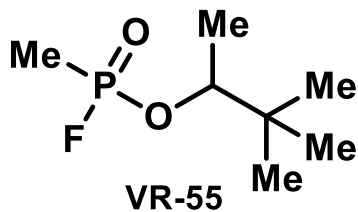


Look inside Ukrainian chemistry: common fluorination and uncommon amines

Institute of Organic Chemistry (IOC), Kyiv

Former “limited access”-facility
with a huge background in fluoro-
and phosphorus chemistry



R. Kuhn, K. Henkel **1944**, test samples
IOC, **1950**-...?, bulk quantities



Together with “Enamine, Ltd.”
provides the vast majority
of organic chemistry output in Ukraine

Main chemistry-oriented periodicals in Cyrillic world

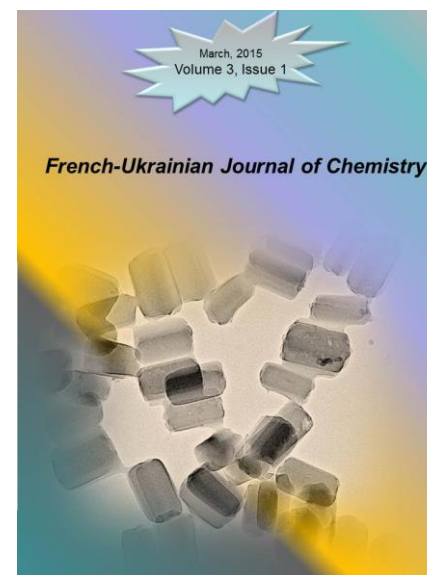


...also recognized by leading experts:

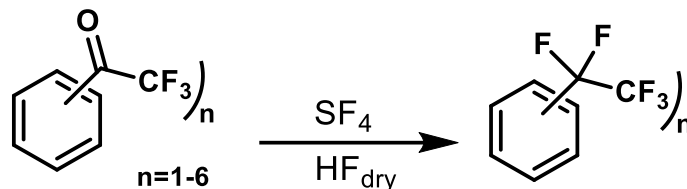
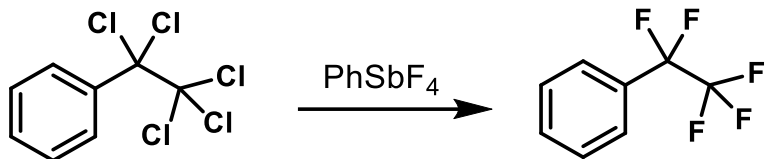
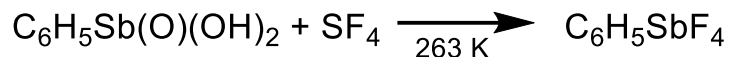
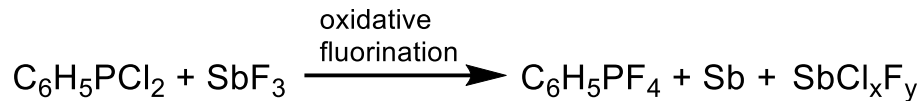
FRENCH-UKRAINIAN JOURNAL OF CHEMISTRY (2015, VOLUME 3, ISSUE 1)

α -Thioalkylation of Zinc Dienolates as an Entry to 4-Substituted 1-*tert*-Butoxy-7a-methylhexahydroindenes^{1,2}

Thomas Köhler^a, Thomas Huhn^{a*} and Ulrich Groth^a

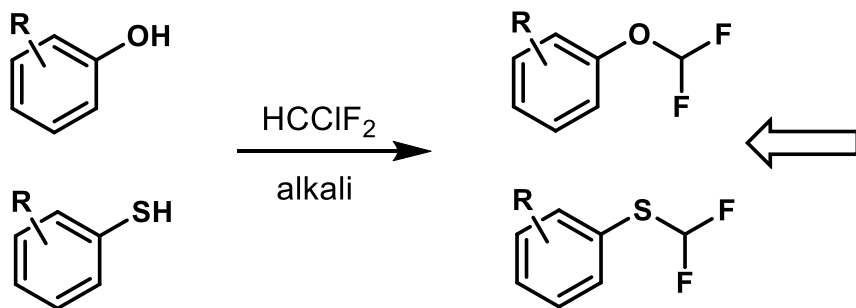


Yagupolskii group: early studies

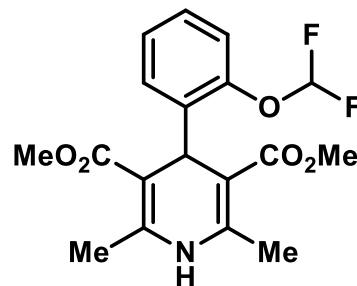


L. Yagupolskii *et al.*, *Zh. Org. Chim.* **1977**, 13 (3), 613-616

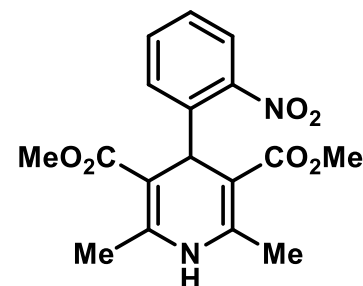
- first polyfluoroalkylarenes
- introduction of difluoromethyl moiety



R=CHO: no Cannizzaro reaction!



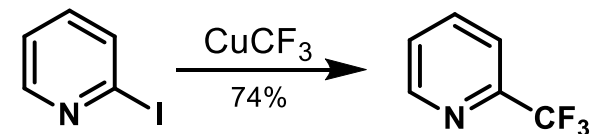
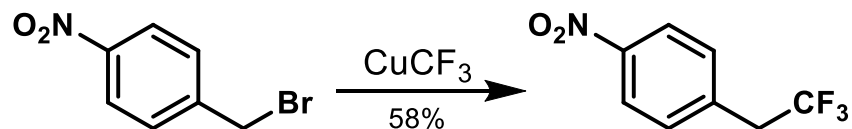
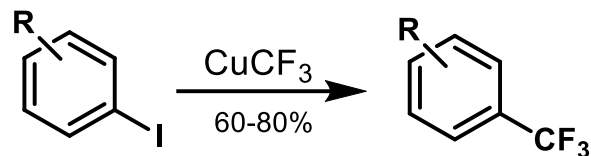
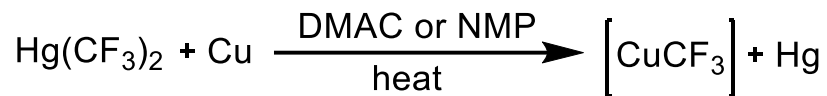
riodipine
Foridon



