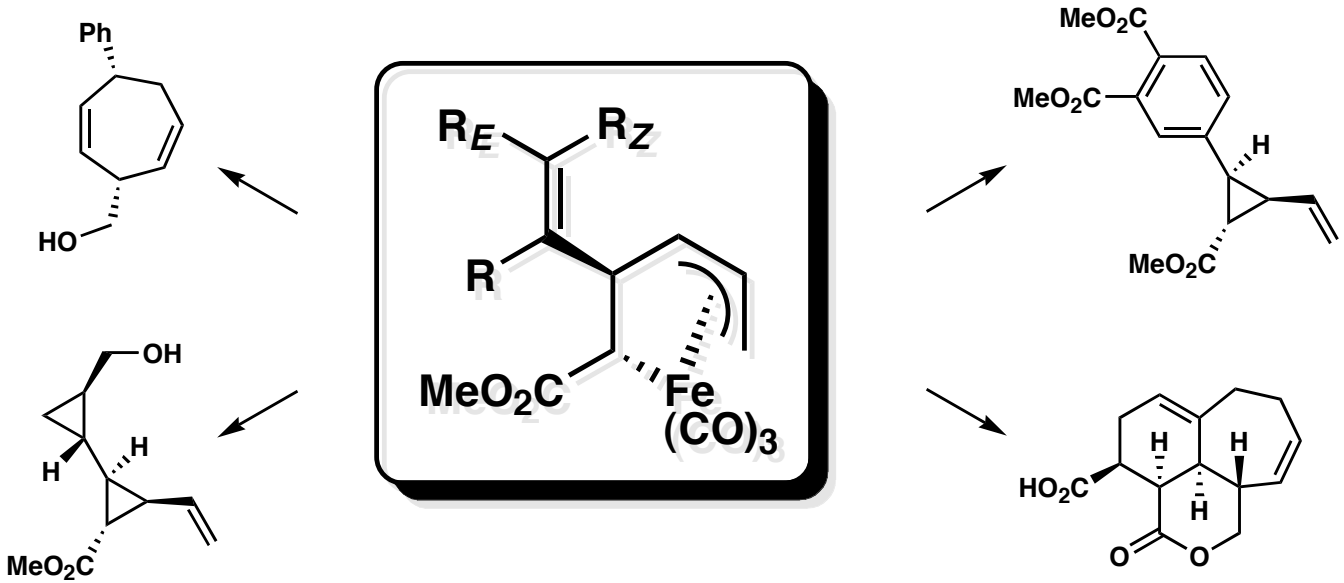
Reactivity of (2-Alkenyl-3-pentene-1,5-diyl)iron Complexes: Preparation of Functionalized Vinylcyclopropanes and Cycloheptadienes

Rajesh K. Pandey, Lizhu Wang, Nathaniel J. Wallock, Sergey Lindeman, and William A. Donaldson*

J. Org. Chem., **2008**, *73* (18), 7236–7245



Adam T. Hoye
Current Literature
Sept. 27th, 2008

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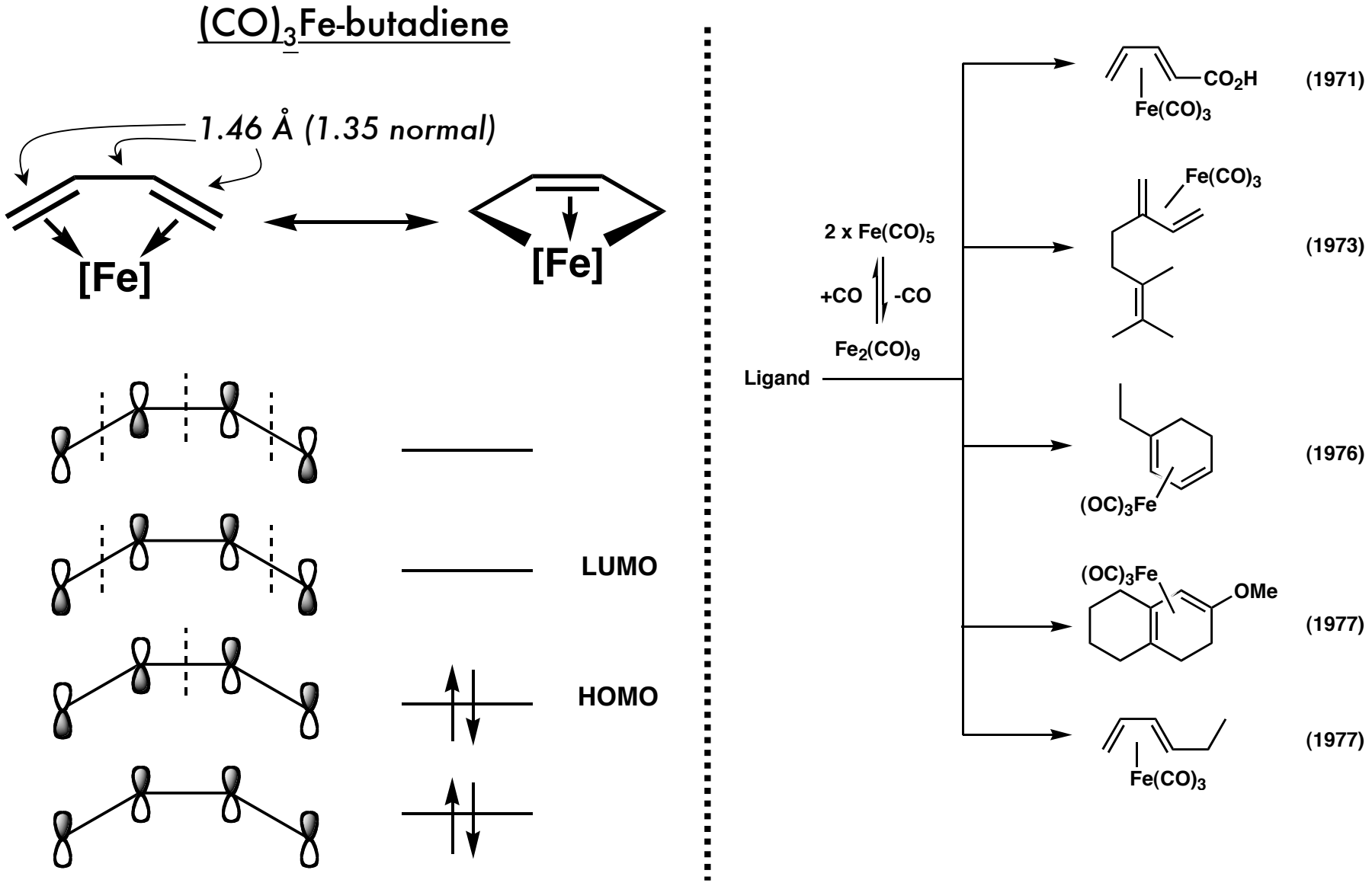
Dienyliron complexes



Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*. 3rd ed. Wiley & Sons, NY. 2001.

