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Scope of the formal [3+2] cycloaddition for the synthesis of substituted 3-arylindanes and related compounds

Beatriz Lantaño [a], José Manuel Aguirre [b], Esteban Ariel Ugliarolo [a],
María Laura Benegas [a], Graciela Yolanda Moltrasio [a,*]

[a] Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Buenos Aires, Argentina
[b] Departamento de Ciencias Básicas, Universidad Nacional de Luján, Luján, Argentina

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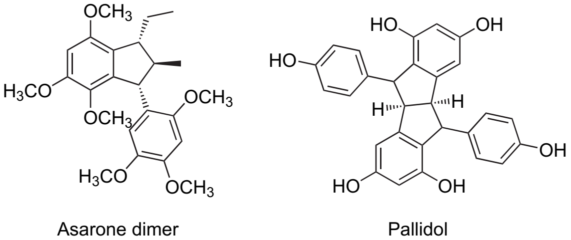
Abstract

We report the single step synthesis of several 3-arylindanes and related compounds via a formal [3+2] cycloaddition. A study of the influence of the aromatic ring substitution pattern on the reaction was carried out.

Keywords: Indanes; Formal [3+2] cycloaddition; Stereochemistry

1. Introduction

There are numerous natural and synthetic products that possess a indane ring system showing significant biological activity, including simple natural compounds such as the asarone dimer a component of the essential oil of *Acarus calamus*[1] or complex compounds, such as pallidol a resveratrol dimer from *Cissus pallida*.[2] In addition, there are many synthetic compounds possessing the indane skeleton that show significant biological activity, for example, indinavir® and indacrinone®.



As a consequence, a large number of methods were developed for their synthesis.[3–7] The first synthetic strategy was the treatment of propenylbenzenes with acidic reagents to obtain dimeric products, but was in 1940 the indane structure was proposed for those dimers.[8] In 1969 MacMillan et al.[9] assigned the correct stereochemical structure for the dimers derived from (*E*)-isosafrole and diisohomogenol. Some years later, Marcuzzi et al.[10] reported that the reaction of phenyl-substituted alkenes and alkynes with diphenylmethyl cations led to good yields of indanes and indenes. The lack of stereoselectivity of these procedures led Angle and Arnaiz[11] to develop a cycloaddition-type method for the preparation of highly substituted indanes in a single step via the reaction of an activated *p*-quinone methide or a benzylic cation with an electron-rich alkene. These reactions are catalyzed by a Lewis acid such as $ZnCl_2$ or a stronger one as $SnCl_4$. Primary and secondary benzylic alcohols led to good yields of cycloadducts as long as there was a phenol *para* to the benzylic alcohol and at least one *meta* alkoxy or alkyl group.

In previous papers we reported the synthesis of several indanes via the reaction of dibenzylic cations, generated from benzhydrols, with several nucleophilic alkenes, such as styrenes, and with other relatively electron-poor alkenes, such as stilbenes and diphenylacetylene.[10] Using this methodology we obtained the natural dimer of asarone[11] and finally, we studied the formal [3+2] cycloaddition reaction using

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* Corresponding author.
E-mail address: gmoltra@ffyb.uba.ar (G.Y. Moltrasio).

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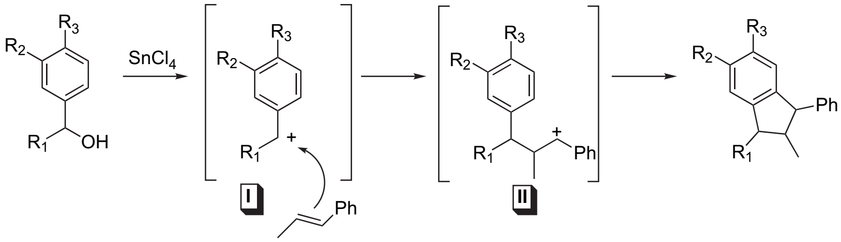


Scheme 1. Proposed mechanism for the formal [3+2] cycloaddition.

silica-supported Keggin heteropolyacids with similar results to those obtained with $SnCl_4$.[14]

The proposed mechanism for the formal [3+2] cycloadditions (Scheme 1) is similar to the dimerization of isosafrole and other styrenes, in acid medium.[11]

It is clear that intermediary **I** carbocation formation is improved by electron releasing substituents in C-4 and the cyclation step due to the presence of substituents in C-3.

The aim of this work is to study the scope of this cycloaddition. We hereby report the results from the formal [3+2] cycloaddition reaction using different starting materials:

- Benzylic alcohols, with a single electron releasing substituent in C-3 or C-4 of the benzenic ring and (*E*)-β-methylstyrene with electron releasing groups.
- Benzylic alcohols substituted with electron releasing groups and cyclic alkenes.
- Benzylic and benzhydrolic alcohols and (*E*)-asarone.
- Benzylic alcohol substituted with methoxyl groups in C-2, C-4, and C-5 and different alkenes.
- Finally we also studied the stereocontrol in formal [3+2] cycloaddition reactions.

2. Results and discussion

Benzylic and benzhydrolic alcohols were prepared from corresponding aldehydes and ethylmagnesium bromide[13,15,16] and phenylmagnesium bromide,[12] respectively. $SnCl_4$ was chosen as catalyst for this study. Experimental conditions were mild (0–25 °C, time: 5–60 min) and methylene chloride was the solvent.

2.1. Reaction of benzylic alcohols with an electron releasing substituent in C-3 or C-4 of the benzenic ring and (E)-β-methylstyrenes with electron releasing groups

The products of the reaction of benzylic alcohols with a substituent in C-4, 1-(4-methoxyphenyl)propan-1-ol (**1**) and in C-3, 1-(3-hydroxyphenyl)propan-1-ol (**2**) and styrenes **11** and **12**, in the presence of $SnCl_4$ are shown in Table 1. The reaction between alcohol **1** with **11** and **12** gave a low yield (about 20%) and the adduct obtained, in each case, corresponded to one single diastereomer (**18** and **19**, respectively) (Table 1, entries 1 and 2). On the other side, alcohol **2** presented lower reactivity and diastereoselectivity than alcohol **1** with the same alkenes (Table 1, entries 3 and 4) producing **20**,**21** and **22**,**23** cyclic dimers as a diastereomeric mixture. The yield did not exceed 15% in any case. We had previously reported that 1-(3,4-dimethoxyphenyl)propan-1-ol (**4**) reacts with **11**, under identical conditions those used in this work, producing the corresponding indane with a 55% yield.[13] Otherwise, Angle and Arnaiz[11] had reported that monosubstituted benzylic alcohols with electron releasing groups in C-3 or C-4 did not react with (*E*)-β-methylstyrene. Our results (Table 1) indicate that the electron richness of the alkenes used (**11** and **12**) compensates the lack of one of the electron releasing substituents in the aryl group of the starting benzylic alcohol.

2.2. Reaction of benzylic alcohols substituted with electron releasing groups and cyclic alkenes

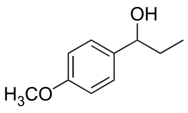
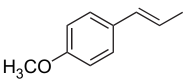
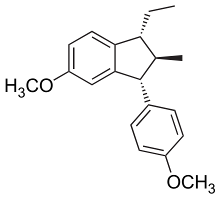
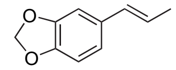
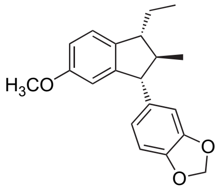
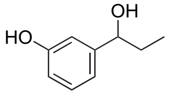
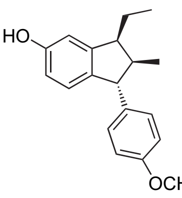
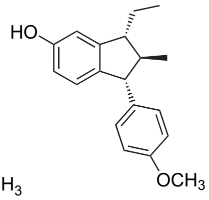
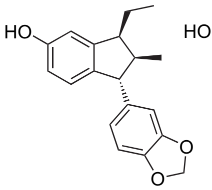
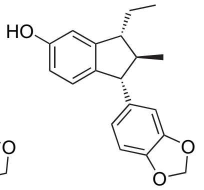
The reaction between benzylic alcohols with diverse substitution type and grade (**1**–**6**) and alkenes such as indene (**13**), 4-phenyl-2,3-dihydronaphthalene (**14**), dihydronaphthalene (**15**), was also explored and the results are shown in Table 2. Alcohols **1** and **2** did not react with **13** (Table 2, entries 5 and 6), however, this alkene reacts with alcohols **3** and **4** leading to formation of tetracyclic systems (**24**, **25**, and **26**) (Table 2, entries 7 and 8). Disubstituted alcohols, with electron releasing groups in C-3 and C-4 (**4** and **5**) react with **14** to give, with poor yield (30 and 40%), one single stereoisomer **27** and **28**, respectively (Table 2, entries 9 and 10). Alcohol **6**, trisubstituted in C-3, C-4, and C-5 with electron releasing groups, showed higher reactivity and lower stereoselectivity when reacting with alkene **14**, and a mixture of two diastereomers **29** and **30** in a 2:1 rate was obtained (Table 2, entry 11).

A similar behavior to alcohols **4**–**6**, with alkene **14** is observed for benzhydrols **7** and **8**. The compound **8** reacts with alkene **14** to obtain the cycloadduct **33**, while **7** reacts with alkenes **13**, **14**, and **15** to obtain, in all cases, a mixture of diastereomers **34**,**35**, **36**,**37** and **38**,**39**, respectively, at similar rates (Table 3).

