

**A Formal [3 + 2] Alkene Addition to
Benzhydryl Cations. A Practical and
Mild Methodology for the Synthesis
of Substituted 1-Arylindanes and
Related Compounds**

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ABSTRACT

We report the single step synthesis of several 1-arylindanes in good yield via a formal [3 + 2] atom cycloaddition. The success of this formal

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cycloaddition relies on the Lewis acid activation of a bibenzylic alcohol in the presence of an alkene. The cation generated from the alcohol can be trapped by the alkene to afford a new benzylic cation which can then undergo cyclization leading to 1-arylidanes with three stereogenic centres.

Key Words: Styrenes; Stilbenes; Indanes; Cycloadditions.

INTRODUCTION

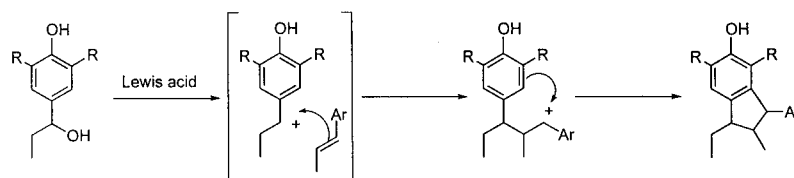
The dihydroindene ring system is a structural subunit found in a large number of naturally occurring compounds.^[1] In addition, there are several synthetic compounds with this skeleton that show a broad range of biological activities.^[2]

Regio- and stereoselective synthesis of highly substituted dihydroindenes has received considerable attention. As part of our program to develop routes to synthesize natural products containing the dihydroindene ring system, we report here our results using a formal [3 + 2] cycloaddition of benzhydryl cations with alkenes.

This synthetic strategy affords the advantage, over others already in use, of the considerable molecular complexity that may be achieved in the final compounds.

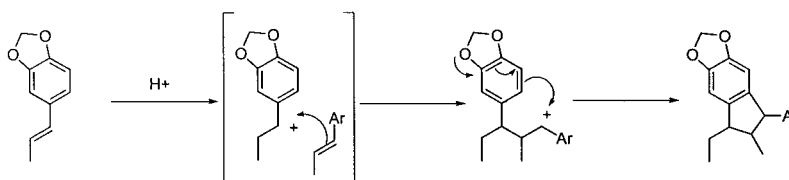
Previous work has already demonstrated that benzylic cations react with alkenes in the presence of Lewis acids to render 2,3-dihydro(1*H*)indenes, via a formal [3 + 2] cycloaddition.^[3] Up to now, the success of such formal cycloaddition relied on selective Lewis acid activation of a quinone methide or benzylic alcohol, both substituted in *p*-position with an hydroxyl group and in *m*-position by a methoxy or methyl group, in the presence of a nucleophilic alkene.

The proposed mechanism for the formal [3 + 2] cycloaddition^[3] (Sch. 1) is similar to the dimerization of isosafrol and other styrenes in acid medium reported by McMillan and coworkers in 1969 (Sch. 2).^[4]



Scheme 1.





Scheme 2.

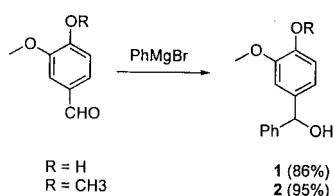
We hereby report the synthesis of several dihydroindenes in a single step via the reaction of bibenzylic cations, generated from benzhydrols **1** or **2** (Sch. 3) with alkenes. As these benzhydrols render a remarkably stable bibenzylic cation, their reactivity was assayed with nucleophilic alkenes such as styrenes,^[3] and with other relatively electron-poor alkenes such as stilbenes and diphenylacetylene.

RESULTS AND DISCUSSION

Benzhydrols **1** and **2** were prepared in good yield using a very well known technique,^[5] starting from the corresponding aldehyde and the Grignard reagent derived from bromobenzene (Sch. 3). SnCl₄ was chosen as catalyst for cycloaddition reactions. Experimental conditions were mild to moderate (0°–40°C; time: 30–180 min) and the solvent employed throughout was methylene chloride.

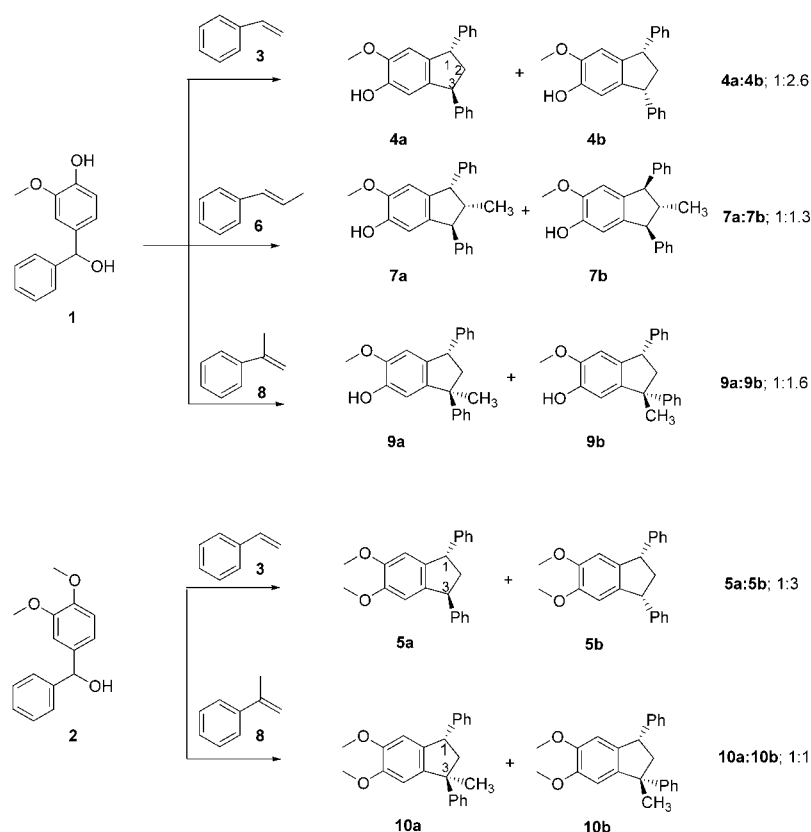
Given the similarity of this formal [3 + 2] cycloaddition to the process of styrene dimerization,^[3] we first chose several styrenes (**3**, **6** and **8**) to react with the bibenzylic cation (Sch. 4).

In contrast to the observations reported by Angle and Arnaiz,^[3] the reaction of benzhydrols **1** and **2** with styrene **3** afforded two pairs of indane diastereoisomers (**4a**, **4b** and **5a**, **5b**) respectively with acceptable yield, indicating that, under those conditions (30 minutes, 0°C), the reaction between



Scheme 3.





