DDQ-induced C-C bond forming reactions

Ying, B. P.; Trogden, B. G.; Kohlman, D. T.; Liang, S. X.; Xu, Y. C. *Organic Letters* **2004,** *6,* 1523

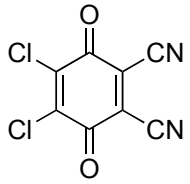
Xu, Y. C.; Kohlman, D. T.; Liang, S. X.; Erikkson, C. *Organic Letters* **1999,** *1,* 1599

Xu, Y. C.; Roy, C.; Lebeau, E. *Tetrahedron Letters* **1993**, *34*, 8189

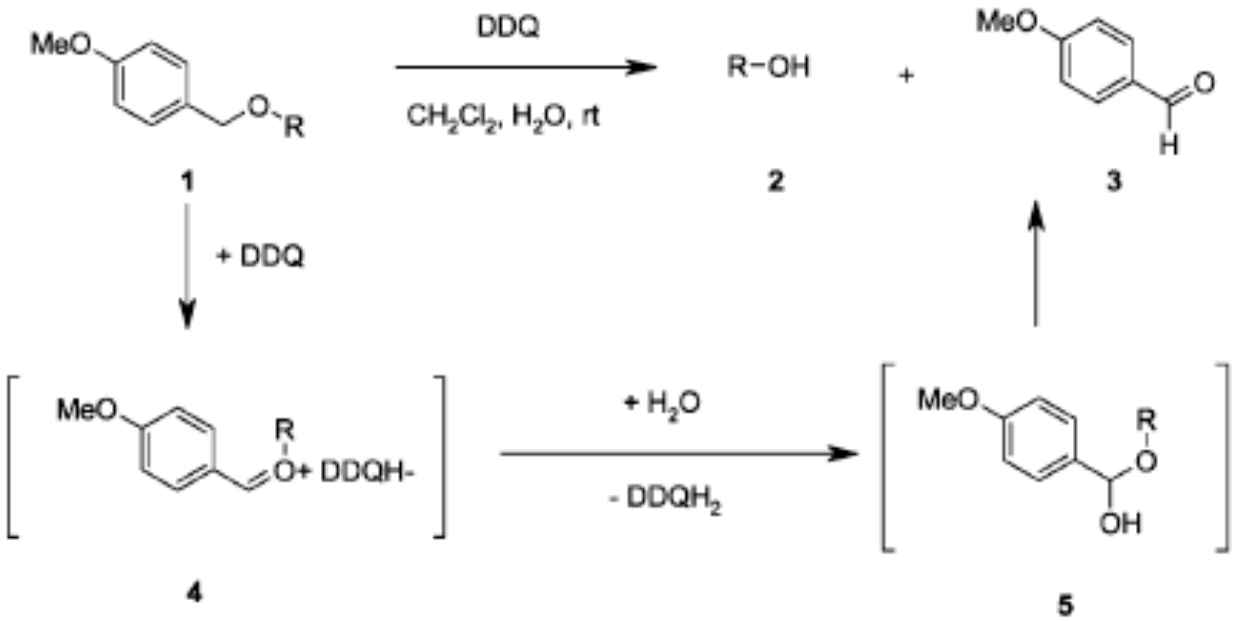
Xu, Y. C.; Lebeau, E.; Gillard, J. W. *Tetrahedron Letters* **1993**, *34*, 3841

(Lilly Research Labs, Indiana)

