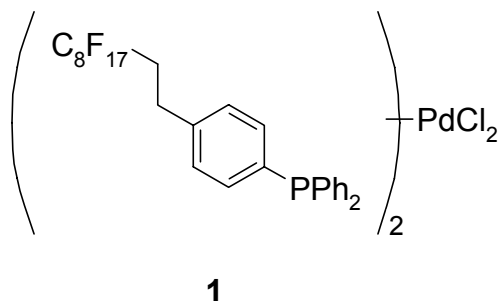


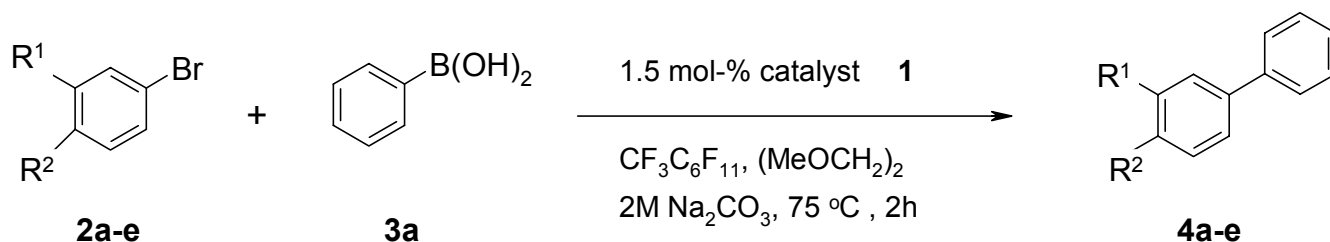
F034092

 Bis[diphenyl-[4-(1H, 1H, 2H, 2H-perfluorodecyl)phenyl]
 phosphine]palladium (II) chloride

Chemical Formula: C₅₆H₃₆Cl₂F₃₄P₂Pd
 Formula Weight: 1594.15
 Description: Catalyst
 Appearance: Yellow solid
 Soluble in: Undecafluoro(trifluoromethyl)cyclohexane
 or CF₃C₆F₁₁
 Stability: Store under N₂ in brown bottle

DESCRIPTION AND USES:

Bis[diphenyl-[4-(1H, 1H, 2H, 2H-perfluorodecyl)phenyl]phosphine]palladium (II) chloride **1** is the fluorinated version of 1,1'-bis(diphenylphosphine) palladium (II) chloride. This heavy fluorinated catalyst is used in carbon-carbon bond formation reactions in a fluorinated biphasic system (FBS).

In a fluorinated biphasic system, an organic solvent is coupled with an immiscible fluorinated solvent to dissolve the organic reactants and the fluorinated reagents. The temperature of this reaction mixture is raised in such a way that both solvents become miscible. Once the reaction is complete, the mixture is cooled to room temperature at which point the 2 solvents become immiscible again and form 2 layers. The organic layer contains the organic product while the fluorinated layer contains the fluorinated catalyst in the example shown. While traditional palladium catalysts such as [Pd(PPh₃)₄], [PdCl₂(PPh₃)₂] or [Pd(OAc)₂/PPh₃] cannot be recovered after the reaction, a FBS catalyst is readily recovered from the reaction mixture after completion and cooling down of the reaction. An example of the use of this FBS catalyst is demonstrated in the Pd-catalyzed Suzuki couplings of bromoarenes **2a-e** with phenylboronic acid **3a** (Table 1).¹ The desired products were obtained in excellent yields and the catalysts could be used in six consecutive runs without loss of activity (Table 1). The scope of the reaction was investigated with electron-deficient and electron-rich bromoarenes (Table 2).



- a = R¹ = H
 R² = *p*-NO₂
 b = R¹ = H
 R² = *p*-CH₃OCO
 c = R¹ = H
 R² = *p*-CHO
 d = R¹ = H
 R² = *p*-MeO
 e = R¹ = H
 R² = *m*-OCH₂O

Table 1. Suzuki Cross-couplings of various bromoarenes **2a-e** in 6 cycles

Entry	Substrate	Product	Yield (%)
1	2a	4a	91, 97, 93, 89, 91, 90
2	2b	4b	98, 96, 95, 89, 92, 89
3	2c	4c	94, 95, 89, 89, 88, 89
4	2d	4d	87, 90, 92, 89, 86, 90
5	2e	4e	95, 84, 89, 87, 91, 92

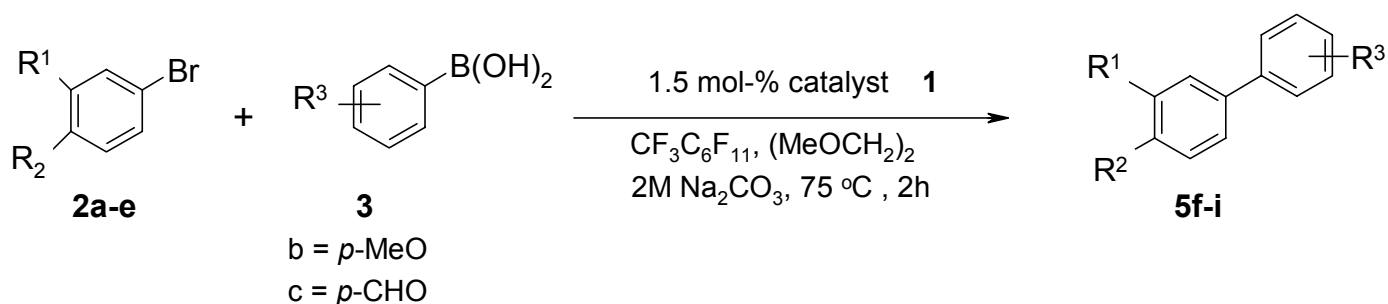


Table 2. Suzuki Cross-couplings with electron-rich and electron-deficient arylboronic acids

Entry	Substrate	Boronic acid (R3)	Product	Yield ^a (%)
1	2a	3b	5f	98, 96, 95, 96, 95, 96
2	2e	3b	5g	95, 96, 91, 93, 98, 99
3	2b	3c	5h	90, 93, 95, 95
4	2e	3c	5i	85, 81, 83, 82

a. Isolated yields from run 1 to 4 (Entries 1-2) and from run 3 to 4 (Entries 3-4). Only 4 runs were performed for entries 3-4.

TYPICAL PROCEDURE:

To a suspension of catalyst (0.003 mmol) in undecafluoro(trifluoromethyl)cyclohexane (1.5 mL) under Ar, bromoarene (0.200 mmol) in $(\text{MeOCH}_2)_2$ (1 mL; 0.2M stock soln) and phenylboronic acid (**2a**; 0.220) in $(\text{MeOCH}_2)_2$ (0.5 mL; 0.44M stock soln) were added. The mixture was heated at 75°C for 2h. After cooling to room temperature, the aqueous and organic phases were separated from the fluororous phase. The fluororous phase was washed with $(\text{MeOCH}_2)_2$ (2 x 1 mL), H_2O (2 x mL), and $(\text{MeOCH}_2)_2$ (2 x 1 mL). The fluororous phase containing the catalyst was removed and used as such for the next run. For the isolation of the product, H_2O (4 mL) was added to the $(\text{MeOCH}_2)_2$ layer, which was extracted with Et_2O (4 x 2 mL). The combined Et_2O solution was evaporated, the residue taken up in Et_2O (1 mL). The solution was passed through a plug of alox (neutral, act. II-III; 2 mL) and silica gel (4 mL). The filtrate was evaporated yielding the desired products.

REFERENCES:

1. Schneider, S. and Bannwarth, W., *Helvetica Chimica Acta*, **2001**, 735.