Supporting Information

[Pt(PPh$_3$)$_4$]-catalyzed selective diboration of symmetrical and unsymmetrical 1,3-diynes

Jakub Szyling,*‡ Jakub Szymańska,*‡ Adrian Franczyk,* Jędrzej Walkowiak*‡

*Center for Advanced Technology, Adam Mickiewicz University in Poznan, Uniwersytetu Poznanskiego 10, 61-614 Poznan, Poland
‡Faculty of Chemistry, Adam Mickiewicz University in Poznan, Uniwersytetu Poznanskiego 8, 61-614 Poznan, Poland

*E-mail: jszyling@amu.edu.pl, jedrzej.walkowiak@amu.edu.pl

Outline

1. Materials........................................................................................................................................... S2
2. General information ........................................................................................................................... S2
   2.1. Products purification ...................................................................................................................... S2
      2.1.1. 1,3-Diynes (2a-z) ................................................................................................................... S2
      2.1.2. Bisboryl-functionalized enynes (3a-z) ................................................................................... S3
3. General procedures for starting materials and product 3a functionalization ........................................ S3
   3.1. Synthesis of alkynyl bromides .................................................................................................... S3
   3.2. Suzuki coupling (for products 6-7) ............................................................................................... S4
   3.3. Hydrosilylation (for product 8) .................................................................................................... S4
   3.4. Sila-Sonogashira (for product 9) ................................................................................................... S4
   3.5. Mechanistic studies ...................................................................................................................... S4
4. Starting materials and diynes characterization ..................................................................................... S4
5. NMR spectra ...................................................................................................................................... S10
6. References .......................................................................................................................................... S97
1. Materials

Phenylacetylene (98%, Sigma-Aldrich), 1-bromo-4-ethynylbenzene (97%, Sigma-Aldrich), 1-ethynyl-4-fluorobenzene (99%, Sigma-Aldrich), 1-ethynyl-4-methoxybenzene (97%, Sigma-Aldrich), 1-ethynyl-4-(trifluoromethyl)benzene (98%, Sigma-Aldrich), 1-ethynyl-2-methylbenzene (97%, Sigma-Aldrich), 2-ethynyl-1,3-dimethylbenzene (abcr, 97%) 1-octyne (97%, Sigma-Aldrich), ethynyltrimethylsilane (98%, abcr), ethynyltriethylsilane (97%, Sigma-Aldrich) (triisopropylsilyl)acetylene (97%, Sigma-Aldrich), 3-phenyl-1-propyne (97%, Sigma-Aldrich), 3-phenoxy-1-propyne (90%, Sigma-Aldrich), prop-2-yn-1-ol (99%, Sigma-Aldrich), 3,3-dimethylbut-1-yne (98%, Sigma-Aldrich), iodobenzene (98%, Sigma-Aldrich), triethylsilane (99%, Sigma-Aldrich), 1,4-diphenylbuta-1,3-diyne (99%, Sigma-Aldrich), hexa-2,4-diyn (99%, abcr), 1,4-bis(trimethylsilyl)buta-1,3-diyne (98%, Sigma-Aldrich), 1,6-diphenoxyhexa-2,4-diyn (98%, Alfa Aesar), bis(pinacolato)diboron (99%, TCI), N-bromosuccinimide (98%, Sigma-Aldrich), hydroxylamine hydrochloride (98%, abcr), tributylamine (99%, Sigma-Aldrich), piperidine (99%, TCI), ammonium chloride (99%, Avantor Performance Materials Poland), 1,1,1,3,3,3-hexamethyldisilazane (99%, Sigma-Aldrich), silver nitrate (99%, Sigma-Aldrich), 2-dicyclohexylphosphino-2',4',6'-trisopropylbiphenyl (98%, Sigma-Aldrich), magnesium sulfate (anhydrous, 99%, Sigma-Aldrich), cesium carbonate (99%, Sigma-Aldrich), hexamethyldisilazane (98%, abcr), silica gel (MN-Kieselgel 60, 0.04-0.063 mm (230-400 mesh ASTM; Sigma-Aldrich)) were used as received. Toluene, tetrahydrofuran (THF), n-hexane, hexanes, ethyl acetate, acetone, were purchased from Avantor Performance Materials Poland. The solvents used in the reactions (toluene and THF) were dried, deoxygenated (SP5-800 MBraun) and stored over molecular sieves 4 Å under argon atmosphere. Argon (99,999%) was purchased from Messer. Platinum(IV) oxide (surface area ≥60 m²/g, Sigma-Aldrich), platinum on carbon (10 wt. % loading, Sigma-Aldrich), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene (Pt ~2 %, Sigma-Aldrich), hexachloroplatinic acid hexahydrate (Sigma-Aldrich), platinum(II) chloride (99.9%, Sigma-Aldrich), tetrakis(triphenylphosphine)palladium(0) (99%, Sigma-Aldrich) were used as received. Tetrakis(triphenylphosphine)platinum(0) was synthesized according to the literature.¹

2. General information:

2.1. Products purification

2.1.1. 1,3-Diynes (2a-z)

The UV-absorbing products (1,3-diynes) were purified on silica by flash chromatography (Biotage IsoleraOne chromatograph) with UV detector (λ1 = 255 nm, λ2= 280 nm). Purification details: cartridge 10 g, flow rate: 12 mL/min, length: 10 CV (CV = column volume), phase: n-hexane/dichloromethane (step 1: n-hexane 100% by 4 CV, step 2: gradient 10%/CV by 4 CV, step 3: n-hexane 50% by 2 CV). The non-aromatic products (1,3-diynes) were purified on silica using standard column chromatography using n-hexane/dichloromethane (95/5–7/3) as eluents. Products were characterized by GC-MS, ¹H, ¹³C, ²⁹Si NMR, FT-IR analyses.
2.1.2. Bisboryl-functionalized enynes (3a-z)

The reaction mixture was evaporated to remove all volatiles. Subsequently, the crude product was dissolved in n-pentane and filtered through the syringe filter (0.2 µm). After evaporation of n-pentane, the product was heated (approx. 70-130 °C) and condensed at cold-finger trap under vacuum (<10⁻³ mbar) (see Scheme 1). The products were obtained as solids (symmetrical substituted 1,3-diynes, excluding 3b) or oils (unsymmetrical substituted 1,3-diynes). Products 3n and 3q could not be condensed on a cold finger trap and were analyzed after the filtration step.

**Purification of 3h-i:** The reaction mixture was evaporated to remove all volatiles. Subsequently, the crude product was dissolved in n-pentane and filtered through the syringe filter (0.2 µm) and placed in the freezer (-18 °C) in 24 hours. The 3h-i precipitate as white solids.

**Purification of 3d-e and 4d-e:** The reaction mixture was evaporated to remove all volatiles. Subsequently, the crude product was dissolved in n-pentane and filtered through the syringe filter (0.2 µm) and excess of diyne or Bpin₂ was removed after the filtration step by heating at 70-110 °C under vacuum (10⁻³ mbar). For 3d-e, the crude products were heated (approx. 90-150 °C) and condensed at cold-finger trap under vacuum (<10⁻³ mbar). For, 4d-e the products were filtered via thick (approx. 3 cm) pad of Florisil and analyzed.

