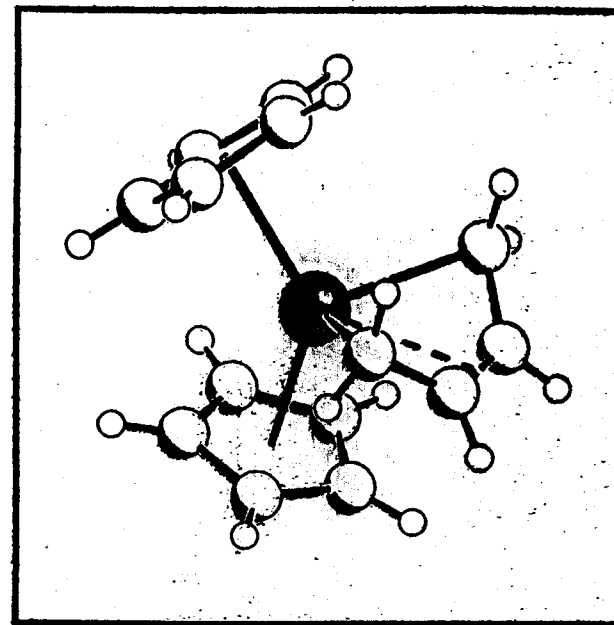
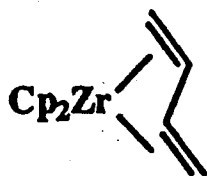


Zr-C1/C4 248.0 pm

Zr-C2/C3 231.0 pm

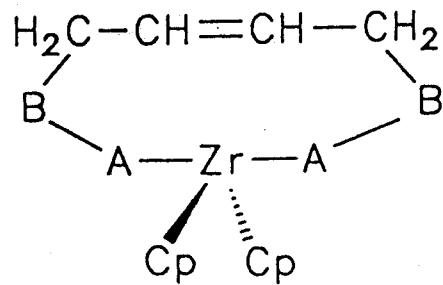
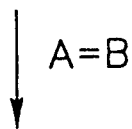
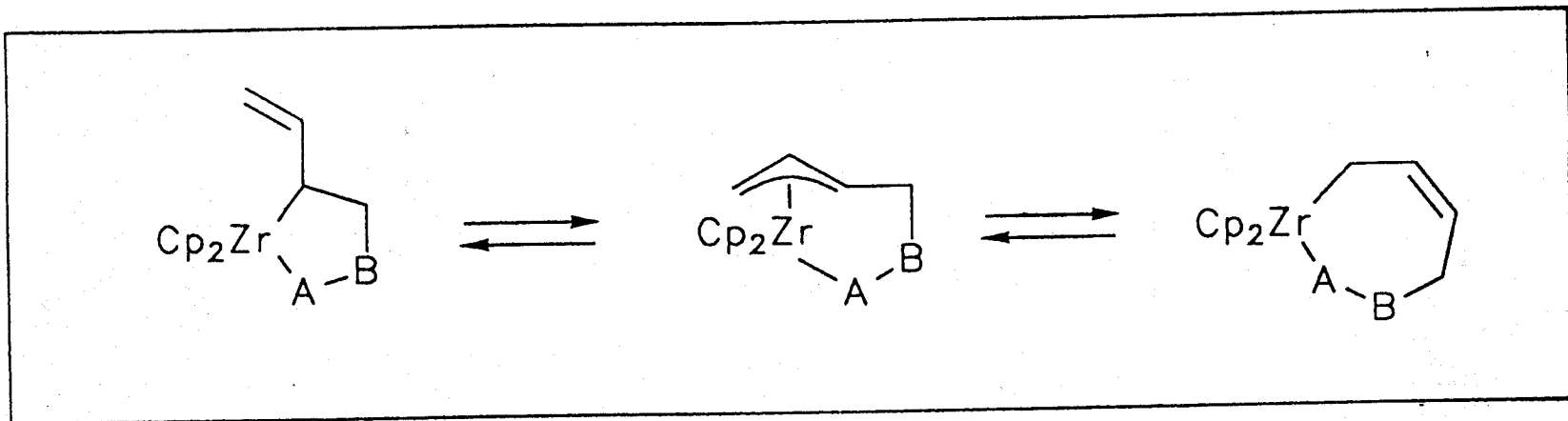
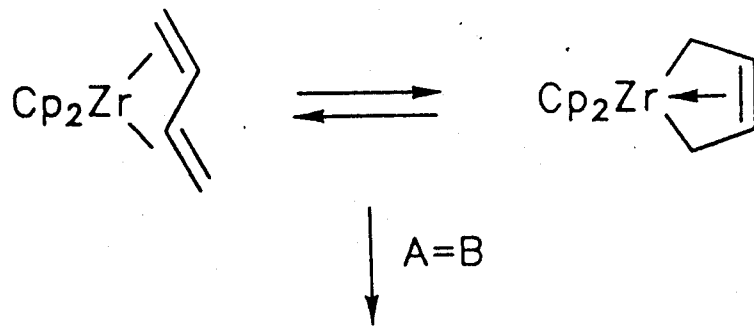
C¹-C²-C³-C⁴
137.5 138.1 136.4 pm

