

Tris(biphenyl-4-yl)silyl-Endcapped Polyynes

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The use of tris(biphenyl-4-yl)silyl (TBPS) as a large protecting group for polyynes has been investigated. The basic building block, TBPS-C≡C-TMS (**1**), is synthesized in a new "one-pot" reaction through the sequential addition of lithiated nucleophiles to tetrachlorosilane. The TMS group of differentially protected **1** and the diyne **5** can be selectively removed in the presence of the TBPS group under mild conditions, allowing for the formation of TBPS-endcapped di-

and tetraynes (**3** and **9**) by oxidative homocoupling. For the triyne, TBPS-(C≡C)₃-TMS (**11**), chemoselectivity for desilylation decreases dramatically, preventing formation of the corresponding hexayne. X-ray crystallographic analysis of **3** confirms a diameter of 20 Å for the TBPS group.

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Introduction

Polyynes have shown potential for new optical materials due to their unique electronic properties.^[1,2] Furthermore, there are many naturally occurring polyynes that have been isolated, and these compounds often show interesting biological activity.^[3] Polyynes are, therefore, desirable synthetic targets, and a number of methods have been reported for their formation.^[4] The synthesis of polyynes can be plagued, however, by decrease of stability as a function of polyne length, and this often leads to decomposition of the polyne resulting from indiscriminate intermolecular reactions (polymerization). It has been shown that the stability of the polyne can be increased by placing bulky endgroups at the termini of the polyne, which act to shield the reactive polyne core from intermolecular reactions that lead to decomposition.^[2,5,6] Excellent examples of this approach have recently been reported by Hirsch and co-workers,^[5] and Gladysz and co-workers.^[6]

The bulky nature of the triisopropylsilyl (TIPS) endgroup has been utilized to increase the stability of polyynes, allowing the successful synthesis of a series of polyynes up to 20 carbon atoms in length.^[2] Increasing the size of the silyl endgroup could serve to increase the stability of the polyne even more. From simple modeling it was determined that the tris(biphenyl-4-yl)silyl (TBPS) group has over twice the diameter of the TIPS group (Figure 1).^[7] It was predicted that the large size of this endgroup should prevent the approach of extended polyne molecules to

within the 4 Å distance required for intermolecular cross-linking to occur (decomposition from polymerization).^[8] Because this endgroup was also reasonably easy to access, we explored its potential as a polyne protecting group.

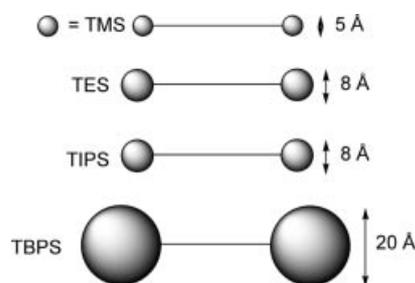
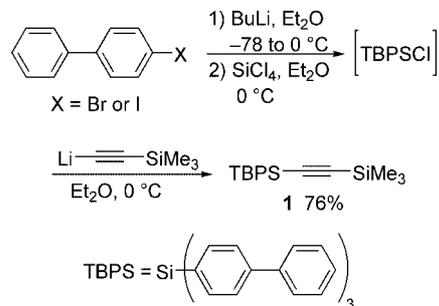


Figure 1. Approximate size relationship of silyl endgroups.

Results and Discussion

The synthesis of the first TBPS-protected target, **1**, was achieved in a one-pot reaction with yields up to 76% by the sequential addition of 3 equiv. of biphenyl-4-yllithium and 1 equiv. of (trimethylsilyl)ethynyllithium to tetrachlorosilane (Scheme 1). While the one-pot synthesis of a tetra-



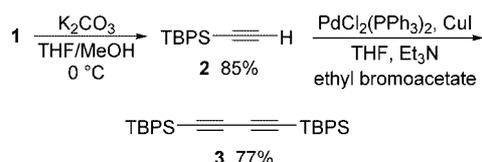
Scheme 1. "One-pot" synthesis of unsymmetrical acetylene **1**.

