Supporting Information

for

Palladium-Catalyzed Intermolecular Fluoroesterification of Styrenes: Exploration and Mechanistic Insight

Haihui Peng, Zheliang Yuan, Hao-yang Wang, Yin-Long Guo and Guosheng Liu*
State Key Laboratory of Organometallics Chemistry, and Shanghai Mass Spectrometry Center,
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road,
Shanghai, China, 200032.
Email: *gliu@mail.sioc.ac.cn*

General Procedure and Characterization of New Compounds

Content

General Considerations.

All commercially available compounds were purchased from Aldrich or Alfa Aesar. NMR spectra were recorded on a Varian Inova 400 (400 MHz for ^{1}H; 376 MHz for ^{19}F; 100 MHz for ^{13}C) spectrometer. The chemical shifts (δ) are given in parts per million relative to internal standard TMS (0 ppm for ^{1}H) and $CDCl_3$ (77.0 ppm for ^{13}C). Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate.

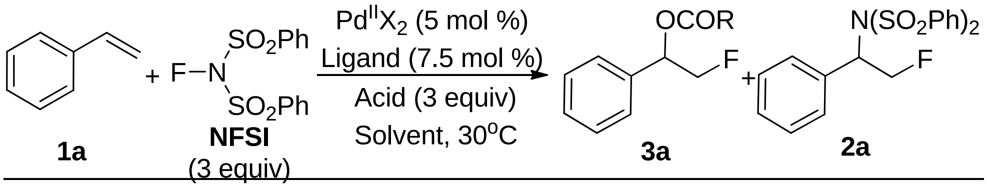
1. General procedure for screening reaction

In a dried glass tube, palladium catalyst (0.01 mmol, 5 mol %), ligand (0.015 mmol, 7.5 mol %), *N*-fluorobenzenesulfonimide (NFSI, 0.6 mmol, 3.0 equivalents) were dissolved in dioxane (1.0 mL). Then styrene (0.2 mmol, 1.0 equivalent) and CF_3CO_2H (0.6 mmol, 3.0 equiv) were added, and the reaction mixture was stirred at 30℃ for 3-5 h. After the reaction completed, a solution of trifluoromethylbenzene was added as an internal standard. The NMR yields were obtained by ^{19}F NMR ananlysis of the crude mixture. The results were summarized in Table **S1**.

2.1. General procedure for Palladium-Catalyzed Fluoroesterification of Styrenes with CF_3COOH as additives: In a dried glass tube, $PdCl_2$ (2.7 mg, 0.015 mmol), **L2** (4.6 mg, 0.023 mmol, 7.5 mol %), NFSI (285.0 mg, 0.9 mmol), Styrene **1** (0.3 mmol) were dissolved in 1,4-Dioxane (0.8 mL), and then CF_3CO_2H (1.5 mmol) was added. The reaction mixture was stirred at 30℃ for 3-5 h. After the reaction completed, a solution of trifluoromethylbenzene was added as an internal standard. The NMR yields of **3** were obtained by ^{19}F NMR ananlysis of the crude mixture. Then methanol (3mL) and 5 drops of wet pyridine (or aq. $NaHCO_3$) were added, and the reaction mixture was stirred for another 1h. After that, the solvent was removed under vacuum, and the residue was purified by silica gel column chromatography with a gradient eluant of petroleum ether and diethyl ether to afford product **5**. The results were showed in Table **2** and equations 2-6.

2.2. General procedure for Palladium-Catalyzed Oxyfluorination of Styrene with CCl_3COOH as additives: In a dried glass tube, $PdCl_2$ (2.7 mg, 0.015 mmol), **L2** (4.6 mg, 0.023 mmol), NFSI (285.0 mg, 0.9 mmol), Styrene **1** (0.3 mmol) were dissolved in 1,4-Dioxane (0.8 mL), and then CCl_3COOH (1.5 mmol) was added. The reaction mixture was stirred at 30℃ for 3-5 h, After the reaction completed, the solvent was removed under vacuum, and the residue was purified by silica gel column chromatography with a gradient eluant of petroleum ether and ethyl acetate to afford product **4**. The results were listed in Table **3**.

Table S1. Screening Results.[a]



Entry	PdX_2	Acid	Ligand	Solvent	Yield(%)[b] **3a/2a**
1	$Pd(OAc)_2$	CH_3CO_2H	Bathcuproine (BC)	dioxane	0/86
2	$Pd(OAc)_2$	*p*-NO_2PhCO_2H	BC	dioxane	0/73
3	$Pd(OAc)_2$	CCl_3CO_2h	BC	dioxane	9/0
4	$Pd(OAc)_2$	CF_3CO_2H	BC	dioxane	13/0
5	$Pd(OAc)_2$	CH_3SO_3H	BC	dioxane	0
6	$Pd(OAc)_2$	CF_3CO_2H	none	dioxane	0
7	$Pd(OAc)_2$	CF_3CO_2H	Pyridine[c]	dioxane	0
8	$Pd(OAc)_2$	CF_3CO_2H	4,4'-di-^{t}Bu-bpy	dioxane	25/7
9	$Pd(OAc)_2$	CF_3CO_2H	Bipyrimidine	dioxane	5/0
10	$Pd(OAc)_2$	CF_3CO_2H	1,10-Phenanthroline	dioxane	30/10
11	$Pd(OAc)_2$	CF_3CO_2H	2,9-Dimerthyl-1,10-Phen	dioxane	31/5
12	$Pd(OAc)_2$	CF_3CO_2H	Bathophenanthroline	dioxane	34/5
13	$Pd(OAc)_2$	CF_3CO_2H	**L2**	dioxane	45/10
14	$PdCl_2$	CF_3CO_2H	**L2**	dioxane	82/9
15	$Pd(OOCCF_3)_2$	CF_3CO_2H	**L2**	dioxane	27/11
16	$Pd(dba)_2$	CF_3CO_2H	**L2**	dioxane	54/7
17	$Pd(PPh_3)_4$	CF_3CO_2H	**L2**	dioxane	63/0
18	$PdCl_2$	CF_3CO_2H	**L2**	DCE	45/0
19	$PdCl_2$	CF_3CO_2H	**L2**	Toluene	39/0
***20*[d]**	**$PdCl_2$**	**CF_3COOH**	**L2**	**dioxane**	**91/0**

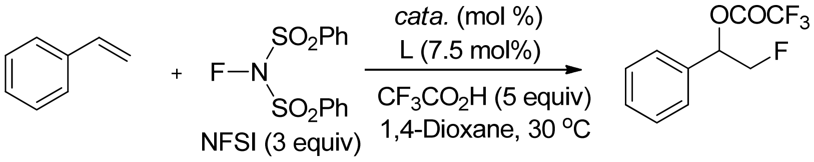
[a]Reaction condition: the reactions were coducted in 0.2 mmol scale in 0.5 mL solvent; [b]F-NMR yield with trifluoromethylbenzene as the internal standard; [c]Pyridine (15 mol%); [d]$PdCl_2$(5 mol%), **L** (7.5 mol%), NFSI (3 equiv), CF_3CO_2H (5 equiv), 1,4-dioxane (0.5 mL), 30°C; DCE = Dichloroethane.

3. Controlling Experiments

3.1. Catalyst screening

Another possibility is that palladium catalyst act as a Lewis acid to activate NFSI. Thus, a variety of metal catalyst, including palladium and other metals, were screened. The typical procedure is the same as described in Table S1. The results were listed in Table **S2**.

Table S2. Catalyst Screening[a]



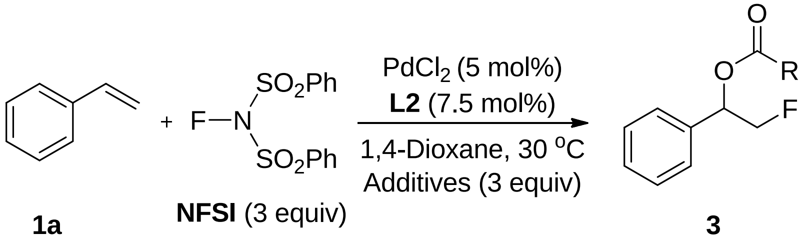
Entry	catalyst	loading (mol%)	Yield(%)[b]	Entry	catalyst	loading (mol%)	Yield(%)[b]
1	$PdCl_2$	5	87	15	$Pd(PhCN)_2(BF_4)_2$	5	15
2	$Pd(OAc)_2$	5	72	16	BF_3 Et_2O	10	0
3	$Pd(TFA)_2$	5	72	17	$PtCl_2$	5	16
4	$Pd(CH_3CN)_2Cl_2$	5	79	18	$AuCl_3$	5	0
5	$Pd(PhCN)_2Cl_2$	5	79	19	$Mg(ClO_4)_2$	10	0
6	$Pd(PPh_3)_2Cl_2$	5	79	20	$(dppp)NiCl_2$	5	0
7	$Pd(dppp)Cl_2$	5	75	21	$Cu(OTf)_2$	5	0
8	$PdCl_2(sp)$	5	85	22	$Zn(OTf)_2$	10	0
9	$PdBr_2$	5	80	23	AgOTf	10	0
10	$Pd(acac)_2$	5	82	24	$Yb(OTf)_3$	10	0
11	Na_2PdCl_4	5	0	25	$Fe(acac)_2$	10	0
12	$Pd(PPh_3)_4$	5	73	26	$FeCl_3$	10	0
13	$Pd(dba)_2$	5	80	27	$FeBr_3$	10	0
14	$Pd(CH_3CN)_2(BF_4)_2$	5	13	28	$SnCl_4$	10	0

[a]Reactions were conducted in 0.2 mmol scale; [b]Using trifluoromethylbenzene as intenal standard.

3.2 Screening Results of Inorganic Carboxylate Salts

In order to investigate C-O bond formation, serial carboyxlate salts were used to instead carboxylic acid. The General procedure is the same with aicd. Results were listed in Table **S3**.

Table S3. Screening of Carboxylate Salts.[a]



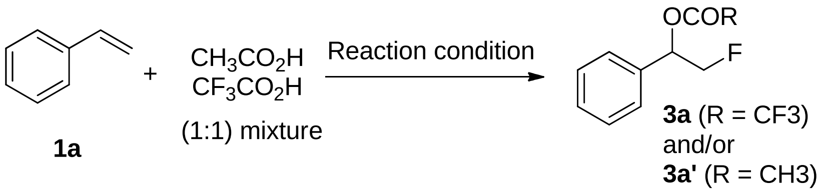
Entry	Additives	Yield[b]
1	CH_3COONa	nd
2	CH_3COOK	nd
3	CF_3COONa	nd
4	CF_3COOCs	nd
5	CF_3COOAg	nd

[a] The reaction condition: **1a** (0.2 mmol), $PdCl_2$ (5 mol%), **L2** (7.5 mol%), NFSI (0.6 mmol) and additives (0.6 mmol) in 1,4-Dioxane (0.5 mL) at 30 °C; [b] ^{19}F NMR yield with trifluoromethylbenzene as internal standard. nd = no detected

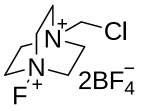
3.3 Controlling Experiments

To detect different electrophilic fluorine reagents, the reaction was taken. As shown in table **S4**, substrate **1a** treated by standard reaction condition in the mixed of HOAc and CF_3CO_2H afforded only product **3a** in 80% yield (entry 1). In contrast, Under the electrophilic fluorination condition, the reaction afforded product 3a', rather than product 3a (entries 2-3).

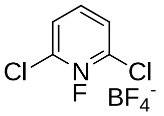
Table S4. Controlling Experiments with different Reaction Conditions.



Entry	Conditions	Yield
1[a]	standard condition (PdCl$_2$/**L2** NFSI)	**3a**, 80%
2[b]	Selectfluor	ND
3[c]	N-Fluoropyridium	**3a'**, 43%



Selelctfluor

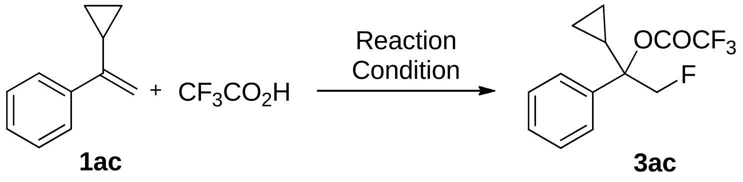


N-Fluoropyridium

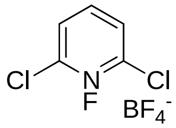
[a] Standard condition with 1:1 ratio of HOAc and CF_3CO_2H, ^{1}HNMR yield with CF_3-DMA as internal standard; [b] **1a** (0.3 mmol), Selectfluor (0.3 mmol), CF_3COOH :CH_3COOH =1:1 (2 mL); [c] **1a** (0.3 mmol), N-Fluoropyridium (0.3 mmol), CF_3COOH : CH_3COOH = 1:1 (2 mL).

