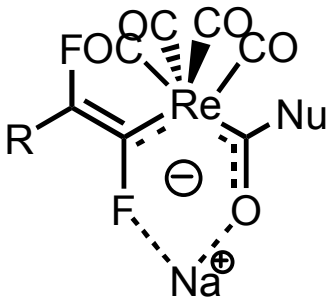
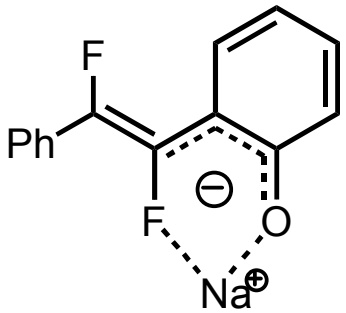
C-F…Na COORDINATION

IN THE SOLUTIONS OF β-FLUOROENOLATES AND α-FLUOROVINYL(ACYL)RHENATES





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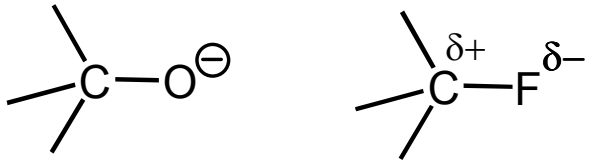
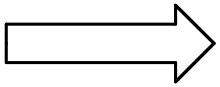
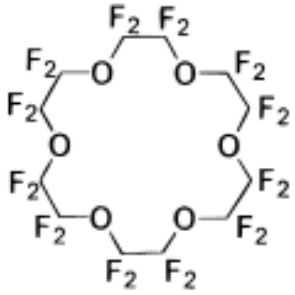


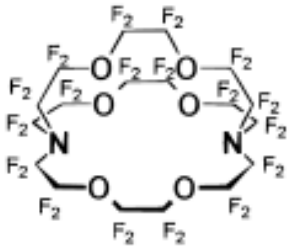
- high electronegativity
- small size



hard donors

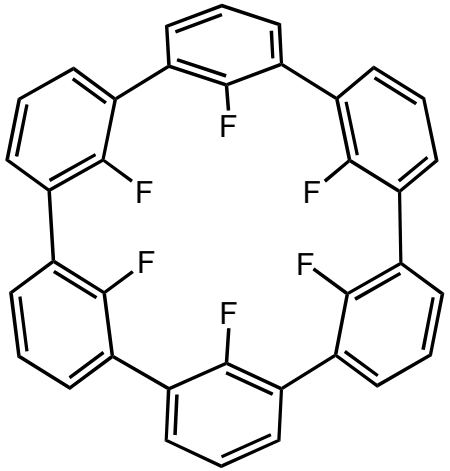


Lagow et al.



Lagow et al.

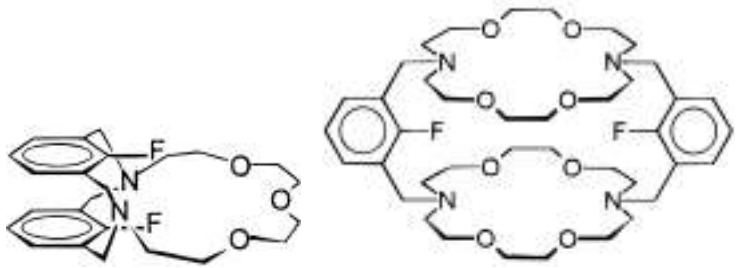
"…are not capable of forming any complexes with metal ions…"

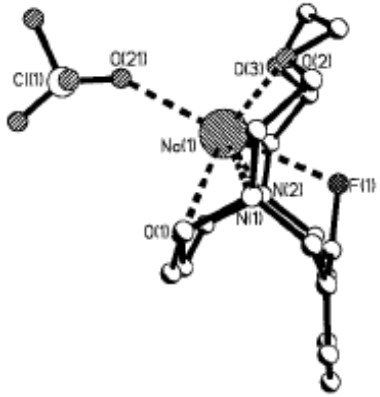


D.J. Cram at al., 1989

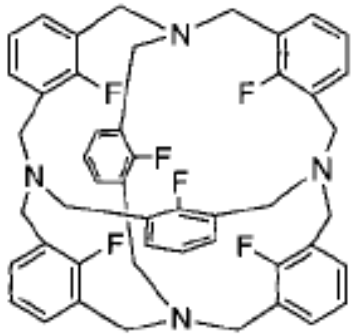
Jenny P. Glusker at al. (*J. Am. Chem. Soc*. **1983**, *105,* 3214)

