The reaction of 2,3-butadien-1-ol

Reporter : Jie Lin

Advisor: Prof. Shengming Ma

20190419

Synthesis of 2,3-butadien-1-ol

Transformation of 2,3-butadien-1-ol

- Coupling reactions of 2,3-butadien-1-ol
- Cyclization reactions of 2,3-butadien-1-ol
- Total synthesis

Transformation of 2,3-butadien-1-ol derivative

Conclusions and outlook

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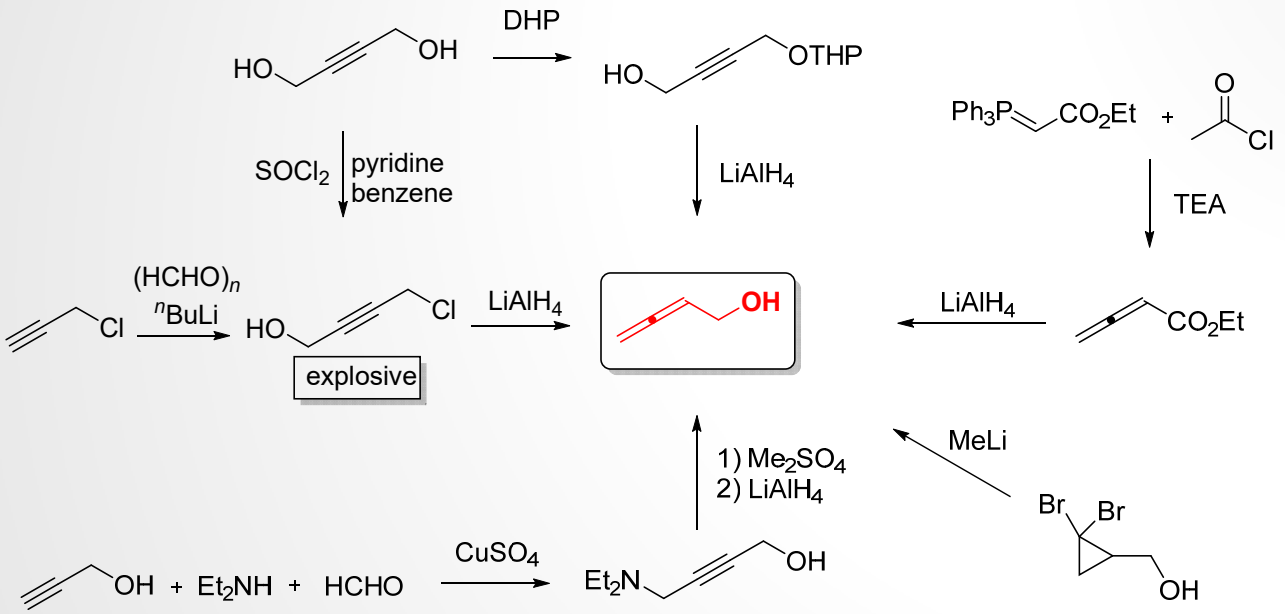
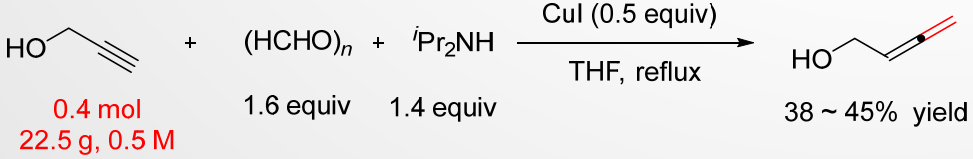
Synthesis of 2,3-butadien-1-ol





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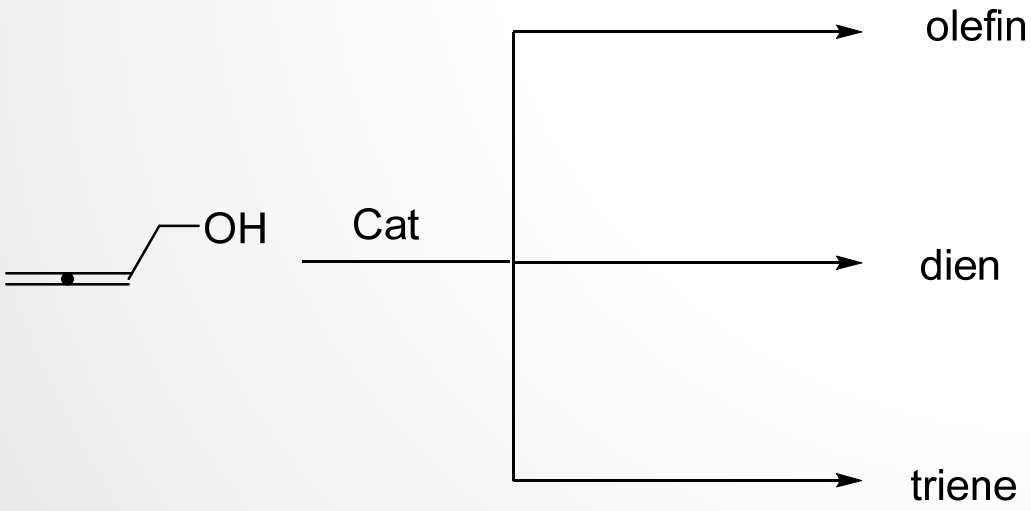
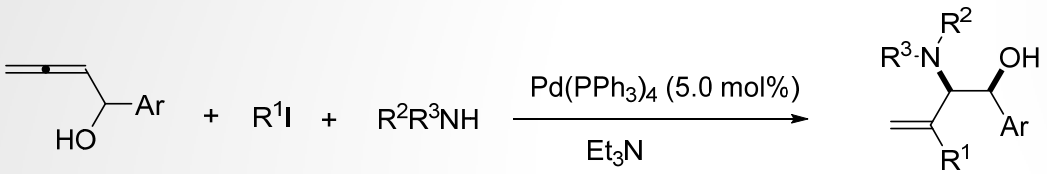
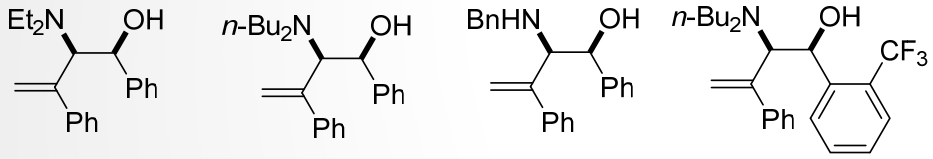
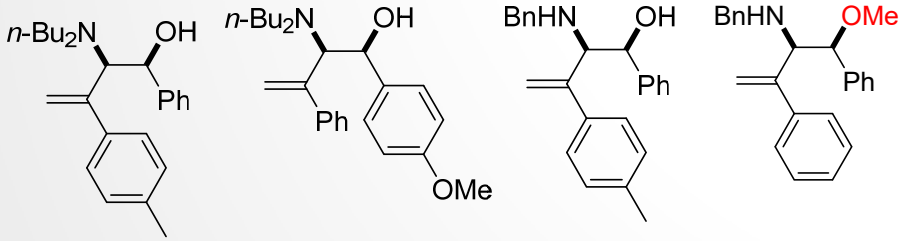


Coupling reactions of 2,3-butadien-1-ol

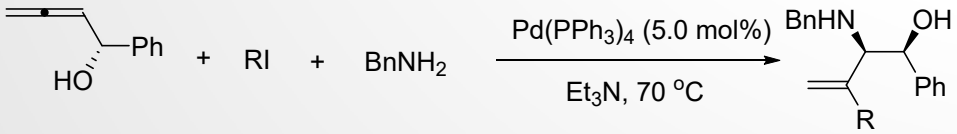




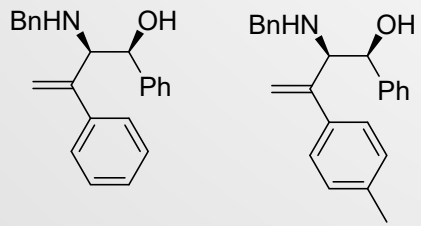
82% 78% 63% 85%



44% 53% 67% 83%



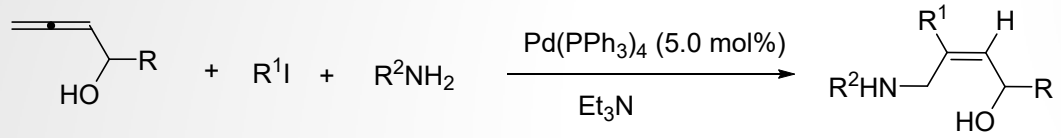
98% ee

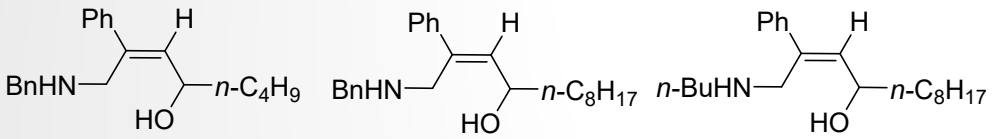


57%, 98% ee 65%, 97% ee

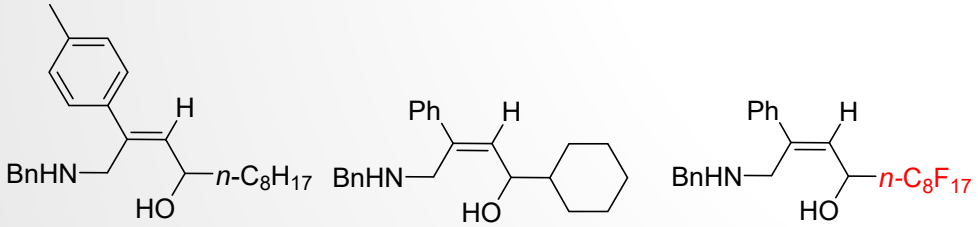
Zhao, S.; Ma, S. *J. Am. Chem. Soc.* **2001**, *123*, 5578

