Prof. Alois Fürstner Group' work

Organometallic Chemistry
and its application in the nature
Product synthesis

Reporter : Zhe Dong
10/10/2012

Prof. Alois Fürstner

2009-2011 Managing Director of the Max-Planck-Institut für Kohlenforschung

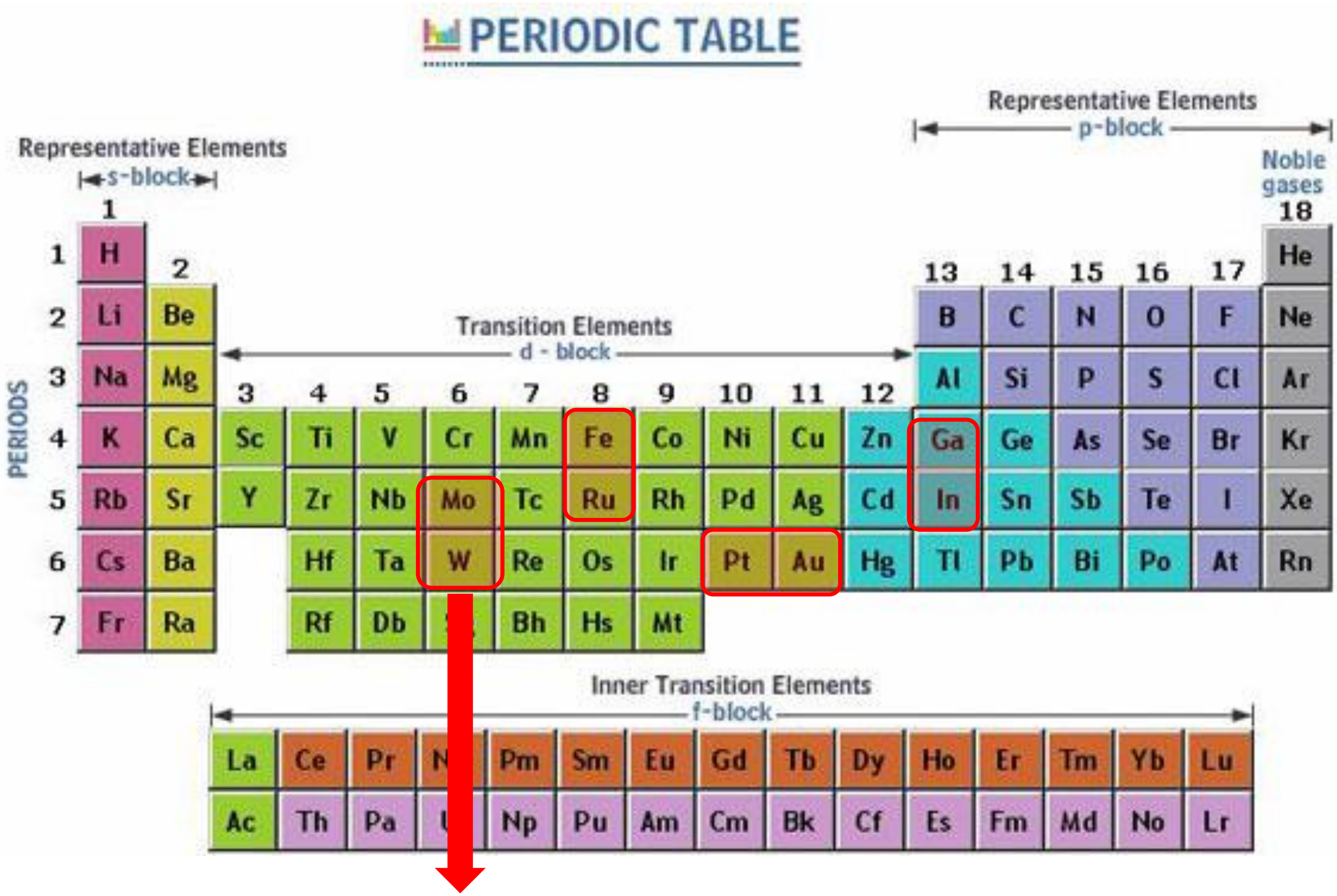
1993-1998 Group leader at the Max-Planck-Institut für Kohlenforschung and Lecturer at the University of Dortmund

1992 “Habilitation” in Organic Chemistry at the Technical University Graz, Austria

1990-1991 Postdoctoral fellow at the University of Geneva, Switzerland (W. Oppolzer)

1987 PhD at the Technical University Graz, Austria (H. Weidmann)
1962 born in Bruck/Mur (Austria）

Research Interest

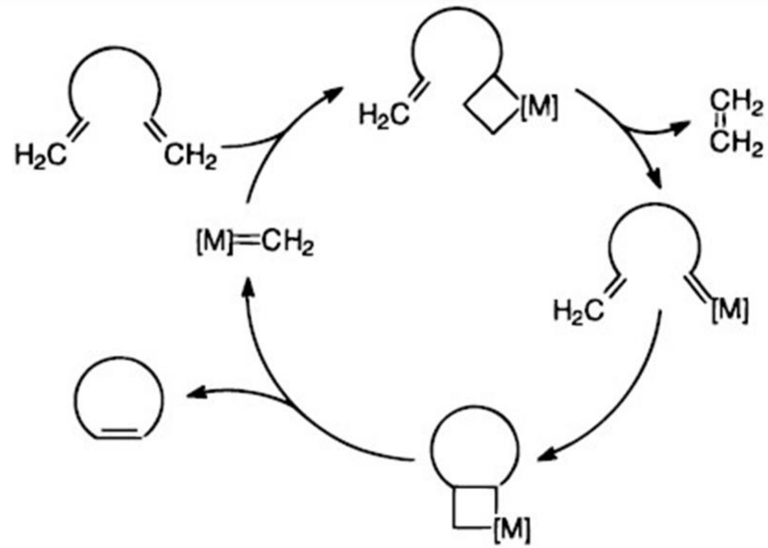


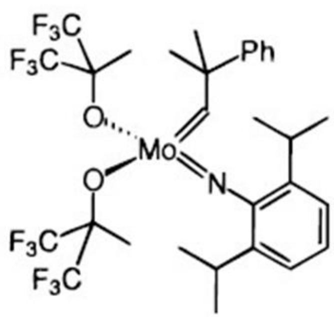
Macrocyclic ring synthesis and nature product synthesis

Outline

1. Macrocyclic ring synthesis
   - Alkene Metathesis Ru
   - Alkyne Metathesis W/Mo
   - RCAM's applications in the complex nature product synthesis
2. Poor man's cataylst Fe
   - Fe catalyzed coupling reaction.
   - Can Fe catalyst work as a expensive metal?
3. Acknowledgement

1. 1Alkene Metathesis





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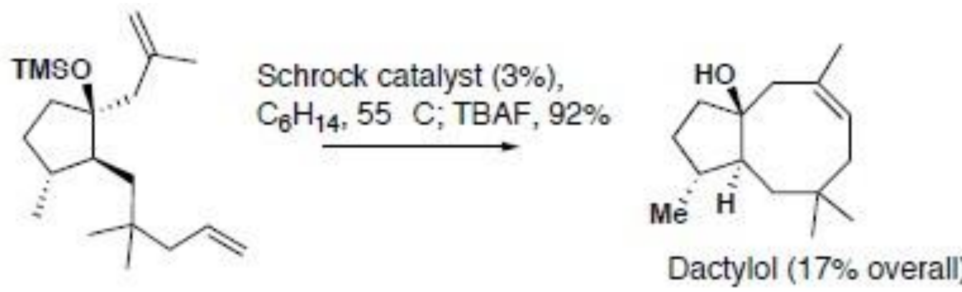
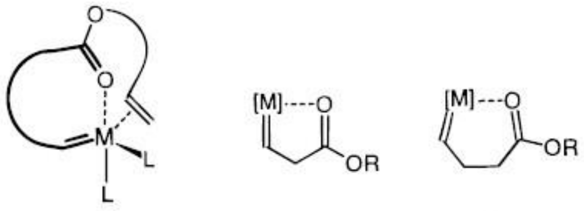
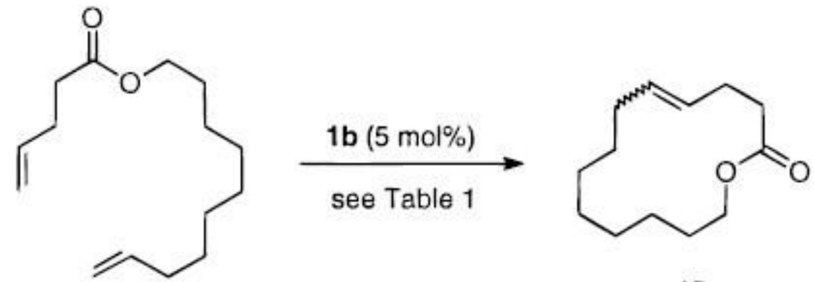


Alois Furstner *J.Org.Chem.*, **1996**, *61*, 8746-9

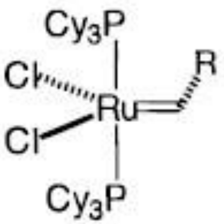
1. 1Alkene Metathesis



A B C



14 15



1a R = Ph

1b R = CH=CPh$_2$

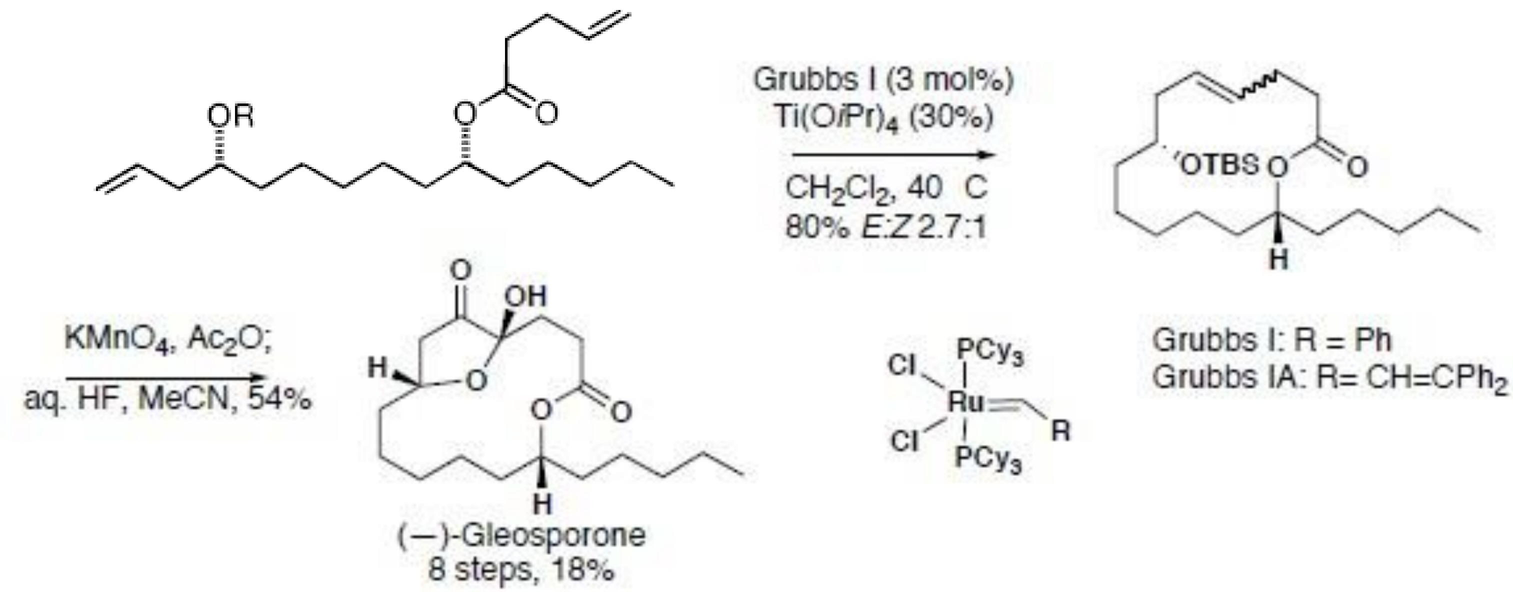
Table 1. Cyclization of the 4-Pentenoate **14** in the Presence of Additives

entry	*t* (d)	*T* (°C)	additive	**14** (%)[a]	**15** (%)[a]
1	3	25		67	22
2	3	25	Ti(OiPr)$_4$ (2 equiv)	49	40
3	3	40	Ti(OiPr)$_4$ (5 mol %)	7	55
4	3	25	LiBr (5 equiv)	79	14

[a] Determined by GC.

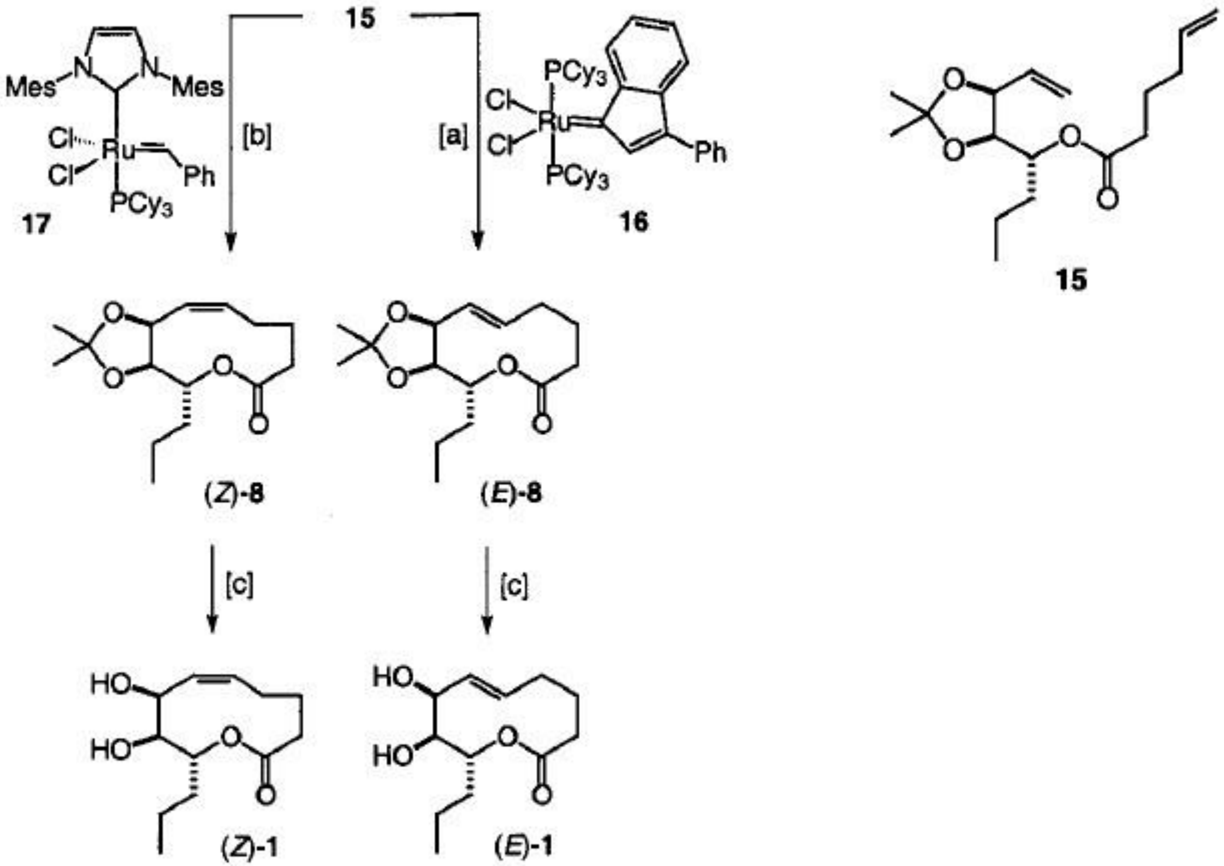
Alois Furstner *J.Am.Chem.Soc.*, **1997**, 119, 9130-6.

1.1 Alkene Metathesis:



Alois Furstner *J.Am.Chem.Soc.*, **1997**, 119, 9130-6.

1. Alkene Metathesis: Selectivity



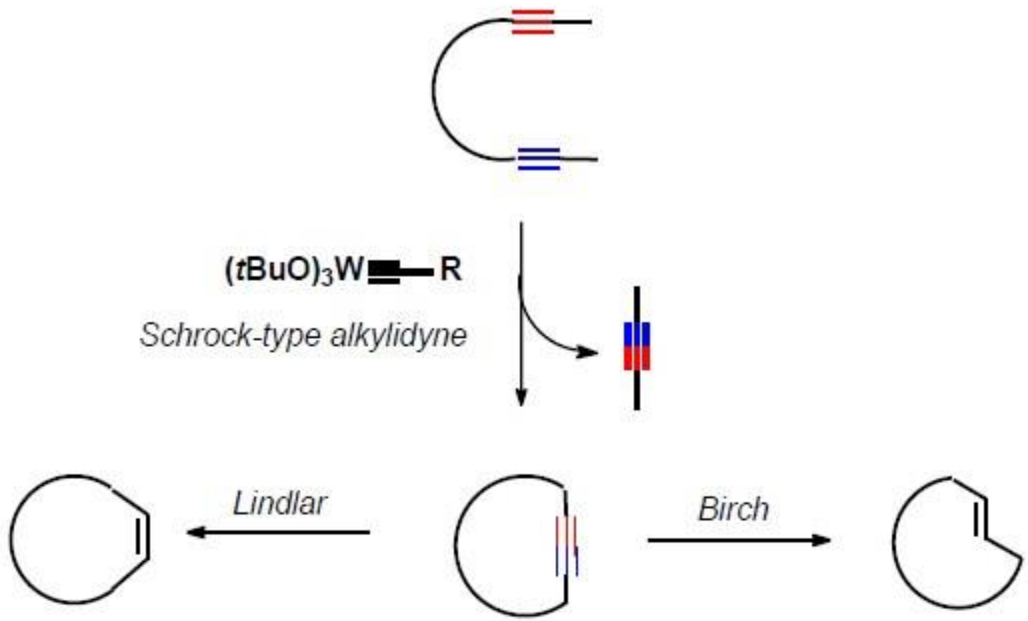
[a] [a] Complex **16** cat., CH_2Cl_2, reflux, 69%; [b] complex **17** cat., CH_2Cl_2, reflux, 86%; [c] aqueous HCl, THF, 47% ((*Z*)-**1**), 90% ((*E*)-**1**).

Alois Furstner *J.Am.Chem.Soc.,* **2002**, 124, 7061-9.