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arylsilane containing at least two different functional groups has been demonstrated,^[9] to the best of our knowledge this is the first example of a multi-component reaction to obtain a triaryl(ethynyl)silane. The synthesis of **1** was also successful using the corresponding biphenyl-4-yl Grignard reagent; however, the yields were lower (ca. 30%).

Under protidesilylation conditions at 0 °C, the trimethylsilyl (TMS) group of **1** could be selectively removed to yield **2** in excellent yield (Scheme 2). At higher temperatures, or prolonged exposure to these conditions, the TBPS group is also cleaved, leading to a decreased yield of **2**. The attempted synthesis of **3** using Hay^[10] conditions was unsuccessful, leading to poor yields. The synthesis of **3** has, however, been carried out in good yield under Pd-catalyzed homocoupling conditions reported by Zhang and co-workers.^[11,12]



Scheme 2. Selective protidesilylation of the TMS group followed by Pd-catalyzed homocoupling to give diyne **3**.

X-ray crystallographic characterization of **3** showed a radius of approximately 10 Å for the TBPS group and clearly demonstrates its larger size in comparison to the TIPS group (Figure 2, a).^[2] This sterically demanding endgroup places each polyyne a distance of > 8 Å from its nearest neighbor in the crystal lattice, double of that required for an intermolecular reaction to occur (Figure 2, b).^[8,13] Diyne **3** shows a melting point (296–298 °C) that is comparable to 1,4-bis(triphenylsilyl)-1,3-butadiyne (304 °C)^[14] and higher than that of 1,4-bis(methyldiphenylsilyl)-1,3-butadiyne (143 °C).^[13] These values are higher than those of trialkylsilyl-encapped diynes such as 1,4-bis(TIPS)-1,3-butadiyne (98–100 °C)^[2] and 1,4-bis(TMS)-1,3-butadiyne (107 °C).^[15] This suggests a possible trend in melting point related to structure of the terminal silyl group (i.e., aryl vs. alkyl substituents), rather than overall size.

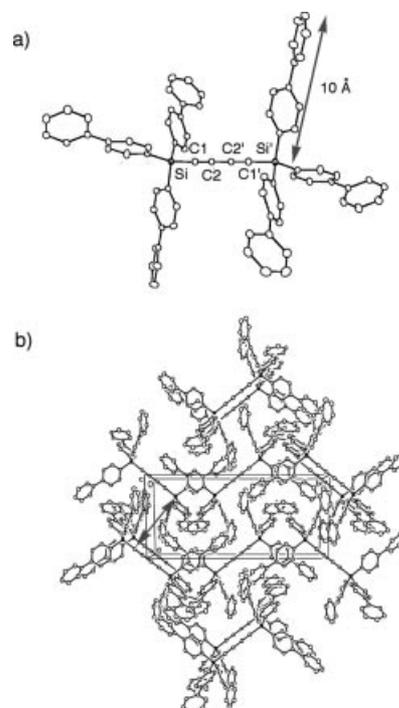


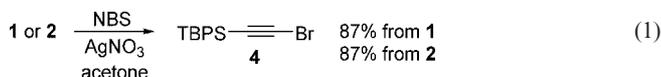
Figure 2. a) A view of molecule **3** with an arrow showing the radius of the TBPS endgroup (Si ↔ H). b) Crystal packing of **3**, with the arrow showing a distance of > 8 Å between neighboring molecules (non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, hydrogen atoms removed for clarity).

Treatment of **1** with *N*-bromosuccinimide in the presence of catalytic silver(I) nitrate gave the bromide **4** directly in excellent yield without the need for prior desilylation [Equation (1)].^[16] The synthesis of **4** could also be carried out using **2** under the same conditions.^[17] The subsequent synthesis of differentially protected **5** was accomplished under Pd-catalyzed cross-coupling conditions between **2** (or **4**) and **6** (or **7**)^[18] in moderate yield (Table 1).^[4c] The main side products from this reaction were the homocoupled product **3** and 1,4-bis(TMS)-1,3-butadiyne, which could be separated chromatographically. Many variations of this reaction were attempted with surprisingly little difference in the

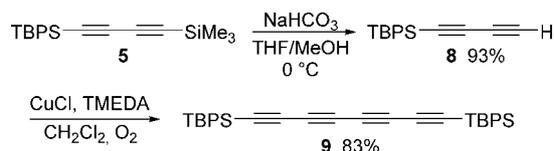
Table 1. Synthesis of **5** by Pd-catalyzed cross-coupling.

