Benzocyclobutadienes via Electrocyclizations of (*Z*,*Z*)-3,5-Octadiene-1,7-diynes Leading to Dimers with Unusual Polycyclic Structures

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Abstract: (*Z*,*Z*)-3,5-Octadiene-1,7-diynes **15a**−**e** were synthesized by condensation of enynyl aldehydes **12a**−**e** with allenylborane **11** to furnish enynyl alcohols **14a**−**e** followed by the elimination step of the Peterson olefination reaction. Desilylation of **15a** with tetrabutylammonium fluoride (TBAF) followed by two consecutive electrocyclizations resulted in the formation of the corresponding benzocyclobutadiene **17a**, leading to the four angular dimers **18a**−**d**. The use of cyclopentadiene to capture **17a** afforded the Diels−Alder adduct **19**. Treatment of **15b** with TBAF produced only one angular dimer **21**. On the other hand, the presence of a phenyl substituent on the four-membered ring directed the dimerization of benzocyclobutadiene **17c** toward the linear dimer **23**, which then underwent a facile thermal rearrangement to dibenzocyclooctadiene **24**. Interestingly, benzocyclobutadienes **17d** and **17e** having an alkenyl substituent on the four-membered ring dimerized via a formal [4 + 4] cycloaddition to the 1,5-cyclooctadienes **26** and **32**, respectively.

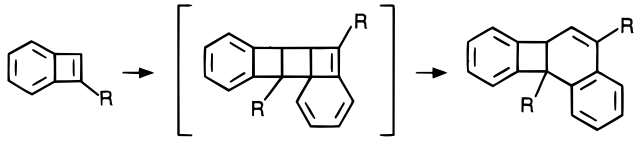
Introduction

The high reactivity of benzocyclobutadienes has been well documented.[1] The parent benzocyclobutadiene (**1a**)[2] and the 1-alkyl-substituted derivatives **1b**−**d**[3] dimerize readily in a Diels−Alder manner via **2** to afford the corresponding angular dimers **3** (Scheme 1). Interestingly, the presence of a phenyl substituent on the four-membered ring in **4** causes the formation of the linear dimers, dibenzocyclooctadienes **6**, presumably via an initial formation of the syn dimer **5** (Scheme 2).[4]

The early demonstration of the existence of benzocyclobutadienes as transient reaction intermediates was achieved by trapping them with reactive dienes, such as cyclopentadiene and 1,3-diphenylisobenzofuran, to form the corresponding Diels−Alder adducts.[5] Direct observation of the infrared and the ultraviolet spectra of the very reactive **1a** was accomplished by matrix isolation in argon at 8 K.[6] The photoelectron spectrum of **1a** was also reported and provided insight into its electronic structure.[7] Because of the high reactivity, it was only until recently that the ^{1}H NMR spectrum of **1a** was obtained by using the technique of flow NMR.[8] In contrast, the sterically hindered 1,2-bis(trimethylsilyl)benzocyclobutadiene is thermally stable even at 150 °C, and the ^{1}H NMR chemical shifts of the protons directly attached to the six-membered ring at δ 5.63 and 6.20 (in CCl_4) gave the first indication of strong paramagnetic ring current contributions to the induced ring current.[9] Similarly, 1,2-di-*tert*-butyl-3,4,5,6-tetramethylbenzocyclobutadiene can be isolated and its X-ray structure permitted the first experimental determination of the molecular geometry of a free benzocyclobutadiene.[10]

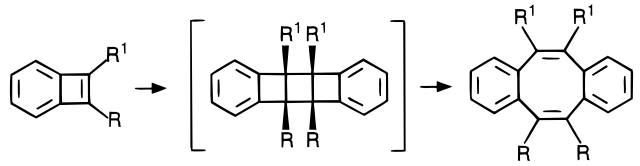
Benzocyclobutadienes have been generated by the dehalogenation of 1,2-dihalobenzocyclobutenes and the dehydroha-

Scheme 1



1a: R = H **2a**: R = H **3a**: R = H
1b: R = Me **2b**: R = Me **3b**: R = Me
1c: R = *i*-Pr **2c**: R = *i*-Pr **3c**: R = *i*-Pr
1d: R = *t*-Bu **2d**: R = *t*-Bu **3d**: R = *t*-Bu

Scheme 2



4a: R = Ph, R^1 = H **5a**: R = Ph, R^1 = H **6a**: R = Ph, R^1 = H
4b: R = Ph, R^1 = CH_3 **5b**: R = Ph, R^1 = CH_3 **6b**: R = Ph, R^1 = CH_3

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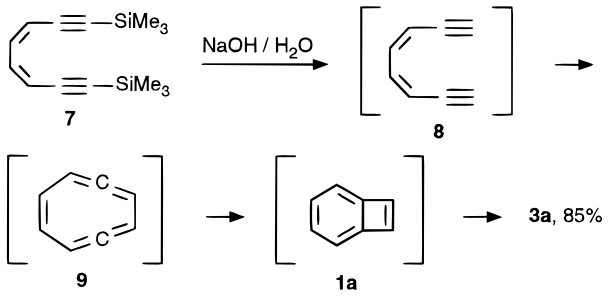
Scheme 3



logenation of 1-halobenzocyclobutenes. These methods have been successfully adopted for the synthesis of **1a**−**d**[2,3] and **4b**.[4b] Treatment of benzyne generated in situ with phenylacetylene and 1-phenyl-1-propyne produced **4a** and **4b**, respectively.[4a] Thermolysis of *trans*-3,4-diethynylcyclobutenes at 100 to 190 °C has also been utilized for the synthesis of benzocyclobutadienes with a permethylated benzene ring.[11] The electrocyclization of (*Z*,*Z*)-3,5-octadiene-1,7-diyne (**8**), obtained by desilylation of the precursor **7**, also provided a highly efficient route to **1a** via an initial formation of 1,2,4,5,7-cyclooctapentaene (**9**) followed by a second electrocyclization (Scheme 3).[12] The reaction occurs at room temperature with a half-life of ca. 10 min, and the dimer **3a** was isolated in 85% yield. However with the exception of one additional case of using **7** for the preparation of 1,2-bis(trimethylsilyl)benzocyclobutadiene,[9] this facile route has not been adopted for the synthesis of other benzocyclobutadienes. This is due mainly to the lack of geometric selectivity in producing predominantly the *E*,*Z*-isomer (35%) and the *E*,*E*-isomer (15%) of **7** instead of the desired *Z*,*Z*-isomer (35%) by dehydrobromination of 1,8-bis(trimethylsilyl)-4,5-dibromo-1,7-octadiyne.

We recently reported a facile synthesis of (*Z*)-1-buten-3-ynes,[13] (*Z*)-3-hexene-1,5-diynes (enediynes),[13] and (*Z*)-1,2,4-heptatrien-6-ynes (enyne-allenes)[14] by condensation of the nonconjugated aldehydes, the conjugated acetylenic and the allenic aldehydes with γ-(trialkylsilyl)allenylboranes, followed by the elimination step of the Peterson olefination reaction. We envisioned that by using the conjugated (*Z*)-enynyl aldehydes for condensation, dienediynes having the *Z* geometry for the two central carbon−carbon double bonds could thus be synthesized. We now report a successful extension of this method to the synthesis of a variety of (*Z*,*Z*)-dienediynes and their electrocyclizations to the corresponding benzocyclobutadienes leading to unusual polycyclic compounds.

