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A New Family of Biisoquinoline Chelates

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Four 8,8′-diaryl-substituted 3,3′-biisoquinoline ligands have been synthesized and characterized. The key feature of this new family of chelates is their endotopic but sterically non-hindering nature. All four ligands were made from a common 8-bromoisoquinolin-3-ol precursor; between three and twelve synthetic steps were necessary to obtain the products. The reported synthetic procedures allow for gram-scale production of these biisoquinolines.

Introduction

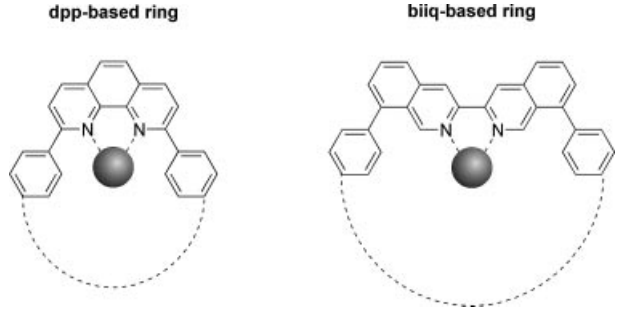
Bidentate chelates of the aromatic polyimine family are among the most universally used ligands in coordination chemistry, the two archetypical structures being 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen).[1] These two ligands have also played a central role, and continue to do so, in the field of coordination photochemistry[2] since the observation that $[Ru(bipy)_3]^{2+}$ solutions are luminescent at room temperature.[3] In particular, this complex and its derivatives, as well as many related second- and third-row transition-metal complexes displaying the d^6 electronic configuration, have been investigated extensively in relation to light-induced electron and energy transfer processes as well as light energy storage.[4]

In this report, we would like to describe the efficient synthesis of a novel series of compounds that display two apparently contradictory structural features: i) Their coordination site is not or is only very slightly hindered by organic substituents borne by the ligand since the ligands have no chemical groups α to the nitrogen atoms and ii) nevertheless, the binding site is oriented towards the *endo* part of the crescent-shaped ligand. In other words, if the chelate is later on included in a ring, the coordination site will unambiguously be endocyclic.

A brief description of the geometrical principles that govern the present family of compounds, namely 8,8′-diaryl-3,3′-biisoquinoline chelates, has been given in a recently published communication.[5]

Note that, very generally speaking, the endotopic and endocyclic nature of the bidentate chelates prepared until now relies on the presence of substituents located α to the nitrogen atoms and thus implies steric hindrance around the coordination site.

Several examples of 2,2′-bipy- and phen-incorporating macrocycles[6] have been reported previously. Many of them share the key structural feature of being substituted at the two positions α to the nitrogen atoms. This (and only this) substitution pattern ensures an endocyclic coordination mode. Substitution at other positions is significantly more likely to yield exocyclic coordination modes as illustrated in Scheme 1.



Scheme 1. Illustration of 2,9-diphenyl-1,10-phenanthroline (dpp) and 8,8′-diaryl-3,3′-biisoquinoline based macrocycles.

Our group has made a large number of catenanes and rotaxanes that include the 2,9-diphenyl-1,10-phenanthroline (dpp) motif because of its highly suitable geometry.[7] The synthesis of these mechanically interlocked molecules is based on a copper(I) template-assisted method. Thereby, the dpp motif plays a key role: It ligates to copper(I) in an endocyclic fashion yielding very stable $[Cu(dpp)_2]^+$ precatenate complexes.

The biisoquinoline-containing ligands described in this paper are such that endocyclic coordination will be certain. In addition, as shown in Scheme 1, the complexed metal center will be remote from any organic group of the organic backbone.

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Results and Discussion

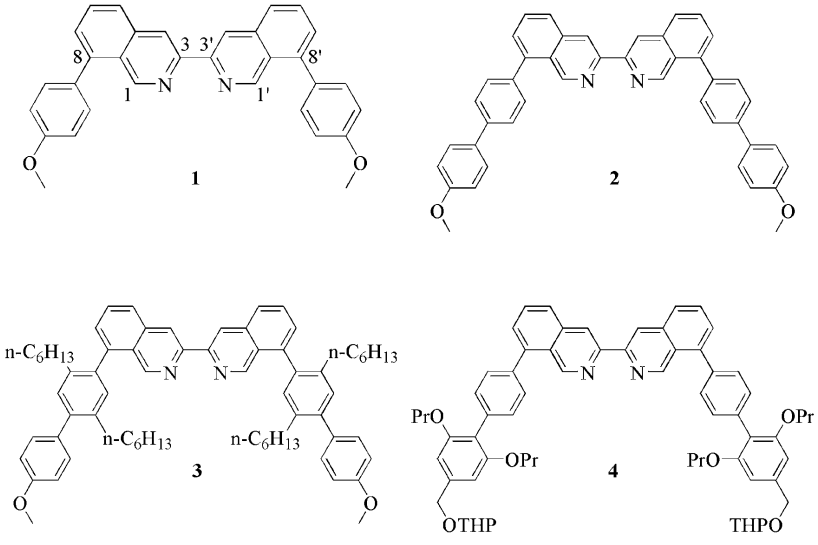
The four ligands shown in Scheme 2 were all made from one common precursor, 8-bromoisoquinolin-3-ol (**8**). This molecule is made in two steps from commercially available starting materials, as illustrated in Scheme 3. The key step is the intramolecular cyclization reaction of *N*-(2-bromobenzyl)-2,2-diethoxyacetamide (**7**) in concentrated sulfuric acid, a so-called Pomeranz–Fritsch reaction. In our hands this reaction led to considerably lower yields (50%) than those reported in a previously published protocol,[8] mainly because the product turned out to be contaminated with an unidentified white side-product from which it had to be purified by recrystallization from methanol. The subsequent reaction steps, described in more detail below and in the Exp. Sect., were developed as part of our research. Hereafter we give an account of the syntheses of the four ligands depicted in Scheme 2 starting with chelate **1**.

8-Bromoisoquinolin-3-ol (**8**) was converted into the triflate **9** with triflic anhydride in dry pyridine in 95% yield following a procedure similar to the one reported by Långström and co-workers.[9] The triflate was treated with 1 equiv. of commercially available 4-methoxyphenylboronic acid (**10**) in a palladium-catalyzed Suzuki coupling reaction. The key was to use the $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone)/P′Bu_3 catalyst system which allows highly selective and efficient C–C coupling at the isoquinoline 8-bromo position,[10] whereas with other catalysts, for example, Pd(triphenylphosphane)$_4$, competitive reactions at both the bromo and triflate functions were observed. Coupling product **11** was treated in a palladium-catalyzed homocoupling reaction with elemental zinc as an electron source to give **1** in 70% average yield (Scheme 3).[11] The use of high triflate concentrations (>1 mM) was of pivotal importance for bimolecular homocoupling to be favored over undesired triflate/hydrogen exchange. Furthermore, the use of dry *N*,*N*-dimethylformamide was imperative.

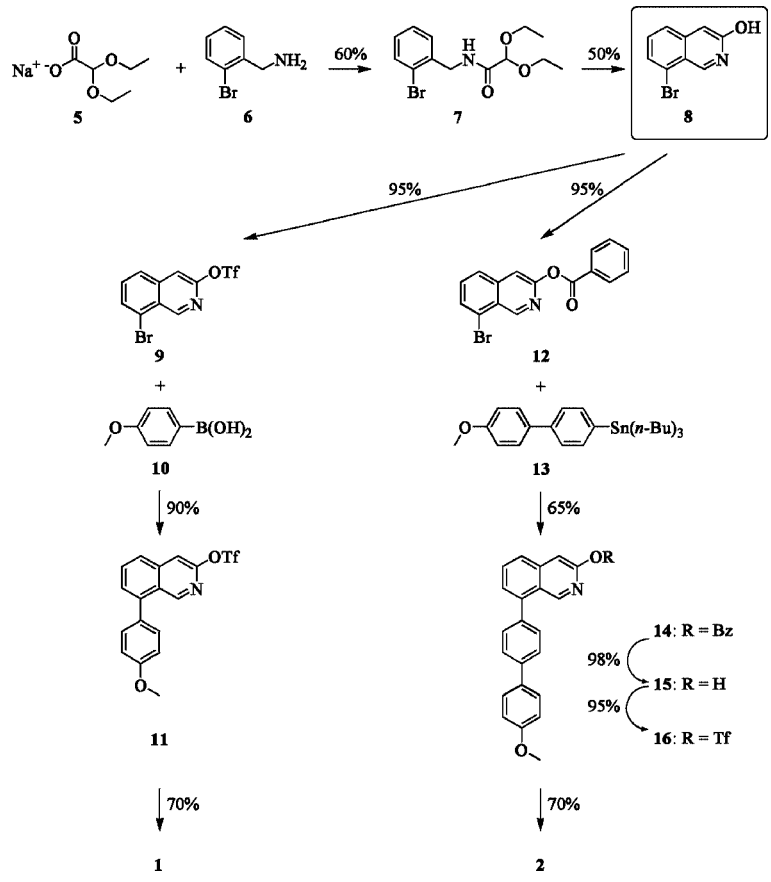
The "longer-legged" equivalent of ligand **1**, chelate **2**, was obtained using a different strategy (Scheme 3, right) in which the phenolic function of **8** was first treated with benzoyl chloride to give the ester 8-bromoisoquinolin-3-yl benzoate (**12**) in very high yields (95%). Attempts to use benzyl ether protecting groups gave unsatisfactory results due to competitive alkylation at both the nitrogen and oxygen heteroatoms of **8**. Since the ester protecting group was incompatible with alkaline Suzuki coupling methodologies, we turned our attention to Stille couplings that can be performed under pH-neutral conditions.[12] 4-Tributylstannylbiphenyl **13** was made in two steps from commercially available 4-bromo-4′-hydroxy-1,1′-biphenyl (>85% overall yield) and coupled to **12** (65% yield). This Stille coupling required significantly more drastic reaction conditions (5 d at reflux in a toluene/tetrahydrofuran mixture) than the Suzuki coupling reaction used to obtain the shorter-legged analogue **11** (2 h at room temperature). The Stille coupling product **14** was subsequently deprotected in tetrahydrofuran/aqueous potassium hydroxide, whereby essentially quantitative conversion of the benzoyl group to the hydroxy function was observed. Reaction of triflic anhydride with **15** gave triflate **16** in excellent yield. The final step in the synthesis of **2** was the same homocoupling reaction as used for **1**; analogous reaction conditions were applied to obtain chelate **2** and yields of the order of 70% were obtained.

