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Stereoselective synthesis of substituted all-*trans* 1,3,5,7-octatetraenes by a modified Ramberg–Bäcklund reaction

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Abstract—The reaction of allylic dienylic sulfone with dibromodifluoromethane in the presence of alumina-supported KOH in dichloromethane solution results in facile rearrangement affording the corresponding all-*trans* 1,3,5,7-octatetraenes in excellent yields. This result shows that the double bonds of stereochemically defined allylic dienylic sulfone retain their stereochemistry and the newly formed double bond has an (*E*)-configuration in the modified Ramberg–Bäcklund procedure.

1. Introduction

The conjugated 1,3,5,7-tetraene is an important structural unit in various classes of natural products such as lipoxin B_4, retinoic acid, navenone C, and chrysophysarin A.[1] It has also been shown that conjugated polyenes are potentially useful compounds for electronic and non-linear optical materials.[2] In the literature, there are only a few general strategies for the stereocontrolled construction of the tetraene unit. This is mainly due to the instability and the facile (*E*)–(*Z*) isomerization of tetraene systems.[3] Synthetic methods for the construction of conjugated octatetraenes that relied on the Wittig olefination invariably gave a mixture of geometrical isomers of octatetraenes.[4] Akhtar[5] utilized a combination of nucleophilic displacement by lithium phenylacetylide with 1,4-dibromobutene and base-catalyzed isomerization, and then copper-catalyzed coupling of styrylacetylene, followed by reduction to prepare the geometrical isomers of 1,8-diphenyl-1,3,5,7-octatetraene. Soullez[6] described the bromine–lithium exchange of ω-bromo polyenol ethers, generated in situ from 5-bromopenta-2,4-dienal, followed by condensation with carbonyl compounds to give conjugated octatetraenes. However, it is only very recently that the stereoselective synthesis of octatetraenes began to emerge. Alami[7] reported that sequential palladium copper co-catalyzed coupling of terminal acetylenes and *trans*-enyne to a stereochemically defined 1,2-dichloroethylene, followed by selective *syn*-reduction of the triple bond moieties with activated zinc gave stereochemically-defined octatetraenes. This synthetic method was applied to an efficient convergent synthesis of lipoxin B_4.[1d] Mestres[1e] reported the addition of lithium trienediolates generated from hexa-2,4-dienoic acid to α,β-unsaturated ketone, which underwent a facile acid-catalyzed dehydration to give retinoic acid. Paquette[8] also reported an interesting [2+2] cycloreversion of *endo*, *endo*-7,8-diphenylbicyclo[4.1.1]octa-2,4-diene, which on irradiation gave all-*trans*-1,8-diphenyl-1,3,5,7-octatetraene. Prompted by these studies, we wish to report our stereoselective construction section of octatetraenes in this paper.

2. Results and discussion

In our previous studies[9] on the stereoselective synthesis of polyenes, we reported that conjugated trienes and enediynes could be prepared by our modified Ramberg–Bäcklund reaction, from the corresponding diallylic sulfones and dipropargylic sulfones. This synthetic method was applied to the synthesis of natural products containing a triene unit such as Galbanolenes. Reported herein are our findings that allylic dienylic sulfones, when subjected to our Ramberg–Bäcklund reaction conditions, provide all-*trans* octatetraenes in good yield. The procedure reported here started with an allylic dienylic sulfone **1** (Scheme 1), with three of the four double bonds already in place and the fourth one to be realized by our modified Ramberg–Bäklund procedure. This disconnection approach relied on the stereocontrolled synthesis of an allylic dienylic sulfone **1**, which was in turn prepared by a stereocontrolled preparation of dienylic halides **2** and dienylic thiolacetate **3**. There are two general approaches for the assembly of allylic dienylic sulfides **4** from which the corresponding sulfone **1** could be obtained after oxidation. One makes use of the coupling reaction between a stereodefined dienylic thiolacetate **3** to a geometrically pure allylic halide **5**. The alternative is to couple an allylic thiolacetate **6** to a dienylic halide **2**. These two procedures invariably demanded a

Keywords: octatetraenes; allylic dienylic sulfones; Ramberg–Bäcklund reaction.

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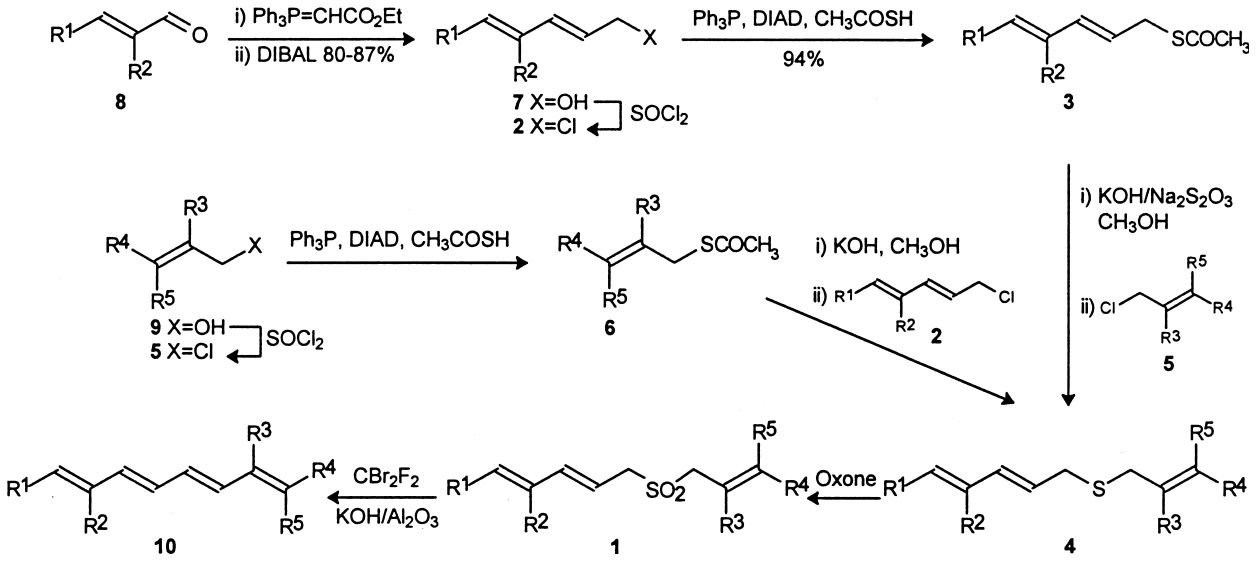
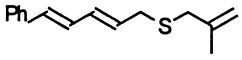
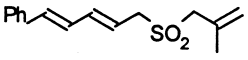
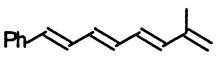
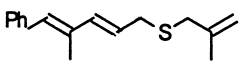
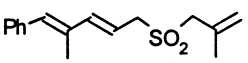
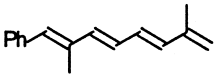
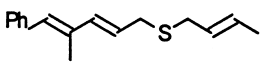
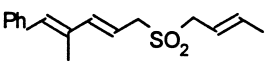
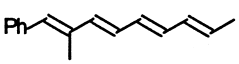
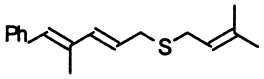
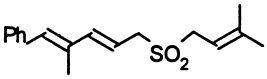
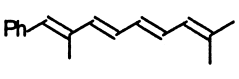
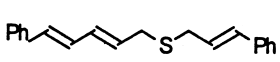
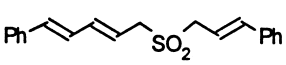
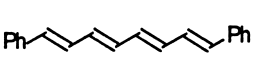
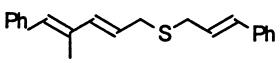
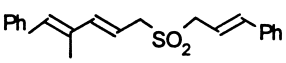
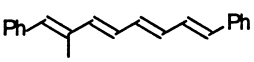
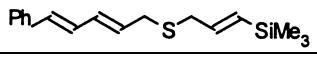
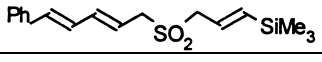
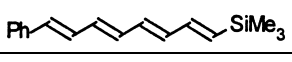


