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Facile Synthesis of the Fused 6-6-5 Ring System Containing Chroman Ring from 2-(1-Hydroxy-5-alkenyl)phenol Derivatives via Intramolecular Inverse-Electron-Demand Diels–Alder Reaction

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A simple and facile synthesis of the fused 6-6-5 ring system, i.e., 1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyrans, was achieved through the intramolecular [4+2] cycloaddition of *o*-quinonemethides generated from 2-(1-hydroxy-5-alkenyl)phenol derivatives under acidic conditions. In general, *cis*-fused tricyclic compounds of 6-6-5 ring system were obtained as the major products. Reactivity and selectivity of the cycloaddition reaction depended on the substituents on the aromatic ring and in the dienophilic olefin moiety.

There has been a great deal of interest in the intramolecular Diels–Alder reaction for many years[1] because the intramolecular Diels–Alder reaction is very often both regioselective and stereospecific.[2] This reaction can lead not only to various carbocyclic compounds but also to heterocyclic systems by introducing heteroatoms in the diene–dienophile system. Therefore, intramolecular Diels–Alder reaction has been used widely as a key reaction for the stereoselective total synthesis of natural products.

o-Quinonemethides are highly reactive intermediates which can be generated in various ways and act as dienes in the Diels–Alder reaction; generation from various precursors is usually the rate-determining step.[3] Since *o*-quinonemethide is an inverse electron demand diene, it reacts with electron-rich dienophiles.[4]

We previously reported facile methods for the generation of alkenyl- and alkenyloxy-substituted *o*-quinonemethides **1** (X = CH_2 and O) to furnish fused 6-6-6 tricyclic compounds **2** with *trans* B/C ring junction (Chart 1).[5] We anticipated that the tricyclic 6-6-5 ring system **3** can be similarly obtained if 6-(5-alkenylidene)-2,4-cyclohexadien-1-one is generated and allowed to react in the intramolecular fashion. In this case, a great interest is placed on the reaction mode, i.e., intramolecular vs. intermolecular mode, and on the stereoselectivity and regioselectivity in the intramolecular reaction.

Three groups have hitherto reported the generation of *o*-quinonemethides by the thermal dehydration of *o*-hydroxybenzyl alcohols and the subsequent intramolecular Diels–Alder cycloaddition leading to fused 6-6-5 tricyclic ring system. Schmid and co-workers[4] reported the thermolysis of **4a** at 147 °C to **5a**, followed by prolonged heating at 270 °C to produce the cycloadducts *cis*-**3a**, *trans*-**3a**, and **7a** in a combined yield of 69% (Chart 2).

Boeckelheide and Mao[6] reported that pyrolysis of **4a** at 700 °C and 0.01 mmHg (1 mmHg = 133.322 Pa) led directly to the chroman *cis*-**3a** in 12% yield. Gutsche and co-workers[7] reported the pyrolysis of **4b** at 280—300 °C in order to dehydrate it to the diene **5b**, furnishing tricyclic compound **3b** in 70% yield. But the detailed stereochemistry of the product was not studied.

As mentioned above, harsh conditions, i.e., vapor phase pyrolysis and prolonged heating at high temperature, were used to generate *o*-quinonemethides; therefore the product selectivity is low or the stereoselectivity is unclear.

Herein we describe a facile synthesis of 6-6-5 tricyclic ring system via *o*-quinonemethides under very mild conditions.

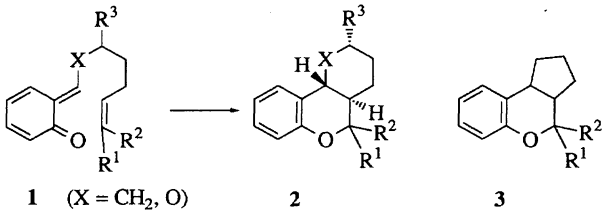


Chart 1.

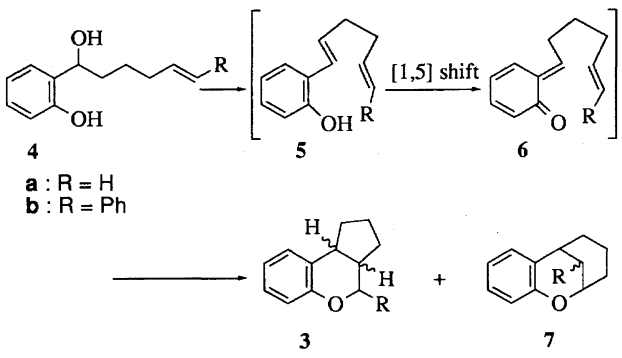
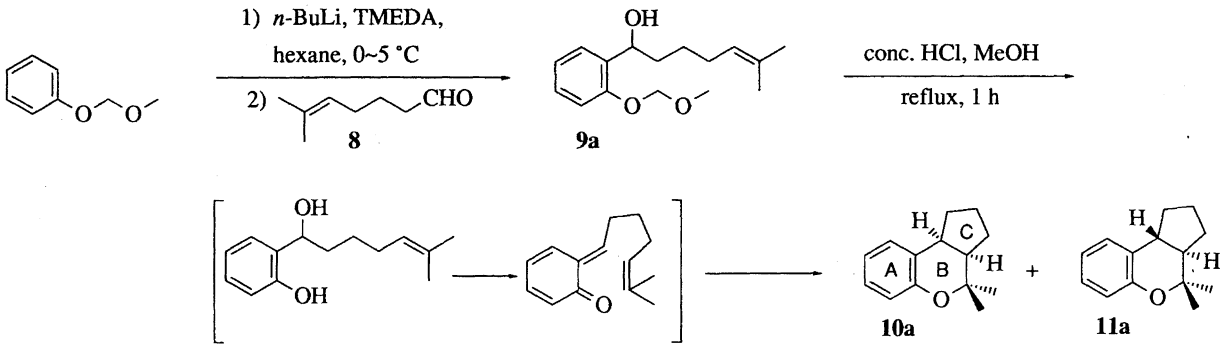


Chart 2.



Scheme 1.

Results and Discussion

With reference to the formation of 6-6-6 ring system (with *trans*-fused B/C ring), we thought that *o*-quinonemethides would be generated easily in the same or slightly modified reaction conditions to furnish 6-6-5 tricyclic ring system with *cis*-fused B/C ring as the *cis*-fused ring is thermodynamically more stable than the *trans*-fused one for 6-6-5 ring system. In view of our previous results that a dimethyl-substituted olefin moiety is very suitable for the intramolecular cycloaddition with *o*-quinonemethides leading to 6-6-6 tricyclic systems, we first synthesized 6-methyl-5-heptenal (**8**) from 4-methyl-3-pentyl bromide[8] via the malonic ester synthesis. It was then coupled with *ortho*-lithiated (methoxymethoxy)-benzene to give an *ortho*-substituted phenol derivative **9a**. This was then heated at reflux in methanol for an hour in the presence of a catalytic amount of hydrochloric acid to give a mixture of *cis*-4,4-dimethyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (**10a**) and its *trans* isomer **11a** in combined yield of 86%. The ratio of **10a** and **11a** was determined by gas chromatography to be 67 : 33 (Scheme 1).

The isolation of individual products from the mixture was quite difficult, but careful column chromatography afforded **10a** in 85% purity and **11a** in 76% purity.

The stereochemistry of both products **10a** and **11a** was determined on the basis of 270-MHz ^{1}H NMR analysis. For **10a**, the proton at C-9b appeared as a triplet at δ = 3.26 (J = 7.26 Hz), which suggested the *cis* relation between B and C rings. For **11a**, the proton at C-9b appeared as ddd at δ = 2.58 (J = 12.21, 11.55, and 7.26 Hz). Irradiation of the C-9b proton (δ = 3.26) in **10a** showed a 9.2% enhancement of the protons at C-3a and C-1, as shown in Fig. 1. Likewise, irradiation of the C-9b proton (δ = 2.58) in **11a** gave a 4.2% enhancement of the C-4 axial methyl (δ = 1.23) and irradiation of the C-4 equatorial methyl (δ = 1.42) gave a 7.2% enhancement of C-3a proton. These NOE experiments confirmed the stereochemistry of **10a** and **11a** as a *cis* and *trans* relationship between B and C rings, respectively.

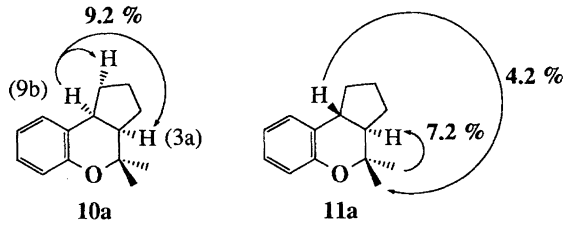
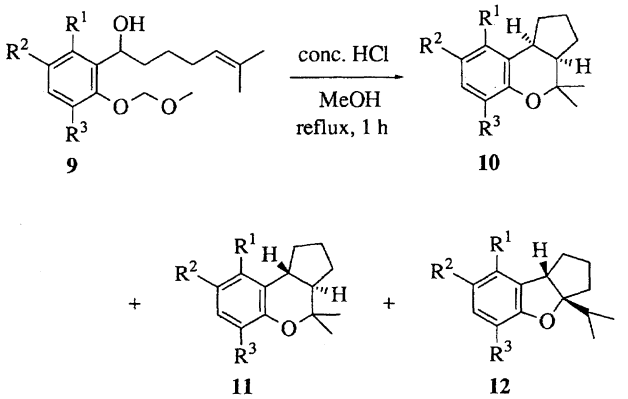


Fig. 1. Results of NOE experiments of **10a** and **11a**.

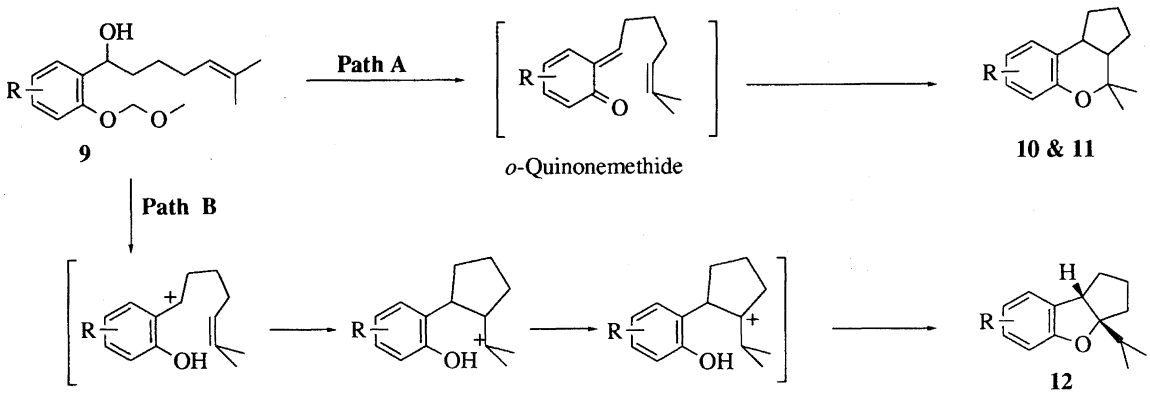
In the case of the 6-6-6 ring system, a single *trans* isomer was obtained stereoselectively.[5] We also reported the *trans* selective formation of 6-6-5 ring system which involved an oxygen atom in the C ring by the intramolecular cycloaddition of 6-(3-alkenyloxymethylene)-2,4-cyclohexadien-1-one.[9] The inversion and decrease of stereoselectivity for the present 6-6-5 ring system may be due to enhancement of steric hindrance between aromatic hydrogen and tethering methylene hydrogen, which retards the *exo*-mode cyclization. Or cyclization may have proceeded not only in a concerted way but via a stepwise mechanism as well.

