

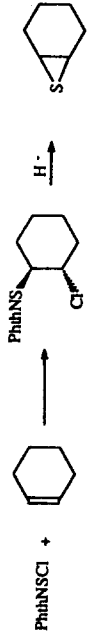
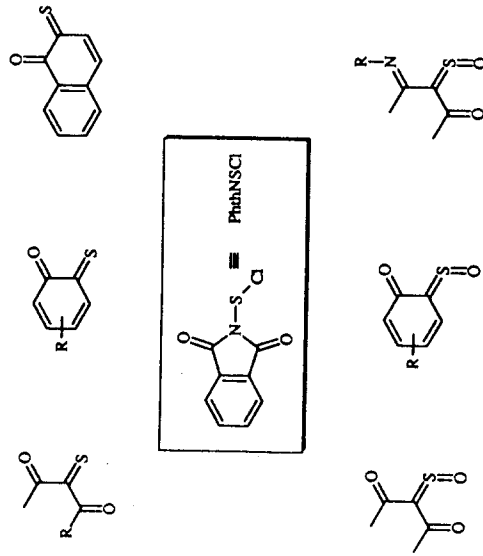
Dioxothiones and *ortho*-Thioquinones: Generation, Trapping and Synthetic Applications

Department of Organic Chemistry, University of Firenze - Italy

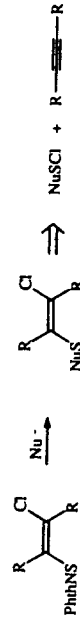
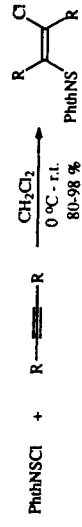
Giuseppe Capozzi
Stefano Menichetti
Cristina Nativi

Hunter College, City University of New York

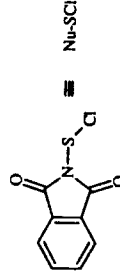
Richard W. Franck



Bombala, M. U.; Ley S. V. *J. Chem. Soc., Perkin Trans. 1*, 1979, 3013

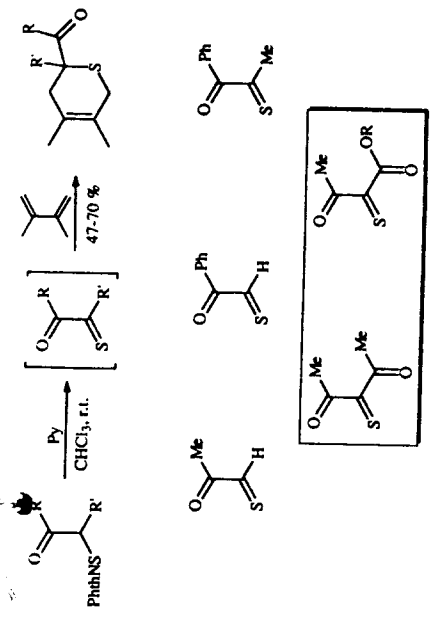


Nu = Me, Ph, *i*-Bu, R₃Sn, (Me₃Si)₂N, R

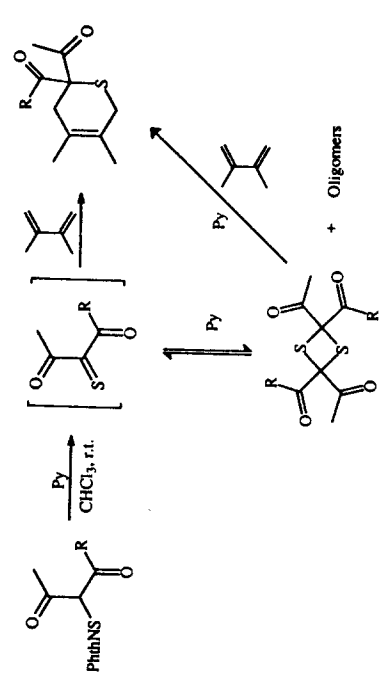


Me₃Si, Ph₃Si, *i*-Bu₃Si, R₃Sn, (Me₃Si)₂N, R, Cl

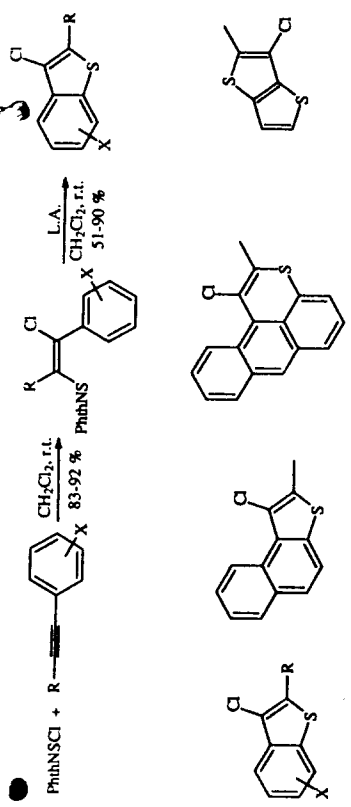
Busi, Gori, Menichetti, Nativi; *Tetrahedron Lett.*, 31, 1990, 6213
Tetrahedron, 47, 1991, 7185
Synthesis, 1992, 643
Perkin Trans. 1, 1992, 1923



