Intramolecular Formal [3 + 2] Cycloaddition of Alkenes and Benzylic Cations. Stereoselective Synthesis of 1,2,3,4,4a,9a-Hexahydrofluorenes

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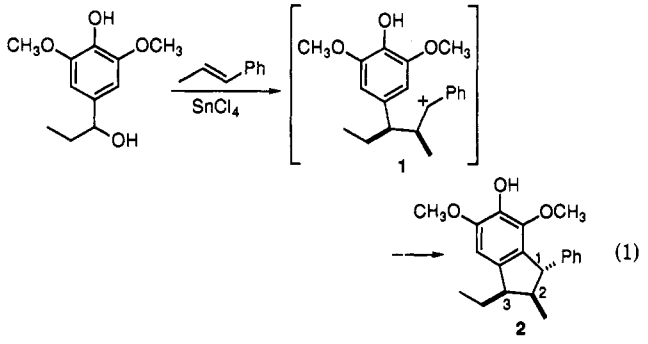
The Lewis acid-promoted intramolecular formal [3 + 2]-atom "cycloaddition" of alkenes with benzylic cations derived from benzylic alcohols and quinone methides affords products in good yield and with remarkable stereoselectivity. Benzylic alcohol **20** affords hexahydrofluorene **36** with three new stereogenic centers in 73% yield as a 10:1 mixture of diastereomers. The scope and limitations of these reactions were explored by varying the substitution pattern on the benzylic cation, the cyclization initiators, and the alkene terminators.

Introduction

Previous work in our laboratory has shown that quinone methides and benzylic cations react with alkenes in the presence of Lewis acids to afford 2,3-dihydro-1*H*-indenes **2** via a formal [3 + 2] "cycloaddition" reaction (eq 1).[1] When *E*-styrenes are used as the 2-atom component, these reactions occur in good yield and allow complete control of the relative stereochemistry at the three newly formed stereogenic centers on the 2,3-dihydro-1*H*-indene. However, *Z*-styrenes afford products with stereocontrol at only two of the three stereogenic centers, C(2) and C(3). This reaction is a formal [3 + 2]-atom "cycloaddition" that appears to involve initial nucleophilic capture of the benzylic cation to afford a new cation **1**, which undergoes intramolecular electrophilic aromatic substitution to afford the product **2**. A priori we had expected both *E*- and



(1)

Z-styrene isomers to afford an identical cationic intermediate (**1**) that should then cyclize to afford the same products in similar ratios. The origin of the difference in their reactivity was unclear; however, it appeared possible that *E*- and *Z*-styrenes might react via different transition states.

One potential way to examine the difference in behavior of the styrene isomers is to construct a substrate for an intramolecular "cycloaddition" differing only in alkene geometry. If the ring to be formed is a six-membered ring, the known preference for cyclization reactions to proceed via a chair conformation[2] should result in *E*- and *Z*-styrenes being constrained to essentially the same transition state. If the intermediate cation (analogous to **1**, eq 1) has a significant lifetime, both alkenes should afford identical product mixtures. In addition, the intramolecular nature of the reaction might allow less-reactive alkenes to be used in the formal cycloaddition as well as styrenes.

We report here the results of such a study using both quinone methides and benzylic alcohols as precursors to the benzylic cations. The scope and limitations of the reaction were explored by varying the substitution pattern on both the benzylic cation and the alkene. The chemistry developed provides a method for the stereoselective synthesis of highly functionalized hydrofluorenes.[3] This skeleton is a common subunit in many natural products.[4] In addition, substituted hydrofluorenes have been used as advanced intermediates in the synthesis of diterpenoids of the gibberellin family.[3] The high level of stereocontrol and the increased complexity available with cycloaddition type methodology make this methodology noteworthy.

Results and Discussion

Synthesis of Substrates. A major challenge in the preparation of the substrates was the stereoselective synthesis of *E*- and *Z*-styrenes. This problem was solved by employing a Still-modified Wittig reaction[5] for the synthesis of *Z*-styrenes with >10:1 *Z*/*E* selectivity. Isomerization of *Z*-styrenes then afforded *E*-styrenes with >20:1 *E*/*Z* selectivity.[6] The Wittig approach requires that the styrene be constructed from an aromatic aldehyde and an aliphatic Wittig reagent. The reverse combination, a benzylic Wittig reagent and an aliphatic aldehyde affords styrenes with ca. 7:3 *E*/*Z* selectivity.[7]

To implement this strategy, the known alcohol **3**[8] was converted to bromide **4** and treated with triphenylphos-

(1) Angle, S. R.; Arnaiz, D. O. *J. Org. Chem.* **1992**, *57*, 5937.

(2) Bartlett, P. A. "Olefin Cyclization Processes that Form Carbon–Carbon Bonds" In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, pp 341–409.

(3) (a) Nagaoka, H.; Shimano, M.; Yamada, Y. *Tetrahedron Lett.* **1989**, *30*, 971, and refs cited therein. (b) Mander, L. N.; Hook, J. M.; Urech, R. *J. Am. Chem. Soc.* **1980**, *102*, 6628. (c) Mori, K.; Shiozaki, M.; Itaya, N. *Tetrahedron Lett.* **1968**, *18*, 2183. For reviews on the synthesis of gibberellins see: (d) Mander, L. N. *Acc. Chem. Res.* **1983**, *16*, 48. (e) Fujita, E.; Node, M. *Heterocycles* **1977**, *7*, 709.

(4) (a) Hanson, J. R. *The Tetracyclic Diterpenes*; Pergamon Press: London, 1968. (b) *Gibberelins*: Crozier, A., Ed.; Praeger: New York, 1983.

(5) Sreekumar, C.; Darst, K. P.; Still, W. C. *J. Org. Chem.* **1980**, *45*, 4260.

(6) Schwarz, M.; Graminski, G. F.; Waters, R. M. *J. Org. Chem.* **1986**, *51*, 260.

(7) Frutos, R. P., unpublished results from these laboratories. To our knowledge the effect of the Still conditions[5] on the *E*/*Z*-selectivity of benzylic Wittig reagents has not been reported.

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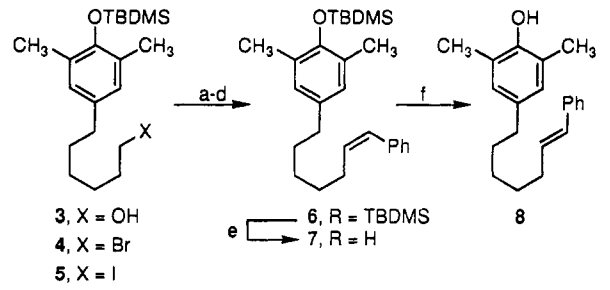
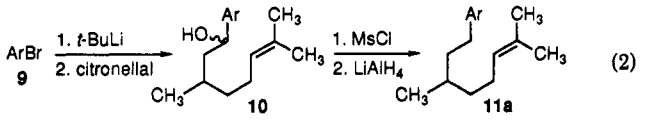
Scheme I[a]



[a] Reagents: (a) CBr_4, Ph_3P, 92%; (b) NaI, acetone, 90%; (c) Ph_3P, 96%; (d) KN(TMS)$_2$, HMPA, $(C_6H_5)CHO$, THF, 70%; (e) $(n\text{-}Bu)_4NF$, THF, 91%; (f) PhSH, AIBN, C_6H_6, reflux, 67%.

phine to afford an oily Wittig salt. Condensation of the conjugate base of this phosphonium bromide with benzaldehyde afforded poor yields of alkenes (Scheme I). However, the corresponding iodide **5** afforded a solid Wittig salt that could be crystallized. Treatment of the purified phosphonium iodide with benzaldehyde under Still-modified Wittig conditions[5] afforded *Z*-styrene **6** in 67% yield from **5** with >10:1 *Z*/*E*-selectivity (^{1}H NMR). Cleavage of the silyl ether afforded **7**. Isomerization of the *Z*-alkene to the *E*-alkene using the method of Schwarz, Graminski, and Waters[6] afforded *E*-styrene **8** in 67% yield with >20:1 *E*/*Z* ratio (^{1}H NMR).

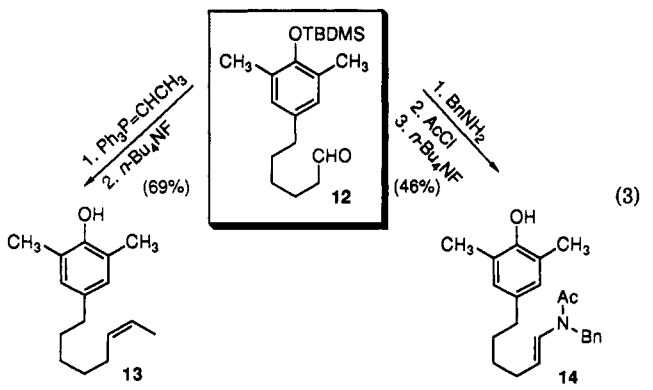
Substrates **10** were readily available as mixtures of diastereomers from (±)-citronellal and the corresponding aryllithiums (eq 2). Cleavage of the benzylic alcohol **10a**



(2)

a Ar = 3,5-dimethyl-4-hydroxyphenyl
b Ar = 4-(*t*-Butyldimethylsilyl)oxy-3-methoxyphenyl
c Ar = 4-methoxyphenyl
d Ar = 3-methoxyphenyl

afforded **11a** in an unoptimized 42% yield. *Z*-Alkene **13** and enamide[9] **14** were both prepared from the known aldehyde **12**[8] as shown in eq 3.



(3)

Benzylic alcohols **20** and **21** (see Table II for structures) were prepared from **18** and **19**, respectively, upon condensation with the appropriate aryllithium. Aldehydes **18** and **19** were prepared as shown in Scheme II. Protection of citronellol, followed by ozonolysis and reduction, afforded **15** in 66% overall yield. Conversion to iodide **16**, followed by reaction with triphenylphosphine and Wittig homologation,[5] afforded styrene **17** in 67% yield. Deprotection of the primary alcohol and oxidation under Swern conditions afforded aldehyde **18** in 80% yield. Isomerization of **18** as described above[6] afforded *E*-styrene **19**.

"Cycloaddition" Studies: Quinone Methides. We elected to first examine the intramolecular "cycloaddition" reactions in which the benzylic cation was derived from the corresponding quinone methide, which was in turn prepared by oxidation of the appropriate phenol with Ag_2O.[10,11] The $SnCl_4$-promoted cyclization of *Z*-styrene **22** at 0 °C afforded hexahydrofluorenes **23a** and **23b** as a 2.3:1 mixture (^{1}H NMR) in 81% yield (entry 1, Table I). Carrying out the reaction at −78 °C resulted in a virtually identical ratio (2.4:1, ^{1}H NMR) of **23a** and **23b** in 57% yield. Treatment of **22** with $TiCl_4$ at −78 °C afforded low yields of **23**.[12] The cyclization of *E*-styrene **24** with $SnCl_4$ afforded **23a** and **23b** as a 4.2:1 ratio in 52% yield. The $TiCl_4$-mediated cyclization of **24** at −78 °C afforded a 9:1 ratio of **23a** to **23b** (entry 5, Table I). The minor difference in product ratios between the isomeric styrenes may be due to conformational differences in the cyclization transition states.

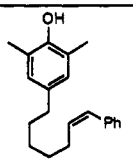
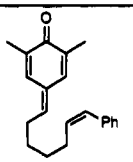
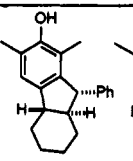
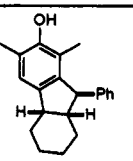
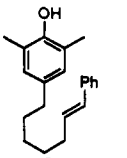
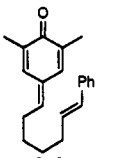
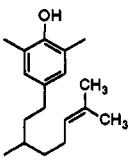
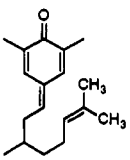
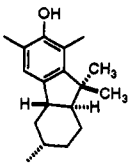
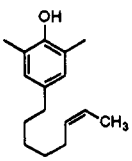
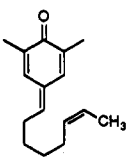
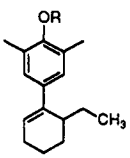
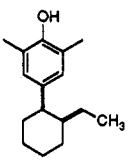
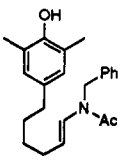
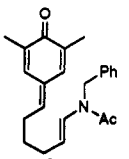
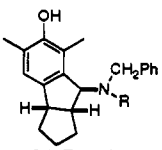
In an effort to probe the generality of the reaction with alkenes other than styrenes, di- and tri-substituted alkenes **25** and **27** were examined. Treatment of quinone methide **25** with $TiCl_4$ at −78 °C afforded **26** in 88% yield as a single diastereomer (entry 6, Table I). This formal "cycloaddition" which is a tandem cationic cyclization–electrophilic aromatic substitution occurs smoothly when a tertiary cation intermediate is formed upon reaction with the benzylic cation.