2.3. Reaction of substituted benzylic alcohols and benzhydrols with asarone (16)

The results of the formal [3+2] cycloaddition between styrene **16** and alcohols **1**–**4**, **6**, **8**, and **9** are presented in Table 4. Compound **16** presents the typical behavior of an electron-rich styrene (Table 4 entries 17, 19–23). However, compound **41**, the result of the cyclodimerization of **16**, was isolated as a sole reaction product between **2** and **16** (Table 4, entry 18). Cyclodimerization products, under these reaction conditions, have not been previously observed. To assess the competition

Table 1
Formal [3+2] cycloaddition of benzylic alcohols and styrenes

Entry	Alcohol	Alkene	Product	Yield %
1	 **1**	 **11**	 **18**[15]	19
2	**1**	 **12**	 **19**	20
3	 **2**	**11**	 **20**  **21** 2:1	7
4	**2**	**12**	 **22**  **23** 1,3:1	15

reaction between cyclodimerization and formal [3+2] cycloaddition, alcohol **5** and styrene **12** were selected. Alkene **12** was treated under same conditions as in cycloaddition ($SnCl_4$, methylene chloride, 0 °C) and the cyclodimer formation could only be observed after 1 h of reaction while the cycloaddition between styrene **12** and alcohol **5** led to the cycloadduct within 5 min of reaction with a 51% yield.

2.4. Reaction of benzylic alcohol substituted with methoxyl groups in C-2, C-4, and C-5 (10) and different alkenes

The results of the reaction of alcohol **10** and alkenes **11**, **13**–**16** are collected in Table 5. As we have previously reported in a synthesis and stereochemistry study on benzylindane natural dimer of asarone,[13] alcohol **10** reacts with alkenes **11** and **16** according to the expected regiochemistry and stereochemistry (Table 5, entry 24). Nevertheless, this alcohol does not react with **13** and the reaction course with **14** and **15** (Table 5, entries 27 and 28) does not lead to expected cycloadducts. In these reactions, the formation of the non-indane compounds **51** (73%) and **52** (70%) is observed. It is clear that the presence of a methoxyl group in C-4 of **10** promotes the formation of cationic intermediaries (Scheme 1), but the presence of methoxyl group in C-2 and the lack of an electron releasing group in C-3 do not promote the formation of the tetracyclic system.

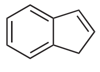
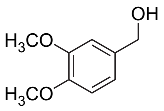
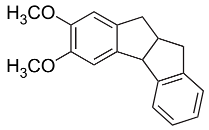
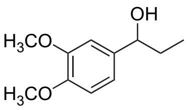
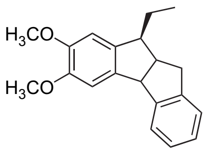
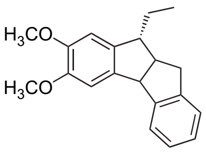
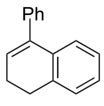
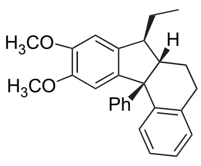
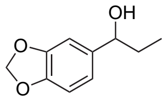
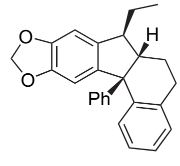
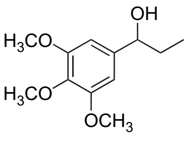
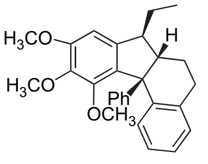
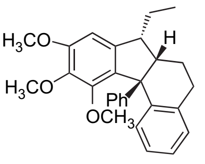
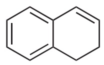
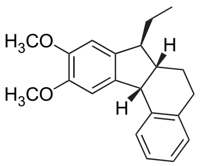
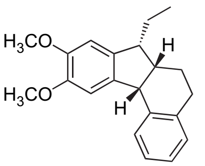
2.5. Stereocontrol in formal [3+2] cycloaddition reactions

Stereocontrol in reactions with adequately substituted benzylic alcohols and (*E*)- and (*Z*)-β-methylstyrenes was studied in the reaction of alcohols **4** and **5** with geometric isomers **16** and **17** (Scheme 2, Table 6). In this case, indane structures with three stereogenic centers are formed thus, four different racemic diastereomers might be obtained named α, β, γ, and δ (Fig. 1).

Likewise, the relation of diastereoisomeric products from benzhydrol alcohols **8** and **9** with styrenes **16** and **17** were analyzed.

In all cases studied, a mixture of the two diastereomers **III** and **IV** was obtained. In the reaction between (*E*)-styrene **16**

Table 2
Formal [3+2] cycloaddition of benzylic alcohols and cyclic alkenes

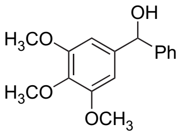
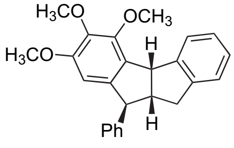
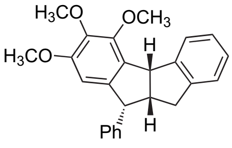
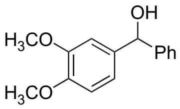
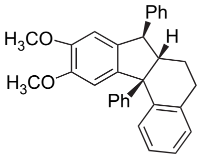
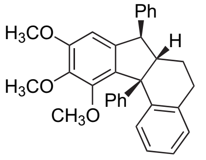
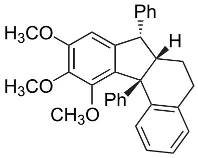
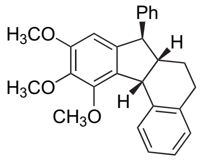
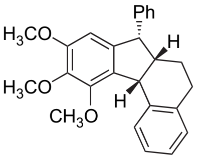
Entry	Alcohol	Alkene	Product	Yield %
5	**1**	 **13**	—	No rxn
6	**2**	**13**	—	No rxn
7	 **3**	**13**	 **24**	36
8	 **4**	**13**	 **25**  **26** 1,5:1	26
9	**4**	 **14**	 **27**	30
10	 **5**	**14**	 **28**	40
11	 **6**	**14**	 **29**  **30** 2:1	65
12	**4**	 **15**	 **31**  **32** 1:1.2	42

and the alcohols **4**, **5**, **8**, **9** the cis–trans diastereomer (**IV**, *r*-1,*t*-2,*t*-3) was mainly obtained. However, (*Z*)-styrene **17** mainly rendered the trans–trans diastereomer (**III**, *r*-1,*t*-2,*c*-3) only with benzylic alcohols **4** and **5**. Benzhydrols **8** and **9** led to the formation of the two indane stereoisomers at equivalent rates.

2.6. Structural and stereochemical assignment

Stereochemical assignment of 3-arylindane-like compounds was conducted taking into consideration ^{1}H NMR spectra, chemical shifts, coupling constants, and double irradiation techniques. MacMillan et al.[9] had already reported

Table 3
Formal [3+2] cycloaddition of benzhydrolic alcohols and cyclic alkenes

Entry	Alcohol	Alkene	Product	Yield %
13	 **7**	**13**	 **34**  **35** 1:1.2	26
14	 **8**	**14**	 **33**	51[12]
15	**7**	**14**	 **36**  **37** 1:1,3	52
16	**7**	**15**	 **38**  **39** 1:1	20

J values for the α, β, and γ configuration for three of the isohomogenol cyclodimers.

As it can be noticed, there is a marked consistency between *J* values (Hz) obtained by MacMillan et al.[9] and those found by us, thus, it would be valid to assign the α-configuration to the 3-arylindanes **20** and **22** and the γ-configuration to the 3-arylindanes **18**, **19**, **21**, **23**, and **40**.

Besides, chemical shifts published for the nonaromatic hydrogens of γ-diisohomogenol are similar to those found for compounds **18**, **19**, **21**, **23**, **40** (Table 7) and identical situation is observed for indanes **20** and **22** respecting α-diisohomogenol. Configuration of cyclodimers **41**, **42–45**, and **50** was assigned by us in a previous work.[13] Coupling constants for the 1,3-diaryl-2-methylindanes **46–49** (Table 8) have similar values to those published by Marcuzzi and Melloni[18] for the 1,3-diphenyl-2-methylindanes **V** and **VI** (Fig. 2). Based on this concordance we have assigned the cis–trans (*r*-1,*c*-2,*t*-3) configuration to the compounds **47** and **49**, and the trans–trans (*r*-1,*t*-2,*c*-3) configuration to **46** and **48**.

Structure assignment for compounds **27–30** was performed taking into consideration the results from the double irradiation experiments in ^{1}H NMR. Chemical shifts in ^{1}H NMR spectrum for compound **28** (Fig. 3) present two multiplets at δ 1.72 and 1.88 ppm, both integrating for two hydrogens, and besides there are four signals corresponding to one hydrogen (δ 2.55, 2.83, 2.98, and 3.05 ppm).