Alkene Synthesis: Selectivity

How to synthesize the double bond by metathesis with high E/Z ratio？
A big problem combined the reactivity and selectivity
Useful in the total Synthesis and industry！

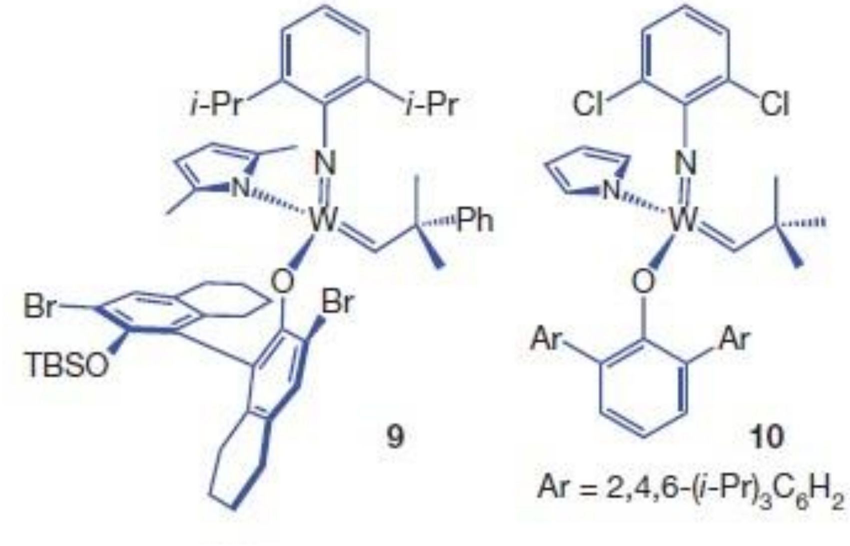
Fürstner’s answer：



Alkene Synthesis: Selectivity

How to synthesize the double bond by metathesis with high E/Z ratio？

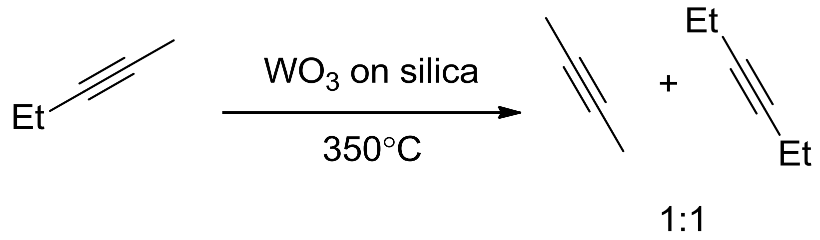
Hoveyda’s answer：



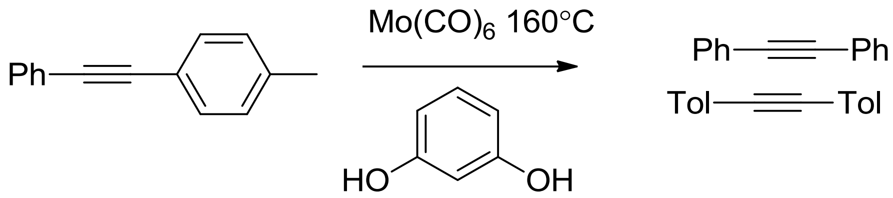
Schrock and Hoveyda *Nature.* **2011**, 479, 88-93

1.2. Alkyne Metathesis:

The discovery of the Alkyne Metathesis：

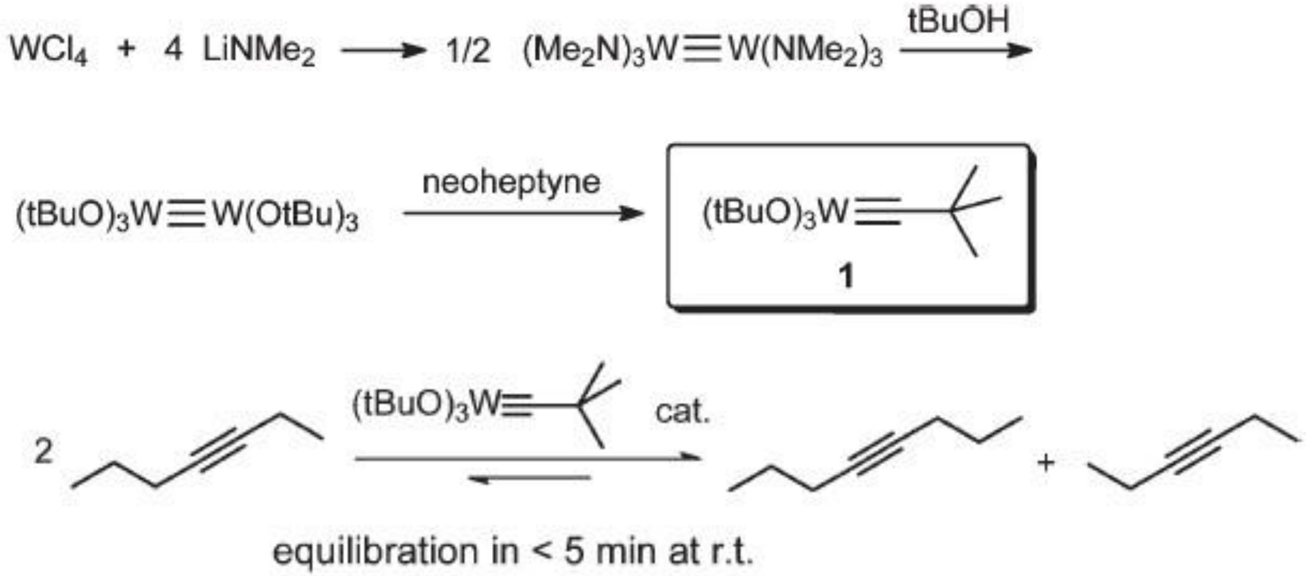


Pennellar, F.; Banks, R. L.; Bailey, G. C. *J. Chem. Soc., Chem. Commun.* **1968**, 1548



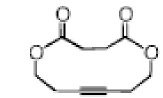
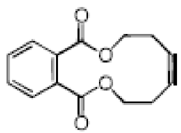
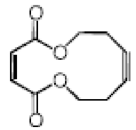
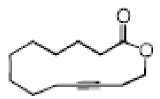
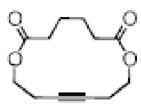
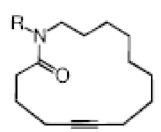
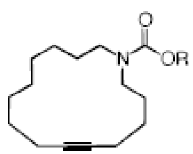
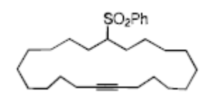
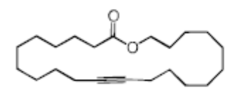
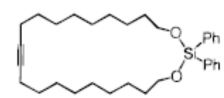
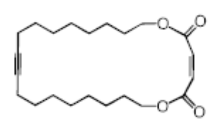
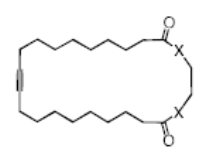
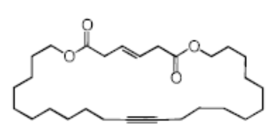
Mortreux, A.; Blanchard, M. *J. Chem. Soc., Chem. Commun.* **1974**, 786

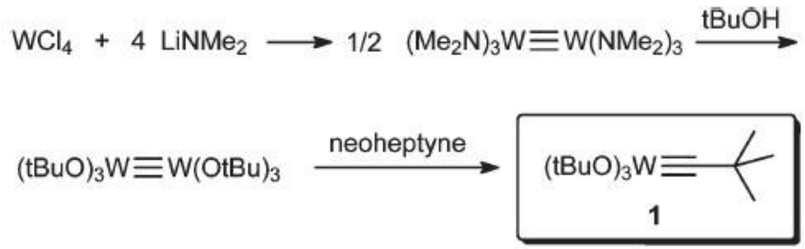
1.2. Alkyne Metathesis:



R. R. Schrock et al., *J. Am. Chem. Soc*. **1981**, *103*, 3932; *Organometallics* **1984**, *3*, 1563.

1.2. Alkyne Metathesis:

Entry	Product		1a[a]	[Mo][b]
1		**3**	73[c]	64
2		**4**	68	0
3		**5**	62	0
4		**6**	52	
5		**7**	79	
6 7		**8a** **8b**	62 (R = H) 72 (R = Me)	0 (R = H) 64 (R = Me)
8	 R = 9-fluorenylmethyl	**9**	62	68
12		**13**	75[d,e]	
13		**14**	64	72
14		**15**	55	decomp.
15		**16**	62	58
16 17		**17a** **17b**	97 (X = O) 90 (X = NH)	
18		**18**	53	70



instant=$Mo(CO)_6$ + *p*-Cl-C_6H_4OH

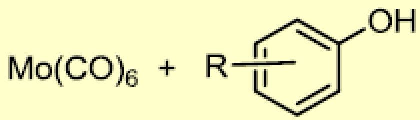
A. Fürstner. *J. Am. Chem. Soc.* **1999,** *121,* 11108-11113

1.2. Alkyne Metathesis:

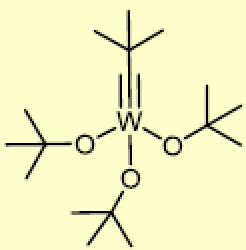
cheap
air stable
user friendly

harsh
slow
limited compatibility

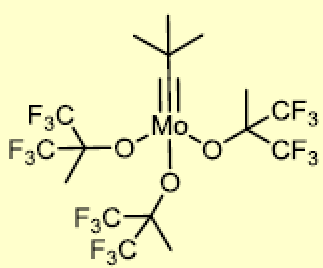
Mortreux Systems



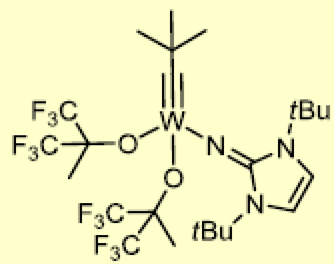
Schrock Alkylidynes



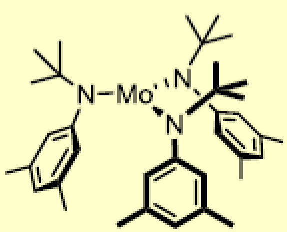
Schrock 1981



Schrock 1984/1985

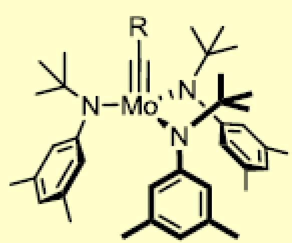


Tamm 2007



+ CH_2Cl_2

Fürstner 1999

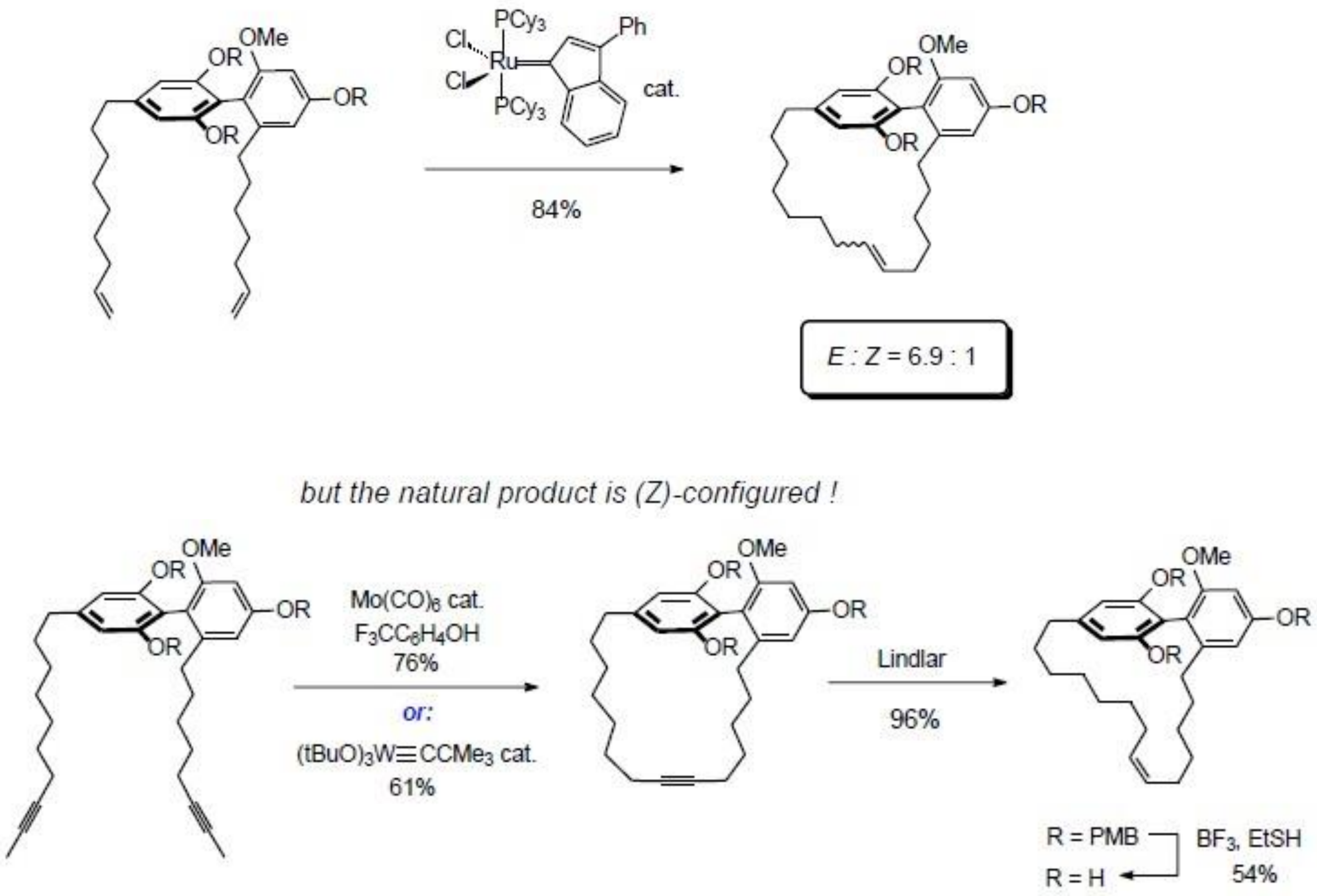


Moore 2004

expensive
laborious
(highly) sensitive (O_2, H_2O, N_2)
short lifetimes

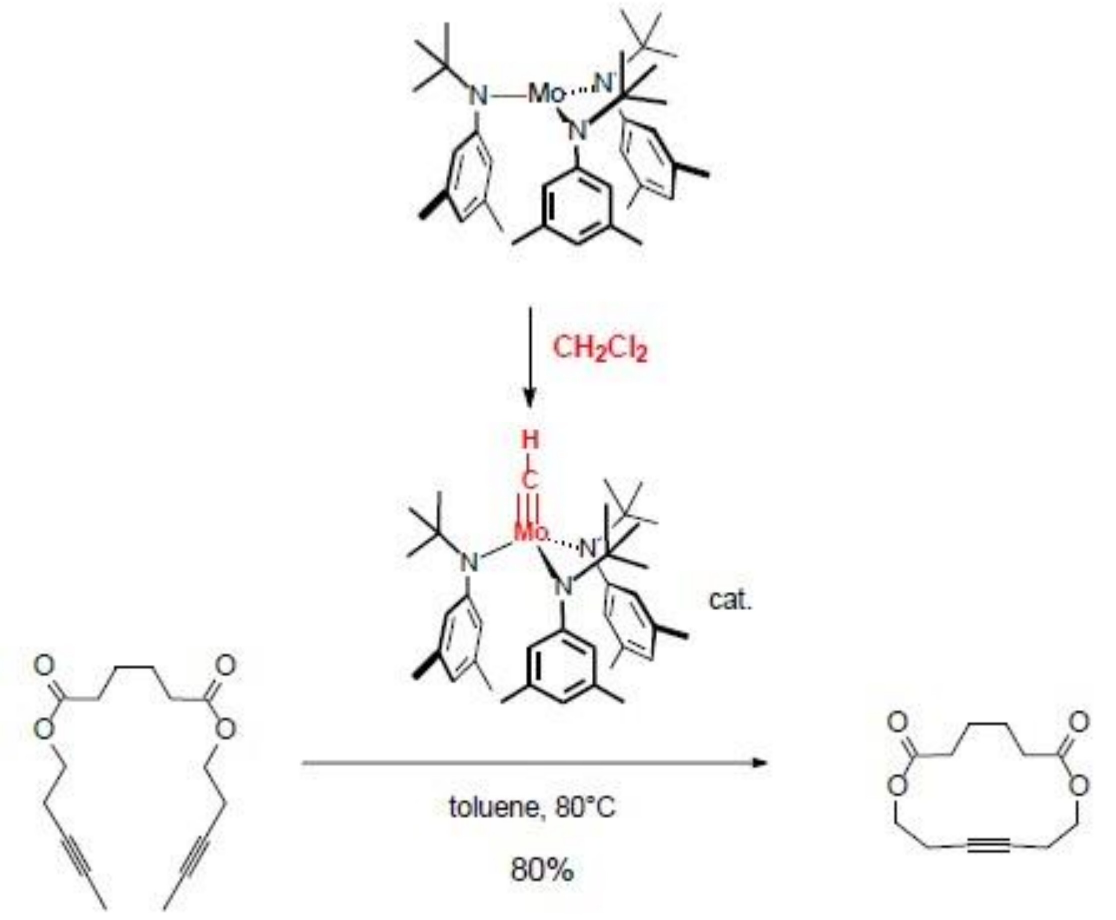
(highly) active: W > Mo
excellent compatibility: Mo > W
broad scope

1.2. Alkyne Metathesis:



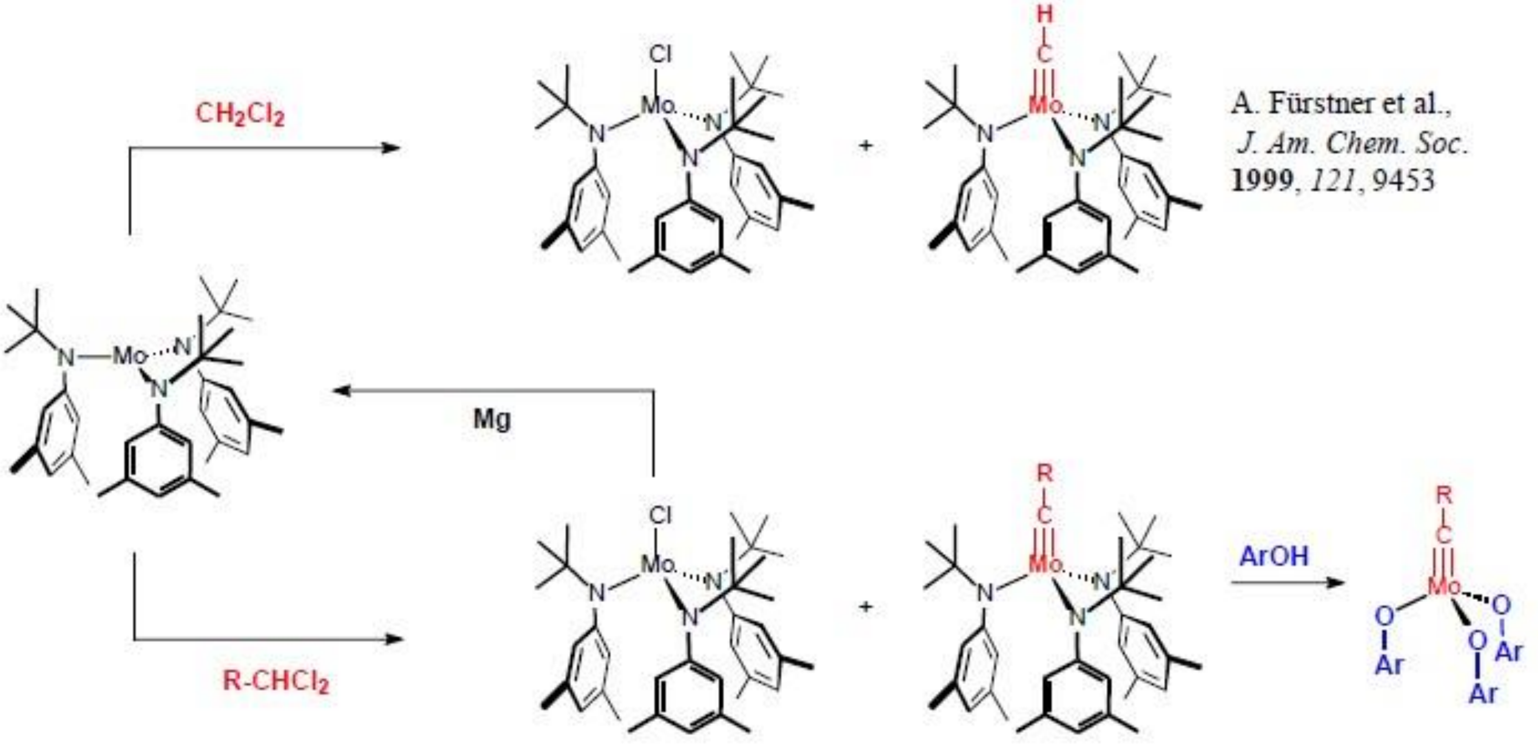
A. Fürstner, F. Stelzer, A. Rumbo, H. Krause, *Chem. Eur. J*. **2002**, *8*, 1856.

1.2. Alkyne Metathesis:



A. F. with C. Mathes, C. W. Lehmann, *J. Am. Chem. Soc.* **1999**, *121*, 9453;

1.2. Alkyne Metathesis:

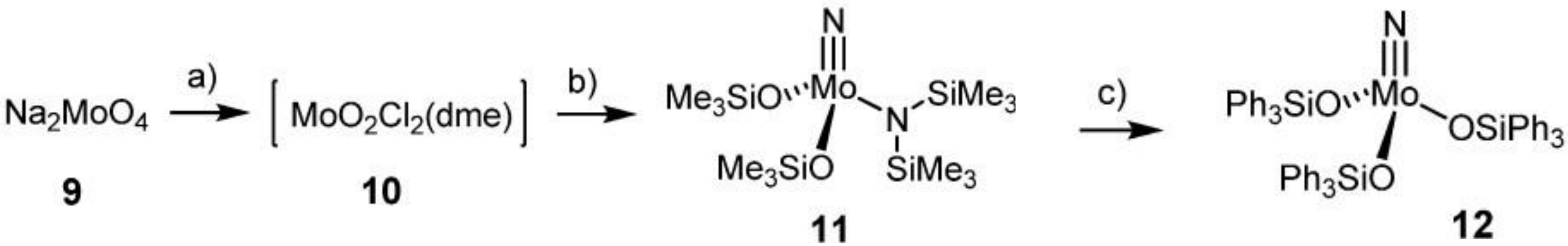


A. Fürstner et al., *J. Am. Chem. Soc.* **1999**, *121*, 9453

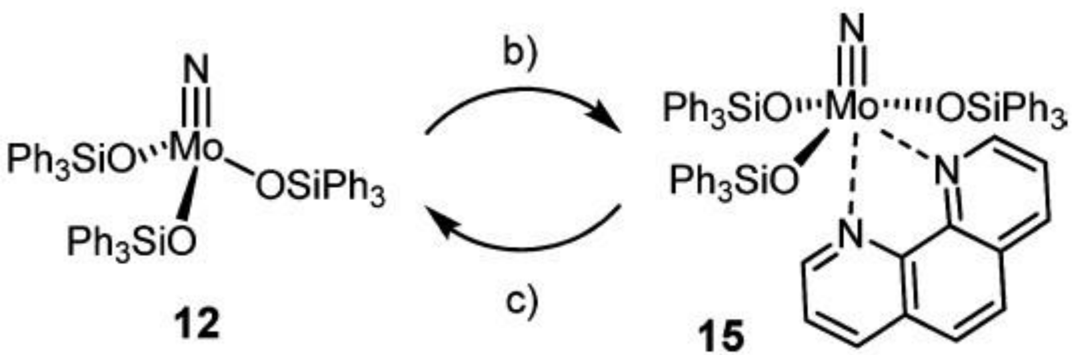
W. Zhang, S. Kraft, J. S. Moore, *Chem. Commun*. **2003**, 832; idem, *J. Am. Chem. Soc*. **2004**, *126*, 392;

See also: C. C. Cummins et al., *Organometallics* **2003**, *22*, 3351.

