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An Iterative Method for the Synthesis of Symmetric Polyynes

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An iterative synthetic route for obtaining symmetric polyynes was developed, consisting of a series of iodination and Stille coupling reactions. The starting materials employed in this pathway are simple and can be prepared easily. Polyynes containing up to seven C≡C bonds were synthesized using this method. This route is particularly effective for accessing polyynes with an odd number of C≡C bonds and has allowed for the synthesis of a new iodine-capped polyyne, diiododecapentayne.

Introduction

The synthesis of polyynes has been the subject of much research in recent years, based on potential applications in optics and electronics.[1] Third-order nonlinear optical properties are of particular interest, with theoretical and experimental studies demonstrating that sp-hybridized carbon chains have large multiphoton absorption cross-sections.[1,2] Several groups have examined the mechanism of charge transport in polyynes and have suggested that they can behave as molecular wires.[3] Polyyne chains may also be used as models to predict the properties of carbyne, the putative linear allotrope of carbon, and more generally to understand the fundamentals of conjugation.[1] Polyynes have also been pursued as possible precursors to polydiacetylenes, nanotubes, fullerenes, graphitic materials, and other carbon-rich compounds.[4] In addition to applications in materials science, polyynes occur in a variety of natural products with biological activity.[5]

Walton and co-workers pioneered the synthesis of extended polyynes with up to 16 C≡C bonds using Hay coupling conditions.[6] Diederich and co-workers used solution-spray flash vacuum pyrolysis (SS-FVP) to form shorter polyynes from substituted 3,4-dialkynyl-3-cyclobutene-1,2-diones.[7] Tykwinski and co-workers recently synthesized chains of as many as 22 C≡C bonds by combining traditional oxidative couplings with the Fritsch–Buttenburg–Wiechell (FBW) rearrangement of dibromoolefinic precursors.[8] While these methods have proven effective in many instances, they require the use of unstable terminal alkynes, complex starting materials, or harsh reactions conditions. Therefore, we envisioned an iterative pathway to moderate-length polyynes based on symmetric couplings to diiodopolyyne intermediates under mild reaction conditions.

Few examples of cross-coupling reactions using diiodopolyynes have been reported. Hirsch and co-workers used Cadiot–Chodkiewicz conditions to couple bridged terminal alkynes and diiodoacetylene, which resulted in low yields and product mixtures.[9] Similarly, after the methods described here were under development, the synthesis of diarylpolyynes from diiodoacetylene was reported by Cataldo and co-workers. These reactions yielded mixtures of polyynes of different lengths, and the individual components were not isolated.[10] In addition, Bruce and co-workers reported the palladium-catalyzed cross-coupling of diiodoalkynes and gold(I) alkynyl complexes.[3a,11] These specific examples highlight the potential of diiodopolyynes to provide a general synthetic route towards symmetric polyynes.

The method presented here provides for the synthesis and isolation of polyynes containing four to seven C≡C bonds, via a series of iodination and Stille coupling reactions (Scheme 1). Palladium-catalyzed coupling reactions bring together short symmetric iodine-capped polyyne rods and silyl-protected tin acetylides. Although there are relatively few examples of Stille-type alkyne–alkyne couplings,[12] we have found efficient conditions for this reaction. The resulting silyl-capped polyyne can subsequently be iodinated to make a new diiodopolyyne for successive coupling reactions. Each iodination/coupling cycle symmetrically increases the length of the resulting polyyne by four carbon atoms, without requiring the preparation or isolation of a terminal alkyne intermediate. The diiodopolyynes that are central to this synthesis are relatively stable compared to analogous terminal or bromoalkynes, thus adding to the appeal of this route. Phenyl alkynyl tin reagents can also be used to prepare the corresponding phenyl-capped polyynes. This method is especially beneficial for providing a straightforward route of accessing symmetric polyynes with an odd number of C≡C bonds.

