

Bulky Trialkylsilyl Acetylenes in the Cadiot-Chodkiewicz Cross-Coupling Reaction

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SUPPORTING INFORMATION

A. General remarks

All needles and syringes were oven-dried and cooled down to room temperature in a desiccator prior to use. All reactions were carried out under a nitrogen (or argon) atmosphere. Unless otherwise indicated, all starting materials were used as received. *n*-Butyl lithium, methylmagnesium bromide, ethylmagnesium bromide, and vinylmagnesium bromide came as a 2.5M solution in tetrahydrofuran, a 3.0M solution in diethyl ether, a 3.0M solution in diethyl ether, and a 1.0M solution in THF respectively, and were titrated prior to use.¹ Diethyl ether was dried over 4 Å molecular sieves and distilled over Na/Benzophenone. Silica gel, 40 microns, was purchased from Scientific Absorbents Incorporated. TLC monitoring was best using Hex:EtOAc solvent systems. The vinylic tellurides were detected using a UV light, iodine, and a vanillin solution (27 mL H₂O, 6 mL concentrated H₂SO₄, 27 mL MeOH and 1.2 g vanillin). Alcohols were best observed in a KMnO₄ solution (1.5 g KMnO₄, 10 g K₂CO₃, 2.5 mL of 5% NaOH and 150 mL water).

Infrared spectra (IR) were recorded on a FT-IR Spectrophotometer with internal calibrations. Spectra were recorded either from a neat oil between sodium chloride salt plates, or from a potassium bromide pellet. IR data were reported in wavenumbers (cm⁻¹).

Proton nuclear magnetic resonance spectra (^1H NMR) were obtained either on a 300, 400, or 500 MHz FT NMR spectrometers. Spectra were recorded in deuteriochloroform (CDCl_3) with residual proteo form as an internal reference or tetramethylsilane (TMS) as the external reference. Data were reported as followed: chemical shift (δ) in ppm (multiplicity, integrated intensity, and coupling constant (J) in Hertz (Hz)). Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), m (multiplet), and br (broad).

Difference nuclear Overhauser effect (NOE) experiments were performed on the 400 and 500 MHz FT NMR spectrometers using automated programs.

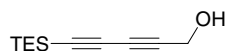
Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained either on the 75, 100 or 125 MHz FT NMR spectrometers. Spectra were recorded in deuteriochloroform with 77.0 ppm resonance of deuteriochloroform as the internal reference.

High resolution mass spectra (HRMS) were determined on a VG 70-250S instrument by the University of Michigan, Department of Chemistry Instrument Services Branch. Sample introduction was *via* direct probe, and ionization was accomplished by electron impact (EI) at 70 eV, by chemical ionization (CI) with methane or ammonia, or by fast atom bombardment (FAB) with sodium. Masses were reported in units of mass over charge (m/z) to four decimal places in conjunction with the relative intensity normalized to 100.

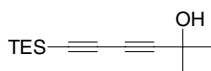
B. General procedure for the diyne synthesis

CuCl (0.06 mmol, 0.02 equiv) was added to a 30% $n\text{-BuNH}_2$ (2.5 mL) aqueous solution at rt that resulted in the formation of a blue solution immediately. A few crystals of hydroxylamine hydrochloride were added to discharge the blue color. The resulting colorless solution indicated the present of Cu(I) salt. The alkyne (3.6 mmol, 1.2 equiv) was added to the solution at rt forming a yellow acetylide suspension that was immediately cooled down with an ice-water mixture. The bromoalkyne (3 mmol, 1 equiv) was added at once and the ice bath was removed (a small amount of diethyl ether could be used in the transfer). More crystals of hydroxylamine hydrochloride were added throughout the reaction as necessary to prevent the solution from turning blue or green. After several additions of hydroxylamine hydrochloride crystals, the reaction mixture had a rusty color (normally after 7 to 30 min, depending on alkynyl substrates). At this point, the reaction was complete according to TLC. The product was repeatedly extracted with diethyl ether (3x20mL), dried over MgSO_4 and concentrated under

reduced pressure. The crude product could be purified further by flash column chromatography on silica gel.



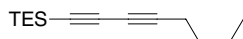
5-Triethylsilyl-penta-2,4-diyne-1-ol (10): $C_{11}H_{18}OSi$; FW = 194; R_f = 0.32 (90:10 Hex:EtOAc). Column chromatography (90:10 Hex:EtOAc) afforded a light yellow oil which was stored in the freezer. Yield 95%. 1H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 4.30 (d, 2H, J = 6.2 Hz), 1.75 (t, 1H, J = 6.2 Hz), 0.95 (t, 9H, J = 8.1 Hz), 0.58 (q, 6H, J = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 88.3, 86.1, 75.2, 71.1, 51.6, 7.5, 4.3; IR (neat) cm^{-1} : 3326 (br), 2957, 2937, 2877, 2224, 2107, 1458, 1414, 1236, 1018, 974, 798, 728; HRMS (CI with NH_3) for $C_{11}H_{18}OSi$ $[M+NH_4]^+$ calcd. 212.1471, found 212.1460; CI with NH_3 , m/z (rel intensity): 120 (40.3), 132 (100), 182 (71.3), 212 (74.5).



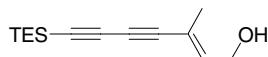
2-Methyl-6-triethylsilyl-hexa-3,5-diyne-2-ol (11): $C_{13}H_{22}OSi$; FW = 222; R_f = 0.38 (90:10 Hex:EtOAc). Column chromatography (90:10 Hex:EtOAc) afforded a colorless oil which was stored in the freezer. Yield 97%. 1H NMR (300 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 2.33 (s, 1H), 1.53 (s, 6H), 0.99 (t, 9H, J = 7.8 Hz), 0.63 (q, 6H, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 88.4, 85.9, 81.4, 67.7, 65.7, 32.3, 7.5, 4.4; IR (neat) cm^{-1} : 3350 (br), 2984, 2958, 2914, 2877, 2231, 2101, 1458, 1415, 1378, 1364, 1236, 1167, 1092, 1018, 951, 859, 728; HRMS (EI, 70 eV) for $C_{13}H_{22}OSi$ $[M^+]$ calcd 222.1440, found 222.1448; m/z (rel intensity): 103 (28.0), 123 (25.3), 137 (23.1), 165 (72.1), 193 (100).