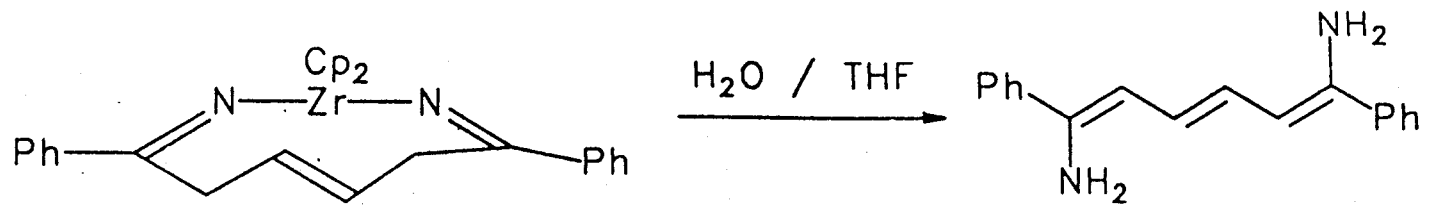


Zr-C1/C4 229.6 pm

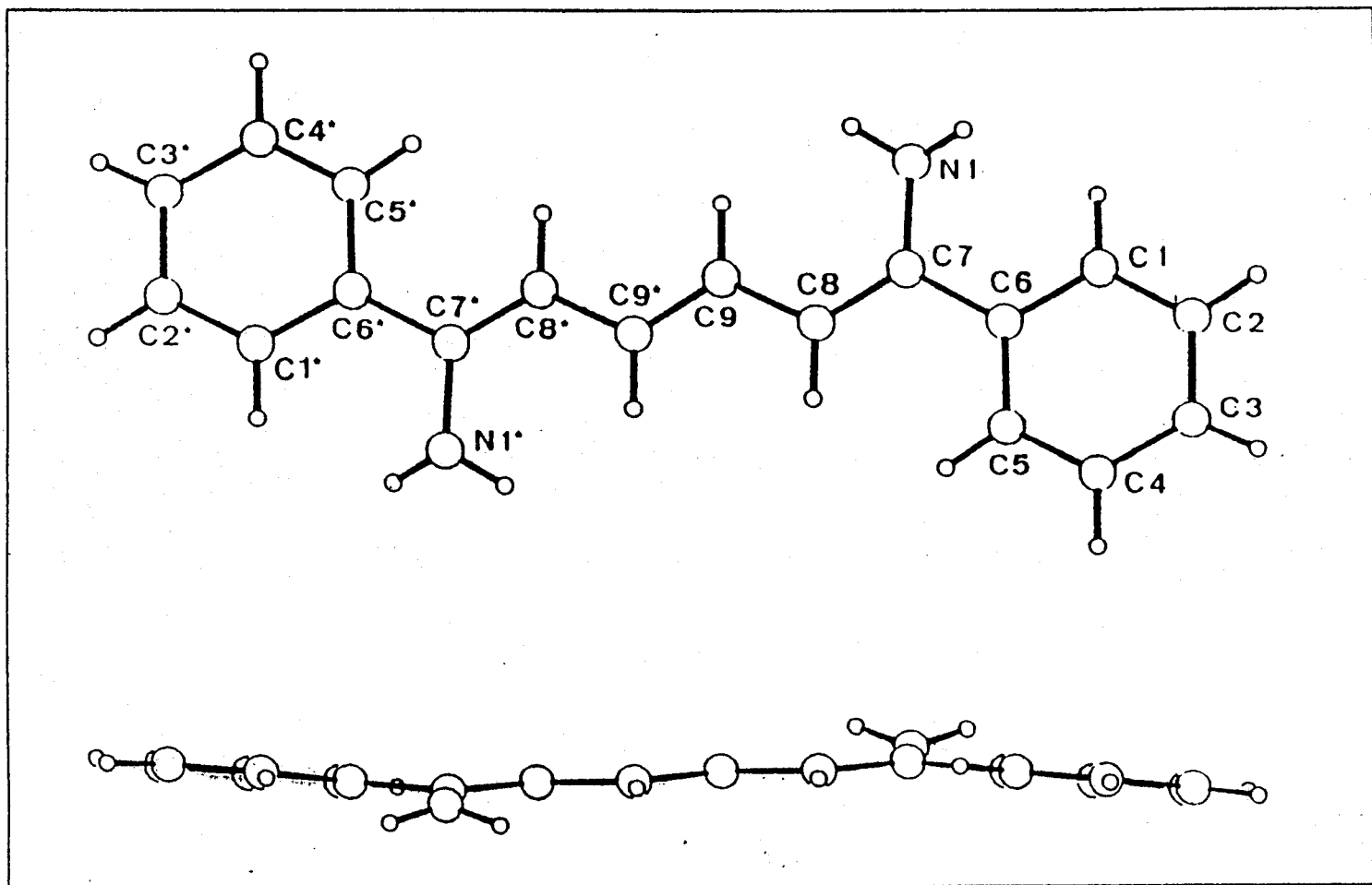
Zr-C2/C3 247.1 pm

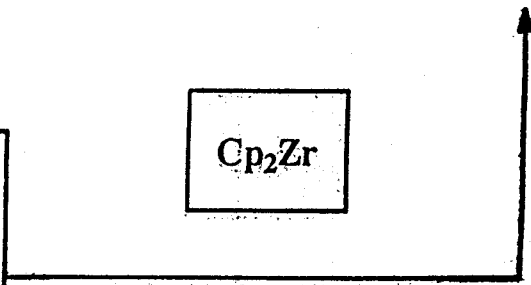
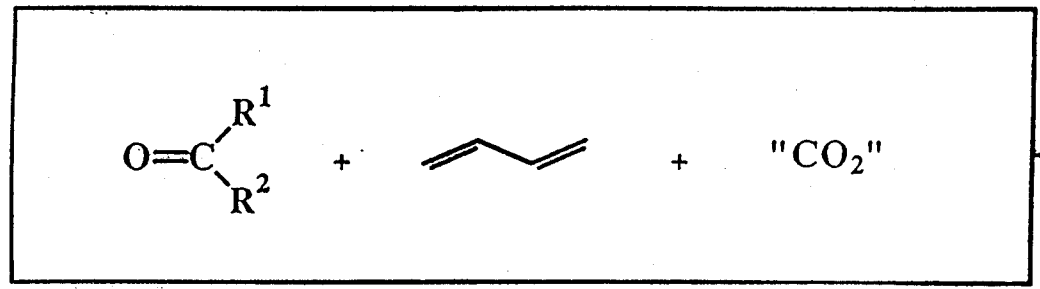
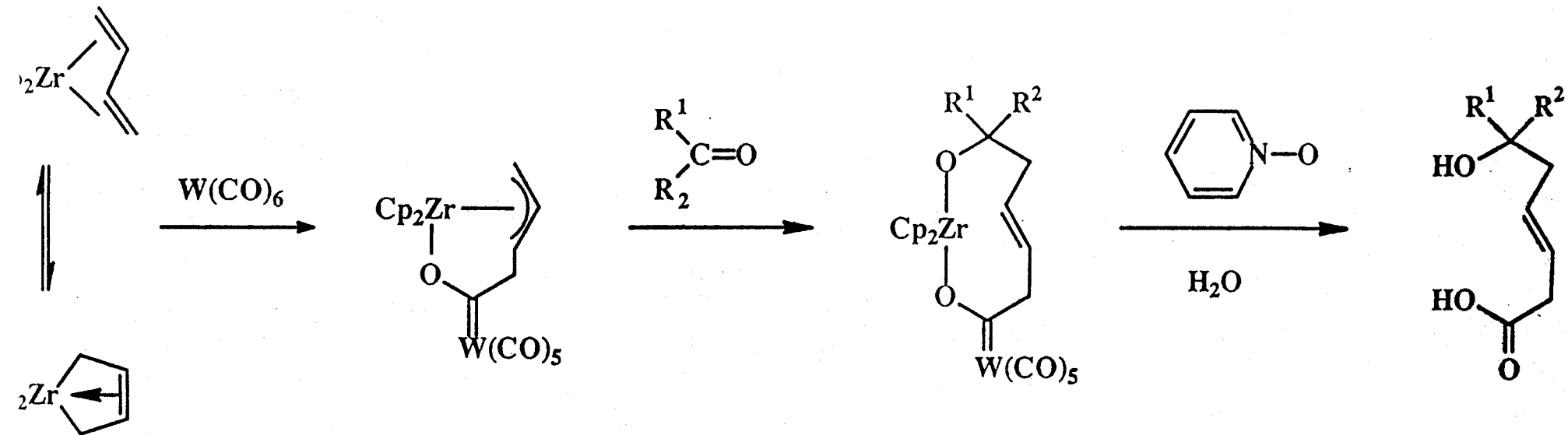
C¹-C²-C³-C⁴
139.9 135.2 139.5 pm

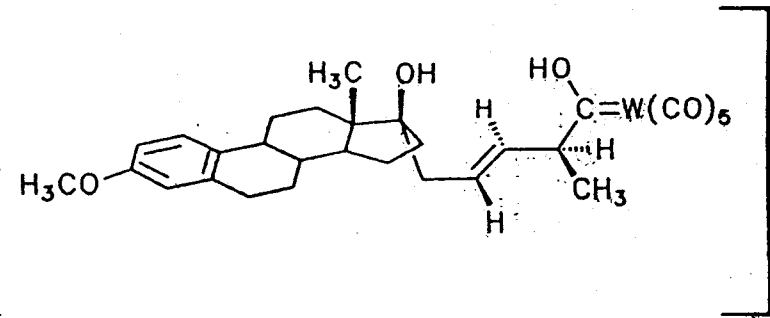
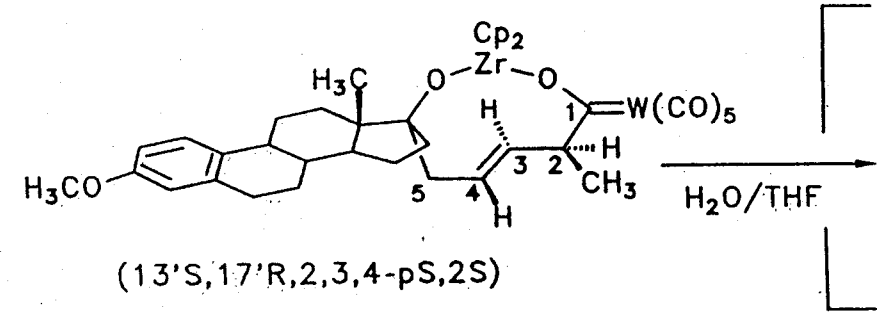
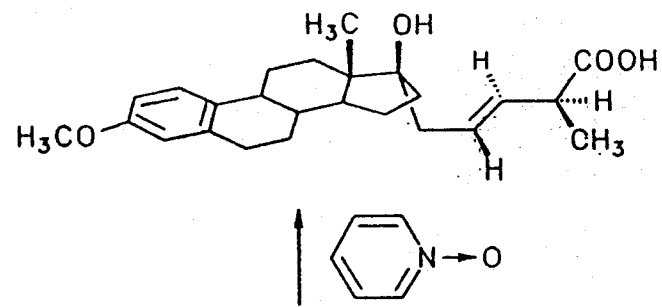
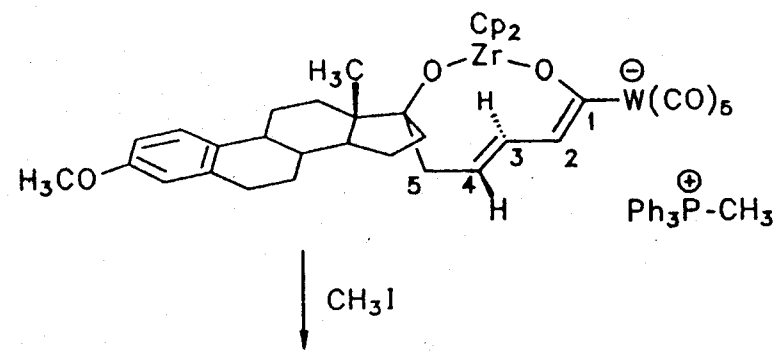
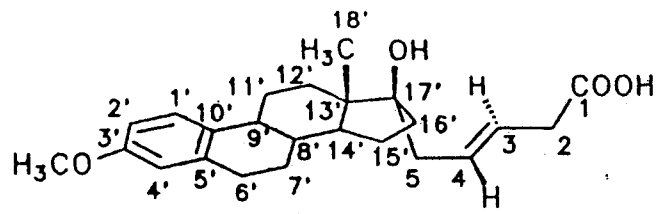
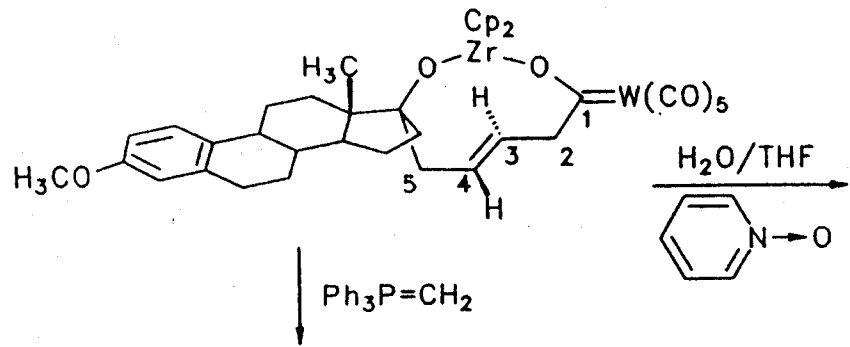