1.2. Alkyne Metathesis:



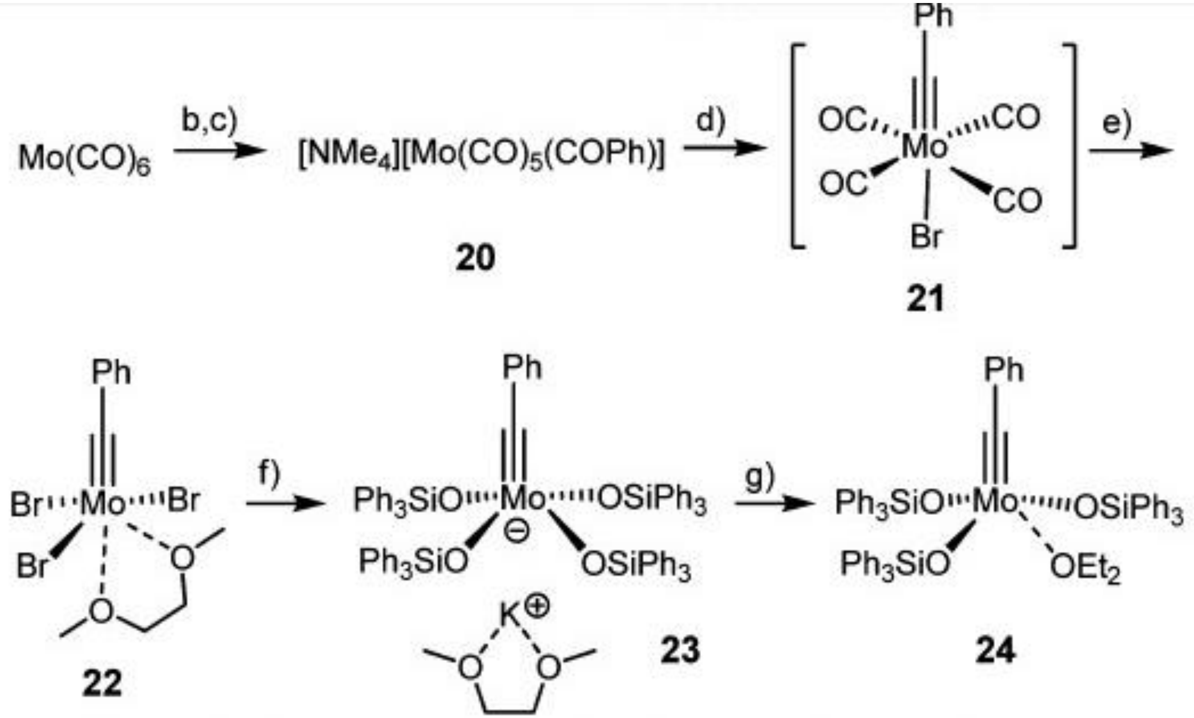
[a] Conditions: (a) TMSCl, 1,2-dimethoxyethane (DME), reflux; (b) LiHMDS, hexane, 64% (over both steps); (c) Ph_3SiOH (3 equiv), toluene,



[a] Reactions and conditions: (a) Ph_3SiOH (3 equiv), toluene; (b) 1,10-phenanthroline, 82%; (c) $MnCl_2$, toluene, 80−100 °C.

A. Fürstner, F. *J. Am. Chem. Soc.* **2010**, *132*, 11045

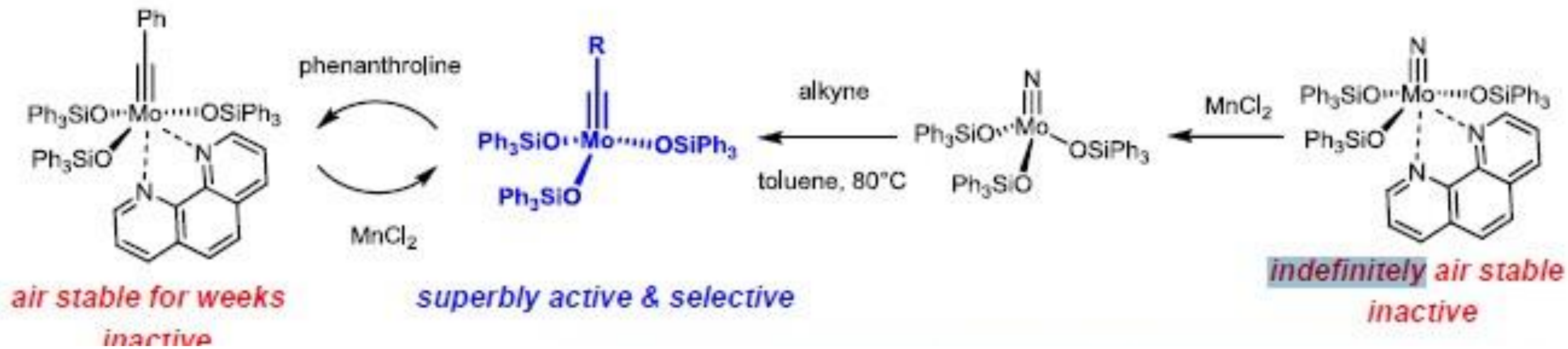
1.2. Alkyne Metathesis:

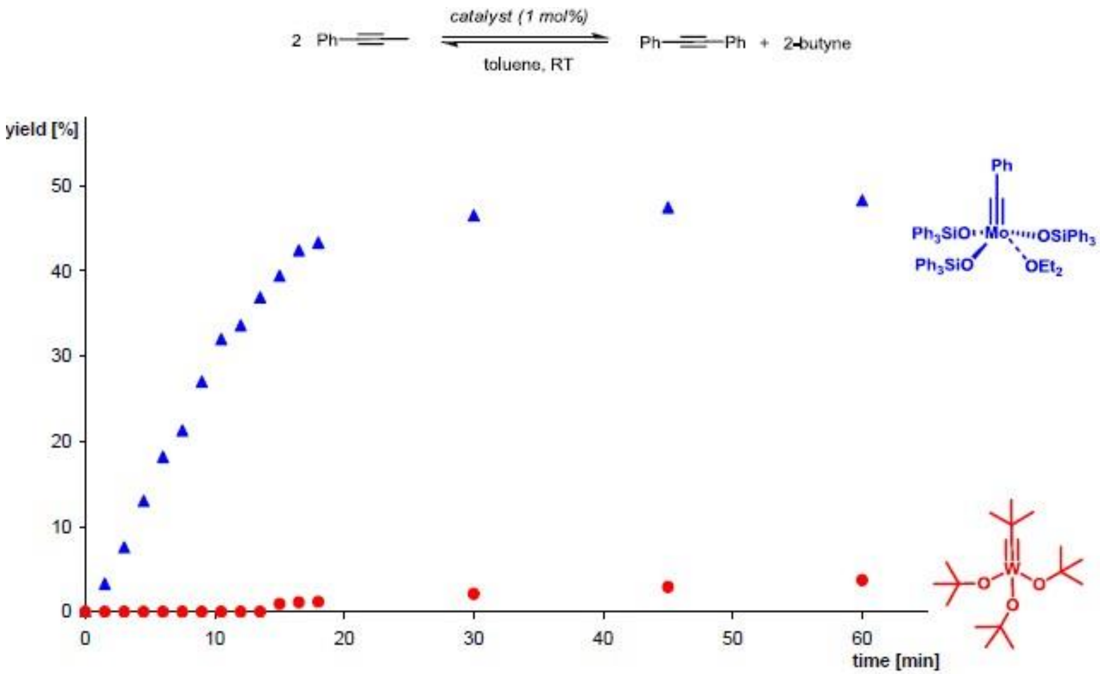


[a] Reagents and conditions: (a) Ph_3SiOLi (3 equiv), Et_2O, −40 °C → rt, then MeCN, 85%; (b) PhLi, Et_2O, reflux; (c) NMe_4Br, H_2O, 52% (over both steps); (d) oxalyl bromide, CH_2Cl_2, −78 °C → −15 °C; (e) Br_2, 1,2-dimethoxyethane (dme, 5 equiv), CH_2Cl_2, −78 °C → rt, 88% (over both steps); (f) Ph_3SiOK (4 equiv), toluene; (g) Et_2O, 92%.

A. Fürstner, F. *J. Am. Chem. Soc.* **2010**, *132*, 11045

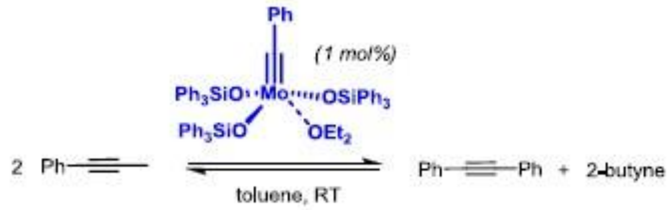
1.2. Alkyne Metathesis:

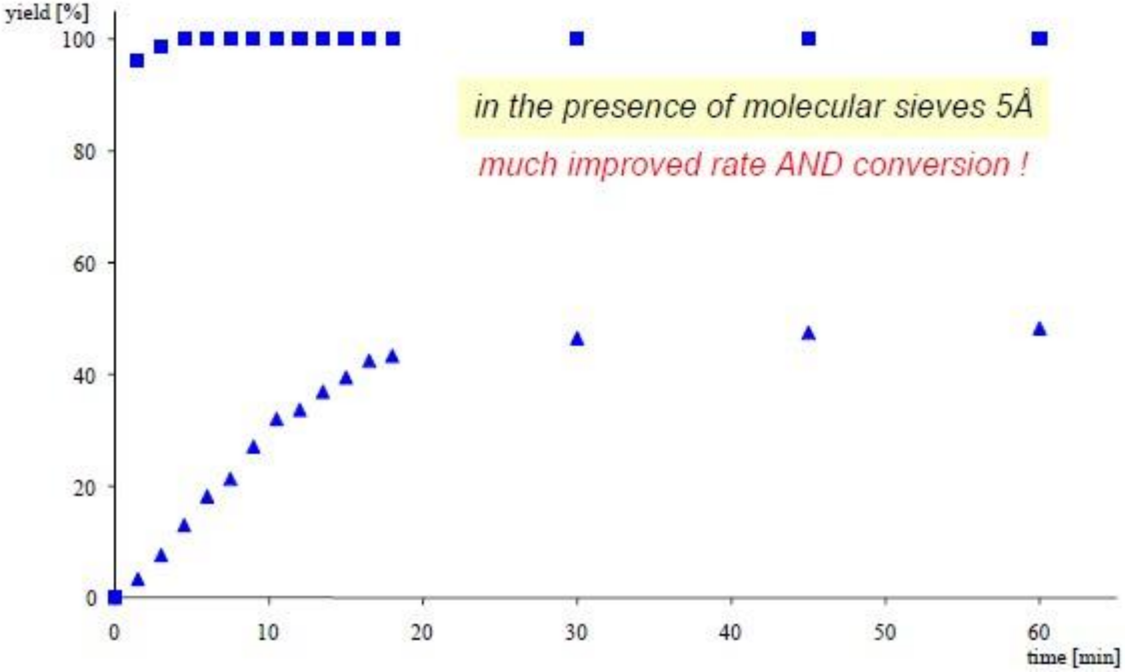




A. Fürstner, F. *J. Am. Chem. Soc.* **2010**, *132*, 11045

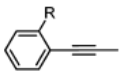
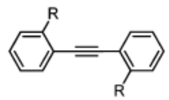
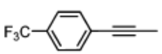
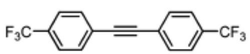
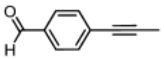
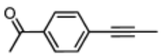
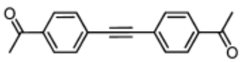
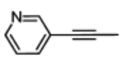
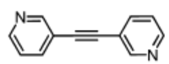
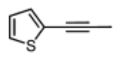
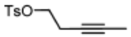
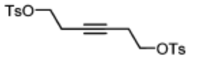
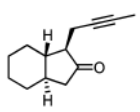
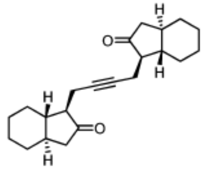
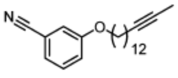
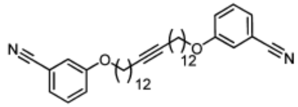
1.2. Alkyne Metathesis:

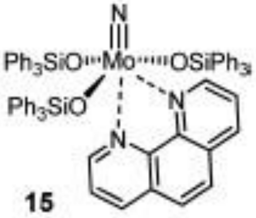




A. Fürstner, F. *J. Am. Chem. Soc.* **2010**, *132*, 11045

1.2. Alkyne Metathesis:

Entry	Substrate	Product		15[a]	24·Et_2O[b]	25[c]
1			R = H	99%	99%	99%
2			R = OMe	96%	97%	97%
3			R = SMe	87%	98%[d]	96%[d]
4			R = COOMe	72%[e]	95%	97%
5				94%	93%	95%
6				NR	NR	NR
7				< 40%[e,f]	84%	84%
8				76%[e]	90%[d]	88%[d]
9				86%	88%	87%
10				95%	92%	92%
11				85%	89%	91%
12					92%	88%
13				81%	87%	89%



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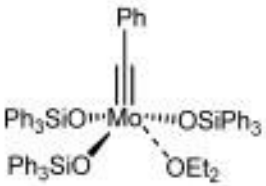

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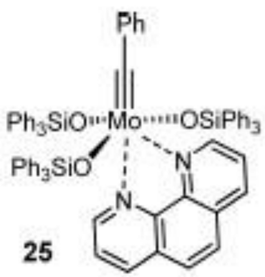

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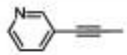
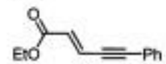
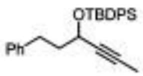
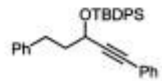
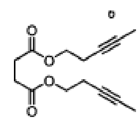
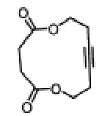
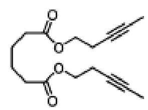
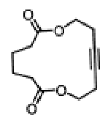
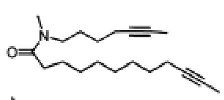
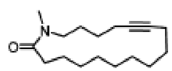
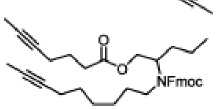
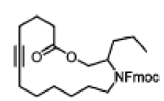
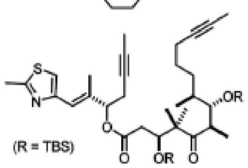
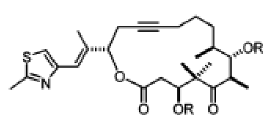
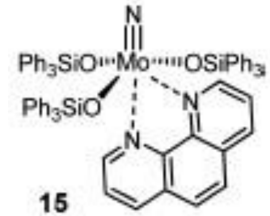
1.2. Alkyne Metathesis:

Entry	Substrates		Product	15[a]	24·Et_2O[b]	25[c]
1		5-decyne		76%	65%	72%
2		tolane		50%	65%	62%
3		tolane		*d*	62%	61%
3				91%	73%	78%
4				85%	92%	90%
5				67%	72%	
6					90%	
7					91%	



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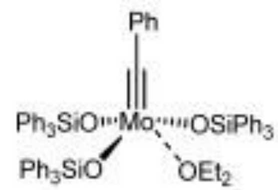

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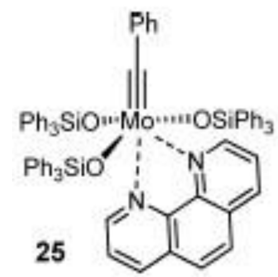

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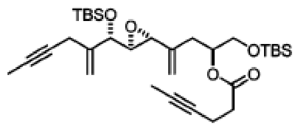
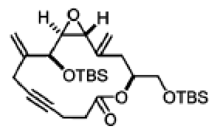
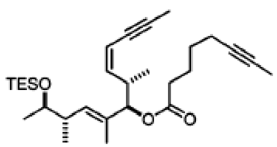
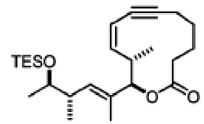
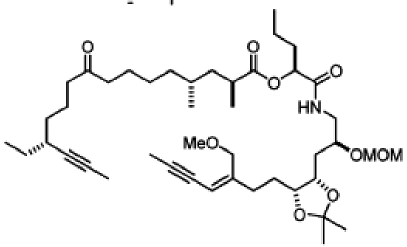
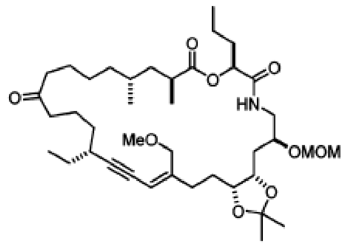
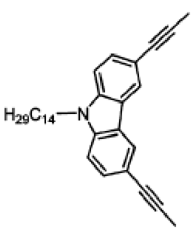
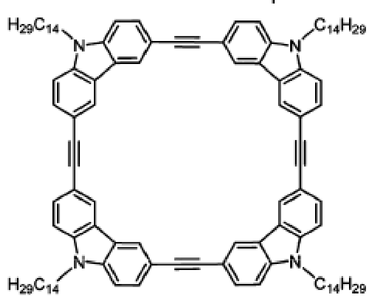
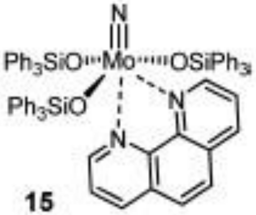
1.2. Alkyne Metathesis:

10				81%	
11				84%[e]	
12				79%	
13			83%	82%	81%



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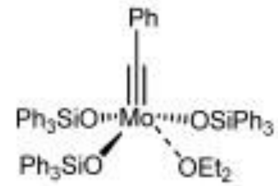

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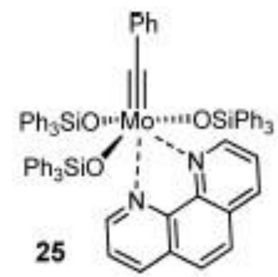

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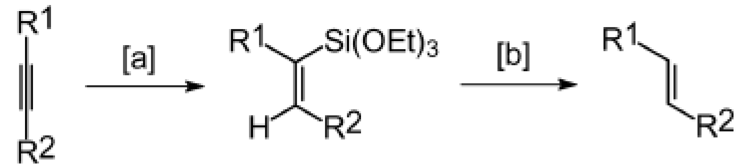
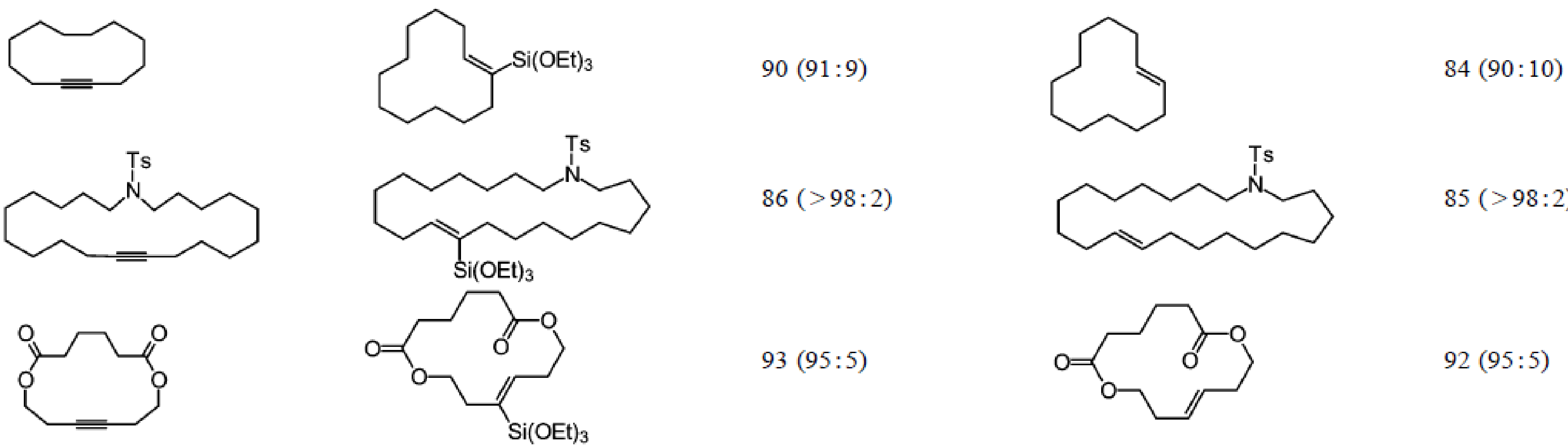
1.2. Alkyne Metathesis:



Scheme 2 *Reagents and conditions*: [a] $(EtO)_3SiH$, $[Cp^*Ru(MeCN)_3]PF_6$ (1 mol%), CH_2Cl_2, r.t.; [b] AgF (2 eq.), THF/aq. MeOH, r.t.