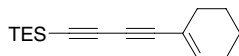
N,N-Dimethyl-(5-triethylsilyl-penta-2,4-diynyl)-amine (12): $C_{13}H_{23}NSi$; FW = 221, R_f = 0.41 (65:35 Hex:EtOAc). Column chromatography (65:35 Hex:EtOAc) afforded a colorless oil which was stored in the freezer. Yield 92%. 1H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 3.33 (s, 2H), 2.28 (s, 6H), 0.97 (t, 9H, J = 7.8 Hz), 0.59 (q, 6H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 88.9, 83.2, 73.7, 70.6, 48.5, 44.3, 7.5, 4.4; IR (neat) cm^{-1} : 2956, 2913, 2876, 2826, 2776, 2212, 2102, 1457, 1321, 1019, 796, 727; HRMS (EI, 70 eV) for $C_{13}H_{23}NSi$ $[M^+]$ calcd 221.1600, found 221.1591; m/z (rel intensity): 58 (35.2), 83 (35.9), 137 (64.6), 164 (100), 192 (50.7), 220 (50.8).



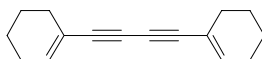
Triethyl-octa-1,3-diynyl-silane (13): C₁₄H₂₄Si; FW = 220; R_f = 0.62 (Hex). Column chromatography (Hex) afforded a colorless oil. Yield 92%. ¹H NMR (400 MHz, CDCl₃ with 0.05% v/v TMS) δ: 2.23 (t, 2H, J = 6.6 Hz), 1.50-1.32 (m, 4H), 0.94 (t, 9H, J = 8.1 Hz), 0.86 (t, 3H, J = 7.3 Hz), 0.58 (q, 6H, J = 8.1 Hz); ¹³C NMR (100 MHz, CDCl₃ with 0.05% v/v TMS) δ: 89.6, 81.0, 79.5, 65.8, 30.3, 22.1, 19.1, 13.7, 7.5, 4.4; IR (neat) cm⁻¹: 2957, 2876, 2223, 2107, 1458, 1181, 1017, 726; HRMS (EI, 70 eV) for C₁₄H₂₄Si [M⁺] calcd 220.1647, found 220.1641; *m/z* (rel intensity): 163 (100), 197 (12.2).



(E)-3-Methyl-7-triethylsilyl-hept-2-ene-4,6-diyn-1-ol (14): C₁₄H₂₂OSi; FW = 234; R_f = 0.29 (80:20 Hex:EtOAc). Column chromatography (80:20 Hex:EtOAc) afforded a light yellow oil which was stored in the freezer. Yield 92%. ¹H NMR (500 MHz, CDCl₃ with 0.05% v/v TMS) δ: 6.13 (t, 1H, J = 6.6 Hz), 4.22 (distorted d, 2H, J = 5.9 Hz), 2.13 (br s, 1H), 1.82 (s, 3H), 1.00 (t, 9H, J = 7.8 Hz), 0.62 (q, 6H, J = 7.8 Hz); ¹³C NMR (126 MHz, CDCl₃ with 0.05% v/v TMS) δ: 139.7, 119.4, 89.0, 88.5, 78.4, 72.9, 59.3, 17.2, 7.6, 4.4; IR (neat) cm⁻¹: 3321 (br), 2957, 2913, 2876, 2201, 2098, 1625, 1457, 1414, 1007, 737; HRMS (EI, 70 eV) for C₁₄H₂₂OSi [M⁺] calcd 234.1440, found 234.1431; *m/z* (rel intensity): 75 (84.5), 103 (73.7), 149 (64.4), 177 (100), 205 (86.0), 234 (16.5).

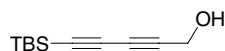


(4-Cyclohex-1-enyl-buta-1,3-diynyl)-triethyl-silane (15): C₁₆H₂₄Si; FW = 244; R_f = 0.51 (Hex). Column chromatography (Hex) afforded a colorless oil. Yield 87% (Dimmer 12%, see below). ¹H NMR (500 MHz, CDCl₃ with 0.05% v/v TMS): 6.31-6.30 (m, 1H), 2.13-2.10 (m, 4H), 1.64-1.57 (m, 4H), 1.01 (t, 9H, J = 7.8 Hz), 0.64 (q, 6H, J = 7.8 Hz); ¹³C NMR (100 MHz, CDCl₃ with 0.05% v/v TMS) δ: 139.5, 119.6, 89.3, 87.4, 78.4, 72.1, 28.7, 26.1, 22.2, 21.4, 7.5, 4.4; IR (neat) cm⁻¹: 3026, 2955, 2936, 2876, 2196, 2096, 1621, 1457, 1240, 1006, 726; HRMS (EI, 70 eV) for C₁₆H₂₄Si [M⁺] calcd 244.1647, found 244.1649; *m/z* (rel intensity): 159 (81.8), 187 (92.3), 215 (100), 244 (27.5).

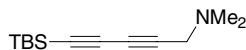


C₁₆H₁₈; FW = 210; R_f = 0.41 (Hex). Column chromatography (Hex) afforded a white solid. Yield 12%. ¹H NMR (500 MHz, CDCl₃ with 0.05% v/v TMS): 6.27-6.25 (m, 2H), 2.15-2.10 (m, 8H),

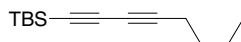
1.66-1.56 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3 with 0.05% v/v TMS) δ : 138.3, 120.1, 82.9, 71.7, 28.9, 26.1, 22.3, 21.5; IR (KBr) cm^{-1} : 3026, 2931, 2861, 2825, 2129, 1616, 1434, 1346, 1336, 1137, 1043, 917, 841, 797; HRMS (EI, 70 eV) for $\text{C}_{16}\text{H}_{18}$ $[\text{M}^+]$ calcd 210.1409, found 210.1405; m/z (rel intensity): 167 (39.8), 210 (100).



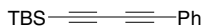
5-(*tert*-Butyldiethylsilyl)-penta-2,4-diyne-1-ol (16): $\text{C}_{11}\text{H}_{18}\text{OSi}$; FW = 194, R_f = 0.24 (90:10 Hex:EtOAc). Column chromatography (80:20 Hex:EtOAc) afforded a light yellow oil which was stored in the freezer. Yield 91%. ^1H NMR (400 MHz, CDCl_3 with 0.05% v/v TMS) δ : 4.28 (s, 2H), 2.19 (br s, 1H), 0.89 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 with 0.05% v/v TMS): 87.9, 86.6, 75.5, 71.0, 51.5, 26.2, 16.9, -4.7; IR (neat) cm^{-1} : 3327 (br), 2954, 2930, 2887, 2859, 2224, 2108, 1471, 1363, 1252, 1017, 826, 777; HRMS (EI, 70 eV) for $\text{C}_{11}\text{H}_{18}\text{OSi}$ $[\text{M}^+]$ calcd 194.1127, found 194.1131; m/z (rel intensity): 75 (25.9), 137 (100), 194 (8.7).