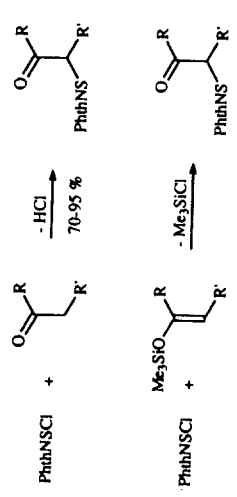
Menichetti, Nativi, Rosi: *Tetrahedron*, 48, 1992, 9023



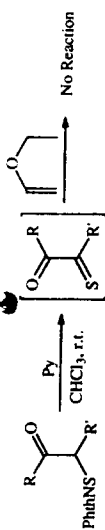
Menichetti, Nativi, Rosi: *Tetrahedron*, 48, 1992, 9023



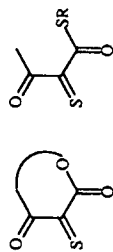
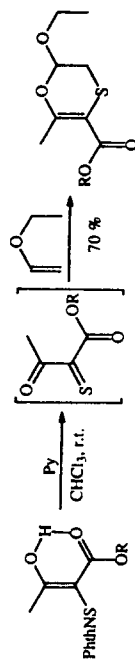
Menichetti, Nativi, Pasini: *Synthesis*, 1994, 522



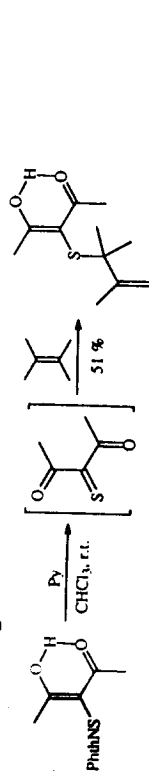
Menichetti, Nativi, Rosi: *Tetrahedron*, 48, 1992, 9023



R = Me, Ph
R' = H, Me, Ph

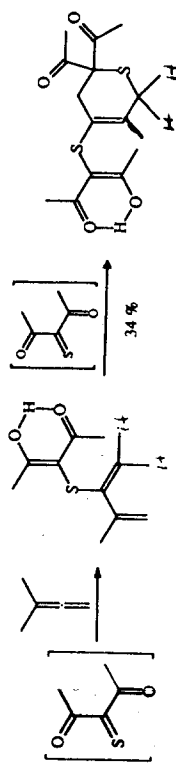


Menichetti, Nativi: *P & S*, 1994, 359

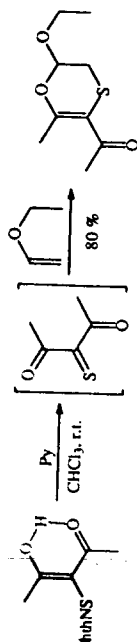


Thioetheric

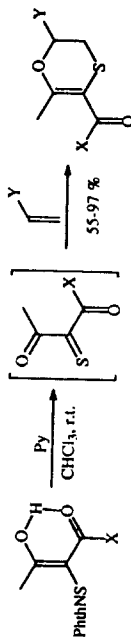
Menichetti, Nativi, Rosi: *Tetrahedron Lett.*, 34, 1993, 4253



