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Auxiliary-Directed Peroxidation Of 1,4-Dienes

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Key words: singlet oxygen; oxygenation; diene; chiral auxiliary; hydroperoxide

Abstract: The addition of singlet oxygen ($^1O_2$) to the proximal alkene of auxiliary-tethered 1,4-dienes and the addition of triplet oxygen ($^3O_2$) to the proximal position of the corresponding pentadienyl radicals both produce conjugated diene hydroperoxides in moderate to high diastereomeric excess. Negligible stereoselection is observed for additions of $^1O_2$ to the distal alkene of *Z,Z*-heptadienes due to the lack of control of alkene conformation. Despite evidence for the intermediacy of highly constrained pentadienyl radicals, poor diastereoselection is also observed for distal addition of $^3O_2$. The extent of olefin isomerization observed during radical oxygenations can be correlated with steric constraints on the intermediate pentadienyl and peroxyl radicals and may be relevant to literature reports of olefin isomerization during enzymatic oxygenations of unnatural fatty acids.

The formation of diene hydroperoxides through enzymatic or free radical oxidation of the 1,4-diene subunits of polyunsaturated fats has been linked with a variety of inflammation-related conditions, including asthma, atherosclerosis, and carcinogenesis.[1-3] Whereas enzymatic oxygenations proceed with high regio- and stereoselectivity, chemical oxygenations typically furnish racemic mixtures of regioisomers (Figure 1).[4-6] We became interested in the development of a strategy able to mimic the high selectivity of the enzymatic oxygenations and now report our investigations into the use of chiral directing groups as a means of controlling the peroxidation of 1,4-dienes.[7]

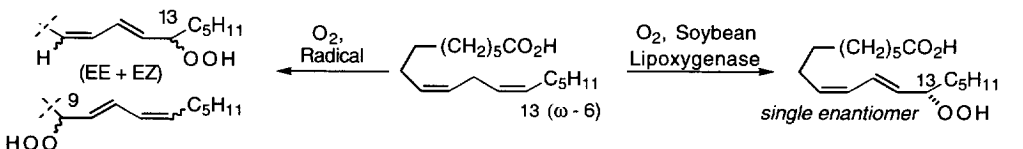


Fig. 1: Comparison of Enzymatic and Chemical Dioxygenations

There are few reports describing stereoselective peroxidation in acyclic systems. Photooxygenation of a prochiral alkene within a chiral inclusion complex was shown to proceed with significant, although unquantified, enantioselectivity.[8] Moderate diastereoselectivity has been achieved in the peroxidation of simple

alkenes based upon the ability of a neighboring chiral center to influence approach of $^1O_2$.[9-11] and several recent extensions of this strategy offer excellent levels of diastereoselection. Chiral allylstannanes undergo highly stereoselective oxygenation to form functionalized allyl hydroperoxides through metal-directed *anti*-S_E2' addition of $^1O_2$.[12] Chiral allylic alcohols or amines undergo diastereoselective addition of $^1O_2$ through a transition state in which the developing perepoxide is stabilized by hydrogen -bonding to the hydroxyl or amino group.[13,14] However, stereoselective peroxidation of 1,4-dienes remains virtually uninvestigated. The only known example is poorly enantioselective oxygenation of a diene fatty acid within a chiral cyclodextrin host.[15]

Lipoxygenases enzymes catalyze the highly enantioselective insertion of $^3O_2$ into 1,4-dienes to form diene hydroperoxides via an intermediate pentadienyl radical.[16-18] Soybean lipoxygenase, the most studied of this class of enzymes, mediates the highly enantioselective and regioselective insertion of oxygen into the ω-6 position of polyunsaturated fatty acids to form diene hydroperoxides. (Fig. 1). Interestingly, the major product derived from ω-6 oxygenation is formed with the same absolute stereochemistry as the regioisomeric hydroperoxide derived from "flip-flopped" substrate binding and oxygenation at ω-10.[17] These reports led us to hypothesize that enzyme-like selectivity could be achieved simply through controlling the approach of oxygen to a constrained pentadienyl fragment.[17]

Our approach to stereoselective diene peroxidation relied upon covalent tethering of a 1,4-pentadiene to arylcyclohexyl chiral auxiliaries as a means of simultaneously limiting the conformational space of the diene and controlling the approach of $^1O_2$ (Figure 2).[7] Conformational control would be provided by the interaction between the Z-alkenyl sidechain and the cyclohexane ring. Molecular modeling suggested the availability of only two low-energy sidechain conformers, "extended" or "folded", of which the extended conformer was predicted to be favored by 1.5 kcal/mole.[19] Control of oxygen approach would by provided by the arene group of the chiral auxiliary. Arylcyclohexyl chiral auxiliaries are well-known to control addition of nucleophiles or electrophiles to tethered trigonal centers and phenylcyclohexyl enoates have been reported to undergo diastereoselective addition of $^1O_2$.[20,21] The substrate design was also intended to result in regioselective peroxidation. Preferential attack of $^1O_2$ on the more electron-rich proximal alkene would produce one major perepoxide regioisomer. Isomerization of this perepoxide was anticipated to proceed via selective migration of a bisallylic hydrogen; the alternative abstraction of the cyclohexylmethine hydrogen was precluded by stereoelectronic considerations (see, for example Figure 4).[22] Taken together, these design elements predicted regio- and stereoselective dioxygenation of the proximal alkene to afford one major hydroperoxide.

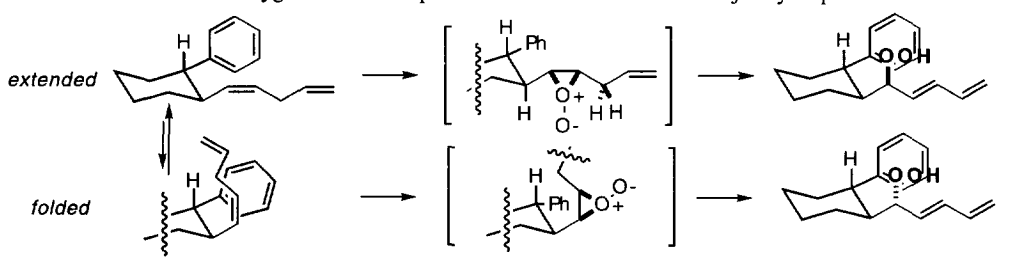
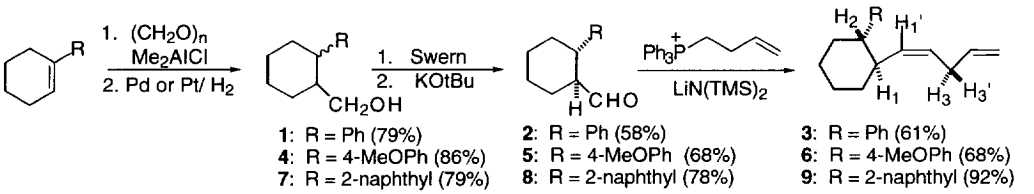


Figure 2: Auxiliary-Directed Oxygenation

Preparation of initial substrates is illustrated in Scheme 1. Prins reaction between formaldehyde and phenylcyclohexene, followed by hydrogenation, provided a mixture of *cis* and *trans*-2-phenylcyclohexane-1-

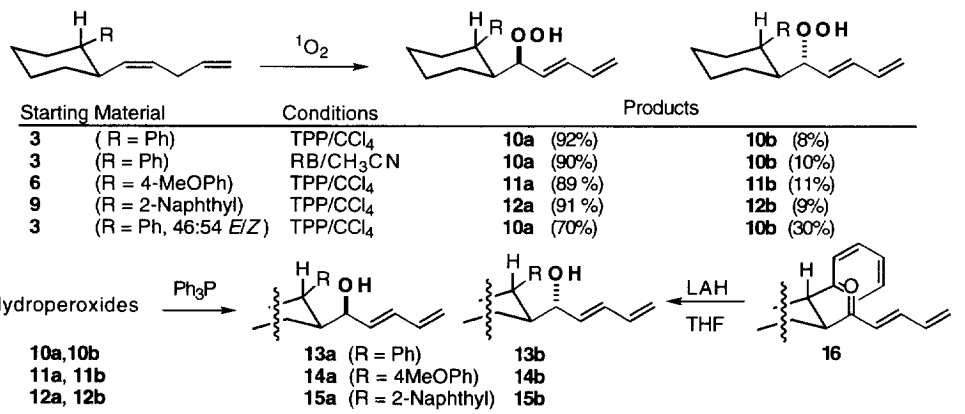
methanol (**1**).[23] Oxidation, followed by base-catalyzed epimerization, furnished the *trans*-aldehyde **2**, which underwent olefination with the ylide derived from 1-bromo-3-butene to afford the Z-1,4-pentadiene **3**. The presence of the chain-extended conformer of **3** was confirmed by the observation of a substantial NOE (5%) between H_2 and $H_{1'}$. The strong influence of the neighboring aromatic ring could be observed both in the diastereotopic character of $H_3/H_{3'}$ as well as the upfield shift of the $H_{1'}$ resonance. Two analogs, **6** and **9**, were similarly prepared from 4-methoxyphenyl-1-cyclohexene and 4-naphthyl-1-cyclohexene.



1: R = Ph (79%) **2**: R = Ph (58%) **3**: R = Ph (61%)
4: R = 4-MeOPh (86%) **5**: R = 4-MeOPh (68%) **6**: R = 4-MeOPh (68%)
7: R = 2-naphthyl (79%) **8**: R = 2-naphthyl (78%) **9**: R = 2-naphthyl (92%)

Scheme 1: Synthesis of 2-Arylcyclohexyl Dienes

Photosensitized oxygenations were performed through visible irradiation of oxygen-saturated solutions of dienes in the presence of either tetraphenylporphyrin (TPP) or Rose Bengal (RB) sensitizers (Scheme 2). Oxygenations were stopped after ≤ 20% conversion to minimize further oxygenation of the diene hydroperoxide products.[24] Oxygenation of **3** proceeded with high selectivity for formation of diastereomer **10a** in both CCl_4 (TPP) and in CH_3CN (RB), indicating the dominance of steric, rather than electronic, effects on the reaction. This was supported by the oxidations of methoxyphenyl and naphthyl dienes **6** and **9**, which were each converted to one major diastereomer, **11a** and **12a**. Product ratios were determined by HPLC of the hydroperoxides **10**, **11**, and **12** as well as the corresponding alcohols **13**, **14**, and **15**. The stereochemical assignment was substantiated by the preferential reduction of dienone **16**, available from either the hydroperoxides or the alcohols, to selectively furnish alcohol **13b**. The importance of the Z-alkene in limiting the conformation of the pentadiene could be tested with the E-isomer, which was predicted to have a greatly



Starting Material		Conditions	Products	
3	(R = Ph)	TPP/CCl_4	**10a** (92%)	**10b** (8%)
3	(R = Ph)	RB/CH_3CN	**10a** (90%)	**10b** (10%)
6	(R = 4-MeOPh)	TPP/CCl_4	**11a** (89 %)	**11b** (11%)
9	(R = 2-Naphthyl)	TPP/CCl_4	**12a** (91 %)	**12b** (9%)
3	(R = Ph, 46:54 *E/Z*)	TPP/CCl_4	**10a** (70%)	**10b** (30%)

10a,10b **13a** (R = Ph) **13b**
11a, 11b **14a** (R = 4MeOPh) **14b**
12a, 12b **15a** (R = 2-Naphthyl) **15b**

Scheme 2: Oxidation of 1,4-Pentadienes

reduced preference (0.5 kcal) for the chain-extended conformer. Schlosser-Wittig olefination of **2** was used to produce **3** as a 56:44 E/Z mixture.[25] Photooxygenation under identical conditions as before now afforded **10a** and **10b** in a 76:24 ratio, implying that the E-alkene underwent oxygenation with only modest (63:37) selectivity. GC analysis of recovered diene indicated no difference in the rate of consumption of the E and Z isomers.

