

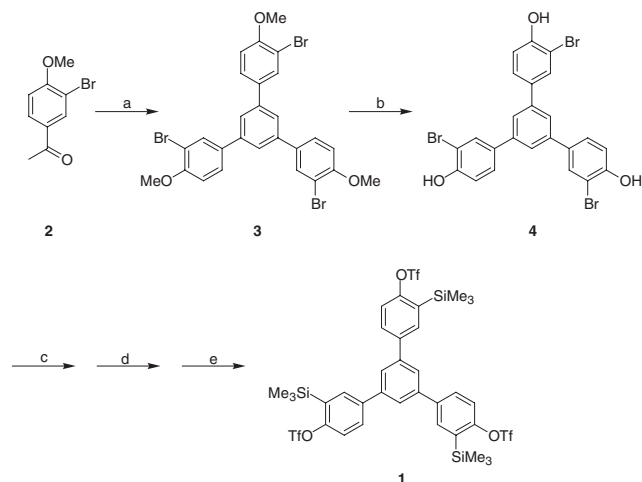
Facile Synthesis of Polycyclic Aromatic Hydrocarbons via a Trisaryne Equivalent

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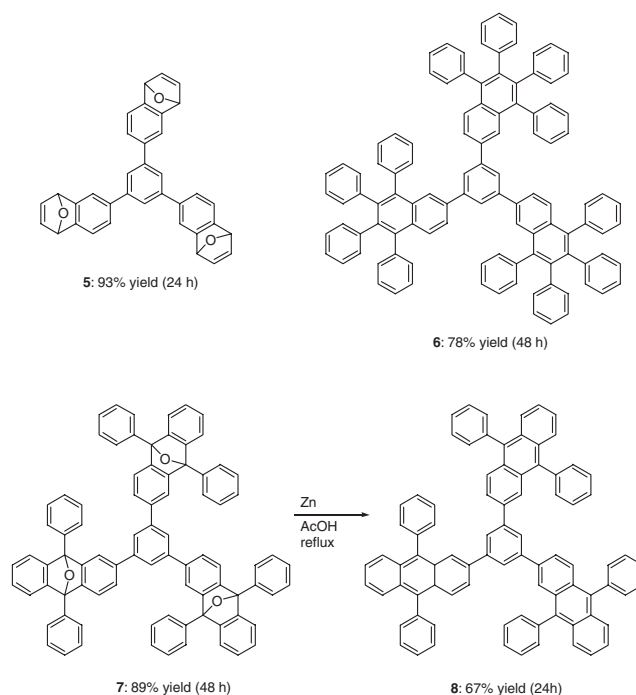
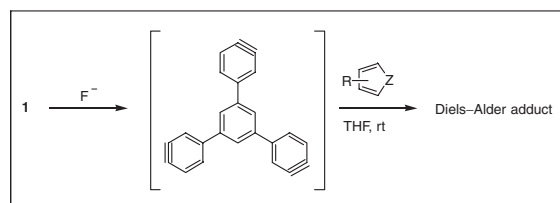
1,3,5-Tris[4-trifluoromethanesulfonyloxy-3-(trimethylsilyl)phenyl]benzene (**1**), a trisaryne equivalent, was synthesized. The Diels–Alder reaction or the palladium-catalyzed hexasilylation by use of **1** gave modest to excellent yields of diverse polyaromatic hydrocarbons straightforwardly.

Arynes are among the most important reactive intermediates in organic synthesis, which are readily convertible into a variety of substituted arenes through pericyclic reactions, electrophilic couplings, and transition metal-catalyzed reactions.¹ In particular, the use of arynes, bearing plural strained triple bonds, in these transformations has proven to be a powerful tool for the synthesis of polycyclic aromatic hydrocarbons (PAHs),² which have attracted considerable attention in materials science due to their shapes and other properties arising from their extended delocalized π -systems.³ Herein we report the synthesis of 1,3,5-tris[4-trifluoromethanesulfonyloxy-3-(trimethylsilyl)phenyl]benzene (**1**), a trisaryne equivalent, and its transformations to PAHs or their silicon-containing-analogues via the Diels–Alder reaction or the palladium-catalyzed hexasilylation.