While a radical "clock" type substrate **1x** was selected to conduct controlling experiments. As shown in Table S7, the reaction under standard reaction condition afforded the desired product **3x** in 50% yield (entry 1, table S5). In contrast, the reaction under electrophilic fluorination conditions, such as N-Fluoropyridium or XeF_2, the reaction delivered the complex mixture. The crude spectrum suggested that cyclopropane was completely opened, and without observation of **3x**. These results exclude the possibility of radical pathway.

Table S5. Controlling Experiments of **1ac** with different Reaction Conditions.



Entry	Conditions	**3ac** (Yield)
1[a]	standard condition ($PdCl_2$/**L2** NFSI)	50%
2[b]	N-Fluoropyridium	0
3[c]	XeF_2	0

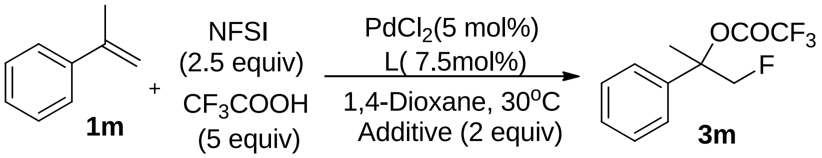


N-Fluoropyridium

[a] Standard Condition, ^{1}HNMR yield with CF_3-DMA as internal standard; [b] **1ac** (0.3 mmol), F^+ (0.3 mmol), in CF_3CO_2H; [c] **1ac** (0.3 mmol), XeF_2 (0.3 mmol), CF_3CO_2H (0.3 mmol), in CH_2Cl_2 (2 mL); both reactions in entries 2 and 3 gave mixture products without **3ac** formation, and the signal of cyclopropayl group was disappeared.

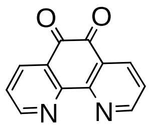
In addition, the possibility pathway involving carbon cationic intermediate was also investigated by using substrate 1m. As shown in Table S6, addition of carbon cationic scavengers did not affect the reaction. Furthermore, if the reaction undergoes electrophilic fluorination process, the reaction of **1m** should be faster than that of **1a**.[S1] Thus, both reactions of **1m** and **1a** were monitored by NMR, and we found that reaction rate of **1m** does be slower than that of styrene **1a**. Those results ruled out the electronic fluorination pathway.

Table S6. Pd-catalyzed Fluoroesterification of 1m with Carbon Cationic Scavenger.[a]



Entry	Additive	Yield/%[b]
1	No	80
2	CF_3CH_2OH	67
3	Toluene	77
4	PhOMe	65
5	CH_3COOH	79[c]

Ligand



[a]All reactions were runed in 0.2 mmol scale. [b]F NMR yield with CF3Ph as internal standard. [c]No **3m'** was observed.

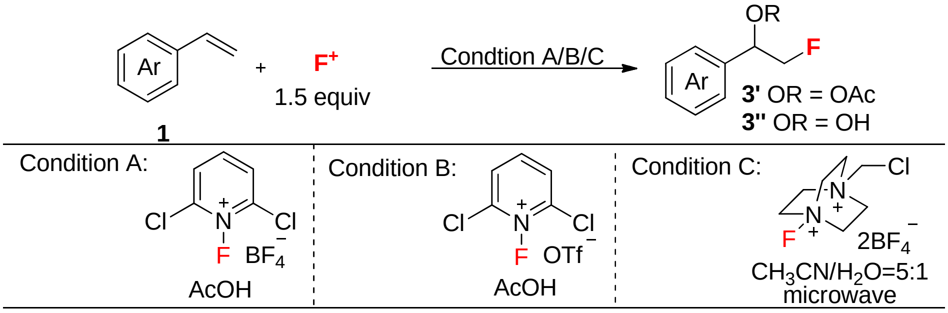
The results in Table S4-S6 indicated that the fluoroesterification catalyzed by palladium catalyst is less likely involving electrophilic fluorination pathway.

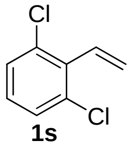
[S1] S. Stavber, S. T. Pečan, M. Zupan, *J. Chem. Soc.*, *Perkin Trans. 2*, **2000**, 1141–1145.

3.4 Results of Electrophilic Fluorination in different conditions

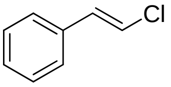
In general, electrophilic fluorination is good for electron-rich alkene substrates. In order to test the reactivity of those styrenes, substrates **1s-1z, 1aa** and **1ab** were treated by F$^+$ reagent under electrophilic fluorination conditions.[S2] As shown in Table S7, the reaction of electro-deficient substrates **1s-1x** didn't occur in the presence of N-Fluoropyridium, and only **1v** or **1x** could afford corresponding product but in low yield (19% or 24%) by using selectfluor under microwave condition. However, electron-rich substrates, such as **1y** and **1z**, proceeded to give fluorination product in 25-52% yield. In addition, the reactions of steroid derivative **1aa** and

Table S7. Results of Electrophilc Fluorination with different conditions.[a]

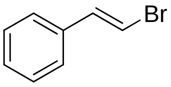




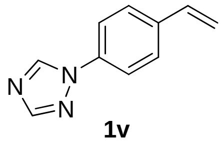
1s
A: N.D.
B :N.D.
C: N.D.



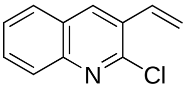
1t
A: N.D.
B :N.D.
C: N.D.



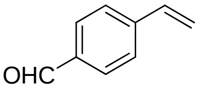
1u
A: N.D.
B :N.D.
C: N.D.



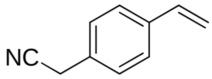
1v
A: N.D.
B :N.D.
C: 19%



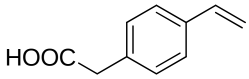
1w
A: N.D.
B: N.D.
C: N.D.



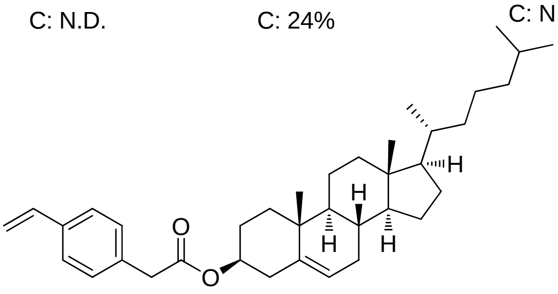
1x
A: N.D.
B: N.D.
C: 24%



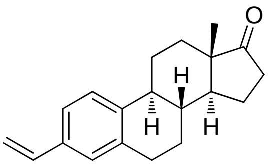
1y
A: N.D.
B: 25%
C: N.D.



1z
A: N.D.
B: 52%
C: 42%



1aa
B: N.D.[b]



1ab
B: complex[c]

[a] ^{19}F NMR yield with trifluoromethylbenzene as internal standard; [b] substrate consumed; [c] reaction gave a complex result. N.D. = Not Detected

---

[S2] (a) T. Umemoto, S. Fukami, G. Tomizawa, K. Harasawa, K. Kawada, K. Tomital *J. Am. Chem. Soc.* **1990,** *112*, 8563-8515; (b) A. Kumar, T. V. Singh, P. Venugopalan *J. Fluorine. Chem.* **2013**, *150*, 72–77.

estrone derivative **1ab** gave complexes results with substrate consumed. These results suggest that significant difference exists between elctrophilic fluorination and palladium-catalyzed fluorination.

4. Kinetic study

4.1 General Information:

Our mechanistic studies focus on the fluoroesterification of styene **1g**. With the optimized reaction condition, the kinetics of the reaction was monitored by ^{19}F NMR with trifluoromethylbenzene as internal standard. Each reaction was monitored to 0~20% conversion, and rate constants were calculated for each reaction using the initial rates method. Error analysis was conducted using standard equations and calculations.

4.2. Preventative Time Course of the Reactions (0.2 mmol scale): To a solution of Pd catalyst, **L2**, NFSI in 1, 4-Dioxane, CF_3CO_2H and trifluoromethylbenzene (internal standard) were added via a syringe. The solution was transferred to a NMR tube. Then styrene was added via a syringe. The mixture was shaken vigorously before collecting data by NMR parameters manually for every 3 min (400 MHz Varian Inova NMR). The conversion of styrene **1g** is obtained based on the internal standard by ^{19}F NMR spectroscopy. The initial rates were calculated from the slopes of line with the zone of 0-10% conversion of styrene **1g**.

As shown in Figure **S1**, A noticeable induction period was found in the reaction with $PdCl_2$ as the catalyst. In contrast, the reaction with $Pd(PPh_3)_4$ and $Pd(dba)_2$ showed a monotonic decrease in styrene concentration, and the lack of an induction period enabled us to obtain much of our kinetics data via initial-rates methods. Thus, the following kinetic studies was conducted by using $Pd(PPh_3)_4$ catalyst.

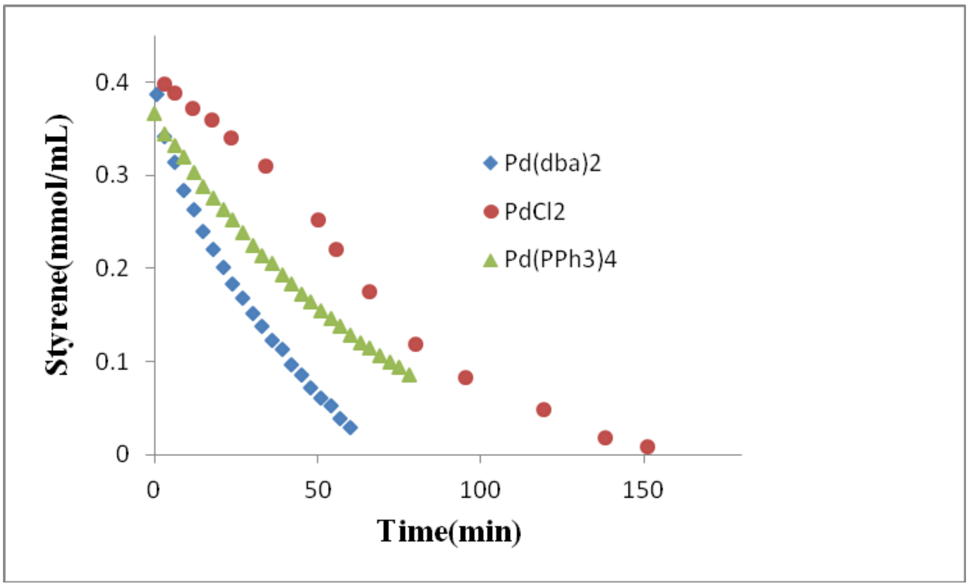


Figure S1. The comparison of the conversion curves for the $PdCl_2$, $Pd(PPh_3)_4$ and $Pd(dba)_2$-catalyzed oxyfluorination of styrene. Note that no inflection point was seen for the Pd(0)-catalyzed transformation. Reaction conditions (initial): [Styrene] = 0.40 M (0.20 mmol), [CF_3COOH] = 2.40 M, [Pd] (5 mol%), [L2] (7.5 mol%), [NFSI] (1.20 M), 1,4- Dioxane, 30^{o}C.