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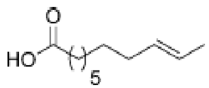
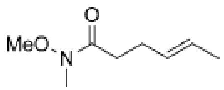
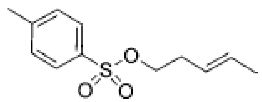
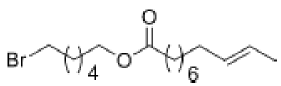
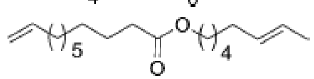
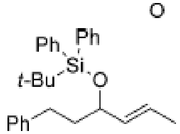
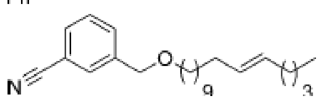
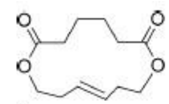
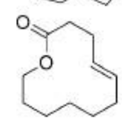
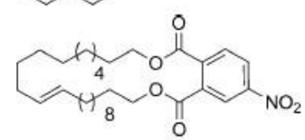
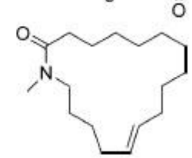
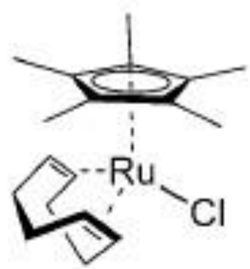
1.2. Alkyne Metathesis:

Table 2: *trans*-Selective reduction of internal alkynes.[a]

Entry	Major Product	*t* [h]	*E*/*Z*[b]	Yield [%][c]
1		0.5	98:2	96
2		0.5	95:5	88
3		4	96:4	66[d]
4		2.5	93:7	95
5		0.5	95:5	87
6		0.5	97:3	60[d]
7		4	93:7	96 (33)[c,d]
8		0.5	87:13	95 (21)[c]
13		0.5	98:2	89[f]
14		0.5	96:4	64 (27)[c,d]
15		16[g]	97:3	81[d]
16		3	92:8	80
17		34[g]	91:9	85
18		1[g]	97:3	77 (26)[c,d]



+AgOTf+H_2(10bar)

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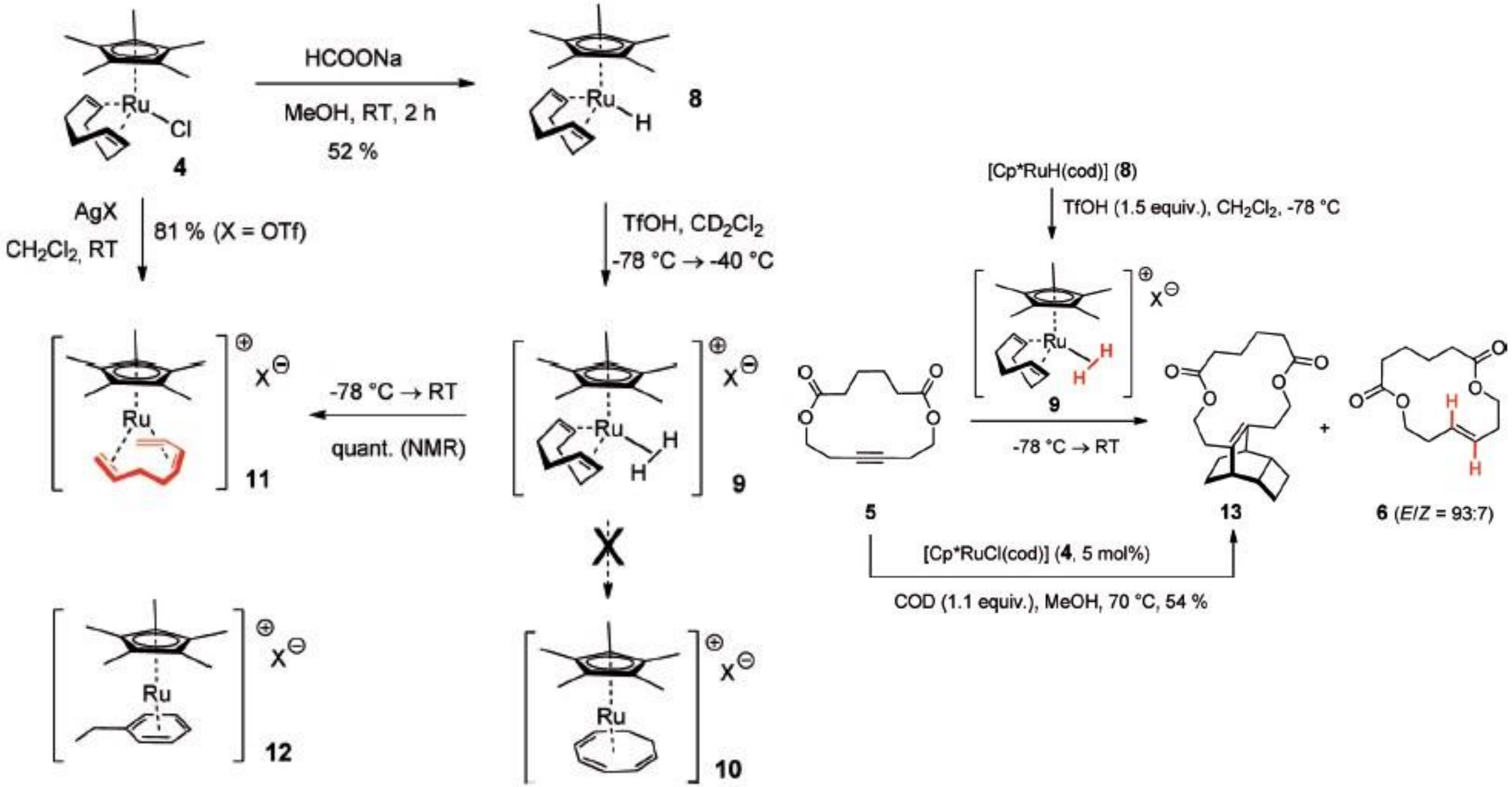
1.2. Alkyne Metathesis:



Scheme 3. Fate of the cationic [Cp*Ru(cod)] fragment.

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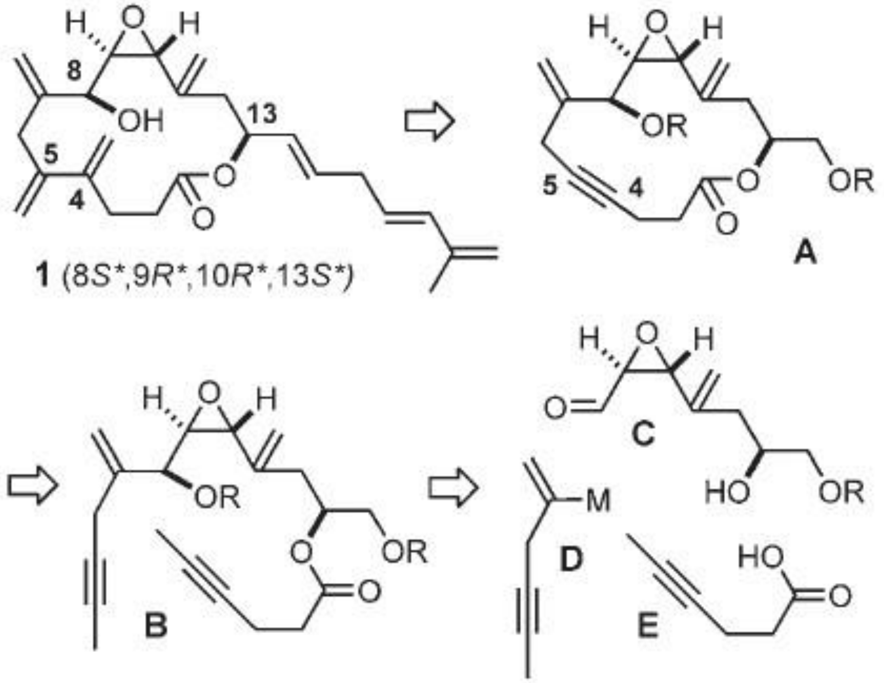
1.2. Alkyne Metathesis in total synthesis

Retrosynthetic analysis of AmphidinolideV.
A nature product born for RCAM



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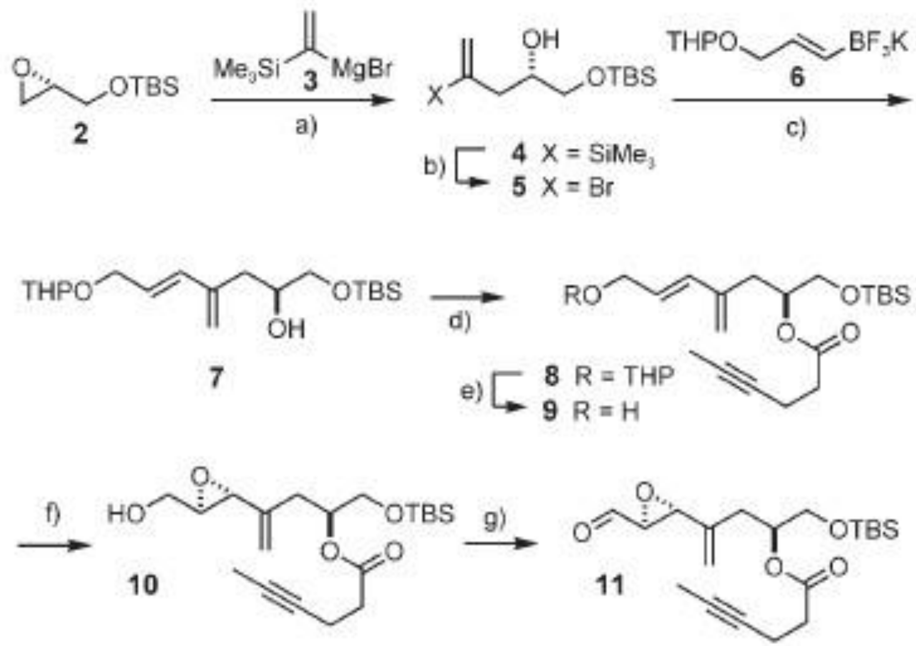
1.2. Alkyne Metathesis in total synthesis



Scheme 2. a) CuCN (10%), THF, 0°C→RT, 99%; b) 1. Br_2, CH_2Cl_2, −78°C; 2. NaOMe, MeOH, −20°C; 3. HOAc, 91% (overall); c) **6**, $Pd(OAc)_2$ (10%), dppf (10%), $tBuNH_2$, THF, reflux (sealed tube), 84%; d) 4-hexynoic acid, EDC, 1-hydroxy-7-azabenzotriazole, $(iPr)_2NEt$, DMAP, CH_2Cl_2/DMF (4:1), 95%; e) PPTS (cat.), *i*PrOH, 70°C, 98%; f) D-(−)-DET (40%), $Ti(OiPr)_4$ (40%), *t*BuOOH, MS (4 Å), CH_2Cl_2, −25°C, 77%; g) Dess–Martin periodinane, $NaHCO_3$, CH_2Cl_2, 90%. dppf = 1,1′-bis(diphenylphosphanyl)ferrocene, EDC = *N*-(3-dimethylaminopropyl)-*N*′-ethyl-carbodiimide, DMAP = 4-dimethylaminopyridine, PPTS = pyridinium *p*-toluenesulfonate, DET = diethyl tartrate.

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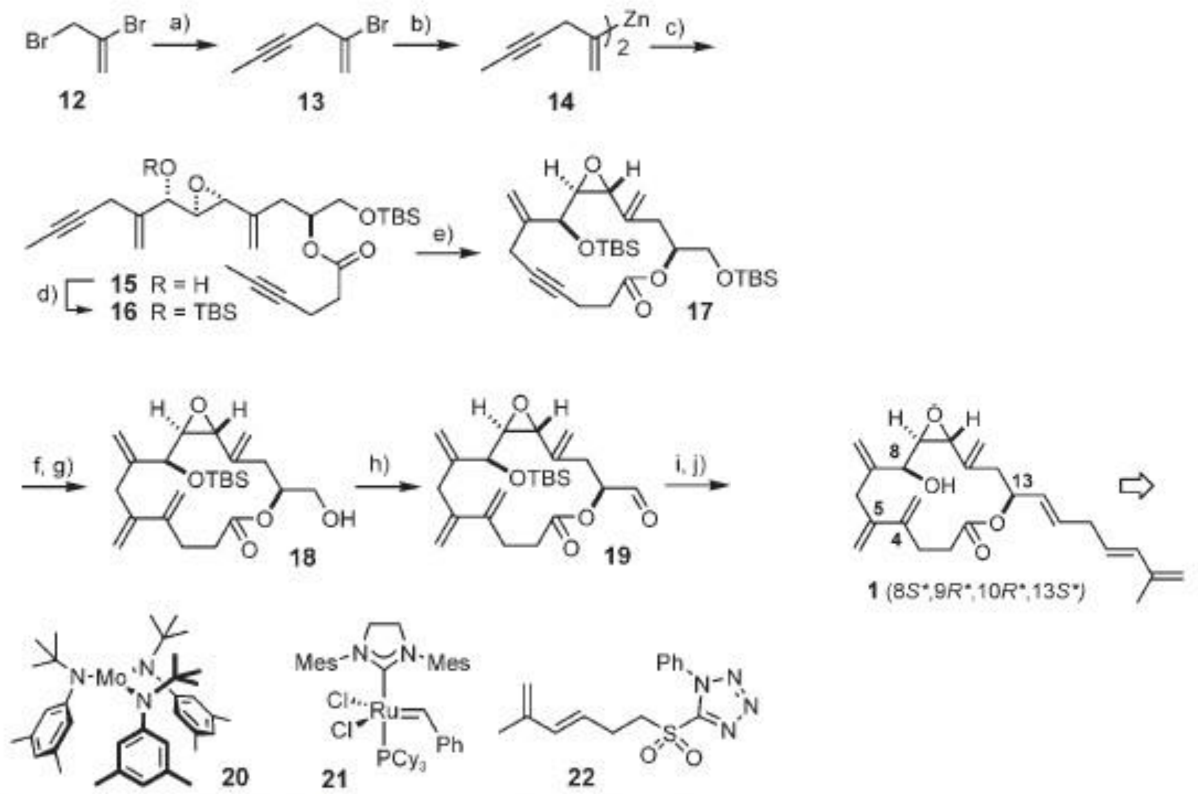
1.2. Alkyne Metathesis in total synthesis



Scheme 3. a) MeC≡CMgBr, CuBr·Me_2S, Et_2O, 99%; b) Li, $ZnBr_2$, THF, 0°C, ultrasound; c) **11**, toluene, (+)-*N*-methylephedrine (60%), −25°C, 69%; d) TBSCl, imidazole, CH_2Cl_2, 10°C, 79%; e) **20** (20%), CH_2Cl_2/toluene, 85°C, 66%; f) **21** (2%), C_2H_4 (1.8 atm), toluene, 45°C, 90%; g) PPTS (cat.), MeOH, 62%; h) Dess–Martin periodinane, $NaHCO_3$, CH_2Cl_2; i) **22**, KHMDS, DME/DMPU, −78°C→RT, 57% (over both steps, *E*:*Z* ≈ 10:1); j) TASF, DMF, −5°C, 82%;

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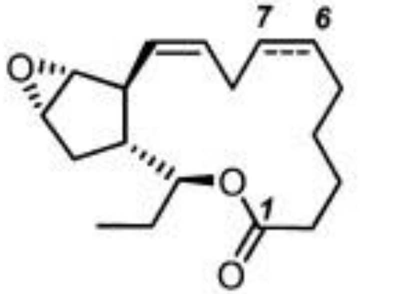
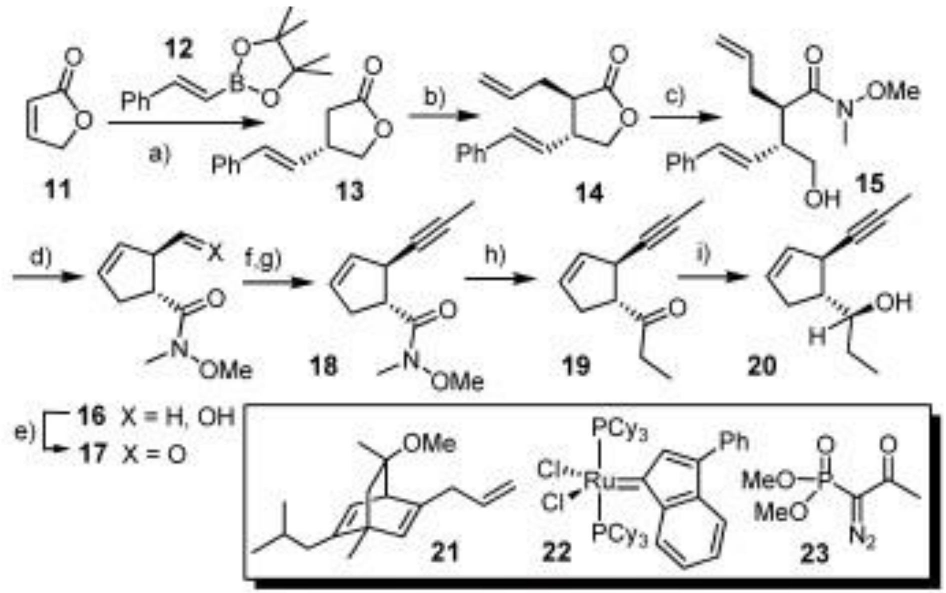
1.2. Alkyne Metathesis in total synthesis

Protecting-Group-Free and Catalysis-Based Total Synthesis of the Ecklonialactones



Ecklonialactone A (**1**): $\Delta^{6,7}$
Ecklonialactone B (**2**)



[a] Reagents and conditions: (a) $[Rh(C_2H_4)_2Cl]_2$ (1.5 mol %), **21** (3.3 mol %), SiO_2 cat., 1,4-dioxane, aq. KOH, 52%, 80% ee (93% ee after recryst.); (b) LDA, THF, −78 °C, then allyl iodide, 87%; (c) HN(OMe)Me·HCl, Me_3Al, CH_2Cl_2, 0 °C → rt; (d) **22** (8 mol %), CH_2Cl_2, 75% (over both steps); (e) Dess−Martin periodinane, $NaHCO_3$, CH_2Cl_2, 73%; (f) **23**, K_2CO_3, MeOH, 75%; (g) LiHMDS, MeOTf, THF, −78 °C, 80%; (h) EtMgBr, THF, 0 °C, 93%; (i) $LiBH(s\text{-}Bu)_3$, THF, −78 °C, 69%.

