

A Facile Cascade Synthesis of 5,6-Diaryldibenzo[*a,e*]cyclooctenes from (*Z,Z*)-1-Aryl-3,5-octadiene-1,7-diyne[†]

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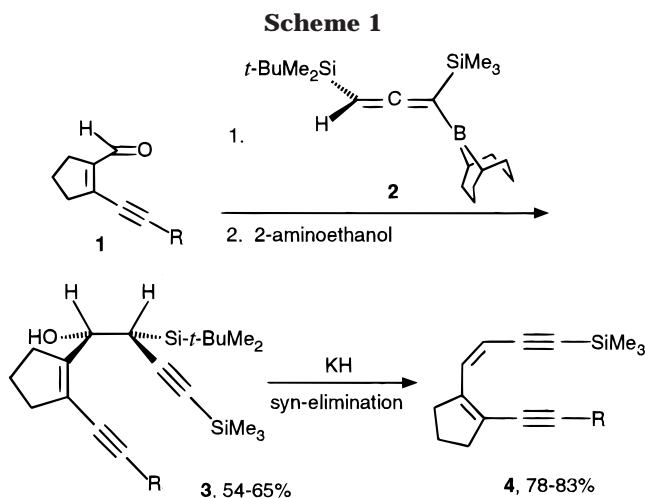
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Sequential treatment of (*Z*)-3-methyl-2-penten-4-ynal (**10**) with the allenylborane **2** and 2-aminoethanol furnished **11**. The use of **11** for cross-coupling with aryl iodides followed by the KH-induced syn elimination of the coupled adducts **13** provided easy access to a variety of dienediynes **14** for subsequent conversions to dibenzo[*a,e*]cyclooctenes (*sym*-dibenzocyclooctatetraenes) **17**. By cross-coupling with 1,2- and 1,4-diiodobenzene, it was possible to obtain **19** and **25** having two dienediynyl moieties. It was anticipated that the oligomers **21** and **26** containing multiple dibenzo[*a,e*]cyclooctenyl units could thus be synthesized. The ¹H NMR spectrum of **32** having three dibenzo[*a,e*]cyclooctenyl units indicates the presence of three diastereomers **32a–c** in a random statistical distribution of 2:1:1. Similarly, the ¹H NMR spectrum of **33** having two dibenzo[*a,e*]cyclooctenyl units exhibits signals that support the presence of two diastereomers **33a** and **33b** in a 1:1 ratio.

Introduction

We recently reported a new synthetic pathway to (*Z,Z*)-3,5-octadiene-1,7-diyne **4** (dieneniynes) as precursors of the highly reactive benzocyclobutadienes leading to dimers with unusual polycyclic structures (Scheme 1).¹ Treatment of enynyl aldehydes **1** with γ -(*tert*-butyldimethylsilyl)allenylborane **2** followed by 2-aminoethanol afforded the condensation adducts **3**. Subsequent KH-induced syn elimination³ of **3** furnished dienediynes **4** with high geometric purity (*Z:E* \geq 92:8). When dienediynes **4a** having a 1-phenyl substituent was treated with tetrabutylammonium fluoride (TBAF) at room temperature, the desilylated adduct **5** underwent two consecutive electrocyclic reactions to produce the benzocyclobutadiene **7**, which then dimerized to form **8** (Scheme 2). The dimer **8** was thermally unstable at room temperature and slowly transformed to the dibenzo[*a,e*]cyclooctene **9**. Fortunately, it was possible to separate a portion of **8** (19%) cleanly by column chromatography for structural elucidation along with a second portion containing a mixture of **8** and **9** (40:60) in 36% yield. On heating at 60 °C, **8** was converted to **9** within 3 h in 89% yield.

The reaction sequence outlined in Schemes 1 and 2 provides a simple and facile route to 5,6-diaryldibenzo[*a,e*]cyclooctenes.⁴ We now have further extended this pathway to the synthesis of several other 5,6-diaryldibenzo[*a,e*]cyclooctenes by using the readily available (*Z*)-3-



methyl-2-penten-4-ynal (**10**)⁵ for condensation with the allenylborane **2**. The presence of a terminal alkynyl group in **10** and consequently in the condensation adduct **11** made it possible to promote a Pd(PPh₃)₄-catalyzed cross-coupling reaction between **11** and a variety of aryl iodides,⁶ enhancing versatility and flexibility of this synthetic strategy for preparation of (*Z,Z*)-1-aryl-3,5-octadiene-1,7-diyne with diverse structures as precursors of 5,6-diaryldibenzo[*a,e*]cyclooctenes.

Results and Discussion

Enynyl aldehyde **10** was synthesized by oxidation of the commercially available (*Z*)-3-methyl-2-penten-4-yn-1-ol.⁵ Treatment of **10** with the allenylborane **2**, prepared in situ by the procedure reported previously,^{1,2} followed by 2-aminoethanol furnished the condensation adduct **11** in 69% yield with high diastereoselectivity (*de* > 99%)

[†] Dedicated to Professor William R. Moore on the occasion of his 70th birthday.

[‡] Author to whom correspondence concerning the X-ray structures should be addressed.

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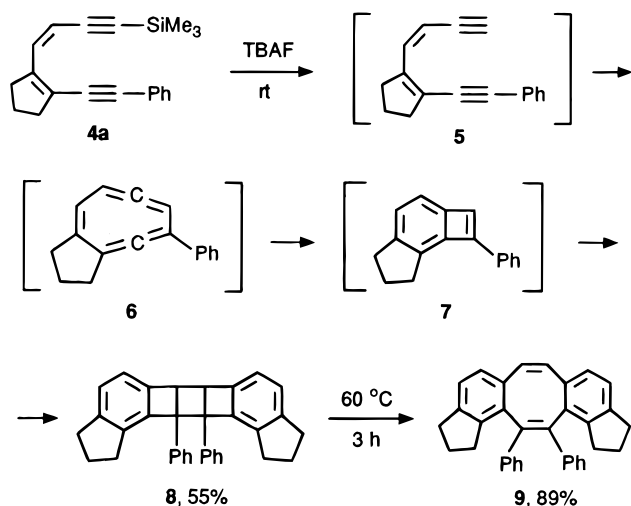
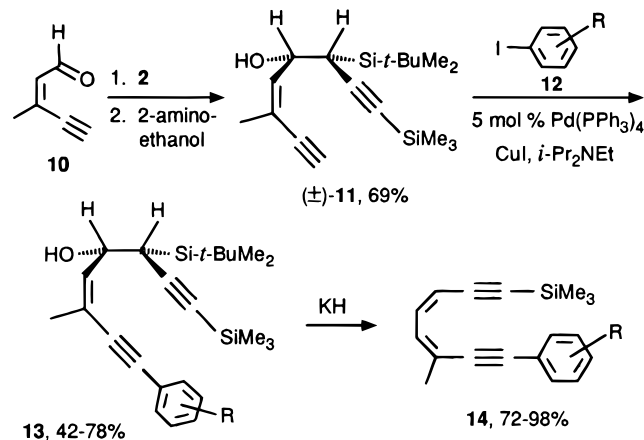
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Table 1. Synthesis of Enynyl Alcohols **13**, Dienediynes **14**, and Dibenzo[*a,e*]cyclooctenes **17**

