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Generation of *o*-quinodimethanes via the electrocyclic reaction of (4*Z*)-1,2,4,6,7-octapentaenes derived from the organoborate complexes and their subsequent reactions

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Abstract

Treatment of allenyldicyclohexylborane (**20**) with 1-lithio-3,4-pentadien-1-yne **21** produced the organoborate complex **22**, which on further treatment with trimethyltin chloride furnished the enediallene **23** in situ. The subsequent electrocyclic reaction then generated the *o*-quinodimethane **24**, which underwent a [1,5]-sigmatropic hydrogen shift to afford **25**. Oxidative work-up followed by protonation gave the phenol **26**. The presence of a boron group and a tin group in **25** also provides handles to allow their transformations to an allyl substituent and an iodo substituent in **27**. Attempts to capture the *o*-quinodimethane in **32** with the carbon–carbon double bond intramolecularly afforded the tricyclic phenol **34** in low yield (6%). By using the combination of the organoborane **36** and 1-lithio-1,2-heptadiene (**37**) to form the organoborate complex **38**, the *o*-quinodimethane **40** could also be generated in situ, leading to the phenol **42** and the styrene **43**.

Keywords: Boron; *o*-Quinodimethanes; Electrocyclization; (*Z*)-1,2,4,6,7-Octapentaenes; Organoborates

1. Introduction

o-Quinodimethanes are reactive intermediates and their chemical reactivities have been exploited for a variety of synthetic applications [1]. The intramolecular Diels–Alder reactions provide efficient pathways to many polycyclic systems. For example, treatment of **1** with tetrabutylammonium fluoride (TBAF) in refluxing acetonitrile induced a 1,4-elimination to form the *o*-quinodimethane **3** having the *E* geometry, which then underwent an intramolecular Diels–Alder reaction to furnish **4** having the *trans* ring junction (Scheme 1) [2]. Alternatively, thermolysis of the sulfone **2** at 210°C to promote extrusion of sulfur dioxide also gave **3** and consequently **4** (*trans*:*cis* = 5:1) in 65% yield [3].

For the α-substituted *o*-quinodimethanes having a (*Z*)-allylic hydrogen, the [1,5]-sigmatropic hydrogen shift is a facile process [4]. Specifically, treatment of the sulfone **5** with TBAF produced both **7a** (45%) and **7b** (3.3%) (see Scheme 2) [4a]. Presumably, the reaction proceeds through an initial 1,4-elimination to form the *o*-quinodimethanes **6a** as the major isomer and **6b** as the minor isomer followed by a [1,5]-sigmatropic hydrogen shift.

In addition to the 1,4-elimination reactions of the α,α′-disubstituted *o*-xylenes, such as those shown in Schemes 1 and 2, many other synthetic routes to *o*-quinodimethanes have been developed [1–8]. An interesting but less studied route to *o*-quinodimethanes involves the electrocyclic reaction of (4*Z*)-1,2,4,6,7-octapentaenes (enediallenes). The parent (*Z*)-1,2,4,6,7-octapentaene (**9**) was generated in situ by treatment of (*Z*)-4-octene-1,7-diyne (**8**) with potassium *tert*-butoxide (Scheme 3) [9]. The subsequent electrocyclic reaction gave the parent *o*-quinodimethane **10**, which then produced the spiro dimer **11** and the linear dimer **12**. Isomerization from **9** to **10** must be a very facile process. The corresponding benzofused [10,11] and naphthofused [10] analogues with a fused central carbon–carbon double bond isomerize rapidly to 2,3-naphthoquinodimethane and 2,3-anthraquinodimethane, respectively, at ambient or subambient tempera-

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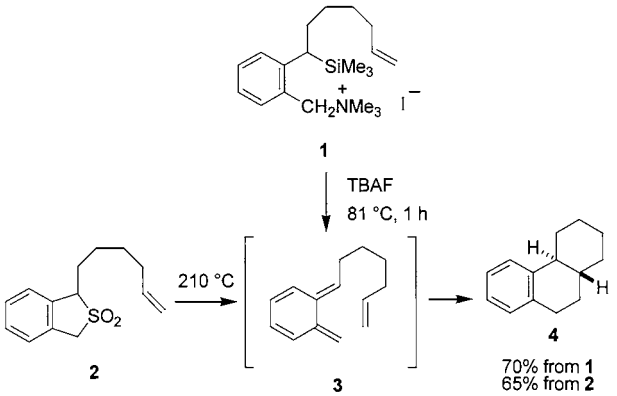
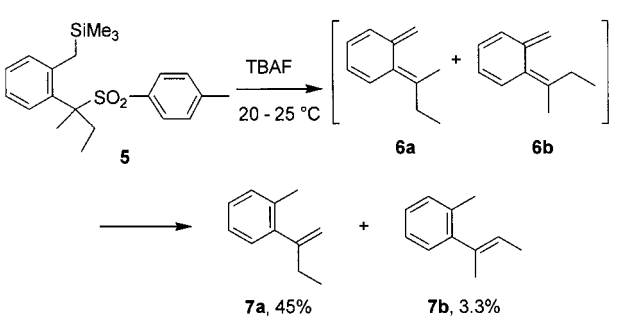


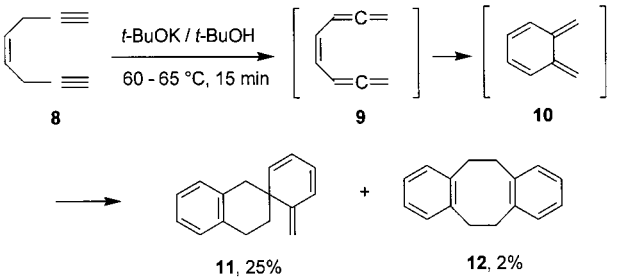
Scheme 1.

tures. In addition, the electrocyclic reaction of (4*Z*)-1,2,4,6-heptatetraenes to 5-methylene-1,3-cyclohexadienes (*o*-isotoluenes) is known to be vary facile [12]. However, with the exception of the benzofused and the naphthofused analogues, other *o*-quinodimethanes have not been prepared via the electrocyclic reaction of enediallenes.