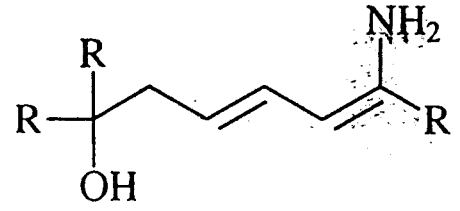
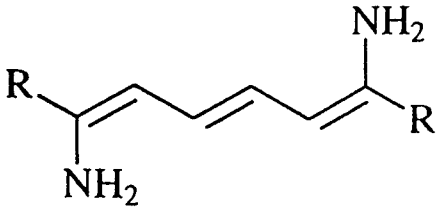
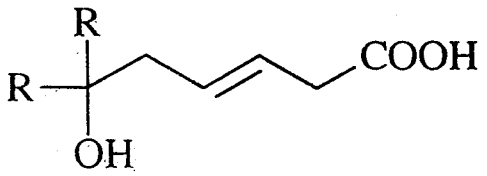
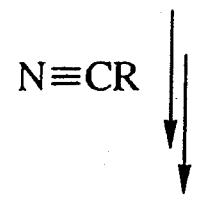
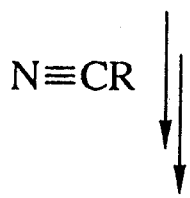
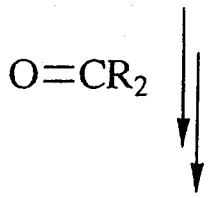
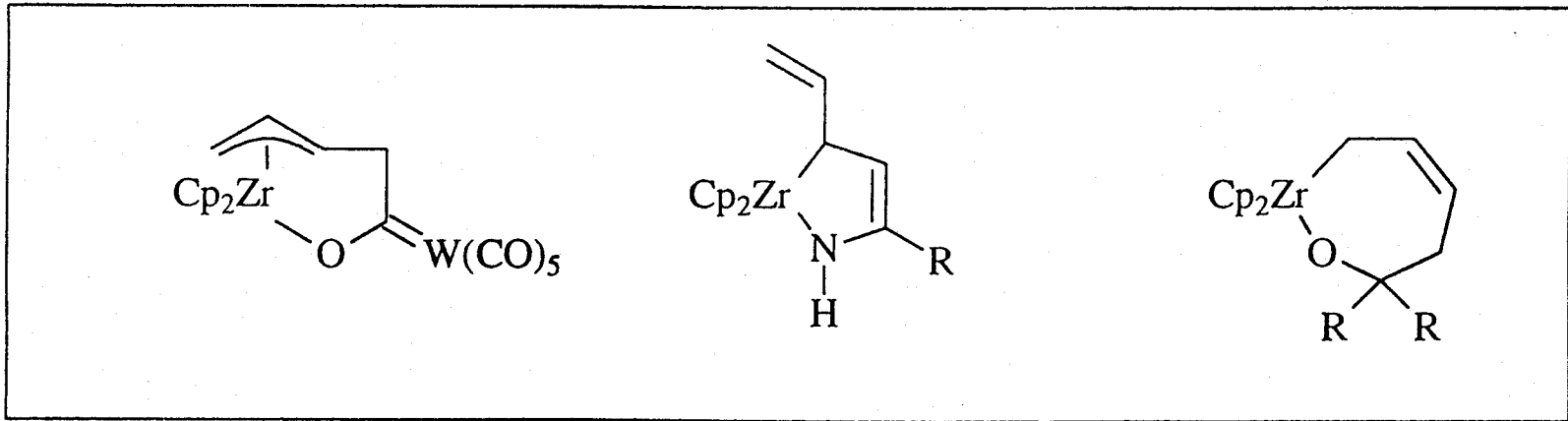
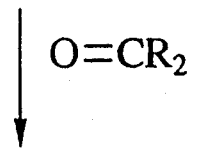
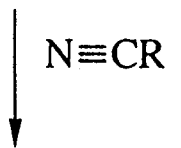
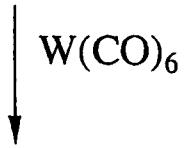
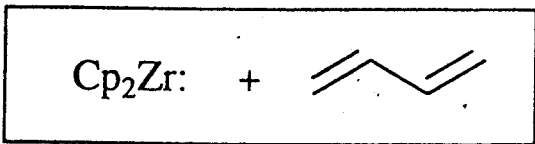


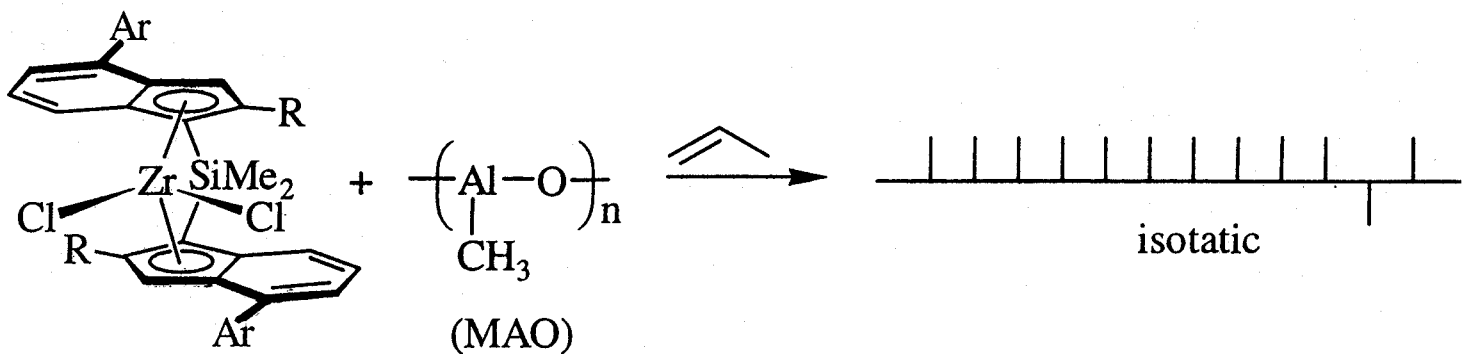
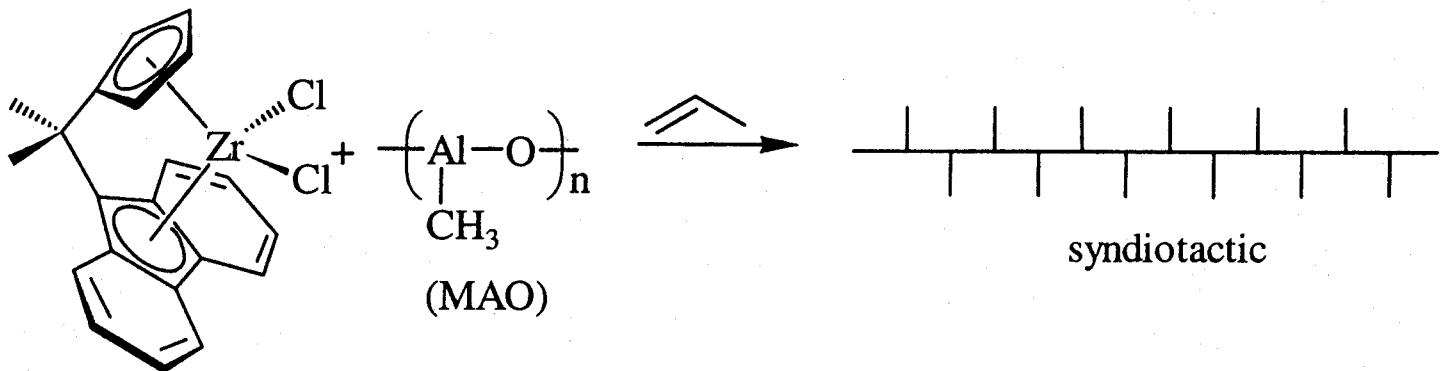
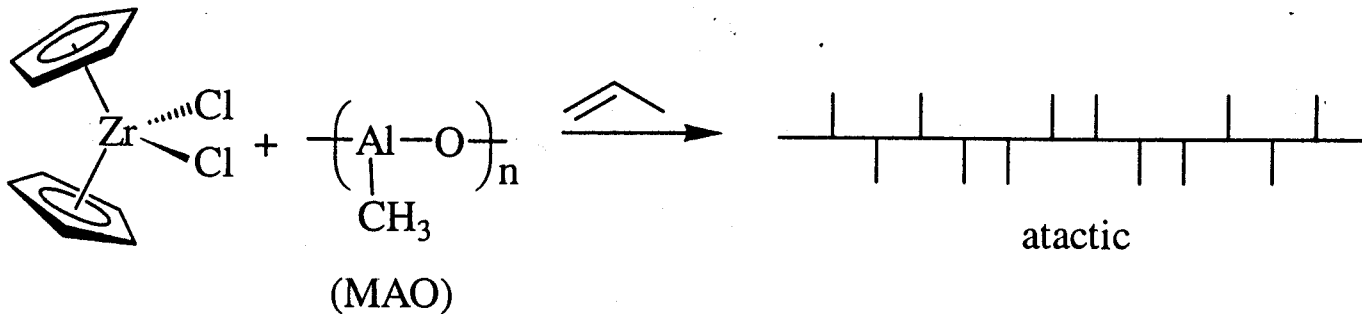
91% yield (350 mg), m.p. = 140°C
 λ_{max} = 403 nm, ϵ = 27000 (CH₂Cl₂)