4.3 Representative Kinetics Data.

Kinetic Data:

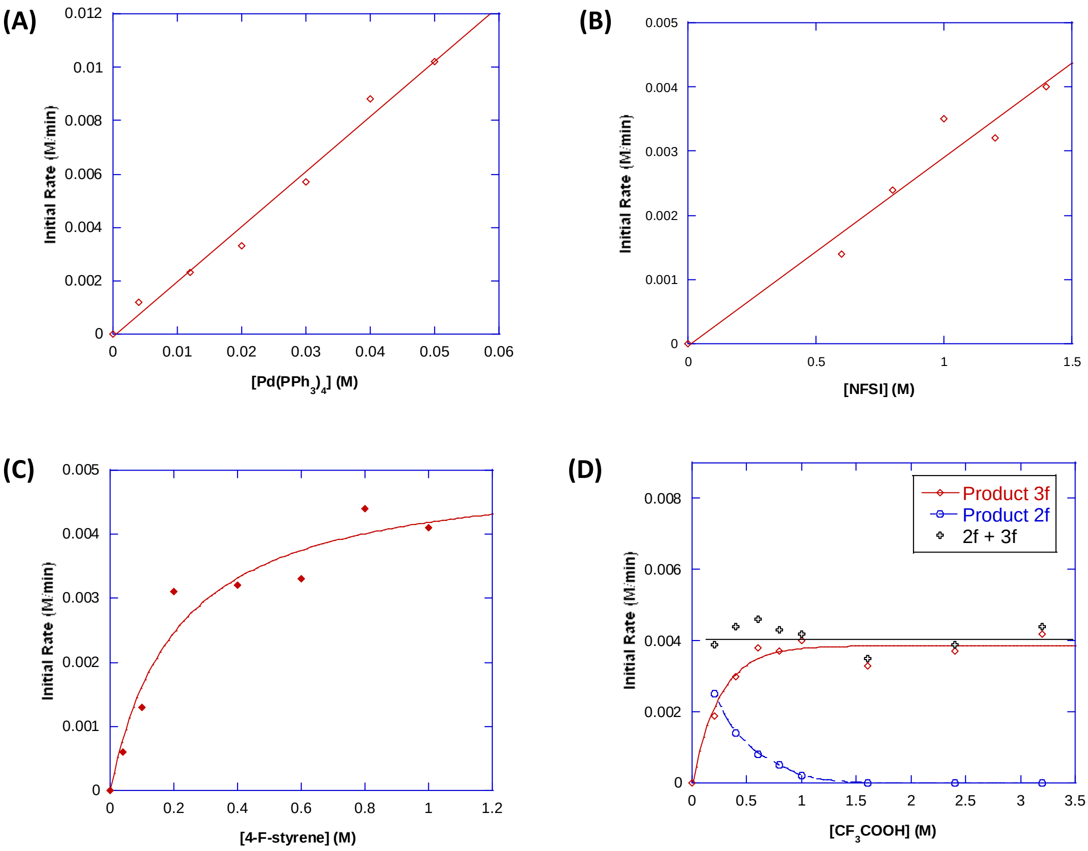


Figure S2. Kinetic Datas: (A) Initial Rate Dependence on the [$Pd(PPh_3)_4$]: [**1g**] = 0.40 M, [CF_3COOH] = 2.40 M, [NFSI] = 1.20 M, [$Pd(PPh_3)_4$] (0-0.05 M) , [**L2**] (0 – 0.075 M) (Pd/**L2** = 1:1.5) in 1,4- Dioxane; (B) Initial Rate Dependence on the [NFSI]: [**1g**] = 0.40 M, [CF_3COOH] = 2.40 M, [$Pd(PPh_3)_4$] (5 mol%), [**L2**] (7.5 mol%), [NFSI] (0.75 -1.75 M) in 1,4- Dioxane; (C) Initial Rate Dependence on the [Styrene]: [NFSI] = 1.20 M, [CF_3COOH] = 2.40 M, [$Pd(PPh_3)_4$] (5 mol%), [**L2**] (7.5 mol%), [**1g**] (0 -1.20 M) in 1,4- Dioxane; (D) Initial Rate Dependence on the [CF_3COOH]: [**1g**] = 0.40 M (0.20 mmol), [NFSI] = 1.20 M, [$Pd(PPh_3)_4$] (5 mol%), [**L2**] (7.5 mol%), [CF_3COOH] (0 -3.20 M) in 1,4- Dioxane at 30^{o}C.

5. Stoichiometric Experiments

5.1 Palladium Complex with Acid without Oxidant:

General procedure 1: under N_2 atmosphere, to a solution of palladium complex **8**[S3] in d_8-Dioxane, CF_3COOH (4 equiv) was added. After the reaction was stirred at room temperature for 3h, the mixture was directly detected by ^1H NMR with N,N-dimethyl-trifluoromethylacetate (DMA-CF_3) as internal standard. Further recrystallization from CH_2Cl_2-Hexane afford pale yellow solid product of complex **10.**

General procedure 2: under N_2 atmosphere, to a solution of palladium complex **8**

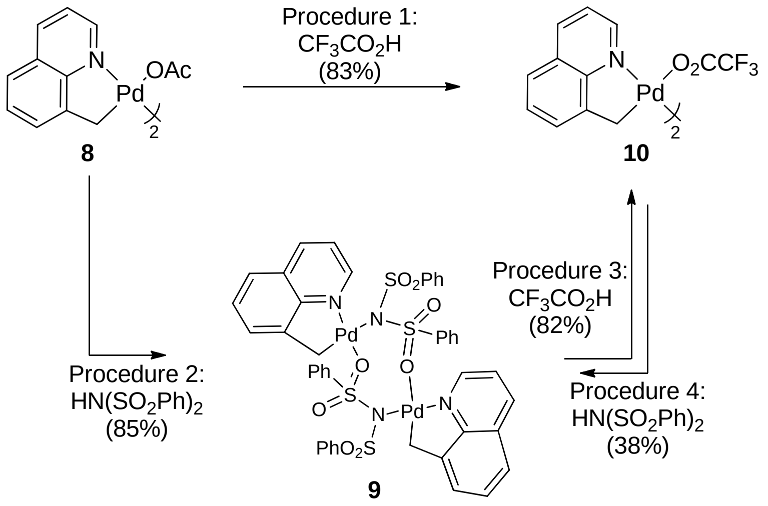
[S3] J. Deeming, I. P. Rothwell, *J.Organometal.Chem.***1981**, *205*, 117-131.

in d_8-Dioxane, $(PhSO_2)_2NH$ (4 equiv) was added. After the reaction was stirred at room temperature for 3h, the mixture was directly detected by ^1H NMR with DMA-CF_3 as internal standard. Further recrystallization from CH_2Cl_2-Hexane afford yellow microcrystalline product of complex **9.**

General procedure 3: In N_2 atmosphere, to a solution of palladium complex **9** in d_8-Dioxane, CF_3COOH (4 equiv) was added. After the reaction was stirred at room temperature for 3h, the solvent was removed in vacuum, the residue was directly detected by ^1HNMR with DMA-CF_3 as internal standard to give the yield.

General procedure 4: under N_2 atmosphere, to a solution of palladium complex **10** in CD_2Cl_2, $(PhSO_2)_2NH$ (4 equiv) was added. After the reaction was stirred at room temperature for 3h, the mixture was directly detected by ^1HNMR with DMA-CF_3 as internal standard to give the yield of complex **9**.

The results were listed in Scheme **S1**.



Scheme S1. Ligands exchange experiment between palladium complex in CH_2Cl_2 or 1,4-Dioxane

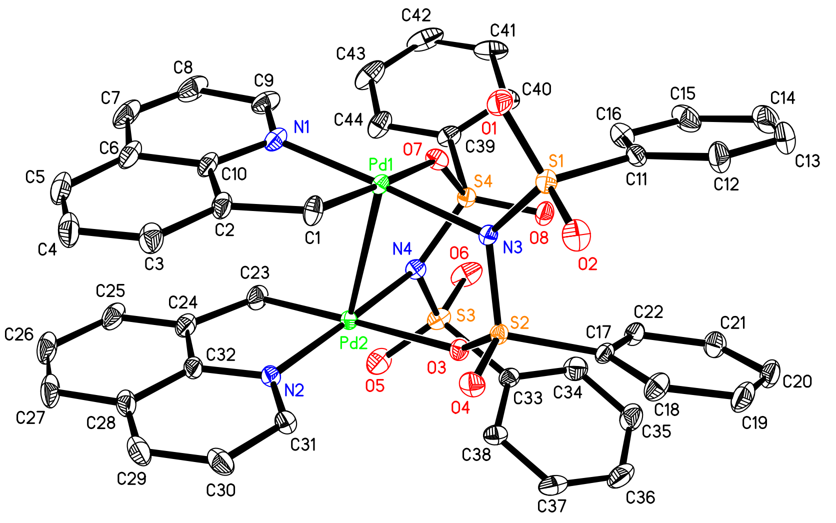
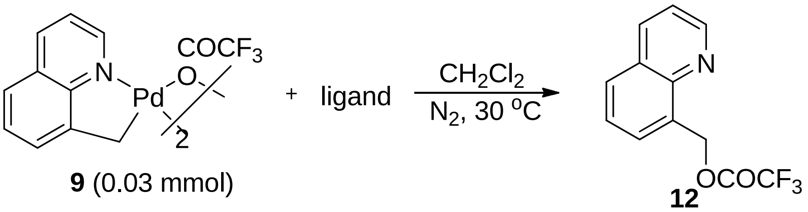


Figure S3. X-Ray Analyses of complex **9**

On the other hand, the palladium dimer complexes **8**-**10** is too stable to give C-O or C-N bond. Thus, ligands were added to promote dissociation of dimer, but the reactions could not afford reductive elimination products, see Table **S8**.

Above results suggest that the possibility of Pd(0)/Pd(II) is unlikely.

Table S8. Reaction of complex **9**



9 (0.03 mmol)

Conditions	Yield[b,c]
PPh_3 (0.18 mmol)	ND
Pyridine (0.18 mmol)	ND
L2 (0.09 mmol)	ND

[a] The reaction condition: complex **9** (0.03 mmol) and ligand in CH_2Cl_2 at 30 °C ; [b] HNMR yield with N,N-dimethyl-trifuluoromethylacetamide as internal standard; [c]All the substrate remained. ND = no dected

5.2 Palladium Complex with Acid with Oxidant:

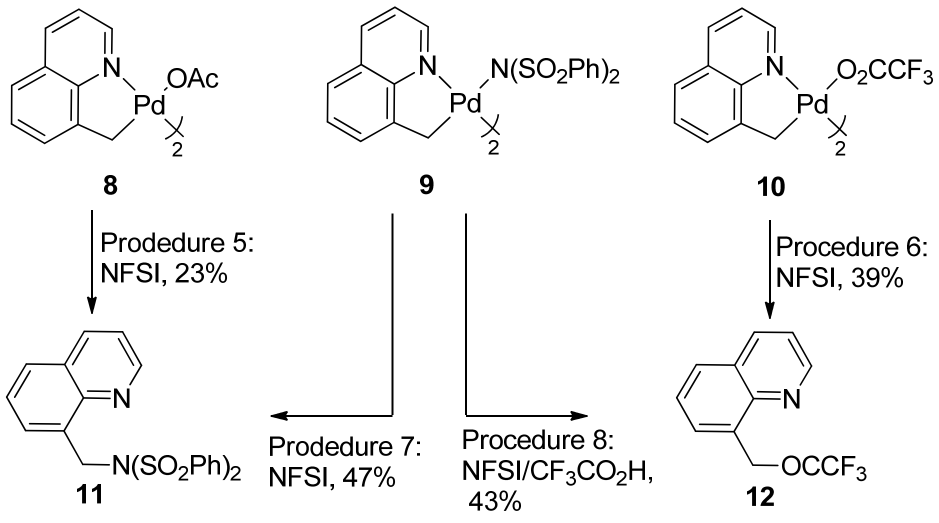
General procedure 5: under N_2 atmosphere, to a solution of palladium complex **8** in *d*$_8$-Dioxane, NFSI (4 equiv) was added. After the reaction was stirred at room temperature for 1h, the mixture was directly detected by ^1H NMR with DMA-CF_3 as internal standard to give product **11** in 23% yield, and no observation of C-O bond formation.

General procedure 6: under N_2 atmosphere, to a solution of palladium complex **10** in CD_2Cl_2, NFSI (4 equiv) was added. After the reaction was stirred at room temperature for 1h, the mixture was directly detected by ^1H NMR with DMA-CF_3 as internal standard to give product **12** in 39% yield, but no product **11** formation.

General procedure 7: under N_2 atmosphere, to a solution of palladium complex **9** in *d*$_8$-Dioxane, NFSI (4 equiv) was added. After the reaction was stirred at room temperature for 1h, the mixture was directly detected by ^1H NMR with DMA-CF_3 as internal standard to give product **11** in 47% yield.

General procedure 8: under N_2 atmosphere, to a solution of palladium complex **9** in *d*$_8$-Dioxane, NFSI (4 equiv) and CF_3COOH (4 equiv) were added. After the reaction was stirred at room temperature for 1h, the mixture was directly detected by ^1H NMR with DMA-CF_3 as internal standard to give product **12** in 43% yield, and the product **11** was inhibited.

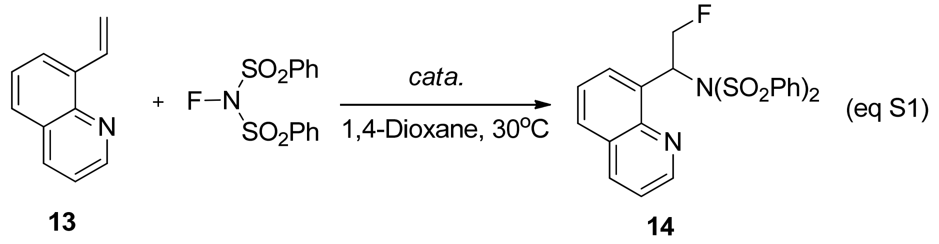
The results were listed in Scheme **S2**.



Scheme S2. Oxidative elimination of palladium complex with NFSi as oxidant

6. Investigation of Fluoropalladation: *in situ* ESI-MS study

Based on the above studies, we turned our attention to investigate fluoropalladation step. Substrate 8-vinyl quionoline **13** was applied, in which nitrogen is proposed to coordinate with palladium complex to give a stabled palladium complex like complex **9**. First, substrate **13** was treated by standard reaction condition, the reaction did provide product **14** around 20% yields, and addition of ligand have no significant effect (eq S1). Although the yield is slightly low, we believe this substrate still can be used to survey fluoropalladation step.