Entry	Substrate 1	Substrate 2	Catalyst system	Base	Oxidant	Yield of 5
1	4	6	[PdCl ₂ (PPh ₃) ₂]/CuI	<i>i</i> Pr ₂ NH	N/A	45%
2	4	6	[Pd(PPh ₃) ₄]/CuI	<i>i</i> Pr ₂ NH	N/A	39%
3	4	6	[PdCl ₂ (PPh ₃) ₂]/CuCl	<i>i</i> Pr ₂ NH	N/A	54%
4	2	7	[PdCl ₂ (PPh ₃) ₂]/CuI	Et ₃ N	N/A	44%
5	2	7	[PdCl ₂ (PPh ₃) ₂]/CuI	<i>i</i> Pr ₂ NH	N/A	48%
6	2	6	[PdCl ₂ (PPh ₃) ₂]/CuI	<i>i</i> Pr ₂ NH	ethyl bromoacetate	57%

yield.^[19] The best yield was ultimately obtained by coupling both terminal acetylenes (**2** and **6**) in the presence of ethyl bromoacetate as the oxidant (Entry 6).

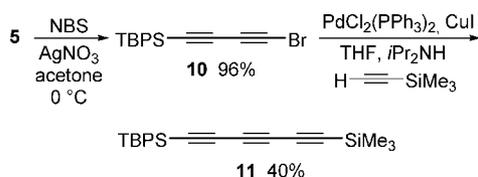


The selective deprotection of **5** proved to be more problematic than anticipated. When the conditions that were used for **1** were applied, the chemoselectivity for the TMS group over the TBPS group was considerably diminished. Using the milder base NaHCO₃ in a 1:1 mixture of THF/MeOH at low temperature gave **8** in excellent yield (Scheme 3). Standard Hay coupling conditions then gave tetrayne **9** in good yield. Tetrayne **9** shows exceptional stability in the solid state, decomposing only at temperatures above 250 °C. By way of comparison, the analogous 1,8-bis(TIPS)tetrayne melts prior to decomposition (M.p. 72–75 °C),^[2] while 1,8-bis(TMS)- and 1,8-bis(triethylsilyl)tetraynes show melting points of 94 °C^[15] and 40 °C,^[20] respectively.



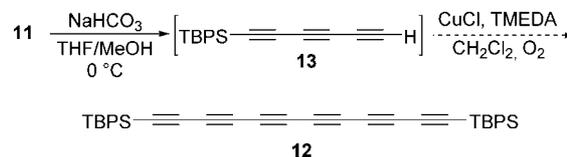
Scheme 3. Desilylation of **5** using mild basic conditions followed by Hay coupling to give tetrayne **9**.

The in situ desilylation/bromination of **5** giving **10** was achieved in excellent yield by cooling the reaction mixture to 0 °C (Scheme 4). An unfortunate problem with this reaction was that it was very slow, requiring 3–6 d to reach completion. Higher temperatures, however, led to a decrease in selectivity. The rate of the reaction could be enhanced by adding five times the amount of silver(I) nitrate, allowing for the complete reaction in 24 h. An interesting spectral feature for **10** is found in the ¹³C NMR spectrum, where the C(1) carbon atom resonates at $\delta = 42.4$ ppm due to the presence of bromine and the “heavy atom effect”.^[21] Cross-coupling with (trimethylsilyl)acetylene gave the unsymmetrical triyne **11** in moderate yield.



Scheme 4. The in situ desilylation/bromination of **5** followed by Pd-catalyzed cross-coupling toward **11**.

The synthesis of hexayne **12** from triyne **11** proved to be frustratingly difficult due to the complete lack of chemoselectivity in the desilylation step (Scheme 5). Using the mildest conditions, only a trace amount of **13** was detected by thin-layer chromatography. The crude reaction mixture was nonetheless subjected to Hay coupling conditions without prior purification in the hope of obtaining quantities of hexayne **12** sufficient for characterization. Only a trace amount of material was obtained, which proved to be difficult to purify and characterize. Due to the apparent chemical instability of the TBPS group, no further attempts were made to isolate or synthesize the hexayne **12**.