Scheme 1. Synthesis of 1,3,5,7-octatraenes via Ramberg–Bäcklund reaction: (a) R^1=C_6H_5, R^2, R^4, R^5=H, R^3=Me; (b) R^1=C_6H_5, R^2, R^3=Me, R^4, R^5=H; (c) R^1=C_6H_5, R^2, R^4=Me, R^3, R^5=H; (d) R^1=C_6H_5, R^2, R^4, R^5=Me, R^3=H; (e) R^1, R^4=C_6H_5, R^2, R^3, R^5=H; (f) R^1, R^4=C_6H_5, R^2=Me, R^3, R^5=H; (g) R^1=C_6H_5, R^2, R^3, R^5=H, R^4=$SiMe_3$.

stereoselective preparation of dienyl alcohol **7**, the common intermediate for the requisite halide **2** and thiolacetate **3**. Several synthetic methods were tried. In the end, the dienylic alcohol **7** was secured by the Wittig reaction followed by reduction.

The starting material was the aromatic aldehyde **8** (R^1=Ph, R^2=H or Me). Reaction of **8** with ethyl (triphenylphosphoranylidene) acetate afforded the dienylic ester with good (*E*)-selectivity, followed by reduction of the ester moiety with DIBAL to furnish the dienylic alcohol **7** in quantitative yield. This dienylic alcohol **7** was converted to the thiolacetate **3** via the Mitsunobu[10] reaction with thiolacetic acid in the presence of triphenylphosphine and diisopropyl azodicarboxylate (DIAD), or it could be converted to the corresponding dienylic chloride **2** by reaction with thionyl chloride. In situ cleavage of the acetyl moiety of **3** with potassium hydroxide in methanol followed by allylation of the resulting dienylic thiol with stereodefined allyl chloride **5** in benzene, provided the allylic dienylic sulfide **4** in good yield. Alternatively, coupling of the dienylic chloride **2** with the thiolacetate **6** prepared from the allylic alcohol **9** also afforded the allylic dienylic sufide **4** in good yield (Table 1) with no S_N2' substitution products. As expected, the stereochemistry of the double bonds was retained during these transformations. The sulfide **4** could be transformed into the corresponding sulfone **1** with retention of double bond geometries by oxone oxidation in dichloromethane or

Table 1. Yields (%) of sulfides **4**, sulfones **1**, and tetraenes **10**

Entry	Sulfide **4**	Yields	Sulfone **1**	Yields	Tetraene **10**	Yields (coupling constants of newly formed C=C bond)
a		81		90		87 (J=15.5)
b		93		85		89 (J=15.6)
c		81		84		92 (J=15.6)
d		90		83		90 (J=15.5)
e		66		70		90[a]
f		82		90		80[a]
g		81		90		87 (J=15.0)

[a] Coupling constants cannot be resolved (500 MHz NMR) due to overlapping signals.

methanol in excellent yield. Subjecting the allylic dienylic sulfone **1** to our previously described modified Ramberg–Bäcklund reaction protocol (CBr_2F_2, KOH-on-Al_2O_3, CH_2Cl_2) invariably gave the geometrically defined 1,3,5,7-octatetraene **10** in good yield with the newly formed double bond having the (*E*)-configuration. Examination of the ^{13}C NMR spectra of the products indicated the presence of one isomer in each case. Thus, the stereoselectivity of the reaction was >95% for this reaction.

The issue of stereochemistry of the newly formed carbon carbon double bond was determined by ^1H NMR spectroscopy. Apart from **10e** and **10f**, the (*E*)-configuration of the newly formed carbon carbon double bond in all cases was readily diagnosed by large $^3J_{HC=CH}$ coupling constants (15.6–15.0 Hz) between the pertinent olefinic protons. The other three double bonds, again retained their stereochemical integrity as suggested by ^1H NMR spectroscopy. For the known diphenyl octatetraene **10e**, the stereochemistry was resolved by comparison of its physical and spectroscopic properties to those reported in the literatures.[5,8] The diphenyl substituted tetraene derivatives **10e** and **10f** have better stability than the other tetraenes towards light and heat. The terminal tetraenes **10a** and **10b** were less stable and tended to decompose in standing at rt.

3. Conclusion

We have presented a rapid route to stereochemically defined octatetraenes. The synthetic transformation utilizes readily available aromatic aldehydes and allylic alcohols as starting materials. The synthetic routes are facile and the reactions can be performed in molar scales. We have also shown that the double bonds of stereochemically defined allylic dienylic sulfone retain their stereochemistry, and that the newly formed double bond has an (*E*)-configuration in our modified Ramberg–Bäcklund procedure. This is similar to the case of dibenzyl sulfones, diallylic sulfones, and dipropargylic sulfones which we reported earlier.[9] Other applications of our procedure are under investigation in our laboratories.

