(2-Fluoroallyl)palladium complexes as intermediates in Pd-catalyzed Tsuji-Trost 2-fluoroallylations: synthesis and reactivity

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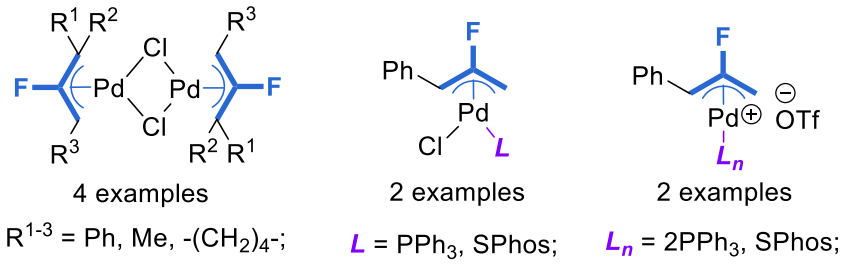
Abstract

The first examples of π-(2-fluoroallyl)palladium complexes were synthesised, isolated and characterized including chloride dimers, neutral chloride or cationic triflate comlexes bearing PPh_3 or SPhos as the ligands. Preliminary reactivity patterns indicating strong dependence of the chemoselectivity on "hardness" of the nucleophile and the ligand type were studied.



Keywords

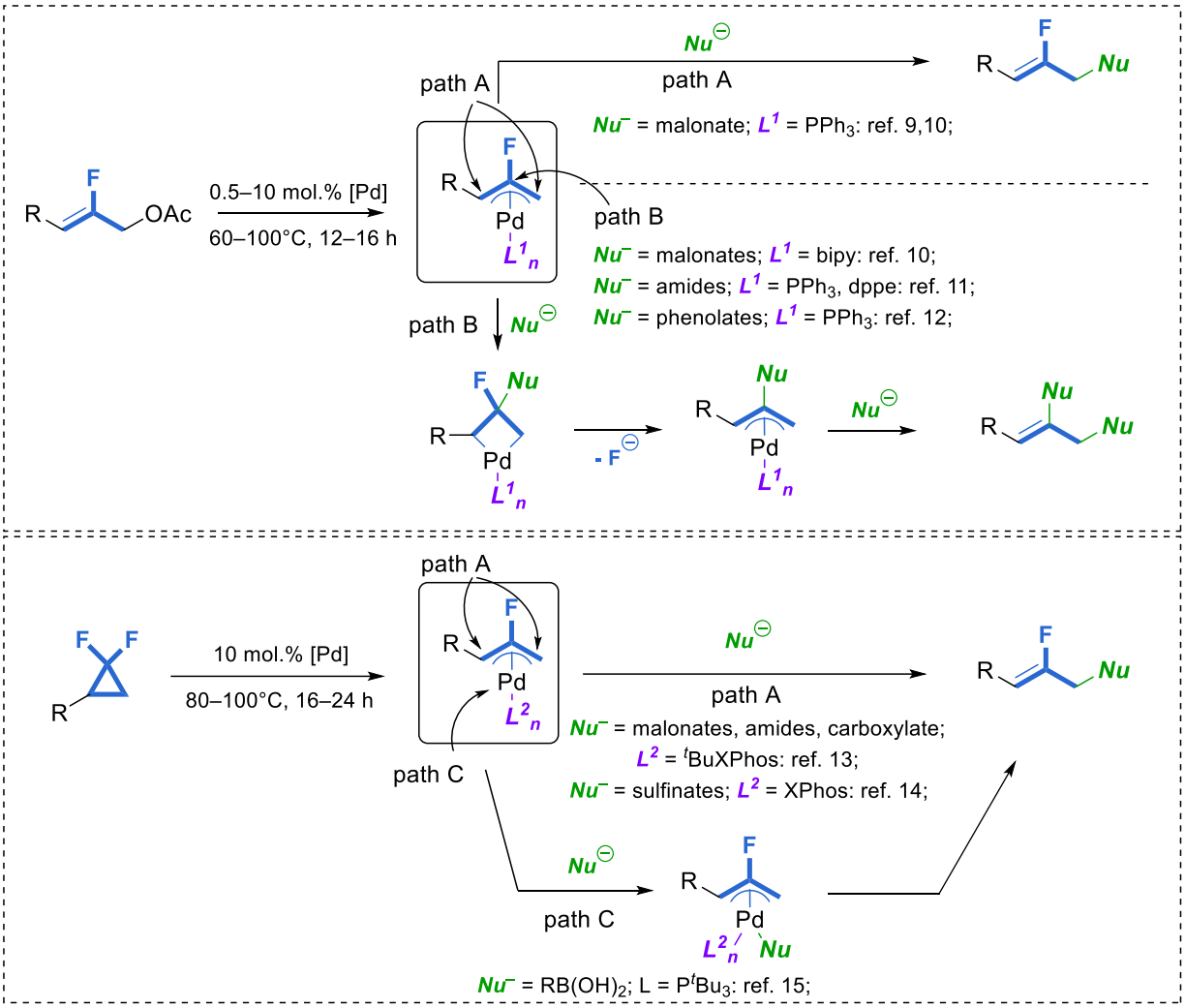
2-fluoroallylation, palladium complexes, Tsuji-Trost allylation, fluoroalkenes

1. Introduction

Tsuji-Trost allylic substitution has found a very broad application in modern organic synthesis in both achiral and enantioselective versions [1–5]. High synthetic potential of allylic alkylation causes a great attention of chemists for synthesis of biologically active organofluorine molecules. In the case of fluorinated allylic electrophiles, it can give easy and highly diastereo- and enantioselective access to functionalized fluoroalkenes — a very important class of bioisosters of amide bond in oligopeptides [6–8].

However, previously studied for this purpose fluorinated allylic esters were found to be challenging substrates [9]. Higher temperatures and longer reaction times compared to *non*-fluorinated analogues are required. Additionally, side substitution of fluorine at central carbon is

a dominant process in many cases (with malonates [10], amides [11], phenolates [12]) that leads to the formation of disubstitution product (Scheme 1, top).



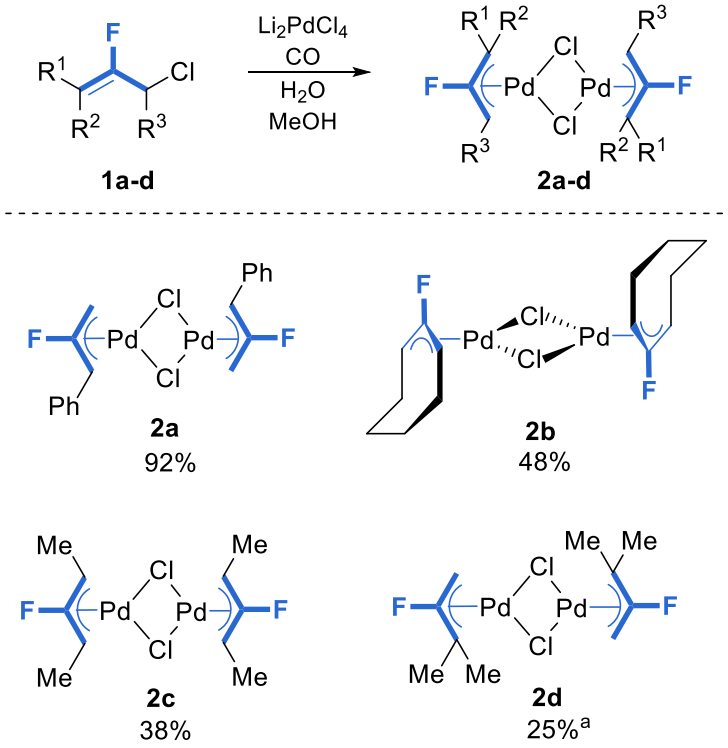
Scheme 1. Application of 2-fluoroallyl acetates and *gem*-difluorocyclopropanes in Pd-catalyzed Tsuji-Trost allylation

