Scheme 1. Metal-catalysed benzylic fluorination

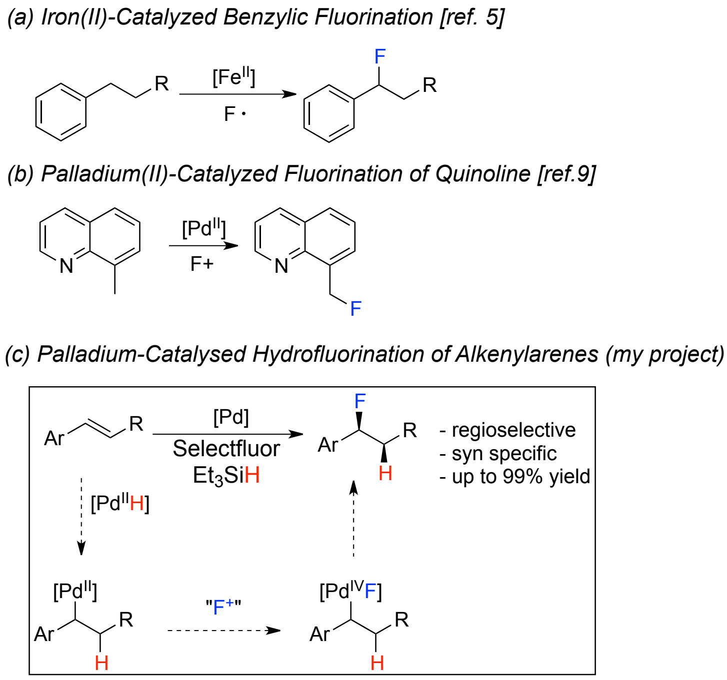
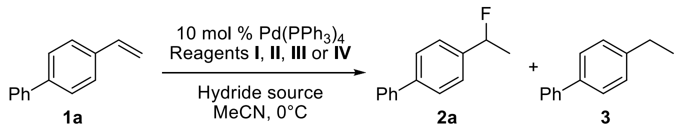
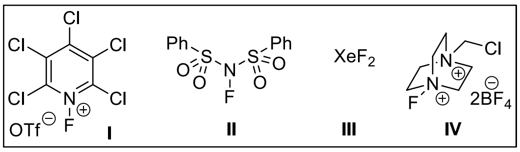


Table 1. Hydrofluorination of styrene **1a**

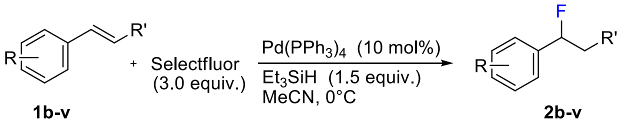




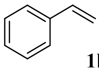
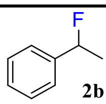
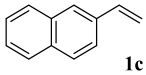
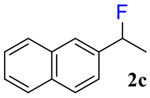
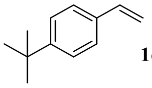
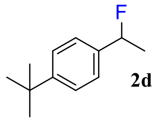
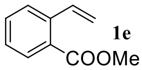
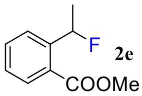
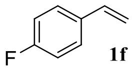
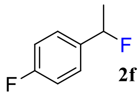
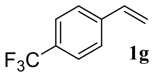
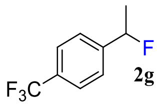
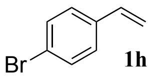
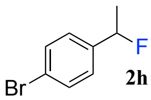
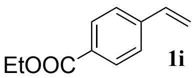
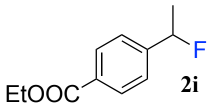
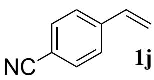
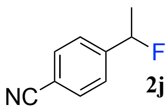
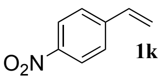
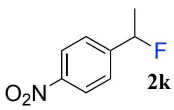
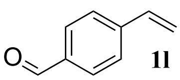
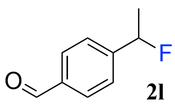
Entry[a]	F+ source (equiv.)	H- source (equiv.)	Solvent (ml)	Conv.(%)[b]	2a(%)[b]	3(%)[b]
1	**I** (2)	*i*Pr$_3$SiH (2)	MeCN (2)	>99	0	23
2	**II** (2)	*i*Pr$_3$SiH (2)	MeCN (2)	23	11	12
3[c]	**III** (2)	*i*Pr$_3$SiH (2)	DCM (2)	72	16	28
4	**IV** (2)	*i*Pr$_3$SiH (2)	MeCN (2)	>99	38	0
5[d]	**IV** (2)	*i*Pr$_3$SiH (2)	MeCN (2)	0	0	0
6	**IV** (2)	-	MeCN (2)	0	0	0
7	**IV** (2)	PhSiH$_3$ (2)	MeCN (2)	95	0	31
8[e]	**IV** (2)	NaBH$_4$ (2)	MeCN (2)	97	18	48
9	**IV** (2)	Bu$_3$SnH (2)	MeCN (2)	9	traces	0
10	**IV** (4)	*i*Pr$_3$SiH (2)	MeCN (4)	>99	54	0
11	**IV** (4)	Ph$_3$SiH (2)	MeCN (4)	>99	37	0
12	**IV** (4)	Et$_3$SiH (2)	MeCN (4)	>99	70	0
13	**IV (3)**	**Et$_3$SiH (1.5)**	MeCN (4)	**>99**	**69**	**0**

