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9-Fluorenylphosphines for the Pd-Catalyzed Sonogashira, Suzuki, and Buchwald–Hartwig Coupling Reactions in Organic Solvents and Water

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Abstract: The lithiation/alkylation of fluorene leads to various 9-alkyl-fluorenes (alkyl = Me, Et, *i*Pr, -Pr, -$C_{18}H_{25}$) in >95% yields, for which lithiation and reaction with R_2PCl (R = Cy, *i*Pr, *t*Bu) generates 9-alkyl, 9-PR_2-fluorenes which constitute electron-rich and bulky phosphine ligands. The in-situ-formed palladium–phosphine complexes ([Na_2PdCl_4], phosphonium salt, base, substrates) were tested in the Sonogashira, Suzuki, and Buchwald–Hartwig reactions of aryl chlorides and aryl bromides in organic solvents. The Sonogashira coupling of aryl chlorides at 100–120 °C leads to >90% yields with 1 mol% of Pd catalyst. The Suzuki coupling of aryl chlorides typically requires 0.05 mol% of Pd catalyst at 100 °C in dioxane for quantitative product formation. To carry out "green" cross-coupling reactions in water, 9-ethylfluorenyldicyclohexylphosphine was reacted in sulphuric acid to generate the respective 2-sulfonated phosphonium salt. The Suzuki coupling of activated aryl chlorides by using this water-soluble catalyst requires only 0.01 mol% of Pd catalyst, while a wide range of aryl chlorides can be quantitatively converted into the respective coupling products by using 0.1–0.5 mol% of catalyst in pure water at 100 °C. Difficult substrate combinations, such as naphthylboronic acid or 3-pyridylboronic acid and aryl chlorides are coupled at 100 °C by using 0.1–0.5 mol% of catalyst in pure water to obtain the respective *N*-heterocycles in quantitative yields. The copper-free aqueous Sonogashira coupling of aryl bromides generates the respective tolane derivatives in >95% yield.

Keywords: Buchwald–Hartwig amination · palladium · phosphines · Sonogashira coupling · Suzuki coupling · water

Introduction

Trialkylphosphines with bulky substituents are highly useful ligands for palladium-complex catalysts in various types of cross-coupling reactions of the Suzuki,[1–11] Sonogashira,[12–21] Heck,[22–27] Buchwald–Hartwig amination[28–34] and ether formation,[35] Negishi,[36] Stille,[37–39] Hiyama,[40] Kumada,[41] α-arylation,[42,43] and carbonylation type.[44] The main reasons for the favorable catalytic properties of trialkylphosphine–palladium complexes are the electron-richness and the steric bulk of trialkylphosphine ligands, which favor the formation of low-coordinate and highly active Pd complexes, possibly of the L_1Pd type,[45–48] also observed with N-heterocyclic carbenes as Pd ligands in cross-coupling reactions.[49] Prominent examples of trialkyl phosphines are PCy_3, $PtBu_3$, and ligands of the Ad_2PR (Ad = 1-adamantyl, R = CH_2Ph, *n*Bu)[50] type. $PtBu_3$, especially, is highly useful; its utility for a wide range of different coupling reactions has been established.[51]

A significant disadvantage of Pd catalysts based on bulky trialkylphosphines, primarily $PtBu_3$, is the lack of flexibility in the design of ligands and catalysts. Detailed structural and electronic modifications (catalyst fine-tuning) are difficult to realize and this could be the reason why in cross-coupling chemistry this class of ligands was "leader of the pack" only about five years ago. Today numerous other specialized and more powerful catalysts, often based on phosphines and *N*-heterocyclic carbenes as ligands for Pd[49,52–61] are available. The advantages of a highly variable ligand backbone are demonstrated convincingly by the enormous success of Buchwald-type biphenyl-based phosphines,[62–64] as evidenced by the excellent performance of the respective Pd complexes in numerous coupling reactions.[65,66] The high level of sophistication concerning the fine-tuning of steric and electronic properties of such ligands was recently demonstrated by Buchwald et al. for Suzuki and amination reactions.[67–69]

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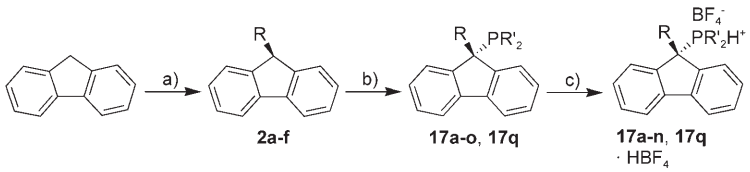
However, as crucial properties for good ligands, such as electron-richness and efficient σ-donation, are perfectly met in trialkyphosphines, we became interested in developing novel phosphines, lacking the disadvantages of P*t*Bu$_3$. In this vain, we want to demonstrate here the synthesis of a new class of trialkylphosphines based on the 9-fluorenyl group and the application of their Pd-complexes in Sonogashira, Suzuki, and Buchwald–Hartwig coupling reactions.



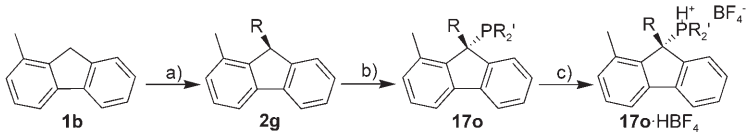
Scheme 1. Reagents and conditions: a) *n*BuLi, RX, THF, −60 °C; b) *n*BuLi, R′$_2$PCl, Et$_2$O, −60 °C; c) HBF$_4$·Et$_2$O.

Results and Discussion

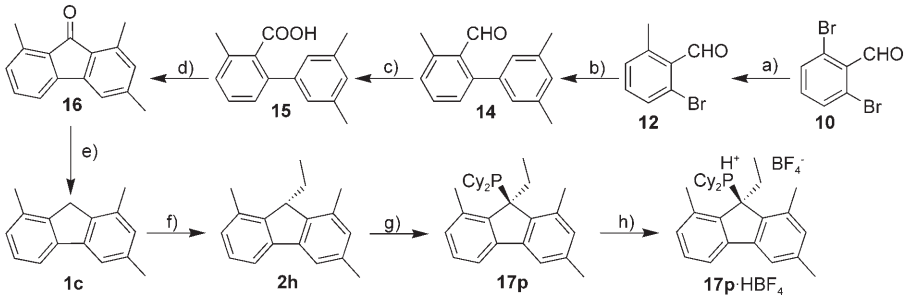
Synthesis of 9-fluorenyldialkylphosphines: The combination of 9-fluorenyl substituents with R$_2$P groups (Figure 1) in the corresponding phosphines appears to have numerous advantages: 1) a 9-fluorenyl group acts as an electron-rich alkyl substituent, 2) due to the formation of a resonance-stabilized anion, the 9-position is easily and selectively deprotonated and reacts smoothly as a soft nucleophile, 3) fluorenone is an umpoled synthon for the 9-fluorenyl group, 4) the close proximity of 6π-systems facilitates the stabilization of low-coordinate Pd species, 5) substituents at the 1,8-position allow the modulation of the steric bulk close the phosphorous donors, 6) the 2,7-positions allow the easy introduction of various functional groups.

Only a few fluorenyl-based trialkyphosphines have been described in the literature and none of them have been utilized in catalysis.[70,71] Simple (no additional substituents) 9-substituted fluorenylphosphines are prepared (Scheme 1) by reactions of the deprotonated fluorene (*n*BuLi) with various alkyl halides (MeI, EtI, *i*PrI, PhCH$_2$Cl, C$_{18}$H$_{37}$Br) to selectively introduce alkyl groups into the 9-position in virtually quantitative yield. This first alkylation step is essential as our very first catalysis screens had revealed that phosphines with 9-R = H produce Pd-complex catalysts with modest activities in cross-coupling reactions. For the introduction of the R$_2$P group, the 9-alkylated fluorene is again deprotonated with *n*BuLi and reacted with various chlorophosphines (*i*Pr$_2$PCl, Cy$_2$PCl) to result in the respective phosphines, which are conveniently converted into the respective phosphonium salts for easier storage and handling.[72]

To further increase the steric bulk close to the phosphine donor, the related 1-methyl- and 1,8-dimethyl-substituted fluorenes were synthesized, as described below (Schemes 2 and 3; Table 10).



Scheme 2. Reagents and conditions: a) *n*BuLi, EtI; b) *n*BuLi, Cy$_2$PCl; c) HBF$_4$·Et$_2$O.



Scheme 3. Reagents and conditions: a) 1,3-propanediol, ZrCl$_4$; *n*BuLi, MeI, H$_2$SO$_4$; b) Pd(OAc)$_2$, SIMES, Cs$_2$CO$_3$, 3,5-Me$_2$-C$_6$H$_3$B(OH)$_2$, dioxane; c) NaClO$_2$, H$_2$O$_2$; d) H$_2$SO$_4$; e) HI, red P, propionic acid; f) *n*BuLi, EtI, THF, −60 °C; g) *n*BuLi, Cy$_2$PCl, Et$_2$O, −60 °C; h) HBF$_4$·Et$_2$O.

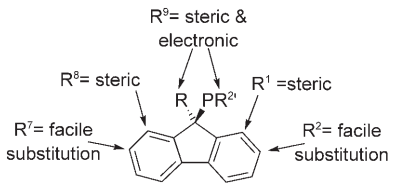


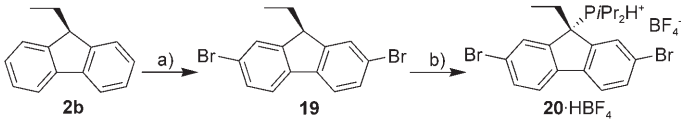
Figure 1. Variability of 9-fluorenylphosphines.

1-Methylfluorenone was prepared according to Mortier et al.,[73] deprotonated and reacted with ethyliodide to result in 1-methyl-9-ethylfluorene. Another sequence of deprotonation and quenching with Cy$_2$PCl gave the 9,9-disubstituted 1-methylfluorene, which was isolated as the respective phosphonium salt after protonation with HBF$_4$ (Scheme 2).

1,3,8-Trimethylfluorenone was prepared by a multistep reaction (Scheme 3). *Ortho* lithiation of 1,3-dibromobenzene by using the protocol of Servatovski et al. and subsequent

quenching with DMF resulted in 1,6-dibromobenzaldehyde,[74] which was protected as an acetal[75] and treated with *n*BuLi, followed by quenching the lithiated intermediate with methyliodide to yield the desired deprotected 1-bromo-6-methylbenzaldehyde in nearly quantitative yield. The Suzuki coupling of the bromo-aldehyde with 3,5-dimethylphenylboronic acid[76] afforded 3,3′,5′-trimethylbiphenylcarbaldehyde, which was converted into the respective carboxylic acid with $H_2O_2/NaClO_2$ by using the method of Dalcanale.[77] The resulting carboxylic acid gave 1,3,8-trimethylfluorenone in quantitative yield after condensation in concentrated sulfuric acid. By using the method of Carruthers,[78] the desired fluorene derivative was obtained by reduction of the fluorenone with HI and red phosphorous in propionic acid. Deprotonation of 1,3,8-trimethylfluorenone with *n*BuLi by using the standard protocol and quenching with ethyliodide gave the 9-ethylated fluorene derivative. Following the next deprotonation with *n*BuLi and reaction with Cy_2PCl, the respective 9-fluorenylphosphine was isolated as the phosphonium salt.

To demonstrate the variability of the 9-fluorenylphosphine chemistry, we have also synthesized a 2,7-dibromo derivative, which enables the easy introduction of additional functional groups at the 2,7-positions (Scheme 4).



Scheme 4. Reagents and conditions: a) bromine, $FeCl_3$, $CHCl_3$, 0 °C–RT; b) LDA, Et_2O, −60 °C, *i*Pr_2PCl, HBF_4·Et_2O.

Pd complexes of 9-fluorenyldialkylphosphines in the Sonogashira reaction: As a first test of the performance of the various Pd 9-fluorenylphosphine complexes, we determined the ton (turnover number) for the Sonogashira cross-coupling of phenylacetylene and 4-bromotoluene, applying the conditions described previously by us (Table 1).[17] In this first screen, the nature of the groups 9-R and 9-PR'_2 were varied. There are a number of phosphines (9-R = H, Ph, *i*Pr, *t*Bu) that display ton of smaller than 1000. This is significantly smaller than that of our reference phosphine Ad_2PBn (ton = 3200). Consequently, these phosphines were excluded from future catalytic test reactions. There are several phosphines for which the performance is comparable or superior to that of our reference system. The best 9-fluorenylphosphines are characterized by an unbranched alkyl group (R = Me, Et, etc.) at the 9-position, -P*i*Pr_2 or -PCy_2 units at the phosphorous atom.

It is known that sp^2–CH bonds close to the binding site of palladium can easily undergo CH-activation reactions,[79,80] which is less likely with sp^3–CH bonds.[68] With this in mind and with a view to further increasing the steric bulk of the phosphines, we synthesized two fluorenyl dialkylphosphines with methyl groups in the 1- or in the 1,8-position. To our surprise, the performance of the 1,8-Me_2-substituted 9-fluorenylphosphines **17p** is poor (ton = 850), while the related compound with a single methyl group at the 1-position shows a good performance (ton = 2600), even though it is not among the top performers. However, given the significantly increased effort required for the synthesis of the 1- and the 1,8-substituted fluorenes, we did not consider it worthwhile to study the performance of these phosphines in more detail.

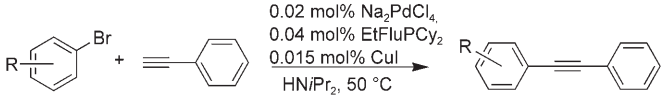
Table 1. Primary Sonogashira screen for the reaction of phenylacetylene and 4-bromotoluene by utilizing various phosphines.

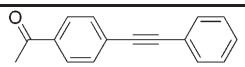
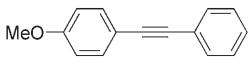
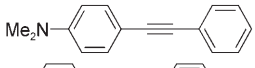
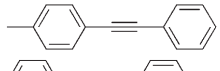
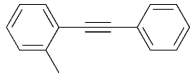
Phosphine	ton[a,b]
$C_{18}FluPCy_2$ (**17i**)	5900
$EtFluPCy_2$ (**17c**)	5600
$MeFluPCy_2$ (**17a**)	5600
$C_{18}FluPiPr_2$ (**17j**)	5500
Ad_2PBn	3600
$MeFluPiPr_2$ (**17b**)	3500
$EtFluPiPr_2$ (**17d**)	3200
1-Me-9-$EtFluPCy_2$ (**17o**)	2600
i$PrFluPCy_2$ (**17e**)	906
1,3,8-$Me_3EtFluPCy_2$ (**17p**)	850
i$PrFluPiPr_2$ (**17f**)	500
$HFluPtBu_2$ (**17h**)	330
$PhFluPiPr_2$ (**17q**)	250

[a] 4-Bromotoluene (10 mmol), phenylacetylene (11 mmol), *i*Pr_2NH (10 mL), 50 °C, 24 h. Catalyst: $[Na_2PdCl_4]$/ligand/CuI 4:8:3, catalyst mixture in *i*Pr_2NH_2Br, max. ton = 15000. [b] Average of two runs. Determined by the mass of the isolated ammonium salt.

