Supporting Information

Synthesis and Derivatization of Ethynyl α,α -Dibromomethyl Ketones: Formation of Highly Functionalized Vinyl Triflates

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1. Experimental details for compounds **7-14**.
2. ^1H and ^{13}C NMR spectra for all unpublished products.

EXPERIMENTAL SECTION

General. Reagents were purchased reagent grade from commercial suppliers and used without further purification. Phenylacetylene,¹ ferrocenylacetylene,² 4-butoxyphenyl boronic acid,³ 2-thienyl tributylstannane,⁴ 2,2'-bithienyltributylstannane,⁴ furyltributylstannane,⁵ were prepared as previously reported. Evaporation and concentration *in vacuo* were done at H₂O-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of argon unless otherwise stated. Flash column chromatography⁶: *silica gel-60* (230-400 mesh) from *General Intermediates of Canada*. Thin Layer Chromatography (TLC): plastic sheets coated with silica gel-60 F₂₅₄ with the fluorescent indicator UV₂₅₄ from Macherey-Nagel; visualization by UV light or KMnO₄ stain. Mp: Fisher-Johns melting point apparatus; uncorrected. IR spectra (cm⁻¹): *Nicolet Magna-IR 750*. ¹H and ¹³C NMR: *Bruker AM-300, Varian Inova 300, 400, 500 or Varian Unity 500* instruments, at rt in CDCl₃ (solvent peaks: 7.24 ppm for ¹H and 77.0 ppm for ¹³C as reference) or CD₂Cl₂ (solvent peaks: 5.3 ppm for ¹H and 53.1 ppm for ¹³C as reference) or (CD₃)₂CO (solvent peaks: 2.05 ppm for ¹H and 29.8 and 206.3 ppm for ¹³C as reference). EIMS: *Kratos MS-50* instrument, peaks as *m/z*. ESIMS: *Micromass Zabspec Hybrid Sector-TOF*, in either positive or negative ion mode, peaks as *m/z*. Elemental analyses were performed by Spectral Services at the University of Alberta, using a *Carlo Era 1108 Elemental Analyzer*.

General Procedure for Sonogashira Cross-Coupling Reactions

To a degassed solution of dibromoacetate **10a** and 3 equiv of the terminal acetylene in triethylamine were added PdCl₂(PPh₃)₂ (5 mol%), and CuI (10 mol%). The mixture was then stirred at rt for ca. 1 day, and monitored by TLC. When complete, the reaction mixture was filtered through celite and diluted with Et₂O. The solution is washed with H₂O (10 mL), brine

(10 mL), dried (Na_2SO_4), filtered, and evaporated. Compounds were isolated by silica gel column chromatography, typically eluted with mixtures of hexanes and Et_2O .

General Procedure for Suzuki Cross-Coupling Reactions

To a dry, degassed solution of the dibromoacetate **10a** and 2.2 equiv of the boronic acid in toluene were added 2.2 equivalents K_2CO_3 and $\text{Pd}(\text{PPh}_3)_4$ (5 mol%). The mixture was then heated to reflux for ca. 24 hr until judged complete, as monitored by TLC. The mixture was then filtered through celite and diluted with Et_2O . The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. Compounds were isolated by silica gel column chromatography, typically eluted with mixtures of hexanes and Et_2O .

General Procedure for Stille Cross-Coupling Reactions

To a degassed solution of the dibromoacetate **10a** and 2.2 equiv of the stannane in DMF was added $\text{Pd}(\text{PPh}_3)_4$ (5 mol%). The mixture was then heated to 120 °C for 2–4 h and monitored by TLC. The mixture was then cooled to rt, poured into H_2O (10 mL) and diluted with Et_2O . The organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was then purified by silica gel column chromatography, typically eluted with mixtures of hexanes and Et_2O .

General Procedure for Triflate Formation

The appropriate vinyl acetate was dissolved in THF and cooled to –78 °C. To this was added 2 equiv of MeLi (1.6 M in Et_2O). The mixture was then stirred at –78 °C for 1 h. To the mixture was then added 2 equiv of Tf_2O . The reaction was typically complete within 20 min, at which time the mixture was poured into sat. NH_4Cl (10 mL) and diluted with Et_2O . The organic layer was then washed twice with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. Compounds were purified by silica gel column chromatography, typically eluted with mixtures of hexanes and Et_2O .

General Procedure for LDA or LiHMDS Formation

To a stirred solution of either *i*-Pr₂NH or HMDS in the appropriate solvent (THF or Et₂O) at –78 °C, was added 1 equiv *n*-BuLi. The mixture was stirred at –78 °C for 30 min and then added to reactions via cannula or syringe.

Triethylsilyl propynoic acid ethyl ester (**7a**).

A solution of ethyl propiolate **6** (4.61 g, 47.0 mmol) in THF (40 mL) was cooled to –78 °C. To this was added LDA (47.0 mmol) in THF (40 mL) over 10 min. The mixture was stirred for 30 min at –78 °C, triethylsilyl chloride (7.08 g, 47.0 mmol) was added and the mixture allowed to warm to rt overnight. The mixture was poured into sat. NH₄Cl (30 mL), extracted with Et₂O (2 x 30 mL), and the organic layer washed with brine (30 mL), dried (MgSO₄), filtered, and evaporated. The residue was filtered through silica gel (hexanes) to yield **7a** (9.36 g, 44.2 mmol, 94%) as a yellow oil. *R*_f = 0.7 (hexane/EtOAc 30:1). IR (neat) 2958, 2913, 2877, 2178, 1713, 1459 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.17 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.66 (q, *J* = 7.8 Hz, 6H); ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 153.1, 96.0, 91.7, 62.0, 14.0, 7.2, 3.8; EIMS *m/z* 212 (*M*⁺, 27), 183 ([*M* - Et]⁺, 100); HRMS calcd for C₁₁H₂₀O₂Si (*M*⁺) 183.0841, found 183.0844. Anal. calcd. for C₁₁H₂₀O₂Si : C, 62.21; H, 9.49. Found: C, 62.30; H, 9.79.

Triisopropylsilyl propynoic acid ethyl ester (**7b**)

A solution of ethyl propynoate **6** (1.93 g, 19.6 mmol) in THF (20 mL) was cooled to -78 °C. To this was added LDA (19.7 mmol) in THF (20 mL) over 10 min. The mixture was then stirred at -78 °C for 30 min, triisopropylsilyltrifluoromethanesulfonate (6.04 g, 19.7 mmol) was added and the mixture allowed to warm to rt overnight. The mixture was poured into sat. NH_4Cl (30 mL), extracted with Et_2O (2 x 30 mL), and the organic layer washed with brine (30 mL), dried (MgSO_4), filtered, and evaporated. The residue was filtered through silica gel (hexanes) to yield **7b** (4.69 g, 18.5 mmol, 94%) as a colorless oil. $R_f = 0.6$ (hexane/ Et_2O 10:1). IR (CH_2Cl_2 , cast) 2945, 2893, 2867, 2177, 1713, 1463, 1385, 1366 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 4.21 (q, $J = 7.2$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.05–1.11 (m, 21H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 153.1, 96.9, 90.8, 61.9, 18.5, 14.1, 11.0; EIMS m/z 254 (M^+ , 20), 211 ($[\text{M} - i\text{-Pr}]^+$, 100); HRMS calcd. for $\text{C}_{14}\text{H}_{26}\text{O}_2\text{Si}$ (M^+) 254.1702, found 254.1704.

