P Ligands

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# Synthesis and Application of 2,6-Bis(trifluoromethyl)-4-pyridyl Phosphanes: The Most Electron-Poor Aryl Phosphanes with Moderate Bulkiness**

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In transition-metal catalysis, $PPh_3$ and more electron-rich tertiary phosphanes are popular ligands for controlling catalytic activity and selectivity. In contrast, efficient catalysts using highly electron-poor phosphanes,[1] such as $P(C_6F_5)_3$, have rarely been reported. However, in recent years this phosphane has been used as an effective ligand, particularly in gold[2] or iridium[3] catalysts. Furthermore, a prominent ligand-acceleration effect (LAE) by a highly electron-poor phosphane has been shown in some cases. Recently, we demonstrated that the Rh/MeO-$F_{12}$-biphep[4] catalyst showed a remarkably high turnover frequency (TOF = 53000 $h^{-1}$) and turnover number (TON = 320000) with 98% *ee* in asymmetric 1,4-addition.[5] These high values are inherently due to the electronic effect of highly electron-poor MeO-$F_{12}$-biphep. Although introduction of perfluoroaromatics into the diphosphane produced a more electron-poor ligand, MeO-$F_{28}$-biphep bearing 4-$CF_3C_6F_4$ groups showed only a low LAE.[5b] The low effect is attributed to the insufficient complexation of MeO-$F_{28}$-biphep with Rh for steric reasons. The *ortho*-fluorine atoms in the PAr moiety significantly increase the cone angle[6] and further destabilize the metal–phosphorus bond, which is inherently weakened by the electron-deficient P atom.[7] This destabilization often had resulted in severe catalyst instability to give lower catalytic activity when aryl phosphanes bearing perfluoroaromatics such as $P(C_6F_5)_3$ were used.[8] These critical problems reduce the utility value of a highly electron-poor phosphane ligand, although it is potentially useful by virtue of its electronic properties.[2,3,9] To overcome this drawback, we designed and developed a novel type of phosphane ligand that has both low σ-donating ability, like $P(C_6F_5)_3$, and moderate bulkiness, like $PPh_3$, to facilitate practical complexation with a metal catalyst.

As an appropriate candidate for the aryl group of the phosphane, we chose the 2,6-bis(trifluoromethyl)-4-pyridyl (BFPy) group (Figure 1). The Taft's σ* value[10] of the BFPy group[11] is larger than those of the $C_6F_5$ or 4-$CF_3C_6F_4$ groups, thus indicating that the BFPy group is the most powerful electron-withdrawing group (EWG) among aromatic groups. The structure of the BFPy group, which has no *ortho*-fluorine atoms, is analogous to that of the 3,5-$(CF_3)_2C_6H_3$ group. The ligand P{3,5-$(CF_3)_2C_6H_3$}$_3$ shows a cone angle similar to that of $PPh_3$ (160° vs. 155° as determined by Howell et al.),[12] thus suggesting that the steric bulkiness of $P(BFPy)_3$ is similar to that of $PPh_3$ and smaller than that of $P(C_6F_5)_3$, the cone angle of which is considerably larger than that of $PPh_3$ (184° vs. 145° as determined by Tolman).[13] Although BFPy phosphane will show lower σ-donating ability than $C_6F_5$ or 4-$CF_3C_6F_4$ phosphanes, its moderate bulkiness will facilitate its complexation with the metal catalyst (Figure 1). Furthermore, the *meta*-$CF_3$ groups in BFPy phosphane assure the 3,5-dialkyl effect.[14] Because these BFPy phosphorous compounds have not been known so far, we attempted to synthesize BFPy phosphanes.

