

Transitional Metal Mediated Pauson–Khand Reaction (PKR)

Kaiji Shen's Farewell
Literature Seminar at Wanbin Group

*Nippon Chemical Industrial-Shanghai Jiao Tong University
Research and Development Center**



* Now move to *Feinberg Graduate School, Weizmann Institute of Science*

Outline

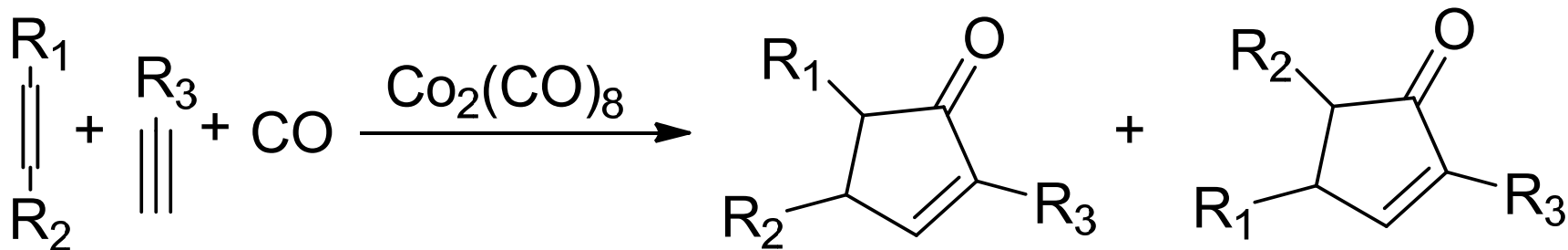


*Prof. P. L. Pauson,
University of Strathclyde,
Glasgow, United Kingdom*

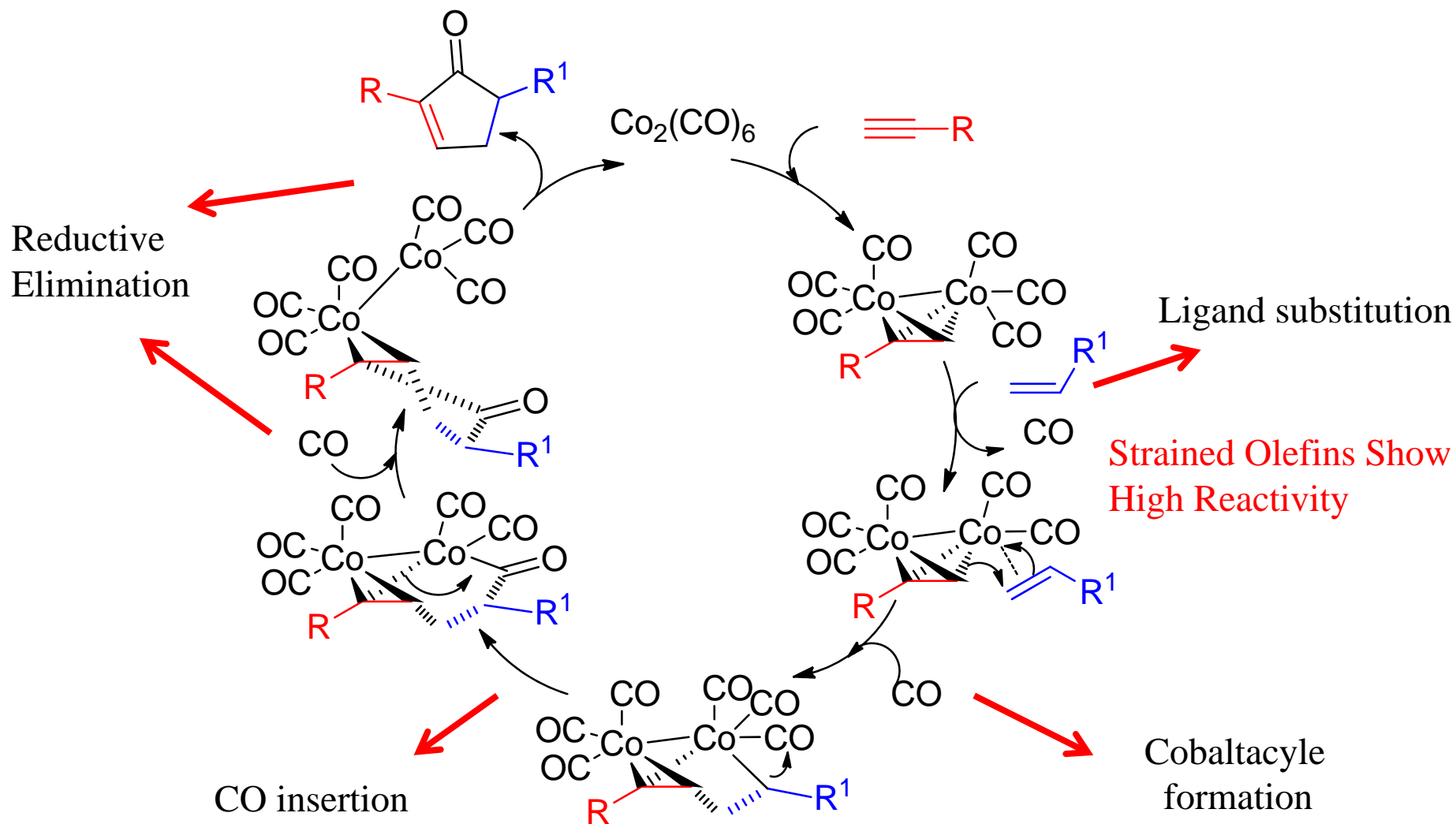
- 1. History
- 2. Mechanism
- 3. Reaction Scope
- 4. Enantioselective PKR
- 5. Applications in total synthesis

History

- Discovered by Pauson and his student Khand in 1977
- $\text{Co}_2(\text{CO})_8$ served as catalyst
- [2+2+1] cycloaddition



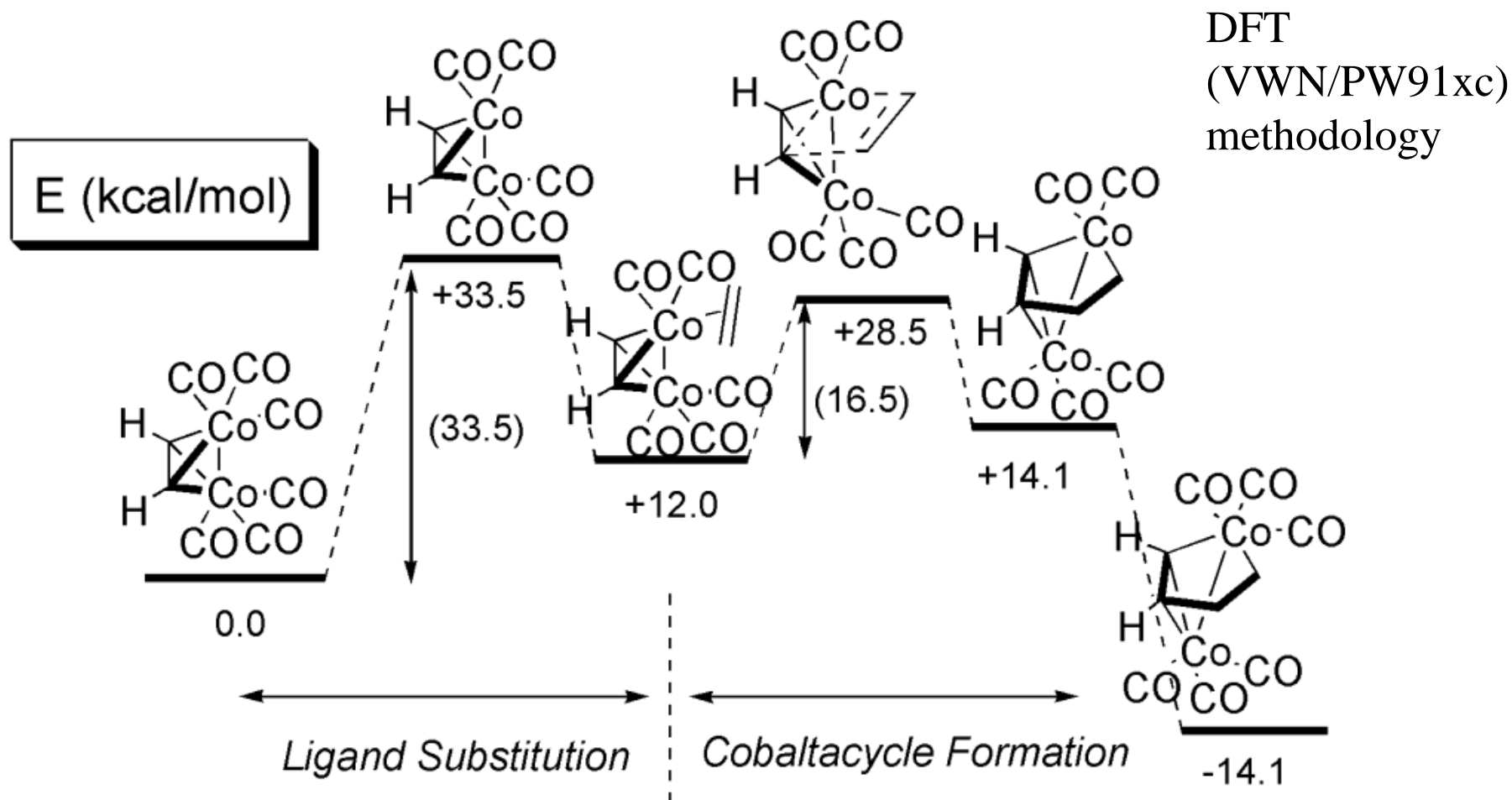
Mechanism



R may also represent larger substituent

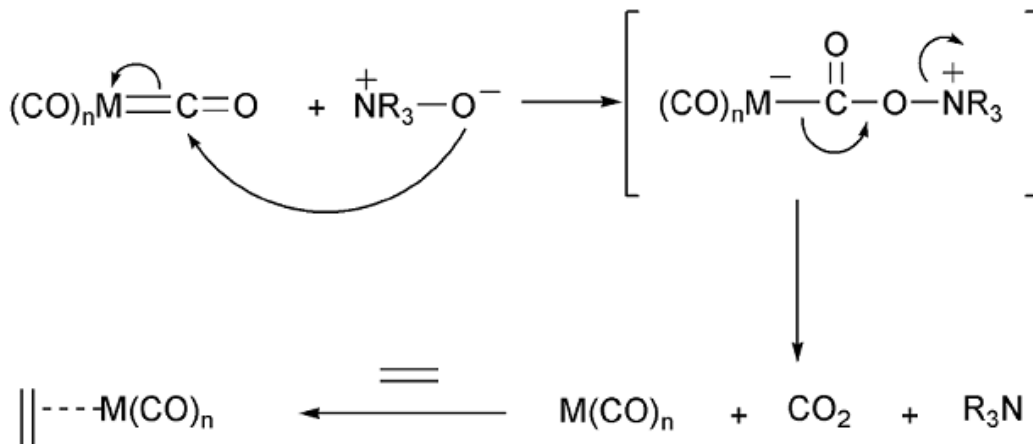
endothermic

Mechanistic Calculations

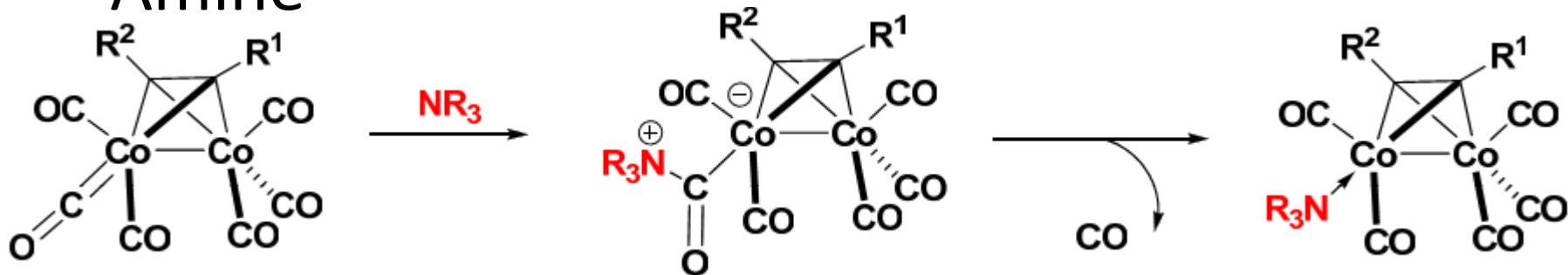


Pauson-Khand Reaction Promoters

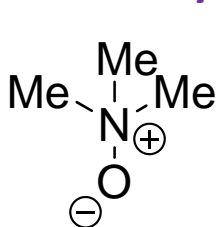
- Amine N-oxides



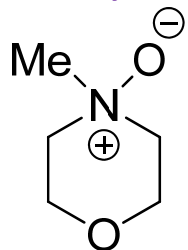
- Amine



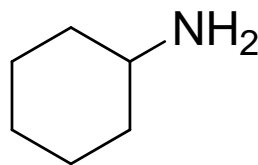
Other: Cyclohexyl amine, sulfides



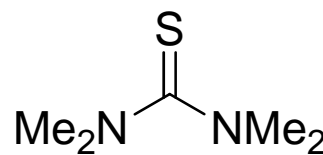
trimethylamine
N-oxide (TMANO)



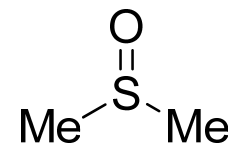
N-methylmorpholine
N-oxide (NMO)



cyclohexanamine

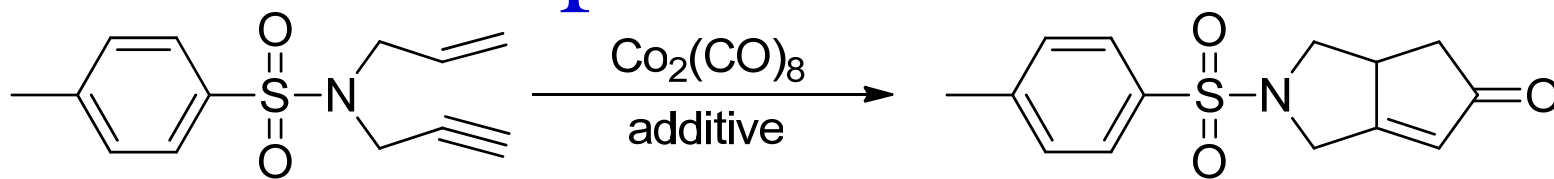


tetramethyl
thiourea (TMTU)

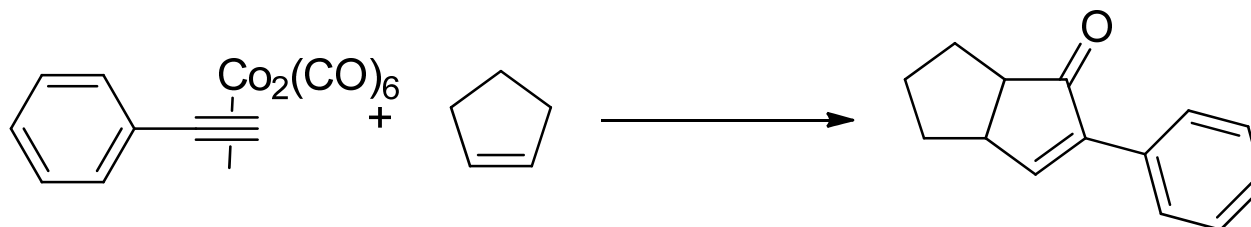


dimethyl sulfoxide
(DMSO)

Examples of additives



Entry	$[\text{Co}_2(\text{CO})_8]$ [mol%]	Additive (mol%)	T [°C]	p(CO) [atm]	Yield [%]
1	7.5	none	60	1	86
2	10	none	70	1	63
3	5	$\text{P}(\text{OPh})_3$ (20)	120	3	94
4	3	DME (12)	120	7	84
5	10	CyNH ₂ (20)	70	1	89
6	5	Bu ₃ PS (30)	70	1	87

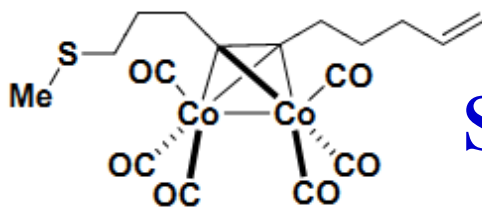


Entry	cyclopentene	Additive (eq)	t, T[°C]	Yield [%]
1	5.3 equiv	none	7 h, 150–160	47
2	5.9 equiv	<i>n</i> Bu ₃ P=O (1)	36 h, 69	70
3	excess	TMANO (6)	10 min, RT, ultrasound	97
4	2 equiv	<i>n</i> BuSMe (5)	2 days, 35	75

Please consult Gibson's 2003 and 2005 reviews on ACIE, links at the last page

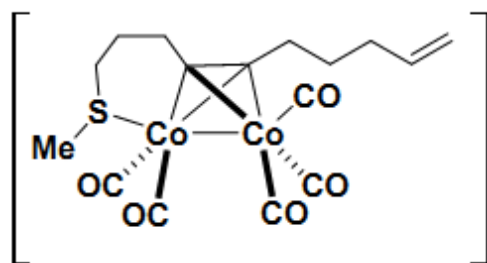
S atom coordination support for Mechanism

