

Towards Benign Synthesis of Indenes from Indanones: Zinc-Mediated Allylation of Ketones in Aqueous Media as a Source of Substituted Indenyl Ligand Precursors

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Keywords: Cyclopentadienyl ligands / Allylation / Zinc / Ketones / Hydrosilylation

Substituted indenenes are valuable ligand precursors for transition-metal complexes. Previously, most of the methods employed for the preparation of alkyl-substituted indenenes have involved the use of air-sensitive organometallic lithium or Grignard reagents, often in combination with expensive metal catalysts. The present work evaluates an approach to the synthesis of 2- and 3-allyl-substituted indenenes by employing a simple, environmentally benign organometallic zinc-mediated Barbier-type allylation of 1- and 2-indanones in aqueous media. A large series of new achiral and racemic indenyl ligand precursors have been prepared in variable yields by reacting substituted and unsubstituted indanones with allyl-, crotyl-, and cinnamyl halides using metallic zinc as the me-

diating metal in THF/NH₄Cl_{aq} followed by acid-catalyzed dehydration. The method described is applicable also for indanones containing unprotected halide- and hydroxyl substituents. As an example of extension of the approach, some indenenes have been further hydrosilylated with achiral silanes and disilanes in the presence of Karstedt's catalyst to provide new silaalkyl-substituted indenenes and bis(indenenes). Hydrosilylation with a chiral silane, (+)-(R)-methyl-1-naphthalenyl-phenylsilane, provides access to new chirally substituted indenenes.

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Introduction

Substituted indenenes and cyclopentadienes serve as versatile ligand precursors for a broad range of transition-metal complexes.^[1] In particular, group 4 bis(indenyl) metallocenes are frequently employed catalyst precursors for stereospecific polymerization of alkenes,^[2] and are being used as reagents and catalysts for various stereo- and/or enantioselective organic transformations.^[3] A remarkable example of an organozirconium success story in organic synthesis is the enantioselective carboalumination of alkenes catalyzed by chiral zirconocene dichlorides,^[4] applied recently to the synthesis of complex natural products.^[5] Other applications of chiral zirconocenes in stereoselective synthesis include those in enantioselective cyclopolymerization of nonconjugated dienes,^[6] as well as applications in other carbon–carbon,^[7] carbon–hydrogen,^[8] and carbon–oxygen^[9] bond forming reactions.

In general, the catalytic performance of group 4 bis(indenyl)metallocene complexes is determined by a combination

of steric and electronic effects, which in turn are induced by the substitution pattern of the indenyl ligand. Thus, the development of new, simple and versatile methods for the synthesis of substituted indenenes and indenyl ligand precursors is nontrivial and of continuous topical interest, especially so, considering the often expensive and complicated methods currently in use for their preparation. Previously, a number of methods have been applied to synthesize 1- and 2-silyl,^[10] 1- (or 3-) and 2-alkyl/aryl,^[1a,11,12] as well as various heteroatom-substituted indenenes.^[13] Most of the earlier approaches to the synthesis of alkyl-substituted indenenes have involved the use of air- and moisture-sensitive organometallic lithium or Grignard reagents, often in combination with expensive metal catalysts. Thus, there exists a demand to develop safer and more economical approaches for their synthesis.

Zinc- and indium-mediated Barbier-type allylations of aldehydes and ketones in aqueous media are powerful methods for creating new C–C bonds under mild and environmentally benign reaction conditions.^[14] Typically, zinc powder is mixed with an allyl halide reagent and reacted with a ketone or aldehyde in a mixture of THF and saturated aqueous ammonium chloride to provide the corresponding allylic alcohols in high yield. Indium, having a lower first ionization potential can be used in nonacidic aqueous solutions without additional proton sources.^[15] In contrast to alkyllithium and Grignard reagents, both zinc

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and indium organometallics tolerate the presence of various other functional groups in the molecule.

In two previous reports, allylation of 1-indanone with allyl bromide^[16] and 2-indanone with tetraallylstannane^[17] in dichloromethane resulted in the formation of the corresponding 1- and 2-substituted allylhydroxyindanes in high yields. Likewise, Bi(OTf)₃-catalyzed allylation of indene oxide with tetraallylstannane^[18] and the indium(I) chloride mediated allylation of indene oxide with allyl bromide catalyzed by Pd^[19] has provided 2-allylhydroxyindane in 85 and 83% yields, respectively. These allylindanol in turn could be easily envisioned to function as precursors to substituted indenenes after elimination of water. We became interested in the applicability of the ketone allylation method in *aqueous media* as a potential simple and environmentally benign source of allylically substituted indenenes, and describe here its scope and application to the synthesis of a large series of new substituted indenenes and cyclopentadienes, suitable as ligand precursors for transition-metal complexes.

Notably, bis(indenyl) group 4 metallocenes incorporating double-bond containing ligand substituents are of current interest as self-supporting olefin polymerization catalysts. By this method, the homogeneous catalysts can be transferred into a heterogeneous system without the use of inorganic carriers.^[20] Also, in recent work, Erker and coworkers have applied alkenyl-substituted metallocene complexes for the preparation of novel bridged and bimolecular zirconocene catalysts through use of the Grubbs ring-closing olefin metathesis reaction.^[21] Likewise, bis(2-alkenylindenyl)zirconium dichlorides were recently converted into

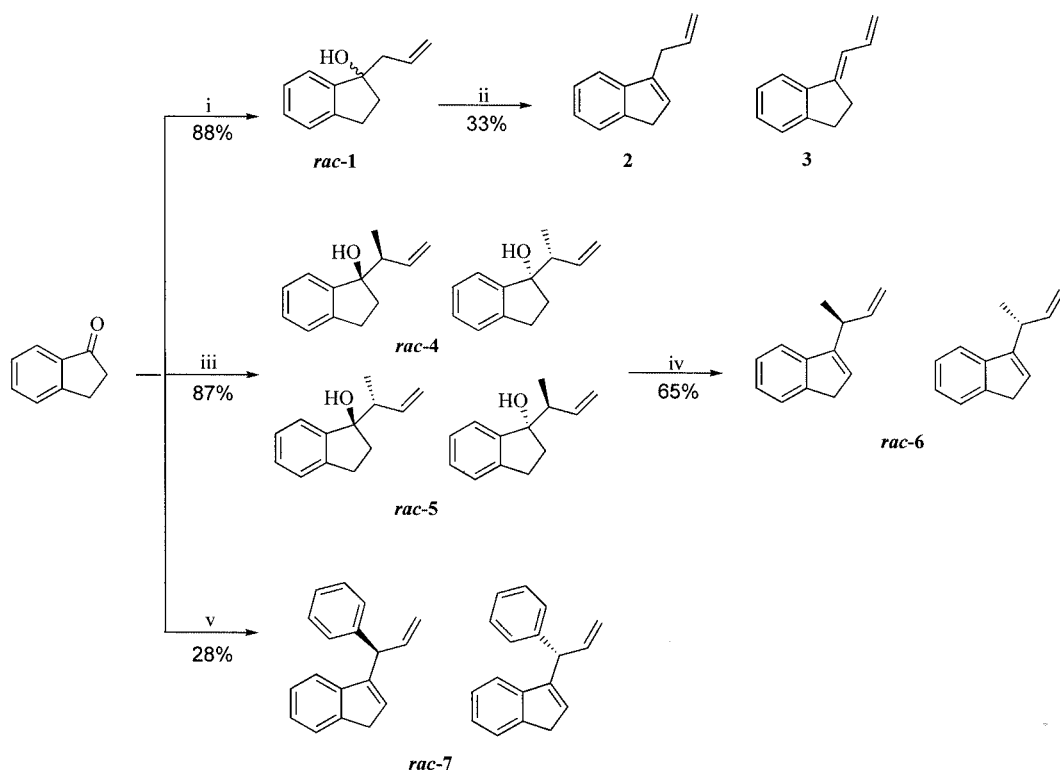
bridged *ansa*-metallocenes by a photochemical [2+2] cycloaddition reaction.^[22] Further examples of developing functional group chemistry on bent group 4 metallocene frameworks have been collected in a recent review.^[23]

Results and Discussion

As a starting point for the present work, various 1- and 2-indanones as well as some substituted cyclopentenones were selected for the metal-mediated allylations in aqueous media with allyl-, crotyl- and cinnamyl bromide as allylating reagents. While a number of metals have been reported to mediate allylations of ketones and aldehydes under aqueous conditions, the efforts here were focused on metallic zinc because of its superiority in terms of low cost and low toxicity. A detailed description of the performed work follows. All of the isolated compounds have been fully characterized by ¹H and ¹³C NMR spectroscopic analysis and by high resolution mass spectroscopy (for details, see the experimental section).

Allylation of 1-Indanones

The reactions of 1-indanone with allyl bromide, crotyl bromide and cinnamyl bromide followed by acid-catalyzed dehydrations are summarized in Scheme 1. The zinc-mediated allylation of 1-indanone with allyl bromide yielded the desired allylindanol in good yield (88%) and as a racemic mixture of two enantiomers *rac-1*. Subsequent dehydration



Scheme 1. (i) Allyl bromide, Zn, NH₄Cl_{aq}/THF. (ii) Amberlyst 15, pentane. (iii) Crotyl bromide, Zn, NH₄Cl_{aq}/THF. (iv) Amberlyst 15, pentane. (v) Cinnamyl chloride, Zn, NH₄Cl_{aq}/THF.

of the *rac*-1 mixture with Amberlyst 15 in pentane gave an inseparable 1:1 mixture of the double-bond isomers **2** and **3** resulting from non-regioselective water elimination in 33% isolated yield. Various dehydration conditions and reagents were investigated for compounds *rac*-1 (sulfuric acid, phosphorus oxychloride, oxalic acid, a mixture of sulfuric acid and acetic acid); however, none of the attempts resulted in the formation of a single product. In previous work, a mixture of 1- and 3-allylindenes was prepared in 69% yield by the conventional addition of allyl chloride to indenyllithium.^[12c,24]

When crotyl bromide was used instead of allyl bromide in the allylation of 1-indanone, a 1:0.3 diastereomeric mixture of two pairs of enantiomers (*rac*-4 versus *rac*-5) was obtained in 87% yield, as evidenced by ¹H NMR spectroscopic analysis. While this mixture was stored at −20 °C overnight, some spontaneous dehydration took place. In order to drive the reaction to completion, the diastereomeric mixture was reacted with Amberlyst 15 in pentane to provide the 3-(1-methylallyl)indene *rac*-6 in 65% yield based on a mixture of *rac*-4 and *rac*-5 and as a racemic mixture of two enantiomers.

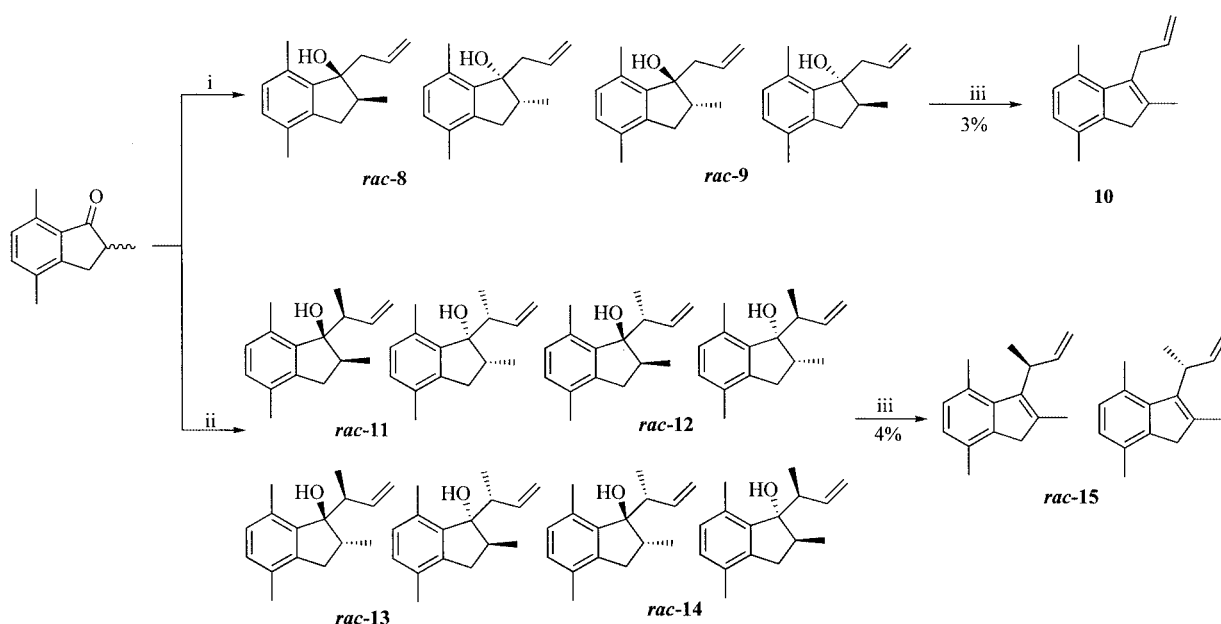
The allylation of 1-indanone with cinnamyl chloride, likewise, initially yielded a diastereomeric mixture of four allylindanol, which, however, due to their high lability, spontaneously eliminated water upon storage at −20 °C overnight to provide the 3-(1-phenylallyl)indene *rac*-7 in 28% isolated overall yield, again as a racemic mixture of two enantiomers.

Allylation of the sterically more congested 2,4,7-trimethyl-1-indanone with allyl bromide and crotyl bromide yielded the desired diastereomeric alcohols *rac*-8/*rac*-9, and *rac*-11/*rac*-12/*rac*-13/*rac*-14, respectively. However, these reactions could not be driven to completion, and the crude products were dehydrated without purification by using

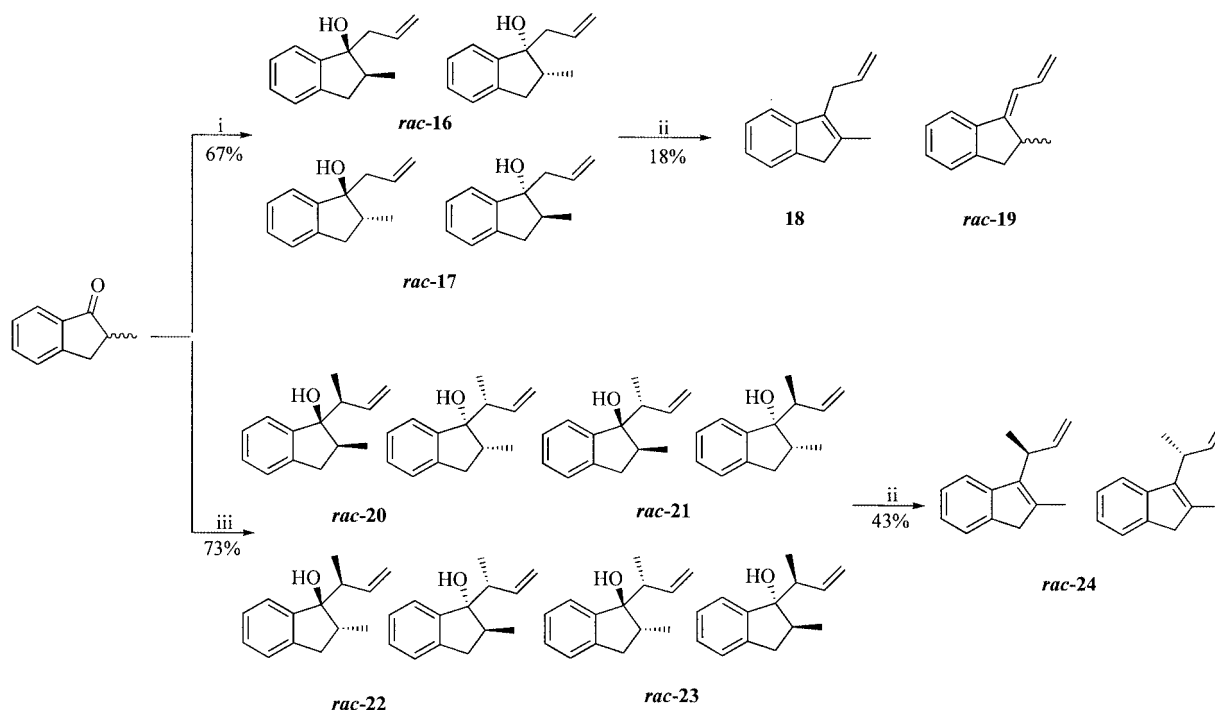
Amberlyst 15 in pentane (Scheme 2). The indenenes **10** and *rac*-15 were obtained in poor overall yields of 3% and 4% over two steps, respectively, after purification by column chromatography. All attempts to react 2,4,7-trimethyl-1-indanone with cinnamyl chloride failed. The total failure with cinnamyl chloride, and the poor yields obtained with crotyl- and allylbromides are likely a result of the increased steric hindrance on the keto side of the indanone induced by the methyl substituents in the 2- and 7-positions, which is even more pronounced when the larger cinnamyl reagent is employed.

In order to further evaluate the influence of methyl substitution on the course of the allylation reaction, 2-methyl-1-indanone was employed as starting material (Scheme 3). The results obtained were similar to the case of 2,4,7-trimethyl-1-indanone; thus, the zinc-mediated allylations of 2-methyl-1-indanone with allyl bromide and crotyl bromide yielded a 1:0.2 diastereomeric mixture of the allylindanol *rac*-16/*rac*-17 in a satisfactory 67% yield and a diastereomeric mixture of *rac*-20/*rac*-21/*rac*-22/*rac*-23 in 73% yield, respectively. Allylation using cinnamyl chloride failed. Apparently, the effect of the methyl substituent in position 7 thus plays a greater role than the substituent in position 2 when steric hindrance towards the allylating reagent is considered. Dehydration of the mixtures of alcohols *rac*-16/*rac*-17, and *rac*-20/*rac*-21/*rac*-22/*rac*-23 with Amberlyst 15 in pentane gave a 1:0.16 mixture of the dehydration products **18** and *rac*-19, and the enantiomeric mixture of the 2-methyl-3-(1-methylallyl)indene *rac*-24 in 18% and 43% yields, respectively.

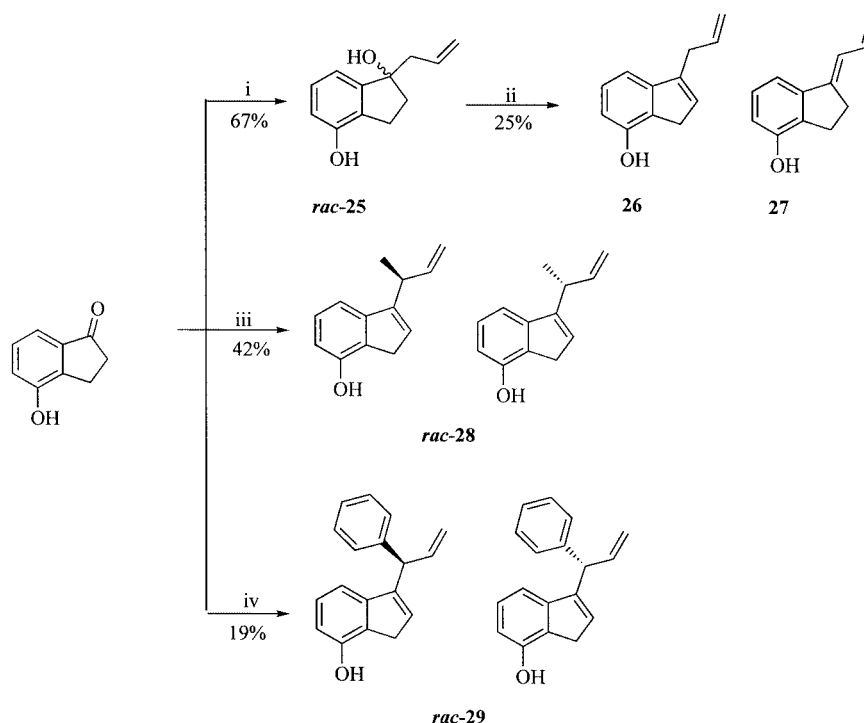
Next, in order to further broaden the usability of the method, a series of functionalized 1-indanones were investigated. The zinc-mediated allylation of 4-hydroxy-1-indanone with allyl bromide yielded the desired allylindandiol *rac*-25 in 67% yield, which upon dehydration, gave an in-



Scheme 2. (i) Allyl bromide, Zn, NH₄Cl_{aq}/THF. (ii) Crotyl bromide, Zn, NH₄Cl_{aq}/THF. (iii) Amberlyst 15, pentane.



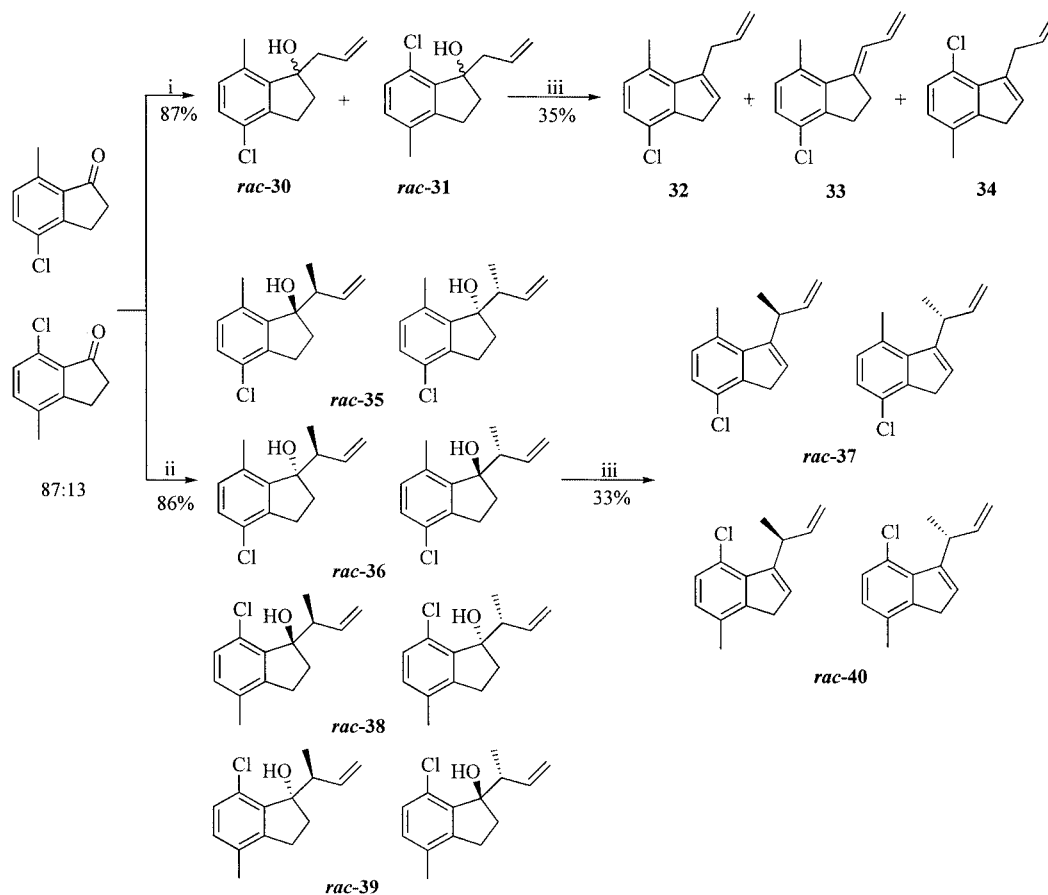
Scheme 3. (i) Allyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii) Amberlyst 15, pentane. (iii) Crotyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF.



