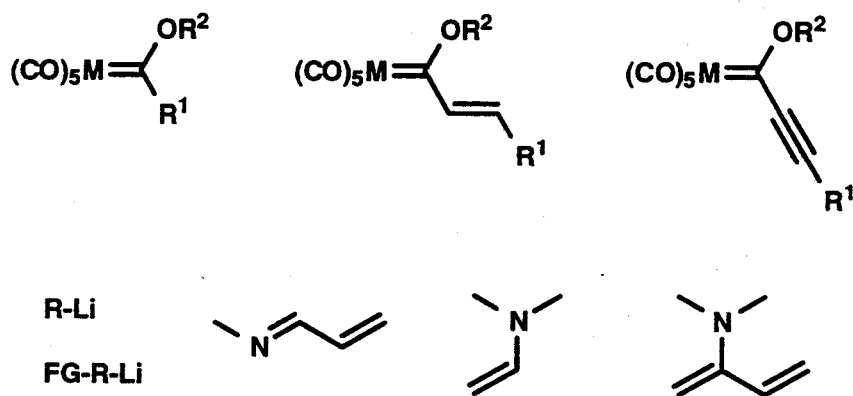
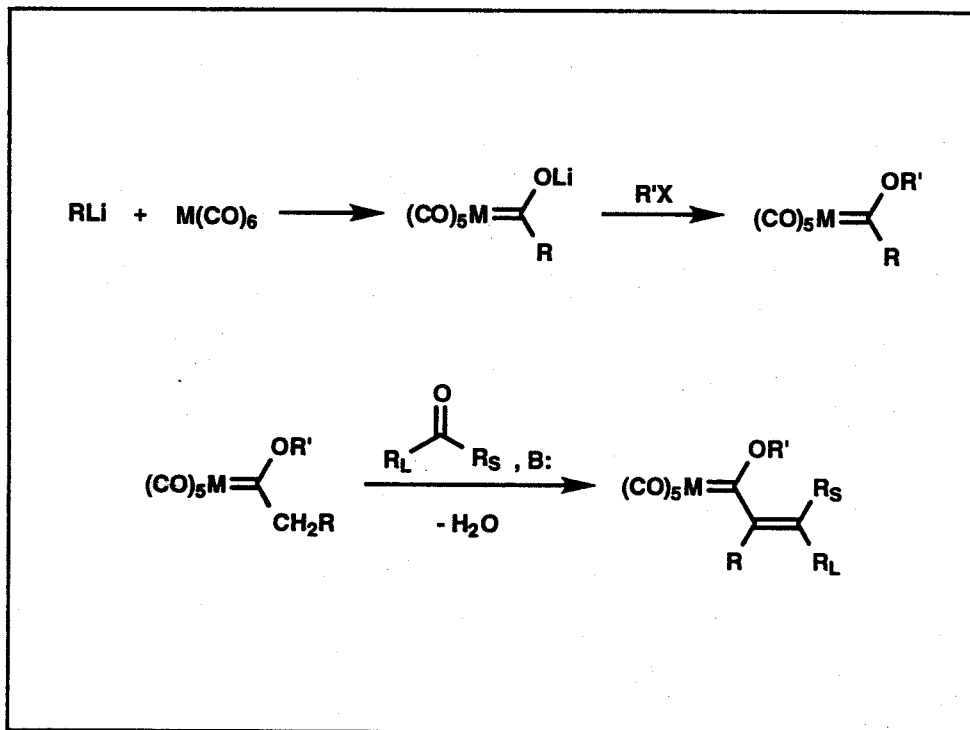


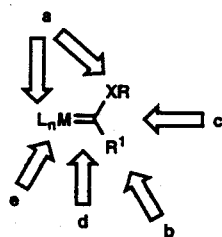
J.B

Synthetic Applications of Transition Metal Carbene Complexes

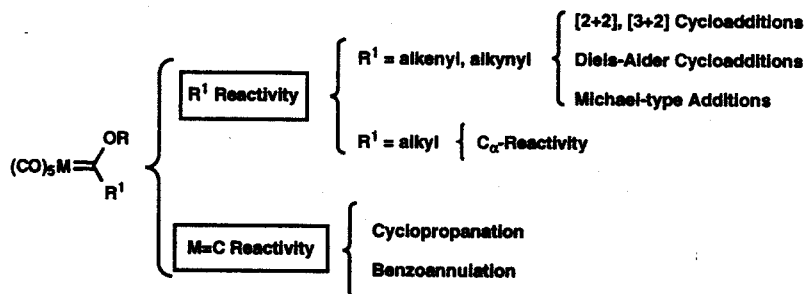




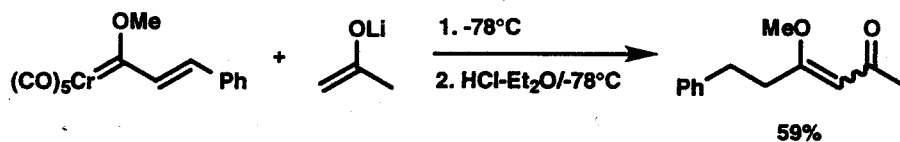
GENERAL PATTERNS OF REACTIVITY



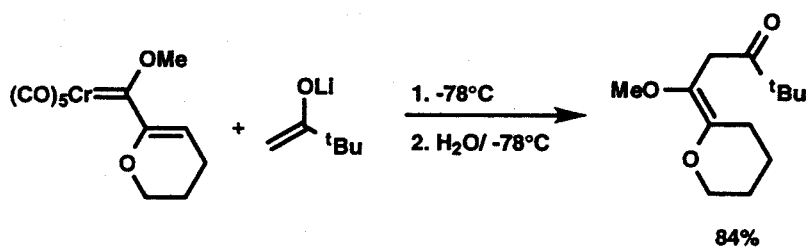
- a: Substitution Reaction
- b: Side Chain Reaction
- c: Nucleophilic Attack
- d: Insertion Reaction
- e: Metal Oxidation