Scheme 4.

the styrene and the benzhydryl cations is faster than the dimerization of styrene itself.^[6]

The reaction between (*E*)- β -methyl styrene **6** and alcohol **1**, had a similar outcome^[3] but gave better yields, rendering indanes **7a**, and **7b**.

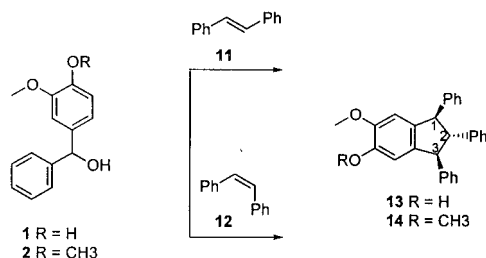
Under the same conditions, the reaction of benzhydrols **1** and **2** with α -methyl styrene **8** led in good yield to indanes **9** and **10**.

An attempt was made to assay the reactivity of benzhydrols **1** and **2** with the less nucleophilic compounds, such as (*E*) and (*Z*) stilbenes **11** and **12**, in each case, benzhydrols **1** and **2** afforded single diastereomers **13** and **14** (Sch. 5), respectively, though under more severe conditions than used for the reaction with styrenes (reflux, 3 h).



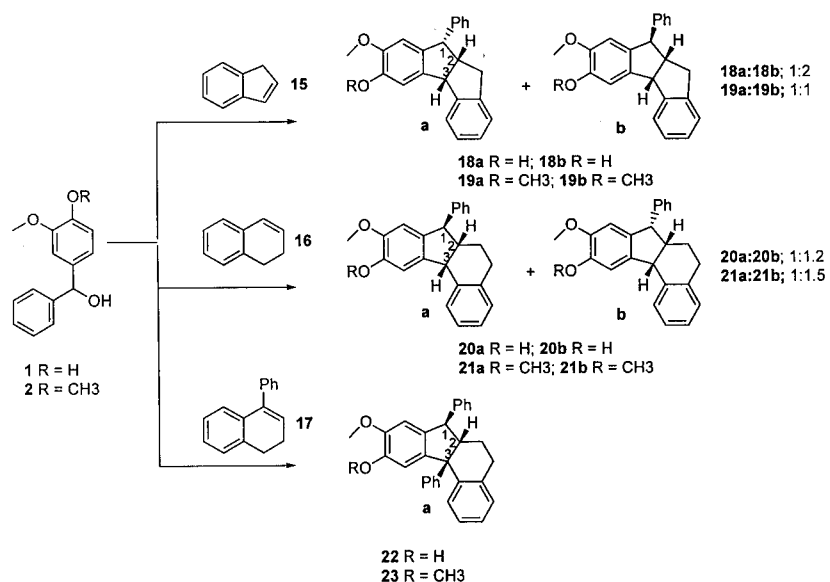
Formal [3 + 2] Alkene Addition to Benzhydrol Cations

629



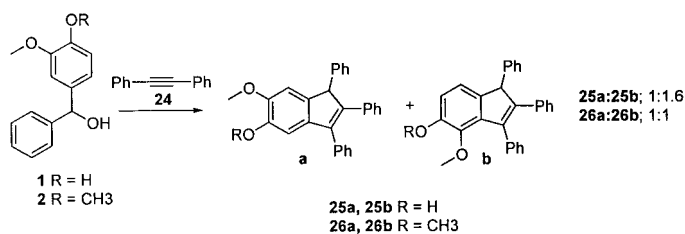
Scheme 5.

To rule out isomerization of (*Z*)-stilbene to (*E*)-stilbene, the former was treated with SnCl₄ at reflux during 3 hours, after which no isomerization had occurred (¹H NMR). This finding supports the formality of the [3 + 2] cycloaddition and its non-concerted, stepwise mechanism, in which the second intermediate planar carbocation (Sch. 2) allows for the formation of the most stable product, regardless of the configuration of the starting stilbene. The reactivity of these benzhydrols was then assayed with molecules presenting the styrene system in a more rigid environment. For this purpose, alkenes **15**, **16** and **17** were chosen (Sch. 6).



Scheme 6.





Scheme 7.

In the case of indene (**15**), tetracyclic compounds **18** and **19** were obtained, which are epimers. Results proved to be similar with 1,2-dihydro-naphthalene (**16**), giving compounds **20** and **21**. Alkene **17**, however, only afforded compounds **22** and **23** starting from alcohols **1** or **2**, respectively.

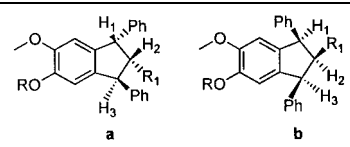
The formal cycloaddition was briefly examined with alkyne **24** (Sch. 7). Formation of regioisomers **25a**, **25b**, and **26a**, **26b** have obtained starting from **1** and **2** respectively. These were the only cases, in our studies, in which regioisomers were formed.

STEREOCHEMICAL ASSIGNMENT

Stereochemical assignment of the cycloadducts was obtained from NMR experiments (^1H , ^{13}C , HMBC (heteronuclear multiple bond correlation)), HMQC (heteronuclear multiple quantum correlation),^[7] NOE and NOESY.

Table 1 provides the values of the coupling constants J_{1-2} and J_{2-3} for the obtained 1,2,3-trisubstituted dihydro(1*H*)indenes **7a**, **7b**, **13** and **14**.

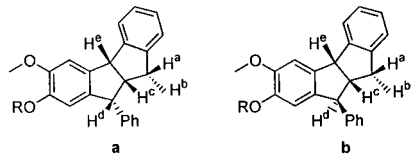
Table 1. Selected coupling constants (Hz) for 1,2,3-trisubstituted indanes.



Compd.	J_{1-2}	J_{2-3}
7a	8.1	9.9
7b	10.3	10.3
13	10.0	10.0
14	9.9	9.9



Table 2. Selected chemical shifts (ppm) and coupling constants (Hz) of bi-indanes.



