Conversion of Bromoalkenes into Alkynes by Wet Tetra-*n*-butylammonium Fluoride

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Supporting Information

General methods. IR spectra were recorded in $CHCl_3$ solution. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution and chemical sift values are reported in ppm (δ) relative to tetramethylsilane and $CDCl_3$ (77.0 ppm) as internal standards, respectively. High resolution electron impact mass spectra were recorded at 70 eV. All air- and moisture-sensitive reactions were carried out under an argon atmosphere in dry, freshly distilled solvents under anhydrous conditions. Flash chromatography was carried out with silica gel 60 (230-400 mesh). The term “dried” refers to the drying of an organic solution over $MgSO_4$ followed by filtration.

Genenral procedure for dehydrobromination of 1,1-dibromoalkenes 1a-1f and (*Z*)-1-bromoalkenes 3a-3d. 1,1-Dibromoalkene (**1**, 0.5 mmol) was dissolved in 2.5 mL of DMF. TBAF·$3H_2O$ (0.78 g, 2.5 mmol) was added to the solution and the reaction mixture was heated at 60 °C for 0.5-1 h (TLC). The reaction mixture was cooled to room temperature and diluted with diethyl ether (50 mL). The organic phase was washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane) to give 1-bromoalkyne **2**.

1-Bromoundec-1-yne (2a). IR ($CHCl_3$) 2210, 1446, 1431 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (3H, d, *J* = 6.8 Hz), 1.26~1.38 (12H, m), 1.51 (2H, q, *J* = 7.3 Hz), 2.19 (2H, t, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.6, 22.6, 28.3, 28.8, 29.4, 29.1, 29.2, 29.41, 31.8, 37.4, 80.5; HREIMS *m/z* calcd for $C_{11}H_{19}{}^{79}Br$ 230.0670, found 230.0672.

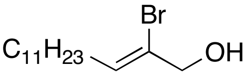
1-Bromo-4,8-dimethylnon-7-en-1-yne (2b). IR ($CHCl_3$) 2213 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.23 (1H, td, *J* = 13.7, 6.6 Hz), 1.65 (1H, m), 1.61 and 1.68 (each 3H, s), 1.94–1.98 (2H, m), 2.10 (1H, dd, *J* = 16.6, 7.3 Hz), 2.19 (1H, dd, *J* = 16.6, 5.4 Hz), 5.11 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 19.4, 25.5, 25.7, 26.9, 32.0, 36.0, 38.1, 79.2, 124.3, 131.5; HREIMS *m/z* calcd for $C_{11}H_{17}{}^{79}Br$ 228.0514, found 228.0521.

1-(4-Bromobut-3-ynyl)benzene (2c). IR ($CHCl_3$) 2215, 1602, 1497 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.48 (2H, t, *J* = 7.6 Hz), 2.83 (2H, t, *J* = 7.6 Hz), 7.19-7.32 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 34.7, 38.7, 79.6, 126.4, 128.3, 128.4, 140.2; HREIMS *m/z* calcd for $C_{10}H_9{}^{79}Br$ 207.9888, found 207.9869.

1-((*E*)-4-Bromobut-1-en-3-ynyl)benzene (2d). IR ($CHCl_3$) 2204, 1613, 1597, 1575, 1489 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.11 (1H, d, *J* = 16.1 Hz), 6.99 (1H, d, *J* = 16.1 Hz), 7.24-7.38 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.3, 79.4, 107.5, 126.3, 128.7, 128.9, 135.8, 142.9; HREIMS *m/z* calcd for $C_{10}H_7{}^{79}Br$ 205.9731, found 205.9744.

1-(2-Bromoethynyl)benzene (2e). IR ($CHCl_3$) 2196, 1597, 1486, 1442 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.46 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.7, 80.0, 122.7, 128.3, 128.7, 132.0; HREIMS *m/z* calcd for $C_8H_5{}^{79}Br$ 179.9575, found 179.9568.

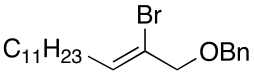
2-(2-Bromoethynyl)naphthalene (2f). IR ($CHCl_3$) 2198, 1597, 1503 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.96 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.0, 80.4, 119.9, 126.6, 126.9, 127.7, 127.8, 128.0, 128.4, 132.2, 132.8, 132.9; HREIMS *m/z* calcd for $C_{12}H_7{}^{79}Br$ 229.9731, found 229.9739.



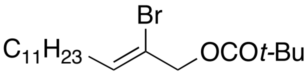
(Z)-2-Bromotetradeac-2-en-1-ol (6a). A solution of dodecanal (2.4 mL, 10.85 mmol) and (triphenylphosphoranylidene)acetaldehyde (3.96 g, 13.02 mmol) in toluene (68 mL) was refluxed for 19 h. The reaction mixture was cooled to room temperature, diluted with hexane (100 mL), and filtered through a short pad of Celite. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (6% EtOAc in hexane) to give (*E*)-tetradec-2-enal (1.30 g, 57%).

To a solution of the above unsaturated aldehyde in CH_2Cl_2 (2.4 mL) was added a solution of Br_2 in CH_2Cl_2 (4.7 mL) at 0 °C. After stirring at 0 °C for 40 min, Et_3N (1.85 mL, 12.41 mmol) was added and the mixture was stirred for 1 h at room temperature. The reaction mixture was diluted with CH_2Cl_2, washed with 10% HCl, water, and brine, dried, and concentrated under reduced pressure. The residue was purified by flash chromatography (40% CH_2Cl_2 in hexane) to give (*Z*)-2-bromotetradec-2-enal (1.07 g, 60%).

To a solution of (*Z*)-2-bromotetradec-2-enal obtained above (1.07 g, 3.70 mmol) in THF-H_2O (9:1, 17 mL) was added $NaBH_4$ (212 mg, 5.55 mmol) at 0 °C, and the reaction mixture was stirred at 0 °C for 45 min. The reaction was quenched with saturated aqueous NH_4Cl and the reaction mixture was extracted with ethyl acetate. The extract was washed with water and brine, dried, and concentrated. The residue was purified by flash chromatography (12% ethyl acetate in hexane) to give **6a** (0.99 g, 92%). IR ($CHCl_3$) 3601, 1657, 1601, 1003 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7.3 Hz), 1.26~1.43 (18H, m), 1.96 (1H, t, J = 6.8 Hz, OH), 2.19 (2H, q, J = 7.3 Hz), 4.25 (2H, d, J = 6.3 Hz), 6.00 (1H, t, J= 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 28.2, 29.2, 29.3, 29.4, 29.5, 29.6 (2xC), 30.8, 31.9, 68.5, 126.5, 130.7; HREIMS *m/z* calcd for $C_{14}H_{27}{}^{79}BrO$ 290.1245, found 290.1287.

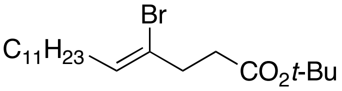


(*Z*)-1-Benzyloxy-2-Bromotetradec-2-ene (6b). A mixture of **6a** (260 mg, 0.896 mmol), trimethylchlorosilane (0.45 mL, 3.584 mmol), benzaldehyde (0.36 mL, 3.549 mmol), triethylsilane (0.6 mL, 3.755 mmol) in dry CH_2Cl_2 (5 mL) was stirred for 6 h at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (3% ethyl acetate in hexane) to give **6b** (330 mg, 98%): IR ($CHCl_3$) 1653, 1601, 1496, 1466, 1455, 1107 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.8), 1.26~1.42 (18H, m), 2.22 (2H, q, J = 6.8), 4.16 (2H, s), 4.52 (2H), 6.00 (1H, t, J = 6.8 Hz), 7.25~7.36 (5H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 28.2, 29.2, 29.3, 29.4, 29.5, 29.6 (2xC), 30.9, 31.9, 71.5, 74.9, 123.3, 127.7, 127.9 (2xC), 128.4 (2xC), 132.4, 137.8; HREIMS *m/z* calcd for $C_{21}H_{33}{}^{79}BrO$ 380.1715, found 380.1757.



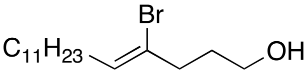
(*Z*)-2-Bromotetradec-2-enyl pivalate (6c). A solution of **6a** (290 mg, 1.00 mmol) and pivaloyl chloride (0.24 mL, 1.948 mmol) in pyridine (3 mL) was stirred for 1.5 h at room temperature. The reaction mixture was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and brine, dried, and concentrated under reduced pressure. The residue was purified by flash chromatography (5% ethyl acetate in hexane) to give **6c** (360 mg, 88%): IR ($CHCl_3$) 1725, 1658 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.8 Hz), 1.23 (9H, s), 1.20~1.39 (16H, m), 1.37~1.46 (2H, m), 2.19

(2H, q, *J* = 6.8 Hz), 4.72 (2H, s), 6.02 (1H, t, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.1, 22.7, 27.1 (3xC), 28.1, 29.1, 29.3, 29.4, 29.5, 29.6 (2xC), 30.9, 31.9, 38.8, 68.6, 120.7, 133.6, 177.7; HREIMS *m/z* calcd for $C_{19}H_{35}{}^{79}BrO$ 374.1820, found 374.1839.

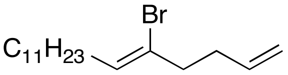


(*Z*)-*tert*-Butyl 4-bromohexadec-4-enoate (6d). To a solution of **6a** (382 mg, 1.312 mmol) in CH_2Cl_2 (6.0 mL) were added triphenylphosphine (516 mg, 1.968 mmol) and carbon tetrabromide (544 mg, 1.640 mmol), and the reaction mixture was stirred at 0 °C for 1.5 h. The reaction mixture was diluted with diethyl ether, passed through a plug of Celite, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane) to give (*Z*)-1,2-dibromo-tetradec-2-ene (416 mg, 90%).

To a solution of LiHMDS (1M solution in THF, 1.55 mL, 1.55 mmol) in THF (1.0 mL) was added *t*-butyl acetate (0.21 mL, 1.544 mmol) at -80 °C. After the reaction mixture was stirred at -80 °C for 45 min, a solution of (*Z*)-1,2-dibromotetradec-2-ene (273 mg, 0.772 mmol) in THF (1.0 mL) and HMPA (134 μL, 0.772 mmol) were added. After stirring at -80 °C for 1.5 h, the reaction was quenched with saturated aqueous NH_4Cl and the reaction mixture was extracted with diethyl ether. The extract was washed with water and brine, dried, and concentrated under reduced pressure. The residue was purified by flash chromatography (3% ethyl acetate in hexane) to give **6d** (121 mg, 70%): IR (CHCl$_3$) 1720, 1654 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26~1.37 (18H, m), 1.44 (9H, s), 2.12 (2H, q, *J* = 6.8 Hz), 2.47 (2H, t, *J* = 6.8 Hz), 2.70 (2H, t, *J* = 6.8 Hz), 5.70 (1H, t, *J* = 6.8 Hz) ; ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.1, 22.7, 28.1 (3xC), 28.4, 29.2, 29.3, 29.4, 29.5, 29.6 (2xC), 31.3, 31.9, 34.6, 37.0, 80.5, 125.9, 129.8, 171.6; HREIMS *m/z* calcd for $C_{20}H_{37}{}^{79}BrO_2$ 388.1977, found 388.1951.



