A Suzuki Coupling Based Route to 2,2'-Bis(2-indenyl)biphenyl Derivatives

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Because of the promising performance in olefin polymerization of 2,2'-bis(2-indenylyl)biphenyl zirconium dichloride, we developed a new and broadly applicable route to 2,2'-bis(2-indenyl)biphenyl derivatives. Reaction of the known 2,2'-diiodobiphenyl (26) with the new 2-indenyl boronic acid (23) did not result in the desired 2,2'-bis(2-indenyl)biphenyl (10); instead an isomer thereof, (spiro-1,1-(2,2'-biphenyl)-2-(2-indenyl)indane) (27), was obtained. It was found that compound 10 could be made via a palladium-catalyzed reaction of 2,2-biphenyl diboronic acid (31) with 2-bromoindene (21) under standard Suzuki reaction conditions. However, the yield of this reaction was low at low palladium catalyst loadings, due to a competitive hydrolysis reaction of 2,2-biphenyl diboronic acid (31). HTE techniques were used to find an economically viable protocol. Thus, use of the commercially available 1.0 molar solution of (n-Bu)4NOH in methanol with cosolvent toluene led to precipitation of the pure product in a fast and clean reaction, using only 0.7 mol % (0.35 mol % per C-C) of the expensive palladium catalyst.

Introduction

For the isotactic polymerization of propylene, an isospecific catalyst is required. Many examples have been reported in the literature, e.g., the ansa bis(1-indenyl)-dimethylsilane (1) derivatives of Hoechst and BASF 1 and the ansa bis-cyclopentadienyl compounds of Chisso.2 The main disadvantage of most of these systems is that two isomers (rac (2) and meso (3)) are formed in the synthesis of these organometallic complexes, often in a ratio of near 1:1 depending on the solvent used in the synthesis (eq 1).

Only the rac-isomer (2) is isospecific and catalyzes formation of isotactic polypropylene. The meso-isomer (3) is nonspecific and produces atactic polypropylene (a-PP). To avoid the presence of undesired, sticky a-PP, a separation of the rac/meso mixture is often necessary. These separations are usually not straightforward and often rely on difficult crystallizations to obtain pure rac-isomer. The unwanted meso-isomer is often discarded at the end of a long route.

The synthesis of an isospecific metallocene is more efficient if the rac/meso separation can be avoided by smart design of the ligand-system. An example is the family of ansa-fluorenly-cyclopentadienyl complexes described by Ewen et al. 3 Another example is the use of biaryl bridged ligands and/or complexes (Figure 1). The spatial arrangement of the biaryl-bridge prohibits formation of the meso-form.

To avoid the introduction of additional isomers, the Cp or indenyl moiety needs to have C2v symmetry. This C2v

Figure 1. Published examples of biaryl-bridged metalloccenes: 4-7,8 (R = H, tert-Bu).8


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symmetry is present in the 2-indenyl moieties that were developed by us,\(^9\) and later by Waymouth,\(^10\) Halterman,\(^11\) and Montell,\(^12\) as ligands for homogeneous Ziegler–Natta (Z–N) polymerization. To the best of our knowledge, biaryl-bridged 2-indenyl-based compounds were reported in only one publication by Bosnich et al. (7 and 8).\(^7\) However, the application of these biaryl-bridged 2-indenyl catalysts in olefin polymerization has not been described. Bosnich et al. studied these complexes as catalysts for enantioselective Diels–Alder reactions.

**Results and Discussion**

The synthesis of 2,2’-bis(2-indenyl)biaryl (10) according to Bosnich et al. was repeated by us (Scheme 1).

**Scheme 1. Synthesis of 2,2’-Bis(2-indenyl)-biaryl According to Bosnich et al.**

Conversion of 10 into the zirconium dichloride complex 7 proceeded in 95% yield.

Initial results in olefin polymerization using zirconium complex 7 were very promising.\(^9\) Therefore, we decided to further develop this type of catalyst system. Unfortunately, the route by Bosnich et al. was not amenable to scale-up, as the yield of bis-Grignard 11 is only high at low concentration (max 0.075 M).\(^13\) We also found that increase of the scale to 0.60 mol (8 L) gave a significant lower yield (10%) at this concentration of bis-Grignard 11, although we could reach similar yields of diol 12 at small scale (37 mmol). It thus became necessary to develop a new route to 10.