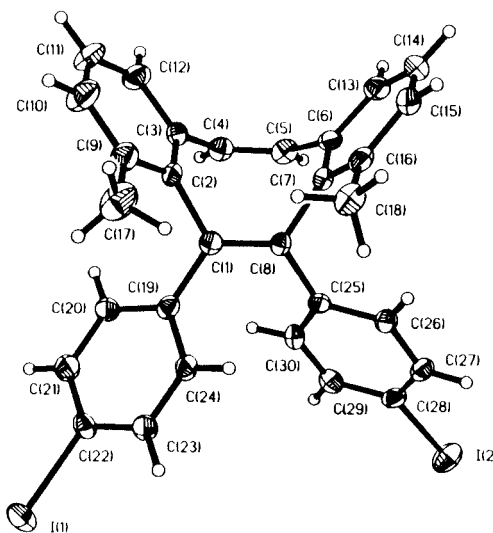
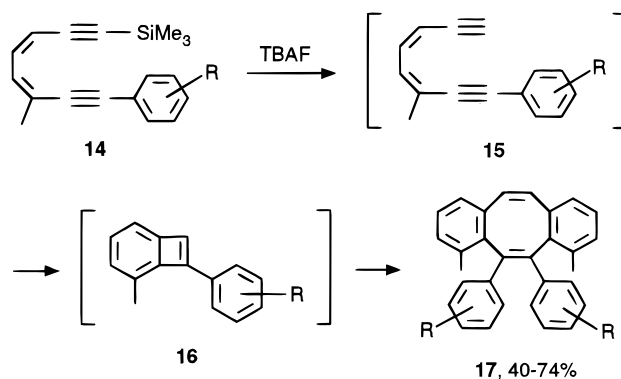
R	13 ^a	isolated yield, %	14	isolated yield, %	17	isolated yield, %
H	13a	78	14a	98	17a	74
4-Me ₃ Si	13b	66	14b	98	17b	54
2-iodo	13c	69	14c	95	17c	47
3-iodo	13d	42	14d	72	17d	40
4-iodo	13e	50	14e	84	17e	43

^a The preferential formation of the *Z,Z* isomer (>98%) of **14** by treatment of **13** with KH to induce syn elimination indicates that the *R,S/SR* pair was produced predominantly.

Scheme 2**Scheme 3**

(Scheme 3). The Pd(PPh₃)₄-catalyzed cross-coupling between **11** and aryl iodides **12** gave **13** in 42–78% yield (Table 1). The adducts **13c–e** were obtained from mono-coupling with 1,2-, 1,3-, and 1,4-diiodobenzene. Conversions of **13** to dienediynes **14** were carried out with potassium hydride in diethyl ether at 0 °C to induce syn elimination (Table 1).³ Dienediynes **14** having predominantly the *Z,Z* geometry (>98%) were thermally stable at room temperature.

Treatment of **14** with TBAF triggered a cascade sequence, starting from the desilylated dienediynes **15** through benzocyclobutadienes **16** and giving rise to dibenzo[*a,e*]cyclooctenes **17** (Scheme 4) in 40–74% isolated yields (Table 1). The X-ray crystal structure of **17e**⁷ showed that it has a tublike shape (Figure 1) resembling the parent dibenzo[*a,e*]cyclooctene.⁸

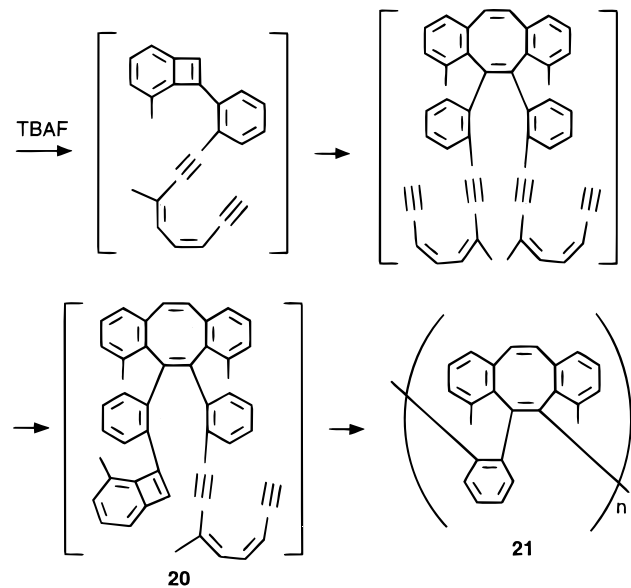
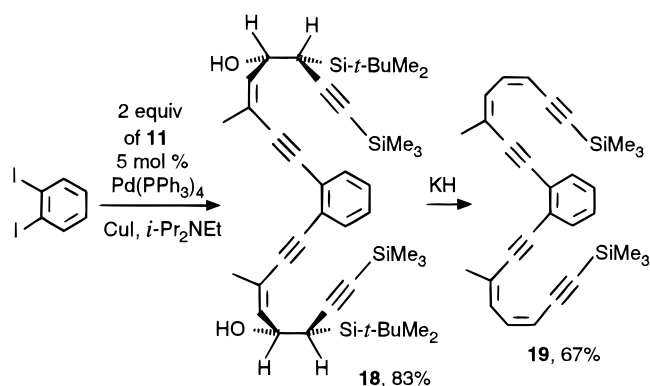
**Figure 1.** ORTEP drawing of the crystal structure of dibenzo[*a,e*]cyclooctene **17e**.**Scheme 4**

