

# 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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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/NH<sub>4</sub>Cl<sub>aq</sub> 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.<sup>[1]</sup> In particular, group 4 bis(indenyl) metallocenes are frequently employed catalyst precursors for stereospecific polymerization of alkenes,<sup>[2]</sup> and are being used as reagents and catalysts for various stereo- and/or enantioselective organic transformations.<sup>[3]</sup> A remarkable example of an organozirconium success story in organic synthesis is the enantioselective carboalumination of alkenes catalyzed by chiral zirconocene dichlorides,<sup>[4]</sup> applied recently to the synthesis of complex natural products.<sup>[5]</sup> Other applications of chiral zirconocenes in stereoselective synthesis include those in enantioselective cyclopolymerization of nonconjugated dienes,<sup>[6]</sup> as well as applications in other carbon–carbon,<sup>[7]</sup> carbon–hydrogen,<sup>[8]</sup> and carbon–oxygen<sup>[9]</sup> 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,<sup>[10]</sup> 1- (or 3-) and 2-alkyl/aryl,<sup>[1a,11,12]</sup> as well as various heteroatom-substituted indenenes.<sup>[13]</sup> 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.<sup>[14]</sup> 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.<sup>[15]</sup> In contrast to alkylolithium 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<sup>[16]</sup> and 2-indanone with tetraallylstannane<sup>[17]</sup> in dichloromethane resulted in the formation of the corresponding 1- and 2-substituted allylhydroxyindanes in high yields. Likewise, Bi(OTf)<sub>3</sub>-catalyzed allylation of indene oxide with tetraallylstannane<sup>[18]</sup> and the indium(I) chloride mediated allylation of indene oxide with allyl bromide catalyzed by Pd<sup>[19]</sup> has provided 2-allylhydroxyindane in 85 and 83% yields, respectively. These allylindanols 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.<sup>[20]</sup> 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.<sup>[21]</sup> Likewise, bis(2-alkenylindenyl)zirconium dichlorides were recently converted into

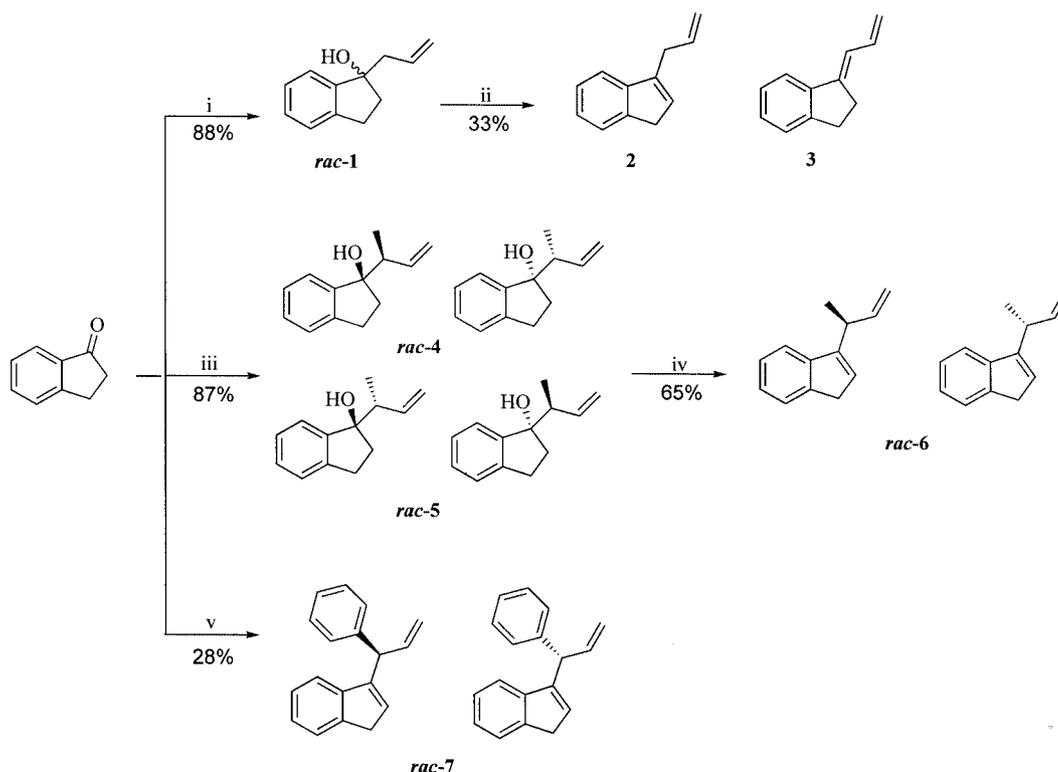
bridged *ansa*-metallocenes by a photochemical [2+2] cycloaddition reaction.<sup>[22]</sup> Further examples of developing functional group chemistry on bent group 4 metallocene frameworks have been collected in a recent review.<sup>[23]</sup>

## 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 <sup>1</sup>H and <sup>13</sup>C 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, NH<sub>4</sub>Cl<sub>aq</sub>/THF. (ii) Amberlyst 15, pentane. (iii) Crotyl bromide, Zn, NH<sub>4</sub>Cl<sub>aq</sub>/THF. (iv) Amberlyst 15, pentane. (v) Cinnamyl chloride, Zn, NH<sub>4</sub>Cl<sub>aq</sub>/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.<sup>[12c,24]</sup>

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 <sup>1</sup>H 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.

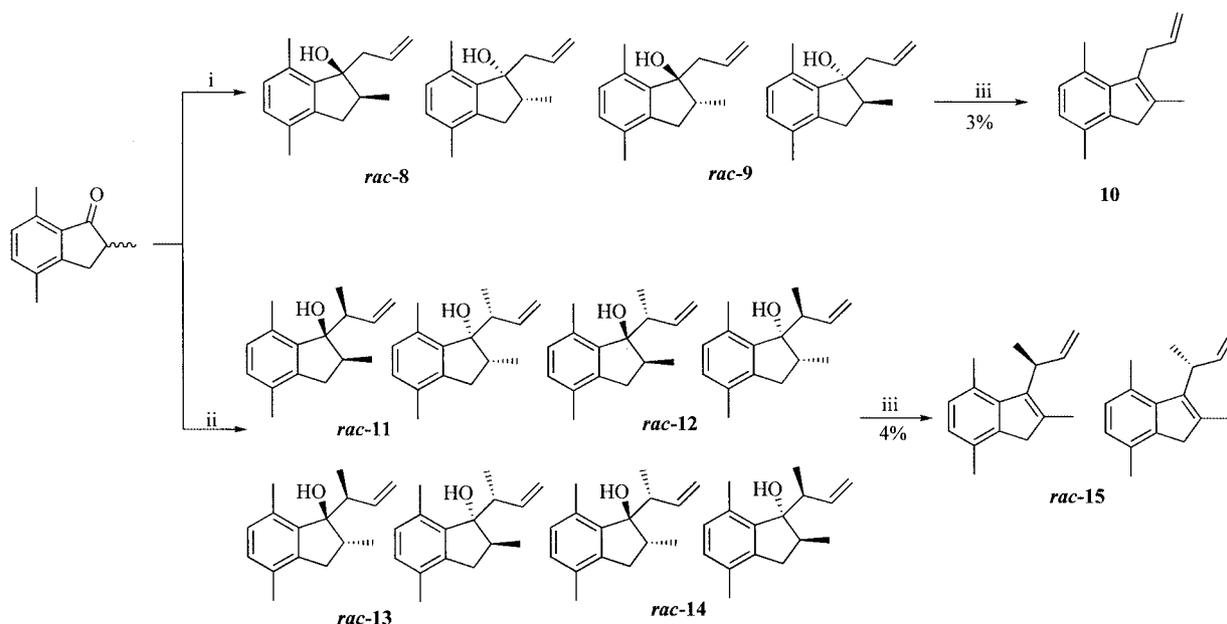
The allylation of 1-indanone with cinnamyl chloride, likewise, initially yielded a diastereomeric mixture of four allylindanol, which, however, due to their high lability, spontaneously eliminated water upon storage at -20 °C overnight to provide the 3-(1-phenylallyl)indene *rac-7* in 28% isolated overall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

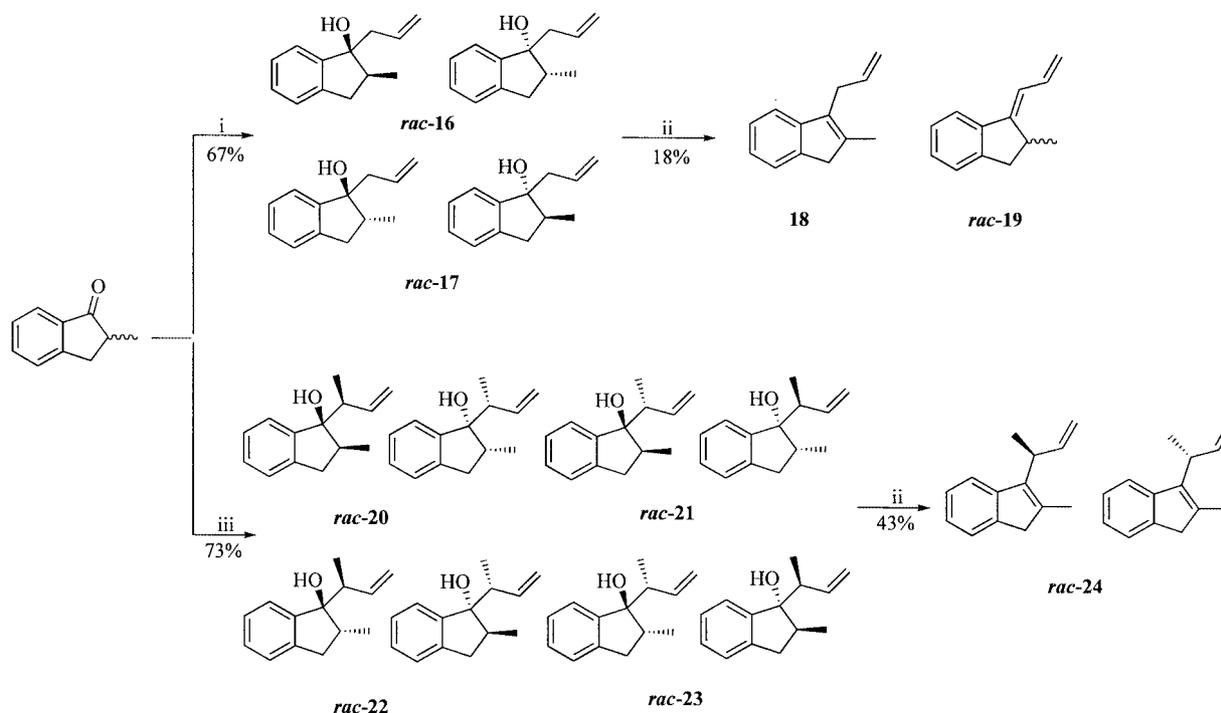
Amberlyst 15 in pentane (Scheme 2). The indenenes **10** and *rac-15* were obtained in poor overall yields of 3% and 4% over two steps, respectively, after purification by column chromatography. All attempts to react 2,4,7-trimethyl-1-indanone with cinnamyl chloride failed. The total failure with cinnamyl 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.

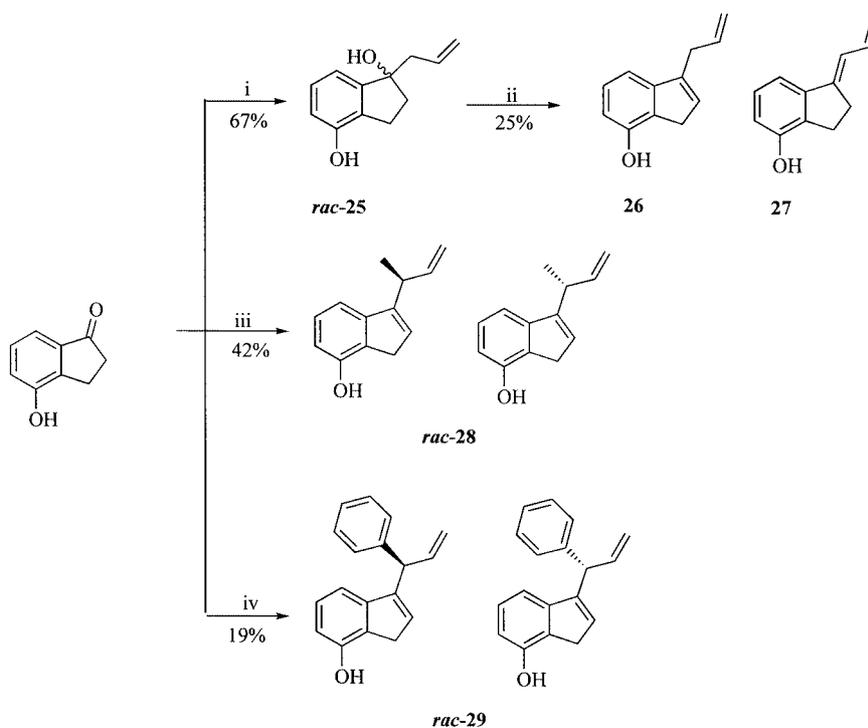
Next, in order to further broaden the usability of the method, a series of functionalized 1-indanones were investigated. The zinc-mediated allylation of 4-hydroxy-1-indanone with allyl bromide yielded the desired allylindandiol *rac-25* in 67% yield, which upon dehydration, gave an in-



Scheme 2. (i) Allyl bromide, Zn, NH<sub>4</sub>Cl<sub>aq</sub>/THF. (ii) Crotyl bromide, Zn, NH<sub>4</sub>Cl<sub>aq</sub>/THF. (iii) Amberlyst 15, pentane.