Fragai, Menichetti, Nativi



Menichetti, Nativi, Rosi: *Tetrahedron Lett.*, 34, 1993, 4253



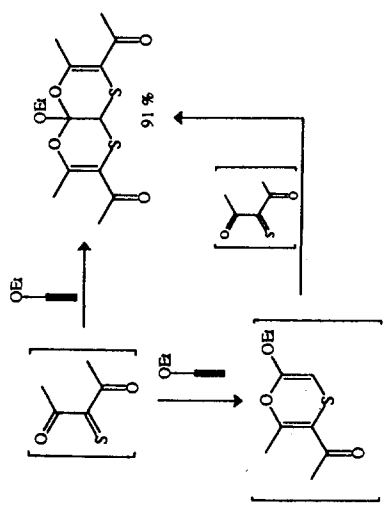
X = Me, OMe



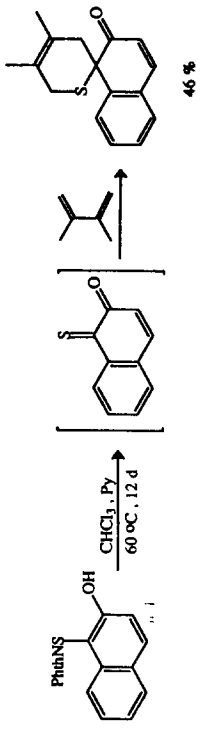
LUMO (eV) 0.190 5.578

HOMO (eV) -9.796 -9.088

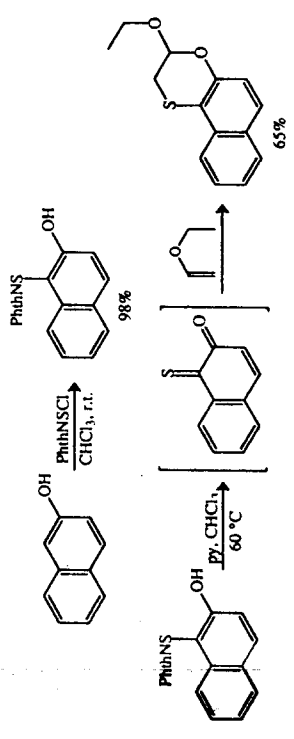
Mattioli, Menichetti, Nativi: *J. Org. Chem.*, 60, 1995, 6416



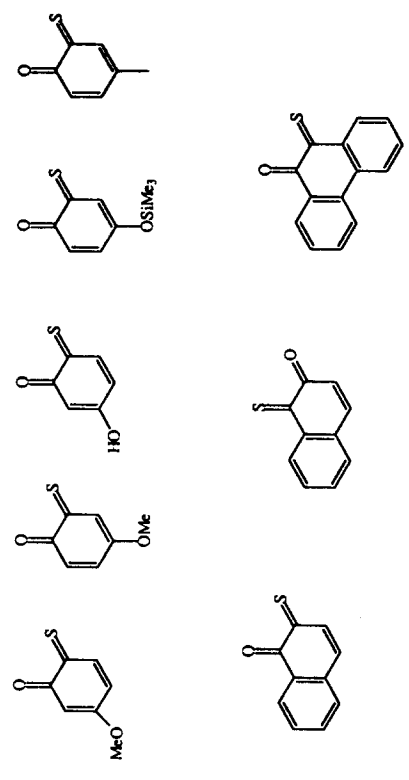
Mattoli, Menichetti, Natvi: *J. Org. Chem.*, 60, 1995, 6416



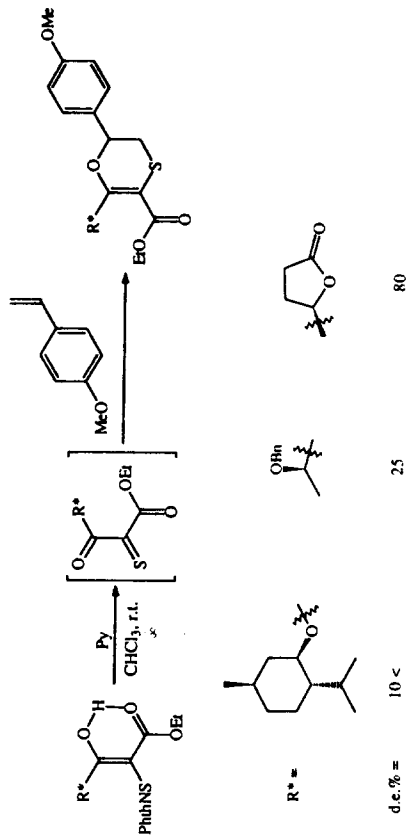
Menichetti, Natvi, Simoni: *Tetrahedron Lett.*, 35, 1994, 9451