**Scheme S1.** Isolation of bisboryl-functionalized enynes. (A) – Crude product after filtration and solvent evaporation. (B) – Purification setup under reduced pressure and elevated temperature. (C) – condensed product (3a) on a cold finger trap.

3. General procedures for starting materials and product 3a functionalization

3.1. Synthesis of alkynyl bromides

The alkynyl bromides were prepared according to the literature with some modification²:

To a solution of alkyne (5 mmol) in acetone (50 mL), N-bromosuccinimide (6 mmol) and silver nitrate (0.5 mmol) were successively added. The reaction mixture was stirred without light access at room temperature over 18 h before adding water (100 mL). The resulting mixture was extracted with hexanes (3 x 100 mL) and the combined organic layers were washed with brine (100 mL), dried over MgSO₄, filtered through a pad of silica and concentrated to give a colourless or slightly yellow liquids.

**Caution:** All synthesized alkynyl bromides are strong lachrymators. The isolation should be performed under the hood.
3.2 Suzuki coupling (for products 6-7)
[Pd(PPh_3)_4] (0.005 mmol), 3a (0.1 mmol), aryl iodide (0.24 mmol) (for 6) or alkenyl iodide (0.12 mmol) (for 7a-b) were placed in the Schlenk vessel and evacuated. Then the toluene (1 mL) and aqueous solution of Cs_2CO_3 (3M, 1mL) were added under argon atmosphere and stirred for 18 h at 60 °C using oil bath as a heat source. Afterwards, crude reaction mixture was analyzed by GC-MS and ^1H NMR analyzes and purified according to the procedure in 2.1.1. subsection.

3.3 Hydrosilylation (for product 8)
To the one-neck round bottom flask, 3a (0.1 mmol), toluene (0.1 mL), triethylsilane (0.12 mmol) were added and heated to 100 °C (oil bath). Subsequently, the Pt(dvs)_3 (10^{-4} mmol) was added and the reaction mixture was stirred for 24 h. Afterwards, crude reaction mixture was analyzed by GC-MS and ^1H NMR analyzes and purified according to the procedure in 2.1.2. subsection.

3.4 Sila-Sonogashira (for product 9)
Pd(PPh_3)_4] (0.005 mmol), CuI (0.05 mmol), 3a (0.1 mmol) and aryl iodide (0.11 mmol) were placed in the Schlenk vessel and evacuated. Then the dry DMF (1 mL) was added under argon atmosphere and stirred for 18 h at 80 °C (oil bath). Afterwards, crude reaction mixture was analyzed by GC-MS and ^1H NMR analyzes and purified according to the procedure in 2.1.1. subsection.

3.5 Mechanistic studies
To the Young’s NMR tube the 1 (15.8 mg, 0.0625 mmol) and Pt(PPh_3)_4 (7.8mg, 0.00625 mmol) were added and kept under the vacuum for 1 h. After that, the 0.7 mL of dry toluene-d8 was added and heated over 1.5 h at 100 °C (oil bath) under Ar atmosphere. The mixture was cooled down to -50 °C (NMR chiller) and low temperature ^31P NMR was performed.

4. Starting materials and diynes characterization
(Bromoethyl)benzene

\[
\begin{array}{c}
\text{Br} \\
\text{C=C=CH}_2
\end{array}
\]

^1H NMR (300 MHz, CDCl_3, δ, ppm): 7.54 – 7.43 (m, 2H, Ph), 7.40 – 7.28 (m, 3H, Ph). ^13C{^1H} NMR (75 MHz, CDCl_3, δ, ppm): 132.1, 128.8, 128.4, 122.7, 80.2 (C≡C-Br), 49.9 (C≡C-Br). MS (EI, m/z): 182 (M+2, 100), 180(M+, 97), 101(93), 75(48), 62(5), 51(8). Pale yellow liquid. Isolated yield: 91% (0.82 g). Analytical data are in agreement with the literature.2

1-Bromooct-1-yne

\[
\begin{array}{c}
\text{Br} \\
\text{C=C=CH}_2
\end{array}
\]

^1H NMR (300 MHz, CDCl_3, δ, ppm): 2.20 (t, J_{H,H} = 7.0 Hz, 2H, CH_2=C), 1.51 (p, J_{H,H} = 6.8 Hz, 2H), 1.38 – 1.24 (m, 6H), 0.89 (t, J_{H,H} = 6.8 Hz, 3H, CH_3CH_2). MS (EI, m/z): 161(M*-28 (C(CH_3)*), 4), 159(M*-30(C(CH_3)*), 4), 147(4), 145(4), 132(7), 119(8), 117(9), 109(15), 79(41), 67(100). Colorless liquid. Isolated yield: 93% (0.88 g). Analytical data are in agreement with the literature.2
(Bromoethyl)trisopropylsilane

\[
\text{Si} \equiv \equiv \text{Br}
\]

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\), \(\delta\), ppm): 1.08 (s, 21H, (Si(CH(CH\(_3\))\(_3\)))\(_2\)). \(^{13}\text{C}[\text{\(1\text{H}\)] \text{NMR}}\) (75 MHz, CDCl\(_3\), \(\delta\), ppm): 83.6 (C≡C-Br), 61.9 (C≡C-Br), 18.6 (Si(CH(CH\(_3\)))\(_3\)), 11.4 (Si(CH(CH\(_3\)))\(_3\)). \text{MS} (EI, m/z): 262 (M\(^+\)-2, 5) 260 (M\(^+\)), 219(83), 217(83), 191(43), 189(42), 163(74), 161(68), 149(100), 147(93), 137(22), 109(31), 95(23), 69(17), 53(22). Colorless liquid. Isolated yield: 91\% (1.18 g). Analytical data are in agreement with the literature.\(^3\)

1,4-Bis(triethylsilyl)buta-1,3-diyne (2b)

\[
\text{Et}_3\text{Si} \equiv \equiv \equiv \text{SiEt}_3
\]

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\), \(\delta\), ppm): 1.00 (t, \(J_{\text{H-H}} = 7.9\) Hz, 18H, Si(CH\(_2\))\(_3\)). \(^{13}\text{C}[\text{\(1\text{H}\)] \text{NMR}}\) (101 MHz, CDCl\(_3\), \(\delta\), ppm): 89.4 (C≡C), 83.3 (C≡C), 7.5, 4.3.

\(^{29}\text{Si NMR}\) (79 MHz, CDCl\(_3\), \(\delta\), ppm): -5.84. \text{MS} (EI, m/z): 278(M\(^+\)-7), 249(100), 221(94), 193(38), 165(27), 137(20), 109(11), 82(17), 68(8). \text{FT-IR} (cm\(^{-1}\)): 2955, 2936, 2875, 2855, 2064, 1457, 1004, 1098, 695, 620. Colorless liquid. Isolated yield: 90\% (1.24 g). Analytical data are in agreement with the literature.\(^4\)

1,4-Bis(triisopropylsilyl)buta-1,3-diyne (2c)

\[
\text{(i-Pr)}_3\text{Si} \equiv \equiv \equiv \text{Si(i-Pr)}_3
\]

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\), \(\delta\), ppm): 1.09 (s, 42H, Si(CH(CH\(_3\))\(_3\)))\(_2\)). \(^{13}\text{C}[\text{\(1\text{H}\)] \text{NMR}}\) (101 MHz, CDCl\(_3\), \(\delta\), ppm): 90.3 (C≡C), 81.7 (C≡C), 18.7, 11.5.