We recently reported a facile synthesis of *o*-isotoluenes via the electrocyclic reaction of (4*Z*)-1,2,4,6-heptatetraenes (Scheme 4) [12d]. Treatment of alkenyldicyclohexylboranes **13** with 1-lithio-3,4-pentadien-1-ynes, derived from lithiation of the corresponding 3,4-pentadien-1-ynes with *n*-butyllithium, followed by trimethyltin chloride and acetic acid furnished the *o*-isotoluenes **18**. Presumably, the reaction proceeds through the formation of the organoborate complexes **15** followed by the trimethyltin chloride-induced transformation to form **16** with the dicyclohexylboryl group and the trimethyltin group *cis* to each other [13]. The electrocyclic reaction of **16** then produces **17** and subsequently, after protonation with acetic acid, the *o*-isotoluenes **18**. We envisioned that the reaction sequence outlined in Scheme 4 could be adopted for the synthesis of enediallenes for subsequent conversion to *o*-quinodimethanes by substitution of the alkenyldicyclohexylboranes **13** with allenyldicyclohexylboranes.



Scheme 2.

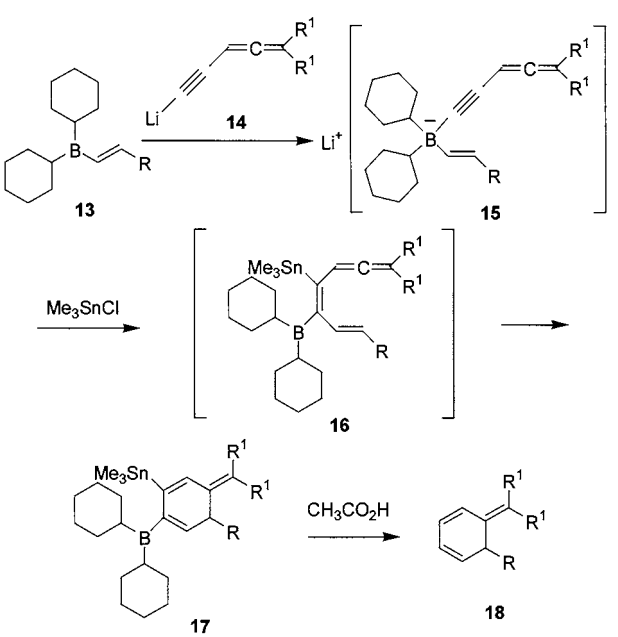


Scheme 3.

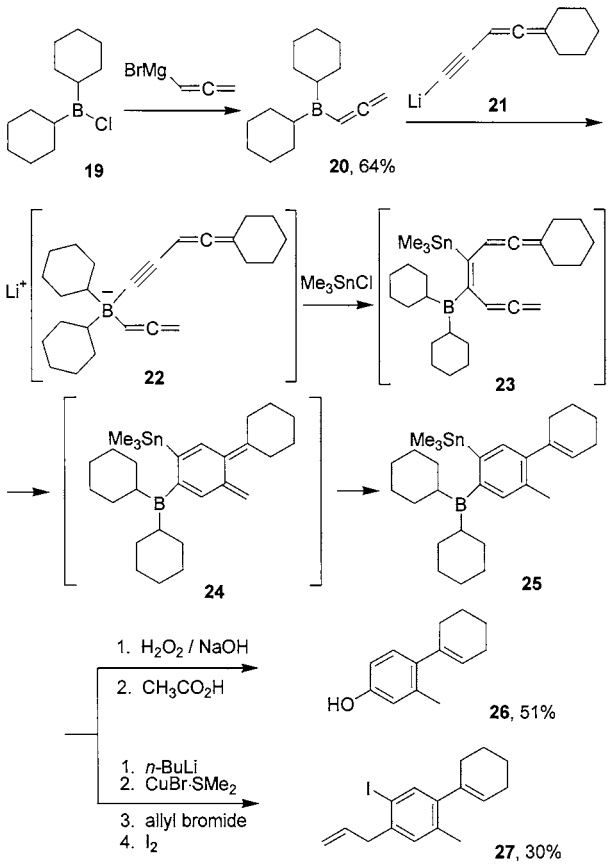
2. Results and discussion

Allenyldicyclohexylborane (**20**) was readily prepared by treatment of chlorodicyclohexylborane (**19**) with allenylmagnesium bromide (Scheme 5). Sequential treatment of **20** with 1-lithio-3,4-pentadien-1-yne **21**, Me_3SnCl, an alkaline H_2O_2 solution, and acetic acid produced the phenol **26** in a single operation. Apparently, trimethyltin chloride also promoted a stereoselective migration of the allenyl group in **22** to the adjacent acetylenic carbon atom to afford the enediallene **23**. The electrocyclic reaction of **23** then generated the *o*-quinodimethane **24**, giving rise to **25** through a [1,5]-sigmatropic hydrogen shift. Oxidative work-up followed by protonation with acetic acid then gave **26** in 51% yield.