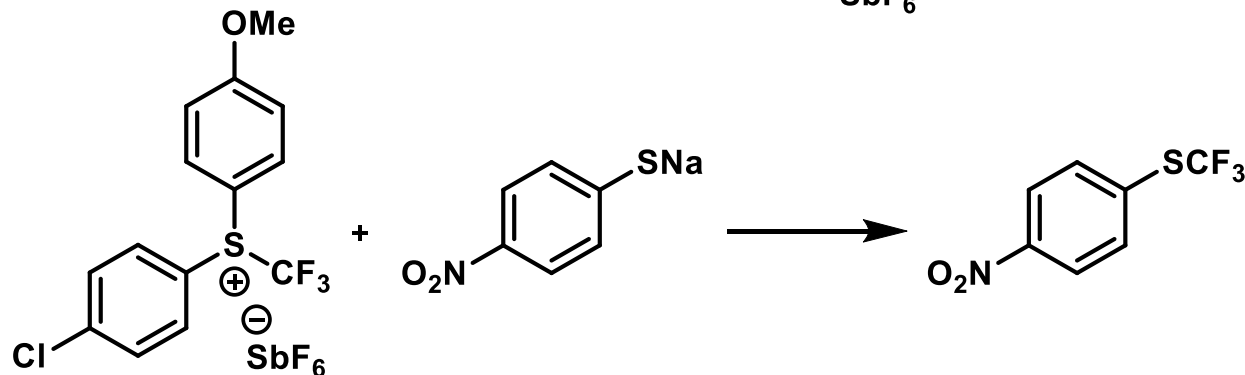
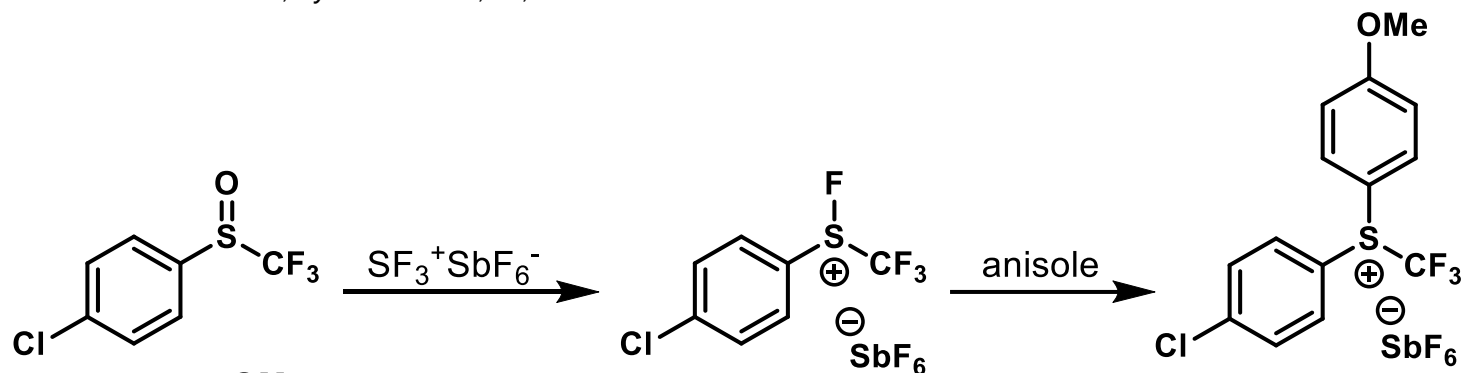
nifedipine
toxic

S. Shelyazhenko *et al.*, *Zh. Org. Chim.* **1992**, 28 (8), 1652-1659

Yagupolskii group: trifluoromethylation



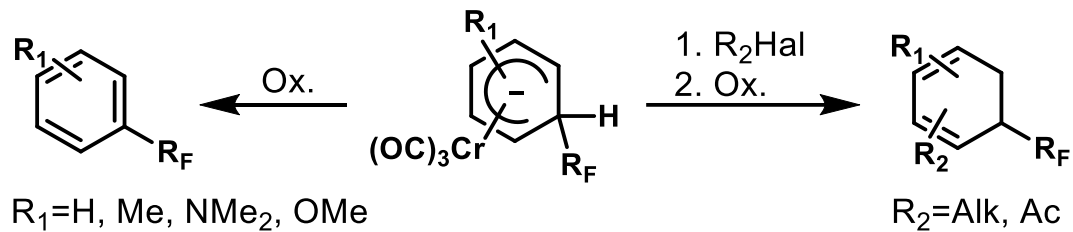
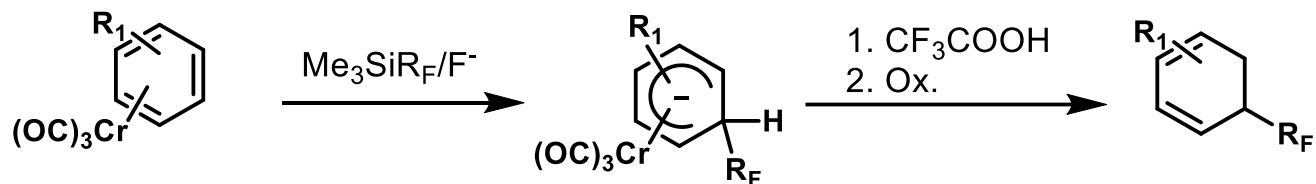
O. Kondratenko *et al.*, *Synthesis* **1980**, 11, 932–933