Coupling reactions of 2,3-butadien-1-ol

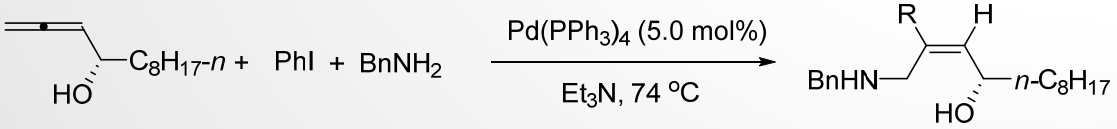




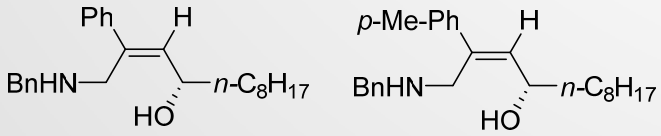
92% 72% 57%



78% 45% 87%



97% ee



58%, 96% ee 63%, 96% ee

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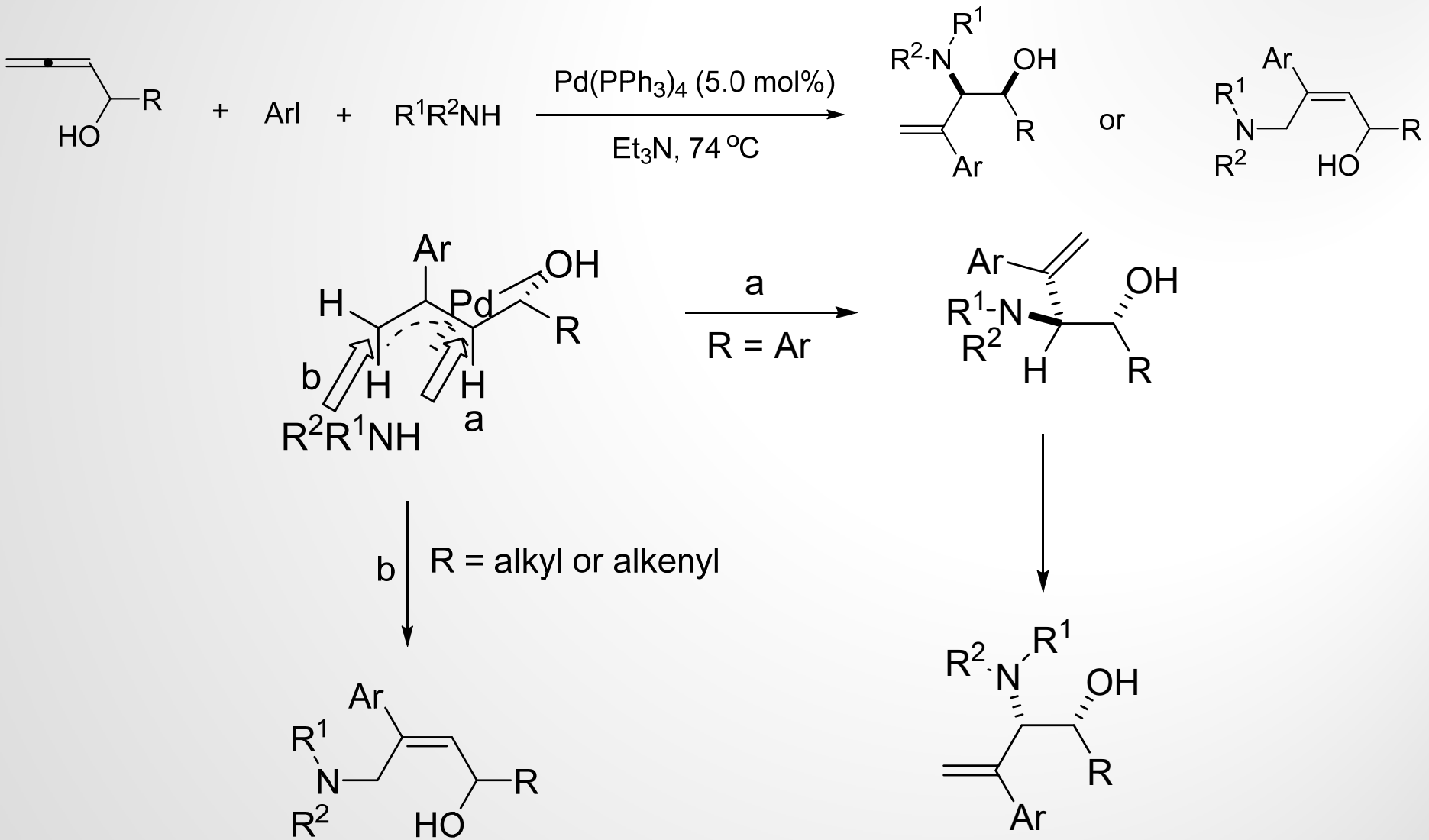
Coupling reactions of 2,3-butadien-1-ol



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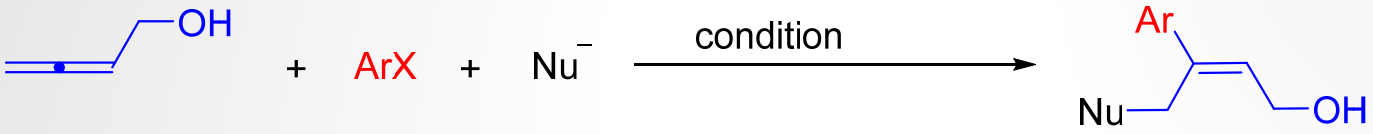
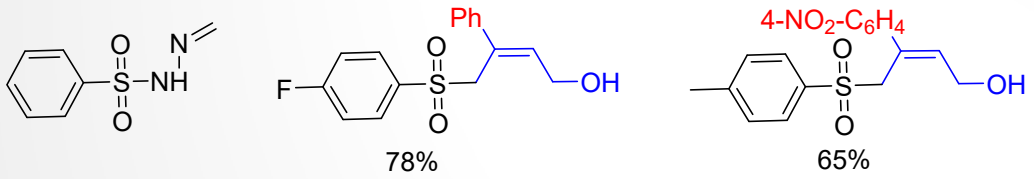
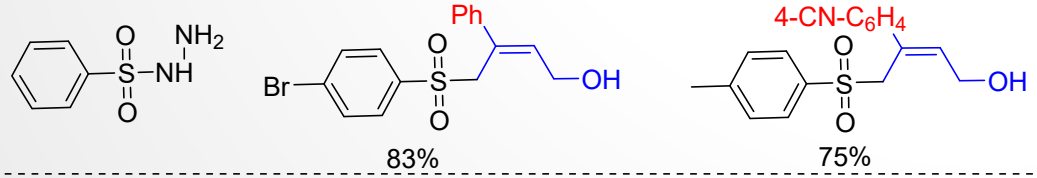


Nu:

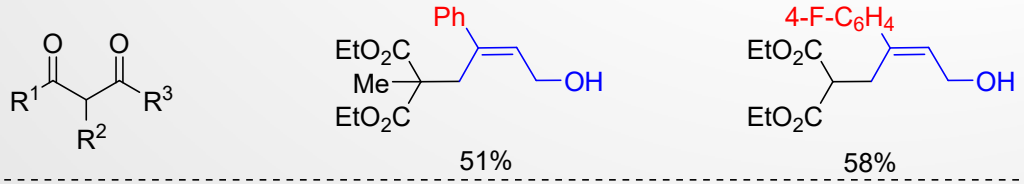
$Pd(PPh_3)_4$ (5.0 mol%), K_2CO_3 (3.0 equiv), Dioxane, 80 °C



$Pd(PPh_3)_4$ (5.0 mol%), K_2CO_3 (3.0 equiv), Dioxane, 80 °C



$Pd(PPh_3)_4$ (5.0 mol%), K_2CO_3 (3.0 equiv), THF, 80 °C

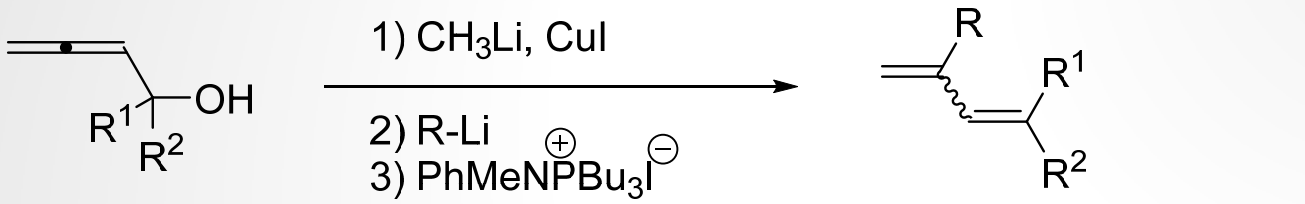


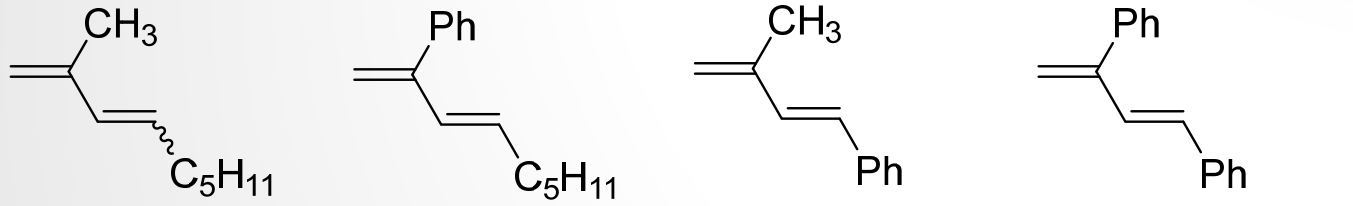
Hou, Y.; Shen, Q.; Zhu, L.; Han, Y.; Zhao, Y.; Qin, M.; Gong, P. *RSC Adv*. **2017**, *7*, 50372

Hou, Y.; Shen, Q.; Li, Z.; Chen, S.; Zhao, Y.; Qin, M.; Gong, P. *Adv. Synth. Catal*. **2018**, *360*, 631

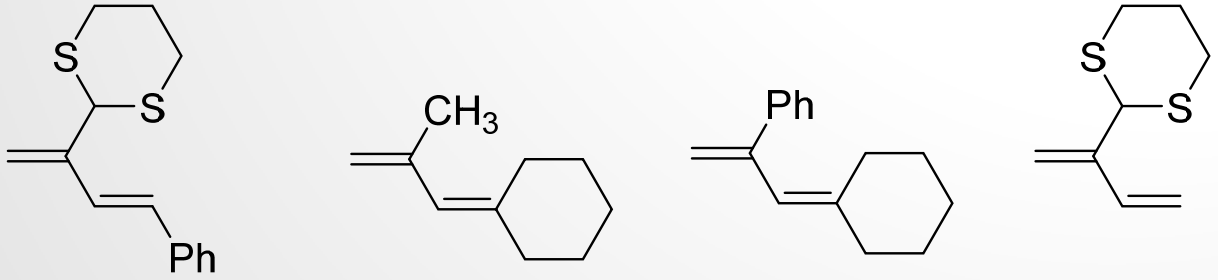
Hu, G.; Wang, J.; Li, Z.; Liu, Y.; Gong, P. *New J. Chem*. **2018**, *42*, 1736

Coupling reactions of 2,3-butadien-1-ol





55% (*E*/*Z* = 1/1) 45% (*E*/*Z* ≥ 20/1) 53% (*E*/*Z* ≥ 20/1) 31% (*E*/*Z* ≥ 20/1)



21% (*E*/*Z* ≥ 20/1) 40% 41% 20%

Fan, C.; Cazes, B. *Tetrahedron. Letters*, **1988**, *29*, 1701

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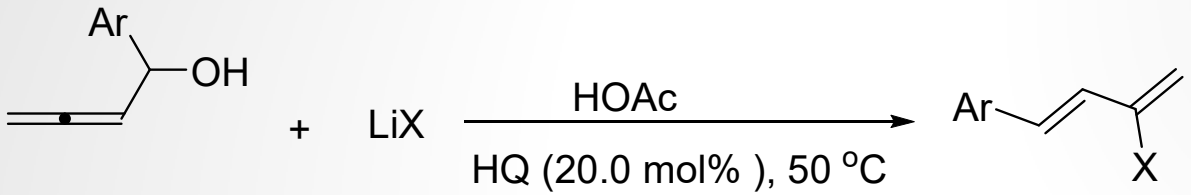
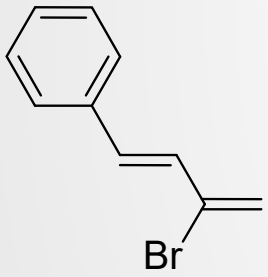
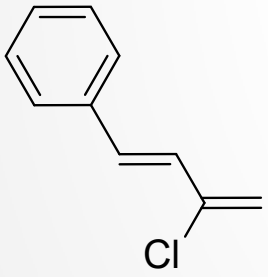
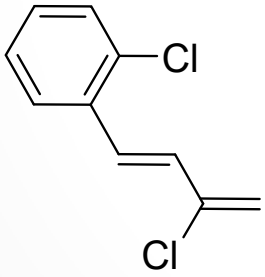