Results and Discussion

Treatment of the readily available 3-(*tert*-butyldimethylsilyl)-1-(trimethylsilyl)-1-propyne (**10**)[15] with *n*-butyllithium followed by *B*-methoxy-9-borabicyclo[3.3.1]nonane (*B*-MeO-9-BBN) and $^4/_3BF_3{\cdot}OEt_2$[16] gave allenylborane **11** (Scheme 4).[13] The requisite (*Z*)-enynyl aldehydes **12** were prepared by a $Pd(PPh_3)_4$-catalyzed

Scheme 4

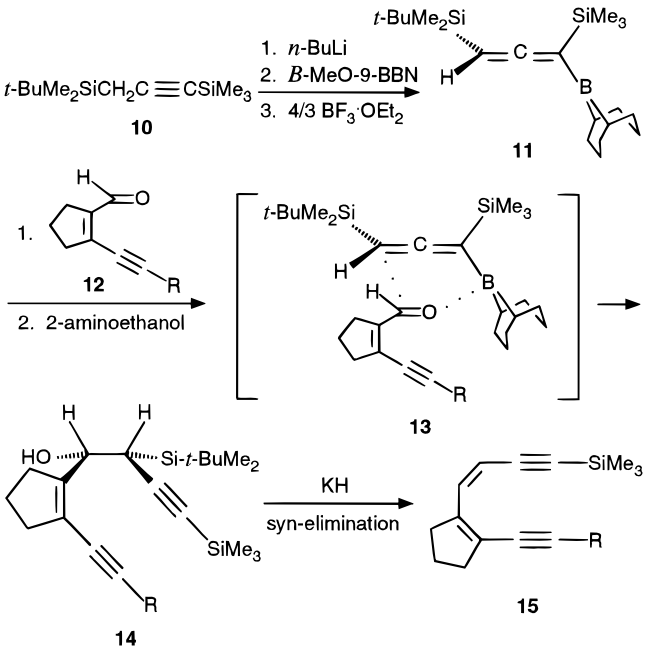


Table 1. Stereoselective Synthesis of Enynyl Alcohols **14** and Dienediynes **15**

R	**14**[a]	isolated yield, %	**15**	isolated yield, % (*Z*:*E*)
Mg_3Si	**14a**	61	**15a**	78 (93:7)
Bu	**14b**	65	**15b**	80 (92:8)
phenyl	**14c**	56	**15c**	83 (95:5)
methylethenyl	**14d**	54	**15d**	81 (95:5)
1-cyclohexenyl	**14e**	55	**15e**	81 (94:6)

[a] The preferential formation of the *Z* isomer **15** by treatment of **14** with potassium hydride indicates that the *SR*/*RS* pair were produced predominantly.

cross coupling between 2-bromo-1-cyclopentenecarboxaldehyde[17] and terminal alkynes.[18] Subsequent condensation of **11**, prepared in situ, with **12** furnished, after treatment with 2-aminoethanol, the condensation adducts **14** with high diastereoselectivity (Table 1). The high diastereoselectivity in forming **14** can be attributed to the preference of the *tert*-butyldimethylsilyl group and the *Z*-enynyl group of aldehydes in adopting the opposite sides of the six-membered transition states **13** in order to minimize nonbonded steric interactions as observed in the earlier cases.[13] Conversion of **14** to dienediynes **15** was carried out with potassium hydride in diethyl ether at 0 °C under a nitrogen atmosphere.[13] Dienediynes **15** having two substituents at the alkynyl terminus were stable enough to allow purification by column chromatography at room temperature and were produced with high geometric purity (*Z*:*E* ≥ 92:8) (Table 1).

Treatment of **15a** with tetrabutylammonium fluoride (TBAF) produced the corresponding desilylated dienediyne **16a**, which then underwent electrocyclization reactions to benzocyclobutadiene **17a**, giving rise to the four possible angular dimers **18a**−**d** with nearly equal proportions in 66% isolated yield (Scheme 5). Apparently there was little preference for the four possible orientations during dimerization.

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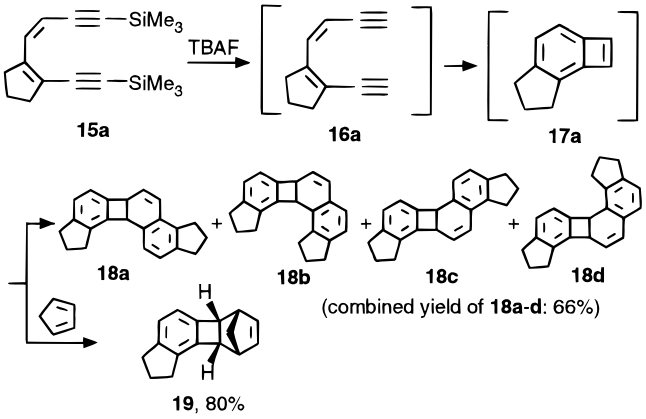
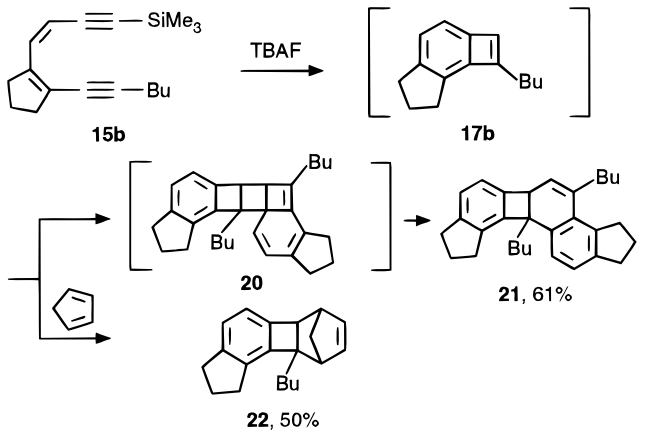
Scheme 5



Scheme 6



It was difficult to separate the four isomers **18a**−**d** by column chromatography. Fortunately, the ^{1}H NMR spectrum of the mixture exhibited clearly seven sets of signals from δ 6.43 to 6.08 with the signal at δ 6.08 having ca. twice the intensity of the other peaks with nearly equal intensities among them. These signals can be attributed to the eight vinylic hydrogens of the four angular dimers with an overlap of two hydrogens at δ 6.08. The ^{13}C NMR spectrum also showed eight well-separated signals from δ 43.58 to 42.28 due to the eight sp^3 carbons on the four-membered rings of the four isomers. In addition, 31 signals (one less than expected because of an overlap at δ 142.42) due to the 32 quaternary sp^2 carbons and 23 signals (two peaks overlapping at δ 123.73) due to the 24 CH sp^2 carbons were clearly discernible. Moreover, 8 signals from δ 25.74 to 25.00 due to the 8 central CH_2 carbons on the five-membered rings along with 10 signals due to the remaining CH_2 carbons (several overlapping peaks) were also observed. Attempts to separate **18a**−**d** by HPLC yielded a fraction which contained predominantly only one of the four isomers, permitting a more definitive analysis of the ^{1}H and ^{13}C NMR spectra for structural elucidation. Indeed, its ^{1}H and ^{13}C NMR spectra are consistent with the structural features of the angular dimers.

In addition to dimerization, it was possible to capture **17a** with cyclopentadiene to form the endo isomer of the Diels−Alder adduct **19** in 80% isolated yield by treating **15a** with TBAF in the presence of an excess of cyclopentadiene (Scheme 5). The endo configuration of **19** was supported by the NOE measurements.

On the other hand, when **15b** was treated with TBAF only one angular dimer **21** was isolated in 61% yield (Scheme 6). Apparently, the butyl group on the four-membered ring in **17b** directs the preferential formation of **20** during dimerization

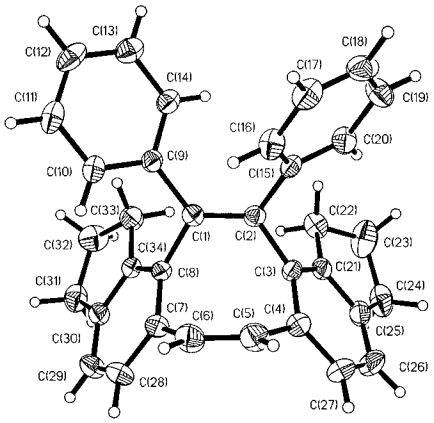
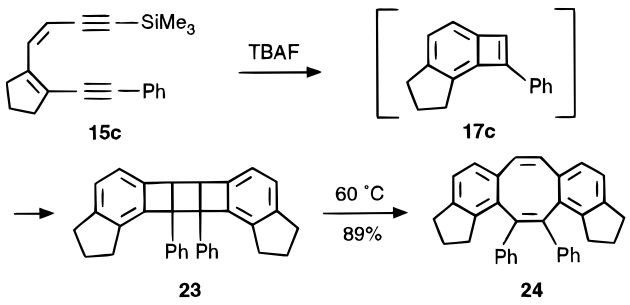


Figure 1. ORTEP drawing of the crystal structure of the dimer **24**.