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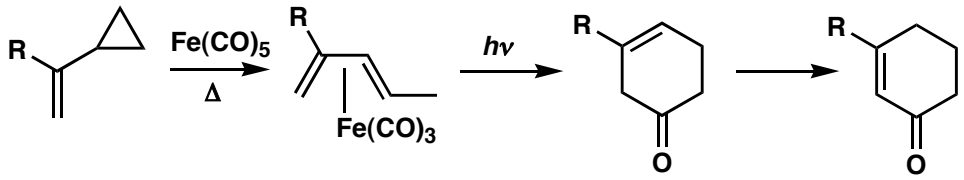
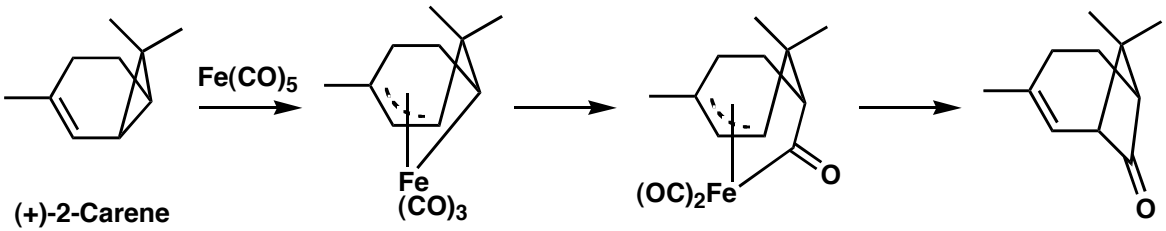
Uses of dienyliron complexes

Rearrangements and CO-insertions



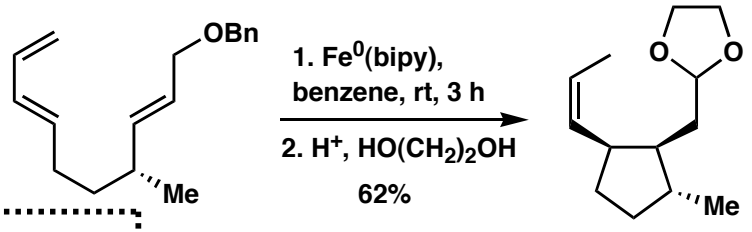
Aumann, R. *J. Am. Chem. Soc.* **1974**, *96*, 2631



(+)-2-Carene

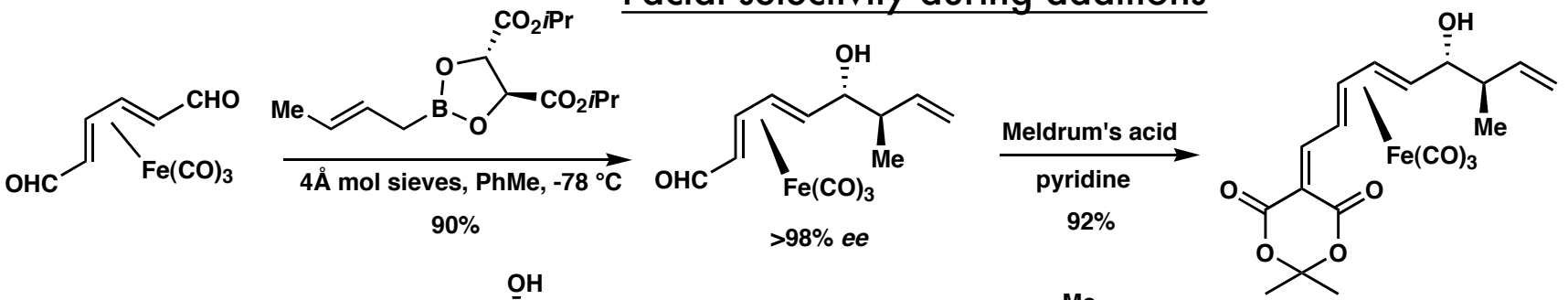
Eilbracht, P.; Winkels, I., *Chem. Ber.*, **1991**, 191.

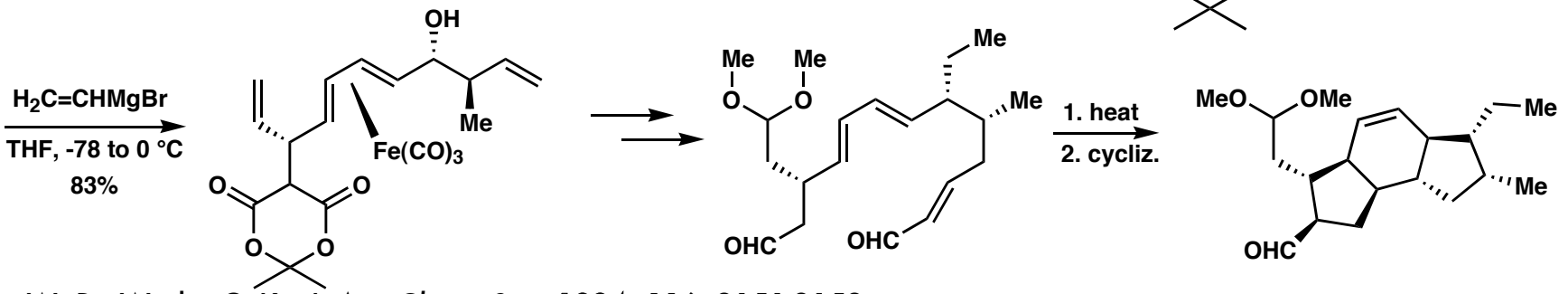
Pericylic catalysis (cisoid conformation)



Takacs, J. M.; Anderson, L. G.; Creswell, M. W. Takacs, B. E. *Tetrahedron Lett.* **1987**, *28*, 5627

Facial selectivity during additions





Roush, W. R.; Wada, C. K., *J. Am. Chem. Soc.* **1994**, *116*, 2151-2152

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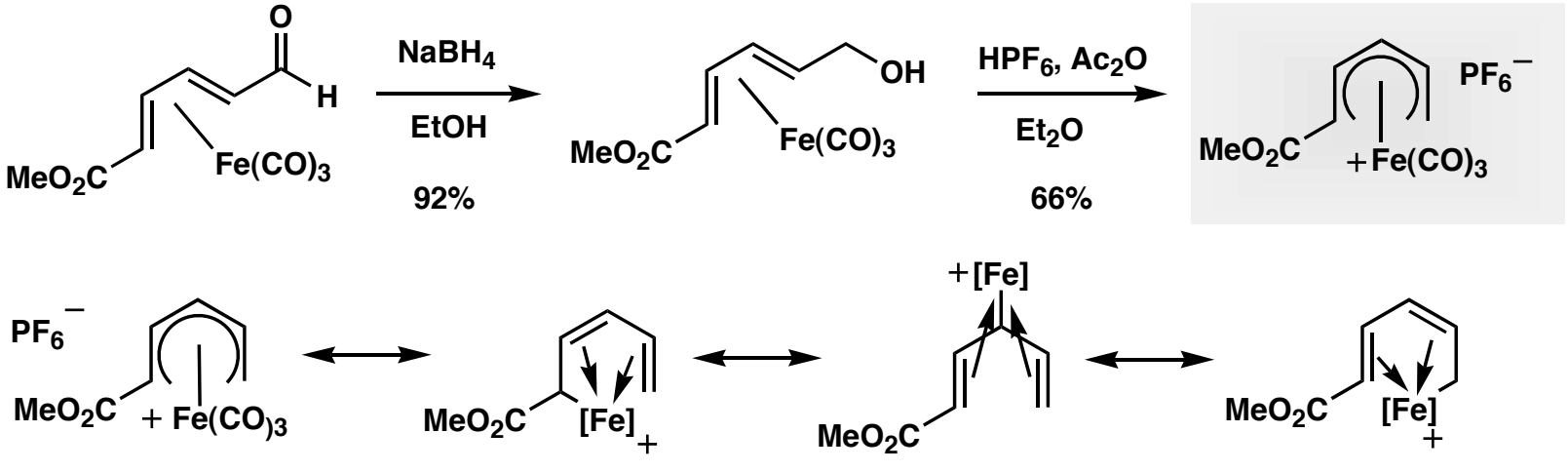
Cationic dienyliron complexes