$Pd(dba)_2$ (5 mol%) **L2** (7.5 mol%)	23%
$Pd(dba)_2$ (5 mol%)	19%

ESI-MS studies: in 4 ml reaction vessel, $Pd(dba)_2$ (50 mol%) and NFSI (0.1 mmol) were dissolved in 1,4-Dioxane (0.5 mL), and then **14 (**0.1 mmol) was added. The mixture was stirred at 30°C for 30 min. Then, 0.01ml of reaction solution was taken out from reaction vessel and diluted with 1.0 ml pure CH_3CN. The injection speed of the diluted reaction solution was set to 5 μL/min. ESI-MS spectrum for the diluted reaction solution (**A**) of at reaction time 10 min was shown in Figure S4a .

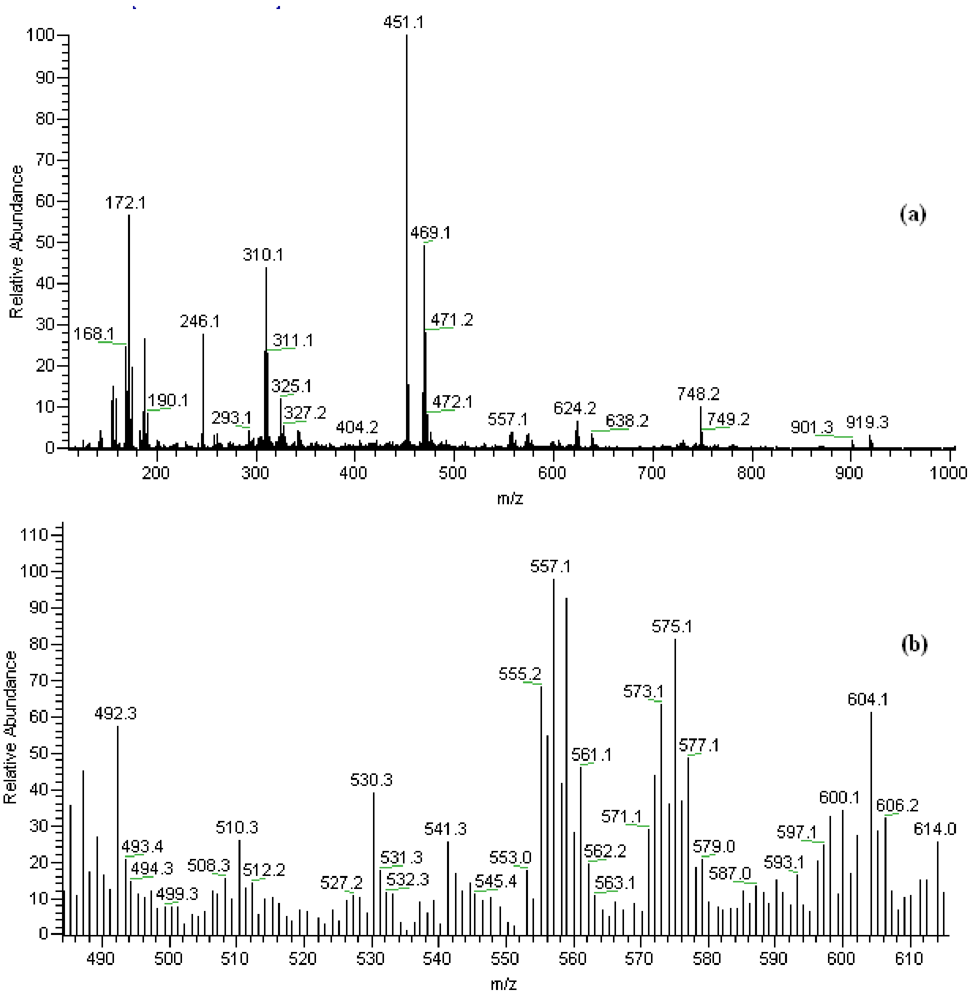
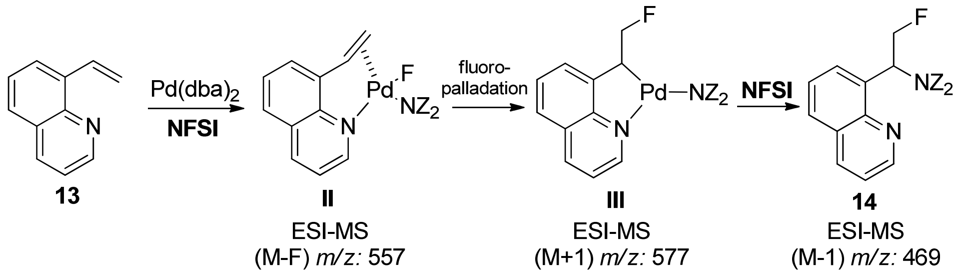


Figure S4. (a) ESI-MS spectrum for the diluted reaction solution, (b) expand ESI-MS spectrum in mass range from *m/z* 400 to *m/z* 800, showing the Pd complexes [**II**-F]$^+$ at *m/z* 557 (in relative high intensity); (b) [**III**+H]$^+$ at *m/z* 577 (in low intensity and mixed with dehydrogenation peak).

As shown in Scheme **S3**, the reactive intermediates **II** and **III** are critically important. The aim of the ESI-MS experiment is to probing the coordination sequence of Pd(II) with **13**. In Figure S1a, the strong signal of product [**14**-H]$^+$ at *m/z* 469 was observed clearly in the ESI-MS spectrum. More importantly, two critical Pd(II) complexes of [**II**-F]$^+$ at *m/z* 557 was formed by loss of anion F$^-$ with Pd(II) complex **II** and the signals of [**II**-F]$^+$ at *m/z* 557 was in low intensity and mixed with dehydrogenation peak. [**III**+H]$^+$ at *m/z* 577 was also detected.



Scheme S3. The Proposed Mechanism and Signal of Palladium Complex.

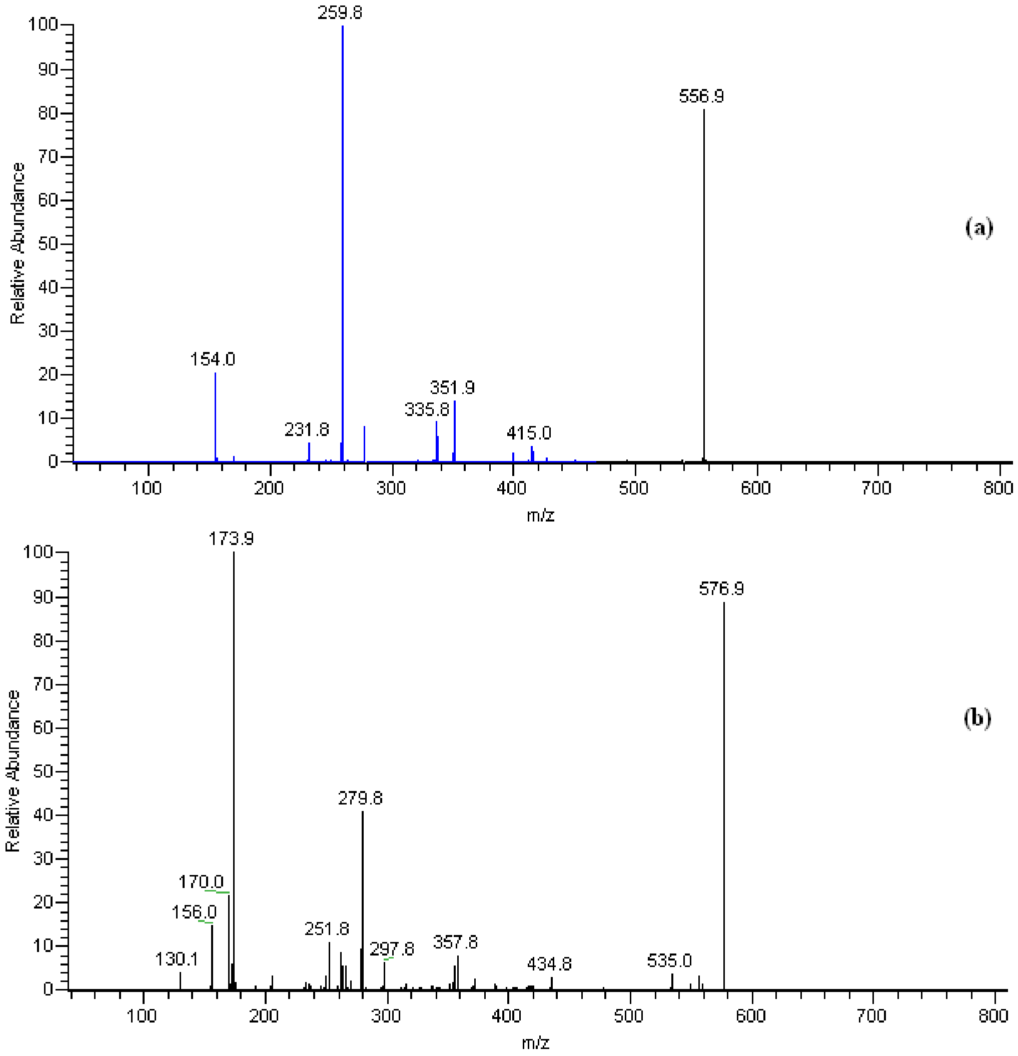
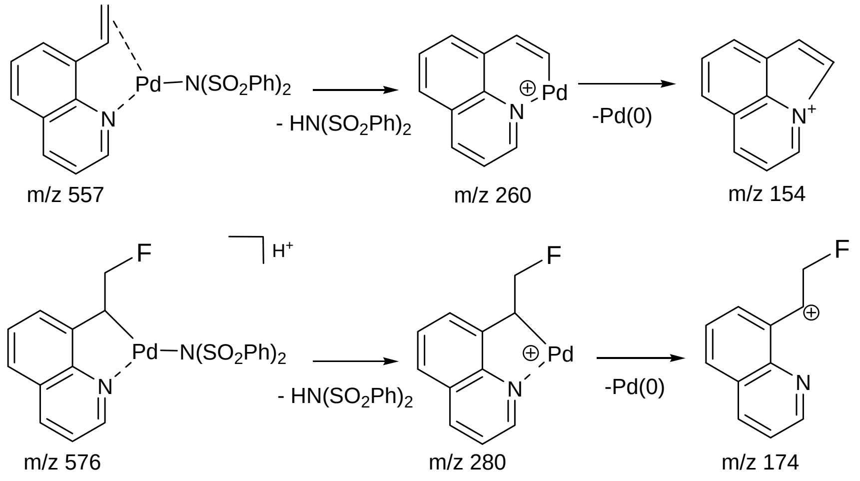


Figure S5. ESI-MS/MS spectra of cationic Pd(II) complexes: (a) [**II**-F]$^+$ at *m/z* 557; (b) [**III**+H]$^+$ at *m/z* 577.



Scheme S4. The proposed dissociation process of formation process of cationic Pd (II) complexes: [**II**-F]$^+$ at *m/z* 557 and [**III**+H]$^+$ at *m/z* 577.

The MS/MS spectrum of Pd complex of [**II**-F]$^+$ at *m/z* 557 was shown in Figure **S5a**. In the MS/MS process, [**II**-F]$^+$ at *m/z* 557 at *m/z* 435 gives its fragment ion at *m/z* 260 by loss of $HN(SO_2Ph)_2$, which would further dissociate to fragment ion at *m/z* 154 by loss of Pd(0) (top, Scheme **S4**);

The MS/MS spectrum of Pd complex of [**III**+H]$^+$ at *m/z* 577 was shown in Figure **S5b**. In the MS/MS process, [**III**+H]$^+$ at *m/z* 577 gives its fragment ion at *m/z* 280 by loss of $HN(SO_2Ph)_2$, which would further dissociate to fragment ion at *m/z* 174 by loss of Pd(0) (Bottom, Scheme **S4**).

7. Further Transformation of product 4f[S4]

General Procedure: Thiolacetic acid (450 mg, 6.0 mmol) [or *p*-methylthiophenol (838 mg, 6.0 mmol] was added to a suspension of NaH (125 mg, 3.0 mmol, 60% suspension in mineral oil) in anhydrous DMF (1 mL) under N_2. After ca. 10 min, compound **4f** (107 mg, 0.3 mmol) was added and the mixture was stirred at room temperature for 30min. The reaction was quenched with saturated NH_4Cl aqueous solution and the mixture was extracted with EtOAc (3 × 15 mL). The organic layer was washed with $NaHCO_3$, dried by Na_2SO_4. Solvent was remolved under vacuum, and the residue was purified by silica gel column chromatography to give product **6** as colorless oil (107.8 mg, 95% yield) [or **7** as a colorless oil (110.5 mg, 90% yield)].