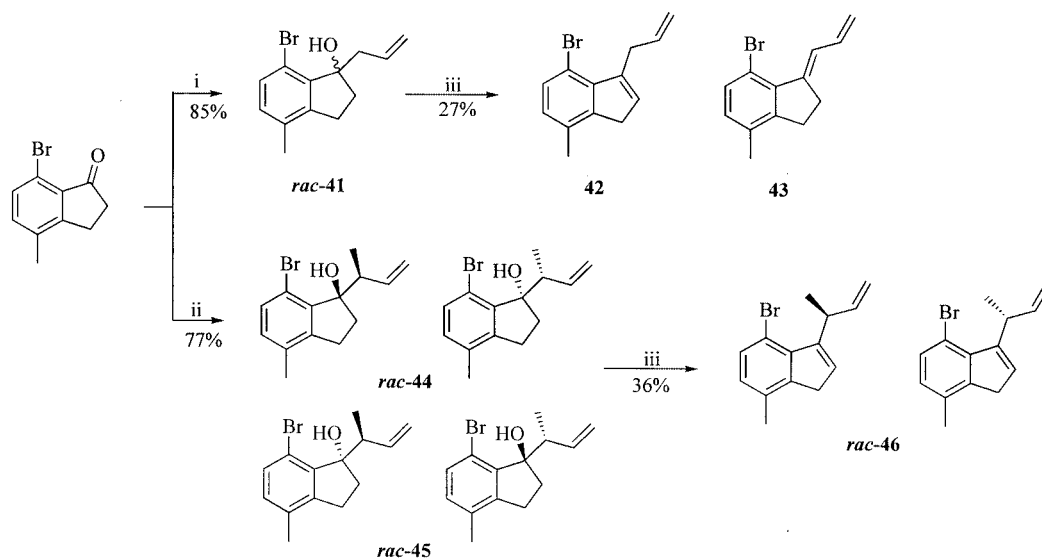
Scheme 4. (i) Allyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii) MgSO_4 , toluene, reflux. (iii) Crotyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (iv) Cinnamyl chloride, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF.

separable 1:0.16 mixture of the double-bond isomers **26** and **27** in 25% isolated yield (Scheme 4). Allylation of 4-hydroxy-1-indanone with crotyl bromide and cinnamyl chloride resulted in spontaneous dehydration upon allylation to give the enantiomeric mixtures of 4-hydroxyindenes *rac*-**28** and *rac*-**29** in 42% and 19% isolated yields, respectively.

The steric effect of the substituent in the 7-position of 1-indanone and the electronic effect of a halogen substituent were further investigated by allylating 4-chloro-7-methyl-1-indanone (containing 13% of 7-chloro-4-methyl-1-indanone as an impurity) with allyl bromide, crotyl bromide and cinnamyl chloride (Scheme 5). Allylation of the chloro-



Scheme 5. (i) Allyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii) Crotyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (iii) Amberlyst 15, pentane.



Scheme 6. (i) Allyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii) Crotyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (iii) Amberlyst 15, pentane.

indanone mixture with allyl bromide and crotyl bromide yielded mixtures of the halogenated indanol derivatives *rac*-30/*rac*-31 and *rac*-35/*rac*-36/*rac*-38/*rac*-39 in 87% and 86% yields respectively. Subsequent dehydration of these mixtures gave mixtures of the dehydration products 32/33/34 and *rac*-37/*rac*-40 in 35% and 33% yields, respectively. Al-

ylation of the chloroindanone mixture with cinnamyl chloride failed, again probably due to the steric hindrance induced by the 7-substituent. Thus, again it appears that of the allylating reagents employed, cinnamyl chloride is the most sensitive towards steric hindrance in the keto substrate.

Allylation of 7-bromo-4-methyl-1-indanone gave results similar to those observed for the chlorinated analogue (Scheme 6). Allylation with allyl bromide and crotyl bromide thus yielded the expected indanol mixtures **rac-41** and **rac-44/rac-45** in 85% and 77% yields, respectively, which upon dehydration in the allyl bromide case provided a 1:0.9 mixture of the double bond isomers **42** and **43** in 27% yield, and in the crotyl bromide case, the enantiomeric mixture **rac-46** in 36% yield.

Allylation of 2-bromo-1-indanone with allyl bromide gave the indanol **rac-1** in 48% yield (Scheme 7). The zinc-mediated allylation reaction thus appears to cleave the bromine at the sp^3 -hybridized carbon atom in position 2 but, as expected, not the aromatic bromine in position 7 as observed in Scheme 6.



Scheme 7. (i) Allyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF.

Finally, allylation of a series of 1-indanones bearing a nitro- or an amino substituent in the six-membered ring, as illustrated in Figure 1, was investigated with crotyl bromide in combination with both zinc and indium as the mediating metal. For reasons remaining unknown at present, no reaction was observed for any of these compounds.

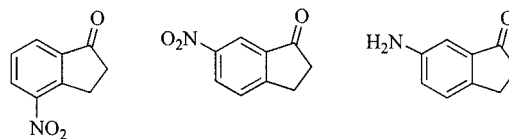
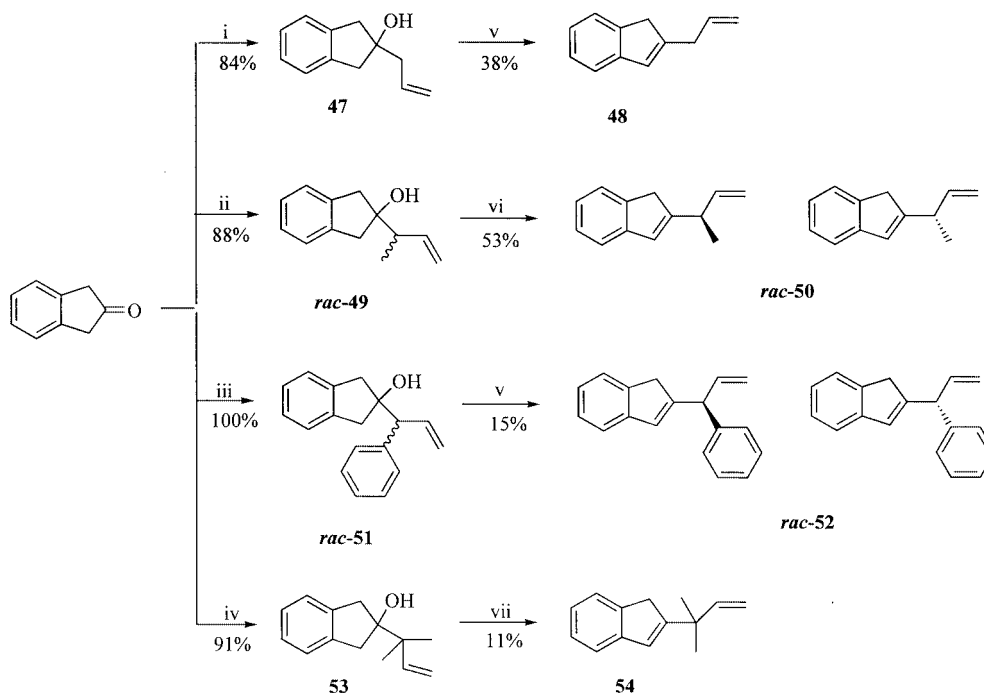


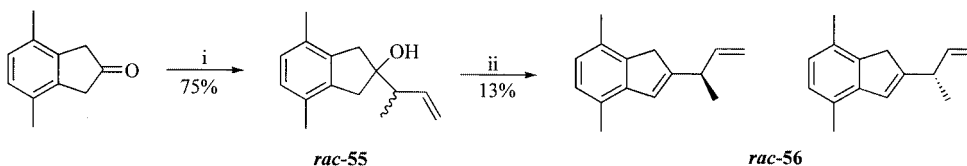
Figure 1. Nitro- and amino-substituted 1-indanones yielding no reaction with crotyl bromide/Zn and crotyl bromide/In.

Allylation of 2-Indanones

Allylation of 2-indanone with allyl bromide, crotyl bromide and cinnamyl chloride yielded the expected allylindanols **47**, **rac-49** and **rac-51** in 84%, 88% and nearly quantitative yields, respectively. Subsequent acid-catalyzed dehydrations in refluxing toluene gave the corresponding substituted indenenes **48**, **rac-50** and **rac-52** in 38%, 53% and 15% yields, respectively (Scheme 8). In a previous work, Schumann and coworkers prepared 2-allylindene by Pd-catalyzed Grignard reaction of 2-bromoindene with allylmagnesium chloride, a considerably more elaborate procedure, which resulted in the formation of the target compound in 25% yield.^[8c] Syntheses of 2-allylindene by Rh-catalyzed allylation of indene with allyl tosylate in 19% yield^[25] and by reaction of 2-indanone with allylmagnesium bromide followed by subsequent dehydration with *p*-TsOH in 30–40% overall yield^[26] have likewise been reported. The overall yield here over two steps for 2-allylindene is 32% and thus entirely satisfactory considering also that none of the ini-



Scheme 8. (i) Allyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii) Crotyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (iii) Cinnamyl chloride, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (iv) Prenyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (v) *p*-TSA, toluene, reflux. (vi) H_2SO_4 , toluene, reflux. (vii) Amberlyst 15, pentane.



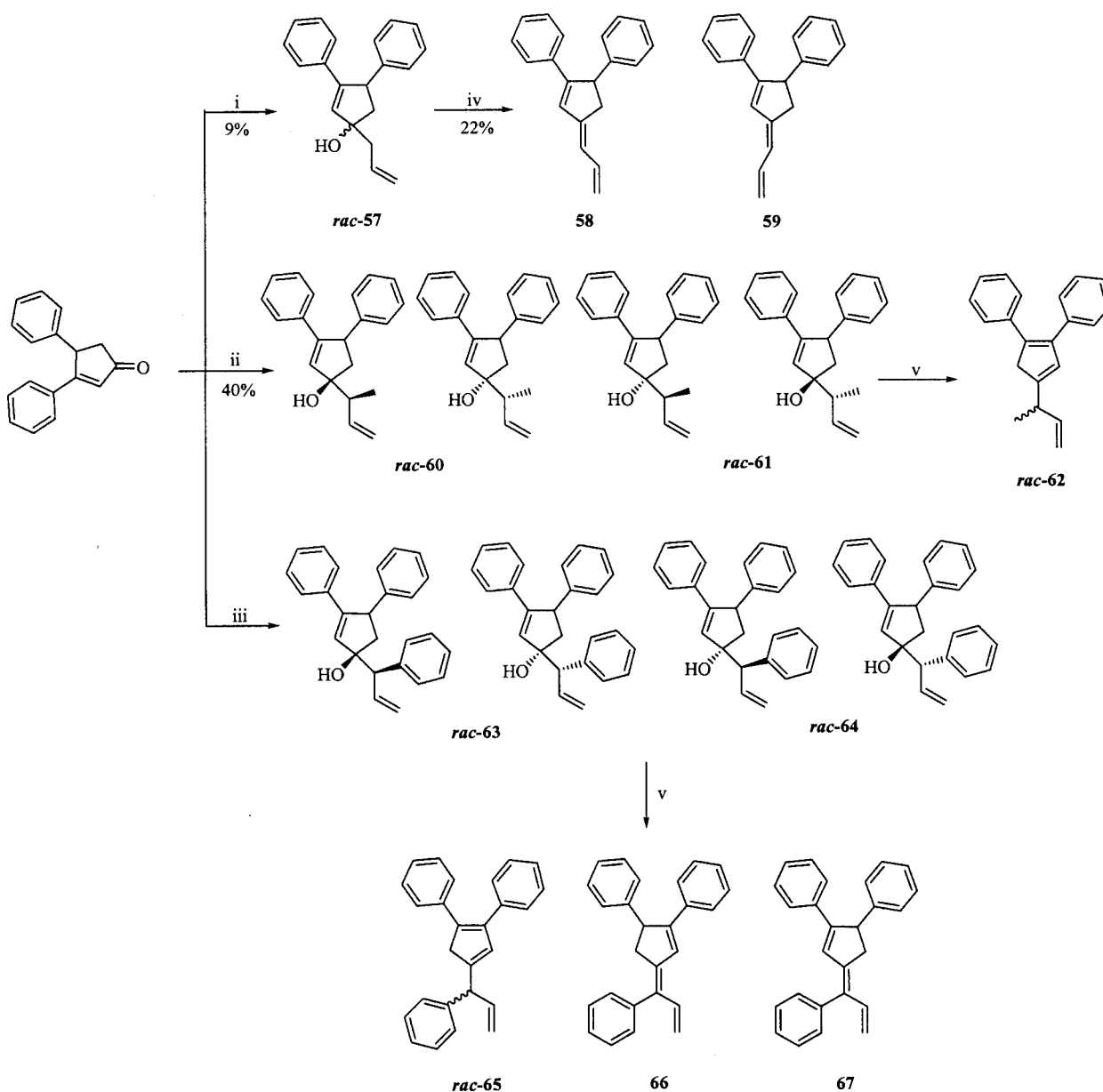
Scheme 9. (i) Crotyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii) Amberlyst 15, pentane.

tially screened reaction conditions reported in this work have been optimized to maximize the formation of the target compounds.

In addition, the zinc-mediated allylation of 2-indanone using prenyl bromide was investigated on a small scale. The indanol **53** was obtained in 91% yield and the indene **54** in

11% isolated yield after subsequent dehydration and purification by flash chromatography.

Finally, one substituted 2-indanone, 4,7-dimethyl-2-indanone, was allylated with crotyl bromide providing the allyl-substituted indanol *rac*-55 in 75% yield. Dehydration of *rac*-55 with Amberlyst 15 in pentane gave the enantiomeric

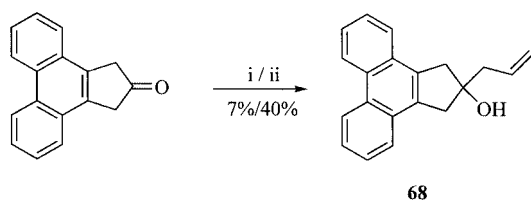


Scheme 10. (i) Allyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii) Crotyl bromide, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (iii) Cinnamyl chloride, Zn, $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (iv) Amberlyst 15, pentane. (v) MgSO_4 , toluene, reflux.

mixture of the corresponding indene **rac-56** in 13% yield (Scheme 9).

Allylation of Cyclopentenones

In order to briefly investigate the applicability of the method for the preparation of substituted cyclopentadienes, some readily available cyclopentenones were screened as starting material. Of these, the allylation of 3-methyl-2-cyclopenten-1-one with allyl bromide was attempted that resulted in a complex mixture of unknown products, possibly containing Diels–Alder adducts. When 3,4-diphenyl-cyclopent-2-enone was reacted with allyl bromide, crotyl bromide and cinnamyl chloride, the cyclopentenol **rac-57** and the mixtures **rac-60/rac-61** and **rac-63/rac-64** were obtained in 9%, 40%, and 51% yields, respectively (Scheme 10). The cyclopentenol derivative **rac-57** was dehydrated with Amberlyst 15 in pentane, and a 2:1 mixture of compounds **58** and **59** with exocyclic double bonds was obtained in 22% yield. The dehydration of the diastereomeric mixtures **rac-60/rac-61** and **rac-63/rac-64** in acidic environment yielded only undesired side products with large molecular weights.



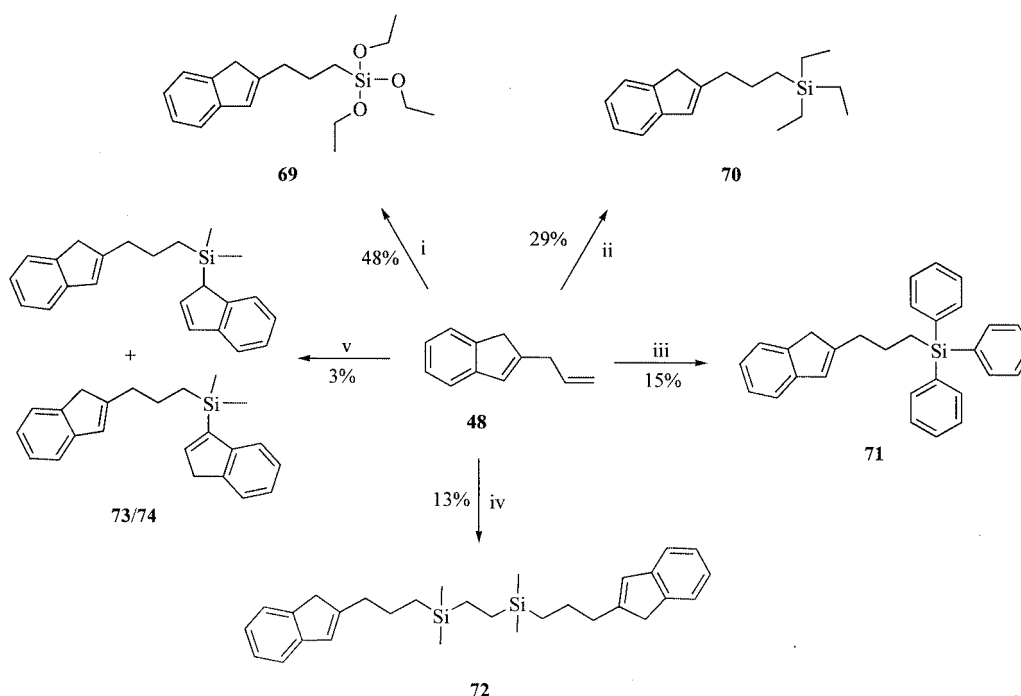
Scheme 11. i) Allyl bromide, Zn, NH₄Cl/THF. (ii) Allyl bromide, In, water/THF.

Cyclopentadienes are prone to form Diels–Alder products, and we assume that the side products formed may consist of such mixtures, although their exact structure remains unknown. Instead, dehydration of the mixtures **rac-60/rac-61** and **rac-63/rac-64** with heat yielded the desired cyclopentadienes **rac-62** and a mixture of **rac-65**, **-66**, and **-67** as main products. Unfortunately, in addition to the desired compounds, inseparable side products were also formed, and the cyclopentadienes could not be obtained in analytically pure form. Thus, at present, the applicability of the zinc-mediated aqueous allylation to the synthesis of substituted cyclopentadienes appears less attractive than its application to the synthesis of substituted indenenes.

Group 4 bis(indenyl) *ansa*-zirconocenes containing benzo-fused indenyl ligands are known to form highly active and stereoselective catalysts for the isospecific polymerization of propylene.^[27] Thus, the zinc-mediated allylation of 1,3-dihydro-cyclopenta[*h*]phenanthren-2-one with allyl bromide was also investigated and provided the alcohol **68** in poor (7%) yield (Scheme 11). When indium was used instead of zinc as the mediating metal, a significantly higher yield (40%) was obtained. Dehydration of **68** under acidic conditions was attempted with *p*-TsOH, H₂SO₄ and Amberlyst 15, and by refluxing in toluene. Unfortunately, none of these attempts provided the desired dehydration product.

Derivatization of the Allyl Group

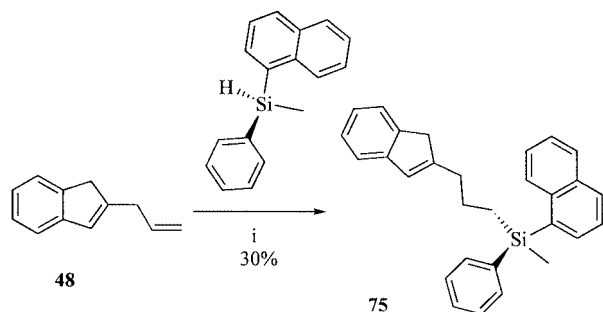
A specific advantage of the allyl substituent is the large variety of postmodifications that can be applied for its derivatization. As an example, we briefly investigated the



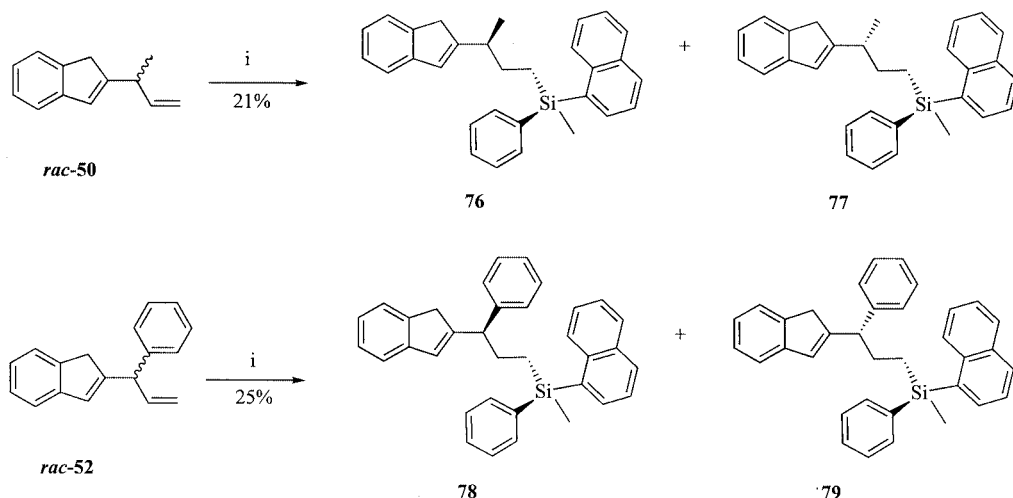
Scheme 12. Karstedt's catalyst in toluene with (i) triethoxysilane, (ii) triethylsilane, (iii) triphenylsilane, (iv) 1,2-bis(dimethylsilyl)ethane, and (v) (1H-inden-1-yl)dimethylsilane (containing about 10% of (3H-inden-1-yl)dimethylsilane as impurity).

hydrosilylation of 2-allylindene (**48**) in the presence of Karstedt's catalyst with triethoxysilane, triethylsilane, triphenylsilane, 1,2-bis(dimethylsilyl)ethane, and a 90:10 mixture of the 1- and 3-indenyl isomers of indenyl dimethylsilane (Scheme 12). In addition, a readily available chiral silane, (+)-(*R*)-methyl-1-naphthalenylphenylsilane, was used for evaluating the applicability of the approach for the preparation of enantiomerically pure chirally substituted indenenes (Scheme 13). Hydrosilylation with the achiral mono- and disilanes thus provided the 2-silaalkyl-substituted indenenes **69–71** in 48%, 29%, and 15% isolated yields, and the bridged bis(indene) **72**, in 13% isolated yield after purification by flash chromatography. The bridged bis(indene) **73/74** (a mixture of 1- and 3-indenyl) isomers were obtained in 3% isolated yield by hydrosilylation of 2-allylindene with the 1- and 3-indenyl dimethylsilane mixture followed by purification by flash chromatography.^[28] Finally, the chiral indene **75** was obtained in 30% isolated yield by hydrosilylation of 2-allylindene with (+)-(*R*)-methyl-1-naphthalenylphenylsilane.^[29] The proposed stereochemistry around the silicon atom, as depicted in Scheme 13, is based on the expected retention of configuration of the chiral silicon atom during the hydrosilylation reaction.^[30]

Finally, for evaluating the potential use of the chiral silane as a resolving agent, the enantiomeric mixtures of 2-(1-methylallyl)-1H-indene (*rac*-**50**) and 2-(1-phenylallyl)-



Scheme 13. (i) (+)-(*R*)-Methyl-1-naphthalenylphenylsilane, Karstedt's catalyst, toluene.



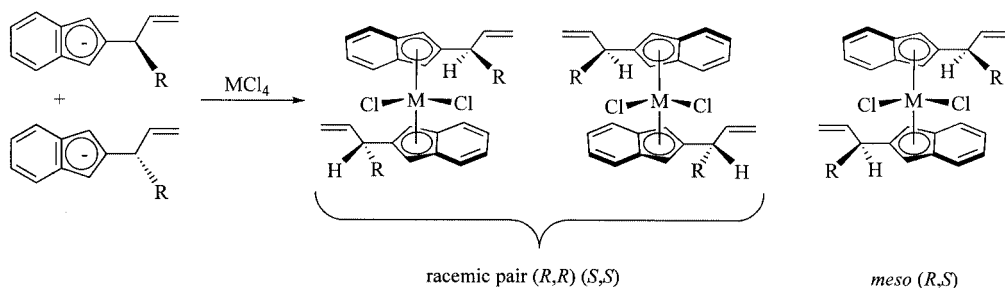
Scheme 14. (i) (+)-(*R*)-Methyl-1-naphthalenylphenylsilane, Karstedt's catalyst, toluene.