Mixed Ar/N₂ Matrix

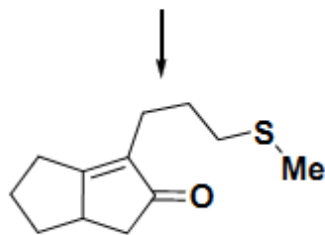


bishomopropargylic sulfide complex

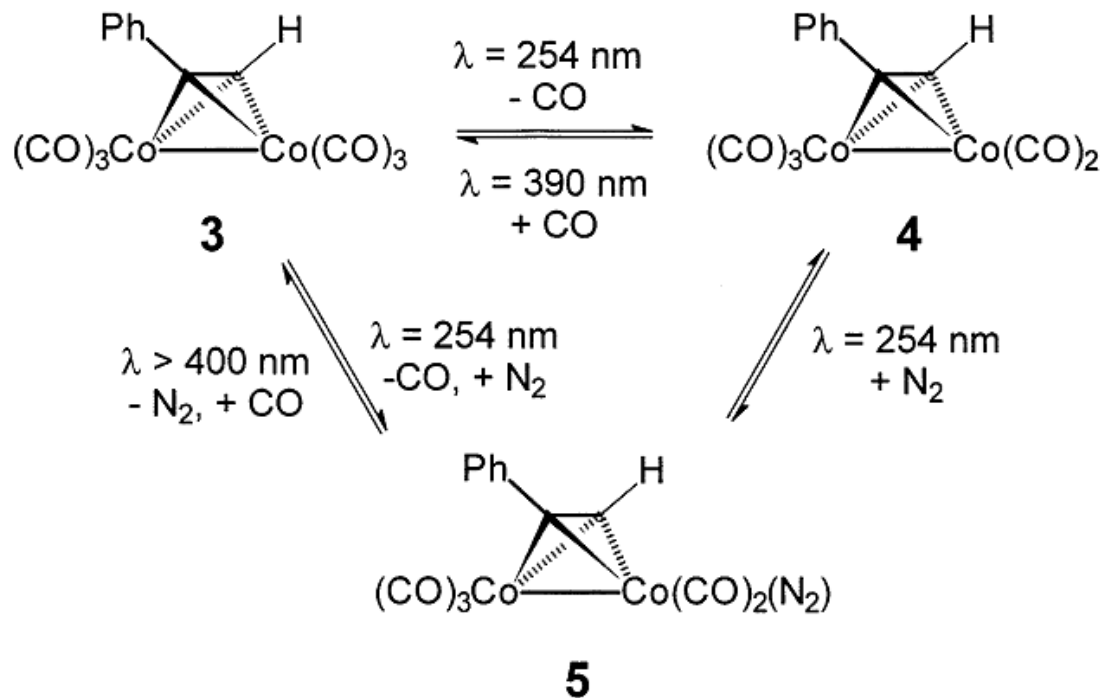
NMO•H₂O,
DCM, rt, 5 d



isolable pentacarbonyl complex



bishomoallylic sulfide



Krafft and coworkers, *J. Am. Chem. Soc.* 1993, **115**, 7199-7207

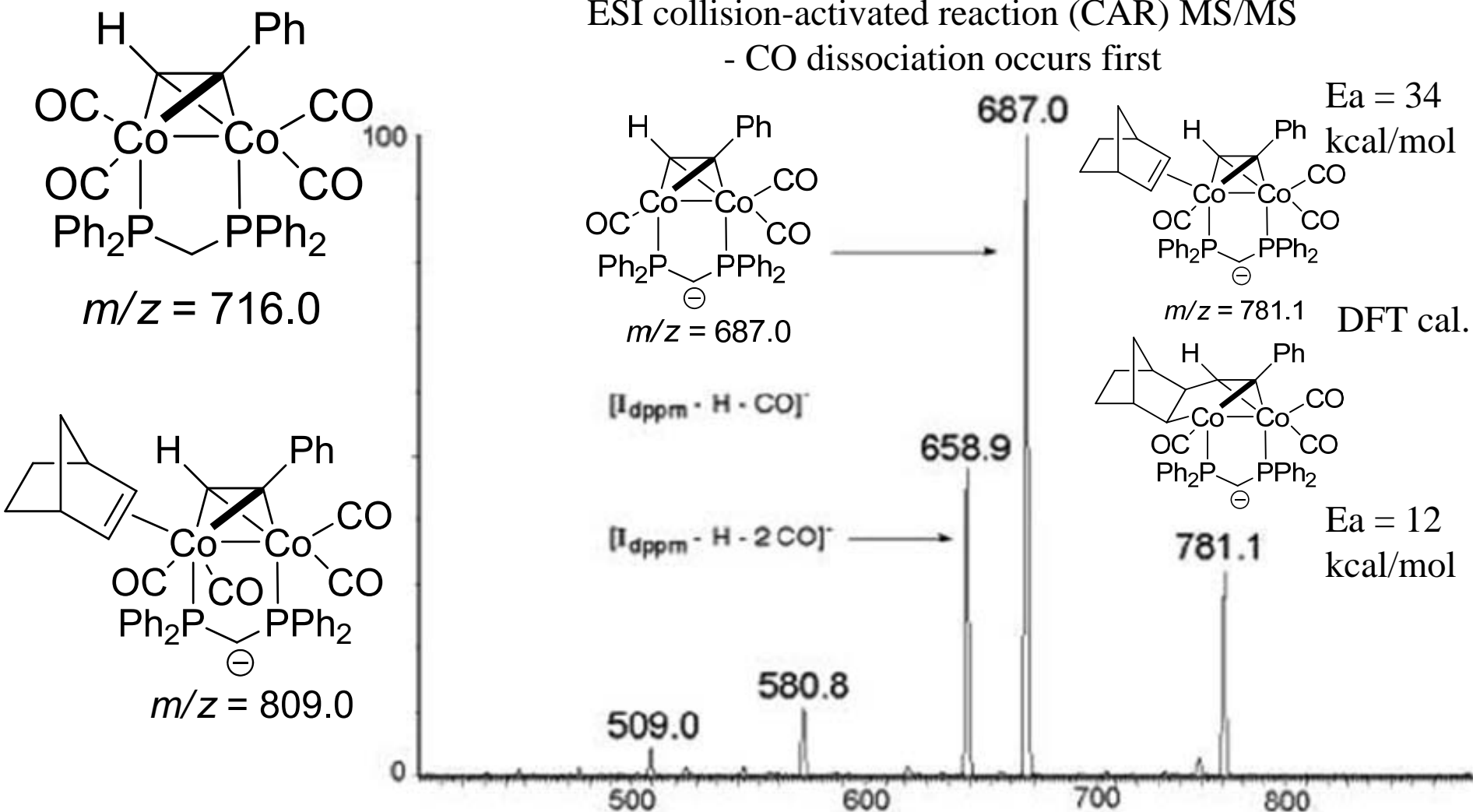
[doi:10.1021/ja00069a017](https://doi.org/10.1021/ja00069a017)

Gordon and coworkers, *J. Organomet. Chem.* 1998, **554**, 147-154

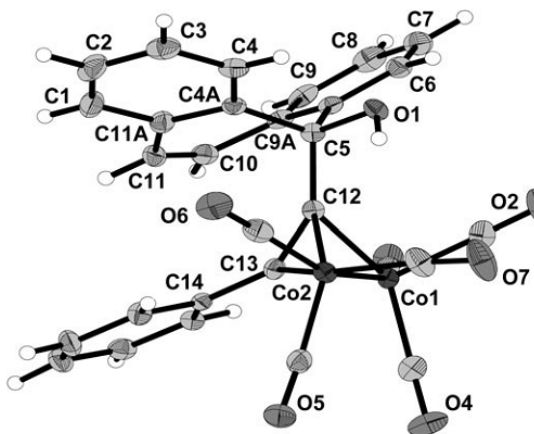
[doi:10.1016/s0022-](https://doi.org/10.1016/s0022-328x(97)00660-8)

[328x\(97\)00660-8](https://doi.org/10.1016/s0022-328x(97)00660-8)

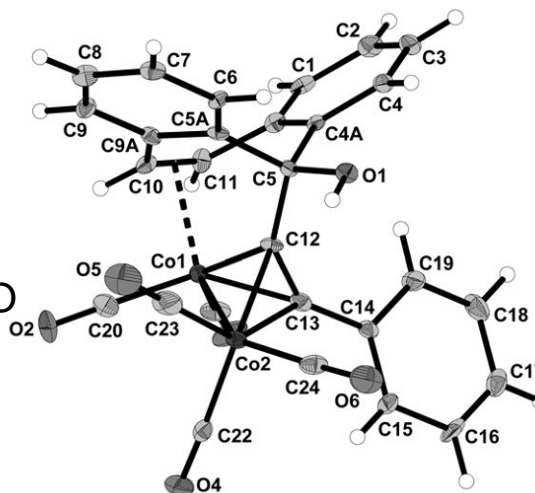
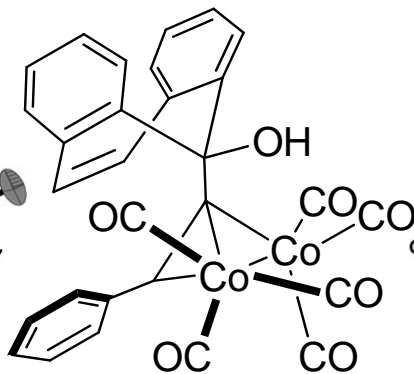
MS Support for Mechanism



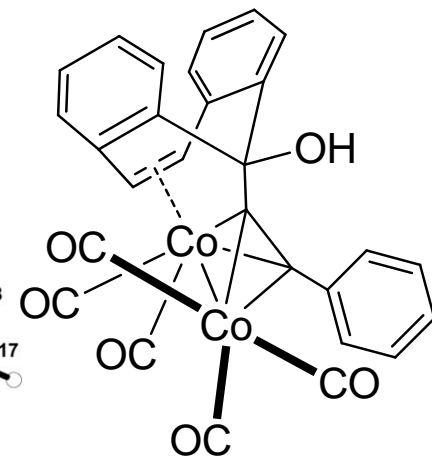
X-ray Crystal Support



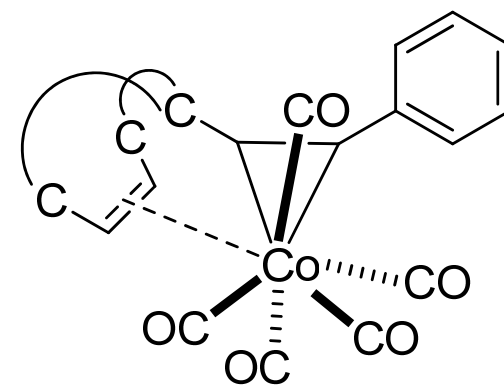
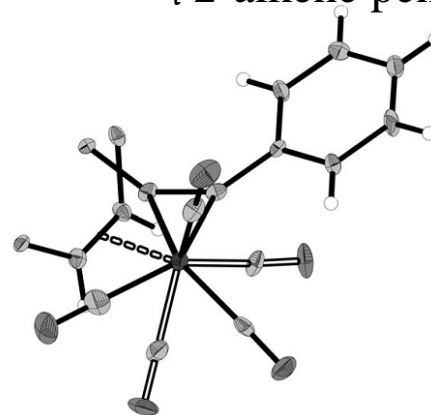
hexacarbonyl alkyne complex



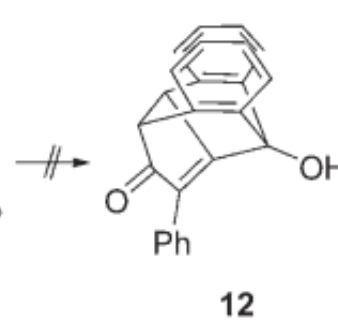
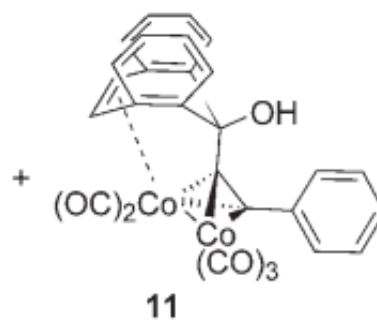
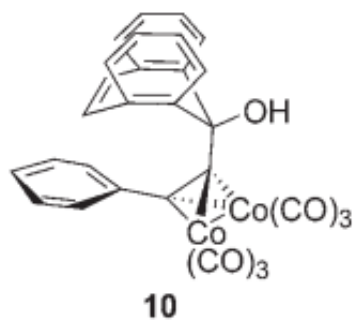
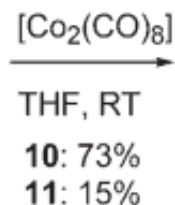
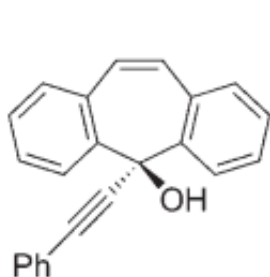
η^2 -alkene pentacarbonyl alkyne complex



Evans and coworkers, *Angew. Chem. Int. Ed.* 2007, **46**, 2907-2910 [doi: 10.1002/anie.200605171](https://doi.org/10.1002/anie.200605171)

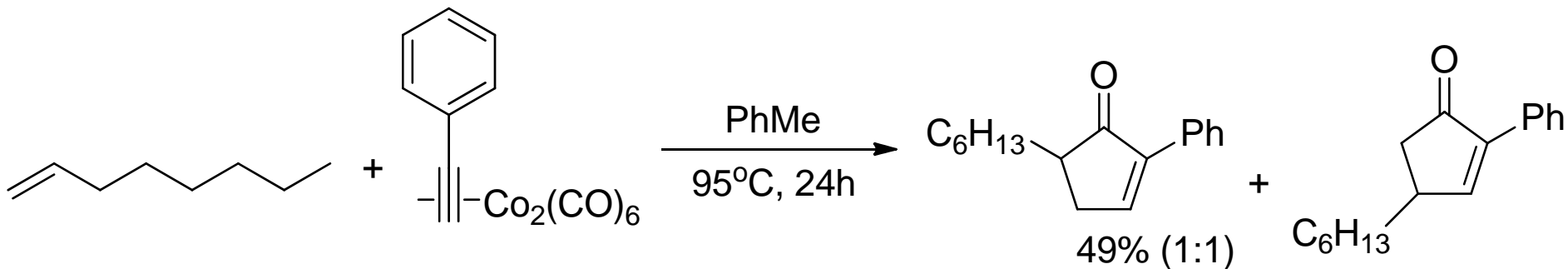
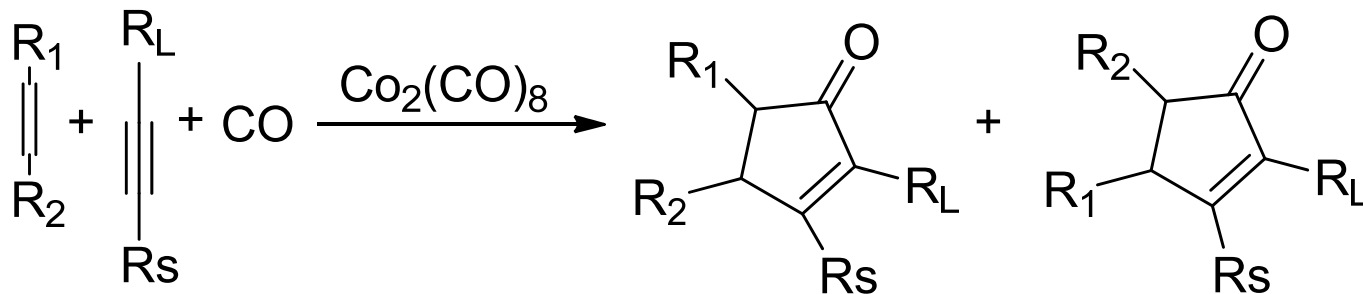


η^2 -alkene pentacarbonyl alkyne complex (viewed down Co-Co bond)



Pauson-Khand Reaction Scope

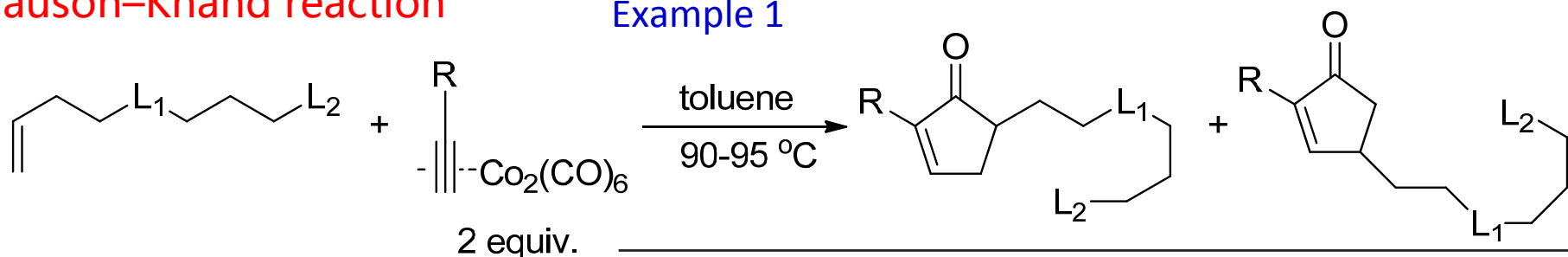
Intermolecular



M. E. Krafft, *J. Am. Chem. Soc.* 1988, *110*, 968 – 970 [doi: 10.1021/ja00211a048](https://doi.org/10.1021/ja00211a048)

Substrate-directed intermolecular Pauson–Khand reaction

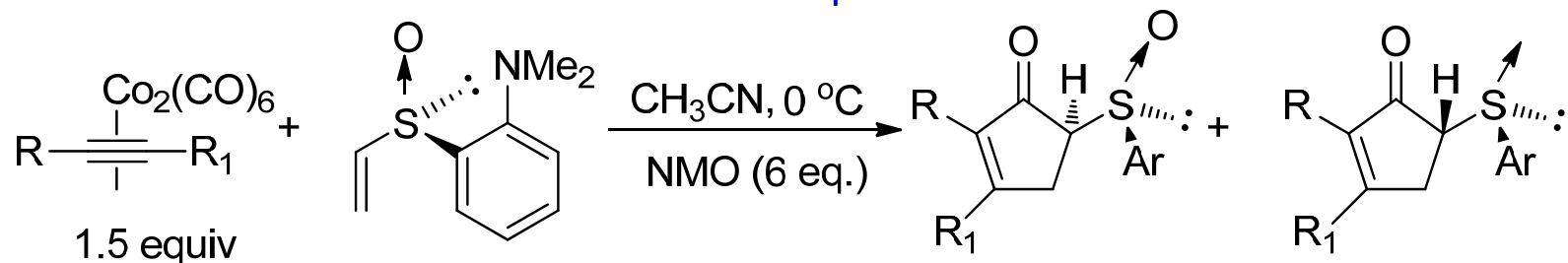
Example 1



Entry	L^1	L^2	R	t [h]	Yield [%] (ratio)
1	S	NMe ₂	Ph	6	85 (15:1)
2	S	SEt	Ph	1.5	70 (8:1)
3	S	SEt	Bu	1.75	85 (>40:1)

M. E. Krafft, C. A. Juliano, *J. Org. Chem.* 1992, **57**, 5106 – 5115 [doi: 10.1021/jo00045a021](https://doi.org/10.1021/jo00045a021)

Example 2



Entry	$R^{[a]}$	R^1	t [h]	Yield (d.r.)
1	<i>n</i> Bu	H	4	74 (93:7)
2	Bn	H	14	58 (93:7)
3	$(\text{CH}_2)_2\text{OTIPS}$	H	7	66 (> 98:2)
4	CH ₃	CH ₃	24	no reaction
5	CH ₃	CH ₃	48 ^[b]	33 (92:8)

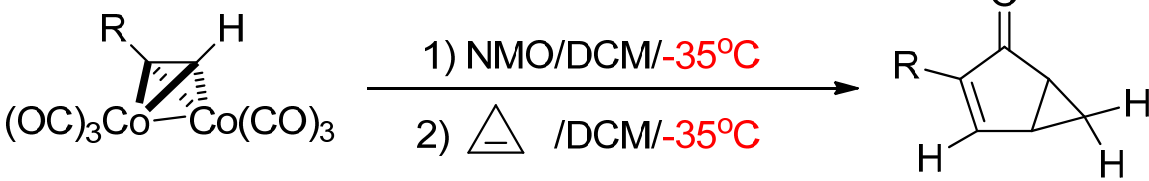
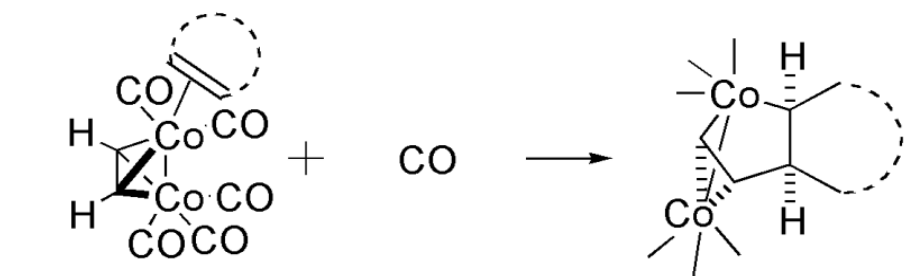
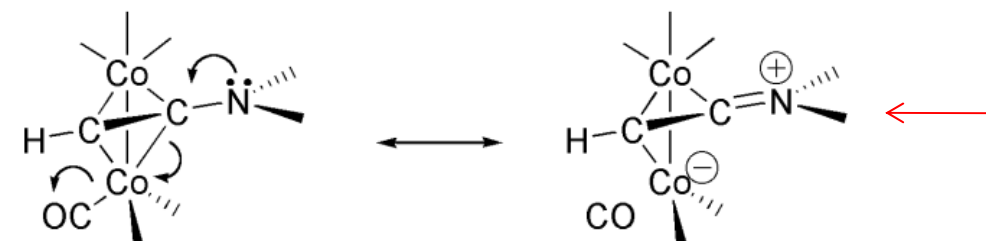
M. R. Rivero and coworkers, *J. Am. Chem. Soc.* 2003, **125**, 14992 – 14993
[doi: 10.1021/ja0384911](https://doi.org/10.1021/ja0384911)

[a] TIPS = triisopropylsilyl. [b] Pressure = 10 kbar.

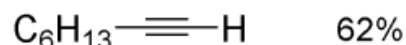
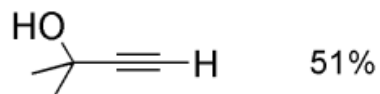
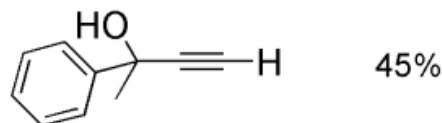
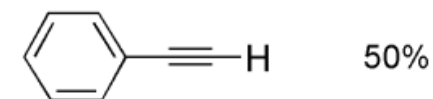
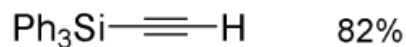
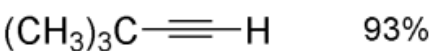
Olefin influence

Strained Olefins Show High Pauson - Khand
 Reactivity Lower the LUMO energy

This ynamine complexes are extremely reactive toward strained olefin, while fail to react with cyclohexene.