**Route Exploration.** Logical disconnections (Figure 2) can be made in the bipyridyl–indenyl bond (disconnection A) or between the two phenyl rings of the bipyridyl moiety (disconnection B). Since bipyridyl is an attractively cheap starting material and 2-indene derivatives are easily accessible, we chose disconnection A.

**Synthesis of 10 Using Noncatalyzed Reactions.** Reaction of 2,2’-dilithiobiphenyl bis TMEDA adduct\(^16\) (16) or its corresponding bis-Grignard 11, obtained via transmetalation of 16 with magnesium bromide, with 2-indanone 18 in diethyl ether did not result in formation of diol 12. Instead, the condensation product of 2-indanone, 1-(2'-indanyliden)-2-indanone (19) (eq 2) was isolated after workup in 46% yield (see Supporting Information). This compound has also been reported by Treibs et al.\(^15\)

**Synthesis of 10 Using Metal-Catalyzed Cross-Coupling Reactions.** Cross-coupling reactions are effective methods to prepare biaryls.\(^16\) However, the double Kumada coupling of 2-(bromomagnesio)indene (20) (prepared by reaction of 2-bromindene (21)\(^17\) with magnesium in THF) with 2,2’-bistrifluoromethylsulfonyl)indenyl-biphenyl (22)\(^18\) was unsuccessful with various catalysts\(^19\)

![Figure 2. Two of the possible disconnections.](image)


\(^{19}\) (a) We tested Ni(acac)\(_2\) with 3 equiv of LiBr (to prevent decomposition of the catalyst), NiCl\(_2\)(dppp), and [Pd(PPh\(_3\))\(_4\)] with and without 3 equiv of LiBr in THF.
All starting materials were still present in the reaction mixture, according to the GC-MS spectra.

To explore the use of a Suzuki approach, 2-indenyl boronic acid (23) was prepared. This was done by the reaction of 20 with an excess (5 equiv) of triisopropoxyborane (at −30 °C) or trimethoxyborane (at −100 °C) and subsequent warming to room temperature, followed by acidic hydrolysis (eq 4).

The yields of the 2-indenyl boronic acid 23 obtained via this reaction varied between 50 and 60%. Higher reaction temperatures (−30 °C) can be applied when triisopropoxyborane is used instead of the more common trimethoxyborane (−100 °C) to reach comparable yields.21

Attempted Suzuki couplings of boronic acid 23 with bistriflate 22 or the bismesylate of 2,2′-biphenol (24) in refluxing toluene, however, did not give the desired product under catalysis of [Pd(PPh3)4] with K2CO3 and LiBr. As indicated by GC-MS, the monosubstituted product (25) was formed when 22 was used in 1,4-dioxane with K3PO4 (eq 5).

Reaction of 2,2′-diiodobiphenyl14 (26) with 2 equiv of boronic acid 23 and K2CO3 in DME/water gave a mixture of 4 products (eq 6) as indicated by GC-MS analysis.

**Scheme 2. Proposed Mechanism (strongly simplified) for the Formation of 27**
The major product was isolated and characterized as spiro-1,1-(2,2′-biphenyl)-2-(2-indenyl)indane (27) by 1H, 13C, 1H-1H COSY, and 13C-1H correlation NMR spectroscopy (see Supporting Information).

For the mechanism for the formation of 27, we propose a cascade as depicted in Scheme 2. Identical Disconnection, Reversed Approach. Since the approach above suffered from the occurrence of an intramolecular Heck-type insertion (26b to 26c), the opposite approach was performed. This translates to a Suzuki-coupling of 2 equiv of 21 with 2,2′-biphenyl diboronic acid (31). Diboronic acid 31 was prepared by the reaction of 16 with trimethoxyborane in diethyl ether at -30 °C (eq 7).

Yields dropped significantly if the temperature exceeded -20 °C. The use of triisopropoxyborane instead of trimethoxyborane in diethyl ether gave only low yields (~10%). These lower yields may be explained by the formation of the monoboronic acid (32) and side products, similar to those in the formation of the described binaphthyldiboronic acid.22

Reaction of 31 with 2 equiv of 21 in DME/water with K2CO3 as base under catalysis of 7 mol % [Pd(PPh3)4] indeed resulted in the formation of 10 (equation 7), which was isolated after crystallization from ethanol-acetone in 79% yield. We wanted to reduce the amount of [Pd(PPh3)4] significantly, since this catalyst is expensive. However, reduction of the Pd-catalyst concentration to 3 mol % resulted in significant lower yields (50% of the desired product). Mono-substituted product 28 was formed as the single side product.