Having achieved stereoselective peroxidation based upon steric shielding, we became interested in the possibility of directing $^1O_2$ *toward* one face of an alkene, an approach based upon the impressive diastereoselection reported for oxygenation of conformationally constrained allylic alcohols (Figure 3).[14]

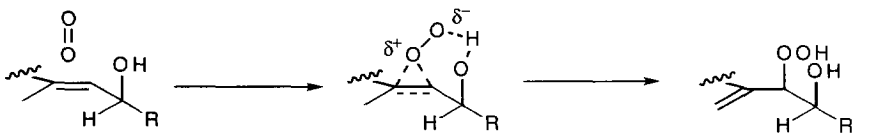
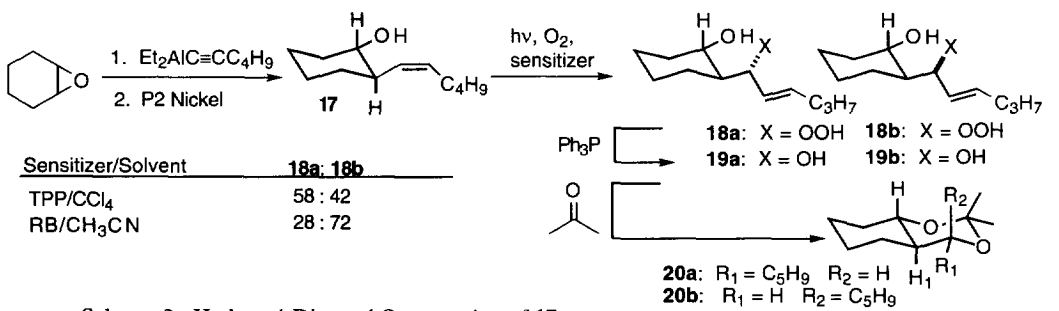


Figure 3: Hydroxyl-Directed Oxygenation (Ref. 14)

An initial substrate, Z-alkenol **17**, was prepared via addition of an alkynyl alane to cyclohexene oxide followed by semihydrogenation of the intermediate alkynol.[26] The Z-alkenyl sidechain of **17** was predicted to be constrained to the same type of "extended" conformation seen for **2**. The observed diastereoselection would therefore depend primarily upon the ability of the hydroxyl group to direct the approach of oxygen. Photooxygenation in CCl_4, a nonpolar medium anticipated to maximize the influence of a hydrogen-bonded transition state,[14] resulted in the formation of a nearly random mixture of diastereomeric hydroperoxides, **18a** and **18b**. Photooxygenation in a more polar solvent, CH_3CN, afforded the same two hydroperoxides in a 27:73 ratio. Product ratios were determined by ^1H NMR of concentrated but unpurified reaction mixtures.



Sensitizer/Solvent	18a: 18b
TPP/CCl_4	58 : 42
RB/CH_3CN	28 : 72

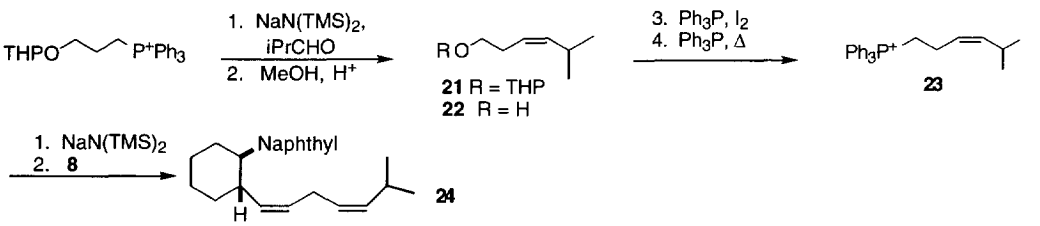
Scheme 3: Hydroxyl-Directed Oxygenation of **17**

Reduction with triphenylphosphine provided the corresponding 1,3-diols **19ab**. We had hoped to assign relative stereochemistry by ^1H NMR following formation of the corresponding acetonides. However, neither acetonide (**20ab**) displayed H_1-$H_{1'}$ coupling constants easily interpreted in terms of a chair 1,3-dioxane. The tentative stereochemical assignments shown in Scheme 3 are therefore based upon the strong influence of solvent polarity on the transition state. Oxygenation in CH_3CN, where a hydrogen-bonded transition state is

presumably less significant, results in net steric control of oxygen delivery, whereas oxygenation in CCl_4, a solvent favoring a hydrogen-bonded transition state, leads to a net cancellation of the two factors.

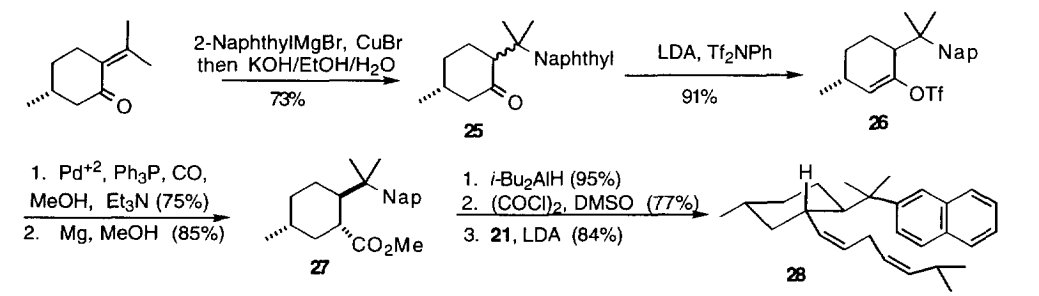
Remote Kinetic Dioxygenation:

We next attempted stereoselective oxygenation of the distal alkene, an endeavor anticipated to be extremely challenging in view of the limited number of reports involving stereoselection at a five-atom distance from a chiral auxiliary.[20] Molecular modeling clearly indicated that a phenylcyclohexyl auxiliary possessed insufficient length to effectively shield the terminus of a pentadiene system. We therefore prepared two new conjugates containing a longer aromatic shielding element. Napthylcyclohexylpentadiene **24** was prepared through olefination of aldehyde **8** with a phosphonium salt derived from 5-methyl-3*Z*-hexenol (Scheme 4).



Scheme 4

Naphthylmenthyl diene **28** was prepared from pulegone (Scheme 5). Copper-catalyzed addition of 2-naphthylmagnesium bromide, followed by base-catalyzed equilibration of the intermediate ketones, furnished a 4:1 trans/cis mixture of 2-(1-methyl-1-naphthylethyl)-4-methylcyclohexanone **25** from which the trans isomer could be purified by chromatography.[27,28] Kinetic enolization, followed by trapping with *N*-phenylbistriflysulfonimide, furnished the enol triflate (**26**). Palladium-mediated carbonylation afforded an unsaturated ester which was reduced with magnesium to furnish methyl ester **27** as a 95:5 mixture of the equatorial and axial epimers. Reduction and reoxidation afforded an aldehyde which underwent Wittig olefination with **23** to afford the *Z,Z*- diene (**28**) in good yield.



Scheme 5: Synthesis of Lengthened Auxiliaries:

The proximal and distal alkenes of both **24** and **28** were expected to undergo reaction with $^1O_2$ at similar rates, resulting in formation of regioisomeric perepoxides. Since each perepoxide could in theory decompose to

give two regioisomeric hydroperoxides, oxygenation might be expected to furnish four regioisomeric peroxides; this exact outcome has in fact been observed during oxidation of fatty acid 1,4-dienes.[5,29] However, the presence of terminal cyclohexyl and isopropyl groups limited the photooxygenation of **24** and **28** to formation of the conjugated 1'- and 5'-hydroperoxides. As illustrated in Figure 4, formation of the nonconjugated hydroperoxides is disfavored by the strained conformation required for hydrogen migration.[22]

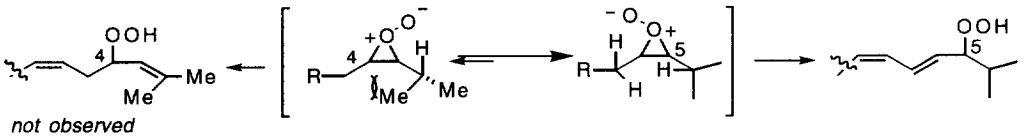
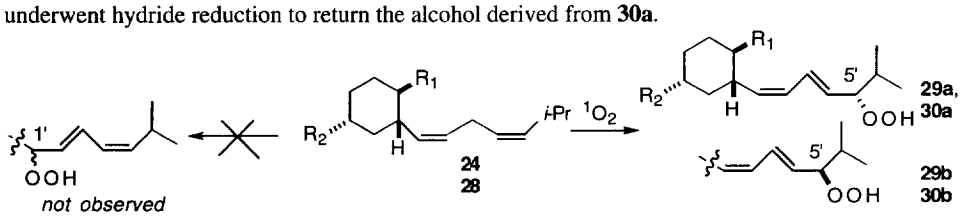


Figure 4: Control of Regioselection with Allylic Strain

Photooxygenation of dienes **24** and **28** was even more regioselective than anticipated, furnishing only the 5'-hydroperoxide isomers **29** and **30** (Scheme 6). Given the identical substitution pattern of the two alkenes, the complete selectivity for distal oxidation probably indicates greater accessibility of the distal alkene. However, while both auxiliaries appeared capable of providing significant shielding, the high degree of conformational freedom in the pentadiene sidechain apparently precluded stereoselective oxidation, as both dienes reacted to form nearly random mixtures of the two 5'-hydroperoxide diastereomers. Products are listed in order of elution; the indicated stereochemical assignments are based upon the observation that the dienone derived from **30ab** underwent hydride reduction to return the alcohol derived from **30a**.

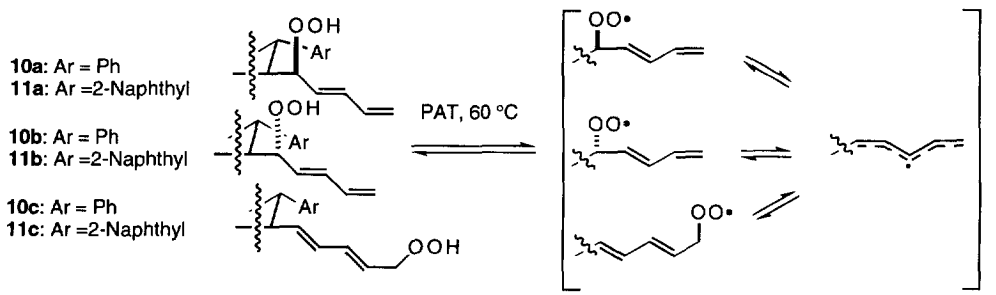


Starting Material	Reaction Conditions	Products	
24 R_1 = 2-naphthyl R_2 = H	TPP/CCl_4	**29a** (60%)	**29b** (40%)
24	RB/CH_3CN	(52%)	(48%)
28 R_1 = 1-methyl-1-(2-napthyl)ethyl R_2 = Me	TPP/CCl_4	**30a** (44%)	**30b** (56%)

Scheme 6: Oxidation of *Z,Z*- Heptadienes

Radical Equilibration

The proposed intermediacy of pentadienyl radicals during lipoxygenase-mediated peroxidation of fatty acid 1,4-dienes led us to investigate whether significant stereoselection could be achieved during oxygenation of auxiliary-tethered pentadienyl radicals.[16-18] Generation of pentadienyl radicals via abstraction of a bisallylic hydrogen is well-established as both an initiation and a chain-carrying step during free radical autoxidation of polyunsaturated fats.[4] However, free radical autoxidation of **3** proved frustatingly slow, even in the presence of radical initiators. Fortunately, pentadienyl radicals are also indirectly available from diene hydroperoxides. Radical abstraction of the peroxyl hydrogen proceeds with surprising facility to furnish diene peroxyl radicals which undergo reversible loss of oxygen to produce pentadienyl radicals (Scheme 7).[30,31]



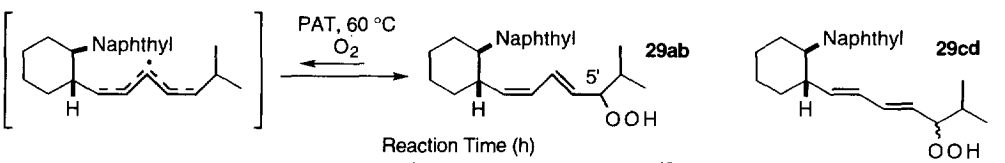
	Reaction Time (h)		
	0	1	2
10a	100	60	50
10b	0	4	5
10c	0	35	44

	Reaction Time (h)		
	0	1	2
10a	0	-	38
10b	100	-	13
10c	0	-	49

	Reaction Time (h)			
	0	1	2	23
11a	100	80	77	45
11b	0	3	3	6
11c	0	17	20	49

Scheme 7: Peroxyl Radical Equilibration

Isomerizations were performed with either 0.1 - 0.2 equivalents of either phenylazotriphenylmethane (PAT)[32,33] or di-*tert*-butylhyponitrite (DTBN) [33-36]under an atmosphere of O_2. Starting with either the major (**10a**) or minor (**10b**) diastereomers from the singlet oxygenations, radical isomerizations furnished a mixture of **10a**, **10b**, and the terminal hydroperoxide **10c** in which the ratio of **10a** to **10b** was consistently >3 : 1.[31] This result is not entirely surprising as the conformational and steric factors governing oxygenation of the pentadienyl radical are essentially identical to those discussed earlier for oxygenation of 1,4-pentadiene **3**.[4,37] However, the observed stereoselection clearly reflects kinetic and not thermodynamic selectivity. Continued equilibration led to a continued increase in the amount of **10c** and attempts to enter the equilibrium with isolated **10c** failed to produce detectable amounts of **10a** or **10b**.