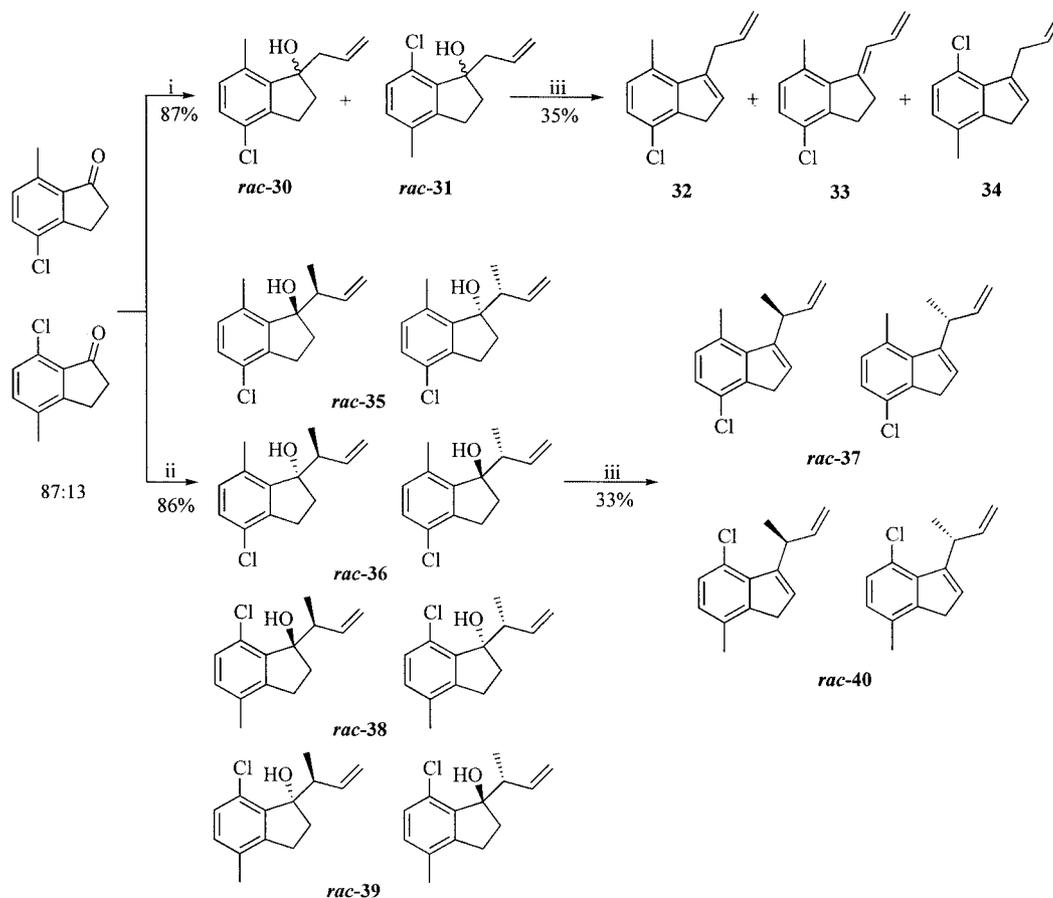
Scheme 3. (i) Allyl bromide, Zn,  $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii) Amberlyst 15, pentane. (iii) Crotyl bromide, Zn,  $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF.



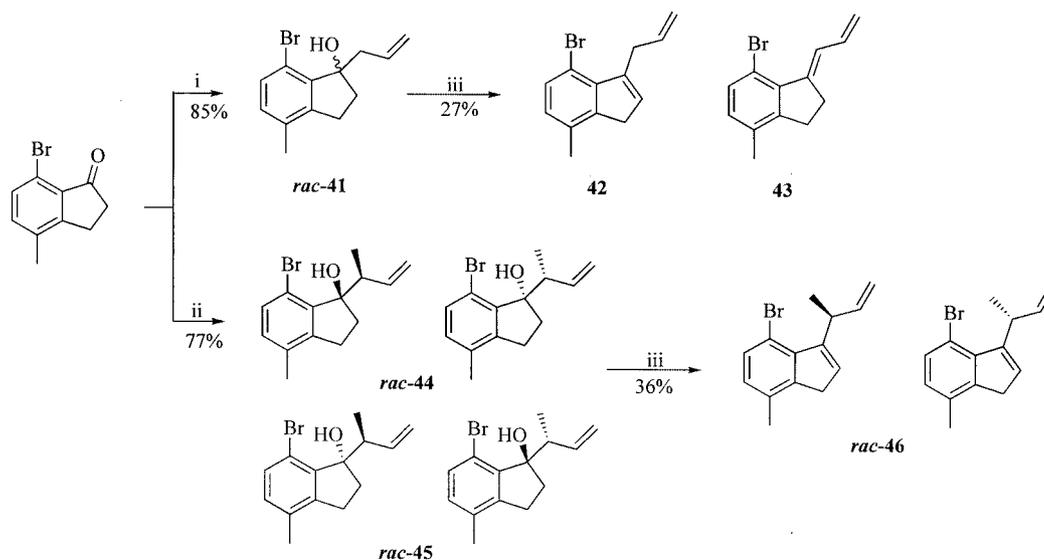
Scheme 4. (i) Allyl bromide, Zn,  $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii)  $\text{MgSO}_4$ , toluene, reflux. (iii) Crotyl bromide, Zn,  $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (iv) Cinnamyl chloride, Zn,  $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF.

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-hydroxyindenones **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<sup>3</sup>-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, NH<sub>4</sub>Cl<sub>aq</sub>/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.

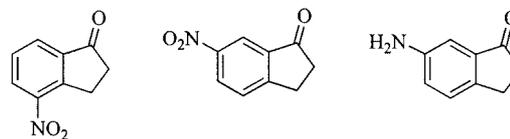
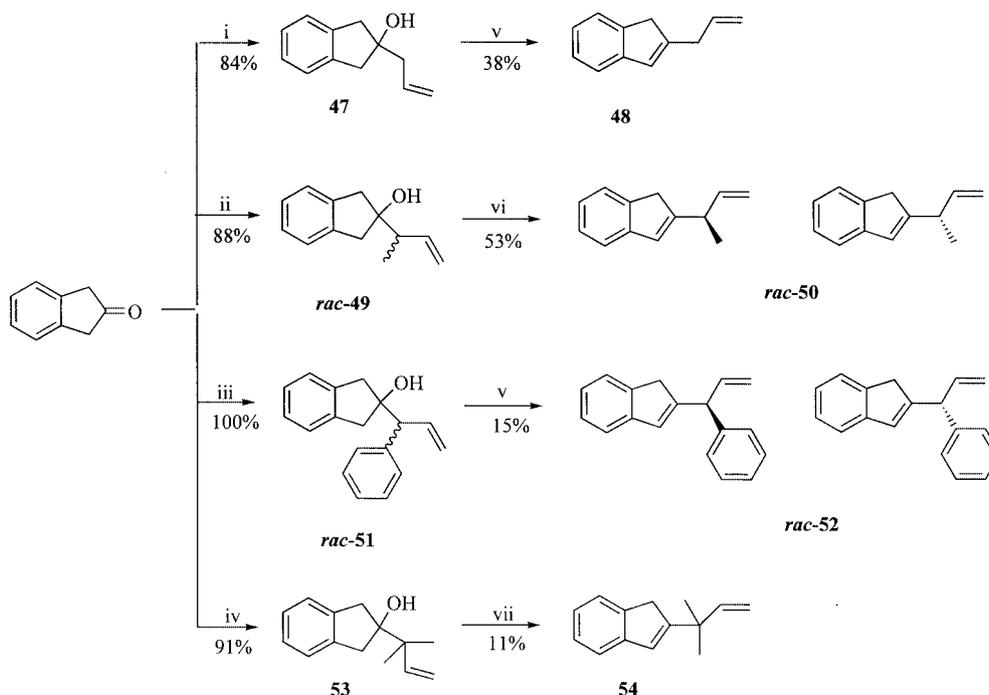


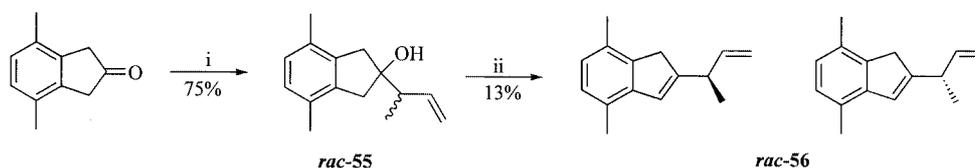
Figure 1. Nitro- and amino-substituted 1-indanones yielding no reaction with crotyl bromide/Zn and crotyl bromide/In.

### 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.<sup>[8c]</sup> Syntheses of 2-allylindene by Rh-catalyzed allylation of indene with allyl tosylate in 19% yield<sup>[25]</sup> and by reaction of 2-indanone with allylmagnesium bromide followed by subsequent dehydration with *p*-TsOH in 30–40% overall yield<sup>[26]</sup> 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, NH<sub>4</sub>Cl<sub>aq</sub>/THF. (ii) Crotyl bromide, Zn, NH<sub>4</sub>Cl<sub>aq</sub>/THF. (iii) Cinnamyl chloride, Zn, NH<sub>4</sub>Cl<sub>aq</sub>/THF. (iv) Prenyl bromide, Zn, NH<sub>4</sub>Cl<sub>aq</sub>/THF. (v) *p*-TSA, toluene, reflux. (vi) H<sub>2</sub>SO<sub>4</sub>, toluene, reflux. (vii) Amberlyst 15, pentane.



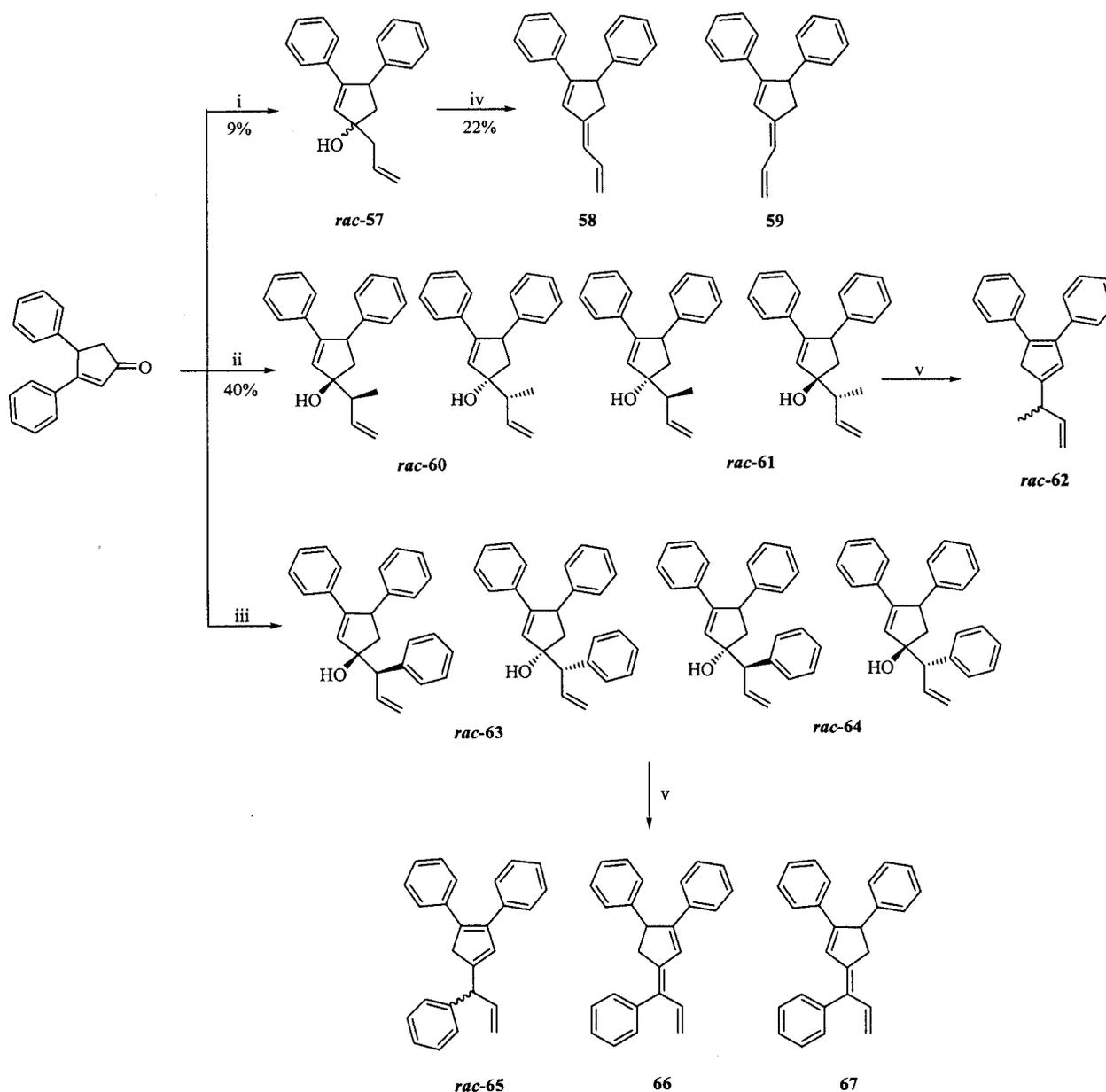
Scheme 9. (i) Crotyl bromide, Zn,  $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii) Amberlyst 15, pentane.

