An iterative synthesis of cross-conjugated iso-polydiacetylene (iso-PDAs) is reported based on three fundamental building blocks: vinyl triflates 8, 9, and 25. An efficient sequence of palladium-catalyzed cross-coupling reactions of vinyl triflates and terminal alkynes has been employed to extend the chain length of these oligomers. The longest member of the series, nonamer 19, spans 3.4 nm from Si to Si atom. The stability and solubility of the conjugated oligomers have been evaluated as a function of pendant substitution. Assessment of solid-state structural properties was achieved via X-ray crystallographic analyses of monomer 12 and trimer 14. The electronic characteristics of the monodisperse oligomers have been fully analyzed by UV–vis spectroscopy in solution and as thin films, and these studies suggest that π-electron communication is present along the enyne framework, but quickly reaches saturation by the stage of nonamer 19.

Chart 1 illustrates the cross-conjugated isomers that arise as the constitutional isomers of the linearly conjugated analogues 1–3: iso-polyacetylenes (iso-PAs) or dendrynes 5,12,17 iso-polydiacetylenes (iso-PDAs) 6,18. 


and iso-polydiacetylenes (iso-PTAs). The obvious difference between the two classes of compounds is that electron density in cross-conjugated isomers cannot be readily delocalized along the carbon framework in a manner analogous to that in their linearly conjugated counterparts in accord with classical resonance theory.

In a simplistic approach, it may be expected that delocalization could be limited to segments composed of linearly conjugated \( \pi \) orbitals. Using this approach, an infinitely cross-conjugated system could be approximated by the attenuated contributions of these linearly conjugated segments. We thought it inappropriate, however, to ascribe the electronic properties of cross-conjugated molecules on the basis of this simple empirical model that might exclude weak electronic interactions between each cross-conjugated segment.

We thus targeted oligomeric iso-PDAs as a class of molecules ideally suited for probing the subtle electronic characteristics of cross-conjugated organic oligomers. We anticipated that a series of monodisperse molecules could lead to a better understanding of cross conjugation and structure–property relationships of conjugated enyne polymers. We report the iterative synthesis and detailed characterization of cross-conjugated iso-PDA oligomers.

**Results and Discussion**

**Synthesis.** The synthesis of iso-PDA oligomers is based on palladium-catalyzed cross-coupling reactions between vinyl triflates and terminal alkynes. The parent series of molecules, with only vinylidene subunits in the carbon chain of the backbone (6, \( R = H \)), represented a desirable target, but were expected to be quite unstable on the basis of the reported synthesis of the parent enediyne of this series. We therefore chose to incorporate an isopropylidene moiety (6, \( R = Me \)) and envisioned a strategy that included an iterative series of desilylation and cross-coupling steps such that the oligomeric chain lengths could be rapidly increased in a divergent manner from enediyne 10–12 (Scheme 1).

The essential vinyl triflate building blocks 8 and 9 were readily obtained through the methods described by Stang et al. Triflates 8 and 9 were cross-coupled with trimethylsilylacetylene (TMSA) or triisopropylsilylacetylene (TIPS) using PdCl\(_2\)(PPh\(_3\))\(_2\) catalyst, Cul cocatalyst, and i-Pr\(_2\)NH base in THF at ambient temperature to give monomers 10, 11, and 12 in yields of 92, 84, and 98%, respectively. Optimization of the cross-coupling conditions of these reactions showed that the choice of catalyst (PdCl\(_2\)(PPh\(_3\))\(_2\) or Pd(PPh\(_3\))\(_4\)), base (Et\(_2\)NH or i-Pr\(_2\)NH), and solvent (THF or DMF) could be altered without significantly affecting the outcome of the coupling reaction. In most cases, the reactions were complete within 2 h as determined by thin layer chromatographic (TLC) analysis.