Whereas the 8,8′-substituents of biisoquinolines **1** and **2** were readily accessible (**10** is commercially available, **13** is made in two steps), more serious synthetic effort was required to obtain the biphenyl substituents of ligands **3** and **4**. The multistep syntheses of these substituents are illustrated in Scheme 4 and are described in the following two paragraphs.

1,4-Dichlorobenzene (**17**) was coupled to organomagnesium compound **18** using a nickel catalyst following a previously published synthetic protocol.[13] 1,4-Di-*n*-hexylben-



Scheme 2. The four new biisoquinoline chelates that were synthesized in this work.

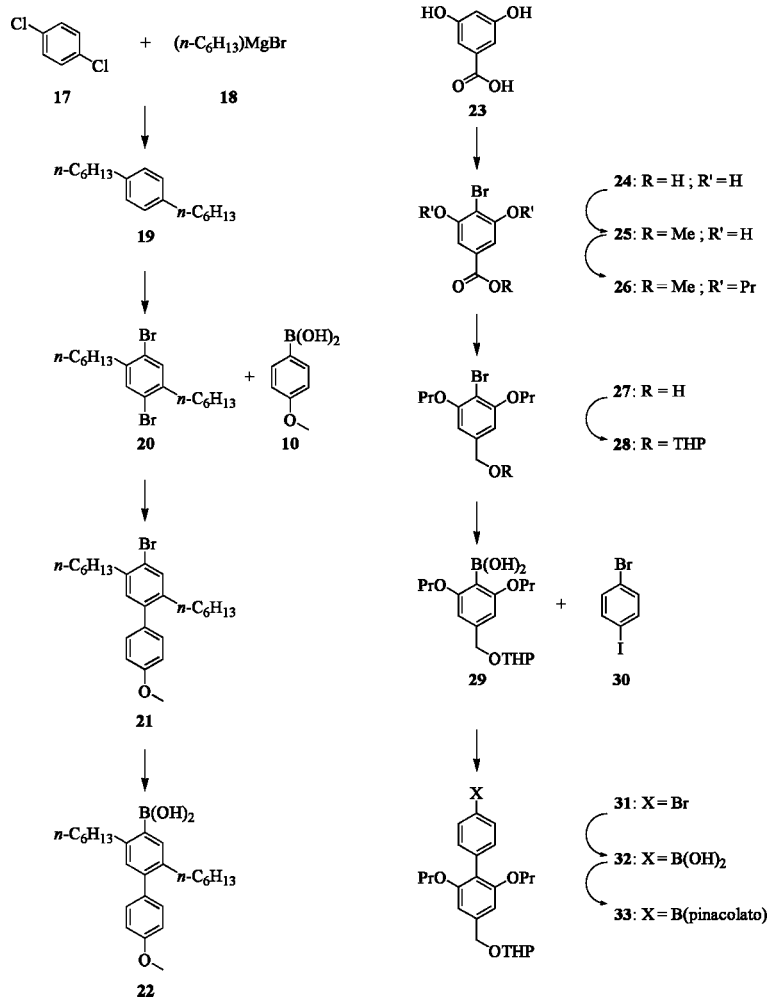


Scheme 3. Synthesis of the chelates **1** and **2**.

zene (**19**) was obtained in excellent yield (90%) and brominated in an electrophilic aromatic substitution reaction with bromine. This reaction, when performed in the dark and when using iodine as a reaction initiator and catalyst, gave 1,4-dibromo-2,5-di-*n*-hexylbenzene (**20**) in high yield (90%) as previously reported by Rehan et al.[13] This molecule was coupled to 4-methoxyphenylboronic acid (**10**) using a palladium(0) catalyst. When using a threefold excess of **20**, Suzuki coupling product **21** was obtained in 65% yield and only very small amounts (<5%) of the undesired double-Suzuki-coupled 4,4′′-dimethoxyterphenyl were obtained. Excess dibromodihexylbenzene **20** was subsequently recovered by column chromatography. The desired coupling product **21** was converted from the bromide to the boronic acid **22** using *n*-butyllithium and trimethyl borate in a yield of about 70%. Before describing the subsequent steps of the synthesis of ligand **3**, we first turn our attention to the synthesis of biphenyl fragment **33** (Scheme 4, right) which was made for the synthesis of ligand **4**.

3,5-Dihydroxybenzoic acid (**23**) was converted quantitatively to 4-bromo-3,5-dihydroxybenzoic acid (**24**) following a literature procedure.[14] The acid was transformed quantitatively into the methyl ester **25** using thionyl chloride in methanol following another previously published protocol.[15] A paper by Lüning et al. served as a valuable basis for the three subsequent reactions steps, namely hydroxyalkylation to **26** with 1-bromopropane, ester reduction to the benzyl alcohol with lithium aluminium hydride to give **27**, and benzyl alcohol protection with 3,4-dihydro-2*H*-pyran to yield **28**.[16] Each of these three reaction steps is essentially quantitative; tedious work up or chromatographic separation was unnecessary. Thus it is possible to generate large quantities (50 g) of **28** with relative ease. Boronic acid **29** was obtained in the same manner as **22**: Treatment with *n*-butyllithium followed by trimethyl borate addition. Compound **29** was treated with one equivalent of commercially available 1-bromo-4-iodobenzene (**30**) under standard Suzuki coupling conditions to afford biphenyl **31** in 90% yield. The bromide was converted into the boronic acid **32** using the *n*-butyllithium/trimethyl borate route from above (yield: 90%). The characterization of this product by both NMR and mass spectrometry turned out to be problematic, presumably as a result of trimer and dimer formation. For this reason we decided to convert the boronic acid **32** into its pinacol ester **33**. The desired product was obtained in quantitative yield by using toluene solvent and a Dean–Stark trap.

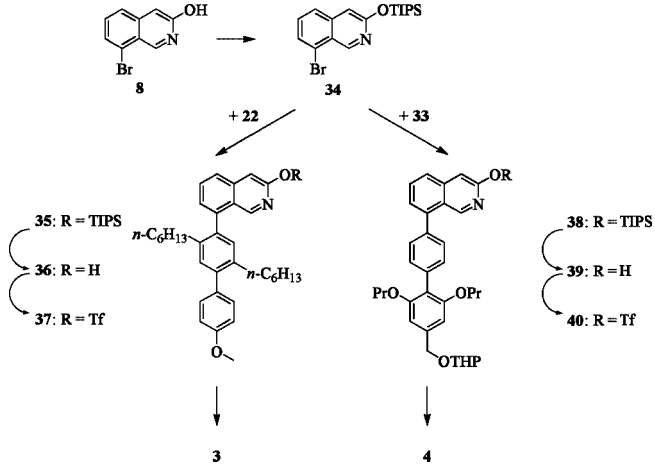
The two biphenylylboronic acids **22** and **32** were then coupled to triisopropylsilyl-protected isoquinoline **34**, see Scheme 5. Isoquinoline **34** was obtained in nearly quantitative yield from 8-bromoisoquinolin-3-ol (**8**) in *N*,*N*-dimethylformamide and triisopropylsilyl chloride (TIPSCl).[17] In contrast to the benzoyl protecting group **12**, the TIPS group is compatible with alkaline Suzuki coupling conditions.



Scheme 4. Synthesis of the 8,8′-subsitutents of chelates **3** and **4**.

Thus **34** was treated with the biphenylylboronic acids **22** and **32** as well as pinacol ester **33** in the presence of a palladium(0) catalyst to give isoquinolines **35** and **38** with yields in the order of 60%. We observed no difference in reactivity between boronic acid **32** and pinacol ester **33**. The silyl ether protecting group was cleaved using tetrabutylammonium fluoride with yields of around 75–80%, that is, TIPS deprotection to give **36** and **39** occurs less efficiently than benzoyl deprotection to **15**. This is in line with previous observations.[18] The phenols **36** and **39** were then converted into the triflates **37** and **40** using trifluoromethanesulfonic anhydride. The respective yields were 95 and 50%. Subsequent homocoupling of the triflates in a palladium-catalyzed reaction using zinc powder as an electron source gave ligands **3** (70% yield) and **4** (15% yield).

Our initial plan was to synthesize only ligands **1** and **2** but the latter turned out to be insoluble in a large variety of solvents including *N*,*N*-dimethylformamide. Therefore we initiated the syntheses of biisoquinolines **3** and **4** which bear solubilizing *n*-hexyl and *n*-propyloxy groups on their 8,8′-biphenyl substituents. This renders these chelates highly soluble in solvents such as dichloromethane, tetrahydrofuran, or ethanol, but this comes at the price of a significantly greater synthetic effort. This is illustrated in Figure 1 which shows the number of synthetic steps required to obtain ligands **1**–**4** from their common precursor, 8-bromoisoquinolin-3-ol (**8**). Chelate **1** is readily available from precursor **8** in three steps in 60% overall yield while



Scheme 5. Synthesis of the chelates **3** and **4**.

ligand **2** requires five steps and has an overall yield of 39%. The 8,8′-biphenyl substituents of ligands **3** and **4** (Scheme 4) are both made in roughly 60% overall yield; they are coupled equally well to the isoquinoline moiety.

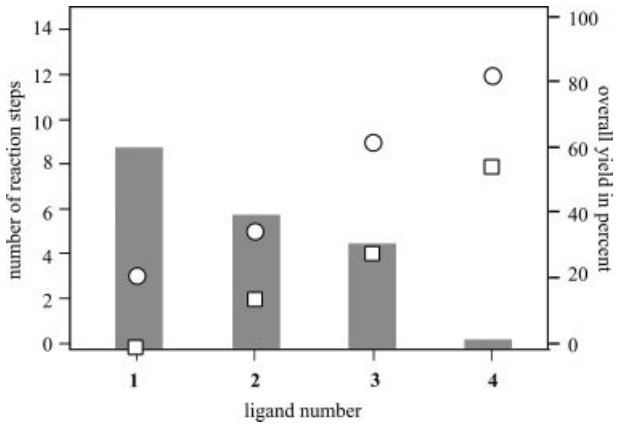


Figure 1. (○) The number of reaction steps required to synthesize the four biisoquinolines in Scheme 2 from their common precursor 8-bromoisoquinolin-3-ol (**8**) (Scheme 3). (□) The number of reaction steps needed to synthesize the 8,8′-aryl substituents. The grey bars represent the overall yields obtained for the syntheses of ligands **1**–**4** from precursor **8**.

