Supporting Information

Synthesis of Unsymmetrically Substituted 1,3–Butadiynes and 1,3,5–Hexatriynes via Alkylidene Carbenoid Rearrangements

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1. Experimental details for compounds **5a–r**, **6a–r**, **7a–r**, **9a–f**, **10a–f**, **12d–f**, **13a–f**, **15-17**, **19-20**.
2. X-ray crystallographic data for compound **18**.
3. ^1H and ^{13}C NMR spectra for all unpublished alcohols, ketones, dibromo-olefins, diynes, and triynes.

Experimental

General. Reagents were purchased reagent grade from commercial suppliers and used without further purification. Et₂O and benzene were distilled from sodium/benzophenone ketyl, and hexanes and dichloromethane were distilled from CaH₂ immediately prior to use. Anh. MgSO₄ or Na₂SO₄ were used as the drying agent after aqueous work-up. Evaporation and concentration *in vacuo* was done at H₂O-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of N₂. Column chromatography: *silica gel-60* (230-400 mesh) from *General Intermediates of Canada*. Thin Layer Chromatography (TLC): aluminum sheets covered with *silica gel-60 F₂₅₄* from *Macherey-Nagel*; visualization by UV light or KMnO₄ stain. Mp: *Gallenkamp* apparatus; uncorrected. IR spectra (cm⁻¹): *Nicolet Magna-IR 750* (neat) or *Nic-Plan IR Microscope* (solids). ¹H- and ¹³C-NMR: *Varian Gemini-300, 400 or 500* and *Bruker AM-300 or 400* instruments, at rt in CD₂Cl₂, CDCl₃, C₆D₆ or CD₃CN; solvent peaks (5.32, 7.24, 7.15 and 1.96 ppm, respectively, for ¹H and 53.8, 77.0, 128.6 and 1.8 ppm, respectively, for ¹³C) as reference. EI MS (*m/z*): *Kratos MS50* instrument. Elemental analyses were effected by Spectral Services at the University of Alberta.

For simplicity, the coupling constants of the aryl protons for *para*-substituted phenyl groups have been reported as pseudo first-order, even though they are second-order spin systems. For mass spectral analyses, low resolution data are provided in cases when M⁺ is not the base peak; otherwise, only high resolution data are provided.

General Procedure for Alcohol Formation. To trimethylsilylacetylene (1.23 g, 12.5 mmol, 1.25 equiv) in Et₂O (50 mL) at -78 °C was added *n*-BuLi (2.5 M in hexanes, 4.8 mL, 12 mmol, 1.2 equiv). After stirring for 30 min, the appropriate aldehyde (10 mmol, 1 equiv) in Et₂O (5 mL) was added. The reaction mixture was slowly warmed to ca. -10 °C until the reaction was judged complete by TLC analysis. The reaction was quenched with satd. aq. NH₄Cl at -78 °C,

the organic layer washed with brine (2×50 mL), and dried (MgSO_4). The resulting alcohol could generally be used without further purification.

General Procedure for Ketone Formation via Oxidation using PCC. To the appropriate alcohol (4 mmol) in CH_2Cl_2 (50 mL) was added sequentially celite (equal amount by mass to PCC), molecular sieves (4 Å, equal amount by mass to PCC), and PCC (5 mmol, 1.25 equiv). After stirring at rt until the reaction was judged complete by TLC analysis, the solution was filtered through a plug of silica (CH_2Cl_2) and the solvent was evaporated to give the corresponding ketone. The ketone was of sufficient purity to be carried on directly to the dibromo-olefination step without further purification or it could be isolated pure by column chromatography.

General Procedure for Ketone Formation via Oxidation using BaMnO_4 . To the appropriate alcohol (4 mmol) in CH_2Cl_2 (50 mL) was added barium manganate (3 equiv). After stirring at rt until the reaction was judged complete by TLC analysis, the solution mixture was filtered through a pad of celite. The solvent was evaporated to give the corresponding ketone.

General Procedure for Ketone Formation via Friedel-Crafts Acylation. The formation of **9a-f** and **12a-f** was accomplished as reported for similar derivatives.³² Commercially available acid chlorides were used except for 4-phenylazobenzoyl chloride, 3-(2-thienyl)acryloyl chloride, and sorbyl chloride which were made from the corresponding carboxylic acids.

General Procedure for Acid Chloride Formation. To the appropriate carboxylic acid (1 equiv) was added thionyl chloride (6 equiv). After stirring for 24 hours, the excess thionyl chloride was evaporated, and the acid chloride was used directly in the next step without further purification.

General Procedure for Dibromo-olefin Formation. Literature procedures were followed as referenced. In some cases, and to date unexplained, reactions conducted under reported conditions would fail to go to completion using the normal amounts of PPh_3 and CBr_4 . In these

cases, an additional equivalent of both PPh_3 and CBr_4 would be added in order to force the reaction to completion.

General Procedure for Diyne formation. Unless otherwise noted, the following procedure was followed. To the appropriate dibromo-olefin (0.368 mmol) in dry hexanes (10 mL) at $-78\text{ }^\circ\text{C}$ was added dropwise over ten minutes 1.1-1.2 equivalent of *n*-BuLi (0.15 mL, 2.5 M in hexanes, 0.38 mmol). The mixture was warmed to approximately $-40\text{ }^\circ\text{C}$ for 30 min, re-cooled to $-78\text{ }^\circ\text{C}$, and quenched with a saturated aqueous solution of NH_4Cl . Et_2O was added (~ 50 mL), the organic layer separated, washed with a saturated aqueous solution NH_4Cl , and dried over magnesium sulfate. Solvent removal *in vacuo* and passing the residue through a short plug of silica gel with the solvent system detailed for each product afforded the desired diyne. If necessary, additional purification could be achieved via flash column chromatography.

1-(1-Naphthyl)-3-trimethylsilylprop-2-yn-1-ol (5a). To (trimethylsilyl)acetylene (0.945 g, 9.62 mmol) in diethyl ether (10 mL) at $-78\text{ }^\circ\text{C}$ was added *n*-BuLi (3.8 mL, 2.5 M in hexanes, 9.5 mmol). After stirring for 0.5 h, 1-naphthaldehyde (1.5 g, 1.3 mL, 9.6 mmol) was added and the general procedure was followed to give **5a** (1.54 g, 64%) as a thick yellow oil: $R_f = 0.25$ (hexanes/ CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 3364, 3050, 2959, 2898, 2173, 1598, 1250 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.28 (d, $J = 8.4$ Hz, 1H), 7.85 (m, 3H), 7.51 (m, 3H), 6.11 (d, $J = 5.0$ Hz, 1H), 2.24 (d, $J = 5.0$ Hz, 1H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, APT, CDCl_3) δ 135.3, 133.9, 130.6, 129.3, 128.6, 126.3, 125.8, 125.2, 124.7, 123.9, 104.7, 92.4, 63.3, -0.1 ; EI HRMS calcd for $\text{C}_{16}\text{H}_{18}\text{OSi}$ (M^+) 254.1127, found 254.1126.

[4,4-Dibromo-3-(1-naphthyl)-buten-1-ynyl]trimethylsilane (7a). To **5a** (1.41 g, 5.52 mmol) in CH_2Cl_2 (60 mL) were sequentially added celite (2 g), molecular sieves ($4\text{ \AA}$, 2 g), and PCC (1.99 g, 9.03 mmol) as per the general procedure to give ketone **6a** that, following workup, was subjected to dibromo-olefination using CBr_4 (2.48 g, 7.36 mmol) and PPh_3 (3.87 g, 14.7 mmol) in CH_2Cl_2 (75 mL) to give **7a** (0.984 g, 44%) as a yellow oil: $R_f = 0.83$ (CH_2Cl_2); IR (CH_2Cl_2 cast) 3058, 2959, 2897, 2141, 1593, 1507 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.99 (d, J

= 8.0 Hz, 1H), 7.89 (m, 2H), 7.52 (m, 4H), 0.21 (s, 9H); ^{13}C NMR (125 MHz, APT, CDCl_3) δ 135.7, 133.6, 129.9, 129.8, 128.9, 128.3, 126.5, 126.3, 126.1, 125.3, 125.0, 104.8, 102.81, 102.80, -0.2; MS (EI, 70 eV) m/z 405.9/407.9/409.9 (M^+ , 18/36/19); HRMS calcd for $\text{C}_{17}\text{H}_{16}\text{Si}^{79}\text{Br}_2/\text{C}_{17}\text{H}_{16}\text{Si}^{79}\text{Br}^{81}\text{Br}/\text{C}_{17}\text{H}_{16}\text{Si}^{81}\text{Br}_2$ (M^+) 405.9388/407.9368/409.9347, found 405.9396/407.9375/409.9357.

1-(1-Pyrenyl)-3-trimethylsilylprop-2-yn-1-ol (5b). To (trimethylsilyl)acetylene (1.30 g, 14.0 mmol) in diethyl ether (30 mL) at -78°C was added *n*-BuLi (5.7 mL, 2.4 M in hexanes, 13.7 mmol). After stirring for 0.5 h, 1-pyrene carboxaldehyde (2.50 g, 10.9 mmol) was added and the general procedure was followed to give **5b** (3.43 g, 96%) as a light yellow solid: mp 100-101 $^\circ\text{C}$; R_f = 0.3 (hexanes/ CH_2Cl_2 1:1); IR (CHCl_3 cast) 3380, 3040, 2958, 2171, 1250 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.51 (d, J = 9.3 Hz, 1H), 8.36 (d, J = 7.9 Hz, 1H), 8.16 (m, 4H), 8.04 (m, 3H), 6.40 (d, J = 5.7 Hz, 1H), 2.37 (d, J = 5.7 Hz, 1H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 132.9, 131.7, 131.2, 130.7, 128.4, 127.9, 127.8, 127.3, 126.0, 125.5, 125.4, 125.1, 124.74, 124.70, 123.1, 105.1, 92.7, 63.4, -0.1 (one coincident signal not observed); MS (EI, 70 eV) m/z 328.1 (M^+ , 73), 73.0 ($[\text{Me}_3\text{Si}]^+$, 100); HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{OSi}$ (M^+) 328.1284, found 328.1276.

1-(1-Pyrenyl)-3-trimethylsilylpropynone (6b). To **5b** (49.4 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) were sequentially added celite (40 mg), molecular sieves (4 $\text{\AA}$, 40 mg), and PCC (39.7 mg, 0.18 mmol) as per the general procedure to give the ketone **6b** (40.9 mg, 83%) as a bright yellow solid: mp 111-112 $^\circ\text{C}$; R_f = 0.62 (hexanes/ Et_2O 7:3); IR (CHCl_3 cast) 2958, 2921, 2120, 1633, 1620, 1592, 1250 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 9.47 (d, J = 9.4 Hz, 1H), 8.92 (d, J = 8.1 Hz, 1H), 8.24 (m, 3H), 8.17 (d, J = 8.7 Hz, 2H), 8.04 (m, 2H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, APT, CDCl_3) δ 179.6, 135.3, 131.8, 130.98, 130.95, 130.8, 130.6, 130.4, 128.8, 127.1, 127.0, 126.7, 126.5, 124.9, 124.7, 124.0, 103.1, 99.4, -0.5; EI HRMS calcd for $\text{C}_{22}\text{H}_{18}\text{OSi}$ (M^+) 326.1127, found 326.1119.

[4,4-Dibromo-3-(1-pyrenyl)-buten-1-ynyl]trimethylsilane (7b). To **5b** (1.64 g, 5.00 mmol) in CH₂Cl₂ (60 mL) were sequentially added celite (1.5 g), molecular sieves (4Å, 1.5 g), and PCC (1.38 g, 6.25 mmol) as per the general procedure to give ketone **6b** that, following workup, was subjected to dibromo-olefination using CBr₄ (2.07 g, 6.25 mmol) and PPh₃ (3.28 g, 12.5 mmol) in CH₂Cl₂ (75 mL) to give **7b** (0.923 g, 39%) as a brown solid: mp 137-139 °C; R_f = 0.7 (CH₂Cl₂); IR (CHCl₃ cast) 3046, 2958, 2134, 1249 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.23 (m, 5H), 8.06 (m, 4H), 0.27 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 132.9, 131.5, 131.1, 130.9, 130.5, 128.2, 128.1, 127.9, 127.2, 126.2, 126.2, 125.5, 125.5, 124.9, 124.6, 124.4, 105.5, 103.3, 103.1, -0.3 (one coincident signal not observed); MS (EI, 70 eV) *m/z* 480.0/482.0/484.0 (M⁺, 19/42/23); HRMS calcd for C₂₃H₁₈OSi⁷⁹Br₂/C₂₃H₁₈OSi⁷⁹Br⁸¹Br/ C₂₃H₁₈OSi⁸¹Br₂ (M⁺) 479.9544/481.9524/483.9504, found 479.9604/481.9585/483.9558.

1-(2-Methoxyphenyl)-3-trimethylsilylprop-2-yn-1-ol (5c).* To (trimethylsilyl)acetylene (1.08 g, 10.7 mmol) in diethyl ether (10 mL) at -78 °C was added *n*-BuLi (4.4 mL, 2.5 M in hexanes, 11.0 mmol). After stirring for 0.5 h, 2-methoxybenzaldehyde (1.50 g, 11.0 mmol) was added. Due to the insolubility of the aldehyde, the reaction mixture was allowed to warm to room temperature and stirred overnight. Workup as per the general procedure gave **5c** (2.33 g, 90%) as a pale yellow oil; R_f = 0.2 (hexanes/CH₂Cl₂ 1:1); IR (CH₂Cl₂ cast) 3426, 2959, 2900, 2838, 2172, 1601, 1590, 1491, 1464 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.57 (m, 1H), 7.29 (m, 1H), 6.97 (m, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 5.69 (d, *J* = 6.0 Hz, 1H), 3.87 (s, 3H), 2.90 (d, *J* = 6.0 Hz, 1H), 0.19 (s, 9H); ¹³C NMR (125 MHz, APT, CDCl₃) δ 156.8, 129.6, 128.5, 127.9, 120.8, 110.8, 104.5, 90.9, 61.4, 55.6, -0.03; MS (EI, 70 eV) *m/z* 234.1 (M⁺, 62); HRMS calcd for C₁₃H₁₈O₂Si (M⁺) 234.1076, found 234.1070. Anal. Calcd for C₁₃H₁₈O₂Si: C, 66.62; H, 7.74. Found C, 66.53; H, 7.86. *Previously reported by: Baldoli, C.; DelButtero, P.; Licandro, E.; Maiorana, S.; Papagni, A.; Torchio, M. *Tetrahedron Lett.* **1993**, *34*, 7943-7946.