		Reaction Time (h)						
		0	0.5	1	3	7	9	12
product distribution	**29a**	100	71	64	49	30	27	26
	29b	0	12	14	18	19	19	17
	29c,d	0	18	22	33	51	54	57

	0	0.5	1.5	3.5	7	9.5	13.0	18
29a	2	5	7	9	9.7	11.7	15	24
29b	98	83	69	55	38.6	28.6	19	16
29c,d	0	12	24	36	51.7	59.7	66	61

Scheme 8: Equilibration of Diene Hydroperoxides **29ab**

We next turned to the pentadienyl radicals derived from the isopropyl-substituted heptadienes **24** and **28**. The poor diastereoselectivity observed for addition of $^1O_2$ to the heptadienes seemed to result from the ability of the dienes to access a number of low-energy conformations and we expected improved results for oxygenation of the corresponding pentadienyl radicals, which were expected to be planar fragments with conformational preferences similar to diene **3**. As before, the pentadienyl radical was accessed via radical equilibration of the diene hydroperoxide. Equilibrations were conducted with PAT in benzene at 60 °C; aliquots were periodically withdrawn from the reaction and analyzed by HPLC. However, isomerization of either 5' diastereomer of the napthylcyclohexyl heptadiene hydroperoxides (**29a** or **29b**) proceeded with minimal stereoselection (Scheme 8). Surprisingly, only terminal (5') hydroperoxides were recovered, implying that the 1'-hydroperoxides may be disfavored by the steric costs associated with developing sp^3 character at this encumbered site. The failure to observe any 1'-hydroperoxide is particularly interesting in view of the fact that a mixture of diastereomeric 5'-hydroperoxy-1E,3E dienes **29cd** gradually accumulated to become the predominant isomerization product. Formation of E,E-diene hydroperoxides is well-precedented during autoxidation of polyunsaturated fats (Figure 5).[4] Loss of oxygen from a rotamer of a 1'-OOH Z,E-peroxyl radical affords an isomerized pentadienyl radical which undergoes readdition of oxygen at the 5'-position to produce the thermodynamically preferred E,E-diene peroxyl. Consequently, in spite of the failure to observe 1'-hydroperoxide, the Z to E isomerization provides strong evidence for the intermediacy of a 1'-peroxyl radical.

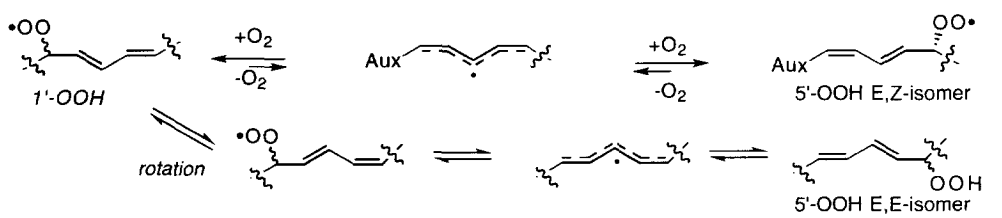
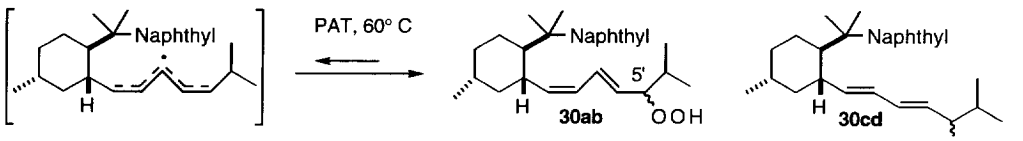


Fig. 5: Equilibration of Pentadiene Hydroperoxides

Our results may be related to observations made during lipoxygenase-mediated peroxidations of unnatural fats. Linoleic (9Z,1Z-octadecadienoic) acid undergoes lipoxygenase-mediated oxygenation to form Z,E-diene hydroperoxides (Fig. 1).[38] The same Z,E-diene hydroperoxide is also formed as the major product upon lipoxygenase-mediated peroxidation of the unnatural 9E,12Z-octadecadienoic acid isomer, a transformation which requires a 9E-to-9Z-isomerization.[38] Our results may indicate that this process could occur via the transient formation of a sterically disfavored 9-peroxyl 10,12-diene intermediate which can undergo rotation and loss of oxygen to form an isomerized pentadienyl radical.

The modest stereoselection and the rapid alkene isomerization both seemed to indicate ineffective shielding by the arylcyclohexyl auxiliary. The relationship of the sidechains in the 1,2-cyclohexyl-based systems is akin to a "widening V" with the aromatic/alkene distance increasing from 3 - 4 Å at the proximal alkene to 5 - 6 Å at the distal alkene.[21,28] We therefore anticipated that oxygenation of a pentadienyl radical derived from the naphthyl menthyl pentadiene **28**, which was anticipated to favor a conformation placing the pentadienyl fragment and the shielding arene parallel at a distance of 4 - 5 Å, might proceed with significantly improved diastereoselection. However, radical isomerization of either diastereomeric hydroperoxide (**30a** or **30b**)

returned a random mixture of stereoisomers (Scheme 9). Interestingly, the formation of E,E-diene hydroperoxide isomers (**30cd**) was greatly reduced relative to the phenylcyclohexyl series, an outcome which may indicate the increased steric constraints exerted by the naphthyl menthyl auxiliary on the intermediate pentadienyl or transient 1-peroxyl radicals, as discussed above. The failure of this shielding to translate into significant diastereoselection stands in sharp constrast to the diastereoselection seen in isomerizations of **10a** and **10b** and probably reflects a true equilibrium in which the product ratios represent only the negligible energy difference of the 5'-hydroperoxides rather than the selectivity of attack on the intermediate radical.



	Reaction Time (h) 0	7
30a	100	47
30b	0	45
30cd	0	<10

	Reaction Time (h) 0	10
30a	0	43
30b	100	43
30cd	0	<15

Scheme 9: Equilibration of Diene Hydroperoxides **30ab**

In summary, we have shown that a chiral auxiliary is able to induce diastereoselective peroxidation of a nonconjugated diene in a predictable manner based upon control of diene conformation and oxidant approach. However, control of oxygenation at a remote site clearly requires greater constraint of substrate conformation than can presently be achieved.

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EXPERIMENTAL PROCEDURES

NMR spectra were acquired in $CDCl_3$ at 300 MHz (^1H) and 75 MHz (^{13}C) unless otherwise indicated. Gas chromatographic (GC) measurements were performed using a 0.25 mm fused silica capillary column (J & W Scientific; Folsom, CA) and flame ionization detection. HPLC was performed with 4.6 mm x 25 cm (analytical) and 21.4 mm x 25 cm (preparative) silica columns using UV, RI, or evaporative light scattering detection. High resolution mass spectra were performed by the Nebraska Center for Mass Spectrometry.

(±)-2-Phenylcyclohexanemethanol (1): 1-Phenyl-1-cyclohexene [771-98-2] was obtained in 66% yield (5.558 g) by refluxing 1-phenylcyclohexanol (7.9482 g, 45.1 mmol) and *p*-toluenesulfonic acid (0.9393 g, 4.9 mmol) in benzene (90 mL) for 4.5 h, followed by concentration and flash chromatography (5% EA/hex).

To a 0 °C solution of the alkene (5.558 g, 35.1 mmol) in CH_2Cl_2 (70 mL) was added paraformaldehyde (1.1138 g, 37.1 mmol), followed by Me_2AlCl (50 mL, 1.0M solution in hexane); the resulting brown solution was stirred for 10 min. The reaction mixture was quenched with excess 10% NaOH, forming a white precipitate which was dissolved by the addition of 1*M* H_2SO_4. Extraction (40% EA/hex) and drying over Na_2SO_4, followed by flash chromatography (10% EA/hex) afforded 5.578 g (84%) of a 2-phenyl-2-cyclohexene-1-methanol [27831-78-3] as a yellow oil.

A mixture of the alcohol (5.578 g, 29.6 mmol) and Pt/C (2.902 g, 5 mol% Pt) in ethyl acetate (60 mL) was placed under a balloon of H_2 for 20 h. Following filtration through a silica plug, flash chromatography (10% EA/hex) afforded 5.295 g (94%) of the saturated alcohol as a mixture of cis and trans isomers: R_f= 0.16 in 10% EA/hex; UV λ_{max} 203 nm (ε = 14,400, hexane); IR (neat) 3332 cm^{-1}; Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.23; H, 9.74. A small sample was purified by NP-HPLC (25% EA/hex), the *trans* and *cis*-isomers eluting at 20.2 and 21.6 minutes, respectively. *Trans*-**1**: ^{1}H NMR δ 7.30-7.15 (m, 5H), 3.34 (dd, 1H, J = 11.9, 6.3), 3.19 (dd, 1H, J = 11.9, 6.3), 2.31 (dt, 1H, J = 11.4, 3.3), 2.1-1.1 (10H); ^{13}C NMR δ 145.7, 128.5, 127.3, 126.1, 66.4, 47.2, 45.1, 35.4, 29.8, 26.6, 26.0. *Cis*-**1**: ^{1}H NMR δ 7.29-7.16 (m, 5H), 3.49 (dd, 1H, J = 10.9, 8.9), 3.30 (dd, 1H, J = 10.9, 5.1), 2.89 (dt, 1H, J = 7.7, 4.6), 2.08-1.38 (10H); ^{13}C NMR δ 144.9, 128.1, 127.3, 125.8, 60.4, 44.4, 42.7, 27.6, 26.1, 26.0, 20.8.

***trans*-2-Phenylcyclohexanecarboxaldehyde (2)** [55278-47-2]: To a -78 °C solution of oxalyl chloride (1.4 mL, 15.9 mmol, freshly distilled) in CH_2Cl_2 (30 mL, dried over 4Å molecular sieves) was added DMSO (2.25 mL, 31.7 mmol). After 2-3 min, a solution of **1** (2.3167 g, 12.2 mmol) in CH_2Cl_2 (10 mL) was added over a 10 min period. The reaction was stirred for 15 minutes whereupon Et_3N (8.4 mL, 60 mmol) was added. After 5 min, the reaction was allowed to warm to RT and diluted with H_2O. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with aq. sat. NaCl, and dried over Na_2SO_4. Purification by flash chromatography (2.5% EA/hex) afforded 1.9064 (83%) of the aldehyde as a 1 : 1.4 mixture of cis and trans isomers based upon the signals at δ 9.58 and δ 9.41. The mixed aldehydes (1.9064 g, 10.1 mmol) in THF (40 mL) were equilibrated with potassium *tert*-butoxide (0.0617 g, 0.55 mmol) for 15 h at RT. The reaction was concentrated and directly subjected to flash chromatography (2.5% EA/hex) to afford 1.3336 g (70%) of pure *trans*-aldehyde: ^{1}H-NMR (360 MHz) δ 9.41 (d, 1H, J = 2.9), 7.31-7.16 (m, 5H), 2.74 (dt, 1H, J = 11.5, 3.5), 2.60 (m, 1H), 2.0-1.3 (8H); ^{13}C-NMR (50 MHz) δ 204.2, 143.9, 128.4, 127.1, 126.4, 55.0, 44.9, 34.6, 26.4, 25.9, 24.6.

2-Phenylcyclohexyl-1*Z*,4-pentadiene (3): To a 0 °C solution of (3-butenyl)triphenylphosphonium bromide (2.6673 g, 6.7 mmol) and HMPA (2.4 mL, 13.8 mmol) in dry THF (9 mL) was added dropwise a solution of LiN(TMS)$_2$ (7.5 mL, 1.0*M* in THF). The red solution was stirred for 30 min at 0° C and then cooled to -78 °C. A solution of aldehyde (0.8546 g, 4.5 mmol) and HMPA (1.5 mL, 8.6 mmol) in THF (4.5 mL) was added dropwise. After 10 min, the reaction was warmed to -20 °C and stirred for 20 min before being quenched with H_2O. Extraction (40% EA/hex) and drying over Na_2SO_4 afforded an oil which was purified by flash chromatography (1% EA/hex) to afford 0.6270 g (61%) of the diene as a 98:2 mixture of 1*Z*:1*E* isomers accompanied by 0.135 g of recovered aldehyde: GC analysis: RT= 11.8 min (1*E*) and 12.2 min (1*Z*), 140 °C-170 °C at 1 °C/min; R_f = 0.72 in 10% EA/hex; ^{1}H NMR (500 MHz) δ 7.24-7.11 (m, 5H), 5.51 (m, 1H, C**H**=CH$_2$; collapses to dd, J = 17.3, 9.2 when δ 2.55 irradiated), 5.08 (m, 2H, CH-C**H**=C**H**-CH$_2$; collapses to 5.11, d, J = 10.8 and 5.06, d, J = 11.0 when δ 2.55 irradiated), 4.84 (apparent dd, 2H, J = 13, 1.6, CH=C**H**$_2$), 2.62 (m, 1H, CH-HC**H**-CH; collapses to dd, J = 15.0, 6.5 when δ 5.05 irradiated), 2.49 (m, 2H, R$_2$**H**-CH=CH, and CH-**H**CH-CH; simplifies when irradiated at δ 5.05 and 2.65), 2.27 (dt, 1H, J = 11.2, 3.3, C**H**-Ph), 1.94-1.17 (m, 8H); ^{13}C NMR (125 MHz) δ 146.3, 137.1, 135.4, 128.0, 127.6, 125.8, 125.7, 114.5, 50.2, 41.7, 34.9, 33.8, 31.8, 26.6, 26.0; Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.17; H, 9.89.

