Supporting Information for:

Synthesis of tri- and tetracynes using a butadiynyl synthon

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General Experimental. Reagents were purchased reagent grade from commercial suppliers and used without further purification. DMF was dried over 4Å molecular sieves. Diisopropylamine was distilled from CaH₂. Anh. MgSO₄ was used as the drying agent after aqueous work-up. Evaporation and concentration in vacuo was performed at H₂O-aspirator pressure.

All reactions were performed in standard, dry glassware under an inert N₂ atmosphere. Column chromatography: silica gel-60 (230-400 mesh) from General Intermediates of Canada. Thin layer chromatography (TLC): Plastic sheets covered with silica gel-60 F254 from Macherey-Nagel; visualization by UV light or KMnO₄ stain. IR spectra (cm⁻¹): Nicolet Magna-IR 750 (neat) or Nic-plan. ¹H- and ¹³C-NMR: Varian Gemini-300 or 400 instruments, at room temperature in CDCl₃; Solvent peaks (7.24 for ¹H and 77.0 for ¹³C) as reference. Coupling constants are reported as observed (±0.5 Hz). For simplicity, the coupling constants of the aryl protons for para-substituted aryl groups have been reported as pseudo first-order (i.e., doublets), even though they are second-order (AA'XX') spin systems.

EI MS (m/z): Kratos MS50 instrument. For mass spectrometrical analyses, low-resolution data are provided in cases when M⁺ is not the base peak; otherwise, only high-resolution data are provided.

1,1-Dibromo-2-trifluoromethanesulfoxy-4-triisopropylsilyl-but-1-en-3-yne (1).

Procedure 1. To a mixture of 4 (200 mg, 0.526 mmol) and HMPA (141 mg, 0.789 mmol) in THF (5 mL) at –78 °C was added LiHMDS (0.684 mmol) in THF (5 mL). The mixture was stirred at –78 °C for 30 min and N-phenyltriflamide (226 mg, 0.631 mmol) in THF (4 mL) was added. The solution was allowed to warm to rt over 3 h. Sat. NH₄Cl (10 mL) was added and the mixture was extracted with Et₂O (2 x 30 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, hexanes) to give 1 (191 mg, 0.372 mmol, 70%) as a colorless oil.

Procedure 2. To a solution of 4 (4.80 g, 12.56 mmol) in dry ether (50 ml) at –78 °C was added LiHMDS (15.07 mmol) in ether (30 mL). The mixture was stirred at –78 °C for 30 min and triflic anhydride (5.14 g, 18.24 mmol) was added slowly via a syringe. The reaction was stirred for 40 min at –78°C and then allowed to reach rt over 2 h. The solution was washed twice with sat. NH₄Cl (50 mL) and once with brine (50 mL). The organic layer was dried (MgSO₄), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexanes) to
give 1 (5.30 g, 10.31 mmol, 82%) as a colorless oil. Rf = 0.7 (hexane/Et2O 30:1). IR (neat) 2946, 2893, 2867, 1571, 1463, 1433, 1385, 1368 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.02-1.10 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 131.6, 118.2 (q, J = 319 Hz, CF₃), 108.7, 100.5, 94.8, 18.4, 11.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -73.54. EIMS m/z 513 (M⁺, 22); HRMS calcd. for C₁₄H₂₁O₃SiF₃S79Br₈₁Br 513.9279, found 513.9273.

General procedure for tri- or tetrayne formation. Triyne 3a. To a degassed solution of dibromovinyltriflate 1 (0.150 g, 0.291 mmol) and phenylacetylene (0.09 g, 0.58 mmol) in DMF (5 mL) and i-Pr₂NH (0.12 g, 0.16 mL, 1.2 mmol) was added P(t-Bu)₃ (0.25 M in toluene, 0.23 mL, 0.058 mmol), CuI (0.011 g, 0.058 mmol) and Pd(OAc)₂ (0.006 g, 0.029 mmol). TLC analysis was used to monitor the reaction, indicating that the dibromovinyltriflate was completely consumed after 30 min of stirring at room temperature. The mixture was then filtered through a plug of silica. Ethyl acetate (20 mL) and satd. aq. NH₄Cl (5 mL) were added. The organic phase separated, washed with water (5 mL) and brine (5 mL), dried over MgSO₄, filtered, and the solvent reduced in vacuo. The crude of the reaction was purified by column chromatography (silica gel, hexanes) and afforded 3a (0.055 g, 62%) as a yellow oil. Rf = 0.6 (hexanes); IR (CH₂Cl₂, cast) 3063, 2944, 2866, 2176, 2074; ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.51 (m, 2H), 7.28-7.39 (m, 3H), 1.05-1.08 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 133.0, 129.7, 128.5, 120.9, 89.7, 86.7, 76.5, 74.3, 67.2, 60.6, 18.5, 11.3. EIMS m/z 306.2 (M⁺, 21), 263.1 ([M – iPr]⁺, 100); HRMS calcd. for C₂₁H₂₆Si (M⁺) 306.1804, found 306.1805.