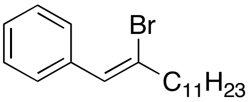
(*Z*)-4-Bromo-5-phenylpent-4-en-1-ol (6e). To a solution of **6d** (375 mg, 0.965 mmol) in CH_2Cl_2 (5 mL) cooled to -20 °C was added DIBALH (0.98 M solution in hexane, 3.95 mL, 3.871 mmol), and the reaction mixture was stirred at -20 °C for 3 h. The reaction was quenched with saturated aqueous potassium sodium tartrate. The mixture was diluted ethyl acetate and stirred vigorously at room temperature until the layer became clear. The organic layer was washed with water and brine, dried, and concentrated under reduced pressure. The residue was purified by flash chromatography (15% ethyl acetate in hexane) to give **6e** (240 mg, 78%): IR (CHCl$_3$) 3628, 3450, 1654 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26~1.38 (18H, m), 1.82 (2H, quint, *J* = 6.8 Hz), 2.14 (2H, q, *J* = 6.8 Hz), 2.54 (2H, t, *J* = 6.8 Hz), 3.67 (2H, t, *J* = 6.4 Hz), 5.68 (1H, t, *J* =6.8 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.1, 22.7, 28.4, 29.2, 29.3, 29.4, 29,5, 29.6 (2xC), 31.1, 31.3, 31.88, 37.8, 61.5, 127.2, 129.4; HREIMS *m/z* calcd for $C_{16}H_{31}{}^{79}BrO$ 318.1588, found 318.1563.



(*Z*)-5-bromoheptadeca-1,5-diene (6f). To a solution of **6d** (285 mg, 0.734 mmol) in CH_2Cl_2 (5 mL) cooled to -80 °C was added DIBALH (0.98 M solution in hexane, 0.75 mL, 0.735 mmol), and the reaction mixture was stirred at -80 °C for 40 min. The reaction was quenched with saturated aqueous potassium sodium tartrate. The mixture was diluted ethyl acetate and stirred vigorously at room temperature until the layer became clear. The organic layer was washed with water and brine, dried, and concentrated under reduced pressure. The residue was purified by flash chromatography

(6% ethyl acetate in hexane) to give (*Z*)-4-bromohexadec-4-enal (162 mg, 70%).

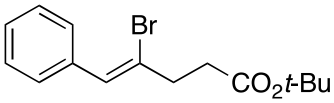
To a suspension of $Ph_3P^+CH_3Br^-$ (345 mg, 0.969 mmol) in THF (3 mL) cooled to 0 °C was added KHMDS (0.5 M solution in toluene, 1.86 mL, 0.930 mmol) and the reaction mixture was stirred at 0 °C for 1 h. The resulting ylide solution was cooled to -80 °C, and a solution of the above aldehyde (162 mg, 0.513 mmol) in THF (1 mL) was added. After reaction mixture was stirred at -80 °C for 40 min and then at room temperature for 1 h, the reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with diethyl ether, washed with water and brine, dried, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane) to give **6f** (46 mg, 85%): IR ($CHCl_3$) 1654, 1641, 1466, 789 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.3 Hz), 1.26~1.39 (18H, m), 2.14 (2H, q, *J* = 6.8 Hz), 2,30 (2H, q, *J* = 6.8 Hz), 2.50 (2H, t, *J* = 6.8 Hz), 4.97~5.00 (1H, m), 5.05 (1H, ddd, *J* = 17.1, 2.9, 1.5 Hz), 5.64 (1H, t, *J* = 6.8 Hz), 5.77 (1H, ddt, *J* = 17.1, 10.2, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 28.5, 29.2, 29.4, 29.5, 29.6 (2xC), 29.7, 31.3, 31.9, 32.5, 41.0, 115.3, 127.2, 129.2, 137.0; HREIMS *m/z* calcd for $C_{17}H_{31}{}^{79}BrO$ 316.1609, found 318.1588.



((*Z*)-2-bromotridec-1-enyl)benzene (6g). To a solution of (*Z*)-2-bromo-3-phenylacrylaldehyde[20b] (1.21 g, 5.741 mmol) in THF-H_2O (9:1, 17 mL) was added $NaBH_4$ (326 mg, 8.612 mmol), and the reaction mixture was stirred at 0 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl and the reaction mixture was extracted with ethyl acetate. The extract was washed with water and brine, dried, and concentrated under reduced pressure. The residue was purified by flash chromatography (30% ethyl acetate in hexane) to give (*Z*)-2-bromo-3- phenylprop-2-en-1-ol (1.21 g, 99%).

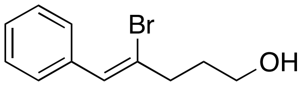
To a solution of the above alcohol (1.16 g, 5.47 mmol) in CH_2Cl_2 (6.4 mL) were added triphenylphosphine (516 mg, 1.968 mmol) and carbon tetrabromide (544 mg, 1.640 mmol) at 0 °C. After being stirred at 0 °C for 20 min, the reaction mixture was diluted with diethyl ether, passed through a plug of Celite, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane) to give ((*Z*)-2,3-dibromoprop-1-enyl)benzene (1.40 g, 93%).

To a suspension of ((*Z*)-2,3-dibromoprop-1-enyl)benzene (315 mg, 1.114 mmol) and CuCl (5.65 mg, 0.057 mmol) cooled to 0 °C was added a THF solution of decylmagnesium bromide prepared from bromodecane (0.71 mL, 3.426 mmol) and Mg (250 mg, 10.28 mmol) in THF (3.4 mL). After stirring at 0°C for 1 h, the reaction was quenched with saturated aqueous NH_4Cl and the reaction mixture was extracted with diethyl ether. The extract was washed with water and brine, dried, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane) to give **6g** (130 mg, 32%): IR ($CHCl_3$) 1628, 1601, 1494, 1466 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 7.3 Hz), 1.25~1.32 (16H), 1.65 (2H, quint, *J* = 7.3 Hz), 2.60 (2H, t, *J* = 7.8 Hz), 6.97 (1H, s), 7.12~7.57 (5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 28.5, 28.6, 29.3 (2xC), 29.5, 29.6 (2xC), 31.9, 36.2, 127.2, 128.1 (2xC), 128.4 (2xC), 131.1, 132.1, 136.2; HREIMS *m/z* calcd for $C_{19}H_{29}{}^{79}Br$ 336.1453, found 336.1462.



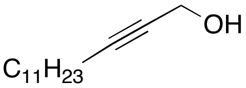
(*Z*)-*tert*-Butyl 4-bromo-5-phenylpent-4-enoate (6h). To a solution of LiHMDS (1M solution in THF, 7.86 mL, 7.860 mmol) in THF (5 mL) was added *t*-butyl acetate (1.05 mL, 7.86 mmol) at -80 °C. After the reaction mixture was stirred at -80 °C for 1 h, a solution of ((*Z*)-2,3-dibromoprop-

1-enyl)benzene (1.08 g, 3.928 mmol) in THF (8 mL) and HMPA (0.68 mL, 3.928 mmol) were added. After stirring at -80 °C for 1 h, the reaction was quenched with saturated aqueous NH_4Cl and the reaction mixture was extracted with diethyl ether. The extract was washed with water and brine, dried, and concentrated under reduced pressure. The residue was purified by flash chromatography (6% ethyl acetate in hexane) to give **6h** (766 mg, 62%): IR ($CHCl_3$) 1722, 1630, 1600, 1494, 1369, 1150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.46 (9H, s), 2.62 (2H, t, *J* = 7.8 Hz), 2.90 (2H, td, *J* = 6.8, 1.0 Hz), 6.81 (1H, s), 7.25~7.55 (5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1 (3xC), 34.5, 38.7, 80.7, 125.5, 127.7 (2xC), 128.1, 128.5, 128.8 (2xC), 135.8, 171.5; HREIMS *m/z* calcd for $C_{15}H_{19}{}^{79}BrO_2$ 310.0568, found 310.0531.

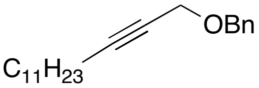


(*Z*)-4-Bromo-5-phenylpent-4-en-1-ol (6i). To a solution of **6h** (504 mg, 1.625 mmol) in CH_2Cl_2 (10 mL) cooled to -20°C was added DIBALH (0.98 M solution in hexane, 5 mL, 4.90 mmol), and the reaction mixture was stirred at -20°C for 2.5 h. The reaction was quenched with saturated aqueous potassium sodium tartrate. The reaction mixture was diluted ethyl acetate and stirred vigorously at room temperature until the layer became clear. The organic layer was washed with water and brine, dried, and concentrated under reduced pressure. The residue was purified by flash chromatography (30% ethyl acetate in hexane) to give **6i** (320 mg, 81%): IR ($CHCl_3$) 3627, 3455, 1638, 1598, 1490, 1444 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (1H, OH), 1.92 (2H, dd, *J* = 7.3, 6.3 Hz), 2.73 (2H, t, *J* = 7.3 Hz), 3.73 (2H, t, *J* = 5.9 Hz), 6.79 (1H, s), 7.23~7.57 (5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 39.5, 61.4, 126.9, 127.7(2xC), 128.1, 128.8 (2xC), 131,5, 135.9; HREIMS *m/z* calcd for $C_{11}H_{13}{}^{79}BrO$ 240.0150, found 240.0173.

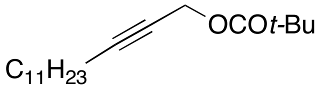
General Procedure for Dehydrobromination of Bromoalkenes. Bromoalkene (0.5 mmol) was dissolved in 2.5 mL of DMF and TBAF·$3H_2O$ (0.78 g, 2.5 mmol) was added to the solution. The reaction mixture was heated at 60 °C for 1~2 h (TLC). The reaction mixture was cooled to room temperature and diluted with diethyl ether (30 mL). The organic phase was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate–hexane) to give the alkyne product.



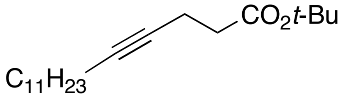
Tetradec-2-yn-1-ol (7a). Purified by flash chromatography (3% ethyl acetate in CH_2Cl_2). IR ($CHCl_3$) 3608, 3442, 2223, 1466, 1379, 1135, 1003 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26~1.39 (16H, m), 1.50 (2H, quint, *J* = 7.3 Hz), 1.62 (1H, t, *J* = 5.8 Hz, OH), 2.21 (2H, tt, *J* = 7.3, 2.0 Hz), 4.25 (2H, dt, *J* = 5.8, 2.0 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 18.7, 22.7, 28.6, 28.9, 29.1, 29.3, 29.5, 29.6 (2xC), 31.9, 51.4, 78.2, 86.7; HREIMS *m/z* calcd for $C_{14}H_{26}O$ 210.1984, found 210.1997.



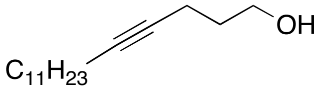
1-Benzyloxytetradec-2-yne (7b). Purified by flash chromatography (5% ethyl acetate in hexane). IR ($CHCl_3$), 2223, 1496, 1455, 1354, 1070 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26~1.41 (16H, m), 1.53 (2H. quint, *J* = 7.3 Hz), 2.24 (2H, tt, *J* = 7.3, 2.4 Hz), 4.16 (2H, t, *J* = 2.4 Hz), 4.58 (2H, s), 7.28~7.37 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 18.8, 22.7, 28.6, 28.9, 29.1, 29.3, 29.5, 29.6 (2xC), 31.9, 57.7, 71.3, 75.8, 87.4, 127.7, 128.1 (2xC), 128.4 (2xC), 137.7; HREIMS *m/z* calcd for $C_{21}H_{32}O$ 300.2453, found 300.2464.



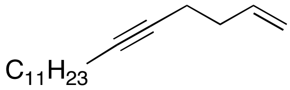
Tetradec-2-ynyl pivalate (7c). Purified by flash chromatography (10% ethyl acetate in hexane). IR ($CHCl_3$) 2231, 1729, 1479, 1461, 1374, 1281, 1249, 1151 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.4 Hz), 1.22 (9H, s), 1.20~1.38 (16H, m), 1.50 (2H, quint, *J* = 7.3 Hz), 2.20 (2H, tt, *J* = 7.3, 2.4 Hz), 4.64 (2H, t, *J* = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 18.7, 22.7, 27.7, 27.2, 28.4, 28.8, 28.9, 29.3, 29.5, 29.6, 31.9, 38.7, 52.8, 74.2, 87.3, 177.9; HREIMS *m/z* calcd for $C_{19}H_{34}O_2$ 294.2559, found 294.2572.