Among the best phosphines in Table 1, $EtFluPCy_2$ **17c** was tested for the conversion of a number of aryl bromides (Table 2). Quantitative yields are possible with various acti-

Table 2. Sonogashira coupling of various aryl bromides with phenylacetylene[a] by using $EtFluPCy_2$·HBF_4.



Entry	Aryl bromide	Product	*t* [h]	Yield [%][b]
1	4-bromoacetophenone		3	≥99
2	4-bromoanisol		24	≥99
3	4-bromodimethylaniline		24	≥99
4	4-bromotoluene		24	≥99
5	2-bromotoluene		24	95

[a] Aryl bromide (10 mmol), phenylacetylene (11 mmol), HN*i*Pr_2 (10 mL), 50 °C, 24 h. Catalyst: $[Na_2PdCl_4]$ (0.02 mol %), phosphine (0.04 mol %), CuI (0.015 mol %), catalyst mixture in *i*Pr_2NH_2Br. [b] Average of two runs, determined by GC analysis (hexadecane as an internal standard) and by the mass of the isolated ammonium salt. Both analytical methods gave similar results.

vated and deactivated aryl bromides when applying 0.02 mol% of Pd complex. To test the limits of catalytic performance, the catalyst concentration was decreased to 0.0033% (Table 3). Even at such low catalyst concentrations, deactivated substrates can be converted in more than 80% yield with ton around 8.500 for sterically hindered substrates and up to 25.000 with deactivated substrates (4-bromoanisol). The turnover frequencies (tof) for two Sonogashira reactions applying MeFluP*i*Pr$_2$ were determined at 80°C: 2-bromotoluene and phenylacetylene at 0.0033 mol% Pd catalyst concentration yield tof of 3600 h^{-1}; the analogous reaction with 4-bromoanisol gives tof of 2650 h^{-1}.

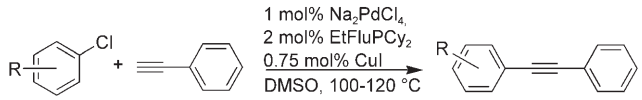
Table 3. Sonogashira coupling of aryl bromides. Determination of ton.[a]

Entry	Aryl bromide	Acetylene	R_3PH^+[b]	Pd [mol%]	t [h]	Yield [%][c]	ton
1	bromobenzene	phenylacetylene	a	0.0033	16	81	24300
2	bromobenzene	phenylacetylene	b	0.0033	16	88	26400
3	2-bromotoluene	phenylacetylene	a	0.0033	16	83	24900
4	2-bromo-*m*-xylene	phenylacetylene	a	0.0067	16	57	8550
5	2-bromo-benzotrifluoride	phenylacetylene	b	0.0033	16	51	15300
6	4-bromoanisol	phenylacetylene	c	0.0033	20	41	12200
7	4-bromoanisol	phenylacetylene	a	0.0033	20	78	23300
8	4-bromoanisol	phenylacetylene	b	0.0033	20	84	25200
9	4-bromoanisol	phenylacetylene	d	0.0033	20	43	12600

[a] Aryl bromide (10 mmol), acetylene (11 mmol), HN*i*Pr$_2$ (10 mL), 80°C, 24 h. Catalyst: [Na$_2$PdCl$_4$]/phosphonium salt/CuI 4:8:3, catalyst mixture in *i*Pr$_2$NH·HBr. [b] Ligand: a: MeFluP*i*Pr$_2$ (**17b**); b: EtFluP*i*Pr$_2$ (**17d**); c: MeFluPCy$_2$ (**17a**); d: *i*PrFluP*i*Pr$_2$ (**17f**). [c] Average of two runs.

Finally, the Sonogashira coupling of phenylacetylene with several aryl chlorides was tested (Table 4). Excellent conversions of the reactants were observed for all substrates at 100–120°C with 1 mol% of catalyst. Again, the 9-fluorenylphosphine-based palladium catalysts compare favorably with other catalytic systems described by us and by others for the conversion of aryl chlorides.[14,19,81–85]

Table 4. Sonogashira reactions with aryl chlorides.[a]



Entry	Aryl chloride	T [°C]	t [h]	Yield [%][b]
1	4-chloroanisol	110	16	43, 44,[c] 47,[d] 23[e]
2	4-nitrochlorobenzene	100	12	88
3	4-chloroacetophenone	100	12	94
4	4-CF_3-chlorobenzene	100	12	92
5	chlorobenzene	120	16	87
6	4-chlorotoluene	120	16	91
7	4-chloroanisol	120	20	73

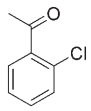
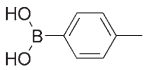
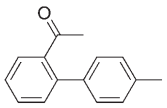
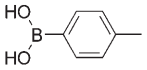
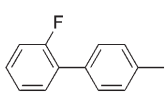
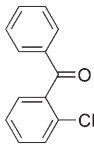
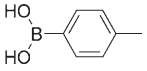
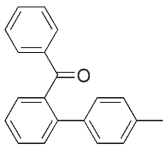
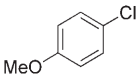
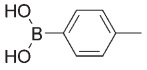
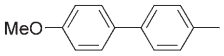
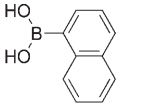
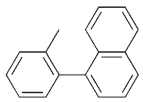
[a] Aryl chloride (1.5 mmol), phenylacetylene (2.1 mmol), Na_2CO_3 (3 mmol), DMSO (5 mL), catalyst: 1 mol% [Na$_2$PdCl$_4$]/ligand/CuI 4:8:3; phosphonium salt: MeFlu*i*Pr$_2$·HBF$_4$ (**17b**·HBF$_4$). Reaction conditions have not been optimized. [b] Average of two runs. Purified by chromatography through a short silica pad. Eluent: cyclohexane/ethyl acetate 100:2. [c] Ligand: EtFluPCy$_2$ (**17c**). [d] Ligand: BnFluPCy$_2$ (**17k**). [e] Ligand: Ad$_2$PBn.

Pd complexes of 9-fluorenyldialkylphosphines in the Suzuki reaction: We first tested Pd complexes of several phosphines, EtFluPCy$_2$ **17c**, BnFluPCy$_2$ **17k**, *i*PrFluPCy$_2$ **17e**, and MeFluP*i*Pr$_2$ **17b**, in the Suzuki coupling. In the reaction of 4-chloroacetophenone with 4-tolylboronic acid by using 0.5 mol% [Na$_2$PdCl$_4$] and 1 mol% phosphonium salt with Cs_2CO_3 in dioxane at 80°C, the following yields were observed: **17c** (77%), **17k** (13%), **17e** (5%), and **17b** (21%). Again, the phosphine with a 9-Et and the 9-PCy$_2$ group is the top performer in this series. It is interesting to observe that too much bulk at the 9-position (*i*Pr, Bn) appears to be detrimental for the coupling reactions (Table 5), while too little bulk of substituents directly attached to the phosphorous atom (9-P*i*Pr$_2$) is not favorable. An amount of 0.05 mol% of catalyst is sufficient to reach full conversion during 24 h; only 4-chloroanisol requires 0.1 mol% of catalyst to reach full conversion.

Pd complexes of 9-fluorenyldialkylphosphines in the Buchwald–Hartwig reaction: To demonstrate the broad applicability of the fluorenyl-based phosphines for coupling reactions, we carried out a few test reactions for the amination of aryl bromides and chlorides.[28,34,66,86] When applying the conditions recently reported by Beller et al. without further optimization,[63] the screening of several fluorenyldialkylphosphines in the reaction of 4-chlorotoluene with 3,5-dimethylaniline revealed EtFluPCy$_2$ as the most active ligand for palladium (Table 6, entry 1). Typical catalyst loadings of between 0.1–0.5 mol% Pd were applied at 120°C by using NaO*t*Bu as the base in toluene (Table 6). Overnight reactions of various aryl bromides gave quantitative conversion of different amines (aniline, morpholine, α-methylbenzylamine). Activated and nonactivated aryl chlorides were converted into the respective anilines under the same conditions in quantitative yields.

Sulfonation of 9-ethylfluorenyldicyclohexylphosphine and the catalytic activity of the respective Pd complexes in the Sonogashira and the Suzuki coupling in water: Water is a cheap, inflammable, and nontoxic solvent from which organic products are easily separated. It is therefore an attractive target to render palladium–phosphine complexes water-soluble in order to allow cross-coupling reactions in this "green" solvent.[87,88] Only a few examples of aqueous Suzuki coupling of aryl chlorides have been described, notable in this respect are recent publications by Buchwald et al.[89,90] and Fu et al.[11] who report on the facile Suzuki coupling in water and water/dioxane for a broad range of substrates.[4,91–93] Consequently, to render the 9-fluorenylphos-

Table 5. Suzuki reaction with aryl chlorides.[a]

Entry	Aryl chloride	Boronic acid	Product	Catalyst [mol%][b]	t [h]	Conversion [%][c]
1				0.5	2	≥99
				0.05	24	≥99
2				0.5	2	≥99
				0.05	24	≥99
3				0.5	2	≥99
				0.05	24	≥99
4				0.5	5	≥99
				0.1	20	≥99
				0.05	24	65
5				0.5	5	≥99
				0.05	24	≥99

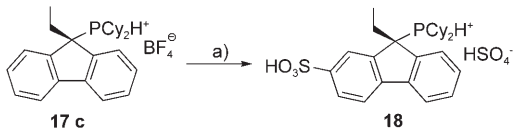
[a] Aryl chloride (1 mmol), boronic acid (1.5 mmol), Cs_2CO_3 (2.0 mmol), dioxane (5 mL), 100 °C, reaction conditions and the amount of catalyst have not been optimized. [b] Catalyst: [Na_2PdCl_4]/ligand 1:2, ligand: Et-FluPCy$_2$ (**17c**). [c] Average of two runs, determined by GC analysis using hexadecane as an internal standard.

phines water soluble, the aromatic ring was sulfonated by treatment of the phosphonium salt **17c** with concentrated sulphuric acid, resulting in the formation of the respective 2-sulfonated fluorene in 77% yield (Scheme 5).

We studied a range of different aryl bromides and aryl chlorides in Suzuki coupling reactions by using 4-toluene-boronic acid, 1-naphthylboronic acid, and 3-pyridylboronic acids (Table 7). Aryl bromides react smoothly at room temperature when using 0.1 mol% of catalyst to form the coupling product in quantitative yield, while a sterically demanding substrate (1-bromo-2,6-dimethylbenzene) requires 1 mol% and overnight reaction at the same temperature. A variety of bases (NaOH, K_2CO_3, Cs_2CO_3, K_3PO_4) were used, significant differences in the outcome of the coupling reaction were not observed and only KF gave poor results in aqueous Suzuki reactions. The addition of a surfactant (Labrasol)[94] leads to slightly improved yields in some cases. The aryl chlorides listed in Table 7 are quantitatively converted by using between 0.1–1 mol% of catalyst during 1–2 h at 100 °C. Activated aryl chlorides, such as 4-chlorobenzonitrile (entry 11), require only 0.1 mol% of catalyst to produce the coupling product in quantitative yield within 30 min. Coupling reactions of 1-naphthylboronic acid (Table 7, entries 19, 20, 23) occur at elevated temperatures with 0.5 mol% of catalyst to produce the respective coupling products in nearly quantitative yields.

N-Heterocycles, such as pyridines, are an important class of substances for pharmaceutical applications.[95] Due to the coordinating nature of pyridines such compounds are a challenging class of substrates in the Suzuki coupling of aryl chlorides.[68,96–98] Recently, Fu et al. and Buchwald et al. reported catalysts that are able to couple various substituted pyridylboronic acids and aryl chlorides in 90–95% yield by using 2–3 mol% of Pd catalyst at 90–100 °C during 24 h in *n*-butanol or in dioxane/water as solvents.[11,68] Encouraged by the high activity of the Pd complexes of the sulfonated fluorenene **18**, we also tried coupling reactions of pyridylboronic acid in the aqueous Suzuki coupling (Table 7, entries 24–28). Activated aryl chlorides (2-CF_3-chlorobenzene, Table 7, entry 26) require only 0.1 mol% of catalyst at 100 °C for quantitative conversion, while nonactivated (chlorobenzene) aryl chlorides work with 0.5 mol% (entry 25). It is remarkable that even pyridyl chlorides can be coupled with pyridyl boronic acids to result in the formation of the respective bipyridines by applying 0.5 mol% of Pd catalyst (entries 27, 28), even at 0.1 mol%, a respectable 43% yield is observed. It is obvious from our experiments carried out in pure water as the solvent that the catalysts reported appear to be the most active ones reported so far for this class of challenging substrates. In conclusion, we were able to demonstrate the excellent activity of the sulfonated **18** in the aqueous Suzuki coupling for a wide range of different substrates.

We also studied the copper-free Sonogashira coupling (also referred to as the Cassar–Heck coupling) by using various aryl bromides in water/isopropanol; yields in excess of 95% are observed for a variety of substrate combinations (Table 8),[18,99–102] while aryl chlorides could not be reacted under these conditions.



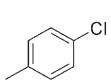
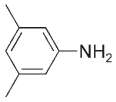
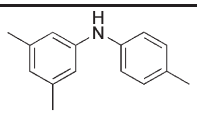
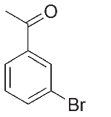
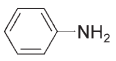
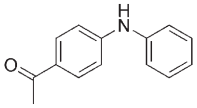
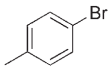
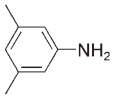
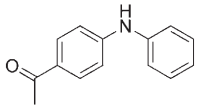
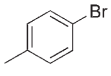
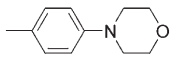
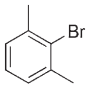
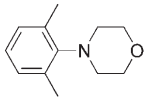
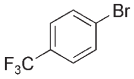
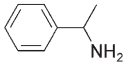
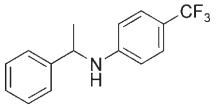
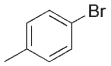
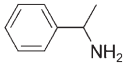
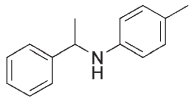
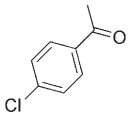
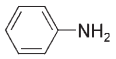
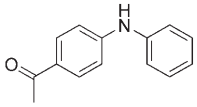
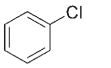
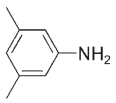
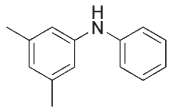
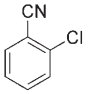
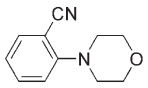
17 c 18

Scheme 5. Reagents and conditions: a) H_2SO_4, 40 °C.