Irradiation of the triplet at δ 0.97 ppm corresponding to the methyl group, simplified the signal at δ 1.72 ppm to a doublet. When irradiated, this signal (δ 1.72 ppm) produces the expected simplification of the signal at δ 0.97 ppm to a singlet and the signal at δ 3.05 ppm (multiplet) to a doublet. These results allow the assignment of the chemical shifts of the aliphatic protons of benzylic alcohol-derived portion of the cycloadduct. The signal at δ 2.55 ppm was assigned to the bridgehead hydrogen as its irradiation reduces signal multiplicity at δ 3.05 ppm and also that of the signal at δ 1.88 ppm. This allows assigning this last 1.88 ppm value to the non-benzylic methylene group, from the hexagonal ring. Remaining signals, δ 2.83 and 2.98 ppm, correspond to benzylic hydrogens from the hexagonal ring. This fact was confirmed as the signal at δ 1.88 ppm is unique to be affected by irradiation of the signals at δ 2.83 and 2.98 ppm. Relative configuration of stereocenters from the structure of **28**, trans between hydrogens (δ 2.55 and 3.05 ppm) and cis between phenyl group and bridgehead hydrogen, was established taking into consideration the value of $J_{\mathrm{H_{benzylic}}/\mathrm{H_{bridgehead}}}$ 8.8 Hz from signal at δ 2.55 ppm, and the results already published for similar structures.[12] The *J* value 8.8 Hz for bridgehead hydrogen (δ

Table 4
Formal [3+2] cycloaddition of benzylic alcohols and asarone

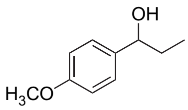
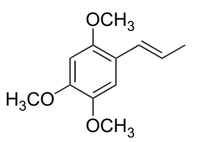
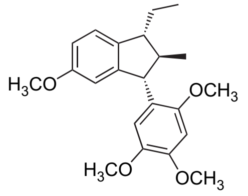
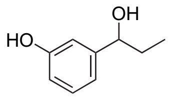
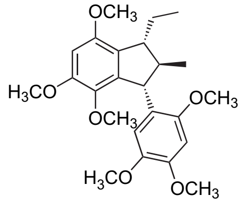
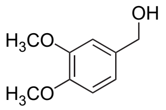
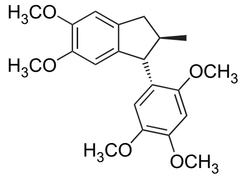
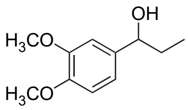
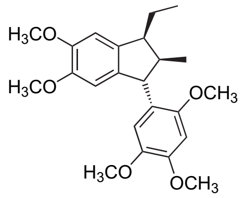
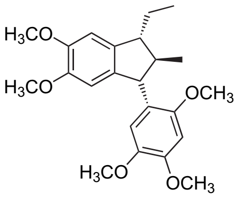
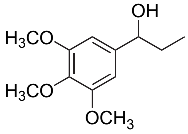
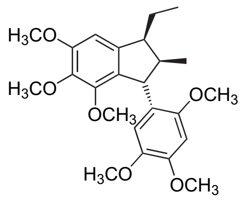
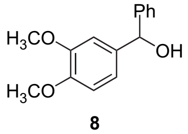
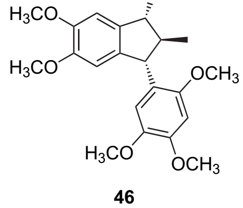
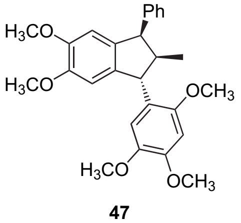
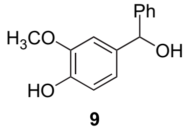
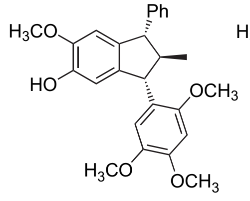
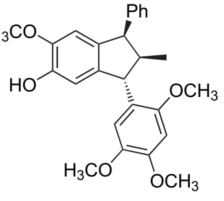
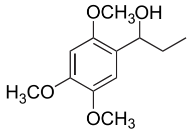
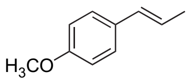
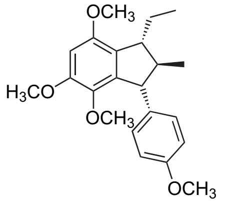
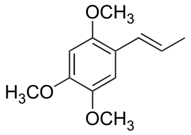
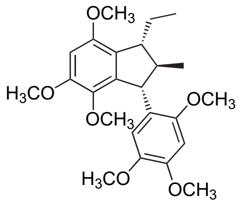
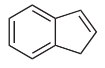
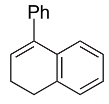
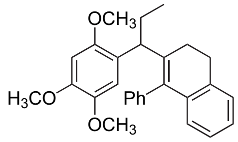
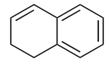
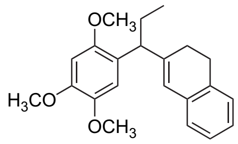
Entry	Alcohol	Alkene	Product	Yield %
17	 **1**	 **16**	 **40**	23
18	 **2**	**16**	 **41**[13]	21
19	 **3**	**16**	 **42**	30
20	 **4**	**16**	  **43** **44** 7:1	84[13]
21	 **6**	**16**	 **45**	98[13]
22	 **8**	**16**	  **46** **47** 1:2.9	55
23	 **9**	**16**	  **48** **49** 1:2.2	40

Table 5
Formal [3+2] cycloaddition of benzylic alcohol and alkenes

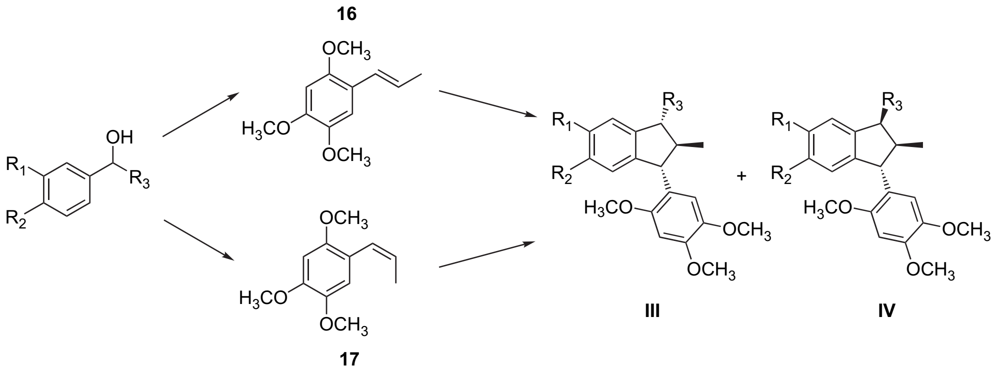
Entry	Alcohol	Alkene	Product	Yield %
24	 **10**	 **11**	 **50**	41[13]
25	**10**	 **16**	 **41**	61[13]
26	**10**	 **13**	—	No rxn
27	**10**	 **14**	 **51**	73
28	**10**	 **15**	 **52**	70

2.55 ppm) was obtained by irradiation of the signal at δ 1.88 ppm. Structures for compounds **27**, **29** and **30** were assigned by comparison with that for compound **28**.

Compounds **36** and **37** (Fig. 4) present a cis fusion between the five- and six-membered rings and are epimers in the dibenzylic carbon. The J value 11.8 Hz in **36** and 7.2 Hz in **37** for the hydrogens bound to these carbons indicate that they present a trans and cis array, respectively, with the bridgehead hydrogen.

The structures of **38** and **39** (Fig. 5) were assigned by comparison with compounds previously published by us.[12] The cycloadduct **38** presents cis fusion of the rings ($J_{a,b}$ 7.7 Hz) and trans configuration by dibenzylic protons H_c and H_b ($J_{b,c}$11.3 Hz). Compound **39** possesses identical fusion rings ($J_{a,b}$ 7.7 Hz) and cis relationship for H_c and H_b ($J_{b,c}$ 7.2 Hz).

Data from ^{1}H and ^{13}C NMR for **51** and **52** (Fig. 6) show that they are dihydronaphthalene-derived structures. Both



Scheme 2.

Table 6

Alcohol	Alkene	Ratio **III** (*t*-*t*):**IV** (*c*-*t*)
4 R_1=R_2=OCH_3; R_3=CH_3CH_2	**16**	1 (**43**):7.1 (**44**)
4 R_1=R_2=OCH_3; R_3=CH_3CH_2	**17**	1.5 (**43**):1 (**44**)
5 R_1=R_2=O–CH_2–O; R_3=CH_3CH_2	**16**	1 (**53**):4.5 (**54**)
5 R_1=R_2=O–CH_2–O; R_3=CH_3CH_2	**17**	4.35 (**53**):1 (**54**)
8 R_1=R_2=OCH_3; R_3=Ph	**16**	1 (**46**):3 (**47**)
8 R_1=R_2=OCH_3; R_3=Ph	**17**	1 (**46**):1 (**47**)
9 R_1=OCH_3; R_2=OH; R_3=Ph	**16**	1 (**48**):3 (**49**)
9 R_1=OCH_3; R_2=OH; R_3=Ph	**17**	1 (**48**):1 (**49**)

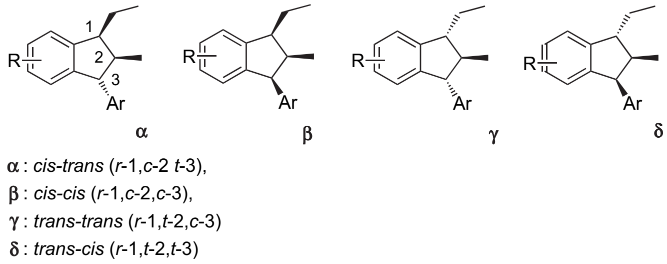
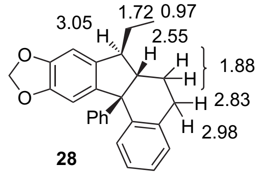
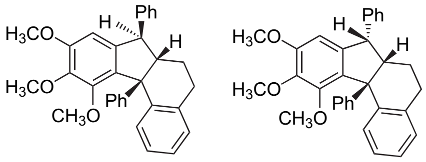


Figure 1.



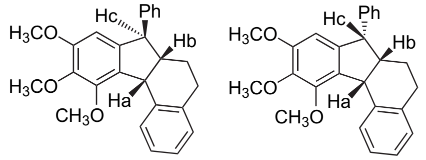
28

Figure 3.



36 **37**

Figure 4.



38 **39**

Figure 5.