Scheme 5. Attempted selective desilylation of **11** using mild basic conditions followed by Hay coupling to give hexayne **12**.

Conclusions

A new and efficient one-pot procedure has been developed for the formation of an ethynylsilane (**1**) substituted with a tris(biphenyl-4-yl)silyl (TBPS) endgroup. From the precursor **1**, the synthesis of unsymmetrical mono-, di- and triynes differentially protected with the TBPS and TMS endgroups has been achieved in good yields. Symmetrical di- and tetraynes substituted at both ends with the TBPS group have been synthesized by oxidative homocoupling. The large size of the TBPS endgroup has been demonstrated by X-ray crystallography of the diyne **3**. Unfortunately, the inability to selectively remove a TMS group in the presence of the TBPS endgroup of longer precursors such as triyne **11** has, to date, prevented the synthesis of longer derivatives.

Experimental Section

General Procedures and Methods: Reagents (reagent grade) were purchased from commercial suppliers and used without further purification. THF and Et₂O were distilled from sodium/benzophenone. Evaporation and concentration in vacuo was done at H₂O aspirator pressure. All reactions were performed in standard, dry glassware under N₂. Column chromatography: Silica gel 60 (230–400 mesh) from Rose Scientific Ltd. Thin-layer chromatography (TLC): aluminum sheets covered with silica gel 60 F₂₅₄ from Macherey–Nagel; visualization by UV light. M.p. (uncorrected): Gallenkamp apparatus. IR spectra [cm⁻¹]: Nicolet Magna 750 FTIR (cast film) or Nic-Plan FTIR Microscope (solids). ¹H and ¹³C NMR: Varian Inova 400, and 500, Varian Mercury 400 or Varian Unity 500 at room temp. in CDCl₃; solvent peaks ($\delta = 7.24$ ppm for ¹H and 77.0 ppm for ¹³C, respectively) as reference. EI MS (*m/z*): Kratos MS50 instrument or Voyager Elite MALDI; the matrix employed was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylid-

ene]malononitrile (DCTB). Elemental analyses were performed by the Microanalytical Laboratory at the University of Alberta.