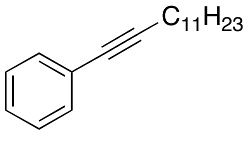
***tert*-Butyl hexadec-4-ynoate (7d).** Purified by flash chromatography (4% ethyl acetate in hexane). IR ($CHCl_3$) 1722, 1469, 1368, 1153 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26~1.36 (16H, m), 1.45 (9H, s), 1.46 (2H, m), 2,12 (2H, t, *J* = 6.8 Hz), 2.41 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.9, 18.7, 22.7, 28.1 (3xC), 28.8, 29.0, 29.2, 29.3, 29.5, 29.6 (2xC), 31.9, 35.3, 78.3, 80.6, 80.9, 171.6; HREIMS *m/z* calcd for $C_{20}H_{36}O_2$ 308.2715, found 308.2702.



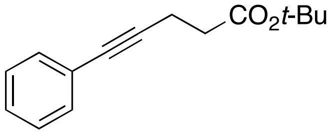
Hexadec-4-yn-1-ol (7e). Purified by flash chromatography (30% ethyl acetate in hexane). IR ($CHCl_3$) 3628, 3529, 1466, 1436, 1053 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26~1.37 (16H, m), 1.47 (2H, quint, *J* = 6.8 Hz), 1.65 (1H, OH), 1.74 (2H, quint, *J* = 6.8 Hz), 2.13 (2H, tt, *J* = 6.8, 2.4 Hz), 2.28 (2H, tt, *J* = 6.8, 2.4 Hz), 3.76 (2H, t, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 15.4, 18.7, 22.7, 28.9, 29.0, 29.1, 29.3, 29.5, 29.6 (2xC), 31.6, 31.9, 62.1, 79.2, 81.2; HREIMS *m/z* calcd for $C_{16}H_{30}O$ 238.2297, found 238.2321.



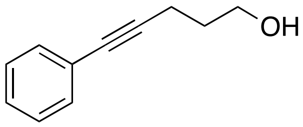
Heptadec-1-en-5-yne (7f). Purified by flash chromatography (hexane). IR ($CHCl_3$) 2336, 1641, 1466 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26~1.37 (16H, m), 1.49 (2H, quint, *J* = 6.8 Hz), 2.12~2.16 (2H, m), 2.22~2.24 (4H, m), 5.01 (1H, dt, *J* = 10.3, 1.0 Hz), 5.06 (1H, dd, *J* = 17.1, 1.5 Hz), 5.86 (1H, ddt, *J* = 17.1, 10.3, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 18.6, 18.7, 22.7, 28.8, 29.1, 29.2, 29.4, 29.5, 29.6 (2xC), 31.9, 33.4, 79.4, 80.8, 115.3, 137.3; HREIMS *m/z* calcd for $C_{17}H_{30}$ 234.2348, found 234.2342.



1-(Tridec-1-ynyl)benzene (7g). Purified by flash chromatography (hexane). IR ($CHCl_3$) 2231, 1599, 1573, 1490, 1466 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26~1.46 (16H, m), 1.60 (2H, q, *J* = 6.8 Hz), 2.39 (2H, t, *J* = 7.3 Hz), 7.24~7.40 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.4, 22.7, 28.8, 28.9, 29.2, 29.3, 29.5, 29.6 (2xC), 31.9, 80.5, 90.5, 124.1, 127.4, 128.1 (2xC), 131.5 (2xC); HREIMS *m/z* calcd for $C_{19}H_{28}$ 256.2191, found 256.2173.

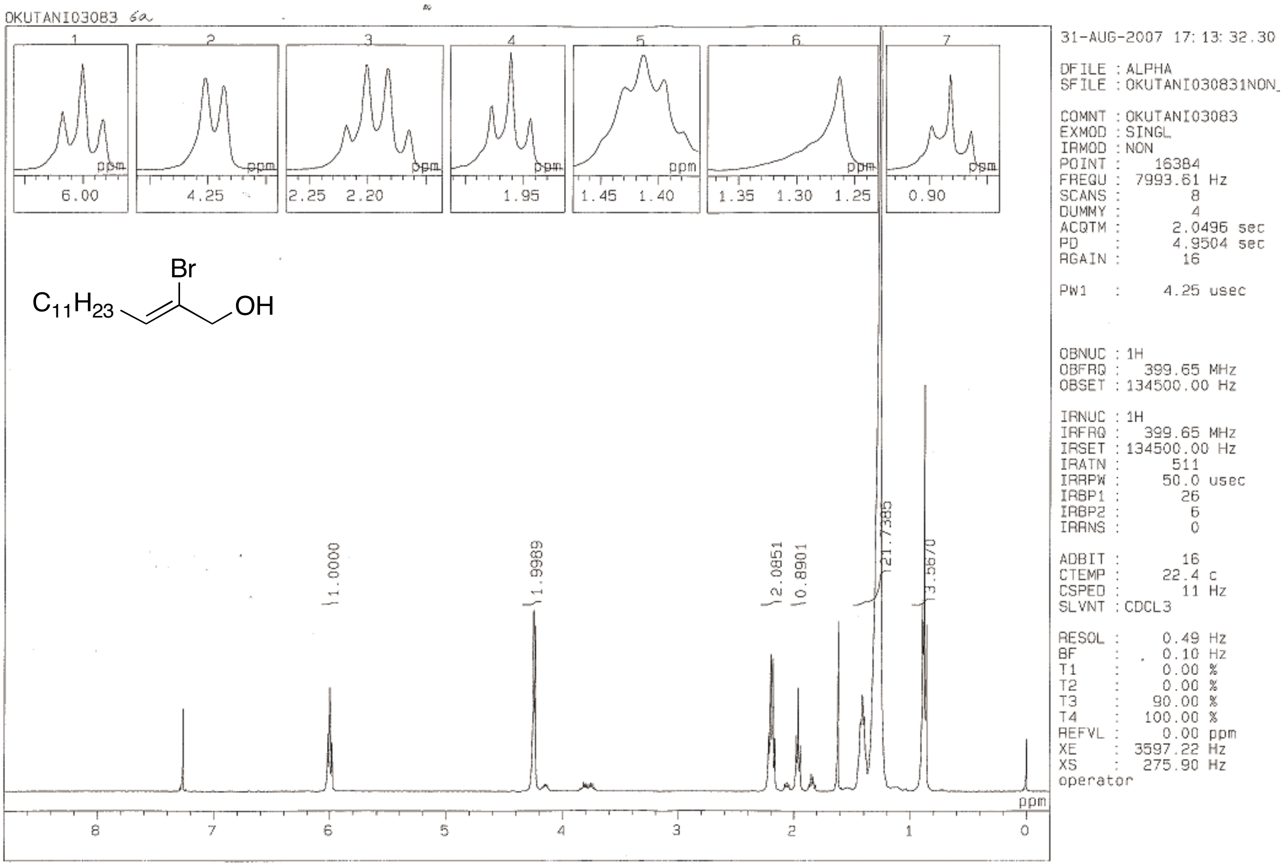


***tert*-Butyl 5-phenylpent-4-ynoate (7h).** Purified by flash chromatography (6% ethyl acetate in hexane). IR ($CHCl_3$) 1722, 1598, 1490, 1368, 1152 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (9H, s), 2.53 (2H, t, J = 7.8 Hz), 2.68 (2H, t, J = 7.8 Hz), 7.25~7.39 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 28.1 (3xC), 34.8, 80.7, 81.0, 88.3, 123.6, 127.7, 128.2 (2xC), 131.5 (2xC), 171.3; HREIMS *m/z* calcd for $C_{15}H_{18}O_2$ 230.1307, found 230.1326.



5-Phenylpent-4-yn-1-ol (7i). Purified by flash chromatography (30% ethyl acetate in hexane). IR ($CHCl_3$) 3626, 3451, 2230, 1598, 1490, 1442, 1070 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (1H, s, OH), 1.85 (2H. quint, J = 6.8 Hz), 2.53 (2H, t, J = 6.8 Hz), 3.80 (2H, t, J = 6.8 Hz), 7.24~7.41 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 31.3, 61.7, 81.1, 89.3, 123.6, 127.6, 128.2 (2xC), 131.5 (2xC); HREIMS *m/z* calcd for $C_{11}H_{12}O$ 160.0888, found 160.08879.

Compound **6a**



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31-AUG-2007 17:13:32.30

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operator
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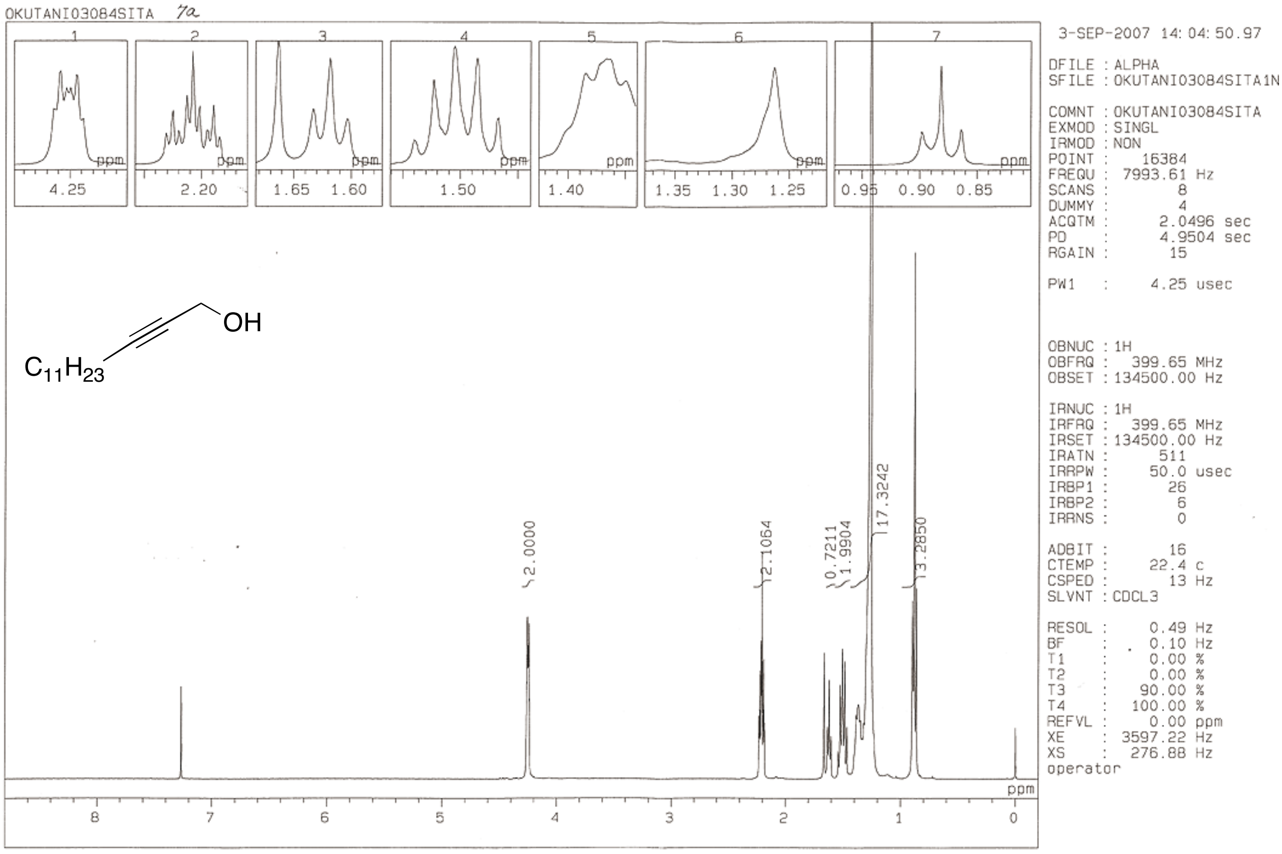
Compound **7a**



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3-SEP-2007 14:04:50.97

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PD    :       4.9504 sec
RGAIN :       15