In an attempt to examine the formation of a secondary cation as an intermediate, disubstituted alkene **27** was subjected to the conditions of the formal cycloaddition. Alkene **27** failed to afford any [3 + 2] "cycloaddition" products. The first step in the reaction, capture of the benzylic cation by the pendant alkene does occur, but, the subsequent electrophilic aromatic substitution does not. The product obtained, **28a**, may be derived from elimination of the secondary cation to an alkene exocyclic to the six-membered ring, followed by acid-mediated alkene isomerization to ultimately afford the observed trisubstituted alkene. The unstable styrene phenol was characterized as the acetate **28b**. It appears that the alkene is nucleophilic enough to capture the benzylic cation, however the resulting secondary cation is not trapped by the adjacent aryl group. Employing a large excess of ethylaluminum dichloride to initiate cyclization and reduce the intermediate cation resulted in the formation of **29** in 69% yield (Table I, entry 8). The formation of **29** provides further evidence that the initial capture of the benzylic cation is an efficient process.

Entry 9 in Table I illustrates that the methodology is applicable to highly functionalized alkenes that contain a Lewis base. Treatment of enamide **14** with $SnCl_4$ or $TiCl_4$ failed to afford any cyclized products. Treatment of **14** with $BF_3{\cdot}Et_2O$ afforded **31** in 70% yield as a single diastereomer.[14] The ^{1}H NMR spectrum of **31** was complicated by the presence of two amide rotational isomers.

(8) Angle, S. R.; Rainier, J. D. *J. Org. Chem.* **1992**, *57*, 6883.
(9) For a general preparation of enamides of this type see: Martin, S. F.; Li, W. *J. Org. Chem.* **1991**, *56*, 642.
(10) Dyall, L. K.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2196.
(11) For examples of the oxidative synthesis of quinone methides from our laboratory see: (a) Angle, S. R.; Turnbull, K. D. *J. Am. Chem. Soc.* **1989**, *111*, 1136. (b) Angle, S. R.; Louie, M. L.; Mattson, H. L.; Yang, W. *Tetrahedron Lett.* **1989**, *30*, 1193.
(12) Examination of the ^{1}H NMR spectrum of the crude reaction mixture showed the presence of ca. 15% of a compound believed to be the [3 + 2] adduct and a similar amount of a compound believed to be the tertiary alkyl chloride.

Table I. "Cycloaddition" Reactions with Benzylic Cations Derived from Quinone Methides

entry	phenol	quinone methide	Lewis acid	temp, °C	product(s)	% yield[a]
1			$SnCl_4$	0	 	81 (2.3:1)
2			$SnCl_4$	-78		57 (2.4:1)
3			$TiCl_4$	-78		-
	7	**22**			**23a** **23b**	
4			$SnCl_4$	0	**23a** **23b**	52 (4.2:1)
5			$TiCl_4$	-78	**23a** **23b**	66 (9:1)
	8	**24**				
6			$TiCl_4$	-78		88
	11a	**25**			**26**	
7			$TiCl_4$	-78		49
	13	**27**			**28a**, R = H **28b**, R = Ac	
8	13	27	$EtAlCl_2$	25		69
					29	
9			BF_3·OEt_2	-78		70
	14	**30**			**31** R = Ac **32** R = Et	

[a] The unoptimized yield is followed by the diastereomer ratio determined by ^1H NMR in parentheses.

Reduction of **31** with $LiAlH_4$ afforded **32** in 52% yield. The ^1H NMR spectrum of **32** was simplified relative to **31** and allowed the assignment of the relative stereochemistry (see below).

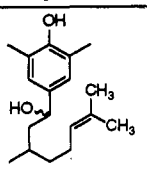
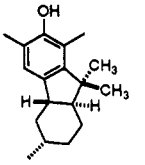
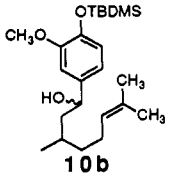
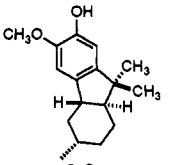
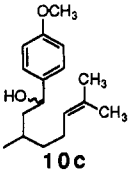
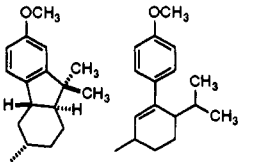
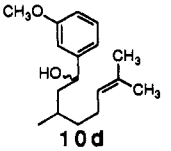
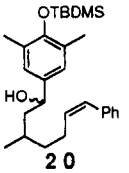
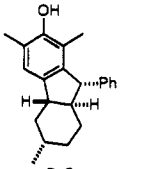
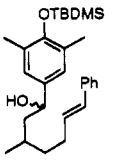
Quinone methide-initiated formal [3 + 2] "cycloadditions" afford products in high yield and with good stereoselectivity. The application of the methodology to cases where benzylic alcohols are used as the precursor to the benzylic cation was investigated next.

"Cycloaddition" Studies: Benzylic Alcohols. In order to ascertain the effect of the source of the cation (quinone methide vs benzylic alcohol) on the reaction, **10a** was treated with $TiCl_4$ at -78 °C to afford **26** in 90% yield as a single diastereomer (entry 1, Table II). This is virtually identical to the result obtained with the corresponding quinone methide (entry 6, Table I). The tolerance of the reaction to varying substitution of the aromatic ring of the cation was next studied (entries 2–4, Table II). Substrate **10b** with one *ortho*-substituent and a *p*-silyl ether afforded **33** in 64% yield, again as a single diastereomer. Substrate **10c** with a single *p*-methoxy substituent afforded the expected product **34** in 59% yield and an unexpected product **35** in 23% yield.[13] Benzylic alcohol **10c** is the first substrate examined that did not possess a *meta*-substituent to facilitate the intramolecular electrophilic aromatic substitution. Capture of the tertiary cation may be slower in this case, allowing time for elimination to an alkene that then undergoes acid-mediated isomerization to styrene **35**.[13] Benzylic alcohol

(13) It is possible that **28a** and **35** are formed by interaction of the initially formed benzylic cation with the alkene, followed by a direct [1,3]-hydrogen shift to afford a new benzylic cation that undergoes elimination to afford the observed styrene products. For a similar reaction that affords a cycloheptene see: Angle, S. R.; Mattson, H. L. *J. Am. Chem. Soc.* **1992**, *114*, 9782. The mechanism of these reactions is currently under investigation.

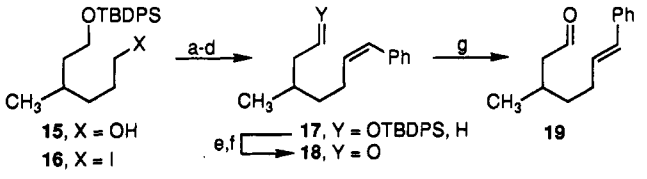
(14) (a) For a preliminary report from our laboratory on the use of enamides as cyclization terminators see: Angle, S. R.; Frutos, R. P. *J. Chem. Soc. Chem. Commun.* **1993**, 171. For examples of the capture of ene carbamates with carbon electrophiles see: (a) Comins, D. L.; Mantlo, N. B. *Tetrahedron Lett.* **1983**, *24*, 3683. (b) Shono, T.; Matsumura, Y.; Tsubata, K.; Sugihara, Y. *Tetrahedron Lett.* **1982**, *23*, 1201.

Table II. "Cycloaddition" Reactions with Benzylic Cations Derived from Benzylic Alcohols

entry	benzylic alcohol	Lewis acid	temp, °C	product(s)	% yield[a]
1	 **10a**	$TiCl_4$	−78	 **26**	90
2	 **10b**	$TiCl_4$	−78	 **33**	64[b]
3	 **10c**	$TiCl_4$	0	 **34** **35**	52/**34** 23/**35**
4	 **10d**	$TiCl_4$	0	–	–
5	 **20**	$TiCl_4$	0	 **36**	93 (2.6:1)[b]
6		$TiCl_4$	−78		73 (10:1)[b]
7	 **21**	$TiCl_4$	−78	**36**	67 (10:1)[b]

[a] The unoptimized yield is followed by the diastereomer ratio determined by ^1H NMR in parentheses. [b] The crude product was treated with $(n\text{-Bu})_4NF$ prior to chromatography.

Scheme II[a]



[a] Reagents: (a) MsCl, Et_3N, Et_2O; (b) NaI, acetone, 85% (two steps); (c) Ph_3P, 89%; (d) $KN(TMS)_2$, HMPA, PhCHO, THF, 84%; (e) TBAF, THF, 89%; (f) $Cl(CO)_2Cl$, DMSO, Et_3N, CH_2Cl_2, 90%; (g) AIBN, PhSH, C_6H_6, reflux, 76%.

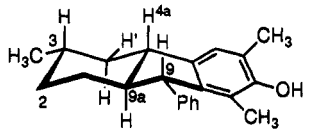
10d possesses a *m*-methoxy group to aid the electrophilic aromatic substitution, but lacks a *para*-substituent to stabilize the initial benzylic cation. It was surprising to find that treatment of **10d** with $TiCl_4$ or $SnCl_4$ at −78 °C, 0 °C, or 25 °C afforded only intractable product mixtures. The disappearance of starting material is likely linked to formation of a cation.[15] Yet neither cyclization nor "cycloaddition" products were observed. These examples show that benzylic cations with both *meta*- and *para*-electron-donating substituents are optimum for good yields of "cycloaddition" products.

Entries 5–7 in Table II examine the formation of three new stereogenic centers relative to an existing stereogenic center. The substrates differ only in the geometry of the alkene. It was hoped that the methyl group on the tether would decrease the available degrees of freedom by providing a preference for a chair transition state with this group in a pseudoequatorial position, thus minimizing the differences between the *E*- and *Z*-styrenes. Treatment of **20** with $SnCl_4$ at −78 °C afforded **36** as a 10:1 mixture of diastereomers (^1H NMR). Conducting the reaction at 0 °C afforded a 2.6:1 ratio of diastereomers (^1H NMR). The stereochemistry of the minor diastereomer was not determined; a pure sample of this less-polar diastereomer could not be obtained. *E*-Styrene **21** was treated with $TiCl_4$ at −78 °C to afford **36** as a 10:1 mixture of the same two diastereomers obtained with **20**. Constrained to similar transition states at low temperature, both styrene isomers afford the same products in identical ratios.

Assignment of Relative Stereochemistry for the Cycloadducts. The relative stereochemistry of the

(15) The substrate with all hydrogens on the aryl ring of the cation also afforded intractable product mixtures; Frutos, R. P., unpublished results from these laboratories.

"cycloaddition" products was assigned on the basis of ^{1}H NMR spectral data and difference NOE experiments. The spectra of the hydrofluorenes were similar, and self-consistent for compounds with *trans*-ring junctions and *cis*-ring junctions. The trans relative stereochemistry of C(9a)-hydrogen to C(9)-hydrogen and C(9a)-hydrogen to C(4a)-hydrogen in **36** was evident from the magnitude of the coupling constants: J[H(9a)–H(9)] = 10.5 Hz, J[H(9a)–H(4a)] = 11.3 Hz (see conformational drawing below for numbering system). The *cis*-orientation of C(4a)-hydrogen and C(9)-hydrogen was confirmed by a difference NOE experiment. Irradiation of the signal for C(9)-hydrogen at δ 3.97 caused a 2.1% enhancement of the



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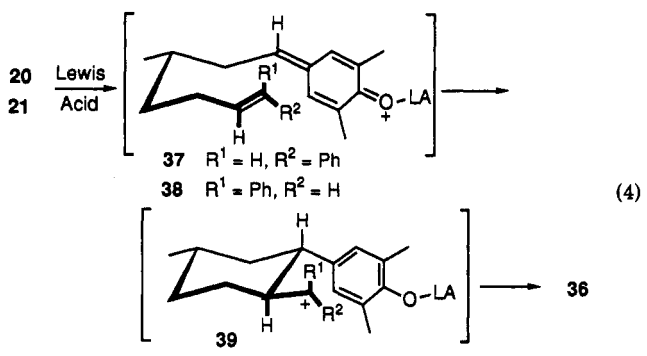
signal for C(4a)-hydrogen at δ 3.21. This places the phenyl in a pseudoequatorial orientation. The equatorial orientation of the C(3)-methyl group was evident from the axial orientation of the C(3)-hydrogen. The signal for the C(4)-axial hydrogen appeared at δ 1.05 as a ddd (all J = 11.5 Hz), consistent with an axial hydrogen with coupling to two adjacent axial hydrogens [C(3)-hydrogen and C(4)-hydrogen] and a geminal hydrogen. In compounds with a *trans*-ring junction (Tables I and II), J[H(9a)–H(4a)] ranged from 10.5 to 11.7 Hz.