Menichetti, Natvi, Simoni: *Tetrahedron Lett.*, 35, 1994, 9451

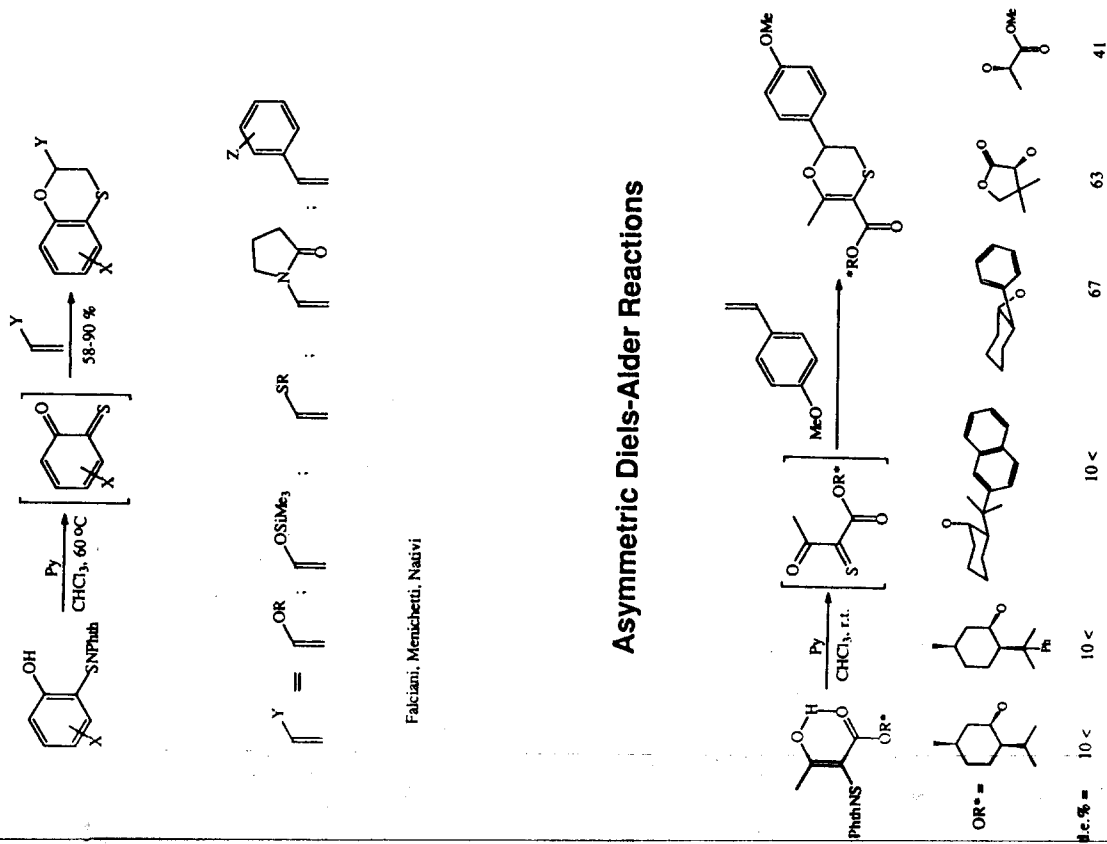


Asymmetric Diels-Alder Reactions



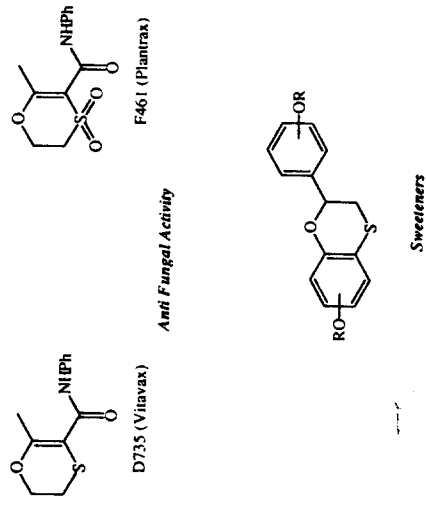
Giuntini, Menichetti, Nativi

Asymmetric Diels-Alder Reactions



Falciani, Menichetti, Nativi

Boccardo, Menichetti, Nativi

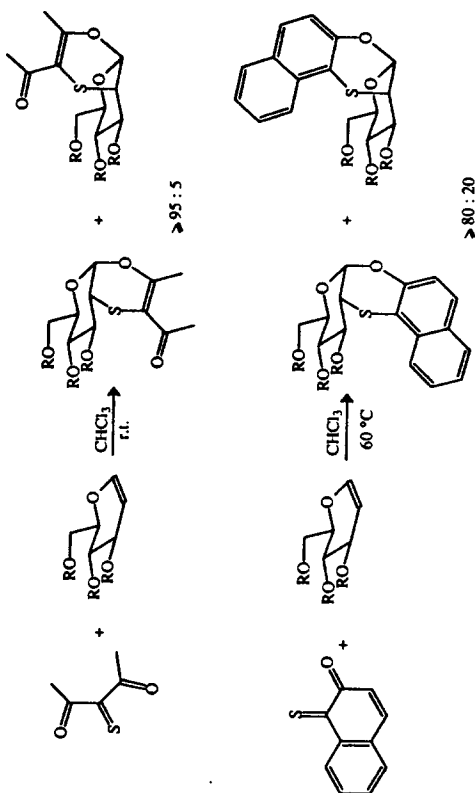


Arnoldi, A.; Bassoli, A.; Merlini, L.; Ragg, E. *J. Chem. Soc., Perkin Trans. 2*, 1991, 1399

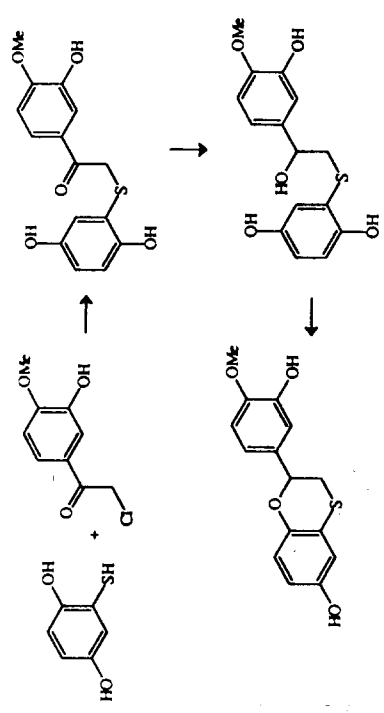
Arnoldi, A.; Bassoli, A.; Merlini, L.; Ragg, E. *J. Chem. Soc., Perkin Trans. 1*, 1993, 1359

