Ligand-Dependent Scope and Divergent Mechanistic Behavior in Nickel-Catalyzed Reductive Couplings of Aldehydes and Alkynes.

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Supporting Information

All reagents were used as received unless otherwise noted. Tetrahydrofuran (THF) was treated under nitrogen using a solvent purification system (Innovative Technology, Inc., Model # SPS-400-3). All aldehydes and alkynes were freshly distilled prior to use. $Ni(COD)_2$ and 1,3-bis(2,4,6-trimethyl-phenyl)imidazolium chloride (Strem Chemicals, Inc., used as received) were stored and weighed in an inert atmosphere glovebox. All reactions were conducted in flame-dried glassware under an oxygen-free atmosphere of argon or nitrogen. ^1H and ^{13}C spectra were obtained in $CDCl_3$, unless otherwise noted, on a Varian Mercury 400, or Varian Unity 500 MHz instrument. Chemical shifts of ^1H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of $CDCl_3$ (77.0 ppm) on the δ scale. High Resolution mass spectra (HRMS) were obtained on a Kratos MS 80 mass spectrometer by the Central Instrumentation Facility, Department of Chemistry, Wayne State University, Detroit, Michigan.

General Procedure A for the $Ni(COD)_2$/carbene catalyzed couplings of aldehydes and alkynes. (Table 1. Examples 1 - 9.)

An 8mL THF solution of $Ni(COD)_2$ (28 mg, 0.1 mmol) and the imidazolium salt **1** (34 mg, 0.1mmol) was prepared. The mixture was cooled to 0º C, and *n*BuLi (1.6 M/hex, 62

μL, 0.1 mmol) was added dropwise. The mixture initially turned green and on standing at 0º C for 50 min had a deep red color. Triethylsilane (320 μL, 2.0 mmol) was then added dropwise and the mixture was heated to 45 º C for 5 min. At the same temperature, the aldehyde (1.0 mmol) was added dropwise followed by addition of the alkyne (1.2 mmol) in 2mL THF over 15 min using a syringe pump. After addition of the alkyne was complete, the mixture was stirred for 15 min at 45 ^{o}C, followed by quenching with aqueous sat. solution of sodium bicarbonate and extracting 3x with ethyl acetate. $MgSO_4$ was then added, the solution was filtered and the solvent was removed using a rotary evaporator. The crude reaction mixture was purified by column chromatography (SiO_2, hexanes, unless otherwise noted), and the protected allyl alcohols were isolated as colorless to pale yellow oils.

General Procedure B for the Ni(COD)$_2$/carbene catalyzed couplings of aldehydes and alkynes. (Table 1. Example 10. **)**

A 5 mL solution of the imidazolium salt **1** (34 mg, 0.1mmol) in THF was prepared. This solution was then cooled to 0 ^{o}C and *n*BuLi (1.6 M/hex, 62 μL, 0.1 mmol) was added dropwise. This mixture was kept at the same temperature for 10 minutes during which the yellow solution went to colorless. Ni(COD)$_2$ (28 mg, 0.1 mmol), dissolved in 3 mL THF was then added by cannula and the solution was stirred at 0 ^{o}C for 10 min. Triethylsilane (320 μL, 2.0 mmol) was then added followed by addition of the aldehyde (1.0 mmol). The alkyne (1.5 mmol) in 2mL THF was then added over 15 minutes by syringe pump. The mixture was then allowed to warm to rt and was stirred overnight. The reaction mixture was quenched with a aqueous sat. solution of sodium bicarbonate and extracted 3x with ethyl acetate. $MgSO_4$ was then added, the solution was filtered, and the solvent

removed by rotary evaporation. The crude reaction mixture was purified by column chromatography (SiO_2, hexanes, unless otherwise noted), and the protected allyl alcohols were isolated as colorless to pale yellow oils.

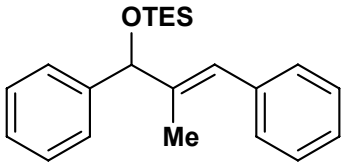


Table 1, Entry 1, Triethyl-(2-methyl-1,3-diphenyl-allyloxy)-silane

Following the general procedure A, $Ni(COD)_2$ (28 mg, 0.1 mmol), imidazolium salt **1** (34 mg, 0.1 mmol), nBuLi (1.6 M/hexanes, 62μL, 0.1 mmol), triethylsilane (320 μL, 2.0 mmol), 1-phenyl-propyne (139 mg, 1.2 mmol), and benzaldeyhde (102 μL, 1.0 mmol) were employed to give triethyl-(2-methyl-1,3-diphenyl-allyloxy)-silane (283 mg, 0.84 mmol, 84 %, >98:2 mixture of regioisomers), after column chromatography (SiO_2, hexanes) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 7.5 Hz, 2H) 7.41-7.45 (m, 6H) 7.30-7.36 (m, 2H) 6.85 (s, 1H), 5.38 (s, 1H) 1.80 (d, J = 1.5 Hz, 3H) 1.09 (t, J = 8.5 Hz, 9H) 0.78 (q, J = 8.0 Hz, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 143.7, 141.2, 138.2, 129.3, 128.4, 128.3, 127.2, 126.7, 126.5, 125.9, 80.3, 13.5, 7.2, 5.3. IR (film, cm^{-1}) 2954.4, 2875.0, 1492.0, 1088.1, 1064.7. HRMS (EI) *m/z* calculated for $C_{22}H_{30}OSi$ 338.2066, found 338.2070 (M^+).

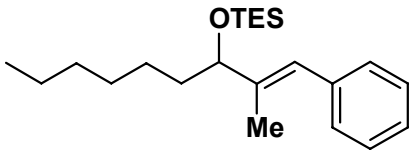


Table 1: Entry 2, Triethyl-(1-hexyl-2-methyl-3-phenyl-allyloxy)-silane

Following the general procedure A, $Ni(COD)_2$ (28 mg, 0.1 mmol), imidazolium salt **1** (34 mg, 0.1 mmol), nBuLi (1.6 M/hexanes, 62μL, 0.1 mmol), triethylsilane (320 μL, 2.0

mmol), 1-phenyl-propyne (139 mg, 1.2 mmol), and heptaldehyde (139 μL, 1.0 mmol) were employed to give triethyl-(1-hexyl-2-methyl-3-phenyl-allyloxy)-silane (284 mg, 0.82 mmol, 82 %, >98:2 mixture of regioisomers) after column chromatography (SiO_2, hexanes) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 8.0 Hz, 2H) 7.35 (d, *J* =7.0 Hz, 2H) 7.26- 7.29 (m, 1H) 6.51 (s, 1H) 5.86 (q, *J* = 7.5 Hz, 0.02 H, minor regioisomer) 4.39 (t, J= 6.5 Hz, 0.02 H, minor regioisomer) 4.21 (t, *J* = 6.0 Hz, 1H) 1.92 (d, *J* = 1.5 Hz, 3H) 1.62- 1.74 (m, 2H) 1.29-1.53 (m, 8H) 1.07 (t, *J* = 8.0 Hz, 9H) 0.99 (t, *J* = 7.0 Hz, 3H) 0.72 (q, *J* = 8.0 Hz, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 141.4, 138.3, 129.2, 128.3, 126.4, 125.3, 79.1, 36.8, 32.2, 29.7, 26.1, 23.0, 14.4, 13.3, 7.2, 5.2. IR (film, cm^{-1}) 2954.8, 2931.0, 1457.5, 1238.1, 1075.0, 1004.9, 745.3. HRMS (EI) *m/z* calculated for $C_{22}H_{38}OSi$ 346.2692, found 346.2698 (M^+).

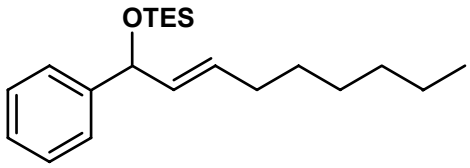


Table 1: Entry 3, Triethyl-(1-phenyl-non-2-enyloxy)-silane

Following the general procedure A, $Ni(COD)_2$ (28 mg, 0.1 mmol), imidazolium salt **1** (34 mg, 0.1 mmol), nBuLi (1.6 M/hexanes, 62μL, 0.1 mmol), triethylsilane (320 μL, 2.0 mmol), 1-octyne (132 mg, 1.2 mmol) and benzaldehyde (102 μL, 1.0 mmol) were employed to give triethyl-(1-phenyl-non-2-enyloxy)-silane (236 mg, 0.71 mmol, 71 %, >98:2 mixture of regioisomers) after column chromatography (SiO_2, hexanes) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dt, *J* = 14.8, 7.2 Hz, 4H) 7.22-7.26 (m, 1H) 5.69 (dt, *J* = 15.6, 6.4 Hz, 1H) 5.58 (dd, *J* = 6.8, 15.6 Hz, 1H) 5.17 (d, *J* = 6.4 Hz, 1H) 2.10 (q, *J* = 7.2 Hz, 2H) 1.24-1.47 (m, 8H) 0.97 (t, *J* = 7.2 Hz, 9H) 0.91 (t, *J* = 6.4Hz, 3H) 0.57-0.71 (m, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 144.8, 133.8, 131.2, 128.3, 127.0,

126.2, 75.8, 32.4, 32.0, 29.37, 29.16, 22.9, 14.3, 7.1, 5.2. IR (film, cm^{-1}) 2954.8, 2925.3, 1457.9, 1240.5, 1100.9, 1056.3, 1105.9, 965.8 HRMS (EI) *m/z* calculated for $C_{21}H_{32}OSi$ 332.2535, found 332.2531 (M^+).

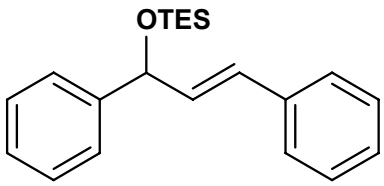


Table 1: Entry 4, (1,3-Diphenyl-allyloxy)-triethyl-silane

Following the general procedure A, $Ni(COD)_2$ (28 mg, 0.1 mmol), imidazolium salt **1** (34 mg, 0.1 mmol), nBuLi (1.6 M/hexanes, 62μL, 0.1 mmol), triethylsilane (320 μL, 2.0 mmol), phenyl acetylene (122 mg, 1.2 mmol), and benzaldeyhde (102 μL, 1.0 mmol) were employed to give (1,3-diphenyl-allyloxy)-triethyl-silane (234 mg, 0.72 mmol, 72 %, >98:2 mixture of regioisomers) after column chromatography (SiO_2, hexanes) as a colorless oil. **Note**: The alkyne was added over 2 h using a syringe drive. ^1H NMR (500 MHz, $CDCl_3$) δ 7.26-7.53 (m, 10H) 6.71 (d, *J* = 16.0 Hz, 1H) 6.38 (ddd, *J* = 15.4, 6.3, 2.5 Hz, 1H) 5.424-5.435 (m, 1H) 1.02-1.06 (m, 9H) 0.66-0.79 (m, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 144.1, 137.2, 133.5, 129.2, 128.8, 128.6, 127.8, 127.4, 126.8, 126.4, 75.7, 7.1, 5.3. IR (film, cm^{-1}) 2954.5, 2875.1, 1493.6, 1449.3, 1103.6, 1059.1, 1004.6, 965.7, 743.4. HRMS (EI) *m/z* calculated for $C_{21}H_{28}OSi$ 324.1909, found 324.1907 (M^+).

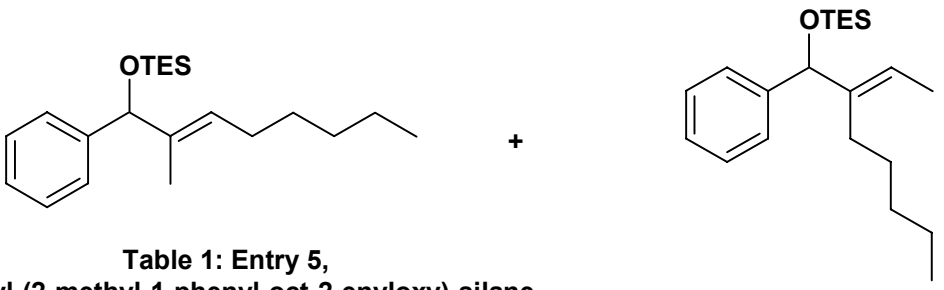


Table 1: Entry 5,
Triethyl-(2-methyl-1-phenyl-oct-2-enyloxy)-silane

Triethyl-(2-pentyl-1-phenyl-but-2-enyloxy)-silane

Following the general procedure A, $Ni(COD)_2$ (28 mg, 0.1 mmol), imidazolium salt **1** (34 mg, 0.1 mmol), nBuLi (1.6 M/hexanes, 62μL, 0.1 mmol), triethylsilane (320 μL, 2.0 mmol), 2-octyne (132 mg, 1.2 mmol), and benzaldeyhde (102 μL, 1.0 mmol) were employed to give a mixture of triethyl-(2-methyl-1-phenyl-oct-2-enyloxy)-silane and triethyl-(2-pentyl-1-phenyl-but-2-enyloxy)-silane (279 mg, 0.84 mmol, 84 %, 1.3:1 mixture of regioisomers) after column chromatography (SiO_2, hexanes) as a colorless oil. **Note**: The alkyne was added over 15 min using a syringe drive, and the reaction mixture was then heated at 60 ^{o}C for 2 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 11.0 Hz, 2H) 7.32 (q, *J* = 8.0 Hz, 2H) 7.22-7.25 (m, 1H) 5.67 (q, *J* = 7.5 Hz, 0.43H) 5.62 (t, *J* = 7.0 Hz, 0.57H) 5.15 (s, 1H) 2.03-2.14 (m, 1.19H) 1.87-1.99 (m, 0.86H) 1.68 (d, *J* = 7.5 Hz, 1.24H) 1.45 (m, 3H) 1.35-1.40 (m, 2.55H) 1.17-1.31 (m, 2.1H) 1.05-1.15 (m, 0.5H) 0.94-1.00(m, 10.7H) 0.87 (t, *J* = 6.5 Hz, 1.36H) 0.6-0.69 (m, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 144.4, 144.1, 143.3, 138.0, 127.99, 127.96, 126.92, 126.89, 126.75, 126.6, 126.2, 120.7, 80.1, 79.2, 32.5, 31.9, 29.5, 29.0, 27.8, 27.0, 22.9, 22.7, 14.3, 14.2, 13.4, 11.3, 7.11, 7.10, 5.15. IR (film, cm^{-1}) 2955.2, 2931.6, 1457.8, 1238.2, 1087.8, 1064.9, 742.5. HRMS (EI) *m/z* calculated for $C_{21}H_{36}OSi$ 332.2535, found 332.2535 (M^+).

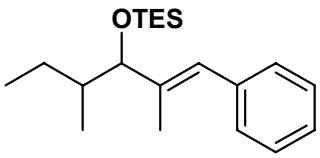


Table 1: Entry 6, (1-*sec*-Butyl-2-methyl-3-phenyl-allyloxy)-triethyl-silane

Following the general procedure A, $Ni(COD)_2$ (28 mg, 0.1 mmol), imidazolium salt **1** (34 mg, 0.1 mmol), nBuLi (1.6 M/hexanes, 62μL, 0.1 mmol), triethylsilane (320 μL, 2.0 mmol), 1-phenyl propyne (139 mg, 1.2 mmol), and 2-methylbutyraldehyde (107 μL, 1.0 mmol) were employed to give (1-sec-butyl-2-methyl-3-phenyl-allyloxy)-triethyl-silane (256 mg, 0.81 mmol, 81 %, 3:2 dr, > 98:2 mixture of regioisomers) after column chromatography (SiO_2, hexanes) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 8.4 Hz, 2H) 7.29 (d, *J* = 8.0 Hz, 2H) 7.21-7.26 (m, 1H) 6.42 (s, 0.6H) 6.39 (s, 0.4H) 3.85 (d, *J* = 7.6Hz, 0.6H) 3.79 (d, *J* = 8.4Hz, 0.4H) 1.83 (s, 3H) 1.56-1.62 (m, 1H) 1.38-1.47 (m, 0.7H) 1.03-1.17 (m, 1H) 0.90-1.01 (m, 14H) 0.80 (d, *J* = 7.2 Hz, 1.3H) 0.65 (q, *J* = 8.0 Hz, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 140.56, 140.45, 138.30, 138.22, 129.1, 128.3, 126.8, 126.43, 126.38, 126.36, 84.0, 83.2, 39.1, 38.9, 26.3, 25.3, 15.7, 14.9, 13.9, 13.3, 12.0, 11.7, 7.2, 5.22, 5.20 IR (film, cm^{-1}) 2957.8, 2875.5, 1458.0, 1064.8, 1006.5 HRMS (EI) *m/z* calculated for $C_{19}H_{31}OSi$ 303.2144, found 303.2143 (M^+).