[4,4-Dibromo-3-(2-methoxyphenyl)-buten-1-ynyl]trimethylsilane (7c). To **5c** (1.93 g, 8.25 mmol) in CH₂Cl₂ (80 mL) were sequentially added celite (3 g), molecular sieves (4Å, 3 g),

and PCC (2.77 g, 12.7 mmol) as per the general procedure to give ketone **6c** that, following workup, was subjected to dibromo-olefination using CBr₄ (3.53 g, 10.7 mmol) and PPh₃ (5.56 g, 21.3 mmol) in CH₂Cl₂ (100 mL) to give **7c** (1.91 g, 59%) as a yellow oil: R_f = 0.85 (CH₂Cl₂); IR (CH₂Cl₂ cast) 3003, 2959, 2898, 2835, 2149, 1597, 1582, 1542, 1489, 1462 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.33 (m, 1H), 7.19 (dd, J = 5.7, 1.7 Hz, 1H), 6.93 (dt, J = 7.4, 1.1 Hz, 1H), 6.90 (d, J = 7.4 Hz, 1H), 3.84 (s, 3H), 0.18 (s, 9H); ¹³C NMR (125 MHz, APT, CDCl₃) δ 155.9, 130.0, 129.7, 127.9, 127.1, 120.5, 111.6, 102.9, 102.8, 102.2, 55.7, -0.2; MS (EI, 70 eV) m/z 385.9/387.9/389.9 (M⁺, 50/100/52); HRMS calcd for C₁₄H₁₆O Si⁷⁹Br₂/C₁₄H₁₆O Si⁷⁹Br⁸¹Br/C₁₄H₁₆O Si⁸¹Br₂ (M⁺) 385.9337/387.9317/389.9296, found 385.9342/387.9325/389.9309.

1-(3-Methoxyphenyl)-3-trimethylsilylprop-2-yn-1-ol (5d). To (trimethylsilyl)acetylene (1.39 g, 14.2 mmol) in diethyl ether (20 mL) at -78 °C was added *n*-BuLi (5.7 mL, 2.5 M in hexanes, 14.3 mmol). After stirring for 0.5 h, 3-methoxybenzaldehyde (1.75 g, 12.9 mmol) was added and the general procedure was followed to give **5d** (2.29 g, 76%) as a light yellow oil: R_f = 0.41 (hexanes/Et₂O 7:3); IR (CHCl₃ cast) 3405, 2959, 2173, 1601, 1251, 1040 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.29 (t, J = 8.0 Hz, 1H), 7.12 (m, 2H), 6.86 (m, 1H), 5.41 (s, 1H), 3.81 (s, 3H), 3.05 (s, 1H), 0.23 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 159.5, 141.9, 129.5, 119.0, 114.1, 111.9, 105.1, 91.2, 64.6, 55.1, -0.3; EI HRMS calcd for C₁₃H₁₈O₂Si (M⁺) 234.1076, found 234.1072.

1-(3-Methoxyphenyl)-3-trimethylsilylpropynone (6d). To alcohol **5d** (0.405 g, 1.73 mmol) in CH₂Cl₂ were sequentially added celite (0.5 g), molecular sieves (4Å, 0.5 g), and PCC (0.45 g, 2.09 mmol) as per the general procedure to give the ketone **6d** (0.305 g, 76%) as a bright yellow oil: R_f = 0.75 (hexanes/Et₂O 7:3); IR (CHCl₃ cast) 3005, 2961, 2153, 1647, 1269, 1028 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (m, 1H), 7.58 (m, 1H), 7.34 (m, 1H), 7.10 (m, 1H), 3.80 (s, 3H), 0.23 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 177.2, 159.7, 137.8, 129.5, 122.7, 121.0, 112.8, 100.8, 100.2, 55.3, -0.8. MS (EI, 70 eV) m/z 232.1 (M⁺, 82), 217.1 ([M - CH₃]⁺, 100). EI HRMS calcd for C₁₃H₁₆O₂Si (M⁺) 232.0920, found 232.0918.

[4,4-Dibromo-3-(3-methoxyphenyl)-buten-1-ynyl]trimethylsilane (7d). To **5d** (0.508 g, 2.17 mmol) in CH₂Cl₂ were sequentially added celite (0.6 g), molecular sieves (4Å, 0.6 g), and PCC (0.585 g, 2.69 mmol) as per the general procedure to give ketone **6d** that, following workup, was subjected to dibromo-olefination using CBr₄ (0.876 g, 2.64 mmol) and PPh₃ (1.36 g, 5.20 mmol) in CH₂Cl₂ (80 mL) to give **7d** (0.407 g, 48%) as an oil: R_f = 0.3 (hexanes); IR (CHCl₃ cast) 2958, 2834, 2145, 1597, 1250 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.31 (t, *J* = 8.0 Hz, 1H), 7.05 (m, 1H), 7.03 (m, 1H), 6.91 (m, 1H), 3.84 (s, 3H), 0.24 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 159.4, 139.0, 130.8, 129.4, 120.9, 114.3, 114.1, 104.2, 103.3, 100.5, 55.3, -0.3; EI HRMS calcd for C₁₄H₁₆OSi⁷⁹Br⁸¹Br (M⁺) 387.9317, found 387.9314.

1-(4-Methoxyphenyl)-3-trimethylsilylprop-2-yn-1-ol (5e).* To (trimethylsilyl)acetylene (1.30 g, 14.0 mmol) in diethyl ether (30 mL) at -78 °C was added *n*-BuLi (5.7 mL, 2.4 M in hexanes, 13.7 mmol). After stirring for 0.5 h, 4-methoxybenzaldehyde (1.52 g, 11.2 mmol) was added and the general procedure was followed to give **5e** (2.54 g, 97%) as a light yellow oil: R_f = 0.79 (hexanes/Et₂O 7:3); IR (CHCl₃ cast) 3407, 2959, 2173, 1587, 1250, 1037 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.38 (d, *J* = 5.5 Hz, 1H), 3.78 (s, 3H), 2.41 (bs, 1H), 0.19 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 159.6, 132.7, 128.1, 113.9, 105.4, 91.1, 64.4, 55.2, -0.2; EI HRMS calcd for C₁₃H₁₈O₂Si (M⁺) 234.1076, found 234.1070. *Previously reported by: Brown, R. F. C.; Jackson, W. R.; McCarthy, T. D. *Tetrahedron* **1994**, *50*, 5469-5488.

[4,4-Dibromo-3-(4-methoxyphenyl)buten-1-ynyl]trimethylsilane (7e). To **5e** (1.90 g, 8.10 mmol) in CH₂Cl₂ were sequentially added celite (2.5 g), molecular sieves (4Å, 2.5 g), and PCC (2.28 g, 10.6 mmol) as per the general procedure. The resulting ketone **6e** was subjected directly to dibromo-olefination conditions, using CBr₄ (3.50 g, 10.6 mmol) and PPh₃ (5.57 g, 21.3 mmol) as per the general procedure to give **7e** (1.47 g, 47%) as a light yellow oil: R_f = 0.6 (hexanes/CH₂Cl₂ 2:1); IR (CH₂Cl₂ cast) 3001, 2959, 2183, 2136, 1607, 1249, 1079 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.45 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H), 0.29

(s, 9H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 159.6, 130.5, 130.0, 129.9, 113.6, 103.7, 103.6, 99.4, 55.2, 0.1; EI HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{OSi}^{79}\text{Br}^{81}\text{Br}$ (M^+) 387.9317, found 387.9318.

1-(4-*n*-Butoxyphenyl)-3-trimethylsilylprop-2-yn-1-ol (5f). To (trimethylsilyl)acetylene (0.61 g, 6.2 mmol) in diethyl ether (20 mL) at -78°C was added *n*-BuLi (2.36 mL, 2.5 M in hexanes, 5.90 mmol). After stirring for 0.5 h, 4-butoxybenzaldehyde (0.97 g, 5.47 mmol) was added and the general procedure was followed to give **5f** (1.04 g, 69%) as a yellow oil: R_f = 0.13 (hexanes/Et₂O 7:3); IR (CH_2Cl_2 cast) 3404, 2959, 2873, 2173, 1611, 1585, 1511, 1475, 1250 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.42 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 5.40 (s, 1H), 3.94 (t, J = 6.5 Hz, 2H), 2.10 (bs, 1H), 1.74 (quint, J = 6.7 Hz, 2H), 1.46 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 159.4, 132.5, 128.2, 114.6, 105.3, 91.3, 67.8, 64.7, 31.3, 19.3, 13.9, -0.1 ; EI HRMS calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{Si}$ (M^+) 276.1546, found 276.1538.

[4,4-Dibromo-3-(4-*n*-butoxyphenyl)buten-1-ynyl]trimethylsilane (7f). To **5f** (0.608 g, 2.17 mmol) in CH_2Cl_2 were sequentially added celite (0.6 g), molecular sieves ($4\text{\AA}$, 0.6 g), and PCC (0.58 g, 2.64 mmol) as per the general procedure. The resulting ketone **6f** was subjected directly to dibromo-olefination conditions, using CBr_4 (0.87 g, 2.60 mmol) and PPh_3 (1.48 g, 5.59 mmol). The reaction mixture was stirred overnight. Since TLC monitoring of the reaction showed that the reaction had not reached completion, more of the brominating mixture (0.38 eq of CBr_4 and 0.75 eq PPh_3) was added. Work-up as per the general procedure and purification by column chromatography (hexanes) yielded **7f** (0.363 g, 38%) as a yellow oil: R_f = 0.9 (hexanes/ CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 2958, 2172, 2134, 1606, 1506, 1469, 1249 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 3.97 (t, J = 6.5 Hz, 2H), 1.77 (quint, J = 6.6 Hz, 2H), 1.49 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 159.2, 130.6, 129.9, 129.7, 114.1, 103.7, 103.6, 99.2, 67.8, 31.4, 19.4, 14.0, -0.2 ; MS (EI, 70 eV) m/z 430.0 (M^+ , 100).

1-(4-Dimethylaminophenyl)-3-trimethylsilylprop-2-yn-1-ol (5g). To (trimethylsilyl)acetylene (1.39 g, 14.2 mmol) in diethyl ether (20 mL) at $-78\text{ }^{\circ}\text{C}$ was added *n*-BuLi (5.4 mL, 2.5 M in hexanes, 13.6 mmol). After stirring for 0.5 h, dimethylaminobenzaldehyde (1.93 g, 12.9 mmol) was added and the general procedure was followed to give **5g** (2.90 g, 91%) as a yellow-green crystalline solid: mp $94\text{--}96\text{ }^{\circ}\text{C}$; $R_f = 0.31$ (hexanes/Et₂O 7:3); IR (CHCl₃ cast) 3376, 2958, 2896, 2169, 1614, 1522, 1249 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.43 (d, $J = 9.0$ Hz, 2H), 6.75 (d, $J = 9.0$ Hz, 2H), 5.39 (d, $J = 5.0$ Hz, 1H), 2.98 (s, 6H), 3.78 (d, $J = 5.0$ Hz, 1H), 0.23 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 150.6, 128.6, 127.9, 112.5, 105.8, 90.5, 64.7, 40.6, -0.3 ; EI HRMS calcd for C₁₄H₂₁ONSi (M⁺) 247.1392, found 247.1387.

1-(2-Furyl)-3-trimethylsilylprop-2-yn-1-ol (5h). To (trimethylsilyl)acetylene (2.10 g, 21.3 mmol) in diethyl ether (30 mL) at $-78\text{ }^{\circ}\text{C}$ was added *n*-BuLi (8.5 mL, 2.4 M in hexanes, 20.4 mmol). After stirring for 0.5 h, 2-furaldehyde (1.83 g, 19.0 mmol) was added and the general procedure was followed to give **5h** (3.15 g, 85%) as a light yellow oil: $R_f = 0.60$ (hexanes/Et₂O 7:3); IR (CHCl₃ cast) 3377, 2960, 2178, 1251 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.36 (m, 1H), 6.42 (m, 1H), 6.29 (m, 1H), 5.38 (d, $J = 6.1$ Hz, 1H), 3.30 (bs, 1H), 0.18 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 152.9, 142.8, 110.2, 107.7, 102.6, 90.4, 58.2, -0.4 ; MS (EI, 70 eV) m/z 194.1 (M⁺, 64), 99.0 ([M – C₆H₇O]⁺, 100); HRMS calcd for C₁₀H₁₄O₂Si (M⁺) 194.0763, found 194.0757. Anal. Calcd for C₁₀H₁₄O₂Si: C, 61.81; H, 7.26. Found C, 61.86; H, 7.28.

[4,4-Dibromo-3-(2-furyl)buten-1-ynyl]trimethylsilane (7h). To **5h** (1.90 g, 9.80 mmol) in CH₂Cl₂ were sequentially added celite (3.0 g), molecular sieves (4Å, 3.0 g), and PCC (2.68 g, 12.5 mmol) as per the general procedure. The resulting ketone **6h*** was subjected directly to dibromo-olefination conditions, using CBr₄ (4.05 g, 12.5 mmol) and PPh₃ (6.42 g, 24.5 mmol) as per the general procedure to give **7h** (1.15 g, 34%) as an oil which decomposes readily even when refrigerated: $R_f = 0.85$ (hexanes/Et₂O 4:1); IR (CHCl₃ cast) 2959, 2148, 1250 cm⁻¹; ¹H

NMR (300 MHz, CDCl_3) δ 7.50 (dd, $J = 1.9, 0.7$ Hz, 1H), 6.90 (dd, $J = 4.3, 0.7$ Hz, 1H), 6.46 (dd, $J = 4.3, 1.9$ Hz, 1H), 0.23 (s, 9H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 149.0, 142.9, 120.8, 112.9, 111.3, 103.2, 101.3, 97.3, -0.3 ; EI HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{OSi}^{79}\text{Br}^{81}\text{Br}$ (M^+) 347.9004, found 347.9006. *Previously reported by: Walton, D. R. M.; Waugh, F. *J. Organomet. Chem.* **1972**, 37, 45-56.

1-(2-Thienyl)-3-trimethylsilylprop-2-yn-1-ol (5i). To (trimethylsilyl)acetylene (2.10 g, 21.3 mmol) in diethyl ether (30 mL) at -78°C was added $n\text{-BuLi}$ (8.5 mL, 2.4 M in hexanes, 20.4 mmol). After stirring for 0.5 h, 2-thiophene carboxaldehyde (2.17 g, 19.0 mmol) was added and the general procedure was followed to give **5i** (3.88 g, 97%) as a light yellow oil: $R_f = 0.56$ (hexanes/ Et_2O 7:3); IR (CHCl_3 cast) 3377, 3106, 2960, 2175, 1251 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.30 (dd, $J = 5.0, 1.1$ Hz, 1H), 7.16 (m, 1H), 6.98 (dd, $J = 5.0, 3.5$ Hz, 1H), 5.63 (d, $J = 6.0$ Hz, 1H), 3.00 (s, 1H), 0.23 (s, 9H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 144.3, 126.7, 126.0, 125.6, 104.3, 91.0, 60.4, -0.3 ; EI HRMS calcd for $\text{C}_{10}\text{H}_{14}\text{OSSi}$ (M^+) 210.0535, found 210.0533. Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{OSSi}$: C, 57.09; H, 6.71. Found C, 57.32; H, 6.58.

1-(2-Thienyl)-3-trimethylsilylpropynone (6i). The alcohol **5i** (1.47g, 6.96 mmol) was oxidized using PCC (2.30 g, 10.5 mmol) in the presence of celite (2.3 g) and molecular sieves ($4\text{\AA}$, 2.3 g) as per the general procedure to give the ketone **6i** (1.26 g, 87%) as a yellow oil: $R_f = 0.65$ (CH_2Cl_2); IR (CH_2Cl_2 cast) 3105, 2961, 2900, 2153, 1625, 1265 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.91 (dd, $J = 4.0, 1.0$ Hz, 1H), 7.69 (dd, $J = 5.0, 1.0$ Hz, 1H), 7.14 (dd, $J = 5.0, 4.0$ Hz, 1H), 0.30 (s, 9H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 169.5, 144.7, 135.6, 135.4, 128.3, 100.5, 99.2, -0.7 ; MS (EI, 70 eV) m/z 208.0 (M^+ , 69), 193.0 ($[\text{M} - \text{CH}_3]^+$, 100); EI HRMS calcd for $\text{C}_{10}\text{H}_{12}\text{OSiS}$ (M^+) 208.0378, found 208.0378.