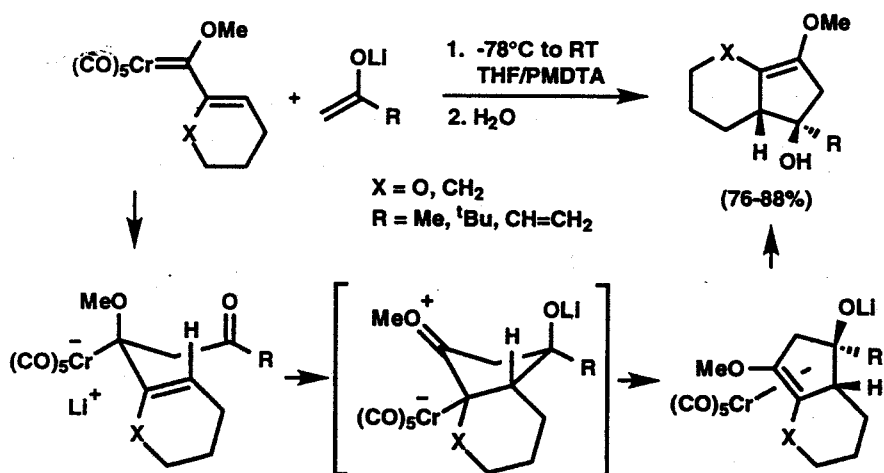
1,2-ADDITION OF METHYL KETONE ENOLATES TO ALKENYL CARBENES



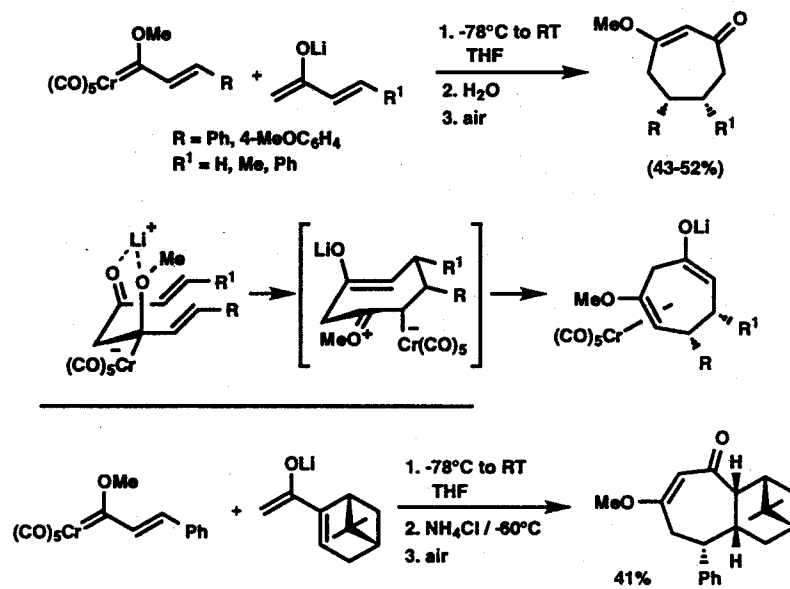
Casey, C.P.; Brunsvold, W. *Inorg. Chem.* 1977, 16, 391



