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Supporting Information

6,6-Dimethoxyhexanal³⁷ and 1-chloro-1-ethynylcyclohexane (**1m**)³⁸ were prepared according to the literature procedure. Propargylic alcohols used for the preparation of mesylates **1a-l** were prepared by the reaction of the corresponding aldehydes with lithium (trimethylsilyl)acetylide followed by desilylation according to the procedure reported previously.³⁹ Spectral data for new compounds are as follows.

5-Phenyl-1-pentyn-3-ol: The alcohol was prepared in 99% overall yield; ¹H-NMR δ 1.86 (1H, br s), 2.05 (2H, m), 2.52 (1H, d, $J = 2.1$ Hz), 2.82 (2H, t, $J = 7.8$ Hz), 4.38 (1H, dt, $J = 2.1$ and 6.6 Hz), 7.17-7.34 (5H, m); IR (liquid film) 3350 (br), 3290, 2120 (m), 1605, 1495, 1450, 1060, 1045, 1010, 750, 700 cm^{-1} ; MS, m/z (relative intensity) 160 (M^+ , 2), 142 (44), 141 (100), 118 (33), 105 (61), 91 (99). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found C, 82.65; H, 7.63.

8,8-Dimethoxy-1-octyn-3-ol: The alcohol was prepared in 79% overall yield; ¹H-NMR δ 1.32-1.82 (9H including OH, m), 2.45 (1H, d, $J = 2.2$ Hz), 3.30 (6H, s), 4.33-4.41 (2H, m, including t (1H, $J = 5.7$ Hz) at 4.36); IR (liquid film) 3420 (br), 3280, 2110 (m), 1735, 1245, 1130, 1045 cm^{-1} ; MS (CI), m/z (relative intensity) 155 ($MH^+ - CH_3OH$, 26), 123 (60), 93 (65), 75 (100). Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found C, 64.16; H, 9.65.

1-Phenyl-4-hexyn-3-ol. Propyne (1.54 g, 38.4 mmol) was bubbled into 20 mL of THF at -40 °C with stirring. To this was added BuLi (1.62 M in hexane) (13.6 mL, 22.0 mmol). To the resulting white suspension of the lithium acetylide was added HMPA (10 mL). After being stirred for 5 min, 3-phenylpropanal (2.68 g, 20 mmol) was added dropwise to the resulting solution of the acetylide. The mixture was allowed to warm to rt during 1 h, poured into 50 mL of water, and extracted three times with ether-hexane (1:1). The combined extracts were dried and concentrated. The residue was purified by flash chromatography (5-15% ethyl acetate in hexane) yielding 1.57 g (45%) of the alcohol; bp 90 °C/0.5 mmHg (Kugelrohr); ¹H-NMR δ 1.64 (1H (OH), br), 1.86 (3H, d, $J = 2.1$ Hz), 1.99 (2H, m), 2.78 (2H, t, $J = 7.9$ Hz), 4.34 (1H, qt, $J = 2.1$ and 6.5 Hz), 7.15-7.32 (5H, m); IR (liquid film) 3350 (br), 2235 (m), 1605, 1495, 1455, 1060, 1030, 1010, 750, 700 cm^{-1} ; MS, m/z (relative intensity) 174 (M^+ , 3), 159 (20), 156 (29), 141 (58), 105 (46), 91 (100); HRMS calcd for $C_{12}H_{14}O$; 174.1045, found; 174.1048. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found C, 82.69; H, 8.09.

Preparation of Propargylic Methanesulfonates. Preparation of **1h**, **1i**, and **1k** has been reported previously.³⁹ Other mesylates were prepared from the corresponding propargylic alcohols by a similar procedure.

5-Phenyl-1-pentyn-3-yl Methanesulfonate (1a): Isolated by flash chromatography (30% ether in hexane) in 99% yield; bp 130 °C/0.03 mmHg (Kugelrohr); ¹H-NMR δ 2.13-2.32 (2H, m), 2.76 (1H, d, $J = 2.2$ Hz), 2.77-2.92

(2H, m), 3.13 (3H, s), 5.16 (1H, dt, $J = 2.2$ and 6.5 Hz), 7.20-7.34 (5H, m); ^{13}C -NMR δ 139.8, 128.6, 128.4, 126.3, 79.1, 77.3, 70.4, 39.1, 37.1, 30.7; IR (liquid film) 3270, 2125, 1495, 1455, 1360, 1330, 1170, 970, 920, 845, 750, 700 cm^{-1} ; MS, m/z (relative intensity) 143 (M^+ - OMs, 9), 142 (53), 141 (100), 91 (64). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3\text{S}$: C, 60.48; H, 5.92; S, 13.45. Found C, 60.74; H, 6.04; S, 13.41.

1-Cyclohexyl-2-propynyl Methanesulfonate (1j): The mesylate was prepared from 1-cyclohexyl-2-propyn-1-ol⁴⁰ and isolated by flash chromatography (20-40% ether in hexane) in 93% yield; bp 120-125 $^\circ\text{C}/0.18$ mmHg (Kugelrohr); ^1H -NMR δ 1.04-1.33 (5H, m), 1.62-1.90 (6H, m), 2.69 (1H, d, $J = 2.2$ Hz), 3.09 (3H, s), 4.94 (1H, dd, $J = 2.2$ and 5.9 Hz); ^{13}C -NMR δ 78.4, 77.4, 75.5, 42.4, 39.0, 28.0, 27.6, 25.9, 25.43, 25.39; IR (liquid film) 3270, 2120, 1360, 1170, 950, 910 cm^{-1} ; MS (CI), m/z (relative intensity) 121 (MH^+ - $\text{CH}_3\text{SO}_3\text{H}$, 100), 93 (82), 83 (89), 81 (82). Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{O}_3\text{S}$: C, 55.53; H, 7.46; S, 14.82. Found C, 55.65; H, 7.55; S, 14.93.

8,8-Dimethoxy-1-octyn-3-yl Methanesulfonate (1i): Isolated by flash chromatography (60-80% ether in hexane) 80% yield; ^1H -NMR δ 1.31-1.64 (6H, m), 1.79-1.97 (2H, m), 2.69 (1H, d, $J = 2.1$ Hz), 3.10 (3H, s), 3.28 (6H, s), 4.33 (1H, t, $J = 5.7$ Hz), 5.13 (1H, dt, $J = 2.1$ and 6.5 Hz); ^{13}C -NMR δ 104.2, 79.2, 76.9, 71.1, 52.70, 52.68, 39.1, 35.4, 32.2, 24.4, 23.8; IR (liquid film) 3270, 2120, 1360, 1175, 1130, 1050, 970, 900 cm^{-1} .

1-Phenyl-4-hexyn-3-yl Methanesulfonate (1n): Isolated by flash chromatography (30-40% ether in hexane) in 95% yield; ^1H -NMR δ 1.92 (3H, d, $J = 2.1$ Hz), 2.09-2.28 (2H, m), 2.74-2.90 (2H, m), 3.11 (3H, s), 5.15 (1H, qt, $J = 2.1$ and 6.4 Hz), 7.18-7.34 (5H, m); ^{13}C -NMR δ 140.1, 128.49, 128.40, 126.2, 85.9, 74.8, 71.9, 39.1, 37.5, 30.9, 3.6; IR (liquid film) 2250, 1360, 1170, 970, 895, 750, 700 cm^{-1} .

2-Propynyl Methanesulfonate (1o): Isolated by flash chromatography (30-50% ether in pentane) in 94% yield; ^1H -NMR δ 2.69 (1H, t, $J = 2.5$ Hz), 3.12 (3H, s), 4.84 (2H, d, $J = 2.5$ Hz); IR (liquid film) 3280, 2130, 1350, 1175, 970, 930, 810, 530 cm^{-1} .

3-Chloro-5-phenyl-1-pentyne (1b): The chloride was prepared by treatment of 1-phenyl-4-pentyn-3-ol with PPh_3 (1.5 equiv) in CCl_4 at 90°C for 1.5 h and isolated by vacuum distillation in 52% yield; bp 100 $^\circ\text{C}/2$ mmHg (Kugelrohr); ^1H -NMR δ 2.27 (2H, m), 2.64 (1H, d, $J = 2.4$ Hz), 2.87 (2H, t, $J = 7.5$ Hz), 4.45 (1H, dt, $J = 2.4$ and 6.8 Hz); MS, m/z (relative intensity) 180 (M^+ , <1), 178 (M^+ , 1), 143 (42), 142 (40), 141 (50), 91 (100); HRMS calcd for $\text{C}_{11}\text{H}_{11}^{37}\text{Cl}$; 180.0520, found; 180.0536, calcd for $\text{C}_{11}\text{H}_{11}^{35}\text{Cl}$; 178.0550, found; 178.0557. Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{Cl}$: C, 73.95; H, 6.21. Found C, 74.17; H, 6.26.

Diethyl 5-Phenyl-1-pentyn-3-yl Phosphate (1c): The phosphate was prepared from 1-phenyl-1-pentyn-3-ol according to the literature procedures⁴¹

and isolated by flash chromatography (30-50 % ethyl acetate in hexane) in 80 % yield; $^1\text{H-NMR}$ δ 1.33 (6H, t, $J = 7.1$ Hz), 2.15 (2H, m), 2.60 (1H, d, $J = 2.2$ Hz), 2.81 (2H, t, $J = 8.0$ Hz), 4.13 (4H, m), 4.98 (1H, dq, $J = 2.1$ and 6.6 Hz), 7.2-7.3 (5H, m); $^{13}\text{C-NMR}$ δ 140.5, 128.4, 128.3, 126.1, 80.7 (d, $J_{\text{CP}} = 4.6$ Hz), 75.1, 67.0 (d, $J_{\text{CP}} = 5.6$ Hz), 66.99, 64.0 (d, $J_{\text{CP}} = 6.3$ Hz), 63.9 (d, $J_{\text{CP}} = 6.6$ Hz), 38.0 (d, $J_{\text{CP}} = 6.1$ Hz), , 30.8, 16.01 (d, $J_{\text{CP}} = 7.1$ Hz), 15.98 (d, $J_{\text{CP}} = 7.4$ Hz); IR (liquid film) 3250, 3175, 2080, 1250, 1010, 730, 680 cm^{-1} ; MS (CI), m/z (relative intensity) 297 (MH^+ , 6), 195 (6), 155 (100), 127 (19), 65 (8); HRMS (CI) calcd for $\text{C}_{15}\text{H}_{22}\text{PO}_4$ (MH^+); 297.1257, found; 297.1262.

5-Phenyl-1-pentyn-3-yl *N,N*-Diphenylcarbamate (1d): The carbamate was prepared from 5-phenyl-1-pentyn-3-ol according to the literature procedure⁴² in 81% yield; mp 69-72 °C (recrystallized from ether/hexane); $^1\text{H-NMR}$ δ 1.95-2.12 (2H, m), 2.52 (1H, d, $J = 1.6$ Hz), 2.56-2.77 (2H, m), 5.40 (1H, dt, $J = 1.6$ Hz), 7.11-7.38 (15H, m); $^{13}\text{C-NMR}$ δ 153.6, 142.3, 140.8, 128.9, 128.4, 128.3, 126.9, 126.2, 126.1, 81.0, 74.1, 65.0, 36.3, 31.0; IR (KBr disk) 3240, 2120, 1720, 1705, 1700, 1690, 735, 690 cm^{-1} ; MS, m/z (relative intensity) 355 (M^+ , 7), 264 (5), 213 (12), 196 (12), 168 (51), 91 (100); HRMS calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_2$; 355.1573, found; 355.1551. Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_2$: C, 81.10; H, 5.96. Found C, 80.85; H, 6.14.

5-Phenyl-1-pentyn-3-yl *N,N*-Diethylcarbamate (1e): The compound was prepared from 1-phenyl-4-pentyn-3-ol according to the literature procedure⁴² and isolated by flash chromatography (5-15 % ethyl acetate in hexane) in 81% yield; $^1\text{H-NMR}$ δ 1.13 (6H, t, $J = 7.0$ Hz), 2.11 (2H, m), 2.48 (1H, d, $J = 1.2$ Hz), 2.80 (1H, t, $J = 8.0$ Hz), 3.28 (4H, br), 5.36 (1H, dt, $J = 2.1$ and 6.5 Hz), 7.2-7.3 (5H, m); $^{13}\text{C-NMR}$ δ 154.7, 140.9, 128.4, 128.3, 126.0, 81.8, 73.4, 63.9, 41.9, 41.2, 36.6, 31.3, 14.1, 13.4; IR (liquid film) 3290, 3240, 2120, 1700, 1420, 1270, 1165, 1060, 765, 745, 695 cm^{-1} ; MS (CI), m/z (relative intensity) 260 (MH^+ , 6), 168 (7), 128 (8), 118 (70), 100 (59), 91 (100); HRMS calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_2$ (MH^+); 260.1652, found; 260.1650.

3-Methoxy-5-phenyl-1-pentyne (1f): The compound was prepared by treating 5-phenyl-1-pentyn-3-ol with sodium hydride (1.5 equiv) in THF at rt followed by the addition of iodomethane (1.5 equiv) and isolated by flash chromatography (1-10% ether in pentane) in 89% yield. $^1\text{H-NMR}$ δ 1.94-2.13 (2H, m), 2.48 (1H, d, $J = 1.9$ Hz), 2.79 (2H, t, $J = 7.8$ Hz), 3.42 (3H, s), 3.91 (1H, dt, $J = 1.9$ and 6.6 Hz), 7.17-7.33 (5H, m); IR (liquid film) 3280, 2110 (m), 1495, 1450, 1335, 1105, 745, 700 cm^{-1} ; MS, m/z (relative intensity) 174 (M^+ , 4), 173 (9), 159 (7), 142 (55), 141 (100), 105 (31), 91 (68); HRMS calcd for $\text{C}_{12}\text{H}_{14}\text{O}$; 174.1045, found; 174.1047. Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}$: C, 82.72; H, 8.10. Found C, 82.96; H, 8.10.

3-[(*tert*-Butyldimethylsilyl)oxy]-5-phenyl-1-pentyne (1g): The compound was prepared by treatment of 5-phenyl-1-pentyn-3-ol with imidazole (1.5 equiv) and *tert*-butylchlorodimethylsilane (1.2 equiv) in DMF at rt for 3 h

and isolated by flash chromatography (1-2% ethyl acetate in hexane) in 98% yield. $^1\text{H-NMR}$ δ 0.12 (3H, s), 0.15 (3H, s), 0.93 (9H, s), 2.01 (2H, td, $J = 6.3$ and 8.8 Hz), 2.43 (1H, d, $J = 2.1$ Hz), 2.70-2.86 (2H, m), 4.38 (1H, dt, $J = 2.1$ and 6.3 Hz), 7.16-7.33 (5H, m); $^{13}\text{C-NMR}$ δ 141.6, 128.43, 128.36, 125.9, 85.3, 72.4, 62.1, 40.2, 31.3, 25.8, 18.2, -4.5, -5.1; IR (liquid film) 3305, 2115 (m), 1250, 1095, 835, 775, 745, 695 cm^{-1} ; MS (CI), m/z (relative intensity) 275 (MH^+ , 0.8), 217 (40), 189 (92), 143 (80), 91 (70), 75 (100); HRMS (CI) calcd for $\text{C}_{17}\text{H}_{27}\text{OSi}$ (MH^+); 275.1832, found; 275.1809.

8,8-Dimethoxy-1-octyn-3-yl *N,N*-Diphenylcarbamate (1p): The compound was prepared from 8,8-dimethoxy-1-octyn-3-ol according to the literature procedure⁴² and isolated by flash chromatography (10-20% ethyl acetate in hexane) in 77 % yield; $^1\text{H-NMR}$ δ 1.30-1.76 (8H, m), 2.45 (1H, d, $J = 2.3$ Hz), 3.30 (6H, s), 4.31 (1H, t, $J = 5.7$ Hz), 5.38 (1H, dt, $J = 2.1$ and 6.5 Hz), 7.2-7.35 (10H, m); IR (liquid film) 3280, 2120, 1720, 1590, 1490, 1360, 1300, 1050, 1020, 760, 695 cm^{-1} ; MS, m/z (relative intensity) 381 (M^+ , 10), 214 (12), 196 (13), 168 (52), 137 (15), 91 (9), 75 (100); HRMS calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_4$; 381.1941, found; 381.1936.

1-Butyn-3-yl *N,N*-Diphenylcarbamate (1q): The compound was prepared from 1-butyn-3-ol according to the literature procedure⁴² in 83% yield; mp 106-107 $^{\circ}\text{C}$ (recrystallized from ether and hexane); $^1\text{H-NMR}$ δ 1.47 (3H, d, $J = 6.7$ Hz), 2.45 (1H, d, $J = 2.2$ Hz), 5.50 (1H, dq, $J = 2.1$ and 6.7 Hz), 7.2-7.35 (10H, m); IR (KBr disk) 3260, 2120, 1700, 1490, 1370, 1305, 760, 695 cm^{-1} ; MS, m/z (relative intensity) 265 (M^+ , 25), 220 (4), 206 (8), 196 (17), 168 (100), 77 (19), 65 (6); HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_2$; 265.1104, found; 265.1104.

6-Methyl-1-phenyl-3,4-octadiene (5c): (a 1:1 mixtures of diastereomers) $^1\text{H-NMR}$ δ 0.90 (3H, t, $J = 7.4$ Hz), 0.970 (1.5 H, d, $J = 6.8$ Hz), 0.974 (1.5H, d, $J = 6.8$ Hz), 1.23-1.43 (2H, m), 2.02 (1H, m), 2.32 (2H, m), 2.74 (2H, br t, $J = ca. 8$ Hz), 5.03-5.11 (1H, m), 5.13-5.22 (1H, m), 7.16-7.33 (5H, m); IR (liquid film) 1965, 1605, 1495, 1455, 875, 745, 730, 700 cm^{-1} ; MS, m/z (relative intensity) 200 (M^+ , 3), 171 (28), 144 (37), 129 (46), 91 (100); HRMS calcd for $\text{C}_{15}\text{H}_{20}$; 200.1566, found; 200.1579. Anal. Calcd for $\text{C}_{15}\text{H}_{20}$: C, 89.94; H, 10.06. Found C, 90.06; H, 10.24.

2,2-Dimethyl-7-phenyl-3,4-heptadiene (5d): $^1\text{H-NMR}$ δ 1.02 (9H, s), 2.32 (2H, m), 2.73 (2H, br t, $J = ca. 8$ Hz), 5.12 (1H, td, $J = 3.1$ and 6.3 Hz), 5.22 (1H, q, $J = 6.3$ Hz), 7.16-7.32 (5H, m); IR (liquid film) 1960, 1605, 1495, 1450, 1360, 875, 730, 695 cm^{-1} ; MS, m/z (relative intensity) 200 (M^+ , 9), 185 (23), 157 (38), 129 (43), 91 (74), 57 (100); HRMS calcd for $\text{C}_{12}\text{H}_{20}$; 200.1566, found; 200.1560. Anal. Calcd for $\text{C}_{15}\text{H}_{20}$: C, 89.94; H, 10.06. Found C, 90.14; H, 10.06.