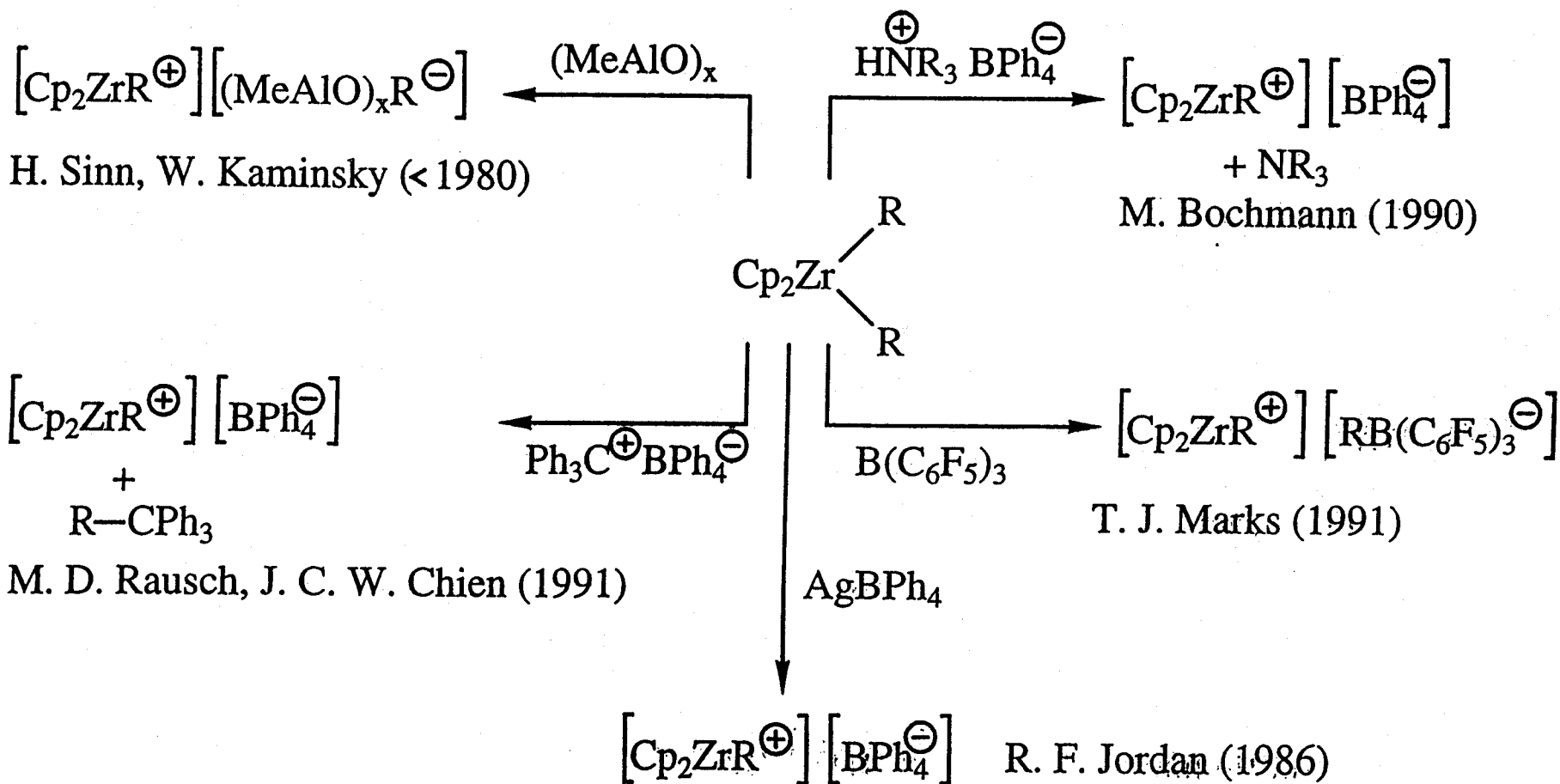
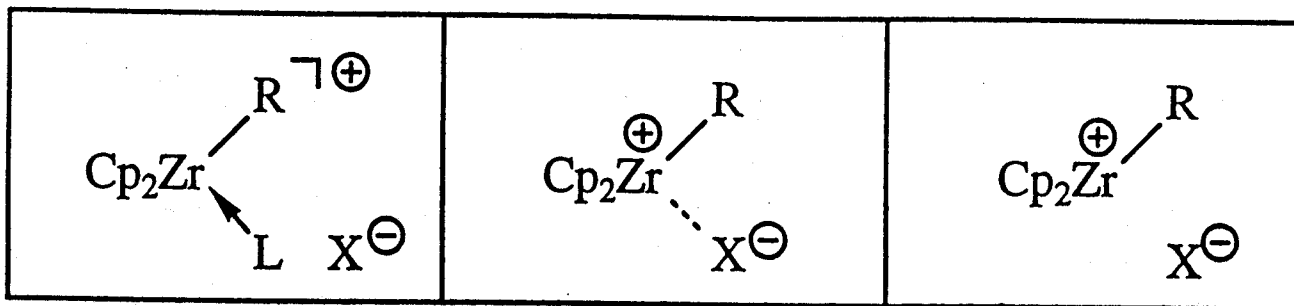


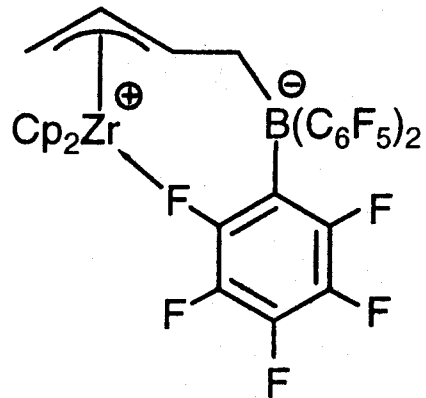
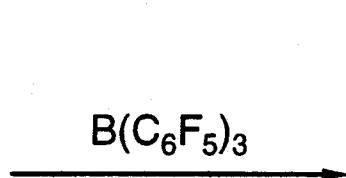
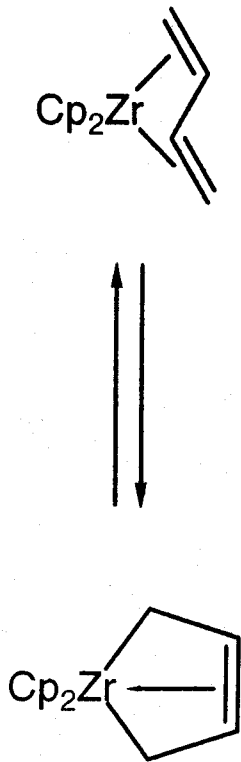