4. Experimental

4.1. General methods and materials

Melting points were measured on a Reichert Microscope apparatus and are uncorrected. IR spectra were recorded on a Nicolet 205 FT-IR spectrophotometer and reported in wavenumbers (cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker Cryospec WM 250 spectrometer (250 MHz for ^1H and 62.5 MHz for ^{13}C) or Bruker ARX 500 spectrometer (500 MHz for ^1H). Samples were measured in $CDCl_3$, with Me_4Si as an internal standard for ^1H NMR, and $CDCl_3$ for ^{13}C NMR. Mass spectra (MS) data were obtained on a Finnegan MAT 95 or VG 7070F mass spectrometer. Elemental analyses were carried out by Medac Ltd, Uxbridge, UK or the Shanghai Institute of Organic Chemistry, People's Republic of China. UV–Visible light spectra were recorded on a Hitachi U-2000 spectrometer. Aromatic aldehydes and allylic alcohols were purchased from Aldrich Chemical Company and used without further purification.

4.2. General procedure for the preparation of allyl dienylic sulfides 4

Method A. The stereochemically pure dienylic thioacetate **3** (5 mmol) was added to a solution of KOH (5 mmol) and $Na_2S_2O_3{\cdot}5H_2O$ (10 mg) in methanol (10 ml). The resulting mixture was stirred at 0°C under nitrogen for 30 min. The methanol was removed in vacuo, and the solvent was changed to benzene (10 ml). To this thiolate solution was then added dropwise the stereochemically pure allylic halide **5** (5 mmol) over a period of 5 min and stirring was continued for 1 h at 20°C. The reaction mixture was poured into water (10 ml) and extracted with Et_2O (3×20 ml). The combined extracts were washed (saturated NaCl solution), dried ($MgSO_4$), filtered and concentrated in vacuo. Flash chromatography of the residue over silica gel (hexane/ethyl acetate=100:1) afforded the sulfide **4**.

Method B. The stereochemically pure allylic thioacetate **6** (5 mmol) was added to a solution of KOH (5 mmol) and $Na_2S_2O_3{\cdot}5H_2O$ (10 mg) in methanol (10 ml). The resulting mixture was stirred at 0°C under nitrogen for 30 min. The methanol was removed in vacuo, and the solvent was changed to benzene (10 ml). To this thiolate solution was then added dropwise the stereochemically pure dienylic halide **2** (5 mmol) over a period of 5 min and stirring was continued for 1 h at 20°C. The reaction mixture was then worked up following the same procedure as that described in Method A.

The following allylic dienylic sulfides were prepared:

4.2.1. 2-Methyl-2-propenyl 5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfide (4a). Oil (Method B, 81%). IR ν_{max} 3022, 2910, 1646, 1371, 987, 895, 748 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.40–7.21 (5H, m, ArH), 6.77 (1H, dd, *J*=15.5, 10.1 Hz, 4′-H), 6.50 (1H, d, *J*=15.5 Hz, 5′-H), 6.20 (1H, dd, *J*=15.4, 10.1 Hz, 3′-H), 5.73 (1H, dt, *J*=15.4, 7.7 Hz, 2′-H), 4.89–4.88 (1H, m, 3-H), 4.84–4.83 (1H, m, 3-H), 3.15 (2H, d, *J*=7.7 Hz, CH_2S), 3.08 (2H, s, CH_2S), 1.83 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 141.2, 137.3, 132.9, 131.9, 130.0, 128.6, 128.3, 127.4, 126.3, 113.4, 38.3 (CH_2S), 33.1 (CH_2S), 20.8; *m/z* (EI) 230 (M^+, 2), 174 ($M^+-C_4H_8$, 9), 143 (34), 131 (100), 103 (66), 91 (33%); HRMS (EI): M^+, found 230.1139. $C_{15}H_{18}S$ requires 230.1129.

4.2.2. 2-Methyl-2-propenyl 4′-methyl-5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfide (4b). Oil (Method A, 93%). (Found: C, 78.59; H, 8.30. $C_{16}H_{20}S$ requires C, 78.65, H, 8.26%); IR ν_{max} 3022, 1597, 1213, 916, 746 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.37–7.22 (5H, m, ArH), 6.47 (1H, s, 5′-H), 6.27 (1H, d, *J*=15.4 Hz, 3′-H), 5.73 (1H, dt, *J*=15.4, 7.9 Hz, 2′-H), 4.89 (1H, s, 3-H), 4.86–4.85 (1H, m, 3-H), 3.19 (2H, d, *J*=7.9 Hz, CH_2S), 3.10 (2H, s, CH_2S), 2.01 (3H, s, Me), 1.84 (3H, d, *J*=0.6 Hz, Me); δ_C (62.5 MHz, $CDCl_3$) 141.3, 137.8, 137.7, 135.0, 130.8, 129.1, 128.0, 126.5, 125.0, 113.4, 38.2 (CH_2S), 33.3 (CH_2S), 20.8, 13.9; *m/z*

(EI) 244 (M^+, 8), 188 ($M^+-C_4H_8$, 31), 157 ($M^+-C_4H_7S$, 92), 142 ($M^+-C_5H_{10}S$, 44), 129 ($M^+-C_6H_{11}S$, 100), 115 (45), 77 (17%).

4.2.3. (2*E*)-Butenyl 4′-methyl-5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfide (4c). Oil (Method A, 81%). IR ν_{max} 3022, 1646, 1371, 987, 895, 748 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.37–7.21 (5H, m, ArH), 6.48 (1H, s, 5′-H), 6.27 (1H, dq, *J*=15.4, 0.8 Hz, 3′-H), 5.73 (1H, dt, *J*=15.4, 7.4 Hz, =CH, 2′-H), 5.53 (1H, dt, *J*=15.4, 7.4 Hz, =CH), 5.42 (1H, dtq, *J*=15.4, 7.4, 1.1 Hz, =CH), 3.21 (2H, d, *J*=7.4 Hz, CH_2S), 3.10 (2H, d, *J*=7.4 Hz, CH_2S), 2.01 (3H, d, *J*=1.1 Hz, Me), 1.67 (3H, d, *J*=7.4 Hz, Me); δ_C (62.5 MHz, $CDCl_3$) 137.8, 137.6, 135.1, 130.8, 129.1, 128.2, 128.1, 127.2, 126.5, 125.3, 33.3 (CH_2S), 33.0 (CH_2S), 17.6, 13.9; *m/z* (EI) 244 (M^+, 9), 189 ($M^+-C_4H_7$, 31), 157 ($M^+-C_4H_7S$, 100), 142 ($M^+-C_5H_{10}S$, 22), 129 ($M^+-C_6H_{11}S$, 53), 115 (23), 91 (18%); HRMS (EI): M^+, found 244.1277. $C_{16}H_{20}S$ requires 244.1286.