The presence of a dicyclohexylboryl group and a trimethyltin group in **25** also affords opportunities for other chemical transformations. Treatment of **25** with *n*-butyllithium followed by $CuBr{\cdot}SMe_2$ and allyl bromide transformed the dicyclohexylboryl substituent to the allyl group, presumably via an organocopper inter-



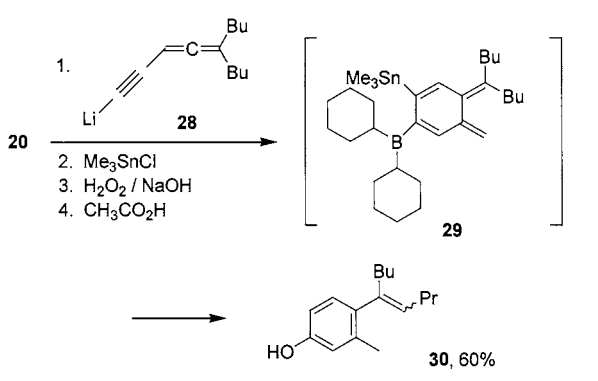
Scheme 4.



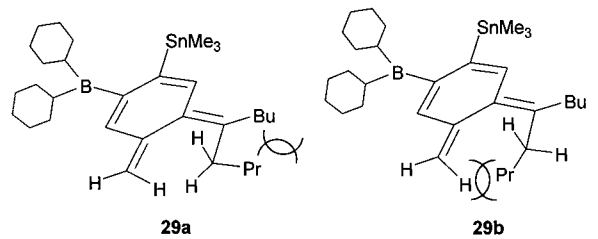
Scheme 5.

mediate [13e–h]. Further treatment of the resulting adduct with I_2 replaced the trimethyltin group with an iodo substituent [13e–h] to furnish **27** having a tetrasubstituted benzene ring.

By using **28** to form the organoborate complex with **20**, the *o*-quinodimethane **29** was generated in situ (Scheme 6). The subsequent [1,5]-sigmatropic hydrogen shift then furnished **30** as a mixture of the *E* and the *Z* isomers (isomer ratio = 84:16) in 60% yield. Whether the *E* isomer or the *Z* isomer was produced as the predominant product has not been determined definitively. However, it is worth noting that the ^{1}H-NMR chemical shift of the alkenyl hydrogen of the major product at δ 5.18 is 0.24 ppm upfield from that of the minor product at δ 5.42. It was reported previously that the ^{1}H-NMR chemical shift of the alkenyl hydrogen of the *Z* isomer of 1-(1-ethyl-1-propenyl)-2-methylbenzene at δ 5.35 is 0.24 ppm upfield from that of the *E* isomer at δ 5.59 [4a]. The chemical shift correlation appears to suggest that the *Z* isomer of **30** is the predominant product. In any event, the *E* isomer is produced from the conformer **29a**, while the *Z* isomer is derived from the conformer **29b**.

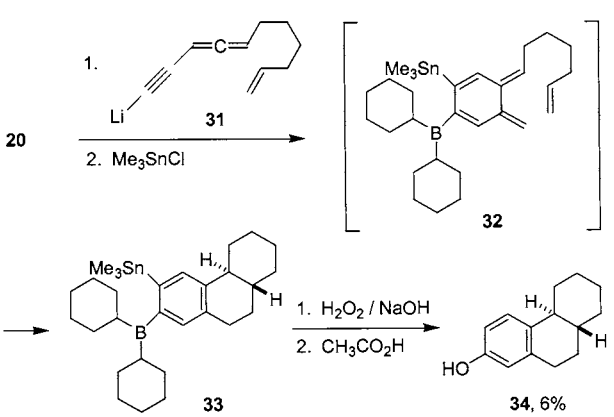


Scheme 6.

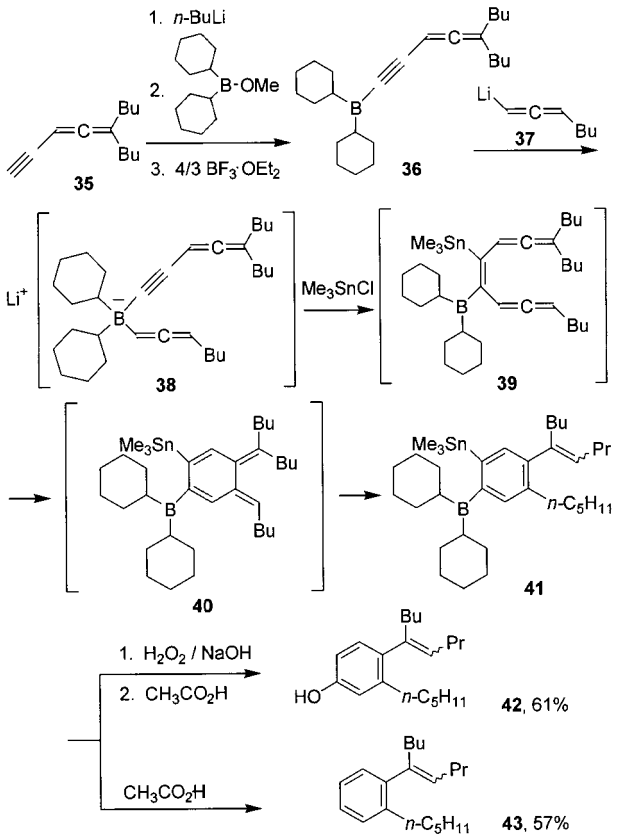


The relative severity of the $A(1,2)$ allylic strain in **29a** versus the $A(1,3)$ allylic strain [14] in **29b** determines the ratio of the resulting *E* and *Z* isomers. The preferential formation of the *E* isomer was reported previously in the system leading to the formation of 1-(1-ethyl-1-propenyl)-2-methylbenzene [4a].

It was possible to capture the *o*-quinodimethane in **32**, derived from **20** and **31**, with the carbon–carbon double bond for the intramolecular Diels–Alder reaction to afford **33**, which on oxidative work-up and protonation gave the tricyclic phenol **34** having predominantly the *trans* ring junction (*trans*:*cis* > 10:1) (Scheme 7). Unfortunately, the overall isolated yield of **34** is only 6%. A small amount of 4-[(1*E*)-1,6-heptadienyl]-3-methylphenol (ca. 1%), presumably derived from a [1,5]-sigmatropic hydrogen shift of the *Z* isomer of **32**, was also produced. The effect of the boron and the tin substituents on the reactivity of the *o*-quinodimethane in **32** for the intramolecular Diels–Alder reaction remains to be determined.