Table 7
Coupling constant and ^{1}H NMR chemical shift data of 3-arylindanes

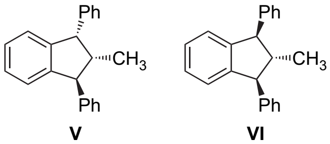
Cycloadducts	$J_{1,2}$	$J_{2,3}$	Configuration	*H*-1	*H*-2	*H*-3	$C\mathit{H}_3$	$CH_3\underline{C}\mathit{H}_2$	$\underline{C}\mathit{H}_3CH_2$
α: cis–trans[a]	7.25	9.5	cis–trans	2.90	2.40	3.77	1.04	1.65	0.96
β: cis–cis[a]	7.0	7.0	cis–cis	2.95	2.77	4.27	0.47	1.61	1.07
γ: trans–trans[a]	9.0	9.0	trans–trans	2.69	2.00	3.65	1.15	1.70	0.97
20	7.1	9.6	cis–trans	2.95	2.49	3.78	1.04	1.83	1.01
22	7.3	9.5	cis–trans	2.92	2.44	3.76	1.03	1.40/1.68	0.97
18	9.9	9.8	trans–trans	2.67	2.02	3.65	1.15	1.83	0.97
19	9.8	9.6	trans–trans	2.67	2.02	3.62	1.14	1.85	0.98
21	9.1	10.1	trans–trans	2.75	2.01	3.63	1.16	1.43/1.75	0.99
23	9.3	9.8	trans–trans	2.69	2.02	3.62	1.12	1.84	0.97
40	10.0	9.5	trans–trans	2.67	2.06	4.22	1.14	1.82	1.00

[a] See Ref. 9.

Table 8
Coupling constants of aliphatic hydrogen atoms in 1,3-diarylindanes

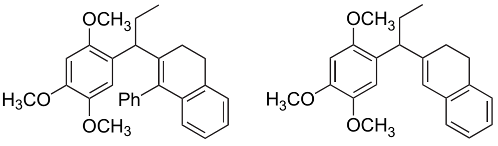
Cycloadducts	$J_{1,2}$ (Hz)	$J_{2,3}$ (Hz)	Configuration
VI[a]	10.5	10.5	trans–trans
46	9.9	9.9	trans–trans
48	9.9	9.9	trans–trans
V[a]	8.5	9.7	cis–trans
47	8.3	9.1	cis–trans
49	7.9	8.8	cis–trans

[a] See Ref. 18.



V **VI**

Figure 2.



51 **52**

Figure 6.

present two singlet signals at δ 6.78, 6.42 for **51** and δ 6.74, 6.54 for **52** corresponding to H-3 and H-6 from the trimethoxy-substituted aryl group (C-2, C-4 and C-5) from the benzylic substrate (alcohol **10**). Besides, compound **52** presents a signal at δ 6.38 ppm, characteristic for a vinylic hydrogen. ^{13}C NMR spectra from **51** and **52** show signals at δ 97.6, 111.2 and at δ 97.9 and 111.8, respectively, which correspond to carbons sp^2, C-3 and C-6, from the aryl group trisubstituted. All these data confirm the proposed structures for compounds **51** and **52**.

3. Conclusions

The reaction of benzylic cations with diverse alkenes allows to obtain complex indane structures. Yields are highly variable and dependent on the electronic effects of the substituents on both the benzylic alcohols and the alkenes. Regiochemistry is controlled and the stereocontrol is excellent at two of the three stereogenic centers formed. We have also found that the formal [3+2] cycloaddition reaction between benzylic alcohols and cyclic alkenes regioselectively afforded 6,6a,7,11b-tetrahydro-5*H*-benzo[*c*]fluorene derivatives in mild conditions. Finally, with a simple one-step process, using readily available starting compounds, several complex structures have been synthetized that makes this cycloaddition reaction an attractive option.

4. Experimental

4.1. General

NMR spectra were recorded ($CDCl_3$) 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 hertz (s: singlet, br s: broad singlet, d: doublet, t: triplet, q: quartet, dd: double doublet, dt: double triplet, m: multiplet). Microanalyses were performed by Elemental Analyser Carlo Erba. Preparative thin layer chromatography (p-TLC) was done on Merck Silica Gel 60 GF_{254} and analytical TLC was performed on Merck aluminum sheets Silica Gel 60 GF_{254}. Commercial compounds were purchased from Aldrich Chemical Co. THF and CH_2Cl_2 were distilled from sodium/benzophenone and CaH_2, 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 $NaCO_3H$ 5%, separate the organic layer, extract the aqueous layer several times with the organic solvent, dry the combined organic extracts over Na_2SO4 and remove the solvent under reduced pressure.

4.2. General procedure for the formal [3+2] cycloaddition of an alcohol and an alkene in the presence of $SnCl_4$

4.2.1. r-1-Ethyl-t-2-methyl-c-3-(4-methoxyphenyl)-5-methoxyindane (*18*)

Styrene **11** (0.10 g, 0.67 mmol) and $SnCl_4$ (0.23 g, 0.90 mmol) were sequentially added to a solution of alcohol **1** (0.11 g, 0.69 mmol) in CH_2Cl_2 (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 $NaCO_3H$ 5%. Aqueous workup ($NaCO_3H$, CH_2Cl_2) followed by p-TLC (95:5, hexane/isopropanol) afforded 0.04 g (19%) of **18** (solid), mp: 134–135 °C.[17] δ_H 0.97 (3H, t, J=7.4 Hz, CH_2CH_3), 1.15 (3H, d, J=6.6 Hz, CH_3), 1.83 (2H, m, CH_2), 2.02 (1H, m, J=6.6, 9.8, 9.9 Hz, $CHCH_3$), 2.67 (1H, m, J=5.3, 9.9 Hz, $ArCHCH_2$), 3.65 (1H, d, J=9.8 Hz, ArCHAr), 3.68 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 6.38 (1H, s, H-4), 6.75 (1H, dd, J=2.3, 8.1 Hz, H-6), 6.86 (2H, d, J=8.6 Hz, H-3′), 7.11 (3H, d, J=8.6 Hz, H-7, H-2′). δ_C 10.9, 17.3, 24.7, 50.9, 51.1, 55.2, 55.4, 58.3, 109.9, 112.6, 113.8, 123.6, 129.7, 136.2, 138.8, 148.3, 158.2, 158.8. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.0; H, 8.2. Found: C, 81.1; H, 8.3.

4.2.2. r-1-Ethyl-t-2-methyl-c-3-(3,4-methylenedioxyphenyl)-5-methoxyindane (*19*)

General procedure was carried out with alcohol **1** (0.11 g, 0.69 mmol), styrene **12** (0.11 g, 0.69 mmol), and $SnCl_4$ (0.23 g, 0.90 mmol). p-TLC (95:5, hexane/isopropanol) afforded 0.04 g (20%) of **19** (pale yellow solid), mp: 99–100 °C. δ_H 0.98 (3H, t, J=7.5 Hz, CH_2CH_3), 1.14 (3H, d, J=6.6 Hz, CH_3), 1.85 (2H, m, CH_2), 2.02 (1H, m, J=6.6, 9.6, 9.8 Hz, $CHCH_3$), 2.67 (1H, m, J=5.3, 9.8 Hz, $ArCHCH_2$), 3.62 (1H, d, J=9.6 Hz, ArCHAr), 3.70 (3H, s, OCH_3), 5.93 (2H, d, J=1.8 Hz, OCH_2O), 6.39 (1H, s, H-4), 6.63 (1H, d, J=1.5 Hz, H-2′), 6.68 (1H, dd, J=1.5, 8.1 Hz, H-6′), 6.75 (1H, dd, J=2.0, 7.6 Hz, H-6), 6.80 (1H, d, J=7.8 Hz, H-7), 7.10 (1H, d, J=8.1 Hz, H-5′). δ_C 10.8, 17.3, 24.6, 29.7, 51.0, 55.4, 58.7, 100.9, 108.0, 108.8, 109.9, 112.6, 122.1, 123.7, 138.1, 138.8, 142.6, 146.2, 148.0, 158.8. Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.4; H, 7.1. Found: C, 77.5; H, 7.2.

4.2.3. r-1-Ethyl-c-2-methyl-t-3-(4-methoxyphenyl)-6-hydroxyindane (*20*) and r-1-ethyl-t-2-methyl-c-3-(4-methoxyphenyl)-6-hydroxyindane (*21*)

General procedure was carried out with alcohol **2** (0.10 g, 0.65 mmol), styrene **11** (0.10 g, 0.66 mmol), and $SnCl_4$ (0.23 g, 0.90 mmol). p-TLC (CH_2Cl_2) afforded 0.01 g (7%) of **20** and **21** as a 2:1 (**20**/**21**) inseparable mixture (clear oil). Major diastereomer **20**: δ_H 1.01 (3H, t, J=7.4 Hz, CH_2CH_3), 1.04 (3H, d, J=7.7 Hz, CH_3), 1.83 (2H, m, CH_2), 2.49 (1H, m, J=7.1, 7.7, 9.6 Hz, $CHCH_3$), 2.95 (1H, m, J=6.0, 7.1 Hz, $ArCHCH_2$), 3.78 (1H, d, J=9.6 Hz, ArCHAr), 3.83 (3H, s, OCH_3), 5.31 (1H, s, OH), 6.59 (1H, d, J=2.9 Hz, H-7), 6.74 (2H, m, H-4, H-5), 6.89 (2H, d, J=9.4 Hz, H-2′), 7.12 (2H, d, J=9.4 Hz, H-3′). δ_C 11.9, 13.4, 21.6, 48.3, 49.0, 55.3, 54.9, 111.6, 113.1, 113.4, 125.3, 129.1, 136.0, 138.9, 149.7, 153.6, 154.0. Minor diastereomer **21**: δ_H 0.99 (3H, t, J=7.4 Hz, CH_2CH_3), 1.16 (3H, d, J=6.5 Hz, CH_3), 1.43 (1H, m, CH_2), 1.75 (1H, m, CH_2), 2.01 (1H, m, J=6.5, 9.1, 10.1 Hz, $CHCH_3$), 2.75 (1H, m, $ArCHCH_2$), 3.63 (1H, d, J=10.1 Hz, ArCHAr), 3.82 (3H, s, OCH_3), 5.18 (1H, s, OH), 6.62 (1H, dd, J=2.9, 9.1 Hz, H-5), 6.70 (1H, d, J=8.4 Hz, H-4), 6.77 (1H, d, J=2.6 Hz, H-7), 6.86 (2H, d, J=9.8 Hz, H-3′), 7.08 (1H, d, J=9.8 Hz, H-2′). δ_C 10.5, 16.9, 23.8, 50.7, 51.3, 54.9, 57.1, 109.8, 113.0, 113.5, 125.0, 129.3, 137.1, 138.8, 148.3, 157.4, 158.2. Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.8; H, 7.8. Found: C, 80.9; H, 7.9.