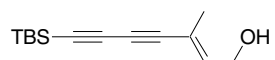
[5-(*tert*-Butyldiethylsilyl)-penta-2,4-diynyl]-dimethyl amine (17): $\text{C}_{13}\text{H}_{23}\text{NSi}$; FW = 221, R_f = 0.43 (65:35 Hex:EtOAc). Column chromatography (65:35 Hex:EtOAc) afforded a light yellow oil which was stored in the freezer. Yield 90%. ^1H NMR (400 MHz, CDCl_3 with 0.05% v/v TMS) δ : 3.29 (s, 2H), 2.24 (s, 6H), 0.88 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 with 0.05% v/v TMS): 88.5, 83.9, 73.9, 70.6, 48.5, 44.3, 26.2, 16.9, -4.7; IR (neat) cm^{-1} : 2930, 2858, 2825, 2774, 2212, 2102, 1470, 1251, 1063, 826, 776; HRMS (EI, 70 eV) for $\text{C}_{13}\text{H}_{23}\text{NSi}$ $[\text{M}^+]$ calcd 221.1600, found 221.1591; m/z (rel intensity): 83 (51.8), 121 (40.3), 138 (35.0), 150 (47.8), 164 (100), 221 (35.8).



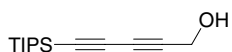
***tert*-Butyl-diethyl-octa-1,3-diynyl-silane (18):** $\text{C}_{14}\text{H}_{24}\text{Si}$; FW = 220; R_f = 0.60 (Hex). Column chromatography (Hex) afforded a colorless oil. Yield 92%. ^1H NMR (400 MHz, CDCl_3 with 0.05% v/v TMS) δ : 2.22 (t, 2H, J = 7.0 Hz), 1.46 (sext, 2H, J = 7.3 Hz), 1.37 (sext, 2H, J = 7.3 Hz), 0.89 (overlapped s, 9H), 0.87 (overlapped t, 3H, J = 7.7 Hz), 0.84 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 with 0.05% v/v TMS) δ : 89.3, 81.5, 79.7, 65.8, 30.3, 26.2, 22.1, 19.1, 16.8, 13.7, -4.6; IR (neat) cm^{-1} : 2956, 2931, 2859, 2224, 2108, 1471, 1251, 1182, 826, 776; HRMS (EI, 70 eV) for $\text{C}_{14}\text{H}_{24}\text{Si}$ $[\text{M}^+]$ calcd 220.1647, found 220.1648; m/z (rel intensity): 135 (59.1), 163 (88.5), 191 (100).



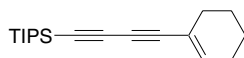
***tert*-Butyl-diethyl-(4-phenyl-buta-1,3-diynyl)-silane (19):** C₁₆H₂₀Si; FW = 240, R_f = 0.56 (90:10 Hex:EtOAc). Column chromatography (Hex) afforded a white solid (mp 45-46 °C) which was stored in the freezer. Yield 82%. A homocoupling product 1,4-diphenyl-1,3-butadiyne was obtained in 14%. ¹H NMR (500 MHz, CDCl₃ with 0.05% v/v TMS) δ: 7.53-7.51 (m, 2H), 7.40-7.32 (m, 3H), 1.00 (s, 9H), 0.19 (s, 6H); ¹³C NMR (100 MHz, CDCl₃ with 0.05% v/v TMS) δ: 132.9, 129.5, 128.6, 121.6, 89.5, 88.7, 76.5, 74.06, 26.3, 17.0, -4.6; IR (neat) cm⁻¹: 3067, 2951, 2927, 2883, 2856, 2204, 2103, 1489, 1469, 1442, 1251, 1020, 1006, 838, 809, 822, 777, 752; HRMS (EI, 70 eV) for C₁₆H₂₀Si [M⁺] calcd 240.4216, found 240.1336; *m/z* (rel intensity): 129 (9.2), 153 (11.9), 169 (8.3), 183 (100), 240 (9.4).



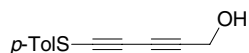
7-(*tert*-Butyldiethylsilyl)-3-methyl-hept-2-ene-4,6-diyn-1-ol (20): C₁₄H₂₂OSi; FW = 234, R_f = 0.33 (80:20 Hex:EtOAc). Column chromatography (80:20 Hex:EtOAc) afforded a white solid which was stored in the freezer. Yield 93%. ¹H NMR (400 MHz, CDCl₃ with 0.05% v/v TMS) δ: 6.07 (td, 1H, J = 6.6, 1.5 Hz), 4.16 (distorted s, 2H), 2.17 (br s, 1H), 1.76 (d, 3H, J = 0.7 Hz), 0.89 (s, 9H), 0.08 (s, 6H); ¹³C NMR (100 MHz, CDCl₃ with 0.05% v/v TMS): 139.7, 119.3, 89.0, 88.6, 78.6, 72.8, 59.2, 26.2, 17.2, 16.9, -4.7; IR (KBr) cm⁻¹: 3294 (br), 2951, 2928, 2883, 2857, 2202, 2098, 1628, 1466, 1251, 1110, 1014, 839, 823, 810, 777; HRMS (EI, 70 eV) for C₁₄H₂₂OSi [M⁺] calcd 234.1440, found 234.1428; *m/z* (rel intensity): 75 (32.0), 123 (31.2), 177 (100), 234 (9.7).



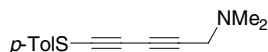
5-Triisopropylsilyl-penta-2,4-diyn-1-ol (21): C₁₄H₂₄OSi; FW = 236, R_f = 0.19 (90:10 Hex:EtOAc). Column chromatography (90:10 Hex:EtOAc) afforded a light yellow oil which was stored in the freezer. Yield 91%. ¹H NMR (400 MHz, CDCl₃ with 0.05% v/v TMS) δ: 4.30 (s, 2H), 1.73 (br s, 1H), 1.04 (m, 21 H); ¹³C NMR (100 MHz, CDCl₃ with 0.05% v/v TMS): 88.9, 85.3, 74.8, 71.3, 51.7, 18.7, 11.4; IR (neat) cm⁻¹: 3326 (br), 2954, 2892, 2867, 2224, 1463, 1018, 883, 794; HRMS (EI, 70 eV) for C₁₄H₂₄OSi [M⁺] calcd 236.1596, found 236.1603; *m/z* (rel intensity): 75 (93.4), 123 (39.4), 165 (37.8), 193 (100), 236 (4.0).