2-Methyl-7-phenyl-1,3,4-heptatriene (5e): $^1\text{H-NMR}$ δ 1.70 (3H, br s), 2.30-2.47 (2H, m), 2.75 (2H, br t, $J = ca. 7.7$ Hz), 4.80 (1H, m), 4.89 (1H, m),

5.43 (1H, br q, $J = 6.4$ Hz), 5.91 (1H, td, $J = 3.0$ and 6.3 Hz), 7.16-7.32 (5H, m); IR (liquid film) 1945, 1450, 885, 745, 695 cm^{-1} ; MS, m/z (relative intensity) 184 (M^+ , 22), 169 (16), 156 (10), 93 (100), 91 (72), 84 (74); HRMS calcd for $C_{14}H_{16}$; 184.1253, found; 184.1254. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found C, 91.29; H, 8.97.

1,5-Diphenyl-1,2-pentadiene (5f): $^1\text{H-NMR}$ δ 2.38-2.58 (2H, m), 2.75-2.91 (2H, m), 5.61 (1H, q, $J = 6.5$ Hz), 6.14 (1H, td, $J = 3.0$ and 6.5 Hz), 7.14-7.34 (10H, m); IR (liquid film) 1950, 1600, 1495, 1450, 775, 745, 720, 695 cm^{-1} ; MS, m/z (relative intensity) 220 (M^+ , 56), 129 (100), 128 (74), 91 (86); HRMS calcd for $C_{17}H_{16}$; 220.1253, found; 220.1250. Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found C, 92.57; H, 7.28.

1-Phenyl-3,4-heptadiene (5g): $^1\text{H-NMR}$ δ 0.97 (3H, t, $J = 7.4$ Hz), 1.97 (2H, m), 2.31 (2H, m), 2.73 (2H, t, $J = 8.0$ Hz), 5.16 (1H, m), 7.15-7.3 (5H, m); IR (liquid film) 1965, 1605, 895, 745, 695 cm^{-1} ; MS, m/z (relative intensity) 172 (M^+ , 4), 157 (12), 143 (29), 129 (84), 91 (100); HRMS calcd for $C_{13}H_{16}$; 172.1252, found; 172.1250. Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found C, 90.70; H, 9.40.

5,6-Pentadecadiene (5h): $^1\text{H-NMR}$ δ 0.88 (3H, t, $J = 6.9$ Hz), 0.89 (3H, t, $J = 7.0$ Hz), 1.20-1.45 (16H, m), 1.92-2.02 (4H, m), 5.01-5.10 (2H, m); IR (liquid film) 1965, 1465, 1455, 870 cm^{-1} ; MS, m/z (relative intensity) 208 (M^+ , 0.2), 124 (3), 110 (43), 95 (31), 81 (76), 67 (92), 54 (100). Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found C, 86.28; H, 13.75.

2,6-Dimethyl-2,8,9-tetradecatriene (5i) (a 1:1 mixture of diastereomers): $^1\text{H-NMR}$ δ 0.90 (1.5H, t, $J = 7.2$ Hz), 0.91 (1.5H, d, $J = 6.7$ Hz), 1.09-1.23 (1H, m), 1.28-1.45 (5H, m), 1.47-1.61 (4H, m, including br s (3H) at 1.61), 1.68 (3H, d, $J = 0.9$ Hz), 1.77-2.06 (6H, m), 4.96-5.13 (3H, m); IR (liquid film) 1965, 1455, 1375, 875 cm^{-1} ; MS, m/z (relative intensity) 220 (M^+ , 3), 205 (3), 177 (22), 163 (8), 149 (11), 135 (14), 121 (22), 107 (40), 95 (76), 81 (74), 69 (100); HRMS calcd for $C_{16}H_{28}$; 220.2192, found; 220.2185. Anal. Calcd for $C_{16}H_{28}$: C, 87.19; H, 12.81. Found C, 87.22; H, 12.80.

1-Cyclohexyl-1,2-heptadiene (5j): $^1\text{H-NMR}$ δ 0.89 (3H, t, $J = 7.1$ Hz), 1.00-1.43 (9H, m), 1.57-1.78 (5H, m), 1.87-2.01 (3H, m), 5.05 (1H, tt, $J = 3.2$ and 6.4 Hz), 5.10 (1H, dq, $J = 3.0$ and 6.4 Hz); $^{13}\text{C-NMR}$ δ 202.7, 97.0, 91.8, 37.3, 33.19, 33.16, 31.5, 28.8, 26.3, 26.1, 22.2, 13.9; IR (liquid film) 1960, 1465, 1455, 1450, 890, 865 cm^{-1} ; MS, m/z (relative intensity) 178 (M^+ , 2), 136 (58), 121 (25), 107 (30), 93 (45), 81 (84), 67 (100); HRMS calcd for $C_{13}H_{22}$; 178.1722, found; 178.1722. Anal. Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44. Found C, 87.38; H, 12.48.

12-[(*tert*-Butyldimethylsilyl)oxy]-5,6-dodecadiene (5k): $^1\text{H-NMR}$ δ 0.05 (6H, s), 0.87-0.93 (12H, m, including s (9H) at 0.89), 1.26-1.48 (8H, m), 1.52 (2H, quint, $J = 6.9$ Hz), 1.92-2.02 (4H, m), 3.60 (2H, t, $J = 6.6$ Hz), 5.02-5.10 (2H, m); $^{13}\text{C-NMR}$ δ 203.8, 90.9, 90.7, 63.3, 32.7, 31.4, 29.0, 28.7, 26.0, 25.3,

22.2, 18.4, 13.9, -5.3; IR (liquid film) 1965, 1255, 1105, 835, 775 cm^{-1} ; MS (CI), m/z (relative intensity) 297 (MH^+ , 6), 239 (19), 163 (22), 109 (53), 95 (66), 75 (100); HRMS (CI) calcd for $\text{C}_{18}\text{H}_{37}\text{OSi}$ (MH^+); 297.2615, found; 297.2617. Anal. Calcd for $\text{C}_{18}\text{H}_{36}\text{OSi}$: C, 72.90; H, 12.24. Found C, 73.05; H, 12.40.

12,12-Dimethoxy-5,6-dodecadiene (5l): $^1\text{H-NMR}$ δ 0.89 (3H, br t, $J = ca. 7$ Hz), 1.27-1.48 (8H, m), 1.57-1.64 (2H, m), 1.92-2.04 (4H, m), 3.31 (6H, s), 4.36 (1H, t, $J = 5.7$ Hz), 5.01-5.11 (2H, m); $^{13}\text{C-NMR}$ δ 203.8, 104.4, 91.0, 90.6, 52.6, 52.5, 32.3, 31.3, 29.0, 28.9, 28.6, 24.1, 22.1, 13.9; IR (liquid film) 1965, 1130, 1075, 1050 cm^{-1} ; MS (CI), m/z (relative intensity) 195 (MH^+ -MeOH, 80), 163 (97), 151 (58), 121 (57), 107 (56), 95 (64), 75 (100). Anal. Calcd for $\text{C}_{14}\text{H}_{26}\text{O}_2$: C, 74.29; H, 11.58. Found C, 74.27; H, 11.76.

(1-Hexenylidene)cyclohexane (5m): bp 105 $^\circ\text{C}/15$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.89 (3H, m), 1.27-1.42 (4H, m), 1.45-1.65 (6H, m), 1.91-1.99 (2H, m), 2.01-2.15 (4H, m), 4.94 (1H, sept t, $J = 2.1$ and 4.3 Hz); IR (liquid film) 1965, 1465, 1455, 1445 cm^{-1} ; MS, m/z (relative intensity) 164 (M^+ , 20), 135 (16), 122 (70), 107 (60), 93 (62), 79 (100); HRMS calcd for $\text{C}_{12}\text{H}_{20}$; 164.1566, found; 164.1564. Anal. Calcd for $\text{C}_{12}\text{H}_{20}$: C, 87.73; H, 12.27. Found C, 87.48; H, 12.41.

The spectral data of the minor products in Table 2 are as follows.

1-Phenyl-4-nonyne (7a): $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.92 (3H, t, $J = 7.1$ Hz), 1.36-1.54 (4H, m), 1.80 (2H, br quint, $J = ca. 7$ Hz), 2.14-2.20 (4H, br t, $J = ca. 7$ Hz), 2.72 (2H, t, $J = 7.6$ Hz), 7.16-7.32 (5H, m); IR (liquid film) 1495 (s), 1450 (s), 745 (s), 700 cm^{-1} (s); MS, m/z (relative intensity) 200 (M^+ , 5), 157 (19), 143 (38), 129 (31), 104 (100), 91 (58); HRMS calcd for $\text{C}_{15}\text{H}_{20}$; 200.1566, found; 200.1562.

3-Methyl-8-phenyl-4-octyne (7c): $^1\text{H-NMR}$ δ 1.00 (3H, t, $J = 7.4$ Hz), 1.15 (3H, d, $J = 6.9$ Hz), 1.34-1.52 (2H, m), 1.80 (2H, tt, $J = 7.0$ and 7.8 Hz), 2.19 (2H, dt, $J = 2.2$ and 7.0 Hz), 2.35 (1H, m), 2.73 (2H, t, $J = 7.8$ Hz), 7.16-7.32 (5H, m); IR (liquid film) 1495, 1450, 745, 700 cm^{-1} ; MS, m/z (relative intensity) 200 (M^+ , 10), 171 (37), 143 (43), 129 (40), 104 (100), 91 (99); HRMS calcd for $\text{C}_{15}\text{H}_{20}$; 200.1566, found; 200.1563.

2,2-Dimethyl-7-phenyl-3-heptyne (7d): $^1\text{H-NMR}$ δ 1.22 (9H, s), 1.79 (2H, br quint, $J = ca. 7$ Hz), 2.16 (2H, t, $J = 7.0$ Hz), 2.71 (2H, t, $J = 7.8$ Hz), 7.16-7.32 (5H, m); IR (liquid film) 1450, 1265, 1205, 745, 695 cm^{-1} ; MS, m/z (relative intensity) 200 (M^+ , 4), 185 (19), 157 (14), 143 (28), 129 (25), 104 (100), 91 (77); HRMS calcd for $\text{C}_{15}\text{H}_{20}$; 200.1566, found; 200.1577.

5-Phenyl-1,2-pentadiene (11): $^1\text{H-NMR}$ δ 2.31 (2H, m), 2.73 (2H, br t, $J = ca. 8$ Hz), 4.67 (2H, td, $J = 3.3$ and 6.7 Hz), 5.15 (1H, quint, $J = 6.7$ Hz), 7.16-7.32 (5H, m); IR (liquid film) 1955, 1605, 1495, 1455, 850, 745, 700 cm^{-1} ; MS,

m/z (relative intensity) 144 (M⁺, 20), 143 (14), 129 (65), 91 (100); HRMS calcd for C₁₁H₁₂; 144.0939, found; 144.0937.

5-Phenyl-1-pentyne (12): ¹H-NMR δ 1.85 (2H, br quint, *J* = ca. 7 Hz), 2.00 (1H, t, *J* = 2.6 Hz), 2.21 (2H, dt, *J* = 2.6 and 7.0 Hz), 2.74 (2H, t, *J* = 7.6 Hz), 7.16-7.33 (5H, m); IR (liquid film) 3300, 2120 (m), 1605, 1495, 1455, 745, 700, 635 cm⁻¹; MS, m/z (relative intensity) 144 (M⁺, 8), 129 (18), 104 (32), 91 (29), 86 (63), 84 (100); HRMS calcd for C₁₁H₁₂; 144.0939, found; 144.0938.

3-(1,1-Dimethylethyl)-5-phenyl-1-pentyne (13): ¹H-NMR δ 1.00 (9H, s), 1.61 (1H, dddd, *J* = 4.7, 9.7, 11.9, and 12.8 Hz), 1.83 (1H, dddd, *J* = 3.4, 7.3, 9.8, and 12.8 Hz), 2.07 (1H, ddd, *J* = 2.5, 3.4, and 11.9 Hz), 2.16 (1H, d, *J* = 2.5 Hz), 2.62 (1H, ddd, *J* = 7.3, 9.7, and 13.6 Hz), 3.00 (1H, ddd, *J* = 4.7, 9.8, and 13.6 Hz), 7.16-7.33 (5H, m); IR (liquid film) 3310, 2110 (m), 1370, 1230, 750, 700, 630 cm⁻¹; MS, m/z (relative intensity) 200 (M⁺, 1), 185 (8), 157 (10), 143 (11), 129 (19), 91 (35), 57 (100); HRMS (CI) calcd for C₁₅H₂₁ (MH⁺); 201.1644, found; 201.1637.

(3*R,4*S**)-2-Methyl-4-octyl-5-decyn-3-ol (anti-14c):** bp 70-80 °C/0.24 mmHg (Kugelrohr); ¹H-NMR δ 0.87 (3H, t, *J* = 7.0 Hz), 0.89 (3H, t, *J* = 7.2 Hz), 0.90 (3H, d, *J* = 6.7 Hz), 0.97 (3H, t, *J* = 6.7 Hz), 1.20-1.59 (18H, m), 1.67 (1H (OH), br d, *J* = 8 Hz), 1.76 (1H, octet, *J* = 6.8 Hz), 2.17 (2H, dt, *J* = 2.2 and 6.9 Hz), 2.52 (1H, m), 3.02 (1H, br dt, *J* = 4 and 8 Hz); ¹³C-NMR δ 84.5, 79.1, 78.4, 36.5, 32.8, 32.4, 31.9, 31.2, 29.5, 29.4, 29.3, 27.6, 22.7, 21.9, 19.5, 18.4, 18.1, 14.1, 13.6; IR (liquid film) 3570 (br), 3480 (br), 1465, 1460, 1380, 995 cm⁻¹; MS (CI), m/z (relative intensity) 281 (MH⁺, 1), 263 (6), 237 (4), 225 (4), 166 (9), 137 (9), 123 (11), 110 (100); HRMS (CI) calcd for C₁₉H₃₇O (MH⁺); 281.2846, found; 281.2840. Anal. Calcd for C₁₉H₃₆O: C, 81.36; H, 12.94. Found C, 81.11; H, 13.15.

(3*S,4*S**)-2,2-Dimethyl-4-octyl-5-decyn-3-ol (anti-14d):** bp 80-90 °C/0.20 mmHg (Kugelrohr); ¹H-NMR δ 0.87 (3H, t, *J* = 6.9 Hz), 0.89 (3H, t, *J* = 7.3 Hz), 0.92 (9H, s), 1.20-1.51 (17H, m), 1.61 (1H, m), 2.06 (1H (OH), d, *J* = 10.2 Hz), 2.17 (2H, dt, *J* = 2.2 and 6.9 Hz), 2.61 (1H, m), 2.99 (1H, d, *J* = 10.2 Hz); ¹³C-NMR δ 86.4, 80.0, 79.1, 35.9, 35.6, 34.2, 31.9, 31.0, 29.5, 29.4, 29.3, 27.5, 26.3, 22.7, 22.0, 18.5, 14.1, 13.6; IR (liquid film) 3540, 1465, 1460, 1075 cm⁻¹; MS (CI), m/z (relative intensity) 295 (MH⁺, 2), 277 (19), 207 (8), 166 (9), 137 (13), 123 (17), 110 (100); HRMS (CI) calcd for C₂₀H₃₉O (MH⁺); 295.3003, found; 295.2999. Anal. Calcd for C₂₀H₃₈O: C, 81.56; H, 13.00. Found C, 81.41; H, 13.00.

2-Octyl-1-phenyl-3-octyn-1-ol (14e) (a 52:48 mixture of diastereomers): bp 135-145 °C/0.17 mmHg (Kugelrohr); ¹H-NMR δ 0.86 (3H for *anti*- and *syn*-isomers, t, *J* = 7.0 Hz), 0.87 (3H for *anti*-isomer, t, *J* = 7.2 Hz), 0.90 (3H for *syn*-isomer, t, *J* = 7.2 Hz), 1.18-1.54 (18H for *anti*- and *syn*-isomers, m), 2.14 (2H for *syn*-isomer, dt, *J* = 2.2 and 6.9 Hz), 2.21 (2H for *anti*-isomer, dt, *J* =

2.2 and 7.0 Hz), 2.27 (1H for *syn*-isomer, br d, $J = 3.8$ Hz), 2.63 (1H for *anti*-isomer, br d, $J = 4.2$ Hz), 2.65 (1H for *anti*-isomer, m), 2.75 (1H for *syn*-isomer, m), 4.47 (1H for *anti*-isomer, dd, $J = 3.9$ and 6.8 Hz), 4.69 (1H for *syn*-isomer, dd, $J = 3.6$ and 5.3 Hz), 7.24-7.38 (5H for *anti*- and *syn*-isomers, m); IR (liquid film) 3530 (sh), 3440 (br), 1465, 1455, 1040, 1025, 760, 700 cm^{-1} ; MS (CI), m/z (relative intensity) 315 (MH^+ , 1), 314 (1), 297 (9), 216 (4), 199 (3), 166 (8), 107 (100); HRMS (CI) calcd for $\text{C}_{22}\text{H}_{35}\text{O}$ (MH^+); 315.2690, found; 315.2688. Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{O}$: C, 84.02; H, 10.90. Found C, 83.94; H, 11.12.

(3R*,4S*)-4-Cyclohexyl-5-decyn-3-ol (anti-14f): bp 80-90 °C/0.20 mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.90 (3H, t, $J = 7.2$ Hz), 0.93 (3H, t, $J = 7.4$ Hz), 0.98-1.31 (5H, m), 1.33-1.58 (7H, m, including quint (2H, $J = 7.4$ Hz) at 1.53), 1.60-1.78 (5H, m), 1.91 (1H, br d, $J = 12.5$ Hz), 2.15-2.22 (3H, m), 3.51 (1H, m); $^{13}\text{C-NMR}$ δ 85.5, 77.8, 71.6, 45.2, 38.7, 31.6, 31.2, 30.6, 29.0, 26.5, 26.3, 22.0, 18.4, 13.6, 10.2; IR (liquid film) 3550 (br), 3460 (br), 1450, 1105, 970 cm^{-1} ; MS (CI), m/z (relative intensity) 237 (MH^+ , 3), 219 (35), 177 (10), 163 (10), 136 (100), 121 (42); HRMS (CI) calcd for $\text{C}_{16}\text{H}_{29}\text{O}$ (MH^+); 237.2220, found; 237.2220. Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{O}$: C, 81.29; H, 11.94. Found C, 81.48; H, 12.18.