4.2.4. r-1-Ethyl-c-2-methyl-t-3-(3,4-methylenedioxyphenyl)-6-hydroxyindane (*22*) and r-1-ethyl-t-2-methyl-c-3-(3,4-methylenedioxyphenyl)-6-hydroxyindane (*23*)

General procedure was carried out with alcohol **2** (0.10 g, 0.66 mmol), styrene **12** (0.10 g, 0.66 mmol), and $SnCl_4$ (0.23 g, 0.90 mmol). p-TLC (CH_2Cl_2) afforded 0.03 g (15%) of **22** and **23** as a 1.3:1 (**22**/**23**) inseparable mixture (clear oil). Major diastereomer **22**: δ_H 0.97 (3H, t, J=7.2 Hz, $\mathrm{CH_2C}H_3$), 1.03 (3H, d, J=6.9 Hz, $\mathrm{CH_3}$), 1.4 (1H, m, $\mathrm{CH_2}$), 1.68 (1H, m, $\mathrm{CH_2}$), 2.44 (1H, m, J=6.9, 7.2, 9.5 Hz, $\mathrm{C}H\mathrm{CH_3}$), 2.92 (1H, m, $\mathrm{ArC}H\mathrm{CH_2}$), 3.76 (1H, d, J=9.5 Hz, ArC*H*Ar), 4.66 (1H, br s, OH), 5.93 (2H, s, $\mathrm{OCH_2O}$), 6.59−6.71 (6H, m, Ar). δ_C 12.1, 13.6, 21.9, 48.5, 49.2, 56.1, 100.7, 107.8, 108.4, 111.8, 113.3, 121.7, 125.6, 129.0, 137.2, 144.0, 145.5, 148.2, 154.8. Minor diastereomer **23**: δ_H 0.97 (3H, t, J=7.2 Hz, $\mathrm{CH_2C}H_3$), 1.12 (3H, d, J=6.4 Hz, $\mathrm{CH_3}$), 1.84 (2H, m, $\mathrm{CH_2}$), 2.02 (1H, m, J=6.4, 9.3, 9.8 Hz, $\mathrm{C}H\mathrm{CH_3}$), 2.69 (1H, m, $\mathrm{ArC}H\mathrm{CH_2}$), 3.62 (1H, d, J=9.8 Hz, ArC*H*Ar), 4.66 (1H, br s, OH), 5.92 (2H, s, $\mathrm{OCH_2O}$), 6.59−6.71 (6H, m, Ar). δ_C 10.7, 17.1, 24.1, 50.9, 51.5, 57.9, 100.7, 107.9, 108.6, 110.0, 113.4, 121.8, 125.2, 128.6, 137.5, 143.1, 145.8, 149.3, 156.7. Anal. Calcd for $\mathrm{C_{19}H_{20}O_3}$: C, 77.0; H, 6.8. Found: C, 77.1; H, 6.9.

*4.2.5. 2,3-Dimethoxyindano[1,2-a]indane (**24**)*

General procedure was carried out with alcohol **3** (0.09 g, 0.58 mmol), indene **13** (0.07 g, 0.62 mmol), and $\mathrm{SnCl_4}$ (0.19 g, 0.75 mmol). p-TLC (80:20, hexane/ethyl acetate) afforded 0.06 g (36%) of **24** (clear oil). δ_H 2.88 (1H, dd, J=4.2, 15.6 Hz, $\mathrm{C}H_2\mathrm{CHCH_2}$), 2.93 (1H, dd, J=5.1, 15.4 Hz, $\mathrm{CH_2CHC}H_2$), 3.38 (2H, m, J=8.5, 8.6, 15.4, 15.6 Hz, $\mathrm{C}H_2\mathrm{CHC}H_2$), 3.60 (1H, m, J=4.2, 5.1, 7.5, 8.5, 8.6 Hz, $\mathrm{CH_2C}H\mathrm{CH_2}$), 3.97 (3H, s, $\mathrm{OCH_3}$), 4.03 (3H, s, $\mathrm{OCH_3}$), 4.74 (1H, d, J=7.5 Hz, ArC*H*Ar), 6.86 (1H, s, Ar), 7.05 (1H, s, Ar), 7.31 (3H, m, Ar), 7.54 (1H, d, J=7.2 Hz, Ar). δ_C 38.9, 39.1, 43.5, 55.9, 56.1, 56.6, 107.3, 107.9, 123.9, 124.8, 126.6, 126.7, 134.4, 136.0, 143.0, 144.7, 148.3, 148.4. Anal. Calcd for $\mathrm{C_{18}H_{18}O_2}$: C, 81.3; H, 6.9. Found: C, 81.2; H, 6.8.

*4.2.6. (5aR/S,5R/S,10bS/R)-5-Ethyl-2,3-dimethoxyindano-[1,2-a]indane (**25**) and (5S/R,5aR/S,10bS/R)-5-ethyl-2,3-dimethoxyindano[1,2-a]indane (**26**)*

General procedure was carried out with alcohol **4** (0.10 g, 0.51 mmol), indene **13** (0.06 g, 0.52 mmol), and $\mathrm{SnCl_4}$ (0.19 g, 0.75 mmol). p-TLC (80:20, hexane/ethyl acetate) afforded 0.09 g (60%) of **25** and **26** as a 1.5:1 (**25**/**26**) inseparable mixture (clear oil). Major diastereomer **25**: δ_H 1.06 (3H, t, J=7.3 Hz, $\mathrm{CH_3}$), 1.59 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 1.85 (1H, m, J=4.6, 7.3, 14.9 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 2.84 (1H, dd, J=4.6, 16.2 Hz, $\mathrm{C}H_2\mathrm{Ar}$), 2.86 (1H, m, $\mathrm{C}H\mathrm{CH_2}$), 3.10 (1H, m, J=4.6, 8.9, 12.0 Hz, $\mathrm{CH_2C}H\mathrm{CH}$), 3.29 (1H, dd, J=8.7, 16.2 Hz, $\mathrm{CH_2Ar}$), 3.84 (3H, s, $\mathrm{OCH_3}$), 3.90 (3H, s, $\mathrm{OCH_3}$), 4.62 (1H, d, J=7.8 Hz, ArC*H*Ar), 6.68 (1H, s, Ar), 6.91 (1H, s, Ar), 7.13−7.24 (3H, m, Ar), 7.39 (1H, d, J=8.3 Hz, Ar). δ_C 11.7, 28.8, 36.8, 49.8, 52.6, 55.4, 56.0, 56.0, 107.2, 107.5, 124.0, 124.8, 126.5, 126.6, 135.9, 138.2, 143.6, 144.7, 148.4, 148.5. Minor diastereomer **26**: δ_H 1.18 (3H, t, J=7.3 Hz, $\mathrm{CH_3}$), 1.59 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 2.08 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 2.75 (1H, dd, J=9.4, 16.0 Hz, $\mathrm{C}H_2\mathrm{Ar}$), 2.92 (1H, dd, J=8.7, 16.0 Hz, $\mathrm{C}H_2\mathrm{Ar}$), 3.25 (1H, m, J=5.5, 5.7, 11.2 Hz, $\mathrm{CH_2C}H\mathrm{CH}$), 3.50 (1H, m, J=5.7, 7.1, 8.7, 9.4 Hz, $\mathrm{CHC}H\mathrm{CH_2}$), 3.81 (3H, s, $\mathrm{OCH_3}$), 3.86 (3H, s, $\mathrm{OCH_3}$), 4.45 (1H, d, J=7.1 Hz, ArCHAr), 6.71 (1H, s, Ar), 6.72 (1H, s, Ar), 7.13−7.24 (3H, m, Ar), 7.50 (1H, d, J=7.8 Hz, Ar). δ_C 12.9, 23.3, 31.9, 47.5, 48.3, 54.9, 55.9, 56.0, 106.8, 107.6, 123.6, 124.6, 126.4, 126.6, 134.4, 137.6, 142.9, 145.3, 148.4, 148.5. Anal. Calcd for $\mathrm{C_{20}H_{22}O_2}$: C, 81.6; H, 7.5. Found: C, 81.7; H, 7.7.