Scheme 7



leading to the formation of **21**. This selectivity is reminiscent of the results observed with **1b**−**d** which produced the angular dimers **3b**−**d**.[3] Treatment of **15b** with TBAF in the presence of an excess of cyclopentadiene also furnished the Diels−Alder adduct **22** in 50% isolated yield along with 20% of the dimer **21**.

Interestingly when **15c** having a phenyl substituent was treated with TBAF, the dimer **23** was formed initially (Scheme 7). As the reaction mixture was stirred at room temperature for 12 h to allow the reaction to go to completion, the linear dimer **24** slowly appeared as observed previously in the cases of **4a** and **4b**.[3a,4] Fortunately, it was possible to separate a portion of **23** (19%) cleanly by column chromatography to allow structural elucidation by ^{1}H and ^{13}C NMR spectroscopy. Only one set of NMR signals due to either the syn or the anti isomer of **23** were observed. A second portion containing a mixture of **23** and **24** (40:60) was also isolated in 36% yield. The dimer **23** was unstable at room temperature and slowly rearranged to **24**. On heating at 60 °C, **23** was converted to **24** within 3 h in 89% yield after purification by column chromatography. The structure of **24** was established by an X-ray structure determination (Figure 1).

While the stereochemistry of **23** was not determined, the facile isomerization of **23** to **24** even at room temperature appears to suggest that the syn isomer of **23** was formed, consistent with the earlier observation that the syn isomer **5b** is prone to thermal isomerization.[4b] The anti isomer of **5b** is thermally much more stable,[4b] and a similar thermal stability could also be expected for the anti isomer of **23**.

The resonance stabilizing effect of a 1-phenyl substituent may significantly alter the electronic structure of benzocyclobutadiene, causing the formation of the linear dimer. Since a 1-alkenyl substituent could also exert a similar stabilizing effect, it is therefore of interest to study the chemical behaviors of such benzocyclobutadiene derivatives. Surprisingly when **15d** was treated with TBAF, the anticipated dibenzocyclooctadiene **25** was not isolated. Instead, a formal [4 + 4] cycloaddition of

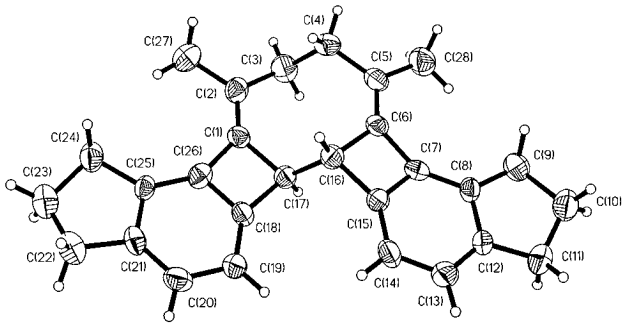
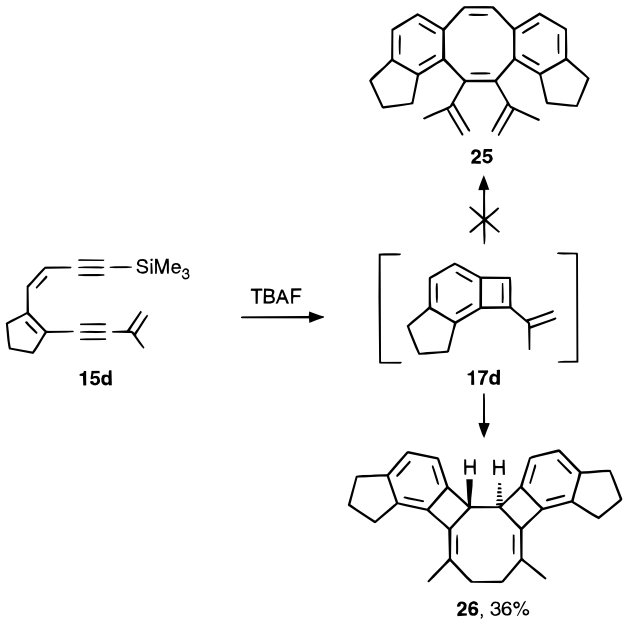


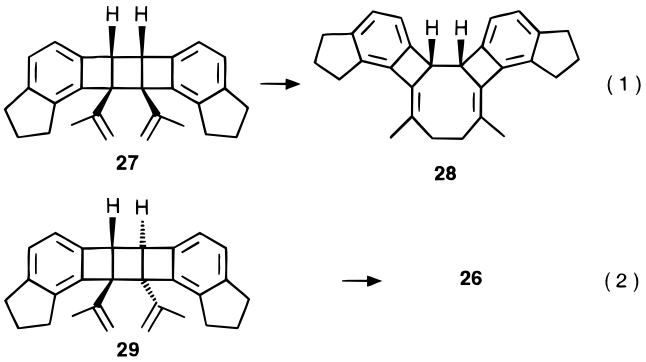
Figure 2. ORTEP drawing of the crystal structure of the dimer **26**.

Scheme 8



17d occurred, producing the 1,5-cyclooctadiene **26** having the trans geometry in 36% isolated yield (Scheme 8). The structure of **26** was unequivocally established by an X-ray structure determination (Figure 2).

The formation of the trans geometry in **26** was particularly unexpected. If the cis isomer **28** had been isolated, a pathway involving an initial formation of the syn dimer **27** as in the case of **23** followed by a facile Cope rearrangement could have accounted for its formation (eq 1). However, such a pathway to the trans isomer **26** would require an initial formation of the anti dimer **29** followed by a nonconcerted rearrangement (eq 2).

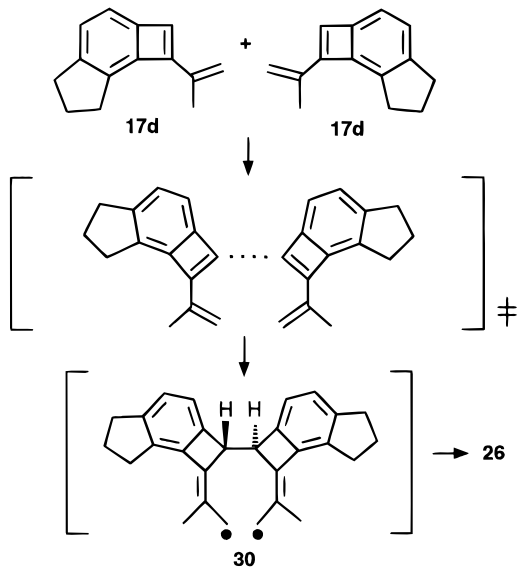


(1)

(2)

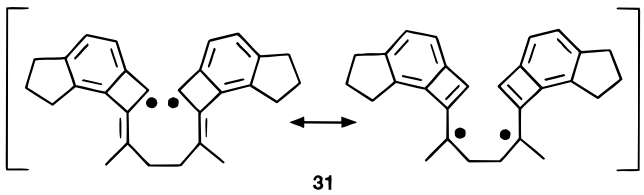
Perhaps the chemical behavior of **17d** resembles those of the benzene-based[19] and the furan-based *o*-quinodimethanes[20] in producing **26** via a two-step diradical mechanism. A radical

Scheme 9



pathway involving an initial head-to-head dimerization to form diradical **30** followed by an intramolecular radical−radical combination could account for the formation of the trans isomer **26** (Scheme 9). There are several possible orientations of the two monomers in the transition state of the first step for dimerization that could lead to **30**, including the one depicted in Scheme 9 with the exo approach and the cisoid encounter of the two diene components in the *s*-cis conformation. It was previously established that dimerizations of the benzene-based[21a] and the furan-based *o*-quinodimethanes[21b] proceed through the exo approach.