[4,4-Dibromo-3-(2-thienyl)buten-1-ynyl]trimethylsilane (7i). Ketone **6i** (0.424 g, 2.04 mmol) was reacted with CBr_4 (0.852 g, 2.54 mmol) and PPh_3 (1.35 g, 5.09 mmol) as per the general procedure to give **7i** (0.628 g, 85%) as a yellow oil: $R_f = 0.77$ (hexanes/ Et_2O 4:1); IR (CHCl_3 cast) 2959, 2898, 2153, 1249 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.67 (dd, $J = 4.0, 1.1$

Hz, 1H), 7.40 (dd, $J = 5.0, 1.1$ Hz, 1H), 7.06 (dd, $J = 5.0, 4.0$ Hz, 1H), 0.38 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.4, 130.6, 127.6, 126.6, 124.4, 103.5, 102.9, 97.5, -0.3 ; EI HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{SiS}^{79}\text{Br}^{81}\text{Br}$ (M^+) 363.8775, found 363.8779.

1-(4-Pyridyl)-3-trimethylsilylprop-2-yn-1-ol (5j). To (trimethylsilyl)acetylene (1.39 g, 14.2 mmol) in diethyl ether (20 mL) at -78°C was added *n*-BuLi (5.7 mL, 2.5 M in hexanes, 14.3 mmol). After stirring for 0.5 h, 4-pyridinecarboxaldehyde (1.39 g, 13.0 mmol) was added and the general procedure was followed to give **5j** (1.33 g, 50%) as a pink solid that slowly decomposes: mp $83\text{--}85^\circ\text{C}$; $R_f = 0.17$ (hexanes/ Et_2O 7:3); IR (CHCl_3 cast) 3096, 2960, 2812, 2176, 1606, 1251 cm^{-1} ; ^1H NMR (300 MHz, CD_3CN) δ 8.57 (d, $J = 6.0$ Hz, 2H), 7.47 (d, $J = 6.0$ Hz, 2H), 5.34 (s, 1H), 2.39 (s, 1H), 0.18 (s, 9H); ^{13}C NMR (75 MHz, APT, CD_3CN) δ 151.3, 150.7, 122.2, 118.3, 106.0, 91.5, 63.4, -0.2 ; MS (EI, 70 eV) m/z 205.1 (M^+ , 78), 162.0 (100); EI HRMS calcd for $\text{C}_{11}\text{H}_{15}\text{ONSi}$ (M^+) 205.0923, found 205.0918.

1-Ferrocenyl-3-trimethylsilylprop-2-yn-1-ol (5k). To (trimethylsilyl)acetylene (1.30 g, 14.0 mmol) in diethyl ether (30 mL) at -78°C was added *n*-BuLi (5.7 mL, 2.4 M in hexanes, 13.7 mmol). After stirring for 0.5 h, ferrocene carboxaldehyde (2.40 g, 11.2 mmol) was added and the general procedure was followed to give **5k** (3.31 g, 95%) as an orange solid: mp $51\text{--}52^\circ\text{C}$; $R_f = 0.41$ (hexanes/ Et_2O 7:3); IR (CHCl_3 cast) 3388, 3097, 2958, 2174, 1250 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.15 (d, $J = 7.5$ Hz, 1H), 4.40 (m, 1H), 4.33 (m, 1H), 4.20 (m, 7H), 2.20 (d, $J = 7.5$ Hz, 1H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 105.4, 89.2, 88.9, 68.9, 68.5, 66.5, 61.4, 0.2 (two coincident signals not observed); EI HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{OSiFe}$ (M^+) 312.0633, found 312.0633.

1-Ferrocenyl-3-trimethylsilylpropynone (6k). To **5k** (0.31 g, 0.99 mmol) in CH_2Cl_2 (70 mL) was added barium manganate (0.76 g, 3.0 mmol). After stirring for 1h, the reaction mixture was filtered through celite and the solvent was evaporated to give **6k** (0.29 g, 94%) as a red solid: mp $68\text{--}69^\circ\text{C}$; IR (CHCl_3 cast) 2958, 2029, 1626, 1251 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.90 (t, $J = 2.0$ Hz, 2H), 4.59 (t, $J = 2.0$ Hz, 2H), 4.24 (s, 5H), 0.30 (s, 9H); ^{13}C NMR (75 MHz,

APT, CDCl₃) δ 180.9, 102.2, 96.3, 80.3, 73.6, 73.4, 70.7, -0.5; EI HRMS calcd for C₁₆H₁₈OSiFe (M⁺) 310.0476, found 310.0475.

[4,4-Dibromo-3-ferrocenyl-buten-1-ynyl]trimethylsilane (7k). To **5k** (0.680 g, 2.20 mmol) in CH₂Cl₂ (50 mL) were sequentially added celite (0.6 g), molecular sieves (4Å, 0.6 g), and PCC (0.58 g, 2.70 mmol). The reaction mixture was stirred and monitored by TLC. Upon completion of the reaction, the reaction mixture was passed through a plug of silica (CH₂Cl₂) and was used directly in the next step. The solution was diluted with 70 mL of benzene and CBr₄ (0.883 g, 2.64 mmol) and PPh₃ (1.50 g, 5.66 mmol) were added. The reaction mixture was refluxed for 2 days and the general work-up procedure was then carried out to give **7k** (0.265 g, 26%) as an orange oil: R_f = 0.84 (hexanes/Et₂O 4:1); IR (CH₂Cl₂ cast) 3096, 2958, 2152, 1249 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 4.71 (t, *J* = 2.0 Hz, 2H), 4.08 (s, 5H), 4.02 (t, *J* = 2.0 Hz, 2H), 0.22 (s, 9H); ¹³C NMR (100 MHz, APT, C₆D₆) δ 129.6, 104.4, 101.9, 94.4, 82.4, 70.5, 70.4, 69.2, -0.2; EI HRMS calcd for C₁₇H₁₈OSi⁷⁹Br⁸¹BrFe (M⁺) 465.8874, found 465.8874.

1-Phenyl-5-trimethylsilylpent-1-en-4-yn-3-ol (5l). To (trimethylsilyl)acetylene (1.39 g, 14.2 mmol) in diethyl ether (20 mL) at -78 °C was added *n*-BuLi (5.7 mL, 2.5 M in hexanes, 14.3 mmol). After stirring for 0.5 h, cinnamaldehyde (1.72 g, 13.0 mmol) was added and the general procedure was followed to give **5l** (2.40 g, 81%) as a light yellow oil: R_f = 0.36 (hexanes/Et₂O 7:3); IR (CHCl₃ cast) 3359, 3027, 2969, 2172, 1627, 1251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (m, 2H), 7.30 (m, 3H), 6.77 (d, *J* = 15.8 Hz, 1H), 6.29 (dd, *J* = 15.8, 6.0 Hz, 1H), 5.05 (m, 1H), 2.39 (bs, 1H), 0.23 (s, 9H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 136.1, 132.0, 128.6, 128.1, 128.0, 126.8, 104.4, 91.3, 63.3, -0.1; MS (EI, 70 eV) *m/z* 230.1 (M⁺, 49), 73.0 ([Me₃Si]⁺, 100); EI HRMS calcd for C₁₄H₁₈OSi (M⁺) 230.1127, found 230.1120. Anal. Calcd for C₁₄H₁₈OSi: C, 72.99; H, 7.88. Found C, 72.92; H, 8.21.

1-Phenyl-5-trimethylsilylpent-1-en-4-yn-3-one (6l).* The alcohol **5l** (0.436 g, 1.89 mmol) was oxidized using barium manganate (1.46 g, 5.68 mmol) as per the general procedure to give the ketone **6l** (0.416 g, 96%) as a yellow oil: R_f = 0.74 (CH₂Cl₂); IR (CHCl₃ cast) 3061,

3027, 2961, 2901, 2157, 1653, 1630, 1599, 1576, 1251 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 16.1$ Hz, 1H), 7.54 (m, 2H), 7.40 (m, 3H), 6.75 (d, $J = 16.1$ Hz, 1H), 0.29 (s, 9H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 177.9, 148.8, 134.0, 131.2, 129.0, 128.6, 128.2, 100.6, 98.6, -0.7; EI HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{OSi}$ (M^+) 228.0971, found 228.0967. *Previously reported by: Walton, D. R. M.; Waugh, F. *J. Organomet. Chem.* **1972**, 37, 45-56.

(3-Dibromomethylene-5-phenylpent-4-en-1-ynyl)trimethylsilane (7l). The alcohol **5l** (0.499 g, 2.16 mmol) was oxidized using barium manganate (1.60 g, 5.62 mmol) and after passing through a plug of silica (CH_2Cl_2), the resulting ketone **6l** was subjected to general dibromo-olefination conditions without additional purification using CBr_4 (1.45 g, 4.36 mmol) and PPh_3 (2.29 g, 8.73 mmol) to give **7l** (0.641 g, 77%) as a yellow oil: $R_f = 0.97$ (CH_2Cl_2); IR (CHCl_3 cast) 3058, 3025, 2959, 2146, 1250 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (m, 2H), 7.35 (m, 3H), 7.20 (d, $J = 15.6$ Hz, 1H), 7.06 (d, $J = 15.6$ Hz, 1H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 136.4, 136.3, 128.82, 128.76, 128.7, 127.2, 124.7, 104.9, 100.6, 99.8, -0.2; MS (EI, 70 eV) m/z 381.9/383.9/385.9 (M^+ , 29/54/29); HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{Si}^{79}\text{Br}_2/\text{C}_{15}\text{H}_{16}\text{Si}^{79}\text{Br}^{81}\text{Br}/\text{C}_{15}\text{H}_{16}\text{Si}^{81}\text{Br}_2$ (M^+) 381.9388/383.9368/385.9347, found 381.9416/383.9386/385.9347. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{SiBr}_2$: C, 46.89; H, 4.20. Found C, 46.73; H, 4.23.

1-[(S)-(-)-perillyl]-3-trimethylsilylprop-2-yn-1-ol (5m). To (trimethylsilyl)acetylene (1.11 g, 11.0 mmol) in diethyl ether (40 mL) at -78°C was added $n\text{-BuLi}$ (4.0 mL, 2.5 M in hexanes, 10.1 mmol). After stirring for 30 minutes, (S)-(-)-perillaldehyde (1.37 g, 9.14 mmol) dissolved in 5 mL of ether was added and stirring was continued for 2 h at -78°C . The reaction was quenched with sat. aq. NH_4Cl at -78°C , extracted with ether, and dried (Na_2SO_4). Column chromatography (CH_2Cl_2 /hexanes, 1:2) gave **5m** (1.42 g, 63%) as a colorless oil which upon refrigeration turned into a clear waxy solid: mp $30\text{--}31^\circ\text{C}$; $R_f = 0.44$ (CH_2Cl_2); IR (CH_2Cl_2 cast) 3332, 3082, 2962, 2920, 2839, 2170, 1644 cm^{-1} ; $[\alpha]_D^{25} -50.5^\circ$ ($c = 0.0020$, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 5.91 (s, 1H), 4.72 (m, 3H), 2.15 (m, 4H), 1.98 (m, 1H), 1.87 (m, 2H), 1.73

(s, 3H), 1.48 (m, 1H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, APT, CDCl_3) δ 149.6, 136.4, 124.4, 108.8, 104.8, 90.9, 66.9, 40.9, 30.6, 27.5, 24.7, 20.8, -0.1; MS (EI, 70 eV) m/z 248.2 (M^+ , 23), 73.0 (Me_3Si^+ , 100); HRMS calcd for $\text{C}_{15}\text{H}_{24}\text{OSi}$ (M^+) 248.1596, found 248.1599. Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{OSi}$: C, 72.52; H, 9.74. Found C, 72.04; H, 10.34.

1-[(S)-(-)-perillyl]-3-trimethylsilylpropynone (6m). To **5m** (0.464 g, 1.87 mmol) in CH_2Cl_2 (20 mL) was added barium manganate (1.60 g, 5.60 mmol). After stirring for 1h, the reaction mixture was filtered through celite. The solvent was evaporated and the crude product was purified by column chromatography (hexanes/ CH_2Cl_2 2:1) to give **6m** (0.390 g, 85%) as a colorless oil: R_f = 0.65 (CH_2Cl_2); IR (CHCl_3 cast) 3082, 2962, 2936, 2151, 1631, 1452, 1251 cm^{-1} ; $[\alpha]_D^{22}$ -85.7° (c = 0.0074, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 7.36 (m, 1H), 4.76 (s, 1H), 4.72 (s, 1H), 2.49 (m, 2H), 2.19 (m, 3H), 1.89 (m, 1H), 1.74 (s, 3H), 1.42 (m, 1H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 178.6, 148.1, 146.8, 139.7, 109.1, 99.9, 97.4, 39.9, 31.5, 26.3, 22.4, 20.4, -1.0; MS (EI, 70 eV) m/z 246.1 (M^+ , 46); HRMS calcd for $\text{C}_{15}\text{H}_{22}\text{OSi}$ (M^+) 246.1440, found 246.1434; Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{OSi}$: C, 73.11; H, 9.00. Found C, 72.96; H, 8.92.

[4-Dibromomethylene-3-[(S)-(-)-perillyl]-but-3-en-1-ynyl]trimethylsilane (7m). CBr_4 (0.499 g, 1.49 mmol) and PPh_3 (1.184 g, 4.47 mmol) were added to CH_2Cl_2 (20 mL) and the mixture stirred for 5 min at rt. Ketone **6m** (0.122 g, 0.50 mmol) in CH_2Cl_2 (5 mL) was added in one portion. The reaction mixture was stirred for 4 h, concentrated to ca. 15 mL, hexanes (15 mL) added, and the inhomogeneous mixture was filtered through celite. Evaporation gave a yellow oil which was purified by passing through a plug of silica (hexanes) to give **7m** (0.054 g, 27%) as a bright yellow oil: R_f = 0.38 (hexanes); IR (CH_2Cl_2 cast) 2958, 2920, 2850, 2145, 1249 cm^{-1} ; $[\alpha]_D$ -23.3° (c = 0.0096, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 5.79 (s, 1H), 4.73 (s, 2H), 2.18 (m, 4H), 2.01 (m, 1H), 1.84 (m, 1H), 1.73 (s, 3H), 1.52 (m, 1H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 149.2, 135.3, 132.8, 129.0, 108.9, 103.2, 102.2, 98.7, 40.2, 30.7, 27.4, 27.2, 20.7, -0.3; MS (EI, 70 eV) m/z 400.0/402.0/404.0 (M^+ , 29/43/22); HRMS calcd for

$\text{C}_{16}\text{H}_{22}\text{Si}^{79}\text{Br}_2/\text{C}_{16}\text{H}_{22}\text{Si}^{79}\text{Br}^{81}\text{Br}/\text{C}_{16}\text{H}_{22}\text{Si}^{81}\text{Br}_2$ (M^+) 399.9858/401.9837/403.9817, found 399.9793/401.9819/403.9814.