According to MM2 calculations, the steric energy of **10a** and **11a** is 7.3 and 8.9 kcal mol^{-1}, respectively. This indicates that for the 6-6-5 ring system *cis* isomer is more stable than *trans* one by 1.6 kcal mol^{-1}. In general, a Diels–Alder reaction is reversible; therefore, a mixture of **10a** and **11a** (**10a** : **11a** = 28 : 72) was heated at reflux in

Table 1. Acid Catalyzed Reaction of **9** in Methanol

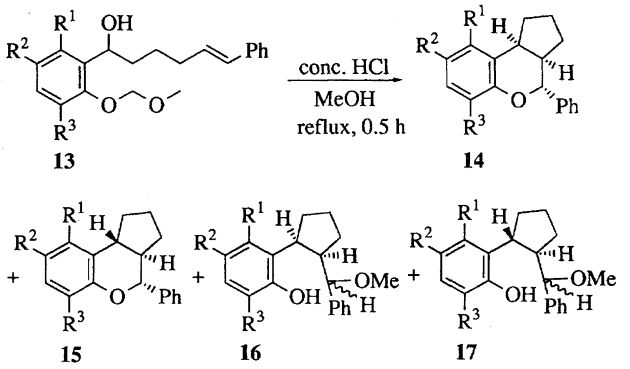


Compd	R^1	R^2	R^3	Product yield/%	Products ratio **10**	**11**	**12**
9a	H	H	H	86	67	33	0
9b	OMe	H	H	58	58	10	32
9c	OMe	OMe	H	52	58	8	34
9d	Me	H	Me	62	48	10	42

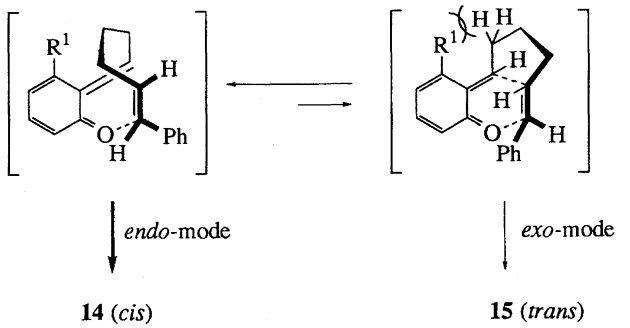


Scheme 2.

Table 2. Acid Catalyzed Reaction of **13** in Methanol



Compd	R^1	R^2	R^3	Solvent	Product yield/%	Products ratio 14	15	16	17
13a	H	H	H	MeOH	97	29	44	3	24
13b	OMe	H	H	MeOH	97	62	0	0	38
13c	Me	H	Me	MeOH	89	58	14	0	28
13d	H	Br	H	MeOH	72	41	24	20	15
13a	H	H	H	MeCN	90	45	55	0	0
13b	OMe	H	H	MeCN	30	100	0	0	0
13d	H	Br	H	MeCN	82	47	53	0	0



Scheme 3.

methanol in the presence of hydrochloric acid for 6 h, but the ratio did not change throughout the reaction period. This fact indicates that the cycloadducts are kinetically controlled products rather than those of thermodynamic control. Next we examined the cyclization reaction using different substituents in the aromatic ring, since the chemical reactivity of *o*-quinonemethides can be significantly affected by substituents.

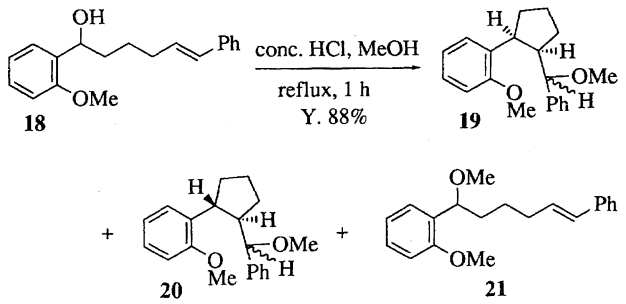
As shown in Table 1, *cis*-fused tricyclic products **10** were produced as predominant products in all cases, but 6-5-5 ring system compounds **12** containing an isopropyl group at the angular position were obtained in the reaction of methoxy- or methyl-substituted phenols. The structure of **12** was determined by ^{1}H NMR and NOE experiments. We assumed that when electron donating groups are substituted to phenols, LUMO level of *o*-quinonemethides would be increased, which would decrease the reaction rate of the inverse electron demand Diels–Alder cyclization reaction. As the result, the reaction proceeded with a stepwise mechanism to form **12** (Scheme 2, Path B).

Next we examined the reaction of compounds **13**, which had a phenyl substituent at the end of the olefin. The results are summarized in Table 2.

In contrast to the cyclization of **9**, the acid treatment of **13a—d** afforded the desired 6-6-5 tricyclic compounds **14** and **15** along with 1,2-disubstituted cyclopentanes **16** and **17** as by-products, without any formation of 6-5-5 tricyclic compounds such as **12**. Such results can be explained on the basis of the relative stability of benzyl cations. Thus the benzyl cation species formed by the stepwise cyclization mechanism did not rearrange to cyclopentyl cations by hydride transfer but was trapped with methanol to furnish **16** and **17**. Examination of the isomer ratio of the 6-6-5 tricyclic compounds indicated that phenols without substituent at R^1 (**13a**, **13d**) underwent cyclization in both *endo*- and *exo*-modes, whereas cyclization took place exclusively or predominantly with *endo*-mode for substituted compounds **13b** and **13c**, because of the steric repulsion between R^1 and the tethering methylene hydrogen in the *exo*-mode, giving *cis*-fused tricyclic compound selectively (Scheme 3).

Careful comparison of ^{1}H NMR spectrum of **3b** reported by Gutsche et al.[7] with those of our compounds revealed that **3b** was a mixture of **14a** and **15a**.

The structure determination of **16** and **17** merits some comments. IR spectra of **17b** indicated the phenolic OH absorption at 3251 cm^{-1}. ^{1}H NMR spectra of **17b** showed two methoxy groups at δ = 3.72 and 3.21, suggesting that one is connected to the aromatic nuclei and the other is connected to an aliphatic carbon. A clear doublet appeared at δ = 4.01, which originated from the benzylidene proton of the starting

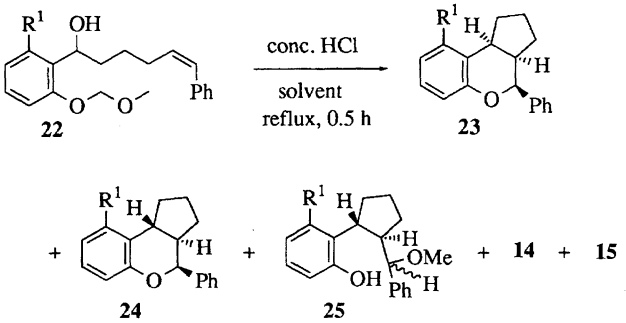


Scheme 4.

material **13b**, suggesting the presence of a methoxy group at the same carbon. Furthermore, the aliphatic methylene signals of **17b** were very similar to the signals of cyclopentane ring protons of 6-6-5 tricyclic compounds **14** and **15**. These spectral characteristics suggested the structure **17b** as 1,2-disubstituted cyclopentane. The stereochemistry was tentatively determined as *trans* because of a very weak NOE between the two methine protons of the cyclopentane ring, and ultimately confirmed by the comparison of the ^{1}H NMR spectra with those of **19** and **20** (vide infra).

In view of possible involvement of **16** and **17** as precursors in the formation of **14** and **15**, the mixture of **16a** and **17a** (1 : 9) and the pure compound **17b** were separately subjected to heating in methanol at reflux in the presence of a catalytic amount of hydrochloric acid for 1 and 3 h, respectively, resulting in the complete recovery of the starting material. It seemed, therefore, very interesting to study the cyclization of **13** in aprotic solvent for the possible inhibition of formation of **16** and **17**. Then the cyclization reaction was carried out in acetonitrile containing a catalytic amount of hydrochloric acid and a drop of water at reflux for half an hour. Very fortunately, the cyclization of **13a** gave **14a** and **15a** in 90% yield in the ratio of 45 : 55 without any formation of **16a** and **17a**. From **13d** were obtained **14d** and **15d** in the ratio of 47 : 53 in 82% yield. Treatment of **13b** under similar conditions, however, gave *cis*-**14b** in only 30% yield with several unidentified by-products (Table 2).

Table 3. Acid Catalyzed Reaction of **22** in Methanol and Acetonitrile



Compd	R^1	Solvent	Product yield/%	Products ratio 23	24	25	14	15
22a	H	MeOH	36	40	50	0	3	7
22a	H	MeCN	77	41	26	0	15	18
22b	OMe	MeOH	83	7	14	70	4	5
22b	OMe	MeCN	30	15	7	0	25	53

In order to see if the formation of cyclopentane compounds such as **16** and **17** (path B in Scheme 2) is a rapid process compared to the formation of tricyclic compounds (**14**, **15**), we synthesized substituted anisol **18** and carried out the reaction in methanol at reflux in the presence of hydrochloric acid. After the reaction for an hour, we found 1,2-disubstituted cyclopentanes **19** and **20**, and substitution product **21** in the ratio of 41 : 35 : 24 (Scheme 4).

As the substitution product **21** is apparently derived from the benzyl cation species formed from **18**, one may safely say that the formation of the cyclopentanes is not a rapid process. The reaction of **13a** under acidic conditions was very rapid and the starting compound disappeared completely in 15 min, therefore the formation of tricyclic compounds such as **14** and **15** via *o*-quinonemethide (path A in Scheme 2) seems to be a relatively rapid process.

The structures of **19** and **20** were determined by comparison of the ^{1}H NMR spectra with that of **17b**. The stereochemistry of **19** and **20** was determined by NOE experiments. Irradiation of the C-1 proton (δ = 3.42) in **19** showed a 8.7% enhancement of the proton at C-2 (δ = 2.75). Likewise, irradiation of the C-1 proton (δ = 3.38) in **20** showed a 1.2% enhancement of the proton at C-2 (δ = 2.37). These facts indicated the stereochemistry of **19** and **20** as *cis* and *trans* isomers, respectively.

It seemed worthwhile to thoroughly examine the stereospecificity of this reaction from synthetic and mechanistic points of view. For this purpose we synthesized **22**, the *cis* isomer of **13**, and the cyclization reaction was examined in methanol and acetonitrile. The results are summarized in Table 3.