The use of 2 equiv of **11** for cross-coupling with 1,2-diiodobenzene was very efficient in producing **18** in 83% yield. Because **11** is a racemic mixture, **18** was obtained most likely as a 1:1 mixture of two diastereomers, but without any chemical consequences for the formation of the *Z* geometry in the next step (Scheme 5). The KH-induced syn elimination of **18** furnished **19** having two dienediynyl moieties. Treatment of **19** with TBAF produced a shining black solid, which exhibited broad ¹H NMR signals (DMSO-*d*₆) around δ 7.3 and 2.1. We suspect that this black solid with the appearance resembling that of graphite is a mixture of the oligomers depicted in **21**, which could be produced from consecutive intermolecular dimerizations as outlined in Scheme 5. A more definitive structural elucidation and characterization of **21** awaits further study. The reaction did not appear to produce the dimer **23**, which would allow structural elucidation by conventional spectroscopic methods. Presumably because of high reactivity of the benzocyclobutadienyl moiety, **20** or its precursors are more likely to undergo intermolecular dimerization rather than to form the second benzocyclobutadienyl unit in **22** for

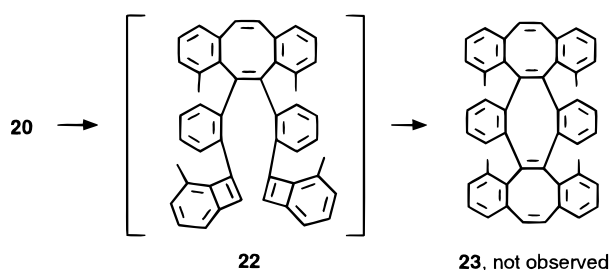
(7) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

(8) Irngartinger, H.; Reibel, W. R. K. *Acta Crystallogr., Sect. B* **1981**, *37*, 1724–1728.

Scheme 5



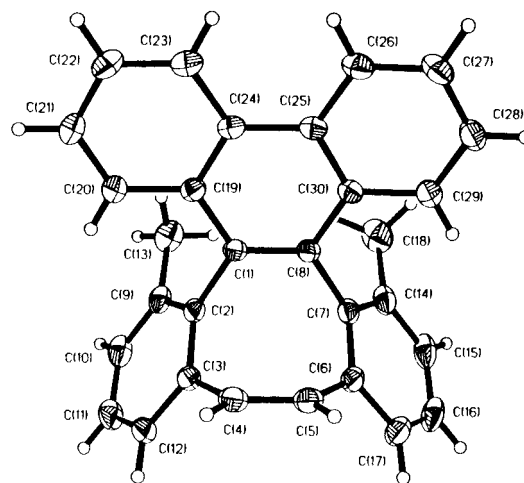
Scheme 6



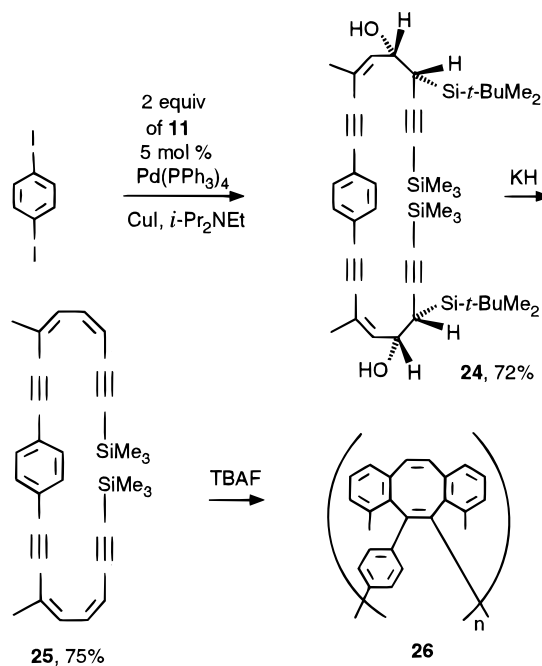
intramolecular cycloaddition to furnish the dimer **23** (Scheme 6).

Similarly, cross-coupling of 1,4-diiodobenzene with 2 equiv of **11** afforded **24** most likely as a 1:1 mixture of two diastereomers which were readily converted to **25** having two dienediynyl functionalities (Scheme 7). Treatment of **25** with TBAF produced a yellow solid exhibiting two broad ¹H NMR signals (C₆D₆) around the regions of δ 6.8 and δ 2.2 with an approximately 2:1 ratio in integration. Again, it is assumed that a mixture of the oligomers depicted in **26** was produced.

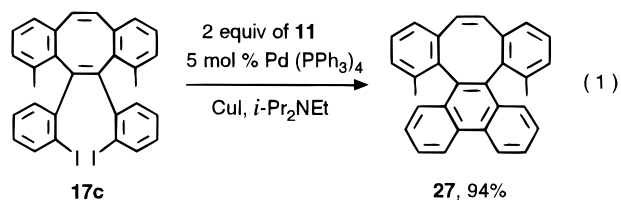
Interestingly, when diiodide **17c** was treated with 2 equiv of **11** for the Pd(PPh₃)₄-catalyzed cross-coupling reaction, the homo-coupling adduct **27** was isolated in 94% yield without formation of the expected cross-coupling product (eq 1). The structure of **27** was established by an X-ray structural analysis (Figure 2).⁷ Apparently, the proximity of the two iodo groups enabled


 Figure 2. ORTEP drawing of the crystal structure of **27**.

Scheme 7



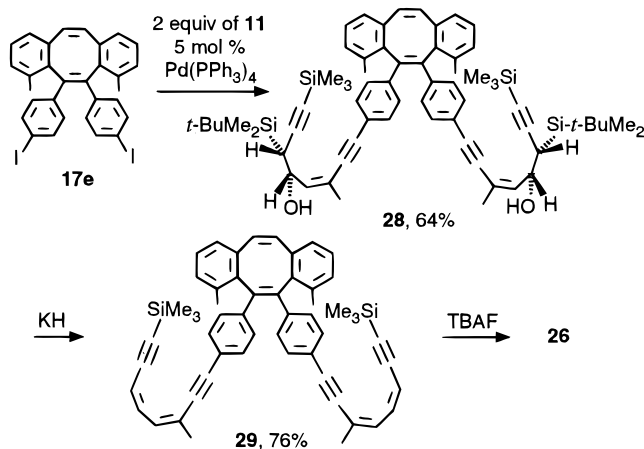
the homo-coupling reaction to occur preferentially.⁹ The homo-coupling adduct **27** was also obtained by treatment of **17c** with 8 mol % of Pd(PPh₃)₄ in the absence of **11**.