Comp.	Ha	Hb	Hc	Hd	He	J_{a-c}	J_{b-c}	J_{a-b}	J_{c-d}	J_{c-e}
19a	2.62	2.52	3.70	4.76	4.65	9.0	7.4	16.7	8.2	7.7
19b	3.22	3.01	3.38	4.03	4.72	2.8	7.7	16.2	6.7	7.7
20a	2.67	2.57	3.75	4.78	4.69	9.2	7.9	16.7	7.9	7.9
20b	3.26	3.07	3.40	4.08	4.76	3.1	7.9	16.2	6.1	7.5

From the values in Table 1, it may be readily appreciated that the J values of the compounds fall into two groups: 8.1 Hz and those ranging from 9.9 to 10.3 Hz, which led us to assign the r -1, c -2, t -3 configuration to compound **7a** and r -1, c -3, t -2 to compounds **7b**, **13** and **14**.^[8]

In the case of 1,3-disubstituted indanes **4** ($R=H$) and **5** ($R=Me$), configurational assignment is straightforward due to symmetry. Isomer **5a** bears a C_2 axis, which makes H-2a and H-2b isochronous (δ 2.57), whereas these protons in **5b**, without that axis, are not (δ 2.05 and 2.98 respectively). In the case of isomers **4** that symmetry does not exist but chemical shifts of H-2a and H-2b should behave in a similar fashion. Coupling constants agreed with those measured for analogue compounds without substituents in the aromatic ring.^[9,10]

The values of δ and J observed for 1,3,3 trisubstituted indanes **9** and **10** are similar to those found by Brook and coworkers^[11] for trisubstituted indanes without substituents in the aromatic ring, who assigned the geometry of the compounds on steric grounds. Thus, analogously, the r -1, t -3-biphenyl configuration was assigned to compounds **9a** and **10a** and the r -1,

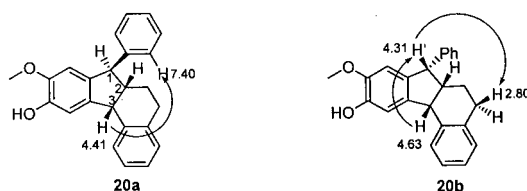


Figure 1. NOEs data of compounds **20a** and **20b**.



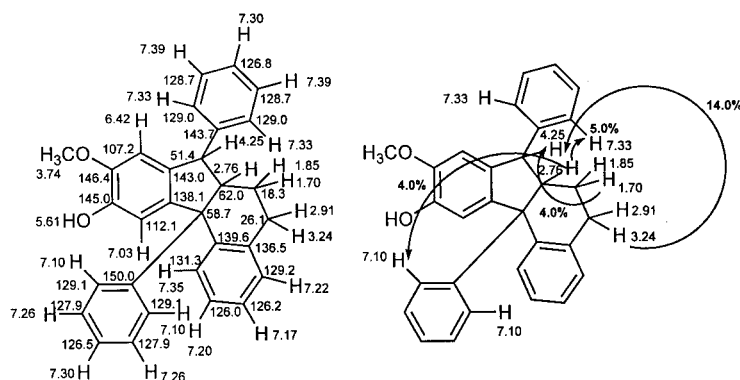


Figure 2. ^1H -NMR and ^{13}C -NMR chemical shifts and NOESY data of compound **22**.

c-3-biphenyl to compounds **9b** and **10b**. It may be inferred from H-2b chemical shifts in compounds **9** (**9a** δ 2.62 ppm, **9b** δ 2.82 ppm) and **10** (**10a** δ 2.64 ppm, **10b** δ 2.78 ppm) that the phenyl moiety exerts a greater shielding effect than the methyl group.^[10] Stereoisomers **18** and **19** presented similar values of chemical shifts and coupling constants (Table 2) as those found by Kuck and coworkers^[12] for compounds with the same type of carbon skeleton, but without substituents, therefore the configuration was assigned by comparison.

Stereochemical assignment for the products **20a** and **20b** was carried out by observing the coupling constants between the bridgehead protons (J 6.1 Hz in **20a** and J 7.5 Hz in **20b**) that indicate a *cis* ring fusion. Additionally, Fig. 1 shows the NOEs found in 1D difference experiments after careful assignment of proton signals by various 2D-NMR techniques. All values are only compatible with the configurations *r*-1-phenyl, *t*-2, *t*-3 for **20a** and *r*-1-phenyl, *c*-2, *c*-3 for **20b**.

Structure determination of compound **22**, obtained from benzhydrol **1** and alkene **17**, by the usual 2D-NMR techniques allowed us to assign the values of protons and carbon atoms. In the ^1H NMR spectrum, the bibenzylic hydrogen atom at δ 4.25 ppm and its neighbour methine at δ 2.76 ppm presented a J 10.6 Hz, which is only compatible with an anti arrangement. Figure 2 shows some NOESY data, which point to a *cis* fusion of the 5- and 6-membered rings so that, the two phenyl substituents at 1,3 positions of the indane moiety are in a syn arrangement. NOE was observed between the protons at δ 2.76 and δ 7.10 ppm, as well as between those at δ 2.76 and δ 7.33 ppm, thus confirming the *cis* configuration between the two phenyl substituents and the *cis* ring linkage. The lack of NOE between the hydrogen atoms at δ 4.25 and 7.10 ppm indicates that H-1 and 3-phenyl should be in an anti arrangement.



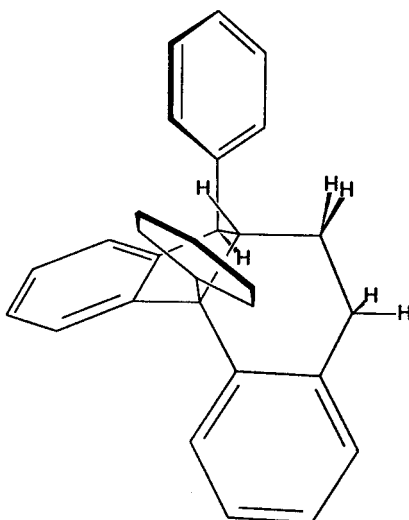


Figure 3. Conformation predicted by computational calculation of compound **22**.

Besides, the shape of most stable conformation predicted by computational calculation employing the semiempirical method AM1 (Austin Model 1)^[13] (Fig. 3), is in good agreement with that deduced from NMR data.

Finally, the structure and configuration of compound **23**, obtained from benzhydryl **2** and alkene **17**, was assigned by comparison with compound **22**.

CONCLUSION

The reaction of benzhydryl cations with diverse alkenes allows to obtain complex indane structures in good yield. It should be highlighted that the skeleton of the type of compounds **20**, **21**, **22** and **23** has not yet been described in the literature, and that benzhydryl cations can react with a wider spectrum of alkenes.

EXPERIMENTAL SECTION

NMR spectra were recorded (CDCl₃) on a Bruker AC 300 or Avance 500 spectrometers. Shifts reported are relative to internal standard Si(Me)₄ and coupling constants are reported in Hz (s: singlet, bs: broad singlet, d: doublet, t: triplet, q: quartet, dd: double doublet, dt: double triplet, m: multiplet). Mass



spectra were recorded on a VG Auto Spec (Micromass Inst.) or a ZAB SEQ (VG, Fisons) spectrometer (FAB+, matrix: glycerol) and are reported as percent relative intensity to the base peak. Preparative thin layer chromatography (p-Tlc) was done on Merck Silica Gel 60 GF₂₅₄; and analytical Tlc was performed on Merck aluminum sheets Silica Gel 60 F₂₅₄. THF and CH₂Cl₂ were distilled from sodium/benzophenone and CaH₂, respectively. Melting points are uncorrected and were determined in a Thomas Hoover apparatus. The products were isolated by quenching the reaction mixture with a solution of NaCO₃H 5%, separate the organic layer, extract the aqueous layer several times with the organic solvent, dry the combined organic extracts over Na₂SO₄, and remove the solvent under reduced pressure.