*4.2.7. (4bS/R,9R/S,9aS/R)-9-Ethyl-6,7-dimethoxy-4b-phenyl-10,11,4b,9a-tetrahydrobenzo[c]fluorene (**27**)*

General procedure was carried out with alcohol **4** (0.04 g, 0.23 mmol), 4-phenyl-1,2-dihydronaphthalene **14** (0.05 g, 0.25 mmol), and $\mathrm{SnCl_4}$ (0.08 g, 0.30 mmol). p-TLC ($\mathrm{CH_2Cl_2}$) afforded 0.03 g (30%) of **27** (white solid), mp: 250−251 °C. δ_H 0.99 (3H, t, J=7.2 Hz, $\mathrm{CH_2CH_3}$), 1.74 (2H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 1.86 (2H, m, $\mathrm{CHC}H_2\mathrm{CH_2}$), 2.51 (1H, m, $\mathrm{CHC}H\mathrm{CH_2}$), 2.84 (1H, m, $\mathrm{CH_2C}H_2\mathrm{Ar}$), 2.96 (1H, m, $\mathrm{CH_2C}H_2\mathrm{Ar}$), 3.03 (1H, m, $\mathrm{ArC}H\mathrm{CH_2CH_3}$), 3.81 (3H, s, $\mathrm{OCH_3}$), 3.87 (3H, s, $\mathrm{OCH_3}$), 6.72 (1H, s, Ar), 6.82 (1H, s, Ar), 7.00−7.31 (9H, m, Ar). δ_C 11.5, 21.1, 26.7, 30.1, 45.1, 54.6, 55.6, 55.7, 58.5, 111.0, 111.6, 125.0, 125.4, 125.6, 126.8, 126.9, 128.9, 131.6, 135.2, 137.8, 138.0, 139.8, 145.3, 146.0, 147.5. Anal. Calcd for $\mathrm{C_{27}H_{28}O_2}$: C, 84.3; H, 7.3. Found: C, 84.5; H, 7.5.

*4.2.8. (4bS/R,9R/S,9aS/R)-9-Ethyl-6,7-methylendioxy-4b-phenyl-10,11,4b,9a-tetrahydrobenzo[c]fluorene (**28**)*

General procedure was carried out with alcohol **5** (0.08 g, 0.46 mmol), 4-phenyl-1,2-dihydronaphthalene **14** (0.10 g, 0.48 mmol), and $\mathrm{SnCl_4}$ (0.15 g, 0.60 mmol). p-TLC (80:20, hexane/ethyl acetate) afforded 0.07 g (40%) of **28** (clear oil). δ_H 0.97 (3H, t, J=7.4 Hz, $\mathrm{CH_2C}H_3$), 1.72 (2H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 1.88 (2H, m, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.55 (1H, m, $\mathrm{CHC}H\mathrm{CH_2}$), 2.83 (1H, m, $\mathrm{CH_2C}H_2\mathrm{Ar}$), 2.98 (1H, m, $\mathrm{CH_2C}H_2\mathrm{Ar}$), 3.05 (1H, m, $\mathrm{ArC}H\mathrm{CH_2CH_3}$), 5.88 (1H, d, J=1.4 Hz, $\mathrm{OCH_2O}$), 5.97 (1H, d, J=1.4 Hz, $\mathrm{OCH_2O}$), 6.68 (1H, s, Ar), 6.78 (1H, s, Ar), 6.98 (1H, m, Ar), 7.0−7.26 (8H, m, Ar). δ_C 11.0, 21.6, 26.4, 29.7, 45.8, 55.7, 58.4, 100.9, 104.2, 106.8, 125.8, 126.0, 127.7, 128.7, 128.8, 128.9, 135.3, 136.5, 140.0, 142.3, 143.5, 144.3, 148.5, 150.3. Anal. Calcd for $\mathrm{C_{26}H_{24}O_2}$: C, 84.7; H, 6.6. Found: C, 84.6; H, 6.7.

*4.2.9. (4bS/R,9R/S,9aS/R)-9-Ethyl-5,6,7-trimethoxy-4b-phenyl-10,11,4b,9a-tetrahydrobenzo[c]fluorene (**29**) and (4bS/R,9S/R,9aS/R)-9-ethyl-5,6,7-trimethoxy-4b-phenyl-10,11,4b,9a-tetrahydrobenzo[c]fluorene (**30**)*

General procedure was carried out with alcohol **6** (0.10 g, 0.46 mmol), 4-phenyl-1,2-dihydronaphthalene **14** (0.10 g, 0.48 mmol), and $\mathrm{SnCl_4}$ (0.15 g, 0.60 mmol). p-TLC ($\mathrm{CH_2Cl_2}$) afforded 0.12 g (65%) of **29** and **30** as a 2:1 (**29**/**30**) mixture and the same chromatographic system allowed the separation of **29** (white solid), mp: 131−133 °C, and **30** (white solid), mp: 132−134 °C. Major diastereomer **29**: δ_H 0.95 (3H, t, J=7.4 Hz, $\mathrm{CH_3}$), 1.58 (2H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 1.81 (2H, m, $\mathrm{C}H_2\mathrm{CH_2Ar}$), 2.74 (2H, m), 2.88 (2H, m), 3.01 (3H, s, $\mathrm{OCH_3}$), 3.85 (3H, s, $\mathrm{OCH_3}$), 3.88 (3H, s, $\mathrm{OCH_3}$), 6.58 (1H, s, Ar), 7.01−7.34 (9H, m, Ar). δ_C 12.0, 20.9, 21.0, 29.3, 46.2, 53.1, 56.0, 59.6, 60.7, 60.8, 102.8, 124.5, 125.6, 125.7, 128.4, 130.6, 131.5, 133.3, 133.9, 138.0, 141.2, 141.4, 142.6, 148.5, 152.2, 153.1. Minor diastereomer **30**: δ_H 1.02 (3H, t, J=7.4 Hz, $\mathrm{CH_3}$), 1.83 (4H, m, $\mathrm{C}H_2\mathrm{CH_3}$, $\mathrm{C}H_2\mathrm{CH_2Ar}$), 2.59

(1H, dt, *J*=3.8, 3.8, 10.5 Hz, CHC*H*CH$_2$), 2.74 (1H, m, ArC*H*CH), 2.93 (2H, m, CH$_2$C*H*$_2$Ar), 3.39 (3H, s, OCH$_3$), 3.78 (3H, s, OCH$_3$), 3.84 (3H, s, OCH$_3$), 6.50 (1H, s, Ar), 7.11–7.21 (8H, m, Ar), 7.74 (1H, m, Ar). δ_C 10.9, 20.4, 23.8, 26.0, 45.3, 56.1, 56.5, 58.8, 59.7, 60.5, 102.2, 125.3, 126.0, 126.3, 127.3, 128.0, 128.5, 131.7, 134.4, 136.9, 140.1, 141.2, 142.2, 150.0, 150.5, 155.4. Anal. Calcd for $C_{28}H_{30}O_3$: C, 81.1; H, 7.3. Found: C, 81.3; H, 7.4.

*4.2.10. (4bR/S,9R/S,9aS/R)-9-Ethyl-6,7-dimethoxy-10,11,4b,9a-tetrahydrobenzo[c]fluorene (**31**) and (4bR/S,9S/R,9aS/R)-9-ethyl-6,7-dimethoxy-10,11,4b,9a-tetrahydrobenzo[c]fluorene (**32**)*

General procedure was carried out with alcohol **4** (0.17 g, 0.86 mmol), 1,2-dihydronaphthalene **15** (0.11 g, 0.85 mmol), and SnCl$_4$ (0.31 g, 1.20 mmol). p-TLC (80:20, hexane/ethyl acetate) afforded 0.11 g (42%) of **31** and **32** as a 1:1.2 (**31/32**) inseparable mixture (clear oil). Mixture diastereomer **31** and **32**: δ_H 0.95 (3H, t, *J*=7.4 Hz, CH$_3$), 1.06 (3H, t, *J*=7.1 Hz, CH$_3$), 1.65 (7H, m), 1.81 (1H, m), 2.55 (1H, m), 2.67 (2H, m), 2.75 (3H, m), 3.80 (3H, s, OCH$_3$), 3.86 (6H, s, OCH$_3$), 3.88 (4H, overlaps with OCH$_3$), 4.39 (1H, d, *J*=6.9 Hz, ArC*H*Ar), 6.76 (6H, m, Ar), 7.15 (2H, m, Ar), 7.27 (3H, m, Ar), 7.41 (d, *J*=7.7 Hz, Ar). δ_C 12.4, 13.8, 18.8, 20.6, 24.7, 27.4, 27.5, 28.6, 37.6, 42.6, 44.2, 46.2, 48.4, 52.7, 55.7, 55.8, 55.9, 56.0, 107.1, 107.8, 107.9, 108.3, 111.1, 111.7, 120.1, 125.6, 125.7, 125.8, 126.0, 135.3, 136.6, 136.7, 136.8, 137.2, 137.5, 137.7, 137.8, 138.0, 147.0, 147.6, 148.0, 148.7. Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.8; H, 7.8. Found: C, 81.9; H, 7.7.