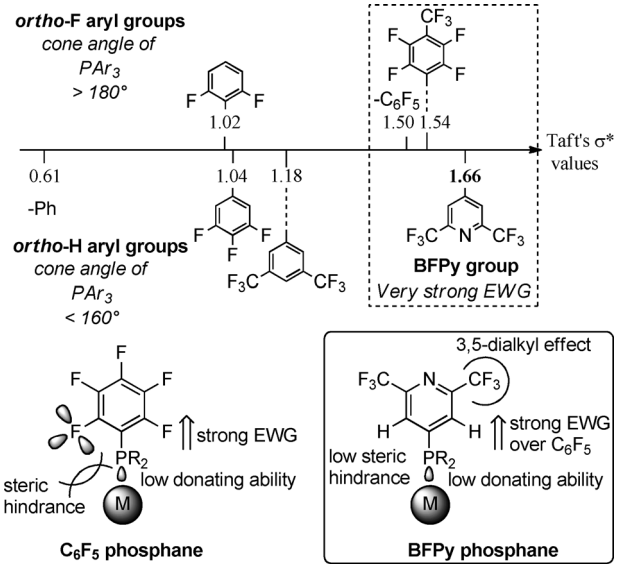


***Figure 1.*** Concept of BFPy phosphane.

The phosphane ligands triaryl phosphane **1a**, dppe analogue **2a**, and MeO-biphep analogue (±)- or enantiomerically pure **3a** could be synthesized from the corresponding $R_{1-x}PCl_{x+2}$ ($x = 0$ or 1) with an excess amount of BFPyMgBr·LiCl,[15] which was prepared from 4-bromo-2,6-bis(trifluoromethyl)pyridine[16] with magnesium and LiCl in the presence of diisobutylaluminum hydride (DIBAL-H) (Scheme 1). The use of a usual Grignard reagent, BFPyMgBr, gave the products in low yield.

The electronic properties of **1a**, **2a**, and **3a** were estimated using metal carbonyl complexes (Table 1). The complexes

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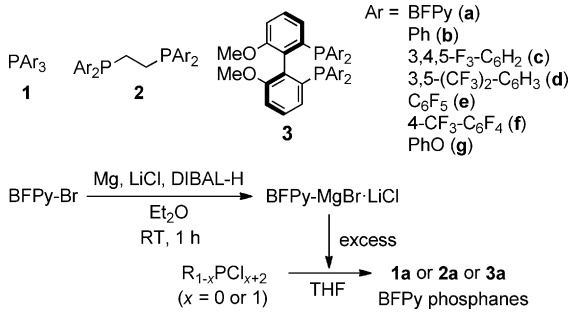
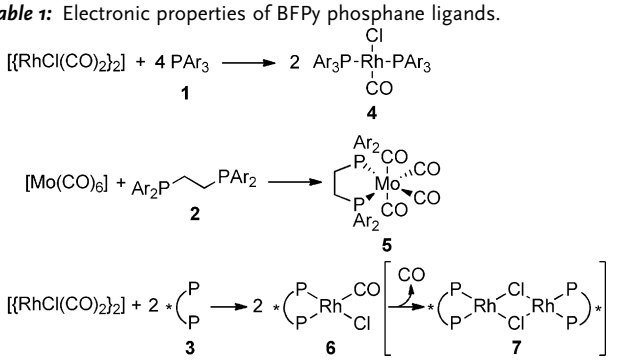



***Scheme 1.*** Synthesis of BFPy phosphanes.

***Table 1:*** Electronic properties of BFPy phosphane ligands.

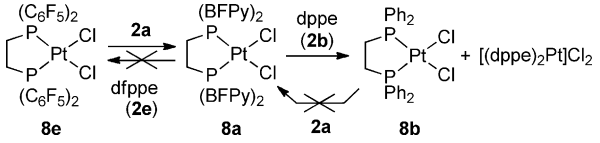



| Ar in phosphane | **4**[a,b] | | **5**[a] | **6**[c] |
|---|---|---|---|---|
| | $\nu^{CO}$ [cm$^{-1}$] | $\delta$ [ppm] ($J_{Rh-P}$ [Hz]) | $\nu^{CO}$ [cm$^{-1}$] | $\nu^{CO}$ [cm$^{-1}$] |
| BFPy (**a**) | 2017 | 31.9 (138.6) | 2047 | (**7a**) |
| PhO (**g**) | 2016 | 113.9 (213.6) | | |
| 4-$CF_3$-$C_6F_4$ (**f**) | 2016 | −22.5 (157.0) | 2045 | (**7f**) |
| $C_6F_5$ (**e**) | 2008 | −23.4 (152.6) | 2041 | |
| 3,5-$(CF_3)_2$-$C_6H_3$ (**d**) | 2000 | 32.7 (133.5) | 2037 | 2044 |
| 3,4,5-$F_3$-$C_6H_2$ (**c**) | 1997 | 34.0 (134.8) | 2031 | 2036 |
| Ph (**b**) | 1978 | 29.5 (125.9) | 2021 | 2014 |

[a] IR spectra in $CH_2Cl_2$. [b] $^{31}$P NMR spectra in $CDCl_3$. [c] IR spectra in $CHCl_3$.