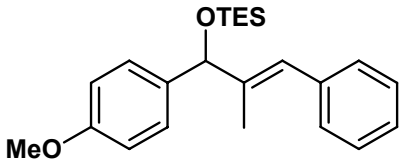


Table 1: Entry 7, Triethyl-[1-(4-methoxy-phenyl)-2-methyl-3-phenyl-allyloxy]-silane

Following the general procedure A, $Ni(COD)_2$ (28 mg, 0.1 mmol), imidazolium salt **1** (34 mg, 0.1 mmol), nBuLi (1.6 M/hexanes, 62μL, 0.1 mmol), triethylsilane (320 μL, 2.0 mmol), 1-phenyl propyne (139 mg, 1.2 mmol), and *p*-methoxybenzaldehyde (122 μL, 1.0

mmol) were employed to give triethyl-[1-(4-methoxy-phenyl)-2-methyl-3-phenyl-allyloxy]-silane (242 mg, 0.66 mmol, 66%, > 98:2 mixture of regioisomers) after silica gel chromatography (10:1 Hex/EtOAc) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) 7.31-7.37 (m, 6H) 7.21-7.26 (m, 1H) 6.88-6.90 (m, 2H) 6.73 (s, 1H) 5.22 (s, 1H) 3.83 (s, 3H) 1.70 (s, 3H) 0.98 (t, J = 8.0 Hz, 9H) 0.67 (q, J = 8.4 Hz, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 158.8, 141.2, 138.2, 135.8, 129.2, 128.3, 127.6, 126.5, 125.4, 113.6, 79.7, 55.5, 13.6, 7.1, 5.2. IR (film, cm^{-1}) 2952.8, 1508.8, 1246.6, 1167.9, 1075.8 HRMS (EI) *m/z* calculated for $C_{23}H_{32}OSi$ 368.2172, found 368.2170 (M^+).

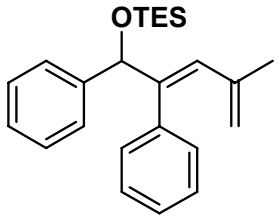


Table 1: Entry 8, Triethyl-(4-methyl-1,2-diphenyl-penta-2,4-dienyloxy)-silane

Following the general procedure A, $Ni(COD)_2$ (28 mg, 0.1 mmol), imidazolium salt **1** (34 mg, 0.1 mmol), nBuLi (1.6 M/hexanes, 62μL, 0.1 mmol), triethylsilane (320 μL, 2.0 mmol), (3-methyl-but-3-en-1-ynyl)-benzene (170 mg, 1.2 mmol), and benzaldehyde (102 μL, 1.0 mmol) were employed to give triethyl-(4-methyl-1,2-diphenyl-penta-2,4-dienyloxy)-silane (305 mg, 0.84 mmol, 84%, > 98:2 mixture of regioisomers) after silica gel chromatography (hexanes) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) 7.14-7.26 (m, 8H) 6.84 (d, J = 7.5 Hz, 2H) 6.59 (s, 1H) 5.33 (s, 1H) 4.94 (s, 1H) 4.89 (s, 1H) 1.37 (s, 3H) 0.95 (t, J = 8.0 Hz, 9H) 0.634 (q, J = 8.0 Hz, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 144.3, 143.1, 142.3, 139.1, 130.1, 128.5, 127.9, 127.4, 127.16, 127.10, 126.90, 118.2, 79.9, 22.5,

7.1, 5.1 IR (film, cm^{-1}) 2956.2, 2875.4, 1492.0, 1452.0, 1101.4, 1006.4 HRMS (EI) *m/z* calculated for $C_{24}H_{32}OSi$ 364.2222, found 364.2225 (M^+).

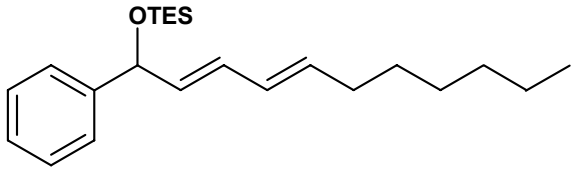


Table 1: Entry 9, Triethyl-(1-phenyl-undeca-2,4-dienyloxy)-silane

Following the general procedure A, $Ni(COD)_2$ (15 mg, 0.055 mmol), imidazolium salt **1** (34 mg, 0.55 mmol), nBuLi (1.6 M/hexanes, 62μL, 0.055 mmol), triethylsilane (166 μL, 1.102 mmol), dec-3-en-1-yne (90 mg, 0.662 mmol), and benzaldehyde (56 μL, 0.55 mmol) were employed to give triethyl-(1-phenyl-undeca-2,4-dienyloxy)-silane (111 mg, 0.31 mmol, 56 %, >98:2 mixture of regioisomers) after silica gel chromatography (hexanes) as a pale yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.29-7.36 (m, 4H) 7.22 (tt, *J* = 6.8, 2.4 Hz, 1H) 6.18 (dd, *J* = 14.8, 10.4 Hz, 1H) 6.00 (dd, *J* = 15.0, 9.6 Hz, 1H) 5.63-5.72 (m, 2H) 5.19 (d, *J* = 6.4 Hz, 1H) 2.06 (q, *J* = 7.2 Hz, 2H) 1.27-1.39 (m, 9H) 0.87-0.95 (m, 12H) 0.53-0.67 (m, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 144.4, 135.4, 134.4, 129.88, 129.77, 128.4, 127.2, 126.2, 75.4, 32.9, 32.0, 29.4, 29.1, 22.8, 14.3, 7.0, 5.2. IR (film, cm^{-1}) 2956.6, 2920.2, 1452.4, 1098.8, 1061.9, 987.6, 742.3, 698.3. HRMS (EI) *m/z* calculated for $C_{23}H_{38}OSi$ 358.2692, found 358.2690 (M^+).

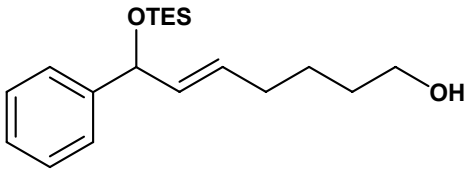
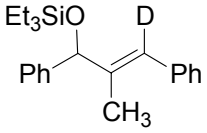


Table 1: Entry 10, 7-Phenyl-7-triethylsilanyloxy-hept-5-en-1-ol

Following the general procedure B, $Ni(COD)_2$ (28 mg, 0.1 mmol), imidazolium salt **1** (34 mg, 0.1 mmol), nBuLi (1.6 M/hexanes, 62μL, 0.1 mmol), triethylsilane (320 μL, 2.0 mmol), 5-hexyn-1-ol (147 mg, 1.5 mmol), and benzaldehyde (102 μL, 1.0 mmol) were employed to give 7-phenyl-7-triethylsilanyloxy-hept-5-en-1-ol (229 mg, 0.72 mmol, 72 %, >98:2 mixture of regioisomers) after silica gel chromatography (3:1 Hex/ EtOAc) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.36 (m, 4H) 7.21-7.26 (m, 1H) 5.68 (dt, *J* = 15.5, 7.0 Hz, 1H) 5.59 (ddt, *J* = 15.3, 6.5, 1.0 Hz, 1H) 5.15 (d, *J* = 7.0 Hz, 1H) 3.61 (t, *J* = 6.5 Hz, 2H) 2.07 (q, *J* = 7.0 Hz, 2H) 1.83-2.00 (m, 1H) 1.57 (quint, *J* = 6.5 Hz, 2H) 1.43-1.49 (m, 2H) 0.93-0.97 (m, 9H) 0.56-0.68 (m, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 144.7, 134.2, 130.5, 128.3, 127.1, 126.1, 75.7, 62.9, 32.5, 32.1, 25.5. IR (film, cm^{-1}) 3378.0, 2951.9, 2875.8, 1454.1, 1240.4, 1057.6. HRMS (EI) *m/z* calculated for $C_{19}H_{32}O_2Si$ 320.2172, found 320.2170 (M^+).

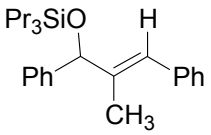


2b

Triethyl-(3-deuterio-2-methyl-1,3-diphenyl-allyloxy)-silane (2b)

Following the general procedure, benzaldehyde (25 μL, 0.25 mmol), 1-phenyl-propyne (38 μL, 0.3 mmol), $Ni(COD)_2$ (7 mg, 0.025 mmol), imidazolium salt **1** (9 mg, 0.025 mmol), n-BuLi (16 μL, 0.025 mmol) and Et_3SiD (80 μL, 0.5 mmol) were employed to give **2b** (68 mg, 80 %) as a colorless oil after chromatography (Hexane) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.0 Hz, 2H), 7.32-7.37 (m, 6H), 7.22-7.28 (m, 2H), 5.28 (s, 1H), 1.70 (s, 3H), 0.99 (t, *J* = 8.0 Hz, 9H), 0.68 (q, *J* = 8.0 Hz, 6H); ^{13}C (125 MHz,

$CDCl_3$) δ 144.6, 141.0, 138.0, 129.2, 128.3, 127.1, 126.6, 126.4, 125.4 (t, *J*=23 Hz), 80.1, 13.5, 7.1, 5.1; IR (film) 2954, 2911, 2874, 1597, 1493, 1065, 744 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{22}H_{29}OSiD$ [M^+] =339.2129, found 339.2125.



2c

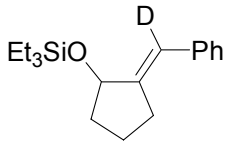
Tripropyl-(2-methyl-1,3-diphenyl-allyloxy)-silane (2c)

Following the general procedure, benzaldehyde (102 μL, 1.0 mmol), 1-phenyl-propyne (150 μL, 1.2 mmol), $Ni(COD)_2$ (28 mg, 0.1 mmol), imidazolium salt **1** (34 mg, 0.1 mmol), n-BuLi (63 μL, 0.1 mmol) and Pr_3SiH (417 μL, 2.0 mmol) were employed to give **2c** (298 mg, 78 %) as a colorless oil after chromatography (Hexane) ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.29-7.36 (m, 6H), 7.20-7.26 (m, 2H), 6.71 (s, 1H), 5.24 (s, 1H), 1.66 (s, 3H), 1.33-1.44 (m, 6H), 0.94 (t, *J* = 7.2 Hz, 9H),0.62-0.66(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 141.1, 138.1, 129.2, 128.3, 128.2, 127.1, 126.6, 126.4, 125.7, 80.2, 18.7, 17.10, 17.07, 13.4; IR (film) 2953, 2923, 2866, 1600, 1491, 1450, 1059, 739, 698 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{25}H_{36}OSi$ [M^+] =380.2535, found 380.2536.

General procedure C for the $Ni(COD)_2$/ carbene catalyzed cyclization of ynals:

Addition of $Ni(COD)_2$ (0.1 equiv.), imidazolium salt **1** (0.1 equiv.), n-Buli (0.1 equiv.) and trialkysilane (1.1-2.0 equiv.) followed the general procedure for intermolecular couplings. Then a 0.5 M THF solution of ynal (1.0 equiv.) was added dropwise. The mixture was stirred for 10 min at 45 º C, followed by quenching with sat. $NaHCO_3$ and

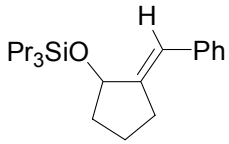
extracting 3x with Et_2O. The combined organic layers were washed with brine, dried with $MgSO_4$, filtered, and concentrated by a rotary evaporation. The crude reaction mixture was purified by column chromatography over silica gel using hexane/ethyl acetate as the eluent.



4b

2-(1-deuteriobenzylidene)-cyclopentyloxy-triethyl-silane (4b)

Following the general procedure, 6-phenyl-hex-5-ynal (90 mg, 0.52 mmol), $Ni(COD)_2$ (14 mg, 0.05 mmol), imidazolium salt **1** (17 mg, 0.05 mmol), n-BuLi (31 μL, 0.05 mmol), and Et_3SiD (91 μL, 0.57 mmol) were employed to give **4b** (95 mg, 63%) as a colorless oil after chromatography (hexane/ethyl acetate: 20:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.30-7.36 (m, 4H), 7.16-7.20 (m, 1H), 4.56 (t, J = 7.0 Hz, 1H), 2.57-2.71 (m, 2H), 1.89-1.97 (m, 2H), 1.51-1.70 (m, 2H), 1.02 (t, J = 8.0 Hz, 9H), 0.69 (q, J = 8.0 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 138.4, 128.6, 128.4, 126.3, 77.1, 35.2, 28.8, 21.7, 7.1, 5.2; IR (film) 2956, 2910, 2875, 1491 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{18}H_{27}OSiD$ [M^+] =289.1972, found 289.1970.



4c

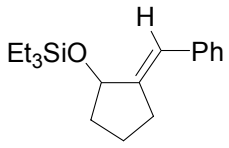
(2-Benzylidene-cyclopentyloxy)-tripropyl-silane (4c)

Following the general procedure, 6-phenyl-hex-5-ynal (150 mg, 0.87 mmol), $Ni(COD)_2$ (25 mg, 0.09 mmol), imidazolium salt **1** (31 mg, 0.09 mmol), n-BuLi (56 μL, 0.09 mmol), and Pr_3SiH (378 μL, 1.74 mmol) were employed to give **4c** (224 mg, 78%) as a

colorless oil after chromatography (hexane/ethyl acetate: 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.36 (m, 4H), 7.17-7.20 (m, 1H), 6.45 (q, *J* = 2.5 Hz, 1H), 4.54 (m, 1H), 2.56-2.70 (m, 2H), 1.88-1.95 (m, 2H), 1.60-1.70 (m, 1H), 1.52-1.57 (m, 1H), 1.40-1.48 (m, 6H), 0.99 (t, *J* = 7.5 Hz, 9H), 0.67-0.70 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 138.4, 128.6, 128.4, 126.3, 122.4, 77.2, 35.2, 28.8, 21.7, 18.7, 17.2, 17.1; IR (film) 2954, 2923, 2867, 1061, 856 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{18}H_{27}OSi$ [M^+] =330.2379, found 330.2382.

General procedure for the $Ni(COD)_2$/ PBu_3 catalyzed cyclization of ynals:

To a 0.1 M THF solution of $Ni(COD)_2$ (0.2 equiv.) was added PBu_3 (0.4 equiv.) at rt. After 5 min at rt., the solution was cooled to 0º C and silane (2.0 equiv.) was added dropwise. The mixture was heated at 45 º C and a 0.5 M THF solution of ynal (1.0 equiv.) was then added dropwise. The temperature was maintained at 45 º C for 20 hours. The reaction mixture was quenched with sat. $NaHCO_3$ at rt. and was extracted 3x with Et_2O. The combined organic layers were washed with brine, dried with $MgSO_4$, filtered, and concentrated using a rotary evaporator. The crude reaction mixture subjected to column chromatography over silica gel using hexane/ethyl acetate as the eluent.