1H-indene (*rac*-**52**) were hydrosilylated with (+)-(*R*)-methyl-1-naphthalenylphenylsilane to yield the 1:1 diastereomeric mixtures of **76/77** and **78/79** in 25% and 21% yields, respectively (Scheme 14). Unfortunately, none of the compounds proved to be crystalline and all preliminary attempts to separate the diastereomers by flash chromatography failed. Nevertheless, considering the simple procedure, the method may prove to be of value for preparation/resolution of other chirally substituted indenenes.

Summary and Conclusions

To summarize, in the present work, we have demonstrated the applicability of metal-mediated allylation of ketones in aqueous media to be a potential source of new substituted indenyl ligand precursors. With limitations, the method would appear to be suitable also for the preparation of substituted cyclopentadienes. It should be borne in mind that the yields and procedures reported in this preliminary screening are by no means optimized. Yields of the zinc-mediated allylations may be highly dependent on reaction conditions, such as temperature, concentration, ammonium chloride/THF mole ratio, and the allyl halide reagent (chloride versus bromide), which, during the course of this investigation, were not varied systematically. Also, as demonstrated by allylation of the cyclopenta[*l*]phenanthren-2-one derivative depicted in Scheme 11, higher yields may simply be obtainable by changing the mediating metal from zinc to indium.

As it stands, yields of the allylation step with allyl bromide, crotyl bromide, and cinnamyl chloride are generally good with the exception of highly substituted indanones, especially when cinnamyl chloride is used. Problems are encountered in some of the dehydration steps, in particular with the 1-allylindanol and allylcyclopentenols, which upon dehydration tend to give mixtures of the desired 3-allylindene or allylcyclopentadiene together with products where water elimination has taken place in an exocyclic fashion. Of some concern, considering the potential use of-



Scheme 15. Metallation of 2-substituted indenyls.

the indenyls prepared as ligand precursors for transition-metal complexes, is also the fact that the 3-(1-methylallyl)- and 3-(1-phenylallyl)indenyls obtained with crotyl and cinnamyl reagents are racemic mixtures that bear a chiral indenyl substituent, which potentially produces a large amount of stereoisomers upon metallation of the 3-substituted indenyl anions. An analogous situation of course exists also with the corresponding 2-substituted indenyls of which 2-(1-methylallyl)indene and 2-(1-phenylallyl)indene are racemic mixtures. However, in contrast to 3-substituted indenyls, the two π faces of a 2-substituted indenyl ligand precursor are equivalent, and thus for racemic 2-substituted indenyls, metallation with group 4 metal tetrahalides potentially results in only three stereoisomers, namely a racemic pair (*R,R*) together with (*S,S*) and a *meso*-form (*R,S*) (Scheme 15),^[1a] a situation analogous to the preparation of conventional bridged bis(indenyl) *ansa*-metallocenes.^[31] These, in turn, are potentially separable into the pure *rac*- and *meso* diastereomers by standard recrystallization techniques.^[32] On the other hand, the racemic nature of some of the ligand precursors reported here should be of less concern when applied, for example, to the synthesis of mono-(indenyl)titanium trichlorides for applications in syndiospecific styrene polymerization^[33] or for use in mixed ligand bis(cyclopentadienyl) metallocene complexes in which one of the ligands does not bear a chiral substituent.

Of particular interest may also prove to be allylations of functionalized indenyls – only preliminarily investigated in this work – which may lead to simplified procedures to new heteroatom-substituted indenyl ligands and metallocene complexes.^[13] Also, a number of functionalized allylation reagents, not evaluated in the present work, should be readily available, providing simple access to further functionalization of the indenyl substitution pattern. As a direct derivatization of the allyl group, the hydrosilylation reaction preliminarily evaluated here may likewise result in new valuable chiral or achiral indenyl ligand precursors.^[34] For example, compound **55** carrying a triethoxysilyl functionality may provide access to immobilization of indenyl ligands and/or metallocenes to silica supports.^[35] We thus believe that the method described herein opens a versatile and simple access to a library of valuable building blocks for organometallic catalyst research. Application of selected ligand precursors reported in this work for preparation of transition-metal complexes is currently in progress in the authors' laboratories and will be reported in forthcoming papers.

Experimental Section

General Considerations: Commercially available solvents and reagents were used without further purification. 2,4,7-Trimethyl-1-indanone,^[36] 2-methyl-1-indanone,^[37] 4-nitro-1-indanone,^[38] 6-nitro-1-indanone,^[38] 6-amino-1-indanone,^[38] 4,7-dimethyl-2-indanone,^[39] 3,4-diphenyl-cyclopent-2-enone,^[40] 1,3-dihydro-cyclopenta[*f*]phenanthren-2-one,^[41] 4-methyl-7-bromo-1-indanone,^[42] the 87:13 mixture of 4-chloro-7-methyl-1-indanone and 4-methyl-7-chloro-1-indanone,^[43] dimethylsilylindene,^[44] and (+)-(*R*)-methyl-1-naphthalenylphenylsilane^[45] were synthesized according to literature procedures. Flash chromatography was performed on silica gel 60 (40–63 μ m). Purification by preparative TLC was performed on a 1 mm silica gel 60 (40–63 μ m) plate containing F₂₅₄. NMR spectra were recorded at 298 K with a Bruker Avance 600 (¹H NMR 600 MHz, ¹³C NMR 150.9 MHz), a Jeol L-400 (¹H NMR 400 MHz, ¹³C 100.6 MHz) or with a Bruker 250 MHz instrument (¹H NMR 250 MHz). ¹H NMR chemical shifts were referenced to residual ¹H impurities in the solvent relative to TMS, and ¹³C NMR chemical shifts, to the solvent signals. The NMR spectra were recorded (in δ values) with deuteriochloroform or [D₄]MeOH as the solvent. Mass spectra were recorded with a high resolution mass spectrometer (Fison's ZapSpec) and an Agilent 1100 Series LC/MSD SL Trap system.

Zinc-Mediated Allylation of a Ketone – General Procedure 1: A solution of the ketone in THF (4 mL) was added dropwise to a well-stirred mixture of zinc, saturated NH₄Cl_{aq} (40 mL) and THF (8 mL). Allyl halide was dissolved in THF (4 mL) and slowly added dropwise to the reaction mixture. The reaction was mildly exothermic, and the mixture began to reflux spontaneously. After refluxing had ceased, the reaction mixture was stirred at room temperature for 1–24 h. The slightly acidic reaction mixture was extracted with Et₂O (3 $\times$ 50 mL) and the combined organic layers were dried with Na₂SO₄, filtered, and evaporated to give the crude product.

Indium-Mediated Allylation of a Ketone – General Procedure 2: Indium powder and allyl halide were added dropwise to a suspension of the ketone in a 1:1 mixture of THF and water (5 mL) at room temperature. The resulting reaction mixture was stirred for 24 h and diluted with dichloromethane (50 mL). The layers formed were separated, and the organic phase was washed with brine (50 mL), dried with Na₂SO₄, filtered, and evaporated to give the crude product.

Dehydration with Amberlyst 15 – General Procedure 3: Amberlyst 15 was added to a solution of allyl indanol in pentane (5–35 mL). The resulting reaction mixture was stirred at room temperature for a period of 15 min–24 h. The solid catalyst was removed by filtration, and the filtrate was evaporated to dryness. The crude product was purified by silica gel column chromatography to yield the desired dehydration product.

Dehydration with *p*-TSA or Sulfuric Acid – General Procedure 4: *p*-TSA or sulfuric acid was added to a solution of allyl indanol in toluene (30–200 mL), and the resulting reaction mixture was refluxed for a period of 2–9.5 h. The solvent was removed under reduced pressure, and the residue was dissolved in Et₂O (50 mL). The organic layer was washed with saturated NH₄Cl_{aq} (50 mL), dried with Na₂SO₄, and filtered, and the solvents, evaporated to dryness. The crude product was purified by silica gel column chromatography to yield the desired dehydration product.

Dehydration with Heat – General Procedure 5: MgSO₄ was added to a solution of allyl cyclopentenol/allyl indandiol in toluene (20 mL), and the resulting reaction mixture was refluxed for 1–2 h. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. The crude product was purified by silica gel column chromatography to yield the desired dehydration product.

Hydrosilylation of Substituted Indenes – General Procedure 6: Karstedt's catalyst (3 drops) was added to a solution of substituted indene in toluene (5 mL). After the reaction mixture was stirred for 10 min, the silane was added. The resulting reaction mixture was stirred at room temperature for 2–23 h, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to yield the desired silaalkyl-substituted indene.

An Enantiomeric Mixture of 1-Allyl-indan-1-ol (*rac*-1): By applying General Procedure 1, zinc (1.4092 g, 21.6 mmol), 1-indanone (1.3777 g, 10.4 mmol), and allyl bromide (1.8 mL, 20.7 mmol) gave, after a 1-h reaction time, 1.5859 g (88%) of the title compound as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (m, 2 H, arom. CH), 7.16 (m, 6 H, arom. CH), 5.77 (m, 2 H, olefinic CH in chain), 5.08 (m, 2 H, olefinic CH in chain), 5.06 (m, 2 H, olefinic CH in chain), 2.93 (m, 2 H, aliphatic CH in five-ring), 2.73 (m, 2 H, aliphatic CH in five-ring), 2.56 (m, 2 H, aliphatic CH in chain), 2.43 (m, 2 H, aliphatic CH in chain), 2.25 (m, 2 H, aliphatic CH in five-ring), 1.99 (m, 4 H, OH and aliphatic CH in five-ring) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 146.99 (2 C_q), 142.95 (2 C_q), 133.73 (2 olefinic CH in chain), 128.22 (2 arom. CH), 126.62 (2 arom. CH), 124.89 (2 arom. CH), 122.85 (2 arom. CH), 118.78 (2 olefinic CH₂ in chain), 82.70 (2 C-OH), 44.94 (2 aliphatic CH₂ in chain), 39.62 (2 aliphatic CH₂ in five-ring), 29.37 (2 aliphatic CH₂ in five-ring) ppm. EIMS (30 eV): calcd. C₁₂H₁₄O 174.1045; found 174.1036.

A Mixture of 3-Allyl-1H-indene (2) and 1-Allylidene-indane (3): By applying General Procedure 3, 1-allyl-indan-1-ol (*rac*-1) (1.2457 g, 7.2 mmol) and Amberlyst 15 (1.0137 g) in pentane (30 mL) gave, after a 30-min reaction time and column chromatography (hexane as eluent), 0.3655 g (33%) of a 1:1 mixture of the title compounds as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.51 (m, 2 H, arom. CH), 7.41 (m, 1 H, arom. CH), 7.33 (m, 1 H, arom. CH), 7.30 (m, 1 H, arom. CH), 7.24 (m, 3 H, arom. CH), 6.65 (m, 2 H, olefinic CH in chain in 3), 6.28 (m, 1 H, aliphatic CH in five-ring in 2), 6.05 (ddt, *J* = 6.33 Hz, 10.07 Hz, 17.09 Hz, 1 H, olefinic CH in chain in 2), 5.32 (dm, *J* = 15.64 Hz, 1 H, olefinic CH in chain in 3), 5.23 (dm, *J* = 17.09 Hz, 1 H, olefinic CH in chain in 2), 5.18 (dm, *J* = 6.56 Hz, 1 H, olefinic CH in chain in 3), 5.16 (dm, *J* = 10.07 Hz, 1 H, olefinic CH in chain in 2), 3.35 (m, 4 H, aliphatic CH₂ in chain in 2 and aliphatic CH₂ in five-ring in 2), 3.06 (m, 2 H, aliphatic CH₂ in five-ring in 3), 2.92 (m, 2 H, aliphatic CH₂ in five-ring in 3) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 146.88 (C_q), 145.07 (2 C_q), 144.47 (C_q), 142.44 (C_q), 141.30 (C_q), 135.59 (olefinic CH in chain in 2), 134.37 (olefinic CH in chain in 3), 128.89 (olefinic CH in five-ring in 2), 128.19 (arom. CH), 126.50 (arom. CH), 125.96 (arom. CH), 125.26 (arom. CH), 124.56 (arom.

CH), 123.71 (arom. CH), 120.33 (arom. CH), 119.15 (arom. CH), 118.78 (olefinic CH in chain in 3), 116.27 (olefinic CH₂ in chain in 2 or 3), 115.92 (olefinic CH₂ in chain in 2 or 3), 37.72 (aliphatic CH₂ in five-ring or chain in 2), 32.43 (aliphatic CH₂ in five-ring or chain in 2), 30.12 (aliphatic CH₂ in five-ring in 3), 28.18 (aliphatic CH₂ in five-ring in 3) ppm. EIMS (30 eV): calcd. C₁₂H₁₂ 156.0939; found 156.0941.

A Mixture of 1-(1-Methyl-allyl)-indan-1-ol (*rac*-4 and *rac*-5): By applying General Procedure 1, zinc (1.6945 g, 25.9 mmol), 1-indanone (1.7007 g, 12.9 mmol), and crotyl bromide (3.1 mL, 30.1 mmol) gave, after a 1-h reaction time, 2.1043 g (87%) of the title compounds as yellow oils. The diastereomeric compounds were formed in a 1:0.3 ratio. ¹H NMR (600 MHz, CDCl₃): δ = 7.37 (m, 4 H, arom. CH in major and arom. CH in minor), 7.29 (m, 12 H, 6 arom. CH in major and 6 arom. CH in minor), 5.99 (ddd, *J* = 7.71 Hz, 10.79 Hz, 17.27 Hz, 2 H, olefinic CH in chain in minor), 5.80 (ddd, *J* = 7.09 Hz, 10.18 Hz, 17.27 Hz, 2 H, olefinic CH in chain in major), 5.27 (dm, *J* = 17.27 Hz, 2 H, olefinic CH in chain in minor), 5.21 (dm, *J* = 10.79 Hz, 2 H, olefinic CH in chain in minor), 5.11 (dm, *J* = 17.27 Hz, 2 H, olefinic CH in chain in major), 5.07 (dm, *J* = 10.18, 2 H, olefinic CH in chain in major), 3.01 (m, 4 H, aliphatic CH in five-ring in major and minor), 2.83 (m, 4 H, aliphatic CH in five-ring in major and minor), 2.76 (m, 4 H, aliphatic CH in chain in major and minor), 2.57 (br. s, 4 H, OH in major and minor), 2.42 (m, 4 H, aliphatic CH in five-ring in major and minor), 2.02 (m, 4 H, aliphatic CH in five-ring in major and minor), 1.19 (d, *J* = 7.22 Hz, 6 H, CH₃ in major), 0.95 (d, *J* = 7.22 Hz, 6 H, CH₃ in minor) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 146.42 (2 C_q in major), 145.94 (2 C_q in minor), 143.81 (2 C_q in minor), 143.53 (2 C_q in major), 139.94 (4 C, olefinic CH in chain in major and minor), 128.24 (2 arom. CH in minor), 128.10 (2 arom. CH in major), 126.57 (2 arom. CH in minor), 126.36 (2 arom. CH in major), 124.82 (2 arom. CH in major), 124.73 (2 arom. CH in minor), 123.74 (2 arom. CH in major), 123.49 (2 arom. CH in minor), 116.48 (2 olefinic CH₂ in minor), 115.65 (2 olefinic CH₂ in major), 85.38 (2 C-OH in minor), 85.33 (2 C-OH in major), 47.42 (2 aliphatic CH in chain in minor), 46.20 (2 aliphatic CH in major), 36.96 (2 aliphatic CH₂ in five-ring in major), 36.29 (2 aliphatic CH₂ in five-ring in minor), 30.08 (2 aliphatic CH₂ in five-ring in minor), 29.83 (2 aliphatic CH₂ in five-ring in major), 15.32 (2 CH₃ in minor), 13.65 (2 CH₃ in major) ppm. EIMS (30 eV): calcd. C₁₃H₁₆O 188.1201; found 188.1188.

An Enantiomeric Mixture of 3-(1-Methyl-allyl)-1H-indene (*rac*-6): By applying General Procedure 3, 1-(1-methyl-allyl)-indan-1-ol (*rac*-4 and *rac*-5) (1.8795 g, 10.0 mmol) and Amberlyst 15 (1.45 g) in pentane (35 mL) gave, after a 15-min reaction time, and column chromatography (hexane as eluent), 1.0949 g (65%) of an enantiomeric mixture of the title compounds as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.51 (dm, *J* = 7.55 Hz, 2 H, arom. CH), 7.46 (dm, *J* = 7.55 Hz, 2 H, arom. CH), 7.32 (tm, *J* = 7.55, 2 H, arom. CH), 7.24 (tm, *J* = 7.55 Hz, 2 H, arom. CH), 6.29 (m, 2 H, olefinic CH in five-ring), 6.07 (ddd, *J* = 6.79 Hz, 10.22 Hz, 17.24 Hz, 2 H, olefinic CH in chain), 5.18 (dt, *J* = 1.53 Hz, 17.24 Hz, 2 H, olefinic CH in chain), 5.10 (ddd, *J* = 1.22 Hz, 1.60 Hz, 10.22 Hz, 2 H, olefinic CH in chain), 3.57 (m, 2 H, aliphatic CH in chain), 3.38 (m, 4 H, aliphatic CH₂ in five-ring), 1.44 (d, *J* = 7.02 Hz, 6 H, CH₃) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 147.64 (2 C_q), 144.71 (2 C_q), 144.66 (2 C_q), 141.87 (2 olefinic CH in chain), 127.27 (2 olefinic CH in five-ring), 125.83 (2 arom. CH), 124.46 (2 arom. CH), 123.78 (2 arom. CH), 119.75 (2 arom. CH), 113.71 (2 olefinic CH₂ in chain), 37.64 (2 aliphatic CH₂ in five-ring), 36.55 (2 aliphatic CH in chain), 19.06 (CH₃) ppm. EIMS (70 eV): calcd. C₁₃H₁₄ 170.1096; found 170.1094.

An Enantiomeric Mixture of 3-(1-Phenyl-allyl)-1H-indene (*rac*-7): 1-indanone (2.1825 g, 16.5 mmol) in THF (4 mL) was added dropwise to a well-stirred mixture of zinc (2.1362 g, 32.7 mmol), saturated $\text{NH}_4\text{Cl}_{\text{aq}}$ (40 mL) and THF (8 mL). Cinnamyl chloride (5.0195 g, 32.9 mmol) was dissolved in THF (4 mL) and slowly added dropwise to the reaction mixture. The reaction mixture began to reflux spontaneously, and after refluxing had ceased, the reaction mixture was stirred at room temperature for 1 h. The slightly acidic (pH $\sim$ 6) reaction mixture was extracted with diethyl ether (3×50 mL), and the combined organic layers were dried with Na_2SO_4 and filtered, and the solvents, evaporated. The TLC analysis (hexane as eluent) of the reaction product showed that a small amount of the alcohol had spontaneously dehydrated. The reaction product was stored at -20°C overnight and analyzed with TLC (hexane as eluent). The TLC analysis indicated complete dehydration during storage. The reaction product was purified by silica gel column chromatography with hexane as eluent and 1.077 g (28%) of an enantiomeric mixture of the title compounds was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.52 (m, 2 H, arom. CH), 7.30 (m, 16 H, arom. CH), 6.35 (m, 4 H, aliphatic CH in five-ring and olefinic CH in chain), 5.27 (dt, J = 1.30 Hz, 1.37 Hz, 10.15 Hz, 2 H, olefinic CH in chain), 5.11 (dt, J = 1.45 Hz, 1.53 Hz, 17.01 Hz, 2 H, olefinic CH in chain), 4.77 (m, 2 H, aliphatic CH in chain), 3.47 (m, 4 H, aliphatic CH_2 in five-ring) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 145.63 (2 C_q), 144.54 (2 C_q), 144.47 (2 C_q), 141.49 (2 C_q), 139.51 (2 olefinic CH in chain), 130.25 (2 olefinic CH in five-ring), 128.47 (4 arom. CH), 128.41 (4 arom. CH), 126.48 (2 arom. CH), 125.86 (2 arom. CH), 124.52 (2 arom. CH), 123.69 (2 arom. CH), 120.21 (2 arom. CH), 115.98 (2 olefinic CH_2 in chain), 48.87 (2 aliphatic CH in chain), 37.76 (2 five-ring aliphatic CH_2) ppm. EIMS (70 eV): calcd. $\text{C}_{18}\text{H}_{18}\text{O}$ 232.1252; found 232.1248.

3-Allyl-2,4,7-trimethyl-1H-indene (10): By applying General Procedure 1, zinc (1.1283 g, 17.3 mmol), 2,4,7-trimethyl-indan-1-one (1.5230 g, 8.7 mmol), and allyl bromide (1.5 mL, 17.5 mmol) gave, after a 5.5-h reaction time, 1.3694 g of the mixture of 2,4,7-trimethyl-indan-1-one and 1-allyl-2,4,7-trimethyl-indan-1-ol (*rac*-8 and *rac*-9). The amount of the alcohol obtained was 27%. This crude product was directly used in the dehydration step without further purification or analysis. By applying General Procedure 3, a mixture of 1-allyl-2,4,7-trimethyl-indan-1-ol (*rac*-8 and *rac*-9) (0.1214 g, 0.56 mmol) and Amberlyst 15 (0.3398 g) in pentane (10 mL) gave, after a 1.5-h reaction time and column chromatography (10% dichloromethane/90% hexane as eluent), 0.0445 g (40%) of the title compound as a yellow oil. The overall yield (over two steps) was 3%. ^1H NMR (400 MHz, CDCl_3): δ = 6.83 (d, J_{AB} = 7.71 Hz, 1 H, arom. CH), 6.74 (d, J_{AB} = 7.71 Hz, 1 H, arom. CH), 5.92 (ddt, J = 5.11 Hz, 10.22 Hz, 17.17 Hz, 1 H, olefinic CH in chain), 4.94 (dq, J = 1.91 Hz, 10.18 Hz, 1 H, olefinic CH in chain), 4.86 (dq, J = 1.99 Hz, 17.17 Hz, 1 H, olefinic CH in chain), 3.34 (m, 2 H, aliphatic CH_2 in chain), 3.10 (m, 2 H, aliphatic CH_2 in five-ring), 2.43 (s, 3 H, CH_3 attached to the aromatic ring), 2.21 (s, 3 H, CH_3 attached to the aromatic ring), 1.98 (s, 3 H, CH_3 attached to the five-ring) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 143.54 (C_q), 141.55 (C_q), 140.05 (C_q), 136.49 (olefinic CH in chain), 135.52 (C_q), 129.87 (C_q), 129.76 (C_q), 129.45 (arom. CH), 124.78 (arom. CH), 115.00 (olefinic CH_2 in chain), 41.51 (aliphatic CH_2 in five-ring), 30.75 (aliphatic CH_2 in chain), 19.30 (CH_3 attached to the aromatic ring), 18.24 (CH_3 attached to the aromatic ring), 13.88 (CH_3 attached to the five-ring) ppm. EIMS (70 eV): calcd. $\text{C}_{15}\text{H}_{18}$ 198.1409; found 198.1409.