Recently developed ring-opening of *gem*-difluorocyclopropanes catalyzed by Pd(0) in the presence of Buchwald's biarylphosphine ligands is a promising alternative to 2-fluoroallyl acetates for allylic alkylation of various nucleophiles (Scheme 1, bottom). All used in these works, *C*-nucleophiles [13], as well as *O,N*- [13] and *S*-nucleophiles [14] gave target products of *mono*-substitution with no evidence of *di*-substitution reported. Also, recently developed application of *gem*-difluorocyclopropanes as sources of 2-fluoroallylic electrophiles in Suzuki cross-coupling with boronic esters should be noted [15].

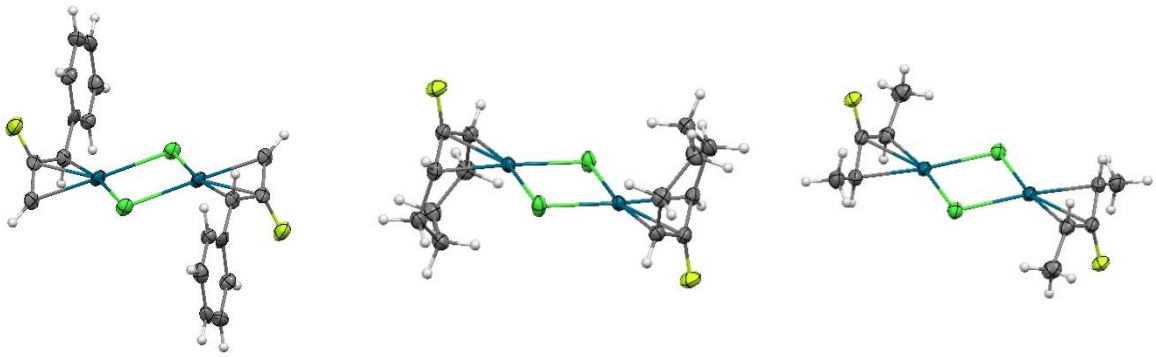
All these reactions were assumed to proceed *via* formation of π-(2-fluoroallyl)palladium complexes that, however, have never been prepared yet or at least detected in reaction mixtures. In the current work, we report isolation of the first examples of (2-fluoroallyl)palladium complexes and studying of their reactivity to the most common nucleophiles.

2. Results and Discussion

After screening of various pathways to (2-fluoroallyl)palladium complexes, we have found that the easiest one is the reaction of 2-fluoroallyl chlorides **1a–d** with Li_2PdCl_4 in MeOH using CO as a reducing agent (Scheme 2). Four examples of (2-fluoroallyl)palladium chloride dimers **2a–d** were prepared in moderate to high yields; and three of them were characterized by X-Ray crystallography (Fig. 1).



Scheme 2. Synthesis of (2-fluoroallyl)palladium chloride dimeres **2a-d** ([a] contaminated with 15 mol.% of unknown impurity contained presumably η_1-[Me_2C=CF–CH_2–Pd] moiety)

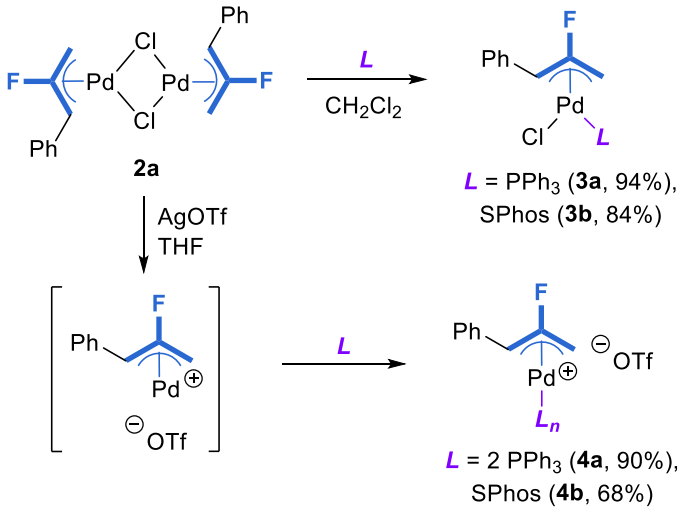


2a	**2b**	**2c**
CCDC 1995196	CCDC 1995198	CCDC 1995197

Figure 1. Single crystal X-ray structures of complexes **2a–c**. Atoms are represented as thermal ellipsoids (p=50%)

Encouraged with these results, we tried to prepare several neutral and ionic 2-fluoroallyl complexes with phosphine ligands. Addition of 1 equiv. of PPh_3 or SPhos to dimer **2a** afforded

complexes **3a,b** in high yields, respectively (Scheme 3). Removing of chloride-anion with AgOTf preceding to addition of ligands, allowed to obtain ionic complexes **4a,b** with two PPh_3 ligands or with one SPhos ligand (Scheme 3). On the contrary, attempts to prepare ionic complexes with Bipy and ^{t}BuXPhos ligands failed, likely due to their instability. Thus, Bipy complex decomposed during crystallization forming free Bipy and unknown products, whereas ^{t}BuXPhos complex decomposed even in THF solution after 1 h forming Pd-black and a complicated by-product mixture.

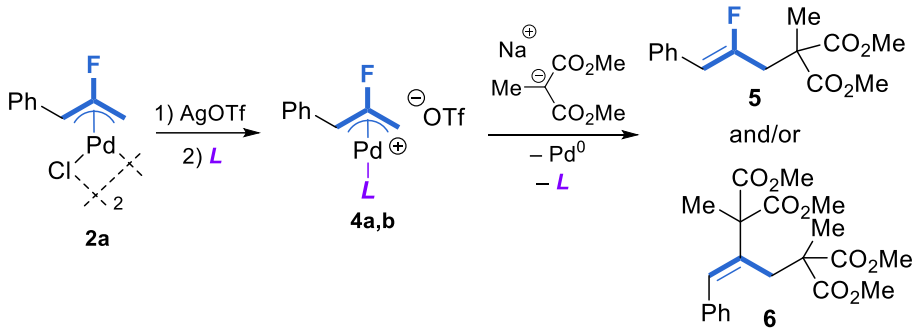


Scheme 3. Synthesis of neutral and ionic π-(2-fluoroallyl)palladium complexes (Abbreviation: SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl)