Conclusions

The 9-fluorenylphosphines described here, constitute a versatile new class of phosphorous ligands, for which the palladium complexes were shown to be high activity catalysts for the Buchwald–Hartwig, Sonogashira, and Suzuki coupling of

Table 6. Buchwald–Hartwig amination[a] of aryl bromides and chlorides.

Entry	Aryl halide	Amine	Product	Catalyst [mol%]	t [h]	Conversion [%][b]
1				0.5	12	16
				0.5[c]	12	<5
				0.5[d]	12	<5
				0.5[e]	12	<5
2				0.1	3	≥99
3				0.5	2	≥99
4				0.5	2	≥99
5				0.5	6	91
6				0.25	2	≥99
7				0.5	2	≥99
8				0.5	12	≥99
9				0.5	12	≥99
10				0.5	12	48

[a] Toluene (5 mL), aryl halide (5 mmol), amine (6 mmol),NaO*t*Bu (6 mmol), Pd/ligand 1:2, phosphonium salt: EtFluPCy$_2$·HBF$_4$ (**17c**·HBF$_4$), 120 °C, reaction conditions have not been optimized. [b] Average of two runs, determined by GC analysis using hexadecane as internal standard. [c] Ligand: PhFluP*i*Pr$_2$ (**17q**). [d] Ligand: *i*PrFluP*i*Pr$_2$ (**17f**). [e] Ligand: BnFluPCy$_2$ (**17k**).

aryl chlorides. Fluorenyl-based phosphines are trialkylphosphines with excellent electron-donating properties and large steric bulk similar to P*t*Bu$_3$. However, in contrast to the latter ligand, the fluorenylphosphines can be modified easily at various positions of the fluorene to allow the design of numerous modified catalysts. The catalytic performance of the Pd complexes of the first generation of 9-alkyl, 9-dialkylphosphinofluorenes reported here is already impressive. Aryl chlorides can be coupled in quantitative yields in the Sonogashira, Suzuki, and Buchwald–Hartwig reaction in organic solvents or in water by using between 0.01 and 1 mol% of catalyst for the various reactions and substrates listed here. Noteworthy, are the excellent activities of Pd complexes of sulfonated 9-dialkylphosphinofluorenes for the Suzuki coupling in pure water with a wide range of substrates, including sterically demanding or heterocyclic boronic acids, which exceed those recently reported by others for the notoriously difficult synthesis of nitrogen-containing heterocycles.

Experimental Section

General experimental: All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. THF was distilled over potassium and benzophenone under an argon atmosphere, diethyl ether was distilled over sodium/potassium alloy and benzophenone under an argon atmosphere. Diisopropylamine was dried over potassium hydroxide, dioxane was dried over calcium hydride. Proton (^{1}H NMR), carbon (^{13}C NMR) and phosphorus (^{31}P NMR) NMR spectra were recorded on Bruker DRX 500 at 500, 125.75, and 202.46 MHz, respectively or on Bruker DRX 300 at 300 and 75.07 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to TMS ($\delta = 0$ ppm), ^{1}H NMR and 65% aq H_3PO_4 ($\delta = 0$ ppm), ^{31}P NMR. Abbreviations for NMR data: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, tt = triplet of triplets, m = multiplet. IR spectra were recorded on Perkin–Elmer 1600 series FTIR. Mass spectra were recorded on a Finigan MAT 95 magnetic sector spectrometer. TLC was performed by using Fluka silica gel 60 F_{254} (0.2 mm) on aluminum plates. Silica-gel columns for chromatography were prepared with E. Merck silica gel 60 (0.063–0.20 mesh ASTM).

General procedure for the preparation of 9-substituted fluorenes (Table 9): *n*BuLi (40 mmol, 2.5 M in hexane) was added at −60 °C to a solution of 9*H*-fluorene (30 mmol) in dry THF (60 mL). The solution immediately turned brownish and was stirred for 1.5 h at RT. After cooling to −60 °C again, the reaction mixture was quenched with alkylhalide (45 mmol, 1.5 equiv), stirred for 10 min at −60 °C, then for an additional 2 h at RT. Water (100 mL) was added to the reaction mixture which was then extracted with diethyl ether (3 × 100 mL). The combined organic phases were subsequently washed with an aqueous solution of $Na_2S_2O_3$, brine, and dried over $MgSO_4$. After filtration and removal of the volatiles under vacuum, the crude product was purified by filtration on a short silica-gel pad (5 cm, eluent: cyclohexane) and concentrated under vacuum, resulting in the pure 9-substituted fluorenes typically in near quantitative yield.

9-Methylfluorene (2a): Fluorene (**1a**) (15.0 g, 90.4 mmol), *n*BuLi (48.1 mL, 120 mmol, 2.5 M in hexane), iodomethane (19.3 g, 136 mmol).

Table 7. Suzuki coupling of aryl bromides and aryl chlorides in water.

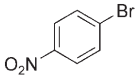
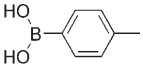
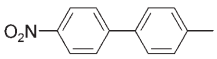
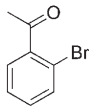
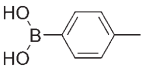
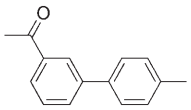
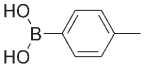
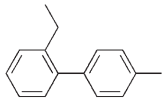
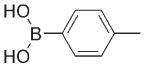
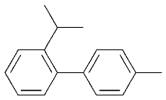
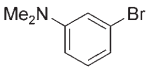
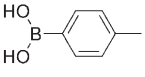
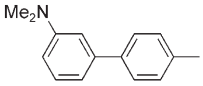
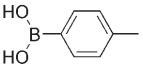
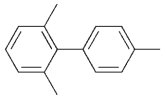
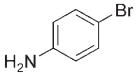
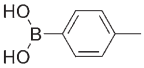
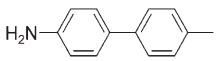
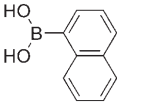
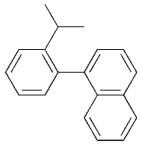
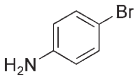
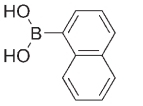
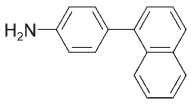
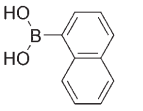
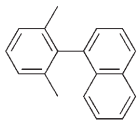
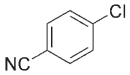
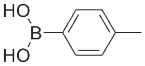
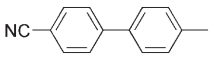
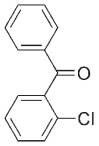
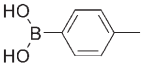
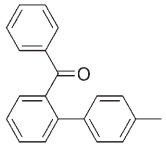
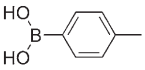
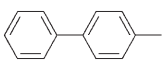
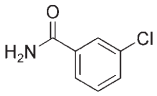
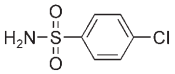
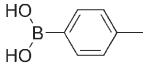
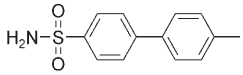
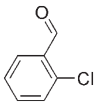
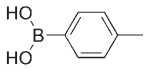
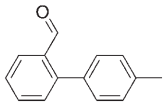
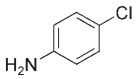
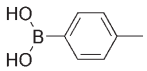
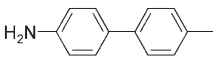
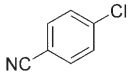
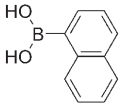
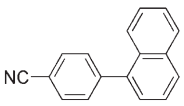
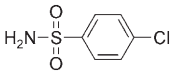
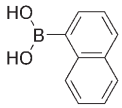
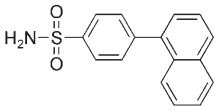
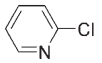
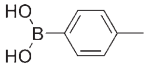
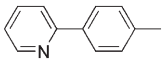
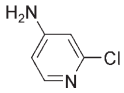
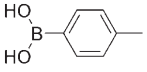
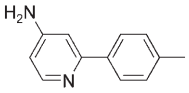
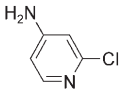
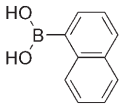
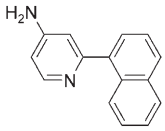
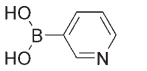
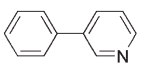
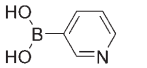
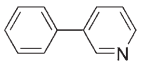
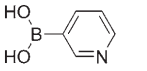
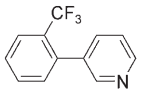
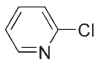
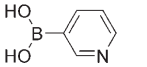
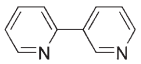
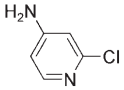
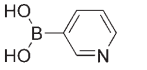
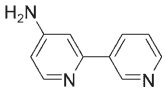
Entry	Halide	Boronic acid	Product	Pd [mol%]	Conditions	Yield [%][f]
1				0.1	RT, 20 h	≥99
				0.01	100°C, 2 h	≥99
				0.005	100°C, 3.5 h	≥99
2				0.5	90°C, 45 min	≥99
				0.5	90°C,30 min[a]	≥99
3				0.5	50°C, 1.5 h	≥99
4				0.5	50°C, 4 h	≥99
5				0.5	50°C, 1.5 h	≥99
6				1	RT, 20 h	≥99
7				0.25	RT, 3 h	≥99
				0.1	RT, 2.5 h	50
				0.1	RT, 2.5 h[a]	66
8				1	100°C, 20 h	≥99
9				0.5	65°C, 20 h	≥99
10				1	90°C, 20 h	≥99
				0.05	100°C, 2 h	≥99
				0.1	100°C, 30 min	≥99
				1	40°C, 10 h	≥99
11				1	RT, 20 h[a]	≥99
				0.1	100°C, 45 min[b]	≥99
				0.1	100°C, 1 h[c]	≥99
				0.1	100°C, 1 h[d]	≥99
				0.1	100°C, 25 min[e]	≥99
				0.5	90°C, 4 h	92
				0.5	90°C, 4 h[a]	98
12						
13				0.5	100°C, 2 h	≥99
				1	RT, 20 h[a]	≥99
14				0.5	100°C, 2.5 h[a]	≥99
				1	RT, 20 h[a]	≥99
15				0.5	100°C, 90 min	≥99

Table 7. (Continued)

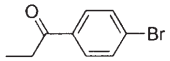
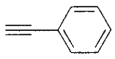
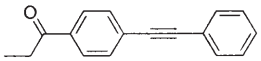
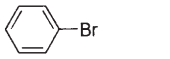
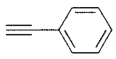
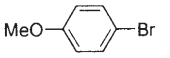
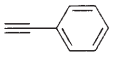
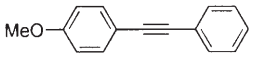
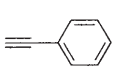
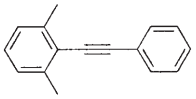
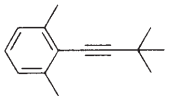
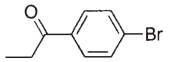
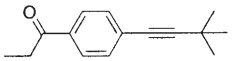
Entry	Halide	Boronic acid	Product	Pd [mol%]	Conditions	Yield [%][f]
16				1	100 °C, 24 h	≥99
17				1 0.5	90 °C, 30 min RT, 4 h	≥99 ≥99
18				0.5	90 °C, 20 h	74
19				0.5	65 °C, 20 h	80
20				0.5	90 °C, 20 h	≥99
21				0.5	100 °C, 12 h[a]	≥99
22				0.5	100 °C, 12 h[a]	≥99
23				0.5	100 °C, 12 h[a]	≥99
24				0.1	100 °C, 12 h[a]	≥99
25				0.5	100 °C, 12 h[a]	≥99
26				0.1	100 °C, 12 h[a]	≥99
27				0.5	100 °C, 12 h[a]	≥99
28				0.5 0.1	100 °C, 20 h[a] 100 °C, 20 h[a]	≥99 43
29				1.0	100 °C, 20 h[a]	97
30				1.0 0.5	100 °C, 20 h[a] 100 °C, 20 h[a]	96 90

Reaction conditions: aryl halide (1.0 equiv), boronic acid (1.2 equiv), K_2CO_3 (3.2 equiv), degassed water (4 mL, mmol^{-1}), cat. [Na_2PdCl_4], ligand **18**, ligand/Pd 2:1. Reaction times and temperatures were not optimized. [a] Additive: Labrasol (0.05 mL). [b] Aryl halide (1 equiv), boronic acid (1.2 equiv), $CsCO_3$ (3.2 equiv). [c] Aryl halide (1 equiv), boronic acid (1.2 equiv), KF (3.2 equiv). [d] Aryl halide (1 equiv), boronic acid (1.2 equiv), NaOH (3.2 equiv). [e] Aryl halide (1 equiv), boronic acid (1.2 equiv), K_3PO_4 (3.2 equiv). [f] Average of two runs, determined by GC analysis using hexadecane as an internal standard.

Product **2a** was isolated as a yellowish waxy solid (16.2 g, quant.). The analytical data were identical to those in the literature.[103] ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.74$ (d, $^3J = 7.5$ Hz, 2H; Ar), 7.49–7.48 (m, 2H; Ar), 7.34–7.28 (m, 4H; Ar), 3.92 (q, $^3J = 7.5$ Hz, 1H; 9*H*Flu), 1.50 ppm (d, $^3J = 5.5$, 7.5 Hz, 3H; CH_3); ^{13}C{^{1}H) NMR (125.77 MHz, $CDCl_3$): $\delta =$ 149.4, 141.0, 127.4 (2×), 124.5, 120.3, 42.9, 18.6 ppm.