E-**3**: To a solution containing (3-butenyl)triphenylphosphonium bromide (0.758 g, 1.9 mmol) in dry THF (3 mL) at -78 °C was added dropwise *n*-BuLi (0.83 mL, 2.5*M* solution in hexane). The red solution was stirred for 5 min whereupon a solution of aldehyde (0.299 g, 1.6 mmol) in dry THF (2 mL) was added dropwise. After 5 min at -78 °C, additional *n*-BuLi (2.1 mmol) was added; the resulting solution was maintained at -78 °C for 5 min and then quenched with *t*-BuOH (0.2 mL, 2 mmol). The opaque solution was allowed to warm to RT and subjected to an extractive workup. Flash chromatography (2.5% EA/hex) afforded 0.273 g (76%) of the diene (colorless oil) as a 44:56 Z:E mixture according to GC.

2-(4-Methoxyphenyl)cyclohexanemethanol (4): To a 0 °C mixture of 4-methoxyphenyl cyclohexene (0.77 g, 4.2 mmol) and paraformaldehyde (148 mg, 4.6 mmol)in CH_2Cl_2 (10 mL) was added Me_2AlCl (6.0 mL, 5.9 mmol, 1M in hexanes) while sweeping the reaction flask with nitrogen gas. After 20 minutes, 10% NaOH was added dropwise until foaming had ceased. Sufficient 1 N H_2SO_4 was then added to dissolve most of the alumina. The reaction was diluted with water and extracted with CH_2Cl_2 (3 x 25 mL). The organic extracts were dried over Na_2SO_4, and concentrated. The crude product was filtered thorugh silica with 20% EA/hex and carried on without further purification.

A mixture of the cyclohexene (1.6 g, 7.33 mmol) and 5% Pt/C (1.1 g) in ethyl acetate (15 mL) was placed under a balloon of H_2 and stirred overnight. After flushing with N_2, the reaction was filtered through silica

(EA). Chromatography (20% EA/hex) afforded 1.38 g (86%) of **4** as a mixture of cis and trans isomers: R_f= 0.08 (10% EA/hex); ^{1}H NMR δ 7.15 (minor), 7.12 (major) (d, 2H, J = 8.8), 6.86 (major) 6.83 (minor) (d, 2H, J = 8.6), 3.78 (s, 3 H), 3.60-3.25 (m, 2 H), 2.90 (dt, 1 H, *J* = 7.6, 4.5), 1.07-2.26 (m, 10 H), ^{13}C NMR (major) δ 157.8, 137.8, 128.3, 113.7, 66.6, 55.2, 46.4, 45.4, 35.6, 29.9, 26.7, 26.1; IR (neat) 3361 cm^{-1}; Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found C, 76.14; H, 9.09.

2-(4-Methoxyphenyl)cyclohexanecarboxaldehyde (5): By a similar procedure as employed for **2**, oxidation of **4** (1.79 g, 8.1 mmol) furnished, after flash chromatography (5% EA/hex), 1.21 g (68%) of the aldehyde: R_f = 0.34 (10% EA/hex); ^{1}H NMR δ 9.40 (d, 1 H, *J* = 3.1), 7.13-6.81 (m, 4 H), 3.75 (s, 3 H), 2.68 (dt, 1 H, *J* = 11.2, 3.4), 2.48-2.62 (m, 1 H), 1.80-2.40 (m, 8 H) ; ^{13}C NMR δ 204.7, 158.1, 136.1, 128.2, 114.0, 55.5, 55.1, 44.2, 34.9, 26.6, 26.0, 24.8; IR (neat) 2931, 1724 cm^{-1}; Anal. calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found C, 76.89; H, 8.41.

2-(4-Methoxyphenyl)cyclohexyl-1Z,4-pentadiene (6): By a procedure similar to that employed for the synthesis of **3**, aldehyde **5** (142 mg, 0.65 mmol) was reacted with the ylide derived from (3-butenyl) triphenylphosphonium bromide (660 mg, 1.6 mmol) and $NaN(TMS)_2$ (1.4 mL, 1.0 M in THF) to furnish, after flash chromatography (1% EA/hex), 113 mg (68%) of pentadiene **6**: R_f = 0.66 (10% EA/hex); ^{1}H NMR δ 7.05-6.76 (m, 4 H), 5.57 (m, 1 H), 5.09 (m, 2 H), 4.84 (m, 2 H), 3.76 (s, 3 H), 2.52 (m, 2H), 2.22 (dt, 1 H, J = 11.2, 3.1), 1.1-2.0 (theory 8H, observed 10 H) ; ^{13}C NMR δ 157.6, 138.6, 137.2, 135.6, 128.4, 125.6, 114.5, 113.4, 55.2, 49.4, 41.9, 35.9, 33.9, 31.7, 26.7, 26.0; Anal. calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found C, 84.12; H, 9.26.

2-(2-Naphthalene)cyclohexane-1-methanol (7): A solution of cyclohexanone (5.21 g, 53 mmol) in 10 mL THF was slowly added to a THF solution of the Grignard reagent prepared from 2-bromonaphthalene (10.34 g, 50 mmol). The reaction was quenched after 3 h by the addition of sat. aq. NH_4Cl (50 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (25 mL) and sat. aq. NaCl (25 mL) and dried over Na_2SO_4. The crude alcohol was dissolved in benzene (100 mL) along with $TsOH{\cdot}H_2O$ (0.45 g, 0.24 mmol) and the reaction was refluxed for 3h. Concentration, followed by flash chromatography, afforded 9.1 g (88%) of napthalenecyclohexene as a white solid: m.p. 59.5 - 60.5°C. lit. 60 - 61°C.[39]

By a similar procedure as used for **4**, napthalenecyclohexene (4.16 g, 0.020 mol.) and paraformaldehyde (0.72 g, 23 mmol) were reacted in the presence of Me_2AlCl (30 mL of a 1M solution in CH_2Cl_2) to afford, after chromatography (25% EA/hex), 3.90 g (82%) of the alkenol: m.p.107-108.5°C; R_f= 0.37 (20% EA/hex); ^{1}H NMR δ 7.82 (m, 4 H), 7.48 (m, 3 H). 6.20 (t, 1 H, J = 3.9), 3.56 (m, 2 H), 3.08 (m, 1 H), 2.26 (m, 2 H), 1.60-2.10 (m, 4 H). ^{13}C NMR δ 139.5, 137.9, 133.5, 132.5, 129.6, 127.9, 127.8, 127.5, 126.0, 125.5, 124.9, 124.3, 64.6, 38.8, 26.1, 25.2, 18.7. IR (neat) 3340 cm^{-1}; Anal. calcd. for $C_{17}H_{18}O$, C: 85.67, H: 7.61, found, C: 85.82, H: 7.40.

A mixture of the unsaturated alcohol (3.90 g, 16.4 mmol) and 5% Pd/C (0.55 g) in ethyl acetate (100 mL) was stirred under a balloon of H_2 until all starting material was consumed (10 h). After removal of the catalyst by filtration, the crude products were purified by flash chromatography (20% EA/hex) to afford 3.80 g (96%) of alcohol **7** as a partially resolved 88:12 mixture of cis:trans isomers: *cis*-**7**: m.p. 90-91°C; R_f = 0.42 (20% EA/hex); ^{1}H NMR δ 7.79 (m , 3 H), 7.61(s, 1 H), 7.47 (m, 3 H), 3.59 (dd, 1 H, J = 11.0, 8.9) , 3.40 (dd, 1 H, J = 11.0, 5.1), 3.10 (m, 1 H), 2.25 (m, 1 H), 2.06-1.85 (m, 4H), 1.66-1.46 (m, 4 H) ^{13}C NMR δ 142.6, 133.5, 132.0, 127.8, 127.7, 127.5, 126.8, 125.9 125.3, 125.1, 60.9, 44.6, 42.8, 28.0, 26.3, 26.2, 21.0; IR (neat) 3332 cm^{-1}; Anal. calcd. for $C_{17}H_{20}O$, C: 84.96, H: 8.36, found, C: 85.15, H, 8.13. *trans*-**7**: R_f = 0.39 (20% EA/Hex); ^{1}H NMR δ 7.80 (m, 3 H), 7.64 (s, 1 H), 7.43 (m, 3 H), 3.41 (dd, 1 H, J = 11.0, 3.8), 3.26 (dd, 1 H, J = 11.0, 6.2), 2.50 (dt, 1 H, J = 11.7, 3.6), 2.06-1.28 (m, 10 H).

2-(2-Naphthalene)cyclohexanecarboxyaldehyde: (8) By a similar procedure as used for **5**, oxidation of alcohol **7** (3.6 g, 15 mmol) afforded a mixture of cis/trans isomers which was equilibrated with potassium *tert*-butoxide to afford, after concentration and flash chromatography, 2.79 g of the trans aldehyde as a white solid: M.p. 85-86°C; R_f = 0.44 (10% EA/hex); ^{1}H NMR δ 9.46 (d, 1 H, J = 2.9), 7.79 (m, 3 H), 7.65 (s, 1 H), 7.43 (m, 3 H), 2.93 (dt, 1 H, J = 11.7, 3.6), 2.76 (m, 1 H), 2.04-1.90 (m, 4 H), 1.65-1.45 (m, 4 H); ^{13}C NMR δ 204.9, 141.6, 133.5, 132.4, 128.4, 127.6, 126.1, 125.8, 125.5, 55.2, 45.3, 34.9, 26.7, 26.1, 24.9; IR (neat) 2916, 1728 cm^{-1}; Anal. calcd for $C_{17}H_{18}O$, C: 85.67, H: 7.61, found, C: 85.63, H: 7.39.

2-(2-napthyl)cyclohexyl-1Z,4-pentadiene (9): By a similar procedure as was employed for **6**, olefination of **8** (0.72 g, 3.0 mmol) with the ylide derived from 3-butenyl triphenylphosphonium bromide (7.5 mmol) afforded, after flash chromatography (1% EA/hex), 0.77 g (92%) of the pentadiene as a colorless oil: R_f = 0.60 (1% EA/hex); ^{1}H NMR δ 7.73 (m, 3 H), 7.53 (s, 1 H), 7.32 (m, 3 H), 5.49 (m, 1 H), 5.15 (m, 1 H), 5.05 (m, 1 H), 4.78 (m, 2 H), 2.67 (m, 2 H), 2.50 (m, 2 H), 1.92-1.32 (m, 8 H); ^{13}C NMR δ 143.9, 137.1,

135.5, 133.6, 132.3, 127.6, 126.4, 126.0, 125.8, 125.7, 125.0, 114.5, 50.6, 41.6, 35.2, 33.9, 31.8, 26.7, 26.1; Anal. calcd. for $C_{21}H_{24}$, C: 91.25, H: 8.75, found, C: 91.46, H: 8.60.

Photooxygenations-Sample Procedure: A water-jacketed glass cell containing a solution of **3** (51.7 mg, 0.23 mmol) in a solution of 5, 10, 15, 20-tetraphenyl-21*H*, 23*H*-porphine in CCl_4 (0.46 mL, 2.5 mM) was irradiated at a distance of 4 cm with a 150 W illuminator for 15 min under continuous O_2 aspiration. The solution was stabilized with a small amount of 2,6-di-*tert*-butyl-4-methylphenol (BHT) (0.1 M in Et_2O) and concentrated. The three hydroperoxides were separated by NP-HPLC (5% EA/hex) with retention times of 8.9 (**10a**), 10.0 (**10b**), and 13.6 (**10c**) min, respectively; only traces of **10c** were detected in photooxygenations. The separated hydroperoxides were concentrated after stabilization with ~0.1% BHT. Photooxygenations in CH_3CN were conducted by the same procedure but with Rose Bengal as a sensitizer.

1-(*trans*-2-Phenylcyclohexyl)-2*E*,4-pentadienyl hydroperoxide (10a): R_f=0.32 in EA/hex; ^{1}H NMR δ 7.56 (s, 1H, CHOO**H**), 7.36-7.18 (m, 5H, phenyl), 6.31 (dt, 1H, J = 16.8, 10.4, CH-C**H**=CH_2), 6.07 (dd, 1H, J = 14.5, 10.5, CH=C**H**-CH=CH_2), 5.72 (dd, 1H, J = 15.3, 7.5, CHOOH-C**H**=CH), 5.17 (d, 1H, J = 16.9, CH=C**H**$_2$), 5.09 (d, 1H, J = 10.3, CH=C**H**$_2$), 4.08 (dd, 1H, J = 7.4, 2.1, C**H**OOH), 2.69 (dt, 1H, J = 11.5, 3.9, C**H**-Phenyl), 1.88-1.24 (m, 9H). ^{13}C NMR δ 145.7, 136.2, 133.6, 131.7, 128.6, 127.6, 126.2, 117.8, 86.2, 47.8, 46.6, 35.7, 26.5, 25.5.

1-(*trans*-2-Phenylcyclohexyl)-2*E*,4-pentadienyl hydroperoxide (10b): ^{1}H-NMR (360 MHz) δ 7.52 (s, 1H, -OO**H**), 7.33-7.14 (m, 5H, phenyl), 6.33 (dt, 1H, J = 17.0, 10.3, CH-C**H**=CH_2), 5.99 (dd, 1H, J = 15.3, 10.6, CH=C**H**-CH=CH_2), 5.63 (dd, 1H, J = 15.4, 8.7, CHOOH-C**H**=CH), 5.21 (d, 1H, J = 17.0, CH=C**H**$_2$), 5.15 (d, 1H, J = 9.4, CH=C**H**$_2$), 4.06 (dd, 1H, J = 8.8, 2.6, C**H**OOH), 2.22 (m, 2H, R_2C**H**-Ph and R_2C**H**-CHOOH), 2.0-1.2 (8H).