X-ray Crystallography: Unit cell parameters and intensity data were obtained with a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated Mo- K_{α} radiation (0.71073 Å). Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. The structures were solved by direct methods using SHELXS-86^[22] and refined by full-matrix least squares on F^2 using SHELXL-93.^[23] The crystallization of **3** was done by slow concentration of a solution of **3** in CH_2Cl_2 /toluene (1:9) at room temp. $\text{C}_{54}\text{H}_{36}\text{Si}_2$, $M = 1023.4$; crystal dimensions: $0.54 \times 0.34 \times 0.28$ mm; crystal system: monoclinic; space group $P2_1/c$ (no. 14), $a = 10.647(2)$, $b = 22.251(4)$, $c = 14.926(3)$ Å; $\beta = 107.929(3)^\circ$; $V = 3364.2(11)$ Å³, $Z = 2$; $\rho_{\text{calcd.}} = 1.192$ g cm⁻³; $\mu = 0.101$ mm⁻¹; absorption correction by multi-scan (SADABS); range of transmission factors 0.9723–0.9475; number of observed reflections 3650; number of independent reflections 5924; $R_1 [F_o^2 \geq 2\sigma(F_o^2)] = 0.0645$; $wR_2 [F_o^2 \geq 3\sigma(F_o^2)] = 0.1701$; $T = -80$ °C; scan mode: ω scans (0.3°) (20 s exposures); largest difference peak and hole 0.588 and -0.265 e Å⁻³. CCDC-623034 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-(TBPS)-2-(TMS)ethyne (1): To a solution of 4-iodobiphenyl (4.279 g, 15.27 mmol) in dry Et_2O (50 mL) at -78 °C under N_2 was added dropwise BuLi (7.3 mL, 2.5 M in hexanes, 18 mmol) over a period of 5 min, and the solution was warmed to 0 °C over a period of 30 min. This solution was added to a solution of SiCl_4 (0.742 g, 0.500 mL, 4.37 mmol) in dry Et_2O (10 mL) through a cannula and the mixture was warmed to room temp. over a period of 10 min and stirred for 1.5 h (solution A). Concurrently, to a solution of (TMS)acetylene (1.28 g, 1.84 mL, 13.1 mmol) in dry Et_2O (10 mL) at -78 °C was added dropwise BuLi (5.2 mL, 2.5 M in hexanes, 13 mmol) over a period of 5 min, and the reaction mixture was warmed to 0 °C over a period of 30 min (solution B). Solution B was added to solution A through a cannula and the mixture stirred under N_2 at room temp. for 7 h. The reaction was quenched with saturated aqueous NH_4Cl (5 mL) and H_2O was then added to dissolve the inorganic salts. The organic layer was washed with brine and then dried with MgSO_4 . The crude product was purified by column chromatography (silica gel, CH_2Cl_2 /hexanes, 1:4) to yield **1** (1.95 g, 76%) as a white solid. M.p. 142–144 °C. $R_f = 0.49$ (CH_2Cl_2 /hexanes, 1:4). IR (microscope): $\tilde{\nu} = 3024, 2955, 1597, 1386, 1248, 1116$ cm⁻¹. ¹H NMR (500 MHz, CDCl_3): $\delta = 7.81$ (d, $^3J = 7.8$ Hz, 6 H), 7.66 (d, $^3J = 7.8$ Hz, 6 H), 7.64 (d, $^3J = 7.5$ Hz, 6 H), 7.46 (app t, $^3J = 7.5$ Hz, 6 H), 7.37 (t, $^3J = 7.5$ Hz, 3 H), 0.31 (s, 9 H) ppm. ¹³C NMR (125 MHz, CDCl_3): $\delta = 142.7, 140.9, 136.1, 132.1, 128.8, 127.5, 127.2, 126.8, 120.0, 107.8, -0.1$ ppm. EI HRMS: calcd. for $\text{C}_{41}\text{H}_{36}\text{Si}_2$ 584.2355 [M^+], found 584.2346. $\text{C}_{41}\text{H}_{36}\text{Si}_2$ (584.90): calcd. C 84.19, H 6.20; found C 84.22, H 6.32.

(TBPS)acetylene (2): A solution of **1** (2.143 g, 3.664 mmol) in a 1:1 mixture of THF (15 mL) and MeOH (15 mL) was cooled to 0 °C and K_2CO_3 (0.506 g, 3.66 mmol) was added. After stirring at 0 °C for 1 h, H_2O (10 mL) was added and the mixture extracted with Et_2O (100 mL). The organic layer was washed with brine and dried with MgSO_4 . The crude product was purified by column chromatography (silica gel, CH_2Cl_2 /hexanes, 1:2) to yield **2** (1.601 g, 85%) as a white solid. M.p. 172–175 °C. $R_f = 0.46$ (CH_2Cl_2 /hexanes, 1:2). IR (CH_2Cl_2 , cast film): $\tilde{\nu} = 3267, 3024, 2035, 1596, 1117$ cm⁻¹. ¹H NMR (400 MHz, CDCl_3): $\delta = 7.79$ (d, $^3J = 8.0$ Hz, 6 H), 7.64 (d, $^3J = 8.0$ Hz, 6 H), 7.60 (d, $^3J = 7.4$ Hz,

6 H), 7.44 (app t, $^3J = 7.4$ Hz, 6 H), 7.35 (t, $^3J = 7.4$ Hz, 3 H), 2.85 (s, 1 H) ppm. ¹³C NMR (125 MHz, CDCl_3): $\delta = 142.9, 140.8, 136.0, 131.4, 128.8, 127.6, 127.2, 126.9, 98.1, 85.3$ ppm. EI HRMS: calcd. for $\text{C}_{38}\text{H}_{28}\text{Si}$ 512.1960 [M^+], found 512.1958. $\text{C}_{38}\text{H}_{28}\text{Si}$ (512.71): calcd. C 89.02, H 5.50; found C 88.76, H 5.74.