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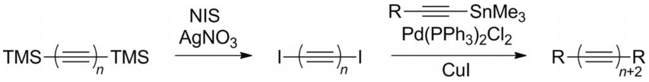


Scheme 1. General scheme for the synthesis of symmetric polyynes.

Results and Discussion

One major advantage of this route is that the required starting materials can be obtained by straightforward synthetic procedures.[13] The diiodoalkyne precursors in this method are prepared via direct iodination of trimethylsilyl-capped alkynes using $AgNO_3$ and *N*-iodosuccinimide (NIS).[13a] Incorporating different tin acetylides (i.e., **1b**–**d**) allows for end cap variety among the polyynes that have been obtained using this method. Trimethylsilyl, triisopropylsilyl, and phenyl tin acetylides, prepared according to literature procedures,[13b] are coupled to C_4I_2 (**2a**), C_6I_2 (**3a**), C_8I_2 (**4a**), and $C_{10}I_2$ (**5a**) to produce the respective tetraynes (i.e., **4b**, **4c**), pentaynes (i.e., **5b**–**d**), hexaynes (i.e., **6b**, **6d**), and heptaynes (i.e., **7b**), as shown in Table 1. Yields for the products are largely dependent on the techniques required for isolation. Byproduct bis(trimethylsilyl)butadiyne (**2c**) is removed from the trimethylsilyl-capped polyynes using vacuum sublimation rather than chromatography, thus avoiding the difficulty of separating compounds with similar polarity on silica. Compounds **4b** and **5b** are isolated via recrystallization techniques. However, similar methods were not effective for purifying longer analogs. The low yield of heptayne **7b** is due to difficulties in isolating the product, but also appears to result from the instability of intermediate diiodopentayne **5a**, as described below. Attempts to prepare a heptayne with bulkier end caps using the tin acetylide of (*tert*-butyl)dimethylsilyl (TBDMS) ethyne were not successful. Thus, heptaynes appear to strain the limits for this method, although there are very few alternatives for heptayne synthesis.

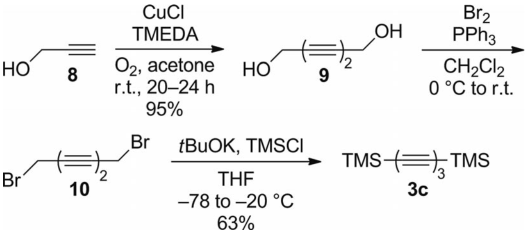
Polyynes containing an even number of C≡C bonds are derived here from diiodobutadiyne (**2a**), which can be obtained from the iodination of commercially available bis(trimethylsilyl)butadiyne (**2c**). Polyynes containing an odd number of C≡C bonds are accessed from diiodohexatriyne (**3a**). Trimethylsilyl-capped precursor **3c** is not commercially available; however, it can be synthesized from propargyl alcohol in three straightforward steps, as shown in Scheme 2.[15] Our initial route towards **3c** encompassed the synthesis of 2,4-hexadiyn-1,6-bis(*p*-toluenesulfonate), as reported by Rubin and co-workers,[7] but we found that going through dibromohexadiyne **10** greatly minimized the risk of undesired polymerization.

To avoid the potential toxicity of the tin reagents and byproducts in the Stille reaction, the synthesis of polyynes using Negishi coupling conditions was also explored.[16] TMS, TIPS, and Ph-capped tetraynes were targeted from reaction of diiodobutadiyne (**2a**) with the corresponding zinc acetylide. Unfortunately, preparing the zinc acetylides proved unreliable in these experiments, and the product yields were typically significantly lower than those obtained

Table 1. Polyyne synthesis via Stille coupling.[a]