*4.2.11. (5aR/S,5S/R,10bS/R,)-1,2,3-Trimethoxy-5-phenylindano[1,2-a]indane (**34**) and (5R/S,5aR/S,10bS/R,)-1,2,3-trimethoxy-5-phenylindano[1,2-a]indane (**35**)*

General procedure was carried out with alcohol **7** (0.13 g, 0.46 mmol), indene **13** (0.08 g, 0.74 mmol), and SnCl$_4$ (0.15 g, 0.60 mmol). p-TLC (CHCl$_3$) afforded 0.02 g (26%) of **34** and **35** as a 1:1.2 (**34/35**) inseparable mixture (yellow solid). Major diastereomer **35**: δ_H 2.59 (2H, d, *J*=7.5 Hz, CHC*H*$_2$Ar), 3.64 (1H, m, *J*=7.5, 7.9, 8.8 Hz, CHPhC*H*CH$_2$), 3.67 (3H, s, OCH$_3$), 3.91 (4H, overlaps with OCH$_3$, ArC*H*Ph), 3.74 (3H, s, OCH$_3$), 3.89 (3H, s, OCH$_3$), 3.94 (3H, s, OCH$_3$), 4.62 (1H, d, *J*=8.8 Hz, ArC*H*Ar), 6.42 (1H, s, Ar), 7.04 (3H, m, Ar), 7.17–7.39 (5H, m, Ar), 7.67 (1H, d, *J*=7.5 Hz, Ar). Minor diastereomer **34**: δ_H 3.00 (1H, dd, *J*=1.8, 16.2 Hz, CH$_2$), 3.15 (1H, dd, *J*=7.2, 16.2 Hz, CH$_2$), 3.31 (1H, m, *J*=1.8, 7.2, 7.5, 7.7 Hz, CHPhC*H*CH$_2$), 3.66 (3H, s, OCH$_3$), 3.90 (3H, s, OCH$_3$), 4.12 (3H, s, OCH$_3$), 4.85 (1H, d, *J*=7.7 Hz, ArC*H*Ph), 4.92 (1H, d, *J*=7.7 Hz, ArC*H*Ar), 6.10 (1H, s, Ar), 6.88 (1H, d, *J*=7.5 Hz, Ar), 7.17–7.39 (7H, m, Ar), 7.58 (1H, m, Ar). Mixture diastereomer **34** and **35**: δ_C 34.1, 36.5, 49.2, 53.1, 54.0, 54.2, 55.3, 56.1, 58.1, 60.5, 60.7, 60.8, 60.9, 103.7, 104.4, 124.0, 125.0, 125.9, 126.0, 126.1, 126.3, 126.5, 126.6, 126.8, 126.9, 127.9, 128.6, 129.3, 141.8, 142.1, 143.4, 144.4. Anal. Calcd for $C_{25}H_{24}O_3$: C, 80.6; H, 6.5. Found: C, 80.7; H, 6.6.

*4.2.12. (4bS/R,9S/R,9aS/R)-5,6,7-Trimethoxy-9,4b-diphenyl-10,11,4b,9a-tetrahydrobenzo[c]fluorene (**36**) and (4bS/R,9R/S,9aS/R)-5,6,7-trimethoxy-9,4b-diphenyl-10,11,4b,9a-tetrahydrobenzo[c]fluorene (**37**)*

General procedure was carried out with alcohol **7** (0.12 g, 0.46 mmol), 4-phenyl-1,2-dihydronaphthalene **14** (0.10 g, 0.50 mmol), and SnCl$_4$ (0.15 g, 0.30 mmol). p-TLC (CHCl$_3$) afforded 0.11 g (52%) of **36** and **37** as a 1:1.3 (**36/37**) mixture and the same chromatographic system allowed the separation of **36** (white solid), mp: 193–195 °C, and **37** (white solid), mp: 210–212 °C. Major diastereomer **37**: δ_H 1.5 (1H, m, CH$_2$), 1.6 (1H, m, CH$_2$), 2.38 (1H, m, CHC*H*CH$_2$), 2.61 (1H, m, CHC*H*$_2$Ar), 3.07 (1H, m, CHC*H*$_2$Ar), 3.10 (3H, s, OCH$_3$), 3.77 (3H, s, OCH$_3$), 3.88 (3H, s, OCH$_3$), 4.36 (1H, d, *J*=7.2 Hz, ArC*H*Ar), 6.50 (1H, d, *J*=0.8 Hz, Ar), 6.94 (2H, m, Ar), 7.02–7.19 (4H, m, Ar), 7.20–7.29 (8H, m, Ar). δ_C 23.1, 28.6, 53.3, 56.0, 56.1, 56.5, 59.8, 60.8, 104.4, 124.9, 125.0, 125.9, 126.8, 127.4, 127.8, 128.0, 128.1, 129.9, 132.8, 133.0, 135.0, 136.8, 138.7, 140.7, 141.0, 149.0, 151.9, 153.4. Minor diastereomer **36**: δ_H 1.68 (2H, m, CH$_2$), 2.81 (2H, m, CH$_2$C*H*$_2$Ar), 3.10 (1H, m, CHC*H*CH$_2$), 3.49 (3H, s, OCH$_3$), 3.67 (3H, s, OCH$_3$), 3.80 (3H, s, OCH$_3$), 4.13 (1H, d, *J*=11.8 Hz, ArC*H*Ar), 6.17 (1H, d, *J*=0.8 Hz, Ar), 7.14–7.40 (13H, m, Ar), 7.86 (1H, m, Ar). δ_C 25.7, 28.5, 51.9, 56.1, 58.3, 59.8, 60.5, 62.2, 103.7, 125.5, 126.3, 126.6, 126.7, 127.5, 128.5, 128.6, 128.8, 128.9, 131.7, 132.4, 133.3, 137.9, 140.8, 143.0, 143.1, 149.4, 152.5, 153.9. Anal. Calcd for $C_{32}H_{30}O_3$: C, 83.1; H, 6.5. Found: C, 83.2; H, 6.6.

*4.2.13. (4bR/S,9S/R,9aS/R)-5,6,7-Trimethoxy-9-phenyl-10,11,4b,9a-tetrahydrobenzo[c]fluorene (**38**) and (4bR/S,9R/S,9aS/R)-5,6,7-trimethoxy-9-phenyl-10,11,4b,9a-tetrahydrobenzo[c]fluorene (**39**)*

General procedure was carried out with alcohol **7** (0.11 g, 0.42 mmol), 1,2-dihydronaphthalene **15** (0.08 g, 0.67 mmol), and SnCl$_4$ (0.14 g, 0.54 mmol). p-TLC (CHCl$_3$) afforded 0.03 g (20%) of **38** and **39** as a 1:1 (**38/39**) mixture (white solid). p-TLC (70:30, hexane/ethyl acetate) allowed the separation of **38** (white solid), mp: 79–80 °C, and **39** (white solid), mp: 58–60 °C. Diastereomer **38**: δ_H 1.72 (1H, m, *J*=4.9, 5.1, 10.0, 15.3 Hz, CHC*H*$_2$), 1.96 (1H, m, *J*=5.1, 5.4, 10.0, 15.3 Hz, CH$_2$), 2.73 (1H, m, *J*=5.1, 5.4, 16.1 Hz, CHC*H*$_2$Ar), 2.88 (1H, m, *J*=5.1, 7.7, 10.2, 11.3 Hz, CHPhC*H*CH$_2$), 2.95 (1H, m, *J*=4.9, 10.0, 16.1 Hz, CHC*H*$_2$Ar), 3.66 (3H, s, OCH$_3$), 3.90 (3H, s, OCH$_3$), 4.02 (3H, s, OCH$_3$), 4.04 (1H, d, *J*=11.3 Hz, ArC*H*Ph), 4.50 (1H, d, *J*=7.7 Hz, ArC*H*Ar), 6.15 (1H, s, Ar), 7.14 (3H, m, Ar), 7.23 (3H, m, Ar), 7.33 (2H, m, Ar), 7.63 (1H, d, *J*=7.2 Hz, Ar). δ_C 23.8, 27.1, 44.4, 50.5, 54.3, 56.3, 60.7, 61.0, 104.3, 125.8, 126.3, 128.2, 128.5, 128.7, 129.5, 129.8, 130.7, 137.3, 138.2, 140.7, 142.6, 143.2, 150.1, 153.3. Diastereomer **39**: δ_H 1.28 (1H, m, CHC*H*$_2$), 1.45 (1H, m, CHC*H*$_2$), 2.51 (2H, m, C*H*CH$_2$Ar, CHC*H*$_2$Ar), 3.01 (1H, m, CHC*H*$_2$Ar), 3.43 (3H, s, OCH$_3$), 3.74 (3H, s, OCH$_3$), 3.87 (3H, s, OCH$_3$), 4.45 (1H, d, *J*=7.2 Hz, ArC*H*Ph), 4.51 (1H, d, *J*=7.7 Hz, ArC*H*Ar), 6.48 (1H, s, Ar), 7.04–7.16 (4H, m, Ar), 7.19–7.26 (4H, m, Ar), 7.53 (1H, d, *J*=7.4 Hz, Ar). δ_C 22.9, 29.0, 45.3, 47.1, 55.4, 56.2, 60.5, 61.0, 104.6, 125.2, 125.8, 126.4, 127.3, 128.1, 129.9, 130.6, 137.4, 138.8, 140.9, 141.2, 141.3, 143.5, 153.1. Anal. Calcd for $C_{26}H_{26}O_3$: C, 80.8; H, 6.8. Found: C, 80.9; H, 6.9.

4.2.14. *r-1-Ethyl-t-2-methyl-c-3-(2,4,5-trimethoxyphenyl)-5-methoxyindane (**40**)*

General procedure was carried out with alcohol **1** (0.11 g, 0.69 mmol), styrene **16** (0.14 g, 0.69 mmol), and $SnCl_4$ (0.23 g, 0.90 mmol). p-TLC (95:5, hexane/isopropanol) afforded 0.09 g (23%) of **40** (clear oil). Compound **40**: δ_H 1.00 (3H, t, J=7.4 Hz, CH_2CH_3), 1.14 (3H, d, J=6.7 Hz, CH_3), 1.82 (2H, m, CH_2CH_3), 2.06 (1H, m, J=6.7, 9.5, 10.0 Hz, $CHCH_3$), 2.67 (1H, m, J=4.6, 5.4, 10.0 Hz, $ArCHCH_2$), 3.69 (3H, s, OCH_3), 3.71 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 4.22 (1H, d, J=9.5 Hz, ArCHAr), 6.38 (1H, d, J=2.5 Hz, H-4), 6.54 (1H, s, Ar), 6.59 (1H, s, Ar), 6.73 (1H, dd, J=2.5, 8.2 Hz, H-6), 7.12 (1H, d, J=8.2 Hz, H-7). δ_C 11.1, 17.8, 25.0, 50.1, 50.6, 51.3, 55.4, 56.1, 56.7, 57.0, 98.1, 109.6, 112.3, 113.2, 123.6, 124.2, 139.1, 143.4, 148.0, 148.3, 152.5, 158.8. Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.1; H, 7.9. Found: C, 74.2; H, 8.0.

