The Role of Bidentate Fluorenylphosphines in Palladium-Catalyzed Cross-Coupling Reactions

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Seven new bidentate phosphine ligands, in which two 9-(dicyclohexylphosphino)fluoren-9′-yl units are bridged with *n*-alkanediyl- (C_1-C_5) or *o/m*-xylenediyl linkers were synthesized and characterized as the respective air-stable phosphonium salts. Pd complexes of the new bidentate ligands proved to be highly active catalysts for Buchwald−Hartwig amination and Suzuki and Sonogashira coupling using aryl bromides and chlorides as substrates. A study comparing the catalytic activity of the Pd complexes of the bidentate phosphine ligands with those of closely related monodentate fluorenyl phosphines gave insights into the influence of the various bridging units on the catalytic transformations. In Suzuki and amination reactions the diphosphine **2b** with the shortest linker, a $-CH_2-$ unit, turned out to be by far the best ligand. In the Sonogashira coupling monodentate phosphines rendered the most active Pd catalysts, while **2b** fails.

Introduction

Pd-mediated cross-coupling reactions are powerful tools for the formation of C−C and C−N bonds and are applied both in chemical laboratories and process development.[1–6] Of those reactions Buchwald−Hartwig amination,[7,8] Suzuki cross-coupling,[9–12] Sonogashira alkynylation,[13–15] and Heck coupling[16] are of special importance.

The most common ligand in the early days of cross-coupling chemistry was Ph_3P in complexes such as $(Ph_3P)_2PdCl_2$ and $Pd(PPh_3)_4$.[11,13,14,17–19] Even though the role of increased steric bulk was recognized by Heck in 1983, when using P(*o*-tolyl)$_3$ as a ligand,[20] Ph_3P continued to dominate. Later the discovery by Beller and Herrmann et al. of the unique catalytic activity of a well-known dimeric complex $Pd_2(P(o\text{-}Tol)_3)_2(OAc)_2$ set a milestone in palladium catalysis.[21] A paradigm shift occurred in the mid 1990s when PPh_3 was replaced with the bulkier and more electron-donating trialkylphosphines Cy_3P and tBu$_3$P,[22] observing hitherto unprecedented catalytic activities in reactions of the amination,[23–26] Suzuki,[27] and Sonogashira[28] type. Hartwig et al. convincingly demonstrated the advantages of sterically demanding and electron-rich phosphines.[29,30]

Since then a plethora of phosphine ligands (and numerous other classes of ligands, most notably NHC ligands)[31,32] have been developed, which enable coupling reactions at much lower catalyst loading compared to Pd-PPh_3 complexes. In Figure 1 a few established representatives of modern monophosphine ligands are summarized.

The trialkylphosphine tBu$_3$P (**L1**, Figure 1) represents a nonproprietary, highly active phosphine ligand for a broad range of Pd-mediated cross-couplings,[33] but lacks facile tuneability. We and the Beller group reported on the use of (1-Ad)$_2$PR (1-Ad = 1-adamantyl) (**L2a**, **L2b**) ligands for Pd catalysis with remarkable activities in amination and Sonogashira and Suzuki coupling.[34–43] Bulky biarylphosphines such as **L3** and its

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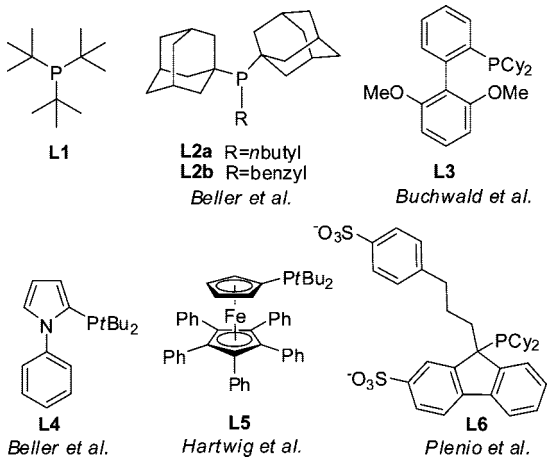

Figure 1. Selected active monodentate phosphines for Pd-mediated C−C and C−N cross-coupling reactions.

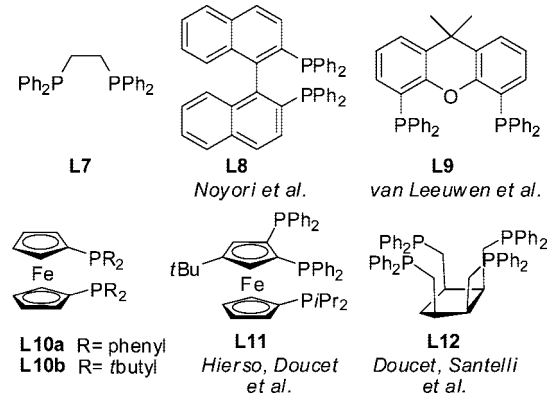

Figure 2. Selected active polydentate phosphine ligands for Pd-mediated C−C and C−N cross-coupling reactions.

derivatives developed by Buchwald et al. turned out to be outstanding ligands for Buchwald−Hartwig amination, Suzuki coupling, and many other Pd-catalyzed reactions.[8,44–50] The related phosphino-*N*-arylpyrrole family was built by Singer et al.[51–53] and subsequently modified to the similar highly active and easily accessible **L4** class by Beller and co-workers.[54–58] Q-Phos (**L5**), which has a ferrocene backbone, was developed by Hartwig and co-workers and is suitable for Pd-mediated etherifications, aminations, and arylations of aryl chlorides under mild conditions.[59–63]

Recognizing the high catalytic activity, but inherent inflexibility of tBu$_3$P (**L1**), we recently developed the class of fluorenyldialkylphosphines (**L6**), whose Pd complexes display excellent activities in various cross-coupling reactions and can be easily modified, also for use in water as the solvent.[64–70]

Bi- or polydentate phosphines are frequently used in Pd-catalyzed cross-coupling reactions, even though they were initially considered as the inferior choice.[16] However, especially in amination reactions chelating diphosphines such as BINAP (**L8**, Figure 2,) Xantphos (**L9**), and DPPF (**L10a**) show excellent activities for aryl bromide and chloride conversions.[7,71–75] Unfortunately there is no clear answer as to whether mono- or bidentates are more suitable. Although comprehensive mechanistic studies for amination reactions with Pd/monophosphine systems such as Pd/tBu$_3$P[76] and Pd/biarylphosphine[77] or with Pd/bidentate systems such as Pd/BINAP[78–80] were performed, it is not well understood why and when bidentate phosphines perform better than monophosphine ligands.

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Despite the popularity of monodentate phosphines, there are numerous examples where bidentates appear to perform better than monodentates.[81–84] As an example, the amination of 9-benzyl-6-bromo-1,2,3,4-tetrahydrocarbazol-1-one with 4-methylbenzamide results in 82% yield with 1 mol % of a Pd/Xantphos catalyst; under the same reaction conditions biphenyl-di-*tert*-butylphosphine affords only 16% conversion.[85] Notoriously difficult substrates such as nucleosides are efficiently aminated with 3-methylindole using 5 mol % PdOAc/Xantphos, affording 69% yield, whereas 2-(dicyclohexylphosphinyl)-2′-(*N,N*-dimethylamino)-1,1′-biphenyl ligands proved to be inefficient.[82]

BINAP was reported to be a useful ligand for the amination of 1,8-dichloroanthracene, while sterically demanding monophosphines tBu$_3$P and Cy$_3$P are poor performers.[86] Even the simple chelating diphosphine DPPE (**L7**) may deliver remarkable results in the amination of 2-anilino-3-chloro-1,4-naphthoquinone with 4-chloroaniline[87] or other Pd-mediated arylation reactions.[88]