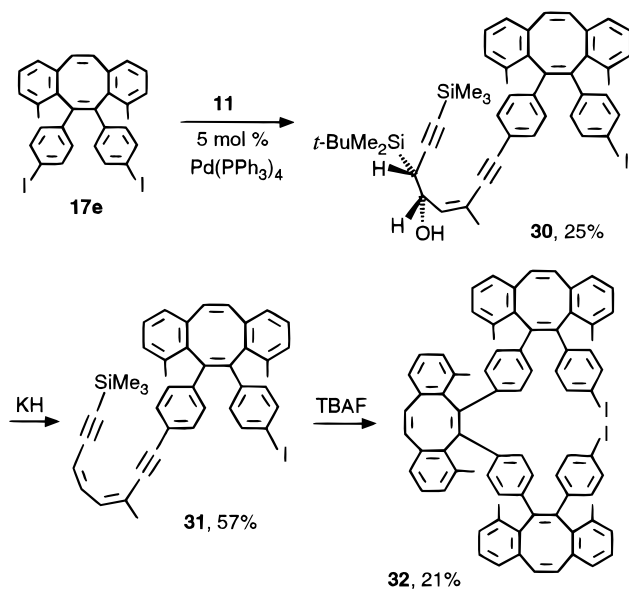
The cross-coupling reaction between diiodide **17e** and 2 equiv of **11** was successful in producing **28** most likely as a 1:1 mixture of two diastereomers in 64% isolated yield (Scheme 8). Conversion of **28** to **29** was again

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Scheme 8



Scheme 9



achieved with KH . Treatment of **29** with TBAF appeared to produce a mixture of the oligomers **26** as well.

Because of difficulties in characterizing the mixtures of the oligomers of **21** and **26**, the polycyclic **32** having only three dibenzo[*a,e*]cyclooctenyl units was synthesized by the sequence outlined in Scheme 9 for structural elucidation by conventional spectroscopic methods. Treatment of **17e** with 1 equiv of **11** for cross-coupling produced the mono-coupling adduct **30** in 25% yield, which was then transformed to **31** (57%) having only one dienediynyl moiety. The cascade sequence triggered by TBAF then led to **32** in 21% isolated yield.

The structure assignment of **32** is based on high-resolution mass spectra and the ^1H and ^{13}C NMR spectra. The molecular ion was detected on a high-resolution mass spectrometer ($m/z = 1248.2604$). The ^1H NMR spectrum (CDCl_3) exhibits 11 singlets between δ 2.36 and 2.12 with 10 of the peaks having approximately the same intensity and the one at δ 2.34 with twice the intensity (Figure 3). This observation could be accounted for on the basis of the presence of the three diastereomers **32a**, **32b**, and **32c** in a random statistical distribution of 2:1:1. Presumably because the rates of ring inversion of the three tublike dibenzo[*a,e*]cyclooctenyl units in **32** are relatively slow, distinct ^1H NMR signals due to the three diastereomers **32a–c** could thus be observed. The rate of ring

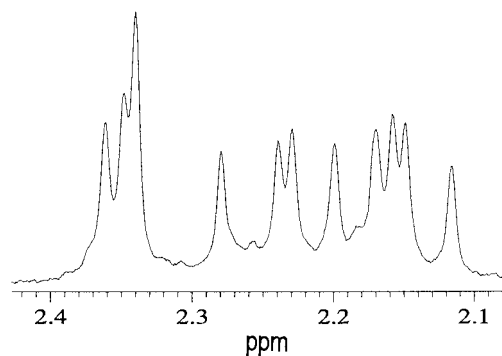
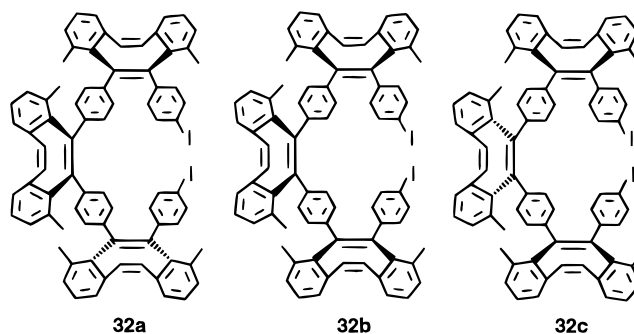


Figure 3. ^1H NMR signals of the methyl groups of **32** in CDCl_3 at 22 °C.



inversion of 5-phenyl-6-(*p*-methoxycarbonylphenyl)dibenzo[*a,e*]cyclooctene was reported to be relatively slow even at 156 °C.¹⁰ The presence of the methyl groups on the fused benzene rings in **32** could further increase the nonbonded steric interactions in the transition states, reducing the rate of ring inversion.¹¹ Since **32a** has no symmetry, all six methyl groups of **32a** are different, while **32b** and **32c** each have a plane of symmetry and consequently each possesses three different types of methyl groups with each signal having twice the intensity of a single methyl group. Because **32a** has twice the population in the 2:1:1 mixture, the ^1H NMR spectrum of the mixture could therefore exhibit a maximum of 12 singlets of equal intensity arising from the methyl groups. The actual spectrum shown in Figure 3 suggests that two of the signals overlap at δ 2.34 with 10 other signals clearly discernible. The aromatic region of the ^1H NMR spectrum has too many overlapping signals to be of use for structural elucidation.

The ^{13}C NMR spectrum of **32** exhibits sets of signals with up to four peaks in each set. For example, a set of four distinct peaks was observed at δ 141.38, 141.32, 141.31, and 141.28 as well as at δ 140.97, 140.79, 140.72, and 140.69. This pattern of signals is consistent with the presence of the three diastereomers **32a–c** with two peaks from **32a** and one peak each from **32b** and **32c** for each set of signals.