(4-Cyclohex-1-enyl-buta-1,3-diynyl)-triisopropyl-silane (22, contaminated with triisopropylsilyl acetylene): $C_{19}H_{30}Si$; FW = 286; R_f = 0.60 (Hex). Column chromatography (Hex) afforded a colorless oil. Yield 75% (along with 11 % of dimer 1,4-dicyclohexene-1,3-butadiyne). 1H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 6.32-6.30 (m, 1H), 2.15-2.11 (m, 4H), 1.65-1.56 (m, 4H), 1.10 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 139.3, 119.8, 90.1, 86.4, 77.9, 72.4, 28.7, 26.1, 22.3, 21.5, 18.7, 11.5; IR (neat) cm^{-1} : 3027, 2943, 2866, 2196, 2095, 1622, 1463, 1010, 996, 883, 677, 661; HRMS (EI, 70 eV) for $C_{19}H_{30}Si$ [M^+] calcd 286.2117, found 286.2112; m/z (rel intensity): 173 (51.0), 243 (100) 286 (15.3).

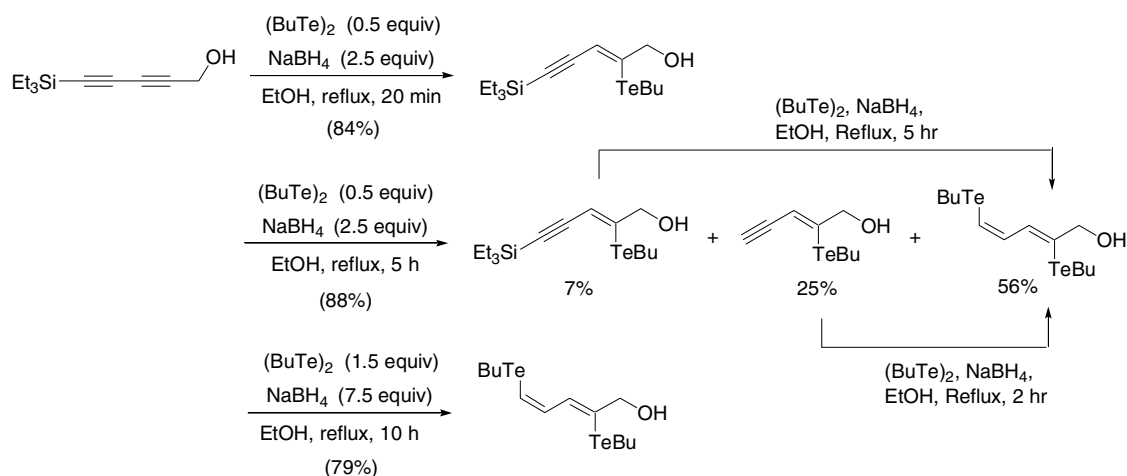


5-*p*-Tolylsulfanyl-penta-2,4-diyn-1-ol (23): $C_{12}H_{10}OS$; FW = 202; R_f = 0.23 (85:15 Hex:EtOAc); mp 63-64 °C. Column chromatography (85:15 Hex:EtOAc) afforded a brown solid which was stored in the freezer cold. Yield 89%. 1H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 7.28 (d, 2H, J = 8.4 Hz), 7.11 (d, 2H, J = 8.4 Hz), 4.36 (s, 2H), 2.57 (br, s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 137.8, 130.5, 127.5, 127.3, 82.8, 81.1, 70.9, 68.4, 51.7, 21.2; IR (KBr) cm^{-1} : 3314, 2898, 2850, 2211, 2116, 1491, 1208, 1014, 805; HRMS (EI, 70 eV) for $C_{11}H_{10}OS$ [M^+] calcd 202.2759, found 202.0457; m/z (rel intensity): 111 (25.0), 202 (100).

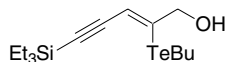


N,N-Dimethyl-(5-*p*-tolylsulfanyl-penta-2,4-diynyl)-amine (24): $C_{14}H_{15}NS$; FW = 229, R_f = 0.22 (70:30 Hex:EtOAc). Column chromatography (70:30 Hex:EtOAc) afforded a light yellow oil but turned brown. Yield 97%. 1H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 7.34 (d, 2H, J = 8.3 Hz), 7.17 (d, 2H, J = 8.3 Hz), 3.42 (s, 2H), 2.34 (s, 3H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$ with 0.05% v/v TMS): 137.6, 130.4, 127.7, 127.5, 83.3, 79.4, 70.5, 65.5, 48.9, 44.4, 21.3; IR (neat) cm^{-1} : 3022, 2974, 2941, 2864, 2823, 2775, 2208, 2114, 1595, 1491, 1451, 1345, 1321, 1034, 1016, 802; HRMS (EI, 70 eV) for $C_{14}H_{15}NS$ [M^+] calcd 229.0925, found 229.0916; m/z (rel intensity): 92 (39.8), 138 (100), 185 (36.3), 229 (54.0).

C. Regio- and stereoselective functionalization of diyne alcohol

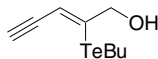


1. Hydrotelluration of diyne-alcohol 10: To a solution of $(\text{BuTe})_2$ (185 mg, 0.5 mmol, 0.5 equiv) in EtOH (30 mL) was added solid NaBH_4 (95 mg, 2.5 mmol, 2.5 equiv) portionwise under nitrogen. The orange solution became light yellow. Diyne-alcohol (194 mg, 1 mmol, 1 equiv) was added to the reaction flask under a nitrogen atmosphere. The reaction mixture was refluxed for 30 min. Careful monitoring of the disappearance of the diyne-alcohol and the appearance of the monotelluration product ($R_f = 0.13$ in 90:10 Hex:EtOAc, iodine detection) was required to avoid the formations of the desilylated monotelluration and the ditelluration products. The reaction was cooled down to room temperature and quenched with saturated aqueous NH_4Cl . The product was extracted with EtOAc, washed with brine, and dried over MgSO_4 . The filtrate was concentrated under reduced pressure and the residue was subjected to flash column chromatography on silica gel (90:10 Hex:EtOAc). Yield 84%.