Arnoldi, A.; Bassoli, A.; Caputo, R.; Merlini, L.; Palumbo, G.; Pedatella, S. *J. Chem. Soc., Perkin Trans. 1*, 1994, 1241

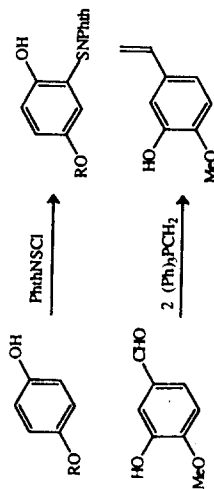
Diels-Alder Approach to Glycosidation



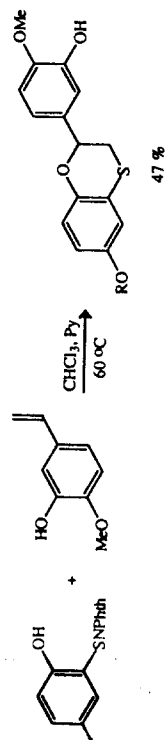
Dienophile	Cycloadduct	Yield	ΔE (HOMO-LUMO) eV
Tri-O-Bn glucal		80	7.91
$\alpha/\beta > 95/5$			
		54	7.91
Tri-O-Bn galactal		73	7.55
Tri-O-Bn allal		68	7.88
Tri-O-Ac glucal	No Reaction	-	8.12



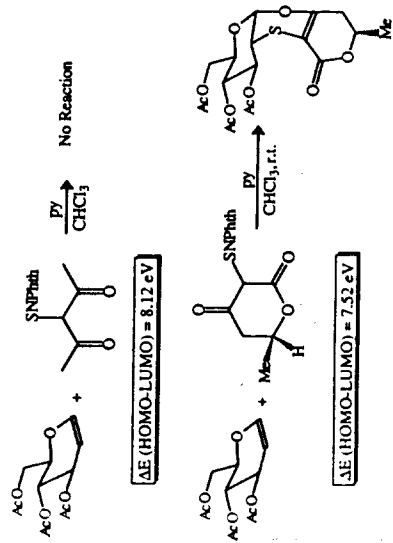
Arnoldi, A.; Bassoli, A.; Merlini, L.; Ragg, E. *J. Chem. Soc., Perkin Trans. 1*, 1993, 1359



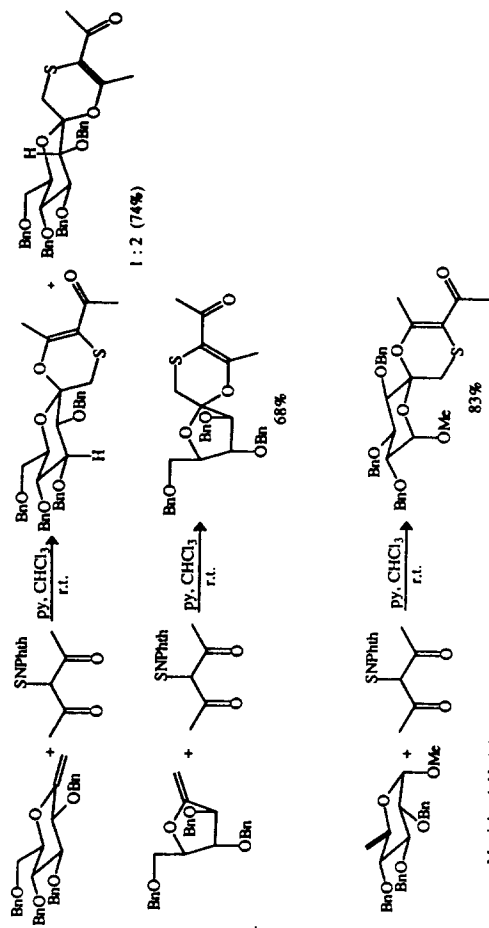
R = Si(Me₂-tBu)