(3R*,4S*)-4-Cyclohexyl-2-methyl-5-decyn-3-ol (anti-14g): bp 80 °C/0.15 mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.88 (3H, d, $J = 6.7$ Hz), 0.90 (3H, t, $J = 7.2$ Hz), 0.95-1.31 (8H, m, including δ (3H, $J = 6.7$ Hz) at 0.96), 1.33-1.53 (5H, m), 1.58-1.83 (6H, m, including octet (1H, $J = 6.9$ Hz) at 1.75), 1.93 (1H, br d, $J = 12.3$ Hz), 2.18 (2H, dt, $J = 2.2$ and 6.9 Hz), 2.31 (1H, br qd, $J = ca. 2.5$ and 7.6 Hz), 3.22 (1H, br dt, $J = ca. 3$ and 7.6 Hz); $^{13}\text{C-NMR}$ δ 85.6, 77.9, 75.2, 42.9, 39.0, 32.6, 31.5, 31.2, 30.8, 26.5, 26.3, 22.0, 19.5, 18.4, 18.1, 13.6; IR (liquid film) 3540 (br), 3500 (br), 1465, 1450, 1040 cm^{-1} ; MS (CI), m/z (relative intensity) 251 (MH^+ , 2), 233 (11), 207 (8), 195 (6), 177 (15), 151 (13), 136 (100), 81 (84); HRMS (CI) calcd for $\text{C}_{17}\text{H}_{31}\text{O}$ (MH^+); 251.2376, found; 251.2370.

(1S*,2S*)-2-Cyclohexyl-1-phenyl-3-octyn-1-ol (anti-14h): bp 95-105 °C/0.14 mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.91 (3H, t, $J = 7.2$ Hz), 1.08-1.32 (5H, m), 1.32-1.54 (4H, m), 1.55-1.76 (5H, m), 1.86 (1H, m), 2.22 (2H, dt, $J = 2.3$ and 6.8 Hz), 2.53 (1H, m), 2.61 (1H (OH), d, $J = 4.7$ Hz), 4.67 (1H, dd, $J = 4.7$ and 6.7 Hz), 7.24-7.36 (5H, m); $^{13}\text{C-NMR}$ δ 142.6, 128.2, 127.6, 126.4, 86.4, 77.7, 73.3, 48.4, 38.2, 32.1, 31.1, 29.1, 26.3, 26.2, 26.0, 21.9, 18.5, 13.6; IR (liquid film) 3540 (br), 3450 (br), 1450, 755, 700 cm^{-1} ; MS (CI), m/z (relative intensity) 285 (MH^+ , 1), 267 (27), 185 (17), 171 (11), 136 (92), 107 (100); HRMS (CI) calcd for $\text{C}_{20}\text{H}_{29}\text{O}$ (MH^+); 285.2220, found; 285.2200. Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{O}$: C, 84.45; H, 9.92. Found C, 84.66; H, 9.92.

(1R*,2S*)-2-Cyclohexyl-1-phenyl-3-octyn-1-ol (syn-14h): bp 95-100 °C/0.14 mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.84 (3H, t, $J = 7.2$ Hz), 1.08-1.41 (9H, m), 1.55-1.90 (6H, m), 2.07 (2H, dt, $J = 2.4$ and 6.9 Hz), 2.09 (1H (OH), br

d, $J = ca.$ 3 Hz), 2.64 (1H, m), 4.68 (1H, dd, $J = 3.6$ and 8.2 Hz), 7.24-7.41 (5H, m); $^{13}\text{C-NMR}$ δ 143.0, 128.0, 127.6, 126.9, 85.4, 78.0, 74.1, 46.6, 36.9, 32.3, 31.0, 28.2, 26.5, 26.1, 21.8, 18.3, 13.6; IR (liquid film) 3425 (br), 1450, 1035, 1025, 755, 700 cm^{-1} ; MS (CI), m/z (relative intensity) 285 (MH^+ , 2), 283 (4), 267 (32), 185 (22), 171 (11), 136 (69), 107 (100); HRMS (CI) calcd for $\text{C}_{20}\text{H}_{29}\text{O}$ (MH^+); 285.2220, found; 285.2218. Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{O}$: C, 84.45; H, 9.92. Found C, 84.37; H, 9.88.

(3R*,4S*)-4-Methyl-1-phenyl-5-decyn-3-ol (anti-14i): bp 88-93 $^{\circ}\text{C}/0.14$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.90 (3H, t, $J = 7.1$ Hz), 1.17 (3H, d, $J = 7.0$ Hz), 1.33-1.52 (4H, m), 1.78-1.91 (3H m, including OH), 2.17 (2H, dt, $J = 2.2$ and 6.9 Hz), 2.51 (1H, tdq, $J = 2.2, 4.7,$ and 7.0 Hz), 2.68 (1H, ddd, $J = 7.3, 9.1,$ and 13.8 Hz), 2.83 (1H, ddd, $J = 6.5, 8.7,$ and 13.8 Hz), 3.37 (1H, br quint, $J = ca.$ 5 Hz), 7.15-7.31 (5H, m); $^{13}\text{C-NMR}$ δ 142.1, 128.4, 128.3, 125.7, 83.8, 80.2, 73.8, 37.0, 33.4, 32.1, 31.1, 21.9, 18.4, 17.9, 13.6; IR (liquid film) 3550 (br), 3450 (br), 1455, 750, 700 cm^{-1} ; MS (CI), m/z (relative intensity) 245 (MH^+ , 3), 227 (12), 199 (4), 185 (4), 171 (12), 117 (26), 91 (76), 68 (100); HRMS (CI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}$ (MH^+); 245.1907, found; 245.1905. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}$: C, 83.55; H, 9.90. Found C, 83.81; H, 9.68.

(3S*,4S*)-4-Methyl-1-phenyl-5-decyn-3-ol (syn-14i): $^1\text{H-NMR}$ δ 0.89 (3H, t, $J = 7.2$ Hz), 1.11 (3H, d, $J = 7.0$ Hz), 1.32-1.51 (4H, m), 1.63 (1H (OH), br s), 1.78 (1H, dtd, $J = 5.4, 9.5,$ and 13.9 Hz), 1.88 (1H, dddd, $J = 3.3, 7.0, 9.8,$ and 13.9 Hz), 2.15 (2H, dt, $J = 2.2$ and 6.9 Hz), 2.58 (1H, tdq, $J = 2.2, 5.1,$ and 7.0 Hz), 2.66 (1H, ddd, $J = 7.0, 9.6,$ and 13.8 Hz), 2.88 (1H, ddd, $J = 5.4, 9.8,$ and 13.8 Hz), 3.52 (1H, ddd, $J = 3.3, 5.1,$ and 9.2 Hz), 7.15-7.31 (5H, m); $^{13}\text{C-NMR}$ δ 142.2, 128.45, 128.36, 125.8, 83.0, 81.3, 73.7, 35.2, 33.1, 32.2, 31.1, 21.9, 18.4, 16.1, 13.6; IR (liquid film) 3550 (sh), 3400 (br), 1455, 745, 700 cm^{-1} ; MS (CI), m/z (relative intensity) 245 (MH^+ , 0.3), 227 (10), 199 (9), 171 (17), 157 (17), 143 (20), 133 (22), 117 (28), 91 (81), 68 (100); HRMS (CI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}$ (MH^+); 245.1907, found; 245.1903.

(3R*,4S*)-2,4-Dimethyl-5-decyn-3-ol (anti-14j): bp 85-90 $^{\circ}\text{C}/9$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.89 (3H, t, $J = 7.2$ Hz), 0.92 (3H, d, $J = 6.7$ Hz), 0.95 (3H, d, $J = 6.7$ Hz), 1.17 (3H, d, $J = 7.0$ Hz), 1.31-1.51 (4H, m), 1.69 (1H (OH), br d, $J = ca.$ 8 Hz), 1.74 (1H, octet, $J = 6.7$ Hz), 2.16 (2H, dt, $J = 2.2$ and 6.9 Hz), 2.66 (1H, tdq, $J = 2.2, 4.7,$ and 7.0 Hz), 2.97 (1H, br dt, $J = ca.$ 4.5 and 7 Hz); $^{13}\text{C-NMR}$ δ 83.5, 80.2, 79.7, 32.0, 31.1, 30.6, 21.9, 19.6, 18.6, 18.4, 17.7, 13.6; IR (liquid film) 3555 (br), 3475 (br), 1465, 1460, 1050, 975 cm^{-1} ; MS, m/z (relative intensity) 182 (M^+ , 3), 167 (7), 139 (7), 95 (20), 81 (52), 68 (100); HRMS calcd for $\text{C}_{12}\text{H}_{22}\text{O}$; 182.1672, found; 182.1674. Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}$: C, 79.06; H, 12.16. Found C, 79.04; H, 12.33.

(3S*,4S*)-2,4-Dimethyl-5-decyn-3-ol (syn-14j): $^1\text{H-NMR}$ δ 0.892 (3H, d, $J = 6.9$ Hz), 0.893 (3H, t, $J = 7.2$ Hz), 0.95 (3H, d, $J = 6.7$ Hz), 1.14 (3H, d, $J = 6.9$ Hz), 1.32-1.51 (4H, m), 1.59 (1H (OH), br s), 1.90 (1H, octet, $J = 6.7$

Hz), 2.15 (2H, dt, $J = 2.2$ and 6.9 Hz), 2.58 (1H, tdq, $J = 2.2, 5.7,$ and 6.9 Hz), 3.25 (1H, t, $J = 5.9$ Hz); $^{13}\text{C-NMR}$ δ 82.4, 82.3, 79.2, 31.1, 30.3, 30.1, 21.9, 19.5, 18.4, 17.2, 15.5, 13.6; IR (liquid film) 3440 (br), 1470, 1460, 990 cm^{-1} ; MS, m/z (relative intensity) 182 (M^+ , 0.7), 180 (2), 165 (12), 139 (22), 95 (75), 81 (98), 73 (99), 67 (100); HRMS calcd for $\text{C}_{12}\text{H}_{22}\text{O}$; 182.1672, found; 182.1662.

(3S*,4S*)-2,2,4-Trimethyl-5-decyn-3-ol (anti-14k): bp 88-90 $^{\circ}\text{C}/8.5$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.89 (3H, t, $J = 7.2$ Hz), 0.93 (9H, s), 1.24 (3H, d, $J = 7.1$ Hz), 1.31-1.50 (4H, m), 1.97 (1H (OH), d, $J = 10$ Hz), 2.15 (2H, dt, $J = 2.2$ and 6.9 Hz), 2.76 (1H, qq, $J = 2$ and 7.1 Hz), 2.93 (1H, dd, $J = 1.1$ and 10 Hz); $^{13}\text{C-NMR}$ δ 85.5, 81.5, 80.2, 35.9, 30.9, 28.3, 26.3, 22.0, 21.8, 18.4, 13.6; IR (liquid film) 3540 (br), 3500 (sh), 1460, 1365, 1090, 970 cm^{-1} ; MS, m/z (relative intensity) 196 (M^+ , 4), 181 (3), 139 (11), 87 (33), 81 (42), 68 (100); HRMS calcd for $\text{C}_{13}\text{H}_{24}\text{O}$; 196.1828, found; 196.1820.

(3R*,4S*)-2,4-Dimethyl-5-heptyn-3-ol (anti-14l): bp 70-75 $^{\circ}\text{C}/23$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.91 (3H, d, $J = 6.8$ Hz), 0.95 (3H, d, $J = 6.7$ Hz), 1.17 (3H, d, $J = 7.0$ Hz), 1.70 (1H (OH), br s), 1.74 (1H, octet, $J = 6.8$ Hz), 1.79 (3H, d, $J = 2.4$ Hz), 2.63 (1H, qdq, $J = 2.4, 4.6,$ and 7.0 Hz), 2.96 (1H, br dd, $J = 4.4$ and 6.4 Hz); $^{13}\text{C-NMR}$ δ 79.8, 79.4, 78.7, 32.0, 30.5, 19.6, 18.6, 17.7, 3.5; IR (liquid film) 3450 (br), 1460, 1390, 1010, 975 cm^{-1} ; MS, m/z (relative intensity) 140 (M^+ , 13), 125 (27), 123 (44), 97 (25), 83 (20), 73 (25), 68 (95), 67 (74), 43 (100); HRMS calcd for $\text{C}_9\text{H}_{16}\text{O}$; 140.1202, found; 140.1200.

(3R*,4S*)-2,4,7-Trimethyl-5-nonyn-3-ol (anti-14m): bp 65 $^{\circ}\text{C}/7.0$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.92 (3H, d, $J = 6.7$ Hz), 0.951 (3H, t, $J = 7.4$ Hz), 0.955 (3H, d, $J = 6.7$ Hz), 1.12 (3H, d, $J = 7.0$ Hz), 1.17 (3H, d, $J = 7.0$ Hz), 1.30-1.51 (2H, m), 1.68 (1H (OH), s), 1.74 (1H, octet, $J = 6.7$ Hz), 2.33 (1H, br δ sext, $J = 2$ and 7 Hz), 2.67 (1H, ddq, $J = 2.1, 4.5,$ and 7.0 Hz), 2.98 (1H, dd, $J = 4.4$ and 6.6 Hz); $^{13}\text{C-NMR}$ δ 88.1, 80.4, 79.6, 32.0, 30.5, 30.1, 27.5, 21.1, 19.6, 18.7, 17.6, 11.7; IR (liquid film) 3565 (br), 3545 (br), 3480 (br), 1460, 1455, 1380 cm^{-1} ; MS, m/z (relative intensity) 182 (M^+ , 1), 180 (2), 167 (5), 165 (6), 151 (11), 95 (100), 81 (98); HRMS calcd for $\text{C}_{12}\text{H}_{22}\text{O}$; 182.1672, found; 182.1669. Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}$: C, 79.06; H, 12.16. Found C, 78.97; H, 12.29.

(3R*,4S*)-2,4,7,7-Tetramethyl-5-octyn-3-ol (anti-14n): bp 65 $^{\circ}\text{C}/8$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.92 (3H, d, $J = 6.8$ Hz), 0.94 (3H, d, $J = 6.8$ Hz), 1.15 (3H, d, $J = 7.0$ Hz), 1.18 (9H, s), 1.70 (1H (OH), s), 1.72 (1H, octet, $J = 6.7$ Hz), 2.63 (1H, dq, $J = 4.5$ and 7.0 Hz), 2.98 (1H, dd, $J = 4.5$ and 6.4 Hz); $^{13}\text{C-NMR}$ δ 92.4, 79.5, 78.5, 32.0, 31.3, 30.5, 27.4, 19.6, 18.6, 17.5; IR (liquid film) 3560 (br), 3490 (br), 1460, 1365, 1000 cm^{-1} ; MS, m/z (relative intensity) 182 (M^+ , 0.9), 180 (4), 165 (20), 137 (6), 121 (4), 110 (74), 95 (90), 57 (100); HRMS calcd for $\text{C}_{12}\text{H}_{22}\text{O}$; 182.1672, found; 182.1720. Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}$: C, 79.06; H, 12.16. Found C, 78.62; H, 12.33.

(3R*,4S*)-2,4-Dimethyl-6-phenyl-5-hexyn-3-ol (anti-14o): bp 85-90 °C/0.25 mmHg (Kugelrohr); mp 53.5-54.0 °C; ¹H-NMR δ 0.98 (3H, d, *J* = 6.8 Hz), 1.01 (3H, d, *J* = 6.7 Hz), 1.32 (3H, d, *J* = 7.0 Hz), 1.72 (1H (OH), br s), 1.86 (1H, octet, *J* = 6.8 Hz), 2.93 (1H, dq, *J* = 4.3 and 7.0 Hz), 3.12 (1H, br dd, *J* = 4.2 and 6.4 Hz), 7.26-7.32 (3H, m), 7.37-7.43 (2H, m); ¹³C-NMR δ 131.7, 128.2, 127.9, 123.3, 90.2, 83.4, 79.8, 32.3, 31.2, 19.6, 18.3, 17.8; IR (liquid film) 3550 (br), 3410 (br), 2225 (m), 1600, 1490, 985, 755, 690 cm⁻¹; MS, *m/z* (relative intensity) 202 (M⁺, 2), 159 (2), 130 (100), 129 (82), 115 (72); HRMS calcd for C₁₄H₁₈O; 202.1358, found; 202.1365.

(3R*,4S*)-2,4,7-Trimethyloct-7-en-5-yn-3-ol (anti-14p): bp 75-80 °C/8 mmHg (Kugelrohr); ¹H-NMR δ 0.94 (3H, d, *J* = 6.8 Hz), 0.97 (3H, d, *J* = 6.7 Hz), 1.23 (3H, d, *J* = 7.0 Hz), 1.63 (1H (OH), br s), 1.77 (1H, octet, *J* = 6.8 Hz), 1.86 (3H, dd, *J* = 1.18 and 1.24 Hz), 2.80 (1H, dq, *J* = 4.3 and 7.0 Hz), 3.05 (1H, dd, *J* = 4.3 and 6.8 Hz), 5.16 (1H, br quint, *J* = ca. 1.6 Hz), 5.22 (1H, br q, *J* = ca. 1.1 Hz); ¹³C-NMR δ 126.8, 121.1, 89.1, 84.6, 79.7, 32.2, 31.0, 23.8, 19.6, 18.2, 17.7; IR (liquid film) 3550 (br), 3450 (br), 2220 (m), 1610, 1000, 890 cm⁻¹; MS, *m/z* (relative intensity) 166 (M⁺, 3), 164 (12), 149 (49), 121 (6), 105 (6), 94 (68), 79 (87), 43 (100); HRMS calcd for C₁₁H₁₈O; 166.1358, found; 166.1362. Anal. Calcd for C₁₁H₁₈O: C, 79.46; H, 10.91. Found C, 79.18; H, 11.08.

(3R*,4S*)-2-Methyl-4-(2-phenylethyl)-5-heptyn-3-ol (anti-14q): bp 85-90 °C/0.21 mmHg (Kugelrohr); ¹H-NMR δ 0.87 (3H, d, *J* = 6.7 Hz), 0.95 (3H, d, *J* = 6.7 Hz), 1.64 (1H (OH), br s), 1.75 (1H, dddd, *J* = 5.4, 7.0, 9.4, and 13.1 Hz), 1.77 (1H, octet, *J* = 7 Hz), 1.85 (3H, d, *J* = 2.4 Hz), 1.91 (1H, dtd, *J* = 5.5, 9.5, and 13.1 Hz), 2.54 (1H, m), 2.68 (1H, ddd, *J* = 7.0, 9.4, and 13.8 Hz), 2.84 (1H, ddd, *J* = 5.5, 9.5, and 13.8 Hz), 3.05 (1H, dd, *J* = 3.6 and 7.4 Hz), 7.14-7.30 (5H, m); ¹³C-NMR δ 141.9, 128.4, 128.3, 125.8, 80.1, 78.4, 77.8, 36.0, 34.4, 33.7, 32.4, 19.4, 18.2, 3.6; IR (liquid film) 3540 (br), 3450 (br), 1450, 1390, 750, 700 cm⁻¹; MS, *m/z* (relative intensity) 230 (M⁺, 1.3), 228 (4), 197 (6), 169 (5), 158 (14), 143 (41), 129 (77), 91 (100); HRMS calcd for C₁₆H₂₂O; 230.1671, found; 230.1676. Anal. Calcd for C₁₆H₂₂O: C, 83.43; H, 9.63. Found C, 83.18; H, 9.81.