- first electrophilic trifluoromethylation agent

L. Yagupolskii *et al.*, *J. Org. Chem. USSR* **1984**, 20, 103–106

Recent results

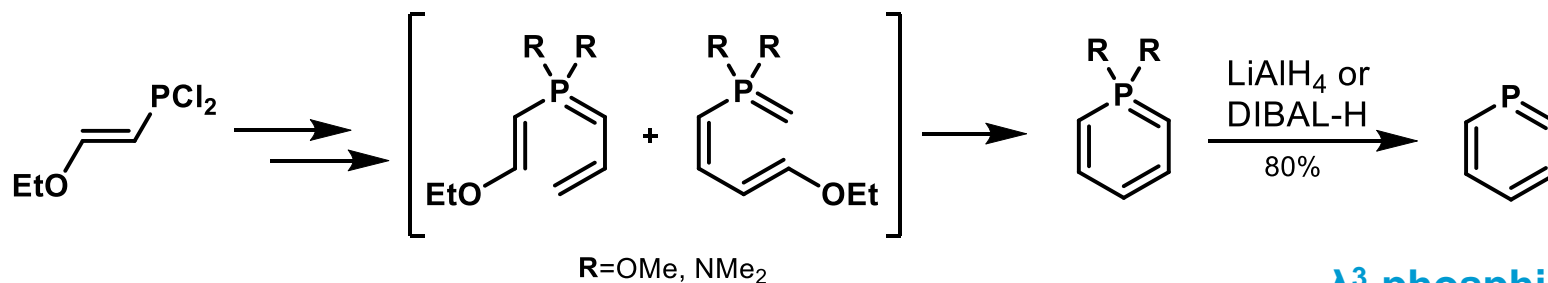


$R_1 = H, Me, NMe_2, OMe$

L. Yagupolskii *et al.*, *Chem. Commun.* **2017**, 53, 2146–2149

$R_2 = Alk, Ac$

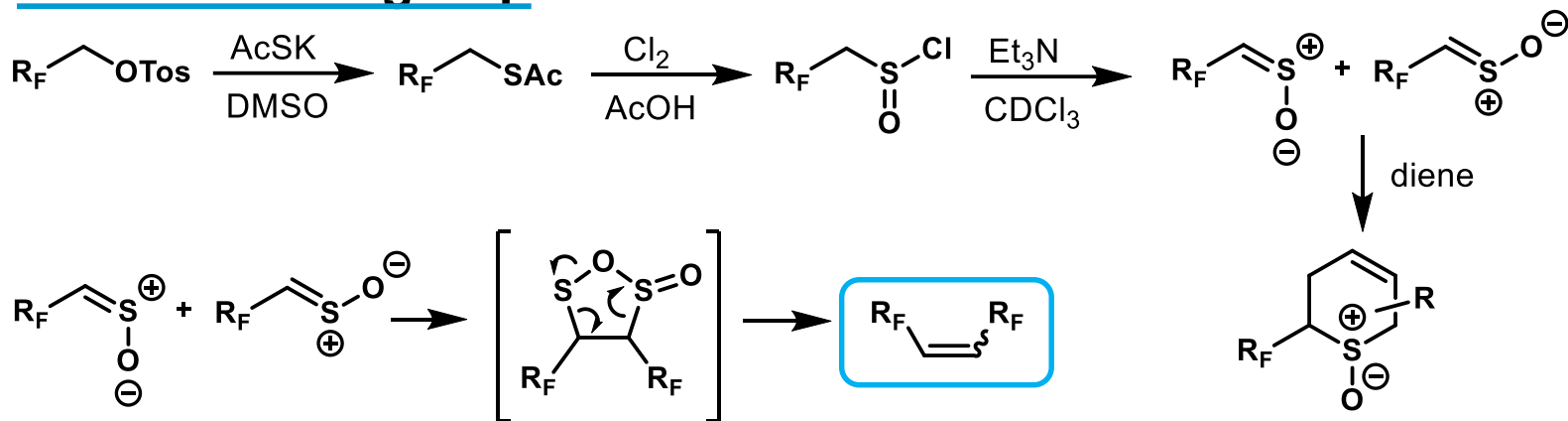
First nucleophilic C-H
perfluoroalkylation of aromatic
compounds *via*
(arene)chromotricarbonyl complexes



A. Savateev *et al.*, *Eur. J. Inorg. Chem.* **2016**, 5, 628–632

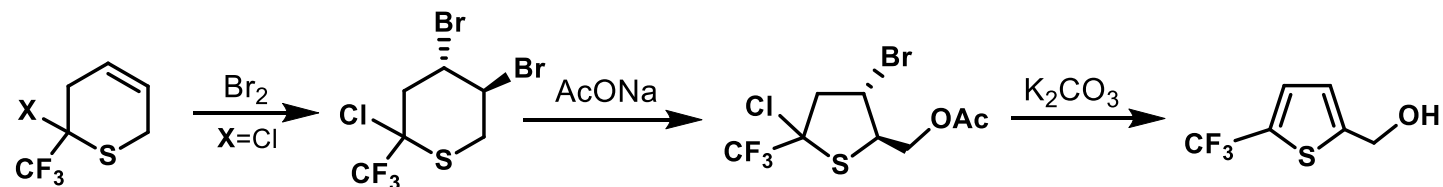
λ^3 -phosphinine (!)
(colorless liquid)