1-[2-(4-Methoxyphenyl)cyclohexyl]-2,4-pentadienyl hydroperoxide (11a): Pentadiene **6**(150mg, 0.59 mmol) was oxygenated with TPP/CCl_4 for 10 min under similar conditions as employed for **3**. The crude products were filtered through silica gel and subjected to NP-HPLC (5% EA/hex) to quantify hydroperoxides **11a** (16.0 minutes) and **11b** (18.5 min): **11a**: R_f = 0.35 (10% EA/hex); ^{1}H NMR δ 7.49 (s, 1 H, 7.16-6.85 (m, 4 H), 6.27 (dt, 1 H, *J* = 17.2, 10.3), 6.06 (dd, 1 H, *J* = 15.3, 10.5), 5.72 (dd, 1 H, *J* = 15.4, 7.6), 5.19 (d, 1 H, *J* = 16.7), 5.10 (d, 1 H, *J* = 10.4), 4.08 (dd, 1 H, *J* = 7.4, 2.0), 3.80 (s, 3 H), 2.63 (dt, 1 H, *J* = 11.2, 3.1), 2.0-1.0 (9 H) ; ^{13}C NMR δ 158.0, 137.8, 136.2, 133.7, 131.8, 128.5, 117.8, 113.9, 86.2, 55.2, 48.1, 45.7, 35.8, 26.60, 26.56, 25.7. Insufficient quantities of **11b** were recovered for spectral analysis.

1-(*trans*-2-(2-Napthyl)cyclohexyl)-2*E*,4-pentadienyl hydroperoxide (12a): Photooxidation of **9** (100 mg 0.36 mmol) in a solution of 0.6 mM TPP/CCl_4 (3.6 mL) was conducted under similar conditions as employed for **3.** The ratio of products was determined by NP-HPLC (1% EtOH/hex), **12a** (91%) eluting at 7.3-7.6 min and **12b** (9%) eluting at 8.5-8.7 minutes. **12a**: R_f = 0.37 (10% EA/hex); ^{1}H NMR δ 7.82 (m, 3 H, Ph), 7.69 (s, 1 H), 7.51 (s, 1 H) 7.44 (m, 3 H,), 6.29 (dt, 1H, J = 16.9, 10.3), 6.03 (dd, 1 H, J = 15.3, 10.5), 5.73 (dd, 1 H, J = 15.5, 7.6), 5.11 (d, 2 H, J = 16.9, 10.3), 4.10 (d, 1 H, J = 7.5), 2.85 (dt, 1 H, J = 11.7, 3.3), 1.93-1.32 (m, 9 H); ^{13}C NMR δ 143.2, 136.1, 133.8, 132.4, 131.6, 128.1, 127.6, 126.2, 126.1, 126.0, 125.2, 117.9, 86.2, 47.7, 46.7, 35.7, 26.6, 25.6. **12b**: ^{1}H NMR δ 7.82 (m, 3 H), 7.55 (s, 1 H), 7.44 (m, 4 H), 6.35 (dt, 1H, J = 17, 10), 5.95 (dd, 1 H, J = 15, 10), 5.68 (dd, 1 H, J = 15, 8), 5.19 (d, 2 H, J = 17), 5.15 (d, 1H, J = 10), 4.10 (dd, 1 H, J = 10,3), 2.4 (m, 1H), 2.35 (m, 1H), 1.93-1.32 (9 H).

1-(*trans*-2-Phenylcyclohexyl)-2*E*,4-pentadien-1-ol (13ab): The mixture of hydroperoxides was dissolved in 1 mL of ethyl acetate and a solution of Ph_3P (0.1 mL, 1.0*M* in EA) was added. The solution was stirred for 5 min and then filtered through silica gel to remove triphenylphosphine oxide. Product ratios were determined by comparison of peaks at 7.1 min and 10.3 min in the NP-HPLC (10% EA/hex), averaging 88.1% **13a** and 11.9% **13b**. *First eluting* **(13a):** R_f=0.31 in 10% EA/hex; ^{1}H NMR (500 MHz) δ 7.31-7.18 (m, 5H), 6.29 (dt, 1H, J = 17.0, 10.2), 6.07 (dd, 1H, J = 15.3, 10.5), 5.67 (dd, 1H, J = 15.3, 5.2), 5.13 (d, 1H, J = 16.9), 5.02 (d, 1H, J = 10.1), 3.89 (s, 1H), 2.64 (dt, 1H, J = 11.6, 3.0), 1.87-1.76 (m, 4H), 1.66 (m, 1H), 1.37-1.21 (5H); ^{13}C NMR (125 MHz) δ 145.8, 136.5, 136.3, 130.2, 128.6, 127.7, 126.2, 116.5, 71.9, 48.4, 46.5, 35.7, 26.7, 26.3, 24.9; IR (neat) 3417 cm^{-1}; UV λ_{max} 228 nm (ε = 34,000, hexane); Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.12; H, 9.20. **13b:** R_f=0.25 in 10% EA/hex; ^{1}H NMR (360 MHz) δ 7.32-7.16 (m, 5H), 6.32 (dt, 1H, J = 17.0,10.3), 5.97 (dd, 1H, J = 15.4, 10.4), 5.67 (dd, 1H, J = 15.4, 7.2), 5.15 (d, 1H, J = 17.0), 5.07 (d, 1H, J = 10.1), 3.89 (dd, 1H, J = 7.0, 3.3), 2.24 (dt, 1H, J = 1.6, 3.3), 2.06-1.11 (m, 10H); ^{13}C NMR δ 145.6, 136.4, 132.6, 132.4, 128.5, 127.5, 126.2, 117.2, 73.2, 48.3, 47.2, 36.5, 26.7, 25.9, 25.6; $C_{17}H_{22}O$ (M^+), calcd 242.1671, obs. 242.1670.

1-[*trans*-2-(4-Methoxyphenyl)cyclohexyl-2E,4-pentadienol (14ab) was prepared in the same manner as **13ab**. NP-HPLC (10% EA/hex) was performed to purify the major product, **14a**: R_f = 0.33 (10%

EA/hex) ; ^{1}H NMR δ 7.16-6.84 (m, 4 H), 6.27 (dt, 1 H, *J* = 17.0, 10.1), 6.06 (dd, 1 H, *J* = 15.1, 10.7), 5.69 (dd, 1 H, *J* = 15.5, 5.4), 5.14 (d, 1 H, *J* = 16.9), 5.02 (d, 1 H, *J* = 10.1), 3.90 (s, 1 H), 3.78 (s, 3 H), 2.58 (dt, 1 H, *J* = 11.7, 3.2), 1.0-2.0 (m, 10 H) ; ^{13}C NMR δ 157.9, 137.9, 136.5, 133.3, 130.2, 128.4, 117.8, 116.6, 71.9, 55.2, 48.1, 46.3, 35.8, 26.6, 26.3, 25.0 ; HRMS m/z calcd. for $C_{18}H_{24}O_2Li$ $[M^+Li]^+$: 279.1936. Found: 279.1936. Insufficient quantities of **14b** were obtained for characterization.

1-[*trans*-2-(2-Napthyl)cyclohexyl]-2*E*,4-pentadienol (15ab) was prepared in the same manner as **13ab** and purified by NP-HPLC (10% EA/hex): **15a**: R_f = 0.29 (10% EA/hex), ^{1}H NMR δ 7.77 (m, 3 H), 7.66 (s, 1 H), 7.41 (m, 3 H), 6.25 (dt, 1 H, J = 16.9, 10.3), 6.03 (dd, 1 H, J = 15.3, 10.5), 5.67 (dd, 1 H, J = 15.3, 5.4), 5.13 (dd, 1H, J =17.0, 1.0), 5.07 (d, 2H, J = 10.3), 3.88 (d, 1 H, J = 5.3), 2.80 (dt, 1 H, J = 11.6, 3.1), 1.88-1.22 (9 H). ^{13}C NMR δ 143.3, 136.4, 136.2, 133.7, 132.4, 130.2, 128.2, 127.7, 127.6, 126.3, 125.9, 125.2, 116.7, 71.9, 48.3, 46.7, 35.6, 26.7, 26.3, 24.8. IR (neat): 3419 cm^{-1}; MS calcd for $C_{21}H_{24}O$ 292.1821, found 292.1824. Insufficient quantities of **15b** were obtained for characterization.

1-*trans*-2-Phenylcyclohexyl-2*E*,4-pentadien-1-one (16): To a solution of alcohols **13ab** (16 mg, 0.07 mmol) in CH_2Cl_2 (0.150 mL) was added pyridinium chlorochromate (20 mg, 0.09 mmol). After 2.5 h additional PCC (19 mg, 0.09 mmol) was added. The reaction was stirred an additional 3.5 h and diluted with anhydrous Et_2O (0.5 mL). After filtration through Florisil with Et_2O, the solution was concentrated and subjected to HPLC (5% EA/hex) to afford 9.5 mg (60%) of the ketone as a white solid: R_f=0.39 in 10% EA/hex; ^{1}H NMR (500 MHz) δ 7.26-7.10 (5H), 6.94 (dd, 1H, J = 15.3, 10.9), 6.30 (dt, 1H, J = 16.9, 10.5), 5.97 (d, 1H, J = 15.7), 5.55 (d, 1H, J = 16.5), 5.45 (d, 1H, J = 10), 2.99 (dt, 1H, J = 11.2, 3.3), 2.87 (dt, 1H, J = 11.4, 3.5), 2.00-1.80 (4H), 1.65-1.40 (4H); ^{13}C NMR (125 MHz) δ 203.1, 144.9, 142.2, 135.3, 129.8, 128.3, 127.3, 126.3, 126.1, 54.4, 46.0, 34.5, 30.2, 26.2, 25.7; IR (neat) 1653 cm^{-1}; UV λ_{max} 259 (ε=12,400, hexane). $C_{17}H_{20}O$ (M^+) calcd 240.1514, obs. 240.1506.

Reduction of 16 to 13b: To a 0 °C solution of ketone **16** (10 mg, 0.04 mmol) in THF (0.4 mL) was added LAH (0.1 mL, 1.0*M* in THF). After 10 min, the reaction was quenched by sequential addition of water (0.1 mL), 15% NaOH (0.1 mL) and water (0.3 mL). Na_2SO_4 was added and the solution was filtered through Celite. Analysis as described for **13ab** above indicated 11.6% **13a** and 88.4% **13b**.

***trans*-2-(1*Z*-Hexenyl)-cyclohexanol (17)**: To a -78 °C solution of 1-hexyne (6.90 mL, 60.0 mmol) in toluene (100 mL)was added nBuLi (24.0 mL, 2.5M in hexanes) and the reaction was stirred for 35 min. Et_2AlCl (34.0 mL, 1.8M in toluene) was then added; after 10 min, the reaction mixture was allowed to warm to RT. After 1 h, the reaction mixture was recooled to -78 °C and cyclohexene oxide (3.00 mL, 29.6 mmol) was added. The resulting reaction was allowed to warm to RT and stirred for 22 h before being quenched into a mixture of 10% HCl (300 mL) and ice (400 mL). The mixture was extracted with CH_2Cl_2 (4x150 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification by flash column chromatography (7-12%EA/hex) gave 3.445 g (64%) of *trans*-2-(hex-1-ynyl)-cyclohexanol as a colorless oil: R*f* = 0.61 (20% EA/hex); ^{1}H NMR δ 3.45-3.33 (1 H), 2.47 (s, 1 H), 2.18 (t, 2 H, J = 6.9), 2.12 (m, 1 H), 2.04-1.90 (2 H), 1.75 (m, 1 H), 1.65 (m, 1 H), 1.54-1.36 (5 H), 1.32-1.10 (5 H), 0.91 (t, 3 H, J = 6.9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 82.7, 81.1, 73.8, 39.0, 32.9, 31.3, 31.1, 24.9, 24.2, 21.9, 18.3, 13.5; IR (ATR) 3393 cm^{-1}; Anal. Calcd for $C_{12}H_{20}O$: C, 79.06; H, 12.16. Found: C, 79.15; H, 11.98.

To a mixture of 5% Pd on $CaCO_3$/Pb (0.160g) and quinoline (0.250 mL from stock solution containing 1 drop quinoline in 2.0 mL EtOH) in EtOH (46.0 mL),under a hydrogen balloon was added a solution of alkynol (0.907g, 5.03 mmol) in EtOH (4.0 mL). After 4.5 hrs, the reaction mixture was filtered through Celite and concentrated in vacuo to give 0.844 g (92%) of alkenol **17** as a colorless oil: ^{1}H NMR δ 5.56 (dt, 1 H, J = 10.5, 7.2), 5.17 (t, 1 H, J = 10.2), 3.20 (m, 1 H), 2.24 (m, 1 H), 2.18-1.90 (4 H), 1.78 (s, 1 H), 1.64 (m, 2 H), 1.40-1.04 (8 H), 0.91 (m, 3 H); ^{13}C NMR δ 132.9, 131.6, 73.6, 44.6, 33.4, 31.9, 31.3, 27.3, 25.1, 24.6, 22.2, 13.7; IR (ATR) 3442 cm^{-1}; HRMS m/z calcd. for $C_{12}H_{22}O$ $[M]^+$: 182.1671. Found: 182.1668.

