ESSOC-2018. The 22nd International Electronic Conference on Synthetic Organic Chemistry.
15/11/2018 - 15/12/2018

Lewis acid-mediated mono- and bis-addition of C-nucleophiles to 1,3-dioxolan-4-ones.

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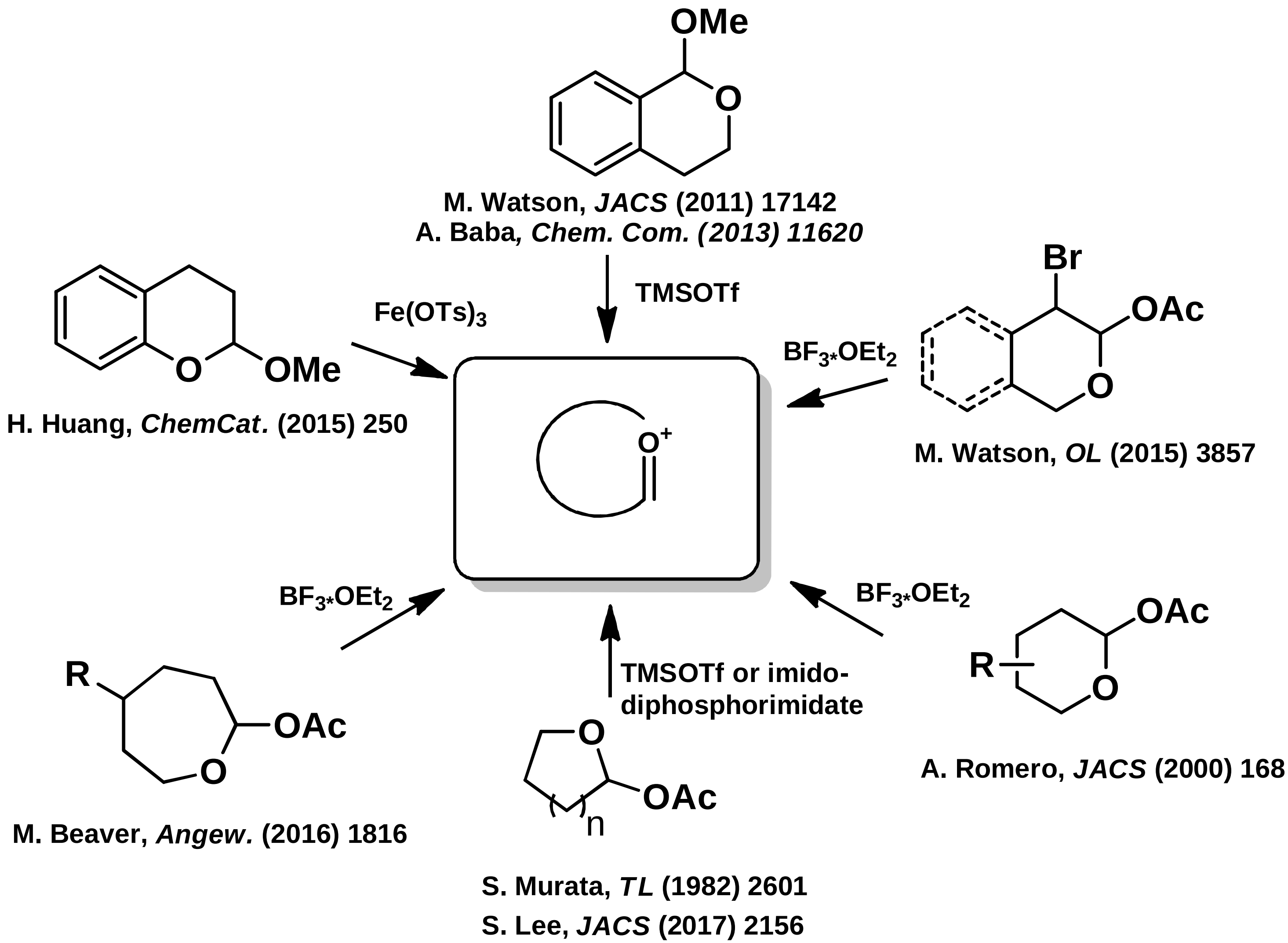
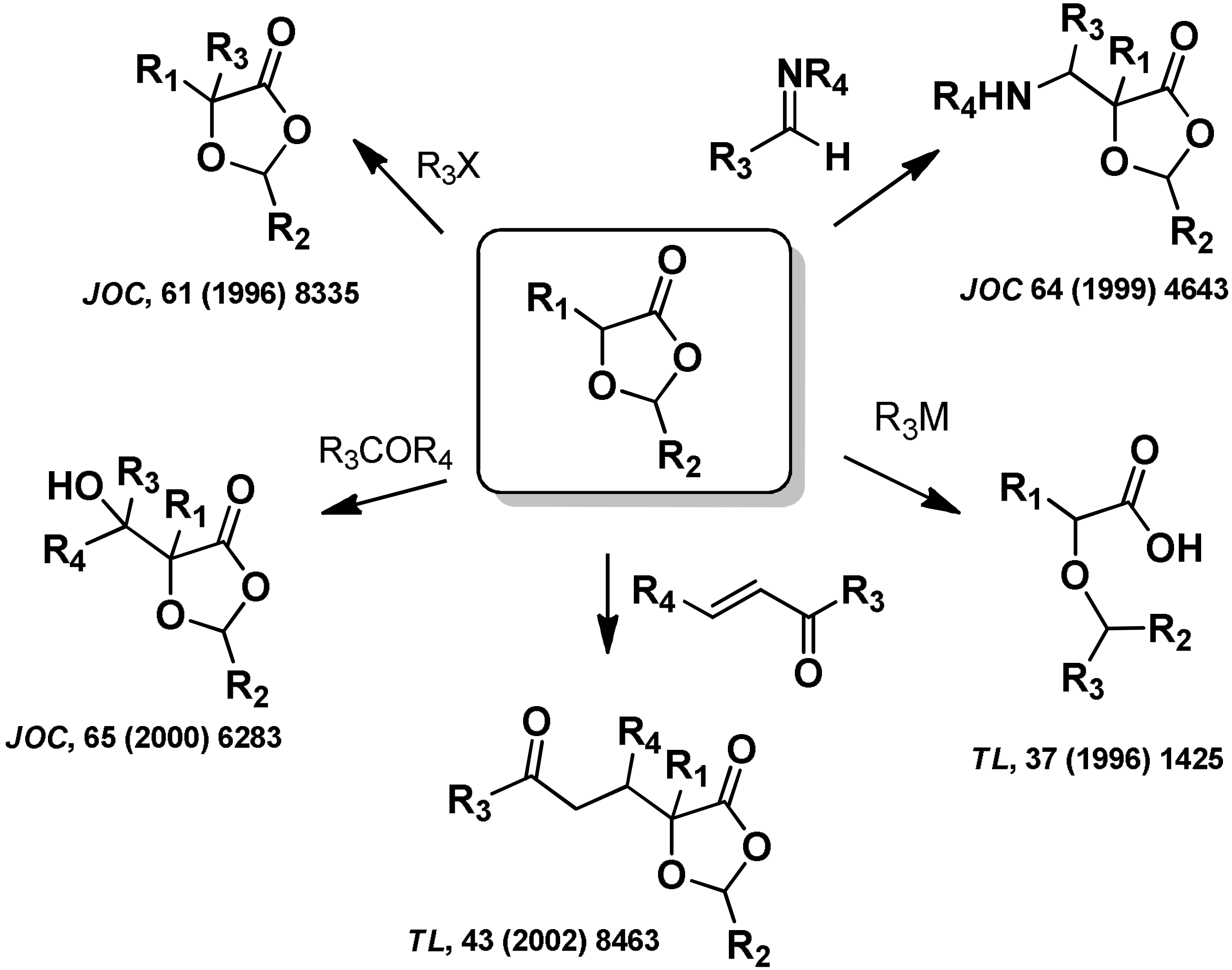
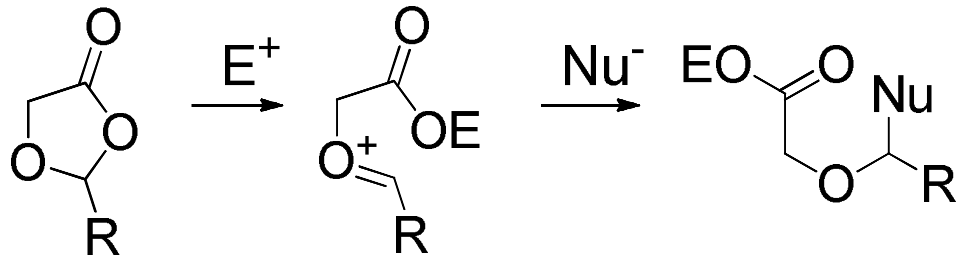
Generation of oxocarbenium cations from acetals and related comounds