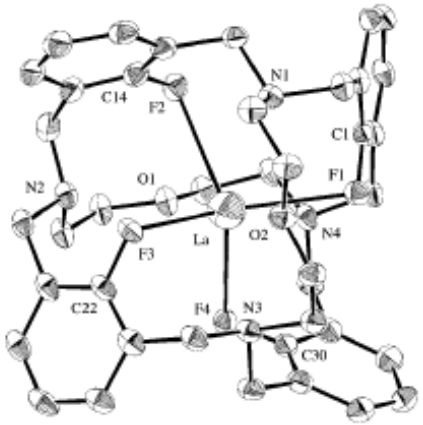
"*We believe that the C-F bond is capable of significant, if not prominent, interactions with both alkaline metal cations and proton donors."*



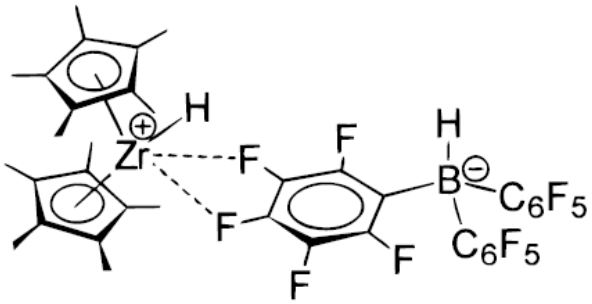


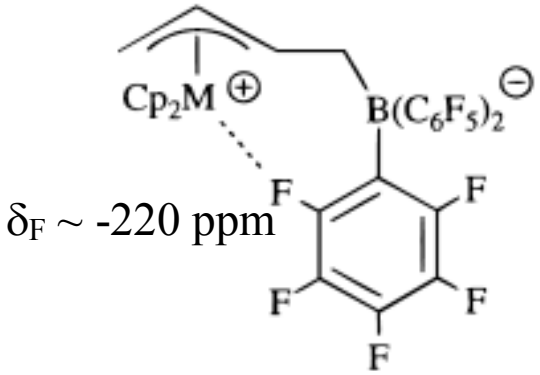
Herbert Plenio at al. (1994-1997)
(*J. Am. Chem. Soc.* **1996,** *118,* 356-367)