The first series of oligomers we targeted were end-capped with trimethylsilyl (TMS) groups, as it was anticipated that removal of this group in subsequent iterations would be more facile than the removal of the more robust triisopropylsilyl (TIPS) group. Thus, monomer 10 was protodesilylated in methanolic K\(_2\)CO\(_3\) to give, in essentially quantitative yield, the deprotected terminal diyne that may be used without further purification. The deprotected enediyne was cross-coupled with 8 to afford trimer 13, which was isolated via flash chromatography as a colorless solid in 92% yield. A subsequent iteration of the protodesilylation and cross-coupling sequence gave pentamer 15 in 69% yield, as a colorless solid that was still quite soluble in chlorinated organic solvents. Desilylation of 15 followed by cross-coupling in DMF, however, was problematic as both deprotected 15 and heptamer 17 were only sparingly soluble in this solvent. Performing the cross-coupling reaction of desilylated 15 with vinyl triflate 8 with THF...
as the solvent helped to solubilize the heptamer product 17 such that it could be isolated in 75% yield as a relatively insoluble, colorless solid. We were unable, however, to effect the next iteration with 17 toward the nonameric derivative due to insolubility. Intermolecular aggregation may contribute to this insolubility, although dilution studies (vide infra) monitored by UV-vis spectroscopy as well as NMR data suggest that aggregation is not a major factor.

In the second series of iso-PDAs, the TIPS group was employed as an endcapping group, which was expected to enhance solubility of the products because of increased steric bulk. Using the iterative sequence outlined above, the formation of the TIPS-protected series employed the respective TMS-endcapped precursor due to the more facile removal of this protecting group. Thus, protodesilylation of enediyne 10 followed directly by cross-coupling with TIPS-protected triflate 9 afforded trimer 14 in 53% yield. Desilylation of TMS-protected trimer 13 followed by cross-coupling with 9 gave pentamer 16 in 82% yield. Desilylation of pentamer 15 and cross-coupling with 9 afforded heptamer 18 as a stable colorless solid in a yield of 44%, which was gratifyingly soluble in most organic solvents. While the increased solubility of 18 circumvented the problems encountered with TMS-protected heptamer 17, there was no way to enhance the solubility of the deprotected heptamer (vide supra). Thus, toward the formation of nonamer 19, the best conditions for deprotection of 17 utilized tetrabutylammonium fluoride (TBAF) in a dilute solution of THF, thus avoiding the less solubilizing MeOH used with K₂CO₃. After reaction of 17 with TBAF for ca. 15 min, the reaction mixture was diluted with a large volume of Et₂O, and aqueous workup provided the terminal alkyne. Following concentration of the ethereal solution, and resolvation with a minimal amount of THF, coupling to triflate 9 gave nonamer 19 in 37% yield. The reasonable solubility of 19 allowed for complete spectroscopic characterization of this nanometer-length oligomer, which measures 3.4 nm from Si to Si. The reaction to produce 19 was always accompanied by the formation of macrocycle 20 (see eq 1), the result of copper-catalyzed, oxidative homocoupling of the two terminal alkynes. Prior to this point, competing homocoupling reactions had not been problematic. Two factors likely contributed to its presence in the current case: (1) a greater amount of O₂ (requisite for the homocoupling reaction) due to the increased amount of solvent employed to accommodate desilylated 17, and (2) higher dilution favoring an intramolecular reaction. To provide sufficient quantities of expanded radialene 20 for characterization, it was synthesized via homocoupling of the deprotected heptamer using Hay catalysis in dry acetone (eq 1). Although the solubility of both the precursor and product complicates this reaction, the cyclic enyne heptamer 20 could be isolated in 31% yield as a rather insoluble colorless solid.

To complete the series of oligomers, and for the purposes of comparison, iso-PDA oligomers with an even number of repeating units were assembled as outlined in Scheme 2. Treatment of differentially protected enediyne 11 with K₂CO₃ in THF/MeOH (1:1) effected selective removal of the TMS group, while leaving the more robust TIPS group unaffected. Following workup, cross-coupling with either vinyl triflate 9 or vinyl triflate 8 gave dimers 21 and 22 in yields of 88 and 81%, respectively.

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Protodesilylation of 21 or 22 in a dilute THF solution using TBAF followed by cross-coupling with 8 or 9 led to tetramers 23 and 24 in yields of 41 and 66%, respectively. 

Irrespective of TMS or TIPS protecting groups, the iso-PDA oligomers incorporating the isopropylidene building block show decreasing stability with increasing chain length. For oligomers longer than the pentamer, stability can vary from a couple of days to several weeks under refrigeration, as evaluated by TLC and 1H NMR analysis. Storing the oligomers under an inert gas afforded better stability, but not substantially. Preliminary evidence suggests that an oxygen ene reaction at the isopropylidene moiety is likely the primary decomposition pathway.