4a

(2-Benzylidene-cyclopentyloxy)-triethyl-silane (4a)

Following the general procedure, 6-phenyl-hex-5-ynal (85 mg, 0.49 mmol), $Ni(COD)_2$ (28 mg, 0.1 mmol), PBu_3 (50 µL, 0.2 mmol), and Et_3SiH (160 µL, 1.0 mmol) were employed to give **4a** (96 mg, 68%) as a colorless oil after chromatography (hexane/ethyl

acetate: 20:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.36 (m, 4H), 7.17-7.20 (m, 1H), 6.48 (m, 1H), 4.56 (m, 1H), 2.57-2.71 (m, 2H), 1.89-1.97 (m, 2H), 1.52-1.70 (m, 2H), 1.02 (t, *J* = 8.0 Hz, 9H), 0.69 (q, *J* = 8.0 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 138.4, 128.6, 128.4, 126.3, 122.4, 77.1, 35.2, 28.8, 21.7, 7.1, 5.2; IR (film) 2955, 2910, 2875, 1598 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{18}H_{27}OSiD$ [M^+] =288.1909, found 288.1909.

Crossover Experiment:

Determination of isotopic distribution in products of catalytic crossover experiments

Representative example: Table 3 with PBu_3:

Pure samples of products derived from Et_3SiH (MW 288), Et_3SiD (MW 289), and Pr_3SiH (MW 330) were independently prepared, and GCMS analysis was performed. Based on similarity of the molecular ion regions of the Et_3SiH and Et_3SiD-derived products, the molecular ion region of the Pr_3SiD-derived product was assumed to appear as the molecular ion region of the Pr_3SiH-derived product, shifted by one mass unit. Relative peak heights in the molecular ion region of the spectra of each pure compound were normalized, with a value of 1 assigned to the base peak.

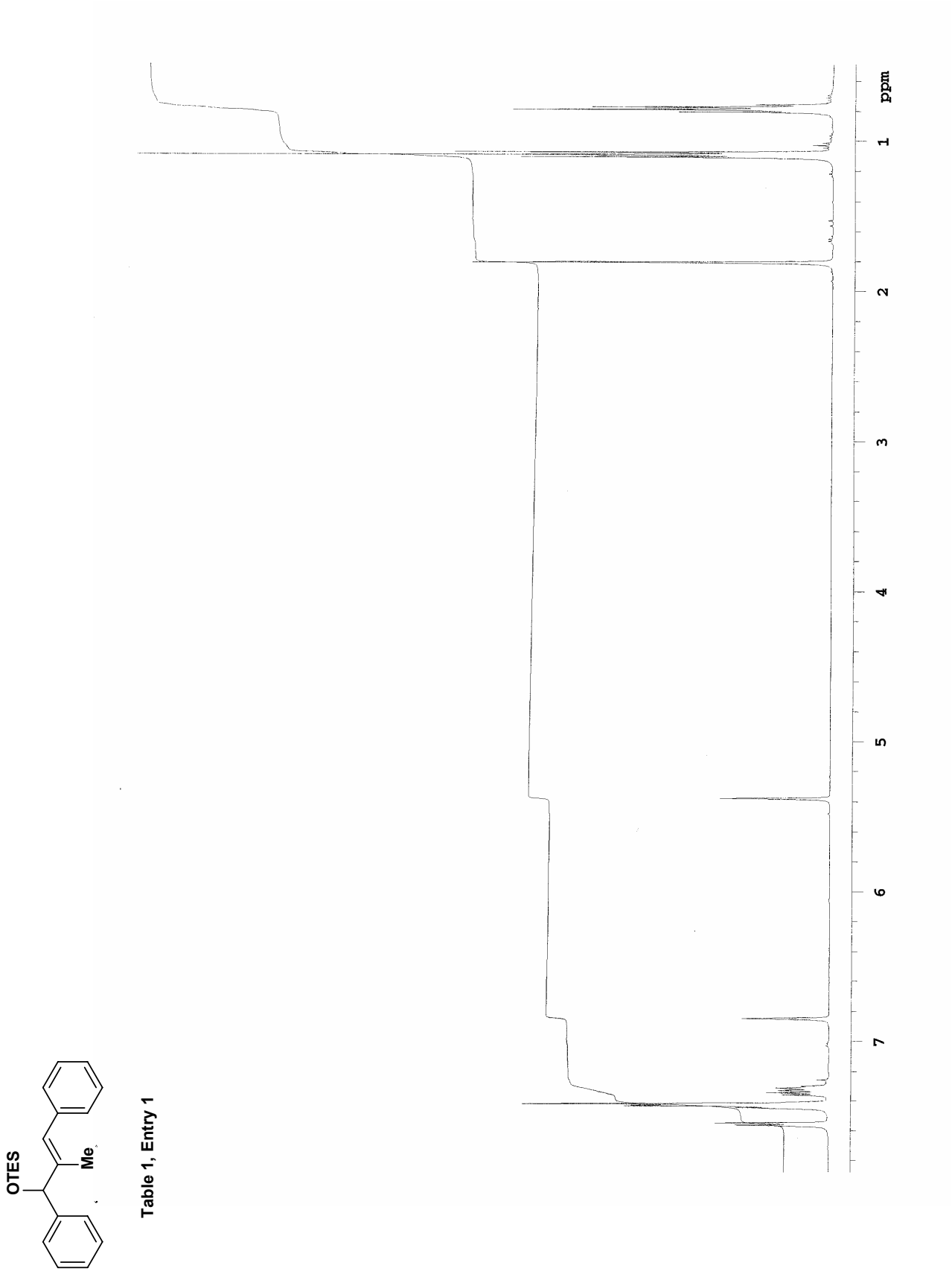
In the crude product of an experiment that employed 1 equiv. each of Et_3SiD and Pr_3SiH, the ratio of Et_3Si products to Pr_3Si products was determined by GC and was verified by NMR integration. From the crude GCMS, the relative intensity of the 289 and 290 peaks were normalized, with a value of 1 assigned to the base peak. The ratio of the Et_3Si-(H) product to Et_3Si-(D) product was determined as follows:

$$\frac{\text{intensity of 288 peak in crossover experiment}}{\text{intensity of 289 peak in crossover experiment}} =$$

$$\frac{[X] \times [\text{rel height of 288 peak in pure } Et_3Si\text{-(H) product}] + [Y] \times [\text{rel height of 288 peak in pure } Et_3Si\text{-(D) product}]}{[X] \times [\text{rel height of 289 peak in pure } Et_3Si\text{-(H) product}] + [Y] \times [\text{rel height of 289 peak in pure } Et_3Si\text{-(D) product}]}$$

X = 1/100 x relative % of Et_3Si-(H) product
Y = 1/100 x relative % of Et_3Si-(D) product = 1 - X

In the above equation, after substitution of [1 - X] for [Y], the experimental values were inserted and the equation was solved for [X]. The ratio of the Pr_3Si-(H) product to Pr_3Si-(D) product was determined in a similar fashion. Merging the GC ratios of Et_3Si products to Pr_3Si products with the data calculated from the above equation, an overall ratio of the four possible products may be obtained.