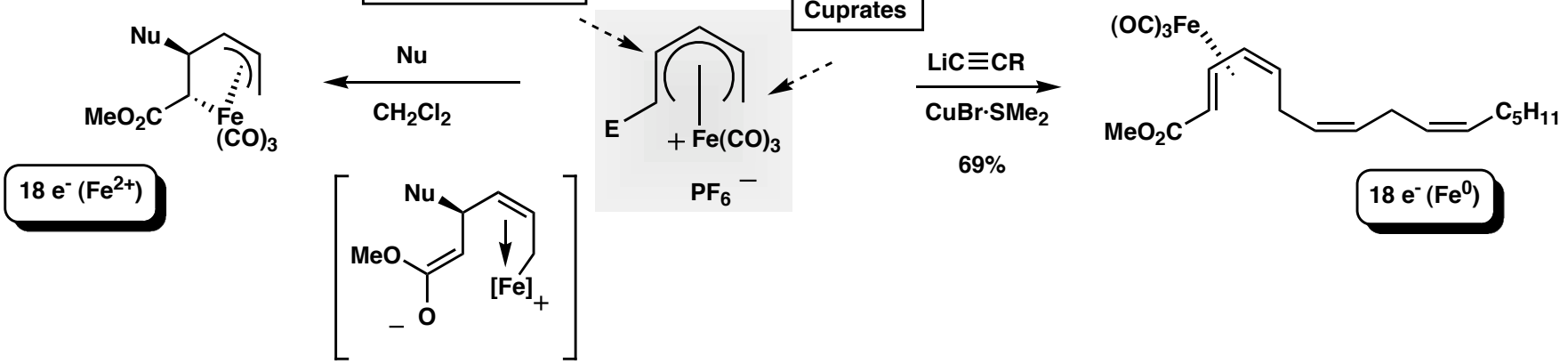


Solvent important

Predominant addition regioselectivities*

α–sulfonyl esters
α-nitro esters
Malonates
Grignards

Cuprates



Tao, C.; Donaldson, W. A. *J. Org. Chem.* **1993**, *58*, 2134-2143

Yun, Y. K.; Godula, K.; Cao, Y.; Donaldson, W. A. *J. Org. Chem.* **2003**, *68*, 901-910

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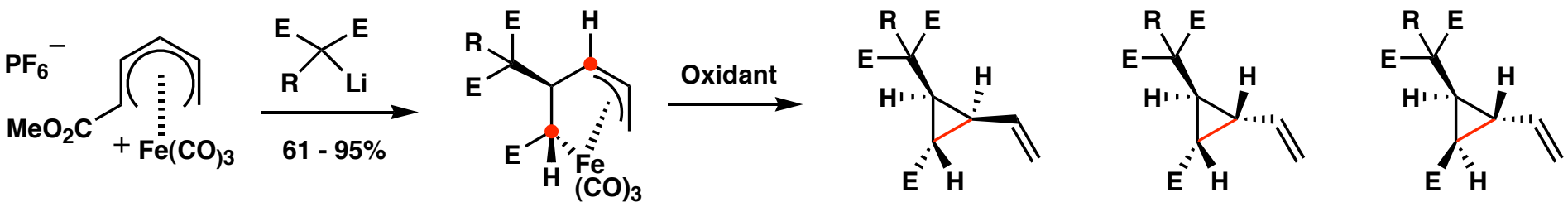
Donaldson group previous work

Vinylcyclopropanes from reductive elimination:



E = CO_2Me

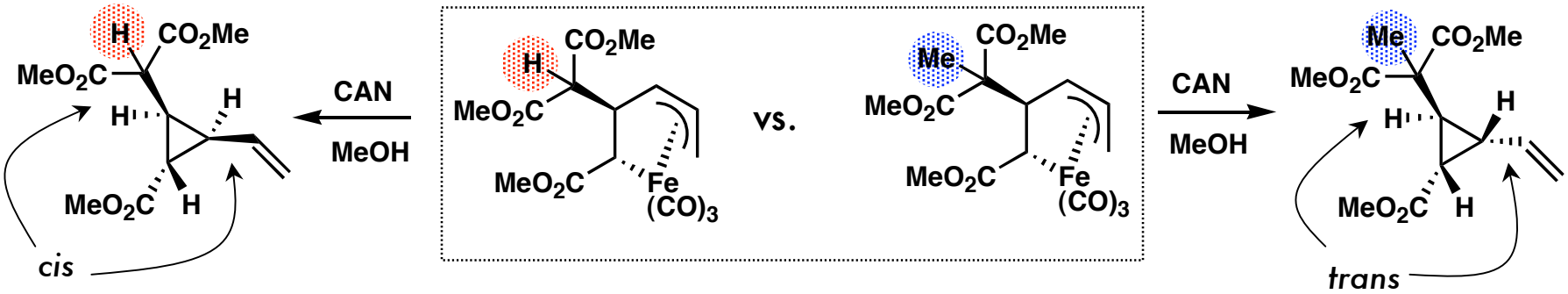
entry	R	conditions	product ratio (**2**:**3**:**4**)	total yield (%)
1	H (**a**)	CAN/DMF/23 °C	10:1:0	70
2	H (**a**)	TMANO/C_6H_6/80 °C	2:4:1	69
3	Me (**b**)	CAN/DMF/23 °C	0:1:0	55
4	Me (**b**)	TMAO/C_6H_6/80 °C	0:1:0	56
5	OMe (**c**)	CAN/DMF/23 °C	0:1:0	25

TMANO = Me_3NO

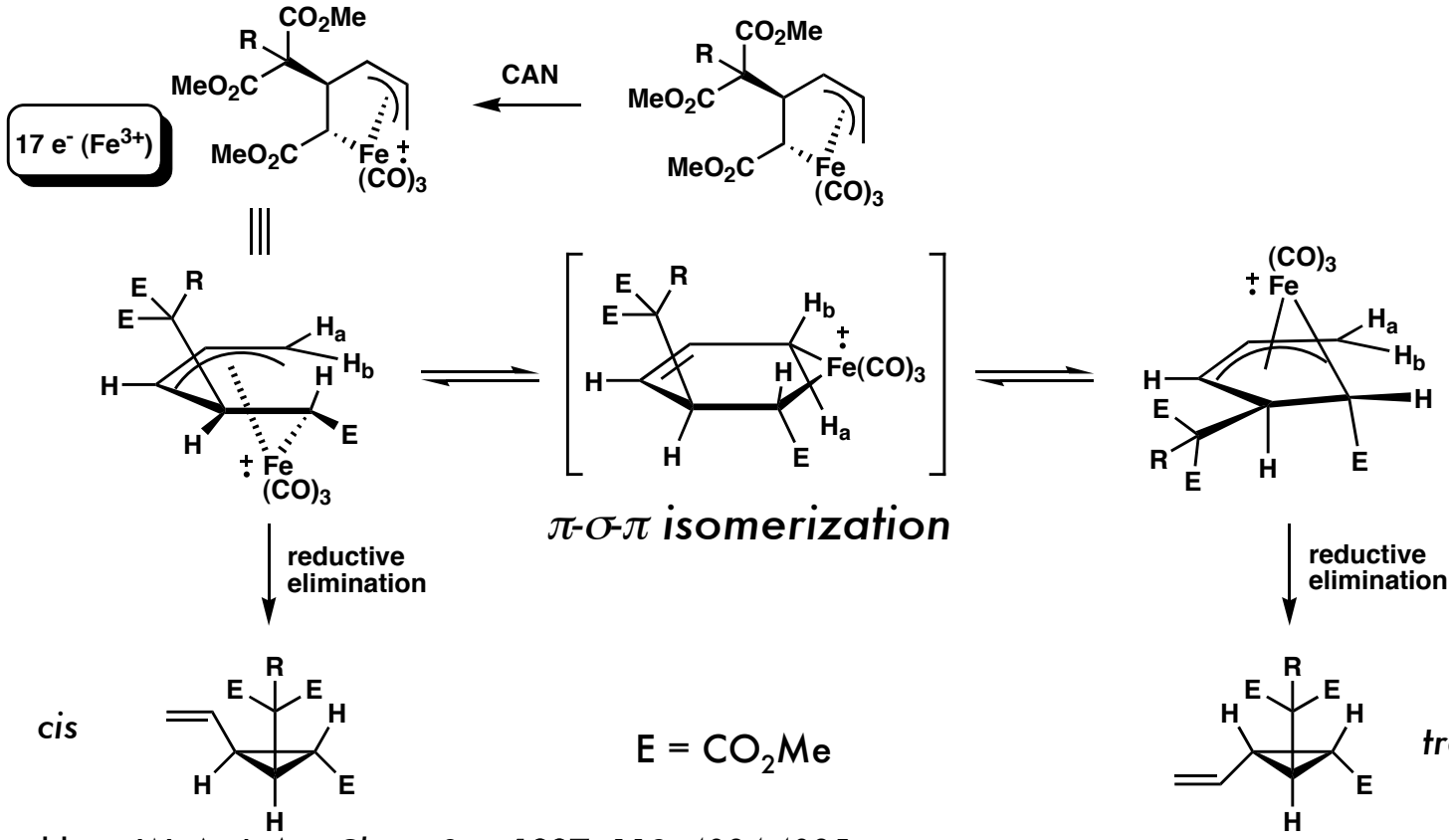
Different diastereoselectivites based on malonate substitutent *AND* temperature