PW1   :     4.25 usec


OBNUC : 1H
OBFRQ :   399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
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IRSET : 134500.00 Hz
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IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     22.4 c
CSPED :       13 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
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operator
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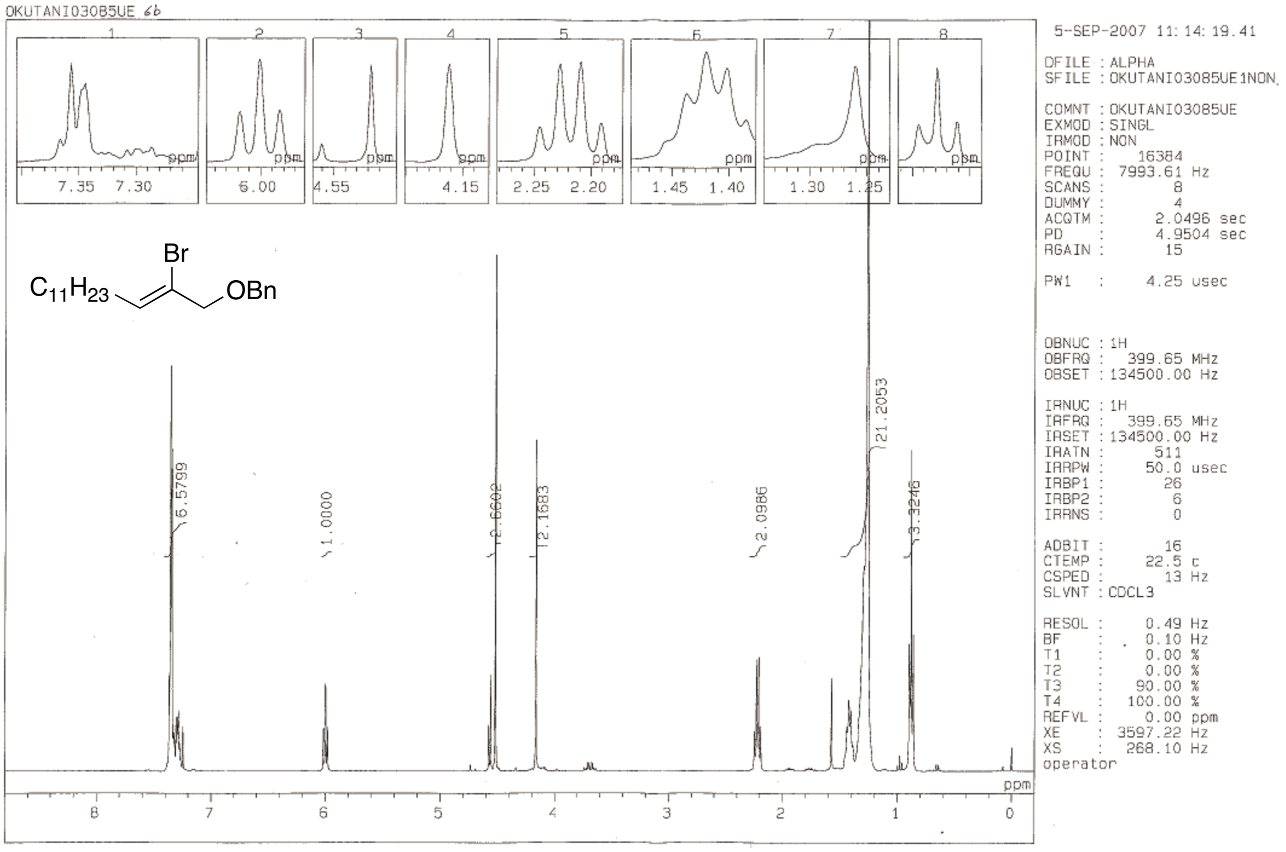
Compound **6b**



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5-SEP-2007 11:14:19.41

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PD    :     4.9504 sec
RGAIN :       15

PW1   :     4.25 usec

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OBFRQ :   399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     22.5 c
CSPED :       13 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
BF    :     0.10 Hz
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operator
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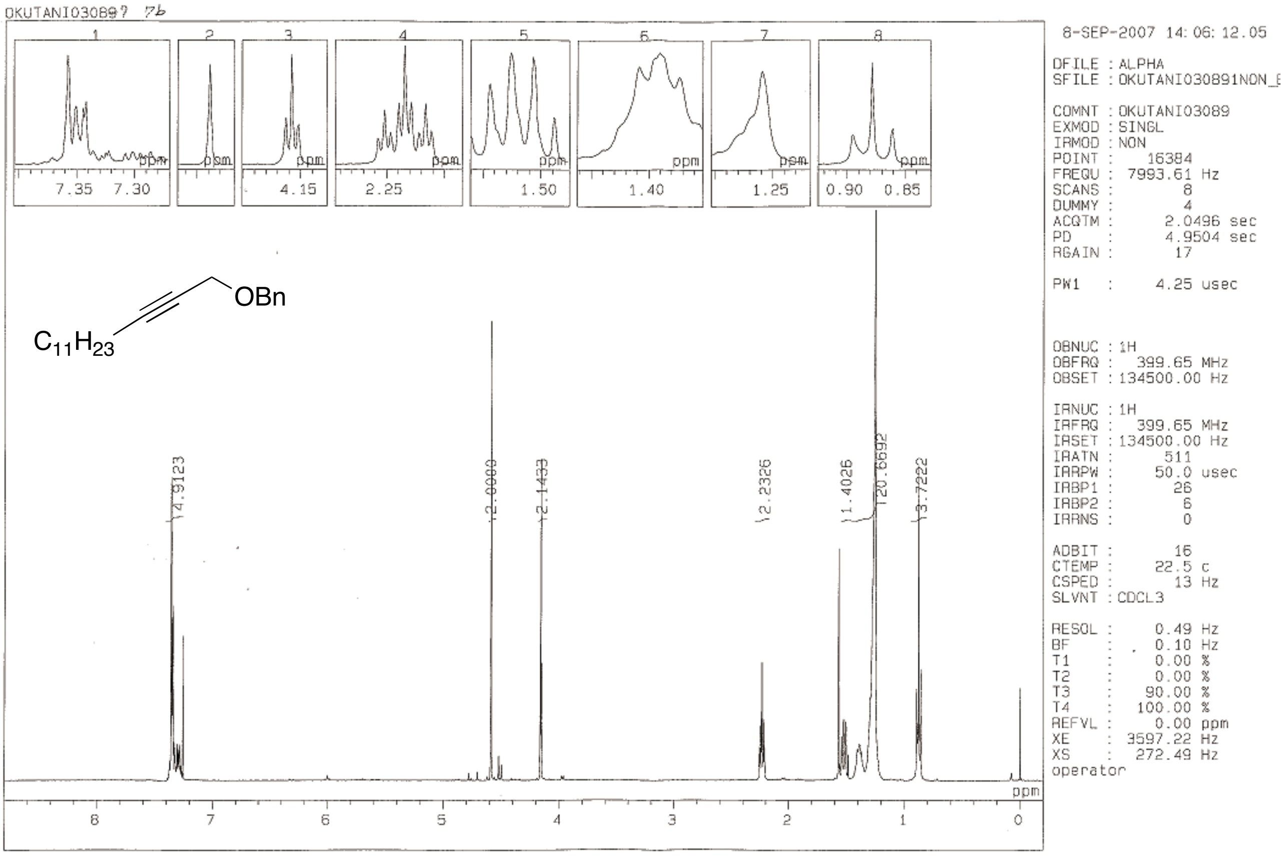
Compound **7b**



