



7-th All-Russian Conference “Fluorine Chemistry”

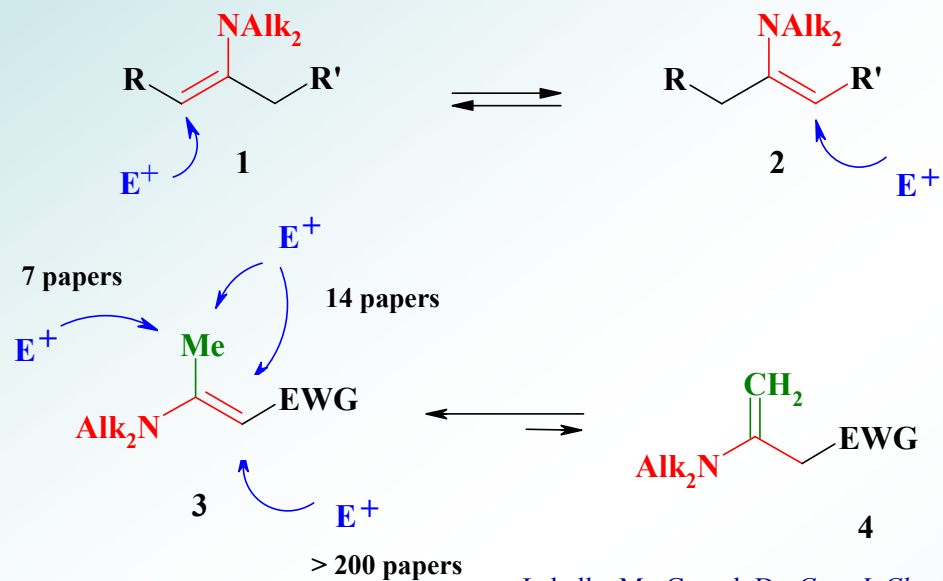
PUSH-PULL ENAMINES IN THE SYNTHESIS OF TRIFLUOROMETHYL CONTAINING ALIPHATIC, CARBO- AND HETEROCYCLIC COMPOUNDS

A.N.Kostyuk, D.M.Volochnyuk, D.A.Sibgatulin, Yu.V. Svyaschenko

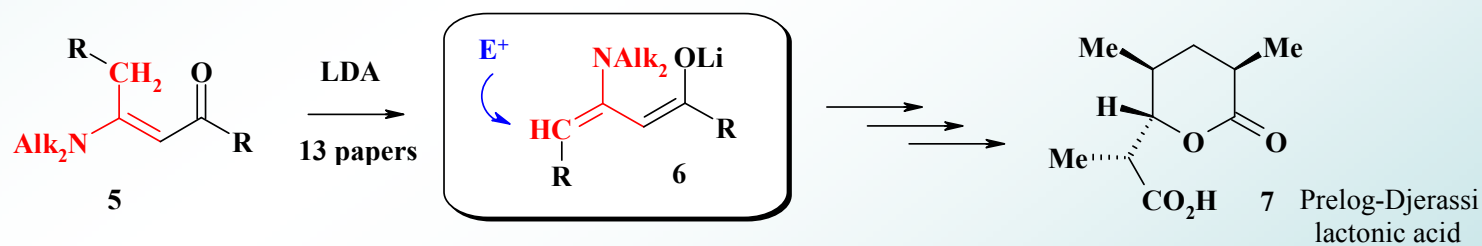
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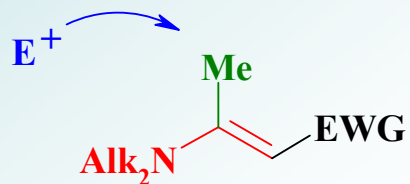


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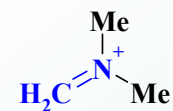
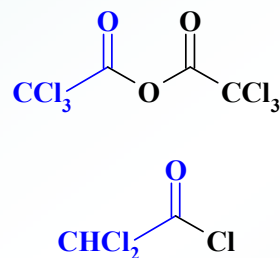
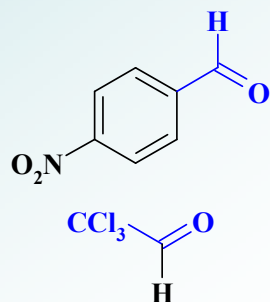
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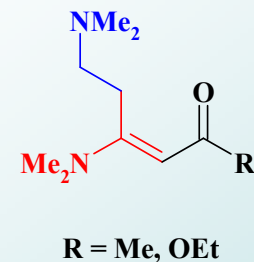
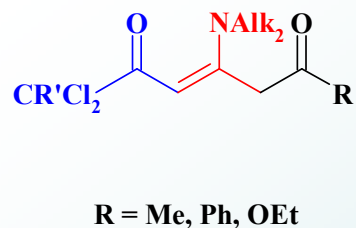
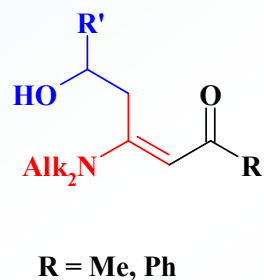
7 papers



Electrophile



Product



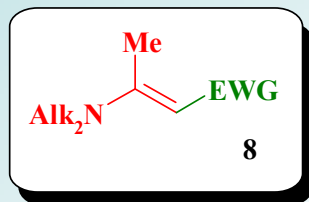
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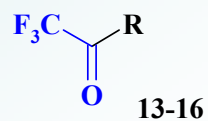
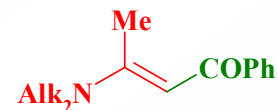
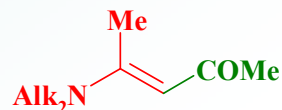
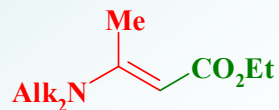
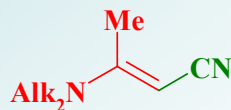
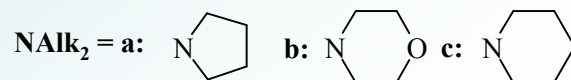
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Arch. Pharm. (Weinheim Ger.) **1984**, 317, 156
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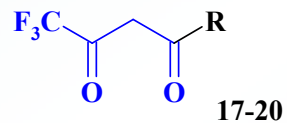
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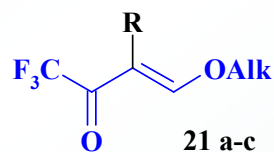
EWG = CN, CO₂Et, COMe, CPh



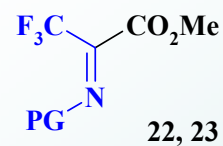
R = 13: CO₂Me, 14: Alk,
15: Ar, 16: Het.