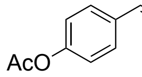
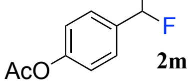
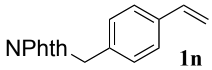
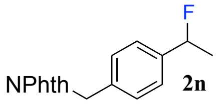
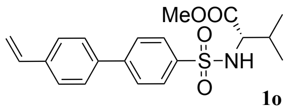
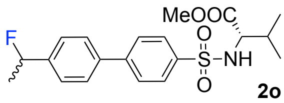
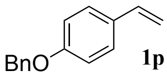
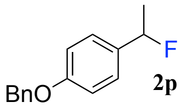
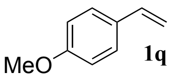
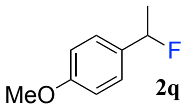
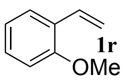
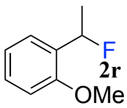
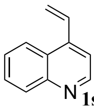
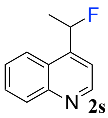
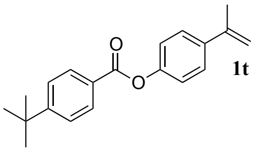
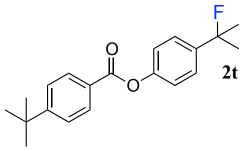
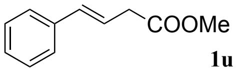
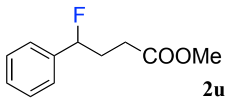
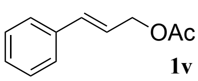
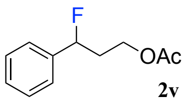
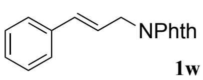
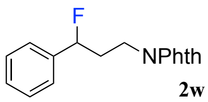
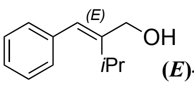
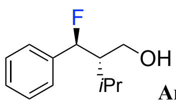
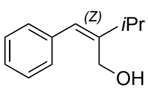
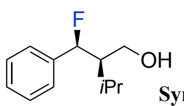
[a] Reaction performed in 0.1 mmol scale, at 0°C in 2.0 ml of MeCN with 2 equiv. of F$^+$ source, 2 equiv. of *i*Pr$_3$SiH and 10 mol% of Pd(PPh$_3$)$_4$; [b] Determined by ^{1}H NMR and ^{19}F NMR using 1-fluoro-3-nitrobenzene as an internal standard; [c] Reaction performed in DCM at -40°C; [d] Reaction performed in absence of Pd(PPh$_3$)$_4$; [e] NaBH$_4$ was added in two portions in 4h.