***trans*-2-(1-Hydroperoxyhex-2*E*-enyl)-cyclohexanol (18)**: Photoxygenation of **17** (0.060g, 0.33 mmol) under similar conditions as employed for diene **3** furnished, after flash chromatography (24% EA/hex), 0.045 g (64%%) of a colorless oil along with 20% of recovered starting material: R*f* = 0.27 (40% EA/hex); ^{1}H NMR δ 9.67 (bs, minor), 9.62 (bs, major), 5.84-5.71 (m, minor), 5.59-5.38 (m, major), 4.50 (dd, J = 8.1, 2.4, minor), 4.31 (t, J = 8.1, major), 3.70-3.49 (m, 2 H), 2.13-1.96 (m, 3 H), 1.74-1.52 (m, 4 H), 1.48-1.38 (m, 2 H), 1.36-1.08 (m, 4 H), 0.92 (t, 3 H, J = 7.5); ^{13}C NMR δ 137.54 (major), 137.46 (minor), 126.9 (major), 125.1 (minor), 92.0 (major), 89.1 (minor), 74.1 (major), 71.2 (minor), 47.1 (minor), 46.6 (major), 34.9 (minor), 34.8 (major), 34.5 (minor), 34.4 (major), 27.2 (major), 26.4 (minor), 25.3 (minor), 25.0 (major), 24.40 (minor), 24.37 (major), 22.1, 13.64 (minor), 13.60 (major); IR (ATR) 3292 cm^{-1}.

***trans*-2-(1Hydroxyhex-2*E*-enyl)-cyclohexanol (19)**: Reduction of hydroperoxide **18** (0.165g/0.774 mmol) with Ph_3P (0.212g, 0.808 mmol) under similar conditons as employed for **10ab**, afforded **19** (0.139g, 91% as a pale yellow oil: R*f* = 0.30 (40% EA/hex); ^1H NMR δ 5.73-5.58 (m, 2 H), 4.16 (bs, 1 H), 3.62 (dt, 1 H, J = 9.6, 3.9), 3.26 (bs, 1 H), 2.87 (bs, 1 H), 2.10-1.94 (m, 3 H), 1.80-1.61 (m, 4 H), 1.47-1.34 (m, 2 H), 1.32-1.14 (m, 3 H), 0.92 (t, J = 7.2, major), 0.90 (t, J = 7.2, minor); ^{13}C NMR δ 134.1 (minor), 133.5 (major), 131.5 (minor), 129.3 (minor), 80.0 (minor), 76.9 (major), 75.9 (minor), 72.1 (major), 49.1 (major), 48.6 (minor), 35.6 (major), 35.3 (minor), 34.4 (major), 34.2 (minor), 27.7 (minor), 27.1 (major), 25.4 (major), 25.2 (minor), 24.6 (minor), 24.4 (major), 22.4 (major), 22.2 (minor), 13.7; IR (ATR) 3323 cm^{-1}; HRMS m/z calcd. for $C_{12}H_{22}O_2$ $[M - H]^+$: 197.1542. Found: 197.1541.

***trans*-2-(1Hydroxyhex-2*E*-enyl)-cyclohexanol, acetonide (20):** To a solution of alcohols **19ab** (0.115g, 0.583 mmol), dimethoxypropane (0.20 mL, 1.6 mmol) and acetone (1.0 mL) in DMF (3.0 mL) was added pyridinium *p*-toluenesulfonate (0.010g). After 43 hrs, additional dimethoxypropane (0.10 mL, 0.80 mmol) was added. After 5.5 hrs, the reaction was diluted with CH_2Cl_2 (50 mL) and sequentially washed with aq. $NaHCO_3$ (15 mL) and H_2O (15 mL). The organic layer was dried (Na_2SO_4) and concentrated. Purification by semi-preparative HPLC provided diastereomers **20a** (0.041g) and **20b** (0.025 g) in a combined 48% yield: **20a**: ^1H NMR δ 5.67 (dt, 1 H, J = 15.0, 6.9), 5.33 (dd, 1 H, J = 15.3, 6.9), 3.92 (dd, 1 H, J = 9.9, 8.1), 3.53 (dt, 1 H, J = 10.2, 4.2), 2.12-1.93 (m, 2 H), 1.90-1.76 (m, 2 H), 1.74-1.56 (m, 2 H), 1.47 (d, 6 H, J = 23.4), 1.44-1.15 (m, 7 H), 0.90 (t, 3 H, J = 7.5); ^{13}C NMR δ 135.0, 128.8, 98.6, 76.1, 73.1, 45.7, 34.4, 32.2, 30.3, 25.9, 25.4, 24.8, 22.2, 20.1, 13.7; Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.70; H, 11.12. **20b**: ^1H NMR δ 5.78-5.63 (m, 2 H), 4.31 (t, 1 H, J = 7.8), 3.65 (dt, 1 H, J = 10.2, 4.2), 2.10-2.00 (m, 2 H), 1.95-1.85 (m, 1 H), 1.83-1.63 (m, 3 H), 1.43 (d, 6 H, J = 17.1), 1.41-1.20 (m, 7 H), 0.91 (t, 3 H, J = 7.5); ^{13}C NMR δ 135.6, 128.1, 98.8, 75.4, 69.1, 43.7, 34.5, 32.6, 29.2, 27.0, 26.6, 25.8, 24.7, 22.2, 13.7; IR (ATR) 2932, 2860, 1450, 1377, 1257, 1192, 1163, 1077, 1020, 948 cm^{-1}; Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.63; H, 10.86.

Tetrahydropyran, 5-methylhex-3*Z*-en-2-yl (21): To 0 °C solution of 3-tetrahydropyranyloxypropyl triphenylphosphonium bromide (7.00 g, 14.4 mmol) in 5:1 THF/toluene (30 mL) was added $NaN(TMS)_2$ (9.50 mL, 1.0M in THF) over 20 min. After 1.5 hr. at RT, the mixture was cooled to -78 °C and isobutyraldehyde (0.863 mL, 9.50 mmol) was added. After 1 h at -78 °C and 40 min. at 0 °C, the mixture was stirred at RT for 50 min. and poured into ice water (300 mL). The mixture was extracted with 50% EA/hex (3x100 mL), dried ($MgSO_4$), and concentrated in vacuo. Purification by extraction with hexanes gave **21** (1.263 g, 68%) as an amber oil: ^1H NMR δ 5.33-5.22 (m, 2 H), 4.61 (m, 1 H), 3.92-3.84 (m, 1 H), 3.73 (dt, 1 H, J = 9.6, 7.2), 3.54-3.47 (m, 1 H), 3.40 (dt, 1 H, J = 9.3, 7.2), 2.62 (d quintet, 1 H, J = 6.6, 1.5), 2.39-2.33 (m, 2 H), 1.90-1.80 (m, 1 H), 1.78-1.65 (m, 1 H), 1.64-1.46 (m, 4 H), 0.95 (d, 6 H, J = 6.6); ^{13}C NMR δ 139.4, 123.1, 98.6, 67.1, 62.2, 30.6, 28.0, 26.5, 25.4, 23.1, 19.5; HRMS m/z calcd. for $C_{12}H_{22}O_2$ $[M - H]^+$: 197.1542. Found: 197.1539.

5-Methylhex-3*Z*-hexenol (22): To a solution of **21** (1.533g, 7.73 mmol) in MeOH (40 mL) was added *p*-TsOH (0.23g, 1.21 mmol). After 12 hrs, the reaction mixture was concentrated and purified by column chromatography (12% EA/hex) to afford 0.292 g (33%) of the alcohol as a colorless oil: R*f* = 0.27 (20% EA/hex); ^1H NMR δ 5.36 (dd, 1 H, J = 10.8, 9.6), 5.28-5.19 (m, 1 H), 3.61 (t, 2 H, J = 6.9), 2.66-2.56 (m, 2 H), 2.32 (q, 2H, J = 6.6), 0.96 (d, 6 H, J = 6.6); ^{13}C NMR δ 140.4, 122.6, 62.2, 30.7, 26.5, 23.0; HRMS m/z calcd. for $C_7H_{14}O$ $[M]^+$: 114.1045. Found: 114.1045.

5-Methylhex-3*Z*-enyl triphenylphosphonium iodide (23): To a 0 °C solution of Ph_3P (3.040g, 11.59 mmol) and imidazole (0.0786g, 11.5 mmol) in 3:1 Et_2O/CH_3CN (60 mL) was added I_2 (2.86g, 11.3 mmol) over a period of 40 min whereupon the reaction was brought to RT for 1 h. The reaction was recooled to 0 °C and **22** (0.29 g) was added as a solution in 3:1 Et_2O/CH_3CN (20 mL). The reaction was allowed to warm to RT. After 2 h, Ph_3PO was precipitated by the addition of hexanes (8 mL) and the reaction was filtered. The filtrate was washed with ether (200 ml) and the combined organic layers were washed with aq. $NaHCO_3$ (100 mL) and dried (Na_2SO_4). Concentration, followed by trituration with hexanes, afforded 0.671 g (78%) of the iodide as a colorless liquid: R*f* = 0.29 (5% EA/hex); ^1H NMR δ 5.36 (t, 1 H, J = 9.6), 5.18 (dt, 1 H, J = 10.8, 7.2), 3.13 (t, 2 H, J =7.5), 2.67-2.50 (m, 3 H), 0.96 (d, 6 H, J = 6.3); ^{13}C NMR δ 140.0, 125.3, 31.6, 26.7, 23.0, 5.5; HRMS m/z calcd. for $C_7H_{13}I$ $[M]^+$: 224.0062. Found: 224.0063.

A solution of iodide (1.499g, 6.690 mmol) and Ph_3P (2.22g, 8.46 mmol) in CH_3CN (15 mL) was refluxed for 10h. After cooling, the solution was concentrated in vacuo to afford a viscous oil which was triturated with toluene (3 x 50 mL). Concentration afforded 3.00 g (92%) of the phosphonium salt as a white solid: ^1H NMR δ 7.90-7.70 (m, 15 H), 5.43 (dt, 1 H, J = 10.5, 7.2), 5.24 (dd, 1 H, J = 10.5, 9.6), 3.74-3.65 (m, 2 H), 2.52-

2.43 (m, 2 H), 2.27-2.20 (m, 1 H), 0.84 (d, 6 H, J = 6.6); ^{13}C NMR (couplings indicate J_{P-C}) δ 139.9, 135.1 (d, J = 3), 133.6 (d, J = 10), 130.5 (d, J = 12), 123.3 (d, J = 14), 117.8 (d, J = 87), 26.5, 23.5 (d, J = 49), 22.8, 20.2 (d, J = 3); HRMS m/z calcd. for $C_{25}H_{28}P[M]^+$: 359.1929. Found: 359.1942.

***trans*-2-(2-Napthyl)cyclohexyl)-6-methyl-1*Z*,4*Z*-hexadiene (24)**: By a similar procedure as employed for synthesis of **3**, aldehyde **8** (288.8 mg, 1.21 mmol) was reacted with the ylide derived from **23** (1.158g, 2.6 mmol) and $NaN(TMS)_2$ to afford, after chromatography (1% EA/hex), 0.34 g (88%) of Z,Z-pentadiene **24**: R_f = 0.66 (1% EA/hex); ^{1}H NMR δ 7.78 (m, 3 H, Ar), 7.58 (s, 1 H, Ar), 7.38 (m, 3 H, Ar). 5.13-4.93 (m, 4 H, olefin), 2.69 (m, 2 H, $=CHCH_2CH=$), 2.46 (m, 3 H, CHPh, CH-CH=), 1.9-1.2 (m, 8 H, cyclohexane ring), 0.90 (d, 3 H, J = 7.6), 0.88 (d, 3 H, J = 6.6); ^{13}C NMR 144.0, 137.6, 134.7, 133.7, 132.3, 127.7, 127.6, 127.4, 126.5, 126.0, 125.7, 125.0, 50.7, 41.9, 35.3, 34.0, 26.8, 26.5, 26.2, 25.9, 23.2, 23.1; Anal. calcd for $C_{24}H_{30}$, C: 90.51, H: 9.49, found C: 90.37, H: 9.34.