HTE Approach in the Optimization of the Suzuki Coupling. Many aspects, such as base, solvent, cosolvent, and catalyst, may have an influence on this standard Suzuki reaction. For this reason, a HTE approach was used for the optimization of the amount of the catalyst. In the first experiment an array of six solvents and eight bases was explored in a custom build 96-well heating block located on the bed of a TECAN Genesis 150 automated pipetting robot. The results are depicted in Figure 3.

It is clear that for most bases, toluene is the best solvent. Additionally, use of K2CO3 as base has hot spots in DME and dioxane. Remarkably, common Lewis bases for Suzuki reactions, such as CsF and Bu4NF,16a gave low yields, even in toluene.

Base, solvent, and catalyst were varied in the second generation 4 by 3 by 4 array: four bases (K2CO3, LiOH.H2O, KOAc, and Ba(OH)2.H2O all as aqueous solutions), three solvents (DMF, DME, and toluene), four catalysts ([Pd(PPh3)4], Pd(OAc)2, [PdCl2(dppe)], and 5% Pd/C. [Pd(PPh3)4] appeared to be the best catalyst, toluene the best solvent, and LiOH.H2O and Ba(OH)2.H2O the best bases. Furthermore, an inert atmosphere (nitrogen) appeared to be very important to avoid degradation.

An important observation made during a control experiment (no catalyst present) was that 31 decomposed to the mono-boronic acid (32) under the reaction conditions, presumably due to hydrolysis (proto-deboronation). Usually, boronic acids are stable toward hydrolysis,
although some boronic acids are reported to hydrolyze under Suzuki reaction conditions. We believe that the decomposition of 31 (and reported compounds in refs 20–24) is related to the high acidity of the boronic acid groups: (i) the protons of the OH groups of diboronic acid 31 have a very low-field chemical shift at 9.15 ppm in DMSO-d$_6$, indicating exceptionally high acidity; (ii) the pK$_a$ was determined by base titration and appeared to be 5.4 (in comparison: the pK$_a$ of phenylboronic acid is 8.8). Diboronic acid 31 and the reported boronic acids in refs 20–24 have in common that they have a neighboring acceptor atom, which can induce hydrogen bond formation that causes increased acidity. Modeling studies of diboronic acid 31 (and the boronic acids from refs 20–24) with Spartan Pro both semiempirical (PM3) and DFT (pBP/DN**+) showed qualitatively significant intramolecular hydrogen bond formation with the neighboring acceptor atom.

Apparently, reduction of the catalyst amount leads to a slow Suzuki reaction. Consequently, the decomposition of 31 becomes more important, resulting in decreasing yields of the desired product. Obviously, to obtain high yields of 10 at low catalyst loadings, the side reaction (presumably proto-deboronation) that leads to the decomposition of 31 has to be prevented by using anhydrous conditions. Remarkably, anhydrous conditions, like DMF/Et$_3$N, also led to decomposition of 31 to 32. As another option to prevent proto-deboronation, diboronic acid 31 was esterified with 2 equiv of pinacol to give 33, in analogy to the method of Gronowitz et al. (eq 8).

Remarkably, we found that pinacol ester 33 was hydrolyzed very rapidly to 31 in DME/water with K$_2$CO$_3$, in contrast to what was observed by Gronowitz.

A much better solution found in the screening was in situ esterification of 31 to 34 in methanol (Scheme 3). This is in contrast to the method described by Suzuki et al., where the boronic esters are prepared in an extra reaction step.

Use of the commercially available 1.0 molar solution of (n-Bu)$_4$NOH in methanol (Scheme 3) yielded 10 in high purity after washing the precipitate with toluene and methanol. Also, the reaction appeared to be very fast, being finished after approximately 10–15 min. On the basis of these observations, even lower Pd-concentrations might be possible.

Scope of the Method. To vary the indenyl moiety of the ligand, the 2-bromindene derivatives 35, 36, and 37 were prepared via the route as depicted in Scheme 4. Bromoindenes 35, 36, and 37 were successfully converted to the corresponding biphenyl-bridged bisindenenes 46, 47, and 48, using the new Suzuki conditions (Figure 4).