Yun, Y. K.; Donaldson, W. A. *J. Am. Chem. Soc.* **1997**, *119*, 4084-4085

Diastereoselectivity in reductive elimination



Proposed Mechanism:



Yun, Y. K.; Donaldson, W. A. *J. Am. Chem. Soc.* **1997**, *119*, 4084-4085

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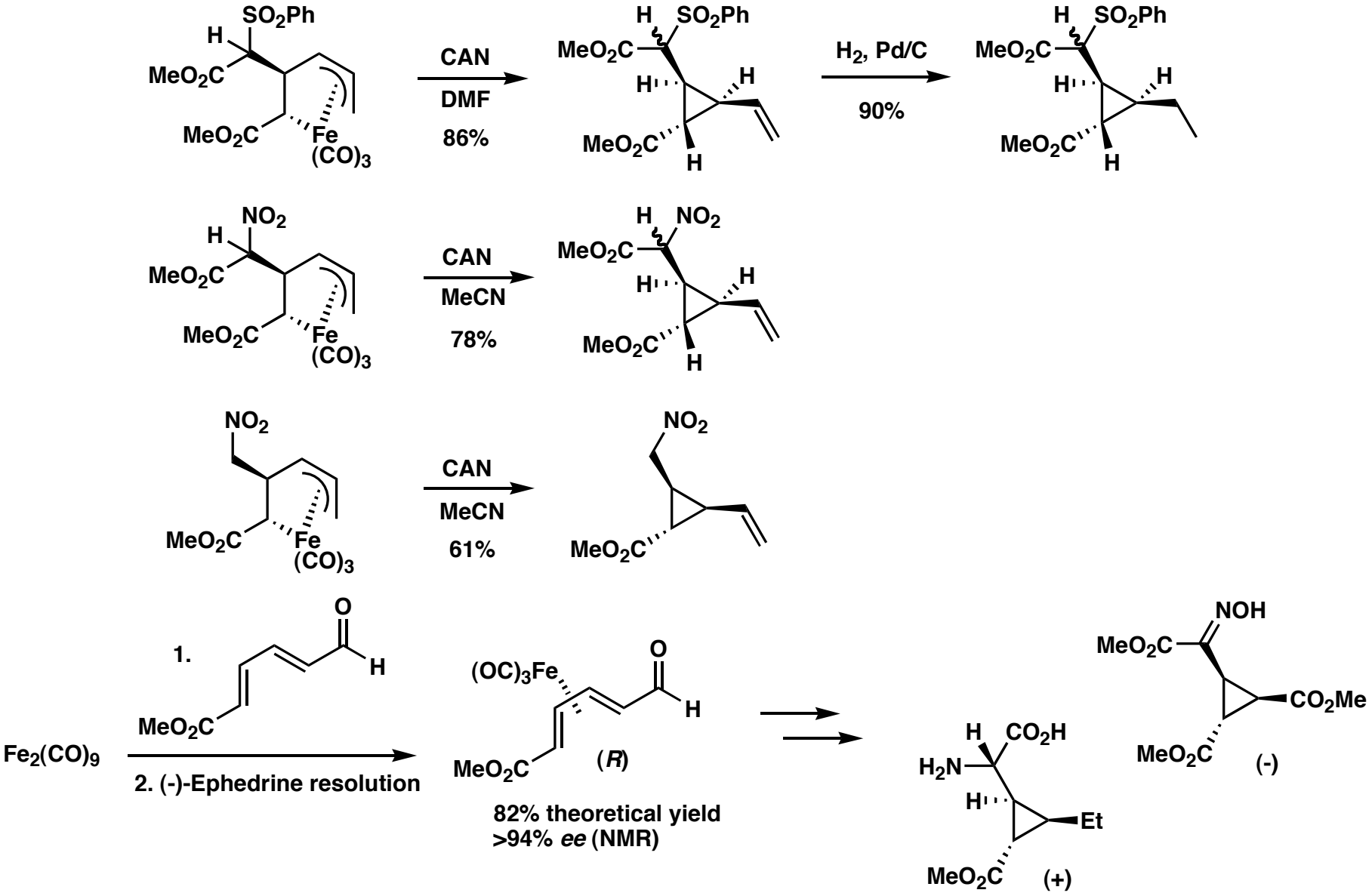
Malonate addition substrate scope



Yun, Y. K.; Godula, K.; Cao, Y.; Donaldson, W. A. *J. Org. Chem.* **2003**, *68*, 901-910

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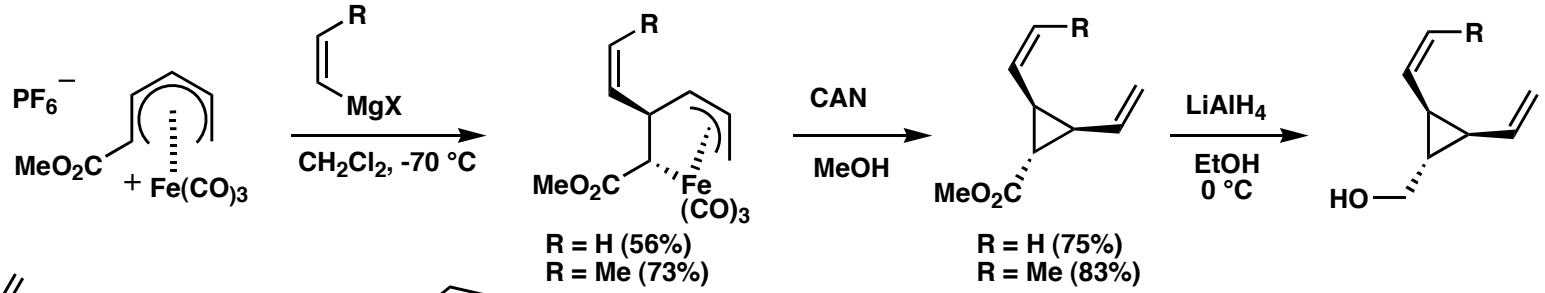
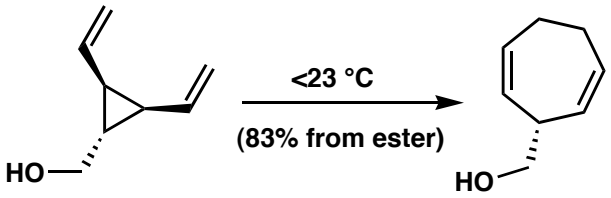
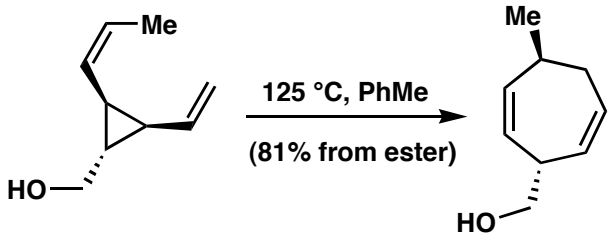
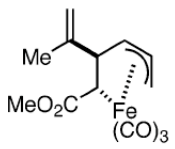
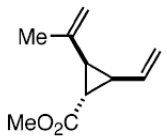
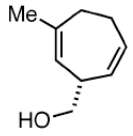
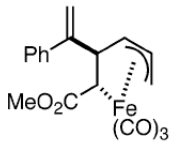
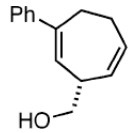
Grignard additions to dienyliron cations