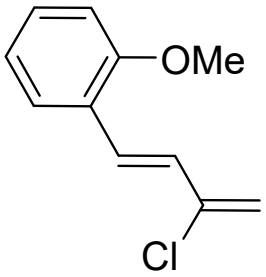
76%



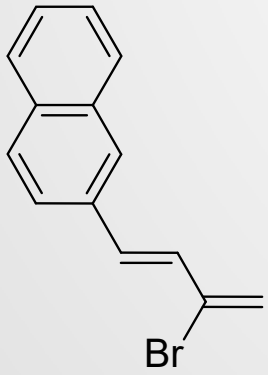
60%



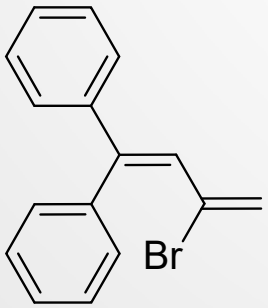
60%



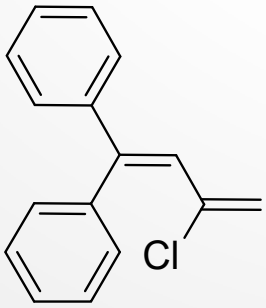
53%



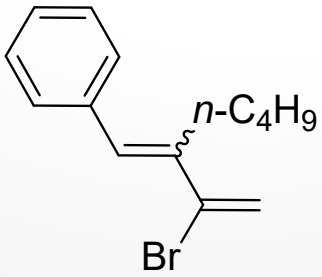
81%



90%



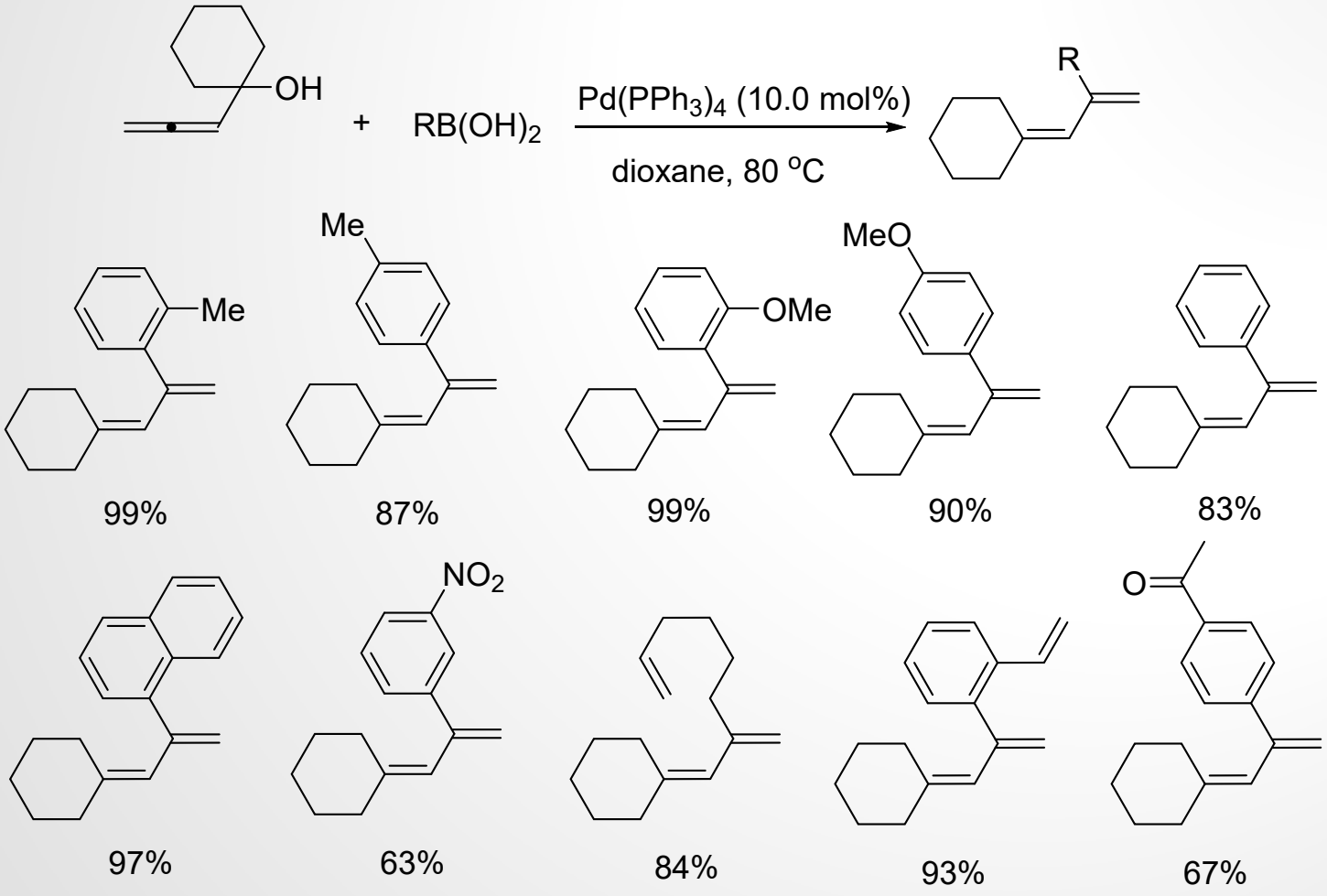
85%



87% (*Z*/*E* = 7/5)

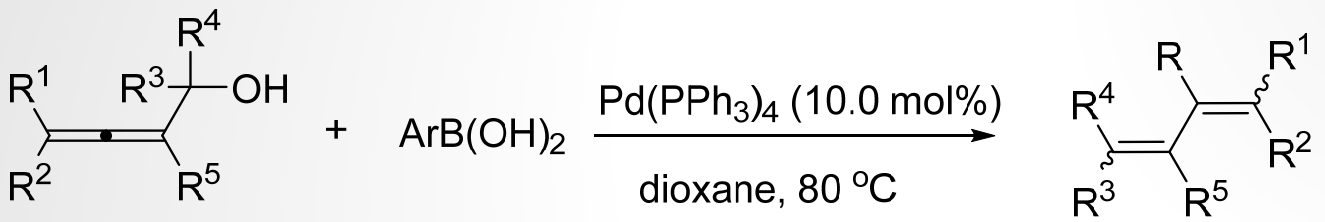
Wang, G.; Ma, S. *Tetrahedron. Lett.* **2002**, *43*, 5723

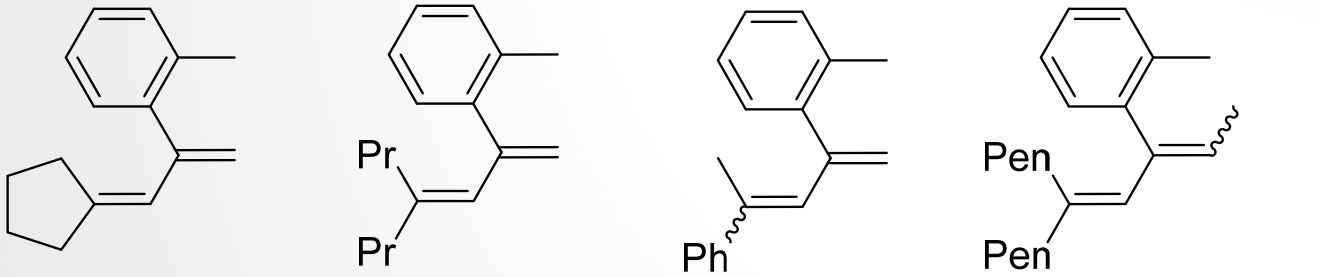
Coupling reactions of 2,3-butadien-1-ol



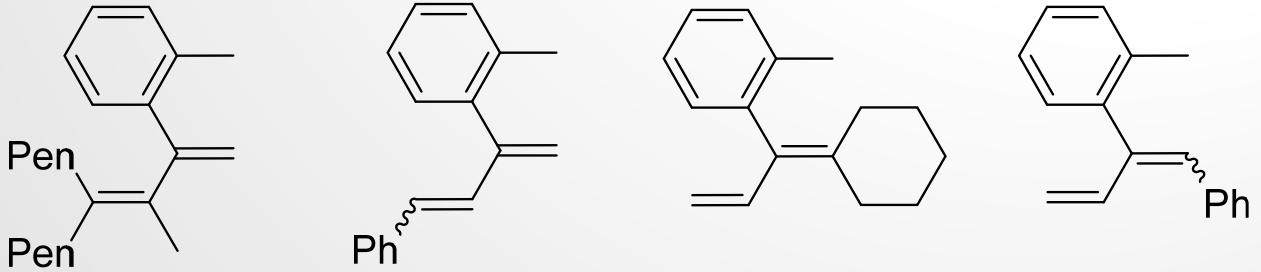
Masahiro, Y.; Takahiro, G.; Masataka, I. *Chem. Commun*. **2004**, 1124

Coupling reactions of 2,3-butadien-1-ol





95% 97% 98% (*E*/*Z* = 1.5/1) 99% (*E*/*Z* = 9/1)



91% 96% (*E*/*Z* = 16/1) 91% 97% (*E*/*Z* > 20/1)

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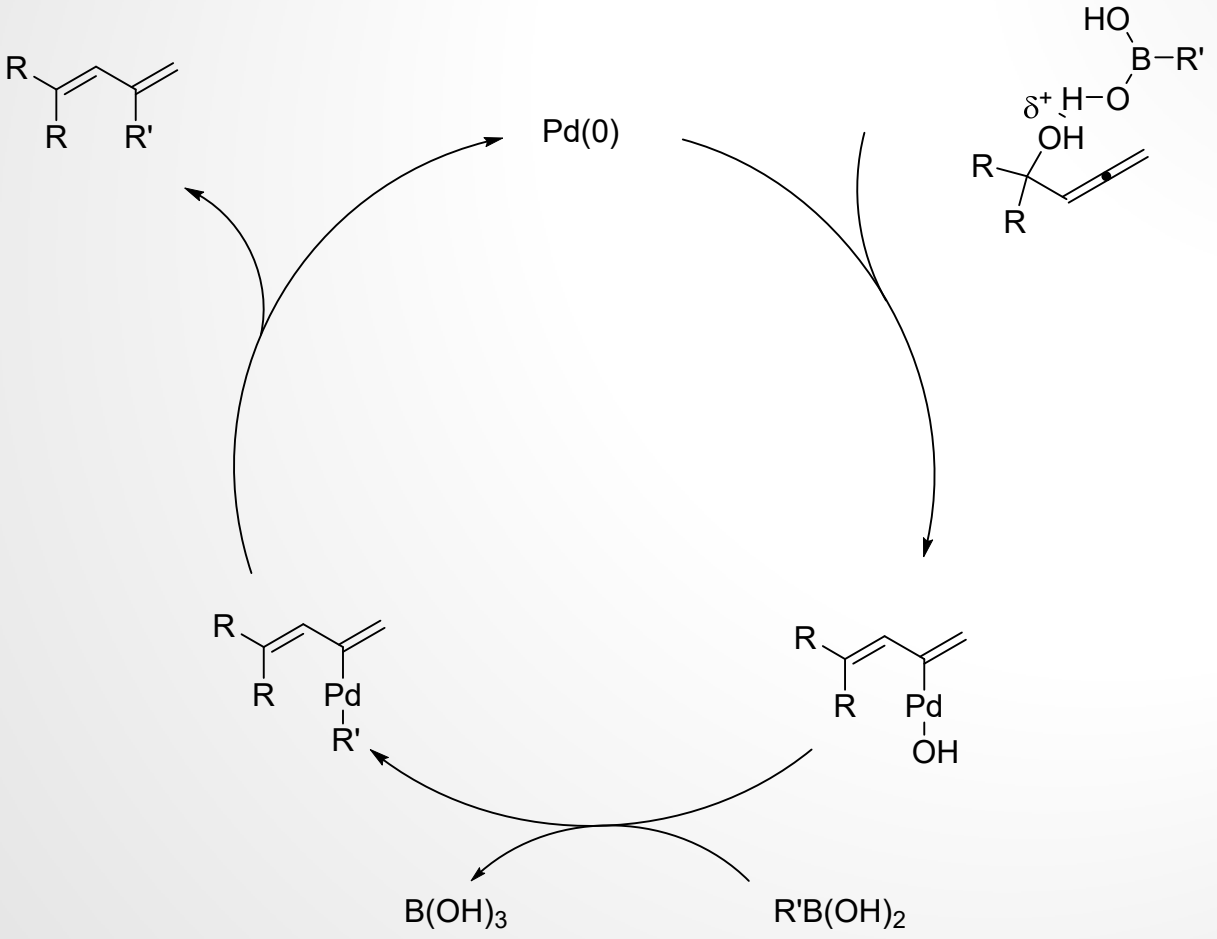

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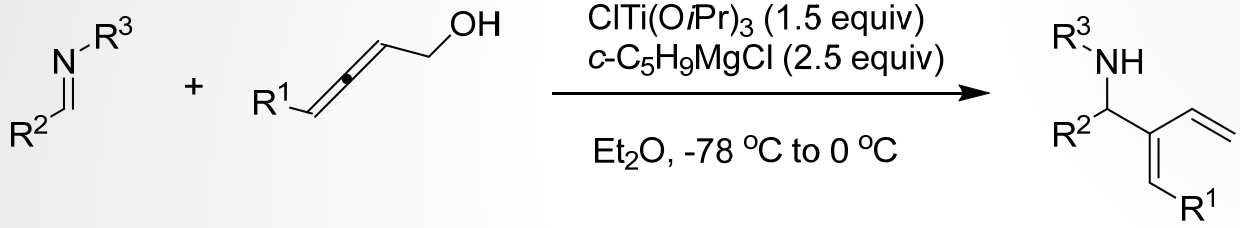
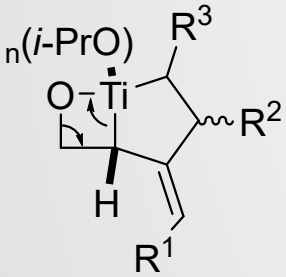
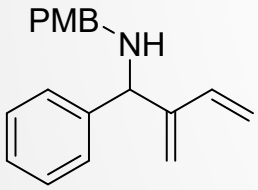
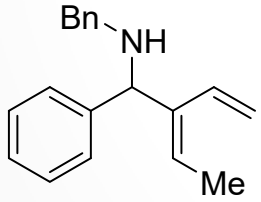




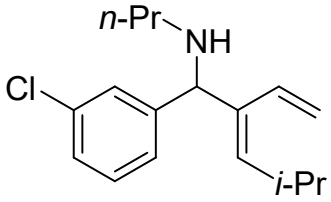
directed carbometalation
then *syn* elimination