1,1-Dibromo-4-triethylsilyl-but-2-one-3-yne (**8a**)

To a stirred solution of dibromomethane (0.331 mL, 4.72 mmol) and compound **7a** (500 mg, 2.32 mmol) in Et_2O (10 mL) was added a solution of LDA (4.72 mmol) in Et_2O (10 mL) over a period of 10 min at -78 °C. The mixture was stirred for 20 min at -78 °C, H_2SO_4 (0.25 mL) in Et_2O (2 mL) was added, this mixture was stirred for 30 min at -78 °C. The now heterogeneous mixture was filtered, the organics were evaporated and the residue passed through a plug of silica gel (hexane/ EtOAc 30:1) to yield **8a** (638 mg, 81%) as a light yellow oil. $R_f = 0.5$ (hexane/ EtOAc 30:1). IR (neat) 3014, 2957, 2936, 2912, 2875, 2156, 1685, 1457, 1413 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.83 (s, 1H), 1.03 (t, $J = 8.1$, 9H), 0.70 (q, $J =$

8.1, 6H); ^{13}C NMR (75.5 MHz, CDCl_3 , APT) δ 173.0, 104.9, 97.6, 42.2, 7.3, 3.8; EIMS m/z 339 (M^+ , 4), 167 ($[\text{M} - \text{CHBr}_2]^+$, 100); HRMS calcd. for $\text{C}_{10}\text{H}_{16}\text{O}^{79}\text{Br}^{81}\text{BrSi}$ (M^+) 339.9317, found 339.9315. Anal calcd for $\text{C}_{10}\text{H}_{16}\text{OBr}_2\text{Si}$: C, 35.31; H, 4.74. Found: C, 35.49; H, 4.95.

1,1-Dibromo-4-triisopropylsilyl-but-3-yne-2-one (8b)

To a stirred solution of dibromomethane (0.240 mL, 3.38 mmol) and compound **7b** (430 mg, 1.69 mmol) in Et_2O (10 mL) at -78°C was added a solution of LDA (3.38 mmol) in Et_2O (10 mL) over a period of 5 min. The mixture was stirred for 20 min at -78°C and then hydrolyzed with HCl (5 mL, 6M). The organic layer was washed with 10% NaHCO_3 (20 mL), brine (30 mL), dried (MgSO_4), filtered, and evaporated. The residue was passed through a plug of silica gel (hexanes/ Et_2O 30:1) to yield **8b** (493 mg, 1.15 mmol, 76%) as a light yellow oil. R_f = 0.5 (hexane/ EtOAc 20:1). IR (neat) 3015, 2944, 2891, 2867, 2155, 1684, 1462, 1385, 1368 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.83 (s, 1H), 1.08-1.21 (m, 21H); ^{13}C NMR (75.5 MHz, CDCl_3 , APT) δ 172.9, 104.3, 98.3, 42.3, 18.5, 11.0; EIMS m/z 381 (M^+ , 9), 209 ($[\text{M} - \text{CHBr}_2]^+$, 100); HRMS calcd. for $\text{C}_{13}\text{H}_{22}\text{OSi}^{79}\text{Br}^{81}\text{Br}$ (M^+) 381.9786, found 381.9778.

1,1-Dibromo-4-triethylsilyl-2-triisopropylsilyloxy-but-1-en-3-yne (9)

To a solution of **8a** (200 mg, 0.59 mmol) in toluene (4 mL) at rt was added Et_3N (89 mg, 0.88 mmol). The mixture was stirred for 15 min and triisopropylsilyltrifluoromethanesulfonate (198 mg, 0.647 mmol) was added. After 30 min the mixture was diluted with Et_2O (10 mL), washed with sat. NH_4Cl (10 mL), dried (MgSO_4), filtered, and evaporated. The residue was

purified by flash column chromatography (silica gel, hexane/EtOAc 10:1) to yield **9** (266 mg, 0.540 mmol, 91%) as a colorless oil. $R_f = 0.7$ (hexane/EtOAc 10:1). IR (neat) 2956, 2869, 2732, 2150, 1555, 1462, 1413, 1384, 1368 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 1.26-1.40 (m, 3H), 1.13 (d, $J = 7.2$ Hz, 18H), 1.04 (t, $J = 8.0$ Hz, 9H), 0.68 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (75.5 MHz, CDCl_3 , APT) δ 136.2, 101.8, 99.4, 85.5, 17.9, 12.8, 7.3, 4.1; EIMS m/z 496 (M^+ , 19), 424 ($[\text{M} - \text{Et} - i\text{Pr}]^+$, 100); HRMS calcd. for $\text{C}_{19}\text{H}_{36}\text{OSi}_2^{79}\text{Br}^{81}\text{Br}$ (M^+) 496.0650, found 496.0653. Anal. Calcd. for $\text{C}_{19}\text{H}_{36}\text{OSi}_2\text{Br}_2$: C, 45.97; H, 7.31. Found: C, 46.36; H, 7.59.

2-Acetoxy-1,1-dibromo-4-triethylsilyl-but-1-en-3-yne (**10a**)

Compound **8a** (457 mg, 1.34 mmol) in THF (10 mL) was cooled to -78°C , LiHMDS (1.61 mmol) in THF (5 mL) was added and the mixture stirred for 30 min at -78°C . Ac_2O was added (0.190 mL, 206 mg, 2.02 mmol) and the mixture allowed to warm to rt over a period of 4 h. The mixture was quenched with sat. NH_4Cl (10 mL), extracted with Et_2O (2 x 20 mL), and the organic layer was washed with brine (20 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by filtration through a plug of silica gel (hexane/ Et_2O 20:1) to yield **10a** (499 mg, 1.31 mmol, 97%) as an amber oil. $R_f = 0.3$ (hexane/ Et_2O 30:1). IR (CHCl_3 , cast) 2956, 2912, 2875, 2735, 2150, 1783, 1711, 1575, 1457, 1414 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.19 (s, 3H) 0.98 (t, $J = 7.8$ Hz, 9H) 0.62 (q, $J = 7.8$ Hz, 6H); ^{13}C NMR (75.5 MHz, CDCl_3 , APT) δ 166.3, 133.2, 104.1, 96.7, 95.6, 20.5, 7.4, 4.0; EIMS m/z 381 (M^+ , 13), 339 ($[\text{M} - \text{C}_2\text{H}_2\text{O}]^+$, 100); HRMS calcd. for $\text{C}_{12}\text{H}_{18}^{79}\text{Br}^{81}\text{BrO}_2\text{Si}$ (M^+) 381.9435, found 381.9422. Anal. calcd. for $\text{C}_{12}\text{H}_{18}\text{Br}_2\text{O}_2\text{Si}$: C, 37.71; H, 4.75. Found: C, 37.99; H, 4.98.