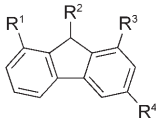
9-Ethylfluorene (2b): Fluorene (**1a**) (5.0 g, 30.1 mmol), *n*BuLi (16 mL, 40 mmol, 2.5 M in hexane), iodoethane (7.04 g, 45.1 mmol). Product **2b**

Table 8. Sonogashira reaction of aryl bromides in an aqueous system.[a]

Entry	Aryl bromide	Acetylene	Product	t [h]	Conversion [%][b]	Yield [%][c]
1				1	≥99	97
2				1.5	≥99	98
3				2	≥99	95
4				4	≥99	95
5				4	≥99	94
6				4	≥99	95

[a] Aryl bromide (1 mmol), acetylene (1.2 mmol), Cs_2CO_3 (1.5 mmol), [Na_2PdCl_4] (1 mol%), ligand ((9-ethyl-2-sulfonic acid-fluorenyl)dicyclohexyl phosphonium HSO_4^-, 2 mol%); 9-SO_3H-EtFluPCy$_2$·H_2SO_4 (**18**), H_2O/isopropanol (4 mL, 1:1), 100 °C. Reaction times and temperatures were not optimized. [b] Average of two runs, determined by GC analysis using hexadecane as an internal standard. [c] Average of two runs. Purified by column chromatography (silica gel, eluent: cyclohexane/ethyl acetate 10:1).

Table 9. 9-Substituted fluorenes.



Compound	R^1	R^2	R^3	R^4
2a	H	Me	H	H
2b	H	Et	H	H
2c	H	*i*Pr	H	H
2d	H	*n*Pr	H	H
2e	H	C_{18}	H	H
2f	H	Bn	H	H
2g	Me	Et	H	H
2h	Me	Et	Me	Me

was isolated as yellow oil (5.7 g, 97%). Analytical data were identical to those in the literature.[104] ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.73 (d, ^3J=10.0 Hz, 2H; Ar), 7.50–7.48 (m, 2H; Ar), 7.36–7.27 (m, 4H; Ar), 3.94 (t, ^3J=6.0 Hz, 1H; 9*H*Flu), 2.07 (dq, ^3J=5.5, 7.0 Hz, 2H; CH_2), 0.71 ppm (t, ^3J=7.5 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ=147.2, 141.3, 126.8, 126.7, 124.3, 119.7, 48.5, 25.7, 9.7 ppm.

9-Isopropylfluorene (2c): Fluorene (**1a**) (15.0 g, 90.4 mmol), *n*BuLi (48.1 mL, 120 mmol, 2.5 M in hexane), 2-iodopropane (14.0 mL, 139.6 mmol). Product **2c** was isolated as a yellowish solid (18.7 g, quant.). The analytical data were identical with these to be found in the literature.[103] ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.73 (d, ^3J=7.5 Hz, 2H; Ar), 7.52–7.51 (m, 2H; Ar), 7.37–7.25 (m, 4H; Ar), 3.91 (d, ^3J=3.0 Hz, 1H; 9*H*Flu), 2.59–2.52 (m, 1H; C*H*), 0.84 ppm (d, ^3J=7.0 Hz, 6H; CH_3); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ=146,7, 142.1, 127.3, 127.1, 125.2, 120.0, 54.2, 32.6, 19.5 ppm (CH_3, 2×).

9-*n*-Propylfluorene (2d): Fluorene (**1a**) (15.0 g, 90.4 mmol), *n*BuLi (48.1 mL, 120 mmol, 2.5 M in hexane), 1-iodopropane (20.8 g, 122.3 mmol). Product **2d** was isolated as a yellowish solid (18.6 g, quant.). The analytical data were identical to those found in the literature.[105] ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.73 (d, ^3J=7.0 Hz, 2H; Ar), 7.51–7.49 (m, 2H; Ar), 7.36–7.27 (m, 4H; Ar), 3.97 (t, ^3J=6.0 Hz, 1H; 9*H*Flu), 1.99–1.94 (m, 2H; CH_2), 1.27–1.19 (m, 2H; CH_2), 0.86 ppm (t, ^3J=7.5 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ=147.7, 141.1, 126.8, 126.7, 124.4, 119.8, 47.4, 35.4, 19.0, 14.4 ppm.

9-*n*-Octadecylfluorene (2e): Fluorene (**1a**) (7.0 g, 42.1 mmol), *n*BuLi (17.35 mL, 43.4 mmol, 2.5 M in hexane), 1-bromooctadecane (14.53 g, 43.6 mmol). Following the usual workup, **2e** was isolated as a white solid (15.5 g, 88%). R_f=0.73 (cyclohexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.76–7.73 (m, 2H; Ar), 7.52–7,49 (m, 2H; Ar), 7.38–7,27 (m, 4H; Ar), 3.96 (t, ^3J=6.0 Hz, 1H; 9*H*Flu), 3.02–1.95 (m, 2H; CH_2), 1.31–1.14 (m, 32H; CH_2), 0.88 ppm (t, ^3J=6.6 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (75.42 MHz, $CDCl_3$): δ=147.7, 141.1, 126.8, 126.7, 124.3, 119.8, 47.5, 33.1, 31.9, 30.0, 29.7 (CH_2, 7×), 29.6 (CH_2, 3×), 29.4, 29.3, 25.7, 22.7, 14.1 ppm.

9-Benzylfluorene (2f): Fluorene (**1a**) (19.0 g, 114 mmol), *n*BuLi (54.9 mL, 137 mmol, 2.5 M in hexane), benzylchloride (17.03 mL, 148 mmol). After the usual workup, **2a** was isolated and recrystallized from heptane to give a white solid (25.8 g, 88.4%). The analytical data were identical to those in the literature.[106] ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.72 (d, ^3J=8 Hz, 2H; Ar), 7.37–7.13 (m, 11H; Ar), 4.22 (t, ^3J=7.5 Hz, 9H; Flu), 3.10 ppm (d, ^3J=7.5 Hz, 2H; CH_2); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ=146.8, 140.8, 139.8, 129.5, 128.3, 127.1, 126.6, 126.4, 124.8, 119.8, 48.7, 40.1 ppm.

1-Methyl-9-ethylfluorene (2g): Fluorene (**1b**) (3.01 g, 16.7 mmol), *n*BuLi (8.06 mL, 20 mmol, 2.5 M in hexane), 1-iodoethane (3.39 g, 21.7 mmol). Product **2h** was isolated to give a colorless oil (3.33 g, 95%). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ=7.79–7.77 (m, 1H; Ar), 7.64 (d, ^3J=7.5 Hz, 1H; Ar), 7.55–7.53 (m, 1H; Ar), 7.34–7.24 (m, 3H; Ar), 7.10–7.08 (m, 1H; Ar), 4.11 (t, ^3J=4.5 Hz, 1H; 9*H*Flu), 2.46 (s, 3H; CH_3), 2.26–2.20 (m, 2H; CH_2), 0.35 ppm (t, ^3J=7.5 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (125.75 MHz, [D$_6$]acetone): δ=148.0, 145.4, 142.6, 142.4, 135.2, 129.4, 128.0, 127.7, 127.6, 124.9, 120.4, 118.1, 48.5, 24.3, 19.2, 8.3 ppm.

1,3,8-Trimethyl-9-ethylfluorene (2h): Fluorene (**1c**) (1.2 g, 5.77 mmol), *n*BuLi (3.0 mL, 2.5 M in hexane, 7.5 mmol), 1-iodoethane (1.35 g, 8.65 mmol). Product **2h** was isolated to give a white solid (1.36 g, quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.55 (d, ^3J=7.2 Hz, 1H; Ar), 7.40 (s, 1H; Ar), 7.27 (t, ^3J=7.2 Hz, 1H; Ar), 7.08 (d, ^3J=7.5 Hz, 1H; Ar), 6.93 (s, 1H; Ar), 4.23 (t, ^3J=4.2 Hz, 1H; 9*H*Flu), 2.49 (s, 3H; CH_3), 2.46 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.30 (dq, ^3J=4.2 Hz, 2H; CH_2), 0.19 ppm (t, ^3J=7.8 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=145.3, 142.1, 136.7, 134.1, 133.7, 129.6, 128.5, 127.0, 118.0, 117.2, 46.7, 21.5, 21.1, 19.2, 19.1, 7.2 ppm.

1-Methylfluorene (1b): 1-Methylfluoren-9-one (**8**) (6.8 g, 35 mmol) was dissolved in propionic acid (450 mL). Red phosphorus (7.4 g) and concentrated HI (100 mL) were added and the reaction mixture was refluxed for 24 h. Quantitative conversion was shown by TLC. The reaction mixture was diluted with water (500 mL), neutralized with NaOH, and extracted with Et_2O (4×125 mL). The combined organic layers were washed with brine (2×125 mL), dried over $MgSO_4$, filtered, and the volatiles removed in vacuo to afford 6.1 g (97%) of **1b** as a white solid. The analytical data were consistent with the literature.[107,108] ^{1}H NMR (500 MHz, [D$_6$]acetone): δ=7.82 (d, ^3J=8.0 Hz, 1H; Ar), 7.67 (d, ^3J=7.5 Hz, 1H; Ar), 7.58–7.56 (m, 1H; Ar), 7.36–7.34 (m, 1H; Ar), 7.30–7.26 (m, 2H; Ar), 7.12–7.10 (m, 1H; Ar), 3.78 (s, 2H; 9*H*Flu), 2.39 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (125.77 MHz, [D$_6$]acetone): δ=144.4, 143.3, 143.3, 142.5, 135.5, 128.9, 128.4, 127.9, 127.9, 126.3, 121.2, 118.6, 36.6, 19.2 ppm.

2-(2,6-Dibromophenyl)-1,3-dioxane (11): 2,6-Dibromobenzaldehyde (**10**) (10.0 g, 37.9 mmol) was dissolved in dry CH_2Cl_2 (160 mL). Propanediol (6.4 mL, 88.5 mL), triethyl orthoformate (6.83 mL, 41 mmol), and anhydrous $ZrCl_4$ (1.0 g) were added at ambient temperature and stirred overnight. Then, NaOH (50 mL of a 10% solution) was added and stirred for an additional 1 h. The organic phase was separated and the aqueous phase was extracted with Et_2O (2×40 mL). The combined organic phases were washed with water (3×60 mL), dried over $MgSO_4$, and the volatiles were removed in vacuo to afford 12.0 g (98%) of **11** as a slightly yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.55 (d, ^3J=8.0 Hz, 2H; Ar), 7.00 (t, ^3J=8.0 Hz, 1H; Ar), 6.19 (s, 1H; C*H*), 4.33–4.29 (m, 2H; CH_2), 4.02–3.97 (m, 2H; CH_2), 2.44–2.34 (m, 1H; CH_2), 1.44–1.40 ppm (m, 1H, CH_2); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ=133.9, 132.5, 129.8, 122.9, 101.6, 66.7, 24.1 ppm.

2-Bromo-6-methylbenzaldehyde (12): Acetal **11** (10.1 g, 31.25 mmol) was dissolved in dry THF (200 mL). At −78°C *n*BuLi (15.1 mL, 2.5 M in hexane, 37.8 mmol) was added within 25 min, followed by 90 min additional stirring at that temperature. Then the reaction mixture was treated with methyliodide (5.99 g, 42.2 mmol) and stirred for 25 min at −78°C. Next, the reaction mixture was allowed to warm to ambient temperature within 1.5 h. The resulting solution was quenched with HCl (290 mL, 5 N) and stirred for 1.5 h at ambient temperature. The complete deprotection of the aldehyde was checked by GC analysis. Then the reaction mixture was subsequently extracted with diethyl ether (4×100 mL), the combined organic layers were washed with a 10% solution of sodium thiosulfate (100 mL), water (100 mL), dried over $MgSO_4$, filtered, and the volatiles were removed in vacuo. The resulting slightly yellow solid was purified by Kugelrohr distillation to afford **12** (5.97 g, 96%) as white crystals. R_f=0.56 (cyclohexane/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ=10.52 (s, 1H; C*H*O), 7.52–7.50 (m, 1H; Ar), 7.26 (t, ^3J=7.0 Hz, 1H; Ar), 7.22–7.20 (m, 2H; Ar), 2.58 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ=194.6, 142.7, 133.6, 131.8, 131.7, 131.4, 128.3, 21.2 ppm.

3,3′,5′-Trimethylbiphenylcarbaldehyde (14): In a 250 mL Schlenk flask, dry dioxane (60 mL), $Pd(OAc)_2$ (175 mg), SIMES (*N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolinium chloride, 777 mg), and Cs_2CO_3 (12.4 g) were stirred for 45 min at 80°C until a grey solution had formed. Benzaldehyde **12** (3.1 g, 15.6 mmol) and 3,5-dimethylphenylboronic acid (**13**) were added and the mixture was stirred for 2 h at 80°C (quantitative conversion, GC analysis). The reaction mixture was left to cool to ambient temperature and was then treated with NaOH (100 mL, 1 N) and diethyl ether (200 mL) and transferred into a separating funnel. The aqueous phase was extracted with Et_2O (2×100 mL) and the combined organic layers were subsequently washed with NaOH (100 mL, 1 N), brine (100 mL), dried over $MgSO_4$, and the volatiles were removed in vacuo. The resulting brown oil was purified by filtration over a short pad of silica gel (10×5 cm, eluent: cyclohexane/ethyl acetate 20:1) to afford **14** (3.1 g, 89%) as a yellow oil. R_f=0.66 (cyclohexane/ethyl acetate 10:1). The product was used without any further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.96 (s, 1H; C*H*O), 7.44 (t, ^3J=7.8 Hz, 1H; Ar), 7.25 (d, ^3J=3.6 Hz, 2H; Ar), 7.04 (s, 1H; Ar), 6.95, (s, 2H; Ar), 2.65 (s, 3H; CH_3), 2.36 ppm (s, 6H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ=195.0, 140.0, 139.0, 138.0, 132.7, 132.2, 131.9, 131.0, 129.7, 128.6, 128.2, 21.7, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3436 (br), 2920, 2858, 2765, 1689, 1677, 1600, 1584, 1463, 1191 cm^{-1}.