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

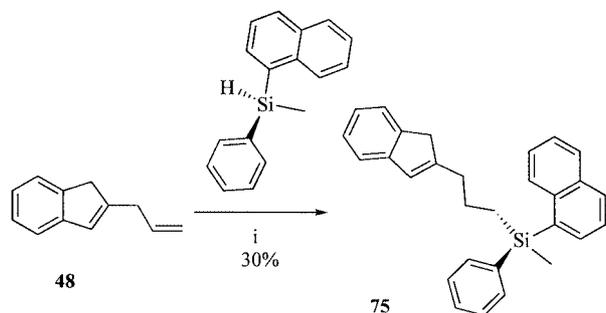


Scheme 10. (i) Allyl bromide, Zn,  $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (ii) Crotyl bromide, Zn,  $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (iii) Cinnamyl chloride, Zn,  $\text{NH}_4\text{Cl}_{\text{aq}}$ /THF. (iv) Amberlyst 15, pentane. (v)  $\text{MgSO}_4$ , toluene, reflux.

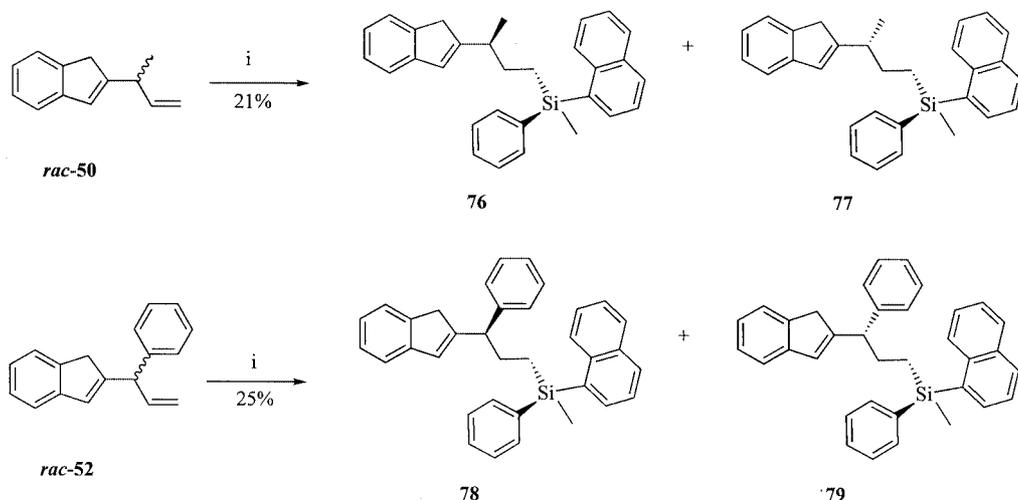


hydrosilylation of 2-allylindene (**48**) in the presence of Karstedt's catalyst with triethoxysilane, triethylsilane, triphenylsilane, 1,2-bis(dimethylsilyl)ethane, and a 90:10 mixture of the 1- and 3-indenyl isomers of indenyl dimethylsilane (Scheme 12). In addition, a readily available chiral silane, (+)-(*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.<sup>[28]</sup> Finally, the chiral indene **75** was obtained in 30% isolated yield by hydrosilylation of 2-allylindene with (+)-(*R*)-methyl-1-naphthalenylphenylsilane.<sup>[29]</sup> 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.<sup>[30]</sup>

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.



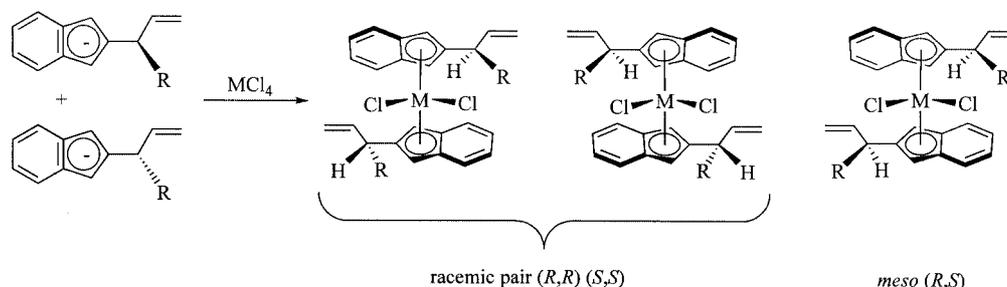
Scheme 14. (i) (+)-(*R*)-Methyl-1-naphthalenylphenylsilane, Karstedt's catalyst, toluene.

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  $\pi$  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),<sup>[1a]</sup> a situation analogous to the preparation of conventional bridged bis(indenyl) *ansa*-metallocenes.<sup>[31]</sup> These, in turn, are potentially separable into the pure *rac*- and *meso* diastereomers by standard recrystallization techniques.<sup>[32]</sup> 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<sup>[33]</sup> 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.<sup>[13]</sup> 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.<sup>[34]</sup> For example, compound **55** carrying a triethoxysilyl functionality may provide access to immobilization of indenyl ligands and/or metallocenes to silica supports.<sup>[35]</sup> 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,<sup>[36]</sup> 2-methyl-1-indanone,<sup>[37]</sup> 4-nitro-1-indanone,<sup>[38]</sup> 6-nitro-1-indanone,<sup>[38]</sup> 6-amino-1-indanone,<sup>[38]</sup> 4,7-dimethyl-2-indanone,<sup>[39]</sup> 3,4-diphenyl-cyclopent-2-enone,<sup>[40]</sup> 1,3-dihydro-cyclopenta[*f*]phenanthren-2-one,<sup>[41]</sup> 4-methyl-7-bromo-1-indanone,<sup>[42]</sup> the 87:13 mixture of 4-chloro-7-methyl-1-indanone and 4-methyl-7-chloro-1-indanone,<sup>[43]</sup> dimethylsilylindene,<sup>[44]</sup> and (+)-(*R*)-methyl-1-naphthalenylphenylsilane<sup>[45]</sup> were synthesized according to literature procedures. Flash chromatography was performed on silica gel 60 (40–63  $\mu$ m). Purification by preparative TLC was performed on a 1 mm silica gel 60 (40–63  $\mu$ m) plate containing F<sub>254</sub>. NMR spectra were recorded at 298 K with a Bruker Avance 600 (<sup>1</sup>H NMR 600 MHz, <sup>13</sup>C NMR 150.9 MHz), a Jeol L-400 (<sup>1</sup>H NMR 400 MHz, <sup>13</sup>C 100.6 MHz) or with a Bruker 250 MHz instrument (<sup>1</sup>H NMR 250 MHz). <sup>1</sup>H NMR chemical shifts were referenced to residual <sup>1</sup>H impurities in the solvent relative to TMS, and <sup>13</sup>C NMR chemical shifts, to the solvent signals. The NMR spectra were recorded (in  $\delta$  values) with deuteriochloroform or [D<sub>4</sub>]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 NH<sub>4</sub>Cl<sub>aq</sub> (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 Et<sub>2</sub>O (3  $\times$  50 mL) and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>, 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 Na<sub>2</sub>SO<sub>4</sub>, 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 Et<sub>2</sub>O (50 mL). The organic layer was washed with saturated NH<sub>4</sub>Cl<sub>aq</sub> (50 mL), dried with Na<sub>2</sub>SO<sub>4</sub>, 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:** MgSO<sub>4</sub> 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 silylalkyl-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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 146.99 (2 C<sub>q</sub>), 142.95 (2 C<sub>q</sub>), 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 CH<sub>2</sub> in chain), 82.70 (2 C-OH), 44.94 (2 aliphatic CH<sub>2</sub> in chain), 39.62 (2 aliphatic CH<sub>2</sub> in five-ring), 29.37 (2 aliphatic CH<sub>2</sub> in five-ring) ppm. EIMS (30 eV): calcd. C<sub>12</sub>H<sub>14</sub>O 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> in chain in 2 and aliphatic CH<sub>2</sub> in five-ring in 2), 3.06 (m, 2 H, aliphatic CH<sub>2</sub> in five-ring in 3), 2.92 (m, 2 H, aliphatic CH<sub>2</sub> in five-ring in 3) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 146.88 (C<sub>q</sub>), 145.07 (2 C<sub>q</sub>), 144.47 (C<sub>q</sub>), 142.44 (C<sub>q</sub>), 141.30 (C<sub>q</sub>), 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 CH<sub>2</sub> in chain in 2 or 3), 115.92 (olefinic CH<sub>2</sub> in chain in 2 or 3), 37.72 (aliphatic CH<sub>2</sub> in five-ring or chain in 2), 32.43 (aliphatic CH<sub>2</sub> in five-ring or chain in 2), 30.12 (aliphatic CH<sub>2</sub> in five-ring in 3), 28.18 (aliphatic CH<sub>2</sub> in five-ring in 3) ppm. EIMS (30 eV): calcd. C<sub>12</sub>H<sub>12</sub> 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. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 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, CH<sub>3</sub> in major), 0.95 (d, *J* = 7.22 Hz, 6 H, CH<sub>3</sub> in minor) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>): δ = 146.42 (2 C<sub>q</sub> in major), 145.94 (2 C<sub>q</sub> in minor), 143.81 (2 C<sub>q</sub> in minor), 143.53 (2 C<sub>q</sub> 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 CH<sub>2</sub> in minor), 115.65 (2 olefinic CH<sub>2</sub> 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 CH<sub>2</sub> in five-ring in major), 36.29 (2 aliphatic CH<sub>2</sub> in five-ring in minor), 30.08 (2 aliphatic CH<sub>2</sub> in five-ring in minor), 29.83 (2 aliphatic CH<sub>2</sub> in five-ring in major), 15.32 (2 CH<sub>3</sub> in minor), 13.65 (2 CH<sub>3</sub> in major) ppm. EIMS (30 eV): calcd. C<sub>13</sub>H<sub>16</sub>O 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> in five-ring), 1.44 (d, *J* = 7.02 Hz, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 147.64 (2 C<sub>q</sub>), 144.71 (2 C<sub>q</sub>), 144.66 (2 C<sub>q</sub>), 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 CH<sub>2</sub> in chain), 37.64 (2 aliphatic CH<sub>2</sub> in five-ring), 36.55 (2 aliphatic CH in chain), 19.06 (CH<sub>3</sub>) ppm. EIMS (70 eV): calcd. C<sub>13</sub>H<sub>14</sub> 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 ~ 6) reaction mixture was extracted with diethyl ether ( $3 \times 50$  mL), and the combined organic layers were dried with  $\text{Na}_2\text{SO}_4$  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  $-20^\circ\text{C}$  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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in five-ring) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 145.63 (2  $\text{C}_q$ ), 144.54 (2  $\text{C}_q$ ), 144.47 (2  $\text{C}_q$ ), 141.49 (2  $\text{C}_q$ ), 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  $\text{CH}_2$  in chain), 48.87 (2 aliphatic CH in chain), 37.76 (2 five-ring aliphatic  $\text{CH}_2$ ) 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%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in chain), 3.10 (m, 2 H, aliphatic  $\text{CH}_2$  in five-ring), 2.43 (s, 3 H,  $\text{CH}_3$  attached to the aromatic ring), 2.21 (s, 3 H,  $\text{CH}_3$  attached to the aromatic ring), 1.98 (s, 3 H,  $\text{CH}_3$  attached to the five-ring) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 143.54 ( $\text{C}_q$ ), 141.55 ( $\text{C}_q$ ), 140.05 ( $\text{C}_q$ ), 136.49 (olefinic CH in chain), 135.52 ( $\text{C}_q$ ), 129.87 ( $\text{C}_q$ ), 129.76 ( $\text{C}_q$ ), 129.45 (arom. CH), 124.78 (arom. CH), 115.00 (olefinic  $\text{CH}_2$  in chain), 41.51 (aliphatic  $\text{CH}_2$  in five-ring), 30.75 (aliphatic  $\text{CH}_2$  in chain), 19.30 ( $\text{CH}_3$  attached to the aromatic ring), 18.24 ( $\text{CH}_3$  attached to the aromatic ring), 13.88 ( $\text{CH}_3$  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%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in five-ring), 2.58 (s, 6 H,  $\text{CH}_3$  attached to the aromatic ring), 2.32 (s, 6 H,  $\text{CH}_3$  attached to the aromatic ring), 2.14 (s, 6 H,  $\text{CH}_3$  attached to the five-ring), 1.44 (d,  $J$  = 7.17 Hz, 6 H,  $\text{CH}_3$  attached to the aliphatic chain) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 143.77 (2  $\text{C}_q$ ), 142.43 (2 olefinic CH in chain), 141.68 (2  $\text{C}_q$ ), 140.88 (2  $\text{C}_q$ ), 139.66 (2  $\text{C}_q$ ), 130.16 (2 arom. CH), 129.91 (2  $\text{C}_q$ ), 126.92 (2  $\text{C}_q$ ), 124.66 (2 arom. CH), 112.44 (2 olefinic  $\text{CH}_2$  in chain), 42.79 (2 aliphatic  $\text{CH}_2$  in five-ring), 34.96 (2 aliphatic CH in chain), 20.98 (2  $\text{CH}_3$  attached to the aromatic ring), 18.19 (2  $\text{CH}_3$  attached to the aromatic ring), 18.16 (2  $\text{CH}_3$  attached to the aliphatic chain), 15.84 (2  $\text{CH}_3$  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  $\mu\text{L}$ , 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.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  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,  $\text{CH}_3$  in *rac-16* or *rac-17*), 1.12 (d,  $J$  = 6.86 Hz, 6 H,  $\text{CH}_3$  in *rac-16* or *rac-17*) ppm.  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.59 (2  $\text{C}_q$  in *rac-16* or *rac-17*), 142.64 (2  $\text{C}_q$  in *rac-16* or *rac-17*), 139.55 (2  $\text{C}_q$  in *rac-16* or *rac-17*), 136.49 (2  $\text{C}_q$  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  $\text{CH}_2$  in chain in *rac-16* or *rac-17*), 115.41 (2 olefinic  $\text{CH}_2$  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 CH<sub>2</sub> in five-ring in *rac-16* or *rac-17* or aliphatic CH<sub>2</sub> 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 CH<sub>2</sub> in five-ring in *rac-16* or *rac-17* or aliphatic CH<sub>2</sub> in chain in *rac-16* or *rac-17*), 35.05 (4 aliphatic CH<sub>2</sub> in five-ring in *rac-16* or *rac-17* or aliphatic CH<sub>2</sub> in chain in *rac-16* or *rac-17*), 13.96 (4 C, CH<sub>3</sub> in *rac-16* and *rac-17*) ppm. EIMS (30 eV): calcd. C<sub>13</sub>H<sub>16</sub>O 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. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> in chain in **18**, aliphatic CH<sub>2</sub> in five-ring in **18** and aliphatic CH in five-ring in *rac-19*), 2.13 (m, 4 H, aliphatic CH<sub>2</sub> in five-ring in *rac-19*), 2.05 (s, 3 H, CH<sub>3</sub> in **18**), 1.95 (d, *J* = 6.42 Hz, 6 H, CH<sub>3</sub> in *rac-19*) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>): δ = 146.56 (C<sub>q</sub> in **18**), 145.42 (2 C<sub>q</sub> in *rac-19*), 142.55 (C<sub>q</sub> in **18**), 140.39 (2 C<sub>q</sub> in *rac-19*), 139.37 (C<sub>q</sub> in **18**), 135.53 (olefinic CH in chain in **18**), 134.54 (2 C<sub>q</sub> in *rac-19*), 134.46 (C<sub>q</sub> 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 CH<sub>2</sub> in chain in **18** and olefinic CH<sub>2</sub> in chain in *rac-19*), 42.93 (2 aliphatic CH in five-ring in *rac-19*), 42.66 (aliphatic CH<sub>2</sub> in chain in **18** or aliphatic CH<sub>2</sub> in five-ring in **18**), 31.76 (2 aliphatic CH<sub>2</sub> in five-ring in *rac-19*), 29.77 (aliphatic CH<sub>2</sub> in chain in **18** or aliphatic CH<sub>2</sub> in five-ring in **18**), 14.84 (2 CH<sub>3</sub> in *rac-19*), 13.93 (CH<sub>3</sub> in **18**) ppm. EIMS (70 eV): calcd. C<sub>13</sub>H<sub>14</sub> 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. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> 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, CH<sub>3</sub> attached to the aliphatic chain in six compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 1.09 (m, 24 H, CH<sub>3</sub> attached to the five-ring in *rac-*