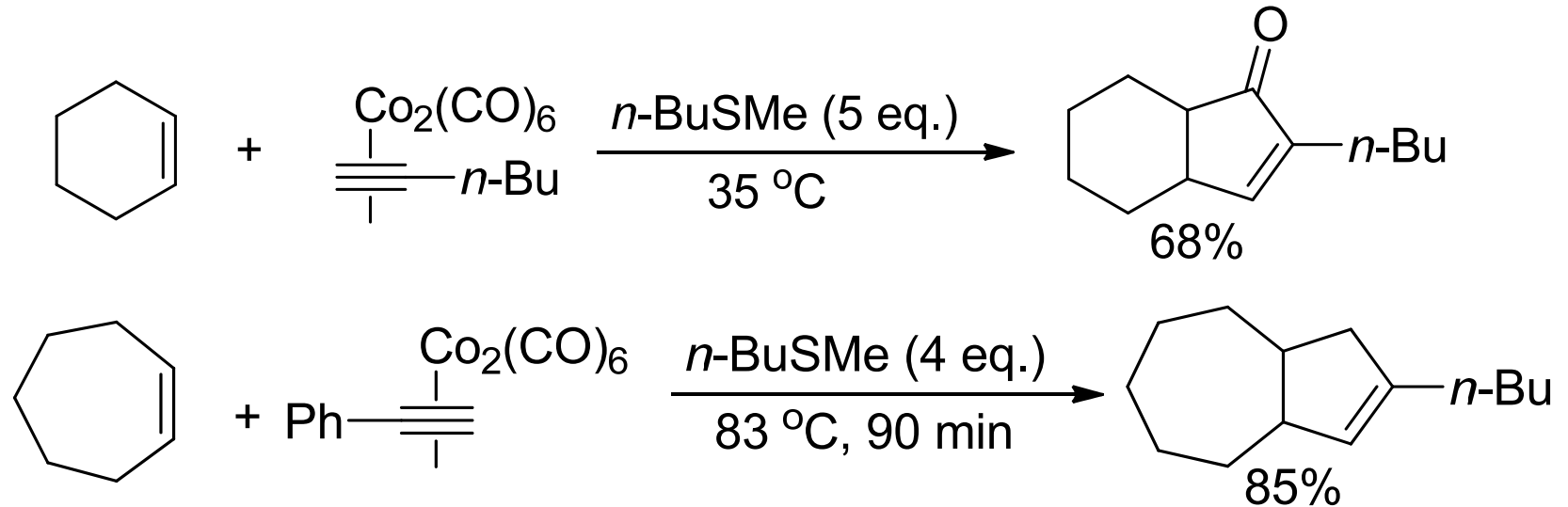


Olefin	ΔH_r° (Kcal/mol)
Methylenecyclopropane	-32.0
Cyclobutene	-31.3
Norbornadiene	-32.5
Norbornene	-27.8
Cyclopentene	-21.7
Cyclohexene	-21.6
Cyclopropene	-47.3



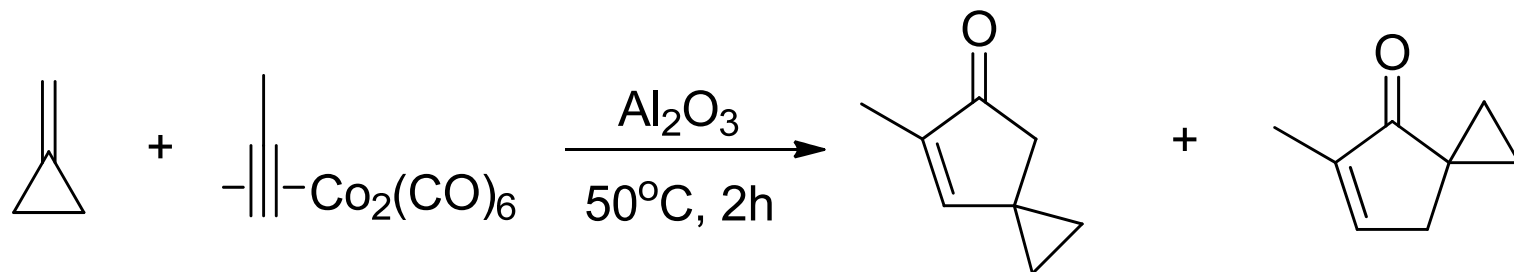
M. A. Pericàs and co-workers, *Org. Lett.* 2001, 3, 3193 – 3196 [doi: 10.1021/o1016505r](https://doi.org/10.1021/o1016505r)

Way to overcome the problem

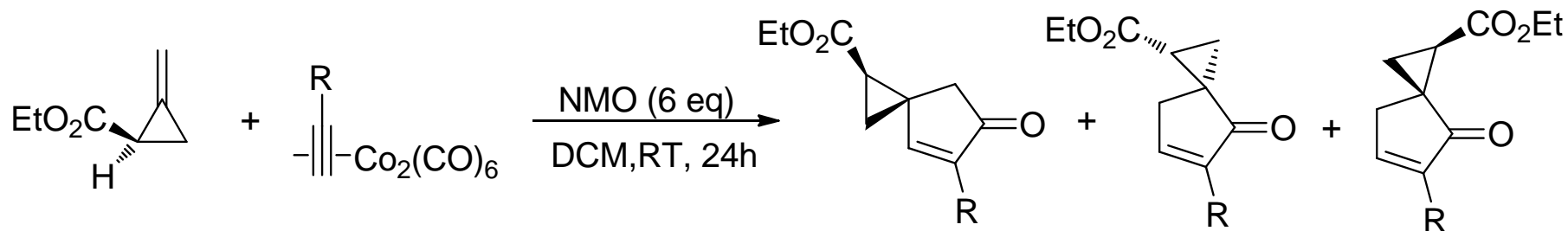
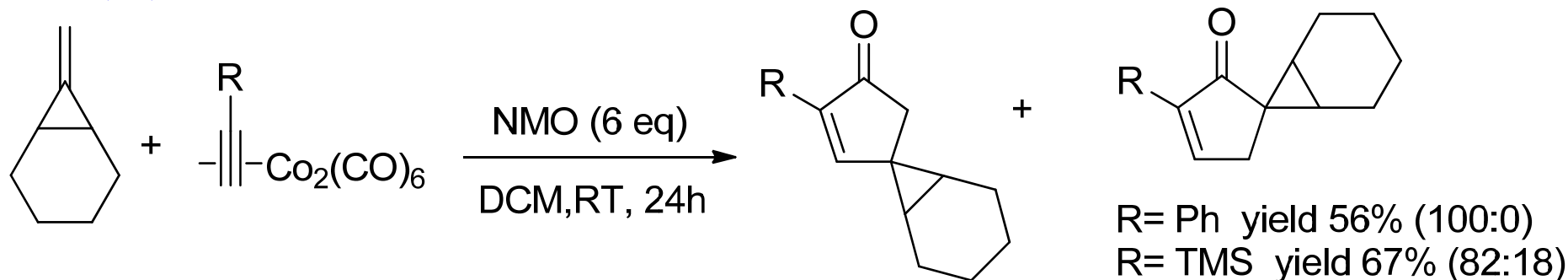


Although it has proven possible to improve reactivity by changing reaction conditions, the relative rates of reactions of different alkenes are always maintained.

The reaction of exocyclic alkenes



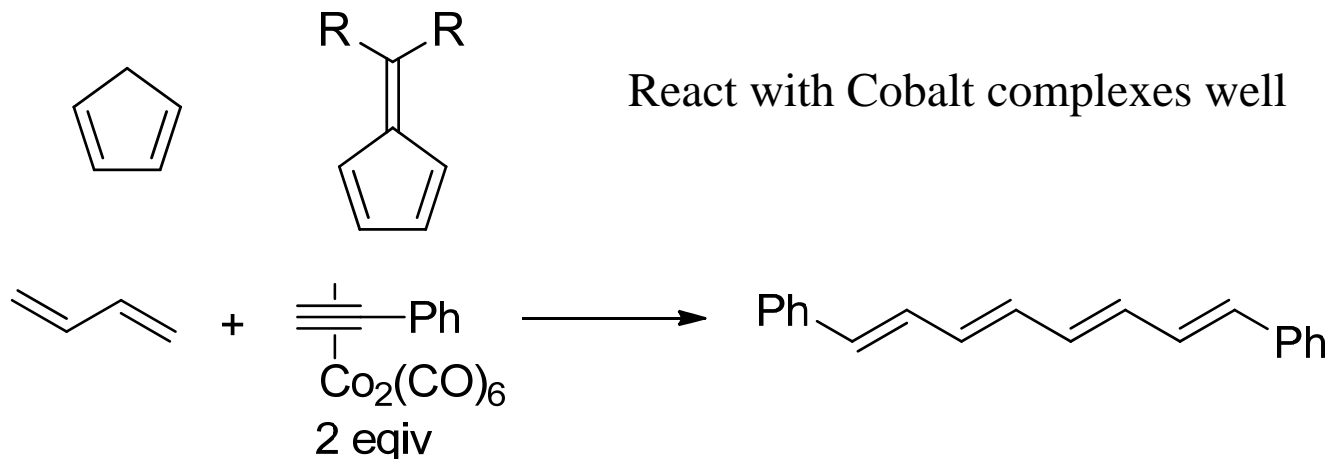
W. A. Smit and co-workers, *Tetrahedron Lett.* 1989, **30**, 4021 – 4024, [doi:10.1016/S0040-4039\(00\)99313-4](https://doi.org/10.1016/S0040-4039(00)99313-4)



B. Motherwell and co-workers, *Synlett*, 1996, **10**, 990 – 992 [doi: 10.1055/s-1996-5645](https://doi.org/10.1055/s-1996-5645)

R=Ph yield 13% 32% 9%
R=TMS yield 17% 31% 3%

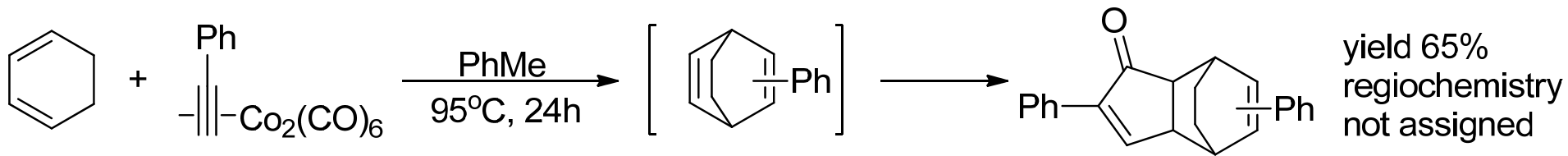
PKR of dienes



Pauson, P.L.; Khand, I.U. *Ann. N.Y. Acad. Sci.* 1977, **295**, 2-14.

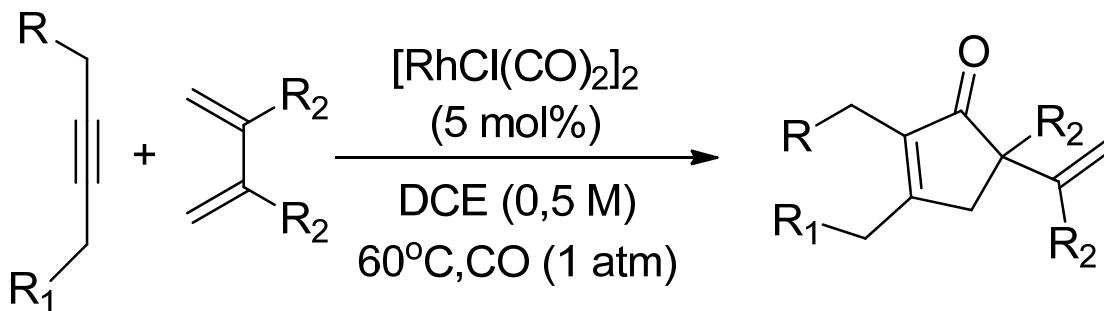
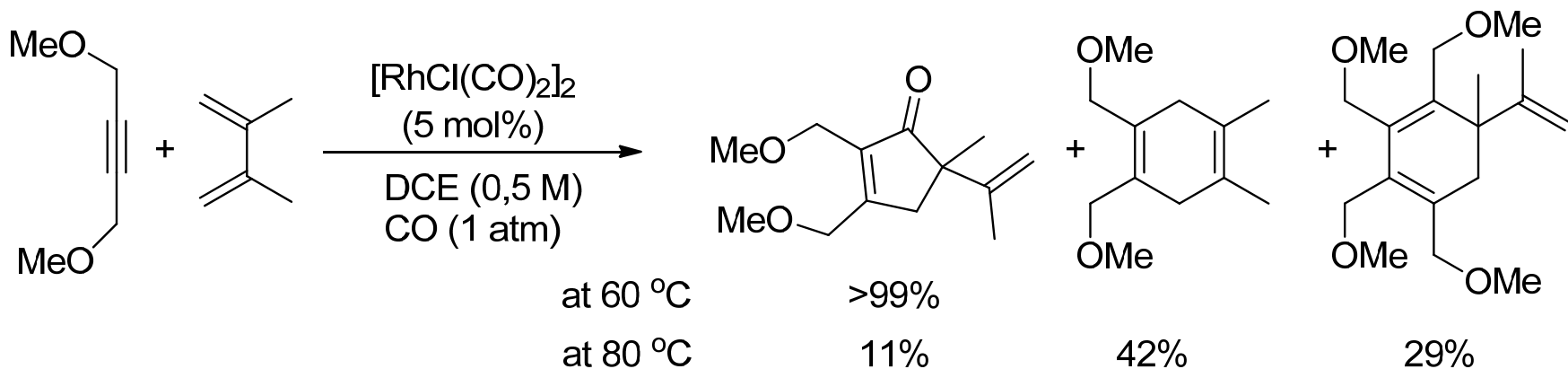
[doi: 10.1111/j.1749-6632.1977.tb41819.x](https://doi.org/10.1111/j.1749-6632.1977.tb41819.x)

I. U. Khand, P. L. Pauson, M. Habib, *J. Chem. Res. Miniprint*, 1978, 4418 – 4433



I. U. Khand, P. L. Pauson, M. Habib, *J. Chem. Res. Miniprint*, 1978, 4401 – 4417

Mechanism Insight



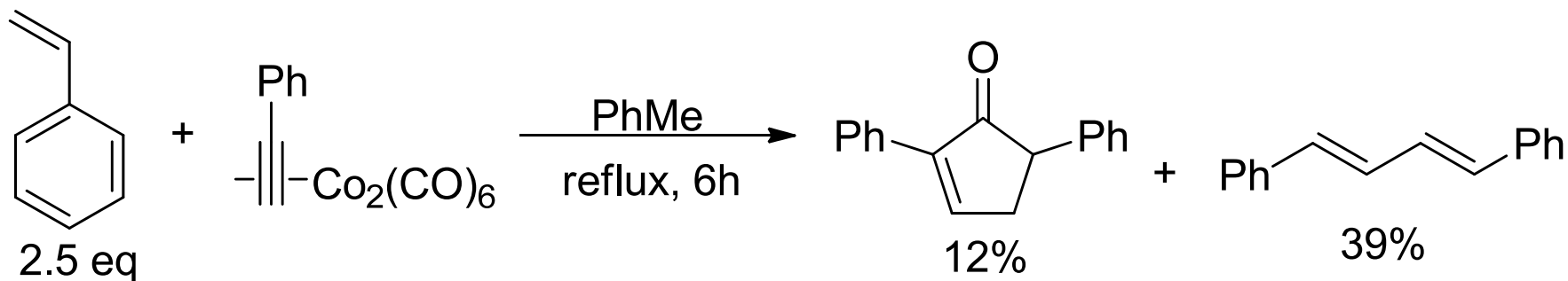
Entry	R ^[a]	R ^{1 [b]}	R ²	<i>t</i>	Yield [%]
1	OMe	OMe	Me	6	98
2	OTBS	OTBS	Me	6	87
3	OMe	OBn	Me	9	81

[a] TBS = *tert*-butyldimethylsilyl. [b] Bn = benzyl.

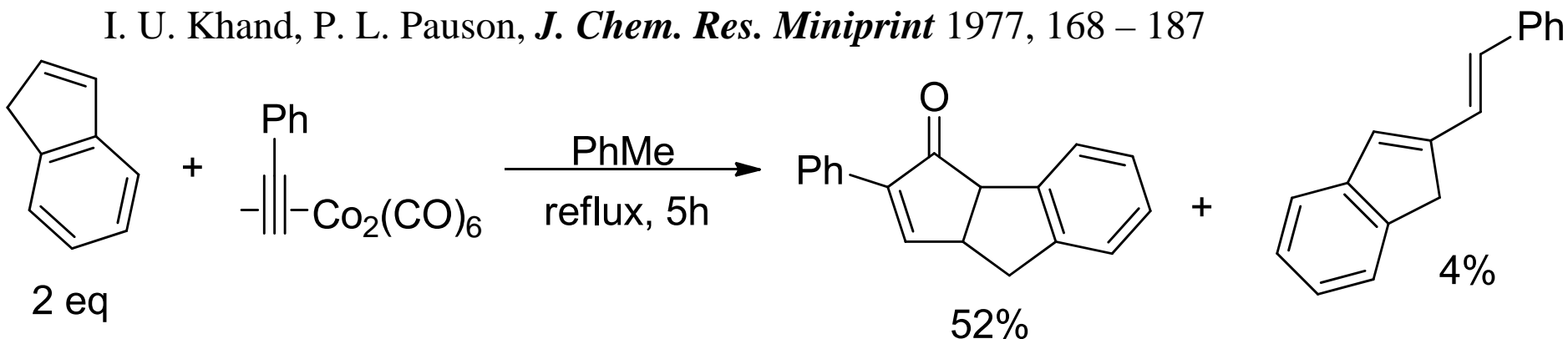
P. A. Wender and co-workers, *Angew. Chem. Int. Ed.* 2004, **43**, 3076–3079

[doi: 10.1002/anie.200454117](https://doi.org/10.1002/anie.200454117)

PKR of Styrene type olefin



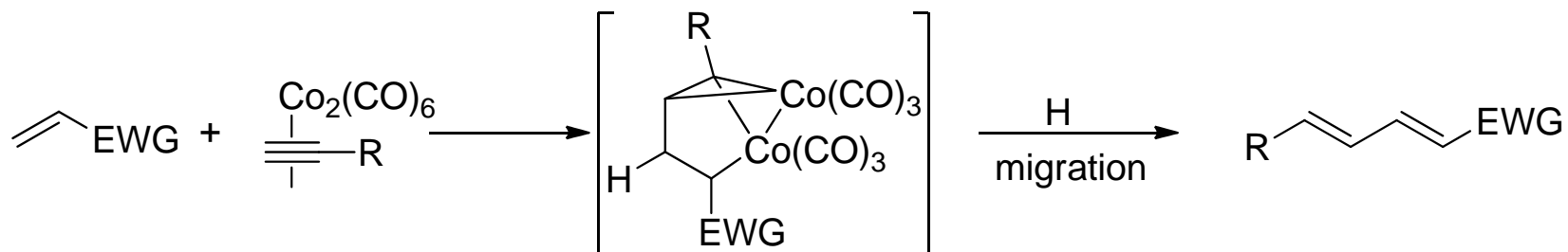
I. U. Khand, P. L. Pauson, *J. Chem. Res. Miniprint* 1977, 168 – 187



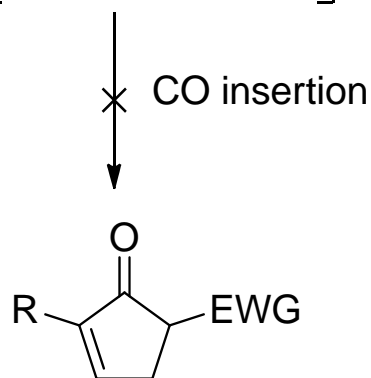
I. U. Khand, P. L. Pauson, M. Habib, *J. Chem. Res. Miniprint*, 1978, 4418 – 4433

An explanation may be found in the polarization of the LUMO of the double bond by the arene ring which may induce the formation of the first C-C bond at the remote carbon atom of the alkene

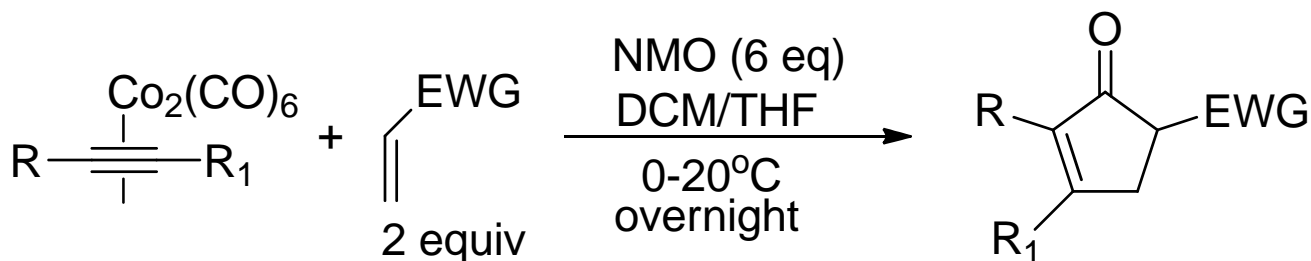
EWG on olefin and its influence



M. Ahmar, F. Antras, B. Cazes,
Tetrahedron Lett. 1999, **40**, 5503 –
 5506 [doi:10.1016/S0040-4039\(99\)01069-2](https://doi.org/10.1016/S0040-4039(99)01069-2)

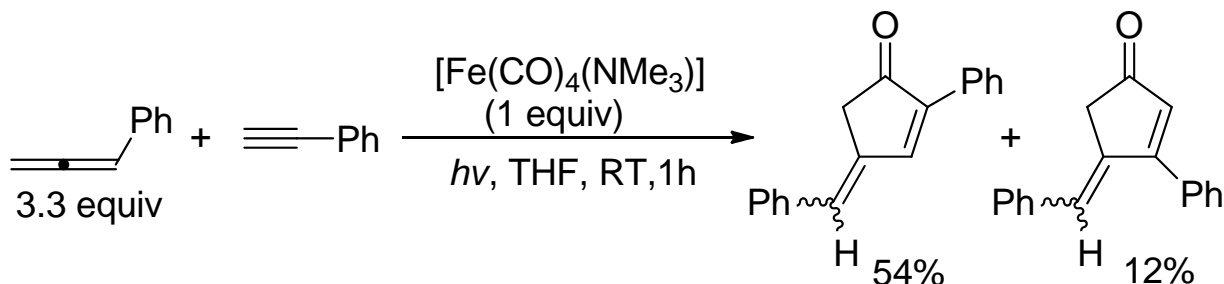


Hydrogen migration (through β -hydride elimination) prevails over CO insertion in the intermolecular Pauson–Khand reaction of electron-poor alkenes.