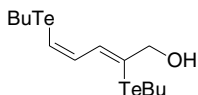


(Z)-2-(Butyltelluro)-5-triethylsilyl-pent-2-en-4-yn-1-ol (25): $\text{C}_{15}\text{H}_{28}\text{OSiTe}$; FW = 382; $R_f = 0.13$ (90:10 Hex:EtOAc). Column chromatography (90:10 Hex:EtOAc) afforded a yellow oil which was stored in the freezer. Yield 84%. ^1H NMR (400 MHz, CDCl_3 with 0.05% v/v TMS) δ : 6.33 (t, 1H, $J = 1.8$ Hz), 4.26 (dd, 2H, $J = 6.2, 1.5$ Hz), 2.86 (t, 2H, $J = 7.7$ Hz), 1.80-1.69 (m, 3H), 2.34 (sext, 2H, $J = 7.3$ Hz), 0.97 (t, 9H, $J = 7.7$ Hz), 0.86 (t, 3H, $J = 7.3$ Hz), 0.60 (t, 6H, $J = 7.7$ Hz); NOE (500 MHz, CDCl_3 with 0.05% v/v TMS): the carbinol hydrogens enhanced (2.1%) when the vinylic hydrogen was irradiated; ^{13}C NMR (100 MHz, CDCl_3 with 0.05% v/v TMS) δ : 136.3, 115.2, 105.1, 100.0, 69.1, 34.4, 25.3, 13.6, 7.8, 5.5, 4.5; IR (neat) cm^{-1} : 3350 (br), 2956, 2932, 2874, 2181, 2127, 1560, 1457, 1414, 1378, 1237, 1087, 1017, 726; HRMS (CI with

methane) for $C_{15}H_{28}OSiTe$ $[M+H]^+$ calcd 383.1050, found 383.1062; CI with ammonia, m/z (rel intensity): 132.1 (100), 197.1 (32.4), 381.1 (16.7).

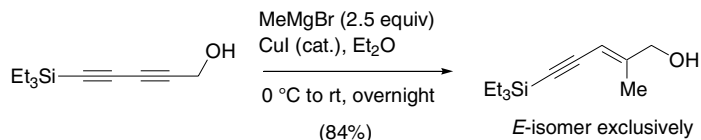


(Z)-2-(Butyltelluro)-pent-2-en-4-yn-1-ol (A byproduct of the hydrotelluration reaction if the hydrotelluration was run for more than one hour): $C_9H_{14}OTe$; FW = 268; Column chromatography (90:10 Hex:EtOAc) afforded a light yellow oil. 1H NMR (300 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 6.37-6.35 (m, 1H), 4.32 (dd, 2H, J = 6.3, 1.4 Hz), 3.37 (d, 1H, J = 2.2 Hz), 2.92 (t, 2H, J = 7.4 Hz), 1.83-1.73 (m, 3H), 1.41 (sext, 2H, J = 7.4 Hz), 0.92 (t, 3H, J = 7.4 Hz); NOE (400 MHz, $CDCl_3$ with 0.05% v/v TMS): the carbinol hydrogens enhanced (0.6%) when the vinylic hydrogen was irradiated; ^{13}C NMR (100 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 136.4, 114.3, 84.2, 82.9, 69.2, 34.4, 25.3, 13.6, 5.9; IR (neat) cm^{-1} : 3289 (br), 2956, 2927, 2870, 2096, 1576, 1457, 1377, 1247, 1079, 991. HRMS (EI, 70 eV) for $C_9H_{14}OTe$ $[M^+]$ calcd 268.0107, found 268.0100; m/z (rel intensity): 57.2 (100), 193.9 (82.9), 268.0 (72.7).

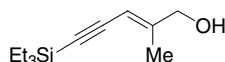


(2Z,5Z)-2,5-(Dibutyltelluro)-penta-2,4-dien-1-ol (26) (A byproduct of the hydrotelluration reaction if the hydrotelluration was run for more than one hour. It was the only product if excess amounts of dibutyltelluride and sodium borohydride were used in the hydrotelluration reaction): $C_{13}H_{24}OTe_2$; FW = 455. Column chromatography (95:05 Hex:EtOAc) afforded a yellow solid which was stored in the freezer. 1H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 7.05 (m, 2H), 6.45 (d, 1H, J = 8.8 Hz), 4.27 (dd, 2H, J = 6.2, 1.1 Hz), 2.71 (overlapped t, 2H, J = 7.7 Hz), 2.70 (overlapped t, 2H, J = 7.3 Hz), 1.87 (t, 1H, J = 6.2 Hz), 1.79-1.64 (m, 4H), 1.40-1.28 (m, 4H), 0.90-0.84 (m, 6H); NOE (400 MHz, $CDCl_3$ with 0.05% v/v TMS): the vinylic hydrogen enhanced (1.5%) when the carbinol hydrogens was irradiated; ^{13}C NMR (100 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 139.4, 137.5, 125.5, 110.9, 70.9, 34.4, 34.3, 25.2, 25.1, 13.6 (overlapped carbons), 7.8, 6.8; APT (125 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 139.4 (methine), 137.5 (methine), 125.5 (quarternary), 110.9 (methine), 70.9 (methylene), 34.4 (methylene), 34.3 (methylene), 25.2 (methylene), 25.1 (methylene), 13.6 (methyl), 7.8 (methylene), 6.8 (methylene); IR (neat) cm^{-1} : 3370 (br), 2955, 2924, 2869, 1539, 1457, 1376, 1278, 1246, 1162,

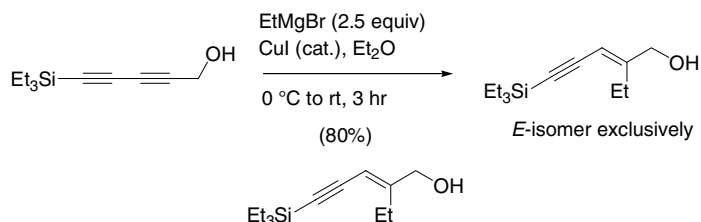
1064, 990, 883; HRMS (EI, 70 eV) for $C_{13}H_{24}OTe_2$ $[M+H]^+$ calcd 455.9952, found 455.9939; m/z (rel intensity): 57.2 (88.3), 194.9 (100), 269 (38.8), 452 (7.3).