\(^{29}\text{Si NMR}\) (79 MHz, CDCl\(_3\), \(\delta\), ppm): -0.86. \text{MS} (EI, m/z): 362(M\(^+\)-10), 319(100), 291(23), 277(26), 263(15), 249(29), 235(15), 207(11), 193(13), 179(11), 165(14), 151(12), 137(16), 82(31), 59(17). \text{FT-IR} (cm\(^{-1}\)): 3055, 3031, 2112, 1587, 1477, 1436, 825, 755, 719, 691. White solid. Isolated yield: 81\% (1.46 g). Analytical data are in agreement with the literature.\(^4\)

Hexadeca-7,9-diyne (2e)

\[
\text{Si} \equiv \equiv \equiv \equiv \text{Si}
\]

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\), \(\delta\), ppm): 2.24 (t, \(J_{\text{H-H}} = 6.9\) Hz, 4H, CH\(_2\)-C\(_\equiv\text{C-C\equivC-CH}_2\)), 1.57 – 1.45 (m, 4H), 1.40 – 1.22 (m, 12H), 0.88 (t, \(J_{\text{H-H}} = 6.8\) Hz, 6H, CH\(_2\)-CH\(_3\)). \(^{13}\text{C}[\text{\(1\text{H}\)] \text{NMR}}\) (101 MHz, CDCl\(_3\), \(\delta\), ppm): 77.7 (C≡C), 65.4 (C≡C), 31.4, 28.7, 28.5, 22.7, 19.3, 14.2. \text{MS} (EI, m/z): 189(M\(^+\)-29, 10), 161(4), 147(11), 133(22), 119(39), 105(58), 91(100), 79(65), 67(54), 55(30). \text{FT-IR} (cm\(^{-1}\)): 2956, 2928, 2858, 1466, 1426, 1323, 725. Colorless oil. Isolated yield: 90\% (0.98 g). Analytical data are in agreement with the literature.\(^5\)

2,2,7,7-Tetramethylocta-3,5-diyne (2f)

\[
\text{Si} \equiv \equiv \equiv \equiv \text{Si}
\]

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\), \(\delta\), ppm): 1.23 (s, 18H, CH\(_3\)))\(_3\)). \(^{13}\text{C}[\text{\(1\text{H}\)] \text{NMR}}\) (101 MHz, CDCl\(_3\), \(\delta\), ppm): 86.4 (C≡C), 63.8 (C≡C), 30.8, 28.1. \text{MS} (EI, m/z): 162(M\(^+\)-74), 147(50), 132(10), 119(100), 105(92), 91(89), 77(36), 55(24). \text{FT-IR} (cm\(^{-1}\)): 2968, 2864, 2141, 1465, 1361, 1239, 1198, 677. White solid. Isolated yield: 87\% (0.7 g). Analytical data are in agreement with the literature.\(^6\)
1,4-Bis(4-fluorophenyl)buta-1,3-diyne (2h)

\[
\text{F} \text{\longrightarrow} \equiv \equiv \equiv \equiv \text{F}
\]

\(^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 7.58 \sim 7.43 \ (m, 4\text{H, Ph}), \ 7.11 \sim 6.96 \ (m, 4\text{H, Ph}), \ ^{13}\text{C}[\text{H}] \text{NMR} \ (101 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 163.2 \ (d, J_{\text{C-F}} = 251.6 \text{ Hz}), \ 134.7 \ (d, J_{\text{C-F}} = 8.6 \text{ Hz}), \ 117.9 \ (d, J_{\text{C-F}} = 3.6 \text{ Hz}), \ 116.1 \ (d, J_{\text{C-F}} = 22.3 \text{ Hz}), \ 80.6 \ (\text{C=C}), \ 73.7 \ (\text{C=C}). \ \text{MS} \ (\text{EI, } m/z): 238(\text{M}^+, \ 100), \ 168(6), \ 119(14). \ \text{FT-IR} \ (\text{cm}^{-1}): \ 1887, \ 1594, \ 1499, \ 1215, \ 1157, \ 1093, \ 825, \ 695, \ 524. \ \text{White solid. Isolated yield: 83}\% \ (0.98 \text{ g}). \ \text{Data are in agreement with the literature.}^7

1,4-Bis(4-(trifluoromethyl)phenyl)buta-1,3-diyne (2i)

\[
\text{F}_3\text{C} \equiv \equiv \equiv \equiv \text{F}
\]

\(^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 7.70 \sim 7.55 \ (m, 8\text{H, Ph}). \ ^{13}\text{C}[\text{H}] \text{NMR} \ (75 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 132.7, \ 131.3 \ (q, J_{\text{C-F}} = 32.9 \text{ Hz}), \ 125.6 \ (q, J_{\text{C-F}} = 3.7 \text{ Hz}), \ 125.4, \ 122.0, \ 81.1, \ 75.8. \ ^{29}\text{Si} \text{NMR} \ (79 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 18.79. \ \text{MS} \ (\text{EI, } m/z): 338(\text{M}^+, \ 100), \ 319(13), \ 288(9), \ 249(5), \ 199(4), \ 169(4), \ 144(5), \ 119(3). \ \text{FT-IR} \ (\text{cm}^{-1}): \ 1607, \ 1306, \ 1166, \ 1121, \ 1104, \ 1062, \ 835. \ \text{White solid. Isolated yield: 91}\% \ (1.53 \text{ g}). \ \text{Analytical data are in agreement with the literature.}^8

1,4-Bis(4-methoxyphenyl)buta-1,3-diyne (2j)

\[
\text{MeO} \equiv \equiv \equiv \equiv \text{OMe}
\]

\(^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 7.46 \ (d, J_{\text{H-H}} = 8.8 \text{ Hz}, \ 4\text{H, Ph}), \ 6.85 \ (d, J_{\text{H-H}} = 8.9 \text{ Hz}, \ 4\text{H, Ph}), \ 3.82 \ (s, 6\text{H, OCH}_3). \ ^{13}\text{C}[\text{H}] \text{NMR} \ (101 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 160.4, \ 134.2, \ 114.3, \ 114.1, \ 81.4 \ (\text{C=C}), \ 73.06 \ (\text{C=C}), \ 55.47 \ (\text{OCH}_3). \ \text{MS} \ (\text{EI, } m/z): 262(\text{M}^+, \ 100), \ 247(43), \ 219(15), \ 203(7), \ 176(13), \ 150(5), \ 131(3). \ \text{FT-IR} \ (\text{cm}^{-1}): \ 3002, \ 2975, \ 2942, \ 2890, \ 2865, \ 1607, \ 1594, \ 1499, \ 1215, \ 1157, \ 1093, \ 825, \ 695, \ 524. \ \text{White solid. Isolated yield: 88}\% \ (1.15 \text{ g}). \ \text{Analytical data are in agreement with the literature.}^7

1,6-Bis(trimethylsiloxy)hexa-2,4-diyne (2l)

\[
\text{Me}_3\text{Si} \equiv \equiv \equiv \equiv \text{OSiMe}_3
\]