In both solvents, cyclization took place very easily. On detailed investigation of products, however, tricyclic compounds consisted of four isomers, two predictable products **23** and **24** and their stereoisomers **14** and **15**. Tricycles **14** and **15** were minor products except in the cyclization of **22b** in acetonitrile. When **22b** was treated with acid in methanol, 1,2-disubstituted cyclopentane **25b** was produced predominantly with very minor amounts of four tricyclic compounds. ^{1}H NMR spectra of **25b** and **17b** are quite similar, but a notable difference is detected in the coupling constant of the methine proton of methoxy(phenyl)methyl group, which shows J = 9.9 Hz in **25b** (δ = 3.95) and J = 4.95 Hz in **17b** (δ = 4.01). These indicate **17b** and **25b** are diastereomers as to the configuration at the methoxy(phenyl)methyl carbon. Here again, **25b** was subjected to heating in methanol at reflux in the presence of hydrochloric acid for 3 h, resulting in the recovery of the starting material. This confirmed that once **25** is formed, it undergoes neither isomerization to give **17** nor cyclization to give tricyclic compound under the reaction conditions.

As **23** and **24** did not isomerize to **14** and **15**, respectively, under the reaction conditions, it seems very likely that **14** and **15** were produced via carbocation species in the stepwise mechanism. These results indicate that the concerted [4+2]

cyclization of **22** is strongly hindered by the terminal (*Z*)-phenyl substituent.

In conclusion we have found that a fused 6-6-5 ring system is easily formed by the intramolecular cyclization of 2-(1-hydroxy-5-alkenyl)phenol derivatives under very mild conditions. In this cyclization, a mixture of B/C-*cis* and -*trans* fused compounds is formed, and in some selected cases *cis*-fused compounds are obtained selectively or predominantly. In addition to tricyclic 6-6-5 compounds, 6-5-5-tricyclic compounds or 1,2-disubstituted cyclopentane derivatives are formed as by-products by the stepwise cyclization process. The ratios of *cis*/*trans* isomers and 6-6-5/6-5-5 or cyclopentanes are greatly affected by substituents in the phenol as well as in the dienophilic olefin moiety.

Experimental

Melting points were determined on a Büchi 535 apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi 260-10 spectrometer, or a Perkin–Elmer Paragon 1000 spectrometer. ^{1}H NMR (270 MHz) and ^{13}C NMR (67.80 MHz) spectra were recorded on a JEOL-EX 270 spectrometer with tetramethylsilane as an internal standard. Mass spectra were recorded with a Perkin–Elmer Q-Mass 910 mass spectrometer or a PROFILE (Shimadzu/KRATOS) instrument. Gas chromatographic determination was performed on a Shimadzu GC-14A. Column chromatography was carried out with Fujidavison silica gel BW-127 ZH (Fuji Davison Chemical Industries) or Wako gel C-200 (Wako Pure Chemical Industries). Thin-layer chromatography (TLC) was carried out with Merck TLC plates with Silica gel 60 F_{254}. Elemental analyses were carried out on a Perkin–Elmer 2400 CHN elemental analyzer.

6-Methyl-5-heptenal (8): To an ethanol (100 cm^3) solution of sodium ethoxide prepared from sodium (2.9 g, 126 mmol) was added diethyl malonate (20.3 g, 125 mmol); the solution was warmed up to 50 °C and stirred for 1 h. To this warm mixture 5-bromo-2-methyl-2-pentene[8] (20.4 g, 125 mmol) was added; then the mixture was refluxed for 3 h. After cooling to room temperature, it was poured into ice-cold saturated NH_4Cl–H_2O (1 : 1) solution. The whole solution was neutralized, then extracted with ethyl acetate four times. The combined organic extracts were dried over $MgSO_4$, then concentrated, and distilled at 92—100 °C/8 mmHg to give 22.0 g (73%) of **diethyl 2-(4-methyl-3-pentenyl)malonate**. IR (neat) 2990, 1740, 1360, 1295, 1250, 1140, 1095, 1020, and 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.23—1.29 (6H, m), 1.58 (3H, s), 1.68 (3H, s), 1.89—2.04 (4H, m), 3.33 (1H, t, J = 7.26 Hz), 4.13—4.23 (4H, m), 5.08 (1H, t, J = 7.26 Hz).

A solution of diethyl 4-methyl-3-pentenylmalonate (22.0 g, 90.8 mmol) and sodium hydroxide (20.0 g, 0.5 mol) in methanol (10 cm^3) was stirred at reflux for 2 h. After the methanol was evaporated under reduced pressure using an aspirator, the residue was acidified with 1 M (1 M = 1 mol dm^{-3}) HCl to pH 1, and extracted with chloroform. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The crude product was recrystallized with hexane/ethyl acetate (10 : 1) to give 15.2 g (90%) of **2-carboxy-6-methyl-5-heptenoic acid**. Mp 88—89 °C; IR (KBr) 3100, 2650, 1710, 1460, 1420, 1300, 1280, 1240, 1210, 1140, 920, 840, and 675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.59 (3H, s), 1.68 (3H, s), 1.96—2.09 (4H, m), 3.48 (1H, t, J = 7.26 Hz), 5.06 (1H, bs).

A mixture of 2-carboxy-6-methyl-5-heptenoic acid (6.4 g, 34.4 mmol), pyridine (16 cm^3), and water (2 cm^3) was refluxed for 5 h. The reaction mixture was acidified with 1 M HCl to pH 1, and extracted with ethyl acetate four times, and the combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by chromatography on silica gel using hexane/ethyl acetate (3 : 1) as eluent to give 4.7 g (96%) of **6-methyl-5-heptenoic acid** as colorless oil. IR (neat) 3110, 2650, 1700, 1450, 1420, 1310, 1280, 1240, 1210, 1140, 920, 850, and 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.59 (3H, s), 1.68 (2H, m), 1.69 (3H, s), 2.05 (2H, m), 2.34 (2H, m), 5.08 (1H, t, J = 8.58 Hz).

A mixture of lithium aluminium hydride (3.3 g, 88.1 mmol) and dry ether (50 cm^3) was stirred for 20 min. Then a solution of 6-methyl-5-heptenoic acid (6.2 g, 43.6 mmol) in dry ether (20 cm^3) was added dropwise to the above solution at 0 °C; then the reaction mixture was stirred for 2 h at r.t. This reaction mixture was quenched by adding cold 2 M HCl. The aqueous layer was extracted with ether four times. The combined organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by chromatography on silica gel using hexane/ether (3 : 2) as eluent to give 4.5 g (80%) of **6-methyl-5-hepten-1-ol**[10]) as colorless oil. IR (neat) 3300, 2940, 2850, 1430, 1360, 1050, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.39 (2H, m), 1.56 (2H, m), 1.60 (3H, s), 1.69 (3H, s), 2.02 (2H, m), 3.64 (2H, t, J = 6.27 Hz), 5.11 (1H, t, J = 8.55 Hz).

To a stirred solution of pyridinium chlorochromate (PCC) (2.6 g, 12.0 mmol) and sodium acetate (0.2 g, 2.4 mmol) in dry dichloromethane (40 cm^3), 6-methyl-5-hepten-1-ol (1.0 g, 8.0 mmol) in dry dichloromethane (10 cm^3) was added slowly and the mixture was stirred for 2 h. The reaction mixture was diluted with ether (30 cm^3) and then filtered by celite and florisil. The filtrate was concentrated and purified by flash chromatography on silica gel using hexane/ethyl acetate (9 : 1) as eluent to give 0.7 g (70%) of **6-methyl-5-heptenal** (**8**) as colorless oil. IR (neat) 2940, 2850, 2700, 1720, 1440, and 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.59 (3H, s), 1.67 (2H, m), 1.69 (3H, s), 2.02 (2H, m), 2.42 (2H, m), 5.08 (1H, t, J = 8.57 Hz), 9.76 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 17.6, 22.2, 25.6, 27.2, 43.2, 123.3, 132.7, 202.7; MS *m*/*z* (rel intensity) 126 (M^+; 4), 82 (100), 67 (35), 55 (20), 41 (50). HRMS Found: *m*/*z* 126.1031. Calcd for $C_8H_{14}O$: M, 126.1045.

***cis*- and *trans*-4,4-Dimethyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (10a, 11a):** To a stirred solution of butyllithium/hexane (1.6 M) (1.88 cm^3, 3.3 mmol) in dry hexane (10 cm^3), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.95 cm^3, 6.3 mmol) and (methoxymethoxy)benzene (0.41 g, 3.0 mmol) diluted with dry hexane (5 cm^3) were added slowly at −5 °C; then the mixture was stirred for 3 h at 0 °C. To this, **8** (0.38 g, 3.0 mmol) in dry hexane (5 cm^3) was added dropwise and the mixture was stirred for 2 h more at 0 °C. Then it was poured into saturated NH_4Cl solution and extracted with ether four times. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated, and column chromatography on silica gel using hexane/ethyl acetate (8 : 2) as eluent gave 0.47 g (60%) of **1-[2-(methoxymethoxy)phenyl]-6-methyl-5-hepten-1-ol** (**9a**) as colorless oil. IR (neat) 3400, 2910, 1600, 1490, 1450, 1230, 1150, 1070, 1000, 920, and 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.38 (2H, m), 1.59 (3H, s), 1.67 (3H, s), 1.79 (2H, m), 2.01 (2H, m), 2.38 (1H, bs), 3.49 (3H, s), 4.93 (1H, t, J = 6.6 Hz), 5.09 (1H, t, J = 5.9 Hz), 5.23 (2H, s), 7.01 (1H, dd, J = 7.59, 1.32 Hz), 7.09 (1H, dd, J = 8.24, 0.99 Hz), 7.22 (1H, dd, J = 1.65, 0.99 Hz), 7.35 (1H, dd, J = 7.59, 1.65 Hz).