Alternatively, an initial tail-to-tail dimerization to form diradical **31** followed by the exo approach for the intramolecular radical−radical combination could also furnish **26**. When compared with the pathway through diradical **30**, the route through an initial tail-to-tail connection is favored by less steric interactions in joining the two tails together. Dimerization of the furan-based *o*-quinodimethanes was found to be sensitive to steric hindrance at the diene terminus.[20b] On the other hand, diradical **31** still retains the reactive benzocyclobutadiene moieties which could make the pathway less favorable. Clearly,



additional studies will be needed to probe into the details of the dimerization mechanism. Nevertheless, it is interesting to note that the absence of the head-to-tail [4 + 4] dimer and the [4 + 2] dimers closely resemble those of the dimerization of 2,3-dimethylene-2,3-dihydrofuran which produces the head-to-head [4 + 4] dimer exclusively.[20]

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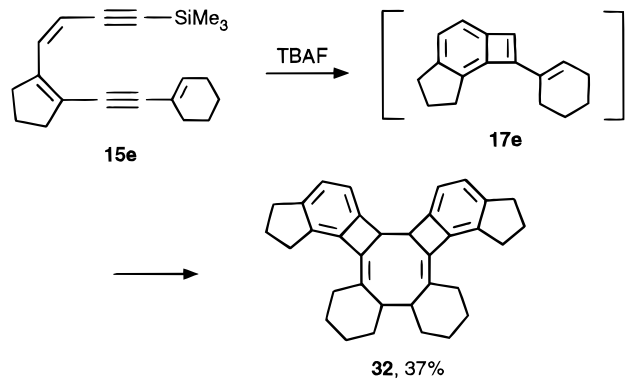
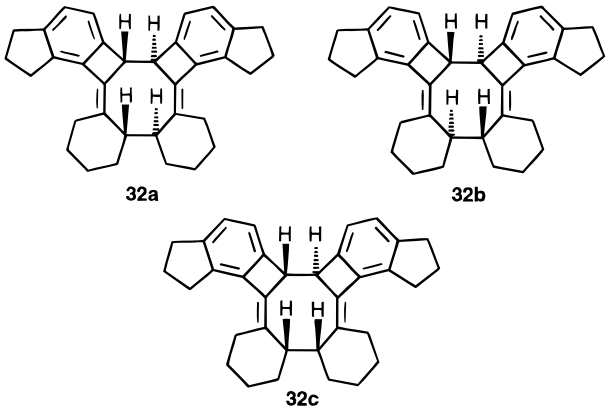
Scheme 10



Similarly, when **15e** was treated with TBAF, the dimer **32** having nine fused rings was isolated in 37% yield (Scheme 10). Of the six possible diastereomers of **32**, only two were present as indicated by two singlet signals in the ^{1}H NMR spectrum at δ 3.97 and 3.92 in a ratio of 35:65 attributable to the hydrogen atoms on the four-membered ring as observed in the case of **26**. If one assumes the preferential formation of the trans junction at the ends of the four-membered ring as in the case of **26**, then the number of possible diastereomers is reduced to three as depicted in **32a**−**c**. Both **32a** and **32b** have a C_2 symmetry, while no symmetry exists with **32c**. The observation of two singlets with unequal intensities at δ 3.97 and 3.92 in the ^{1}H NMR spectrum along with only 18 sp^3-carbon and 14 (two signals less than expected presumably due to overlaps) sp^2-carbon signals strongly suggest that the two isolated isomers are **32a** and **32b**. Because of the lack of symmetry in **32c**, the



presence of **32c** as one of the two isomers would have produced a more complex pattern at ca. δ 3.9 in the ^{1}H NMR spectrum and additional ^{13}C signals. As in the case of **26**, an initial step involving the exo approach of two molecules of **17e** with the cisoid encounter of the two diene components in the *s*-cis conformation followed by the two diastereomeric exo approaches for the intramolecular radical−radical combination could produce the two trans junctions in **32a** and **32b**.

Conclusions

The ability to synthesize a variety of (*Z*,*Z*)-3,5-octadiene-1,7-diynes provides an easy access to the reactive benzocyclobutadienes with diverse structures. Benzocyclobutadienes with no substituent on the four-membered ring or with a 1-alkyl or a 1-phenyl substituent dimerize by the pathways observed previously.[1] On the other hand, benzocyclobutadienes substituted with a 1-alkenyl group exhibit a new reaction pathway via a formal [4 + 4] cycloaddition to polycyclic compounds having unusual carbon frameworks.

Experimental Section

General procedures for manipulation of organoboranes and other organometallic reagents were described previously.[22] All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Tetrahydrofuran (THF) and diethyl ether were distilled from benzophenone ketyl prior to use. *n*-Butyllithium (2.5 M) in hexanes, tetrabutylammonium fluoride (TBAF) (1.0 M in THF), and 1-(trimethylsilyl)-1-propyne were purchased from Aldrich Chemical Co., Inc. and were used as received. Potassium hydride (35 wt % dispersion in mineral oil) was also purchased from Aldrich, and mineral oil was removed by washing with pentane prior to use. Silica gel (70−230 mesh) for column chromatography was also purchased from Aldrich. *B*-Methoxy-9-borabicyclo[3.3.1]nonane (*B*-MeO-9-BBN),[23] 3-(*tert*-butyldimethylsilyl)-1-(trimethylsilyl)-1-propyne,[15] and enynyl aldehydes **12**[18] were prepared according to the reported procedures. ^{1}H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ or C_6D_6 using Me_4Si, $CHCl_3$ (^{1}H δ 7.26), $CDCl_3$ (^{13}C δ 77.02), C_6D_5H (^{1}H δ 7.15), or C_6D_6 (^{13}C δ 128.00) as internal standard. The isomer ratios were determined by integration of the ^{1}H NMR spectra.

2-(Trimethylsilylethynyl)-1-cyclopentenecarboxaldehyde (12a). The following procedure for the preparation of **12a** is representative. A flask containing 0.867 g (0.75 mmol) of $Pd(PPh_3)_4$ and 0.29 g (1.50 mmol) of CuI was evacuated and then purged with nitrogen. To a second flask were added 2.68 g (15.0 mmol) of 2-bromo-1-cyclopentenecarboxaldehyde, 5.82 g (45.0 mmol, 7.8 mL) of ethyldiisopropylamine, and 20 mL of DMF. The mixture was degassed by three cycles of freeze-thaw before it was transferred via cannula into the first flask at room temperature. Then a degassed solution of trimethylsilylacetylene (2.26 g, 23.0 mmol) in 10 mL of DMF was introduced into the reaction mixture. After 12 h, the mixture was poured into 200 mL of an aqueous NH_4Cl solution, filtrated, and extracted with pentane (3 × 30 mL). The combined organic layers were washed with water (3 × 30 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel/5% diethyl ether in hexanes) to furnish 2.79 g (97%) of **12a** as a light yellow oil: IR (neat) 2138, 1672, 1593, 1250, 1199, 992, 852, 761, 689 cm^{-1}; ^{1}H NMR (C_6D_6) δ 10.32 (1 H, s), 2.36 (2 H, tt, J = 7.7 and 2.3 Hz), 2.25 (2 H, tt, J = 7.7 and 2.3 Hz), 1.32 (2 H, quintet, J = 7.7 Hz), 0.13 (9 H, s); ^{13}C NMR (C_6D_6) δ 187.45, 149.85, 141.29, 106.43, 99.16, 38.67, 29.81, 21.98, −0.37; MS (*m*/*e*) 192 (M$^+$), 191, 177, 164, 149, 117, 103, 83, 75, 73.

2-(1-Hexynyl)-1-cyclopentenecarboxaldehyde (12b): isolated in 97% yield as a light yellow oil; IR (neat) 2211, 1668, 1596, 1466, 1430, 1383, 1352, 1224, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 10.01 (1 H, s), 2.65 (2 H, tt, J = 7.7 and 2.2 Hz), 2.57 (2 H, t, J = 7.6 Hz), 2.43 (2 H, t, J = 6.9 Hz), 1.92 (2 H, quintet, J = 7.6 Hz), 1.62−1.5 (2 H, m), 1.5−1.35 (2 H, m), 0.92 (3 H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 189.23, 146.94, 144.71, 103.24, 74.99, 39.21, 30.42, 29.28, 21.99, 21.96, 19.51, 13.54; MS (*m*/*e*) 176 (M$^+$), 175, 161, 147, 134, 117, 105, 91, 77.