\(^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 4.34 \ (s, 4\text{H, CCH}_2\text{O}), \ 0.16 \ (s, 18\text{H, OSi(CH}_3)_3). \ ^{13}\text{C}[\text{H}] \text{NMR} \ (75 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 77.5, \ 69.4, \ 51.5, \ -0.3. \ ^{29}\text{Si} \text{NMR} \ (79 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 22.26. \ \text{MS} \ (\text{EI, } m/z): 254(\text{M}^+, \ 23), \ 239(7), \ 209(25), \ 179(73), \ 147(28), \ 73(100). \ \text{FT-IR} \ (\text{cm}^{-1}): \ 2958, \ 2856, \ 1362, \ 1250, \ 1078, \ 834, \ 748. \ \text{Brown oil. Isolated yield: 77}\% \ (0.97 \text{ g}). \ \text{Despite previous report, 2l is fully characterized for the first time.}^9

(Phenylbuta-1,3-diyne-1-yl)trisopropylsilane (2m)

\[
\text{C}_3\text{H}_6\text{Si} \equiv \equiv \equiv \equiv \text{Si(OPr}_3)_3
\]

\(^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 7.55 \sim 7.27 \ (m, 5\text{H, Ph}), \ 1.12 \ (s, 21\text{H, Si(CH}_3)_3). \ ^{13}\text{C}[\text{H}] \text{NMR} \ (75 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): 132.8, \ 129.4, \ 128.5, \ 121.7, \ 89.6 \ (\text{C=C}), \ 88.0 \ (\text{C=C}), \ 75.7 \ (\text{C=C}), \ 74.8 \ (\text{C=C}), \ 18.7, \ 11.6. \ ^{29}\text{Si} \text{NMR} \ (79 \text{ MHz, CDCl}_3, \delta, \text{ ppm}): -0.65. \ \text{MS} \ (\text{EI, } m/z): 282(\text{M}^+, \ 8), \ 239(98), \ 211(44), \ 197(40), \ 183(54), \ 169(100), \ 159(21), \ 153(27), \ 91(20) 90(10). \ \text{FT-IR} \ (\text{cm}^{-1}): \ 2942, \ 2890, \ 2865, \ 2204, \ 2101, \ 1488, \ 1461, \ 1070, \ 1018, \ 995, \ 881, \ 752, \ 729, \ 675, \ 602. \ \text{Colorless oil. Isolated yield: 75}\% \ (1.05 \text{ g}). \ \text{Analytical data are in agreement with the literature.}^{10}

(4-Bromophenyl)buta-1,3-diyne-1-yl)trisopropylsilane (2n)

\[
\text{C}_3\text{H}_6\text{Si} \equiv \equiv \equiv \equiv \text{Br}
\]
\(^{1}H\) NMR (300 MHz, CDCl\(_3\), \(\delta\), ppm): 7.49 - 7.43 (m, 2H, Ph), 7.39 - 7.33 (m, 2H, Ph), 1.11 (s, 21H, Si(CH(CH\(_3\))\(_2\))). \(^{13}C\{H\}\) NMR (75 MHz, CDCl\(_3\), \(\delta\), ppm): 134.2, 131.9, 123.9, 120.7, 89.4 (C=C), 89.0 (C=C), 75.9 (C=C), 74.5 (C=C), 18.7, 11.4. \(^{29}Si\) NMR (79 MHz, CDCl\(_3\), \(\delta\), ppm): -0.46. MS (EI, m/z): 362(M\(^+\)), 360(M\(^+\) - 2), 319(100), 317(98), 291(33), 289(33), 277(28), 275(26), 249(61), 247(61), 153(16), 151(17), 109(10), 59(8). FT-IR (cm\(^{-1}\)): 2942, 2890, 2864, 2102, 1485, 1462, 1070, 1009, 881, 820, 745, 676, 613. **Analytical Calculated for C\(_{59}H_{82}BrSi\): C, 63.15; H, 6.97.** Found: C, 63.09; H, 6.93. White solid. Isolated yield: 74% (1.33 g). Analytical data are in agreement with the literature.\(^{11}\)

**Trisopropyl(((4-(trifluoromethyl)phenyl)buta-1,3-diyyn-1-yl)silane (2o)**

\[\text{\textbullet}{\text{Pr}}_3\text{Si} \equiv \equiv \equiv \overset{\text{CF}_3}{\text{C}}\]

\(^{1}H\) NMR (300 MHz, CDCl\(_3\), \(\delta\), ppm): 7.68 - 7.50 (m, 4H, Ph), 1.12 (s, 21H, Si(CH(CH\(_3\))\(_2\))). \(^{13}C\{H\}\) NMR (101 MHz, CDCl\(_3\), \(\delta\), ppm): 133.1, 131.1, 130.8, 125.5 (q, \(J_{C,F} = 3.8\) Hz), 122.5, 89.9 (C=C), 89.1 (C=C), 74.0 (C=C), 18.7, 11.4. \(^{29}Si\) NMR (79 MHz, CDCl\(_3\), \(\delta\), ppm): -0.28. MS (EI, m/z): 350(M\(^+\)), 307(100), 279(38), 265(26), 251(55), 237(82), 197(12), 175(17), 137(8), 125(6). FT-IR (cm\(^{-1}\)): 2944, 2892, 2867, 2104, 1614, 1462, 1318, 1168, 1129, 1055, 1017, 1015, 881, 839, 676, 659, 613, 595. **Analytical Calculated for C\(_{59}H_{82}BrSi\): C, 68.54; H, 7.19.** Found: C, 68.58; H, 7.21. Colorless oil. Isolated yield: 81% (1.42 g). Analytical data are in agreement with the literature.\(^{11}\)

**Trioisopropyl(m-tolyl)buta-1,3-diyyn-1-yl)silane (2p)**

\[\text{\textbullet}{\text{Pr}}_3\text{Si} \equiv \equiv \equiv \overset{\text{H}}{\text{C}}\]

\(^{1}H\) NMR (400 MHz, CDCl\(_3\), \(\delta\), ppm): 7.35 - 7.29 (m, 2H, Ph), 7.23 - 7.14 (m, 2H, Ph), 2.33 (s, 3H PhCH\(_3\)), 1.12 (s, 21H, Si(CH(CH\(_3\))\(_2\))). \(^{13}C\{H\}\) NMR (101 MHz, CDCl\(_3\), \(\delta\), ppm): 138.3, 133.4, 130.3, 129.9, 128.4, 121.5, 89.8 (C=C), 87.7 (C=C), 76.0 (C=C), 74.5 (C=C), 21.3 (PhCH\(_3\)), 18.7, 11.5. \(^{29}Si\) NMR (79 MHz, CDCl\(_3\), \(\delta\), ppm): -0.70. MS (EI, m/z): 296(M\(^+\)), 253(98), 225(44), 211(41), 197(50), 183(100), 167(24), 143(24), 98(19), 59(10). **Analytical Calculated for C\(_{59}H_{82}Si\): C, 81.01; H, 9.52.** Found: C, 81.19; H, 9.60. Yellow oil. Isolated yield: 77% (1.14 g).