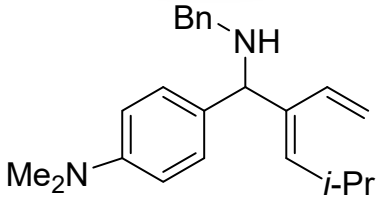
57%



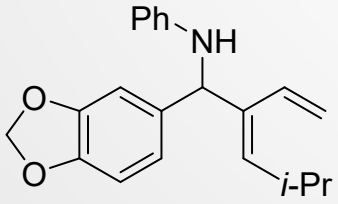
50% (*E*/*Z* = 4/1)



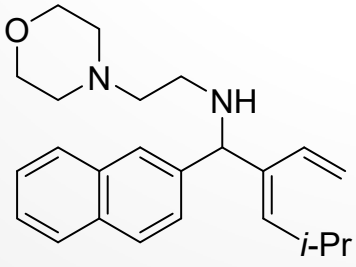
63% (*E*/*Z* ≥ 20/1)



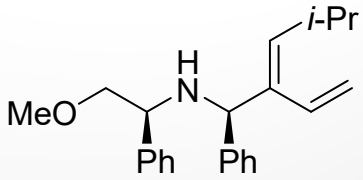
54% (*E*/*Z* ≥20/1)



57% (*E*/*Z* ≥20/1)



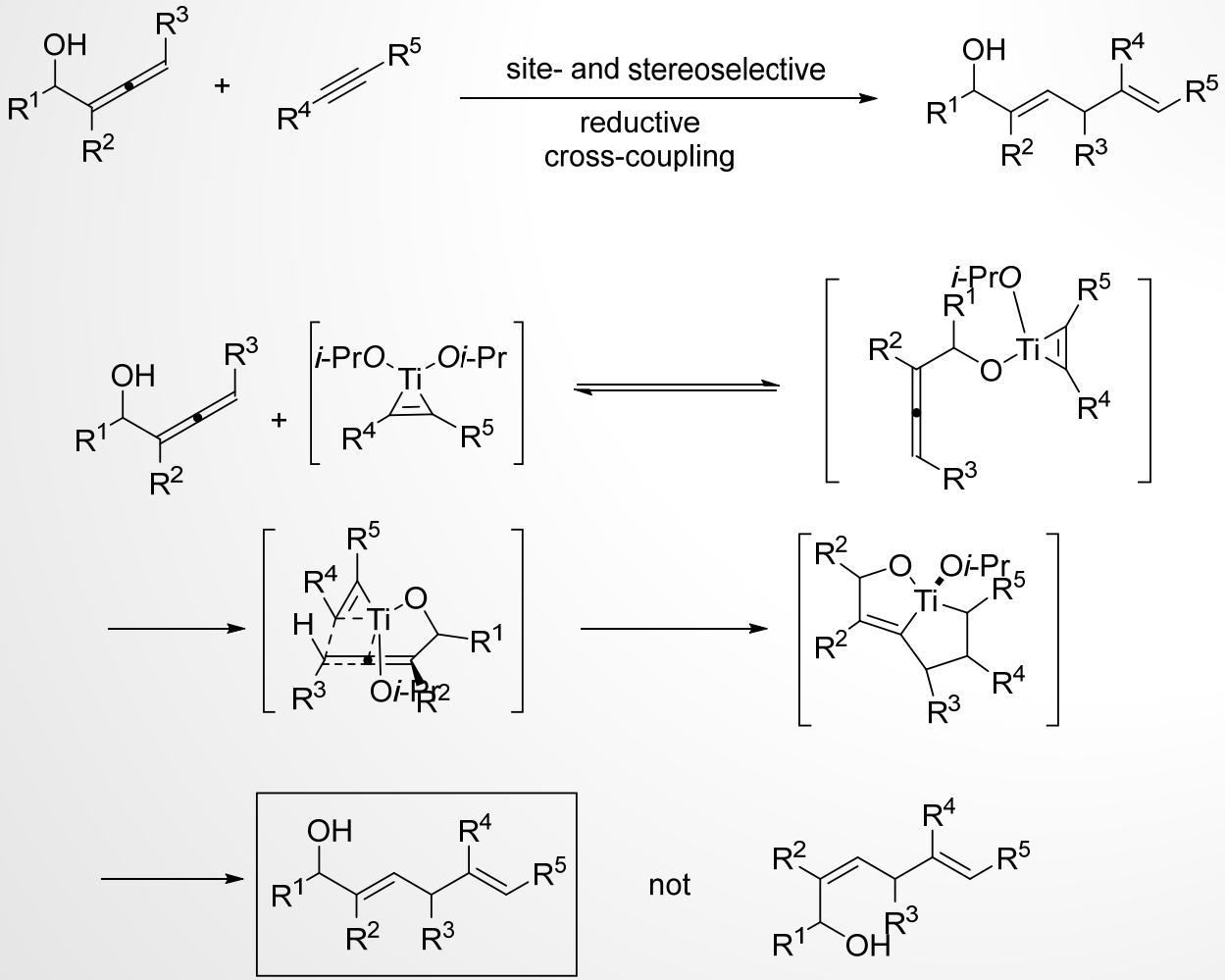
51% (*E*/*Z* ≥20/1)



78% (*E*/*Z* ≥20/1)

McLaughlin, M.; Shimp, H. L.; Navarro, R.; Micalizio, G.C. *Synlett.* **2008**, *5*, 735

Coupling reactions of 2,3-butadien-1-ol



Shimp, H. L.; Micalizio, G. C. *Chem. Commun*. **2007**, 4531

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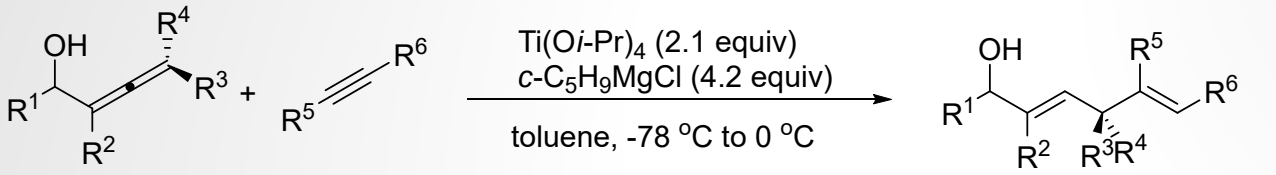

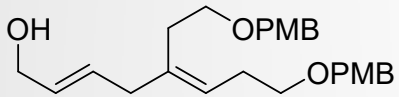

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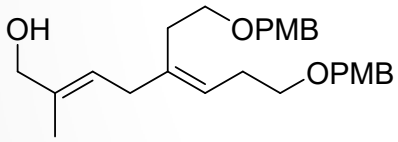
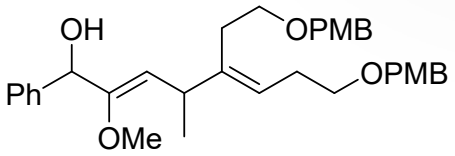
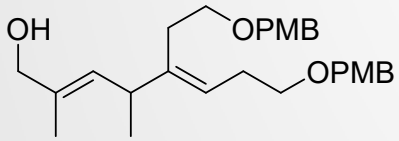


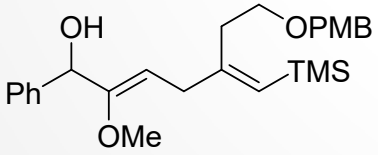
74%



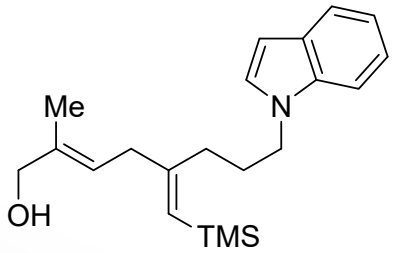
87%



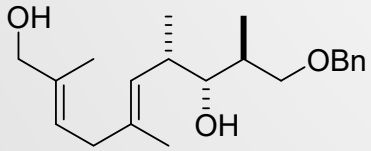
53%



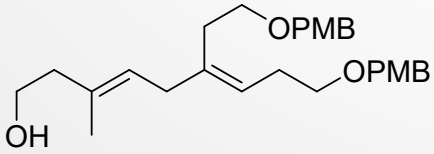
66% (rs = 4/1)



48% (rs = 4/1)



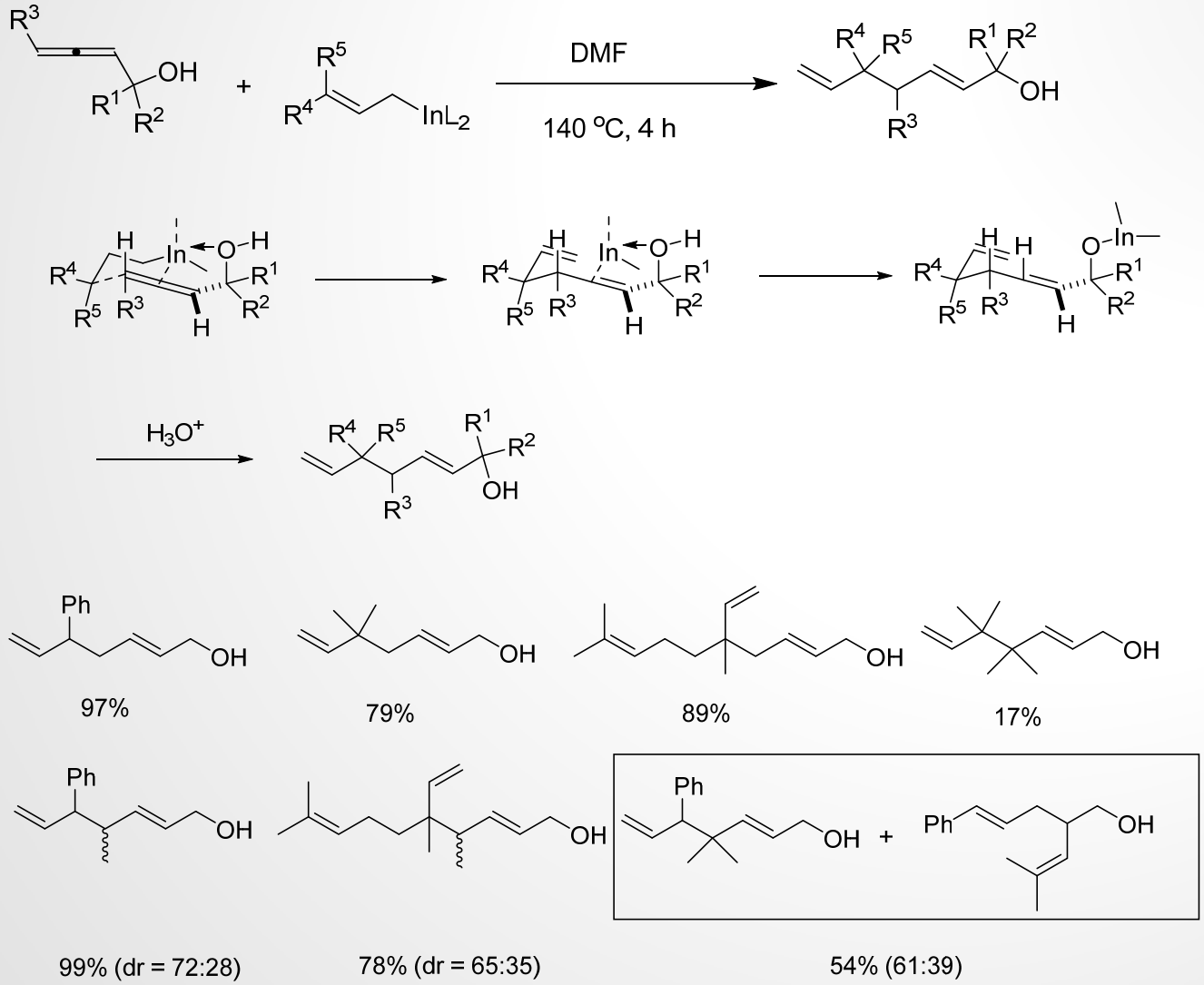
62% (rr = 4/1)



64% (*E*/*Z* = 64/1)