Diiodopolyyne	Sn Acetylide	Product	Temperature [°C]	Yield[b] [%]
$I-\equiv-\equiv-I$ **2a**	$\text{TIPS}-\equiv-\text{SnMe}_3$ **1b**	$\text{TIPS}-\equiv-(\equiv)_2-\equiv-\text{TIPS}$ **4b**	25	77
2a	$\text{TMS}-\equiv-\text{SnMe}_3$ **1c**	$\text{TMS}-\equiv-(\equiv)_2-\equiv-\text{TMS}$ **4c**	0	59
$I-\equiv-\equiv-\equiv-I$ **3a**	**1b**	$\text{TIPS}-\equiv-(\equiv)_3-\equiv-\text{TIPS}$ **5b**	0	40
3a	**1c**	$\text{TMS}-\equiv-(\equiv)_3-\equiv-\text{TMS}$ **5c**	0	61
3a	$\text{Ph}-\equiv-\text{SnMe}_3$ **1d**	$\text{Ph}-\equiv-(\equiv)_3-\equiv-\text{Ph}$ **5d**	0	28
$I-\equiv-(\equiv)_2-\equiv-I$ **4a**	**1b**[c]	$\text{TIPS}-\equiv-(\equiv)_4-\equiv-\text{TIPS}$ **6b**	0	47
4a	**1d**	$\text{Ph}-\equiv-(\equiv)_4-\equiv-\text{Ph}$ **6d**	0	16
$I-\equiv-(\equiv)_3-\equiv-I$ **5a**	**1b**	$\text{TIPS}-\equiv-(\equiv)_5-\equiv-\text{TIPS}$ **7b**	–15	10

[a] Compounds are numbered according to the number of triple bonds they contain, with letters designating the end groups: **a** = iodine, **b** = TIPS, **c** = TMS, **d** = Ph. Conditions: Mole ratio of organostannane/diiodoalkyne = 2:1, $Pd(PPh_3)_2Cl_2$ (12 mol-%), CuI (23 mol-%),[14] THF, 10 h. [b] All yields are for the isolated product, based on diiodopolyyne starting material. [c] An excess amount of the organostannane was used, CuI (13 mol-%).



Scheme 2. Synthesis of bis(trimethylsilyl)hexatriyne (**3c**).

under Stille coupling conditions. Similarly, copper acetylides were prepared and employed under Cadiot–Chodkiewicz conditions.[17] Unfortunately, these reactions did not favor cross-coupling, as product mixtures consistently contained significant amounts of homocoupled starting materials.

Stille couplings between tin acetylides and haloalkynes are relatively rare, with only a few reported examples.[12] We therefore carried out model experiments based on the Stille coupling of iodophenylacetylene and trimethylsilyl tin acetylide **1c**. These experiments indicated that the concentration of copper iodide is particularly important to promote cross-coupling in this reaction. Previous studies of the coupling of tin acetylides with aryl halides have suggested that a copper cocatalyst transmetalates with the organostannane to form a copper acetylide, which in turn may transmetalate with palladium at a faster rate than the stannane alone.[18] The presence of copper iodide thus minimizes homocoupling of the iodoalkyne. Optimizing the reaction conditions gave catalyst ratios for the symmetric double coupling of the diiodopolyynes of 12 mol-% palladium (6 mol-% per iodine) and 23 mol-% copper (11.5 mol-% per iodine).

In addition to catalyst load, we examined the order and rate of reagent addition. Initial investigations revealed the importance of both these parameters. Experimental trials where compound **2a** and tin acetylide **1c** were combined in solution and then slowly added together to the catalyst mixture provided better results than when all reagents were combined in one pot. This method increases the effective concentration of the catalyst, relative to the alkyne reactants. Adding the diiodoalkyne and the tin acetylide to the catalyst mixture over a period of 10–11 h proved optimal, whereas shorter addition times resulted in increased homocoupling of the tin acetylide, as well as the unwanted formation of longer polyynes, as determined by ^{13}C NMR spectroscopy. Rapid addition evidently promotes decomposition of diiodobutadiyne (**2a**), via successive homocoupling reactions. However, diyne **2c**, formed from homocoupling of organostannane **1c**, is easily separated from the product using vacuum sublimation. The ability to recover the diyne and use it in future iodination reactions adds to the overall efficiency of this method.