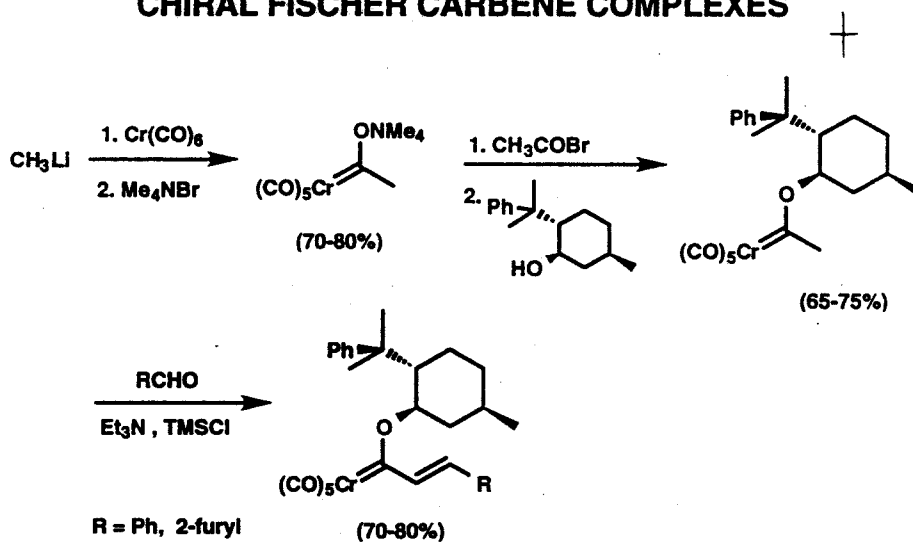
[3+2] CYCLOADDITION OF ALKENYL CARBENES AND METHYL KETONE ENOLATES



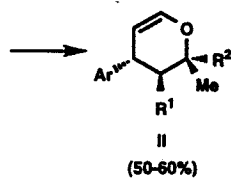
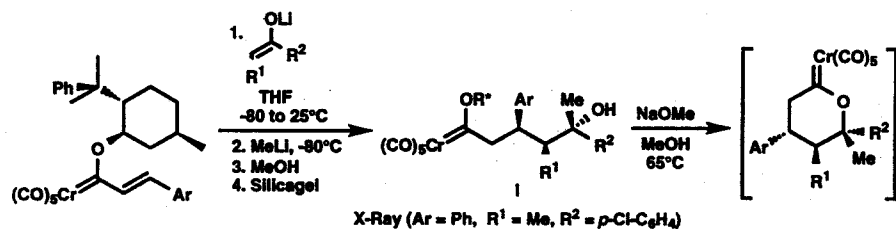
**[4+3] CYCLOADDITION OF ALKENYL CARBENES
AND METHYL VINYL KETONE ENOLATES**



CHIRAL FISCHER CARBENE COMPLEXES

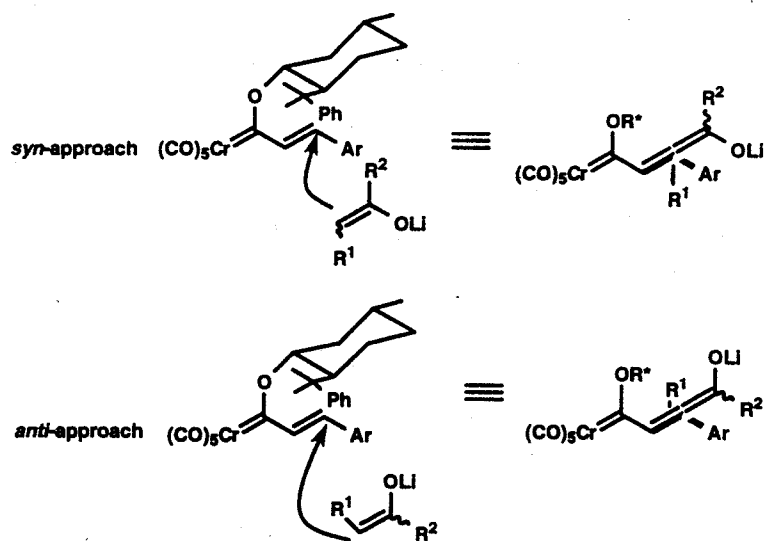


syn-DIASTEREOSELECTIVE MICHAEL ADDITION

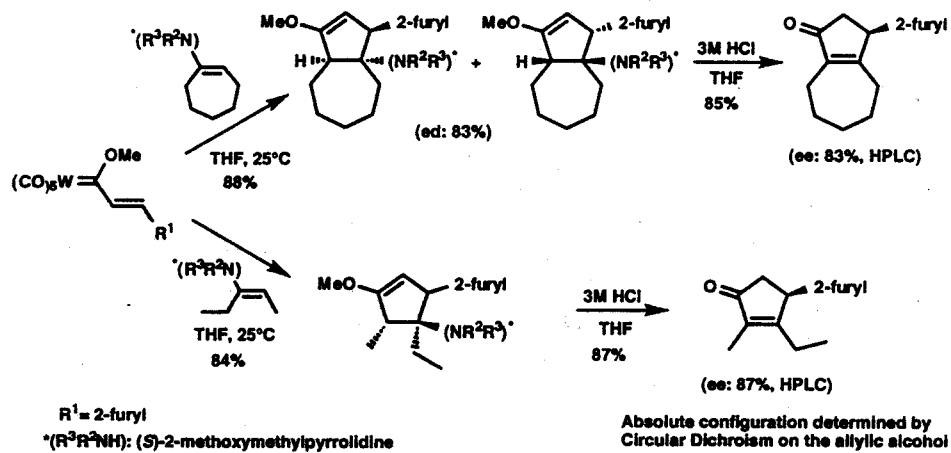
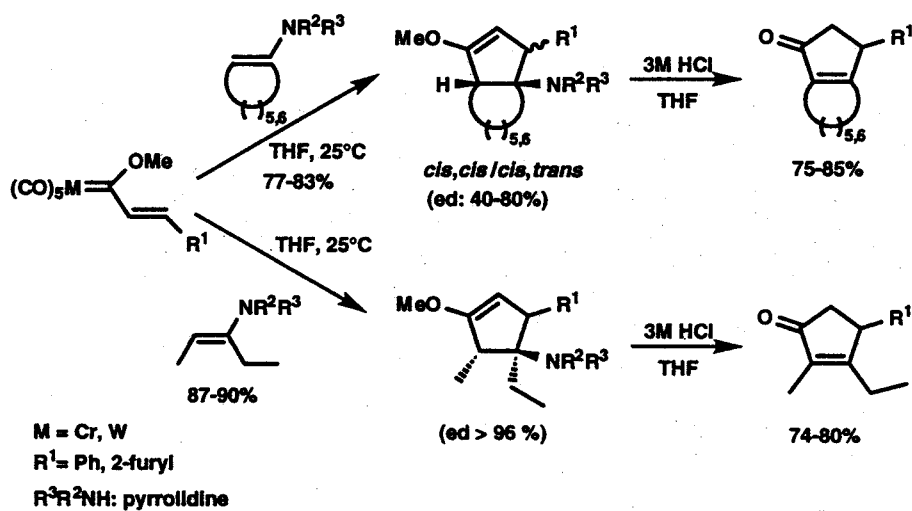