In an effort to improve the stability of the iso-PDA derivatives, as well as their solubility, an alternative pendant transformation was targeted, with adamantanylidene functionalization as illustrated in Scheme 3. The adamantyl-substituted vinyl triflate 25 was synthesized as previously described. Palladium-catalyzed cross-coupling of this building block with TMSA gave monomer 26 in a yield of 61%. Desilylation of the adamantyl derivatives always proceeds more efficiently using TBAF in THF rather than methanolic K2CO3. Thus, deprotection of 26 using TBAF followed by cross-coupling of the terminal diyne to triflate 25 afforded trimer 27 in 67% yield. The trimer was subsequently deprotected and cross-coupled with an additional 2 equiv of triflate 25 to provide the pentamer 28 in 74% yield. The adamantylidene-substituted iso-PDAs 27 and 28 did indeed show greater long-term stability than the isopropylidene-substituted derivatives and could be stored at ambient conditions for weeks or under refrigeration for months. They were, however, far less soluble than expected. Even at the stage of the pentamer, solubility in organic solvents was already quite limited, which precluded our ability to further elaborate this series. For the molecular mass characterization of trimer 27 and pentamer 28, electrospray mass spectrometry proved particularly beneficial. Specifically, analysis (positive mode) of a nitromethane solution of 28 with added AgOTf provided a signal at m/z 1129.6 expected for [M + Ag]+, as silver coordinates to an alkyn unit of the iso-PDA.

Physical Characteristics. The spectroscopic data for the iso-PDA oligomers are consistent with their proposed structures. In the 13C NMR spectra for members of the isopropylidene series, the resonances of the pendant methyl groups are observed in a range of 22–23 ppm. The vinylidene carbons outside of the main chain of the oligomers (R2C=C) are quite deshielded, resonating in a range of 152–155 ppm for the isopropylidene and 167–169 ppm for the adamantylidene derivatives, respectively. The other vinylidene carbons (R2C=C) fall into the chemical shift range of the acetylenic carbons, from 88 to 104 ppm. Even at 125 MHz, significant chemical shift degeneracy is observed in the 13C NMR analysis of the longest oligomer, nonamer 19, for which only 11 of 20 unique sp and sp2 carbon resonances are discernible. In comparison, all unique sp and sp2 resonances for the pentameromic species 15 and 28 are observed in the expected ranges.

All iso-PDAs show significant thermal stability. For the TMS-endcapped series, trimeric 13 melts at 136 °C, whereas pentamer 15 and heptamer 17 show only decomposition points at 196 and >170 °C, respectively. For TIPS derivatives, dimeric 21, trimeric 14, and tetrameric 24 showed well-defined melting points at 65–66, 70–71, and 89–90 °C, respectively. Heptamer 18 and nonamer 19 show only decomposition at 148 and 190 °C, respectively. Although adamantyl derivatives 27 and 28 show greater stability under ambient conditions, their thermal stability is comparable to that of dimethyl-substituted iso-PDAs; adamantyl trimer 27 shows a melting point of 176–178 °C, and pentamer 28 decomposes at 164 °C. These data suggest that, despite their highly unsaturated structure, longer oligomeric or poly-

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than the anticipated angle of 120 °C for an sp2-hybridized carbon atom, and (2) the Si–C(C6) bond is 1.191(5) Å, C–Si bond is 1.699(5) Å, and C(6)–C(7) bond is 1.439(5) Å, respectively. Of the two C=C bonds in the central symmetric structure, one is 1.206(5) Å and the other is 1.199(5) Å. Of the two C=C bonds, one is 1.347(5) Å and the other is 1.349(5) Å, respectively.

solid-state structures are also available. The two C=C bonds in the central symmetric structure, one is 1.206(5) Å and the other is 1.199(5) Å. Of the two C=C bonds, one is 1.347(5) Å and the other is 1.349(5) Å, respectively. Of the two C=C bonds, one is 1.206(5) Å and the other is 1.199(5) Å. Of the two C=C bonds, one is 1.347(5) Å and the other is 1.349(5) Å, respectively.

**Electronic Properties.** From our perspective, the most interesting feature of the iso-PDA oligomers is their unique cross-conjugated π framework. As demonstrated by the diagrams in Chart 2 for a cisoid iso-PDA dimer, two sets of orthogonal sp orbitals can potentially contribute to electron communication. The out-of-plane p orbitals (right) form the longest π-conjugated segment in an iso-PDA oligomer, and it is anticipated that the lowest-energy electronic absorption would be due to this sequence of sp² and sp orbitals. Because of the nature of cross conjugation, the out-of-plane π electrons would be expected to be delocalized across the alkylidene segments only in the lowest-energy π orbital, that is, the fully symmetrical orbital as depicted in Chart 2. The in-plane set of orbitals (left) are essentially isolated, but could allow for a certain amount of overlap between each conjugated segment as a result of homocoupling.