A solution of **9a** (0.11 g, 0.6 mmol) in methanol (10 cm^3) containing one drop of hydrochloric acid was heated at reflux for an

hour. After the methanol was evaporated, 2 cm^3 of water was added to the residue and the mixture was extracted with ether five times. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, concentrated; column chromatography on silica gel using hexane/ethyl acetate (9 : 1) as eluent gave 0.098 g (86%) of mixture of *cis*- 4,4-dimethyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (**10a**) and *trans*-4,4-dimethyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (**11a**) as viscous oil in the ratio of 2 : 1. The isolation of individual **10a** and **11a** from the mixture was quite difficult, but careful column chromatography on silica gel using hexane/ethyl acetate (98 : 2) as eluent afforded **10a** in 85% purity and **11a** in 76% purity. IR (neat) as mixture of **10a** and **11a**: 2950, 2870, 1690, 1480, 1380, 1360, 1300, 1240, 1210, 1100, 1030, 945, 910, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) **10a**: δ = 1.26 (3H, s, CH_3-4^{ax}), 1.36 (3H, s, CH_3-4^{eq}), 1.47—1.60 (3H, m), 1.76 (1H, m, H-3), 1.91 (1H, m, H-1), 2.02—2.13 (2H, m, H-1 and H-3a), 3.26 (1H, t, J = 7.26 Hz, H-9b), 6.75 (1H, d, J = 7.26 Hz, Ar-H), 6.87 (1H, dd, J = 7.26, 7.59 Hz, Ar-H), 7.06 (1H, dd, J = 7.26, 7.59 Hz, Ar-H), 7.14 (1H, d, J = 7.59 Hz, Ar-H); ^{13}C NMR ($CDCl_3$) **10a**: δ = 23.1, 25.5, 26.3, 27.4, 33.7, 37.1, 47.7, 75.1, 117.2, 120.4, 126.9, 128.7, 153.4 (one carbon peak is overlapping); ^{1}H NMR ($CDCl_3$) **11a**: δ = 1.23 (3H, s, CH_3-4^{ax}), 1.27—1.94 (6H, m), 1.42 (3H, s, CH_3-4^{eq}), 2.33 (1H, m, H-1), 2.58 (1H, ddd, J = 12.21, 11.55, 7.26 Hz, H-9b), 6.73—6.89 (2H, m, Ar-H), 7.04—7.15 (2H, m, Ar-H); ^{13}C NMR ($CDCl_3$) **11a**: δ = 21.1, 23.3, 26.3, 28.9, 29.6, 39.3, 51.8, 79.6, 116.7, 119.7, 127.3, 127.8, 129.1, 154.3. Found: C, 82.73; H, 9.09% for mixture of **10a** and **11a**. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

***cis*- and *trans*-9-Methoxy-4,4-dimethyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (10b, 11b) and 3a-Isopropyl-8-methoxy-2,3,3a,8b-tetrahydro-1*H*-cyclopenta[*b*]benzofuran (12b):** A mixture of butyllithium/hexane (1 cm^3, 1.7 mmol), TMEDA (0.46 g, 3.2 mmol), 1-methoxy-3-(methoxymethoxy)benzene (0.26 g, 1.6 mmol), and aldehyde **8** (0.2 g, 1.6 mmol) was reacted as before to give 0.42 g (91%) of **1-[2-methoxy-6-(methoxymethoxy)phenyl]-6-methyl-5-hepten-1-ol (9b)** as colorless oil. IR (neat) 3550, 2900, 1590, 1460, 1430, 1230, 1150, 1090, 1000, 920, 780, and 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.30 (1H, m), 1.52 (1H, m), 1.58 (3H, s), 1.66 (3H, s), 1.82 (2H, m), 2.00 (2H, q, J = 7.26 Hz), 3.48 (3H, s), 3.65 (1H, d, J = 11.88 Hz, OH), 3.84 (3H, s), 5.11—5.17 (2H, m), 5.20 (2H, d, J = 1.98 Hz), 6.59 (1H, d, J = 8.25 Hz, Ar-H), 6.74 (1H, d, J = 8.25 Hz, Ar-H), 7.14 (1H, dd, J = 8.25 Hz, Ar-H).

A solution of **9b** (0.15 g, 0.5 mmol) in methanol (10 cm^3) was refluxed in the presence of a catalytic amount of hydrochloric acid as before to give 0.07 g (57%) of mixture of *cis*-9-methoxy-4,4-dimethyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (**10b**), *trans*-9-methoxy-4,4-dimethyl-1,2,3,3a,4,9b-hexahydrocyclopenta-[*c*][1]benzopyran (**11b**), and **12b** as liquid in the ratio of 58 : 10 : 32. Careful column chromatography on silica gel using hexane/ethyl acetate (95 : 5) as eluent afforded **10b** in 80% purity, **11b** in 60% purity, and **12b** in 90% purity. IR (neat) as mixture of **10b**, **11b**, and **12b**: 2950, 1600, 1480, 1460, 1325, 1280, 1240, 1190, 920, 760, and 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) **10b**: δ = 1.21 (3H, s, CH_3-4^{ax}), 1.34 (3H, s, CH_3-4^{eq}), 1.47—1.92 (6H, m), 2.35 (1H, m, H-3a), 3.25 (1H, m, H-9b), 3.80 (3H, s, CH_3O), 6.32—6.45 (2H, m, Ar-H), 7.02 (1H, m, Ar-H); **11b**: δ = 1.16 (3H, s, CH_3-4^{ax}), 1.40 (3H, s, CH_3-4^{eq}), 1.47—1.92 (6H, m), 2.42—2.68 (2H, m, H-1 and H-9b), 3.80 (3H, s, CH_3O), 6.32—6.45 (2H, m, Ar-H), 7.02 (1H, m, Ar-H); **12b**: δ = 0.94 (3H, d, J = 7.03 Hz, CH**Me**$_2$), 0.99 (3H, d, J = 6.6 Hz, CH**Me**$_2$), 1.47—1.92 (6H, m), 1.99 (1H, m, C**H**Me$_2$), 3.56 (1H, d, J = 7.19 Hz, H-9b), 3.82 (3H, s, CH_3O), 6.32—6.45 (2H, m, Ar-H), 7.02 (1H, m, Ar-H); ^{13}C NMR ($CDCl_3$) as mixture of **10b**, **11b**, and **12b**: δ = 17.3, 17.4, 22.7, 24.4, 24.6, 25.7, 26.9, 27.2, 32.3, 33.4, 36.0, 37.1, 47.0, 47.8, 55.2, 55.3, 75.5, 78.2, 78.9, 101.8, 102.1, 102.5, 103.8, 110.0, 117.9, 126.5, 128.9, 156.2. HRMS Found: *m/z* 232.1484 for **10b**; 232.1477 for **11b**; 232.1478 for **12b**. Calcd for $C_{15}H_{20}O_2$: M, 232.1463.

***cis*- and *trans*-8,9-Dimethoxy-4,4-dimethyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (10c, 11c) and 3a-Isopropyl-7,8-dimethoxy-2,3,3a,8b-tetrahydro-1*H*-cyclopenta[*b*]benzofuran (12c):** A mixture of butyllithium/hexane (0.9 cm^3, 1.7 mmol), TMEDA (0.49 cm^3, 3.3 mmol), 1,2-dimethoxy-4-(methoxymethoxy)benzene (0.18 g, 1.5 mmol), and aldehyde **8** (0.18 g, 1.5 mmol) was reacted as before to give 0.26 g (53%) of **1-[2,3-dimethoxy-6-(methoxymethoxy)phenyl]-6-methyl-5-hepten-1-ol (9c)** as colorless oil. IR (neat) 3500, 2910, 1580, 1480, 1240, 1140, 1040, 915, 790, and 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.32 (1H, m), 1.52 (1H, m), 1.58 (3H, s), 1.67 (3H, s), 1.82 (2H, m), 2.02 (2H, q, J = 7.26 Hz), 3.48 (3H, s), 3.62 (1H, d, J = 11.51 Hz, OH), 3.82 (3H, s), 3.88 (3H, s), 5.03—5.13 (2H, m), 5.16 (2H, d, J = 3.63 Hz), 6.73 (1H, d, J = 9.24 Hz, Ar-H), 6.82 (1H, d, J = 9.24 Hz, Ar-H).

A solution of **9c** (0.16 g, 0.5 mmol) in methanol (10 cm^3) was refluxed in the presence of a catalytic amount of hydrochloric acid as before to give 0.07 g (52%) of mixture of *cis*-8,9-dimethoxy-4,4-dimethyl-1,2,3,3a,4,9b-hexahydrocyclocyclopenta[*c*][1]benzopyran (**10c**), *trans*-8,9-dimethoxy-4,4-dimethyl-1,2,3,3a,4,9b-hexahydrocyclocyclopenta[*c*][1]benzopyran (**11c**), and **12c** as solid in the ratio of 58 : 8 : 34. Careful column chromatography on silica gel using hexane/ethyl acetate (98 : 2) as eluent afforded **10c** in 70% purity, **11c** in 60% purity, and **12c** in 80% purity. IR (neat) as mixture of **10c**, **11c** and **12c**: 2950, 1600, 1580, 1480, 1380, 1360, 1290, 1280, 1250, 1140, 1080, 1050, 980, 940, 850, 800, and 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) **10c**: δ = 1.19 (3H, s, CH_3-4^{ax}), 1.33 (3H, s, CH_3-4^{eq}), 1.46—2.13 (7H, m), 3.31 (1H, m, H-9b), 3.80 (3H, s, CH_3O), 3.86 (3H, s, CH_3O), 6.33—6.71 (2H, m, Ar-H); **11c**: δ = 1.15 (3H, s, CH_3-4^{ax}), 1.39 (3H, s, CH_3-4^{eq}), 1.46—2.13 (7H, m), 2.41 (1H, m, H-9b), 3.79 (3H, s, CH_3O), 3.90 (3H, s, CH_3O), 6.33—6.71 (2H, m, Ar-H); **12c**: δ = 0.93 (3H, d, J = 6.6 Hz, CH**Me**$_2$), 0.99 (3H, d, J = 6.9 Hz, CH**Me**$_2$), 1.46—1.92 (6H, m), 2.05 (1H, m, C**H**Me$_2$), 3.62 (1H, d, J = 7.59 Hz, H-9b), 3.80 (3H, s, CH_3O), 3.85 (3H, s, CH_3O), 6.33—6.71 (2H, m, Ar-H); MS *m/z* (rel intensity) **10c**: 262 (M^+; 100), 247 (33), 219 (35), 191 (34), 177 (32), 152 (25), 133 (17), 115 (17), 91 (25), 77 (20), 55 (22); MS *m/z* (rel intensity) **11c**: 262 (M^+; 100), 219 (28), 207 (10), 191 (9), 167 (18), 152 (15), 91 (12), 77 (6); MS *m/z* (rel intensity) **12c**: 262 (M^+; 100), 247 (32), 219 (36), 205 (16), 191 (46), 177 (40), 162 (18), 152 (24), 133 (15), 115 (16), 105 (18), 95 (20), 91 (26), 77 (17), 69 (16), 55 (16). HRMS Found: *m/z* 262.1585 for **10c**; 262.1597 for **11c**; 262.1599 for **12c**. Calcd for $C_{16}H_{22}O_3$: M, 262.1569.

***cis*- and *trans*-4,4,6,9-Tetramethyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (10d, 11d) and 3a-Isopropyl-5,8-dimethyl-2,3,3a,8b-tetrahydro-1*H*-cyclopenta[*b*]benzofuran (12d):** A mixture of butyllithium/hexane (1 cm^3, 1.7 mmol), TMEDA (0.47 cm^3, 3.1 mmol), 1-(methoxymethoxy)-2,5-dimethylbenzene (0.27g, 1.7 mmol), and aldehyde **8** (0.19 g, 1.5 mmol) was reacted as before to give 0.22 g (50%) of **1-(2-methoxymethoxy-3,6-dimethylphenyl)-6-methyl-5-hepten-1-ol (9d)** as colorless oil. IR (neat) 3410, 2930, 1440, 1380, 1250, 1200, 1160, 1070, 1040, 990, 930, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.32 (1H, m), 1.52 (1H, m), 1.58 (3H, s), 1.67 (3H, s), 1.83 (2H, m), 2.02 (2H, m), 2.23 (3H, s), 2.35 (3H, s), 3.61 (3H, s), 3.71 (1H, d, J = 9.24 Hz, OH),

4.89—5.13 (4H, m), 6.87 (1H, d, J = 7.92 Hz, Ar-H), 6.97 (1H, d, J = 7.92 Hz, Ar-H).