Deprotection of benzyl ethers

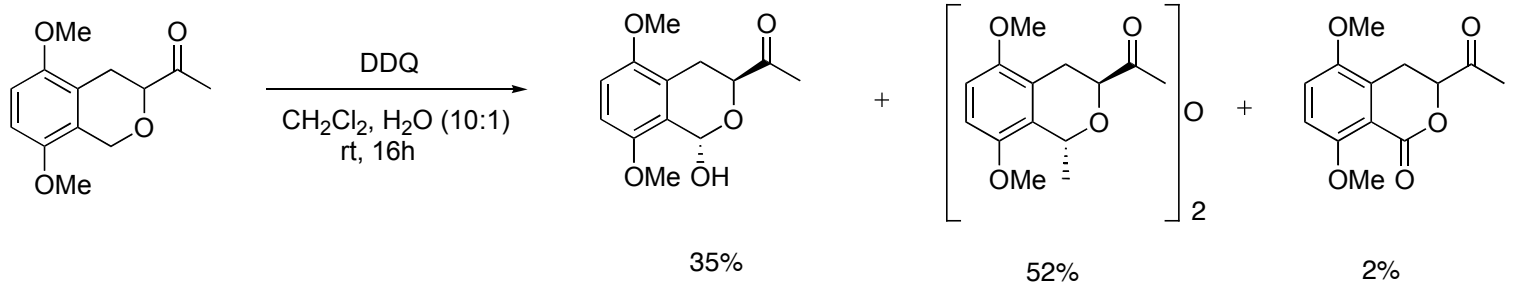


DDQ



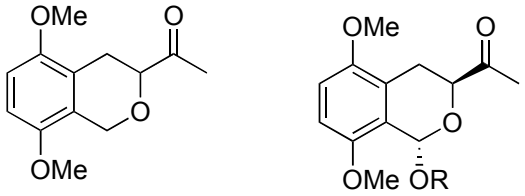
Addition of O- nucleophiles

-Water



-Alcohols

Isochromans Product



R=Me 93% (trans only)

R=iPrO 90%

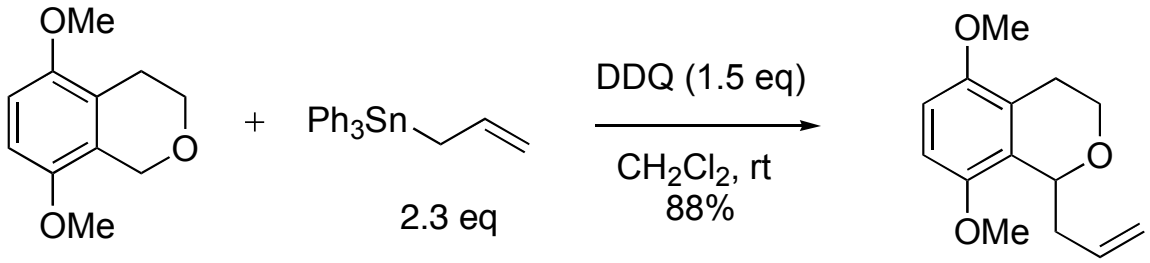
R=tBu 90%

R=H 85%

R=Me 78%

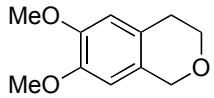
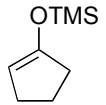
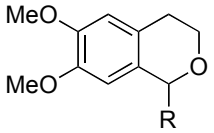
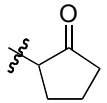
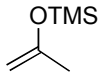
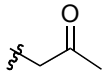
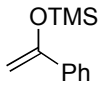
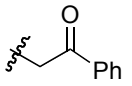
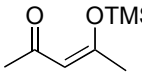
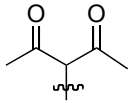
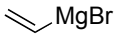
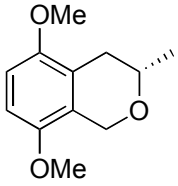
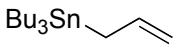
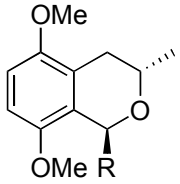
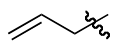
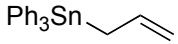
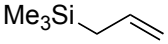
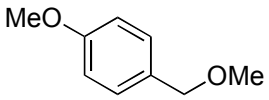
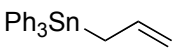
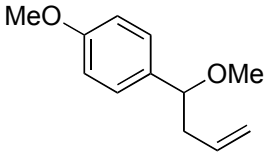
Xu et al. *Tetrahedron Letters* **1993**, *34*, 3841