*trans*-[RhCl(CO)(**1a**)$_2$] (**4a**) and [Mo(CO)$_4$(**2a**)] (**5a**) were easily synthesized according to the typical method.[17,18] The chemical shift of **4a** in the $^{31}$P NMR spectrum was within the range of those of **4b**–**4d**, which have *ortho*-H aryl phosphanes. The $J_{Rh-P}$ value of **4a** was higher than those of the complexes **4b**–**d**, indicating that P atoms of **1a** have a high electron-withdrawing character.[19] The $\nu^{CO}$ values of both **4a** and **5a** were highest among each analogue, indicating that **1a** and **2a** have the lowest σ-donating ability and the highest π-acceptor ability among each type of aryl phosphane ligand, including $C_6F_5$ and 4-$CF_3C_6F_4$ phosphanes (**1e**, **1f**, **2e** and **2f**). Note that the π-acceptor ability of **1a** was comparable with that of triphenyl phosphite (P(OPh)$_3$, **1g**). In the synthesis of *cis*-[RhCl(CO)(**3a**)] (**6a**),[20] *cis*-[{RhCl(**3a**)}$_2$] (**7a**) was obtained instead of **6a**. This decarbonylation indicates that **3a** is a more electron-poor ligand than MeO-$F_{12}$-biphep **3c**[5b] or **3d**[21] in a similar case when MeO-$F_{28}$-biphep (**3f**) was used to obtain **7f**.[5b]

The stability of the BFPy phosphane ligand towards metal complex formation was confirmed using [$PtCl_2$(**2**)] complex **8**. The chelate effect of highly fluorinated dfppe (**2e** bearing $C_6F_5$) stabilizes the metal–phosphorus bond, although **2e** has a large cone angle.[1] However, ligand **2e** in complex **8e** was replaced with **2a** to give **8a** quantitatively in $(CD_3)_2CO$ in 24 h at room temperature (Scheme 2). In contrast, complex

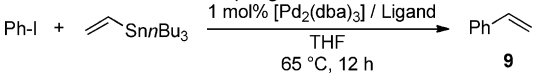



***Scheme 2.*** Stabilization of BFPy phosphane **2a** toward Pt complex.

**8a** was stable in the presence of **2e**. When the more basic dppe (**2b**) ligand was added to the solution of **8a**, ligand exchange occurred to give a mixture of **8b** and [(dppe)$_2$Pt]Cl$_2$,[22] and **8b** did not react with **2a**. The stabilities of ligand **2** towards platinum complex **8** decreased in the order of **2b** > **2a** > **2e**, which is inconsistent with the σ-donating ability of the ligand (**2a** vs. **2e**, see Table 1 **5a** vs. **5e**). These results show that less hindered and highly electron-poor **2a** constructs a stronger bond with Pt than the sterically hindered dfppe (**2e**).

The LAE of BFPy phosphanes was demonstrated by using several metal-catalyzed reactions. First, we performed Pd/**1a**-catalyzed Stille coupling. The Stille coupling of iodobenzene prefers less σ-donating ligands. Farina and Krishnan reported that triphenyl arsine ($AsPh_3$) considerably accelerated the Stille coupling.[23] However, highly electron-poor $P(C_6F_5)_3$ did not accelerate the reaction because of catalyst decomposition.[23] We performed the Stille coupling of iodobenzene with tributyl(vinyl)stannane using **1a** (Table 2). The reaction in the presence of 1 mol% [$Pd_2$(dba)$_3$] (dba = dibenzylideneacetone) with 4 mol% **1a** (**1a**/Pd = 2) in THF at 65 °C for 12 h gave styrene (**9**) in 94% yield (Table 2, entry 2), which exceeded the yields obtained with other ligands including $AsPh_3$ and P(OPh)$_3$ (Table 2, entries 3 and 4). In this reaction, the rate-determining step is known to be the transmetalation of the vinyl group to Pd.[23,24] The ligand effect in this step was evaluated by DFT calculation of the reaction of [L(Ph)PdI] (L = **1a**, **1b** and $AsPh_3$) with (vinyl)$SnMe_3$ (Figure 2).[24,25] Although we found the T-shaped intermediate *trans*-