1-Trimethylsilyl-hex-4-en-1-yn-3-ol (5n). To (trimethylsilyl)acetylene (1.72 g, 17.1 mmol) in diethyl ether (60 mL) at -78°C was added *n*-BuLi (6.3 mL, 2.5 M in hexanes, 15.7 mmol). After stirring for 30 minutes, crotonaldehyde (1.00 g, 14.3 mmol, 1.19 mL) was added and stirring was continued for 2 h at -78°C . The reaction was quenched with sat. aq. NH_4Cl at -78°C , extracted with ether, and dried (Na_2SO_4). Column chromatography (hexanes/ CH_2Cl_2 2:1) gave **5n** (0.930 g, 39%) as a pale yellow oil: $R_f = 0.4$ (CH_2Cl_2); IR (CH_2Cl_2 cast) 3329, 3031, 2961, 2918, 2899, 2173, 1449, 1251 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.86 (m, 1H), 5.61 (m, 1H), 4.79 (t, $J = 6.1$ Hz, 1H), 1.87 (d, $J = 6.0$ Hz, 1H), 1.71 (dd, $J = 6.5, 1.1$ Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 129.9, 129.0, 104.8, 90.5, 63.3, 17.5, -0.2; MS (EI, 70 eV) m/z 168.1 (M^+ , 54); HRMS calcd for $\text{C}_9\text{H}_{16}\text{OSi}$ (M^+) 168.0971, found 168.0971.

1-Trimethylsilyl-hex-4-en-1-yn-3-one (6n). To **5n** (0.010 g, 0.59 mmol) in CH_2Cl_2 was added 3 equivalents of barium manganate (0.505 g, 1.77 mmol). After stirring for 1h, the reaction mixture was filtered through celite. The solvent was evaporated to give **6n** (0.087 g, 89%) as a yellow oil: IR (CHCl_3 cast) 3037, 2963, 2902, 2156, 1663, 1641, 1628, 1442, 1253 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.16 (dq, $J = 15.4, 6.8$ Hz, 1H), 6.12 (dq, $J = 15.4, 1.6$ Hz, 1H), 1.94 (dd, $J = 6.8, 1.6$ Hz, 3H), 0.23 (s, 9H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 178.0, 150.0, 133.6, 100.3, 98.0, 18.4, -0.7; MS (EI, 70 eV) m/z 166.1 (M^+ , 16), 151.1 ($[\text{M} - \text{CH}_3]^+$, 100); HRMS calcd for $\text{C}_9\text{H}_{14}\text{OSi}$ (M^+) 166.0814, found 166.0813.

1-(2-Thienyl)hex-4-en-1-yn-3-ol (5o). To a solution of 2-(2-thienyl)-ethynyltrimethylsilane (0.818 g, 4.53 mmol) in wet methanol (25 mL) was added potassium carbonate (ca. 0.2 eq), the mixture stirred for 30 min., ether and water added, the organic phase separated, washed with brine, dried and reduced under vacuo to give the corresponding terminal acetylene, 2-ethynyl-thiophene, as a yellow oil that was used in the next step without additional purification. To 2-ethynyl-thiophene (4.53 mmol) in diethyl ether at -78°C was added *n*-BuLi

(1.7 mL, 2.5 M in hexanes, 4.25 mmol). After stirring for 30 minutes, crotonaldehyde (0.267 g, 3.82 mmol, 0.300 mL) was added and stirring was continued for 2 h at $-78\text{ }^{\circ}\text{C}$. The reaction was quenched with sat. aq. NH_4Cl at $-78\text{ }^{\circ}\text{C}$, extracted with ether, and dried (Na_2SO_4). Column chromatography (CH_2Cl_2 /hexanes, 1:2) gave **5o** (0.548 g, 80%) as a yellow oil: $R_f = 0.37$ (CH_2Cl_2); IR (CH_2Cl_2 cast) 3300, 3106, 3029, 2966, 2939, 2915, 2854, 2221, 1672, 1517, 1189 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.16 (m, 2H), 6.88 (m, 1H), 5.90 (m, 1H), 5.63 (m, 1H), 5.00 (m, 1H), 1.91 (m, 1H), 1.67 (m, 3H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 132.4, 130.3, 129.4, 127.6, 127.0, 122.7, 93.6, 80.0, 63.9, 18.2; MS (EI, 70 eV) m/z 178.0 (M^+ , 100); HRMS calcd for $\text{C}_{10}\text{H}_{10}\text{OS}$ (M^+) 178.0452, found 178.0452.

1-(2-Thienyl)hex-4-en-1-yn-3-one (6o). (a) *PCC oxidation*: To **5o** (0.523 g, 2.93 mmol) in CH_2Cl_2 were sequentially added celite (1 g), molecular sieves ($4\text{\AA}$, 1 g), and PCC (0.968 g, 4.40 mmol). The reaction mixture was stirred for 2 h at rt and the solution mixture was filtered through a plug (SiO_2 , CH_2Cl_2) to give **6o** (0.179 g, 35%) as a yellow oil: $R_f = 0.48$ (CH_2Cl_2); IR (CH_2Cl_2 cast) 2189, 1647, 1620, 1513 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.44 (m, 2H), 7.19 (dq, $J = 15.7, 6.9$ Hz, 1H), 7.03 (dd, $J = 5.0, 3.8$ Hz, 1H), 6.21 (dq, $J = 15.7, 1.6$ Hz, 1H), 1.98 (dd, $J = 6.9, 1.6$ Hz, 3H); ^{13}C NMR (125 MHz, APT, CDCl_3) δ 177.8, 149.3, 136.2, 133.6, 131.1, 127.6, 119.9, 90.8, 84.9, 18.5; MS (EI, 70 eV) m/z 176.0 (M^+ , 100); HRMS calcd for $\text{C}_{10}\text{H}_8\text{OS}$ (M^+) 176.0296, found 176.0297. Anal. Calcd for $\text{C}_{10}\text{H}_8\text{OS}$: C, 68.15; H, 4.58. Found C, 67.73; H, 4.67. (b) *Barium manganate oxidation*: To **5o** (0.434 g, 2.43 mmol) in CH_2Cl_2 (20 mL) was added 3 equivalents of barium manganate (2.078 g, 7.30 mmol). After stirring for 1h, the reaction mixture was filtered through celite and the solvent was evaporated to give **6o** as a yellow oil (0.352 g, 82%).

1-(3-Methoxyphenyl)hept-2-yn-1-ol (5p). To 1-hexyne (1.54 g, 19.3 mmol) in diethyl ether (50 mL) at $-78\text{ }^{\circ}\text{C}$ was added $n\text{-BuLi}$ (12.1 mL, 1.6 M in hexanes, 19.4 mmol). After stirring for 0.5 h, *m*-anisaldehyde (2.37 g, 17.4 mmol) was added. The reaction mixture was allowed to warm up such that the aldehyde, which froze at $-78\text{ }^{\circ}\text{C}$ dissolved completely and

stirring was then continued for 1 h. The reaction mixture was quenched and extracted as per the general procedure to give **5p** (3.33 g, 88%) as a yellow oil: $R_f = 0.11$ (hexanes/ CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 3405, 2957, 2872, 2226, 1601, 1587, 1488, 1466, 1259 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.26 (m, 1H), 7.10 (m, 2H), 6.84 (m, 1H), 5.40 (s, 1H), 3.81 (s, 3H), 2.26 (t, $J = 7.0$, 2.0 Hz, 2H), 2.13 (bs, 1H), 1.53 (quint, $J = 7.0$ Hz, 2H), 1.42 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 159.8, 142.9, 129.5, 118.9, 113.9, 112.0, 87.6, 79.8, 64.8, 55.2, 30.6, 22.0, 18.5, 13.5; EI HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$ (M^+) 218.1307, found 218.1301.

1-(3-Methoxyphenyl)hept-2-yn-1-one (6p). To **5p** (2.32 g, 10.6 mmol) in CH_2Cl_2 were sequentially added celite (2.7 g), molecular sieves (4Å, 2.7 g), and PCC (2.74 g, 12.8 mmol) as per the general procedure to give **6p** (1.05 g, 46%) as a yellow oil: $R_f = 0.35$ (hexanes/ CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 2958, 2934, 2872, 2221, 1645, 1595, 1582, 1484, 1465, 1430 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (dd, $J = 7.3$, 1.4 Hz, 1H), 7.63 (dd, $J = 2.5$, 1.4 Hz, 1H), 7.35 (t, $J = 7.9$ Hz, 1H), 7.13 (ddd, $J = 8.5$, 2.5, 1.4 Hz, 1H), 3.83 (s, 3H), 2.47 (t, $J = 7.1$ Hz, 2H), 1.64 (m, 2H), 1.49 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 177.9, 160.0, 138.3, 129.5, 122.7, 120.7, 112.9, 96.6, 79.7, 55.4, 29.8, 22.0, 18.9, 13.5; EI HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$ (M^+) 216.1150, found 216.1146.

1-(1-Dibromomethylene-hept-2-ynyl)-3-methoxybenzene (7p). Ketone **6p** (0.880 g, 4.67 mmol) was reacted with CBr_4 (1.65 g, 4.99 mmol) and PPh_3 (2.89 g, 10.9 mmol) as per the general procedure. After work-up as per the general procedure, the product was purified by column chromatography (hexanes/ CH_2Cl_2 1:1) to give **7p** (0.126 g, 7%) as a yellow/orange oil: $R_f = 0.70$ (hexanes/ CH_2Cl_2 1:1). IR (CH_2Cl_2 cast) 2956, 2215, 1597, 1580 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , APT) δ 7.26 (t, $J = 8.0$ Hz, 1H), 6.99 (d, $J = 7.6$ Hz, 1H), 6.94 (m, 1H), 6.86 (dd, $J = 2.8$, 8.0 Hz, 1H), 3.80 (s, 3H), 2.34 (t, $J = 7.0$ Hz, 2H), 1.54 (tt, $J = 6.8$, 7.7 Hz, 2H), 1.44 (tq, $J = 7.2$, 7.6 Hz, 2H), 0.90 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.2, 139.7, 131.1, 129.2, 120.8, 114.0, 113.9, 100.1, 97.4, 80.5, 55.3, 30.4, 22.0, 19.6, 13.6; EIMS m/z 371.9 (M^+ , 100), 329.9 ($[\text{M} - i\text{-Pr}]^+$, 14); HRMS calcd. for $\text{C}_{15}\text{H}_{16}\text{O}^{79}\text{Br}^{81}\text{Br}$ (M^+) 371.9547, found 371.9549.

1-(2-Thienyl)hept-2-yn-1-ol (5q). To 1-hexyne (1.46 g, 18.3 mmol) in diethyl ether (50 mL) at $-78\text{ }^{\circ}\text{C}$ was added *n*-BuLi (11.4 mL, 1.6 M in hexanes, 18.2 mmol). After stirring for 0.5 h, 2-thiophene carboxaldehyde (1.88 g, 16.7 mmol) was added and the general procedure was followed to give **5q** (3.04 g, 94%) as a yellow oil: $R_f = 0.14$ (hexanes/ CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 3374, 3105, 2957, 2932, 2871, 2227, 1652, 1538, 1465, 1251 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.26 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.14 (dt, $J = 3.5, 1.2$ Hz, 1H), 6.95 (dd, $J = 5.0, 3.5$ Hz, 1H), 5.62 (s, 1H), 2.37 (bs, 1H), 2.27 (dt, $J = 7.0, 2.0$ Hz, 2H), 1.53 (quint, $J = 7.0$ Hz, 2H), 1.43 (sext, $J = 7.0$ Hz, 2H), 0.91 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 145.5, 126.7, 125.8, 125.3, 87.1, 79.4, 60.4, 30.5, 21.9, 18.4, 13.5; EI HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{OS}$ (M^+) 194.0765, found 194.0761.

1-(2-Thienyl)hept-2-yn-1-one (6q). To **5q** (1.95 g, 10.3 mmol) in CH_2Cl_2 were sequentially added celite (2.6 g), molecular sieves ($4\text{\AA}$, 2.6 g), and PCC (2.60 g, 12.1 mmol) as per the general procedure to give **6q** (1.62 g, 82%) as a red oil: $R_f = 0.36$ (hexanes/ CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 3103, 2958, 2932, 2871, 2229, 2202, 1623, 1515, 1465, 1257 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (dd, $J = 3.8, 1.2$ Hz, 1H), 7.66 (dd, $J = 4.9, 1.2$ Hz, 1H), 7.12 (dd, $J = 4.9, 3.8$ Hz, 1H), 2.46 (t, $J = 7.0$ Hz, 2H), 1.62 (quint, $J = 7.0$ Hz, 2H), 1.49 (sext, $J = 7.2$ Hz, 2H), 0.94 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 170.0, 145.1, 134.77, 134.76, 128.1, 95.3, 79.3, 29.7, 22.0, 18.8, 13.5; EI HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{OS}$ (M^+) 192.0609, found 192.0610.

2-(1-Dibromomethylene-2-heptynyl)thiophene (7q). Ketone **6q** (0.043 g, 0.223 mmol) was reacted with CBr_4 (0.100 g, 0.325 mmol) and PPh_3 (0.177 g, 0.650 mmol) as per the general procedure. Another equivalent of CBr_4 and PPh_3 was required for completion of the reaction. After work-up as per the general procedure, the product was purified by column chromatography (hexanes/ CH_2Cl_2 1:1) to give **7q** (0.013 g, 16%) as a yellow oil: $R_f = 0.75$ (hexanes/ CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 2956, 2930, 2870, 2223, 1464 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dd, $J = 3.8, 1.2$ Hz, 1H), 7.35 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.00 (dd, $J = 5.1, 3.8$ Hz, 1H), 2.41 (t, $J = 7.0$

Hz, 2H), 1.60 (m, 2H), 1.49 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 139.3, 130.1, 127.3, 126.5, 124.6, 99.3, 95.2, 80.2, 30.3, 22.0, 19.4, 13.6; MS (EI, 70 eV) m/z 345.9/347.9/349.9 (M^+ , 60/100/63); HRMS calcd for $\text{C}_{12}\text{H}_{12}\text{S}^{79}\text{Br}_2/\text{C}_{12}\text{H}_{12}\text{S}^{79}\text{Br}^{81}\text{Br}/\text{C}_{12}\text{H}_{12}\text{S}^{81}\text{Br}_2$ (M^+) 345.9027/347.9006/349.8986, found 345.9037/347.9019/349.8999.

1-(2-Thienyl)but-2-yn-1-ol (5r). Propyne gas was bubbled through a solution of *n*-BuLi (2.5 M in hexanes, 26.7 mmol, 10.7 mL) in diethyl ether (60 mL) at -78°C . After stirring for 30 minutes, 2-thiophenecarboxaldehyde (2.00 g, 17.8 mmol, 1.7 mL) was added and stirring was continued for 2 h at -78°C . The reaction was quenched with sat. aq. NH_4Cl at -78°C , extracted with ether, and dried (Na_2SO_4). Column chromatography (hexanes/ CH_2Cl_2 2:1) gave **5r** (2.65 g, 98%) as a yellow oil: $R_f = 0.3$ (CH_2Cl_2); IR (CHCl_3 cast) 3372, 2228, 1435, 1380 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.28 (dd, $J = 5.3, 1.3$ Hz, 1H), 7.15 (dt, $J = 3.5, 1.0$ Hz, 1H), 6.97 (dd, $J = 5.3, 3.5$ Hz, 1H), 5.61 (s, 1H), 2.72 (d, $J = 6.5$ Hz, 1H), 1.90 (s, 3H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 145.4, 126.6, 125.7, 125.2, 82.6, 78.7, 60.3, 3.6; MS (EI, 70 eV) m/z 152.0 (M^+ , 100); HRMS calcd for $\text{C}_8\text{H}_8\text{OS}$ (M^+) 152.0296, found 152.0296. Anal. Calcd for $\text{C}_8\text{H}_8\text{OS}$: C, 63.13; H, 5.30. Found C, 63.03; H, 5.28.