The UV–vis spectra in CHCl₃ of the TIPS-endcapped oligomers ranging from dimer to nonamer are shown in Figure 3. The predominant feature of the electronic absorption behavior of the iso-PDA oligomers is a steadily increasing molar absorptivity as the number of enyne monomer units is increased. In the spectrum of dimer 21, two distinct, low-energy absorptions are discernible at 291 and 306 nm. These low-energy absorptions are due to the π → π* transition from HOMO to LUMO. In the cisoid orientation (C₂ᵥ), the HOMO to LUMO (A₁ − B₁) and HOMO to LUMO + 1 (A₁ − A₁) transitions are both symmetry-allowed. However, in the centrally symmetric transoid orientation (C₂ᵥ), only the HOMO to LUMO (A₂ → B₂) transition is symmetry-allowed, whereas the HOMO to LUMO + 1 (A₂ → A₂) transition is symmetry-forbidden. The low-energy absorption peak at 306 nm is

Single crystals of 14 were obtained by diffusion of MeOH into a CH₂Cl₂ solution at 4 °C, and the structure was solved at low temperature. The C₂ᵥ symmetrical structure of 14 is essentially planar with a maximum deviation from the least-squares plane of carbon and silicon framework (excluding the isopropyl groups) of 0.126(4) Å. Of three possible planar geometries, 14 assumes an all-transoid orientation of the olefins with respect to the acetylenic linkers. Unlike their linearly conjugated isomers, polydiacetylenes,¹⁹ no observable reduction in bond length alternation is observed in the iso-PDA trimer. Single bonds of the conjugated framework, for example, C(3)–C(5) and C(6)–C(7) at 1.435(5) Å and 1.439(5) Å, respectively, are in the range expected for single bonds linking sp and sp² carbons. The two C=C bonds at 1.206(5) Å and 1.199(5) Å and the two C=C bonds at 1.347(5) Å and 1.349(5) Å are also in the range expected. Bond lengths for 14 are comparable to those found in monomer 12. The alkylidene bond angles C(2)–C(3)–C(5) at 115.4(3)° and C(6)–C(7)–C(6) at 115.5(5)° are also similar to the analogous angle of endyne 12. **Electronic Properties.** From our perspective, the most interesting feature of the iso-PDA oligomers is their unique cross-conjugated π framework. As demonstrated by the diagrams in Chart 2 for a cisoid iso-PDA dimer, two sets of orthogonal sp orbitals can potentially contribute to electron communication. The out-of-plane p orbitals (right) form the longest π-conjugated segment in an iso-PDA oligomer, and it is anticipated that the lowest-energy electronic absorption would be due to this sequence of sp² and sp orbitals. Because of the nature of cross conjugation, the out-of-plane π electrons would be expected to be delocalized across the alkylidene segments only in the lowest-energy π orbital, that is, the fully symmetrical orbital as depicted in Chart 2. The in-plane set of orbitals (left) are essentially isolated, but could allow for a certain amount of overlap between each conjugated segment as a result of homocoupling.
from cross conjugation, the absorbance spectrum of (Scheme 2). In the absence of electronic contributions iso-PDAs, that is the ene-yne-ene sequence shown in bold longest linearly conjugated segment found in any of the oligomers. As can be seen in Figure 3, however, a slight (or 22) dimer cyclic or the acyclic iso-PDAs. As one progresses from the transoid orientation, whereas the higher-energy absorption peak seen at 291 nm likely corresponds to HOMO to LUMO or a combination of the HOMO to LUMO + 1 transitions of the cisoid orientation. Unfortunately, the absence of a second, clear absorbance at 305 nm is absent, whereas the higher-energy absorption at 283 nm remains.18c

Figure 3. Electronic absorption spectra (ε [L M⁻¹ cm⁻¹]) in CHCl₃ comparing the effects of oligomer length between 14, 16, 18, 19, 21, and 24.

Figure 4. Plot of estimated optical band gap (Eₒ) versus reciprocal number of monomer units (1/n) of TIPS and TMS endcapped iso-PDAs via method A (○, TMS; □, TIPS) and method B (●, TMS; ▲, TIPS).

