Supporting Information

Pd-Catalyzed Pathways to Aryl-Substituted Indenes:

Efficient Synthesis of Ligands and the Respective *ansa*-Zirconocenes.

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Experimental Details

General Procedure. All manipulations with compounds, which are sensitive to both moisture and air, were performed either in an atmosphere of thoroughly purified argon using a standard Schlenk technique or in a controlled-atmosphere glove box (VAC). Tetrahydrofuran and diethyl ether were purified by distillation over LiAlH_4 and kept over sodium benzophenone ketyl. Hydrocarbon solvents (including C_6D_6) were distilled and stored over CaH_2 or Na/K alloy. Methylene chloride (and CD_2Cl_2) was distilled over P_4O_{10} and stored over CaH_2 . Chloroform-d was distilled over P_4O_{10} and stored over molecular sieves (3 Å). DMSO- d_6 was stored over KOH, distilled under reduced pressure, and stored over molecular sieves (3 Å). 2-Bromobenzyl bromide, 2-chlorobenzyl chloride, 2-bromobenzaldehyde, o-toluidine, 4-isopropylaniline, tetralin, 3,5-dibromotoluene, 2-bromoisobutyl bromide, diethylmethylmalonate, 4-bromotoluene, 1-naphthyl bromide, 1-naphthyl chloride, mesityl bromide, 2-bromothiophene, 2-

bromopyridine, 4-bromoisoquinoline, acetic anhydride, 3-bromo-1-benzothiophene, 2-fluorobromobenzene, perfluorobromobenzene, phenyl bromide, sodium tetraphenylborate, o-tolylboronic acid, p-tolylboronic acid, perfluorophenylboronic acid, 4-tert-butylphenylboronic acid, mesitylboronic acid, 2-thienylboronic acid, 3-nitrophenylboronic acid, 1-naphthylboronic acid, 2-methoxyphenylboronic acid, 1.0 M phenylmagnesium bromide, 1.0 M p-tolylmagnesium bromide in THF, 0.25 M 1-naphthylmagnesium bromide in THF, 1.0 M mesitylmagnesium bromide in THF, 0.5 M phenylzinc bromide in THF, triethyltin chloride, p-toluenesulfonic acid, NaBH₄, thionyl chloride, N-bromosuccinimide, triethyl 2-phosphonopropionate, powdered AlCl₃ (Merck), dibenzoyl peroxide, 0.5 M ZnCl₂ in THF, 2.5 M ⁿBuLi in hexanes, 1.6 M MeLi in ether, BrCF₂CF₂Br, Pd(OAc)₂, PdCl₂, Pd(P^tBu₃)₂, Pd(PPh₃)₄, triphenylphosphine, 2-[di(tert-butyl)phosphino]-1,1'-biphenyl, K₃PO₄ (Fluka), Na₂CO₃, methyl iodide, triisopropylborate, ZrCl₄ (Alfa Aesar), ZrCl₄(THF)₂ (Aldrich), anhydrous ethanol, copper powder, CuBr, and CuI were used as received. Pd(dba)₂ was prepared from PdCl₂ and dibenzolidenacetone as described in the literature [(a) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121. (b) Ukai, T.; Kawazawa, H.; Ishii, Y.; Bonnett, J.J.; Ibers, J.A. *J. Organomet. Chem.* **1974**, *65*, 253.]. Dichlorodimethylsilane was distilled over quinoline before use. TMEDA was distilled and stored over CaH₂. Powder of anhydrous ZnCl₂ (Merck) was dried in vacuum (10⁻²-10⁻³ mm/Hg) with vigorous stirring for 15 h at 170°C (oil bath). This product was stored and weighed in a glove box. Celite 503 (Fluka) was dried in vacuum for 20 h at 170°C (oil bath). 1-Bromo-2-methylnaphthalene was obtained via bromination of 2-methylnaphthalene [Budac, D.; Wan, P. *Can. J. Chem.* **1996**, *74*, 1447.]. 2,6-Dimethylindan-1-one was synthesized via the described procedure [Fukuoka, M.; Yoshihira, K.; Natori, S.; Mihashi, K.; Nishi, M. *Chem. Pharm. Bull.* **1983**, *31*, 3113.]. 5-Methyl-4,5-dihydro-6H-cyclopenta[b]thiophen-6-one was synthesized as described previously [Ryabov, A. N.; Gribkov, D. V.; Izmer, V. V.; Voskoboynikov, A. Z. *Organometallics* **2002**, *21*, 2842.]. Dicyclohexyl[2-(9-phenanthryl)phenyl]phosphine was synthesized from 2-chlorobromobenzene, 9-bromophenanthrene, and chlorodicyclohexylphosphine [Yin, J.; Rainka, M. P.; Zhang, X.-X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162.]. 2-(Tributylstannyl)pyridine was obtained by a published procedure [McWhinnie, W.R.; Poller, R.C.; Thevarasa, M. *J. Organomet. Chem.*

1968, 11, 499.], whereas tributyl(2-thienyl)stannane was obtained as described for trimethyl(2-thienyl)stannane starting from tri(*n*-butyl)tin chloride [Rocca, P.; Marsais, F.; Godard, A.; Queguiner, G. *Tetrahedron* **1993**, 49, 3325.]. Thienylmagnesium bromide was obtained by a standard procedure starting from 2-bromothiophene and magnesium turnings in THF. Silica Gel 60 (230-400 mesh, Merck) was used for flash chromatographic separations. Analytical and semipreparative liquid chromatography was performed using a Waters Delta 600 HPLC system including a 996 Photodiode Array Detector, Symmetry C18 (Waters, 60 Å, 5 µm, 4.6 x 250 mm) or Chromolith RP-18 (Merck, 4.6 x 100 mm) columns, and a Nova-Pack C18 column (Waters, 60 Å, 6 µm, 3.9 and 19 x 300 mm), respectively, in a methanol-water mobile phase. For analytical runs, calculations of yields of the products were performed under the assumption that extinction coefficients of isomeric indenenes and diastereomeric methoxyindanes are equal. ¹H and ¹³C spectra were recorded with Bruker DPX-300 or Avance-400 spectrometers for 1-10% solutions in deuterated solvents. Chemical shifts for ¹H and ¹³C were measured relatively to TMS. In ¹H NMR spectra, the assignment was made on the evidence of double resonance and NOE experiments. C, H microanalyses were done using a Carlo Erba 1106 analyzer.

3-(2-Bromophenyl)-2-methylpropanoic acid, 3-(2-bromophenyl)-2-methylpropanoyl chloride, 4-bromo-2-methyl-1-indanone. In a three-necked round-bottom 2000-ml flask equipped with a reflux condenser, a dropping funnel with pressure-equalizing bypass, and a magnetic stirring bar, 20.5 g (0.89 mol) of sodium metal was dissolved in 450 ml of dry ethanol. To the resulting solution, 155 g (0.89 mol) of diethylmethylmalonate in 150 ml of dry ethanol was added dropwise over 15 min. This mixture was stirred for 15 min; then, 186 g (0.89 mol) of 2-bromobenzyl bromide was added with vigorous stirring at such a rate as to maintain gentle reflux. This mixture was refluxed for an additional 4 h and cooled to room temperature. A solution of 151 g of KOH in 400 ml of water was then added. This mixture was refluxed for 3 h to saponify the ester formed. Ethanol and water were distilled off. To the residue, 500 ml of water and then 12 M HCl (to pH 1) were added. The substituted methylmalonic acid was precipitated and filtered off, washed with 2 x 200 ml of cold water, and dried overnight in air. Crude 3-(2-bromophenyl)-2-methylpropanoic acid was obtained after decarboxylation of this substituted methylmalonic acid for 2 h at

160°C. The product was used without further purification. A mixture of this acid and 160 ml of SOCl₂ was stirred for 24 h at ambient temperature. Thionyl chloride was distilled off. Crude 3-(2-bromophenyl)-2-methylpropanoyl chloride dissolved in 270 ml of CH₂Cl₂ was added dropwise with vigorous stirring to a suspension of 136 g (1.02 mol) of AlCl₃ in 1350 ml of CH₂Cl₂ over 1 h at 0°C. Then, this mixture was refluxed for 3 h, cooled to ambient temperature, and poured onto 500 cm³ of ice. The organic layer was separated. The aqueous layer was extracted with 3 x 300 ml of methyl-*tert*-butyl ether. The combined extract was dried over K₂CO₃ and evaporated to dryness. Fractional distillation gave the title indanone, b.p. 131-134°C/2 mm Hg. Yield 125.5 g (75%) of colorless solid. Anal. calc. for C₁₀H₉BrO: C, 53.36; H, 4.03. Found: C, 53.19; H, 3.98. ¹H NMR (CDCl₃): δ 7.76 (d, J = 7.6 Hz, 1H, 7-H), 7.71 (d, J = 7.6 Hz, 1H, 5-H), 7.28 (t, J = 7.6 Hz, 1H, 6-H), 3.36 (dd, J = 17.5 Hz, J = 7.6 Hz, 1H, 3-H), 2.70-2.82 (m, 1H, 2-H), 2.67 (dd, J = 17.5 Hz, J = 3.8 Hz, 1H, 3'-H), 1.34 (d, J = 7.3 Hz, 3H, 2-Me). ¹³C{¹H} NMR (CDCl₃): δ 208.3, 152.9, 138.2, 137.2, 129.0, 122.6, 122.0, 41.8, 35.7, 16.0.

(2*E/Z*)-3-(2-Bromophenyl)-2-methyl-2-propenoic acid. To a mixture of 57 ml of 50% NaOH and 100 ml of dichloromethane, a mixture of 18.5 g (0.10 mol) of 2-bromobenzaldehyde, 23.8 g (0.10 mol) of ethyl 2-(diethoxyphosphoryl)propanoate, and 14 ml of dichloromethane was added dropwise with vigorous stirring at ambient temperature over 30 min. The resulting mixture was refluxed for 4 h and then cooled to room temperature. The white crystals precipitated from this mixture were separated and then added to 300 ml of 4 M HCl with vigorous stirring. The precipitate formed was filtered off, washed with 30 ml of cold water, and dried in vacuum over P₄O₁₀. Yield 20.0 g (83%) of a ca. 9:1 mixture of *E*- and *Z*-isomers. Anal. calc. for C₁₀H₉BrO₂: C, 49.82; H, 3.76. Found: C, 49.89.19; H, 3.70. ¹H NMR (DMSO-*d*₆) of *E*-isomer: δ 12.71 (br.s, 1H, COOH), 7.69 (m, 1H, 6-H in C₆H₄), 7.56 (q, J = 1.3 Hz, CH=C(Me)COOH), 7.41-7.45 (m, 2H, 3,5-H in C₆H₄), 7.29 (m, 1H, 4-H in C₆H₄), 1.87 (d, J = 1.4 Hz, 3H, Me). ¹³C{¹H} NMR (DMSO-*d*₆) of *E*-isomer: δ 168.8, 136.6, 135.6, 132.6, 130.8, 130.7, 130.2, 127.7, 123.5, 13.8.

3-(2-Bromophenyl)-2-methylpropanoic acid. (2*E*)-3-(2-Bromophenyl)-2-methyl-2-propenoic acid (14.7 g, 61.0 mmol) and 7.6 g of red phosphorus were suspended in 95 ml of 57% HI and heated at reflux for 3.5 h. The reaction mixture was cooled to room temperature and 100 ml of dichloromethane was added; then,

this mixture was filtered through glass frit (G3). The filtrate consisted of two layers. The organic layer was separated, and the aqueous layer was extracted with 2 x 50 ml of dichloromethane. The combined extract was dried over MgSO_4 , evaporated to ca. 50 ml volume, and then passed through a short column with Silica Gel 60 (40-63 μm , d 50 mm, l 40 mm). The column was additionally washed by dichloromethane to isolate the product. The combined extract was evaporated to dryness, and the resulting white solid was dried in vacuum. Yield 13.3 g (90%). Anal. calc. for $\text{C}_{10}\text{H}_{11}\text{BrO}_2$: C, 49.41; H, 4.56. Found: C, 49.37; H, 4.51. ^1H NMR (CDCl_3): δ 11.87 (br.s, 1H, COOH), 7.54 (m, 1H, 3-H in C_6H_4), 7.21-7.25 (m, 2H, 5,6-H in C_6H_4), 7.08 (m, 1H, 4-H in C_6H_4), 3.19 (dd, $J=13.3$ Hz, $J=6.9$ Hz, 1H, CHH'), 2.93 (hex, $J=6.9$ Hz, 1H, CHMe), 2.81 (dd, $J=13.3$ Hz, $J=6.9$ Hz, 1H, CHH'), 1.22 (d, $J=6.9$ Hz, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 182.4, 138.4, 132.9, 131.3, 128.2, 127.3, 124.7, 39.4, 39.3, 16.7.

Mixture of 4- and 7-bromo-2-methyl-1H-indenes (1). To a solution of 116 g (0.52 mol) of 4-bromo-2-methyl-1-indanone in 950 ml of THF-methanol (2:1, vol.) 38.3 g (1.02 mol) of NaBH_4 was added in small portions over 2 h at -5°C (Caution: the temperature must be lower than 0°C). The mixture was stirred overnight at ambient temperature. The resulting mixture was poured onto 1000 cm^3 of ice and acidified with 10% HCl to pH 4. The organic layer was separated; the aqueous layer was extracted with 3 x 300 ml of methyl-*tert*-butyl ether. This combined extract was dried over K_2CO_3 and evaporated to dryness, and 1500 ml of toluene were added to the residue. This toluene solution was treated with a catalytic amount of $p\text{TolSO}_3\text{H}$ (ca. 2 g) for 2 h at reflux. Then this mixture was cooled to room temperature and passed through a short column with Silica Gel 60 (40-63 μm , d 60 mm, l 40 mm). This column was additionally eluted with 250 ml of toluene. The combined extract was evaporated to dryness. Fractional distillation gave a mixture of the title indene, b.p. $104\text{--}108^\circ\text{C}/5$ mm Hg. Yield 100 g (93%) of colorless solid mainly consisting of 7-bromo-2-methyl-1H-indene. Anal. calc. for $\text{C}_{10}\text{H}_9\text{Br}$: C, 57.44; H, 4.34. Found: C, 57.59; H, 4.40. ^1H NMR (CDCl_3) of 7-bromo-2-methyl-1H-indene: δ 7.23 (dd, $J=7.9$ Hz, $J=1.0$ Hz, 1H, 6-H), 7.18 (dd, $J=7.4$ Hz, $J=1.0$ Hz, 1H, 4-H), 7.10 (m, 1H, 5-H), 6.51 (m, 1H, 3-H), 3.28 (m, 2H, 1,1'-H), 2.17 (s, 3H, 2-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) of 7-bromo-2-methyl-1H-indene: δ 147.3, 146.8, 143.3, 128.2, 127.1, 126.6, 118.7, 118.3, 44.2, 16.7.

3-(2-Chlorophenyl)-2-methylpropanoic acid, 3-(2-chlorophenyl)-2-methylpropanoyl chloride, and 4-chloro-2-methyl-1-indanone. In a three-necked round-bottom 2000-ml flask equipped with a reflux condenser, a dropping funnel with a pressure-equalizing bypass, and a magnetic stirring bar, 19.5 g (0.87 mol) of sodium metal was dissolved in 480 ml of dry ethanol. To the resulting solution, 141 g (0.84 mol) of diethylmethylmalonate in 150 ml of dry ethanol was added dropwise over 15 min. This mixture was stirred for 15 min; then, 108 ml (138 g, 0.86 mol) of 2-chlorobenzyl chloride was added with vigorous stirring at such a rate as to maintain gentle reflux. This mixture was refluxed for an additional 4 h and then cooled to room temperature. A solution of 168 g of KOH in 450 ml of water was then added. This mixture was refluxed for 3 h to saponify the ester formed. Ethanol and water were distilled off. To the residue, 500 ml of water and then 12 M HCl (to pH 1) were added. The substituted methylmalonic acid was precipitated and separated, washed with 2 x 200 ml of cold water, and dried in vacuum. Crude 3-(2-chlorophenyl)-2-methylpropanoic acid was obtained after decarboxylation of the substituted methylmalonic acid for 2 h at 180°C. This product was used without further purification. A mixture of this acid and 210 ml of SOCl₂ was stirred for 24 h at ambient temperature. Thionyl chloride was distilled off. Fractional distillation gave 147 g of a colorless oil of 3-(2-chlorophenyl)-2-methylpropanoyl chloride, b.p. 115-117°C/7 mm Hg. This acid chloride was dissolved in 300 ml of CH₂Cl₂ and added dropwise with vigorous stirring to a suspension of 170 g (1.28 mol) of AlCl₃ in 1500 ml of CH₂Cl₂ over 2 h at 0°C. Then, this mixture was refluxed for 3 h, cooled to room temperature, and poured onto 500 cm³ of ice. The organic layer was separated. The aqueous layer was extracted with 3 x 300 ml of methyl-*tert*-butyl ether. The combined extract was dried over K₂CO₃ and evaporated to dryness. Fractional distillation gave 106 g (76%) of 4-chloro-2-methyl-1-indanone, b.p. 128°C/10 mm Hg. Anal. calc. for C₁₀H₉ClO: C, 66.49; H, 5.02. Found: C, 66.32; H, 4.95. ¹H NMR (CDCl₃): δ 7.60 (m, 1H, 7-H), 7.52 (dd, J = 7.8 Hz, J = 0.9 Hz, 1H, 5-H), 7.29 (m, 1H, 6-H), 3.35 (m, 1H, 2-H), 2.69 (m, 2H, CH₂), 1.30 (d, 3H, Me). ¹³C{¹H} NMR (CDCl₃): δ 207.5, 150.4, 137.7, 133.6, 132.2, 128.4, 121.6, 41.3, 33.3, 15.5.

Mixture of 4- and 7-chloro-2-methyl-1H-indenes (2). To a solution of 106 g (0.59 mol) of 4-chloro-2-methyl-1-indanone in 1000 ml of THF-methanol (2:1, vol.), 48.4 g (1.29 mol) of NaBH₄ was added in

small portions over 2 h at -5°C (Caution: the temperature must be lower than 0°C). The mixture was stirred for 12 h at ambient temperature and then poured onto 1000 cm^3 of ice and acidified with 10% HCl to pH 4. The organic layer was separated, and the aqueous layer was extracted with 3 x 300 ml of methyl-*tert*-butyl ether. The combined extract was dried over K_2CO_3 and evaporated to dryness, and 1500 ml of toluene was added to the yellowish oil obtained. This toluene solution was treated with a catalytic amount of $p\text{-TolSO}_3\text{H}$ (ca. 2 g) for 2 h at reflux. Then, the mixture was cooled to room temperature and passed through a short column with Silica Gel 60 (40-63 μm , d 80 mm, l 50 mm). This column was additionally eluted with 500 ml of toluene. The combined extract was evaporated to dryness. Fractional distillation gave chloro-substituted indene, b.p. $120\text{-}125^{\circ}\text{C}/10\text{ mm Hg}$. Yield 89.9 g (97%) of colorless oil of a ca. 1:9 mixture of 4-chloro-2-methylindene and 7-chloro-2-methylindene. Anal. calc. for $\text{C}_{10}\text{H}_9\text{Cl}$: C, 72.96; H, 5.51. Found: C, 72.80; H, 5.47. ^1H NMR (CDCl_3) of 4-chloro-2-methylindene: δ 7.14-7.31 (m, 3H, 5,6,7-H), 6.72 (m, 1H, 3-H), 3.38 (m, 2H, 1,1'-H), 2.23 (s, 3H, 2-Me); 7-chloro-2-methylindene: δ 7.14-7.31 (m, 3H, 4,5,6-H), 6.53 (m, 1H, 3-H), 3.36 (m, 2H, 1,1'-H), 2.23 (s, 3H, 2-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) of 7-chloro-2-methylindene: δ 147.9, 147.2, 141.3, 129.7, 128.3, 127.4, 124.1, 118.5, 42.6, 17.0.

3-(2-Bromo-3-methylphenyl)-2-methylpropanoic acid, 3-(2-bromo-3-methylphenyl)-2-

methylpropanoyl chloride, and 4-bromo-2,5-dimethyl-1-indanone. In a three-necked round-bottom 500-ml flask equipped with a reflux condenser, a dropping funnel with pressure-equalizing bypass, and a magnetic stirring bar, 5.95 g (0.26 mol) of sodium metal was dissolved in 200 ml of dry ethanol. To the resulting solution, 45.1 g (0.26 mol) of diethylmethylmalonate was added dropwise over 15 min. This mixture was stirred for 15 min; then, 62.1 g (0.24 mol) of 2-bromo-1-(bromomethyl)-3-methylbenzene in 50 ml of ethanol was added with vigorous stirring at such a rate as to maintain gentle reflux. This mixture was refluxed for an additional 4 h and cooled to room temperature. A solution of 51.8 g of KOH in 150 ml of water was added. This mixture was refluxed for 3 h to saponify the ester formed. Ethanol and water were distilled off. To the residue, 200 ml of water and then 12 M HCl (to pH 1) were added. The substituted methylmalonic acid was precipitated and separated, washed with 2 x 60 ml of cold water, and dried overnight in air. Crude 3-(2-bromo-3-methylphenyl)-2-methylpropanoic acid was obtained after

decarboxylation of this substituted methylmalonic acid for 2 h at 160°C. The product was used without further purification. A mixture of this acid and 60 ml of SOCl₂ was stirred for 24 h at ambient temperature. Thionyl chloride was distilled off. Crude 3-(2-bromo-3-methylphenyl)-2-methylpropanoyl chloride was dissolved in 200 ml of CH₂Cl₂ and added dropwise with vigorous stirring to a suspension of 37.7 g (0.28 mol) of AlCl₃ in 800 ml of CH₂Cl₂ over 1 h at 0°C. Then, this mixture was refluxed for 3 h, cooled to ambient temperature, and poured onto 300 cm³ of ice. The organic layer was separated. The aqueous layer was extracted with 3 x 100 ml of methyl-*tert*-butyl ether. The combined extract was dried over K₂CO₃ and evaporated to dryness. Fractional distillation gave the title indanone, b.p. 120-121°C/1 mm Hg. Yield 47.6 g (85%) of a colorless solid. Anal. calc. for C₁₁H₁₁BrO: C, 55.25; H, 4.64. Found: C, 55.35; H, 4.66. ¹H NMR (CDCl₃): δ 7.64 (d, J = 7.8 Hz, 1H, 7-H), 7.22 (d, J = 7.8 Hz, 1H, 6-H), 3.29 (dd, J = 17.6 Hz, J = 7.9 Hz, 1H, 3-H), 2.70 (m, 1H, 2-H), 2.59 (dd, J = 17.6 Hz, J = 3.9 Hz, 1H, 3'-H), 2.45 (s, 3H, 5-Me), 1.28 (d, J = 7.6 Hz, 2-Me). ¹³C{¹H} NMR (CDCl₃): δ 208.1, 153.8, 145.1, 136.1, 130.3, 124.1, 122.3, 42.2, 36.5, 23.1, 16.2.

Mixture of 4-bromo-2,5-dimethyl-1*H*-indene and 7-bromo-2,6-dimethyl-1*H*-indene (3). To a solution of 47.6 g (199 mmol) of 4-bromo-2,5-dimethyl-1-indanone in 270 ml of THF-methanol (2:1, vol.) 11.3 g (299 mmol) of NaBH₄ was added in small portions over 1 h at 0°C (Caution: the temperature must be kept below 5°C). The mixture was stirred overnight at ambient temperature and then poured onto 300 cm³ of ice and acidified with 10% HCl to pH 4. The organic layer was separated, and the aqueous layer was extracted with 3 x 200 ml of dichloromethane. This combined extract was dried over Na₂SO₄, and evaporated to dryness, and 500 ml of toluene were added to the white solid obtained. This toluene solution was treated with a catalytic amount of *p*-TolSO₃H (ca. 2 g) using a Dean-Stark trap for 2 h at reflux. Then, the mixture was cooled to room temperature, washed with aqueous NaHCO₃, and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm, d 80 mm, l 50 mm; eluent: hexanes). Yield 38.7 g (87%) of a ca. 1:8 mixture of 4-bromo-2,5-dimethyl-1*H*-indene and 7-bromo-2,6-dimethyl-1*H*-indene as a white solid. Anal. calc. for C₁₁H₁₀Br: C, 59.22; H, 4.97. Found: C, 59.35; H, 5.03. ¹H NMR (CDCl₃) of 4-bromo-2,5-dimethyl-1*H*-indene: δ 7.03 (m, 1H, 7-H in indenyl), 6.97 (d, J = 7.4 Hz, 1H, 6-H

on indenyl), 6.36 (m, 1H, 3-H in indenyl), 3.22 (m, 2H, CH₂), 2.35 (s, 3H, 5-Me in indenyl), 2.09 (m, 3H, 2-Me in indenyl); 7-bromo-2,6-dimethyl-1*H*-indene: δ 7.03 (m, 1H, 4-H in indenyl), 7.00 (d, *J* = 7.5 Hz, 1H, 5-H on indenyl), 6.40 (m, 1H, 3-H in indenyl), 3.20 (m, 2H, CH₂), 2.38 (s, 3H, 6-Me in indenyl), 2.09 (m, 3H, 2-Me in indenyl). ¹³C{¹H} NMR (CDCl₃) of 7-bromo-2,6-dimethyl-1*H*-indene: δ 145.6, 144.6, 144.0, 132.5, 128.7, 126.9, 121.0, 118.3, 44.8, 22.3, 16.6.