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8-SEP-2007 14:06:12.05

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PW1   :     4.25 usec

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OBSET : 134500.00 Hz

IRNUC : 1H
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IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     22.5 c
CSPED :       13 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
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operator
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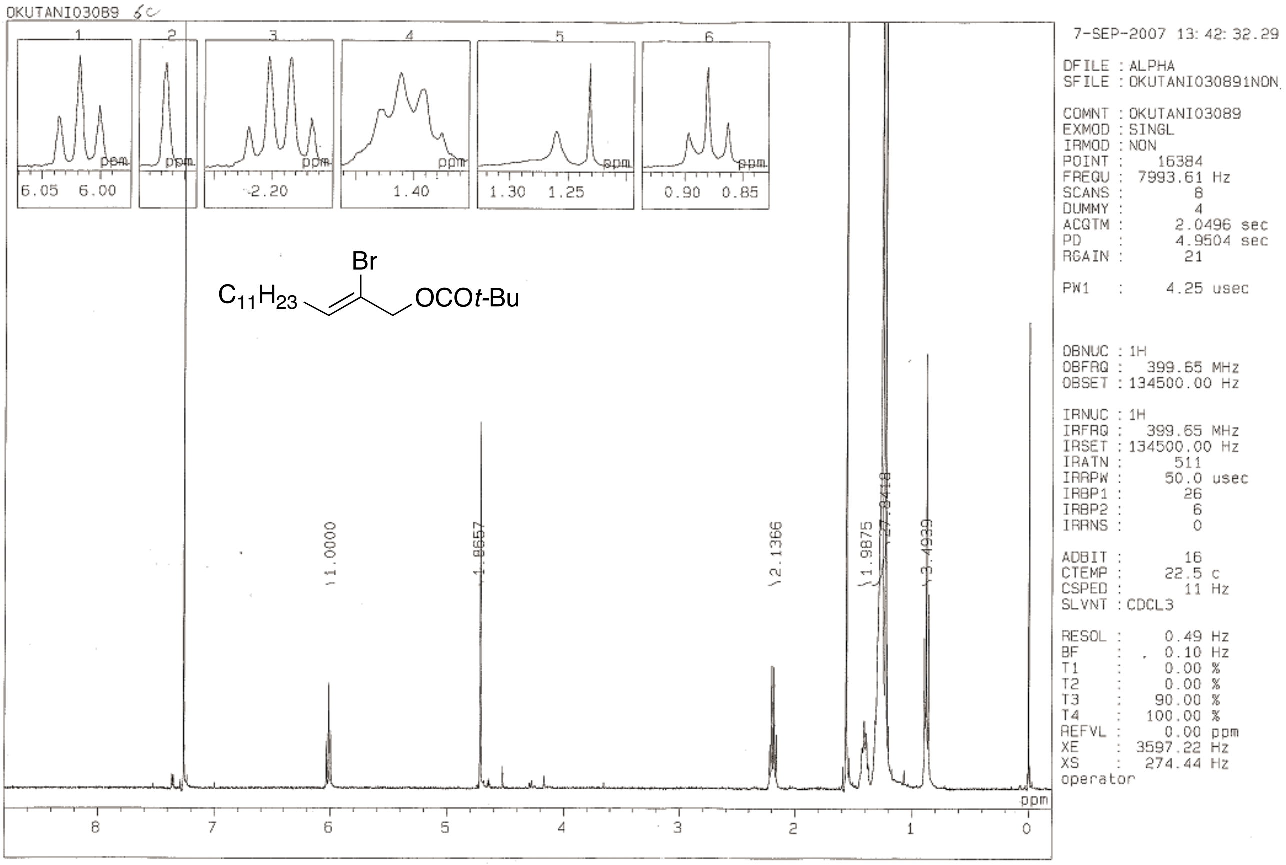
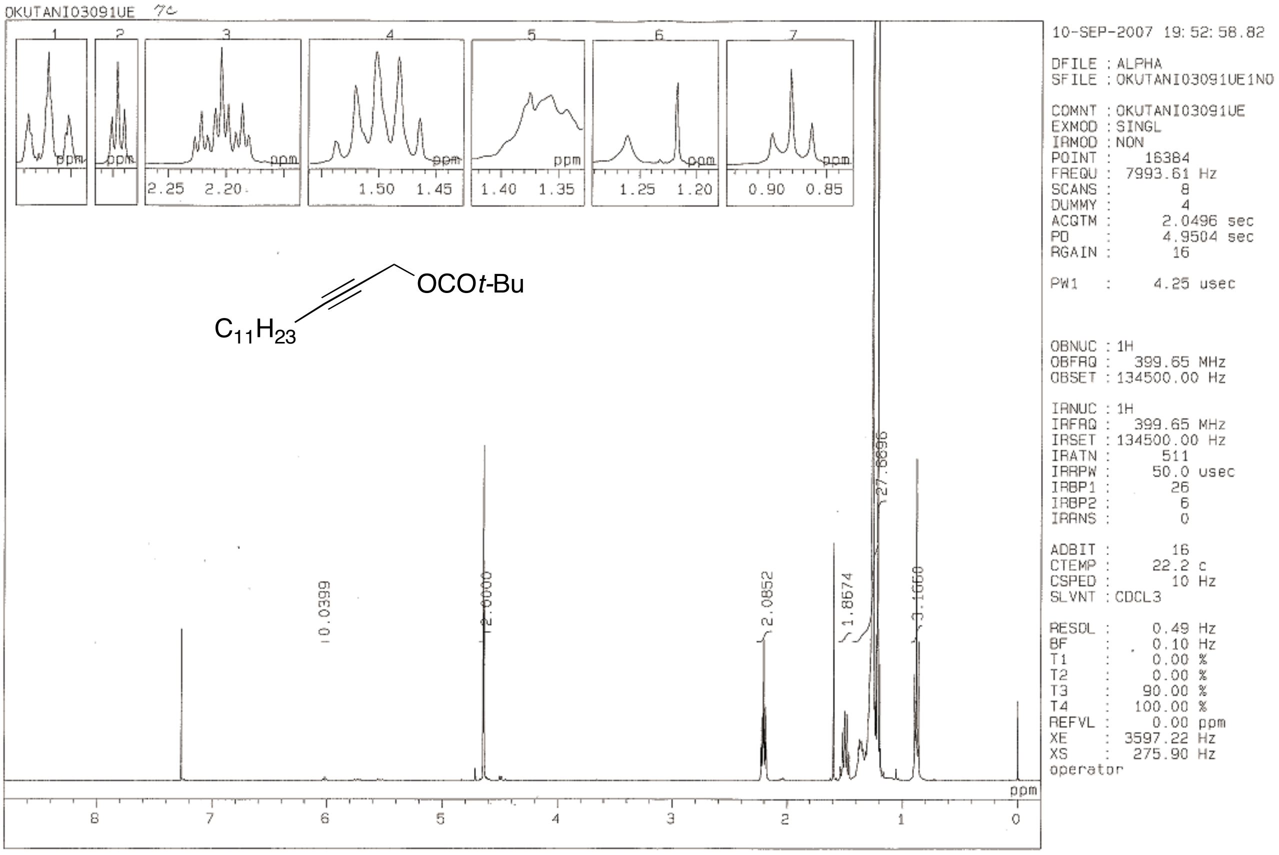
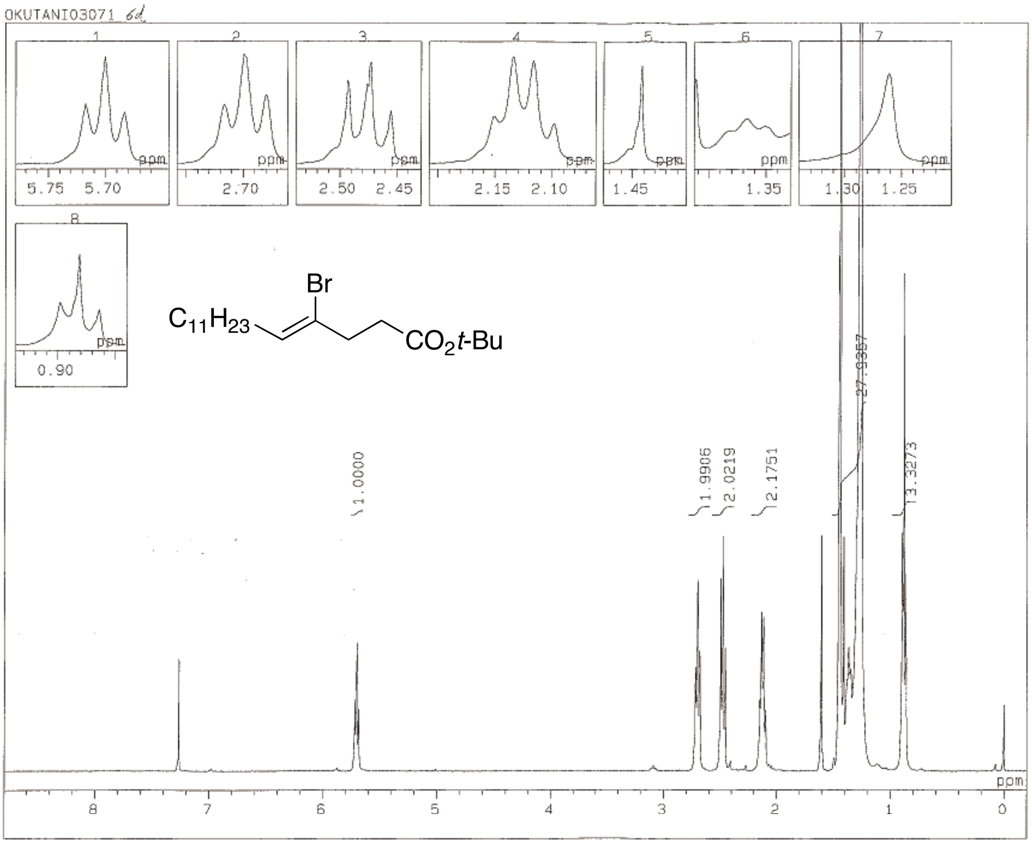


Compound **7c**



Compound **6d**



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1-AUG-2007 11:02:34.04

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DUMMY :        4
ACQTM :      2.0496 sec
PD    :      4.9504 sec
RGAIN :       15

PW1   :     4.25 usec


OBNUC : 1H
OBFRQ :   399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     22.2 c
CSPED :       12 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
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XS    :   276.39 Hz
operator
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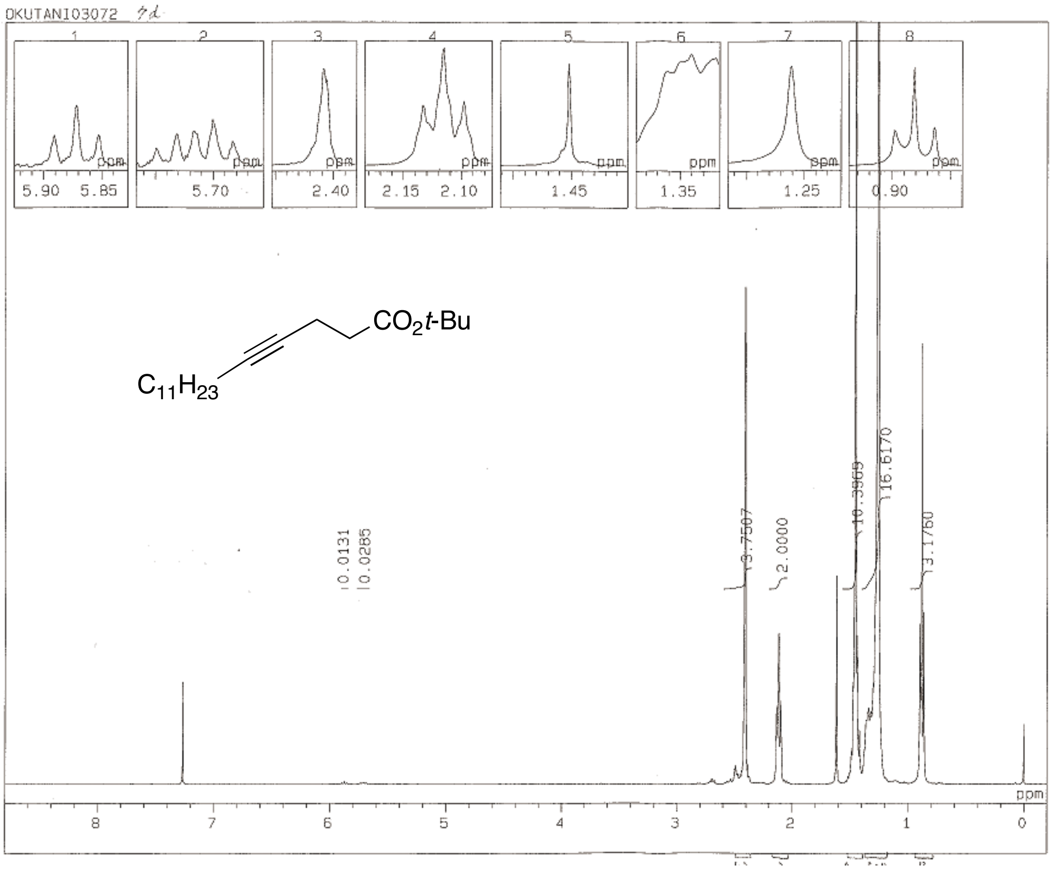
Compound **7d**



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2-AUG-2007 12:31:01.04

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SCANS :        8
DUMMY :        4
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PD    :      4.9504 sec
RGAIN :       15

PW1   :     4.25 usec


OBNUC : 1H
OBFRQ :   399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     22.2 c
CSPED :       13 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
BF    :   . 0.24 Hz
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operator
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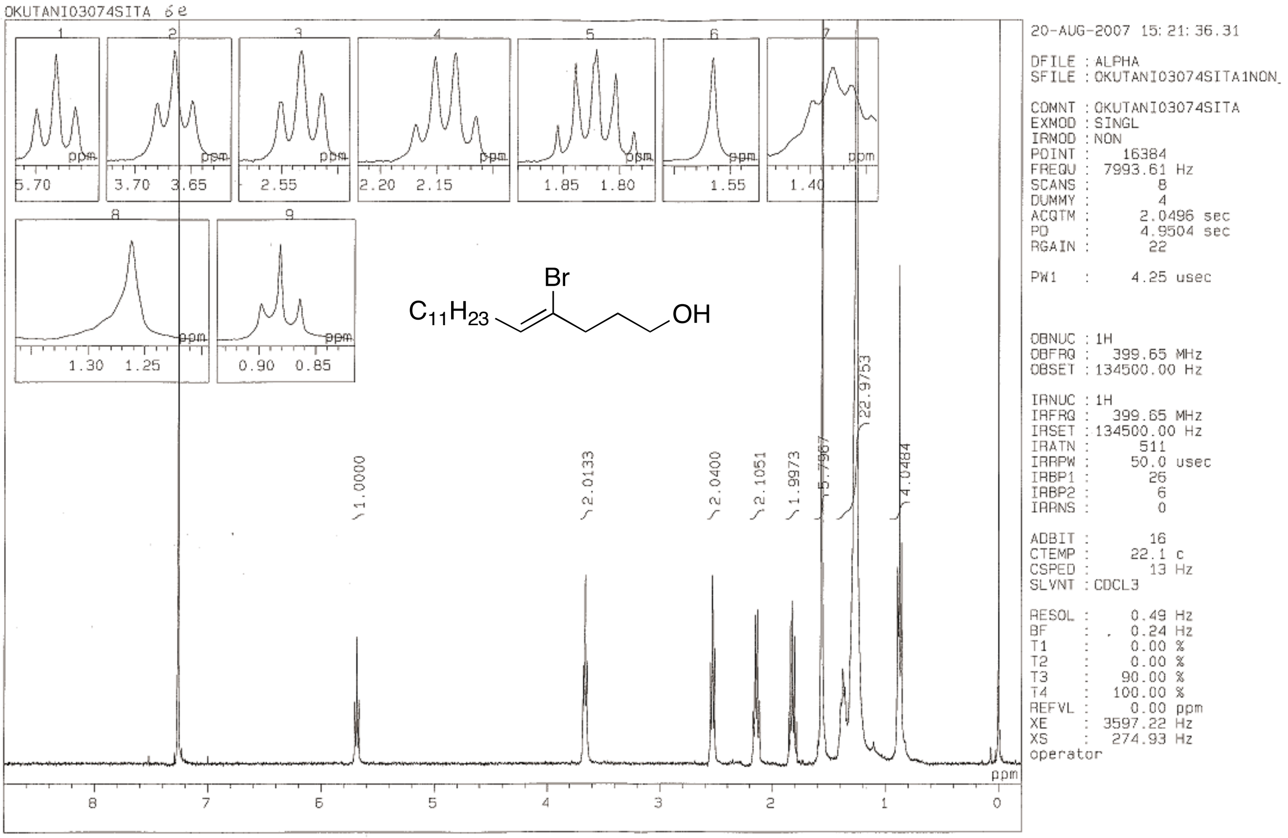
Compound **6e**