Bidentate phosphines also form active Pd complexes for Suzuki couplings[89–92] and are well established in the Novartis discodermolide synthesis.[93] Ostentatiously, the classic bidentates BINAP and DPPF proved to be the better choice, when heteroaryl chlorides or bromides such as chloroquinoline[94] or bromoimidazole[95] were subjected to Suzuki couplings. Pd complexes with the sterically demanding 1,1′-Fc(PtBu$_2$)$_2$ (D-t-BPF) (**L10b**) were found to be active catalysts for Suzuki arylation of aminochloropyrimidines, while various monodentates such as the Buchwald biarylphosphines or tBu$_3$P failed.[96] Bidentate ligands are reported to enable Sonogashira cross-coupling reactions, using Cu(I) as a cocatalyst. The reported catalytic activity of the respective Pd complexes[97,98] is clearly inferior to that of potent monophosphine systems;[35,45,64,99,100] however, with copper-free protocols good results were reported on coupling N-heteroaryl chlorides using BINAP[101] or bis-diphenylphosphinebutane (dppb). With arylsulfonate substrates, bidentate phosphines appear to be the better choice: aryl nonaflates are efficiently aminated using Pd/Xantphos as catalyst;[102] the carbonylation of various aryltosylates and -mesylates was very recently reported by the Buchwald group utilizing Pd(OAc)$_2$ with bisdicyclohexylphosphinopropane.[103] In addition to the bidentate phosphine ligands, a few polydentate ligands have been applied, of which Tedicyp (**L12**) by Doucet and Santelli may be the most prominent one. Tedicyp is powerful in Sonogashira and Suzuki couplings of heteroaryl halides[104,105] or heteroboronic acids.[106,107]

With diphosphines steric bulk, electronic properties, and the bite angle have to be taken into account. Although preliminary studies concerning the correlation between bite angle and catalytic activity of Pd complexes have been made,[108,109] there is no clear rule as to which distance between the donor atoms is ideal.[75] Recently the Wills' group tested a number of bidentate ligands in Suzuki, Sonogashira, and amination reactions, to observe drastic effects on catalytic activity depending on the lengths of the bridging unit.[110] In order to get a better idea of the influence of the donor atom separation in electron-rich and sterically demanding diphosphine ligands on the catalytic properties, we decided to synthesize a number of bidentate fluorenyldialkylphosphines with variable length and nature of the bridging unit.

Results and Discussion

Synthesis of Ligands. In order to prepare bidentate fluorenyldialkylphosphines, we first synthesized a number of alkanediyl- and xylenediyl-linked difluorenes (**2a**−**8a**). The 9-position of fluorene serves as the anchor for the respective linkers. Difluoren-9-yl-methane **2a** was conveniently available from **1** and paraformaldehyde in 52% yield utilizing a slightly modified reaction protocol originally reported by Resconi et al.[111] Difluorenes **3a**, **4a**, **7a**, and **8a** were obtained by stoichiometric deprotonation of **1** with nBuLi and subsequent quenching of the fluorenyl anion with the respective α,ω-alkyldibromide in 44−75% yield. n-Pentyl- and n-butyl-linked difluorenes **5a** and **6a** were conveniently prepared in 45−47% yield by KOH-catalyzed condensation of fluorene (**1**) with 1,4-butanediol or 1,5-pentanediol at elevated temperatures.[112] Due to the lower boiling points of the respective glycols, this route turned out to be inconvenient for formation of the respective difluorenes with shorter linkers.

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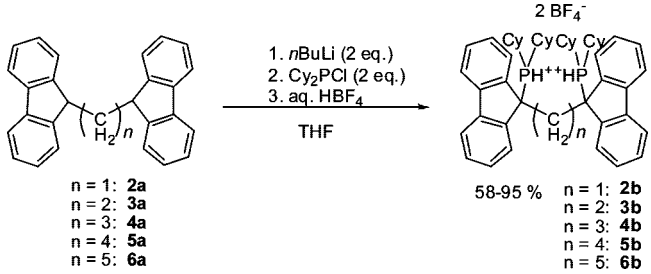
Scheme 1. Synthesis of the *n*-Alkanediyl-Linked Diphosphines 2b−6b[a]



[a] Reagents and conditions: (1) *n*BuLi, THF, 0 °C; (2) Cy_2PCl, 0 °C; (3) aq HBF_4.

The respective difluorenes **2a**−**8a** were doubly deprotonated with *n*BuLi and reacted with 2 equiv of Cy_2PCl to obtain the respective bidentate phosphines **2b**−**8b** (Scheme 2.) Subsequent treatment of the reaction mixture with aqueous HBF_4 led to the precipitation of the respective air-stable diphosphonium salts (**2b**−**6b**)·$2H^+$ (Scheme 1) and **7b**·$2H^+$ and **8b**·$2H^+$ (Scheme 2) in good yields and high purities. The synthesis of the CH_2-bridged and sterically congested diphosphine **2b** requires elevated temperatures (50 °C) to effect the full conversion of the reactants.

The phosphines synthesized here are potential chelating ligands. Whether chelated metal complexes represent the catalytically active Pd species remains unclear. It is known that especially the long chain linked diphosphines are variable in their coordination chemistry. McAuliffe et al.,[113] Shaw et al.,[114] and Sijbesma/Paulusse[115] reported on the formation of cis- and trans-configured Pd complexes and on polymeric species.

Depicted in Figure 3 are two related monodentate fluorenylphosphines **A** and **B** used as catalysis benchmarks.

Cross-Coupling Reactions. With this set of ligands we tested Pd complexes of the bidentate phosphines **2b**−**8b** in various cross-coupling reactions and compared their catalytic efficiency with those of the Pd complexes with the monodentates **A** and **B**. In the Buchwald−Hartwig amination of 4-bromotoluene with 3,5-dimethylaniline in toluene and NaO*t*Bu as a base, all Pd catalysts were formed *in situ* from $Pd(OAc)_2$ and the respective phosphonium salts. The catalysts showed high activity and led to good conversions (Figure 4.) However, starting with full conversion for a catalyst loading of 0.5 mol % Pd/**2b**, a continuous decrease of activity could be observed with increased length of the *n*-alkyl linker. With Pd/**6b** only a 57% yield was observed.

For a more detailed understanding a related set of screening experiments was done with *p*-chlorotoluene. Using ligand **2b** led to significantly higher conversions (65%) than with all other ligands. With Pd/**2b** as a catalyst the amination turned out to be highly selective toward the secondary aniline, whereas significant amounts of tertiary aniline were detected with the monodentate system Pd/**B**.[116] The remaining diphosphines (**3b**−**8b**) perform poorly compared to the monodentates **A** and **B**. These results are surprising, because normally diphosphines with well-separated donor atoms render high catalytic activity in amination reactions, whereas diphosphines with small bite angles such as dppe and dppp were reported to fail.[117,75,118]

Next, we applied the various *in situ* formed Pd complexes in Suzuki couplings by reacting *p*-chloroacetophenone with *p*-tolylboronic acid. Using 0.5 mol % of the respective catalysts, only the bidentates **2b** and **6b** showed high activities (Figure 5). The diphosphines with an intermediate number of atoms separating the two donor atom are less efficient. **5b** and **6b** behave similarly to monodentate ligands.

In order to better understand which catalyst performs best, the four most active complexes, Pd/**A**, Pd/**2b**, Pd/**6b**, and Pd/**7b**, were subjected to a second screening. Here less catalyst (0.1 mol %) was applied, while maintaining all other reaction parameters. The three selected bidentate phosphine ligands possess significantly higher catalytic activities than the monodentate ligand **A**. The diphosphine **2b**, bearing the shortest linker, proved to be most active one: more than 5 times higher than the monodentate ligand **A**. Thus among the phosphines tested here, **2b** turned out to be the most active ligand.

Finally, we applied the various mono- and bidentate phosphines in the Sonogashira coupling of 4-bromotoluene with phenylacetylene using diisopropylamine as solvent and CuI as cocatalyst at 50 °C. Fluorenyldialkylphosphines are known to be highly active in Sonogashira coupling of aryl bromides;[64] the required low catalyst concentrations (0.00667 mol % Pd) could be handled easily by application of premixed "ready-made catalyst".[119] In two independent screening reactions we applied an *in situ* formed catalyst consisting of [Na_2PdCl_4], ligand, and CuI in 4:4:3 and 4:8:3 ratio, respectively (Figure 6.) In general, Sonogashira reactions effected by a catalyst mixture with a higher phosphine ratio (Pd/L 1:2) led to significantly higher yield.