3,5-Dibromobenzyl bromide. A mixture of 390 g (1.56 mol) of 3,5-dibromotoluene, 278 g (1.56 mol) of *N*-bromosuccinimide, and 1 g of benzoyl peroxide in 1500 cm³ of CCl₄ was refluxed for 3 h. Then, this mixture was cooled to ambient temperature and one more portion of benzoyl peroxide (1 g) was added. The resulting mixture was refluxed for 3 h and then filtered through glass frit (G2). The filtrate was evaporated to dryness, and the residue was recrystallized from 200 ml of hexanes at 5°C. The crystals precipitated were collected, washed with 2 x 20 ml of cold hexanes, and dried in vacuum. Yield 309 g (60%) of a white crystalline solid. Anal. calc. for C₇H₅Br₃: C, 25.57; H, 1.53. Found: C, 25.70; H, 1.62. ¹H NMR (CDCl₃): δ 7.58 (t, *J* = 1.7 Hz, 1H, 2-H), 7.46 (d, *J* = 1.7 Hz, 2H, 4,6-H), 4.34 (s, 2H, CH₂). ¹³C{¹H} NMR (CDCl₃): δ 141.2, 133.9, 130.7, 123.0, 30.7.

3-(3,5-Dibromophenyl)-2-methylpropanoic acid, 3-(3,5-dibromophenyl)-2-methylpropanoyl chloride, and 5,7-dibromo-2-methyl-1-indanone. In a three-necked round-bottom 2000-ml flask equipped with a reflux condenser, a dropping funnel with a pressure-equalizing bypass, and a magnetic stirring bar, 22.0 g (0.96 mol) of sodium metal was dissolved in 700 ml of dry ethanol. To the resulting solution, 164 g (0.94 mol) of diethylmethylmalonate was added dropwise over 30 min. This mixture was stirred for 15 min; then, 309 g (0.94 mol) of 3,5-dibromobenzylbromide in 200 ml of ethanol was added with vigorous stirring at such a rate as to maintain gentle reflux. This mixture was refluxed for an additional 4 h and cooled to room temperature. A solution of 188 g of KOH in 500 ml of water was added. This mixture was refluxed for 3 h to saponify the ester formed. Ethanol and water were distilled off, and 600 ml of water and then 12 M HCl (to pH 1) were added to the residue. The substituted methylmalonic acid was precipitated and separated, washed with 2 x 200 ml of cold water, and dried overnight in air. Crude 3-(3,5-dibromophenyl)-2-methylpropanoic acid was obtained after decarboxylation of this substituted methylmalonic acid for 4 h

at 160°C. The product was used without further purification. A mixture of this acid and 200 ml of SOCl₂ was stirred for 24 h at ambient temperature. Thionyl chloride was distilled off (at <50°C), and the residue was dried in vacuum for 3 h at ambient temperature. Crude 3-(3,5-dibromophenyl)-2-methylpropanoyl chloride dissolved in 500 ml of CH₂Cl₂ was added dropwise with vigorous stirring to a suspension of 150 g (1.13 mol) of AlCl₃ in 1000 ml of CH₂Cl₂ over 2 h at 0°C. Then, this mixture was refluxed for 6 h, cooled to ambient temperature, and poured onto 800 cm³ of ice. The organic layer was separated. The aqueous layer was extracted with 3 x 400 ml of CH₂Cl₂. The combined extract was dried over K₂CO₃ and evaporated to dryness. The crude product was isolated by flash chromatography on Silica Gel 60 (40-63 μm, d 60 mm, l 500 mm; eluent: hexanes-dichloromethane from 1:1 to 1:2). The eluate was evaporated to dryness, and the residue was recrystallized from hexanes. Yield 211 g (74%) of a yellowish solid of 5,7-dibromo-2-methyl-1-indanone. Anal. calc. for C₁₀H₈Br₂O: C, 39.51; H, 2.65. Found: C, 39.45; H, 2.58. ¹H NMR (CDCl₃): δ 7.66 (m, 1H, 4-H), 7.54 (m, 1H, 6-H), 3.31 (m, 1H, 3-H), 2.71 (m, 1H, 2-H), 2.66 (m, 1H, 3'-H), 1.29 (d, J= 7.2 Hz, 3H, 2-Me).

Mixture of 4,6- and 5,7-dibromo-2-methyl-1*H*-indenenes (4). To a solution of 210 g (0.69 mol) of 5,7-dibromo-2-methyl-1-indanone in 900 ml of THF-methanol (2:1, vol.), 35.8 g (0.95 mol) of NaBH₄ was added in small portions over 1 h at 0°C (Caution: the temperature must be lower than 5°C). The mixture was stirred overnight at ambient temperature and then poured onto 300 cm³ of ice and acidified with 10% HCl to pH 4. The organic layer was separated, and the aqueous layer was extracted with 2 x 200 ml of methyl-*tert*-butyl ether. The combined extract was dried over Na₂SO₄ and evaporated to dryness, and 1700 ml of toluene was added to the white solid obtained. This toluene solution was treated with a catalytic amount of *p*-TolSO₃H (ca. 5 g) using a Dean-Stark trap for 7 h at reflux. Then, the mixture was cooled to room temperature, washed with aqueous NaHCO₃, and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm, d 80 mm, l 50 mm; eluent: hexanes). Yield 181 g (91%) of a ca. 10:1 mixture of 4,6- and 5,7-dibromo-2-methyl-1*H*-indenenes as a white solid. Anal. calc. for C₁₀H₈Br₂: C, 41.71; H, 2.80. Found: C, 41.61; H, 2.86. 4,6-Dibromo-2-methyl-1*H*-indene. ¹H NMR

(CDCl₃): δ 7.49 (m, 1H, 5-H), 7.37 (m, 1H, 7-H), 6.51 (m, 1H, 3-H), 3.33 (m, 2H, 1,1'-H), 2.13 (m, 3H, 2-Me). ¹³C{¹H} NMR (CDCl₃): δ 147.9, 146.0, 145.0, 131.6, 126.2, 125.4, 117.4, 113.7, 43.7, 16.7.

2-Methyl-1-indanol. To a solution of 119 g (0.815 mol) of 2-methyl-1-indanone in 1100 cm³ of THF-methanol (2:1, vol.), 46.3 g (1.22 mol) of NaBH₄ was added with vigorous stirring for 4 h at 0°C. This mixture was stirred overnight at room temperature and then added to 1000 cm³ of cold water. The organic layer was separated, and the aqueous layer was extracted with 3 x 400 ml of dichloromethane. The combined extract was passed through a short column with Silica Gel 60 (40-63 μ m, d 80 mm, l 100 mm). The eluate was evaporated to dryness. Yield 118 g (98%) of a ca. 1:1 mixture of (*R,S/S,R*)-2-methyl-1-indanol and (*R,R/S,S*)-2-methyl-1-indanol that can be rectified at 122-125°C/13 mm Hg. Anal. calc. for C₁₀H₁₂O: C, 81.04; H, 8.16. Found: C, 81.03; H, 8.25. (*R,S/S,R*)-2-Methyl-1-indanol (53.8 g) of 93% purity was obtained by crystallization of the above-described mixture of isomers from hexanes at -30°C. ¹H NMR (CDCl₃), (*R,S/S,R*)- 2-methyl-1-indanol: δ 7.17-7.39 (m, 4H, 4,5,6,7-H), 4.69 (d, J= 6.7 Hz, 1H, CHOH), 3.10 (dd, J= 15.7 Hz, J= 7.7 Hz, 1H, CHH'), 2.45 (dd, J= 15.7 Hz, J= 8.3 Hz, 1H, CHH'), 2.23 (m, 1H, CHMe), 1.86 (br.s, 1H, OH), 1.24 (d, J= 6.9 Hz, 3H, Me); (*R,R/S,S*)-2-methyl-1-indanol: δ 7.18-7.41 (m, 4H, 4,5,6,7-H), 4.98 (d, J= 5.9 Hz, 1H, CHOH), 2.94 (dd, J= 15.7 Hz, J= 7.4 Hz, 1H, CHH'), 2.66 (dd, J= 15.7 Hz, J= 7.2 Hz, 1H, CHH'), 2.53 (m, 1H, CHMe), 1.82 (br.s, 1H, OH), 1.12 (d, J= 7.0 Hz, 3H, Me). ¹³C{¹H} NMR (CDCl₃), (*R,S/S,R*)- 2-methyl-1-indanol: δ 144.9, 142.0, 128.0, 126.6, 124.7, 123.9, 82.8, 45.4, 37.8, 17.8; (*R,R/S,S*)-2-methyl-1-indanol: δ 144.7, 143.3, 128.3, 126.6, 124.9, 124.7, 77.6, 39.2, 37.9, 13.6.

7-Bromo-2-methyl-1-indanol (5). To a mixture of 7.11 g (48.0 mmol) of (*R,S/S,R*)- and (*R,R/S,S*)-2-methyl-1-indanol, 16.0 ml (12.3 g, 106 mmol) of TMEDA and 720 ml of *n*-pentane, 42.4 ml of 2.5 M (106 mmol) of ⁿBuLi in hexanes was added dropwise with vigorous stirring over 10 min at 0°C. This mixture was stirred for an additional 10 min at this temperature and then refluxed for 10 h. The resulting mixture was cooled to -80°C, and 31.2 g (120 mmol) of BrCF₂CF₂Br was added at this temperature. The mixture was warmed to ambient temperature and then stirred for 12 h. Then, 100 ml of water was added at 0°C. The organic layer was separated, and the aqueous layer was extracted with 4 x 30 ml of dichloromethane.

The combined organic extracts were dried over K_2CO_3 and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 40 mm, l 300 mm; eluent: hexanes-ether = 5:1, vol.). Yield 9.05 g (83%) of a mixture of (*R,S/S,R*)- and (*R,R/S,S*)-7-bromo-2-methyl-1-indanol. Anal. calc. for $C_{10}H_{11}BrO$: C, 52.89; H, 4.88. Found: C, 53.02; H, 4.81. 1H NMR ($CDCl_3$) (*R,S/S,R*)-7-bromo-2-methyl-1-indanol: δ 7.31-7.35 (m, 1H, 6-H), 7.08-7.18 (m, 2H, 4,5-H), 4.86 (m, 1H, *CHOH*), 3.31 (m, 1H, *CHH'*CHMe), 2.55 (br.s, 1H, OH), 2.48 (m, 1H, *CHH'*CHMe), 2.39-2.51 (m, 1H, CHMe), 1.16 (d, $J = 7.0$ Hz, 3H, Me); (*R,R/S,S*)-7-bromo-2-methyl-1-indanol: δ 7.31-7.35 (m, 1H, 6-H), 7.07-7.18 (m, 2H, 4,5-H), 5.04 (m, 1H, *CHOH*), 2.99 (dd, $J = 15.9$ Hz, $J = 7.6$ Hz, 1H, *CHH'*CHMe), 2.82 (dd, $J = 15.9$ Hz, $J = 9.7$ Hz, 1H, *CHH'*CHMe), 2.55 (br.s, 1H, OH), 2.45 (m, 1H, CHMe), 1.24 (d, $J = 7.1$ Hz, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$), (*R,S/S,R*)-7-bromo-2-methyl-1-indanol: δ 145.6, 143.2, 130.14, 130.08, 124.3, 120.0, 83.3, 41.8, 38.6, 18.7.

Mixture of 4- and 7-bromo-2-methyl-1*H*-indenes (1). A mixture of 4.54 g (20.0 mmol) of **5**, 200 mg of *para*-toluenesulfonic acid, and 100 ml of toluene was refluxed for 1 h. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 15 mm, l 200 mm; eluent: hexanes). Yield 4.01 g (96%) of colorless solid mainly consisting of 4-bromo-2-methyl-1*H*-indene. Anal. calc. for $C_{10}H_9Br$: C, 57.44; H, 4.34. Found: C, 57.52; H, 4.30. 1H NMR ($CDCl_3$) of 4-bromo-2-methyl-1*H*-indene: δ 7.32 (m, 1H, 5-H), 7.24 (m, 1H, 7-H), 6.93 (m, 1H, 6-H), 6.57 (m, 1H, 3-H), 3.34 (m, 2H, 1,1'-H), 2.14 (m, 3H, 2-Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$) of 4-bromo-2-methyl-1*H*-indene: δ 147.4, 145.9, 144.7, 129.3, 126.7, 125.0, 122.1, 113.7, 43.8, 16.8.

(*R,S/S,R*)-7-Iodo-2-methyl-1-indanol (6). To a mixture of 5.00 g (33.7 mmol) of (*R,S/S,R*)-2-methyl-1-indanol, 10.2 ml (7.85 g, 67.5 mmol) of TMEDA and 65 ml of *n*-pentane, 27.0 ml of 2.5 M (67.5 mmol) of n BuLi in hexanes was added dropwise with vigorous stirring over 10 min at 0°C. This mixture was stirred for an additional 10 min at this temperature and then refluxed for 7 h. The resulting mixture was cooled to -40°C, and 8.38 g (33.0 mmol) of iodine and 30 ml of ether were added at this temperature. The mixture was warmed to ambient temperature and then stirred for 4 h. Then, 100 ml of water was added at 0°C. The organic layer was separated, and the aqueous layer was extracted with 3 x 30 ml of ether. The combined

organic extracts were dried over K_2CO_3 and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 45 mm, l 300 mm; eluent: hexanes-dichloromethane = 1:2, vol.). Yield 2.52 g (27%) of yellowish solid. Anal. calc. for $C_{10}H_{11}IO$: C, 43.82; H, 4.05. Found: C, 43.92; H, 4.11. 1H NMR ($CDCl_3$): δ 7.57 (m, 1H, 6-H), 7.18 (d, J = 7.6 Hz, 1H, 4-H), 6.94 (t, J = 7.6 Hz, 6-H), 4.69 (d, J = 3.4 Hz, 1H, $CHOH$), 3.33 (m, 1H, CHH'), 2.38-2.52 (m, 3H, CHH' , $CHMe$, and OH), 1.13 (d, J = 7.0 Hz, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.7, 144.9, 136.4, 130.2, 125.2, 93.4, 85.4, 41.4, 38.7, 18.8.

4-Iodo-2-methyl-1H-indene (7). A mixture of 0.41 g (1.58 mmol) of **7**, 10 mg of p TolSO $_3$ H, and 5 ml of toluene was refluxed for 40 min. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 15 mm, l 250 mm; eluent: hexanes). Yield 0.38 g (94%) of yellowish oil. Anal. calc. for $C_{10}H_9I$: C, 46.90; H, 3.54. Found: C, 46.77; H, 3.52. 1H NMR ($CDCl_3$): δ 7.51 (d, J = 7.6 Hz, 1H, 5-H), 7.21 (m, 1H, 7-H), 6.75 (t, J = 7.6 Hz, 6-H), 6.43 (m, 1H, 3-H), 3.31 (m, 2H, CH_2), 2.10 (m, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.7, 147.3, 143.6, 135.4, 130.2, 125.2, 122.8, 86.6, 44.2, 16.7.

2,6-Dimethylindan-1-ol. To a solution of 131 g (0.818 mol) of 2,6-dimethyl-1-indanone in 1100 cm 3 of THF-methanol (2:1, vol.), 46.3 g (1.22 mol) of $NaBH_4$ was added with vigorous stirring for 4 h at 0°C. This mixture was stirred overnight at room temperature and then added to 1000 cm 3 of cold water. The organic layer was separated, and the aqueous layer was extracted with 3 x 400 ml of dichloromethane. The combined extract was passed through a short column with Silica Gel 60 (40-63 μm , d 80 mm, l 100 mm). The solution was evaporated to dryness, and the residue was dried in vacuum. Yield 130 g (98%) of a mixture of (*R,S/S,R*)- and (*R,R/S,S*)-2,6-dimethyl-1-indanol. Anal. calc. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.60; H, 8.83. 1H NMR ($CDCl_3$) (*R,S/S,R*)-2,6-dimethyl-1-indanol: δ 7.16 (s, 1H, 7-H), 7.01-7.11 (m, 2H, 4,5-H), 4.65 (t, J = 7.1 Hz, 1H, $CHOH$), 3.04 (dd, J = 15.5 Hz, J = 7.8 Hz, 1H, CHH' CHMe), 2.39 (dd, J = 15.5 Hz, J = 8.2 Hz, 1H, CHH' CHMe), 2.33 (br.s, 4H, 6-Me and OH), 2.21 (m, 1H, CHMe), 1.22 (d, J = 6.8 Hz, 3H, Me); (*R,R/S,S*)-2,6-dimethyl-1-indanol: δ 7.20 (s, 1H, 7-H), 7.01-7.09 (m, 2H, 4,5-H), 4.93 (t, J = 6.3 Hz, 1H, $CHOH$), 2.89 (dd, J = 15.4 Hz, J = 7.3 Hz, 1H, CHH' CHMe), 2.60 (dd, J = 15.4 Hz, J = 7.1 Hz, 1H, CHH' CHMe), 2.51 (m, 1H, CHMe), 2.33 (br.s, 4H, 6-Me and OH), 1.11 (d, J = 7.0 Hz,

3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 145.1, 144.9, 140.2, 139.0, 136.2, 129.1, 128.8, 125.3, 124.6, 124.4, 82.7, 77.6, 45.5, 39.4, 37.5, 37.4, 30.8, 21.2, 17.7, 13.6.

7-Bromo-2,6-dimethyl-1-indanol (8). To a mixture of 4.87 g (30.0 mmol) of 2,6-dimethylindan-1-ol, 9.96 ml (7.68 g, 66 mmol) of TMEDA and 450 ml of *n*-pentane, 26.4 ml of 2.5 M (66 mmol) of $n\text{BuLi}$ in hexanes was added dropwise with vigorous stirring over 10 min at 0°C . This mixture was stirred for an additional 10 min at this temperature and then refluxed for 10 h. The resulting mixture was cooled to -80°C , and 19.6 g (75.4 mmol) of $\text{BrCF}_2\text{CF}_2\text{Br}$ was added at this temperature. The mixture was warmed to ambient temperature and then stirred for 12 h. Then, 100 ml of water was added at 0°C . The organic layer was separated, and the aqueous layer was extracted with 4 x 30 ml of dichloromethane. The combined organic extracts were dried over K_2CO_3 and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 40 mm, l 250 mm; eluent: hexanes-ether = 5:1, vol.). Yield 2.68 g (37%) of a ca. 1:1 mixture of (*R,S/S,R*)- and (*R,R/S,S*)-7-bromo-2,6-dimethyl-1-indanol. Anal. calc. for $\text{C}_{11}\text{H}_{13}\text{BrO}$: C, 54.79; H, 5.43. Found: C, 54.60; H, 5.56. ^1H NMR (CDCl_3), (*R,S/S,R*)-7-bromo-2,6-dimethyl-1-indanol: δ 6.97-7.15 (m, 2H, 4,5-H), 4.87 (d, $J = 3.4$ Hz, 1H, CHOH), 3.31 (m, 1H, $\text{CHH}'\text{CHMe}$), 2.40-2.54 (m, 2H, $\text{CHH}'\text{CHMe}$ and CHMe), 2.38 (s, 3H, 6-Me), 1.68 (br.s, 1H, OH), 1.24 (d, $J = 7.0$ Hz, 3H, 2-Me); (*R,R/S,S*)-7-bromo-2,6-dimethyl-1-indanol: δ 6.97-7.15 (m, 2H, 4,5-H), 5.04 (d, $J = 5.9$ Hz, 1H, CHOH), 2.97 (m, 1H, $\text{CHH}'\text{CHMe}$), 2.80 (m, 1H, $\text{CHH}'\text{CHMe}$), 2.44 (m, 1H, CHMe), 2.38 (s, 3H, 6-Me), 1.68 (br.s, 1H, OH), 1.15 (d, $J = 7.0$ Hz, 3H, 2-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 145.4, 143.64, 143.59, 142.7, 136.0, 135.9, 131.1, 131.0, 124.0, 123.5, 122.5, 122.4, 83.8, 78.2, 41.7, 39.0, 38.3, 30.3, 22.3, 22.2, 19.0, 13.5.

Mixture of 4-bromo-2,5-dimethyl-1*H*-indene and 7-bromo-2,6-dimethyl-1*H*-indene (3). A mixture of 2.41 g (10.0 mmol) of **8**, 100 mg of $p\text{TolSO}_3\text{H}$, and 50 ml of toluene was refluxed for 1 hour. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 15 mm, l 200 mm; eluent: hexanes). Yield 2.19 g (98%) of colorless solid mainly consisting of 4-bromo-2,5-dimethyl-1*H*-indene. Anal. calc. for $\text{C}_{11}\text{H}_{11}\text{Br}$: C, 59.22; H, 4.97. Found: C, 59.37; H, 5.04.

2-Methyl-2,3,5,6,7,8-hexahydro-1*H*-cyclopenta[*b*]naphthalen-1-one and 2-methyl-1,2,6,7,8,9-

hexahydro-3*H*-cyclopenta[*a*]naphthalen-3-one. To a suspension of 223 g (1.67 mol) AlCl₃ in 200 ml of CH₂Cl₂ 145 g (0.63 mol) of 2-bromoisobutyryl bromide was added dropwise with vigorous stirring over 15 min at 0°C. This mixture was stirred for 45 min at this temperature; then, a solution of 83.4 g (0.63 mol) of tetralin in 200 ml of CH₂Cl₂ was added dropwise. The mixture was slowly warmed to ambient temperature, stirred additionally overnight, and then poured onto 1000 cm³ of ice. The organic layer was separated, and the aqueous layer was extracted with 3 x 300 ml of CH₂Cl₂. The combined extract was dried over MgSO₄ and evaporated to dryness. Fractional distillation gave a yellowish mixture of the title indanones, b.p. 183-190°C/7 mm Hg. This mixture was recrystallized from 300 ml of *n*-hexane. Crystals of 2-methyl-1,2,6,7,8,9-hexahydro-3*H*-cyclopenta[*a*]naphthalen-3-one precipitated at -30°C were filtered off, washed with 2 x 25 ml of cold *n*-hexane, and dried in vacuum. Yield 56.5 g (45%) of 2-methyl-1,2,6,7,8,9-hexahydro-3*H*-cyclopenta[*a*]naphthalen-3-one. The filtrate was evaporated to dryness and dried in vacuum. This procedure gave 39.3 g (31%) of pure 2-methyl-2,3,5,6,7,8-hexahydro-1*H*-cyclopenta[*b*]naphthalen-1-one. 2-Methyl-2,3,5,6,7,8-hexahydro-1*H*-cyclopenta[*b*]naphthalen-1-one: Anal. calc. for C₁₄H₁₆O: C, 83.96; H, 8.05. Found: C, 84.20; H, 8.14. ¹H NMR (CDCl₃): δ 7.42 (s, 1H, 9-H), 7.09 (s, 1H, 4-H), 3.26 (dd, J= 16.7 Hz, J= 7.6 Hz, 1H, 3-H), 2.78 (m, 3H, 2,8,8'-H), 2.63 (m, 2H, 5,5'-H), 2.59 (dd, J= 16.7 Hz, J= 3.8 Hz, 1H, 3'-H), 1.77 (m, 4H, 6,6',7,7'-H), 1.25 (d, J= 7.3 Hz, 2-Me). ¹³C{¹H} NMR (CDCl₃): δ 209.0, 150.3, 145.2, 136.6, 133.9, 126.5, 123.8, 42.0, 34.3, 30.2, 29.2, 22.8, 22.7, 16.3. 2-Methyl-1,2,6,7,8,9-hexahydro-3*H*-cyclopenta[*a*]naphthalen-3-one: Anal. calc. for C₁₄H₁₆O: C, 83.96; H, 8.05. Found: C, 83.79; H, 8.16. ¹H NMR (CDCl₃): δ 7.46 (d, J= 7.9 Hz, 1H, 9-H), 7.06 (d, J= 7.9 Hz, 1H, 8-H), 3.18 (dd, J= 17.3 Hz, J= 7.9 Hz, 1H, 3-H), 2.81 (m, 2H, 7,7'-H), 2.66 (m, 3H, 2,4,4'-H), 2.48 (dd, J= 17.3 Hz, J= 3.5 Hz, 1H, 3'-H), 1.83 (m, 4H, 5,5',6,6'-H), 1.28 (d, J= 7.3 Hz, 3H, 2-Me). ¹³C{¹H} NMR (CDCl₃): δ 209.3, 153.1, 144.4, 134.4, 133.7, 128.8, 120.5, 41.9, 33.4, 30.1, 25.4, 22.6, 22.5, 16.5.