Addition of C- nucleophiles

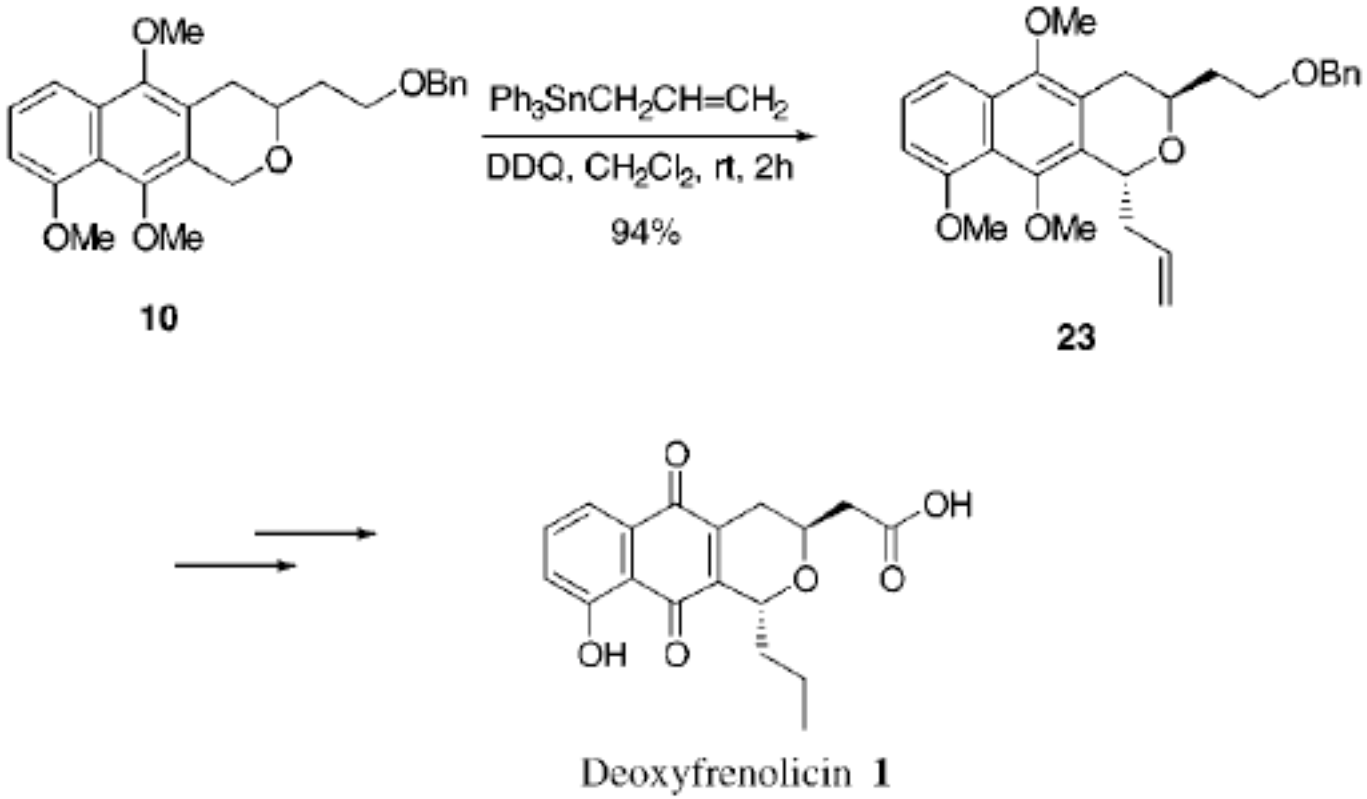


Xu et al. *Tetrahedron Letters* **1993**, *34*, 8189

Addition of C- nucleophiles

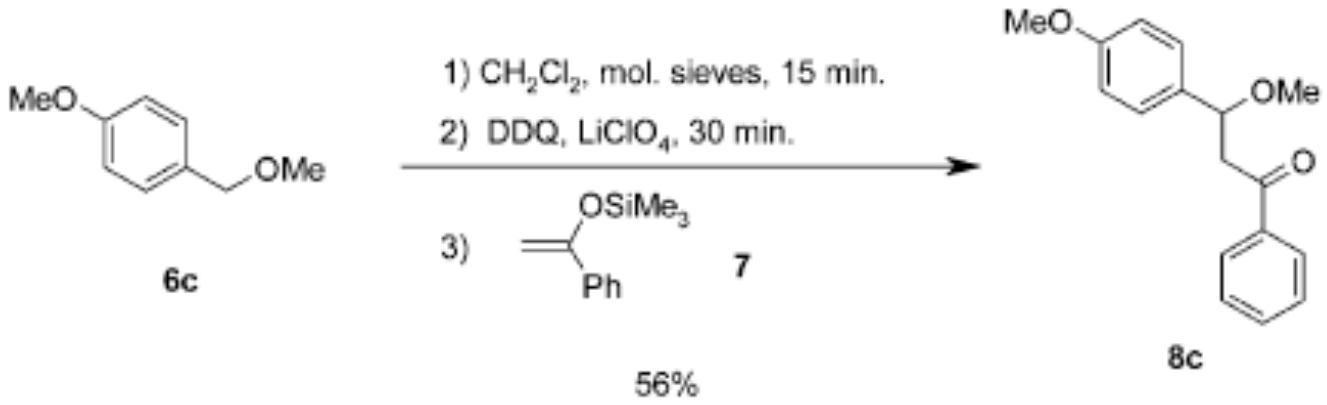
Substrate	Nucleophile	Product	R	Yields	trans / cis
				78	
				49	
				50	
				73	
				25	
				77	10 / 1
				97	13 / 1
				45	trans only
	BuMgCl		Bu	54	>>
	BuLi			48	>>
				71	

Application of the allylation protocol



Xu et al. *Organic Letters* **1999,** *1,* 1599

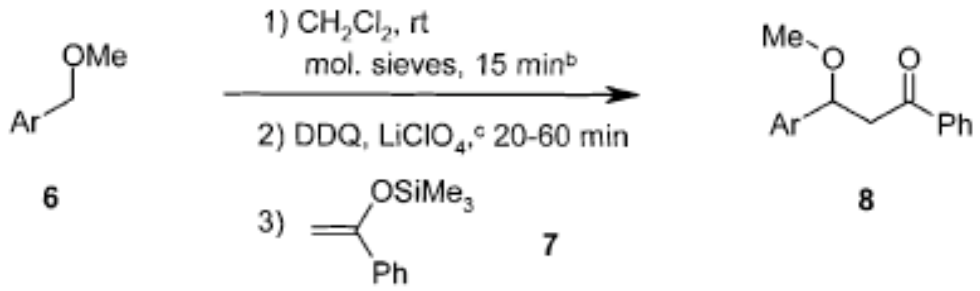