Alternate procedure:

To a solution of **8a** (1.38 g, 4.08 mmol) in THF (30 mL) was added Et₃N (0.85 mL, 620 mg, 6.10 mmol), then Ac₂O (0.960 mL, 1.04g, 10.2 mmol). The solution was stirred for 5 min, and DMAP (49.8 mg, 0.408 mmol) was added. After TLC analysis indicated completion (1 h) the mixture was poured into sat. NH₄Cl (20 mL), diluted with Et₂O (20 mL), the organic layer washed with brine (30 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by filtration through silica gel (hexane/Et₂O 20:1) to yield **10a** (1.38 g, 3.62 mmol, 89%).

2-Acetoxy-1,1-dibromo-4-triisopropylsilyl-but-1-en-3-yne (**10b**)

Compound **8b** (400 mg, 1.05 mmol) in THF (10 mL) was cooled to -78°C , LiHMDS (1.26 mmol) in THF (5 mL) was added and the mixture stirred for 30 min at -78°C . Ac₂O was added (160 mg, 1.58 mmol) and the mixture allowed to warm to rt over a period of 4 h. The mixture was quenched with sat. NH₄Cl (10 mL) and extracted with Et₂O (2 x 20 mL). The organic layer was washed with brine (20 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by filtration through silica gel (hexane/Et₂O 20:1) to yield **10b** (438 mg, 1.04 mmol, 99%) as an amber oil. $R_f = 0.5$ (hexane/Et₂O 15:1). IR (CH₂Cl₂, cast) 2944, 2891, 2866, 1784, 1711, 1463, 1367 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.19 (s, 3H), 1.02–1.14 (m, 21H); ¹³C NMR (100 MHz, CDCl₃, APT) δ 166.3, 133.3, 103.3, 97.4, 95.3, 20.4, 18.5, 11.0; EIMS m/z 423 (M^+ , 7); HRMS calculated for C₁₅H₂₄O₂Si ⁷⁹Br⁸¹Br (M^+) 423.9892, found 423.9879.

3-Acetoxy-1-triethylsilyl-4-triisopropylsilylethynyl-6-triisopropylsilyl-hex-3-en-1,5-diyne (**11a**)

To a degassed solution of compound **10a** (100 mg, 0.262 mmol) and triisopropylacetylene (238 mg, 1.31 mmol) in Et_3N (20 mL) was added $\text{PdCl}_2(\text{PPh}_3)_2$ (9.2 mg, 0.0013 mmol), and CuI (18 mg, 0.095 mmol). The mixture was stirred at rt for 3 days, then filtered through celite and evaporated. The residue was diluted with Et_2O (10 mL), washed with H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/ Et_2O 50:1) to yield **11a** (101 mg, 0.173 mmol, 66%) as a yellow oil. $R_f = 0.5$ (hexane/ Et_2O 40:1); IR (CH_2Cl_2 , cast) 2943, 2865, 2159, 1785, 1463, 1414, 1383, 1367 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.15 (s, 3H), 1.07 (s, 21H), 1.04 (s, 21H), 0.96 (t, $J = 8.1$ Hz, 9H), 0.61 (q, $J = 8.1$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.9, 141.5, 106.4, 105.3, 101.2, 100.6, 99.8, 98.9, 98.4, 20.6, 18.6, 18.5, 11.4, 11.2, 7.4, 4.0; EIMS m/z 584 (M^+ , 14), 542 ($[\text{M} - \text{C}_2\text{H}_2\text{O}]^+$, 100); HRMS calcd. for $\text{C}_{34}\text{H}_{60}\text{O}_2\text{Si}_3$ (M^+) 584.3901, found 584.3910.

3-Acetoxy-4-phenylethynyl-6-phenyl-1-triethylsilyl-hex-3-en-1,5-diyne (**11b**)

To a degassed solution of compound **10a** (50 mg, 0.13 mmol) and phenylacetylene (114 mg, 0.654 mmol) in Et₃N (10 mL) was added PdCl₂(PPh₃)₂ (4.6 mg, 0.0066 mmol), and Cul (10 mg, 0.053 mmol). The mixture was stirred at rt for 24 h, then filtered through celite and evaporated. The residue was diluted with Et₂O (10 mL), washed with H₂O (10 mL), brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 60:1) to yield **11b** (37 mg, 0.087 mmol, 66%) as a light yellow oil. R_f = 0.4 (hexane/Et₂O 5:1). IR (CH₂Cl₂, cast) 3060, 2956, 2911, 2874, 2205, 2136, 1781, 1596, 1571, 1491, 1457, 1442, 1413 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.4-7.52 (m, 4H), 7.26-7.36 (m, 6H), 2.26 (s, 3H), 0.98 (t, *J* = 8.1 Hz, 9H), 0.65 (q, *J* = 8.1 Hz, 6H); ¹³C NMR (75.5 MHz, CDCl₃) δ 167.1, 141.1, 131.8, 131.7, 129.1, 128.8, 128.4, 128.2, 122.6, 122.4, 106.8, 105.4, 99.1, 98.8, 95.0, 84.0, 82.8, 20.7, 7.5, 4.2; EIMS *m/z* 424 (M⁺, 16), 382 ([M – C₂H₂O]⁺, 100); HRMS calcd. for C₂₈H₂₈O₂Si (M⁺) 424.1859, found 424.1859.

3-Acetoxy-4-ferrocenylethynyl-6-ferrocenyl-1-triethylsilyl-hex-3-en-1,5-diyne (**11c**)

To a degassed solution of compound **10a** (50 mg, 0.131 mmol) and ethynylferrocene (137 mg, 0.654 mmol) in Et₃N (10 mL) was added PdCl₂(PPh₃)₂ (4.6 mg, 0.0066 mmol), and Cul (10 mg, 0.053 mmol). The mixture was stirred at rt for 48 h, filtered through celite and evaporated. The residue was diluted with Et₂O (10 mL), washed with H₂O (10 mL), brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 20:1) to yield **11c** (52 mg, 0.081 mmol, 62%) as a

red solid, Mp 89-91 °C. R_f = 0.2 (hexane/Et₂O 10:1). IR (CH₂Cl₂, cast) 3096, 2955, 2911, 2874, 2200, 2130, 1776, 1427, 1412, 1366, 1324 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.43-4.47 (m, 4H), 4.19-4.24 (m, 14H), 2.30 (s, 3H), 1.0 (t, J = 7.5 Hz, 9H), 0.67 (q, J = 7.5 Hz, 6H); ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 167.1, 138.8, 106.4, 105.4, 99.5, 98.8, 94.9, 80.7, 79.7, 71.6, 70.2, 70.1, 69.4, 69.2, 64.4, 64.0, 20.8, 7.6, 4.3, (1 coincident signal); EIMS m/z 640 (M^+ , 100); HRMS calcd. for C₃₆H₃₆O₂SiFe₂ (M^+) 640.1184, found 640.1168.