Scheme 7.

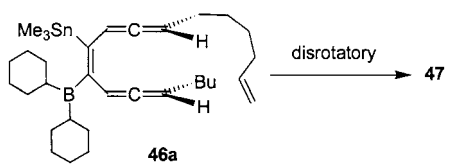


Scheme 8.

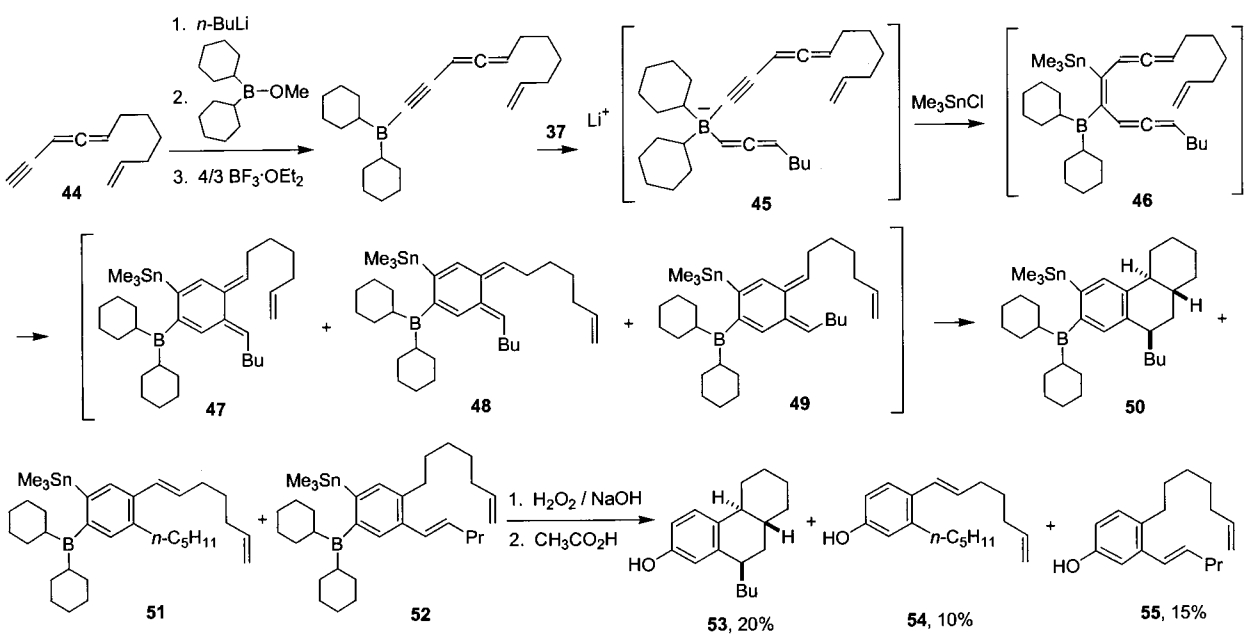
An alternative pathway to the organoborate complexes for the subsequent formation of *o*-quinodimethanes has also been developed. Sequential treatment of 5-butyl-3,4-nonadien-1-yne (**35**) with *n*-butyllithium, *B*-methoxydicyclohexylborane, and $4/3BF_3{\cdot}OEt_2$ [15] generated **36** in situ (Scheme 8). Further treatment of **36** with 1-lithio-1,2-heptadiene (**37**) gave the requisite organoborate complex **38** for transformation to the *o*-quinodimethane **40**, leading to **41** and subsequently, after oxidative work-up and protonation, to the phenol **42** (61% yield, isomer ratio = 87:13). Direct protonation of **41** with acetic acid furnished **43** in 57% yield.

By using the combination of 3,4,10-undecatrien-1-yne (**44**) and **37** to form the organoborate complex **45**, the phenols **53** (20%), **54** (10%) and **55** (15%) were obtained (Scheme 9). Apparently, **53** was produced via the intramolecular Diels–Alder reaction of **47** to form **50**, whereas **54** and **55** were produced via the [1,5]-sigmatropic hydrogen shift of **48** and **49** to form **51** and **52**, respectively.

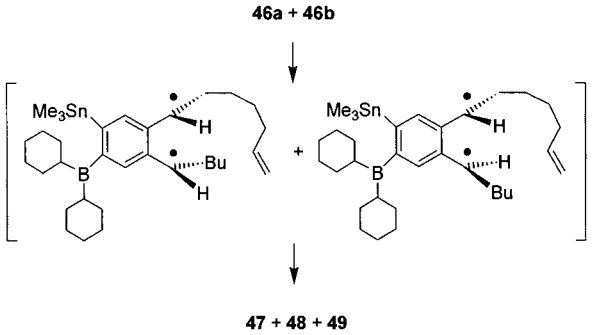
It is worth noting that the enediallene **46** is most likely a 1:1 mixture of the two diastereomers **46a** and **46b**. If the disrotatory motion of the six π-electron system is also required for the thermally induced electrocyclic reactions of **46a** and **46b**, then **46a** will be the precursor of **47** (Eq. (1)) whereas **46b** will be the precursor of both **48** and **49** (Eq. (2)) [16].



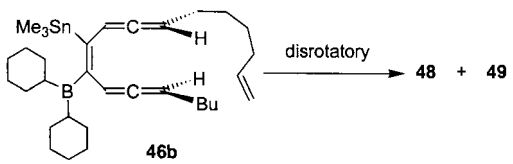
(1)



Scheme 9.



Scheme 10.