An Enantiomeric Mixture of 2,4,7-Trimethyl-3-(1-methyl-allyl)-1H-indene (*rac*-15): By applying General Procedure 1, zinc (1.1470 g,

17.5 mmol), 2,4,7-trimethyl-indan-1-one (1.4956 g, 8.6 mmol), and crotyl bromide (2.0 mL, 17.5 mmol) gave, after a 6-h reaction time, 1.4364 g of the mixture of 2,4,7-trimethyl-indan-1-one and 2,4,7-trimethyl-1-(1-methyl-allyl)-indan-1-ol (*rac*-11, *rac*-12, *rac*-13 and *rac*-14). The amount of the alcohol obtained was 40%. This crude product was directly used in the dehydration step without further purification or analysis. By applying General Procedure 3, the mixture of 2,4,7-trimethyl-1-(1-methyl-allyl)-indan-1-ol (*rac*-11, *rac*-12, *rac*-13 and *rac*-14) [0.1774 g, 0.77 mmol] and Amberlyst 15 (0.3022 g) in pentane (10 mL) gave, after a 2-h reaction time and column chromatography (10% dichloromethane/90% hexane as eluent), 0.0686 g (42%) of the enantiomeric mixture of the title compounds as a pale slightly yellowish oil. The overall yield (over two steps) was 4%. ^1H NMR (400 MHz, CDCl_3): δ = 6.97 (d, J_{AB} = 7.59 Hz, 2 H, arom. CH), 6.87 (d, J_{AB} = 7.59 Hz, 2 H, arom. CH), 6.20 (ddd, J = 4.35 Hz, 10.43 Hz, 17.78 Hz, 2 H, olefinic CH in chain), 5.13 (m, 2 H, olefinic CH in chain), 5.10 (m, 2 H, olefinic CH in chain), 4.14 (m, 2 H, aliphatic CH in chain), 3.17 (m, 4 H, aliphatic CH_2 in five-ring), 2.58 (s, 6 H, CH_3 attached to the aromatic ring), 2.32 (s, 6 H, CH_3 attached to the aromatic ring), 2.14 (s, 6 H, CH_3 attached to the five-ring), 1.44 (d, J = 7.17 Hz, 6 H, CH_3 attached to the aliphatic chain) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 143.77 (2 C_q), 142.43 (2 olefinic CH in chain), 141.68 (2 C_q), 140.88 (2 C_q), 139.66 (2 C_q), 130.16 (2 arom. CH), 129.91 (2 C_q), 126.92 (2 C_q), 124.66 (2 arom. CH), 112.44 (2 olefinic CH_2 in chain), 42.79 (2 aliphatic CH_2 in five-ring), 34.96 (2 aliphatic CH in chain), 20.98 (2 CH_3 attached to the aromatic ring), 18.19 (2 CH_3 attached to the aromatic ring), 18.16 (2 CH_3 attached to the aliphatic chain), 15.84 (2 CH_3 attached to the five-ring) ppm. EIMS (70 eV): calcd. $\text{C}_{16}\text{H}_{20}$ 212.1565; found 212.1560.

A Mixture of 1-Allyl-2-methyl-indan-1-ol (*rac*-16 and *rac*-17): By applying General Procedure 1, zinc (0.7386 g, 11.3 mmol), 2-methyl-indan-1-one (0.7838 g, 5.4 mmol), and allyl bromide (940 μL , 10.7 mmol) gave, after a 2.5-h reaction time, 0.6743 g (67%) of a mixture of the title compounds as a yellow oil. ^1H NMR (600 MHz, CDCl_3): δ = 7.38 (m, 4 H, arom. CH in *rac*-16 and *rac*-17), 7.26 (m, 12 H, arom. CH in *rac*-16 and *rac*-17), 5.94 (ddt, J = 5.87 Hz, 13.39 Hz, 16.01 Hz, 2 H, olefinic CH in chain in *rac*-16 or *rac*-17), 5.82 (ddt, J = 6.70 Hz, 9.38 Hz, 17.41 Hz, 2 H, olefinic CH in chain in *rac*-16 or *rac*-17), 5.17 (dm, J = 17.41 Hz, 2 H, olefinic CH in chain in *rac*-16 or *rac*-17), 5.16 (dm, J = 16.01 Hz, 2 H, olefinic CH in chain in *rac*-16 or *rac*-17), 5.12 (dm, J = 9.38 Hz, 2 H, olefinic CH in chain in *rac*-16 or *rac*-17), 5.04 (dm, J = 13.39 Hz, 2 H, olefinic CH in chain in *rac*-16 or *rac*-17), 3.32 (s, 2 H, OH in *rac*-16 or *rac*-17), 3.02 (m, 4 H, aliphatic CH in five-ring in *rac*-16 and *rac*-17), 2.74 (m, 2 H, aliphatic CH in five-ring in *rac*-16 or *rac*-17), 2.65 (m, 12 H, aliphatic CH_2 in chain in *rac*-16 and *rac*-17 and aliphatic CH in five-ring in *rac*-16 and *rac*-17), 2.45 (m, 2 H, aliphatic CH in five-ring in *rac*-16 or *rac*-17), 2.10 (s, 2 H, OH in *rac*-16 or *rac*-17), 1.34 (d, J = 6.86 Hz, 6 H, CH_3 in *rac*-16 or *rac*-17), 1.12 (d, J = 6.86 Hz, 6 H, CH_3 in *rac*-16 or *rac*-17) ppm. ^{13}C NMR (150.9 MHz, CDCl_3): δ = 146.59 (2 C_q in *rac*-16 or *rac*-17), 142.64 (2 C_q in *rac*-16 or *rac*-17), 139.55 (2 C_q in *rac*-16 or *rac*-17), 136.49 (2 C_q in *rac*-16 or *rac*-17), 134.81 (2 olefinic CH in chain in *rac*-16 or *rac*-17), 134.29 (2 olefinic CH in chain in *rac*-16 or *rac*-17), 128.41 (2 arom. CH in *rac*-16 or *rac*-17), 127.50 (2 arom. CH in *rac*-16 or *rac*-17), 126.71 (2 arom. CH in *rac*-16 or *rac*-17), 126.63 (2 arom. CH in *rac*-16 or *rac*-17), 125.11 (2 arom. CH in *rac*-16 or *rac*-17), 124.14 (2 arom. CH in *rac*-16 or *rac*-17), 123.50 (2 arom. CH in *rac*-16 or *rac*-17), two arom. CH in *rac*-16 or *rac*-17 are overlapping with other signals, 118.53 (2 olefinic CH_2 in chain in *rac*-16 or *rac*-17), 115.41 (2 olefinic CH_2 in chain in *rac*-16 or *rac*-17), 82.73 (2 C-OH in *rac*-16 or

rac-17), 68.07 (2 C-OH in *rac*-16 or *rac*-17), 43.69 (4 C, aliphatic CH₂ in five-ring in *rac*-16 or *rac*-17 or aliphatic CH₂ in chain in *rac*-16 or *rac*-17), 42.06 (2 aliphatic CH in five-ring in *rac*-16 or *rac*-17), 41.73 (2 aliphatic CH in five-ring in *rac*-16 or *rac*-17), 38.19 (4 aliphatic CH₂ in five-ring in *rac*-16 or *rac*-17 or aliphatic CH₂ in chain in *rac*-16 or *rac*-17), 35.05 (4 aliphatic CH₂ in five-ring in *rac*-16 or *rac*-17 or aliphatic CH₂ in chain in *rac*-16 or *rac*-17), 13.96 (4 C, CH₃ in *rac*-16 and *rac*-17) ppm. EIMS (30 eV): calcd. C₁₃H₁₆O 188.1201; found 188.1196.

A Mixture of 3-Allyl-2-methyl-1H-indene (18) and 2-Methyl-1-prop-2-en-(E)-ylidene-indane (*rac*-19): By applying General Procedure 3, a mixture of 1-allyl-2-methyl-indan-1-ol (*rac*-16 and *rac*-17) (0.2479 g, 1.3 mmol) and Amberlyst 15 (0.1923 g) in pentane (10 mL) gave, after a 1.5-h reaction time and column chromatography (hexane as eluent), 0.0406 g (18%) of the mixture of the title compounds as a colorless oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.51 (m, 2 H, arom. CH in *rac*-19), 7.35 (m, 3 H, 1 arom. CH in *rac*-19 and 1 arom. CH in 18), 7.24 (m, 4 H, 1 arom. CH in *rac*-19 and 2 arom. CH in 18), 7.13 (m, 3 H, 1 arom. CH in *rac*-19 and 1 arom. CH in 18), 6.46 (d, *J* = 16.33 Hz, 2 H, olefinic CH in chain in *rac*-19), 6.23 (m, 2 H, olefinic CH in chain in *rac*-19), 5.91 (ddt, *J* = 6.16 Hz, 10.15 Hz, 17.29 Hz, 1 H, olefinic CH in chain in 18), 5.10 (dm, *J* = 17.29 Hz, 1 H, olefinic CH in chain in 18), 5.03 (dm, *J* = 10.15 Hz, 1 H, olefinic CH in chain in 18), 4 olefinic CH in chain in *rac*-19 overlap with the corresponding signals from 18, 3.27 (m, 6 H, aliphatic CH₂ in chain in 18, aliphatic CH₂ in five-ring in 18 and aliphatic CH in five-ring in *rac*-19), 2.13 (m, 4 H, aliphatic CH₂ in five-ring in *rac*-19), 2.05 (s, 3 H, CH₃ in 18), 1.95 (d, *J* = 6.42 Hz, 6 H, CH₃ in *rac*-19) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 146.56 (C_q in 18), 145.42 (2 C_q in *rac*-19), 142.55 (C_q in 18), 140.39 (2 C_q in *rac*-19), 139.37 (C_q in 18), 135.53 (olefinic CH in chain in 18), 134.54 (2 C_q in *rac*-19), 134.46 (C_q in 18), 127.81 (2 olefinic CH in chain in *rac*-19), 126.15 (2 arom. CH in *rac*-19), 126.09 (arom. CH in 18), 124.03 (2 arom. CH in *rac*-19 or 2 olefinic CH in chain in *rac*-19), 123.87 (2 arom. CH in *rac*-19 or 2 olefinic CH in chain in *rac*-19), 123.72 (arom. CH in 18), 123.33 (2 arom. CH in *rac*-19), 123.21 (arom. CH in 18), 119.47 (2 arom. CH in *rac*-19), 118.56 (arom. CH in 18), 115.37 (3 C, olefinic CH₂ in chain in 18 and olefinic CH₂ in chain in *rac*-19), 42.93 (2 aliphatic CH in five-ring in *rac*-19), 42.66 (aliphatic CH₂ in chain in 18 or aliphatic CH₂ in five-ring in 18), 31.76 (2 aliphatic CH₂ in five-ring in *rac*-19), 29.77 (aliphatic CH₂ in chain in 18 or aliphatic CH₂ in five-ring in 18), 14.84 (2 CH₃ in *rac*-19), 13.93 (CH₃ in 18) ppm. EIMS (70 eV): calcd. C₁₃H₁₄ 170.1096, found 170.1102.

A Mixture of 2-Methyl-1-(1-methyl-allyl)-indan-1-ol (*rac*-20, *rac*-21, *rac*-22 and *rac*-23): By applying General Procedure 1, zinc (0.7949 g, 12.2 mmol), 2-methyl-1-indanone (0.8209 g, 5.6 mmol), and crotyl bromide (1.4 mL, 11.5 mmol) gave, after a 2.5-h reaction time, 0.8232 g (73%) of a mixture of the title compounds as a yellow oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.38 (m, 8 H, arom. CH in *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 7.26 (m, 24 H, arom. CH in *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 5.93 (m, 8 H, olefinic CH in chain in *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 5.16 (m, 16 H, olefinic CH₂ in chain in *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 3.10 (m, 8 H, aliphatic CH in five-ring in *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 2.69 (m, 8 H, aliphatic CH in chain in *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 2.63 (m, 8 H, aliphatic CH in five-ring in *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 2.59 (m, 8 H, aliphatic CH in five-ring in *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 1.92 (br. s, 8 H, C-OH in *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 1.16 (d, *J* = 6.73 Hz, 18 H, CH₃ attached to the aliphatic chain in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 1.09 (m, 24 H, CH₃ attached to the five-ring in *rac*-

20, *rac*-21, *rac*-22 and *rac*-23), 0.98 (d, *J* = 6.73 Hz, 3 H, CH₃ attached to the aliphatic chain in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 145.98 (6 C_q in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 145.63 (2 C_q in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 142.75 (2 C_q in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 142.23 (6 C_q in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 140.30 (6 olefinic CH in chain in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 140.15 (2 olefinic CH in chain in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 128.30 (2 arom. CH in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 128.15 (6 arom. CH in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 126.65 (2 arom. CH in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 126.42 (6 arom. CH in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 125.07 (6 arom. CH in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 124.84 (2 arom. CH in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 124.52 (6 arom. CH in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 124.01 (2 arom. CH in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 116.56 (2 olefinic CH₂ in chain in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 115.83 (6 olefinic CH₂ in chain in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 85.42 (6 C-OH in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 85.19 (2 C-OH in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 47.65 (2 aliphatic CH in chain in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 45.89 (6 aliphatic CH in chain in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 39.74 (6 C, aliphatic CH or CH₂ in five-ring in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 39.46 (2 C, aliphatic CH or CH₂ in five-ring in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 38.88 (6C, aliphatic CH or CH₂ in five-ring in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 38.18 (2 C, aliphatic CH or CH₂ in five-ring in two diastereomers of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 16.45 (2 C, CH₃ attached to the aliphatic chain or five-ring in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 15.93 (6C, CH₃ attached to the five-ring in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 15.53 (2 C, CH₃ attached to the aliphatic chain or five-ring in two compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23), 14.06 (6 C, CH₃ attached to the chain in six compounds of *rac*-20, *rac*-21, *rac*-22 and *rac*-23) ppm. EIMS (30 eV): calcd. C₁₄H₁₈O 202.1358; found 202.1368.

An Enantiomeric Mixture of 2-Methyl-3-(1-methyl-allyl)-1H-indene (*rac*-24): By applying General Procedure 3, a mixture of 2-methyl-1-(1-methyl-allyl)-indan-1-ol (*rac*-20, *rac*-21, *rac*-22 and *rac*-23) [0.2283 g, 1.1 mmol] and Amberlyst 15 (0.1822 g) in pentane (10 mL) gave, after a 1.5-h reaction time and column chromatography (hexane as eluent), 0.0888 g (43%) of the enantiomeric mixture of the title compounds as a colorless oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.25 (d, *J* = 7.92 Hz, 4 H, arom. CH), 7.10 (t, *J* = 7.92 Hz, 2 H, arom. CH), 6.99 (t, *J* = 7.92 Hz, 2 H, arom. CH), 6.04 (ddt, *J* = 5.08 Hz, 10.28 Hz, 17.05 Hz, 2 H, olefinic CH in chain), 5.03 (dm, *J* = 17.05 Hz, 2 H, olefinic CH in chain), 4.98 (dm, *J* = 10.28 Hz, 2 H, olefinic CH in chain), 3.58 (m, 2 H, aliphatic CH in chain), 3.16 (m, 4 H, aliphatic CH₂ in five-ring), 1.98 (s, 6 H, CH₃ attached to the five-ring), 1.31 (d, *J* = 7.42 Hz, 6 H, CH₃ attached to the chain) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 145.57 (2 C_q), 142.96 (2 C_q), 141.58 (2 olefinic CH in chain), 139.20 (2 C_q), 138.36 (2 C_q), 125.86 (2 arom. CH), 123.48 (2 arom. CH), 120.03 (2 arom. CH), overlapping of two arom. CH, 113.59 (2 olefinic CH₂ in chain), 43.10 (2 aliphatic CH₂ in five-ring), 35.05 (2 aliphatic CH in chain), 18.44 (2 CH₃ attached to the chain), 14.70 (2 CH₃ attached to the five-ring) ppm. EIMS (70 eV): calcd. C₁₄H₁₆ 184.1252; found 184.1255.

An Enantiomeric Mixture of 1-Allyl-indan-1,4-diol (*rac*-25): By applying General Procedure 1, zinc (0.6556 g, 10.0 mmol), 4-hydroxy-indan-1-one (0.7321 g, 5.0 mmol), and allyl bromide (870 μ L, 9.9 mmol) gave, after a 1.5-h reaction time, 0.6185 g of a mixture of 4-hydroxy-1-indanone and the title compounds as white crystals. The amount of the title compound was 67%. The yield from the reaction was 43%. ^1H NMR (400 MHz, CD_3OD): δ = 7.03 (m, 2 H, arom. CH), 6.84 (dm, J = 7.48 Hz, 2 H, arom. CH), 6.65 (dd, J = 0.88 Hz, 7.89 Hz, 2 H, arom. CH), 5.74 (m, 2 H, olefinic CH in chain), 5.04 (m, 4 H, olefinic CH_2 in chain), 2.89 (m, 2 H, aliphatic CH in five-ring), 2.66 (m, 2 H, aliphatic CH in five-ring), 2.58 (ddt, J_{AB} = 1.07 Hz, 7.44 Hz, 13.74 Hz, 2 H, aliphatic CH in chain), 2.48 (ddt, J_{AB} = 1.22 Hz, 6.95 Hz, 13.74 Hz, 2 H, aliphatic CH in chain), 2.28 (m, 2 H, aliphatic CH in five-ring), 2.02 (m, 2 H, aliphatic CH in five-ring) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 154.50 (2 C_q), 150.44 (2 C_q), 143.85 (2 C_q), 135.48 (2 olefinic CH in chain), 128.95 (2 arom. CH), 118.07 (2 olefinic CH_2 in chain), 115.35 (2 arom. CH), 115.08 (2 arom. CH), 84.22 (2 C-OH), 46.49 (2 aliphatic CH_2 in chain), 39.63 (2 aliphatic CH_2 in five-ring), 26.80 (2 aliphatic CH_2 in five-ring) ppm. EIMS (70 eV): calcd. $\text{C}_{12}\text{H}_{14}\text{O}_2$ 190.0994; found 190.0996.

A Mixture of 1-Allyl-3H-inden-4-ol (26) and 1-Prop-2-en-(*E*)-ylidene-indan-4-ol (27): By applying General Procedure 5, the enantiomeric mixture of 1-allyl-indan-1,4-diol (*rac*-25) (0.5371 g; 2.8 mmol) and Mg_2SO_4 in toluene (20 mL) gave, after refluxing for 1.5 h and column chromatography (dichloromethane as eluent), 0.1188 g (25%) of a 1:0.16 mixture of the title compounds as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.19 (ddt, J = 0.53 Hz, 7.48 Hz, 8.01 Hz, 1 H, arom. CH in 26), 7.09 (m, 1 H, arom. CH in 27), 7.08 (m, 1 H, arom. CH in 27), 6.99 (dm, J = 7.48 Hz, 1 H, arom. CH in 26), 6.67 (dm, J = 8.01 Hz, 1 H, arom. CH in 26), 6.66 (m, 1 H, arom. CH in 27), 6.58 (m, 2 H, olefinic CH in chain in 27), 6.23 (m, 1 H, olefinic CH in five-ring in 26), 6.02 (ddt, J = 6.56 Hz, 10.07 Hz, 17.09 Hz, 1 H, olefinic CH in chain in 26), 5.29 (m, 1 H, olefinic CH in chain in 27), 5.25 (m, 1 H, olefinic CH in chain in 27), 5.16 (ddd, J = 1.52 Hz, 3.43 Hz, 17.09 Hz, 1 H, olefinic CH in chain in 26), 5.10 (dm, J = 10.07 Hz, 1 H, olefinic CH in chain in 26), 4.74 (br. s, 2 H, OH in 26 and OH in 27), 3.29 (m, 4 H, aliphatic CH_2 in chain in 26 and five-ring aliphatic CH_2 in 26), 2.93 (m, 4 H, five-ring aliphatic CH_2 in 27) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 151.09 (C_q in 26), 147.48 (C_q in 26), 142.74 (C_q in 26), 135.52 (olefinic CH in chain in 26), 134.22 (olefinic CH in 27), 128.88 (C_q in 26), 128.60 (olefinic CH in five-ring in 26), 128.27 (arom. CH in 27), 127.92 (arom. CH in 26), 119.41 (olefinic CH in chain in 27), 116.32 (olefinic CH_2 in chain in 26 and 27), 114.19 (arom. CH in 27), 113.06 (arom. CH in 27), 112.61 (arom. CH in 26), 112.07 (arom. CH in 26), 34.30 (aliphatic CH_2 in chain in 26 or aliphatic CH_2 in five-ring in 26), 32.53 (aliphatic CH_2 in chain in 26 or aliphatic CH_2 in five-ring in 26), 28.23 (aliphatic CH_2 in five-ring in 27), 26.26 (aliphatic CH_2 in five-ring in 27) ppm. The quaternary carbon atoms of the minor product could not be detected in the carbon spectrum due to their low intensity. EIMS (70 eV): calcd. $\text{C}_{12}\text{H}_{12}\text{O}$ 172.0888; found 172.0886.

An Enantiomeric Mixture of 1-(1-Methyl-allyl)-3H-inden-4-ol (*rac*-28): By applying General Procedure 1, zinc (0.5064 g, 7.74 mmol), 4-hydroxy-1-indanone (0.5660 g, 3.82 mmol), and crotyl bromide (930 μ L, 7.64 mmol) gave, after a 2-h reaction time and column chromatography (dichloromethane as eluent), 0.2953 g (42%) of the enantiomeric mixture of the title compounds as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.18 (tm, J = 7.75 Hz, 2 H, arom. CH), 7.04 (dd, J = 0.80 Hz, 7.75 Hz, 2 H, arom. CH), 6.66 (dm, J = 7.75 Hz, 2 H, arom. CH), 6.23 (m, 2 H, olefinic CH in five-ring), 5.99 (ddd, J = 6.79 Hz, 10.22 Hz, 17.17 Hz, 2 H, olefinic CH in

chain), 5.12 (dt, J = 1.53 Hz, 17.17 Hz, 2 H, olefinic CH in chain), 5.04 (ddd, J = 1.18 Hz, 1.56 Hz, 10.22 Hz, 2 H, olefinic CH in chain), 4.73 (br. s, 2 H, OH), 3.49 (m, 2 H, aliphatic CH in chain), 3.27 (m, 4 H, aliphatic CH_2 in five-ring), 1.38 (d, J = 6.94 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 151.12 (2 C_q), 147.96 (2 C_q), 147.06 (2 C_q), 141.82 (2 olefinic CH in chain), 129.14 (2 C_q), 127.78 (2 arom. CH), 127.01 (2 arom. CH), 113.72 (2 olefinic CH_2 in chain), 113.21 (2 arom. CH), 111.90 (2 arom. CH), 36.64 (2 aliphatic CH in chain), 34.18 (2 aliphatic CH_2 in five-ring), 19.12 (2 CH_3) ppm. EIMS (70 eV): calcd. $\text{C}_{13}\text{H}_{14}\text{O}_1$ 186.1045; found 186.1043.

An Enantiomeric Mixture of 1-(1-Phenyl-allyl)-3H-inden-4-ol (*rac*-29): By applying General Procedure 1, zinc (0.4575 g, 7.00 mmol), 4-hydroxy-1-indanone (0.4963 g, 3.35 mmol), and cinnamyl chloride (1.0336 g, 6.77 mmol) gave, after a 6-h reaction time and column chromatography (dichloromethane as eluent), 0.1576 g (19%) of the enantiomeric mixture of the title compounds as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.19 (m, 10 H, arom. CH in phenyl substituent), 6.98 (m, 2 H, arom. CH), 6.70 (dd, J = 0.76 Hz, 7.56 Hz, 2 H, arom. CH), 6.53 (dq, J = 0.38 Hz, 7.97 Hz, 2 H, arom. CH), 6.19 (m, 4 H, olefinic CH in chain and olefinic CH in five-ring), 5.10 (ddd, J = 1.11 Hz, 1.56 Hz, 10.15 Hz, 2 H, olefinic CH in chain), 4.97 (br. s, 2 H, OH), 4.95 (dt, J = 1.49 Hz, 17.09 Hz, 2 H, olefinic CH in chain), 4.59 (m, 2 H, aliphatic CH in chain), 3.24 (m, 4 H, aliphatic CH_2 in chain) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 151.06 (2 C_q), 146.81 (2 C_q), 145.85 (2 C_q), 141.47 (2 C_q), 139.48 (2 olefinic CH in chain), 130.00 (2 olefinic CH in five-ring), 128.44 and 128.40 (10 C, overlapping signals from arom. CH in phenyl), 127.75 (2 arom. CH), 126.49 (2 C_q), 115.99 (2 olefinic CH_2 in chain), 113.60 (2 arom. CH), 111.96 (2 arom. CH), 48.92 (2 aliphatic CH in chain), 34.39 (2 aliphatic CH_2 in five-ring) ppm. EIMS (70 eV): calcd. $\text{C}_{18}\text{H}_{16}\text{O}_1$ 248.1201; found 248.1198.