4-(Hydroxyphenylmethyl)-2-methoxyphenol (1). Phenylmagnesium bromide (58 mmol in 29 mL of THF) was added dropwise to a stirred solution of vanillin (5 mL, 19.7 mmol) at 0°C for 15 min and then allowed to warm to room temperature. After the solution was stirred for 2 h. at room temperature, CH₃OH (5 mL) was added. Aqueous workup (H₂O, AcOH, ether) afforded 3.89 g (86%) of **1** as white crystals (recrystallization: ether–hexane, 80%) mp: 84–86°C. δ_{H} 2.35 (1H, s, OH), 3.84 (3H, s, OCH₃), 5.64 (1H, s, ArCHAr), 5.77 (1H, s, OH), 6.82 (1H, dd, *J*: 1.6 and 8.2, Ar), 6.87 (1H, d, *J*: 8.2, Ar), 6.90 (1H, d, *J*: 1.6, Ar), 7.24–7.39 (5H, m, Ar), δ_{C} 56.6, 76.0, 109.7, 114.8, 120.4, 127.1, 128.2, 129.1, 136.6, 144.6, 145.8, 147.3.

(3,4-Dimethoxyphenyl)phenylmethan-1-ol (2). The same procedure described for the preparation of **1** was carried out with 3,4-dimethoxy benzaldehyde (4.34 g, 26.2 mmol) and PhMgBr (56 mmol in 28 mL of THF). Recrystallization (ethanol) afforded 6.05 g (95%) of **2** as white crystals; mp: 94–95°C. δ_{H} 2.32 (1H, s, OH), 3.84 (3H, s, OCH₃), 3.85 (3H, s, OCH₃), 5.79 (1H, s, ArCHAr), 6.81 (1H, d, *J*: 8.3, Ar), 6.87 (1H, d, *J*: 1.3, Ar), 6.91 (1H, dd, *J*: 8.3 and 1.3, Ar), 7.26–7.39 (5H, m, Ar); δ_{C} 55.8, 55.9, 76.2, 109.7, 110.9, 118.9, 126.4, 127.5, 128.4, 136.5, 143.8, 148.4, 149.0.

General Procedure for the Formal [3 + 2] Cycloaddition of a Benzhydrol and an Alkene in the Presence of SnCl₄

(1R/S,3S/R)-6-Methoxy-1,3-diphenylindan-5-ol (4a) and (1R/S,3R/S)-6-methoxy-1,3-diphenylindan-5-ol (4b). Styrene **3** (0.09 g, 0.92 mmol) and SnCl₄ (0.19 g, 0.75 mmol) were sequentially added to a solution of alcohol **1** (0.13 g, 0.58 mmol) in CH₂Cl₂ (10 mL) at 0°C. The resulting solution was stirred for 30 min at 0°C and then poured into a rapidly stirred solution of NaHCO₃ 5%. Aqueous workup (NaHCO₃, CH₂Cl₂) followed by p-Tlc (CHCl₃) afforded 0.07 g (40%) of **4a** and **4b** as a 1 : 2.6 (**4a/4b**) inseparable mixture (clear oil). Found: C, 83.6; H, 6.38. C₂₂H₂₀O₂. Calcd: C, 83.5; H, 6.4.



Formal [3 + 2] Alkene Addition to Benzhydryl Cations

635

Mayor diastereomer **4b**: δ_{H} 2.05 (1H, dt, J : 10.7 and 12.4, CH₂), 2.94 (1H, dt, J : 7.2 and 12.4, CH₂), 3.75 (3H, s, OCH₃), 4.28 (2H, m, J : 10.7 and 6.8, ArCHAr), 5.51 (1H, s, OH), 6.43 (1H, s, Ar), 6.52 (1H, s, Ar), 7.13–7.39 (10H, m, Ar); δ_{C} 48.4, 50.4, 50.6, 56.1, 106.9, 110.5, 126.4, 127.8, 128.2, 128.3, 128.4, 128.5, 138.2, 139.8, 144.5, 144.8, 144.9, 145.9. Minor diastereomer **4a**: δ_{H} 2.55 (2H, m, CH₂), 3.79 (3H, s, OCH₃), 4.47 (2H, m, J : 7.0, ArCHAr), 5.56 (1H, s, OH), 6.58 (1H, s, Ar), 6.66 (1H, s, Ar), 7.13–7.39 (10H, m, Ar); δ_{C} 47.0, 49.6, 50.0, 56.0, 107.1, 110.8, 126.2, 127.7, 128.2, 128.3, 128.4, 128.5, 137.8, 139.3, 145.1, 145.4, 145.8, 146.1.

(1R/S,3S/R)-5,6-Dimethoxy-1,3-diphenylindane (5a) and (1R/S,3R/S)-5,6-dimethoxy-1,3-diphenylindane (5b). General procedure was carried out with alcohol **2** (0.14 g, 0.58 mmol), styrene **3** (0.09 g, 0.92 mmol) and SnCl₄ (0.19 g, 0.75 mmol). p-Tlc (CHCl₃) afforded: 0.08 g (42%) of **5a** and **5b** as a 1 : 3 (**5a/5b**) inseparable mixture (clear oil). Found: C, 83.5; H, 6.8. C₂₃H₂₂O₂. Calcd: C, 83.6; H, 6.7. Mayor diastereomer **5b**: δ_{H} 2.05 (1H, dt, J : 10.7 and 12.5, CH₂), 2.98 (1H, dt, J : 7.2 and 12.5, CH₂), 3.76 (6H, s, OCH₃), 4.33 (2H, dd, J : 10.5 and 7.2, ArCHAr), 6.49 (2H, s, Ar), 7.15–7.40 (10H, m, Ar); δ_{C} 48.7, 50.7, 56.1, 107.6, 126.5, 128.2, 128.3, 138.8, 144.8, 148.6. Minor diastereomer **5a**: δ_{H} 2.57 (2H, t, J : 7.0, CH₂), 3.80 (6 H, s, OCH₃), 4.52 (2H, t, J : 7.0, CH₂), 6.63 (2H, s, Ar), 7.15–7.40 (10H, m, Ar); δ_{C} 47.4, 50.0, 55.9, 107.7, 126.2, 127.7, 128.5, 138.4, 147.7, 148.7.