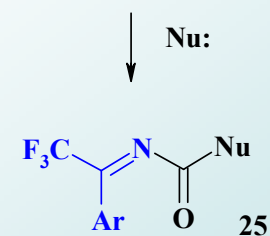
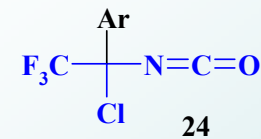
R = 17: CF₃, 18: Ar,
19: Me, 20: OEt



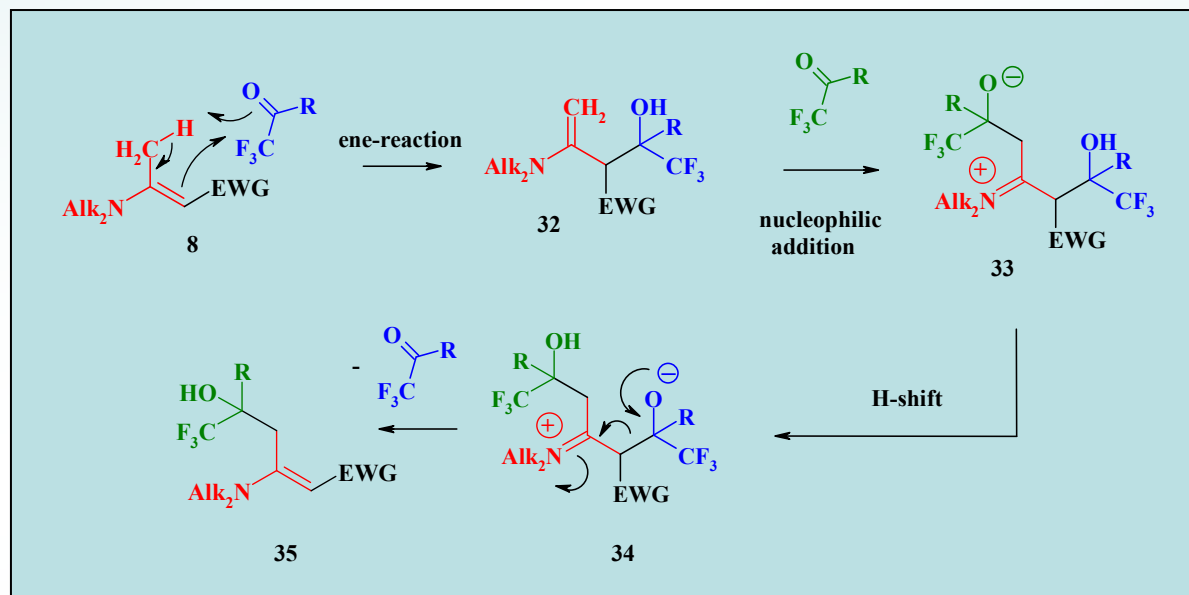
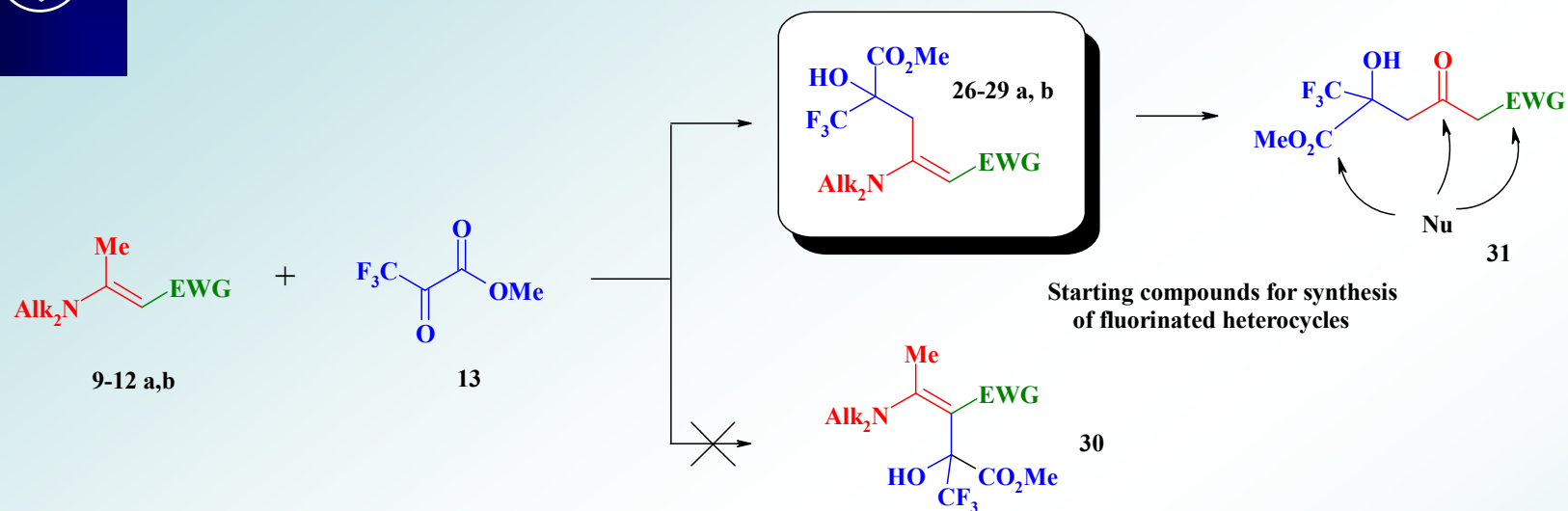
R = a: H, b: COCF₃,
c: CO₂Et