(2)

The fact that substantial amounts of **54** and **55** (combined yield = 25%) were produced appears to suggest that the stereoelectronic requirement for the electrocyclic reaction dictates the transformation of **46b** to the sterically less favorable **48** and **49** with one of the exocyclic double bonds having the *Z* geometry. Otherwise, one would expect a preferential formation of **47** with both of the exocyclic double bonds having the *E* geometry. However, the possibility of producing **47**–**49** from **46** via a biradical pathway without the requirement of an initial disrotatory motion (Scheme 10) could not be ruled out. A one-step intramolecular ene reaction of **46** could also produce **51** and **52** directly [17].

3. Conclusions

A new synthetic pathway to (4*Z*)-1,2,4,6,7-octapentaenes as precursors of *o*-quinodimethanes has been developed. The ability to generate enediallenes with high geometric purity via the corresponding organoborate complexes in a single operation is an especially attractive feature. The process is very flexible, allowing easy assembly of various readily available fragments to produce the requisite organoborate complexes. The presence of the boron and the tin substituents in the cyclized adducts also affords opportunities to introduce other functional groups onto the benzene ring.

4. Experimental

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. Chlorodicyclohexylborane (**19**, 1.0 M solution in hexanes), trimethyltin chloride (1.0 M solution in THF), *n*-butyllithium (2.5 M solution in hexanes), $CuBr{\cdot}SMe_2$, $BF_3{\cdot}OEt_2$, propargyl bromide (80 wt.% solution in toluene) were purchased from Aldrich Chemical Co., and were used as received. Allenylmagnesium bromide was prepared according to the reported procedure [18]. *B*-Methoxydicyclohexylborane was prepared by treatment of dicyclohexylborane with methanol [19]. 5,5-(Pentamethylene)-3,4-pentadienl-1-yne and 5-butyl-3,4-nonadienl-1-yne (**35**) were prepared as reported previously [12d]. Similarly, 3,4,10-undecatrien-1-yne (**44**) was synthesized in 52% overall yield from cross-coupling of 1,2,8-nonatriene [20] with 1-iodo-2-(trimethylsilyl)ethyne (69%) followed by desilylation (75%). 1,2-Heptadiene was prepared as reported previously [21]. ^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 77.00) as internal standards.

4.1. Allenyldicyclohexylborane (*20*)

The procedure for the synthesis of *B*-allenyl-9-borabicyclo[3.3.1]nonane [22] was adopted for the preparation of **20**. Allenylmagnesium bromide was prepared as described previously [18]. To 0.48 g (20.0 mmol) of magnesium turnings under a nitrogen atmosphere were added 20 ml of anhydrous diethyl ether and 2 drops of 1,2-dibromoethane. After 10 min, 0.010 g of mercury(II) chloride was added followed by dropwise addition of 1.34 ml of a 80 wt.% solution of propargyl bromide (12.0 mmol) in toluene over 20 min. The reaction flask was immersed in a cold water bath when the Grignard reaction became too vigorous. The reaction mixture was stirred at r.t. for 1 h. The resulting mixture was then transferred via cannula to a flask containing 10.0 ml of a 1.0 M solution of chlorodicyclohexylborane (10.0 mmol) in hexanes and 20 ml of diethyl ether maintained at −78°C. After 30 min, the mixture was allowed to warm to r.t. After 1 h, stirring was discontinued to allow magnesium salt to settle. The solution was transferred via cannula to centrifuge tubes for centrifugation. The clear supernatant liquid was transferred via cannula to a flask and was concentrated in vacuo. The residue was distilled in vacuo (b.p. 98°C, 0.02 Torr) to give 1.372 g (6.35 mmol, 64%) of **20** as a colorless liquid: ^1H δ 5.56 (1 H, t, $J = 6.5$ Hz), 4.56 (2 H, d, $J = 6.7$ Hz), 1.76–1.62 (6 H, m), 1.53–1.43 (4 H, m), 1.28–1.14 (12 H, m); ^{13}C δ 220.15, 87.5 (br), 68.54, 34.5 (br), 27.49, 27.43, 27.01.

4.2. 4-(1-Cyclohexenyl)-3-methylphenol (*26*)

The following procedure for the preparation of **26** is representative. To 0.264 g (2.00 mmol) of 5,5-(pentamethylene)-3,4-pentadien-1-yne in 20 ml of THF at

−78°C was added 1.25 ml (2.00 mmol) of a 1.6 M solution of *n*-butyllithium in hexanes. After 30 min at −78°C, 0.475 g (2.20 mmol) of **20** in 10.0 ml of THF was introduced via cannula. After 30 min, the mixture was allowed to warm to r.t. After an additional 2 h, the mixture was cooled to 0°C, and 2.0 ml of a 1.0 M solution of trimethyltin chloride (2.0 mmol) in THF were added with a syringe. After 15 h of stirring at r.t., the mixture was transferred via cannula to a flask containing a mixture of 2.0 ml of a 30% H_2O_2 solution and 2 ml a 6 N NaOH solution in 15 ml of methanol at 0°C. The reaction mixture was heated at 50°C for 1 h before it was allowed to cool to rt. Glacial acetic acid (2.0 ml) was added, and the mixture was heated at 50°C for 2 h. The organic layer was separated, and the aqueous layer was extracted with pentane (3 × 20 ml). The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/20% Et_2O in hexanes) to furnish 0.192 g (1.02 mmol, 51%) of **26** as a light yellow liquid: IR (neat) 3331, 1605, 1581, 1226, 857, 812 cm^{-1}; ^1H δ 6.96 (1 H, d, $J = 8.1$ Hz), 6.68 (1 H, d, $J = 2.6$ Hz), 6.65 (1 H, dd, $J = 8.1$ and 2.6 Hz), 5.60 (1 H, s), 5.54 (1 H, tt, $J = 3.6$ and 1.8 Hz), 2.25 (3 H, s), 2.21–2.14 (4 H, m), 1.82–1.65 (4 H, m); ^{13}C δ 153.60, 138.17, 137.47, 136.66, 129.37, 125.76, 116.61, 112.23, 30.32, 25.38, 23.09, 22.15, 19.84; MS (*m*/*z*) 188 (M^+), 173, 160, 159, 145.

