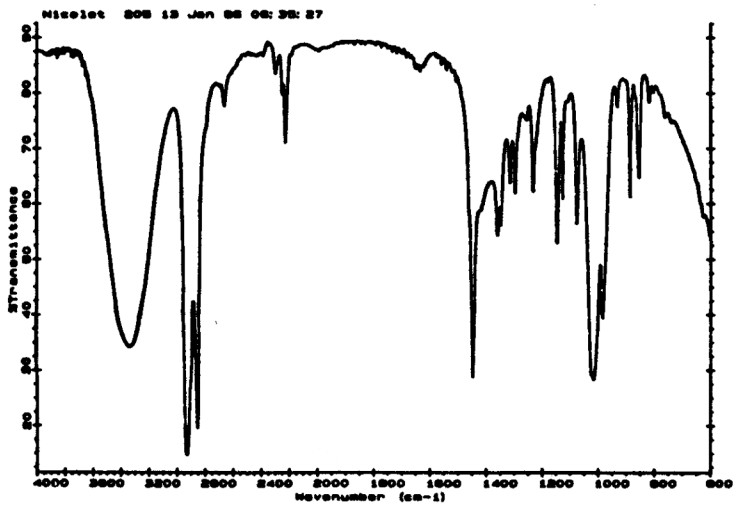
combined extracts were dried over magnesium sulfate. Removal of the solvent under reduced pressure and flash chromatography on silica (5:1 pet ether:ethyl acetate) gave 180 mg of clear oil (27% yield) and 315 mg of recovered starting material (67% yield BRSM). IR (film): 3454, 2932, 2859, 1739, 1428, 1363, 1172, 1112, 1071, 986, 740, 703 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): d 7.68-7.60(m, 4H), 7.44-7.32 (m, 6H), 6.48 (dd, J = 15.5, 10.6 Hz, 1H), 6.00 (dd, J = 15.3, 10.6 Hz, 1H), 5.83 (dd, J = 15.1, 6.1 Hz, 1H), 5.45 (d, J = 15.6 Hz, 1H), 4.52 (d, J = 4.9 Hz, 1H), 4.26 (q, J = 6.1 Hz, 1H), 3.67 (s, 3H), 2.40-2.29 (m, 4H), 2.08-2.03 (m, 2H), 1.92 (d, J = 5.1 Hz, 1H), 1.83-1.72 (m, 4H), 1.40-1.26 (m, 6H), 1.05 (s, 9H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): d 173.9, 141.7, 137.9, 135.9 (4), 133.9, 133.6, 129.7 (2), 129.4, 127.5 (4), 110.1, 91.9, 84.3, 82.6, 75.9, 72.4, 62.5, 51.6, 37.0, 33.5, 31.0, 28.6, 28.3, 26.9 (3), 22.2, 20.5, 19.3, 18.7, 14.0; HRMS calcd for $C_{33}H_{39}O_4Si$ (M^+ - C_4H_9): 527.2618. Found 527.2623.

(8*E*,10*E*)-Methyl 5,12-bis[(*t*-butyldiphenylsilyl)oxy]-8,10-eicosadiene-6,14-diynoate. To alcohol **22** (220 mg, 0.38 mmol) in methylene chloride (5 mL) at 0 °C was added imidazole (39 mg, 0.57 mmol) and catalytic DMAP followed by *t*-butyldiphenylsilyl chloride (120 mL, 126 mg, 0.46 mmol). After stirring 3 h at room temperature, the mixture was worked up with 1M aqueous sodium bisulfate (10 mL) and methylene chloride (3x10 mL). The combined extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. Flash chromatography on silica (20:1 pet ether:ethyl acetate) gave 256 mg of clear oil (82% yield). All spectral data compared favorably with those reported in the literature.[15] IR (film): 3072, 2932, 2859, 1741, 1590, 1472, 1428, 1362, 1112, 985, 823, 740, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): d 7.74-7.61 (m, 8H), 7.44-7.32 (m, 12H), 6.23-6.13 (m, 1H), 5.97-5.89 (m, 1H), 5.76 (dd, J = 15.9, 6.3 Hz, 1H), 5.29 (d, J = 15.6 Hz, 1H), 4.49-4.47 (m, 1H), 4.25 (q, J = 6.2 Hz, 1H), 3.65 (s, 3H), 2.34-2.25 (m, 4H), 2.07 (t, J = 6.8 Hz, 2H), 1.79-1.69 (m, 4H), 1.44-1.25 (m, 6H), 1.07 (s, 9H), 1.06 (s, 9H), 0.86 (t, J = 7.1 Hz, 3H).

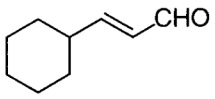
3-Cyclohexyl-2-propyn-1-ol (**3.7**)

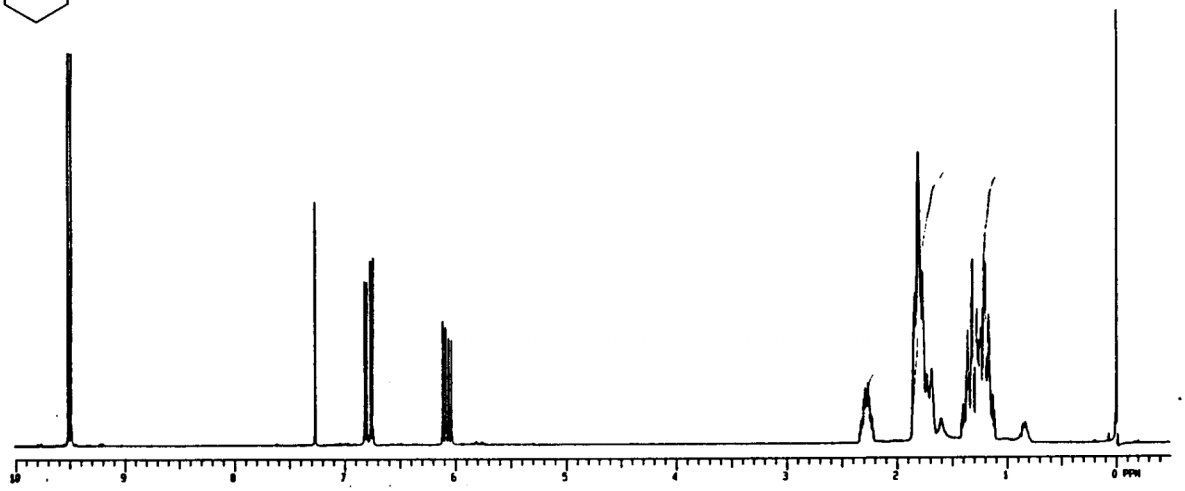


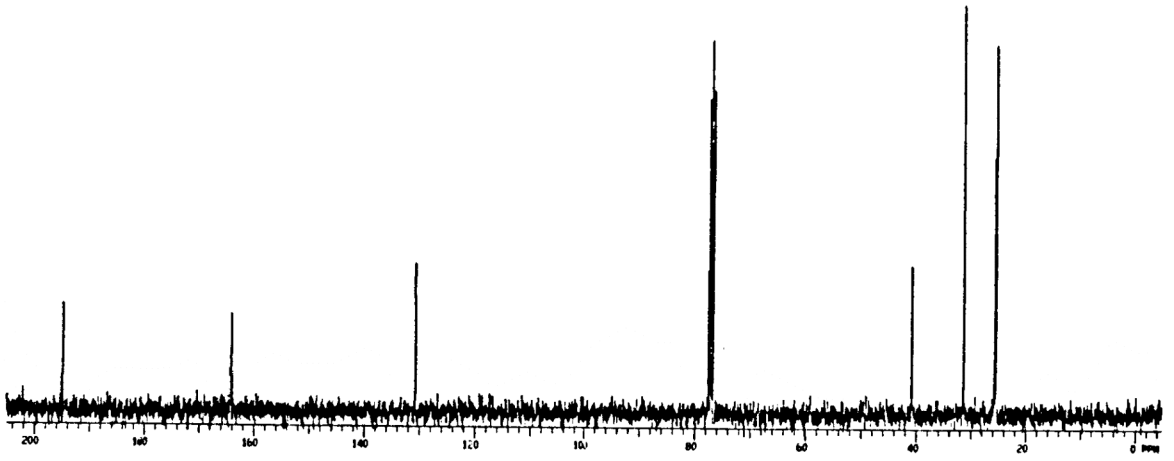


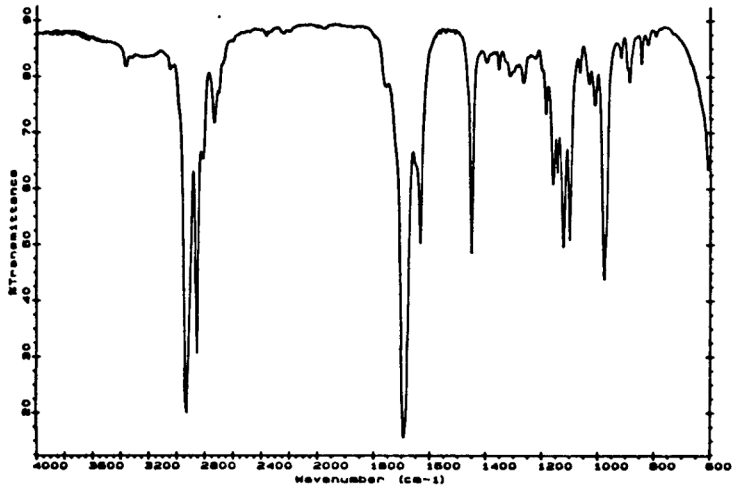


(*E*)-3-Cyclohexyl-2-propenal (**3.8**)

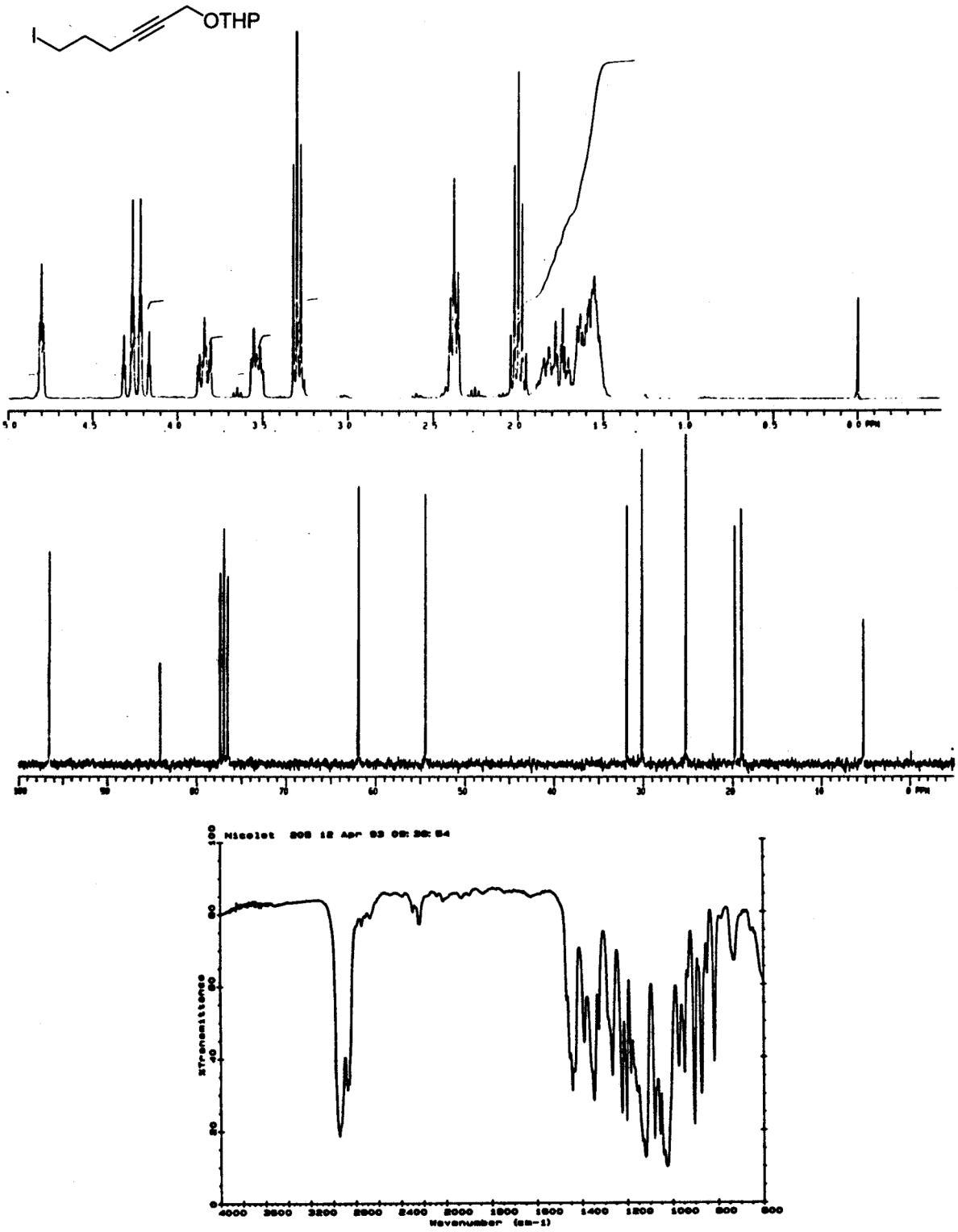




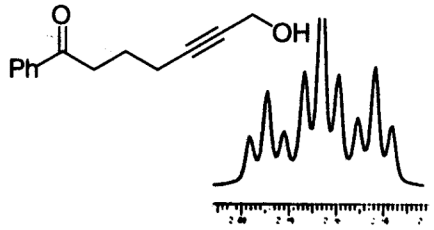


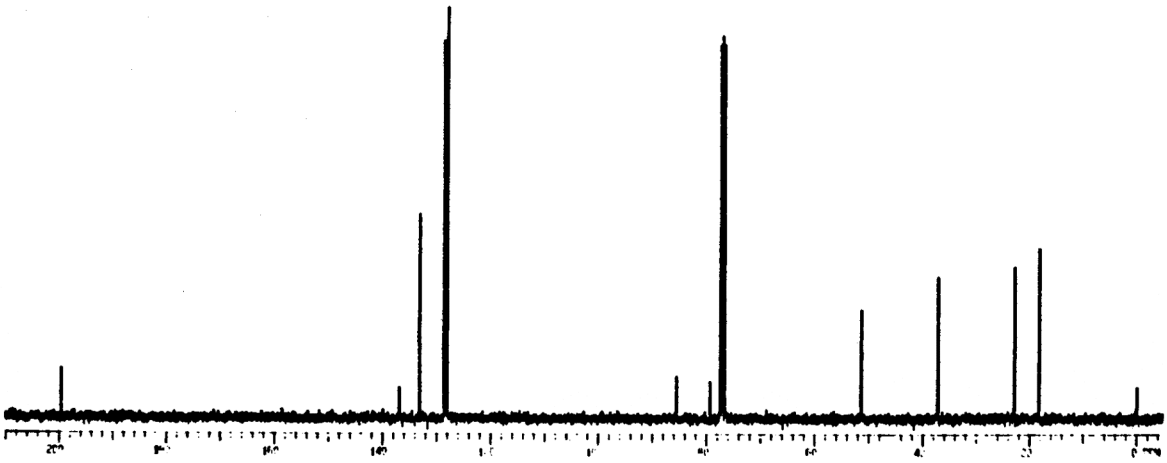


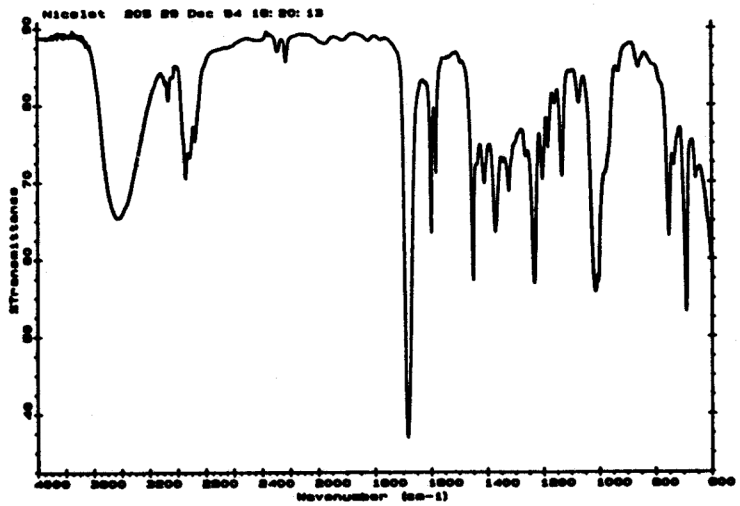
1-Tetrahydropyranyloxy-6-iodo-2-hexyne



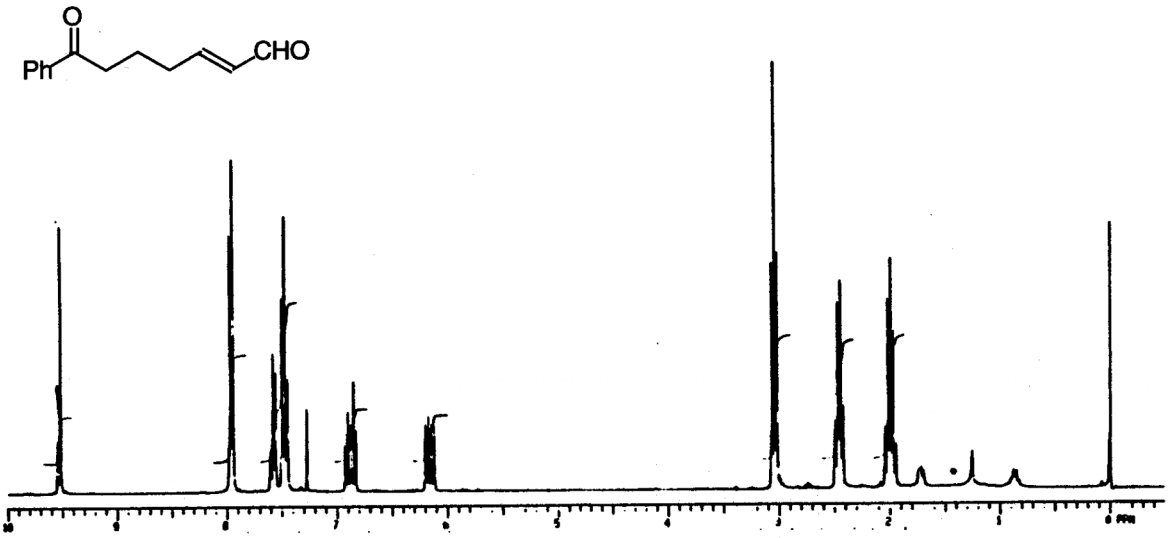
7-Oxo-7-phenyl-2-heptyn-1-ol (**3.9**)

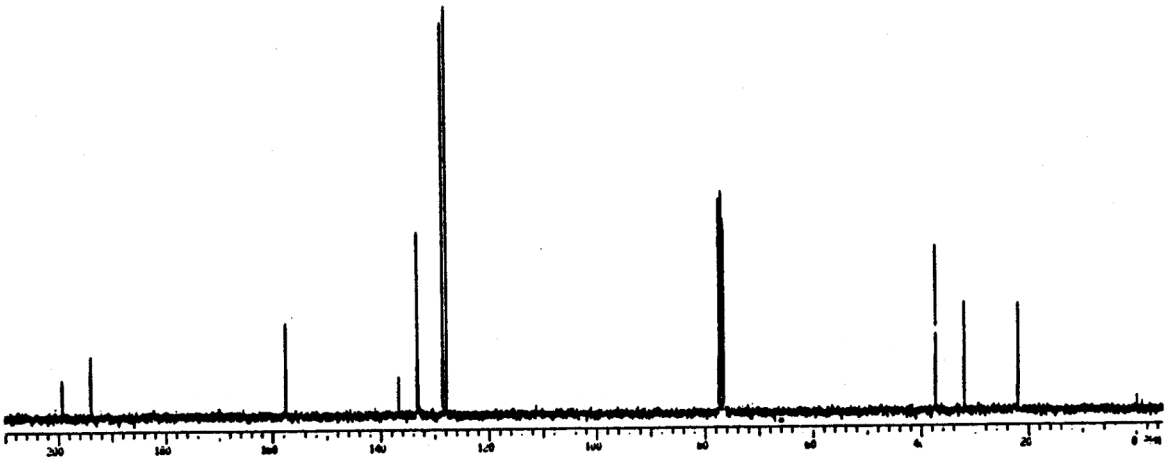


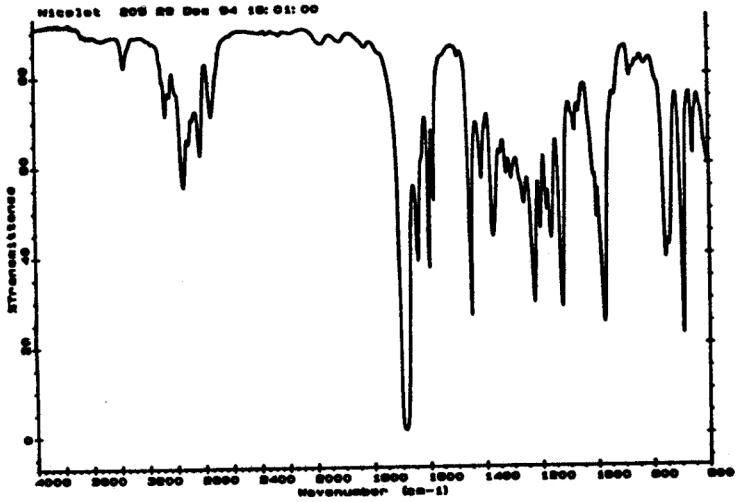




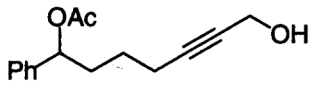
(*E*)-7-Oxo-7-phenyl-2-heptenal **(3.10)**