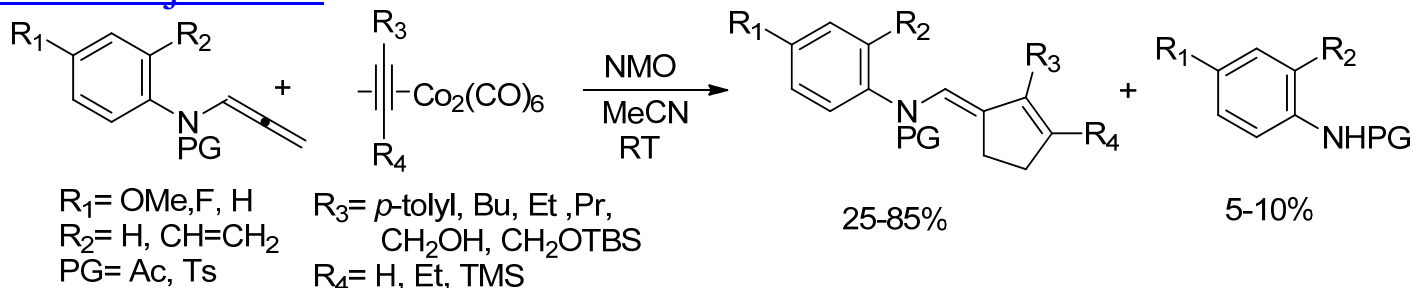
Entry	R	R ₁	EWG	Yield [%]
1	CH ₃	CH ₃	CO ₂ Me	59
2	CH ₃	CH ₃	SO ₂ Ph	71
3	C ₃ H ₇	H	CO ₂ Me	47
4	Ph	H	CO ₂ Me	41

The reaction of allene



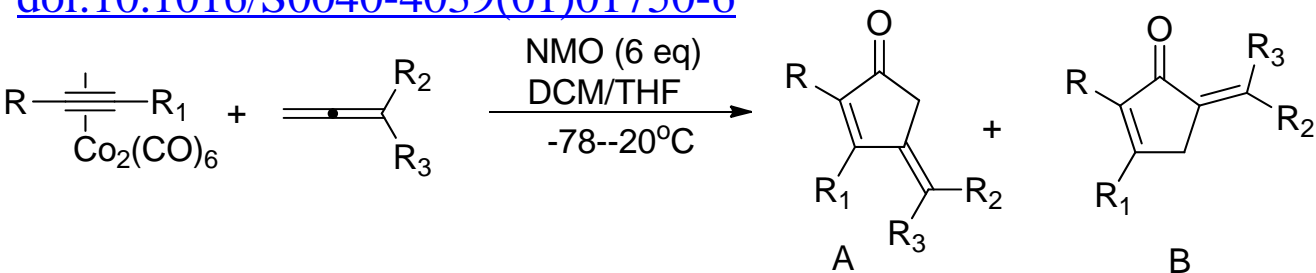
T. Shibata, Y. Koga, K. Narasaka, *Bull. Chem. Soc. Jpn.* 1995, **68**, 911 – 919

[doi:10.1246/bcsj.68.911](https://doi.org/10.1246/bcsj.68.911)



F. Antras, M. Ahmar, B. Cazes, *Tetrahedron Lett.* 2001, **42**, 8157 – 8160

[doi:10.1016/S0040-4039\(01\)01750-6](https://doi.org/10.1016/S0040-4039(01)01750-6)

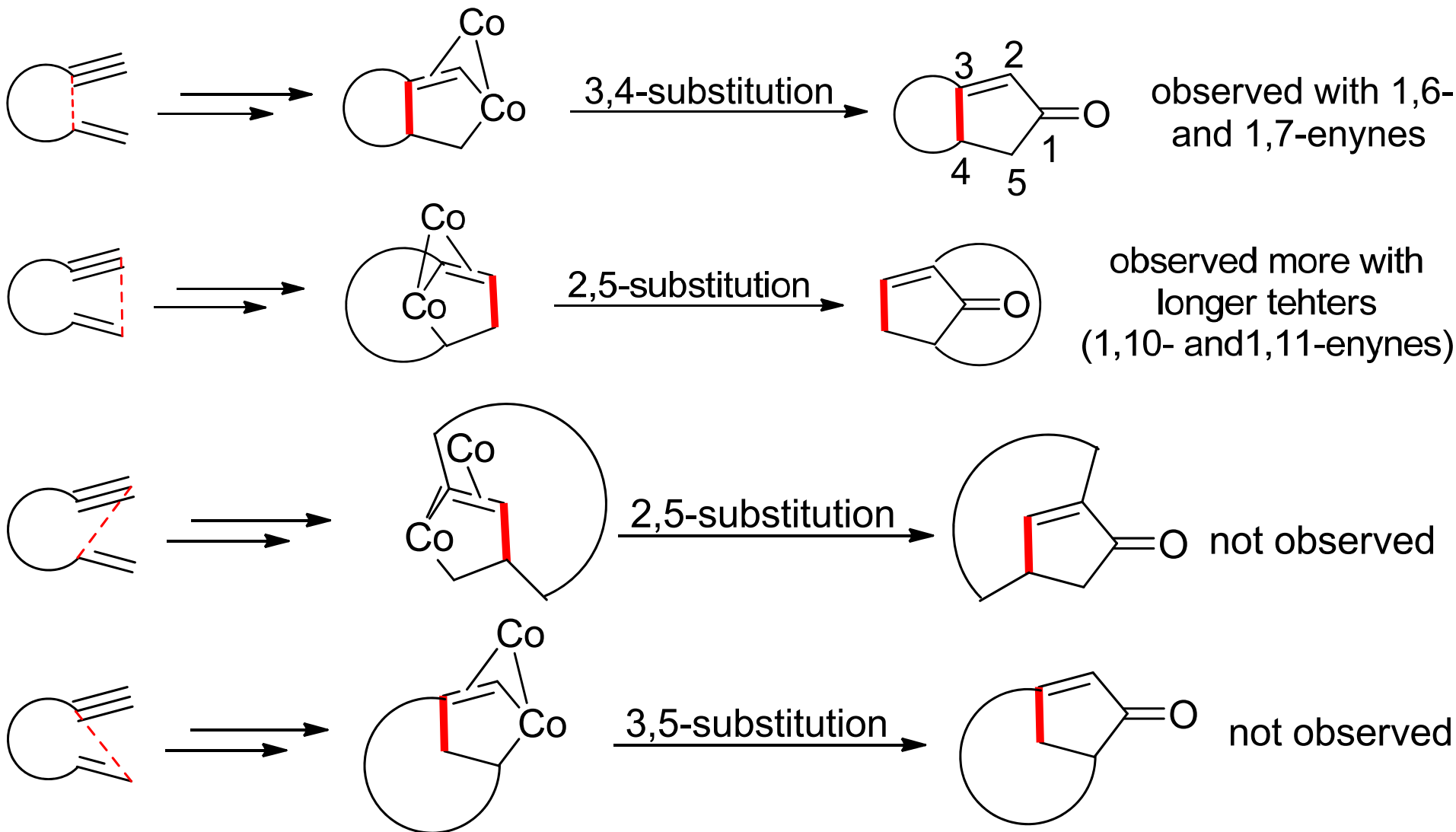


L. Añorbe, A. Poblador, G. Domínguez, J. Pérez-Castells, *Tetrahedron Lett.* 2004, **45**, 4441 – 4444

[doi:10.1016/j.tetlet.2004.04.061](https://doi.org/10.1016/j.tetlet.2004.04.061)

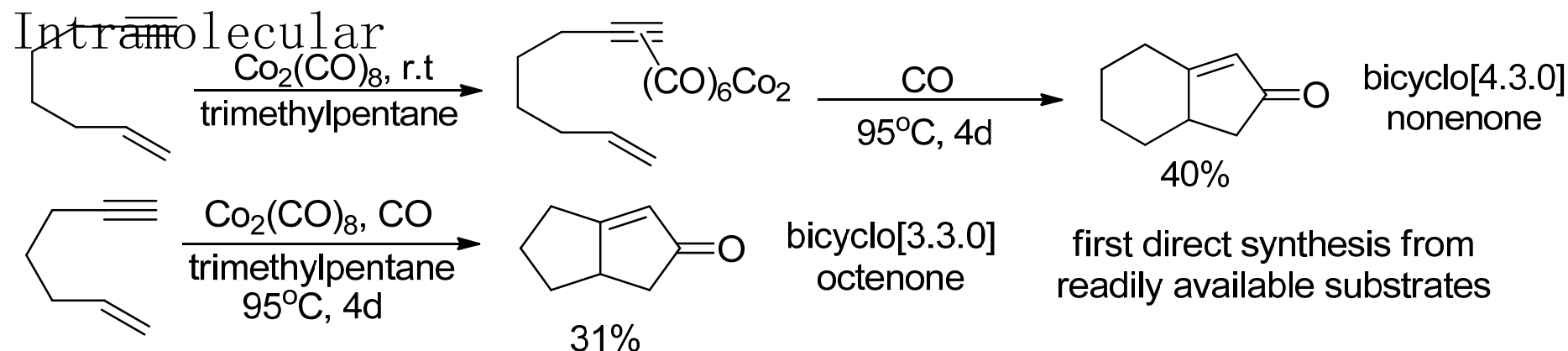
Entry	R	R ₁	R ₂	R ₃	Yield [%]	
					A	B
1	CH ₃	CH ₃	<i>Or</i> -Bu	H	30	
2	C ₃ H ₇	C ₃ H ₇	CO ₂ Me	H	33	14

Intramolecular PKR

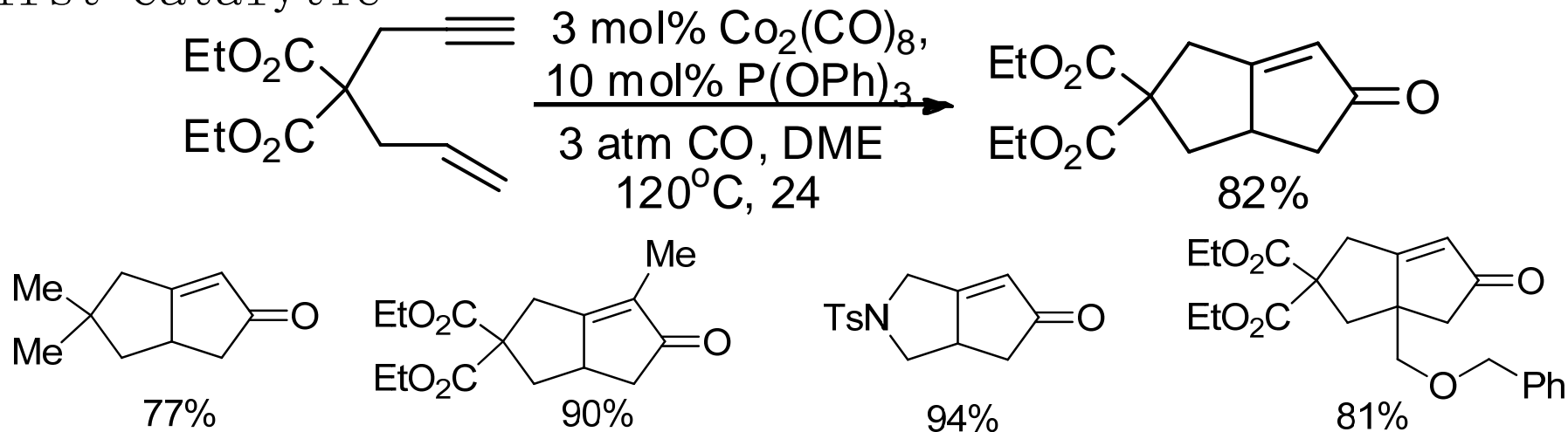


Catalytic and Intramolecular Pauson-Khand Examples

First



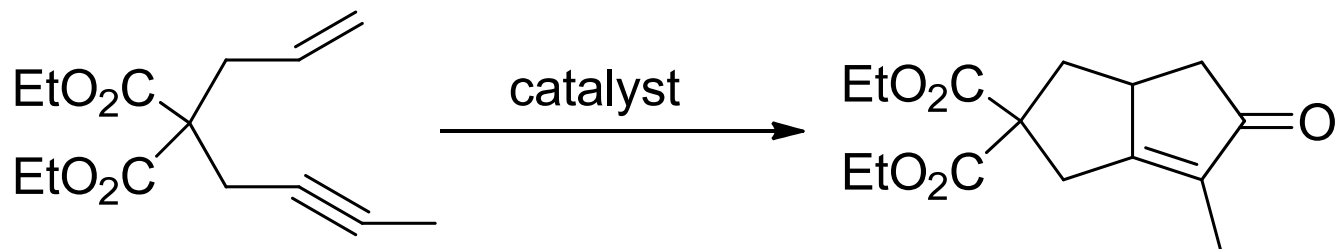
First Catalytic



Schore, N. E.; Croudace, M. C. *J. Org. Chem.* 1981, **46**, 5436-5438 [doi: 10.1021/jo00339a046](https://doi.org/10.1021/jo00339a046)

Jeong and coworkers, *J. Am. Chem. Soc.* 1994, **116**, 3159-3160 [doi: 10.1021/ja00098a042](https://doi.org/10.1021/ja00098a042)

Ti serves as catalyst



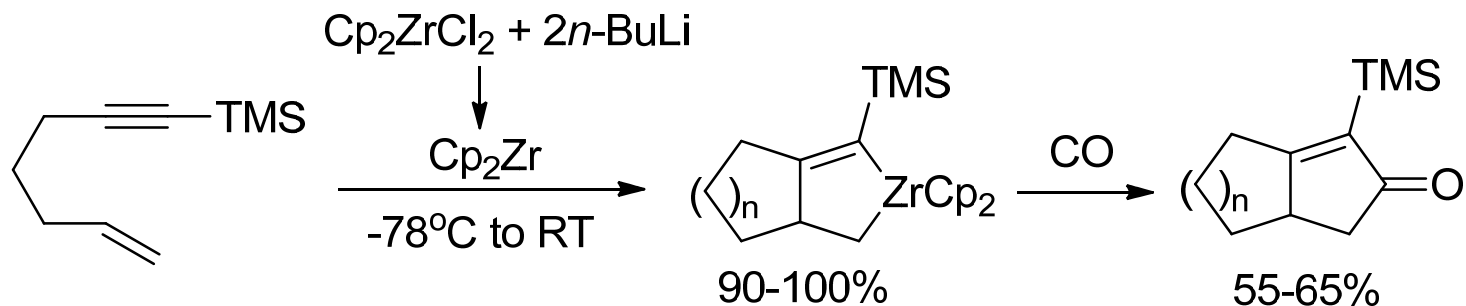
Entry	Catalyst (mol%)	R ₃ SiCN (equiv)	p(CO) [atm]	Yield [%]
1 ^[a]	[Cp ₂ Ti(PMe ₃) ₂] (10)	Et ₃ SiCN (1.3)	–	71
2 ^[b]	[Cp ₂ Ti(CO) ₂] (5)	–	1.22	91

[a] Ar, benzene, 45 °C, 16–24 h, then CuSO₄ (sat. aq.), room temperature, 3–5 h. [b] Toluene, 90 °C, 12–48 h.