2-Methyl-2,3,6,7,8,9-hexahydro-1*H*-cyclopenta[*a*]naphthalen-3-ol (9). To a solution of 163 g (0.814 mol) of 2-methyl-1,2,6,7,8,9-hexahydro-3*H*-cyclopenta[*a*]naphthalen-3-one in 1100 cm³ of THF-methanol (2:1, vol.), 46.3 g (1.22 mol) of NaBH₄ was added with vigorous stirring for 4 h at 0°C. This mixture was

stirred overnight at room temperature and then added to 1000 cm³ of cold water. The organic layer was separated, and the aqueous layer was extracted with 3 x 400 ml of dichloromethane. The combined extract was passed through a short column with Silica Gel 60 (40-63 µm, d 80 mm, l 100 mm). The solution was evaporated to dryness, and the residue was dried in vacuum. Yield 161 g (98%) of a mixture of (*R,S/S,R*)- and (*R,R/S,S*)-2-methyl-2,3,6,7,8,9-hexahydro-1*H*-cyclopenta[*a*]naphthalen-3-ol. Anal. calc. for C₁₄H₁₈O: C, 83.12; H, 8.97. Found: C, 83.01; H, 9.11. ¹H NMR (CDCl₃): δ 7.14 (d, J = 7.7 Hz), 7.10 (d, J = 7.7 Hz), 6.96 (d, J = 7.7 Hz), 6.94 (d, J = 7.7 Hz), 4.92 (d, J = 5.6 Hz), 4.66 (d, J = 5.6 Hz), 3.00 (m), 2.82 (m), 2.75 (m), 2.41-2.67 (m), 2.15-2.29 (m), 1.92 (br.s), 1.79 (m), 1.22 (d, J = 6.7 Hz), 1.15 (d, J = 6.8 Hz). ¹³C{¹H} NMR (CDCl₃), (*R,S/S,R*)-2-methyl-2,3,6,7,8,9-hexahydro-1*H*-cyclopenta[*a*]naphthalen-3-ol: δ 141.8, 140.8, 136.9, 133.1, 127.9, 120.9, 83.0, 44.8, 36.1, 29.6, 26.4, 23.1, 23.0, 18.2.

4-Bromo-2-methyl-2,3,6,7,8,9-hexahydro-1*H*-cyclopenta[*a*]naphthalen-3-ol (10). To a mixture of 6.07 g (30.0 mmol) of **9**, 9.96 ml (7.68 g, 66 mmol) of TMEDA and 450 ml of *n*-pentane, 26.4 ml of 2.5 M (66 mmol) of ^{*n*}BuLi in hexanes was added dropwise with vigorous stirring over 10 min at 0°C. This mixture was stirred for an additional 10 min at this temperature and then refluxed for 10 h. The resulting mixture was cooled to -80°C, and 19.6 g (75.4 mmol) of BrCF₂CF₂Br was added at this temperature. The mixture was warmed to ambient temperature and then stirred for 12 h. Then, 100 ml of water was added at 0°C. The organic layer was separated, and the aqueous layer was extracted with 4 x 30 ml of dichloromethane. The combined organic extracts were dried over K₂CO₃ and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 µm, d 40 mm, l 250 mm; eluent: hexanes-ether = 5:1, vol.). Yield 3.46 g (41%). Anal. calc. for C₁₄H₁₇BrO: C, 59.80; H, 6.09. Found: C, 59.72; H, 6.17. ¹H NMR (CDCl₃): δ 7.10 (s), 5.01 (m), 4.83 (t, J = 3.1 Hz), 3.48 (m), 3.17 (dd, J = 16.4 Hz, J = 7.8 Hz), 2.89 (dd, J = 15.9 Hz, J = 7.6 Hz), 2.73 (t, J = 6.3 Hz), 2.53 (t, J = 5.9 Hz), 2.36-2.50 (m), 2.31 (dd, J = 16.4 Hz, J = 4.5 Hz), 1.78 (m), 1.69 (br.s), 1.24 (d, J = 7.0 Hz), 1.16 (d, J = 7.3 Hz). ¹³C{¹H} NMR (CDCl₃), (*R,S/S,R*)-4-bromo-2-methyl-2,3,6,7,8,9-hexahydro-1*H*-cyclopenta[*a*]naphthalen-3-ol: δ 144.2, 139.9, 139.7, 133.0, 130.7, 116.3, 83.5, 41.4, 37.1, 29.4, 26.3, 22.8, 19.2.

4-Bromo-2-methyl-6,7,8,9-tetrahydro-1H-cyclopenta[a]naphthalene (11). A mixture of 2.81 g (10.0 mmol) of **10**, 100 mg of *para*-toluenesulfonic acid, and 50 ml of toluene was refluxed for 1 h. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μ m, d 15 mm, l 200 mm; eluent: hexanes). Yield 2.53 g (96%). Anal. calc. for C₁₄H₁₅Br: C, 63.89; H, 5.74. Found: C, 64.01; H, 5.85. ¹H NMR (CDCl₃): δ 7.10 (s, 1H, 5-H), 6.53 (m, 1H, 3-H), 3.18 (s, 2H, 1-CH₂), 2.76 (t, J= 6.2 Hz, 2H, 9-CH₂), 2.63 (t, J= 5.9 Hz, 2H, 6-CH₂), 2.15 (s, 3H, Me), 1.80 (m, 4H, 7,8-CH₂). ¹³C{¹H} NMR (CDCl₃): δ 145.8, 143.2, 142.8, 134.8, 131.0, 129.8, 126.6, 110.8, 42.4, 29.3, 26.2, 23.3, 22.9, 16.8.

2-Bromo-4-isopropylaniline. A mixture of 99 g (0.73 mol) of 4-isopropylaniline and 300 ml of acetic acid was refluxed for 1 h; then, 75 g of acetic anhydride was added dropwise with vigorous stirring. The resulting solution was cooled to 50°C, and 37.4 ml of bromine was added dropwise with vigorous stirring over ca. 30 min. Then, 370 ml of 12 M HCl was added and this mixture was refluxed until a precipitate was formed. This precipitate was separated, washed with 2 x 150 ml of methyl-*tert*-butyl ether, and dried in vacuum. A mixture of the solid obtained and a solution of 112 g of KOH in 300 ml of water was stirred at 50-60°C for 1 h. The organic layer was separated, and the aqueous layer was extracted with 2 x 150 ml of methyl-*tert*-butyl ether. The combined extract was dried over K₂CO₃ and evaporated to dryness. Fractional distillation gave the title product, b.p. 107-111°C/3 mm Hg. Yield 83.7 g (77%) of yellowish oil. Anal. calc. for C₉H₁₂BrN: C, 50.49; H, 5.65. Found: C, 50.45; H, 5.69. ¹H NMR (CDCl₃): δ 7.26 (d, J= 2.0 Hz, 1H, 3-H), 6.95 (dd, J= 8.1 Hz, J= 2.0 Hz, 1H, 5-H), 6.68 (d, J= 8.1 Hz, 1H, 6-H), 3.89 (br.s, 2H, NH₂), 2.77 (sept, J= 6.9 Hz, CHMe₂), 1.18 (d, J= 6.9 Hz, 6H, CHMe₂).

1-Bromo-3-isopropylbenzene. To a mixture of 1000 ml of 96% ethanol and 94 ml of 98% H₂SO₄, 117 g (0.55 mol) of 2-bromo-4-isopropylaniline was added with vigorous stirring at -5°C over 15 min. Then, a solution of 63 g of NaNO₂ in 125 ml of water was added at this temperature over 1 h, and the resulting mixture was stirred for about 30 min longer. Then, 12 g of copper powder was added. The reaction mixture was refluxed for 4 h and then filtered through glass frit (G3). The filtrate was poured into 2500 cm³ of cold water. The organic product was extracted with 4 x 400 ml of dichloromethane. The combined extract was dried over K₂CO₃ and evaporated to dryness. Fractional distillation gave the title product, b.p. 64-67°C/3

mm Hg. Yield 117.4 g (75%) of yellowish oil. Anal. calc. for $C_9H_{11}Br$: C, 54.30; H, 5.57. Found: C, 54.44; H, 5.49. 1H NMR ($CDCl_3$): δ 7.37 (m, 1H, 2-H), 7.28-7.34 (m, 1H, 5-H), 7.15-7.16 (m, 1H, 6-H), 7.14 (d, J = 1.0 Hz, 1H, 2-H), 2.87 (sept, J = 6.9 Hz, 1H, $CHMe_2$), 1.24 (d, J = 6.9 Hz, 6H, $CHMe_2$).

7-Bromo-5-isopropyl-2-methyl-1-indanone (12). To a mixture of 34.9 g (0.26 mol) of $AlCl_3$ and 350 ml of dichloromethane, a solution of 50.9 g (0.22 mol) of 2-bromoisobutyryl bromide in 120 ml of dichloromethane was added dropwise with vigorous stirring at $-10^\circ C$. Then, a solution of 40.0 g (0.20 mol) of 1-bromo-3-isopropylbenzene in 70 ml of dichloromethane was added dropwise at this temperature. The resulting mixture was refluxed for 12 h and then poured onto 2000 cm^3 of ice. The organic product was extracted with 4 x 300 ml of dichloromethane. The combined extract was dried over K_2CO_3 and evaporated to dryness. Fractional distillation gave the title product, b.p. $130-135^\circ C/1.5$ mm Hg. Yield 36.2 g (67%). Anal. calc. for $C_{13}H_{15}BrO$: C, 58.44; H, 5.66. Found: C, 58.40; H, 5.67. 1H NMR ($CDCl_3$): δ 7.37 (s, 1H, 6-H), 7.23 (s, 1H, 4-H), 3.31 (dd, J = 16.7 Hz, J = 8.0 Hz, 1H, 3-H), 2.94 (sept, J = 6.8 Hz, 1H, $CHMe_2$), 2.71 (m, 1H, 2-H), 2.65 (m, 1H, 3'-H), 1.30 (d, J = 7.4 Hz, 3H, 2-Me), 1.27 (d, J = 6.8 Hz, 6H, $CHMe_2$).

4-Bromo-6-isopropyl-2-methyl-1H-indene (13). To a solution of 22.2 g (83.2 mmol) of **12** in 120 ml of THF-methanol (2:1, vol.) 5.06 g (133 mmol) of $NaBH_4$ was added with vigorous stirring over 3 h at $0^\circ C$. This mixture was stirred overnight at room temperature; then, 300 ml of cold water was added and the resulting mixture was acidified with 1 M HCl to pH 1. The organic layer was separated, and the aqueous layer was extracted with 3 x 150 ml of dichloromethane. The combined extract was dried over K_2CO_3 and evaporated to dryness, and 200 ml of toluene was added to the yellowish oil obtained. This toluene solution was treated with a catalytic amount of p -TolSO $_3$ H (ca. 0.2 g) for 1 h at reflux, cooled to room temperature, and evaporated to dryness. The crude product was purified using flash chromatography on Silica Gel 60 (40-63 μm , d 40 mm, l 400 mm; eluent: hexanes). Yield 19.6 g (94%) of **13**. Anal. calc. for $C_{13}H_{15}Br$: C, 62.17; H, 6.02. Found: C, 61.99; H, 6.08. 1H NMR ($CDCl_3$): δ 7.20 (s, 1H, 5-H), 7.13 (s, 1H, 7-H), 6.52 (m, 1H, 3-H), 3.32 (s, 2H, 1,1'-H), 2.86 (sept, J = 6.9 Hz, 1H, $CHMe_2$), 2.12 (m, 3H, 2-Me), 1.23 (d, J = 6.9 Hz, 6H, $CHMe_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.5, 146.4, 144.9, 143.6, 127.4, 126.5, 120.6, 113.4, 43.7, 33.9, 24.2, 16.8.

3-Bromo-5-methyl-4,5-dihydro-6H-cyclopenta[*b*]thiophen-6-one (15). To a suspension of 250 g (1.89 mol) of AlCl₃ (anhydrous powder) in 350 ml of CHCl₃, a solution of 129 g (0.85 mol) of 5-methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one in 130 ml of CHCl₃ was added at 0°C over 30 min. The reaction mixture was stirred for 10 min at this temperature; then, a solution of 46.7 ml of Br₂ (0.91 mol) in 90 ml of CHCl₃ was added dropwise over 1 h. The resulting mixture was stirred for 1 h at room temperature and then poured onto 2000 cm³ of ice. The organic layer was separated. The aqueous layer was extracted with 4 x 200 ml of CH₂Cl₂. The combined extract was washed with 1000 ml of saturated aqueous Na₂CO₃, dried over K₂CO₃, passed through a short column with Silica Gel 60 (40-63 µm, d 40 mm, l 50 mm), and evaporated to dryness. Fractional distillation gave a white crystalline product, b.p. 128°C/0.8 mm Hg. Yield 185 g (94%). Anal. calc. for C₈H₇BrOS: C, 41.58; H, 3.05. Found: C, 41.78; H, 3.16. ¹H NMR (CDCl₃): δ 7.77 (s, 1H, 2-H), 3.15 (dd, J = 17.2 Hz, J = 7.0 Hz, 1H, 4-H), 3.04 (m, 1H, 5-H), 2.50 (dd, J = 17.2 Hz, J = 2.9 Hz, 1H, 4'-H), 1.34 (d, J = 7.5 Hz, 3H, 5-Me). ¹³C NMR (CDCl₃): δ 199.3, 165.6, 140.2, 136.7, 108.4, 47.4, 32.3, 16.7.

3-Bromo-5-methyl-4H-cyclopenta[*b*]thiophene (16). To a solution of 5.0 g (21.5 mmol) of **15** in 60 ml of THF-methanol (2:1, vol.), 1.30 g (34.4 mmol) of NaBH₄ was added over 1 h at -5°C (Caution: the temperature must be lower than 0°C). The mixture was stirred for 10 h at ambient temperature and then diluted with 20 ml of water and acidified with 10% HCl to pH 1. The crude product was extracted with 3 x 100 ml of CH₂Cl₂. This extract was washed with saturated aqueous Na₂CO₃, dried over K₂CO₃, and evaporated to dryness. Then 150 ml of toluene was added to the yellow oil obtained. This toluene solution was treated with a catalytic amount of ^{*p*}TolSO₃H (ca. 0.2 g) for 10 min at reflux, cooled to room temperature, and then passed through a short column with Silica Gel 60 (40-63 µm, d 20 mm, l 50 mm). This column was additionally eluted with 300 ml of a hexanes-methyl-*tert*-butyl ether mixture (10:1, vol.). The combined extract was evaporated to dryness. This procedure gave 4.61 g (99%) of beige crystalline product of 3-bromo-5-methyl-4*H*-cyclopenta[*b*]thiophene (containing 3-5% of 3-bromo-5-methyl-6*H*-cyclopenta[*b*]thiophene). Anal. calc. for C₈H₇BrS: C, 44.67; H, 3.28. Found: C, 44.80; H, 3.34. ¹H NMR

(CDCl₃): δ 6.94 (s, 1H, 2-H), 6.43 (m, 1H, 6-H), 3.10 (d, J = 1.3 Hz, 2H, CH₂), 2.16 (d, J = 1.5 Hz, 3H, Me).

¹³C NMR (CDCl₃): δ 129.0, 127.6, 127.5, 122.6, 120.2, 106.5, 40.0, 17.4.

Mixture of 2-methyl-4-phenyl-1*H*-indene and 2-methyl-7-phenyl-1*H*-indene (17). To a mixture of 5.30 g (25.4 mmol) of **1**, 2.50 g (7.31 mmol) of NaBPh₄, 9.40 g of Na₂CO₃, and 120 ml of acetone-water (3:1, vol.), a solution of 115 mg (0.51 mmol) Pd(OAc)₂ in 50 ml of acetone was added dropwise with vigorous stirring for 6 h at reflux. The solution was decanted from the precipitate, and this precipitate was washed with 2 x 75 ml of dichloromethane. The combined extract was evaporated, and 150 ml of dichloromethane was added to the residue. The organic layer was separated, dried over MgSO₄, and evaporated to dryness. Fractional distillation gave a yellowish liquid, b.p. 138-140°C/1 mm Hg. Yield 4.81 g (92%) of a mixture of isomeric indenenes. Anal. calc. for C₁₆H₁₄: C, 93.16; H, 6.84. Found: C, 93.10; H, 6.80. 2-Methyl-7-phenyl-1*H*-indene. ¹H NMR (CDCl₃): δ 7.47-7.51 (m, 2H, 2,6-H in Ph), 7.36-7.42 (m, 2H, 3,5-H in Ph), 7.31 (m, 1H, 4-H in Ph), 7.27 (d, J = 7.5 Hz, 1H, 6-H in indenyl), 7.21 (dd, J = 7.5 Hz, J = 1.2 Hz, 1H, 4-H in indenyl), 7.10 (dd, J = 1.2 Hz, J = 7.5 Hz, 1H, 5-H in indenyl), 6.50 (hex, J = 1.6 Hz, 1H, 3-H in indenyl), 3.33 (m, 2H, 1,1'-H in indenyl), 2.08 (m, 3H, 2-Me in indenyl). ¹³C{¹H} NMR (CDCl₃): δ 146.4, 146.2, 141.3, 140.8, 137.3, 128.4 (two resonances), 128.3, 127.1, 127.0, 124.2, 118.9, 42.7, 16.6.

Mixture of 4-(4-*tert*-butylphenyl)-2-methyl-1*H*-indene and 7-(4-*tert*-butylphenyl)-2-methyl-1*H*-indene (18). To a mixture of 4.58 g (21.9 mmol) of **1**, 4.45 g (25.0 mmol) of 4-*tert*-butylphenylboronic acid, 9.50 g of Na₂CO₃, and 50 ml of acetone-water (3:1, vol.), a solution of 100 mg (0.45 mmol) Pd(OAc)₂ in 50 ml of acetone was added dropwise with vigorous stirring for 6 h at reflux. The solution was decanted from the precipitate, and this precipitate was washed with 2 x 60 ml of dichloromethane. The combined extract was evaporated, and 150 ml of dichloromethane was added to the residue. The organic layer was separated, dried over MgSO₄, and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μ m, d 40 mm, l 200 mm; eluent: hexanes). Yield 5.16 g (90%) of a mixture of isomeric indenenes. Anal. calc. for C₂₀H₂₂: C, 91.55; H, 8.45. Found: C, 91.51; H, 8.39. 7-(4-*tert*-Butylphenyl)-2-methyl-1*H*-indene. ¹H NMR (CDCl₃): δ 7.42-7.48 (m, 4H, 2,3,5,6-H in C₆H₄), 7.27 (d, J = 7.5 Hz, 1H, 6-H in indenyl), 7.21 (dd, J = 7.5 Hz, J = 1.2 Hz, 1H, 4-H in indenyl), 7.13 (dd, J = 7.5 Hz, J = 1.2 Hz, 1H, 5-H in

indenyl), 6.52 (hex, $J = 1.5$ Hz, 1H, 3-H in indenyl), 3.39 (m, 2H, 1,1'-H in indenyl), 2.12 (m, 3H, 2-Me in indenyl), 1.37 (s, 9H, t Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 149.8, 146.4, 146.3, 140.8, 138.3, 137.2, 128.0, 127.1, 126.9, 125.3, 124.2, 118.7, 42.9, 34.5, 31.4, 16.7.

Mixture of 2-methyl-4-(2-methylphenyl)-1*H*-indene and 2-methyl-7-(2-methylphenyl)-1*H*-indene

(19). To a mixture of 7.96 g (38.1 mmol) of **1**, 5.43 g (39.9 mmol) of *o*-tolylboronic acid, 16.0 g (151 mmol) of Na_2CO_3 , and 70 ml of acetone-water (3:1, vol.), a solution of 165 mg (0.74 mmol) $\text{Pd}(\text{OAc})_2$ in 80 ml of acetone was added dropwise with vigorous stirring for 6 h at reflux. The solution was decanted from the precipitate, and this precipitate was additionally washed with 100 ml of ether. The combined extract was evaporated, and 150 ml of dichloromethane was added to the residue. The organic layer was separated, dried over MgSO_4 , and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 40 mm, l 300 mm; eluent: hexanes). Yield 7.46 g (89%) of a mixture of isomeric indenenes. Anal. calc. for $\text{C}_{17}\text{H}_{16}$: C, 92.68; H, 7.32. Found: C, 92.53; H, 7.38. 2-Methyl-4-(2-methylphenyl)-1*H*-indene. ^1H NMR (CDCl_3): δ 7.32 (d, $J = 7.0$ Hz, 1H, 3-H in C_6H_4), 7.18-7.27 (m, 4H, 5-H in indenyl and 4,5,6-H in C_6H_4), 7.13 (d, $J = 7.5$ Hz, 1H, 7-H in indenyl), 7.08 (dd, $J = 7.5$ Hz, $J = 1.2$ Hz, 1H, 6-H in indenyl), 6.20 (m, 1H, 3-H in indenyl), 3.32 (br.s, 2H, 1,1'-H in indenyl), 2.15 (s, 3H, 2-Me in C_6H_4), 2.07 (m, 3H, 2-Me in indenyl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 146.0, 144.3, 143.2, 140.6, 135.9, 133.6, 130.0, 129.9, 127.1 (two resonances), 126.5, 125.4, 123.3, 122.0, 43.0, 20.2, 16.8. 2-Methyl-7-(2-methylphenyl)-1*H*-indene. ^1H NMR (CDCl_3): δ 7.18-7.27 (m, 6H, 4,6-H in indenyl and C_6H_4), 6.92 (dd, $J = 1.9$ Hz, $J = 6.7$ Hz, 1H, 5-H in indenyl), 6.51 (hex, $J = 1.5$ Hz, 1H, 3-H in indenyl), 3.03 (br.s, 2H, 1,1'-H in indenyl), 2.12 (s, 3H, 2-Me in C_6H_4), 2.06 (m, 3H, 2-Me in indenyl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 146.3, 145.8, 141.6, 140.8, 137.2, 135.6, 130.0, 129.1, 127.2 (two resonances), 126.3, 125.4, 124.6, 118.6, 42.2, 19.9, 16.7.

Mixture of 1-(2-methyl-1*H*-inden-4-yl)naphthalene and 1-(2-methyl-1*H*-inden-7-yl)naphthalene (20).

To a mixture of 5.00 g (23.9 mmol) of **1**, 4.90 g (83.7 mmol) of naphthylboronic acid, 8.87 g (83.7 mmol) of Na_2CO_3 , and 120 ml of acetone-water (3:1, vol.), a solution of 110 mg (0.49 mmol) $\text{Pd}(\text{OAc})_2$ in 50 ml of acetone was added dropwise with vigorous stirring for 6 h at reflux. The solution was decanted from the

precipitate, and this precipitate was additionally washed with 150 ml of ether. The combined extract was evaporated, and 150 ml of dichloromethane was added to the residue. The organic layer was separated, dried over MgSO_4 , and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 40 mm, l 300 mm; eluent: hexanes). Yield 5.75 g (94%) of a mixture of isomeric indenenes. Anal. calc. for $\text{C}_{20}\text{H}_{16}$: C, 93.71; H, 6.29. Found: C, 93.79; H, 6.14. ^1H NMR (CDCl_3) of 1-(2-methyl-1*H*-inden-4-yl)naphthalene: δ 7.86 (d, J = 8.3 Hz, 1H, 4-H in naphthyl), 7.82 (d, J = 8.1 Hz, 1H, 8-H in naphthyl), 7.70 (d, J = 8.5 Hz, 1H, 5-H in naphthyl), 7.16-7.53 (m, 7H, 5,6,7-H in indenyl and 2,3,6,7-H in naphthyl), 6.09 (m, 1H, 3-H in indenyl), 3.36 (m, 2H, CH_2), 2.00 (m, 3H, Me); 1-(2-methyl-1*H*-inden-7-yl)naphthalene: δ 7.86 (d, J = 8.3 Hz, 1H, 4-H in naphthyl), 7.82 (d, J = 8.1 Hz, 1H, 8-H in naphthyl), 7.61 (d, J = 8.5 Hz, 1H, 5-H in naphthyl), 7.28-7.53 (m, 6H, 4,6-H in indenyl and 2,3,6,7-H in naphthyl), 7.09 (dd, J = Hz, J = Hz, 1H, 5-H in indenyl), 6.53 (m, 1H, 3-H in indenyl), 2.99 (m, 2H, CH_2), 1.99 (m, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) of 1-(2-methyl-1*H*-inden-4-yl)naphthalene: δ 146.0, 145.2, 143.3, 138.9, 133.7, 132.2, 131.9, 128.1, 127.4, 127.2, 126.6, 126.5, 125.8, 125.6, 125.3, 123.5, 122.4, 43.0, 16.7; 1-(2-methyl-1*H*-inden-7-yl)naphthalene: δ 146.4, 145.9, 142.6, 139.2, 136.0, 133.6, 131.5, 128.2, 127.5, 127.1, 126.5, 126.3, 126.1, 125.8, 125.7, 125.5, 125.3, 119.0, 42.3, 16.6.

Mixture of 4- and 7-(2-methoxyphenyl)-2-methyl-1*H*-indenenes (22). To a mixture of 9.61 g (46.0 mmol) of **1**, 7.50 g (49.3 mmol) of 2-methoxyphenylboronic acid, 20.0 g (189 mmol) of Na_2CO_3 , and 100 ml of acetone-water (3:1, vol.), a solution of 210 mg (0.94 mmol) $\text{Pd}(\text{OAc})_2$ in 100 ml of acetone was added dropwise with vigorous stirring for 6 h at reflux. The solution was decanted from the precipitate, and this precipitate was additionally washed with 2 x 150 ml of ether. The combined extract was evaporated. The residue was extracted with 2 x 200 ml of hexanes. Crystals precipitated from this hexane solution at -30°C were separated and dried in vacuum. This procedure gave 7.15 g of the product. The solution was evaporated to a volume of ca. 100 ml. An additional quantity of the product was obtained from this solution at -30°C . Yield 7.75 g (71%) of a ca. 1:3 mixture of 4- and 7-aryl-substituted indenenes. Anal. calc. for $\text{C}_{17}\text{H}_{16}\text{O}$: C, 86.40; H, 6.82. Found: C, 86.40; H, 6.75. 4-(2-Methoxyphenyl)-2-methyl-1*H*-indenenes. ^1H NMR (CDCl_3): δ 6.96-7.36 (m, 7H, 5,6,7-H in indenyl and 3,4,5,6-H in C_6H_4), 6.51 (hex, J = 1.5 Hz, 1H, 3-

H in indenyl), 3.75 (s, 3H, 2-MeO in C₆H₄), 3.33 (m, 2H, 1,1'-H in indenyl), 2.10 (m, 3H, 2-Me in indenyl). ¹³C NMR (CDCl₃): δ 156.6, 146.2, 145.6, 144.7, 143.2, 134.9, 131.5, 130.1, 128.4, 127.7, 127.0, 123.3, 122.2, 111.0, 55.5, 42.9, 16.8. 7-(2-Methoxyphenyl)-2-methyl-1*H*-indenes. ¹H NMR (CDCl₃): δ 6.96-7.36 (m, 7H, 4,5,6-H in indenyl and 3,4,5,6-H in C₆H₄), 6.51 (m, 1H, 3-H in indenyl), 3.75 (s, 3H, 2-MeO in C₆H₄), 3.18 (m, 2H, 1,1'-H in indenyl), 2.10 (m, 3H, 2-Me in indenyl). ¹³C{¹H} NMR (CDCl₃): δ 156.5, 146.2, 145.6, 145.4, 142.4, 134.2, 130.9, 128.5, 127.0, 126.3, 125.2, 120.4, 118.8, 110.9, 55.4, 42.5, 16.7.