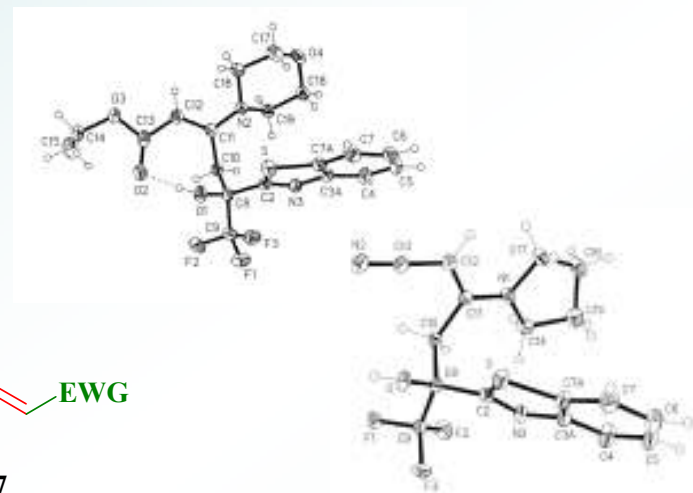
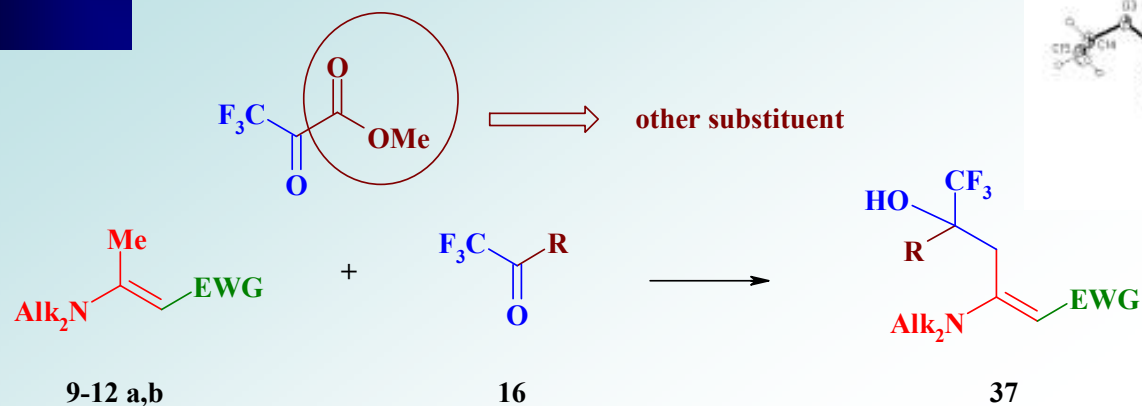
PG = 22: CO₂Et
23: PMP



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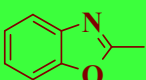
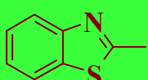
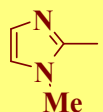
react

don't react

R =

σ_I =

σ_R^0 =

R =			CO ₂ Me		CH ₂ COCF ₃	CH ₂ COPh	CH ₂ CO ₂ Et	Me	Ph
σ_I =	0.41	0.37	0.30	0.26	0.22	0.12	0.12	-0.01	0.12
σ_R^0 =	0.14	0.16	0.11	-0.01	-0.09	-0.14	-0.14	-0.16	-0.17

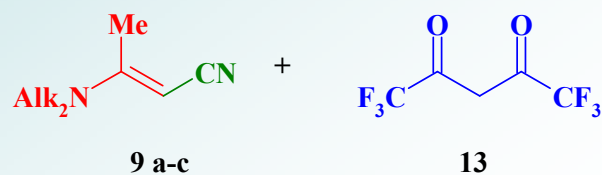
doesn't enter in the reaction with enamines having EWG = CN
 reacts with enamines having EWG = CO₂Et, COPh
 reacts with enamines having EWG = COMe (!) selectively