OTES
Me
Table 1, Entry 1
ppm
1
2
3
4
5
6
7

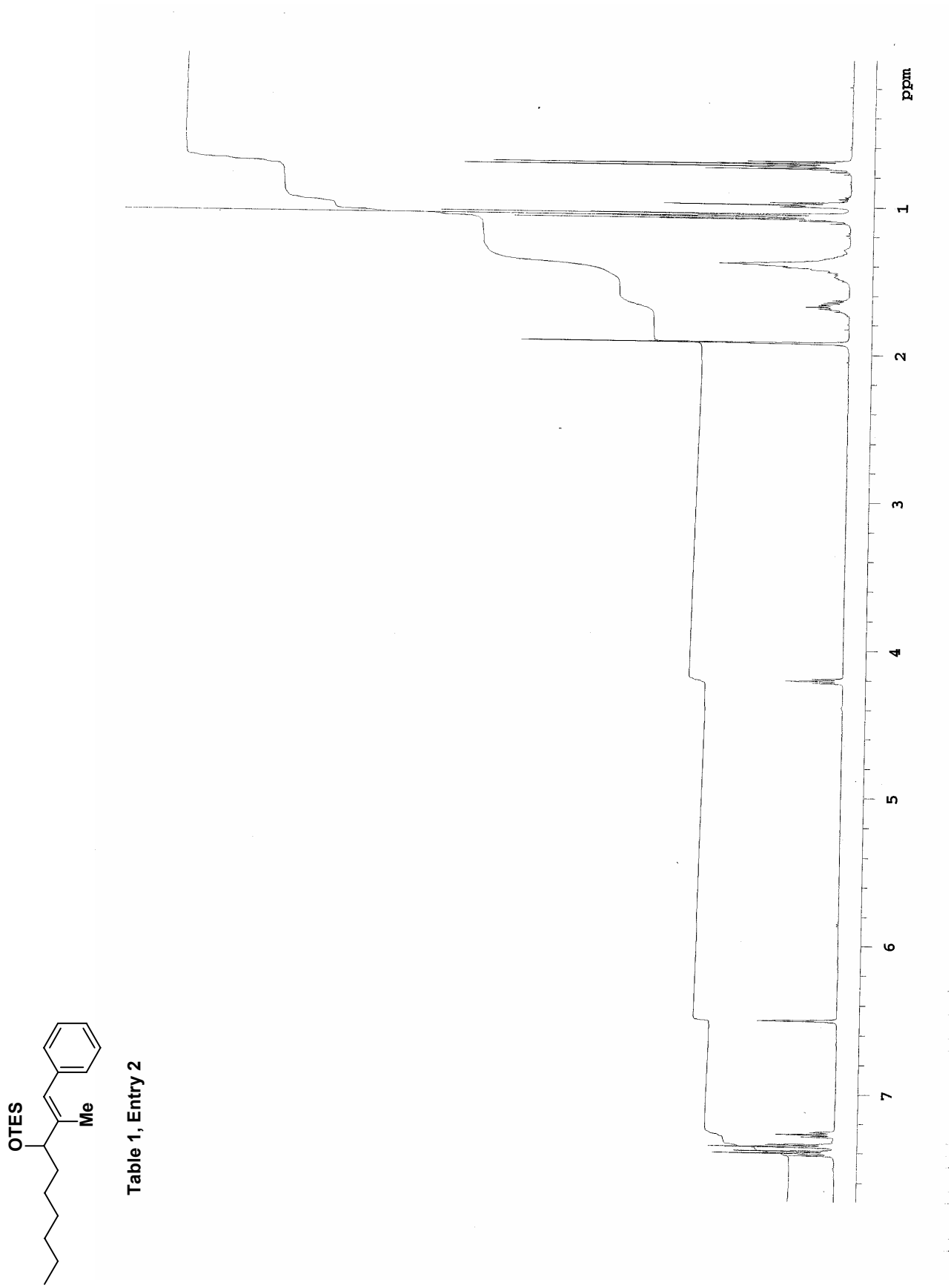


Table 1, Entry 2

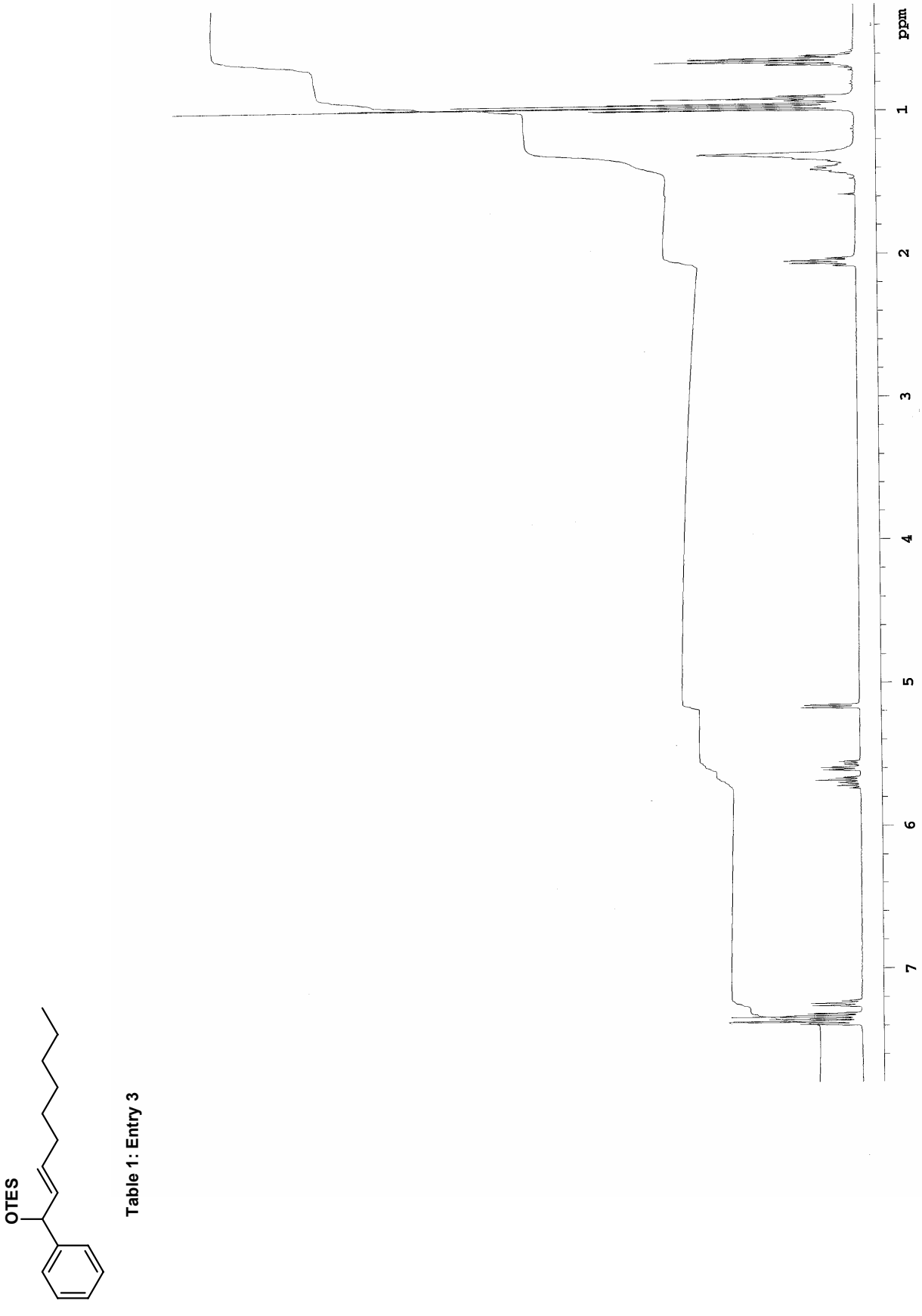


Table 1: Entry 3

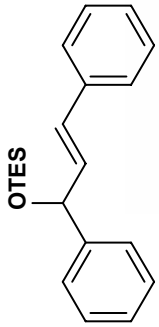
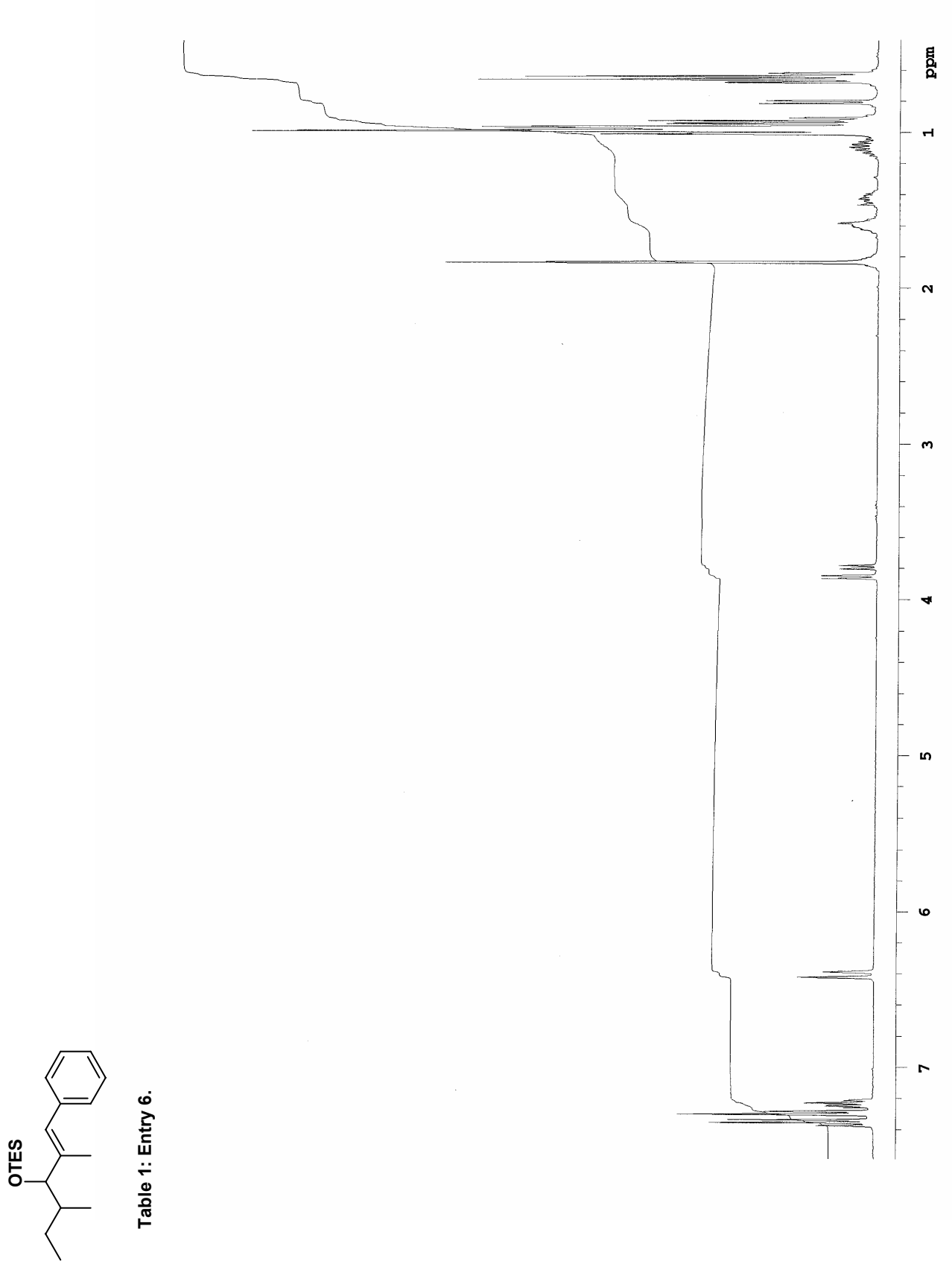


Table 1: Entry 4.

Table 1: Entry 5 (major)



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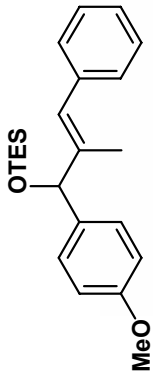

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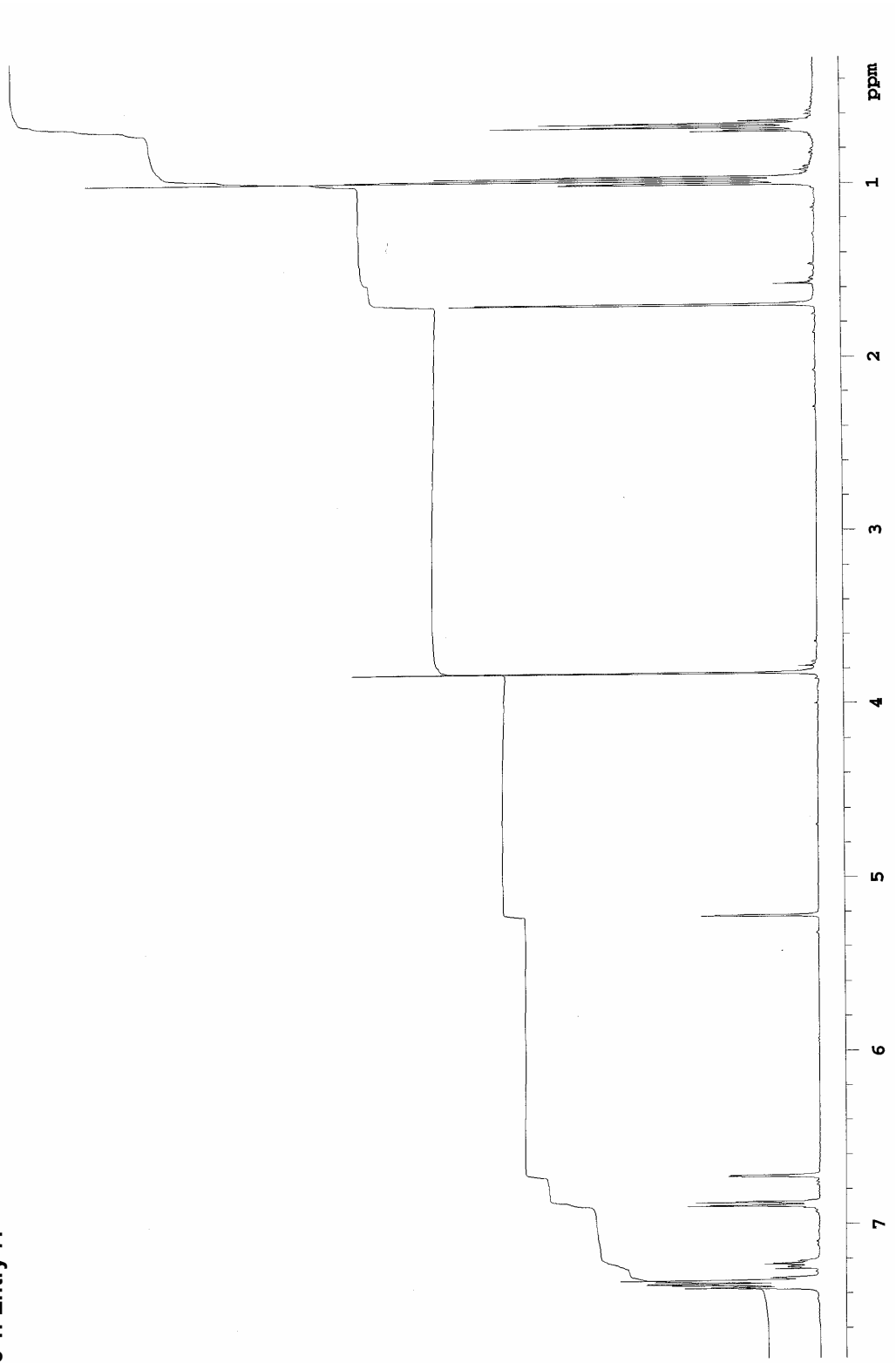


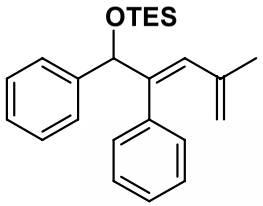
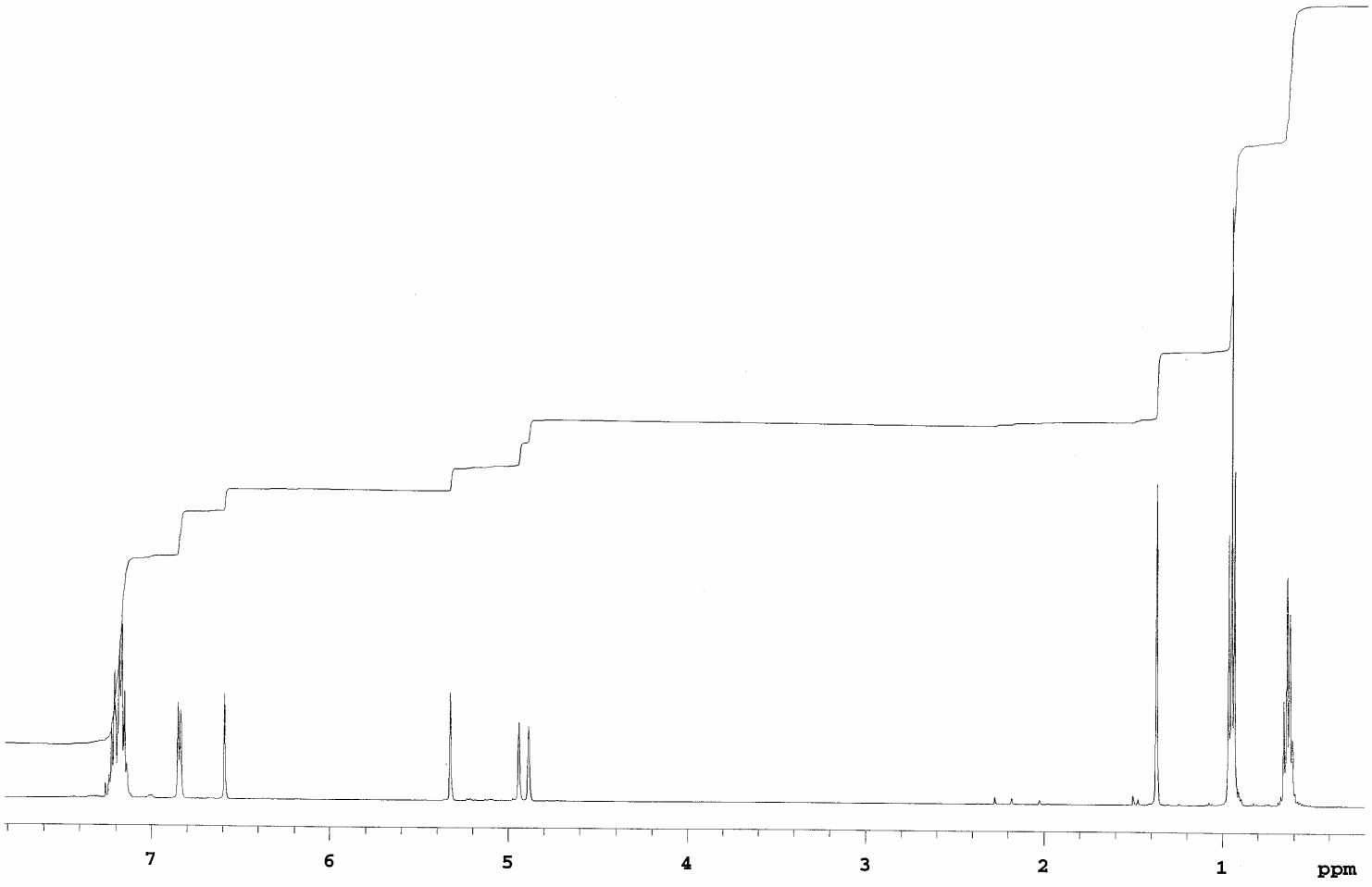
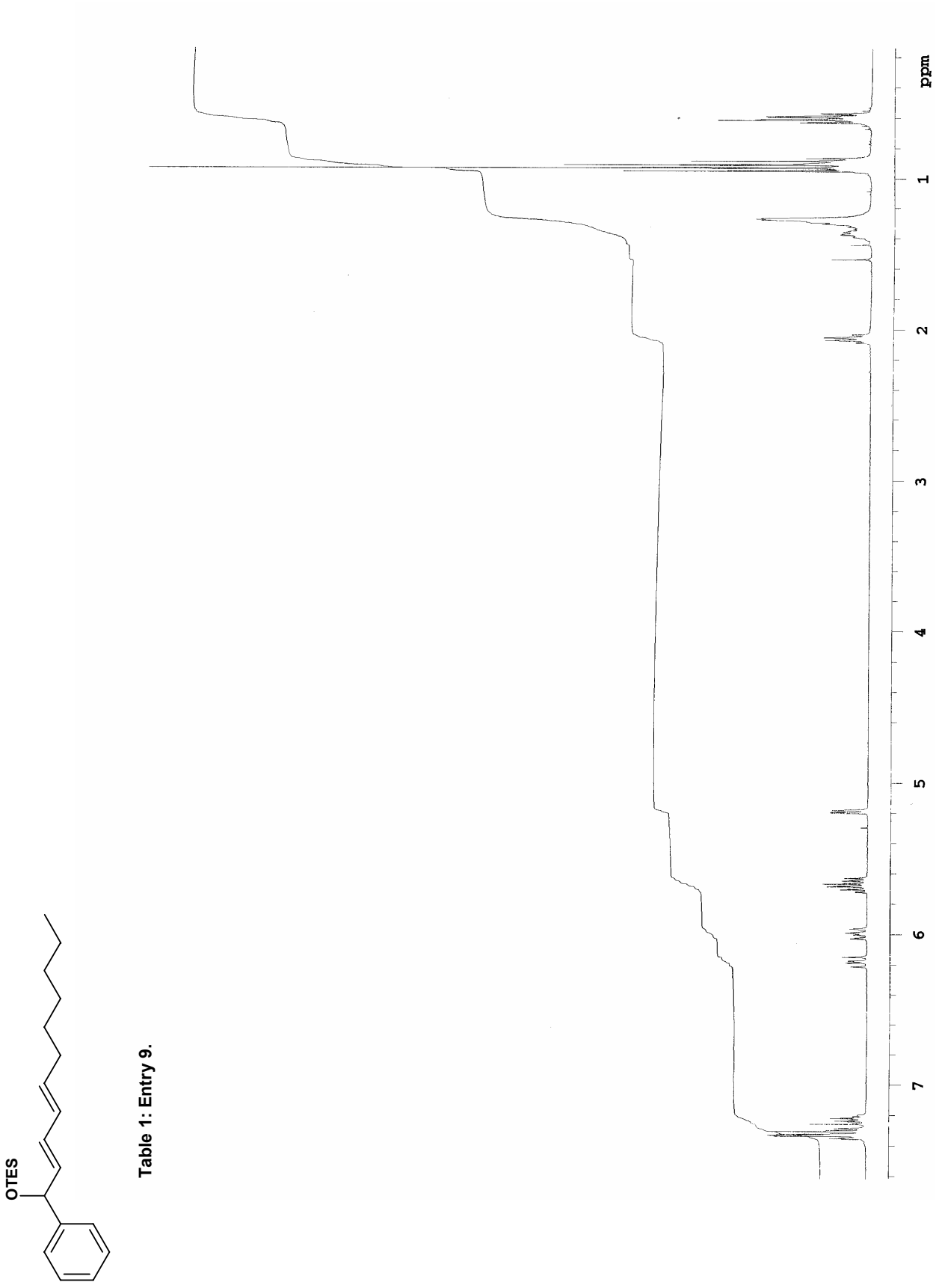


Table 1: Entry 8.





