



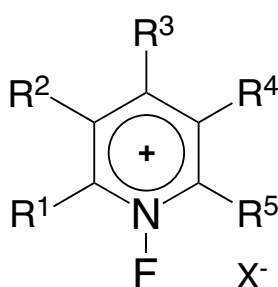
TOSOH F-TECH, INC.

Fluorinating Reagents

F - P L U S

(N-Fluoropyridinium Salts)

(PATENTED)



FP-T series : $X^- = \text{CF}_3\text{SO}_3^-$

FP-B series : $X^- = \text{BF}_4^-$

N-Fluoropyridinium salts are electrophilic fluorinating reagents, consisting of a pyridinium ring and its counter anions. Using these reagents, a fluorine atom can be easily introduced into aromatics, carbanion and active methylene compounds.

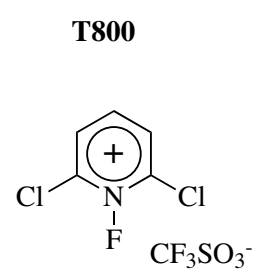
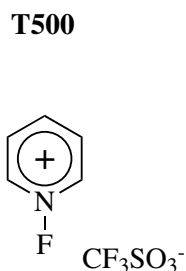
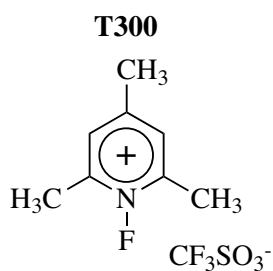
The degree of fluorinating ability is determined by substituents on the pyridine ring. Methyl groups decrease this ability, thus making these reagents ideal for reactions with carbanions and the like with high basicity. Chlorine groups have the opposite effect, thus making these reagents suitable for reactions with aromatics.

F-TECH offers two series of these reagents, each having different anion groups. The **FP-T series** is characterized by high chlorohydrocarbon solubility while the **FP-B series** have a higher fluorine content and are less expensive.

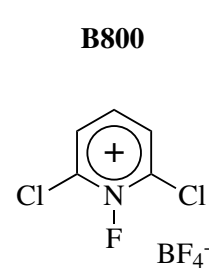
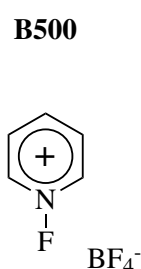
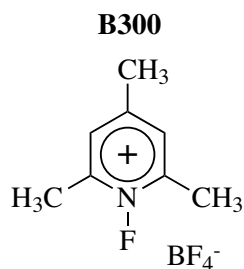
Features

- (1) Electrophilic chemical species : F^+ or $\text{F} \cdot$
- (2) High Selectivity
- (3) Wide range of fluorinating capacity (see below)
- (4) Low cost due to high active fluorine contents

FP-T series



FP-B series

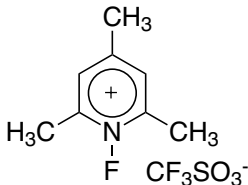
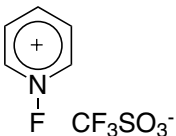
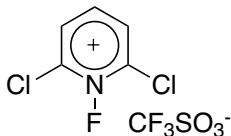


moderate \longleftarrow Fluorinating Abilities \longrightarrow high

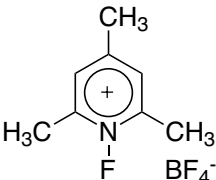
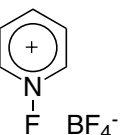
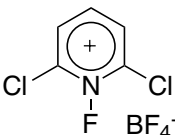


PHYSICAL PROPERTIES

FP-T series

Type	FP-T300	FP-T500	FP-T800
Chemical name	N-Fluoro-2,4,6-trimethylpyridinium triflate	N-Fluoropyridinium triflate	N-Fluoro-2,6-dichloropyridinium triflate
			