A Mixture of 1-Allyl-4-chloro-7-methyl-indan-1-ol (*rac*-30) and 1-Allyl-7-chloro-4-methyl-indan-1-ol (*rac*-31): By applying General Procedure 1, zinc (0.4379 g, 6.7 mmol), 4-chloro-7-methyl-indan-1-one (containing 13% of 7-chloro-4-methyl-indan-1-one as impurity) [0.5179 g, 2.9 mmol], and allyl bromide (500 μ L, 5.7 mmol) gave, after a 1.5-h reaction time, 0.5620 g (87%) of a mixture of the title compounds as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.10 (d, J = 8.01 Hz, 2 H, arom. CH in *rac*-30), 7.05 (dm, J = 8.01 Hz, 2 H, arom. CH in *rac*-31), 6.97 (dm, J = 8.01 Hz, 2 H, arom. CH in *rac*-31), 6.91 (dm, J = 8.01 Hz, 2 H, arom. CH in *rac*-30), 5.71 (m, 4 H, olefinic CH in chain in *rac*-30 and olefinic CH in chain in *rac*-31), 5.11 (m, 8 H, olefinic CH_2 in chain in *rac*-30 and olefinic CH_2 in chain in *rac*-31), 3.04–2.45 and 2.00–1.90 (m, 24 H, overlapping signals from aliphatic CH_2 in chain in *rac*-30, aliphatic CH_2 in five-ring in *rac*-30, aliphatic CH_2 in chain in *rac*-31 and aliphatic CH_2 in five-ring in *rac*-31), 2.43 (s, 12 H, CH_3 attached to the aromatic ring in *rac*-30 and CH_3 attached to the aromatic ring in *rac*-31), 2.19 (br. s, 4 H, OH in *rac*-30 and OH in *rac*-31) ppm. The ratio between the enantiomeric mixture of 1-allyl-4-chloro-7-methyl-indan-1-ol (*rac*-30) and the enantiomeric mixture of 1-allyl-7-chloro-4-methyl-indan-1-ol (*rac*-31) was approximately 83% of *rac*-30 and 17% of *rac*-31. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 145.70 (2 C_q in *rac*-30), 144.33 (2 C_q in *rac*-31), 141.75 (2 C_q in *rac*-31), 140.69 (2 C_q in *rac*-30), 137.25 (2 C_q in *rac*-31), 132.54 (2 C_q in *rac*-31), overlapping of two C_q in *rac*-30 with other signals, 133.29 (2 olefinic CH in chain in *rac*-30), 133.17 (2 olefinic CH in chain in *rac*-31), 130.94 (2 arom. CH in *rac*-30), 130.26 (2 arom. CH in *rac*-31), 128.16 (2 C_q in *rac*-30), 127.85 (2 arom. CH in *rac*-30), 127.98 (2 arom. CH in *rac*-31), 119.03 (2 olefinic CH_2 in chain in *rac*-30), 118.49 (2 olefinic CH_2 in chain in *rac*-31), 85.25

(2 C-OH in *rac*-30), 84.88 (2 C-OH in *rac*-31), 44.35 (2 aliphatic CH₂ in five-ring or in chain in *rac*-31), 43.55 (2 aliphatic CH₂ in five-ring or in chain in *rac*-30), 39.58 (2 aliphatic CH₂ in five-ring or in chain in *rac*-30), 37.56 (2 aliphatic CH₂ in five-ring or in chain in *rac*-31), 28.33 (2 aliphatic CH₂ in five-ring or in chain in *rac*-30), 28.19 (2 aliphatic CH₂ in five-ring or in chain in *rac*-31), 18.23 (2 CH₃ attached to the aromatic ring in *rac*-31), 17.52 (2 CH₃ attached to the aromatic ring in *rac*-30) ppm. EIMS (30 eV): calcd. C₁₃H₁₅OCl 222.0811; found 222.0815.

A Mixture of 3-Allyl-7-chloro-4-methyl-1H-indene (32), 4-Chloro-7-methyl-1-prop-2-en-(E)-ylidene-indane (33), and 3-Allyl-4-chloro-7-methyl-1H-indene (34): By applying General Procedure 3, a mixture of 1-allyl-4-chloro-7-methyl-indan-1-ol (*rac*-30) and 1-allyl-7-chloro-4-methyl-indan-1-ol (*rac*-31) [0.1729 g, 0.78 mmol] and Amberlyst 15 (0.1169 g) in pentane (10 mL) gave, after a 2-h reaction time and column chromatography (hexane as eluent), 0.0554 g (35%) of a mixture of the title compounds as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.13 (dm, *J* = 8.09 Hz, 1 H, arom. CH in 34), 7.06 (d, *J* = 8.01 Hz, 1 H, arom. CH in 32 or 33), 7.05 (d, *J* = 8.01 Hz, 1 H, arom. CH in 32 or 33), 6.96 (dm, *J* = 8.01 Hz, 1 H, arom. CH in 32 or 33), 6.91 (dm, *J* = 8.01 Hz, 1 H, arom. CH in 32 or 33), 6.91 (m, 1 H, arom. CH in 34), 6.63 (m, 2 H, olefinic CH in chain in 33), 6.25 (m, 2 H, olefinic CH in five-ring in 32 and olefinic CH in five-ring in 34), 6.09 (m, 2 H, olefinic CH in chain in 32 and olefinic CH in chain in 34), 5.31 (m, 1 H, olefinic CH in chain in 33), 5.19 (m, 1 H, olefinic CH in chain in 33), 5.14 (m, 2 H, olefinic CH in chain in 32 and olefinic CH in chain in 34), 5.08 (m, 2 H, olefinic CH in chain in 32 and olefinic CH in chain in 34), 3.61 (m, 2 H, aliphatic CH₂ in chain in 34), 3.45 (m, 2 H, aliphatic CH₂ in chain in 32), 3.30 (m, 2 H, aliphatic CH₂ in five-ring in 32), 3.19 (m, 2 H, aliphatic CH₂ in five-ring in 34), 2.98 (m, 2 H, aliphatic CH₂ in five-ring in 33), 2.90 (m, 2 H, aliphatic CH₂ in five-ring in 33), 2.52 (s, 3 H, CH₃ attached to the aromatic ring in 32), 2.47 (s, 3 H, CH₃ attached to the aromatic ring in 33), 2.30 (s, 3 H, CH₃ attached to the aromatic ring in 34) ppm. The ratio between 3-allyl-7-chloro-4-methyl-1H-indene (32), 4-chloro-7-methyl-1-prop-2-en-(E)-ylidene-indane (33), and 3-allyl-4-chloro-7-methyl-1H-indene (34) was 47% of 32, 42% of 33 and 11% of 34. ¹³C NMR (100.6 MHz, CDCl₃): δ = 146.28 (C_q in 32, 33 or 34), 145.78 (C_q in 32, 33 or 34), 145.42 (C_q in 32, 33 or 34), 144.23 (C_q in 32, 33 or 34), 143.88 (C_q in 32, 33 or 34), 143.54 (C_q in 32, 33 or 34), 142.76 (C_q in 32, 33 or 34), 142.63 (C_q in 32, 33 or 34), 140.61 (C_q in 32, 33 or 34), 140.38 (C_q in 32, 33 or 34), 132.58 (C_q in 32, 33 or 34), 131.40 (C_q in 32, 33 or 34), 129.52 (C_q in 32, 33 or 34), 128.66 (C_q in 32, 33 or 34), 127.47 (C_q in 32, 33 or 34), 136.42 (olefinic CH in chain in 34), 136.21 (olefinic CH in chain in 32), 134.89 (olefinic CH in chain in 33), 130.75 (arom. CH in 32 or 33 or olefinic CH in five-ring in 32), 130.64 (arom. CH in 34 and in 32 or 33 or olefinic CH in five-ring in 32), 130.62 (arom. CH in 32 or 33 or olefinic CH in five-ring in 32), 130.57 (olefinic CH in five-ring in 34), 128.10 (arom. CH in 34), 127.05 (arom. CH in 32 or 33), 124.58 (arom. CH in 32 or 33), 124.27 (olefinic CH in chain in 33), 117.25 (olefinic CH₂ in chain in 33), 116.33 (olefinic CH₂ in chain in 32), 115.92 (olefinic CH₂ in chain in 34), 37.12 (aliphatic CH₂ in five-ring in 32), 36.75 (aliphatic CH₂ in five-ring in 34), 34.80 (aliphatic CH₂ in chain in 32), 34.66 (aliphatic CH₂ in chain in 34), 29.45 (aliphatic CH₂ in five-ring in 33), 28.55 (aliphatic CH₂ in five-ring in 33), 21.54 (CH₃ attached to the aromatic ring in 33), 19.40 (CH₃ attached to the aromatic ring in 32), 18.05 (CH₃ attached to the aromatic ring in 34) ppm. EIMS (70 eV): calcd. C₁₃H₁₃Cl 204.0706; found 204.0700.

A Mixture of 4-Chloro-7-methyl-1-(1-methyl-allyl)-indan-1-ol (*rac*-35 and *rac*-36) and 7-Chloro-4-methyl-1-(1-methyl-allyl)-indan-1-ol

(*rac*-38 and *rac*-39): By applying General Procedure 1, zinc (0.4321 g, 6.6 mmol), 4-chloro-7-methyl-indan-1-one (containing 13% of 7-chloro-4-methyl-indan-1-one as impurity) [0.5797 g, 3.2 mmol], and crotyl bromide (800 μL, 6.4 mmol) gave, after a 3-h reaction time, 0.6539 g (86%) of a mixture of the title compound as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.10 (m, 4 H, arom. CH in *rac*-35 and *rac*-36), 7.05 (m, 4 H, arom. CH in *rac*-38 and *rac*-39), 6.97 (m, 4 H, arom. CH in *rac*-38 and *rac*-39), 6.92 (m, 4 H, arom. CH in *rac*-35 and *rac*-36), 6.11 (m, 2 H, olefinic CH in chain in *rac*-38 and *rac*-39), 6.01 (m, 2 H, olefinic CH in chain in *rac*-35 and *rac*-36), 5.45 (ddd, *J* = 6.68 Hz, 10.53 Hz, 17.24 Hz, 2 H, olefinic CH in *rac*-35 and *rac*-36 and m, 2 H, olefinic CH in *rac*-38 and *rac*-39), 5.22 (m, 8 H, olefinic CH₂ in chain in *rac*-35 and *rac*-36 and olefinic CH₂ in chain in *rac*-38 and *rac*-39), 4.92 (dm, *J* = 17.24 Hz, 2 H, olefinic CH in chain in *rac*-35 and *rac*-36 and m, 2 H, olefinic CH in chain in *rac*-38 and *rac*-39), 4.86 (dm, *J* = 10.53 Hz, 2 H, olefinic CH in chain in *rac*-35 and *rac*-36), 4.81 (ddd, *J* = 0.61 Hz, 1.22 Hz, 10.45 Hz, 2 H, olefinic CH in chain in *rac*-38 and *rac*-39), 3.26 (m, 4 H, aliphatic CH in chain in *rac*-38 and *rac*-39), 2.79 (m, 36 H, overlapping signals from aliphatic CH in chain in *rac*-35 and *rac*-36, aliphatic CH₂ in five-ring in *rac*-35 and *rac*-36, aliphatic CH₂ in five-ring in *rac*-38 and *rac*-39), 2.44 (m, 24 H, overlapping signals from CH₃ attached to the aromatic ring in *rac*-35, *rac*-36, *rac*-38 and *rac*-39), 2.19 (br. s, 8 H, OH in *rac*-35, *rac*-36, *rac*-38 and *rac*-39), 1.20 (d, *J* = 6.72 Hz, 12 H, CH₃ attached to the aliphatic chain in *rac*-35, *rac*-36, *rac*-38 and *rac*-39), 0.77 (d, *J* = 7.01 Hz, 12 H, CH₃ attached to the aliphatic chain in *rac*-35, *rac*-36, *rac*-38 and *rac*-39) ppm. The ratio between the mixtures could not be determined by ¹H NMR spectroscopy due to overlapping signals. ¹³C NMR (100.6 MHz, CDCl₃): overlapping of some of the quaternary carbons with signals from other carbons δ = 145.74 (C_q), 144.53 (C_q), 141.83 (C_q), 141.42 (C_q), 139.49 (2 olefinic CH in chain in *rac*-35 and *rac*-36 and 2 olefinic CH in chain in *rac*-38 and *rac*-39), 138.92 (2 olefinic CH in chain in *rac*-38 and *rac*-39), 138.80 (2 olefinic CH in chain in *rac*-35 and *rac*-36), 133.51 (C_q), 133.23 (C_q), 131.14 and 131.05 (signals from aromatic carbons in *rac*-35, *rac*-36, *rac*-38 and *rac*-39), 128.18–127.73 (signals from aromatic carbons in *rac*-35, *rac*-36, *rac*-38 and *rac*-39), 117.57 (2 olefinic CH₂ in chain in *rac*-35 and *rac*-36), 116.40 (2 olefinic CH₂ in chain in *rac*-38 and *rac*-39), 115.39 (2 olefinic CH₂ in chain in *rac*-35 and *rac*-36), 115.23 (2 olefinic CH₂ in chain in *rac*-38 and *rac*-39), 88.39 (2 C-OH in *rac*-35 and *rac*-36), 88.03 (2 C-OH in *rac*-35 and *rac*-36), 87.92 (2 C-OH in *rac*-38 and *rac*-39), 46.14 (2 aliphatic CH in chain in *rac*-35 and *rac*-36), 45.45 (2 aliphatic CH in chain in *rac*-38 and *rac*-39), 45.00 (2 aliphatic CH in chain in *rac*-38 and *rac*-39), 44.46 (2 aliphatic CH in chain in *rac*-35 and *rac*-36), 35.67 (2 aliphatic CH₂ in five-ring in *rac*-35 and *rac*-36 and/or *rac*-38 and *rac*-39), 35.56 (2 aliphatic CH₂ in five-ring in *rac*-35 and *rac*-36 and/or *rac*-38 and *rac*-39), 29.68 (2 aliphatic CH₂ in five-ring in *rac*-35 and *rac*-36 and/or *rac*-38 and *rac*-39), 29.14 (2 aliphatic CH₂ in five-ring in *rac*-35 and *rac*-36 and/or *rac*-38 and *rac*-39), 18.01 (2 CH₃ attached to the aromatic ring in *rac*-35 and *rac*-36 and/or *rac*-38 and *rac*-39), 17.81 (2 CH₃ attached to the aromatic ring in *rac*-35 and *rac*-36 and/or *rac*-38 and *rac*-39), 17.51 (2 CH₃ attached to the aromatic ring in *rac*-35 and *rac*-36 and/or *rac*-38 and *rac*-39), 14.83 (2 CH₃ attached to the chain in *rac*-35 and *rac*-36), 14.74 (2 CH₃ attached to the chain in *rac*-38 and *rac*-39), 13.24 (2 CH₃ attached to the chain in *rac*-35 and *rac*-36), 13.17 (2 CH₃ attached to the chain in *rac*-38 and *rac*-39) ppm. EIMS (30 eV): calcd. C₁₄H₁₇OCl 236.0968; found 236.0978.

A Mixture of 7-Chloro-4-methyl-3-(1-methyl-allyl)-1H-indene (*rac*-37) and 4-Chloro-7-methyl-3-(1-methyl-allyl)-1H-indene (*rac*-40): By

applying General Procedure 3, a mixture of 4-chloro-7-methyl-1-(1-methyl-allyl)-indan-1-ol (*rac*-**35** and *rac*-**36**) and 7-chloro-4-methyl-1-(1-methyl-allyl)-indan-1-ol (*rac*-**38** and *rac*-**39**) [0.1828 g, 0.77 mmol] and Amberlyst 15 (0.1189 g) in pentane (10 mL) gave, after a 2-h reaction time and column chromatography (hexane as eluent), 0.0560 g (33%) of a mixture of the title compounds as a colorless, cloudy oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.13 (dm, *J* = 8.09 Hz, 2 H, arom. CH in *rac*-**40**), 7.04 (dm, *J* = 8.09 Hz, 2 H, arom. CH in *rac*-**37**), 6.96 (dm, *J* = 8.09 Hz, 2 H, arom. CH in *rac*-**37**), 6.91 (dm, *J* = 8.09 Hz, 2 H, arom. CH in *rac*-**40**), 6.33 (m, 4 H, olefinic CH in five-ring in *rac*-**37** and *rac*-**40**), 6.15 (m, 2 H, olefinic CH in chain in *rac*-**40**), 6.10 (ddd, *J* = 5.72 Hz, 10.38 Hz, 17.31 Hz, 2 H, olefinic CH in chain in *rac*-**37**), 5.04 (m, 4 H, olefinic CH₂ in chain in *rac*-**40**), 5.02 (dt, *J* = 1.45 Hz, 10.38 Hz, 2 H, olefinic CH in chain in *rac*-**37**), 4.93 (dt, *J* = 1.57 Hz, 17.31 Hz, 2 H, olefinic CH in chain in *rac*-**37**), 4.14 (m, 2 H, aliphatic CH in chain in *rac*-**40**), 3.74 (m, 2 H, aliphatic CH in chain in *rac*-**37**), 3.32 (m, 4 H, aliphatic CH₂ in five-ring in *rac*-**37**), 3.20 (m, 4 H, aliphatic CH₂ in chain in *rac*-**40**), 2.53 (s, 6 H, CH₃ attached to the aromatic ring in *rac*-**37**), 2.30 (s, 6 H, CH₃ attached to the aromatic ring in *rac*-**40**), 1.35 (d, *J* = 6.87 Hz, 6 H, CH₃ attached to the chain in *rac*-**37**), 1.36 (d, *J* = 6.87 Hz, 6 H, CH₃ attached to the chain in *rac*-**40**) ppm. The mixture contained 78% of an enantiomeric mixture of 7-chloro-4-methyl-3-(1-methyl-allyl)-1H-indene and 22% of an enantiomeric mixture of 4-chloro-7-methyl-3-(1-methyl-allyl)-1H-indene. ¹³C NMR (100.6 MHz, CDCl₃): δ = 149.37 (4C, C_q in *rac*-**37** and *rac*-**40**), 144.11 (4C, C_q in *rac*-**37** and *rac*-**40**), 142.83 (4C, C_q in *rac*-**37** and *rac*-**40**), 142.61 (2 olefinic CH in chain in *rac*-**37**), 142.53 (2 olefinic CH in chain in *rac*-**40**), 131.00 (2 arom. CH in *rac*-**37**), 129.42 (4C, C_q in *rac*-**37** and *rac*-**40**), 129.15 (2 olefinic CH in five-ring in *rac*-**40**), 129.05 (2 olefinic CH in five-ring in *rac*-**37**), 128.46 (2 arom. CH in *rac*-**40**), 127.53 (4C, C_q in *rac*-**37** and *rac*-**40**), 126.96 (2 arom. CH in *rac*-**40**), 124.49 (2 arom. CH in *rac*-**37**), 113.56 (2 olefinic CH₂ in chain in *rac*-**37**), 112.81 (2 olefinic CH₂ in chain in *rac*-**40**), 37.19 (2 aliphatic CH₂ in five-ring in *rac*-**37**), 36.80 (2 aliphatic CH₂ in five-ring in *rac*-**40**), 36.65 (2 aliphatic CH in chain in *rac*-**37**), 35.97 (2 aliphatic CH in chain in *rac*-**40**), 20.46 (2 CH₃ attached to the chain in *rac*-**37**), 19.96 (2 CH₃ attached to the chain in *rac*-**40**), 19.65 (2 CH₃ attached to the aromatic ring in *rac*-**37**), 18.11 (2 CH₃ attached to the aromatic ring in *rac*-**40**). EIMS (70 eV): calcd. C₁₄H₁₅Cl 218.0862; found 218.0864.

An Enantiomeric Mixture of 1-Allyl-7-bromo-4-methyl-indan-1-ol (*rac*-41**):** By applying General Procedure 1, zinc (0.3655 g, 5.6 mmol), 7-bromo-4-methyl-indan-1-one (0.5577 g, 2.5 mmol), and allyl bromide (430 μL, 5.0 mmol) gave, after a 3-h reaction time, 0.566 g (85%) of the enantiomeric mixture of the title compounds as a yellow oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.15 (m, 2 H, arom. CH), 6.82 (m, 2 H, arom. CH), 5.63 (ddt, *J* = 7.36 Hz, 10.41 Hz, 17.17 Hz, 2 H, olefinic CH in chain), 5.05 (dm, *J* = 17.17 Hz, 2 H, olefinic CH in chain), 4.99 (dm, *J* = 10.41 Hz, 2 H, olefinic CH in chain), 2.73 (m, 2 H, aliphatic CH in five-ring), 2.69 (dd, *J* = 7.36 Hz, 13.75 Hz, 2 H, aliphatic CH in chain), 2.62 (dd, *J* = 7.36 Hz, 13.75 Hz, 2 H, aliphatic CH in chain), 2.53 (m, 2 H, aliphatic CH in five-ring), 2.35 (m, 2 H, aliphatic CH in five-ring), 2.21 (br. s, 2 H, OH), 2.11 (s, 6 H, CH₃), 2.02 (m, 2 H, aliphatic CH in five-ring) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 144.70 (2 C_q), 143.24 (2 C_q), 133.47 (2 C_q), 133.22 (2 olefinic CH in chain), 131.10 (2 arom. CH), 130.28 (2 arom. CH), 118.18 (2 olefinic CH₂ in chain), 115.13 (2 C_q), 84.99 (2 C-OH), 43.85 (2 aliphatic CH₂ in chain), 38.01 (2 aliphatic CH₂ in five-ring), 27.86 (2 aliphatic CH₂ in five-ring), 18.20 (2 CH₃) ppm. EIMS (30 eV): calcd. C₁₃H₁₅OBr 266.0306; found 266.0313.