Important efficiency differences in the syntheses of ligands **3** and **4** were observed in the last two steps, namely the conversion of the hydroxy function into the triflate (**37** and **40**) and the subsequent homocoupling reactions. For chelate **3**, these two reactions give yields comparable to those observed for ligands **1** and **2**, that is, a conversion of the hydroxy group to the triflate that is very nearly quantitative and a homocoupling yield of about 70%. By contrast, for ligand **4** the triflate yield is about 50% and the homocoupling yield 15%. An important chemical difference between ligand **4** and chelates **1**, **2**, and **3** is of course the presence of a tetrahydropyran (THP)-protected benzyl alcohol in **4**; ligands **1**–**3** contain methyl-protected phenols. The methoxy groups are known to be chemically more robust than OTHP groups and thus it seems plausible that the lower yields of the last two steps in the synthesis of ligand **4** are due to THP deprotection and subsequent undesired side-reactions.

However, despite the relatively large number of steps required to make these four 8,8′-diaryl-substituted 3,3′-biisoquinolines, it is possible to produce gram quantities of each of the four ligands in Scheme 2 with relative ease.

Addition of ligand **1** to a solution of iron(II) tetrafluoroborate at room temperature led to the rapid formation of the red $[Fe(\mathbf{1})_3]^{2+}$ complex **41** in nearly quantitative yield. An X-ray crystal structure of this complex is shown in Figure 2. The FeN_6 first coordination sphere is very nearly octahedral: Fe–N distances in the 1.958–1.972 Å range were determined and all N–Fe–N angles are between 86 and 94°. This strongly supports our hypothesis that this family of ligands coordinates transition-metal ions in an endotopic but sterically nonhindering fashion.

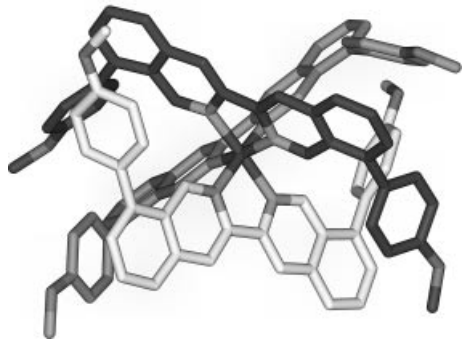


Figure 2. Crystallographic structure of the $[Fe(\mathbf{1})_3]^{2+}$ cation **41**.

Conclusions

In summary we have developed efficient multistep syntheses of four endotopic biisoquinoline ligands. These chelates are ideally suited for macrocycle formation around transition-metal ions and are thus valuable new building blocks for topological chemistry. In contrast to the vast majority of previously reported endotopic α-diimine ligands, the 8,8′-diaryl-3,3′-biisoquinolines are sterically nonhindering, as confirmed by the crystal structure analysis of an homoleptic tris(biisoquinoline)iron(II) complex. This is expected to pave the way to the synthesis of molecules with highly unusual topologies.

Experimental Section

The following chemicals were obtained commercially and used without further purification: Ammonium chloride (Aldrich), barium hydroxide octahydrate (Aldrich), 1,3-bis(triphenylphosphanyl)-propanenickel(II) chloride (Strem), benzoyl chloride (Aldrich), 1,1′-bis(diphenylphosphanyl)ferrocenedichloropalladium(II) (Aldrich), bromine (Aldrich), 2-bromobenzylamine (Alfa Aesar), 1-bromohexane (Aldrich), 4-bromo-4′-hydroxy-1,1′-biphenyl (Aldrich), 1-bromo-4-iodobenzene (Acros), 1-bromopropane (Aldrich), *n*-butyllithium in hexanes (1.6 M solution) (Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Aldrich), 1,4-dichlorobenzene (Alfa Aesar), dichlorobis(triphenylphosphane)palladium(II) (Aldrich), 3,4-dihydro-2*H*-pyran (Aldrich), 3,5-dihydroxybenzoic acid (Acros), 1,2-dimethoxyethane (Aldrich), ethyl diethoxyacetate (Aldrich), imidazole (Acros), iron(II) tetrafluoroborate hexahydrate (Aldrich), lithium aluminium hydride (Aldrich), lithium chloride (Merck), magnesium as ribbons (Riedel-de Haën), 4-methoxyphenylboronic acid (Aldrich), potassium carbonate (Prolabo), potassium hydroxide (Riedel-de Haën), potassium iodide (Prolabo), tetrabutylammonium chloride hydrate (Acros), tetrabutylammonium fluoride trihydrate (Acros), tetrabutylammonium iodide (Aldrich), tetrakis(triphenylphosphane)palladium(0) (Aldrich), thionyl chloride (Prolabo), tri-*tert*-butylphosphonium tetrafluoroborate (Strem), tri-*n*-butyltin chloride (Aldrich), triethylamine (Riedel-de Haën), trifluoromethanesulfonic anhydride (Alfa Aesar) triisopropylsilyl chloride (Acros), trimethyl borate (Aldrich), tris(dibenzylideneacetone)dipalladium(0) (Strem), pinacol (Aldrich), potassium fluoride (Aldrich), potassium iodide (Prolabo), sulfuric acid (Riedel-de Haën), *p*-toluenesulfonic acid monohydrate (Aldrich), zinc powder (Fluka).

Dry solvents were obtained with suitable desiccants. Diethyl ether and tetrahydrofuran were distilled from sodium, triethylamine and

pyridine from potassium hydroxide. *N*,*N*-Dimethylformamide was distilled from anhydrous aluminium oxide.

All silica column chromatography was performed using Merck silica gel 60 (0.063–0.200 mm). Fluka aluminium oxide 17994 was used in alumina columns and for filtrations.

^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE 300 [300 MHz (^{1}H); 75 MHz (^{13}C)] spectrometer using deuteriated solvent as the lock. The spectra were collected at 25 °C and the chemical shifts were referenced to residual solvent protons as internal standards. ^{1}H: $CDCl_3$ 7.27 ppm, CD_2Cl_2 5.32 ppm, [D_6]acetone, 2.05 ppm, [D_6]DMSO 2.50 ppm; ^{13}C: CD_3Cl 77 ppm, CD_2Cl_2 53.7 ppm, [D_6]acetone 30.6 ppm.[19] Mass spectra were obtained with a VG ZAB-HF spectrometer (FAB) and a VG-BIOQ triple quadrupole in positive or negative mode (ES-MS).

Single-crystal X-ray diffraction experiments were carried out with a Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The SHELX-97[20] program was used for structure solution and refinement.

***N*-(2-Bromobenzyl)-2,2-diethoxyacetamide (7):** Sodium diethoxyacetate (22.95 g, 135 mmol) was dissolved in dry diethyl ether (110 mL) and to this mixture was added thionyl chloride (10.0 mL, 16.2 g, 136 mmol) with stirring for 10 min at 10 °C. The reaction mixture was refluxed for 30 min and then cooled. A solution of 2-bromobenzylamine (25 g, 13.4 mmol) in dry toluene (70 mL) and freshly distilled pyridine (41 mL) was added to this reaction mixture through a cannula with vigorous stirring. The resulting mixture was refluxed for 30 min and then cooled to room temperature. Then the mixture was poured into ice–water (ca. 200 mL) and extracted with toluene (3 × 100 mL). The organic extracts were combined and washed with a solution of hydrochloric acid (2%, 100 mL) and water. The organic solvents were evaporated and the residue purified by chromatography [silica; pentane/ethyl acetate 9:1 (v/v)]. Thereby pure **7** was obtained as a yellow oil (23.6 g, 60%). ^{1}H NMR ($CDCl_3$): δ = 7.34 (m, 2 H), 7.23 (m, 2 H), 7.04 (br. s, 1 H), 4.82 (s, 1 H), 4.55 (d, 2 H, J = 6.2 Hz), 3.63 (m, 4 H), 1.23 (t, 6 H, J = 7.1 Hz) ppm.

8-Bromoisoquinolin-3-ol (8): *N*-(2-Bromobenzyl)-2,2-diethoxyacetamide (**7**) (23.6 g, 74.6 mmol) was added carefully to concentrated sulfuric acid (120 mL) with stirring under ice cooling. The reaction mixture was stirred at room temperature for 16 h, poured into ice–water, and filtered. The filtrate was slowly neutralized with 33% aqueous ammonium hydroxide and the resulting precipitate was filtered, dried, and then recrystallized from methanol to give 10.7 g (47.8 mmol, 64%) of pure **8** as yellow needles. ^{1}H NMR (CD_2Cl_2): δ = 9.13 (s, 1 H, 1-H), 7.66 (d, J = 8.7 Hz, 1 H, 7-H), 7.60 (d, J = 7.2 Hz, 1 H, 5-H), 7.42 (dd, J = 8.7, 7.2 Hz, 1 H, 6-H), 7.03 (s, 1 H, 4-H) ppm. ES-MS: calcd. for $C_9H_6BrNO + H^+$ 223.9711; found 223.9694. C_9H_6BrNO: C 48.25, H 2.70, N 6.25; found C 47.99, H 3.06, N 6.46.

8-Bromoisoquinolin-3-yl Trifluoromethanesulfonate (9): A solution of 8-bromoisoquinolin-3-ol (4.0 g, 17.9 mmol) in dry pyridine (125 mL) was cooled to 0 °C and carefully treated with trifluoromethanesulfonic anhydride (4.0 mL, 6.8 g, 23 mmol). The mixture was warmed to room temperature and stirred overnight. Then the solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel using pentane/diethyl ether (1:4) as eluent to afford pure **9** as colorless crystals (6.06 g, 95%). ^{1}H NMR (CD_2Cl_2): δ = 9.43 (s, 1 H, 1-H), 7.95 (d, J = 7.5 Hz, 1 H), 7.91 (d, J = 7.9 Hz, 1 H), 7.65 (dd, J = 7.9, 7.5 Hz, 1 H, 7-H), 7.60 (s, 1 H, 4-H) ppm. ES-MS: calcd. for $C_{10}H_5BrF_3NO_3S + Li^+$ 361.9280; found 361.9404.