Mol. weight	289.25	247.17	316.06
MP(°C)	168.5-170	185-187	151-153
Active Fluorine (mM/g)	3.46	4.05	3.16
Appearance	colorless crystal	colorless crystal	colorless crystal
Solubility(MeCN) (g/ml,25°C)	0.37	0.69	0.38
CAS Reg.No.	107264-00-6	107263-95-6	130433-68-0

FP-B series

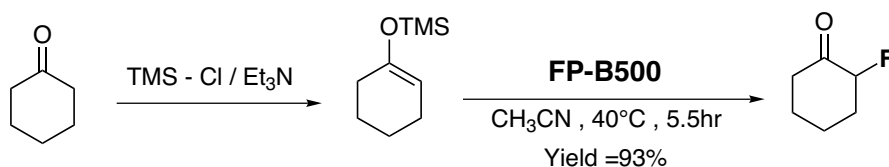
Type	FP-B300	FP-B500	FP-B800
Chemical name	N-Fluoro-2,4,6-trimethylpyridinium tetrafluoroborate	N-Fluoropyridinium tetrafluoroborate	N-Fluoro-2,6-dichloropyridinium tetrafluoroborate
			
Mol. weight	226.98	184.90	253.79
MP (°C)	217-217	197-198	203-205
Active Fluorine (mM/g)	4.40	5.41	3.94
Appearance	colorless crystal	colorless crystal	colorless crystal
Solubility(MeCN) (g/ml,25°C)	0.10	0.20	0.16
CAS Reg.No.	109705-14-8	107264-09-5	140623-89-8



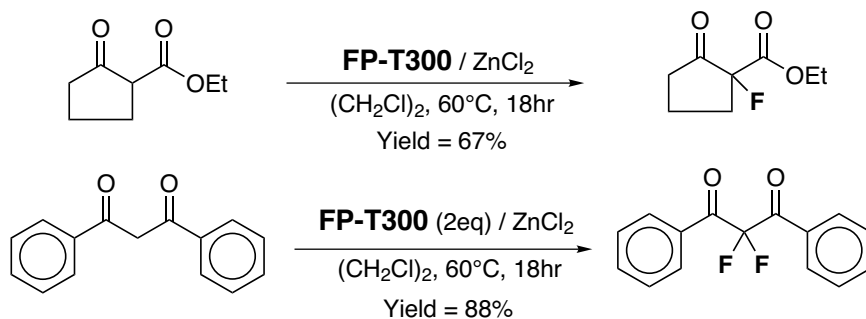
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EXAMPLES OF BASIC FLUORINATION REACTION

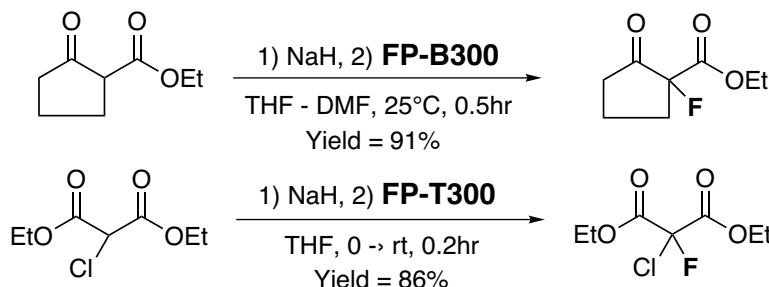
1) Enole compounds¹⁾



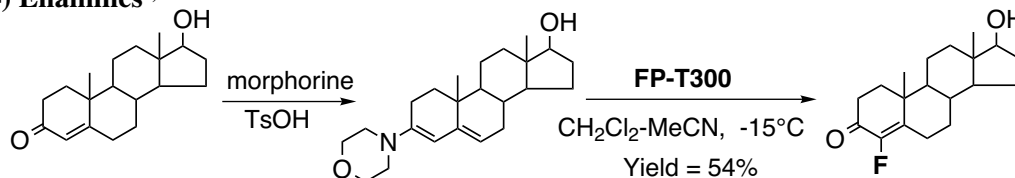
2) Active methylene compounds with Lewis acid²⁾