Un fortunately, the absence of a second, clear absorption band in the spectrum of 29 makes it impossible to distinguish between the HOMO to LUMO and HOMO to LUMO + 1 transitions in the spectra of either the cyclic or the acyclic iso-PDAs. As one progresses from the dimer 21 to longer oligomers, the absorption bands broaden significantly due to an increasing number of rotational degrees of freedom, and beyond the stage of trimer 14 only one broad, featureless absorption is observed. The spectra of TMS-endcapped iso-PDAs showed similar characteristics.35

The framework of dimeric 21 and 22 contains the longest linearly conjugated segment found in any of the iso-PDAs, that is the ene-ene-ene sequence shown in bold (Scheme 2). In the absence of electronic contributions from cross conjugation, the absorbance spectrum of 21 (or 22) should be representative of the longer iso-PDA oligomers. As can be seen in Figure 3, however, a slight lowering of the cutoff energy for elongated oligomers is observed as one progresses from dimer 21 to nonamer 19.

The solution state optical band gap Eₒ of the iso-PDA oligomers has been approximated by two methods: (a) from the intersection between the tangent passing through the turning point of the shoulder of the lowest-energy absorption band and the x axis, and (b) from maximal wavelength at one-half intensity of the maximal absorption.36 Figure 4 shows that plots of estimated band gap (Eₒ) versus the reciprocal of monomer unit numbers (1/n) are similar for both methods. The band gap values decrease slightly with an increasing monomer unit number (n) from dimer to heptamer, eventually reaching a constant at the stage of nonamer. By extrapolation, it is reasonable to suggest that any further extension of the oligomer chain length will not lower Eₒ; that is, the band gap of a polymer containing an infinite number of monomer units would be the same as that of the nonamer, 3.75 eV (as measured by method A). As this value represents the π→π⁺ transition, it is clear that π-electron communication along the iso-PDA framework (between adjacent cross-conjugated enyne subunits) quickly reaches saturation by the stage of the nonamer, and transparency should be preserved beyond this energy level.

Changing the pendant functionality of iso-PDAs from isopropylidene to adamantylidene has only a small effect on the overall shape and molar absorptivity of the solution state spectra, albeit there is a pronounced broadening in the spectra of both adamantyl oligomers 27 and 28.37 The lower energy cutoff for the adamantyl trimer 27 and pentamer 28, however, is red shifted by about 10 nm versus that of analogous dimethyl derivatives 14 and 16, likely the result of the larger alkyl group (i.e., adamantyl vs dimethyl). Unfortunately, the featureless spectra of 27 and 28 made it impossible to tell if a similar red shift was present for specific λmax values.

The influence of solvent polarity on the electronic absorptions for dimeric 21 was investigated via measurement in chloroform, THF, benzene, Et₂O, and hexanes.

18c The UV–vis spectra for 13, 15, and 17 are supplied as Supporting Information.

19 The UV–vis spectra for 27 and 28, as well as spectra comparing characteristics of 15, 16, and 28, are supplied as Supporting Information.

(35) The UV–vis spectra for 13, 15, and 17 are supplied as Supporting Information.

(36) A table of values for Figure 4 is supplied as Supporting Information.

(37) The UV–vis spectra for 27 and 28, as well as spectra comparing characteristics of 15, 16, and 28, are supplied as Supporting Information.
The concentration range accessible for UV–vis spectra for thin films of 14, 16, 21, and 24 acquired in more polar solvents display a maximum absorption peak (λ_{max}) slightly shifted to longer wavelengths. This shift, however, is rather small; it ranges from a minimum value in hexane of 303 nm to a maximum value in THF or CHCl₃ of 306 nm. The overall shape and molar absorptivities for the spectra are essentially independent of solvent.38

The consistent profiles and molar absorptivity values observed at different concentrations suggest that aggregation may become a factor for longer oligomers.16 Red shift in the lowest-energy absorption to 331 nm that was reproducibly demonstrated a measurable small; it was noted in the respective experimental paragraphs. ESI MS analysis was done in nitromethane with added AgOTf.

X-ray crystal data for 12: monoclinic space group P1 (No. 2), Dₐ = 0.973 g cm⁻³, Z = 4, a = 14.440(3) Å, b = 14.464(3) Å, c = 15.314(2) Å, α = 111.702(3)°, β = 105.415(4)°, γ = 90.142(3)°. V = 2846.6(8) Å³, R(F₀) = 0.0911, wR²(F²) = 0.2607 for 522 variables and 11521 data with F₂ > 2σ(F²). Details are provided as Supporting Information.