Mixture of 2-methyl-4-(3-nitrophenyl)-1*H*-indene and 2-methyl-7-(3-nitrophenyl)-1*H*-indene (23). To a mixture of 250 mg (1.20 mmol) of **1**, 219 mg (1.31 mmol) of 3-nitrophenylboronic acid, 530 mg (5.0 mmol) of Na₂CO₃, and 5 ml of acetone-water (3:1, vol.), a solution of 5.4 mg (0.94 mmol) Pd(OAc)₂ in 3 ml of acetone was added dropwise with vigorous stirring for 3 h at reflux. The solution was decanted from the precipitate, and this precipitate was additionally washed with 5 ml of ether. The combined extract was evaporated. The residue was extracted with 2 x 5 ml of hexanes. The extract was evaporated to dryness. The residue was dissolved in 4 ml of acetonitrile. The product was isolated by preparative HPLC. Yield 278 mg (92%) of a ca. 1:1 mixture of 4- and 7-aryl-substituted indenenes. Anal. calc. for C₁₆H₁₃NO₂: C, 76.48; H, 5.21. Found: C, 76.64; H, 5.27. ¹H NMR (CDCl₃): δ 7.09-7.52 (m, 12H, 5,6,7-H in indenyl of 4-aryllindene, 4,5,6-H in indenyl of 7-aryllindene, and 2,4,5,6-H in C₆H₄ of 4- and 7-aryllindene), 6.66 (m, 1H, 3-H in indenyl of 7-aryllindene), 6.50 (hex, J= 1.5 Hz, 1H, 3-H in indenyl of 4-aryllindene), 3.34 (m, 2H, 1,1'-H in indenyl of 4-aryllindene), 3.31 (m, 2H, 1,1'-H in indenyl of 7-aryllindene), 2.08-2.11 (m, 6H, 2-Me of 4- and 7-aryllindenenes). ¹³C NMR (CDCl₃): δ 146.44 (two resonances), 146.39, 146.26 (two resonances), 143.9 (two resonances), 141.3, 141.1, 140.8, 137.3, 133.9, 128.8, 128.4 (two resonances), 128.3 (two resonances), 127.1, 126.9, 126.7, 126.6, 126.2, 124.2, 123.8, 122.3, 118.9, 42.9, 42.7, 16.8, 16.6.

Mixture of 2,5-dimethyl-4-phenyl-1*H*-indene and 2,6-dimethyl-7-phenyl-1*H*-indene (26). To a mixture of 15.2 g (68.1 mmol) of **3**, 8.82 g (25.8 mmol) of NaBPh₄, 25.3 g (238 mmol) of Na₂CO₃, and 330 ml of acetone-water (3:1, vol.), a solution of 612 mg (2.8 mmol) of Pd(OAc)₂ in 250 ml of acetone was added

dropwise with vigorous stirring for 11 h at reflux. The acetone was evaporated, and 200 ml of water were added. The product was extracted with 3 x 300 ml of methyl-*tert*-butyl ether; the extract was dried over K_2CO_3 and evaporated to dryness. Fractional distillation gave a yellowish liquid, b.p. 100-109°C/0.1 mm Hg. Yield 12.0 g (80%). Anal. calc. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.70; H, 7.35. 1H NMR ($CDCl_3$) of 2,5-dimethyl-4-phenyl-1*H*-indene: δ 7.35-7.41 (m, 2H, 3,5-H in Ph), 7.19-7.41 (m, 4H, 6-H in indenyl and 2,4,6-H in Ph), 7.12 (s, 1H, 6-H in indenyl), 6.18 (m, 1H, 3-H in indenyl), 3.27 (m, 2H, CH_2), 2.17 (s, 3H, 5-Me in indenyl), 2.03 (m, 3H, 2-Me in indenyl); 2,6-dimethyl-7-phenyl-1*H*-indene: δ 7.35-7.41 (m, 2H, 3,5-H in Ph), 7.19-7.41 (m, 4H, 4-H in indenyl and 2,4,6-H in Ph), 7.12 (s, 1H, 5-H in indenyl), 6.44 (m, 1H, 3-H in indenyl), 3.00 (m, 2H, CH_2), 2.12 (s, 3H, 6-H in indenyl), 2.02 (m, 3H, 2-Me in indenyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$) of 2,5-dimethyl-4-phenyl-1*H*-indene: δ 145.9, 140.7, 140.1, 137.6, 133.7, 133.1, 126.5, 129.7, 128.9, 128.15, 128.01, 42.8, 20.1, 16.7; 2,6-dimethyl-7-phenyl-1*H*-indene: δ 145.5, 143.4, 142.5, 140.5, 130.7, 125.4, 122.1, 128.3, 126.9, 126.7, 118.6, 42.5, 19.9, 16.6.

6-Isopropyl-2-methyl-4-phenyl-1*H*-indene (27). To a mixture of 12.8 g (37.5 mmol) of $NaBPh_4$, 37.7 g (150 mmol) of **13**, 71.6 g of Na_2CO_3 , 130 ml of water, and 130 ml of acetone, a solution of 560 mg (2.50 mmol) of $Pd(OAc)_2$ in 200 ml of acetone was added dropwise with vigorous stirring for 5 h at reflux. Then acetone was distilled off under a reduced vacuum. The crude product was extracted with 3 x 200 ml of methyl-*tert*-butyl ether. The combined extract was evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 60 mm, l 300 mm; eluent: hexanes-dichloromethane = 5:1). Yield 31.3 g (84%) of **27**. Anal. calc. for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.79; H, 8.06. 1H NMR ($DMSO-d_6$): δ 7.29-7.48 (m, 5H, Ph), 7.23 (s, 1H, 7-H in indenyl), 7.06 (d, $J = 1.3$ Hz, 5-H in indenyl), 6.56 (m, 1H, 3-H in indenyl), 3.32 (s, 2H, CH_2), 2.91 (sept, $J = 6.8$ Hz, 1H, $CHMe_2$), 2.08 (d, $J = 1.3$ Hz, 3H, 2-Me), 1.22 (d, $J = 7.0$ Hz, 6H, $CHMe_2$). $^{13}C\{^1H\}$ NMR ($DMSO-d_6$): δ 146.1, 144.3, 144.1, 140.7, 140.6, 132.7, 128.5, 128.4, 126.7, 126.2, 124.4, 120.6, 42.4, 33.4, 24.2, 16.6.

Mixture of 2-methyl-4,6-diphenyl-1*H*-indene and 2-methyl-5,7-diphenyl-1*H*-indene (28). To a mixture of 10.0 g (34.7 mmol) of **4**, 6.20 g (18.1 mmol) of $NaBPh_4$, 25.8 g (243 mmol) of Na_2CO_3 , and 250 ml of acetone-water (3:1, vol.), a solution of 310 mg (1.39 mmol) of $Pd(OAc)_2$ in 100 ml of acetone was added

dropwise with vigorous stirring for 7 h at reflux. The reaction mixture was cooled to room temperature, and acetone was distilled off under a reduced pressure. The crude product was extracted with 2 x 150 ml of dichloromethane. The combined extract was dried over K_2CO_3 and then evaporated to dryness. The crude product was purified on a short column with Silica Gel 60 (40-63 μm , d 70 mm, l 60 mm; eluent: hexanes-dichloromethane, 5:1, vol.). An analytically pure sample was obtained by recrystallization from hexanes. Yield 7.41 g (76%) of white solid. Anal. calc. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.64; H, 6.32. 1H NMR ($CDCl_3$): δ 7.30-7.68 (m, 12H, 5,7-H in indenyl of 4,6-diphenylindene, 4,6-H in indenyl of 5,7-diphenylindene, and Ph of both isomers), 6.70 and 6.60 (two m, 1H, 3-H in indenyls), 3.45 and 3.43 (two s, 2H, 1,1'-H in indenyls), 2.16-2.19 (m, 3H, Me).

4-Bromo-1-methoxy-2-methylindane (37). To a solution of 149.5 g (0.664 mol) of 4-bromo-2-methyl-1-indanone in 900 ml of THF-methanol (2:1, vol.) 37.6 g (0.995 mol) of $NaBH_4$ was added in small portions with vigorous stirring over 1.5 h at 5°C. This mixture was stirred at room temperature for 12 h and then added to 2000 cm^3 of cold water. The hydrogenation product was extracted with 5 x 200 ml of dichloromethane, and the combined extract was evaporated to dryness. To 149 g (2.65 mol) of KOH in 420 ml of DMSO, 188 g (82.5 ml, 1.33 mol) MeI and a solution of crude 4-bromo-2-methylindan-1-ol in 220 ml of DMSO were added. This mixture was stirred for 2 h at ambient temperature; then, 92.0 g (40.4 ml, 0.664 mol) of MeI was added, and the mixture was additionally stirred for 2 h. The resulting mixture was added to 2.5 L of cold water. The crude product was extracted with 5 x 200 ml of dichloromethane. The combined extract was dried over Na_2SO_4 and then evaporated to dryness. Fractional distillation gave a mixture of two diastereomeric compounds, b.p. 108°C/3 mm Hg. Yield 148.5 g (93%) of colorless oil. Anal. calc. for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43. Found: C, 54.86; H, 5.40. 1H NMR ($CDCl_3$): δ 7.41 (d, J= 7.9 Hz, 1H, 5-H of *cis*-product), 7.40 (d, J= 7.9 Hz, 1H, 5-H of *trans*-product), 7.31 (d, J= 7.2 Hz, 1H, 7-H of *cis*-product), 7.29 (d, J= 7.2 Hz, 1H, 7-H of *trans*-product), 7.08 (m, 1H, 6-H of *cis*-product), 7.07 (m, 1H, 6-H of *trans*-product), 4.57 (d, J= 5.8 Hz, 1H, CHOMe of *trans*-product), 4.45 (d, J= 4.2 Hz, 1H, CHOMe of *cis*-product), 3.45 (m, 3H, OMe of *cis*-product), 3.40 (m, 3H, OMe of *trans*-product), 2.40-3.30 (m, 6H, CH_2 and CHMe of *cis*-products), 1.18 (m, 3H, CHMe of *cis*-product), 1.11 (m, 3H, CHMe of

trans-product). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 144.6, 144.1, 143.7, 143.4, 131.3, 131.2, 128.2, 127.8, 124.1, 123.9, 120.4, 91.9, 86.6, 56.9, 56.5, 39.7, 39.5, 39.0, 37.9, 19.2, 13.4.

2-Methyl-1*H*-inden-7-ylboronic acid (38). To a solution of 50.0 g (0.207 mol) of **37** in 270 ml of THF 91.2 ml of 2.5 M (0.228 mol) $n\text{BuLi}$ was added dropwise with vigorous stirring for 45 min at -80°C . The resulting mixture was additionally stirred for 1 h at this temperature. Then, it was cooled to -100°C and 81.6 ml (66.5 g, 0.354 mmol) of triisopropylborate was added with vigorous stirring in one portion at this temperature. The resulting mixture was stirred overnight at room temperature. Then, the mixture was cooled to 0°C and 100 ml of cold 12 M HCl and 150 ml of ether were added. This mixture was stirred for 5 min, and then the crude product was extracted with 3 x 150 ml of ether. The combined extract was evaporated to dryness. A solution of 33 g of KOH in 100 ml of water was added to the residue. The resulting mixture was washed with 3 x 150 ml of ether. The aqueous layer was cooled to 0°C , acidified with 4 M HCl to pH 3.0, and stirred overnight at room temperature. The precipitate formed was separated, washed with 2 x 100 ml of cold water, and dried in vacuum. Yield 19.1 g (53%) of yellowish solid of **38**.
 Anal. calc. for $\text{C}_{10}\text{H}_{11}\text{BO}_2$: C, 69.03; H, 6.37. Found: C, 69.21; H, 6.48. ^1H NMR (acetone- d_6): δ 7.55 (dd, $J = 7.3$ Hz, $J = 1.1$ Hz, 1H, 6-H), 7.29 (dd, $J = 7.3$ Hz, $J = 1.1$ Hz, 1H, 4-H), 7.17 (t, $J = 7.3$ Hz, 1H, 5-H), 6.50 (m, 1H, 3-H), 3.54 (m, 2H, CH_2), 3.08 (br.s, 2H, BOH), 2.16 (m, 3H, Me).

1-Methoxy-2-methyl-2,3-dihydro-1*H*-inden-4-ylboronic acid (39). To a solution of 50.0 g (0.207 mol) of **37** in 270 ml of THF, 91.2 ml of 2.5 M (0.228 mol) $n\text{BuLi}$ was added dropwise with vigorous stirring for 45 min at -80°C . The resulting mixture was stirred for an additional 1 h at this temperature. Then, it was cooled to -100°C and 81.6 ml (66.5 g, 0.354 mmol) of triisopropylborate was added with vigorous stirring in one portion at this temperature. The resulting mixture was stirred overnight at room temperature. Then, the mixture was cooled to 0°C and 100 ml of cold 12 M HCl and 150 ml of ether were added. This mixture was stirred for 5 min, and then the crude product was extracted with 3 x 150 ml of ether. The combined extract was evaporated to dryness. A solution of 33 g of KOH in 100 ml of water was added to the residue. The resulting mixture was washed with 3 x 150 ml of ether. The aqueous layer was cooled to 0°C and acidified with cold 4 M HCl to pH 3.0. The precipitate formed was immediately separated, washed with 2

x 100 ml of cold water, and dried in vacuum. Yield 18.3 g (43%) of white solid of a mixture of diastereomers of **39**. Analytically pure *cis*-diastereomer, i.e., (*R,S/S,R*)-**39**, can be obtained by recrystallization of **39** from ethylacetate. Anal. calc. for C₁₁H₁₅BO₃: C, 64.12; H, 7.34. Found: C, 63.95; H, 7.22. ¹H NMR (acetone-d₆): δ 7.92 (br.s, 2H, BOH of *trans*- and *cis*-products), 7.83 (d, J= 7.1 Hz, 1H, 5-H in indanyl of *cis*-product), 7.60 (d, J= 7.3 Hz, 1H, 5-H in indanyl of *trans*-product), 7.88 (d, J= 7.1 Hz, 1H, 7-H in indanyl of *cis*-product), 7.86 (d, J= 7.3 Hz, 1H, 7-H in indanyl of *trans*-product), 7.22 (t, J= 7.1 Hz, 1H, 6-H in indanyl of *cis*-product), 7.17 (t, J= 7.3 Hz, 1H, 6-H in indanyl of *trans*-product), 4.35 (d, J= 3.7 Hz, 1H, CHOMe of *cis*-product), 4.31 (d, J= 4.1 Hz, 1H, CHOMe of *trans*-product), 3.53 (dd, J= 16.6 Hz, J= 7.5 Hz, 1H, CHH' of *cis*-product), 3.36 (s, OMe of *cis*-product), 3.35 (s, OMe of *trans*-product), 3.33 (dd, J= 16.7 Hz, J= 6.8 Hz, 1H, CHH' of *trans*-product), 2.82 (dd, J= 16.6 Hz, J= 5.0 Hz, 1H, CHH' of *cis*-product), 2.57 (dd, J= 16.7 Hz, J= 5.2 Hz, 1H, CHH' of *trans*-product), 2.51 (m, 1H, CHMe of *cis*-product), 2.34 (m, 1H, CHMe of *trans*-product), 1.12 (d, J= 7.3 Hz, 3H, CHMe of *cis*-product), 1.08 (d, J= 7.0 Hz, 3H, CHMe of *trans*-product).

Bromo(1-methoxy-2-methyl-2,3-dihydro-1*H*-inden-4-yl)magnesium (40). To 1.05 g (43 mmol) of magnesium turnings in 10 ml of THF, ca. 10% of a solution of 8.68 g (36 mmol) of **37** in 60 ml of THF was added in one portion, and the mixture was heated to reflux. Then the rest of the solution of **37** was added with vigorous stirring over 1 h at 30°C. The resulting mixture was refluxed for 2 h. The organomagnesium reagent solution was decanted from the excess of magnesium turnings and transferred to a flask equipped with a PTFE stopcock. This procedure gave 45 ml of a 0.779 M (97% yield) solution of **40** in THF. Titration of this reagent was performed using the procedure described in the following book [Ioffe, S.T.; Nesmeyanov, A.S. *Methods of Elementoorganic Chemistry: Magnesium, Berilium, Calcium, Stroncium, Barium*, Moscow, 1963.].

Bromo(1-methoxy-2-methyl-2,3-dihydro-1*H*-inden-4-yl)zinc (41). To a solution of 2.94 g (21.5 mmol) of anhydrous ZnCl₂ in 25 ml of THF, 22.5 ml of a 0.779 M (22.5 mmol) solution of **40** in THF was added in one portion at ambient temperature. The resulting mixture was stirred for an additional 1 h. The product

yield is assumed to be almost quantitative. This Negishi reagent was kept in a glass flask equipped with a PTFE stopcock.

Mixture of 4- and 7-mesityl-2-methyl-1*H*-indenes (21). Method **A** starting from mesitylboronic acid and **1** gave 236 mg (95%) of **21**. Anal. calc. for C₁₉H₂₀: C, 91.88; H, 8.12. Found: C, 91.77; H, 8.03. ¹H NMR (CDCl₃) of 4-mesityl-2-methyl-1*H*-indene: δ 7.32 (m, 1H, 7-H in indenyl), 7.21 (d, J = 7.5 Hz, 1H, 5-H in indenyl), 7.12 (t, J = 7.5 Hz, 1H, 6-H in indenyl), 6.93 (s, 2H, 3,5-H in mesityl), 6.04 (m, 1H, 3-H in indenyl), 3.34 (m, 2H, CH₂), 2.33 (s, 3H, 4-Me in mesityl), 2.07 (s, 3H, 2-Me in indenyl), 1.96 (s, 6H, 2,6-Me in mesityl); 7-mesityl-2-methyl-1*H*-indene: δ 7.25 (m, 1H, 4-H in indenyl), 7.22 (d, J = 1.5 Hz, 1H, 6-H in indenyl), 6.94 (s, 2H, 3,5-H in mesityl), 6.82 (dd, J = 7.0 Hz, J = 1.5 Hz, 1H, 5-H in indenyl), 6.51 (m, 1H, 3-H in indenyl), 2.90 (s, 2H, CH₂), 2.33 (s, 3H, 4-Me in mesityl), 2.06 (s, 3H, 2-Me in indenyl), 1.95 (s, 6H, 2,6-Me in mesityl). ¹³C{¹H} NMR (CDCl₃) of 7-mesityl-2-methyl-1*H*-indene: δ 145.9, 145.8, 141.6, 137.5, 136.4, 136.3, 135.7, 128.0, 127.3, 126.8, 124.6, 118.4, 42.1, 21.1, 20.1, 16.7.

Mixture of 2-methyl-4-(4-methylphenyl)-1*H*-indene and 2-methyl-7-(4-methylphenyl)-1*H*-indene (25). Method **C** starting from p-tolylzinc chloride and **1** gave 218 mg (99%) of **25**. Anal. calc. for C₁₇H₁₆: C, 92.68; H, 7.32. Found: C, 92.59; H, 7.24. ¹H NMR (CDCl₃) of 2-methyl-4-(4-methylphenyl)-1*H*-indene: δ 7.38-7.42 (m, 2H, 3,5-H in *p*-tolyl), 7.23-7.27 (m, 3H, 7-H in indenyl and 2,6-H in *p*-tolyl), 7.22 (dd, J = 7.4 Hz, J = 1.1 Hz, 1H, 5-H in indenyl), 7.15 (t, J = 7.4 Hz, 6-H in indenyl), 6.67 (m, 1H, 3-H in indenyl), 3.35 (m, 1H, CH₂), 2.41 (s, 1H, 4-Me in *p*-tolyl), 2.14 (m, 1H, 2-Me in indenyl); 2-methyl-7-(4-methylphenyl)-1*H*-indene: δ 7.41-7.45 (m, 2H, 3,5-H in tolyl), 7.33 (m, 1H, 6-H in indenyl), 7.29 (t, J = 7.4 Hz, 1H, 5-H in indenyl), 7.22-7.27 (m, 2H, 2,6-H in tolyl), 7.11 (dd, J = 7.4 Hz, J = 1.1 Hz, 1H, 6-H in indenyl), 6.53 (m, 1H, 3-H in indenyl), 3.37 (m, 1H, CH₂), 2.41 (s, 1H, 4-Me in *p*-tolyl), 2.13 (m, 1H, 2-Me in indenyl). ¹³C{¹H} NMR (CDCl₃) of 2-methyl-4-(4-methylphenyl)-1*H*-indene: δ 146.7, 144.8, 138.6, 136.9, 136.7, 134.2, 129.4, 129.0, 126.9, 126.6, 124.1, 122.4, 43.3, 21.5, 17.2; 2-methyl-7-(4-methylphenyl)-1*H*-indene: δ 146.6, 144.3, 141.1, 138.8, 137.6, 137.0, 129.4, 128.6, 127.5, 127.3, 124.5, 119.0, 43.1, 21.5, 17.0.

Mixture of 4-mesityl-2,5-dimethyl-1*H*-indene and 7-mesityl-2,6-dimethyl-1*H*-indene (29). Method A starting from mesitylboronic acid and **3** in the presence of 11.5 mg (0.02 mmol) of Pd(dba)₂ and 36.0 mg (0.08 mmol) of dicyclohexyl[2-(9-phenanthryl)phenyl]phosphine gave 110 mg (42%) of **29**. Anal. calc. for C₂₀H₂₂: C, 91.55; H, 8.45. Found: C, 91.41; H, 8.42. ¹H NMR (CDCl₃) of 4-mesityl-2,5-dimethyl-1*H*-indene: δ 7.13 (s, 1H, 6-H in indenyl), 6.94 (m, 1H, 7-H in indenyl), 5.90 (m, 1H, 3-H in indenyl), 3.30 (m, 2H, CH₂), 2.33 (s, 3H, 5-Me in indenyl), 2.03 (m, 3H, 2-Me in indenyl), 1.97 (s, 3H, 4-Me in mesityl), 1.88 (s, 6H, 2,6-Me in mesityl); 7-mesityl-2,6-dimethyl-1*H*-indene: δ 7.13 (s, 1H, 5-H in indenyl), 6.95 (m, 1H, 4-H in indenyl), 6.47 (m, 1H, 3-H in indenyl), 2.80 (m, 2H, CH₂), 2.33 (s, 3H, 6-Me in indenyl), 2.03 (m, 3H, 2-Me in indenyl), 1.96 (s, 3H, 4-Me in mesityl), 1.88 (s, 6H, 2,6-Me in mesityl). ¹³C{¹H} NMR (CDCl₃) of 7-mesityl-2,6-dimethyl-1*H*-indene: δ 145.0, 143.5, 141.9, 136.2, 135.9, 135.3, 137.1, 128.2, 128.0, 127.2, 118.3, 42.2, 21.1, 19.7, 19.2, 16.7.

1-Methoxy-2-methyl-4-(4-methylphenyl)indane (42). Method A starting from 4-bromotoluene and **45** gave 245 mg (97%) of **42**. Anal. calc. for C₁₈H₂₀O: C, 85.67; H, 7.99. Found: C, 85.73; H, 8.07. ¹H NMR (CDCl₃): δ 7.22-7.36 (m, 10H, 5,6,7-H in indanyl and 2,5-H in tolyl of *trans*- and *cis*-products), 7.16-7.22 (m, 4H, 3,5-H in tolyl of *trans*- and *cis*-products), 4.50 (d, J = 5.7 Hz, 1H, CHOMe of *trans*-product), 4.41 (d, J = 4.2 Hz, 1H, CHOMe of *cis*-product), 3.46 (s, 3H, OMe of *cis*-product), 3.41 (s, 3H, OMe of *trans*-product), 3.28 (dd, J = 17.4 Hz, J = 8.8 Hz, 1H, CHH' of *cis*-product), 2.91 (dd, J = 15.6 Hz, J = 7.2 Hz, 1H, CHH' of *trans*-product), 2.81 (dd, J = 15.6 Hz, J = 6.8 Hz, 1H, CHH' of *trans*-product), 2.40-2.58 (m, 3H, CHH' of *cis*-product and CHMe of *trans*- and *cis*-products), 2.35 (s, 6H, 4-Me in tolyl of *trans*- and *cis*-products), 1.09 (d, J = 6.5 Hz, 3H, CHMe of *cis*-product), 1.07 (d, J = 6.7 Hz, 3H, CHMe of *trans*-product). ¹³C{¹H} NMR (CDCl₃): δ 143.3, 142.8, 141.1, 140.5, 138.6, 138.5, 137.8, 136.5, 128.9, 128.5, 128.3, 128.2, 126.8, 126.4, 123.9, 123.8, 91.2, 86.0, 56.6, 56.4, 39.9, 39.0, 38.3, 38.2, 21.0, 19.0, 13.4.