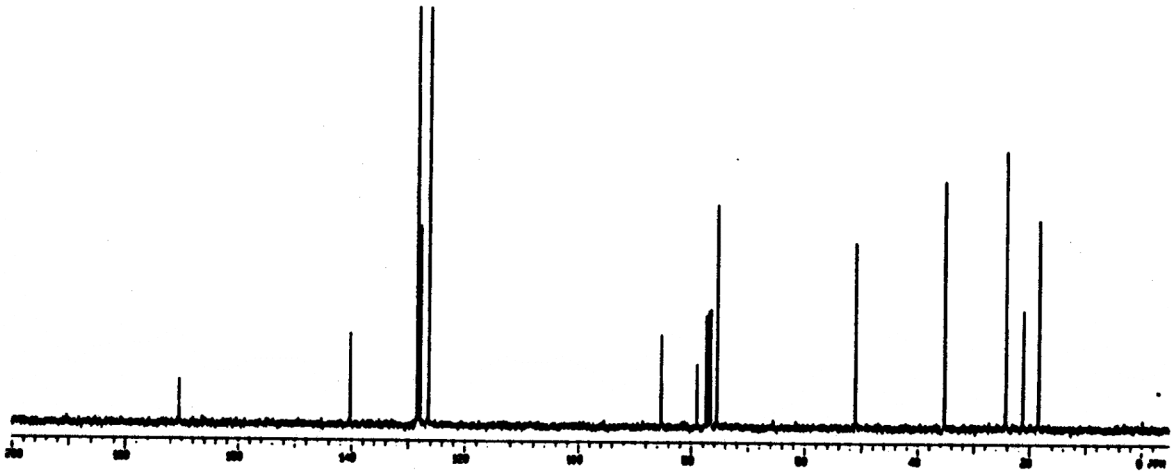


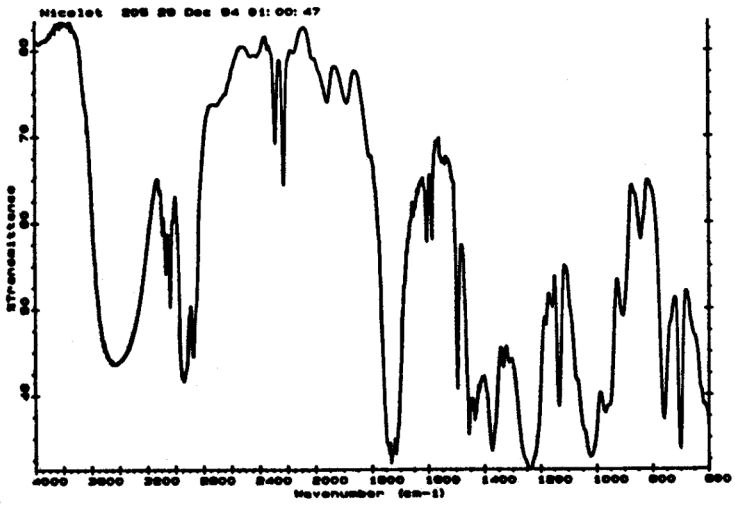




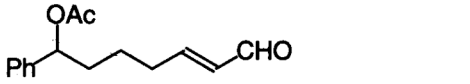
7-Acetoxy-7-phenyl-2-heptyn-1-ol (**3.13**)

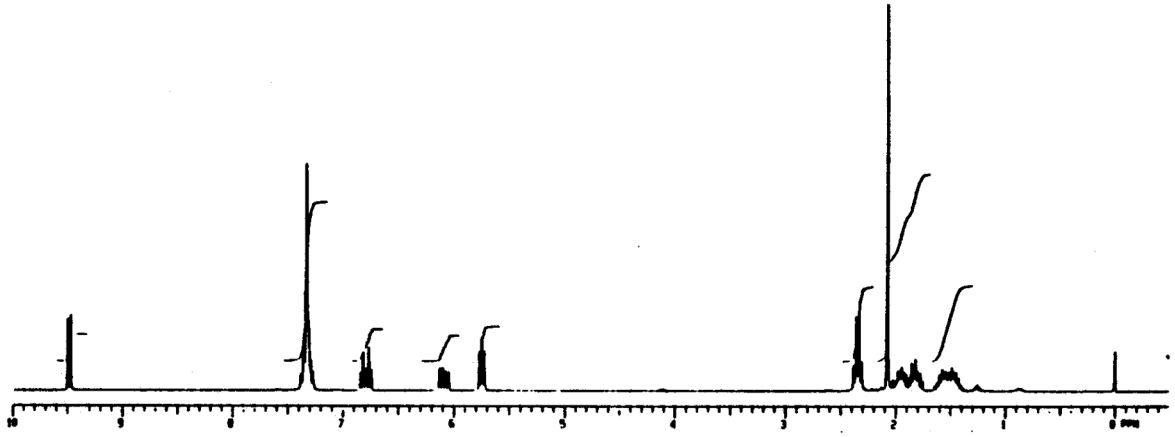


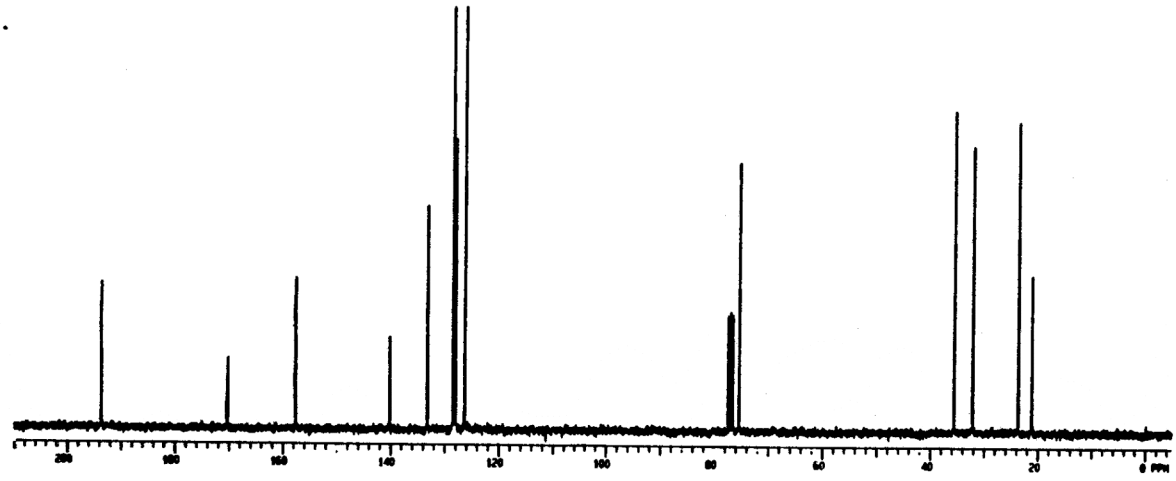


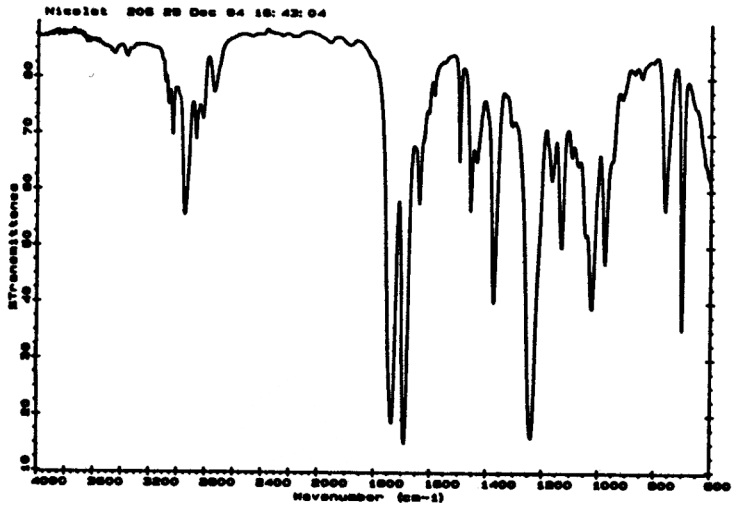


(*E*)-7-Acetoxy-7-phenyl-2-heptenal (**3.14**)

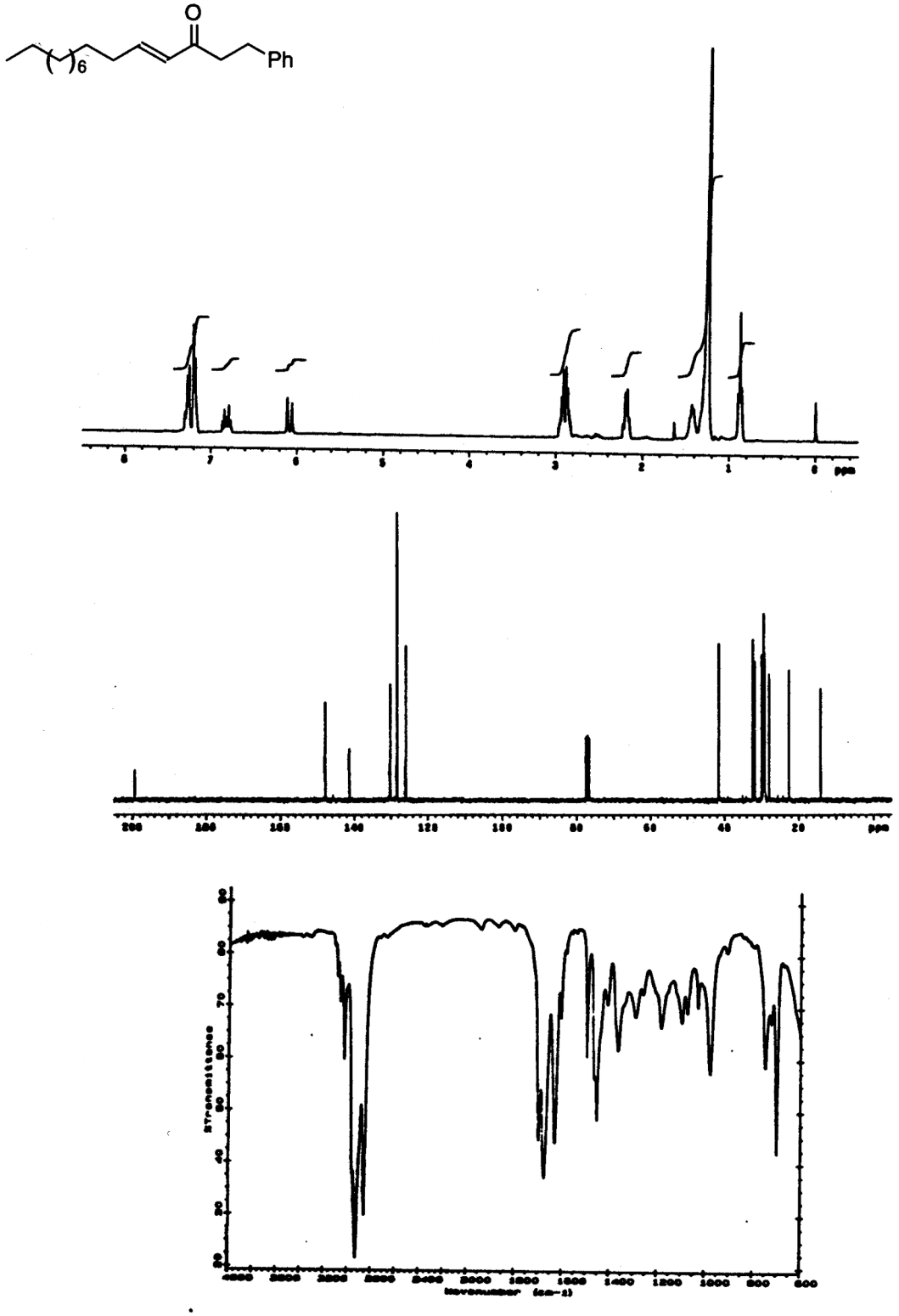




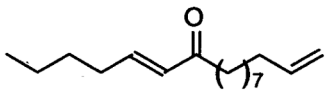


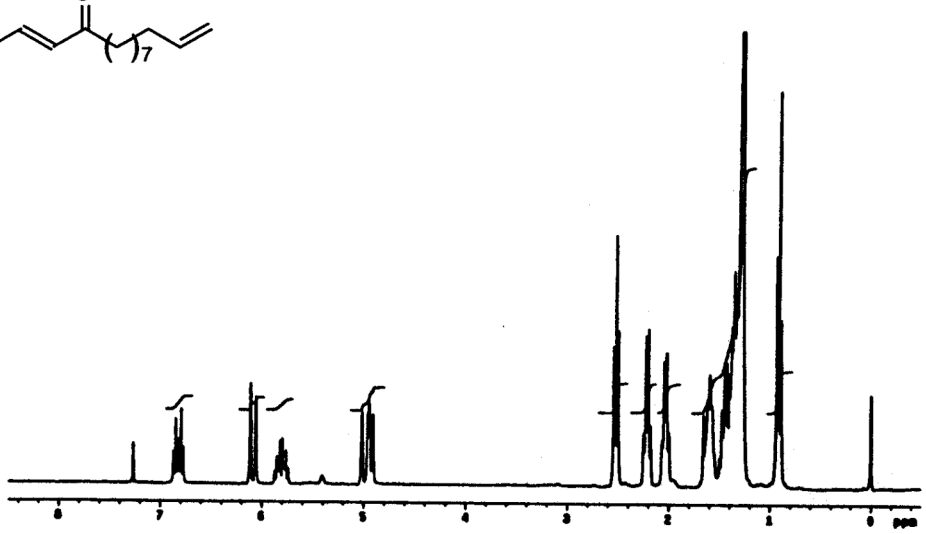


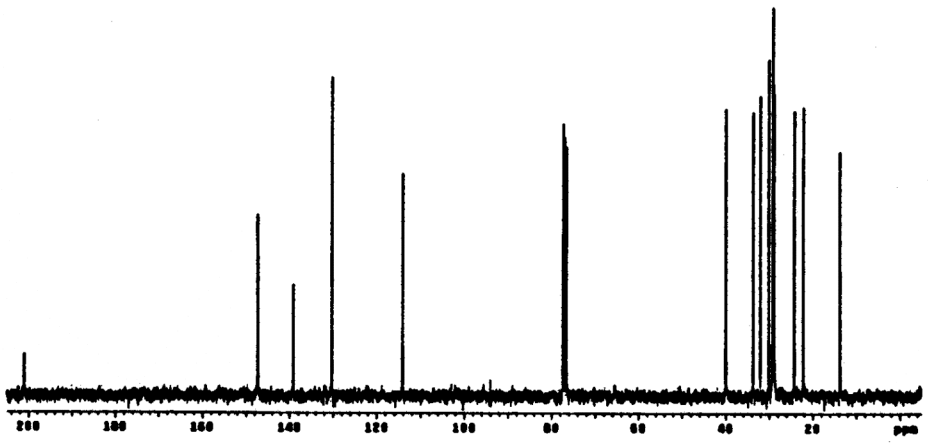
(*E*)-1-Phenyl-4-pentadecen-3-one (**3.20**)

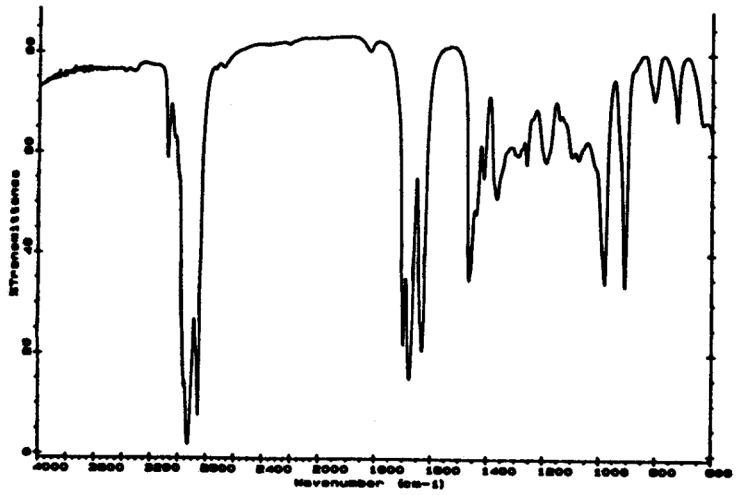


(*E*)-5,16-Heptadecadien-7-one (**3.22**)

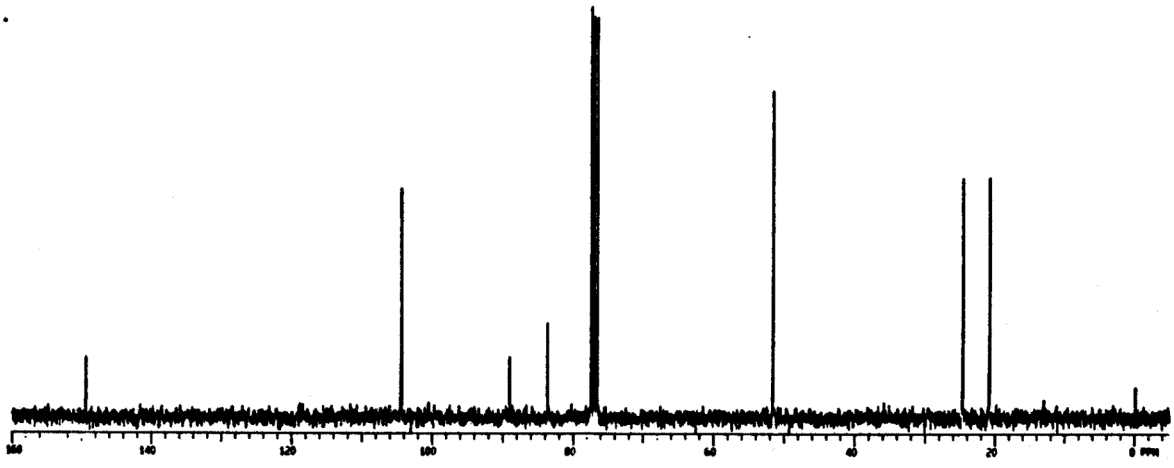


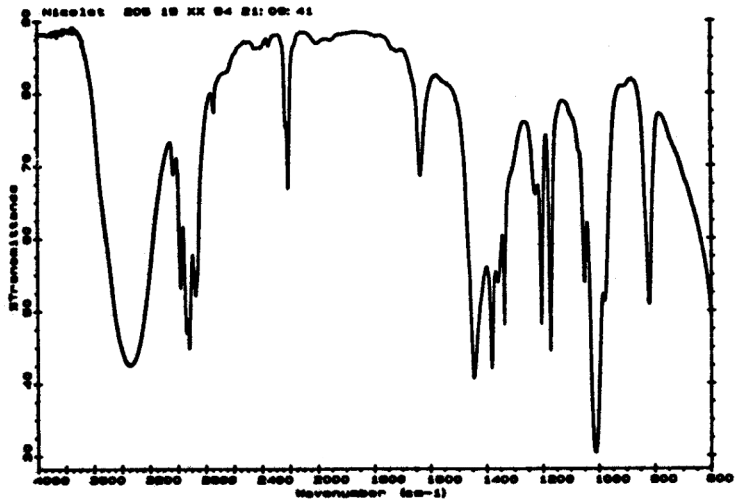




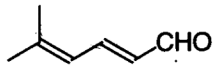


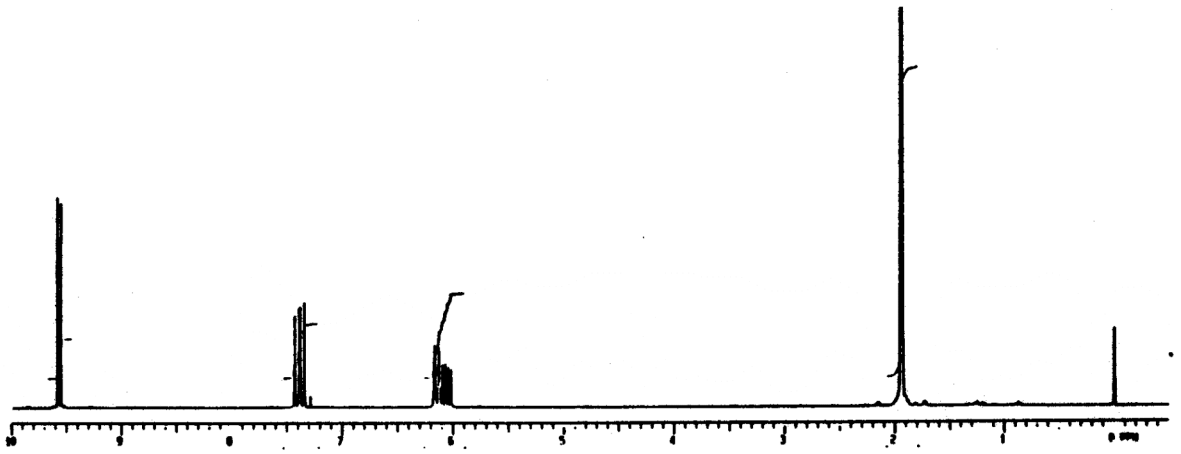
5-Methyl-4-hexen-2-yn-1-ol (**3.17**)