Shermolovich group

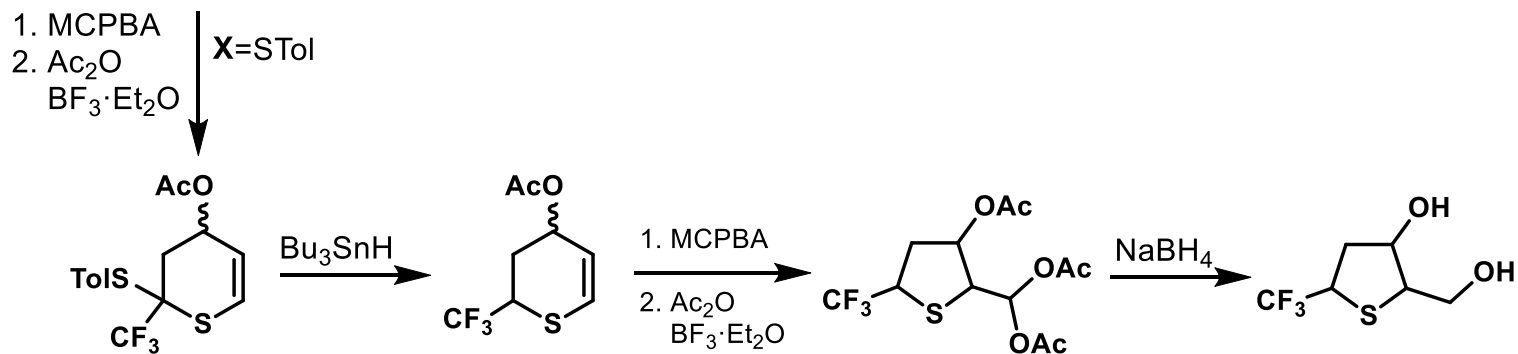


Yu. Shermolovich *et al.*, *J. Fluor. Chem.* **2016**, *185*, 119-126

Access to the symmetrical polyfluorinated alkenes

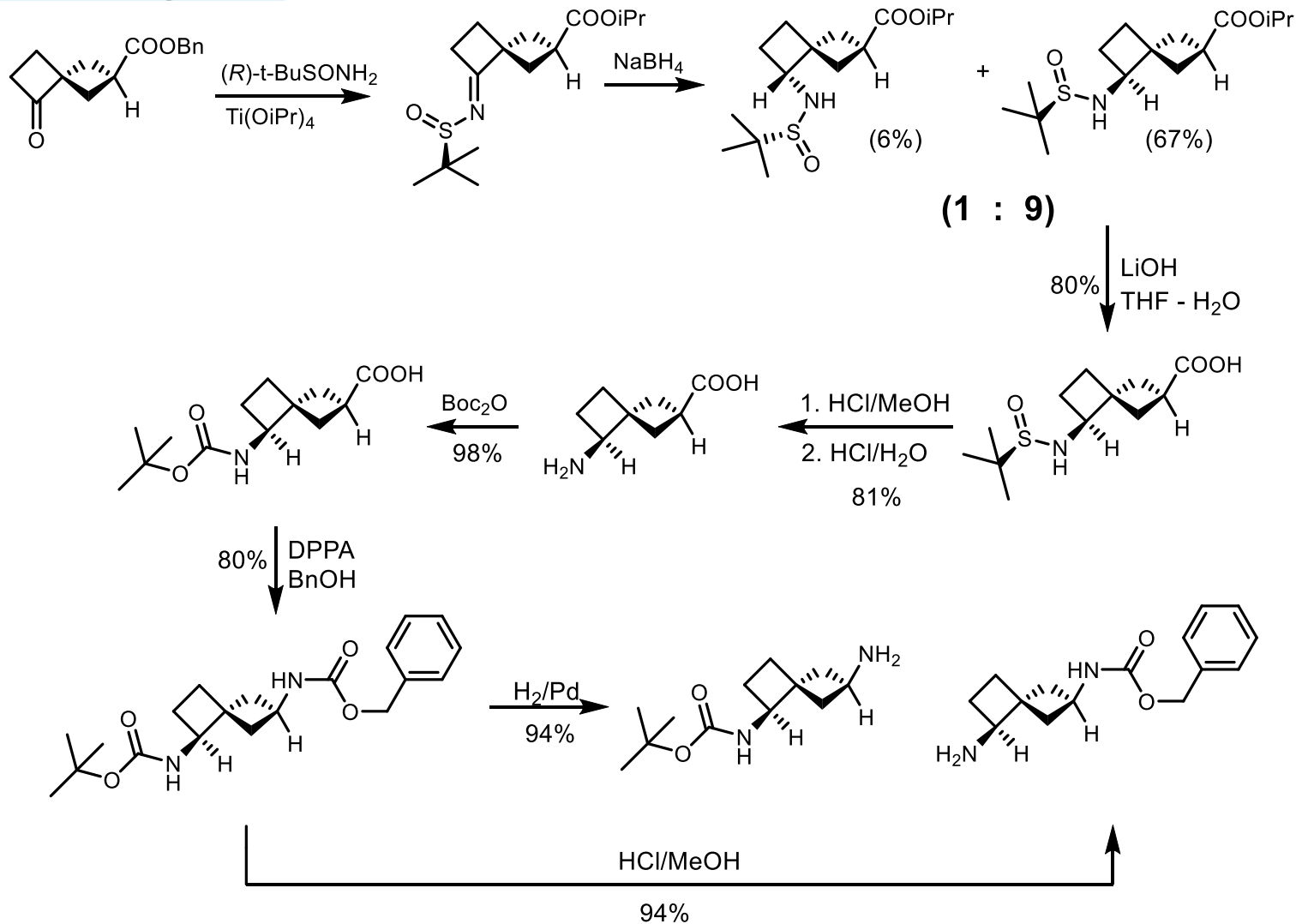


X=Cl, STol



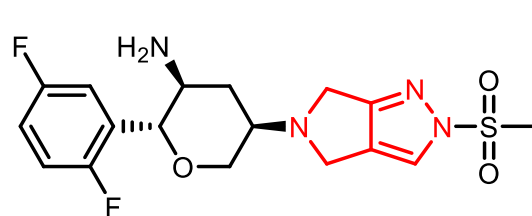
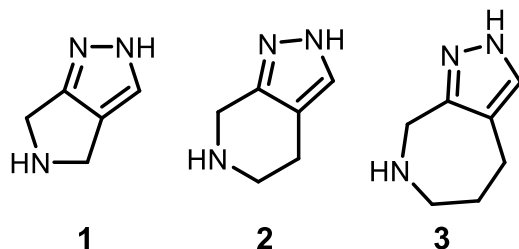
Yu. Shermolovich *et al.*, *J. Fluor. Chem.* **2016**, *181*, 17-21