A solution of **9d** (0.08 g, 0.3 mmol) in methanol (5 cm^3) was refluxed in the presence of a catalytic amount of hydrochloric acid as before to give 0.04 g (62%) of mixture of *cis*- 4,4,6,9-tetramethyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (**10d**), *trans*-4,4,6,9-tetramethyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*]-[1]benzopyran (**11d**), and **12d** as liquid in the ratio of 48 : 10 : 42. Careful column chromatography using hexane/ethyl acetate (98 : 2) as eluent afforded **10d** in 75% purity, **11d** in 95% purity, and **12d** in 65% purity. IR (neat) as mixture of **10d**, **11d**, and **12d** : 2960, 1590, 1460, 1420, 1370, 1350, 1260, 1220, 1150, 910, and 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) **10d** : δ = 1.15 (3H, s, CH_3-4^{ax}), 1.36 (3H, s, CH_3-4^{eq}), 1.42—1.74 (5H, m), 2.05 (1H, m, H-3), 2.15 (3H, s, CH_3-6), 2.21 (3H, s, CH_3-9), 2.41 (1H, m, H-3a), 3.26 (1H, m, H-9b), 6.62 (1H, d, J = 7.58 Hz, Ar-H), 6.81 (1H, m, Ar-H); **11d** : δ = 1.14 (3H, s, CH_3-4^{ax}), 1.19—1.54 (2H, m), 1.40 (3H, s, CH_3-4^{eq}), 1.71—1.90 (4H, m), 2.15 (3H, s, CH_3-6), 2.21 (3H, s, CH_3-9), 2.49—2.61 (2H, m, H-1 and H9b), 6.55 (1H, d, J = 7.26 Hz, Ar-H), 6.86 (1H, d, J = 7.59 Hz, Ar-H); ^{13}C NMR ($CDCl_3$) **11d** : δ = 16.6, 19.9, 22.0, 22.8, 25.1, 28.9, 30.3, 39.2, 52.3, 77.2, 120.9, 128.1; ^{1}H NMR ($CDCl_3$) **12d** : δ = 0.91 (3H, d, J = 6.6 Hz, CH**Me**$_2$), 0.99 (3H, d, J = 6.6 Hz, CH**Me**$_2$), 1.46—1.74 (6H, m), 1.85 (1H, m, C**H**Me$_2$), 2.13 (3H, s, CH_3-6), 2.23 (3H, s, CH_3-9), 3.46 (1H, dd, J = 6.3, 6.59 Hz, H-8b), 6.51 (1H, d, J = 7.26 Hz, Ar-H), 6.82 (1H, d, J = 7.59 Hz, Ar-H); ^{13}C NMR ($CDCl_3$) as mixture of **10d** and **12d** : δ = 15.1, 15.9, 17.4, 17.5, 18.0, 19.8, 24.5, 25.3, 26.0, 27.0, 28.1, 33.7, 34.3, 35.3, 36.0, 36.9, 48.4, 48.7, 75.0, 102.5, 115.5, 120.6, 121.8, 124.0, 127.2, 128.9, 129.3, 131.3, 134.3, 150.9, 158.8; MS *m/z* (rel intensity) **10d** : 230 (M^+; 70), 215 (15), 187 (100), 173 (23), 159 (35), 145 (55), 115 (20), 91 (25), 77 (17), 55 (6); MS *m/z* (rel intensity) **12d** : 230 (M^+; 65), 215 (13), 187 (100), 173 (15), 159 (41), 145 (56), 115 (20), 91 (28), 77 (12). HRMS Found: *m/z* 230.1695 for **10d**; 230.1663 for **11d**; 230.1691 for **12d**. Calcd for $C_{16}H_{22}O$: M, 230.1671.

(*E*)-6-Phenyl-5-hexenal: To a stirred solution of 3-chloro-1-propanol (4.15 cm^3, 50.0 mmol) in dry THF (50 cm^3), methylmagnesium chloride (3 M THF solution, 16.7 cm^3, 50.0 mmol) was added dropwise at −20 °C and the solution was stirred for 20 min more. To this, magnesium (1.82 g, 75 mmol) was added and the mixture was heated at reflux. Then 1,2-dibromoethane (0.09 cm^3, 1.0 mmol) was added twice at the interval of 1 h. After having been heated at reflux for 2 h more, the Grignard reagent was cooled to room temperature.[11]

To a solution of cinnamyl bromide (7.4 cm^3, 50 mmol) in dry THF (10 cm^3), the freshly prepared Grignard reagent as described above was added dropwise over 30 min period at −10 °C. After stirring for 1 h at −10 °C, the reaction mixture was poured into ice-cold saturated NH_4Cl–H_2O (30 cm^3) and extracted with ether four times. The combined organic layers were washed with water, brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane/ether (1 : 1) as eluent to give 5.68 g (65%) of **(*E*)-6-phenyl-5-hexen-1-ol** as yellowish oil. IR (neat) 3356, 3025, 2934, 2860, 1652, 1598, 1495, 1060, 965, 745, and 693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.43—1.68 (5H, m), 2.24 (2H, m), 3.67 (2H, m), 6.22 (1H, m), 6.39 (1H, d, J = 15.84 Hz), 7.15—7.36 (5H, m, Ar-H); MS *m/z* (rel intensity) 176 (M^+; 40), 158 (25), 143 (16), 129 (45), 117 (72), 115 (100), 104 (25), 91 (75), 65 (8).

(*E*)-6-Phenyl-5-hexen-1-ol (2.64 g, 15.0 mmol) was reacted with PCC (4.8 g, 22.5 mmol) in dichloromethane (30 cm^3) as described before to give 2.1 g (80%) of **(*E*)-6-phenyl-5-hexenal**[12] as clear liquid. IR (neat) 3025, 2935, 2835, 2722, 1724, 1589, 1493, 1448, 968, 745, and 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.80 (2H, m), 2.25 (2H, m), 2.47 (2H, m), 6.16 (1H, m), 6.40 (1H, d, J = 15.84 Hz), 7.16—7.35 (5H, m, Ar-H), 9.77 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 21.4, 32.0, 42.8, 125.8, 126.8, 128.3, 129.3, 130.6, 137.3, 201.8; MS *m/z* (rel intensity) 174 (M^+; 11), 130 (100), 115 (48), 104 (13), 91 (37), 77 (9), 39 (13). HRMS Found: *m/z* 174.1026. Calcd for $C_{12}H_{14}O$: M, 174.1045.

(3a*R, 4*R**, 9b*S**)- and (3a*R**, 4*R**, 9b*R**)-(±)-4-Phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (14a, 15a) and (±)-2-{(1*R**, 2*S**)- and (1*R**, 2*R**)-2-[methoxy(phenyl)-methyl]cyclopentyl}phenol (16a, 17a):** A mixture of butyllithium/hexane (2.3 cm^3, 3.4 mmol), TMEDA (0.7 g, 6.0 mmol), (methoxymethoxy)benzene (0.43 g, 3.2 mmol), and (*E*)-6-phenyl-5-hexenal (0.5 g, 2.9 mmol) was reacted as described before to give 0.58 g (65%) of **(*E*)-1-[2-(methoxymethoxy)phenyl]-6-phenyl-5-hexen-1-ol (13a)** as slightly greenish oil. IR (neat) 3423, 2934, 1489, 1231, 1153, 1077, 1003, 755, and 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.61 (2H, m), 1.84 (2H, m), 2.25 (2H, m), 2.42 (1H, d, J = 6.6 Hz, OH), 3.43 (3H, s), 4.96 (1H, m), 5.19 (2H, s), 6.20 (1H, m), 6.38 (1H, d, J = 15.84 Hz), 6.97—7.09 (2H, m, Ar-H), 7.17—7.36 (7H, m, Ar-H).

A solution of **13a** (0.16 g, 0.5 mmol) in methanol (10 cm^3) was refluxed in the presence of a catalytic amount of hydrochloric acid as before to give 0.13 g (97%) of mixture of (3a*R**, 4*R**, 9b*S**)-(±)-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (**14a**), (3a*R**, 4*R**, 9b*R**)-(±)-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (**15a**), (±)-2-{(1*R**, 2*S**)-2-[methoxy-(phenyl)methyl]cyclopentyl}phenol (**16a**), and (±)-2-{(1*R**, 2*R**)-2-[methoxy(phenyl)methyl]cyclopentyl}phenol (**17a**) as solid in the ratio of 29 : 44 : 3 : 24. Mixture of **14a** and **15a**, and mixture of **16a** and **17a** was separated by column chromatography on silica gel using hexane/ethyl acetate (9 : 1) as eluent. Further isolation of individual **14a** and **15a** was quite difficult, but careful column chromatography on silica gel using hexane/ethyl acetate (98 : 2) as eluent afforded **14a** in 80% purity and **15a** in 70% purity. Similarly, isolation of **16a** and **17a** by chromatography afforded **16a** in 30% purity and **17a** in 90% purity.

When a solution of **13a** (0.012 g, 0.04 mmol) in acetonitrile/water (9 : 1) (10 cm^3) was refluxed for 30 min in the presence of a catalytic amount of hydrochloric acid, 0.008 g (90%) of mixture of **14a** and **15a** was obtained as solid in the ratio of 45 : 55. IR (KBr) as mixture of **14a** and **15a** : 3032, 2953, 2871, 1580, 1486, 1454, 1351, 1237, 1192, 1118, 1038, 995, 915, 754, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) **14a** : δ = 1.28—1.96 (5H, m), 2.34 (1H, m, H-1), 2.58 (1H, m, H-3a), 3.10 (1H, m, H-9b), 4.36 (1H, d, J = 10.9 Hz, H-4), 6.85—7.43 (9H, m, Ar-H); **15a** : δ = 1.28—1.96 (6H, m), 2.34 (1H, m, H-3a), 2.75 (1H, m, H-9b), 5.07 (1H, d, J = 10.9 Hz, H-4), 6.85—7.43 (9H, m, Ar-H); ^{13}C NMR ($CDCl_3$) as mixture of **14a** and **15a** : δ = 22.7, 23.9, 27.2, 28.0, 28.3, 34.8, 40.0, 41.7, 43.5, 48.8, 80.0, 85.0, 115.8, 117.0, 120.0, 120.9, 126.3, 126.4, 126.8, 127.5, 127.9, 128.1, 128.2, 128.5, 129.7, 141.5; MS *m/z* (rel intensity) **14a** : 250 (M^+; 100), 221 (6), 207 (22), 159 (92), 91 (40), 91 (44), 77 (5); MS *m/z* (rel intensity) **15a** : 250 (M^+; 100), 207 (23), 159 (72), 131 (9), 117 (24), 77 (5). Found: C, 85.89; H, 7.39% for mixture of **14a** and **15a**. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%.