2-(Phenylethynyl)-1-cyclopentenecarboxaldehyde (12c): isolated in 84% yield as a yellow solid; IR (KBr) 2197, 1670, 1603, 1488, 1441, 1355, 1245, 754, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 10.16 (1 H, s), 7.50−7.48 (2 H, m), 7.38−7.34 (3 H, m), 2.80 (2 H, tt, J = 7.6 and 2.2 Hz), 2.66 (2 H, tt, J = 7.7 and 2.2 Hz), 2.00 (2 H, quintet, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 188.65, 147.79, 142.94, 131.72, 129.26, 128.40, 121.92, 100.58, 83.17, 38.79, 29.49, 22.00; MS (*m*/*e*) 196 (M$^+$), 167, 153, 152, 139, 115.

2-(3-Methyl-3-buten-1-ynyl)-1-cyclopentenecarboxaldehyde (12d): isolated in 84% yield as a light yellow oil; IR (neat) 2194, 1670, 1614, 1587, 1434, 1384, 1353, 1304, 1247, 1198, 904, 724 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 10.02 (1 H, s), 5.40 (1 H, br s), 5.35 (1 H, quintet, J = 1.6 Hz), 2.69 (2 H, tt, J = 7.4 and 2.2 Hz), 2.58 (2 H, tt, J = 7.7 and 2.2 Hz), 1.99−1.87 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 188.82, 147.78, 143.07, 126.06, 124.10, 101.71, 82.09, 38.80, 29.47, 22.99, 22.03; MS (*m*/*e*) 160 (M$^+$), 159, 145, 131, 117, 115, 103, 91, 77.

(22) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.
(23) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1−15.

2-(1-Cyclohexenylethynyl)-1-cyclopentenecarboxaldehyde (12e): isolated in 98% yield as a yellow oil; IR (neat) 2183, 1667, 1584, 1434, 1386, 1350, 1238, 919, 842, 799, 737, 645 cm^{-1}; ^1H NMR (C_6D_6) δ 10.38 (1 H, s), 6.09 (1 H, tt, J = 4.1 and 2.0 Hz), 2.44 (2 H, tt, J = 7.6 and 2.2 Hz), 2.31 (2 H, tt, J = 7.7 and 2.2 Hz), 2.05−2.0 (2 H, m), 1.82−1.7 (2 H, m), 1.46−1.2 (6 H, m); ^{13}C NMR (C_6D_6) δ 187.69, 147.65, 142.35, 137.58, 120.77, 102.77, 81.72, 38.89, 29.87, 29.15, 25.96, 22.34, 22.09, 21.50; MS (*m/e*) 200 (M^+), 199, 185, 171, 157, 129, 128, 115, 108, 91, 77.

(1*S*,2*R*)-2-(*tert*-Butyldimethylsilyl)-4-(trimethylsilyl)-1-[2-(trimethylsilylethynyl)-1-cyclopentenyl]-3-butyn-1-ol (14a). The following procedure for the synthesis of **14a** is representative. To a solution of 0.68 g (3.00 mmol) of 3-(*tert*-butyldimethylsilyl)-1-(trimethylsilyl)-1-propyne in 10 mL of THF was added 1.2 mL (3.00 mmol) of a 2.5 M solution of *n*-butyllithium in hexanes at −10 °C. After 30 min at −10 °C, 0.5 mL of *B*-MeO-9-BBN (0.46 g, 3.00 mmol) was introduced with a syringe. After an additional 45 min at 0 °C, 0.5 mL of $BF_3{\cdot}OEt_2$ (0.57 g, 4.0 mmol) was added and the mixture was stirred at 0 °C for 20 min to form the 3-(*tert*-butyldimethylsilyl)-1-(trimethylsilyl)-1-allenylborane **11** before 0.576 g of the enynyl aldehyde **12a** (3.00 mmol) in 5 mL of THF was introduced. The mixture was allowed to warm to room temperature and stirred for 6 h. THF and hexanes were evaporated at reduced pressure and pressure was then restored with nitrogen. Hexanes (20 mL) was added followed by 0.5 mL of 2-aminoethanol, and a precipitate was formed almost immediately. After 15 min of stirring, the precipitate was removed by filtration, and the filtrate was washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/5% diethyl ether in hexanes) to afford 0.76 g (1.82 mmol, 61%) of **14a** as a yellow oil: IR (neat) 3532, 2157, 2136, 1674, 1593, 1470, 1249, 842, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.76 (1 H, d, J = 9 Hz), 2.65−2.5 (2 H, m), 2.5−2.4 (2 H, m), 2.47 (1 H, d, J = 9 Hz), 2.21 (1 H, d, J = 3.1 Hz), 1.9−1.8 (2 H, m), 0.96 (9 H, s), 0.17 (12 H, s), 0.13 (9 H, s), 0.12 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 155.81, 118.07, 105.65, 101.14, 100.00, 90.30, 68.50, 36.73, 32.83, 27.06, 26.94, 22.57, 17.71, 0.07, 0.04, −6.60, −6.63.

(1*S*,2*R*)-2-(*tert*-Butyldimethylsilyl)-1-[2-(1-hexynyl)-1-cyclopentenyl]-4-(trimethylsilyl)-3-butyn-1-ol (14b): a yellow oil; IR (neat) 3463, 2157, 1464, 1249, 841 cm^{-1}; ^1H NMR (C_6D_6) δ 4.97 (1 H, dd, J = 8.6 and 3.1 Hz), 2.75−2.4 (4 H, m), 2.55 (1 H, d, J = 8.6 Hz), 2.43 (1 H, d, J = 3.1 Hz), 2.17 (2 H, t, J = 6.8 Hz), 1.75−1.64 (2 H, m), 1.48−1.26 (4 H, m), 1.04 (9 H, s), 0.79 (3 H, t, J = 7.0 Hz), 0.37 (3 H, s), 0.25 (3 H, s), 0.16 (9 H, s); ^{13}C NMR (C_6D_6) δ 152.73, 118.79, 107.09, 96.48, 89.55, 77.28, 69.45, 37.53, 33.23, 31.26, 27.45, 27.25, 22.77, 22.25, 19.59, 17.88, 13.72, 0.17, −6.17, −6.42.

(1*S*,2*R*)-2-(*tert*-Butyldimethylsilyl)-1-[2-(phenylethynyl)-1-cyclopentenyl]-4-(trimethylsilyl)-3-butyn-1-ol (14c): a yellow oil; IR (neat) 3545, 2155, 1489, 1469, 1249, 841, 755, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41−7.37 (2 H, m), 7.29−7.24 (3 H, m), 4.84 (1 H, dd, J = 9.0 and 3.3 Hz), 2.60 (4 H, m), 2.57 (1 H, d, J = 9.0 Hz), 2.28 (1 H, d, J = 3.3 Hz), 1.92 (2 H, quintet, J = 7.5 Hz), 0.95 (9 H, s), 0.18 (3 H, s), 0.14 (3 H, s), 0.13 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 154.27, 131.27, 128.24, 127.97, 123.48, 118.21, 105.64, 95.12, 90.37, 85.41, 68.53, 36.83, 32.83, 27.07, 27.01, 22.55, 17.62, 0.04, −6.53, −6.65.

(1*S*,2*R*)-2-(*tert*-Butyldimethylsilyl)-1-[2-(3-methyl-3-buten-1-ynyl)-1-cyclopentenyl]-4-(trimethylsilyl)-3-butyn-1-ol (14d): a yellow oil; IR (neat) 3540, 2156, 1673, 1605, 1470, 1249, 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.24 (1 H, m), 5.20 (1 H, quintet, J = 1.7 Hz), 4.74 (1 H, dm, J = 9 Hz), 2.64−2.46 (5 H, m), 2.23 (1 H, d, J = 3.3 Hz), 1.99−1.83 (2 H, m), 1.89 (3 H, t, J = 1.5 Hz), 0.96 (9 H, s), 0.16 (3 H, s), 0.13 (9 H, s), 0.12 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 154.02, 126.87, 121.28, 118.14, 105.65, 96.33, 90.34, 84.38, 68.50, 36.79, 32.80, 27.02, 23.57, 22.54, 17.64, 0.05, −6.61, −6.66.