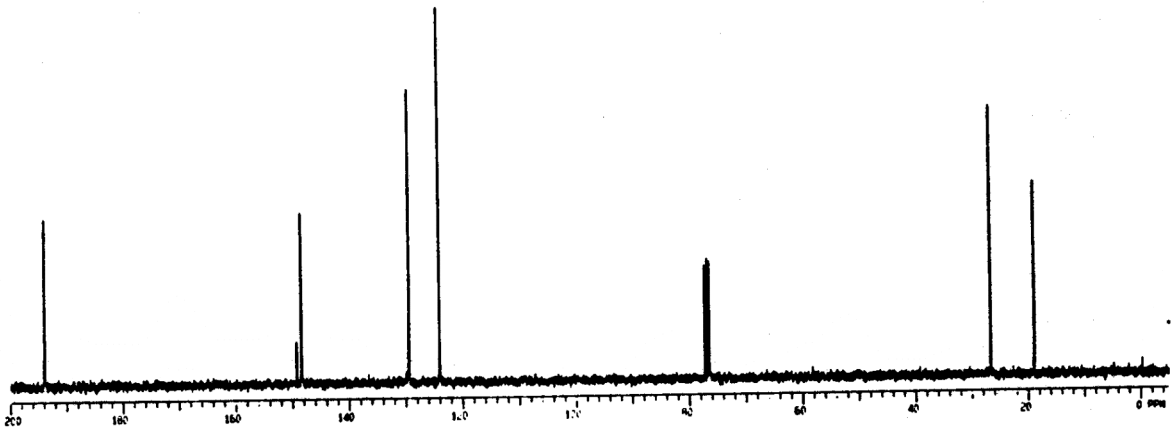


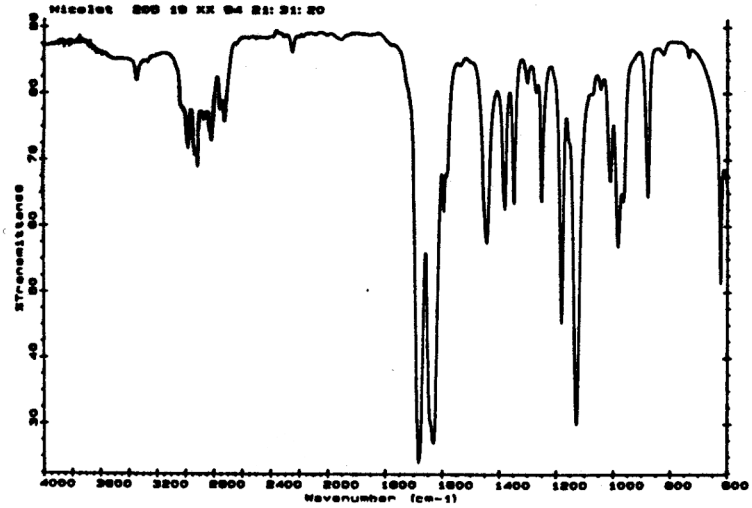


(*E*)-5-Methyl-2,4-hexadienal **(3.18)**

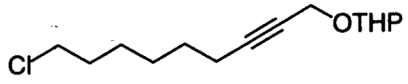


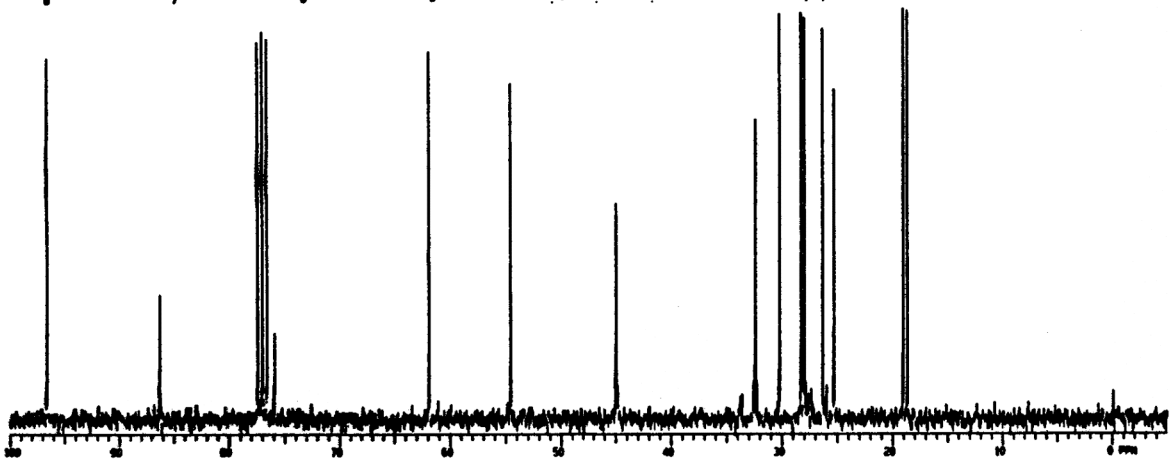


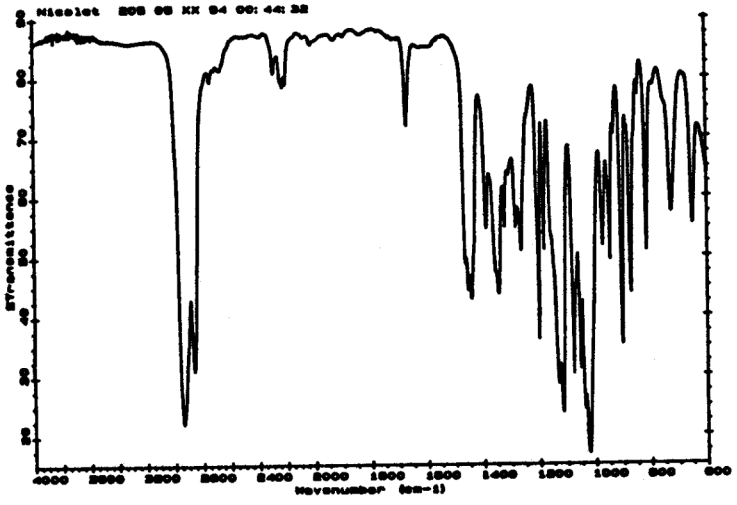




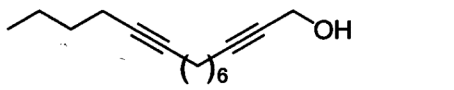
1-Tetrahydropyranyloxy-9-chloro-2-nonyne

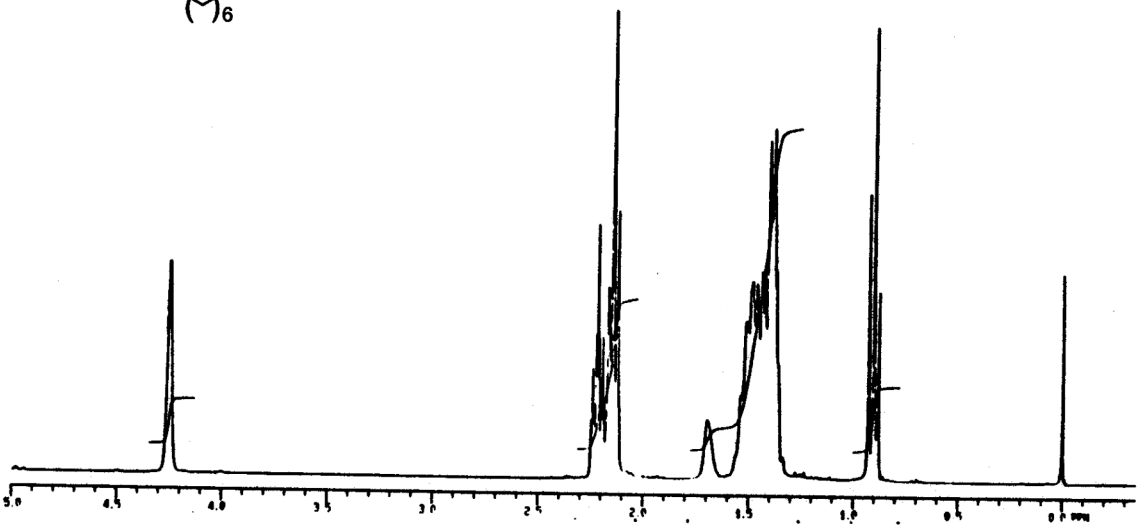


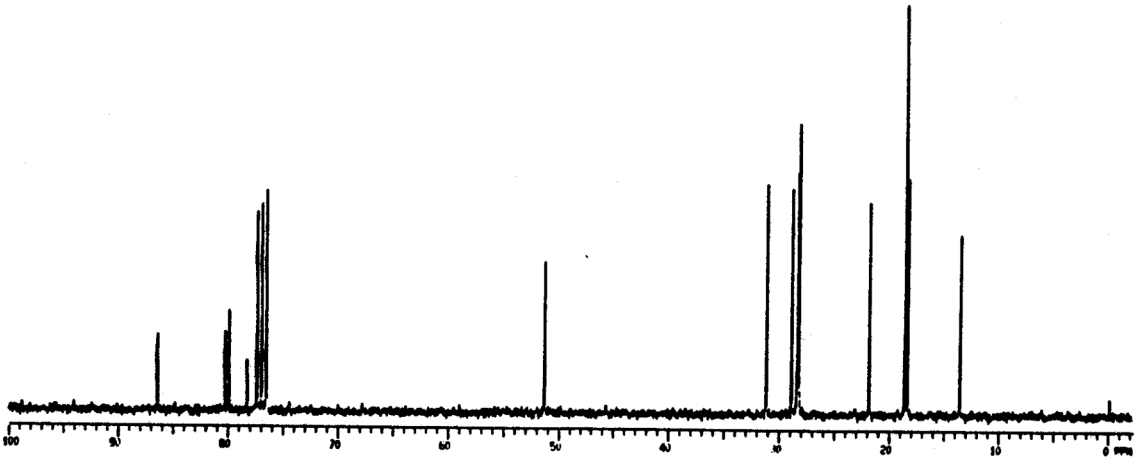


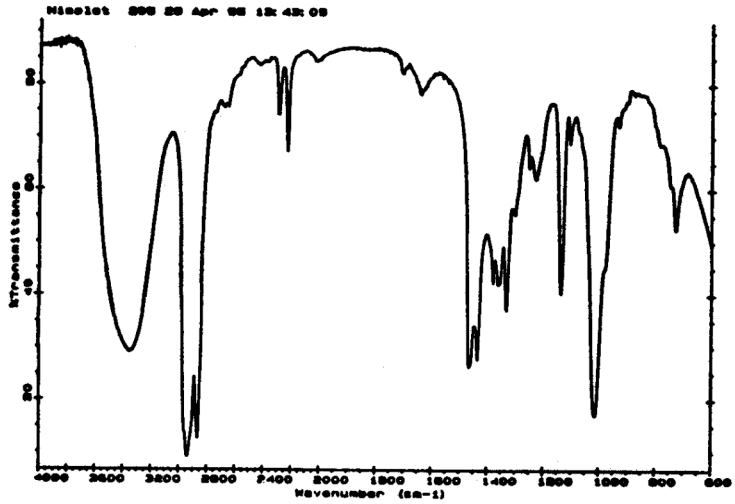


2,10-Pentadecadiyn-1-ol (**3.15**)

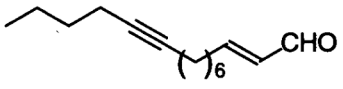


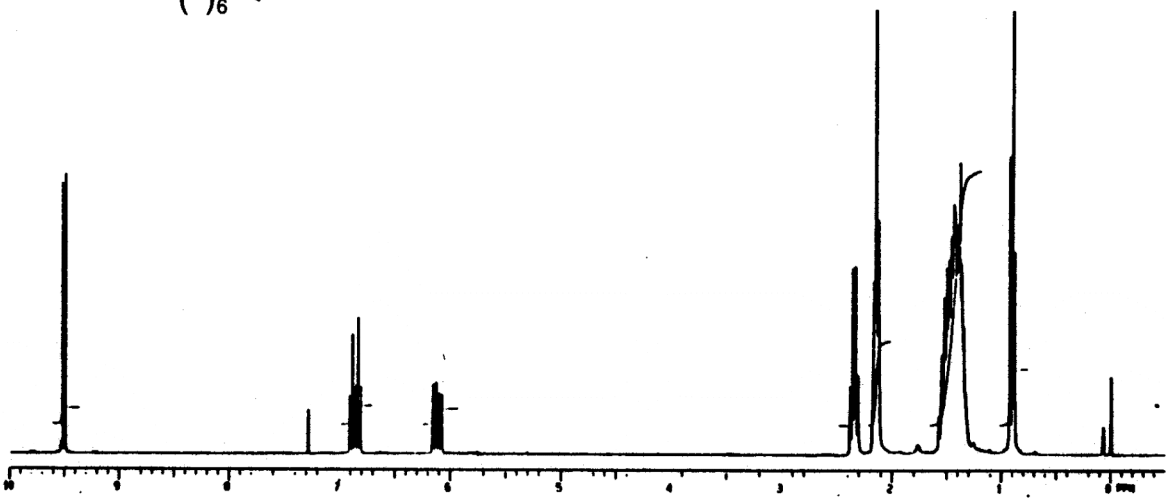


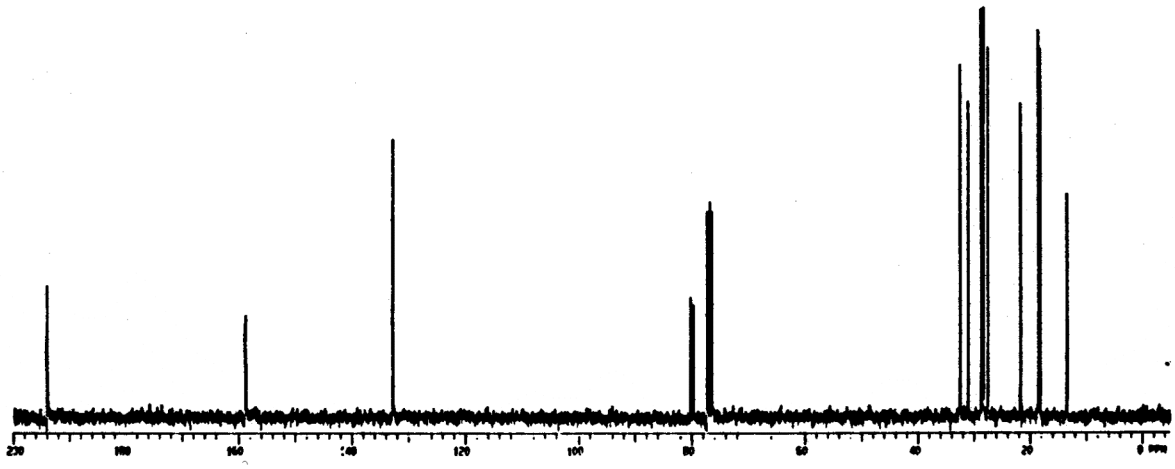


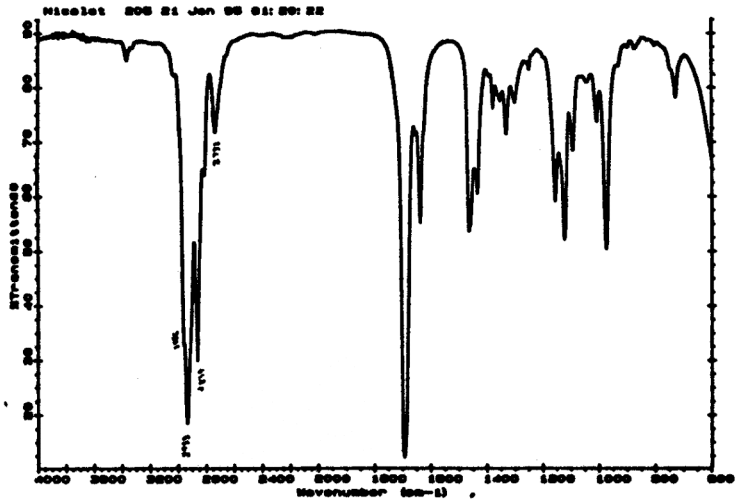


(*E*)-2-Pentadecen-10-ynal (**3.16**)