The *cis*-ring junction of **23b** was clearly evident from the C(4a)-hydrogen and C(9a)-hydrogen coupling constant of 5.4 Hz. The *cis*-orientation of the phenyl to the C(4a)-hydrogen was deduced by a NOE experiment. Irradiation of the signal for the C(4a)-hydrogen at δ 3.21 caused no enhancement of the signal for the C(9)-hydrogen, but did cause a 1.7% enhancement of the signal for the *o*-hydrogens on the phenyl ring.

Comparison of the Intramolecular and Intermolecular "Cycloaddition" Reactions. The results with styrenes **20** and **21** (entries 6 and 7, Table II) show that if constrained to the same transition state both *E*- and *Z*-styrenes afford virtually identical mixtures of products. This is probably due to the fact that both reactions are preceeding through similar transition states (**37** and **38**) and a common cationic intermediate (**39**) which collapses to **36**, placing the phenyl substituent in the α-orientation to minimize steric interactions (eq 4). It seems likely that



the intermolecular reactions of *E*- and *Z*-styrenes (eq 1) previously examined proceed through different transition states.

Conclusion

The intramolecular reaction of benzylic cations with alkenes was found to be a general reaction that is compatible with a range of alkene components. The choice of precursor to the cation, benzylic alcohol or quinone methide, is governed by the ease of substrate preparation, since both afford good yields of "cycloadducts". The reaction requires the cation to have an electron-donating group on the ring for stabilization. The major requirement of the alkene terminator is that it possesses a stabilizing group to allow sufficient lifetime for the cation to undergo intramolecular electrophilic aromatic substitution. A tertiary cation, benzylic cation, and acyliminiun ion all allowed trapping of the intermediate cation. A secondary cation failed to undergo the electrophilic aromatic substitution. The exploitation of this methodology in the synthesis of functionalized hydrofluorenes is currently under investigation.

Experimental Section[16a]

General Information: NMR spectra were recorded on a General Electric QE-300 or GN-500 NMR. Shifts reported are relative to internal tetramethylsilane; coupling constants (J) are reported in hertz, refer to apparent peak multiplicities, and may not necessarily be true coupling constants. Abbreviations used are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentuplet, br = broad. Mass spectra are reported as % relative intensity to the parent peak. HPLC was carried out with an RI detector using a 25-cm column (4.6 mm or 1.0 cm i.d.) packed with 8 μm silica gel. Melting points were determined using a capillary melting point apparatus and are uncorrected. The molarities indicated for alkyllithiums were established by titration with 2,5-dimethoxybenzyl alcohol.[16b] In cases where products were isolated by "aqueous workup (solvent, drying agent)" the procedure was to dilute the reaction mixture with water, extract the aqueous layer several times with the indicated organic solvent, wash the combined organic layers with brine, dry over the indicated drying agent, and concentrate the reaction mixture. "Concentration" in the experimental procedures refers to isolation of product(s) from a solvent/product mixture by removal of the solvent under reduced pressure (water aspirator) with a Rotavapor. Unless stated otherwise, all reactions were run under an atmosphere of nitrogen or argon in oven-dried glassware.

1-[(*tert*-Butyldimethylsilyl)oxy]-4-(6-bromohexyl)-2,6-dimethylbenzene (4). Triphenylphosphine (1.36 g, 5.19 mmol) was added a stirred solution of alcohol **3**[8] (896 mg, 2.66 mmol) and CBr_4 (1.75 g, 5.29 mmol) in ether (40 mL) at room temperature. The resulting mixture was stirred for 2.5 h and then water (60 mL) was added. After stirring for 10 min, the solution was filtered to remove triphenylphosphine oxide. Aqueous workup (ethyl acetate, $MgSO_4$) and flash chromatography (hexane) afforded 1.03 g of 4 contaminated with CBr_4. The CBr_4 was removed by heating the resulting oil under high vacuum to afford 982 mg (92%) of 4 as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (s, 2H, ArH), 3.42 (t, J = 6.8 Hz, 2H, CH_2Br), 2.50 (t, J = 7.7 Hz, 2H, $ArCH_2$), 2.21 (s, 6H, $Ar(CH_3)_2$), 1.89 (p, J = 7.2 Hz, 2H, CH_2), 1.62 (m, 2H), 1.49 (m, 2H), 1.38 (m, 2H), 1.06 (s, 9H, $C(CH_3)_3$), 0.21 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 134.9, 128.6, 128.0, 34.9, 33.8, 32.7, 31.3, 28.4, 28.0, 26.2, 18.7, 17.8, –2.9; IR (CCl_4) 2932, 1483, 1255, 1230 cm^{-1}; MS (EI, 50 eV) m/z 400 (M^+, 34), 398 (M^+, 36), 273 (100), 271 (97), 73 (42); HRMS calcd for $C_{20}H_{35}BrOSi$ 398.1641, found 398.1640.

1-[(*tert*-Butyldimethylsilyl)oxy]-4-(6-iodohexyl)-2,6-dimethylbenzene (5). NaI (473 mg, 3.15 mmol) was added to a solution of 4 (400 mg, 1.00 mmol) and acetone (3.2 mL) at room temperature. The resulting solution was refluxed for 3 h, allowed to cool to room temperature, filtered through Celite, and concentrated to afford a yellow oil. Aqueous workup (ethyl

(16) (a) Some general experimental details have recently been reported: see ref 8. (b) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. J. *J. Chem. Soc. Chem. Commun.* **1980**, 87.

acetate, Na_2SO_4) afforded 404 mg (90%) of **5** as a clear oil: ^1H NMR (300 MHz, $CDCl_3$) δ 6.76 (s, 2H, ArH), 3.18 (t, J = 7.1 Hz, 2H, CH_2I), 2.47 (t, J = 7.7 Hz, 2H, $ArCH_2$), 2.18 (s, 6H, $Ar(CH_3)_2$), 1.83 (p, J = 7.2 Hz, 2H, CH_2), 1.58 (m, 2H), 1.45–1.31 (m, 4H), 1.03 (s, 9H, $C(CH_3)_3$), 0.18 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 135.0, 128.6, 128.1, 34.9, 33.5, 31.3, 30.3, 28.2, 26.1, 18.7, 17.8, 7.0, –2.9; IR ($CDCl_3$) 2932, 1484, 1473, 1255, 1232 cm^{-1}; MS (EI, 50 eV) m/z 446 (M^+, 42), 319 (100), 73 (46); HRMS calcd for $C_{20}H_{35}OSiI$ 446.1502, found 446.1521.

(*Z*)-7-[4-[(*tert*-Butyldimethylsilyl)oxy]-3,5-dimethylphenyl]-1-phenyl-1-heptene (6). Triphenylphosphine (262 mg, 1.25 mmol) was added to iodide **4** (387 mg, 0.866 mmol) and the mixture was heated neat for 20 h at 70 °C.[17] The resulting amorphous solid was allowed to cool to room temperature, dissolved in a minimum amount of $CHCl_3$, and crystallized by addition of hot ether to afford 591 mg (96%) of {6-[4-[(*tert*-butyldimethylsilyl)oxy]-3,5-dimethylphenyl]hexyl}-triphenylphosphonium iodide as a white solid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.85–7.65 (m, 15H, $(C_6H_5)_3P$), 6.67 (s, 2H, ArH), 3.58 (m, 2H, CH_2P), 2.37 (t, J = 7.7 Hz, 2H, $ArCH_2$), 2.12 (s, 6H, $Ar(CH_3)_2$), 1.71–1.54 (m, 4H), 1.47 (m, 2H), 1.27 (m, 2H), 0.98 (s, 9H, $C(CH_3)_3$), 0.13 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 135.0 (d, J = 9.8 Hz), 134.8, 133.5 (d, J = 9.8 Hz), 130.5 (d, J = 12.3 Hz), 128.5, 127.9, 118.0 (d, J = 85.4 Hz), 34.7, 30.9, 30.2 (d, J = 15.1 Hz), 28.7, 26.0, 23.1 (d, J = 49.7 Hz), 22.6 (d, J = 4.4 Hz), 18.6, 17.7, –3.1; IR ($CDCl_3$) 2933, 1440, 1232, 1113 cm^{-1}. Using the general procedure of Sreekumar, Darst, and Still,[5] hexamethyldisilazane (280 μL, 1.33 mmol) was added to a stirred suspension of potassium hydride (52.7 mg, 1.31 mmol) and THF (1.3 mL) at room temperature. After stirring for 1 h this mixture was added *via* cannula to a stirred solution of the above Wittig salt (625 mg, 0.882 mmol) and HMPA (280 μL, 1.61 mmol) in THF (4.0 mL). The resulting orange solution was stirred for 20 min at room temperature and then cooled to –78 °C for 10 min. Benzaldehyde (300 μL, 2.95 mmol) was then added dropwise, and the resulting solution was allowed to warm to room temperature over 1 h and stirred for an additional 1 h. Aqueous workup, (ethyl acetate, $MgSO_4$) afforded 937 mg of crude product as a brown oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 253 mg (70%) of **6** as a clear oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (m, 5H, C_6H_5), 6.94 (s, 2H, ArH), 6.59 (d, J = 11.4 Hz, 1H, CH=C*H*Ar), 5.86 (dt, J = 11.4 Hz, 7.5 Hz, 1H, CH_2CH=CH), 2.65 (t, 2H, J = 7.7 Hz, $ArCH_2$), 2.52 (dq, J = 1.4, 7.5 Hz, 2H, CH_2CH_2CH), 2.38 (s, 6H, $Ar(CH_3)_2$), 1.76 (m, 2H), 1.67 (m, 2H), 1.56 (m, 2H), 1.24 (s, 9H, $C(CH_3)_3$), 0.38 (s, 6H, $Si(CH_3)_2$; ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 137.8, 135.2, 133.0, 128.8, 128.7, 128.6, 128.0, 128.0, 126.4, 35.0, 31.5, 29.8, 29.0, 28.5, 26.1, 18.7, 17.8, –3.0; IR ($CDCl_3$) 2931, 1484, 1473, 1255, 1232 cm^{-1}; MS (EI, 50 eV) m/z 408 (M^+, 100), 351 (35), 117 (48); HRMS calcd for $C_{27}H_{40}OSi$ 408.2848, found 408.2862.

(*Z*)-7-(3,5-Dimethyl-4-hydroxyphenyl)-1-phenyl-1-heptene (7). *n*-Bu_4NF (300 μL of a 1 M solution in THF, 0.30 mmol) was added dropwise to a stirred solution of **6** (253 mg, 0.620 mmol) and THF (4.0 mL) at room temperature. The resulting solution was stirred at room temperature for 8 h. Aqueous workup (ethyl acetate, Na_2SO_4), afforded 267 mg of crude product as a brown oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 165 mg (91%) of **7** as a clear oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.36–7.22 (m, 5H, C_6H_5), 6.77 (s, 2H, ArH), 6.41 (d, J = 11.7 Hz, 1H, CH=C*H*Ar), 5.66 (dt, J = 11.7, 7.2 Hz, 1H, CH_2CH=CH), 4.46 (s, 1H, OH), 2.46 (t, J = 7.7 Hz, 2H, $ArCH_2$), 2.34 (dq, J = 1.4, 7.5 Hz, 2H, CH_2CH), 2.22 (s, 6H, $Ar(CH_3)_2$), 1.80–1.30 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 137.8, 134.3, 133.1, 128.7, 128.7, 128.4, 128.1, 126.4, 122.7, 35.0, 31.7, 29.8, 29.0, 28.5, 15.8; IR ($CDCl_3$) 3611, 2931, 1489, 1198 cm^{-1}; MS (EI, 50 eV) m/z 294 (M^+, 26), 161 (60), 135 (100), 91 (33); HRMS calcd for $C_{21}H_{26}O$ 294.1984, found 294.1992.