8-(*p*-Anisyl)isoquinolin-3-yl Trifluoromethanesulfonate (11): Because of the very air-sensitive phosphane, the subsequently described manipulations must be carried out under argon. 4-Methoxyphenylboronic acid (**10**) (3.01 g, 19.8 mmol), potassium fluoride (3.45 g, 59.4 mmol), and tris(dibenzylideneacetone)dipalladium(0) (825 mg, 0.9 mmol) were added to a dry two-necked flask equipped with a stirring bar. A solution of 8-bromoisoquinolin-3-yl trifluoromethanesulfonate (**9**) (6.41 g, 18 mmol) in dry and degassed tetrahydrofuran (20 mL) was first added through a cannula. A mixture of tri-*tert*-butylphosphonium tetrafluoroborate (627 mg, 2.16 mmol) and DBU (about 0.35 mL, 2.3 mmol) in dry and degassed tetrahydrofuran (20 mL) was then added through a cannula. The reaction mixture was stirred at room temperature (25 °C) for 2 h and subjected to thin-layer chromatography [silica; dichloromethane/pentane 3:2 (v/v)]. In case the reaction had not finished, it was then stirred for two more hours at room temperature. Finally, the reaction mixture was diluted with diethyl ether and filtered through a pad of silica gel with copious washings. The solvent was evaporated and the residue purified by chromatography on silica gel using dichloromethane/pentane (3:7, 4:6, and 5:5) as the eluent to give pure **11** as colorless crystals (6.18 g, 90%). ^{1}H NMR (CD_2Cl_2): δ = 9.12 (s, 1 H, 1-H), 7.90 (d, J = 8.2 Hz, 1 H), 7.82 (dd, J = 7.1, 8.2 Hz, 1 H, 7-H), 7.63 (s, 1 H, 4-H), 7.59 (d, J = 7.1 Hz, 1 H), 7.44 (d, J = 8.8 Hz, 2 H), 7.06 (d, J = 8.8 Hz, 2 H), 3.89 (s, 3 H, OCH_3) ppm. ES-MS: calcd. for $C_{17}H_{12}F_3NO_4S + Li^+$ 390.0594; found 390.0575.

8,8-Di-*p*-anisyl-3,3′-biisoquinoline (1): Zinc powder (20 g) was activated in acetic acid (100 mL) for 1 h. After filtration, the powder was washed three times with distilled water and dried under vacuum for 6 h at 120 °C. Dichloro[1,1′-bis(diphenylphosphanyl)ferrocene]palladium(II) dichloromethane adduct (800 mg, 1.09 mmol), zinc powder (10.2 g, 156 mmol), potassium iodide (10.3 g, 62 mmol), and 8-(*p*-anisyl)isoquinolin-3-yl trifluoromethanesulfonate (**11**) (6.02 g, 15.7 mmol) were stirred in the smallest possible volume of dry and degassed *N*,*N*-dimethylformamide (about 10 mL) for 2 h at 90 °C. Then the solvent was evaporated and the residue dissolved in dichloromethane (100 mL), distilled water (100 mL), and a 32% ammonium hydroxide solution (10 mL). The organic phase was separated and the aqueous phase extracted twice with dichloromethane. The combined organic phases were washed once with distilled water and then evaporated. Dichloromethane (20 mL) was added to the crude product and the mixture was filtered through a glass frit with porosity 4. The solid was washed with acetone and diethyl ether to give pure **1** as a white powder (2.47 g, 67%). ^{1}H NMR ($CDCl_3$): δ = 9.48 (s, 2 H, 1-H), 8.92 (s, 2 H, 4-H), 7.94 (d, J = 8.2 Hz, 2 H), 7.72 (dd, J = 7.1, 8.2 Hz, 2 H), 7.52 (d, J = 8.8 Hz, 4 H), 7.51 (d, J = 7.1 Hz, 2 H), 7.08 (d, J = 8.8 Hz, 4 H), 3.93 (s, 6 H, OCH_3) ppm. ES-MS: calcd. for $C_{32}H_{24}N_2O_2 + H^+$ 469.1911; found 469.1907.

8-Bromoisoquinolin-3-yl Benzoate (12): Benzoyl chloride (0.62 mL, 5.36 mmol) was added dropwise to a solution of 8-bromoisoquinolin-3-ol (1.0 g, 4.47 mmol) in freshly distilled pyridine (15 mL) at 0 °C under argon. The resulting mixture was stirred for 2 h at room temperature. After evaporation of the pyridine solvent, the crude product was dissolved in dichloromethane and filtered through alumina to yield 1.42 g (4.36 mmol; 97%) of pure compound **12**. ^{1}H NMR (CD_2Cl_2): δ = 9.47 (s, 1 H, 1-H), 8.27 (d, J = 7.7 Hz, 2 H, H^a), 7.85 (d, J = 7.7 Hz, 2 H, H^b), 7.70 (ddd, J = 7.4, 7.4 Hz, 1 H, 6-H), 7.59–7.54 (m, 4 H) ppm. ES-MS: calcd. for $C_{16}H_{10}BrNO_2$ 329.995; found 329.999. $C_{16}H_{10}BrNO_2$: C 58.56, H 3.07, N 4.27; found C 58.81, H 3.41, N 4.02.

4-Methoxy-4′-tri-*n*-butylstannyl-1,1′-biphenyl (13): This compound was obtained in two steps: commercially available 4-bromo-4′-hy-

droxy-1,1′-biphenyl (10.0 g, 40.14 mmol) was treated with methyl iodide (17.1 g, 120.42 mmol) and tetrabutylammonium iodide (0.74 g, 2.00 mmol) in a biphasic system consisting of 1 M aqueous potassium carbonate (50 mL) and acetonitrile (100 mL). After refluxing for 16 h the reaction mixture was evaporated to dryness and the solids were taken up in water (100 mL) and dichloromethane (300 mL). Filtration of the organic phase through silica gel and solvent evaporation yielded 9.38 g (35.65 mmol; 89%) of pure 4-bromo-4′-methoxy-1,1′-biphenyl as a white powder. The latter was dissolved in freshly distilled tetrahydrofuran (125 mL) and dry toluene (125 mL) and cooled to –78 °C. After dropwise addition of 1.6 M *n*-butyllithium (24.5 mL) in hexanes solution, the reaction mixture was stirred for 2 h at –78 °C under argon before tri-*n*-butyltin chloride (10.7 mL, 39.45 mmol) was slowly added. The solution was subsequently warmed to room temperature and stirred for another 4 h. The solvents were evaporated and the remaining oil was dissolved in pentane and filtered through neutral alumina. Pentane evaporation yielded 16.2 g (34.23 mmol; 96%) of pure compound **13** as a colorless oil. ^{1}H NMR (CD_2Cl_2): δ = 7.56 [d, J = 8.8 Hz, 2 H, -C_6(-*m*)H_2(*o*-)H_2OCH_3], 7.53 (s, 2 H, -SnC_6H_4–), 6.99 [d, J = 8.8 Hz, 2 H, -C_6(-*m*)H_2(*o*-)H_2OCH_3], 3.85 (s, 3 H, OCH_3), 1.64–1.54 (m, 6 H, -$CH_2CH_2CH_2CH_3$), 1.37 (tt, J = 7.5, 7.5 Hz, 6 H, -$CH_2CH_2CH_2CH_3$), 1.13–1.08 (m, 6 H, -CH_2CH_2-CH_2CH_3), 0.92 (t, J = 7.3 Hz, 9 H, -$CH_2CH_2CH_2CH_3$) ppm.

8-(*p*-Anisyl-*p*-phenyl)isoquinolin-3-yl Benzoate (14): 8-Bromoisoquinolin-3-yl benzoate (**12**) (8.20 g, 25.0 mmol) and 4-methoxy-4′-tri-*n*-butylstannyl-1,1′-biphenyl (**13**) (13.3 g, 28.1 mmol), and dichlorobis(triphenylphosphane)palladium(II) (0.95 g, 1.4 mmol) were dissolved in a mixture of tetrahydrofuran and toluene (200 mL, 1:1, v/v). After addition of dry lithium chloride (5.3 g, 125 mmol), the reaction mixture was placed under argon and refluxed for 5 d and the reaction progress was monitored by thin-layer chromatography [silica; pentane/ethyl acetate 4:1 (v/v)]. Then the solvents were evaporated, the residue taken up in dichloromethane (200 mL) and washed with water (200 mL). Evaporation of the dichloromethane yielded a yellow solid which was subjected to column chromatography [silica; pentane/ethyl acetate 4:1 (v/v)]. This procedure yielded 5.26 g (12.19 mmol; 49%) of the coupling product **14** as a white solid. ^{1}H NMR (CD_2Cl_2): δ = 9.23 (s, 1 H, 1-H), 8.27 (d, J = 6.9 Hz, 2 H, H^a), 7.90–7.55 (m, 13 H), 7.03 (d, J = 9.0 Hz, 2 H), 3.86 (s, 3 H, OCH_3) ppm. ES-MS: calcd. for $C_{28}H_{22}NO_3$ + H^+ 432.1594; found 432.1541.

8-(*p*-Anisyl-*p*-phenyl)isoquinolin-3-ol (15): Benzoate-protected isoquinoline **14** (5.26 g (12.19 mmol) was dissolved in tetrahydrofuran (150 mL). After addition of 2 M aqueous potassium hydroxide (150 mL) the resulting biphasic solution was stirred vigorously for 2 h at room temperature during which time it turned yellow. After neutralizing it with 1 M hydrochloric acid under ice cooling, the solution was filtered through a glass frit (porosity 3) and the yellow solid was vacuum-dried overnight to yield 3.87 g (11.83 mmol; 97%) of pure compound **15**. ES-MS: calcd. for $C_{22}H_{18}NO_2$ 328.1332; found 328.1342. $C_{22}H_{18}NO_2$: C 80.71, H 5.23, N 4.28; found C 82.46, H 5.14, N 4.16.