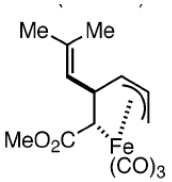
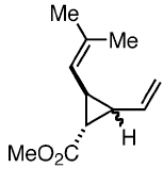
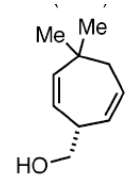
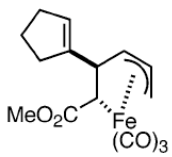
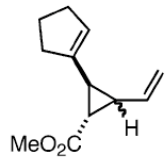
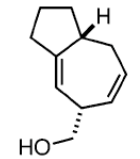




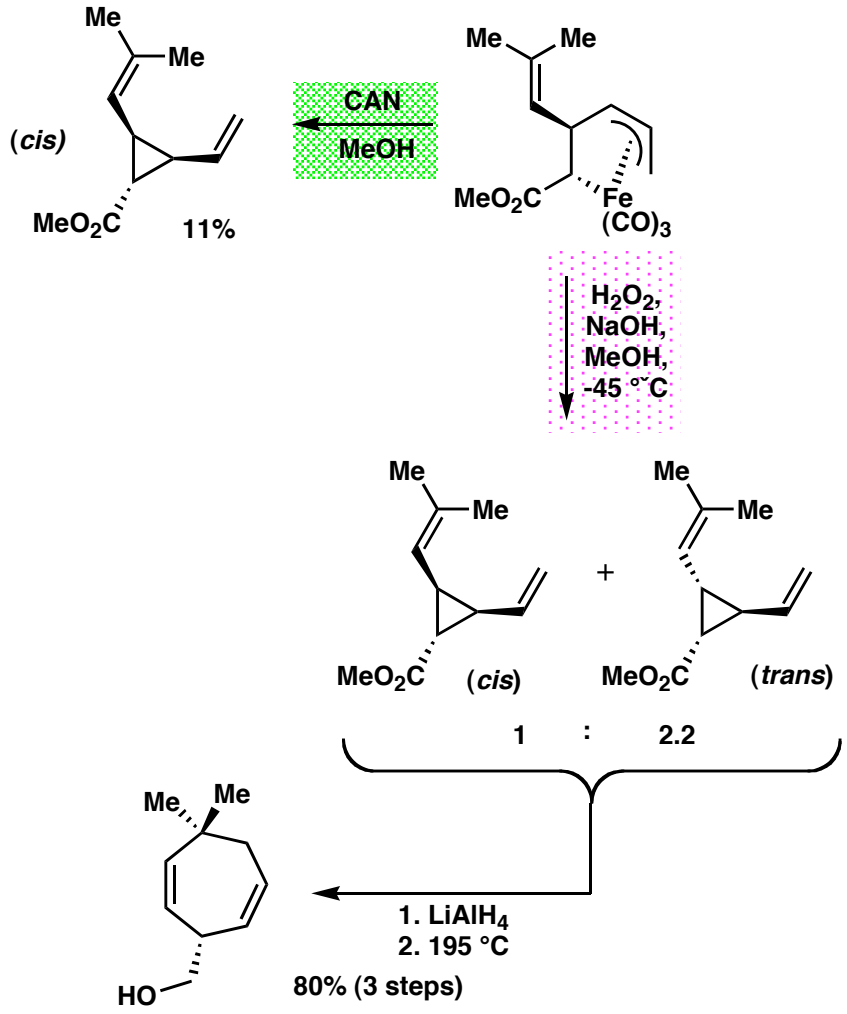


"It is known that the presence of an electron-withdrawing group strengthens the distal cyclopropane ring bond, and this should have an effect on the rate of the Cope rearrangement."

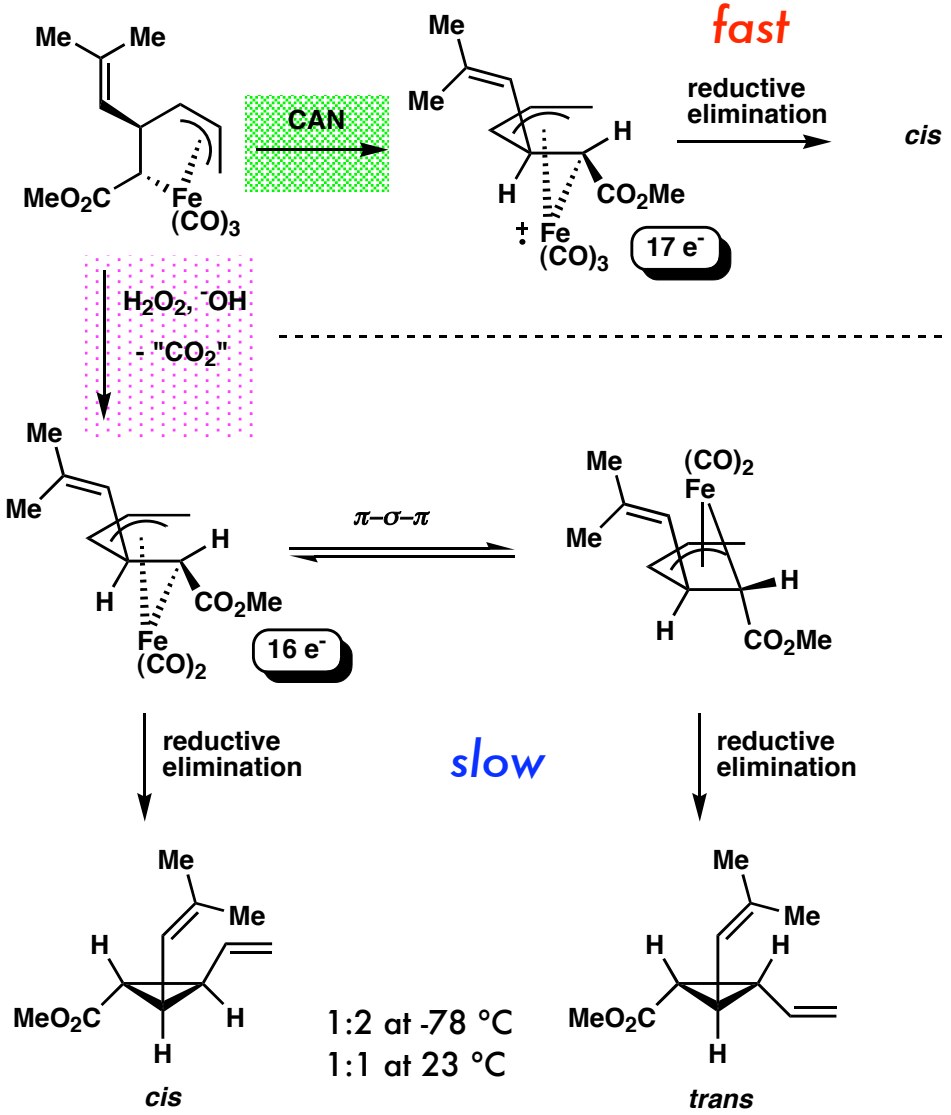
pentenediyl complex	oxidation conditions[a]	divinyl-cyclopropane	Cope conditions[a]	1,4-cyclo-heptadiene
	A		C	
4c (42-52%)		**5c**[c]		**6c** (82%)[b]
	A	not observed	C	
4d (38-49%)				**6d** (33%)[b]