Preliminary screening of reactivity patterns depending on the ligand was made using sodium dimethyl methylmalonate as a model nucleophile. (2-Fluorocinnamyl)palladium complexes were generated using the same strategy as for complexes **4a,b** — elimination of chloride in **2a** with AgOTf followed by addition of a ligand (See Table 1). Reactions with the malonate proceeded smoothly at room temperature in most cases affording products of mono- or disubstitution **5** or **6** depending on the ligand according to the mechanism presented in Scheme 1 (see path A for mono-adduct **5** and path B for bis-adduct **6**). The highest yields of monosubtitution product **5** were obtained using PPh_3, SPhos, ^{t}BuXPhos and XantPhos as the ligands (Table 1, Entries 1–4). Other monodentate phosphine ligands PCy_3 and P^tBu_3 gave low yield of **5** (Entries 5, 6). Notably, in the case of P^tBu_3, formation of fluorinated side product was observed that was preliminary assigned as the isomer of **5** with terminal double bond (Entry 6, product **7**). Other bidentate ligands dppp, dppb and (*R*)-BINAP (Table 1, Entries 8–10) except dppe (Entry 7) gave **5** as the major product along with impurity of side product of disubstitution **6**. Weakly bonded pyridine and tmeda gave low yields (Entries 11, 12); whereas bidentate Bipy and Phen gave disubstitution product **6** selectively, however, in moderate yields (Entries 13, 14). All these results are in a good agreement with previously studied reactivity of (2-

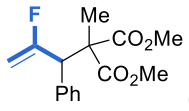
chloroallyl)palladium complexes [16], as well as with ligand screening in catalytic version of this reaction in ref. [10]. However, analyzing these results, one should not forget that complexes suggested as intermediate in these reactions could be instable (as shown above for ^{t}BuXPhos and Bipy complexes, Entries 3 and 13 in Table 1) and so other structures are probably involved in reaction mechanism in these cases.

Table 1. Reaction of ionic complexes **4a,b** with sodium dimethyl methylmalonate



Entry	Ligand (*L*)	Yield, (%)	
		Mono-adduct **5**	Bis-adduct **6**
1	2 PPh_3	89	0
2	SPhos	79	0
3	^{t}BuXPhos	79	0
4	XantPhos	87	0
5	2 PCy_3	6	0
6	2 $P^{t}Bu_3$ [a]	29	0
7	dppe	6	22
8	dppp	71	21
9	dppb	85	8
10	(*R*)-BINAP	87	7
11	2 Py	7	1
12	tmeda	0	25
13	Bipy	0	66
14	Phen	0	55

[a] A fluorinated side product is formed in 15% yield (NMR data) which may be preliminary assigned to compound **7**

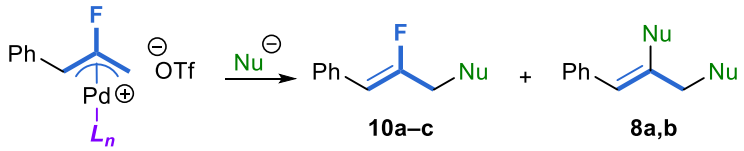


(**7**)

Abbreviations: ^{t}BuXPhos = 2-di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl; XantPhos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; (*R*)-BINAP = (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene; tmeda = 1,2-bis(dimethylamino)ethane; Bipy = 2,2′-bipyridine; Phen = 1,10-phenanthroline.

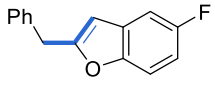
Isolated complexes **4a,b** were further studied in reactions with model *O*-, *N*- and *S*-nucleophiles. On the contrary to malonates, almost all these nucleophiles require elevated reaction temperatures. A ratio between central and terminal additions strongly depends on nucleophile hardness (see Table 2). Phenoxide gave only products of central addition; but depending on the ligand the major product was either diaryl ether **8a** (with PPh_3, entry 1), or benzofuran derivative **9**. The selectivity of sodium butyl(tosyl)amide addition depends on the ligand — SPhos gave only 2-fluoroallyl sulfamide **10a** *via* terminal addition (Entry 4); whereas PPh_3 resulted in major central addition affording disulfamido substituted product **8b** (Entry 3). On the opposite, both diethylamine and sodium 4-methylbenzenesulfinate reacted *via* pure terminal addition with the formation of 2-fluoroallyl amine **10b** or sulfone **10c** (Entries 5–8). Notably, reaction with $HNEt_2$ proceeded smoothly even at room temperature affording more than 90% yields of allylamine **10b**.

Table 2. Reaction of ionic complexes **4a,b** with *O*-, *N*- and *S*-nucleophiles.[a]



Entry	Nucleophile	Complex **4**	Yield (%)	
			Mono-adduct	Bis-adduct
1	4-FC_6H_4OK	**4a** (2 PPh_3)	–	**8a** (24%, *Z/E* 76:24)[b]
2		**4b** (SPhos)	–	– [c]
3	Bn(Ts)NNa	**4a** (2 PPh_3)	**10a** (7)	**8b** (23%, *E/Z* 71:29)
4		**4b** (SPhos)	**10a** (69)	–
5	$HNEt_2$ [d]	**4a** (2 PPh_3)	**10b** (97)	–
6		**4b** (SPhos)	**10b** (91)	–
7	4-$MeC_6H_4SO_2Na$	**4a** (2 PPh_3)	**10c** (86%, *Z/E* 98:2)	–
8		**4b** (SPhos)	**10c** (64%, *Z/E* 96:4)	–

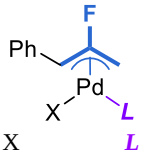
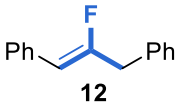
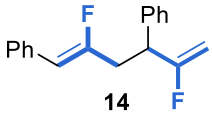
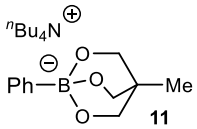
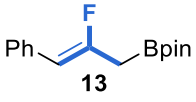
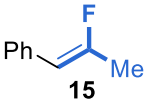
[a] Reaction conditions: Pd-complex **4** (0.025 mmol), Nucleophile (0.075 mmol), THF (2.5 mL), 80°C, 4 h. [b] Additionally 2-benzyl-5-fluorobenzofuran (**9**) was obtained in yield 28%. [c] Benzofuran **9** was obtained in yield 43%. [d] Room temperature, 24 h.



(**9**)

Another known mode of reactivity of allyl palladium complexes is transmetalation followed by reductive elimination that is operated under cross-coupling conditions. To test the reactivity of (2-fluoroallyl)palladium complexes in the processes of this type, we used neutral complexes **3a,b** with PPh_3 or SPhos as the ligands, respectively. These complexes successfully reacted with phenyltriolborate **11** and diboron reagent B_2pin_2 as model cross-coupling partners leading to 2-fluoro-1,3-diphenylpropene **12** or 2-fluorocinnamyl boronate **13**, respectively (Table 3). In both cases elevated temperatures were required again. Notable is Replacement of halide counterion with acetate is well-known way to accelerate transmetalation step in Suzuki and Suzuki-Miyaura reactions. However, in the cases of complexes **3a,b** the influence of acetate counterion was not large. For Suzuki coupling with triolborate **11**, addition of AgOAc lowered the yields (Entries 3,4 vs. 1,2). Moreover, for PPh_3-complex **3a** it induced side dimerization of 2-fluorocinnamyl fragment giving **14** as a single isomer (Entry 3). For Suzuki-Miayura coupling with B_2pin_2, AgOAc did not affect on PPh_3-complex reaction, whereas accelerate slightly the reaction of SPhos-complex **3b** (Entry 8 vs. 6). Also notable is formation of side fuoroalkene **15** in the case PPh_3-complex — a product of formal "hydrolysis" of **3a** (Entries 5, 7).