8-(*p*-Anisyl-*p*-phenyl)isoquinolin-3-yl Trifluoromethanesulfonate (16): 8-(*p*-Anisyl-*p*-phenyl)isoquinolin-3-ol (**15**) (3.87 g, 11.83 mmol) was dissolved in freshly distilled pyridine (250 mL). Triflic anhydride (3.29 mL, 19.56 mmol) was added dropwise under argon at 0 °C; thereby the solution turned red-brown. After stirring for 16 h at room temperature the pyridine solvent was removed and the remaining dark brown solid was subjected to column chromatography (silica; dichloromethane). This yielded 4.51 g (9.82 mmol; 83%) of pure triflate **16** as a white solid. ^{1}H NMR (CD_2Cl_2): δ = 9.19 (s, 1 H, 1-H), 7.99 (d, J = 8.4 Hz, 1 H, 7-H), 7.87 (dd, J = 8.4, 6.9 Hz, 1 H, 6-H), 7.77–7.57 (m, 8 H), 7.04 (d, J = 8.7 Hz, 2 H) 6.97 (s, 1 H, 4-H), 3.87 (s, 3 H, OCH_3) ppm. ES-MS: calcd. for $C_{22}H_{17}NO_4F_3S$ + H^+ 460.082; found 460.081. $C_{22}H_{17}NO_4F_3S$: C 60.13, H 3.51, N 3.05; found C 60.10, H 3.86, N 2.74.

8,8′-Bis(*p*-anisyl-*p*-phenyl)-3,3′-biisoquinoline (2): Triflate **16** (6.50 g, 14.15 mmol) and 1,1′-bis(diphenylphosphanyl)ferrocenedichloropalladium(II) (1.17 g, 1.28 mmol) were dissolved in freshly distilled *N*,*N*-dimethylformamide (19 mL). After addition of freshly activated zinc powder (9.26 g, 141.6 mmol) (for activation procedure, see **1**) and dry potassium iodide (9.39 g, 56.56 mmol), the reaction mixture was heated to 90 °C for 8 h. Then the mixture was filtered through a glass frit (porosity 4) and the residue taken up in dichloromethane (100 mL) and a 10% aqueous ammonia solution (100 mL). Filtration of the organic phase and repeated washings of the filtered residue with dichloromethane and diethyl ether yielded 3.19 g of biisoquinoline **2** (5.14 mmol; 73%) as a white powder. ^{1}H NMR ($CDCl_3$, 5% TFA): δ = 9.72 (s, 2 H, 1-H), 9.07 (s, 2 H, 4-H), 8.36–8.34 (m, 4 H, 5-H, 7-H), 8.12 (dd, J = 5.0, 3.4 Hz, 2 H, 6-H) 7.83 (d, J = 8.8 Hz, 4 H), 7.66 (d, J = 8.8 Hz, 4 H), 7.61 (d, J = 8.8 Hz, 4 H), 7.08 (d, J = 8.8 Hz, 4 H), 3.93 (s, 6 H, OCH_3) ppm. ES-MS: calcd. for $C_{44}H_{32}N_2O_2$ + H^+ 621.2537; found 621.2529.

1,4-Di-*n*-hexylbenzene (19): 1-Hexyl bromide (70 mL, 500 mmol) in dry diethyl ether (50 mL) was added dropwise, over 30 min, to a suspension of magnesium ribbons (13.4 g, 550 mmol) in dry diethyl ether (100 mL) maintained at slight reflux. After complete addition, the solution was refluxed for an additional 30 min. When cooled to room temperature, the *n*-hexylmagnesium bromide was transferred, over 30 min, to an ice-cooled and stirred solution of 1,4-dichlorobenzene (29.4 g, 200 mmol) and 1,3-bis(triphenylphosphanyl)propanenickel(II) chloride (108 mg, 200 μmol) in dry diethyl ether (200 mL). Then the cooling bath was removed and the solvent began to boil after an induction period of about 1 h. The mixture was refluxed overnight, cooled to 0 °C, and quenched carefully with water (10 mL), followed by 2 M hydrochloric acid (100 mL). After phase separation, the aqueous phase was extracted with diethyl ether (2 × 50 mL) and the combined organic phases were washed with water (50 mL) and dried (anhydrous magnesium sulfate). The solvent was removed to yield the crude but analytically pure **19** (48.2 g, 98%) as a slightly yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.09 (s, 4 H, aryl-H), 2.57 [t, J = 7.7 Hz, 4 H, $CH_2(\alpha)$], 1.65–1.52 [m, 4 H, $CH_2(\beta)$], 1.37–1.26 (m, 12 H), 0.89 (t, J = 7.1 Hz, 6 H, CH_3) ppm.

1,4-Dibromo-2,5-di-*n*-hexylbenzene (20): Bromine (67.1 g, 420 mmol) was added dropwise, over 30 min, to a stirred and ice-cooled solution of 1,4-dihexylbenzene (**19**) (49.3 g, 200 mmol) and iodine (≈500 mg, 0.01 equiv.) under rigorous exclusion of light. After 1 d at room temperature, 20% aqueous potassium hydroxide solution (100 mL) was added and the mixture was shaken under slight warming until the color disappeared. The mixture was then cooled to room temperature, the aqueous solution decanted, and the remaining residue was recrystallized from ethanol to give **20** (65.9 g, 82%) as colorless crystals. ^{1}H NMR ($CDCl_3$): δ = 7.35 (s, 2 H, aryl-H), 2.64 [t, J = 7.7 Hz, 4 H, $CH_2(\alpha)$], 1.60–1.49 [m, 4 H, $CH_2(\beta)$], 1.41–1.24 (m, 12 H), 0.90 (t, J = 7.1 Hz, 6 H, CH_3) ppm.

4-Bromo-2,5-di-*n*-hexyl-4′-methoxy-1,1′-biphenyl (21): 1,4-Dibromo-2,5-dihexylbenzene (**20**) (23.9 g, 59.2 mmol), 4-methoxyphenylboronic acid (**10**) (4.50 g, 29.6 mmol), and sodium carbonate (5.02 g, 47.4 mmol) were dissolved in toluene (800 mL), ethanol (150 mL), and water (50 mL). The solution was degassed with ar-

gon (30 min) before addition of tetrakis(triphenylphosphane)palladium(0) (867 mg, 750 μmol). The reaction mixture was refluxed for 16 h, extracted twice with water (200 mL), and purified by column chromatography [silica; 0.4% ethyl acetate in pentane (v/v)] to yield **21** (10.1 g, 79%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ = 7.41 (s, 1 H, aryl-H), 7.19 (d, J = 8.8 Hz, 2 H, aryl-H), 7.01 (s, 1 H, aryl-H), 6.93 (d, J = 8.8 Hz, 2 H, aryl-H), 3.85 (s, 3 H, OCH_3), 2.68 [t, J = 7.7 Hz, 2 H, $CH_2(\alpha)$], 2.49 [t, J = 7.7 Hz, 2 H, $CH_2(\alpha')$], 1.65–1.52 (m, 2 H), 1.46–1.11 (m, 14 H), 0.88–0.75 (m, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.6, 140.7, 140.0, 139.1, 133.5, 133.0, 131.8, 130.2, 123.0, 113.5, 55.3 (OCH_3), 35.8, 32.4, 31.7, 31.5, 31.1, 30.0, 20.2, 20.1, 22.6, 22.5, 14.1 (CH_3) ppm. ES-MS: calcd. for $C_{25}H_{35}BrO$ 432.1849; found 432.1855.

Boronic Acid 22: Bromide **21** (4.28 g, 9.92 mmol) was dissolved in anhydrous tetrahydrofuran (500 mL) and cooled to –78 °C. *N*-Butyllithium (12.4 mL, 1.6 M solution in hexanes, 19.8 mmol) was added dropwise to this solution. The reaction mixture was stirred over a period of 2 h at this temperature whereby a slight yellow coloring was observed. Trimethyl borate (2.2 mL, 19.8 mmol) was added and the reaction mixture (now colorless) was stirred at room temperature overnight. Hydrochloric acid (200 mL, 4 M) was added and the solvents removed in vacuo. The white precipitate was dissolved in diethyl ether (150 mL) and water (150 mL). The organic phase was separated and the solvent removed to yield a white solid (4.06 g, quantitative) which was used without further purification in the next step. ^{1}H NMR ([D$_6$]acetone/D_2O ≈ 6:1): δ = 7.47 (s, 1 H, aryl-H), 7.17 (d, J = 8.8 Hz, 2 H, aryl-H), 6.94 (d, J = 8.8 Hz, 2 H, aryl-H), 6.87 (s, 1 H, aryl-H), 3.79 (s, 3 H, OCH_3), 2.79 [t, J = 7.7 Hz, 2 H, $CH_2(\alpha)$], 2.49 [t, J = 7.7 Hz, 2 H, $CH_2(\alpha')$], 1.58–1.46 (m, 2 H), 1.42–1.03 (m, 14 H), 0.83–0.72 (m, 6 H, CH_3) ppm. ES-MS: calcd. for $C_{25}H_{37}BO_3$ + $CF_3SO_2^-$ 509.2696; found 509.2658.

8-Bromoisoquinolin-3-yl Triisopropylsilyl Ether (34): 8-Bromoisoquinolin-3-ol (**8**) (10.03 g, 44.8 mmol) and imidazole (7.62 g, 112 mmol) were dissolved in *N*,*N*-dimethylformamide (250 mL). After dropwise addition of triisopropylsilyl chloride (11.4 mL) at 0 °C the reaction mixture was stirred for 12 h at room temperature. Then the *N*,*N*-dimethylformamide was evaporated and the residue was taken up in dichloromethane (200 mL) and water (200 mL). After phase separation, the water phase was extracted once with dichloromethane (100 mL). The combined organic phases were evaporated and the residue subjected to column chromatography (silica; dichloromethane). This procedure yielded 16.01 g (42.1 mmol; 94%) of pure **34** as a slightly yellow oil which crystallized within several hours upon standing at room temperature. ^{1}H NMR ($CDCl_3$): δ = 9.20 (s, 1 H, 1-H), 7.61–7.57 (m, 2 H, 6,7-H), 7.34 (dd, J = 8.4, 7.3 Hz, 1 H, 5-H), 6.97 (s, 1 H, 4-H), 1.45 [hept, J = 7.9 Hz, 3 H, C*H*(CH_3)$_3$], 1.13 [d, J = 7.9 Hz, 18 H, C*H*(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 160.10 (C-3), 150.40 (C-1), 141.12 (C-10), 130.29, 128.02, 125.50, 123.28, 122.58, 103.97, 18.07 [CH(*C*H$_3$)$_3$], 12.70 [*C*H(CH$_3$)$_3$] ppm. ES-MS: calcd. for $C_{18}H_{26}BrNOSi$ + H^+ 382.1021; found 382.1014; calcd. for $C_{18}H_{26}BrNOSi$ + Na^+ 404.0841; found 404.0820.