We were surprised to learn that ligand **2b**, which was extremely useful in Suzuki and amination reactions, failed in the Sonogashira coupling. All other diphosphines provide medium catalytic activity, independent of the nature of the bridging unit. Catalysts [Pd/**A**] and [Pd/**B**] derived from monodentate ligands are by far the most active catalysts. Complex [Pd/**8b**] shows activity comparable to that of the mondentates and phosphine **B**. We ascribe the lower activity of the bidentate ligands, especially of **2b** in Sonogashira cross-coupling, to a strong chelation and thus inhibition of the copper cocatalyst, whose presence is essential for these high-activity catalysts. Consequently, optimization of catalysts for Sonogashira cross-coupling reactions must follow other principles than Suzuki coupling or amination.

Summary and Conclusion

Motivated by the success of monodentate fluorenyldialkylphosphines ligands in Pd-mediated cross-coupling reactions, we synthesized seven new *n*-alkanediyl- and xylenediyl-linked fluorenyldiphosphines, **2b**−**8b**. The new diphosphines were tested in Buchwald−Hartwig amination and Suzuki and Sonogashira reactions using aryl bromides and chlorides as substrates. The catalytic activity of the Pd complexes is

(113) Hill, W. E.; McAuliffe, C. A.; Niven, I. E.; Parish, R. V. *Inorg. Chim. Acta* **1980**, *38*, 273.

(114) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1979**, 1972.

(115) Paulusse, J. M. J.; Sijbesma, R. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4460.

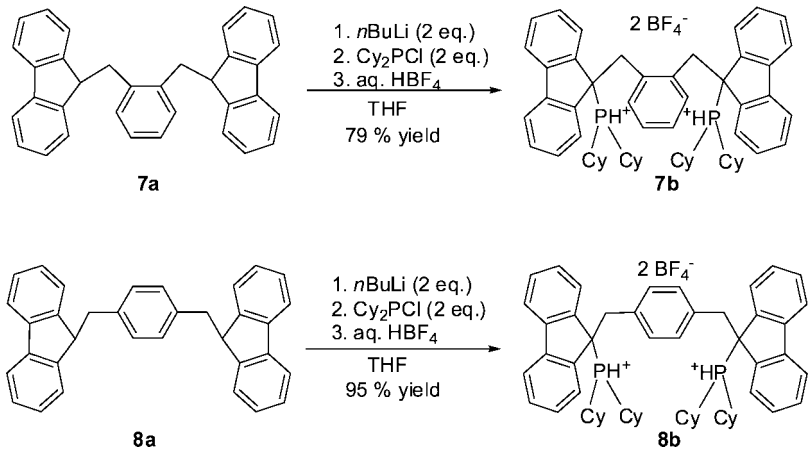
(116) In contrast to all other *in situ* formed colorless Pd/phosphine complexes in solution, the *in situ* formed Pd/**2b** has a brownish appearance.

(117) Regarding the bite angle, in a first approximation diphosphine **2b** shows similarity with dppp.

(118) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741.

(119) Köllhofer, A.; Plenio, H. *Adv. Synth. Catal.* **2005**, *347*, 1295.

Scheme 2. Synthesis of the Xylendiyl-Linked Diphosphines 7b and 8b[a]



[a] Reagents and conditions: (1) *n*BuLi, THF, 0 °C; (2) Cy_2PCl, 0 °C; (3) aq HBF_4.

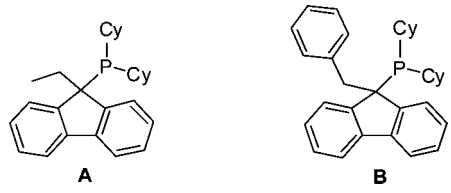


Figure 3. 9-Ethylfluorenyldicyclohexylphosphine (**A**) and 9-benzylfluorenyldicyclohexylphosphine (**B**).

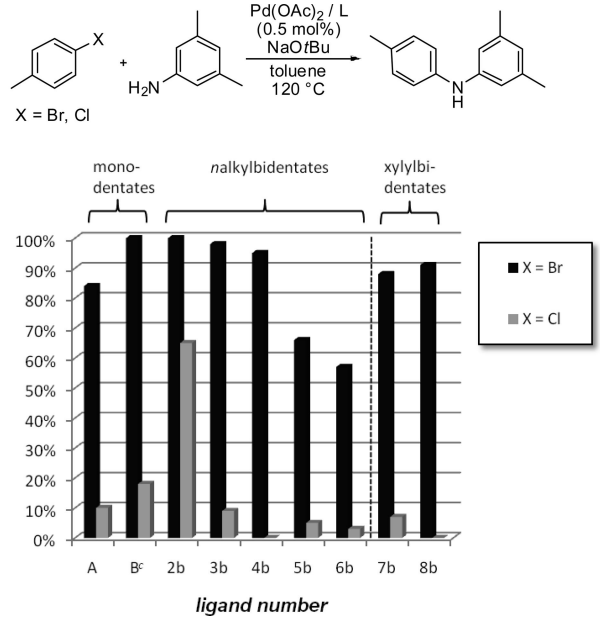


Figure 4. Buchwald−Hartwig amination. [a]Reaction conditions: 1.0 mmol of aryl halide, 1.5 mmol of aniline, 2.0 mmol of NaO*t*Bu, 0.5 mol % $Pd(OAc)_2$ 0.5 mol% ligand (in case of monodentate ligands **A** and **B** 1 mol % ligand was used), toluene (5 mL), 120 °C, 12 h. [b]Average of two runs, determined by GC using heptadecane as internal standard. [c]Formation of significant amounts (4%) of tertiary aniline was observed.

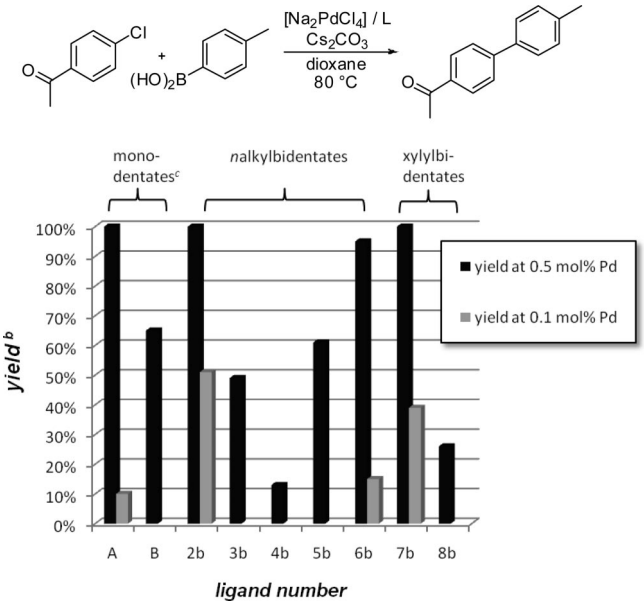


Figure 5. Suzuki cross-coupling. [a]Reaction conditions: 1.0 equiv of *p*chloroacetophenone, 1.5 equiv of tolylboronic acid, 2.0 equiv of Cs_2CO_3, dioxane (5.0 mL $mmol^{-1}$), cat.: the respective volume of aqueous catalyst stock solution (c_{Pd} = 0.005 mol/L), $[Na_2PdCl_4]$/ligand, 1:1; 80 °C, 15 h. [b]Average of two runs, determined by GC using heptadecane as internal standard. [c]For monodentate ligands **A** and **B** the Pd/ligand ratio was 1:2 in the catalyst stock solution.

systematically modulated, depending on the nature of the bridge linking the two P donors. On the basis of our study we can draw the following conclusions:

(a) In Buchwald−Hartwig amination and in Suzuki reactions Pd complexes of diphosphines with short-chain-linked P donors display superior catalytic activity compared to complexes of monophosphines. The fluorenylphosphine **2b**, with a CH_2 linker, renders a Pd complex of excellent activity.

(b) Pd complexes of diphosphines with distant P donors are comparable to those of the respective monodentate ligands.

(c) In Sonogashira coupling reactions monophosphines appear to be superior to diphosphines; especially ligand **2b**, with excellent properties in amination and Suzuki reactions, fails in the Sonogashira coupling.