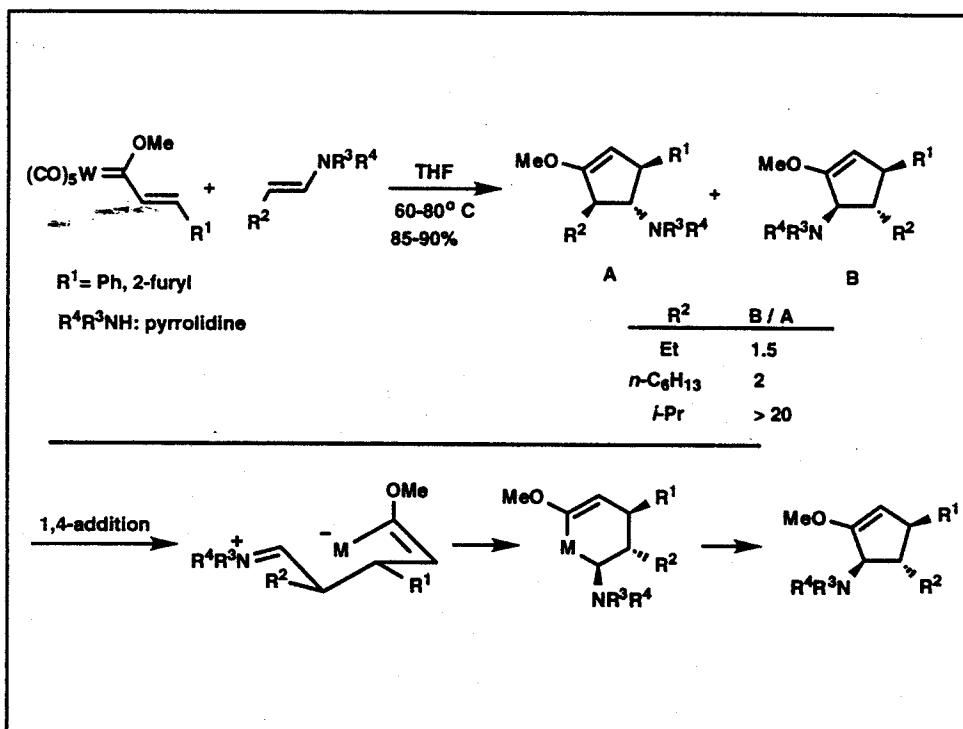
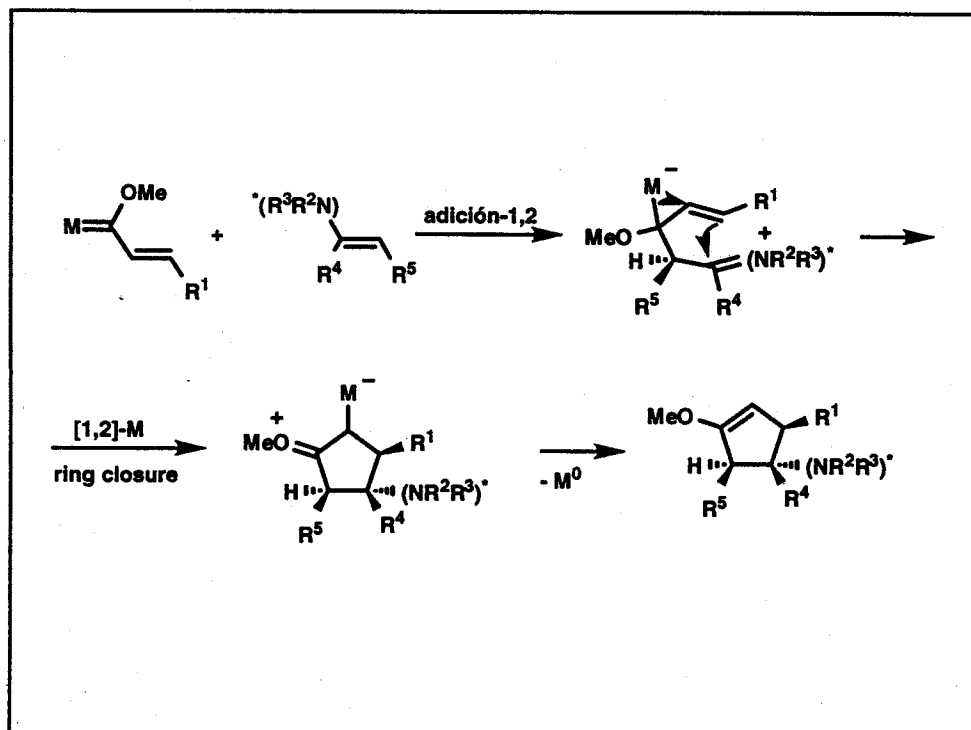
Ar	Enolate config.	R^1	R^2	% I	de(%) I	ee(%) II
Ph	E	(CH ₂) ₄		40	>99	95
Ph	E	(CH ₂) ₅		84	>99	93
Ph	Z	Me	Ph	89	>99	98
Ph	Z	Me	<i>p</i> -Cl-C ₆ H ₄	83	>99	96
Ph	Z	Et	Pr	75	69	93
2-furyl	E	(CH ₂) ₄		30	>99	93
2-furyl	Z	Me	Ph	75	>99	97