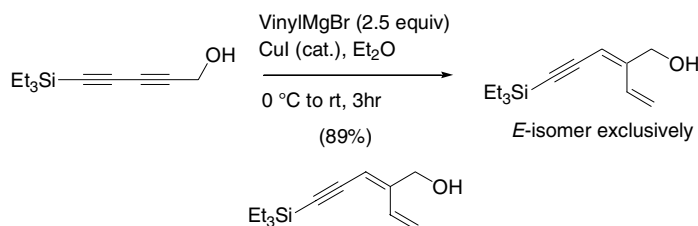
2. Carbometalations² of diyne alcohol 10: MeMgBr (2.5 mL of a 3.0M solution in diethyl ether, 7.5 mmol, 2.5 equiv) was added to a suspension of CuI (57 mg, 0.3 mmol, 0.1 equiv) and Et₂O (20 mL) at 0 °C. A dark brown solution formed immediately. To this solution was added a solution of diyne-alcohol (582 mg, 3 mmol, 1 equiv) in 2 mL of Et₂O at 0 °C. The ice-bath was removed and the reaction was stirred overnight. The reaction was quenched slowly at 0 °C with 2N HCl under nitrogen until the reaction mixture was acidic. The product was extracted with diethyl ether, washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The crude product was pure enough for characterizations. Only the *E*-isomer was detected in the crude ¹H NMR (84% yield).



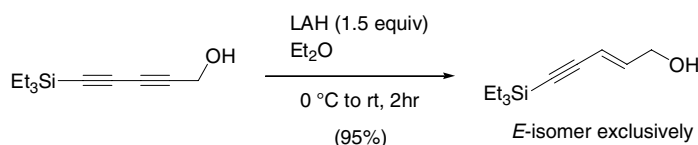
(E)-2-Methyl-5-triethylsilyl-pent-2-en-4-yn-1-ol (27): C₁₂H₂₂OSi; FW = 210; R_f = 0.26 (85:15 Hex:EtOAc). Column chromatography (90:10 Hex:EtOAc) afforded a yellow oil which was stored in the freezer. Yield 84%. ¹H NMR (500 MHz, CDCl₃ with 0.05% v/v TMS) δ: 5.63 (s, 1H), 4.11 (d, 2H, J = 5.1 Hz), 1.92 (s, 3H), 1.51 (distorted t, 1H), 1.01 (t, 9H, J = 7.8 Hz), 0.62 (q, 6H, J = 8.0 Hz); NOE (500 MHz, CDCl₃ with 0.05% v/v TMS): the carbinol hydrogens enhanced (0.6%) when the vinylic hydrogen was irradiated; ¹³C NMR (100 MHz, CDCl₃ with 0.05% v/v TMS) δ: 151.6, 105.2, 103.7, 96.1, 67.0, 16.8, 7.7, 4.7; IR (neat) cm⁻¹: 3340 (br), 2955, 2913, 2875, 2133, 1635, 1457, 1415, 1377, 1235, 1099, 1017, 723; HRMS (EI, 70 eV) for C₁₂H₂₂O₂Si $[M^+]$ calcd 210.1440, found 210.1444; m/z (rel intensity): 25 (33.6), 153 (57.2), 181 (100), 205 (21.6).



(E)-2-Ethyl-5-triethylsilyl-pent-2-en-4-yn-1-ol (28): C₁₃H₂₄OSi; FW = 224; R_f = 0.33 (80:20 Hex:EtOAc); a yellow oil; yield 80%. ¹H NMR (300 MHz, CDCl₃ with 0.05% v/v TMS) δ: 5.58 (s, 1H), 4.15 (d, 2H, J = 4.9 Hz), 2.38 (q, 2H, J = 7.7 Hz), 1.82 (br s, 1H), 1.06 (t, 3H, J = 7.7 Hz), 1.00 (t, 9H, J = 8.0 Hz), 0.62 (q, 6H, J = 8.0 Hz); NOE (500 MHz, CDCl₃ with 0.05% v/v TMS): the carbinol hydrogens enhanced (0.2%) when the vinylic hydrogen was irradiated; ¹³C NMR (125 MHz, CDCl₃ with 0.05% v/v TMS) δ: 157.3, 104.6, 103.5, 96.1, 65.1, 24.3, 12.6, 7.6, 4.7; IR (neat) cm⁻¹: 3327 (br), 2957, 2913, 2876, 2137, 1634, 1458, 1102, 1017, 724; HRMS (DCI with ammonia) for C₁₃H₂₄OSi [M+H]⁺ calcd 225.1674, found 225.1669; CI with ammonia, *m/z* (rel intensity): 132 (100), 225 (43.2).

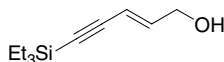


(E)-5-Triethylsilyl-2-vinyl-pent-2-en-4-yn-1-ol (29): C₁₃H₂₂OSi; FW = 222; R_f = 0.15 (90:10 Hex:EtOAc); a yellow oil; yield 89%. ¹H NMR (300 MHz, CDCl₃ with 0.05% v/v TMS) δ: 6.97 (dd, 1H, J = 18.1, 11.3 Hz), 5.78 (m, 1H), 5.38 (d, 1H, J = 17.9 Hz), 5.30 (dm, 1H, J = 11.0 Hz), 4.35 (m, 2H), 2.16 (br s, 1H), 1.00 (t, 9H, J = 7.7 Hz), 0.64 (q, 6H, J = 7.7 Hz); NOE (500 MHz, CDCl₃ with 0.05% v/v TMS): the carbinol hydrogens enhanced (0.8%) when the vinylic hydrogen was irradiated; ¹³C NMR (125 MHz, CDCl₃ with 0.05% v/v TMS) δ: 148.7, 133.0, 116.9, 109.1, 103.1, 100.1, 62.6, 7.7, 4.6; IR (neat) cm⁻¹: 3336 (br), 3091, 2956, 2912, 2875, 2127, 1458, 1415, 1236, 1094, 1005, 911, 724; HRMS (DCI with ammonia) for C₁₃H₂₂OSi [M+H]⁺ calcd 223.1518, found 223.1509; CI with ammonia, *m/z* (rel intensity): 120 (100), 223 (25.2); EI 70 eV, *m/z* (rel intensity): 45 (38.4), 75 (55.3), 103 (60.3), 137 (68.4), 165 (100), 193 (60.0), 251 (19.3).