**Trifluoromethanesulfonic Acid 2-Methyl-1-trisopropylsilanylenethynyl-propenyl Ester (9)**. Reaction of 4-methyl-1-trisopropylsilanylenethynyl-1-yn-3-one with trifluoromethanesulfonic anhydride (4.53 g, 16.1 mmol) and 2,6-di-tert-butyl-4-methylpyridine (2.72 g, 13.2 mmol) in CH₂Cl₂ (50 mL) was conducted under Ar for 24 h. The CH₂Cl₂ was removed in vacuo, and the residue was extracted with pentane. The organic solution was washed with 10% HCl, saturated aqueous NaHCO₃, and brine. Evaporation followed by flash chromatography (hexane/CH₂Cl₂ 2:1) gave 9 (2.72 g, 66%) as a clear light-yellow oil. IR (neat): 2946, 2968, 2150 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 1.99 (s, 3H), 1.90 (s, 3H), 1.07 (m, 21H). ¹³C NMR (125 MHz, CDCl₃): δ 138.1, 126.6, 118.3 (q, J = 263.4 Hz), 100.1, 96.2, 21.1, 18.7, 18.5, 11.2. HRMS calc for C₁₂H₁₂₂F₃O₅Si (M⁺): 384.1402, found, 384.1402.

**General Cross-Coupling Procedure**. A mixture of the appropriate trimethylsilyl- or trisopropylsilyl-protected polyyne and K₂CO₃ (ca. 0.2 equiv) or TBAF (2.2 equiv) in wet THF/MeOH (1:3, 20 mL) or THF (20 mL), respectively, was stirred at room temperature for 2 h. Ether and saturated aqueous NaHCO₃ were added, and the organic phase was separated. Washing with saturated aqueous NH₄Cl (2 × 50 mL), dried, reduced to ca. 1 mL, and added to a degassed solution of vinyl triflate 8, or 25 in THF or DMF (20 mL). Pd(PPh₃)₄ or PdCl₂(PPh₃)₂ (ca. 0.05 equiv) and i-Pr₂NH or Et₂NH were sequentially added, the solution was stirred for 5 min, Cuc (ca. 0.15 equiv) was added, and the solution was then subjected to TLC analysis. No longer showed the presence of the deprotected polyyne starting material. Ether and H₂O were added, and the organic phase was separated. Washing with saturated aqueous NH₄Cl (2 × 50 mL), dried, and the solvent was removed in vacuo. Flash column chromatography and/or precipitation from MeOH gave the desired iso-PDA oligomer.
1-Triethylsilyl-3-trimethylsilylletynyl-4-methyl-pent-3-en-1-yne (10). Triflate 8 (0.300 g, 1.00 mmol) was cross-coupled with trimethylsilylacetylene (0.200 g, 2.04 mmol) in degassed THF (20 mL) in the presence of PdCl₂(PPh₃)₂ (35 mg, 0.18 mmol), diethylamine (3 mL), and CuI (29 mg, 0.15 mmol) for 2 h as described in the general procedure. Final chromatography (hexane/CHCl₃, 5:1) afforded 9 (0.220 g, 92%) as a colorless solid. mp 70 °C. UV–Vis (CHCl₃): λmax (ε): 2943, 2147, 1605 cm⁻¹. 1H NMR (300 MHz, CDCl₃): δ 1.09 (s, 42H), 2.05 (s, 6H), 2.03 (s, 6H), 1.01 (s, 6H), 0.18 (s, 12H). 13C NMR (75 MHz, CDCl₃): δ 153.8, 152.5, 152.4, 152.0, 151.8, 151.9, 151.7, 151.6, 22.7, 22.6, 22.5, 22.4, 22.3. HRMS calcd for C₁₉H₂₆Si₂ (M⁺): 343.1534; found, 343.1534. Anal. Calcd for C₁₉H₂₆Si₂: C, 72.21; H, 10.91. Found: C, 72.25; H, 10.77.