(*E*)-7-(3,5-Dimethyl-4-hydroxyphenyl)-1-phenyl-1-heptene (8). According to the general procedure of Schwarz et al.,[6] AIBN (22.6 mg, 0.138 mmol) was added in three equal portions over a period of 5 h to a refluxing solution of **7** (30.9 mg, 0.105 mmol) and thiophenol (5.5 μL, 0.0536 mmol) in benzene (2 mL). The mixture was allowed to cool to room temperature and concentrated to afford 48.6 mg of a brown oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 20.8 mg (67%) of **8** as a clear oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.41–7.18 (m, 5H, C_6H_5), 6.82 (s, 2H, ArH), 6.41 (d, J = 15.9 Hz, 1H, CH=C*H*Ph), 6.47 (dt, J = 15.9, 6.6 Hz, 1H, CH_2CH=CH), 4.51 (s, 1H, OH), 2.52 (t, J = 7.5 Hz, 2H, CH_2Ar), 2.31–2.14 (m, 2H), 2.25 (s, 6H, $Ar(CH_3)_2$), 1.69–1.46 (m, 6H); ^{13}C (75 MHz, $CDCl_3$) δ 150.0, 137.9, 134.4, 131.0, 129.7, 128.4, 126.7, 125.9, 122.7, 35.0, 32.9, 31.7, 29.2, 28.8, 15.8; IR ($CDCl_3$) 3611, 1489, 1198, 1150 cm^{-1}; MS (EI, 50 eV) m/z 294 (M^+, 73), 161 (77), 135 (100); HRMS calcd for $C_{21}H_{26}O$ 294.1984, found 294.1975.

(±)-1-(3,5-Dimethyl-4-hydroxyphenyl)-3,7-dimethyl-6-octen-1-ol (10a). *n*-BuLi (9.70 mL of a 1.96 M solution in hexanes, 19.0 mmol) was added dropwise to a stirred solution of 4-bromo-2,6-dimethylphenol (3.82 g, 19.0 mmol) and THF (102 mL) at –78 °C. The resulting solution was stirred for 40 min and then *t*-BuLi (22.0 mL of a 1.27 M solution in pentane, 27.9 mmol) was added dropwise. The mixture was stirred vigorously for 2 h and then citronellal (4.40 mL, 30.0 mmol) was added dropwise. The resulting solution was allowed to warm to room temperature, stirred for 40 min, and then poured into saturated aqueous $NaHCO_3$ solution (500 mL). Aqueous workup (ethyl acetate, $MgSO_4$) afforded 7.40 g of crude product as a yellow oil. Crystallization (ether/hexane) afforded 1.97 g (38%) of **10a** (mp 80–81 °C) as a 1:1 mixture of diastereomers: mp 80–81 °C; ^1H NMR (300 MHz, $CDCl_3$; mixture of diastereomers) δ 6.96 (s, 1H, ArH), 6.95 (s, 1H ArH), 5.14–5.04 (m, 1H, CH=C), 4.60–4.50 (m, 1H, C*H*OH), 4.58 (s, 1H, OH), 2.25 (s, 6H, $Ar(CH_3)_2$), 2.05–1.91 (m, 2H), 1.86–1.75 (m, 1H, CH_3CH), 1.70–1.54 (m, 6H, C=C-$(CH_3)_2$), 1.50–1.30 (m, 2H), 1.08–1.28 (m, 2H), 0.97–0.92 (m, 3H, $CHCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 151.5, 136.9, 136.3, 131.1, 126.3, 126.0, 124.8, 123.1, 72.6, 72.1, 46.5, 45.9, 37.5, 36.9, 29.3, 29.2, 25.6, 25.3, 25.2, 20.0, 19.2, 17.6, 16.0; IR (CCl_4) 3619, 2927, 1488, 1196 cm^{-1}; MS (EI, 70 eV) m/z 276 (M^+, 19), 191 (69), 151 (100) 123 (44); Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.00; H, 10.24.

(±)-1-{4-[(*tert*-Butyldimethylsilyl)oxy]-3-methoxyphenyl}-3,7-dimethyl-6-octen-1-ol (10b). *t*-BuLi (4.20 mL of a 1.5 M solution in pentane, 1.88 mmol) was added dropwise to a stirred solution of 4-bromo-2-methoxy-1-[(*tert*-butyldimethylsilyl)oxy]-benzene[18] (1.01 g, 3.35 mmol) and ether (25 mL) at –78 °C. The resulting solution was stirred for 1 h and then citronellal (730 μL, 4.03 mmol) was added dropwise. The resulting solution was allowed to warm to room temperature over a period of 7 h and then poured into a rapidly stirred solution of saturated aqueous $NaHCO_3$ (100 mL). Aqueous workup (ethyl acetate, $MgSO_4$) afforded 1.40 g of crude product as a yellow oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 1.04 g (80%) of **10b** as a 1:1 mixture of diastereomers (clear oil): ^1H NMR (300 MHz, $CDCl_3$, mixture of diastereomers) δ 6.88–6.74 (m, 3H), 5.14–5.02 (m, 1H, CH=C), 4.79–4.65 (m, 1H, C*H*OH), 3.81 (s, 3H, OCH_3), 2.05–1.75 (m, 3H), 1.68–1.66 (m, 3H, C=CCH_3), 1.60–1.58 (m, 3H, C=CCH_3), 1.51–1.09 (m, 4H), 0.99 (s, 9H, $C(CH_3)_3$), 0.94 (d, J = 6.3 Hz, 3H, $CHCH_3$), 0.15 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) (mixture of diastereomers) δ 150.9, 150.9, 144.3, 139.0, 138.5, 131.1, 124.7, 120.5, 118.4, 118.1, 109.7, 109.6, 72.7, 72.2, 55.4, 46.6, 46.2, 37.6, 36.8, 29.3, 29.2, 25.7, 25.4, 25.3, 20.1, 19.2, 18.4, 17.6, –4.7; IR (CCl_4) 3616, 2930, 1515, 1464, 1282 cm^{-1}; MS (FAB, CH_2Cl_2/NBA) m/z 392 (M^+, 23), 375 (76), 335 (100), 251 (56); HRMS calcd for $C_{23}H_{40}O_3Si$ 392.2747, found 392.2755.

(±)-1-(4-Methoxyphenyl)-2,6-dimethyl-6-octen-1-ol (10c). The same procedure used for the preparation of **10b** was carried out with 4-bromoanisole (0.420 mL, 3.36 mmol) to afford 927 mg of crude product as a yellow oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 437 mg (50%) of **10c** as a clear oil (1:1 mixture of diastereomers by HPLC). The diastereomers were separated by HPLC (4.6 mm i.d. column, 9:1 hexane/ethyl acetate, 0.8 mL min^{-1}) to afford analytical samples of each diastereomer. Slower eluting diastereomer (t_R = 21.2 min, clear oil): ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.7 Hz, 2H, ArH), 6.87 (d, J = 8.7 Hz, 2H, ArH), 5.05 (t, J = 7.2 Hz, 1H, CH=C), 4.69 (t, J = 7.2 Hz, 1H, C*H*OH), 3.80 (s, 3H, OCH_3), 2.05–1.83 (m, 3H), 1.77–1.63 (m, 1H), 1.66 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 1.41 (m, 2H), 1.16 (m, 1H), 0.93 (d, J = 6.3 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 137.1, 131.1, 127.2, 124.7, 113.8, 72.4, 55.2, 46.1, 36.9, 29.3, 25.6, 25.2, 20.0, 17.6; IR ($CDCl_3$) 3606,

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2930, 1513, 1248 cm^{-1}; MS (EI, 50 eV) m/z 262 (M$^+$, 10), 244 (50), 161 (100), 137 (79), 121 (67); HRMS calcd for $C_{17}H_{26}O_2$ 262.1933, found 262.1928. Faster eluting diastereomer (t_R = 18.3 min, clear oil): ^{1}H NMR ($CDCl_3$) δ 7.27 (d, J = 8.4 Hz, 2H, ArH), 6.88 (d, J = 8.7 Hz, 2H, ArH), 5.10 (t, J = 7.2 Hz, 1H, CH=C), 4.72 (dd, J = 9.0, 4.5 Hz, 1H, CHOH), 3.80 (s, 3H, OCH_3), 2.10–1.91 (m, 2H), 1.81 (m, 1H), 1.74–1.52 (m, 1H), 1.68 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.47–1.31 (m, 2H), 1.21 (m, 1H), 0.94 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 137.6, 131.2, 127.0, 124.8, 113.8, 72.0, 55.3, 46.6, 37.5, 29.2, 25.7, 25.4, 19.3, 17.6; IR ($CDCl_3$) 3608, 2930, 1513, 1248 cm^{-1}; MS (EI, 50 eV) m/z 262 (M$^+$, 4), 244 (55), 161 (100), 137 (36), 121 (70); HRMS calcd for $C_{17}H_{26}O_2$ 262.1933, found 262.1924.

(±)-3,7-Dimethyl-1-(3-methoxyphenyl)-6-octen-1-ol (10d). The same procedure used for the preparation of **10b** was carried out with 3-bromoanisole (600 μL, 4.7 mmol) to afford 1.55 g of crude **10d** as a yellow oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 740 mg (60%) of **10d** as a clear oil, 1:1 mixture of diastereomers: ^{1}H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers) δ 7.29–7.23 (m, 1H), 6.92 (m, 2H), 6.81 (m, 1H), 5.09 (m, 1H, CH=C), 4.75 (m, 1H, CHOH), 3.82 (s, 3H, OCH_3), 2.09–1.89 (m, 2H), 1.81 (m, 1H), 1.72–1.64 (m, 4H), 1.60–1.58 (m, 3H), 1.55–1.31 (m, 2H), 1.25–1.09 (m, 1H), 0.98–0.94 (m, 3H, $CHCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 147.3, 146.7, 131.1, 129.4, 124.7, 118.3, 118.0, 112.8, 112.7, 111.4, 111.2, 72.7, 72.2, 55.1, 46.7, 46.3, 37.5, 36.7, 29.2, 29.1, 25.6, 25.6, 25.3, 25.2, 20.0, 19.1, 17.6; IR ($CDCl_3$) 3605, 2929, 1456, 1262, 1049 cm^{-1}; MS (EI, 50 eV) m/z 262 (M$^+$, 40), 177 (100), 122 (56), 109 (95); HRMS calcd for $C_{17}H_{26}O_2$ 262.1933 found 262.1925.

(±)-2,6-Dimethyl-8-(3,5-dimethyl-4-hydroxyphenyl)-2-octene (11a). Methanesulfonyl chloride (50.0 μL, 0.65 mmol) was added dropwise to a stirred solution of **10a** (156 mg, 0.565 mmol), triethylamine (90.6 μL, 0.650 mmol), and ether (3.6 mL) at −5 °C. The resulting solution was stirred for 20 min and then $LiAlH_4$ (108 mg, 2.72 mmol) was slowly added. The resulting suspension was allowed to warm to room temperature and stirred for 40 min. The reaction mixture was then cooled to 0 °C, and H_2O (0.10 mL), 15% NaOH (0.10 mL) and H_2O (0.30 mL) were added sequentially. The resulting suspension was allowed to warm to room temperature, stirred for 1 h, filtered, dried ($MgSO_4$), and concentrated to afford 160 mg of crude product as a yellow oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 61.3 mg (42%) of **11a** as a white solid: mp 33–34 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (s, 2H, ArH), 5.11 (br, t, J = 7.2 Hz, 1H, CH_2CH=C), 4.44 (s, 1H, OH), 2.58–2.33 (m, 2H, $ArCH_2CH$), 2.22 (s, 6H, $Ar(CH_3)_2$), 2.05–1.91 (m, 2H), 1.69 (s, 3H, CH_3), 1.68–1.62 (m, 1H), 1.61 (s, 3H, CH_3), 1.50–1.30 (m, 3H), 1.29–1.11 (m, 1H), 0.93 (d, J = 6 Hz, 3H, $CHCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 134.8, 131.0, 128.4, 125.0, 122.7, 39.4, 37.0, 32.6, 32.2, 25.7, 25.5, 19.6, 17.6, 15.9; IR (CCl_4) 3622, 2916, 1488, 1196 cm^{-1}; MS (EI, 50 eV) m/z 260 (M$^+$, 28), 175 (65), 135 (100); HRMS calcd for $C_{18}H_{28}O$ 260.2140, found 260.2138.