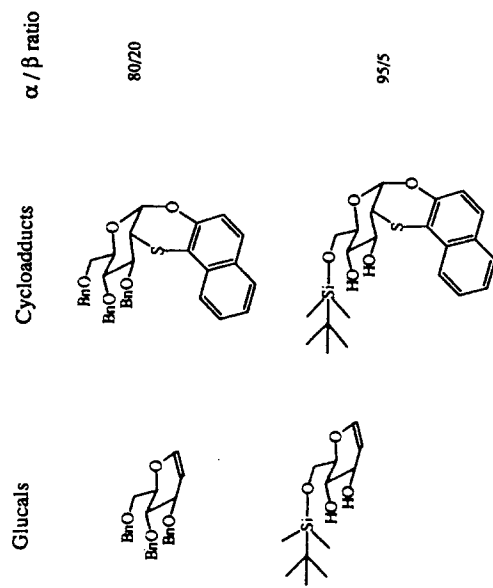
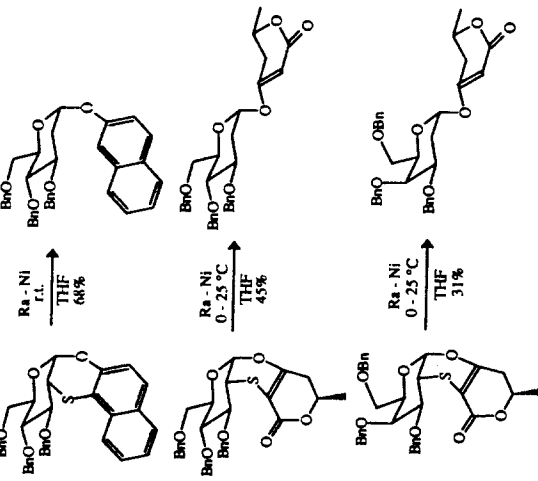
Falciani, Menichetti, Nativi



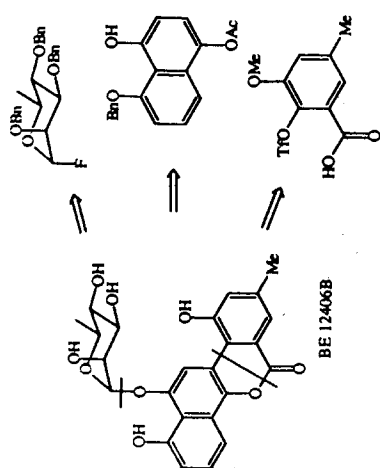
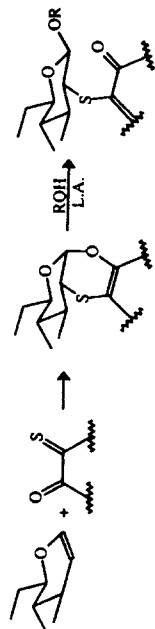
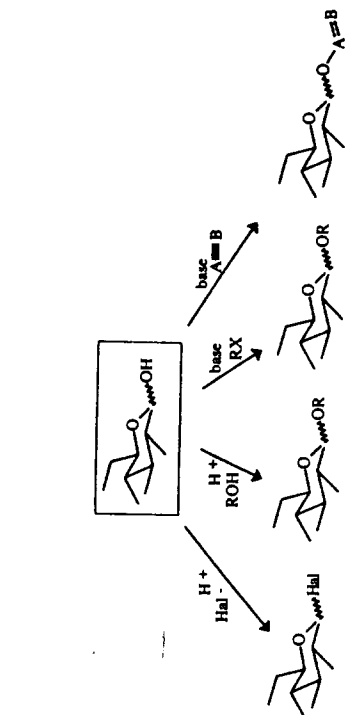
Dios, Franck, Geer, Marzabadi, Menichetti, Nativi, Tananez, *Angew. Chem. Int. Ed. Engl.*, 1996, 35, 777