8-(1,1′-Biphenyl-4-yl)isoquinolin-3-yl Trifluoromethanesulfonate 37: Three synthetic steps were performed without isolation of the intermediates **35** and **36**: First, triisopropylsilyl ether **34** (6.77 g, 17.8 mmol) and boronic acid **22** (8.72 g, 22.0 mmol) were dissolved in 1,2-dimethoxyethane (90 mL) and water (15 mL). The solution was degassed with argon (30 min) before addition of tetrakis(triphenylphosphane)palladium(0) (825 mg, 712 μmol) and barium hydroxide octahydrate (7.30 g, 23.2 mmol). The mixture was refluxed overnight. The triisopropylsilyl ether protecting group was removed partially during the reaction. In order to complete the deprotection process, the reaction mixture was then evaporated to dryness, dissolved in tetrahydrofuran (100 mL), and tetrabutylammonium fluoride trihydrate (6.18 g, 19.6 mmol) was added. This reaction mixture was stirred for a period of 30 min. Then the solvent was evaporated and the residue filtered through silica [washings with dichloromethane and a 9:1 (v/v) mixture of dichloromethane and methanol] in order to remove less polar impurities. Finally, the crude phenol was dissolved in anhydrous dichloromethane (250 mL) and anhydrous triethylamine (40 mL). The solution was cooled to –10 °C and trifluoromethanesulfonic anhydride (4.5 mL, 26.7 mmol) was added slowly. The reaction mixture was stirred for 16 h at room temperature, washed with saturated ammonium chloride solution, and purified by column chromatography [silica; pentane/diethyl ether 20:1 (v/v)] to yield triflate **37** (7.22 g, 65% with respect to **34**) as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ = 8.81 (t, J = 0.8 Hz, 1 H, 1-H), 7.93–7.81 (m, 2 H), 7.62–7.56 (m, 2 H), 7.32 [d, J = 8.8 Hz, 2 H(10)], 7.19 (s, 1 H), 7.10 (s, 1 H), 7.00 (d, J = 9.0 Hz, 2 H), 3.89 (s, 3 H, OCH_3), 2.58–2.55 [m, 2 H, C*H*$_2(\alpha)$], 2.42–2.28 [m, 2 H, C*H*$_2(\alpha')$], 1.40–0.91 (m, 16 H), 0.80 (t, J = 6.8 Hz, 3 H, CH_3), 0.73 (t, J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.6, 152.4, 151.7, 141.7, 141.2, 138.6, 138.4, 137.9, 135.4, 134.0, 131.4, 131.2, 131.0, 130.3, 129.3, 127.8, 126.0, 113.5, 110.6, 76.6 (CF_3), 55.3 (OCH_3), 32.8, 32.6, 31.5, 31.3, 31.1, 29.7, 29.2, 28.9, 22.5, 22.3, 14.0, 13.9 ppm. ^{19}F NMR ($CDCl_3$): δ = –73.4 (s) ppm. ES-MS: calcd. for $C_{35}H_{40}F_3NO_4S$ + H^+ 628.2703; found 628.2727.

8,8′-Diaryl-3,3′-biisoquinoline 3: Triflate **37** (1.68 g, 2.68 mmol), freshly activated zinc powder (1.75 g, 10 equiv., for activation procedure, see **1**), dry potassium iodide (1.78 g, 10.7 mmol), and 1,1′-bis(diphenylphosphanyl)ferrocenedichloropalladium(II) (218 mg, 268 μmol) were dissolved in dry *N*,*N*-dimethylformamide (1.8 mL) and stirred for 16 h at 90 °C. The mixture was hydrolyzed with 10% aqueous hydrochloric acid (40 mL) and extracted with diethyl ether. The red solution was filtered three times through alumina before purification by column chromatography [silica; pentane/diethyl ether 20:1 (v/v)] to yield **3** (950 mg, 74%) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 9.12 (s, 2 H, 1-H), 8.94 (s, 2 H, 4-H), 7.98 (d, J = 8.1 Hz, 2 H, 6-H), 7.76 (t, J = 7.5 Hz, 2 H, 7-H), 7.52 (d, J = 7.6 Hz, 2 H, 8-H), 7.36 (d, J = 7.7 Hz, 4 H, anisyl-H), 7.23 (s, 2 H, aryl-H), 7.20 (s, 2 H, aryl-H), 7.02 (d, J = 7.7 Hz, 4 H, anisyl-H), 3.91 (s, 6 H, OCH_3), 2.65–2.55 [m, 4 H, $CH_2(\alpha)$], 2.49–2.37 [m, 2 H, $CH_2(\alpha')$], 2.36–2.22 [m, 2 H, $CH_2(\alpha'')$], 1.52–0.93 (m, 32 H), 0.82 (t, J = 7.2 Hz, 6 H, CH_3), 0.71 (t, J = 7.2 Hz, 6 H, CH_3') ppm. ^{13}C NMR ($CDCl_3$): δ = 158.6, 151.4, 149.8, 141.2, 140.6, 138.6, 137.7, 136.9, 136.4, 134.4, 131.4, 130.9, 130.4, 130.0, 128.4, 127.6, 126.9, 117.5, 113.5, 55.3, 32.9, 32.7, 31.5, 31.4, 31.3, 31.1, 29.2, 28.9, 22.5, 22.3, 14.0, 13.9 ppm. ES-MS: calcd. for $C_{68}H_{80}N_2O_2$ + H^+ 957.6298; found 957.6266.

4-Bromo-3,5-dihydroxybenzoic Acid (24): 3,5-Dihydroxybenzoic acid (**23**) (100 g, 649 mmol) and bromine (103.6 g, 649 mmol) were refluxed in 20% hydrochloric acid (1.1 L) for 2 h. The initially inhomogeneous reaction mixture temporarily became a homogeneous solution before the reappearance of a white precipitate towards the end of the reaction time. Then the reaction mixture was extracted with diethyl ether (3 × 500 mL). The combined organic phases were dried with anhydrous sodium sulfate. Evaporation of the solvent yielded 151.2 g (649 mmol; 100%) of pure 4-bromo-3,5-dihydroxybenzoic acid (**24**) as a sticky white solid. ^{1}H NMR ([D$_6$]acetone): δ = 7.19 (s, 2 H, aryl-H) ppm. ES-MS: calcd. for $C_7H_5BrO_4$ + Na^+ 254.9460; found 254.9263.

Methyl 4-Bromo-3,5-dihydroxybenzoate (25): 4-Bromo-3,5-dihydroxybenzoic acid (**24**) (151.2 g, 649 mmol) was dissolved in dry

methanol (750 mL). After dropwise addition of thionyl chloride (52.1 mL, 714 mmol) at 0 °C under argon the reaction mixture was refluxed for 6 h. Evaporation of the solvent and vacuum drying of the white residue yielded 150.12 g (608 mmol; 94%) of methyl 4-bromo-3,5-dihydroxybenzoate (**25**) as a white powder. ^{1}H NMR ([D$_6$]acetone): δ = 9.16 (s, 2 H, OH), 7.15 (s, 2 H, aryl-H), 3.83 (s, 3 H, OCH_3) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 165.76 (COO), 155.29 (C-2), 130.24 (C-4), 107.66 (C-3), 51.57 (OCH_3) ppm. ES-MS: calcd. for $C_8H_7BrO_4$ + H^+ 246.9606; found 246.9792.

Methyl 4-Bromo-3,5-bis(*n*-propyloxy)benzoate (26): Methyl 4-bromo-3,5-dihydroxybenzoate (**25**) (50 g, 202 mmol) was dissolved in acetone (800 mL) along with 1-bromopropane (52 mL, 606 mmol) and tetrabutylammonium iodide (14.8 g, 40 mmol). After addition of potassium carbonate (84 g, 518 mmol) the reaction mixture was refluxed for 16 h under argon. Then the acetone was evaporated and the residue taken up in as much diethyl ether and water as was needed to obtain two homogeneous phases. The aqueous phase was extracted diethyl ether (2 × 150 mL). The combined organic phases were dried with anhydrous sodium sulfate, filtered, and the ether evaporated. This procedure yielded 64.67 g (195 mmol; 96%) of a slightly brown oil that crystallized within 4 h upon standing at room temperature. This product turned out to be NMR-pure methyl 4-bromo-3,5-di-*n*-propoxybenzoate (**26**). ^{1}H NMR ($CDCl_3$): δ = 7.20 (s, 2 H, aryl-H), 4.04 (t, J = 6.6 Hz, 4 H, OCH_2), 3.93 (s, 3 H, OCH_3), 1.88 (tq, J = 7.5, 6.6 Hz, 4 H, $OCH_2CH_2CH_3$), 1.09 (t, J = 7.5 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 166.63 (COO), 156.58 (C-2), 129.87 (C-4), 107.79 (C-1), 106.05 (C-3), 70.99 (OCH_2), 52.36 (OCH_3), 22.48 ($OCH_2CH_2CH_3$), 10.55 (CH_3) ppm. ES-MS: calcd. for $C_{14}H_{19}BrO_4$ + H^+ 331.0539; found 331.0511.