Coupling of benzyl ether with enol ethers

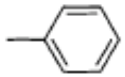
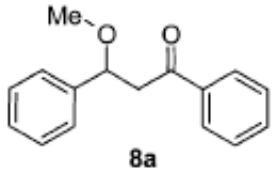
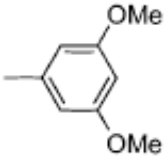
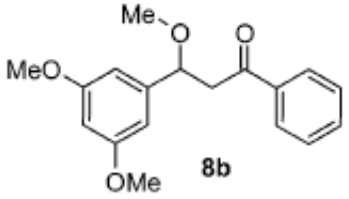
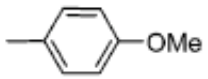
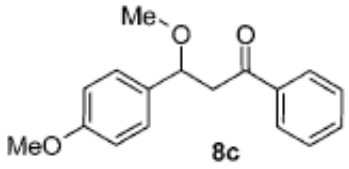
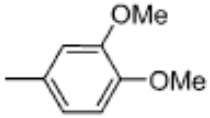
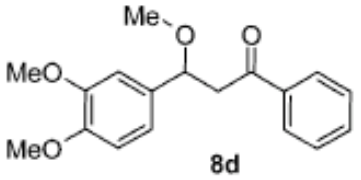
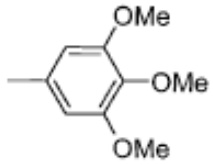
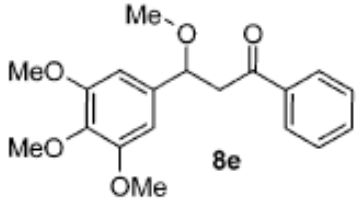
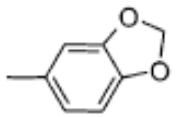
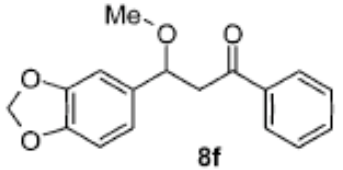