(3R*,4S*)-2-Methyl-6-phenyl-4-(2-phenylethyl)-5-hexyn-3-ol (anti-14r): ¹H-NMR δ 0.94 (3H, d, *J* = 6.7 Hz), 1.01 (3H, d, *J* = 6.7 Hz), 1.73 (1H (OH), br s), 1.88 (1H, octet, *J* = 6.7 Hz), 1.89 (1H, dddd, *J* = 5.4, 7.2, 9.3, and 13.3 Hz), 2.08 (1H, dtd, *J* = 5.5, 9.4, and 13.3 Hz), 2.79 (1H, ddd, *J* = 7.2, 9.2, and 13.8 Hz), 2.82 (1H, ddd, *J* = 3.5, 5.4, and 9.4 Hz), 2.94 (1H, ddd, *J* = 5.5, 9.3, and 13.8 Hz), 3.20 (1H, br s), 7.17-7.34 (8H, m), 7.42-7.47 (2H, m); ¹³C-NMR δ 141.8, 131.7, 128.5, 128.4, 128.3, 128.0, 125.9, 123.3, 90.9, 85.0, 78.5, 36.6, 34.2, 33.8, 32.7, 19.5, 18.3; IR (liquid film) 3560 (br), 3420 (br), 2230 (m), 1600, 1490, 1455, 755, 695 cm⁻¹; MS (CI), *m/z* (relative intensity) 293 (MH⁺, 2), 275 (4), 237 (61), 220 (96), 219 (43), 129 (80), 91 (100); HRMS (CI) calcd for C₂₁H₂₅O (MH⁺); 293.1907, found; 293.1904.

(3R*,4S*)-4-(5,5-Dimethoxypentyl)-5-decyn-3-ol (anti-14s): bp 85-90 °C/0.16 mmHg (Kugelrohr); ¹H-NMR δ 0.89 (3H, t, *J* = 7.2 Hz), 0.94 (3H, t, *J* = 7.4 Hz), 1.28-1.66 (14H, m), 1.72 (1H (OH), br d, *J* = 7.3 Hz), 2.17 (2H, dt, *J* = 2.2 and 6.9 Hz), 2.38 (1H, m), 3.28-3.35 (7H, m, including s (6H) at 3.30), 4.35 (1H, t, *J* = 5.7 Hz); ¹³C-NMR δ 104.4, 84.6, 78.9, 74.7, 52.6, 52.5, 38.7, 32.4, 32.1, 31.1, 28.5, 27.5, 24.4, 21.9, 18.4, 13.6, 10.2; IR (liquid film) 3465 (br), 1460, 1385, 1125, 1070, 1050, 960 cm⁻¹; MS (CI), *m/z* (relative intensity) 253 (MH⁺-MeOH, 0.8), 221 (85), 203 (9), 151 (28), 137 (17), 75 (100); Anal. Calcd for C₁₇H₃₂O₃: C, 71.79; H, 11.34. Found C, 71.69; H, 11.05.

(3S*,4S*)-4-(5,5-Dimethoxypentyl)-5-decyn-3-ol (syn-14s): ¹H-NMR δ 0.89 (3H, t, *J* = 7.2 Hz), 0.97 (3H, t, *J* = 7.4 Hz), 1.28-1.71 (15H, m), 2.16 (2H, dt, *J* = 2.2 and 6.9 Hz), 2.45 (1H, m), 3.30 (6H, s), 3.42 (1H, m), 4.35 (1H, t, *J* = 5.7 Hz); ¹³C-NMR δ 104.5, 83.7, 80.1, 75.1, 52.6, 38.9, 32.4, 31.2, 30.2, 27.4, 26.5, 24.5, 21.9, 18.4, 13.6, 10.2; IR (liquid film) 3450 (br), 1460, 1130, 1075, 1050, 970 cm⁻¹; MS (CI), *m/z* (relative intensity) 253 (MH⁺-MeOH, 0.6), 235 (6), 221 (100), 207 (17), 151 (23), 75 (84).

(3R*,4S*)-4-(5,5-Dimethoxypentyl)-2-methyl-5-decyn-3-ol (anti-14t): bp 88-95 °C/0.14 mmHg (Kugelrohr); ¹H-NMR δ 0.891 (3H, t, *J* = 7.2 Hz), 0.898 (3H, d, *J* = 6.7 Hz), 0.97 (3H, d, *J* = 6.7 Hz), 1.28-1.63 (12H, m), 1.66 (1H (OH), d, *J* = 8.5 Hz), 1.75 (1H, octet, *J* = 6.8 Hz), 2.17 (2H, dt, *J* = 2.2 and 6.9 Hz), 2.53 (1H, m), 3.01 (1H, ddd, *J* = 3.6, 7.4, and 8.5 Hz), 3.30 (6H, s), 4.35 (1H, t, *J* = 5.7 Hz); ¹³C-NMR δ 104.4, 84.6, 78.9, 78.4, 52.6, 36.5, 32.7, 32.4, 31.1, 27.5, 24.4, 21.9, 19.5, 18.4, 18.2, 13.6; IR (liquid film) 3490 (br), 1470, 1390, 1130, 1080, 1055, 960 cm⁻¹; MS (CI), *m/z* (relative intensity) 267 (MH⁺-MeOH, 1), 235 (54), 217 (9), 179 (46), 151 (34), 75 (100). Anal. Calcd for C₁₈H₃₄O₃: C, 72.44; H, 11.48. Found C, 72.23; H, 11.67.

1-(1-Hexynyl)-1-[(hydroxy)(phenyl)methyl]cyclohexane (14u): bp 105-115 °C/0.15 mmHg (Kugelrohr); ¹H-NMR δ 0.92 (3H, t, *J* = 7.2 Hz), 0.97-1.11 (2H, m), 1.22 (1H, br dt, *J* = 4 and 12 Hz), 1.34-1.73 (10H, m), 1.96 (1H, m), 2.25 (2H, t, *J* = 6.9 Hz), 2.55 (1H (OH), d, *J* = 5 Hz), 4.36 (1H, d, *J* = 5 Hz), 7.23-7.41 (5H, m); ¹³C-NMR δ 140.4, 127.9, 127.5, 127.4, 86.4, 81.9, 81.0, 44.1, 35.5, 33.1, 31.2, 26.0, 22.9, 22.7, 22.0, 18.5, 13.6; IR (liquid film) 3520 (sh), 3450 (br), 1450, 1040, 1025, 770, 705 cm⁻¹; MS (CI), *m/z* (relative intensity) 271 (MH⁺, 1), 253 (18), 197 (8), 171 (8), 122 (100); HRMS (CI) calcd for C₁₉H₂₇O (MH⁺); 271.2063, found; 271.2065. Anal. Calcd for C₁₉H₂₆O: C, 84.39; H, 9.69. Found C, 84.16; H, 9.69.

1-(1-Hexynyl)-1-(1-hydroxy-3-phenylpropyl)cyclohexane (14v): bp 108-110 °C/0.16 mmHg (Kugelrohr); ¹H-NMR δ 0.91 (3H, t, *J* = 7.2 Hz), 1.00-1.27 (3H, m), 1.35-1.79 (12H, m), 1.82-1.99 (2H, m, including dddd (1H, *J* = 2.1, 7.0, 9.9, and 13.8 Hz) at 1.94), 2.20 (2H, t, *J* = 6.8 Hz), 2.66 (1H, ddd, *J* = 7.0, 9.6, and 13.7 Hz), 2.95 (1H, ddd, *J* = 5.0, 9.9, and 13.7 Hz), 3.22 (1H, dd, *J* = 2.1 and 10.5 Hz), 7.14-7.31 (5H, m); ¹³C-NMR δ 142.5, 128.5, 128.3, 125.6, 85.3,

82.2, 77.7, 43.3, 34.5, 33.7, 33.3, 32.7, 31.3, 26.1, 22.97, 22.90, 21.9, 18.4, 13.6; IR (liquid film) 3550 (br), 3440 (br), 1500, 1450, 1050, 750, 700 cm^{-1} ; MS (CI), m/z (relative intensity) 299 (MH^+ , 0.2), 298 (0.2), 281 (3), 194 (17), 163 (3), 151 (6), 122 (100), 91 (59); HRMS (CI) calcd for $\text{C}_{21}\text{H}_{31}\text{O}$ (MH^+); 299.2376, found; 299.2355. Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{O}$: C, 84.51; H, 10.13. Found C, 84.50; H, 10.13.

1-Phenyl-3-octyn-1-ol (14w): bp 91-93 $^{\circ}\text{C}/0.17$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.89 (3H, t, $J = 7.2$ Hz), 1.30-1.51 (4H, m), 2.16 (2H, tt, $J = 2.4$ and 6.9 Hz), 2.32 (1H (OH), br), 2.56 (1H, tdd, $J = 2.4, 7.4,$ and 16.5 Hz), 2.63 (1H, tdd, $J = 2.4, 5.3,$ and 16.5 Hz), 4.80 (1H, dd, $J = 5.3$ and 7.4 Hz), 7.25-7.40 (5H, m); $^{13}\text{C-NMR}$ δ 142.8, 128.3, 127.7, 125.7, 83.6, 75.9, 72.6, 30.9, 30.1, 21.9, 18.4, 13.6; IR (liquid film) 3520 (sh), 3400 (br), 1450, 1050, 755, 695 cm^{-1} ; MS, m/z (relative intensity) 202 (M^+ , 1), 160 (2), 115 (4), 107 (100), 79 (70); HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}$; 202.1358, found; 202.1354. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97. Found C, 82.98; H, 8.90.

2-Butyl-1-phenyl-2,3-butadien-1-ol (15w): bp 88-90 $^{\circ}\text{C}/0.17$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.83 (3H, t, $J = 7.2$ Hz), 1.20-1.42 (4H, m), 1.77 (1H, ttd, $J = 3.5, 7.4,$ and 15 Hz), 1.84 (1H, ttd, $J = 3.6, 7.5,$ and 15 Hz), 2.28 (1H (OH), br s), 4.94-5.05 (2H, m), 5.09 (1H, br t, $J = 2.3$ Hz), 7.25-7.39 (5H, m); $^{13}\text{C-NMR}$ δ 204.0, 142.1, 128.3, 127.7, 126.7, 108.2, 79.8, 74.1, 29.6, 27.6, 22.3, 13.9; IR (liquid film) 3390 (br), 1955, 1450, 1035, 1020, 850, 740, 700 cm^{-1} ; MS, m/z (relative intensity) 202 (M^+ , 2), 201 (2), 187 (3), 115 (7), 107 (100), 79 (68); HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}$; 202.1358, found; 202.1358. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97. Found C, 83.21; H, 8.99.

1-Phenyl-5-decyn-3-ol (14x): $^1\text{H-NMR}$ δ 0.90 (3H, t, $J = 7.2$ Hz), 1.33-1.52 (4H, m), 1.83 (2H, br td, $J = 7$ and 8 Hz), 1.98 (1H (OH), br s), 2.16 (2H, tt, $J = 2.4$ and 6.9 Hz), 2.30 (1H, tdd, $J = 2.4, 6.8,$ and 16.5 Hz), 2.42 (1H, tdd, $J = 2.4, 4.7,$ and 16.5 Hz), 2.68 (1H, td, $J = 8.1$ and 13.9 Hz), 2.80 (1H, td, $J = 7.5$ and 13.9 Hz), 3.70 (1H, br quint, $J = ca. 6$ Hz), 7.15-7.31 (5H, m); $^{13}\text{C-NMR}$ δ 141.9, 128.41, 128.38, 125.8, 83.5, 75.7, 69.4, 37.8, 31.9, 31.0, 27.9, 22.0, 18.4, 13.6; IR (liquid film) 3550 (sh), 3400 (br), 1460, 1055, 750, 705 cm^{-1} ; MS (CI), m/z (relative intensity) 231 (MH^+ , 0.6), 213 (7), 185 (5), 171 (10), 157 (20), 134 (38), 117 (44), 91 (100); HRMS (CI) calcd for $\text{C}_{16}\text{H}_{23}\text{O}$ (MH^+); 231.1750, found; 231.1740.

4-Butyl-1-phenyl-4,5-hexadien-3-ol (15x): bp 105-108 $^{\circ}\text{C}/0.25$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.90 (3H, t, $J = 7.1$ Hz), 1.28-1.47 (4H, m), 1.62 (1H (OH), br d, $J = 4$ Hz), 1.83 (1H, dddd, $J = 5.9, 7.6, 9.8,$ and 13.7 Hz), 1.90-2.07 (3H, m), 2.67 (1H, ddd, $J = 6.4, 9.7,$ and 13.8 Hz), 2.77 (1H, ddd, $J = 5.8, 9.9,$ and 13.8 Hz), 4.04 (1H, br s), 4.88 (2H, dt, $J = 2.3$ and 3.5 Hz), 7.15-7.31 (5H, m); $^{13}\text{C-NMR}$ δ 204.3, 142.0, 128.5, 128.3, 125.8, 107.5, 78.9, 71.2, 37.3, 31.9, 29.8, 27.7, 22.5, 13.9; IR (liquid film) 3550 (sh), 3350 (br), 1950, 1450, 1050, 1030, 845, 745, 695 cm^{-1} ; MS, m/z (relative intensity) 230 (M^+ , 0.2), 212 (1),

197 (8), 183 (5), 170 (4), 155 (3), 134 (10), 117 (13), 105 (13), 91 (100); HRMS calcd for C₁₆H₂₂O; 230.1671, found; 230.1639. Anal. Calcd for C₁₆H₂₂O: C, 83.43; H, 9.63. Found C, 83.38; H, 9.45.

(3R*,4S*)-cis-2,4-Dimethyl-3-[(methoxymethyl)oxy]-5-decene

(16): To a mixture of alcohol *anti*-14j (78 mg, 0.43 mmol) and (*i*Pr)₂NEt (0.37 mL, 2.1 mmol) in CH₂Cl₂ (5 mL) was added chloromethyl methyl ether (0.16 mL, 2.1 mmol). The mixture was stirred at rt for 18 h. The reaction was quenched by the addition of saturated NaHCO₃. The mixture was extracted three times with ether, dried, and concentrated in *vacuo*. Purification of the residue by flash chromatography (10-20% ether in hexane) gave 91 mg (94% yield) of (3R*,4S*)-2,4-dimethyl-3-[(methoxymethyl)oxy]-5-decyne: ¹H-NMR δ 0.88 (3H, t, *J* = 7.1 Hz), 0.93 (3H, d, *J* = 6.8 Hz), 0.97 (3H, d, *J* = 6.9 Hz), 1.15 (3H, d, *J* = 7.0 Hz), 1.31-1.50 (4H, m), 1.92 (1H, octet, *J* = 6.7 Hz), 2.14 (2H, dt, *J* = 2.3 and 6.9 Hz), 2.69 (1H, tdq, *J* = 2.3, 5.0, and 7.0 Hz), 3.09 (1H, br t, *J* = 5.5 Hz), 3.40 (3H, s), 4.68 (1H, d, *J* = 6.9 Hz), 4.79 (1H, d, *J* = 6.9 Hz); ¹³C-NMR δ 98.0, 87.0, 81.9, 81.6, 56.0, 31.1, 30.7, 29.5, 21.9, 20.0, 18.5, 18.2, 17.9, 13.6; IR (liquid film) 1470, 1460, 1150, 1135, 1090, 1035, 920 cm⁻¹; MS (CI), *m/z* (relative intensity) 195 (MH⁺-MeOH, 9), 153 (6), 139 (6), 123 (68), 82 (64), 45 (100); HRMS (CI) calcd for C₁₃H₂₃O (MH⁺-MeOH); 195.1750, found; 195.1718.

A mixture of the MOM ether derivative (84 mg, 0.37 mmol) and Lindlar's catalyst (Pd-CaCO₃) (29 mg) in dry benzene (3 mL) was stirred at rt under H₂ for 1 h. The filtration of the mixture through a pad of celite followed by the concentration of the filtrate gave 83.5 mg (99% yield) of **16**: ¹H-NMR δ 0.88 (3H, t, *J* = 6.9 Hz), 0.90 (3H, d, *J* = 7.0 Hz), 0.92 (3H, d, *J* = 7.1 Hz), 0.97 (3H, d, *J* = 6.9 Hz), 1.24-1.38 (4H, m), 1.77 (1H, octet, *J* = 6.7 Hz), 1.94-2.12 (2H, m), 2.72 (1H, dd quint, *J* = 2.3, 4.5, and 6.8 Hz), 3.05 (1H, dd, *J* = 4.5 and 6.2 Hz), 3.39 (3H, s), 4.62 (1H, d, *J* = 6.8 Hz), 4.67 (1H, d, *J* = 6.8 Hz), 5.30-5.40 (2H, m); ¹³C-NMR δ 132.0, 129.6, 98.3, 88.7, 56.0, 34.4, 32.0, 31.0, 27.2, 22.4, 19.9, 18.8, 18.2, 14.0; IR (liquid film) 1150, 1090, 1035 cm⁻¹; MS (CI), *m/z* (relative intensity) 197 (MH⁺-MeOH, 3), 167 (3), 125 (40), 117 (64), 69 (74), 45 (100).

(2S*,3R*)-2,4-Dimethyl-3-[(methoxymethyl)oxy]-1-pentanol (17):

Ozone was bubbled through a solution of **16** (71 mg, 0.31 mmol) in methanol (2.5 mL) at -78 °C until a blue color persisted. Nitrogen was bubbled through the solution until it was colorless, then NaBH₄ (36 mg, 0.81 mmol) was added, and the reaction mixture was allowed to slowly warm to rt. After being stirred for 0.5 h, the mixture was quenched with saturated NaHCO₃ and extracted three times with ether. After concentration of the dried extracts in *vacuo*, purification of the residue by flash chromatography (20-30% ethyl acetate in hexane) gave 10 mg (18% yield) of **17**: ¹H-NMR δ 0.87 (3H, d, *J* = 6.8 Hz), 0.94 (3H, d, *J* = 6.8 Hz), 0.97 (3H, d, *J* = 6.9 Hz), 1.79 (1H, t quint, *J* = 3.6 and 7.2 Hz), 1.86 (1H, δ sept, *J* = 3.6 and 6.9 Hz), 2.59 (1H (OH), br s), 3.24 (1H, dd, *J* = 3.6 and 8.0 Hz), 3.42

(3H, s), 3.49 (1H, dd, $J = 4.0$ and 11.3 Hz), 3.83 (1H, dd, $J = 3.4$ and 11.3 Hz), 4.66 (2H, s); $^{13}\text{C-NMR}$ δ 99.1, 87.8, 65.3, 56.3, 37.2, 30.3, 20.2, 16.2, 15.2.