Conclusions

A new route to 10 has been developed, which is broadly applicable and economically feasible. This route involves a Suzuki coupling of 2 equiv of 2-bromindene (21) with 2,2′-biphenyl diboronic acid (31) with [Pd(PPh$_3$)$_4$]. Standard Suzuki reaction conditions (in DME/water with K$_2$CO$_3$ as base) proved unsatisfactory for our needs due to a competitive proto-deboronation of the 2,2′-biphenyl diboronic acid (31), necessitating the use of high loadings of the expensive palladium catalyst.

HTE techniques proved a very useful tool to rapidly optimize the scale-up of this Suzuki reaction. By use of the commercially available 1.0 molar solution of (n-Bu)$_4$NOH in methanol optionally with cosolvent toluene, pure product could be easily obtained in a fast and clean reaction, using only 0.7 mol % (0.35 mol % per C–C) of the expensive palladium catalyst.

Experimental Section

Experiments were performed under a dry and oxygen-free nitrogen atmosphere using Schlenk-line techniques. $^1$H NMR (200, 300 or 400 MHz) and $^{13}$C NMR spectra (50, 75 or 100 MHz) were measured on a Bruker AC200, Bruker Avance 300, Varian Unity 300 or Bruker DPX 400. GC-MS spectra were measured on a Fisons MD-800 GC-MS equipped with a CPSil8 low bleed column (dimensions: 30 m × 0.25 mm, film thickness: 1.0 μm) or on a HP5890–HP5971-MS equipped with a CPSil8 low bleed column (dimensions: 25 m × 0.25 mm; film thickness: 0.4 μm). Diethyl ether and ligroin were distilled from sodium/potassium alloy; THF and toluene from potassium and sodium, respectively, all having benzophenone as indica-

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**Figure 4.** Suzuki coupling products of the substituted 2-bromoindenes (isolated yields between parentheses).

2-Indenyl Boronic Acid (23). Magnesium turnings (9.72 g, 0.40 mol) covered with dry THF (50 mL) were activated with 10 drops of 1,2-dibromoethane. A solution of 2-bromoindene (39.01 g, 0.20 mol) in dry THF (200 mL) was added slowly during 45 min under cooling with an ice-bath to maintain the temperature below 20 °C. The mixture was stirred at room temperature for 2 h after complete addition. Via a syringe, the Grignard solution was decanted from the excess magnesium turnings and added slowly to a solution of triisopropoxyborane (92 mL, 0.40 mol) in dry THF (250 mL) keeping the temperature between 0 to 50 °C. After addition, the temperature was allowed to rise to room temperature, and stirring was continued overnight. The mixture was quenched with water (100 mL), and then dilute hydrochloric acid (25 mL, 37 weight % in 250 mL water) was added. The mixture was stirred for 30 min and then transferred into a separatory funnel. The organic phase was separated, and the aqueous phase extracted with ether (3 × 100 mL). The combined organic phases were extracted 3× with 50 mL of saturated brine. The organic phase was dried over sodium sulfate, filtered, and evaporated to dryness. The residue was dissolved in boiling ether (200 mL), and then hexanes were added (400 mL). Quick filtration of the hazy solution through paper gave a clear filtrate. The clear filtrate was evaporated slowly and partly on the rotary evaporator to afford a white powder. After filtration, washing, and drying, 23 was obtained as a white powder (18.54 g, 58%), mp 222 °C (dec). 1H NMR (CDCl3): ã 8.0–7.6 (3 peaks, ratio and exact shift concentration dependent; sum 1H), 7.45 (m, 2H), 7.20 (m, 2H), 3.7–3.5 (multiple peaks, ratio and exact shift concentration dependent; sum 2H) ppm. 13C NMR (CDCl3): ã 148.5, 147.8, 147.5, 146.8, 146.0, 145.1, 144.9, 126.5 (m), 124.2, 124.1, 122.5, 122.2, 42.1, 41.5, 41.0 ppm. Anal. Calcd for C27H21B3O3·2H2O: C, 70.20; H, 5.46. Found: C, 69.99; H, 5.39.