depend on structure of enamine, see next slides

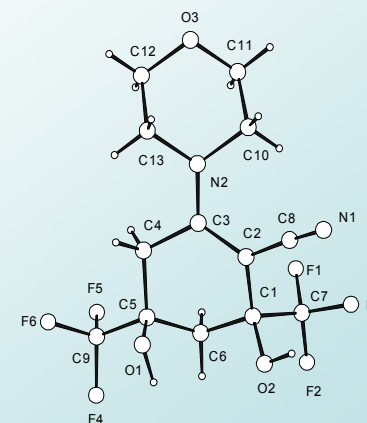
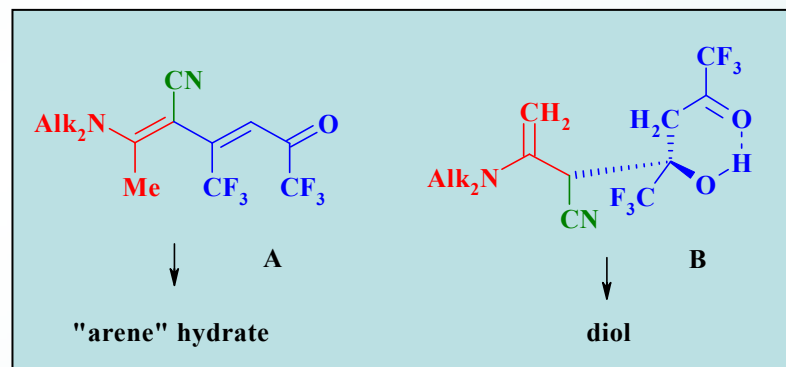
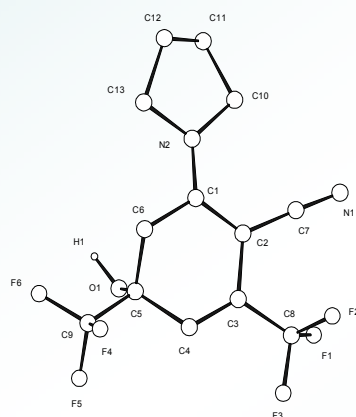
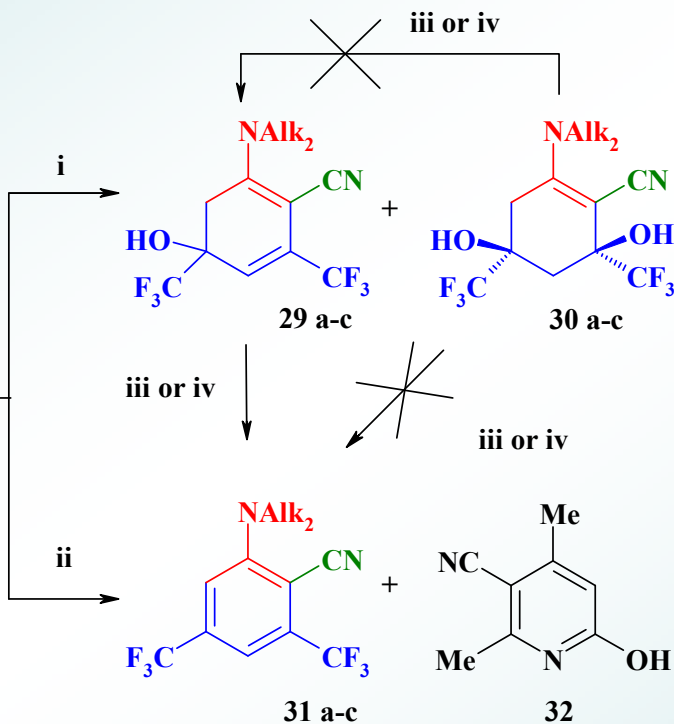
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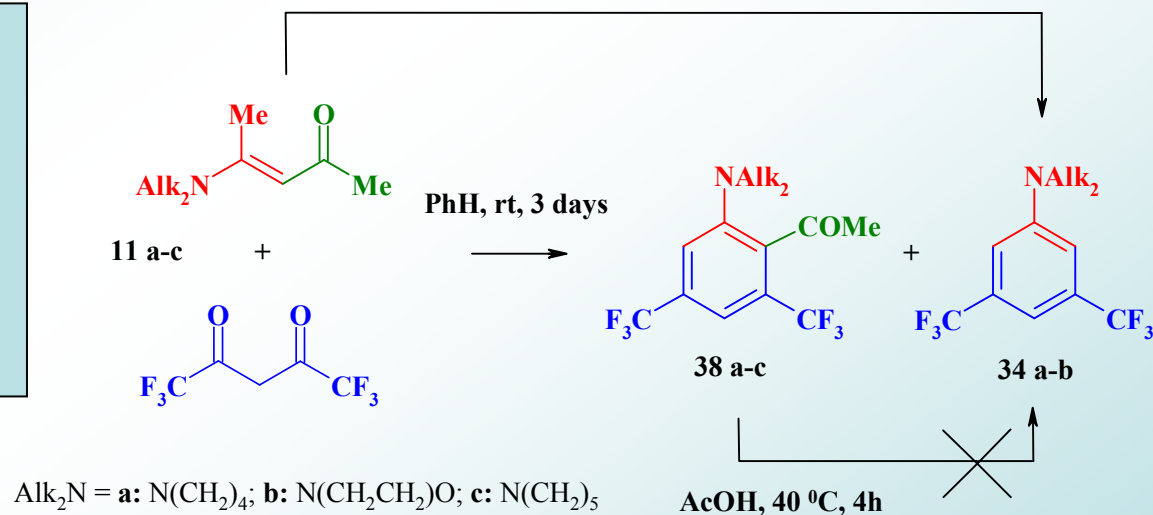
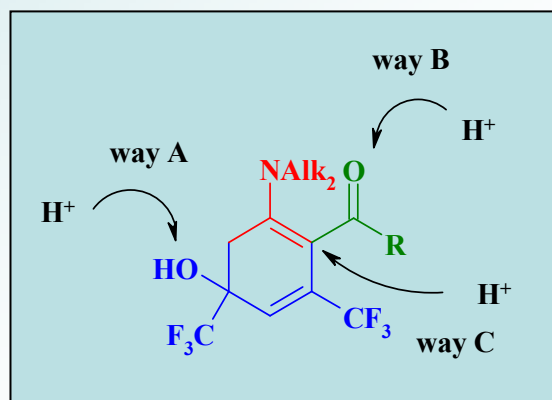
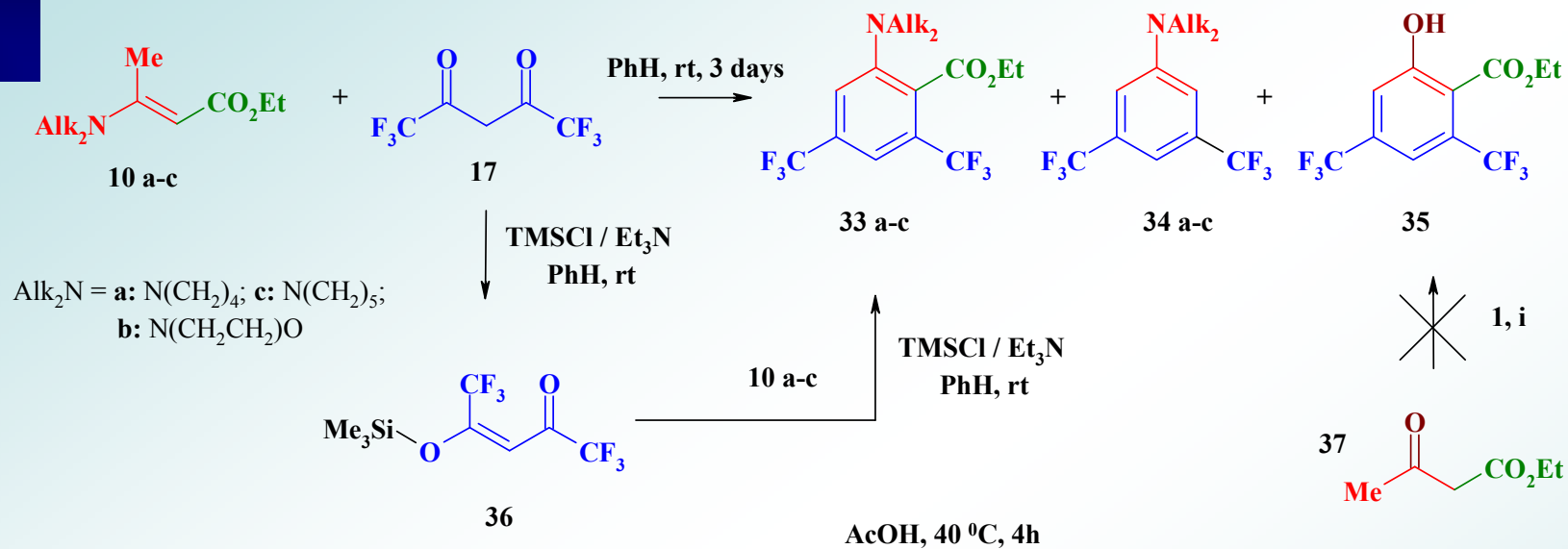
iii or iv = PhMe, reflux, PTSA
or acetone, 10 days, rt