1-(1-Methoxy-2-methyl-2,3-dihydro-1*H*-inden-4-yl)naphthalene (43). Method B starting from 1-naphthylbromide and **40** gave 268 mg (93%) of **43**. Anal. calc. for C₂₁H₂₀O: C, 87.46; H, 6.99. Found: C, 87.39; H, 7.05. ¹H NMR (CDCl₃): δ 7.84 (d, J = 8.3 Hz, 0.5H, 5-H in indanyl of *trans*-product), 7.80 (d, J = 8.1 Hz, 0.5H, 5-H in indanyl of *trans*-product), 7.22-7.82 (m, 19H, 6,7-H in indanyl and naphthyl of *trans*-

product and 5,6,7-H in indanyl and naphthyl of *cis*-product), 4.56 (m, 1H, *CHOMe* of *cis*-product), 4.46 (m, 1H, *CHOMe* of *trans*-product), 3.52 (s, 1.5H, *OMe* of *trans*-product), 3.58 (s, 1.5H, *OMe* of *trans*-product), 3.46 (s, 1.5H, *OMe* of *cis*-product), 3.43 (s, 1.5H, *OMe* of *cis*-product), 2.92 (dd, *J* = 16.2 Hz, *J* = 7.5 Hz, 0.5H, *CHH'* of *trans*-product), 2.86 (dd, *J* = 16.3 Hz, *J* = 7.7 Hz, 0.5H, *CHH'* of *trans*-product), 2.13 (dd, *J* = 16.2 Hz, *J* = 5.7 Hz, 0.5H, *CHH'* of *trans*-product), 2.08 (dd, *J* = 16.3 Hz, *J* = 5.0 Hz, 0.5H, *CHH'* of *trans*-product), 2.32-2.59 (m, 4H, *CHMe* of *trans*-product and *CH₂* and *CHMe* of *cis*-product), 1.06 (d, *J* = 7.0 Hz, 1.5H, *CHMe* of *trans*-product), 1.04 (d, *J* = 7.0 Hz, 1.5H, *CHMe* of *trans*-product), 1.01 (d, *J* = 6.7 Hz, 1.5H, *CHMe* of *cis*-product), 0.99 (d, *J* = 6.6 Hz, 1.5H, *CHMe* of *cis*-product). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 142.8, 142.72, 142.69, 142.43, 142.35, 142.23, 142.20, 138.8, 138.73, 138.68, 137.52, 137.46, 137.3, 133.53, 133.50, 133.46, 131.45, 131.42, 131.39, 129.9, 129.83, 129.80, 129.6, 128.2, 128.1, 127.49, 127.46, 127.43, 126.7, 126.6, 126.5, 126.42, 126.38, 126.2, 126.1, 125.93, 125.87, 125.8, 125.7, 125.58, 125.55, 125.28, 125.26, 125.1, 124.43, 124.37, 124.29, 124.23, 91.53, 91.47, 86.18, 86.15, 56.8, 56.7, 56.6, 39.8, 39.6, 38.7, 38.4, 37.7, 37.6, 37.5, 37.4, 19.3, 19.0, 13.5, 13.3.

4-Mesityl-1-methoxy-2-methylindane (44). Method A starting from mesitylbromide and **39** gave 277 mg (99%) of **44**. Anal. calc. for $\text{C}_{20}\text{H}_{24}\text{O}$: C, 85.67; H, 8.63. Found: C, 85.48; H, 8.56. ^1H NMR (CDCl_3): δ 7.35 (t, *J* = 6.9 Hz, 2H, 6-H in indanyl of *trans*- and *cis*-products), 7.26 (dd, *J* = 7.5 Hz, *J* = 4.4 Hz, 1H, 7-H in indanyl of *cis*-product), 7.24 (dd, *J* = 7.4 Hz, *J* = 4.3 Hz, 1H, 7-H in indanyl of *trans*-product), 6.98 (dd, *J* = 7.5 Hz, *J* = 4.4 Hz, 1H, 5-H in indanyl of *cis*-product), 6.97 (dd, *J* = 7.5 Hz, *J* = 4.3 Hz, 1H, 5-H in indanyl of *trans*-product), 6.91 (s, 4H, 3,5-H in mesityl of *trans*- and *cis*-products), 4.62 (d, *J* = 5.7 Hz, 1H, *CHOMe* of *trans*-product), 4.44 (d, *J* = 3.9 Hz, 1H, *CHOMe* of *cis*-product), 3.48 (s, 3H, *OMe* of *cis*-product), 3.44 (s, 3H, *OMe* of *trans*-product), 2.83 (dd, *J* = 16.2 Hz, *J* = 7.6 Hz, 1H, *CHH'* of *cis*-product), 2.39-2.65 (m, 3H, *CHH'* of *trans*-product and *CHMe* of *trans*- and *cis*-products), 2.31 (s, 6H, 4-Me in mesityl of *trans*- and *cis*-products), 2.28 (dd, *J* = 15.8 Hz, *J* = 5.3 Hz, 1H, *CHH'* of *trans*-product), 2.02 (dd, *J* = 16.2 Hz, *J* = 5.0 Hz, 1H, *CHH'* of *cis*-product), 1.93 (s, 6H, 2-Me in mesityl of *trans*- and *cis*-products), 1.92 (s, 6H, 6-Me in mesityl of *trans*- and *cis*-products), 1.09 (d, *J* = 7.0 Hz, 3H, *CHMe* of *cis*-product), 1.00 (d, *J* = 6.8 Hz, 3H, *CHMe* of *trans*-product). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 142.6, 142.2, 141.7, 141.5,

138.0, 137.8, 137.2, 136.3, 135.7, 135.4, 135.3, 128.8, 128.5, 127.9, 127.8, 126.8, 126.5, 123.9, 123.5, 91.6, 86.2, 56.8, 56.6, 39.5, 38.1, 37.5, 37.0, 21.0, 20.2, 19.3, 13.5.

2-(1-Methoxy-2-methyl-2,3-dihydro-1*H*-inden-4-yl)thiophene (45). Method A starting from 2-bromothiophene and **39** gave 168 mg (69%) of **45**. Anal. calc. for C₁₅H₁₆OS: C, 73.73; H, 6.60. Found: C, 73.84; H, 6.51. ¹H NMR (CDCl₃): δ 7.49 (dd, J = 7.5 Hz, J = 1.1 Hz, 1H, 5-H in indanyl of *cis*-product), 7.48 (dd, J = 7.6 Hz, J = 1.2 Hz, 1H, 5-H in indanyl of *trans*-product), 7.18-7.39 (m, 4H, 6,7-H in indanyl and 3,4-H in thienyl of *trans*- and *cis*-products), 7.09 (dd, J = 5.1 Hz, J = 3.7 Hz, 5-H in thienyl of *trans*- and *cis*-products), 4.53 (d, J = 5.9 Hz, 1H, CHOMe of *trans*-product), 4.42 (d, J = 4.1 Hz, 1H, CHOMe of *cis*-product), 3.47 (s, 3H, OMe of *cis*-product), 3.44 (dd, J = 16.1 Hz, J = 7.6 Hz, 1H, CHH' of *cis*-product), 3.43 (s, 3H, OMe of *trans*-product), 3.11 (dd, J = 15.9 Hz, J = 7.4 Hz, 1H, CHH' of *trans*-product), 2.90 (dd, J = 15.9 Hz, J = 6.8 Hz, 1H, CHH' of *trans*-product), 2.47-2.67 (m, 3H, CHH' of *cis*-product and CHMe of *trans*- and *cis*-products), 1.15 (d, J = 6.8 Hz, 3H, CHMe of *cis*-product), 1.12 (d, J = 7.1 Hz, 3H, CHMe of *trans*-product). ¹³C{¹H} NMR (CDCl₃): δ 143.9, 143.3, 143.0, 140.5, 131.5, 127.9, 127.7, 127.5, 127.0, 126.6, 125.3, 125.0, 124.5, 124.3, 91.2, 86.0, 56.8, 56.5, 39.7, 39.2, 38.9, 38.7, 19.3, 13.6.

(*R,S,S,R*)-2-(1-Methoxy-2-methyl-2,3-dihydro-1*H*-inden-4-yl)pyridine (46). Method A starting from 2-bromopyridine and (*R,S,S,R*)-**39** gave 62 mg (26%) of **46**. Anal. calc. for C₁₆H₁₇NO: C, 80.30; H, 7.16. Found: C, 80.45; H, 7.23. ¹H NMR (CDCl₃): δ 8.67 (ddd, J = 4.9 Hz, J = 1.8 Hz, J = 1.0 Hz, 1H, 6-H in Py), 7.67 (dt, J = 7.8 Hz, J = 1.8 Hz, 1H, 4-H in Py), 7.64 (dd, J = 7.5 Hz, J = 1.0 Hz, 1H, 5-H in indanyl), 7.49 (dt, J = 7.8 Hz, J = 1.0 Hz, 3-H in Py), 7.42 (m, 1H, 7-H in indanyl), 7.32 (t, J = 7.5 Hz, 1H, 6-H in indanyl), 7.16 (ddd, J = 7.5 Hz, J = 4.9 Hz, J = 1.0 Hz, 1H, 5-H in Py), 4.44 (d, J = 4.4 Hz, 1H, CHOMe of *cis*-product), 3.47 (s, 3H, OMe of *cis*-product), 3.42 (dd, J = 16.3 Hz, J = 7.5 Hz, 1H, CHH' of *cis*-product), 2.65 (dd, J = 16.3 Hz, J = 5.5 Hz, 1H, CHH' of *cis*-product), 2.50 (m, 1H, CHMe of *cis*-products), 1.13 (d, J = 6.9 Hz, 3H, CHMe of *cis*-product). ¹³C{¹H} NMR (CDCl₃): δ 158.1, 149.2, 143.1, 141.0, 137.0, 135.9, 128.3, 126.7, 125.3, 122.7, 121.4, 90.8, 56.2, 39.8, 38.5, 18.8.

Mixture of 2-(2-methyl-1*H*-inden-4-yl)pyridine and 2-(2-methyl-1*H*-inden-7-yl)pyridine (47). A

mixture of 242 mg (1.01 mmol) of **46**, 5 ml of methanol, and 1 ml of 12 M HCl was refluxed for 3 h. Then a solution of 2.5 g of KOH in 10 ml of water was added. The crude product was extracted with 4 x 5 ml of methyl-*tert*-butyl ether. The combined extract was dried over Na₂SO₄ and evaporated to dryness. The residue was dissolved in 4 ml of acetonitrile. The product was isolated by preparative HPLC. Yield 178 mg (85%) of **47**. Anal. calc. for C₁₅H₁₃N: C, 86.92; H, 6.32. Found: C, 87.02; H, 6.40. ¹H NMR (CDCl₃) for 2-(2-methyl-1*H*-inden-4-yl)pyridine: δ 8.73 (m, 1H, 6-H in Py), 7.66 (m, 1H, 5-H in Py), 7.62 (m, 1H, 6-H in Py), 7.58 (m, 1H, 7-H in indenyl), 7.52 (dd, J= 7.47 Hz, J= 1.19 Hz, 5-H in indenyl), 7.40 (m, 1H, 6-H in indenyl), 7.16 (ddd, J= 7.21 Hz, J= 4.89 Hz, J= 1.30 Hz, 1H, 4-H in Py), 6.55 (m, 1H, 3-H in indenyl), 3.65 (s, 2H, CH₂), 2.16 (m, 3H, Me); 2-(2-methyl-1*H*-inden-7-yl)pyridine: δ 8.75 (m, 1H, 6-H in Py), 7.68 (m, 1H, 5-H in Py), 7.59 (m, 1H, 6-H in Py), 7.37 (m, 1H, 4-H in indenyl), 7.33 (dd, J= 7.47 Hz, J= 1.19 Hz, 1H, 6-H in indenyl), 7.23 (t, J= 7.47 Hz, 1H, 5-H in indenyl), 7.16 (ddd, J= 7.21 Hz, J= 4.89 Hz, J= 1.30 Hz, 1H, 4-H in Py), 7.06 (m, 1H, 3-H in indenyl), 3.33 (s, 2H, CH₂), 2.17 (m, 3H, Me). ¹³C{¹H} NMR (CDCl₃) for 2-(2-methyl-1*H*-inden-4-yl)pyridine: δ 158.7, 149.1, 146.7, 144.2, 143.7, 135.94, 132.0, 126.5, 126.1, 123.5, 123.2, 122.6, 121.0, 42.4, 16.6. 2-(2-methyl-1*H*-inden-7-yl)pyridine: δ 158.5, 148.9, 146.9, 146.4, 141.2, 135.90, 135.0, 126.6, 126.4, 123.2, 122.1, 121.3, 119.9, 43.4, 16.3.

(*R,S/S,R*)-4-(1-Methoxy-2-methyl-2,3-dihydro-1*H*-inden-4-yl)isoquinoline (48). Method A starting

from 4-bromoisoquinoline and (*R,S/S,R*)-**39** gave 179 mg (62%) of **48**. At room temperature, this compound is a mixture of two conformers. Anal. calc. for C₂₀H₁₉NO: C, 83.01; H, 6.62. Found: C, 83.27; H, 6.55. ¹H NMR (CDCl₃): δ 9.27 (s, 1H, 4-H in isoquinolyl), 8.45 (d, J= 5.3 Hz, 1H, 8-H in isoquinolyl), 8.02 (m, 1H, 5-H in isoquinolyl), 7.55-7.64 (m, 3H, 2,6,7-H in isoquinolyl), 7.51 (d, J= 7.5 Hz, 1H, 5-H in indanyl), 7.37 (t, J= 7.5 Hz, 1H, 6-H in indanyl), 7.28 (d, J= 7.5 Hz, 1H, 7-H in indanyl), 4.50 (m, 1H, CHOMe), 3.56 (s, 1.5H, OMe), 3.51 (s, 1.5H, OMe), 2.98 (dd, J= 16.2 Hz, J= 7.6 Hz, 0.5H, CHH'), 2.88 (dd, J= 16.2 Hz, J= 7.7 Hz, 0.5H, CHH'), 2.47 (m, 1H, CHMe), 2.20 (dd, J= 16.2 Hz, J= 5.5 Hz, 0.5H, CHH'), 2.10 (dd, J= 16.2 Hz, J= 5.0 Hz, 0.5H, CHH'), 1.10 (d, J= 7.0 Hz, 1.5H, CHMe), 1.09 (d, J= 7.0 Hz, 1.5H, CHMe). ¹³C{¹H} NMR (CDCl₃): δ 151.9, 144.6, 142.7, 142.6, 134.1, 133.7, 131.8, 131.5, 130.4,

130.3, 130.0, 128.6, 128.2, 127.7, 127.1, 126.7, 125.7, 125.1, 124.9, 124.8, 91.4, 91.3, 56.9, 56.5, 39.8, 39.5, 37.7, 37.6, 19.2, 19.0.

Mixture of 4-(2-methyl-1*H*-inden-4-yl)isoquinoline and 4-(2-methyl-1*H*-inden-7-yl)isoquinoline (49).

A mixture of 160 mg (0.55 mmol) of **48**, 5 ml of methanol, and 1 ml of 12 M HCl was refluxed for 5 h. Then a solution of 2.5 g of KOH in 10 ml of water was added. The crude product was extracted with 4 x 5 ml of methyl-*tert*-butyl ether. The combined extract was dried over Na₂SO₄ and evaporated to dryness. The residue was dissolved in 4 ml of acetonitrile. The product was isolated by preparative HPLC. Yield 99 mg (69%) of **49**. Anal. calc. for C₁₉H₁₅N: C, 88.68; H, 5.88. Found: C, 88.54; H, 5.79. ¹H NMR (CDCl₃) for 2-methyl-4-(2,3,4,5,6-pentafluorophenyl)-1*H*-indene: δ 9.27 (s, 1H, 1-H in isoquinolyl), 8.53 (s, 1H, 3-H in isoquinolyl), 8.05 (d, J = 2.9 Hz, 1H, 5-H in isoquinolyl), 7.08-7.76 (m, 6H, 5,6,7-H in indenyl and 6,7,8-H in isoquinolyl), 6.12 (m, 1H, 3-H in indenyl), 3.41 (s, 2H, CH₂), 2.06 (m, 3H, Me); 2-methyl-7-(2,3,4,5,6-pentafluorophenyl)-1*H*-indene: δ 9.28 (s, 1H, 1-H in isoquinolyl), 8.52 (s, 1H, 3-H in isoquinolyl), 8.03 (d, J = 2.3 Hz, 1H, 5-H in isoquinolyl), 7.08-7.76 (m, 6H, 4,5,6-H in indenyl and 6,7,8-H in isoquinolyl), 6.57 (m, 1H, 3-H in indenyl), 3.05 (m, 2H, CH₂), 2.06 (m, 3H, Me). ¹³C{¹H} NMR (CDCl₃) of a mixture: δ 151.9, 151.8, 146.8, 146.6, 146.2, 145.4, 143.6, 143.3, 142.9, 142.6, 134.5, 134.2, 132.3, 132.1, 130.3, 128.3, 128.2, 127.8, 127.7, 127.0, 126.7, 126.1, 125.5, 125.3, 123.7, 123.0, 119.6, 43.0, 42.2, 16.8, 16.6.

Mixture of 3-(2-methyl-1*H*-inden-4-yl)-1-benzothiophene and 3-(2-methyl-1*H*-inden-7-yl)-1-benzothiophene (50).

A mixture of 45.0 ml of a 0.78 M (35 mmol) solution of **41** in THF, 7.46 g (35 mmol) of 3-bromo-1-benzothiophene, 0.37 g (0.72 mmol) of Pd(P^{*t*}Bu₃)₂, and 100 ml of THF was refluxed for 8 h. The resulting mixture was cooled to ambient temperature and then filtered through glass frit (G4). The filtrate was evaporated to dryness. The oil obtained was dried in vacuum. Then 0.50 g of *p*-TolSO₃H and 150 ml of toluene were added. This mixture was refluxed for 1 h and then evaporated to dryness. The crude product was purified using flash chromatography on Silica Gel 60 (40-63 μm, d 45 mm, l 500 mm; eluent: hexanes). Yield 7.82 g (85%) of **50** as a ca. 1:10 mixture of 4- and 7-substituted indenenes. Anal. calc. for C₁₈H₁₄S: C, 82.40; H, 5.38. Found: C, 82.39; H, 5.22. 3-(2-Methyl-1*H*-inden-7-yl)-1-benzothiophene. ¹H NMR (CDCl₃): δ 7.90 (m, 1H, 4-H in benzothienyl), 7.62 (m, 1H, 7-H in benzothienyl), 7.38 (s, 1H, 2-

H in benzothienyl), 7.27-7.37 (m, 4H, 4,5,6-H in indenyl and 5-H in benzothienyl), 7.17 (m, 1H, 6-H in benzothienyl), 6.53 (hex, $J = 1.5$ Hz, 1H, 3-H in indenyl), 3.20 (s, 2H, 1,1'-H in indenyl), 2.07 (m, 3H, 2-Me in indenyl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 146.5, 146.4, 142.3, 140.2, 138.5, 136.9, 131.2, 127.1, 126.7, 124.9, 124.3, 124.1, 123.4, 123.2, 122.8, 119.3, 42.6, 16.7.

(*R,S/S,R*)-4-(2-Fluorophenyl)-1-methoxy-2-methylindane (51). Method **A** starting from 2-fluorobromobenzene and (*R,S/S,R*)-**39** gave 105 mg (41%) of **51**. Anal. calc. for $\text{C}_{17}\text{H}_{17}\text{FO}$: C, 79.66; H, 6.69. Found: C, 79.57; H, 6.61. ^1H NMR (CDCl_3): δ 7.40 (d, $J = 6.9$ Hz, $J = 1.3$ Hz, 1H, 5-H in indanyl), 7.06-7.33 (m, 6H, 6,7-H in indanyl and C_6H_4), 4.45 (d, $J = 4.5$ Hz, 1H, *CHOMe*), 3.49 (s, 3H, OMe), 3.10 (dd, $J = 15.8$ Hz, $J = 7.3$ Hz, 1H, *CHH'*), 2.42-2.52 (m, 1H, *CHMe*), 2.37 (dd, $J = 15.8$ Hz, $J = 5.6$ Hz, 1H, *CHH'*), 1.13 (d, $J = 6.9$ Hz, 3H, *CHMe*).

7-(2-Fluorophenyl)-2-methyl-1*H*-indene (52). A mixture of 64 mg (0.25 mmol) of **51**, 5 mg of $p\text{-TolSO}_3\text{H}$, and 3 ml of toluene was refluxed for 1 h. The resulting mixture was passed through a short column with Silica Gel 60 (40-63 μm , d 20 mm, l 20 mm). This column was additionally washed with 25 ml of toluene. The combined extract was evaporated to dryness. The residue was dissolved in 4 ml of acetonitrile. The product was isolated by preparative HPLC. Yield 44 mg (79%) of **52**. Anal. calc. for $\text{C}_{16}\text{H}_{13}\text{F}$: C, 85.69; H, 5.84. Found: C, 85.47; H, 5.90. ^1H NMR (CDCl_3): δ 7.05-7.41 (m, 7H, 4,5,6-H in indenyl and C_6H_4), 6.52 (m, 1H, 3-H in indenyl), 3.24 (m, 2H, CH_2), 2.11 (m, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 159.6 (d, $J = 246.0$ Hz), 146.5, 146.1, 142.2, 131.5, 131.3, 129.0, 128.9 (d, $J = 7.4$ Hz), 127.0, 126.6, 125.0, 124.0, 119.4, 115.7 (d, $J = 22.5$ Hz), 42.4, 16.7.

1-Methoxy-2-methyl-4-(2,3,4,5,6-pentafluorophenyl)indane (53). Method **A** starting from perfluorobromobenzene and **39** gave 89 mg (27%) of **53**. Anal. calc. for $\text{C}_{17}\text{H}_{13}\text{F}_5\text{O}$: C, 62.20; H, 3.99. Found: C, 62.01; H, 4.07. ^1H NMR (CDCl_3): δ 7.49 (d, $J = 7.5$ Hz, 1H, 5-H in inanyl of *trans*-product), 7.48 (d, $J = 7.5$ Hz, 1H, 5-H in inanyl of *cis*-product), 7.34 (t, $J = 7.5$ Hz, 1H, 6-H in inanyl of *trans*-product), 7.32 (t, $J = 7.5$ Hz, 1H, 6-H in inanyl of *cis*-product), 7.20 (d, $J = 7.5$ Hz, 1H, 7-H of *trans*- and *cis*-products), 4.61 (d, $J = 5.5$ Hz, 1H, *CHOMe* of *cis*-product), 4.47 (d, $J = 4.5$ Hz, 1H, *CHOMe* of *trans*-

product), 3.51 (s, 3H, OMe of *trans*-product), 3.46 (s, 3H, OMe of *cis*-product), 3.02 (dd, $J = 15.9$ Hz, $J = 7.6$ Hz, 1H, CHH' of *trans*-product), 2.44-2.77 (m, $CHMe$ of *trans*-product and CH_2 and $CHMe$ of *cis*-product), 2.29 (dd, $J = 15.9$ Hz, $J = 5.6$ Hz, 1H, CHH' of *trans*-product), 1.16 (d, $J = 7.0$ Hz, 3H, $CHMe$ of *trans*-product), 1.06 (d, $J = 6.7$ Hz, 3H, $CHMe$ of *cis*-product).

Mixture of 2-methyl-4-(2,3,4,5,6-pentafluorophenyl)-1*H*-indene and 2-methyl-7-(2,3,4,5,6-pentafluorophenyl)-1*H*-indene (54). A mixture of 101 mg (0.31 mmol) of **53**, 5 ml of methanol, and 5 ml of 12 M HCl was refluxed for 5 h. The crude product was extracted with 3 x 25 ml of methyl-*tert*-butyl ether. The combined extract was dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in 4 ml of acetonitrile. The product was isolated by preparative HPLC. Yield 92 mg (99%) of **54**. Anal. calc. for $C_{16}H_9F_5$: C, 64.87; H, 3.06. Found: C, 64.72; H, 2.99. 1H NMR ($CDCl_3$) for 2-methyl-4-(2,3,4,5,6-pentafluorophenyl)-1*H*-indene: δ 7.44 (m, 1H, 5-H in indenyl), 7.31 (m, 1H, 6-H in indenyl), 7.18 (m, 1H, 7-H in indenyl), 6.24 (m, 1H, 3-H), 3.37 (m, 2H, CH_2), 2.15 (m, 3H, Me); 2-methyl-7-(2,3,4,5,6-pentafluorophenyl)-1*H*-indene: δ 7.27-7.36 (m, 2H, 5,6-H in indenyl), 7.01 (m, 1H, 4-H in indenyl), 6.52 (m, 1H, 3-H), 3.14 (m, 2H, CH_2), 2.13 (m, 3H, Me).