S. C. Berk, R. B. Grossman, S. L. Buchwald, *J. Am. Chem. Soc.* 1994, **116**, 8593
[doi: 10.1021/ja00098a020](https://doi.org/10.1021/ja00098a020)

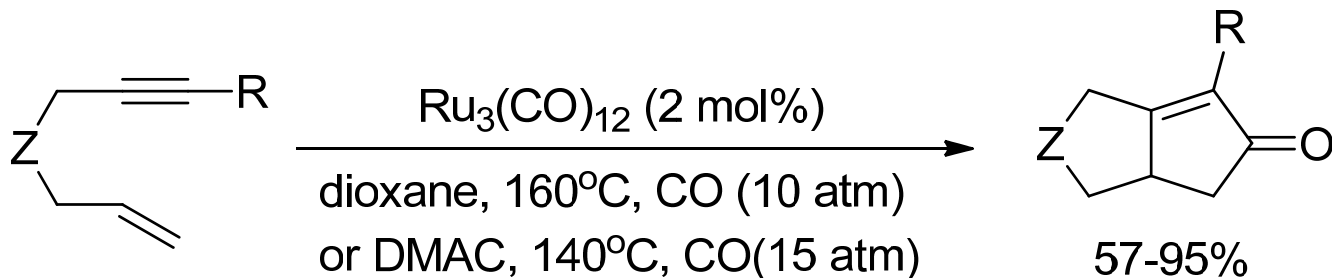
F. A. Hicks, N. M. Kablaoui, S. L. Buchwald, *J. Am. Chem. Soc.* 1999, **121**, 5881
[doi: 10.1021/ja990682u](https://doi.org/10.1021/ja990682u)

Zr serves as catalyst



E.I. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, *J. Am. Chem. Soc.* 1985, **107**, 2568 – 2569
[doi: 10.1021/ja00294a071](https://doi.org/10.1021/ja00294a071)

Ru serves as catalyst

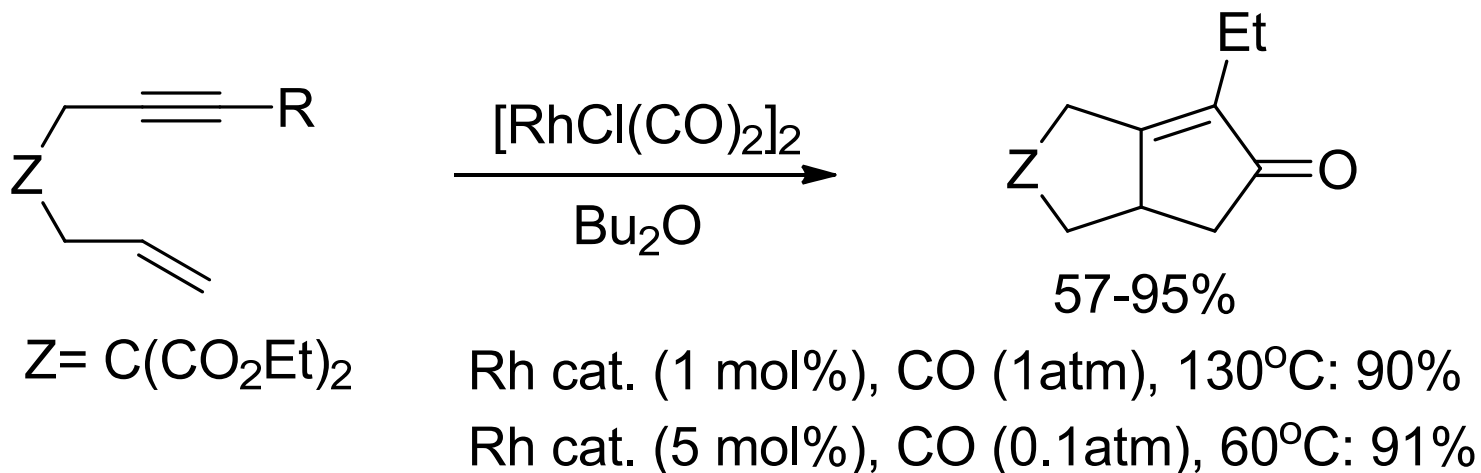


R= Ar, Alkyl, TMS
Z= C(CO₂Et)₂, O, NTs

T. Kondo, N. Suzuki, T. Okada, T. Mitsudo, *J. Am. Chem. Soc.* 1997, **119**, 6187 – 6188
[doi: 10.1021/ja970793y](https://doi.org/10.1021/ja970793y)

Mechanism of Ru catalyzed PKR, please click this: Yun-dong Wu and co-workers,
[Organometallics](https://doi.org/10.1021/ja00294a071), 2008, **27**, 6152–6162

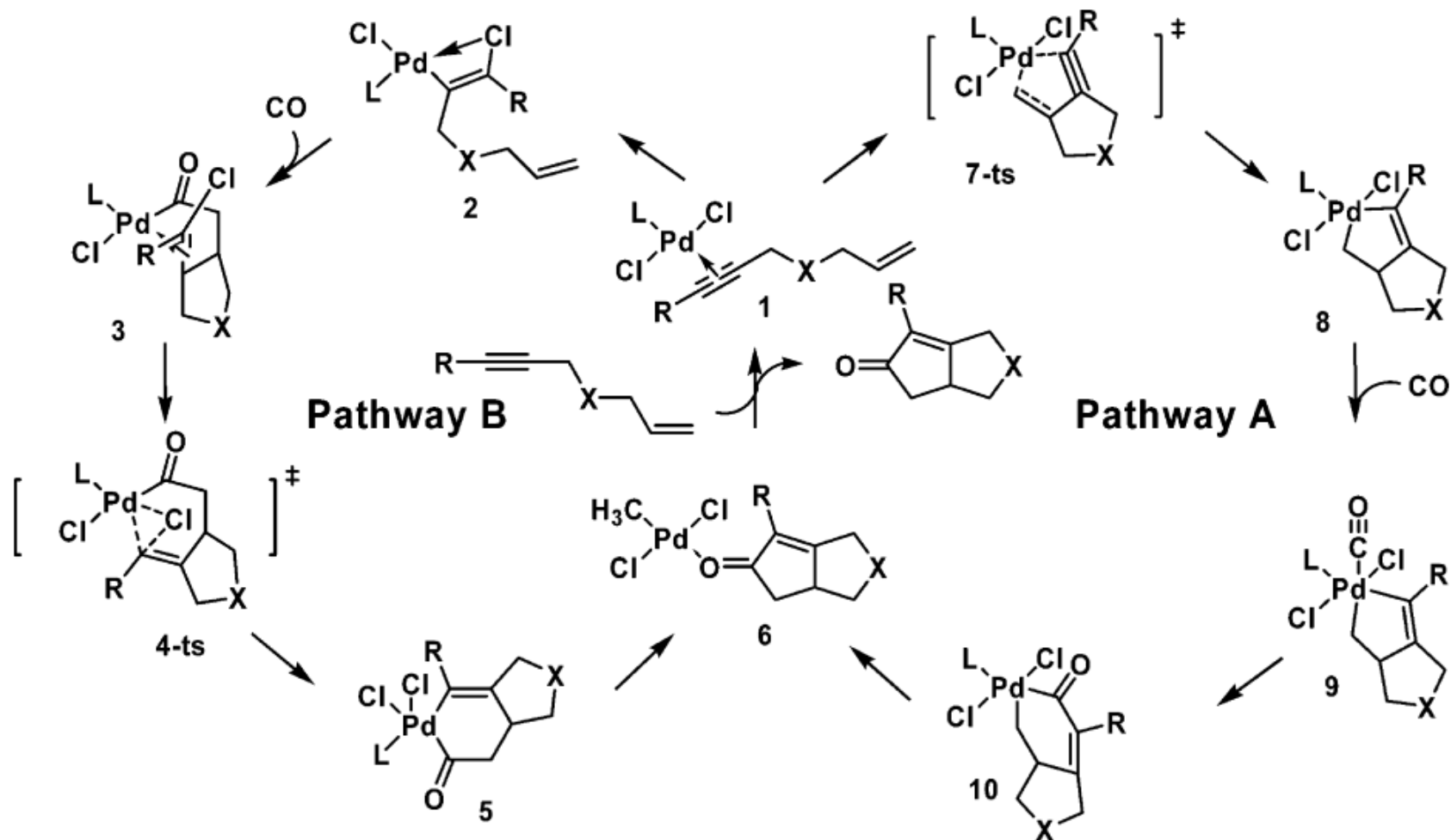
Rh serves as catalyst



T. Kobayashi, Y. Koga, K. Narasaka, *J. Organomet. Chem.* 2001., **624** 73 – 87
[doi:10.1016/S0022-328X\(00\)00835-4](https://doi.org/10.1016/S0022-328X(00)00835-4)

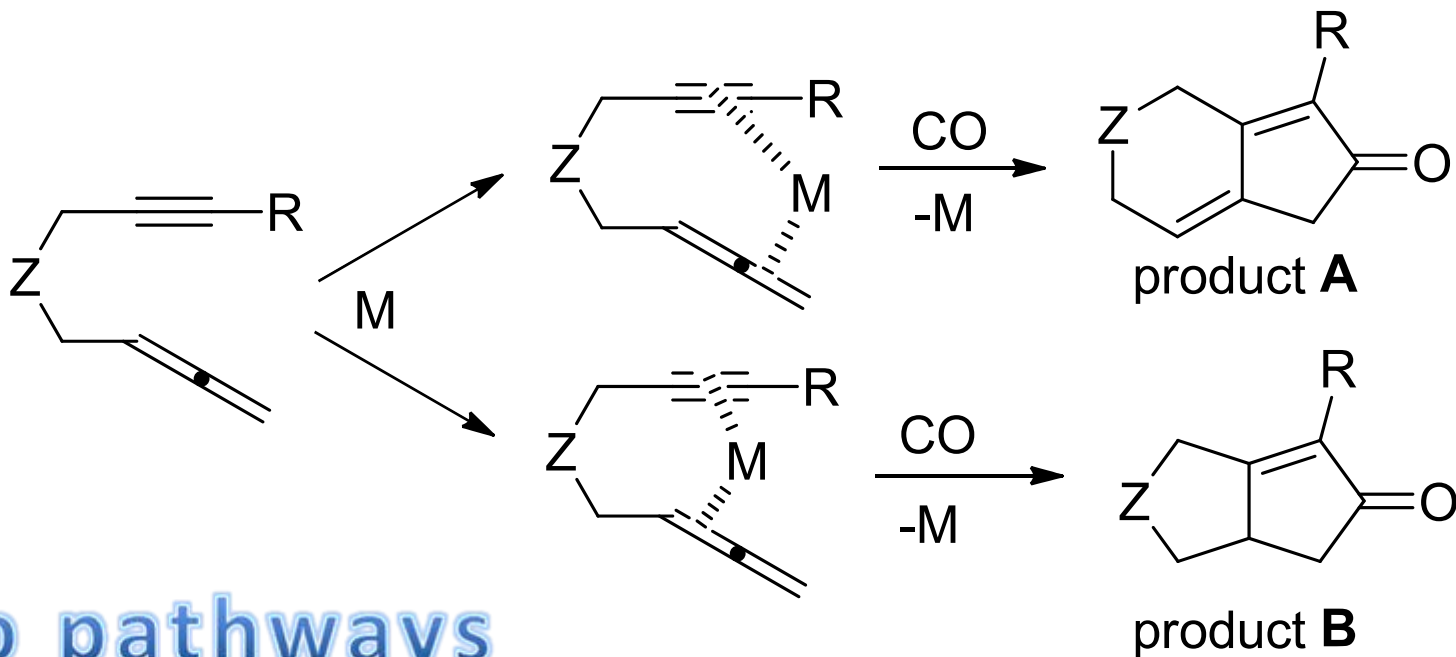
N. Jeong, S. Lee, B. K. Sung, *Organometallics*, 1998, **17**, 3642 – 3644
[doi: 10.1021/om980410k](https://doi.org/10.1021/om980410k)

Pd serves as catalyst



Zhen Yang and co-workers, *J. Org. Chem.* 2009, *74*, 5049–5058
[doi:10.1021/jo900919v](https://doi.org/10.1021/jo900919v)

Intramolecular PKR with allenes

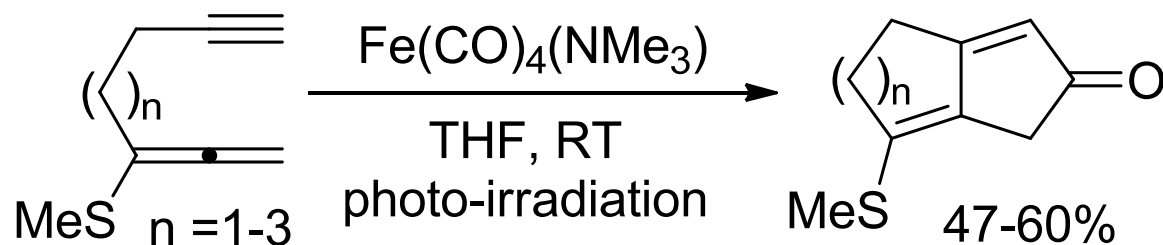


Two pathways

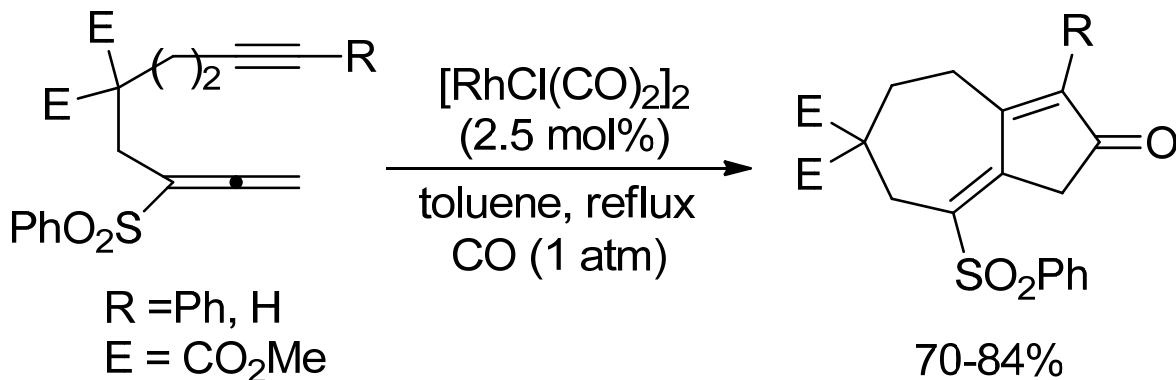
A: reaction of an external π -bond

B: reaction of an internal π -bond

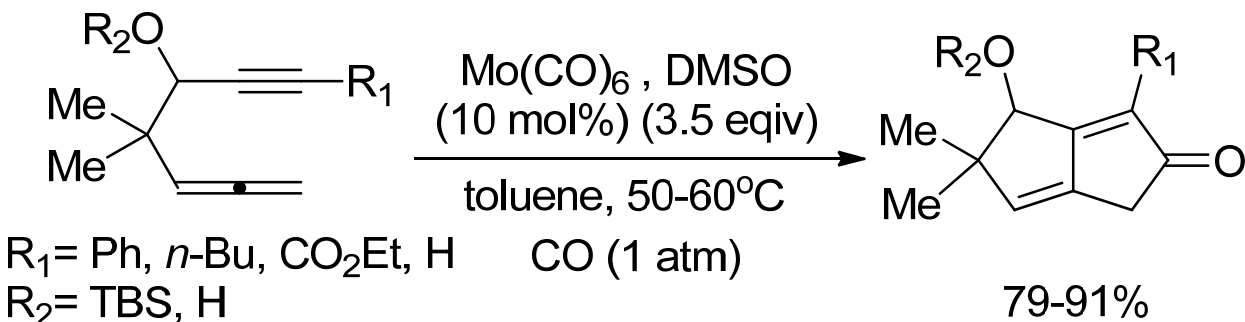
The reaction of an external π -bond --product A



K. Narasaka, T. Shibata, *Chem. Lett.* 1994, 315 – 318
[doi:10.1246/cl.1994.315](https://doi.org/10.1246/cl.1994.315)

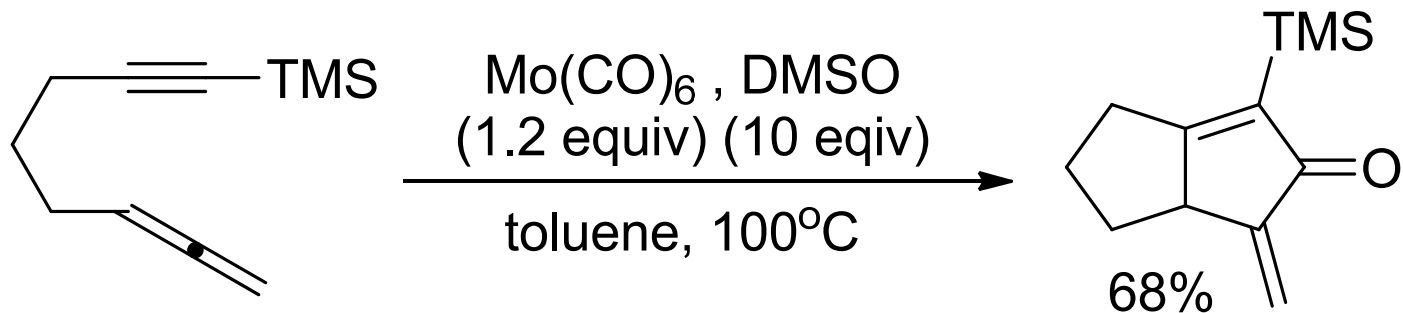


K. M. Brummond and co-workers, *Org. Lett.* 2002, 4, 1931 – 1934
[doi: 10.1021/ol025955w](https://doi.org/10.1021/ol025955w)

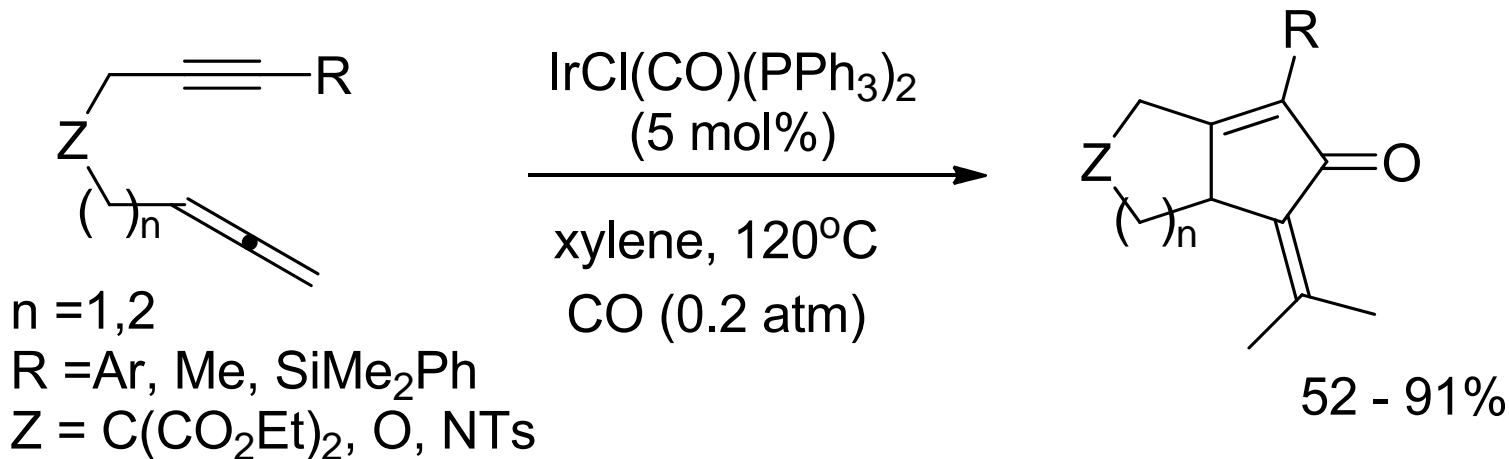


A. K. Gupta and co-workers, *Tetrahedron Lett.* 2005, 46, 4171 – 4174
[doi:10.1016/j.tetlet.2005.04.071](https://doi.org/10.1016/j.tetlet.2005.04.071)

The reaction of an internal π -bond --product B

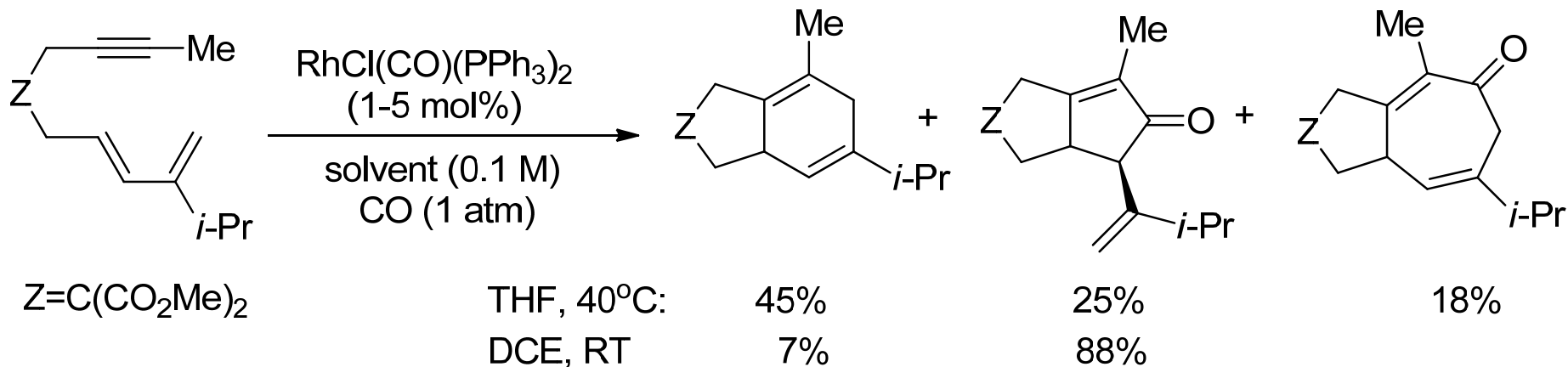


K. M. Brummond and co-workers, *Tetrahedron Lett.* 1995, **36**, 2407 – 2410
[doi:10.1016/0040-4039\(95\)00315-4](https://doi.org/10.1016/0040-4039(95)00315-4)