***Table 2:*** LAE of **1a** on Stille coupling.




| Entry | Pd/Ligand | Ligand | Yield of **9** [%][a] |
|---|---|---|---|
| 1 | 1:0 | none | 7 |
| 2 | 1:2 | **1a** | 94 |
| 3 | 1:2 | $AsPh_3$ | 72 |
| 4 | 1:2 | P(OPh)$_3$ (**1g**) | 84 |
| 5 | 1:2 | $PPh_3$ (**1b**) | 65 |
| 6 | 1:2 | $P(C_6F_5)_3$ (**1e**) | 6 |
| 7 | 1:3 | **1a** | 92 |
| 8 | 1:3 | $AsPh_3$ | 73 |
| 9 | 1:3 | P(OPh)$_3$ (**1g**) | 62 |
| 10 | 1:3 | $PPh_3$ (**1b**) | 6 |
| 11 | 1:3 | $P(C_6F_5)_3$ (**1e**) | 6 |

[a] Yields were determined by $^1$H NMR spectroscopy.

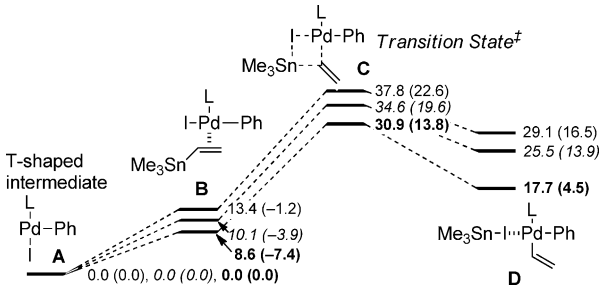
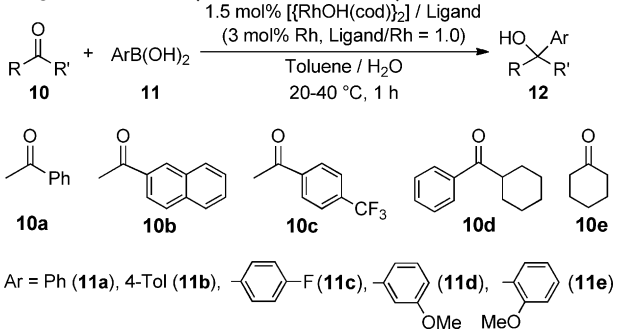



***Figure 2.*** Energy profile for the transmetalation of the Stille coupling. The relative free energies and potential energies (in parentheses) obtained from the DFT calculations are given in kcal mol$^{-1}$. Plain typeface L = **1b**, *italic* L = $AsPh_3$, **bold** L = **1a**.

[L(I)PdPh] (**A**), the isomer with *cis* arrangement of L and I was not obtained in all cases. The overall relative energy profile (**A**–**D**) of the **1a** system is smaller than those of the other systems. In particular, the activation barrier of the **1a** system (30.9 kcal mol$^{-1}$) is significantly lower than that of the corresponding $AsPh_3$ or **1b** systems (34.6 and 37.8 kcal mol$^{-1}$, respectively), thus indicating that highly electron-poor **1a** electronically accelerates the transmetalation step. However, similar electron-poor ligand **1e** showed no LAE in the Stille coupling (Table 2, entries 6 and 11 vs. 1). $^{31}$P NMR spectroscopy revealed that a large amount of **1e** was not complexed with Pd in the reaction mixture.[23] In the **1a** system, no inhibitory effect of excess ligand was observed (Table 2, entry 2 vs. 7) although the effect was apparent in the **1b** system (Table 2, entry 5 vs. 10).[23] The results show that the lower σ-donating ability of **1a** enables it to control the electronic properties of the catalyst while avoiding catalyst inactivation caused by coordination of additional ligands.[26]

The BFPy phosphane ligand accelerated the rhodium-catalyzed 1,2-addition of aryl boronic acid to an unactivated ketone. Although many examples of similar reactions using aldehyde have been reported, this type of 1,2-addition to a ketone had been limited, except for a few examples,[27] to activated ketones,[28] intramolecular reactions,[28] and the side reaction of 1,4-addition to an enone.[29] Furthermore, the exceptional successful cases[27] required high reaction temperatures (80–120 °C), a long reaction times (10–24 h), an equivalent amount of additive, and aryl boron derivatives instead of aryl boronic acid. The reaction of acetophenone (**10a**) with three equivalents phenylboronic acid (**11a**) in the presence of 1.5 mol % [{RhOH(cod)}$_2$] and 3 mol % (±)-**3a** in toluene/$H_2O$ gave 94 % yield of 1,1-diphenylethanol (**12aa**) when the reaction was carried out at 40 °C for 1 h without any additives (Table 3, entry 6). It is obvious that the large LAE of (±)-**3a** can be attributed to its electronic effect. [{RhOH-(cod)}$_2$] (1.5 mol %) showed no catalytic activity (Table 3, entry 1) and further addition of (±)-binap or (±)-**3f** resulted in no acceleration (Table 3, entries 2 or 5). The Rh catalyst with electron-poor phosphanes (±)-**3c** and **3d** gave the product in poor to moderate yields (Table 3, entries 3 and 4). The Rh/(±)-**3a** catalyst provided an excellent yield of the product in the reactions with other ketones and aryl boronic acids when allowed to react for 1 h at a temperature between 20 and 40 °C (Table 3, entries 7–14). The reaction mechanism