Table 3. Neutral complexes **3a,b** in cross-coupling conditions [a]

Entry	Nucleophile	Complexes **3**		Yields (%)	
				 **12**	 **14**
		X	*L*		
1	 **11**	Cl	PPh_3	40	–
2		Cl	SPhos	48	–
3		OAc	PPh_3	30	33
4		OAc	SPhos	33	–
				 **13**	 **15**
5	B_2pin_2	Cl	PPh_3	70	21
6		Cl	SPhos	50[b]	–
7		OAc	PPh_3	72	23
8		OAc	SPhos	64[c]	–

[a] Reaction conditions: Pd-complex **3a** or **3b** (0.025 mmol), AgOAc (0–0.025 mmol), Nucleophile (0.075 mmol), THF (2.5 mL), 80°C (for $PhB(OR)_3^-$) or 60° (for B_2pin_2), 4 h; [b] 48% of **3b** were recovered; [c] 24% of **3b** were recovered;

3. Conclusions

In summary, we have synthesized and fully characterized the first examples of π-(2-fluoroallyl)palladium complexes. The key point is preparation of π-(2-fluoroallyl)palladium

chloride dimers from 2-fluoroallyl chlorides with Li_2PdCl_4 in MeOH using CO as a reducing agent. Using 2-fluorocinnamyl dimer so obtained, we have demonstrated the possibility of isolation of neutral chloride and ionic triflate complexes bearing PPh_3 or SPhos as the ligands, whereas similar complexes with ^{t}BuXPhos and Bipy were found to be unstable. Synthesized complexes with PPh_3 and SPhos ligands, as well as generated *one pot* with various *P*- and *N*-mono- and bidentate ligands were studied in reactions with *C*-, *N*-, *O*- and *S*-nucleophiles showing strong dependence of the chemoselectivity on "hardness" of the nucleophile and the ligand type.

4. Experimental part

4.1. *General Information*

2-Fluoroallyl chlorides **1a–c** were prepared by CuCl-catalyzed ring-opening isomerization of corresponding *gem*-chlorofluorocyclopropanes according to [17]. Pure sample of **1d** was prepared by chlorination of 3,3-dimethyl-2-fluoroallyl alcohol (ref. [18]) with $SOCl_2$ in pyridine. Carbon monooxide was generated by portionwise addition of HCO_2H to conc. H_2SO_4 and passed through a washing bottle with conc. H_2SO_4 for drying. Nucleophiles for the reaction with Pd-complexes were obtained in following ways: a 0.05 *M* batch solution of sodium dimethyl methylmalonate was prepared prior to use from NaH (dispersion in mineral oil) and 1.2 excess of dimethyl methylmalonate in THF for 1 h at 0°C. Potassium 4-fluorophenolate was prepared from 4-fluorophenol and KOH in anhydrous EtOH. A suspension of sodium *N*-benzyl-*N*-tosylamide in THF ("concentration" ca. 0.03 *M*) was prepared for each reaction separately prior to use from NaH and 1.2 excess of BnNHTs in THF for 1 h at 0°C. Diethylamine was distilled over KOH prior to use. Sodium *para*-tolylsulfinate was prepared by reduction of TsCl with Zn in water followed by quenching with NaOH. Tetrabutylammonium 4-methyl-1-phenyl-2,6,7-trioxa-1-borabicyclo[2.2.2]octan-1-uide **11** was prepared as previously published [19]. Ligand B_2pin_2 was purchased from ABCR and used as received. THF was distilled over $LiAlH_4$, stored over 4A Linde type molecular sieves. Dichloromethane was distilled over KOH prior to use.

All reactions were carried out under argon atmosphere using standard Schlenk technique unless otherwise stated. Silica gel 60 (40–63 μm, Merck) was used for column chromatography. TLC analysis was made on standard Merck plates with F_{254}-inducator using UV or $KMnO_4$ solution for visualization. GC analysis was performed on Chromatec Crystal 2000M gas chromatograph (capillary column Macherey-Nagel OPTIMA-1, 300 × 0.025 cm, 100% dimethylpolysiloxane (0.25 μm), carrier gas – He, detector – FID). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Varian Inova 400 (400.1, 376.4 and 100.6 MHz, respectively) or Bruker AVANCE II 300 (300.1, 282.3 and 75.4 MHz, respectively) in $CDCl_3$ or C_6D_6 containing TMS

(δ = 0 ppm) and C_6F_6 (δ = –162.2 ppm) as internal standards. GC/MS analysis was performed on gas chromatographer Chromatec Crystal 5000.2 with Thermo DSQ II (EI, 70 eV, 200°C) mass-detector. HRMS were recorded on Bruker micrOTOF equipment using electro spray ionization (ESI). Elemental analyses were made in Laboratory of microanalysis IOC RAS on Perkin-Elmer Series II 2400 CHN Analyzer.

4.2. *Synthesis of (2-fluoroallyl)palladium chloride dimers **2a–d**. General Procedure.*

Modified procedure from ref. [16] was used. A mixture of $PdCl_2$ (1–5 mmol) and LiCl (4 equiv., 4–20 mmol) was dissolved in water (0.3–1.5 mL) under gentle heating on a plate of magnetic stirrer. After cooling to room temperature, this solution was transferred to a three-neck round bottom flask and diluted with MeOH (6–30 mL). Then, 2-fluoroallyl chloride **1a–d** (4 equiv., 1–20 mmol) was added; and CO was bubbled through the solution with stirring on a magnetic stirrer for 30 min to 2 h. During this period color changed from deep brown to yellow and a yellow precipitate formed; then bubbling was continued for 1 h more. Next, the reaction mixture was diluted with CH_2Cl_2 and water. Organic layer was separated, dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was washed with hexane and recrystallized by slow diffusion of hexane into CH_2Cl_2 solution in a fridge overnight (except **2d**, see below). The crystals were collected, washed with hexane and dried under high vacuum.

*4.2.1. η^3-(2-Fluoro-3-phenylallyl)palladium chloride dimer **2a***

This compound was obtained by the general procedure on a 5 mmol scale as yellow microcrystals (1.308 g, 92% yield, *Z/E* = 92:8).

Z-isomer: ^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 7.65–7.55 (m, 2H, arom.), 7.45–7.33 (m, 1H), 7.36–7.17 (m, 2H), 4.47 (d, *J* = 22.1 Hz, 1H, Ph*CH*=), 3.86 (dd, *J* = 8.9, 4.5 Hz, 1H, =CH_2 (*cis* to F)), 2.88 (dd, *J* = 28.4, 4.5 Hz, 1H, =CH_2 (*trans* to F)). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ: –107.1 (m). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ: 144.3 (d, *J* = 299.6 Hz, -CF=), 132.9 (d, *J* = 3.0 Hz, C-arom.), 129.9 (d, *J* = 4.4 Hz, CH-arom.), 129.0 (d, *J* = 0.8 Hz, CH-arom.), 129.0 (s, CH-arom.), 69.8 (d, *J* = 6.6 Hz, Ph*CH*=), 47.4 (d, *J* = 14.4 Hz, =CH_2). HRMS (ESI) *m/z*: [(2-F-cinnamyl)Pd(CH_3CN)]$^+$, Calcd. for $C_{11}H_{11}FNPd^+$ 281.9905; Found 281.9917. Anal.: calcd. for C_9H_8FClPd: C, 39.02; H, 2.91. Found: C, 38.91, H, 3.01.