(2*R,3*S**)-2-(2-Methylethyl)-3-methyl-1,5-**

dioxaspiro[5,5]undecane (18).²¹ To a solution of alcohol **17** (7.3 mg, 0.041 mmol) in methanol (0.2 mL) was added a drop of conc. HCl. The mixture was stirred at rt for 4 h, quenched with saturated NaHCO_3 , and extracted five times with ether. After concentration of the dried extracts in vacuo, the residue was purified by flash chromatography (50-100% ether in hexane) to give 3.0 mg (56% yield) of (2*S**,3*R**)-2,4-dimethyl-pentan-1,3-diol: $^1\text{H-NMR}$ δ 0.86 (3H, d, $J = 7.0$ Hz), 0.89 (3H, d, $J = 6.8$ Hz), 0.95 (3H, d, $J = 6.9$ Hz), 1.75-1.91 (2H, m, including δ sept (1H, $J = 3.8$ and 6.9 Hz) at 1.83), 2.33 (2H (OH), br s), 3.34 (1H, dd, $J = 3.8$ and 8.0 Hz), 3.63 (1H, dd, $J = 7.2$ and 10.7 Hz), 3.75 (1H, dd, $J = 3.6$ and 10.7 Hz); $^{13}\text{C-NMR}$ δ 82.1, 68.2, 37.2, 30.3, 19.8, 15.0, 13.9; IR (liquid film) 3350 (br), 1465, 1065, 1030, 990, 970 cm^{-1} ; MS (CI), m/z (relative intensity) 133 (MH^+ , 2), 115 (37), 97 (100), 89 (50), 73 (95).

1,1-Dimethoxycyclohexane (11 mg, 0.049 mmol) was added to a solution of the diol (3.0 mg, 0.023 mmol) and pyridinium *p*-toluenesulfonate (*ca.* 1 mg) in CH_2Cl_2 (0.2 mL). The mixture was stirred at rt for 18 h and then directly subjected to flash chromatography (5% ethyl acetate in hexane) to give 4.8 mg (98% yield) of spiroacetal **18**: $^1\text{H-NMR}$ δ 0.69 (3H, d, $J = 6.7$ Hz), 0.87 (3H, d, $J = 6.8$ Hz), 0.97 (3H, d, $J = 6.9$ Hz), 1.20-1.69 (9H, m), 1.72-1.91 (2H, m, including δ sept (1H, $J = 2.5$ and 6.9 Hz) at 1.83), 2.18 (1H, m), 3.30 (1H, dd, $J = 2.5$ and 10.2 Hz), 3.52 (1H, dd, $J = 11.0$ and 11.4 Hz), 3.64 (1H, dd, $J = 5.2$ and 11.4 Hz); $^{13}\text{C-NMR}$ δ 97.9, 77.4, 65.6, 38.6, 31.4, 28.5, 27.8, 25.9, 22.7, 22.4, 20.1, 14.5, 12.6; IR (liquid film) 1155, 1110, 1095, 1015 cm^{-1} ; MS, m/z (relative intensity) 212 (M^+ , 8), 169 (13), 140 (2), 99 (30), 97 (100); HRMS calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2$; 212.1777, found; 212.1779.

6-(2-Phenylethyl)-7-dodecyn-5-one (19b): $^1\text{H-NMR}$ δ 0.90 (3H, t, $J = 7.3$ Hz), 0.93 (3H, t, $J = 7.2$ Hz), 1.24-1.60 (8H, m), 1.91 (1H, dtd, $J = 5.7, 8.9,$ and 13.3 Hz), 2.01 (1H, dddd, $J = 5.6, 7.3, 9.1,$ and 13.3 Hz), 2.24 (2H, dt, $J = 2.4$ and 6.9 Hz), 2.58 (1H, td, $J = 7.3$ and 17.2 Hz), 2.676 (1H, ddd, $J = 7.3, 9.0,$ and 13.6 Hz), 2.684 (1H, td, $J = 7.5$ and 17.2 Hz), 2.79 (1H, ddd, $J = 5.7, 9.1,$ and 13.6 Hz), 3.15 (1H, tdd, $J = 2.4, 5.6,$ and 8.7 Hz), 7.15-7.31 (5H, m) [a minor product **20b** resonated at 5.55 (1H, tt, $J = 2.4$ and 7.0 Hz)]; $^{13}\text{C-NMR}$ δ 208.1, 141.3, 128.5, 128.4, 126.0, 85.5, 76.96, 44.4, 40.0, 33.1, 32.8, 30.9, 25.9, 22.3, 21.9, 18.5, 13.8, 13.6; IR (liquid film) 1720, 1455, 750, 700 cm^{-1} ; MS, m/z (relative intensity) 284 (M^+ , 4), 283 (9), 227 (19), 180 (14), 91 (65), 85 (99), 57 (100); HRMS calcd for $\text{C}_{20}\text{H}_{28}\text{O}$; 284.2141, found; 284.2141.

2-Methyl-4-(2-phenylethyl)-5-decyn-3-one (19c): bp 115-120 $^\circ\text{C}/0.06$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.91 (3H, t, $J = 7.2$ Hz), 1.08 (3H, d, $J = 7.0$ Hz), 1.10 (3H, d, $J = 6.8$ Hz), 1.36-1.56 (4H, m), 1.85-2.08 (2H, m), 2.22 (2H,

dt, $J = 2.4$ and 6.9 Hz), 2.67 (1H, ddd, $J = 7.1, 9.0,$ and 13.7 Hz), 2.77 (1H, ddd, $J = 5.7, 9.1,$ and 13.7 Hz), 3.08 (1H, sept, $J = 6.9$ Hz), 3.27 (1H, tdd, $J = 2.4, 5.8,$ and 8.5 Hz), 7.15-7.30 (5H, m) [a minor product **20c** resonated at 5.54 (1H, tt, $J = 2.5$ and 7.0 Hz)]; $^{13}\text{C-NMR}$ δ 211.4, 141.4, 128.5, 128.3, 125.9, 85.1, 76.8, 42.8, 38.4, 33.1, 32.7, 30.9, 21.9, 19.0, 18.54, 18.46, 13.6; IR (liquid film) 1715, 1465, 1455, 745, 700 cm^{-1} ; MS, m/z (relative intensity) 270 (M^+ , 2), 269 (2), 227 (11), 179 (6), 166 (7), 91 (64), 71 (59), 43 (100); HRMS calcd for $\text{C}_{19}\text{H}_{26}\text{O}$; 270.1985, found; 270.1982.

2,2-Dimethyl-4-(2-phenylethyl)-5-decyn-3-one (19d): bp 140-145 $^{\circ}\text{C}/0.06$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.90 (3H, t, $J = 7.2$ Hz), 1.16 (9H, s), 1.33-1.52 (4H, m), 1.87-2.06 (2H, m), 2.17 (2H, dt, $J = 2.3$ and 6.9 Hz), 2.62 (1H, ddd, $J = 7.5, 8.6,$ and 13.7 Hz), 2.75 (1H, ddd, $J = 5.9, 8.8,$ and 13.7 Hz), 3.60 (1H, tdd, $J = 2.4, 6.4,$ and 8.2 Hz), 7.15-7.31 (5H, m) [a minor product **20d** resonated at 5.40 (1H, tt, $J = 2.4$ and 6.9 Hz)]; $^{13}\text{C-NMR}$ δ 211.7, 141.4, 128.4, 128.3, 125.9, 84.1, 77.3, 44.8, 37.5, 33.5, 33.3, 30.8, 26.5, 21.9, 18.4, 13.5; IR (liquid film) 1710, 1495, 1475, 1465, 1455, 1365, 745, 700 cm^{-1} ; MS, m/z (relative intensity) 284 (M^+ , 2), 283 (2), 269 (4), 227 (20), 180 (16), 91 (73), 57 (100); HRMS calcd for $\text{C}_{20}\text{H}_{28}\text{O}$; 284.2141, found; 284.2133. Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{O}$: C, 84.45; H, 9.92. Found C, 84.42; H, 9.78.

Ethyl 2-(2-Phenylethyl)-3-Octynoate (19e): $^1\text{H-NMR}$ δ 0.93 (3H, t, $J = 7.2$ Hz), 1.28 (3H, t, $J = 7.1$ Hz), 1.38-1.58 (4H, m), 1.97-2.14 (2H, m), 2.24 (2H, dt, $J = 2.3$ and 6.9 Hz), 2.69-2.86 (2H, m), 3.28 (1H, tdd, $J = 2.4, 6.0,$ and 8.4 Hz), 4.18 (2H, q, $J = 7.1$ Hz), 7.17-7.32 (5H, m) [a minor product **20e** resonated at 5.55 (1H, tt, $J = 2.8$ and 6.8 Hz)]; $^{13}\text{C-NMR}$ δ 171.4, 141.1, 128.5, 128.4, 126.0, 84.4, 76.1, 61.2, 37.5, 34.2, 33.1, 30.8, 21.9, 18.5, 14.1, 13.6; IR (liquid film) 1740, 1255, 1180, 1155, 1030, 750, 700 cm^{-1} ; MS (CI), m/z (relative intensity) 273 (MH^+ , 14), 245 (5), 227 (6), 199 (52), 168 (90), 91 (100); HRMS (CI) calcd for $\text{C}_{18}\text{H}_{25}\text{O}_2$; 273.1856 (MH^+), found; 273.1846.

2-Methyl-4-(2-phenylethyl)-4,5-decadien-3-one (21c): bp 125-135 $^{\circ}\text{C}/0.06$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.90 (3H, m), 1.04 (3H, d, $J = 6.9$ Hz), 1.05 (3H, d, $J = 6.9$ Hz), 1.26-1.41 (4H, m), 1.98-2.07 (2H, m), 2.45 (1H, dtd, $J = 2.4, 8.0,$ and 14.4 Hz), 2.54 (1H, dddd, $J = 2.5, 6.7, 7.8,$ and 14.4 Hz), 2.70 (2H, br t, $J = 7.6$ Hz), 3.25 (1H, sept, $J = 6.9$ Hz), 5.46 (1H, tt, $J = 2.4$ and 7.1 Hz), 7.13-7.29 (5H, m); $^{13}\text{C-NMR}$ δ 211.5, 205.7, 141.7, 128.5, 128.2, 125.7, 106.9, 95.6, 36.1, 34.2, 31.2, 28.8, 27.9, 22.2, 19.6, 19.2, 13.8; IR (liquid film) 1945, 1675, 745, 700 cm^{-1} ; MS, m/z (relative intensity) 270 (M^+ , 14), 269 (13), 255 (8), 227 (9), 213 (8), 179 (29), 91 (51), 71 (49), 43 (100); HRMS calcd for $\text{C}_{19}\text{H}_{26}\text{O}$; 270.1985, found; 270.1972. Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{O}$: C, 84.39; H, 9.69. Found C, 84.18; H, 9.67.

2,2-Dimethyl-4-(2-phenylethyl)-4,5-decadien-3-one (21d): bp 140-145 $^{\circ}\text{C}/0.05$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.89 (3H, m), 1.21 (9H, s), 1.26-

1.42 (4H, m), 1.97-2.05 (2H, m), 2.37-2.57 (2H, m), 2.67 (2H, br t, $J = ca. 8$ Hz), 5.29 (1H, tt, $J = 2.3$ and 7.2 Hz), 7.12-7.28 (5H, m); $^{13}\text{C-NMR}$ δ 210.0, 206.3, 141.8, 128.6, 128.1, 125.7, 102.8, 94.4, 45.0, 34.3, 31.2, 31.1, 28.1, 28.0, 22.3, 13.8; IR (liquid film) 1945, 1665, 1475, 1450, 1130, 745, 695 cm^{-1} ; MS, m/z (relative intensity) 284 (M^+ , 8), 283 (5), 269 (8), 227 (6), 193 (6), 91 (31), 57 (100); HRMS calcd for $\text{C}_{20}\text{H}_{28}\text{O}$; 284.2141, found; 284.2148. Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{O}$: C, 84.45; H, 9.92. Found C, 84.52; H, 10.07.

1-Phenyl-3-[(chloromethyl)dimethylsilyl]-4-nonyne (24c): bp 140-150 $^{\circ}\text{C}/1.9$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.16 (3H, s), 0.18 (3H, s), 0.93 (3H, t, $J = 7.2$ Hz), 1.37-1.55 (4H, m), 1.61-1.82 (3H, m), 2.21 (2H, dt, $J = 2.4$ and 6.8 Hz), 2.66 (1H, ddd, $J = 7.8, 8.7,$ and 13.4 Hz), 2.87 (2H, s), 2.98 (1H, ddd, $J = 6.3, 7.8,$ and 13.4 Hz), 7.15-7.31 (5H, m); $^{13}\text{C-NMR}$ δ 142.0, 128.6, 128.3, 125.8, 82.2, 79.8, 35.6, 31.5, 31.4, 28.9, 21.9, 18.6, 17.3, 13.6, -6.2, -6.3; IR (liquid film) 2220 (m), 1250, 840, 815, 745, 695 cm^{-1} ; MS, m/z (relative intensity) 306 (M^+ , 0.2), 257 (8), 249 (9), 199 (15), 107 (79), 93 (79), 91 (92), 79 (100); HRMS calcd for $\text{C}_{18}\text{H}_{27}\text{SiCl}$; 306.1572, found; 306.1566. Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{SiCl}$: C, 70.43; H, 8.87; Cl, 11.55. Found C, 70.34; H, 8.81; Cl, 11.36.

1-Phenyl-5-[(chloromethyl)dimethylsilyl]-3,4-nonadiene (25c): bp 120-130 $^{\circ}\text{C}/1.5$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.18 (6H, s), 0.89 (3H, t, $J = 7.1$ Hz), 1.24-1.41 (4H, m), 1.92 (2H, m), 2.29 (2H, br td, $J = ca. 6.8$ and 8.1 Hz), 2.70 (2H, br t, $J = ca. 7.8$ Hz), 2.78 (2H, s), 4.90 (1H, tt, $J = 3.0$ and 6.6 Hz), 7.15-7.31 (5H, m); $^{13}\text{C-NMR}$ δ 206.4, 141.9, 128.5, 128.3, 125.8, 94.1, 85.9, 36.0, 31.3, 30.3, 30.2, 29.2, 22.3, 13.9, -4.58, -4.63; IR (liquid film) 1930, 1250, 835, 810, 740, 695 cm^{-1} ; MS, m/z (relative intensity) 306 (M^+ , 0.9), 257 (6), 249 (8), 199 (14), 107 (91), 93 (90), 91 (96), 79 (100); HRMS calcd for $\text{C}_{18}\text{H}_{27}\text{SiCl}$; 306.1572, found; 306.1571. Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{SiCl}$: C, 70.43; H, 8.87; Cl, 11.55. Found C, 70.32; H, 8.75; Cl, 11.41.

1-Phenyl-3-triethylsilyl-4-nonyne (24d): bp 125-135 $^{\circ}\text{C}/1.9$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.60 (6H, m), 0.92 (3H, t, $J = 6.6$ Hz), 0.94 (9H, t, $J = 7.9$ Hz), 1.37-1.54 (4H, m), 1.60-1.73 (3H, m), 2.20 (2H, br t, $J = ca. 6$ Hz), 2.62 (1H, m), 3.01 (1H, m), 7.14-7.30 (5H, m); $^{13}\text{C-NMR}$ δ 142.5, 128.6, 128.2, 125.6, 81.4, 81.1, 35.9, 31.9, 31.6, 22.0, 18.7, 16.0, 13.6, 7.5, 2.4; IR (liquid film) 2220 (m), 1450, 1015, 745, 730, 695 cm^{-1} ; MS, m/z (relative intensity) 314 (M^+ , 0.1), 285 (13), 198 (11), 167 (4), 139 (5), 115 (100), 87 (84); HRMS calcd for $\text{C}_{21}\text{H}_{34}\text{Si}$; 314.2431, found; 314.2429. Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{Si}$: C, 80.18; H, 10.89. Found C, 79.98; H, 10.75.

1-Phenyl-5-triethylsilyl-3,4-nonadiene (25d): bp 125-135 $^{\circ}\text{C}/1.0$ mmHg (Kugelrohr); $^1\text{H-NMR}$ δ 0.57 (6H, q, $J = 7.8$ Hz), 0.88 (3H, t, $J = 7.2$ Hz), 0.93 (9H, t, $J = 7.8$ Hz), 1.24-1.42 (4H, m), 1.84-1.90 (2H, m), 2.23-2.31 (2H, m), 2.69 (2H, br t, $J = ca. 8$ Hz), 4.80 (1H, tt, $J = 3.2$ and 6.7 Hz), 7.14-7.31 (5H, m); $^{13}\text{C-NMR}$ δ 206.0, 142.2, 128.5, 128.2, 125.7, 93.6, 84.7, 36.3, 31.2, 30.9, 29.3,

22.5, 14.0, 7.4, 3.2; IR (liquid film) 1935, 1015, 730, 715, 695 cm^{-1} ; MS, m/z (relative intensity) 314 (M^+ , 0.1), 285 (7), 198 (11), 167 (3), 139 (4), 115 (100), 87 (86); HRMS calcd for $\text{C}_{21}\text{H}_{34}\text{Si}$; 314.2431, found; 314.2425. Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{Si}$: C, 80.18; H, 10.89. Found C, 80.26; H, 10.90.

1-Bromo-5-phenyl-1-pentyn-3-ol (39a): To a solution of 5-phenyl-1-pentyn-3-ol (1.00 g, 6.2 mmol) in 19 mL of THF under argon at $-85\text{ }^\circ\text{C}$ was added BuLi (1.62 M in hexane) (7.65 mL, 12.4 mmol) and the mixture was stirred for 30 min. A solution of bromine (1.20 g, 7.5 mmol) in pentane (6 mL) was added dropwise and the mixture was allowed to warm to $0\text{ }^\circ\text{C}$ over 3 h. The mixture was poured into water and extracted twice with hexane (80 mL). The combined organic extracts were washed successively with saturated NaHSO_3 and 5% NaHCO_3 , dried and concentrated in vacuo. Purification of the residue by flash chromatography (10 % ethyl acetate in hexane) gave 1.16g (78%) of **39a**: $^1\text{H-NMR}$ δ 1.87 (1H, d, $J = 5.4\text{ Hz}$), 2.03 (2H, m), 2.79 (2H, t, $J = 7.8\text{ Hz}$), 4.39 (1H, q, $J = \text{ca. } 6.5\text{ Hz}$), 7.18-7.32 (5H, m); IR (liquid film), 3350 (br), 2210, 1050, 750, 700 cm^{-1} ;

1-Bromo-5-phenyl-1-pentyn-3-yl Methanesulfonate (40a). The mesylate was prepared from **39a** by a procedure similar to that described previously.³⁸ Purification of the residue by flash chromatography (10-30% ethyl acetate in hexane) gave **40a** (87%): $^1\text{H-NMR}$ δ 1.22 (2H, m), 2.82 (2H, m), 3.11 (3H, s), 5.17 (1H, dd, $J = 6.3$ and 6.8 Hz), 7.18-7.35 (5H, m); IR (liquid film) 2190, 1345, 1160, 745, 695 cm^{-1} ; MS (CI), m/z (relative intensity) 223, 221 ($\text{MH}^+ - \text{CH}_3\text{SO}_3\text{H}$, 28), 141 (83), 91 (100); HRMS (EI) calcd for $\text{C}_{11}\text{H}_9^{79}\text{Br}$ ($\text{MH}^+ - \text{CH}_3\text{SO}_3\text{H}$); 219.9888, found; 219.9889, calcd for $\text{C}_{11}\text{H}_9^{81}\text{Br}$ ($\text{MH}^+ - \text{CH}_3\text{SO}_3\text{H}$); 221.9868, found; 221.9868. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{O}_3\text{SBr}$: C, 45.44; H, 4.13. Found C, 45.42; H, 3.99.