The procedure used for iodinating the silyl-capped polyynes required modification to prepare longer diiodoalkyne intermediates. Iodination of longer chains was observed to proceed more slowly than shorter analogs, which may be due to complexation of the silver to the internal C≡C bonds. To compensate for this effect and to enhance the rate of reaction for longer polyynes, the concentration of $AgNO_3$ and NIS was increased. By reducing the time required for complete iodination, we minimized decomposition of the target diiodopolyynes.

As part of this iterative route, we have prepared the novel compound 1,10-diiodo-1,3,5,7,9-decapentayne (**5a**). This diiodopolyyne is less stable than its shorter analogs, decomposing rapidly at room temperature and exploding at 55–56 °C. When working with this compound, it is crucial to keep it in solution and cooled below 0 °C, as black insoluble material forms in solution relatively quickly above 0 °C. Keeping the diiodopentayne in a dry ice/acetone bath allowed successful reaction with triisopropyl tin acetylide **1b** to make bis(triisopropylsilyl)heptayne (**7b**), which has also not been reported until now.

The diiodopolyynes prepared here are interesting compounds in their own right. Based on their Lewis acidity, they can be aligned in the solid state for topochemical polymerization, as a means of accessing carbon-rich materials.[19] We have prepared the ordered polymer of diiodobutadiyne (**2a**) and are currently pursuing methods for controlled polymerization of the longer analogs.

Conclusions

The iterative iodination/Stille coupling method described here has proven to be an effective route towards tetraynes, pentaynes, and hexaynes. Polyynes with an even number of C≡C bonds are all derived from bis(trimethylsilyl)butadiyne (**2c**), whereas the polyynes with an odd number of C≡C bonds are prepared from bis(trimethylsilyl)hexatriyne (**3c**). The choice of end group is not made until the final step, thus adding flexibility to this route. The decreased stability of the longer diiodoalkyne precursors is addressed by simple modifications in temperature, reaction rate, and order of reagent addition. Thus, starting from simple building blocks, we can prepare polyynes with a range of lengths and end groups.

Experimental Section

General Methods: Reagents were purchased reagent grade from Aldrich, Fischer Scientific/Acros Organics, VWR, Strem, or GFS Chemicals and were used without further purification, except where stated. Tetrahydrofuran was distilled under an atmosphere of argon from sodium/benzophenone. Copper iodide was purified by recrystallization. High-purity hexanes should be used when preparing silyl-capped polyynes to avoid possible grease contamination caused by the low polarity of these compounds. All reactions were performed under an inert argon atmosphere, unless stated otherwise. Iodination and coupling reactions of polyynes were carried out in aluminum-foil-wrapped flasks in an unlighted hood. All diiodopolyynes were washed with aqueous $Na_2S_2O_3$ immediately prior to use. Column chromatography: alumina (50–200 mesh) from Acros Organics, silica gel-60 (230–400 mesh) from Sorbent Technologies. Thin-Layer Chromatography (TLC): plastic sheets covered with silica gel purchased from Acros. Melting points were measured with a Thomas Hoover Capillary melting point apparatus. ^1H NMR and ^{13}C NMR spectra were obtained by using Varian Gemini 300 MHz, Inova 400 MHz, or Inova 500 MHz instruments and were taken in deuterated chloroform unless noted otherwise. Mass spectra (EI) and high-resolution mass spectra (EI) were obtained from the University of Illinois SCS Mass Spectrometry Laboratory.