4.2.4. 3-Methyl-2-butenyl 4′-methyl-5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfide (4d). Oil (Method A, 90%). IR ν_{max} 3012, 1488, 1291, 751 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.40–7.22 (5H, m, ArH), 6.51 (1H, s, 5′-H), 6.32 (1H, d, *J*=15.5 Hz, 3′-H), 5.84 (1H, dt, *J*=15.5, 7.6 Hz, 2′-H), 5.30–5.26 (1H, m, 2-H), 3.23 (2H, d, *J*=7.6 Hz, CH_2S), 3.17 (2H, d, *J*=7.6 Hz, CH_2S), 2.05 (3H, s, Me), 1.79 (3H, s, Me), 1.71 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 137.8, 137.4, 135.1, 130.8, 129.3, 129.1, 128.1, 126.5, 125.5, 120.7, 33.8 (CH_2S), 28.8 (CH_2S), 25.6, 17.8, 13.9; *m/z* (EI) 258 (M^+, 9), 189 ($M^+-C_5H_9$, 46), 157 ($M^+-C_5H_9S$, 100), 105 (35%); HRMS (EI): M^+, found 258.1434. $C_{17}H_{22}S$ requires 258.1442.

4.2.5. (*E*)-Cinnamyl 5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfide (4e). Oil (Method B, 66%). IR ν_{max} 3021, 1597, 1213, 960, 696 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.34–7.14 (10H, m, ArH), 6.72 (1H, dd, *J*=15.4, 10.4 Hz, =CH), 6.44 (1H, d, *J*=15.4 Hz, =CH), 6.38 (1H, *J*=15.4 Hz, =CH), 6.18 (1H, dd, *J*=15.4, 10.4 Hz, =CH), 6.11 (1H, dt, *J*=15.4, 7.5 Hz, =CH), 5.70 (1H, dt, *J*=15.4, 7.5 Hz, =CH), 3.21 (2H, d, *J*=7.5 Hz, CH_2S), 3.20 (2H, d, *J*=7.5 Hz, CH_2S); δ_C (62.5 MHz, $CDCl_3$) 137.9, 137.4, 133.8, 133.1, 132.7, 130.7, 129.3 (overlapping signals), 128.9, 128.2 (overlapping signals), 127.0 (overlapping signals), 126.6, 33.9 (CH_2S), 33.6 (CH_2S); *m/z* (EI) 292 (M^+, 2), 143 ($M^+-PhC_3H_4S$, 40), 117 ($M^+-PhC_5H_6S$, 100), 91 (67), 77 (34%); HRMS (EI): M^+, found 292.1277. $C_{20}H_{20}S$ requires 292.1286.

4.2.6. (*E*)-Cinnamyl 4′-methyl-5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfide (4f). Oil (Method A, 82%). (Found: C, 82.35; H, 7.47. $C_{21}H_{22}S$ requires C, 82.31, H, 7.24%); IR ν_{max} 3054, 1492, 1394, 808 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.41–7.20 (10H, m, ArH), 6.48 (1H, s, 5′-H), 6.46 (1H, d, *J*=15.4 Hz, =CH), 6.30 (1H, d, *J*=15.3 Hz, =CH), 6.19 (1H, dt, *J*=15.4, 7.3 Hz, =CH), 5.74 (1H, dt, *J*=15.3, 7.3 Hz, =CH), 3.32 (2H, d, *J*=7.3 Hz, SCH_2), 3.28 (2H, d, *J*=7.3 Hz, SCH_2), 2.01 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 137.9, 137.7, 136.8, 135.1, 132.4, 130.9, 129.2, 128.5, 128.1, 127.5, 126.6, 126.3, 126.1, 125.2, 33.4 (overlapping signals, CH_2S), 14.0 (Me); *m/z* (EI) 306 (M^+, 5), 67 (100%).

4.2.7. 5-Phenyl-(2*E*,4*E*)-pentadienyl 3′-trimethylsilyl-(2′*E*)-propenyl sulfide (4g). Oil (Method A, 81%). IR ν_{max} 3022, 1597, 1213, 745 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.44–7.29 (5H, m, ArH), 6.81 (1H, dd, *J*=15.7, 10.4 Hz, 4-H), 6.53 (1H, d, *J*=15.7 Hz, 5-H), 6.24 (1H, dd, *J*=15.1, 10.4 Hz, =CH), 5.98 (1H, dt, *J*=18.4, 6.5 Hz, 2′-H), 5.80 (1H, dt, *J*=15.0, 10.4 Hz, =CH), 5.75 (1H, d, *J*=18.4 Hz, 3′-H), 3.19 (4H, d, *J*=6.5 Hz, CH_2S), 0.10 (9H, s, $Si(CH_3)_3$); δ_C (62.5 MHz, $CDCl_3$) 141.6, 137.3, 133.5, 133.0, 132.0, 130.1, 128.6, 128.3, 127.5, 126.3, 36.3 (CH_2S), 32.9 (CH_2S), −1.2 ($Si(CH_3)_3$); *m/z* (EI) 288 (M^+, <1), 43 (100%); HRMS (EI): M^+-H, found 287.1302. $C_{17}H_{23}SSi$ requires 287.1290.

4.2.8. Dienylic alcohol 7. To a stirred solution of ethyl-(triphenylphosphoranylidene)acetate (100 mmol) in dry benzene (100 ml) was added cinnamaldehyde or 4-methyl cinnamaldehyde **8** (90 mmol) dropwise at 0°C under nitrogen. The resulting solution was stirred at rt for 5 h. The reaction mixture was then poured into ice water and the aqueous phase extracted with ethyl acetate (3×50 ml). The combined organic solvents were dried ($MgSO_4$), filtered, evaporated in vacuo and purified by flash chromatography on silica gel with hexane/ethyl acetate (3:1 gradient to 1:1) as eluent to give ethyl 5-phenyl-(2*E*,4*E*)-pentadioate (91% yield) and ethyl 4-methyl-5-phenyl-(2*E*,4*E*)-pentadienoate (88% yield), respectively. To a stirred solution of DIBAL (100 ml, 1.0 M in hexane) was added the ester (50 mmol) at 0°C under nitrogen. The resulting solution was stirred at rt for 1 h. The reaction mixture was then poured into ice water and the aqueous phase extracted with ethyl acetate (3×50 ml). The combined organic solvents were dried ($MgSO_4$), filtered, concentrated in vacuo to give either 5-phenyl-(2*E*,4*E*)-pentadienol (95% yield) or 4-methyl-5-phenyl-(2*E*,4*E*)-pentadienol (91% yield). These dienylic alcohols have already been described.[11,12] For 5-phenyl-(2*E*,4*E*)-pentadienol: IR ν_{max} 3412, 2969, 1635, 1213, 930, 721 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.34–7.19 (5H, m, ArH), 6.52–5.90 (4H, m, =CH), 4.26 (2H, d, *J*=6.0 Hz, CH_2), 1.86 (1H, s, OH); δ_C (62.5 MHz, $CDCl_3$) 137.2, 132.6, 132.1, 131.6, 129.0, 128.7, 127.5, 126.4, 63.2; HRMS (EI): M^+, found 160.0883. $C_{11}H_{12}O$ requires 160.0889. For 4-methyl-5-phenyl-(2*E*,4*E*)-pentadienol: IR ν_{max} 3401, 2987, 1610, 1213, 948, 725 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.34–7.19 (5H, m, ArH), 6.52 (1H, s, 5-H), 6.44 (1H, d, *J*=15.7 Hz, 3-H), 5.92 (1H, dt, *J*=15.7, 6.0 Hz, 2-H), 4.26 (2H, d, *J*=6.0 Hz, CH_2), 2.35 (3H, s, 4-Me), 1.86 (1H, s, OH); δ_C (62.5 MHz, $CDCl_3$) 137.0, 132.7, 132.5, 131.6, 129.3, 128.1, 127.6, 126.4, 63.3, 13.8; *m/z* (EI) 174 (M^+, 23), 156 (M^+-H_2O, 33), 143 (100), 128 (56), 115 (43), 91 (74%); HRMS (EI): M^+, found 174.1039. $C_{12}H_{14}O$ requires 174.1045.