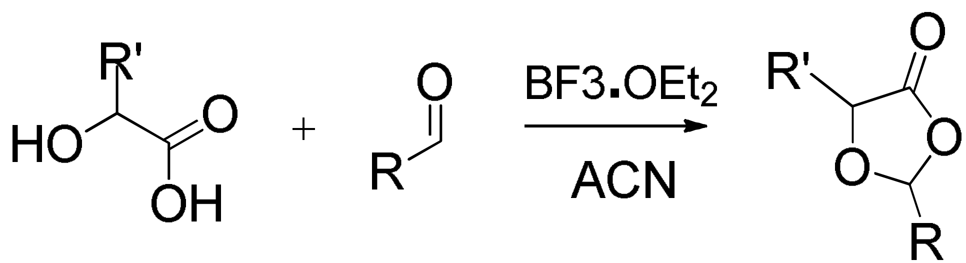


Synthetic application of 1,3-dioxolan-4-ones



Nucleophilic addition to an oxocarbenium cation generated from 1,3-dioxolan-4-ones



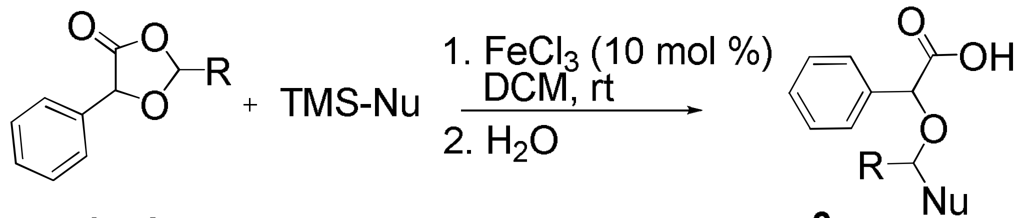


48-73%

R=Ph, t-Bu, CCl_3;

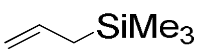
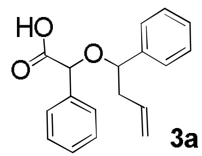
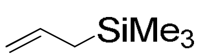
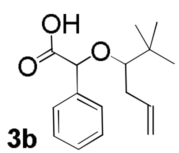
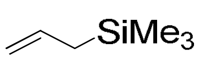
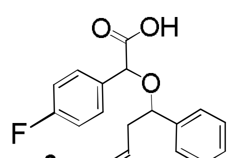
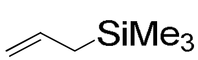
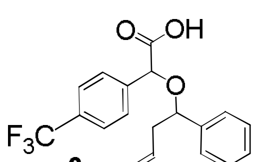
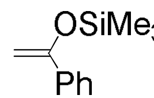
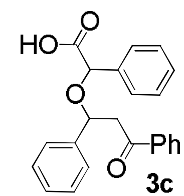
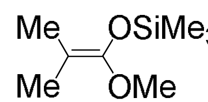
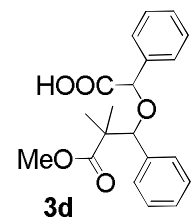
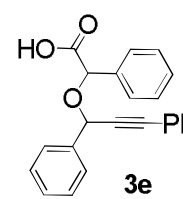
R'=Ph, *p*-FC_6H_4; *p*-$CF_3C_6H_4$; CH_2COOH