Experimental Section

General Procedures. All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. Toluene was freshly distilled over sodium, dioxane was dried over CaH_2, and $HNiPr_2$ was dried over KOH. Solvents used in cross-coupling experiments were deaerated

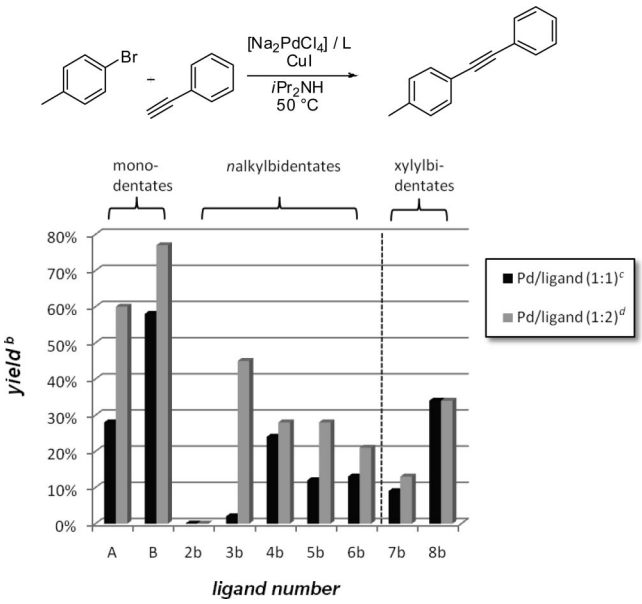


Figure 6. Sonogashira cross-coupling. [a]Reaction conditions: 10 mmol of 4-bromotoluene, 11 mmol of phenylacetylene, 10 mL of iPr$_2$NH, cat.: the respective amount of ready made catalyst, triturated with iPr$_2$NH$_2$Br (cat. loading: 0.00667 mol %), 50 °C, 24 h. [b]Determined via GC, external calibration calculated with the response factors of analytically pure samples of starting material (4-bromotoluene) and product. [c]Catalyst composition: [Na$_2$PdCl$_4$]/ligand/CuI (4:4:3). [d]Catalyst composition: [Na$_2$PdCl$_4$]/ligand/CuI (4:8:3).

via freeze and thaw technique (2×). Cs_2CO_3 (99.5%) was purchased from Chemetall; NaOtBu (98%) was purchased from Acros. All "phosphines" mentioned in this publication were used as their air-stable phosphonium salts and deprotonated *in situ* during the catalyst preparation. All experiments were carried out under an argon atmosphere, unless otherwise noted. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and ^{15}N NMR spectra were recorded on a Bruker DRX 500 at 500, 125.75, 202.46, and 50.69 MHz, respectively, at 293 K. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to tetramethylsilane (δ = 0 ppm), ^{1}H NMR; 65% aqueous H_3PO_4 (δ = 0 ppm), ^{31}P NMR; and nitromethane (δ = 0 ppm), ^{15}N NMR. Abbreviations for NMR data: s = singlet; d = doublet; t = triplet; q = quartet; qi = quintet; dd = doublet of doublets; dt = doublet of triplets; dq = doublet of quartets; tt = triplet of triplets; m = multiplet. Mass spectra were recorded on a Finnigan MAT 95 magnetic sector spectrometer. Melting points were determined on a Büchi type B-540 melting point apparatus and corrected versus caffeine (p.a. quality, mp 236.1 °C) as standard.

Thin-layer chromatography (TLC) was performed using Fluka silica gel 60 F 254 (0.2 mm) on Al plates. Silica gel columns for chromatography were prepared with E. Merck silica gel 60 (0.063−0.20 mesh ASTM). GC experiments were run on a Clarus 500 GC with autosampler and FID detector. Column: Varian CP-Sil 8 CB (l = 15 m, d_i = 0.25 mm, d_F = 1.0 μm), N_2 (flow 17 cm/s; split 1:50); injector temperature 270 °C, detector temperature 350 °C. Temperature program: isotherm 150 °C for 5 min, heating to 300 °C at 25 °C/min, isotherm for 15 min.

Difluoren-9-ylmethane (2a). In a 250 mL Schlenk flask fluorene (15 g, 90.2 mmol) paraformaldehyde (1.41 g, 50 mmol) was dissolved in dry DMF (150 mL). KOtBu (12.15 g, 108 mmol) was added, and the resulting red reaction mixture was stirred at ambient temperature for 12 h, then for an additional 2 h at 70 °C. The reaction mixture was poured into water (300 mL) and extracted with THF/MTBE (1:1, 4 × 150 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent volume was reduced *in vacuo* to about 100 mL. Addition of cyclohexane (200 mL) and removal of the remaining THF via rotary evaporation afforded a slightly yellowish crude solid, which was separated via suction filtration. Recrystallization from cyclohexane (1 L) afforded **2a** as white crystals (8.1 g, 52%). The ^{1}H and ^{13}C NMR spectra are identical to those in the literature.[111]

Mp 207.5 °C (cyclohexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, ^3J = 7.6 Hz, 4 H, *CH*, ar), 7.54 (d, ^3J = 7.6 Hz, 4 H, *CH*, ar), 7.39 (t, ^3J = 7.5 Hz, 4 H, *CH*, ar), 7.27 (dt, ^3J = 7.5 Hz, J = 1.1 Hz, 4 H, *CH*, ar), 4.39 (t, ^3J = 7.5 Hz, 2 H, *H*Flu), 2.24 (t, ^3J = 7.6 Hz, 2 H, C*H*$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 147.5, 141.0, 127.2, 127.0, 125.0, 120.1, 45.9, 38.8; HRMS calcd for $C_{27}H_{20}$ 344.1565, found 344.15884. Anal. Calcd (%) for $C_{27}H_{20}$: C 94.15, H 5.85. Found: C 94.07, H 5.89.

1,2-Difluoren-9-ylethane (3a). In a 500 mL Schlenk flask fluorene (20 g, 120 mmol) was dissolved in dry THF (350 mL). nBuLi (50 mL, 2.5 M solution in hexane, 125 mmol) was added to the stirred solution at −50 °C. The resulting orange solution was stirred at that temperature for 5 min, allowed to come to ambient temperature, and stirred for an additional 1 h. At −50 °C 1,2-dibromoethane (11.9 g, 5.46 mL, 63.5 mmol) was added to the stirred solution within 1 min via a syringe. The reaction mixture was allowed to come to ambient temperature and stirred for 1 h. The reaction mixture was evaporated *in vacuo* to afford a white solid residue. The solid was stirred in water/EtOH (1:1, 500 mL) for 40 min. Then the solid was separated via suction filtration and recrystallized from hot xylene (400 mL) to afford **3a** as white crystals (10.5 g, 48.7%). The ^{1}H and ^{13}C NMR spectra are identical to those in the literature.[120]

Mp 228.0 °C (xylene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, ^3J = 7.5 Hz, 4 H, *CH*, ar), 7.38−7.34 (m, 4 H, *CH*, ar), 7.32−7.26 (m, 8 H, *CH*, ar), 3.84 (m, 2 H, *H*Flu), 1.74−1.72 (m, 4H, Flu-C*H*$_2$); ^{13}C[121] NMR (125.8 MHz, $CDCl_3$) δ 147.2, 141.7, 127.4, 127.3, 124.6, 120.2, 47.4, 27.0; HRMS calcd for $C_{28}H_{22}$ 358.1721, found 358.17463. Anal. Calcd (%) for $C_{28}H_{22}$: C 93.81, H 6.19. Found: C 93.72, H 6.13.

1,3-Difluoren-9-ylpropane (4a). In a 500 mL Schlenk flask fluorene (20 g, 120 mmol) was dissolved in dry THF (350 mL). nBuLi (50 mL, 2.5 M solution in hexane, 125 mmol) was added to the stirred solution at −50 °C. The resulting orange solution was stirred at that temperature for 5 min, allowed to come to ambient temperature, and stirred for an additional 1 h. At −50 °C 1,3-dibromopropane (12.6 g, 6.38 mL, 62.6 mmol) was added to the stirred solution within 1 min via a syringe. The reaction mixture was allowed to come to ambient temperature, stirred for 1 h, and then quenched with water (100 mL). After addition of MTBE (100 mL) the organic layer was separated, washed with saturated aqueous $Na_2S_2O_3$ solution (100 mL) and water (100 mL), dried over $MgSO_4$, and filtered, and the volatiles were removed *in vacuo* to afford crude **4a** as a white solid. The solid was dissolved in Et_2O (500 mL), n-pentane (50 mL) was added, and the solution was allowed to stand in an open 1 L Erlenmeyer flask at room temperature. Slow evaporation of the solvent within 2 days afforded the product **4a** (16.9 g, 75%) as pure white crystals. The ^{1}H and ^{13}C NMR spectra are identical to those in the literature.[122]

Mp 115.9 °C (Et_2O/n-pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, ^3J = 7.6 Hz, 4 H, *CH*, ar), 7.35 (d, ^3J = 7.2 Hz, 4 H, *CH*, ar), 7.33 (t, ^3J = 7.5 Hz, 4 H, *CH*, ar), 7.24 (dt, ^3J = 7.4 Hz, J = 1.1 Hz, 4 H, *CH*, ar), 3.88 (t, ^3J = 6.2 Hz, 2 H, *H*Flu), 1.94−1.88 (m, 4 H, C*H*$_2$(propyl)), 1.35−1.27 (m, 2 H, C*H*$_2$(propyl)); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ 147.9, 141.5, 127.3, 127.2, 124.8, 120.2, 47.6, 33.7, 23.2; HRMS calcd for $C_{29}H_{24}$ 372.1878, found

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(121) Schulte, J. P., II; Tweedie, S. R. *Synlett* **2007**, *15*, 2331.
(122) Fritze, C.; Erker, G.; Fröhlich, R. *J. Organomet. Chem.* **1995**, *501*, 41.