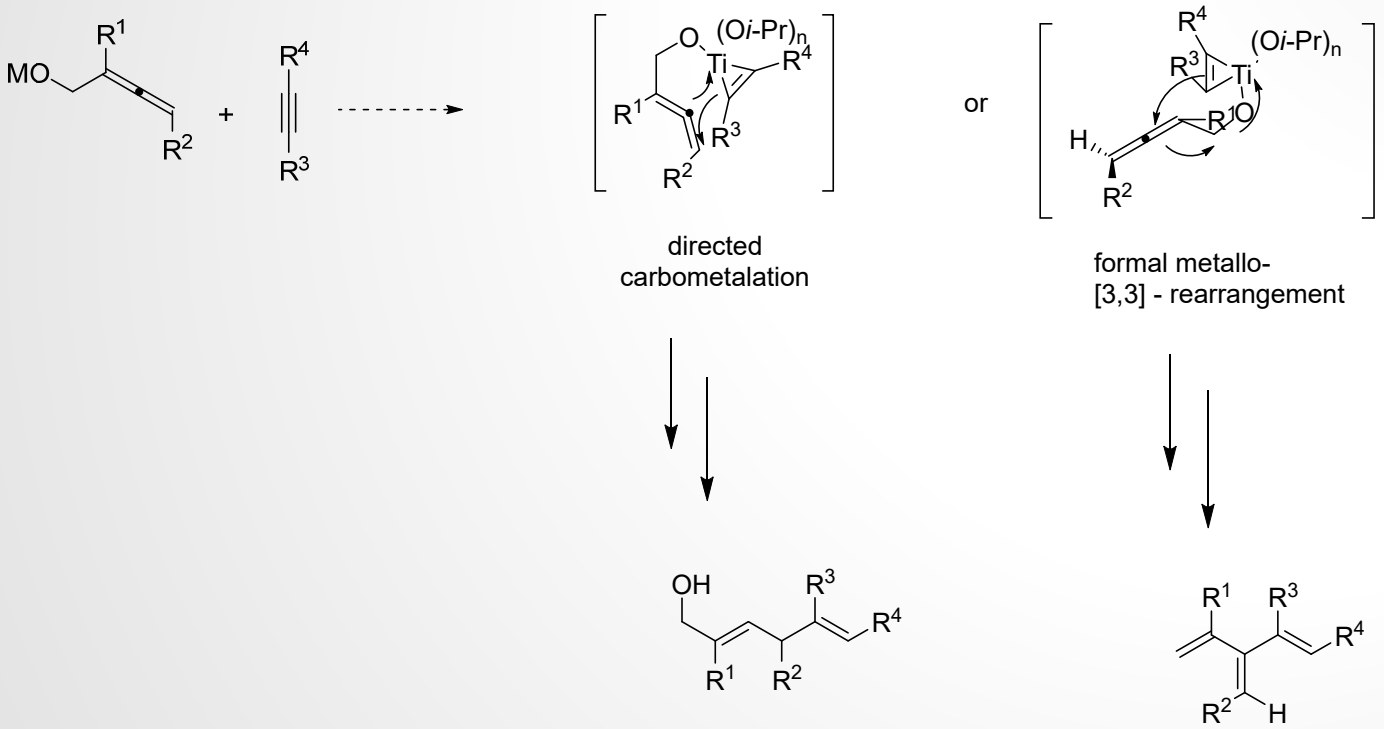
Shimp, H. L.; Micalizio, G. C. *Chem. Commun*. **2007**, 4531

Coupling reactions of 2,3-butadien-1-ol



Araki, S.; Usui, H.; Kato, M.; Butsugan, Y. *J. Am. Chem. Soc.* **1996**, *118*, 4699

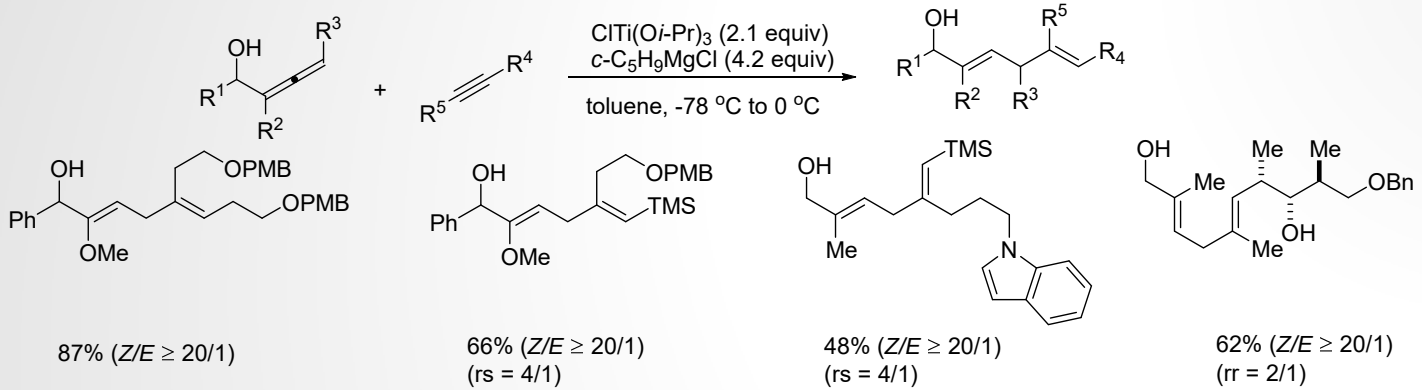
Coupling reactions of 2,3-butadien-1-ol



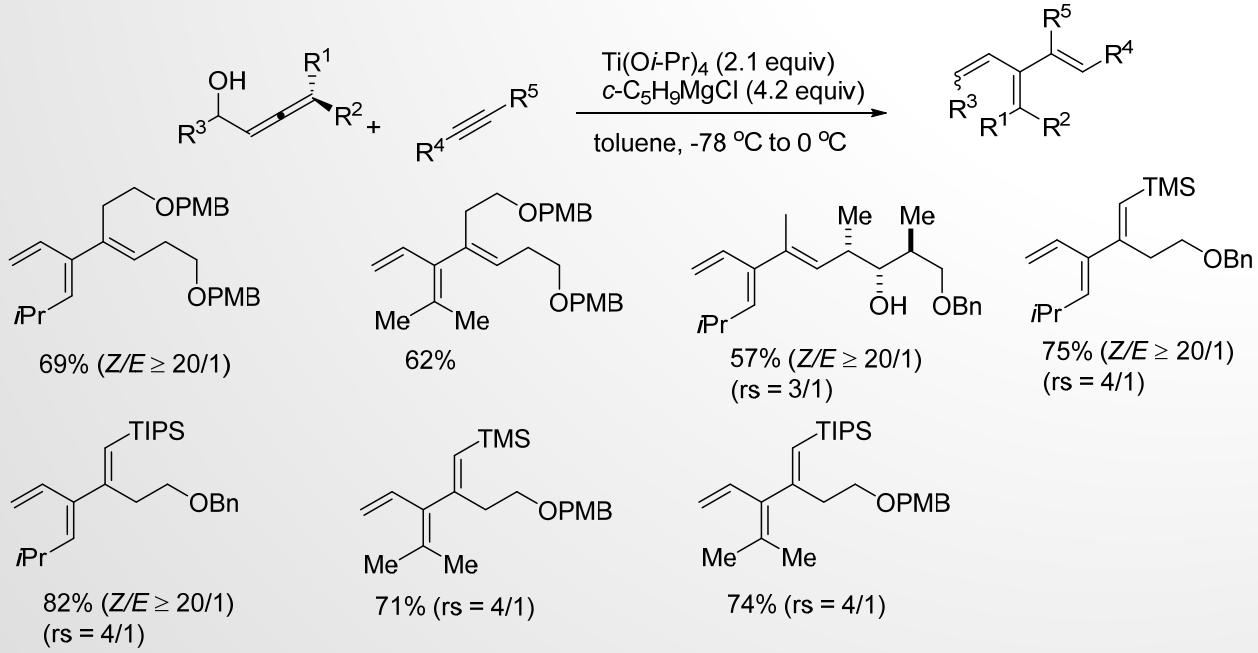
Shimp, H. L.; Hare, A.; McLaughlin, M.; Micalizio, G. C. *Tetrahedron.* **2008**, *64*, 6831.

Coupling reactions of 2,3-butadien-1-ol

alkoxide-directed cross-coupling

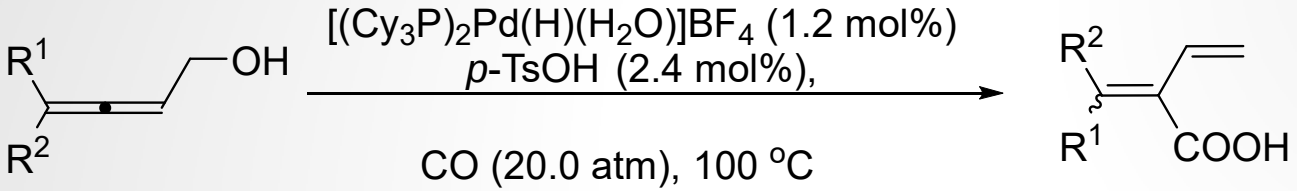


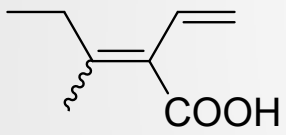
titanium-mediated cross-coupling



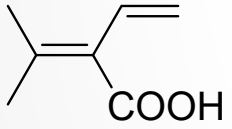
Shimp, H. L.; Hare, A.; McLaughlin, M.; Micalizio, G. C. *Tetrahedron.* **2008**, *64*, 6831.