pentenediyl complex	oxidation conditions[a]	divinyl-cyclopropane	Cope conditions[a]	1,4-cyclo-heptadiene
	A B		D	
4e (71-76%)		**5e** (11%, *cis* only) **5e/e'** (63-84%)[d]		**6e** (80%)[b]
	B		E	
4f (50%)		**5f** (85%)[e]		**6f** (76%)[b]

Wallock, N. J.; Donaldson, W. A. *Org. Lett.* **2005**, *10*, 2047-2049



Mechanistic Rationale:



Wallock, N. J.; Bennett, D. W.; Siddiquee, T.; Haworth, D. T.; Donaldson, W. A. *Synthesis*, **2006**, *21*, 3639-3646

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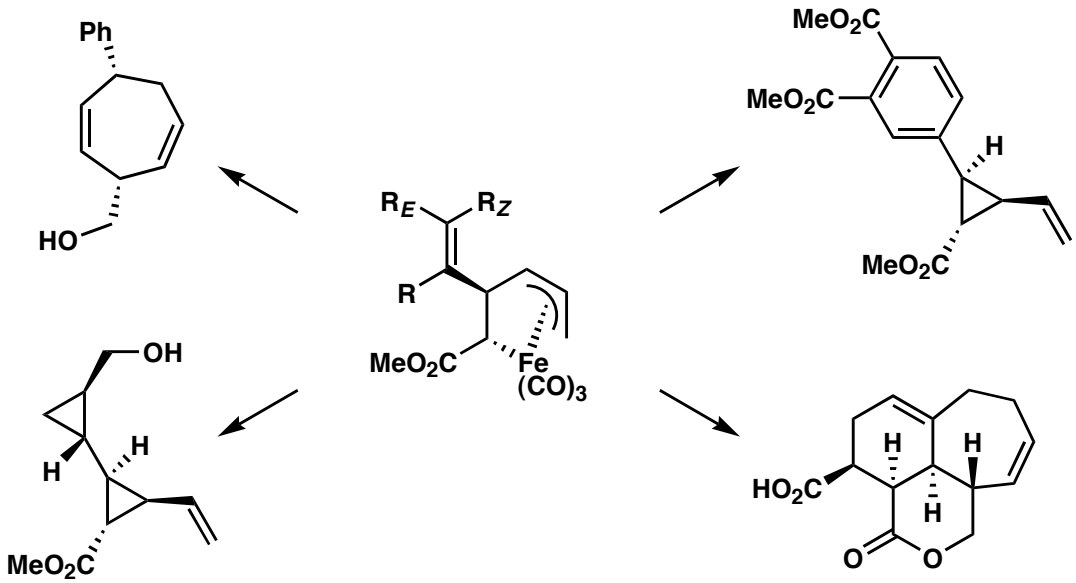
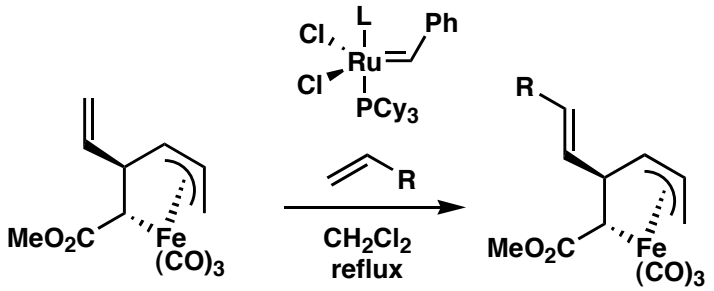
Current paper- scaffold diversification



Metathesis strategy

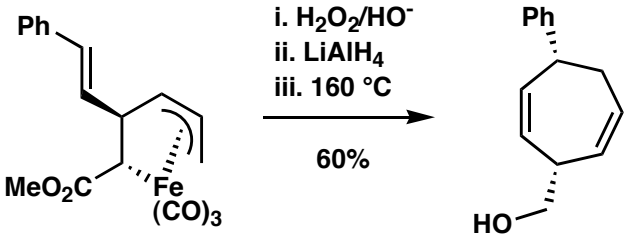


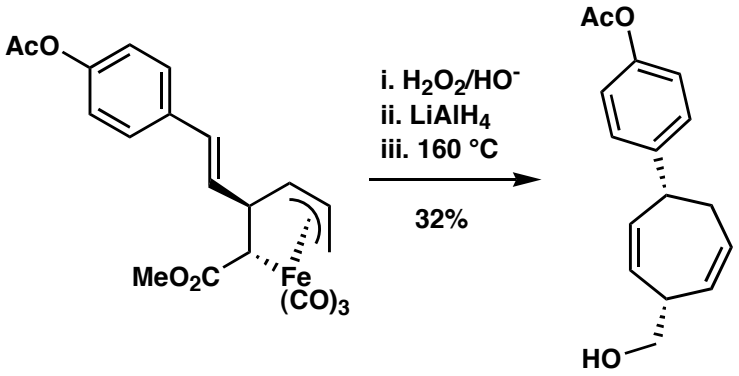
E- isomer exclusively

53 - 80%

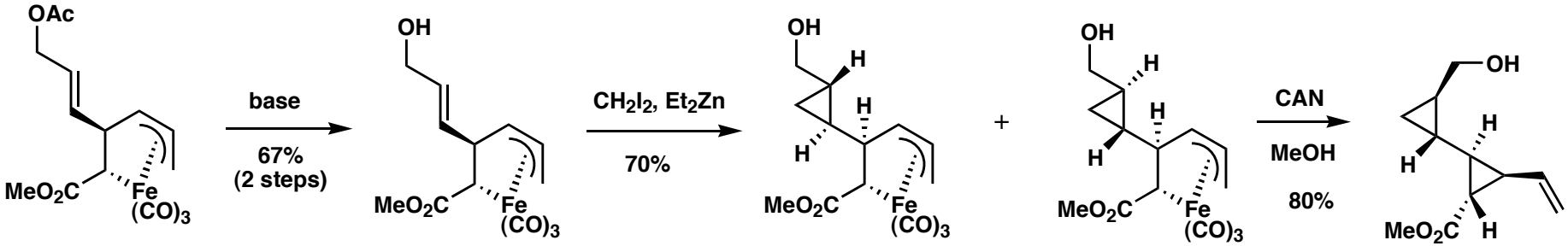
R = Ph, OAc, *p*-C_6H_4OAc, *c*-C_6H_{11}, $(CH_2)_4OTBS$, CH_2SiMe_3

Divinylcyclopropane rearrangement:





Cyclopropanation (Simmons-Smith):