Reaction of 1,3-dioxolan-4-ones with silicon containing nucleophiles

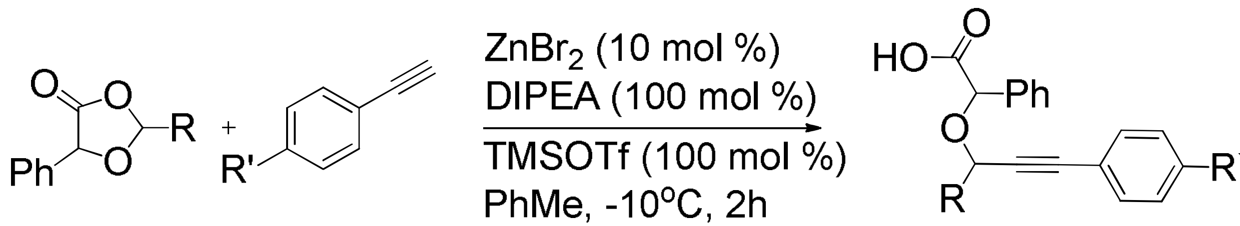


1a,d **2** **3a-e**

1a: R=Ph; **1d**: R=*t*-Bu

	Nucleophile	Product	Yield, %
1			84 (62:38)
2			76 (76:24)
3			62 (61:39)
4			82 (57:43)
5			55 (61:39)
6			63 (64:36)
7	Ph-C≡C-$SiMe_3$		–
8	Ph-C≡C-H		–

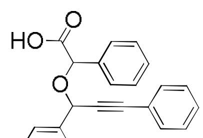
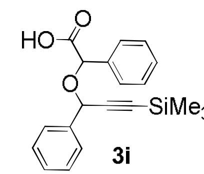
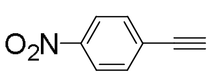
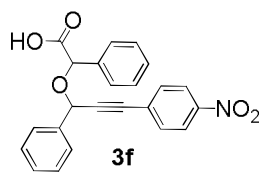
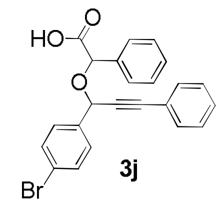
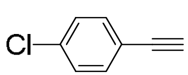
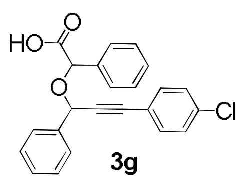
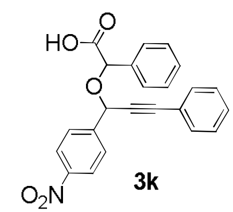
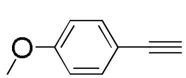
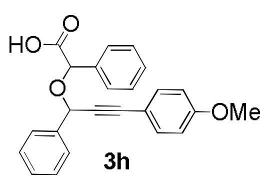
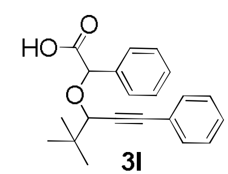
Reaction of 1,3-dioxolan-4-ones with 1-alkynes