*20*, *rac-21*, *rac-22* and *rac-23*), 0.98 (d, *J* = 6.73 Hz, 3 H, CH<sub>3</sub> attached to the aliphatic chain in two compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>): δ = 145.98 (6 C<sub>q</sub> in six compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 145.63 (2 C<sub>q</sub> in two compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 142.75 (2 C<sub>q</sub> in two compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 142.23 (6 C<sub>q</sub> 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 CH<sub>2</sub> in chain in two compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 115.83 (6 olefinic CH<sub>2</sub> 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 CH<sub>2</sub> in five-ring in six compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 39.46 (2 C, aliphatic CH or CH<sub>2</sub> in five-ring in two compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 38.88 (6C, aliphatic CH or CH<sub>2</sub> in five-ring in six compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 38.18 (2 C, aliphatic CH or CH<sub>2</sub> in five-ring in two diastereomers of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 16.45 (2 C, CH<sub>3</sub> attached to the aliphatic chain or five-ring in two compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 15.93 (6C, CH<sub>3</sub> attached to the five-ring in six compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*), 15.53 (2 C, CH<sub>3</sub> 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, CH<sub>3</sub> attached to the chain in six compounds of *rac-20*, *rac-21*, *rac-22* and *rac-23*) ppm. EIMS (30 eV): calcd. C<sub>14</sub>H<sub>18</sub>O 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. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> in five-ring), 1.98 (s, 6 H, CH<sub>3</sub> attached to the five-ring), 1.31 (d, *J* = 7.42 Hz, 6 H, CH<sub>3</sub> attached to the chain) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>): δ = 145.57 (2 C<sub>q</sub>), 142.96 (2 C<sub>q</sub>), 141.58 (2 olefinic CH in chain), 139.20 (2 C<sub>q</sub>), 138.36 (2 C<sub>q</sub>), 125.86 (2 arom. CH), 123.48 (2 arom. CH), 120.03 (2 arom. CH), overlapping of two arom. CH, 113.59 (2 olefinic CH<sub>2</sub> in chain), 43.10 (2 aliphatic CH<sub>2</sub> in five-ring), 35.05 (2 aliphatic CH in chain), 18.44 (2 CH<sub>3</sub> attached to the chain), 14.70 (2 CH<sub>3</sub> attached to the five-ring) ppm. EIMS (70 eV): calcd. C<sub>14</sub>H<sub>16</sub> 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  $\mu$ 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%.  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  = 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  $\text{CH}_2$  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.  $^{13}\text{C NMR}$  (100.6 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  = 154.50 (2  $\text{C}_q$ ), 150.44 (2  $\text{C}_q$ ), 143.85 (2  $\text{C}_q$ ), 135.48 (2 olefinic CH in chain), 128.95 (2 arom. CH), 118.07 (2 olefinic  $\text{CH}_2$  in chain), 115.35 (2 arom. CH), 115.08 (2 arom. CH), 84.22 (2 C-OH), 46.49 (2 aliphatic  $\text{CH}_2$  in chain), 39.63 (2 aliphatic  $\text{CH}_2$  in five-ring), 26.80 (2 aliphatic  $\text{CH}_2$  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  $\text{Mg}_2\text{SO}_4$  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.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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 26), 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  $\text{CH}_2$  in chain in 26 and five-ring aliphatic  $\text{CH}_2$  in 26), 2.93 (m, 4 H, five-ring aliphatic  $\text{CH}_2$  in 27) ppm.  $^{13}\text{C NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 151.09 ( $\text{C}_q$  in 26), 147.48 ( $\text{C}_q$  in 26), 142.74 ( $\text{C}_q$  in 26), 135.52 (olefinic CH in chain in 26), 134.22 (olefinic CH in 27), 128.88 ( $\text{C}_q$  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  $\text{CH}_2$  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  $\text{CH}_2$  in chain in 26 or aliphatic  $\text{CH}_2$  in five-ring in 26), 32.53 (aliphatic  $\text{CH}_2$  in chain in 26 or aliphatic  $\text{CH}_2$  in five-ring in 26), 28.23 (aliphatic  $\text{CH}_2$  in five-ring in 27), 26.26 (aliphatic  $\text{CH}_2$  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  $\mu$ 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.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in five-ring), 1.38 (d,  $J$  = 6.94 Hz, 6 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 151.12 (2  $\text{C}_q$ ), 147.96 (2  $\text{C}_q$ ), 147.06 (2  $\text{C}_q$ ), 141.82 (2 olefinic CH in chain), 129.14 (2  $\text{C}_q$ ), 127.78 (2 arom. CH), 127.01 (2 arom. CH), 113.72 (2 olefinic  $\text{CH}_2$  in chain), 113.21 (2 arom. CH), 111.90 (2 arom. CH), 36.64 (2 aliphatic CH in chain), 34.18 (2 aliphatic  $\text{CH}_2$  in five-ring), 19.12 (2  $\text{CH}_3$ ) 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.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in chain) ppm.  $^{13}\text{C NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 151.06 (2  $\text{C}_q$ ), 146.81 (2  $\text{C}_q$ ), 145.85 (2  $\text{C}_q$ ), 141.47 (2  $\text{C}_q$ ), 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  $\text{C}_q$ ), 115.99 (2 olefinic  $\text{CH}_2$  in chain), 113.60 (2 arom. CH), 111.96 (2 arom. CH), 48.92 (2 aliphatic CH in chain), 34.39 (2 aliphatic  $\text{CH}_2$  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  $\mu$ 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.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in chain in *rac*-30 and olefinic  $\text{CH}_2$  in chain in *rac*-31), 3.04–2.45 and 2.00–1.90 (m, 24 H, overlapping signals from aliphatic  $\text{CH}_2$  in chain in *rac*-30, aliphatic  $\text{CH}_2$  in five-ring in *rac*-30, aliphatic  $\text{CH}_2$  in chain in *rac*-31 and aliphatic  $\text{CH}_2$  in five-ring in *rac*-31), 2.43 (s, 12 H,  $\text{CH}_3$  attached to the aromatic ring in *rac*-30 and  $\text{CH}_3$  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.  $^{13}\text{C NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 145.70 (2  $\text{C}_q$  in *rac*-30), 144.33 (2  $\text{C}_q$  in *rac*-31), 141.75 (2  $\text{C}_q$  in *rac*-31), 140.69 (2  $\text{C}_q$  in *rac*-30), 137.25 (2  $\text{C}_q$  in *rac*-31), 132.54 (2  $\text{C}_q$  in *rac*-31), overlapping of two  $\text{C}_q$  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  $\text{C}_q$  in *rac*-30), 127.85 (2 arom. CH in *rac*-30), 127.98 (2 arom. CH in *rac*-31), 119.03 (2 olefinic  $\text{CH}_2$  in chain in *rac*-30), 118.49 (2 olefinic  $\text{CH}_2$  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 CH<sub>2</sub> in five-ring or in chain in *rac-31*), 43.55 (2 aliphatic CH<sub>2</sub> in five-ring or in chain in *rac-30*), 39.58 (2 aliphatic CH<sub>2</sub> in five-ring or in chain in *rac-30*), 37.56 (2 aliphatic CH<sub>2</sub> in five-ring or in chain in *rac-31*), 28.33 (2 aliphatic CH<sub>2</sub> in five-ring or in chain in *rac-30*), 28.19 (2 aliphatic CH<sub>2</sub> in five-ring or in chain in *rac-31*), 18.23 (2 CH<sub>3</sub> attached to the aromatic ring in *rac-31*), 17.52 (2 CH<sub>3</sub> attached to the aromatic ring in *rac-30*) ppm. EIMS (30 eV): calcd. C<sub>13</sub>H<sub>15</sub>OCl 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> in chain in **34**), 3.45 (m, 2 H, aliphatic CH<sub>2</sub> in chain in **32**), 3.30 (m, 2 H, aliphatic CH<sub>2</sub> in five-ring in **32**), 3.19 (m, 2 H, aliphatic CH<sub>2</sub> in five-ring in **34**), 2.98 (m, 2 H, aliphatic CH<sub>2</sub> in five-ring in **33**), 2.90 (m, 2 H, aliphatic CH<sub>2</sub> in five-ring in **33**), 2.52 (s, 3 H, CH<sub>3</sub> attached to the aromatic ring in **32**), 2.47 (s, 3 H, CH<sub>3</sub> attached to the aromatic ring in **33**), 2.30 (s, 3 H, CH<sub>3</sub> 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**. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 146.28 (C<sub>q</sub> in **32**, **33** or **34**), 145.78 (C<sub>q</sub> in **32**, **33** or **34**), 145.42 (C<sub>q</sub> in **32**, **33** or **34**), 144.23 (C<sub>q</sub> in **32**, **33** or **34**), 143.88 (C<sub>q</sub> in **32**, **33** or **34**), 143.54 (C<sub>q</sub> in **32**, **33** or **34**), 142.76 (C<sub>q</sub> in **32**, **33** or **34**), 142.63 (C<sub>q</sub> in **32**, **33** or **34**), 140.61 (C<sub>q</sub> in **32**, **33** or **34**), 140.38 (C<sub>q</sub> in **32**, **33** or **34**), 132.58 (C<sub>q</sub> in **32**, **33** or **34**), 131.40 (C<sub>q</sub> in **32**, **33** or **34**), 129.52 (C<sub>q</sub> in **32**, **33** or **34**), 128.66 (C<sub>q</sub> in **32**, **33** or **34**), 127.47 (C<sub>q</sub> 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 CH<sub>2</sub> in chain in **33**), 116.33 (olefinic CH<sub>2</sub> in chain in **32**), 115.92 (olefinic CH<sub>2</sub> in chain in **34**), 37.12 (aliphatic CH<sub>2</sub> in five-ring in **32**), 36.75 (aliphatic CH<sub>2</sub> in five-ring in **34**), 34.80 (aliphatic CH<sub>2</sub> in chain in **32**), 34.66 (aliphatic CH<sub>2</sub> in chain in **34**), 29.45 (aliphatic CH<sub>2</sub> in five-ring in **33**), 28.55 (aliphatic CH<sub>2</sub> in five-ring in **33**), 21.54 (CH<sub>3</sub> attached to the aromatic ring in **33**), 19.40 (CH<sub>3</sub> attached to the aromatic ring in **32**), 18.05 (CH<sub>3</sub> attached to the aromatic ring in **34**) ppm. EIMS (70 eV): calcd. C<sub>13</sub>H<sub>13</sub>Cl 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> in chain in *rac-35* and *rac-36* and olefinic CH<sub>2</sub> 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 CH<sub>2</sub> in five-ring in *rac-35* and *rac-36*, aliphatic CH<sub>2</sub> in five-ring in *rac-38* and *rac-39*), 2.44 (m, 24 H, overlapping signals from CH<sub>3</sub> 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, CH<sub>3</sub> attached to the aliphatic chain in *rac-35*, *rac-36*, *rac-38* and *rac-39*), 0.77 (d, *J* = 7.01 Hz, 12 H, CH<sub>3</sub> 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 <sup>1</sup>H NMR spectroscopy due to overlapping signals. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): overlapping of some of the quaternary carbons with signals from other carbons δ = 145.74 (C<sub>q</sub>), 144.53 (C<sub>q</sub>), 141.83 (C<sub>q</sub>), 141.42 (C<sub>q</sub>), 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<sub>q</sub>), 133.23 (C<sub>q</sub>), 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 CH<sub>2</sub> in chain in *rac-35* and *rac-36*), 116.40 (2 olefinic CH<sub>2</sub> in chain in *rac-38* and *rac-39*), 115.39 (2 olefinic CH<sub>2</sub> in chain in *rac-35* and *rac-36*), 115.23 (2 olefinic CH<sub>2</sub> 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 CH<sub>2</sub> in five-ring in *rac-35* and *rac-36* and/or *rac-38* and *rac-39*), 35.56 (2 aliphatic CH<sub>2</sub> in five-ring in *rac-35* and *rac-36* and/or *rac-38* and *rac-39*), 29.68 (2 aliphatic CH<sub>2</sub> in five-ring in *rac-35* and *rac-36* and/or *rac-38* and *rac-39*), 29.14 (2 aliphatic CH<sub>2</sub> in five-ring in *rac-35* and *rac-36* and/or *rac-38* and *rac-39*), 18.01 (2 CH<sub>3</sub> attached to the aromatic ring in *rac-35* and *rac-36* and/or *rac-38* and *rac-39*), 17.81 (2 CH<sub>3</sub> attached to the aromatic ring in *rac-35* and *rac-36* and/or *rac-38* and *rac-39*), 17.51 (2 CH<sub>3</sub> attached to the aromatic ring in *rac-35* and *rac-36* and/or *rac-38* and *rac-39*), 14.83 (2 CH<sub>3</sub> attached to the chain in *rac-35* and *rac-36*), 14.74 (2 CH<sub>3</sub> attached to the chain in *rac-38* and *rac-39*), 13.24 (2 CH<sub>3</sub> attached to the chain in *rac-35* and *rac-36*), 13.17 (2 CH<sub>3</sub> attached to the chain in *rac-38* and *rac-39*) ppm. EIMS (30 eV): calcd. C<sub>14</sub>H<sub>17</sub>OCl 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.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  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  $\text{CH}_2$  in five-ring in *rac-37*), 3.20 (m, 4 H, aliphatic  $\text{CH}_2$  in chain in *rac-40*), 2.53 (s, 6 H,  $\text{CH}_3$  attached to the aromatic ring in *rac-37*), 2.30 (s, 6 H,  $\text{CH}_3$  attached to the aromatic ring in *rac-40*), 1.35 (d,  $J$  = 6.87 Hz, 6 H,  $\text{CH}_3$  attached to the chain in *rac-37*), 1.36 (d,  $J$  = 6.87 Hz, 6 H,  $\text{CH}_3$  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.  $^{13}\text{C NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.37 (4C,  $\text{C}_q$  in *rac-37* and *rac-40*), 144.11 (4C,  $\text{C}_q$  in *rac-37* and *rac-40*), 142.83 (4C,  $\text{C}_q$  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,  $\text{C}_q$  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,  $\text{C}_q$  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  $\text{CH}_2$  in chain in *rac-37*), 112.81 (2 olefinic  $\text{CH}_2$  in chain in *rac-40*), 37.19 (2 aliphatic  $\text{CH}_2$  in five-ring in *rac-37*), 36.80 (2 aliphatic  $\text{CH}_2$  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  $\text{CH}_3$  attached to the chain in *rac-37*), 19.96 (2  $\text{CH}_3$  attached to the chain in *rac-40*), 19.65 (2  $\text{CH}_3$  attached to the aromatic ring in *rac-37*), 18.11 (2  $\text{CH}_3$  attached to the aromatic ring in *rac-40*). EIMS (70 eV): calcd.  $\text{C}_{14}\text{H}_{15}\text{Cl}$  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  $\mu\text{L}$ , 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.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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,  $\text{CH}_3$ ), 2.02 (m, 2 H, aliphatic CH in five-ring) ppm.  $^{13}\text{C NMR}$  (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 144.70 (2  $\text{C}_q$ ), 143.24 (2  $\text{C}_q$ ), 133.47 (2  $\text{C}_q$ ), 133.22 (2 olefinic CH in chain), 131.10 (2 arom. CH), 130.28 (2 arom. CH), 118.18 (2 olefinic  $\text{CH}_2$  in chain), 115.13 (2  $\text{C}_q$ ), 84.99 (2 C-OH), 43.85 (2 aliphatic  $\text{CH}_2$  in chain), 38.01 (2 aliphatic  $\text{CH}_2$  in five-ring), 27.86 (2 aliphatic  $\text{CH}_2$  in five-ring), 18.20 (2  $\text{CH}_3$ ) ppm. EIMS (30 eV): calcd.  $\text{C}_{13}\text{H}_{15}\text{OBr}$  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.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in chain in *42* or aliphatic  $\text{CH}_2$  in five-ring in *42*), 3.18 (m, 2 H, aliphatic  $\text{CH}_2$  in chain in *42* or aliphatic  $\text{CH}_2$  in five-ring in *42*), 2.89 (m, 4 H, aliphatic  $\text{CH}_2$  in five-ring in *43*), 2.28 (s, 3 H,  $\text{CH}_3$  attached to the aromatic ring in *42*), 2.18 (s, 3 H,  $\text{CH}_3$  attached to the aromatic ring in *43*) ppm.  $^{13}\text{C NMR}$  (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.16 ( $\text{C}_q$  in *43*), 146.16 ( $\text{C}_q$  in *42*), 144.23 ( $\text{C}_q$  in *43*), 143.97 ( $\text{C}_q$  in *42*), 141.95 ( $\text{C}_q$  in *42*), 137.88 ( $\text{C}_q$  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 ( $\text{C}_q$  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 ( $\text{C}_q$  in *43*), 117.88 (olefinic CH in chain in *43*), 116.05 (olefinic CH in chain in *42*), 115.15 ( $\text{C}_q$  in *43*), 112.07 ( $\text{C}_q$  in *42*), 36.71 (aliphatic  $\text{CH}_2$  in chain in *42* or aliphatic  $\text{CH}_2$  in five-ring in *42*), 34.74 (aliphatic  $\text{CH}_2$  in chain in *42* or aliphatic  $\text{CH}_2$  in five-ring in *42*), 29.13 (aliphatic  $\text{CH}_2$  in five-ring in *43*), 28.81 (aliphatic  $\text{CH}_2$  in five-ring in *43*), 18.46 ( $\text{CH}_3$  attached to the aromatic ring in *43*), 18.15 ( $\text{CH}_3$  attached to the aromatic ring in *42*) ppm. EIMS (70 eV): calcd.  $\text{C}_{13}\text{H}_{13}\text{Br}$  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  $\mu\text{L}$ , 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.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  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  $\text{CH}_2$  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,  $\text{CH}_3$  attached to the aromatic ring in *rac-44* or *rac-45*), 2.15 (s, 6 H,  $\text{CH}_3$  attached to the aromatic ring in *rac-44* or *rac-45*), 1.23 (d,  $J$  = 6.72 Hz, 6 H,  $\text{CH}_3$  attached to the chain in *rac-44* or *rac-45*), 0.72 (d,  $J$  = 6.94 Hz, 6 H,  $\text{CH}_3$  attached to the chain in *rac-44* or *rac-45*) ppm.  $^{13}\text{C NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 145.68 (2  $\text{C}_q$  in *rac-44* or *rac-45*), 145.50 (2  $\text{C}_q$  in *rac-44* or *rac-45*), 143.17 (2  $\text{C}_q$  in *rac-44* or *rac-45*), 142.49 (2  $\text{C}_q$  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  $\text{C}_q$  in *rac-44* or *rac-45*), 133.61 (2  $\text{C}_q$  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 CH<sub>2</sub> in chain in *rac-44* or *rac-45*), 115.45 (2 C<sub>q</sub> in *rac-44* or *rac-45*), 115.20 (2 olefinic CH<sub>2</sub> in chain in *rac-44* or *rac-45*), 115.16 (2 C<sub>q</sub> 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 CH<sub>2</sub> in five-ring in *rac-44* or *rac-45*), 33.62 (2 aliphatic CH<sub>2</sub> in five-ring in *rac-44* or *rac-45*), 29.23 (2 aliphatic CH<sub>2</sub> in five-ring in *rac-44* or *rac-45*), 28.94 (2 aliphatic CH<sub>2</sub> in five-ring in *rac-44* or *rac-45*), 18.38 (4 CH<sub>3</sub> attached to the aromatic ring in *rac-44* and *rac-45*), 14.54 (2 CH<sub>3</sub> attached to the chain in *rac-44* or *rac-45*), 13.05 (2 CH<sub>3</sub> attached to the chain in *rac-44* or *rac-45*) ppm. EIMS (30 eV): calcd. C<sub>14</sub>H<sub>17</sub>OBr 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> in five-ring), 2.30 (s, 6 H, CH<sub>3</sub> attached to the aromatic ring), 1.38 (d, *J* = 6.87 Hz, 6 H, CH<sub>3</sub> attached to the chain) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 149.38 (2 C<sub>q</sub>), 146.35 (2 C<sub>q</sub>), 142.49 (2 olefinic CH in chain), 141.43 (2 C<sub>q</sub>), 132.02 (2 C<sub>q</sub>), 131.95 (2 arom. CH), 129.74 (2 olefinic CH in five-ring), 127.27 (2 arom. CH), 112.79 (2 olefinic CH<sub>2</sub> in chain), 111.96 (2 C<sub>q</sub>), 36.71 (2 aliphatic CH<sub>2</sub> in five-ring), 35.42 (2 aliphatic CH in chain), 20.03 (2 CH<sub>3</sub> attached to the chain), 18.14 (2 CH<sub>3</sub> attached to the aromatic ring) ppm. EIMS (70 eV): calcd. C<sub>14</sub>H<sub>15</sub>Br 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. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 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. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>): δ = 146.99 (2 C<sub>q</sub>), 142.95 (2 C<sub>q</sub>), 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 CH<sub>2</sub> in chain), 82.70 (2 C-OH), 44.94 (2 aliphatic CH<sub>2</sub> in chain), 39.62 (2 aliphatic CH<sub>2</sub> in five-ring), 29.37 (2 aliphatic CH<sub>2</sub> in five-ring) ppm. EIMS (30 eV): calcd. C<sub>12</sub>H<sub>14</sub>O 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.25 (m, 4 H, arom. CH), 6.03 (m, 1 H, olefinic CH in chain), 5.27 (m, 2 H, olefinic CH<sub>2</sub> 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