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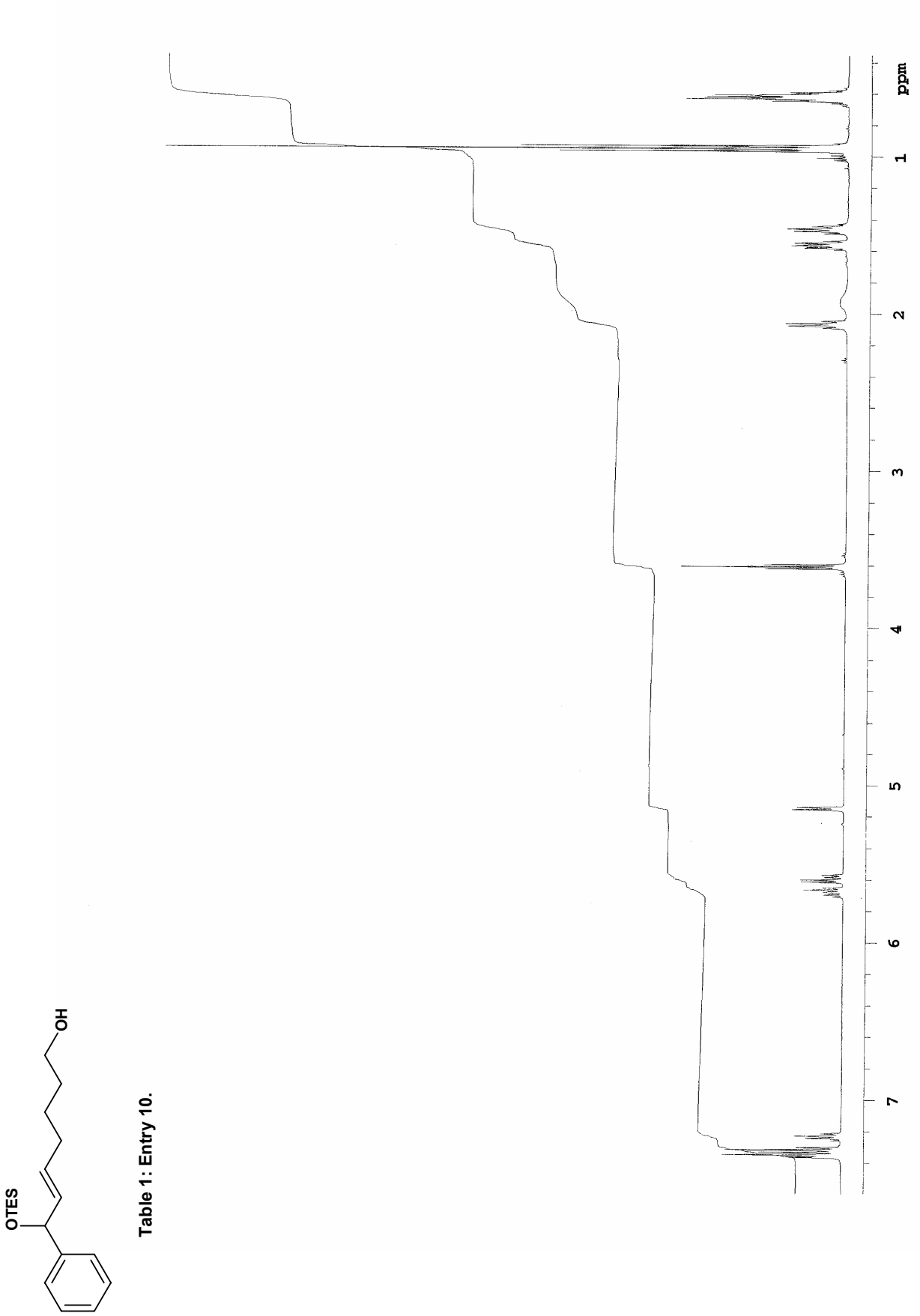

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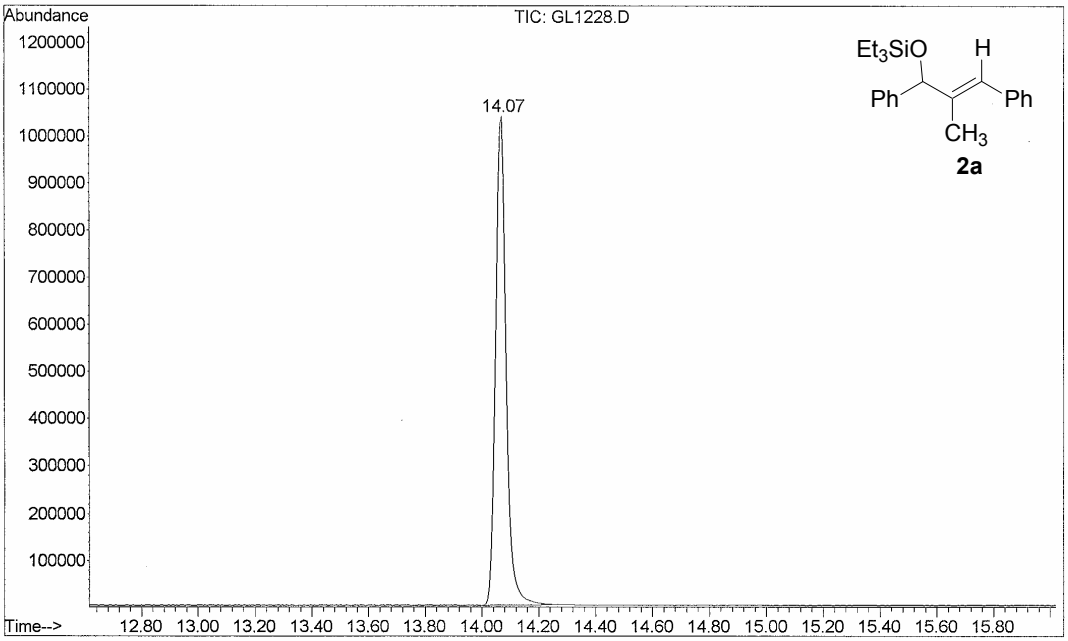
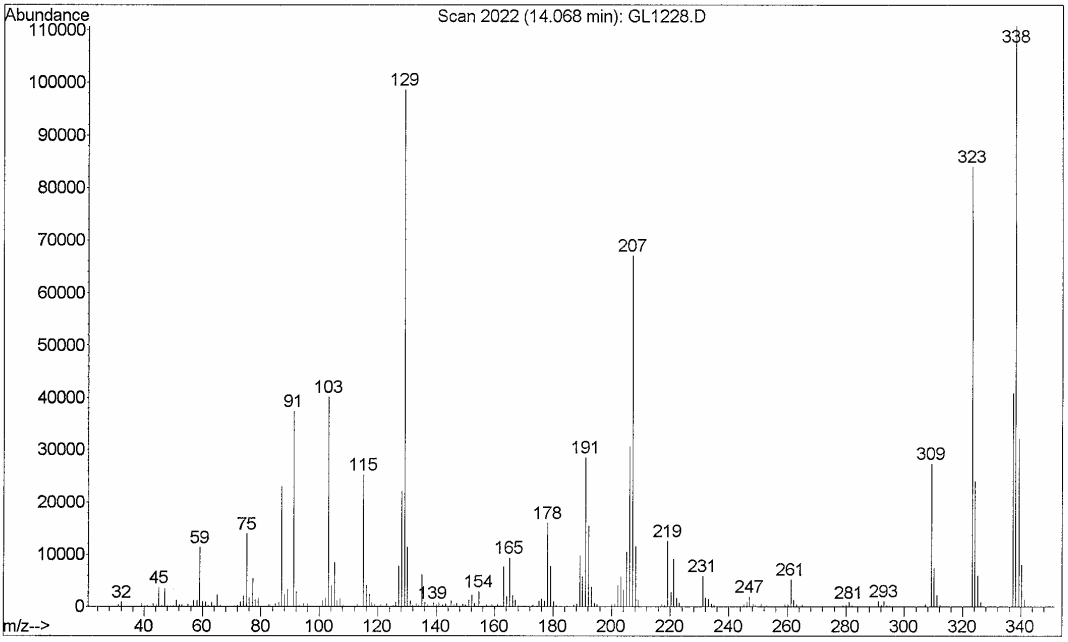
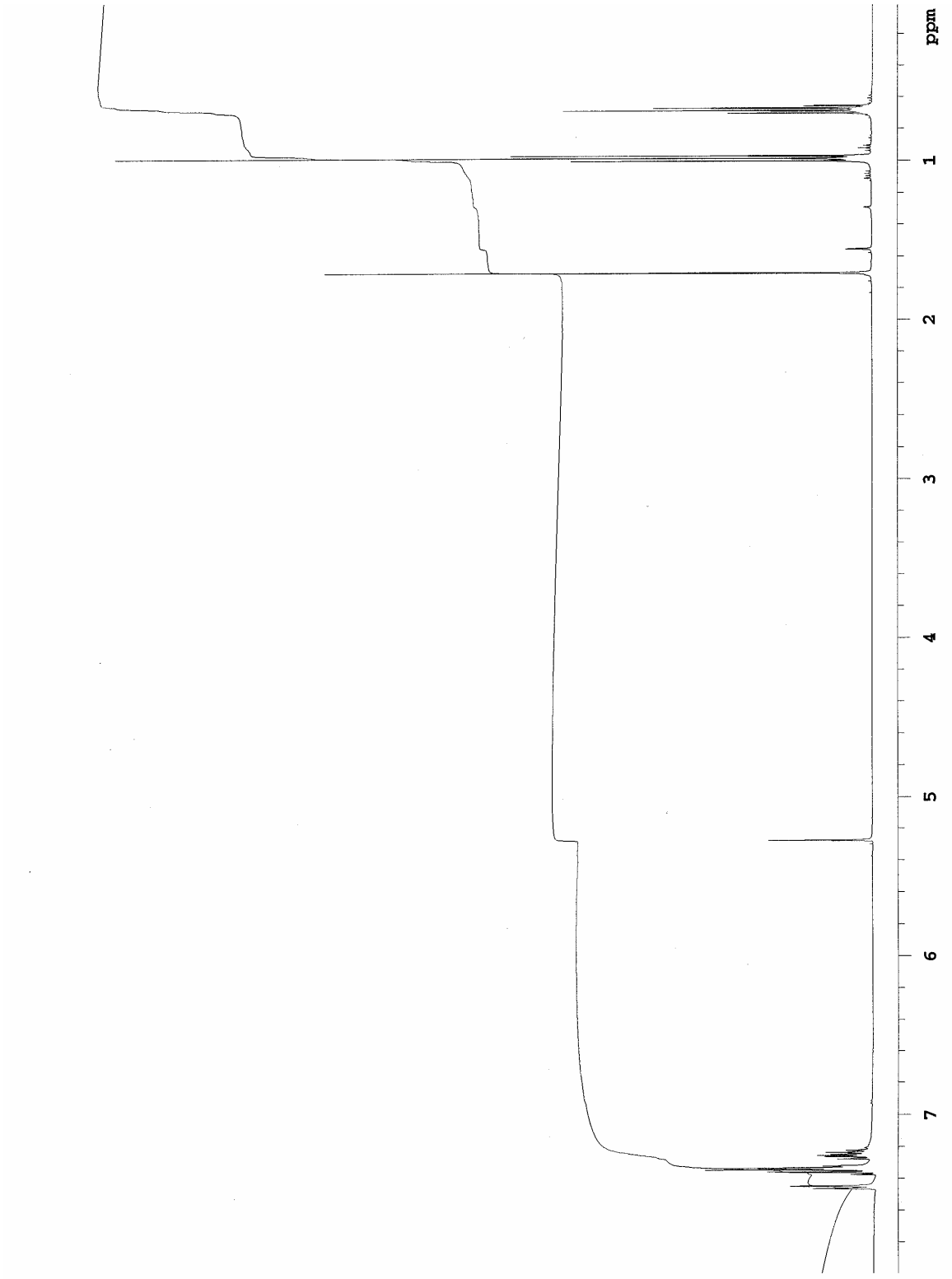
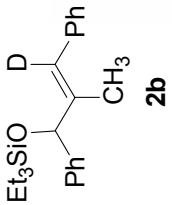


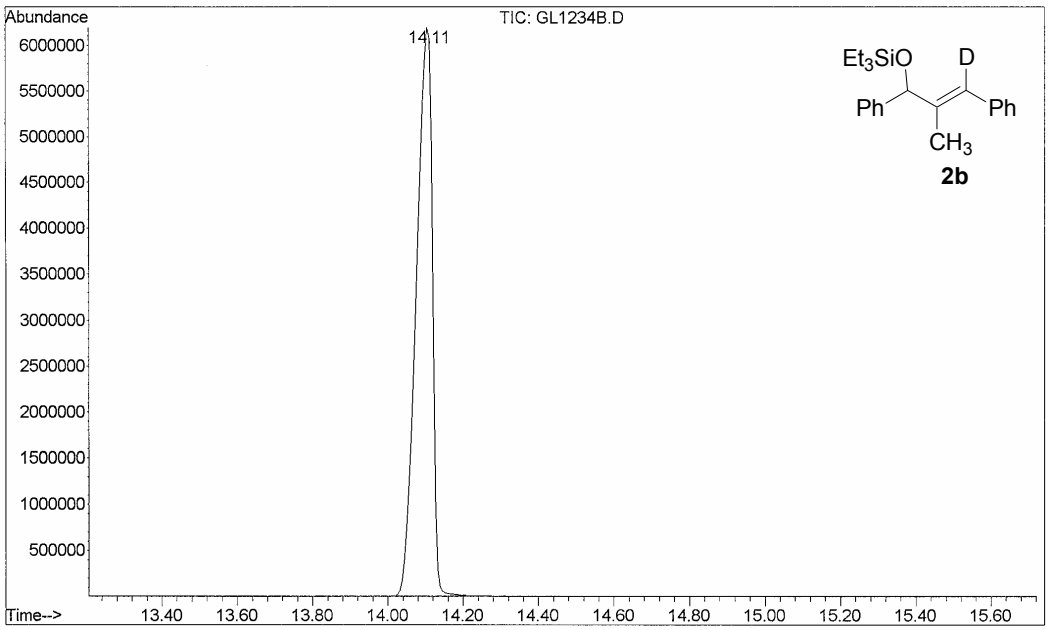


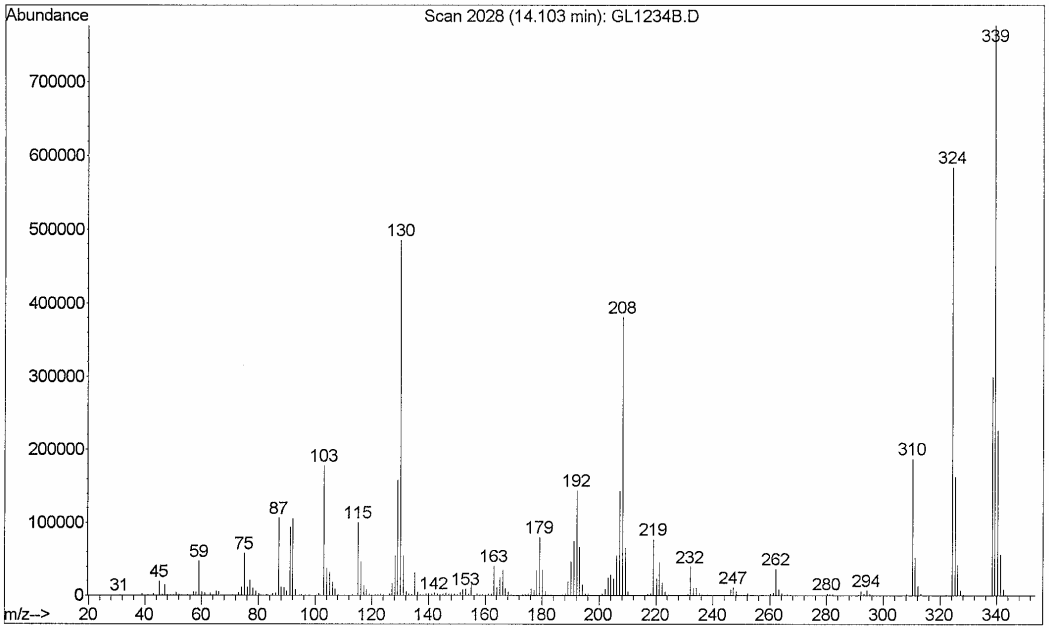
M/z	Abundance
337	40888
338	110688
339	32144
340	8132
341	1343