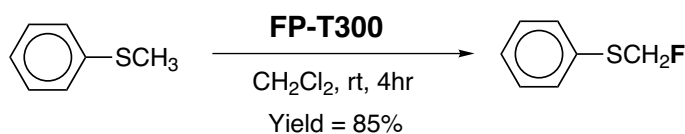
3) Carbanions^{1),2),3)}



4) Enamines²⁾



5) Sulfides⁴⁾



1) T.Tamura, K.Nukui and K.Kawada, *18th Symposium on Fluorine Chemistry Jpn.*, Abstract, p135 (1993)

2) T. Umemoto et al, *J.Am.Chem.Soc.*, **112** (23), 8563-8575, (1990)

3) K.Kawada and K. Nukui, *Chemistry and Chemical Industry*, **46** (11), 1730-1732, (1993)

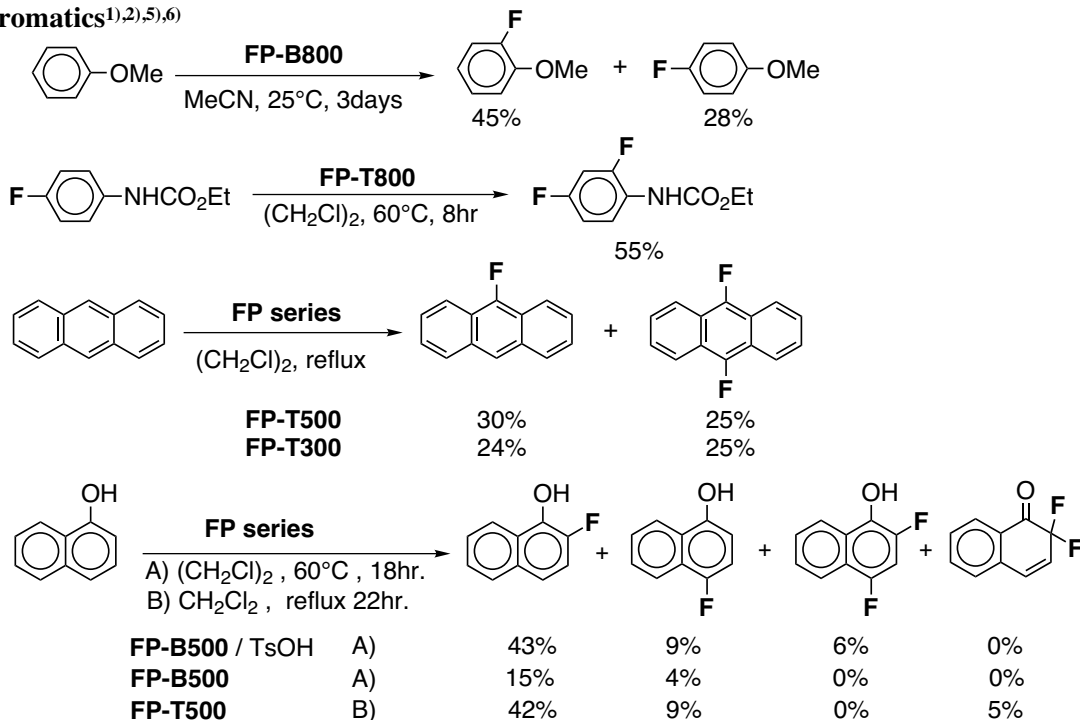
4) T.Umemoto and G.Tomizawa, *Bull.Chem.Soc.Jpn.* **59**, 3625, (1990)