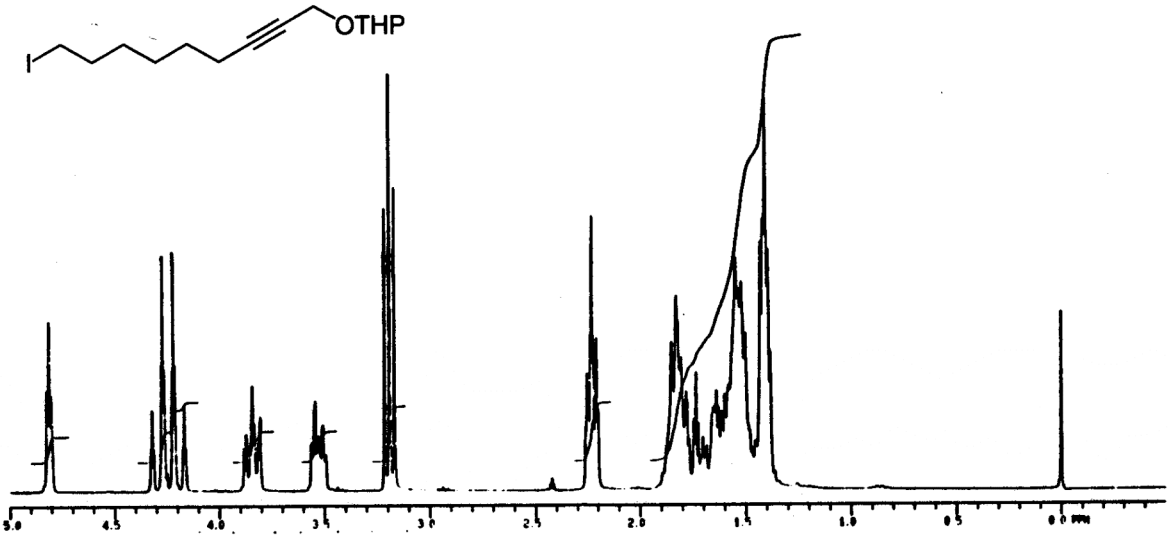


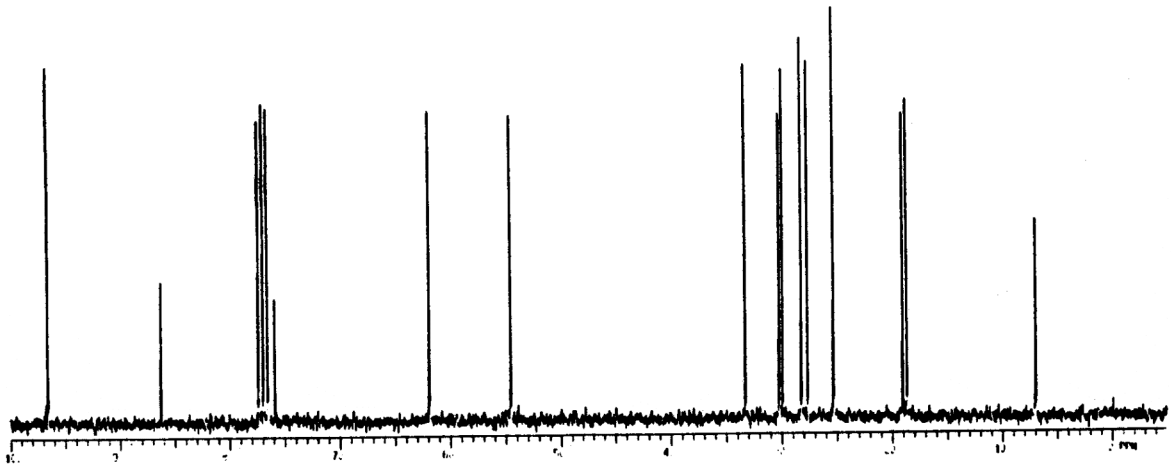


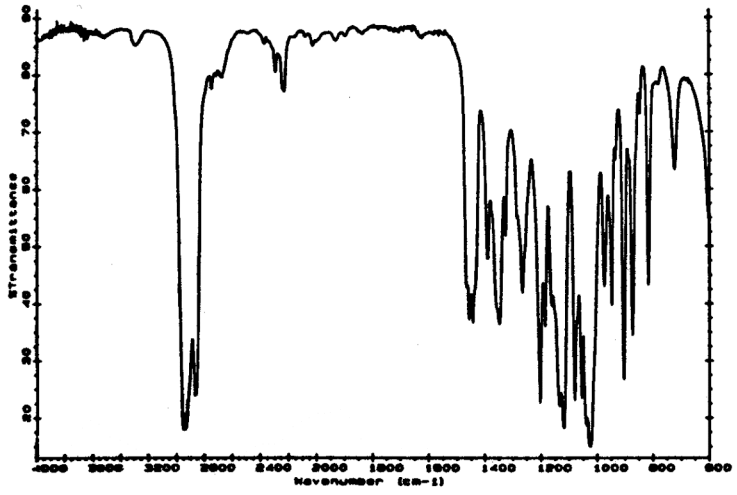


171

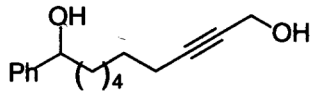
1-Tetrahydropyranyloxy-9-iodo-2-nonyne

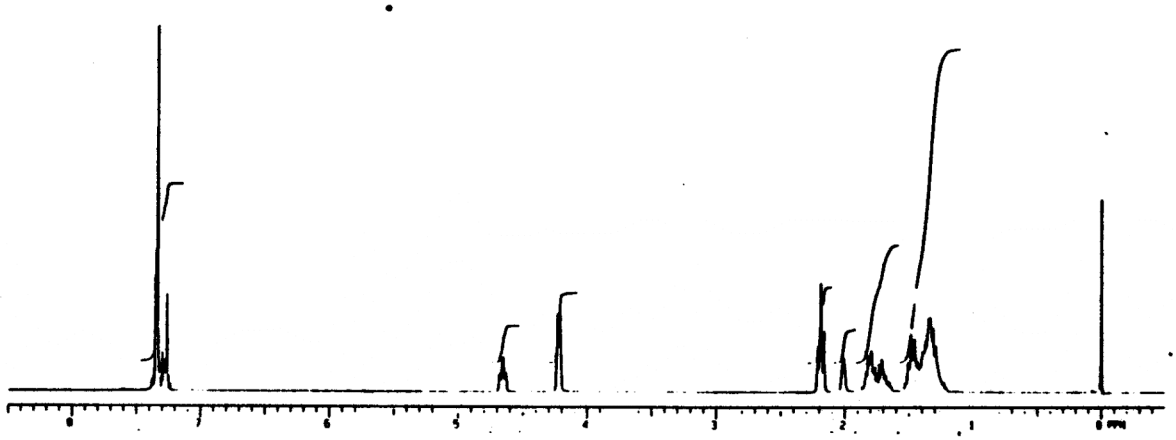


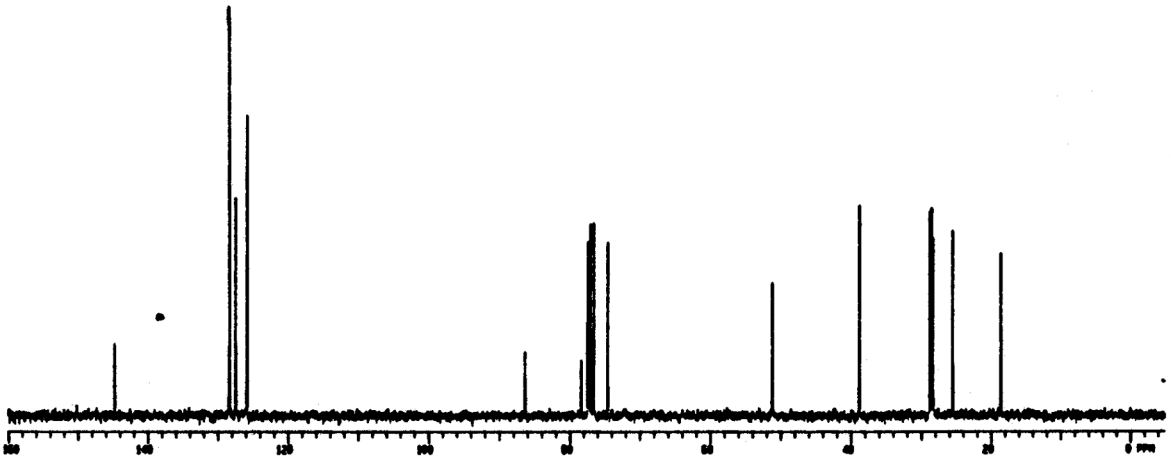


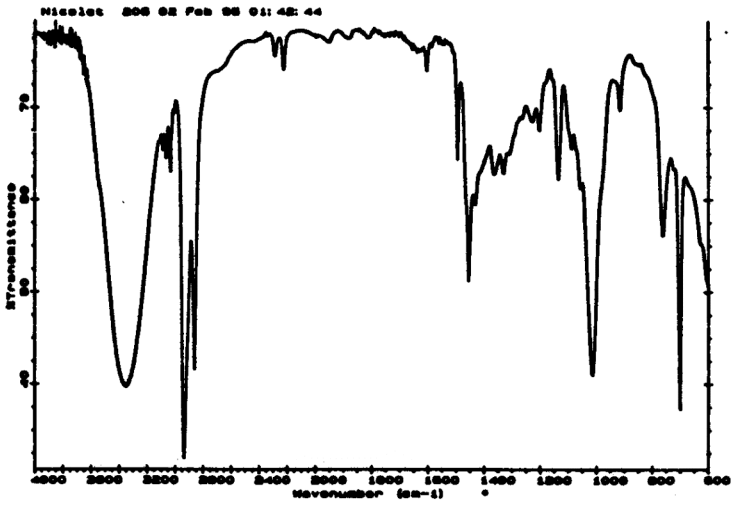


10-Phenyl-2-decyn-1,10-diol **(3.11)**

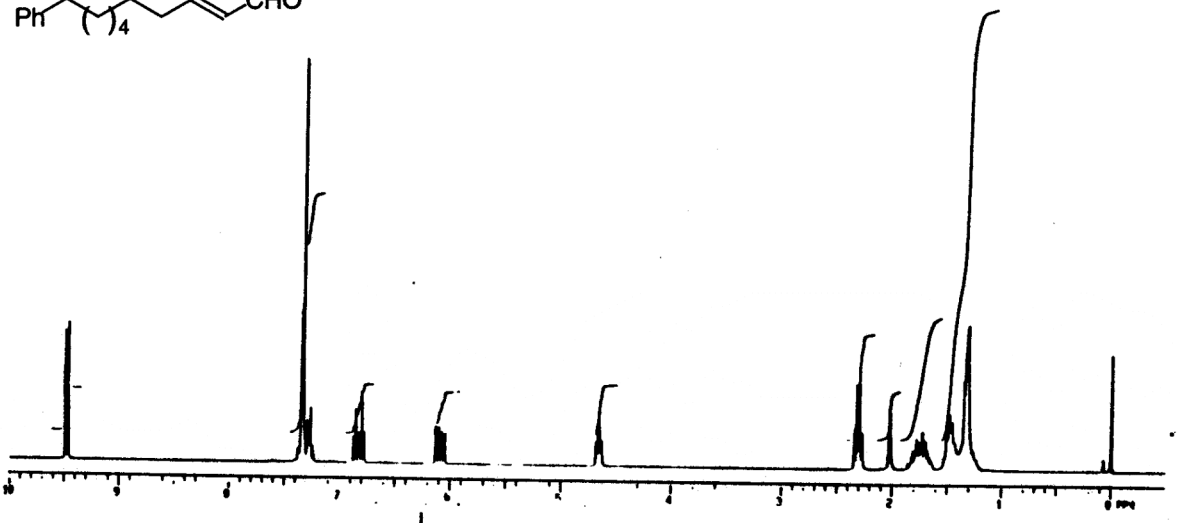


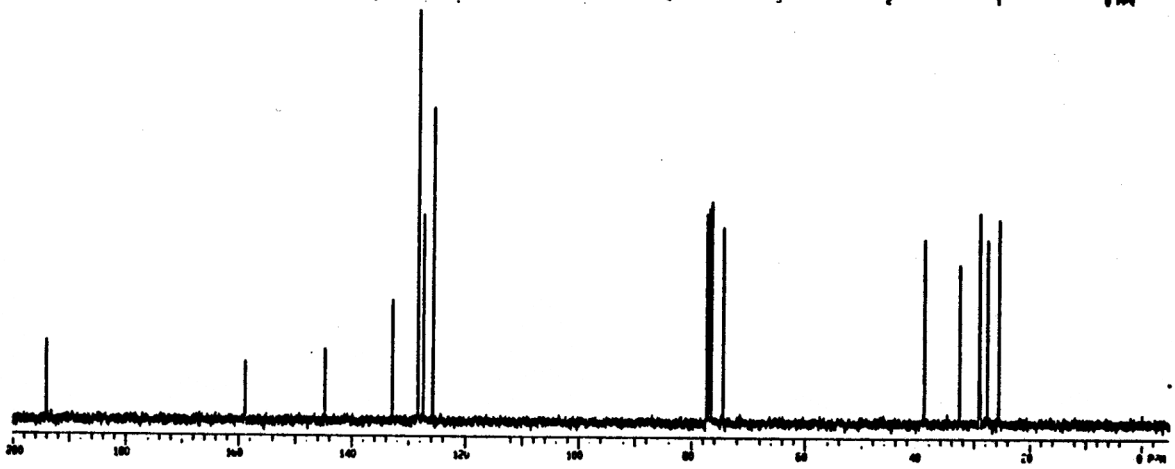


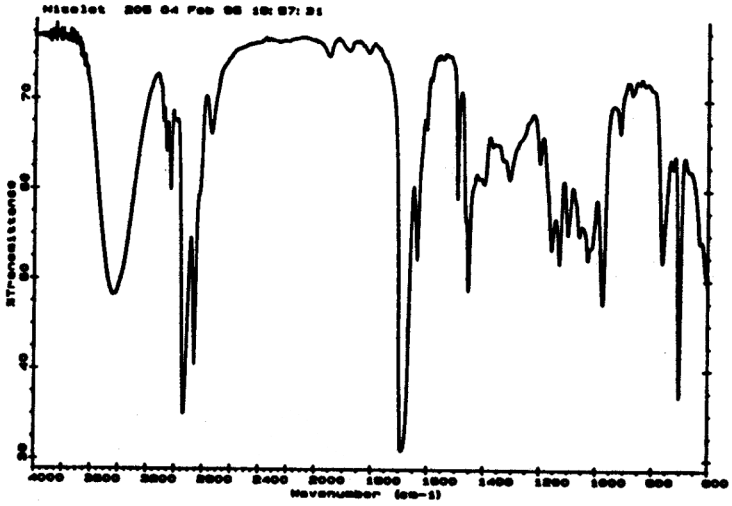




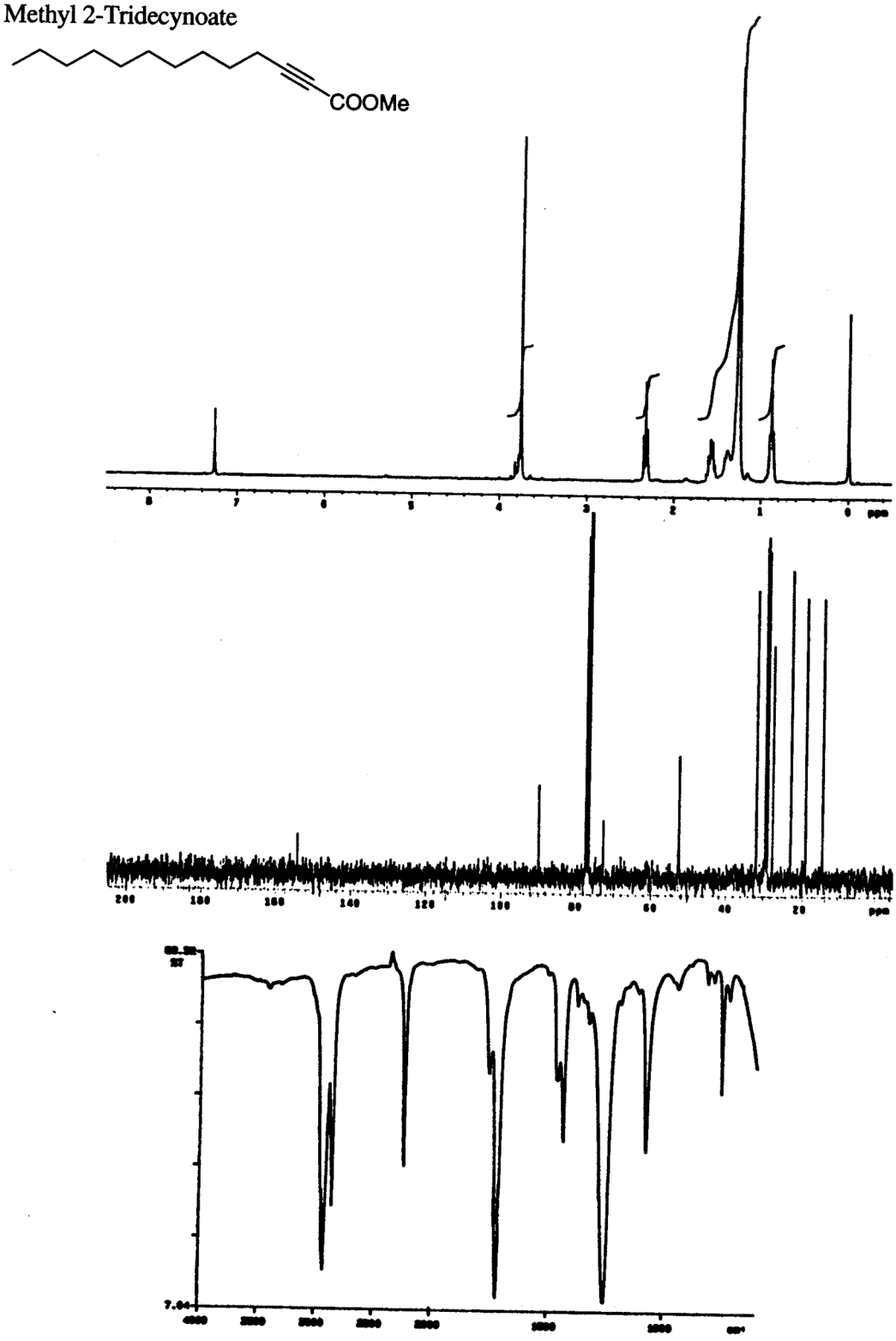
(*E*)-10-Hydroxy-10-phenyl-2-decenal **(3.12)**