3. Reduction³ of diyne alcohol 10: Powdered LiAlH₄ (35.6 mg, 0.9 mmol, 1.5 equiv) was added quickly to a solution of diyne-alcohol (121 mg, 0.6 mmol, 1 equiv) in 15 mL of diethyl ether at 0 °C. The reaction was warmed to rt and stirred for 2 hours. The reaction was cooled with an ice/water bath and quenched with 2N HCl until acidic. Saturated aqueous Na₂SO₄ was added and

the reaction was stirred vigorously until a bilayer was formed. The product was extracted with diethyl ether several times, washed with brine, dried over MgSO_4 and concentrated under reduced pressure. The crude product (95% yield) was pure enough to perform physical characterizations.

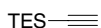


(E)-5-Triethylsilyl-pent-2-en-4-yn-1-ol (30): $\text{C}_{11}\text{H}_{20}\text{OSi}$; FW = 196; R_f = 0.23 (80:20 Hex:EtOAc); a light yellow oil, 95% yield. ^1H NMR (300 MHz, CDCl_3 with 0.05% v/v TMS) δ : 6.31 (dt, 1H, J = 15.9, 4.9 Hz), 5.79 (dm, 1H, J = 15.9 Hz), 4.18 (dd, 2H, J = 5.2, 1.9 Hz), 1.83 (br s, 1H), 0.99 (t, 9H, J = 8.0 Hz), 0.62 (q, 6H, J = 8.0 Hz); ^{13}C NMR (125 MHz, CDCl_3 with 0.05% v/v TMS) δ : 143.1, 110.8, 104.4, 93.0, 63.1, 7.7, 4.6; IR (neat) cm^{-1} : 3326 (br), 2955, 2912, 2876, 2175, 2133, 1938, 1630, 1458, 1415, 1378, 1236, 1083, 1008, 954, 724. HRMS (EI, 70 eV); HRMS (DCI with ammonia) for $[\text{M}+\text{H}]^+$ for $\text{C}_{11}\text{H}_{20}\text{OSi}$ calcd 197.1362, found 197.1355; CI with ammonia, m/z (rel intensity) 132 (100), 186 (23.7), 197 (39.1); EI 70 eV, m/z (rel intensity): 75 (44.2), 103 (62.8), 139 (85.7), 167 (100), 205 (26.1).

D. Preparation of starting materials

1. Alkyne Synthesis

A 2L, three-necked, round-bottomed flask was equipped with a stir bar, an acetylene gas inlet, a pressure equalizing addition funnel and a gas outlet connected to a drierite drying tube. The acetylene gas was passed through a $-78\text{ }^\circ\text{C}$ trap, and bubbling slowly via a gas inlet into a vigorously stirred solution of $n\text{-BuLi}$ (159 mL of a 2.5M solution in THF, 398 mmol, 1.2 equiv) in THF (700 mL) at $0\text{ }^\circ\text{C}$ for about 1 hour to ensure the complete formation of the alkynyl acetylide. Then freshly distilled triethylsilyl chloride (50 g, 332 mmol, 1 equiv) was added dropwise via an addition funnel at $0\text{ }^\circ\text{C}$. The cold bath was removed and the reaction was stirred overnight under an acetylenic atmosphere using the balloon technique. The reaction was quenched slowly with brine. The product was extracted with diethyl ether, dried over MgSO_4 and concentrated under reduced pressure. The trialkylsilyl acetylene could be purified further by distillation. This procedure⁴ was used to prepare triethylsilyl, tert-butyldimethylsilyl, and triisopropylsilyl acetylenes.



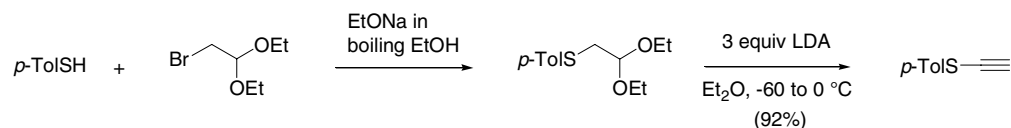
Triethylsilyl acetylene: $C_8H_{16}Si$; FW = 140; a colorless oil, bp 136-137 °C,⁵ 75-70 °C at 95 mmHg, 43 °C at 42 mmHg. Yield 83%.⁶



***tert*-Butyldimethylsilyl acetylene:** $C_8H_{16}Si$; FW = 140; a colorless and volatile oil. Yield 81%.
¹H NMR (300 MHz, CDCl₃ with 0.05% v/v TMS) δ : 2.35 (s, 1H), 0.95 (s, 9H), 0.09 (s, 6H).⁷

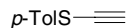


Triisopropylsilyl acetylene: $C_{11}H_{22}Si$; FW = 182; a colorless oil. Physical characterizations matched with the literature.⁸



The literature did not provide experimental details for either the first or the second step.⁹ The first step was straightforward but because of a minor modification in the second step, the actual experimental procedure was provided here. In the second step, three equiv of LDA were employed to avoid the formation of an olefinic compound (*via* ¹H-NMR) when two equiv of LDA were used. As thioethyne was formed, its acetylenic proton was acidic enough to consume the LDA base. Brandsma described in a similar procedure using three equiv of sodamide in liquid ammonia to make alkylthioethyne from 1,2-dibromoalkyl compound. These observations prompted us to use three equiv of LDA and as expected, the olefinic product was no longer detected.

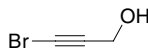
In a flamed-dried, 500-mL, three-necked, round-bottom flask equipped with a stir bar and an addition funnel, was added 150 mL of freshly distilled diethyl ether. After cooling the reaction vessel down to -78 °C, diisopropyl amine (15.7 mL, 112 mmol, 3 equiv) were added to the cold diethyl ether dropwise via a syringe and the reaction was stirred at -78 °C for 10 min. *n*-Butyl lithium (44.8 mL of a 2.5M solution in hexanes, 112 mmol, 3 equiv) was added dropwise *via* an addition funnel. The 1,1-diethoxy-2-(4-methylphenylthio)ethane (8.97 g, 37.3 mmol, 1 equiv) in 5 mL of diethyl ether was cannulated into the LDA solution at -78 °C. A milky solution was observed as the cold bath was removed and the temperature was brought up to 0 °C. TLC (Hex) showed that the reaction was complete in 15 min. The reaction mixture was diluted with 100 mL of diethyl ether, quenched with 30 mL of saturated NH₄Cl, and neutralized with 1M HCl. The organic layer was extracted, dried with MgSO₄, and concentrated under reduced pressure to afford the title compound which was used without further purification.