E-isomer: ^{1}H NMR (400.0 MHz, $CDCl_3$) δ: (aromatic signal overlapped with *Z*-isomer), 5.95 (d, *J* = 10.8 Hz, 1H, Ph*CH*=), 4.14–4.07 (m, 1H, =CH_2 (*cis* to F)), 3.47 (dd, *J* = 32.0, 4.5 Hz, 1H, =CH_2 (*trans* to F)). ^{19}F NMR (376.4 MHz, $CDCl_3$) δ: –102.7 (m).

*4.2.2. η_3-(2-Fluorocyclohept-2-enyl)palladium chloride dimer **2b***

This compound was obtained by the general procedure on a 1 mmol scale as yellow octahedrons (123.2 mg, 48% yield).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 5.01–4.90 (m, 2H, 2 -CH=), 2.06–1.88 (m, 4H, CH_2), 1.62–1.50 (m, 2H, CH_2), 1.50 – 1.38 (m, 2H, CH_2). ^{19}F NMR (376.4 MHz, $CDCl_3$) δ: –103.2 (br. s). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 140.8 (d, *J* = 287.8 Hz, CF), 72.9 (d, *J* = 14.5 Hz, 2 -CH=), 29.53 (d, *J* = 4.1 Hz, 2 CH_2), 26.31 (s, 2 CH_2). HRMS (ESI) *m/z*: [(2-F-cycloheptenyl)Pd]$^+$, Calcd. for $C_7H_{10}FPd^+$ 218.9799; Found 218.9798. [(2-F-cycloheptenyl)Pd(CH_3CN)]$^+$, Calcd. for $C_9H_{13}FNPd^+$ 260.0065; Found 260.0072. Anal.: calcd. for $C_7H_{10}FClPd$: C, 32.97; H, 3.95. Found: C, 32.89, H, 3.80.

*4.2.3. η_3-(3-Fluoropent-3-en-2-yl)palladium chloride dimer **2c***

This compound was obtained by the general procedure on a 1 mmol scale as yellow microcrystals (83.8 mg, 38% yield, *Z/E* > 99/1).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 3.54 (dq, *J* = 20.9, 6.6 Hz, 2H, 2 -CH=), 1.28 (d, *J* = 6.5 Hz, 6H, 2 CH_3). ^{19}F NMR (376.4 MHz, $CDCl_3$) δ: –118.8 (t, *J* = 21.0 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 145.8 (d, *J* = 294.9 Hz, CF), 63.2 (d, *J* = 12.3 Hz, 2 -CH=), 11.4 (d, *J* = 2.6 Hz, 2 CH_3). HRMS (ESI) *m/z*: [(2-F-3,3-Me_2All)Pd]$^+$, Calcd. for $C_5H_8FNPd^+$ 281.9905; Found 281.9917. [(2-F-3,3-Me_2All)Pd(CH_3CN)]$^+$, Calcd. for $C_{11}H_{11}FNPd^+$ 281.9905; Found 281.9917. HRMS (ESI) *m/z*: [(2-F-1,3-Me_2All)Pd]$^+$, Calcd. for $C_5H_8FPd^+$ 192.9641; Found 192.9642. [(2-F-1,3-Me_2All)Pd(CH_3CN)]$^+$, Calcd. for $C_7H_{11}FNPd^+$ 233.9908; Found 233.9909. Anal.: calcd. for C_5H_8FClPd: C, 26.23; H, 3.52. Found: C, 26.25; H, 3.47.

*4.2.4. η_3-(2-Fluoro-3-methylbut-2-enyl)palladium chloride dimer **2d***

Obtained by the general procedure on a 1 mmol scale as yellow solids. Complex **2d** was found to be soluble in hexane and precipitated as yellow oil during attempts to recrystallize. (68.1 g, 25% yield, contaminated with 15 mol.% of unknown impurity contained presumably η_1-[Me_2C=CFCH_2Pd] moiety).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 3.86 (dd, *J* = 9.7, 4.7 Hz, 1H, =CH_2 (*cis* to F)), 3.15 (dd, *J* = 30.9, 4.7 Hz, 1H, =CH_2 (*trans* to F)), 1.42 (d, *J* = 1.8 Hz, 3H, CH_3), 1.25 (d, *J* = 1.8 Hz, 3H, CH_3). ^{19}F NMR (376.4 MHz, $CDCl_3$) δ: –108.5 (br. d, *J* = 30.8 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 143.3 (d, *J* = 291.2 Hz, CF), 81.3 (d, *J* = 11.2 Hz, Me_2C=), 45.6 (d, *J* = 15.7 Hz, =CH_2), 22.8 (s, CH_3), 20.0 (d, *J* = 5.0 Hz, CH_3). HRMS (ESI) *m/z*: [(2-F-3,3-Me_2All)Pd]$^+$, Calcd. for $C_5H_8FPd^+$ 192.9641; Found 192.9644. [(2-F-3,3-Me_2All)Pd(CH_3CN)]$^+$, Calcd. for $C_7H_{11}FNPd^+$ 233.9908; Found 233.9913. Anal.: calcd. for C_5H_8FClPd: C, 26.23; H, 3.52. Found: C, 25.49; H, 3.25.

(Impurity): ^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 3.80 (dd, *J* = 4.1, 1.6 Hz, 1H, in CH_2), 2.98 (t, *J* = 1.4 Hz, 1H, in CH_2), 2.17 (d, *J* = 2.5 Hz, 3H, CH_3), 1.66 (d, *J* = 19.0 Hz, 3H, CH_3). ^{19}F NMR (376.4 MHz, $CDCl_3$) δ: –113.3 (m). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 124.2 (d, *J* = 272 Hz, CF, from {^{1}H,^{13}C}-HMBC), 111.7 (d, *J* = 17.4 Hz, Me_2C=), 57.7 (d, *J* = 6.2 Hz, CH_2), 20.6 (d, *J* = 25.4 Hz, CH_3), 17.4 (d, *J* = 3.9 Hz, CH_3).

4.3. *Synthesis of (triphenylphosphine)(η$_3$-2-fluoro-3-phenylallyl)palladium chloride **3a***

A Schlenk flask was charged with **2a** (0.10 mmol, 64.0 mg) and PPh_3 (0.20 mmol, 63.8 mg) and filled with argon on a Schlenk line. Benzene (4.2 mL) was added and the yellow solution was stirred at room temperature for 3 h; then, evaporated to dryness on a rotary evaporator and redissolved in CH_2Cl_2 (1.0 mL). The product was precipitated by addition of hexane (5.0 mL) and crystallization in a fridge overnight. The precipitate was filtered off, washed with hexane and dried under high vacuum, affording **3a** as yellow solids (125.7 mg, 94% yield).