4.3. 1-(1-Cyclohexenyl)-5-iodo-2-methyl-4-(2-propenyl)benzene (27)

The same procedure was repeated as described for **26** except that after 15 h of stirring following the introduction of trimethyltin chloride, the mixture was cooled to −78°C. A solution of a 1.6 M *n*-butyllithium in hexanes (1.25 ml, 2.0 mmol) was added with a syringe. After 15 min, the reaction mixture was transferred via cannula to a flask containing 0.452 g (2.20 mmol) of $CuBr{\cdot}SMe_2$ and 15 ml of THF maintained at −78°C. After 1 h at −78°C, 0.726 g (6.00 mmol) of allyl bromide was introduced dropwise, and the reaction mixture was stirred at −78°C for 1 h before it was allowed to warm to r.t. A solution of 1.02 g of iodine (4.00 mmol) in 10 ml of diethyl ether was added via cannula. The resulting mixture was stirred at r.t. for 1 h followed by the addition of a saturated $Na_2S_2O_3$ solution to destroy excess I_2. An additional 30 ml of water and 40 ml of Et_2O were added, and the organic layer was then separated, washed with a saturated NaCl solution, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/hexanes) to afford 0.203 g (0.60 mmol, 30%) of **27** as a yellow oil: IR (neat) 991, 914 cm^{-1}; ^1H δ 7.54 (1 H, s), 7.00 (1 H, s), 5.96 (1 H, ddt, $J = 16.6$, 10.3, and 6.6 Hz), 5.55 (1 H, tt, $J = 5.5$ and 2.8 Hz), 5.14 (1 H, dq, $J = 10$ and 1.6 Hz), 5.12 (1 H, dq, $J = 17$ and 1.8 Hz), 3.44 (2 H, dt, $J = 6.5$ and 1.5 Hz), 2.20 (3 H, s), 2.19–2.11 (4 H, m), 1.79–1.62 (4 H, m); ^{13}C δ 144.70, 140.34, 138.73, 137.31, 136.01, 135.51, 131.04, 126.48, 116.44, 96.75, 44.42, 29.89, 25.33, 22.96, 22.06, 19.36; MS (*m*/*z*) 338 (M^+), 297, 211, 170, 169. Anal. Calc. for $C_{16}H_{19}I$: C, 56.82; H, 5.66. Found: C, 57.04; H, 5.68.

4.4. 4-(1-Butyl-1-pentenyl)-3-methylphenol (30)

The same procedure was repeated as described for **26** except that 0.352 g (2.00 mmol) of 5-butyl-3,4-nonadien-1-yne (**35**) was treated with 0.80 ml (2.00 mmol) of a 2.5 M solution of *n*-butyllithium in hexanes to produce **28** followed by 0.561 g (2.6 mmol) of **20**. The phenol **30** (0.279 g, 1.20 mmol, 60%) was isolated as a light yellow liquid: IR (neat) 3353, 1607, 1581, 1235, 860, 816 cm^{-1}; ^1H δ 6.89 (1 H, d, $J = 8.1$ Hz), 6.63 (1 H, dd, $J = 2.6$ Hz), 6.58 (1 H, dd, $J = 8.1$ and 2.6 Hz), 5.18 (1 H, t, $J = 7.3$ Hz), 4.65 (1 H, br s, OH), 2.28 (2 H, t, $J = 7.4$ Hz), 2.20 (3 H, s), 2.12 (2 H, q, $J = 7.3$ Hz), 1.43 (2 H, sextet, $J = 7.3$ Hz), 1.34–1.20 (4 H, m), 0.94 (3 H, t, $J = 7.3$ Hz), 0.87 (3 H, t, $J = 6.8$ Hz); ^{13}C δ 153.68, 140.09, 137.39, 136.93, 130.09, 129.69, 116.48, 111.91, 31.71, 30.36, 30.11, 23.02, 22.83, 20.04, 14.01, 13.90; MS (*m*/*z*) 232 [M^+], 217, 203, 190, 175, 161, 148, 147. A minor set of the ^1H-NMR signals attributable to the presence of the other geometric isomer (isomer ratio = 84:16) at δ (partial) 6.80 (1 H, d, $J = 8.1$ Hz), 6.66 (1 H, d, $J = 2.6$ Hz), and 5.42 (1 H, tt, $J = 7.3$ and 1.1 Hz) was also observed.

4.5. trans-(±)-4b,5,6,7,8,8a,9,10-Octahydro-2-phenanthrenol (34)

The same procedure was repeated as described for **26** except that 0.292 g (2.00 mmol) of 3,4,10-undecatrien-1-yne (**44**) was used to prepare **31**. To facilitate purification of **34**, the products isolated after column chromatography were treated with an excess of a 2.0 M solution of $BH_3{\cdot}SMe_2$ in THF followed by oxidation with an alkaline 30% H_2O_2 solution. This treatment allowed conversion of undesired side products containing a terminal carbon–carbon double bond to more polar adducts having a hydroxyl group. Further purification by column chromatography afforded 0.023 g (0.11 mmol, 6%) of **34** [23] as a white solid: IR 3302, 1610, 1247, 802 cm^{-1}; ^1H δ 7.14 (1 H, d, $J = 8.3$ Hz), 6.61 (1 H, dd, $J = 8.4$ and 2.9 Hz), 6.54 (1 H, d, $J = 2.8$ Hz), 4.51 (1 H, br s, OH), 2.84 (1 H, ddd, $J = 17.0$, 11.5 and 5.9 Hz), 2.73 (1 H, ddd, $J = 16.8$, 6.0 and 2.4 Hz), 2.39 (1 H, dm, $J = 12.9$ and 3.4 Hz), 2.18 (1 H, td, $J = 10.7$ and 2 Hz), 1.93–1.84 (1 H, m), 1.8–1.7 (3 H, m), 1.5–1.1 (6 H, m); ^{13}C δ 153.09, 138.68, 133.10, 126.61, 115.16, 112.62, 43.24, 40.80, 34.24, 31.19, 30.64, 30.01, 26.89, 26.31; MS (*m*/*z*) 202 [M^+], 174, 159, 145.