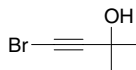
1-Ethynylsulfanyl-4-methyl-benzene: $\text{C}_9\text{H}_8\text{S}$; FW = 148; TLC (Hex) R_f = 0.61; a light yellow liquid but turned orange/red quickly, 92% yield; ^1H NMR (300 MHz, CDCl_3 with 0.05% v/v TMS) δ 7.33 (m, 2H), 7.13 (m, 2H), 3.19 (s, 1H), 2.33 (s, 3H).⁹

2. Synthesis of haloalkynes

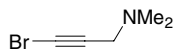
The Strauss method was used to prepare bromo-alkynes which had polar functional groups such as alcohols and amines.^{10,11} To a cold (-5 to 0 °C) solution of KOH (111.5 g, 1.75 mol, 7 equiv) in water (440 mL) was added pure bromine (42.4 g, 250 mmol, 1 equiv) slowly in a hood. After 15 min, propargyl alcohol (19.5 mL, 335 mmol, 1.34 equiv) was added dropwise via an addition funnel to the light orange solution while maintaining the temperature between 0 and 5 °C. After 30 minutes of stirring at 0 °C, the reaction was allowed to reach rt and the product was extracted several times with diethyl ether (4x100 mL). Solvent removal afforded a pure product in 91% yield.



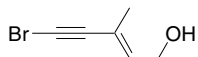
3-Bromo-prop-2-yn-1-ol: $\text{C}_3\text{H}_3\text{OBr}$; FW = 135; a colorless oil which was stored in the freezer. Yield 91%. ^1H NMR (300 MHz, CDCl_3 with 0.05% v/v TMS) δ : 4.30 (d, 2H, J = 5.2 Hz), 1.65 (t, 1H, J = 6.0 Hz).



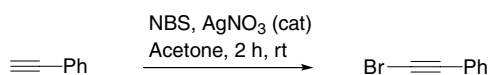
4-Bromo-2-methylbut-3-yn-2-ol: $\text{C}_5\text{H}_7\text{Br}$; FW = 163; TLC (80:20 Hex:EtOAc) R_f = 0.66, (90:10 Hex:EtOAc) R_f = 0.33; a colorless oil (bp 68 °C, 12 mmHg) which was stored in the freezer. Yield 95%. ^1H NMR (300 MHz, CDCl_3 with 0.05% v/v TMS) δ : 1.99 (s, 1H), 1.53 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 with 0.05% v/v TMS) δ : 84.5, 66.3, 42.8, 31.2.¹¹



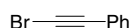
N,N-Dimethyl-(3-bromo-prop-2-ynyl)-amine: $\text{C}_5\text{H}_8\text{NBr}$; FW = 160; a light orange solid; an irritant and a lachrymator which was stored in the freezer. Yield 76%. ^1H NMR (300 MHz, CDCl_3 with 0.05% v/v TMS) δ : 3.23 (s, 2H), 2.23 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 with 0.05% v/v TMS) δ : 75.6, 49.0, 44.2, 43.5; IR (KBr) cm^{-1} : 2974, 2943, 2860, 2830, 2786, 2195, 1472, 1328, 1157, 1095, 1036, 978, 815; HRMS (EI, 70 eV) for $\text{C}_5\text{H}_8\text{NBr}$ [M^+] cackled 160.9840, found 160.9838; m/z (rel intensity): 42 (100), 82 (56.3), 117 (51.8), 119 (53.7), 160 (83.4), 162 (84.8).



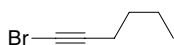
(E)-5-Bromo-3-methyl-pent-2-en-4-yn-1-ol: C_6H_7OBr ; FW = 175; a light yellow oil; bp 78-80 °C at 0.35 mmHg; stored cold. Yield 68%. 1H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 5.91 (t, 1H, J = 6.6 Hz), 4.11 (d, 2H, J = 6.6 Hz), 2.92 (br s, 1H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 137.2, 120.3, 82.3, 58.9, 48.0, 17.4; IR (neat) cm^{-1} : 3309 (br), 3032, 2990, 2924, 2875, 2184, 1633, 1437, 1378, 1245, 1091, 100; HRMS (EI, 70 eV) for C_6H_7OBr [M^+] calcd 173.9680, found 173.9685; m/z (rel intensity): 41 (56.5), 51 (100), 67 (70.6), 95 (86.5), 159 (38.3), 174 (9.7).



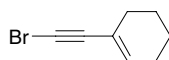
For nonpolar alkynes such as phenyl acetylene or 1-hexyne, NBS/ $AgNO_3$ bromination conditions worked the best.¹² To a solution of phenyl acetylene (1.65 mL, 15 mmol, 1 equiv), in acetone (100 mL) was added recrystallized NBS (5.34 g, 30 mmol, 2 equiv) and $AgNO_3$ (250 mg, 1.47 mmol) at room temperature. After stirring for 4 hours, acetone was removed under reduced pressure. The residue was treated with diethyl ether and hexanes to induce a solid formation. The mixture was passed through a pad of silica gel using hexanes as an eluent. The filtrate was collected and solvents were removed under reduced pressure to afford a pure, colorless alkynyl bromide in 98% yield.



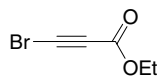
Bromoethynyl-benzene: C_8H_5Br ; FW = 181. 98% yield.



1-Bromo-hex-1-yne: C_6H_9Br ; FW = 161. A colorless oil which turned light yellow upon standing. Physical characterizations matched with the literature.¹³



1-Bromoethynyl-cyclohexene: C_8H_9Br ; FW = 185; R_f = 0.63 (Hex); a light yellow oil. Yield 99%. 1H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 6.11-6.09 (m, 1H), 2.08-2.01 (m, 4H), 1.61-1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$ with 0.05% v/v TMS) δ : 136.6, 120.7, 82.0, 46.4, 29.0, 25.8, 22.4, 21.6; IR (neat) cm^{-1} : 3028, 2934, 2859, 2839, 2187, 1630, 1446, 1435, 918; HRMS (EI, 70 eV) for C_8H_9Br [M^+] calcd. 183.9888, found 183.9887; m/z (rel intensity): 51 (52.6), 77 (100), 105 (79.9), 184 (55.7).



Bromo-propynoic acid ethyl ester: $C_5H_5O_2Br$. 1H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS): 4.21 (q, 2H, $J = 7.3$ Hz), 1.27 (t, 3H, $J = 7.3$ Hz).

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