4-Bromo-3-butyn-2-ol (39b). The compound was prepared from 1-butyn-3-ol by a procedure similar to that described for **39a**. Purification of the crude product Kugelrohr distillation ($80\text{ }^\circ\text{C}$, 40 mmHg) gave **39b** (49 %): $^1\text{H-NMR}$ δ 1.46 (3H, d, $J = 6.6\text{ Hz}$), 1.96 (1H, br d, $J = \text{ca. } 4\text{ Hz}$), 4.54 (1H, m); IR (liquid film) 3330 (br), 2210, 1120, 1050, 950, 855 cm^{-1} .

4-Bromo-3-butyn-2-yl Methanesulfonate (40b). The mesylate was prepared from **39b** by a procedure described previously³⁹. Purification of the crude mixture by flash chromatography (10-50% ethyl acetate in hexane) gave **40b** (64%): $^1\text{H-NMR}$ δ 1.65 (3H, d, $J = 6.7\text{ Hz}$), 3.10 (3H, s), 5.30 (q, $J = 6.6\text{ Hz}$); IR (liquid film) 2210, 1355, 1175, 935, 890 cm^{-1} ; MS (CI), m/z (relative intensity) 229, 227 (MH^+ , 5), 133, 131 (100), 97 (51); HRMS (CI) calcd for $\text{C}_5\text{H}_8\text{SO}_3^{79}\text{Br}$ (MH^+); 226.9377, found; 226.9337, calcd for $\text{C}_5\text{H}_8\text{SO}_3^{81}\text{Br}$ (MH^+); 228.9357, found; 228.9299. Anal. Calcd for $\text{C}_5\text{H}_7\text{SO}_3^{79}\text{Br}$: C, 26.45; H, 3.11. Found C, 26.69; H, 3.11.

1-Bromo-8,8-dimethoxy-1-butyn-3-ol (39c). The compound was prepared from 8,8-dimethoxy-1-butyn-3-ol by a procedure similar to that described for 39a. Purification of the crude mixture by flash chromatography (20% ethyl acetate in hexane) gave 39c (68%): $^1\text{H-NMR}$ δ 1.3-1.55 (4H, m), 1.55-1.75 (4H, m), 1.86 (1H, d, $J = 5.6$ Hz), 3.31 (6H, s), 4.34-4.42 (2H, m); IR (liquid film) 3420 (br), 2210, 1125, 1130 cm^{-1} .

1-Bromo-8,8-dimethoxy-1-butyn-3-yl Methanesulfonate (40c). The mesylate was prepared from 39c by a procedure described previously³⁹. Purification of the crude mixture by flash chromatography (20% ethyl acetate in hexane) gave 40c (84%): $^1\text{H-NMR}$ δ 1.35-1.65 (6H, m), 1.89 (2H, m), 3.10 (3H, s), 3.31 (6H, s), 4.35 (1H, t, $J = 5.7$ Hz), 5.17 (1H, t, $J = 6.5$ Hz); IR (liquid film) 2220, 1360, 1175, 900 cm^{-1} ; MS (CI), m/z (relative intensity) 311, 313 ($\text{MH}^+ - \text{CH}_3\text{OH}$, 2), 247, 249 (6), 215, 217 (40), 75 (100); HRMS (CI) calcd for $\text{C}_{10}\text{H}_{16}\text{SO}_4^{79}\text{Br}$ ($\text{MH}^+ - \text{CH}_3\text{OH}$); 310.9953, found; 310.9945, calcd for $\text{C}_{10}\text{H}_{16}\text{SO}_4^{81}\text{Br}$ ($\text{MH}^+ - \text{CH}_3\text{OH}$); 312.9933, found; 312.9967.

(3R*,4S*)-6-(Dimethylphenylsilyl)-2,4-dimethyl-5-hexyn-3-ol (44c): The reaction of allenic zinc 29 ($\text{R} = \text{Me}$), prepared by the reaction of 40b with $(\text{PhMe}_2\text{Si})_3\text{ZnLi}$, with 2-methylpropanal (1.5 equiv) was carried out using 1.6 equiv of ZnCl_2 by a procedure similar to that described in a general procedure for the preparation of homopropargyl alcohols. Purification of the crude products by flash chromatography (2-10 % ethyl acetate in hexane) gave 44c (62%): $^1\text{H-NMR}$ δ 0.39 (6H, s), 0.96 (3H, d, $J = 7.8$ Hz), 0.97 (3H, d, $J = 7.8$ Hz), 1.25 (3H, d, $J = 6.8$ Hz), 1.69 (1H, d, $J = 7.6$ Hz), 1.79 (1H, m); 2.77 (1H, dq, $J = 4.8$ and 6.8 Hz), 3.07 (1H, ddd, $J = 4.8, 6.6,$ and 7.6 Hz), 7.37 (3H, m), 7.61 (2H, m); IR (liquid film) 3570 (br), 3470 (br), 2170, 1250, 1115, 815, 780, 730, 700 cm^{-1} ; MS (CI), m/z (relative intensity) 243 ($\text{MH}^+ - \text{H}_2\text{O}$, <1), 183 (54), 135 (100), 135 (62), 75 (100); HRMS (CI) calcd for $\text{C}_{16}\text{H}_{25}\text{OSi}$ (MH^+); 261.1675, found; 261.1649. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{SiO}$: C, 73.79; H, 9.29. Found C, 73.56; H, 9.55.

(3R*,4S*)-2-Methyl-4-(5,5-dimethoxypentyl)-6-(dimethylphenylsilyl)-5-hexyn-3-ol (44d): The reaction of allenic zinc 29 ($\text{R} = (\text{MeO})_2\text{CH}(\text{CH}_2)_4$), prepared by the reaction of 40c with $(\text{PhMe}_2\text{Si})_3\text{ZnLi}$, with 2-methylpropanal (1.5 equiv) was carried out using 1.6 equiv of ZnCl_2 by a procedure similar to that described in a general procedure for the preparation of homopropargyl alcohols. Purification of the crude products by flash chromatography (5-30 % ethyl acetate in benzene) gave 44d (58%): $^1\text{H-NMR}$ δ 0.39 (6H, s), 0.94 (3H, d, $J = 6.7$ Hz), 0.98 (3H, d, $J = 6.7$ Hz), 1.3-1.7 (8H, m), 1.79 (1H, m), 2.66 (1H, td, $J = 4.0$ and 9.0 Hz), 3.10 (1H, ddd, $J = 4.0, 7.3,$ and 8.4 Hz), 3.33 (6H, s), 4.35 (1H, t, $J = 5.7$ Hz), 7.37 (3H, m), 7.60 (2H, m); IR (liquid film) 3480 (br), 2160, 1250, 1125, 1150, 780, 730, 700 cm^{-1} ; MS (CI),

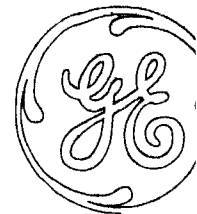
m/z (relative intensity) 377 (MH⁺, <1), 345 (MH⁺ - H₂O, 1), 327 (2), 267 (92), 89 (100).

4-Bromo-1-phenyl-3,4-nonadiene (48): ¹H-NMR δ 0.88 (3H, t, *J* = 7.1Hz), 1.25-1.45 (4H, m), 1.96 (2H, m), 2.33 (2H, dt, *J* = 2.9 and 7.6 Hz), 2.43 (2H, m), 2.76 (2H, br t, *J* = ca. 7 Hz), 5.31 (1H, tt, *J* = 2.9 and 6.5 Hz), 7.16-7.32 (5H, m); IR (liquid film) 1970, 1605, 1110, 1450, 745, 700 cm⁻¹; MS, m/z (relative intensity) 278, 280 (M⁺, <1), 199 (7), 143 (25), 91 (100).

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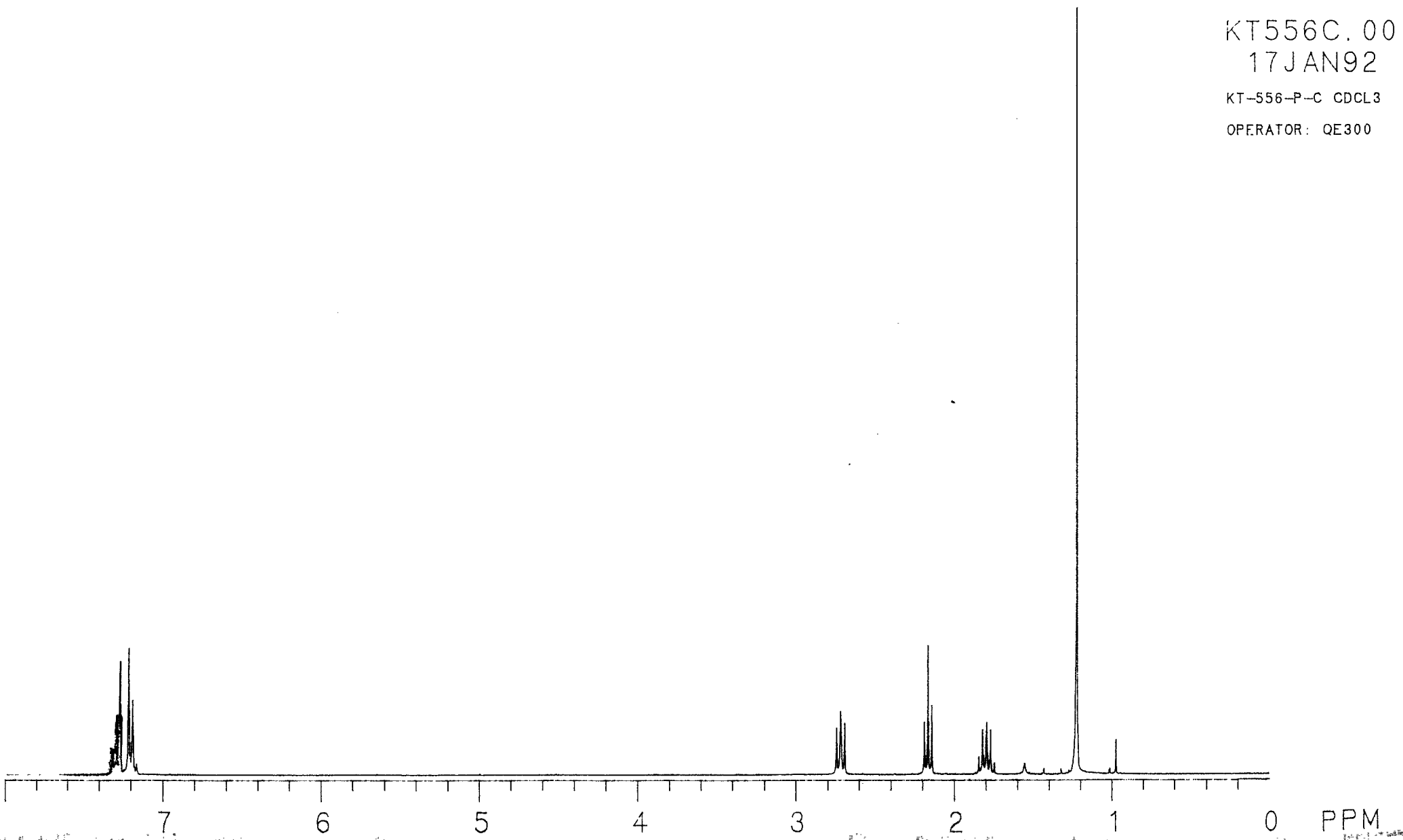
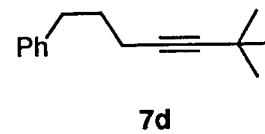


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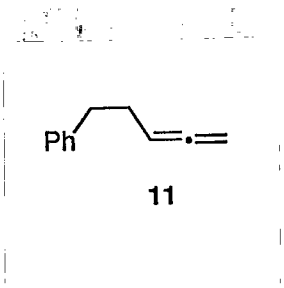
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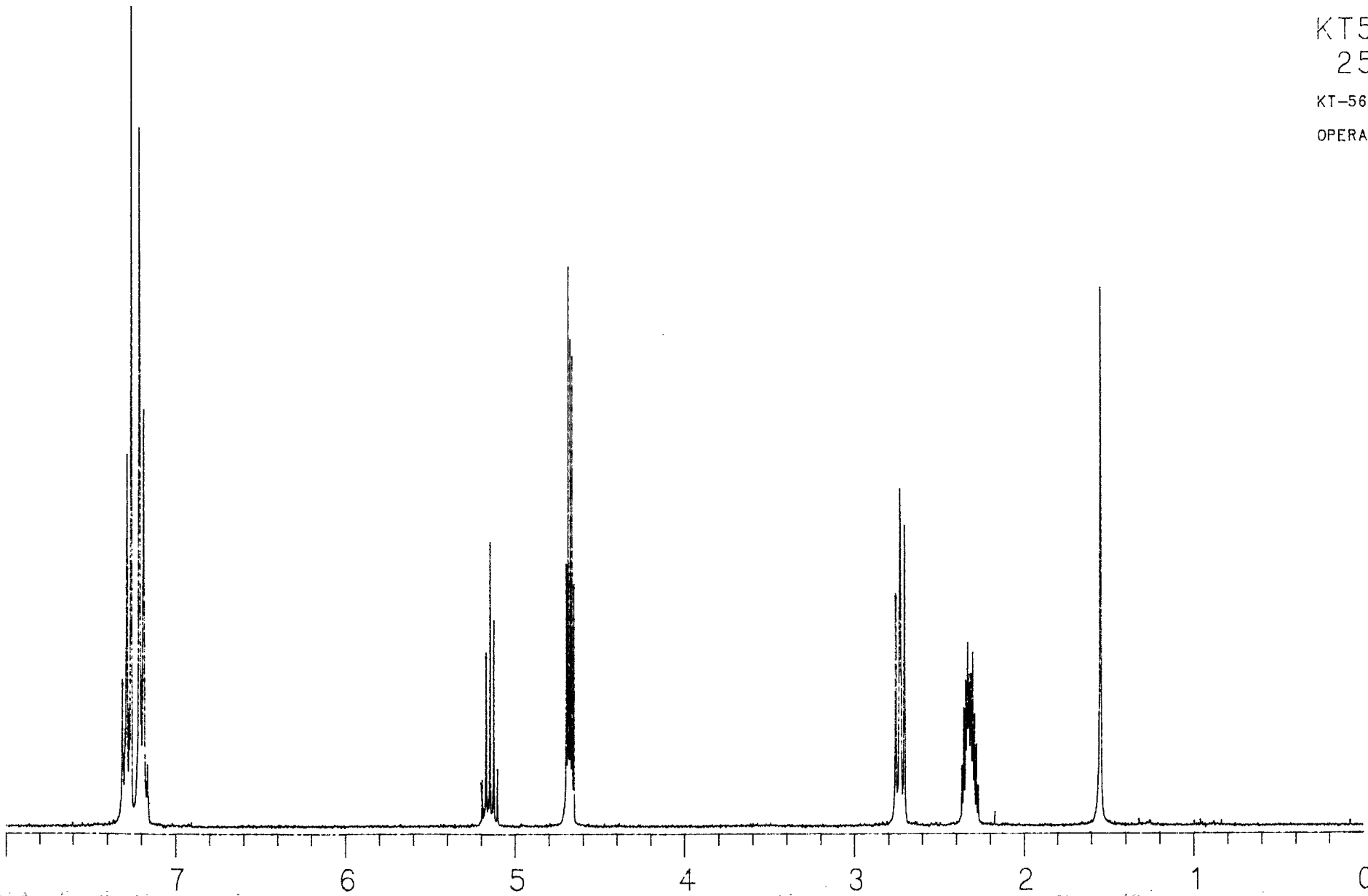
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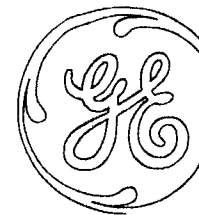


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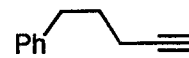