^{1}H NMR (400.0 MHz, C_6D_6) δ: 7.83 (d, *J* = 7.7 Hz, 2H in Ph), 7.76–7.68 (m, 6H in PPh_3), 7.20 (t, *J* = 7.7 Hz, 2H in Ph), 7.09 (d, *J* = 7.4, 1H in Ph), 7.04–6.87 (m, 9H in PPh_3), 4.72 (dd, *J* = 29.2, 10.0 Hz, 1H, Ph*CH*=), 2.26 (br. s, 2H, =CH_2). ^{19}F NMR (376.4 MHz, C_6D_6) δ: –101.1 (br. s). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6) δ: 27.0 (br. s). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 147.5 (dd, *J* = 290.6, 7.5 Hz, CF), 134.2 (d, *J* = 12.6 Hz, CH-arom.), 130.7 (d, *J* = 2.5 Hz, CH-arom.), 130.0 (t, *J* = 4.9, 3.8 Hz, CH-arom.), 128.8 (d, *J* = 8.2 Hz, CH-arom.), 128.7 (s, CH-arom.), 128.4 (s, CH-arom.), 85.0 (dd, *J* = 30.6, 6.7 Hz, Ph*CH*=), 46.3 (d, *J* = 16.1 Hz, =CH_2). HRMS (ESI) *m/z*: [(2-F-cinnamyl)Pd(PPh_3)]$^+$, Calcd. for $C_{27}H_{23}FPPd^+$ 503.0561; Found 503.0565. [(2-F-cinnamyl)Pd(PPh_3)(CH_3CN)]$^+$, Calcd. for $C_{29}H_{26}FNPPd^+$ 544.0827; Found 544.0831. Anal.: calcd. for $C_{27}H_{23}FClPPd$: C, 60.13; H, 4.30. Found: C, 59.81, H, 3.32.

4.4. *Synthesis of (η$_3$-2-fluoro-3-phenylallyl)palladium(2-cyclohexylphosphino-2',6'-dimethoxybiphenyl) chloride **3b***

A Schlenk flask was charged with **2a** (0.68 mmol, 377.4 mg) and SPhos (1.36 mmol, 560.0 mg) and filled with argon on a Schlenk line. Toluene (2.4 mL) was added and the reaction mixture was stirred at room temperature for 2 h. During the first 15 min, precipitation of a yellow solid was observed. Next, the mixture was diluted with pentane (5.7 mL) and left in a freezer overnight for complete crystallization. The precipitate was filtered off, washed with pentane and dried under high vacuum, affording **3b** as yellow solids (788.1 mg, 84% yield).

^{1}H NMR (400.0 MHz, C_6D_6) δ: 7.85 (d, *J* = 7.7 Hz, 2H, arom.), 7.58 (t, *J* = 8.5 Hz, 1H, arom.), 7.24 (t, *J* = 7.6 Hz, 2H, arom.), 7.14–6.95 (m, 5H, arom.), 6.31 (br. s, 2H, 2CH *orto* to OMe in

SPhos), 4.13 (dd, *J* = 29.9, 9.6 Hz, 1H, Ph*CH*=), 3.51–3.02 (m, 8H, 2OMe + $=CH_2$), 2.54–2.15 (m, 2H, Cy), 2.10–1.96, 1.91–1.38, 1.34–0.98 (m, Cy, 20H total). ^{19}F NMR (376.4 MHz, C_6D_6) δ: –103.6 (dt, *J* = 29.8, 21.2 Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6) δ: 38.8 (br. s). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ: 158.1 (s), 146.1 (dd, *J* = 288.2, 6.8 Hz), 139.9 (d, *J* = 7.6 Hz), 135.8 (d, *J* = 11.2 Hz), 133.4–133.0 (m), 131.1 (d, *J* = 31.5 Hz), 129.6 (dd, *J* = 6.0, 3.0 Hz), 129.2 (s), 128.5 (d, *J* = 1.7 Hz), 127.7 (s), 125.8 (d, *J* = 9.1 Hz), 120.0–119.4 (m), 103.8 (s), 86.1 (dd, *J* = 29.3, 5.7 Hz), 55.5 (s), 40.7 (d, *J* = 15.4 Hz), 35.6 (d, *J* = 21.0 Hz), 29.8 (s), 27.4 (d, *J* = 11.9 Hz), 27.2 (d, *J* = 13.5 Hz), 26.2 (d, *J* = 1.6 Hz). HRMS (ESI) *m/z*: [(2-F-cinnamyl)Pd(SPhos)]$^+$, Calcd. for $C_{35}H_{43}FO_2PPd^+$ 651.2027; Found 651.2018. Anal.: calcd. for $C_{35}H_{43}ClFO_2PPd$: C, 61.14; H, 6.30. Found: C, 60.28, H, 6.39.

4.5. *Synthesis of bis(triphenylphosphine)(η3-2-fluoro-3-phenylallyl)palladium triflate* ***4a***

A Schlenk flask was charged with **2a** (0.25 mmol, 138.5 mg) and AgOTf (0.50 mmol, 129.5 mg) and filled with argon on a Schlenk line. THF (10 mL) was added and the reaction mixture was stirred for 1 hour. The resulted suspension was filtered under argon through a pad of *Celite* (Sigma-Aldrich, cat. no. 06858). Addition 5 mL of THF were used to wash the *Celite® S*. To the filtrate, PPh_3 (1.0 mmol, 262.3 mg) was added; and the resulted solution was stirred for 2 h. Then it was concentrated on a rotary evaporator to ca. 5 mL and diluted with 100 mL of *n*-hexane. Immediately formation of light beige precipitate was observed. The mixture was left for 2 hours at room temperature; the solids were filtered off, washed with hexane and dried under high vacuum, affording **4a** as light beige solids (409.8 mg, 90% yield).

^1H NMR (400.0 MHz, $CDCl_3$) δ: 7.42–7.22 (m, 18H, PPh_3), 7.16–7.05 (m, 12H, PPh_3), 6.96 (t, *J* = 7.5 Hz, 1H, Ph), 6.91 (d, *J* = 7.8 Hz, 2H, Ph), 6.74 (t, *J* = 7.7 Hz, 2H, Ph), 5.62 (dd, *J* = 31.6, 10.4 Hz, 1H, Ph*CH*=), 3.92 (ddd, *J* = 34.9, 9.8, 5.0 Hz, 1H, $=CH_2$ (*trans* to F)), 3.35 (dt, *J* = 11.9, 5.7 Hz, 1H, *cis* to F)). ^{19}F NMR (376.4 MHz, $CDCl_3$) δ: –78.6 (s, 3F, OTf), –94.7 (td, *J* = 33.2, 12.5 Hz, 1F, CF). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ: 27.1 (dd, *J* = 45.8, 2.2 Hz), 25.9 (d, *J* = 45.8 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ: 147.9 (dt, *J* = 288.6, 7.2 Hz, CF), 133.8 (d, *J* = 8.5 Hz, CH in PPh_3), 133.7 (d, *J* = 8.7 Hz, CH in PPh_3), 131.0 (d, *J* = 2.5 Hz, CH in PPh_3), 130.9 (dd, *J* = 44.2, 1.7 Hz, C in PPh_3), 130.6 (d, *J* = 2.4 Hz, CH in PPh_3), 130.2–130.0 (m, CH in Ph), 129.3 (dd, *J* = 42.6, 1.4 Hz, C in PPh_3), 129.0 (d, *J* = 10.7 Hz, CH in PPh_3), 128.7 (d, *J* = 10.5 Hz, CH in PPh_3), 128.1 (br. s, CH in Ph), 127.7 (br. s, CH in Ph), 85.4 (d, *J* = 28.7 Hz, Ph*CH*=), 61.9 (dd, *J* = 29.9, 14.1 Hz, $=CH_2$). HRMS (ESI) *m/z*: [(2-F-cinnamyl)Pd$(PPh_3)_2$]$^+$, Calcd. for $C_{45}H_{38}FP_2Pd^+$ 765.1478; Found 765.1476. Anal.: calcd. for $C_{46}H_{38}F_4O_3P_2PdS$: C, 60.37; H, 4.19. Found: C, 61.08, H, 3.99.