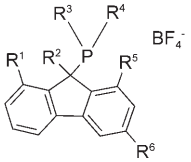
3,3′,5′-Trimethylbiphenylcarboxylic acid (15): Aldehyde **14** (2.75 g, 11.5 mmol) was dissolved in acetonitrile (18 mL, technical grade). NaH_2PO_4 (0.453 g, dissolved in 5.5 mL water) and H_2O_2 (1.93 mL of a 30% solution) were added. The reaction mixture was cooled to 0°C (ice/water) and $NaClO_2$ (2.2 g, dissolved in 19 mL water) was added within 60 min by a syringe. The solution was left to warm to ambient temperature and was stirred for an additional 3.5 h. Then Na_2SO_3 (100 mg) was added and the resulting reaction mixture was stirred for 5 min. After treatment with HCl (50 mL of a 10% solution), the reaction mixture was extracted with ether (3×75 mL). The combined organic phase was extracted with NaOH (4×75 mL, 1 N). The combined NaOH layers were acidified with HCl to pH 1 and extracted again with Et_2O. The combined organic layers were dried over $MgSO_4$ and the volatiles were removed in vacuo to afford **15** (2.95 g, quant.) as a colorless oil. The product was used without any further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.36–7.18 (m, 3H; Ar), 7.04 (s, 2H; Ar), 6.98 (s, 1H; Ar), 2.45 (s, 3H; CH_3), 2.32 ppm (s, 6H, CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=180.7, 140.6, 140.4, 138.0, 135.4, 132.1, 129.8, 129.4, 129.1, 127.6, 126.3, 21.4, 20.0 ppm.

1,3,8-Trimethylfluoren-9-one (16): In a 250 mL one-necked round-bottomed flask, the biphenylcarboxylic acid **15** (3.0 g, 12.9 mmol) was treated with concentrated sulphuric acid (40 mL) at 0°C (ice bath). The resulting dark-brown solution was stirred for 15 min at 0°C, then for additional 1 h at ambient temperature. After this time, the reaction mixture was poured onto ice (100 g) whereupon the color changed to a bright yellow. The suspension was neutralized with K_2CO_3 and extracted with Et_2O (3×100 mL). The combined organic phases were washed with brine (75 mL), dried over $MgSO_4$, filtered, and the volatiles removed in vacuo to afford **16** (2.8 g, 98%) as yellow crystals. R_f=0.52 (cyclohexane/ethyl acetate 10:1). The product was used without any further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.30–7.28 (m, 2H; Ar), 7.14 (s, 1H; Ar), 7.02–7.00 (m, 1H; Ar), 6.82 (s, 1H; Ar), 2.61 (s, 3H; CH_3), 2.57 (s, 3H; CH_3), 2.38 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ=196.3, 144.7, 144.5, 144.2, 138.9, 138.8, 133.4, 132.2, 131.7, 131.5, 128.8, 118.6, 117.4, 21.9, 17.7, 17.6 ppm; IR (KBr): ν=3049, 3020, 2919, 1698, 1615, 1595, 1454, 1373, 1296, 1170 cm^{-1}.

1,3,8-Trimethylfluorene (1c): 1,3,8-Trimethylfluoren-9-one (**16**) was reduced according to the general procedure of Carruthers et al.[8] 1,3,8-Trimethylfluoren-9-one (**16**) (2.74 g, 12.3 mmol) was dissolved in propionic acid (235 mL). Red phosphorus (3.0 g) and concentrated HI (40 mL) were added and the reaction mixture was refluxed for 24 h. Quantitative conversion was shown by TLC. The reaction mixture was diluted with water (250 mL), neutralized with NaOH, and extracted with Et_2O (4×125 mL). The combined organic layers were washed with brine (2×125 mL), dried over $MgSO_4$, filtered, and the volatiles were removed in vacuo to afford 2.56 g (quant.) of **1c** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.60 (d, ^3J=7.5 Hz, 1H; Ar), 7.44 (s, 1H; Ar), 7.28 (t, ^3J=7.5 Hz, 1H; Ar), 7.10 (d, ^3J=7.0 Hz, 1H; Ar), 6.95 (s, 1H; Ar), 3.63 (s, 2H; CH_2), 2.44 (s, 3H; CH_3), 2.42 (s, 3H; CH_3), 2.40 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (125.77 MHz; $CDCl_3$): δ=141.3, 140.9, 140.8, 138.0, 135.6, 133.1, 132.8, 127.6, 126.4, 125.9, 117.1, 116.4, 33.4, 20.4, 17.9, 17.8 ppm; IR (KBr): $\tilde{\nu}$=3038, 3012, 2964, 2917, 2874, 1612, 1592, 1455, 1261 cm^{-1}.

9-Ethyl-2,7-dibromofluorene (19): In a 250 mL four-necked round-bottomed flask (wrapped with aluminum foil), 9-ethylfluorene (**2b**) (5 g, 25.7 mmol) was dissolved in dry $CHCl_3$ (50 mL). Anhydrous $FeCl_3$ (0.1 g, 0.63 mmol) was added. Under an argon atmosphere, bromine (8.64 g, 54.1 mmol, dissolved in 25 mL $CHCl_3$) was added dropwise at 0°C over 20 min while stirring. After completion of the addition, the reaction mixture was stirred for 3 h at ambient temperature. Then a solution of $Na_2S_2O_3$ (20% w/w in water) was added and the mixture was transferred to a separation funnel. The aqueous phase was discarded and the organic layer was subsequently washed with a solution of $NaHCO_3$ (saturated, 3×40 mL) and water (1×40 mL). The organic layer was dried over $MgSO_4$, filtered, and the volatiles were removed in vacuo to afford a yellow solid. Recrystallization from ethanol afforded **19** (6.3 g, 70%) as

Table 10. Fluorenyl phosphonium salts.



HBF_4 salt	R^1	R^2	R^3	R^4	R^5	R^6
17a	H	Me	Cy	Cy	H	H
17b	H	Me	*i*Pr	*i*Pr	H	H
17c	H	Et	Cy	Cy	H	H
17d	H	Et	*i*Pr	*i*Pr	H	H
17e	H	*i*Pr	Cy	Cy	H	H
17f	H	*i*Pr	*i*Pr	*i*Pr	H	H
17g	H	*n*Pr	Cy	Cy	H	H
17h	H	H	*t*Bu	*t*Bu	H	H
17i	H	$C_{18}H_{25}$	Cy	Cy	H	H
17j	H	$C_{18}H_{25}$	*i*Pr	*i*Pr	H	H
17k	H	Bn	Cy	Cy	H	H
17L	H	Bn	*i*Pr	*i*Pr	H	H
17m	H	Bn	*t*Bu	*n*Bu	H	H
17n	H	Et	*t*Bu	*n*Bu	H	H
17o	Me	Et	Cy	Cy	H	H
17p	Me	Et	Cy	Cy	Me	Me
17q	H	Ph	*i*Pr	*i*Pr	H	H

white crystals. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.61$ (s, 2H; Ar), 7.56 (d, $^3J = 8.5$ Hz, 2H; Ar), 7.48 (dd, $^3J = 8.5$, $^4J = 1.5$ Hz, 2H; Ar), 3.94 (t, $^3J = 5.0$ Hz, 1H; 9*H*Flu), 2.06 (dq, $^3J = 5.5$, 7.5 Hz, 2H; CH_2), 0.68 ppm (t, $^3J = 7.5$ Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): $\delta = 148.9$, 139.4, 130.3, 127.7, 121.2, 48.4, 25.3, 9.4 ppm; HRMS: *m*/*z*: calcd. for $C_{15}H_{12}Br_2$: 349.9305; found: 349.9286.

General procedure for the synthesis of fluorenyl phosphonium salts (Table 10): *n*BuLi (29 mmol, 2.5 M solution in hexane) was added to a solution of 9-substituted fluorene (31 mmol) in dry Et_2O (100 mL) at −60 °C. The solution immediately turned red and was stirred for 10 min at −60 °C, then for additional 2 h at ambient temperature. After cooling to −60 °C again, the dialkyl phosphonium chloride (22 mmol) was added. The reaction mixture was stirred for 10 min at −60 °C, then overnight at RT. After removing the LiCl by filtration over a short pad of Celite, the resulting clear filtrate was quenched with HBF_4 (31.5 mmol of a diethyl ether complex). After separation by means of suction filtration, the crude product was dissolved in $CHCl_3$ (20 mL) and added dropwise into Et_2O (1 L, vigorously stirred). Filtration and removal of the volatiles in vacuo afforded the pure product as a white solid.

MeFluPCy$_2$·HBF$_4$ (17a·HBF$_4$): 9-Methylfluorene (**2a**) (1.0 g, 5.55 mmol), *n*BuLi (2.7 mL of a 2.0 M in hexane, 5.4 mmol), Cy_2PCl (0.95 g, 4.08 mmol), HBF_4·Et_2O (1.4 mL, 5.55 mmol). **17a**·HBF_4 was isolated to give a white solid (1.35 g, 71 %). ^{1}H NMR (300 MHz, CD_3CN) $\delta = 8.02$–7.99 (m, 2H; Ar), 7.81–7.78 (m, 2H; Ar), 7.66–7.61 (m, 2H; Ar), 7.56–7.50 (m, 2H; Ar), 6.00 (d, $^1J = 464$ Hz, 1H; P*H*), 2.44–2.30 (m, 4H; CH_2), 2.03 (d, $^3J = 16.8$ Hz, 3H; CH_3), 1.96–1.92 (m, 2H; C*H*), 1.75–1.49 (m, 8H; CH_2), 1.31–1.04 ppm (m, 8H; CH_2); ^{13}C{^{1}H} NMR (75.4 MHz, CD_3CN): $\delta = 140.9$ (d, J(P,C) = 3.1 Hz), 140.1 (d, J(P,C) = 4.3 Hz), 130.0 (d, J(P,C) = 2.0 Hz), 128.6 (d, J(P,C) = 2.0 Hz), 124.6 (d, J(P,C) = 3.3 Hz), 121.3, 47.6 (d, J(P,C) = 33.9 Hz), 30.4 (d, J(P,C) = 35 Hz), 28.5 (d, J(P,C) = 3.9 Hz), 27.5 (d, J(P,C) = 3.8 Hz), 25.8 (d, J(P,C) = 13 Hz), 25.6 (d, J(P,C) = 13 Hz), 24.4, 21.6 ppm; ^{31}P{^{1}H} NMR (121.4 MHz, CD_3CN): $\delta = 38.8$ ppm; ^{31}P NMR (121.4 MHz, CD_3CN): $\delta = 38.8$ ppm (d, J(P,H) = 463 Hz).

MeFluP*i*Pr$_2$·HBF$_4$ (17b·HBF$_4$): 9-Methylfluorene (**2a**) (1.5 g, 8.31 mmol), *n*BuLi (4.05 mL, 2.0 M in hexane, 8.1 mmol), iPr_2PCl (0.9 mL, 5.67 mmol), HBF_4·Et_2O (2.4 mL, 9.51 mmol). Product **17b**·HBF_4 was isolated as a white solid (1.37 g, 63 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.94$–7.86 (m, 4H; Ar), 7.60–7.49 (m, 4H; Ar), 7.27 (d, $^1J = 483$ Hz, 1H; P*H*), 2.65–2.50 (m, 2H; C*H*), 2.15 (d, ^3J(P,H) = 16.8 Hz, 3H; CH_3), 1.33 (dd, $^3J = 7.2$, ^3J(P,H) = 18.3 Hz, 6H; CH_3), 1.06 ppm (dd, $^3J = 7.5$, ^3J(P,H) = 17.7 Hz, 6H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): $\delta = 142.2$ (d, J(P,C) = 2.2 Hz), 140.2 (d, J(P,C) = 4.3 Hz), 130.3, 129.2 (d, J(P,C) = 1.7 Hz), 125.2 (d, J(P,C) = 3.7 Hz), 121.2, 47.9 (d, J(P,C) = 34 Hz), 22.7, 21.2 (d, J(P,C) = 36.3 Hz), 19.3 (d, J(P,C) = 2.9 Hz), 17.8 ppm (d, J(P,C) = 3.0 Hz); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): $\delta = 39.4$ ppm; ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = 39.4$ ppm (d, J(P,H) = 482 Hz).

EtFluPCy$_2$·HBF$_4$ (17c·HBF$_4$): 9-Ethylfluorene (**2b**) (1.65 g, 8.55 mmol), *n*BuLi (3.3 mL, 2.5 M in hexane, 8.25 mmol), Cy_2PCl (1.26 g, 5.43 mmol), HBF_4·Et_2O (2.2 mL, 8.7 mmol). Product **17c**·HBF_4 was isolated as a white solid (1.97 g, 76 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.90$–7.87 (m, 2H; Ar), 7.79 (d, $^3J = 7.9$ Hz, 2H; Ar), 7.61–7.49 (m, 4H; Ar), 6.54 (d, $^1J = 480$ Hz, 1H; P*H*), 2.80–2.71 (m, 2H; CH_2 (ethyl)), 2.30–2.18 (m, 2H; C*H*), 1.91–1.08 (m, 19H; CH_2), 0.32 ppm (t, $^3J = 6.9$ Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) $\delta = 141.6$ (d, J(P,C) = 4.5 Hz), 139.7 (d, J(P,C) = 3.0 Hz), 130.2, 129.1, 125.1 (d, J(P,C) = 3.0 Hz), 121.1, 52.9 (d, J(P,C) = 33 Hz), 31.2 (d, J(P,C) = 35 Hz), 29.4 (d, J(P,C) = 2.6 Hz), 28.0 (d, J(P,C) = 4 Hz), 27.4, 26.7 (d, J(P,C) = 13 Hz), 26.5 (d, J(P,C) = 13 Hz), 24.9, 6.7 ppm (d, J(P,C) = 11 Hz); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): $\delta = 34.4$ ppm; ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = 34.4$ ppm (d, J(P,H) = 480 Hz).

EtFluP*i*Pr$_2$·HBF$_4$ (17d·HBF$_4$): 9-Ethylfluorene (**2b**) (0.54 g, 2.78 mmol), *n*BuLi (1.35 mL, 2.0 M in hexane, 2.7 mmol), iPr_2PCl (0.269 g, 1.76 mmol), HBF_4·Et_2O (0.55 mL, 2.7 mmol). Product **17d**·HBF_4 was isolated as a white solid (0.69 g, 99 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.90$–7.82 (m, 4H; Ar), 7.61–7.50 (m, 4H; Ar), 6.70 (d, $^1J = 480$ Hz, 1H; P*H*), 2.79–2.72 (m, 2H; CH_2 (ethyl)), 2.64–2.54 (m, 2H; C*H*), 1.30 (dd, $^3J = 7.2$, ^3J(P,H) = 18.3 Hz, 6H; CH_3), 1.05 (dd, $^3J = 7.2$, ^3J(P,H) = 17.4 Hz, 6H; CH_3), 0.33 ppm (t, $^3J = 6.9$ Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): $\delta = 141.6$ (d, J(P,C) = 4.8 Hz), 139.5 (d, J(P,C) = 3.0 Hz), 130.3 (d, J(P,C) = 2.1 Hz), 129.2 (d, J(P,C) = 3.4 Hz), 125.1 (d, J(P,C) = 3.4 Hz), 121.3, 52.7 (d, J(P,C) = 34 Hz), 27.6, 21.3 (d, J(P,C) = 36.7 Hz), 19.5 (d, J(P,C) = 2.4 Hz), 17.8 (d, J(P,C) = 3.5 Hz), 6.6 ppm (d, J(P,C) = 11 Hz); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): $\delta = 40.8$ ppm; ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = 40.8$ ppm (d, J(P,H) = 478 Hz).