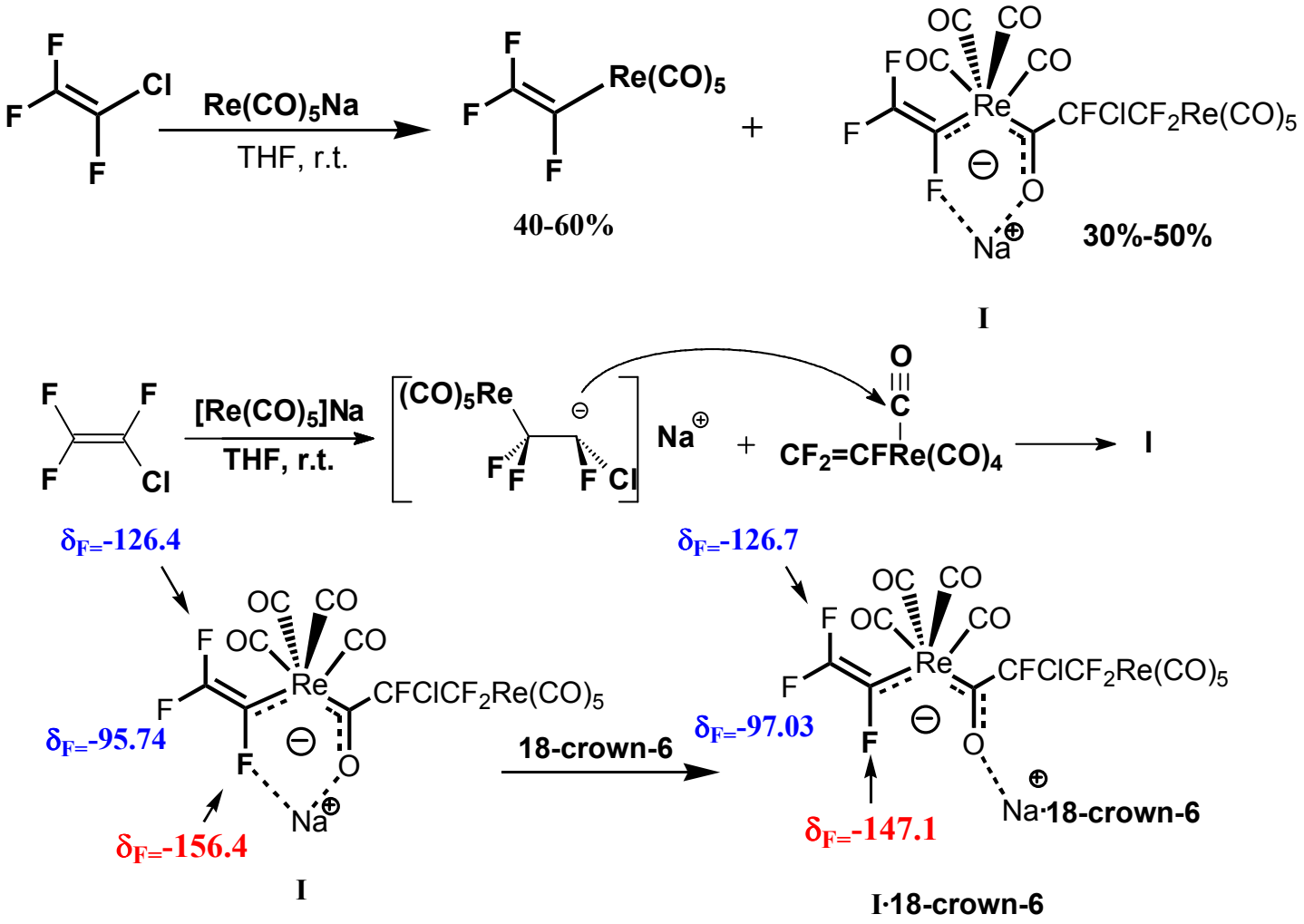


H.Takemura et al. (1999-2003)
(*J. Am. Chem. Soc.* **2001,** *123,* 9293)