Triyne 3b. Dibromovinyltriflate 1 (0.140 g, 0.272 mmol) and 2-methylphenylacetylene (0.09 g, 0.54 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)₂ (0.006 g, 0.027 mmol), P(t-Bu)₃ (0.22 mL, 0.25 M in toluene, 0.054 mmol), CuI (0.010, 0.054 mmol) and i-Pr₂NH (0.11 g, 0.15 mL, 1.1 mmol) in DMF (5 mL) to afford 3b (0.054 g, 62%) as a yellow oil. Rf = 0.6 (hexanes); IR (CH₂Cl₂, cast) 2945, 2867, 2178, 2072; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.28-7.39 (m, 3H), 1.05-1.08 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 133.0, 129.7, 128.5, 120.9, 89.7, 86.7, 76.5, 74.3, 67.2, 60.6, 18.5, 11.3. EIMS m/z 320.2 (M⁺, 21), 263.1 ([M – iPr]⁺, 100); HRMS calcd. for C₂₂H₂₈Si (M⁺) 320.1960, found 320.1965.
Triyne 3c. Dibromovinyltriflate 1 (0.135 g, 0.262 mmol) and 4-cyanophenylacetylene (0.067 g, 0.520 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)$_2$ (0.006 g, 0.026 mmol), P(t-Bu)$_3$ (0.21 mL, 0.25 M in toluene, 0.05 mmol), Cul (0.010, 0.052 mmol) and i-Pr$_2$NH (0.11 g, 0.14 mL, 1.0 mmol) in DMF (5 mL) to afford 3c (0.053 g, 61%) as a brown solid. Mp = 95-97 °C. R$_f$ = 0.59 (hexanes/ether 4:1); IR (CH$_2$Cl$_2$, cast); 2944, 2866, 2175, 2074; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56-7.62 (m, 4H), 1.02-1.08 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 133.4, 132.1, 125.9, 118.0, 112.9, 89.2, 88.7, 78.3, 74.1, 69.4, 59.6, 18.5, 11.2. EIMS m/z 331.2 (M$^+$, 24), 288.1 ([M – iPr]$^+$, 100); HRMS calcd. for C$_{22}$H$_{25}$NSi (M$^+$) 331.1756, found 331.1752. Data are consistent with those reported in ref. 1.

Triyne 3d. Dibromovinyltriflate 1 (0.150 g, 0.290 mmol) and 4-nitro-phenylacetylene (0.085 g, 0.58 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)$_2$ (0.006 g, 0.029 mmol), P(t-Bu)$_3$ (0.23 mL, 0.25 M in toluene, 0.058 mmol), Cul (0.011, 0.058 mmol) and i-Pr$_2$NH (0.11 g, 0.14 mL, 1.0 mmol) in DMF (5 mL) to afford 3d (0.069 g, 68%) as a yellow solid. Mp = 105-108 °C. R$_f$ = 0.6 (hexanes/ether 95:5); IR (CH$_2$Cl$_2$, cast) 3102, 2953, 2867, 2071, 1523, 1343; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J$ = 9.2 Hz, 2H), 7.63 (d, $J$ = 9.2 Hz, 2H), 1.05-1.11 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.7, 133.7, 127.8, 123.6, 89.1, 88.9, 79.0, 73.7, 69.7, 59.5, 18.5, 11.1. EIMS m/z 351.2 (M$^+$, 22), 308.1 ([M – iPr]$^+$, 100); HRMS calcd. for C$_{21}$H$_{25}$NO$_2$Si (M$^+$) 351.1655, found 351.1662.