Safety Statement: *The diiodopolyynes, while more stable than analogous terminal polyynes or dibromopolyynes, still must be handled with caution. These compounds are shock explosives and have been observed to become less stable over time. They should therefore be stored in solution below 0 °C and should be used within a week of preparation. Caution should also be taken when preparing and handling the tin acetylides, as trimethyltin chloride and analogous organotin compounds have been declared toxic by all means of exposure.*[20]

Diiodobutadiyne (**2a**), diiodohexatriyne (**3a**), and diiodooctatetrayne (**4a**) were each prepared from the corresponding trimethylsilyl-capped polyynes (that is, **2c**, **3c**, and **4c**, respectively) according to previously described methods.[19b,21] 2,4-Hexadiyne-1,6-diol (**9**) and 1,6-dibromo-2,4-hexadiyne (**10**) were also prepared using previously reported methods.[15b,15c]

General Procedure for the Preparation of Tin Acetylides[13b]

Triisopropylsilyl(trimethylstannyl)ethyne (1b): Triisopropylsilyl acetylene (4.50 g, 25.0 mmol) was dissolved in THF (50 mL), and the solution was cooled to –30 °C using a dry ice/acetone bath. *n*BuLi (1.6 M in hexanes, 15.0 mL, 25.0 mmol) was added dropwise over 15 min. After stirring for 15 min at –30 °C, $SnMe_3Cl$ (1 M in THF, 25.0 mL, 25.0 mmol) was added, and the mixture was stirred for an additional 30 min before warming to room temperature and stirring for 1 h. Hexanes (100 mL) was added to the reaction mixture, resulting in the formation of a white precipitate. The mixture was extracted with H_2O (25 mL), and the organic layer was dried with $MgSO_4$. The solution was filtered, and the solvent was removed in vacuo, leaving a cloudy yellow liquid. Vacuum distillation (≈90 °C) was used to isolate **1b** as a colorless liquid (5.50 g, 64% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.07 (br., 21 H), 0.28 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 115.1, 113.5, 18.6, 11.2, –7.6 ppm.[22]

Trimethylsilyl(trimethylstannyl)ethyne (1c): Colorless liquid (79% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.27 (s, 9 H), 0.15 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 117.4, 113.1, 0.2, –7.7 ppm.[23]

Phenyl(trimethylstannyl)ethyne (1d): Yellow liquid (55% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.45–7.44 (m, 2 H), 7.26–7.25 (m, 3 H), 0.35 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 131.8, 128.1, 128.0, 123.5, 108.9, 93.2, –7.7 ppm.[24]

1,8-Bis(triisopropylsilyl)-1,3,5,7-octatetrayne (4b): Diiodobutadiyne (**2a**; 0.150 g, 0.500 mmol) and triisopropylsilyl(trimethylstannyl)ethyne (**1b**; 0.370 g, 1.07 mmol) were dissolved in dry THF (15 mL) in a heart-shaped flask wrapped in aluminum foil. CuI (0.019 g, 0.10 mmol, 20 mol-%) and $Pd(PPh_3)_2Cl_2$ (0.035 g, 0.050 mmol, 10 mol-%) were combined in a round-bottom flask wrapped with foil, and the system was degassed and backfilled with Ar. THF (8 mL) was added to the flask. The solution of **2a** and **1b** was added to the catalyst mixture via cannula over 10 h. After addition, the mixture was stirred for 2 h, and the solvent was removed. The residue was purified by column chromatography (Al_2O_3/hexanes). To recrystallize **4b**, the mixture of **4b** and 1,4-bis(triisopropylsilyl)-1,3-butadiyne (**2b**) was dissolved in a minimum amount of warm $CHCl_3$ ≈45 °C, causing a white precipitate to appear. Upon stirring after the first HCl additions, the cloudy precipitate disappeared, but the addition was continued until the white cloudy suspension remained steady. This warm solution was allowed to cool down to room temperature and placed in the freezer. Compound **4b** was isolated as a light yellow solid (0.16 g, 77% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.09 ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 89.6, 85.6, 62.2, 61.4, 18.5, 11.3 ppm.[1]