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20-AUG-2007 15:21:36.31

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IRMOD : NON
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SCANS :        8
DUMMY :        4
ACQTM :     2.0496 sec
PD    :     4.9504 sec
RGAIN :       22

PW1   :     4.25 usec


OBNUC : 1H
OBFRQ :   399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
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IRSET : 134500.00 Hz
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IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
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CSPED :       13 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
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operator
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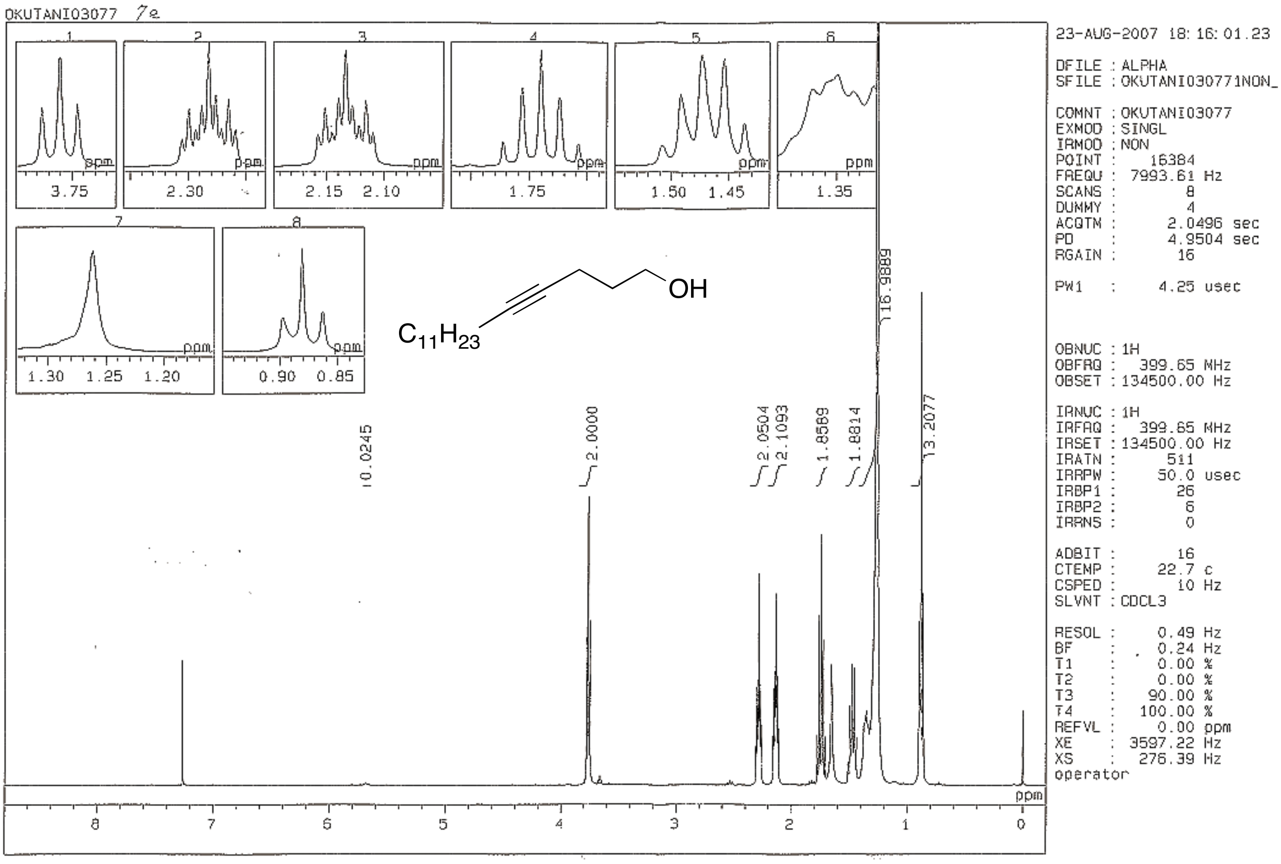
Compound **7e**



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23-AUG-2007 18:16:01.23

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PD    :     4.9504 sec
RGAIN :       16

PW1   :     4.25 usec


OBNUC : 1H
OBFRQ :   399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
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CSPED :       10 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
BF    :     0.24 Hz
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T2    :     0.00 %
T3    :    90.00 %
T4    :   100.00 %
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XE    :  3597.22 Hz
XS    :   276.39 Hz
operator
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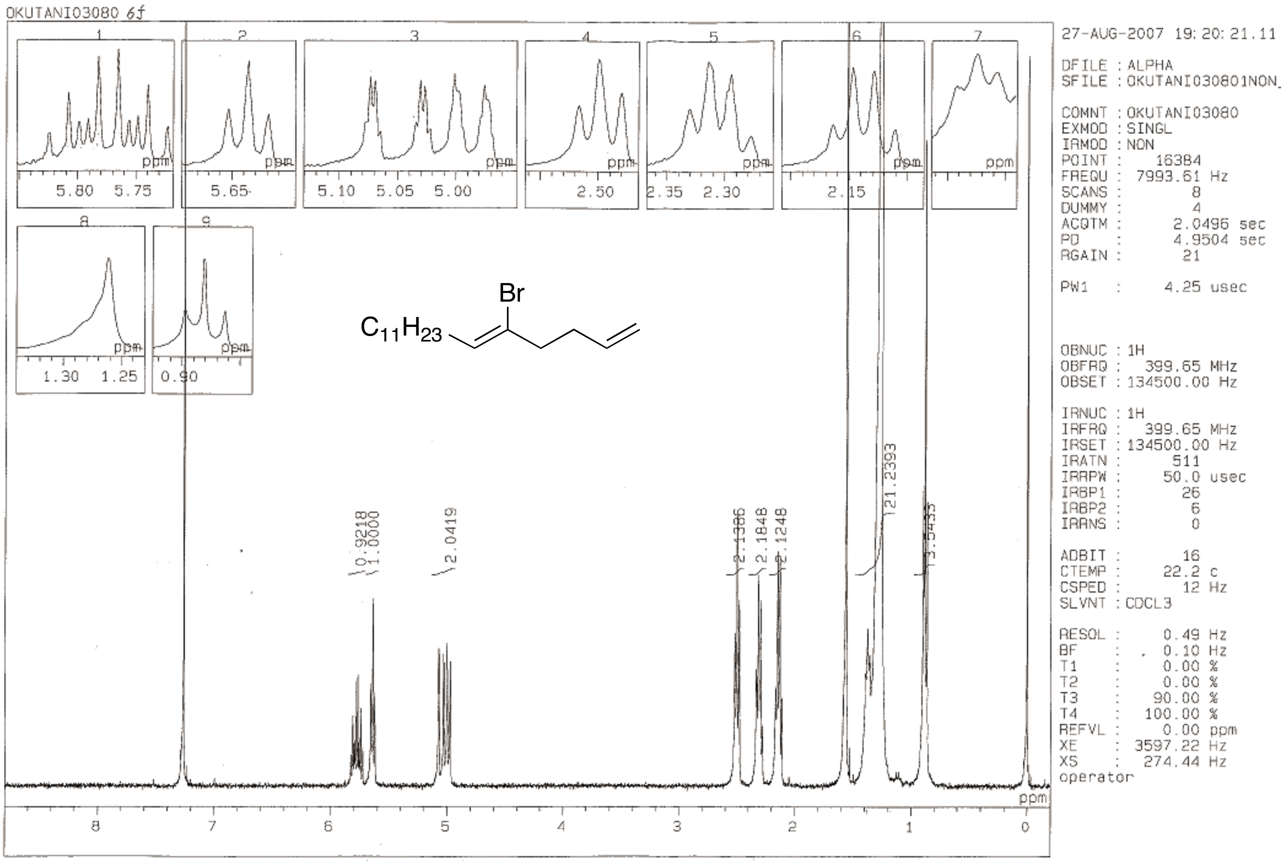
Compound **6f**



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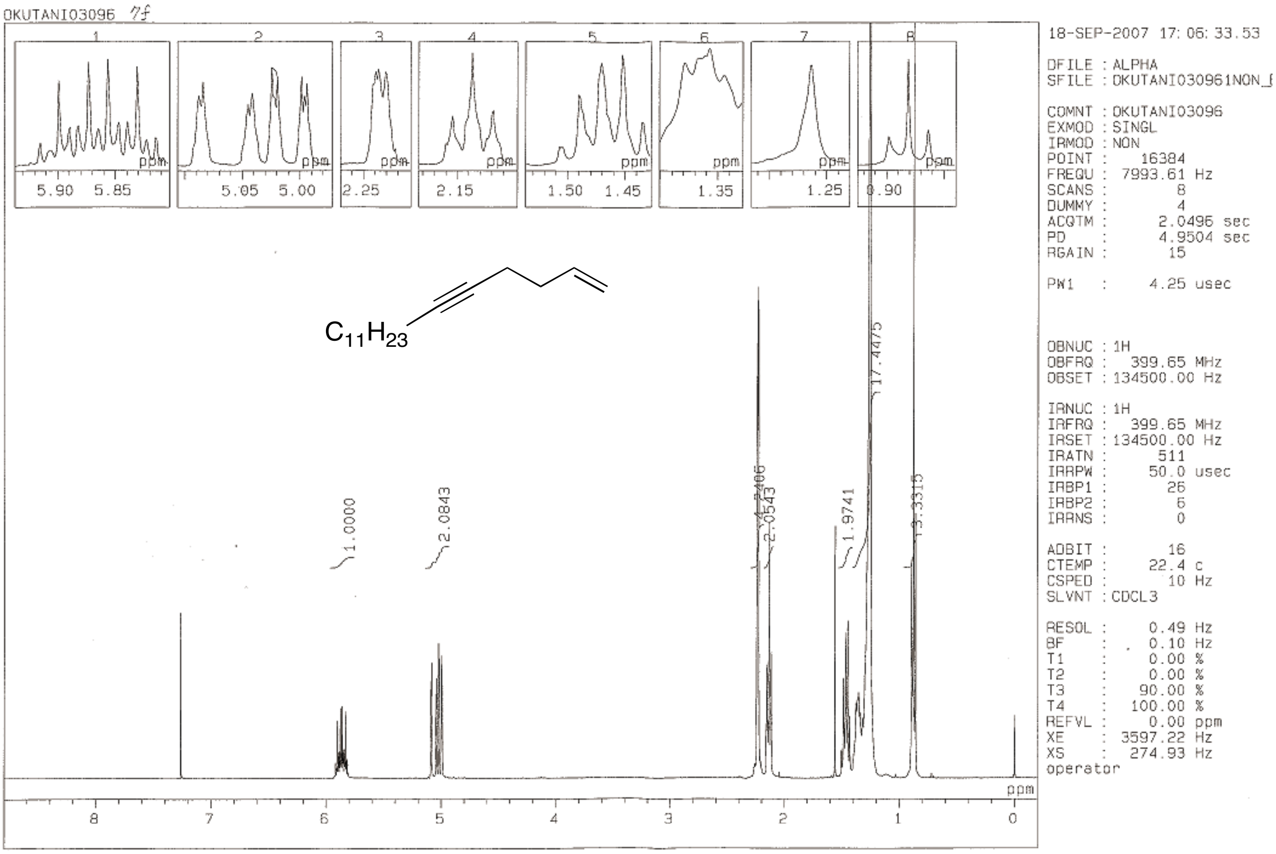