***trans*-2-(1-Methyl-1-(2-naphthyl)ethyl-5-methylcyclohexanone (25)** was prepared from the reaction of pulegone (3.95 g, 26 mmol) and 2-napthylmagnesium bromide (40 mL, 1M in THF) following a procedure reported for the phenyl analog except that THF was used as a reaction solvent.[27] Following equilibration in base, the ether extract was dried over Na_2SO_4 and concentrated to afford a crude oil which was subjected to flash chromatography (5% EA/hex) to afford 5.44 g (75%) of the ketone as a partially resolved 85:15 trans/cis mixture: *Trans*-**25**: R_f = 0.35 (5% EA/hex); ^{1}H NMR δ 7.77 (m, 4 H), 7.46 (m, 3 H), 2.78 (dd, 1 H, J = 4.8, 13.0), 2.26 (ddd, 1 H, J = 4.2, 1.9, 12.4), 2.04 (dt, 1 H, J = 1.2, 12.6), 1.77 (m, 1 H), 1.71-1.20 (m, 4 H), 1.56 (s, 3 H), 1.52 (s, 3 H), 0.96 (d, 3 H, J = 6.2); ^{13}C NMR δ 211.2, 147.2, 133.2, 131.6, 128. 0, 127.5, 127.3, 125.8, 125.3, 124.5, 124.2, 59.2, 52.4, 39.2, 36.2, 34.6, 29.1, 26.7, 23.5, 22.2. *Cis*-**25**: R_f = 0.28 (5% EA/hex); ^{1}H NMR δ 7.77 (m, 4 H), 7.44 (m, 3 H), 2.78 (dd, J = 5.6, 10.4), 2.52 (dd, 1 H, J = 5.7, 13.1), 2.28 (m, 1H), 2.03 (ddd, J = 1.5, 4.8, 13.0), 1.74-1.41 (4 H), 1.55 (s, 3 H), 1.53 (s, 3 H), 0.90 (d, 3 H, J = 7.2); ^{13}C NMR 212.1, 146.8, 133.2, 131.6, 128.0, 127.5, 127.3, 125.8, 125.3, 124.6, 124.3, 59.3, 50.3, 39.7, 32.2, 31.2, 27.3, 24.9, 23.6, 19.2.

2-(1-Methyl-1-(2-naphthyl)ethyl-5-methylcyclohexene trifluoromethanesulfonate (26):
To a 0 °C solution of $(i\text{-Pr})_2NH$ (2.5 mL, 0.18 mmol) in THF (40 mL) was added *n*-BuLi (7.5 mL, 2.4 M in hexane). The solution was cooled to -78 °C prior to addition of *trans*-**25**(4.5 g, 16 mmol), resulting in a green solution which was stirred at -78 °C for 1 h. A solution of Tf_2NPh (6.43 g, 18 mmol) in THF (17 mL) was added dropwise and the reaction mixture was warmed to 0 °C. After 1 h, the reaction was concentrated and subjected to flash chromatography (4% EA/hex) to afford 5.98 g (91%) of the enol triflate: R_f = 0.63 (5% EA/hex); ^{1}H NMR δ 7.80 (m, 3 H), 7.68 (s, 1 H), 7.46 (m, 3 H), 5.74 (s, 1 H), 3.05 (m, 1 H), 2.18 (m, 1 H), 1.58 (s, 3 H), 1.43 (s, 3 H), 1.63-1.22 (m,4 H),0.97 (d, 3 H, J = 7.2); ^{13}C NMR δ 151.3, 145.8, 133.3, 131.8, 128.5, 127.9, 127.8, 127.3, 125.9, 125.5, 124.7, 123.9, 118.6 (q, J_{C-F} = 321), 47.3, 41.1, 30.5, 29.9, 29.2, 26.8, 24.0, 21.1; Anal. calcd for $C_{21}H_{23}F_3SO_3$, C: 61.65, H: 5.62, found, 60.97, 5.57.

2-(1-Methyl-1-(2-naphthyl)ethyl-5-methylcyclohexenecarboxylic acid, methyl ester: (27)
A solution of the triflate (3.12 g, 7.7 mmol) and $Pd(OAc)_2(Ph_3P)_2$ (200 mg, 0.26 mmol) in 1:1 MeOH/DMF (28 mL) was stirred under a balloon of CO for 4 days. The resulting mixture was diluted with EtOAc and ether (60 mL, 1:1), washed with water (3 x 30 mL) and dried over Na_2SO_4. After concentration, the residue was subjected to flash chromatography (5% EA/hex) to afford 1.87 g (75 %) of 2-(1-methyl-1-(2-naphthyl)ethyl-5-methylcyclohexenecarboxylic acid, methyl ester: $[\alpha]_D$ = +54.0, (c - 1.1, $CHCl_3$); mp 73-74 °C; R_f =0.45 (5% EA/hex); ^{1}H NMR δ 7.78 (m, 3 H), 7.68 (d, 1 H), 7.58 (dd, 1 H, J = 1.9, 8.8), 7.41 (m, 2 H), 6.58 (d, 1 H, J = 2.4), 3.39 (s, 3 H), 3.29 (t, 1 H, J = 6.7, 5.5), 2.01 (m, 1 H), 1.49 (m, 4 H), 1.35 (s, 6 H), 0.95 (d, 3 H, J = 7.2); ^{13}C NMR δ 170.9, 146.5, 146.0, 133.6, 133.2, 131.8, 128.0, 127.3, 125.7, 125.6, 125.3, 124.4, 51.3, 42.8, 42.6, 29.9, 29.8, 27.9, 24.9, 23.8, 21.2; IR (neat) 1718 cm^{-1}; Anal. calcd for $C_{22}H_{26}O_2$, C: 81.95, H: 8.13, found, C: 81.89, H: 8.26.

Thereafter was eluted 0.48 g (21%) of the corresponding anhydride: mp 65-67 °C (dec); R_f = 0.39 (5% EA/hex); ^{1}H NMR δ 7.80 (m, 4 H), 7.61 (d, 1 H, J = 8.8), 7.44 (m, 2 H), 6.95 (d, 1 H, J = 2.6), 3.40 (t, 1 H, J = 6.7, 5.5), 2.10 (m, 1 H), 1.46(s, 3 H), 1.42 (s, 3 H), 1.58-0.83 (m, 4 H), 1.00 (d, 3 H, J = 5.5); ^{13}C NMR δ 165.6, 151.5, 146.0, 133.3, 132.9, 131.9, 128.0, 127.6, 127.4, 125.9, 125.5, 125.4, 124.5,43.3, 42.1, 30.4, 30.3, 29.2, 24.1, 23.6, 21.2; IR (neat) 1776, 1716 cm^{-1}; Anal. calcd for $C_{42}H_{46}O_3$, C: 84.24, H: 7.74, found, C: 84.22, H: 7.76.

To a solution of the unsaturated ester (1.8 g, 5.58 mmol) in MeOH (80 mL) was added Mg turnings (6.75 g, 280 mmol) over a period of 10 h. Excess Mg was destroyed with 10% HCl and the mixture was extracted with ether (4 x 30 mL). The combined layers were washed with sat. $NaHCO_3$ and dried over Na_2SO_4. Concentration, followed by filtration thorugh silica, furnished 1.54 g (85%) of the ester as a 5: 95 cis/trans

mixture which was separable by HPLC (7% EA/hex): *trans*-**27** $[\alpha]_D$ = + 5.4 (c = 1.2, $CHCl_3$); R_f = 0.45 (5% EA/hex); ^1H NMR δ 7.79 (m, 3 H), 7.66 (d, 1 H, J = 1.4), 7.60 (d, 1 H, J = 8.8), 7.42 (m, 2 H), 3.14 (s, 3 H), 2.43 (dt, 1 H, J = 11.2, 3.1), 2.24 (dt, 1 H, J = 11.5, 3.1), 1.77 (m, 1 H), 1.63-0.87 (m, 6 H, 1.35 (s, 3 H), 1.34 (s, 3 H), 0.84 (d, 3 H, J = 6.2); ^{13}C NMR δ 176.9, 147.4, 133.1, 131.7, 127.9, 127.2, 125.7, 125.4, 125.2, 124.1, 51.0, 47.5, 46.1, 41.0, 40.3, 34.7, 31.7, 27.3, 25.7, 25.6, 22.0. IR (neat)1734 cm^{-1}; Anal. calcd for $C_{22}H_{28}O_2$, C: 81.44, H: 8.70, found, C: 81.27, H: 8.78. *cis*-**27**: R_f = 0.47 (5% EA/hex); ^1H NMR δ 7.79 (m, 3 H) 7.68 (d, 1 H, J = 1.7), 7.46 (m, 3 H), 3.54 (s, 3 H), 2.69 (m, 1 H), 2.05-1.20(m, 8 H), 1.38 (s, 3 H), 1.34 (s, 3 H), 0.79 (d, 3 H, J = 6.4); ^{13}C NMR δ 176.0. 147.1, 133.2, 131.6, 127.9, 127.4, 127.3, 125.7, 125.3, 124.9, 124.5, 51.7, 50.9, 40.7, 40.5, 39.0, 35.8, 26.7, 26.2, 25.7, 22.3, 22.2.

1-(*trans*-2-(2-Naphthyl)cyclohexyl)-6-methyl-1Z-4Z-heptadiene (28): To a 0 °C solution of the ester (1.25 g, 3.85 mmol) in THF (40 mL) was dropwise added a solution of DIBAL (15.4 mL, 1.0M in toluene). After 2 h, the reaction was quenched with 10% HCl (20 mL). The aqueous layer was extracted with ether (2 x 40 mL) and the combined organic layers were dried over Na_2SO_4. After concentration, the residue was subjected to flash chromatography (10% EA/hex) to furnish 1.10 g (96%) of *trans*-2-(1-methyl-1-(2-naphthyl)ethyl-5-methylcyclohexanemethanol: $[\alpha]_D$ = -13.9 (c = 0.5, $CHCl_3$) R_f = 0.29 (10% EA/hex); ^1H NMR δ 7.70 (m, 4 H), 7.59 (d, 1 H, J = 8.8), 7.44 (m, 2 H), 3.02 (bs, 2 H), 2.02-0.92 (m, 9 H), 1.43 (s, 3 H), 1.20 (s, 3 H), 0.89 (d, 3 H, J = 6.4); ^{13}C NMR δ 150.1, 133.4, 131.7, 128.0, 127.9, 127.4, 126.0, 125.4, 124.4, 123.1, 65.5, 46.4, 42.9, 40.3, 39.9, 35.6, 32.5, 32.1, 28.0, 22.5, 21.2; IR (neat) 3396 cm^{-1}; Anal. calcd for $C_{21}H_{28}O$, C: 85.08, H: 9.52, found, C: 85.11, H: 9.38.

Oxidation of the alcohol (1.10 g, 3.71 mmol) as for **2** afforded, after chromatography (10% EA/hex), 0.841 g (77%) of 2-(1-methyl-1-(2-naphthyl)ethyl-5-methylcyclohexane carboxaldehyde (77%): $[\alpha]_D$ = -9.2 (c = 1, $CHCl_3$) m.p. 60-61.5°C; R_f = 0.40 (5% EA/hex); ^1H NMR δ 8.68 (d, 1 H, J = 5.5), 7.79 (m, 3 H), 7.65 (s, 1 H), 7.47 (m, 3 H), 2.29 (m, 1 H), 2.14 (dt, 1 H, J = 3.3, 11.7), 1.74 (m, 2 H), 1.46-0.86 (theory 5H, observed 6 H), 1.38 (s, 3 H), 1.36 (s, 3 H), 0.88 (d, 3 H, J = 6.2); ^{13}C NMR δ 203.1, 146.4, 133.1, 131.8, 128.1, 127.7, 127.3, 126.0, 125.6, 125.2, 125.1, 53.7, 47.9, 40.8, 35.9, 34.6, 31.1, 27.2, 26.7, 24.8, 21.2; IR (neat) 2949, 1716 cm^{-1}. Anal. calcd for $C_{21}H_{26}O$, C: 85.67, H: 8.90, found, C: 85.81, H: 8.74.

Under similar conditions as employed for **24**, olefination of the aldehyde (0.187 g, 0.635 mmol) with the ylide derived from **23** (1.00 g, 2.06 mmol) afforded, after flash chromatography (hexanes) 0.20 g (84%) of pure Z,Z-heptadiene **28** as a colorless oil: R_f = 0.65 (1% EA/Hex); ^1H NMR δ 7.76 (m, 3 H), 7.61 (s, 1 H), 7.44 (m, 3 H), 5.21 (m, 2 H), 5.02 (t, 1 H, J = 10.3), 4.84 (m, 1 H), 2.79 (m, 2 H), 2.64 (heptet, 1 H), 2.38 (dq, 1 H, J = 10.7, 11.6, 2.4, 3.3), 1.73-0.85 (8 H), 1.42 (s, 3 H), 1.33 (s, 3 H), 0.98 (d, 3 H, J = 5.7), 0.80 (d, 3 H, J = 6.4); ^{13}C NMR δ 149.1, 137.6, 137.5, 133.2, 131.5, 127.9, 127.3, 127.1, 125.6, 125.5, 125.4, 125.0, 124.1, 123.1, 51.2, 44.3, 41.4, 39.5, 35.4, 32.3, 28.5, 27.8, 26.5, 25.7, 25.6, 23.2, 23.1, 22.3; Anal. calcd for $C_{28}H_{38}$, C: 89.78, H: 10.22, found, C: 89.55, H: 9.95.