CH<sub>2</sub> in chain), 2.25 (s, 1 H, OH) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 141.11 (2 C<sub>q</sub>), 133.93 (olefinic CH in chain), 126.51 (2 arom. CH), 124.88 (2 arom. CH), 118.85 (olefinic CH<sub>2</sub> in chain), 81.41 (C-OH), 46.34 (2 aliphatic CH<sub>2</sub> in five-ring), 44.92 (aliphatic CH<sub>2</sub> in chain) ppm. EIMS (70 eV): calcd. C<sub>12</sub>H<sub>14</sub>O 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. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 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 (ddt, *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 CH<sub>2</sub> in five-ring), 3.40 (m, 2 H, aliphatic CH<sub>2</sub> in chain) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>): δ = 148.11 (C<sub>q</sub>), 145.38 (C<sub>q</sub>), 143.15 (C<sub>q</sub>), 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 CH<sub>2</sub> in chain), 40.88 (aliphatic CH<sub>2</sub> in five-ring), 35.65 (aliphatic CH<sub>2</sub> in chain) ppm. EIMS (70 eV): calcd. C<sub>12</sub>H<sub>12</sub> 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> in five-ring), 2.93 (m, 4 H, aliphatic CH<sub>2</sub> 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, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 141.25 (2 C<sub>q</sub>), 141.23 (2 C<sub>q</sub>), 140.14 (2 olefinic CH in chain), 126.46 (4 C, arom. CH), 124.91 (4 C, arom. CH), 115.92 (2 olefinic CH<sub>2</sub> in chain), 83.81 (2 C-OH), 46.86 (2 aliphatic CH in chain), 45.73 (2 aliphatic CH<sub>2</sub> in five-ring), 45.18 (2 aliphatic CH<sub>2</sub> in five-ring), 14.87 (2 CH<sub>3</sub>) ppm. EIMS (70 eV): calcd. C<sub>13</sub>H<sub>16</sub>O 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> in five-ring and aliphatic CH in chain), 1.22 (d, *J* = 6.9 Hz, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 153.57 (2 C<sub>q</sub>), 145.31 (2 C<sub>q</sub>), 143.14 (2 C<sub>q</sub>), 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 CH<sub>2</sub> in chain), 39.69 (2 aliphatic CH<sub>2</sub> in five-ring or aliphatic CH in chain), 39.49 (2 aliphatic CH<sub>2</sub> in five-ring or aliphatic CH in chain), 19.53 (2 CH<sub>3</sub>) ppm. EIMS (70 eV): calcd. C<sub>13</sub>H<sub>14</sub> 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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 141.03 (6 $\text{C}_q$ ), 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  $\text{CH}_2$  in chain), 84.14 (2 C–OH), 59.24 (2 aliphatic CH in chain), 46.15 (2 aliphatic  $\text{CH}_2$  in five-ring), 45.94 (2 aliphatic  $\text{CH}_2$  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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in five-ring) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 151.35 (2  $\text{C}_q$ ), 144.95 (2  $\text{C}_q$ ), 143.34 (2  $\text{C}_q$ ), 142.49 (2  $\text{C}_q$ ), 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  $\text{CH}_2$  in chain), 51.78 (2 aliphatic CH in chain), 40.20 (2 aliphatic  $\text{CH}_2$  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.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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,  $\text{CH}_3$  attached to the chain) ppm.  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 141.39 (olefinic CH in chain), 137.90 ( $\text{C}_q$ ), 126.73 (arom. CH), 126.52 (arom. CH), 125.29 (arom. CH), 125.11 (arom. CH), 114.06 (olefinic  $\text{CH}_2$  in chain), 86.49 (C–OH), 42.96 (2 aliphatic  $\text{CH}_2$  in five-ring), 22.86 ( $\text{CH}_3$  attached to the chain), 22.81 ( $\text{CH}_3$  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.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in the five-ring), 1.35 (s, 6 H,  $\text{CH}_3$  attached to the chain) ppm.  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 157.46 ( $\text{C}_q$ ), 147.43 (olefinic CH in chain), 145.30 ( $\text{C}_q$ ), 143.43 ( $\text{C}_q$ ), 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  $\text{CH}_2$  in chain), 38.28 (aliphatic  $\text{CH}_2$  in the five-ring), 27.46 ( $\text{CH}_3$  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  $\mu\text{L}$ , 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.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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,  $\text{CH}_3$  attached to the aromatic ring), 2.20 (s, 6 H,  $\text{CH}_3$  attached to the aromatic ring), 1.71 (br. s, 2 H, OH), 1.17 (d,  $J$  = 6.87 Hz, 6 H,  $\text{CH}_3$  attached to the aliphatic chain) ppm.  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 140.40 (2 olefinic CH in chain), 139.80 (2  $\text{C}_q$ ), 131.69 (2  $\text{C}_q$ ), 127.76 (4C, arom. CH), 116.22 (2 olefinic  $\text{CH}_2$  in chain), 83.30 (2 C–OH), 47.25 (2 aliphatic CH in chain), 45.01 (2 aliphatic  $\text{CH}_2$  in five-ring), 44.41 (2 aliphatic  $\text{CH}_2$  in five-ring), 18.95 (4  $\text{CH}_3$  attached to the aromatic ring), 15.23 (2  $\text{CH}_3$  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.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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,  $\text{CH}_3$  attached to the aromatic ring), 2.30 (s, 6 H,  $\text{CH}_3$  attached to the aromatic ring), 1.35 (d,  $J$  = 6.96 Hz, 6 H,  $\text{CH}_3$  attached to the aliphatic chain) ppm.  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 152.74 (2  $\text{C}_q$ ), 143.10 (2 olefinic CH in chain), 141.69 (2  $\text{C}_q$ ), 130.20 (2  $\text{C}_q$ ), 127.81 (2 arom. CH), 125.41 (2 arom. CH), 124.19 (2 olefinic CH in five-ring), 113.56 (2 olefinic  $\text{CH}_2$  in chain), 39.98 (2 aliphatic CH in chain), 38.82 (2 aliphatic  $\text{CH}_2$  in five-ring), 19.84 (2  $\text{CH}_3$  attached to the aliphatic chain), 18.61 (2  $\text{CH}_3$  attached to the aromatic ring), 18.30 (2  $\text{CH}_3$  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  $\mu$ 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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  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  $\text{CH}_2$  in chain), 1.86 (m, 2 H, aliphatic CH in five-ring), 1.82 (s, 2 H, OH) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.25 (2  $\text{C}_q$ ), 144.84 (2  $\text{C}_q$ ), 134.92 (2  $\text{C}_q$ ), 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  $\text{CH}_2$  in chain), 83.32 (2 C-OH), 50.30 (2 aliphatic CH in five-ring), 48.91 (2 aliphatic  $\text{CH}_2$  five-ring), 45.67 (2 aliphatic  $\text{CH}_2$  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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 151.92, 150.98, 148.23, 147.12, 145.32, 145.06 (8 C, overlapping signals from  $\text{C}_q$  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  $\text{CH}_2$  in 58), 114.09 (1 C, olefinic chain  $\text{CH}_2$  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  $\text{CH}_2$  in 59), 39.00 (1 C, five-ring aliphatic  $\text{CH}_2$  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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  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,  $\text{CH}_3$  in *rac*-60 or *rac*-61), 1.11 (d,  $J$  = 6.9 Hz, 6 H,  $\text{CH}_3$  in *rac*-60 or *rac*-61) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.84 (2  $\text{C}_q$  in *rac*-60 or *rac*-61), 146.71 (2  $\text{C}_q$  in *rac*-60 or *rac*-61), 145.07 (4  $\text{C}_q$  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  $\text{C}_q$  in *rac*-60 or *rac*-61), 134.96 (2  $\text{C}_q$  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  $\text{CH}_2$  in chain in *rac*-60 or *rac*-61), 116.36 (2 olefinic  $\text{CH}_2$  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  $\text{CH}_2$  in five-ring in *rac*-60 and *rac*-61), 15.16 (2  $\text{CH}_3$  in *rac*-60 or *rac*-61), 14.36 (2  $\text{CH}_3$  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  $\text{MgSO}_4$  (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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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,  $\text{CH}_3$  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.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ): 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,  $\delta$  = 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  $\text{CH}_2$  in chain), 45.78 (2 aliphatic  $\text{CH}_2$  in five-ring), 39.43 (2 aliphatic CH in chain), 19.79 (2  $\text{CH}_3$  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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  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.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):