Table 2. Substrate Scope for Hydrofluorination[a]



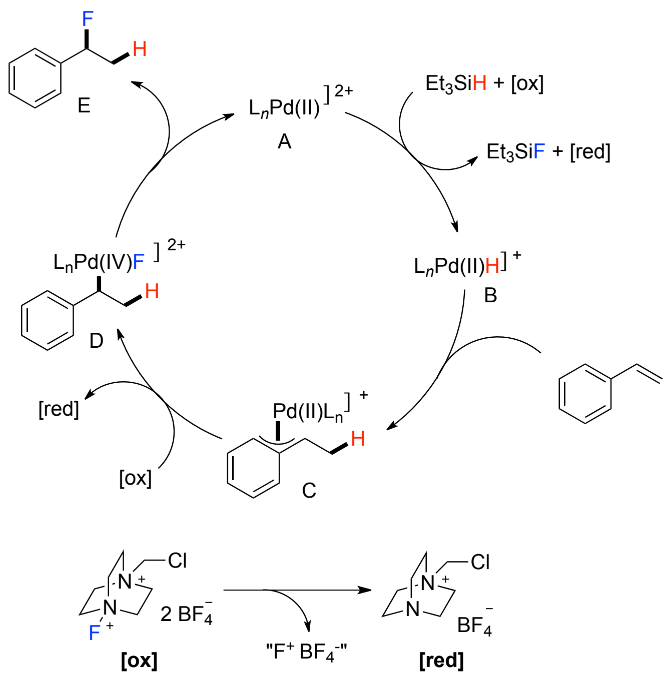
1b-v **2b-v**

Entry[a]	Substrate	Product	Yield (%)[b]
1[c]	 **1b**	 **2b**	58
2	 **1c**	 **2c**	46
3[c]	 **1d**	 **2d**	43
4	 **1e**	 **2e**	58
5[c]	 **1f**	 **2f**	55
6[c]	 **1g**	 **2g**	72
7[c]	 **1h**	 **2h**	78
8	 **1i**	 **2i**	64
9	 **1j**	 **2j**	70
10	 **1k**	 **2k**	61
11[c]	 **1l**	 **2l**	76

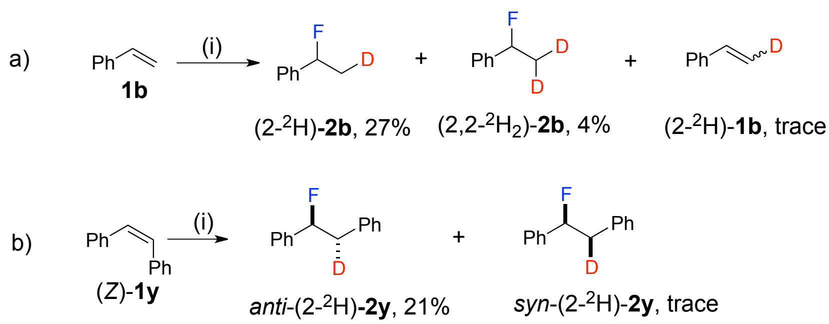
12	 **1m**	 **2m**	99
13	 **1n**	 **2n**	87
14	 **1o**	 **2o**	80 (d.r. 1:1)
15	 **1p**	 **2p**	8
16	 **1q**	 **2q**	0
17[c]	 **1r**	 **2r**	43
18[c]	 **1s**	 **2s**	13
19	 **1t**	 **2t**	65
20	 **1u**	 **2u**	51
21	 **1v**	 **2v**	54
22	 **1w**	 **2w**	66
23	 **(*E*)-1x**	 **Anti-2x**	67 (d.r. >20:1)
24	 **(*Z*)-1x**	 **Syn-2x**	41 (d.r. >20:1)

[a] Reaction conditions: 0.1mmol scale reaction with 4 ml of MeCN. Reaction time: 2h; [b] Yields determined by ^{19}F NMR using 1-fluoro-3-nitrobenzene as an internal standard; [c] Reaction performed in CD_3CN.

Scheme 2. Proposed catalytic cycle



Scheme 3. Deutherium-labelled experiments. Conditions: (i) $Pd(PPh_3)_4$, 10 mol%, Selectfluor (3 equiv) Et_3SiD (1.5 equiv), CH_3CN, 0 ˚C, 2 h.



Scheme 4. Oxidative fluorination of palladacomplexes **C1** and **C2**