4.6. *Synthesis of (η_3-2-fluoro-3-phenylallyl)palladium(2-cyclohexylphosphino-2′,6′-dimethoxybiphenyl) triflate **4b***

This complex was prepared using the procedure described for **4a**, using **2a** (0.25 mmol, 139.3 mg), AgOTf (0.50 mmol, 129.2 mg) and SPhos (206.3 mg). After the reaction completed, the formation of light-yellow precipitate was observed. The reaction mixture was diluted with 45 mL of anhydrous Et_2O and left in a freezer for 3 h. The solids were filtered off, washed with anhydrous Et_2O and dried under high vacuum, affording **4b** as light-yellow solids (273.4 mg, 68% yield).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.72–7.65 (m, 1H, arom.), 7.54–7.42 (m, 5H, arom), 7.35–7.27 (m, 2H, arom.), 6.83–6.76 (m, 1H, arom.), 6.48 (br. s, 1H, SPhos, CH *orto* to MeO), 6.19 (t, *J* = 8.3 Hz, 1H, SPhos, CH *meta* to MeO), 5.63 (br. s, 1H, SPhos, CH *orto* to MeO), 5.12 (dd, *J* = 33.0, 9.5 Hz, 1H, Ph*CH*=), 3.95–3.28 (m, 8H, 2MeO + =CH_2), 2.53–2.15 (m, 2H, CH in Cy), 2.09–1.61 (m, 10H, CH_2 in Cy), 1.61–1.04 (m, 10H, CH_2 in Cy). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ: –78.6 (s, 3F, OTf), –100.3 (dtd, *J* = 32.8, 21.7, 4.1 Hz, 1F, CF). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$) δ: –60.7 (br. s). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ: 159.2 (s), 145.1 (s), 144.8 (s), 144.3 (dd, *J* = 285.6, 8.4 Hz), 135.7 (s), 135.1 (s), 132.8 (br. s), 132.5 (d, *J* = 2.3 Hz), 132.4 (s), 131.8 (s), 131.4 (d, *J* = 12.9 Hz), 129.4 (t, *J* = 2.5, 1.4 Hz), 129.0 (dd, *J* = 6.2, 3.1 Hz), 128.7 (d, *J* = 2.4 Hz), 128.2 (d, *J* = 5.5 Hz), 103.6 (br. s), 100.2 (d, *J* = 4.4 Hz), 96.4 (dd, *J* = 24.8, 3.9 Hz), 56.3 (br. s), 40.6 (d, *J* = 15.9 Hz), 37.0 (d, *J* = 24.3 Hz), 29.3 (br. s), 28.7 (s), 27.1 (d, *J* = 13.7 Hz), 27.0 (d, *J* = 11.6 Hz), 25.7 (s). HRMS (ESI) *m/z*: [(2-F-cinnamyl)Pd(SPhos)]$^+$, Calcd. for $C_{35}H_{43}FO_2PPd^+$ 651.2027; Found 651.2017. Anal.: calcd. for $C_{36}H_{43}F_4O_5PPdS$: C, 53.90; H, 5.41. Found: C, 54.12, H, 5.31.

4.7. *Reactions of (2-fluoroallyl)palladium complexes with sodium dimethyl methylmalonate (Table 1)*

A modified procedure from ref. [16] was used. A 20-mL screw neck vial was charged with a Ligand (0.025 mmol for bidentate ligands, 0.050 mmol for monodentate ligands), sealed with a septum and filled with argon on a Schlenk line through a needle. An aliquot of 0.10 *M* solution of (2-fluorocinnamyl)palladium triflate in THF was added (0.025 mmol, 2.5 mL, freshly prepared from dimer **2a** and AgOTf), and the mixture was stirred for 30 min. Then, a 0.50M solution of sodium dimethyl methylmalonate in THF was added (0.125 mmol, 2.5 mL, 5 equiv.). The reaction mixture was stirred at room temperature for 24 h, then quenched with 5.7 *M* solution of HCl in dioxane (30–40 μL, 7–9 equiv.) and evaporated on a rotary evaporator to dryness. Then mesitylene and 4-fluorobenzotrifluoride were added (internal standards for ^{1}H and ^{19}F NMR, respectively), and the mixture was dissolved in ca. 0.8 mL of $CDCl_3$, filtered through

a short pad of *Celite® S* and analyzed by ^{1}H and ^{19}F NMR and GC/MS. Results are presented in the Table 1.

Products **5** and **6** were identified by characteristic signals that were the same to previously published [10]. Side product **7** could only be preliminary identified (see characteristic NMR signals and MS data below) as *dimethyl 2-(2-fluoro-1-phenylallyl)-2-methylmalonate*.

^{1}H NMR (400.0 MHz, $CDCl_3$) (selected peaks) δ: 4.71 (dd, *J* = 18.6, 3.1 Hz, 1H, Ph*CH*<), 4.58 (d, *J* = 18.8 Hz, 1H, $=CH_2$ (*cis* to F)), 4.41 (dd, *J* = 50.1, 3.1 Hz, 1H, $=CH_2$ (*trans* to F)). ^{19}F NMR (376.4 MHz, $CDCl_3$) δ: –96.7 (dt, *J* = 50.3, 18.7 Hz). MS (EI) *m/z*: 280 ([M^+], 5), 221 (43), 201 (9), 188 (10), 146 (14), 135 (100), 115 (53), 109 (9).

4.8. *Reactions of (2-fluoroallyl)palladium complexes **3** and **4** with nucleophiles (Tables 2, 3)*

A 20 mL screw neck vial was charged with a complex **3** or **4** (0.025 mmol). In a stream of argon, THF (2.5 mL) and Nucleophile (4-FC_6H_4OK, Bn(Ts)NNa, $HNEt_2$, 4-$MeC_6H_4SO_2Na$, triolborate **11** or B_2pin_2) (0.075 mmol, 3 equiv.) were added. The vial was sealed and stirred at 80°C (or 60°C for B_2pin_2) on an oil bath for 4 h. The reaction mixture was concentrated on a rotary evaporator to ca. 1 mL; 4-fluorobenzotrifluoride as an internal standard was added; the mixture was filtered through a short pad of *Celite® S* and analyzed by ^{19}F NMR and GC/MS.

To detect the formation of products of disubstitution that do not contain any fluorine atom, the reaction mixture was quenched with 5.7 *M* solution of HCl in dioxane (30–40 μL, 7–9 equiv.) and evaporated on a rotary evaporator to dryness (except reactions with diethylamine, that were diluted with Et_2O, washed with 10% K_2CO_3 solution, dried over K_2CO_3, concentrated on a rotary evaporator). Then, mesitylene and 4-fluorobenzotrifluoride as internal standards were added; the mixture was dissolved in ca. 0.8 mL of $CDCl_3$, filtered through a short pad of *Celite® S* and analyzed by ^{1}H and ^{19}F NMR and GC/MS.

The products were identified by characteristic NMR signals using previously published data or compared to authentic samples: **8b** — [11], **10a** — [13], **10b** — [20], **12** — [15], **13** — [17], **14** — [18], **15** — [21]. Compounds **8a** and **9** are unpublished, authentic samples were prepared by previously published procedures for similar compounds [12] (see below). Compound **10c** was previously published only in a PhD. thesis of one the author of the current paper [22], therefore, the procedure is listed below.