A Mixture of 3-Allyl-4-bromo-7-methyl-1H-indene (42**) and 7-Bromo-4-methyl-1-prop-2-en-(*E*)-ylidene-indane (**43**):** By applying General Procedure 3, an enantiomeric mixture of 1-allyl-7-bromo-4-methyl-indan-1-ol (*rac*-**41**) [0.1462 g, 0.55 mmol] and Amberlyst 15 (0.0805 g) in pentane (5 mL) gave, after a 2-h reaction time and column chromatography (hexane as eluent), 0.0368 g (27%) of a mixture of the title compounds as a colorless oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.51 (m, 1 H, arom. CH in **43**), 7.33 (dm, *J* = 8.09 Hz, 1 H, arom. CH in **42**), 7.28 (m, 1 H, arom. CH in **43**), 6.84 (dm, *J* = 8.09 Hz, 1 H, arom. CH in **42**), 6.80 (m, 1 H, olefinic CH in chain in **43**), 6.64 (ddd, *J* = 10.07 Hz, 10.98 Hz, 16.86 Hz, 1 H, olefinic CH in chain in **43**), 6.31 (m, 1 H, olefinic CH in five-ring in **42**), 6.11 (mt, *J* = 6.48 Hz, 1 H, olefinic CH in chain in **42**), 5.37 (dm, *J* = 16.86 Hz, 1 H, olefinic CH in chain in **43**), 5.21 (dm, *J* = 10.07 Hz, 1 H, olefinic CH in chain in **43**), 5.12 (m, 1 H, olefinic CH in chain in **42**), 5.11 (m, 1 H, olefinic CH in chain in **42**), 3.62 (m, 2 H, aliphatic CH₂ in chain in **42** or aliphatic CH₂ in five-ring in **42**), 3.18 (m, 2 H, aliphatic CH₂ in chain in **42** or aliphatic CH₂ in five-ring in **42**), 2.89 (m, 4 H, aliphatic CH₂ in five-ring in **43**), 2.28 (s, 3 H, CH₃ attached to the aromatic ring in **42**), 2.18 (s, 3 H, CH₃ attached to the aromatic ring in **43**) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 149.16 (C_q in **43**), 146.16 (C_q in **42**), 144.23 (C_q in **43**), 143.97 (C_q in **42**), 141.95 (C_q in **42**), 137.88 (C_q in **43**), 136.38 (olefinic CH in chain in **42**), 134.60 (olefinic CH in chain in **43**), 132.32 (arom. CH in **43**), 132.06 (C_q in **42**), 131.59 (arom. CH in **42**), 131.15 (olefinic CH in five-ring in **42**), 129.50 (olefinic CH in chain in **43**), 127.39 (arom. CH in **42**), 124.41 (arom. CH in **43**), 122.35 (C_q in **43**), 117.88 (olefinic CH in chain in **43**), 116.05 (olefinic CH in chain in **42**), 115.15 (C_q in **43**), 112.07 (C_q in **42**), 36.71 (aliphatic CH₂ in chain in **42** or aliphatic CH₂ in five-ring in **42**), 34.74 (aliphatic CH₂ in chain in **42** or aliphatic CH₂ in five-ring in **42**), 29.13 (aliphatic CH₂ in five-ring in **43**), 28.81 (aliphatic CH₂ in five-ring in **43**), 18.46 (CH₃ attached to the aromatic ring in **43**), 18.15 (CH₃ attached to the aromatic ring in **42**) ppm. EIMS (70 eV): calcd. C₁₃H₁₃Br 248.0201; found 248.0195.

A Mixture of 7-Bromo-4-methyl-1-(1-methyl-allyl)-indan-1-ol (*rac*-44** and *rac*-**45**):** By applying General Procedure 1, zinc (0.5132 g, 7.8 mmol), 7-bromo-4-methyl-indan-1-one (0.8606 g, 3.8 mmol), and crotyl bromide (930 μL, 7.6 mmol) gave, after a 3-h reaction time, 0.8213 g (77%) of a mixture of the title compounds as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.23 (m, 4 H, arom. CH in *rac*-**44** and/or *rac*-**45**), 6.90 (m, 4 H, arom. CH in CH in *rac*-**44** and/or *rac*-**45**), 6.14 (m, 2 H, olefinic CH in chain in CH in *rac*-**44** or *rac*-**45**), 5.40 (ddd, *J* = 6.79 Hz, 10.45 Hz, 17.25 Hz, 2 H, olefinic CH in chain in *rac*-**44** or *rac*-**45**), 5.20 (m, 4 H, olefinic CH₂ in chain in *rac*-**44** or *rac*-**45**), 4.91 (dt, *J* = 1.54 Hz, 17.25 Hz, 2 H, olefinic CH in chain in *rac*-**44** or *rac*-**45**), 4.79 (dt, *J* = 1.37 Hz, 10.45 Hz, 2 H, olefinic CH in chain in *rac*-**44** or *rac*-**45**), 3.29 (m, 4 H, aliphatic CH in chain in *rac*-**44** and *rac*-**45**), 2.95–2.35 and 2.02–1.90 (m, 16 H, overlapping signals from aliphatic CH₂ in five-ring in *rac*-**44** and *rac*-**45**), 2.29 (br. s, 2 H, OH in *rac*-**44** or *rac*-**45**), 2.28 (br. s, 2 H, OH in *rac*-**44** or *rac*-**45**), 2.17 (s, 6 H, CH₃ attached to the aromatic ring in *rac*-**44** or *rac*-**45**), 2.15 (s, 6 H, CH₃ attached to the aromatic ring in *rac*-**44** or *rac*-**45**), 1.23 (d, *J* = 6.72 Hz, 6 H, CH₃ attached to the chain in *rac*-**44** or *rac*-**45**), 0.72 (d, *J* = 6.94 Hz, 6 H, CH₃ attached to the chain in *rac*-**44** or *rac*-**45**) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 145.68 (2 C_q in *rac*-**44** or *rac*-**45**), 145.50 (2 C_q in *rac*-**44** or *rac*-**45**), 143.17 (2 C_q in *rac*-**44** or *rac*-**45**), 142.49 (2 C_q in *rac*-**44** or *rac*-**45**), 139.38 (2 olefinic CH in chain in *rac*-**44** or *rac*-**45**), 138.73 (2 olefinic CH in chain in *rac*-**44** or *rac*-**45**), 133.65 (2 C_q in *rac*-**44** or *rac*-**45**), 133.61 (2 C_q in *rac*-**44** or *rac*-**45**), 131.61 (2 arom. CH in *rac*-**44** or *rac*-**45**), 131.30 (2 arom. CH in *rac*-**44** or *rac*-**45**), 130.57 (2 arom. CH in *rac*-**44** or

rac-45), 130.49 (2 arom. CH in **rac-44** or **rac-45**), 116.39 (2 olefinic CH₂ in chain in **rac-44** or **rac-45**), 115.45 (2 C_q in **rac-44** or **rac-45**), 115.20 (2 olefinic CH₂ in chain in **rac-44** or **rac-45**), 115.16 (2 C_q in **rac-44** or **rac-45**), 88.21 (4 C-OH in **rac-44** or **rac-45**), 45.27 (2 aliphatic CH in chain in **rac-44** or **rac-45**), 44.72 (2 aliphatic CH in chain **rac-44** or **rac-45**), 34.33 (2 aliphatic CH₂ in five-ring in **rac-44** or **rac-45**), 33.62 (2 aliphatic CH₂ in five-ring in **rac-44** or **rac-45**), 29.23 (2 aliphatic CH₂ in five-ring in **rac-44** or **rac-45**), 28.94 (2 aliphatic CH₂ in five-ring in **rac-44** or **rac-45**), 18.38 (4 CH₃ attached to the aromatic ring in **rac-44** and **rac-45**), 14.54 (2 CH₃ attached to the chain in **rac-44** or **rac-45**), 13.05 (2 CH₃ attached to the chain in **rac-44** or **rac-45**) ppm. EIMS (30 eV): calcd. C₁₄H₁₇OBr 280.0463; found 280.0451.

An Enantiomeric Mixture of 4-Bromo-7-methyl-3-(1-methyl-allyl)-1H-indene (rac-46): By applying General Procedure 3, a mixture of 7-bromo-4-methyl-1-(1-methyl-allyl)-indan-1-ol (**rac-44** and **rac-45**) [0.2042 g, 0.73 mmol] and Amberlyst 15 (0.1159 g) in pentane (10 mL) gave, after a 1-h reaction time and column chromatography (hexane as eluent), 0.0701 g (36%) of an enantiomeric mixture of the title compounds as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.35 (d, *J* = 8.01 Hz, 2 H, arom. CH), 6.85 (dm, *J* = 8.01 Hz, 2 H, arom. CH), 6.37 (m, 2 H, olefinic CH in five-ring), 6.19 (ddd, *J* = 5.64 Hz, 9.84 Hz, 17.85 Hz, 2 H, olefinic CH in chain), 5.05 (dt, *J* = 1.57 Hz, 9.84 Hz, 2 H, olefinic CH in chain), 5.04 (dt, *J* = 1.68 Hz, 17.85 Hz, 2 H, olefinic CH in chain), 4.27 (m, 2 H, aliphatic CH in chain), 3.19 (m, 4 H, aliphatic CH₂ in five-ring), 2.30 (s, 6 H, CH₃ attached to the aromatic ring), 1.38 (d, *J* = 6.87 Hz, 6 H, CH₃ attached to the chain) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 149.38 (2 C_q), 146.35 (2 C_q), 142.49 (2 olefinic CH in chain), 141.43 (2 C_q), 132.02 (2 C_q), 131.95 (2 arom. CH), 129.74 (2 olefinic CH in five-ring), 127.27 (2 arom. CH), 112.79 (2 olefinic CH₂ in chain), 111.96 (2 C_q), 36.71 (2 aliphatic CH₂ in five-ring), 35.42 (2 aliphatic CH in chain), 20.03 (2 CH₃ attached to the chain), 18.14 (2 CH₃ attached to the aromatic ring) ppm. EIMS (70 eV): calcd. C₁₄H₁₅Br 262.0357; found 262.0360.

An Enantiomeric Mixture of 1-Allyl-indan-1-ol (rac-1) from Alkylation of 2-Bromo-indan-1-one: By applying General Procedure 1, zinc (0.4719 g, 7.2 mmol), 2-bromo-indan-1-one (0.6706 g, 3.2 mmol), and allyl bromide (550 μL, 6.4 mmol) gave, after a 2-h reaction time, 0.3855 g (48%) of an enantiomeric mixture of the title compounds as a brown oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.25 (m, 2 H, arom. CH), 7.16 (m, 2 H, arom. CH), 5.77 (m, 2 H, olefinic CH in chain), 5.08 (m, 2 H, olefinic CH in chain), 5.06 (m, 2 H, olefinic CH in chain), 2.93 (m, 2 H, aliphatic CH in five-ring), 2.73 (m, 2 H, aliphatic CH in five-ring), 2.56 (m, 2 H, aliphatic CH in chain), 2.43 (m, 2 H, aliphatic CH in chain), 2.25 (m, 4 H, OH and aliphatic CH in five-ring), 1.99 (m, 2 H, aliphatic CH in five-ring) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 146.99 (2 C_q), 142.95 (2 C_q), 133.73 (2 olefinic CH in chain), 128.22 (2 arom. CH), 126.62 (2 arom. CH), 124.89 (2 arom. CH), 122.85 (2 arom. CH), 118.78 (2 olefinic CH₂ in chain), 82.70 (2 C-OH), 44.94 (2 aliphatic CH₂ in chain), 39.62 (2 aliphatic CH₂ in five-ring), 29.37 (2 aliphatic CH₂ in five-ring) ppm. EIMS (30 eV): calcd. C₁₂H₁₄O 174.1045; found 174.1032.

2-Allyl-indan-2-ol (47): By applying General Procedure 1, zinc (13.08 g, 200 mmol), 2-indanone (13.215 g, 100 mmol), and allyl bromide (24.194 g, 200 mmol) gave, after a 19-h reaction time, 14.674 g (84%) of the title compound as a green oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (m, 4 H, arom. CH), 6.03 (m, 1 H, olefinic CH in chain), 5.27 (m, 2 H, olefinic CH₂ in chain), 3.14 (d, *J* = 16.2 Hz, 2 H, aliphatic CH in five-ring), 2.99 (d, *J* = 16.2 Hz, 2 H, aliphatic CH in five-ring), 2.56 (d, *J* = 7.25 Hz, 2 H, aliphatic

CH₂ in chain), 2.25 (s, 1 H, OH) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 141.11 (2 C_q), 133.93 (olefinic CH in chain), 126.51 (2 arom. CH), 124.88 (2 arom. CH), 118.85 (olefinic CH₂ in chain), 81.41 (C-OH), 46.34 (2 aliphatic CH₂ in five-ring), 44.92 (aliphatic CH₂ in chain) ppm. EIMS (70 eV): calcd. C₁₂H₁₄O 174.1045; found 174.1044.

2-Allyl-1H-indene (48): By applying General Procedure 4, 2-allyl-indan-2-ol (47) [14.67 g, 84.2 mmol] and *p*-TSA (1.4 g, 7.4 mmol) in toluene (200 mL) gave, after a 2-h reaction time and column chromatography (hexane as eluent), 5.031 g (38%) of the title compound as a colorless oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.55 (ddd, *J* = 0.84 Hz, 1.83 Hz, 7.32 Hz, 1 H, arom. CH), 7.44 (m, 2 H, arom. CH), 7.31 (td, *J* = 1.30 Hz, 7.32 Hz, 1 H, arom. CH), 6.72 (m, 1 H, olefinic CH in five-ring), 6.16 (ddd, *J* = 6.79 Hz, 10.0 Hz, 16.86 Hz, 1 H, olefinic CH in chain), 5.35 (dm, *J* = 16.86 Hz, 1 H, olefinic CH in chain), 5.31 (dm, *J* = 10.0 Hz, 1 H, olefinic CH in chain), 3.46 (m, 2 H, aliphatic CH₂ in five-ring), 3.40 (m, 2 H, aliphatic CH₂ in chain) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 148.11 (C_q), 145.38 (C_q), 143.15 (C_q), 136.04 (olefinic CH in chain), 126.99 (olefinic CH in five-ring), 126.16 (arom. CH), 123.70 (arom. CH), 123.33 (arom. CH), 120.01 (arom. CH), 115.98 (olefinic CH₂ in chain), 40.88 (aliphatic CH₂ in five-ring), 35.65 (aliphatic CH₂ in chain) ppm. EIMS (70 eV): calcd. C₁₂H₁₂ 156.0939; found 156.0939.

An Enantiomeric Mixture of 2-(1-Methyl-allyl)-indan-2-ol (rac-49): By applying General Procedure 1, zinc (13.08 g, 200 mmol), 2-indanone (13.22 g, 100 mmol), and crotyl bromide (27.0 g, 200 mmol) gave, after a 4-h reaction time, 16.5 g (88%) of an enantiomeric mixture of the title compounds as a green oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.26 (m, 8 H, arom. CH), 6.02 (ddd, *J* = 8.01 Hz, 10.38 Hz, 17.17 Hz, 2 H, olefinic CH in chain), 5.23 (dm, *J* = 17.17 Hz, 2 H, olefinic CH in chain), 5.21 (dm, *J* = 10.38 Hz, 2 H, olefinic CH in chain), 3.18 (m, 4 H, aliphatic CH₂ in five-ring), 2.93 (m, 4 H, aliphatic CH₂ in five-ring), 2.55 (m, 2 H, aliphatic CH in chain), 2.00 (br. s, 2 H, OH), 1.22 (d, *J* = 6.9 Hz, 3 H, CH₃) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 141.25 (2 C_q), 141.23 (2 C_q), 140.14 (2 olefinic CH in chain), 126.46 (4 C, arom. CH), 124.91 (4 C, arom. CH), 115.92 (2 olefinic CH₂ in chain), 83.81 (2 C-OH), 46.86 (2 aliphatic CH in chain), 45.73 (2 aliphatic CH₂ in five-ring), 45.18 (2 aliphatic CH₂ in five-ring), 14.87 (2 CH₃) ppm. EIMS (70 eV): calcd. C₁₃H₁₆O 188.1201; found 188.1200.

An Enantiomeric Mixture of 2-(1-Methyl-allyl)-1H-indene (rac-50): By applying General Procedure 4, an enantiomeric mixture of 2-(1-methyl-allyl)-indan-2-ol (**rac-49**) (16.5 g, 88 mmol) and concentrated sulfuric acid (22 drops) in toluene (30 mL) gave, after a 9.5-h reaction time and column chromatography (hexane as eluent), 7.93 g (53%) of an enantiomeric mixture of the title compounds as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (dm, *J* = 7.40, 2 H, arom. CH), 7.16 (dm, *J* = 7.40, 2 H, arom. CH), 7.10 (tm, *J* = 7.40 Hz, 2 H, arom. CH), 6.99 (tm, *J* = 7.40 Hz, 2 H, arom. CH), 6.43 (m, 2 H, olefinic CH in five-ring), 5.78 (ddd, *J* = 7.33 Hz, 10.15 Hz, 17.24 Hz, 2 H, olefinic CH in chain), 4.98 (dt, *J* = 1.30 Hz, 17.24 Hz, 2 H, olefinic CH in chain), 4.91 (ddd, *J* = 0.99 Hz, 1.60 Hz, 10.15 Hz, 2 H, olefinic CH in chain), 3.19 (m, 6 H, aliphatic CH₂ in five-ring and aliphatic CH in chain), 1.22 (d, *J* = 6.9 Hz, 6 H, CH₃) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 153.57 (2 C_q), 145.31 (2 C_q), 143.14 (2 C_q), 142.52 (2 olefinic CH in chain), 126.24 (2 arom. CH), 125.57 (2 olefinic CH in five-ring), 123.78 (2 arom. CH), 123.47 (2 arom. CH), 120.19 (2 arom. CH), 113.47 (2 olefinic CH₂ in chain), 39.69 (2 aliphatic CH₂ in five-ring or aliphatic CH in chain), 39.49 (2 aliphatic CH₂ in five-ring or aliphatic CH in chain), 19.53 (2 CH₃) ppm. EIMS (70 eV): calcd. C₁₃H₁₄ 170.1096; found 170.1093.

An Enantiomeric Mixture of 2-(1-Phenyl-allyl)-indan-2-ol (*rac*-51):

By applying General Procedure 1, zinc (13.08 g, 200 mmol), 2-indanone (13.215 g, 100 mmol), and cinnamyl chloride (30.522 g, 200 mmol) gave, after a 19-h reaction time, 34.9 g (100%, contains some solvent) of an enantiomeric mixture of the title compounds as a dark oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.39–7.10 (m, 18 H, arom. CH), 6.40 (ddd, J = 9.08 Hz, 10.22 Hz, 17.01 Hz, 2 H, olefinic CH in chain), 5.22 (dm, J = 10.22 Hz, 2 H, olefinic CH in chain), 5.18 (dm, J = 17.01 Hz, 2 H, olefinic CH in chain), 3.54 (d, J = 9.08 Hz, 2 H, aliphatic CH in chain), 3.20 (m, 4 H, aliphatic CH in five-ring), 2.95 (m, 2 H, aliphatic CH in five-ring), 2.57 (m, 2 H, aliphatic CH in five-ring), 1.75 (br. s, 2 H, OH) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 141.03 (6 C_q), 137.81 (2 olefinic CH in chain), 129.00 (2 arom. CH), 128.49 (2 arom. CH), 126.88 (2 arom. CH), 126.60 (2 arom. CH), 125.01 (2 arom. CH), 124.93 (2 arom. CH), 117.56 (2 olefinic CH_2 in chain), 84.14 (2 C–OH), 59.24 (2 aliphatic CH in chain), 46.15 (2 aliphatic CH_2 in five-ring), 45.94 (2 aliphatic CH_2 in five-ring) ppm. EIMS (30 eV): calcd. $\text{C}_{18}\text{H}_{18}\text{O}$ 250.1358; found 250.1353.

An Enantiomeric Mixture of 2-(1-Phenyl-allyl)-1H-indene (*rac*-52):

By applying General Procedure 4, an enantiomeric mixture of 2-(1-phenyl-allyl)-indan-2-ol (*rac*-51) [34.9 g, 139 mmol] and *p*-TSA (1.7 g, 8.9 mmol) in toluene (200 mL) gave, after a 6.5-h reaction time and column chromatography (hexane as eluent), 3.18 g (15%) of an enantiomeric mixture of the title compounds as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.31 (m, 8 H, arom. CH), 7.22 (m, 8 H, arom. CH), 7.10 (m, 2 H, arom. CH), 6.59 (m, 2 H, olefinic CH in five-ring), 6.27 (ddd, J = 7.47 Hz, 10.07 Hz, 17.09 Hz, 2 H, olefinic CH in chain), 5.19 (ddd, J = 1.07 Hz, 1.60 Hz, 10.07 Hz, 2 H, olefinic CH in chain), 5.08 (ddd, J = 1.30 Hz, 1.60 Hz, 17.09 Hz, 2 H, olefinic CH in chain), 4.50 (dm, J = 7.47 Hz, 2 H, aliphatic CH in chain), 3.26 (m, 4 H, aliphatic CH_2 in five-ring) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 151.35 (2 C_q), 144.95 (2 C_q), 143.34 (2 C_q), 142.49 (2 C_q), 139.78 (2 olefinic CH in chain), 128.49, 128.23, 128.03, 126.52, 126.28, 124.05, 123.48, 120.45 (18 C, overlapping arom. CH), 115.88 (2 olefinic CH_2 in chain), 51.78 (2 aliphatic CH in chain), 40.20 (2 aliphatic CH_2 in five-ring) ppm. EIMS (70 eV): calcd. $\text{C}_{18}\text{H}_{16}$ 232.1252; found 232.1251.

2-(1,1-Dimethyl-allyl)-indan-2-ol (53): By applying General Procedure 1, zinc (1.134 g, 17.34 mmol), 2-indanone (1.119 g, 8.47 mmol), and prenyl bromide (2.0 mL, 16.96 mmol) gave, after a 3-h reaction time, 1.5617 g (91%) of the title compound as a brown oil. ^1H NMR (600 MHz, CDCl_3): δ = 7.20 (m, 2 H, arom. CH), 7.15 (m, 2 H, arom. CH), 6.04 (dd, J = 10.46 Hz, 17.0 Hz, 1 H, olefinic CH in chain), 5.17 (dm, J = 17.0 Hz, 1 H, olefinic CH in chain), 5.11 (dm, J = 10.46 Hz, 1 H, olefinic CH in chain), 3.32 (s, 1 H, aliphatic CH in five-ring), 3.30 (s, 1 H, aliphatic CH in five-ring), 2.76 (s, 1 H, aliphatic CH in five-ring), 2.73 (s, 1 H, aliphatic CH in five-ring), 1.16 (s, 6 H, CH_3 attached to the chain) ppm. ^{13}C NMR (150.9 MHz, CDCl_3): δ = 141.39 (olefinic CH in chain), 137.90 (C_q), 126.73 (arom. CH), 126.52 (arom. CH), 125.29 (arom. CH), 125.11 (arom. CH), 114.06 (olefinic CH_2 in chain), 86.49 (C–OH), 42.96 (2 aliphatic CH_2 in five-ring), 22.86 (CH_3 attached to the chain), 22.81 (CH_3 attached to the chain) ppm. EIMS (30 eV): calcd. $\text{C}_{14}\text{H}_{18}\text{O}$ 202.1358; found 202.1363.

2-(1,1-Dimethyl-allyl)-1H-indene (54): By applying General Procedure 3, 2-(1,1-dimethyl-allyl)-indan-2-ol (53) [0.0865 g, 0.43 mmol] and Amberlyst 15 (0.0751 g) in pentane (3 mL) gave, after a 19-h reaction time and column chromatography (hexane as eluent), 0.0088 g (11%) of the title compound as a colorless oil. ^1H NMR (600 MHz, CDCl_3): δ = 7.37 (d, J = 7.25 Hz, 1 H, arom.

CH), 7.29 (d, J = 7.25 Hz, 1 H, arom. CH), 7.22 (t, J = 7.25 Hz, 1 H, arom. CH), 7.11 (t, J = 7.25 Hz, 1 H, arom. CH), 6.57 (s, 1 H, olefinic CH in five-ring), 5.97 (dd, J = 11.32 Hz, 17.89 Hz, 1 H, olefinic CH in chain), 5.03 (dm, J = 17.89 Hz, 1 H, olefinic CH in chain), 4.97 (dm, J = 11.32 Hz, 1 H, olefinic CH in chain), 3.35 (s, 2 H, aliphatic CH_2 in the five-ring), 1.35 (s, 6 H, CH_3 attached to the chain) ppm. ^{13}C NMR (150.9 MHz, CDCl_3): δ = 157.46 (C_q), 147.43 (olefinic CH in chain), 145.30 (C_q), 143.43 (C_q), 126.39 (arom. CH), 125.19 (olefinic CH in the five-ring), 123.99 (arom. CH), 123.65 (arom. CH), 120.45 (arom. CH), 110.96 (olefinic CH_2 in chain), 38.28 (aliphatic CH_2 in the five-ring), 27.46 (CH_3 attached to the chain) ppm. EIMS (70 eV): calcd. $\text{C}_{14}\text{H}_{16}$ 184.1252; found 184.1253.