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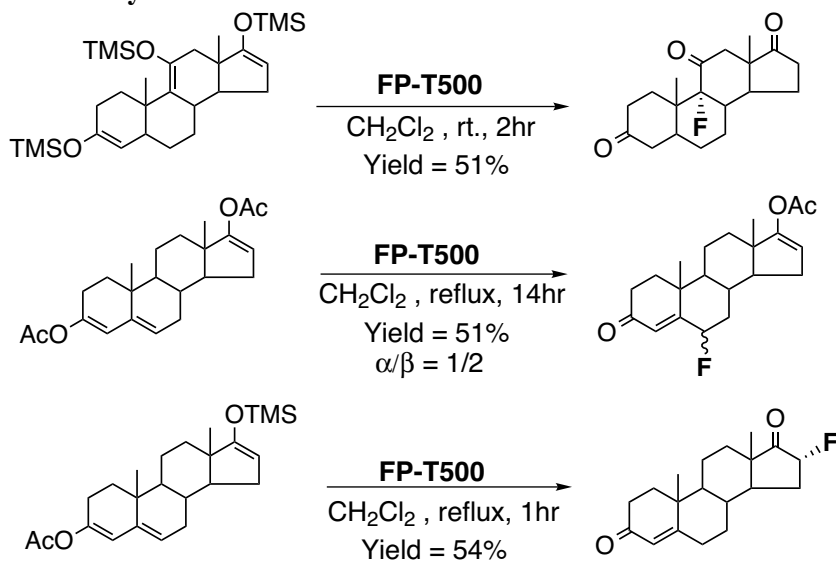
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6) Aromatics^{1),2),5),6)}



APPLICATIONS

Regioselectivity^{2),7)}



5) T. Umemoto et al, *52th Symposium on Organic Synthesis*, Abstract,111-114, (1986)

6) Yongseog Chung et al, *J. Org. Chem.* **54**, 1018 - 32, (1989)

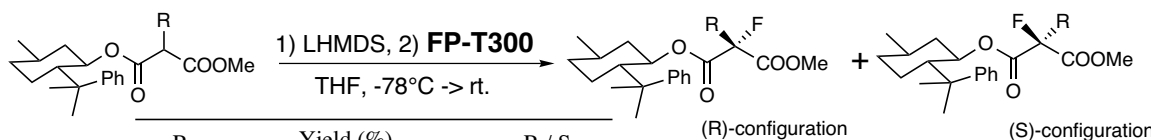
7) *Organic Syntheses*, **69**, 129-143, (1990)



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TOSOH

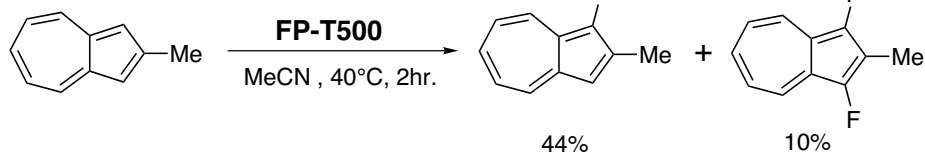
Stereospecificity⁸⁾



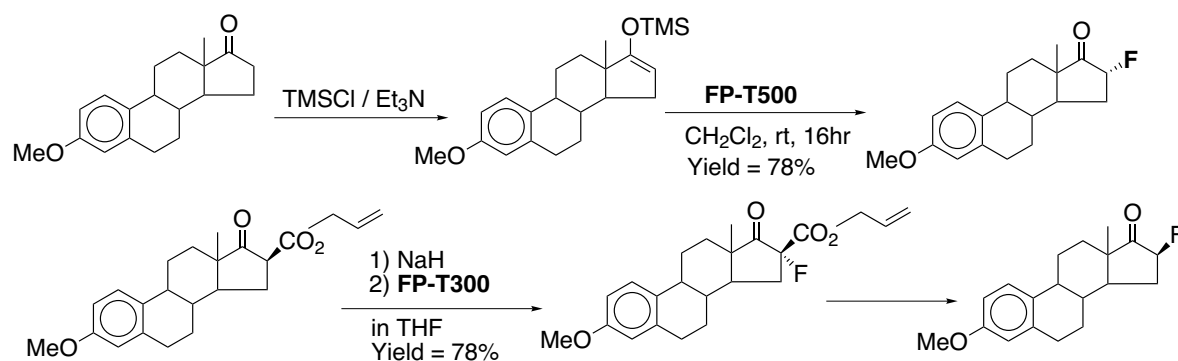
R	Yield (%)	R / S
Me	87	3.8 / 1
Et	96	1 / 2
Pr	96	1 / 2
PhCH ₂	88	1 / 16