***i*PrFluPCy$_2$·HBF$_4$ (17e·HBF$_4$)**: 9-Isopropylfluorene (**2c**) (1.15 g, 5.54 mmol), *n*BuLi (2.7 mL, 2.0 M in hexane, 5.4 mmol), Cy_2PCl (0.9 mL, 4.08 mmol), HBF_4·Et_2O (1.2 mL, 4.76 mmol). Product **17e**·HBF_4 was isolated as a white solid (1.30 g, 64 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.89$ (d, $^3J = 6.9$ Hz, 2H; Ar), 7.79 (d, $^3J = 7.5$ Hz, 2H; Ar), 7.62–7.50 (m, 4H; Ar), 6.79 (d, $^1J = 479$ Hz, 1H; P*H*), 3.01 (dq, $^3J = 6.6$, 4.8 Hz, 1H; C*H*CH$_3$), 2.21–2.09 (m, 2H; C*H*), 1.97–1.86 (m, 2H; CH_2), 1.81–1.59 (m, 6H; CH_2), 1.51–1.37 (m, 4H; CH_2), 1.23–1.07 (m, 8H; CH_2), 0.93 ppm (d, $^3J = 6.6$ Hz, 6H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) $\delta = 141.5$ (d, J(P,C) = 5.1 Hz), 139.6 (d, J(P,C) = J = 2.6 Hz), 130.3, 129.0, 125.7 (d, J(P,C) = 2.9 Hz), 121.1, 56.4 (d, J(P,C) = 33 Hz), 34.4, (d, J(P,C) = 35.6 Hz), 29.3 (d, J(P,C) = 3.8 Hz), 28.1 (d, J(P,C) = 3.7 Hz), 26.9 (d, J(P,C) = 12.9 Hz), 26.6 (d, J(P,C) = 12.5 Hz), 24.9, 17.8 ppm (d, J(P,C) = 6.6 Hz); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): $\delta = 25.0$ ppm; ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = 25.0$ ppm (d, J(P,H) = 477 Hz).

***i*PrFluP*i*Pr$_2$·HBF$_4$ (17f·HBF$_4$)**: 9-Isopropylfluorene (**2c**) (1.16 g, 5.57 mmol), *n*BuLi (2.7 mL, 2.0 M in hexane, 5.4 mmol), iPr_2PCl (0.66 g, 4.1 mmol), HBF_4·Et_2O (1.2 mL, 4.76 mmol). Product **17f**·HBF_4 was isolated as a white solid (1.20 g, 71 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.90$–7.82 (m, 4H; Ar), 7.62–7.50 (m, 4H; Ar), 6.99 (d, $^1J = 477$ Hz, 1H; P*H*), 3.09–2.99 (m, 1H; C*H*), 2.59–2.44 (m, 2H; C*H*), 1.32 (dd, $^3J = 7.5$, ^3J(P,H) = 18.9 Hz, 6H; CH_3), 1.03 (dd, $^3J = 7.5$, ^3J(P,H) = 17.7 Hz, 6H; CH_3), 0.94 ppm (d, $^3J = 6.9$ Hz, 6H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): $\delta = 141.5$ (d, J(P,C) = 5.1 Hz), 139.4 (d, J(P,C) = 2.4 Hz), 130.3 (d, J(P,C) = 1.6 Hz), 129.1 (d, J(P,C) = 1.3 Hz), 125.7 (d, J(P,C) = 3.6 Hz), 121.2, 56.1 (d, J(P,C) = 33.2 Hz), 34.4, 21.1 (d, J(P,C) = 38.5 Hz), 19.5 (d, J(P,C) = 2.2 Hz), 17.8 (d, J(P,C) = 2.6 Hz), 6.6 ppm (d, J(P,C) = 6.5 Hz); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): $\delta = 31.3$ ppm; ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = 31.3$ ppm (d, J(P,H) = 473 Hz).

***n*PrFluPCy$_2$·HBF$_4$ (17g·HBF$_4$)**: 9-*n*-Propylfluorene (**2d**) (3.0 g, 14.4 mmol), *n*BuLi (5.6 mL, 2.5 M in hexane, 14.0 mmol), Cy_2PCl (2.37 g, 10.2 mmol), HBF_4·Et_2O (2.0 mL, 14 mmol). Product **17g**·HBF_4 was isolat-

ed as a white solid (4.13 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, ^3J = 7.5 Hz, 2H; Ar), 7.79 (d, ^3J = 7.5 Hz, 2H; Ar), 7.59–7.50 (m, 4H; Ar), 6.54 (d, ^1J = 480.5 Hz, 1H; P*H*), 2.67–2.63 (m, 2H; CH_2 (propyl)), 2.24–2.21 (m, 2H; C*H*), 1.91–1.10 (m, 19H; CH_2), 0.73 (t, ^3J = 7.5 Hz, 3H; CH_3), 0.66–0.58 ppm (m, 2H; CH_2 (propyl)); ^{13}C{^{1}H} NMR (125.75 MHz, $CDCl_3$): δ = 141.4 (d, J(P,C) = 4.5 Hz), 140.2 (d, J(P,C) = 3.8 Hz), 130.2, 129.1, 125.1 (d, J(P,C) = 2.8 Hz), 121.1, 52.4 (d, J(P,C) = 33 Hz), 40.0, 31.3 (d, J(P,C) = 34.6 Hz), 29.4 (d, J(P,C) = 3.6 Hz), 28.1 (d, J(P,C) = 3.3 Hz), 26.8 (d, J(P,C) = 13.8 Hz), 26.5 (d, J(P,C) = 12.4 Hz), 24.9, 16.0 (d, J(P,C) = 10.4 Hz), 13.6 ppm; ^{31}P{^{1}H} NMR (202.45 MHz, $CDCl_3$): δ = 34.9 ppm; ^{31}P NMR (202.45 MHz, $CDCl_3$): δ = 34.9 ppm (d, J(P,H) = 483 Hz).

HFluP*t*Bu$_2$·HBF$_4$ (17h·HBF$_4$): Fluorene (**1a**) (0.505 g, 3.04 mmol) dissolved in dry THF (10 mL) was treated with *n*BuLi (1.5 mL, 2.0 M in hexane) at −80 °C. The mixture turned orange and was stirred for an additional 4 h at ambient temperature. Then *t*Bu$_2$PCl (0.476 g, 2.6 mmol) and dry heptane (10 mL) were added at −80 °C. The reaction mixture was refluxed overnight, filtered under Schlenk conditions over a short pad of Celite, and the clear filtrate was quenched with HBF$_4$·Et$_2$O (0.7 mL, 2.8 mmol) to afford a white residue, which could be crystallized from ethyl acetate. After separation of the solids by means of suction filtration, the crude product was dissolved in $CHCl_3$ (3 mL) and added dropwise into Et$_2$O (200 mL, vigorously stirred). Filtration and removal of the volatiles in vacuo afforded pure **17h**·HBF$_4$ (0.54 g, 52%) as a white solid. ^{1}H NMR (300 MHz, CD_3CN): δ = 8.05–7.98 (m, 2H; Ar), 7.86–7.77 (m, 2H; Ar), 7.63–7.54 (m, 4H; Ar), 6.27 (d, ^1J = 463 Hz, 1H; P*H*), 5.37 (d, ^2J(P,H) = 15.6 Hz, 1H; C*H*), 1.85 (d, ^3J(P,H) = 17.1 Hz, 9H; CH_3), 0.91 ppm (d, ^3J(P,H) = 17.1 Hz, 9H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, CD_3CN): δ = 139.0, 135.1, 129.4 (d, J(P,C) = 10 Hz), 128.1 (d, J(P,C) = 32 Hz), 125.7 (d, J(P,C) = 87 Hz), 121.2 (d, J(P,C) = 28.0 Hz), 38.4 (d, J(P,C) = 34 Hz), 36.5 (d, J(P,C) = 23.7 Hz), 34.5 (d, J(P,C) = 30.0 Hz), 27.5, 26.6 ppm; ^{31}P{^{1}H} NMR (121.4 MHz, CD_3CN): δ = 52.1 ppm; ^{31}P NMR (121.4 MHz, CD_3CN): δ = 52.1 ppm (d, J(P,H) = 462 Hz).

C$_{18}$FluPCy$_2$·HBF$_4$ (17i·HBF$_4$): 9-Octadecylfluorene (**2e**) (2.48 g, 5.9 mmol), *n*BuLi (2.1 mL, 2.5 M in hexane, 5.25 mmol), Cy$_2$PCl (0.92 g, 3.94 mmol), HBF$_4$·Et$_2$O (1.8 mL). In the absence of precipitation, water (80 mL, treated with aqueous HBF$_4$ (8 N)) was added, whereupon a white solid precipitated. The solid was removed by means of suction filtration to afford **17i**·HBF$_4$ as a white solid (2.6 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, ^3J = 7.2 Hz, 2H; Ar), 7.79–7.77 (m, 2H; Ar), 7.60–7.50 (m, 4H; Ar), 6.59 (d, ^1J = 483 Hz, 1H; P*H*), 2.71–2.59 (m, 2H; CH_2), 2.27–2.13 (m, 2H; C*H*), 1.92–1.02 (m, 50H; CH_2), 0.87 (t, ^3J = 6.6 Hz, 3H; CH_3), 0.60–0.49 ppm (m, 2H; CH_2); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 141.4 (d, J(P,C) = 4.2 Hz), 140.2, 130.2, 129.1, 125.1, 121.0, 52.4 (d, J(P,C) = 32.2 Hz), 34.0, 31.9, 31.3 (d, J(P,C) = 34.5 Hz), 29.7–29.1 (CH$_2$, 14×), 28.1 (d, J(P,C) = 3.2 Hz), 26.8(d, J(P,C) = 13.2 Hz), 26.6 (d, J(P,C) = 12.6 Hz), 24.9, 22.7, 22.4 (d, J(P,C) = 9.9 Hz), 14.1 ppm; ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ = 34.1 ppm; ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = 34.1 ppm (d, J(P,H) = 482 Hz).

C$_{18}$FluP*i*Pr$_2$·HBF$_4$ (17j·HBF$_4$): 9-Octadecylfluorene (**2e**) (2.38 g, 5.7 mmol), *n*BuLi (2.0 mL, 2.5 M in hexane, 5.0 mmol), *i*Pr$_2$PCl (0.575 g, 3.77 mmol), HBF$_4$·Et$_2$O (2.0 mL, 9.8 mmol). In the absence of precipitation, the volatiles were evaporated in vacuo to give a colorless solid, which was dissolved in diethyl ether (50 mL) and treated with HBF$_4$·Et$_2$O (1 mL). Aqueous HBF$_4$ (50 mL, 4 N) was added, the mixture was stirred vigorously, and then the aqueous phase was separated and kept in an open beaker overnight. After this time, the crystals which had formed were separated by means of suction filtration and dried in vacuo to afford **17j**·HBF$_4$ (1.90 g, 81%) as white crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, ^3J = 6.9 Hz, 2H; Ar), 7.81 (d, ^3J = 6.9 Hz, 2H; Ar), 7.59–7.53 (m, 4H; Ar), 6.65 (d, ^1J = 481 Hz, 1H; P*H*), 2.71–2.61 (m, 2H; CH_2), 2.61–2.49 (m, 2H; C*H*), 1.31 (dd, ^3J = 7.2, ^3J(P,H) = 12.3 Hz, 6H; CH_3), 1.27–1.11 (m, 30H; CH_2), 1.05 (dd, ^3J = 7.5, ^3J(P,H) = 17.4 Hz, 6H; CH_3), 0.88 (t, ^3J = 6.9 Hz, 3H; CH_3), 0.61–0.50 ppm (m, 2H; CH_2); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 141.4 (d, J(P,C) = 5.1 Hz), 139.9 (d, J(P,C) = 2.9 Hz), 130.3, 129.2, 125.0 (d, J(P,C) = 2.9 Hz), 121.3, 52.3 (d, J(P,C) = 33.5 Hz), 34.1, 31.9, 29.6 (CH$_2$, 11×), 29.5, 29.4, 29.3, 29.1, 22.7, 22.2 (d, J(P,C) = 10.5 Hz), 21.3 (d, J(P,C) = 37 Hz), 19.5 (d, J(P,C) = 1.8 Hz), 17.8 (d, J(P,C) = 2.5 Hz), 14.1 ppm; ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ = 40.8 ppm; ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = 40.8 ppm (d, J(P,H) = 480 Hz).

BnFluPCy$_2$·HBF$_4$ (17k·HBF$_4$): 9-Benzylfluorene (**2f**) (6.0 g, 23.2 mmol), *n*BuLi (8.6 mL, 2.5 M in hexane, 21.5 mmol), Cy$_2$PCl (3.85 g, 16.5 mmol), HBF$_4$·Et$_2$O (3.22 mL, 23.6 mmol). Product **17k**·HBF$_4$ was isolated as a white solid (5.43 g, 61%). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 8.32–8.30 (m, 2H; Ar), 7.88–7.86 (m, 2H; Ar), 7.60–7.57 (m, 4H; Ar), 6.90–6.87 (m, 1H; Ar), 6.82–6.79 (m, 2H; Ar), 6.70 (d, ^1J = 472.5 Hz, 1H; P*H*), 6.69–6.67 (m, 2H; Ar), 4.25 (d, ^3J = 7 Hz, 2H; CH_2), 2.88–2.79 (m, 2H; C*H*), 1.96–1.94 (m, 2H; CH_2), 1.77–1.08 ppm (m, 18H; CH_2); ^{13}C{^{1}H} NMR (125.77 MHz, [D$_6$]acetone): δ = 142.7 ppm (d, J(P,C) = 4.5 Hz), 140.5 (d, J(P,C) = 3.5 Hz), 133.8, 133.7, 131.1, 129.3, 128.1, 127.7, 127.3 (d, J(P,C) = 3.9 Hz), 122.1, 53.8 (d, J(P,C) = 32.2 Hz), 39.5, 32.0 (d, J(P,C) = 34.5 Hz), 30.0 (d, J(P,C) = 3.5), 29.0 (d, J(P,C) = 3.0), 27.2 (d, J(P,C) = 12.0), 27.0 (d, J(P,C) = 13.3), 25.6 ppm; ^{31}P{^{1}H} NMR (202.46 MHz, [D$_6$]acetone) δ = 35.7 ppm; ^{31}P NMR (202.46 MHz, [D$_6$]acetone) δ = 35.7 ppm (d, J(P,H) = 472.6 Hz).