(1R/S,2S/R,3S/R)-6-Methoxy-2-methyl-1,3-diphenylindan-5-ol (7a) and (1R/S,2R/S,3R/S)-6-methoxy-2-methyl-1,3-diphenylindan-5-ol (7b). General procedure was carried out with alcohol **1** (0.13 g, 0.58 mmol), styrene **6** (0.11 g, 0.92 mmol) and SnCl₄ (0.19 g, 0.75 mmol). p-Tlc (CHCl₃) afforded 0.15 g (80%) of **7a** and **7b** as a 1 : 1.3 (**7a/7b**) mixture (clear oil). p-Tlc (9 : 1 hexane : ethyl acetate) allowed the separation of **7a** (clear oil) and **7b** (clear oil). Found: C, 83.5; H, 6.8. C₂₃H₂₂O₂. Calcd: C, 83.6; H, 6.7. Mayor diastereomer **7b**: δ_{H} 1.07 (3H, d, J : 6.3, CH₃), 2.29 (1H, m, J : 6.3 and 10.3, CHCH₃), 3.75 (3 H, s, OCH₃), 3.80 (1H, d, J : 10.3, ArCHAr), 3.81 (1H, d, J : 10.3, ArCHAr), 5.51 (1H, s, OH), 6.42 (1H, s, Ar), 6.48 (1H, s, Ar), 7.27–7.36 (10H, m, Ar); δ_{C} 14.9, 54.5, 56.0, 57.0, 107.2, 110.6, 126.5, 128.3, 128.4, 137.7, 137.9, 142.2, 143.6, 145.1, 146.1. Minor diastereomer **7a**: δ_{H} 0.68 (3H, d, J : 7.0, CH₃), 2.73 (1H, m, J : 7.0, 8.1, and 9.9, CHCH₃), 3.81 (3H, s, OCH₃), 3.87 (1H, d, J : 9.9, ArCHAr), 4.40 (1H, d, J : 8.1, ArCHAr), 5.55 (1H, s, OH), 6.53 (1H, s, Ar), 6.68 (1H, s, Ar), 6.94 (2H, d, J : 8.1, Ar), 7.16–7.36 (8H, m, Ar); δ_{C} 15.5, 50.4, 56.2, 58.4, 58.2, 106.9, 110.4, 126.2, 126.4, 128.0, 128.8, 128.9, 137.8, 139.4, 143.4, 143.7, 144.9, 145.9.

(1R/S,3S/R)-6-Methoxy-3-methyl-1,3-diphenylindan-5-ol (9a) and (1R/S,3R/S)-6-methoxy-3-methyl-1,3-diphenylindan-5-ol (9b). General procedure was carried out with alcohol **1** (0.13 g, 0.58 mmol), styrene **8** (0.11 g, 0.92 mmol) and SnCl₄ (0.19 g, 0.75 mmol). p-Tlc (CHCl₃) afforded



0.092 g (50%) of **9a** and **9b** as a 1 : 1.6 (**9a/9b**) inseparable mixture (yellow solid). Found: C, 83.4; H, 6.6. $C_{23}H_{22}O_2$. Calcd: C, 83.6; H, 6.7. Major diastereomer **9b** δ_H 1.75 (3H, s, CH_3), 2.22 (1H, dd, J : 10.7 and 12.3, CH_2), 2.82 (1H, dd, J : 6.8 and 12.3, CH_2), 3.77 (3H, s, OCH_3), 4.10 (1H, dd, J : 6.8 and 10.7, ArCHAr), 5.63 (1H, s, OH), 6.42 (1H, s, Ar), 6.86 (1H, s, Ar), 7.12–7.43 (10H, m, Ar); δ_C 28.9, 48.8, 50.9, 55.5, 56.1, 107.0, 109.8, 125.8, 126.9, 128.0, 128.3, 128.4, 128.5, 137.9, 142.7, 144.9, 145.0, 146.0, 148.7. Minor diastereomer **9a** δ_H 1.64 (3H, s, CH_3), 2.35 (1H, dd, J : 10.3 and 12.7, CH_2), 2.62 (1H, dd, J : 7.7 and 12.7, CH_2), 3.76 (3H, s, OCH_3), 4.43 (1H, dd, J : 8.6 and 9.2, ArCHAr), 5.54 (1H, s, OH), 6.43 (1H, s, Ar), 6.49 (1H, s, Ar), 7.12–7.43 (10H, m, Ar); δ_C 26.3, 49.5, 51.1, 55.9, 56.1, 107.2, 110.0, 125.8, 126.9, 128.0, 128.3, 128.4, 128.5, 136.7, 142.6, 144.8, 145.0, 146.1, 149.0.

(1R/S,3S/R)-5,6-Dimethoxy-1-methyl-1,3-diphenylindane (10a) and (1R/S,3R/S)-5,6-dimethoxy-1-methyl-1,3-diphenylindane (10b). General procedure was carried out with alcohol **2** (0.14 g, 0.81 mmol), styrene **8** (0.09 g, 0.75 mmol) and $SnCl_4$ (0.19 g, 0.75 mmol). p-Tlc ($CHCl_3$) afforded 0.12 g (60%) of **10a** and **10b** as a 1 : 1 (**10a/10b**) inseparable mixture (white solid). Found: C, 83.6; H, 6.6. $C_{24}H_{24}O_2$. Calcd: C, 83.7; H, 7.0. Diastereomer **10b** δ_H 1.80 (3H, s, CH_3), 2.24 (1H, dd, J : 10.5 and 12.3, CH_2), 2.78 (1H, dd, J : 7.0 and 12.3, CH_2), 3.75 (3H, s, OCH_3), 3.76 (3H, s, OCH_3), 4.1 (1H, dd, J : 6.8 and 10.3, ArCHAr), 6.46 (1H, s, Ar), 6.77 (1H, s, Ar), 7.10 (2H, dd, J : 1.3 and 8.3, Ar), 7.19–7.36 (8H, m, Ar). Diastereomer **10a** δ_H 1.66 (3H, s, CH_3), 2.33 (1H, dd, J : 10.1 and 12.7, CH_2), 2.64 (1H, dd, J : 7.5 and 12.9, CH_2), 3.77 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 4.4 (1H, dd, J : 7.7 and 9.9, ArCHAr), 6.42 (1H, s, Ar), 6.46 (1H, s, Ar), 7.19–7.36 (8H, m, Ar), 7.43 (2H, dd, J : 1.3 and 8.4, Ar). δ_C of the mixture of diastereomers **10a** and **10b**: δ 26.2, 28.8, 48.8, 49.5, 51.0, 51.3, 55.8, 55.9, 56.0, 56.3, 106.8, 107.5, 107.7, 125.8, 126.4, 127.0, 128.1, 128.3, 128.4, 137.2, 138.4, 141.8, 144.1, 144.7, 145.0, 148.5, 148.8, 148.9, 149.2.