372.18669. Anal. Calcd (%) for $C_{29}H_{24}$: C 93.51, H 6.49. Found: C 93.33, H 6.50.

1,4-Difluoren-9-ylbutane (5a). In a 500 mL three-necked round-bottomed flask fitted with a mechanical stirrer, reflux condenser (Liebig condenser), and a metal bath, fluorene (100 g, 602 mmol) and potassium hydroxide (33.6 g, 600 mmol) were suspended in 1,4-butanediol (357 g, 350 mL, 3.96 mol) and stirred at 250 °C for 6 h. During the first hour unreacted fluorene sublimed in the Liebig condenser and was mechanically returned into the reaction mixture. After the reaction time the mixture was allowed to come to 80 °C and then poured into water (1.5 L) while stirring. After standing overnight the white solid that precipitated was separated via suction filtration and washed thoroughly with water (5 × 60 mL). The white solid was refluxed twice in MeOH and hot filtered to remove 4-(9*H*-fluoren-9-yl)butan-1-ol (**5c**) byproduct. The residual solid was purified via short column chromatography (silica, 10 × 10 cm; eluent: cyclohexane/ethyl acetate (95:5)) to afford **5a** as a white solid (51 g, 45%).

Mp 161.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, ^3J = 7.5 Hz, 4 H, *CH*, ar), 7.41 (dd, ^3J = 7.5 Hz, J = 0.8 Hz, 4 H, *CH*, ar), 7.33 (tt, ^3J = 7.3 Hz, J = 0.8 Hz, 4 H, *CH*, ar), 7.26 (dt, ^3J = 7.4 Hz, J = 1.2 Hz, 4 H, *CH*, ar), 3.88 (t, ^3J = 5.8 Hz, 2 H, *H*Flu), 1.94−1.87 (m, 4H, Flu-CH_2), 1.13−1.08 (m, 4H, CH_2(butyl)); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ 147.4, 141.1, 126.8, 126.7, 124.3, 119.7, 47.4, 32.8, 25.9; HRMS calcd for $C_{30}H_{26}$ 386.2034, found 386.20289. Anal. Calcd (%) for $C_{30}H_{26}$: C 93.22, H 6.78. Found: C 93.02, H 6.73.

1,5-Difluoren-9-ylpentane (6a). In a 500 mL three-necked round-bottomed flask fitted with a mechanical stirrer, reflux condenser (Liebig condenser) and a metal bath, fluorene (100 g, 602 mmol) and KOH (33.6 g, 600 mmol) were suspended in 1,5-pentanediol (368 g, 370 mL, 3.53 mol) and stirred at 250 °C for 6 h. During the first hour unreacted fluorene sublimed in the Liebig condenser and was mechanically returned into the reaction mixture. After 6 h the mixture was allowed to come to 80 °C and poured into water (1.5 L) while stirring. The product was extracted with MTBE (3 × 400 mL). The combined organic phases were dried over $MgSO_4$ and filtered, and the volatiles were removed *in vacuo*. The residue was adsorbed on silica gel (100 g) and purified via column chromatography (silica, 20 × 10 cm; eluent: cyclohexane/ethyl acetate (95:5)) to afford **6a** as a white solid (55 g, 47%).

Mp 82.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, ^3J = 7.6 Hz, 4 H, *CH*, ar), 7.43 (d, ^3J = 7.6 Hz, 4 H, *CH*, ar), 7.32 (t, ^3J = 7.6 Hz, 4 H, *CH*, ar), 7.26 (dt, ^3J = 7.5 Hz, J = 1.2 Hz,4 H, *CH*, ar), 3.90 (t, ^3J = 5.8 Hz, 2 H, Flu-C*H*), 1.93−1.87 (m, 4 H, Flu-CH_2), 1.23−1.16 (m, 2 H, Flu-CH$_2$-CH$_2$-CH_2), 1.10−1.02 (m, 4 H, Flu-CH$_2$-CH_2) ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ 147.5, 141.1, 126.8, 126.7, 124.3, 119.8, 47.3, 32.9, 30.2, 25.2; HRMS calcd for $C_{31}H_{28}$ 400.2191, found 400.21767. Anal. Calcd (%) for $C_{31}H_{28}$: C 92.95, H 7.05. Found: C 92.73, H 7.04.

α,α′-Difluoren-9-yl-*o*-xylene (7a). In a 500 mL Schlenk flask fluorene (20 g, 120 mmol) was dissolved in dry THF (350 mL). *n*BuLi (50 mL, 2.5 M solution in hexane, 125 mmol) was added to the stirred solution at −50 °C. The resulting orange solution was stirred at this temperature for 5 min, allowed to come to ambient temperature, and stirred for an additional 60 min. After recooling to −50 °C a solution of α,α′-dibromo-*o*-xylene (16.5 g, 62.6 mmol in 50 mL of dry THF) was syringed into the stirred solution within 2 min. The reaction mixture was allowed to come to ambient temperature, stirred for 1 h, and then quenched with water (100 mL). The organic layer was separated, washed with saturated $Na_2S_2O_3$ solution (100 mL) and water (100 mL), dried over $MgSO_4$, and filtered, and the volatiles were removed *in vacuo* to afford crude **7a** as a yellow, oily residue. The residue was taken up in xylene (200 mL); after a few minutes a white precipitate was formed. The resulting suspension was stirred at ambient temperature for 1 h, and the solid was isolated via suction filtration, washed with xylene (2 × 20 mL), and dried *in vacuo* (90 °C, 1 mbar), affording **7a** (11.5 g, 44%) as pure white crystals.

Mp 165.3 °C (xylene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, ^3J = 7.6 Hz, 4 H, C*H*, ar), 7.38 − 7.31 (m, 4 H, C*H*, ar), 7.29 (t, ^3J = 7.6 Hz, 4 H, C*H*, ar), 7.13 (dt, ^3J = 7.5 Hz, J = 1.1 Hz,4 H, CH, ar), 7.01−6.98 (m, 4 H, C*H*, ar), 4.10 (t, ^3J = 8.0 Hz, 2 H, *H*Flu), 2.99 (d, ^3J = 8.0 Hz, 4 H, C$H_{2(benzyl)}$); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ 146.8, 140.6, 138.8, 130.8, 127.1, 126.6, 124.8, 119.8, 48.1, 37.2; HRMS calcd for $C_{34}H_{26}$ 434.2034, found 434.20710. Anal. Calcd (%) for $C_{34}H_{26}$: C 93.97, H 6.03. Found: C 93.78, H 6.03.