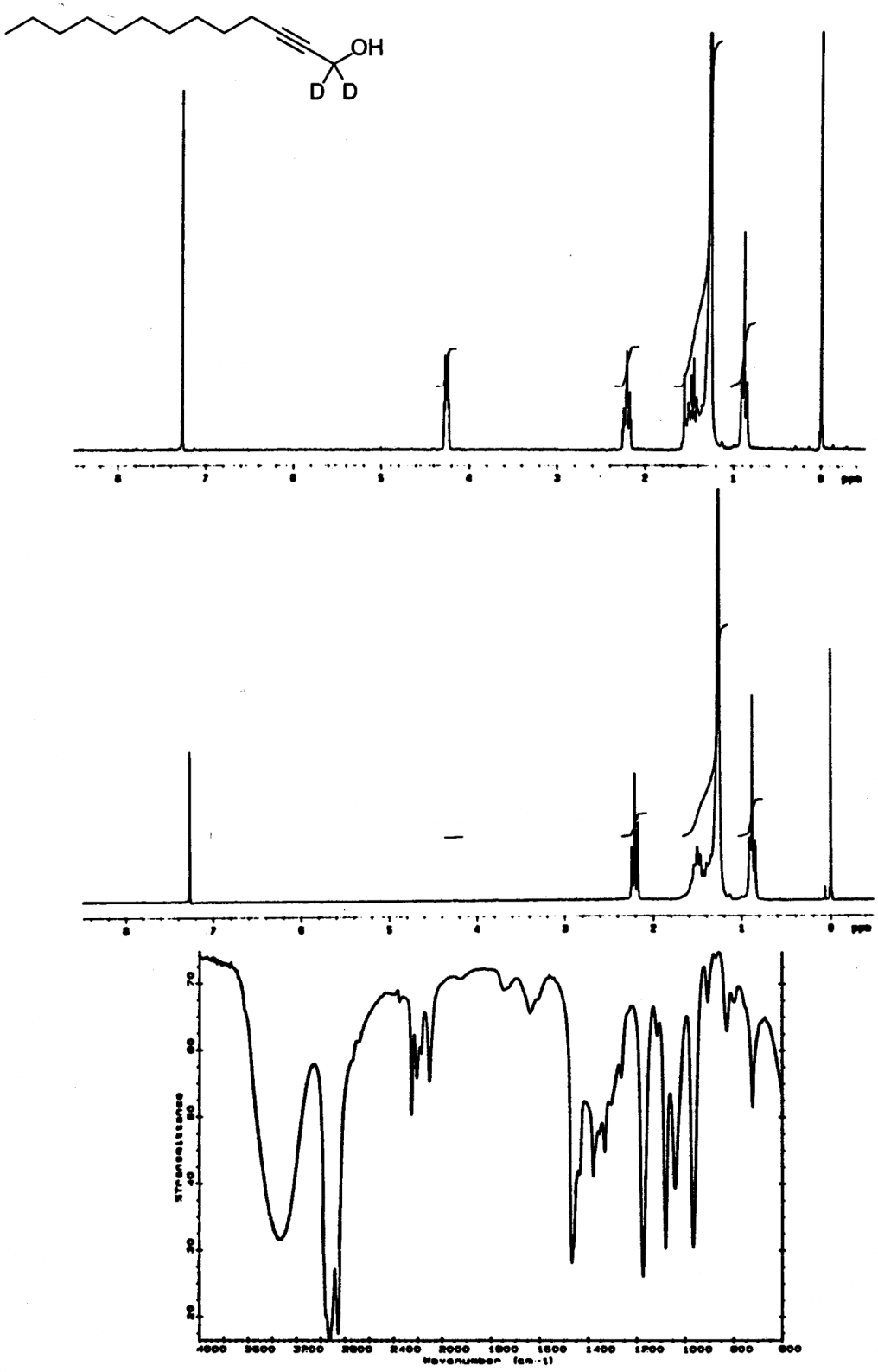




Methyl 2-Tridecynoate

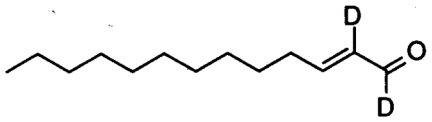


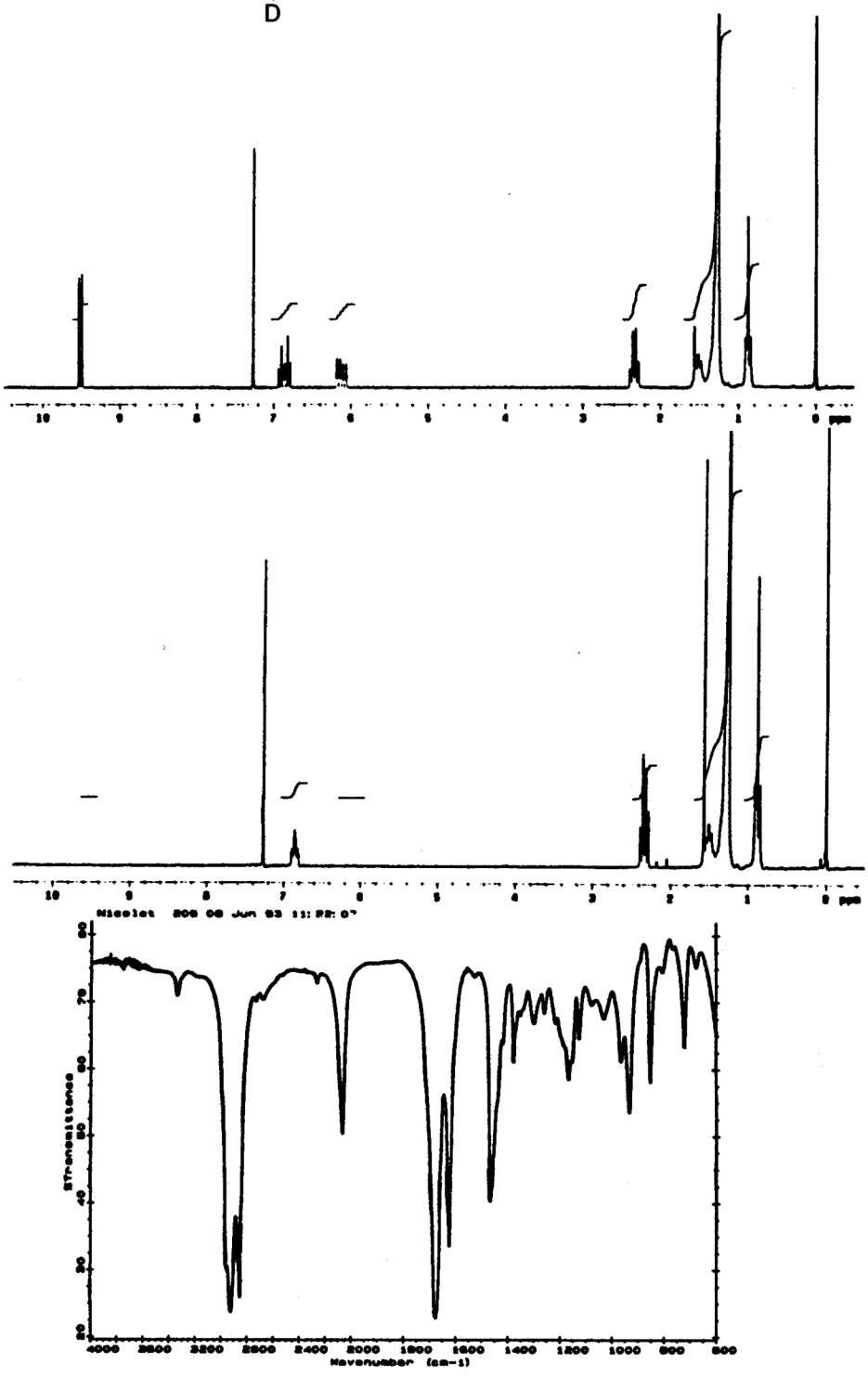
1,1-Dideutero-2-tridecyn-1-ol (**3.23**)



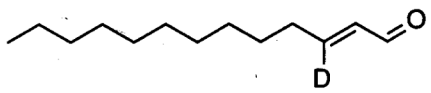
176

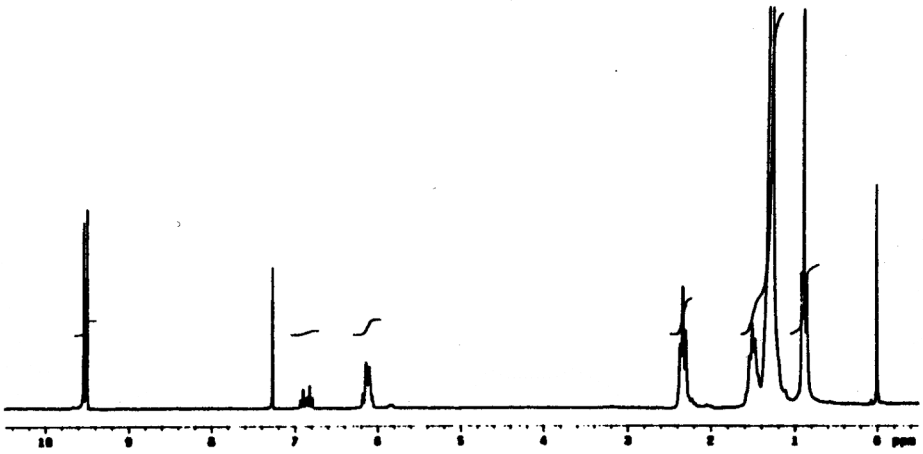
(*E*)-1,2-Dideutero-2-tridecenal (**3.24**)

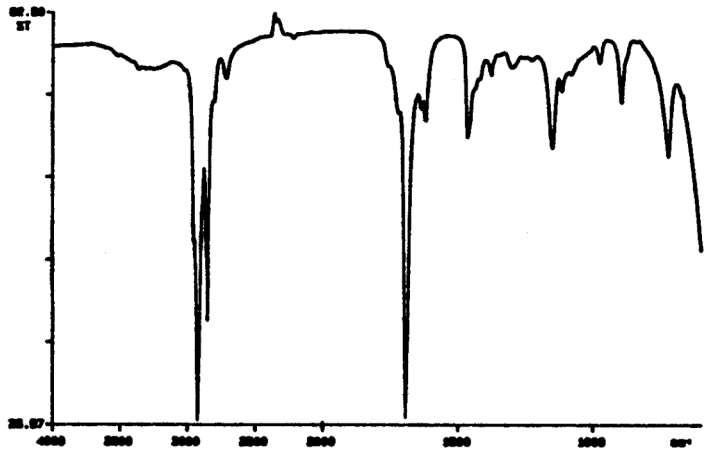




(*E*)-3-Deutero-2-tridecenal (**3.26**)

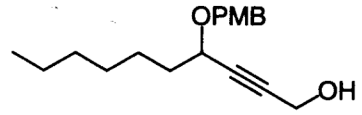


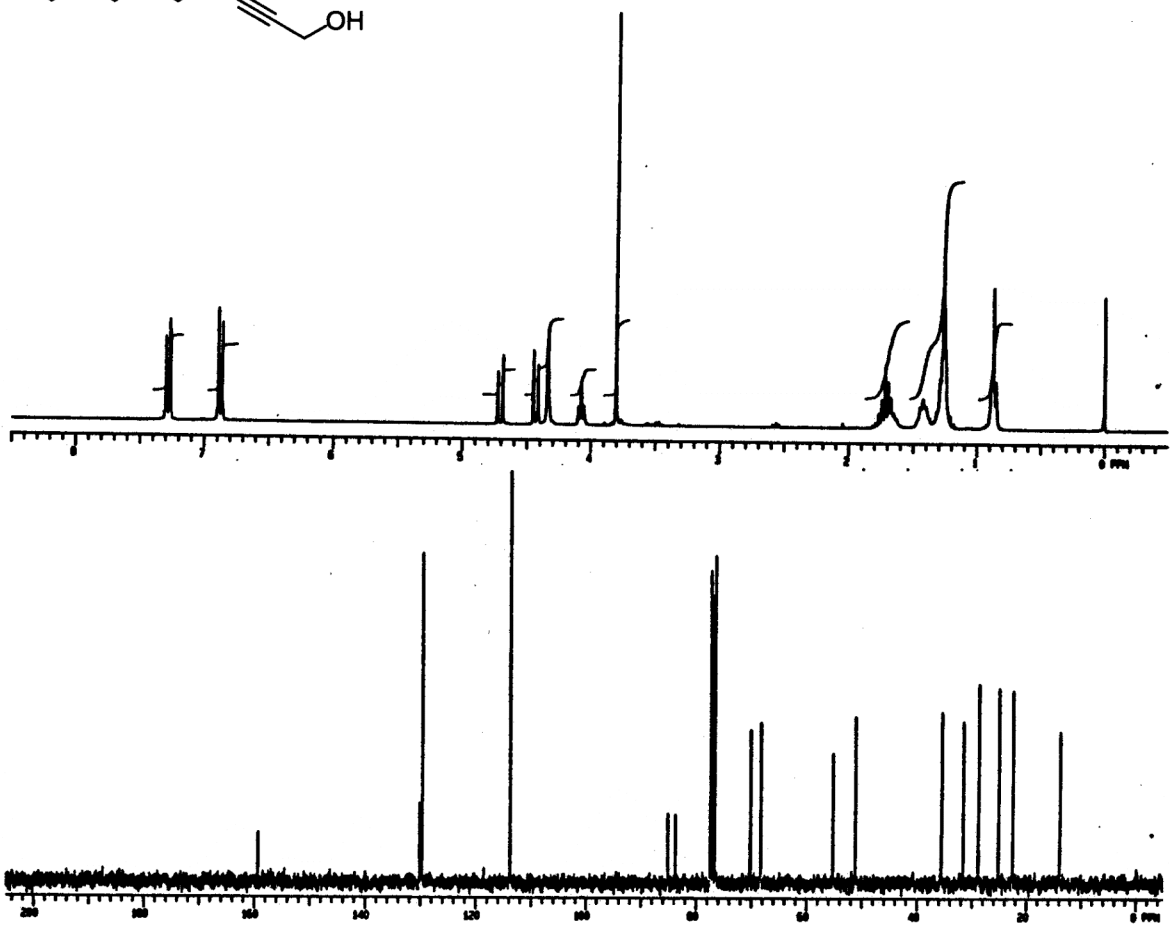


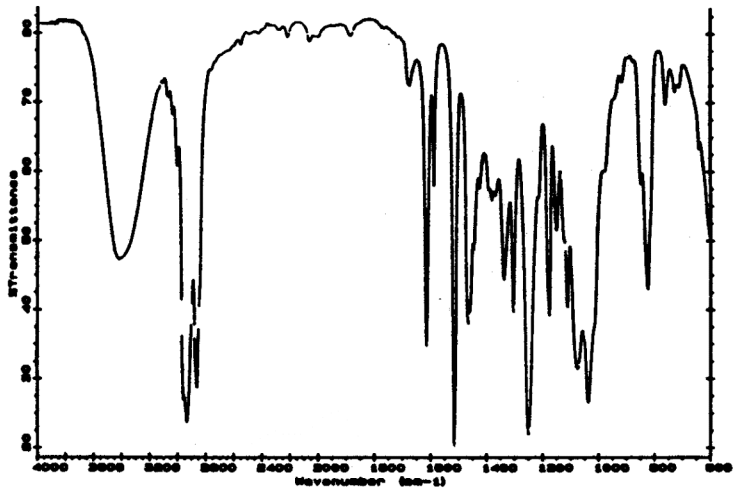


178

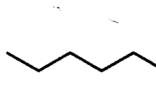
4-(4-Methoxybenzyl)oxy-2-decyn-1-ol **(3.51)**

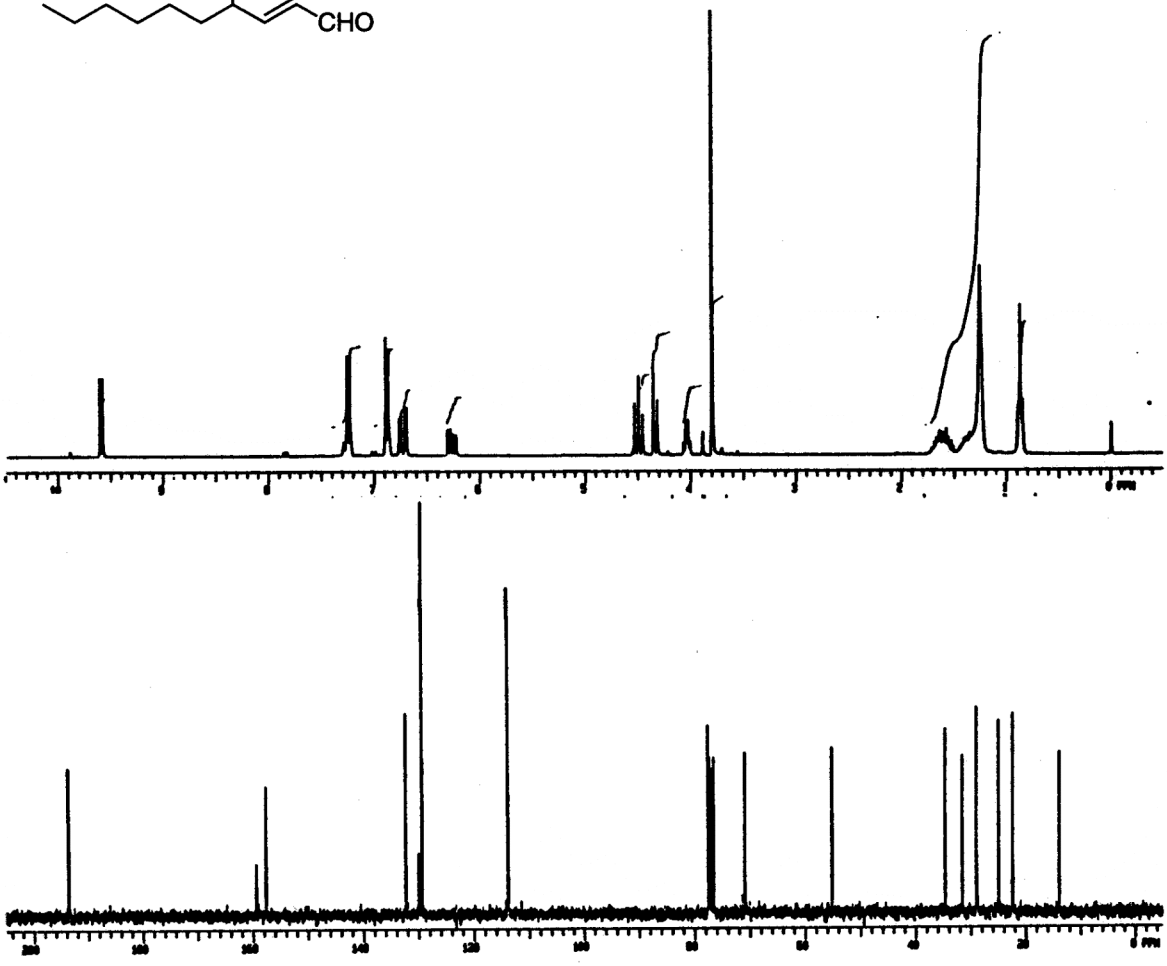


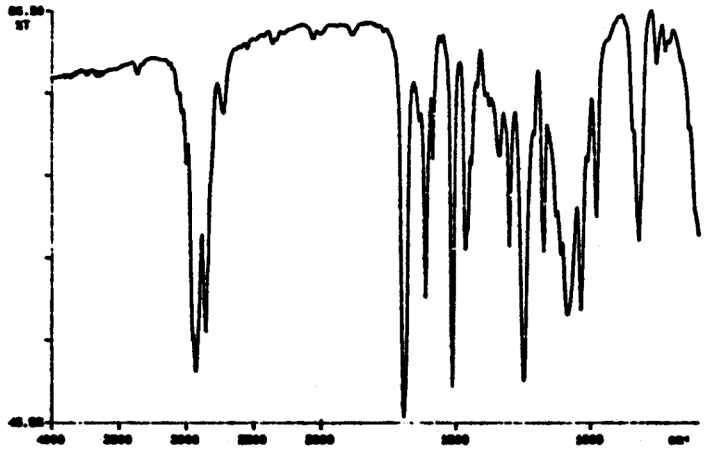




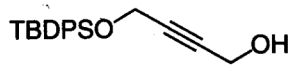
(*E*)-4-(4-Methoxybenzyl)oxy-2-decenal (**3.52**)