(1*S*,2*R*)-2-(*tert*-Butyldimethylsilyl)-1-[2-(1-cyclohexenylethynyl)-1-cyclopentenyl]-4-(trimethylsilyl)-3-butyn-1-ol (14e): a yellow oil; IR (neat) 3538, 2156, 1470, 1249, 1030, 838 cm^{-1}; ^1H NMR (C_6D_6) δ 6.12 (1 H, tt, J = 4 and 2 Hz), 4.99 (1 H, br s), 2.86−2.40 (4 H, m), 2.45 (1 H, d, J = 3.1 Hz), 2.18−2.12 (2 H, m), 1.86−1.77 (2 H, m), 1.75−1.65 (2 H, m), 1.44−1.24 (4 H, m), 1.02 (9 H, s), 0.36 (3 H, s), 0.25 (3 H, s), 0.16 (9 H, s); ^{13}C NMR (C_6D_6) δ 153.71, 134.35, 121.44, 118.59, 107.02, 97.88, 89.62, 83.52, 69.50, 37.38, 33.48, 29.75, 27.26, 27.17, 25.85, 22.85, 22.56, 21.74, 17.87, 0.17, −6.16, −6.35.

(*Z*)-4-(Trimethylsilyl)-1-[2-(trimethylsilylethynyl)-1-cyclopentenyl]-1-buten-3-yne (15a). The following procedure for the synthesis of **15a** is representative. To a dispersion of 0.16 g (4.0 mmol) of KH in 10 mL of diethyl ether at 0 °C under a nitrogen atmosphere was added 0.418 g (1.0 mmol) of **14a** in 6 mL of diethyl ether. After 45 min of stirring, the reaction mixture was filtrated to remove excess KH, washed with an aqueous solution of NH_4Cl, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes) to furnish 0.223 g (78%) of **15a** (*Z*:*E* = 93:7) as a yellow solid: mp 69−71 °C; IR (KBr) 2139, 2130, 1438, 1249, 1173, 1007, 986, 850, 758 cm^{-1}; ^1H NMR (C_6D_6) δ 7.06 (1 H, d, J = 11.7 Hz), 5.48 (1 H, d, J = 11.9 Hz), 3.07 (2 H, t, J = 7.4 Hz), 2.39 (2 H, t, J = 7.6 Hz), 1.59 (2 H, quintet, J = 7.6 Hz), 0.19 (9 H, s), 0.14 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 148.89, 134.94, 126.96, 108.23, 104.33, 103.16, 101.96, 101.35, 36.38, 33.70, 23.15, 0.08, −0.32; MS (*m/e*) 286 (M^+), 271, 255, 213, 197, 175, 128, 73. A minor set of ^1H NMR (C_6D_6) signals at δ 7.50 (1 H, d, J = 16 Hz) and 5.57 (1 H, d, J = 16 Hz) attributable to the *E* isomer (7%) were also observed. The *E* isomer was separated by column chromatography.

(*Z*)-1-[2-(1-Hexynyl)-1-cyclopentenyl]-4-(trimethylsilyl)-1-buten-3-yne (15b): a yellow liquid; IR (neat) 2136, 1588, 1464, 1249, 1180, 1000, 842, 760 cm^{-1}; ^1H NMR (C_6D_6) δ 7.05 (1 H, d, J = 11.7 Hz), 5.50 (1 H, d, J = 11.7 Hz), 3.13 (2 H, t, J = 7.4 Hz), 2.43 (2 H, t, J = 7.4 Hz), 2.21 (2 H, t, J = 6.6 Hz), 1.66 (2 H, quintet, J = 7.5 Hz), 1.39−1.24 (4 H, m), 0.77 (3 H, t, J = 7.1 Hz), 0.16 (9 H, s).; ^{13}C NMR (C_6D_6) δ 146.17, 135.74, 128.88, 107.67, 105.31, 101.35, 99.52, 77.76, 37.13, 33.93, 31.21, 23.19, 22.23, 19.78, 13.68, −0.23; MS (*m/e*) 270 (M^+), 196, 167, 141, 115, 73. Anal. Calcd for $C_{18}H_{26}Si$: C, 79.93; H, 9.69. Found: C, 79.79; H, 9.55. A minor set of ^1H NMR ($CDCl_3$) signals at δ 7.10 (1 H, d, J = 16 Hz) and 5.53 (1 H, d, J = 16 Hz) attributable to the *E* isomer (8%) were also observed. The *E* isomer was separated by column chromatography.

(*Z*)-1-[2-(Phenylethynyl)-1-cyclopentenyl]-4-(trimethylsilyl)-1-buten-3-yne (15c): a yellow liquid; IR (neat) 2135, 1599, 1489, 1442, 1412, 1249, 1180, 1018, 977, 846, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44−7.40 (2 H, m), 7.28−7.25 (3 H, m), 6.85 (1 H, d, J = 11.7 Hz), 5.52 (1 H, d, J = 11.9 Hz), 3.02 (2 H, t, J = 7.4 Hz), 2.58 (2 H, t, J = 7.6 Hz), 1.93 (2 H, quintet, J = 7.6 Hz), 0.17 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 147.66, 135.06, 131.41, 128.28, 128.20, 127.09, 123.33, 107.93, 104.42, 101.87, 97.89, 85.89, 36.44, 33.76, 23.16, −0.32; MS (*m/e*) 290 (M^+), 275, 259, 247, 231, 215, 202, 173, 159, 145, 135, 121, 105, 73.

(*Z*)-1-[2-(3-Methyl-3-buten-1-ynyl)-1-cyclopentenyl]-4-(trimethylsilyl)-1-buten-3-yne (15d): a yellow liquid; IR (neat) 2135, 1612, 1438, 1250, 1180, 1025, 995, 893, 843, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.76 (1 H, d, J = 11.7 Hz), 5.51 (1 H, d, J = 11.7 Hz), 5.32 (1 H, m), 5.25 (1 H, quintet, J = 1.6 Hz), 3.01 (2 H, t, J = 7.5 Hz), 2.52 (2 H, t, J = 7.7 Hz), 1.98−1.87 (2 H, m), 1.94 (3 H, dd, J = 1.6 and 1.0 Hz), 0.19 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 147.46, 135.01, 127.10, 126.88, 121.76, 107.81, 104.42, 101.77, 99.09, 84.84, 36.42, 33.70, 23.53, 23.13, −0.33; MS (*m/e*) 254 (M^+), 239, 223, 211, 195, 181, 179, 165, 153, 141, 128, 115, 97, 83, 73. A minor set of ^1H NMR ($CDCl_3$) signals at δ 7.08 (1 H, d, J = 16 Hz) and 5.58 (1 H, d, J = 16 Hz) attributable to the *E* isomer (5%) were also observed.

(*Z*)-1-[2-(1-Cyclohexenylethynyl)-1-cyclopentenyl]-4-(trimethylsilyl)-1-buten-3-yne (15e): a yellow liquid; IR (neat) 2136, 1583, 1552, 1437, 1249, 1017, 842, 759 cm^{-1}; ^1H NMR (C_6D_6) δ 7.07 (1 H, d, J = 11.7 Hz), 6.13 (1 H, tt, J = 4.1 and 1.9 Hz), 5.51 (1 H, d, J = 11.9 Hz), 3.13 (2 H, t, J = 7.5 Hz), 2.44 (2 H, t, J = 7.6 Hz), 2.16−2.10 (2 H, m), 1.87−1.80 (2 H, m), 1.65 (2 H, quintet, J = 7.5 Hz), 1.42−1.26 (4 H, m), 0.16 (9 H, s); ^{13}C NMR (C_6D_6) δ 146.78, 135.66, 135.05, 128.45, 121.51, 107.93, 105.35, 101.66, 100.76, 84.11, 36.93, 34.10, 29.68, 25.94, 23.28, 22.56, 21.73, −0.23; MS (*m/e*) 294 (M^+), 220, 191, 165, 115, 73. Anal. Calcd for $C_{20}H_{26}Si$: C, 81.57; H, 8.90. Found: C, 80.96; H, 9.03. A minor set of ^1H NMR (C_6D_6) signals at δ 7.60 (1 H, d, J = 16 Hz) and 5.63 (1H, d, J = 16 Hz) attributable to the *E* isomer (6%) were also observed.