Volochniuk group

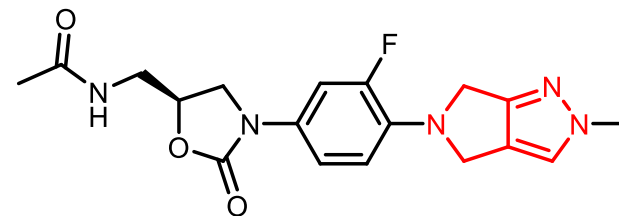


2,6-disubstituted spiro[3.3]heptanes

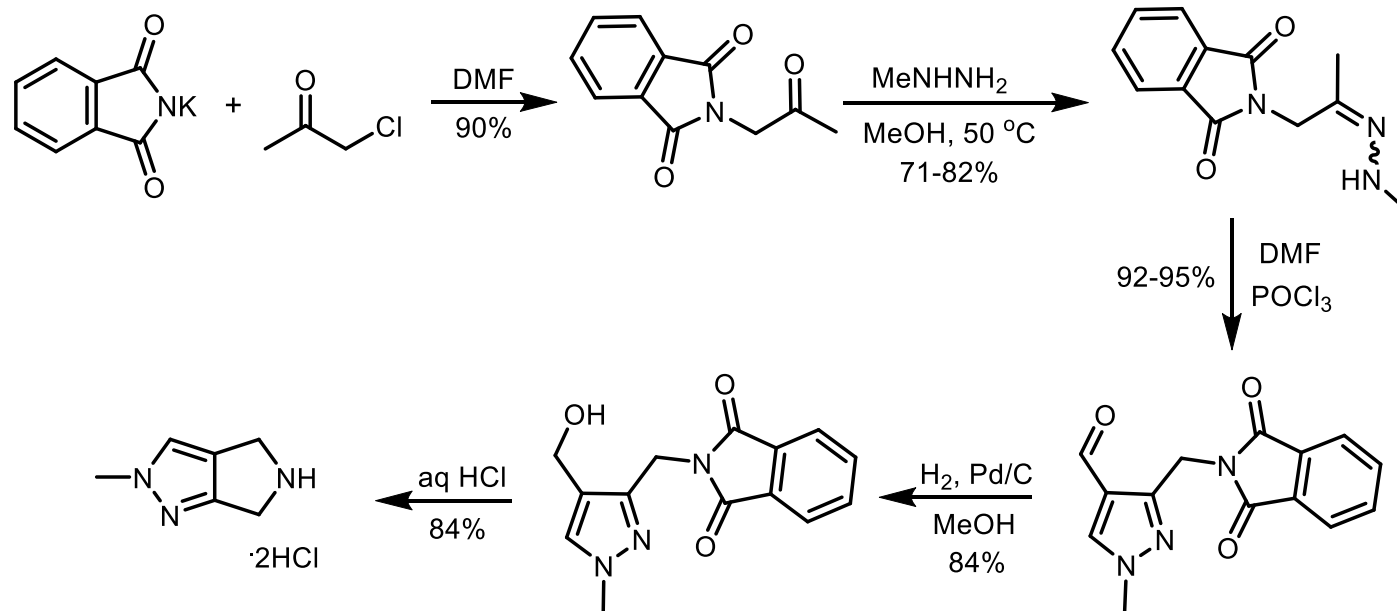
Volochniuk group



Omarigliptin
DPP-4 inhibitor

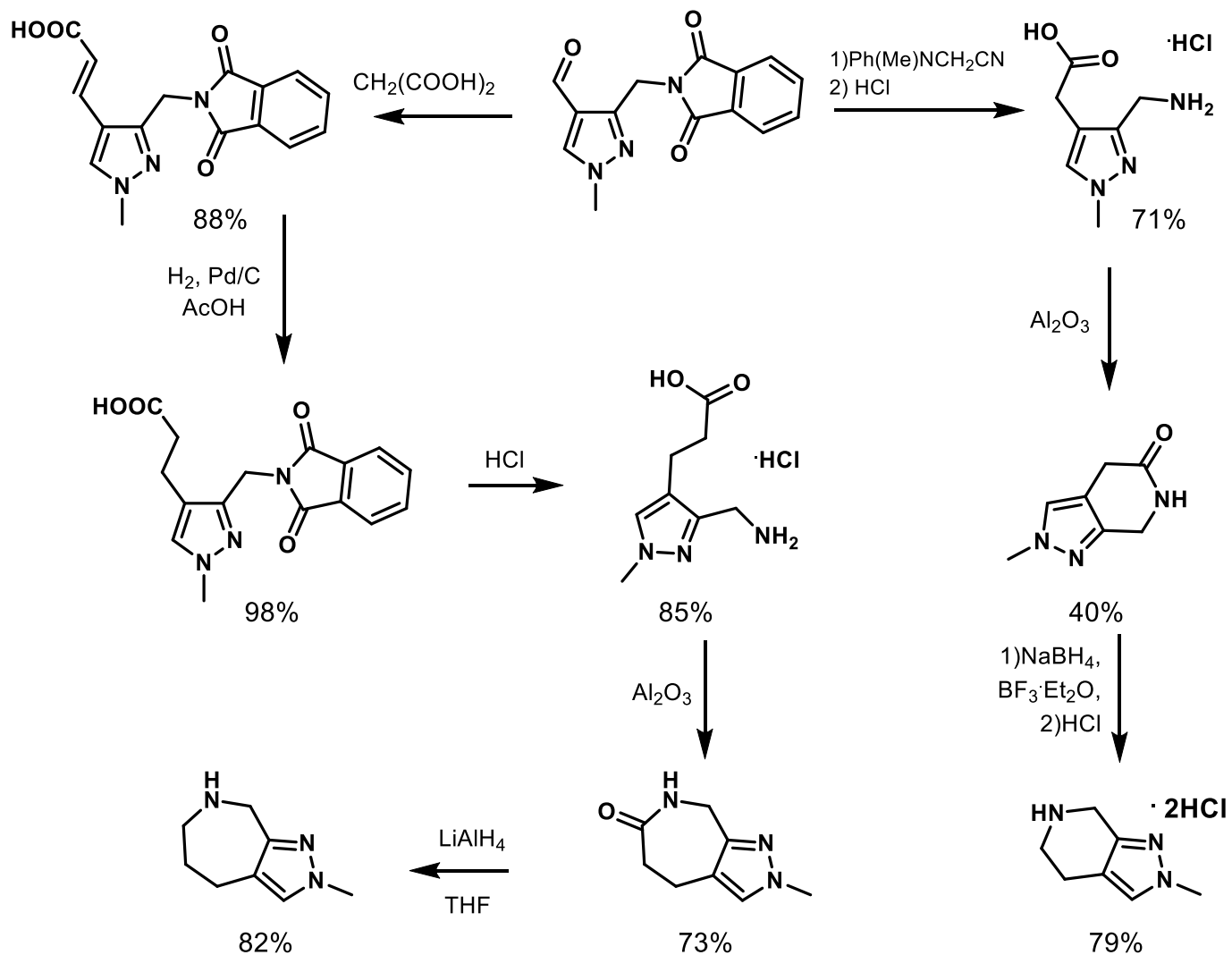


RWJ-416457
antibiotic

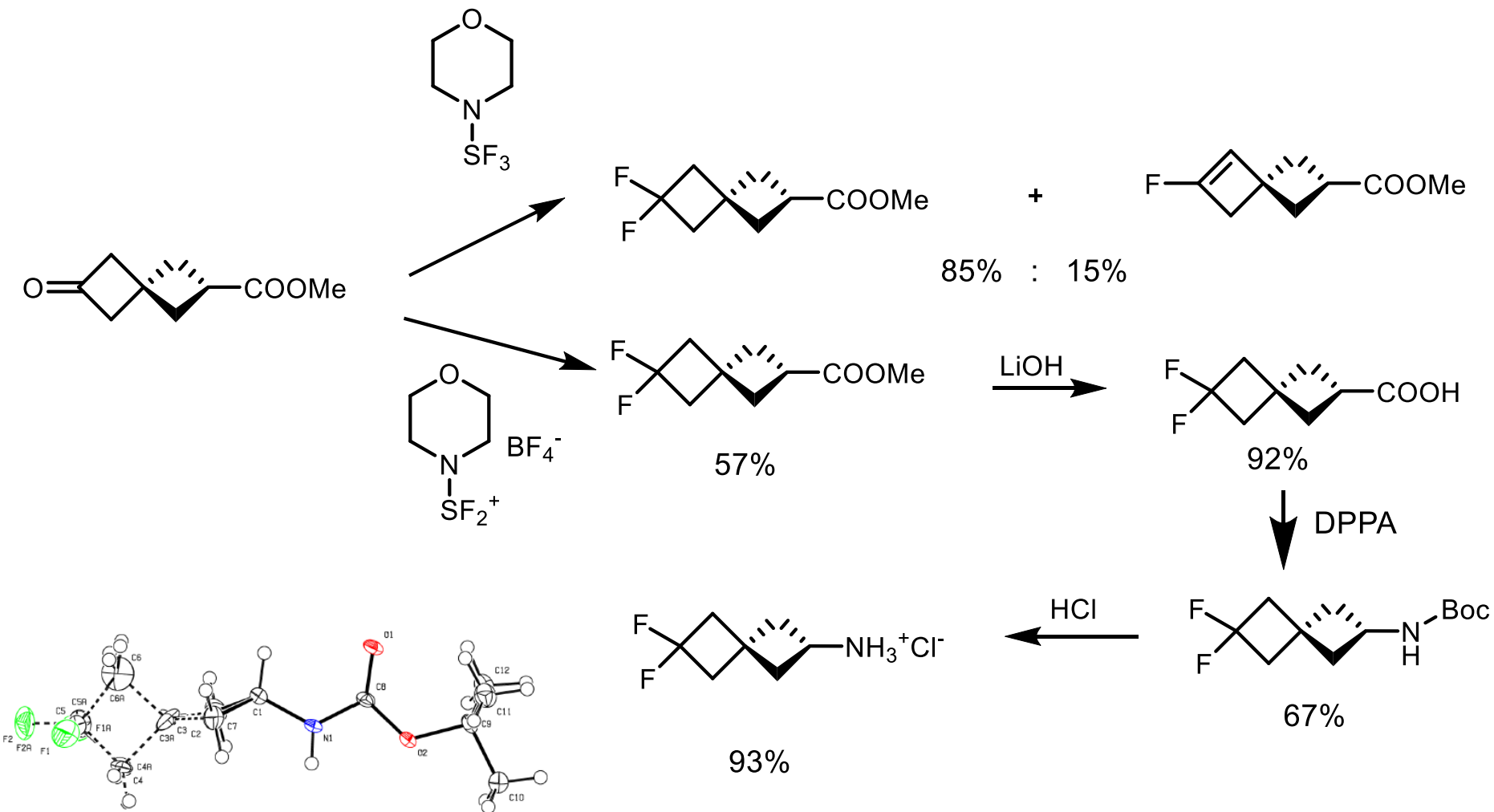