Without $LiClO_4$: 45% yield

Xu et al. *Organic Letters* **2004,** *6,* 1523

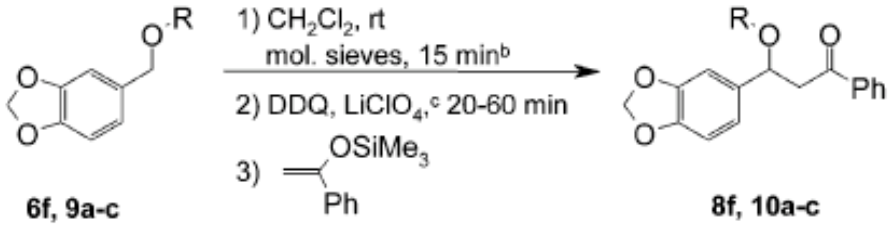
Various benzyl ethers



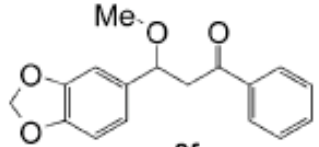
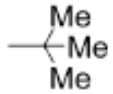
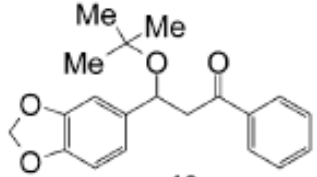
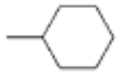
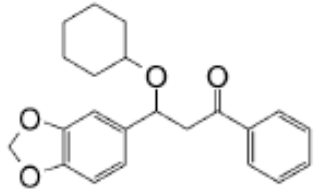
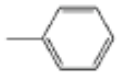
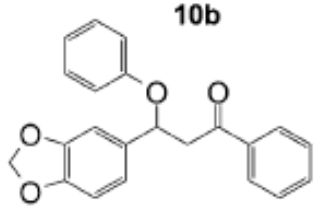
starting material	-Ar	product **8**[d]	yield[e]
6a		 **8a**	0%
6b		 **8b**	10%
6c		 **8c**	56%
6d		 **8d**	32%
6e		 **8e**	55%
6f		 **8f**	84%

[a] All reactions were carried out in anhydrous conditions at room mperature under nitrogen pressure with 0.1 M solution of compound **6** in H_2Cl_2. [b] Anhydrous dichloromethane purchased from Aldrich in a Sure Seal bottle was used. [c] Performed with about 0.2−0.5 equiv of $LiClO_4$. [d] All products were characterized by ^1H NMR, MS, and elemental analysis. [e] Isolated yield after flash chromatography separation.