Dimers 18a−d. To a solution containing 0.334 g (1.17 mmol) of **15a** in 10 mL of THF and 5 mL of ethanol was added 6 mL (6.0 mmol) of a 1.0 M solution of TBAF in THF at room temperature under a nitrogen atmosphere. After 4 h of stirring, 100 mL of diethyl ether was added. The mixture was washed with water (3 × 30 mL), dried

over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes) to afford 0.11 g (66%) of **18a**−**d** as a white solid: ^{1}H NMR ($CDCl_3$) δ 7.2−6.8 (4 H, m) [6.43 (dm, J = 9.9 and 1 Hz), 6.41 (dm, J = 10.1 and 1 Hz), 6.31 (dd, J = 9.9 and 1 Hz), 6.29 (dd, J = 9.9 and 1 Hz), 6.20 (dd, J = 10.1 and 4.5 Hz), 6.19 (dd, J = 9.9 and 4.5 Hz), 6.08 (dd, J = 9.9 and 4.4 Hz), signals due to the eight vinylic hydrogens of the four isomers with one overlap at δ 6.08 which has ca. twice the intensity of the other signals with nearly equal intensities among them], 4.83 (1 H, m), 4.41 (1 H, m), 3.3−2.6 (8 H, m), 2.3−1.9 (4 H, m); ^{13}C NMR ($CDCl_3$) δ [148.46, 146.94, 146.82, 146.42, 144.79, 144.66, 144.62, 144.50, 144.42, 144.23, 144.18, 144.13, 143.99, 143.24, 142.42 (2 carbons), 142.26, 142.16, 141.21, 141.10, 137.93, 137.78, 136.82, 136.78, 132.66, 131.77, 130.82, 129.78, 129.72, 129.19, 126.96, 126.70 (31 signals due to the 32 quaternary sp^2 carbons of the four isomers)], [127.37, 126.46, 126.36, 126.31, 126.24, 126.20, 126.12, 125.95, 125.60, 124.76, 123.90, 123.77, 123.73 (2 carbons), 123.42, 123.14, 123.00, 122.66, 122.40, 122.25, 119.33, 118.72, 117.94, 117.78 (23 signals due to the 24 CH sp^2 carbons)], [43.58, 43.48, 42.98, 42.88, 42.76, 42.68, 42.48, 42.24 (8 signals of the 8 sp^3 carbons on the four-membered rings)], [32.96, 32.93, 32.79, 32.72, 32.56, 31.33, 30.85, 30.72, 30.18, 29.29 (benzylic CH_2 carbons on the five-membered rings with several overlapping peaks)], [25.74, 25.57, 25.55, 25.38, 25.35, 25.16, 25.03, 25.00 (8 signals due to the 8 central CH_2 carbons on the five-membered rings)]; MS (*m/e*) 284 (M^+), 269, 256, 241, 239, 228, 214, 167, 152, 142, 128, 114. Attempts to separate **18a**−**d** by HPLC produced a fraction which contained predominantly only one of the four isomers. Its NMR spectral data are consistent with the structural features of the angular dimers: ^{1}H NMR ($CDCl_3$) δ 7.16 (1 H, d, J = 8 Hz), 7.13 (1 H, d, J = 7 Hz), 7.10 (1 H, d, J = 8 Hz), 6.93 (1 H, d, J = 7.5 Hz), 6.41 (1 H, dd, J = 10.1 and 1 Hz), 6.19 (1 H, dd, J = 10.1 and 4.5 Hz), 4.85 (1 H, d, J = 6.0 Hz), 4.42 (1 H, t, J = 5 Hz), 2.95−2.75 (8 H, m), 2.15−1.95 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 146.93, 144.66, 144.17, 142.44, 141.24, 137.97, 131.74, 127.38, 126.94, 126.36, 123.74, 123.16, 122.66, 117.96, 43.45, 42.86, 32.80, 32.56, 30.73, 29.28, 25.39, 25.01. The additional ^{1}H NMR decoupling experiments further support the assigned structures.

Diels−**Alder Adduct 19.** To a solution containing 0.30 g (1.05 mmol) of **15a** and 1.32 g (20.0 mmol) of cyclopentadiene in 10 mL of THF and 10 mL of ethanol at 0 °C under a nitrogen atmosphere was added 3.0 mL (3.00 mmol) of a 1.0 M solution of TBAF in THF. The resulting mixture was stirred at 0 °C for 3 h. Pentane (100 mL) was added, and the mixture was washed with water (3 × 20 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes) to afford 0.175 g (80%) of **19** as a colorless oil: IR (neat) 1454, 1437, 1338, 1294, 1268, 1294, 1195, 1101, 1071, 906, 806, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.96 (1 H, d, J = 7.3 Hz), 6.66 (1 H, d, J = 7.5 Hz), 5.65 (2 H, d, J = 1.5 Hz), 3.64 (2 H, m), 2.93 (2 H, m), 2.80 (2 H, t, J = 7.4 Hz), 2.73−2.58 (2 H, m), 2.00 (2 H, quintet, J = 7.4 Hz), 1.93 (1 H, d, J = 8.2 Hz), 1.63 (1 H, d, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 145.57, 143.41, 143.00, 138.09, 132.46, 132.14, 122.66, 119.52, 54.75, 45.49, 44.97, 43.58, 43.21, 32.70, 29.70, 25.41; MS (*m/e*) 208 (M^+) 193, 179, 165, 152, 142, 115, 102, 89. Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.59; H, 7.77. The endo configuration of **19** was supported by the NOE measurements by irradiating the hydrogens on the four-membered ring at δ 3.64 and the methylene hydrogens on the bridge at δ 1.63 (syn to the four-membered ring) and at δ 1.93 (anti to the four-membered ring).

Dimer 21. To a solution containing 0.091 g (0.34 mmol) of **15b** in a mixture of 15 mL of THF and 5 mL of ethanol at room temperature under a nitrogen atmosphere was added 1.02 mL (1.02 mmol) of a 1.0 M solution of TBAF in THF. The resulting mixture was stirred for 18 h. Pentane (100 mL) was added, and the mixture was washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes) to afford 0.041 g (61%) of **21** as a colorless oil: IR (neat) 1453, 1378, 1118, 808 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.38 (1 H, d, J = 7.7 Hz), 7.12 (1 H, d, J = 7.7 Hz), 7.07 (1 H, d, J = 7.5 Hz), 6.86 (1 H, d, J = 7.3 Hz), 6.01 (1 H, d, J = 6.0 Hz), 3.88 (1 H, d, J = 6.0 Hz), 3.20−3.04 (2 H, m), 2.95−2.66 (8 H, m), 2.48−2.30 (2 H, m), 2.04 (4 H, quintet, J = 7.3 Hz), 2.00−1.75 (2 H, m), 1.52−1.18 (6 H, m), 0.93 (3 H, t, J = 7.0 Hz), 0.85 (3 H, t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 149.38, 144.05, 143.34, 143.06, 139.61, 138.20, 136.24, 136.20, 129.85, 125.75, 125.58, 123.65, 123.14, 118.50, 51.56, 48.57, 40.77, 36.40, 35.40, 32.52, 32.37, 32.24, 29.67, 27.89, 25.45, 25.38, 23.11, 22.38, 14.11, 14.03; MS (*m/e*) 396 (M^+), 339, 312, 297, 283; HRMS calcd for $C_{30}H_{36}$ 396.2819, found 396.2794.