\([(4,6-Dihydropyren-1-yl)buta-1,3-diyyn-1-yl)]trioisopropylsilane (2q)**

\[\text{\textbullet}{\text{Pr}}_3\text{Si} \equiv \equiv \equiv \overset{\circ}\text{H}_{\circ}\]

\(^{1}H\) NMR (300 MHz, CDCl\(_3\), \(\delta\), ppm): 8.58 (d, \(J_{H,H} = 9.1\) Hz, 1H), 8.28 - 7.99 (m, 8H), 1.18 (s, 21H, Si(CH(CH\(_3\))\(_2\))). \(^{13}C\{H\}\) NMR (101 MHz, CDCl\(_3\), \(\delta\), ppm): 133.7, 132.0, 131.3, 131.2, 131.0, 129.0, 128.9, 127.3, 126.5, 126.1, 126.0, 125.5, 124.6, 124.5, 124.3, 116.0, 90.0 (C=C), 89.7 (C=C), 80.2 (C=C), 75.1 (C=C), 18.8, 11.6. \(^{29}Si\) NMR (79 MHz, CDCl\(_3\), \(\delta\), ppm): -0.57. FT-IR (cm\(^{-1}\)): 2940, 2889, 2863, 2191, 2089, 1459, 1069, 1016, 993, 880, 844, 670. **Analytical Calculated for C\(_{59}H_{82}Si\): C, 85.23; H, 7.89.** Found: C, 84.98; H, 7.77. Yellow solid. Isolated yield: 48% (0.97g). Analytical data are in agreement with the literature.\(^{12}\)

\[(Cyclopropylbuta-1,3-diyyn-1-yl)]trioisopropylsilane (2r)**

\[\text{\textbullet}{\text{Pr}}_3\text{Si} \equiv \equiv \equiv \overset{\circ}\text{H}_{\circ}\]

\(^{1}H\) NMR (300 MHz, CDCl\(_3\), \(\delta\), ppm): 1.37 - 1.28 (m, 1H, CH), 1.07 (s, 21H, Si(CH(CH\(_3\))\(_2\))), 0.85 - 0.78 (m, 4H, CH\(_2\)CH\(_2\))). \(^{13}C\{H\}\) NMR (75 MHz, CDCl\(_3\), \(\delta\), ppm): 90.4 (C=C), 81.9 (C=C), 79.7 (C=C), 61.5 (C=C), 18.7, 11.5, 8.9, 0.2. \(^{29}Si\) NMR (79 MHz, CDCl\(_3\), \(\delta\), ppm): -1.15. MS (EI, m/z): 246(M\(^+\)), 203(93), 175(42), 161(50), 147(48), 133(100), 118(17), 93(27), 59(23). **Analytical Calculated for C\(_{59}H_{82}Si\)): C, 77.97; H, 10.63. Found: C, 78.08; H, 10.72. Yellow oil. Isolated yield: 83% (1.02 g).
(5-Phenylpenta-1,3-diyn-1-yl)trisopropylsilane (2s)

\[\text{(5-Phenylpenta-1,3-diyn-1-yl)trisopropylsilane (2s)}\]

\[\text{\((\text{CH}_3)_{2}Si\)}\]

\(\text{\textbf{1H NMR}}\) (300 MHz, CDCl\(_3\), \(\delta\), ppm): 6.75 – 6.58 (m, 5H), 3.09 (s, 2H, =CCH\(_2\)Ph), 1.11 (s, 21H, Si(CH\(_2\)(CH\(_3\)))\(_3\)). \(\text{\textbf{13C}[\text{H}] NMR}\) (75 MHz, CDCl\(_3\), \(\delta\), ppm): 135.4, 128.8, 128.2, 127.1, 90.0 (C=C), 81.5 (C=C), 75.8 (C=C), 67.9 (C=C), 25.8, 18.7, 11.4. \(\text{\textbf{29Si NMR}}\) (79 MHz, CDCl\(_3\), \(\delta\), ppm): -0.93. \(\text{MS}\) (EI, m/z): 296(M\(^+\), 4), 253(100), 225(30), 211(27), 197(29), 183(58), 155(14), 115(7), 98(5), 59(11). \(\text{FT-IR (cm}\(^{-1}\)): 2942, 2890, 2865, 2225, 2105, 1495, 1455, 1188, 1073, 995, 882, 727, 675, 611. \text{Anal. Calcd for C\(_{20}\)H\(_{28}\)Si: C, 81.01; H, 9.52. Found: C, 80.98; H, 9.53. Yellow oil. Isolated yield: 73% (1.08 g).}

(5-Phenoxy penta-1,3-diyn-1-yl)trisopropylsilane (2t)

\[\text{(5-Phenoxy penta-1,3-diyn-1-yl)trisopropylsilane (2t)}\]

\[\text{\((\text{CH}_3)_{2}Si\)}\]

\(\text{\textbf{1H NMR}}\) (300 MHz, CDCl\(_3\), \(\delta\), ppm): 7.42 – 7.31 (m, 2H, Ph), 7.08 – 6.96 (m, 3H, Ph) 4.80 (s, 2H, =CCH\(_2\)OPh), 1.11 (s, 21H, Si(CH\(_2\)(CH\(_3\)))\(_3\)). \(\text{\textbf{13C}[\text{H}] NMR}\) (75 MHz, CDCl\(_3\), \(\delta\), ppm): 157.7, 129.7, 125.3, 121.8, 115.0, 88.8 (C=C), 85.5 (C=C), 72.5 (C=C), 71.5 (C=C), 56.4, 18.6, 11.4. \(\text{\textbf{29Si NMR}}\) (79 MHz, CDCl\(_3\), \(\delta\), ppm): -0.45. \(\text{MS}\) (EI, m/z): 312(M\(^+\), 26), 269(100), 241(50), 225(29), 213(24), 199(38), 185(20), 173(30), 151(81), 137(32), 121(22), 106(34), 92(19), 59(25). \(\text{FT-IR (cm}\(^{-1}\)): 2943, 2891, 2865, 2225, 2106, 1598, 1588, 1494, 1461, 1211, 1172, 1032, 1015, 994, 881, 801, 750, 676. \text{Anal. Calcd for C\(_{20}\)H\(_{31}\)OSi: C, 76.86; H, 9.03. Found: C, 76.88; H, 9.01. Yellow oil. Isolated yield: 69% (1.07 g).}

Deca-1,3-diyn-1-yltrisopropylsilane (2u)

\[\text{(Deca-1,3-diyn-1-yl)trisopropylsilane (2u)}\]

\[\text{\((\text{CH}_3)_{2}Si\)}\]

\(\text{\textbf{1H NMR}}\) (300 MHz, CDCl\(_3\), \(\delta\), ppm): 2.28 (d, \(J_{\text{H-H}} = 7.0\) Hz, 2H, =CCH\(_3\)), 1.59 – 1.18 (m, 8H), 1.08 (s, 21H, Si(CH\(_2\)(CH\(_3\)))\(_3\)), 0.89 (t, \(J_{\text{H-H}} = 6.8\) Hz, 3H, CH\(_3\)CH\(_3\)). \(\text{\textbf{13C}[\text{H}] NMR}\) (75 MHz, CDCl\(_3\), \(\delta\), ppm): 90.3 (C=C), 80.1 (C=C), 79.1 (C=C), 65.9 (C=C), 31.4, 28.6, 28.3, 22.6, 19.4, 18.7, 14.2, 11.4. \(\text{\textbf{29Si NMR}}\) (79 MHz, CDCl\(_3\), \(\delta\), ppm): -1.14. \(\text{MS}\) (EI, m/z): 290(M\(^+\), 3), 247(100), 219(38), 205(33), 191(28), 177(52), 163(5), 149(9), 137(11), 109(13), 95(10), 83(15), 59(20). \(\text{FT-IR (cm}\(^{-1}\)): 2941, 2865, 2223, 2104, 1462, 1181, 995, 881, 675. \text{Anal. Calcd for C\(_{40}\)H\(_{70}\)Si: C, 78.54; H, 11.79. Found: C, 78.50; H, 11.81. Pale yellow oil. Isolated yield: 82% (1.19g). Analytical data are in agreement with the literature.}