Scheme 1. (a) TiF_2O , toluene, reflux, 55%; (b) HBr , AcOH , 75°C , 67%; (c) HMDS , 70°C ; (d) Me_3SiCl , Na , toluene, reflux; (e) (i) $n\text{-BuLi}$, Et_2O , 0°C to rt; (ii) TiF_2O , 0°C to rt, 27% (from **4**).

Trisaryne equivalent **1**⁴ was prepared from readily available 3-bromo-4-methoxyacetophenone (**2**)⁵ as shown in Scheme 1. According to a literature procedure,⁶ condensation of **2** in the presence of TiF_2O gave 1,3,5-tris(4-bromo-3-methoxyphenyl)benzene (**3**). Subsequent cleavage of the phenolic ether moieties in **3** with HBr provided **4**, which was converted into **1** in a similar manner to the preparation of a simple arylene precursor (10% overall yield from **2**).⁷



Scheme 2.

With this trisaryne equivalent in hand, we first investigated the Diels–Alder reaction with furan in the presence of a fluorene ion ($\text{KF}/18\text{-crown-6}$), and observed that all of the three triple bonds were efficiently trapped to afford 1,3,5-tris(5,8-dihydro-5,8-epoxy-2-naphthyl)benzene (**5**) in 93% yield (Scheme 2).⁸ Similarly, the reaction with tetraphenylcyclopentadienone took place smoothly with release of carbon monoxide, providing 1,3,5-tris(5,6,7,8-tetraphenyl-2-naphthyl)benzene (**6**) in 78% yield. Moreover, 1,3-diphenylisobenzofuran was also coupled with **1** to give 89% yield of 1,3,5-tris(9,10-diphenyl-9,10-epoxy-2-anthryl)benzene (**7**), which could be further converted into 1,3,5-tris(9,10-diphenyl-2-anthryl)benzene (**8**)⁹ in 67% yield under reductive deoxygenation conditions.¹⁰ Although the *syn:anti* ratio of **7** was elucidated to be ca. 1:3 by ^{13}C NMR spectrometry, we could not determine the diastereoselectivity of **5**.

Figure 1 depicts the absorption and emission spectra of **8**, in comparison with those of 9,10-diphenylanthracene (DPA). The

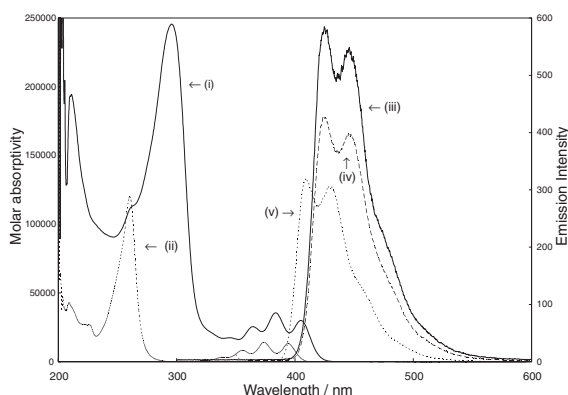
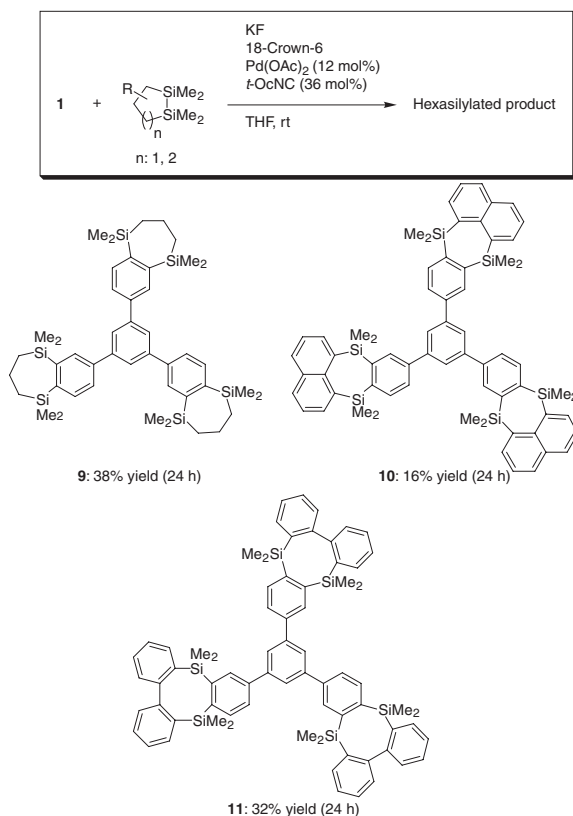