IR (KBr) as mixture of **16a** and **17a** : 3423, 3037, 2955, 2869, 1608, 1580, 1486, 1453, 1352, 1237, 1194, 1125, 1036, 995, 977, 755, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) **16a** : δ = 1.53—1.94 (5H, m), 2.13 (1H, m, H-5), 2.63 (1H, m, H-2), 2.81 (3H, s, C**H**$_3$OCHPh), 3.49 (1H, m, H-1), 3.78 (1H, d, J = 3.30 Hz, PhC**H**OMe), 6.79—6.94 (4H, m, Ar-H), 7.09—7.31 (5H, m, Ar-

H); **17a**: δ = 1.53—1.94 (6H, m), 2.13 (1H, m, H-2), 3.29 (3H, s, C**H**$_3$OCHPh), 3.30 (1H, m, H-1), 4.18 (1H, d, J = 3.95 Hz, PhC**H**OMe), 5.28 (1H, bs, OH), 6.79—6.94 (4H, m, Ar-H), 7.09—7.30 (5H, m, Ar-H). MS m/z (rel intensity) **16a**: 250 ($M^+ - CH_3OH$; 100), 207 (22), 159 (98), 121 (97), 117 (30), 107 (14), 91 (58), 77 (25); **17a**: 250 ($M^+ - CH_3OH$; 70), 207 (5), 159 (100), 131 (16), 91 (35), 84 (10).

(3aR^*, 4R^*, 9bS^*)-(±)-9-Methoxy-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (14b) and (±)-3-Methoxy-2-{(1R^*, 2R^*)-2-[methoxy(phenyl)methyl]cyclopentyl}phenol (17b): A mixture of butyllithium/hexane (2.3 cm^3, 3.4 mmol), TMEDA (0.7 g, 6.0 mmol), 1-methoxy-3-(methoxymethoxy)benzene (0.53 g, 3.2 mmol), and (*E*)-6-phenyl-5-hexenal (0.5 g, 2.9 mmol) was reacted as before to give 0.44 g (45%) of **(*E*)-1-[2-methoxy-6-(methoxymethoxy)phenyl]-6-phenyl-5-hexen-1-ol (13b)** as viscous oil. IR (neat) 3558, 2934, 1736, 1596, 1473, 1440, 1233, 1154, 1101, 1069, 1007, 967, 734, and 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.42—2.03 (4H, m), 2.23 (2H, m), 3.43 (3H, s), 3.72 (1H, d, J = 10.55 Hz, OH), 3.87 (3H, s), 5.15—5.21 (3H, m), 6.20 (1H, m), 6.36 (1H, d, J = 15.84 Hz), 6.59 (1H, d, J = 8.58 Hz, Ar-H), 6.75 (1H, d, J = 8.25 Hz, Ar-H), 7.15 (1H, m, Ar-H), 7.23—7.33 (5H, m, Ar-H).

A solution of **13b** (0.15 g, 0.44 mmol) in methanol (10 cm^3) was refluxed in the presence of a catalytic amount of hydrochloric acid as before to give 0.12g (97%) of mixture of **14b** and **17b** as solid in the ratio of 62 : 38. The isolation by column chromatography on silica gel using hexane/ethyl acetate (95 : 5) as eluent afforded crystallines of individual **14b** and **17b** in 100% purity.

A solution of **13b** (0.012 g, 0.035 mmol) in acetonitrile/water (9 : 1) (10 cm^3) was stirred at 50 °C for 30 min in the presence of a catalytic amount of hydrochloric acid to give 0.003 g (30%) of **14b** as pure crystals.

14b: Mp 99—101 °C; IR (KBr) 2945, 2878, 1602, 1588, 1466, 1348, 1267, 1234, 1165, 1091, 1000, 780, 700, and 546 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.32—1.80 (5H, m), 2.43 (1H, m, H-3a), 2.55 (1H, m, H-1), 3.12 (1H, dt, J = 7.26, 10.55 Hz, H-9b), 3.84 (3H, s, CH_3O), 4.38 (1H, d, J = 10.89 Hz, H-4), 6.55 (1H, d, J = 8.25 Hz, Ar-H), 6.58 (1H, d, J = 8.25 Hz, Ar-H), 7.06 (1H, dd, J = 8.24, 7.92 Hz, Ar-H), 7.31—7.43 (5H, m, Ar-H); ^{13}C NMR ($CDCl_3$) δ = 23.2, 27.4, 32.7, 36.7, 41.2, 55.4, 79.1, 102.3, 109.7, 115.4, 126.4, 126.5, 126.8, 128.0, 128.2, 128.4, 140.0, 155.4, 158.8; MS m/z (rel intensity) 280 (M^+; 48), 189 (100), 161 (15), 147 (25), 107 (24), 91 (31). Found: C, 81.42; H, 7.14%. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19%.

17b: Mp 140—143 °C. IR (KBr) 3251, 2951, 2862, 1598, 1463, 1351, 1281, 1242, 1171, 1078, 925, 838, 765, 614, and 544 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.60—1.83 (5H, m), 2.13 (1H, m, H-5), 2.66 (1H, m, H-2), 3.21 (3H, s, C**H**$_3$OCHPh), 3.34 (1H, m, H-1), 3.72 (3H, s, CH_3O-Ar), 4.01 (1H, d, J = 4.95 Hz, PhC**H**OMe), 5.62 (1H, s, OH), 6.39 (1H, d, J = 8.25 Hz, Ar-H), 6.42 (1H, d, J = 8.25 Hz, Ar-H), 6.98 (1H, t, J = 8.25 Hz, Ar-H), 7.14—7.25 (5H, m, Ar-H); ^{13}C NMR ($CDCl_3$) δ = 24.5, 27.6, 30.1, 37.2, 50.5, 55.2, 56.7, 84.8, 103.4, 109.1, 118.1, 126.7, 127.0, 127.2, 127.8, 141.0, 155.2, 159.1; MS m/z (rel intensity) 280 ($M^+ - CH_3OH$; 48), 189 (100), 161 (15), 147 (24), 115 (16), 107 (22), 91 (39), 77 (12). Found: C, 76.79; H, 7.75%. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74%.

(3aR^*, 4R^*, 9bS^*)- and (3aR^*, 4R^*, 9bR^*)-(±)-6,9-Dimethyl-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (14c, 15c) and (±)-3,6-Dimethly-2-{(1R^*, 2R^*)-2-[methoxy(phenyl)methyl]cyclopentyl}phenol (17c): A mixture of butyllithium/hexane (2.3 cm^3, 3.4 mmol), TMEDA (0.7 g, 6.0 mmol), 1-(methoxymethoxy)-2,5-dimethylbenzene (0.52 g, 3.2 mmol), and (*E*)-6-phenyl-5-hexenal (0.5 g, 2.9 mmol) was reacted as before to give 0.29 g (30%) of **(*E*)-1-[2-(methoxymethoxy)-3,6-dimethylphenyl]-6-phenyl-5-hexen-1-ol (13c)** as viscous oil. IR (neat) 3453, 2930, 1737, 1599, 1496, 1250, 1194, 1159, 1035, 973, 927, 810, 744, and 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.48—2.12 (4H, m), 2.22 (3H, s), 2.27 (2H, m), 2.35 (3H, s), 3.58 (3H, s), 3.76 (1H, d, J = 10.24 Hz, OH), 4.96 (2H, m), 5.09 (1H, d, J = 5.61 Hz), 6.22 (1H, m), 6.37 (1H, d, J = 15.84 Hz), 6.83 (1H, d, J = 7.59 Hz, Ar-H), 6.97 (1H, d, J = 7.92 Hz, Ar-H), 7.17—7.34 (5H, m, Ar-H).

A solution of **13c** (0.11 g, 0.3 mmol) in methanol (7 cm^3) was refluxed in the presence of a catalytic amount of hydrochloric acid as before to give 0.083 g (89%) of mixture of (3aR^*, 4R^*, 9bS^*)-(±)-6,9-dimethyl-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*]-[1]benzopyran (**14c**), (3aR^*, 4R^*, 9bR^*)-(±)-6,9-dimethyl-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (**15c**), and (±)-3,6-dimethly-2-{(1R^*, 2R^*)-2-[methoxy(phenyl)methyl]cyclopentyl}phenol (**17c**) as solid in the ratio of 58 : 14 : 28. Purification by further column chromatography on silica gel using hexane/ethyl acetate (98 : 2) as eluent afforded **14c** in 80% purity, **15c** in 90% purity, and pure crystals of **17c**. IR (neat) as mixture of **14c** and **15c**: 3031, 2954, 2875, 1588, 1457, 1417, 1350, 1260, 1214, 1165, 1071, 1003, 802, 764, 700, 645, and 587 cm^{-1}; ^{1}H NMR ($CDCl_3$) **14c**: δ = 1.40—1.85 (5H, m), 2.13 (3H, s, CH_3-9), 2.31 (3H, s, CH_3-6), 2.36—2.49 (2H, m), 3.06 (1H, m, H-9b), 4.46 (1H, d, J = 10.89 Hz, H-4), 6.68 (1H, d, J = 7.59 Hz, Ar-H), 6.91(1H, d, J = 7.16 Hz, Ar-H), 7.31—7.44 (5H, m, Ar-H); **15c**: δ = 1.40—1.85 (6H, m), 2.18 (3H, s, CH_3-9), 2.33 (3H, s, CH_3-6), 2.50 (1H, m, H-3a), 2.79 (1H, m, H-9b), 5.00 (1H, d, J = 10.56 Hz, H-4), 6.62 (1H, d, J = 7.58 Hz, Ar-H), 6.90 (1H, d, J = 7.16 Hz, Ar-H), 7.31—7.44 (5H, m, Ar-H); ^{13}C NMR ($CDCl_3$) as mixture of **14c** and **15c**: δ = 16.2, 19.4, 22.4, 22.6, 26.2, 27.5, 30.5, 32.1, 39.2, 42.4, 44.0, 50.2, 77.7, 83.7, 121.1, 123.5, 124.2, 126.2, 127.7, 127.8, 127.9, 128.2, 128.4, 134.9, 135.1, 140.8. Found: C, 86.03; H, 7.99% for mixture of **14c** and **15c**. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97%.

17c: IR (KBr) 3412, 3027, 2950, 2870, 1578, 1467, 1362, 1271, 1214, 1154, 1077, 959, 905, 797, 761, 703, and 628 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.57—2.01 (6H, m), 2.20 (6H, s, CH_3-Ar), 2.81 (1H, m, H-2), 3.21 (3H, s, C**H**$_3$OCHPh), 3.55 (1H, m, H-1), 3.99 (1H, d, J = 4.29 Hz, PhC**H**OMe), 4.92 (1H, bs, OH), 6.61 (1H, d, J = 7.58 Hz, Ar-H), 6.84 (1H, d, J = 59 Hz, Ar-H), 7.13—7.29 (5H, m, Ar-H).