2-Acetoxy-1,1-diphenyl-4-triethylsilyl-but-1-en-3-yne (**12a**)

To a dry, degassed solution of compound **10a** (100 mg, 0.262 mmol) and phenyl boronic acid (70.2 mg, 0.576 mmol) in toluene (7 mL) was added K₂CO₃ (80 mg, 0.58 mmol) and Pd(PPh₃)₄ (15.1 mg, 0.0131 mmol). The mixture was refluxed for 12 h, filtered through celite and diluted with Et₂O (10 mL). The organic layer was washed with sat. NH₄Cl (2 x 10 mL), H₂O (10 mL), brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 10:1) to yield **12a** (62 mg, 0.17 mmol, 63%) as a light yellow solid, Mp 72-73 °C. R_f = 0.4 (hexane/Et₂O 10:1). IR (CH₂Cl₂, cast) 3056, 2955, 2911, 2874, 2144, 1769, 1600, 1494, 1457, 1443, 1414, 1367, 1214 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.43-7.50 (m, 2H), 7.22-7.32 (m, 6H), 7.15-7.20 (m, 2H), 1.97 (s, 3H), 0.89 (t, J = 7.8 Hz, 9H), 0.54 (q, J = 7.8 Hz, 6H); ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 168.3, 140.1, 138.1, 137.8, 130.4, 129.4, 128.2, 128.0, 127.9, 127.8, 126.8, 100.3, 98.3, 20.7, 7.4, 4.1; EIMS m/z 376 (M^+ , 17), 334 ([M - C₂H₂O]⁺, 100); HRMS calcd. for C₂₄H₂₈O₂Si (M^+) 376.1859, found 376.1862.

2-Acetoxy-1,1-bis(p-methylphenyl)-4-triethylsilylbut-1-en-3-yne (**12b**)

To a dry, degassed solution of compound **10a** (200 mg, 0.524 mmol) and *p*-tolylboronic acid (157 mg, 1.15 mmol) in toluene (7 mL) was added K_2CO_3 (159 mg, 1.15 mmol) and $Pd(PPh_3)_4$ (30.3 mg, 0.0262 mmol). The mixture was refluxed for 12 h, filtered through celite and diluted with Et_2O (10 mL). The organic layer was washed with sat. NH_4Cl (2 x 10 mL), H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/ Et_2O 10:1) to yield **12b** (146 mg, 0.36 mmol, 69%) as a yellow oil. R_f = 0.4 (hexane/ Et_2O 10:1). IR (CH_2Cl_2 , cast) 3025, 2955, 2913, 2874, 2147, 1769, 1610, 1511, 1457, 1413, 1367, 1213 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.05-7.10 (m, 6H), 2.32 (br s, 2 x CH_3), 0.90 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 169.2, 140.0, 137.9, 137.6, 135.3, 135.0, 130.2, 129.2, 128.6, 128.3, 126.1, 100.6, 97.9, 21.4, 21.3, 20.9, 7.4, 4.3; EIMS m/z 404 (M^+ , 24), 362 ($[M - C_2H_2O]^+$, 100); HRMS calcd. for $C_{26}H_{32}O_2Si$ (M^+) 404.2171, found 404.2171. Anal. calcd. for $C_{26}H_{32}O_2Si$: C, 76.22; H, 7.99. Found: C, 76.66; H, 7.94.

2-Acetoxy-1,1-bis-(4-methoxyphenyl)-4-triethylsilyl-but-1-en-3-yne (12c)

To a dry, degassed solution of compound **10a** (200 mg, 0.524 mmol) and *p*-methoxyphenyl boronic acid (176 mg, 1.16 mmol) in toluene (7 mL) was added K₂CO₃ (160 mg, 1.16 mmol) and Pd(PPh₃)₄ (30.2 mg, 0.0262 mmol). The mixture was refluxed for 12 h, filtered through celite and diluted with Et₂O (10 mL). The organic layer was washed with sat. NH₄Cl (2 x 10 mL), H₂O (10 mL), brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 5:1) to yield **12c** (115 mg, 0.263 mmol, 50%) as a light yellow oil. *R*_f = 0.2 (hexane/Et₂O 5:1). IR (CH₂Cl₂, cast) 3000, 2955, 2910, 2874, 2836, 2143, 1765, 1606, 1572, 1510, 1463, 1441, 1414, 1367 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 1.99 (s, 3H); 0.90 (t, *J* = 8.9 Hz, 9H), 0.54 (q, *J* = 8.9 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 168.3, 159.4, 159.0, 139.3, 131.7, 130.7, 130.5, 130.3, 125.4, 113.3, 113.0, 100.8, 97.5, 55.3, 55.2, 20.9, 7.4, 4.2; EIMS *m/z* 436 (M⁺, 26), 394 ([M – C₂H₂O]⁺, 100); HRMS calcd. for C₂₆H₃₂O₄Si (M⁺) 436.2070, found 436.2066.

2-Acetoxy-1,1-bis-(4-butoxyphenyl)-4-triethylsilyl-but-1-en-3-yne (12d)

To a dry, degassed solution of compound **10a** (200 mg, 0.524 mmol) and *p*-butoxyphenyl boronic acid (398 mg, 2.09 mmol) in toluene (7 mL) was added K₂CO₃ (362 mg, 2.62 mmol) and Pd(PPh₃)₄ (30.3 mg, 0.0262 mmol). The mixture was refluxed for 12 h, filtered through celite and diluted with Et₂O (10 mL). The organic layer was washed with sat.

NH₄Cl (2 x 10 mL), H₂O (10 mL), brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 15:1) to yield **12d** (239 mg, 0.460 mmol, 85%) as a light yellow oil. *R*_f = 0.2 (hexane/Et₂O 15:1). IR (CH₂Cl₂, cast) 3039, 2957, 2934, 2873, 2144, 1768, 1606, 1570, 1467, 1414, 1367, 1304 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.91-3.98 (m, 4H), 2.00 (s, 3H), 1.70-1.79 (m, 4H), 1.43-1.53 (m, 4H), 0.96 (t, *J* = 7.6 Hz, 6H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 159.1, 158.8, 139.6, 131.8, 130.8, 130.4, 130.2, 125.3, 113.8, 113.6, 100.9, 97.5, 67.6, 67.5, 31.3, 31.2, 20.8, 19.2, 19.1, 13.8, 13.7, 7.3, 4.1; EIMS *m/z* 520 (M⁺, 34), 478 ([M – C₂H₂O]⁺, 100); HRMS calcd. for C₃₂H₄₄O₄Si (M⁺) 520.3009, found 520.3000.

2-Acetoxy-1,1-bis(2-thienyl)-4-triethylsilyl-but-1-en-3-yne (**13a**)

To a degassed solution of compound **10a** (50 mg, 0.131 mmol) and 2-tributylstannylthiophene (150 mg, 0.393 mmol) in DMF (5 mL) was added Pd(PPh₃)₄ (7.5 mg, 0.007 mmol). The mixture was heated to 120 °C for 2 h, then cooled to rt and poured into H₂O (10 mL) and diluted with Et₂O (10 mL). The organic layer was washed with brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 25:1) to yield **13a** (34 mg, 0.088 mmol, 66%) as a light green oil. *R*_f = 0.3 (hexanes/Et₂O 20:1). IR (CH₂Cl₂, cast) 3105, 2955, 2910, 2874, 2141, 1774, 1457, 1420, 1367, 1349 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.37 (t, *J* = 5.5 Hz, 1H), 7.36 (t, *J* = 5.5 Hz, 1H), 7.24 (dd, *J* = 1.0, 4.0 Hz, 1H), 7.01 (dd, *J* = 4.0, 5.5 Hz, 1H),

6.96 (dd, $J = 4.0, 5.5$ Hz, 1H), 6.92 (dd, $J = 1.0, 4.0$ Hz, 1H), 2.24 (s, 3H), 0.89 (t, $J = 8.0$ Hz, 9H), 0.54 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3 , APT) δ 167.5, 138.5, 138.0, 129.9, 129.8, 127.9, 126.8, 126.7, 126.6, 126.4, 126.3, 102.4, 99.6, 21.3, 7.4, 4.1; EIMS m/z 388 (M^+ , 3); HRMS calcd. for $\text{C}_{20}\text{H}_{24}\text{SiS}_2\text{O}_2$ (M^+) 388.0986, found 388.0983.