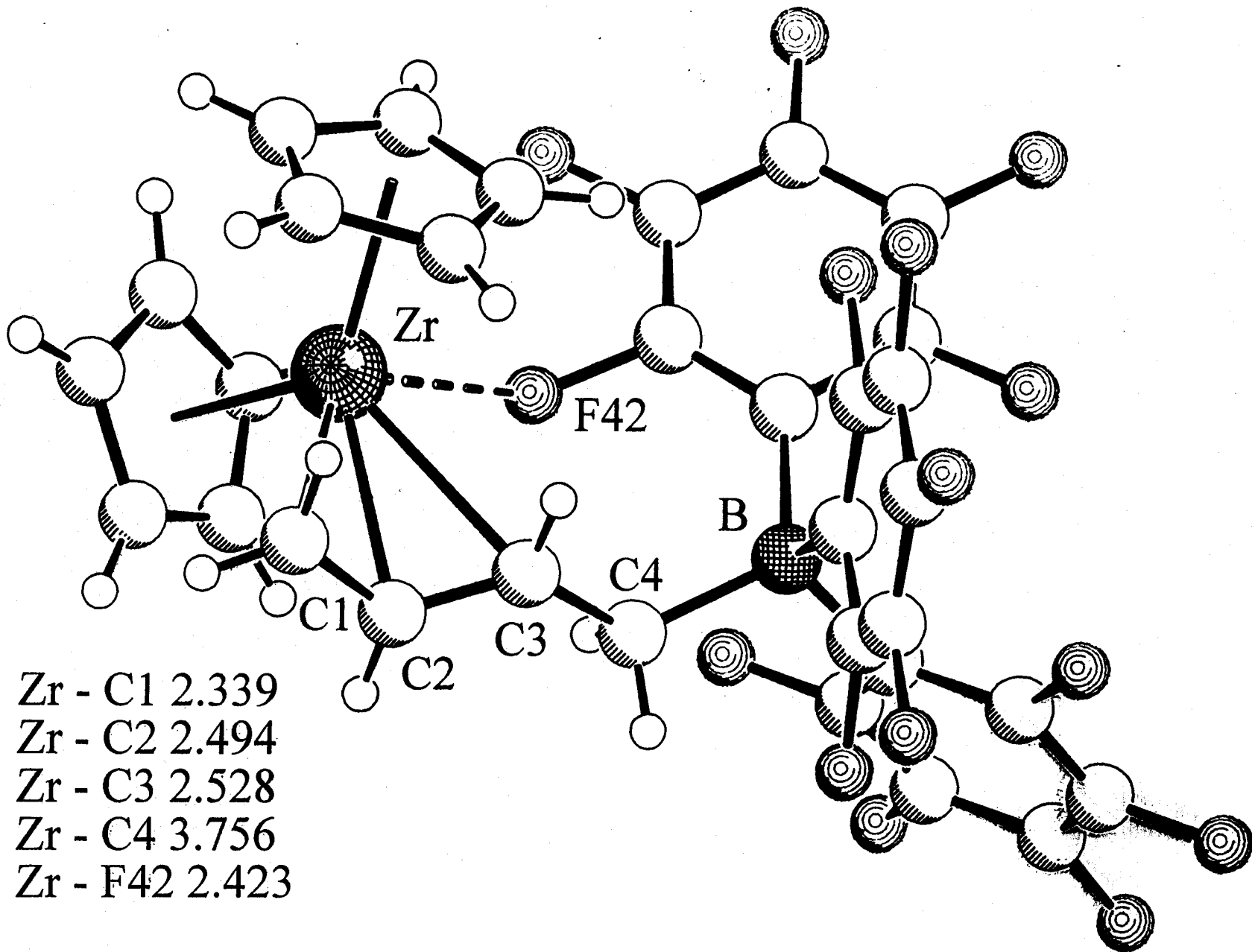
$\text{R} = \text{CH}_3$

Sinn, Kaminsky, Brintzinger, Spaleck, Herrmann, Ewen, Razawi, and others





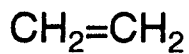
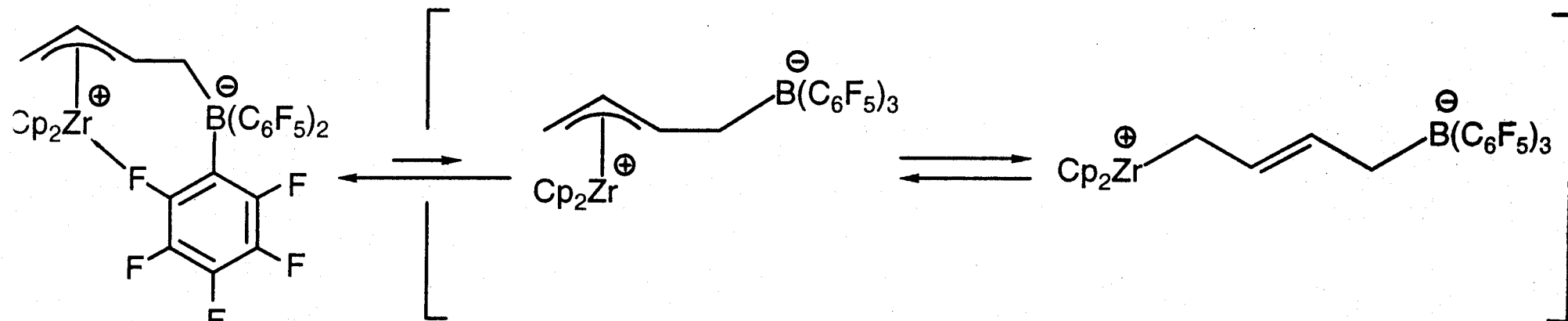
^{19}F - NMR: -126.4, -130.6, -131.8
 (o-F; 193 K) -134.0, -137.5, -213.2 ppm





(toluene)

$\Delta G^\ddagger(233 \text{ K}) = 8.1 \pm 0.5 \text{ kcal/mol}$

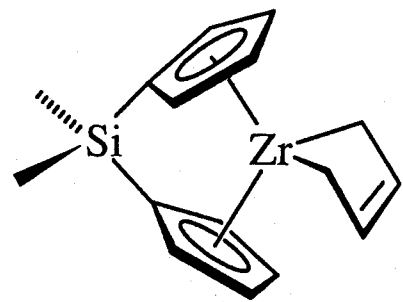


polyethylene $\text{-(CH}_2\text{-CH}_2\text{)}_n\text{-}$

$\text{-(CH(CH}_3\text{)-CH}_2\text{)}_n\text{-}$ polypropylene

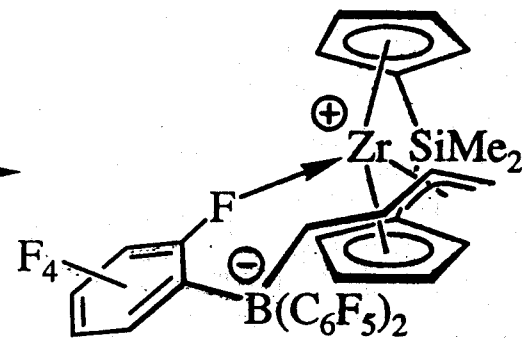
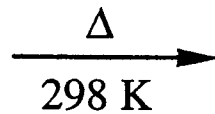
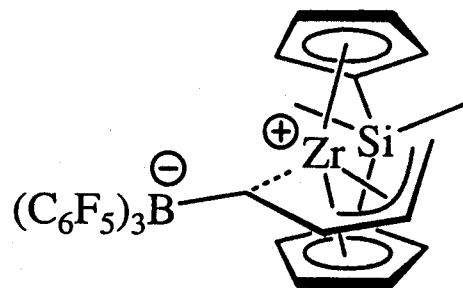
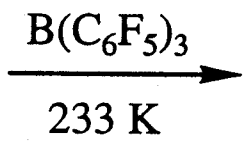
act.: 135 g / mmol [Zr] · h
(20°C, 1 bar)

2.2 kg / mmol [Zr] · h
(70°C)