Coupling reactions of 2,3-butadien-1-ol

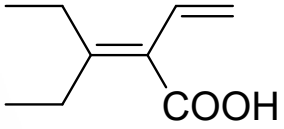




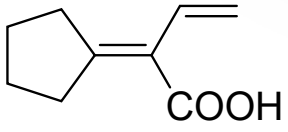
64%



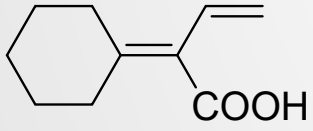
59%



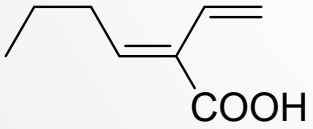
55%



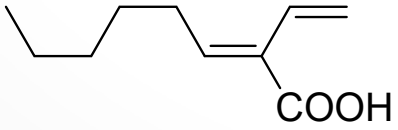
43%



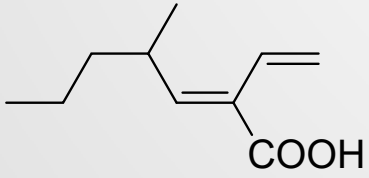
58%



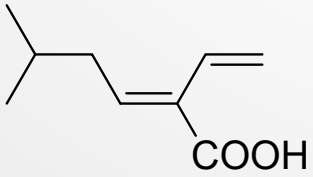
61%



74%



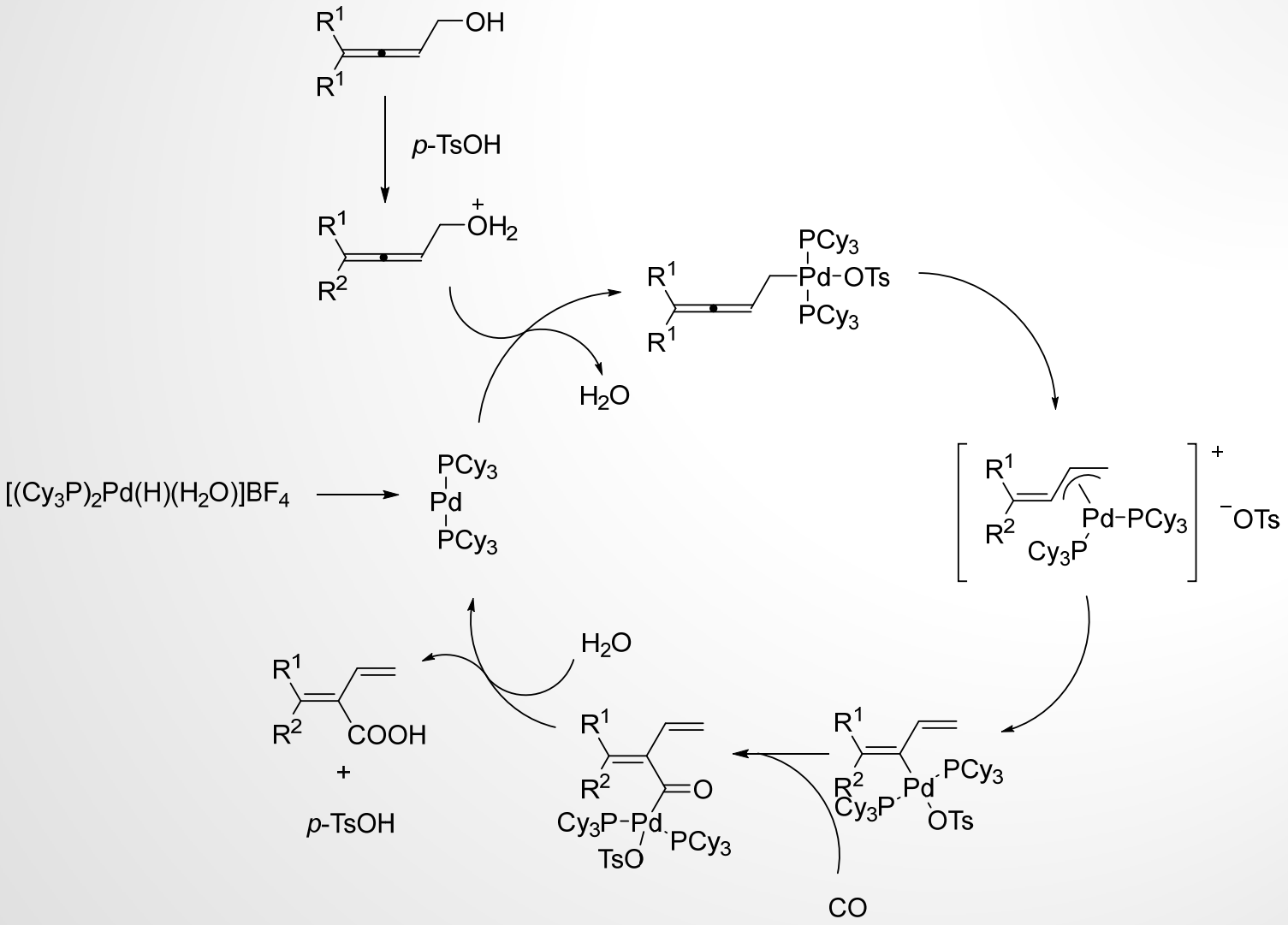
72%



64%

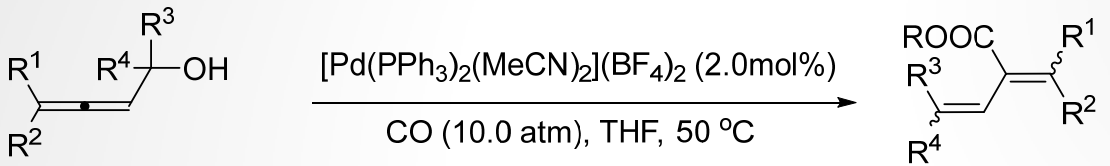
Marcelo, E.; Howard, A. *J. Org. Chem.* **1994**,*59*, 1956

Coupling reactions of 2,3-butadien-1-ol



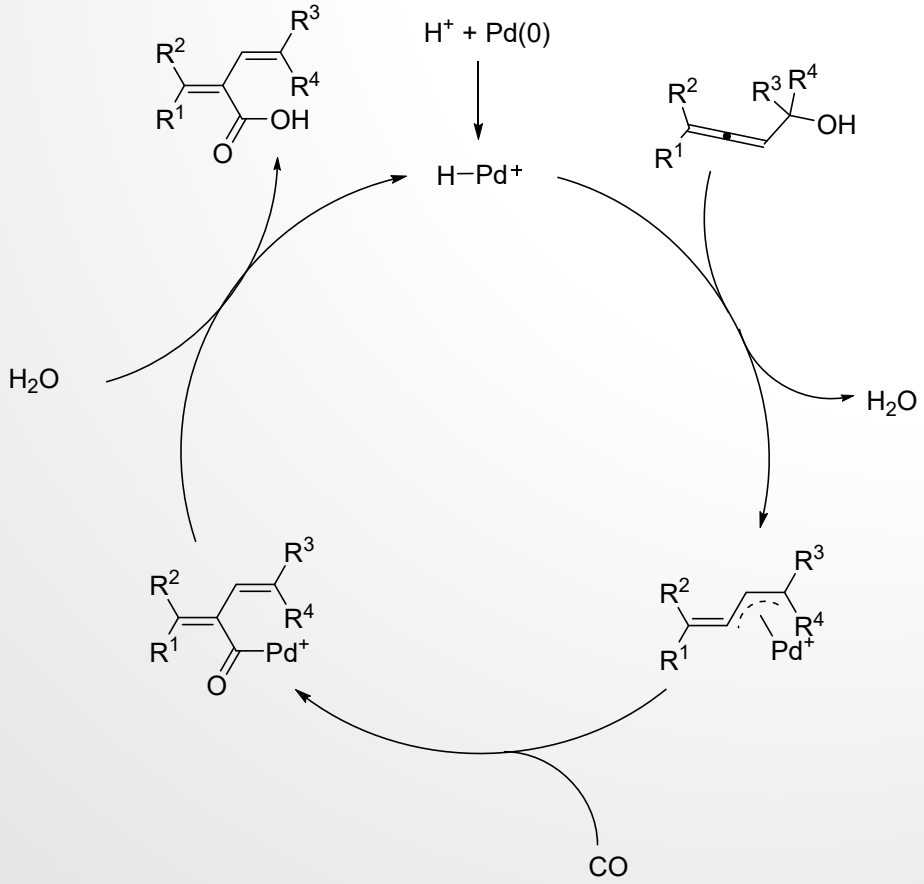
Marcelo, E.; Howard, A. *J. Org. Chem.* **1994**,*59*, 1956

Coupling reactions of 2,3-butadien-1-ol



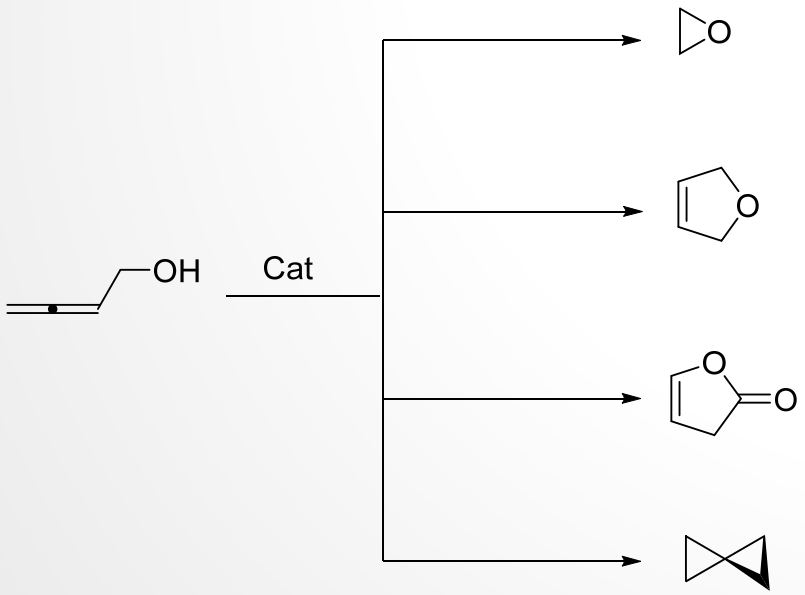
R^1,R^2, R^3, R^4 = H, alkyl, aryl
Solvent: THF, R = H
MeOH, R = Me

10 examples
yield up to 60%

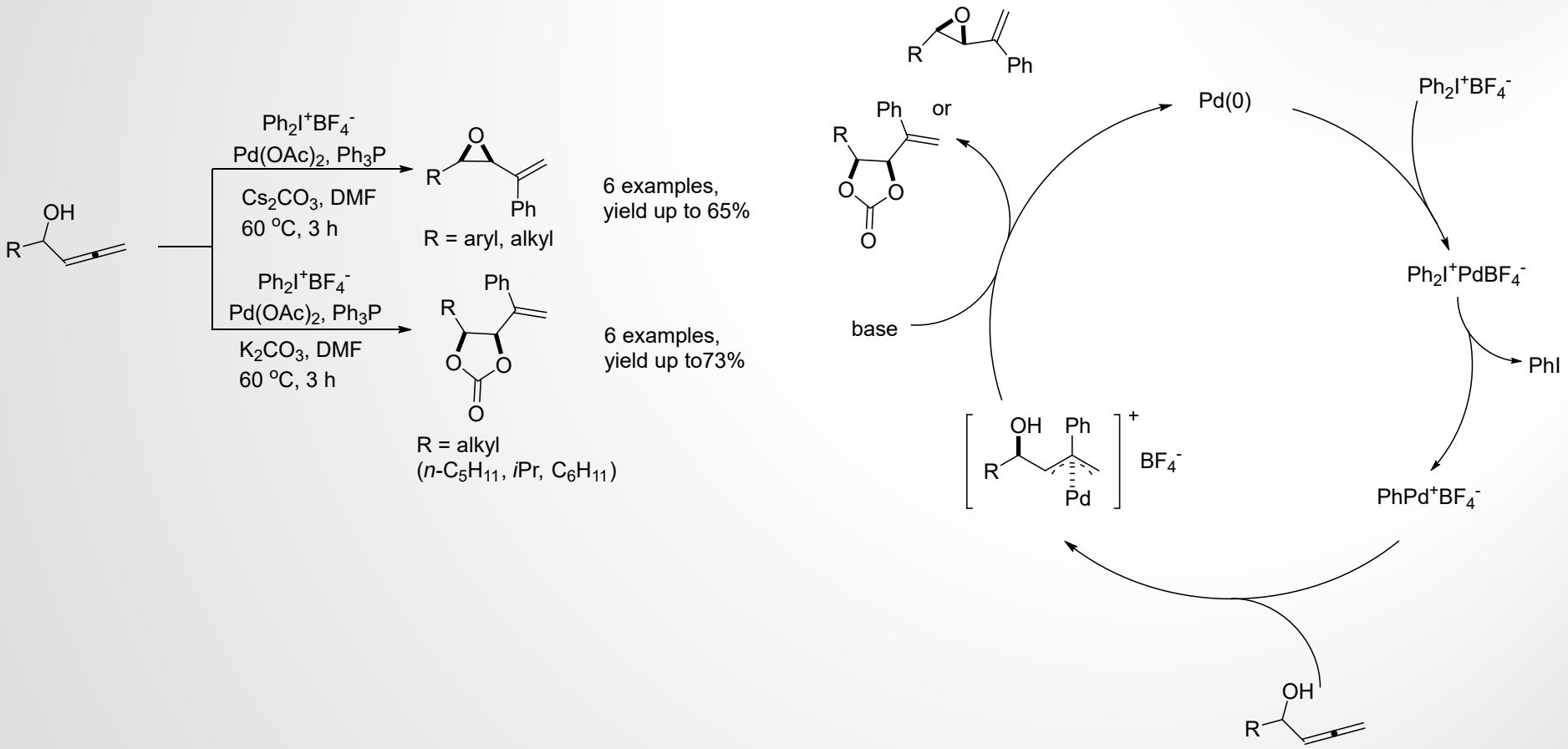


Uemura, K.; Inoue, Y. *Appl. Organometal. Chem.* **2000**, *14*, 8.

Cyclization reactions of 2,3-butadien-1-ol

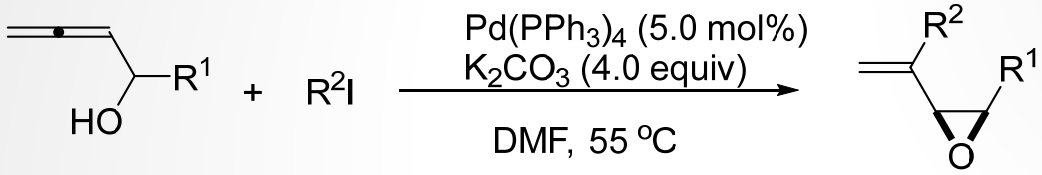


Cyclization reactions of 2,3-butadien-1-ol

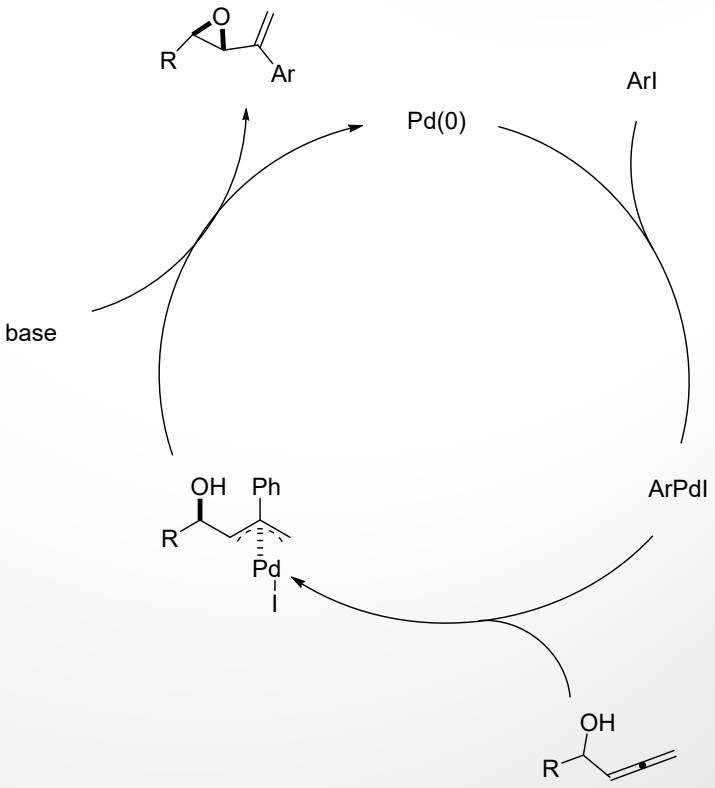


Kang, S.; Yamaguchi, T.; Pyun, S.; Lee, Y.; Baik, T. *Tetrahedron. Letters.* **1998,** *39*, 2127