Triyne 3e. Dibromovinyltriflate 1 (0.135 g, 0.262 mmol) and 4-(acetylamino)-phenylacetylene (0.067 g, 0.520 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)$_2$ (0.006 g, 0.026 mmol), P(t-Bu)$_3$ (0.21 mL, 0.250 M in toluene, 0.052 mmol) Cul (0.010, 0.052 mmol) and i-Pr$_2$NH (0.11 g, 0.14 mL, 1.0 mmol) in DMF (5 mL) to afford 3e (0.050 g, 53%) as a brown solid. Mp = 182-185 °C. R$_f$ = 0.6 (hexanes/ether 95:5); IR (CH$_2$Cl$_2$, cast) 3305, 3257, 3106, 3054, 2944, 2867, 2167, 2070, 1671; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (br s, 1H), 7.47 (d, $J$ = 8.4 Hz, 2H), 7.42 (d, $J$ = 8.4 Hz, 2H), 2.15 (s, 3H), 1.03-1.08 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) d 168.5, 139.2, 134.0, 119.3, 116.1, 89.8, 86.8, 76.4, 74.1, 67.3;

60.7, 24.7, 18.5, 11.3. EIMS m/z 363.2 (M⁺, 68), 320.1 ([M – iPr]⁺, 100); HRMS calcd. for C₂₃H₂₉NO₅Si (M⁺) 363.2018, found 363.2013.

\[ {^3} \text{Pr}_3 \text{Si} \quad \text{NH}_2 \]

**Triyne 3f.** Dibromovinyltriflate 1 (0.200 g, 0.390 mmol) and 4-amino-phenylacetylene (0.09 g, 0.78 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)₂ (0.009 g, 0.078 mmol), P(t-Bu)₃ (0.31 mL, 0.25 M in toluene, 0.078 mmol) Cul (0.015, 0.078 mmol) and i-Pr₂NH (0.16 g, 0.22 mL, 1.6 mmol) in DMF (8 mL) to afford 3f (0.041 g, 33%) as a red oil. Rᵥ = 0.46 (hexanes/ethyl acetate 2:3); IR (CH₂Cl₂, cast) 3470, 3375, 3286, 3226, 2925, 2865, 2185, 2099, 1622, 1511; ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, J = 8.8 Hz, 2H), 6.50 (d, J = 8.8 Hz, 2H), 3.86 (b s, NH₂), 1.03-1.06 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 147.9, 134.7, 114.5, 109.3, 90.0, 85.9, 77.9, 72.6, 66.8, 61.2, 18.4, 11.2. HRMS calcd. for C₂₁H₂₇NSi (M⁺) 321.1913, found 321.1917.

\[ {^3} \text{Pr}_3 \text{Si} \quad \text{N(Pr)}_2 \]

**Triyne 3g.** Dibromovinyltriflate 1 (0.120 g, 0.234 mmol) and 4-(diisopropylamino)-phenylacetylene (0.093 g, 0.460 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)₂ (0.005 g, 0.023 mmol), P(Cy)₃ (0.013 g, 0.046 mmol), Cul (0.009, 0.046 mmol) and i-Pr₂NH (0.093 g, 0.13 mL, 0.92 mmol) in DMF (5 mL) to afford 3g (0.046 g, 48%) as a yellow oil. Rᵥ = 0.64 (hexanes/ether 9:1); IR (CH₂Cl₂, cast) 3470, 2943, 2866, 2166, 2068, 1601, 1517; ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 3.87 (sept, J = 6.8 Hz, 2H), 1.26 (d, J = 6.8 Hz, 12H), 1.07-1.11 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 134.0, 115.0, 106.1, 90.2, 85.8, 78.8, 72.8, 66.9, 61.7, 47.3, 21.0, 18.4, 11.2. EIMS m/z 405.3 (M⁺, 87), 390.3 ([M – ³Pr]⁺, 100); HRMS calcd. for C₂₇H₃₉NSi (M⁺) 405.2852, found 405.2852.

\[ {^3} \text{Pr}_3 \text{Si} \quad \text{CHO} \]

**Triyne 3h.** Dibromovinyltriflate 1 (0.140 g, 0.272 mmol) and para-ethynylbenzaldehyde (0.07 g, 0.54 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)₂ (0.006 g, 0.027 mmol), P(t-Bu)₃ (0.22 mL, 0.25 M in toluene, 0.054 mmol), Cul (0.010, 0.054 mmol) and i-Pr₂NH (0.11 g, 0.15 mL, 1.1 mmol) in DMF (5 mL) to afford 3h (0.036 g, 40%) as a yellow solid. Mp = 66-68 °C. Rᵥ = 0.6 (hexanes/ether 99:1); IR (CH₂Cl₂, cast) 2945, 2866, 2074, 1705, 1601; ¹H NMR (400 MHz, CDCl₃) δ 9.99 (s, 1H), 7.81 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 1.05-1.10 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 191.0, 136.3, 133.5, 129.5, 127.1,
89.4, 88.4, 78.0, 75.0, 69.1, 59.9, 18.6, 11.3. EIMS m/z 334.2 (M+, 21), 291.1 ([M – iPr]+, 100); HRMS calcd. for C_{22}H_{26}O_{Si} (M+) 334.1753, found 334.1751.