***Table 3:*** Rhodium-catalyzed 1,2-addition of aryl boronic acid to ketone.




| Entry | 10 | 11 | Ligand | T [°C] | Yield [%][a] |
|---|---|---|---|---|---|
| 1 | **10a** | **11a**[b] | none | 40 | 0 (**12aa**) |
| 2 | **10a** | **11a**[b] | (±)-binap[d] | 40 | 0 (**12aa**) |
| 3 | **10a** | **11a**[b] | (±)-**3c** | 40 | 35 (**12aa**) |
| 4 | **10a** | **11a**[b] | (±)-**3d** | 40 | 72 (**12aa**) |
| 5 | **10a** | **11a**[b] | (±)-**3f** | 40 | 2 (**12aa**) |
| 6 | **10a** | **11a**[b] | (±)-**3a** | 40 | 94 (**12aa**) |
| 7 | **10b** | **11a**[b] | (±)-**3a** | 40 | 91 (**12ba**) |
| 8 | **10c** | **11a**[c] | (±)-**3a** | 20 | 99 (**12ca**) |
| 9 | **10d** | **11a**[b] | (±)-**3a** | 30 | 81 (**12da**) |
| 10 | **10e** | **11a**[c] | (±)-**3a** | 20 | 98 (**12ea**) |
| 11 | **10e** | **11b**[c] | (±)-**3a** | 20 | 95 (**12eb**) |
| 12 | **10e** | **11c**[c] | (±)-**3a** | 20 | 96 (**12ec**) |
| 13 | **10e** | **11d**[c] | (±)-**3a** | 20 | 94 (**12ed**) |
| 14 | **10e** | **11e**[b] | (±)-**3a** | 20 | 93 (**12ee**) |

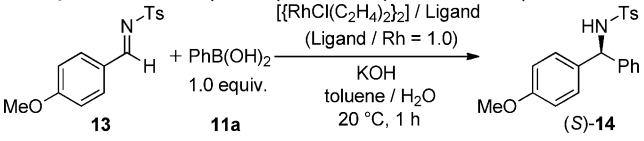
[a] Yield of isolated product. [b] 3 equiv was used. [c] 2 equiv was used. [d] binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl.

is presumed to be similar to that of Rh- or Pd-catalyzed 1,2-addition to an aldehyde[27a] involving the transmetalation of **11** to Rh, insertion of **10** into the Rh–Ar bond and then hydrolysis to give **12**. Because an excess amount of **11** was required, the rate-determining step is assumed to be the insertion step,[30] and highly electron-poor **3a** is expected to substantially accelerate the insertion.[5] As a result, an efficient Rh-catalyzed 1,2-addition of aryl boronic acids to unactivated ketones near room temperature was achieved using highly electron-poor ligand (±)-**3a** without any additives. We are currently making efforts to develop the asymmetric variants.[31]

Highly enantioselective catalysis using (*R*)-**3a** was achieved in the asymmetric arylation of aryl imine (Table 4).[32,33] The reaction of *N*-tosylimine **13** with one equivalent **11a** in the presence of 0.025 mol % [{RhCl($C_2H_4$)$_2$}$_2$] (0.05 mol % Rh) and 0.05 mol % (*R*)-**3a** in toluene/$H_2O$ with 20 mol % KOH at 20 °C for 1 h gave *N*-tosylamine (*S*)-**14** in 98 % yield and with 98 % *ee* (Table 4, entry 1). When 0.008 mol % Rh/(*R*)-**3a** was used, the TOF was 6900 h$^{-1}$ (Table 4, entry 2). This value is notable because similar known catalytic reactions using activated imine required 1.5–3 mol % catalyst loading, a longer reaction time (3–12 h, typically TOF < 10 h$^{-1}$ [34]), and higher reaction temperature.[32,33] The catalysis using (*R*)-binap or (*R*)-**3f** gave no product under these conditions (Table 4, entries 4 and 7). Although the use of the electron-poor phosphanes (*R*)-**3c** or (*R*)-**3d** showed acceptable TOF values (Table 4, entries 5 and 6), the values were much lower than that obtained with (*R*)-**3a**. Ultimately, the