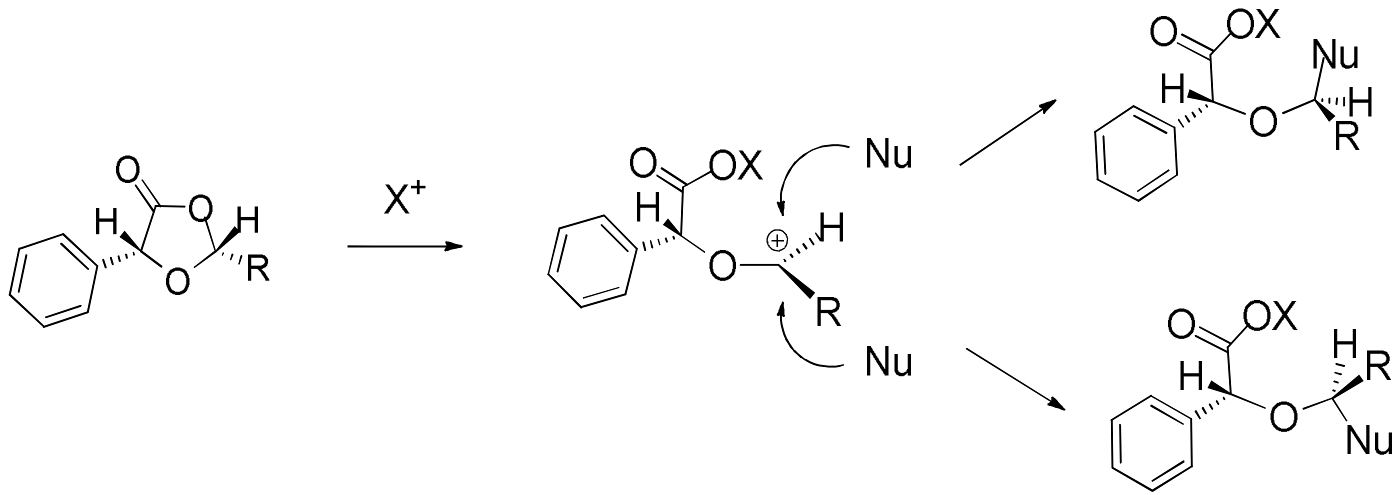
1a-d

3e-l

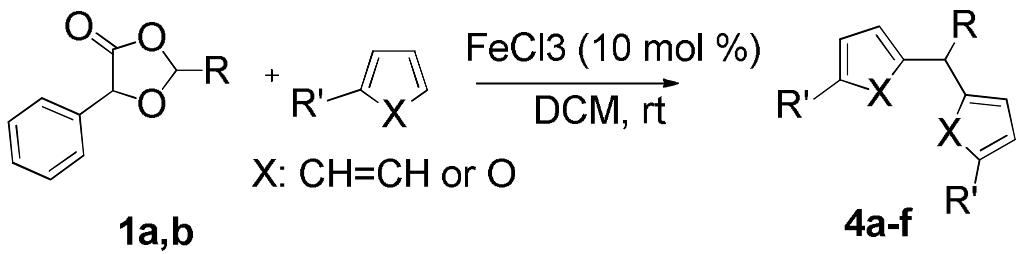
1b: R= p-NO_2Ph;
1c: R= p-BrPh

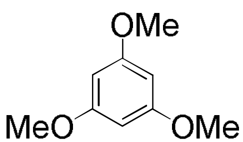
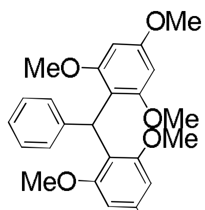
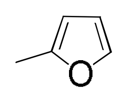
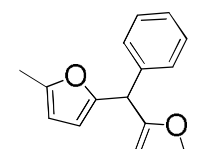
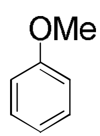
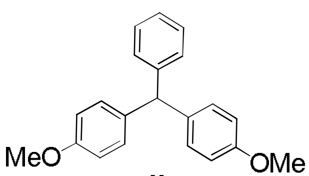
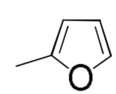
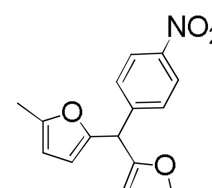
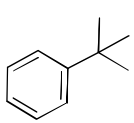
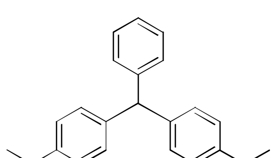
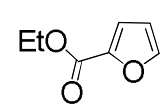
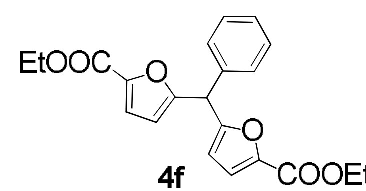
	Nucleophile	Product	Yield, %		Nucleophile	Product	Yield, %
1	Ph—≡	 **3e**	75 (60:40)	5	Me_3Si—≡	 **3i**	50 (75:25)
2		 **3f**	73 (80:20)	6	Ph—≡	 **3j**	53 (75:25)
3		 **3g**	67 (75:25)	7	Ph—≡	 **3k**	45 (82:18)
4		 **3h**	45 (80:20)	8	Ph—≡	 **3l**	33 (83:17)