The possibility of interconversions among **32a**, **32b**, and **32c** by ring inversion of the tublike dibenzo[*a,e*]cyclooctenyl units was studied by recording their ^1H NMR signals at elevated temperatures using 1,1,2,2-tetrachloroethane-*d*₂ as the solvent. At 22 °C, nine distinct signals were observed for the methyl groups with the peak at δ

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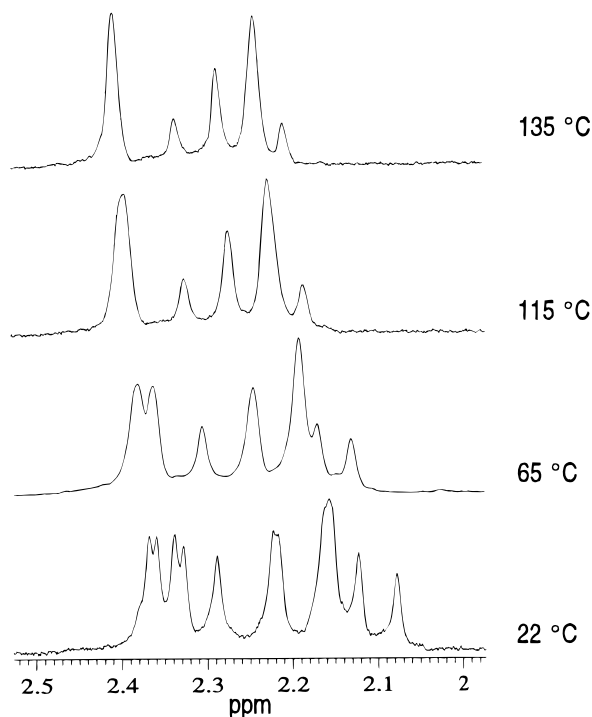
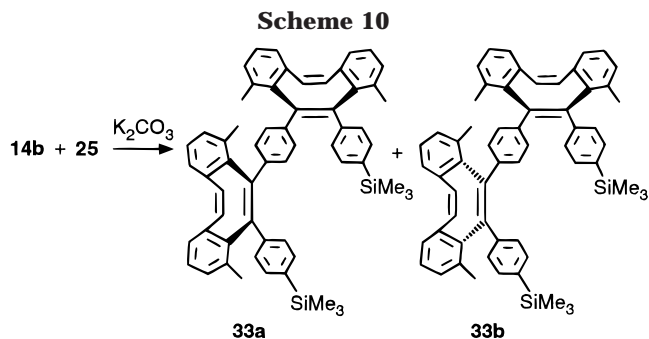


Figure 4. ^1H NMR signals of the methyl groups of **32** in 1,1,2,2-tetrachloroethane- d_2 .

2.22 having twice the intensity and the peak at δ 2.16 having three times the intensity (Figure 4). At 65 °C, the two most downfield signals and the next two most downfield signals collapsed into two singlets. At 115 °C, they further coalesced into a singlet. In addition, the second and the third most upfield signals also collapsed into a singlet. However, the three other signals remained clearly separated at 135 °C and exhibited no significant line broadening. These variable-temperature studies appear to suggest that ring inversion is relatively slow on the NMR time scale even at 135 °C. The overlapping of some signals beginning at 65 °C is due to accidental isochrony arising from dependence of chemical shift on temperature and cannot be attributed to lower coalescence temperatures due to smaller differences of chemical shifts. The ^1H NMR spectrum of the same sample retaken at 22 °C is identical to the one recorded before heating, indicating no decomposition of the sample and no rearrangement to the isomer having the aryl groups on the opposite sides of the eight-membered ring.^{10,12}

A small amount of **33** (4% yield) having two dibenzo[*a,e*]cyclooctenyl units was isolated from treatment of a mixture of **25** and an excess of **14b** with K_2CO_3 (Scheme 10). The molecular ion of **33** ($m/z = 834.4064$) was detected as the base peak on a high resolution mass spectrometer. Because there are only two dibenzo[*a,e*]cyclooctenyl units in **33**, the two diastereomers **33a** and **33b** could exist in a random statistical distribution of 1:1. With the presence of a plane of symmetry in **33a** and C_2 symmetry in **33b**, one can expect to observe four ^1H NMR signals as singlets of equal intensity arising from the methyl groups as well as two signals from the trimethylsilyl groups. Indeed, the ^1H NMR spectrum (CDCl_3) exhibits four singlets of essentially equal intensity at δ 2.42, 2.39, 2.16, and 2.12 from the methyl groups and



two singlets at δ 0.18 and 0.17 from the trimethylsilyl groups. At 115 °C in 1,1,2,2-tetrachloroethane- d_2 , the two trimethylsilyl signals collapsed into a singlet and the two aromatic signals originally at δ 6.67 and 6.65 at 22 °C also coalesced into a singlet. However, the four methyl signals remained well separated at 135 °C and exhibited no significant line broadening. Again, these observations suggest a relatively slow rate of ring inversion.

Conclusions

A new and versatile pathway to (*Z,Z*)-1-aryl-3,5-octadiene-1,7-diyne as precursors of 5,6-diaryldibenzo[*a,e*]cyclooctenes has been established. Specifically, **11** serves as a latent dienediyne moiety to allow cross-coupling with aryl iodides, providing easy access to a variety of dienediynes for subsequent conversions to 5,6-diaryldibenzo[*a,e*]cyclooctenes. By placing two dienediynyl moieties in the same molecule, it was possible to produce oligomers having multiple dibenzo[*a,e*]cyclooctenyl units.

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from benzophenone ketyl prior to use. (*Z*)-3-Methyl-2-penten-4-yn-1-ol, KH (35 wt % dispersion in mineral oil), a 1.0 M solution of tetrabutylammonium fluoride (TBAF) in THF, a 1.0 M solution of *B*-methoxy-9-borabicyclo[3.3.1]nonane (*B*-methoxy-9-BBN) in hexanes, and $\text{Pd}(\text{PPh}_3)_4$ were purchased from Aldrich Chemical Co. and were used as received. Diiodobenzenes were obtained from Oakwood Products, Inc., and were used without further purification. (*Z*)-3-Methyl-2-penten-4-ynal (**10**) was synthesized by oxidation of (*Z*)-3-methyl-2-penten-4-yn-1-ol as described previously.⁵ Allenylborane **2** was prepared from 3-(*tert*-butyldimethylsilyl)-1-(trimethylsilyl)-1-propyne according to the reported procedure.^{1,2} 1-Iodo-4-(trimethylsilyl)benzene (97% yield) was prepared by treatment of 1,4-diiodobenzene in THF at -78 °C with *n*-butyllithium followed by trimethylsilyl chloride. ^1H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in CDCl_3 using CHCl_3 (^1H δ 7.25) and CDCl_3 (^{13}C δ 77.10) as internal standards.