LHMDS: lithium hexamethyl disilazide

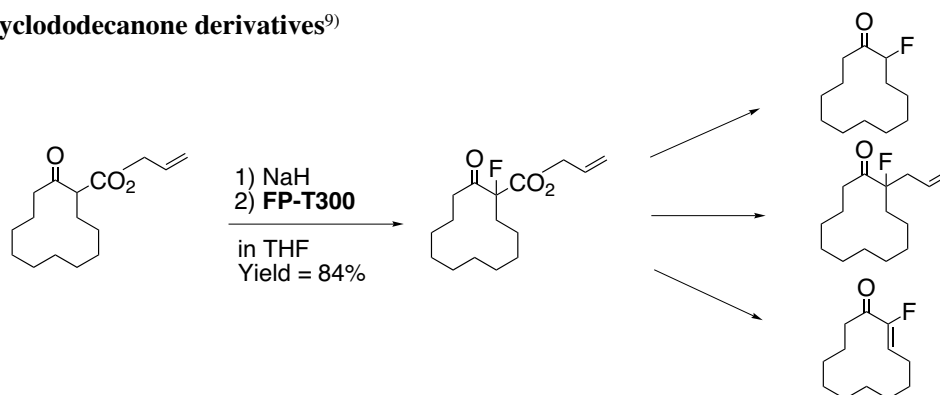
Azulene derivatives



Estrone derivatives^{2),7),9)}



Cyclododecanone derivatives⁹⁾



8) M.Ihara et al, *Tetrahedron Letters*, **27**(37), 4465-4468, (1986)

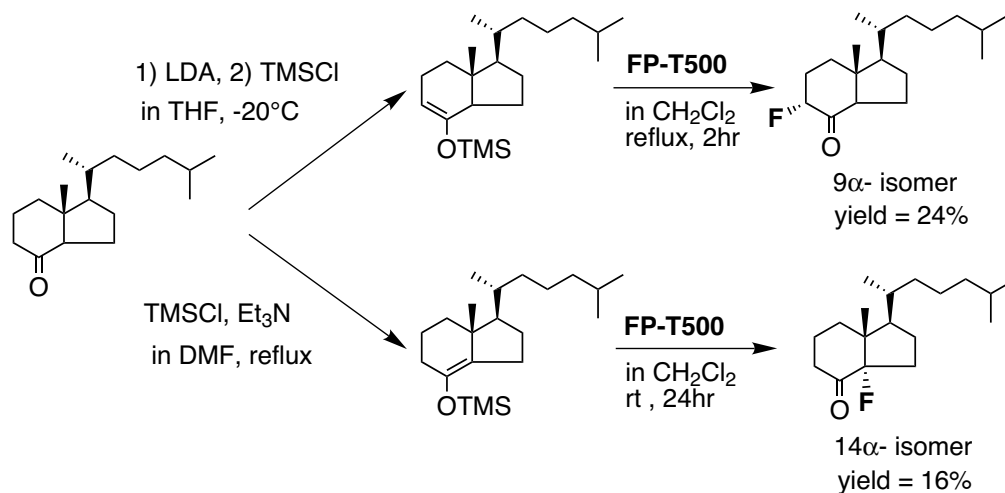
9) I.Shimizu and H.Ishii, *Tetrahedron*, **50** (2), 487-495, (1994)



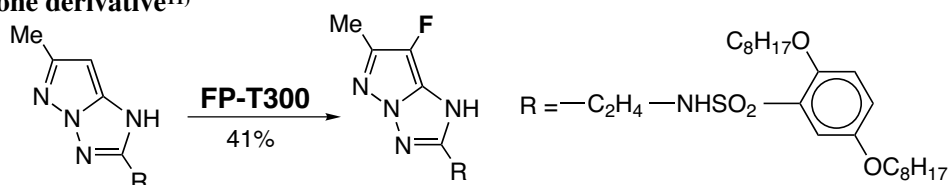
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Building block of vitamin D₃¹⁰⁾