\[ \text{Triyne 3i. Dibromovinyl triflate 1 (0.100 g, 0.194 mmol) and 4-(trifluoromethyl)phenylacetylene (0.06 g, 0.38 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)\textsubscript{2} (0.004 g, 0.019 mmol), P(t-Bu)\textsubscript{3} (0.15 mL, 0.25 M in toluene, 0.038 mmol), Cul (0.007, 0.038 mmol) and i-Pr\textsubscript{2}NH (0.077 g, 0.11 mL, 0.76 mmol) in DMF (3 mL) to afford 3i (0.029 g, 40%) as a yellow oil. R\textsubscript{f} = 0.6 (hexanes/ether 99:1); IR (CH\textsubscript{2}Cl\textsubscript{2}, cast) 2946, 2868, 2076, 1322; }^{1}\text{H NMR (400 MHz, CDCl\textsubscript{3}) }\delta 7.60-7.55 (m, 4H), 1.06-1.11 (m, 21H); 13C NMR (100 MHz, CDCl\textsubscript{3}) \delta 133.1, 131.1 (q, J_{CF} = 32.8 Hz), 125.3 (q, J_{CF} = 3.7 Hz), 124.7, 123.4 (q, J_{CF} = 270.3 Hz), 89.3, 87.8, 76.5, 74.5, 68.3, 59.8, 18.5, 11.2; {^{19}}\text{F NMR (376 MHz, CDCl\textsubscript{3}) }\delta -63.43. \\ 
\text{EIMS m/z 374.2 (M+, 11), 331.1 ([M – iPr]+, 100); HRMS calcd. for C_{22}H_{25}F_{3}Si (M+) 374.1678, found 374.1677.} \]

\[ \text{Tetrayne 3k. Dibromovinyl triflate 1 (0.100 g, 0.194 mmol) and 1-butadiynyladamantane (0.07 g, 0.38 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)\textsubscript{2} (0.004 g, 0.019 mmol), P(t-Bu)\textsubscript{3} (0.15 mL, 0.25 M in toluene, 0.038 mmol), Cul (0.007, 0.038 mmol) and i-Pr\textsubscript{2}NH (0.077 g, 0.11 mL, 0.76 mmol) in DMF (3 mL) to afford 3k (0.020 g, 26%) as a white solid. Mp = 130-132 °C. R\textsubscript{f} = 0.6 (hexanes); IR (CH\textsubscript{2}Cl\textsubscript{2}, cast) 2930, 2867, 2206, 2138, 2057; }^{1}\text{H NMR (400 MHz, CDCl\textsubscript{3}) }\delta 1.94 (br s, 3H), 1.84-1.95 (m, 6H), 1.64-1.71 (m, 6H), 1.05-1.08 (m, 6H); 13C NMR (100 MHz, CDCl\textsubscript{3}) \delta 89.7, 87.5, 82.1, 67.3, 65.5, 64.2, 62.8, 41.8, 41.7, 35.9, 30.2, 27.4, 18.4, 11.2. EIMS m/z 388.3 (M+, 13), 345.2 ([M – iPr]+, 66); HRMS calcd. for C_{27}H_{36}Si (M+) 388.2587, found 388.2583.} \]

\[ \text{Tetrayne 3l. Dibromovinyl triflate 1 (0.100 g, 0.194 mmol) and 2-methylhexa-3,5-diyn-2-ol (0.04 g, 0.38 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)\textsubscript{2} (0.004 g, 0.019 mmol), P(t-Bu)\textsubscript{3} (0.15 mL, 0.25 M in toluene, 0.038 mmol), Cul (0.007, 0.038 mmol) and i-Pr\textsubscript{2}NH (0.077 g, 0.11 mL, 0.76 mmol) in DMF (3 mL) to afford 3l (0.027 g, 45%) as a red oil. R\textsubscript{f} = 0.6 (hexanes/ether 4:1); }^{1}\text{H NMR (400 MHz, CDCl\textsubscript{3}) }\delta 2.22 (br s, 1H), 1.54 (s, 6H), 1.08-1.03 (m, 6H); 13C NMR (100 MHz, CDCl\textsubscript{3}) \delta 89.4, 85.9, 82.1, 67.3, 65.5, 64.2, 62.8,}
61.0, 60.8, 30.8, 18.4, 11.2. EIMS m/z 312.2 (M+, 6), 269.1 ([M – iPr]+, 78); HRMS calcd. for C_{20}H_{28}OSi (M+) 312.1910, found 312.1909.