Diels−**Alder Adduct 22.** To a solution of **15b** (320 mg, 1.2 mmol) and 2.1 g (32 mmol) of cyclopentadiene in a mixture of 10 mL of THF and 10 mL of ethanol was added 3.0 mL of a 1.0 M solution of TBAF (3.0 mmol) in THF at room temperature under a nitrogen atmosphere. After 10 h, 100 mL of pentane was added and the mixture was washed with water (3 × 30 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes) to afford 157 mg (50%) of **22** as a light yellow oil: IR (neat) 1454, 1438, 1378, 1335, 1251, 906, 808, 756, 732, 716 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.02 (1 H, d, J = 7.3 Hz), 6.70 (1 H, d, J = 7.3 Hz), 5.80 (1 H, dd, J = 5.5 and 3.1 Hz), 5.65 (1 H, dd, J = 5.5 and 3.1 Hz), 3.37 (1 H, d, J = 4.6 Hz), 3.00 (1 H, br s), 2.87 (2 H, t, J = 7.3 Hz), 2.79 (2 H, t, J = 8.0 Hz), 2.71 (1 H, br s), 2.13−2.02 (2 H, m), 1.99−1.86 (4 H, m), 1.55−1.34 (4 H, m), 0.96 (3 H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 146.42, 143.92, 142.85, 137.76, 134.24, 133.27, 122.61, 119.47, 58.06, 53.93, 51.35, 47.53, 44.92, 35.63, 32.75, 30.88, 30.01, 25.56, 23.53, 14.15; MS (*m/e*) 264 (M^+), 249, 235, 221, 207, 193, 179, 165, 152, 115, 91; HRMS calcd for $C_{20}H_{24}$ 264.1879, found 264.1890. In addition, the dimer **21** (47 mg) was also isolated in 20% yield.

Dimer 23. To a solution of **15c** (162 mg, 0.559 mmol) in a mixture of THF (10 mL) and ethanol (2 mL) was added 1.7 mL of a 1.0 M solution of TBAF (1.7 mmol) in THF at room temperature under a nitrogen atmosphere and the reaction was followed by TLC. Immediately after the addition of TBAF, only one major spot, presumably the desilylated product of **15c**, appeared on TLC. After 30 min of stirring, a second spot, the dimer **23**, appeared followed by the appearance of a third spot due to the dimer **24** with a very close R_f value 2 h later. As the mixture was stirred for 12 h, the desilylated product of **15c** completely disappeared. Diethyl ether (100 mL) was added and the mixture was washed with water (3 × 10 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes) to afford 23 mg (19%) of the dimer **23** as a light yellow solid and 44 mg (36%) of a mixture of **23** and **24** (**23**:**24** = 40:60). Dimer **23**: ^{1}H NMR ($CDCl_3$) δ 7.18−7.05 (10 H, m), 6.88−6.84 (4 H, m), 4.07 (2 H, s), 2.75 (4 H, t, J = 7 Hz), 2.64−2.55 (2 H, m), 1.93−1.83 (2 H, m), 1.64−1.53 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 144.03, 143.62, 143.03, 140.63, 140.59, 127.42, 127.17, 126.00, 124.04, 119.71, 68.07, 51.94, 32.88, 30.83, 25.86; MS (*m/e*) 436 (M^+), 421, 408, 359, 345, 331, 258, 218, 202. The dimer **23** was thermally labile and slowly rearranged to **24** even at room temperature.

Dimer 24. A solution containing 22.0 mg (0.0504 mmol) of **23** in 0.5 mL of C_6D_6 was heated at 60 °C in an NMR tube, and the rearrangement of **23** to **24** was found to be complete in 3 h as indicated by ^{1}H NMR. Benzene was removed and the residue was purified by column chromatography (silica gel/hexanes) to afford 19.6 mg (89%) of **24** as a yellow solid: IR ($CDCl_3$) 718, 651 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.33 (4 H, d, J = 7.1 Hz), 6.97−6.85 (10 H, m), 6.79 (2 H, d, J = 7.9 Hz), 2.69 (2 H, dt, J = 15.9 and 7.2 Hz), 2.81 (2 H, dt, J = 15.9 and 7.6 Hz), 2.55 (2 H, dt, J = 15.7 and 7.7 Hz), 2.41 (2 H, dt, J = 15.7 and 7.1 Hz), 1.76 (4 H, quintet, J = 7.5 Hz); ^{13}C NMR (C_6D_6) δ 143.36, 142.07, 141.39, 140.83, 140.47, 135.53, 133.88, 131.05, 128.01, 126.82, 126.28, 122.93, 33.27, 32.88, 25.52; MS (*m/e*) 436 (M^+), 408, 359, 345, 331, 315, 302, 258, 239, 165; HRMS calcd for $C_{34}H_{28}$ 436.2192, found 436.2179. The dimer **24** was recrystallized from a 1:1 mixture of hexanes and chloroform for the X-ray structure determination.

Dimer 26. To a solution of **15d** (120 mg, 0.47 mmol) in a mixture of THF (10 mL) and ethanol (2 mL) was added 1.5 mL of a 1.0 M solution of TBAF (1.5 mmol) in THF at room temperature under a nitrogen atmosphere. After 16 h, 50 mL of diethyl ether was added and the reaction mixture was washed with water (3 × 10 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes) and HPLC (silica/hexanes) to furnish 31 mg (36%) of the dimer **26** as a white solid: ^{1}H NMR ($CDCl_3$) δ 7.18 (2 H, d, J = 7.3 Hz), 7.10 (2 H, d, J = 7.3 Hz), 3.89 (2 H, s), 3.14−3.00 (4 H, m), 2.91 (4 H, t, J = 7.5 Hz), 2.58 (2 H, dt, J = 12.5 and 3 Hz), 2.16 (2 H, dt, J = 12 and 3 Hz), 2.13 (6 H, s), 2.10 (4 H,

m); ^{13}C NMR ($CDCl_3$) δ 146.01, 144.92, 140.50, 136.97, 134.92, 132.17, 123.54, 119.71, 55.07, 34.59, 33.15, 32.95, 25.54, 22.83; MS (*m/e*) 364 (M^+), 349, 334, 219, 166, 152, 145, 139; HRMS calcd for $C_{28}H_{28}$ 364.2192, found 364.2203. The dimer **26** was recrystallized from chloroform for the X-ray structure determination.

Dimer 32. The same procedure was repeated as described for **26** except that 186 mg (0.63 mmol) of **15e** was used to furnish 52 mg (37%) of **32** (two isomers, 35:65) as a white solid. The two isomers tentatively assigned to **32a** and **32b** were inseparable by HPLC (silica/hexanes). IR ($CDCl_3$) 736, 651 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.20−7.09 (4 H, m), 3.97 and 3.92 (2 H, two singlets, 35 : 65), 3.25−2.85 (10 H, m), 2.60−1.40 (20 H, m); ^{13}C NMR ($CDCl_3$) δ 145.98, 144.93, 144.74, 144.41, 140.81, 140.25, 139.81, 135.27, 134.72, 134.67, 133.74, 123.32, 119.65, 119.53, 55.20, 54.47, 51.97, 45.40, 37.30, 36.88, 33.30, 33.14, 33.06, 33.02, 30.58, 28.29, 27.22, 25.53, 25.48, 25.39, 23.81, 22.64; MS (*m/e*) 444 (M^+), 401, 387, 375, 363, 222, 193, 179, 165, 149, 129, 115, 105; HRMS calcd for $C_{34}H_{36}$ 444.2819, found 444.2825. The two singlets in the ^{1}H NMR spectrum at δ 3.97 and 3.92 could be attributed to the hydrogen atoms on the four-membered rings of **32a** and **32b** as observed in the case of **26**. These two signals could not be attributed to the presence of only one isomer without symmetry in its structure, such as **32c**, which could be expected to exhibit two AB pattern doublets with equal intensities. The two ^{13}C NMR signals at δ 55.20 and 54.47 were found to be CH carbons by the DEPT experiment. They are attributable to the sp^3 carbons on the four-membered rings of **32a** and **32b** as observed in the case of **26**. In addition, the two ^{13}C NMR signals at δ 51.97 and 45.40 were also found to be CH carbons by the DEPT experiment and are attributable to the CH carbons on the six-membered rings of **32a** and **32b**.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **12a**−**e**, **14a**−**e**, **15a**−**e**, **18**, **19**, **21**, **22**, **23**, **24**, **26**, and **32** and tables of crystallographic data for the X-ray diffraction analyses of **24** and **26** (59 pages). See any current masthead page for ordering and Internet access instructions.

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