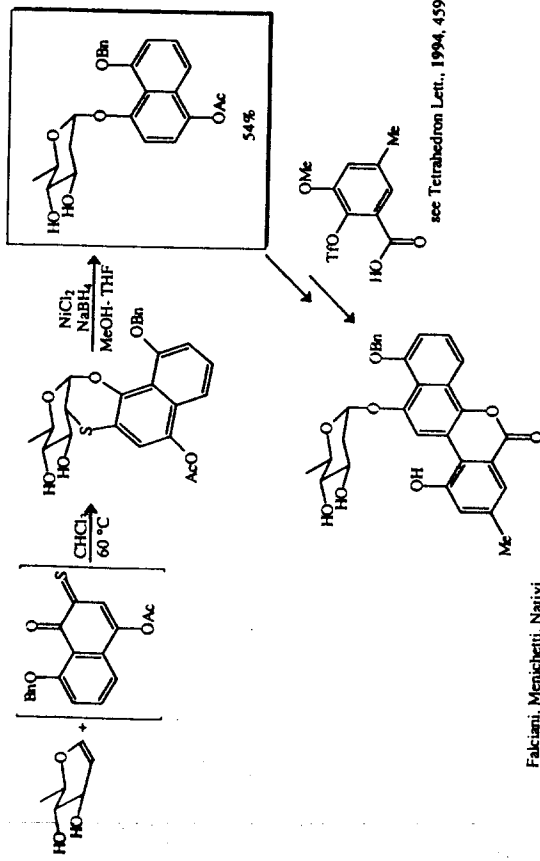
Menichetti, Nativi, Paolacci



Falciani, Menichetti, Nativi, Franck *Tetrahedron Lett.*, 1995, 6755

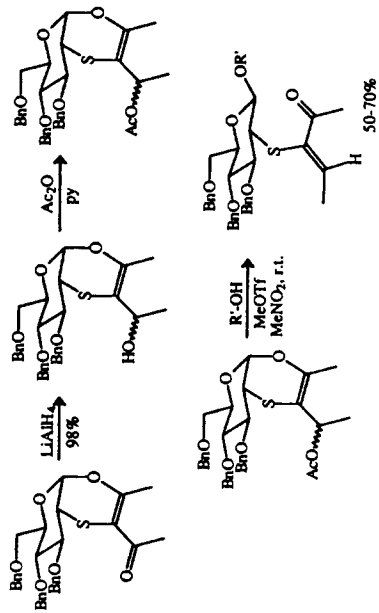


Suzuki et al. *Tetrahedron Lett.*, 1994, 4591



Falciani, Menichetti, Nativi

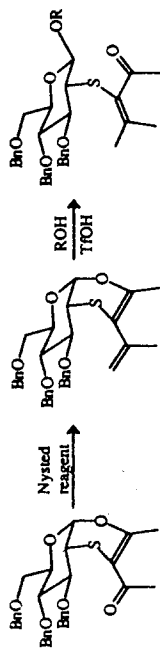
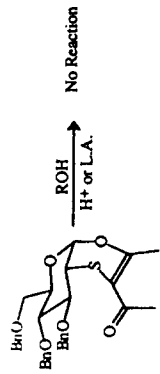
The Firenze Approach



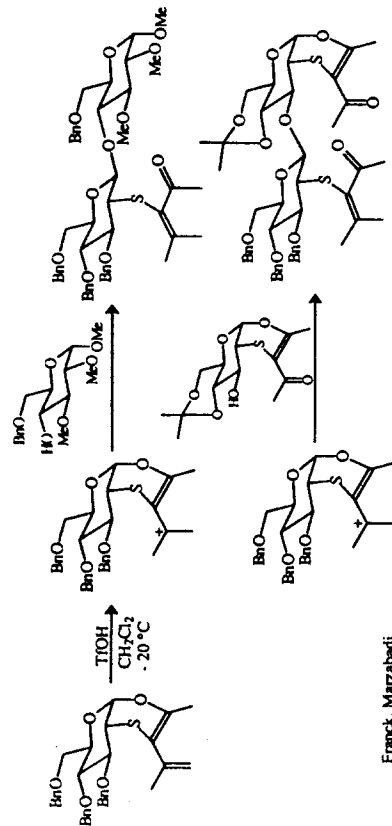
Menichetti, Nativi, Paoletti

O-GLYCOSIDE	DONOR	ACCEPTOR	REACTION TIME (min)	YIELD (%)
			135 min r.t.	35.7%
			5 min r.t.	61%
			40 min r.t.	68%
			45 min r.t.	10%

The Hunter Approach

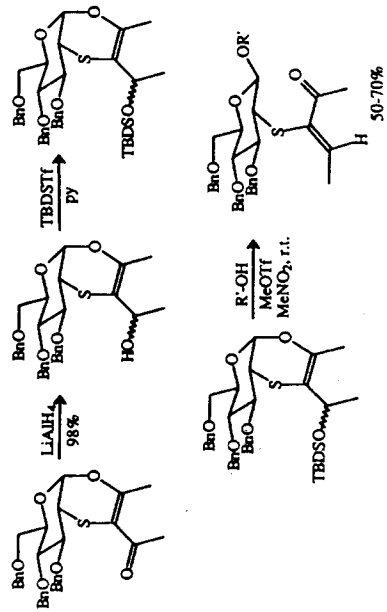


Franck, Marzabadi



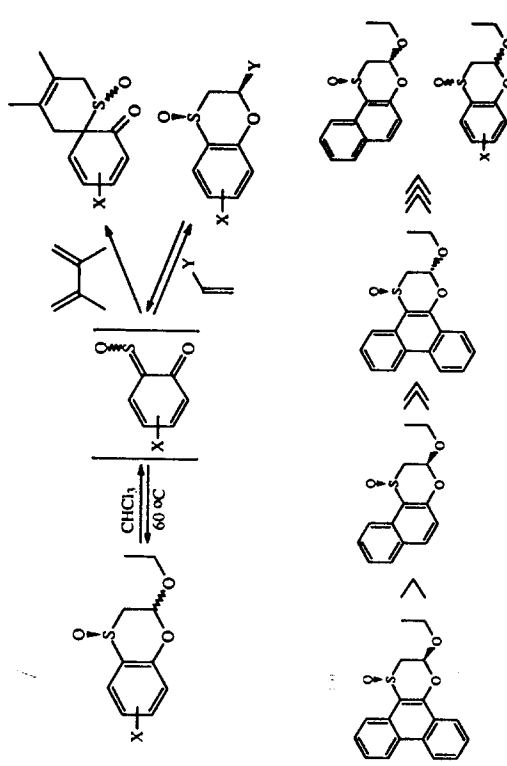
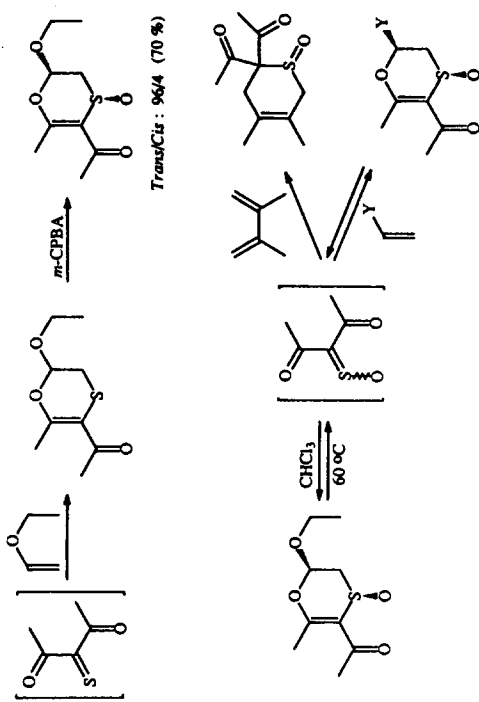
Franck, Marzabadi