BnFluP*i*Pr$_2$·HBF$_4$ (17 L·HBF$_4$): 9-Benzylfluorene (**2f**) (8.1 g, 31.3 mmol), *n*BuLi (11.6 mL, 2.5 M in hexane, 29 mmol), (*i*Pr)$_2$PCl (3.32 g, 22.3 mmol), HBF$_4$·Et$_2$O (4.35 mL, 31.9 mmol). After separation by means of suction filtration, the crude product was dissolved in acetonitrile (20 mL) and added dropwise into Et$_2$O (1 L, vigorous stirring). Filtration and removal of the volatiles in vacuo afforded the pure product **17l**·HBF$_4$ as a white solid (9.8 g, 95%). ^{1}H NMR (500 MHz, CD_3CN): δ = 8.04–8.02 (m, 2H; Ar), 7.79–7.77 (m, 2H; Ar), 7.56–7.54 (m, 4H; Ar), 6.92–6.90 (m, 1H; Ar), 6.84–6.81 (m, 2H; Ar), 6.61–6.60 (m, 2H; Ar), 6.35 (d, ^1J = 470 Hz, 1H; P*H*), 4.00 (d, ^3J = 6.00 Hz, 2H; CH_2), 2.83–2.75 (m, 2H; C*H*), 1.18 (dd, ^3J = 7.5, ^3J(P,H) = 18.5 Hz, 6H; CH_3), 1.00 ppm (dd, ^3J = 7.0, ^3J(P,H) = 17.5 Hz, 6H; CH_3); ^{13}C{^{1}H} NMR (125.8 MHz, CD_3CN): δ = 141.2 (d, J(P,C) = 4.8 Hz), 138.7, 132.2 (d, J(P,C) = 14.3 Hz), 130.0, 129.9, 128.2, 127.1, 126.7, 125.8 (d, J(P,C) = 31.8 Hz), 38.5, 21.0 (d, J(P,C) = 36.2 Hz), 18.3 (d, J(P,C) = 2.3 Hz), 17.0 ppm (d, J(P,C) = 1.4 Hz); ^{31}P{^{1}H} NMR (202.5 MHz, CD_3CN): δ = 43.8 ppm; ^{31}P NMR (202.5 MHz, CD_3CN): δ = 43.8 ppm (d, J(P,H) = 465.2 Hz).

Synthesis of the fluorenyl phosphonium salts 17m and 17n

BnFluP(*n*Bu*t*Bu)·HBF$_4$ (17m·HBF$_4$): *n*BuLi (13.8 mL, 2.5 M in hexane, 34.7 mmol) was added to a solution of 9-benzylfluorene (**2f**) (9.24 g, 35.7 mmol) in dry THF (75 mL at −60 °C. The solution immediately turned red. After stirring for 1 h at ambient temperature, the reaction mixture was added to a solution of *t*BuPCl$_2$[109] (5.2 g, 32.7 mmol, dissolved in 50 mL dry Et$_2$O) at −80 °C. At the end of the addition, the red color remained. After stirring overnight at ambient temperature, *n*BuLi (16.8 mL, 2.5 M in hexane, 41.9 mmol) was added at −60 °C. The reaction mixture was stirred for 10 min at −60 °C, then for 2 h at ambient temperature. The suspension was filtered over a small pad of Celite and the clear reddish filtrate was quenched with HBF$_4$·Et$_2$O (4.0 mL, 29.3 mmol) to precipitate the phosphonium salt. After separation by means of suction filtration, the crude product was dissolved in acetonitrile (20 mL) and the solution was added dropwise to vigorously stirred Et$_2$O (1 L) to obtain a colorless precipitate. Filtration and removal of the volatiles in vacuo afforded **17m**·HBF$_4$ as a white solid (2.65 g, 17%). ^{1}H NMR (500 MHz, CD_3CN): δ = 8.19–8.18 (m, 1H; Ar), 8.10–8.08 (m, 1H; Ar), 7.78–7.77 (m, 1H; Ar), 7.73–7.71 (m, 1H; Ar), 7.56–7.50 (m, 4H; Ar), 6.93–6.89 (m, 1H; Ar), 6.82–6.79 (m, 2H; Ar), 6.62–6.60 (m, 2H; Ar), 4.09–4.00 (m, 2H; CH_2, Bn), 2.81–2.77 (m, 1H; CH_2, *n*Bu), 2.42–2.38 (m, 1H; CH_2, *n*Bu), 1.95–1.94 (m, 2H; CH_2, *n*Bu), 1.66–1.59 (m, 2H; CH_2, *n*Bu), 1.01 (t, ^3J = 7.6 Hz, 3H; CH_3, *n*Bu), 0.74 ppm (d, ^3J = 17.5 Hz, 9H; CH_3, *t*Bu); ^{13}C{^{1}H} NMR (125.77 MHz, CD_3CN): δ = 141.2 (d, J(P,C) = 4.5 Hz), 141.0 (d, J(P,C) = 4.4 Hz), 139.5 (d, J(P,C) = 2.5 Hz), 138.4 (d, J(P,C) = 1.9 Hz), 132.0 (d, J(P,C) = 13.8), 132.1, 131.9, 130.0, 130.0, 129.8, 128.0 (d, J(P,C) = 6.5 Hz), 127.0, 126.7, 126.4 (d, J(P,C) = 3.4 Hz), 125.7 (d, J(P,C) = 2.8 Hz), 121.1, 120.9, 52.1 (d, J(P,C) = 32.8 Hz), 38.9, 33.5 (d, J(P,C) = 34.0 Hz), 29.1 (d, J(P,C) = 7.5 Hz), 25.2, 23.2 (d, J(P,C) = 14.5 Hz), 14.5 (d, J(P,C) = 37.7 Hz), 12.3 ppm; ^{31}P{^{1}H} NMR (202.5 MHz, CD_3CN): δ = 39.8 ppm.

EtFluP(*n*Bu*t*Bu)·HBF$_4$ (17n·HBF$_4$): 9-Ethylfluorene (**2b**) (5.85 g, 30.0 mmol) was dissolved in dry THF (50 mL), treated with *n*BuLi

(11.5 mL, 2.5 M in hexane, 29.0 mmol) at −30 °C and stirred for 1 h at ambient temperature. Then *t*BuPCl$_2$[12] (4.36 g, 27.4 mmol) dissolved in dry THF (50 mL) was added at −80 °C to the red solution. The reaction mixture was stirred at ambient temperature for 14 h and the color turned slightly greenish. Completeness of the conversion was checked by ^{31}P NMR spectroscopy which showed one single signal at $\delta = 162.91$ ppm (in benzene) for EtFluP*t*BuCl. At −30 °C, *n*BuLi (14.0 mL, 2.5 M in hexane, 35.0 mmol) was added and the reaction mixture stirred at ambient temperature overnight. The suspension was filtered over a small pad of Celite by using Schlenk technique. The clear reddish filtrate was treated with HBF$_4$·Et$_2$O (5.2 mL, 38 mmol). The volatiles were removed in vacuo to give a yellow residue, which was extracted with chloroform (6 mL), filtered, and the clear filtrate was added dropwise into Et$_2$O (200 mL, vigorously stirred) to precipitate the product. Filtration and removal of the volatiles in vacuo afforded **17n**·HBF$_4$ (5.3 g, 45 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 7.95$ (d, $^3J = 6.5$ Hz, 1H; Ar), 7.89–7.84 (m, 2H; Ar), 7.72 (d, $^3J = 8$ Hz, 1H; Ar), 7.60–7.49 (m, 4H; Ar), 6.77 (d, $^1J = 481$ Hz, 1H; P*H*), 2.81–2.73 (m, 1H; CH_2 (ethyl)), 2.69–2.61 (m, 1H; CH_2 (ethyl)), 2.42–2.32 (m, 1H; CH_2 (butyl)), 2.18–2.08 (m, 1H; CH_2 (butyl)), 1.88–1.77 (m, 2H; CH_2 (butyl)), 1.57–1.43 (m, 2H; CH_2 (butyl)), 0.97 (t, $^3J = 7.5$ Hz, 3H; (butyl)), 0.85 (d, ^3J(P,H) = 17 Hz, 9H; CH_3), 0.32 ppm (t, $^3J = 7.5$ Hz, 3H; (ethyl)); ^{13}C{^{1}H} NMR (125.75 MHz, CDCl$_3$): $\delta = 141.7$ (d, J(P,C) = 4.4 Hz), 141.3 (d, J(P,C) = 4.5 Hz), 139.9, 139.0 (d, J(P,C) = 2.8 Hz), 130.4, 130.2, 129.3, 128.9, 125.9 (d, J(P,C) = 3.3 Hz), 124.7 (d, J(P,C) = 2.3 Hz), 121.4, 121.0, 52.2 (d, J(P,C) = 34 Hz), 33.7 (d, J(P,C) = 36.3 Hz), 28.8 (d, J(P,C) = 5.5 Hz), 28.1, 26.5, 24.1 (d, J(P,C) = 13.1 Hz), 15.0 (d, J(P,C) = 37.7 Hz), 13.2, 6.3 ppm (d, J(P,C) = 9.3 Hz); ^{31}P{^{1}H} NMR (202.45 MHz, CDCl$_3$): $\delta = 39.4$ ppm; ^{31}P NMR (202.45 MHz, CDCl$_3$): $\delta = 39.4$ ppm (d, J(P,H) = 480 Hz).

9-Et-1-MeFluPCy$_2$·HBF$_4$ (17o·HBF$_4$): 9-Ethyl-1-methylfluorene (**2g**) (2.0 g, 9.56 mmol), *n*BuLi (3.67 mL, 2.5 M in hexane, 9.18 mmol), Cy$_2$PCl (1.78 g, 7.65 mmol), HBF$_4$·Et$_2$O (1.25 mL, 9.18 mmol). Product **17o**·HBF$_4$ was isolated as a white solid (3.5 g, 93 %). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 7.86$ (d, $^3J = 7.5$ Hz, 1H; Ar), 7.74 (d, $^3J = 7.5$ Hz, 1H; Ar), 7.68 (d, $^3J = 7.5$ Hz, 1H; Ar), 7.59 (t, $^3J = 7.5$ Hz, 1H; Ar), 7.54–7.47 (m, 2H; Ar), 7.24 (d, $^3J = 7.5$ Hz, 1H; Ar), 6.50 (dd, $^1J = 465.5$, $^3J = 4.0$ Hz, 1H; P*H*), 3.06–2.97 (m, 1H; CH_2 (ethyl)), 2.79–2.68 (m, 2H; CH_2 (ethyl) + C*H* (Cy)), 2.66 (s, 3H; CH_3), 2.35–2.32 (m, 1H; C*H*(Cy)), 2.02–1.65 (m, 7H; CH_2), 1.56–1.34 (m, 7H; CH_2), 1.13–1.08 (m, 1H; CH_2), 0.91–0.87 (m, 4H; CH_2), 0.68–0.59 (m, 1H; CH_2), 0.39 ppm (t, $^3J = 7.0$ Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (125.75 MHz, CDCl$_3$): $\delta = 142.6$ (d, J(P,C) = 4.0 Hz), 142.3 (d, J(P,C) = 4.5 Hz), 139.8 (d, J(P,C) = 4.5 Hz), 137.4 (d, J(P,C) = 3.3 Hz), 136.8 (d, J(P,C) = 2.8 Hz), 132.2, 131.0, 130.8, 129.2 (d, J(P,C) = 2.3 Hz), 124.6 (d, J(P,C) = 4.1 Hz), 121.4, 119.1, 54.7 (d, J(P,C) = 31.3 Hz), 32.1 (d, J(P,C) = 37.3 Hz), 31.8 (d, J(P,C) = 33.3 Hz), 30.6 (d, J(P,C) = 3.8 Hz), 28.7 (d, J(P,C) = 3.6 Hz), 28.5 (d, J(P,C) = 3.4 Hz), 27.2, 27.2, 27.2, 27.1, 27.1, 27.0, 26.9, 26.8, (d, J(P,C) = 13.2 Hz), 27.1 (d, J(P,C) = 13.2 Hz),25.2, 20.1, 7.4 ppm (d, J(P,C) = 11 Hz); ^{31}P{^{1}H} NMR (202.5 MHz, CDCl$_3$) $\delta = 27.5$ ppm; ^{31}P NMR (202.5 MHz, CDCl$_3$): $\delta = 27.5$ ppm (d, J(P,H) = 471 Hz).

9-Et-1,3,8-Me$_3$-FluPCy$_2$·HBF$_4$ (17p·HBF$_4$): 9-Ethyl-1,3,8-trimethylfluorene (**2h**) (0.8 g, 3.4 mmol), *n*BuLi (1.29 mL, 2.5 M in hexane), Cy$_2$PCl (0.633 g, 2.72 mmol), HBF$_4$·Et$_2$O (0.8 mL, 3.2 mmol). Product **17p**·HBF$_4$ was isolated as a white solid (1.29 g, 92 %). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.89$ (d, $^3J = 7.5$ Hz, 1H; Ar), 7.52 (s, 1H; Ar), 7.49–7.43 (m, 1H; Ar), 7.22 (d, $^3J = 7.5$ Hz, 1H; Ar), 7.05 (s, 1H; Ar), 6.30 (dt, $^1J = 469$, $^3J = 4.5$ Hz, 1H; P*H*), 2.96 (dq, ^3J(P,H) = 5.7, 7.2 Hz, 2H; CH_2 (ethyl)), 2.66 (s, 3H; CH_3), 2.62 (s, 3H; CH_3), 2.44 (s, 3H; CH_3), 2.24–2.19 (m, 2H; C*H*), 2.12–1.04 (m, 20H; CH_2), 0.44 ppm (t, $^3J = 7.2$ Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): $\delta = 142.6$ (d, J(P,C) = 4.8 Hz), 142.5 (d, J(P,C) = 4.5 Hz), 140.8, 137.0 (d, J(P,C) = 4.4 Hz), 135.4 (d, J(P,C) = 3.2 Hz), 135.0 (d, J(P,C) = 3.2 Hz), 133.8 (d, J(P,C) = 4.1 Hz), 133.3 (d, J(P,C) = 2.3 Hz), 132.1 (d, J(P,C) = 2.3 Hz), 130.5 (d, J(P,C) = 2.4 Hz), 119.3, 118.6, 56.8 (d, J(P,C) = 28.9 Hz), 32.9 (d, J(P,C) = 17.3 Hz), 32.5 (d, J(P,C) = 17.7 Hz), 29.4 (d, J(P,C) = 3.3 Hz), 27.6 (d, J(P,C) = 4.8 Hz), 27.5 (d, J(P,C) = 4.8 Hz), 26.9 (d, J(P,C) = 13.5 Hz), 26.7 (d, J(P,C) = 13.1 Hz), 24.8, 23.7, 21.3, 20.3, 20.1, 7.1 ppm (d, J(P,C) = 11 Hz); ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$) $\delta = 27.7$ ppm; ^{31}P NMR (121.4 MHz, CDCl$_3$): $\delta = 27.7$ ppm (d, J(P,H) = 469 Hz).