4.2.9. Dienylic thioacetate 3 or allylic thioacetate 6. A solution of DIAD (10 mmol) in dry benzene (10 ml) was added to a stirred solution of triphenylphosphine (10 mmol) in benzene (100 ml) at 0°C. The resulting red solution was kept at 0°C for 15 min and then a precooled (0°C) mixture of the stereochemically pure dienylic alcohol **7** or allyl alcohol **9** (10 mmol) and thioacetic acid (10 mmol) in dry benzene (20 ml) was added in one portion. The mixture was stirred at 20°C for 1 h and solvent was removed in vacuo. Flash chromatography of the residue over silica

gel (hexane/ethyl acetate=10:1) afforded either the dienylic thioacetate **3** or allylic thioacetate **6**. For 4-methyl-5-phenyl-(2*E*,4*E*)-pentadienyl thioacetate **3**: (Found: C, 72.08; H, 6.74. $C_{14}H_{16}OS$ requires C, 72.37, H, 6.94); IR ν_{max} 3067, 2965, 1635, 965, 687 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.36–7.18 (5H, m, ArH), 6.49 (1H, s, 5-H), 6.41 (1H, d, *J*=15.4 Hz, 3-H), 5.72 (1H, dt, *J*=15.4, 7.0 Hz, 2-H), 3.64 (2H, d, *J*=7.0 Hz, CH_2), 2.34 (3H, s, CH_3C=O), 1.96 (3H, s, CH_3); δ_C (62.5 MHz, $CDCl_3$) 195.0 (C=O), 138.5, 137.7, 134.9, 131.5, 129.1, 128.1, 126.6, 123.6, 31.8, 30.4, 13.8; *m/z* (EI) 232 (M^+, 18), 189 (M^+-CH_3CO, 13), 157 (M^+-CH_3COS, 100), 142 (45), 129 (87), 115 (45), 105 (41), 91 (44), 77 (23%). Cinnamyl thioacetate has already been described.[13] For 2-methyl-2-propenyl thioacetate **6**: IR ν_{max} 3022, 2910, 1646, 1371, 691 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 4.89–4.88 (1H, m, 3-H), 4.84–4.83 (1H, m, 3-H), 3.08 (2H, s, CH_2S), 2.34 (3H, s, CH_3C=O), 1.83 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 190.1 (C=O), 141.2, 113.4, 38.3 (CH_2S), 30.4, 20.8; *m/z* (EI) 130 (M^+, 2), 75 ($M^+-C_4H_7$, 9), 55 (100%); HRMS (EI): M^+, found 130.0450. $C_6H_{10}OS$ requires 130.0453.

4.3. General procedure for the preparation of allylic dienylic sulfones 1

A mixture of the sulfide **4** (5 mmol) and oxone (25 mmol) in CH_2Cl_2/MeOH (2:1, 30 ml) was stirred at rt for 3–5 days. The reaction mixture was filtered through a pad of silica gel and the filtered cake was washed with CH_2Cl_2/EtOAc (2:1, 50 ml). The filtrate was concentrated in vacuo. Flash chromatography of the residue over silica gel (hexane/ethyl acetate=10:1 gradient to 1:1) afforded the following sulfone:

4.3.1. 2-Methyl-2-propenyl 5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfone (1a). White solid (90%). Mp 110°C; (Found: C, 68.80; H, 7.11. $C_{15}H_{18}O_2S$ requires C, 68.67, H, 6.91%); IR ν_{max} 3030, 1492, 1290 (O=S=O), 1120 (O=S=O), 924, 795, 691 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.43–7.26 (5H, m, ArH), 6.81 (1H, dd, *J*=15.5, 10.4 Hz, 4′-H), 6.62 (1H, d, *J*=15.5 Hz, 5′-H), 6.49 (1H, dd, *J*=15.5, 10.4 Hz, 3′-H), 5.82 (1H, dt, *J*=15.5, 7.7 Hz, 2′-H), 5.25 (1H, t, *J*=1.4 Hz, 3-H), 5.10 (1H, s, 3-H), 3.83 (2H, d, *J*=7.7 Hz, CH_2SO_2), 3.68 (2H, s, CH_2SO_2), 1.99 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 139.4, 136.6, 135.0, 134.0, 128.7, 128.2, 127.2, 126.6, 120.5, 118.6, 60.0 (CH_2SO_2), 56.1 (CH_2SO_2), 22.7 (Me); *m/z* (EI, 20 eV) 262 (M^+, 2), 144 (40), 143 ($M^+-C_4H_7SO_2$, 100), 128 (98), 91 (17%); HRMS (EI): M^+, found 262.1032. $C_{15}H_{18}O_2S$ requires 262.1028.