1-Trisopropylsilyl-3-trimethylsilylletynyl-4-methyl-pent-3-en-1-ynyl (11). Triflate 8 (0.300 g, 1.00 mmol) was cross-coupled with trimethylsilylacetylene (0.364 g, 4.00 mmol) in degassed DMF (20 mL) in the presence of Pd(PPh₃)₄ (58 mg, 0.05 mmol), diethylamine (3 mL), and CuI (29 mg, 0.15 mmol) for 2 h as described in the general procedure. Final chromatography (hexane/CHCl₃, 5:1) afforded 9 (0.280 g, 84%) as a colorless oil. IR (neat): 2959, 2944, 2215, 1461 cm⁻¹. 1H NMR (300 MHz, CDCl₃): δ 150.6, 103.5, 102.3, 101.9, 96.1, 92.8, 22.7 (6H), 22.6 (4H), 18.7, 11.4, 0.0. 13C NMR (75 MHz, CDCl₃, APT): δ 154.9, 103.8, 102.6, 92.5, 22.7, 18.7, 11.4. EIMS m/z: 416.3 (M⁺, 63), 373.3 ([M + i-Pr⁺]⁺, 100). HRMS calcd for C₂₀H₂₆Si₂ (M⁺): 343.1534; found, 343.1530. Anal. Calcd for C₂₀H₂₆Si₂: C, 72.21; H, 10.77. Found: C, 72.25; H, 10.77.

1-Trisopropylsilyl-3-trimethylsilylletynyl-4-methyl-pent-3-en-1-ynyl (12). Triflate 8 (0.770 g, 2.00 mmol) was cross-coupled with trimethylsilylacetylene (0.730 g, 4.00 mmol) in degassed THF (40 mL) in the presence of Pd(PPh₃)₂(P₃)₃ (70 mg, 0.10 mmol), diethylamine (6 mL), and CuI (58 mg, 0.30 mmol) for 2 h as described in the general procedure. Final chromatography (hexane/CHCl₃, 5:1) afforded 9 (0.126 g, 98%) as a colorless solid. mp 52.5 °C. UV–Vis (CHCl₃) λmax (ε): 265 (1600) nm. IR (µscope): 2956, 2941, 2891, 1461 cm⁻¹. 1H NMR (300 MHz, CDCl₃, APT): δ 150.6, 103.9, 102.3, 101.9, 96.1, 92.8, 22.7 (7H, 22.6 (3H), 18.7, 11.4. 13C NMR (75 MHz, CDCl₃): δ 154.9, 103.8, 102.6, 92.5, 22.7, 18.7, 11.4. EIMS m/z: 416.3 (M⁺, 63), 373.3 ([M + i-Pr⁺]⁺, 100). HRMS calcd for C₂₀H₂₆Si₂ (M⁺): 343.1534; found, 343.1530. Anal. Calcd for C₂₀H₂₆Si₂: C, 72.21; H, 10.77. Found: C, 72.25; H, 10.77.

3,15-Bis(trimethylsilylletynyl)-2,10-dimethyl-6-isopropylidene-2,9-undecadiyne-4,7-diyne (13). Enediyne 10 (0.146 g, 0.590 mmol) was desilylated with K₂CO₃/MeOH and cross-coupled with triflate 8 (0.360 g, 1.20 mmol) in degassed DMF (20 mL) in the presence of Pd(PPh₃)₂(P₃)₃ (70 mg, 0.10 mmol), diethylamine (6 mL), and CuI (35 mg, 0.18 mmol) for 2 h as described in the general procedure. Final chromatography (hexane/CHCl₃, 5:1) afforded 13 (0.220 g, 92%) as a colorless solid. mp 136 °C. UV–Vis (CHCl₃) λmax (ε): 286 (25 900), 309 (18 000) nm. IR (µscope): 2958, 2907, 2147, 1605 cm⁻¹. 1H NMR (300 MHz, CDCl₃): δ 1.87 (s, 6H), 1.84 (s, 6H), 1.82 (s, 6H), 0.19 (s, 18H). 13C NMR (75 MHz, CDCl₃, APT): 154.6, 152.8, 101.8, 101.7, 95.7, 88.7, 88.0, 22.8, 22.7 (2x, 2.0). (one coincident peak not observed). EIMS m/z: 404.2 (M⁺, 50), 73.0 (Me₂Si⁺, 100). HRMS calcd for C₂₁H₂₄Si₂ (M⁺): 345.1534; found, 345.1534. Anal. Calcd for C₂₁H₂₄Si₂: C, 72.21; H, 10.77. Found: C, 72.25; H, 10.77.