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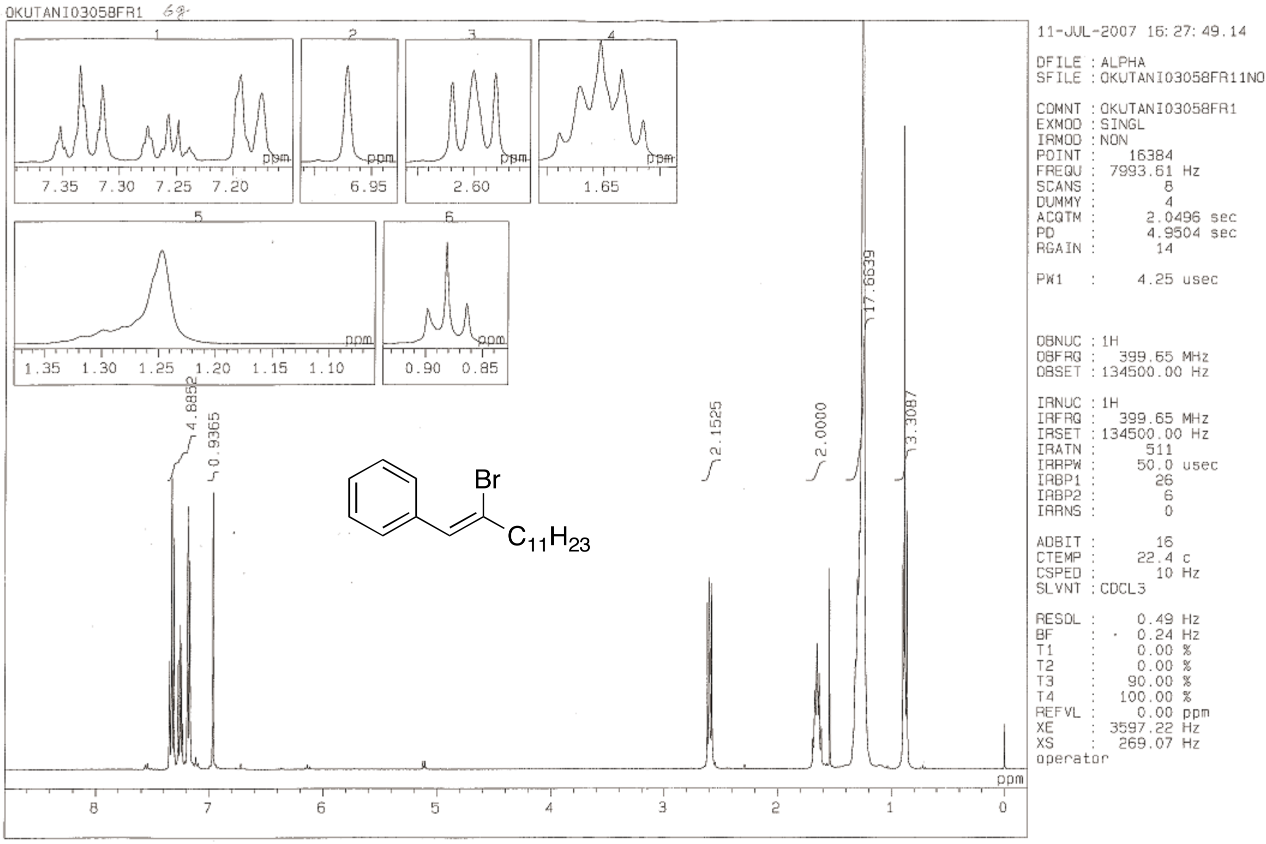

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11-JUL-2007 16:27:49.14

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SCANS :        8
DUMMY :        4
ACQTM :       2.0496 sec
PD    :       4.9504 sec
RGAIN :       14

PW1   :     4.25 usec

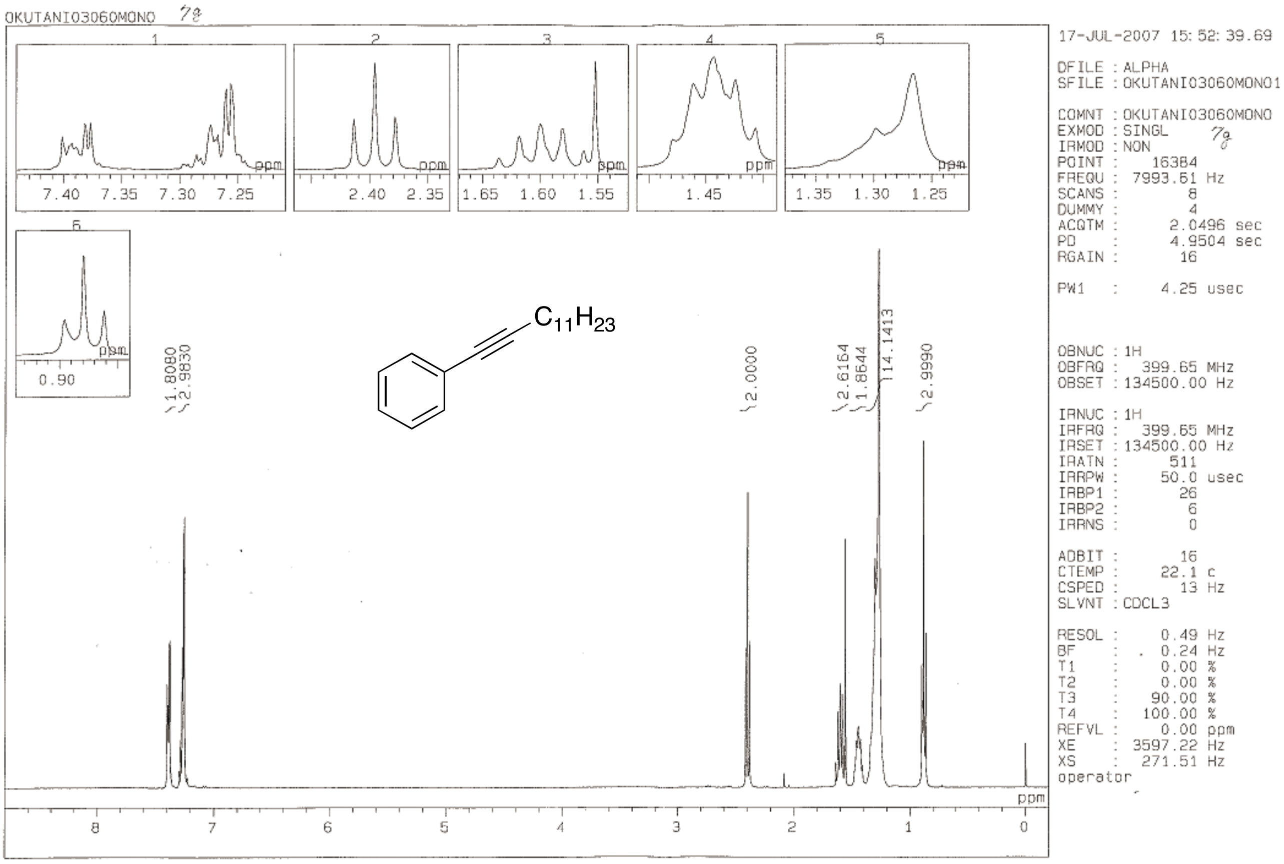

OBNUC : 1H
OBFRQ :   399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     22.4 c
CSPED :       10 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
BF    :  .  0.24 Hz
T1    :     0.00 %
T2    :     0.00 %
T3    :    90.00 %
T4    :   100.00 %
REFVL :     0.00 ppm
XE    :  3597.22 Hz
XS    :   269.07 Hz
operator
```

Compound **7g**



```
17-JUL-2007 15:52:39.69

DFILE : ALPHA
SFILE : OKUTANI03060MONO1

COMNT : OKUTANI03060MONO
EXMOD : SINGL      7g
IRMOD : NON
POINT :    16384
FREQU :  7993.61 Hz
SCANS :        8
DUMMY :        4
ACQTM :       2.0496 sec
PD    :       4.9504 sec
RGAIN :       16

PW1   :     4.25 usec

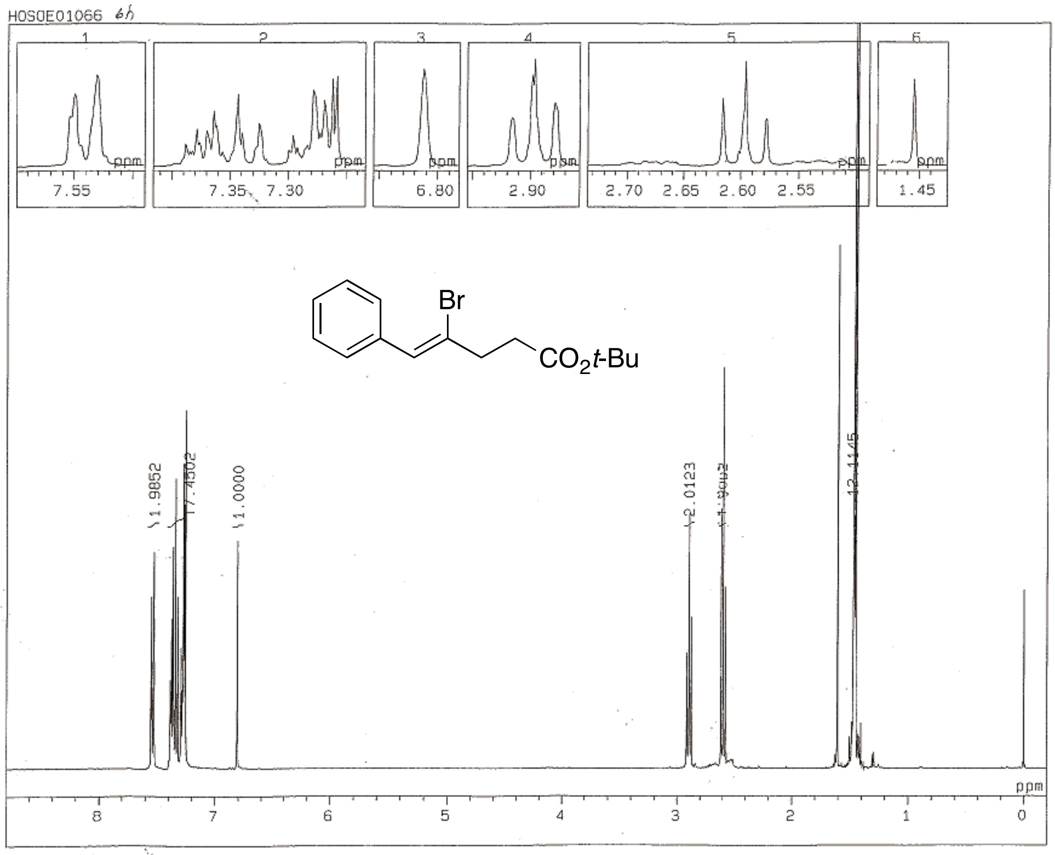

OBNUC : 1H
OBFRQ :   399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     22.1 c
CSPED :       13 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
BF    :  .  0.24 Hz
T1    :     0.00 %
T2    :     0.00 %
T3    :    90.00 %
T4    :   100.00 %
REFVL :     0.00 ppm
XE    :  3597.22 Hz
XS    :   271.51 Hz
operator
```

Compound **6h**



```
10-OCT-2007 11:38:40.37

DFILE : ALPHA
SFILE : HOSOE010661NON_E1

COMNT : HOSOE01066
EXMOD : SINGL
IRMOD : NON
POINT :    16384
FREQU :  7993.61 Hz
SCANS :        8
DUMMY :        4
ACQTM :      2.0496 sec
PD    :      4.9504 sec
RGAIN :       17