(Z)-8-(3,5-Dimethyl-4-hydroxyphenyl)-2-octene (13). The Still-modified Wittig[5] procedure used to prepare **6** was carried out with ethyltriphenylphosphonium bromide (2.53 g, 6.82 mmol) and the known aldehyde **12**[8] (442 mg, 1.32 mmol). Flash chromatography (15:1 hexane/ethyl acetate) afforded 350 mg (76%) of (*Z*)-8-{[(4-*tert*-butyldimethylsilyl)oxy]-3,5-dimethylphenyl}-2-octene as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (s, 2H, ArH), 5.44 (m, 2H), 2.49 (t, J = 8.1 Hz, 2H, $ArCH_2$), 2.21 (s, 6H, $Ar(CH_3)_2$), 2.06 (dt, J = 6.6, 5.7 Hz, 2H, $CHCH_2CH_2$), 1.62 (d, J = 5.4 Hz, 3H, $CHCH_3$), 1.58 (m, 2H), 1.39 (m, 4H), 1.06 (s, 9H, $C(CH_3)_3$), 0.20 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 135.3, 130.8, 128.6, 128.0, 123.6, 35.1, 31.6, 29.5, 29.1, 26.8, 26.1, 18.7, 17.8, 12.7, −3.0. *n*-Bu_4NF (500 μL, of a 1 M solution in THF, 0.500 mmol) was added dropwise to a solution of the above silyl ether (350 mg, 1.01 mmol) and THF (5.0 mL) at room temperature. After 10 h, aqueous workup (ether, $MgSO_4$) afforded 321 mg of crude product as a clear oil. Flash chromatography (20:1 hexane/ethyl acetate) afforded 214 mg (91%) of **13** as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (s, 2H, ArH), 5.60–5.40 (m, 2H, CH=CHCH$_3$), 4.39 (bs, 1H, OH), 2.55 (t, J = 7.7 Hz, 2H, $ArCH_2$), 2.29 (s, 6H, $Ar(CH_3)_2$), 2.12 (m, 2H), 1.76–1.58 (m, 5H), 1.54–1.34 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 134.5, 130.7, 128.4, 123.6, 122.7, 35.0, 31.8, 29.4, 29.0, 26.7, 15.9, 12.7; IR ($CDCl_3$) 3611, 2931, 1489, 1198 cm^{-1}; MS (EI, 70 eV) 232 (M$^+$, 27), 161 (33), 135 (100); HRMS calcd for $C_{16}H_{24}O$ 232.1827, found 232.1825.

***N*-Acetyl-*N*-(phenylmethyl)-6-(3,5-dimethyl-4-hydroxyphenyl)hex-1-enamine (14).** Benzylamine (0.110 mL, 1.01 mmol) was added to a suspension of aldehyde **12**[8] (272 mg, 0.815 mmol), $MgSO_4$ (117 mg, 0.972 mmol), and CH_2Cl_2 (2.0 mL) at room temperature. The resulting suspension was stirred for 3 h, filtered, and concentrated. The resulting imine was dissolved in benzene (2.0 mL) and cooled to 0 °C. Pyridine (250 μL, 3.09 mmol), acetyl chloride (75.0 μL, 1.05 mmol), and DMAP (ca. 2 mg) were added sequentially. The resulting solution was stirred for 5 min and then allowed to warm to room temperature and stirred overnight. Aqueous workup (ether, $MgSO_4$) afforded crude enamide. The crude product was dissolved in THF (2.0 mL) and treated with *n*-Bu_4NF (0.15 mL, of a 1.0 M solution in THF, 0.15 mmol). The resulting solution was stirred at room temperature for 1 h. Aqueous workup (ether, $MgSO_4$) afforded 171.1 mg of crude product as an amber oil. Flash chromatography afforded 129.8 mg (46% overall) of 14 as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$, 7:3 mixture of amide rotational isomers) δ 7.40–7.14 (m, 5.3 H), 6.74 (s, 2H, ArH), 6.52 (d, J = 14.1 Hz, 0.7 H, NCHCH), 5.00 (dt, J = 14.1, 7.2 Hz, 1.4 H, $NCHCHCH_2$), 4.91 (dt, J = 14.1, 7.2 Hz, 0.6 H, $NCHCHCH_2$), 4.86 (s, 1.4 H, $PhCH_2N$), 4.82 (s, 0.7 H, OH), 4.78 (s, 0.3 H, OH), 4.75 (s, 0.6 H, $PhCH_2N$) 2.43 (t, J = 7.5 Hz, 2H, $ArCH_2CH_2$), 2.29 (s, 2.1 H, $NC(O)CH_3$), 2.23 (s, 6H, $Ar(CH_3)_2$), 2.15 (s, 0.9 H, $NC(O)CH_3$), 2.03 (m, 2H), 1.48 (m, 2H), 1.34 (m, 2H); IR (CCl_4) 3622, 3437, 2930, 1678, 1650, 1401, 1196 cm^{-1}; MS (CI, NH_3), m/z 352 (MH$^+$, 100), 202 (38); HRMS calcd for $C_{23}H_{30}O_2N$ (M + H) 352.2277, found 352.2264.

(±)-1-[(*tert*-Butyldiphenylsilyl)oxy]-6-hydroxy-3-methylhexane (15). *t*-Butyldiphenylchlorosilane (7.80 mL, 30.5 mmol) was added to a solution of citronellol (5.00 mL, 27.4 mmol), imidazole (2.16 g, 31.7 mmol), and DMAP (41.3 mg, 0.337 mmol) in CH_2Cl_2 (50 mL) at room temperature. The resulting solution was stirred for 5 h. Aqueous workup (CH_2Cl_2, Na_2SO_4) afforded 10.2 g (94%) of crude product as a clear oil. A portion of the resulting oil (2.50 g, 6.33 mmol) was dissolved in CH_2Cl_2/methanol (20 mL, 1:1 v/v). Ozone was bubbled through the solution for 12 min at −78 °C (solution turns blue). The ozone flow was stopped and nitrogen was bubbled through until the blue color disappeared. Methyl sulfide (10.0 mL, 136 mmol) was added and the reaction mixture was allowed to warm to room temperature and stirred for 8 h. The reaction mixture was then concentrated to ca. one-fourth of its original volume in vacuo. Aqueous workup (ethyl acetate, Na_2SO_4) afforded crude aldehyde as a yellow oil. The resulting oil was dissolved in ether (50 mL) and cooled to 0 °C. $LiAlH_4$ (267 mg, 7.04 mmol) was slowly added to the solution. The resulting solution was allowed to warm to room temperature for 8 h, cooled back to 0 °C, and treated sequentially with H_2O (0.30 mL), 15% NaOH (0.30 mL), and H_2O (0.90 mL). The resulting suspension was filtered, dried (Na_2SO_4), and concentrated to afford 778 mg of crude product as a brown oil. Flash chromatography (4:1 hexane/ethyl acetate) afforded 632 mg (70%) of alcohol **15** as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72–7.63 (m, 4H), 7.48–7.33 (m, 6H), 3.70 (m, 2H, CH_2OSi), 3.60 (t, J = 6.6 Hz, 2H, CH_2OH), 1.69–1.47 (m, 4H), 1.46–1.10 (m, 4H), 1.05 (s, 9H), 0.86 (d, J = 6.3 Hz, 3H, $CHCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5, 134.0, 129.4, 127.5, 63.1, 62.0, 39.4, 32.9, 30.1, 29.2, 26.8, 19.6, 19.1; IR (CCl_4) 3639, 2932, 1428, 1112, 1091 cm^{-1}; MS (FAB, CH_2Cl_2/NBA) m/z 371 (MH$^+$, 6), 199 (100), 137 (45), 135 (51); HRMS calcd for $C_{23}H_{35}O_2Si$ (M + H) 371.2406, found 371.2420.

(±)-1-[(*tert*-Butyldiphenylsilyl)oxy]-6-iodo-3-methylhexane (16). Methanesulfonyl chloride (600 μL, 6.14 mmol) was added dropwise to a stirred solution of **15**, triethylamine (1.30 mL, 9.33 mmol), and ether (18 mL) at 0 °C. The resulting solution was allowed to warm to room temperature over a period of 30 min and stirred for 1 h. Aqueous workup (ether, combined organic extracts washed with saturated $CuSO_4$ aqueous solution, Na_2SO_4) afforded crude mesylate as a yellow oil. The crude mesylate was dissolved in acetone (10 mL) and the resulting solution was cooled to 0 °C. NaI (1.92 g, 12.8 mmol) was added and the resulting orange solution was allowed to warm to room temperature and stirred for 8 h. Aqueous workup (ethyl acetate, organic layers washed with dilute aqueous $Na_2S_2O_3$, Na_2SO_4) afforded 1.87 g of crude product as a yellow oil. Flash chromatography

(20:1 hexane/ethyl acetate) afforded 1.75 g (85%) of iodide **16** as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72–7.63 (m, 4H), 7.48–7.35 (m, 6H), 3.69 (m, 2H, CH_2OSi), 3.14 (dt, J = 1.2, 6.9 Hz, 2H, CH_2I), 1.80 (m, 2H), 1.70–1.53 (m, 2H), 1.44–1.29 (m, 2H), 1.28–1.12 (m, 1H), 1.06 (s, 9H, $C(CH_3)_3$), 0.84 (d, J = 6.6 Hz, 3H, $CHCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5, 133.9, 129.5, 127.6, 61.9, 39.3, 37.7, 31.1, 28.6, 26.9, 19.6, 19.2, 7.2; IR (CCl_4) 2960, 1428, 1112, 1092 cm^{-1}; MS (FAB, CH_2Cl_2/NBA) m/z 479 (M^+ – H, 4), 199 (76), 135 (100); HRMS calcd for $C_{23}H_{32}IOSi$ (M – H) 479.1267, found 479.1298.

(±)-(*Z*)-7-[(*tert*-Butyldiphenylsilyl)oxy]-5-methyl-1-phenyl-1-heptene (17). The same procedure used for the preparation of **6** from **5** was carried out with triphenylphosphine (509 mg, 1.94 mmol) and iodide **16** (536 mg, 1.12 mmol). The crude salt was triturated with hot ether to afford 726 mg (89%) of {6-[(*tert*-butyldiphenylsilyl)oxy]-4-methylhexyl}triphenylphosphonium iodide as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.52 (m, 17H), 7.41–7.22 (m, 8H), 3.69–3.43 (m, 4H), 1.73–1.38 (m, 6H), 1.32–1.15 (m, 1H), 0.96 (s, 9H), 0.72 (d, J = 5.7 Hz, 3H, $CHCH_3$). Still-modified Wittig reaction[5] with benzaldehyde (1.50 mL, 14.7 mmol) afforded 6.59 g of crude product as a brown oil. Flash chromatography (20:1 hexane/ethyl acetate) afforded 2.02 g (84%) of **17** as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72–7.61 (m, 4H), 7.45–7.18 (m, 11H), 6.40 (d, J = 11.7 Hz, 1H, CH=C*H*Ph), 5.63 (dt, J = 11.7, 7.2 Hz, 1H, C*H*=CHPh), 3.70 (m, 2H, CH_2OSi), 2.34 (m, 2H, CH_2CH=CH), 1.74–1.56 (m, 2H), 1.52–1.18 (m, 3H), 1.05 (s, 9H, $C(CH_3)_3$), 0.81 (d, J = 6.3 Hz, 3H, $CHCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 135.5, 134.1, 133.1, 129.5, 128.7, 128.1, 127.6, 126.4, 62.1, 39.5, 37.2, 29.2, 26.9, 26.2, 19.5, 19.2; IR ($CDCl_3$) 2932, 1428, 1112, 1089 cm^{-1}; MS (FAB, CH_2Cl_2/NBA) m/z 441 (M^+ – H, 6), 199 (100), 135 (75), 117 (93); HRMS calcd for $C_{30}H_{37}OSi$ (M – H) 441.2614, found 441.2623.