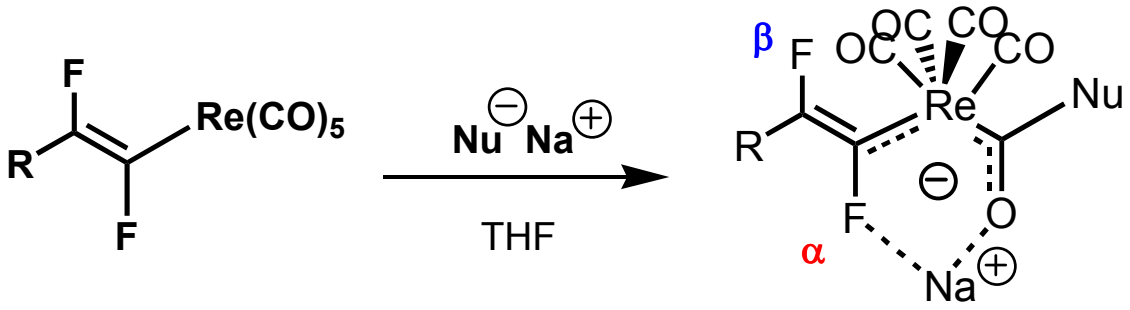




$\delta_F \sim -220$ ppm

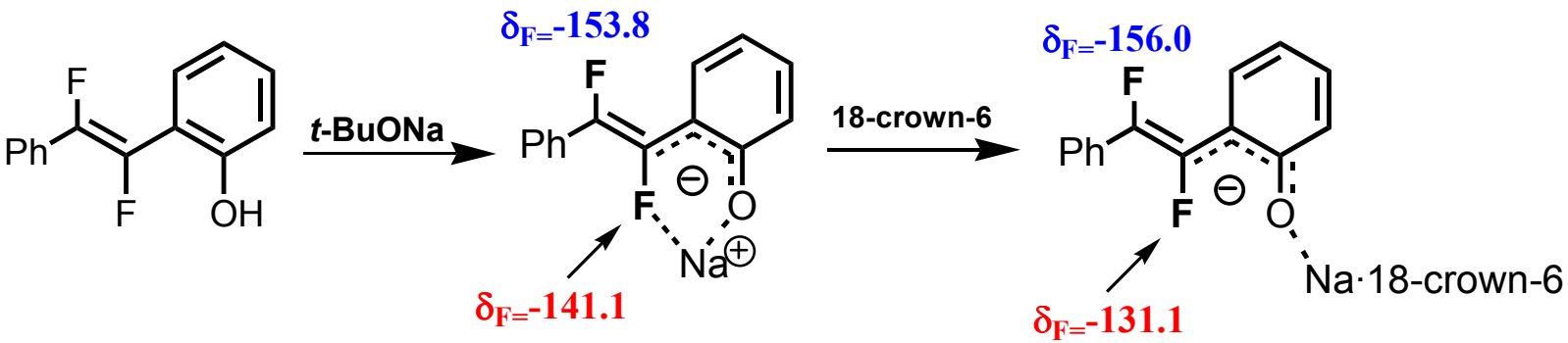


$\Delta\delta_{F\alpha}$=9.3 ppm

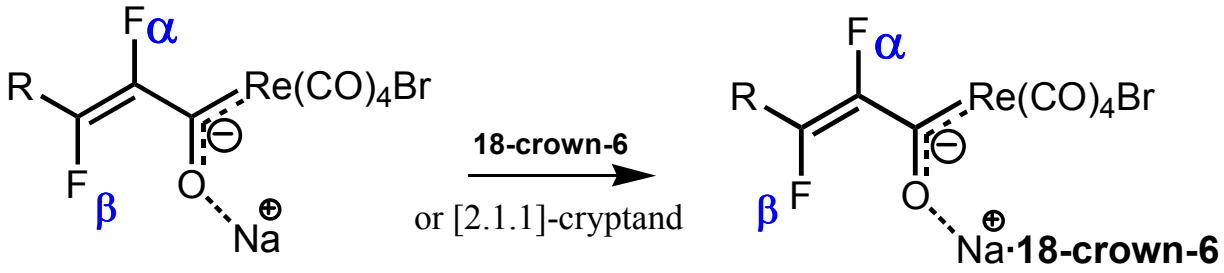


$_{\Delta}\delta_{F}$ - change of the δ_F on the addition of 18-crown-6 in **THF**

Compound number	**R**	**Nu⁻**	$_{\Delta}\delta_{F\alpha}$	$_{\Delta}\delta_{F\beta}$
I	F	$[(CO)_5ReF_2CFClC]^-$	**9.3**	**-0.3**
II	F	*t*-BuO⁻	**14.9**	**-1.9**
III	$(CF_3)_3C$-	*t*-BuO⁻	**7.2**	**-1.8**
IV	Ph	*t*-BuO⁻	**14.8**	**-2.1**
V	F	[PhC≡C]⁻	**7.2**	**-0.9**
VI	Ph	[PhC≡C]⁻	**5.0**	**-0.9**



$\Delta\delta_{F\alpha}$=10 ppm

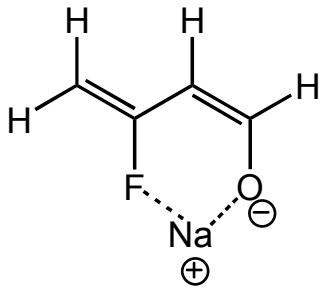


R=F, $(CF_3)_3C^-$

$\Delta\delta_{F\alpha}$~1 ppm

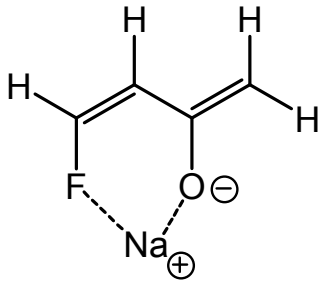
$\Delta\delta_{F\beta}$ – (3–5) ppm, *i.e. shifts to **higher** field*

Direction (upfield) and value of $\Delta\delta_F$ shift upon C-F…Na+ coordination as predicted by B3LYP/6-31+G(d) calculations.