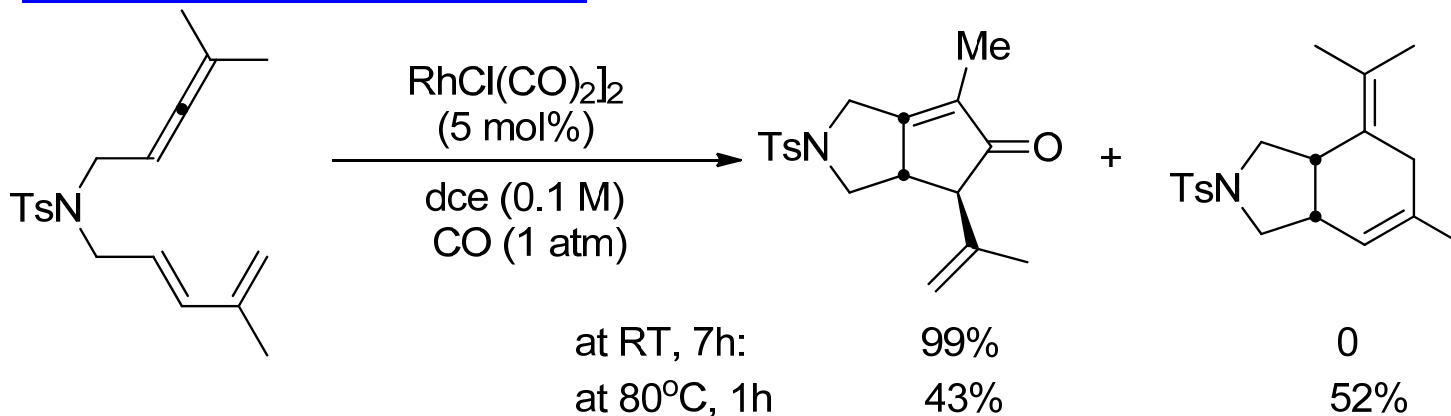


T. Shibata and co-workers, *Synlett*, 2003, 573 – 575
[doi: 10.1055/s-2003-37532](https://doi.org/10.1055/s-2003-37532)

Reaction of dienes



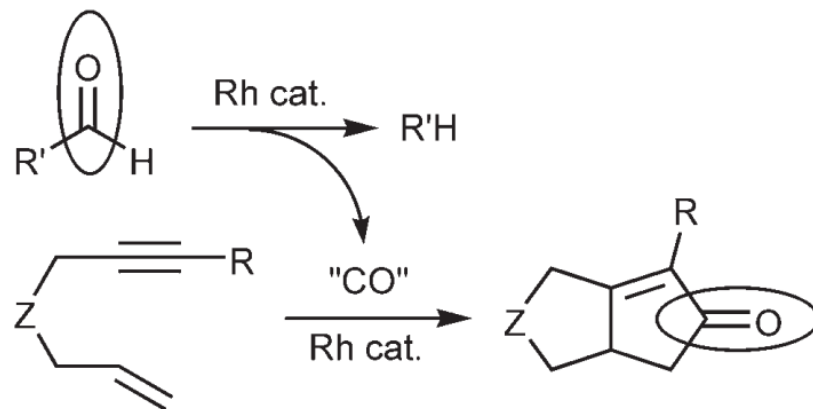
P. A. Wender and co-workers, *Angew. Chem. Int. Ed.* 2003, **42**, 1853 – 1857
[doi: 10.1002/anie.200350949](https://doi.org/10.1002/anie.200350949)



P. A. Wender and co-workers, *Angew. Chem. Int. Ed.* 2006, **45**, 2459 – 2462
[doi: 10.1002/anie.200600300](https://doi.org/10.1002/anie.200600300)

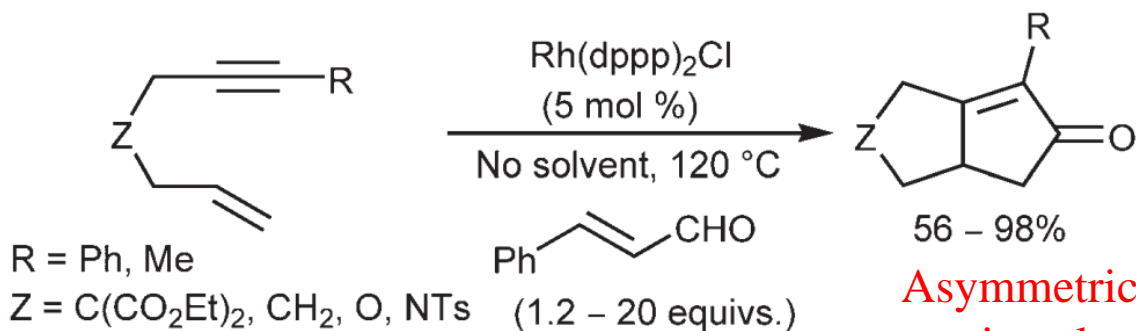
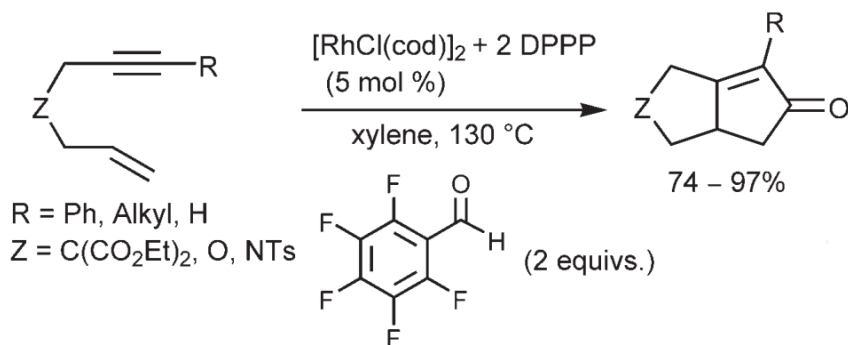
Other carbonyl sources

Aldehydes serve as
CO source



T. Morimoto, K. Fuji, K. Tsutsumi, K. Kakiuchi, *J. Am. Chem. Soc.* 2002, **124**, 3806 – 3807

[doi: 10.1021/ja0126881](https://doi.org/10.1021/ja0126881)



Asymmetric
version also
Possible !

T. Shibata, N. Toshida, K. Takagi, *Org. Lett.* 2002, **4**, 1619 – 1621

[doi: 10.1021/ol025836g](https://doi.org/10.1021/ol025836g)

BINAP as Ligand, Z = O
yield 89%
ee 82%

Alcohol serve as CO source

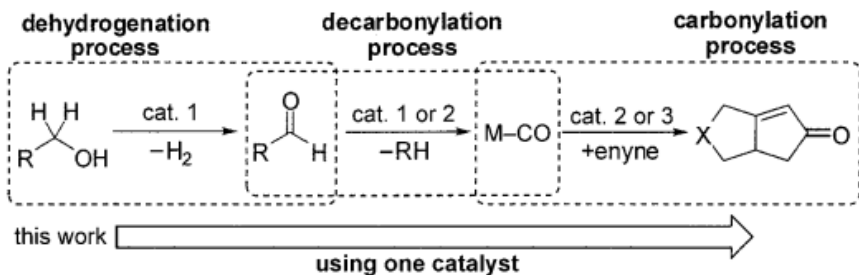
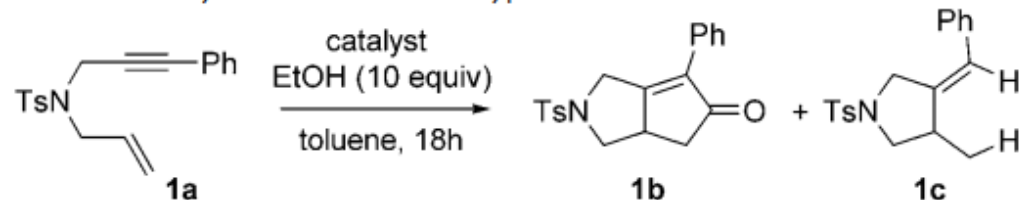


Table 1: Catalytic Pauson–Khand-type reaction of **1a** with ethanol.^[a]



Entry	Catalyst	mol %	T [°C]	1b [%] ^[b]	1c [%] ^[b]
1	[{Rh(CO)Cl(dppp)} ₂]	8	120	61	36
2	[{Rh(CO)Cl(dppp)} ₂]	8	70	66	33
3	[{Rh(CO)Cl(dppp)} ₂]	8	40	31 (45) ^[c]	22
4	[Rh(CO)Cl(dppe)]	16	70	trace	trace
5	[{Rh(CO)Cl(dppb)} ₂]	8	70	18 (65) ^[c]	16
6	[Rh(dppp) ₂ Cl]	16	70	24 (32) ^[c]	34
7	[{Rh(cod)Cl} ₂] /binap	8 (16) ^[d]	70	n.r.	
8	[{Rh(cod)Cl} ₂] /dppp	8 (16) ^[d]	70	48	49
9	[RhCl(PPh ₃) ₃]	16	70	n.r.	
10 ^[e]	[{Rh(CO)Cl(dppp)} ₂]	8	70	n.r.	
11	[{Rh(CO)Cl(dppp)} ₂]	4	70	58	37
12	[{Rh(CO)Cl(dppp)} ₂]	2	70	41	53

It should be noted that the CO actually comes from the acetaldehyde which is generated from the oxidation of ethanol

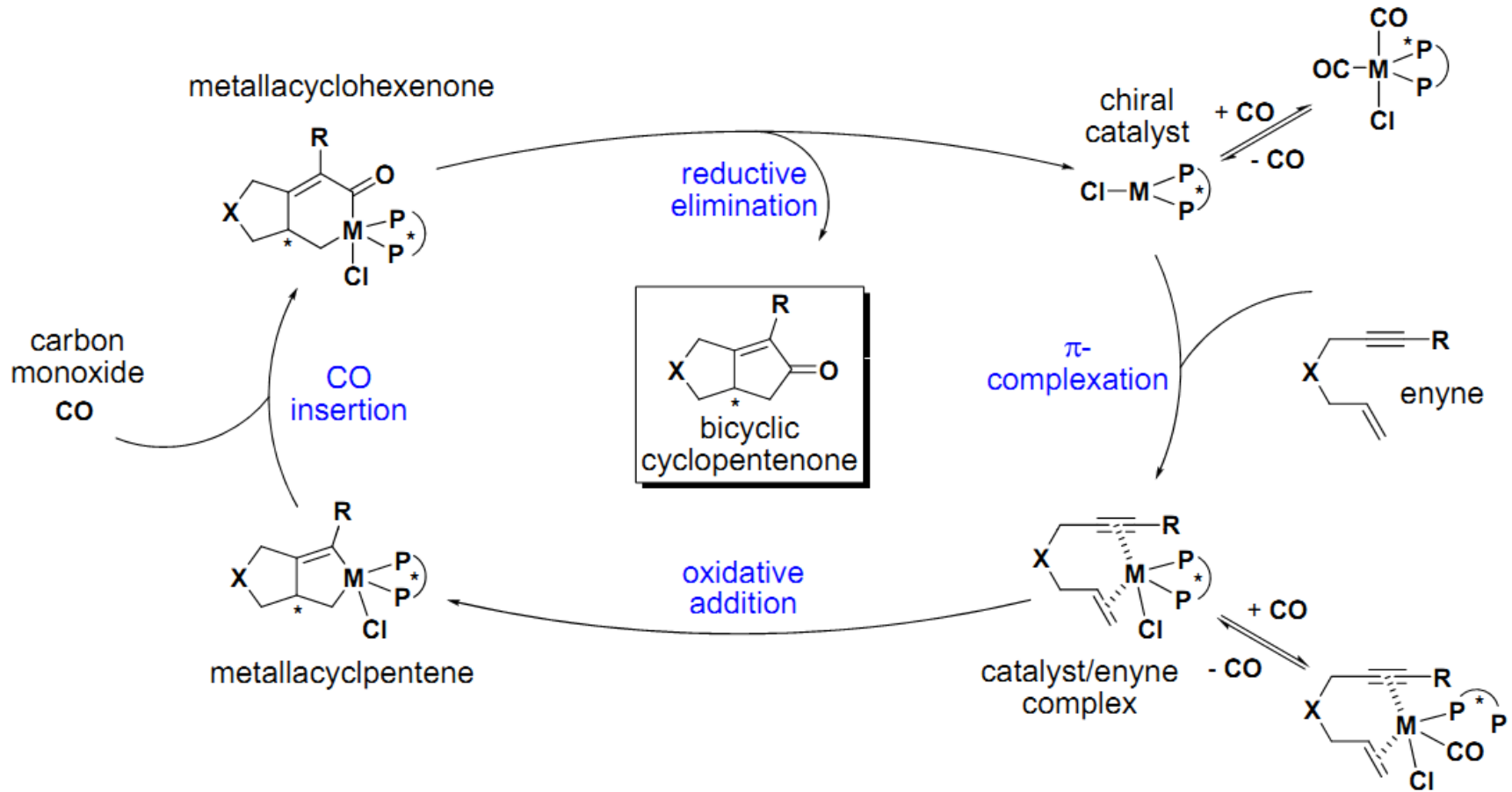
Park, Ji Hoon, Cho, Yoonhee, Chung, Young Keun. *Angew. Chem. Int. Ed.* 2010, **49**, 5138–5141

[doi:10.1002/anie.201001246](https://doi.org/10.1002/anie.201001246)

Asymmetric PKR

- Chirality transfer from substrate [link](#)
- Chiral auxiliaries
- Chiral metal complexes
- Chiral promoters
- Metals include *Co*, *Rh*, Ti, Mo, Ir etc.

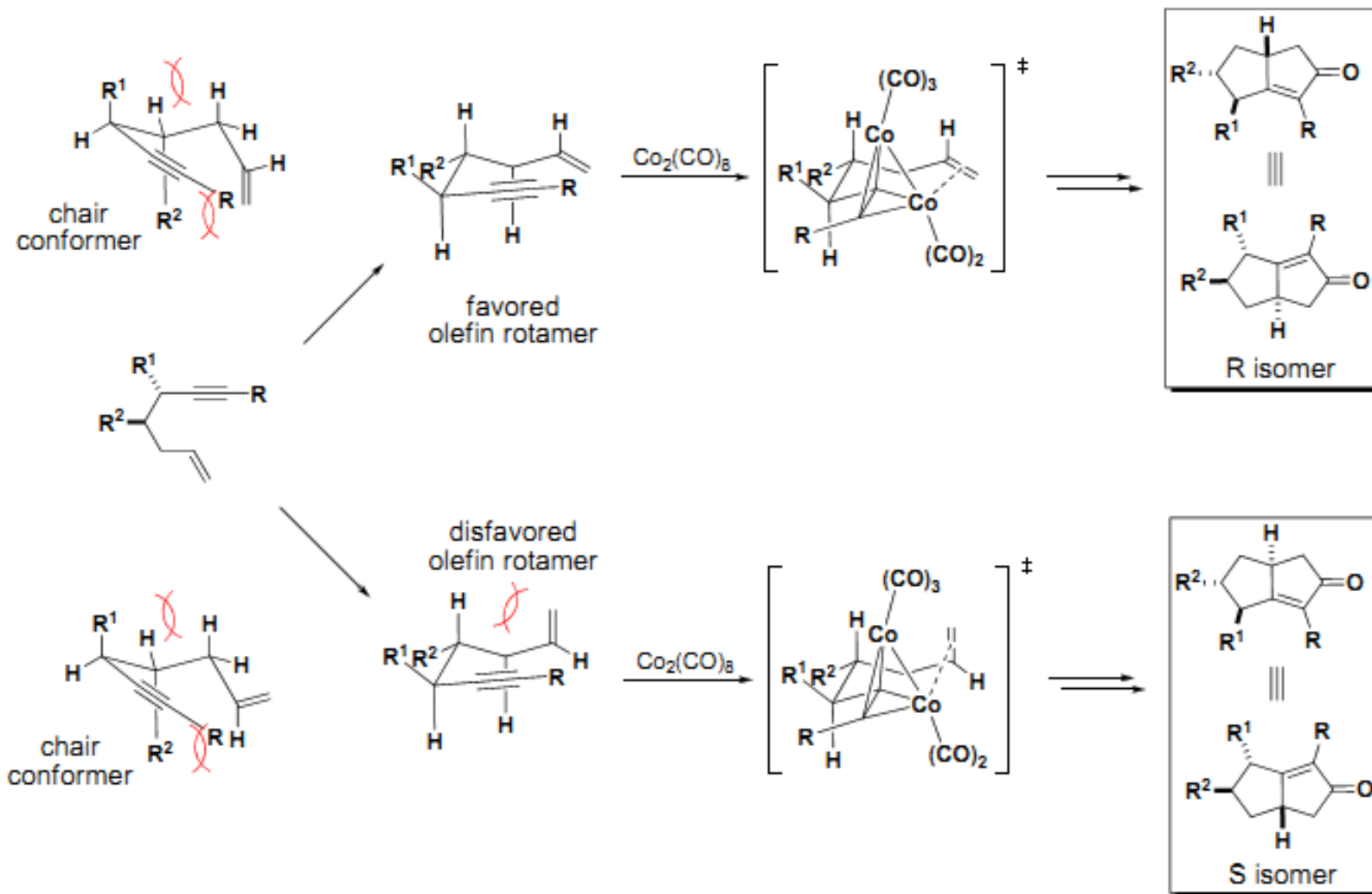
Asymmetric Catalytic Cycle



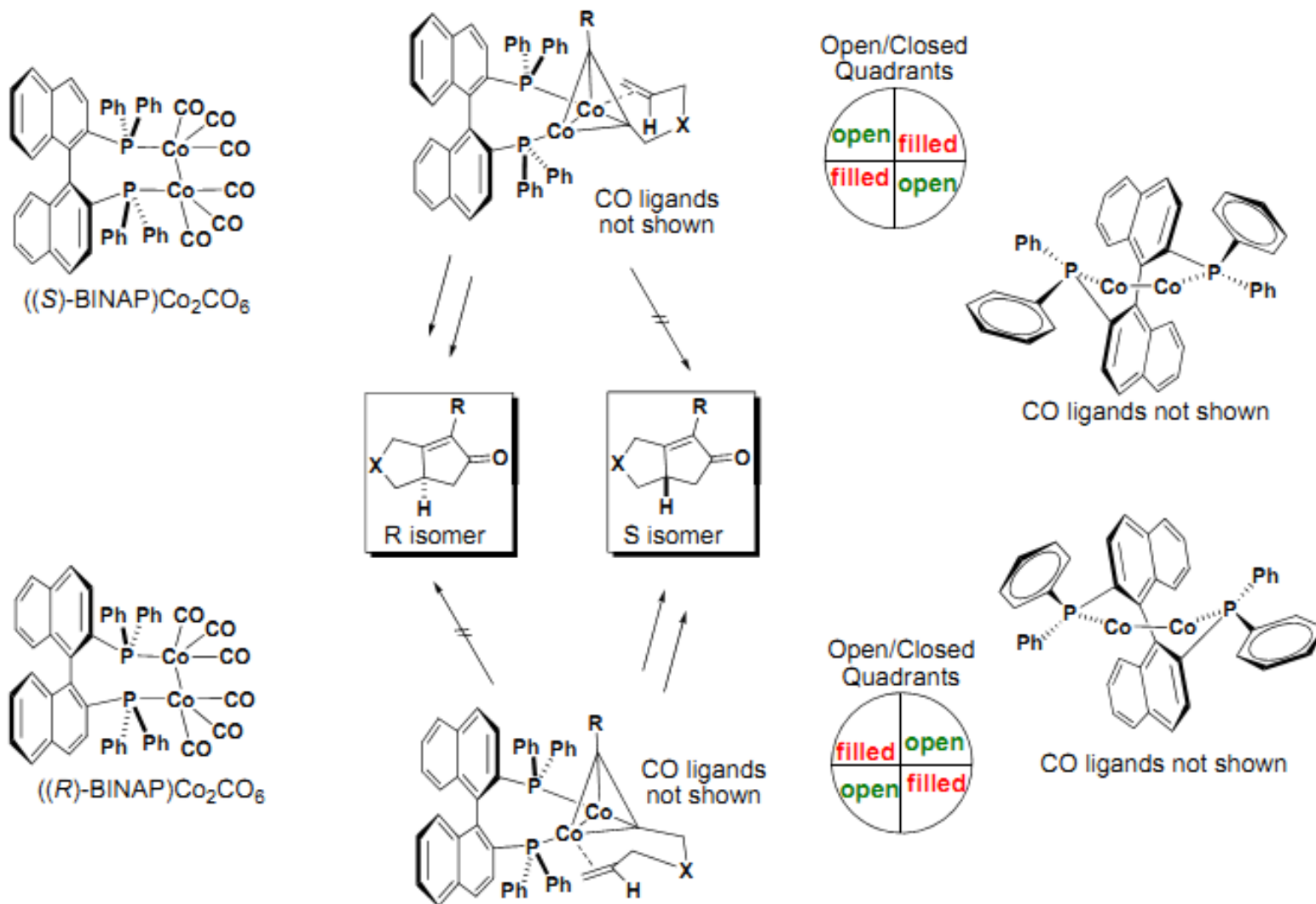
CO pressure-dependence

- reaction rate decreases with increased CO pressure
- enantioselectivity decreases with increased CO pressure