***Table 4:*** Rhodium-catalyzed asymmetric arylation of *N*-tosylimine.




**13** **11a** (*S*)-**14**

| Entry | Ligand | Rh [mol%] | Yield [%][a] | *ee* [%][b] | TOF [$h^{-1}$] |
|---|---|---|---|---|---|
| 1 | (*R*)-**3a** | 0.05 | 98 | 98 | 1960 |
| 2 | (*R*)-**3a** | 0.008 | 55 | 96 | 6900 |
| 3[c] | (*R*)-**3a** | 0.008 | 87 | 95 | 10900 |
| 4 | (*R*)-**3f** | 0.05 | 0 | – | 0 |
| 5 | (*R*)-**3d** | 0.05 | 31 | 98 | 620 |
| 6 | (*R*)-**3c** | 0.05 | 25 | 97 | 500 |
| 7 | (*R*)-binap | 0.05 | 0 | – | 0 |

[a] Yield of isolated product. [b] Determined by HPLC on a chiral stationary phase. [c] 2 equiv **11a** was used at 40 °C.

TOF value using 0.008 mol% Rh/(*R*)-**3a** reached 10900 $h^{-1}$ at 40 °C (Table 4, entry 3). The prominent activity of the Rh/(*R*)-**3a** catalyst is considered to come from the large acceleration of the insertion step by the strong electronic effect of (*R*)-**3a**,[5b] and the scope and the detailed mechanism of this catalytic reaction will be explored in near future.

In summary, BFPy phosphanes were developed as a novel type of aryl phosphane ligand, in which the low σ-donating ability and low steric demands enabled them to control the electronic properties of the metal catalyst, providing a large LAE in the Stille coupling, the Rh-catalyzed 1,2-addition of aryl boronic acid to unactivated ketone, and the asymmetric arylation of *N*-tosylimine. Particularly in the last two cases, the BFPy phosphane achieved the record of the highest catalytic activity. BFPy phosphanes will be effective ligands for many metal-catalyzed reactions, in particular those involving transmetalation, insertion, or reductive elimination[18] processes.

## *Experimental Section*

Synthesis of **1a**: A dried flask was flushed with argon and charged with magnesium turnings (365 mg, 15 mmol), LiCl (318 mg, 7.5 mmol), and $Et_2O$ (20 mL). A solution of DIBAL in hexane (1.0 M, 100 μL, 0.10 mmol) was added and stirred for 5 min. Then 4-bromo-2,6-bis(trifluoromethyl)pyridine (1.77 g, 6.0 mmol) was added and the reaction mixture was stirred for 1 h. After addition of trichlorophosphane (131 μL, 1.5 mmol), the solution was stirred for 1 h and then saturated $NH_4Cl$(aq) was added. After extraction with EtOAc, the organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting solid was purified by silica gel column chromatography (hexane/EtOAc = 6:1) to give **1a** (0.79 g, 78% yield) as a white solid. M.p. > 220 °C (decomp.). $^1$H NMR (300 MHz, [D$_6$]acetone): $\delta = 8.48$ ppm (d, $J = 6.6$ Hz). $^{13}$C NMR (100 MHz, [D$_6$]acetone): $\delta = 121.9$ (q, $^1J_{F\text{-}C} = 274.3$ Hz), 129.6 (d, $^2J_{P\text{-}C} = 17.8$ Hz), 149.2 (dq, $^2J_{F\text{-}C} = 35.8$ Hz, $^3J_{P\text{-}C} = 5.9$ Hz), 150.0 ppm (d, $^1J_{P\text{-}C} = 22.5$ Hz). $^{19}$F NMR (282 MHz, [D$_6$]acetone): $\delta = -64.6$ (s). $^{31}$P NMR (121 MHz, [D$_6$]acetone): $\delta = 0.53$ ppm (s). Elemental anal. calcd (%) for $C_{21}H_6F_{18}N_3P$: C 37.46, H 0.90, N 6.24; found: C 37.39, H 1.26, N 6.37.

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**Keywords:** asymmetric catalysis · electrophilic addition · insertion · ligand effects · P ligands

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