2-Acetoxy-1,1-[bis-(2,2'-bithienyl)]-4-triethylsilyl-but-1-en-3-yne (**13b**)

To a degassed solution of compound **10a** (60 mg, 0.157 mmol) and 2-tributylstannyl-2,2'-bithiophene (180 mg, 0.396 mmol) in DMF (5 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (8.0 mg, 0.0069 mmol). The mixture was heated to 120 °C for 2 h, then cooled to rt and poured into H_2O (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/ Et_2O 5:1) to yield **13b** (43 mg, 0.078 mmol, 50%) as a light green oil. $R_f = 0.4$ (hexane/ Et_2O 5:1). IR (CH_2Cl_2 , cast) 3106, 3070, 2954, 2909, 2873, 2137, 1774, 1456, 1444, 1423, 1367, 1308 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 6.90-7.26 (m, 10H), 2.26 (s, 3H), 0.92 (t, $J = 8.0$ Hz, 9H), 0.57 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3 , APT) δ 167.9, 140.1, 139.2, 137.4, 137.1, 136.9, 131.3, 131.1, 128.2, 128.1, 126.9, 126.5, 125.3, 124.9, 124.3, 124.1, 123.5, 123.4, 104.1, 100.1, 21.6, 7.6, 4.4, (1 coincident signal); EIMS m/z 552 (M^+ , 29), 510 ($[\text{M} - \text{C}_2\text{H}_2\text{O}]^+$, 100); HRMS calcd. for $\text{C}_{28}\text{H}_{28}\text{O}_2\text{SiS}_4$ (M^+) 552.0741, found 552.0738.

2-Acetoxy-1,1-(di-2-furanyl)-4-triethylsilyl-but-1-en-3-yne (**13c**)

To a degassed solution of compound **10a** (100 mg, 0.262 mmol) and 2-tributylstannylfuran (280 mg, 0.785 mmol) in DMF (5 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (15.0 mg, 0.0131 mmol). The mixture was heated to 120 °C for 4 h, then cooled to rt and poured into H_2O (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/ Et_2O gradient elution 20:1-5:1) to yield **13c** (53 mg, 0.15 mmol, 57%) as a light red oil. $R_f = 0.3$ (hexane/ Et_2O 10:1). IR (CH_2Cl_2 , cast) 3120, 2956, 2911, 2875, 2139, 1772, 1546, 1466, 1414, 1367, 1313 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.44 (m, 2H), 6.80 (d, $J = 3.3$ Hz, 1H), 6.40-6.50 (m, 3H), 2.19 (s, 3H), 0.95 (t, $J = 7.8$ Hz, 9H), 0.60 (q, $J = 7.8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , APT) δ 168.3, 148.3, 147.8, 143.3, 142.7, 126.3, 119.7, 113.4, 113.3, 111.4, 111.0, 101.8, 100.2, 20.9, 7.4, 4.1; EIMS m/z 356 (M^+ , 15), 314 ($[\text{M} - \text{C}_2\text{H}_2\text{O}]^+$, 100); HRMS calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_4\text{Si}$ (M^+) 356.1443, found 356.1441.

1-Triethylsilyl-3-[[[(trifluoromethyl)sulfonyl]oxy]-4-triisopropylsilylethynyl-6-triisopropylsilyl-hex-3-en-1,5-diyne (14a)

Compound **11a** (118 mg, 0.202 mmol) was dissolved in THF (5 mL) and cooled to -78°C . To this was added MeLi (0.25 mL, 0.40 mmol, 1.6 M in Et₂O). The mixture was stirred at -78°C for 1 h, and Tf₂O (114 mg, 0.404 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH₄Cl (10 mL) and diluted with Et₂O (10 mL). The organic layer was washed with H₂O (2 x 10 mL), brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 10:1) to yield **14a** (110 mg, 0.148 mmol, 81%) as a light yellow oil. $R_f = 0.5$ (hexane). IR (CDCl₃, cast) 2958, 2944, 2911, 2867, 1463, 1432, 1384, 1273 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.05-1.10 (m, 42H), 0.97 (t, $J = 8.1$ Hz, 9H), 0.64 (q, $J = 8.1$ Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 138.9, 118.4 (q, $J = 320$ Hz, CF₃), 111.3, 108.8, 106.8, 102.5, 99.3, 98.1, 95.8, 18.6, 18.5, 11.2, 11.1, 7.3, 3.9. EIMS m/z 674 (M⁺, 66), 589 ([M – 2 *i*-Pr]⁺, 100); HRMS calcd. for C₃₃H₅₇F₃O₃SSi₃ (M⁺) 674.3289, found 674.3307. Anal. calcd. for C₃₃H₅₇F₃O₃SSi₃: C, 58.71; H, 8.51. Found: C, 58.78; H, 8.83.

4-Phenylethynyl-6-phenyl-1-triethylsilyl-3-[[[(trifluoromethyl)sulfonyl]oxy]-hex-3-en-1,5-diyne (14b)

Compound **11b** (60 mg, 0.17 mmol) was dissolved in THF (3 mL) and cooled to -78°C . To this was added MeLi (0.21 mL, 0.34 mmol, 1.6 M in Et₂O). The mixture was stirred at -78°C for 1 h, and Tf₂O (96 mg, 0.34 mmol) was added. The mixture was stirred for 20 min,

poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/ Et_2O 10:1) to yield **14b** (53 mg, 0.10 mmol, 60%) as a colorless oil. R_f = 0.6 (hexane/ Et_2O 5:1). IR (CH_2Cl_2 , cast) 3063, 2958, 2913, 2195, 2136, 1597, 1492, 1457, 1427, 1357, 1249 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.5-7.6 (m, 4H), 7.34-7.46 (m, 6H), 1.02 (t, J = 7.8 Hz, 9H), 0.71 (q, J = 7.8 Hz, 6H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 138.6, 132.3, 132.2, 130.3, 130.0, 128.97, 128.90, 121.9, 121.8, 118.8 (q, J = 321 Hz, CF_3), 112.3, 109.2, 102.6, 98.3, 96.4, 82.8, 82.0, 7.4, 4.3; EIMS m/z 514 (M^+ , 23), 381 ($[\text{M} - \text{SO}_2\text{CF}_3]^+$, 100); HRMS calcd. for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{O}_3\text{SSi}$ (M^+) 514.1243, found 514.1239.