2b





M/z	Abundance
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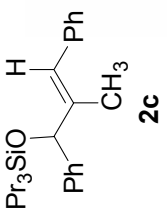
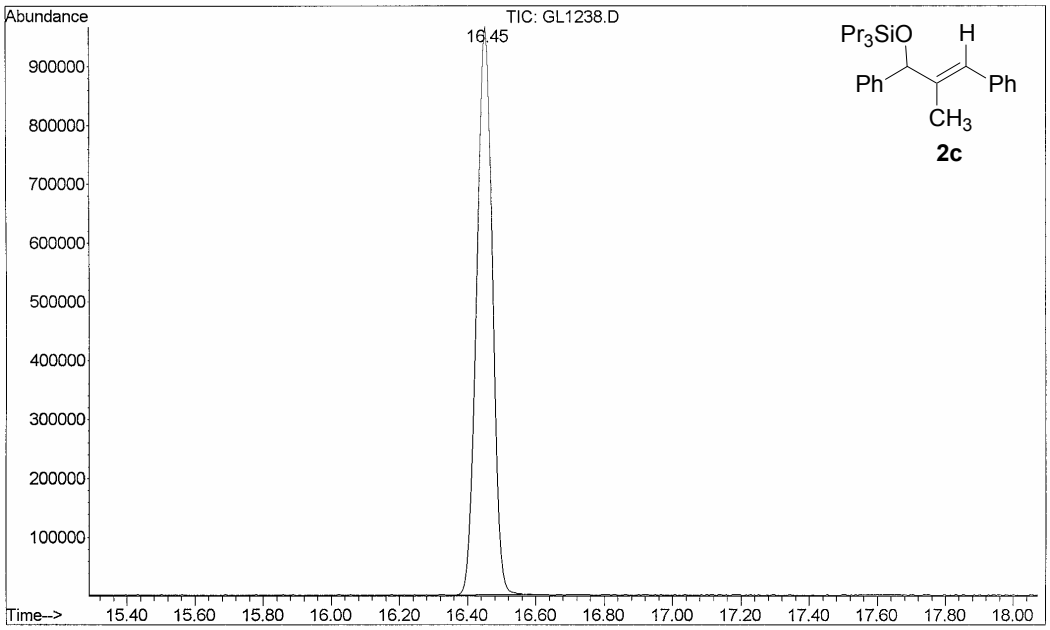
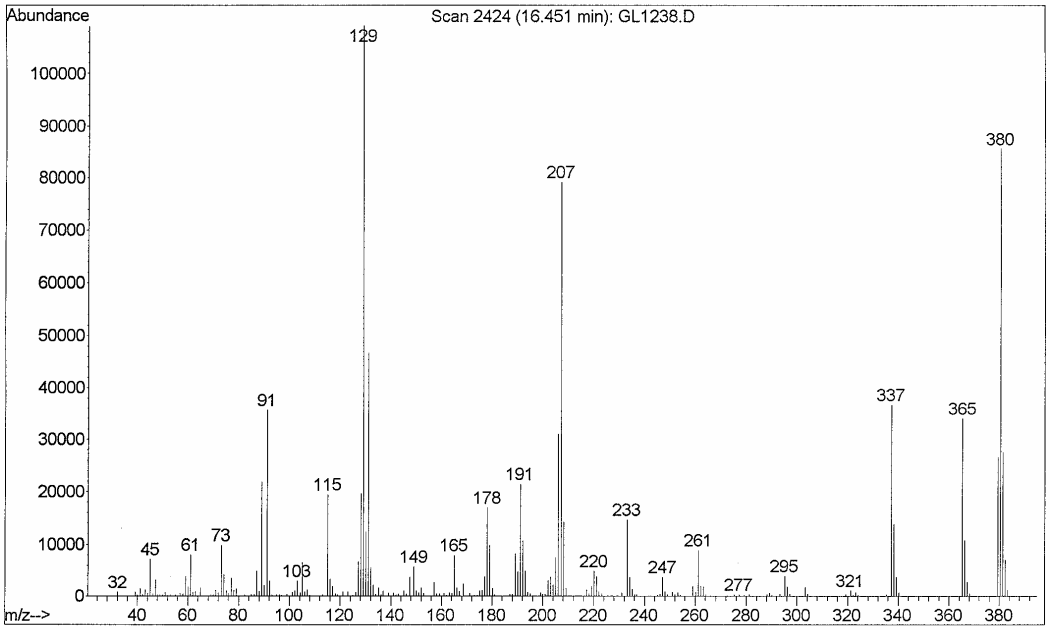
339	776576
340	225728
341	56808
342	8694



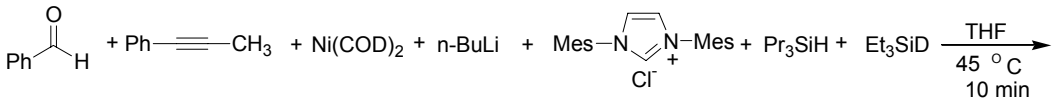
2c



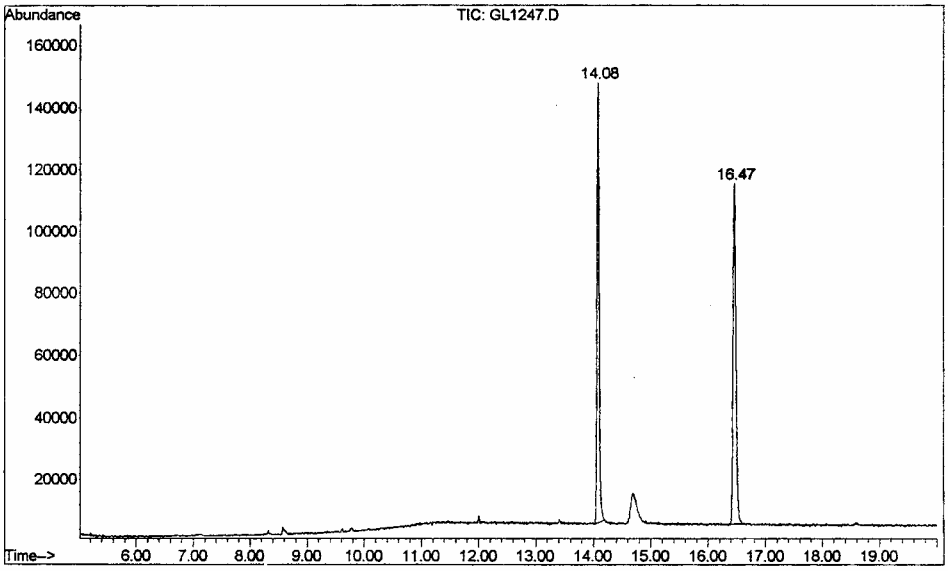


M/z	Abundance
379	26720
380	85624
381	27528
382	6985
383	1137

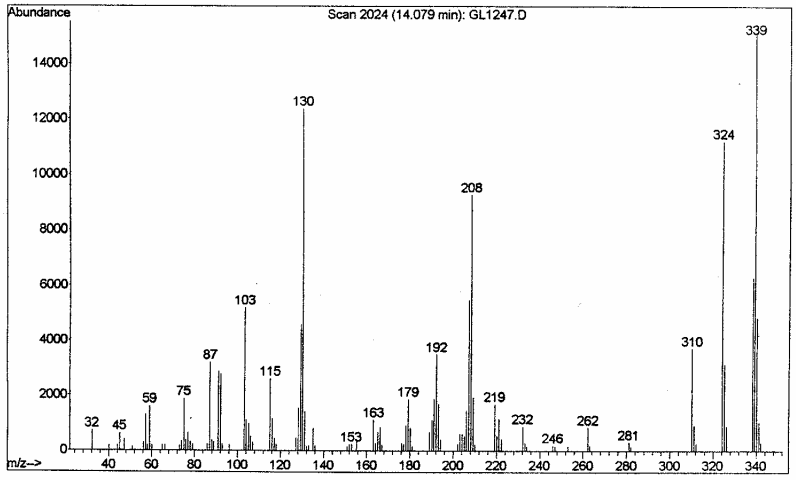
Crossover experiment of $Ni(COD)_2$/ carbene catalyzed coupling of aldehyde and alkyne:

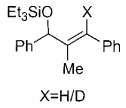


2a <1% **2b** 48% **2c** 50% **2d** <1%



peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	14.085	2014	2025	2052	BB	141979	3764817	96.41%	49.087%
2	16.469	2407	2427	2450	BB 2	109561	3904939	100.00%	50.913%





M/z	Abundance
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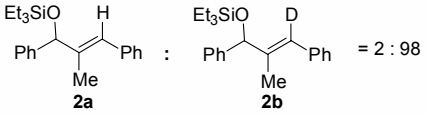
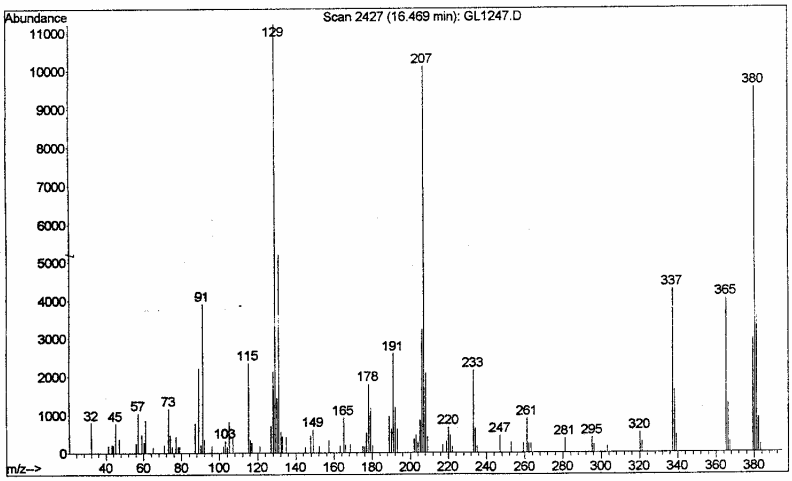
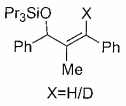
339.20	15526.0
340.30	4844.0
341.20	1035.0
342.20	297.0



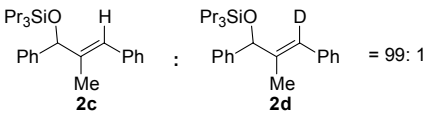
= 2 : 98

2a **2b**



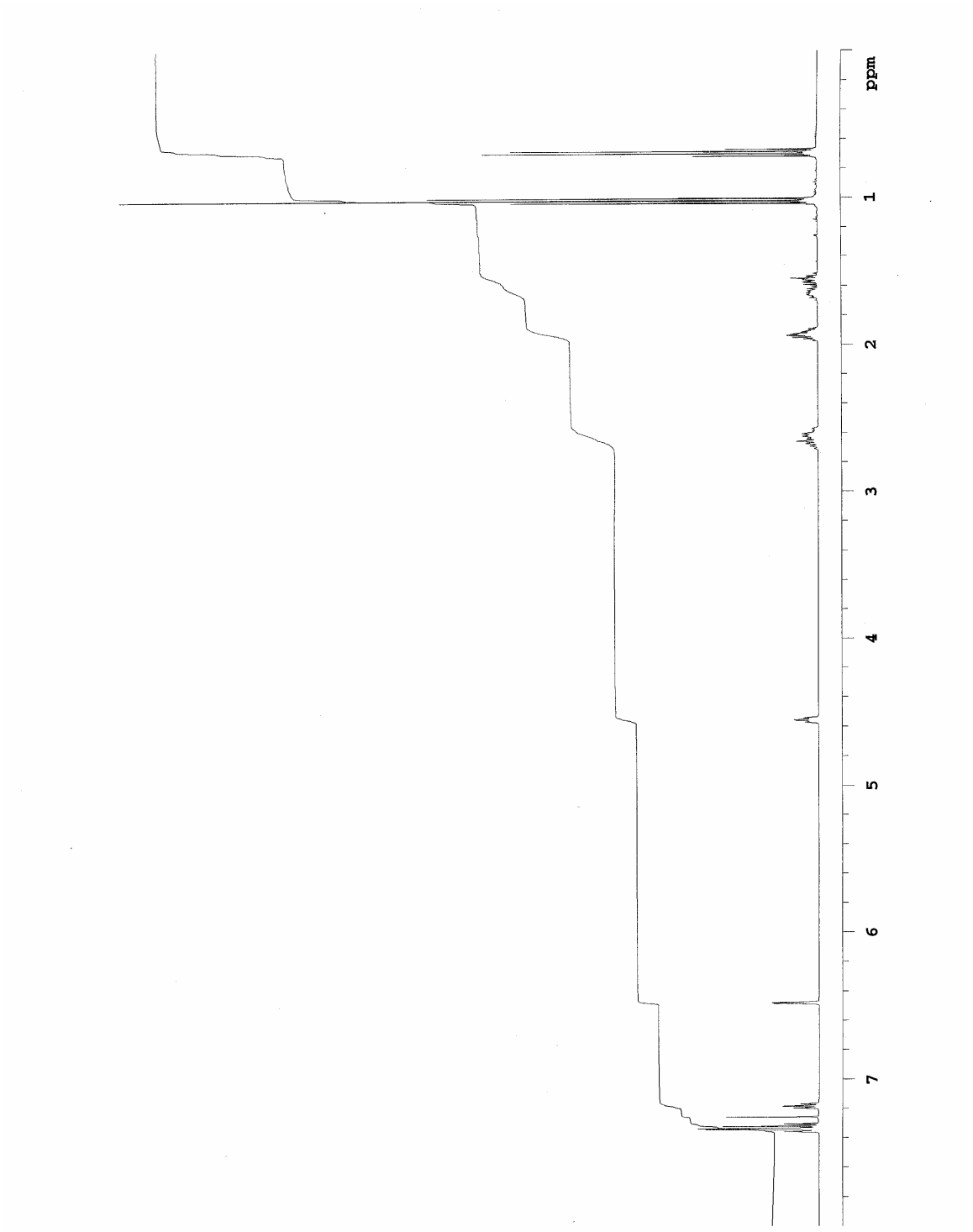


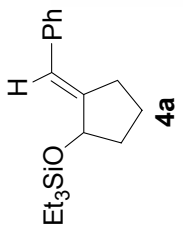
M/z	Abundance
379.30	2970.0
380.30	9529.0
381.30	3568.0
382.30	913.0
383.30	210.0