4.2.15. *r-1-(2,4,5-Trimethoxyphenyl)-t-2-methylindane (**42**)*

General procedure was carried out with alcohol **3** (0.08 g, 0.46 mmol), styrene **16** (0.11 g, 0.56 mmol), and $SnCl_4$ (0.15 g, 0.60 mmol). p-TLC (70:30, hexane/ethyl acetate) afforded 0.05 g (30%) of **42** (clear oil). Compound **42**: δ_H 1.15 (3H, d, J=6.7 Hz, CH_3), 2.35 (1H, m, $CHCH_3$), 2.55 (1H, dd, J=8.7, 14.9 Hz, CH_2), 3.04 (1H, dd, J=7.5, 14.9 Hz, CH_2), 3.68 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 4.28 (1H, d, J=8.5 Hz, ArCH), 6.41 (1H, s, Ar), 6.49 (1H, s, Ar), 6.59 (1H, s, Ar), 6.79 (1H, s, Ar). δ_C 17.9, 39.6, 42.8, 52.5, 55.6, 55.7, 55.8, 56.7, 56.4, 96.4, 111.3, 113.1, 116.2, 123.8, 131.4, 132.2, 141.0, 147.2, 147.7, 148.1, 149.5. Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.4; H, 7.3. Found: C, 70.5; H, 7.4.

4.2.16. *r-1-(2,4,5-Trimethoxyphenyl)-t-2-methyl-c-3-phenyl-5,6-dimethoxyindane (**46**) and r-1-(2,4,5-trimethoxyphenyl)-t-2-methyl-t-3-phenyl-5,6-dimethoxyindane (**47**)*

General procedure was carried out with alcohol **8** (0.13 g, 0.53 mmol), styrene **16** (0.14 g, 0.69 mmol), and $SnCl_4$ (0.18 g, 0.69 mmol). p-TLC ($CHCl_3$) afforded 0.09 g (40%) of **46** and **47** as a 1:2.9 (**46**/**47**) inseparable mixture (clear oil). Major diastereomer **47**: δ_H 0.68 (3H, d, J=7.1 Hz, CH_3), 2.68 (1H, m, $CHCH_3$), 3.70 (3H, s, OCH_3), 3.78 (6H, s, OCH_3), 3.80 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 4.38 (1H, d, J=8.3 Hz, ArCH), 4.43 (1H, d, J=9.1 Hz, ArCH), 6.49 (1H, s, Ar), 6.52 (1H, s, Ar), 6.58 (1H, s, Ar), 6.70 (1H, s, Ar), 6.98 (2H, m, Ar), 7.21–7.36 (3H, m, Ar). δ_C 15.4, 48.9, 50.0, 54.3, 55.8, 55.9, 56.0, 56.5, 56.6, 97.6, 107.4, 107.8, 112.4, 126.1, 127.9, 128.7, 129.0, 138.3, 138.8, 142.1, 143.2, 147.8, 148.3, 148.4, 152.3. Minor diastereomer **46**: δ_H 1.07 (3H, d, J=6.7 Hz, CH_3), 2.28 (1H, m, J=6.7, 9.8, 9.9 Hz, $CHCH_3$), 3.73 (3H, s, OCH_3), 3.74 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 3.92 (5H, overlaps with OCH_3, CHAr, CHPh), 6.40 (1H, s, Ar), 6.46 (1H, s, Ar), 6.47 (1H, s, Ar), 6.58 (1H, s, Ar), 7.21–7.36 (5H, m, Ar). δ_C 15.9, 54.3, 55.8, 55.9, 56.0, 56.6, 56.7, 56.8, 58.3, 97.8, 107.2, 107.5, 112.7, 123.3, 123.8, 126.4, 138.1, 138.7, 143.3, 143.8, 147.9, 148.1, 148.3, 152.3, 152.4. Anal. Calcd for $C_{27}H_{30}O_5$: C, 74.6; H, 6.9. Found: C, 74.7; H, 7.0.

4.2.17. *r-1-(2,4,5-Trimethoxyphenyl)-t-2-methyl-c-3-phenyl-5-methoxy-6-hydroxyindane (**48**) and r-1-(2,4,5-trimethoxyphenyl)-t-2-methyl-t-3-phenyl-5-methoxy-6-hydroxyindane (**49**)*

General procedure was carried out with alcohol **9** (0.12 g, 0.53 mmol), styrene **16** (0.14 g, 0.69 mmol), and $SnCl_4$ (0.18 g, 0.69 mmol). p-TLC ($CHCl_3$) afforded 0.12 g (55%) of **48** and **49** as a 1:2.2 (**48**/**49**) mixture(solid). P-TLC (80:20 hexane/ethyl acetate) allowed the separation of **48** (yellow solid), mp: 155–157 °C, and **49** (yellow solid), mp: 168–170 °C. Major diastereomer **49**: δ_H 0.68 (3H, d, J=7.0 Hz, CH_3), 2.72 (1H, m, $CHCH_3$), 3.72 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 4.38 (1H, d, J=8.1 Hz, ArCH), 4.41 (1H, d, J=9.2 Hz, ArCH), 5.54 (1H, s, OH), 6.54 (1H, s, Ar), 6.55 (1H, s, Ar), 6.56 (1H, s, Ar), 6.67 (1H, s, Ar), 6.99 (2H, m, Ar), 7.00–7.31 (3H, m, Ar). δ_C 15.6, 48.6, 49.4, 54.2, 55.9, 56.0, 56.6, 56.7, 97.7, 107.3, 110.4, 112.4, 123.6, 126.0, 127.9, 129.0, 137.6, 139.8, 142.2, 143.2, 144.9, 145.8, 147.9, 152.4. Minor diastereomer **48**: δ_H 1.05 (3H, d, J=6.6 Hz, CH_3), 2.40 (1H, m, J=6.6, 9.9, 9.9 Hz, $CHCH_3$), 3.74 (4H, overlaps with OCH_3, CHAr), 3.75 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 4.31 (1H, d, J=9.9 Hz, ArCH), 5.49 (1H, s, OH), 6.40 (1H, s, Ar), 6.46 (1H, s, Ar), 6.47 (1H, s, Ar), 6.58 (1H, s, Ar), 7.25–7.39 (5H, m, Ar). δ_C 15.9, 56.1, 56.2, 56.7, 57.0, 58.4, 98.0, 107.0, 110.1, 112.7, 123.1, 126.4, 128.4, 128.8, 137.5, 139.7, 143.4, 143.9, 144.8, 145.6, 148.0, 152.5. Anal. Calcd for $C_{26}H_{28}O_5$: C, 74.2; H, 6.7. Found: C, 74.3; H, 6.8.

4.2.18. *3-[1-(2,4,5-Trimethoxyphenyl)-propyl]-1,2-dihydronaphthalene (**51**)*

General procedure was carried out with alcohol **10** (0.10 g, 0.46 mmol), 4-phenyl-1,2-dihydronaphthalene **14** (0.10 g, 0.50 mmol), and $SnCl_4$ (0.15 g, 0.30 mmol). p-TLC (80:20, hexane/ethyl acetate) afforded 0.14 g (73%) of **51** (clear oil). δ_H 0.83 (3H, t, J=7.4 Hz, CH_2CH_3), 1.80 (2H, m, J=6.5, 7.4 Hz, CH_2CH_3), 2.24 (1H, m, CH_2CH_2Ar), 2.36 (1H, m, CH_2CH_2Ar), 2.75 (3H, m, CH_2Ar, $CHCH_2$), 3.59 (3H, s, OCH_3), 3.84 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 6.42 (1H, s, Ar), 6.55 (1H, dd, J=6.6, 7.7 Hz, Ar), 6.78 (1H, s, Ar), 6.96–7.11 (3H, m, Ar), 7.26 (2H, m, Ar), 7.29–7.44 (3H, m). δ_C 12.6, 24.1, 25.6, 28.8, 43.0, 55.9, 56.1, 56.9, 97.6, 111.2, 122.9, 125.8, 126.0, 126.1, 126.4, 126.7, 127.8, 129.5, 134.8, 138.1, 138.2, 140.9, 141.8, 148.2, 148.6, 157.3. Anal. Calcd for $C_{28}H_{30}O_3$: C, 81.1; H, 7.3. Found: C, 81.2; H, 7.4.

4.2.19. *4-Phenyl-3-[1-(2,4,5-trimethoxyphenyl)-propyl]-1,2-dihydronaphthalene (**52**)*

General procedure was carried out with alcohol **10** (0.10 g, 0.46 mmol), 1,2-dihydronaphthalene **15** (0.097 g, 0.74 mmol), and $SnCl_4$ (0.15 g, 0.60 mmol). p-TLC (70:30, hexane/ethyl acetate) afforded 0.11 g (70%) of **52** (clear oil). δ_H 0.90 (3H, t, J=7.4 Hz, CH_2CH_3), 1.71 (1H, m, CH_2CH_3), 1.96 (1H, m, CH_2CH_3), 2.12 (3H, m, $CHCH_2$, CH_2CH_2Ar), 2.70 (2H, m, CH_2CH_2Ar), 3.80 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 6.38 (1H, s, CH=), 6.54 (1H, s, Ar), 6.74 (1H, s, Ar), 7.04–7.12 (4H, m, Ar). δ_C 12.3, 25.8, 26.8, 28.4, 44.9, 56.0, 56.7, 56.8, 97.9, 111.8, 121.7, 123.8, 125.6, 126.1, 126.3, 127.1, 134.7, 135.0, 143.2, 144.6, 147.7, 152.0. Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.1; H, 7.7. Found: C, 78.2; H, 7.8.

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