Pyrazoles fused with heteroaliphatic amines

Volochniuk group

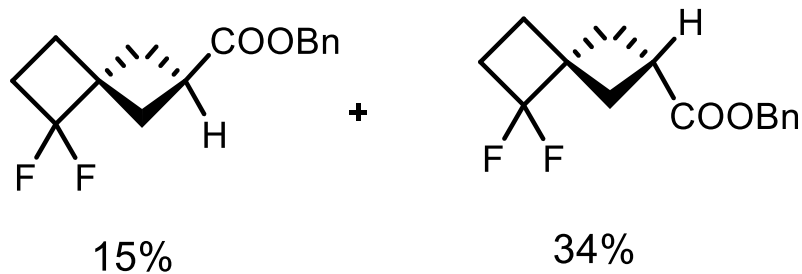
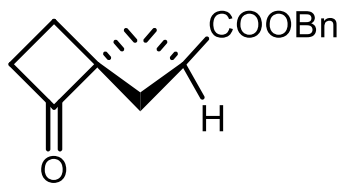


Volochniuk group



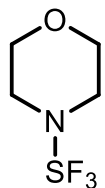
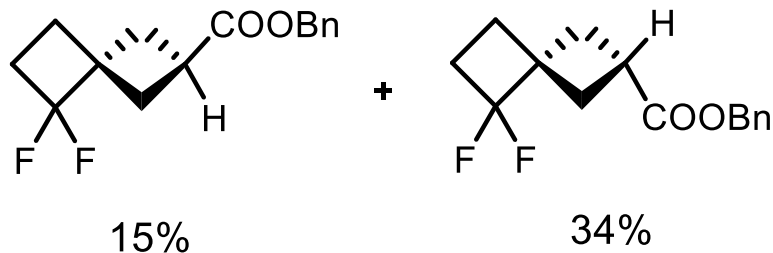
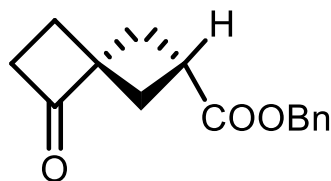
Model study of the spiro[3.3]heptane fluorination