4.3.2. 2-Methyl-2-propenyl 4′-methyl-5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfone (1b). White solid (85%). Mp 121°C; IR ν_{max} 3086, 1413, 1282 (O=S=O), 1119 (O=S=O), 978, 712, 696 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.35–7.17 (5H, m, ArH), 6.54 (1H, s, 5′-H), 6.48 (1H, d, *J*=15.5 Hz, 3′-H), 5.74 (1H, dt, *J*=15.5, 7.5 Hz, 2′-H), 5.23–5.21 (1H, m, 2-H), 5.07 (1H, s, 2-H), 3.82 (2H, d, *J*=7.5 Hz, CH_2SO_2), 3.65 (2H, s, CH_2SO_2), 1.99 (3H, s, Me), 1.96 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 144.4, 137.1, 134.5, 134.5, 133.8, 129.2, 128.2, 127.1, 120.5, 114.3, 59.9 (CH_2SO_2), 56.2 (CH_2SO_2), 22.7 (Me), 13.8 (Me); *m/z* (EI, 20 eV) 276 (M^+, <1), 157 ($M^+-C_4H_7SO_2$, 100), 129 (61%); HRMS (EI): M^+, found 276.1183. $C_{16}H_{20}O_2S$ requires 276.1185.

4.3.3. (2*E*)-Butenyl 4′-methyl-5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfone (1c). White solid (84%). Mp 124°C; IR ν_{max} 3051, 1414, 1292 (O=S=O), 1119 (O=S=O), 978, 758, 728 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.39–7.22 (5H, m, ArH), 6.58 (1H, s, 5′-H), 6.40 (1H, d, *J*=15.6 Hz, 3′-H), 5.88 (1H, dt, *J*=15.6, 6.5 Hz, =CH), 5.78 (1H, dt, *J*=15.6, 7.6 Hz, =CH), 5.58 (1H, dtq, *J*=15.6, 7.6, 1.6 Hz, =CH), 3.80 (2H, d, *J*=7.6 Hz, CH_2SO_2), 3.67 (2H, d, *J*=7.6 Hz, CH_2SO_2), 2.03 (3H, s, Me), 1.80 (3H, d, *J*=7.6 Hz, Me); δ_C (62.5 MHz, $CDCl_3$) 143.9, 136.9, 136.1, 134.3, 133.5, 129.0, 128.0, 126.9, 117.2, 114.1, 55.6 (CH_2SO_2), 55.4 (CH_2SO_2), 18.0 (Me), 13.6 (Me); *m/z* (EI, 20 eV) 276 (M^+, <1), 157 ($M^+-C_4H_7SO_2$, 100), 91 (22%); HRMS (EI): M^+, found 276.1180. $C_{16}H_{20}O_2S$ requires 276.1185.

4.3.4. 3-Methyl-2-butenyl 4′-methyl-5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfone (1d). White solid (83%). Mp 132°C; IR ν_{max} 2978, 1668, 1291 (O=S=O), 1119 (O=S=O), 977, 734, 695 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.38–7.22 (5H, m, ArH), 6.57 (1H, s, 5′-H), 6.50 (1H, d, *J*=15.6 Hz, 3′-H), 5.77 (1H, dt, *J*=15.6, 7.8 Hz, 2′-H), 5.32 (1H, t, *J*=7.8 Hz, 2-H), 3.74 (2H, d, *J*=7.8 Hz, CH_2SO_2), 3.70 (2H, d, *J*=7.8 Hz, CH_2SO_2), 2.03 (3H, s, Me), 1.85 (3H, s, Me), 1.61 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 143.0, 142.5, 137.1, 134.4, 133.7, 129.2, 128.2, 127.0, 114.3, 110.4, 56.2 (CH_2SO_2), 52.0 (CH_2SO_2), 25.9 (Me), 18.5 (Me), 13.8 (Me); *m/z* (EI, 20 eV) 290 (M^+, <1), 157 ($M^+-C_5H_9SO_2$, 100), 69 (45%); HRMS (EI): M^+, found 290.1350. $C_{17}H_{22}O_2S$ requires 290.1341.

4.3.5. (*E*)-Cinnamyl 5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfone (1e). White solid (70%). Mp 201°C; (Found: C, 73.82; H, 6.09. $C_{20}H_{20}O_2S$ requires C, 74.04, H, 6.21%); IR ν_{max} 2959, 1325 (O=S=O), 1135 (O=S=O), 892, 760, 691 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.45–7.25 (10H, m, ArH), 6.82 (1H, dd, *J*=15.5, 10.0 Hz, =CH), 6.69 (1H, d, *J*=15.5 Hz, =CH), 6.61 (1H, d, *J*=15.5 Hz, =CH), 6.49 (1H, dd, *J*=15.5, 10.0 Hz, =CH), 6.26 (1H, dt, *J*=15.5, 7.6 Hz, =CH), 5.84 (1H, dt, *J*=15.5, 7.6 Hz, =CH), 3.88 (2H, d, *J*=7.6 Hz, CH_2SO_2), 3.82 (2H, d, *J*=7.6 Hz, CH_2SO_2); δ_C (62.5 MHz, $CDCl_3$) 140.2, 139.8, 137.0, 136.1, 135.8 (overlapping signals), 129.4, 129.3, 128.9, 127.7, 127.4, 127.3, 119.0, 115.9, 56.8 (CH_2SO_2), 56.6 (CH_2SO_2); *m/z* (EI, 20 eV) 324 (M^+, 1), 143 ($M^+-C_9H_9SO_2$ 100), 91 (13%).

4.3.6. (*E*)-Cinnamyl 4′-methyl-5′-phenyl-(2′*E*,4′*E*)-pentadienyl sulfone (1f). White solid (90%). Mp 228°C; (Found: C, 74.61; H, 6.32. $C_{21}H_{22}O_2S$ requires C, 74.52, H, 6.55%); IR ν_{max} 3058, 1451, 1292 (O=S=O), 1116 (O=S=O), 957, 751, 692 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.41–7.25 (10H, m, ArH), 6.70 (1H, d, *J*=15.9 Hz, =CH), 6.55 (1H, s, 5′-H), 6.51 (1H, d, *J*=15.5 Hz, =CH), 6.27 (1H, dt, *J*=15.9, 7.5 Hz, =CH), 5.81 (1H, dt, *J*=15.5, 7.7 Hz, =CH), 3.90 (2H, d, *J*=7.5 Hz, CH_2SO_2), 3.85 (2H, *J*=7.7 Hz, CH_2SO_2), 2.03 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 144.4, 139.1, 137.1, 135.6, 134.5, 133.9, 129.2, 128.8, 128.7, 128.2, 127.1, 126.7, 115.4, 114.2, 56.3 (CH_2SO_2), 56.2 (CH_2SO_2), 13.8 (Me); *m/z* (EI,

20 eV) 338 (M^+, <1), 189 (1), 157 ($M^+ - PhC_3H_4O_2S$, 100), 129 (42), 91 (19%).