1-(2-Thienyl)but-2-yn-1-one (6r). To **5r** (2.04 g, 13.4 mmol) in CH_2Cl_2 (60 mL) was added sequentially celite (4.5 g), molecular sieves ($4\text{\AA}$, 4.5 g), and PCC (4.43 g, 20.1 mmol). The reaction mixture was stirred for 2 h at rt and the solution mixture was filtered through a plug (SiO_2 , CH_2Cl_2) to give **6r** (1.48 g, 73%) as a yellow oil: $R_f = 0.52$ (CH_2Cl_2); IR (CHCl_3 cast) 3102, 2237, 2198, 1620 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.91 (dd, $J = 4.0, 1.0$ Hz, 1H), 7.69 (dd, $J = 5.0, 1.0$ Hz, 1H), 7.15 (dd, $J = 5.0, 4.0$ Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.1, 145.0, 135.0, 134.9, 128.2, 91.0, 78.7, 4.3; EI HRMS calcd for $\text{C}_8\text{H}_6\text{OS}$ (M^+) 150.0139, found 150.0140.

2-(1-Dibromomethylene-2-butynyl)thiophene (7r). CBr_4 (0.240 g, 0.72 mmol) and PPh_3 (0.380 g, 1.43 mmol) were added to CH_2Cl_2 (40 mL) and the mixture stirred for 5 min at rt. Ketone **6r** (0.086 g, 0.57 mmol) in CH_2Cl_2 was added in one portion, the reaction stirred for 4 h,

then concentrated to ca. 15 mL, hexanes (15 mL) was added, and the inhomogeneous mixture was filtered through celite. Evaporation gave a yellow oil which was purified by passing through a plug of silica (hexanes) to give **7r** (0.029 g, 17%) as a yellow oil: $R_f = 0.97$ (CH_2Cl_2); IR (CH_2Cl_2 cast) 3104, 2922, 2851, 2232 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (dd, $J = 3.7, 1.2$ Hz, 1H), 7.35 (dd, $J = 5.2, 1.2$ Hz, 1H), 7.00 (dd, $J = 5.2, 3.7$ Hz, 1H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.2, 130.1, 127.3, 126.5, 124.6, 95.5, 94.8, 79.2, 4.7; MS (EI, 70 eV) m/z 303.9/305.9/307.9 (M^+ , 43/86/45); HRMS calcd for $\text{C}_9\text{H}_6\text{S}^{79}\text{Br}_2/\text{C}_9\text{H}_6\text{S}^{79}\text{Br}^{81}\text{Br}/\text{C}_9\text{H}_6\text{S}^{81}\text{Br}_2$ (M^+) 303.8557/305.8536/307.8516, found 303.8562/305.8543/307.8522.

1-(4-Hexylphenyl)-3-trimethylsilylpropynone (9a). 4-Hexylbenzoyl chloride (1.65 g, 7.3 mmol) was reacted with bis(trimethylsilyl)acetylene (1.25 g, 7.3 mmol) and AlCl_3 (0.97 g, 7.3 mmol) as per the general procedure, with more AlCl_3 (0.4 g, 3.0 mmol) being added until the reaction was deemed complete by TLC, to give ketone **9a** (1.88 g, 90%) as a greenish yellow oil: $R_f = 0.76$ (hexanes/ Et_2O 7:3); IR (CHCl_3 cast) 2958, 2929, 2153, 1644, 1255 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 2.64 (t, $J = 7.7$ Hz, 2H), 1.60 (m, 2H), 1.27 (m, 6H), 0.85 (m, 3H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 177.3, 150.1, 134.4, 129.7, 128.6, 101.0, 99.8, 36.1, 31.6, 30.9, 28.8, 22.5, 14.0, -0.7; MS (EI, 70 eV) m/z 286.2 (M^+ , 46), 271.2 ($[\text{M} - \text{CH}_3]^+$, 100); EI HRMS calcd for $\text{C}_{18}\text{H}_{26}\text{OSi}$ (M^+) 286.1753, found 286.1756. Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{OSi}$: C, 75.46; H, 9.15. Found C, 75.32; H, 9.21.

[4,4-Dibromo-3-(4-hexylphenyl)buten-1-ynyl]trimethylsilane (10a). Ketone **9a** (1.00 g, 3.5 mmol) was reacted with CBr_4 (1.40 g, 4.2 mmol) and PPh_3 (2.40 g, 9.1 mmol) as per the general procedure to give **10a** (1.22 g, 79%) as a yellow oil: $R_f = 0.70$ (hexanes); IR (CHCl_3 cast) 3036, 2957, 2135, 1250 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, $J = 8.2$ Hz, 2H), 7.14 (d, $J = 8.2$ Hz, 2H), 2.57 (t, $J = 7.8$ Hz, 2H), 1.58 (m, 2H), 1.28 (m, 6H), 0.86 (m, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 143.5, 134.9, 130.9, 128.4, 128.2, 103.8, 103.5, 99.7, 35.8, 31.6, 31.1, 29.0, 22.5, 14.0, -0.4; EI HRMS calcd for $\text{C}_{19}\text{H}_{26}\text{Si}^{79}\text{Br}^{81}\text{Br}$ (M^+) 442.0150, found 442.0129. Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{SiBr}_2$: C, 51.59; H, 5.93. Found C, 51.87; H, 5.91.

1-(4-*tert*-Butylphenyl)-3-trimethylsilylpropynone (9b).* 4-*tert*-Butylbenzoyl chloride (1.02 g, 5.19 mmol) was reacted with bis(trimethylsilyl)acetylene (0.88 g, 5.19 mmol) and AlCl₃ (0.69 g, 5.17 mmol) as per the general procedure, with more AlCl₃ (0.26 g, 2.0 mmol) being added until the reaction was deemed complete by TLC, to give ketone **9b** (1.04 g, 78%) as a yellow oil: R_f = 0.79 (hexanes/Et₂O 7:3); IR (CH₂Cl₂ cast) 2964, 2904, 2154, 1645, 1261 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 1.28 (s, 9H), 0.26 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 177.4, 158.2, 134.2, 129.7, 125.6, 101.1, 100.0, 35.3, 31.1, -0.6; MS (EI, 70 eV) *m/z* 258.1 (M⁺, 25), 243.1 ([M - CH₃]⁺, 100); HRMS calcd for C₁₆H₂₂OSi (M⁺) 258.1440, found 258.1444. *Previously reported by: Suzuki, R.; Tsukuda, H.; Watanabe, N.; Kuwatani, Y.; Ueda, I. *Tetrahedron* **1998**, 54, 2477-2496.

[4,4-Dibromo-3-(4-*tert*-butylphenyl)buten-1-ynyl]trimethylsilane (10b). Ketone **9b** (0.25 g, 0.97 mmol) was reacted with CBr₄ (0.39 g, 1.2 mmol) and PPh₃ (0.66 g, 2.5 mmol) as per the general procedure to give **10b** (0.245 g, 61%) as a white solid: mp 69-70 °C; R_f = 0.75 (hexanes); IR (CH₂Cl₂ cast) 2962, 2183, 2134, 1250 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (s, 4H), 1.36 (s, 9H), 0.23 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 151.7, 134.7, 130.9, 128.4, 125.2, 103.8, 103.6, 99.8, 31.3, -0.3; EI HRMS calcd for C₁₇H₂₂Si⁷⁹Br⁸¹Br (M⁺) 413.9837, found 413.9801.

1-(4-Phenylazophenyl)-3-trimethylsilylpropynone (9c). To a solution of 4-phenylazobenzoyl chloride (2.00 g, 8.17 mmol) in dry CH₂Cl₂ (80 mL) at 0 °C, bis(trimethylsilyl)acetylene (1.39 g, 8.17 mmol) was added, followed by slow addition of AlCl₃ (1.09 g, 8.17 mmol) as per the general procedure to give the ketone **9c** (1.07 g, 43%) as a red solid: mp 68-69 °C; R_f = 0.67 (hexanes/CH₂Cl₂ 1:1); IR (CH₂Cl₂ cast) 2956, 2159, 1635, 1249 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.70 (m, 4H), 7.54 (m, 3H), 0.34 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 176.9, 155.7, 152.6, 137.8, 132.0, 130.8, 129.3, 123.3, 122.9, 101.4, 100.9, -0.6; MS (EI, 70 eV) *m/z* 306.1 (M⁺, 86), 77.0 (C₆H₅⁺, 100); EI HRMS calcd

for $C_{18}H_{18}ON_2Si$ (M^+) 306.1188, found 306.1183. Anal. Calcd. for $C_{18}H_{18}ON_2Si$: C, 70.55; H, 5.92; N, 9.14. Found C, 70.64; H, 5.70; N, 9.11.

[4-(1-Dibromomethylene-3-trimethylsilylprop-2-ynyl)phenyl]phenyldiazene (10c).

Ketone **9c** (0.448 g, 1.46 mmol) was reacted with CBr_4 (0.75 g, 2.2 mmol) and PPh_3 (1.50 g, 5.66 mmol) as per the general procedure to give **10c** (0.560 g, 83%) as a bright orange solid: mp 92-94 °C; R_f = 0.57 (hexanes/ CH_2Cl_2 2:1); IR ($CHCl_3$ cast) 2958, 2132, 2028, 1250 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.93 (m, 4H), 7.62 (d, J = 8.8 Hz, 2H), 7.51 (m, 3H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 152.2, 140.1, 131.2, 130.3, 129.5, 129.1, 122.9, 122.8, 104.7, 103.0, 100.9, -0.4; EI HRMS calcd for $C_{19}H_{18}N_2Si^{79}Br_2/C_{19}H_{18}N_2Si^{79}Br^{81}Br/C_{19}H_{18}N_2Si^{81}Br_2$ (M^+) 459.9606/461.9586/463.9565, found 459.9633/461.9585/463.9574. Anal. Calcd for $C_{19}H_{18}N_2SiBr_2$: C, 49.37; H, 3.93; N, 6.06. Found C, 49.76; H, 3.69; N, 5.91.

1-(3,4,5-Trimethoxyphenyl)-3-trimethylsilylpropynone (9d). To a solution of 3,4,5-trimethoxybenzoyl chloride (0.47 g, 2.0 mmol) in dry CH_2Cl_2 at 0 °C, bis(trimethylsilyl)acetylene (0.35 g, 2.0 mmol) was added, followed by slow addition of $AlCl_3$ (0.27 g, 2.0 mmol) as per the general procedure to give the ketone **9d** (0.54 g, 91%) as a white solid: mp 54-55 °C; R_f = 0.39 (hexanes/ Et_2O 7:3); IR (CH_2Cl_2 cast) 2959, 2837, 2154, 1642, 1251 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.37(s, 2H), 3.87 (s, 3H), 3.86 (s, 6H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 176.7, 152.9, 143.3, 131.7, 106.9, 100.7, 100.2, 60.9, 56.1, -0.8; EI HRMS calcd for $C_{15}H_{20}O_4Si$ (M^+) 292.1131, found 292.1132. Anal. Calcd for $C_{15}H_{20}O_4Si$: C, 61.61; H, 6.89. Found C, 61.58; H, 7.06.

[4,4-Dibromo-3-(3,4,5-trimethoxyphenyl)buten-1-ynyl]trimethylsilane (10d). Ketone **9d** (0.19 g, 0.64 mmol) was reacted with CBr_4 (0.16 g, 0.48 mmol) and PPh_3 (0.44 g, 1.7 mmol) as per the general procedure to give **10d** (0.263 g, 91%) as a white solid: mp 48-49 °C; R_f = 0.2 (hexanes/ CH_2Cl_2 1:3); IR (microscope) 2958, 2836, 2154, 2139, 1247 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 6.64 (s, 2H), 3.83 (s, 3H), 3.82 (s, 6H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, APT, $CDCl_3$)

δ 153.0, 138.3, 132.9, 130.8, 106.1, 104.4, 103.3, 100.1, 60.9, 56.2, -0.3 ; EI HRMS calcd for $C_{16}H_{20}O_3Si^{79}Br^{81}Br$ (M^+) 447.9528, found 447.9557.

1-(2-Thienyl)-5-trimethylsilylpent-1-en-4-yn-3-one (9e). To a solution of 3-(2-thienyl)acryloyl chloride (2.18 g, 12.6 mmol) in dry CH_2Cl_2 at $0^\circ C$, bis(trimethylsilyl)acetylene (2.15 g, 12.6 mmol) was added, followed by slow addition of $AlCl_3$ (1.68 g, 12.6 mmol). The reaction mixture was stirred for 3 h. Aqueous work-up and purification by column chromatography (hexanes/ CH_2Cl_2 2:1) gave the ketone **9e** (1.82 g, 62%) as an orange oil: R_f = 0.65 (CH_2Cl_2); IR ($CHCl_3$ cast) 2960, 2156, 1622, 1583, 1421, 1240, 1185 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 15.8, 0.7 Hz, 1H), 7.45 (dd, J = 4.8, 0.7 Hz, 1H), 7.34 (m, 1H), 7.07 (ddd, J = 4.8, 3.7, 1.3 Hz, 1H), 6.55 (dd, J = 15.8, 1.3 Hz, 1H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 177.1, 140.6, 139.2, 132.4, 130.2, 128.4, 126.9, 100.6, 98.4, -0.7 ; MS (EI, 70 eV) m/z 234.1 (M^+ , 80), 219.0 ($[M - CH_3]^+$, 100); EI HRMS calcd for $C_{12}H_{14}OSSi$ (M^+) 234.0535, found 234.0533. Anal. Calcd for $C_{12}H_{14}OSiS$: C, 61.49; H, 6.02. Found C, 61.00; H, 6.23.

[3-Dibromomethylene-5-(2-thienyl)-pent-4-en-1-ynyl]trimethylsilane (10e). Ketone **9e** (0.877 g, 3.74 mmol) was reacted with CBr_4 (2.51 g, 7.48 mmol) and PPh_3 (3.97 g, 15.0 mmol) as per the general procedure to give **10e** (0.971 g, 67%) as a pale yellow crystalline solid: mp $67-69^\circ C$; R_f = 0.48 (hexanes); IR ($CHCl_3$ cast) 2958, 2898, 2145, 1605, 1424, 1250 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 5.1 Hz, 1H), 7.25 (d, J = 15.4 Hz, 1H), 7.13 (d, J = 3.7 Hz, 1H), 7.00 (dd, J = 5.1, 3.7 Hz, 1H), 6.83 (d, J = 15.5 Hz, 1H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 141.6, 128.9, 128.4, 128.0, 127.8, 126.1, 124.1, 104.9, 100.1, 99.5, -0.3 ; MS (EI, 70 eV) m/z 387.9/389.9/391.9 (M^+ , 10/19/10); HRMS calcd for $C_{13}H_{14}SSi^{79}Br_2/C_{13}H_{14}SSi^{79}Br^{81}Br/C_{13}H_{14}SSi^{81}Br_2$ (M^+) 387.8952/389.8932/391.8911, found 387.8947/389.8930/391.8915. Anal. Calcd for $C_{13}H_{14}SiSBr_2$: C, 40.01; H, 3.62. Found C, 40.33; H, 3.81.