4-Bromo-3,5-bis(*n*-propyloxy)benzyl Alcohol (27): Ester **26** (34.4 g, 104 mmol) was dissolved in freshly distilled diethyl ether (300 mL) and added dropwise to lithium aluminium hydride (7.89 g, 208 mmol) in dry diethyl ether (200 mL) at 0 °C under argon. After addition was completed, the reaction mixture was stirred for 2 h at room temperature. Excess lithium aluminium hydride was destroyed by slow sequential addition of ethyl acetate, water, and concentrated hydrochloric acid. The organic phase was separated from the aqueous phase and the latter was extracted diethyl ether (2 × 150 mL). The combined organic phases were dried with anhydrous sodium sulfate, filtered, and the solvents evaporated to dryness. Thereby 30.0 g (98.9 mmol; 95%) of pure **27** were isolated as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ = 6.55 (s, 2 H, aryl-H), 4.63 (s, 2 H, CH_2OH), 3.99 (t, J = 6.6 Hz, 4 H, OCH_2), 1.85 (tq, J = 7.5, 6.6 Hz, 4 H, $OCH_2CH_2CH_3$), 1.07 (t, J = 7.5 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 156.73 (C-2), 141.36 (C-4), 104.04 (C-3), 70.83 (OCH_2), 65.21 (CH_2OH), 22.53 ($OCH_2CH_2CH_3$), 10.53 (CH_3) ppm. ES-MS: calcd. for $C_{13}H_{19}BrO_3$ + H^+ 303.0590; found 303.0594.

2-[4-Bromo-3,5-bis(*n*-propyloxy)]benzyloxytetrahydro-2*H*-pyran (28): Alcohol **27** (28.0 g, 92.4 mmol), 3,4-dihydro-2*H*-pyran (18.0 g, 214 mmol), and *p*-toluenesulfonic acid (0.32 g, 1.7 mmol) were dissolved in tetrahydrofuran (250 mL) and stirred for 16 h. Filtration through silica and solvent evaporation yielded 34.4 g (88.9 mmol; 96%) of pure **28** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ = 6.55 (s, 2 H, aryl-H), 4.70 (d, J = 12.4 Hz, 1 H, H$^\alpha$), 4.66 (m, 1 H, OCHO), 4.45 (d, J = 12.4 Hz, 1 H, H$^\alpha$), 3.99 (t, J = 6.6 Hz, 4 H, $OCH_2CH_2CH_3$), 3.96–3.86 (m, 1 H), 3.55–3.50 (m, 1 H), 1.85 [tq, J = 7.5, 6.6 Hz, 4 H, ($OCH_2CH_2CH_3$)], 1.80–1.48 (m, 6 H), 1.07 (t, J = 7.5 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 156.61 (C-2), 138.67 (C-4), 105.19 (C-3), 97.64, 70.79 ($OCH_2CH_2CH_3$), 68.63, 62.35, 30.58, 25.42, 22.54 ($OCH_2CH_2CH_3$), 19.44, 10.56 (CH_3) ppm. ES-MS: calcd. for $C_{18}H_{27}BrO_4$ + Na^+ 409.0985; found 409.1046.

Phenylboronic Acid 29: Compound **28** (34.4 g, 88.9 mmol) was dissolved in freshly distilled tetrahydrofuran (450 mL). After cooling to –78 °C a 1.6 M *n*-butyllithium solution in hexanes (61 mL) was added dropwise and the reaction mixture was stirred at –78 °C for 2 h under argon. After addition of trimethyl borate (11 mL, 98.7 mmol), the solution was warmed to room temperature and stirred for another 12 h. Diethyl ether (150 mL) and water (200 mL) were then added. The aqueous phase was discarded and the ether phase evaporated to dryness. A 1 g portion of crude product **29** was subjected to column chromatography (silica; diethyl ether) yielding 0.746 g (2.12 mmol; 82%) of pure **29** as a white solid. ^{1}H NMR ($CDCl_3$): δ = 7.34 (s, 2 H, OH), 6.61 (s, 2 H, aryl-H), 4.75 (d, J = 12.8 Hz, 1 H, H$^\alpha$), 4.73 (m, 1 H), 4.49 (d, J = 12.8 Hz, 1 H, H$^\alpha$), 4.04 (t, J = 6.4 Hz, 4 H, $OCH_2CH_2CH_3$), 3.96–3.85 (m, 1 H), 3.62–3.52 (m, 1 H), 1.87 (tq, J = 7.5, 6.4 Hz, 4 H, $OCH_2CH_2CH_3$), 1.80–1.53 (m, 6 H, pyran-H), 1.07 (t, J = 7.5 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 165.09, 143.91, 104.17, 97.88, 70.61 ($OCH_2CH_2CH_3$), 68.53, 62.38, 30.56, 25.40, 22.49 ($OCH_2CH_2CH_3$), 19.42, 10.55 (CH_3) ppm. ES-MS: calcd. for $C_{18}H_{29}O_6B$ 352.2057; found 352.2449.

1,1′-Biphenyl-4-yl Bromide 31: Crude **29** (i.e. the non-column-chromatography purified portion from above) (27.5 g) was dissolved in tetrahydrofuran (350 mL) along with 1-bromo-4-iodobenzene (25.0 g, 88.4 mmol) and tetrakis(triphenylphosphane)palladium(0) (2.57 g, 2.22 mmol). After addition of 2 M aqueous potassium carbonate (350 mL) the resulting biphasic mixture was reacted for 20 h at 70 °C under argon. Then the organic phase was evaporated to yield 47.4 g of a brown oil which was purified by column chromatography [silica; pentane/diethyl ether 1:1 (v/v)]. This yielded 39.5 g (88.3 mmol; 98%) of **31** as a slightly orange oil. ^{1}H NMR ($CDCl_3$): δ = 7.46 (d, J = 8.8 Hz, 2 H), 7.24 (d, J = 8.8 Hz, 2 H), 6.62 (s, 2 H, 3-H), 4.77 (d, J = 12.1 Hz, 1 H, H$^\alpha$), 4.74 (m, 1 H), 4.50 (d, J = 12.1 Hz, 1 H, α-H), 4.01–3.91 (m, 1 H), 3.86 (t, J = 6.4 Hz, 4 H, $OCH_2CH_2CH_3$), 3.60–3.55 (m, 1 H), 1.92–1.53 (m, 6 H), 1.63 (tq, J = 7.3, 6.4 Hz, 4 H, $OCH_2CH_2CH_3$), 0.87 (t, J = 7.3 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 156.93 (C-2), 139.33 (C-4), 132.96, 130.28, 120.26, 117.95, 104.77 (C-3), 97.79, 70.14 ($OCH_2CH_2CH_3$), 69.07, 62.35, 30.63, 25.47, 22.49, 19.48, 10.60 (CH_3) ppm. ES-MS: calcd. for $C_{24}H_{31}BrO_4$ + Na^+ 487.1281; found 487.1119.

1,1′-Biphenyl-4-ylboronic Acid 32: Bromide **31** (27.76 g, 60 mmol) was dissolved in freshly distilled tetrahydrofuran (300 mL) and cooled to –78 °C before a 1.6 M *n*-butyllithium in hexanes solution (52.4 mL) was added dropwise under argon. After stirring for 2 h at –78 °C trimethyl borate (8.0 mL, 71.8 mmol) was slowly added. Then the reaction mixture was warmed to room temperature and stirred for another 20 h. Then dichloromethane (100 mL) and water (300 mL) were added to the reaction mixture. The water phase was extracted once each with dichloromethane and diethyl ether. The combined organic phases were dried with anhydrous sodium sulfate, filtered, and evaporated to yield 24.38 g (56.9 mmol; 95%) of pure boronic acid **32** (white solid). ^{1}H NMR ([D$_6$]acetone/D$_2$O 3:1): δ = 7.78 (d, J = 8.2 Hz, 2 H), 7.24 (d, J = 8.8 Hz, 2 H), 6.66 (s, 2 H, 3-H), 4.67 (m, 1 H), 4.66 (d, J = 12.2 Hz, 1 H, H$^\alpha$), 4.44 (d, J = 12.2 Hz, 1 H, H$^\alpha$), 3.85–3.75 (m, 1 H), 3.80 (t, J = 6.6 Hz, 4 H, $OCH_2CH_2CH_3$), 3.57–3.45 (m, 1 H), 1.80–1.40 (m, 10 H), 0.77 (t, J = 7.2 Hz, 6 H, CH_3) ppm. ^{13}C NMR ([D$_6$]acetone/D$_2$O 3:1): δ = 156.87 (C-2), 139.51, 136.59, 133.02, 130.30, 118.97, 104.83 (C-3), 97.61, 69.86, 68.56, 65.42, 61.79, 25.13, 22.21, 19.04, 10.02 (CH_3) ppm. ES-MS: calcd. for $C_{24}H_{31}O_2B(OCH_3)_2$ 479.2581;

found 479.2655; calcd. for $C_{24}H_{31}O_2B(OCH_3)H$ 479.2581; found 465.2497.

Pinacol (1,1′-Biphenyl-4-yl)boronate 33: Boronic acid **32** (11.91 g, 27.8 mmol) and pinacol (5.19 g, 43.9 mmol) were dissolved in toluene (250 mL) and refluxed for 4 h using a Dean–Stark trap. After toluene evaporation the residue was taken up in diethyl ether and filtered through silica. Ether evaporation yielded 13.83 g (27.1 mmol; 97%) of pinacol ester **33** as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.79 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 8.4 Hz, 2 H), 6.62 (s, 2 H), 4.78 (d, J = 12.1 Hz, 1 H, H$^{\alpha}$), 4.73 (m, 1 H), 4.50 (d, J = 12.1 Hz, 1 H, H$^{\alpha}$), 4.04–3.96 (m, 1 H), 3.85 (t, J = 6.4 Hz, 3 H, OCH_2CH$_2$CH$_3$), 3.62–3.55 (m, 1 H), 1.95–1.55 (m, 10 H), 1.38 [s, 12 H, CH(CH_3)$_2$], 0.87 (t, J = 7.3 Hz, 6 H, OCH$_2$CH$_2$CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 157.11 (C-2), 139.23, 134.56, 130.84, 119.36, 105.00, 97.76, 70.27, 69.12, 62.35, 30.66, 25.50, 22.53, 19.50, 14.04, 10.61 ppm. ES-MS: calcd. for $C_{30}H_{43}O_6B$ + H^+ 511.3231; found 511.3177; calcd. for $C_{30}H_{43}O_6B$ + Na^+ 533.3050; found 533.2996.