Mixture of 5-methyl-3-phenyl-6*H*-cyclopenta[*b*]thiophene and 5-methyl-3-phenyl-4*H*-cyclopenta[*b*]thiophene (30). To a solution of 4.78 g (20.7 mmol) of **16** in 300 ml of THF, 41.4 ml of 0.5 M (20.7 mmol) phenylzinc bromide in THF and then 4.14 ml of 0.1 M (0.414 mmol) of $Pd(P^tBu_3)_2$ in THF were added at room temperature. This mixture was stirred for 10 h at reflux and then evaporated to dryness. The product was isolated by flash chromatography on SilicaGel 60 (40-63 μm , d 40 mm, l 300 mm; eluent: hexanes). Yield 4.37 g (99%) of **30** as a ca. 1:4 mixture of 5-methyl-3-phenyl-6*H*-cyclopenta[*b*]thiophene and 5-methyl-3-phenyl-4*H*-cyclopenta[*b*]thiophene. Anal. calc. for $C_{14}H_{12}S$: C, 79.20; H, 5.70. Found: C, 79.00; H, 5.79. 1H NMR ($CDCl_3$) of a mixture of isomers: δ 7.53-7.57 and 7.47-7.50 (two m, 4H, 2,6-H in Ph of major and minor isomers), 7.28-7.34 (m, 4H, 3,5-H in Ph of both isomers), 7.17-7.22 (m, 2H, 4-H in Ph of both isomers), 7.14 and 7.12 (two s, 2H, 2-H in cyclopentathienyl of minor and major isomers), 6.53 and 6.39 (two m, 2H, 4-H and 6-H of cyclopentathienyl of minor and major isomers, respectively), 3.23 and 3.20 (m and br.s, 4H, CH_2 of major and minor isomers), 2.10 and 2.07

(two d, $J = 1.4$ and 1.5 Hz, 6H, Me of major and minor isomers). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) of 5-methyl-3-phenyl-4*H*-cyclopenta[*b*]thiophene: δ 146.9, 146.1, 143.1, 136.6, 136.0, 128.6, 126.9, 126.4, 122.1, 119.1, 40.8, 17.0.

Mixture of 5-methyl-3-(1-naphthyl)-6*H*-cyclopenta[*b*]thiophene and 5-methyl-3-(1-naphthyl)-4*H*-cyclopenta[*b*]thiophene (31). To a solution of 15.2 ml of 0.1 M (15.2 mmol) of ZnCl_2 in THF, 55.2 ml of 0.25 M (13.8 mmol) 1-naphthylmagnesium bromide in THF was added at ambient temperature. The resulting mixture was stirred for 1 h; then, a solution of 3.20 g (13.8 mmol) of **16** in 50 ml of THF and 2.76 ml of 0.1 M (0.276 mmol) $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ in THF were added at ambient temperature. This mixture was stirred for 10 h at reflux and then evaporated to dryness. The product was isolated by flash chromatography on SilicaGel 60 (40-63 μm , d 40 mm, l 300 mm; eluent: hexanes). Yield 3.61 g (99%) of **31** as a ca. 1:2 mixture of 5-methyl-3-(1-naphthyl)-6*H*-cyclopenta[*b*]thiophene and 5-methyl-3-(1-naphthyl)-4*H*-cyclopenta[*b*]thiophene. Anal. calc. for $\text{C}_{18}\text{H}_{14}\text{S}$: C, 82.40; H, 5.38. Found: C, 82.28; H, 5.30. ^1H NMR (CDCl_3): δ 7.82-8.02 (m, 6H, 8,7,5-H in naphthyl of both isomers), 7.41-7.45 (m, 8H, 1,2,3,6-H in naphthyl of both isomers), 7.25 and 7.11 (two s, 2H, 2-H in cyclopentathienyl of minor and major isomers), 6.53 and 6.18 (two m, 2H, 6-H and 4-H of cyclopentathienyl of major and minor isomers, respectively), 3.37 and 3.03 (br.s and m, 4H, CH_2 of minor and major isomers), 2.13 and 2.11 (two d, $J = 1.4$ and 1.4 Hz, 6H, Me of major and minor isomers).

Mixture of 5-methyl-3-(4-*tert*-butylphenyl)-6*H*-cyclopenta[*b*]thiophene and 5-methyl-3-(4-*tert*-butyl)-4*H*-cyclopenta[*b*]thiophene (32). To a solution of 160 ml of 0.25 M (40 mmol) of ZnCl_2 in THF, 40.0 ml of 1.0 M (40 mmol) 4-*tert*-butylphenylmagnesium bromide in THF was added at ambient temperature. The resulting mixture was stirred for 1 h; then, a solution of 8.60 g (40 mmol) of **16** in 50 ml of THF and 6.0 ml of 0.1 M (0.6 mmol) $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ in THF were added at ambient temperature. This mixture was stirred for 5 h at reflux and then evaporated to dryness. The product was isolated by flash chromatography on SilicaGel 60 (40-63 μm , d 40 mm, l 200 mm; eluent: hexanes). Yield 10.1 g (94%) of **32**. Anal. calc. for $\text{C}_{18}\text{H}_{14}\text{S}$: C, 80.54; H, 7.51. Found: C, 80.59; H, 7.39. ^1H NMR (CDCl_3): δ 7.58-7.40 (m, 4H, C_6H_4), 7.17 (s, 1H, 2-H in cyclopenta[*b*]thienyl), 6.47 (m, 1H, 4-H in cyclopenta[*b*]thienyl), 3.32 (m, 2H, CH_2), 2.17 (m, 3H, 2-Me in

cyclopenta[*b*]thienyl), 1.35 (s, 9H, ^{*t*}Bu). ¹³C{¹H} NMR (CDCl₃): δ 149.8, 146.9, 145.8, 143.2, 136.5, 133.2, 126.1, 125.5, 122.1, 118.6, 77.4, 76.6, 40.8, 34.5, 31.3, 29.7, 17.1.

2-Methyl-7-(4-dimethylaminophenyl)-1*H*-indene (33). To a solution of 172 ml of 0.25 M (43 mmol) of ZnCl₂ in THF, 39.0 ml of 1.0 M (39 mmol) 4-dimethylaminophenylmagnesium bromide in THF was added at ambient temperature. The resulting mixture was stirred for 1 h; then, a solution of 6.27 g (30 mmol) of **1** in 50 ml of THF and 6.0 ml of 0.1 M (0.6 mmol) Pd(P^{*t*}Bu₃)₂ in THF were added at ambient temperature. This mixture was stirred for 5 h at reflux and then evaporated to dryness. The product was isolated by flash chromatography on SilicaGel 60 (40-63 μm, d 40 mm, l 200 mm; eluent: hexanes). Yield 7.17 g (96%) of **33**. Anal. calc. for C₁₈H₁₉N: C, 86.70; H, 7.67. Found: C, 86.79; H, 7.55. ¹H NMR (CDCl₃) δ 7.42 (m, 2H, 2,6-H in 4-Me₂NC₆H₄), 7.26 (m, 1H, 5-H in indenyl), 7.16 (d, J = 7.4 Hz, 1H, 6-H in indenyl), 7.11 (d, J = 7.6 Hz, 1H, 4-H in indenyl), 6.76 (m, 2H, 3,5-H in 4-Me₂NC₆H₄), 6.49 (m, 1H, 3-H in indenyl), 3.38 (s, 2H, 1,1'-H in indenyl), 2.94 (s, 6H, Me₂N), 2.10 (s, 3H, 2-Me). ¹³C{¹H} NMR (CDCl₃): δ 149.7, 146.6, 146.3, 140.6, 137.5, 129.5, 129.3, 127.5, 127.1, 124.2, 118.3, 112.5, 43.2, 40.7, 16.9.

2-Methyl-7-(2-trifluoromethylphenyl)-1*H*-indene (34). To a solution of 172 ml of 0.25 M (43 mmol) of ZnCl₂ in THF, 39.0 ml of 1.0 M (39 mmol) 2-trifluorophenylmagnesium bromide in THF was added at ambient temperature. The resulting mixture was stirred for 1 h; then, a solution of 6.27 g (30 mmol) of **1** in 50 ml of THF and 6.0 ml of 0.1 M (0.6 mmol) Pd(P^{*t*}Bu₃)₂ in THF were added at ambient temperature. This mixture was stirred for 5 h at reflux and then evaporated to dryness. The product was isolated by flash chromatography on SilicaGel 60 (40-63 μm, d 40 mm, l 200 mm; eluent: hexanes). Yield 8.06 g (98%) of **34**. Anal. calc. for C₁₇H₁₃F₃: C, 74.44; H, 4.78. Found: C, 74.55; H, 4.86. ¹H NMR (CDCl₃) δ 7.88 (d, J = 7.6 Hz, 1H, 3-H in C₆H₄), 7.64 (t, J = 7.6 Hz, 1H, 4-H in C₆H₄), 7.56 (t, J = 7.6 Hz, 1H, 5-H in C₆H₄), 7.44 (d, J = 7.6 Hz, 1H, 6-H in C₆H₄), 7.33-7.41 (m, 2H, 5,6-H in indenyl), 7.10 (d, J = 6.8 Hz, 1H, 4-H in indenyl), 6.64 (m, 1H, 3-H in indenyl), 3.18 (d, J = 22.4 Hz, 1H, 1-H in indenyl), 3.09 (d, J = 22.4 Hz, 1H, 1'-H in indenyl), 2.19 (s, 3H, 2-Me). ¹³C{¹H} NMR (CDCl₃): δ 146.4, 145.6, 142.1, 140.3 (q, J = 1.7 Hz), 135.0, 131.5, 131.4, 128.8 (q, J = 30.0 Hz), 127.5, 127.2, 126.1 (q, J = 5.1 Hz), 125.9, 124.7 (q, J = 1.5 Hz), 124.6 (q, J = 273.7 Hz), 119.4, 42.1, 16.7.

Mixture of 2,5-dimethyl-4-[3,5-bis(trifluoromethyl)phenyl]-1*H*-indene and 2,6-dimethyl-7-[3,5-bis(trifluoromethyl)phenyl]-1*H*-indene (35). To a solution of 172 ml of 0.25 M (43 mmol) of ZnCl₂ in THF, 39.0 ml of 1.0 M (39 mmol) 3,5-bis(trifluoromethyl)phenylmagnesium bromide in THF was added at ambient temperature. The resulting mixture was stirred for 1 h; then, a solution of 6.69 g (30 mmol) of **3** in 50 ml of THF and 6.0 ml of 0.1 M (0.6 mmol) Pd(P^{*t*}Bu₃)₂ in THF were added at ambient temperature. This mixture was stirred for 5 h at reflux and then evaporated to dryness. The product was isolated by flash chromatography on SilicaGel 60 (40-63 μm, d 40 mm, l 200 mm; eluent: hexanes). Yield 9.83 g (92%) of ca. 1:1 mixture of the title isomeric indenenes. Anal. calc. for C₁₉H₁₄F₆: C, 64.05; H, 3.96. Found: C, 63.90; H, 4.08. ¹H NMR (CDCl₃): δ 8.00 (m, 2H, 4-H in 3,5-(CF₃)₂C₆H₃ of both isomers), 7.87 (m, 4H, 2,6-H in 3,5-(CF₃)₂C₆H₃ of both isomers), 7.40 (d, J = 7.6 Hz, 1H, 6-H of 4-aryllindene), 7.24-7.31 (m, 2H, 4,5-H of 7-aryllindenyl), 7.14 (d, J = 7.6 Hz, 1H, 7-H of 4-aryllindenyl), 6.59 (m, 1H, 3-H of 7-aryllindene), 6.20 (m, 1H, 3-H of 4-aryllindene), 3.44 (s, 2H, 1,1'-H of 4-aryllindene), 3.09 (s, 2H, 1,1'-H of 7-aryllindene), 2.27 (s, 3H, 2-Me of 4-aryllindene), 2.23 (s, 3H, 2-Me of 7-aryllindene), 2.19 (s, 3H, 5-Me of 4-aryllindene), 2.17 (s, 3H, 6-Me of 7-aryllindene). ¹³C{¹H} NMR (CDCl₃): δ 147.9, 145.9, 144.9, 144.1, 142.8, 142.5, 142.3, 141.3, 134.6, 133.0, 131.9 (q, J = 32.9 Hz), 131.6 (q, J = 32.9 Hz), 130.5, 130.4, 130.1 (q, J = 2.9 Hz), 129.4 (q, J = 2.9 Hz), 128.8, 127.1, 125.8, 125.5, 123.51 (q, J = 272.3 Hz), 123.49 (q, J = 272.3 Hz), 123.3, 120.9 (sept, J = 4.4 Hz), 120.7 (sept, J = 3.7 Hz), 119.8, 42.9, 42.3, 20.0, 19.8, 16.8, 16.6.

Dimethyl{bis[2-methyl-4-(2-methylphenyl)-1*H*-inden-1-yl]}silane (55). To a solution of 10.0 g (45.4 mmol) of **19** in 500 ml of ether, 18.2 ml of 2.5 M (45.4 mmol) of ^{*n*}BuLi in hexanes was added with vigorous stirring at room temperature. This mixture was additionally stirred for 3 h and then cooled to 0°C. Then 2.75 ml (2.93 g, 22.7 mmol) of dichlorodimethylsilane was added in one portion. The resulting mixture was heated to ambient temperature and stirred for 24 h. Then, 50 ml of water was added. The organic layer was separated, dried over K₂CO₃, and evaporated to dryness. The crude product was purified using flash chromatography on Silica Gel 60 (40-63 μm, d 50 mm, l 350 mm; eluent: hexanes, 100 ml/min). Yield 6.23 g (55%) of ca. 1:1 mixture of *rac*- and *meso*-isomers. Anal. calc. for C₃₆H₃₆Si: C, 87.04; H, 7.30. Found: C, 87.30; H, 7.19. ¹H NMR (CDCl₃): δ 7.08-7.42 (m, 14H, 5,5',6,6',7,7'-H in

indenyls and 3,3',4,4',5,5',6,6'-H in C₆H₄), 6.33 (br.s, 2H, 3,3'-H in indenyls), 3.79-3.89 (m, 2H, 1,1'-H in indenyls), 2.12-2.27 (m, 12H, 2,2'-Me in indenyls and 2,2'-Me in C₆H₄), -0.25 and -0.28 (two br.s, 6H, Me₂Si in *rac*- and *meso*-compounds).

Bis[4-(2-methoxyphenyl)-2-methyl-1*H*-inden-1-yl](dimethyl)silane (56). To a solution of 18.1 g (76.4 mmol) of **22** in a mixture of 230 ml of toluene and 15 ml of THF, 30.6 ml of 2.5 M (76.5 mmol) ^{*n*}BuLi in hexanes was added dropwise. This mixture was additionally stirred for 2 h at ambient temperature and cooled to -35°C, and then 4.64 ml (4.94 g, 38.3 mmol) of dichlorodimethylsilane was added in one portion. The resulting mixture was stirred overnight at room temperature and then 75 ml of cold water was added. The organic layer was separated, dried over MgSO₄, and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm, d 40 mm, l 300 mm; eluent: hexanes-dichloromethane, 2:1, vol.). Yield 11.7 g (58%) of yellowish solid of ca. 1:1 mixture of *rac*- and *meso*-isomers. Anal. calc. for C₃₆H₃₆O₂Si: C, 81.77; H, 6.86. Found: C, 81.96; H, 6.79. ¹H NMR (CDCl₃): δ 7.51 (m, 2H, 7,7'-H in indenyl of *rac*-compound), 7.37 (m, 2H, 5,5'-H in indenyl of *meso*-compound), 7.34 (m, 4H, 7,7'-H in C₆H₄ of *rac*- and *meso*-compounds), 7.32 (m, 4H, 3,3'-H in C₆H₄ of *rac*- and *meso*-compounds), 7.24 (m, 2H, 5,5'-H in indenyl of *rac*-compound), 7.22 (m, 2H, 5,5'-H in indenyl of *meso*-compound), 7.17 (d, J = 7.5 Hz, 2H, 6,6'-H in indenyl of *rac*-compound), 7.16 (d, J = 7.5 Hz, 2H, 6,6'-H in indenyl of *meso*-compound), 7.05 (dt, J = 7.4 Hz, J = 1.0 Hz, 4H, 4,4'-H in C₆H₄ of *rac*- and *meso*-compounds), 7.01 (m, 4H, 6,6'-H in C₆H₄ of *rac*- and *meso*-compounds). ¹³C{¹H} NMR (CDCl₃): δ 156.7 (two resonances), 146.7, 146.6, 144.61, 144.58, 144.2 (two resonances), 130.66, 131.4 (two resonances), 130.63, 130.24, 130.19, 128.4 (two resonances), 126.9, 126.8, 126.43, 126.39, 122.6, 122.5, 122.14, 122.06, 120.5 (two resonances), 111.15, 111.12, 55.52, 55.49, 47.6, 47.5, 17.7, 17.2, -6.0, -6.1, -6.4.

Bis[4-(2-trifluoromethylphenyl)-2-methyl-1*H*-inden-1-yl](dimethyl)silane (57). To a solution of 7.40 g (27.0 mmol) of **34** in a mixture of 100 ml of toluene and 7 ml of THF, 10.8 ml of 2.5 M (27.0 mmol) ^{*n*}BuLi in hexanes was added dropwise. This mixture was additionally stirred for 2 h at ambient temperature and cooled to -35°C, and then 1.65 ml (1.76 g, 13.6 mmol) of dichlorodimethylsilane was added in one portion. The resulting mixture was stirred overnight at room temperature and then 50 ml of cold water was added.

The organic layer was separated, dried over MgSO_4 , and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 40 mm, l 200 mm; eluent: hexanes-dichloromethane, 2:1, vol.). Yield 5.79 g (71%) of yellowish solid of ca. 1:1 mixture of *rac*- and *meso*-isomers. Anal. calc. for $\text{C}_{36}\text{H}_{30}\text{F}_6\text{Si}$: C, 71.50; H, 5.00. Found: C, 71.66; H, 5.12. ^1H NMR (CDCl_3): δ 7.21-7.94 (m, 28H, 5,5',6,6',7,7'-H in indenyl and 3,3',4,4',5,5',6,6'-H in C_6H_4 of *rac*- and *meso*-isomers), 6.40 (m, 4H, 3,3'-H in indenyl of *rac*- and *meso*-isomers), 3.92-4.07 (m, 4H, 1,1'-H in indenyl of *rac*- and *meso*-isomers), 2.21-2.39 (m, 12H, 2,2'-Me in indenyl of *rac*- and *meso*-isomers), -0.04-0.24 (m, 12H, Me_2Si in indenyl of *rac*- and *meso*-isomers).

Bis[4-(4-methylphenyl)-2-methyl-1*H*-inden-1-yl](dimethyl)silane (58). To a solution of 6.60 g (30.0 mmol) of **25** in a mixture of 100 ml of toluene and 7 ml of THF, 12.0 ml of 2.5 M (30.0 mmol) $n\text{BuLi}$ in hexanes was added dropwise. This mixture was additionally stirred for 2 h at ambient temperature and cooled to -35°C , and then 1.84 ml (1.96 g, 15.2 mmol) of dichlorodimethylsilane was added in one portion. The resulting mixture was stirred overnight at room temperature and then 50 ml of cold water was added. The organic layer was separated, dried over MgSO_4 , and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 40 mm, l 200 mm; eluent: hexanes-dichloromethane, 2:1, vol.). Yield 4.84 g (65%) of yellowish solid of ca. 1:1 mixture of *rac*- and *meso*-isomers. Anal. calc. for $\text{C}_{36}\text{H}_{36}\text{Si}$: C, 87.04; H, 7.30. Found: C, 87.10; H, 7.23. ^1H NMR (CDCl_3): δ 7.49-7.54 (m, 10H, 7,7'-H in indenyl of *rac*- or *meso*-isomers and 3,3',5,5'-H in C_6H_4 of *rac*- and *meso*-isomers), 7.40-7.43 (m, 2H, 7,7'-H in indenyl of *meso*- or *rac*-isomers), 7.30-7.35 (m, 12H, 5,5'-H in indenyl and 3,3',5,5'-H in C_6H_4 of *rac*- and *meso*-isomers), 7.19-7.25 (m, 4H, 6,6'-H in indenyl of *rac*- or *meso*-isomers), 6.87 (m, 2H, 3,3'-H in indenyl of *meso*-isomer), 6.85 (m, 2H, 3,3'-H in indenyl of *rac*-isomer), 3.86 (m, 4H, 1,1'-H in indenyl of *rac*- and *meso*-isomer), 2.494 (s, 6H, 4,4'-Me in C_6H_4 of *rac*-isomer), 2.487 (s, 6H, 4,4'-Me in C_6H_4 of *meso*-isomer), 2.30 (m, 6H, 2,2'-Me in indenyl of *meso*-isomer), 2.22 (m, 6H, 2,2'-Me in indenyl of *rac*-isomer), -0.12 (s, 9H, Me_2Si of *rac*-isomer and $\text{MeMe}'\text{Si}$ of *meso*-isomer), -0.14 (s, 3H, $\text{MeMe}'\text{Si}$ of *meso*-isomer). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 147.6, 147.4, 145.5, 145.4,

143.0, 142.9, 138.5, 138.4, 136.4, 136.3, 134.1, 129.1, 128.8, 126.1, 126.0, 125.5, 125.4, 123.1, 123.0, 122.0, 121.9, 47.6, 47.5, 21.2, 18.0, 17.9, -5.68 (br).

Bis[4-(4-*tert*-butylphenyl)-2-methyl-1*H*-inden-1-yl](dimethyl)silane (59). To a solution of 5.05 g (19.3 mmol) of **18** in a mixture of 60 ml of toluene and 5 ml of THF, 7.75 ml of 2.5 M (19.4 mmol) ^{*n*}BuLi in hexanes was added dropwise. This mixture was additionally stirred for 2 h at ambient temperature and cooled to -35°C, and then 1.18 ml (1.25 g, 9.7 mmol) of dichlorodimethylsilane was added in one portion. The resulting mixture was stirred overnight at room temperature and then 30 ml of cold water was added. The organic layer was separated, dried over MgSO₄, and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm, d 30 mm, l 200 mm; eluent: hexanes-dichloromethane, 2:1, vol.). Yield 3.36 g (60%) of yellowish solid of ca. 1:1 mixture of *rac*- and *meso*-isomers. Anal. calc. for C₄₂H₄₈Si: C, 86.84; H, 8.33. Found: C, 86.90; H, 8.39. ¹H NMR (CDCl₃): δ 7.52-7.57 (m, 18H, 7,7'-H in indenyl of *rac*- or *meso*-isomers and 2,2',3,3',5,5',6,6'-H in C₆H₄ of *rac*- and *meso*-isomers), 7.39-7.43 (m, 2H, 7,7'-H in indenyl of *meso*- or *rac*-isomers), 7.31-7.36 (m, 4H, 5,5'-H in indenyl of *rac*- and *meso*-isomers), 7.19-7.26 (m, 4H, 6,6'-H in indenyl of *rac*- and *meso*-isomers), 6.92 (m, 4H, 3,3'-H in indenyl of *rac*- and *meso*-isomers), 3.88 (m, 2H, 1,1'-H in indenyl of *rac*- or *meso*-isomer), 3.85 (m, 2H, 1,1'-H in indenyl of *meso*- or *rac*-isomer), 2.30 (m, 6H, 2,2'-Me in indenyl of *rac*- or *meso*-isomer), 2.24 (m, 6H, 2,2'-Me in indenyl of *meso*- or *rac*-isomer), 1.46 (s, 18H, ^{*t*}Bu of *rac*- or *meso*-isomer), 1.45 (s, 18H, ^{*t*}Bu of *meso*- or *rac*-isomer), -0.13 (s, 3H, MeMe'Si of *meso*-isomer), -0.15 (s, 3H, MeMe'Si of *meso*-isomer), -0.16 (s, 6H, Me₂Si of *rac*-isomer). ¹³C{¹H} NMR (CDCl₃): δ 149.6, 147.5, 147.4, 145.52, 145.50, 143.00, 142.95, 138.49, 138.45, 134.09, 134.04, 128.6, 126.3, 126.2, 125.63, 125.58, 125.3, 123.14, 123.06, 122.05, 122.00, 47.7, 47.6, 34.6, 31.5, 18.03, 18.01, -5.58, -5.59, -5.8.

Bis[4-(4-dimethylaminophenyl)-2-methyl-1*H*-inden-1-yl](dimethyl)silane (60). To a solution of 7.02 g (28.2 mmol) of **33** in a mixture of 100 ml of toluene and 7 ml of THF, 11.3 ml of 2.5 M (28.2 mmol) ^{*n*}BuLi in hexanes was added dropwise. This mixture was additionally stirred for 2 h at ambient temperature and cooled to -35°C, and then 1.72 ml (1.83 g, 14.2 mmol) of dichlorodimethylsilane was added in one portion. The resulting mixture was stirred overnight at room temperature and then 50 ml of cold water was added.