(\pm)-**(3*R*,4*S*,5*Z*)-3-(*tert*-Butyldimethylsilyl)-6-methyl-1-(trimethylsilyl)-5-octene-1,7-diyne-4-ol (11)**. To a solution of 1.67 g (7.38 mmol) of 3-(*tert*-butyldimethylsilyl)-1-(trimethylsilyl)-1-propyne in 20 mL of THF at -10 °C was added 2.95 mL of a 2.5 M solution of *n*-butyllithium (7.38 mmol) in hexanes. After 30 min of stirring at -10 °C, 7.38 mL (7.38 mmol) of a 1.0 M solution of *B*-methoxy-9-BBN in hexanes was introduced with a syringe. After an additional 45 min at 0 °C, 1.25 mL of $\text{BF}_3 \cdot \text{OEt}_2$ (1.40 g, 9.84 mmol) was added, and the mixture was stirred at 0 °C for 20 min to allow for the formation of the allenylborane **2** before 0.694 g of **10** (7.38 mmol) in 10 mL of THF was introduced. The mixture was allowed to warm to room temperature and stirred for 5 h. THF and hexanes were evaporated at reduced pressure, and the

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pressure was then restored with nitrogen. Hexanes (40 mL) was added followed by 1.0 mL of 2-aminoethanol, and a precipitate appeared almost immediately. After 20 min of stirring, the precipitate was removed by filtration, and the filtrate was washed with water, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (silica gel/5–10% diethyl ether in hexanes) to afford 1.63 g (5.09 mmol, 69%) of **11** (de > 99%) as a light yellow oil: IR (neat) 3538, 3310, 2156, 1249, 841 cm⁻¹; ¹H δ 6.00 (1 H, dm, *J* = 8.5 and 1 Hz), 4.65 (1 H, td, *J* = 8.5 and 2.9 Hz), 3.12 (1 H, s), 2.13 (1 H, d, *J* = 8.9 Hz), 2.10 (1 H, d, *J* = 3.0 Hz), 1.87 (3 H, d, *J* = 1.4 Hz), 0.94 (9 H, s), 0.13 (12 H, s), 0.10 (3 H, s); ¹³C δ 141.55, 117.72, 105.27, 89.79, 82.12, 82.07, 68.82, 27.40, 27.02, 22.88, 17.66, 0.22, -6.41, -6.60; MS *m/z* 320 (M⁺), 305, 263, 205, 190, 73; HRMS calcd for C₁₈H₃₅OSi₂ (MH⁺) 321.2070, found 321.2077. Anal. Calcd for C₁₈H₃₂OSi₂: C, 67.43; H, 10.06. Found: C, 67.54; H, 10.04.

(±)-(3*R*,4*S*,5*Z*)-3-(*tert*-Butyldimethylsilyl)-6-methyl-8-phenyl-1-(trimethylsilyl)-5-octene-1,7-diyn-4-ol (**13a**). The following procedure for the preparation of **13a** is representative for the cases using **11** for cross-coupling. A suspension of 0.685 g of **11** (2.14 mmol), 0.479 g of iodobenzene (2.35 mmol), 0.033 g of CuI (0.17 mmol), 0.127 g of Pd(PPh₃)₄ (0.11 mmol), and 1.12 mL of diisopropylethylamine (6.42 mmol) in 8 mL of DMF was cooled to -78 °C and degassed by three cycles of freeze-thaw. The resulting mixture was stirred at 42 °C under a nitrogen atmosphere for 22 h before 30 mL of a saturated ammonium chloride solution and 100 mL of Et₂O were added. The solid material was removed by filtration, and the aqueous layer was separated and extracted with Et₂O. The combined organic layers were washed with a saturated NH₄Cl solution, dried over MgSO₄, and concentrated. The residue was purified by column chromatography (silica gel/5–10% diethyl ether in hexanes) to furnish 0.664 g of **13a** (1.68 mmol, 78%) as a pale yellow oil: IR (neat) 3510, 2155, 1249, 840 cm⁻¹; ¹H δ 7.43–7.39 (2 H, m), 7.33–7.29 (3 H, m), 5.99 (1 H, dq, *J* = 8.7 and 1.4 Hz), 4.78 (1 H, td, *J* = 8.3 and 2.8 Hz), 2.20 (1 H, d, *J* = 8.9 Hz), 2.16 (1 H, d, *J* = 3.0 Hz), 1.97 (3 H, d, *J* = 1.2 Hz), 0.95 (9 H, s), 0.17 (3 H, s), 0.16 (9 H, s), 0.14 (3 H, s); ¹³C δ 139.66, 131.50, 128.38, 128.33, 123.17, 118.80, 105.34, 94.18, 89.85, 87.71, 69.10, 27.52, 27.05, 23.18, 17.64, 0.25, -6.37, -6.47; MS *m/z* 378 (M⁺ - H₂O), 339, 264, 249, 233, 171.

(3*Z*,5*Z*)-3-Methyl-1-phenyl-8-(trimethylsilyl)-1,7-octadiene-3,5-diene (**14a**). The following procedure for the preparation of **14a** is representative. To a dispersion of 0.514 g (12.8 mmol) of KH in 15 mL of diethyl ether at 0 °C under a nitrogen atmosphere was added 1.271 g (3.21 mmol) of **13a** in 15 mL of diethyl ether. After 1 h of stirring, the reaction mixture was filtered through a short Florisil column to remove excess KH. The filtrate was washed with a saturated aqueous solution of NH₄Cl, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes) to furnish 0.828 g (3.14 mmol, 98%) of **14a** (geometric purity >98%) as a yellow oil: IR (neat) 2141, 1250, 845, 755, 689 cm⁻¹; ¹H δ 7.49–7.45 (2 H, m), 7.35–7.31 (3 H, m), 6.97 (1 H, t, *J* = 11.1 Hz), 6.81 (1 H, d, *J* = 11.5 Hz), 5.52 (1 H, d, *J* = 10.7 Hz), 2.10 (3 H, s), 0.24 (9 H, s); ¹³C δ 138.76, 133.01, 131.60, 128.51, 128.43, 123.51, 123.16, 109.18, 102.36, 102.33, 97.01, 88.56, 23.72, 0.08; MS *m/z* 264 (M⁺), 249, 247, 205, 73.