An Enantiomeric Mixture of 4,7-Dimethyl-2-(1-methyl-allyl)-indan-2-ol (*rac*-55):

By applying General Procedure 1, zinc (0.1930 g, 2.95 mmol), 4,7-dimethyl-indan-2-one (0.2323 g, 1.45 mmol), and crotyl bromide (350 μL , 2.90 mmol) gave, after a 2-h reaction time, 0.2345 g (75%) of an enantiomeric mixture of the title compounds as a very pale brown oil. ^1H NMR (600 MHz, CDCl_3): δ = 6.91 (m, 4 H, arom. CH), 5.98 (ddd, J = 8.12 Hz, 10.61 Hz, 17.48 Hz, 2 H, olefinic CH in chain), 5.18 (dm, J = 17.48 Hz, 2 H, olefinic CH in chain), 5.15 (dm, J = 10.61 Hz, 2 H, olefinic CH in chain), 3.02 (d, J = 16.70 Hz, 2 H, aliphatic CH in five-ring), 3.01 (d, J = 16.70 Hz, 2 H, aliphatic CH in five-ring), 2.86 (d, J = 16.23 Hz, 2 H, aliphatic CH in five-ring), 2.82 (d, J = 16.23 Hz, 2 H, aliphatic CH in five-ring), 2.50 (m, 2 H, aliphatic CH in chain), 2.21 (s, 6 H, CH_3 attached to the aromatic ring), 2.20 (s, 6 H, CH_3 attached to the aromatic ring), 1.71 (br. s, 2 H, OH), 1.17 (d, J = 6.87 Hz, 6 H, CH_3 attached to the aliphatic chain) ppm. ^{13}C NMR (150.9 MHz, CDCl_3): δ = 140.40 (2 olefinic CH in chain), 139.80 (2 C_q), 131.69 (2 C_q), 127.76 (4C, arom. CH), 116.22 (2 olefinic CH_2 in chain), 83.30 (2 C–OH), 47.25 (2 aliphatic CH in chain), 45.01 (2 aliphatic CH_2 in five-ring), 44.41 (2 aliphatic CH_2 in five-ring), 18.95 (4 CH_3 attached to the aromatic ring), 15.23 (2 CH_3 attached to the aliphatic chain) ppm. EIMS (70 eV): calcd. $\text{C}_{15}\text{H}_{20}\text{O}$ 216.1514; found 216.1514.

An Enantiomeric Mixture of 4,7-Dimethyl-2-(1-methyl-allyl)-1H-indene (*rac*-56):

By applying General Procedure 3, an enantiomeric mixture of 4,7-dimethyl-2-(1-methyl-allyl)-indan-2-ol (*rac*-55) (0.0796 g, 0.37 mmol) and Amberlyst 15 (0.0598 g) in pentane (5 mL) gave, after a 24-h reaction time and column chromatography (hexane as eluent), 0.0094 g (13%) of an enantiomeric mixture of the title compounds as a colorless oil. ^1H NMR (600 MHz, CDCl_3): δ = 6.97 (d, J = 7.69 Hz, 2 H, arom. CH), 6.85 (d, J = 7.69 Hz, 2 H, arom. CH), 6.65 (m, 2 H, olefinic CH in five-ring), 5.93 (ddd, J = 7.02 Hz, 10.23 Hz, 17.66 Hz, 2 H, olefinic CH in chain), 5.10 (dm, J = 17.66 Hz, 2 H, olefinic CH in chain), 5.04 (dm, J = 10.23 Hz, 2 H, olefinic CH in chain), 3.37 (m, 2 H, aliphatic CH in chain), 3.25 (d, J = 22.36 Hz, 2 H, aliphatic CH in five-ring), 3.20 (d, J = 22.36 Hz, 2 H, aliphatic CH in five-ring), 2.39 (s, 6 H, CH_3 attached to the aromatic ring), 2.30 (s, 6 H, CH_3 attached to the aromatic ring), 1.35 (d, J = 6.96 Hz, 6 H, CH_3 attached to the aliphatic chain) ppm. ^{13}C NMR (150.9 MHz, CDCl_3): δ = 152.74 (2 C_q), 143.10 (2 olefinic CH in chain), 141.69 (2 C_q), 130.20 (2 C_q), 127.81 (2 arom. CH), 125.41 (2 arom. CH), 124.19 (2 olefinic CH in five-ring), 113.56 (2 olefinic CH_2 in chain), 39.98 (2 aliphatic CH in chain), 38.82 (2 aliphatic CH_2 in five-ring), 19.84 (2 CH_3 attached to the aliphatic chain), 18.61 (2 CH_3 attached to the aromatic ring), 18.30 (2 CH_3 attached to the aromatic ring) ppm. EIMS (70 eV): calcd. $\text{C}_{15}\text{H}_{18}$ 198.1409; found 198.1409.

An Enantiomeric Mixture of 1-Allyl-3,4-diphenyl-cyclopent-2-enol (*rac*-57):

By applying General Procedure 1, zinc (0.5332 g,

8.2 mmol), 3,4-diphenyl-cyclopent-2-enone (0.9379 g, 4.0 mmol), and allyl bromide (700 μ L, 8.0 mmol) gave, after a 19-h reaction time and column chromatography (dichloromethane as eluent), 0.1035 g (9%) of the title compound as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.17 (m, 20 H, arom. CH), 6.25 (m, 2 H, olefinic CH in five-ring), 5.85 (m, 2 H, olefinic CH in chain), 5.12 (m, 4 H, olefinic CH_2 in chain), 4.22 (m, 2 H, aliphatic CH in five-ring), 2.71 (m, 2 H, aliphatic CH in five-ring), 2.44 (m, 4 H, aliphatic CH_2 in chain), 1.86 (m, 2 H, aliphatic CH in five-ring), 1.82 (s, 2 H, OH) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 146.25 (2 C_q), 144.84 (2 C_q), 134.92 (2 C_q), 133.68 (2 olefinic CH in chain), 133.03 (2 olefinic CH in five-ring), 128.64, 128.21, 127.63, 126.93, 126.20 (20 overlapping arom. CH), 118.98 (2 olefinic CH_2 in chain), 83.32 (2 C-OH), 50.30 (2 aliphatic CH in five-ring), 48.91 (2 aliphatic CH_2 five-ring), 45.67 (2 aliphatic CH_2 five-ring) ppm.

A Mixture of 1,5-Diphenyl-3-prop-2-en-(Z)-ylidene-cyclopentene (58) and 1,5-Diphenyl-3-prop-2-en-(E)-ylidene-cyclopentene (59): By applying General Procedure 3, an enantiomeric mixture of 1-allyl-3,4-diphenyl-cyclopent-2-enol (*rac*-57) [103.5 mg, 0.37 mmol] and Amberlyst 15 (0.0430 g) in pentane (5 mL) gave, after a 23-h reaction time and purification by preparative TLC (10% dichloromethane/90% hexane as eluent), 0.0207 g (22%) of a 2:1 mixture of the title compounds as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.20 (m, 20 H, arom. CH from 58 and 59), 6.80 (m, 2 H, five-ring olefinic CH in 58 and 59), 6.77 (ddd, J = 16.9 Hz, 11.1 Hz, 10.1 Hz, 1 H, chain olefinic CH in 59), 6.42 (ddd, J = 16.9 Hz, 11.3 Hz, 10.1 Hz, 1 H, chain olefinic CH in 58), 6.18 (dm, J = 11.1 Hz, 1 H, chain olefinic CH in 58), 5.91 (dm, J = 11.2 Hz, 1 H, chain olefinic CH in 59), 5.17 (dm, J = 16.7 Hz, 1 H, chain olefinic CH in 58), 5.11 (dm, J = 16.7 Hz, 1 H, chain olefinic CH in 59), 5.03 (dm, J = 10.2 Hz, 1 H, chain olefinic CH in 58), 5.02 (dm, J = 10.4 Hz, 1 H, chain olefinic CH in 59), 4.48 (dm, J = 8.7 Hz, 1 H, five-ring aliphatic CH in 58), 4.41 (dm, J = 8.5 Hz, 1 H, five-ring aliphatic CH in 59), 3.30 (ddd, J = 17.1 Hz, 8.6 Hz, 2.6 Hz, 1 H, five-ring aliphatic CH in 58), 3.29 (ddm, J = 17 Hz, 8 Hz, 1 H, five-ring aliphatic CH in 59), 2.66 (dt, J = 17.2 Hz, 2.4 Hz, 1 H, five-ring aliphatic CH in 58), 2.57 (dm, J = 16.9 Hz, 1 H, five-ring aliphatic CH in 59) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 151.92, 150.98, 148.23, 147.12, 145.32, 145.06 (8 C, overlapping signals from C_q from both stereoisomers), 134.52 (1 C, olefinic CH in chain in 58), 134.00 (1 C, olefinic CH in chain in 59), 131.53 (2 C, five-ring olefinic CH in 58 and 59), 128.70 (4 C, overlapping arom. CH in 58 and 59), 128.29 (4 C, overlapping arom. CH in 58 and 59), 127.12 (4 C, overlapping arom. CH in 58 and 59), 126.54 (4 C, overlapping arom. CH in 58 and 59), 126.28 (4 C, overlapping arom. CH in 58 and 59), 121.22 (1 C, olefinic CH in chain in 58), 120.50 (1 C, olefinic CH in chain in 59), 115.35 (1 C, olefinic chain CH_2 in 58), 114.09 (1 C, olefinic chain CH_2 in 59), 50.44 (1 C, five-ring aliphatic CH in 58), 49.70 (1 C, five-ring aliphatic CH in 59), 42.18 (1 C, five-ring aliphatic CH_2 in 59), 39.00 (1 C, five-ring aliphatic CH_2 in 58) ppm.

A Mixture of 1-(1-Methyl-allyl)-3,4-diphenyl-cyclopent-2-enol (*rac*-60 and *rac*-61): By applying General Procedure 1, zinc (0.5797 g, 8.9 mmol), 3,4-diphenyl-cyclopent-2-enone (1.2405 g, 5.3 mmol), and crotyl bromide (1.05 mL, 8.7 mmol) gave, after a 5.5-h reaction time and column chromatography (dichloromethane as eluent), 0.5012 g (40%) of a mixture of the title compounds as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.35 (m, 8 H, arom. CH in *rac*-60 and *rac*-61), 7.17 (m, 32 H, arom. CH in *rac*-60 and *rac*-61), 6.34 (m, 4 H, olefinic CH in five-ring in *rac*-60 and *rac*-61), 5.92 (m, 4 H, olefinic CH in chain in *rac*-60 and *rac*-61), 5.17 (m, 8 H, olefinic CH_2 in chain in *rac*-60 and *rac*-61), 4.27 (m, 4 H, aliphatic CH in five-ring in *rac*-60 and *rac*-61), 2.84 (m, 4 H, aliphatic CH

in five-ring in *rac*-60 and *rac*-61), 2.53 (m, 4 H, aliphatic CH in chain in *rac*-60 and *rac*-61), 1.88 (m, 4 H, aliphatic CH in five-ring in *rac*-60 and *rac*-61), 1.82 (m, 4 H, OH in *rac*-60 and *rac*-61), 1.15 (d, J = 6.8 Hz, 6 H, CH_3 in *rac*-60 or *rac*-61), 1.11 (d, J = 6.9 Hz, 6 H, CH_3 in *rac*-60 or *rac*-61) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): δ = 146.84 (2 C_q in *rac*-60 or *rac*-61), 146.71 (2 C_q in *rac*-60 or *rac*-61), 145.07 (4 C_q in *rac*-60 and *rac*-61), 139.95 (2 olefinic CH in chain in *rac*-60 or *rac*-61), 139.85 (2 olefinic CH in chain in *rac*-60 or *rac*-61), 135.00 (2 C_q *rac*-60 or *rac*-61), 134.96 (2 C_q in *rac*-60 or *rac*-61), 131.99 (2 olefinic CH in five-ring in *rac*-60 or *rac*-61), 131.81 (2 olefinic CH in five-ring in *rac*-60 or *rac*-61), 128.63, 128.21, 127.62, 126.95, 126.16 (40 C, overlapping arom. CH in *rac*-60 and *rac*-61), 116.54 (2 olefinic CH_2 in chain in *rac*-60 or *rac*-61), 116.36 (2 olefinic CH_2 in chain in *rac*-60 or *rac*-61), 85.99 (2 C-OH in *rac*-60 or *rac*-61), 85.91 (2 C-OH in *rac*-60 or *rac*-61), 50.44 (2 aliphatic CH in five-ring in *rac*-60 or *rac*-61), 50.12 (2 aliphatic CH in five-ring in *rac*-60 or *rac*-61), 47.55 (2 aliphatic CH in chain in *rac*-60 or *rac*-61), 47.23 (2 aliphatic CH in chain in *rac*-60 or *rac*-61), 45.76 (4 C, aliphatic CH_2 in five-ring in *rac*-60 and *rac*-61), 15.16 (2 CH_3 in *rac*-60 or *rac*-61), 14.36 (2 CH_3 in *rac*-60 or *rac*-61).

An Enantiomeric Mixture of 1,2-Diphenyl-4-(1-methyl-allyl)-cyclopenta-1,3-diene (*rac*-62): By applying General Procedure 5, a mixture of 1-(1-methyl-allyl)-3,4-diphenyl-cyclopent-2-enol (*rac*-60 and *rac*-61) [0.6969 g, 2.4 mmol] and MgSO_4 (0.3652 g, 3.0 mmol) in toluene (20 mL) gave, after a 1-h reaction time and column chromatography (a mixture of 30% of dichloromethane and 70% of hexane as eluent), 0.2210 g of a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.31 (m, 20 H, arom. CH), 6.42 (m, 2 H, olefinic CH in five-ring), 5.98 (m, 2 H, olefinic CH in chain), 5.16 (dm, J = 17.17 Hz, 2 H, olefinic CH in chain), 5.07 (dm, J = 10.07 Hz, 2 H, olefinic CH in chain), 3.55 (dm, J = 23.23 Hz, 2 H, aliphatic CH in five-ring), 3.50 (dm, J = 23.23 Hz, 2 H, aliphatic CH in five-ring), 3.38 (m, 2 H, aliphatic CH in chain), 1.38 (d, J = 6.94 Hz, 6 H, CH_3 attached to the chain) ppm. The yield of the desired compound could not be determined due to the high-molecular-weight side-products present in the reaction product. ^{13}C NMR (100.6 MHz, CDCl_3): the signals for the quaternary carbon atoms of the desired reaction product could not be separated from the signals which originate from the high-molecular-weight side-products, δ = 142.94 (2 olefinic CH in chain), 130.45 (2 olefinic CH in five-ring), 128.77–126.11 (overlapping signals from arom. CH both in the desired compound and in the side products), 113.20 (2 olefinic CH_2 in chain), 45.78 (2 aliphatic CH_2 in five-ring), 39.43 (2 aliphatic CH in chain), 19.79 (2 CH_3 attached to the chain) ppm. EIMS (70 eV): calcd. $\text{C}_{21}\text{H}_{20}$ 272.1565; found 272.1567.

A Mixture of 3,4-Diphenyl-1-(1-phenyl-allyl)-cyclopent-2-enol (*rac*-63 and *rac*-64): By applying General Procedure 1, zinc (0.7079 g, 10.8 mmol), 3,4-diphenyl-cyclopent-2-enone (1.2405 g, 5.3 mmol), and cinnamyl chloride (1.6218 g, 10.6 mmol) gave, after a 5-h reaction time and column chromatography (dichloromethane as eluent), 0.9521 g (51%) of a mixture of the title compounds as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.32 (m, 60 H, arom. CH in *rac*-63 and *rac*-64), 6.48 (m, 2 H, olefinic CH in five-ring in *rac*-63 or *rac*-64), 6.40 (m, 4 H, olefinic CH in chain in *rac*-63 and *rac*-64), 6.25 (m, 2 H, olefinic CH in five-ring in *rac*-63 or *rac*-64), 5.29 (m, 8 H, olefinic CH_2 in chain in *rac*-63 and *rac*-64), 4.21 (m, 2 H, aliphatic CH in five-ring in *rac*-63 or *rac*-64), 3.95 (m, 2 H, aliphatic CH in five-ring in *rac*-63 or *rac*-64), 3.61 (m, 4 H, aliphatic CH in chain in *rac*-63 and *rac*-64), 2.93 (m, 4 H, aliphatic CH in five-ring in *rac*-63 and *rac*-64), 2.10 (s, 2 H, OH in *rac*-63 or *rac*-64), 1.94 (m, 6 H, aliphatic CH in five-ring in *rac*-63 and *rac*-64 and OH in *rac*-63 or *rac*-64) ppm. ^{13}C NMR (100.6 MHz, CDCl_3):

δ = 147.41 (2 C_q in *rac*-63 or *rac*-64), 147.05 (2 C_q in *rac*-63 or *rac*-64), 144.77 (2 C_q in *rac*-63 or *rac*-64), 144.62 (2 C_q in *rac*-63 or *rac*-64), 140.57 (2 C_q in *rac*-63 or *rac*-64), 140.38 (2 C_q in *rac*-63 or *rac*-64), 137.52 (2 olefinic CH in chain in *rac*-63 or *rac*-64), 137.46 (2 olefinic CH in chain in *rac*-63 or *rac*-64), 135.00 (2 C_q in *rac*-63 or *rac*-64), 134.96 (2 C_q in *rac*-63 or *rac*-64), 131.59 (2 olefinic CH in five-ring in *rac*-63 or *rac*-64), 131.57 (2 olefinic CH in five-ring in *rac*-63 or *rac*-64), 129.25, 129.10, 128.54, 128.49, 128.31, 128.25, 128.18, 128.15, 127.64, 126.95, 126.89, 126.80, 126.78, 126.13, 126.11 (60C, overlapping signals from arom. CH in *rac*-63 and *rac*-64), 117.94 (2 olefinic CH₂ in chain in *rac*-63 or *rac*-64), 117.89 (2 olefinic CH₂ in chain in *rac*-63 or *rac*-64), 85.82 (2 C–OH in *rac*-63 or *rac*-64), 85.73 (2 C–OH in *rac*-63 or *rac*-64), 60.28 (2 aliphatic CH in chain in *rac*-63 or *rac*-64), 60.09 (2 aliphatic CH in chain in *rac*-63 or *rac*-64), 50.41 (2 aliphatic CH in five-ring in *rac*-63 or *rac*-64), 50.29 (2 aliphatic CH in five-ring in *rac*-63 or *rac*-64), 48.12 (2 aliphatic CH in five-ring in *rac*-63 or *rac*-64), 47.94 (2 aliphatic CH in five-ring in *rac*-63 or *rac*-64) ppm.

A Mixture of [1-(3,4-Diphenyl-cyclopenta-1,3-dienyl)-allyl]benzene (*rac*-65), 1-[3,4-Diphenyl-cyclopent-2-en-(*Z*)-ylidene]-allyl]-benzene (66), and 1-[3,4-Dimethyl-cyclopent-2-en-(*E*)-ylidene]-allyl]-benzene (67): By applying General Procedure 5, a mixture of 3,4-diphenyl-1-(1-phenyl-allyl)-cyclopent-2-enol (*rac*-63 and *rac*-64) [0.3172 g, 0.90 mmol] and MgSO₄ (0.3404 g, 2.83 mmol) in toluene (20 mL) gave, after a 1-h reaction time and column chromatography (a mixture of 30% of dichloromethane and 70% of hexane as eluent), 0.0944 g of a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.16 (m, 45 H, arom. CH), 6.60 (m, 3 H, olefinic CH in five-ring in 66, olefinic CH in five-ring in 67 and olefinic CH in chain in 66 or 67), 6.30 (m, 2 H, olefinic CH in five-ring in *rac*-65), 6.19 (m, 3 H, olefinic CH in chain in *rac*-65 and olefinic CH in chain in 66 or 67), 5.08 (ddd, J = 0.61 Hz, 0.99 Hz, 10.07 Hz, 2 H, olefinic CH in chain in *rac*-65, 66 or 67), 5.00 (ddd, J = 0.3 Hz, 1.3 Hz, 17.01 Hz, 2 H, olefinic CH in chain in *rac*-65, 66 or 67), 4.98 (m, 3 H, olefinic CH₂ in chain in *rac*-65, 66 or 67), 4.75 (dm, J = 17.24, 2 H, olefinic CH in chain in *rac*-65, 66 or 67), 4.65 (dm, J = 17.17 Hz, 2 H, olefinic CH in chain in *rac*-65, 66 or 67), 4.44 (m, 1 H, aliphatic CH in five-ring in 66 or olefinic CH in five-ring in 67), 4.40 (m, 2 H, aliphatic CH in chain in *rac*-65), 4.27 (m, 1 H, aliphatic CH in five-ring in 66 or olefinic CH in five-ring in 67), 3.38 (m, 1 H, aliphatic CH in five-ring in 67), 3.32 (m, 4 H, aliphatic CH₂ in five-ring in *rac*-65), 2.98 (m, 1 H, aliphatic CH in five-ring in 67), 2.73 (dd, J = 2.52 Hz, 17.47 Hz, 1 H, aliphatic CH in five-ring in 67), 2.28 (dd, J = 2.48 Hz, 17.47 Hz, 1 H, aliphatic CH in five-ring in 66) ppm. The ratio between *rac*-65, 66 and 67 was 1.3:1:1. The yield of the reaction could not be determined due to the high-molecular-weight side-products present in the reaction product. ¹³C NMR (100.6 MHz, CDCl₃): quaternary carbons could not be determined from the carbon spectrum due to excessive number of signals from the side products, δ = 140.16 (2C, olefinic CH in chain in *rac*-65, 66 or 67), 136.22 (olefinic CH in five-ring in 66 and 67), 134.09 (2C, olefinic CH in chain in *rac*-65, 66 or 67), 132.84 (2 olefinic CH in five-ring in *rac*-65), 124.87 (2C, olefinic CH in chain in *rac*-65, 66 or 67), 115.61 (2 olefinic CH₂ in chain in *rac*-65), 115.20 (olefinic CH₂ in chain in 66 or 67), 114.10 (olefinic CH₂ in chain in 66 or 67), 51.58 (2 aliphatic CH in chain in *rac*-65), 50.29 (aliphatic CH in five-ring in 66 or olefinic CH in five-ring in 67), 49.81 (aliphatic CH in five-ring in 66 or olefinic CH in five-ring in 67), 46.37 (2 aliphatic CH₂ in five-ring in *rac*-65), 41.91 (aliphatic CH₂ in five-ring in 66 or 67) ppm. EIMS (70 eV): calcd. C₂₆H₂₂ 334.1722; found 334.1722.

2-Allyl-2,3-dihydro-1H-cyclopenta[*l*]phenanthren-2-ol (68) – Alkylation in the Presence of Zinc: By applying General Procedure 1,

zinc (0.5501 g; 8.4 mmol), 1,3-dihydro-cyclopenta[*l*]phenanthren-2-one (0.9793 g, 4.2 mmol), and allyl bromide (740 μ L, 8.4 mmol) gave, after a 24-h reaction time and column chromatography (dichloromethane as eluent), 0.0747 g (7%) of the title compound as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (m, 2 H, arom. CH), 7.79 (m, 2 H, arom. CH), 7.61 (m, 4 H, arom. CH), 6.06 (ddt, J = 7.25 Hz, 10.22 Hz, 17.47 Hz, 1 H, olefinic CH in chain), 5.26 (dm, J = 17.47 Hz, 1 H, olefinic CH in chain), 5.25 (dm, J = 10.22 Hz, 1 H, olefinic CH in chain) 3.43 (m, 4 H, aliphatic CH₂ in five-ring), 2.66 (m, 2 H, aliphatic CH₂ in chain), 2.13 (m, 1 H, OH) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 134.67 (2 C, C_q), 133.93 (olefinic CH in chain), 130.30 (2 C, C_q), 129.78 (2 C, C_q), 126.70 (2C, arom. CH), 125.83 (2 C, C_q), 124.73 (2 C, C_q), 123.15 (2 C, C_q), 119.26 (olefinic CH₂ in chain), 80.66 (C–OH), 46.22 (2 C, aliphatic CH₂ in five-ring), 45.91 (aliphatic CH₂ in chain) ppm. EIMS (70 eV): calcd. C₂₀H₁₈O 274.1358; found 274.1355.