Volochniuk group

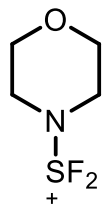


Deoxofluorination

1 : 2.2



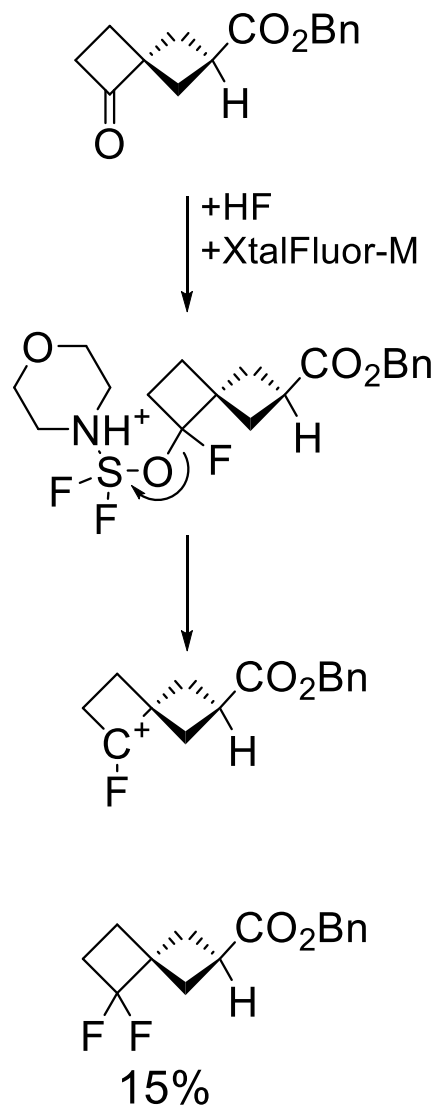
MOST



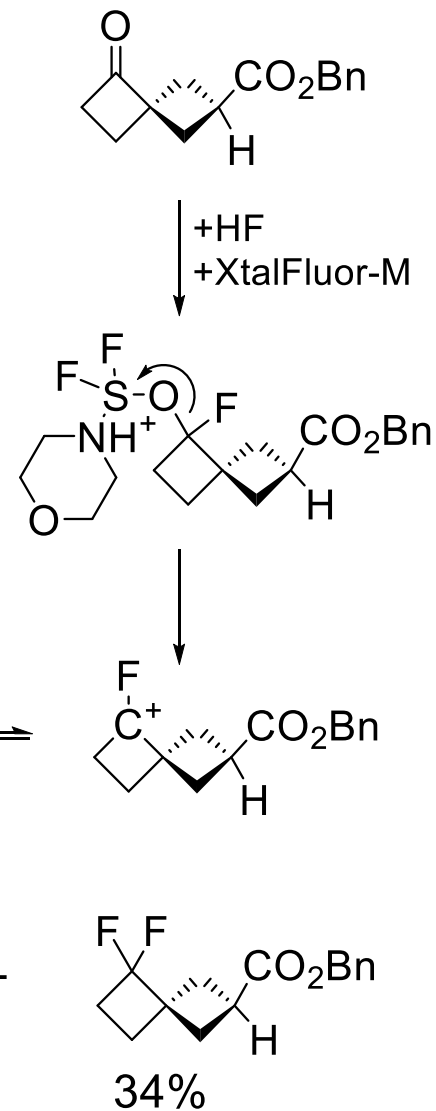
XtalFluor-M

Agent	Conversion
SF ₄	Unidentified mixture
SF ₄ B Et ₂ O	0 %
MOST	5%
MOST B DCM	3%
XtalFluor-M	55%

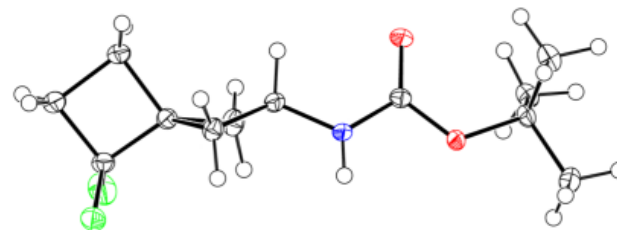
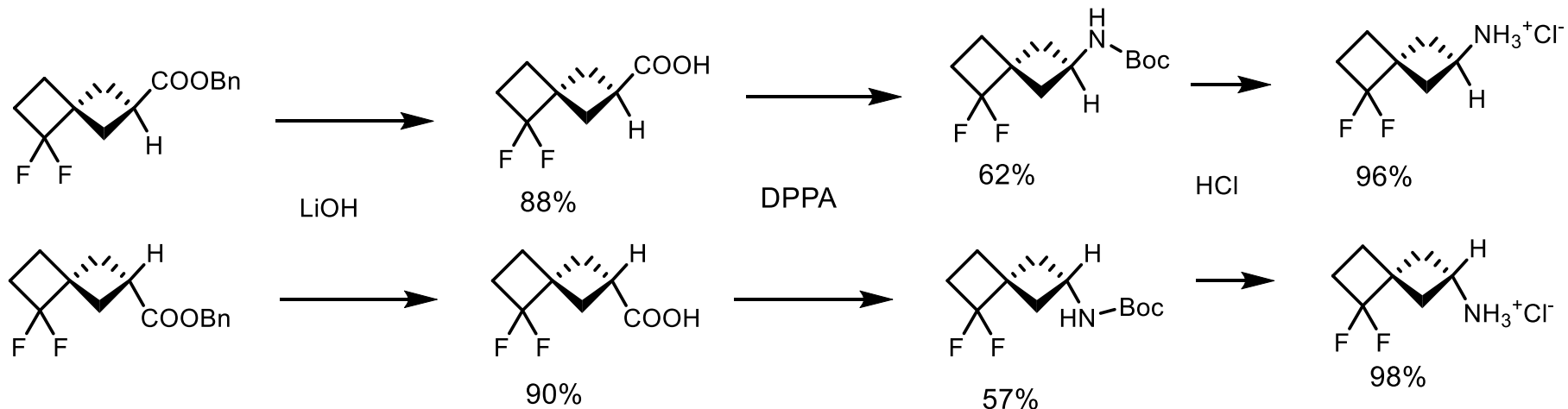
Volochniuk group