*4.8.1. 2,3-Bis(4-fluorophenyloxy)-1-phenylpropene **8a***

According to published procedure [12], starting from 2-fluorocinnamyl acetate (195.1 mg, 1.0 mmol), 4-fluorophenol (341.1 mg, 3.0 mmol), $Pd(PPh_3)_4$ (116.8 mg, 0.10 mmol) and Cs_2CO_3 (925.3 mg, 2.8 mmol) in toluene (5.0 mL) at 100°C for 10 h, **8a** was obtained as a clear viscous oil that slowly crystallized at 20°C (169.9 mg, 53% yield, *Z/E* = 84/16, R_f = 0.28, eluent — *n*-

hexane/benzene/EtOAc 300:100:1). *Z*-Configuration of the major isomer was confirmed by nOe cross-peak between =CH– and –CH_2OAr protons in {^{1}H,^{1}H}-NOESY.

Z-**8a**: ^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.60–7.53 (m, 2H, arom.), 7.42–7.17 (m, 4H, arom.), 7.10–6.90 (m, 5H, arom.), 6.89 – 6.78 (m, 2H, arom.), 6.29 (s, 1H, =CH), 4.52 (s, 2H, -CH_2OAr). ^{19}F NMR (376.4 MHz, $CDCl_3$) δ: –121.2 (tt, *J* = 8.3, 4.6 Hz, 1F), –123.4 (tt, *J* = 8.4, 4.3 Hz, 1F). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 158.6 (d, *J* = 241.1 Hz, CF-arom.), 157.7 (d, *J* = 239.1 Hz, CF-arom.), 154.4 (d, *J* = 2.1 Hz, C-arom.), 151.2 (d, *J* = 2.2 Hz, C-arom.), 147.1 (s, C-arom.), 128.9 (s, CH-arom.), 128.6 (s, CH-arom.), 127.8 (s, CH-arom.), 118.5 (d, *J* = 8.3 Hz, CH-arom.), 117.9 (s, =CH), 116.3 (d, *J* = 23.9 Hz, CH-arom.), 116.2 (d, *J* = 7.5 Hz, CH-arom.), 115.9 (d, *J* = 23.1 Hz, CH-arom.), 67.9 (s, CH_2O).

E-**8a**: ^{1}H NMR (400.0 MHz, $CDCl_3$) δ: (aromatic signals are overlapped with *Z*-isomer), 6.04 (s, 1H, =CH), 4.71 (s, 2H, CH_2OAr). ^{19}F NMR (376.4 MHz, $CDCl_3$) δ: –119.4 (tt, *J* = 7.9, 4.8 Hz, 1F), –123.7 (tt, *J* = 8.4, 4.4 Hz, 1F).

*4.8.2. 2-Benzyl-5-fluorobenzofuran **9***

According to published procedure [12], starting from 2-fluorocinnamyl acetate (201.5 mg, 1.0 mmol), 4-fluorophenol (579.9 mg, 5.2 mmol), [(2-Methallyl)PdCl]$_2$ (19.5 mg, 0.05 mmol), dppp (41.3 mg, 0.10 mmol) and Cs_2CO_3 (933.0 mg, 2.9 mmol) in dioxane(5.0 mL) at 100°C for 10 h, **9** was obtained as a clear oil (112.7 mg, 55% yield, R_f = 0.31, eluent — *n*-hexane/benzene/EtOAc 100:10:0.1).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.36–7.22 (m, 6H, arom.), 7.10 (dd, *J* = 8.6, 2.6 Hz, 1H, CH-arom.), 6.90 (td, *J* = 9.1, 2.7 Hz, 1H, CH-arom.), 6.32 (d, *J* = 1.1 Hz, 1H, CH-furan), 4.07 (s, 2H, CH_2). ^{19}F NMR (376.4 MHz, $CDCl_3$) δ: –122.1 (td, *J* = 9.0, 4.1 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 159.8 (s, C-arom.), 159.2 (d, *J* = 237.3 Hz, CF-arom.), 151.2 (s, C-arom.), 136.9 (s, C-arom.), 129.6 (d, *J* = 10.7 Hz, C-arom.), 129.0 (s, CH-arom.), 128.7 (s, CH-arom.), 127.0 (s, CH-arom.), 111.5 (d, *J* = 9.7 Hz, CH-arom.), 111.0 (d, *J* = 26.3 Hz, CH-arom.), 106.1 (d, *J* = 25.0 Hz, CH-arom.), 103.7 (d, *J* = 3.8 Hz, CH-arom.), 35.1 (s, CH_2). MS (EI) *m/z*: 226 ([M^+], 53), 225 (100), 207 (5), 196 (23), 149 (47).

*4.8.3. 1-[(2-fluoro-3-phenylallyl)sulfonyl]-4-methylbenzene **10c***

A vial was charged with 2-bromo-2-fluoro-1-phenylcyclopropane (108.2 mg, 0.50 mmol), *p*-TolSO_2Na (107.1 mg, 0.60 mmol) and CuBr (14.3 mg, 0.10 mmol). In a steam of argon, anhydrous DMSO was added (0.50 mL); the vial was sealed and heated on an oil bath at 100°C for 24 h. The reaction mixture was diluted with CH_2Cl_2, washed with satd. NH_3, water and brine, and dried over K_2CO_3. After evaporation of the solvent on a rotary evaporator, the residue was

purified by column chromatography on silica eluting with n-hexane/EtOAc (gradient from 50:1 to 5:1) to give **10c** as colorless solvent solids (137.3 mg, 95% yield, *Z/E* 80:20).

Z-**10c**: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 7.75–7.85 (m., 2H, arom.), 7.19–7.44 (m., 7H, arom.), 5.62 (d, *J* = 37.2 Hz, 1H, =CH), 4.05 (d, *J* = 18.7 Hz, 2H, CH_2SO_2), 2.43 (s, 3H, CH_3). ^{19}F NMR (188.3 MHz, $CDCl_3$) δ: –101.6 (dt, *J* = 37.2, 18.7 Hz). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$) δ: 148.4 (d, *J* = 265 Hz, =CF), 145.3 (s, C-arom.), 135.3 (s, C-arom.), 132.1 (d, *J* = 3.3 Hz, C-arom.), 129.9 (s, CH-arom.), 128.9 (d, *J* = 7.5 Hz, CH-arom.), 128.6 (s, CH-arom.), 128.6 (s, CH-arom.), 128.2 (d, *J* = 2.3 Hz, CH-arom.), 114.2 (d, *J* = 6.7 Hz, =CH), 61.0 (d, *J* = 29.4 Hz, CH_2SO_2), 21.7 (s, CH_3). HRMS (ESI) *m/z*: $[M+Na]^+$, Calcd. for $C_{16}H_{15}FO_2SNa^+$ 313.0669; Found 313.0658.

E-**10c**: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ: (aromatic signals are overlapped with *Z*-**10c**) 6.53 (d, *J* = 19.6 Hz, 1H, –CH=), 4.18 (d, *J* = 20.5 Hz, 2H, CH_2SO_2). ^{19}F NMR (188.3 MHz, $CDCl_3$) δ: –99.0 (td, *J* = 20.5, 19.6 Hz).

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Supplementary Data

Copies of ^{1}H, ^{19}F, ^{31}P and ^{13}C NMR spectra.

X-Ray crystallography data for compounds **2a-c**.

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