α,α′-Difluoren-9-yl-*p*-xylene (8a). In a 1 L Schlenk flask fluorene (20 g, 120 mmol) was dissolved in dry THF (350 mL). *n*BuLi (50 mL, 2.5 molar solution in hexane, 125 mmol) was added to the stirred solution at −50 °C. The resulting orange solution was stirred at that temperature for 5 min, allowed to come to ambient temperature and stirred for additional 1 h. After recooling to −50 °C a solution of α,α′-dibromo-*p*-xylene (16.5 g, 62.6 mmol in 100 mL dry THF) was syringed into the stirred solution within 5 min. The reaction mixture was allowed to come to ambient temperature, stirred for 1 h and then quenched with water (100 mL) and MTBE (100 mL). The precipitated solid was separated via suction filtration and dissolved in hot chloroform (1 L). The product containing solution was transferred into a wide necked Erlenmeyer flask and left standing. Slow evaporation of the solvent (to a volume of 600 mL) at ambient temperature within 4 days afforded **8a** (17.6 g, 67%) as pure white crystals. The ^{1}H- and ^{13}C NMR spectra are identical to those in the literature.[123]

Mp 244.4 °C (chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, ^3J = 7.5 Hz, 4 H, *CH*, ar), 7.35 (t, ^3J = 7.5 Hz, 4 H, *CH*, ar), 7.23 (dt, ^3J = 7.5 Hz, J = 1.0 Hz,4 H, *CH*, ar), 7.18 (d, ^3J = 7.5 Hz, 4 H, *CH*, ar), 7.09 (s, 4 H, C*H*, ar$_{(benzyl)}$), 4.23 (t, ^3J = 7.5 Hz, 2 H, Flu-C*H*), 3.12 (d, ^3J = 7.5 Hz, 4 H, CH_2) ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ 146.8, 140.9, 137.6, 129.4, 127.1, 126.6, 124.9, 119.8, 48.7, 39.7; HRMS calcd for $C_{34}H_{26}$: 434.2034, found 434.20478. Anal. Calcd (%) for $C_{34}H_{26}$: C 93.97, H 6.03; found: C 93.69, H 6.10.

General Procedure for Synthesis of Phosphines 2b−8b. In a 500 mL Schlenk flask the respective difluorene **2a**−**8a** (1.0 equiv) was dissolved in dry THF (150 mL). At 0 °C (ice/water cooling) *n*BuLi (2.0 equiv, 2.5 M solution in hexane) was added dropwise within 2 min, and the resulting red reaction mixture was stirred for an additional 2 h at ambient temperature. Then the mixture was cooled to 0 °C and Cy_2PCl (∼2.0 equiv) was added until the red color of the solution disappeared. After stirring for 10 min at ambient temperature aqueous HBF_4 (48%, 2.5 equiv) was added while stirring. Additional HBF_4 (2 M in water, 25 mL) and MTBE (100 mL) were added to precipitate product. Filtration and drying *in vacuo* (1 mbar, 60 °C) afforded the respective phosphonium salts **2b**−**8b** as white powders in 58−95% yield.

1,1-Bis(9-(dicyclohexylphosphinotetrafluoroborate)fluorenyl)methane (2b). Difluorenylmethane (**2a**) (2.5 g, 7.26 mmol), *n*BuLi (5.81 mL, 14.5 mmol), and Cy_2PCl (3.38 g, 14.5 mmol) afforded **2b** (3.9 g, 58%) as a white powder. *Note*: Reaction temperature after addition of Cy_2PCl was raised to 50 °C for 20 min. Mp 202 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, ^3J = 7.6 Hz, 4 H, *CH*, ar), 7.77 (t, ^3J = 7.6 Hz, 4 H, *CH*, ar), 7.56 (t, ^3J = 7.6 Hz, 4 H, *CH*, ar), 7.47 (dt, ^3J = 7.6 Hz, J = 1.0 Hz, 4 H, *CH*, ar), 6.69 (d, ^1J = 487 Hz, 2 H, P*H*), 5.22 (d, ^3J*(P,H)* = 16.7 Hz, 2 H, CH_2), 2.23−2.11 (m, 4 H, PC*H*), 1.91−1.77 (m, 8 H, Cy-CH_2), 1.76−1.61 (m, 8 H, Cy-CH_2), 1.58−1.39 (m, 8 H, Cy-CH_2), 1.32−1.11 (m, 16 H, Cy-CH_2); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ 141.6 (d, *J(P,C)* = 4.6 Hz), 135.9 (d, *J(P,C)* = 5.3 Hz), 130.0 (d, *J(P,C)* = 2.1 Hz), 128.8 (d, *J(P,C)* = 2.2 Hz), 125.6, (d, *J(P,C)* = 3.4 Hz), 121.2, 36.4 (d, *J(P,C)* = 38.5 Hz), 28.5, 28.2, 27.5 (d, *J(P,C)* =

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10.0 Hz), 27.5 (d, *J(P,C)* = 2.2 Hz), 26.4 (d, *J(P,C)* = 13.3 Hz), 26.1 (d, *J(P,C)* = 13.2 Hz), 24.7; $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 28.7; ^{31}P NMR (202.5 MHz, $CDCl_3$) δ 28.7 (d, *J(P,H)* = 485 Hz); MS (70 eV) *m/z* 737.6 $[M - H^+]^+$, 541.3 $[M - PHCy_2]^+$, 363.3 $[FluPHCy_2 + H]^+$.

1,2-Bis(9-(dicyclohexylphosphinotetrafluoroborate)fluorenyl)methane (3b). 1,2-Difluorenylethane (**3a**) (3.03 g, 8.44 mmol), *n*BuLi (6.75 mL, 16.9 mmol), and Cy_2PCl (3.93 g, 16.9 mmol) afforded **3b** (6.6 g, 84%) as a white powder. Mp 262.5 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, ^{3}J = 7.6 Hz, 4 H, *CH*, ar), 7.61 (t, ^{3}J = 7.6 Hz, 4 H, *CH*, ar), 7.56−7.47 (m, 8 H, *CH*, ar), 6.29 (d, ^{1}J = 477 Hz, 2 H, P*H*), 2.14−2.03 (m, 4 H, PC*H*), 1.98−1.94 (m, 4 H, Flu-CH_2), 1.65−1.51 (m, 16 H, Cy-CH_2), 1.39−1.31 (m, 4 H, Cy-CH_2), 1.20−0.90 (m, 20 H, Cy-CH_2); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 141.1 (d, *J(P,C)* = 4.1 Hz), 138.7 (d, *J(P,C)* = 2.5 Hz), 130.8, 129.5, 125.3, (d, *J(P,C)* = 2.8 Hz), 121.4, 51.0 (d, *J(P,C)* = 34.4 Hz), 31.3, 31.0, 29.2 (d, *J(P,C)* = 2.8 Hz), 28.1 (d, *J(P,C)* = 10.6 Hz), 27.9 (d, *J(P,C)* = 2.8 Hz), 26.5 (d, *J(P,C)* = 13.1 Hz), 26.3 (d, *J(P,C)* = 13.1 Hz), 24.8; $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 33.1; ^{31}P NMR (202.5 MHz, $CDCl_3$) δ 33.1 (d, *J(P,H)* = 477 Hz); MS (70 eV) *m/z* 751.6 $[M - H^+]^+$, 553.4 $[M - PHCy_2 - H^+]^+$.

1,3-Bis(9-(dicyclohexylphosphinotetrafluoroborate)fluorenyl)propane (4b). 1,3-Difluorenylpropane (**4a**) (2.5 g, 6.71 mmol), *n*BuLi (5.37 mL, 13.42 mmol), and Cy_2PCl (3.12 g, 13.42 mmol) afforded **4b** (4.99 g, 79%) as a white powder. Mp 248.9−250.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, ^{3}J = 7.6 Hz, 4 H, *CH*, ar), 7.62 (d, ^{3}J = 7.6 Hz, 4 H, *CH*, ar), 7.46 (t, ^{3}J = 7.6 Hz, 4 H, *CH*, ar), 7.37 (dt, ^{3}J = 7.6 Hz, *J* = 1.0 Hz, 4 H, *CH*, ar), 6.09 (d, ^{1}J = 473 Hz, 2 H, P*H*), 2.63−2.54 (m, 4 H, Flu-CH_2), 2.28−2.16 (m, 4 H, Cy-C*H*), 1.78−1.56 (m, 16 H, Cy-CH_2), 1.47−1.38 (m, 4 H, Cy-CH_2), 1.29−0.95 (m, 20 H, Cy-CH_2), 0.15−0.07 (m, 2 H, CH_2 (propyl)); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 141.1 (d, *J(P,C)* = 4.3 Hz), 139.3 (d, *J(P,C)* = 3.3 Hz), 130.1, 129.1, 125.3, (d, *J(P,C)* = 2.8 Hz), 121.0, 51.9 (d, *J(P,C)* = 32.9 Hz), 32.3, 31.1, 30.9, 29.6 (d, *J(P,C)* = 3.2 Hz), 28.1 (d, *J(P,C)* = 3.2 Hz), 26.6 (d, *J(P,C)* = 13.0 Hz), 26.3 (d, *J(P,C)* = 12.7 Hz), 24.9; $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$) δ 37.3; ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 37.3 (d, *J(P,H)* = 473 Hz); MS (70 eV) *m/z* 765.6 $[M - H^+]^+$, 568.3 $[M - PHCy_2]^+$.