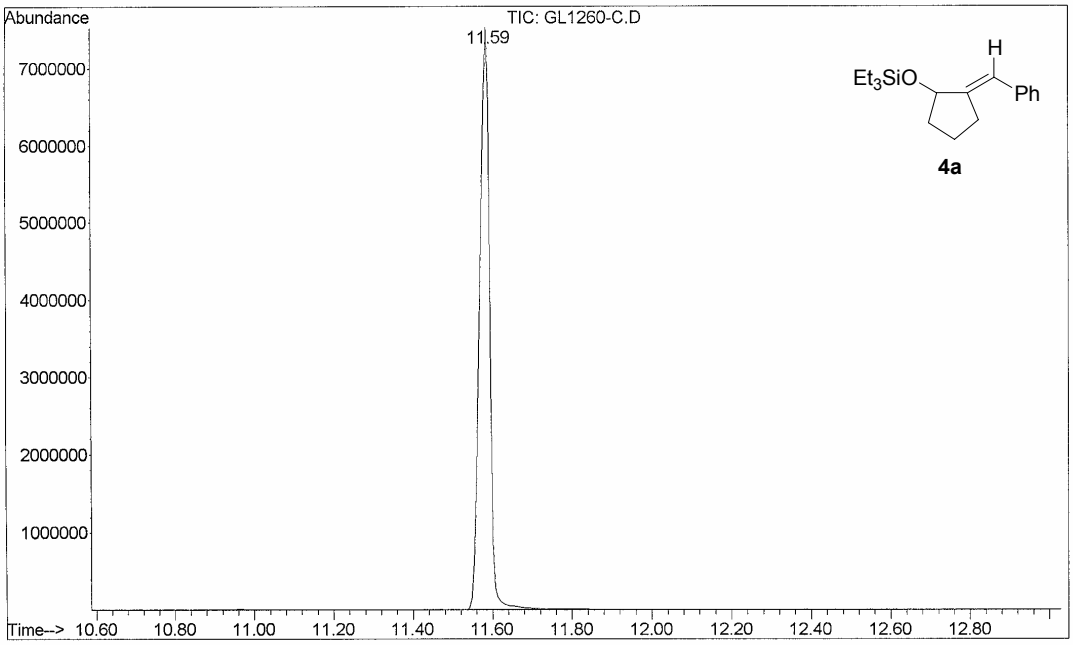
= 99: 1

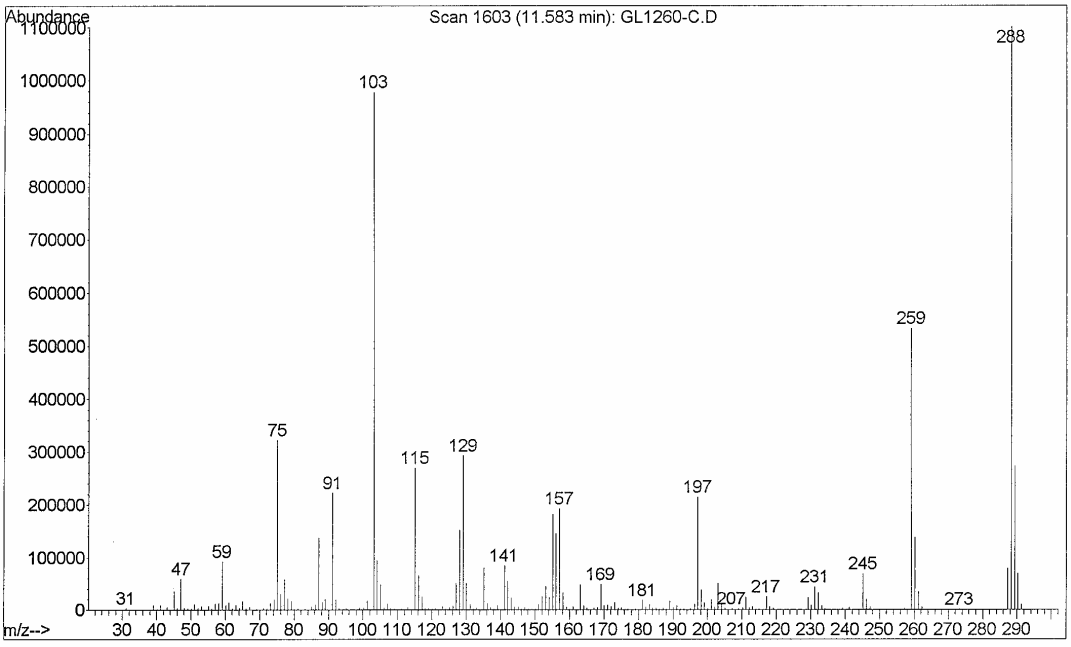
2c **2d**



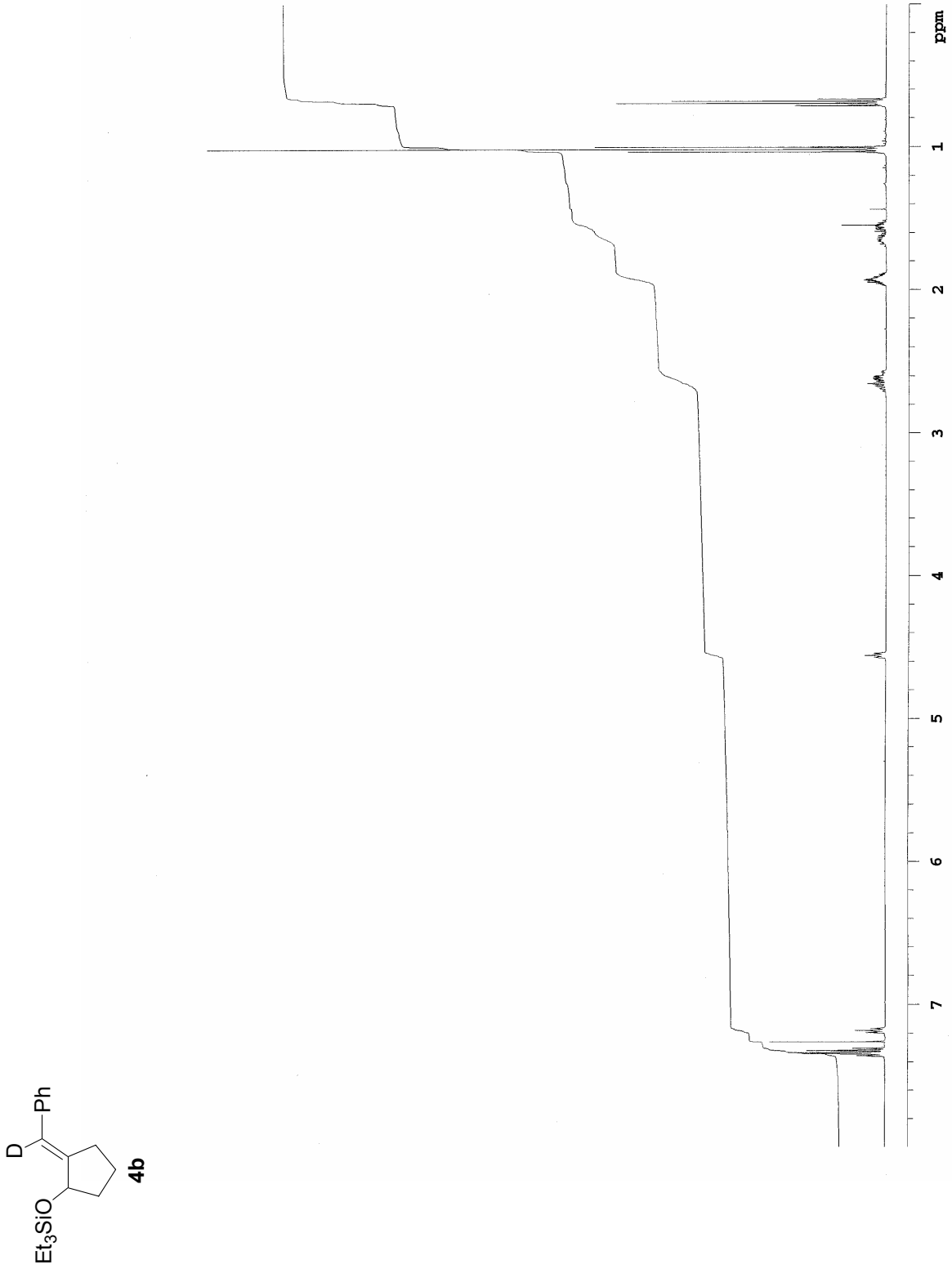


4a

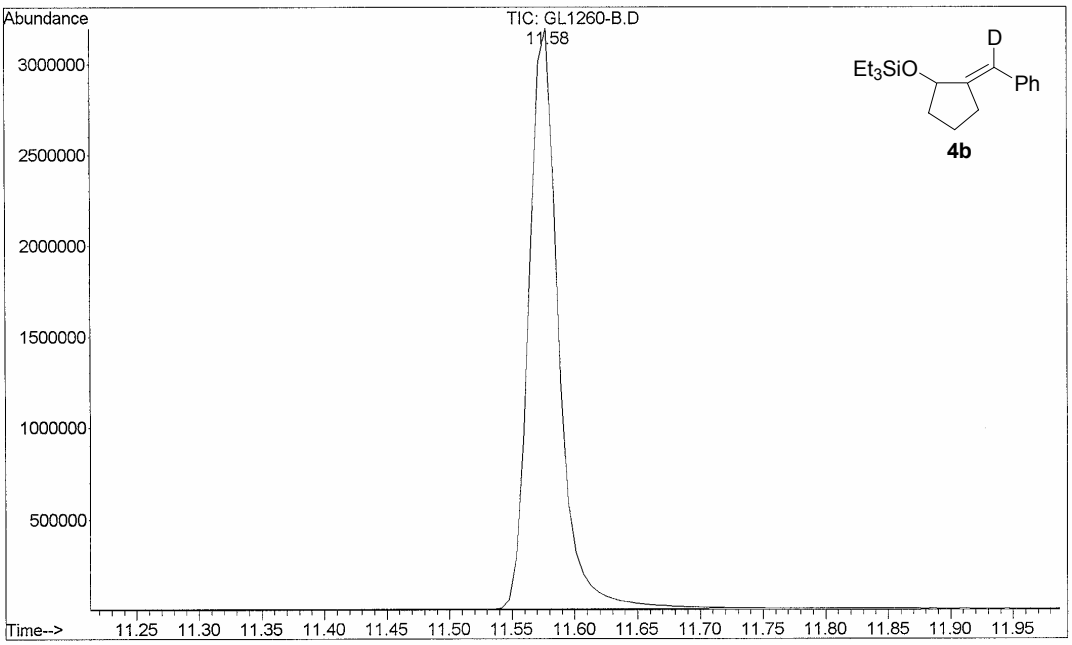


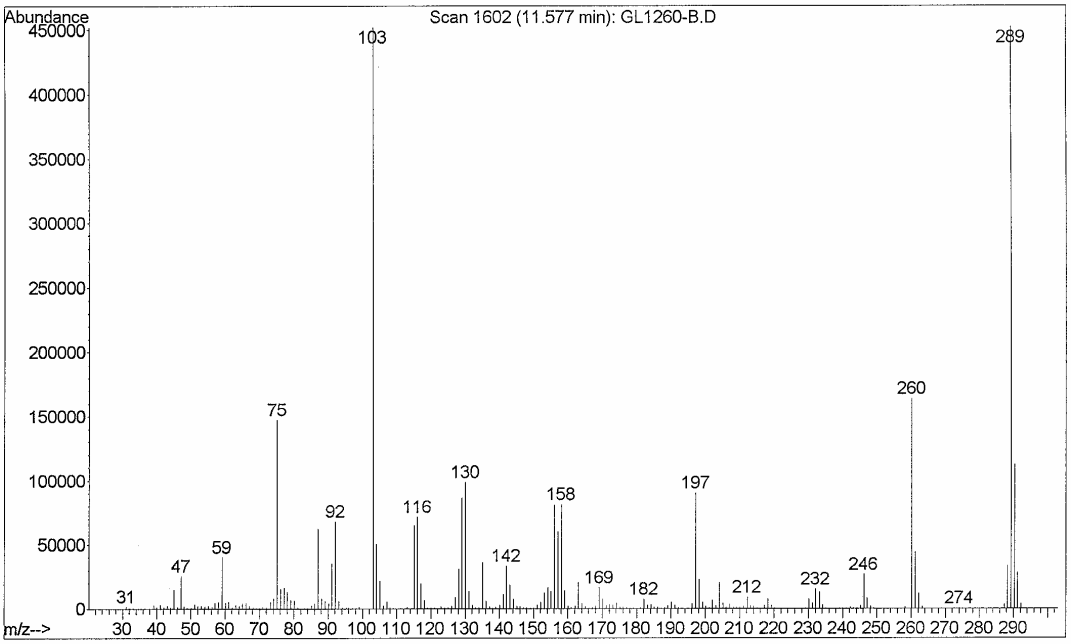


M/z	Abundance
287	79856
288	1100800
289	273408
290	70160
291	10276
292	1034

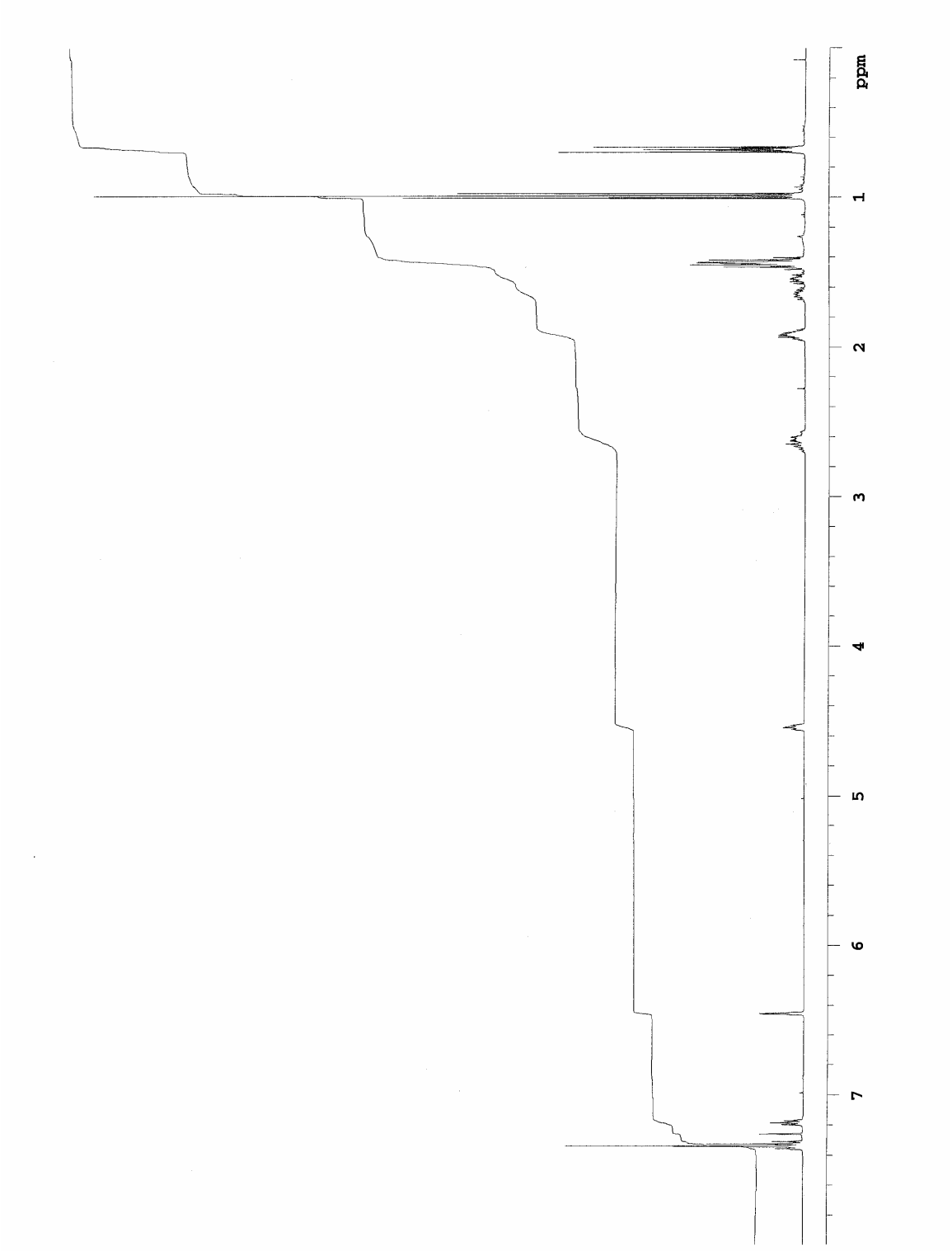


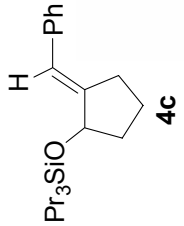
4b



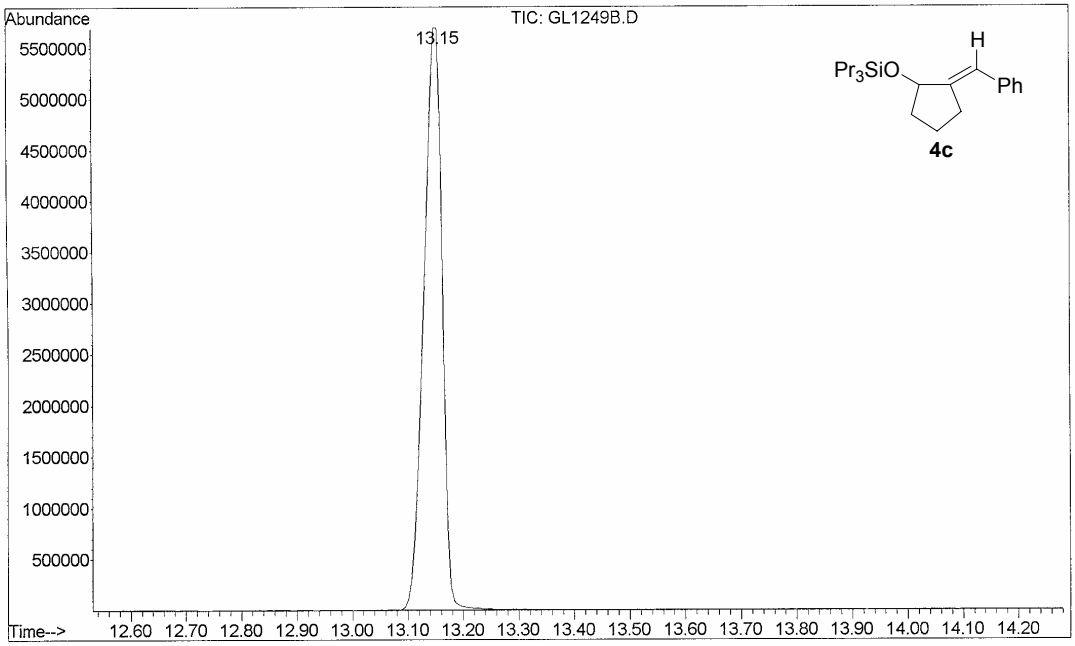


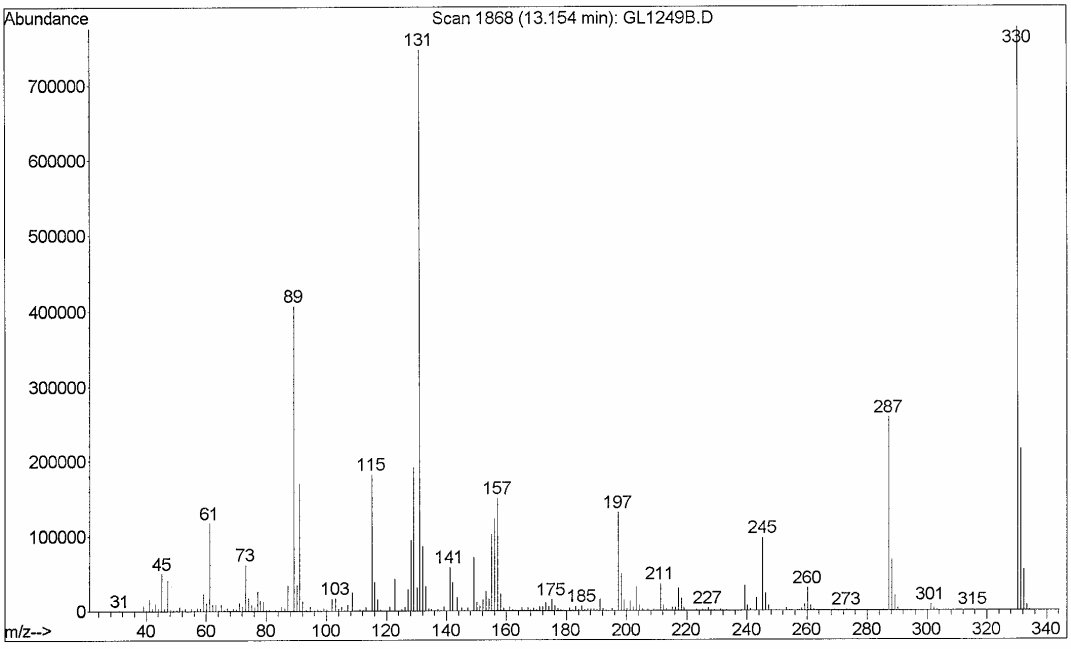
M/z	Abundance
287	3575
288	33784
289	452032
290	112624
291	28336
292	3828





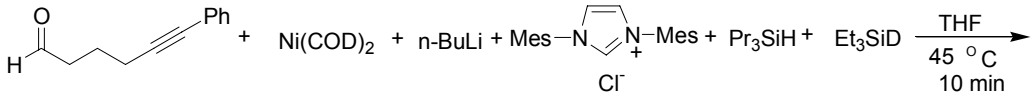
4c

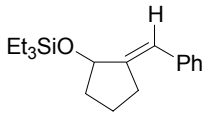




M/z	Abundance
330	776256
331	215424
332	55408
333	8349
334	1043

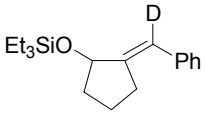
Crossover experiment of $Ni(COD)_2$/ carbene catalyzed cyclization of ynals:





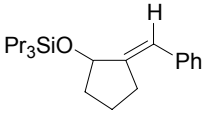
4a

<2%



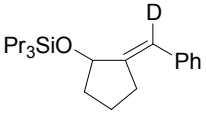
4b

55%



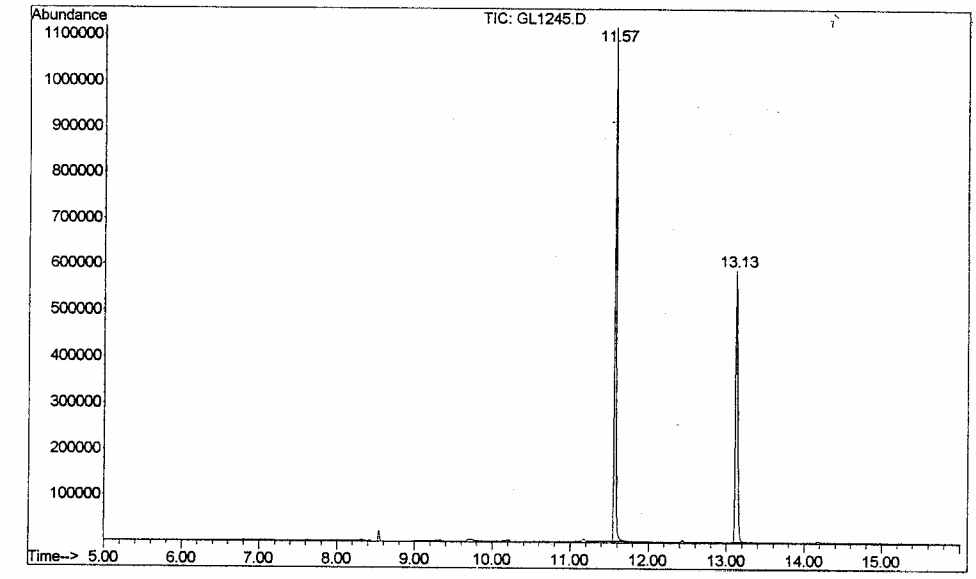
4c

41%

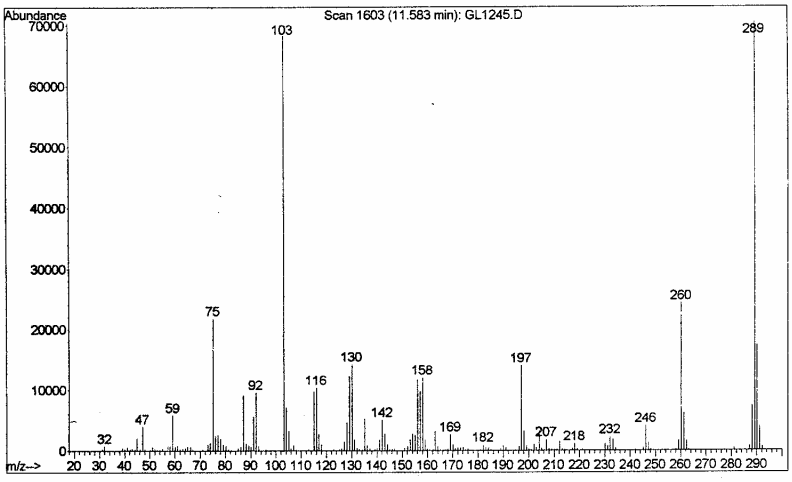


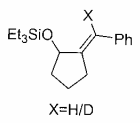
4d

<2%

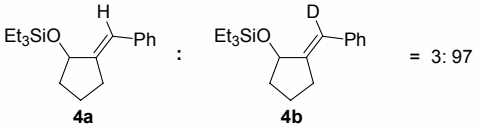


peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	11.571	1594	1601	1626	BB	1070471	15408799	100.00%	56.843%