The Firenze Approach



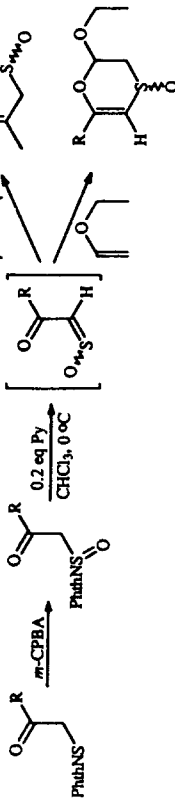
Menichetti, Nativi, *Procedi*

Fratini, Menichetti, Nativi: *Tetrahedron Lett.*, 36, 1995, 5089
 Fratini, Menichetti, Nativi: *Tetrahedron*, 52, 1996, 12233



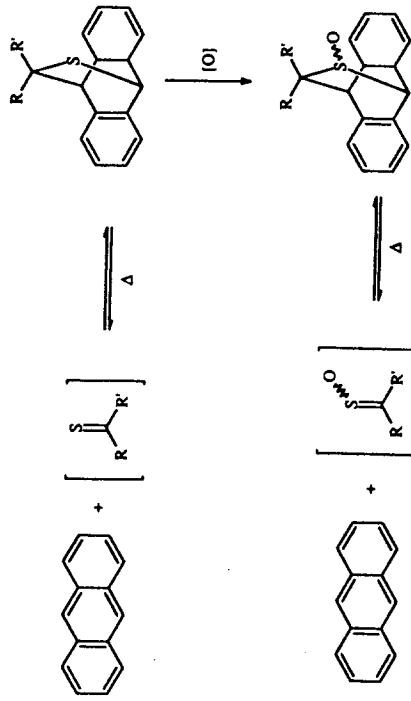
O-GLYCOSIDE	DONOR	ACCEPTOR	REACTION TIME (min)	YIELD (%)
		HO-CH(CH3)2 2 eq	5 min r.t.	58%
		HO-CH(CH3)2 2 eq	10 min -26°C	37%

Fratini, Menichetti, Nativi: *Tetrahedron*, 52, 1996, 12247

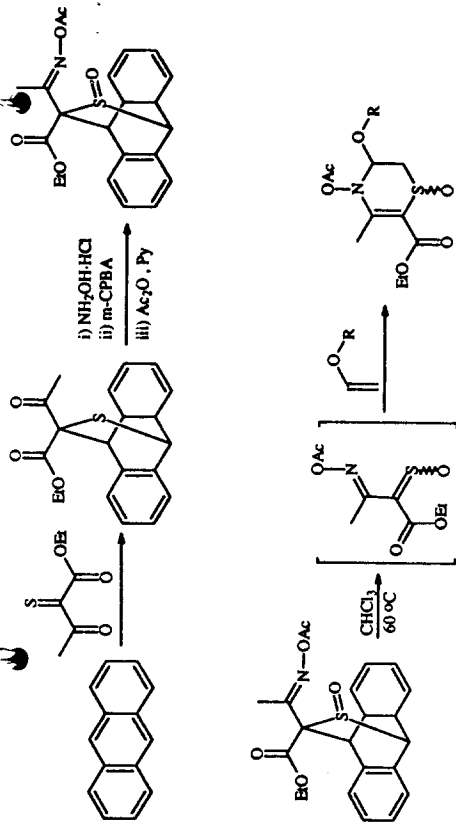


R = CH₃, Ph, 1-Naphthyl, 2-Thienyl, COCH₃

Corti, Menichetti, Nativi



Kirby, G.; McGregor, W. M. *J. Chem. Soc., Perkin Trans. J.* 1990, 3175



Corti, Menichetti, Nativi

Ph

18th International Symposium on The Organic Chemistry of Sulfur

Firenze, Italy July 13 - 18, 1998



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