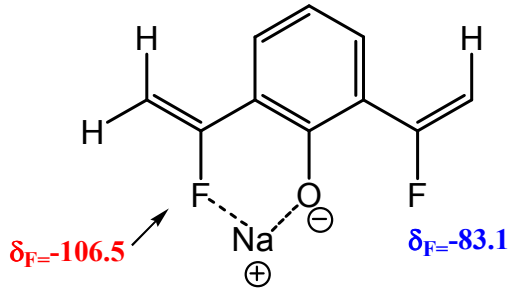


$\Delta\delta_{F\alpha}$=21.8 ppm

Flat chelate cycle



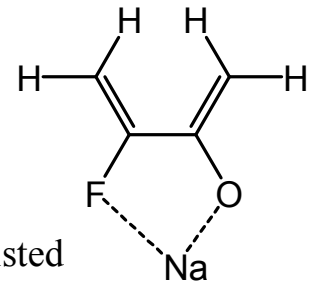
$\Delta\delta_{F\alpha}$=28.5 ppm



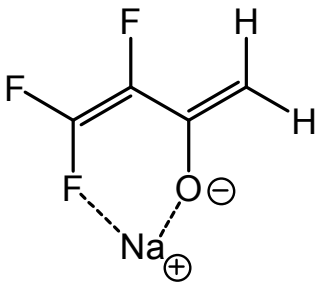
$\Delta\delta_F$=23.4 ppm

Twisted chelate cycle

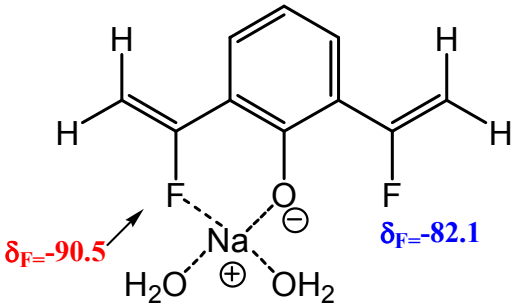
Twisted



$\Delta\delta_{F\alpha}$=21.5 ppm



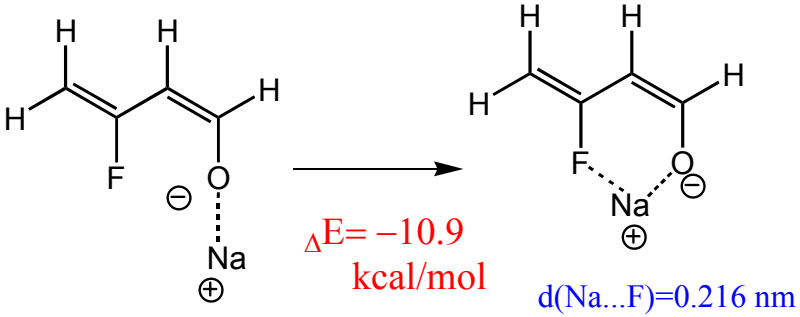
$\Delta\delta_{F\alpha}$=23 ppm



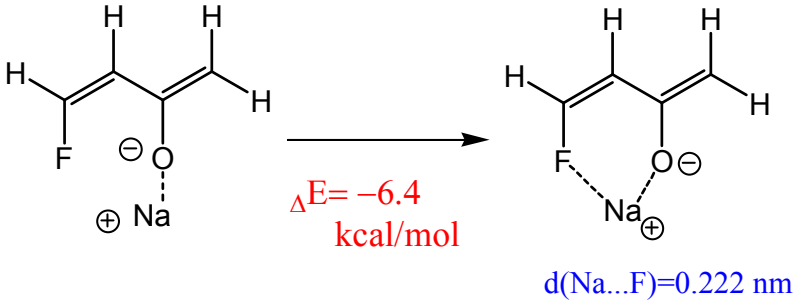
$\Delta\delta_F$=8.4 ppm

Stabilization energy of C-F…Na+ coordination ($_{\Delta}$E, kcal/mol) calculated at B3LYP/6-31+G(d) level.