(±)-(*Z*)-3-Methyl-7-phenyl-6-heptenal (18). The same procedure used for the preparation of **7** from **6** was carried out with **17** (2.02 g, 4.57 mmol) to afford 1.51 g of crude alcohol as a brown oil. Flash chromatography (4:1 hexane/ethyl acetate) afforded 829 mg (89%) of (*Z*)-3-methyl-7-phenyl-6-hepten-1-ol as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.18 (m, 5H, C_6H_5), 6.42 (d, J = 11.7 Hz, 1H, CH=C*H*Ph), 5.65 (dt, J = 11.7, 7.2 Hz, 1H, C*H*=CHPh), 3.66 (m, 2H, CH_2OH), 2.36 (m, 2H, CH_2CH=CH), 1.69–1.24 (m, 5H), 0.89 (d, J = 6.3 Hz, 3H, $CHCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 132.9, 128.8, 128.6, 128.0, 126.4, 60.8, 39.6, 37.2, 29.2, 26.0, 19.4; IR (CCl_4) 3637, 2929, 1448, 1058 cm^{-1}; MS (EI, 50 eV) m/z 204 (M^+, 10), 117 (98), 104 (100), 91 (79); HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1411. Using the general procedure of Swern, Mancuso, and Huang,[19] a solution of DMSO (860 μL, 12.1 mmol) and CH_2Cl_2 (2.8 mL) was added dropwise to a stirred solution of oxalyl chloride (530 μL, 6.08 mmol) and CH_2Cl_2 (14 mL) at –60 °C. The resulting solution was stirred for 2 min and then a solution of the above alcohol (829 mg) and CH_2Cl_2 (4 mL) was added dropwise. The resulting solution was stirred for an additional 15 min and then triethylamine (2.80 mL, 20.1 mmol) was added dropwise. After stirring for 5 min, the cold bath was removed and the reaction mixture was allowed to warm to room temperature. Aqueous workup (CH_2Cl_2, $MgSO_4$) afforded 896 mg of crude aldehyde as a yellow oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 739 mg (90%) of **18** (10:1 mixture of alkene isomers, **18**/**19**, ^{1}H NMR) as a clear oil. *Z*-alkene **18**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.72 (t, J = 2.3 Hz, 1H, CHO), 7.41–7.18 (m, 5H, C_6H_5), 6.45 (d, J = 11.7 Hz, 1H, CH=C*H*Ph), 5.64 (dt, J = 11.7, 7.2 Hz, 1H, C*H*=CHPh), 2.48–2.02 (m, 5H), 1.58–1.28 (m, 2H), 0.95 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 137.4, 132.1, 129.2, 128.6, 128.1, 126.5, 50.7, 36.8, 27.6, 25.9, 19.7; IR (CCl_4) 2960, 2917, 1729, 1494 cm^{-1}; MS (EI, 50 eV) m/z 202 (M^+, 16), 117 (100), 91 (76); HRMS calcd for $C_{14}H_{18}O$ 202.1358, found 202.1362.

(±)-(*E*)-3-Methyl-7-phenyl-6-heptenal (19). The same procedure used for the preparation of **8** from **7** was carried out with **18** (341 mg, 1.68 mmol) (45 min, 80 °C) to afford 375 mg of crude product as a brown oil. Flash chromatography (20:1 hexane/ethyl acetate) afforded 259 mg (76%) of **19** as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (t, J = 2.1 Hz, 1H, CHO), 7.43–7.15 (m, 5H, C_6H_5), 6.42 (d, J = 15.9 Hz, 1H, CH=C*H*Ph), 6.21 (dt, J = 15.9, 6.6 Hz, 1H, C*H*=CHPh), 2.44 (ddd, J = 1.8, 5.7, 10.2 Hz, 1H, CH*H*CHO), 2.35–2.07 (m, 4H), 1.61–1.35 (m, 2H), 1.02 (d, J = 6.6 Hz, 3H, $CHCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 137.5, 130.1, 128.4, 126.8, 125.8, 50.8, 36.2, 30.3, 27.5, 19.7; IR ($CDCl_3$) 2931, 2919, 1724, 1448 cm^{-1}; MS (EI, 50 eV) m/z 202 (M^+, 25) 117 (100), 91 (74) HRMS calcd for $C_{14}H_{18}O$ 202.1358, found 202.1352.

(±)-(*Z*)-1-{4-[(*tert*-Butyldimethylsilyl)oxy]-3,5-dimethylphenyl}-3-methyl-7-phenyl-6-hepten-1-ol (20). The same procedure used for the preparation of **10b** was carried out with 1-bromo-4-[(*tert*-butyldimethylsilyl)oxy]-3,5-dimethylbenzene[18] (475 mg, 1.51 mmol) and aldehyde **18** (200 mg, 0.989 mmol) to afford 618 mg of crude product as a yellow oil. Flash chromatography (40:1 hexane/ethyl acetate) afforded 362 mg (83%) of **20** as a 1:1 mixture of diastereomers (clear oil): ^{1}H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers) δ 7.42–7.17 (m, 5H, C_6H_5), 6.93 (s, 2H, ArH), 6.48–6.37 (m, 1H, CH_2=C*H*Ph), 5.75–5.59 (m, 1H, C*H*=CHPh), 4.70–4.58 (m, 1H, C*H*OH), 2.50–2.30 (m, 2H, CH_2CH=CH), 2.25 (s, 6H, $Ar(CH_3)_2$), 1.91–1.47 (m, 3H), 1.47–1.18 (m, 2H), 1.07 (s, 9H, $C(CH_3)_3$), 0.95 (d, J = 6.3 Hz, 3H, $CHCH_3$), 0.22 (s, 6H, $Si(CH_3)_2$); IR (CCl_4) 3617, 2931, 1472, 1255, 1232 cm^{-1}; MS (FAB, CH_2Cl_2/NBA) m/z 438 (M^+, 15), 421 (100), 265 (92), 249 (99); HRMS calcd for $C_{28}H_{42}O_2Si$ 438.2954, found 438.2949. Two early chromatography fractions afforded a sample of the faster eluting diastereomer for chaaracterization: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.21 (m, 5H, C_6H_5), 6.94 (s, 2H, ArH), 6.44 (d, J = 11.4 Hz, 1H, CH=C*H*Ph), 5.68 (dt, J = 11.7, 7.2 Hz, 1H, C*H*=CHPh), 4.64 (m, 1H, C*H*OH), 2.50–2.30 (m, 2H, CH_2CH=CH), 2.24 (s, 6H, ArH), 1.89–1.66 (m, 2H), 1.60–1.46 (m, 1H), 1.46–1.32 (m, 2H), 1.07 (s, 9H, $C(CH_3)_3$), 0.96 (d, J = 6.3 Hz, 3H, $CHCH_3$), 0.22 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 137.8, 137.7, 133.0, 128.8, 128.7, 128.5, 128.1, 126.4, 126.1, 71.9, 46.3, 37.6, 29.2, 26.1, 26.0, 19.2, 18.7, 17.9, –3.0.

(±)-(*E*)-1-{4-[(*tert*-Butyldimethylsilyl)oxy]-3,5-dimethylphenyl}-3-methyl-7-phenyl-6-hepten-1-ol (21). The same procedure used for the preparation of **10b** was carried out with 1-bromo-4-[(*tert*-butyldimethylsilyl)oxy]-3,5-dimethylbenzene (614 mg, 1.95 mmol) and aldehyde **19** (255 mg, 1.29 mmol) to afford 764 mg of **21** as an amber oil. Flash chromatography (40:1 hexane/ethyl acetate) afforded 547 mg (99%) of **21** as a 1:1 mixture of diastereomers (clear oil): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.14 (m, 5H), 6.95 (s, 1H, ArH), 6.95 (s, 1H, ArH), 6.48–6.31 (m, 1H, CH_2=C*H*Ph), 6.28–6.12 (m, 1H, C*H*=CHPh), 4.70–4.61 (m, 1H, C*H*OH), 2.32–2.10 (m, 2H, CH_2CH=CH), 2.21 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 1.91–1.15 (m, 5H), 1.04 (s, 9H, $C(CH_3)_3$), 1.00–0.95 (m, 3H, $CHCH_3$), 0.18 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 137.8, 137.7, 137.2, 130.8, 130.8, 129.6, 128.2, 126.5, 126.4, 126.1, 125.8, 115.2, 72.3, 71.7, 46.3, 45.8, 37.0, 36.2, 30.3, 30.1, 29.0, 29.0, 26.0, 20.0, 19.1, 18.6, 17.8, –3.1; IR (CCl_4) 3617, 2931, 1473, 1230; MS (FAB, CH_2Cl_2/NBA) m/z 438 (M^+, 10), 421 (100), 265 (81), 249 (72); HRMS calcd for $C_{28}H_{42}O_2Si$ 438.2954, found 438.2943.

General Procedure for Quinone Methide Formation. Using a modification of the procedure by Dyall and Winstein,[10] Ag_2O (5 to 10 equiv) was added to a solution of the appropriate phenol in CD_2Cl_2 (0.5–0.2 M) at room temperature. The reaction mixture was stirred for 25 min and then checked by ^{1}H NMR to ensure the oxidation was complete. The solution was filtered through a plug of Celite/Na_2SO_4 to afford a yellow solution of the quinone methide. The quinone methide was diluted with CH_2Cl_2 to give a solution ca. 0.15 M in quinone methide.

General Procedure for the Formal Cycloaddition. A CH_2Cl_2 solution of the quinone methide or benzylic alcohol was cooled to the temperature noted, the appropriate Lewis acid was added, and the resulting solution was stirred for the time indicated [concentration, temperature, Lewis acid (amount), time]. The reaction mixture was then poured into a rapidly stirred two-phase solution of CH_2Cl_2 and $NaHCO_3$ and stirred for 30 min. The aqueous layer was extracted with CH_2Cl_2 (3×), and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to afford the crude products. In several cases the starting material was a silylated phenol. The products of these reactions were mixtures of phenols and silyl phenols. Accordingly, the crude product was treated with *n*-Bu_4NF as described for the preparation of **7** from **6** to afford the unprotected phenols in the yields indicated.

(19) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

(±)-(4a*S,9*S**,9a*S**) and (4a*S**,9*R**,9a*R**)-6,8-Dimethyl-7-hydroxy-9-phenyl-1,2,3,4,4a,9,9a-heptahydrofluorene (23a and 23b, respectively). From 22.** Phenol **7** (43.5 mg, 0.148 mmol) was oxidized according to the general quinone methide preparation to afford a yellow solution of quinone methide **22** (*Z*)-7-(3,5-dimethyl-4-oxo-2,5-cyclohexadien-1-ylidene)-1-phenyl-1-heptene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.18 (m, 6H), 6.86 (s, 1H), 6.44 (d, *J* = 11.7 Hz, 1H, CH=C*H*Ph), 6.27 (t, *J* = 8.1 Hz, 1H, C=C*H*CH_2), 5.64 (dt, *J* = 11.7 Hz, *J* = 7.2 Hz, 1H, CH_2CH=CH), 2.47 (m, 2H), 2.37 (m, 2H), 2.04 (s, 3H, CH_3) 2.00 (s, 3H, CH_3), 1.63–1.46 (m, 4H). **Method A, $SnCl_4$, −78 °C.** According to the general procedure for the formal cycloaddition, **22** (0.148 mmol) [0.10 M, −78 °C, $SnCl_4$ (70.0 μL, 0.598 mmol), 10 min] afforded 46.5 mg of crude product as a yellow oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 24.6 mg (57%) of **23a** and **23b** as a 2.4:1 (**23a/23b**, ^{1}H NMR) mixture (clear oil). **Method B, $SnCl_4$, 0 °C.** According to the general procedure for the formal cycloaddition, **22** (0.129 mmol) [0.07 M, 0 °C, $SnCl_4$ (60.0 μL, 0.513 mmol), 10 min] afforded 38.6 mg of crude product as a yellow oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 30.7 mg (81%) of **23a** and **23b** as a 2.3:1 (**23a/23b**, ^{1}H NMR) mixture (clear oil).