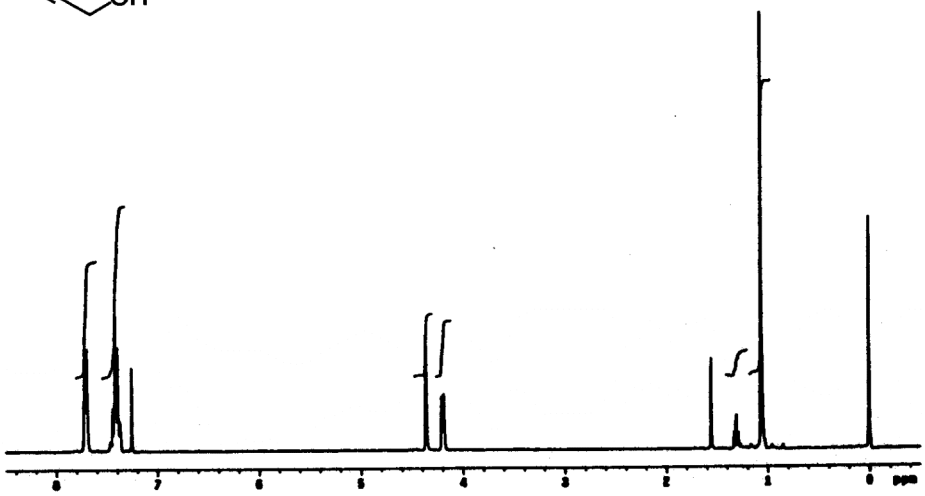


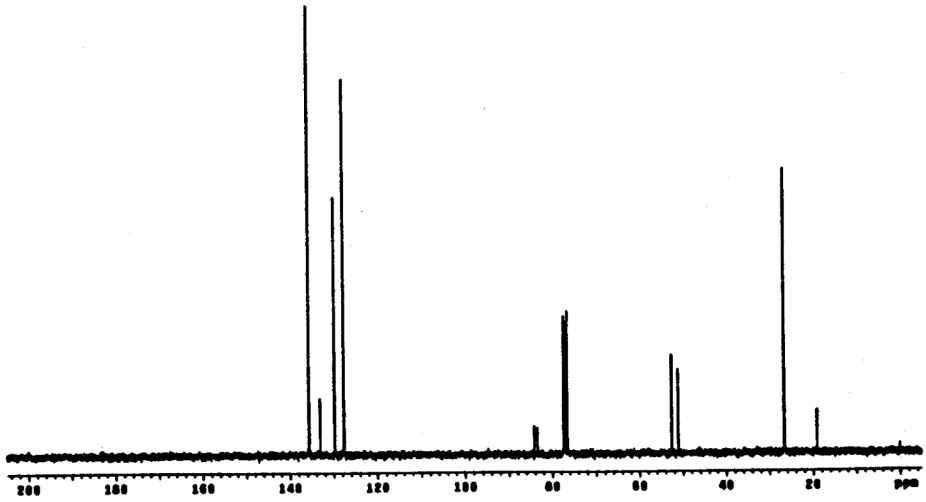


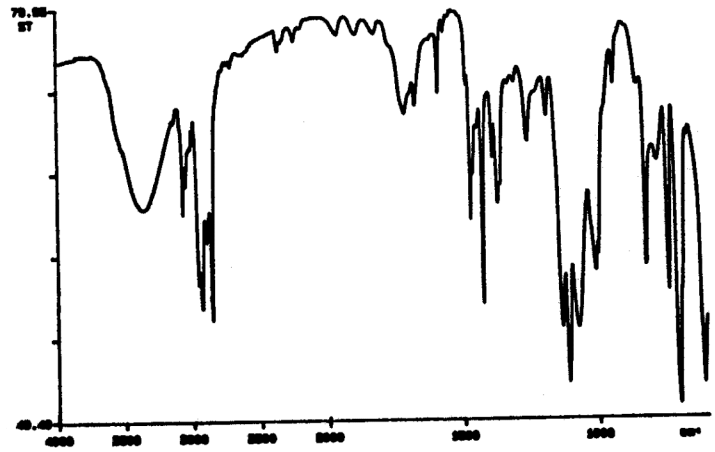


4-(*t*-Butyldiphenylsilyl)oxy-2-butyn-1-ol **(3.53)**

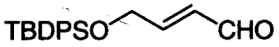


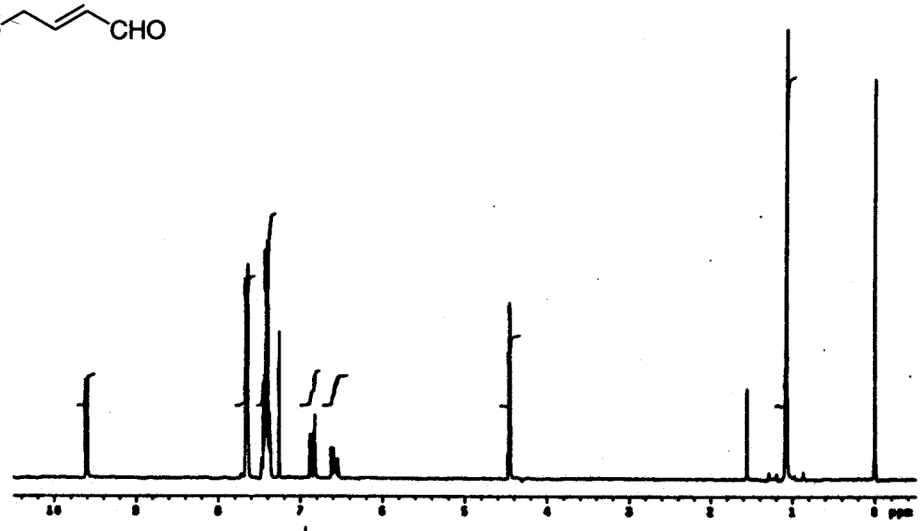


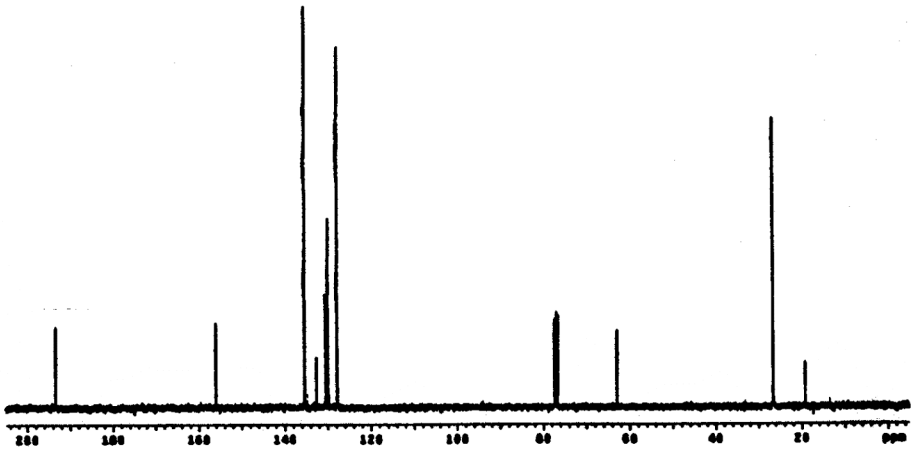


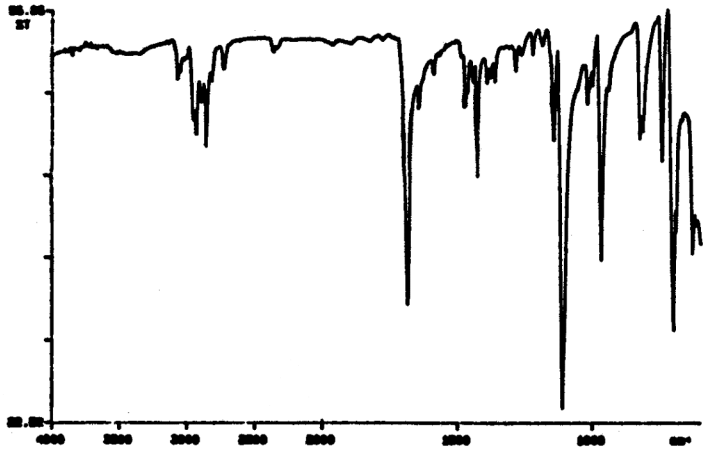


(*E*)-4-(*t*-Butyldiphenylsilyl)oxy-2-butenal (**3.54**)

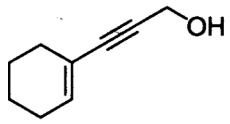


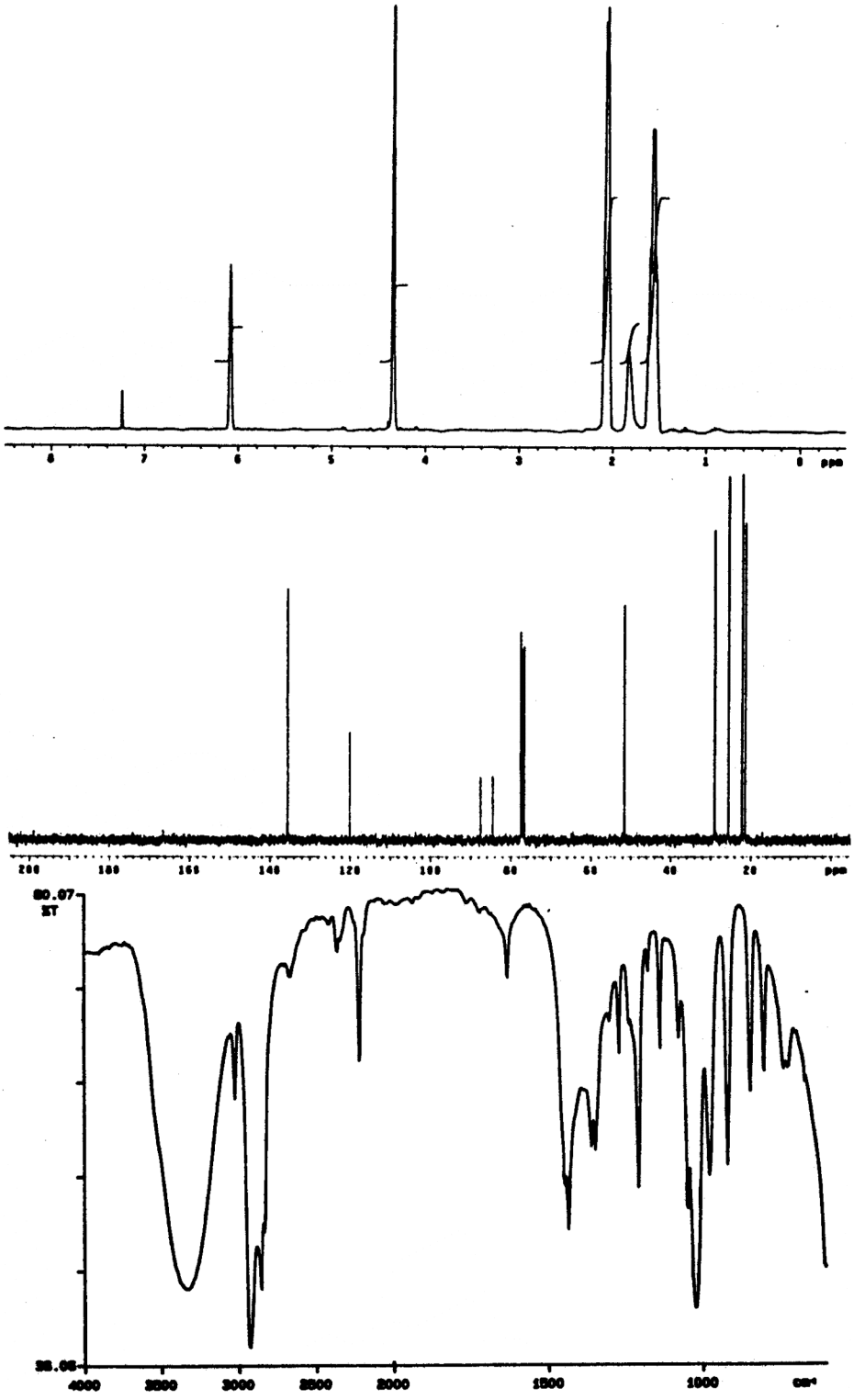




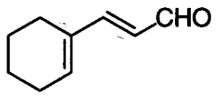


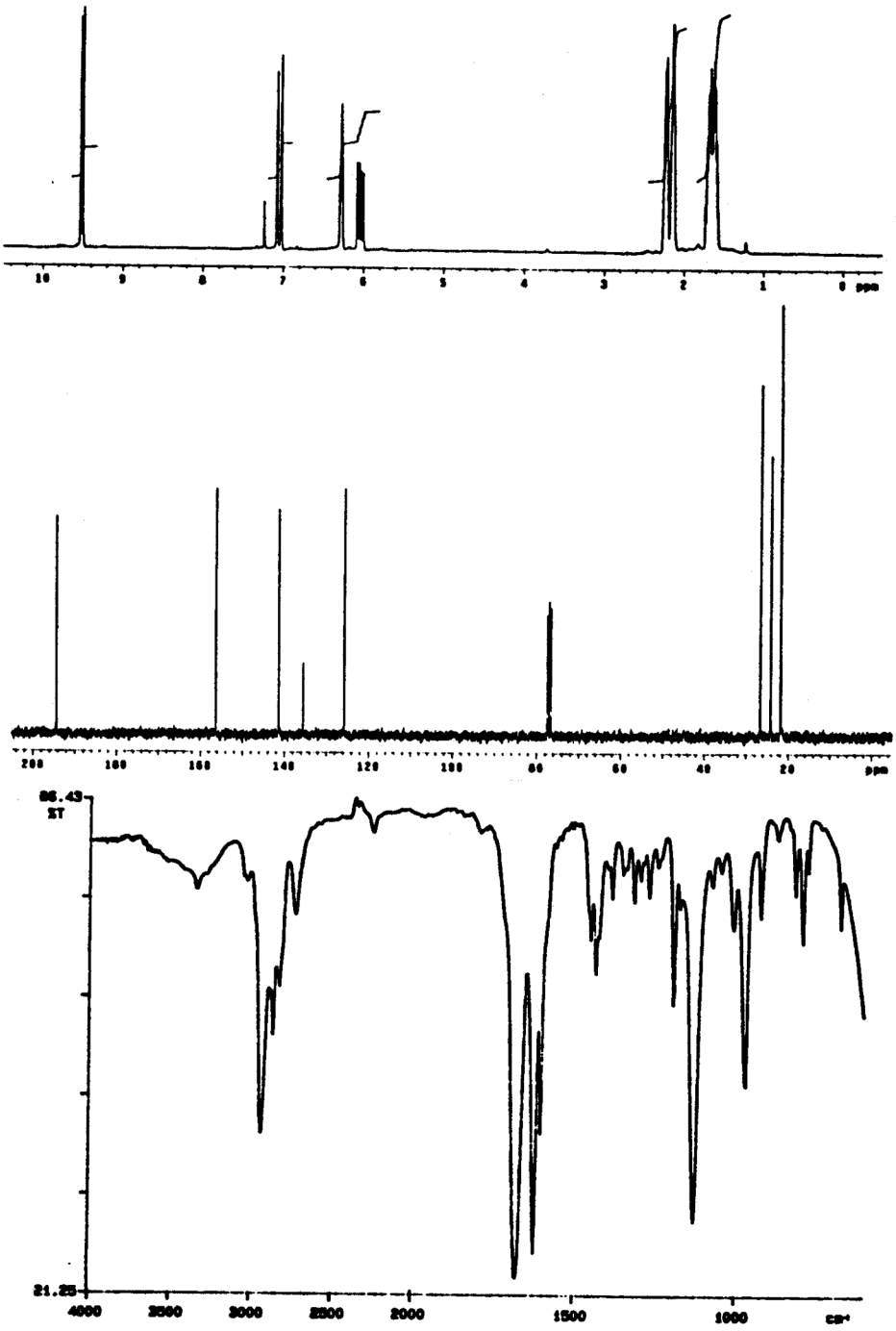
3-(1-Cyclohexenyl)-2-propyn-1-ol (**3.55**)





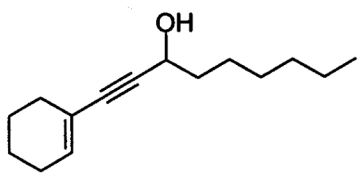
(*E*)-3-(1-Cyclohexenyl)-2-propenal





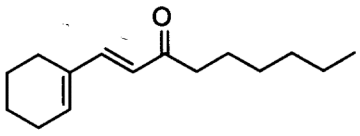
199

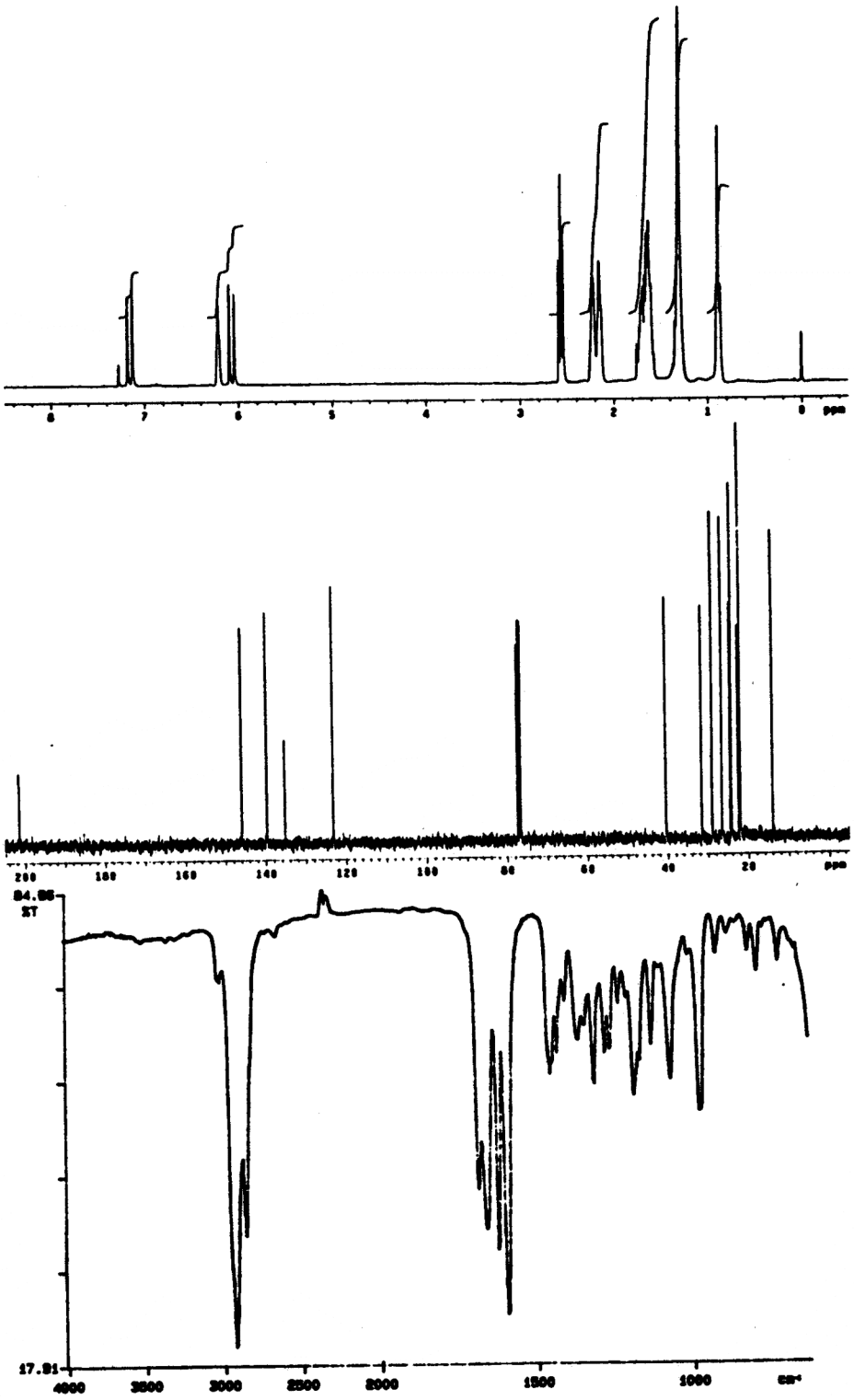
1-(1-Cyclohexenyl)-1-nonyn-3-ol **(3.56)**