1-Trimethylsilyl-octa-4,6-dien-1-yn-3-one (9f). Bis(trimethylsilyl)acetylene (0.976 g, 5.72 mmol) was added to sorbyl chloride (0.748 g, 5.72 mmol) in CH₂Cl₂ (16 mL) in an ice bath. The reaction mixture was stirred and anhydrous aluminium trichloride (0.763 g, 5.72 mmol) was slowly added. After stirring for 3 h at 0-5 °C, the solution was poured into a mixture of 10% aq. HCl (5 mL) and ice (15 mL). The aqueous layer was extracted with diethyl ether (4 x 25 mL) and the combined organic phases were washed with saturated sodium hydrogencarbonate solution, followed by brine, and then dried over anhydrous MgSO₄. The solvent was evaporated to give a yellow oil which was purified by column chromatography (hexanes/CH₂Cl₂ 2:1) to afford ketone **9f** (0.722 g, 66%) as a yellow oil: R_f = 0.58 (CH₂Cl₂); IR (CH₂Cl₂ cast) 2962, 2155, 1625 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.38 (m, 1H), 6.26 (m, 2H), 6.09 (d, *J* = 15.3 Hz, 1H), 1.88 (d, *J* = 5.1 Hz, 3H), 0.24 (s, 9H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 178.2, 149.1, 142.4, 130.1, 129.6, 100.7, 97.9, 18.9, -0.7; MS (EI, 70 eV) *m/z* 192.1 (M⁺, 14), 177.1 ([M - CH₃]⁺, 39); HRMS calcd for C₁₁H₁₆OSi (M⁺) 192.0971, found 192.0963. Anal. Calcd for C₁₁H₁₆OSi: C, 68.69; H, 8.39. Found C, 68.26; H, 8.38.

(3-Dibromomethylene-octa-4,6-dien-1-ynyl)trimethylsilane (10f). CBr₄ (1.46 g, 4.36 mmol) and PPh₃ (2.31 g, 8.71 mmol) were added to CH₂Cl₂ (25 mL) and the mixture stirred for 5 min at rt. Ketone **9f** (0.419 g, 2.18 mmol) in CH₂Cl₂ (5 mL) was added in one portion. The reaction mixture was stirred for 4 h, concentrated to ca. 15 mL, hexanes (15 mL) added, and the inhomogeneous mixture was filtered through celite. Evaporation gave a yellow oil which was purified by passing through a plug of silica (hexanes) to give **10f** (0.310 g, 41%) as a yellow oil: R_f = 0.97 (CH₂Cl₂); IR (CH₂Cl₂ cast) 2959, 2924, 2852, 2145 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.74 (dd, *J* = 15.0, 10.6 Hz, 1H), 6.33 (d, *J* = 15.0 Hz, 1H), 6.15 (m, 1H), 5.95 (m, 1H), 1.77 (d, *J* = 6.7 Hz, 3H), 0.23 (s, 9H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 136.8, 134.2, 131.0, 128.9, 125.7, 104.3, 99.8, 98.9, 18.5, -0.3; MS (EI, 70 eV) *m/z* 345.9/347.9/349.9 (M⁺, 10/20/10); HRMS calcd for C₁₂H₁₆Si⁷⁹Br₂/C₁₂H₁₆Si⁷⁹Br⁸¹Br/ C₁₂H₁₆Si⁸¹Br₂ (M⁺) 345.9388/347.9368/ 349.9347, found 345.9383/347.9363/349.9339.

[6,6-Dibromo-5-(4-*n*-hexylphenyl)hex-5-ene-1,3-diynyl]trimethylsilane (13a). To a solution of 4-hexylbenzoyl chloride (0.456 g, 2.03 mmol) in dry CH₂Cl₂ (40 mL) at 0 °C, was added 1,4-bis(trimethylsilyl)-1,3-butadiyne (0.414 g, 2.13 mmol), followed by slow addition of AlCl₃ (0.325 g, 2.44 mmol). The reaction mixture was stirred for 3 h and worked up as per the general procedure. The resulting ketone **12a** was reacted overnight with CBr₄ (0.815 g, 2.43 mmol) and PPh₃ (1.38 g, 5.21 mmol). Then, more of the brominating mixture (0.20 g CBr₄ and 0.69 g PPh₃) was added. Work-up and purification by column chromatography (hexanes) gave dibromo-olefin **13a** (0.202 g, 21%) as a yellow oil: R_f = 0.69 (hexanes); IR (CHCl₃ cast) 2956, 2927, 2855, 2167, 2092, 1251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.56 (m, 2H), 1.26 (m, 6H), 0.85 (m, 3H), 0.17 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 143.9, 134.4, 130.0, 128.5, 128.4, 102.1, 95.2, 87.5, 82.0, 75.2, 35.9, 31.8, 31.3, 29.1, 22.7, 14.2, -0.4; EI HRMS calcd. for C₂₁H₂₆Si⁷⁹Br₂/C₂₁H₂₆Si⁷⁹Br⁸¹Br/C₂₁H₂₆Si⁸¹Br₂ (M⁺) 464.0171/466.0150/468.0130, found 464.0157/466.0138/468.0132. Anal. Calcd for C₂₁H₂₆SiBr₂: C, 54.09; H, 5.62. Found C, 54.41; H, 5.49.

[6,6-Dibromo-5-(4-*tert*-butylphenyl)hex-5-ene-1,3-diynyl]trimethylsilane (13b). To a solution of 4-*tert*-butylbenzoyl chloride (0.503 g, 2.56 mmol) in dry CH₂Cl₂ (50 mL) at 0 °C, 1,4-bis(trimethylsilyl)-1,3-butadiyne (0.519 g, 2.67 mmol) was added, followed by slow addition of AlCl₃ (0.406 g, 3.04 mmol). The reaction mixture was stirred for 3 h and aqueous work-up as per the general procedure was carried out. The resulting ketone **12b** was reacted with CBr₄ (1.02 g, 3.04 mmol) and PPh₃ (1.73 g, 6.60 mmol) as per the general procedure and stirred overnight. Then, more of the brominating mixture (0.26 g CBr₄ and 0.87 g PPh₃) was added and the reaction mixture was heated. Work-up and purification by column chromatography (hexanes) gave dibromo-olefin **13b** (0.269 g, 24%) as a yellow crystalline solid: mp 96-98 °C; R_f = 0.93 (hexanes/CH₂Cl₂ 1:1); IR (CHCl₃ cast) 2962, 2902, 2195, 2095, 1251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (m, 4H), 1.32 (s, 9H), 0.20 (s, 9H); ¹³C NMR (75 MHz, APT, CDCl₃) δ 152.0,

134.2, 130.0, 128.3, 125.5, 102.1, 95.2, 87.5, 82.0, 75.2, 34.8, 31.3, -0.5; MS (EI, 70 eV) m/z 436.0/438.0/440.0 (M^+ , 40/79/40); HRMS calcd. for $C_{19}H_{22}Si^{79}Br_2/C_{19}H_{22}Si^{79}Br^{81}Br/C_{19}H_{22}Si^{81}Br_2$ (M^+) 435.9858/437.9837/439.9817, found 435.9860/437.9833/439.9820.

[4-(1-Dibromomethylene-5-trimethylsilylpenta-2,4-diynyl)phenyl]phenyldiazene

(13c). To a solution of 4-phenylazobenzoyl chloride (0.874 g, 3.57 mmol) in dry CH_2Cl_2 (90 mL) at 0 °C, 1,4-bis(trimethylsilyl)-1,3-butadiyne (0.698 g, 3.59 mmol) was added, followed by slow addition of $AlCl_3$ (0.48 g, 3.60 mmol). The reaction mixture was stirred for 3 h and aqueous work-up as per the general procedure was carried out. The resulting ketone **12c** was reacted with CBr_4 (1.44 g, 4.30 mmol) and PPh_3 (2.46 g, 9.29 mmol) as per the general procedure to give dibromo-olefin **13c** (0.136 g, 8%) as a bright orange solid: mp 94-95 °C; R_f = 0.13 (hexanes); IR (CH_2Cl_2 cast) 3065, 2960, 2093, 2067, 1250 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.91 (m, 4H), 7.52 (m, 5H), 0.16 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 152.6, 152.3, 139.4, 131.3, 129.4, 129.1, 122.93, 122.90, 103.4, 95.9, 88.0, 87.2, 85.9, 74.5, -0.6; EI HRMS calcd for $C_{21}H_{18}N_2Si^{79}Br^{81}Br$ (M^+) 485.9586, found 485.9580.

1-Phenyl-7-trimethylsilyl-hept-1-ene-4,6-diyn-3-one (12d). To a solution of cinnamoyl chloride (0.779 g, 4.63 mmol) in dry CH_2Cl_2 (40 mL) at 0 °C, 1,4-bis(trimethylsilyl)-1,3-butadiyne (1.00 g, 5.14 mmol) was added, followed by slow addition of $AlCl_3$ (0.617 g, 4.63 mmol). The reaction mixture was stirred for 3 h. Aqueous work-up and purification by column chromatography (hexanes/ CH_2Cl_2 2:1) gave the ketone **12d** (0.528 g, 45%) as a pale yellow solid: mp 60-61 °C; R_f = 0.69 (CH_2Cl_2); IR ($CHCl_3$ cast) 2961, 2209, 2097, 1630, 1449 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 16.2 Hz, 1H), 7.58 (m, 2H), 7.43 (m, 3H), 6.79 (d, J = 16.2 Hz, 1H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 176.8, 149.4, 133.8, 131.4, 129.1, 128.7, 128.3, 96.5, 86.0, 75.6, 72.2, -0.7. MS (EI, 70 eV) m/z 252.1 (M^+ , 98), 237.1 ($[M-CH_3]^+$, 100); EI HRMS calcd for $C_{16}H_{16}OSi$ (M^+) 252.0971, found 252.0967. Anal. Calcd for $C_{16}H_{16}OSi$: C, 76.14; H, 6.39. Found C, 76.17; H, 6.31.

(5-Dibromomethylene-7-phenyl-hept-6-ene-1,3-diynyl)trimethylsilane (13d). Ketone **12d** (0.469 g, 1.86 mmol) was reacted with CBr₄ (1.24 g, 3.72 mmol) and PPh₃ (1.97 g, 7.43 mmol) as per the general procedure to give **13d** (0.548 g, 72%) as a white solid: mp 74-75 °C; R_f = 0.33 (hexanes); IR (CHCl₃ cast) 2959, 2227, 2104, 1493, 1250 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (m, 2H), 7.33 (m, 3H), 7.13 (d, *J* = 15.8 Hz, 1H), 6.99 (d, *J* = 15.8 Hz, 1H), 0.25 (s, 9H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 136.3, 136.0, 128.8, 128.7, 127.7, 127.2, 124.5, 102.5, 94.3, 87.2, 82.6, 71.6, -0.5; MS (EI, 70 eV) *m/z* 405.9/407.9/409.9 (M⁺, 21/42/22); HRMS calcd for C₁₇H₁₆Si⁷⁹Br₂/C₁₇H₁₆Si⁷⁹Br⁸¹Br/C₁₇H₁₆Si⁸¹Br₂ (M⁺) 405.9388/407.9361/409.9346, found 405.9386/407.9361/409.9346. Anal. Calcd for C₁₇H₁₆OSiBr₂: C, 50.02; H, 3.95. Found C, 49.76; H, 3.68.

1-(2-Thienyl)-7-trimethylsilyl-hept-1-ene-4,6-diyn-3-one (12e). To a solution of 3-(2-thienyl)acryloyl chloride (1.10 g, 6.38 mmol) in dry CH₂Cl₂ (30 mL) at 0 °C, 1,4-bis(trimethylsilyl)-1,3-butadiyne (1.24 g, 6.38 mmol) was added, followed by slow addition of AlCl₃ (0.85 g, 6.38 mmol). The reaction mixture was stirred for 3 h. Aqueous work-up and purification by column chromatography (hexanes/CH₂Cl₂ 2:1) gave ketone **12e** (1.13 g, 69%) as an orange oil: R_f = 0.67 (CH₂Cl₂); IR (CHCl₃ cast) 2959, 2925, 2853, 2208, 2098, 1623, 1582, 1512, 1253 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.88 (bd, *J* = 15.8 Hz, 1H), 7.48 (bd, *J* = 5.1 Hz, 1H), 7.38 (m, 1H), 7.10 (ddd, *J* = 5.3, 3.7, 1.1 Hz, 1H), 6.58 (dd, *J* = 15.8, 2.2 Hz, 1H), 0.24 (s, 9H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 176.0, 141.3, 139.1, 132.8, 130.7, 128.6, 127.1, 96.4, 86.0, 75.4, 72.2, -0.7; MS (EI, 70 eV) *m/z* 258.1 (M⁺, 31), 243.0 ([M - CH₃]⁺, 54); HRMS calcd for C₁₂H₁₄OSSi (M⁺) 258.0535, found 258.0532. Anal. Calcd for C₁₄H₁₄OSiS: C, 65.07; H, 5.46. Found C, 64.98; H, 5.28.

[5-Dibromomethylene-7-(2-thienyl)hept-6-ene-1,3-diynyl]trimethylsilane (13e). Ketone **12e** (0.429 g, 1.66 mmol) was reacted with CBr₄ (1.11 g, 3.32 mmol) and PPh₃ (1.76 g, 6.65 mmol) as per the general procedure to give **13e** (0.517 g, 75%) as a pale yellow solid upon refrigeration: mp 94-95 °C; R_f = 0.48 (hexanes); IR (CH₂Cl₂ cast) 2958, 2924, 2852, 2227, 2104,

1606, 1250 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.26 (d, $J = 5.0$ Hz, 1H), 7.24 (d, $J = 15.5$ Hz, 1H), 7.16 (d, $J = 3.6$ Hz, 1H), 7.00 (dd, $J = 5.0, 3.6$ Hz, 1H), 6.80 (d, $J = 15.5$ Hz, 1H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 141.3, 129.0, 128.3, 127.9, 127.3, 126.3, 123.9, 102.0, 94.3, 87.1, 82.5, 71.4, -0.5 ; MS (EI, 70 eV) m/z 411.9/413.9/415.9 (M^+ , 15/32/18); HRMS calcd for $\text{C}_{15}\text{H}_{14}\text{SSi}^{79}\text{Br}_2/\text{C}_{15}\text{H}_{14}\text{SSi}^{79}\text{Br}^{81}\text{Br}/\text{C}_{15}\text{H}_{14}\text{SSi}^{81}\text{Br}_2$ (M^+) 411.8952/413.8932/415.8911, found 411.8945/413.8926/415.8903. Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{SSiBr}_2$: C, 43.49; H, 3.41; S, 7.74. Found C, 43.65; H, 3.36; S, 7.51.