**Spiro-1,1-(2,2′-Biphenyl)-2-(2-indenyli)indane (27).** To a solution of 2-indenyl boronic acid (1.72 g, 10.73 mmol) and 2,2′-diiodobiphenyl (1.98 g, 4.88 mmol) in dimethoxyethane (10 mL), a solution of K2CO3 (1.54 g; 11.1 mmol) in degassed water was added. Then, [Pd(PPh3)4] (0.11 g, 0.1 mmol, 2.0 mol %) was added, and the yellow mixture was heated to reflux. During this process, the color quickly changed (within one minute) to cognac brown. Reflux was continued for a period of 16 h. After cooling, the mixture was poured into 5% aqueous HCl (50 mL). The mixture was extracted with ether (3 × 50 mL). The combined organic phases were subsequently extracted with an aqueous solution of HCl (5 wt %, 3 × 25 mL), saturated sodium bicarbonate, and saturated brine. The organic phase was dried over sodium sulfate, filtered, and evaporated to dryness. The residue was dissolved in warm
ethanol/water 9:1 v/v, and treated with active carbon. Cooling followed by slow partial evaporation gave a yellow-brown solid powder (1.08 g; 58%). An analytical pure sample was obtained by crystallization from acetone/ethanol 1:1 v/v by slow evaporation in air, mp 158–159 °C.1H NMR (CDCl3): δ 7.7 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 6.8–7.5 (m, 13H), 6.47 (s, 1H), 5.03 (s, 1H), 3.72 (d, J = 16 Hz, 2H), 2.0 (s, 6H), 1.35 (d, J = 16 Hz, 6H), 0.7 (s, 3H).13C NMR (CDCl3): δ 150.0, 148.8, 147.0, 140.5, 144.2, 143.0, 142.5, 140.1, 139.6, 129.5, 128.4, 127.1, 126.7, 126.0, 125.6, 124.9, 124.5, 124.1, 123.6, 122.9, 122.1, 121.0, 119.5, 63.2, 57.3, 143.8, 40.7 ppm. Anal. Calcd for C39H38B2O4: C, 70.98; H, 4.25; B, 6.18%. Found: C, 71.0; H, 4.25; B, 6.29%. 

To a solution of 41 (6.50 g; 24.9 mmol) in THF (65 mL) and methanol (35 mL) was added sodium borohydride (1.03 g; 27.1 mmol) at 0 °C. A gas evolved, and the yellow color disappeared during this event. The ice bath was removed and stirred for 1 h at room temperature. A solution of hydrochloric acid in water (5%, 100 mL) was added to the reaction mixture. The reaction mixture was extracted with dichloromethane (2 × 150 mL). The combined organic phases were dried over sodium sulfate and filtered. The organic solvents were removed under reduced pressure to give 6.54 g (100%) of white powder of 44.1H NMR (CDCl3): δ 8.14 (d, J = 8.1 Hz, 1H), 7.76 (m, 2H), 7.43 (m, 2H), 7.26 (d, J = 8.3 Hz, 1H), 5.38 (d, J = 4.9 Hz, 1H), 4.77 (m, 1H), 3.43 (d, J = 6.4 Hz, 2H) ppm. The crude indanol (44) was dissolved in toluene (150 mL), and p-toluenesulfonic acid (0.82 g; 4.3 mmol) was added. The mixture was heated to reflux for 2 h, and a Dean–Stark trap was dried over the evolved water. After stirring and extraction with chloroform (50 mL), the solvents were removed under reduced pressure. Filtration of the residue over silica (eluent: ligroin) gave 35 as a light yellow solid (3.23 g, 53%), mp 92.0–93.8 °C.1H NMR (CDCl3): δ 8.07–7.1 (m, 4H), 7.45–7.39 (m, 3H), 7.39–7.31 (m, 3H), 7.27–7.20 (m, 2H), 7.10–7.03 (m, 2H), 3.82 (m, 2H), 3.76 (s, 3H), 3.67 (m, 2H) ppm. Anal. Calcd for C25H32B2O4: C, 70.98; H, 4.25; B, 6.18%. Found: C, 71.2; H, 4.37; B, 6.35%. 