Mechanism of formation of diastereomeric pair

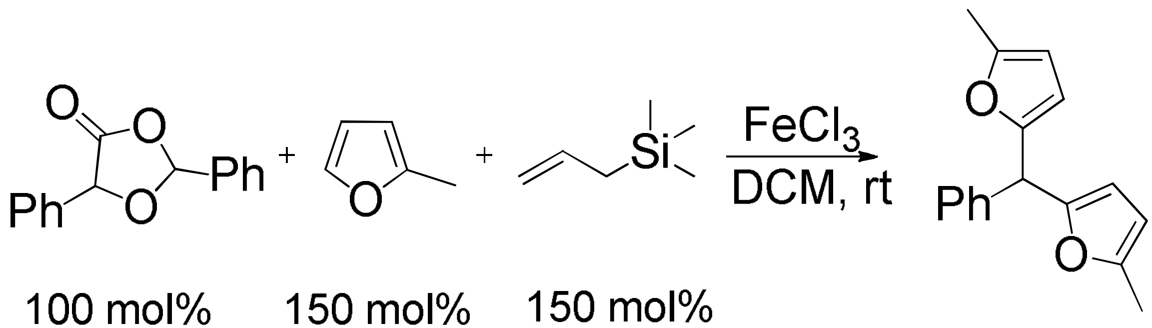


Reaction of 1,3-dioxolan-4-ones with aromatic compounds



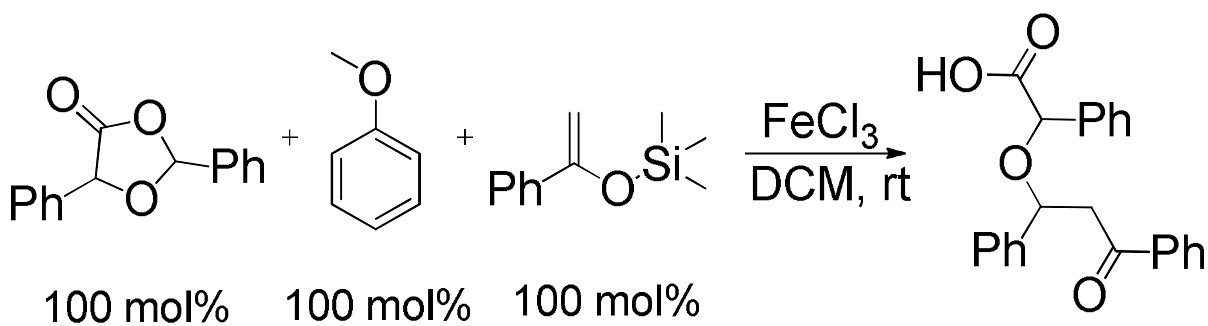
R	Nucleophile	Product	Yield, %	R	Nucleophile	Product	Yield, %
Ph		 4a	54	Ph		 4d	76
Ph		 4b	28	p-NO_2Ph		 4e	15
Ph		 4c	trace	Ph		 4f	-