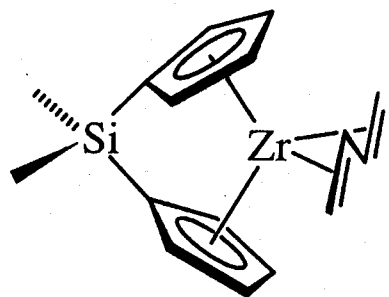


s-cis

+



$\Delta G^\ddagger = 21.5\text{ kcal/mol}$

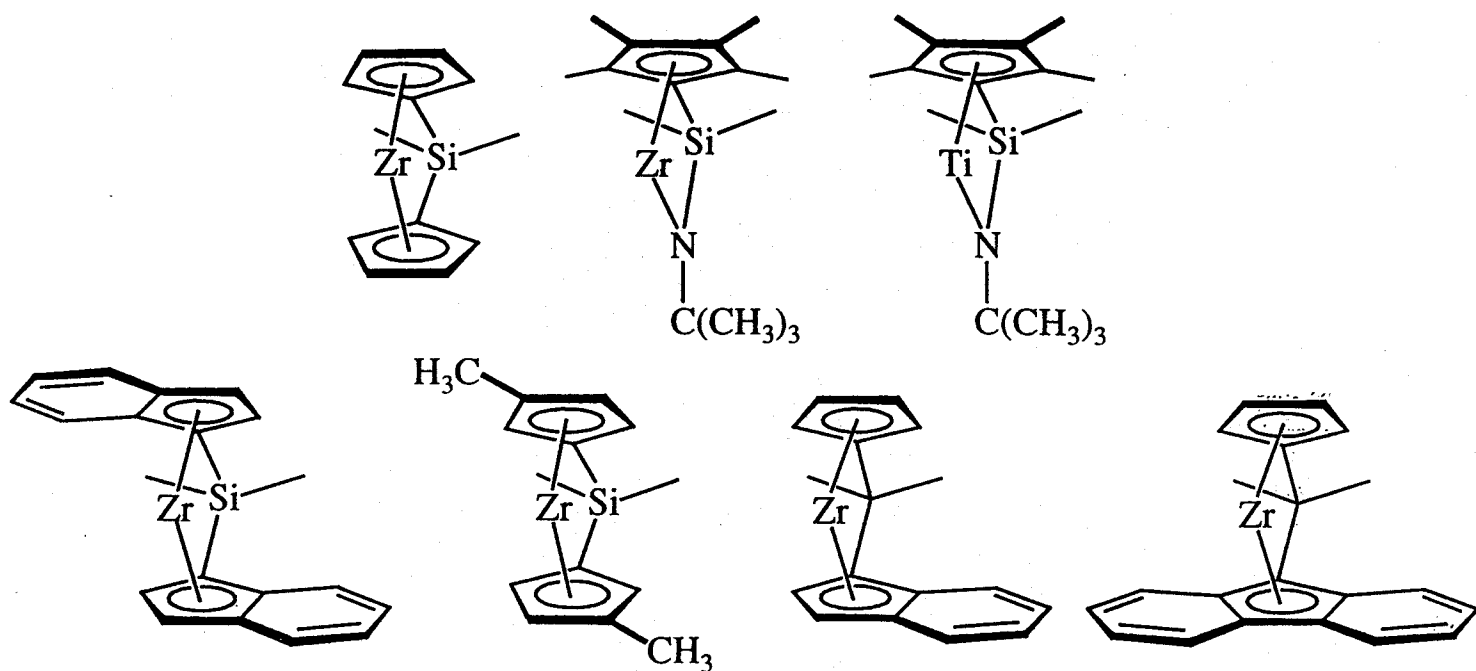


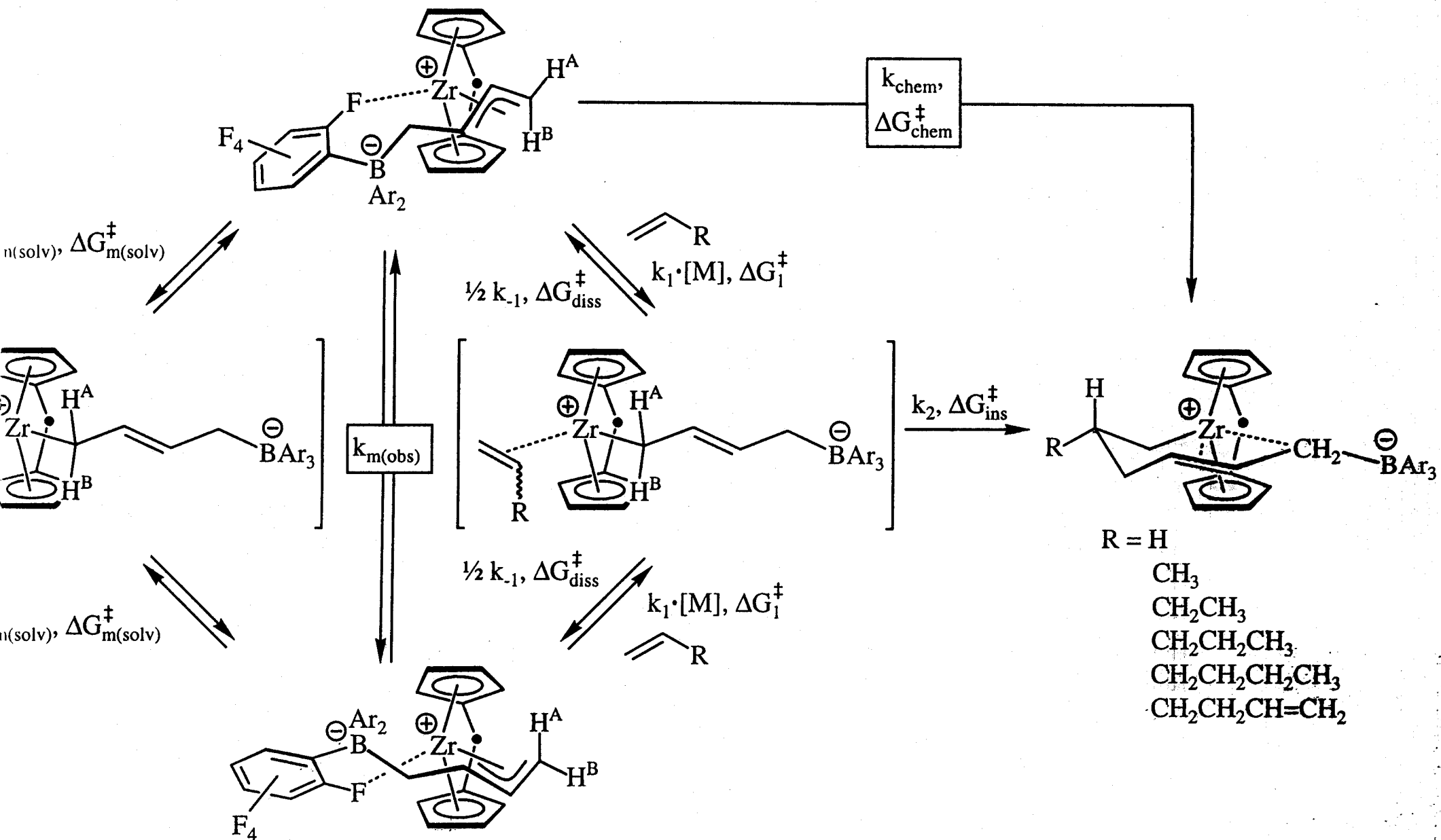
s-trans

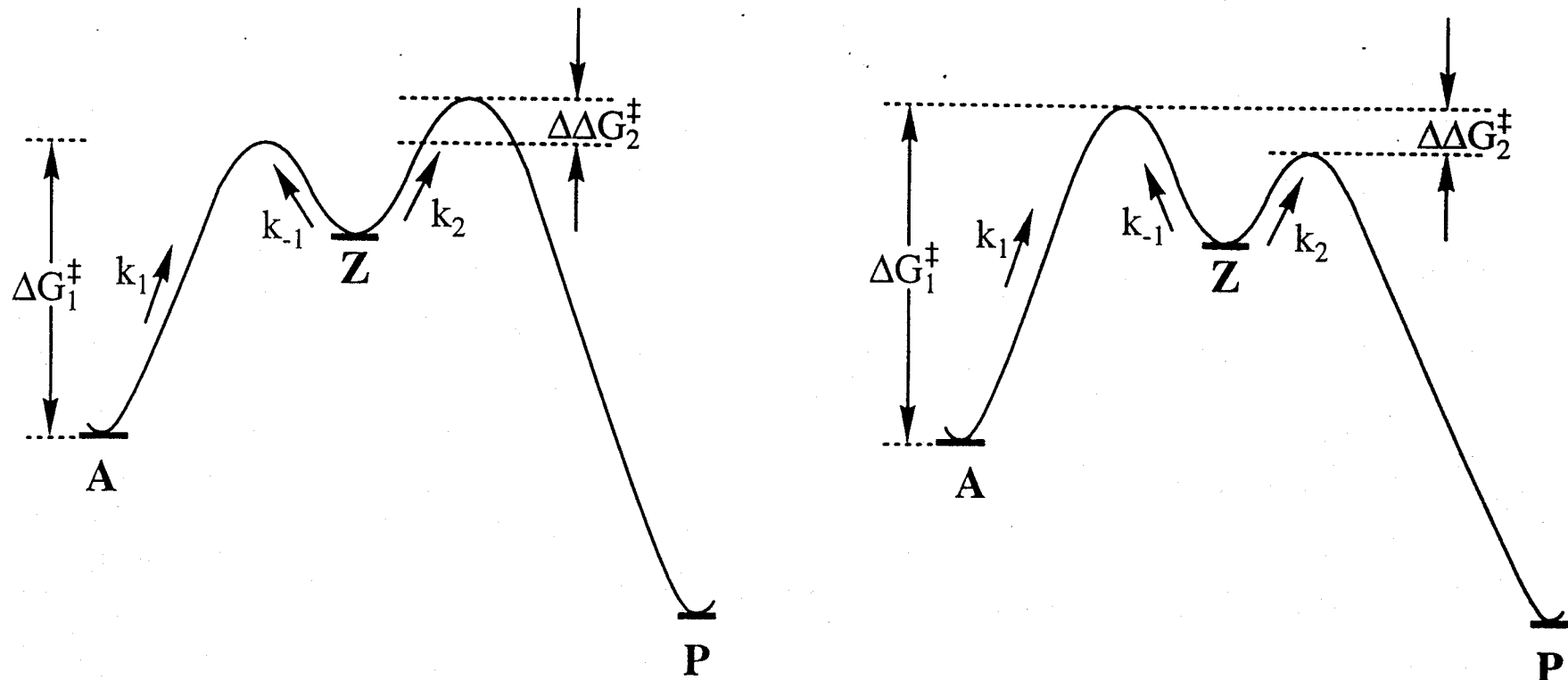
Ethene Polymerization

metallocene	activator	B/Zr (Al/Zr)	activity
$[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{Zr}(\text{C}_4\text{H}_6)$	$\text{B}(\text{C}_6\text{F}_5)_3$	1.05	1550
$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{Zr}(\text{C}_4\text{H}_6)^*$	$\text{B}(\text{C}_6\text{F}_5)_3$	1.02	30
$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{Ti}(\text{C}_4\text{H}_6)^*$	$\text{B}(\text{C}_6\text{F}_5)_3$	1.03	390
$[\text{Me}_2\text{Si}(\text{Ind})_2]\text{Zr}(\text{C}_4\text{H}_6)$	$\text{B}(\text{C}_6\text{F}_5)_3$	1.24	2310
$[\text{Me}_2\text{Si}(3\text{-Me-C}_5\text{H}_3)_2]\text{Zr}(\text{C}_4\text{H}_6)$	$\text{B}(\text{C}_6\text{F}_5)_3$	1.03	3370
$[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{Ind})]\text{Zr}(\text{C}_4\text{H}_6)$	$\text{B}(\text{C}_6\text{F}_5)_3$	1.21	340
$[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{Ind})]\text{ZrCl}_2$	MAO	1065	410
$[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{Flu})]\text{Zr}(\text{C}_4\text{H}_6)$	$\text{B}(\text{C}_6\text{F}_5)_3$	1.10	114
$[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{Flu})]\text{ZrCl}_2$	MAO	1117	147