200

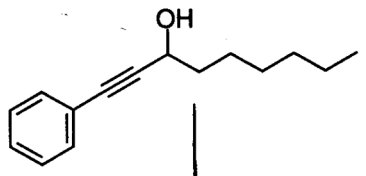
(*E*)-1-(1-Cyclohexenyl)-1-nonen-3-one

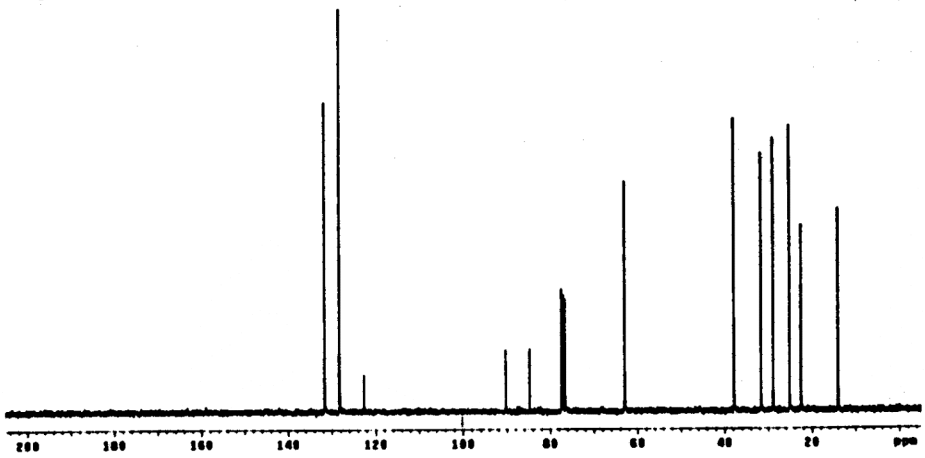


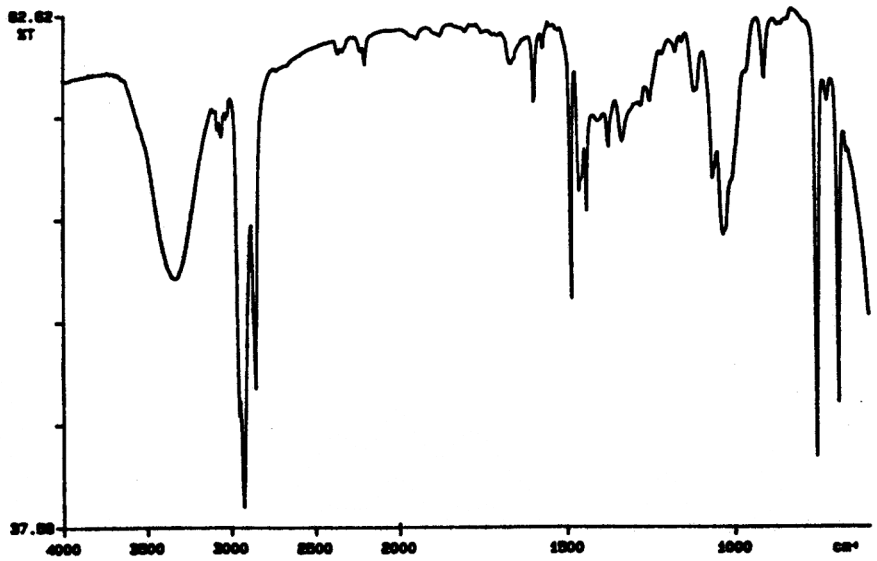


201

1-Phenyl-1-nonyn-3-ol **(3.57)**

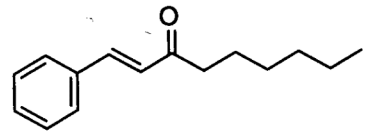


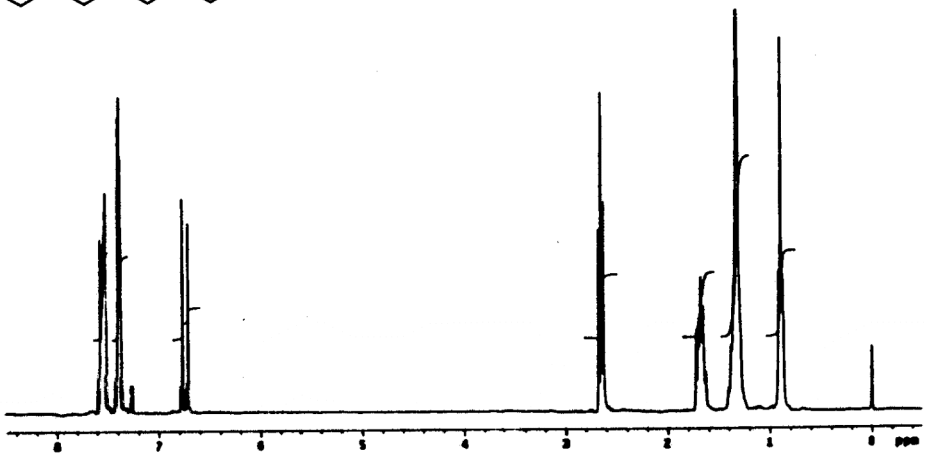


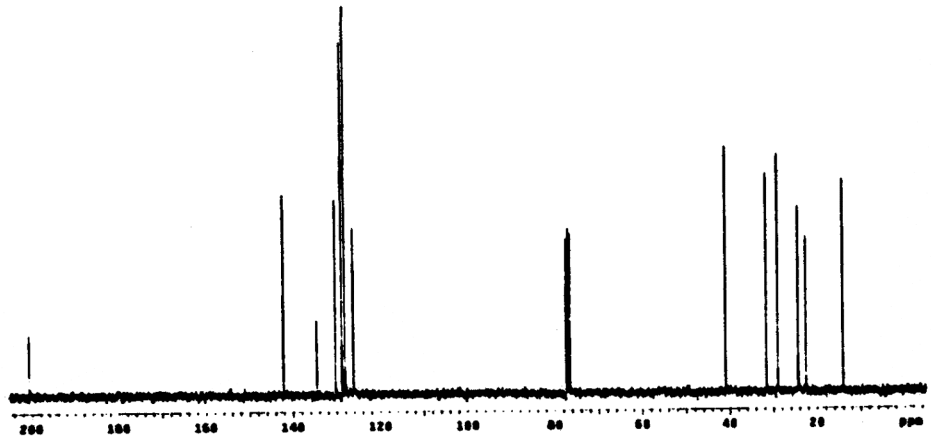


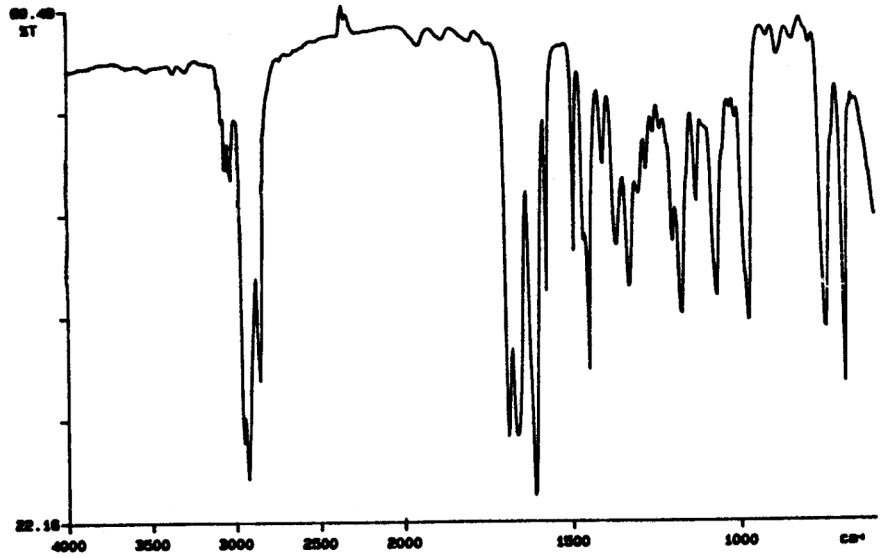
202

(*E*)-1-Phenyl-1-nonen-3-one



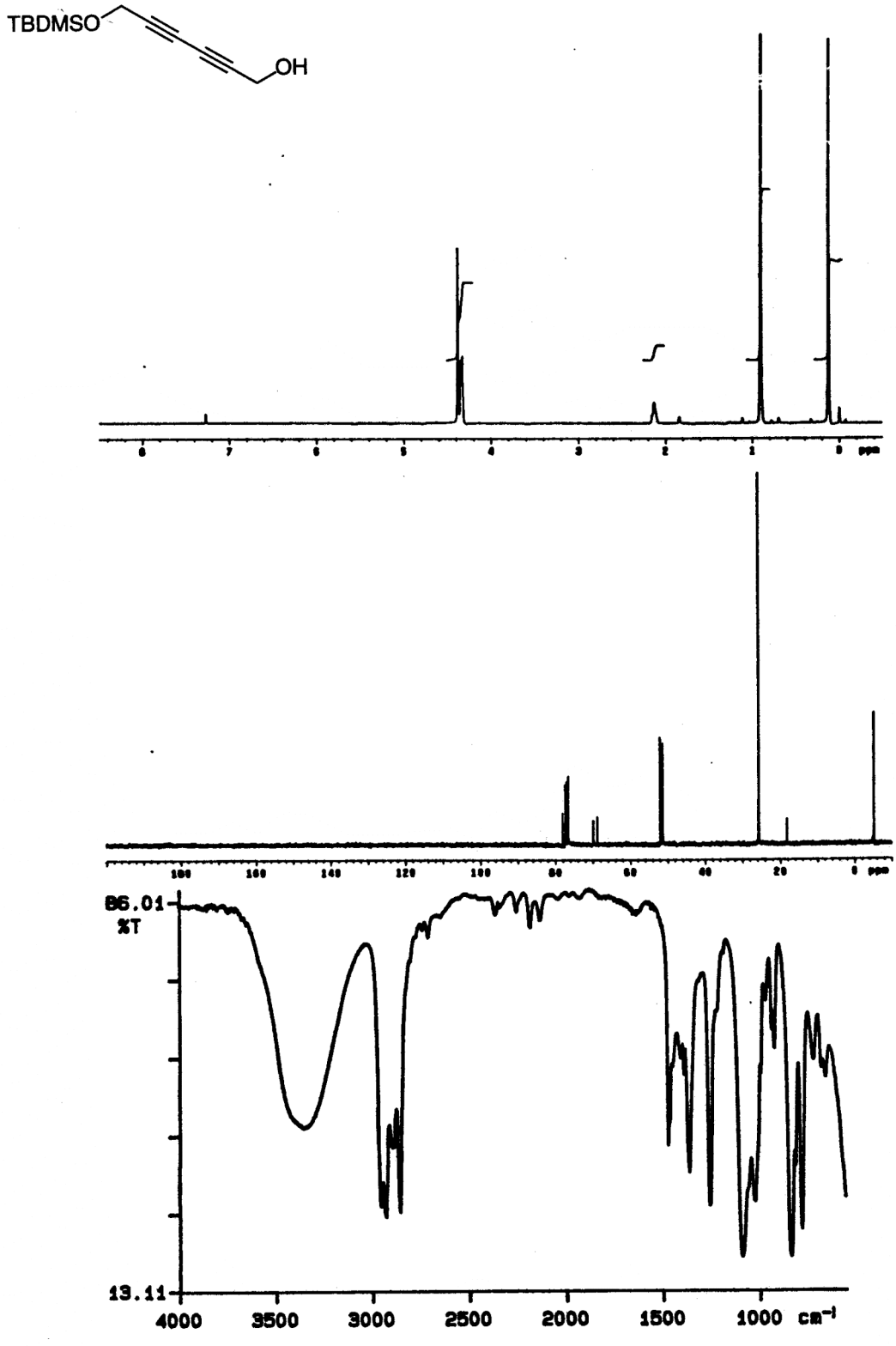




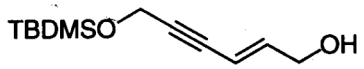


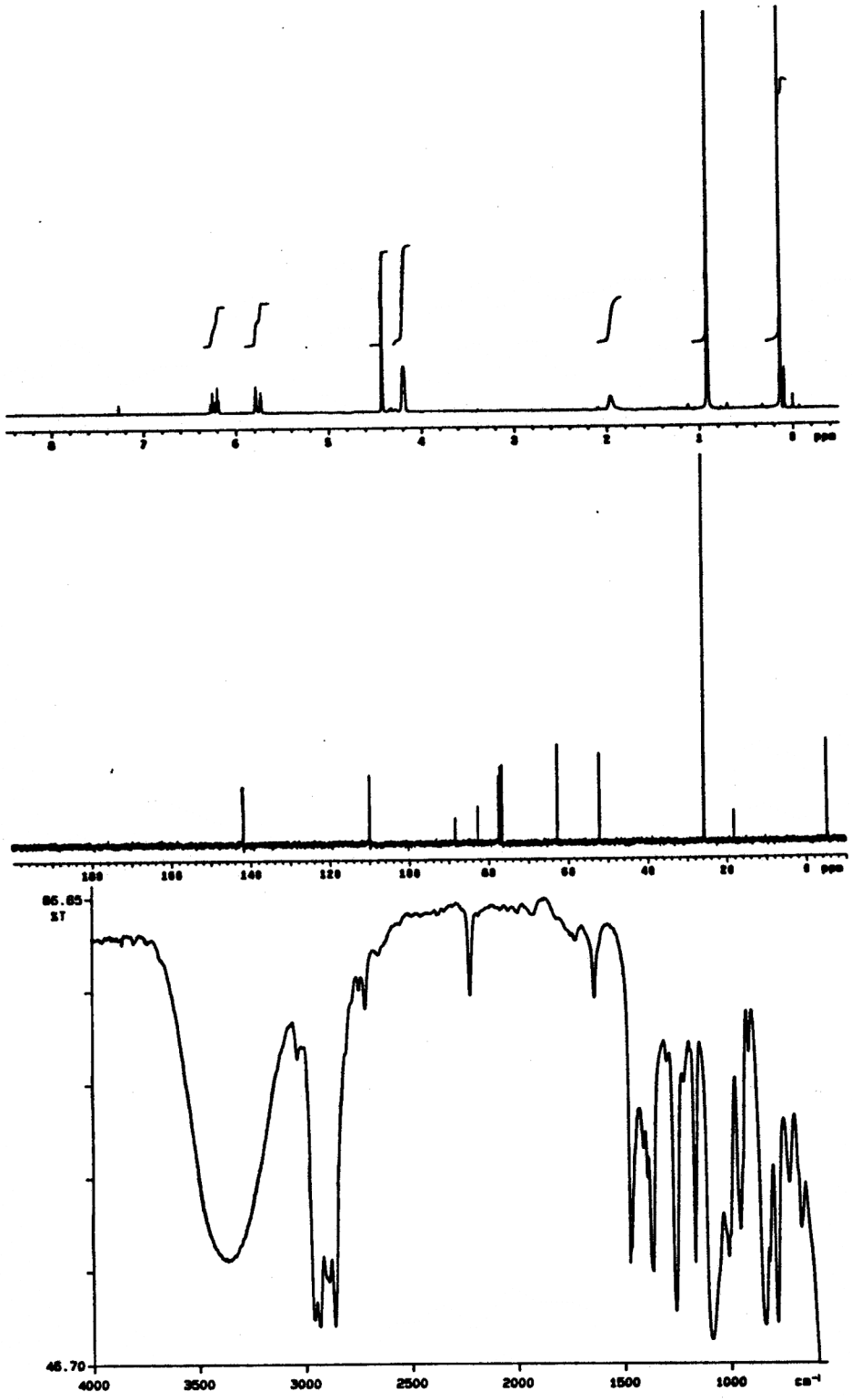
203

6-(*t*-Butyldimethylsilyl)oxy-2,4-hexadiyn-1-ol **(4.14)**

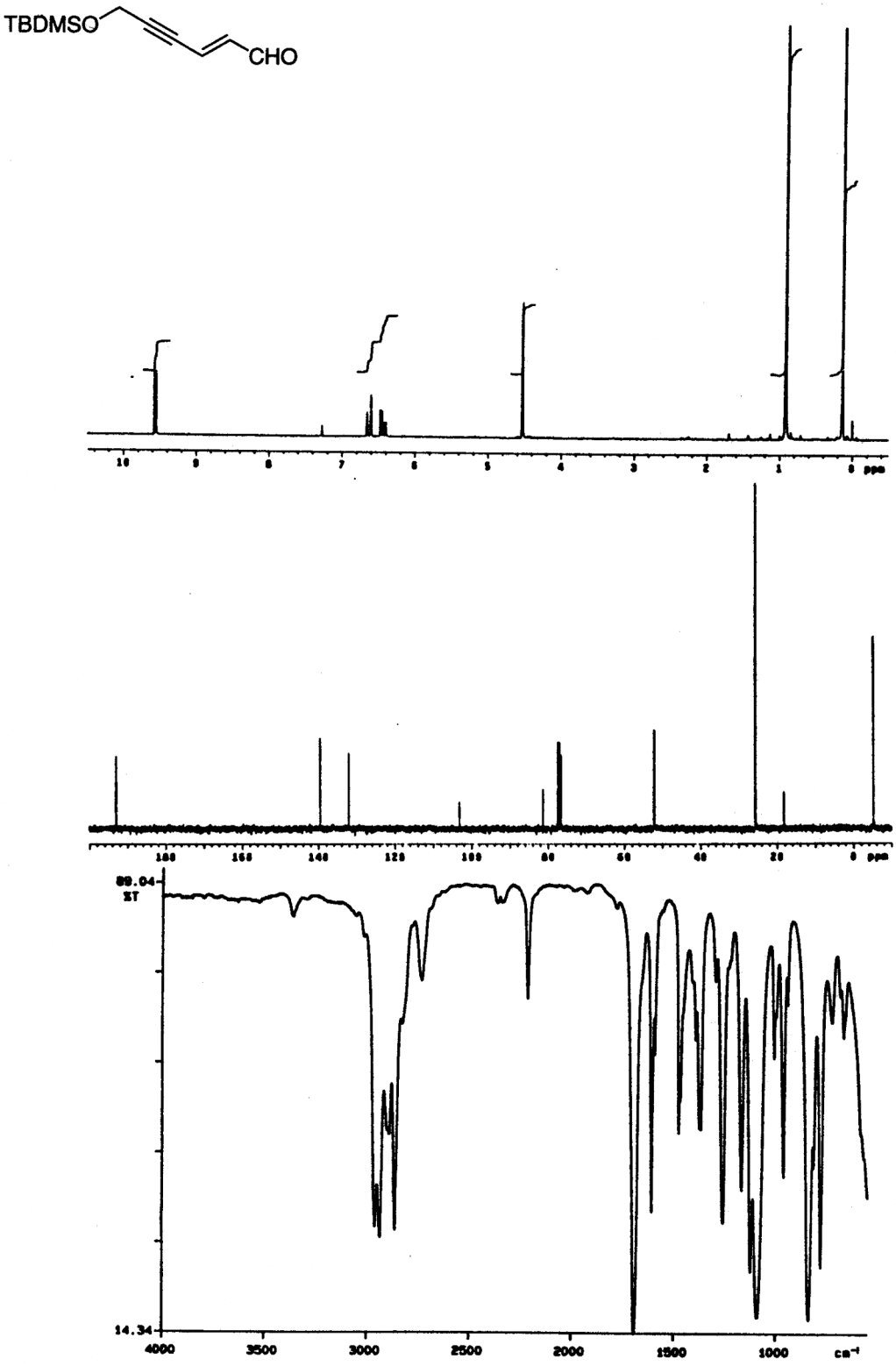


(*E*)-6-(*t*-Butyldimethylsilyl)oxy-2-hexen-4-yn-1-ol **(4.22)**

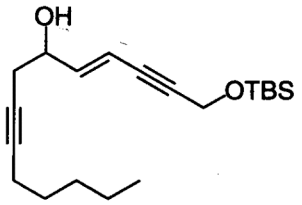


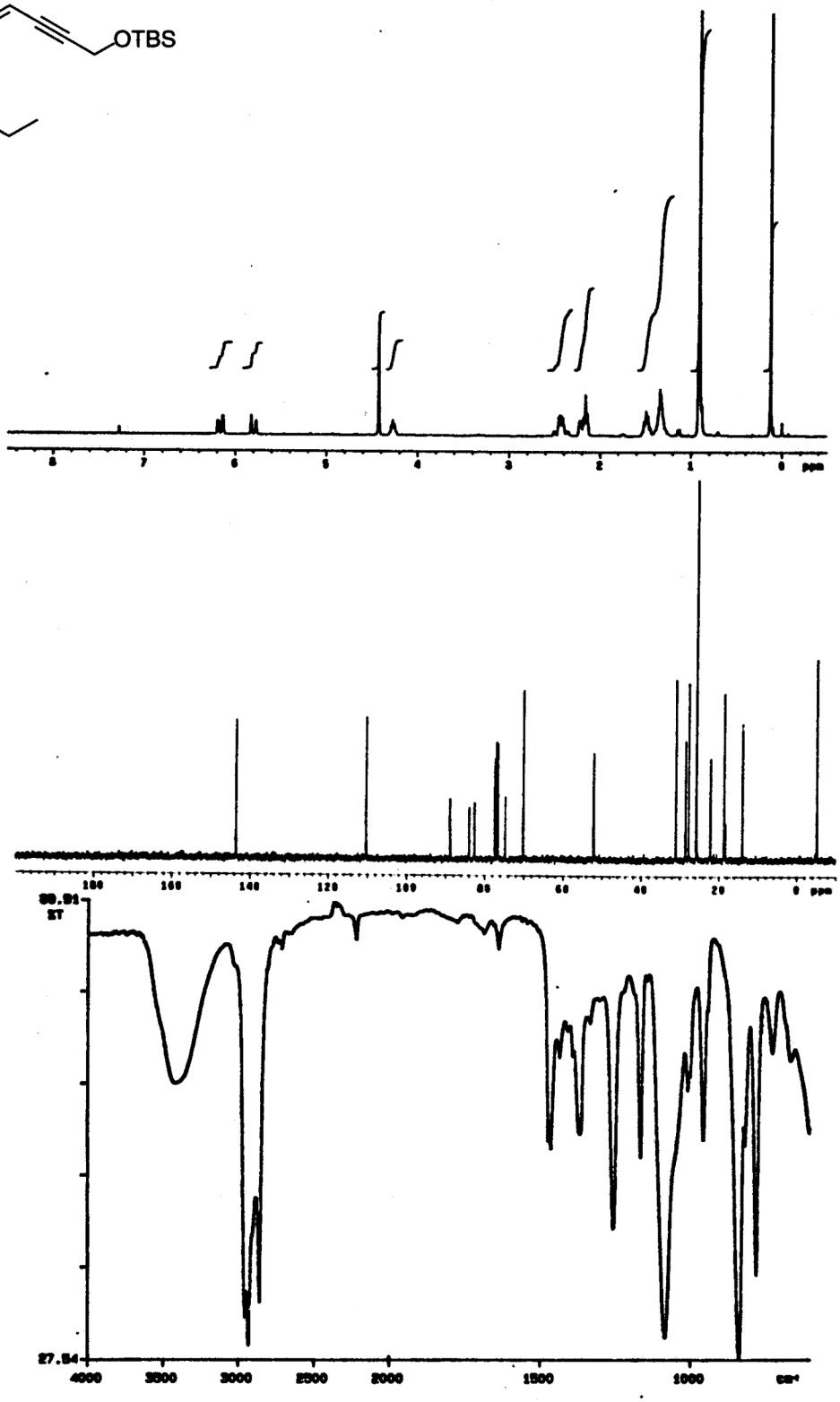


(*E*)-6-(*t*-Butyldimethylsilyl)oxy-2-hexen-4-ynal **(4.23)**



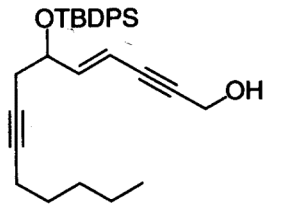
(*E*)-1-(*t*-Butyldimethylsilyl)oxy-4-tetradecen-2,8-diyn-6-ol (**4.25**)