1,4-Bis(9-(dicyclohexylphosphinotetrafluoroborate)fluorenyl)butane (5b). 1,4-Difluorenylbutane (**5a**) (2.58 g, 6.68 mmol), *n*BuLi (5.34 mL, 13.4 mmol), and Cy_2PCl (3.11 g, 13.4 mmol) afforded **5b** (5.64 g, 88%) as a white powder. Mp 262.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99−7.94 (m, 4 H, *CH*, ar), 7.78−7.74 (m, 4 H, *CH*, ar), 7.50−7.46 (m, 8 H, C*H*, ar), 6.29 (d, ^{1}J = 472 Hz, 2 H, P*H*), 2.88−2.82 (m, 4 H, Flu-CH_2), 2.53−2.42 (m, 4 H, PC*H*), 1.96−1.89 (m, 4 H, Cy-CH_2), 1.79−1.71 (m, 4 H, Cy-CH_2), 1.69−1.62 (m, 8 H, Cy-CH_2), 1.58−1.51 (m, 4 H, Cy-CH_2), 1.40−1.20 (m, 12 H, Cy-CH_2), 1.12−1.01 (m, 8 H, Cy-CH_2), 0.51−0.46 (m, 4H, CH_2 (butyl)); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 141.7 (d, *J(P,C)* = 4.7 Hz), 140.3 (d, *J(P,C)* = 2.7 Hz), 130.3, 129.5, 126.1, (d, *J(P,C)* = 2.8 Hz), 121.0, 52.4 (d, *J(P,C)* = 33.3 Hz), 31.5 (d, *J(P,C)* = 8.7 Hz), 31.2, 30.1 (d, *J(P,C)* = 3.3 Hz), 28.7 (d, *J(P,C)* = 3.3 Hz), 27.0 (d, *J(P,C)* = 13.2 Hz), 26.6 (d, *J(P,C)* = 12.4 Hz), 25.5, 21.2 (d, *J(P,C)* = 11.2 Hz); $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 37.2; ^{31}P NMR (202.5 MHz, $CDCl_3$) δ 37.2 (d, *J(P,H)* = 471 Hz); MS (70 eV) *m/z* 779.6 $[M - H^+]^+$, 795.6 $[MO - H^+]^+$, 597.5 $[MO - PHCy_2 - H^+]^+$.

1,5-Bis(9-(dicyclohexylphosphinotetrafluoroborate)fluorenyl)pentane (6b). 1,5-Difluorenylpentane (**6a**) (2.40 g, 6.00 mmol), *n*BuLi (4.80 mL, 12.0 mmol), and Cy_2PCl (2.78 g, 12.0 mmol) afforded **6b** (4.63 g, 80%) as a white powder. Mp 165.1−170.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, ^{3}J = 7.0 Hz, 4 H, *CH*, ar), 7.81 (dd, ^{3}J = 7.0 Hz, *J* = 1.6 Hz, 4 H, *CH*, ar), 7.54−7.47 (m, 8 H, *CH*, ar), 6.43 (d, ^{1}J = 475 Hz, 2 H, P*H*), 2.75−2.64 (m, 4 H, Flu-CH_2), 2.43−2.31 (m, 4 H, Cy-C*H*), 1.93−1.85 (m, 4 H, Cy-CH_2), 1.76−1.69 (m, 4 H, Cy-CH_2), 1.69−1.60 (m, 8 H, Cy-CH_2), 1.56−1.48 (m, 4 H, Cy-CH_2), 1.35−1.26 (m, 8 H, Cy-CH_2), 1.23−1.01 (m, 14 H, Cy-CH_2 and Flu-$CH_2CH_2CH_2$), 0.57−0.48 (m, 4 H, CH_2 (pentyl)); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 141.3 (d, *J(P,C)* = 4.6 Hz), 140.2 (d, *J(P,C)* = 2.6 Hz), 130.1, 129.2, 125.5, (d, *J(P,C)* = 3.1 Hz), 120.8, 52.2 (d, *J(P,C)* = 33.1 Hz), 33.6, 31.1, 30.8, 29.6 (d, *J(P,C)* = 3.3 Hz), 28.2 (d, *J(P,C)* = 3.7 Hz), 26.6 (d, *J(P,C)* = 13.1 Hz), 26.3 (d, *J(P,C)* = 12.6 Hz), 25.0, 22.1 (d, *J(P,C)* = 9.8 Hz); $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$) δ 34.6; ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 34.6 (d, *J(P,H)* = 475 Hz); MS (70 eV) *m/z* 793.6 $[M - H^+]^+$, 809.6 $[MO - H^+]^+$, 596.5 $[M - PHCy_2 - H^+]^+$.

α,α′-Bis(9-(dicyclohexylphosphinotetrafluoroborate)fluorenyl)-*o*-xylene (7b). α,α′-Difluoren-9-yl-*o*-xylene (**7a**) (3.02 g, 6.90 mmol), *n*BuLi (5.53 mL, 13.8 mmol), and Cy_2PCl (3.21 g, 13.8 mmol) afforded **7b** (5.5 g, 79%) as a white powder. Mp 250.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, ^{3}J = 7.0 Hz, 4 H, *CH*, ar), 7.67−7.64 (m, 4 H, *CH*, ar), 7.51−7.45 (m, 8 H, *CH*, ar), 6.65 (d, ^{1}J = 474 Hz, 2 H, P*H*), 6.12−6.07 (m, 2 H, *CH*, ar), 5.64−5.58 (m, 2 H, *CH*, ar), 4.13 (d, $^{3}J(P,H)$ = 7.4 Hz, 4 H, Flu$CH_{2benzyl}$), 2.44−2.32 (m, 4 H, Cy-C*H*), 2.10−2.02 (m, 4 H, Cy-CH_2), 1.85−1.77 (m, 4 H, Cy-CH_2), 1.73−1.63 (m, 8 H, Cy-CH_2), 1.61−1.45 (m, 8 H, Cy-CH_2), 1.41−1.30 (m, 4 H, Cy-CH_2), 1.29−1.09 (m, 12 H, Cy-CH_2); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 141.3 (d, *J(P,C)* = 5.0 Hz), 139.5 (d, *J(P,C)* = 3.5 Hz), 131.7 (d, *J(P,C)* = 13.6 Hz), 130.3, (d, *J(P,C)* = 1.8 Hz), 129.0, (d, *J(P,C)* = 1.8 Hz), 128.1, 125.7 (d, *J(P,C)* = 3.3 Hz), 125.6, 121.0, 53.4 (d, *J(P,C)* = 32.0 Hz), 34.8 (d, *J(P,C)* = 2.2 Hz), 31.2 (d, *J(P,C)* = 34.4 Hz), 29.9 (d, *J(P,C)* = 3.4 Hz), 28.1 (d, *J(P,C)* = 3.1 Hz), 26.7 (d, *J(P,C)* = 12.8 Hz), 26.2 (d, *J(P,C)* = 12.7 Hz), 25.0; $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 36.9; ^{31}P NMR (202.5 MHz, $CDCl_3$) δ 36.9 (d, *J(P,H)* = 474 Hz); MS (70 eV) *m/z* 827.7 $[M - H^+]^+$, 630.5 $[M - PHCy_2]^+$.