Trimethyl(phenylbuta-1,3-diyn-1-yl)silane (2v)

\[\text{\((\text{CH}_3)_{2}Si\)}\]

\(\text{\textbf{1H NMR}}\) (300 MHz, CDCl\(_3\), \(\delta\), ppm): 7.62 – 7.43 (m, 2H, Ph), 7.43 – 7.18 (m, 3H, Ph), 0.24 (s, 9H, Si(CH\(_3\)))\(_3\)). \(\text{\textbf{13C}[\text{H}] NMR}\) (75 MHz, CDCl\(_3\), \(\delta\), ppm): 132.8, 129.5, 128.6, 121.5, 90.8 (C=C), 88.0 (C=C), 76.9 (C=C), 74.3 (C=C), -0.2 (Si(CH\(_3\)))\(_3\)). \(\text{\textbf{29Si NMR}}\) (79 MHz, CDCl\(_3\), \(\delta\), ppm): -16.1. \(\text{MS}\) (EI, m/z): 198(M\(^+\), 26), 183(100), 167(3), 153(5), 129(8). \(\text{FT-IR (cm}\(^{-1}\)): 2959, 2205, 2104, 1489, 1442, 1250, 837, 751, 686, 632. Pale yellow oil. Isolated yield: 66% (0.65 g). Analytical data are in agreement with the literature.

2,2-Dimethyldecadiyne (2w)

\[\text{\((\text{CH}_3)_{2}Si\)}\]
$^1$H NMR (300 MHz, CDCl$_3$, δ, ppm): 2.25 (d, $J_{H-H} = 7.0$ Hz, 2H, =CCH$_3$), 1.59 – 1.24 (m, 8H), 1.23 (s, 9H, CH$_3$)$\beta$), 0.88 (t, $J_{H-H} = 6.8$ Hz, 3H, CH$_2$CH$_3$). $^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$, δ, ppm): 85.2 (C=, C), 79.0 (C=), 65.1 (C=C), 64.0 (C=C), 31.5, 30.8, 28.7, 28.5, 28.1, 22.7, 19.4, 14.2. MS (EI, m/z): 175(M$^+$15, 20), 161(20), 147(19), 133(1), 119(70), 105(100), 91(67), 79(38), 67(22), 55(25). FT-IR (cm$^{-1}$): 2966, 2930, 2861, 1706, 1456, 1363, 1281, 1201, 1169. **Anal. Calcd for C$_{18}$H$_{22}$:** C, 88.35; H, 11.65. Found: C, 88.38; H, 11.62. Yellow oil. Isolated yield: 89% (0.84 g) Despite previous report, 2v is fully characterized for the first time.$^{15}$

**Deca-1,3-diynyl-ylbenzene (2x)**

$^1$H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.51 – 7.27 (m, 5H, Ph), 2.36 (d, $J_{H-H} = 7.0$ Hz, 2H, =CCH$_3$), 1.65 – 1.25 (m, 8H), 0.91 (t, $J_{H-H} = 6.7$ Hz, 3H, CH$_2$CH$_3$). $^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$, δ, ppm): 132.6, 128.9, 128.5, 122.3, 85.1 (C=), 74.8 (C=C), 74.6 (C=C), 65.2 (C=C), 31.4, 28.7, 28.4, 22.7, 19.7, 14.2. MS (EI, m/z): 210(M$^+$, 53), 195(16), 181(72), 165(76), 153(53), 139(100), 126(39), 115(39), 91(22), 79(14), 63(8). FT-IR (cm$^{-1}$): 2955, 2929, 2858, 1489, 1422, 752, 687. Yellow oil. Isolated yield: 88% (0.92 g). Analytical data are in agreement with the literature.$^{16}$

**1-(Deca-1,3-diynyl-yl)-2-methylbenzene (2y)**

$^1$H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.37 (dd, $J_{H-H} = 7.6$, 1.4 Hz, 1H, Ph), 7.20 – 6.99 (m, 3H, Ph), 2.37 (s, 3H, PhCH$_3$), 2.30 (d, $J_{H-H} = 6.7$ Hz, 2H, =CCH$_3$), 1.58 – 1.41 (m, 2H), 1.39 – 1.12 (m, 6H) 0.83 (t, $J_{H-H} = 6.7$ Hz, 3H, CH$_2$CH$_3$). $^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$, δ, ppm): 141.7, 133.1, 129.6, 128.7, 125.7, 122.1, 85.5 (C=), 78.1 (C=C), 73.9 (C=C), 65.3 (C=C), 31.5, 28.7, 28.4, 22.7, 20.8, 19.8, 14.2. MS (EI, m/z): 224(M$^+$, 78), 209(14), 195(62), 181(26), 165(83), 152(100), 139(30), 129(23), 115(39), 105(7), 91(15), 79(18), 67(24) 51(7). FT-IR (cm$^{-1}$): 2954, 2929, 2857, 1484, 1456, 753, 713. **Anal. Calcd for C$_{19}$H$_{22}$:** C, 91.01; H, 8.99. Found: C, 90.99; H, 9.01. Pale-orange oil. Isolated yield: 85% (0.95 g).

**2-(Deca-1,3-diynyl-yl)-1,3-dimethylbenzene (2z)**

$^1$H NMR (600 MHz, CDCl$_3$, δ, ppm): 7.14 – 7.09 (m, 1H, Ph), 7.03 (m, 2H, Ph), 2.45 (s, 6H, PhCH$_3$), 2.39 (t, $J_{H-H} = 7.2$ Hz, 2H), 1.60 (p, $J_{H-H} = 7.2$ Hz, 2H), 1.48 – 1.41 (m, 2H), 1.37 – 1.29 (m, 4H), 0.92 (t, $J_{H-H} = 7.0$ Hz, 3H). $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$, δ, ppm): 142.0, 128.2, 126.8, 122.1, 86.1 (C=C), 82.3 (C=C), 72.7 (C=C), 65.3 (C=C), 31.5, 28.8, 28.4, 27.4, 22.7, 21.2, 19.9, 14.2. MS (EI, m/z): 238(M$^+$, 100), 223(10), 209(39), 195(20), 180(27), 164(56), 152(39), 115(16), 91(15), 79(26). FT-IR (cm$^{-1}$): 2954, 2927, 2858, 1466, 1377, 769. **Anal. Calcd for C$_{19}$H$_{22}$:** C, 90.70; H, 9.30. Found: C, 91.04; H, 8.96. Colourless oil. Isolated yield: 88% (1.04 g).
4. NMR spectra

Figure S1. $^1$H NMR spectrum of (bromoethynyl)benzene.

Figure S2. $^{13}$C NMR spectrum of (bromoethynyl)benzene.
Figure S3. $^1$H NMR spectrum of 1-bromo-1-ynes.