(1R/S, 2R/S, 3R/S)-6-Methoxy-1,2,3-triphenylindan-5-ol (13). *Trans*-stilbene **11** (0.17 g, 0.93 mmol) and $SnCl_4$ (0.19 g, 0.75 mmol) were sequentially added to a solution of alcohol **1** (0.13 g, 0.58 mmol) in CH_2Cl_2 (10 mL) at 0°C. The resulting solution was stirred for 30 min at 0°C, 1 h at room temperature. p-Tlc ($CHCl_3$) afforded 0.12 g (50%) of **13** (yellow oil). *Cis*-stilbene **12** (0.17 g, 0.93 mmol) and $SnCl_4$ (0.19 g, 0.75 mmol) were sequentially added to a solution of alcohol **1** (0.13 g, 0.58 mmol) in CH_2Cl_2 (10 mL) at room temperature. The resulting solution was stirred for 180 min at 40°C. p-Tlc ($CHCl_3$) afforded 0.04 g (20%) of **13** (yellow oil). Found: C, 85.6; H, 6.2. $C_{28}H_{24}O_2$. Calcd: C, 85.7; H, 6.1. δ_H 3.45 (1H, t, J : 10.0, CHAr), 3.77 (3H, s, OCH_3), 4.5 (2H, d, J : 10.0, ArCHAr), 5.62 (1H, s, OH), 6.49 (1H, s, Ar), 6.59 (1H, s, Ar), 7.07 (2H, dd, J : 1.7 and 7.5, Ar), 7.13–7.32 (13H, m, Ar),



7.77 (3H, s, OCH₃); δ_C 56.2, 58.2, 58.6, 68.2, 107.1, 110.6, 126.5, 126.6, 128.3, 128.4, 128.5, 128.6, 136.5, 138.2, 140.8, 142.9, 143.3, 146.3.

(1R/S,3R/S)-5,6-Dimethoxy-1,2,3-triphenylindane (14). The same procedure described for the preparation of **13** was carried out with alcohol **2** (0.14 g, 0.58 mmol), stilbene **11** (0.17 g, 0.93 mmol) and SnCl₄ (0.19 g, 0.75 mmol). p-Tlc (CHCl₃) afforded 0.12 g (51%) of **14** (clear oil). The same procedure described for the preparation of **14** was carried out with alcohol **2** (0.14 g, 0.58 mmol), stilbene **12** (0.17 g, 0.93 mmol) and SnCl₄ (0.14 g, 0.5 mmol). p-Tlc (CHCl₃) afforded 0.04 g (25%) of **14**. Found: C, 85.5; H, 6.3. C₂₉H₂₆O₂. Calcd: C, 85.7; H, 6.4. δ_H 3.45 (1H, t, *J*: 9.9, CHAr), 3.79 (6H, s, OCH₃), 4.56 (2H, d, *J*: 9.9, CHAr₂), 6.56 (2H, s, Ar), 7.09 (2H, dd, *J*: 1.6 and 7.7, Ar), 7.16–7.33 (13H, m, Ar); δ_C 56.1, 58.6, 68.6, 107.6, 126.5, 126.6, 128.3, 128.5, 137.1, 140.8, 143.2, 148.9.

(5R/S, 5aR/S, 10bS/R)-3-Methoxy-5-phenylindano[1,2-a]indan-2-ol (18a) and (5aR/S,5S/R,10bS/R)-3-methoxy-5-phenylindano[1,2-a]indan-2-ol (18b). General procedure was carried out with alcohol **1** (0.11 g, 0.46 mmol), indene **15** (0.08 g, 0.74 mmol) and SnCl₄ (0.15 g, 0.6 mmol). p-Tlc (CHCl₃) afforded 0.10 g (66%) of **18a** and **18b** as a 1:2 (**18a/18b**) inseparable mixture (white solid). (Found: C, 84.3; H, 6.3. C₂₃H₂₀O₂. Calcd: C, 84.1; H, 6.1). Major diastereomer **18b** δ_H 3.01 (1H, dd, *J*: 16.1 and 2.8, CH₂), 3.22 (1H, dd, *J*: 16.1 and 7.7, CH₂), 3.38 (1H, m, *J*: 2.8 and 7.7, CH₂CHCHAR), 3.72 (3H, s, OCH₃), 4.03 (1H, d, *J*: 6.7, ArCHAR), 4.72 (1H, d, *J*: 7.7, ArCHAR), 5.5 (1H, s, OH), 6.41 (1H, s, Ar), 7.15 (1H, s, Ar), 7.20–7.41 (9H, m, Ar); δ_C 34.0, 49.9, 53.2, 55.9, 56.2, 108.1, 110.3, 123.8, 124.4, 126.4, 126.5, 126.7, 128.4, 128.8, 135.2, 137.3, 142.1, 143.3, 144.9, 145.3, 146.1. Minor diastereomer **18a** δ_H 2.52 (1H, dd, *J*: 8.9 and 16.7, CH₂), 2.62 (1H, dd, *J*: 7.4 and 16.7, CH₂), 3.70 (1H, m, overlaps with OCH₃, CH₂CHAR), 3.79 (3H, s, OCH₃), 4.65 (1H, d, *J*: 7.7, ArCHAR), 4.76 (1H, d, *J*: 8.2, ArCHAR), 5.61 (1H, s, OH), 6.67 (1H, s, Ar), 7.03 (1H, s, Ar), 7.0–7.5 (9H, m, Ar); δ_C 37.3, 55.3, 55.4, 56.1, 57.9, 107.6, 109.9, 124.5, 125.1, 126.5, 126.8, 126.9, 128.3, 128.6, 137.3, 137.6, 143.4, 143.8, 145.3, 145.5, 146.3.

(5R/S, 5aR/S, 10bS/R)-2,3-Dimethoxy-5-phenylindano[1,2-a]indane (19a) and (5aR/S,5S/R,10bS/R)-2,3-dimethoxy-5-phenylindano[1,2-a]indane (19b). General procedure was carried out with alcohol **2** (0.09 g, 0.38 mmol), indene **15** (0.08 g, 0.74 mmol) and SnCl₄ (0.15 g, 0.6 mmol). p-Tlc (CHCl₃) afforded 0.10 g (76%) of **19a** and **19b** as a 1:1 (**19a/19b**) inseparable mixture (clear oil). Found: C, 84.2; H, 6.6. C₂₄H₂₂O₂. Calcd: C, 84; H, 6.5. Diastereomer **19b**. δ_H 3.07 (1H, dd, *J*: 3.1 and 16.2, CH₂), 3.26 (1H, dd, *J*: 7.9 and 16.2, CH₂), 3.40 (1H, m, *J*: 3.1, 6.1, 7.5 and 7.9, CH₂CHCHAR), 3.74 (3H, s, OCH₃), 4.0 (3H, s, OCH₃), 4.08 (1H, d, *J*: 6.1, ArCHAR), 4.76 (1H, d, *J*: 7.4 Hz, ArCHAR), 6.46 (1H, s, Ar), 7.10 (1H, s, Ar), 7.26–7.44 (9H, m, Ar); δ_C 37.4, 55.5, 56.0, 56.1, 57.9, 107.1, 108.3, 124.3,