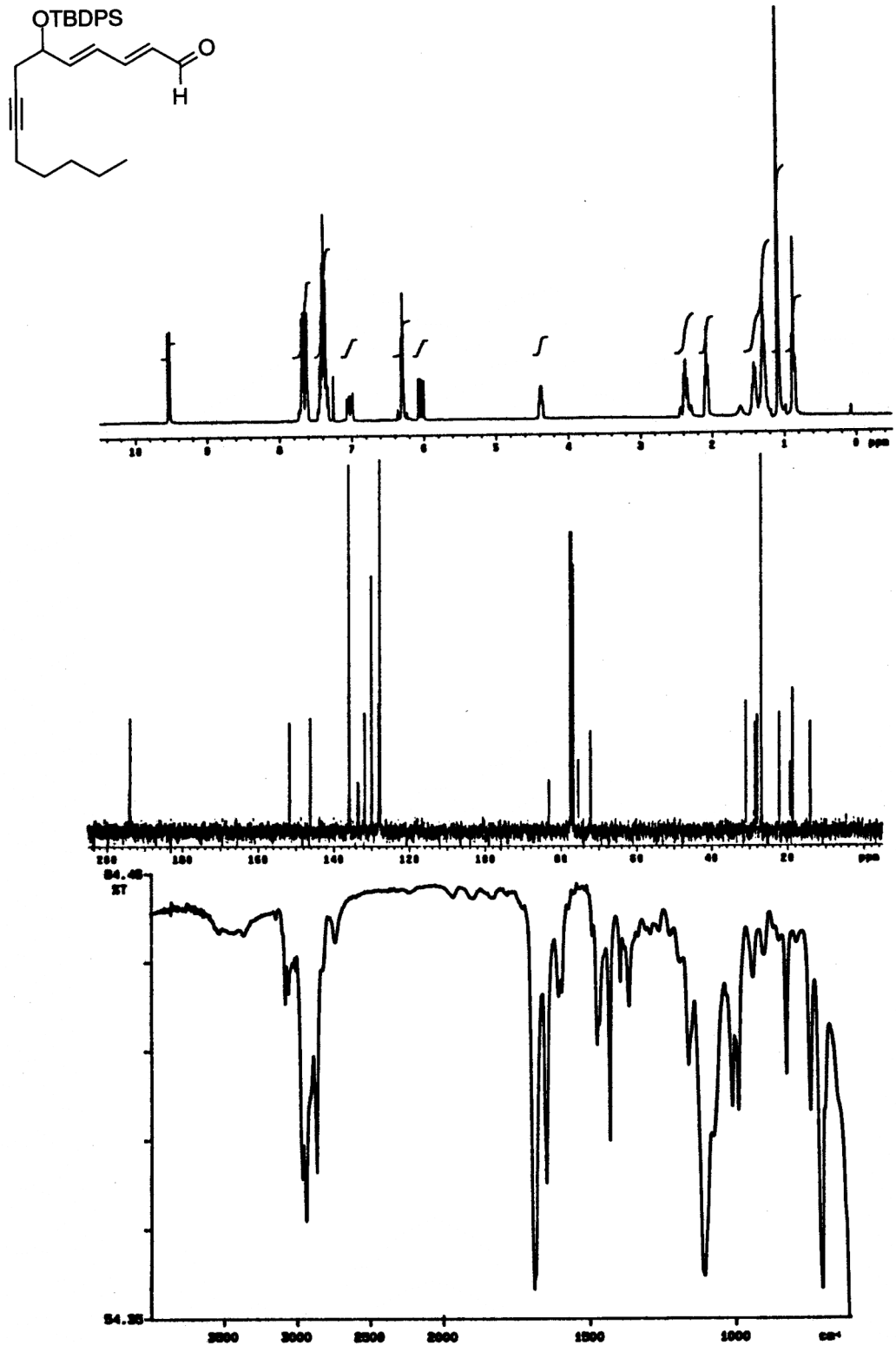


208

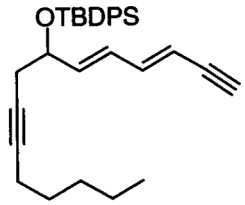
(*E*)-6-(*t*-Butyldiphenylsilyl)oxy-4-tetradecen-2,8-diyn-1-ol **(4.27)**

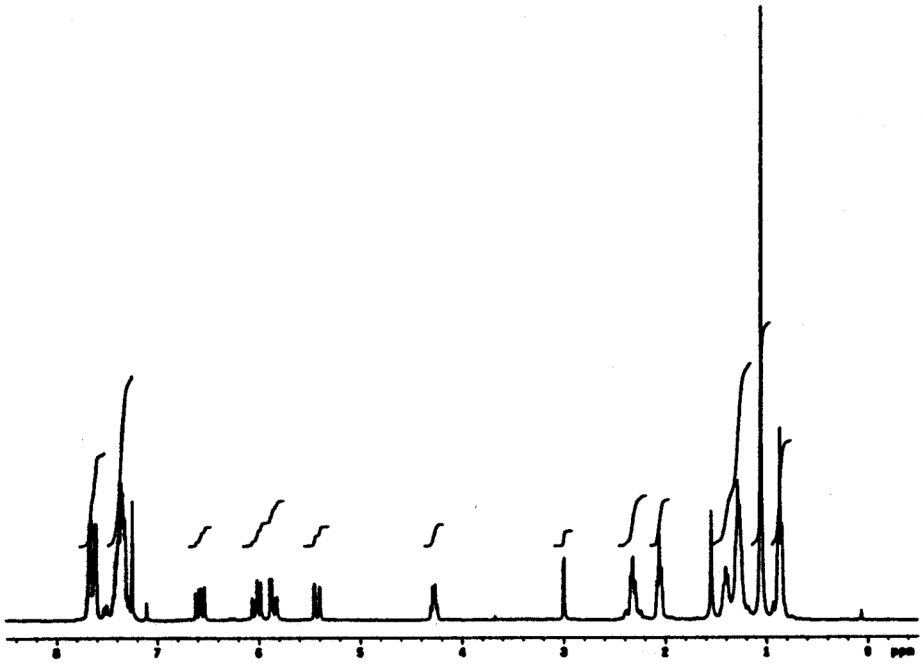


(2*E*,4*E*)-6-(*t*-Butyldiphenylsilyl)oxy-2,4-tetradecadien-8-ynal (**4.29**)



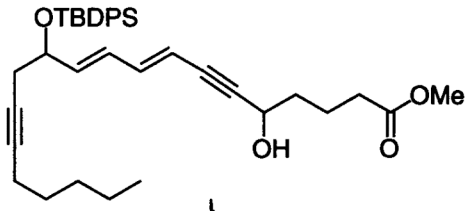
(3*E*,5*E*)-7-(*t*-Butyldiphenylsilyl)oxy-3,5-pentadecadien-1,9-diyne **(4.30)**

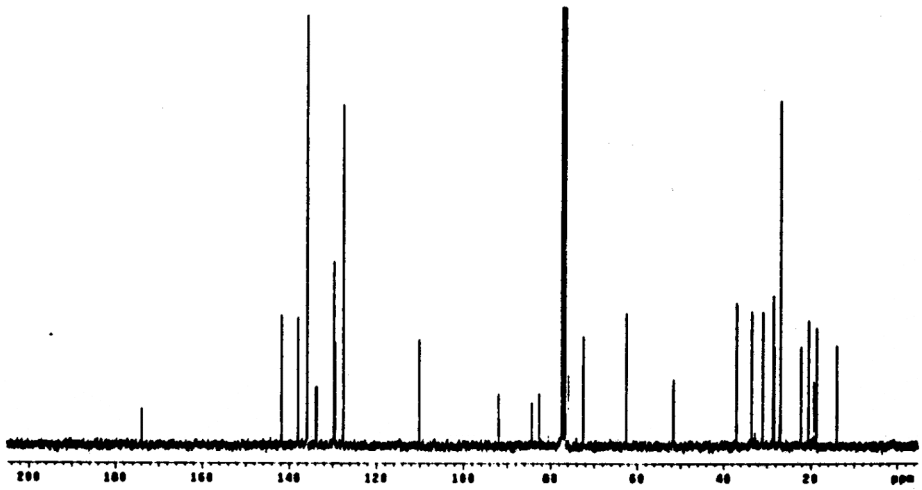


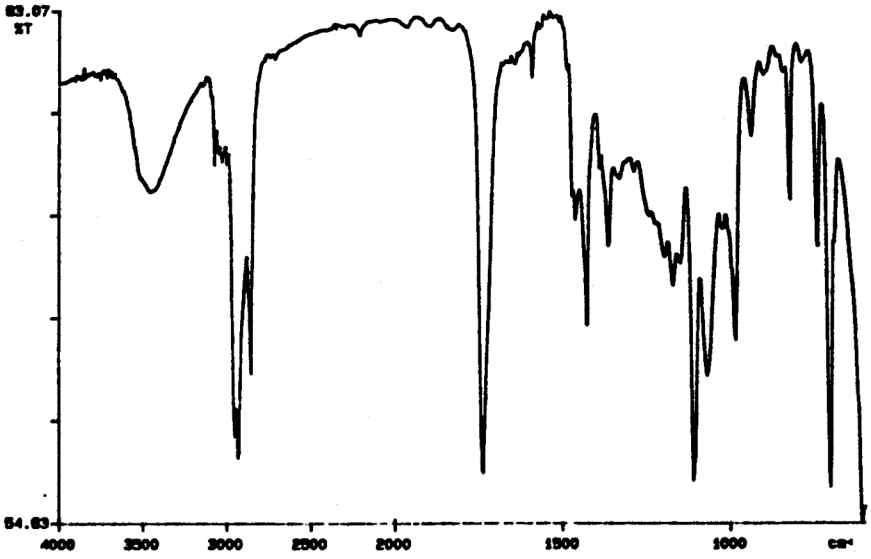


(8*E*,10*E*)-Methyl 5-Hydroxy-12-(*t*-butyldiphenylsilyl)oxy-8,10-eicosadiene-6,14-diynoate

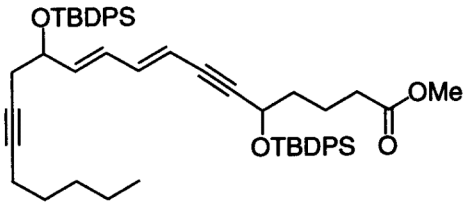
(4.31)

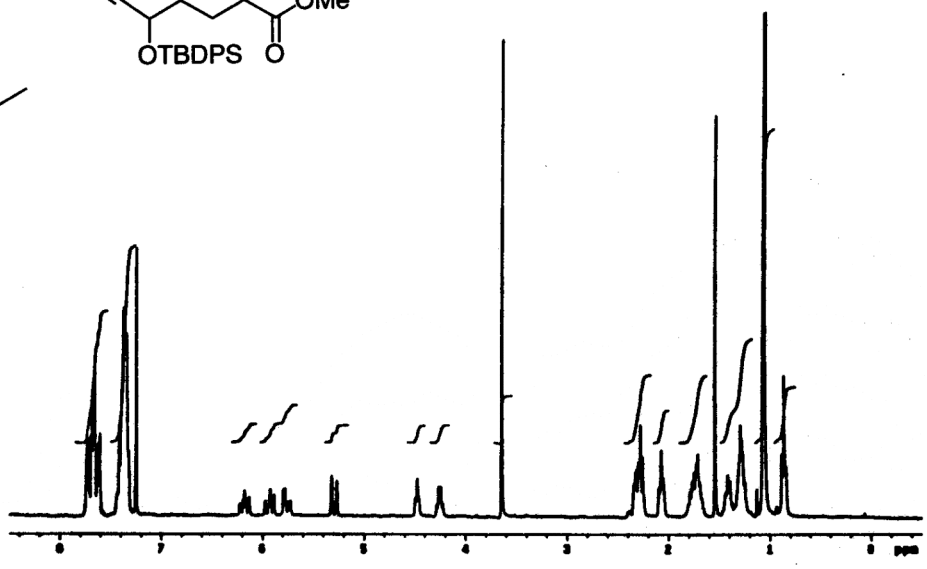


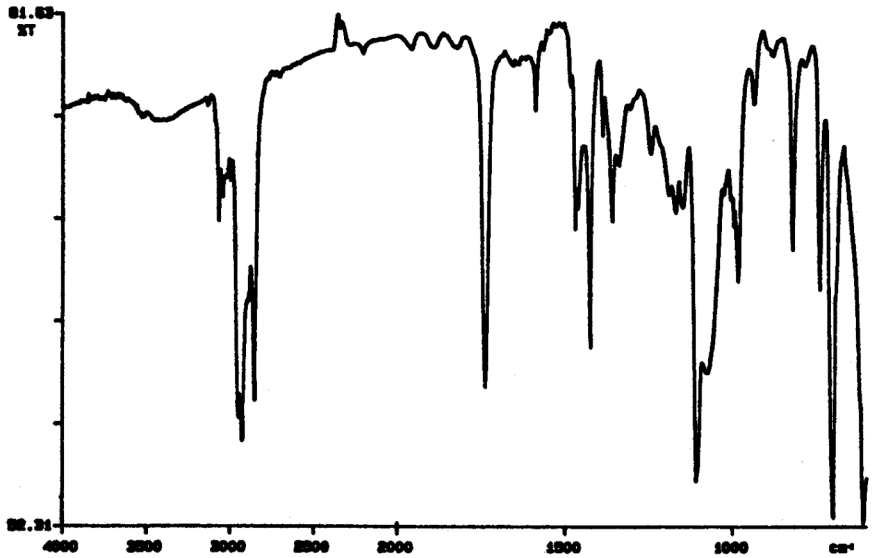




(8*E*,10*E*)-Methyl 5,12-Bis[(*t*-butyldiphenylsilyl)oxy]-8,10-eicosadiene-6,14-diynoate

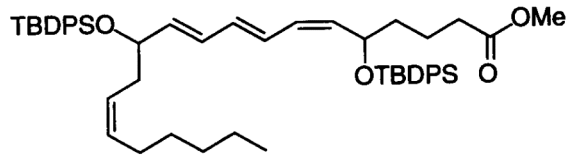


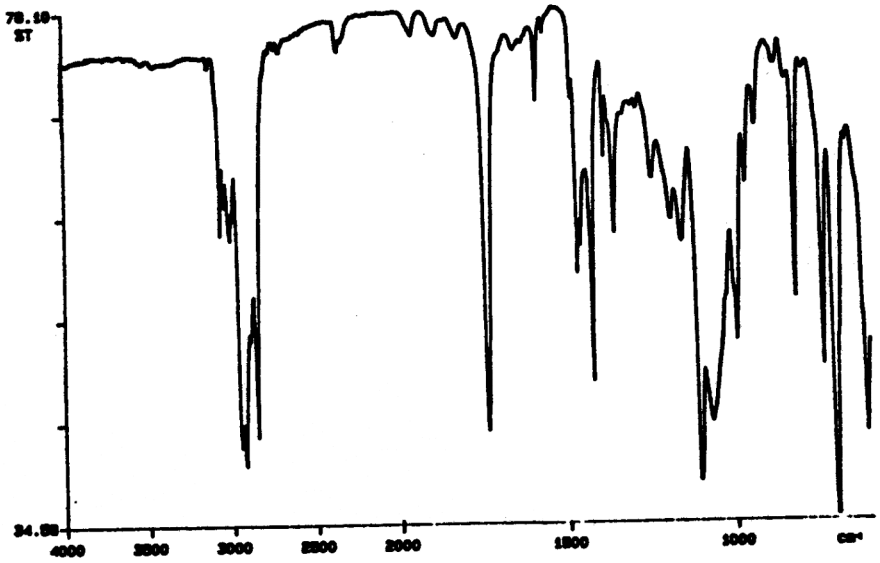




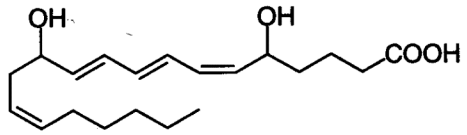
(6*Z*,8*E*,10*E*,14*Z*)-Methyl 5,12-Bis[(*t*-butyldiphenylsilyl)oxy]-6,8,10,14-eicosatetraenoate

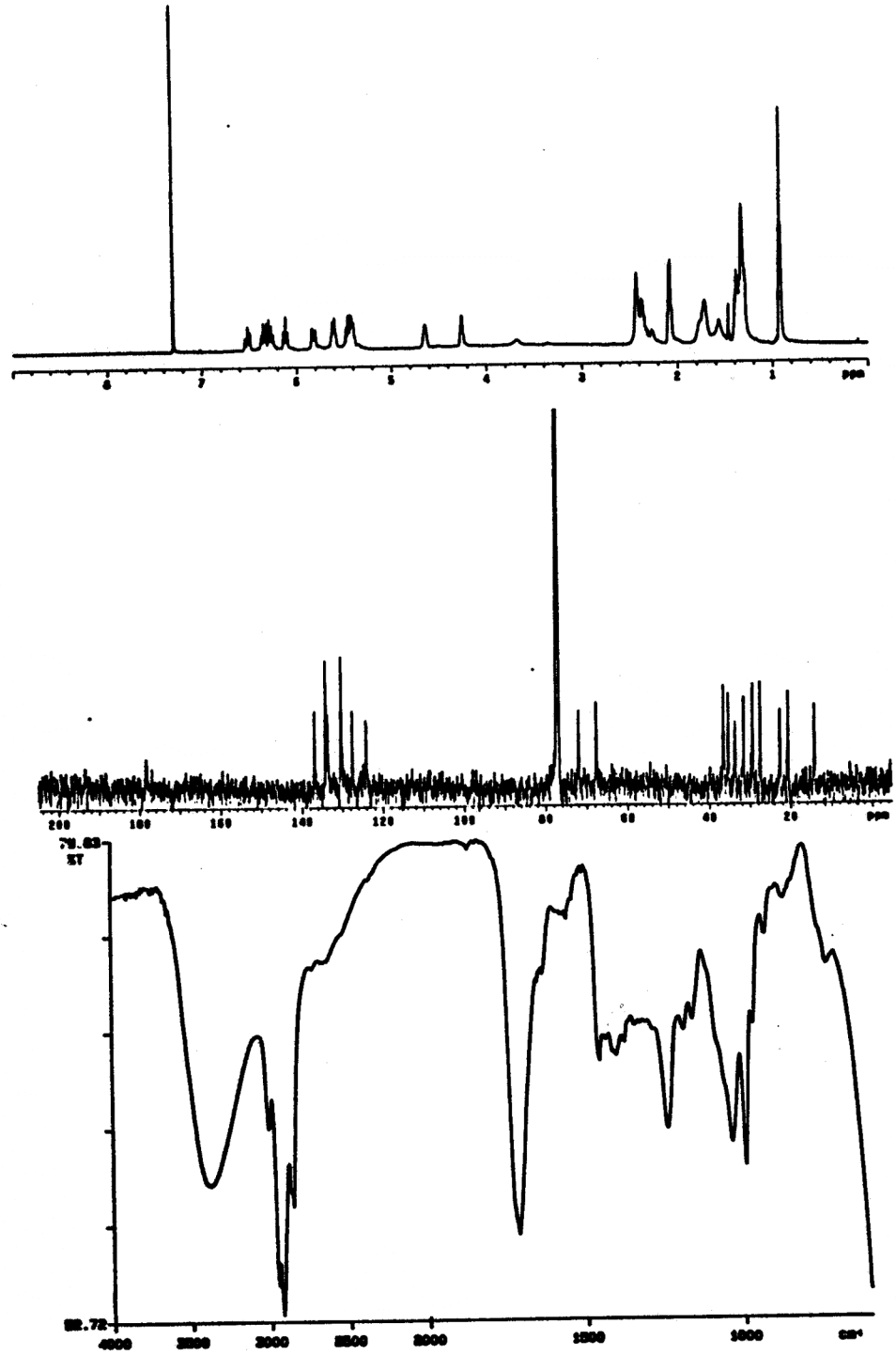
(4.32)





Leukotriene B_4 (**4.1**)





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