1-Trimethylsilyl-deca-6,8-diene-1,3-diyn-5-one (12f). 1,4-Bis(trimethylsilyl)-1,3-butadiyne (0.301 g, 1.54 mmol) was added to sorbyl chloride (0.202 g, 1.54 mmol) in CH_2Cl_2 (20 mL) cooled in an ice bath. The reaction mixture was stirred and anhydrous aluminium trichloride (0.206 g, 1.54 mmol) was slowly added. After 3 h of continuous stirring at $0-5^\circ\text{C}$, the solution was poured into a mixture of 10% aq. HCl (5 mL) and ice (15 mL). The aqueous layer was extracted with diethyl ether (4 x 25 mL) and the combined organic phase was washed with saturated sodium hydrogencarbonate solution, followed by brine, and then dried over anhydrous MgSO_4 . The solvent was evaporated to give a yellow oil which was purified by column chromatography (hexanes/ CH_2Cl_2 2:1) to afford ketone **12f** (0.217 g, 65%) as a yellow oil: $R_f = 0.72$ (CH_2Cl_2); IR (CH_2Cl_2 cast) 2209, 2097, 1621 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.36 (dd, $J = 15.6, 10.1$ Hz, 1H), 6.28 (m, 2H), 6.10 (d, $J = 15.6$ Hz, 1H), 1.88 (d, $J = 5.7$ Hz, 3H), 0.21 (s, 9H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 177.0, 149.8, 143.3, 130.1, 129.7, 96.0, 86.1, 75.1, 72.4, 19.1, -0.7 ; MS (EI, 70 eV) m/z 216.1 (M^+ , 63), 201.1 ($[\text{M} - \text{CH}_3]^+$, 100); HRMS calcd for $\text{C}_{13}\text{H}_{16}\text{OSi}$ (M^+) 216.0971, found 216.0971.

(5-Dibromomethylene-deca-6,8-diene-1,3-diynyl)trimethylsilane (13f). CBr_4 (0.324 g, 0.97 mmol) and PPh_3 (0.513 g, 1.94 mmol) were added to CH_2Cl_2 (30 mL) and the mixture stirred for 5 min at rt. Ketone **12f** (0.168 g, 0.77 mmol) in CH_2Cl_2 was added in one portion. The reaction mixture was stirred and the mixture was monitored by TLC. After 1 h, another equivalent of the brominating agent was added. After 4 h, the solution was concentrated to ca.

15 mL, hexanes (15 mL) was added, and the inhomogeneous mixture filtered through celite. Evaporation gave a yellow oil which was purified by passing through a plug of silica (hexanes) to give **13f** (0.116 g, 40%) as a reddish-orange oil: $R_f = 0.97$ (CH_2Cl_2); IR (CHCl_3 cast) 2960, 2257, 2103, 1717, 1251 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 6.68 (dd, $J = 15.1, 10.4$ Hz, 1H), 6.30 (d, $J = 15.1$, 1H), 6.13 (m, 1H), 5.99 (m, 1H), 1.76 (d, $J = 6.6$ Hz, 3H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, APT, CDCl_3) δ 137.0, 135.0, 131.0, 127.9, 125.6, 101.0, 94.0, 87.3, 82.2, 71.9, 18.7, -0.4 ; MS (EI, 70 eV) m/z 369.9/371.9/373.9 (M^+ , 12/26/14); HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{Si}^{79}\text{Br}_2/\text{C}_{14}\text{H}_{16}\text{S}^{79}\text{Br}^{81}\text{Br}/\text{C}_{14}\text{H}_{16}\text{S}^{81}\text{Br}_2$ (M^+) 369.9388/371.9368/373.9347, found 369.9348/371.9329/373.9304.

1,4-Bis(1-hydroxy-3-trimethylsilylprop-2-ynyl)benzene 15. To (trimethylsilyl)acetylene (9.42 g, 94.0 mmol) in diethyl ether (150 mL) at -78°C was added $n\text{-BuLi}$ (32.9 mL, 2.5 M in hexanes, 82.2 mmol). After stirring for 0.5 h, a solution of terephthalaldehyde (5.25 g, 39.1 mmol) in THF (45 mL) was added and the reaction mixture was stirred at -78°C for 3 h. The general work-up procedure was followed to give **15** (11.41 g, 88%), presumably a mixture of stereoisomers, as a white solid: mp $117\text{--}119^\circ\text{C}$; $R_f = 0.16$ (CH_2Cl_2); IR (CH_2Cl_2 cast) 3334, 2960, 2899, 2174, 1612, 1420, 1250 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (s, 4H), 5.44 (d, $J = 6.1$ Hz, 2H), 2.34 (d, $J = 6.1$ Hz, 2H), 0.19 (s, 18H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 140.4, 126.9, 104.8, -91.7 , 64.6, -0.2 ; MS (EI, 70 eV) m/z 330.1 (M^+ , 9), 203.1 ($[\text{C}_{12}\text{H}_{15}\text{OSi}]^+$, 100); HRMS calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Si}_2$ (M^+) 330.1471, found 330.1472.

3-Trimethylsilyl-1-[4-(3-trimethylsilylpropynoyl)phenyl]propynone 16.* To **15** (4.84 g, 14.7 mmol) in CH_2Cl_2 (150 mL) was added sequentially celite (11.3 g), molecular sieves ($4\text{\AA}$, 11.3 g), and PCC (11.28 g, 51.3 mmol). The reaction mixture was stirred for 2 h at rt and the solution mixture was filtered through a plug (SiO_2 , CH_2Cl_2) to give **16** (3.58 g, 75%) as a white fluffy solid: mp $143\text{--}144^\circ\text{C}$; $R_f = 0.80$ (CH_2Cl_2); IR (CH_2Cl_2 cast) 2961, 2157, 1643, 1262, 1245 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.22 (s, 4H), 0.32 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.8, 140.1, 129.7, 102.3, 100.6, -0.7 ; MS (EI, 70 eV) m/z 326.1 (M^+ , 42), 311.1 ($[\text{M} - \text{CH}_3]^+$,

100); HRMS calcd for $C_{18}H_{22}O_2Si_2$ (M^+) 326.1174, found 326.1157. Anal. Calcd for $C_{18}H_{22}O_2Si_2$: C, 66.21; H, 6.79. Found C, 66.16; H, 6.81. *Previously reported by: Walton, D. R. M.; Waugh, F. *J. Organomet. Chem.* **1972**, 37, 45-56.

1,4-Bis(1-dibromomethylene-3-trimethylsilylprop-2-ynyl)benzene 17. CBr_4 (6.65 g, 19.9 mmol) and PPh_3 (10.52 g, 39.7 mmol) were added to CH_2Cl_2 (150 mL) and the mixture stirred for 5 min at rt. Diketone **16** (3.24 g, 9.93 mmol) in CH_2Cl_2 was added in one portion and reacted as per the general procedure to give **17** (4.79 g, 76%) as a pale yellow solid: mp 107-108 °C; R_f = 0.85 (CH_2Cl_2); IR ($CHCl_3$ cast) 2959, 2898, 2135, 1400, 1250 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 4H), 0.21 (s, 18H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 137.7, 130.3, 128.6, 104.4, 103.2, 100.7, -0.4; MS (EI, 70 eV) m/z 633.8/635.8/637.8/639.8/641.8 (M^+ , 23/78/100/84/30); HRMS calcd for $C_{20}H_{22}Si_2^{79}Br_4/C_{20}H_{22}Si_2^{79}Br_3^{81}Br/C_{20}H_{22}Si_2^{79}Br_2^{81}Br_2/C_{20}H_{22}Si_2^{79}Br^{81}Br_3/C_{20}H_{22}Si_2^{81}Br_4$ (M^+) 633.7994/635.7973/637.7953/639.7932/641.7911, found 633.7990/635.7975/637.7959/639.7944/641.7922. Anal. Calcd for $C_{20}H_{22}Si_2Br_4$: C, 37.64; H, 3.48. Found C, 37.66; H, 3.34.

1,4-Bis[3-hydroxy-3-(2-thienyl)propynyl]benzene (S1). To 1,4-diethynylbenzene (0.45 g, 3.6 mmol) in diethyl ether at -78 °C was added $n-BuLi$ (2.85 mL, 2.5 M in hexanes, 7.13 mmol). After stirring for 1 h, 2-thiophene carboxaldehyde (0.733 g, 6.41 mmol) was added and the reaction mixture was stirred at -78 °C for 3 h. The general work-up procedure was followed to give 1,4-bis[3-hydroxy-3-(2-thienyl)propynyl]benzene, **S1**, (0.868 g, 76%) as a tan solid: mp 92-94 °C; R_f = 0.2 (CH_2Cl_2); IR ($CHCl_3$ cast) 3334, 3105, 2229, 1506 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 4H), 7.30 (m, 2H), 7.22 (m, 2H), 6.97 (dd, J = 5.1, 3.5 Hz, 2H), 5.86 (d, J = 6.8

Hz, 2H), 2.35 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 144.4, 131.7, 126.9, 126.2, 125.7, 122.6, 90.1, 85.5, 60.8; EI HRMS calcd for $\text{C}_{20}\text{H}_{14}\text{O}_2\text{S}_2$ (M^+) 350.0435, found 350.0421.

1,4-Bis[3-oxo-3-(2-thienyl)propynyl]benzene S2. The bis-alcohol **S1** (0.228 g, 0.65 mmol) was reacted with barium manganate (1.60 g, 6.24 mmol) as per the general procedure to give 1,4-bis[3-oxo-3-(2-thienyl)propynyl]benzene (0.209 g, 93%) as a tan solid: decomposition at 202 °C; $R_f = 0.6$ (CH_2Cl_2 /hexanes/ Et_2O 5:3:1); IR (CH_2Cl_2 cast) 3097, 2200, 1622 cm^{-1} ; ^1H NMR (300 MHz, CD_2Cl_2) δ 8.03 (dd, $J = 3.8, 1.2$ Hz, 2H), 7.80 (dd, $J = 4.7, 1.2$ Hz, 2H), 7.24 (dd, $J = 4.7, 3.8$ Hz, 4H), 7.24 (m, 2H); ^{13}C NMR (75 MHz, APT, CD_2Cl_2) δ 169.5, 151.6, 136.0, 135.8, 133.5, 128.9, 122.7, 89.9, 88.7; EI HRMS calcd for $\text{C}_{20}\text{H}_{10}\text{O}_2\text{S}_2$ (M^+) 346.0122, found 346.0110. Anal. Calcd for $\text{C}_{20}\text{H}_{10}\text{O}_2\text{S}_2$: C, 69.34; H, 2.91. Found C, 69.46; H, 2.94. **With PCC:** To **S1** (0.626 g, 1.71 mmol) in CH_2Cl_2 (70 mL) was added sequentially celite (1 g), molecular sieves (4Å, 1 g), and PCC (0.92 g, 4.3 mmol). The reaction mixture was stirred for 2 h at rt and the solution mixture was filtered through a plug (SiO_2 , CH_2Cl_2) to give **S2** (0.44 g, 74%).

1,4-Bis[3-dibromomethylene-3-(2-thienyl)propynyl]benzene 19. CBr_4 (1.4 g, 4.2 mmol) and PPh_3 (2.21 g, 8.5 mmol) were added to CH_2Cl_2 (150 mL) and the mixture stirred for 5 min at rt. Diketone **S2** (0.44 g, 1.3 mmol) in CH_2Cl_2 (10 mL) was added in one portion and reacted as per the general procedure to give **19** (0.281 g, 33%) as a pale yellow solid: mp 128-129 °C; $R_f = 0.63$ (hexanes/ Et_2O 4:1); IR (CH_2Cl_2 cast) 3100, 2207, 1508, 1489, 1420, 1404, 1343 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (m, 2H), 7.48 (s, 4H), 7.39 (m, 2H), 7.03 (m, 2H); ^{13}C NMR (75 MHz, APT, CDCl_3) δ 138.5, 131.5, 130.3, 127.7, 126.8, 124.2, 123.0, 97.3, 96.3, 90.6; EI HRMS calcd for $\text{C}_{22}\text{H}_{10}\text{S}_2^{79}\text{Br}_2^{81}\text{Br}_2$ (M^+) 657.6917, found 657.6862.

1,4-Bis[3-(4-*tert*-butylphenyl)-3-oxopropynyl]-2,5-bis(octyloxy)benzene **S3.** To a solution of *tert*-butylbenzoyl chloride (0.274 g, 1.40 mmol) in dry CH₂Cl₂ (10 mL) at 0 °C, was added 1,4-bis(trimethylsilylacetylene)-2,5-octyloxybenzene (0.368 g, 0.698 mmol), followed by slow addition of AlCl₃ (0.200 g, 1.54 mmol). The reaction was stirred for 3 h and aqueous work-up as per the general procedure was carried out. The crude product was rinsed with hexanes and filtered to give **S3**, (0.214 g, 44%) an orange waxy solid: mp 113-115 °C; R_f = 0.52 (hexanes/EtOAc 4:1); IR (CH₂Cl₂ cast) 2955, 2926, 2854, 2193, 1638, 1603, 1566, 1499, 1270 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.4 Hz, 4H), 7.50 (d, *J* = 8.4 Hz, 4H), 7.16 (s, 2H), 4.05 (t, *J* = 6.4 Hz, 4H), 1.92 (m, 4H), 1.51 (m, 4H), 1.35 (s, 18H), 1.24 (m, 16H), 0.84 (m, 6H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 177.5, 158.1, 155.0, 134.5, 129.8, 125.5, 117.5, 113.2, 92.8, 88.6, 69.5, 35.3, 31.8, 31.0, 29.5, 29.4, 29.2, 26.0, 22.6, 14.0; MS (EI, 70 eV) *m/z* 702.5 (M⁺, 34), 161.1 ([M – C₃₇H₄₉O₃]⁺, 100); HRMS calcd for C₄₈H₆₂O₄ (M⁺) 702.4648, found 702.4644.

1,4-Bis[3-(4-*tert*-butylphenyl)-3-dibromomethylenepropynyl]-2,5-bis(octyloxy)benzene **20.** To a solution of CBr₄ (0.190 g, 0.572 mmol) and PPh₃ (0.300 g, 1.14 mmol) in acetonitrile (18 mL) was added a solution of the diketone precursor **S3** (0.996 g, 1.42 mmol) in CH₂Cl₂ (8 mL). The mixture was stirred and monitored by TLC. More brominating solution mixture of CBr₄ (0.190 g, 0.572 mmol) and PPh₃ (0.190 g, 1.14 mmol) was added and the reaction mixture was stirred until judged complete by TLC analysis. The reaction was worked-up as per the general procedure and the crude compound was purified by passing a plug of silica (hexanes/CH₂Cl₂ 4:1) to give **20** (245 mg, 17%) as a yellow solid: mp 108-109 °C; R_f = 0.75 (hexanes/EtOAc 19:1); IR (CH₂Cl₂ cast) 2955, 2924, 2855, 2196, 1495, 1415, 1221 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.6 Hz, 4H), 7.38 (d, *J* = 8.6 Hz, 4H), 6.84 (s, 2H), 3.89 (t, *J* = 6.6 Hz, 4H), 1.71 (m, 4H), 1.42 (m, 4H), 1.32 (m, 18H), 1.31 (m, 16H), 0.87 (m, 6H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 153.7, 151.6, 134.9, 131.0, 128.4, 125.1, 116.4, 113.8, 98.1,

94.5, 94.0, 69.5, 34.7, 31.8, 31.2, 29.4, 29.3, 29.2, 26.0, 22.6, 14.1. ESI HRMS calcd for $C_{50}H_{62}O_2Br_4Na$ ($M + Na^+$) 1033.1381, found 1033.1382. Anal. Calcd for $C_{50}H_{62}O_2Br_4$: C, 59.19; H, 6.16. Found C, 58.97; H, 6.28.