$\delta$  = 147.41 (2 C<sub>q</sub> in *rac*-63 or *rac*-64), 147.05 (2 C<sub>q</sub> in *rac*-63 or *rac*-64), 144.77 (2 C<sub>q</sub> in *rac*-63 or *rac*-64), 144.62 (2 C<sub>q</sub> in *rac*-63 or *rac*-64), 140.57 (2 C<sub>q</sub> in *rac*-63 or *rac*-64), 140.38 (2 C<sub>q</sub> 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<sub>q</sub> in *rac*-63 or *rac*-64), 134.96 (2 C<sub>q</sub> 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 CH<sub>2</sub> in chain in *rac*-63 or *rac*-64), 117.89 (2 olefinic CH<sub>2</sub> 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 MgSO<sub>4</sub> (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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 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 CH<sub>2</sub> 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 CH<sub>2</sub> 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. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): quaternary carbons could not be determined from the carbon spectrum due to excessive number of signals from the side products,  $\delta$  = 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 CH<sub>2</sub> in chain in *rac*-65), 115.20 (olefinic CH<sub>2</sub> in chain in 66 or 67), 114.10 (olefinic CH<sub>2</sub> 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 CH<sub>2</sub> in five-ring in *rac*-65), 41.91 (aliphatic CH<sub>2</sub> in five-ring in 66 or 67) ppm. EIMS (70 eV): calcd. C<sub>26</sub>H<sub>22</sub> 334.1722; found 334.1722.

**2-Allyl-2,3-dihydro-1H-cyclopenta[*b*]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[*b*]phenanthren-2-one (0.9793 g, 4.2 mmol), and allyl bromide (740  $\mu$ 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 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 CH<sub>2</sub> in five-ring), 2.66 (m, 2 H, aliphatic CH<sub>2</sub> in chain), 2.13 (m, 1 H, OH) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 134.67 (2 C, C<sub>q</sub>), 133.93 (olefinic CH in chain), 130.30 (2 C, C<sub>q</sub>), 129.78 (2 C, C<sub>q</sub>), 126.70 (2C, arom. CH), 125.83 (2 C, C<sub>q</sub>), 124.73 (2 C, C<sub>q</sub>), 123.15 (2 C, C<sub>q</sub>), 119.26 (olefinic CH<sub>2</sub> in chain), 80.66 (C–OH), 46.22 (2 C, aliphatic CH<sub>2</sub> in five-ring), 45.91 (aliphatic CH<sub>2</sub> in chain) ppm. EIMS (70 eV): calcd. C<sub>20</sub>H<sub>18</sub>O 274.1358; found 274.1355.

**2-Allyl-2,3-dihydro-1H-cyclopenta[*b*]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[*b*]phenanthren-2-one (0.067 g, 0.3 mmol), and allyl bromide (40  $\mu$ 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  $\mu$ L, 5.2 mmol) gave, after column chromatography (dichloromethane as eluent), 0.797 g (48%) of the title compound as a pale yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 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, CH<sub>2</sub> in EtO groups), 3.33 (m, 2 H, aliphatic CH<sub>2</sub> in five-ring), 2.56 (m, 2 H, aliphatic CH<sub>2</sub> in chain), 1.77 (m, 2 H, aliphatic CH<sub>2</sub> in chain), 1.27 (m, 9 H, CH<sub>3</sub> in EtO groups), 0.74 (m, 2 H, aliphatic CH<sub>2</sub> in chain) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.57 (C<sub>q</sub>), 145.80 (C<sub>q</sub>), 143.27 (C<sub>q</sub>), 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, CH<sub>2</sub> in EtO groups), 41.07 (aliphatic CH<sub>2</sub> in five-ring), 34.64 (aliphatic CH<sub>2</sub> in chain), 22.60 (aliphatic CH<sub>2</sub> in chain), 18.44 (3C, CH<sub>3</sub> in EtO groups), 10.42 (aliphatic CH<sub>2</sub> in chain) ppm. EIMS (70 eV): calcd. C<sub>18</sub>H<sub>28</sub>O<sub>3</sub>Si 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  $\mu$ L, 4.4 mmol) gave, after column chromatography (hexane as eluent), 0.3434 g (29%) of the title compound as a colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 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 CH<sub>2</sub> in five-ring), 2.66 (m, 2 H, aliphatic CH<sub>2</sub> in chain), 1.79 (m, 2 H, aliphatic CH<sub>2</sub> in chain), 1.13 (m, 9 H, CH<sub>3</sub> in Et groups), 0.77 (m, 2 H, aliphatic CH<sub>2</sub> in chain), 0.71 (m, 6 H, CH<sub>2</sub> in Et groups) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.79 (C<sub>q</sub>), 145.86 (C<sub>q</sub>), 143.24 (C<sub>q</sub>), 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 CH<sub>2</sub> in five-ring), 35.56 (aliphatic CH<sub>2</sub> in chain), 23.74 (aliphatic CH<sub>2</sub> in chain), 11.61 (aliphatic CH<sub>2</sub> in chain), 7.63 (3C, CH<sub>3</sub> in Et- groups), 3.47 (3C, CH<sub>2</sub> in Et groups) ppm. EIMS (70 eV): calcd. C<sub>18</sub>H<sub>28</sub>Si 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  $-20^{\circ}\text{C}$  yielded 0.1118 g (7%) of white crystals.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in five-ring), 2.45 (m, 2 H, aliphatic  $\text{CH}_2$  in chain), 1.71 (m, 2 H, aliphatic  $\text{CH}_2$  in chain), 1.35 (m, 2 H, aliphatic  $\text{CH}_2$  in chain) ppm.  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.29 ( $\text{C}_q$ ), 145.67 ( $\text{C}_q$ ), 143.24 ( $\text{C}_q$ ), 135.81 (6C, arom. CH), 135.25 ( $\text{C}_q$ ), 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  $\text{CH}_2$  in five-ring), 35.14 (aliphatic  $\text{CH}_2$  in chain), 23.66 (aliphatic  $\text{CH}_2$  in chain), 13.16 (aliphatic  $\text{CH}_2$  in chain) ppm. M.p. 127–128  $^{\circ}\text{C}$ . 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.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in five-ring), 2.59 (m, 4 H, aliphatic  $\text{CH}_2$  in chain), 1.69 (m, 4 H, aliphatic  $\text{CH}_2$  in chain), 0.66 (m, 4 H, aliphatic  $\text{CH}_2$  in chain), 0.48 (m, 4 H, aliphatic  $\text{CH}_2$  in chain between Si atoms), 0.07 (m, 12 H,  $\text{CH}_3$  attached to Si) ppm.  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.88 (2C,  $\text{C}_q$ ), 145.88 (2C,  $\text{C}_q$ ), 143.30 (2C,  $\text{C}_q$ ), 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  $\text{CH}_2$  in chain), 35.28 (2C, aliphatic  $\text{CH}_2$  in chain), 23.76 (2C, aliphatic  $\text{CH}_2$  in chain), 14.79 (2C, aliphatic  $\text{CH}_2$  in chain), 7.30 (2C, aliphatic  $\text{CH}_2$  in chain between Si atoms), 3.76 (4C,  $\text{CH}_3$  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.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in five-ring in **74**), 3.27 (m, 4 H, aliphatic  $\text{CH}_2$  in five-ring in **73** and **74**), 2.53 (m, 2 H, aliphatic  $\text{CH}_2$  in chain in **74**), 2.47 (m, 2 H, aliphatic  $\text{CH}_2$  in chain in **73**), 1.69 (m, 2 H, aliphatic  $\text{CH}_2$  in chain in **74**), 1.55 (m, 2 H, aliphatic  $\text{CH}_2$  in chain in **73**), 0.92 (m, 2 H, aliphatic  $\text{CH}_2$  in chain in **74**), 0.58 (m, 2 H, aliphatic  $\text{CH}_2$  in chain in **73**), 0.35 (s, 6 H,  $\text{CH}_3$  attached to Si in **74**), 0.01 (s, 3 H,  $\text{CH}_3$  attached to Si in **73**),  $-0.03$  (s, 3 H,  $\text{CH}_3$  attached to Si in **73**) ppm.  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.74 ( $\text{C}_q$  in **74**), 150.51 ( $\text{C}_q$  in **73**), 148.26 ( $\text{C}_q$  in **74**), 145.81 ( $\text{C}_q$  in **74**), 145.77 ( $\text{C}_q$  in **73**), 145.40 ( $\text{C}_q$  in **73**), 144.87 (olefinic CH in five-ring in **74**), 144.72 ( $\text{C}_q$  in **74**), 144.52 ( $\text{C}_q$  in **74**), 144.28 ( $\text{C}_q$  in **73**), 143.27 ( $\text{C}_q$  in **74**), 143.23 ( $\text{C}_q$