2-Allyl-2,3-dihydro-1H-cyclopenta[*l*]phenanthren-2-ol (68) – Alkylation in the Presence of Indium. By applying General Procedure 2, indium powder (0.1812 g, 1.6 mmol), 1,3-dihydro-cyclopenta[*l*]phenanthren-2-one (0.067 g, 0.3 mmol), and allyl bromide (40 μ L, 0.4 mmol) gave, after column chromatography (dichloromethane as eluent), 0.0319 g (40%) of the title compound as a pale yellow oil.

2-(3-Triethoxysilylpropyl)indene (69): By applying General Procedure 6, 2-allyl-1H-indene (48) [0.8171 g, 5.2 mmol] and triethoxysilane (990 μ L, 5.2 mmol) gave, after column chromatography (dichloromethane as eluent), 0.797 g (48%) of the title compound as a pale yellow oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.41 (m, 1 H, arom. CH), 7.29 (m, 1 H, arom. CH), 7.25 (m, 1 H, arom. CH), 7.13 (m, 1 H, arom. CH), 6.54 (m, 1 H, olefinic CH in five-ring), 3.86 (m, 6 H, CH₂ in EtO groups), 3.33 (m, 2 H, aliphatic CH₂ in five-ring), 2.56 (m, 2 H, aliphatic CH₂ in chain), 1.77 (m, 2 H, aliphatic CH₂ in chain), 1.27 (m, 9 H, CH₃ in EtO groups), 0.74 (m, 2 H, aliphatic CH₂ in chain) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 150.57 (C_q), 145.80 (C_q), 143.27 (C_q), 126.64 (olefinic CH in five-ring), 126.31 (arom. CH), 123.65 (arom. CH), 123.48 (arom. CH), 119.99 (arom. CH), 58.48 (3C, CH₂ in EtO groups), 41.07 (aliphatic CH₂ in five-ring), 34.64 (aliphatic CH₂ in chain), 22.60 (aliphatic CH₂ in chain), 18.44 (3C, CH₃ in EtO groups), 10.42 (aliphatic CH₂ in chain) ppm. EIMS (70 eV): calcd. C₁₈H₂₈O₃Si 320.1808; found 320.1812.

2-(3-Triethylsilylpropyl)indene (70): By applying General Procedure 6, 2-allyl-1H-indene (48) [0.6880 g; 4.4 mmol] and triethylsilane (700 μ L, 4.4 mmol) gave, after column chromatography (hexane as eluent), 0.3434 g (29%) of the title compound as a colorless oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.53 (m, 1 H, arom. CH), 7.43 (m, 1 H, arom. CH), 7.38 (m, 1 H, arom. CH), 7.26 (m, 1 H, arom. CH), 6.67 (m, 1 H, olefinic CH in five-ring), 3.44 (m, 2 H, aliphatic CH₂ in five-ring), 2.66 (m, 2 H, aliphatic CH₂ in chain), 1.79 (m, 2 H, aliphatic CH₂ in chain), 1.13 (m, 9 H, CH₃ in Et groups), 0.77 (m, 2 H, aliphatic CH₂ in chain), 0.71 (m, 6 H, CH₂ in Et groups) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 150.79 (C_q), 145.86 (C_q), 143.24 (C_q), 126.50 (olefinic CH in five-ring), 126.33 (arom. CH), 123.64 (arom. CH), 123.48 (arom. CH), 119.94 (arom. CH), 41.08 (aliphatic CH₂ in five-ring), 35.56 (aliphatic CH₂ in chain), 23.74 (aliphatic CH₂ in chain), 11.61 (aliphatic CH₂ in chain), 7.63 (3C, CH₃ in Et- groups), 3.47 (3C, CH₂ in Et groups) ppm. EIMS (70 eV): calcd. C₁₈H₂₈Si 272.1960; found 272.1960.

2-(3-Triphenylsilylpropyl)indene (71): By applying General Procedure 6, 2-allyl-1H-indene (48) [0.6119 g, 3.9 mmol] and triphenylsilane (1.0459, 4.2 mmol) gave, after column chromatography (a mixture of 10% dichloromethane and 90% hexane as elu-

ent), 0.2467 g (15%) of the title compound as white crystals. Recrystallization from pentane at -20°C yielded 0.1118 g (7%) of white crystals. ^1H NMR (600 MHz, CDCl_3): δ = 7.43 (m, 6 H, arom. CH), 7.30 (m, 10 H, arom. CH), 7.14 (m, 2 H, arom. CH), 7.00 (m, 1 H, arom. CH), 6.36 (m, 1 H, olefinic CH in five-ring), 3.11 (m, 2 H, aliphatic CH_2 in five-ring), 2.45 (m, 2 H, aliphatic CH_2 in chain), 1.71 (m, 2 H, aliphatic CH_2 in chain), 1.35 (m, 2 H, aliphatic CH_2 in chain) ppm. ^{13}C NMR (150.9 MHz, CDCl_3): δ = 150.29 (C_q), 145.67 (C_q), 143.24 (C_q), 135.81 (6C, arom. CH), 135.25 (C_q), 129.56 (3C, arom. CH), 128.01 (6C, arom. CH), 126.87 (olefinic CH in five-ring), 126.37 (arom. CH), 123.73 (arom. CH), 123.51 (arom. CH), 119.98 (arom. CH), 41.06 (aliphatic CH_2 in five-ring), 35.14 (aliphatic CH_2 in chain), 23.66 (aliphatic CH_2 in chain), 13.16 (aliphatic CH_2 in chain) ppm. M.p. $127\text{--}128^{\circ}\text{C}$. EIMS (70 eV): calcd. $\text{C}_{30}\text{H}_{28}\text{Si}$ 416.1960; found 416.1953.

1-{[2-(Dimethyl-indenyl-silanyl)-ethyl]-dimethyl-silanyl}-indene (72): By applying General Procedure 6, 2-allyl-1H-indene (**48**) [0.3717 g, 2.4 mmol] and 1,2-bis-dimethyl-silyl-ethane (0.1782 g, 1.2 mmol) gave, after column chromatography (a mixture of 10% dichloromethane and 90% hexane as eluent), 0.3255 g (30%) of the title compound as a colorless oil. ^1H NMR (600 MHz, CDCl_3): δ = 7.45 (m, 2 H, arom. CH), 7.35 (m, 2 H, arom. CH), 7.30 (m, 2 H, arom. CH), 7.18 (m, 2 H, arom. CH), 6.59 (m, 2 H, olefinic CH in five-ring), 3.37 (m, 4 H, aliphatic CH_2 in five-ring), 2.59 (m, 4 H, aliphatic CH_2 in chain), 1.69 (m, 4 H, aliphatic CH_2 in chain), 0.66 (m, 4 H, aliphatic CH_2 in chain), 0.48 (m, 4 H, aliphatic CH_2 in chain between Si atoms), 0.07 (m, 12 H, CH_3 attached to Si) ppm. ^{13}C NMR (150.9 MHz, CDCl_3): δ = 150.88 (2C, C_q), 145.88 (2C, C_q), 143.30 (2C, C_q), 126.52 (2C, olefinic CH in five-ring), 126.34 (2C, arom. CH), 123.63 (2C, arom. CH), 123.49 (2C, arom. CH), 119.97 (2C, arom. CH), 41.08 (2C, aliphatic CH_2 in chain), 35.28 (2C, aliphatic CH_2 in chain), 23.76 (2C, aliphatic CH_2 in chain), 14.79 (2C, aliphatic CH_2 in chain), 7.30 (2C, aliphatic CH_2 in chain between Si atoms), 3.76 (4C, CH_3 attached to Si) ppm. EIMS (70 eV): calcd. $\text{C}_{30}\text{H}_{42}\text{Si}_2$ 458.2825; found 458.2829.

A Mixture of (1H-Inden-1-yl)-[3-(1H-inden-2-yl)propyl]-dimethyl-silane (73) and (3H-Inden-1-yl)-[3-(1H-inden-2-yl)propyl]-dimethyl-silane (74): By applying General Procedure 6, 2-allyl-1H-indene (**48**) [0.4618 g, 3.0 mmol] and (1H-Inden-1-yl)-dimethyl-silane (containing ca 10% of (3H-inden-1-yl)-dimethyl-silane as impurity, 0.5221, 1.3 mmol) gave, after column chromatography (a mixture of 10% dichloromethane and 90% hexane as eluent), 0.0310 g (3%) of the mixture of the title compounds as a pale yellow oil. ^1H NMR (600 MHz, CDCl_3): δ = 7.54 (m, 2 H, arom. CH in **74**), 7.50 (m, 2 H, arom. CH in **73** and **74**), 7.46 (m, 1 H, arom. CH in **73**), 7.41 (m, 1 H, arom. CH in **73**), 7.28 (m, 6 H, arom. CH in **73** and **74**), 7.19 (m, 2 H, arom. CH in **73** and **74**), 7.14 (m, 2 H, arom. CH in **73** and **74**), 6.95 (m, 1 H, olefinic CH in five-ring in **74**), 6.94 (m, 1 H, olefinic CH in five-ring in **73**), 6.81 (m, 1 H, olefinic CH in five-ring in **74**), 6.67 (m, 1 H, olefinic CH in five-ring in **73**), 6.49 (m, 1 H, olefinic CH in five-ring in **73**), 3.59 (m, 1 H, aliphatic CH in five-ring in **73**), 3.46 (m, 2 H, aliphatic CH_2 in five-ring in **74**), 3.27 (m, 4 H, aliphatic CH_2 in five-ring in **73** and **74**), 2.53 (m, 2 H, aliphatic CH_2 in chain in **74**), 2.47 (m, 2 H, aliphatic CH_2 in chain in **73**), 1.69 (m, 2 H, aliphatic CH_2 in chain in **74**), 1.55 (m, 2 H, aliphatic CH_2 in chain in **73**), 0.92 (m, 2 H, aliphatic CH_2 in chain in **74**), 0.58 (m, 2 H, aliphatic CH_2 in chain in **73**), 0.35 (s, 6 H, CH_3 attached to Si in **74**), 0.01 (s, 3 H, CH_3 attached to Si in **73**), -0.03 (s, 3 H, CH_3 attached to Si in **73**) ppm. ^{13}C NMR (150.9 MHz, CDCl_3): δ = 150.74 (C_q in **74**), 150.51 (C_q in **73**), 148.26 (C_q in **74**), 145.81 (C_q in **74**), 145.77 (C_q in **73**), 145.40 (C_q in **73**), 144.87 (olefinic CH in five-ring in **74**), 144.72 (C_q in **74**), 144.52 (C_q in **74**), 144.28 (C_q in **73**), 143.27 (C_q in **74**), 143.23 (C_q

in **73**), 135.74 (olefinic CH in five-ring in **73**), 134.99 (olefinic CH in five-ring in **74**), 129.07 (olefinic CH in five-ring in **73**), 126.60 (olefinic CH in five-ring in **73**), 126.36 (arom. CH in **73**), 126.20 (arom. CH in **74**), 125.10 (arom. CH in **74**), 124.93 (arom. CH in **73**), 124.38 (arom. CH in **74**), 123.89 (arom. CH in **74**), 123.85 (arom. CH in **74**), 123.74 (arom. CH in **73**), 123.69 (arom. CH in **73**), 123.62 (arom. CH in **74**), 123.53 (arom. CH in **73**), 122.83 (arom. CH in **73**), 122.10 (arom. CH in **74**), 121.16 (arom. CH in **73**), 120.01 (arom. CH in **73**), 119.97 (arom. CH in **74**), 45.71 (aliphatic CH in five-ring in **73**), 41.06 (3C, aliphatic CH_2 in five-ring in **73** and **74**), 35.06 (2 C, aliphatic CH_2 in chain in **73** and **74**), 23.60 (2 C, aliphatic CH_2 in chain in **73** and **74**), 14.50 (2 C, aliphatic CH_2 in chain in **73** and **74**), -2.73 (2C, CH_3 attached to Si in **74**), -3.77 (CH_3 attached to Si in **73**), -4.17 (CH_3 attached to Si in **73**) ppm. EIMS (70 eV): calcd. $\text{C}_{23}\text{H}_{26}\text{Si}$ 330.1804; found 330.1807.

2-(3-Naphthylphenylmethylsilylpropyl)indene (75): By applying General Procedure 6, 2-allyl-1H-indene (**48**) [0.1812 g, 1.2 mmol] and (+)-(R)-methyl-1-naphthalenylphenylsilane (0.3112, 1.3 mmol) gave, after column chromatography (a mixture of 10% dichloromethane and 90% hexane as eluent), 0.0627 g (13%) of the title compound as a colorless oil. ^1H NMR (600 MHz, CDCl_3): δ = 7.91 (m, 2 H, arom. CH), 7.86 (m, 1 H, arom. CH), 7.75 (m, 1 H, arom. CH), 7.53 (m, 2 H, arom. CH), 7.46 (m, 1 H, arom. CH), 7.42 (m, 1 H, arom. CH), 7.31 (m, 5 H, arom. CH), 7.21 (m, 2 H, arom. CH), 7.10 (m, 1 H, arom. CH), 6.43 (m, 1 H, olefinic CH in five-ring), 3.17 (m, 2 H, aliphatic CH_2 in five-ring), 2.52 (m, 2 H, aliphatic CH_2 in chain), 1.70 (m, 2 H, aliphatic CH_2 in chain), 1.34 (m, 2 H, aliphatic CH_2 in chain), 0.73 (s, 3 H, CH_3 attached to Si) ppm. ^{13}C NMR (150.9 MHz, CDCl_3): δ = 150.39 (C_q), 145.75 (C_q), 143.25 (C_q), 138.14 (C_q), 137.19 (C_q), 135.06 (arom. CH), 134.81 (C_q), 134.53 (2C, arom. CH), 133.56 (C_q), 130.40 (arom. CH), 129.23 (arom. CH), 129.09 (arom. CH), 128.64 (arom. CH), 128.02 (2C, arom. CH), 126.79 (arom. CH), 126.34 (olefinic CH in five-ring), 125.80 (arom. CH), 125.54 (arom. CH), 125.21 (arom. CH), 123.63 (arom. CH), 213.48 (arom. CH), 119.93 (arom. CH), 41.00 (aliphatic CH_2 in five-ring), 34.93 (aliphatic CH_2 in chain), 23.62 (aliphatic CH_2 in chain), 14.92 (aliphatic CH_2 in chain), -2.67 (CH_3 attached to Si) ppm. $[\alpha]_D^{25} -0.9^{\circ}$ (c, 0.0264 g/mL CHCl_3). EIMS (70 eV): calcd. $\text{C}_{29}\text{H}_{28}\text{Si}$ 404.1960; found 404.1957.

A Diastereomeric Mixture of 2-(1-Methyl-3-naphthylphenylmethylsilylpropyl)indene (76 and 77): By applying General Procedure 6, an enantiomeric mixture of 2-(1-methyl-allyl)-1H-indene (*rac*-**50**) [0.4039 g, 2.4 mmol] and (+)-(R)-methyl-1-naphthalenylphenylsilane (0.6014, 2.4 mmol) gave, after column chromatography (a mixture of 10% dichloromethane and 90% hexane as eluent), 0.2057 g (21%) of a 1:1 diastereomeric mixture of the title compounds as a colorless oil. ^1H NMR (600 MHz, CDCl_3): δ = 7.78 (m, 6 H, arom. CH in **76** and/or **77**), 7.61 (m, 2 H, arom. CH in **76** and/or **77**), 7.39 (m, 4 H, arom. CH in **76** and/or **77**), 7.35 (m, 4 H, arom. CH in **76** and/or **77**), 7.22 (m, 8 H, arom. CH in **76** and/or **77**), 7.14 (m, 6 H, arom. CH in **76** and/or **77**), 7.00 (m, 2 H, arom. CH in **76** and/or **77**), 6.35 (m, 2 H, olefinic CH in five-ring in **76** and **77**), 3.03 (m, 4 H, aliphatic CH_2 in five-ring in **76** and **77**), 2.53 (m, 2 H, aliphatic CH in chain in **76** and **77**), 1.48 (m, 4 H, aliphatic CH_2 in chain in **76** and/or **77**), 1.15 (m, 4 H, aliphatic CH_2 in chain in **76** and/or **77**), 1.06 (m, 6 H, CH_3 attached to the aliphatic chain in **76** and **77**), 0.60 (s, 6 H, CH_3 attached to Si in **76** and **77**) ppm. ^{13}C NMR (150.9 MHz, CDCl_3): δ = 153.31 (C_q in **76** and/or **77**), 145.63 (C_q in **76** and/or **77**), 143.22 (C_q in **76** and/or **77**), 137.16 (C_q in **76** and/or **77**), 133.52 (C_q in **76** and/or **77**), 135.08 (arom. CH in **76** and/or **77**), 134.48 (arom. CH in **76** and/or **77**), 130.35 (arom. CH in **76** and/or **77**), 129.19 (arom. CH in **76** and/or **77**),

129.08 (arom. CH in **76** and/or **77**), 128.58 (arom. CH in **76** and/or **77**), 127.99 (arom. CH in **76** and/or **77**), 126.31 (arom. CH in **76** and/or **77**), 126.03 (olefinic CH in five-ring in **76** and **77**), 125.75 (arom. CH in **76** and/or **77**), 125.50 (arom. CH in **76** and/or **77**), 125.19 (arom. CH in **76** and/or **77**), 123.66 (arom. CH in **76** and/or **77**), 123.62 (arom. CH in **76** and/or **77**), 120.08 (arom. CH in **76** and/or **77**), 38.63 (aliphatic CH in chain in **76** or **77**), 38.57 (aliphatic CH in chain in **76** or **77**), 38.51 (aliphatic CH₂ in five-ring in **76** or **77**), 38.48 (aliphatic CH₂ in five-ring in **76** or **77**), 30.93 (aliphatic CH₂ in **76** and **77**), 20.54 (CH₃ attached to the aliphatic chain in **76** or **77**), 20.40 (CH₃ attached to the aliphatic chain in **76** or **77**), 12.56 (aliphatic CH₂ in chain in **76** or **77**), 12.38 (aliphatic CH₂ in chain in **76** or **77**), -2.72 (CH₃ attached to Si in **76** or **77**), -2.76 (CH₃ attached to Si in **76** or **77**) ppm. EIMS (70 eV): calcd. C₃₀H₃₀Si 418.2117; found 418.2115.

A Diastereomeric Mixture of 2-(1-Phenyl-3-naphthylphenylmethylsilylpropyl)indene (78 and 79): By applying General Procedure 6, an enantiomeric mixture of 2-(1-phenyl-allyl)-1H-indene (*rac*-**52**) [0.2590 g, 1.1 mmol] and (+)-(*R*)-methyl-1-naphthalenylphenylsilane (0.2716, 1.1 mmol) gave, after column chromatography (a mixture of 10% dichloromethane and 90% hexane as eluent), 0.1318 g (25%) of a 1:1 diastereomeric mixture of the title compounds as a colorless oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.95 (m, 6 H, arom. CH in **78** and/or **79**), 7.76 (m, 2 H, arom. CH in **78** and/or **79**), 7.57 (m, 4 H, arom. CH in **78** and/or **79**), 7.54 (m, 4 H, arom. CH in **78** and/or **79**), 7.42 (m, 2 H, arom. CH in **78** and/or **79**), 7.35 (m, 6 H, arom. CH in **78** and/or **79**), 7.31 (m, 12 H, arom. CH in **78** and/or **79**), 7.19 (m, 4 H, arom. CH in **78** and/or **79**), 7.14 (m, 2 H, arom. CH in **78** and/or **79**), 6.55 (m, 1 H, olefinic CH in five-ring in **78** or **79**), 6.53 (m, 1 H, olefinic CH in five-ring in **78** or **79**), 3.73 (m, 2 H, aliphatic CH in chain in **78** and **79**), 3.16 (m, 4 H, aliphatic CH₂ in five-ring in **78** and **79**), 2.13 (m, 4 H, aliphatic CH₂ in chain in **78** and **79**), 1.37 (m, 4 H, aliphatic CH₂ in chain in **78** and **79**), 0.80 (s, 3 H, CH₃ attached to Si in **78** or **79**) ppm. ¹³C NMR (150.9 MHz, CDCl₃): δ = 153.12 (C_q in **78** and/or **79**), 152.98 (C_q in **78** and/or **79**), 145.25 (C_q in **78** and/or **79**), 144.22 (C_q in **78** and/or **79**), 144.10 (C_q in **78** and/or **79**), 143.31 (C_q in **78** and/or **79**), 138.01 (C_q in **78** and/or **79**), 137.92 (C_q in **78** and/or **79**), 137.19 (C_q in **78** and/or **79**), 135.16 (arom. CH in **78** and/or **79**), 135.12 (arom. CH in **78** and/or **79**), 134.59 (C_q in **78** and/or **79**), 134.56 (C_q in **78** and/or **79**), 134.52 (arom. CH in **78** and/or **79**), 133.58 (C_q in **78** and/or **79**), 133.56 (C_q in **78** and/or **79**), 130.46 (arom. CH in **78** and/or **79**), 129.26 (arom. CH in **78** and/or **79**), 129.12 (arom. CH in **78** and/or **79**), 129.09 (arom. CH in **78** and/or **79**), 128.60 (arom. CH in **78** and/or **79**), 128.52 (arom. CH in **78** and/or **79**), 128.09 (arom. CH in **78** and/or **79**), 128.05 (arom. CH in **78** and/or **79**), 126.44 (arom. CH in **78** and/or **79**), 126.41 (arom. CH in **78** and/or **79**), 126.34 (olefinic CH in five-ring in **78** and **79**), 125.81 (arom. CH in **78** and/or **79**), 125.54 (arom. CH in **78** and/or **79**), 125.51 (arom. CH in **78** and/or **79**), 125.21 (arom. CH in **78** and/or **79**), 123.95 (arom. CH in **78** and/or **79**), 123.54 (arom. CH in **78** and/or **79**), 120.39 (arom. CH in **78** and/or **79**), 51.10 (aliphatic CH in chain in **78** or **79**), 51.04 (aliphatic CH in chain in **78** or **79**), 40.04 (aliphatic CH₂ in five-ring in **78** and **79**), 29.26 (aliphatic CH₂ in chain in **78** or **79**), 29.20 (aliphatic CH₂ in chain in **78** or **79**), 13.48 (aliphatic CH₂ in chain in **78** or **79**), 13.44 (aliphatic CH₂ in chain in **78** or **79**), -2.67 (CH₃ attached to Si in **78** or **79**), -2.70 (CH₃ attached to Si in **78** or **79**) ppm. EIMS (70 eV): calcd. C₃₅H₃₂Si 480.2273; found 480.2267.

Supporting Information: Copies of ¹³C NMR spectra of the compounds reported are provided.

Acknowledgments

Financial support from the Neste Research Foundation is gratefully acknowledged. We also thank Doc. Leif Kronberg, Mr. Markku Reunanen and Mrs. Päivi Pennanen for their assistance with the ESIMS, EIMS and NMR analyses, and Ms. Elise Johansson for preparing the chiral (+)-(*R*)-methyl-1-naphthalenylphenylsilane.

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Received November 3, 2004