8. X-Ray data

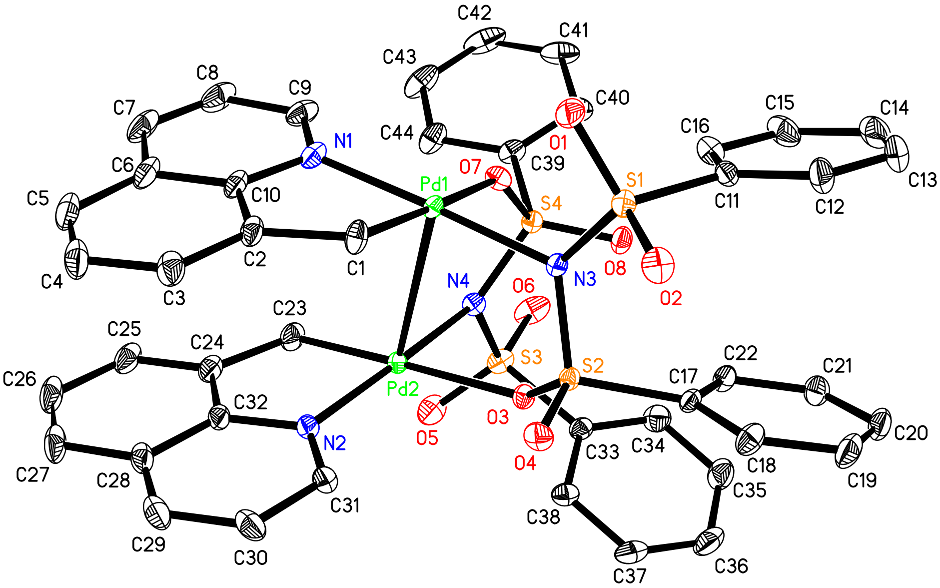


***Table S9*. Crystal Data and Summary of Data Collection and Refinement for**

[S4] R. O. Moisés, R. Horacio, C. Z. Adrián, C. Raymundo,A. Z. José Gustavo *Synthesis* **2003**, *18*, 2765-2767

di(μ-Dibenzolsulfimide)bis[8-methylenylquinoline]dipalladium(II)

	di(μ-Dibenzolsulfimide)bis[8-methylenylquinoline] dipalladium(II)
formula	$C_{51}H_{43}Cl_2N_4O_{11}Pd_2S_5$
crystal size (mm)	2593.8(4)
fw	1331.89
crystal system	Triclinic
space group	P-1
a, Å	12.398(1)
b, Å	14.865(1)
c, Å	15.105(1)
α, deg	88.522(2)
β, deg	68.745(1)
γ, deg	89.787(1)
V, $Å^3$	2593.8(4)
Z	2
D_{calcd}, Mg/m^3	1.705
radiation (*λ*), Å	0.71073
2*θ* range, deg	3.52 to 63.24
μ, mm^{-1}	1.063
F(000)	1342
no. of obsd reflns	17094
no. of params refnd	704
goodness of fit	0.979
R1	0.0413
*w*R2	0.1119

Pd1 C1 1.996(3)

Pd1 N1 2.024(3)

Pd1 N3 2.085(2)

Pd1 O7 2.231(2)

S2 C17 1.758(3)

S1 C11 1.771(3)

S2 N3 1.623(3)

S3 O5 1.431(3)

Pd1 Pd2 3.0322(4)

Pd2 C23 1.999(3)

Pd2 N2 2.027(3)

Pd2 N4 2.117(2)

S3 N4 1.650(3)

S2 O4 1.439(2)

S5 O10 1.437(3)

S3 C33 1.772(3)

Pd2 O3 2.285(2)

S1 O1 1.434(2)

S1 O2 1.447(2)

S1 N3 1.640(2)

S4 O7 1.453(2)

S2 O3 1.453(2)

S5 O9 1.437(3)

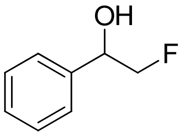
S4 N4 1.619(3)

S3 O6 1.436(3)	S4 O8 1.434(2)	S4 C39 1.768(3)
S5 C45 1.764(4)	S5 O11 1.619(3)	C1 Pd1 N1 83.78(12)
C1 Pd1 N3 91.75(11)	N1 Pd1 N3 175.53(10)	C1 Pd1 O7 174.55(10)
N1 Pd1 O7 91.45(10)	N3 Pd1 O7 93.02(9)	C1 Pd1 Pd2 104.00(10)
N1 Pd1 Pd2 86.43(8)	N3 Pd1 Pd2 94.76(7)	O7 Pd1 Pd2 72.98(6)
C23 Pd2 N2 83.44(13)	C23 Pd2 N4 90.70(13)	N2 Pd2 N4 173.17(10)
C23 Pd2 O3 178.66(12)	N2 Pd2 O3 95.29(9)	N4 Pd2 O3 90.54(9)
C23 Pd2 Pd1 109.85(11)	N2 Pd2 Pd1 93.15(7)	N4 Pd2 Pd1 92.14(7)
O3 Pd2 Pd1 70.62(5)	O1 S1 O2 118.74(15)	O1 S1 N3 106.02(13)
O2 S1 N3 111.89(14)	O1 S1 C11 107.84(15)	O2 S1 C11 107.54(15)
N3 S1 C11 103.75(13)	O4 S2 O3 116.56(13)	O4 S2 N3 112.36(13)
O3 S2 N3 105.41(12)	O4 S2 C17 107.49(13)	O3 S2 C17 107.18(13)
N3 S2 C17 107.41(13)	O5 S3 O6 118.36(17)	O5 S3 N4 106.43(15)
O6 S3 N4 109.68(15)	O5 S3 C33 107.55(16)	O6 S3 C33 107.14(16)
N4 S3 C33 107.20(14)	O8 S4 O7 116.24(14)	O8 S4 N4 113.16(14)
O7 S4 N4 106.42(13)	O8 S4 C39 108.08(14)	O7 S4 C39 104.25(14)
N4 S4 C39 108.09(15)	O10 S5 O9 120.6(2)	O10 S5 O11 106.99(19)
O9 S5 O11 106.41(17)	O10 S5 C45 106.79(18)	O9 S5 C45 106.43(18)
O11 S5 C45 109.25(18)	S2 O3 Pd2 140.23(13)	S4 O7 Pd1 141.25(14)
C9 N1 C10 119.3(3)	C9 N1 Pd1 127.9(2)	C10 N1 Pd1 112.1(2)
C31 N2 C32 118.6(3)	C31 N2 Pd2 127.2(2)	C32 N2 Pd2 114.2(2)
S2 N3 S1 120.82(15)	S2 N3 Pd1 116.82(13)	S1 N3 Pd1 119.43(13)

S4 N4 S3 116.71(16)	S4 N4 Pd2 120.76(14)	S3 N4 Pd2 118.36(14)
C2 C1 Pd1 107.8(2)	Pd1 C1 H1A 110.1	Pd1 C1 H1B 110.1

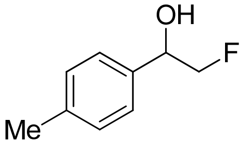
10. New compounds characterization

Compounds **3a**[S5] **5g**[S6],**5m-5n**[S7], **5p-5q**[S8], **5r**[S3], **5t**[S9], **11**[S10], **12**[S11] were reported in literature.



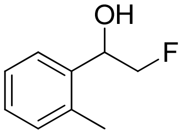
5a

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.35 (m, 5H), 4.97 (t, *J* = 10.8 Hz, 1H), 4.57-4.28 (m, 2H), 2.89 (br s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.1 (d, *J* = 8.2 Hz), 128.6, 128.3, 126.3, 87.1 (d, *J* = 174.0 Hz), 72.8 (d, *J* = 19.3 Hz). ^{19}F NMR (282 MHz, CDCl$_3$) δ -220.8 (dt, *J* = 13.8, 48.3 Hz, 1F). IR cm^{-1}: 3386, 2950, 1604, 1494, 1454, 1311, 1198, 1097, 1010, 897, 759, 701. HRMS: m/z (EI) calculated [M]$^+$ 140.0637, measured 140.0634.



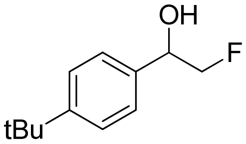
5b

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.23 (d, *J* = 6.8 Hz, 2H), 7.15 (d, *J* = 10.4 Hz, 2H), 4.92 (t, *J* = 12.8 Hz, 1H), 4.53-4.25 (m, 2H), 2.94 (br s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.1, 135.2 (d, *J* = 8.2 Hz), 129.2, 126.2, 87.1 (d, *J* = 173.3 Hz), 72.6 (d, *J* = 19.3 Hz), 21.0. ^{19}F NMR (282 MHz, CDCl$_3$) δ -220.5 (dt, *J* = 13.8, 48.3 Hz, 1F). IR cm^{-1}: 3422, 2949, 1701, 1609, 1514, 1450, 1382, 1179, 1092, 1013, 897, 815, 771. HRMS: m/z (EI) calculated [M]$^+$ 154.0794, measured 154.0793



5c

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.47 (m, 1H), 7.22 (m, 2H), 7.13 (m, 1H), 5.19 (t, *J* = 11.1 Hz, 1H), 4.51-4.22 (m, 2H), 2.98 (br s, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.1 (d, *J* = 8.2 Hz), 134.9, 130.4, 128.0, 126.3, 126.0, 86.2 (d, *J* = 174.0 Hz), 69.5 (d, *J* = 19.4 Hz), 18.9. ^{19}F NMR (282 MHz, CDCl$_3$) δ -219.3 (dt, J = 13.8, 48.3 Hz, 1F). IR cm^{-1}: 3373, 2961, 1606, 1488, 1461, 1343, 1180, 1085, 1012, 894, 757, 726. HRMS: m/z (EI) calculated [M]$^+$ 154.0794, measured 154.0798

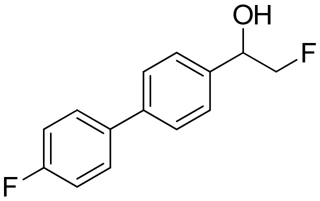


5d

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.92

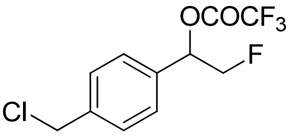
[S5] A. Gregorcic, M. Zupa,n *J. Org. Chem.* **1979**, *44*, 4120 – 4122.
[S6] E. Fuglseth, E. Sundby, P. Bruheim, B. H. Hoff, *Tetrahedron: Asymmetry*, **2008**, *19*, 1941-1946.
[S7] G. S. Lal, *J. Org. Chem.* **1993**, *58*, 2791-2796.
[S8] P. K. Mohanta, T. A. Davis, J. R. Gooch, R. A. Flowers, *J. Am. Chem. Soc.* **2005**, *127*, 11896-11897.
[S9] Y. Takashi, T. Tsukasa, K.-T. Tomoko, *Tetrahedron*, **2008**, 64, 2419 - 2424
[S10] Á. Iglesias, R. Álvarez, Á. R. de Lera, K. Muñiz, *Angew. Chem. Int. Ed.* **2012**, *51*, 2225-2228.
[S11] R. Alam, L. T. Pilarski, E. Pershagen, K. J. Szabo, *J. Am. Chem. Soc.* **2012** , *134*, 8778-8781.

(ddd, *J* = 3.6, 8.0, 14.4 Hz, 1H), 4.52-4.30 (m, 2H), 3.02 (br s, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.2, 135.3 (d, *J* = 8.2 Hz), 126.0, 125.4, 87.0 (d, *J* = 173.2 Hz), 72.6 (d, *J* = 20.1 Hz), 34.5, 31.2. ^{19}F NMR (376 MHz, CDCl$_3$) δ -220.2 (dt, J = 14.3, 47.3 Hz, 1F). IR cm^{-1}: 3377, 2962, 1614, 1509, 1462, 1361, 1204, 1109, 1019, 900, 831, 703. HRMS: m/z (EI) calculated [M]$^+$ 196.1263, measured 196.1259.