Cyclization reactions of 2,3-butadien-1-ol

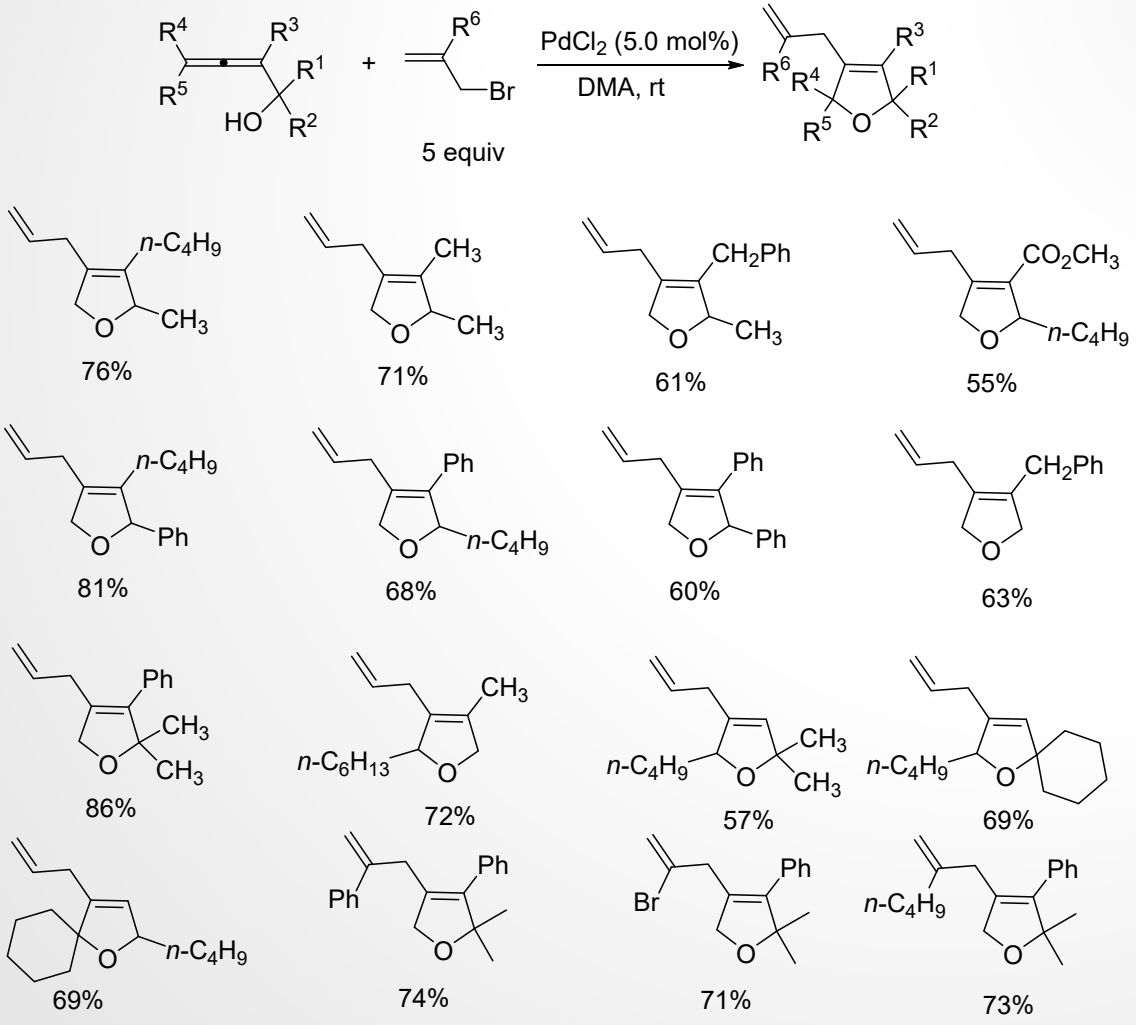


entry	R^1	R^2	Yield, %	dr
1	*n*-C_4H_9	Ph	71	96/4
2	*n*-C_4H_9	*p*-MeO-C_6H_4	71	97/3
3	*n*-C_4H_9	*E*-2-Ph-ethenyl	65	92/8
4	*n*-C_4H_9	Naphthyl	76	96/4
5	Ph	*p*-Me-C_6H_4	55	95/5
6	*n*-C_7H_{15}	*p*-MeO-C_6H_4	81	99/1
7	*n*-C_8H_{17}	*p*-Br-C_6H_4	46	99/1
8	*n*-C_8H_{17} (98% ee)	*E*-1-hexenyl	52	98% ee
9	*n*-C_8H_{17} (95% ee)	*p*-Me-C_6H_4	85	95% ee



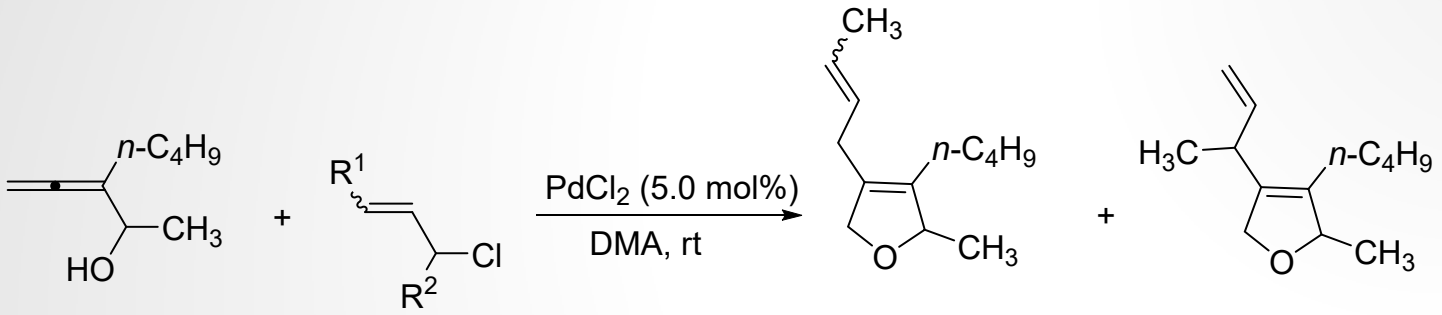
Zhao, S.; Ma, S. *J. Am. Chem. Soc.* **1999**, *121*, 7943

Cyclization reactions of 2,3-butadien-1-ol



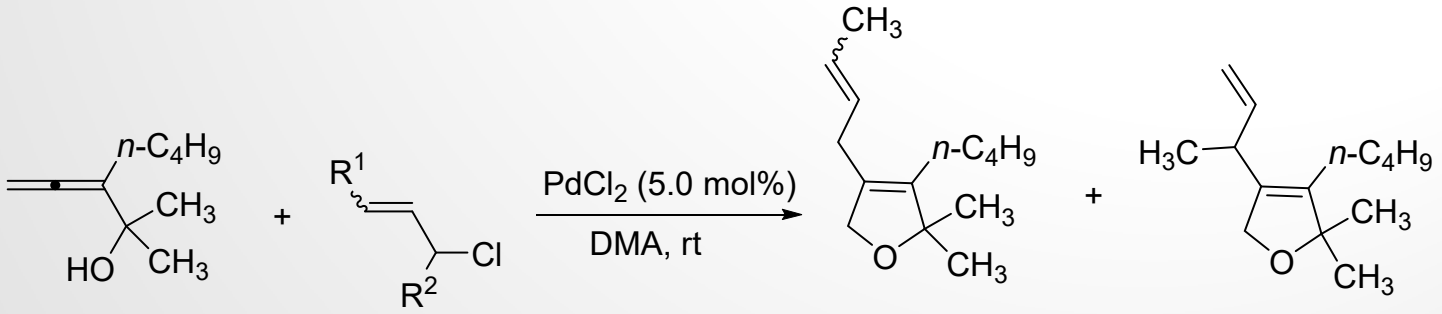
Gao, W.; Ma, S. *J. Org. Chem.* **2002**, *67*, 6104

Cyclization reactions of 2,3-butadien-1-ol



1aa *(E+Z)* **1ab**

R^1 = H, R^2 = CH_3,	9 h	63% (**1aa**:**1ab** = 98:2)
	3 d	50% (**1aa**:**1ab** = 98:2)
R^1 = CH_3, R^2 = H,	21 h	21% (**1aa**:**1ab** = 14:86)
	7 d	22% (**1aa**:**1ab** = 13:87)

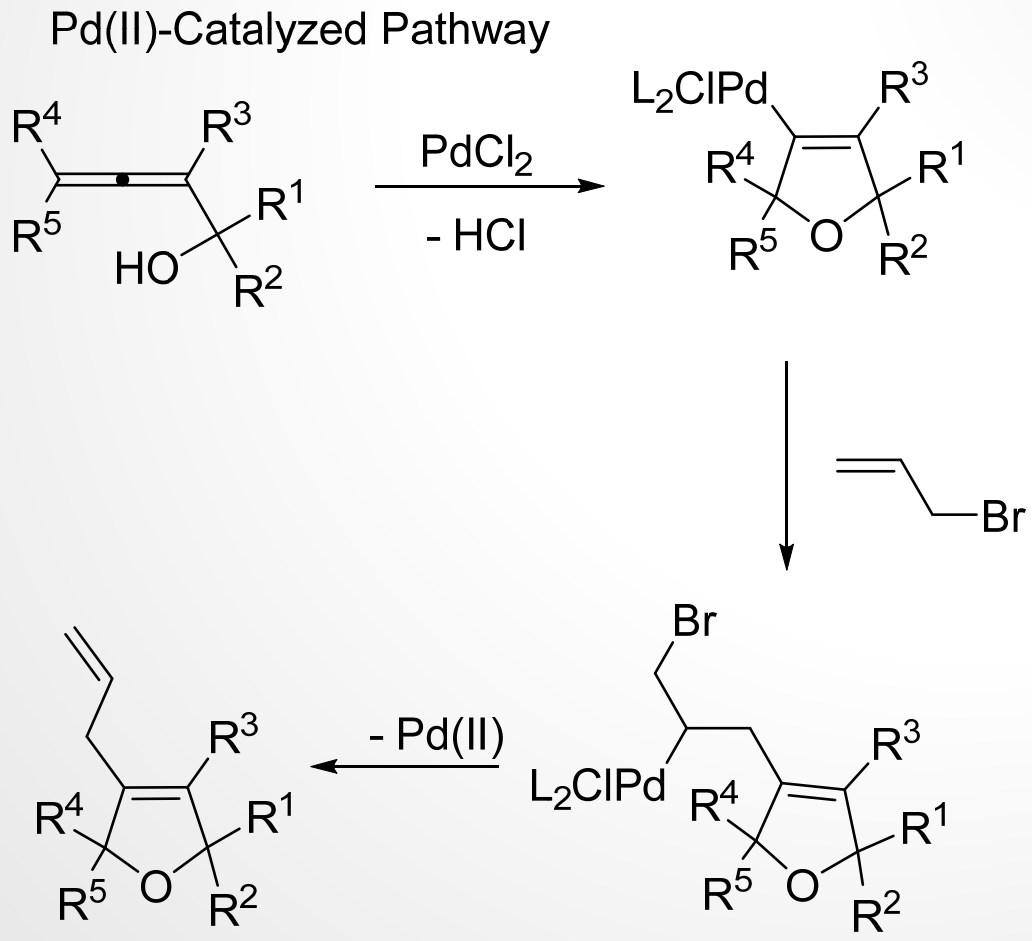


2aa *(E+Z)* **2ab**

R^1 = H, R^2 = CH_3,	14 h	69% (**2aa**:**2ab** = 89:11)
R^1 = CH_3, R^2 = H,	40 h	34% (**2aa**:**2ab** = 15:85)

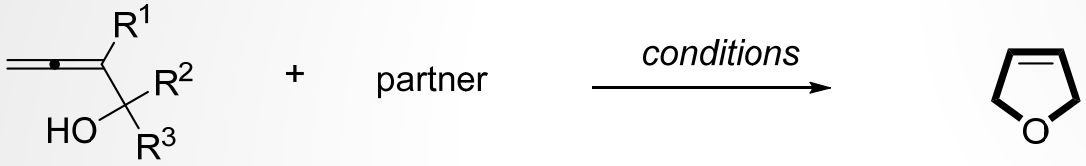
Gao, W.; Ma, S. *J. Org. Chem.* **2002**, *67*, 6104