(3aR^*, 4R^*, 9bS^*)- and (3aR^*, 4R^*, 9bR^*)-(±)-8-Bromo-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (14d, 15d) and 4-Bromo-2-{(1R^*, 2S^*)- and (1R^*, 2R^*)-2-[methoxy(phenyl)methyl]cyclopentyl}phenol (16d, 17d): A mixture of butyllithium/hexane (1.5 cm^3, 2.4 mmol), TMEDA (0.64 g, 4.2 mmol), 4-bromo-1-(methoxymethoxy)benzene (0.43 g, 3.2 mmol), and (*E*)-6-phenyl-5-hexenal (0.35 g, 2.0 mmol) was reacted as before to give 0.39 g (50%) of **(*E*)-1-[5-bromo-2-(methoxymethoxy)phenyl]-6-phenyl-5-hexen-1-ol (13d)** as slightly greenish oil. IR (neat) 3421, 2931, 1734, 1595, 1482, 1400, 1309, 1234, 1198, 1179, 1155, 1078, 997, 923, 811, 744, and 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.52—1.83 (4H, m), 2.21—2.29 (3H, m), 3.40 (3H, s), 4.94 (1H, d, J = 5.93 Hz), 5.15 (2H, s), 6.20 (1H, m), 6.37 (1H, d, J = 15.84 Hz), 6.96 (1H, d, J = 8.91 Hz, Ar-H), 7.16—7.34 (6H, m, Ar-H), 7.51 (1H, s, Ar-H).

A solution of **13d** (0.10 g, 0.25 mmol) in methanol (7 cm^3) was refluxed in the presence of a catalytic amount of hydrochloric acid as before to give 0.06 g (74%) of mixture of **14d**, **15d**, **16d**, and **17d** as solid in the ratio of 41 : 24 : 15 : 20. The isolation by chromatography on silica gel using hexane/ethyl acetate (9 : 1) as

eluent gave a mixture of **14d** and **15d**, and a mixture of **16d** and **17d**. Further careful column chromatography of the mixture of **14d** and **15d** on silica gel using hexane/ethyl acetate (98 : 2) as eluent afforded **14d** in 70% purity and **15d** in 65% purity. Similarly column chromatography of mixture of **16d** and **17d** afforded **16d** in 65% purity and **17d** in 70% purity.

A solution of **13d** (0.16 g, 0.41 mmol) in acetonitrile/water (9 : 1) (10 cm^3) was refluxed for 30 min in the presence of a catalytic amount of hydrochloric acid to give 0.11 g (82%) of mixture of **14d** and **15d** in the ratio of 47 : 53. IR (KBr) as mixture of **14d** and **15d**: 3033, 2954, 2872, 1571, 1474, 1410, 1351, 1240, 1189, 1126, 1075, 995, 908, 876, 815, 756, 697, and 574 cm^{-1}; ^{1}H NMR ($CDCl_3$) **14d**: δ = 1.28—1.96 (5H, m), 2.32 (1H, m, H-1), 2.55 (1H, m, H-3a), 3.07 (1H, m, H-9b), 4.33 (1H, d, J = 10.55 Hz, H-4), 6.79 (1H, d, J = 8.57 Hz, Ar-H), 7.17—7.25 (2H, m, Ar-H), 7.31—7.41 (5H, m, Ar-H); **15d**: δ = 1.28—1.96 (6H, m), 2.33 (1H, m, H-3a), 2.73 (1H, m, H-9b), 5.04 (1H, d, J = 10.56 Hz, H-4), 6.79 (1H, d, J = 8.57 Hz, Ar-H), 7.17—7.25 (2H, m, Ar-H), 7.31—7.41 (5H, m, Ar-H); ^{13}C NMR ($CDCl_3$) as a mixture of **14d** and **15d**: δ = 23.0, 23.8, 27.2, 28.0, 28.2, 34.7, 39.9, 41.4, 43.5, 48.5, 80.1, 85.0, 118.8, 126.3, 127.8, 128.2, 128.4, 128.5, 129.7, 132.2. Found: C, 65.51; H, 5.16% for the mixture of **14d** and **15d**. Calcd for $C_{18}H_{17}BrO$: C, 65.67; H, 5.20%.

IR (KBr) as a mixture of **16d** and **17d**: 3234, 2951, 2865, 1596, 1470, 1350, 1239, 1082, 995, 762, and 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) **16d**: δ = 1.43—1.96 (5H, m), 2.14 (1H, m, H-5), 2.62 (1H, m, H-2), 2.85 (3H, s, C**H**$_3$OCHPh), 3.27 (1H, m, H-1), 3.76 (1H, d, J = 2.97 Hz, PhC**H**OMe), 5.58 (1H, bs, OH), 6.69 (1H, d, J = 8.58 Hz, Ar-H), 7.10—7.41 (7H, m, Ar-H); **17d**: δ = 1.43—1.96 (6H, m), 2.14 (1H, m, H-2), 3.25 (1H, m, H-1), 3.28 (3H, s, C**H**$_3$OCHPh), 4.17 (1H, d, J = 4.19 Hz, PhC**H**OMe), 5.37 (1H, bs, OH), 6.78 (1H, d, J = 8.56 Hz, Ar-H), 7.10—7.41 (7H, m, Ar-H).

(*E*)-1-(2-Methoxyphenyl)-6-phenyl-5-hexen-1-ol (18): A mixture of butyllithium/hexane (1.1 cm^3, 1.7 mmol), TMEDA (0.35 g, 3 mmol), anisol (0.2 g, 1.7 mmol), and (*E*)-6-phenyl-5-hexenal (0.25 g, 1.4 mmol) was reacted as before to give 0.17 g (42%) of **18** as viscous oil. IR (neat) 3407, 2936, 2838, 1599, 1491, 1266, 1240, 1049, 1029, 976, 751, and 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.46—1.88 (4H, m), 2.24 (2H, m), 2.59 (1H, d, J = 4.94 Hz, OH), 3.81 (3H, s, CH_3O), 4.88 (1H, d, J = 5.28 Hz), 6.19 (1H, m), 6.36 (1H, d, J = 15.84 Hz), 6.87—6.99 (2H, m, Ar-H), 7.14—7.33 (7H, m, Ar-H).

Acid-Catalyzed Reaction of 18: A solution of **18** (0.12 g, 0.4 mmol) in methanol (10 cm^3) was refluxed in the presence of a catalytic amount of hydrochloric acid as before to give 0.11 g (88%) of mixture of ***cis*-1-(2-methoxyphenyl)-2-[methoxy(phenyl)methyl]cyclopentane (19)**, ***trans*-1-(2-methoxyphenyl)-2-[methoxy(phenyl)methyl]cyclopentane (20)**, and **(*E*)-6-methoxy-6-(2-methoxyphenyl)-6-phenyl-1-hexene (21)** in the ratio of 41 : 35 : 24. Isolation by column chromatography on silica gel using hexane/ethyl acetate (9 : 1) as eluent afforded **19** in 78% purity, **20** in 70% purity, and **21** in 65% purity. IR (neat) as mixture of **19** and **20**: 3026, 2951, 2867, 1600, 1585, 1492, 1453, 1360, 1289, 1241, 1153, 1111, 1080, 1031, 968, 800, 750, 701, 597, and 509 cm^{-1}; ^{1}H NMR ($CDCl_3$) **19**: δ = 1.47—1.91 (5H, m), 2.08 (1H, m, H-5), 2.69 (3H, s, C**H**$_3$OCHPh), 2.75 (1H, m, H-2), 3.42 (1H, m, H-1), 3.59 (1H, d, J = 3.30 Hz, PhC**H**OMe), 3.83 (3H, s, CH_3O-Ar), 6.73—7.36 (9H, m, Ar-H); **20**: δ = 1.47—1.91 (5H, m), 2.05 (1H, m, H-5), 2.37 (1H, m, H-2), 3.20 (3H, s, C**H**$_3$OCHPh), 3.38 (1H, m, H-1), 3.73 (3H, s, CH_3O-Ar), 3.95 (1H, d, J = 4.95 Hz, PhC**H**OMe), 6.73—7.36 (9H, m, Ar-H); ^{13}C NMR ($CDCl_3$) as mixture of **19** and **20**: δ = 24.6, 24.9, 25.1, 30.9, 34.3, 41.3, 42.7, 47.4, 53.6, 55.1, 56.1, 57.0, 83.3, 84.5, 109.5, 110.3, 120.1, 120.4, 126.4, 126.6, 126.8, 127.8, 128.0, 128.4, 131.3, 133.7, 141.9, 142.6, 157.4, 157.6. Found: C, 80.77; H, 8.24% for mixture of **20** and **21**. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%. HRMS Found: m/z 296.1761 for **20**; 296.1764 for **21**. Calcd for $C_{20}H_{24}O_2$: M, 296.1776.

(*Z*)-6-Phenyl-5-hexenal: To a solution of phenylacetylene (3.06 g, 30.0 mmol) in THF (40 cm^3), butyllithium (19.7 cm^3, 31.1 mmol) was added dropwise at 0 °C. Then, 4-bromobutyl 2-tetrahydropyranyl ether[13] (7.36 g, 31.1 mmol) in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (35 cm^3) was added slowly. After the reaction mixture was stirred at 0 °C for an additional 30 min and at room temperature for 1.5 h, the reaction was quenched in ice water (50 cm^3), then extracted with hexane four times. The combined organic extracts were washed with water and brine, dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel using hexane/ethyl acetate (9 : 1) as eluent to give 7.28 g (94%) of **6-phenyl-5-hexynyl 2-tetrahydropyranyl ether** as colorless oil. IR (neat) 3056, 2943, 2868, 1664, 1598, 1490, 1442, 1351, 1201, 1136, 1073, 1034, 989, 907, 870, 757, and 693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.50—1.87 (10H, m), 2.44 (2H, m), 3.46 (2H, m), 3.83 (2H, m), 4.58 (1H, bs), 7.24—7.40 (5H, m, Ar-H).

A reaction flask of a low-pressure hydrogenation apparatus was charged with 6-phenyl-5-hexynyl 2-tetrahydropyranyl ether (4.0 g, 15.5 mmol), Lindlar catalyst (5% Pd-$CaCO_3$) (0.1 g), and quinoline (1 g, 7.7 mmol) in methanol (20 cm^3). The apparatus was evacuated, and hydrogen was admitted to a pressure slightly above 1 atm. After the mixture had been shaken for 10 h, it was washed with 2M HCl (20 cm^3) and extracted with ether four times. The combined organic layer was dried over $MgSO_4$, concentrated in vacuo, and residue was purified by column chromatography on silica gel using hexane/ethyl acetate (9 : 1) as eluent to give 3.07 g (76%) of **(*Z*)-6-phenyl-5-hexenyl 2-tetrahydropyranyl ether** as colorless liquid. IR (neat) 3055, 2940, 2867, 1664, 1494, 1446, 1351, 1201, 1137, 1122, 1075, 1032, 990, 908, 812, 770, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.45—1.85 (10H, m), 2.36 (2H, m), 3.42 (2H, m), 3.78 (2H, m), 4.55 (1H, bs), 5.65 (1H, m), 6.43 (1H, d, J = 11.88 Hz), 7.17—7.35 (5H, m, Ar-H).