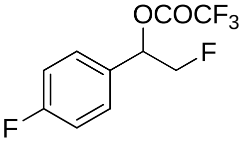
5e

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 (m, 4H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.10 (t, *J* = 8.8 Hz, 2H), 5.03 (ddd, *J* = 3.2, 8.0, 14.0 Hz, 1H), 4.59-4.35 (m, 2H), 2.89 (br s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 162. 5(d, *J* = 245.4 Hz), 140.3, 137.2 (d, *J* = 8.2 Hz), 136.6 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 7.4 Hz), 127.1, 126.8, 115.6 (d, *J* = 21.6 Hz), 87.0 (d, *J* = 174.0 Hz),72.6 (d, *J* = 20.1 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -115.3 (m, 1 F), -220.7 (dt, *J* = 14.3, 48.5 Hz, 1F). IR cm^{-1}: 3331, 2962, 1604, 1527, 1498, 1394, 1252, 1088, 1005, 821, 790. HRMS: m/z (EI) calculated [M]$^+$ 234.0856, measured 234.0855



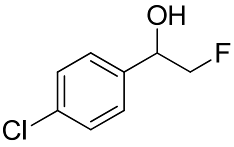
3f

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.18 (ddd, *J* = 3.2, 8.4, 14.8 Hz, 1H), 4.78-4.53 (m, 2H), 4.59 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.5 (d, *J* = 42.7 Hz), 139.2, 132.7 (d, *J* = 6.9 Hz), 129.3, 127.3, 114.4 (d, *J* = 284.0 Hz), 83.0 (d, *J* = 180.7 Hz), 77.7 (d, *J* = 19.8 Hz), 45.3 ^{19}F NMR (376 MHz, CDCl$_3$) δ -221.2 (dt, *J* = 14.3, 47.0 Hz, 1F), -75.0 (s, 3F). IR cm^{-1}: 3392, 2951, 1781, 1683, 1515, 1452, 1417, 1265, 1212, 1091, 1012, 898, 790, 682. HRMS: m/z (EI) calculated [M]$^+$ 284.0227, measured 284.0231



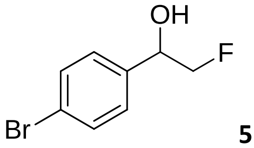
3g

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (dd, *J* = 5.6, 8.8 Hz, 2H), 7.11 (t, *J* = 8.8 Hz, 2H), 6.18 (ddd, *J* = 3.2, 8.4, 14.8 Hz, 1H), 6.16 (ddd, *J* = 3.2, 8.0, 14.8 Hz, 1H), 4.78-4.52 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 163.4 (d, *J* = 248 Hz), 156.5 (q, *J* = 42.9 Hz), 128.9 (d, *J* = 11.3 Hz), 128.6 (dd, *J* = 3.6, 6.8 Hz), 116.2 (d, *J* = 22.1 Hz) 113.9 (q, *J* = 284.2 Hz), 83.0 (d, *J* = 180.7 Hz), 77.7 (d, *J* = 19.8 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -224.4 (dt, *J* = 14.3, 47.0 Hz, 1F), -113.5 (m, 1F), -77.8 (s, 3F). IR cm^{-1}: 3387, 2972, 2866, 2572, 1785, 1514, 1456, 1374, 1218, 1169, 1121, 1081, 870, 699. HRMS: m/z (EI) calculated [M]$^+$ 254.0366, measured 254.0369



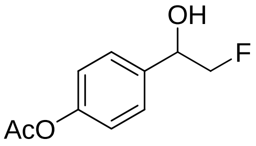
5h

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 4.92 (t, *J* = 8.8 Hz, 1H), 4.51-4.26 (m, 2H), 3.30 (br s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.7 (d, *J* = 8.1 Hz), 134.0, 128.7, 127.6, 86.7 (d, *J* = 173.2 Hz), 72.1 (d, *J* = 19.3 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -220.9 (dt, *J* = 14.3, 48.5 Hz, 1F). IR cm^{-1}: 3384, 2951, 1598, 1493, 1407, 1327, 1197, 1090, 1013, 897, 827, 743. HRMS: m/z (EI) calculated [M]$^+$ 174.0248, measured 174.0246



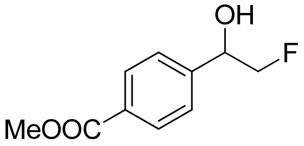
5i

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 4.91 (m, 1H), 4.51-4.26 (m, 2H), 3.22 (br s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.2 (d, *J* = 8.2 Hz), 131.6, 127.9, 122.2, 86.7 (d, *J* = 174.0 Hz), 72.1 (d, *J* = 20.0 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -221.0 (dt, *J* = 15.0, 47.8 Hz, 1F). IR cm^{-1}: 3384, 2950, 1701, 1593, 1488, 1403, 1230, 1195, 1089, 1072, 1010, 897, 822, 734. HRMS: m/z (EI) calculated [M]$^+$ 217.9743, measured 217.9744



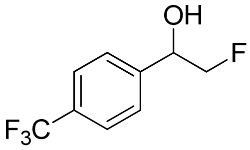
5j

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.91 (ddd, *J* = 3.2, 8.0, 14.4 Hz, 1H), 4.51-4.27 (m, 2H), 3.22 (br s, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.6, 150.3, 136.0 (d, *J* = 8.2 Hz), 127.4, 121.6, 86.8 (d, *J* = 174.0 Hz), 72.1 (d, *J* = 19.3 Hz), 20.9. ^{19}F NMR (376 MHz, CDCl$_3$) δ -220.8 (dt, *J* = 14.3, 46.6 Hz, 1F). IR cm^{-1}: 3373, 2953, 1713, 1614, 1515, 1449, 1373, 1236, 1202, 1111, 1088, 1013, 836. HRMS: m/z (EI) calculated [M]$^+$ 198.0692, measured 198.0688.



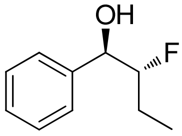
5k

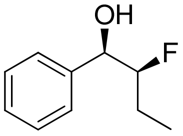
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 5.04 (dd, *J* = 7.2, 14.4 Hz, 1H), 4.56-4.33 (m, 2H), 3.90 (s, 3H), 3.62 (br s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.8, 143.5 (d, *J* = 8.2 Hz), 129.8, 129.7, 126.2, 86.7 (d, *J* = 174.0 Hz), 72.3 (d, *J* = 20.1 Hz), 52.1. ^{19}F NMR (376 MHz, CDCl$_3$) δ -221.7 (dt, *J* = 14.7, 46.6 Hz, 1F). IR cm^{-1}: 3323, 2957, 1723, 1613, 1514, 1450, 1436, 1288, 1189, 1112, 1092, 1001, 964, 862, 760, 704. HRMS: m/z (EI) calculated [M]$^+$ 198.0692, measured 198.0694



5l

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 5.07 (dd, *J* = 7.8, 10.8 Hz, 1H), 4.62-4.29 (m, 2H), 2.92 (br s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ142.1 (d, J = 7.5 Hz), 130.6 (d, J = 32.7 Hz), 126.6, 125.5 (d, J = 3.7 Hz), 123.9 (q, J = 270 Hz), 86.8 (d, J = 174.0 Hz), 72.3 (d, J = 20.1 Hz). ^{19}F NMR (282 MHz, CDCl$_3$) δ -63.1 (s, 3F), -222.2 (dt, J = 13.5, 46.5 Hz, 1F). IR cm^{-1}: 3392, 2917, 1621, 1457, 1418, 1327, 1166, 1125, 1067, 1017, 898, 844. HRMS: m/z (EI) calculated [M]$^+$ 208.0511, measured 208.0514.

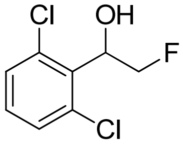

tran-5o and


Syn-5o

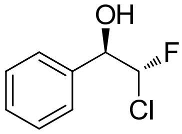
Compounds *anti*-**5o** and *syn*-**5o** could not be separated.

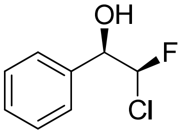
Syn-**5o:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (m, 5H), 4.85 (dd, J = 4.0, 14.8 Hz, 1H), 4.62 (ddd, J = 3.2, 6.4, 9.6 Hz, 0.5H), 4.48 (ddd, J = 3.2, 4.0, 9.2 Hz, 0.5H), 2.40 (s, 1H), 1.65 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.3 (d, J = 4.5 Hz), 128.4, 128.2, 126.5, 97.6 (d, J = 172.5 Hz), 74.9 (d, J = 22.3 Hz), 22.3 (d, J = 20.8Hz), 9.4 (d, J = 3.7 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -191.4 (ddt, J = 15.0, 30.5, 36.5, 47.8, 51.9 Hz, 1F).

Anti-**5o:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (m, 5H), 4.67 (dd, J = 7.2, 13.6 Hz, 1H), 4.53 (ddd, J = 3.6, 7.2, 10.4 Hz, 0.5H), 4.40 (ddd, J = 3.2, 6.8, 10.4 Hz, 0.5H), 2.69 (s, 1H), 1.43 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.2 (d, J = 5.2 Hz), 128.2, 127.8, 126.9, 98.3 (d, J = 173.3 Hz), 76.0 (d, J = 20.9 Hz), 23.9 (d, J = 21.5 Hz), 9.2 (d, J = 4.4 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -191.1 (m, 1F). IR cm^{-1}: 3388, 2969, 2925, 1507, 1455, 1382, 1261, 1198, 1117, 1082, 1052, 955, 759, 701. HRMS: m/z (EI) calculated [M]$^+$ 168.0950, measured 168.0945.


5s

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, J = 8.0 Hz, 2H), 7.19 (dd, J = 7.6, 8.8 Hz, 1H), 5.77 (m, 1H), 4.88 (ddd, J = 8.0, 9.6, 45.5 Hz, 1H), 4.63 (ddd, J = 8.0, 9.6, 46.4 Hz, 1H), 3.18 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 134.9, 133.3 (d, J = 7.6 Hz), 129.9, 129.5, 83.8 (d, J = 173.4 Hz), 71.0 (d, J = 22.8 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -222.5 (dt, J = 16.9, 47.4 Hz, 1F). IR cm^{-1}: 3575, 3433, 2957, 1704, 1580, 1562, 1436, 1185, 1104, 1010, 895, 838, 768, 728, 665. HRMS: m/z (EI) calculated [M]$^+$ 207.9858, measured 207.9859.

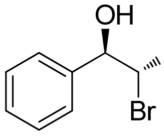

trans-5t and


Syn-5t

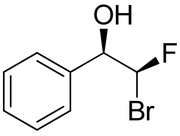
syn-**5t** : ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (m, 5H), 6.21 (dd, J = 5.2, 50.8 Hz, 1H), 4.92 (dt, J = 3.6, 13.2 Hz, 1H), 2.60 (br s, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.5 (d, J = 3.3 Hz), 129.1, 128.6, 127.3, 103.8 (d, J = 239.0 Hz), 76.1 (d, J = 23.4 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -140.3 (dd, J = 9.0, 50.8 Hz, 1F).

trans-**5t:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (m, 5H), 6.21 (dd, J = 5.2, 50.8 Hz, 1H), 4.92 (dt, J = 3.6, 13.2 Hz, 1H), 2.74 (br s, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.5

(d, J = 2.2 Hz), 129.0, 128.6, 127.0, 102.6 (d, J = 246.2 Hz), 77.0 (d, J = 20.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.2 (dd, J = 13.2, 49.3 Hz, 1F).



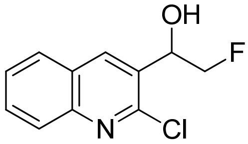
***tran*-5u and**



***Syn*-5u**

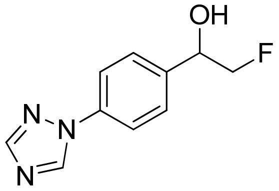
Syn-**5u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 5H), 6.44 (dd, J = 4.8, 48.8 Hz, 1H), 4.98 (m, 1H), 2.69 (d, J = 4.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 129.0, 128.6, 126.9, 98.3 (d, J = 256.6 Hz), 76.4 (d, J = 22.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.7 (dd, J = 8.3, 48.9 Hz, 1F).

trans-**5u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 5H), 6.46 (dd, J = 4.8, 49.6 Hz, 1H), 4.99 (dt, J = 4.8, 14.4 Hz, 1H), 2.87 (J = 3.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 129.1, 128.5, 127.3, 96.1 (d, J = 257.7 Hz), 77.4 (d, J = 20.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -146.5 (dd, J = 14.3, 49.3 Hz, 1F). IR cm^{-1}: 3388, 2963, 1495, 1453, 1260, 1089, 1017, 798, 732, 698. HRMS: m/z (EI) calculated [M]$^+$ 217.9743, measured 217.9745.



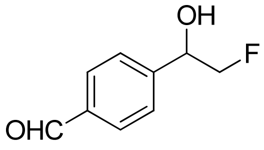
5v

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.77 (m, 1H), 7.71 (m, 1H), 7.53 (m, 1H), 5.51 (dd, J = 7.2, 16.4 Hz, 1H), 4.76 (dd, J = 9.6, 46.4 Hz, 1H), 4.41 (ddd, J = 7.2, 9.6, 48.0 Hz, 1H), 3.95 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 146.9, 137.5 (d, J = 7.2 Hz), 130.7 (t, J = 6.8 Hz), 130.2, 127.8, 127.6, 127.3 (d, J = 12.9 Hz), 127.0, 87.7 (d, J = 175.3 Hz), 69.3 (dd, J = 6.1, 20.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -222.9 (ddt, J = 4.1, 16.5, 47.4 Hz, 1F). IR cm^{-1}: 3359, 2953, 1619, 1591, 1564, 1491, 1377, 1328, 1169, 1138, 1097, 1065, 1014, 909, 780, 749, 666. HRMS: m/z (EI) calculated [M]$^+$ 225.0357, measured 225.0359..