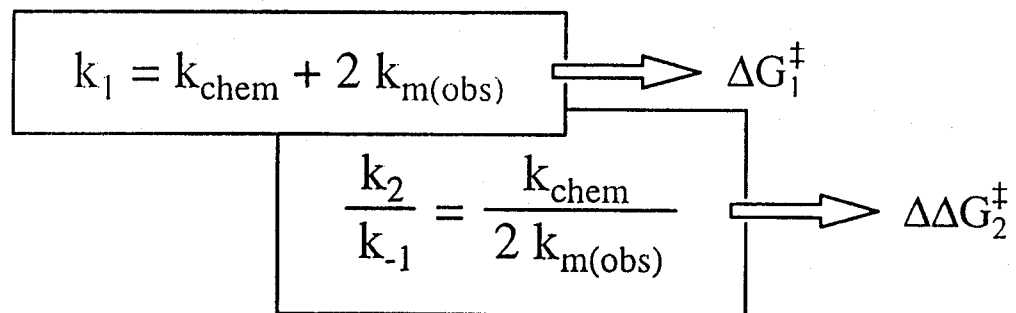
at 40°C, activity in g polymer/mmol[Ti/Zr]·h·bar; * at 90°C



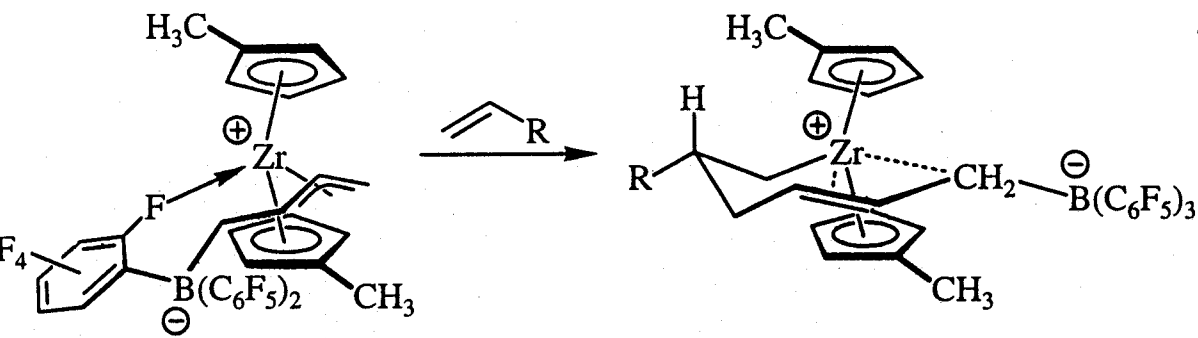
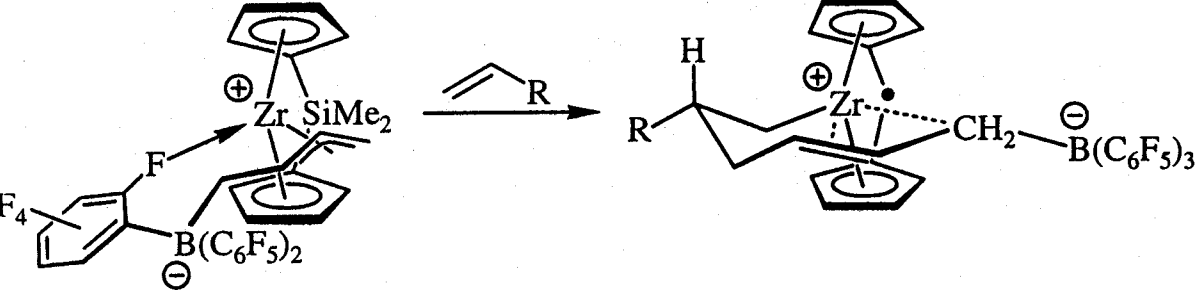
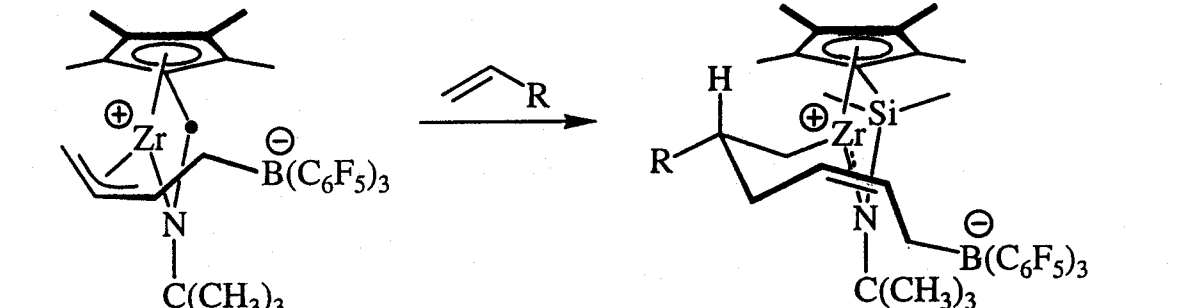


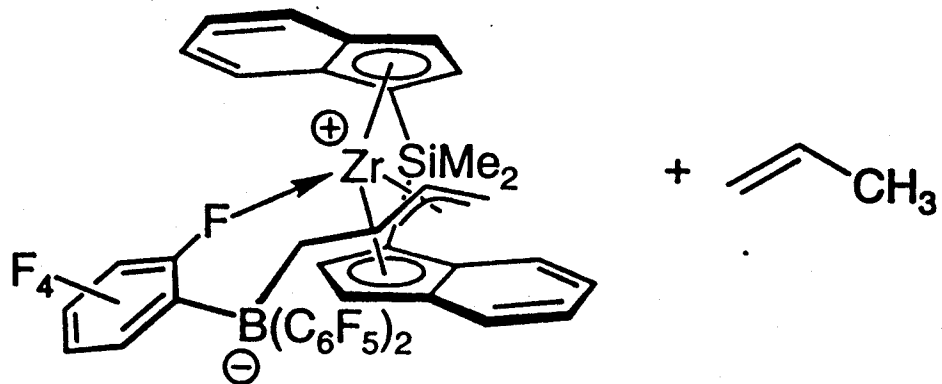


$$k_{m(\text{obs})} = \frac{1}{2} \frac{k_1}{1 + \Delta} ; k_{\text{chem}} = k_1 - \frac{k_1}{1 + \Delta} ; \Delta = \frac{k_2}{k_{-1}}$$



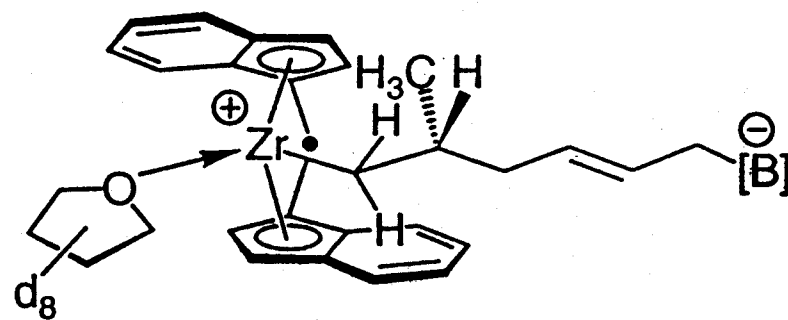
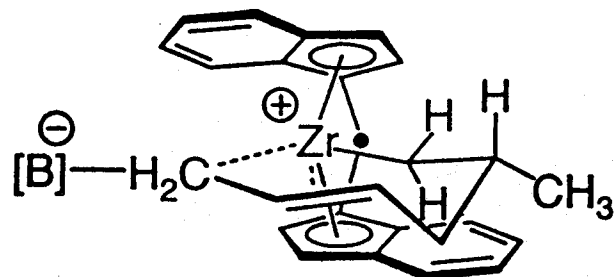
Stoichiometric 1-Butene (Propene) Insertion Reactions

	$\Delta G^{\ddagger}_{\text{chem}}$	ΔG^{\ddagger}_1	$\Delta\Delta G^{\ddagger}_2$	k_1/k_2	$\Delta G^{\ddagger}_{\text{ins}}$
	18.4 (17.3)	17.1 (16.5)	1.2 (0.7)	8 (3)	10.8 (10.9)
	14.9	13.2	1.7	31	10.6
	19.0 (18.8)	16.5 (16.4)	2.5 (2.4)	85 (83)	9.7 (9.7)