PW1   :      4.25 usec

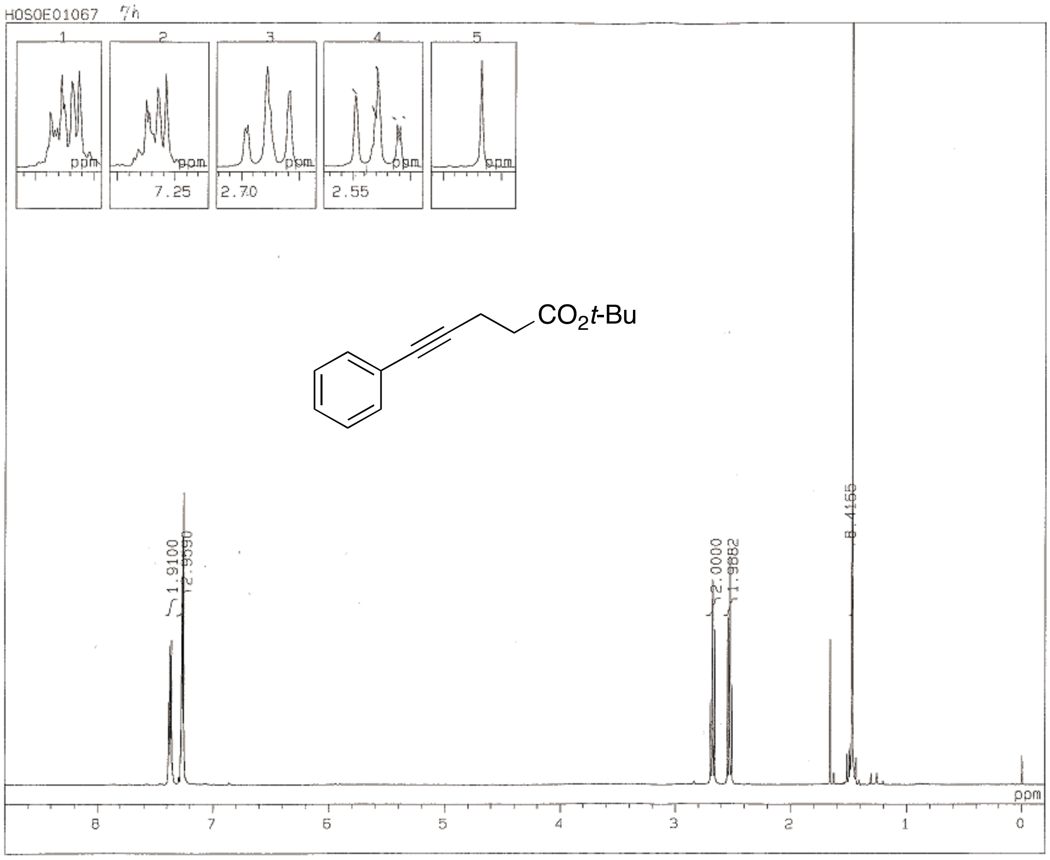
OBNUC : 1H
OBFRQ :    399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
IRFRQ :    399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :      50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :      21.6 c
CSPED :       14 Hz
SLVNT : CDCL3

RESOL :      0.49 Hz
BF    :      0.10 Hz
T1    :      0.00 %
T2    :      0.00 %
T3    :     90.00 %
T4    :    100.00 %
REFVL :      0.00 ppm
XE    :   3597.22 Hz
XS    :    272.97 Hz
operator
```

Compound **7h**



```
11-OCT-2007 13:08:31.59

DFILE : ALPHA
SFILE : HOSOE010671NON_E1

COMNT : HOSOE01067
EXMOD : SINGL
IRMOD : NON
POINT :    16384
FREQU :  7993.61 Hz
SCANS :        8
DUMMY :        4
ACQTM :      2.0496 sec
PD    :      4.9504 sec
RGAIN :       15

PW1   :      4.25 usec

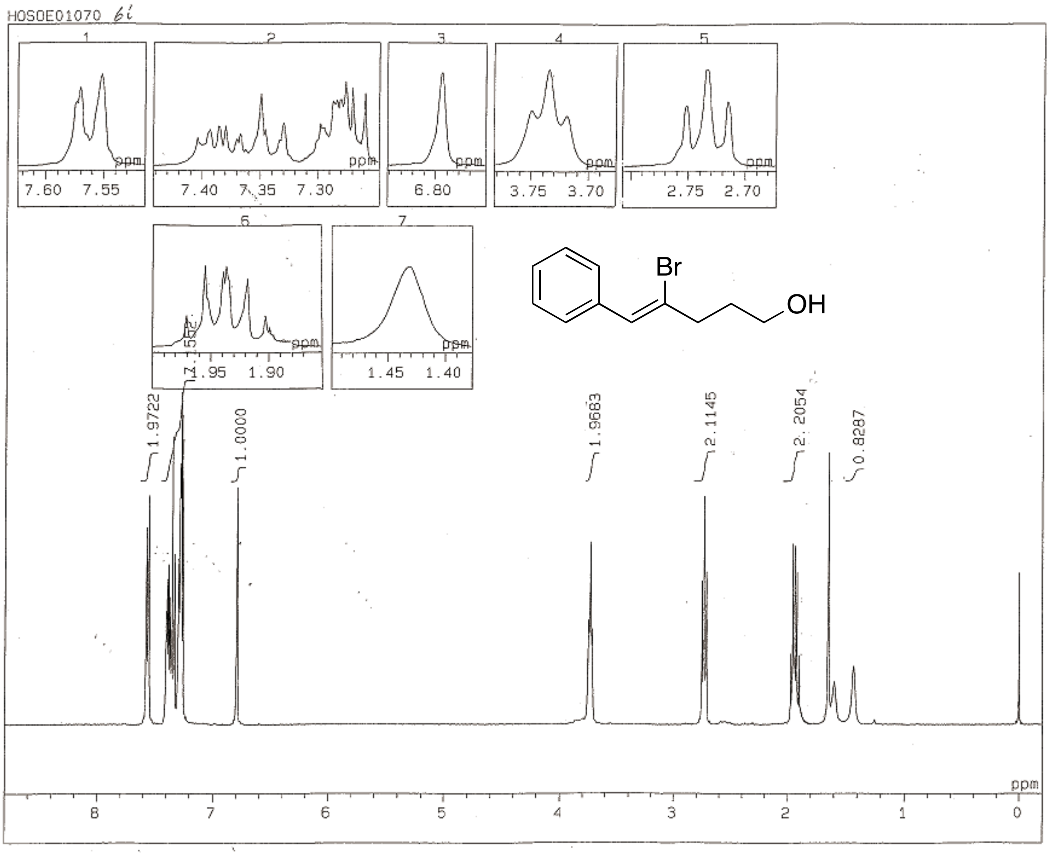
OBNUC : 1H
OBFRQ :    399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
IRFRQ :    399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :      50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :      22.0 c
CSPED :       14 Hz
SLVNT : CDCL3

RESOL :      0.49 Hz
BF    :      0.10 Hz
T1    :      0.00 %
T2    :      0.00 %
T3    :     90.00 %
T4    :    100.00 %
REFVL :      0.00 ppm
XE    :   3597.22 Hz
XS    :    272.49 Hz
operator
```

Compound **6i**



```
16-OCT-2007 11:08:21.41

DFILE : ALPHA
SFILE : HOSOE010701NON_E1

COMNT : HOSOE01070
EXMOD : SINGL
IRMOD : NON
POINT :    16384
FREQU :  7993.61 Hz
SCANS :        8
DUMMY :        4
ACQTM :      2.0496 sec
PD    :      4.9504 sec
RGAIN :       18

PW1   :     4.25 usec

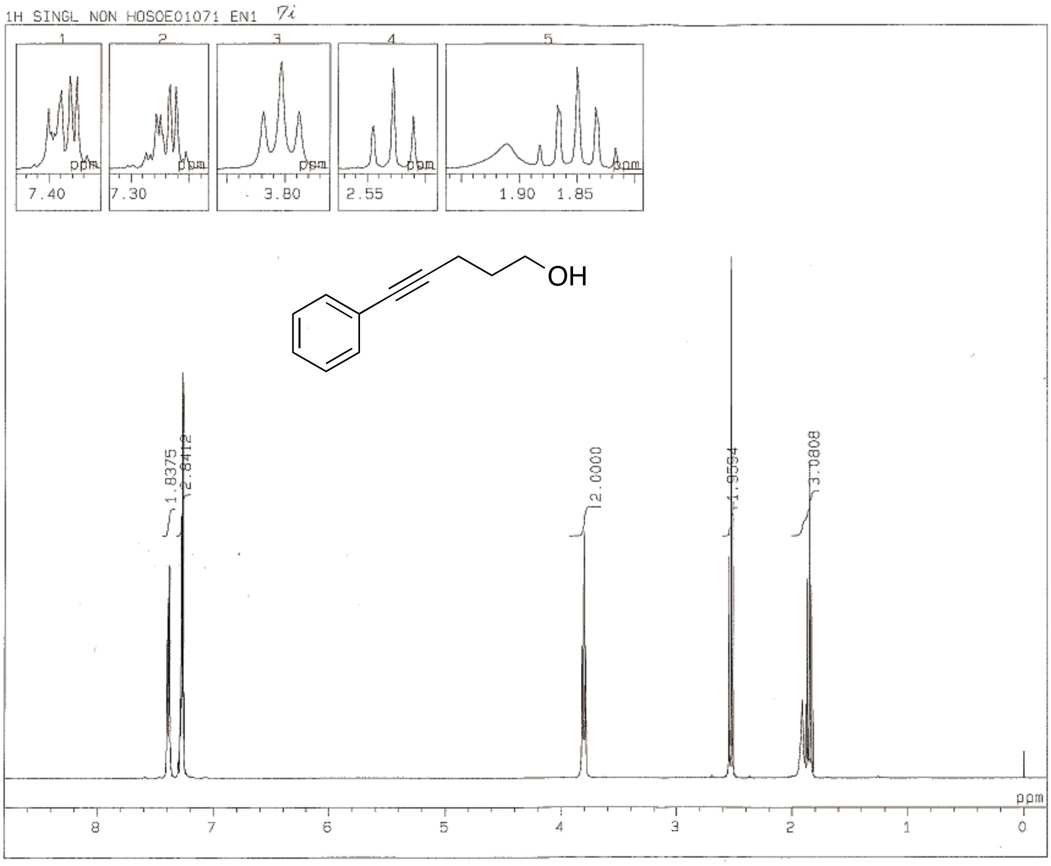

OBNUC : 1H
OBFRQ :   399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     21.5 c
CSPED :       10 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
BF    :     0.10 Hz
T1    :     0.00 %
T2    :     0.00 %
T3    :    90.00 %
T4    :   100.00 %
REFVL :     0.00 ppm
XE    :  3597.22 Hz
XS    :   272.97 Hz
operator
```

Compound **7i**



```
17-OCT-2007 13:50:49.20

DFILE : ALPHA
SFILE : HOSOE010711NON_E

COMNT : 1H SINGL NON HOS
EXMOD : SINGL
IRMOD : NON
POINT :    16384
FREQU :  7993.61 Hz
SCANS :        8
DUMMY :        4
ACQTM :      2.0496 sec
PD    :      4.9504 sec
RGAIN :       15

PW1   :     4.25 usec


OBNUC : 1H
OBFRQ :   399.65 MHz
OBSET : 134500.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     21.5 c
CSPED :       12 Hz
SLVNT : CDCL3

RESOL :     0.49 Hz
BF    :     0.10 Hz
T1    :     0.00 %
T2    :     0.00 %
T3    :    90.00 %
T4    :   100.00 %
REFVL :     0.00 ppm
XE    :  3597.22 Hz
XS    :   271.02 Hz
operator
```