4-Ferrocenylethynyl-6-ferrocenyl-1-triethylsilyl-3-[[trifluoromethyl)sulfonyl]oxy]-hex-3-en-1,5-diyne (14c**)**

Compound **11c** (105 mg, 0.163 mmol) was dissolved in THF (7 mL) and cooled to -78°C . To this was added MeLi (0.21 mL, 0.33 mmol, 1.6 M in Et_2O). The mixture was stirred at -78°C for 1 h, and Tf_2O (92 mg, 0.33 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/ Et_2O 15:1) to yield **14c** (86 mg, 0.12 mmol, 72%) as a dark red oil. R_f = 0.2 (hexane/ Et_2O 18:1). IR (CH_2Cl_2 , cast) 3096, 2956, 2874, 2196, 2135, 1457, 1425, 1324, 1248 cm^{-1} ; ^1H NMR (300 MHz,

CDCl₃) δ 4.57 (t, J = 1.8 Hz, 2H), 4.50 (t, J = 1.8 Hz, 2H), 4.31 (t, J = 1.8 Hz, 2H), 4.29 (t, J = 1.8 Hz, 2H), 4.28 (s, 5H), 4.25 (s, 5H), 1.0 (t, J = 8.1 Hz, 9H), 0.71 (q, J = 8.1 Hz, 6H); ¹³C NMR (75.5 MHz, CDCl₃) δ 136.3, 118.4 (q, J = 321 Hz, CF₃), 110.1, 109.9, 103.4, 98.4, 97.0, 79.6, 79.2, 72.0, 71.9, 70.4, 70.3, 69.9, 69.7, 63.3, 62.9, 7.5, 4.1; EIMS m/z 730 (M⁺, 10), 597 ([M - SO₂CF₃]⁺, 17); HRMS calcd. for C₃₅H₃₃F₃FeO₃SSi (M⁺) 730.0571, found 730.0573.

1,1-Diphenyl-4-triethylsilyl-2-[(trifluoromethyl)sulfonyl]oxy-3-butyn-1-ene (**14d**)

Compound **12a** (52 mg, 0.138 mmol) was dissolved in THF (3 mL) and cooled to -20 °C. To this was added MeLi (0.17 mL, 0.27 mmol, 1.6 M in Et₂O). The mixture was stirred at -20 °C for 1 h, and Tf₂O (78.2 mg, 0.277 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH₄Cl (10 mL) and diluted with Et₂O (10 mL). The organic layer was washed with H₂O (2 x 10 mL), brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 10:1) to yield **14d** (43 mg, 0.092 mmol, 67%) as a light yellow oil. Spectral data consistent with those previously reported (Zhao, Tykwinski, unpublished results). R_f = 0.5 (hexane/Et₂O 10:1). ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.47 (m, 2H), 7.23-7.37 (m, 8H) 0.91 (t, J = 7.8 Hz, 9H), 0.57 (q, J = 7.8 Hz, 6H), ¹³C (100 MHz, CDCl₃, APT) δ 143.9, 136.9, 136.1, 130.4, 130.1, 139.6, 129.1, 128.4, 128.1, 126.4, 118.2 (q, J = 319 Hz, CF₃), 103.1, 97.4, 7.21, 3.93.

4-Triethylsilyl-2-[[trifluoromethyl)sulfonyl]oxy]-1,1-bis(p-methylphenyl)-but-1-en-3-yne (**14e**)

Compound **12b** (100 mg, 0.248 mmol) was dissolved in THF (5 mL) and cooled to -78°C . To this was added MeLi (0.31 mL, 0.50 mmol, 1.6 M in Et₂O). The mixture was stirred at -78°C for 1 h, and Tf₂O (140 mg, 0.495 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH₄Cl (10 mL) and diluted with Et₂O (10 mL). The organic layer was washed with H₂O (2 x 10 mL), brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 15:1) to yield **14e** (77 mg, 0.16 mmol, 63%) as a brown solid, Mp 50-52 $^{\circ}\text{C}$. $R_f = 0.7$ (hexane/Et₂O 10:1). IR (CH₂Cl₂, cast) 3029, 2957, 2914, 2877, 2147, 1610, 1511, 1458, 1423, 1379, 1246, 1209, cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.32 (d, $J = 8.0$ Hz, 2H) 7.08-7.15 (M, 6H), 2.34 (br s, 2 x CH₃), 0.91 (t, $J = 7.6$ Hz, 9H), 0.57 (q, $J = 7.6$ Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, APT) δ 143.9, 139.3, 139.1, 134.0, 133.2, 130.8, 130.3, 129.9, 128.6, 125.8, 118.2 (q, $J = 318$ Hz, CF₃), 102.5, 97.7, 21.5, 21.4, 7.3, 4.1; EIMS m/z 494 (M⁺, 18), 361 ([M – SO₂CF₃]⁺, 100); HRMS calcd. for C₂₅H₂₉O₃SSiF₃ (M⁺) 494.1559, found 494.1562. Anal calcd. for C₂₅H₂₉O₃SSiF₃: C, 60.73; H, 5.87. Found: C, 60.82; H, 6.34.

1,1-Bis(4-methoxyphenyl)-4-triethylsilyl-2-[[[(trifluoromethyl)sulfonyl]oxy]-but-1-en-3-yne (14f)

Compound **12c** (59 mg, 0.135 mmol) was dissolved in THF (3 mL) and cooled to -20°C . To this was added MeLi (0.17 mL, 0.27 mmol, 1.6 M in Et₂O). The mixture was stirred at -20°C for 1 h, and Tf₂O (76.5 mg, 0.271 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH₄Cl (10 mL) and diluted with Et₂O (10 mL). The organic layer was washed with H₂O (2 x 10 mL), brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 5:1) to yield **14f** (46 mg, 0.087 mmol, 65%) as a colorless oil. $R_f = 0.6$ (hexane/Et₂O 5:1). IR (CH₂Cl₂, cast) 2957, 2912, 2876, 2839, 2144, 1606, 1574, 1511, 1463, 1442, 1420 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.37 (d, $J = 9.0$ Hz, 2H), 7.17 (d, $J = 9.0$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 6.82 (d, $J = 9.0$ Hz, 2H), 3.8 (s, 3H), 3.79 (s, 3H), 0.91 (t, $J = 7.8$ Hz, 9H), 0.57 (q, $J = 7.8$ Hz, 6H); ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 160.5, 130.2, 143.1, 132.1, 131.8, 129.3, 128.5, 125.2, 118.3 (q, $J = 321$ Hz, CF₃), 113.7, 113.4, 102.2, 98.1, 55.4, 55.3, 7.2, 4.0; EIMS m/z 526 (M⁺, 19), 393 ([M – SO₂CF₃]⁺, 100); HRMS calcd. for C₂₅H₂₉O₃SSiF₃ (M⁺) 526.1456, found 526.1457.