1,8-Bis(trimethylsilyl)-1,3,5,7-octatetrayne (4c): Diiodobutadiyne (**2a**; 0.239 g, 0.792 mmol) and trimethylsilyl(trimethylstannyl)ethyne (**1c**; 0.414 g, 1.58 mmol) were dissolved in dry THF (20 mL) in a heart-shaped flask wrapped in aluminum foil. The flask was placed in an ice bath (0 °C). CuI (0.036 g, 0.19 mmol, 24 mol-%) and $Pd(PPh_3)_2Cl_2$ (0.065 g, 0.093 mmol, 12 mol-%) were combined in a round-bottom flask wrapped with foil, and the system was degassed and backfilled with Ar. THF (5 mL) was added to the flask, and the solution of **2a** and **1c** was added to the catalyst mixture via cannula over a period of 10 h. The mixture was stirred for 2 h after the addition, solvent was removed in vacuo, and the excess amount of the catalyst was removed using a short plug (SiO_2/hexanes). Vacuum sublimation was used to isolate **4c** as a brown oil that contained solid needles (0.11 g, 59% yield). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.21 ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 88.01, 87.83, 62.16, 62.14, –0.57 ppm.[21]

1,12-Bis(triisopropylsilyl)-1,3,5,7,9,11-dodecahexayne (6b): In a heart-shaped flask wrapped in aluminum foil, diiodotetrayne (**4a**; 0.150 g, 0.430 mmol) and triisopropylsilyl(trimethylstannyl)ethyne (**1b**; 0.57 g, 1.6 mmol) were dissolved in dry THF (20 mL). CuI (0.010 g, 0.053 mmol, 13 mol-%), and $Pd(PPh_3)_2Cl_2$ (0.035 g, 0.05 mmol, 12 mol-%) were combined in a round-bottom flask wrapped with foil, and the system was degassed and backfilled with Ar. THF (5 mL) was added to the flask, and both flasks were kept in ice baths (0 °C). The solution of **4a** and **1b** was added to the catalyst mixture via cannula, over a period of 10 h. After addition, the mixture was stirred for 2 h at room temperature, and the solvent was removed in vacuo. Column chromatography (SiO_2/hexanes) was used to isolate **6b** as a light yellow solid (0.092 g, 47% yield). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.08 ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 89.40, 87.03, 62.71, 62.66, 62.36, 61.26, 18.56, 11.29 ppm.[1]

1,12-Bis(diphenyl)-1,3,5,7,9,11-dodecahexayne (6d): In a heart-shaped flask wrapped in aluminum foil, diiodotetrayne (**4a**; 0.132 g, 0.377 mmol) and phenyl(trimetylstannyl)ethyne (**1d**; 0.194 g, 0.732 mmol) were dissolved in dry THF (20 mL). CuI (0.018 g, 0.095 mmol, 25 mol-%) and $Pd(PPh_3)_2Cl_2$ (0.032 g, 0.046 mmol, 12 mol-%) were combined in a round-bottom flask wrapped with foil, and the system was degassed and backfilled with Ar. THF (5 mL) was added to the flask, and both flasks were kept in ice baths (0 °C). The solution of **4a** and **1d** was added to the catalyst mixture via cannula, over a period of 11 h. After addition, the mixture was stirred for 2 h at room temperature, and solvent was removed in vacuo. The excess amount of the catalyst was removed using a short plug (SiO_2/hexanes). Column chromatography (SiO_2/hexanes) was used to isolate **6d** as a light orange solid (0.018 g, 16% yield). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.56–7.54 (m, 4 H), 7.42–7.41 (m, 2 H), 7.36–7.33 (m, 4 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 133.5, 130.4, 128.5, 120.1, 77.5, 74.3, 67.2, 64.6, 63.6, 62.5 ppm.[25]