7-(*trans*-2-(2-Napthyl)cyclohexyl)-2-methyl-4*E*,6Z-heptadienyl-3-hydroperoxide (29ab): Singlet oxygenation of diene **24** was conducted under similar conditons as emplyed for diene **3** to afford a 60:40 mixture of diastereomeric hydroperoxides **29a** and **29b**, which were separable by HPLC (5% EA/hex): **29a**: R_f = 0.38 (10% EA/Hex); ^1H NMR δ 7.70 (m, 3 H, Ar), 7.53 (s, 1 H, Ar), 7.40 (m, 3 H, Ar), 7.18 (s, 1 H, OOH), 6.38 (dd, 1 H, J = 11.1, 15.6, =CH-C**H**=), 5.66 (t, 1 H, J = 11.0, CH=C**H**-CH=), 5.25 (dd, 1 H, J = 7.2, 8.6, 15.2, =C**H**CHOOH), 5.18 (t, 1 H, J = 11.0, C**H**=CH-CH=), 3.97 (t, 1 H, J = 7.2, 8.6, CHOOH), 2.81 (m, 1 H), 2.48 (td, 1H, J = 11.0, 3.6, CHAr), 2.0-1.2 (m, 9 H, cyclohexane ring), 0.91 (d, 3 H, J = 6.7), 0.79 (d, 3 H, J = 6.7). ^{13}C NMR δ 143.5, 138.0, 133.6, 132.2, 131.5, 129.3, 127.7, 127.6, 126.6, 126.4, 126.1, 125.9, 125.2, 91.9, 50.6, 42.5, 34.9, 33.8, 30.8, 26.7, 26.0, 18.9, 18.4. **29b**: R_f = 0.34 (10% EA/hex); ^1H NMR δ 7.70 (m, 3 H), 7.61 (s, 1 H), 7.54 (s, 1 H), 7.37 (m, 3 H), 6.36 (dd, 1H, J = 11.1, 15.2), 5.67 (t, 1 H, J = 11.0), 5.29 (dd, 1H, J = 8.5, 15.1), 5.20 (t, 1 H, J = 10.7), 3.97 (t, 1 H, J = 8.4), 2.81 (qd, 1 H, J = 10.7, 3.3), 2.47 (td, 1 H, J = 11.0, 3.3), 1.96-1.27 (m, 9 H), 0.81 (d, 3 H, J = 6.7), 0.66 (d, 3 H. J = 6.9); ^{13}C NMR δ 143.5, 137.8, 133.6, 132.2, 130.8, 129.5, 127.6, 126.6, 126.4, 126.0, 125.7, 125.1, 91.8, 50.5, 42.4, 34.9, 33.8, 30.7, 26.7, 25.9, 18.8, 18.1.

7-(*trans*-2-(2-Napthyl)cyclohexyl)-2-methyl-4*E*,6Z-heptadien-3-ol: Ph_3P reduction of the crude hydroperoxides provided a 61:39 mixture of alcohols which eluted at 10.0 and 12.5 min on HPLC (5% EA/hex): *First eluting:* R_f = 0.33 (10% EA/Hex); ^1H NMR δ 7.75 (m, 3 H, Ar), 7.59 (s, 1H, Ar), 7.39 (m, Ar), 6.17 (dd, 1 H, J = 11.1, 15.2), 5.64 (t, 1 H, J = 11.1), 5.30 (dd, 1 H, J =15.0, 6.9), 5.14 (t, 1 H, J = 10.3), 3.68 (t, 1 H, J = 6.7), 2.78 (qd, 1 H, J = 10.5, 3.0), 2.48 (td, 1 H, J = 3.3, 11.7), 2.00-1.20 (m, 9 H), 0.82 (d. 1 H, J = 6.7), 0.78 (d, 1 H, J = 6.9); ^{13}C NMR δ 143.6, 136.5, 133.9, 133.5, 132.2, 127.6, 127.5,127.4, 127.2, 127.0, 126.7, 126.1, 125.8, 125.1, 77.7, 50.4, 42.6, 34.7, 34.0, 33.7, 26.7, 26.0,

18.2, 18.0; IR (neat) 3438 cm^{-1}; HRMS, calcd for $C_{24}H_{30}O$ 334.2289, found, 334.2297. *Second eluting:* R_f = 0.26 (10% EA /hex); ^1H NMR δ 7.72 (m, 3 H), 7.56 (s, 1 H), 7.38 (m, 3 H), 6.30 (dd, 1 H, J = 15.2, 11.1), 5.62 (t, 1 H, J = 11.1), 5.39 (dd, 1 H, J = 15.3, 7.2), 5.15 (t, 1 H, J = 10.3), 3.75 (t, 1 H, J = 7.0), 2.82 (qd, 1 H, J = 10.7, 3.0), 2.48 (td, 1 H, J = 11.3, 3.3), 2.0-1.2 (m, 9 H), 0.85 (d, 3 H, J = 6.9), 0.74 (d, 3 H, J = 6.7); ^{13}C NMR δ 143.6, 136.7, 134.0, 133.5, 132.3, 127.6, 127.5, 126.9, 126.8, 126.5, 125.9, 125.7, 125.0, 78.0, 50.4, 42.2, 35.0, 33.9, 33.8, 26.6, 25.9, 18.1, 18.0; IR (neat) 3400 cm^{-1}; HRMS caldd for $C_{24}H_{30}O$ 334.2289, found, 334.2294.

7-(*trans*-2-(1-Methyl-1-(2-naphthyl)ethyl)cyclohexyl)-2-methyl-4*E*,6Z-heptadienyl-3-hydroperoxide (30ab): Photoxygenation of diene **28** under similar conditions as employed for diene **3** resulted in a 44:56 mixture of diastereomeric hydroperoxides **30ab** which could be separated by NP-HPLC (eluting at 17.3 min, 18.5 min in 10% EA/hex): **30a**: R_f = 0.35 (10 % EA/hex); ^1H NMR δ 7.76 (m, 4 H, Ar & OOH), 7.61 (s, 1 H, Ar), 7.45 (m, 3 H, Ar), 6.56 (dd, 1 H, J = 11.2, 15.3, C**H**=CHCHOOH), 5.52 (dd, 1 H, J = 9.1, 14.9, CH=C**H**CHOOH), 5.47 (t, 1 H, J = 10.8, CH=C**H**-CH=), 5.08 (t, 1 H, J = 10.7, C**H**=CH-CH=), 4.17 (dd, 1 H, J = 8.3, 6.7, CHOOH), 2.54 (m, 1 H, CHAr), 1.91 (hept., 1 H, iPr), 1.76-1.46 (4 H), 1.40 (s, 3 H), 1.31 (s, 3 H), 0.97 (d, 3 H, J = 6.9, iPr), 0.90 (d, 3 H, J = 6.9, iPr), 0.82 (d, 3 H, J = 6.2), 1.46-0.74 (m, 4 H, ring); ^{13}C NMR δ 148.7, 140.9, 133.2, 131.6, 131.0, 128.8, 128.0, 127.2, 127.1, 125.6, 125.4, 125.1, 124.3, 123.1, 91.8, 51.4, 44.0, 41.3, 40.1, 35.3, 32.2, 30.7, 28.2, 26.9, 26.6, 22.2, 18.7, 18.1; IR (neat) 3419 cm^{-1}; HRMS, calcd for $C_{28}H_{38}O_2$ 406.2862, found 406.2877. **30b**: R_f = 0.34 (10% EA/hex); ^1H NMR δ 7.78 (m, 4 H), 7.59 (s, 1 H), 7.42 (m, 3 H), 6.57 (dd, 1 H, J = 15.4, 11.1), 5.47 (dd, 1 H, J = 8.5, 14.9), 5.45 (t, 1 H, J = 10.6), 4.96 (t, 1 H, J = 10.6), 4.16 (dd, 1 H, J = 6.9, 8.3), 2.52 (m, 1 H), 1.92 (hept., 1 H, J = 6.7), 1.38 (s, 3 H), 1.30 (s, 3 H), 1.02 (d, 3 H, J =6.9), 0.96 (d, 3 H, J = 6.9), 0.82 (d, 3 H, J = 6.2), 1.8-0.7 (m, 8 H); ^{13}C NMR δ 148.9, 140.8, 133.2, 131.1, 128.9, 128.0, 127.9, 127.2, 127.0, 125.6, 125.4, 125.1, 124.3, 123.1, 92.0, 51.4, 43.9, 41.3, 40.1, 35.3, 32.1, 30.7, 28.2, 28.8, 26.4, 22.2, 18.9, 18.1.

Hydroperoxide Equilibration: HPLC-purified samples of either **10a** or **10b** (typically 3.8 mg, 0.0147 mmol) were dissolved in benzene-d_6 (0.37 mL, Cambridge Isotope Laboratories) in a 5 mm NMR tube. DTBN (0.15 - 0.20 eq) was added and the tube was mixed by vortexing. The tube was flushed with O_2 and heated to 60 °C. The tube was removed from the heat source at desired intervals for ^1H NMR analysis. Product ratios were determined based upon relative integration of peaks at δ 2.7 (**10a**), 4.15 (**10c**), and 4.2 (**10a + 10b**) and/or by comparison of integrations at 8.9 (**10a**), 10.0 (**10b**), and 13.6 (**10c**) min on analytical HPLC (5% EA/hex, 1.0 mL/min).

5-(*trans*-2-phenylcyclohexyl)-2*E*,4*E*-pentadiene hydroperoxide (10c): ^1H-NMR δ 7.85 (s, 1H, CH_2OOH), 7.28 (m, 5H, phenyl), 6.09 (dd, 1H, J = 15.2, 10.5 , RCH=CH-C**H**=CHCH$_2$OOH), 5.84 (dd, 1H, J = 15.1, 10.6 , RCH=C**H**-CH=CH), 5.50 (m, 2H, CH=C**H**-CH$_2$OOH and RC**H**=CH-CH=CH), 4.40 (d, 2H, J = 6.4 , -C**H**$_2$OOH) 2.29 (m, 2H, R$_2$C**H**-Ph and R$_2$C**H**-CH=CH), 1.8-1.3 (8H).

5-(*trans*-2-phenylcyclohexyl)-2*E*,4*E*-pentadienol (14c) was prepared from **10c** by reduction with Ph_3P as described earlier: R_f =0.25, 20% EA/hex; ^1H NMR δ 7.27-7.10 (5H), 5.99 (dd, 1H, J = 15.2, 10.4), 5.81 (dd, 1H, J = 15.3, 10.4), 5.58 (dt, 1H, J = 15.2, 6.1), 5.41 (dd, 1H, J = 15.3, 6.8), 4.05 (d, 2H, J = 5.9), 2.32-2.22 (m, 2H), 1.90-1.24 (9H); ^{13}C NMR (125 MHz) δ 145.9, 139.1, 131.1, 129.2, 128.2, 128.1, 127.5, 125.7, 63.1, 50.3, 45.8, 35.5, 33.0, 26.5, 25.9; IR (neat) 3340 cm^{-1}; UV λ_{max} 234 (ε = 22,600, Hex); Anal. Calcd for $C_{17}H_{23}0$: C, 83.90; H, 9.52. Found: C, 84.13; H, 9.38.

Equilibration of 11a (12 mg, 0.039 mmol) was conducted in the presence of PAT (1.6 mg) under similar conditons as described above. The products were analyzed as described earlier.

Radical Equilibration of 29a:

A solution of **29a** hydroperoxide (0.06 M) and PAT (0.0066 M) in benzene was flushed with oxygen and placed in a 60°C bath. The reaction was monitored by HPLC. The reaction was analyzed as described for **29a**.

Radical Equilibration of 29b: A solution of **29b** (0.017 M) and PAT (0.0016 M) in benzene was equilibrated and analyzed in the same manner as described above.

7-(*trans*-2-(2-Napthyl)cyclohexyl)-2-methyl-4*E*,6*E*-heptadienyl-3-hydroperoxide (29cd): R_f = 0.31 (10% EA/hex); ^1H NMR δ 7.76 (m, 3 H, Ar), 7.56 (s, 1 H, Ar), 7.52 (s, 1 H, OOH), 7.36 (m, 3 H, Ar), 5.99 (dd, 1 H, J = 15.2, 10.5, =CH-C**H**=), 5.84 (dd,1 H, J = 15.2, 10.5, =C**H**-CH=), 5.49 (dd, 1 H, J = 15.3, 6.4, =C**H**CHOOH), 5.30 (dd, 1 H, J = 15.2, 8.8, C**H**=CH-CH=), 3.90 (dd, 1 H, J = 8.8, 6.4, CHOOH), 2.50 (m, 1 H, CHAr), 1.94-1.41 (m, 9 H, ring), 0.83 (d, 3 H, J = 6.8), 0.73 (d, 3 H, J = 6.9).

Radical Equilibration of 30ab:

A benzene solution containing 0.042M **30a** and 0.0043 M PAT was flushed with O_2 and placed in a 60°C bath. After 7h, HPLC analysis (10% EA/hexane) indicated the presence of **30a**, **30b**, and small quantities of a third peak tentatively identified, on the basis of comparison with **29cd**, as the *E,E*-dienes **30cd.** Equilibration of **30b** (0.043 M) was conducted in a similar manner.

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