4.3.7. 5-Phenyl-(2*E*,4*E*)-pentadienyl 3′-trimethylsilyl-(2′*E*)-propenyl sulfone (1g). White solid (90%). Mp 175°C; IR ν_{max} 3028, 1377, 1290 (O=S=O), 1119 (O=S=O), 978, 921, 720 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.38–7.18 (5H, m, ArH), 6.75 (1H, dd, *J*=15.6, 10.4 Hz, 4-H), 6.56 (1H, d, *J*=15.6 Hz, 5-H), 6.39 (1H, dd, *J*=15.6, 10.4 Hz, 3-H), 6.10 (1H, d, *J*=18.5 Hz, 3′-H), 6.05–5.94 (1H, m, 2′-H), 5.75 (1H, dt, *J*=15.2, 7.5 Hz, 2-H), 3.73 (2H, d, *J*=7.5 Hz, CH_2SO_2), 3.70 (2H, d, *J*=7.5 Hz, CH_2SO_2), −0.60 (9H, s, $Si(CH_3)_3$); δ_C (62.5 MHz, $CDCl_3$) 143.0, 139.4, 136.6, 135.1, 131.4, 128.7, 128.2, 127.1, 126.6, 118.5, 59.0 (CH_2SO_2), 56.0 (CH_2SO_2), −1.6 ($Si(CH_3)_3$); *m/z* (EI, 20 eV) 320 (M^+, 4), 128 (100), 115 (55), 77 (49%); HRMS (EI): M^+, found 320.1265. $C_{17}H_{24}O_2SSi$ requires 320.1267.

4.4. General procedure for the preparation of 1,3,5,7-octatraenes 10

The sulfone **1** (1 mmol) was added to a stirred suspension of alumina-supported KOH (10 mmol of KOH)[9] in CF_2Br_2/CH_2Cl_2 (1:10 10 ml) at 0°C. The mixture was then stirred for 10 min to 2 h. The reaction mixture was filtered through a pad of celite and the filtered cake was washed thoroughly with CH_2Cl_2. The filtrate was concentrated in vacuo to give the crude octatetraene **10**. Flash chromatography over silica gel (hexane) afforded the 1,3,5,7-octatetraenes. Phenyl substituted octatetraenes are more stable. However, terminal octatetraenes are less stable and tend to polymerize upon concentration to give white precipitates even stored at −20°C in the dark in hexane solution. As a result, we were unable to obtain satisfactory high-resolution mass data or elemental analysis data for compounds **10a** and **10b**.

The following 1,3,5,7-octatetraenes were prepared:

4.4.1. (1*E*,3*E*,5*E*)-7-Methyl-1-phenyl-1,3,5,7-octatetraene (10a). Yellow oil (87%). IR ν_{max} 3029, 1878, 1360, 993, 734, 700 cm^{-1}; UV λ_{max} (log ε): 242 (4.6), 278 (4.6), 311 (4.4), 324 (4.5), 337 (4.5), 381 (4.4) nm; δ_H (500 MHz, $CDCl_3$) 7.40 (2H, t, *J*=7.6 Hz, ArH), 7.31 (2H, t, *J*=7.6 Hz, ArH), 7.21 (1H, t, *J*=7.6 Hz, ArH), 6.85 (1H, dd, *J*=15.5, 10.3 Hz, =CH), 6.56 (1H, d, *J*=15.5 Hz, 1-H), 6.45 (1H, dd, *J*=15.5, 10.3 Hz, =CH), 6.40 (1H, dd, *J*=15.5, 8.4 Hz, =CH), 6.38 (1H, d, *J*=15.5 Hz, 6-H), 6.31 (1H, dd, *J*=15.5, 8.4 Hz, =CH), 5.03 (1H, s, 8-H), 5.01 (1H, s, 8-H), 1.90 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 142.2, 137.5, 135.9, 133.6, 133.3, 132.4, 129.3, 129.2, 128.6, 127.5, 126.4, 117.0, 18.5 (Me); *m/z* (EI) 196 (M^+, 2),165 (5), 131 (19), 117 (16), 105 (57), 91 (42), 77 (46%); HRMS (EI): M^+, found 196.1243. $C_{15}H_{16}$ requires 196.1253.

4.4.2. (1*E*,3*E*,5*E*)-2,7-Dimethyl-1-phenyl-1,3,5,7-octatetraene (10b). Yellow oil (89%). IR ν_{max} 2983, 1679, 1453, 1377, 1002, 912, 734, 701 cm^{-1}; UV λ_{max} (log ε): 210 (5.1), 250 (4.5), 300 (4.7), 315 (4.7), 329 (4.8), 345 (4.9), 381 (3.7) nm; δ_H (500 MHz, $CDCl_3$) 7.36–7.30 (4H, m, ArH), 7.23 (1H, t, *J*=7.5 Hz, ArH), 6.54 (1H, s, 1-H), 6.49 (1H, d, *J*=15.5 Hz, 3-H), 6.45 (1H, dd, *J*=15.5, 10.0 Hz, =CH, 4-H), 6.39 (1H, d, *J*=15.6 Hz, 6-H), 6.36 (1H, dd, *J*=15.6, 10.0 Hz, =CH, 5-H), 5.01 (1H, s, 8-H), 5.00 (1H, s, 8-H), 2.05 (3H, s, Me), 1.91 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 142.3, 138.4, 137.9, 136.0, 135.4, 131.7, 129.7, 129.2, 128.8, 128.1, 126.5, 116.6, 18.5 (Me), 13.9 (Me); *m/z* (EI) 210 (M^+, 100), 195 (27), 165 (18), 155 (16), 131 (22), 115 (28), 91 (47), 77 (23%); HRMS (EI): M^+, found 210.1418. $C_{16}H_{18}$ requires 210.1409.

4.4.3. (1*E*,3*E*,5*E*,7*E*)-2-Methyl-1-phenyl-1,3,5,7-nonatetraene (10c). Yellow oil (92%). IR ν_{max} 2984, 1674, 1367, 992, 734, 701 cm^{-1}; UV λ_{max} (log ε): 244 (4.6), 278 (4.6), 381 (3.8) nm; δ_H (500 MHz, $CDCl_3$) 7.35–7.29 (4H, m, ArH), 7.21 (1H, t, *J*=7.5 Hz, ArH), 6.51 (1H, s, 1-H), 6.38 (1H, d, *J*=15.5 Hz, 3-H), 6.34 (1H, dd, *J*=15.6, 10.1 Hz, =CH), 6.27 (1H, dd, *J*=15.6, 10.1 Hz, =CH), 6.23 (1H, dd, *J*=15.6, 10.1 Hz, =CH), 6.14 (1H, ddq, *J*=15.1, 10.1, 2.0 Hz, 7-H), 5.74 (1H, dq, *J*=15.1, 6.5 Hz, 8-H), 2.04 (3H, s, Me), 1.80 (3H, d, *J*=6.5 Hz, Me); δ_C (62.5 MHz, $CDCl_3$) 138.6, 137.3, 136.1, 133.1, 132.0, 131.3, 130.8, 129.8, 129.2, 128.9, 128.1, 126.5, 18.3, 13.9; *m/z* (EI) 210 (M^+, 30), 169 (18), 115 (26), 91 (53), 77 (40%); HRMS (EI): M^+, found 210.1404. $C_{16}H_{18}$ requires 210.1409.