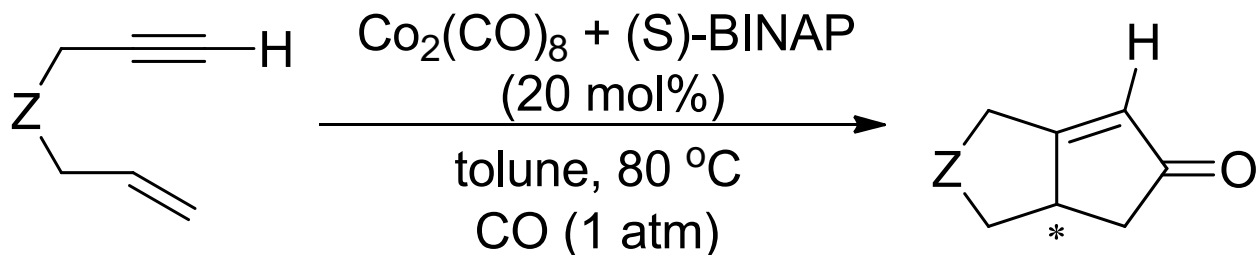
Substrate-Directed Stereocontrol



Reagent-Directed Stereocontrol

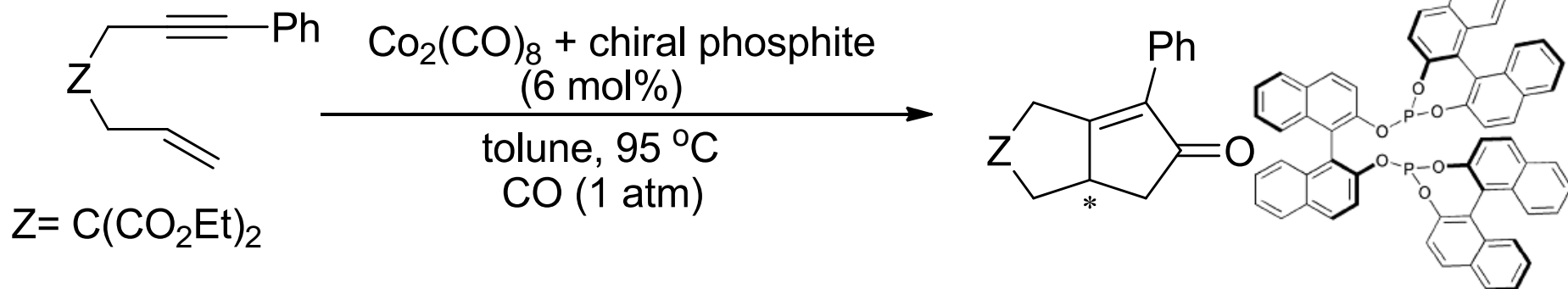


Commonly used Chiral ligands



Z = $\text{C}(\text{CO}_2\text{Et})_2$, NTs

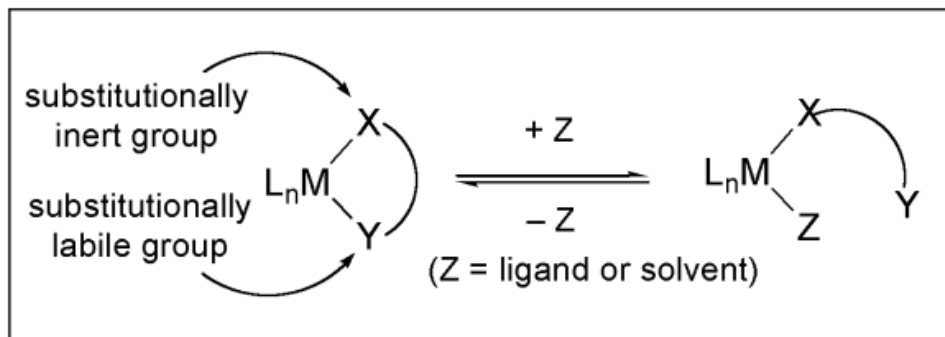
K. Hiroi and co-workers, *Tetrahedron Lett.* 2000, **41**, 891 – 895
[doi:10.1016/S0040-4039\(99\)02141-3](https://doi.org/10.1016/S0040-4039(99)02141-3)



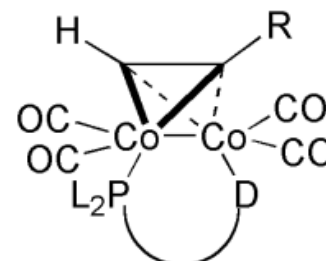
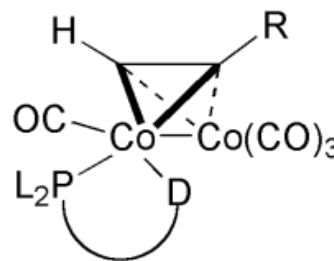
Z = $\text{C}(\text{CO}_2\text{Et})_2$

S. J. Sturla, S. L. Buchwald, *J. Org. Chem.* 2002, **67**, 3398 – 3403
[doi: 10.1021/jo016038r](https://doi.org/10.1021/jo016038r)

The mechanism based design of Chiral cobalt catalyst ligands

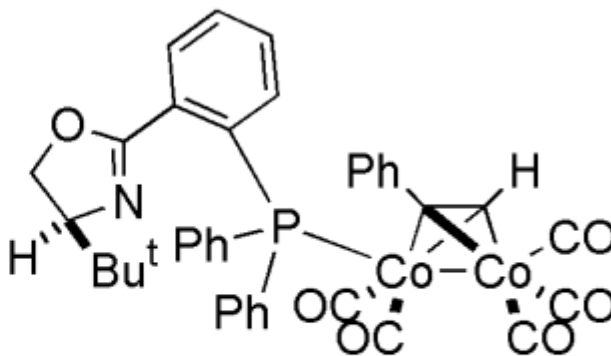
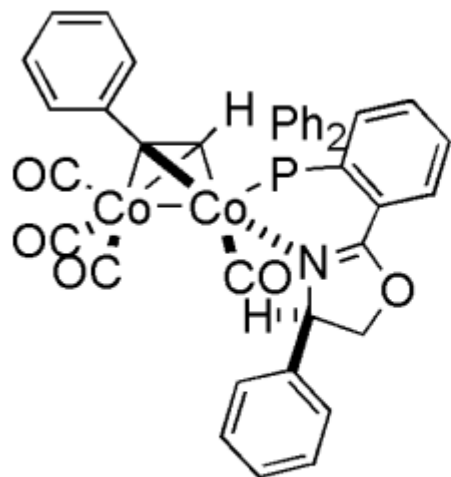


Semi-Labile Ligands in Dicobalt Hexacarbonyl Complexes



D = N, S

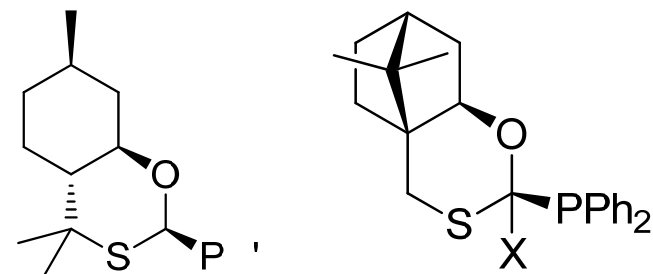
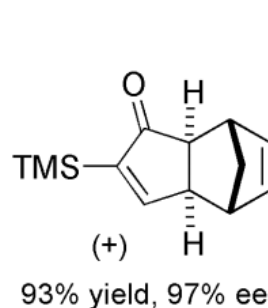
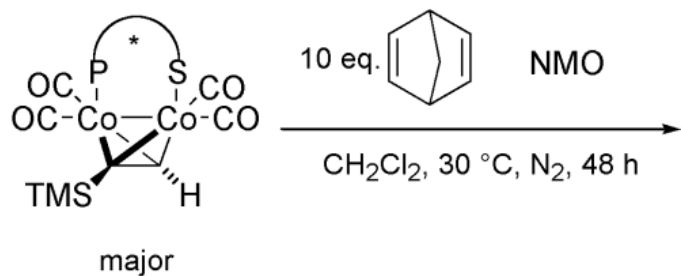
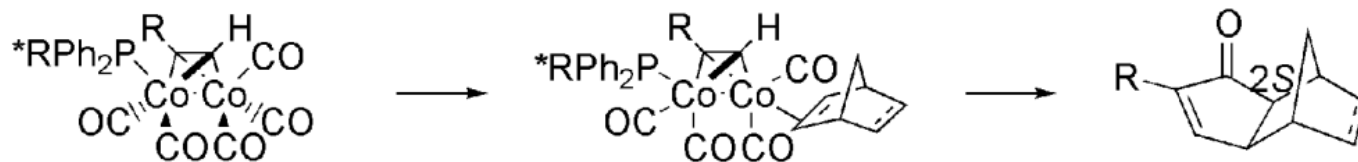
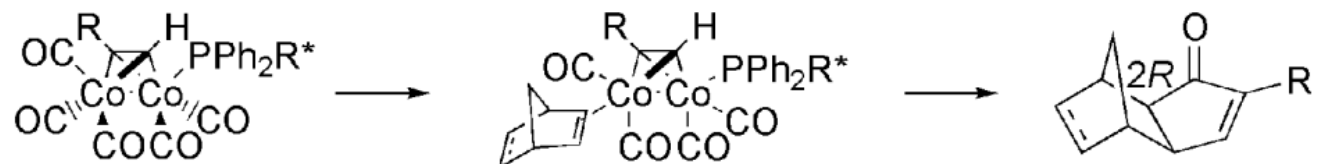
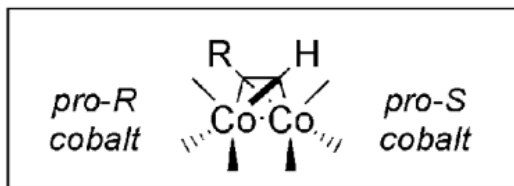
85:15 dr



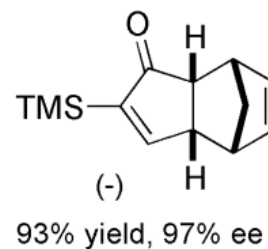
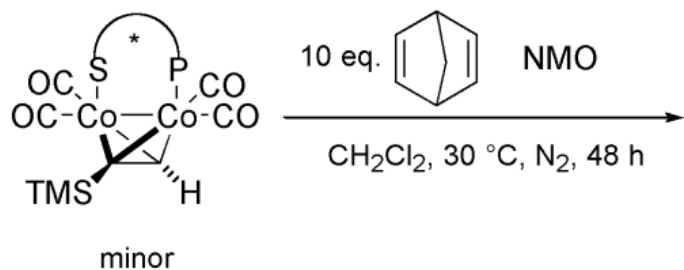
51 ee%

Added into reaction

Pseudoenantiomeric complexes



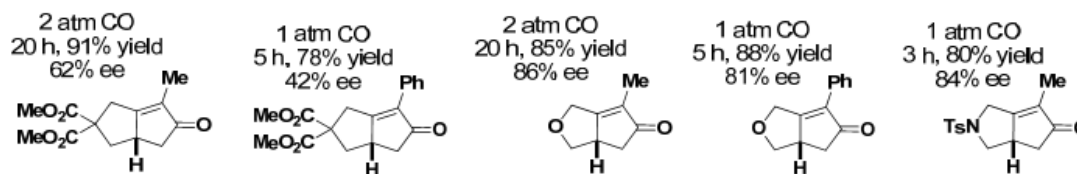
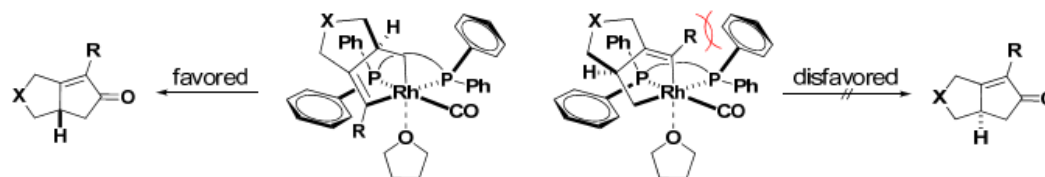
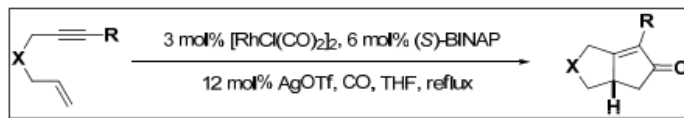
Ligand Example



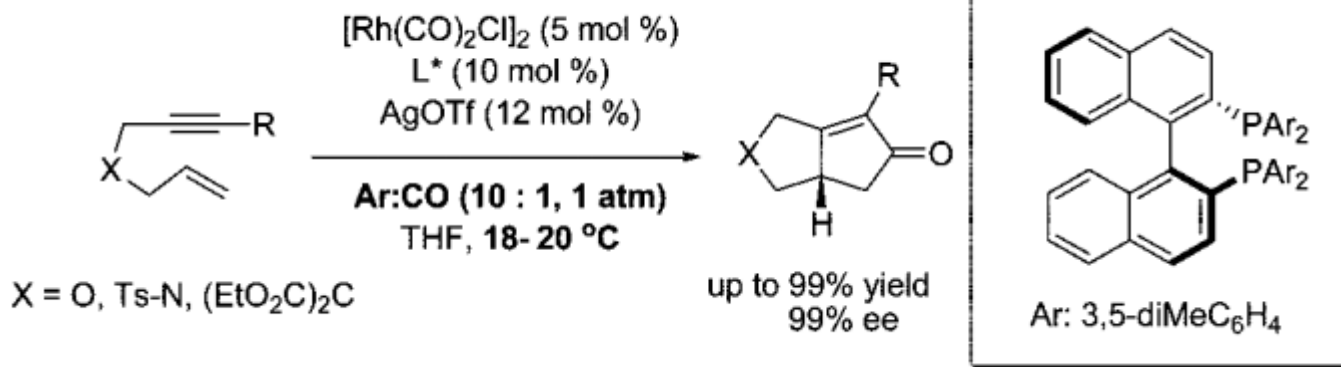
Pericàs et al. *Pure Appl. Chem.* 2002, **74**, 167-174

[doi:10.1351/pac200274010167](https://doi.org/10.1351/pac200274010167)

Enantioselective Rh catalysts

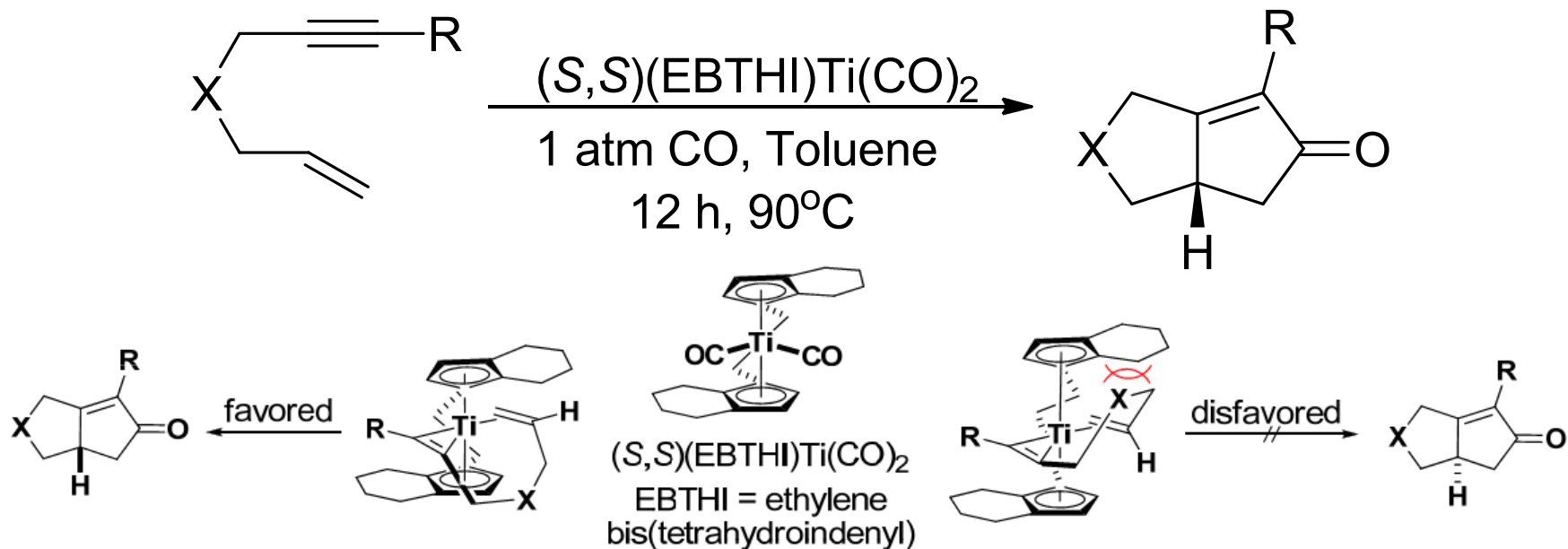


Nakcheol Jeong and coworkers, *J. Am. Chem. Soc.* 2000, **122**, 6771-6772
[doi:10.1021/ja0007049](https://doi.org/10.1021/ja0007049)

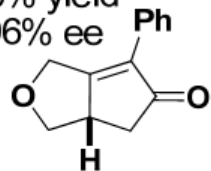


Nakcheol Jeong and co-workers, *J. Org. Chem.* 2008, **73**, 7985–7989
[doi:10.1021/jo801236c](https://doi.org/10.1021/jo801236c)

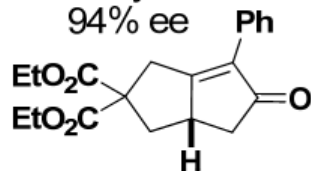
Asymmetric Titanium Catalysts



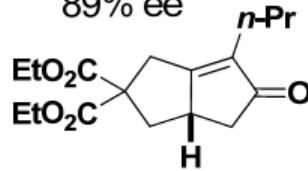
20 mol % Ti
85% yield
96% ee



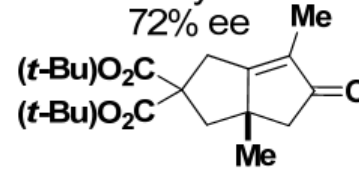
7.5 mol % Ti
92% yield
94% ee



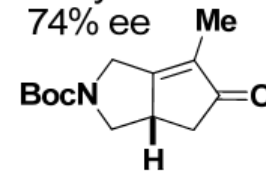
5 mol % Ti
94% yield
89% ee



20 mol % Ti
90% yield
72% ee



10 mol % Ti
84% yield
74% ee



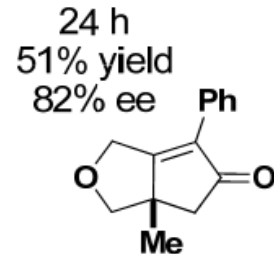
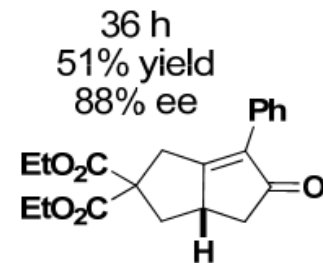
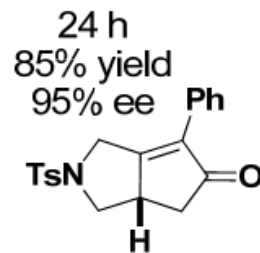
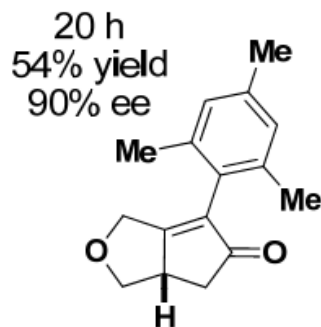
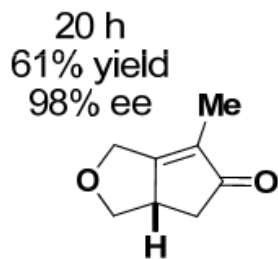
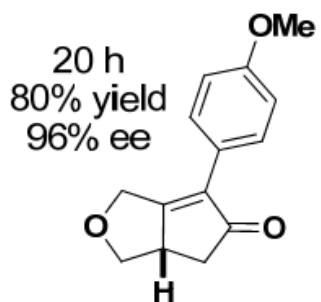
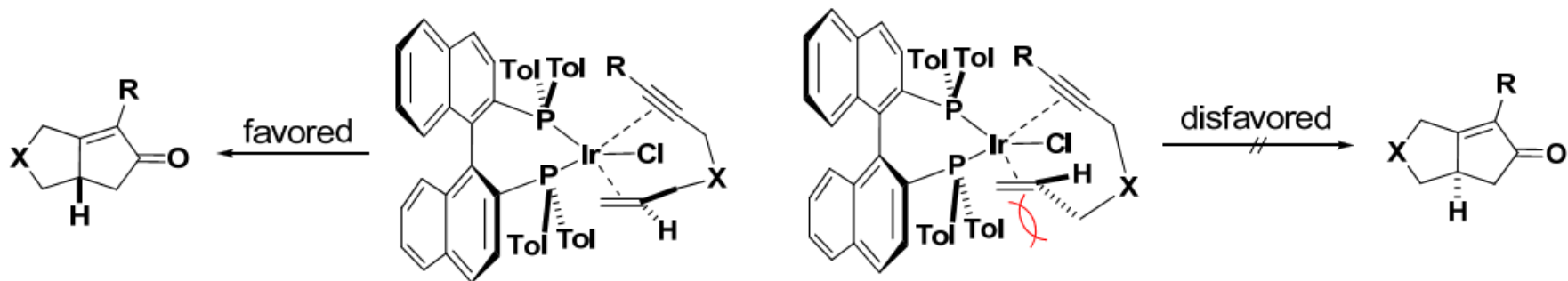
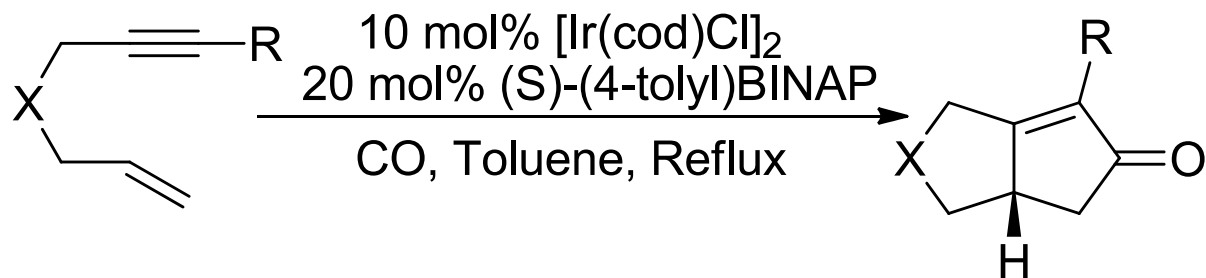
Buchwald and coworkers, *J. Am. Chem. Soc.* 1996, *118*, 9450-9451.