125.2, 126.5, 126.6, 126.8, 128.2, 128.7, 136.7, 137.9, 142.5, 143.9, 145.4, 148.9. Diastereomer **19a**. δ_{H} 2.57 (1H, dd, J : 9.2 and 16.7, CH₂), 2.67 (1H, dd, J : 7.9 and 16.7, CH₂), 3.75 (1H, m, overlaps with OCH₃, CH₂CH), 3.81 (3H, s, OCH₃), 3.95 (3H, s, OCH₃), 4.69 (1H, d, J : 7.9, ArCHAR), 4.78 (1H, d, J : 7.9 Hz, ArCHAR), 6.72 (1H, s, Ar), 6.97 (1H, s, Ar), 7.01–7.55 (9H, m, Ar); δ_{C} 34.1, 50.0, 53.2, 55.6, 56.1, 107.3, 108.7, 123.7, 124.6, 126.4, 126.5, 128.2, 129.2, 135.7, 136.4, 141.9, 143.5, 145.0, 148.7, 148.9.

(4bR/S,9S/R,9aS/R)-7-Methoxy-9-phenyl-10,11,4b,9a-tetrahydrobenzo[c]fluoren-6-ol (20a) and (4bR/S,9R/S,9aS/R)-7-methoxy-9-phenyl-10,11,4b,9a-tetrahydrobenzo[c]fluoren-6-ol (20b). General procedure was carried out with alcohol **1** (0.13 g, 0.58 mmol), dihydronaphthalene **16** (0.12 g, 0.92 mmol) and SnCl₄ (0.19 g, 0.75 mmol). p-Tlc (80:20 hexane:ethyl acetate) afforded 0.08 g (41%) of **20a** and **20b** as a 1.6:1 (**20a/20b**) (clear oil). Found: C, 84.3; H, 6.6. C₂₄H₂₂O₂. Calcd: C, 84.2; H, 6.5. Mayor diastereomer **20a**. δ_{H} 1.79 (1H, m, CHCH₂CH₂), 1.95 (1H, m, CHCH₂CH₂), 2.80 (3H, m, CHArCHCH₂, CHCH₂Ar), 3.75 (3H, s, OCH₃), 4.12 (1H, d, J : 5.7, ArCHAR), 4.41 (1H, d, J : 7.5, ArCHAR), 5.55 (1H, s, OH), 6.52 (1H, s, Ar), 7.03 (1H, s, Ar), 7.10–7.45 (9H, m, Ar); δ_{C} 25.9, 27.6, 45.9, 49.5, 55.7, 56.0, 107.8, 110.8, 125.8, 126.0, 126.3, 128.0, 128.5, 128.7, 129.3, 136.2, 137.1, 137.4, 138.6, 144.7, 144.8, 145.9. Minor diastereomer **20b** δ_{H} 1.1 (1H, m, CHCH₂CH₂), 1.3 (1H, m, CHCH₂CH₂), 2.60 (2H, m, CHCH₂CH₂Ar), 2.80 (1H, m, CHArCHCH₂), 3.79 (3H, s, OCH₃), 4.31 (1H, d, J : 5.7 Hz, ArCHAR), 4.63 (1H, d, J : 6.1, ArCHAR), 5.53 (1H, s, OH), 6.69 (1H, s, Ar), 6.90 (1H, s, Ar), 7.08 (1H, d, J : 7.5 Hz, Ar), 7.18 (1H, d, J : 7.2, Ar), 7.26–7.46 (7H, m, Ar); δ_{C} 21.3, 28.9, 46.7, 47.3, 54.5, 56.3, 108.1, 110.5, 125.7, 126.1, 126.6, 128.2, 128.9, 129.7, 130.1, 134.0, 136.3, 137.2, 139.1, 140.0, 144.5, 145.3.

(4bR/S,9S/R,9aS/R)-6,7-dimethoxy-9-phenyl-10,11,4b,9a-tetrahydrobenzo[c]fluorene (21a) and (4bR/S,9R/S,9aS/R)-6,7-dimethoxy-9-phenyl-10,11,4b,9a-tetrahydrobenzo[c]fluorene (21b). General procedure was carried out with alcohol **2** (0.14 g, 0.58 mmol), dihydronaphthalene **16** (0.12 g, 0.92 mmol) and SnCl₄ (0.19 g, 0.75 mmol). p-Tlc (80:20 hexane:ethyl acetate) afforded 0.10 g (54%) of **21a** and **21b** as a 1.5:1 (**21a/21b**) (clear oil). m/z (EI) 356.1884 (M⁺, 356 C₂₅H₂₄O₂) requires 356.1776, 356 (100), 227 (17) and 91 (13%). Mayor diastereomer **21a** δ_{H} 1.79 (1H, m, J : 4.9, 5.1 and 13.3, CHCH₂CH₂Ar), 1.95 (1H, m, J : 4.9, 5.1, 7.9 and 13.3, CHCH₂CH₂Ar), 2.80 (3H, m, J : 5.1, 7.4 and 7.9, CHArCHCH₂, CH₂Ar), 3.73 (3H, s, OCH₃), 3.87 (3H, s, OCH₃), 4.13 (1H, d, J : 5.4, ArCHAR), 4.42 (1H, d, J : 7.4, ArCHAR), 6.54 (1H, s, Ar), 6.94 (1H, s, Ar), 7.11–7.33 (8H, m, Ar), 7.42 (1H, d, J : 7.7, Ar); δ_{C} 26.2, 27.8, 46.3, 49.5, 55.9, 56.0, 56.1, 108.1, 108.6, 125.9, 126.0, 126.3, 127.9, 128.5, 128.9, 129.0, 136.5, 136.8, 137.4, 137.6, 137.8, 148.4, 148.5. Minor diastereomer **21b** δ_{H} 1.09 (1H, dd, J : 3.6 and 13.1,



CHCH₂CH₂), 1.29 (1H, m, *J*: 6.7 and 11.0, CHCH₂CH₂Ar), 2.60 (2H, m, *J*: 4.1 and 6.1, CH₂CH₂Ar), 2.85 (1H, m, CHArCHCH₂), 3.76 (3H, s, OCH₃), 3.92 (3H, s, OCH₃), 4.33 (1H, d, *J*: 5.9, ArCHAr), 4.64 (1H, d, *J*: 6.2, ArCHAr), 6.70 (1H, s, Ar), 6.78 (1H, s, Ar), 7.20–7.47 (9H, m, Ar), δ_C 21.8, 29.4, 47.1, 48.0, 54.9, 56.5, 56.6, 108.1, 109.3, 126.1, 126.5, 127.0, 128.6, 129.6, 130.1, 130.3, 135.1, 136.9, 137.8, 139.0, 140.3, 148.4, 148.5.