Competitive addition of nucleophiles to 1,3-dioxolan-4-one



1a

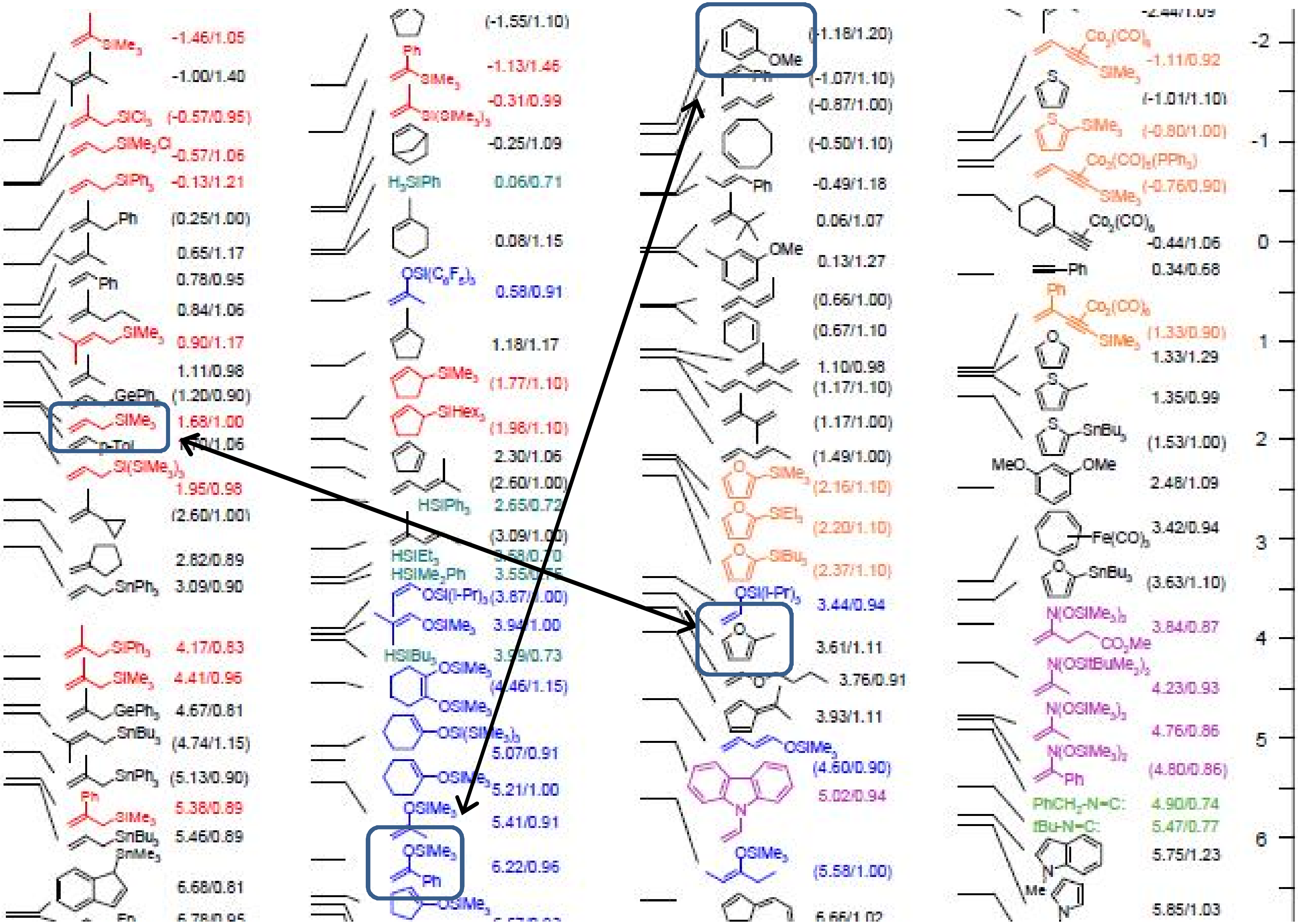
4d 64%



1a

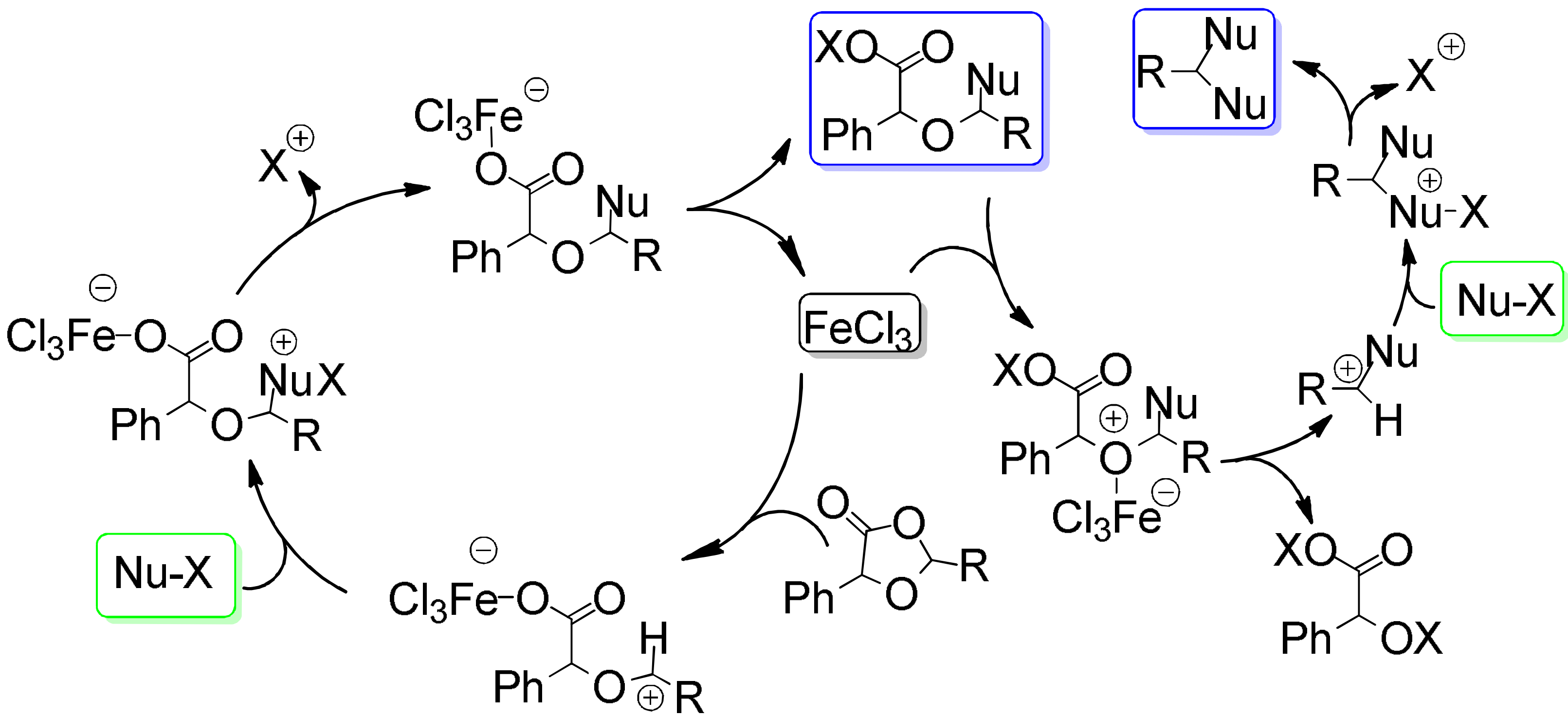
3c 40%

Comparison of the nucleophilicity of the reagents involved in competitive addition

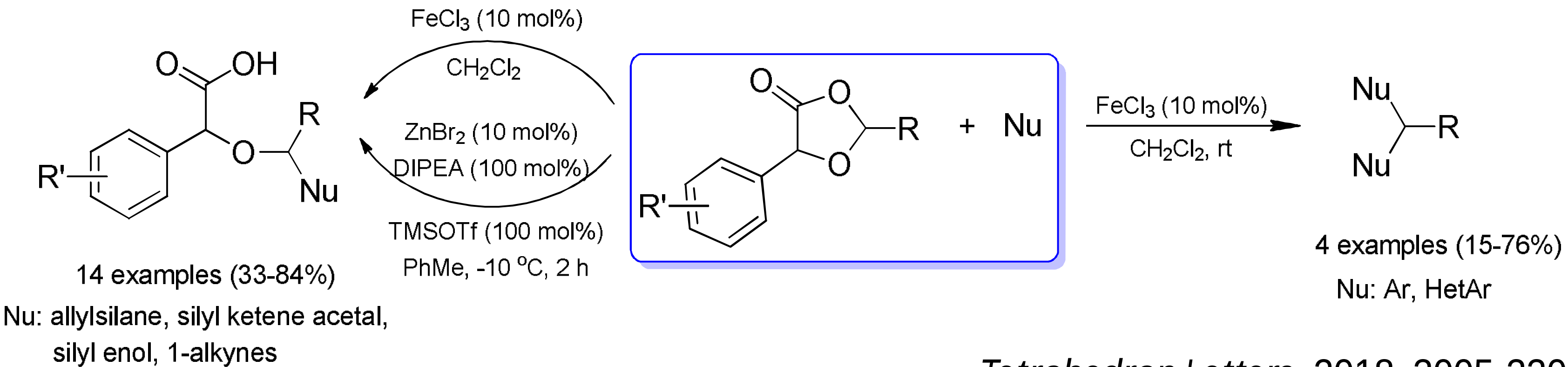


Prof. H. Mayr, http://www.cup.lmu.de/oc/mayr/DBintro.html

Proposed mechanistic scheme for the transformations



Conclusion



Tetrahedron Letters, 2018, 3005-3309

This work was financially supported by the Russian Science Foundation (project No. 17-73-10251)

Thanks for your kind attantion!