1,4-Bis(TBPS)-1,3-butadiyne (3): To a mixture of $[\text{PdCl}_2(\text{PPh}_3)_2]$ (10 mg, 0.016 mmol), CuI (3 mg, 0.02 mmol) and Et_3N (95 mg, 0.13 mL, 0.94 mmol) was added **2** (200 mg, 0.390 mmol) in THF (5 mL). Ethyl bromoacetate (65 mg, 43 μL , 0.39 mmol) was added and the mixture stirred at room temp. under N_2 for 24 h. H_2O (5 mL) was added and the resulting mixture extracted with CH_2Cl_2 (2×20 mL). The organic layers were combined, washed with brine and dried with MgSO_4 . The resulting solution was concentrated under vacuum. Et_2O was added to the crude product, which formed a precipitate. The mixture was filtered and the solid washed with Et_2O to give **3** (0.156 g, 77%) as a white solid. M.p. 296–298 °C. $R_f = 0.43$ (CH_2Cl_2 /hexanes, 1:2). IR (microscope): $\tilde{\nu} = 3024, 2068, 1595, 1385, 1115$ cm⁻¹. ¹H NMR (400 MHz, CDCl_3): $\delta = 7.78$ (d, $^3J = 7.9$ Hz, 12 H), 7.65 (d, $^3J = 7.9$ Hz, 12 H), 7.60 (d, $^3J = 7.5$ Hz, 12 H), 7.43 (app t, $^3J = 7.5$ Hz, 12 H), 7.34 (t, $^3J = 7.5$ Hz, 6 H) ppm. ¹³C NMR (125 MHz, CDCl_3): $\delta = 143.1, 140.8, 136.1, 130.9, 128.8, 127.7, 127.2, 127.0, 92.3, 82.4$ ppm. MALDI MS (DCTB): m/z (%) = 1272.5 (100) [M^+ + matrix], 1022.4 (30) [M^+].

1-Bromo-2-(TBPS)ethyne (4): To a solution of **1** (163 mg, 0.279 mmol) and *N*-bromosuccinimide (58 mg, 0.33 mmol) in acetone (10 mL) was added AgNO_3 (5 mg, 0.03 mmol). The mixture was stirred at room temp. under N_2 for 30 min. H_2O (5 mL) was added and the resulting mixture extracted with hexanes (2×20 mL). The organic layers were combined, washed with brine and dried with MgSO_4 . The crude product was purified by column chromatography (silica gel, CH_2Cl_2 /hexanes, 1:2) to yield **4** (143 mg, 87%) as a white solid. M.p. 166–168 °C. $R_f = 0.61$ (CH_2Cl_2 /hexanes, 1:2). IR (CH_2Cl_2 , cast film): $\tilde{\nu} = 3060, 3025, 2122, 1596, 1386, 1117$ cm⁻¹. ¹H NMR (500 MHz, CDCl_3): $\delta = 7.78$ (d, $^3J = 8.0$ Hz, 6 H), 7.65 (d, $^3J = 8.0$ Hz, 6 H), 7.62 (d, $^3J = 7.5$ Hz, 6 H), 7.45 (app t, $^3J = 7.5$ Hz, 6 H), 7.36 (t, $^3J = 7.5$ Hz, 3 H) ppm. ¹³C NMR (125 MHz, CDCl_3): $\delta = 143.0, 140.8, 136.0, 131.4, 128.8, 127.6, 127.2, 126.9, 82.5, 67.2$ ppm. EI HRMS: calcd. for $\text{C}_{38}\text{H}_{27}\text{Si}^{\text{Br}}$ 592.1045 [M^+], found 592.1048. $\text{C}_{38}\text{H}_{27}\text{BrSi}$ (591.61): calcd. C 77.15, H 4.60; found C 77.40, H 4.67.