4.4.4. (1*E*,3*E*,5*E*)-2,8-Dimethyl-1-phenyl-1,3,5,7-nonatetraene (10d). Yellow oil (90%). (Found: C, 90.85; H, 8.70. $C_{17}H_{20}$ requires C, 91.01, H, 8.99); IR ν_{max} 2984, 1674, 1376, 992, 734, 701 cm^{-1}; UV λ_{max} (log ε): 215 (4.5), 241 (4.7), 284 (4.7), 381 (2.5) nm; δ_H (500 MHz, $CDCl_3$) 7.35–7.20 (5H, m, ArH), 6.51 (1H, s, 1-H), 6.49 (1H, dd, *J*=15.5, 11.0 Hz, =CH), 6.44 (1H, dd, *J*=15.5, 9.5 Hz, =CH), 6.40 (1H, d, *J*=15.1 Hz, 3-H), 6.24 (1H, dd, *J*=15.1, 9.5 Hz, =CH), 5.92 (1H, d, *J*=11.0 Hz, 7-H), 2.05 (3H, s, Me), 1.83 (3H, s, Me), 1.81 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 137.9, 136.6, 135.4, 135.0, 131.7, 130.9, 130.1, 129.7, 129.4, 128.1, 126.4, 125.7, 26.2 (Me), 21.0 (Me), 18.5 (Me); *m/z* (EI) 224 (M^+, 43), 210 (28), 165 (47), 129 (37), 115 (59), 105 (31), 91 (84%).

4.4.5. (1*E*,3*E*,5*E*,7*E*)-1,8-Diphenyl-1,3,5,7-octatetraene (10e). Yellow solid (90%). Mp 233–235°C (lit.[8] 235°C); IR ν_{max} 3012, 1488, 1072, 996, 748, 692 cm^{-1}; UV λ_{max} (log ε): 211 (5.4), 250 (2.1), 256 (2.9), 350 (4.9) nm; δ_H (500 MHz, $CDCl_3$) 7.41 (4H, d, *J*=7.5 Hz, ArH), 7.33 (4H, t, *J*=7.5 Hz, ArH), 7.22 (2H, t, *J*=7.5 Hz, ArH), 6.86 (2H, dd, *J*=15.0, 7.7 Hz, =CH), 6.58 (2H, d, *J*=7.7 Hz, =CH), 6.45 (4H, m, =CH); δ_C (62.5 MHz, $CDCl_3$) 137.6, 133.5 (overlapping signals), 132.8, 129.3, 128.7, 127.6, 126.4; *m/z* (EI) 258 (M^+, 100), 215 (10), 167 (72), 154 (51), 128 (38), 91 (32%); HRMS (EI): M^+, found 258.1420. $C_{20}H_{18}$ requires 258.1409.

4.4.6. (1*E*,3*E*,5*E*,7*E*)-1,8-Diphenyl-2-methyl-1,3,5,7-octatraene (10f). Yellow solid (80%). Mp 210°C; IR ν_{max} 3021, 1446, 1120, 997, 810, 752, 703 cm^{-1}; UV λ_{max} (log ε): 231 (4.9), 287 (3.9), 361 (4.8), 381 (4.9), 402 (4.9) nm; δ_H (500 MHz, $CDCl_3$) 7.33 (2H, d, *J*=7.5 Hz, ArH), 7.29–7.23 (6H, m, ArH), 7.16–7.13 (2H, m, ArH), 6.81 (1H, ddd, *J*=15.5, 7.5, 3.5 Hz, =CH), 6.49 (1H, s, 1-H), 6.48 (1H, d, *J*=15.5 Hz), 6.44–6.35 (4H, m), 2.00 (3H, s, Me); δ_C (62.5 MHz, $CDCl_3$) 138.6, 137.9, 137.6, 136.1, 133.9, 133.0, 132.3, 132.1, 129.4, 129.2, 128.8, 128.6, 128.2,

127.4, 126.6, 126.3, 13.9 (Me); *m/z* (EI) 272 (M^+, 100), 180 (23), 164 (19), 117 (55), 91 (17%); HRMS (EI): M^+, found 272.1571. $C_{21}H_{20}$ requires 272.1566.

4.4.7. (1*E*,3*E*,5*E*,7*E*)-1-Phenyl-8-trimethylsilyl-1,3,5,7-octatetraene (10g). Yellow oil (87%). (Found: C, 80.02; H, 8.53. $C_{17}H_{22}Si$ requires C, 80.25, H, 8.71); IR ν_{max} 2956, 1682, 1455, 1251, 1014, 843, 750, 692 cm^{-1}; UV λ_{max} (log ε): 250 (4.4), 329 (4.7) nm; δ_H (500 MHz, $CDCl_3$) 7.40 (2H, d, *J*=7.5 Hz, ArH), 7.32 (2H, t, *J*=7.5 Hz, ArH), 7.23 (1H, t, *J*=7.5 Hz, ArH), 6.85 (1H, dd, *J*=15.5, 10.5 Hz, =CH), 6.59 (1H, d, *J*=18.0, 10.5 Hz, 7-H), 6.57 (1H, d, *J*=15.5 Hz, 1-H), 6.44 (1H, dd, *J*=15.5, 10.5 Hz, =CH), 6.41 (1H, dd, *J*=15.0, 10.5 Hz, =CH), 6.34 (1H, dd, *J*=15.0, 10.5 Hz, =CH), 6.29 (1H, dd, *J*=15.5, 10.5 Hz, =CH), 5.93 (1H, d, *J*=18.0 Hz, 8-H), −0.10 (9H, s, $Si(CH_3)_3$); δ_C (62.5 MHz, $CDCl_3$) 144.1, 137.5, 135.8, 135.1, 134.0, 133.4, 133.3, 132.8, 129.2, 128.7, 127.5, 126.4, −1.28 ($Si(CH_3)_3$); *m/z* (EI) 254 (M^+, 19), 180 (6), 115 (5), 73 (100), 59 (23%).

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