2	13.131	1851	1864	1882	BB	584802	11699063	75.92%	43.157%

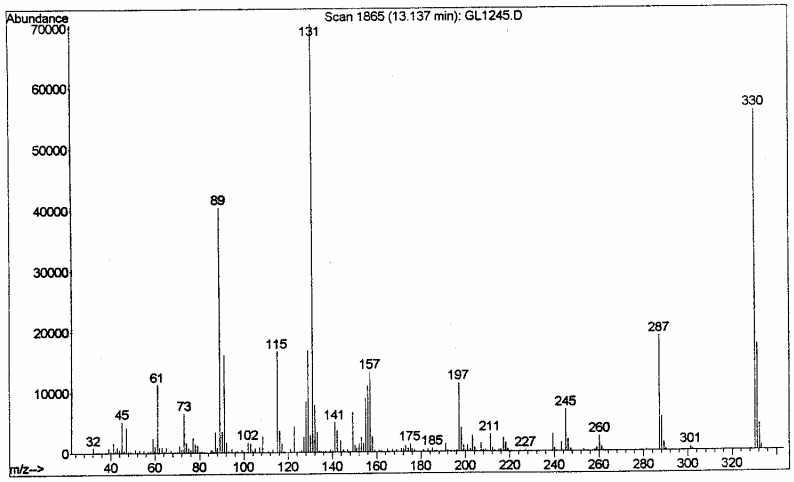


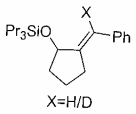


M/z	Abundance
287.20	789.0
288.20	7317.0
289.20	70416.0
290.20	17352.0
291.20	4001.0
292.20	625.0

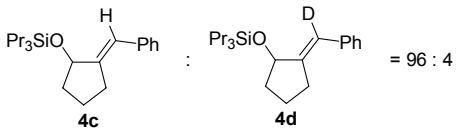


4a **4b**



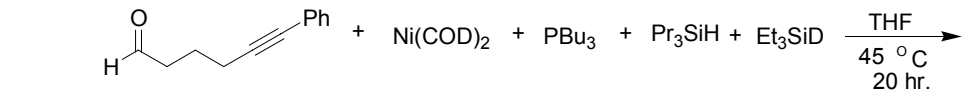


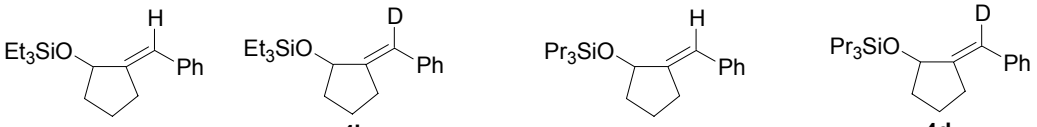
M/z	Abundance
328.20	194.0
330.30	56040.0
331.30	17544.0
332.30	4356.0
333.30	863.0



4c **4d**

Crossover experiment of $Ni(COD)_2$/ PBu_3 catalyzed cyclization of ynals:



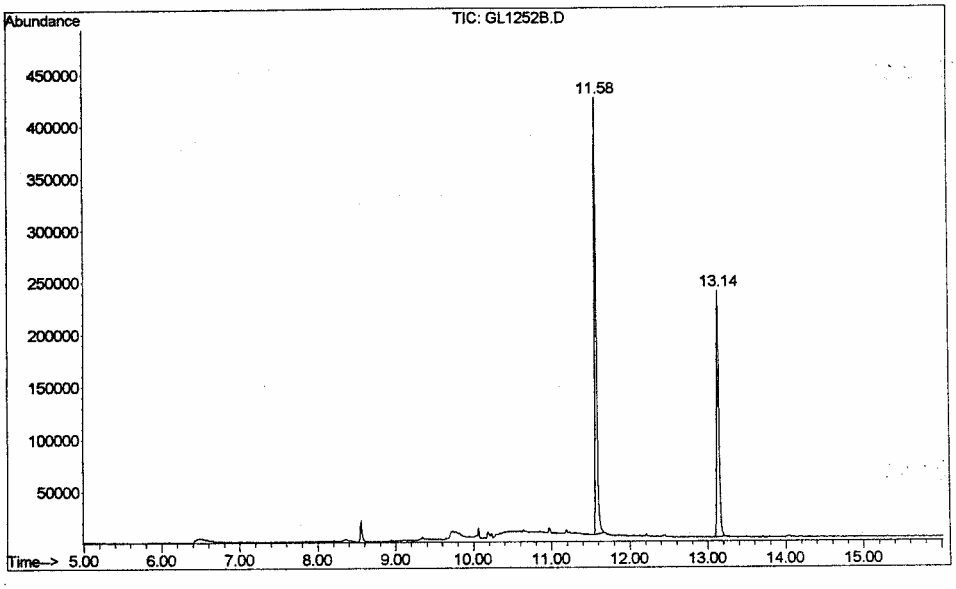


4a 25%

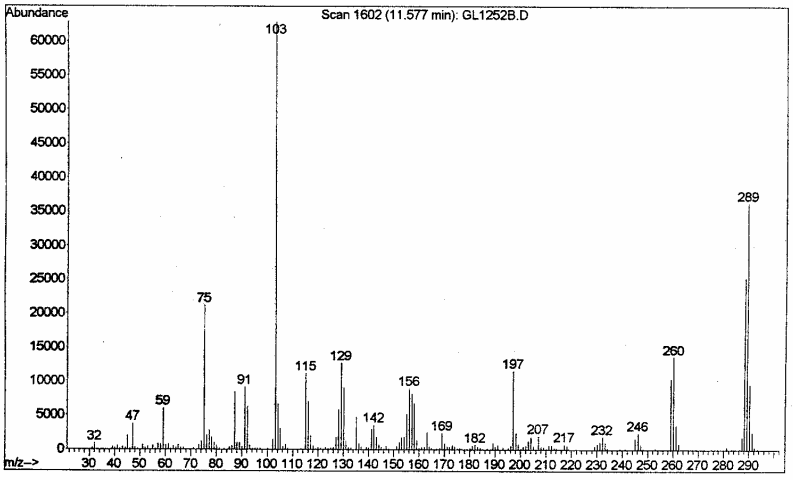
4b 34%

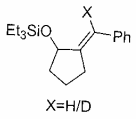
4c 23%

4d 18%

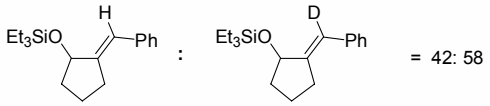


peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	11.577	1596	1602	1631	BB	405585	6464420	100.00%	58.018%
2	13.137	1857	1865	1881	BB	230147	4677618	72.36%	41.982%

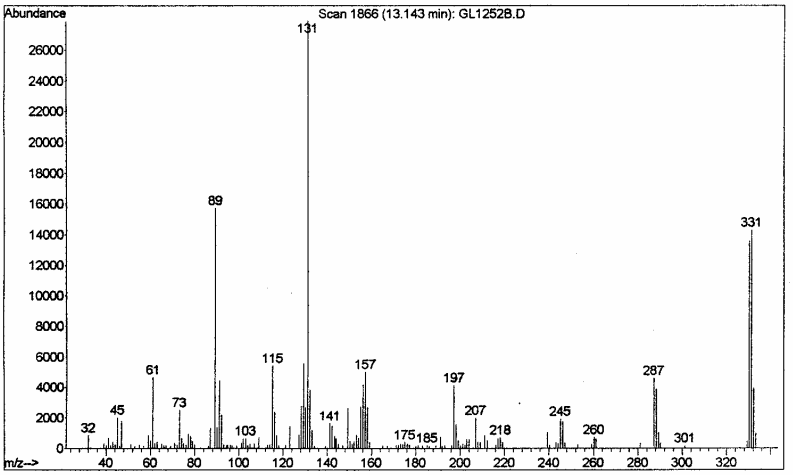


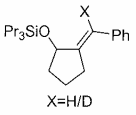


M/z	Abundance
286.30	169.0
287.30	1806.0
288.20	25296.0
289.20	36296.0
290.20	9608.0
291.30	2510.0

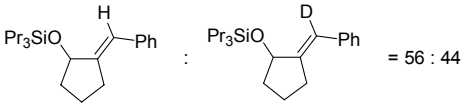


4a **4b**





M/z	Abundance
329.30	463.0
330.30	13589.0
331.30	14304.0
332.30	3971.0
333.30	986.0



4c **4d**