1,1-Bis(4-butoxyphenyl)-4-triethylsilyl-2-[[[(trifluoromethyl)sulfonyl]oxy]-but-1-en-3-yne (14g)

Compound **12d** (200 mg, 0.385 mmol) was dissolved in THF (5 mL) and cooled to -78°C . To this was added MeLi (0.48 mL, 0.77 mmol, 1.6 M in Et₂O). The mixture was stirred at

–78 °C for 1 h, and TiF_2O (217 mg, 0.769 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/ Et_2O 10:1) to yield **14g** (164 mg, 0.269 mmol, 70%) as a yellow semi-solid. $R_f = 0.5$ (hexane/ Et_2O 10:1). IR (CH_2Cl_2 , cast) 3041, 2958, 2875, 2144, 1606, 1572, 1511, 1468, 1421, 1305 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 9.2$ Hz, 2H), 7.16 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 9.2$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 3.93-3.98 (m, 4H), 1.7-1.8 (m, 4H), 1.42-1.54 (m, 4H), 0.97 (t, $J = 7.2$ Hz, 6H), 0.92 (t, $J = 8.0$ Hz, 9H), 0.57 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ 160.6, 160.3, 144.2, 132.4, 132.1, 129.2, 128.6, 125.4, 118.6 (q, $J = 319$ Hz, CF_3), 114.5, 114.3, 102.0, 98.2, 68.2, 68.1, 31.7, 31.6, 19.6, 19.5, 14.0, 13.9, 7.3, 4.3; EIMS m/z 610 (M^+ , 34), 477 ($[\text{M} - \text{SO}_2\text{CF}_3]^+$, 100); HRMS calcd. for $\text{C}_{31}\text{H}_{41}\text{O}_5\text{F}_3\text{SSi}$ (M^+) 610.2396, found 610.2394.

1,1-Bis(2-thienyl)-4-triethylsilyl-2-[(trifluoromethyl)sulfonyl]oxy]-but-1-en-3-yne (**14h**)

Compound **13a** (35 mg, 0.090 mmol) was dissolved in THF (3 mL) and cooled to –78 °C. To this was added MeLi (0.11 mL, 0.18 mmol, 1.6 M in Et_2O). The mixture was stirred at –78 °C for 1 h, and TiF_2O (51 mg, 0.016 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/ Et_2O 15:1) to yield

14h (37 mg, 0.077 mmol, 85%) as a light green oil. R_f = 0.6 (hexane/ Et₂O 10:1). IR (CH₂Cl₂, cast) 3109, 3077, 2958, 2913, 2877, 2142, 1579, 1523, 1504, 1457, 1424, 1380, 1365, 1348 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.49 (dd, J = 1.2, 5.1 Hz, 1H), 7.43 (dd, J = 1.2, 5.1 Hz, 1H), 7.33 (dd, J = 1.2, 5.1 Hz, 1H), 7.19 (dd, J = 1.2, 5.1 Hz, 1H), 7.06 (dd, J = 3.6, 5.1 Hz, 1H), 7.02 (dd, J = 3.6, 5.1 Hz, 1H), 0.96 (t, J = 7.8 Hz, 9H), 0.63 (q, J = 7.8 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 137.6, 136.4, 131.7, 131.3, 130.3, 129.3, 128.7, 127.1, 126.8, 125.2, 118.2 (q, J = 320 Hz, CF₃), 108.2, 97.1, 7.2, 3.8; EIMS m/z 478 (M⁺, 10), 345 ([M – SO₂CF₃]⁺, 100); HRMS calcd. for C₁₉H₂₁S₃O₃F₃Si (M⁺) 478.0374, found 478.0382.

1,1-[Bis-(2,2'-bithienyl)]-4-triethylsilyl-2-[[[(trifluoromethyl)sulfonyl]oxy]-but-1-en-3-yne (14i)

Compound **13b** (35 mg, 0.063 mmol) was dissolved in THF (3 mL) and cooled to –78 °C. To this was added MeLi (0.079 mL, 0.13 mmol, 1.6 M in Et₂O). The mixture was stirred at –78 °C for 1 h, and Tf₂O (36 mg, 0.13 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH₄Cl (10 mL) and diluted with Et₂O (10 mL). The organic layer was washed with H₂O (2 x 10 mL), brine (10 mL), dried (Na₂SO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O 15:1) to yield **14i** (24 mg, 0.037 mmol, 60%) as a dark green oil. R_f = 0.6 (hexane/ Et₂O 10:1). IR (CH₂Cl₂, cast) 3072, 2956, 2911, 2875, 2138, 1441, 1423, 1308 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.23-7.27 (m, 3H), 7.20 (dd, J = 0.9, 3.6 Hz, 1H), 7.18 (dd, J = 0.9, 3.6 Hz, 1H), 7.14 (s, br, 2H), 7.09 (dd, J = 0.9, 3.6 Hz, 1H), 7.02 (t, J = 3.6 Hz, 1H), 7.00 (t, J = 3.9 Hz, 1H), 0.98 (t,

$J = 7.8$ Hz, 9H), 0.66 (q, $J = 7.8$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.4, 140.7, 136.7, 136.4, 135.6, 134.4, 133.0, 132.2, 129.7, 128.07, 128.05, 125.4, 125.0, 124.6, 124.4, 123.6, 123.2, 118.3 (q, $J = 321$ Hz, CF_3), 109.5, 97.3, 7.3, 3.9 (1 coincident signal); ESI HRMS calcd. for $\text{C}_{27}\text{H}_{26}\text{O}_3\text{F}_3\text{SiS}_5$ ($\text{M} + \text{H}$) $^+$ 643.0206, found 643.0206, solvent: MeOH/toluene 4:1.

1,1-Bis(2-furanyl)-4-triethylsilyl-2-[[trifluoromethyl)sulfonyl]oxy]-but-1-en-3-yne (14j)

Compound **13c** (43 mg, 0.121 mmol) was dissolved in THF (5 mL) and cooled to -78 $^{\circ}\text{C}$. To this was added MeLi (0.15 mL, 0.24 mmol, 1.6 M in Et_2O). The mixture was stirred at -78 $^{\circ}\text{C}$ for 1 h, and Tf_2O (68 mg, 0.24 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/ Et_2O 10:1) to yield **14j** (31 mg, 0.069 mmol, 57%) as a light yellow oil. $R_f = 0.4$ (hexane/ Et_2O 10:1). IR (CH_2Cl_2 , cast) 3154, 2958, 2914, 2877, 2141, 1568, 1467, 1425, 1380, 1316 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.54-7.58 (m, 1H), 7.46-7.52 (m, 1H), 6.82-6.88 (m, 1H), 6.62-6.68 (m, 1H), 6.46-6.54 (m, 2H), 0.97 (t, $J = 8.1$ Hz, 9H), 0.63 (q, $J = 8.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 144.6, 143.9, 124.8, 122.1, 118.3 (q, $J = 319$ Hz, CF_3), 116.1, 115.3, 111.9, 111.5, 106.7, 97.5, 7.2, 3.9 (1 coincident signal); EIMS m/z 446 (M^+ , 9), 313 ($[\text{M} - \text{SO}_2\text{CF}_3]^+$, 100); HRMS calcd. for $\text{C}_{19}\text{H}_{21}\text{O}_5\text{F}_3\text{SiS}$ (M^+) 446.0831, found 446.0834.