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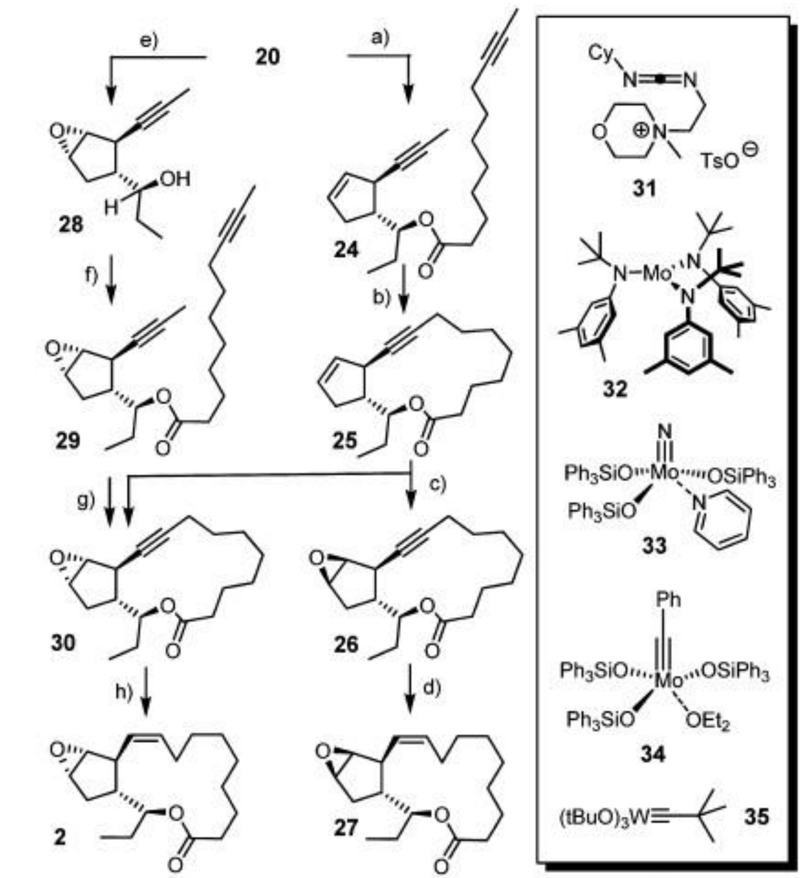
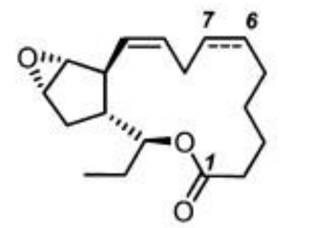
1.2. Alkyne Metathesis in total synthesis

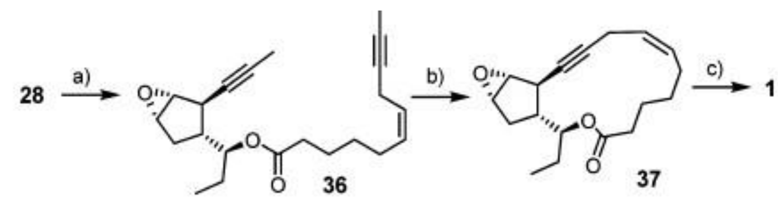


^{a} Reagents and conditions: (a) 9-undecynoyl chloride, DMAP, CH_2Cl_2, 70%; (b) **32** (20 mol %), toluene/CH_2Cl_2, 80 °C, 71%; (c) dimethyl dioxirane, acetone/CH_2Cl_2, −78 °C → rt, 75% (**26**:**30** = 3:1); (d) Lindlar catalyst, H_2, CH_2Cl_2, 80%; (e) $VO(acac)_2$ (8 mol %), *t*-BuOOH, CH_2Cl_2, 94%; (f) 9-undecynoic acid, **31**, DMAP, CH_2Cl_2, 61%; (g) **34** (5 mol %), toluene, MS 5 Å, 80%; (h) Lindlar catalyst, H_2, CH_2Cl_2, 90%.



Ecklonialactone A (**1**): $\Delta^{6,7}$

Ecklonialactone B (**2**)

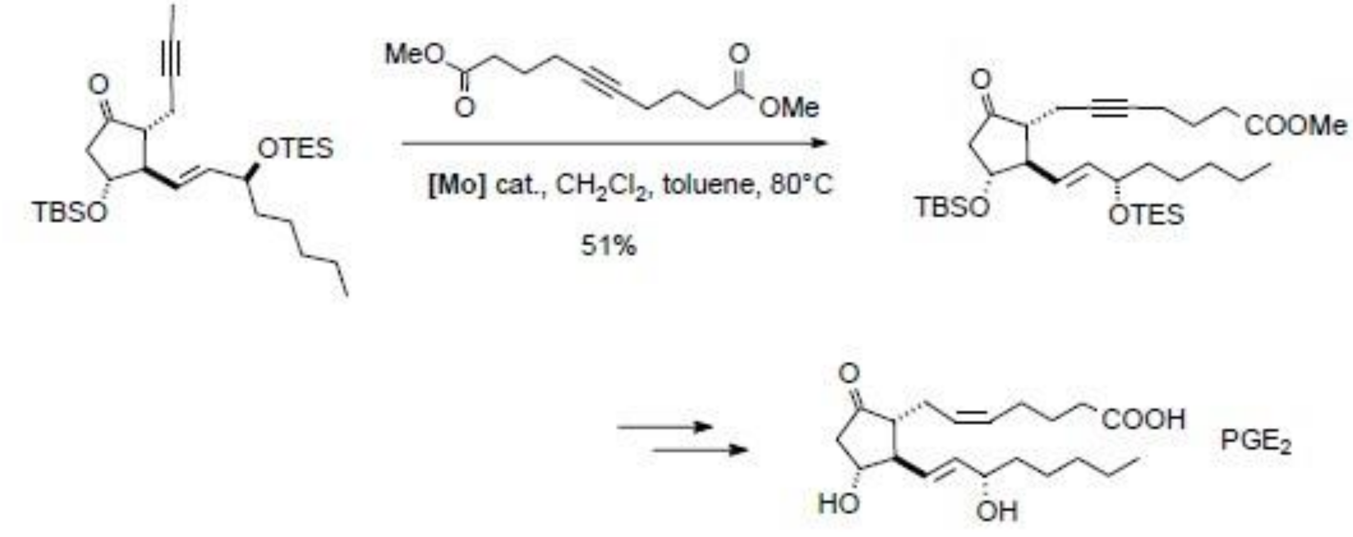


^{a} Reagents and conditions: (a) undec-6(*Z*)-en-9-ynoic acid, **31**, DMAP, CH_2Cl_2, 65%; (b) **34** (5 mol %), MS 5 Å, toluene, 90%; (c) P_2Ni (25 mol %), H_2, EtOH, 69%.

A. Fürstner, F. *J. Am. Chem. Soc.* **2010**, *132*, 11042

1.2. Alkyne Metathesis in total synthesis

Cross Alkyne Metathesis：

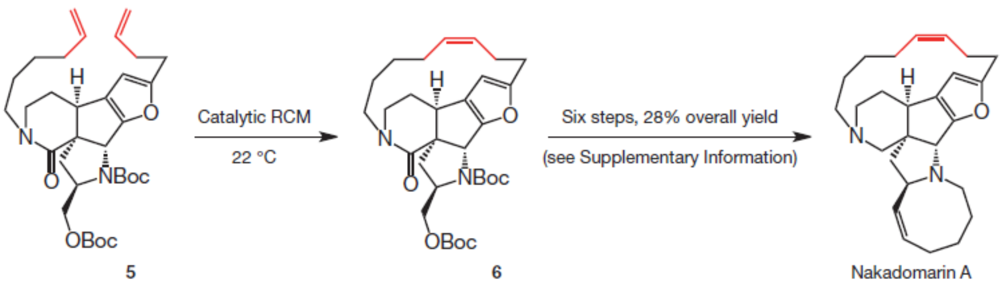


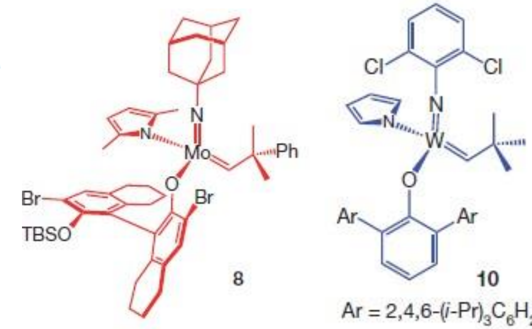
A. Fürstner, *Org. Lett*. **2001**, *3*, 221.

1.3. Compare Alkyne metathesis and Alkene in the selectivity

Alkene Metathesis

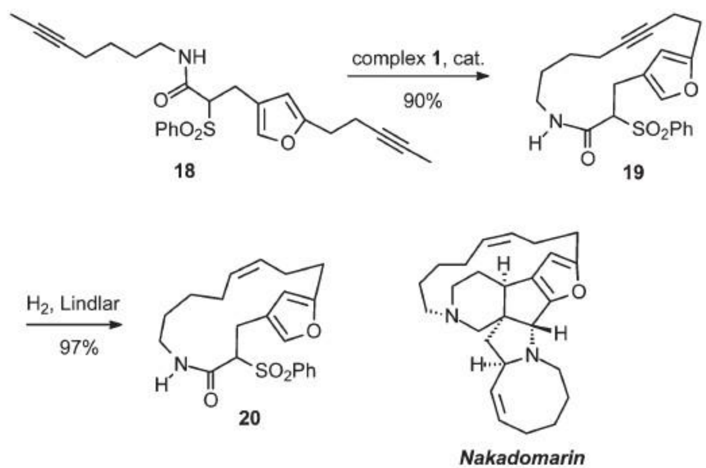
Table 3 | *Z*-selective catalytic RCM for stereoselective synthesis of 6 en route to nakadomarin A

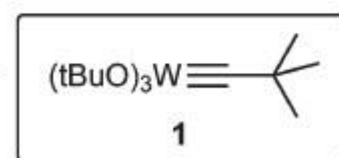




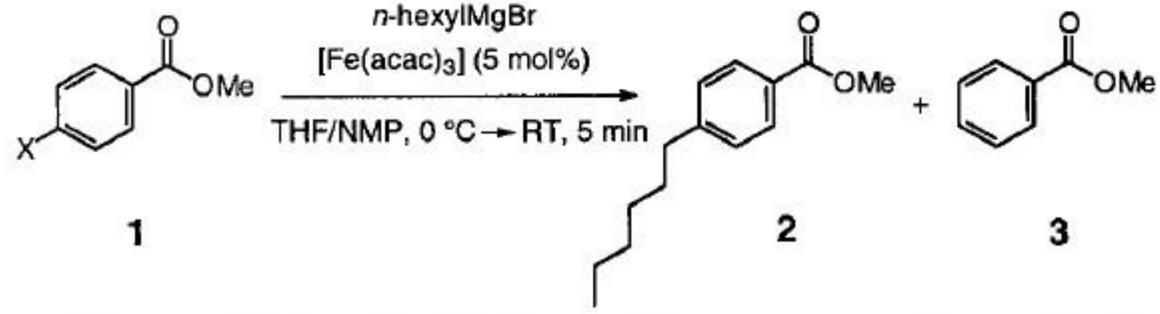
Entry no.	Complex; loading (mol%)	Pressure; concentration	Time	Conv.* (%); yield† (%)	*Z*:*E**
1	**7b**; 5.0	7.0 torr; 5.0 mM	2.0 h	10; ND	ND
2	**8**; 6.0	7.0 torr; 5.0 mM	2.0 h	95; 71	69:31
3	**9**; 5.0	7.0 torr; 5.0 mM	2.0 h	26; ND	ND
4	**10**; 5.0	7.0 torr; 5.0 mM	2.0 h	98; 90	97:3
5	**10**; 5.0	7.0 torr; 0.1 M	0.5 h	>98; 39	90:10
6	**10**; 5.0	Ambient; 0.1 M	2.0 h	95; 52	94:6

Alkyne Metathesis





2.1 Fe catalyzed coupling reaction



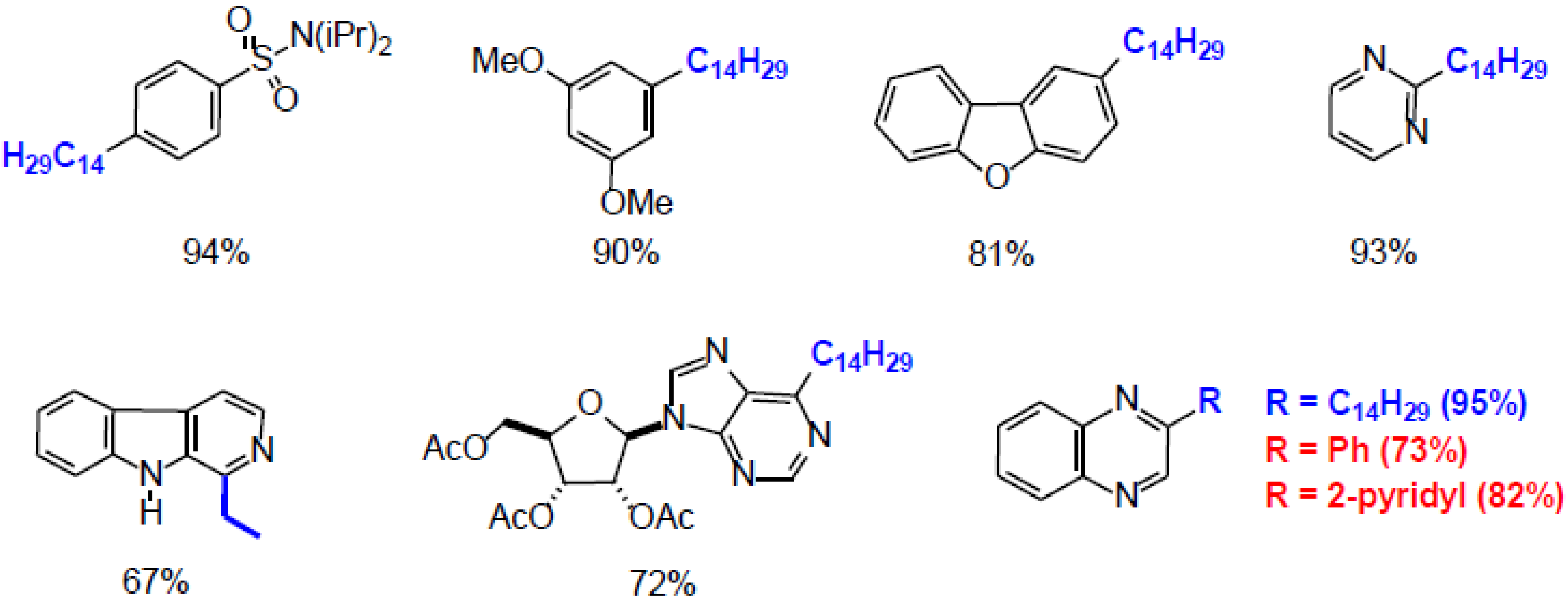
Scheme 3. Optimization of the iron-catalyzed cross-coupling reaction of substrate **1**, (see Table 1). NMP = *N*-methylpyrrolidone.

Table 1. Screening of different substrates in the iron catalyzed cross coupling reaction depicted in Scheme 3.

Entry	X	Yield [GC, %]	
		2	**3**
1	I	27	46
2	Br	38	50
3	Cl	>95	–
4	OTf	>95	–
5	OTs	>95	–

A. Fürstner et al.*Angew. Chem. Int. Ed*. **2002**, *41*, 609;

2.1 Fe catalyzed coupling reaction

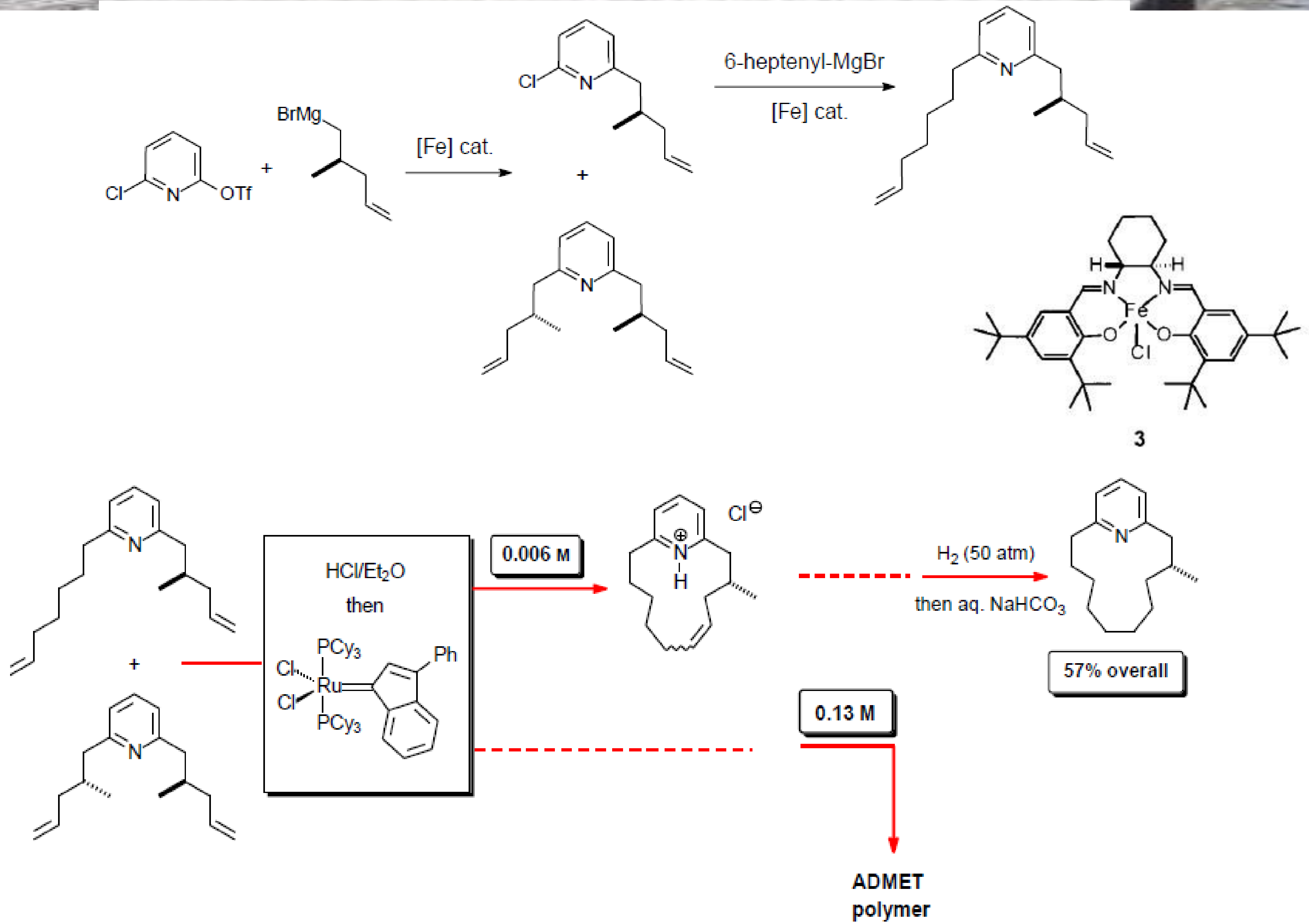


alkyl-MgX >> **aryl-MgX** (homocoupling)

the reaction is sensitive to steric hindrance

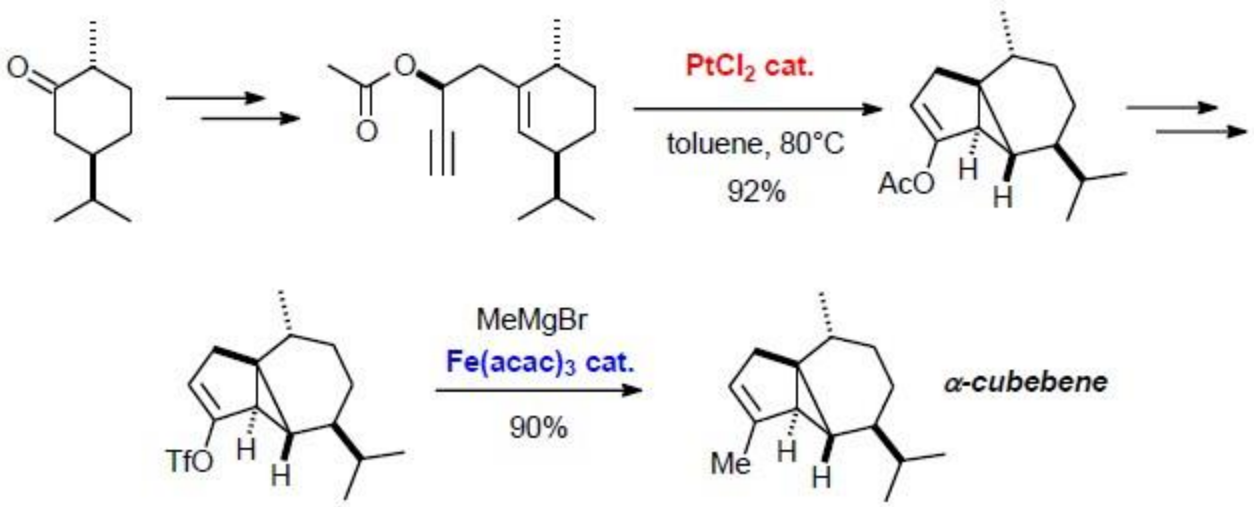
A. Fürstner et al. . *J. Am. Chem. Soc.* **2002**, *124*, 13856