α,α′-Bis(9-(dicyclohexylphosphinotetrafluoroborate)fluorenyl)-*p*-xylene (8b). α,α′-Difluoren-9-yl-*p*-xylene (**8a**) (1.5 g, 3.45 mmol), *n*BuLi (2.76 mL, 6.90 mmol), and Cy_2PCl (1.60 g, 6.90 mmol) afforded **8b** (3.3 g, 95%) as a white powder. Mp 256.8 °C; ^{1}H NMR (500 MHz, CD_3CN) δ 7.78 (d, ^{3}J = 7.6 Hz, 4 H, *CH*, ar), 7.71 (d, ^{3}J = 7.6 Hz, 4 H, *CH*, ar), 7.53 (t, ^{3}J = 7.6 Hz, 4 H, *CH*, ar), 7.41 (dt, ^{3}J = 7.6 Hz, *J* = 1.0 Hz, 4 H, *CH*, ar), 6.05 (d, ^{1}J = 463 Hz, 2 H, P*H*), 6.00 (s, 4 H, CH_{benzyl}, ar), 3.67 (d, $^{3}J(P,H)$ = 6.5 Hz, 4 H, Flu$CH_{2benzyl}$), 2.48−2.38 (m, 4 H, Cy-C*H*), 1.72−1.46 (m, 22 H, Cy-CH_2), 1.24−0.98 (m, 22 H, Cy-CH_2); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_3CN) δ 142.0 (d, *J(P,C)* = 5.0 Hz), 139.5 (d, *J(P,C)* = 3.0 Hz), 131.7 (d, *J(P,C)* = 13.9 Hz), 130.9, (d, *J(P,C)* = 1.8 Hz), 129.7, 128.8, (d, *J(P,C)* = 1.8 Hz), 126.5, (d, *J(P,C)* = 3.3 Hz), 122.0, 53.2 (d, *J(P,C)* = 32.3 Hz), 39.0, 31.6 (d, *J(P,C)* = 34.2 Hz), 29.7 (d, *J(P,C)* = 3.4 Hz), 28.7 (d, *J(P,C)* = 3.9 Hz), 26.9 (d, *J(P,C)* = 13.4 Hz), 26.7 (d, *J(P,C)* = 12.7 Hz), 25.2; $^{31}P\{^{1}H\}$ NMR (121.4 MHz, CD_3CN) δ 37.4; ^{31}P NMR (121.4 MHz, CD_3CN) δ 37.4 (d, *J(P,H)* = 464 Hz); MS (70 eV) *m/z* 827.7 $[M - H^+]^+$, 630.5 $[M - PHCy_2]^+$.

General Cross-Coupling Screening Protocols. Buchwald−Hartwig Amination of Aryl Halides with 3,5-Dimethylaniline. The aryl halide (1 mmol), amine (1.5 mmol), NaO*t*Bu (2 mmol), $Pd(OAc)_2$ (1.12 mg, 0.005 mmol, 0.5 mol %), and the respective ligand (**2b**−**8b**) (0.01 mmol, 1 mol %) and dry toluene (5 mL) were placed in a Schlenk tube under an Ar atmosphere. Heptadecane (200 μL) was added as an internal standard, and the reaction mixture was stirred at 120 °C for 12 h in an Al block. After cooling to RT, the reaction mixture was analyzed via GC. For the isolation of the amination product the reaction mixture was diluted with diethyl ether (15 mL) and washed with water (10 mL). Then the organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*.

The product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate/NEt_3, 9:1:1) to afford (3,5-dimethylphenyl)-*p*-tolylamine as colorless needles.

Suzuki Coupling of *p*-Chloroacetophenone with Tolylboronic Acid. (a) Preparation of the catalyst stock solution: [Na_2PdCl_4](0.025 mmol), the respective ligand (**2b**−**8b**) (0.05 mmol), and Cs_2CO_3 (66 mg, 0.2 mmol) were placed in a Schlenk tube and evacuated and backfilled with argon three times. Dioxane (5.0 mL) was added, and the mixture was stirred at 60 °C for 2 h until the solution turned off-white. This stock solution has a concentration of 0.005 mol %/(mL·mmol aryl halide).

(b) Cross-coupling reaction: *p*-Tolylboronic acid (204 mg, 1.5 mmol) and Cs_2CO_3 (652 mg, 2.0 mmol) were placed in a 25 mL Schlenk tube, evacuated, and backfilled with argon three times. Dioxane (5 mL), *p*-chloroacetophenone (129.8 μL, 1 mmol), and the respective volume of the catalyst stock solution (1 mL of catalyst stock solution effects a cat. loading of 0.5 mol % per mmol of arylchloride) and heptadecane (200 μL) as an internal standard were added, and the reaction mixture was stirred for 15 h at 80 °C in an Al block. After cooling to RT, the reaction mixture was analyzed via GC. For isolation of the coupling product the reaction mixture was diluted with diethyl ether (15 mL) and washed with water (10 mL). Then the organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 9:1) to afford 1-(4′-methylbiphenyl-4-yl)ethanone as white crystals.

Sonogashira Reaction of 4-Bromotoluene with Phenylacetylene. Dry HN*i*Pr_2 (10 mL), 4-bromotoluene (1.71 g, 1.22 mL, 10 mmol), and phenylacetylene (1.12 g, 1.21 mL, 11 mmol) were placed in a Schlenk tube and deaerated twice via freeze and thaw technique. Then the catalyst (0.00667 mol % Pd) was added in the given concentration as a ready-made mixture of [Na_2PdCl_4]/ligand (phosphonium salt)/CuI (4:4:3 or 4:8:3), respectively, under argon. The reaction mixture was stirred for 24 h at 50 °C in an Al block. After cooling to RT, the reaction mixture was analyzed via GC, and quantitative analysis was performed via external calibration by calculating the response factors of pure samples of starting material (4-bromotoluene) and product. For isolation of the coupling product the reaction mixture was diluted with diethyl ether (15 mL) and washed with water (2 × 10 mL), then the organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was isolated by column chromatography (silica gel, cyclohexane/ethyl acetate, 100:2) to afford 1-methyl-4-phenylethynylbenzene as white crystals.

(3,5-Dimethylphenyl)-*p*-tolylamine. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, ^3J = 8.2 Hz, 2 H, C*H*, ar), 7.03 (d, ^3J = 8.2 Hz, 2 H, C*H*, ar), 6.69 (s, 2 H, C*H*, ar), 6.59 (s, 1 H, C*H*, ar), 5.53 (s (br), 1 H, N*H*), 2.35 (s, 3 H, CH_3), 2.30 (s, 6 H, CH_3); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ 144.0, 140.6, 139.0, 130.8, 129.9, 122.3, 119.1, 114.8, 21.5, 20.7; ^{15}N NMR (50.69 MHz, $CDCl_3$) δ −294.6; HRMS calcd for $C_{15}H_{17}N$ 211.1361, found 211.13511. Anal. Calcd (%) for $C_{15}H_{17}N$: C 85.26, H 8.11, N 6.63. Found: C 84.89, H 8.08, N 6.64.

1-(4′-Methylbiphenyl-4-yl)ethanone. Mp 121.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, ^3J = 8.5 Hz, 2 H, C*H*, ar), 7.66 (d, ^3J = 8.5 Hz, 2 H, C*H*, ar), 7.52 (d, ^3J = 8.2 Hz, 2 H, C*H*, ar),7.27 (d, ^3J = 8.2 Hz, 2 H, C*H*, ar), 2.62 (s, 3 H, (CO)CH_3), 2.40 (s, 3 H, CH_3); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ 197.7, 145.7, 138.2, 137.0, 135.6, 129.7, 128.9, 127.1, 127.0, 26.6, 21.2; HRMS calcd for $C_{18}H_{14}N_2$ 210.1044, found 210.10444. Anal. Calcd (%) for $C_{15}H_{14}O$: C 85.68, H 6.71. Found: C 85.60, H 6.74. The ^{1}H and ^{13}C NMR spectra were identical to those in the literature.[124]

1-Methyl-4-phenylethynylbenzene. Mp 79.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, ^3J = 7.8 Hz, J = 1.9 Hz, 2 H, C*H*, ar), 7.42 (d, ^3J = 8.0 Hz, 2 H, C*H*, ar), 7.35−7.29 (m, 3 H, C*H*, ar), 7.15 (dd, ^3J = 8.0 Hz, J = 0.6 Hz, 2 H, C*H*, ar), 2.36 (s, 3 H, CH_3); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ 138.8, 132.0, 131.9, 129.5, 128.7, 128.5, 123.9, 120.6, 90.0, 89.1, 21.9; HRMS calcd for $C_{15}H_{12}$ 192.0939, found 192.09198. Anal. Calcd (%) for $C_{15}H_{12}$: C 93.71, H 6.29. Found: C 93.58, H 6.28. The ^{1}H and ^{13}C NMR spectra were identical to those in the literature.[125]

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Supporting Information Available: Full set of ^{1}H, ^{13}C, ^{31}P, and ^{15}N NMR spectra of all compounds synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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