1-(TBPS)-4-(TMS)-1,3-butadiyne (5): To a mixture of **4** (208 mg, 0.352 mmol) and (TMS)acetylene (**6**) (70 mg, 0.10 mL, 0.71 mmol) in THF (5 mL) was added $[\text{PdCl}_2(\text{PPh}_3)_2]$ (12 mg, 0.018 mmol), CuI (3 mg, 0.02 mmol) and *t*- Pr_2NH (0.18 g, 0.25 mL, 1.8 mmol) in that order. The mixture was stirred at room temp. under N_2 for 2 h. H_2O (5 mL) was added and the resulting mixture was extracted with Et_2O (2×20 mL). The organic layers were combined, washed with brine and dried with MgSO_4 . The crude product was purified by column chromatography (silica gel, EtOAc /hexanes, 1:10) to give **5** (96 mg, 45%) as a white solid. M.p. 222–223 °C. $R_f = 0.55$ (CH_2Cl_2 /hexanes, 1:2). IR (microscope): $\tilde{\nu} = 3073, 3025, 2961, 2070, 1597, 1386, 1253, 1118$ cm⁻¹. ¹H NMR (400 MHz, CDCl_3): $\delta = 7.76$ (d, $^3J = 8.1$ Hz, 6 H), 7.63 (d, $^3J = 8.1$ Hz, 6 H), 7.60 (d, $^3J = 7.4$ Hz, 6 H), 7.44 (app t, $^3J = 7.4$ Hz, 6 H), 7.35 (t, $^3J = 7.4$ Hz, 3 H), 0.22 (s, 9 H) ppm. ¹³C NMR (125 MHz, CDCl_3): $\delta = 143.0, 140.8, 136.1, 131.1, 128.8, 127.6, 127.2, 126.9, 92.4, 88.1, 87.8, 80.5, -0.5$ ppm. EI HRMS: calcd. for $\text{C}_{43}\text{H}_{36}\text{Si}_2$ 608.2355 [M^+], found 608.2360.

1-(TBPS)-1,3-butadiyne (8): A solution of **5** (31 mg, 0.051 mmol) in a 1:1 mixture of THF (5 mL) and MeOH (5 mL) was cooled to 0 °C and NaHCO_3 (21 mg, 0.25 mmol) was added. After stirring

at 0 °C for 28 h, H₂O (10 mL) was added and the mixture extracted with hexanes (2 × 30 mL). The organic layer was washed with brine and dried with MgSO₄. The crude product was purified by column chromatography (silica gel, CH₂Cl₂/hexanes, 1:3) to yield **8** (25 mg, 93%) as a colorless oil: *R*_f = 0.50 (CH₂Cl₂/hexanes, 1:2). IR (CH₂Cl₂, cast film): $\tilde{\nu}$ = 3272, 3024, 2188, 2035, 1596, 1116 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 7.78 (d, ³*J* = 8.0 Hz, 6 H), 7.66 (d, ³*J* = 8.0 Hz, 6 H), 7.62 (d, ³*J* = 7.5 Hz, 6 H), 7.45 (app t, ³*J* = 7.5 Hz, 6 H), 7.37 (t, ³*J* = 7.5 Hz, 3 H), 2.25 (s, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 143.1, 140.8, 136.1, 130.8, 128.8, 127.7, 127.2, 126.9, 91.7, 79.6, 68.4, 68.2 ppm. EI HRMS: calcd. for C₄₀H₂₈Si 536.1960 [M⁺], found 536.1989.

1,8-Bis(TBPS)-1,3,5,7-octatetrayne (9): To a mixture of CuCl (4 mg, 0.05 mmol) in CH₂Cl₂ (5 mL) was added TMEDA (10 mg, 14 μ L, 0.090 mmol). O₂ was bubbled through the solution for 5 min and a solution of **8** (24 mg, 0.045 mmol) in CH₂Cl₂ (1 mL) was added and stirred for 5 min. The reaction mixture was passed through a plug of silica gel with CH₂Cl₂ and then concentrated under vacuum to give **9** (20 mg, 83%) as a yellow solid. M.p. 273–275 °C (decomposition observed at > 250 °C). *R*_f = 0.43 (CH₂Cl₂/hexanes, 1:2). IR (microscope): $\tilde{\nu}$ = 3071, 3024, 2041, 1595, 1386, 1115 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.76 (d, ³*J* = 8.0 Hz, 12 H), 7.66 (d, ³*J* = 8.0 Hz, 12 H), 7.61 (d, ³*J* = 7.5 Hz, 12 H), 7.45 (app t, ³*J* = 7.5 Hz, 12 H), 7.36 (t, ³*J* = 7.5 Hz, 6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 143.3, 140.7, 136.1, 130.4, 128.8, 127.7, 127.2, 127.0, 91.8, 83.3, 63.5, 62.9 ppm. MALDI MS (DCTB): *m/z* (%) = 1321.6 (100) [M⁺ + matrix + H].