The assignment of the *trans* geometry to **34** is based on the coupling constant of ca. 10.7 Hz for the two anti hydrogen atoms with the benzylic methine hydrogen at 2.18 ppm. The ^{1}H-NMR chemical shift of the benzylic methine hydrogen and the ^{13}C-NMR chemical shifts of the aliphatic carbons are also consistent with the assignment of the *trans* geometry to **34** when compared with those of *trans*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene reported previously [3a]. A minor set of the ^{1}H-NMR signals (partial) attributable to 4-[(1*E*)-1,6-heptadienyl]-3-methylphenol (ca. 1%) at δ 7.28 (1 H, d, $J = 9$ Hz), 6.48 (1 H, dt, $J = 15.8$ and 1.5 Hz), 5.94 (1 H, dt, $J = 15.6$ and 6.9 Hz) was also observed.

4.6. 4-(1-Butyl-1-pentenyl)-3-pentylphenol (42)

The following procedure for the preparation of **42** is representative. To 0.352 g (2.00 mmol) of 5-butyl-3,4-nonadien-1-yne (**35**) in 20 ml of THF at -78°C under a nitrogen atmosphere was added 0.80 ml (2.0 mmol) of a 2.5 M solution of *n*-butyllithium in hexanes. After 30 min at -78°C, 0.416 g (2.00 mmol) of *B*-methoxydicyclohexylborane in 10.0 ml of THF was introduced via cannula. After 1.5 h of stirring at -78°C, 0.33 ml (2.67 mmol) of $BF_3{\cdot}OEt_2$ was added with a syringe, and the mixture was allowed to warm to r.t. Solvent was removed in vacuo, and the remaining yellow viscous residue was dissolved in 30 ml of pentane. The solution was transferred to centrifuge tubes via cannula for centrifugation. The supernatant liquid was then transferred via cannula to a flask. Pentane was removed in vacuo to furnish **36** as a colorless viscous liquid. Anhydrous THF (35 ml) was added, and the solution was cooled to -78°C. To a second flask containing 0.202 g (2.1 mmol) of 1,2-heptadiene in 15 ml of THF at -78°C was added 0.80 ml (2.0 mmol) of a 2.5 M solution of *n*-butyllithium in hexanes. After 30 min of stirring at -78°C, 1-lithio-1,2-heptadiene (**37**) was added via cannula to the flask containing **36**. After 1 h of stirring at -78°C, the mixture was allowed to warm to r.t. and stirred for an additional 3 h. The mixture was then cooled to 0°C, and 2.0 ml of a 1.0 M solution of trimethyltin chloride in THF was introduced with a syringe. After 14 h of stirring at r.t., the mixture was transferred via cannula to a flask containing 2 ml of 30% H_2O_2, 2.0 ml of a 6 N NaOH solution, and 15 ml of methanol at 0°C. The reaction mixture was heated at 50°C for 1 h. Glacial acetic acid (2 ml) was added, and the mixture was heated at 50°C for an additional 2 h before it was allowed to cool to r.t. The organic layer was separated, and the aqueous layer was extracted with pentane (3×20 ml). The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/20% Et_2O in hexanes) to furnish 0.351 g (1.22 mmol, 61%) of **42** as a light yellow liquid: IR (neat) 3341, 1606, 1581, 1230, 817 cm^{-1}; ^{1}H δ 6.91 (1 H, d, $J = 8.3$ Hz), 6.70 (1 H, d, $J = 2.6$ Hz), 6.61 (1 H, dd, $J = 8.1$ and 2.8 Hz), 5.21 (1 H, t, $J = 7.3$ Hz), 5.17 (1 H, br s, OH), 2.52 (2 H, t, $J = 8.0$ Hz), 2.29 (2 H, t, $J = 7.3$ Hz), 2.15 (2 H, q, $J = 7.3$ Hz), 1.6–1.5 (2 H, m), 1.45 (2 H, sextet, $J = 7.3$ Hz), 1.37–1.23 (8 H, m), 0.97 (3 H, t, $J = 7.3$ Hz), 0.90 (3 H, t, $J = 6.7$ Hz), 0.87 (3 H, t, $J = 6.9$ Hz); ^{13}C δ 153.73, 141.96, 140.03, 137.12, 130.41, 129.80, 115.30, 111.93, 32.94, 32.27, 31.98, 31.28, 30.41, 30.14, 23.03, 22.86, 22.54, 14.02, 13.99, 13.90; MS (*m*/*z*) 288 [M$^+$], 259, 231, 217, 189, 175, 161; HRMS calc. for $C_{20}H_{32}O$ 288.2453, found 288.2442. Anal. Calc. for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.15; H, 11.19. A minor set of the ^{1}H-NMR signals (partial) at δ 6.81 (1 H, d, $J = 8.3$ Hz), 6.74 (1 H, d, $J = 2.6$ Hz), 6.64 (1 H, dd, $J = 8$ and 2.6 Hz), and 5.45 (1 H, tt, $J = 7.1$ and 1.2 Hz) attributable to the presence of the other geometric isomer (isomer ratio = 87:13) was also observed.