To a solution of (*Z*)-6-phenyl-5-hexenyl 2-tetrahydropyranyl ether (2.7 g, 10.4 mmol) in methanol–water (48 : 2) (30 cm^3) solvent, *p*-toluenesulfonic acid (0.15 g, 0.79 mmol) was added. The mixture was stirred at 60 °C for 1 h. After the methanol was evaporated, the residue was washed with saturated $NaHCO_3$ solution (20 cm^3) and then extracted with ether three times. Ether extracts were washed with brine, dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography on silica gel using hexane/ethyl acetate (3 : 1) as eluent to give 1.80 g (98.7%) of **(*Z*)-6-phenyl-5-hexen-1-ol** as colorless oil. IR (neat) 3334, 2933, 2862, 1493, 1448, 1068, 770, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.45—1.65 (4H, m), 2.36 (2H, m), 3.62 (2H, bs), 5.65 (1H, m), 6.43 (1H, d, J = 11.88 Hz), 7.18—7.39 (5H, m, Ar-H).

(*Z*)-6-Phenyl-5-hexen-1-ol (1.76 g, 9.9 mmol) and sodium acetate (0.24 g, 2.9 mmol) with PCC (3.22 g, 14.9 mmol) was reacted in dichloromethane (50 cm^3) as described before to give 1.47 g (85%) of **(*Z*)-6-phenyl-5-hexenal**[12] as clear liquid. IR (neat) 3011, 2938, 2827, 2723, 1724, 1494, 1448, 769, and 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.77 (2H, m), 2.33—2.48 (4H, m), 5.62 (1H, m), 6.47 (1H, d, J = 11.54 Hz), 7.20—7.36 (5H, m, Ar-H), 9.74 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 22.2, 27.8, 42.3, 126.6, 128.2, 128.6, 130.0, 131.4, 137.3, 202.3; MS m/z (rel intensity) 174 (M^+; 11), 130 (100), 115 (46), 104 (13), 91 (29), 77 (7), 39 (11). HRMS Found: m/z 174.1040. Calcd for $C_{12}H_{14}O$: M, 174.1045.

(*Z*)-1-[2-(Methoxymethoxy)phenyl]-6-phenyl-5-hexen-1-ol (22a): A mixture of butyllithium/hexane (2.15 cm^3, 3.4 mmol), TMEDA (0.70 g, 6.2 mmol), (methoxymethoxy)benzene (0.43 g, 3.2 mmol), and (*Z*)-6-phenyl-5-hexenal (0.5 g, 2.7 mmol) was reacted as before to give 0.54 g (60%) of **22a** as viscous oil. IR (neat) 3421, 2936, 1601, 1490, 1453, 1406, 1310, 1231, 1200, 1154, 1077, 1002, 922, 758, and 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.47—1.88 (4H, m), 2.36—2.42 (3H, m), 3.45 (3H, s), 4.93 (1H, m), 5.19 (2H, s), 5.64 (1H, m), 6.40 (1H, d, J = 11.55 Hz), 6.97—7.17 (2H, m, Ar-H), 7.18—7.33 (7H, m, Ar-H).

(*Z*)-1-[2-Methoxy-6-(methoxymethoxy)phenyl]-6-phenyl-5-hexen-1ol (22b): A mixture of butyllithium/hexane (2.2 cm^3, 3.4 mmol), TMEDA (0.7 g, 6.0 mmol), 3-methoxy-1-(methoxymethoxy)benzene (0.54 g, 3.2 mmol), and (*Z*)-6-phenyl-5-hexenal (0.5 g, 2.87 mmol) was reacted as before to give 0.49 g (50%) of **22b** as viscous oil. IR (neat) 3557, 2937, 1736, 1597, 1473, 1441, 1407, 1234, 1180, 1101, 1070, 1009, 923, 783, and 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.43—1.97 (4H, m), 2.37 (2H, m), 3.44 (3H, s), 3.69 (1H, d, J = 11.55 Hz), 3.80 (3H, s), 5.11—5.21 (3H, m), 5.62 (1H, m), 6.38 (1H, d, J = 11.55 Hz), 6.57 (1H, d, J = 7.92, Hz, Ar-H), 6.74 (1H, d, J = 7.92, Hz, Ar-H), 7.09—7.34 (6H, m, Ar-H).

Acid-Catalyzed Reaction of 22a: A solution of **22a** (0.11 g, 0.25 mmol) in methanol (10 cm^3) was refluxed in the presence of a catalytic amount of hydrochloric acid as before to give 0.03 g (36%) of mixture of **(3a*R**, 4*S**, 9b*S**)-(±)-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (23a)**, **(3a*R**, 4*S**, 9b*R**)-(±)-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]-benzopyran (24a)**, **14a**, and **15a** in the ratio of 40 : 50 : 3 : 7. Isolation by column chromatography on silica gel using hexane/ethyl acetate (98 : 2) afforded **23a** in 75% purity as solid and **24a** in 95% purity as solid.

A solution of **22a** (0.012 g, 0.38 mmol) in acetonitrile/water (9 : 1) (10 cm^3) was refluxed for 30 min in the presence of a catalytic amount of hydrochloric acid to give 0.07 g (77%) of mixture of **23a**, **24a**, **14a**, and **15a** in the ratio of 41 : 26 : 15 : 18. IR (KBr) as mixture of **23a**, **24a**, **14a**, and **15a** : 3030, 2956, 2870, 1608, 1579, 1486, 1451, 1300, 1231, 1195, 1124, 1035, 982, 754, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) **23a** : δ = 1.25—1.70 (4H, m), 1.81 (1H, m, H-1), 2.16 (1H, m, H-1), 2.64 (1H, m, H-3a), 3.53 (1H, t, J = 7.92, 7.59 Hz, H-9b), 5.18 (1H, d, J = 1.98 Hz, H-4), 6.91—7.48 (9H, m, Ar-H); **24a** : δ = 0.81—1.90 (6H, m), 2.19 (1H, m, H-3a), 2.37 (1H, m, H-9b), 5.64 (1H, d, J = 5.61 Hz, H-4), 6.91—7.48 (9H, m, Ar-H); ^{13}C NMR ($CDCl_3$) as a mixture of **23a**, **24a**, **14a**, and **15a** : δ = 22.7, 22.8, 23.5, 23.7, 23.9, 26.4, 27.1, 27.5, 28.0, 28.2, 34.8, 34.9, 35.6, 39.6, 40.0, 41.6, 43.5, 45.2, 48.7, 77.2, 80.0, 80.6, 85.0, 115.5, 115.8, 117.0, 117.1, 199.9, 120.8, 121.4, 125.6, 126.3, 126.4, 126.6, 126.7, 127.1, 127.4, 127.5, 127.8, 128.2, 128.4, 128.5, 129.1, 129.7, 139.2, 141.1, 141.2. HRMS Found: *m/z* 250.1333 for **23a**; 250.1336 for **24a**. Calcd for $C_{18}H_{18}O$: M, 250.1358.

Acid-Catalyzed Reaction of 22b: A solution of **22b** (0.11 g, 0.3 mmol) in methanol (10 cm^3) was refluxed in the presence of a catalytic amount of hydrochloric acid as before to give 0.08 g (83%) of mixture of **(3a*R**, 4*S**, 9b*S**)-(±)-9-methoxy-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclopenta[*c*][1]benzopyran (23b)**, **(3a*R**, 4*S**, 9b*R**)-(±)-9-methoxy-4-phenyl-1,2,3,3a,4,9b-hexahydrocyclo-penta[*c*][1]benzopyran (24b)**, **(±)-3-methoxy-2-{(1*R**, 2*R**)-2-[methoxy(phenyl)methyl]cyclopentyl}phenol (25b)**, **14b**, and **15b** in the ratio of 7 : 14 : 70 : 4 : 5. Mixture of **23b**, **24b**, **14b**, **15b**, and pure **25b** was separated by column chromatography on silica gel using hexane/ethyl acetate (9 : 1) as eluent. Further isolation of individual **23b**, **24b**, **14b**, and **15b** by column chromatography on silica gel using hexane/ethyl acetate (95 : 5) as eluent afforded **23b** in 55% purity and **24b** in 70% purity.

A solution of **22b** (0.012 g, 0.035 mmol) in acetonitrile/water (9 : 1) (10 cm^3) was refluxed for 30 min in the presence of a catalytic amount of hydrochloric acid to give 0.03 g (30%) of mixture of **23b**, **24b**, **14b**, and **15b** in the ratio of 15 : 7 : 25 : 53. IR (KBr) as mixture of **23b**, **24b**, **14b**, and **15b** : 3027, 2953, 2871, 1586, 1486, 1465, 1342, 1263, 1235, 1167, 1106, 1011, 959, 918, 775, and 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) **23b** : δ = 1.25—1.84 (5H, m), 2.24 (1H, m, H-1), 2.64 (1H, m, H-3a), 3.57 (1H, m, H-9b), 3.83 (3H, s, CH_3O), 5.05 (1H, d, J = 2.39 Hz, H-4), 6.46 (1H, m, Ar-H), 6.60 (1H, m, Ar-H), 7.08 (1H, m, Ar-H), 7.22—7.48 (5H, m, Ar-H); **24b** : δ = 0.85—1.84 (6H, m), 2.17—2.32 (2H, m, H-3a and H-9b), 3.77 (3H, s, CH_3O), 5.56 (1H, d, J = 4.29 Hz, H-4), 6.46 (1H, m, Ar-H), 6.61 (1H, m, Ar-H), 7.08 (1H, m, Ar-H), 7.22—7.48 (5H, m, Ar-H). HRMS Found: *m/z* 280.1473 for **23b**; 280.1452 for **24b**. Calcd for $C_{19}H_{20}O_2$: M, 280.1463.

25b: Mp 116—118 °C; IR (KBr) 3290, 2951, 2867, 1605, 1500, 1467, 1440, 1362, 1281, 1246, 1190, 1139, 1084, 956, 904, 782, 700, and 615 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.30 (1H, m, H-3), 1.63 (2H, m, H-4), 1.83—1.92 (2H, m, H-3 and H-5), 2.19 (1H, m, H-5), 2.45 (1H, m, H-2), 3.15 (3H, s, C**H**$_3$OCHPh), 3.39 (1H, m, H-1), 3.76 (3H, s, CH_3O-Ar), 3.95 (1H, d, J = 9.90 Hz, PhC**H**OMe), 6.48 (1H, d, J = 7.26 Hz, Ar-H), 6.61 (1H, d, J = 7.36 Hz, Ar-H), 7.06 (1H, m, Ar-H), 7.22—7.33 (5H, m, Ar-H); ^{13}C NMR ($CDCl_3$) δ = 26.4, 31.1, 31.9, 39.2, 52.5, 55.1, 56.2, 89.6, 104.0, 110.5, 126.8, 127.0, 127.9, 128.2, 141.0, 155.2. Found: C, 76.87; H, 7.74%. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74%.

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