1,6-Bis(trimethylsilyl)-1,3,5-hexatriyne (3c): Potassium *tert*-butoxide (0.551 g, 4.91 mmol) was dissolved in THF (20 mL), and this solution was cooled to –78 °C using a dry ice/acetone bath. A solution of 1,6-dibromo-2,4-hexadiyne (**2g**; 0.290 g, 1.23 mmol) in THF (20 mL) was added to the reaction mixture via cannula. After stirring for 2 h, the mixture reached –60 °C, and trimethylsilyl chloride (0.63 mL, 4.9 mmol) was added. The reaction was allowed to stir for 3.5 h, without further cooling. Saturated aq. NH_4Cl (30 mL) was added, and the mixture was extracted with hexanes (3× 30 mL). Removal of the solvent resulted in **3c** as a mixture of brown oil and short needle-like crystals (0.17 g, 63% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.20 ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 87.9, 87.4, 61.9, –0.6 ppm.[7]

1,10-Bis(triisopropylsilyl)-1,3,5,7,9-decapentayne (5b): In a heart-shaped flask wrapped in aluminum foil, diiodohexatriyne (**3a**; 0.123 g, 0.377 mmol) and triisopropylsilyl(trimethylstannyl)ethyne (**1b**; 0.253 g, 0.734 mmol) were dissolved in dry THF (20 mL). CuI (0.016 g, 0.084 mmol, 22 mol-%) and $Pd(PPh_3)_2Cl_2$ (0.035 g, 0.050 mmol, 13 mol-%) were combined in a round-bottom flask wrapped with foil, and the system was degassed and backfilled with Ar. THF (5 mL) was added to this flask, and both flasks were kept in ice baths (0 °C). The solution of **3a** and **1b** was added to the catalyst mixture via cannula over a period of 9 h. After stirring for an additional 2 h at room temperature, the solvent was removed in vacuo, and the excess amount of the catalyst was removed using a short plug (SiO_2/hexanes). Warm MeOH/$CHCl_3$ (10:1) was used for recrystallization. The mixture was placed in a 45 °C water bath, and 3 N HCl was added dropwise until a visible yellow suspension formed. The liquid was cooled to room temperature and placed in the freezer. Vacuum filtration was used to isolate **5b** as a yellow solid (0.065 g, 40% yield). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.99 ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 90.65, 87.18, 63.42, 63.41, 62.49, 18.95, 11.87 ppm.[7]

1,10-Bis(trimethylsilyl)-1,3,5,7,9-decapentayne (5c): In a heart-shaped flask wrapped in aluminum foil, diiodohexatriyne (**3a**; 0.113 g, 0.347 mmol) and trimethylsilyl[(trimethylstannyl)ethynyl]ethyne (**1c**; 0.179 g, 0.686 mmol) were dissolved in dry THF (20 mL). CuI (0.015 g, 0.079 mmol, 23 mol-%) and $Pd(PPh_3)_2Cl_2$ (0.028 g, 0.041 mmol, 12 mol-%) were combined in a round-bottom flask wrapped with foil, and the system was degassed and backfilled with Ar. THF (5 mL) was added to the flask, and both flasks were kept in ice baths (0 °C). The solution of **3a** and **1c** was added to the catalyst mixture via cannula over a period of 10 h. After stirring for an additional 2 h at room temperature, the solvent was removed in vacuo and the excess amount of the catalyst was removed using a short plug (SiO_2/hexanes). Vacuum sublimation was used to isolate **5c** as a brown solid (0.060 g, 61% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.21 ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 88.63, 87.71, 62.62, 62.23, 62.17, –0.65 ppm.[26]

1,10-Bis(phenyl)-1,3,5,7,9-decapentayne (5d): In a heart-shaped flask wrapped in aluminum foil, diiodohexatriyne (**3a**; 0.198 g, 0.608 mmol) and phenyl(trimethylstannyl)ethyne (**1d**; 0.321 g, 1.21 mmol) were dissolved in dry THF (20 mL). CuI (0.026 g, 0.14 mmol, 22 mol-%) and $Pd(PPh_3)_2Cl_2$ (0.051 g, 0.073 mmol, 12 mol-%) were combined in a round-bottom flask wrapped with foil, and the system was degassed and backfilled with Ar. THF (5 mL) was added to the flask, and both flasks were kept in ice baths (0 °C). The solution of **3a** and **1d** was added to the catalyst mixture via cannula over a period of 9 h. After stirring for an additional 2 h at room temperature, the solvent was removed in vacuo and the excess amount of the catalyst was removed using a short plug (SiO_2/hexanes). Column chromatography (SiO_2/hexanes) was used to isolate **5d** as a light yellow solid (0.47 g, 28% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.56–7.54 (m, 4 H), 7.44–7.40 (m, 2 H), 7.36–7.32, (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 133.3, 130.2, 128.6, 120.3, 77.5, 74.4, 67.3, 64.5, 62.8 ppm.[7]