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  $\text{CH}_2$  in five-ring in **73** and **74**), 35.06 (2 C, aliphatic  $\text{CH}_2$  in chain in **73** and **74**), 23.60 (2 C, aliphatic  $\text{CH}_2$  in chain in **73** and **74**), 14.50 (2 C, aliphatic  $\text{CH}_2$  in chain in **73** and **74**),  $-2.73$  (2C,  $\text{CH}_3$  attached to Si in **74**),  $-3.77$  ( $\text{CH}_3$  attached to Si in **73**),  $-4.17$  ( $\text{CH}_3$  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.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  in five-ring), 2.52 (m, 2 H, aliphatic  $\text{CH}_2$  in chain), 1.70 (m, 2 H, aliphatic  $\text{CH}_2$  in chain), 1.34 (m, 2 H, aliphatic  $\text{CH}_2$  in chain), 0.73 (s, 3 H,  $\text{CH}_3$  attached to Si) ppm.  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.39 ( $\text{C}_q$ ), 145.75 ( $\text{C}_q$ ), 143.25 ( $\text{C}_q$ ), 138.14 ( $\text{C}_q$ ), 137.19 ( $\text{C}_q$ ), 135.06 (arom. CH), 134.81 ( $\text{C}_q$ ), 134.53 (2C, arom. CH), 133.56 ( $\text{C}_q$ ), 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  $\text{CH}_2$  in five-ring), 34.93 (aliphatic  $\text{CH}_2$  in chain), 23.62 (aliphatic  $\text{CH}_2$  in chain), 14.92 (aliphatic  $\text{CH}_2$  in chain),  $-2.67$  ( $\text{CH}_3$  attached to Si) ppm.  $[\alpha]_D^{25} -0.9^{\circ}$  (c, 0.0264 g/ml  $\text{CHCl}_3$ ). 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.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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  $\text{CH}_2$  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  $\text{CH}_2$  in chain in **76** and/or **77**), 1.15 (m, 4 H, aliphatic  $\text{CH}_2$  in chain in **76** and/or **77**), 1.06 (m, 6 H,  $\text{CH}_3$  attached to the aliphatic chain in **76** and **77**), 0.60 (s, 6 H,  $\text{CH}_3$  attached to Si in **76** and **77**) ppm.  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 153.31 ( $\text{C}_q$  in **76** and/or **77**), 145.63 ( $\text{C}_q$  in **76** and/or **77**), 143.22 ( $\text{C}_q$  in **76** and/or **77**), 137.16 ( $\text{C}_q$  in **76** and/or **77**), 133.52 ( $\text{C}_q$  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 CH<sub>2</sub> in five-ring in **76** or **77**), 38.48 (aliphatic CH<sub>2</sub> in five-ring in **76** or **77**), 30.93 (aliphatic CH<sub>2</sub> in **76** and **77**), 20.54 (CH<sub>3</sub> attached to the aliphatic chain in **76** or **77**), 20.40 (CH<sub>3</sub> attached to the aliphatic chain in **76** or **77**), 12.56 (aliphatic CH<sub>2</sub> in chain in **76** or **77**), 12.38 (aliphatic CH<sub>2</sub> in chain in **76** or **77**), -2.72 (CH<sub>3</sub> attached to Si in **76** or **77**), -2.76 (CH<sub>3</sub> attached to Si in **76** or **77**) ppm. EIMS (70 eV): calcd. C<sub>30</sub>H<sub>30</sub>Si 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. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 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 CH<sub>2</sub> in five-ring in **78** and **79**), 2.13 (m, 4 H, aliphatic CH<sub>2</sub> in chain in **78** and **79**), 1.37 (m, 4 H, aliphatic CH<sub>2</sub> in chain in **78** and **79**), 0.80 (s, 3 H, CH<sub>3</sub> attached to Si in **78** or **79**), 0.79 (s, 3 H, CH<sub>3</sub> attached to Si in **78** or **79**) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>): δ = 153.12 (C<sub>q</sub> in **78** and/or **79**), 152.98 (C<sub>q</sub> in **78** and/or **79**), 145.25 (C<sub>q</sub> in **78** and/or **79**), 144.22 (C<sub>q</sub> in **78** and/or **79**), 144.10 (C<sub>q</sub> in **78** and/or **79**), 143.31 (C<sub>q</sub> in **78** and/or **79**), 138.01 (C<sub>q</sub> in **78** and/or **79**), 137.92 (C<sub>q</sub> in **78** and/or **79**), 137.19 (C<sub>q</sub> 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<sub>q</sub> in **78** and/or **79**), 134.56 (C<sub>q</sub> in **78** and/or **79**), 134.52 (arom. CH in **78** and/or **79**), 133.58 (C<sub>q</sub> in **78** and/or **79**), 133.56 (C<sub>q</sub> 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 CH<sub>2</sub> in five-ring in **78** and **79**), 29.26 (aliphatic CH<sub>2</sub> in chain in **78** or **79**), 29.20 (aliphatic CH<sub>2</sub> in chain in **78** or **79**), 13.48 (aliphatic CH<sub>2</sub> in chain in **78** or **79**), 13.44 (aliphatic CH<sub>2</sub> in chain in **78** or **79**), -2.67 (CH<sub>3</sub> attached to Si in **78** or **79**), -2.70 (CH<sub>3</sub> attached to Si in **78** or **79**) ppm. EIMS (70 eV): calcd. C<sub>35</sub>H<sub>32</sub>Si 480.2273; found 480.2267.

**Supporting Information:** Copies of <sup>13</sup>C NMR spectra of the compounds reported are provided.

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- a) R. L. Halterman, in *Metallocenes* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, **1998**, pp. 455–544; b) V. Cadierno, J. Diéz, M. P. Gamasa, J. Gimeno, E. Lastra, *Coord. Chem. Rev.* **1999**, *193–195*, 147–205; c) M. Stradiotto, M. J. McGlinchey, *Coord. Chem. Rev.* **2001**, *219–221*, 311–378.
- For recent reviews, see: a) G. W. Coates, *Chem. Rev.* **2000**, *100*, 1223–1252; b) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* **2000**, *100*, 1253–1346; c) R. Leino, in *Encyclopedia of Polymer Science and Technology*, 3rd ed. (Ed.: J. I. Kroschwitz); Wiley & Sons, New York, **2003**, vol. 4, pp. 136–179.
- For reviews, see: a) R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965–994; b) A. H. Hoveyda, J. P. Morken, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1263–1284; c) A. H. Hoveyda, J. P. Morken, in *Metallocenes* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, **1998**, pp. 625–683.
- a) D. Y. Kondakov, E. Negishi, *J. Am. Chem. Soc.* **1995**, *117*, 10771–10772; b) D. Y. Kondakov, E. Negishi, *J. Am. Chem. Soc.* **1996**, *118*, 1577–1578; c) K. H. Shaughnessy, R. M. Waymouth, *Organometallics* **1998**, *17*, 5728–5745; d) P. Wipf, S. Ribe, *Org. Lett.* **2000**, *2*, 1713–1716; e) P. Wipf, S. Ribe, *Org. Lett.* **2001**, *3*, 1503–1505.
- a) S. Huo, E. Negishi, *Org. Lett.* **2001**, *3*, 3253–3256; b) M. Magnin-Lachaux, Z. Tan, B. Liang, E. Negishi, *Org. Lett.* **2004**, *6*, 1425–1427; c) E. Negishi, Z. Tan, B. Liang, T. Novak, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5782–5787.
- a) G. W. Coates, R. M. Waymouth, *J. Am. Chem. Soc.* **1991**, *113*, 6270–6271; b) G. W. Coates, R. M. Waymouth, *J. Am. Chem. Soc.* **1993**, *115*, 91–98.
- See, for example: a) J. P. Morken, M. T. Didiuk, A. H. Hoveyda, *J. Am. Chem. Soc.* **1993**, *115*, 6997–6998; b) M. S. Visser, N. M. Heron, M. T. Didiuk, J. F. Sagal, A. H. Hoveyda, *J. Am. Chem. Soc.* **1996**, *118*, 4291–4298.
- See, for example: a) R. L. Halterman, K. P. C. Vollhardt, M. E. Welker, D. Bläser, R. Boese, *J. Am. Chem. Soc.* **1987**, *109*, 8105–8107; b) R. L. Halterman, T. M. Ramsey, Z. Chen, *J. Org. Chem.* **1994**, *59*, 2642–2644; c) C. A. Willoughby, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 8952–8965; d) M. B. Carter, B. Schiott, A. Gutiérrez, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 11667–11670; e) C. A. Willoughby, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 11703–11714.
- See, for example: a) S. L. Colletti, R. L. Halterman, *Tetrahedron Lett.* **1992**, *33*, 1005–1008; b) S. L. Colletti, R. L. Halterman, *J. Organomet. Chem.* **1993**, *455*, 99–106.
- a) A. Davison, P. E. Rakita, *J. Organomet. Chem.* **1970**, *23*, 407–426; b) N. E. Grimmer, N. J. Coville, C. B. de Koning, J. M. Smith, L. M. Cook, *J. Organomet. Chem.* **2000**, *616*, 112–127; c) A. C. Möller, R. H. Heyn, R. Blom, O. Swang, C. H. Görbitz, J. Kopf, *J. Chem. Soc., Dalton Trans.* **2004**, 1578–1589.
- For synthesis of 1-(or 3)-alkyl- and 1-(or 3)-aryl-substituted indenes, see for example: a) L. Meurling, *Acta Chem. Scand. B* **1974**, *28*, 295–300; b) T. H. Warren, G. Erker, R. Fröhlich, B. Wibbeling, *Organometallics* **2000**, *19*, 127–134 (addition of alkyl halides or alkyl tosylates to indenyl anions); c) L. G. Greifenstein, J. B. Lambert, R. J. Nienhuis, H. E. Fried, G. A. Pagani, *J. Org. Chem.* **1981**, *46*, 5125–5132; d) M. Adamczyk, D. S. Watt, D. A. Netzel, *J. Org. Chem.* **1984**, *49*, 4226–4237; e) T. M. Böhme, C. Keim, K. Kreutzmann, M. Linder, T. Dingermann, G. Dannhardt, E. Mutschler, G. Lambrecht, *J. Med. Chem.* **2003**, *46*, 856–867 (addition of alkyl- or arylmetals