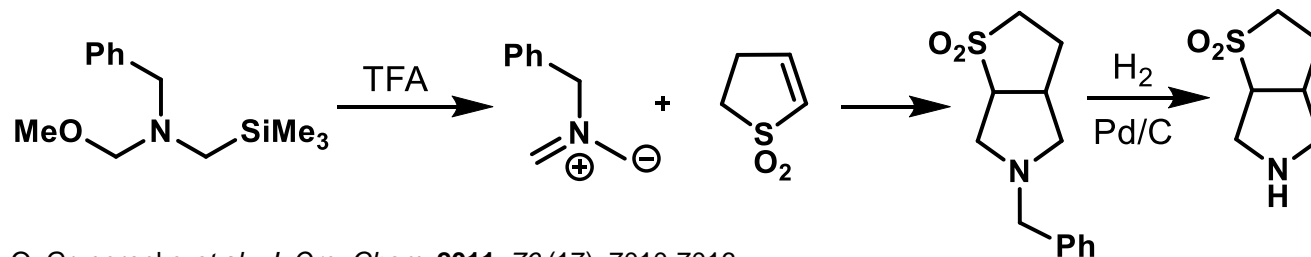
suggested mechanism



Komarov group

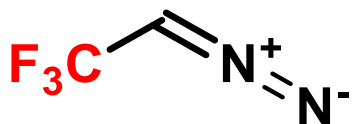


uncommon conformationally rigid amines



O. Grygorenko *et al.*, *J. Org. Chem.* **2011**, 76 (17), 7010-7016

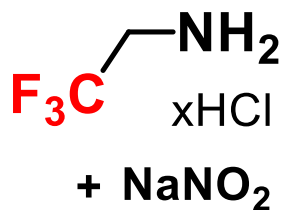
Mikhailiuk group



J. Gilman, *J. Am. Chem. Soc.* **1943**, 65, 1459
over 60 years was not applied for synthesis

Drying flask with MgSO_4

Reaction flask

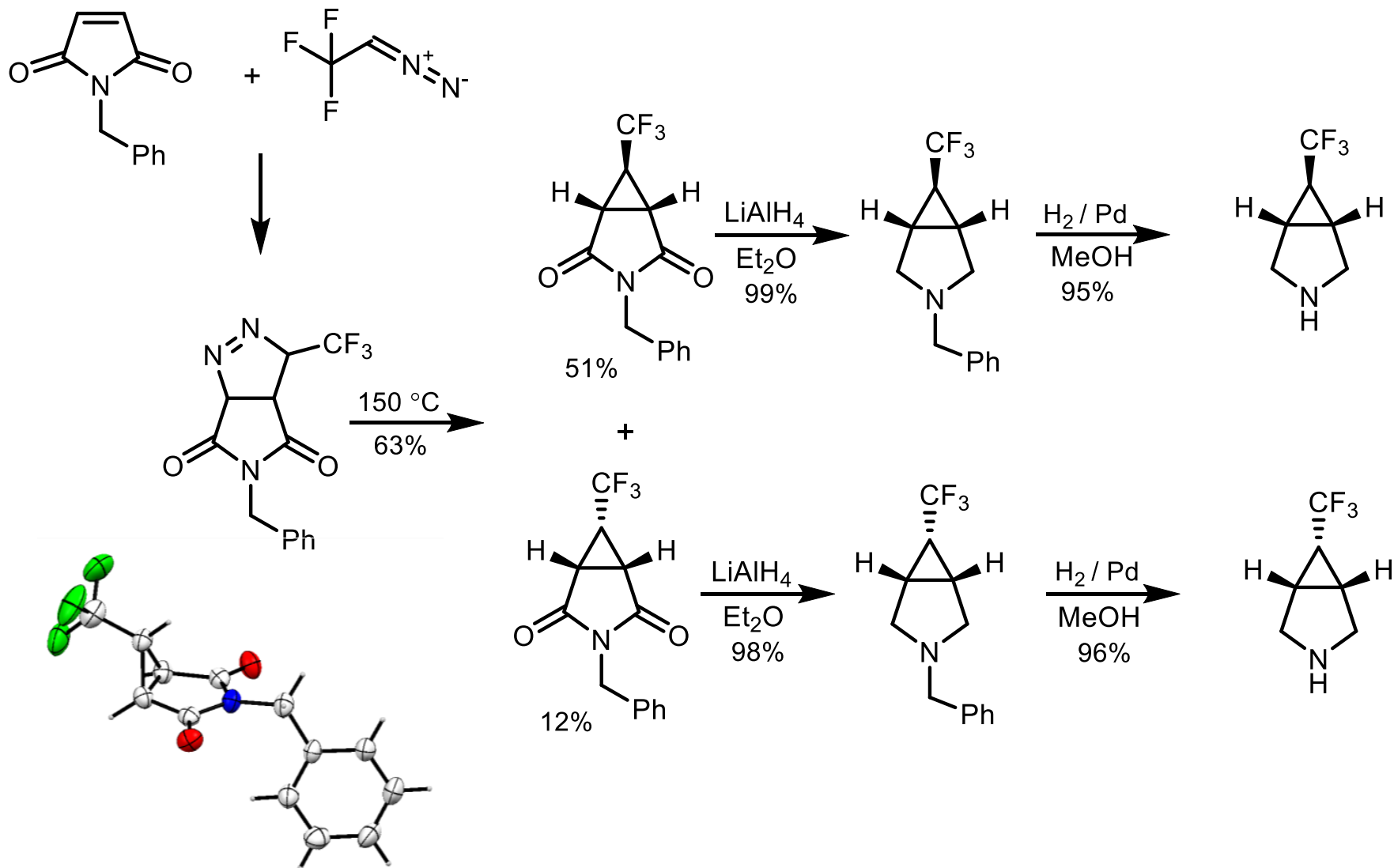


Ar



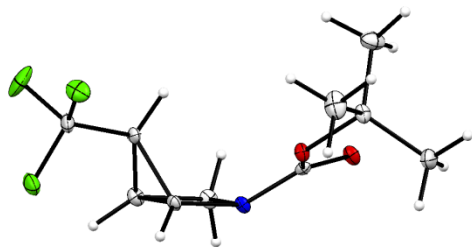
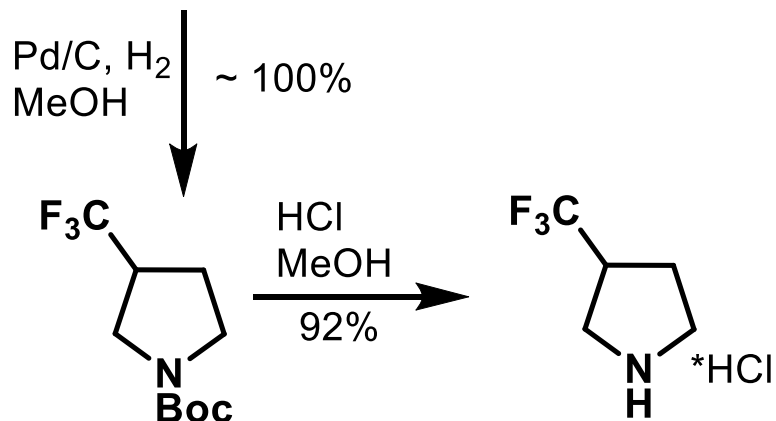
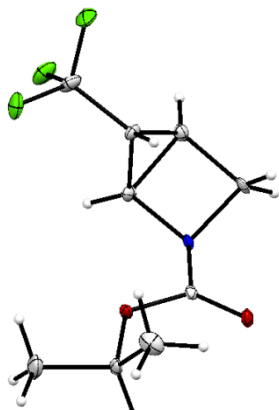
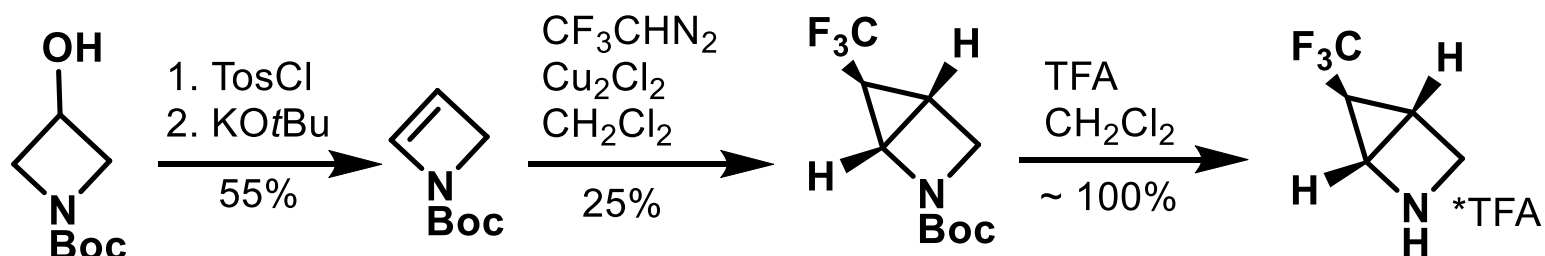
trap

Mikhailiuk group



O. Artamonov *et al.*, *Synthesis*, **2013**, 45, 225-230

Mikhailiuk group



the sum of bond angles at the N atom (341°)
indicates on its pyramidal surrounding

Acknowledgements

Kyiv Taras Shevchenko University

Dr. O. Grygorenko

Y. Sokolenko

Enamine, Ltd.

Dr. Dr. P. Mikhailiuk

**Herzlichen
Dank!**