University of Alberta Department of Chemistry
X-Ray Crystallography Laboratory

STRUCTURE REPORT

XCL Code: RRT0204

Date: 13 March 2002

Compound: 1,4-di(trimethylsilyl)buta-1,3-diyne

Formula: C₂₀H₂₂Si₂

Supervisor: R. R. Tykwinski

Crystallographer: M. J. Ferguson

Figure 1. Perspective view of the 1,4-di(trimethylsilylbuta-1,3-diynyl)benzene molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

Table 1. Crystallographic Experimental Details**A. Crystal Data**

formula	C ₂₀ H ₂₂ Si ₂
formula weight	318.56
crystal dimensions (mm)	0.22 × 0.14 × 0.05
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters ^a	
<i>a</i> (Å)	5.8635 (7)
<i>b</i> (Å)	6.0746 (7)
<i>c</i> (Å)	14.7262 (18)
α (deg)	87.686 (3)
β (deg)	80.087 (2)
γ (deg)	74.929 (2)
<i>V</i> (Å ³)	498.92 (10)
<i>Z</i>	1

ρ_{calcd} (g cm⁻³) 1.060

μ (mm⁻¹) 0.173

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCDb
radiation (_ [Å])	graphite-monochromated Mo K_ (0.71073)
temperature (°C)	−80
scan type	_ scans (0.2() (25 s exposures)
data collection 2_ limit (deg)	52.82
total data collected	2729 (−7 (h (6, −7 (k (6, −18 (l (17)
independent reflections	2011 ($R_{\text{int}} = 0.0235$)
number of observed reflections (<i>NO</i>)	1505 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS</i> −86 ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL</i> −93 ^d)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9914–0.9629
data/restraints/parameters	2011 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 103
goodness-of-fit (<i>S</i>) ^e	1.037 [$F_o^2 \geq -3\sigma(F_o^2)$]
final <i>R</i> indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0467
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1305
largest difference peak and hole	0.265 and −0.244 e Å ⁻³

^aObtained from least-squares refinement of 1096 reflections with $5.62^\circ < 2\theta < 50.97^\circ$.

(continued)

Table 1. Crystallographic Experimental Details (continued)

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

^cSheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted R -factors wR_2 and all goodnesses of fit S are based on F_o^2 ; conventional R -factors R_1 are based on F_o , with F_o set to zero for negative F_o^2 . The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 , and is not relevant to the choice of reflections for refinement. R -factors based on F_o^2 are statistically about twice as large as those based on F_o , and R -factors based on ALL data will be even larger.

^e $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0758P)^2]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

^f $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
Si	0.59019(11)	0.74793(10)	0.32511(4)	0.0369(2)*
C1	0.0947(4)	0.1222(3)	0.05529(14)	0.0381(5)*
C2	0.2144(4)	-0.1040(4)	0.02970(15)	0.0397(5)*
C3	-0.1201(4)	0.2232(4)	0.02469(15)	0.0395(5)*
C4	0.1927(4)	0.2458(4)	0.11270(15)	0.0410(5)*
C5	0.2767(4)	0.3504(4)	0.15927(16)	0.0419(5)*
C6	0.3768(4)	0.4715(4)	0.21119(16)	0.0414(5)*
C7	0.4634(4)	0.5787(4)	0.25685(16)	0.0434(6)*
C8	0.3331(5)	0.9526(4)	0.39395(18)	0.0588(7)*
C9	0.7756(5)	0.5481(4)	0.39862(18)	0.0569(7)*
C10	0.7751(4)	0.8988(4)	0.2450(2)	0.0567(7)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3. Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Si	C7	1.832(2)	C1	C4	1.432(3)
Si	C8	1.857(2)	C2	C3'	1.371(3) [†]
Si	C9	1.855(2)	C2	C3'	1.371(3) [†]
Si	C10	1.843(3)	C4	C5	1.196(3)
C1	C2	1.404(3)	C5	C6	1.377(3)
C1	C3	1.392(3)	C6	C7	1.208(3)

Table 4. Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C7	Si	C8	106.66(11)	C3	C1	C4	120.71(19)
C7	Si	C9	107.58(11)	C1	C2	C3'	120.2(2) [†]
C7	Si	C10	108.17(12)	C1	C3	C2'	120.61(19) [†]
C8	Si	C9	112.36(12)	C1	C4	C5	178.8(2)
C8	Si	C10	111.00(13)	C4	C5	C6	178.7(2)
C9	Si	C10	110.83(12)	C5	C6	C7	179.6(2)
C2	C1	C3	119.2(2)	Si	C7	C6	178.57(19)
C2	C1	C4	120.1(2)				

Table 5. Torsional Angles (deg)

Atom1	Atom2	Atom3	Atom4	Angle	A
C8	Si	C7	C6	51(9)	
C9	Si	C7	C6	172(9)	
C10	Si	C7	C6	-68(9)	
C3	C1	C2	C3'	0.0(4) [†]	
C4	C1	C2	C3'	179.5(2) [†]	
C2	C1	C3	C2'	0.0(4) [†]	
C4	C1	C3	C2'	-179.5(2) [†]	
C2	C1	C4	C5	90(11)	
C3	C1	C4	C5	-90(11)	
C1	C2	C3'	C1'	0.0(4) [†]	
C1	C4	C5	C6	-12(20)	
C4	C5	C6	C7	117(37)	
C5	C6	C7	Si	-35(45)	

[†]Primed atoms are related to unprimed atoms by the crystallographic inversion centre (0, 0, 0).

Table 6. Anisotropic Displacement Parameters (U_{ij} , Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si	0.0349(4)	0.0344(3)	0.0401(4)	-0.0032(2)	-0.0099(2)	-0.0039(2)
C1	0.0396(12)	0.0399(12)	0.0356(11)	0.0007(9)	-0.0046(9)	-0.0131(9)
C2	0.0361(12)	0.0391(12)	0.0426(12)	0.0031(9)	-0.0081(10)	-0.0069(9)
C3	0.0403(12)	0.0340(11)	0.0423(12)	-0.0014(9)	-0.0040(10)	-0.0080(9)
C4	0.0403(13)	0.0409(12)	0.0408(12)	-0.0010(10)	-0.0055(10)	-0.0091(10)
C5	0.0399(13)	0.0401(12)	0.0438(13)	-0.0039(10)	-0.0082(10)	-0.0056(10)
C6	0.0385(12)	0.0366(12)	0.0468(13)	-0.0029(10)	-0.0092(10)	-0.0038(9)
C7	0.0414(13)	0.0382(12)	0.0483(13)	-0.0047(10)	-0.0075(11)	-0.0056(10)
C8	0.0518(16)	0.0600(16)	0.0564(16)	-0.0167(13)	-0.0084(13)	0.0020(12)
C9	0.0523(16)	0.0598(16)	0.0534(15)	0.0070(12)	-0.0154(13)	-0.0022(12)
C10	0.0459(15)	0.0457(14)	0.0761(18)	0.0115(13)	-0.0100(13)	-0.0096(11)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$$

Table 7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	x	y	z	U_{eq} , Å ²
H2	0.3612	-0.1746	0.0501	0.048
H3	-0.2021	0.3762	0.0417	0.047
H8A	0.2293	1.0414	0.3527	0.088
H8B	0.3926	1.0558	0.4277	0.088
H8C	0.2416	0.8688	0.4378	0.088
H9A	0.9070	0.4420	0.3594	0.085
H9B	0.6762	0.4622	0.4376	0.085
H9C	0.8415	0.6344	0.4376	0.085
H10A	0.9097	0.7874	0.2097	0.085
H10B	0.8364	0.9979	0.2800	0.085
H10C	0.6774	0.9912	0.2026	0.085

Figure S1. ¹H and ¹³C NMR spectra of compound **8a**.

Figure S2. ^1H and ^{13}C NMR spectra of compound **8b**.

Figure S4. ^1H and ^{13}C NMR spectra of compound **8d**.

Figure S5. ^1H and ^{13}C NMR spectra of compound **8f**.

Figure S6. ^1H and ^{13}C NMR spectra of compound **8h**.

Figure S7. ^1H and ^{13}C NMR spectra of compound **8i**.

INDEX	FREQUENCY	PPM	HEIGHT
1	8914.788	88.671	-10.0
2	8802.177	87.550	-7.2
3	7774.024	77.324	-9.4
4	7770.972	77.294	-13.3
5	7738.328	76.975	-12.5
6	7706.884	76.656	-13.3
7	7269.866	72.309	28.7
8	7090.725	70.528	-5.7
9	7052.272	70.145	70.6
10	6973.536	69.362	31.4
11	6287.185	62.535	-5.8
12	-35.544	-0.354	21.2

Figure S8. ^1H and ^{13}C NMR spectra of compound **8k**.

Figure S9. ^1H and ^{13}C NMR spectra of compound **8l**.

Figure S10. ¹H and ¹³C NMR spectra of compound **8m**.

Figure S11. ¹H and ¹³C NMR spectra of compound **8p**.

Figure S12. ^1H and ^{13}C NMR spectra of compound **8q**.

Figure S13. ^1H and ^{13}C NMR spectra of compound **8r**.

Figure S14. ^1H and ^{13}C NMR spectra of compound **11a**.

Figure S15. ^1H and ^{13}C NMR spectra of compound **11c**.

Figure S16. ^1H and ^{13}C NMR spectra of compound **11d**.

Figure S17. ^1H and ^{13}C NMR spectra of compound **11e**.

Figure S18. ^1H and ^{13}C NMR spectra of compound **14a**.

Figure S19. ^1H and ^{13}C NMR spectra of compound **14b**.

Figure S20. ¹H and ¹³C NMR spectra of compound **14c**.

Figure S21. ^1H and ^{13}C NMR spectra of compound **14d**.

Figure S22. ¹H and ¹³C NMR spectra of compound **14e**.

Figure S23. ^1H and ^{13}C NMR spectrum of compound **14f**.

Figure S24. ^1H and ^{13}C NMR spectra of compound **18**.

Figure S25. ¹H and ¹³C NMR spectra of compound **21**.

Figure S26. ^1H and ^{13}C NMR of compound **22**.

Figure S27. ^1H and ^{13}C NMR spectra of compound **5a**.

Figure S28. ¹H and ¹³C NMR spectra of compound **7a**.

Figure S29. ^1H and ^{13}C NMR spectra of compound **5b**.

Figure S30. ^1H and ^{13}C NMR spectra of compound **6b**.

Figure S31. ^1H and ^{13}C NMR spectra of compound **7b**.

Figure S33. ^1H and ^{13}C NMR spectra of compound **7c**.

Figure S34. ^1H and ^{13}C NMR spectra of compound **5d**.

Figure S35. ^1H and ^{13}C NMR spectra of compound **6d**.

Figure S36. ^1H and ^{13}C NMR spectra of compound **7d**.

Figure S37. ^1H and ^{13}C NMR spectra of compound **5e**.

Figure S38. ^1H and ^{13}C NMR spectra of compound **7e**.

Figure S39. ^1H and ^{13}C NMR spectra of compound **5f**.

Figure S40. ^1H and ^{13}C NMR spectra of compound **7f**.

Figure S41. ^1H and ^{13}C NMR spectra of compound **5g**.

Figure S42. ^1H and ^{13}C NMR spectra of compound **5h**.

Figure S43. ^1H and ^{13}C NMR spectra of compound **7h**.

Figure S44. ^1H and ^{13}C NMR spectrum of compound **5i**.

Figure S45. ^1H and ^{13}C NMR spectra of compound **6i**.

Figure S46. ^1H and ^{13}C NMR spectrum of compound **7i**.

Figure S47. ^1H and ^{13}C NMR spectrum of compound **5j**.

Figure S48. ^1H and ^{13}C NMR spectrum of compound **5k**.

Figure S49. ^1H and ^{13}C NMR spectra of compound **6k**.

Figure S50. ^1H and ^{13}C NMR spectra of compound **7k**.

Figure S51. ^1H and ^{13}C NMR spectra of compound **51**.

Figure S52. ^1H and ^{13}C NMR spectra of compound **6l**.

Figure S53. ^1H and ^{13}C NMR spectra of compound **7l**.

Figure S54. ^1H and ^{13}C NMR spectra of compound **5m**.

Figure S55. ^1H and ^{13}C NMR spectra of compound **6m**.

Figure S56. ^1H and ^{13}C NMR spectra of compound **7m**.

Figure S57. ^1H and ^{13}C NMR spectra of compound **5n**.

Figure S58. ^1H and ^{13}C NMR spectra of compound **6n**.

Figure S59. ^1H and ^{13}C NMR spectra of compound **5o**.

Figure S60. ^1H and ^{13}C NMR spectra of compound **60**.

Figure S61. ¹H and ¹³C NMR spectra of compound **5p**.

Figure S62. ^1H and ^{13}C NMR spectra of compound **6p**.

Figure S63. ¹H and ¹³C NMR spectra of compound **7p**.

Figure S64. ^1H and ^{13}C NMR spectra of compound **5q**.

Figure S66. ^1H and ^{13}C NMR spectra of compound **7q**.

Figure S68. ^1H and ^{13}C NMR spectra of compound **6r**.

Figure S69. ^1H and ^{13}C NMR spectra of compound **7r**.

Figure S70. ^1H and ^{13}C NMR spectra of compound **9a**.

Figure S71. ^1H and ^{13}C NMR spectra of compound **10a**.

Figure S72. ^1H and ^{13}C NMR spectra of compound **9b**.

Figure S73. ^1H and ^{13}C NMR spectra of compound **10b**.

Figure S74. ^1H and ^{13}C NMR spectra of compound **9c**.

Figure S75. ^1H and ^{13}C NMR spectra of compound **10c**.

Figure S76. ^1H and ^{13}C NMR spectra of compound **9d**.

Figure S77. ^1H and ^{13}C NMR spectra of compound **10d**.

Figure S78. ^1H and ^{13}C NMR spectra of compound **9e**.

Figure S79. ^1H and ^{13}C NMR spectra of compound **10e**.

Figure S80. ^1H and ^{13}C NMR spectra of compound **9f**.

Figure S81. ^1H and ^{13}C NMR spectra of compound **10f**.

Figure S82. ^1H and ^{13}C NMR spectra of compound **13a**.

Figure S83. ^1H and ^{13}C NMR spectra of compound **13b**.

Figure S84. ^1H and ^{13}C NMR spectra of compound **13c**.

Figure S85. ¹H and ¹³C NMR spectra of compound **12d**.

Figure S86. 1H and ^{13}C NMR spectra of compound **13d**.

Figure S87. ¹H and ¹³C NMR spectra of compound **12e**.

Figure S88. ¹H and ¹³C NMR spectra of compound **13e**.

Figure S89. ^1H and ^{13}C NMR spectra of compound **12f**.

Figure S90. ^1H and ^{13}C NMR spectra of compound **13f**.

Figure S91. ^1H and ^{13}C NMR spectra of compound **15**.

Figure S92. ^1H and ^{13}C NMR spectra of compound **16**.

Figure S93. ^1H and ^{13}C NMR spectra of compound **17**.

Figure S94. ^1H and ^{13}C NMR spectra of compound **S1**.

Figure S95. ^1H and ^{13}C NMR spectra of compound **S2**.

Figure S96. ¹H and ¹³C NMR spectra of compound **19**.

Figure S97. ^1H and ^{13}C NMR spectra of compound **S3**.

Figure S98. ^1H and ^{13}C NMR spectra of compound **20**.