1,10-Dimethyl-11,12-diphenyldibenzo[*a,e*]cyclooctene (**17a**). The following procedure for the preparation of **17a** is representative. To a solution of **14a** (0.828 g, 3.14 mmol) in a mixture of THF (35 mL) and ethanol (5 mL) was added 9.4 mL of a 1.0 M solution of TBAF (9.4 mmol) in THF at room temperature under a nitrogen atmosphere. After 5 min of stirring, the reaction mixture was heated under reflux for 14 h. Diethyl ether was added, and the mixture was washed with water, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (silica gel/5–10% diethyl ether in hexanes) to give 0.445 g (1.16 mmol, 74%) of **17a** as colorless crystals: IR 3053, 3011, 700 cm⁻¹; ¹H δ 7.07–6.88 (18 H, m), 2.35 (6 H, s); ¹³C δ 142.83, 140.77, 140.61, 137.31, 135.31, 133.61, 130.50, 129.00, 127.69, 126.52,

126.17, 124.96, 20.76; MS *m/z* 307 (M⁺ - C₆H₅), 293, 206. Anal. Calcd for C₃₀H₂₄: C, 93.71; H, 6.29. Found: C, 93.55; H, 6.36.

1,10-Dimethyl-11,12-bis[4-(trimethylsilyl)phenyl]dibenzo[*a,e*]cyclooctene (**17b**). To a suspension of 0.370 g of K₂CO₃ (2.68 mmol) in 5 mL of ethanol was added a solution of 0.450 g of **14b** (1.34 mmol) in 5 mL of Et₂O at room temperature under a nitrogen atmosphere. After 5 min of stirring, the reaction mixture was heated to 60 °C for 14 h. Ethanol was then evaporated in vacuo, and a mixture of Et₂O and water was introduced. After filtration, the organic layer was separated, washed with water, and concentrated. The residue was purified by column chromatography (silica gel/5–10% diethyl ether in hexanes) to afford 0.190 g of **17b** (0.36 mmol, 54%) as colorless crystals: IR 1248, 839 cm⁻¹; ¹H δ 7.21 (4 H, d, *J* = 8.3 Hz), 7.03–6.86 (12 H, m), 2.32 (6 H, s), 0.19 (18 H, s); ¹³C δ 142.91, 140.95, 140.53, 138.34, 137.28, 135.38, 133.56, 132.66, 129.63, 128.92, 126.11, 124.89, 20.76, -1.06; MS *m/z* 528 (M⁺), 513, 455, 440, 249, 206, 73; HRMS calcd for C₃₆H₄₀Si₂ 528.2669, found 528.2651.

Diol **18**. The same procedure was repeated as described for **13a** except that 0.704 g of **11** (2.2 mmol) was used to couple with 0.330 g of 1,2-diiodobenzene (1.0 mmol) to afford 0.593 g of **18** (0.83 mmol, 83%, most likely a 1:1 mixture of two diastereomers) as a pale yellow solid: IR 3514, 2156, 1249, 840 cm⁻¹; ¹H δ 7.38 (2 H, dd, *J* = 5.7 and 3.4 Hz), 7.24 (2 H, dd, *J* = 5.9 and 3.4 Hz), 6.01 (2 H, dm, *J* = 8.7 and 1.4 Hz), 4.78 (2 H, tm, *J* = 7.9 and 2.2 Hz), 2.23 (2 H, br d, *J* = 8.3 Hz), 2.14 (2 H, d, *J* = 3.0 Hz), 1.97 (6 H, d, *J* = 1.0 Hz), 0.92 (18 H, s), 0.15 (6 H, s), 0.14 (18 H, s), 0.11 (6 H, s); ¹³C δ 140.24, 131.76, 128.00, 125.49, 118.60, 105.43, 92.91, 91.69, 89.72, 69.12, 27.50, 27.04, 23.18, 17.61, 0.25, -6.36, -6.48. The ¹H NMR spectrum showed the presence of 14% of the homo-coupling adduct of **11** derived from joining the acetylenic CH terminus of two molecules of **11**.

Dienediyne **19**. The same procedure was repeated as described for **14a** except that 0.270 g of **18** (0.38 mmol) and 0.121 g of KH (3.03 mmol) were used to afford 0.115 g (0.256 mmol, 67%) of **19** (geometric purity >98%) as a brown oil: IR (neat) 2141, 1249, 843 cm⁻¹; ¹H δ 7.47 (2 H, dd, *J* = 5.9 and 3.3 Hz), 7.27 (2 H, dd, *J* = 5.7 and 3.4 Hz), 6.99 (2 H, t, *J* = 11.1 Hz), 6.82 (2 H, dm, *J* = 11.1 and 1 Hz), 5.46 (2 H, d, *J* = 10.7 Hz), 2.08 (6 H, s), 0.23 (18 H, s); ¹³C δ 138.79, 133.57, 132.09, 128.23, 125.40, 123.16, 109.55, 102.44, 102.37, 95.67, 92.59, 23.72, 0.09.

5,14-Dimethyldibenzo[3,4:7,8]cycloocta[1,2-*l*]phenanthrene (**27**). A suspension of 0.366 g of **17c** (0.58 mmol), 0.422 g of **11** (1.32 mmol), 0.005 g of CuI (0.024 mmol), 0.035 g of Pd(PPh₃)₄ (0.03 mmol), and 0.5 mL of diisopropylethylamine (3.0 mmol) in 7 mL of DMF was cooled to -78 °C and degassed by three cycles of freeze-thaw. The resulting mixture was stirred at 42 °C under a nitrogen atmosphere for 46 h before 20 mL of a saturated ammonium chloride solution and 30 mL of Et₂O were introduced. The solid material was removed by filtration, and the aqueous layer was separated and extracted with Et₂O. The combined organic layers were washed with a saturated NH₄Cl solution, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (silica gel/5–10% diethyl ether in hexanes) to furnish 0.212 g (0.55 mmol, 94%) of **27** as colorless crystals: ¹H δ 8.77 (2 H, d, *J* = 8.3 Hz), 7.61 (2 H, td, *J* = 7.6 and 1.4 Hz), 7.43 (2 H, td, *J* = 7.6 and 1.2 Hz), 7.20–7.09 (6 H, m), 6.99 (2 H, dd, *J* = 7.2 and 1.5 Hz), 6.68 (2 H, s), 2.00 (6 H, s); ¹³C δ 138.84, 138.29, 136.64, 135.94, 133.13, 130.49, 130.10, 128.38, 126.89, 126.68 (two signals overlapped), 126.29, 125.03, 122.74, 20.60. The structure of **27** was unequivocally established by an X-ray structural analysis.⁷ Similarly, **27** was obtained by treatment of **17c** with 8 mol % of Pd(PPh₃)₄, 8 mol % of CuI, and 5 equiv of diisopropylethylamine in DMF at 52 °C for 66 h without **11**.