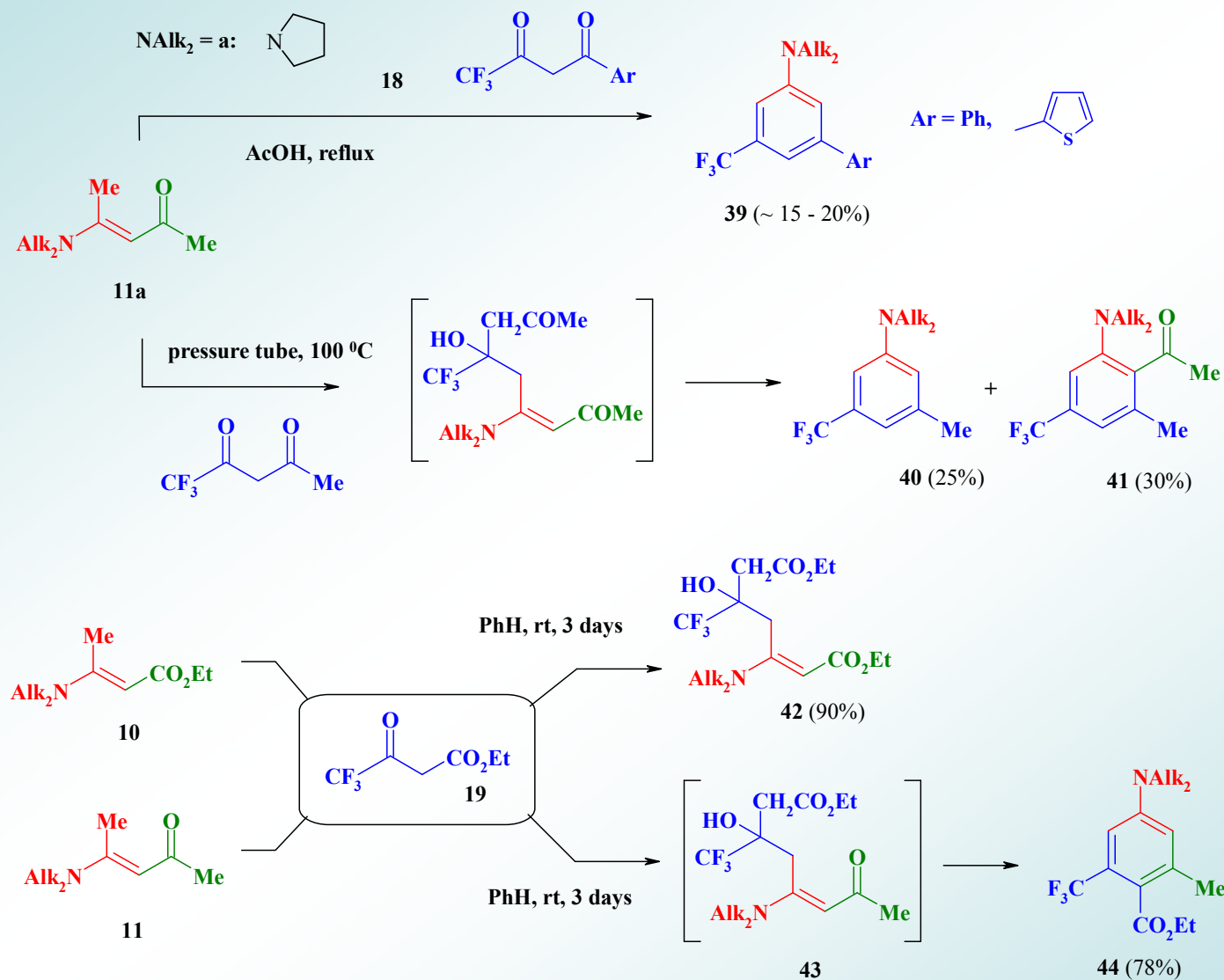
Alk₂N = **a**: N(CH₂)₄; **c**: N(CH₂)₅;
b: N(CH₂CH₂)O