- to 1-indanone followed by acid-promoted dehydration); f) T. Hayashi, T. Suzuka, A. Okada, M. Kawatsura, *Tetrahedron: Asymmetry* **2004**, *15*, 545–548 (Pd-catalyzed alkylation with indenyl anions); g) R. L. Halterman, C. Zhu, *Tetrahedron Lett.* **1999**, *40*, 7445–7448 (Ni-catalyzed Cr<sup>II</sup>-promoted addition of aryl bromides to tethered ketone carbonyls); h) J. de Arman, S. P. Kolis, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 5977–5983 (Zr-catalyzed addition of alkyl tosylates to indenenes); i) Z. Xi, R. Guo, S. Mito, H. Yan, K. Kanno, K. Nakajima, T. Takahashi, *J. Org. Chem.* **2003**, *68*, 1252–1257 (Zr-mediated coupling of aromatic ketones and alkynes followed by hydrolysis); j) R. W. Baker, M. A. Foulkes, M. Griggs, B. N. Nguyen, *Tetrahedron Lett.* **2002**, *43*, 9319–9322 (reaction of carboxylate esters with *o*-( $\beta$ -magnesiioalkyl)phenylmagnesium dihalides).
- [12] For synthesis of 2-alkyl- and 2-aryl-substituted indenenes, see for example ref.<sup>[11c]</sup> and a) E. C. Ribakove, R. C. Kerber, *Organometallics* **1990**, *9*, 531–534; b) E. Hauptman, R. M. Waymouth, J. W. Ziller, *J. Am. Chem. Soc.* **1995**, *117*, 11586–11587 (addition of alkyl- or aryl metals to 2-indanone followed by dehydration); ref.<sup>[11d]</sup> and c) H. Schumann, D. F. Karasiak, S. H. Mühle, R. L. Halterman, W. Kaminsky, U. Weingarten, *J. Organomet. Chem.* **1999**, *579*, 356–372 (cross coupling of Grignard reagents with 2-bromoindene); d) M. F. Lappert, T. R. Martin, C. L. Raston, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1982**, 1959–1963; e) W. W. Ellis, T. K. Hollis, W. Odenkirk, J. Whelan, R. Ostrander, A. L. Rheingold, B. Bosnich, *Organometallics* **1993**, *12*, 4391–4401; f) P. Witte, T. K. Lal, R. M. Waymouth, *Organometallics* **1999**, *18*, 4147–4155 [reaction of 1,2-di(magnesiomethyl)benzene dichloride with a carboxylic acid methyl esters followed by dehydration]; g) E. G. Ijpeij, F. H. Beijer, H. J. Arts, C. Newton, J. G. de Vries, G.-J. M. Gruter, *J. Org. Chem.* **2002**, *67*, 169–176 (Suzuki coupling of 2-bromoindene with diboronic acid); h) W.-L. Nie, G. Erker, G. Kehr, R. Fröhlich, *Angew. Chem. Int. Ed.* **2004**, *43*, 310–313 (addition of 2-indenylmagnesium bromide to a ketone followed by dehydration); i) I. E. Nifant'ev, A. A. Sitnikov, N. V. Andriukhova, I. P. Laishev'tsev, Y. N. Luzikov, *Tetrahedron Lett.* **2002**, *43*, 3213–3215 (Pd-catalyzed addition of aryl iodides to indenenes); and ref.<sup>[11j]</sup> (Zr-mediated coupling of aromatic ketones and alkynes followed by hydrolysis).
- [13] For a review, see: R. Leino, P. Lehmus, A. Lehtonen, *Eur. J. Inorg. Chem.* **2004**, 3201–3222.
- [14] a) S. E. Denmark, J. Fu, *Chem. Rev.* **2003**, *103*, 2763–2793; b) C.-J. Li, *Tetrahedron* **1996**, *52*, 5643–5668; c) C. Pétrier, J.-L. Luche, *J. Org. Chem.* **1985**, *50*, 912–915; d) K.-T. Tan, S.-S. Chng, H.-S. Cheng, T.-P. Loh, *J. Am. Chem. Soc.* **2003**, *125*, 2958–2963.
- [15] a) J. Podlech, T. C. Maier, *Synthesis* **2003**, 633–655; b) L. Paquette, *Synthesis* **2003**, 765–774.
- [16] T.-P. Loh, J.-R. Zhou, X.-R. Li, *Tetrahedron Lett.* **1999**, *40*, 9333–9336.
- [17] R. M. Kamble, V. K. Singh, *Tetrahedron Lett.* **2001**, *42*, 7525–7526.
- [18] J. S. Yadav, B. V. S. Reddy, G. Satheesh, *Tetrahedron Lett.* **2003**, *44*, 6501–6504.
- [19] N. Jiang, Q. Hu, C. S. Reid, Y. Lu, C.-J. Li, *Chem. Commun.* **2003**, 2318–2319.
- [20] a) H. G. Alt, M. Jung, *J. Organomet. Chem.* **1999**, *580*, 1–16; b) H. G. Alt, *J. Chem. Soc., Dalton Trans.* **1999**, 1703–1709; c) D. Zhang, G.-X. Jin, N.-H. Hu, *Eur. J. Inorg. Chem.* **2003**, 1570–1576; d) F. A. R. Kaul, G. T. Puchta, H. Schneider, F. Bielert, D. Mihalios, W. A. Herrmann, *Organometallics* **2002**, *21*, 74–82.
- [21] a) D. Hürcländer, N. Kleigrew, G. Kehr, G. Erker, R. Fröhlich, *Eur. J. Inorg. Chem.* **2002**, 2633–2642; b) J. C. Sierra, D. Hürcländer, M. Hill, G. Kehr, G. Erker, R. Fröhlich, *Chem. Eur. J.* **2003**, *9*, 3618–3622.
- [22] a) W.-L. Nie, G. Erker, G. Kehr, R. Fröhlich, *Angew. Chem. Int. Ed.* **2004**, *43*, 310–313. For similar work on cyclopentadienyl complexes, see: b) G. Erker, S. Wilker, C. Krüger, R. Goddard, *J. Am. Chem. Soc.* **1992**, *114*, 10983–10984; c) G. Erker, S. Wilker, C. Krüger, M. Nolte, *Organometallics* **1993**, *12*, 2140–2151.
- [23] G. Erker, G. Kehr, R. Fröhlich, *J. Organomet. Chem.* **2004**, *689*, 1402–1412.
- [24] See also: a) A. Padwa, S. Goldstein, M. Pulwer, *J. Org. Chem.* **1982**, *47*, 3893–3902; b) T. E. Ready, J. C. W. Chien, M. D. Rausch, *J. Organomet. Chem.* **1999**, *583*, 11–27.
- [25] N. Tsukada, T. Sato, Y. Inoue, *Chem. Commun.* **2001**, 237–238.
- [26] H. G. Alt, A. Weis, A. Reb, R. Ernst, *Inorg. Chim. Acta* **2003**, *343*, 253–274.
- [27] a) U. Stehling, J. Diebold, R. Kirsten, W. Röhl, H. H. Brintzinger, S. Jüngling, R. Mülhaupt, F. Langhauser, *Organometallics* **1994**, *13*, 964–970; b) N. Schneider, M. E. Huttenloch, U. Stehling, R. Kirsten, F. Schaper, H. H. Brintzinger, *Organometallics* **1997**, *16*, 3413–3420; c) N. Schneider, F. Schaper, K. Schmidt, R. Kirsten, A. Geyer, H. H. Brintzinger, *Organometallics* **2000**, *19*, 3597–3604.
- [28] In previous work, we have, without success, attempted the hydrosilylation of  $\beta$ -pinene by using the 1- and 3-indenyl mixture of indenyldimethylsilane in the presence of Karstedt's catalyst. Thus, for some reason, the reactivity of this compound under hydrosilylation conditions appears to be very low.
- [29] For other approaches to the synthesis of chirally substituted indenenes, see: a) Z. Chen, R. L. Halterman, *J. Am. Chem. Soc.* **1992**, *114*, 2276–2277; b) G. Erker, M. Aulbach, M. Knickmeier, D. Wingbermhühle, C. Krüger, M. Nolte, S. Werner, *J. Am. Chem. Soc.* **1993**, *115*, 4590–4601; c) G. Erker, M. Aulbach, C. Krüger, S. Werner, *J. Organomet. Chem.* **1993**, *450*, 1–7; d) M. Knickmeier, G. Erker, T. Fox, *J. Am. Chem. Soc.* **1996**, *118*, 9623–9630; e) R. L. Halterman, D. R. Fahey, E. F. Bailly, D. W. Dockter, O. Stenzel, J. L. Shipman, M. A. Khan, S. Dechert, H. Schumann, *Organometallics* **2000**, *19*, 5464–5470; f) H. Schumann, O. Stenzel, F. Girgsdies, R. L. Halterman, *Organometallics* **2001**, *20*, 1743–1751; g) R. L. Halterman, L. D. Crow, *Tetrahedron Lett.* **2003**, *44*, 2907–2909; h) S. Silver, E. Johansson, R. Sjöholm, R. Leino, *Tetrahedron Lett.* **2004**, *45*, 249–252.
- [30] a) L. H. Sommer, J. E. Lyons, H. Fujimoto, *J. Am. Chem. Soc.* **1969**, *91*, 7051–7061; b) M. A. Brook, *Silicon in Organic, Organometallic and Polymer Chemistry*, John Wiley & Sons, New York, **2000**, pp. 409–412.
- [31] For representative examples, see: a) F. R. W. P. Wild, L. Zsolnai, G. Huttner, H. H. Brintzinger, *J. Organomet. Chem.* **1982**, *232*, 233–247; b) F. R. W. P. Wild, M. Wasucioneck, G. Huttner, H. H. Brintzinger, *J. Organomet. Chem.* **1985**, *288*, 63–67; c) F. Piemontesi, I. Camurati, L. Resconi, D. Balboni, A. Sironi, M. Moret, R. Zeigler, N. Piccolrovazzi, *Organometallics* **1995**, *14*, 1256–1266.
- [32] Preliminary metallation attempts of the indenyl anions generated from compounds **38ab** and **40ab** with ZrCl<sub>4</sub> indeed support this hypothesis. <sup>1</sup>H NMR analyses of the crude products indicate the formation of the corresponding metallocene complexes as mixtures of the *rac*- and *meso* diastereomers in reasonably high yields. Detailed studies and optimization of the work-up/separation procedures are currently in progress.
- [33] See, for example: J. Schellenberg, N. Tomotsu, *Prog. Polym. Sci.* **2002**, *27*, 1925–1982.
- [34] Examples of hydrosilylation as postfunctionalization method for *ansa*-zirconocene complexes have been reported recently, see: a) C. J. Miller, D. O'Hare, *Chem. Commun.* **2004**, 1710–1711; b) A. Antinolo, M. Fajardo, S. Gomez-Ruiz, I. Lopez-Solera, A. Otero, S. Prashar, *Organometallics* **2004**, *23*, 4062–4069.
- [35] For a review on heterogeneous metallocene olefin polymerization catalysts, see: G. G. Hlatky, *Chem. Rev.* **2000**, *100*, 1347–1376.
- [36] W. Kaminsky, O. Rabe, A.-M. Schauwienold, G. U. Schupfner, J. Hanss, J. Kopf, *J. Organomet. Chem.* **1995**, *497*, 181–193.

- [37] H. W. Pinnick, S. P. Brown, E. A. McLean, L. W. Zoller, *J. Org. Chem.* **1981**, *46*, 3758–3760.
- [38] D. L. Musso, F. R. Cochran, J. L. Kelley, E. W. McLean, J. L. Selph, G. C. Rigdon, G. F. Orr, R. G. Davis, B. R. Cooper, V. L. Styles, J. B. Thompson, W. R. Hall, *J. Med. Chem.* **2003**, *46*, 399–408.
- [39] R. Leino, H. J. G. Luttikhedde, A. Lehtonen, R. Sillanpää, A. Penninkangas, J. Strandén, J. Mattinen, J. Näsman, *J. Organomet. Chem.* **1998**, *558*, 171–179.
- [40] H. Plenio, D. Burth, *Organometallics* **1996**, *15*, 4054–4062.
- [41] a) R. B. Shankar, US Pat. Appl. 0002308, 2002. See also: b) F. R. Japp, F. W. Streatfeild, *J. Chem. Soc.* **1883**, *43*, 27–34; c) A. C. Cope, L. Field, D. W. H. MacDowell, M. E. Wright, *J. Am. Chem. Soc.* **1949**, *71*, 1589–1593.
- [42] L. F. Fieser, A. M. Seligman, *J. Am. Chem. Soc.* **1935**, *57*, 942–946.
- [43] L. F. Fieser, A. M. Seligman, *J. Am. Chem. Soc.* **1936**, *58*, 2482–2487.
- [44] J. Eppinger, M. Spiegler, W. Hieringer, W. A. Herrmann, R. Anwänder, *J. Am. Chem. Soc.* **2000**, *122*, 3080–3096.
- [45] L. H. Sommer, C. L. Frye, G. A. Parker, K. W. Michael, *J. Am. Chem. Soc.* **1964**, *86*, 3271–3276.

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