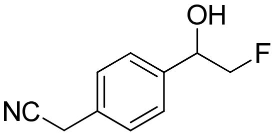
5w

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.09 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 5.09 (ddd, J = 3.0, 7.8，13.5 Hz, 1H), 4.50 (dm, J = 46.5 Hz, 2H), 3.70 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 140.8, 138.8 (d, J = 7.8 Hz), 136.7, 127.8, 120.1, 86.9 (d, J = 174.3 Hz), 72.0 (d, J = 20.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.3 (dt, J = 14.3, 47.0 Hz, 1F). IR cm^{-1}: 3226, 3129, 2922, 2852, 1609, 1523, 1444, 1410, 1281, 1218, 1200, 1146, 1090, 1048, 997, 981, 964, 894, 867, 836, 672. HRMS: m/z (EI) calculated [M]$^+$ 207.0808, measured 207.0805.



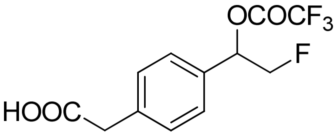
5x

^{1}H NMR (400 MHz, CDCl$_3$) δ 10.02 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 5.12 (ddd, *J* = 3.2, 8.0, 14.4 Hz, 1H), 4.49 (m, 2H), 2.80 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 191.9, 144.8 (d, *J* = 7.5 Hz), 136.3, 130.0, 126.9, 86.7 (d, *J* = 174.0 Hz), 72.5 (d, *J* = 20.1 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -222.4 (dt, *J* = 15.0, 46.6 Hz, 1F). IR cm^{-1}: 3384, 2952, 1685, 1607, 1577, 1382, 1305, 1208, 1089, 995, 897, 824, 803. HRMS: m/z (EI) calculated [M]$^+$ 168.0587, measured 168.0589.



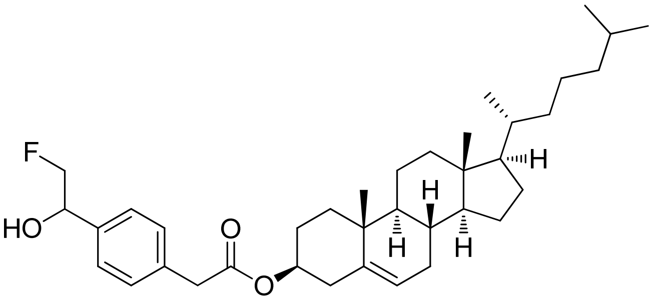
5y

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.97 (ddd, *J* = 2.8, 7.6, 14.0 Hz, 1H), 4.44 (m, 2H), 3.72 (s, 2H), 3.27 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.3 (d, *J* = 8.0 Hz), 129.8, 128.0, 127.0, 117.8, 86.7 (d, *J* = 173.8 Hz), 72.1 (d, *J* = 19.8 Hz), 23.1. ^{19}F NMR (376 MHz, CDCl$_3$) δ -221.2 (dt, *J* = 14.7, 48.1 Hz, 1F). IR cm^{-1}: 3437, 2956, 2253, 1515, 1417, 1168, 1090, 1005, 813, 731. HRMS: m/z (EI) calculated [M]$^+$ 179.0746, measured 179.0743.



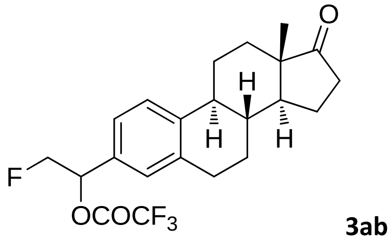
3z

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.16 (s, 1H), 7.35 (s, 4H), 6.17 (ddd, *J* = 2.8, 8.4 , 14.0 Hz, 1H), 4.64 (m, 2H), 3.67 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 177.3, 156.6 (d, *J* = 159.8 Hz), 135.0, 131.8 (d, *J* = 6.4 Hz), 120.2, 127.2, 114.4 (q, *J* = 284.2 Hz), 83.1 (d, *J* = 180.7 Hz), 77.8 (d, *J* = 19.7 Hz), 40.6. ^{19}F NMR (376 MHz, CDCl$_3$) δ -222.0 (ddd, *J* = 15.0, 46.2, 48.1 Hz, 1F), -75.0 (s, 3F). IR cm^{-1}: 2922, 1783, 1713, 1406, 1346, 1223, 1152, 1018, 833, 729,677. HRMS: m/z (EI) calculated [M]$^+$ 294.0515, measured 294.0517.



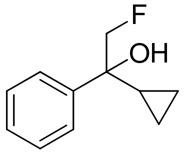
5aa

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.36 (d, *J* = 4.5 Hz, 1H), 5.02 (dm, *J* = 10.0 Hz, 1H), 4.61 (m, 1H), 4.45 (m, 2H), 3.59 (s, 2H), 2.44 (br s, 1H), 2.30 (d, *J* = 8.0 Hz, 2H), 1.99 (m, 2H), 1.83 (m, 3H), 1.51 (m, 8H), 1.33 (m, 5 H), 1.12 (m, 8H), 1.01 (s, 3H), 1.00 (m, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 1.5 Hz, 3H), 0.85 (d, *J* = 1.5 Hz, 3H), 0.67 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 170.8, 139.5, 136.8 (d, *J* = 7.5 Hz), 134.6, 129.5 126.5, 122.7, 87.1 (d, *J* = 173.5 Hz), 74.6, 72.7 (d, *J* = 19.8 Hz), 56.7, 56.1, 49.9, 42.3, 41.3, 39.7, 39.5, 38.0, 36.9, 36.5, 36.1, 35.8, 31.8 (d, *J* = 6.7 Hz), 28.2, 28.0, 27.7, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8. ^{19}F NMR (376 MHz, CDCl$_3$) δ -221.0 (dt, *J* = 14.3, 48.9 Hz, 1F). IR cm^{-1}: 2963, 1733, 1261, 1092, 1019, 799. HRMS: m/z (ESI) calculated [M-H]$^+$ 565.4052, measured 565.4074.



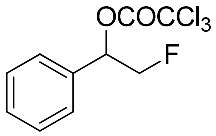
3ab

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 6.13 (ddd, *J* = 3.2, 8.4, 14.4 Hz, 1H), 4.64 (m, 2H), 2.93 (dd, *J* = 4.0, 9.2 Hz, 2H), 5.21 (dd, *J* = 8.8, 18.8 Hz, 1H), 2.40 (m, 1H), 2.31 (m, 1H), 2.07 (m, 4H), 1.55 (m, 6H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 220.7, 156.6 (d, *J* = 42.9 Hz), 141.6, 137.5, 129.9 (d, *J* = 7.2 Hz), 127.5, 126.1, 124.1, 114.4 (q, *J* = 284.3 Hz), 83.1 (d, *J* = 180.2 Hz), 78.1 (dd, *J* = 9.5, 19.7 Hz), 50.3, 47.8, 44.3, 37.8, 35.7, 31.4, 29.2 (d, *J* = 2.2 Hz), 26.2, 25.5 (d, *J* = 1.9 Hz), 21.5, 13.7. ^{19}F NMR (376 MHz, CDCl$_3$) δ -222.0 (dt, *J* = 14.3, 47.4 Hz, 1F), -75.5 (d, *J* = 2.3 Hz, 3F). IR cm^{-1}: 2933, 2864, 1787, 1737, 1454, 1377, 1219, 1149, 1027, 755, 730. HRMS: m/z (EI) calculated [M]$^+$ 412.1662, measured 412.1668.



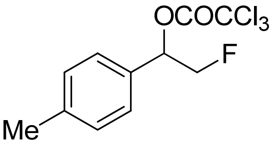
5ac

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.50 (m, 2H), 7.36 (m, 2H), 7.28 (m, 1H), 4.66 (dd, *J* = 9.0, 47.7 Hz, 1H), 4.55 (dd, *J* = 9.3, 48.3 Hz, 1H), 2.23 (br s, 1H), 1.20 (m, 1H), 0.52 (m, 2H), 0.38 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 142.2 (d, *J* = 2.8 Hz), 128.2, 127.5, 125.7, 88.9 (d, *J* = 177.0 Hz), 74.2 (d, *J* = 17.7 Hz), 17.6 (d, *J* = 4.5 Hz), 1.0. ^{19}F NMR (282 MHz, CDCl$_3$) δ -225.0 (t, *J* = 48.2 Hz, 1F). IR cm^{-1}: 3356, 2945, 2833, 1653, 1449, 1113, 1028, 759, 703. HRMS: m/z (EI) calculated [M]$^+$ 180.0950, measured 180.0948.



4a

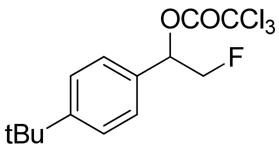
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (m, 5H), 6.11 (ddd, *J* = 2.8, 7.6, 14.4 Hz, 1H), 4.80-4.54 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.9, 132.9 (d, *J* = 6.7 Hz), 129.6, 129.0, 126.7, 89.6, 83.4 (d, *J* = 180.0 Hz), 79.3 (d, *J* = 20.1 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -220.9 (dt, *J* = 14.3, 47.4 Hz, 1F). IR cm^{-1}: 3503, 2954, 2585, 1954, 1762, 1495, 1455, 1394, 1240, 1077, 1026, 846, 831, 760, 700, 680. HRMS: m/z (EI) calculated [M]$^+$ 283.9574, measured 283.9573.



4b

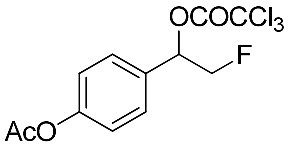
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.09

(ddd, *J* = 2.8, 8.0, 13.6 Hz, 1H), 4.79-4.51 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 139.6, 129.9 (d, *J* = 7.2 Hz), 129.7, 126.7, 89.7, 83.4 (d, *J* = 180.1 Hz), 79.3 (d, *J* = 19.8 Hz), 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -220.6 (dt, *J* = 14.7, 47.8 Hz, 1F). IR cm^{-1}: 3373, 2967, 2580, 1942, 1760, 1516, 1450, 1372, 1256, 1167, 1120, 1081, 870, 845, 830, 677. HRMS: m/z (EI) calculated $[M+Na]^+$ 297.9730, measured 297.9726



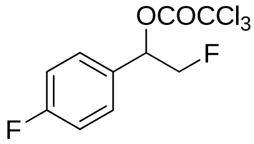
4c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.11 (m, 1H), 4.79-4.52 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 152.7, 129.9 (d, *J* = 7.4 Hz), 126.5, 125.9, 89.7, 83.4 (d, *J* = 180.7 Hz), 79.2 (d, *J* = 21.7 Hz), 34.7, 31.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -220.4 (dt, *J* = 13.9, 46.6 Hz, 1F). IR cm^{-1}: 3363, 2962, 1780, 1615, 1511, 1462, 1449, 1365, 1249, 1103, 1010, 979, 880, 829, 816, 702, 675, 572. HRMS: m/z (EI) calculated $[M]^+$ 340.0200, measured 340.0201



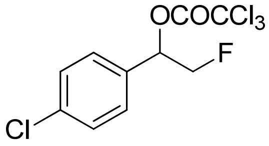
4g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.12 (ddd, *J* = 3.2, 8.0, 14.8 Hz, 1H), 4.77-4.54 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 160.9, 151.4, 130.5 (d, *J* = 6.7 Hz), 128.0, 122.3, 84.2, 83.1 (d, *J* = 180.7 Hz), 78.6 (d, *J* = 20.1 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.4 (dt, *J* = 15.0, 46.6 Hz, 1F). IR cm^{-1}: 3404, 2949, 2837, 1562, 1518, 1451, 1259, 1122, 1022, 837, 683. HRMS: m/z (EI) calculated $[M+Na]^+$ 364.9521, measured 364.9527



4d

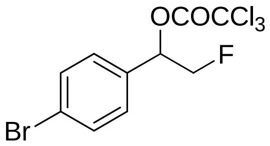
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 5.2, 8.4 Hz, 2H), 7.11 (t, *J* = 8.4 Hz, 2H), 6.09 (ddd, *J* = 3.2, 8.0, 15.2 Hz, 1H), 4.80-4.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 247.6 Hz), 160.9, 128.8 (d, J = 8.5 Hz), 116.1 (d, *J* = 21.6 Hz), 89.5, , 83.2 (d, *J* = 180.4 Hz), 78.5 (d, *J* = 20.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.6 (dd, *J* = 15.4, 47.8 Hz, 1F), -111.1 (m, 1F). IR cm^{-1}: 3522, 2958, 2588, 1959, 1770, 1608, 1513, 1455, 1455, 1428, 1160, 1035, 979, 830, 749, 680, 533. HRMS: m/z (EI) calculated $[M]^+$ 301.9480, measured 301.9485.



4e

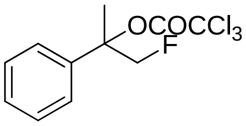
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 4.8 Hz, 4H), 6.07 (ddd, *J* = 3.2, 7.6, 15.2 Hz, 1H), 4.78-4.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 135.6, 131.5 (d, *J*

= 6.7 Hz), 129.2, 128.1, 89.4, 83.1 (d, *J* = 180.7 Hz), 78.4 (d, *J* = 20.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -222.0 (dt, *J* = 14.7, 47.4 Hz, 1F). IR cm^{-1}: 3474, 2955, 2589, 1905, 1762, 1599, 1494, 1456, 1411, 1239, 1091, 1014, 979, 889, 830, 753, 678. HRMS: m/z (EI) calculated [M]$^+$ 317.9184, measured 317.9189.