(4bS/R,9S/R,9aS/R)-7-methoxy-9,4b-diphenyl-10,11,4b,9a-tetrahydrobenzo[c]fluoren-6-ol (22). General procedure was carried out with alcohol **1** (0.10 g, 0.46 mmol), 1-phenyl-3,4-dihydronaphthalene **17** (0.15 g, 0.74 mmol) and SnCl₄ (0.15 g, 0.6 mmol). p-Tlc (CHCl₃) afforded 0.08 g (40%) of **22** (white solid); mp: 180–182°C (see Fig. 2).

(4bS/R,9S/R,9aS/R)-6,7-Dimethoxy-9,4b-diphenyl-10,11,4b,9a tetrahydrobenzo[c]fluorene (23). General procedure was carried out with alcohol **2** (0.11 g, 0.64 mmol), 1-phenyl-3,4-dihydronaphthalene **17** (0.15 g, 0.74 mmol) and SnCl₄ (0.15 g, 0.6 mmol). p-Tlc (CHCl₃) afforded 0.1 g (51%) of **23** (white solid); mp: 210–212°C m/z (CI) 418.1933 (M⁺, 418. C₃₀H₂₆O₂ requires 418.1997), 418 (100), 341(58), 327 (23). HRMS calcd. for C₃₀H₂₆O₂ found: 418.1977. δ_H 1.7 (1H, m, *J*: 3.6 and 13.8, CHCH₂CH₂), 1.8 (1H, m, CHCH₂CH₂), 2.70 (1H, dt, *J*: 3.6 and 10.8, CHArCHCH₂), 2.9 (1H, m, *J*: 5.9, 7.9 and 17.2, CH₂CH₂Ar), 3.25 (1H, m, *J*: 6.1, 12.9 and 16.9, CH₂CH₂Ar), 3.71 (3H, s, OCH₃), 3.86 (3H, s, OCH₃), 4.25 (1H, d, *J*: 10.8, CHAr₂), 6.42 (1H, s, Ar), 6.93 (1H, s, Ar), 7.05–7.38 (14H, m, Ar); δ_C 18.2, 25.7, 51.2, 56.0, 56.3, 58.7, 62.0, 107.8, 109.2, 125.9, 126.0, 126.3, 126.6, 127.7, 128.5, 128.7, 128.9, 129.1, 130.8, 136.9, 138.5, 139.5, 141.8, 143.4, 148.5, 148.9, 149.9.

6-Methoxy-1,2,3-triphenylinden-5-ol 25a and 4-methoxy-1,2,3-triphenylinden-5-ol (25b). General procedure was carried out with alcohol **1** (0.11 g, 0.5 mmol), diphenylacetylene **24** (0.09 g, 0.5 mmol) and SnCl₄ (0.17 g, 0.65 mmol). The reaction was carried out at 0°C during 150 min. p-Tlc (CHCl₃) afforded 0.09 g (47%) of **25a** and **25b** as a 1 : 1.6 (**25a/25b**) mixture. The separation of the regioisomers was made by p-Tlc (CHCl₂). Diastereomer **25a**, white solid, mp: 67–69°C, δ_H 3.70 (3 H, s, OCH₃), 5.03 (1H, s, CH), 5.41 (1H, s, OH), 6.51 (1H, s, Ar), 6.77 (1H, s, Ar), 7.05–7.10 (5H, m, Ar), 7.18–7.30 (5H, m, Ar), 7.35–7.41 (5H, m, Ar); δ_C 55.8, 57.7, 110.1, 114.4, 121.4, 123.8, 125.7, 126.7, 127.4, 127.8, 128.7, 129.3, 129.5, 131.3, 135.6, 137.0, 140.5, 144.2, 144.7, 145.6, 146.5, 148.2, m/z (CI) 390.1622 (M⁺, 390. C₂₈H₂₂O₂ requires 390.1620), 390 (100), 313 (17) and 213 (14%). Diastereomer **25b**, white solid, mp: 65–67°C, δ_H 3.83 (3H, s, OCH₃), 5.01 (1H, s, CH), 5.57 (1H, s, OH), 6.76 (1H, d: *J*: 6.8, Ar), 6.86 (1H, d: *J*: 7.9, Ar), 7.01–7.18 (10H, m, Ar), 7.36–7.42 (5H, m, Ar), δ_C 55.7, 57.1, 102.1, 104.2, 126.7, 127.5, 127.6, 127.8, 128.3, 128.4, 128.8, 129.6, 129.7, 129.9, 129.9, 130.0, 130.1, 136.9, 140.5, 144.0, 144.1, 144.4, m/z (CI) 390.1625 (M⁺, 390. C₂₈H₂₂O₂) requires 390.1620, 390 (100), 313 (6), 267 (15%).



5,6-Dimethoxy-1,2,3-triphenylindene 26a and 4,5-dimethoxy-1,2,3-triphenylindene 26b. General procedure was carried out with alcohol **2** (0.11 g, 0.46 mmol), diphenylacetylene **24** (0.13 g, 0.74 mmol) and SnCl₄ (0.15 g, 0.6 mmol). p-Tlc (CHCl₃) afforded 0.11 g (60%) of **26a** and **26b** as a 1 : 1 (**26a/26b**) inseparable mixture (white solid). Found: C, 86.0; H, 5.96. C₂₈H₂₄O₂. Calcd: C, 85.7; H, 6.1. Spectroscopic data of the mixture of regioisomers **26a** and **26b**: δ_{H} 3.71 (3H, s, OCH₃), 3.80 (3H, s, OCH₃), 3.82 (3H, s, OCH₃), 3.83 (3H, s, OCH₃), 5.02 (1H, s, ArCHAR), 5.05 (1H, s, ArCHAR), 6.56 (1H, d, *J*: 1.8, Ar), 6.73 (1H, s, Ar), 6.80 (3H, m, Ar), 7.02–7.29 (19H, m, Ar), 7.38–7.42 (10H, m, Ar); δ_{C} 54.6, 55.2, 57.0, 57.1, 104.2, 107.9, 110.9, 111.3, 119.7, 123.0, 124.8, 125.6, 125.9, 126.6, 127.0, 127.1, 127.4, 127.8, 128.3, 128.5, 128.7, 128.8, 131.0, 134.9, 135.2, 139.4, 139.7, 140.2, 143.6, 143.8, 144.8, 147.0. MS (FAB, glycerol) 405 (M + 1).

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Formal [3 + 2] Alkene Addition to Benzhydrol Cations

641

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