1 : 4.5

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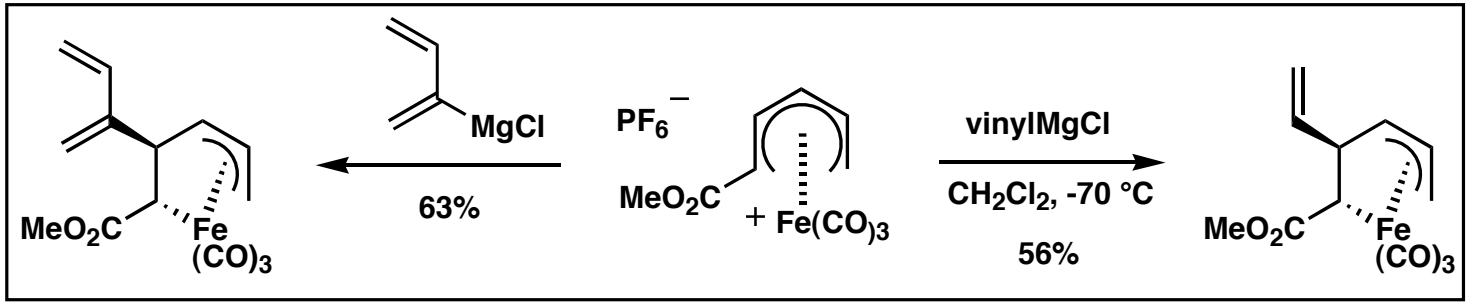
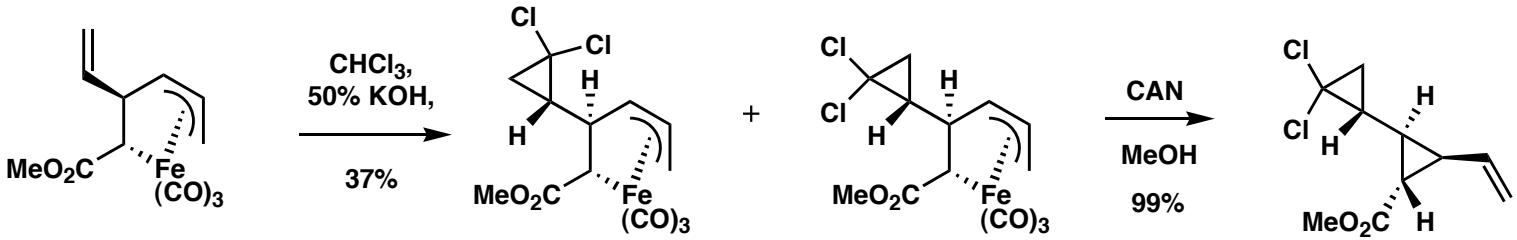
Grignard additions

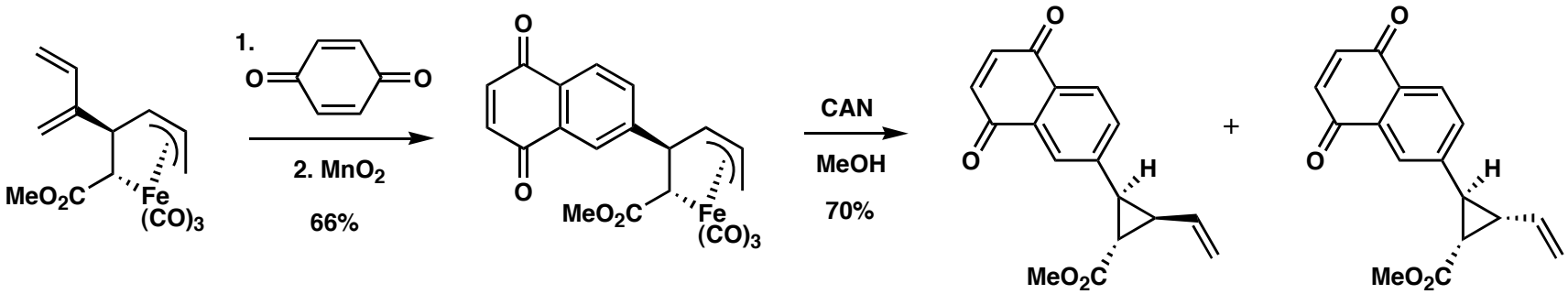


Dichlorocyclopropanation:



1 : 2

[4+2] Cycloadditions:



7 : 3

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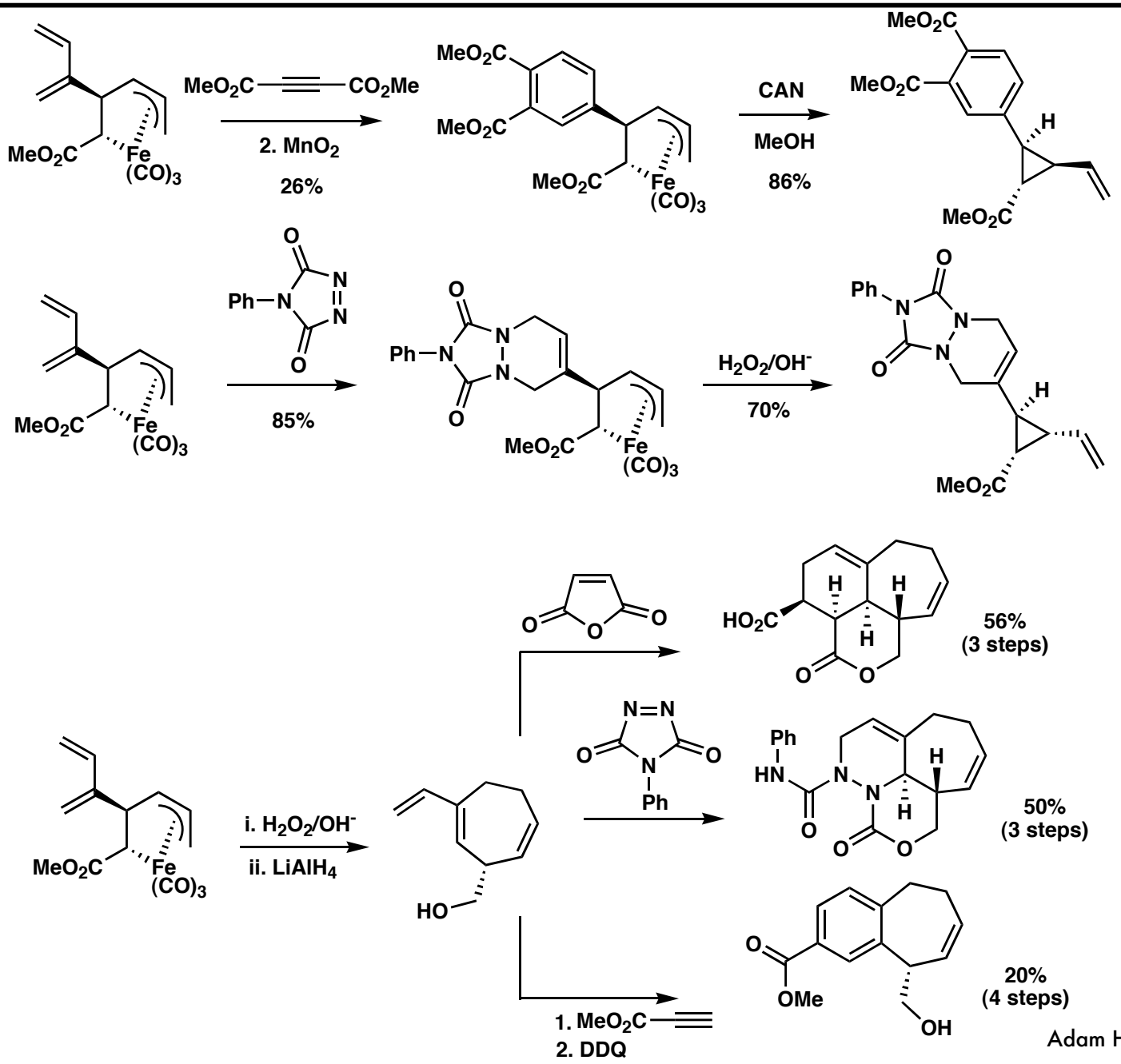
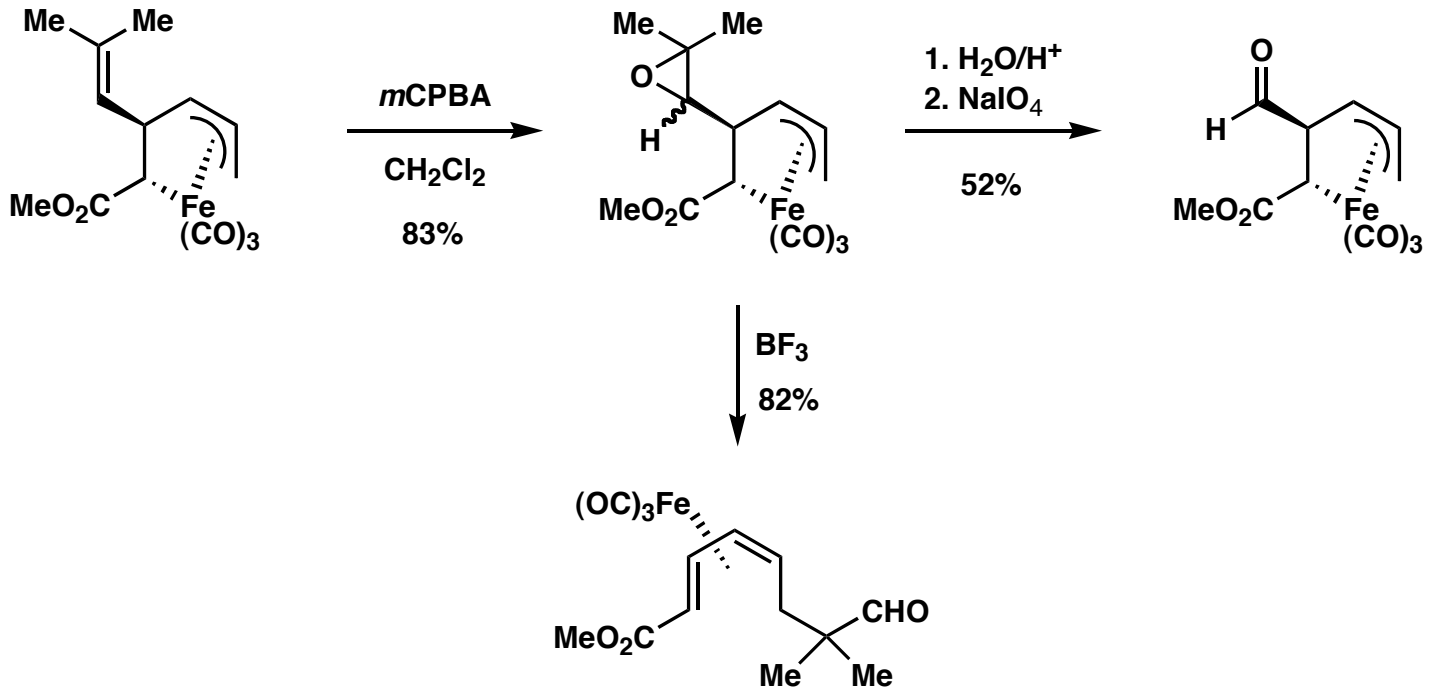
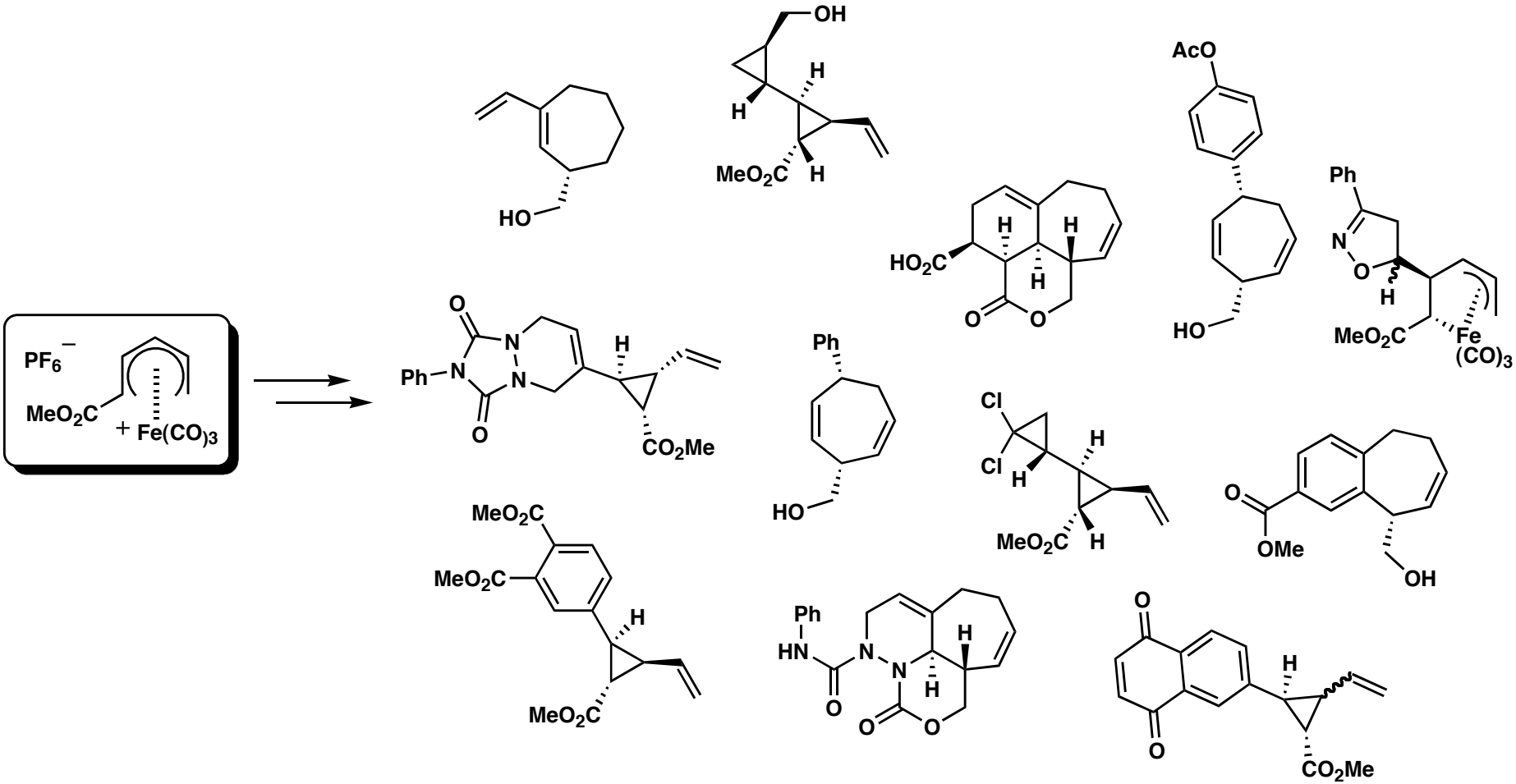
Cycloadditions continued



Epoxidation strategy



Summary



-diverse molecular scaffolds accessible from a single organometallic intermediate
-tolerant of a variety of reaction conditions to access a broad range of functionality with many points amenable to structural diversification

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