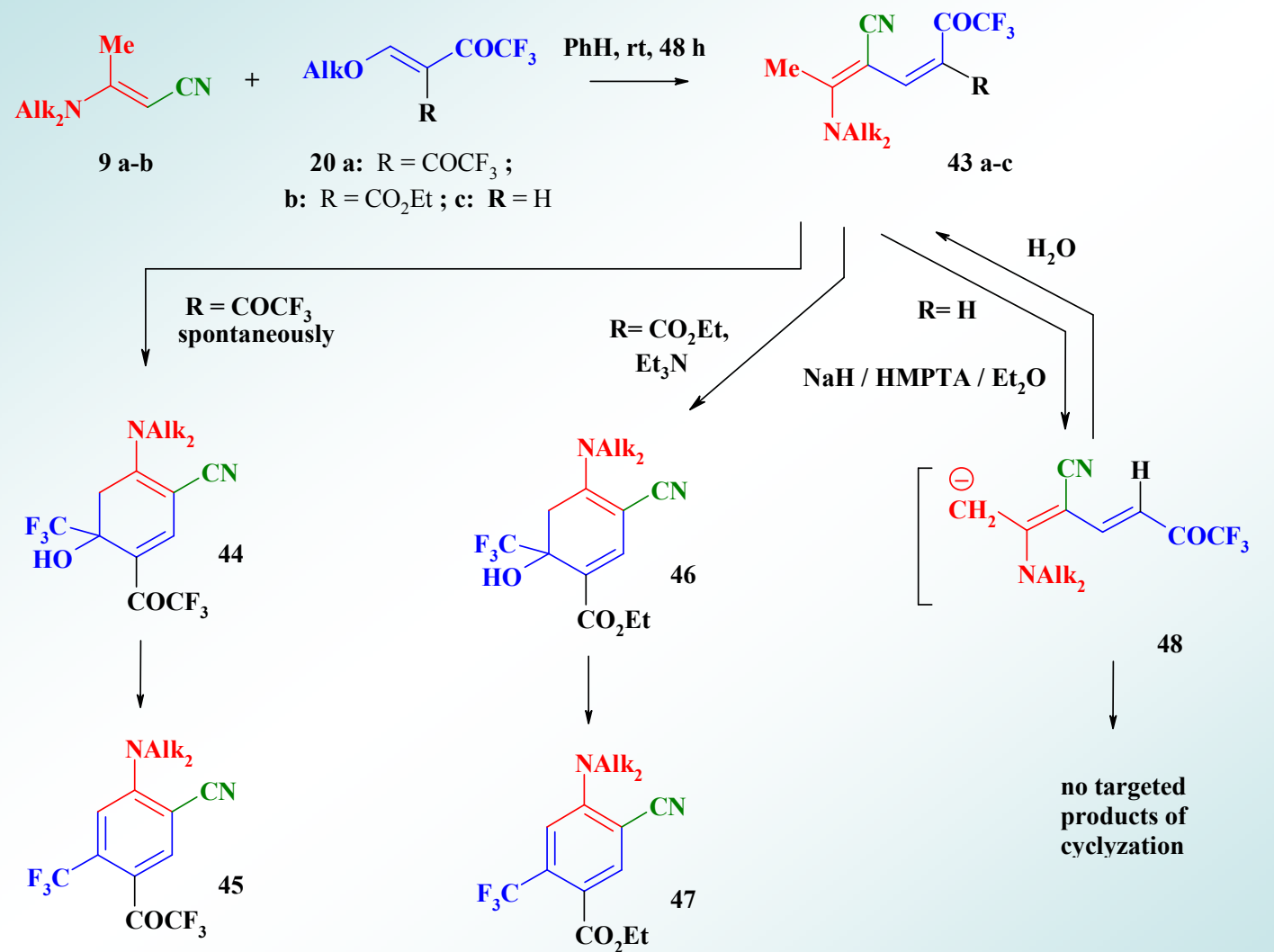
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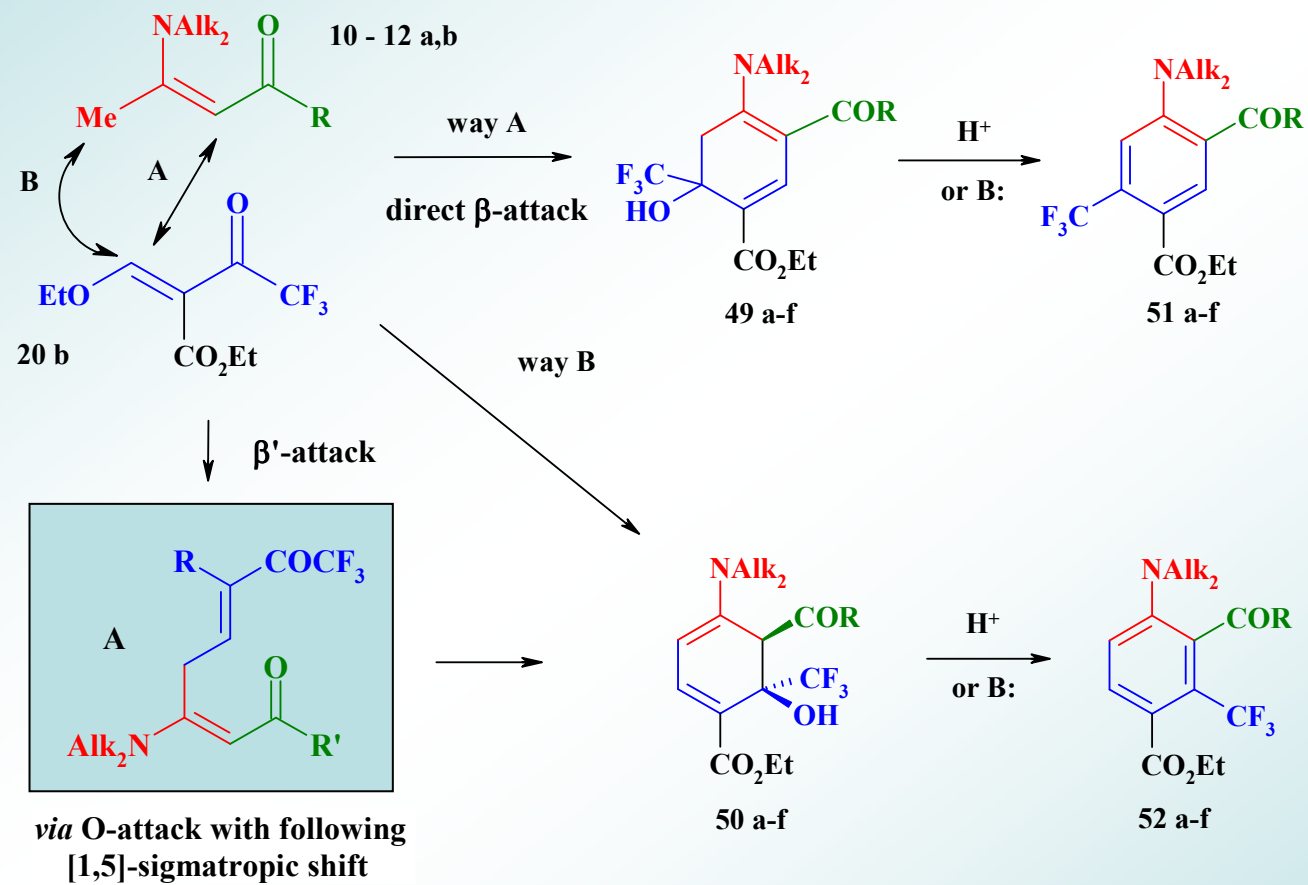