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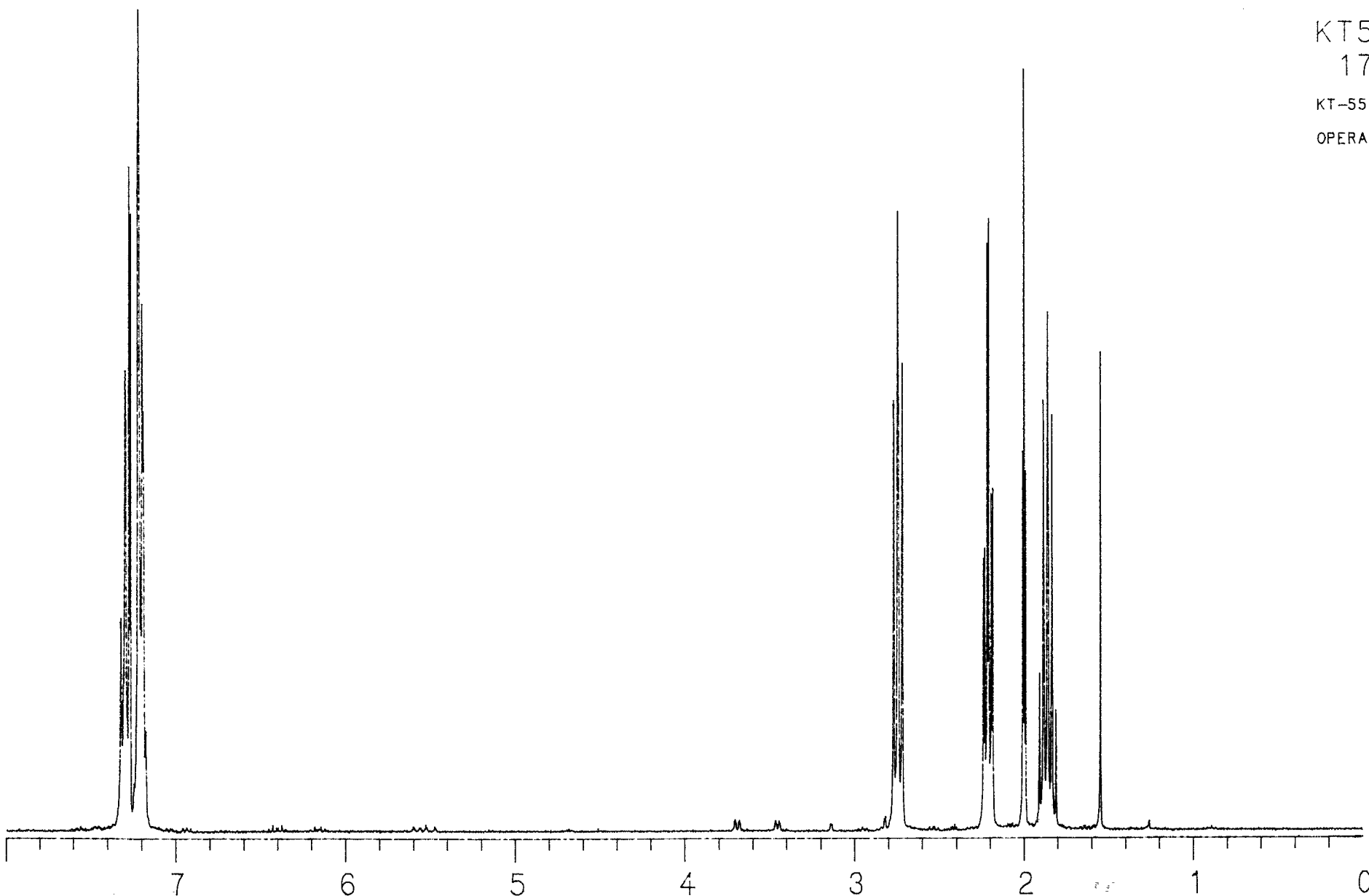
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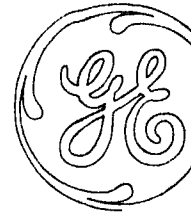
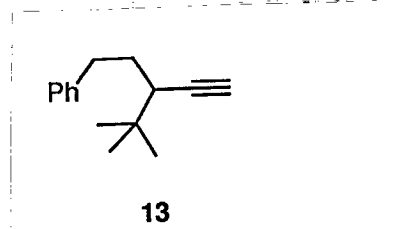
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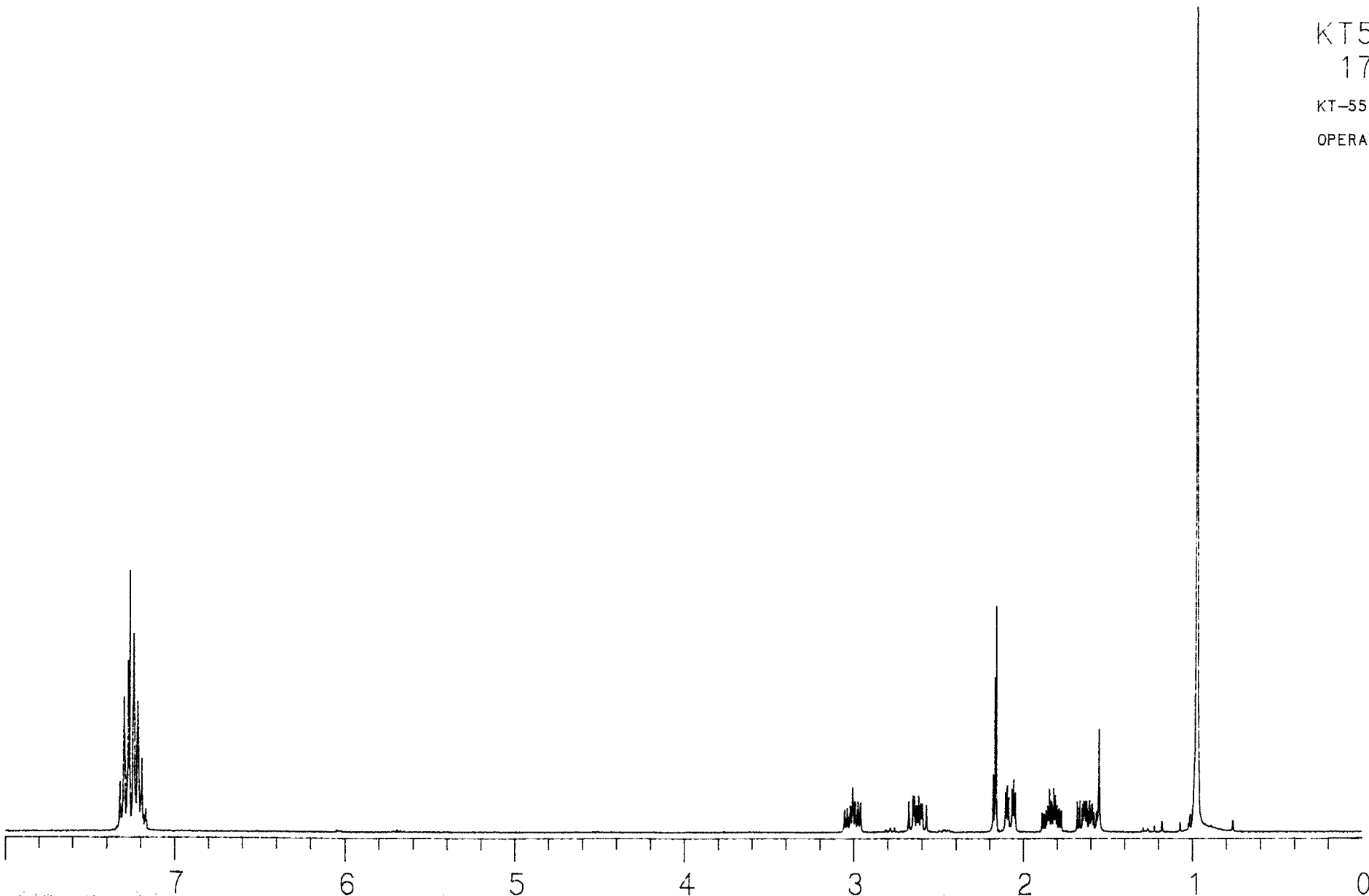
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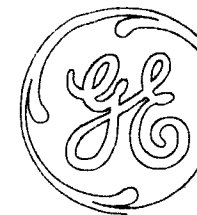


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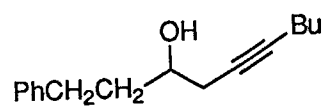


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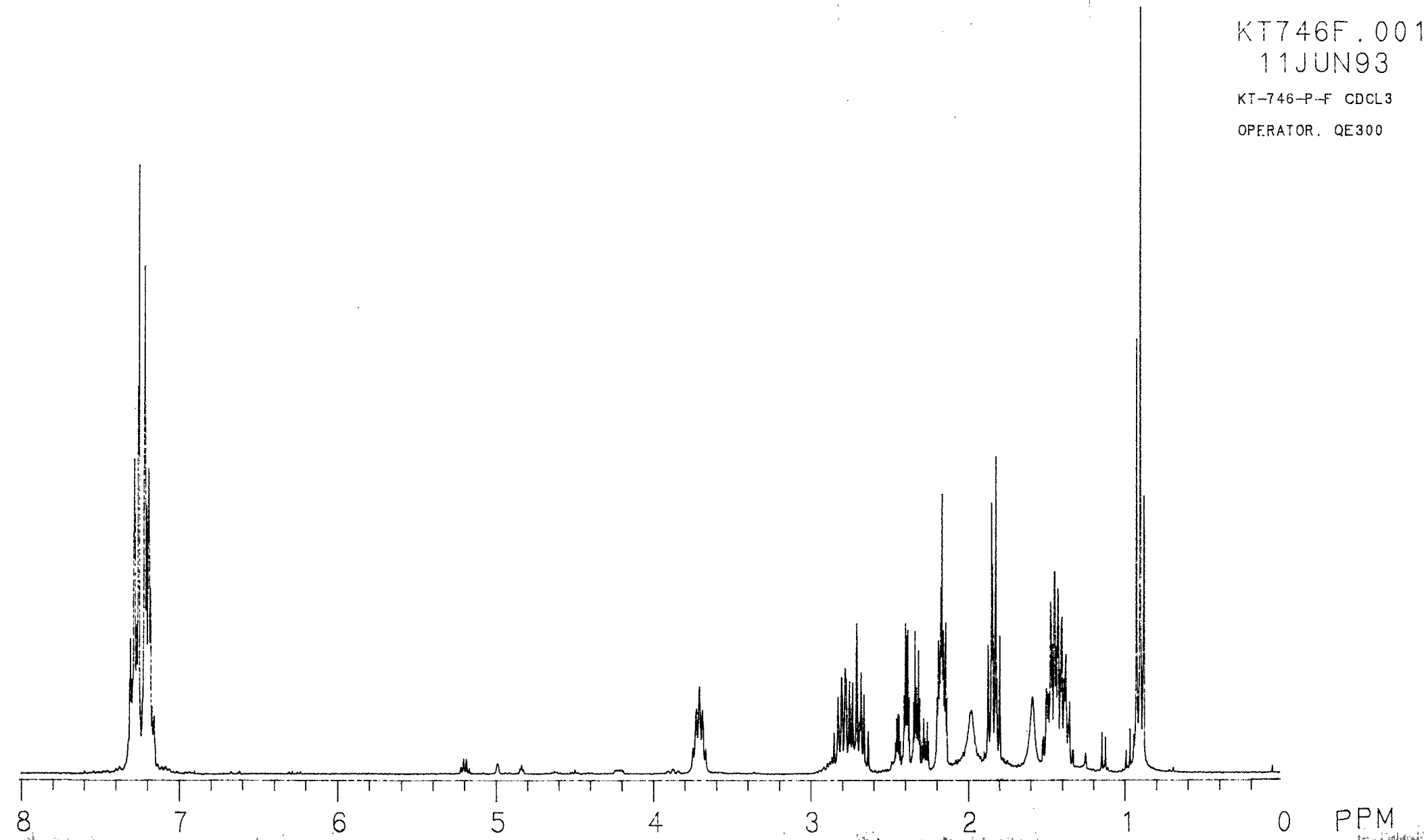
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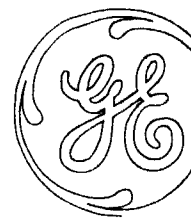
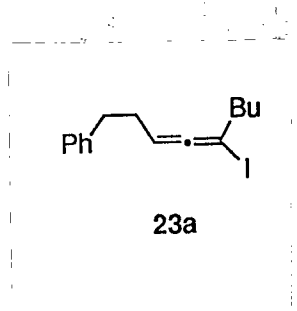
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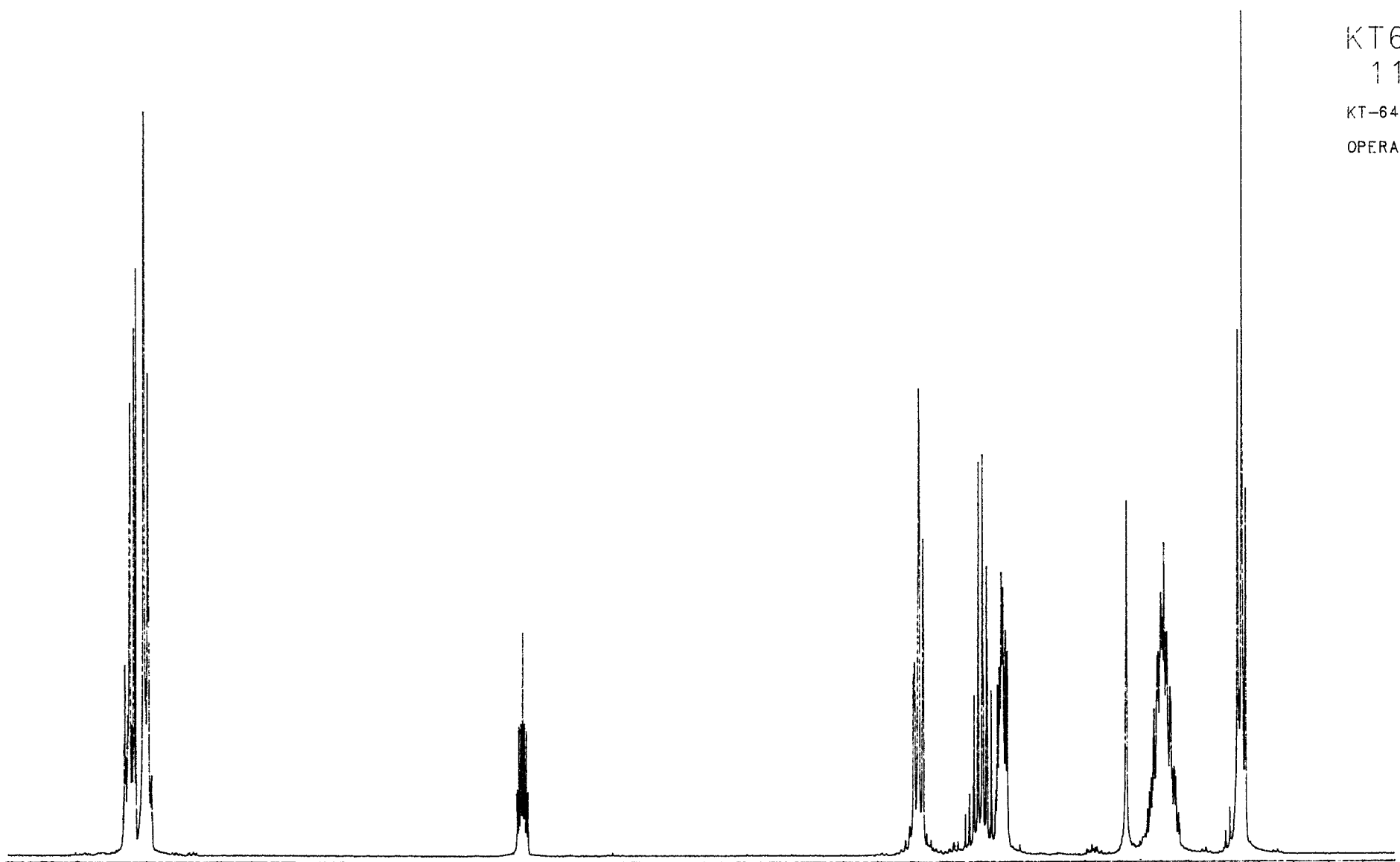
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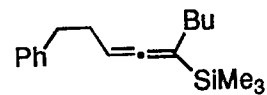
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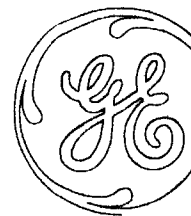


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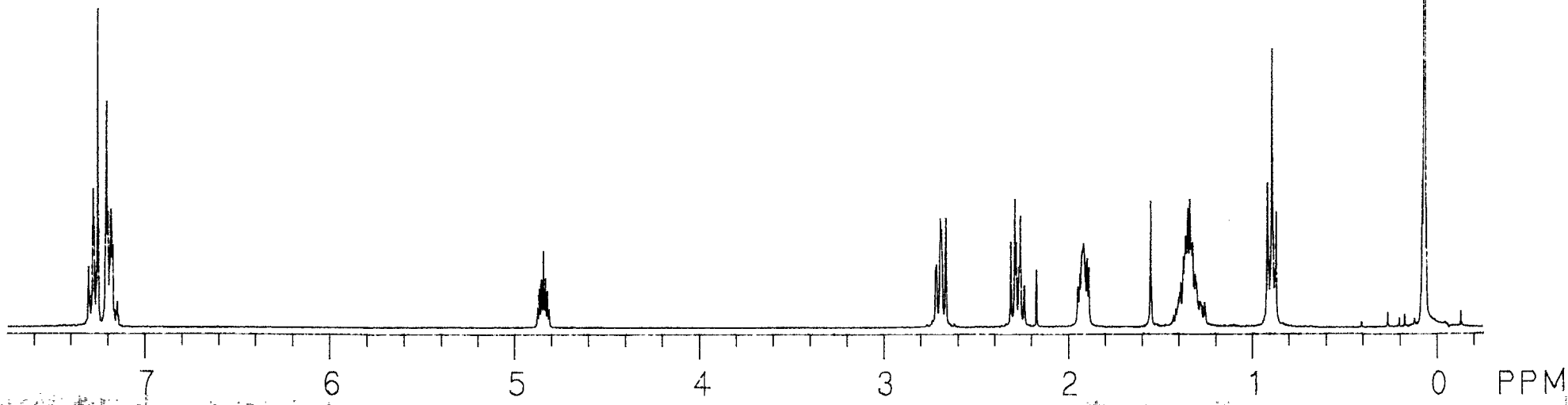
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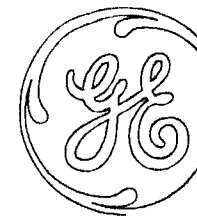
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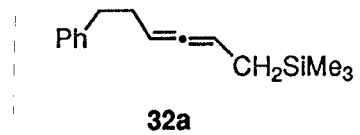
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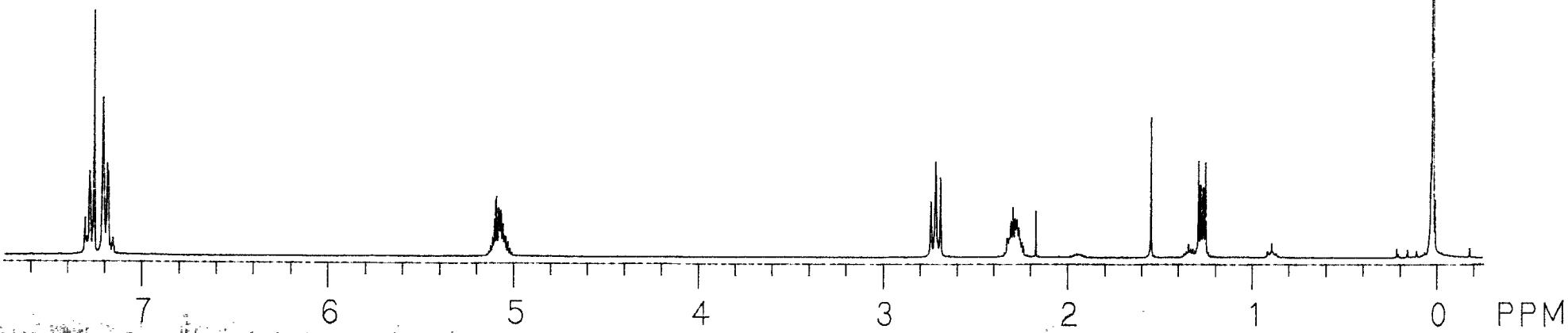