Figure S4. $^1$H NMR spectrum of (bromoethyl)trisopropylsilane.
Figure S5. $^{13}$C NMR spectrum of (bromoethynyl)trisopropylsilane.

$^{13}$C NMR spectrum of (bromoethynyl)trisopropylsilane.

Figure S6. $^1$H NMR spectrum of 2b.
Figure S7. $^{13}$C NMR spectrum of 2b.

Figure S8. $^{29}$Si NMR spectrum of 2b.
**Figure S9.** $^1$H NMR spectrum of 2c.

**Figure S10.** $^{13}$C NMR spectrum of 2c.
Figure S11. $^29$Si NMR spectrum of 2c.

Figure S12. $^1$H NMR spectrum of 2f.
Figure S13. $^{13}$C NMR spectrum of 2f.

Figure S14. $^{1}$H NMR spectrum of 2e. * - Traces of CHCl₃.
Figure S15. $^{13}$C NMR spectrum of 2e. * - Traces of CH$_2$Cl$_2$

Figure S16. $^1$H NMR spectrum of 2h. * - Grease.
Figure S17. $^{13}$C NMR spectrum of 2h.

$^{1}$H NMR spectrum of 2i.

(101 MHz, CDCl$_3$)

(300 MHz, CDCl$_3$)
Figure S19. $^{13}$C NMR spectrum of 2i.

Figure S20. $^1$H NMR spectrum of 2j.
Figure S21. $^{13}$C NMR spectrum of 2j.

(101 MHz, CDCl$_3$)

Figure S22. $^1$H NMR spectrum of 2l.

(300 MHz, CDCl$_3$)
Figure S23. $^{13}$C NMR spectrum of 2l.

Figure S24. $^{29}$Si NMR spectrum of 2l.
Figure S25. $^1$H NMR spectrum of 2m.

Figure S26. $^{13}$C NMR spectrum of 2m.
Figure 27. $^{29}\text{Si}$ NMR spectrum of 2m.

Figure S28. $^1\text{H}$ NMR spectrum of 2n.
Figure S29. $^{13}$C NMR spectrum of 2n.

(75 MHz, CDCl$_3$)

Figure S30. $^{29}$Si NMR spectrum of 2n.

(79 MHz, CDCl$_3$)
Figure S31. $^1$H NMR spectrum of 2o.

Figure S32. $^{13}$C NMR spectrum of 2o.
Figure S33. $^{29}$Si NMR spectrum of 2o.

Figure S34. $^1$H NMR spectrum of (2p)
Figure S35. $^{13}$C NMR spectrum of (2p)

Figure S36. $^{29}$Si NMR spectrum of (2p)
Figure S37. $^1$H NMR spectrum of 2q.

(300 MHz, CDCl$_3$)

Figure S38. $^{13}$C NMR spectrum of 2q.
Figure S39. $^{29}$Si NMR spectrum of 2q.

Figure S40. $^1$H NMR spectrum of (2r)
Figure S41. $^{13}$C NMR spectrum of (2r)

\[
\text{($i$-Pr)$_3$Si} \quad \text{($75$ MHz, CDCl$_3$)}
\]

Figure S42. $^{29}$Si NMR spectrum of (2r)

\[
\text{($i$-Pr)$_3$Si} \quad \text{($79$ MHz, CDCl$_3$)}
\]
Figure S43. $^1$H NMR spectrum of 2s.

(300 MHz, CDCl$_3$)

Figure S44. $^{13}$C NMR spectrum of 2s.

(75 MHz, CDCl$_3$)
Figure S45. $^2$SiNMR spectrum of 2s.

\[
\text{\text{(79 MHz, CDCl}_3\text{)}}
\]

Figure S46. $^1$H NMR spectrum of 2t.

\[
\text{\text{(300 MHz, CDCl}_3\text{)}}
\]
Figure S47. $^{13}$C NMR spectrum of 2t.

Figure S48. $^{29}$Si NMR spectrum of 2t.
Figure S49. $^1$H NMR spectrum of 2u.

Figure S50. $^{13}$C NMR spectrum of 2u.
Figure S51. $^{29}$Si NMR spectrum of 2u.

Figure S52. $^1$H NMR spectrum of 2v.
Figure S53. $^{13}$C NMR spectrum of 2v.

Figure S54. $^{29}$Si NMR spectrum of 2v.
Figure S55. $^1$H NMR spectrum of 2w.

(300 MHz, CDCl₃)

Figure S56. $^{13}$C NMR spectrum of 2w.

(75 MHz, CDCl₃)
Figure S57. $^1$H NMR spectrum of 2x.

Figure S58. $^{13}$C NMR spectrum of 2x.
Figure S59. $^1$H NMR spectrum of 2y.

Figure S60. $^{13}$C NMR spectrum of 2y.
Figure S61. $^1$H NMR spectrum of 2z.

Figure S62. $^{13}$C NMR spectrum of 2z.
Figure S63. $^1$H NMR spectrum of 3a.

Figure S64. $^{13}$C NMR spectrum of 3a.
Figure S65. $^{29}$Si NMR spectrum of 3a.

Figure S66. $^{11}$B NMR spectrum of 3a.
Figure S67. $^1$H NMR spectrum of 3b.

Figure S68. $^{13}$C NMR spectrum of 3b.
Figure S69. $^2$Si NMR spectrum of 3b.

Figure S70. $^1$B NMR spectrum of 3b.
Figure S71. $^1$H NMR spectrum of 3d.

Figure S72. $^{13}$C NMR spectrum of 3d.
Figure S73. $^1$B NMR spectrum of 3d.

Figure S74. $^1$H NMR spectrum of 3e.
Figure S75. $^{13}$C NMR spectrum of 3e.

Figure S76. $^{13}$C NMR spectrum of 3e.
Figure S77. $^1$H NMR spectrum of 3f. *-Grease.

Figure S78. $^{13}$C NMR spectrum of 3f. *-Grease
Figure S79. $^1$B NMR spectrum of 3f.

Figure S80. $^1$H NMR spectrum of 3g.
Figure S81. $^{13}$C NMR spectrum of 3g.

(75 MHz, CDCl$_3$)

Figure S82. $^{11}$B NMR spectrum of 3g.

(128 MHz, CDCl$_3$)
Figure S83. $^1$H NMR spectrum of 3h.

Figure S84. 1D selective gradient NOESY of 3h (freq. 1.33 ppm)
Figure S85. $^{13}$C NMR spectrum of 3h.

Figure S86. $^{11}$B NMR spectrum of 3h.
Figure S87. $^1$H NMR spectrum of 3i.

Figure S88. $^{13}$C NMR spectrum of 3i.
Figure S89. $^1$H NMR spectrum of 3j.

Figure S90. $^1$B NMR spectrum of 3i.
Figure S91. $^{13}$C NMR spectrum of 3j.

Figure S92. $^{11}$B NMR spectrum of 3j.
Figure S93. $^1$H NMR spectrum of 3m.

Figure S94. $^{13}$C NMR spectrum of 3m.
Figure S95. $^{29}$Si NMR spectrum of 3m.