syn-STEREOSELECTIVE MICHAEL ADDITION

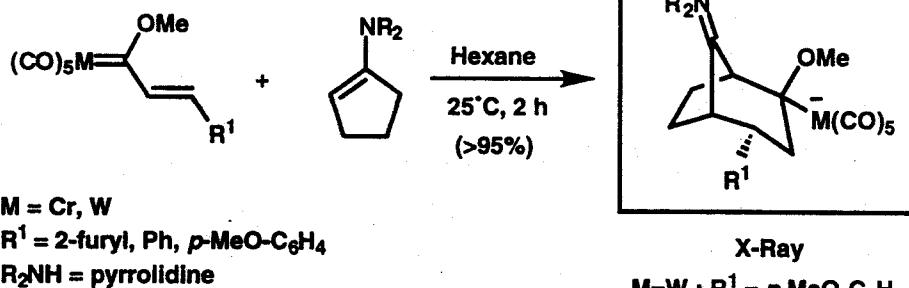
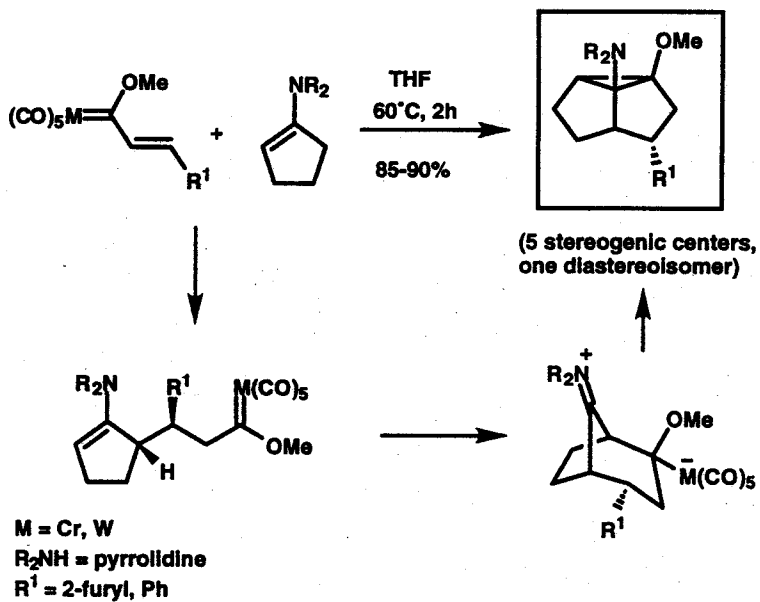


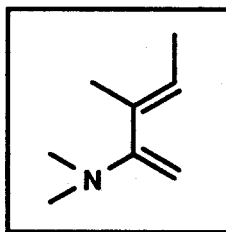
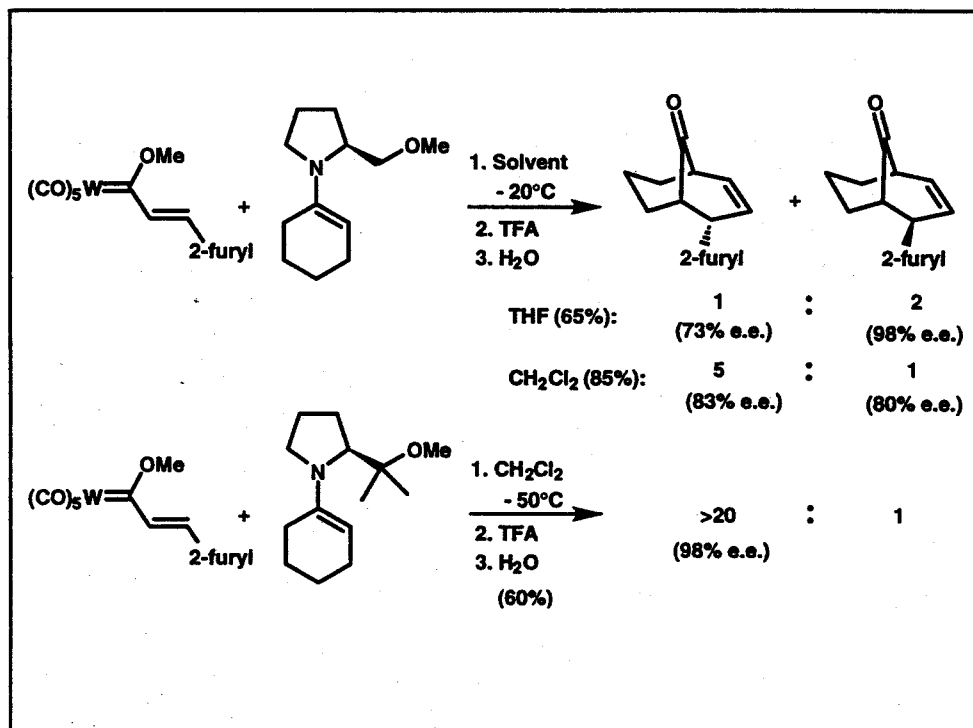
[3+2] CYCLOADDITION OF FISCHER ALKENYL CARBENES WITH ENAMINES