3,15-Bis(trimethylsilylletynyl)-2,10-dimethyl-6-isopropylidene-2,9-undecadiyne-4,7-diyne (14). Enediyne 10 (0.279 g, 1.12 mmol) was desilylated with K₂CO₃/MeOH and cross-coupled with triflate 8 (0.870 g, 2.26 mmol) in degassed DMF (40 mL) in the presence of Pd(PPh₃)₂(P₃)₃ (0.13 g, 0.11 mmol), diethylamine (6 mL), and CuI (63 mg, 0.33 mmol) for 2 h as described in the general procedure. Final chromatography (hexane/CHCl₃, 5:1) followed by precipitation from MeOH gave 14 (0.338 g, 53%) as a colorless solid. mp 70–71 °C. UV–Vis (CHCl₃) λmax (ε): 286 (29 100), 312 (20 200) nm. IR (µscope): 2944, 2864, 2146, 1604 cm⁻¹. 1H NMR (300 MHz, CDCl₃): δ 2.07 (s, 6H), 2.05 (s, 6H), 2.03 (s, 6H), 1.09 (s, 2H). 13C NMR (75 MHz, CDCl₃, APT): δ 154.7, 152.7, 103.8, 102.2, 101.6, 92.2, 88.6, 88.4, 22.8, 22.6 (2x, 18.7, 11.4. EIMS m/z: 572.4 (M⁺, 73), 157.1 (i-Pr₂Si⁺, 100). HRMS calcd for C₂₀H₂₄Si₂ (M⁺): 572.4233; found, 572.4223. X-ray.
(s, 42H). 13C NMR (75 MHz, CDCl3): δ 153.8, 152.6, 152.4, 103.8, 102.2, 101.8 (3×), 92.2, 88.7, 88.4, 22.8, 22.7 (2×), 22.6 (2×), 18.7, 11.4 (thirteen coincident peaks not observed). Attempts for MS analyses were unsuccessful.

8.11,14,17,20-23-Heptaisopropylidinencyclooctos triangener 3,6,9,12,15,18,21-octayne (20). Heptamer 17 (20 mg, 0.028 mmol) was desilylated with K2CO3/MeOH as described in the general procedure and then oxidatively homocoupled in the presence of CuI (16 mg, 0.084 mmol), TMEDA (4.9 mg, 0.042 mmol), and THF (10 mL) under air for 2 h. Flash chromatography (hexane/CH2Cl2 5:1) gave 20 (5 mg, 31%) as a colorless solid. mp > 115 °C (dec). UV–vis (CHCl3) λmax (ε): 280 (44 400), 336 (6200) nm. 1H NMR (300 MHz, CDCl3): δ 2.07 (s, 12H), 2.04 (m, 30H), and CuI (39 mg, 0.20 mmol) for 2 h as described in the general procedure. Flash chromatography (hexane/CH2Cl2 5:1) followed by precipitation from hexane/CH2Cl2 2:1 afforded 26 (0.127 g, 88%) as a colorless solid. mp 176–178 °C. UV–vis (CHCl3) λmax (ε): 291 (21 200), 291 (29 900) nm. IR (µscope): 2942, 2850, 2146, 1668 cm−1. 1H NMR (300 MHz, CDCl3): δ 1.75–1.95 (m, 36H), 1.06 (s, 42H). 13C NMR (75 MHz, CDCl3): δ 153.8, 103.7, 102.2, 92.2, 88.6, 22.8, 22.5, 18.7, 11.4. HRMS calcld for C26H42Si2 (M+): 494.3764, found, 494.3768.

3.6-Bis(trimethylsilyl)-2,7-dimethyl-2,6-octadiene-4-yne (21). Enediyne 11 (79 mg, 0.24 mmol) was desilylated with K2CO3/MeOH and cross-coupled with triflate 9 (91 mg, 0.24 mmol) in degassed DMF (20 mL) in the presence of Pd(PPh3)4 (27 mg, 0.023 mmol), diethylamine (3 mL), and CuI (12 mg, 0.063 mmol) for 40 min as described in the general procedure. Flash chromatography (hexane/CH2Cl2 5:1) followed by precipitation from hexane/CH2Cl2 2:1 afforded 21 (43 mg, 60%) as a colorless solid. mp 65 °C (dec). UV–vis (CH2Cl2) λmax (ε): 260 (43 900), 289 (47 700) nm. IR (µscope): 2906, 2849, 2146, 1670 cm−1. 1H NMR (300 MHz, CDCl3): δ 1.60 (m, 10H), 1.35 (s, 21H), 0.46 (s, 9H). 13C NMR (75 MHz, CDCl3): δ 154.4, 153.8, 103.8, 102.2, 101.9, 95.8, 95.3, 88.8, 22.8, 22.3, 18.7, 11.4. HRMS calcld for C21H26Si2 (M+) 360.2825; found, 360.2829.