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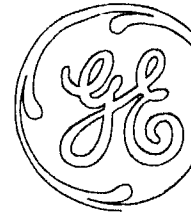
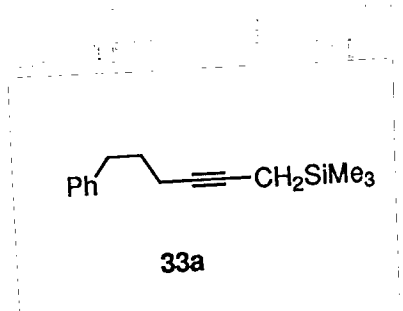
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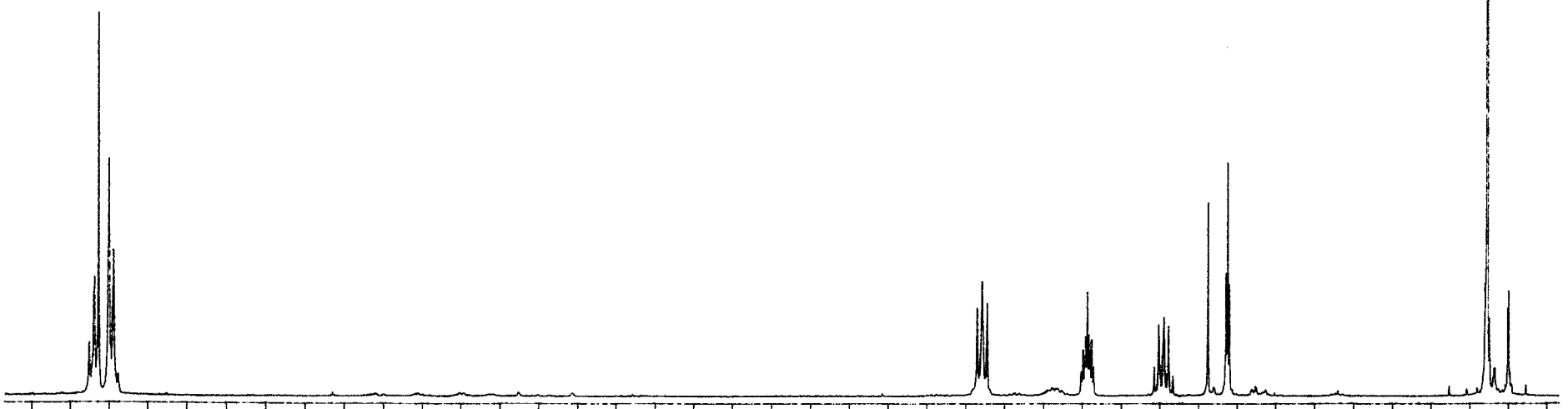


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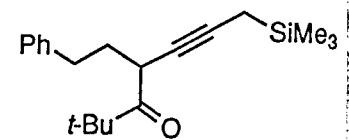
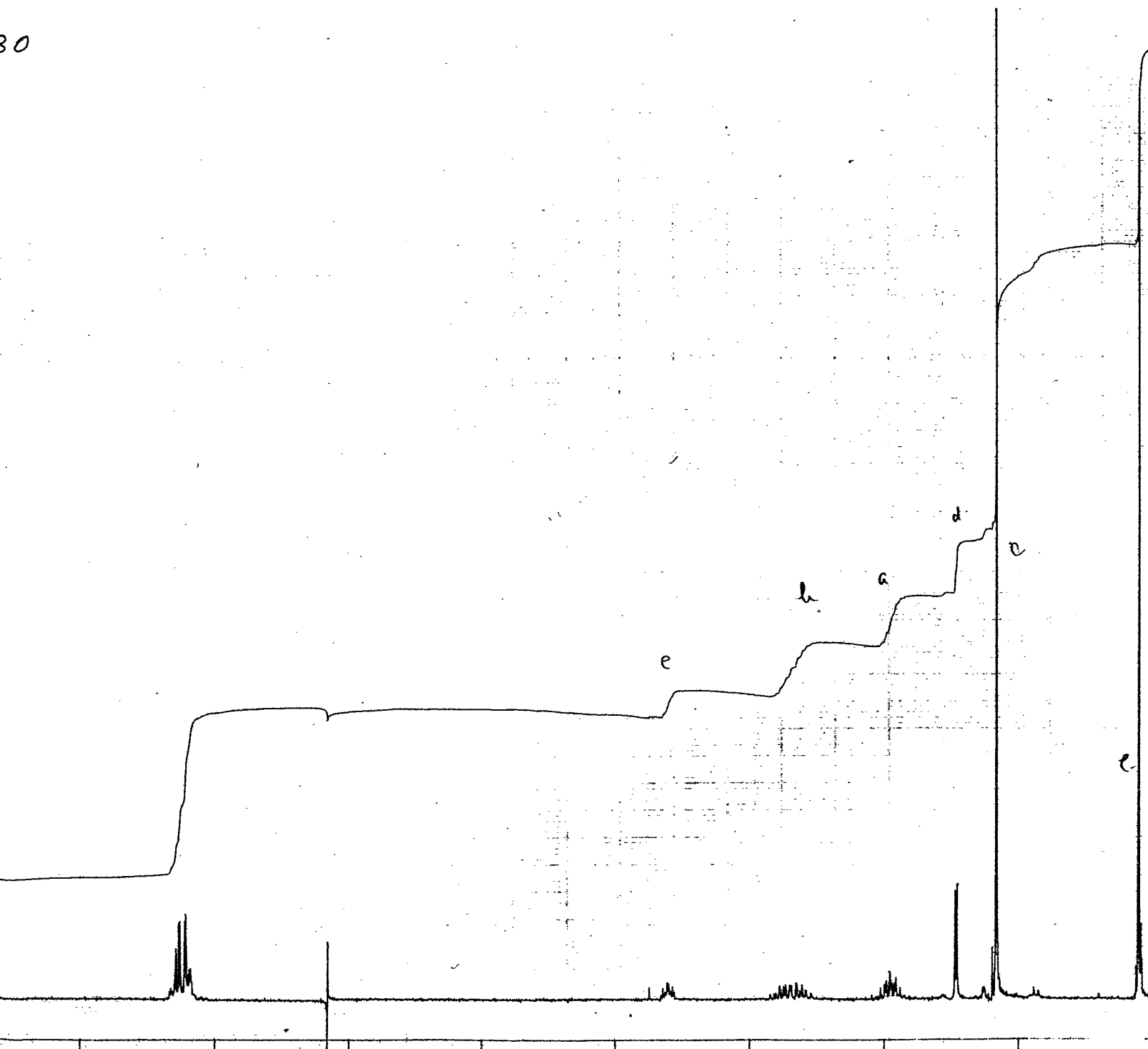


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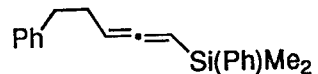
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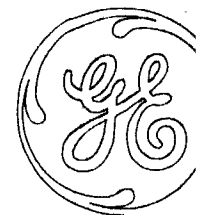


37a

3/



42a



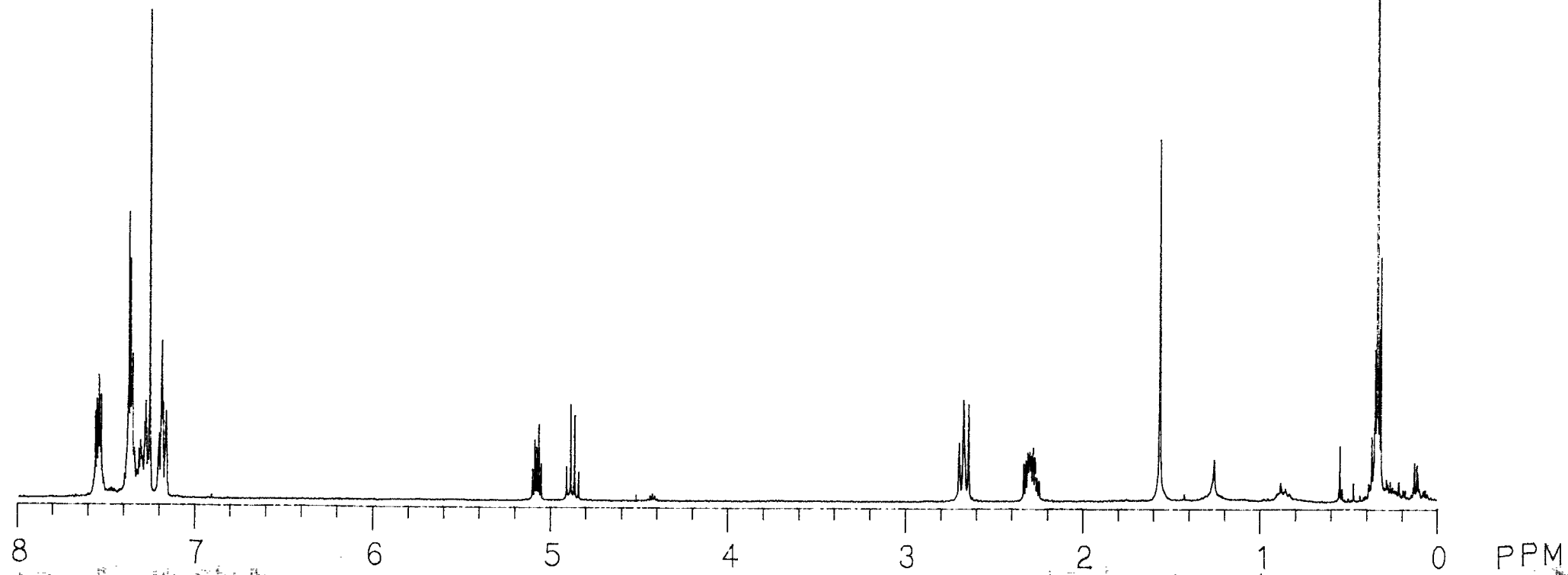
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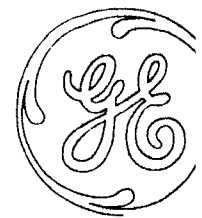
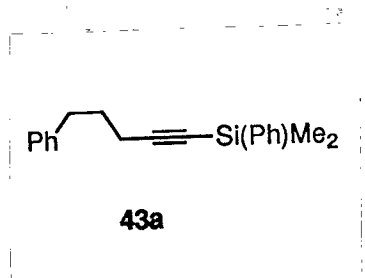
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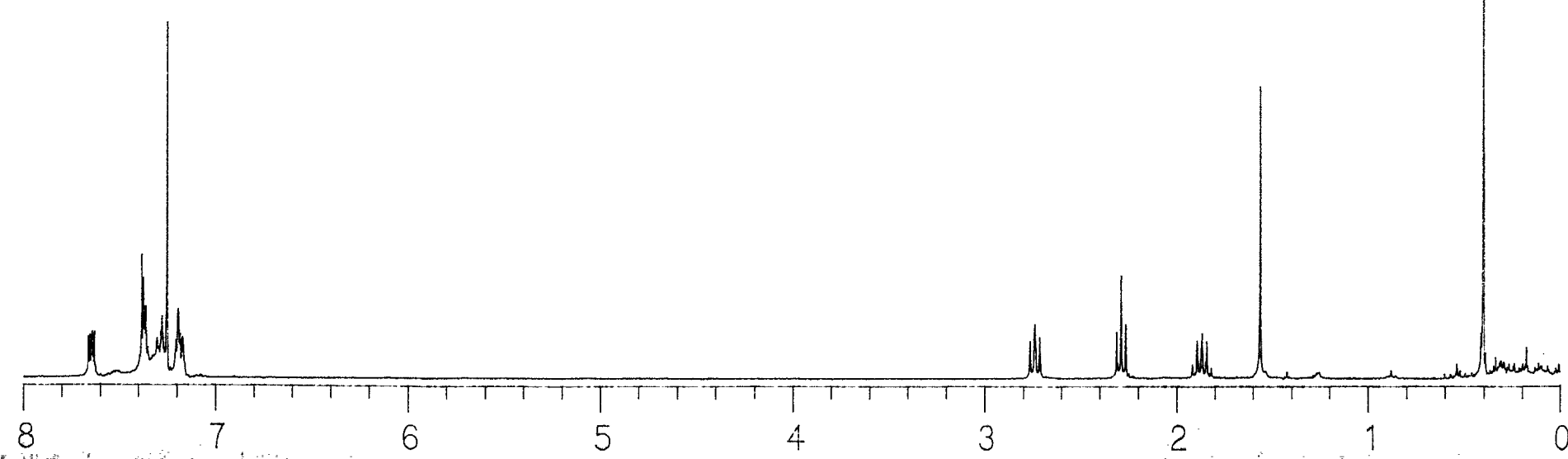
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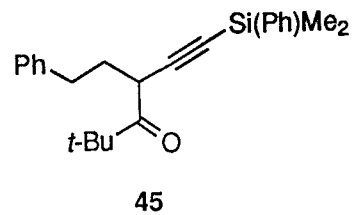


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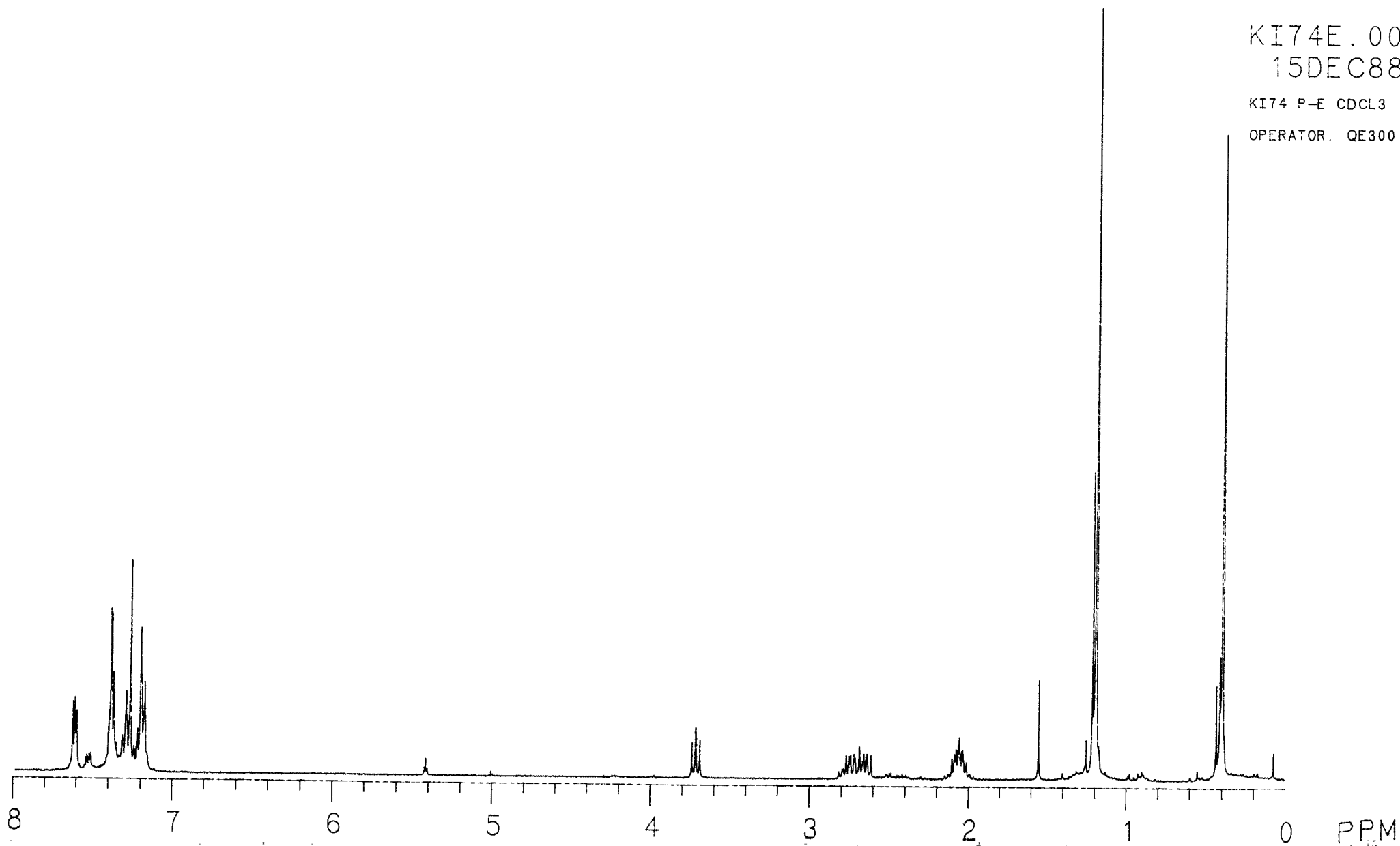
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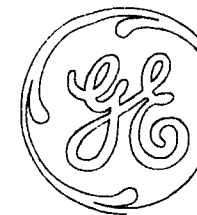
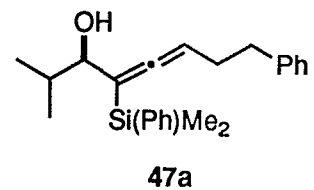
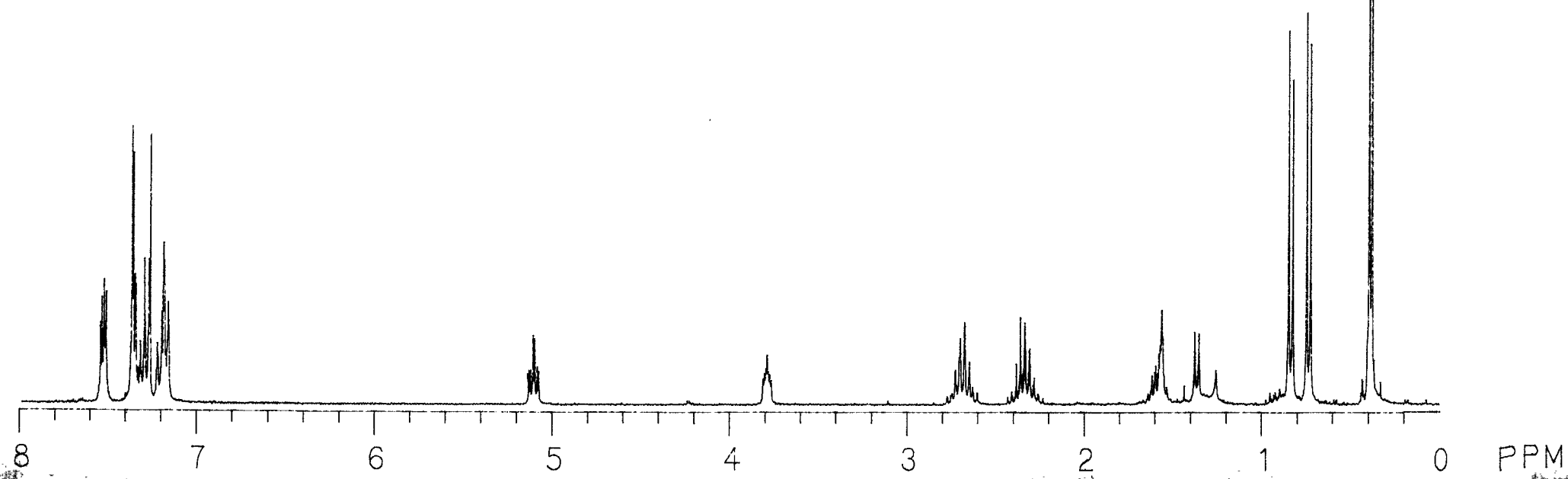


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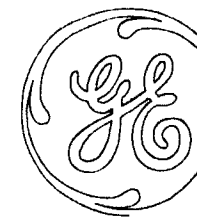
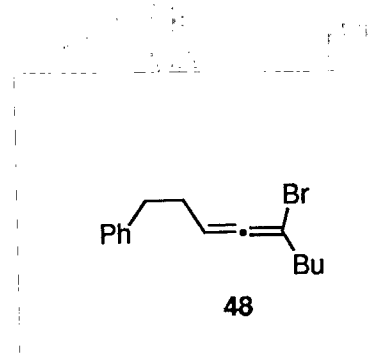
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35



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