Alcohol **30**. The same procedure was repeated as described for **13a** except that 0.240 g of **11** (0.75 mmol) was used to couple with 0.477 g of **17e** (0.75 mmol) to afford 0.152 g of **30** (0.184 mmol, 25%) as a pale yellow solid: IR 3540, 2153, 1250, 842 cm⁻¹; ¹H δ 7.38 (2 H, d, *J* = 8.3 Hz), 7.12 (2 H, d, *J* = 8.3 Hz), 7.04–6.85 (10 H, m), 6.74 (2 H, d, *J* = 8.3 Hz), 5.96 (1 H,

dg, $J = 8.6$ and 1.5 Hz), 4.72 (1 H, tm, $J = 6.8$ and 1 Hz), 2.32 (3 H, s), 2.25 (3 H, s), 2.15 (1 H, br), 2.13 (1 H, d, $J = 3.0$ Hz), 1.92 (3 H, d, $J = 1.2$ Hz), 0.93 (9 H, s), 0.15 (12 H, s), 0.11 (3 H, s); ^{13}C δ 142.09, 140.74, 140.59, 140.24, 139.88, 139.72, 137.41, 137.34, 137.16, 137.00, 135.30, 134.98, 133.58, 133.56, 132.27, 131.04, 130.35, 129.30, 129.17, 129.11, 126.52, 126.47, 125.07, 121.38, 118.80, 105.36, 94.26, 92.53, 89.84, 88.27, 69.08, 27.53, 27.09, 23.14, 20.71, 20.68, 17.65, 0.26, -6.35 , -6.42 .

Dienediynes 31. The same procedure was repeated as described for **14a** except that 0.063 g of **30** (0.076 mmol) and 0.012 g of KH (0.30 mmol) were used to afford 0.030 g of **31** (0.043 mmol, 57%) as a yellow solid: ^1H δ 7.38 (2 H, d, $J = 8.5$ Hz), 7.17 (2 H, d, $J = 8.5$ Hz), 7.03–6.86 (11 H, m), 6.76 (1 H, dm), 6.74 (2 H, d, $J = 8.5$ Hz), 5.47 (1 H, d, $J = 10.5$ Hz), 2.31 (3 H, s), 2.25 (3 H, s), 2.04 (3 H, s), 0.21 (9 H, s); ^{13}C δ 142.09, 140.75, 140.33, 139.95, 138.75, 137.51, 137.41, 137.31, 137.16, 137.03, 135.25, 135.00, 133.56, 133.03, 132.26, 131.14, 130.39, 129.44, 129.28, 129.16, 126.53, 125.08, 123.46, 121.31, 109.15, 102.35, 97.08, 92.59, 89.15, 23.68, 20.68, 0.07.

Dibenzo[a,e]cyclooctene 32. The same procedure was repeated as described for **17a** except that 0.123 g of **31** (0.177 mmol) and 1.7 mL of a 1.0 M solution of TBAF (1.7 mmol) in THF were used, and the product was purified further by HPLC (5% diethyl ether in hexanes) to afford 0.023 g of **32** (0.0184 mmol, 21%) as a yellow solid: ^1H δ 7.31 (2 H, d, $J = 8.5$ Hz), 7.26 (2 H, dd, $J = 8.7$ and 1.8 Hz), 7.01–6.82 (24 H, m), 6.74–6.64 (12 H, m), 2.36 (1.5 H, s), 2.35 (1.5 H, s), 2.34 (3 H, s), 2.28 (1.5 H, s), 2.24 (1.5 H, s), 2.23 (1.5 H, s), 2.20 (1.5 H, s), 2.17 (1.5 H, s), 2.16 (1.5 H, s), 2.15 (1.5 H, s), 2.12 (1.5 H, s); ^{13}C δ 142.55, 142.53, 142.51, 142.47, 142.34, 142.29, 142.25, 142.23, 142.19, 141.38, 141.33, 141.31, 141.28, 140.97, 140.79, 140.72, 140.69, 139.99, 139.93, 139.89, 139.88, 139.68, 139.61, 139.54, 139.10, 139.03, 139.02, 139.00, 138.94, 138.92, 138.82, 137.41, 137.40, 137.38, 137.33, 137.31, 137.28, 137.13, 137.07, 137.02, 136.77, 136.74, 136.71, 135.52, 135.49, 135.42, 135.34, 135.30, 135.16, 134.98, 134.89, 134.84, 133.56, 133.50, 133.44, 132.37, 132.34, 132.31, 130.16, 129.55, 129.52, 129.12, 128.99, 126.46, 126.39, 126.34, 126.30, 126.20, 125.06, 125.02, 124.91, 124.87, 92.30, 92.27, 20.82, 20.79, 20.77, 20.66, 20.62; HRMS calcd for $\text{C}_{78}\text{H}_{58}\text{I}_2$ 1248.2620, found 1248.2604.

Dibenzo[a,e]cyclooctene 33. To a suspension of 2.76 g of K_2CO_3 (20 mmol) in 50 mL of ethanol were added a solution of 0.396 g of **25** (0.88 mmol) and 2.496 g of **14b** (7.43 mmol) in 20 mL of Et_2O via cannula at room temperature under a nitrogen atmosphere. After 5 min of stirring, the reaction mixture was heated to 60°C for 14 h. Ethanol was then evaporated in vacuo, and a mixture of Et_2O and water was introduced. After filtration, the organic layer was separated, washed with water, dried over MgSO_4 , and concentrated. The residue was purified by column chromatography (silica gel/5–10% diethyl ether in hexanes) to give 0.554 g of **17b** (1.05 mmol, 28%) and, after further purification by HPLC (7% diethyl ether in hexanes), 0.029 g of **33** (0.035 mmol, 4%) as a pale yellow solid: ^1H δ 7.14 (2 H, m), 7.0–6.9 (18 H, m), 6.87 (4 H, s), 6.74 (2 H, s), 6.72 (2 H, s), 2.40 (3 H, s), 2.37 (3 H, s), 2.14 (3 H, s), 2.10 (3 H, s), 0.18 (9 H, s), 0.17 (9 H, s); MS m/z 834 (M^+ , base peak), 455, 379, 206; HRMS calcd for $\text{C}_{60}\text{H}_{58}\text{Si}_2$ 834.4075, found 834.4064.

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Supporting Information Available: Experimental procedures and spectroscopic data for **13b–e**, **14b–e**, **17c–e**, **24**, **25**, **28**, and **29** and ^1H and ^{13}C NMR spectra of **11**, **13a–e**, **14a–e**, **17a–e**, **18**, **19**, **24**, **25**, and **27–33** (59 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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