2.1 Fe catalyzed coupling reaction

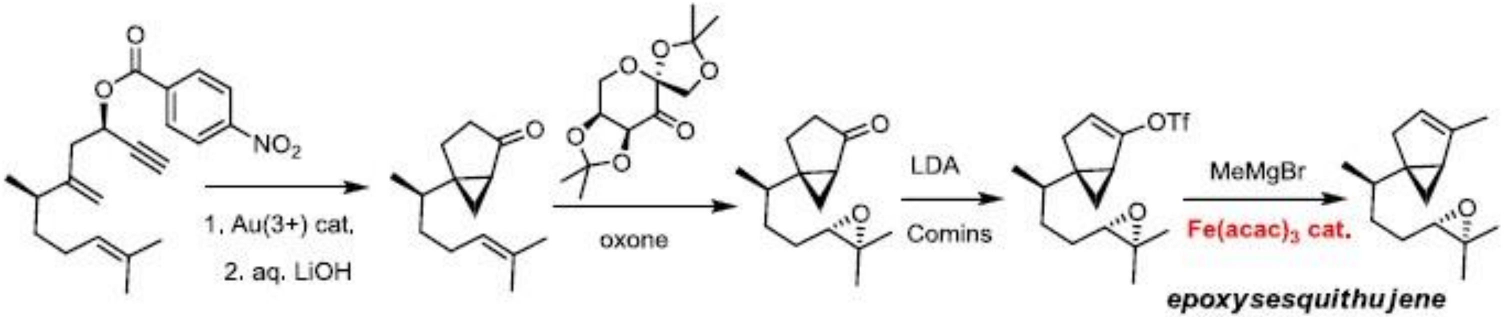


A. Fürstner et al. *Angew. Chem. Int. Ed*. **2003**, *42*, 308

2.1 Fe catalyzed coupling reaction

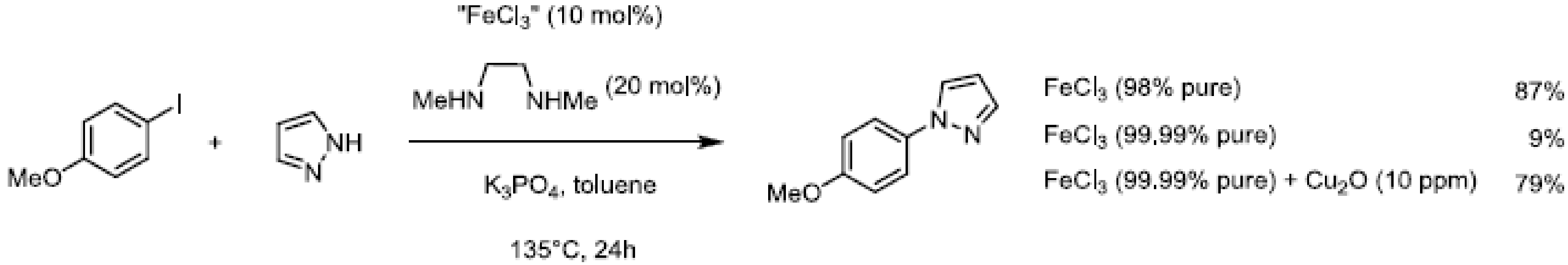


A. Fürstner, P. Hannen, *Chem. Eur. J.* **2006**, *12*, 3006



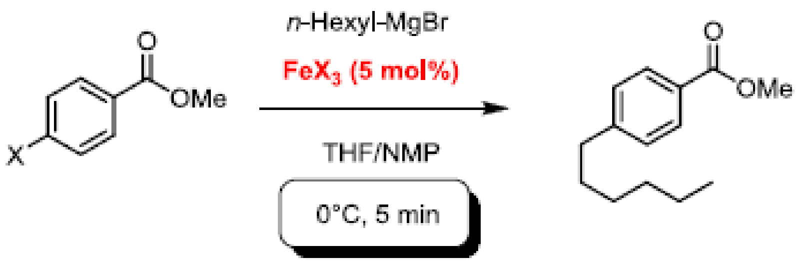
A. Fürstner, A. Schlecker, *Chem. Eur. J*. **2008**, *14*, 9181

2.1 Fe catalyzed coupling reaction



C. Bolm et al., *Angew. Chem., Int. Ed.* **2007**, *46*, 8862

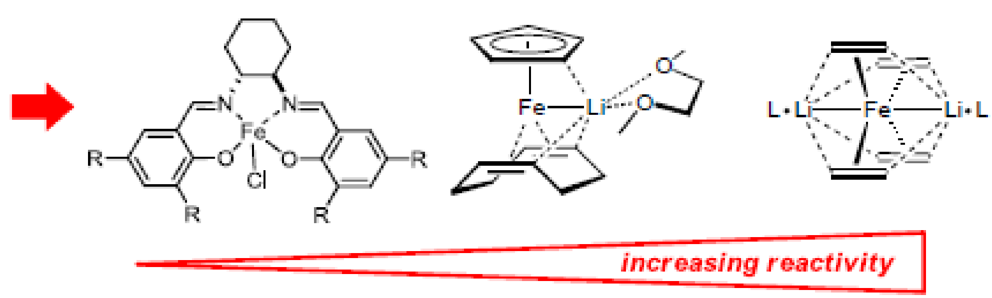
S. L. Buchwald, C. Bolm, *Angew. Chem. Int. Ed.* **2009**, *48*, 5586



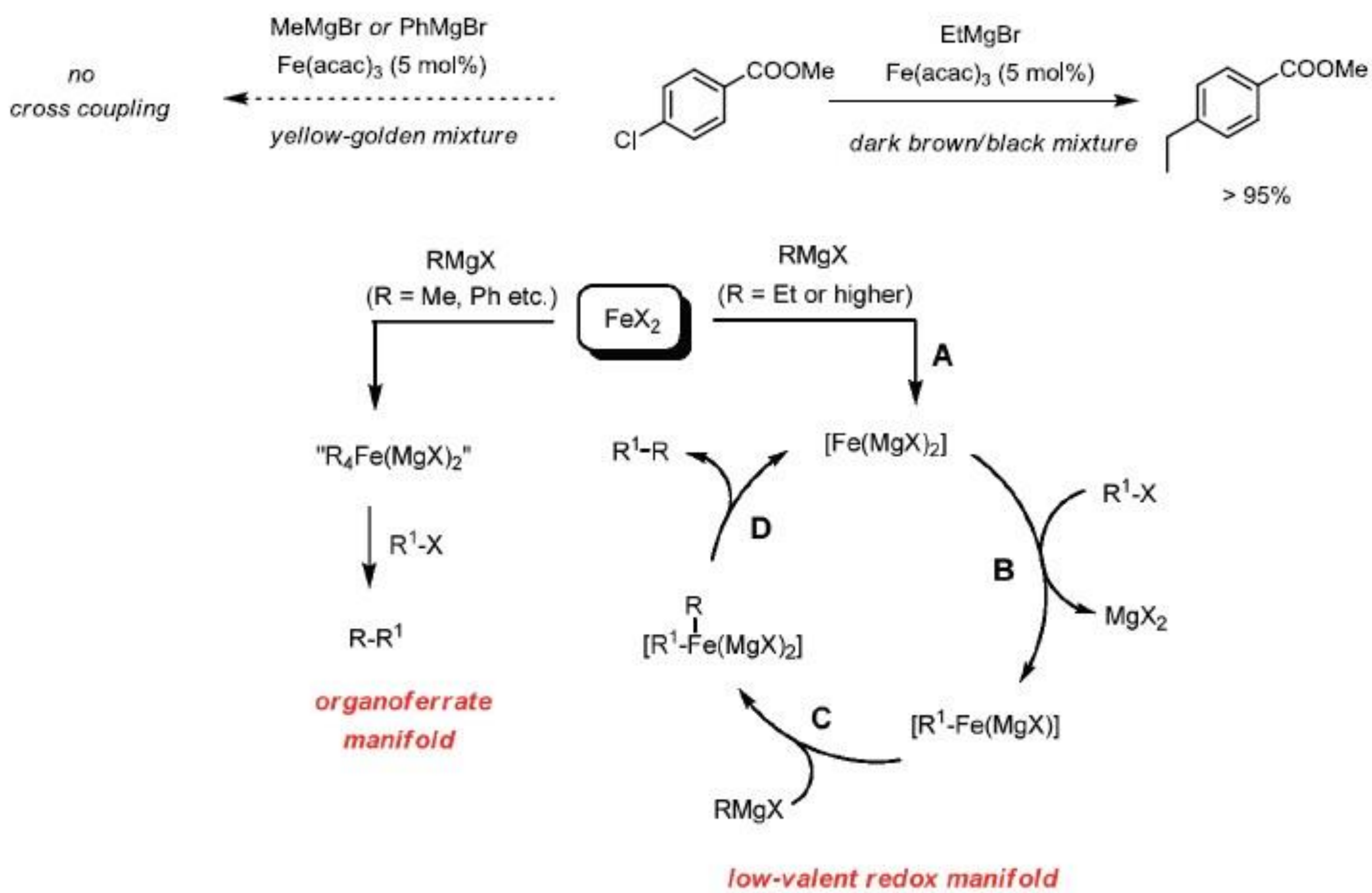
$Fe(acac)_3$ (99.9+% pure)	91%
$FeCl_3$ (99.99+% pure)	93%

X = Cl >> Br, I

extremely fast even at -20°C

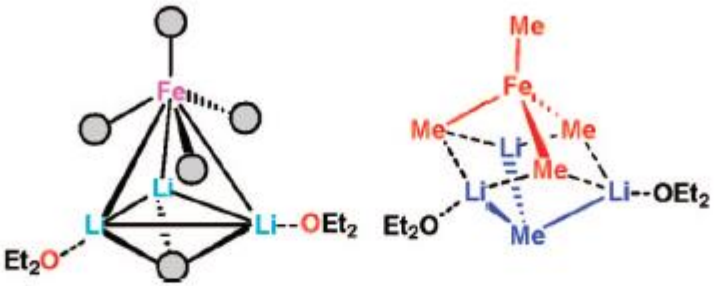


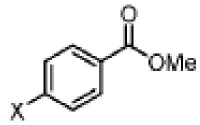
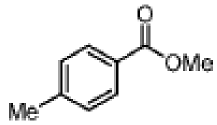
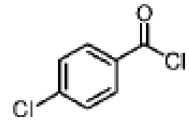
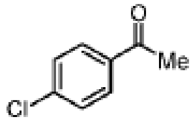
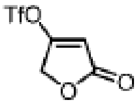
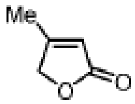
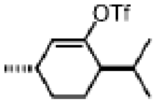
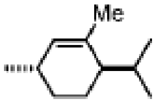
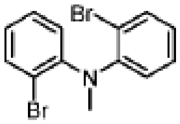
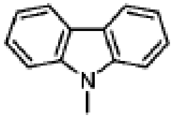
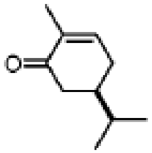
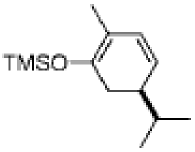
2.1 Fe catalyzed coupling reaction



A. Fürstner et al. . *J. Am. Chem. Soc.* **2008**, *130*, 8773

2.1 Fe catalyzed coupling reaction



Nr	Substrate	Product	Yield
1			< 20% (X = Cl, I)
2			60%
3			70%
4			80%
5			83%
6			45%[b,c]

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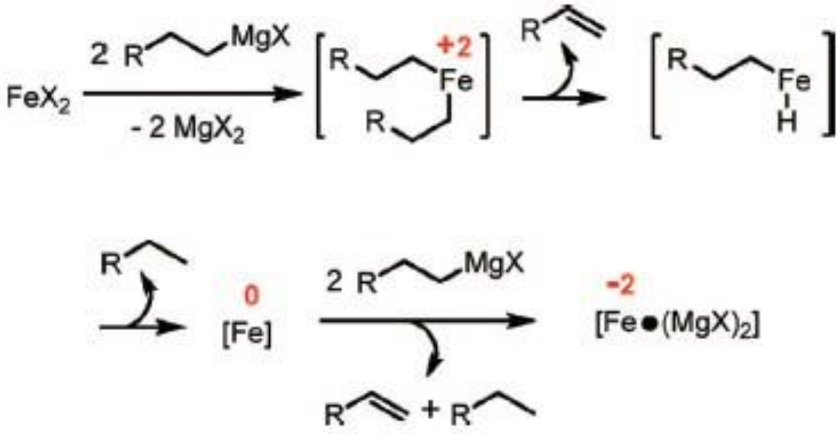
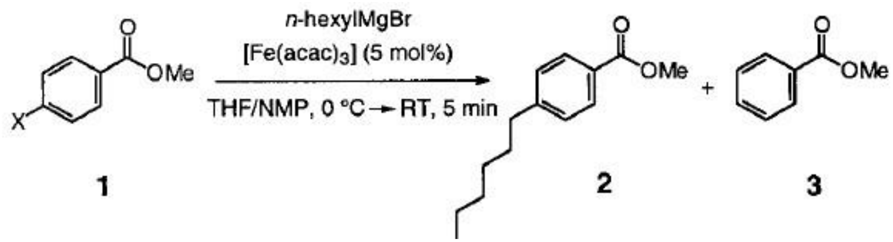
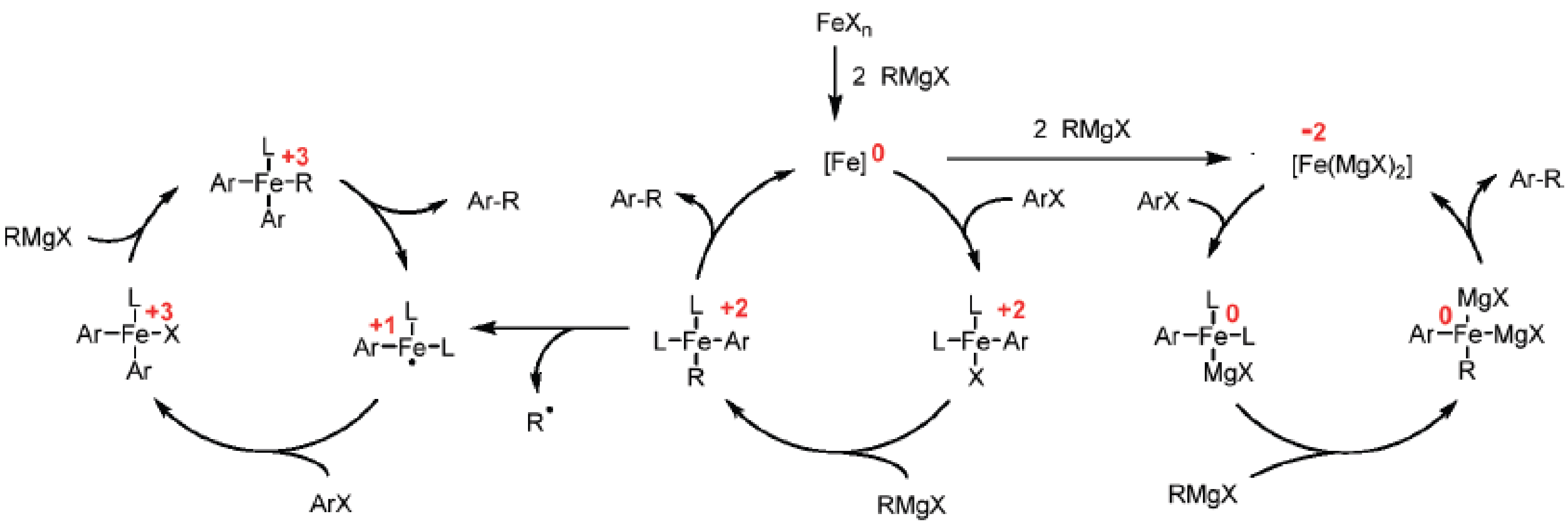
2 Fe catalyzed coupling reaction







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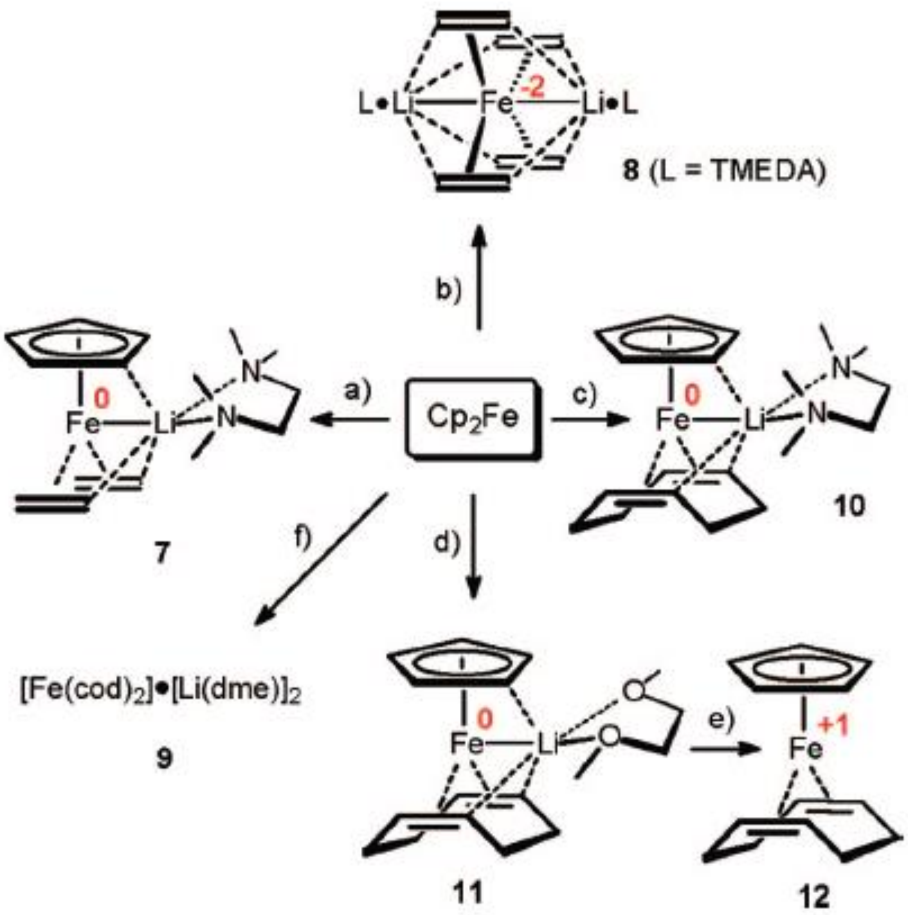
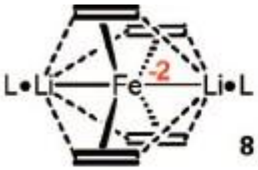
2 Fe catalyzed coupling reaction

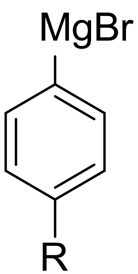


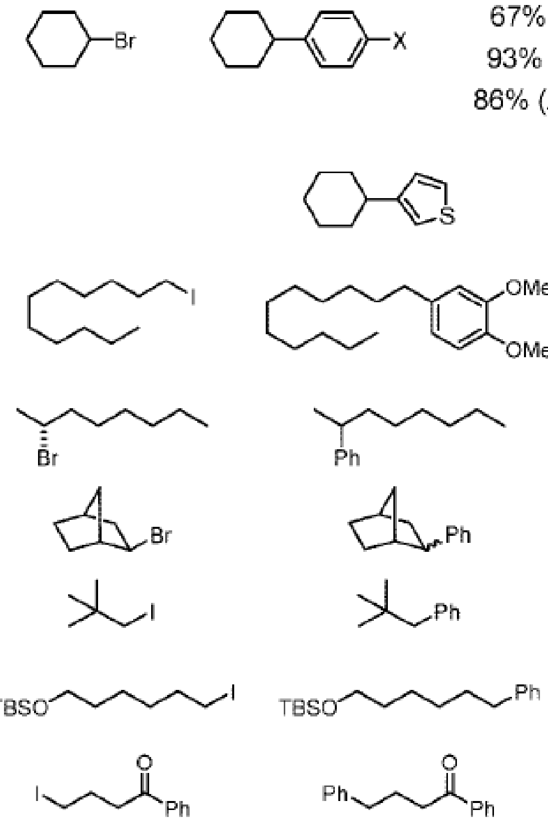
A. Fürstner et al. . *J. Am. Chem. Soc.* **2008**, *130*, 8773

2 Fe catalyzed coupling reaction



8 (L = TMEDA)





Nr	Substrate	Product	Yield
1			95% (X = OMe)
2			67% (X = Cl)[c]
3			93% (X = Ph)[c]
4			86% (X = NMe_2)
5			77%
6			94%
7			93%[d]
8			58%[e]
9			74%
10			84%
11			91%