1,10-Diiodo-1,3,5,7,9-decapentayne (5a): 1,10-Bis(trimethylsilyl)-1,3,5,7,9-decapentayne (**5c**; 0.096 g, 0.36 mmol) was dissolved in acetone (200 mL) in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.186 g, 1.09 mmol) and *N*-iodosuccinimide (0.488 g, 2.17 mmol) were added, and the reaction mixture was allowed to stir at room temperature for 4.5 h. Ice water (200 mL) and hexanes (200 mL) were added, and the aqueous layer was extracted with hexanes (3× 100 mL). The combined organic layers were washed with 15% aq. $Na_2S_2O_3$. The resulting yellow solution was dried with $MgSO_4$. Filtration and removal of solvent resulted in **5a** as a yellow solid that decomposed at 55–56 °C (0.11 g, 82% yield). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 79.0, 62.6, 61.4, 59.3, 2.3 ppm. MS (EI): *m/z* (%): 373 (100) $[M]^+$, 246 (18) $[M - I]^+$, 128 (60) $[I]^+$, 119 (42) $[M - 2I]^+$. HRMS (EI): calcd. for $C_{10}I_2$ 373.80900; found 373.80923.

1,14-Bis(triisopropylsilyl)-1,3,5,7,9,11,13-tetradecaheptayne (7b): In a heart-shaped flask wrapped in aluminum foil, diiodopentayne (**5a**; 0.056 g, 0.15 mmol) and triisopropylsilyl(trimethylstannyl)ethyne (**1b**; 0.10 g, 0.29 mmol) were dissolved in dry THF (20 mL). CuI (0.007 g, 0.037 mmol, 24 mol-%) and $Pd(PPh_3)_2Cl_2$ (0.013 g, 0.018 mmol, 12 mol-%) were combined in a round-bottom flask wrapped with foil, and the system was degassed and backfilled with Ar. THF (5 mL) was added to the flask, and both flasks were kept in ice baths (the diiodopentayne and tin solution was kept between –15 and –30 °C, and the catalyst mixture was kept at 0 °C). The solution of **5a** and **1b** was added to the catalyst mixture via cannula over a period of 10 h. After stirring for an additional 2 h at room temperature, the solvent was removed in vacuo and the excess amount of the catalyst was removed using a short plug (SiO_2/hexanes). Column chromatography (SiO_2/hexanes) was used to isolate **7b** as dark yellow oil (0.007 g, 10% yield). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.09 ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 89.34, 87.39, 62.97, 62.93, 62.62, 62.26, 61.20, 18.49, 11.27 ppm. HRMS (EI): calcd. for $C_{32}H_{42}Si_2$ 482.28251; found 482.28314.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H NMR and ^{13}C NMR for the prepared compounds and HRMS for novel compounds.

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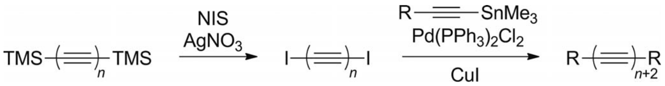
Symmetric Polyynes



Symmetric polyynes containing four to seven C≡C bonds were prepared by using a series of iodination and Stille coupling reactions. The simple starting materials that are required in this iterative route are easily prepared and relatively stable. This route is especially effective when targeting polyynes with an odd number of C≡C bonds.

Keywords: Alkynes / Cross-coupling / Synthetic methods / Palladium