The organic layer was separated, dried over MgSO_4 , and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 40 mm, l 200 mm; eluent: hexanes-dichloromethane, 2:1, vol.). Yield 3.84 g (49%) of yellowish solid of ca. 1:1 mixture of *rac*- and *meso*-isomers. Anal. calc. for $\text{C}_{38}\text{H}_{42}\text{N}_2\text{Si}$: C, 82.26; H, 7.63. Found: C, 82.39; H, 7.66. ^1H NMR (CDCl_3): δ 7.45-7.51 (m, 10H, 7,7'-H in indenyl of *rac*-isomer and 2,2',6,6'-H in C_6H_4 of *rac*- and *meso*-isomers), 7.34 (m, 2H, 7,7'-H in indenyl of *meso*-isomer), 7.29 (m, 2H, 5,5'-H in indenyl of *rac*-isomer), 7.26 (m, 2H, 5,5'-H in indenyl of *meso*-isomer), 7.18 (m, 2H, 6,6'-H in indenyl of *meso*-isomer), 7.16 (m, 2H, 6,6'-H in indenyl of *rac*-isomer), 6.84-6.91 (m, 12H, 3,3'-H in indenyl and 3,3',5,5'-H in C_6H_4 of *rac*- and *meso*-isomers), 3.82 (m, 4H, 1,1'-H in indenyl of *rac*- and *meso*-isomer), 3.04 (s, 12H, Me_2N of *rac*-isomer), 3.03 (s, 12H, Me_2N of *meso*-isomer), 2.27 (m, 6H, 2,2'-Me in indenyl of *meso*-isomer), 2.18 (m, 6H, 2,2'-Me in indenyl of *rac*-isomer), -0.16 (s, 6H, Me_2Si of *rac*-isomer), -0.17 (s, 3H, $\text{MeMe}'\text{Si}$ of *meso*-isomer), -0.19 (s, 3H, $\text{MeMe}'\text{Si}$ of *meso*-isomer). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 149.5, 147.1, 146.9, 145.51, 145.46, 142.84, 142.76, 134.3, 129.8, 129.6, 126.35, 126.30, 125.18, 125.14, 123.02, 122.97, 121.38, 121.32, 112.6, 47.6, 47.5, 40.7, 17.9, 17.8, -5.67.

Bis[4-(1-benzothien-3-yl)-2-methyl-1*H*-inden-1-yl](dimethyl)silane (62). To a solution of 7.35 g (28.0 mmol) of **50** in 300 ml of ether, 11.3 ml of 2.5 M (28.3 mmol) $n\text{BuLi}$ in hexanes was added dropwise at 0°C . This mixture was stirred for an additional 16 h at ambient temperature. Then 1.70 ml (1.81 g, 14.0 mmol) of dichlorodimethylsilane was added in one portion. The resulting mixture was stirred for 30 h at room temperature, and then 150 ml of cold water was added. The organic layer was separated. The aqueous layer was washed with 2 x 100 ml of methyl-*tert*-butyl ether. The combined organic extract was dried over MgSO_4 and evaporated to dryness. The obtained oil was recrystallized from 150 ml of hot hexanes. The precipitate formed at ambient temperature was separated, washed with 20 ml of cold hexanes, and dried in vacuum. Yield 3.81 g (47%) of yellowish solid of ca. 1:1 mixture of *rac*- and *meso*-isomers. Anal. calc. for $\text{C}_{38}\text{H}_{32}\text{S}_2\text{Si}$: C, 78.57; H, 5.55. Found: C, 78.42; H, 5.63. ^1H NMR (CDCl_3): δ 7.92-7.96 (m, 4H, 4,4'-H in benzothienyl of *rac*- and *meso*-compounds), 7.66-7.72 (m, 4H, 7,7'-H in benzothienyl of *rac*- and *meso*-compounds), 7.58 (m, 2H, 7,7'-H in indenyl of *rac*-compound), 7.46 (m, 2H, 7,7'-H in indenyl of *meso*-

compound), 7.42 (s, 2H, 2,2'-H in benzothienyl of *meso*-compound), 7.40 (s, 2H, 2,2'-H in benzothienyl of *rac*-compound), 7.31-7.40 (m, 12H, 6,6'-H in indenyl and 5,5',6,6'-H in benzothienyl of *rac*- and *meso*-compound), 7.25 (d, J= 7.5 Hz, 2H, 5,5'-H in indenyl of *rac*-compound), 7.23 (d, J= 7.5 Hz, 2H, 5,5'-H in indenyl of *meso*-compound), 6.55 (m, 2H, 3,3'-H in indenyl of *meso*-compound), 6.53 (m, 2H, 3,3'-H in indenyl of *rac*-compound), 3.86 (m, 4H, 1,1'-H in indenyls of *rac*- and *meso*-compounds), 2.24 (m, 6H, 2,2'-Me in *meso*-compound), 2.15 (m, 6H, 2,2'-Me in *rac*-compound), -0.12 (s, 6H, SiMe₂ in *rac*-compound), -0.13(s, 3H, SiMeMe' in *meso*-compound), -0.15 (s, 3H, SiMeMe' in *meso*-compound).

Bis(2,5-dimethyl-4-phenylinden-1-yl)(dimethyl)silane (63). To a solution of 11.8 g (53.7 mmol) of **26** in a mixture of 140 ml of toluene and 10 ml of THF, 22.0 ml of 2.5 M (55.0 mmol) of ⁿBuLi was added dropwise with vigorous stirring at -80°C. This mixture was stirred overnight at room temperature and then cooled to -40°C. To the resulting mixture, 3.27 ml (3.48 g, 27.0 mmol) of dichlorodimethylsilane was added in one portion. This mixture was stirred overnight at room temperature, and then 100 ml of cold water was added. The organic layer was separated, dried over K₂CO₃, and evaporated to dryness. The residue was recrystallized from hexanes-methyl-*tert*-butyl ether (20:1, vol.). Yield 7.22 g (54%) of white solid of ca. 1:1 mixture of *rac*-and *meso*-isomers. Anal. calc. for C₃₆H₃₆Si: C, 87.04; H, 7.30. Found: C, 87.19; H, 7.34. ¹H NMR (CDCl₃): δ 7.25-7.45 (m, 12H, 6-H of indenyl and Ph of *rac*- and *meso*-compounds), 7.03 (d, J= 8.0 Hz, 7-H in indenyl of *rac*-compound), 7.01 (d, J= 8.0 Hz, 7-H in indenyl of *meso*-compound), 6.31 (m, 2H, 3-H in indenyl of *rac*- and *meso*-compounds), 3.76 (s, 1H, 1-H in indenyl of *rac*-compound), 3.75 (s, 1H, 1-H in indenyl of *meso*-compound), 2.22 (s, 3H, 5-Me in indenyl of *rac*-compound), 2.21 (s, 3H, 5-Me in indenyl of *meso*-compound), 2.17 (s, 3H, 2-Me in indenyl of *meso*-compound), 2.09 (s, 3H, 2-Me in indenyl of *rac*-compound), -0.23 (s, 3H, SiMeMe' of *meso*-compound), -0.24 (s, 6H, SiMe₂ of *rac*-compound), -0.25 (s, 3H, SiMeMe' of *meso*-compound). ¹³C{¹H} NMR (CDCl₃): δ 147.1, 147.0, 144.5, 142.2, 140.3, 133.8, 132.0, 129.9, 129.7, 126.01, 126.52, 126.4, 124.9, 122.0, 47.3, 20.1, 17.9, -5.9, -6.0, -6.1.

Bis[4-[3,5-bis(trifluoromethyl)phenyl]-2,5-dimethyl-1H-inden-1-yl](dimethyl)silane (64). To a solution of 9.40 g (26.4 mmol) of **35** in a mixture of 120 ml of toluene and 8 ml of THF, 10.6 ml of 2.5 M (26.5

mmol) of n BuLi was added dropwise with vigorous stirring at -80°C . This mixture was stirred overnight at room temperature and then cooled to -40°C . To the resulting mixture, 3.21 ml (3.42 g, 26.5 mmol) of dichlorodimethylsilane was added in one portion. This mixture was stirred overnight at room temperature, and then 70 ml of cold water was added. The organic layer was separated, dried over MgSO_4 , and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 40 mm, l 200 mm; eluent: hexanes-dichloromethane, 2:1, vol.). Yield 7.31 g (72%) of yellowish solid of ca. 1:1 mixture of *rac*- and *meso*-isomers. Anal. calc. for $\text{C}_{40}\text{H}_{32}\text{F}_{12}\text{Si}$: C, 62.49; H, 4.20. Found: C, 62.55; H, 4.28. ^1H NMR (CDCl_3): δ 8.02 (m, 4H, 4,4'-H in aryl of *rac*- and *meso*-isomers), 7.93 (m, 4H, 2,2',6,6'-H in aryl of *rac*- or *meso*-isomer), 7.89 (m, 4H, 2,2',6,6'-H in aryl of *meso*- or *rac*-isomer), 7.57 (m, 2H, 7,7'-H in indenyl of *rac*- or *meso*-isomer), 7.46 (m, 2H, 7,7'-H in indenyl of *meso*- or *rac*-isomer), 7.20 (m, 2H, 6,6'-H in indenyl of *rac*- or *meso*-isomer), 7.17 (m, 2H, 6,6'-H in indenyl of *meso*- or *rac*-isomer), 6.36 (m, 4H, 3,3'-H in indenyl of *rac*- and *meso*-isomers), 3.92 (m, 2H, 1,1'-H in indenyl of *rac*- or *meso*-isomer), 3.91 (m, 2H, 1,1'-H in indenyl of *meso*- or *rac*-isomer), 2.34 (m, 6H, 2,2'-Me of *rac*- or *meso*-isomer), 2.33 (s, 6H, 5,5'-Me of *rac*- or *meso*-isomer), 2.32 (s, 6H, 5,5'-Me of *meso*- or *rac*-isomer), 2.28 (m, 6H, 2,2'-Me of *meso*- or *rac*-isomer), -0.05 (s, 3H, SiMeMe' of *meso*-isomer), -0.08 (s, 3H, SiMeMe' of *meso*-isomer), -0.09 (s, 6H, SiMe₂ of *rac*-isomer).

Bis[4-phenyl-2-methyl-6-isopropyl-1*H*-inden-1-yl](dimethyl)silane (65). To a solution of 15.6 g (62.9 mmol) of **27** in a mixture of 140 ml of toluene and 10 ml of THF, 25.2 ml of 2.5 M (63.0 mmol) of n BuLi was added dropwise with vigorous stirring at -80°C . This mixture was stirred overnight at room temperature and then cooled to -40°C . To the resulting mixture, 3.82 ml (4.06 g, 31.5 mmol) of dichlorodimethylsilane was added in one portion. This mixture was stirred overnight at room temperature, and then 70 ml of cold water was added. The organic layer was separated, dried over MgSO_4 , and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 50 mm, l 300 mm; eluent: hexanes-dichloromethane, 2:1, vol.). Yield 17.4 g (55%) of yellowish solid of ca. 1:1 mixture of *rac*- and *meso*-isomers. Anal. calc. for $\text{C}_{40}\text{H}_{44}\text{Si}$: C, 86.90; H, 8.02. Found: C, 87.11; H, 8.10. ^1H NMR (CDCl_3): δ 7.57-7.61 (m, 8H, 2,2',6,6'-H in Ph of *rac*- and *meso*-isomers), 7.46-7.52 (m, 8H,

3,3',5,5'-H in Ph of *rac*- and *meso*-isomers), 7.35-7.42 (m, 8H, 5,5'-H in indenyl and 4,4'-H in Ph of *rac*- and *meso*-isomers), 7.16-7.19 (m, 4H, 7,7'-H in indenyl of *rac*- and *meso*-isomers), 6.81 (m, 2H, 3,3'-H in indenyl of *rac*- or *meso*-isomer), 6.77 (m, 2H, 3,3'-H in indenyl of *meso*- or *rac*-isomer), 3.76 (s, 2H, 1,1'-H in indenyl of *rac*- or *meso*-isomer), 3.75 (s, 2H, 1,1'-H in indenyl of *meso*- or *rac*-isomer), 3.01 (sept, J = Hz, 4H, CHMe₂ of *rac*- and *meso*-isomers), 2.25 (s, 6H, 2,2'-Me in indenyl of *rac*- or *meso*-isomer), 2.18 (s, 6H, 2,2'-Me in indenyl of *meso*- or *rac*-isomer), 1.30-1.35 (m, 24H, CHMe₂ of *rac*- and *meso*-isomers), -0.09 (s, 3H, SiMeMe' of *meso*-isomer), -0.10 (s, 6H, SiMe₂ of *rac*-isomer), -0.16 (s, 3H, SiMeMe' of *meso*-isomer). ¹³C{¹H} NMR (CDCl₃): δ 147.0, 146.8, 145.92, 145.86, 143.95, 143.93, 141.71, 141.65, 140.9, 140.8, 133.73, 133.70, 128.9, 128.4, 126.67, 126.65, 125.73, 125.66, 124.13, 124.06, 120.45, 120.42, 47.5, 47.4, 34.21, 34.20, 24.6, 24.5, 24.4, 24.3, 18.0, 17.9, -5.13 (two resonances), -5.24.

Dimethyl[bis(2-methyl-4,6-diphenyl-1*H*-inden-1-yl)]silane (66). To a solution of 20.9 g (74.1 mmol) of **28** in a mixture of 200 ml of toluene and 10 ml of THF, 29.6 ml of 2.5 M (74.1 mmol) ⁿBuLi in hexanes was added dropwise with vigorous stirring. This mixture was additionally stirred for 1 h and cooled to -30°C, and then 4.49 ml (4.78 g, 37.0 mmol) of dichlorodimethylsilane was added in one portion. The resulting mixture was stirred overnight at room temperature. Then 100 ml of cold water were added. The organic layer was separated, dried over MgSO₄, and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm, d 40 mm, l 350 mm; eluent: hexanes-dichloromethane, 3:1, vol.). Yield 14.1 g (61%) of a ca. 1:1 mixture of *rac*- and *meso*-**66**. Anal. calc. for C₄₆H₄₀Si: C, 88.98; H, 6.49. Found: C, 89.14; H, 6.33. ¹H NMR (CDCl₃): δ 7.24-7.69 (m, 24H, 5,5',7,7'-H in indenyl and Ph of *rac*- and *meso*-isomers), 6.82 (m, 2H, 3,3'-H in indenyl of *meso*-isomer), 6.81 (m, 2H, 3,3'-H in indenyl of *rac*-isomer), 3.88 (br.s, 2H, 1,1'-H in indenyl of *meso*-isomer), 3.85 (br.s, 2H, 1,1'-H in indenyl of *rac*-isomer), 2.28 (d, J= 0.8 Hz, 6H, 2,2'-Me in indenyl of *meso*-isomer), 2.20 (d, J= 0.8 Hz, 6H, 2,2'-Me in indenyl of *rac*-isomer), -0.04 (s, 3H, SiMeMe' of *meso*-isomer), -0.05 (s, 6H, SiMe₂ of *rac*-isomer), -0.07 (s, 3H, SiMeMe' of *meso*-isomer). ¹³C{¹H} NMR (CDCl₃): δ 148.3, 148.2, 146.3, 146.2, 142.3, 142.2, 141.77, 141.74, 141.22, 141.19, 136.32, 136.28, 134.3, 128.9, 128.7, 128.4, 127.13, 127.10, 126.9, 126.73, 126.72, 125.8, 125.1, 125.0, 121.0, 120.9, 47.91, 47.87, 18.1, 18.0, -4.9, -5.05, -5.08.

Dimethyl[bis(5-methyl-3-phenyl-6*H*-cyclopenta[*b*]thien-6-yl)]silane (67). To a solution of 5.20 g (24.5 mmol) of **30** in 200 ml of ether, 15.3 ml of 1.6 M (24.5 mmol) MeLi in ether was added at 20°C. This mixture was stirred for 24 h at room temperature and then cooled to 10°C. To this mixture, 1.48 ml (1.57 g, 12.3 mmol) of dichlorodimethylsilane was added at this temperature. The resulting mixture was stirred for 24 h at ambient temperature. Then 50 ml of water was added. The organic layer was separated, dried over K₂CO₃, and evaporated to dryness in vacuum. The residue was recrystallized from 50 ml of hexanes. Yield 2.71 g (46%) of pure *rac*-**67**. Anal. calc. for C₃₀H₂₈S₂Si: C, 74.95; H, 5.87. Found: C, 74.88; H, 5.95. ¹H NMR (CDCl₃): δ 7.08-7.69 (m, 12H, 5,5'-H in cyclopentathienyl and Ph), 6.81 (m, 2H, 3,3'-H in cyclopentathienyl), 3.94 (s, 2H, 1,1'-H in cyclopentathienyl), 2.20 (m, 6H, 2,2'-Me in cyclopentathienyl), -0.22 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃): δ 147.8, 147.4, 142.0, 136.5, 134.1, 128.7, 127.1, 126.9, 123.1, 121.8, 45.8, 18.1, -7.6.

Dimethyl{bis[5-methyl-3-(1-naphthyl)-6*H*-cyclopenta[*b*]thien-6-yl]}silane (68). In an argon atmosphere, to a solution of 4.00 g (15.2 mmol) of **31** in 200 ml of diethyl ether, 9.4 ml of 1.6 M MeLi (15.2 mmol) in ether was added at 20°C. This mixture was stirred for 24 h at room temperature and then cooled to 10°C. To this mixture, 0.922 ml (7.60 mmol) of Me₂SiCl₂ was added at this temperature. The resulting mixture was stirred for 24 h at ambient temperature. Then 50 ml of water were added. The organic layer was separated, dried over K₂CO₃, and evaporated to dryness in vacuum. The residue was recrystallized from 30 ml of hexanes. Yield 1.38 g (31%) of pure *rac*-**68**. Anal. calc. for C₃₈H₃₂S₂Si: C, 78.57; H, 5.55. Found: C, 78.64; H, 5.42. ¹H NMR (CDCl₃): δ 7.20-8.07 (m, 16H, 5,5'-H in cyclopentathienyl and naphthyls), 6.37 (m, 2H, 3,3'-H in cyclopentathienyl), 3.95 (s, 2H, 1,1'-H in cyclopentathienyl), 2.29 (s, 6H, 2,2'-Me in cyclopentathienyl), -0.11 (s, 6H, SiMe₂).

Dimethyl{bis[5-methyl-3-(4-*tert*-butylphenyl)-6*H*-cyclopenta[*b*]thien-6-yl]}silane (69). To a solution of 9.65 g (36.0 mmol) of **32** in a mixture of 100 ml of toluene and 8 ml of THF, 14.4 ml of 2.5 M (36.0 mmol) of ^{*n*}BuLi was added dropwise with vigorous stirring at -80°C. This mixture was stirred overnight at room temperature and then cooled to -40°C. To the resulting mixture, 2.19 ml (2.33 g, 18.1 mmol) of dichlorodimethylsilane was added in one portion. This mixture was stirred overnight at room temperature,

and then 50 ml of cold water was added. The organic layer was separated, dried over MgSO_4 , and evaporated to dryness. The product was isolated by flash chromatography on Silica Gel 60 (40-63 μm , d 40 mm, l 200 mm; eluent: hexanes-dichloromethane, 2:1, vol.). Yield 6.08 g (57%) of yellowish solid of ca. 1:1 mixture of *rac*- and *meso*-isomers. Anal. calc. for $\text{C}_{38}\text{H}_{44}\text{S}_2\text{Si}$: C, 76.97; H, 7.48. Found: C, 77.08; H, 7.56. ^1H NMR (CDCl_3): δ 7.59-7.64 (m, 8H, 2,2',6,6'-H in C_6H_4 of *rac*- and *meso*-isomers), 7.47-7.51 (m, 8H, 3,3',5,5'-H in C_6H_4 of *rac*- and *meso*-isomers), 7.29 (m, 2H, 2,2'-H in cyclopenta[*b*]thienyl of *rac*-isomer), 7.26 (m, 2H, 2,2'-H in cyclopenta[*b*]thienyl of *meso*-isomer), 6.84 (m, 4H, 4,4'-H in cyclopenta[*b*]thienyl of *rac*- and *meso*-isomers), 3.97 (s, 2H, 6,6'-H in cyclopenta[*b*]thienyl of *rac*-isomer), 3.86 (s, 2H, 6,6'-H in cyclopenta[*b*]thienyl of *meso*-isomer), 2.35 (m, 6H, 2,2'-Me in cyclopenta[*b*]thienyl of *meso*-isomer), 2.22 (m, 6H, 2,2'-Me in cyclopenta[*b*]thienyl of *rac*-isomer), 1.399 (s, 18H, ^tBu of *rac*-isomer), 1.396 (s, 18H, ^tBu of *meso*-isomer), -0.20 (s, 3H, SiMeMe' of *meso*-isomer), -0.21 (s, 3H, SiMeMe' of *meso*-isomer), -0.22 (s, 6H, SiMe_2 of *rac*-isomer). ^{13}C NMR (CDCl_3 , 25°C): δ 149.8, 147.7, 147.6, 147.5, 141.91, 141.88, 133.9, 133.7, 126.8, 125.6, 123.2, 121.41, 121.38, 46.0, 45.7, 34.6, 31.4, 30.9, 18.2, -7.2, -7.7, -8.5.

Complex *rac*-70. To a solution of 4.84 g (8.0 mmol) of **57** in 150 ml of ether, 6.50 ml 2.5 M (16.3 mmol) of $^n\text{BuLi}$ in hexanes was added dropwise over 15 min at 0°C . This mixture was stirred for 5 h at room temperature and then cooled to -78°C . Next, 3.02 g (8.0 mmol) of $\text{ZrCl}_4(\text{THF})_2$ was added. The resulting mixture was slowly (ca. 2 h) warmed to ambient temperature with vigorous stirring and then stirred for 24 h. The organic solvents were distilled off under reduced pressure, and 200 ml of toluene was added. This mixture was stirred for 1 h at 80°C and then filtered through glass frit (G4) at this temperature. The filtrate was evaporated to ca. 80 ml. The orange crystals precipitated at -30°C were collected, washed with 2 x 5 ml of cold toluene and 3 x 30 ml of hexanes, and dried in vacuum. This procedure gave 1.71 g (28%) of pure *rac*-**70**. Anal. calc. for $\text{C}_{36}\text{H}_{28}\text{Cl}_2\text{F}_6\text{SiZr}$: C, 56.53; H, 3.69. Found: C, 56.60; H, 3.77. ^1H NMR (CD_2Cl_2): δ 7.85 (m, 2H, 6,6'-H in C_6H_4), 7.77 (m, 2H, 3,3'-H in C_6H_4), 7.73 (m, 5,5'-H in indenyl), 7.65 (m, 4,4'-H in C_6H_4), 7.53 (m, 5,5'-H in C_6H_4), 7.26 (m, 7,7'-H in indenyl), 7.09 (dd, $J = 8.8$ Hz, $J = 7.0$ Hz,

2H, 6,6'-H in indenyl), 6.41 (s, 2H, 3,3'-H in indenyl), 2.23 (s, 6H, 2,2'-Me in indenyl), 1.34 (s, 6H, SiMe₂).

Complex *rac*-71. To a solution of 4.47 g (9.0 mmol) of **58** in 150 ml of ether, 7.30 ml 2.5 M (18.3 mmol) of ⁿBuLi in hexanes was added dropwise over 15 min at 0°C. This mixture was stirred for 10 h at room temperature and then cooled to -78°C. Next, 3.39 g (9.0 mmol) of ZrCl₄(THF)₂ was added. The resulting mixture was slowly (ca. 1.5 h) warmed to ambient temperature with vigorous stirring and then stirred for 15 h. The organic solvents were distilled off under reduced pressure, and 200 ml of toluene was added. This mixture was stirred for 1 h at 80°C and then filtered through glass frit (G4) at this temperature. The filtrate was evaporated to ca. 100 ml. The orange-yellow crystals precipitated at -30°C were collected, washed with 2 x 5 ml of cold toluene and 3 x 30 ml of hexanes, and dried in vacuum. This procedure gave 2.07 g (35%) of pure *rac*-71. Anal. calc. for C₃₆H₃₄Cl₂SiZr: C, 65.83; H, 5.22. Found: C, 65.94; H, 5.00. ¹H NMR (CD₂Cl₂): δ 7.63 (d, J = 8.7 Hz, 2H, 7,7'-H of indenyl), 7.46 (m, 4H, 2,2',6,6'-H of *p*-tolyl), 7.30 (d, J = 7.0 Hz, 2H, 5,5'-H of indenyl), 7.21 (m, 4H, 3,3',5,5'-H of *p*-tolyl), 7.06 (dd, J = 8.7 Hz, J = 7.0 Hz, 2H, 6,6'-H of indenyl), 6.86 (s, 2H, 3,3'-H of indenyl), 2.33 (s, 6H, 4,4'-Me of *p*-tolyl), 2.20 (s, 6H, 2,2'-Me of indenyl), 1.30 (s, 6H, SiMe₂).

Complex *rac*-72. To a solution of 2.91 g (5.0 mmol) of **59** in 100 ml of ether, 4.10 ml 2.5 M (10.3 mmol) of ⁿBuLi in hexanes was added dropwise over 15 min at 0°C. This mixture was stirred for 12 h at room temperature and then cooled to -78°C. Next, 1.89 g (5.0 mmol) of ZrCl₄(THF)₂ was added. The resulting mixture was slowly (ca. 1.5 h) warmed to ambient temperature with vigorous stirring and then stirred for 12 h. The organic solvents were distilled off under reduced pressure, and 100 ml of toluene was added. This mixture was stirred for 1 h at 80°C and then filtered through glass frit (G4) at this temperature. The filtrate was evaporated to ca. 30 ml. The yellow crystals precipitated at -30°C were collected, washed with 2 x 5 ml of cold toluene and 3 x 30 ml of hexanes, and dried in vacuum. This procedure gave 0.67 g (18%) of pure *rac*-72. Anal. calc. for C₄₂H₄₆Cl₂SiZr: C, 68.07; H, 6.26. Found: C, 68.22; H, 6.05. ¹H NMR (CD₂Cl₂): δ 7.64 (m, 2H, 7,7'-H of indenyl), 7.50-7.56 (m, 4H, 2,2',6,6'-H of C₆H₄), 7.41-7.47 (m, 4H, 3,3',5,5'-H of C₆H₄), 7.33 (dd, J = 7.0 Hz, J = 0.8 Hz, 2H, 5,5'-H of indenyl), 7.08 (dd, J = 8.7 Hz, J = 7.0 Hz,

2H, 6,6'-H of indenyl), 6.91 (m, 2H, 3,3'-H of indenyl), 2.21 (d, $J = 0.4$ Hz, 6H, 2,2'-Me of indenyl), 1.31 (s, 6H, SiMe₂), 1.30 (s, 18H, ^tBu).