Bis-2-(indenyl)biphenyl Derivatives

2,2'-Bis(2-indenyl)biphenyl (10) via the Standard Suzuki Procedure. To a solution of 21 (15.60 g; 80.0 mmol) in degassed DME (800 mL) were added 31 (9.40 g; 38.8 mmol), [Pd(PPh3)4] (3.23 g; 2.80 mmol), and a degassed solution of K2CO3 (16.72 g; 121 mmol) in water (400 mL). After stirring at room temperature, the reaction mixture was poured in a solution of hydrochloric acid in water (5%, 250 mL). The organic phase was dried over sodium sulfate and filtered. The solvents were removed under reduced pressure. Crystallization of the residue from ethanol gave analytically pure 10 (11.6 g, 79%), mp 210–212 °C (lit. 211–213 °C).7

First Generation Array HTE Run for the Synthesis of 10. The 48 reaction vessels were charged with 2-bromoindene (50 mg; 0.256 mmol), 2,2'-biphenyl diboronic acid (31 mg; 0.128 mmol), and [Pd(PPh3)4] (3.0 mg; 2.60 μmol). To each vessel was added the desired solvent (1 mL). Then, all bases were added to the mixtures at 10 °C. The 48 reaction vessels were charged with 2-Bromobenz(5,6)indene (36). 2-Bromobenz(4,5)indanone (42) was prepared in the same way as 41 from 39 with the difference that the reaction mixture was extracted with dichloromethane instead of diethyl ether. The solvents were removed under reduced pressure, and the crude mixture of the bromoindanone syntheses (9.78 g) was treated as described in the synthesis for 42. The trituration solvents were divided in 6.54 g, pure bromoindanone 45 was obtained (3.41 g, 36%).1H NMR (CDCl3): δ 7.75 (m, 3H), 7.61 (s, 1H), 7.30 (m, 2H), 5.05 (d, J = 9.5 and 4.4 Hz, 1H), 4.91 (m, 1H), 3.48 (bs, 2H), 2.50 (d, 10.0 Hz) ppm. After dehydrogenation and crystallization from ligroin, pure 36 (decomposes slowly at room temperature) was obtained (1.72 g, 55%).1H NMR (CDCl3): δ 7.73 (m, 3H), 7.60 (s, 1H), 7.37 (m, 2H), 6.96 (bs, 1H), 3.67 (tr, J = 1.4 Hz, 2H) ppm.13C NMR (CDCl3): δ 142.6, 140.2, 131.3, 132.8, 131.6, 131.7, 129.7, 129.6, 128.6, 125.6, 125.1, 121.7, 117.9, 117.5, 117.2 ppm.

2,2'-Bis(2-indenyl)biphenyl (10) via the Standard Suzuki Procedure. To a solution of 21 (15.60 g; 80.0 mmol) in degassed DME (800 mL) were added 31 (9.40 g; 38.8 mmol), [Pd(PPh3)4] (3.23 g; 2.80 mmol), and a degassed solution of K2CO3 (16.72 g; 121 mmol) in water (400 mL). After stirring at room temperature, the reaction mixture was poured in a solution of hydrochloric acid in water (5%, 250 mL). The organic phase was dried over sodium sulfate and filtered. The solvents were removed under reduced pressure. Crystallization of the residue from ethanol gave analytically pure 10 (11.6 g, 79%), mp 210–212 °C (lit. 211–213 °C).7

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Second Generation Array HTE Run for the Synthesis of 10. The 48 reaction vessels were charged with 2-bromoindene (50 mg; 0.256 mmol) and 2,2'-biphenyl diboronic acid (31 mg; 0.128 mmol). Then, the 48 mini reactors were divided in blocks of 12 vessels, and those were charged with catalyst [Pd(PPh3)4] (8.9 mg; 77.1 μmol); [PdCl2(dppf)] (5.6 mg; 77.1 μmol); Pd(OAc)2 (1.7 mg; 7.71 μmol) and PdCl2 (5%, 10 mg). These 4 blocks of 12 mini reactors each were divided in blocks of 4 mini reactors and each block of 4 reactors was charged with the...
solvent (1 mL; toluene; DMF and DME). Then, each reactor was charged with an aqueous solution of the base (1.5 M; K$_2$CO$_3$, LiOH, KOAc or Ba(OH)$_2$). The reactor block was heated to 70 °C for 6 h. After being cooled to room temperature, the reaction mixtures were filtered, and the residues were extracted with acetone. Combined filtrate and acetone extract were analyzed by LC-MS.