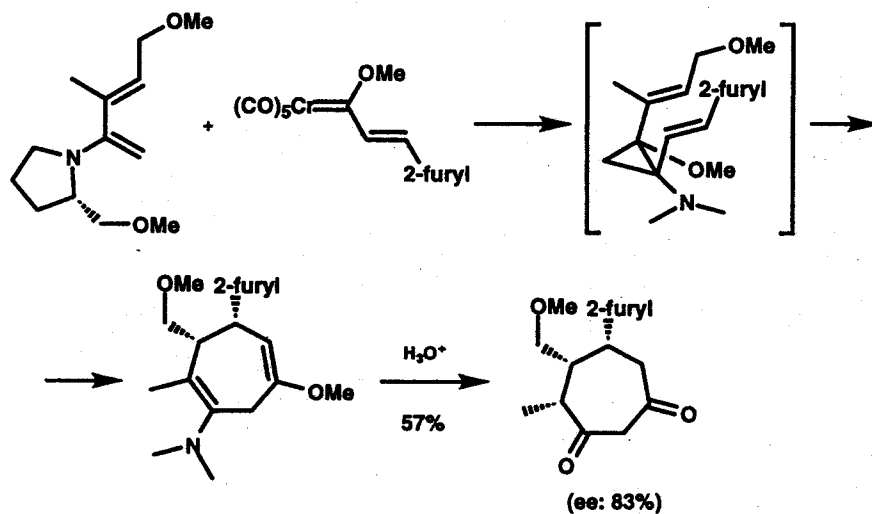
[3+3] CYCLOADDITION OF FISCHER ALKENYL CARBENES WITH ENAMINES



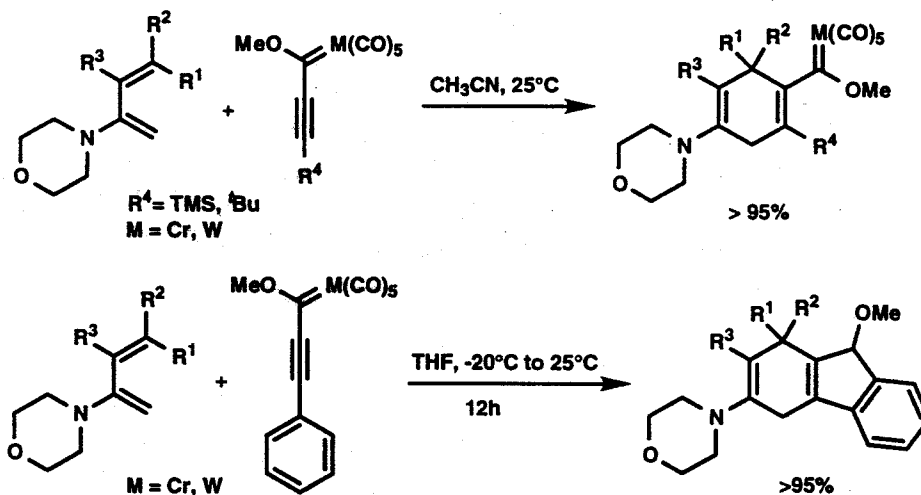


2-Amino-1,3-butadiene

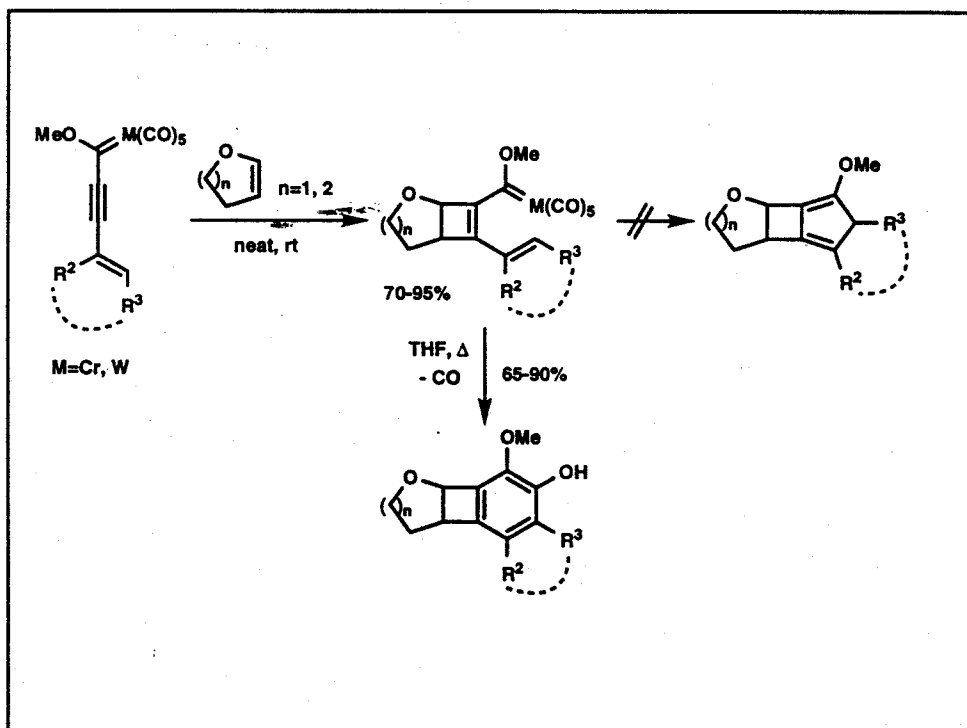
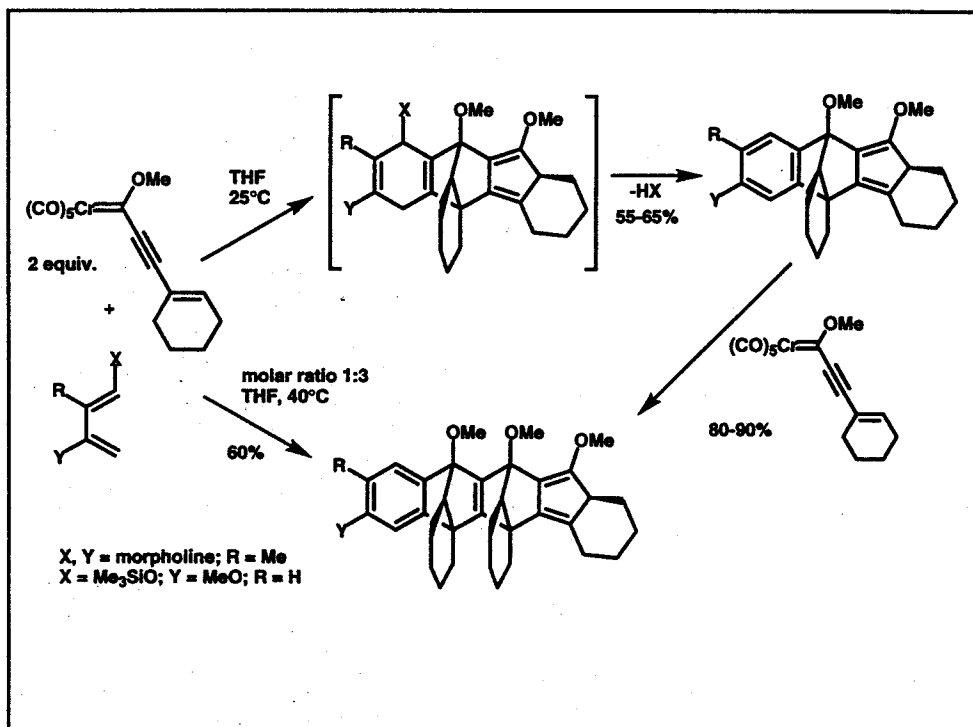
CHIRAL 2-AMINODIENES IN ASYMMETRIC [4+3] CYCLOADDITIONS