Complex *rac*-73. To a solution of 3.33 g (6.0 mmol) of **60** in 100 ml of ether, 4.90 ml 2.5 M (12.3 mmol) of ⁿBuLi in hexanes was added dropwise over 15 min at 0°C. This mixture was stirred for 5 h at room temperature and then cooled to -78°C. Next, 2.26 g (6.0 mmol) of ZrCl₄(THF)₂ was added. The resulting mixture was slowly (ca. 1.5 h) warmed to ambient temperature with vigorous stirring and then stirred for 10 h. The organic solvents were distilled off under reduced pressure, and 100 ml of dichloromethane was added. This mixture was filtered through glass frit (G4). The precipitate was washed by 4 x 20 ml of dichloromethane and dried in vacuum. This procedure gave 1.29 g (30%) of pure *rac*-**73** as orange powder. Anal. calc. for C₃₈H₄₀Cl₂N₂SiZr: C, 63.84; H, 5.64. Found: C, 63.71; H, 5.55. ¹H NMR (CD₂Cl₂): δ 7.61-7.69 (m, 6H, 5,5'-H in indenyl and 2,2',6,6'-H in C₆H₄), 7.35 (m, 4H, 3,3',5,5'-H in C₆H₄), 7.31 (m, 2H, 7,7'-H in indenyl), 7.09 (dd, $J = 8.7$ Hz, $J = 7.2$ Hz, 2H, 6,6'-H in indenyl), 6.87 (s, 3,3'-H in indenyl), 3.15 (s, 12H, NMe₂), 2.20 (s, 6H, 2,2'-Me), 1.32 (s, 6H, SiMe₂).

Complexes *rac*- and *meso*-75. To a solution of 3.25 g (5.60 mmol) of **62** in 120 ml of ether, 4.49 ml 2.5 M (11.2 mmol) of ⁿBuLi in hexanes was added dropwise over 15 min at 0°C. This mixture was stirred for 20 h at room temperature and then cooled to -78°C. Next, 2.11 g (5.60 mmol) of ZrCl₄(THF)₂ was added. The resulting mixture was slowly (ca. 1.5 h) warmed to ambient temperature with vigorous stirring and then stirred for 30 h. The organic solvents were distilled off under reduced pressure, and 150 ml of toluene was added. This mixture was stirred for 1 h at 80°C and then filtered through glass frit (G4) at this temperature. The precipitate was additionally washed with 20 ml of hot toluene. Crystals precipitated at -30°C from the combined filtrate were collected, washed with 3 x 5 ml of cold toluene and 4 x 30 ml of hexanes, and dried in vacuum. This procedure gave 0.62 g (15%) of pure *meso*-**75**. Anal. calc. for C₃₈H₃₀Cl₂S₂SiZr: C, 61.59; H, 4.08. Found: C, 61.48; H, 4.07. The mother solution was evaporated to ca. 50 ml. Crystals precipitated from this solution at -30°C were collected, washed with 2 x 5 ml of cold toluene and 3 x 30 ml of hexanes, and dried in vacuum. This procedure gave 0.83 g (20%) of a ca. 4:1 mixture of *rac*- and *meso*-**75**. Found: C, 61.51; H, 4.16. *rac*-**75**. ¹H NMR (CD₂Cl₂): δ 7.81-7.92 (m, 4H, 4,4',7,7'-H in benzothienyl), 7.72 (m,

2H, 6,6'-H in benzothienyl), 7.69 (s, 2H, 2,2'-H in benzothienyl), 7.50 (dd, $J = 7.0$ Hz, $J = 0.8$ Hz, 2H, 7,7'-H in indenyl), 7.29-7.36 (m, 4H, 5,5'-H in indenyl and 5,5'-H in benzothienyl), 7.14 (dd, $J = 8.7$ Hz, $J = 7.0$ Hz, 2H, 6,6'-H in indenyl), 6.84 (m, 2H, 3,3'-H in indenyl), 2.21 (s, 6H, 2,2'-Me in indenyl), 1.34 (s, 6H, SiMe₂). **meso-75**. ¹H NMR (CD₂Cl₂): δ 7.88 (m, 2H, 4,4'-H in benzothienyl), 7.75 (m, 2H, 7,7'-H in indenyl), 7.72 (m, 2H, 7,7'-H in benzothienyl), 7.64 (s, 2H, 2,2'-H in benzothienyl), 7.25-7.36 (m, 6H, 5,5'-H in indenyl and 5,5',6,6'-H in benzothienyl), 6.93 (dd, $J = 8.7$ Hz, $J = 6.9$ Hz, 2H, 6,6'-H in indenyl), 6.69 (m, 2H, 3,3'-H in indenyl), 2.40 (s, 6H, 2,2'-Me in indenyl), 1.50 (s, 3H, SiMeMe'), 1.25 (s, 3H, SiMeMe'). ¹³C{¹H} NMR (CD₂Cl₂): δ 142.0, 139.7, 139.6, 137.3, 136.3, 133.0, 130.0, 128.1, 127.6, 127.2, 126.0, 125.9, 125.7, 124.5, 124.4, 121.7, 87.2, 20.4, 4.1, 3.9.

Complex rac-76. To a solution of 6.15 g (8.0 mmol) of **64** in 100 ml of ether, 6.50 ml 2.5 M (16.3 mmol) of ⁿBuLi in hexanes was added dropwise over 15 min at 0°C. This mixture was stirred for 12 h at room temperature and then cooled to -78°C. Next, 3.02 g (8.0 mmol) of ZrCl₄(THF)₂ was added. The resulting mixture was slowly (ca. 1.5 h) warmed to ambient temperature with vigorous stirring and then stirred for 20 h. The organic solvents were distilled off under reduced pressure, and 100 ml of dichloromethane was added. This mixture was filtered through glass frit (G4). The precipitate was washed by 4 x 20 ml of dichloromethane and dried in vacuum. This procedure gave 1.41 g (19%) of pure **rac-76** as orange-red powder. Anal. calc. for C₄₀H₃₀Cl₂F₁₂SiZr: C, 51.72; H, 3.26. Found: C, 51.60; H, 3.14. ¹H NMR (CD₂Cl₂): δ 7.47-7.57 (m, 6H, 2,2',4,4',6,6'-H in aryl), 6.95-6.99 (m, 4H, 6,6',7,7'-H in indenyl), 6.43 (s, 2H, 3,3'-H in indenyl), 2.29 (s, 6H, 5,5'-Me in indenyl), 2.19 (s, 6H, 2,2'-Me in indenyl), 1.29 (s, 6H, SiMe₂).

Complex rac-77. To a solution of 5.53 g (10.0 mmol) of **65** in 150 ml of ether, 8.10 ml 2.5 M (20.3 mmol) of ⁿBuLi in hexanes was added dropwise over 15 min at 0°C. This mixture was stirred for 12 h at room temperature and then cooled to -78°C. Next, 3.77 g (10.0 mmol) of ZrCl₄(THF)₂ was added. The resulting mixture was slowly (ca. 1.5 h) warmed to ambient temperature with vigorous stirring and then stirred for 24 h. The organic solvents were distilled off under reduced pressure, and 100 ml of dichloromethane was added. This mixture was filtered through glass frit (G4). The precipitate was washed by 4 x 20 ml of dichloromethane and dried in vacuum. The crude product was recrystallized from toluene. This procedure

gave 1.00 g (14%) of pure *rac*-**77** as orange crystalline solid. Anal. calc. for $C_{40}H_{42}Cl_2SiZr$: C, 67.38; H, 5.94. Found: C, 67.47; H, 6.00. 1H NMR (CD_2Cl_2): δ 7.60-7.65 (m, 4H, 2,2',6,6'-H in Ph), 7.47 (m, 2H, 5,5'-H in indenyl), 7.41-7.46 (m, 3,3',5,5'-H in Ph), 7.34-7.39 (m, 4,4'-H in Ph), 7.29 (d, $J = 1.2$ Hz, 2H, 7,7'-H in indenyl), 6.87 (s, 2H, 3,3'-H in indenyl), 2.93 (sept, $J = 6.9$ Hz, 2H, $CHMe_2$), 2.26 (s, 6H, 2,2'-Me), 1.36 (s, 6H, $SiMe_2$), 1.26 (d, $J = 6.9$ Hz, $CHMe_2$).

Complex *rac*-78. To a solution of 7.83 g (12.6 mmol) of **66** in 250 ml of ether, 10.1 ml of 2.5 M (25.2 mmol) $nBuLi$ in hexanes was added at room temperature. This mixture was stirred for 3 h and then cooled to $-80^\circ C$. Next, 4.57 g (12.6 mmol) of $ZrCl_4(THF)_2$ was added and the resulting mixture was slowly (ca. 1.5 h) warmed to room temperature with vigorous stirring. The mixture was additionally stirred for 30 h. Then, the organic solvents were distilled off under reduced vacuum and 250 ml of toluene were added. This mixture was stirred for 1 h at $80^\circ C$ and then filtered through glass frit (G4) at this temperature. The precipitate was additionally washed with 3 x 40 ml of hot toluene. Crystals precipitated at $-30^\circ C$ from the combined filtrate were collected, washed with 3 x 20 ml of cold toluene, and 3 x 20 ml of hexanes, and dried in vacuum. Yield 2.86 g (29%) of orange crystals of pure *rac*-**78**. Additional crystallization of the mother solution at $-30^\circ C$ gave several crystals of *meso*-**78** suitable for X-ray crystal structure analysis. Anal. calc. for $C_{46}H_{38}Cl_2SiZr$: C, 70.74; H, 4.90. Found: C, 70.89; H, 4.93. 1H NMR (CD_2Cl_2): δ 7.83 (m, 2H, 5,5'-H in indenyl), 7.63-7.67 (m, 4H, 2,2',6,6'-H in 4-,4'-,7-, or 7'-Ph), 7.62 (d, $J = 1.4$ Hz, 2H, 7,7'-H in indenyl), 7.55-7.59 (m, 4H, 2,2',6,6'-H in 4-,4'-,7-, or 7'-Ph), 7.40-7.46 (m, 8H, 3,3',5,5'-H in 4,4',6,6'-Ph), 7.31-7.38 (m, 4H, 4,4'-H in 4,4',6,6'-Ph), 6.93 (m, 2H, 3,3'-H in indenyl), 2.29 (s, 6H, 2,2'-Me in indenyl), 1.39 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 142.5, 141.1, 140.5, 140.4, 137.8, 132.7, 130.5, 130.19, 130.15, 129.5, 129.2, 128.7, 128.6, 126.8, 123.8, 123.4, 20.2, 4.2.

Complex *rac*-79. To a solution of 2.15 g (4.47 mmol) of **67** in 250 ml of ether, 5.6 ml of 1.6 M MeLi (8.94 mmol) in ether were added at room temperature. This mixture was stirred for 24 h and cooled to $-80^\circ C$, and then 1.69 g (4.47 mmol) of $ZrCl_4(THF)_2$ was added. The resulting mixture was stirred for 24 h at room temperature and then evaporated to dryness. To the residue, 200 ml of toluene was added. This mixture was additionally stirred for 10 h at $70^\circ C$. This hot mixture was filtered through glass frit (G4). The

precipitate was additionally washed with 3 x 50 ml of hot toluene. The combined filtrate was evaporated to dryness. The residue was recrystallized from dichloromethane. Yield 1.07 g (37%) of pure *rac*-**79**. Anal. calc. for $C_{30}H_{26}Cl_2S_2SiZr$: C, 56.22; H, 4.09. Found: C, 56.10; H, 4.17. 1H NMR (CD_2Cl_2): δ 7.54-7.60 (m, 4H, 2,2',6,6'-H in Ph), 7.49 (s, 2H, 5,5'-H in cyclopentathienyl), 7.35-7.42 (m, 4H, 3,3',5,5'-H in cyclopentathienyl), 7.25-7.33 (m, 2H, 4,4'-H in cyclopentathienyl), 6.86 (s, 2H, 3,3'-H in cyclopentathienyl), 2.32 (s, 6H, 2,2'-Me in cyclopentathienyl), 1.09 (s, 6H, SiMe₂). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 144.7, 133.7, 136.2, 135.7, 130.8, 130.4, 129.4, 128.5, 121.4, 120.4, 72.4, 20.7, 0.7.

Complex *rac*-80. To a solution of 1.14 g (1.96 mmol) of **68** in 200 ml of ether, 2.45 ml of 1.6 M MeLi (3.92 mmol) in ether was added at room temperature. This mixture was stirred for 24 h and cooled to -80°C, and then 0.74 g (1.96 mmol) of $ZrCl_4(THF)_2$ was added. The resulting mixture was stirred for 24 h at room temperature and then evaporated to dryness. To the residue, 150 ml of toluene were added. This mixture was additionally stirred for 10 h at 70°C and then filtered through glass frit (G4). The precipitate was additionally washed with 3 x 30 ml of hot toluene. The combined filtrate was evaporated to dryness. The residue was recrystallized from dichloromethane. Yield 0.59 g (41%) of pure *rac*-**80**. Anal. calc. for $C_{38}H_{30}Cl_2S_2SiZr$: C, 61.59; H, 4.08. Found: C, 61.69; H, 4.18. 1H NMR (CD_2Cl_2): δ 8.06 (m, 2H, 2,2'-, 4,4'-, 5,5'-, or 8,8'-H in naphthyl), 7.87 (m, 2H, 2,2'-, 4,4'-, 5,5'-, or 8,8'-H in naphthyl), 7.83 (m, 2H, 2,2'-, 4,4'-, 5,5'-, or 8,8'-H in naphthyl), 7.72 (m, 2H, 2,2'-, 4,4'-, 5,5'-, or 8,8'-H in naphthyl), 7.53 (s, 2H, 3,3'-H in cyclopentathienyl), 7.48 (m, 2H, 3,3'-H in naphthyl), 7.46 (m, 2H, 6,6'- or 7,7'-H in naphthyl), 7.41 (m, 2H, 7,7'- or 6,6'-H in naphthyl), 6.58 (s, 2H, 3,3'-H in cyclopentathienyl), 2.34 (s, 6H, 2,2'-Me in cyclopentathienyl), 1.14 (s, 6H, SiMe₂). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 147.5, 140.4, 137.6, 135.6, 134.2, 133.9, 133.7, 133.1, 130.1, 129.8, 128.9, 127.7, 127.4, 127.2, 127.0, 120.6, 76.4, 20.8, 0.7.

Complex *rac*-81. To a solution of 5.93 g (10.0 mmol) of **69** in 180 ml of ether, 8.10 ml 2.5 M (20.3 mmol) of *n*BuLi in hexanes was added dropwise over 15 min at 0°C. This mixture was stirred for 12 h at room temperature and then cooled to -78°C. Next, 3.77 g (10.0 mmol) of $ZrCl_4(THF)_2$ was added. The resulting mixture was slowly (ca. 1.5 h) warmed to ambient temperature with vigorous stirring and then stirred for 10 h. The organic solvents were distilled off under reduced pressure, and 200 ml of toluene was added.

This mixture was stirred for 1 h at 80°C and then filtered through glass frit (G4) at this temperature. The filtrate was evaporated to ca. 50 ml. The orange crystals precipitated at -30°C were collected, washed with 2 x 5 ml of cold toluene and 3 x 30 ml of hexanes, and dried in vacuum. This procedure gave 1.80 g (24%) of pure *rac*-**81**. Anal. calc. for C₃₈H₄₂Cl₂S₂SiZr: C, 60.60; H, 5.62. Found: C, 60.86; H, 5.75. ¹H NMR (CD₂Cl₂): δ 7.37-7.61 (m, 10H, 5,5'-H of cyclopentathienyl and 2,2',3,3',5,5',6,6'-H of C₆H₄), 6.85 (s, 2H, 3,3'-H of cyclopentathienyl), 2.31 (s, 6H, 2,2'-Me of cyclopentathienyl), 1.29 (s, 18H, ^tBu), 1.09 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 138.3, 138.1, 137.6, 135.6, 133.3, 130.1, 128.1, 127.4, 121.5, 120.6, 72.5, 36.1, 32.6, 20.7, 0.7.

Complexes *rac*- and *meso*-82. To a solution of 8.39 g (16.9 mmol) of **55** in 150 ml of THF, 13.5 ml of 2.5 M (33.8 mmol) ⁿBuLi in hexanes was added at -80°C. This mixture was slowly (ca. 1 h) warmed to room temperature and stirred for 2 h. The solution of Li salt was cooled to -80°C, and 8.16 g (33.8 mmol) of Et₃SnCl was added. The resulting mixture was stirred and slowly (ca. 1 h) warmed to room temperature and then additionally stirred for 3 h. The organic solvents were distilled off under reduced pressure, and 100 ml of toluene was added. Next, the toluene solution was evaporated under reduced pressure to eliminate THF traces. One more portion of toluene (100 ml) was added to the residue. The resulting mixture was filtered through Celite 503. To the filtrate 3.93 g (16.9 mmol) ZrCl₄ was added. The resulting mixture was stirred for 10 h at room temperature and then for 30 h at reflux. This hot mixture was filtered through glass frit (G4). The precipitate was washed with 4 x 100 ml of hot toluene. Crystals precipitated at -30°C from the combined filtrate were collected, washed with 3 x 30 ml of toluene and 3 x 20 ml of hexanes, and dried in vacuum. Yield 4.19 g (38%) of pure *rac*-**82**. Anal. calc. for C₃₆H₃₄Cl₂SiZr: C, 65.83; H, 5.22. Found: C, 65.75; H, 5.11. The mother solution was evaporated to dryness. Fractional crystallization of the residue from toluene-dichloromethane gave 1.65 g (15%) of pure *meso*-**82**. Found: C, 65.69; H, 5.06. *rac*-**82**. ¹H NMR (CD₂Cl₂): δ 7.64 (dt, J= 8.7 Hz, J= 0.9 Hz, 2H, 7,7'-H in indenyl), 7.45 (br.m, 2H, 6,6'-H in C₆H₄), 7.17-7.25 (m, 6H, 3,3',4,4',5,5'-H in C₆H₄), 7.16 (dd, J= 6.9 Hz, J= 0.7 Hz, 5,5'-H in indenyl), 7.05 (dd, J= 8.7 Hz, J= 6.9 Hz, 2H, 6,6'-H in indenyl), 6.44 (br.s, 2H, 3,3'-H in indenyl), 2.21 (s, 6H, 2,2'-Me in indenyl), 2.04 (br.s, 6H, 2,2'-Me in C₆H₄), 1.30 (s, 6H, SiMe₂). *meso*-**82**.

^1H NMR (CD_2Cl_2): δ 7.70 (dt, $J = 8.7$ Hz, $J = 0.9$ Hz, 2H, 7,7'-H in indenyl), 7.48 (br.m, 2H, 6,6'-H in C_6H_4), 7.18-7.25 (m, 6H, 3,3',4,4',5,5'-H in C_6H_4), 6.99 (dd, $J = 6.9$ Hz, $J = 0.7$ Hz, 5,5'-H in indenyl), 6.87 (dd, $J = 8.7$ Hz, $J = 6.9$ Hz, 2H, 6,6'-H in indenyl), 6.33 (br.s, 2H, 3,3'-H in indenyl), 2.37 (s, 6H, 2,2'-Me in indenyl), 1.99 (br.s, 6H, 2,2'-Me in C_6H_4), 1.46 (s, 3H, SiMeMe'), 1.22 (s, 3H, SiMeMe').

Complexes *rac*-83. To a solution of 11.3 g (21.4 mmol) of **56** in 200 ml of toluene, 18.2 ml of 2.5 M (45.6 mmol) $n\text{BuLi}$ in hexanes was added at -30°C . Next, the reaction mixture was warmed to room temperature and additionally stirred for 2 h. The resulting mixture was cooled to -30°C , and 12.5 g (51.79 mmol) of Et_3SnCl was added. The solution was stirred for 24 h at room temperature and then filtered through Celite 503. Hexanes were distilled off from the filtrate under reduced pressure. The resulting mixture was cooled to -30°C , and 5.00 g (21.5 mmol) of ZrCl_4 was added. The mixture was stirred for 24 h at ambient temperature and for 4 h at 100°C , cooled to ambient temperature, and then filtered through glass frit (G4). The precipitate was additionally washed with 2 x 50 ml of toluene. The combined filtrate was evaporated to ca. 200 ml. Crystals precipitated at -30°C were collected. The filtrate was evaporated to dryness. To the residue, 200 ml of hexanes were added. The resulting mixture was filtered through glass frit (G4). The precipitate was additionally washed with 3 x 100 ml of hot hexanes and dried in vacuum. Yield 6.85 g (46%) of orange powder of *rac*-**83** including ca. 8% of the respective *meso*-isomer. Anal. calc. for $\text{C}_{36}\text{H}_{34}\text{Cl}_2\text{O}_2\text{SiZr}$: C, 62.77; H, 4.97. Found: C, 62.69; H, 5.12. ^1H NMR (CD_2Cl_2): δ 7.63 (dt, $J = 8.7$ Hz, $J = 0.9$ Hz, 2H, 7,7'-H in indenyl), 7.45 (dd, $J = 7.4$ Hz, $J = 1.8$ Hz, 2H, 3,3'-H in C_6H_4), 7.31 (ddd, $J = 8.3$ Hz, $J = 7.4$ Hz, $J = 1.8$ Hz, 2H, 3,3'-H in C_6H_4), 7.27 (dd, $J = 6.9$ Hz, $J = 0.8$ Hz, 2H, 5,5'-H in indenyl), 7.03 (dd, $J = 8.7$ Hz, $J = 6.9$ Hz, 2H, 6,6'-H in indenyl), 6.97 (dt, $J = 8.3$ Hz, $J = 7.4$ Hz, 2H, 5,5'-H in C_6H_4), 6.95 (m, 2H, 6,6'-H in C_6H_4), 6.53 (m, 2H, 3,3'-H in indenyl), 3.67 (s, 6H, 2-OMe in C_6H_4), 2.19 (s, 2-Me in indenyl), 1.30 (s, 6H, SiMe₂).

Complexes *rac*- and *meso*-84. To a solution of 4.97 g (10 mmol) of **63** in a mixture of 24 ml of toluene and 4 ml of ether, 8.4 ml of 2.5 M (21 mmol) of $n\text{BuLi}$ in hexanes was added with vigorous stirring. This mixture was stirred overnight at room temperature, and then 5.31 g (3.69 ml, 22 mmol) of Et_3SnCl was added. The resulting mixture was stirred overnight and then filtered through Celite 503. The Celite layer

was additionally washed with small amount of toluene. The solution was evaporated to ca. 70 ml, and 2.33 g (10 mmol) of ZrCl_4 was added. This mixture was stirred for 24 h at reflux and then filtered through glass frit (G4). The filtrate was evaporated to ca. 40 ml. Crystals precipitated from this solution at -30°C were separated, washed with 100 ml of cold hexanes and 50 ml of dichloromethane, and dried in vacuum. This procedure gave 0.85 g (13%) of analytically pure *meso*-**84**. Anal. calc. for $\text{C}_{36}\text{H}_{34}\text{Cl}_2\text{SiZr}$: C, 65.83; H, 5.22. Found: C, 65.85; H, 5.14. The dichloromethane solution was evaporated to dryness to give 1.10 g (17%) of a ca. 3:1 mixture of *rac*- and *meso*-**84**. Found: C, 66.03; H, 5.34. *rac*-**84**. ^1H NMR (CD_2Cl_2): δ 7.51 (d, $J = 8.9$ Hz, 2H, 7,7'-H in indenyl), 7.40 (m, 4H, 2,2',6,6'-H in Ph), 7.35 (m, 4H, 3,3',5,5'-H in Ph), 7.20 (m, 2H, 4,4'-H in Ph), 6.95 (d, $J = 8.9$ Hz, 2H, 6,6'-H in indenyl), 6.35 (m, 2H, 3,3'-H in indenyl), 2.23 (s, 6H, 5,5'-Me), 2.14 (s, 6H, 2,2'-Me), 1.26 (s, 6H, SiMe_2). *meso*-**84**. ^1H NMR (CD_2Cl_2): δ 7.55 (d, $J = 8.9$ Hz, 2H, 7,7'-H in indenyl), 7.39 (br.s, 6H, 2,2',3,3',5,5'-H in Ph), 7.31 (m, 2H, 4,4'-H in Ph), 7.12 (br.s, 2H, 6,6'-H in Ph), 6.76 (d, $J = 8.9$ Hz, 2H, 6,6'-H in indenyl), 6.23 (m, 2H, 3,3'-H in indenyl), 2.29 (s, 6H, 5,5'-Me), 2.13 (s, 6H, 2,2'-Me), 1.40 (s, 3H, SiMeMe'), 1.17 (s, 3H, SiMeMe'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 139.3, 137.8, 137.2, 134.9, 134.1, 131.8, 129.8, 128.7, 128.5 (br), 127.5, 125.6, 120.3, 85.0, 20.0, 19.0, 2.8, 2.6.