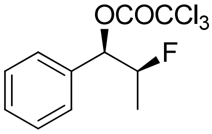
4f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.06 (ddd, *J* = 2.8, 7.6, 15.2 Hz, 1H), 4.78-4.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 132.2, 132.0 (d, *J* = 6.8 Hz), 128.4, 123.8, 89.4, 83.0 (d, *J* = 180.5 Hz), 78.4 (d, *J* = 19.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -222.1 (dt, *J* = 15.0, 46.6 Hz, 1F). IR cm^{-1}: 3449, 2954, 2587, 1906, 1760, 1594, 1490, 1455, 1405, 1238, 1073, 1011, 895, 847, 830, 749, 679. HRMS: m/z (EI) calculated [M]$^+$ 361.8679, measured 361.8683.

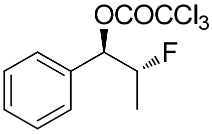


4h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 5H), 4.70 (dd, *J* = 10.0, 48.0 Hz, 1H), 4.47 (dd, *J* = 10.4, 46.8 Hz, 1H), 2.03 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 137.7 (d, *J* = 3.8 Hz), 128.9, 128.8, 124.9, 90.3, 86.9 (d, *J* = 184.5 Hz), 87.0 (d, *J* = 17.9 Hz), 19.6 (d, *J* = 3.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.5 (t, *J* = 47.8 Hz, 1F). IR cm^{-1}: 3417, 2985, 2952, 1770, 1644, 1495, 1448, 1254, 1181, 1074, 1017, 831, 762, 710, 682. HRMS: m/z (EI) calculated [M]$^+$ 297.9730, measured 297.9731.

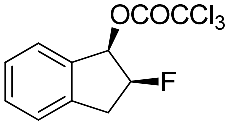


Syn-**4i** and

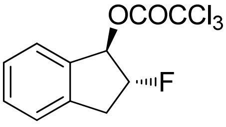


Anti-**4i**

Syn-**4i:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 5H), 5.82 (dd, *J* = 6.8, 14.4 Hz, 1H), 4.90 (m, 1H),1.26 (dd, *J* = 6.4, 23.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 134.1 (d, *J* = 5.2 Hz), 129.5, 128.9, 127.2, 90.0 (d, *J* = 177.8 Hz), 89.7, 82.7 (d, *J* = 20.9 Hz), 17.0 (d, *J* = 22.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -180.9 (m, 1F).
Anti-**4i:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 5H), 5.96 (dd, *J* = 4.0, 15.2 Hz, 1H), 5.02 (m, 1H),1.37 (dd, *J* = 6.4, 24.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 133.6 (d, *J* = 4.4 Hz), 129.1, 128.7, 126.9, 90.9 (d, *J* = 176.3 Hz), 89.7, 81.4 (d, *J* = 23.0 Hz), 15.4 (d, *J* = 22.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -181.1 (m, 1F). IR cm^{-1}: 3523, 2989, 1939, 2584, 1955, 1766, 1495, 1455, 1384, 1242, 1141, 1039, 1025, 993, 925, 845, 759, 700, 680. HRMS: m/z (EI) calculated [M]$^+$ 297.9730, measured 297.9728.



Syn-**4j** and

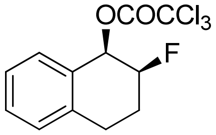


Anti-**4j**

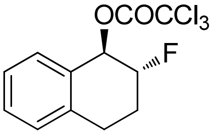
Compounds *syn*-**4j** and *anti*-**4j** could not be separated.

Syn-**4j:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40 (m, 4H), 6.40 (d, *J* = 16.5 Hz, 1H), 5.54 (dm, *J* = 51.9 Hz, 1H), 3.53 (ddd, *J* = 6.3, 17.4 Hz, 1H), 3.27 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.6, 140.5, 135.6, 130.5, 128.0, 126.0, 125.4, 96.4 (d, *J* = 183.7 Hz), 89.6, 85.5 (d, *J* = 30.5 Hz), 37.1 (d, *J* = 23.1 Hz). ^{19}F NMR (282 MHz, CDCl$_3$) δ -184.7 (dddd, *J* = 17.8, 37.0, 52.1 Hz, 1F).

Anti-**4j:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40 (m, 4H), 6.16 (dd, *J* = 4.5, 10.0 Hz, 1H), 5.46 (dm, *J* = 51.3 Hz, 1H), 3.30 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.8, 139.4, 135.3, 130.6, 127.9, 125.8, 125.3, 90.9 (d, *J* = 194.1 Hz), 89.6, 80.1 (d, *J* = 15.6 Hz), 36.7 (d, *J* = 22.3 Hz). ^{19}F NMR (282 MHz, CDCl$_3$) δ -198.6 (dddd, *J* = 9.6, 20.6, 49.4 Hz, 1F). IR cm^{-1}: 3510, 2959, 2582, 1915, 1763, 1611, 1479, 1463, 1239, 1104, 1061, 1018, 952, 845, 830, 746, 680. HRMS: m/z (EI) calculated [M]$^+$ 295.9574, measured 295.9571.



syn-**4j**

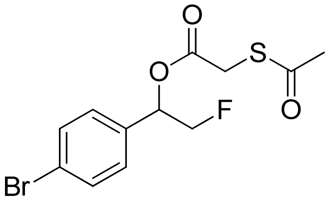


anti-**4j**

Compounds *syn*-**4j** and *anti*-**4j** could not be separated.

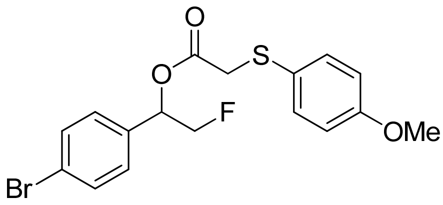
Syn-**4j:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (m, 4H), 6.23 (dd, *J* = 5.6, 12.8 Hz, 1H), 5.01 (dddd, *J* = 3.2, 6.0, 49.2 Hz, 1H), 2.95 (m, 2H), 2.21 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.7, 136.3, 130.1 (d, *J* = 4.8 Hz), 129.7, 129.1, 128.7, 126.8 , 89.7, 89.4 (d, *J* = 176.9 Hz), 89.7, 77.0 (d, *J* = 26.7 Hz), 26.5 (d, *J* = 10.4 Hz), 25.4 (d, *J* = 8.9 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -186.3 (dddd, J = 2.3, 7.1, 12.4, 20.3, 30.8, 36.1, 43.3, 46.3 Hz, 1F).

Anti-**4j:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (m, 4H), 6.25 (d, *J* = 4.4, 11.2 Hz, 1H), 5.09 (dddd, *J* = 2.8, 10.4, 47.2 Hz, 1H), 3.05 (m, 2H), 2.36 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.5, 136.5, 130.2, 129.9 (d, *J* = 5.2 Hz), 128.8, 128.6, 126.8, 89.9, 88.2 (d, *J* = 182.9 Hz), 75.1 (d, *J* = 17.9 Hz), 25.9 (d, *J* = 19.4 Hz), 23.9 (d, *J* = 19.3 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ -190.7 (dm, *J* = 47.8 Hz, 1F). IR cm^{-1}: 3513, 2949, 2581, 1915, 1764, 1607, 1493, 1459, 1437, 1382, 1239, 1123, 1036, 952, 908, 846, 830, 756, 680. HRMS: m/z (EI) calculated [M]$^+$ 309.9730, measured 309.9732.



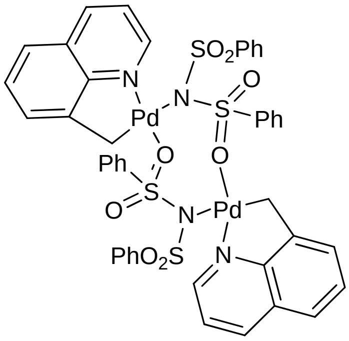
6

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.97 (ddd, *J* = 3.6, 6.8, 16.8 Hz, 1H), 4.66-4.46 (m, 2H), 3.78 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.5, 167.7, 133.6 (d, *J* = 6.4 Hz), 131.8, 128.4, 122.9, 83.4 (d, *J* = 178.5 Hz), 74.6 (d, *J* = 20.1 Hz), 31.3, 30.0. ^{19}F NMR (376 MHz, CDCl$_3$) δ -223.2 (dt, *J* = 16.5, 47.0 Hz, 1F). Anal. Calcd for $C_{12}H_{12}BrFO_3S$: C, 43.12; H, 3.63; S, 9.57. Found: C, 42.90; H, 3.83; S, 9.69. IR cm^{-1}: 2953, 1748, 1698, 1594, 1490, 1385, 1355, 1291, 1260, 1155, 1131, 1073, 1011, 956, 822,625.



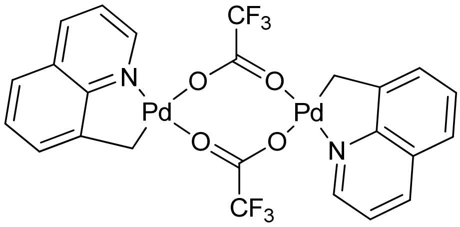
7

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.24 (m, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 5.93 (ddd, *J* = 3.6, 6.8, 16.4 Hz, 1H), 4.59-4.38 (m, 2H), 3.63 (d, J = 15.2 Hz, 1H), 3.60 (d, J = 14.8 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 137.4, 133.7 (d, *J* = 6.3 Hz), 131.7, 131.0, 130.4, 129.7, 128.5, 122.7, 83.4 (d, *J* = 178.5 Hz), 74.2 (d, *J* = 20.5 Hz), 37.1, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -222.8 (dt, *J* = 16.9, 47.0 Hz, 1F). IR cm^{-1}: 3016, 2920, 1908, 1741, 1591, 1493, 1457, 1390, 1273, 1212, 1188, 1127, 1089, 1009, 953, 865, 815, 795, 722, 692, 500. HRMS: m/z (EI) calculated [M]$^{+}$ 382.0034, measured 382.0038.



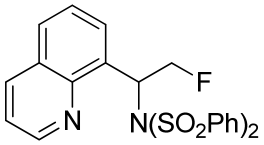
9

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.90 (m, 4H), 7.26 (m, 11H), 3.83 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 150.0, 146.4, 141.6, 137.5, 132.5, 131.8, 129.0, 128.1, 127.8, 127.3, 126.8, 126.3, 123.6, 121.2, 53.4, 26.2. LRMS: m/z (MALDI) calculated [M+Pd]$^{+}$ 649.8778, measured 649.8784



10

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 1.2, 4.8 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 5.2 Hz, 0.5 H), 7.81 (d, *J* = 8.4 Hz, 0.5 H), 7.32 (dd, *J* = 5.2, 8.8 Hz, 1 H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 0.5 H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 8.0 Hz, 0.5H),6.75 (d, *J* = 7.2 Hz, 1H), 3.93 (s, 0.5 H), 3.68 (s, 1.6 H), 2.71(s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.9, 152.4, 152.3, 148.7, 147.5, 147.3, 146.6, 137.2, 136.8, 128.2, 128.0, 127.6, 127.2, 126.6, 123.3, 122.9, 121.3, 120.8, 117.2, 114.3, 25.3, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.4 (s), -74.1 (s), -74.6 (s).



14

^{1}H NMR (400 MHz, C_7D_8) δ 8.58 (dd, *J* = 1.6, 4.0 Hz, 1H), 8.35 (dd, *J* = 4.0, 7.2 Hz, 4H), 7.74 (d, *J* = 7.2 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 1 H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.09 (s, 1H), 6.98 (m, 6H), 6.80 (dd, *J* = 4.0, 8.4 Hz, 1H), 4.38 (m, 1H), 4.18 (m, 1H). ^{13}C NMR (100 MHz, C_7D_8) δ 149.6, 145.3 (d, *J* = 4.9 Hz), 140.7, 137.5, 136.3 (d, *J* = 18.6 Hz), 135.9, 133.4, 129.2, 128.7, 128.3, 126.6, 126.3 (d, *J* = 11.9 Hz), 121.2, 90.2 (d, *J* = 176.2Hz), 52.1 (d, *J* = 22.3 Hz). ^{19}F NMR (376 MHz, C_7D_8) δ -192.6 (ddd, *J* = 12.8, 35.7, 49.6 Hz, 1F). IR cm^{-1}: 3065, 2962, 1597, 1582, 1499, 1448, 1375, 1354, 1262, 1170, 1085, 1048, 904, 866, 799, 736, 686, 581, 549. HRMS: m/z (ESI) calculated $[M+H]^+$ 471.0849, measured 471.0852.