From 24. Phenol **8** (54.7 mg, 0.186 mmol) was oxidized according to the general quinone methide preparation to afford a yellow solution of quinone methide **24** (*E*)-7-(3,5-dimethyl-4-oxo-2,5-cyclohexadien-1-ylidene)-1-phenyl-1-hexene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.14 (m, 6H), 6.89 (s, 1H, C=CHC), 6.40 (d, *J* = 15.6 Hz, 1H, C*H*Ph), 6.32 (t, *J* = 8.1 Hz, 1H, C=C*H*CH_2), 6.20 (dt, *J* = 6.9 Hz, *J* = 15.6 Hz, 1H, C*H*=CHPh), 2.52 (m, 2H), 2.26 (m, 2H), 2.05 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.67–1.49 (m, 4H). **Method C.** According to the general procedure for the formal cycloaddition, **24** (0.186 mmol) [0.10 M, 0 °C, $SnCl_4$ (90.0 μL, 0.769 mmol), 10 min] afforded 39.5 mg of crude product as a yellow oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 28.1 mg (52%) of **23a** and **23b** as a 4.2:1 (**23a/23b**, ^{1}H NMR) mixture (clear oil). **Method D.** According to the general procedure for the formal cycloaddition, **24** (0.0934 mmol) [0.10 M, −78 °C, $TiCl_4$ (40.0 μL, 0.364 mmol), 30 min] afforded 39.8 mg of crude product as a yellow oil. Flash chromatography (9:1 hexane/ethyl acetate) afforded 18.1 mg (66%) of **23a** and **23b** as a 4.2:1 (**23a/23b**, ^{1}H NMR) mixture (clear oil). Analytical samples of both diastereomers were obtained by HPLC (4.6 mm i.d. column, 40:1 hexane/ethyl acetate, 0.8 mL/min, **23a**, t_R = 10.6 min, **23b**, t_R = 11.0 min) purification. Major diastereomer **23a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.09 (m, 5H, C_6H_5), 6.87 (s, 1H, ArH), 4.47 (s, 1H, OH), 3.74 (d, *J* = 10.5 Hz, 1H, C*H*(C_6H_5), 2.48–2.32 (m, 2H), 2.29 (s, 3H, $ArCH_3$), 1.88 (m, 1H), 1.84–1.69 (m, 2H), 1.65 (s, 3H, $ArCH_3$), 1.60 (dddd, *J* = 3, 11, 11, 11 Hz, 1H, C_6H_5CHCH(CH)CH_2), 1.48–1.28 (m, 3H), 1.21 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 144.5, 143.0, 139.3, 128.3 (br), 126.0, 120.9, 120.8, 120.5, 61.2, 56.1, 49.0, 29.3, 28.5, 26.5, 26.2, 16.2, 12.6; IR ($CDCl_3$) 3610, 2929, 1451, 1223, 1217 cm^{-1}; MS (EI, 50 eV) *m/z* 292 (M^+, 100), 249 (24), 91 (26); HRMS calcd for $C_{21}H_{24}O$ 292.1827, found 292.1827. Minor diastereomer **23b** (1:11 mixture of **23a/23b**, ^{1}H NMR): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.17 (m, 3H), 7.03–7.00 (m, 2H), 6.87 (s, 1H, ArH), 4.47 (s, 1H, OH), 3.97 (d, *J* = 3.0 Hz, 1H, CHPh, H(9)), 3.21 (apparent q, *J* = 5.4 Hz, 1H, ArCH, H(4a)), 2.36–2.21 (partially obscured m, 1H, H(9a)), 2.30 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.85–1.81 (m, 1H), 1.79–1.65 (m, 2H), 1.54 (m, 1H), 1.48–1.25 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 143.9, 142.9, 138.7, 128.2, 127.7, 125.9, 122.3, 121.5, 120.9, 55.2, 50.3, 41.2, 28.5, 27.3, 24.2, 22.4, 16.4, 12.3; IR ($CDCl_3$) 3611, 2928, 1450, 1217, 1190 cm^{-1}; MS (EI, 70 eV) *m/z* 292 (M^+, 100), 249 (62), 91 (21); HRMS calcd $C_{21}H_{24}O$ 292.1827, found 292.1815.

(±)-(3*S,4a*S**,9a*S**)-7-Hydroxy-3,6,8,9,9-pentamethyl-1,2,3,4,4a,9a-hexahydrofluorene (26). From Benzylic Alcohol 10a:** According to the general procedure for the formal cycloaddition, **10a** (103 mg, 0.373 mmol) [0.035 M, −78 °C, $TiCl_4$ (1.9 mL of a 1 M solution in CH_2Cl_2, 1.9 mmol), 14 min] afforded 98.0 mg of crude product as a yellow solid. Flash chromatography gave 85.6 mg (90%) of a **26** as a white solid (mp 153–154 °C).

From Quinone Methide 25: Phenol **11a** (23.5 mg, 0.090 mmol) was oxidized according to the general quinone methide preparation to afford a yellow solution of quinone methide **25** 8-(3,5-dimethyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2,6-dimethyl-2-octene. Concentration afforded 22.5 mg (97%) of a **25** as a bright yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (s, 1H, C=CH), 6.90 (s, 1H, C=CH), 6.33 (t, *J* = 8.3 Hz, 1H, C=C*H*CH_2), 5.05–5.10 (m, 1H, $(CH_3)_2C$=C*H*), 2.55–2.41 (m, 1H), 2.41–2.25 (m, 1H), 2.07–1.90 (m, 2H), 2.04 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.75–1.65 (m, 1H), 1.68 (s, 3H, CH_3), 1.60 (s, 3H), 1.46–1.34 (m, 1H), 1.33–1.17 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$), δ (C=O not observed) 147.6, 138.7, 136.4, 134.5, 132.5, 131.6, 130.0, 124.2, 36.8, 36.2, 33.3, 25.7, 25.5, 19.7, 17.6, 16.8, 16.0. According to the general procedure for the formal cycloaddition, **25** (22.5 mg, 0.087 mmol) [0.015 M, −78 °C, $TiCl_4$ (0.36 mL of a 1 M solution in CH_2Cl_2, 0.36 mmol), 9 min] afforded 23.1 mg of crude product as a yellow solid. Flash chromatography (9:1 hexane/ethyl acetate) afforded 19.7 mg (88%) of **26** as a white solid. Recrystallization (ether/hexane) afforded an analytical sample: mp 154–155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.75 (s, 1H, ArH), 4.47 (s, 1H, ArOH), 2.45 (dt, *J* = 3.3, 10.8 Hz, 1H, ArCH, H(4a)), 2.33–2.13 (m, 1H), 2.29 (s, 3H, $ArCH_3$), 2.22 (s, 3H, $ArCH_3$), 1.93–1.85 (m, 1H), 1.78–1.70 (m, 1H), 1.63–1.50 (m, 1H, C*H*CH_3), 1.39 (s, 3H, CH_3), 1.35–1.25 (m, 2H), 1.04 (s, 3H, CH_3), 1.05–0.99 (m, 1H), 1.00 (d, *J* = 6.6 Hz, 3H, CH_3), 0.92 (q, *J* = 11.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9, 149.3, 137.4, 121.0, 120.3, 119.8, 59.6, 45.4, 44.6, 38.3, 35.7, 33.1, 26.7, 24.7, 22.6, 19.4, 16.2, 11.4; IR (CCl_4), 3623, 2918, 1457, 1231, 1193 cm^{-1}; MS (EI, 20 eV) *m/z* 258 (M^+, 100), 243 (76). Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.09. Found: C, 83.81, H, 10.23.

(±)-1-[4-(Acetyloxy)-3,5-dimethylphenyl]-6-ethyl-1-cyclohexene (28b). Phenol **13** (60.6 mg, 0.261 mmol) was oxidized according to the general quinone methide preparation to afford a yellow solution of quinone methide **27** (*Z*)-8-(3,5-dimethyl-4-oxo-2,5-cyclohexadien-1-ylidene)]-2-octene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.88 (s, 1H), 6.31 (t, *J* = 8.1 Hz, 1H, C=C*H*CH_2), 5.53–5.30 (m, 2H, C*H*=C*H*CH_3), 2.49 (q, *J* = 7.5 Hz, 2H, CH_2), 2.16–2.02 (m, 2H, C*H*CH=C), 2.04 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.60 (d, *J* = 6 Hz, 3H, CHC*H*$_3$), 1.60–1.36 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.7, 148.3, 138.6, 136.3, 134.5, 131.8, 129.9, 129.8, 124.2, 29.1, 28.9, 28.8, 26.4, 16.7, 16.0, 12.7; IR (CCl_4) 2924, 1646, 1628, 1579, 1447. According to the general procedure for the formal cycloaddition, **27** (0.261 mmol), [0.052 M, −78 °C, $TiCl_4$ (110 μL, 1.00 mmol), 40 min] afforded 59.5 mg of crude phenol **28a** as an unstable yellow oil. Flash chromatography of similar material (9:1 hexane/ethyl acetate) afforded styrene **28a** 1-(4-hydroxy-3,5-dimethylphenyl)-6-ethyl-1-cyclohexene, which rapidly decomposed: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (s, 2H, ArH), 5.77 (t, *J* = 3.6 Hz, 1H, C=C*H*CH_2), 4.53 (s, 1H, OH), 2.52 (br, m, 1H, CH_3CH_2CH), 2.24 (s, 6H, Ar-$(CH_3)_2$) 2.13 (m, 2H, C=CHC*H*$_2$), 1.80–1.52 (m, 4H), 1.41 (m, 1H, C*H*HCH$_3$), 1.20 (m, 1H, CH*H*CH$_3$), 0.83 (t, *J* = 7.5 Hz, 3H, CH_2CH_3). The crude **28a** prepared above was dissolved in CH_2Cl_2 (5.0 mL), and acetic anhydride (50.0 μL, 0.530 mmol), pyridine (0.150 mL, 1.86 mmol), and DMAP (ca. 2 mg, catalytic) were added. The resulting solution was stirred for 8 h and then poured into rapidly stirred saturated aqueous $NaHCO_3$ (20 mL). Aqueous workup (CH_2Cl_2, Na_2SO_4) afforded 68.7 mg of crude product. Flash chromatography (9:1 hexane/ethyl acetate) afforded 34.6 mg (49%) of **28b** as clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (s, 2H, ArH), 5.82 (dt, *J* = 0.9, 4.1 Hz, 1H, CH_2CH=C), 2.52 (br m, 1H, CH_3CH_2CH), 2.33 (s, 3H, C(O)CH_3), 2.20–2.08 (m, 2H), 2.14 (s, 6H, $ArCH_3$), 1.78–1.52 (m, 4H), 1.40 (m, 1H, C*H*HCH$_3$), 1.20 (m, 1H, CH*H*CH$_3$), 0.82 (t, *J* = 7.5 Hz, 3H, CHC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 146.8, 141.8, 140.7, 129.4, 126.4, 125.8, 37.3, 26.3, 26.1, 25.9, 20.5, 18.7, 16.4, 12.0; IR ($CDCl_3$) 2933, 1228, 1208, 1147 cm^{-1}; MS (EI, 50 eV) 272 (M^+, 26), 230 (100), 174 (33); HRMS calcd for $C_{18}H_{24}O_2$ 272.1776, found 272.1762.

(±)-(1*R,2*S**)-1-(3,5-Dimethyl-4-hydroxyphenyl)-2-ethylcyclohexane (29).** According to the general procedure for the formal cycloaddition, **27** (0.125 mmol), [0.021 M, −78 °C, $EtAlCl_2$ (4.00 mL of a 1 M solution in CH_2Cl_2), 12 min] afforded 23.2 mg of crude product as a yellow oil. Flash chromatography (20:1 hexane/ethyl acetate) afforded 20.0 mg (69%) of **29** as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (s, 2H, ArH), 4.43 (bs, 1H, OH), 2.74 (dt, *J* = 12, 3.6 Hz, 1H, ArCH), 2.24 (s, 6H, $ArCH_3$), 1.92–1.18 (m, 10H), 0.99 (m, 1H), 0.70 (t, *J* = 7.5 Hz, 3H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 137.8, 127.9, 122.2, 46.0, 42.0, 28.6, 26.7, 25.9, 20.4, 17.8, 16.0, 12.4; IR ($CDCl_3$) 3612, 2962, 2930, 2859, 1489, 1201 cm^{-1}; MS (EI, 50 eV) 232 (M^+, 82), 161 (100), 135 (68); HRMS calcd for $C_{16}H_{24}O$ 232.1827, found 232.1821.