1-Bromo-4-(TBPS)-1,3-butadiyne (10): A solution of **5** (28 mg, 0.046 mmol) and *N*-bromosuccinimide (18 mg, 0.10 mmol) in acetone (5 mL) was cooled to 0 °C and AgNO₃ (5 mg, 0.03 mmol) was added. The mixture was stirred at 0 °C under N₂ for 24 h. H₂O (10 mL) was added and the resulting mixture extracted with hexanes (2 × 20 mL). The organic layers were combined, washed with brine and dried with MgSO₄. The crude product was purified by column chromatography (silica gel, EtOAc/hexanes, 1:10) to yield **10** (27 mg, 96%) as a pale yellow oil: *R*_f = 0.49 (CH₂Cl₂/hexanes, 1:2). IR (CH₂Cl₂, cast film): $\tilde{\nu}$ = 3057, 3024, 2247, 2179, 2093, 1596, 1117 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, ³*J* = 8.0 Hz, 6 H), 7.65 (d, ³*J* = 8.0 Hz, 6 H), 7.62 (d, ³*J* = 7.4 Hz, 6 H), 7.45 (app t, ³*J* = 7.4 Hz, 6 H), 7.36 (t, ³*J* = 7.4 Hz, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 143.1, 140.8, 136.1, 130.9, 128.8, 127.7, 127.2, 126.9, 92.4, 78.3, 66.1, 42.4 ppm. EI HRMS: calcd. for C₃₆H₂₇Si 487.1882 [M⁺ - C₄Br], found 487.1890.

1-(TBPS)-6-(TMS)-1,3,5-hexatriyne (11): To a mixture of **10** (141 mg, 0.229 mmol) and (TMS)acetylene (112 mg, 161 μ L, 1.14 mmol) in THF (25 mL) was added [PdCl₂(PPh₃)₂] (8 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol) and *i*Pr₂NH (116 mg, 161 μ L, 1.15 mmol) in that order. The mixture was stirred at room temp. under N₂ for 18 h. The reaction mixture was concentrated to ca. 5 mL, then co-evaporated with 2 × 30 mL of CH₂Cl₂. The crude product was purified by column chromatography (silica gel, CH₂Cl₂/hexanes, 1:4) to give **11** (58 mg, 40%) as a yellow solid. M.p. 142–144 °C (decomposition observed at > 100 °C). *R*_f = 0.34 (CH₂Cl₂/hexanes, 1:4). IR (microscope): $\tilde{\nu}$ = 3060, 3025, 2960, 2160, 2068, 1597, 1386, 1245, 1114 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 7.78 (d, ³*J* = 8.1 Hz, 6 H), 7.65 (d, ³*J* = 8.1 Hz, 6 H), 7.61 (d, ³*J* = 7.4 Hz, 6 H), 7.45 (app t, ³*J* = 7.4 Hz, 6 H), 7.36 (t, ³*J* = 7.4 Hz, 3 H), 0.21 (s, 9 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 143.2, 140.7, 136.1, 130.7, 128.8, 127.7, 127.2, 127.0, 92.2, 88.7, 87.7, 82.1, 63.5, 61.9, -0.6 ppm. EI HRMS: calcd. for C₄₅H₃₆Si₂ 632.2355 [M⁺], found 632.2348.

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Attempts to refine peaks of residual electron density as solvent toluene carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure (P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194–201) as implemented in PLATON (A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C34; *PLATON – a multipurpose crystallographic tool*, Utrecht University, Utrecht, The Netherlands). A total solvent-accessible void volume of 738 Å³ with a total electron count of 197 (consistent with four molecules of solvent toluene) was found in the unit cell.

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