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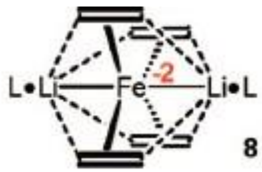
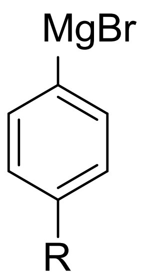
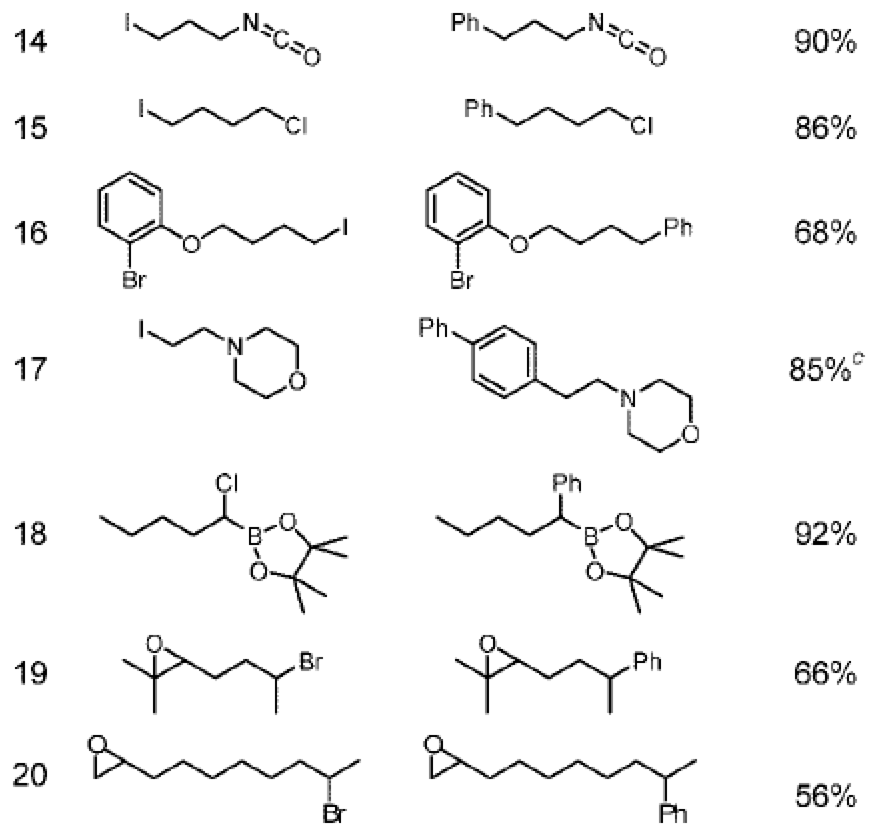
2 Fe catalyzed coupling reaction



8 (L = TMEDA)





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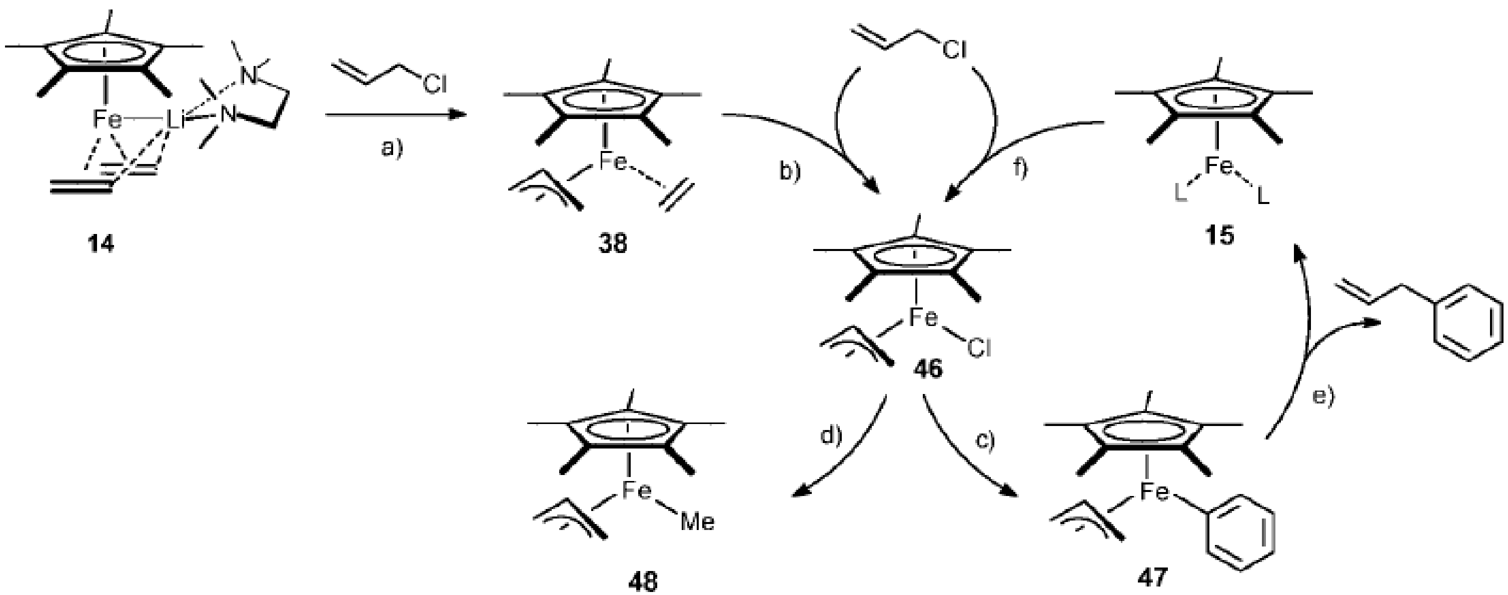
2 Fe catalyzed coupling reaction

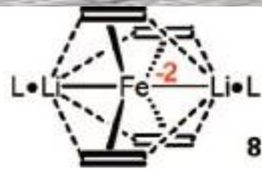
Scheme 14. Experimental Evidence for the Cross Coupling of Allyl Chloride by an Fe(1+)/Fe(3+) Redox Couple that Is Innately Connected with Lower-Valent Organoiron Precursors[a]



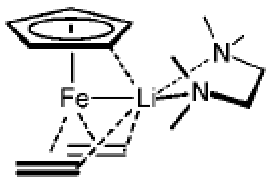
[a] Reagents and conditions: (a) allyl chloride, pentane, −20 °C → 0 °C, 16 h, 43%, cf. Scheme 9; (b) allyl chloride, Et_2O, 0 °C, 24 h, 61%, cf. Scheme 13; (c) PhLi or PhMgBr, Et_2O, −35 °C, 2 h; (d) MeLi, pentane, −78 °C → 0 °C, ca. 70%; (e) THF-d_8, ethene (1 atm), ambient temperature, 46% (NMR, allylbenzene), see text; (f) allyl chloride, Et_2O, −40 °C, 20 h, 58%.

A. Fürstner et al. . *J. Am. Chem. Soc.* **2008**, *130*, 8773

2 Fe catalyzed coupling reaction



8 (L = TMEDA)



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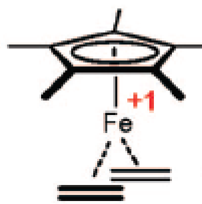

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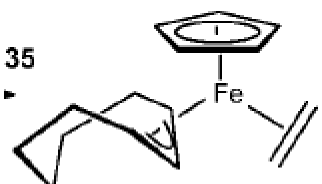

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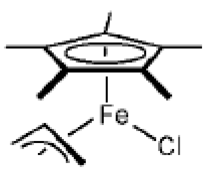
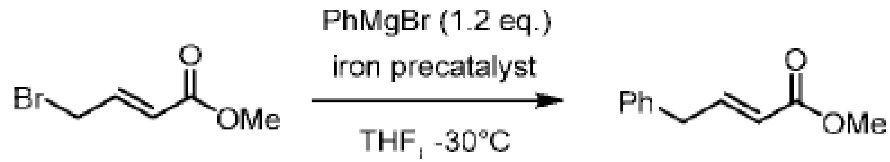


46



entry	complex (loading)	formal oxidation state	t^a	yield[b]
1	**8** (5%)	−2	< 10 min	94%
2	**7** (5%)	0	30 min	45%
3	**15** (10%)	+1	30 min	50%
4	**36** (10%)	+2	30 min	46%
5	**46** (10%)	+3	30 min	73%

[a] Time necessary to reach complete conversion of the substrate. [b] Isolated yield of pure product; variable amounts of biphenyl were removed by flash chromatography.

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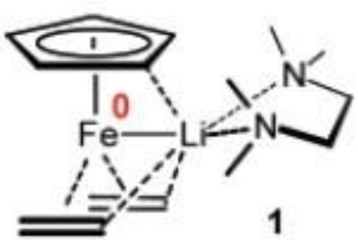
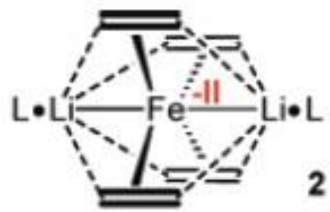
2.2 Can Fe work as Expensive metal?

A CHEAP METAL FOR A NOBLE TASK ?

Fe^{0}: [Ar] $3d^{6}$ $4s^{2}$	Fe^{-II}: [Ar] $3d^{8}$ $4s^{2}$
Ru^{0}: [Kr] $3d^{6}$ $4s^{2}$	Pd^{0}: [Kr] $3d^{10}$ $4s^{0}$
Rh^{I}: [Kr] $3d^{8}$ $4s^{0}$	Ni^{0}: [Ar] $3d^{8}$ $4s^{2}$
Ir^{I}: [Xe] $3d^{8}$ $4s^{0}$	Cu^{+I}: [Kr] $3d^{10}$ $4s^{0}$



1

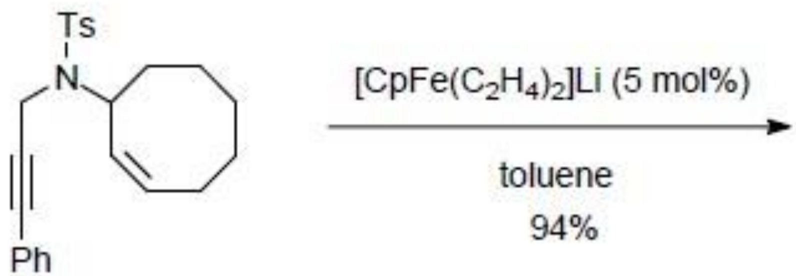


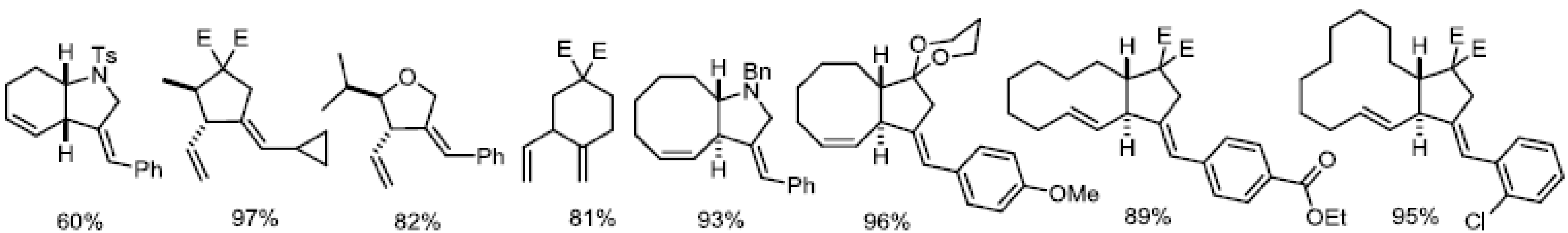
2 (L = TMEDA)

A. Fürstner et al. . *J. Am. Chem. Soc.* **2008**, *130*,1992-2004

2.2 Can Fe work as Expensive metal?

Alder-Ene Reation.

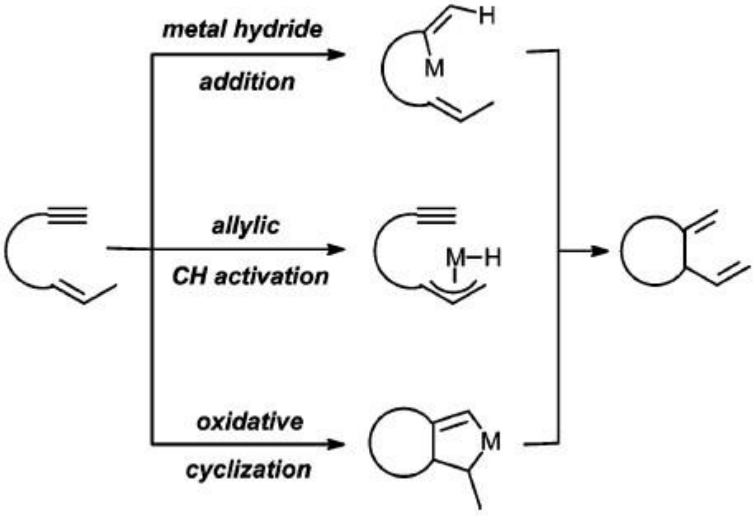


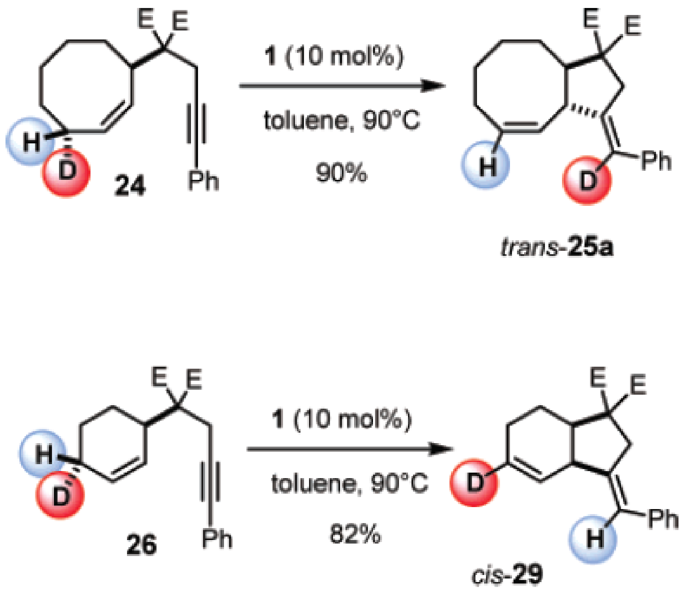


A. Fürstner et al. . *J. Am. Chem. Soc.* **2008***, 130***,**1992-2004

2.2 Can Fe work as Expensive metal?

Alder-Ene Reation.

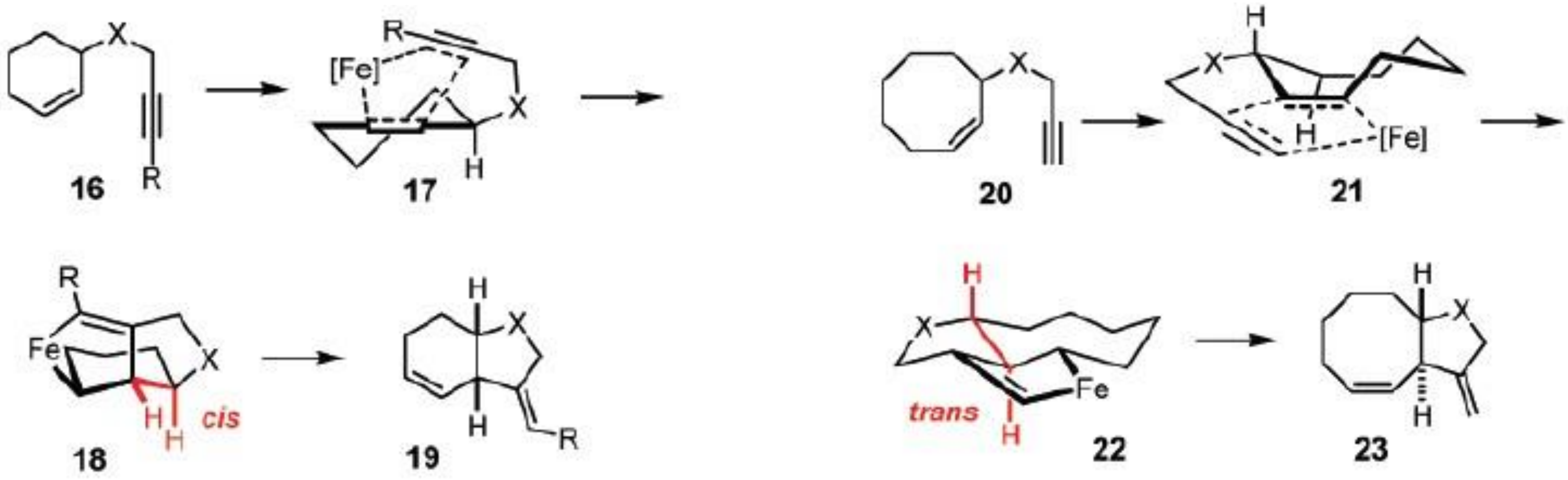




A. Fürstner et al. . *J. Am. Chem. Soc.* **2008**, *130*,1992-2004

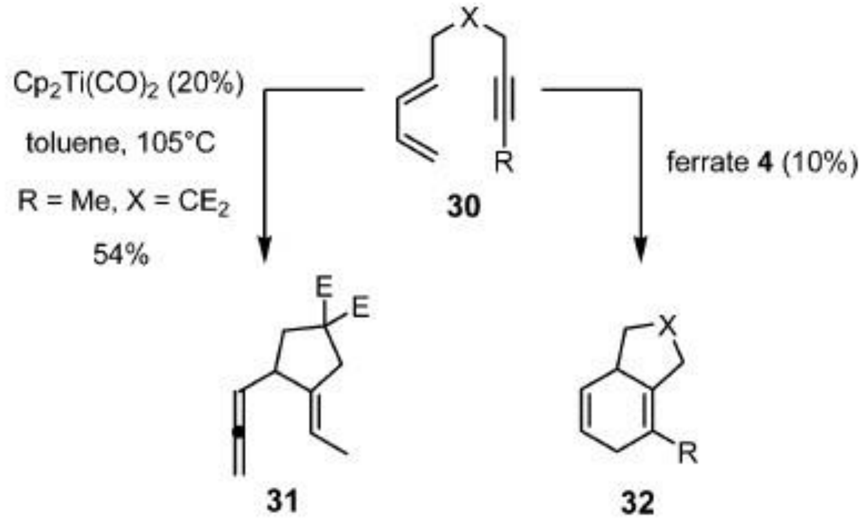
2.2 Can Fe work as Expensive metal?

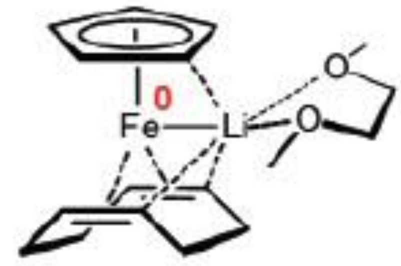
Alder-Ene Reation.



A. Fürstner et al. . *J. Am. Chem. Soc.* **2008**, *130*,1992-2004

2.2 Can Fe work as Expensive metal?





4

entry	X	R	catalyst	*t* (h)	conversion	yield[b]
1	NTs	H	–	1.5	23%	
2		H	**4** (10%)	1.5	>90%	54%
3	CE_2	H	–	7	25%	
4		H	**4** (10%)	7	85%	67%
5		Me	–	16	10%	
6		Me	**4** (20%)	16	100%	57%
7		$SiMe_3$	–	6	25%	
8		$SiMe_3$	**4** (10%)	6	100%	66%

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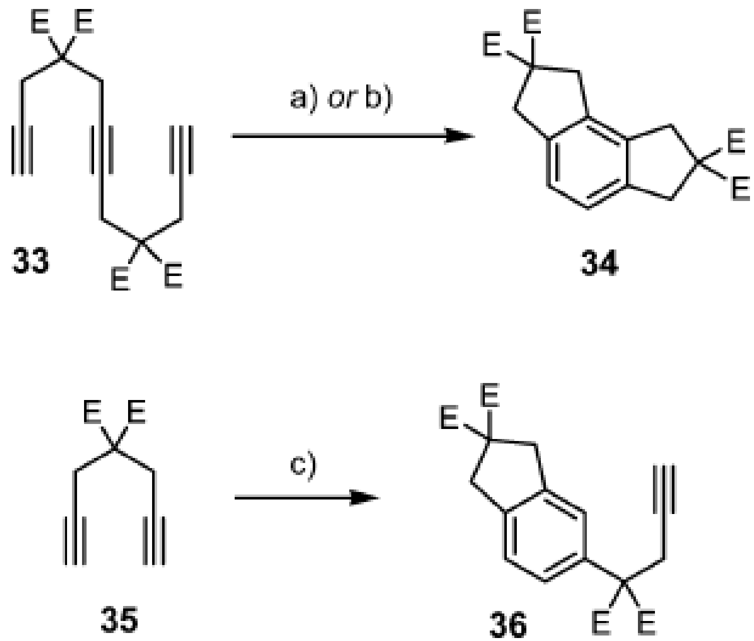
2.2 Can Fe work as Expensive metal?



[a] Reagents and conditions: (a) complex **4** (10 mol %), toluene (0.08 M), reflux, 2 h, 89%; (b) complex **6** (20 mol %), toluene (0.08 M), reflux, 21 h, 80%; (c) complex **4** (5 mol %), toluene (0.1 M), 90 °C, 24 h, 70%; E = COOEt.