(±)-(3a*R,8*S**,8a*R**)-5,7-Dimethyl-8-[(*N*-ethyl-*N*-(phenylmethyl)amino]-6-hydroxy-1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene (32).** Phenol **14** (40.7 mg, 0.117 mmol) was oxidized according to the general quinone methide preparation to afford a yellow solution of quinone methide **30** *N*-acetyl-*N*-(phenylmethyl)-6-(3,5-dimethyl-4-oxo-2,5-cyclohexadien-1-ylidene-)hex-1-enamine: ^{1}H NMR (300 MHz, $CDCl_3$, 6:4 mixture of amide rotational isomers) δ 7.42–7.13 (m, 6.4 H), 6.85 (s, 1H), 6.54 (d, *J* = 14.1 Hz, 0.6 H, NC*H*=CH), 6.22 (m, 1H), 4.94–4.84 (m, 1H, NCH=C*H*), 4.87 (s, 1.2 H), 4.76 (s, 0.8 H), 2.37 (m, 2H), 2.28 (s, 1.8 H, NC(O)CH_3), 2.16 (s, 1.2 H, NC(O)CH_3), 2.06 (m, 2H), 2.03 (s, 3H), 1.99 (s, 3H), 1.52 (m, 2H); IR ($CDCl_3$) 2925, 1645, 1620, 1576, 1407, 1333 cm^{-1}. According to the general procedure for the formal cycloaddition, **30** (0.125 mmol), [0.012 M, −5 °C, BF_3·OEt_2 (60.0 μL, 0.488 mmol), 10 min] afforded 38.2 mg of crude product as a yellow oil. Flash chromatography (5:1 hexane/ethyl acetate) gave 28.2 mg (70%) of **31** as a clear viscous oil: ^{1}H NMR (300 MHz, $CDCl_3$, 1:1 mixture of amide rotational isomers) δ 7.35–6.73 (m, 6H), 5.99 and 5.04 (s, 1H), 5.00 (bs, 1H, OH), 4.35 (m, 1H, PhC*H*N), 4.01 (m, 1H, PhC*H*N), 3.25 and 3.17 (dt, *J* = 2.1, 7.8 Hz, 1H), 2.46 (m, 1H), 2.41 (s, 1.5 H), 2.27 (s, 1.5 H), 2.27 (s, 1.5 H), 2.13 (s, 1.5 H), 2.07 (s, 1.5 H), 1.99–1.70 (m, 2H), 1.83 (s, 1.5 H), 1.58 (m, 2H), 1.45 (m, 1H), 1.30 (m, 1H); IR ($CDCl_3$) 3609, 2954, 1626, 1416, 1222 cm^{-1}; MS (CI, NH_3) 350 (MH^+, 59), 258 (22), 201 (100); HRMS calcd for $C_{23}H_{28}O_2N$ 350.2120, found 350.2124. Due to the presence of amide rotational isomers, **31** was reduced to amine **32**. $LiAlH_4$ (32.1 mg, 0.846 mmol) was added slowly to a solution of **31** (26.4 mg, 0.762 mmol) in ether (5.0 mL) at 0 °C. The mixture was refluxed for 3 h, and then excess ethyl acetate was added to destroy any remaining hydride. The mixture was filtered through Celite and concentrated to afford 13.2 mg (52%) of **32** as a clear oil: ^{1}H NMR (300 MHz, C_6D_6) δ 7.33 (d, *J* = 7.5 Hz, 2H), 7.12 (m, 3H, C_6H_5N), 6.70 (s, 1H, ArH), 4.21 (s, 1H, NCH), 3.64 (d, *J* = 13.2 Hz, 1H, PhC*H*HN), 3.49 (dt, *J* = 2.7, 8.0 Hz, 1H, ArCH), 3.18 (d, *J* = 13.2 Hz, 1H, PhCH*H*N), 2.67 (m, 1H), 2.50 (dq, *J* = 12.9, 7.2 Hz, 1H, CH_3C*H*H), 2.31 (s, 3H, $ArCH_3$), 2.29 (partially obscured dq, *J* = 12.9, 7.2 Hz, 1H, CH_3CH*H*), 2.05 (s, 3H, $ArCH_3$), 1.86 (m, 1H), 1.73 (m, 2H), 1.44 (m, 1H), 1.28 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), O*H* not observed; ^{13}C NMR (75 MHz, C_6D_6) δ 152.0, 141.2, 141.1, 140.4, 129.3, 128.3, 126.9, 124.0, 123.4, 120.4, 72.9, 54.8, 49.4, 44.3, 41.1, 35.0, 34.4, 26.1, 16.5, 13.9, 11.8; IR ($CDCl_3$) 3611, 2940, 1468, 1220, 1195 cm^{-1}; MS (EI, 70 eV) *m/z* 355 (M^+, 8), 201 (100), 200 (32), 136 (27); HRMS calcd for $C_{23}H_{29}NO$ 335.2249, found 335.2261.

(±)-(3*S,4a*S**,9a*S**)-7-Hydroxy-6-methoxy-3,9,9-trimethyl-1,2,3,4,4a,9a-hexahydrofluorene (33).** According to the general procedure for the formal cycloaddition, **10b** (214 mg, 0.546 mmol), [0.099 M, −78 °C, $TiCl_4$ (180 μL, 1.64 mmol), 12 min] afforded 209 mg of crude product as a brown oil. Desilylation [*n*-Bu_4NF (0.25 mL of a 1 M solution in THF, 0.25 mmol)] and aqueous workup (ether, $MgSO_4$) followed by flash chromatography (9:1 hexane/ethyl acetate) afforded 90.9 mg (64%) of **33** as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (s, 1H, ArH), 6.67 (s, 1H, ArH), 5.23 (s, 1H, OH), 3.88 (s, 3H, OCH_3), 2.57 (dt, *J* = 3.0, 10.8 Hz, 1H), 2.27 (br d, *J* = 12.6 Hz, 1H), 1.87 (m, 1H), 1.73 (m, 1H), 1.57 (m, 1H), 1.39–1.30 (m, 2H), 1.24 (s, 3H, CCH_3), 1.08–0.85 (m, 2H), 1.01 (d, *J* = 6.6 Hz, 3H, $CHCH_3$), 0.93 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 144.9, 144.3, 136.3, 108.6, 104.8, 59.7, 56.1, 46.3, 43.2, 38.2, 35.6, 33.2, 26.2, 25.1, 22.6, 21.8; IR (CCl_4) 3617, 3558, 2929, 1494, 1307, 1230; MS (EI, 70 eV) *m/z* 260 (M^+, 58), 245 (100), 189 (26); HRMS calcd for $C_{17}H_{24}O_2$ 260.1776, found 260.1777.

(±)-(3*S,4a*S**,9a*S**)-7-Methoxy-3,9,9a-trimethyl-1,2,3,4,-4a,9a-hexahydrofluorene (34) and (±)-6-isopropyl-1-(4-methoxyphenyl)-3-methyl-1-cyclohexene (35):** According to the general procedure for the formal cycloaddition, **10c** (216 mg, 0.822 mmol) [0.091 M, −78 °C, $TiCl_4$ (0.230 mL, 2.10 mmol), 13 min] afforded 216 mg of an amber oil. Flash chromatography (hexane) gave 106 mg (52%) of **34** (clear oil) and 45.2 mg (23%) of styrene **35** (clear oil). Major product **34**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.1 Hz, 1H, ArH), 6.75 (d, *J* = 2.4 Hz, 1H, ArH), 6.70 (dd, *J* = 2.4, 8.1 Hz, 1H, ArH), 3.81 (s, 3H, OCH_3), 2.58 (dt, *J* = 2.7, 10.8 Hz, 1H, ArCH), 2.31 (br d, *J* = 12.2 Hz, 1H), 1.89 (br d, *J* = 12.0 Hz, 1H), 1.76 (m, 1H), 1.59 (m, 1H), 1.42–1.33 (m, 2H), 1.29 (s, 3H, CH_3), 1.12–0.85 (m, 2H), 1.01 (d, *J* = 6.6 Hz, 3H, CH_3), 0.98 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 155.3, 137.5, 122.1, 110.8, 108.5, 59.7, 55.4, 45.8, 43.5, 38.1, 35.6, 33.2, 26.0, 25.0, 22.6, 21.9; IR ($CDCl_3$) 2957, 2923, 1479, 1281, 1210 cm^{-1}; MS (EI, 50 eV) 244 (M^+, 100), 229 (67), 173 (41); HRMS calcd for $C_{17}H_{24}O$, 244.1827 found 244.1820. Minor product **35**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (dm, *J* = 8.7 Hz, 2H, ArH), 6.83 (dm, *J* = 8.7 Hz, 2H, ArH), 5.71 (m, 1H, CH=C), 3.80 (s, 3H, OCH_3), 2.57 (m, 1H), 2.30 (m, 1H), 1.89–1.53 (m, 4H), 1.48–1.21 (m, 1H), 1.05 (d, *J* = 7.2 Hz, 3H, CH_3), 0.85 (d, *J* = 6.9 Hz, 3H, CH_3), 0.67 (d, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 140.7, 136.2, 133.0, 127.5, 113.4, 55.1, 40.9, 30.4, 29.4, 28.5, 21.4, 21.4, 20.9, 17.8; IR ($CDCl_3$) 2959, 1510, 1242, 1180 cm^{-1}; MS (CI, NH_3) 245 (M^+ + H), 203 (9), 174 (8); HRMS calcd for $C_{17}H_{25}O$ (M + H) 245.1905, found 245.1915.

(±)-(3*S,4*S**,9*S**,9a*S**)-7-Hydroxy-9-phenyl-3,6,8-trimethyl-1,2,3,4,4a,9,9a-heptahydrofluorene (36). From 20. Method A, $TiCl_4$, 0 °C.** According to the general procedure for the formal cycloaddition, **20** (89.9 mg, 0.205 mmol) [0.051 M, 0 °C, $TiCl_4$ (50.0 μL, 0.455 mmol), 8 min] afforded 84.6 mg of crude product as a brown oil. Desilylation [*n*-Bu_4NF (0.10 mL of a 1 M solution in THF, 0.10 mmol)] followed by aqueous workup (ether, $MgSO_4$) afforded crude phenol. Flash chromatography (9:1 hexane/ethyl acetate) afforded 58.7 mg (93%) of **36** as a 2.6:1 mixture (^{1}H NMR). **Method B, $TiCl_4$, −78 °C.** According to the general procedure for the formal cycloaddition, **20** (28.1 mg, 0.0641 mmol), [0.25 M, −78 °C, $TiCl_4$ (30.0 μL, 0.273 mmol), 20 min] afforded 27.3 mg of crude product as a brown oil. Desilylation [*n*-Bu_4NF (0.032 mL of a 1 M solution in THF, 0.032 mmol)] followed by aqueous workup (ether, $MgSO_4$) and flash chromatography afforded 14.4 mg (73%) of **36** as a 10:1 mixture (^{1}H NMR) of diastereomers (clear oil).

From 21. According to the general procedure for the formal cycloaddition, **21** (99.8 mg, 0.228 mmol) [0.09 M, −78 °C, $TiCl_4$ (45.0 μL, 0.410 mmol), 20 min] afforded 92.9 mg of crude product as a brown oil. Desilylation [*n*-Bu_4NF (0.11 mL of a 1 M solution in THF, 0.11 mmol)] followed by aqueous workup (ether, $MgSO_4$) afforded crude phenol. Flash chromatography (9:1 hexane/ethyl acetate) afforded 46.8 mg (67%) of **36** as a 10:1 mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–6.96 (m, 5H, C_6H_5), 6.87 (s, 1H, ArH), 4.48 (s, 1H, OH), 3.73 (d, *J* = 10.5 Hz, 1H, C*H*(C_6H_5)), 2.48 (br t, *J* = 11.5, 1H, C*H*Ar), 2.35 (br d, *J* = 12.0 Hz, 1H), 2.29 (s, 3H, $ArCH_3$), 1.78 (m, 1H), 1.71 (m, 1H), 1.68–1.60 (m, 1H, C*H*CH_3), 1.65 (s, 3H, $ArCH_3$), 1.56 (dq, *J* = 2.3, 11.3 Hz, 1H, CH_2CH(CH)-CH(C_6H_5); 1.42 (dq, *J* = 2.5, 12.0 Hz, 1H), 1.05 (q, *J* = 11.5 Hz, 1H), 1.01 (d, *J* = 6.5 Hz, 3H, $CHCH_3$), 0.91 (dq, *J* = 4.0, 12.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 145.0, 143.9, 139.6, 128.8 (br), 126.5, 121.4, 121.3, 121.0, 61.5, 56.2, 49.4, 38.3, 36.0, 33.4, 28.5, 23.0, 16.8, 13.2; IR ($CDCl_3$) 3611, 2916, 1454, 1230, 1216, 1196 cm^{-1}; MS (EI, 50 eV) *m/z* 306 (M^+, 100), 291 (21), 249 (24); HRMS calcd for $C_{22}H_{26}O$ 306.1984, found 306.1987. Anal. Calcd for $C_{22}H_{26}O$: C, 86.22; H, 8.56. Found: C, 85.92; H, 8.60.

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Supplementary Material Available: Summary of key NOE and decoupling experiments and copies of ^{1}H NMR and ^{13}C NMR spectra for new compounds (69 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.