Bisindenyl Compound 10 via the Optimized Suzuki Procedure (0.70 mol % [Pd(PPh$_3$)$_4$]). To a solution of tetra(n-butyl)ammonium hydroxide (25.0 mL; 1.0 M; 25 mol) in methanol (used as obtained from Aldrich) were added toluene (30 mL), 2-bromoindene (3.20 g, 16.5 mmol), 2,2′-biphenyl diboronic acid (31) (2.00 g, 8.30 mmol), and [Pd(PPh$_3$)$_4$] (44 mg, 30 µmol, 0.7 mol %). The mixture was heated to reflux. At the boiling point, the color changed from yellow to cognac brown, and the product immediately started to precipitate. After stirring overnight at reflux, the reaction mixture was cooled to room temperature. Diluted hydrochloric acid (5%, 75 mL) was added, and the precipitate was filtered off. The residue was subsequently washed with water, ligroin, and ethanol and dried, resulting in pure 10 (2.49 g, 79%).

Bis(2-benz(4,5)indenyl)biphenyl (46) via the Optimized Suzuki Procedure. The same procedure as described for 10, using 31 (1.18 g; 15.7 mmol), 35 (2.39 g; 9.76 mmol), tetra(n-butyl)ammonium hydroxide (14.0 mL; 1.0 M in MeOH; 14.0 mmol). Yield: 4.0 g (66%), mp 229–230 °C. $^1$H NMR (CDCl$_3$): $\delta$ 7.97–7.1 (m, 12H), 6.28 and 6.25 (2 s, sum: 2H), 3.6–3.0 (m, sum: 4H) ppm, remark: mixture of double bond isomers. $^{13}$C NMR (CDCl$_3$): 146.9, 141.3, 141.0, 140.8, 139.8, 136.3, 132.5, 131.4, 131.0, 128.8, 128.3, 128.0, 127.8, 127.6, 127.4, 127.0, 126.0, 125.4, 124.9, 124.6, 124.4, 123.6, 123.4, 122.1, 120.4, 42.0, 42.0 ppm, remark: mixture of double bond isomers. HRMS calcd for C$_{38}$H$_{26}$: 582.20345. Found: 582.20486.

Bis(2-benz(5,6)indenyl)biphenyl (47) via the Optimized Suzuki Procedure. The same procedure as described for 10, using 31 (0.86 g; 3.55 mmol), 36 (1.76 g; 7.19 mmol), and tetra(n-butyl)ammonium hydroxide (11.0 mL; 1.0 M in MeOH; 11.0 mmol). Yield: 1.13 g (66%), mp. 229–230 °C (dec). $^1$H NMR (CDCl$_3$): $\delta$ 7.69 (dd, 4H), 7.55 (s, 2H), 7.43–7.29 (m, 14H), 6.24 (s, 2H), 3.39 (d, $J$ = 22.5 Hz, 2H), 3.09 (d, $J$ = 22.5 Hz, 2H) ppm. $^{13}$C NMR (CDCl$_3$): 146.8, 144.9, 142.0, 141.5, 136.7, 133.7, 132.5, 131.7, 131.2, 129.4, 128.3 (three peaks), 125.7, 125.3, 122.3, 119.1, 40.6 ppm. HRMS calcd for C$_{38}$H$_{26}$: 482.20345. Found: 482.20486.

Bis(4,7-dimethyl-2-indenyl)biphenyl (48) via the Optimized Suzuki Procedure. The same procedure as described for 10, using 31 (3.80 g; 15.7 mmol), 37 (6.20 g; 27.8 mmol), and tetra(n-butyl)ammonium hydroxide (50.0 mL; 1.0 M in MeOH; 50.0 mmol). Yield: 4.0 g (66%), mp 229–230 °C. $^1$H NMR (CDCl$_3$): $\delta$ 7.97–7.1 (m, 12H), 6.28 and 6.25 (2 s, sum: 2H), 3.6–3.0 (m, sum: 4H) ppm, remark: mixture of double bond isomers. $^{13}$C NMR (CDCl$_3$): 146.9, 141.3, 141.0, 140.8, 139.8, 136.3, 132.5, 131.4, 131.0, 128.8, 128.3, 128.0, 127.8, 127.6, 127.4, 127.0, 126.0, 125.4, 124.9, 124.6, 124.4, 123.6, 123.4, 122.1, 120.4, 42.0, 42.0 ppm, remark: mixture of double bond isomers. HRMS calcd for C$_{34}$H$_{26}$: 482.20345. Found: 482.20486.

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Supporting Information Available: An experimental procedure for 19 and spectral data for 27, 41, 44, 35, 46, 36, 47, and 48 are available free of charge via the Internet at http://pubs.acs.org.