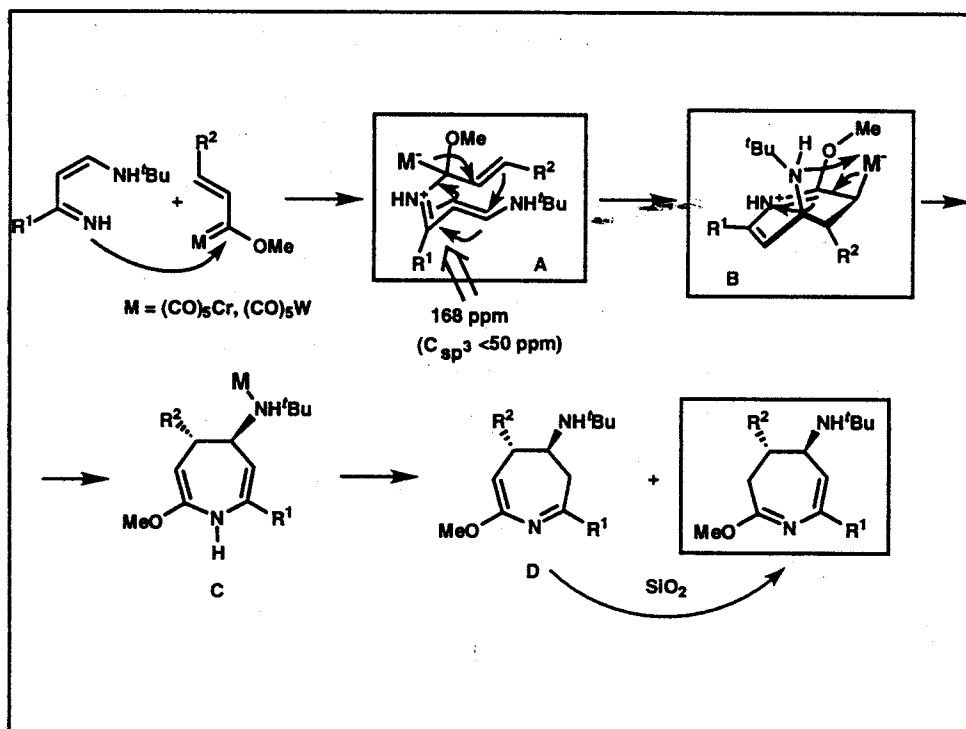
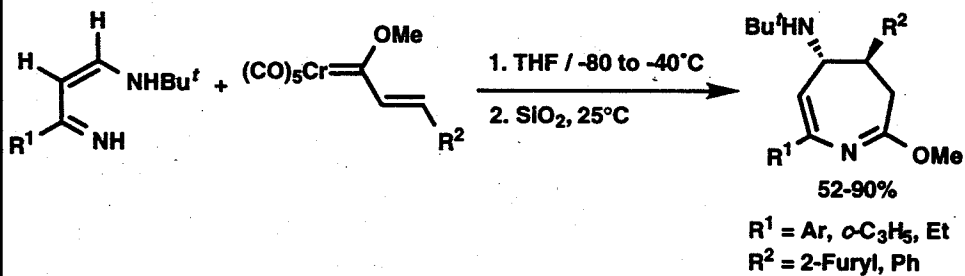
2-AMINO-1,3 BUTADIENES vs. ALKYNYL FISCHER CARBENE COMPLEXES