Figure 1. Absorption: (i) = **8**, (ii) = DPA, Fluorescence: (iii) = **8** ($\lambda_{\text{ex}} = \lambda_{\text{max}}$), (iv) = **8** ($\lambda_{\text{ex}} = 350 \text{ nm}$), (v) = DPA ($\lambda_{\text{ex}} = 350 \text{ nm}$);

absorption and emission maxima of **8** were somewhat red-shifted from those of DPA probably owing to the elongated conjugation in **8**, while the quantum yield of **8** ($\Phi_F = 0.44$) was lower than that of DPA ($\Phi_F = 0.90$).

The trisaryne equivalent was found to be applicable to the palladium-catalyzed coupling reaction with cyclic disilanes (Scheme 3).¹¹ Thus, treatment of **1** with a five-membered cyclic disilane, 1,1,2,2-tetramethyl-1,2-disilacyclopentane or 1,1,2,2-tetramethyl-1,2-(1,8-naphthylene)disilane, in the presence of a palladium-*t*-OcNC complex provided the corresponding hexasilylated products (**9** or **10**) in 38 or 16% yield, where all triple bonds were inserted into the Si-Si σ -bond. A six-membered cyclic disilane, 1,1,2,2-tetramethyl-1,2-(2,2'-biphenylene)disilane,



Scheme 3.

was also added to the trisaryne to offer 32% yield of **11**, containing three benzodisilocene moieties.

In conclusion, we have disclosed the synthesis of the trisaryne equivalent and its utilization for assembling diverse PAHs via the Diels-Alder reaction or the palladium-catalyzed hexasilylation. Further studies on synthetic application of the trisaryne equivalent to the construction of other PAHs are in progress.

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- 1**; ¹H NMR (CDCl₃) δ 0.43 (s, 27 H), 7.47 (d, $J = 8.4 \text{ Hz}$, 3 H), 7.68 (s, 3 H), 7.70 (dd, $J = 8.4, 2.4 \text{ Hz}$, 3 H), 7.77 (d, $J = 2.4 \text{ Hz}$, 3 H); ¹³C NMR (CDCl₃) δ -0.8, 118.5 (q, $J = 320 \text{ Hz}$), 120.1, 125.9, 130.2, 133.5, 135.2, 140.0, 141.5, 154.8; Anal. Calcd for C₃₆H₃₉O₉F₉S₃Si₃: C, 44.71; H, 4.06%. Found: C, 44.73; H, 3.99%.
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- A THF solution (1.0 mL) of **1** (0.195 g, 0.20 mmol), a 1,3-diene (0.90 mmol), 18-Crown-6 (0.334 g 1.26 mmol) and KF (0.071 g, 1.23 mmol) was stirred for the time specified in Scheme 2. The mixture was diluted with ethyl acetate, washed with brine and concentrated. The residue was purified by GPC to give the corresponding product.
- 8**; ¹H NMR (50 °C) (CDCl₃) δ 7.34 (dd, $J = 6.8, 3.4 \text{ Hz}$, 6 H), 7.43–7.62 (m, 36 H), 7.70 (dd, $J = 6.8, 2.9 \text{ Hz}$, 6 H), 7.74 (dd, $J = 8.8, 1.9 \text{ Hz}$, 3 H), 7.90 (s, 3 H); ¹³C NMR (50 °C) (CDCl₃) δ 124.8, 125.1, 125.2, 125.3, 125.7, 127.0, 127.6, 127.67, 127.72, 128.5, 129.2, 130.0, 130.2, 130.5, 131.3, 131.4, 137.1, 137.4, 137.6, 138.9, 139.1, 142.5; HRMS (FAB) Calcd for C₈₄H₅₄: 1062.4226, Found 1062.4240.
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