**Tetrayne 3m.** Dibromovinyltriflate 1 (0.100 g, 0.194 mmol) and 5,5-dimethylhexa-1,3-diyne (0.04 g, 0.38 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)$_2$ (0.004 g, 0.019 mmol), P(t-Bu)$_3$ (0.15 mL, 0.25 M in toluene, 0.038 mmol), Cul (0.007, 0.038 mmol) and i-Pr$_2$NH (0.077 g, 0.11 mL, 0.76 mmol) in DMF (3 mL) to afford 3m (0.009 g, 15%) as a yellow oil. R$_f$ = 0.63 (hexanes); IR (CH$_2$Cl$_2$, cast) 2945, 2867, 2210, 2149, 2058, 1239; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.23 (s, 9H), 1.05-1.08 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 89.7, 88.0, 64.3, 62.0, 61.5, 61.4, 30.1, 28.1, 18.4, 11.2 (one coincident signal not observed). EIMS m/z 310.2 (M+, 28), 267.1 ([M – iPr]+, 100); HRMS calcd. for C$_{21}$H$_{30}$Si (M+) 310.2117, found 310.2116.

**Triyne 6a.** Dibromovinyltriflate 1 (0.150 g, 0.291 mmol) and 5a (0.23 g, 0.58 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)$_2$ (0.006 g, 0.029 mmol), P(t-Bu)$_3$ (0.23 mL, 0.25 M in toluene, 0.058 mmol), Cul (0.011, 0.058 mmol), and i-Pr$_2$NH (0.12 g, 0.16 mL, 1.2 mmol) in DMF (5 mL) to afford 6a (0.086 g, 50%) as a yellow oil. R$_f$ = 0.6 (hexanes); IR (CH$_2$Cl$_2$, cast) 2944, 2891, 2866, 2181, 2071, 2043; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.05-1.10 (m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 113.3, 113.2, 101.2, 100.7, 89.5, 89.2, 80.2, 72.0, 70.7, 60.0, 18.6, 18.5, 11.2, 11.1. EIMS m/z 594.1 (M+, 2), 367.2 ([M – C$_5$H$_7$Br$_2$]+, 100); HRMS calcd. for C$_{28}$H$_{42}$$_{79}$Br$_{81}$BrSi (M+) 594.1171, found 594.1178.

**Triyne 6b.** Dibromovinyltriflate 1 (0.150 g, 0.291 mmol) and 5b (0.17 g, 0.58 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)$_2$ (0.006 g, 0.029 mmol), P(t-Bu)$_3$ (0.23 mL, 0.25 M in toluene, 0.058 mmol), Cul (0.011, 0.058 mmol), and i-Pr$_2$NH (0.12 g, 0.16 mL, 1.2 mmol) in DMF (5 mL) to afford 6b (0.044 g, 31%) as a yellow oil.
Rf = 0.68 (hexanes/ether 95:5); IR (CH₂Cl₂, cast) 2944, 2866, 2237, 2180, 2072; ¹H NMR (400 MHz, CDCl₃) δ 2.32 (t, J = 7.2 Hz, 2H), 1.55 (sext, J = 7.2 Hz, 2H), 1.42 (quint, J = 7.2 Hz, 2H), 1.05-1.08 (m, 21H), 0.90 (t, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 113.3, 111.0, 99.6, 89.5, 89.0, 79.8, 72.5, 70.5, 59.9, 30.0, 21.9, 19.4, 18.5, 13.5, 11.2 (one coincident signal not observed). EIMS m/z 494.0 (M⁺, 67), 57 (Bu⁺, 100); HRMS calcd. for C₂₃H₃₀⁷⁹Br₈¹BrSi (M⁺) 494.0463, found 494.0460.