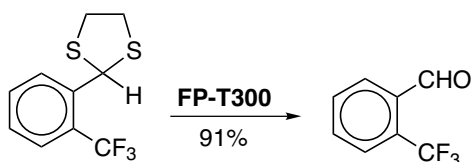


Pyrazolone derivative¹¹⁾



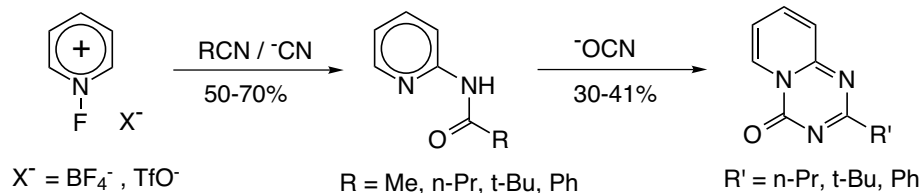
HYDROLYSIS

Hydrolysis of dithioacetal¹²⁾



OTHERS

Synthesis of 2-substituted pyrido[1,2-a]-1,3,5-triazin-4-ones¹³⁾



10) William G. Dauben et al (University of California), *J. Org. Chem.* **57**, 1597 - 1600, (1992)

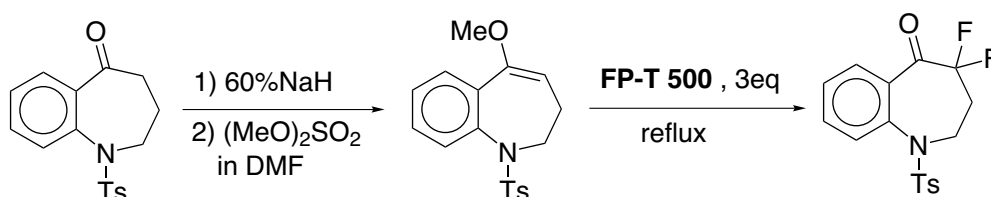
11) FUJI PHOTO FILM CO., LTD., JP 277236/88

12) Alexander S Kiselyov et al, *Tetrahedron*, **49**, 2151, (1992)

13) Alexander S Kiselyov et al, *Tetrahedron*, **35**, 207, (1994)

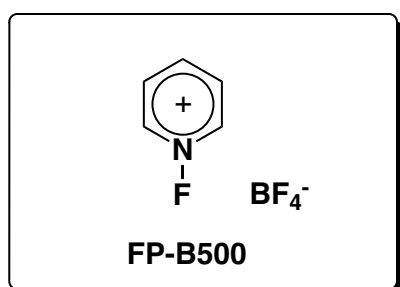
New Reaction

Example of difluorination¹⁴⁾

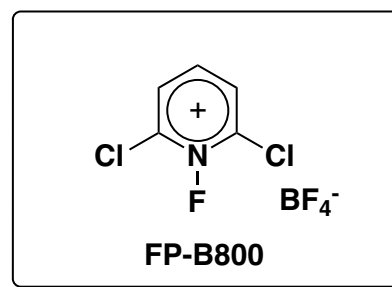


Comparison with N-Fluoropyridinium Salts and other electrophilic fluorinating agents

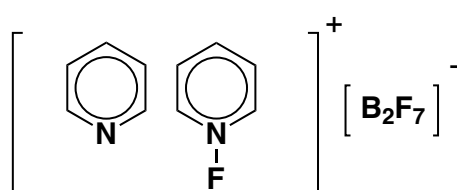
- Content of Active fluorine -



Active fluorine 10.3%

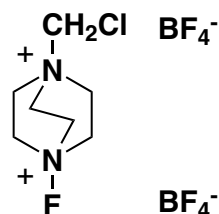


Active fluorine 7.5%



NFPy

Active fluorine 5.7%



SELECTFLUOR

Active fluorine 5.4%