4.7. 1-(1-Butyl-1-pentenyl)-2-pentylbenzene (43)

The same procedure was repeated as described for **42** except that the reaction mixture was treated with acetic acid directly. Purification by column chromatography (silica gel/hexanes) furnished 0.310 g (1.14 mmol, 57%) of **43** as a yellow oil: IR (neat) 1457, 758 cm^{-1}; ^{1}H δ 7.24–7.20 (2 H, m), 7.19–7.11 (1 H, m), 7.07 (1 H, dm, $J = 6.9$ and 1.3 Hz), 5.28 (1 H, t, $J = 7.3$ Hz), 2.61 (2 H, t, $J = 8.0$ Hz), 2.38 (2 H, t, $J = 7.3$ Hz), 2.21 (2 H, q, $J = 7.3$ Hz), 1.63 (2 H, m), 1.50 (2 H, sextet, $J = 7.3$ Hz), 1.42–1.28 (8 H, m), 1.02 (3 H, t, $J = 7.3$ Hz), 0.94 (3 H, t, $J = 6.7$ Hz), 0.91 (3 H, t, $J = 6.7$ Hz); ^{13}C δ 144.31, 140.63, 140.20, 129.60, 129.34, 128.75, 126.30, 124.97, 32.98, 32.19, 32.10, 31.55, 30.49, 30.14, 23.06, 22.91, 22.59, 14.05, 13.99. 13.92; MS (*m*/*z*) 272 [M$^+$], 215, 201, 173, 159, 145, 117; HRMS Calc. for $C_{20}H_{32}$ 272.2504, Found 272.2481. A minor ^{1}H-NMR signal of the alkenyl hydrogen of the other geometric isomer at δ 5.50 (tt, $J = 7.1$ and 1 Hz) was also observed.

4.8. (±)-10β-Butyl-4bα,5,6,7,8,8aβ,9,10-octahydro-2-phenanthrenol (53), 4-[(1E)-1,6-heptadienyl]-3-pentylphenol (54), and 4-(6-heptenyl)-3-[(E)-1-pentenyl]phenol (55)

The same procedure was repeated as described for **42** except that 0.292 g (2.0 mmol) of **44** was used. Purification by column chromatography (silica gel/10% diethyl ether in hexanes) furnished 0.232 g (0.90 mmol, 45%) of a mixture of **53** (20%), **54** (10%) and **55** (15%) as a colorless liquid. The amounts of **53**, **54** and **55** in the mixture were determined by integration of the ^{1}H-NMR spectrum. It was possible to separate **53** and **55** from the mixture by HPLC. A fraction containing predominantly **54** was also obtained. **53**: IR (neat)

3342, 1609, 1582, 1244, 733 cm^{-1}. ^1H δ 7.13(1 H, d, $J = 8.8$ Hz), 6.63 (1 H, d, $J = 8$ Hz), 6.60 (1 H, s), 4.77 (1 H, br s, OH), 2.66 (1 H, m), 2.39 (1 H, dm, $J = 12$ and 3 Hz), 2.12 (1 H, tm, $J = 11$ and 3 Hz), 1.94–1.1 (16 H, m), 0.92 (3 H, t, $J = 7.1$ Hz); ^{13}C δ 153.13, 143.85, 132.76, 126.21, 115.38, 112.71, 43.74, 38.21, 37.84. 35.61, 34.34, 33.92, 30.96, 30.38, 26.92, 26.43, 22.84, 14.13; MS (m/z) 258 [M^+], 201, 174, 159, 145, 133. **54**: ^1H (partial) δ 7.29 (1 H, d, $J = 8.2$ Hz), 6.60 (2 H, m), 6.51 (1 H, dt, $J = 15.4$ and 1.6 Hz), 5.94 (1 H, dt, $J = 15.4$ and 6.9 Hz); ^{13}C δ 154.36, 141.50, 138.76, 130.22, 129.43, 127.11 (2 carbons), 115.86, 114.55, 112.97, 33.32, 33.20, 32.65, 31.72, 30.46, 28.73, 22.53, 14.03. **55**: IR (neat) 3354, 1640, 1607, 1578, 1245, 993, 964, 909, 867, 821 cm^{-1}; ^1H δ 6.96 (1 H, d, $J = 8.2$ Hz), 6.90 (1 H, d, $J = 2.6$ Hz), 6.62 (1 H, dd, $J = 8.3$ and 2.7 Hz), 6.54 (1 H, dt, $J = 15.7$ and 1.1 Hz), 6.05 (1 H, tt, $J = 15.6$ and 6.9 Hz), 5.80 (1 H, ddt, $J = 17.0$, 10.2 and 6.6 Hz), 4.98 (1 H, dm, $J = 17$ and 2 Hz), 4.93 (1 H, dm, $J = 10$ and 1 Hz), 4.73 (1 H, br s, OH), 2.56 (2 H, t, $J = 7.7$ Hz), 2.19 (2 H, qd, $J = 7.3$ and 1.7 Hz), 2.04 (2 H, qm, $J = 6.6$ and 1 Hz), 1.6–1.3 (8 H, m), 0.95 (3 H, t, $J = 7.3$ Hz); ^{13}C δ 153.57, 139.08, 137.74, 132.58, 132.22, 130.51, 127.27, 114.20, 113.77, 112.24, 35.31, 33.71, 32.49, 31.06, 28.94, 28.75, 22.55, 13.68; MS (m/z) 258 (M^+), 229, 215, 201, 187, 175, 145, 133. The assignment of the *trans* ring junction to **53** is based on the ^1H-NMR chemical shift of the benzylic methine hydrogen at 2.12 ppm as observed in the case of **34**. The structures of **54** and **55** were assigned on the basis of the ^1H-NMR chemical shifts of the aromatic hydrogens at the *meta* position. The chemical shift of the *meta* aromatic hydrogen of **54** at 7.29 ppm is essentially identical to that of 4-[(1*E*)-1,6-heptadienyl]-3-methylphenol at 7.28 ppm.

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