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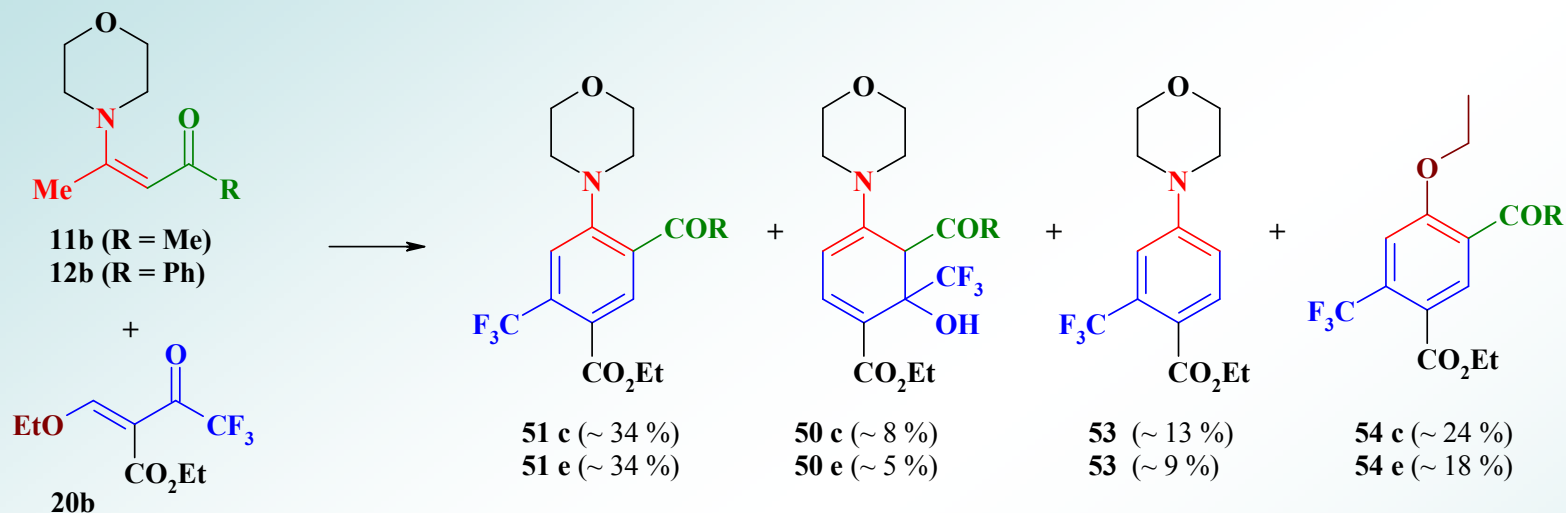


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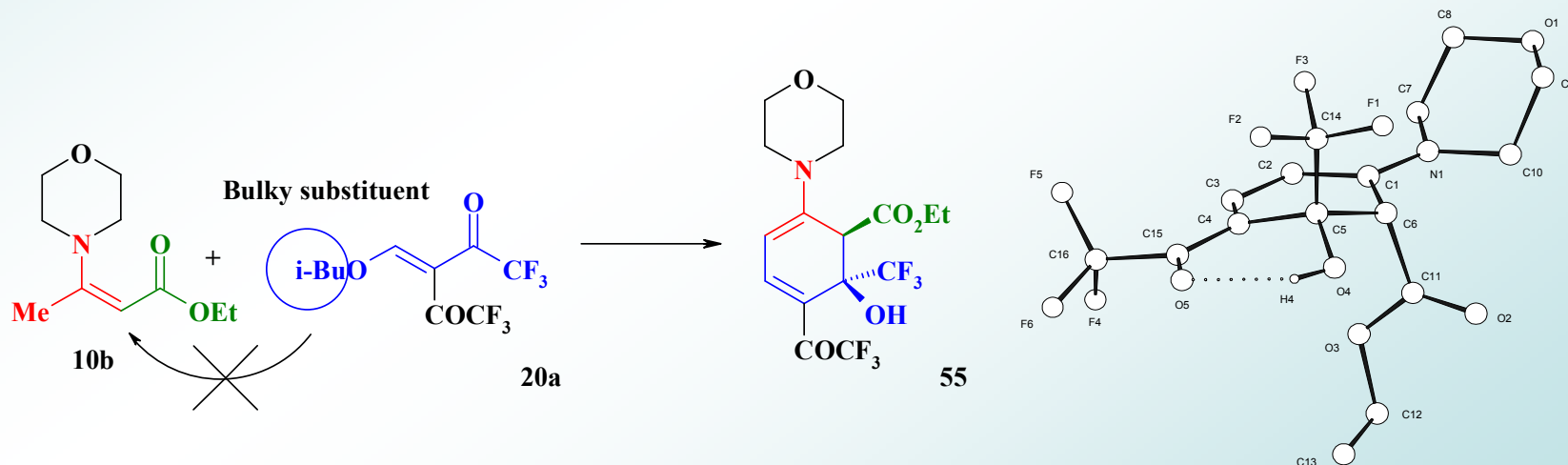




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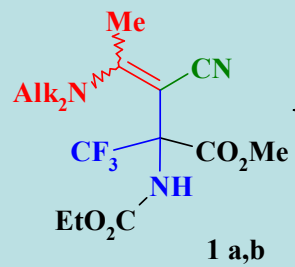
Data of ^{19}F NMR spectra and GC/MS of reaction mixture



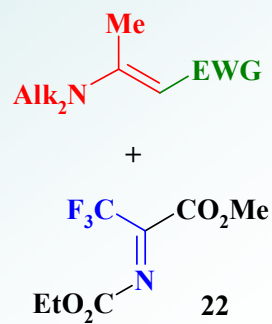
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EWG = CN

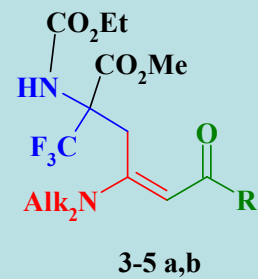


1 a,b

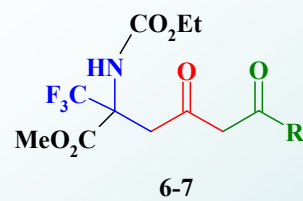


22

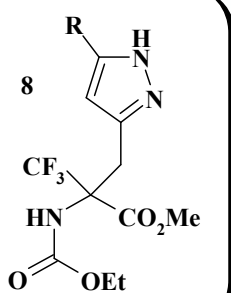
EWG = COR,
R = OEt, Me, Ph



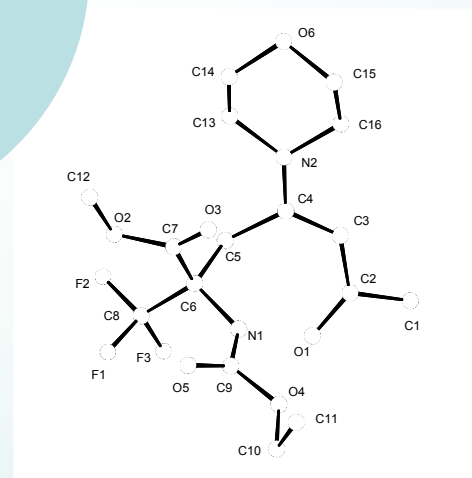
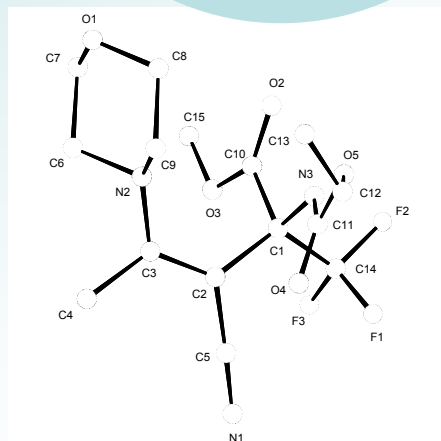
3-5 a,b