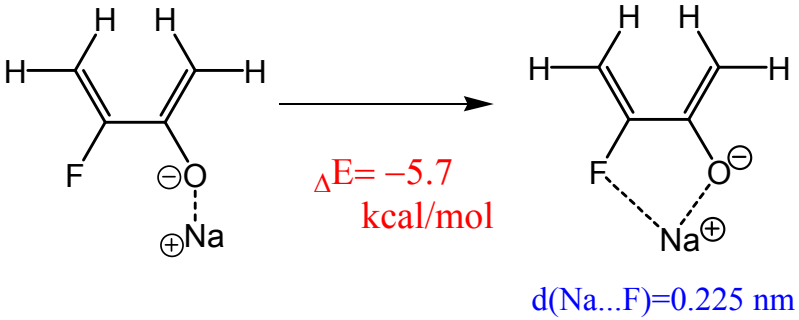
6-member chelate, α-fluorine



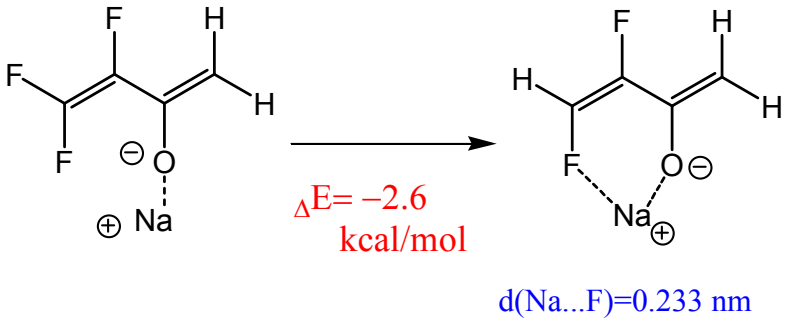
6-member chelate, β-fluorine (terminal CHF= group)

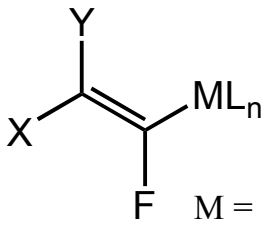


5-member chelate, α-fluorine



6-member chelate, β-fluorine (terminal CF_2= group)

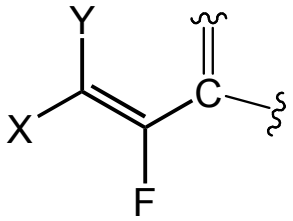




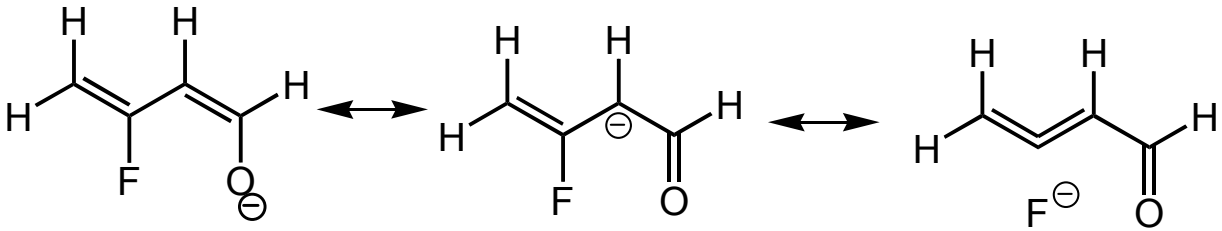
M = transition metal

Search in
Cambridge Crystallographic Data Base
http://www.ccdc.cam.ac.uk

d(C-F)=0.138-0.14 nm - *longer than in monofluoroalkanes !*



d(C-F)=0.137-0.138 nm



Negative fluorine hyperconjugation in β-fluoroenolate anions should further increase
(a) negative charge on fluorine and
(b) d(C-F) bond

Acknowledgements

- Organizing committee
- Financial support from RFBR Project No. 05-03-32905
- "P&M" Scientific Industrial Association (Moscow) for a gift of CF_2=CFCl (used in the synthesis of α-fluorovinyl(acyl)renate (I))