PhFluP*i*Pr$_2$·HBF$_4$ (17q·HBF$_4$): 9-Phenylfluorene (**5**) (0.72 g, 2.97 mmol), *n*BuLi (1.08 mL, 2.5 M solution in hexane), *i*Pr$_2$PCl (0.33 mL, 2.03 mmol), HBF$_4$·Et$_2$O (0.6 mL, 2.37 mmol). Product **17q**·HBF$_4$ was isolated to give a white solid (0.84 g, 93 %). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 9.49$ (d, $^1J = 490$ Hz, 1H; P*H*), 7.98–7.91 (m, 4H; Ar), 7.85 (d, $^3J = 8.1$ Hz, 2H; Ar), 7.64–7.52 (m, 4H; Ar), 7.45 (t, $^3J = 7.2$ Hz, 2H; Ar), 7.37–7.32 (m, 1H; Ar), 2.30–2.21 (m, 2H; C*H*), 1.14 (dd, $^3J = 7.2$, ^3J(P,H) = 18.0 Hz, 6H; CH_3), 1.02 ppm (dd, $^3J = 7.5$, ^3J(P,H) = 17.7 Hz, 6H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): $\delta = 140.6$ (d, J(P,C) = 4.5 Hz), 140.3 (d, J(P,C) = 2.9 Hz), 135.2, 130.5, 130.0, 129.4, 129.1, 127.3 (d, J(P,C) = 5.9 Hz), 126.7 (d, J(P,C) = 3.1 Hz), 121.5, 56.5 (d, J(P,C) = 33.8 Hz), 21.0 (d, J(P,C) = 37.3 Hz), 19.6 (d, J(P,C) = 2.4 Hz), 17.7 ppm (d, J(P,C) = 2.5 Hz); ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$): $\delta = 30.6$ ppm; ^{31}P NMR (121.4 MHz, CDCl$_3$): $\delta = 30.6$ ppm (d, J(P,H) = 489 Hz).

Synthesis of a monosulfonated 9-fluorenylphosphine, 9-Et-2-SO$_3$H-FluP-Cy$_2$·H$_2$SO$_4$ (18·H$_2$SO$_4$): Concentrated sulfuric acid (2.3 mL) was added to a solution of EtFluPCy$_2$·HBF$_4$ (**17c**·HBF$_4$) (2.35 g, 4.92 mmol) in dry CH$_2$Cl$_2$ (1 mL) at 0 °C. After stirring the solution at 40 °C overnight, ice was added (5 g). The reaction mixture was extracted with chloroform (3 × 10 mL). The combined organic layers were dried over MgSO$_4$. After filtration, the clear filtrate was reduced to a final volume of 5 mL in vacuo. The concentrate was added dropwise to diethyl ether (500 mL, vigorously stirred) to precipitate the product. Filtration and removal of the volatiles in vacuo afforded the pure product **18**·H$_2$SO$_4$ (1.8 g, 77 %) as a white solid. ^{1}H NMR (500 MHz, [D$_4$]methanol): $\delta = 8.22$ (s, 1H; Ar), 8.10 (s, 2H; Ar), 8.09 (s, 1H; Ar), 7.86 (d, $^3J = 10$ Hz, 1H; Ar), 7.68 (t, $^3J = 7.5$ Hz, 1H; Ar), 7.60 (t, $^3J = 7.5$ Hz, 1H; Ar), 2.87–2.81 (m, 1H; CH_2), 2.79–2.74 (m, 1H; CH_2), 2.69–2.61 (m, 1H; C*H*), 2.51–2.46 (m, 1H; C*H*), 2.05–1.05 (m, 20H; CH_2), 0.34 ppm (t, $^3J = 6.5$ Hz, 3H; CH_3). ^{13}C{^{1}H} NMR (125.75 MHz, [D$_4$]methanol): $\delta = 147.5$, 144.8 (d, J(P,C) = 4.8 Hz), 142.5 (d, J(P,C) = 4.5 Hz), 141.8 (d, J(P,C) = 2.9 Hz), 141.0 (d, J(P,C) = 2.0 Hz), 131.8, 130.6, 129.4, 126.4 (d, J(P,C) = 4.0 Hz), 124.0 (d, J(P,C) = 3.9 Hz), 123.2, 122.4, 53.9 (d, J(P,C) = 33.7 Hz), 32.4 (d, J(P,C) = 9.2 Hz), 32.1 (d, J(P,C) = 8.7 Hz), 30.8 (d, J(P,C) = 3.8 Hz), 30.4 (d, J(P,C) = 3.4 Hz), 29.6 (d, J(P,C) = 4.0 Hz), 29.5 (d, J(P,C) = 5.4 Hz), 28.9 (d, J(P,C) = 3.8 Hz), 28.5, 27.7 (d, J(P,C) = 4.9 Hz), 27.6 (d, J(P,C) = 4.3 Hz), 27.4 (d, J(P,C) = 11.3 Hz), 27.2 (d, J(P,C) = 11.9 Hz), 26.0 (d, J(P,C) = 2.8 Hz), 6.9 ppm (d, J(P,C) = 11.7 Hz); ^{31}P{^{1}H} NMR (202.46 MHz, [D$_4$]methanol): $\delta = 34.9$ ppm; ESI-MS: positive ions **18**$^+$ (471.3), negative ions HSO_3^- (97.3), BF_4^- not observed. elemental analysis calcd for $C_{27}H_{37}O_7PS_2$ (568.7): C 57.02, H 6.56; found: C 56.93, H 7.26.

9-Et-2,7-dibromo-FluP*i*Pr$_2$·HBF$_4$ (20·HBF$_4$): In a 100 mL Schlenk flask, diisopropylamine (1.03 mL, 7.4 mmol) was dissolved in dry THF (20 mL). At −60 °C, *n*BuLi (2.7 mL of a 2.0 M solution in hexane, 6.8 mmol) was added. The solution was stirred at −60 °C for 10 min, then for an additional 30 min at 0 °C. The formed LDA (LDA = lithium diisopropylamide) solution was added to a solution of 9-ethyl-2,7-dibromofluorene (**19**·HBF$_4$) (2.5 g, 7.08 mmol) in Et$_2$O (40 mL) at −60 °C. The red reaction mixture was stirred for 30 min at −60 °C, then for 1.5 h at ambient temperature (at lower temperatures a thick reddish precipitate was formed). Then *i*Pr$_2$PCl (0.9 mL, 5.66 mmol) was added at −60 °C. The reaction mixture was stirred at ambient temperature for 2 h (color changed from red to yellow) and filtered over a small pad of Celite. The clear, slightly yellow filtrate was quenched with HBF$_4$·Et$_2$O (1.80 mL, 13.2 mmol) which led to precipitation of the phosphonium salt as a white solid. The solid was separated by means of suction filtration, slurried in water (15 mL, to remove residual ammonium salt) and filtered again. The collected white solid was dissolved in CHCl$_3$ (10 mL) and acetonitrile (1 mL), and the solution was added dropwise to vigorously stirred Et$_2$O (400 mL) to give a colorless precipitate. Filtration and removal of the volatiles in vacuo afforded **20**·HBF$_4$ as a white solid (2.82 g, 90 %). ^{1}H NMR (500 MHz, CD$_3$CN): $\delta = 7.98$ (t, $^4J = 1.5$ Hz, 2H; Ar), 7.91 (d, $^3J = 8.0$ Hz, 2H; Ar), 7.81 (dt, $^3J = 8.0$, $^4J = 1.5$ Hz, 2H; Ar), 6.24 (d, $^1J = 470$ Hz, 1H; P*H*), 2.80–2.71 (m, 2H; C*H*), 2.70–2.64 (m, 2H; CH_2), 1.17 (dd, $^3J = 7.5$, ^3J(P,H) = 19 Hz, 6H; CH_3), 1.01 (dd, $^3J = 7.0$, ^3J(P,H) = 18 Hz, 6H; CH_3), 0.30 ppm (t, $^3J = 7.0$ Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (125.75 MHz, CD$_3$CN): $\delta = 141.3$ (d, J(P,C) = 2.1 Hz), 139.7 (d, J(P,C) = 4.5 Hz), 133.4, 127.9 (d, J(P,C) = 3.8 Hz), 123.1, 122.2 (d, J(P,C) = 2.0 Hz), 52.5 (d, J(P,C) = 33.9 Hz), 26.9, 20.9 (d, J(P,C) = 35.1 Hz), 18.3 (d, J(P,C) = 2.0 Hz), 16.9 (d,

J(P,C) = 1.4 Hz), 18.1 (d, J(P,C) = 3.4 Hz), 5.4 ppm (d, J(P,C) = 10.1 Hz); $^{31}P\{^1H\}$ NMR (202.45 MHz, CD_3CN): δ = 42.1 ppm; ^{31}P NMR (202.45 MHz, CD_3CN): δ = 34.9 ppm (d, J(P,H) = 470.1 Hz).

General procedures for the cross-coupling reactions: All cross-coupling reactions were carried out under an argon atmosphere in deaerated solvents (freeze and thaw).

Sonogashira reaction of aryl bromides (in diisopropylamine): Dry diisopropylamine (10 mL), aryl bromide (10 mmol), and acetylene (11 mmol) were placed in a Schlenk tube. Then the catalyst was added in the given concentration as a ready-made mixture[17] of $[Na_2PdCl_4]$/ligand (phosphonium salt)/CuI 4:8:3 under argon. Unless otherwise noted, the reaction mixture was stirred at 50 °C in an aluminum block. After cooling to RT, 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 isolated by column chromatography (silica gel, cyclohexane/ethyl acetate 100:2). Alternatively, the yield was either determined by GC analysis with hexadecane or diethylene glycol di-*n*-butyl ether as an internal standard or by determination of the mass of the isolated $i Pr_2NH_2^+Br^-$.

Sonogashira reaction of aryl chlorides (in DMSO): Dry DMSO (5 mL, crown cap), aryl chloride (1.5 mmol), acetylene (2.1 mmol), and Na_2CO_3 (3 mmol) were placed in a Schlenk tube. Then the catalyst was added in the given concentration, $[Na_2PdCl_4]$/ligand (phosphonium salt)/CuI 4:8:3 under argon. The reaction mixture was stirred at 100–120 °C in an aluminum block for 12 to 20 h. After cooling to RT, 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 isolated by column chromatography (silica, cyclohexane/ethyl acetate 100:2. Alternatively, the yield was determined by GC analysis with hexadecane or diethylene glycol di-*n*-butyl ether as an internal standard.

Sonogashira reaction of aryl bromides (in water)

Preparation of the catalyst stock solution: $[Na_2PdCl_4]$ (0.05 mmol), 9-Et-2-SO_3HFlu-$PCy_2{\cdot}HSO_4^-$ (**18**·H_2SO_4) (0.1 mmol) and Cs_2CO_3 (0.4 mmol) were placed in a Schlenk tube under argon. Degassed water (5.0 mL) was added and the mixture was stirred at 45 °C for 2 h until the solution turned off white. The stock solution had a concentration of 1 mol % mL^{-1} $mmol^{-1}$ aryl halide).

Cross-coupling reaction: Water (2 mL), isopropanol (2 mL), and the catalyst stock solution were added to the aryl bromide (1 mmol), acetylene (1.1 mmol), and Cs_2CO_3 (2 mmol) in a Schlenk tube. The reaction mixture was stirred at 100 °C in an aluminum block for 1.5 to 4 h. After cooling to RT, 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 isolated by column chromatography (silica gel, cyclohexane/ethyl acetate 100:2. Alternatively the yield was determined by means of GC analysis with hexadecane or diethylene glycol di-*n*-butyl ether as an internal standard.

Suzuki reaction of aryl halides (in dioxane)

Preparation of the catalyst stock solution: $[Na_2PdCl_4]$ (0.05 mmol), phosphonium salt (0.1 mmol), and Cs_2CO_3 (0.2 mmol) were placed in Schlenk tube. Dioxane (5.0 mL) was added and the mixture was stirred at 45 °C for 2 h until the solution turned off white. This stock solution has a concentration of 1 mol % mL^{-1}·mmol aryl halide.

Cross-coupling reaction: Boronic acid (1.5 mmol), Cs_2CO_3 (2 mmol) in dioxane (5 mL), and the catalyst stock solution were added to the aryl halide (1 mmol). The reaction mixture was stirred at 100 °C in an aluminum block. After cooling to RT, 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 isolated by column chromatography (silica gel, cyclohexane/ethyl acetate 100:2). Alternatively, the yield was determined by GC analysis with hexadecane or diethylene glycol di-*n*-butyl ether as an internal standard.

Suzuki reaction of aryl halides (in water)

Preparation of the catalyst stock solution: The catalyst stock solution was prepared as described for the aqueous Sonogshira reaction; K_2CO_3 instead of Cs_2CO_3.

Cross-coupling reaction: Water (4 mL), the catalyst stock solution, and two drops of Labrasol were added to a mixture of aryl halide (1 mmol), boronic acid (1.2 mmol), and K_2CO_3 (3.2 mmol). The reaction mixture was stirred at the respective temperatures (see tables) for 0.5–20 h (see tables). After cooling to RT, 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 isolated by column chromatography (silica gel, cyclohexane/ethyl acetate 100:2). Alternatively, the yield was determined by GC analysis with hexadecane or diethylene glycol di-*n*-butyl ether as an internal standard.

Buchwald–Hartwig amination of aryl halides: Dry toluene (5 mL), aryl halide (5 mmol), amine (6 mmol), and NaO*t*Bu (6 mmol) were placed in a Schlenk tube. Next, the catalyst was added in the given concentration ($[Na_2PdCl_4]$/ligand phosphonium salt 1:2). The reaction mixture was stirred at 120 °C in an aluminum block. After cooling to RT, 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 isolated by column chromatography (silica gel, cyclohexane/ethyl acetate 9:1). Alternatively, the yield was determined by GC analysis with hexadecane or diethylene glycol di-*n*-butyl ether as an internal standard.

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