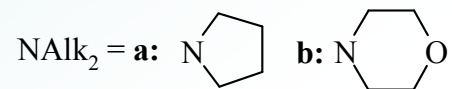
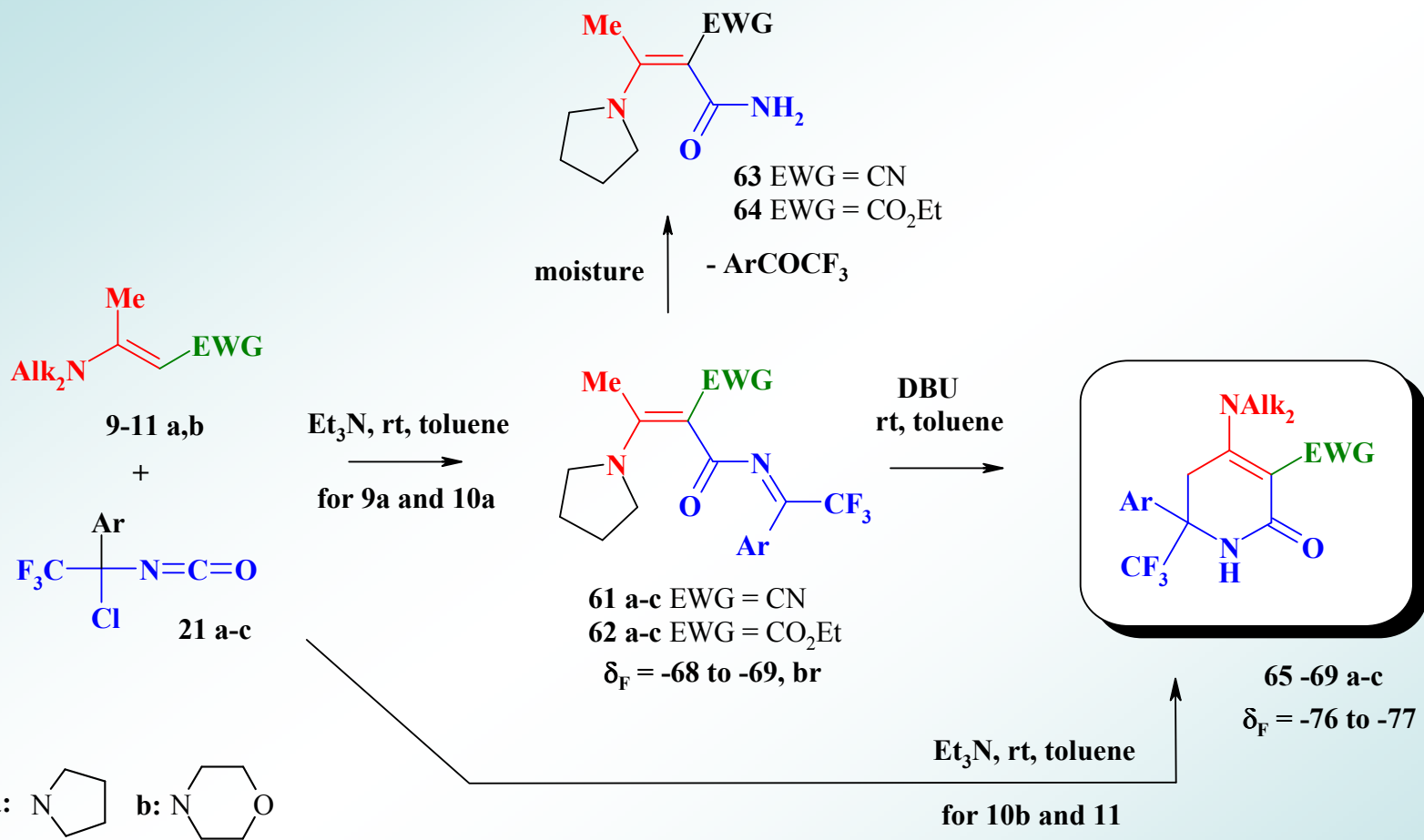
6-7



8



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EWG = 9: CN; 10: CO₂Et; 11: COMe

Ar = a: Ph, b: Tol, c: Anz

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α -Methyl “push-pull” enamines as mono C(β')-nucleophiles

Sequence of stages	Key intermediates	Examples of E-philes
Lithiation – E-philic functionalization of vinylogous enolate		$RR'C=O$
E-philic O-attack – deprotonation – [1,5]-sigmatropic shift		Ph_2PCl , Me_3SiCl , $TCAA$, $CCl_2=C=O$
Ene-reaction – nucleophilic C(β') addition – C(β)-C(E-ophile) cleavage		$CF_3-C(=O)CO_2Me$ $CF_3-C(=O)CO_2Me$ $Ph-C(=O)H$

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α -Methyl “push-pull” enamines as 1,3-CCC-binucleophiles

Sequence of stages	Examples of key intermediates	Examples of products
C(β') functionalization <i>via</i> [1.5]-shift – cyclization with participation of C(β)-position		
C(β) functionalization <i>via</i> ene-reaction – cyclization with participation of terminal enamine		
C(β) functionalization – cyclization with participation of CH-acidic Me-group		

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Acknowledgement

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- **NMR study**

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- Pirozhenko V. V. (*IOCh NAS of Ukraine*)
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- **IR study**

- Alekseev S. A. (*Kiev National University*)

- **MS study**

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- **X-ray study**

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