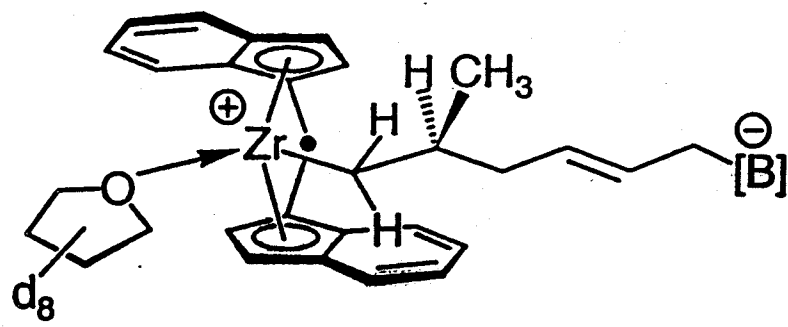
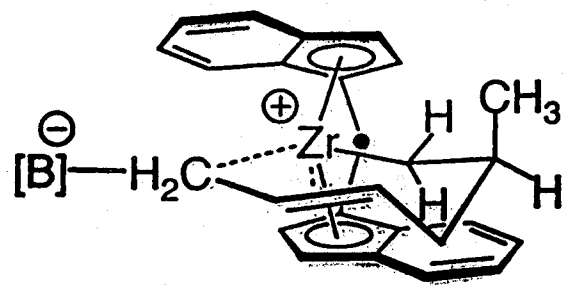


-15°C
 \downarrow
 $\text{d}_8\text{-toluene}$

$[\text{B}] = \text{B}(\text{C}_6\text{F}_5)_3$; $\bullet = \text{SiMe}_2$

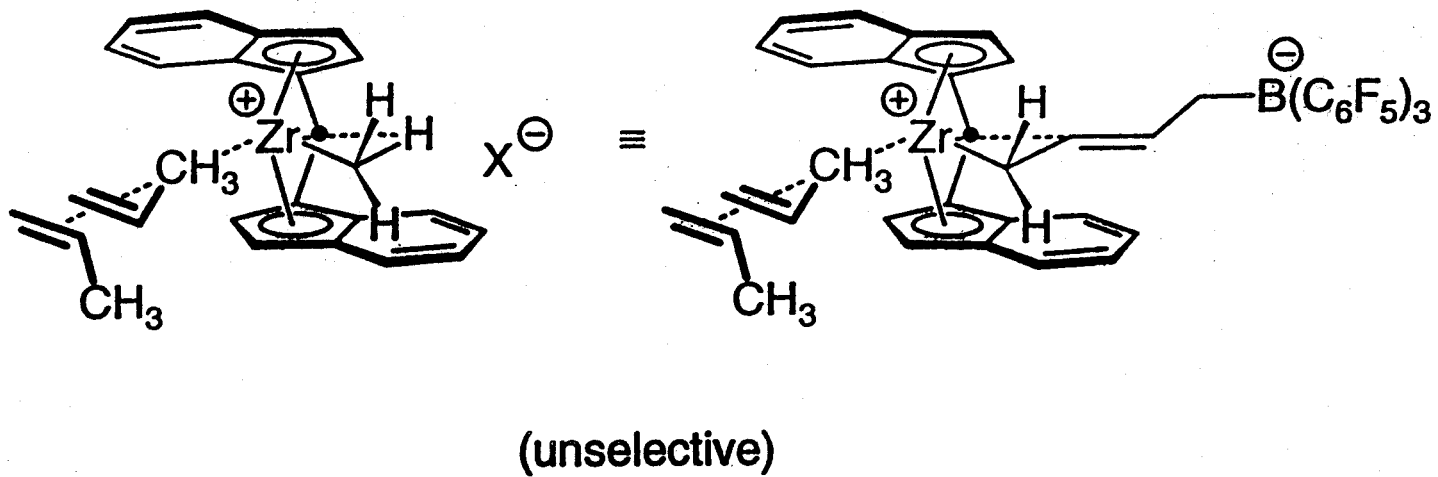
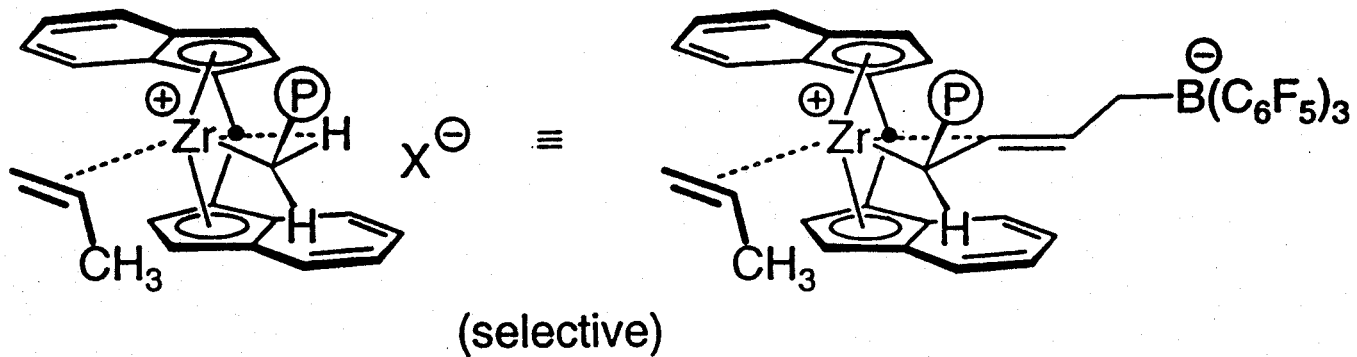


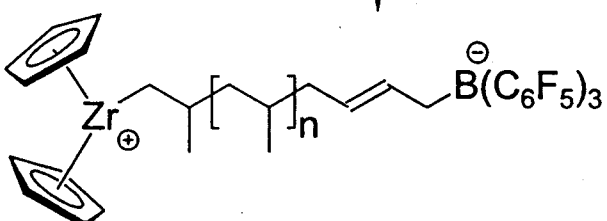
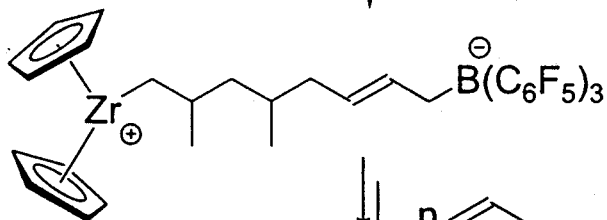
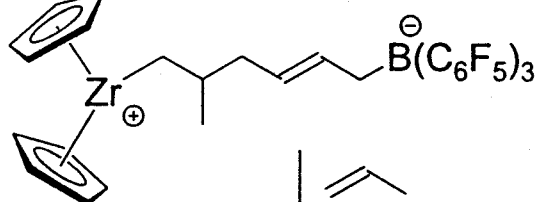
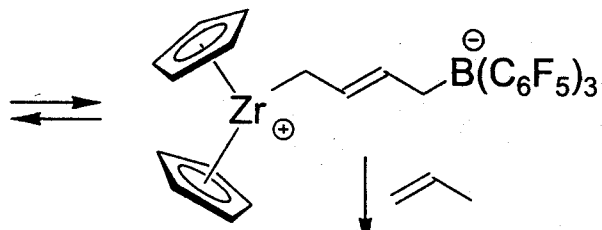
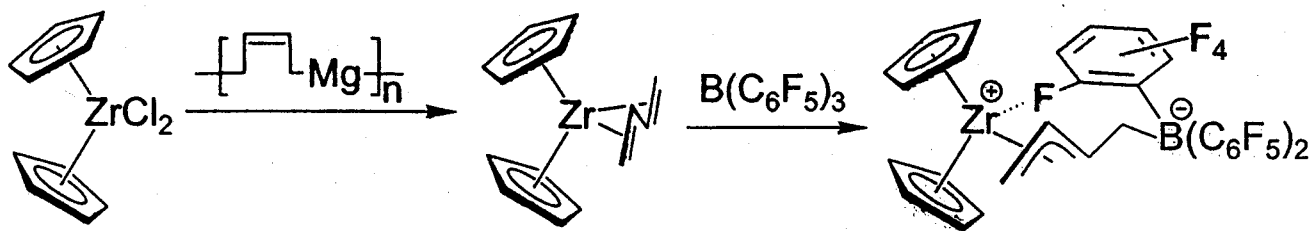
$\xrightarrow{\text{d}_8\text{-THF}}$



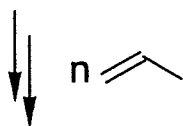
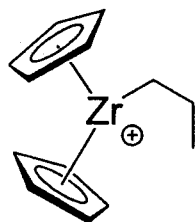
$\approx 60 : 40$

$\approx 60 : 40$



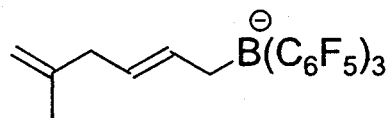


chain transfer
(H₂O)

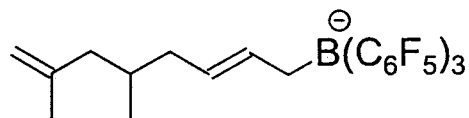


polypropylene

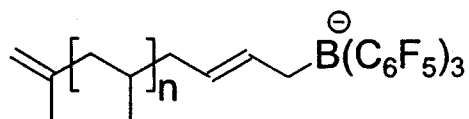
chain transfer products:



m/z = 607



m/z = 607 + 42 = 649



m/z = 607 + (n x 42)