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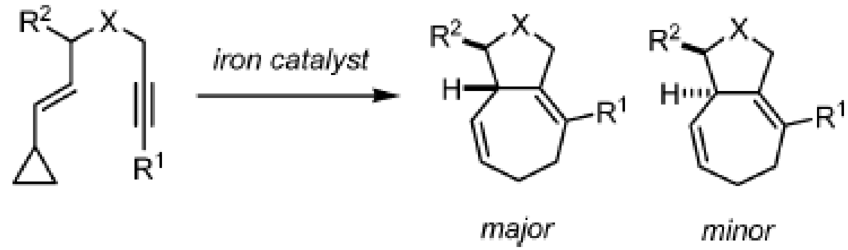
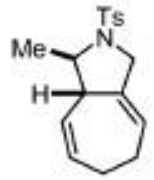
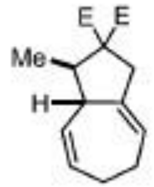
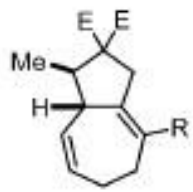
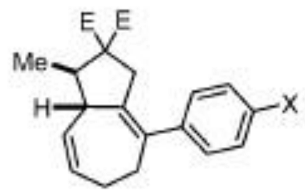
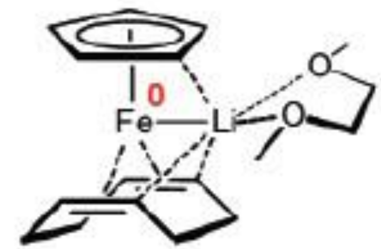
2.2 Can Fe work as Expensive metal?



9		A	56%[d]	5.5:1
10		B	70%	5.7:1
11		A	91%[e]	6.7:1
12		A	92% (R = Me)[d]	9.4:1
13		A	76% (R = COOEt)[d]	2.3:1
14		A	99% (R = $SiMe_3$)	15:1
15		A	98% (X = H)	6.2:1
16		A	98% (X = OMe)	7.3:1
17		A	97% (X = F)	6.6:1



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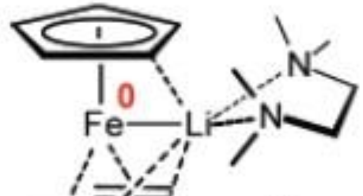

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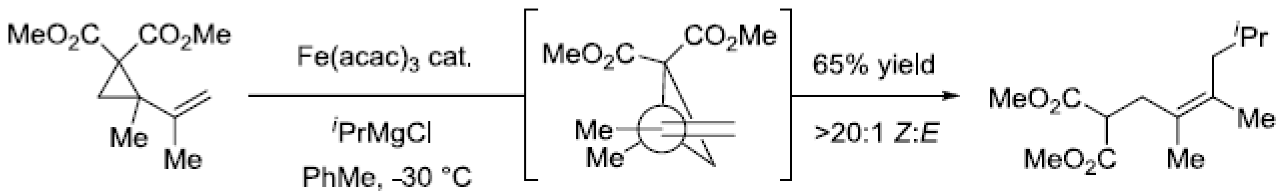
A. Fürstner et al. . *J. Am. Chem. Soc.* **2008***, 130***,**1992-2004

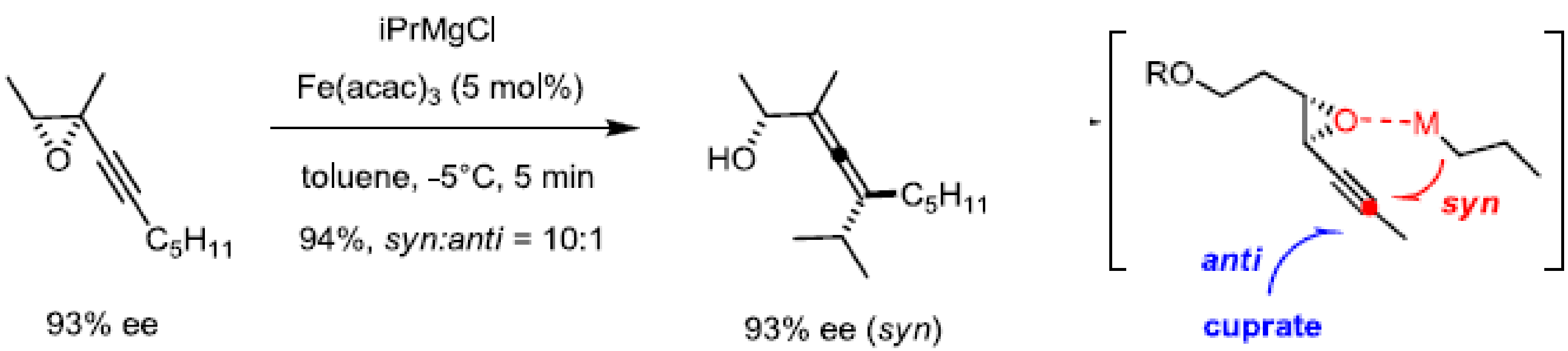
3. Acknowledgement

Thank you for your attention

3. Acknowledgement

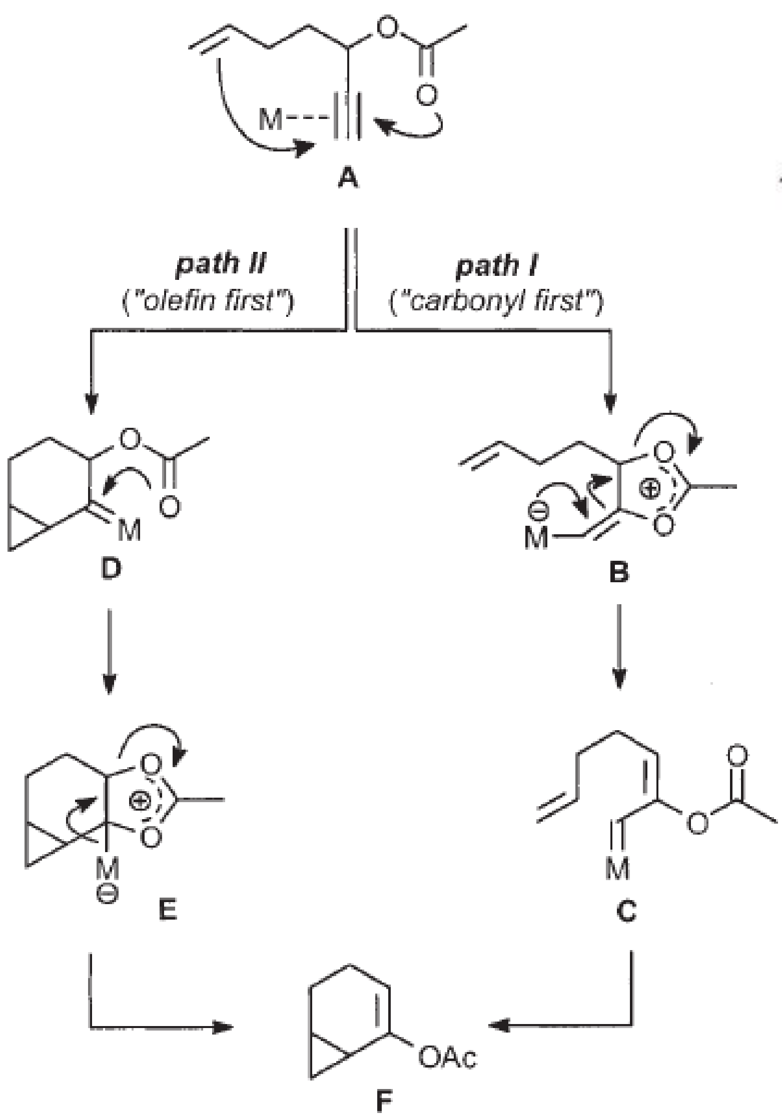


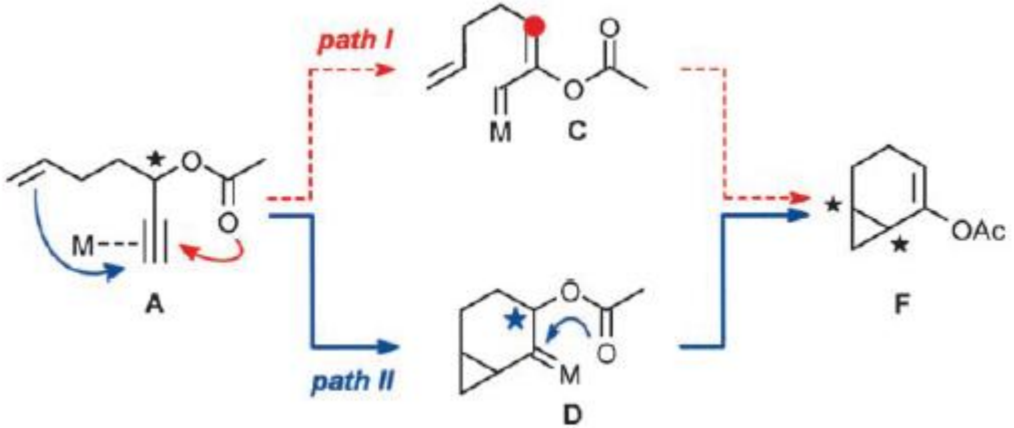
B. D. Sherry, A. Fürstner, *Chem. Commun.* **2009**, 7116



A. Fürstner, M. Méndez, *Angew. Chem. Int. Ed.* **2003**, *42*, 5355

3. Acknowledgement





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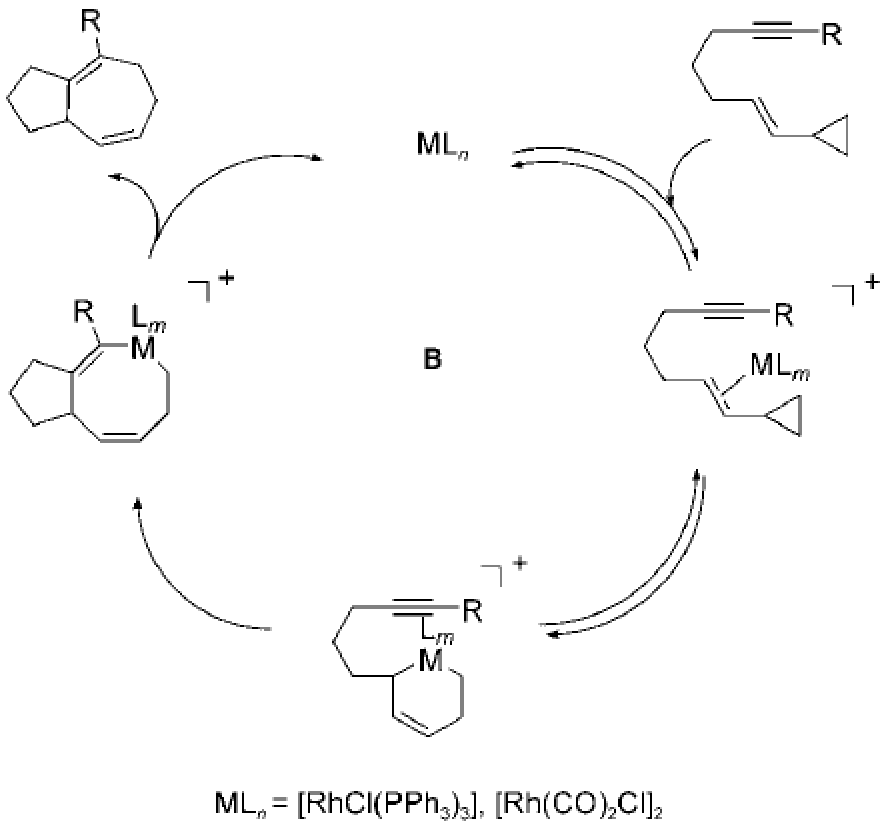
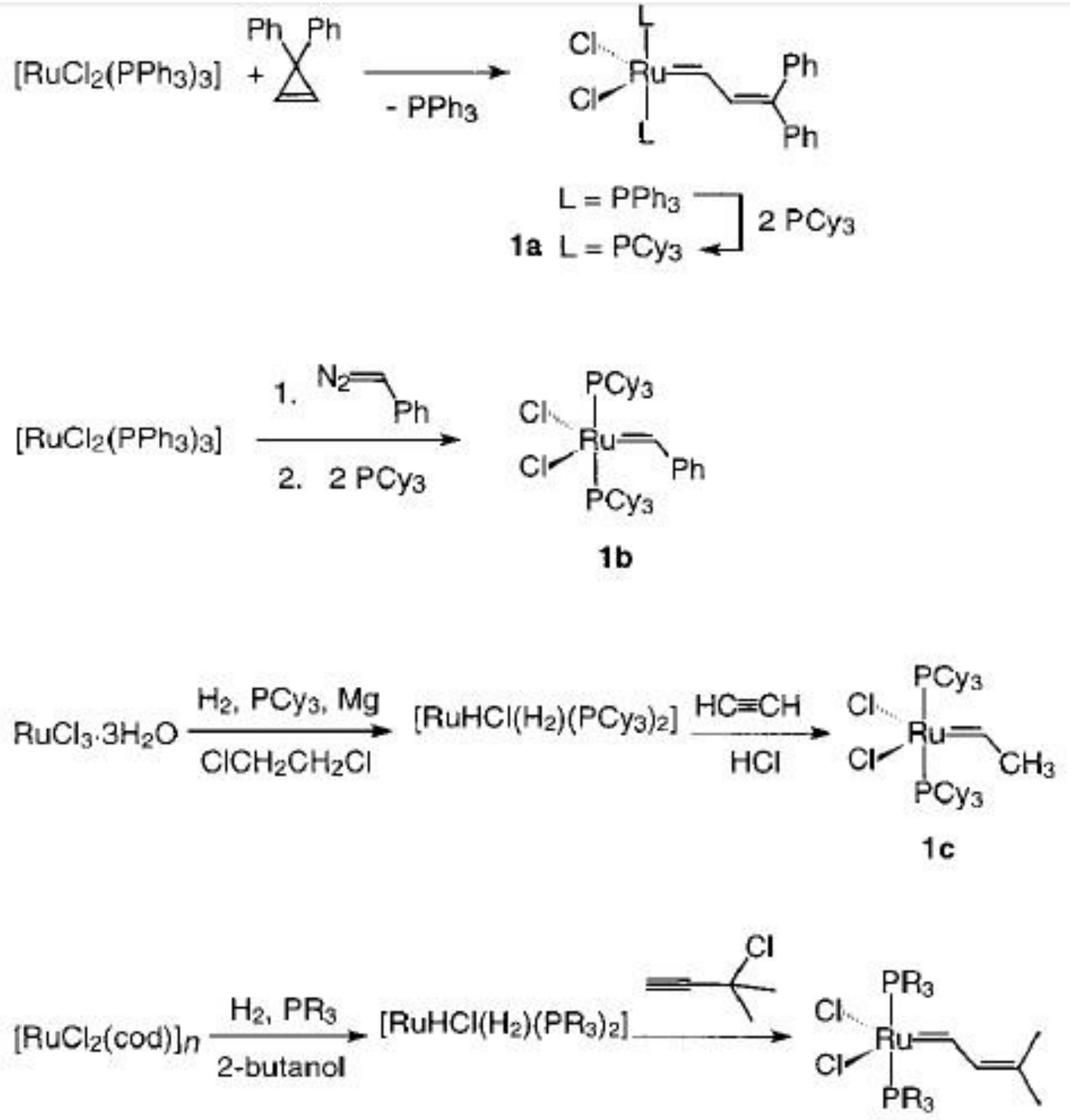
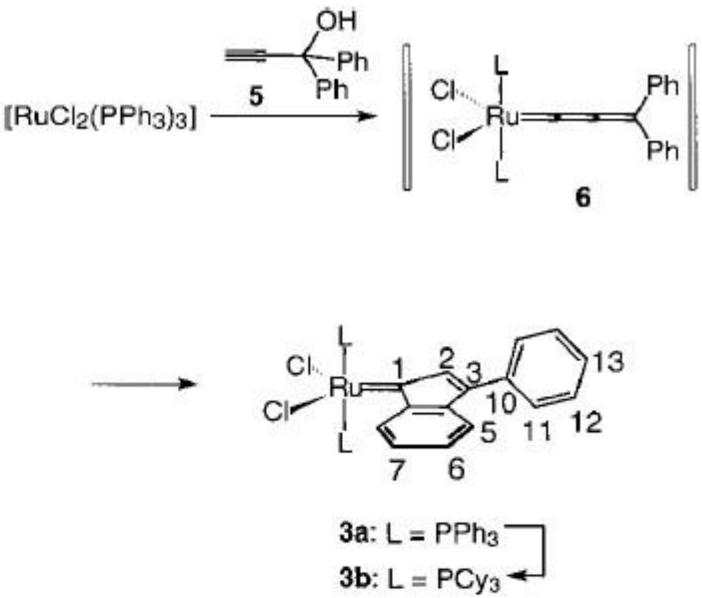


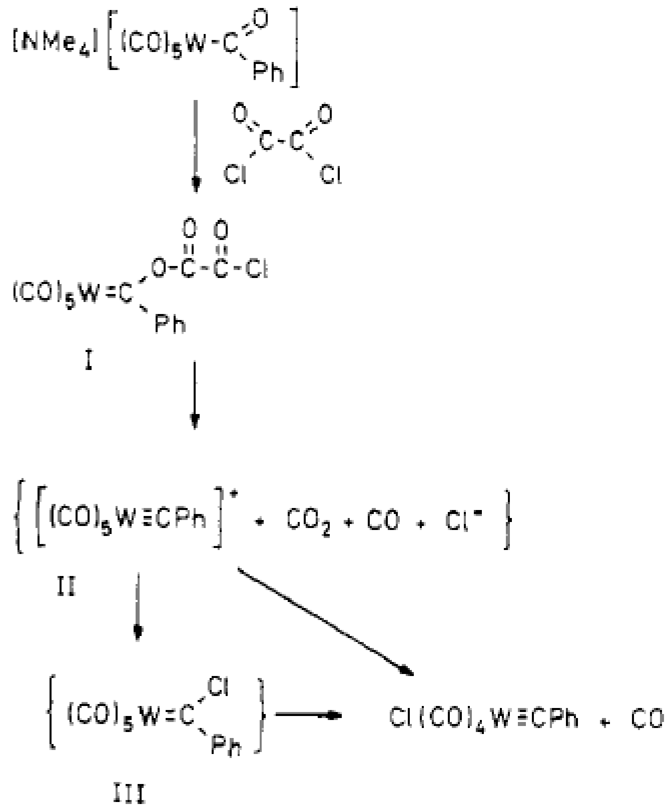
5. Acknowledgement



5. Acknowledgement

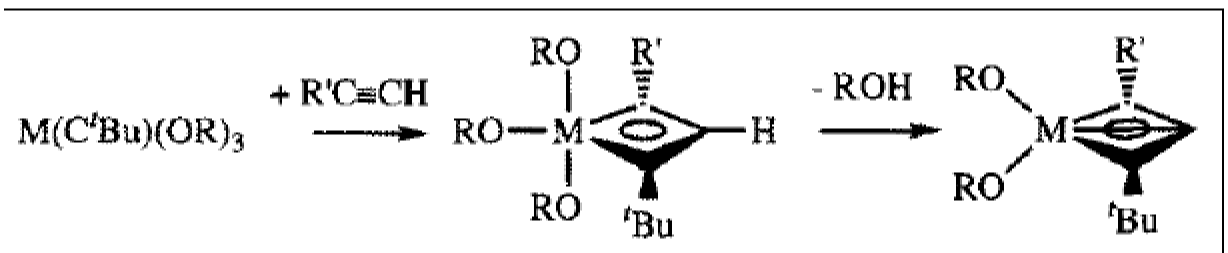


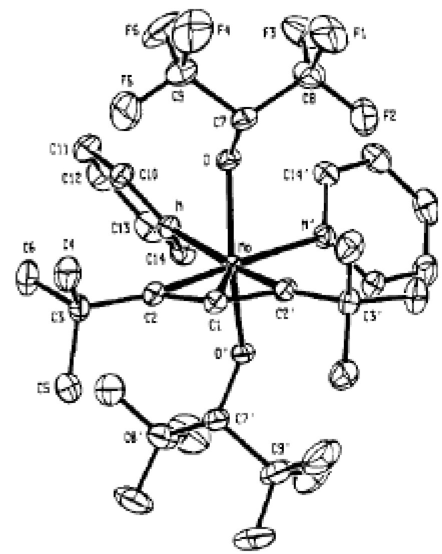
Scheme I



5. Acknowledgement

Why is **3** not catalytically active?
Why are terminal alkynes not viable substrates?
"Deprotiometallacyclobutadiene"





$Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$

Schrock et. al. *J. Am. Chem. Soc.* **1985**, *107*, 5987
Polyhedron **1995**, *15*, 3177