[Doi: 10.1021/ja9621509](https://doi.org/10.1021/ja9621509)

Buchwald and coworkers, *J. Am. Chem. Soc.* 1996, *118*, 11688-11689

[doi: 10.1021/ja9630452](https://doi.org/10.1021/ja9630452)

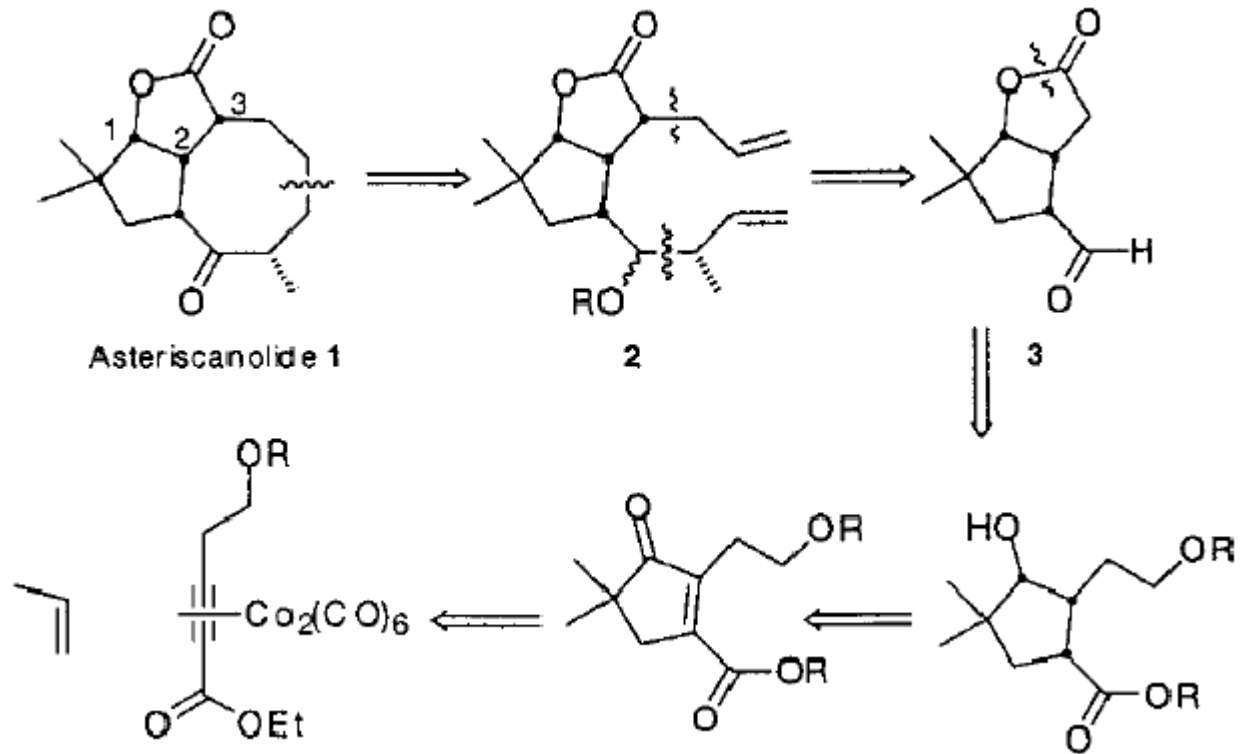
Asymmetric Iridium Catalysts



Shibata, T.; Takagi, K. *J. Am. Chem. Soc.* 2000, *122*, 9852-9853

[doi: 10.1021/ja000899k](https://doi.org/10.1021/ja000899k)

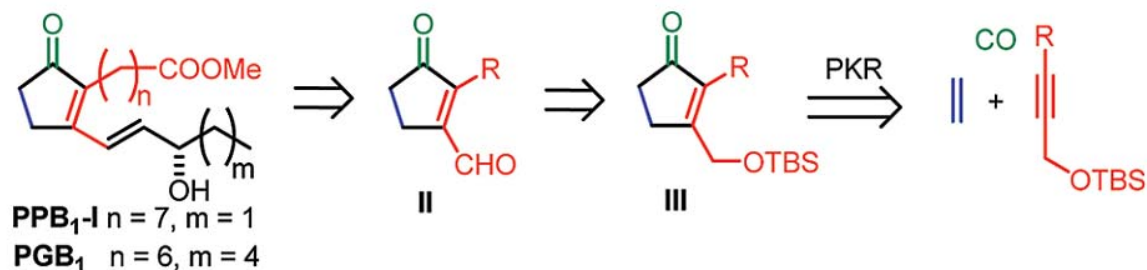
Total Synthesis of (\pm)-Asteriscanolide



Intermolecular PKR!

Krafft, M.E. and co-workers, *J. Org. Chem.* 2001, **66**, 7443-7448
[doi: 10.1021/jo010623a](https://doi.org/10.1021/jo010623a)

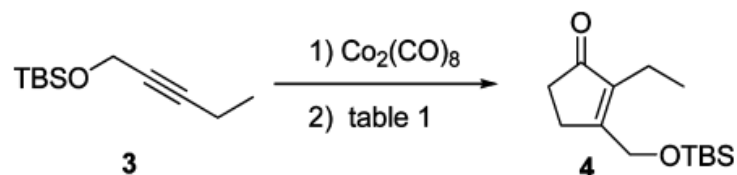
Synthesis of Prostaglandin and Phytoprostane B₁



Antoni Riera and co-workers, *Org. Lett.*, 2009, *11*, 3104-3107

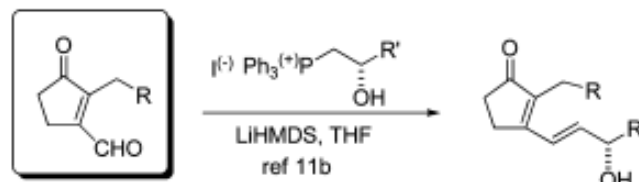
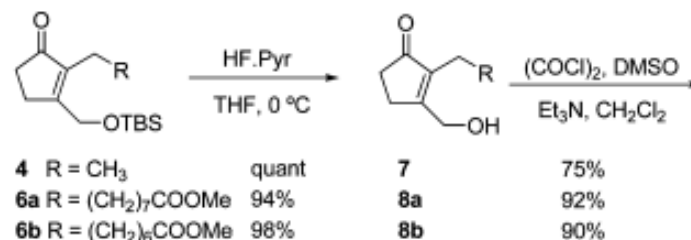
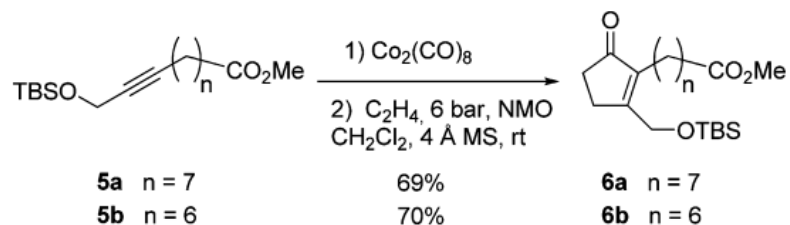
[doi: 10.1021/ol901213d](https://doi.org/10.1021/ol901213d)

Table 1. Pauson–Khand Synthesis of the Cyclopentenone **4** Using Ethylene or Equivalent Compounds

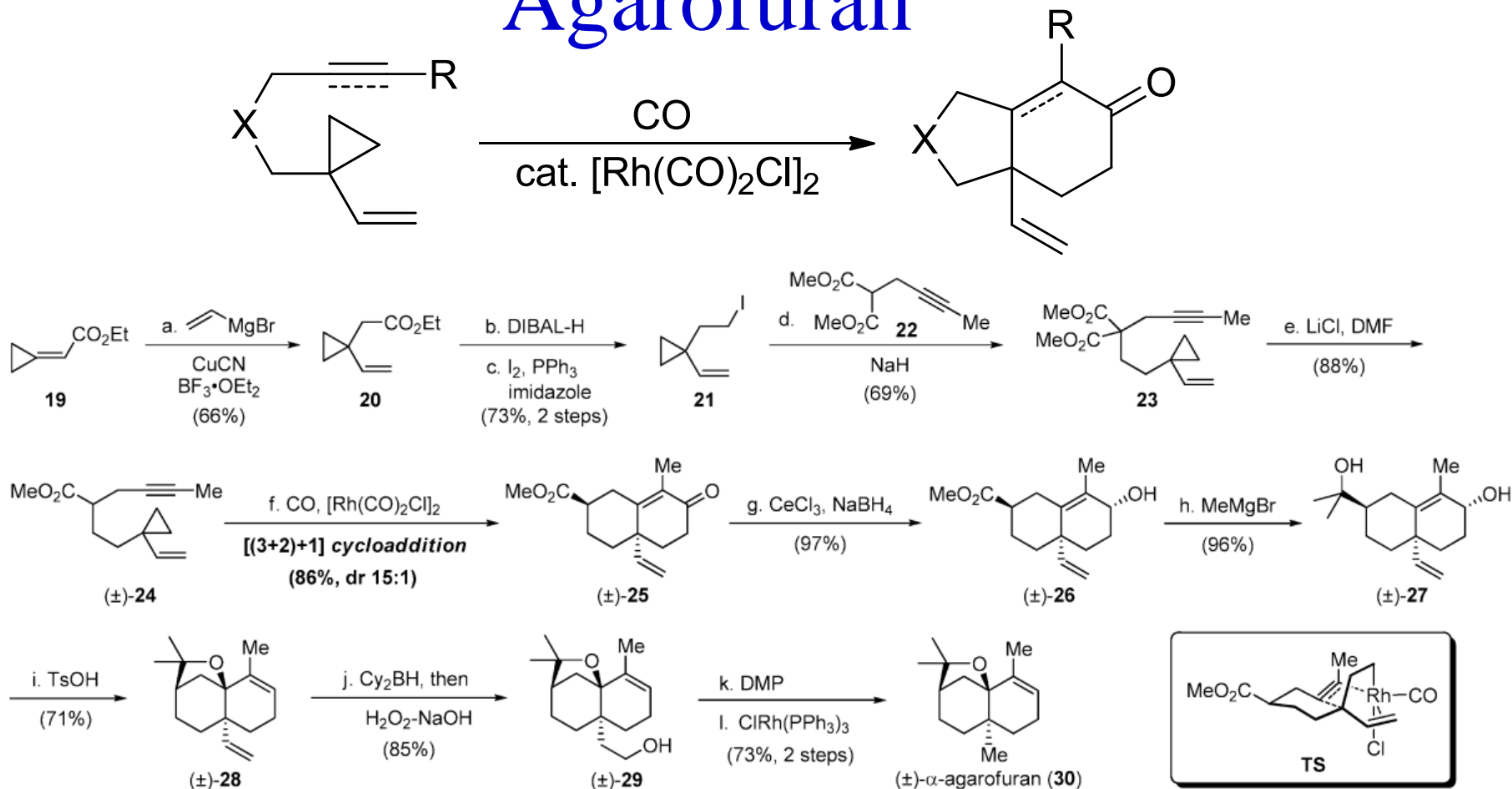


reagent	conditions	Yield
CH ₂ =CH ₂ , 7.5 bar	toluene, 90 °C	25%
CH ₂ =CH–OBz	CH ₂ Cl ₂ , NMO, rt	19%
CH ₂ =CH–OAc	CH ₂ Cl ₂ , NMO, rt	22%
CH ₂ =CH ₂ , 6 bar	Tol/MeOH, NMO, rt	46%
CH ₂ =CH ₂ , 6 bar	CH ₂ Cl ₂ , NMO, rt	54%
CH ₂ =CH ₂ , 6 bar	CH ₂ Cl ₂ , 4 Å MS, NMO, rt	67%

Scheme 1. Pauson–Khand Syntheses of the Cyclopentenones **6a** and **6b**



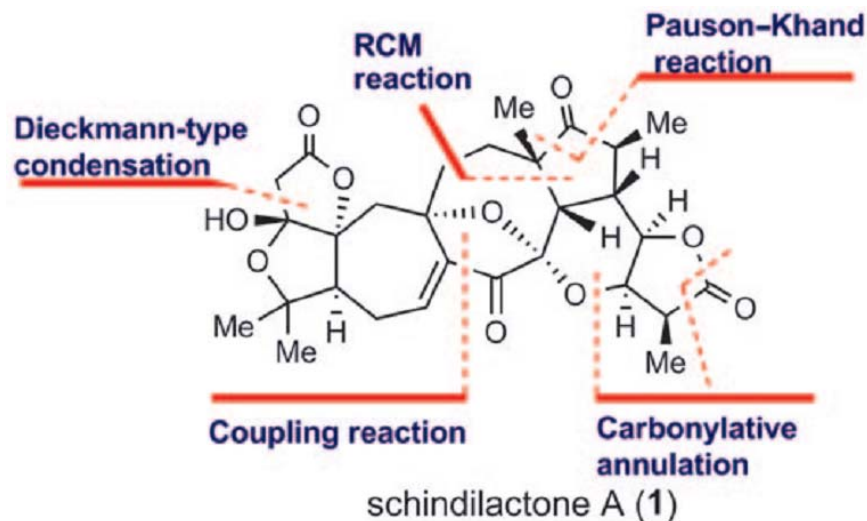
The total synthesis of (\pm)- α -Agarofuran



^a DIBAL-H = diisobutylaluminum hydride, DMF = dimethylformamide, DMP = Dess–Martin periodinane.

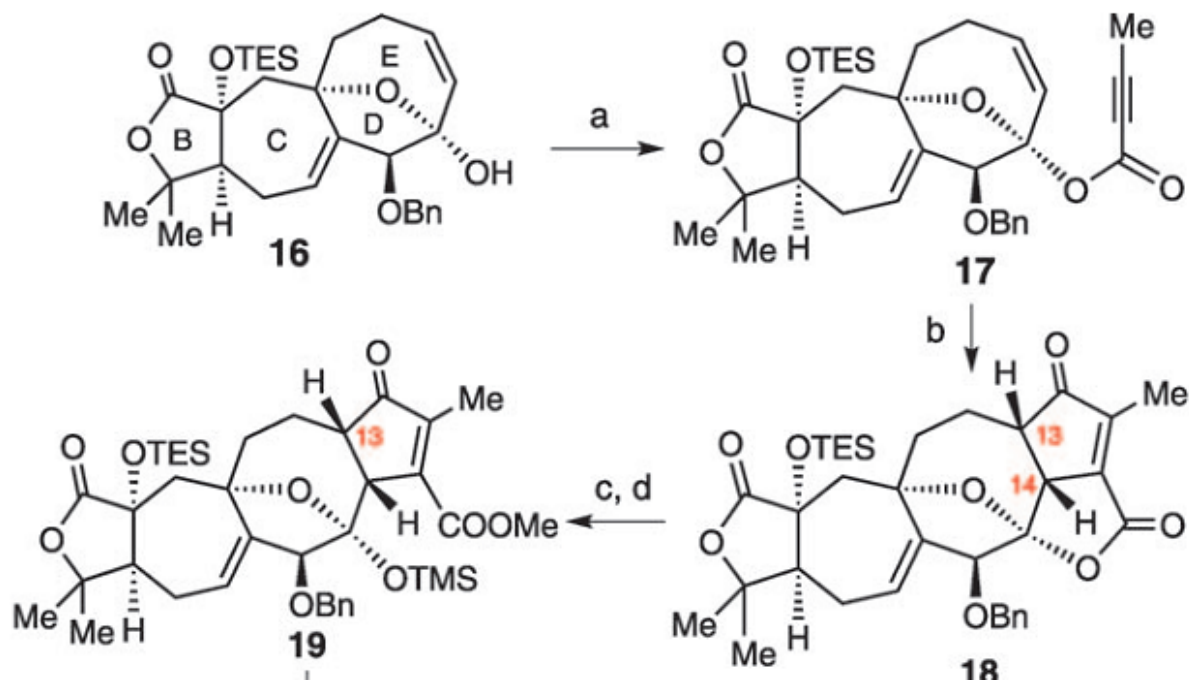
Zhi-Xiang Yu and coworkers, *Org. Lett.* 2010, **12**, 2528-2531
[doi:10.1021/ol100625e](https://doi.org/10.1021/ol100625e)

The total synthesis of (\pm)-Schindilactone A

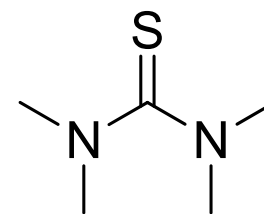


Zhen Yang and co-workers,
Angew. Chem. Int. Ed. 2011, **50**,
7373 –7377

[doi:10.1002/anie.201103088](https://doi.org/10.1002/anie.201103088)



b) $[\text{Co}_2(\text{CO})_8]$ (0.5 equiv),
TMTU (3.0 equiv), PhH,
70°C, 4 h (74%).



tetramethylthiourea

Acknowledgements

Credits should be given to those who pioneering in preparing PKR literature seminar

- Mindy Levine @ WISC
- Nathan Bennett @Caltech
- R. Paolillo @ Politecnico di Bari (巴里理工大学, 意大利)
- Steven Ballmer @UIUC

Useful Review on this topic

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Blanco-Urgoiti et al. The Pauson-Khand reaction, a powerful synthetic tool for the synthesis of complex molecules. *Chemical Society Reviews*, 2004, **33**, 32-42. [Link](#)

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Shibata. Recent Advances in the Catalytic Pauson–Khand-Type Reaction. *Adv. Synth. Catal.* 2006, **348**, 2328–2336 [Link](#)

Thanks for watching!