8-(1,1′-Biphenyl-4-yl)isoquinolin-3-yl Triisopropylsilyl Ether 38: Protected bromoisoquinoline (**34**) (10.21 g, 26.8 mmol), boronic acid pinacol ester **33** (15.46 g, 30.3 mmol), and tetrakis(triphenylphosphane)palladium(0) (1.25 g, 1.1 mmol) were dissolved in tetrahydrofuran (400 mL). After addition of 1 M aqueous potassium carbonate solution (200 mL), the reaction mixture was refluxed for 48 h under argon. Then the aqueous phase was discarded and the organic phase evaporated to dryness. The residue was subjected to column chromatography [silica; pentane/ethyl acetate 4:1 (v/v)] giving 10.4 g (15.2 mmol; 57%) of pure **38** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ = 9.02 (s, 1 H, 1-H), 7.66–7.55 (m, 2 H, 6,7-H), 7.51 (s, 4 H, Aryl-H), 7.32 (d, J = 6.8 Hz, 1 H, 5-H), 7.04 (s, 1 H, 4-H), 6.69 [s, 2 H, Aryl-(OC$_3$H$_7$)$_2$$H_2$], 4.81 (d, J = 12.1 Hz, 1 H, H$^{\alpha}$), 4.77 (m, 1 H), 4.53 (d, J = 12.1 Hz, 1 H, H$^{\alpha}$), 4.03–3.95 (m, 1 H), 3.93 (t, 4 H, OCH_2CH$_2$CH$_3$), 3.61–3.57 (m, 1 H), 1.95–1.58 (m, 10 H), 1.14 [hept, J = 6.6 Hz, 3 H, CH(CH$_3$)$_3$],1.11 [d, J = 6.6 Hz, 18 H, CH(CH_3)$_3$], 0.92 (t, J = 7.5 Hz, 6 H, OCH$_2$CH$_2$CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 159.14, 157.21, 149.73, 141.42, 140.17, 139.08, 136.97, 133.69, 131.23, 129.63, 128.86, 125.04, 123.43, 105.08, 104.13, 97.83, 70.28, 69.16, 62.35, 30.66, 25.50, 22.56, 19.50, 18.09, 12.72, 10.58 ppm. ES-MS: calcd. for $C_{42}H_{57}N_5OSi$ + H^+ 684.4079; found 684.3787.

8-(1,1′-Biphenyl-4-yl)isoquinolin-3-ol 39: The triisopropylsilyl ether protected isoquinoline (0.75 g, 1.1 mmol) was dissolved in dichloromethane (5 mL). A solution of tetrabutylammonium fluoride trihydrate (0.52 g, 1.5 mmol) in dichloromethane (10 mL) was added to this solution. The reaction mixture immediately turned yellow and it was stirred at room temperature for 4 h. Then water (30 mL) was added and the organic phase separated from the aqueous phase. The latter was extracted once with dichloromethane (10 mL). The combined organic phases were evaporated to yield 0.88 g of an orange oil which was subjected to column chromatography [silica; dichloromethane/methanol 50:1 (v/v)] yielding 0.42 g (0.8 mmol; 73%) of pure **39** as a yellow oil. ^{1}H NMR ($CDCl_3$): δ = 9.12 (s, 1 H, 1-H), 8.66 (s, 1 H, OH), 7.59–7.51 (m, 2 H, 6,7-H), 7.43 (s, 4 H, Aryl-H), 7.38 (d, J = 7.0 Hz, 1 H, 5-H), 6.82 (s, 1 H, 4-H), 6.52 [s, 2 H, Aryl-(OC$_3$H$_7$)$_2$$H_2$], 4.85 (d, J = 12.1 Hz, 1 H, H$^{\alpha}$), 4.78 (m, 1 H), 4.54 (d, J = 12.1 Hz, 1 H, H$^{\alpha}$), 4.05–3.82 (m, 5 H, pyran-H, OCH_2CH$_2$CH$_3$), 3.67–3.55 (m, 1 H), 2.01–1.53 (m, 10 H), 0.87 (t, J = 7.5 Hz, 6 H, OCH$_2$CH$_2$CH_3) ppm. ES-MS: calcd. for $C_{33}H_{37}NO_5^-$ 526.2584; found 526.2593.

8-(1,1′-Biphenyl-4-yl)isoquinolin-3-yl Trifluoromethanesulfonate 40: The protected isoquinoline **38** (3.1 g, 4.5 mmol) was dissolved in dichloromethane (120 mL). A solution of tetrabutylammonium fluoride trihydrate (2.15 g, 6.8 mmol) was slowly added to the isoquinoline solution and the yellow reaction mixture was stirred for 12 h at room temperature. Then the solution was washed with water (100 mL) and the dichloromethane phase was dried with anhydrous sodium sulfate, filtered, and the solvents evaporated to dryness. The yellow residue was then dissolved in dry dichloromethane (150 mL) and freshly distilled triethylamine (50 mL). Trifluoromethanesulfonic anhydride (2.29 mL, 13.6 mmol) was added dropwise to this solution at 0 °C under argon. This solution was stirred at room temperature for 12 h before the solvents were evaporated. The red-brown residue was subjected to column chromatography [silica; pentane/diethyl ether 1:1 (v/v)] giving 1.14 g [1.7 mmol; 38% (two steps)] of pure **40** as a pale yellow oil that crystallized within several hours upon standing at room temperature. ^{1}H NMR ($CDCl_3$): δ = 9.27 (s, 1 H, 1-H), 7.91–7.80 (m, 2 H, 6,7-H), 7.68 (dd, J = 8.2, 1.4 Hz, 1 H, 5-H), 7.63 (s, 1 H, 4-H), 7.57 (d, J = 8.9 Hz, 2 H, ArH_2H$_2$), 7.48 (d, J = 8.9 Hz, 2 H, ArH$_2$$H_2$), 6.70 [s, 2 H, Aryl-(OC$_3$H$_7$)$_2$$H_2$], 4.83 (d, J = 12.1 Hz, 1 H, H$^{\alpha}$), 4.78 (m, 1 H), 4.55 (d, J = 12.1 Hz, 1 H, H$^{\alpha}$), 4.05–3.95 (m, 1 H), 3.94 (t, J = 6.4 Hz, 4 H, OCH_2CH$_2$CH$_3$), 3.65–3.55 (m, 1 H), 1.97–1.55 (m, 10 H), 0.92 (t, J = 7.3 Hz, 6 H, OCH$_2$CH$_2$CH_3) ppm. ES-MS: calcd. for $C_{34}H_{36}NO_7F_3S$ + H^+ 660.2243; found 660.2161.

8,8′-Diaryl-3,3′-biisoquinoline 4: Triflate **40** (873 mg, 1.32 mmol) and dichloro[1,1′-bis(diphenylphosphanyl)ferrocene]palladium(0) (108 mg, 0.15 mmol) were dissolved in freshly distilled *N*,*N*-dimethylformamide (4.5 mL). Freshly activated zinc powder (865 mg, 13.2 mmol) (for activation procedure, see **1**) and anhydrous potassium iodide (879 mg, 5.28 mmol) were added to this solution. The resulting reaction mixture was heated at 90 °C for 16 h. Then water (20 mL) and dichloromethane (20 mL) were added and the aqueous phase was separated from the organic phase. The latter was evaporated to dryness and the brown oily residue subjected to column chromatography [silica; dichloromethane/methanol 50:1 (v/v)] to yield 101 mg (0.1 mmol; 15%) of pure **4** as a white solid. ^{1}H NMR ($CDCl_3$): δ = 9.61 (s, 2 H, 1-H), 8.95 (s, 2 H, 4-H), 8.01–7.96 (m, 2 H), 7.78–7.53 (m, 12 H), 6.70 [s, 4 H, Aryl-(OC$_3$H$_7$)$_2$$H_2$], 4.81 (d, J = 12.0 Hz, 2 H, H$^{\alpha}$), 4.78 (m, 2 H, H^{a}), 4.54 (d, J = 12.0 Hz, 2 H, H$^{\alpha}$), 4.00–3.90 (m, 2 H, H^{e}), 3.95 (t, J = 6.6 Hz, 8 H, OCH$_2$CH$_2$CH$_3$), 3.64–3.55 (m, 2 H, H^{e}), 1.97–1.51 (m, 20 H), 0.94 (t, J = 7.2 Hz, 12 H, OCH$_2$CH$_2$CH_3) ppm. MALDI-TOF MS: calcd. for $C_{66}H_{72}N_2O_8$ + H^+ 1021.5367; found 1021.546.

Tris(8,8′-di-*p*-anisyl-3,3′-biisoquinoline)iron(II) Hexafluorophosphate (41): By stirring a dichloromethane solution of bis(tetrafluoroborate)iron(II) and ligand **1** for 2 h at room temperature and subsequent anion exchange, **41** was obtained in quantitative yields. Single crystals suitable for crystal structure determination were obtained by slow diffusion of diisopropyl ether into acetone solutions at room temperature. ^{1}H NMR (CD_2Cl_2): δ = 8.89 (s, 6 H, 1-H), 8.10 (d, J = 8.4 Hz, 6 H), 7.87 (s, 6 H, 4-H), 7.84 (dd, J = 8.4, 7.2 Hz, 6 H, 6-H), 7.45 (d, J = 7.2 Hz, 6 H), 6.62 (d, J = 8.7 Hz, 12 H), 6.31 (d, J = 8.7 Hz, 12 H), 3.58 (s, 18 H, OCH$_3$) ppm. ES-MS: calcd. for $C_{96}H_{72}N_6O_6Fe^{2+}$ 730.443; found 730.7444. Crystal structure analysis: $C_{96}H_{72}F_{12}Fe_1N_6O_6P_2$, M = 1751.39, monoclinic, a = 15.4180(3), b = 34.4150(6), c = 17.0120(4) Å, β = 116.3621(8)°, V = 8088.0(3) Å^3, T = 173(2) K, space group $P2_1/n$, Z = 4, μ(Mo-K_α) = 0.316 mm^{-1}, 45635 collected reflections, 23640 independent reflections [R(int) = 0.048], final R indices R_1 = 0.052, wR_2 = 0.1261.

CCDC-283554 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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