Figure S96. $^{11}$B NMR spectrum of 3m.
Figure S97. $^1$H NMR spectrum of 3n.*-Grease

Figure S98. $^{13}$C NMR spectrum of 3n.*-Grease
Figure S99. $^29$Si NMR spectrum of 3n. *-Grease

Figure S100. $^{11}$B NMR spectrum of 3n.
Figure S101. $^1$H NMR spectrum of 3o. $^*-Grease.$

$^{31}$C NMR spectrum of 3o. $^*-Grease.$

(400 MHz, CDCl$_3$)

(101 MHz, CDCl$_3$)
Figure S103. $^{29}$Si NMR spectrum of 3o. *-Grease

Figure S104. $^{11}$B NMR spectrum of 3o.
Figure S105. $^1$H NMR spectrum of (3p)

Figure S106. $^{13}$C NMR spectrum of (3p)
Figure S107. $^{29}$Si NMR spectrum of (3p)

(79 MHz, CDCl₃)

Figure S108. $^{11}$B NMR spectrum of (3p)

(128 MHz, CDCl₃)
Figure S109. $^1$H NMR spectrum of 3q.

Figure S110. $^{13}$C NMR spectrum of 3q.
Figure S11. $^{11}$B NMR spectrum of 3q.

Figure S12. $^{29}$Si NMR spectrum of 3q.
Figure S113. $^1$H NMR spectrum of (3r)

Figure S114. $^{13}$C NMR spectrum of (3r)
Figure S115. $^{13}$C NMR spectrum of (3r)

Figure S116. $^{29}$Si NMR spectrum of (3r)
Figure S117. $^1$H NMR spectrum of 3s.

Figure S118. $^{13}$C NMR spectrum of 3s.
Figure S119. $^{29}$Si NMR spectrum of 3s.

Figure S120. $^{11}$B NMR spectrum of 3s.
Figure S121. $^1$H NMR spectrum of 3t.

Figure S122. $^{13}$C NMR spectrum of 3t.
Figure S123. $^1$H-$^{13}$C HSQC NMR spectrum of 3t.

Figure S124. $^1$H-$^{13}$C HMBC NMR spectrum of 3t.
Figure S125. $^{29}$Si NMR spectrum of 3t.

Figure S126. $^{11}$B NMR spectrum of 3t.
Figure S127. $^1$H NMR spectrum of 3u.

Figure S128. $^{13}$C NMR spectrum of 3u.
Figure S129. $^{29}$Si NMR spectrum of 3u.

Figure S130. $^{11}$B NMR spectrum of 3u.
Figure S131. $^1$H NMR spectrum of 3v.

Figure S132. $^{13}$C NMR spectrum of 3v.
Figure S133. $^{29}$Si NMR spectrum of $3v$.

Figure S134. $^{11}$B NMR spectrum of $3v$. 
Figure S135. $^1$H NMR spectrum of $3w$.

Figure S136. $^{13}$C NMR spectrum of $3w$. * - traces of PPh$_3$
Figure S137. $^1$H NMR spectrum of 3w.

Figure S138. $^1$H NMR spectrum of 3x/3’x.
Figure S139. $^{13}$C NMR spectrum of 3x/3'x.

Figure S140. $^1$H NMR spectrum of 3y/3'y.
Figure S141. $^1$H NMR spectrum of 3z.

Figure S142. $^{13}$C NMR spectrum of 3z.
Figure S143. $^1$H-$^{13}$C HSQC NMR spectrum of 3z.

Figure S144. $^1$H-$^{13}$C HMBC NMR spectrum of 3z.
Figure S145. $^1$H NMR spectrum of 3z.

Figure S146. $^1$H NMR spectrum of 4d. * - Grease
Figure S147. $^{13}$C NMR spectrum of 4d.

(101 MHz, CDCl$_3$)

Figure S148. $^{11}$B NMR spectrum of 4d.

(128 MHz, CDCl$_3$)
Figure S149. $^1$H NMR spectrum of 4e. * - Grease

Figure S150. $^{13}$C NMR spectrum of 4d. * - Grease
Figure S151. $^{11}$B NMR spectrum of 4d.

Figure S152. $^1$H NMR spectrum of 6.
Figure S153. $^{13}$C NMR spectrum of 6.

Figure S154. $^{29}$Si NMR spectrum of 6.
Figure S155. $^1$H NMR spectrum of 7a.

Figure S156. $^{13}$C NMR spectrum of 7a.
Figure S157. $^{29}$Si NMR spectrum of 7a.

Figure S158. $^1$H-$^{13}$C HSQC NMR spectrum of 7a.
Figure S159. $^1$H-$^{13}$C HMBC NMR spectrum of 7a.

Figure S160. Selective 1D NOESY spectrum of 7a directed at the singlet at 6.12 ppm.
Figure S161. $^1$H NMR spectrum of 7b.

Figure S162. $^{13}$C NMR spectrum of 7b. * - Unknown impurities.
Figure S163. $^{29}$Si NMR spectrum of 7b.

Figure S164. $^1$H NMR spectrum of 8.
Figure S165. $^{13}$C NMR spectrum of 8.

Figure S166. $^{29}$Si NMR spectrum of 8. * - Grease
Figure S167. $^{11}$B NMR spectrum of 8.

Figure S168. $^1$H NMR spectrum of 9.
Figure S169. $^{13}$C NMR spectrum of 9.

Figure S170. $^{29}$Si NMR spectrum of 9.
Figure S171. $^{11}$B NMR spectrum of 9.

Figure S172. Formation of a new (A) specie via addition of Bpin to [Pt(PPh$_3$)$_4$].
6. References

1. Il’inich, G. N.; Zudin, V. N.; Nosov, A. V.; Rogov, V. A.; Likholobov, V. A., The mechanism of the catalytic behaviour of platinum triphenylphosphine complexes in the ethylene hydrocarbonylation. *Journal of Molecular Catalysis A: Chemical* 1995, 101 (3), 221-235.

2. Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H., Nucleophilic addition of sulfonamides to bromoacetylenes: facile preparation of pyrroles. *Organic letters* 2011, 13 (18), 4873-4875.

3. Lutter, F. H.; Grokenberger, L.; Spieß, P.; Hammann, J. M.; Karaghiosoff, K.; Knochel, P., Cobalt-Catalyzed Cross-Coupling of Functionalized Alkylzinc Reagents with (Hetero)Aryl Halides. *Angewandte Chemie International Edition* 2020, 59 (14), 5546-5550.

4. Arisawa, M.; Tagami, Y.; Yamaguchi, M., Two types of rhodium-catalyzed CS/CS metathesis reactions: formation of CS/CS bonds and CC/SS bonds. *Tetrahedron Letters* 2008, 49 (10), 5648-5651.

5. Schwarz, H.; Köppel, C.; Bohlmann, F., Elektronenstossinduzierte fragmentierung von acetylenverbindungen—XII: Umlagerungen von bis-(trimethylsilyl)-äthern ungesättigter α,ω-diole und massenspektrometrische identifizierung isomerer phenole. *Tetrahedron* 1974, 30 (5), 689-693.

6. Pelter, A.; Hughes, R.; Smith, K.; Tabata, M., A new synthesis of unsymmetrical conjugated diynes. *Tetrahedron Letters* 1976, 17 (48), 4385-4388.

7. Li, X.; Liu, X.; Chen, H.; Wu, W.; Qi, C.; Jiang, H., Copper-Catalyzed Aerobic Oxidative Transformation of Ketone-Derived N-Tosyl Hydrazones: An Entry to Alkynes. *Angewandte Chemie* 2014, 126 (52), 14713-14717.