**Tetrayne 6c.** Dibromovinyltriflate 1 (0.150 g, 0.291 mmol) and 5c (0.24 g, 0.58 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)₂ (0.006 g, 0.029 mmol), P(t-Bu)₃ (0.23 mL, 0.25 M in toluene, 0.058 mmol), CuI (0.011, 0.058 mmol) and i-Pr₂NH (0.12 g, 0.16 mL, 1.2 mmol) in DMF (5 mL) to afford 6c (0.088 g, 49%) as a yellow oil. Rf = 0.64 (hexanes/ether 95:5); IR (CH₂Cl₂, cast) 2943, 2929, 2866, 2186, 2122, 2054; ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 1.62 (quint, J = 7.2 Hz, 2H), 1.30-1.28 (m, 6H), 1.04-1.08 (m, 21H), 0.86 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 133.9, 129.5, 128.6, 128.3, 104.4, 89.5, 88.0, 81.9, 74.6, 71.2, 66.3, 61.0, 60.8, 35.8, 31.7, 31.2, 29.0, 22.6, 18.5, 14.0, 11.2. EIMS m/z 598.2 (M⁺, 2), 555.1 ([M – iPr⁺], 7); HRMS calcd. for C₃₃H₃₈⁷⁹Br₈¹BrSi (M⁺) 598.1089, found 598.1072.

**Triyne 6d.** Dibromovinyltriflate 1 (0.150 g, 0.291 mmol) and 5d (0.205 g, 0.58 mmol) were subjected to the conditions outlined in the general procedure using Pd(OAc)₂ (0.006 g, 0.029 mmol), P(t-Bu)₃ (0.23 mL, 0.25 M in toluene, 0.058 mmol) CuI (0.011, 0.058 mmol) and i-Pr₂NH (0.12 g, 0.16 mL, 1.2 mmol) in DMF (5 mL) to afford 6d (0.057 g, 35%) as a yellow oil. Rf = 0.64 (hexanes/ether 95:5); IR (CH₂Cl₂, cast) 2943, 2866, 2179, 2073, 1523, 1343; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 7.2 Hz, 2H), 1.06-1.08 (s, 21H), ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 132.4, 128.4, 123.7, 114.4, 112.6, 94.1, 89.9, 89.32, 89.30, 81.1, 71.30,
71.26, 59.7, 18.5, 11.2. EIMS $m/z$ 559.0 ($M^+$, 5), 516.0 ($[M - iPr]^+$, 100); HRMS analysis was not successful due to the apparent instability of the compound to the analysis conditions.
Figure S1. $^1$H NMR Spectrum of I
Figure S2. $^{13}$C NMR Spectrum of 1
Figure S1. $^1$H NMR Spectrum of 3a
Figure S2. $^{13}$C NMR Spectrum of 3a
Figure S3. $^1$H NMR Spectrum of 3b
Figure S4. $^{13}$C NMR Spectrum of 3b
Figure S5. $^1$H NMR Spectrum of 3e
Figure S6. $^{13}$C NMR Spectrum of 3c
Figure S7. $^1$H NMR Spectrum of 3d
Figure S8. $^{13}$C NMR Spectrum of 3d
Figure S9. $^1$H NMR Spectrum of 3e
Figure S10. $^{13}$C NMR Spectrum of 3e
Figure S11. $^1$H NMR Spectrum of 3f
Figure S12. $^{13}$C NMR Spectrum of 3f
Figure S13. $^1$H NMR Spectrum of 3g
Figure S14. $^{13}$C NMR Spectrum of 3g
Figure S15. $^1$H NMR Spectrum of $3g$
Figure S16. $^{13}$C NMR Spectrum of 3g
Figure S17. $^1$H NMR Spectrum of 3i
Figure S18. $^{13}$C NMR Spectrum of 3i
Figure S19. $^1$H NMR Spectrum of 3k
Figure S20. $^{13}$C NMR Spectrum of 3k
Figure S21. $^1$H NMR Spectrum of 31
Figure S22. $^{13}$C NMR Spectrum of 3I
Figure S23. $^1$H NMR Spectrum of 3m
Figure S24. $^{13}$C NMR Spectrum of 3m
Figure S25. $^1$H NMR Spectrum of 6a
Figure S26. $^{13}$C NMR Spectrum of 6a
Figure S27. $^{13}$C NMR Spectrum of 6b
Figure S28. $^{13}$C NMR Spectrum of 6b
Figure S29. $^1$H NMR Spectrum of 6c
Figure S30. $^{13}$C NMR Spectrum of 6c
Figure S31. $^1$H NMR Spectrum of 6d
Figure S32. $^{13}$C NMR Spectrum of 6d