Figure S1. ^1H and ^{13}C NMR spectra of Compound 7a

INDEX	FREQUENCY	PPM	HEIGHT
1	1268.788	4.230	8.7
2	1261.643	4.206	28.1
3	1254.489	4.182	28.5
4	1247.355	4.158	9.2
5	391.518	1.305	28.7
6	384.374	1.281	58.3
7	377.230	1.258	27.4
8	326.579	1.083	36.8
9	323.373	1.078	233.8
10	320.351	1.068	98.6
11	314.764	1.049	7.4

Figure S2. ^1H and ^{13}C NMR Spectra of Compound 7b

Figure S3. ^1H and ^{13}C NMR Spectra of Compound 8a

INDEX	FREQUENCY	PPM	HEIGHT
1	2172.253	7.242	9.9
2	1749.005	5.831	35.5
3	372.833	1.243	13.9
4	365.414	1.218	11.3
5	356.072	1.187	10.8
6	354.698	1.182	17.1
7	353.049	1.177	9.9
8	347.462	1.158	36.5
9	343.243	1.144	39.9
10	338.669	1.123	237.7
11	333.998	1.113	97.7
12	330.792	1.103	36.7
13	329.327	1.098	23.3
14	327.403	1.091	17.7
15	325.480	1.085	12.7
16	320.351	1.068	8.3
17	316.184	1.034	42.1

Figure S4. ^1H and ^{13}C NMR Spectra of Compound 8b

Figure S5. ^1H and ^{13}C NMR Spectra of Compound 9

Figure S6. ¹H and ¹³C NMR Spectra of Compound 10a

Figure S7. ^1H and ^{13}C NMR Spectra of Compound 10b

Chemical Shift (ppm)	Integration	Assignment
297.097	0.990	10.8
296.547	0.989	12.6
288.945	0.963	26.6
288.487	0.982	26.8
280.885	0.936	15.1
187.095	0.624	13.7
179.218	0.597	11.6

10a

13C NMR (400 MHz, CDCl₃)

Chemical Shift (ppm): 297.097, 296.547, 288.945, 288.487, 280.885, 187.095, 179.218

Integration: 3.00, 19.29, 6.29

Figure S9. ^1H and ^{13}C NMR Spectra of Compound 11b

Figure S11. ^1H and ^{13}C NMR Spectra of Compound 12a

Figure S12. ¹H and ¹³C NMR Spectra of Compound 12b

Figure S13. ^1H and ^{13}C NMR Spectra of Compound 12c

Figure S14. ^1H and ^{13}C NMR Spectra of Compound 12d

Figure S15. ¹H and ¹³C NMR Spectra of Compound 13a

Figure S16. ^1H and ^{13}C NMR Spectra of Compound 13b

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exp2 apt
SAMPLE
date Jun 26 2002 dfrq 400.023 DEC. & VT
solvent CDCl3 dn HI
file /mnt/d800/nmr~ dpwr 40
tabdata/MISCELLANE~ dof 0
OUS/JUNE21-30/jn26~ dm yny
s408c_APT.fid dnm w
ACQUISITION dmf 10582
sfrq 100.598 dseq 1.0
tn C13 dres 1.0
at 1.184 homo n
np 65536 temp 24.0
sw 28149.2 DEC2
fb not used dfrq2 0
bs 4 dn2
tpwr 55 dpwr2 1
pw 3.0 dof2 0
p1 17.6 dm2 n
d1 0.500 dnm2 c
d2 0.007 dm2 10582
d3 0.001 dseq2
tof 1546.3 dres2 1.0
nt 50000 homo2 n
ct 314 PROCESSING
alock n lb 2.00
gain not used vtfile
flaqs n fn 262144
in n math f
dp y
hs nn wexp
DISPLAY -20.9 wbs procplot
sp 18107.5 wmt testn
vs 33
sc 0
wc 180
hzm 100.60
ls 500.00
rfl 10781.3
rfp 7751.2
th 4
lms 100.000
nm no ph

```

Figure S17. ^1H and ^{13}C NMR Spectra of Compound 13c

Figure S18. ^1H and ^{13}C NMR Spectra of Compound 14a

Figure S20. ^1H and ^{13}C NMR Spectra of Compound 14c

Figure S21 ¹H and ¹³C NMR Spectra of Compound 14d

Figure S22. ¹H and ¹³C NMR Spectra of Compound 14e

Trent Rankin, TR-3-163, BB
STANDARD CARBON PARAMETERS cdc13

Figure S25. ^1H and ^{13}C NMR Spectra of Compound 14h

Trent Rankin TR-3-177
400.15 MHz ¹H in CDCl₃

exp1 stidh

```

SAMPLE          DEC. & VT
date Jun 26 2002 dfrq 400.029
solvent CDCl3   dn H1
file /mnt/d600/nmr~ dpwr 40
labdata/MISCELLANE~ dof 0
OUS/JUNE21-30/jn26~ dm nmh
s410h.fid      dm C
ACQUISITION     dmf 10582
sfrq 400.0288410 dseq 1.0
tn H1 dres 24.0
at 3.744 homo n
np 44932 temp DEC2
sw 6000.5 dfrq2 0
fb not used dn2 1
bs 1 dn2 1
ss 2 dpwr2 1
tpwr 80 dof2 0
pw 4.0 dm2 n
d1 0.100 dme2 C
tof 0 dm2 200
nt 16 dseq2 1.0
ct 16 dres2 n
alock n homo2 n
gain not used PROCESSING n
FLAGS          wtf file
il n proc ft
in n fn not used f
dp y math
hs nn
DISPLAY        verr
sp -80.1 wexp
vp 4000.1 wnt
vs 151
sc 0
wc 240
h2mm 16.67
is 1079.67
rf1 3865.6
rfp 2906.2
th 20
lms 1.000
nm cdc ph

```

Trent Rankin TR-3-177
100.6 MHz ¹³C APT in CDCl₃

exp2 apt

```

SAMPLE          DEC. & VT
date Jun 26 2002 dfrq 400.029
solvent CDCl3   dn H1
file /mnt/d600/nmr~ dpwr 40
labdata/MISCELLANE~ dof 0
OUS/JUNE21-30/jn26~ dm yny
s410c.APT.fid   dm w
ACQUISITION     dmf 10582
sfrq 100.588 dseq 1.0
tn C13 dres 24.0
at 1.164 homo n
np 85536 temp DEC2
sw 28149.2 dfrq2 0
fb not used dn2 1
bs 1 dn2 1
ss 55 dpwr2 1
tpwr 3.0 dof2 0
p1 17.6 dm2 n
d1 0.500 dme2 C
d2 0.007 dm2 10582
d3 0.001 dseq2 1.0
tof 1546.3 dres2 n
nt 1000 homo2 n
ct 1000 PROCESSING 1.00
alock n lb
gain not used wtf file
il n proc ft
in n fn 262144
dp y math
hs nn
DISPLAY        verr
sp -503.0 wexp
vp 18608.6 wnt
vs 90
sc 0
wc 185
h2mm 100.59
is 500.00
rf1 10779.2
rfp 7751.2
th 7
lms 100.000
nm no ph

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Figure S27. ¹H and ¹³C NMR Spectra of Compound 14j

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