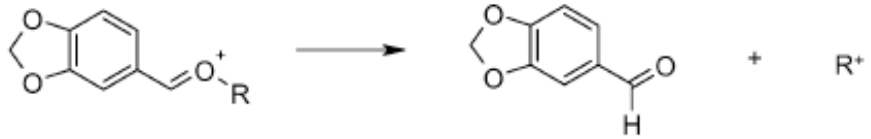
Various R groups



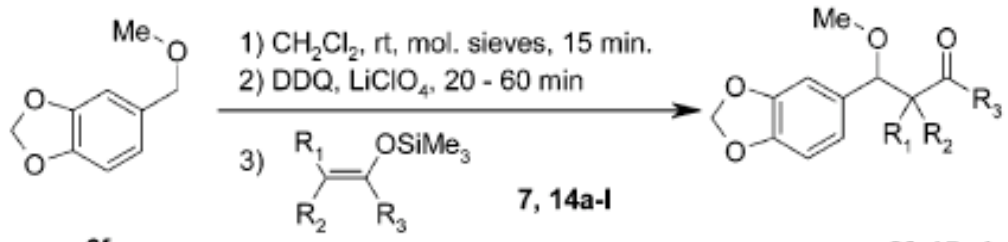
[a] All reactions were carried out in anhydrous conditions at room temperature under nitrogen pressure with 0.1 M solution of compound **6** or **9** in CH_2Cl_2. [b] Anhydrous dichloromethane purchased from Aldrich in aSure/ Seal bottle was used. [c] Performed with about 0.2−0.5 equiv of $LiClO_4$.[d] All products were characterized by ^1H NMR, MS, and elemental analysis. [e] Isolated yield after flash chromatography separation.

starting material	-R	product[d]	yield[e]
6f	—Me	 **8f**	84%
9a		 **10a**	0%
9b		 **10b**	85%
9c		 **10c**	0%

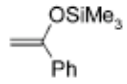
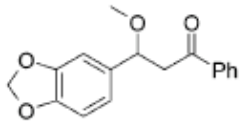
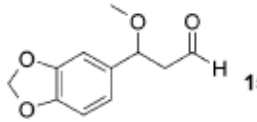
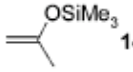
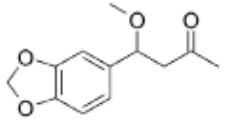
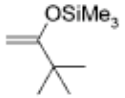
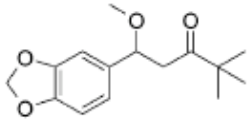
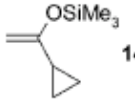
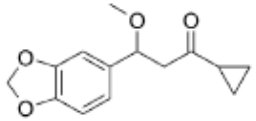
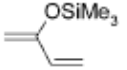
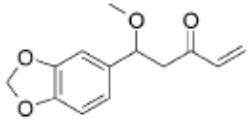
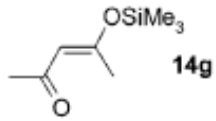
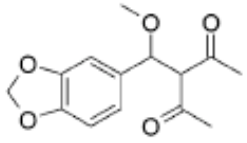
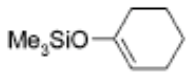
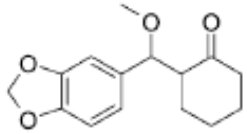
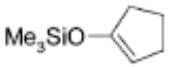
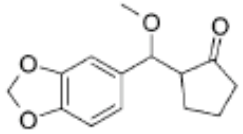
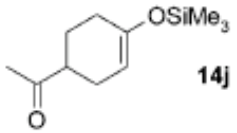
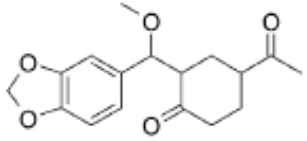
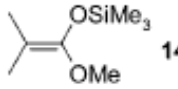
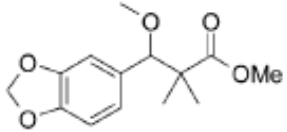
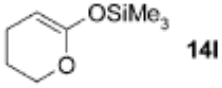
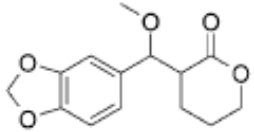
Possible explanation of low yields for 10a, 10c :



Various enol ethers



6f **8f, 15a-l**

trimethylvinyloxysilane[b]	product[c]	yield[d]
 **7**	 **8f**	84%
14a	 **15a**	65%
 **14b**	 **15b**	53%
 **14c**	 **15c**	69%
 **14d**	 **15d**	77%
 **14f**	 **15f**	68%
 **14g**	 **15g**	67%
 **14h**	 **15h**	75%
 **14i**	 **15i**	53%
 **14j**	 **15j**	30%
 **14k**	 **15k**	71%
 **14l**	 **15l**	44%