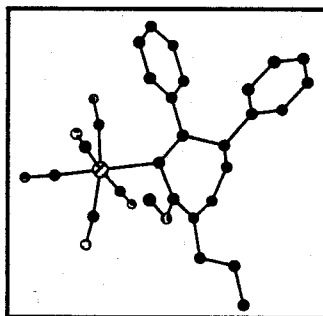
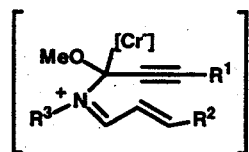
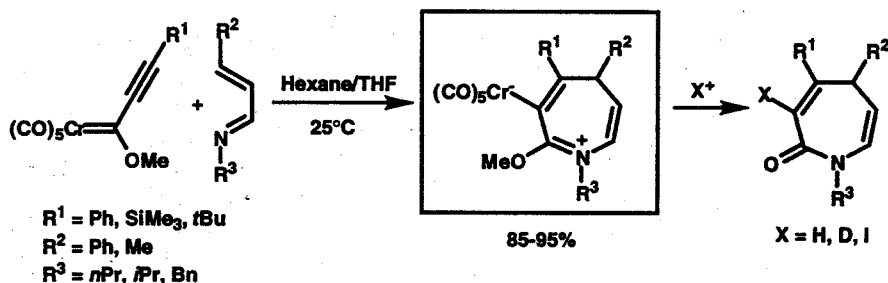
a part of the paper



[4+3] ANNULATION OF AZADIENES WITH FISCHER CARBENE COMPLEXES

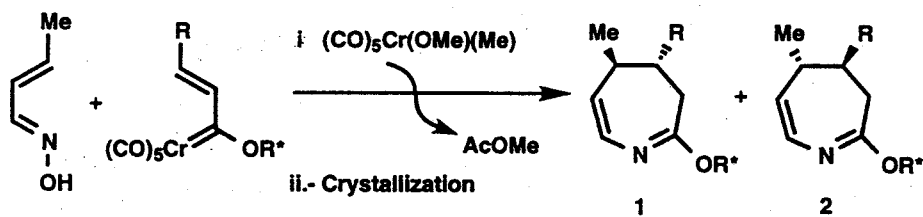


[4+3] CYCLOADDITION OF ALKYNYL FISCHER CARBENES



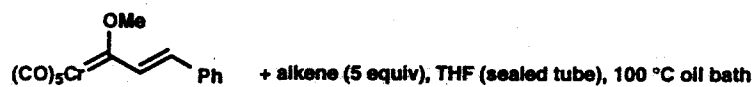
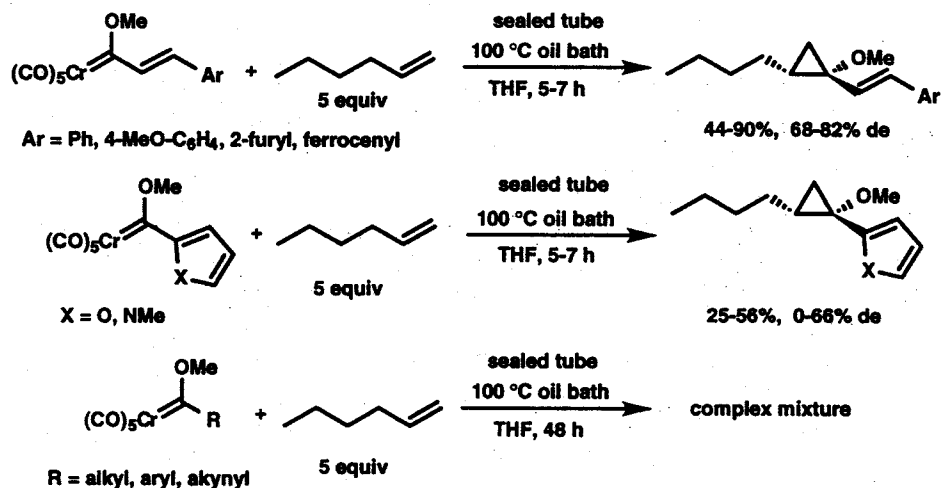
$\text{R}^1 = \text{R}^2 = \text{Ph}; \text{R}^3 = n\text{Pr}$

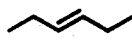
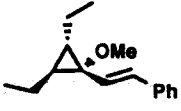

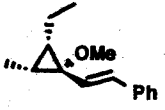

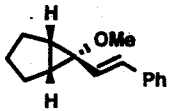
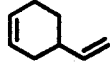


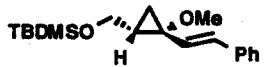
USE OF CHIRAL, NON RACEMIC CARBENE COMPLEXES



HOR*	R	Yield	1 + 2 Ratio	Isolated Product	Yield (d.e.)
a (-)-Menthol	Ph	87	70:30	1a	50% (>97%) (X-Ray)
b (-)-Menthol	2-Furyl	90	72:28	1b	48% (>97%)
c (+)-Menthol	Ph	80	30:70	2c	46% (>97%)

DIASTEREOSELECTIVE CYCLOPROPANATION OF SIMPLE ALKENES BY ALKENYL AND HETEROARYL FISCHER CARBENE OF CHROMIUM



alkene	cyclopropane	yield (%)	de (%)
		40	-
		40	>96
		70	>96
		52	-
TBDMSO (1 equiv) 	TBDMSO 	95	73