Cyclization reactions of 2,3-butadien-1-ol

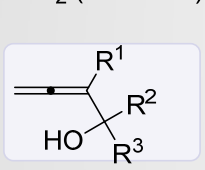


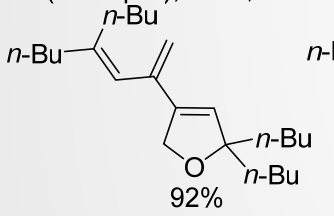
Gao, W.; Ma, S. *J. Org. Chem.* **2002**, *67*, 6104

Cyclization reactions of 2,3-butadien-1-ol

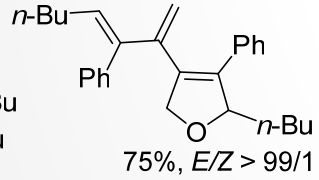


$PdCl_2$ (5.0 mol%), NaI (0.5 equiv), DMA, 80 °C



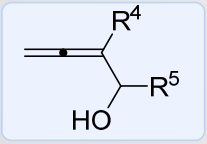


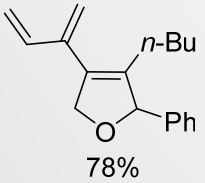
92%



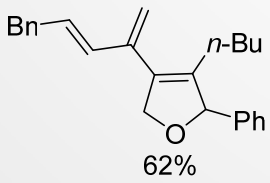
75%, *E*/*Z* > 99/1

PdI_2 (5.0 mol%), $BF_3{\bullet}Et_2O$ (1.0 equiv), DMSO, 80 °C

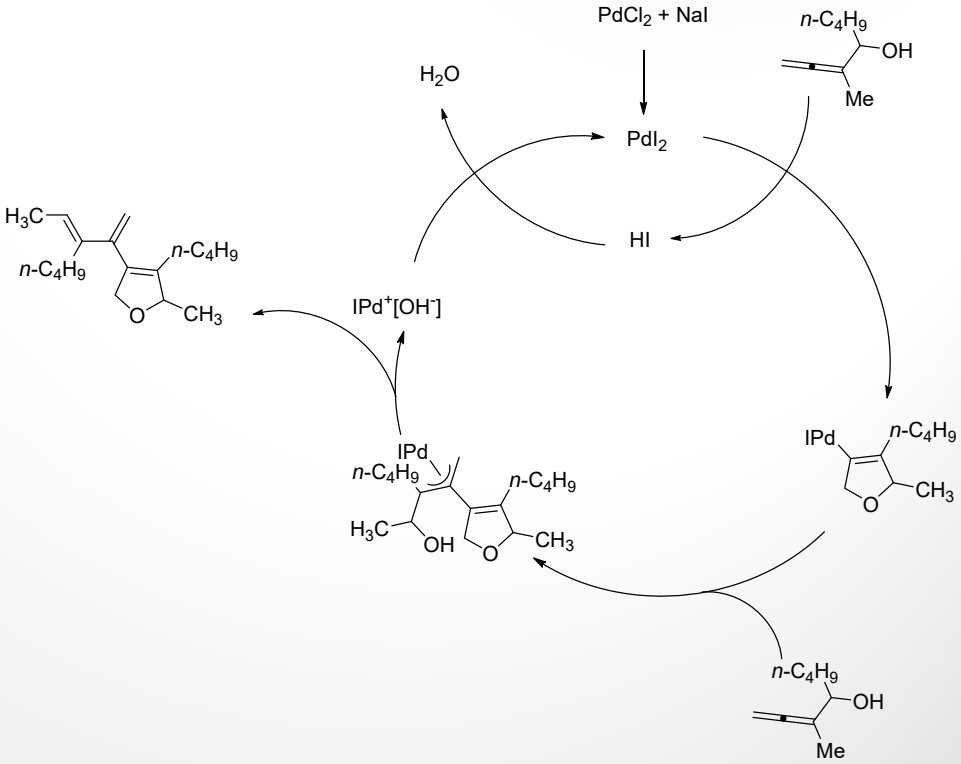




78%



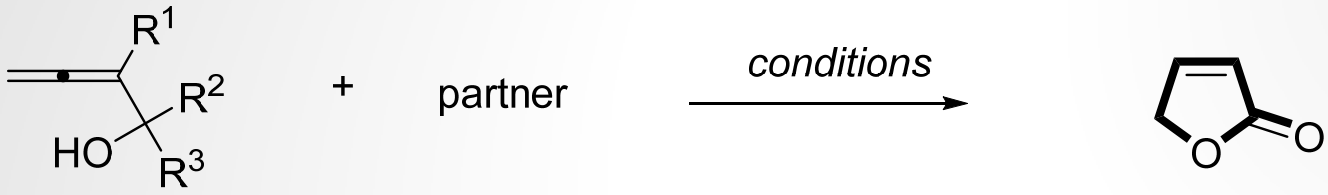
62%



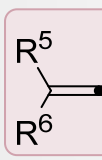
Deng, Y.; Yu, Y.; Ma, S. *J. Org. Chem.* **2008**, *73*, 585

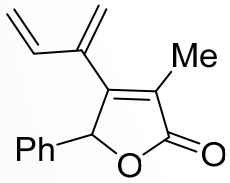
Deng, Y.; Li, J.; Ma, S**.** *Chem. Eur. J.* **2008**, *14*, 4263

Cyclization reactions of 2,3-butadien-1-ol

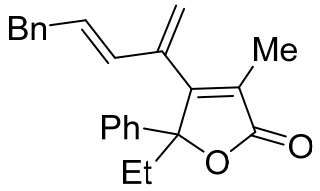


$PdCl_2$ (5.0 mol%), DMA, 80 °C





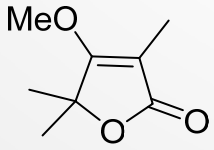
59%



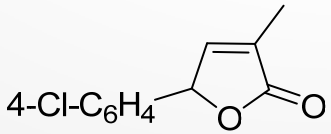
66%

$Ru_3(CO)_{12}$ (1.0 mol%), Et_3N (1.5 equiv), dioxane, 110 °C

CO (10 atm)



95%

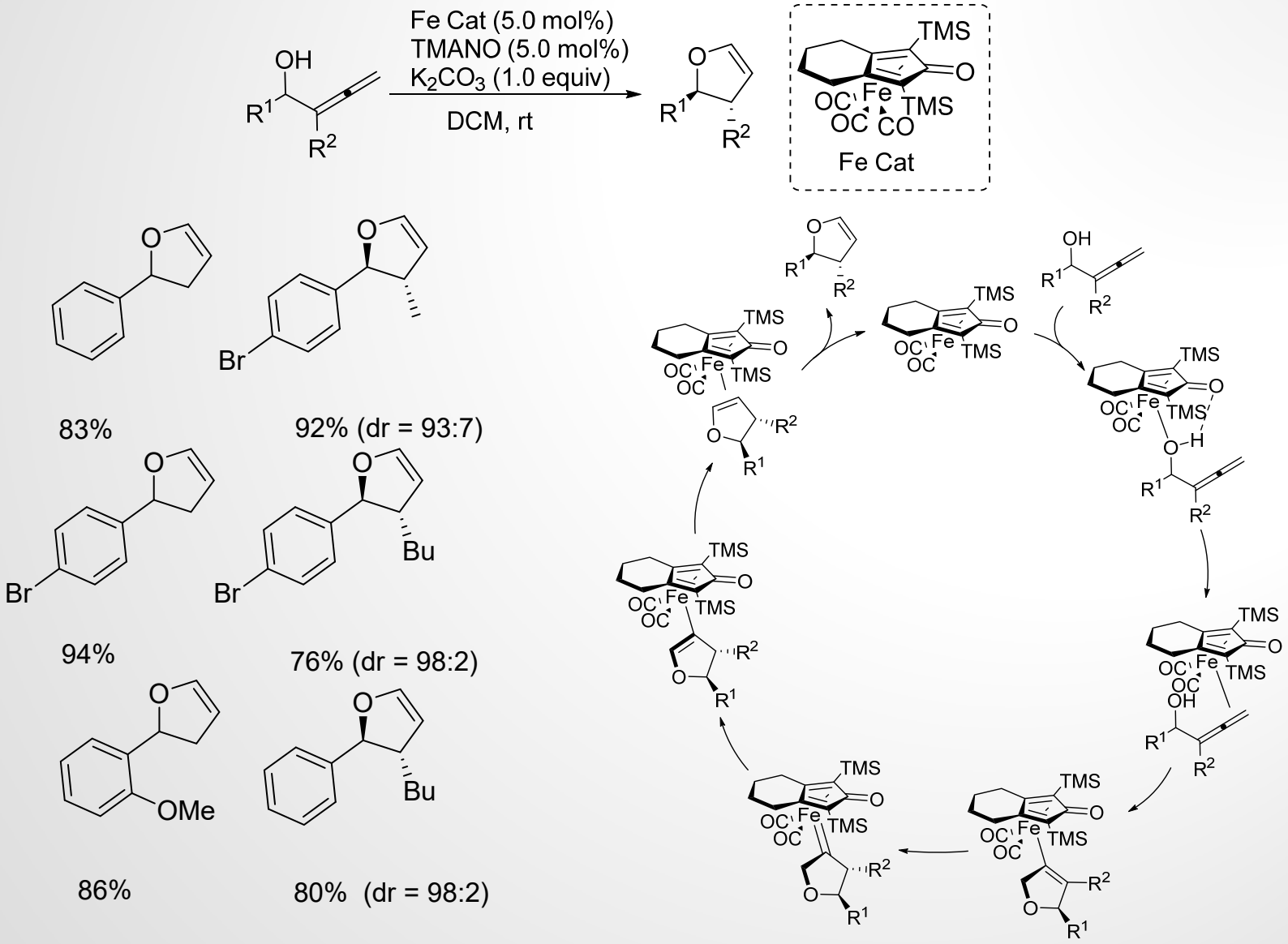


94%

Gu, Z.; Ma, S. *J. Am. Chem. Soc*. **2005**, *127*, 6182

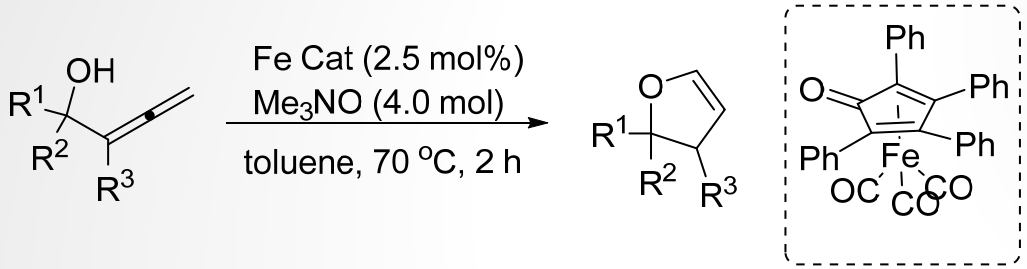
Yoneda, E.; Zhang, S.; Zhou, D.; Onitsuka, K.; Takahashi, J. S. *J. Org. Chem.* **2003**, *68*, 8571

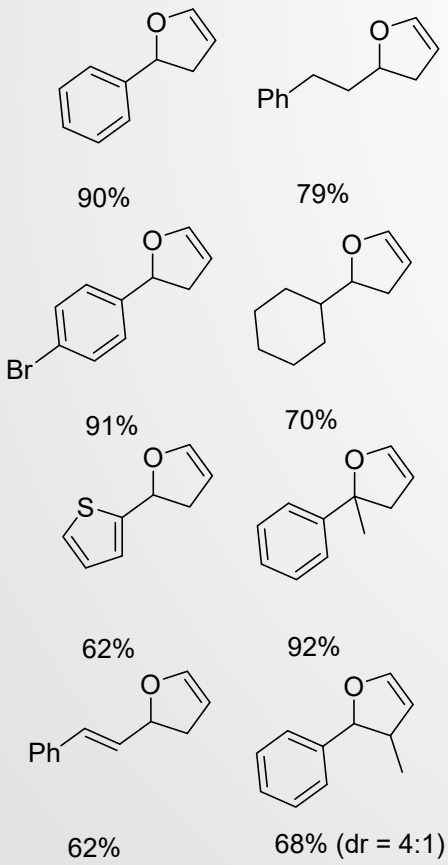
Cyclization reactions of 2,3-butadien-1-ol

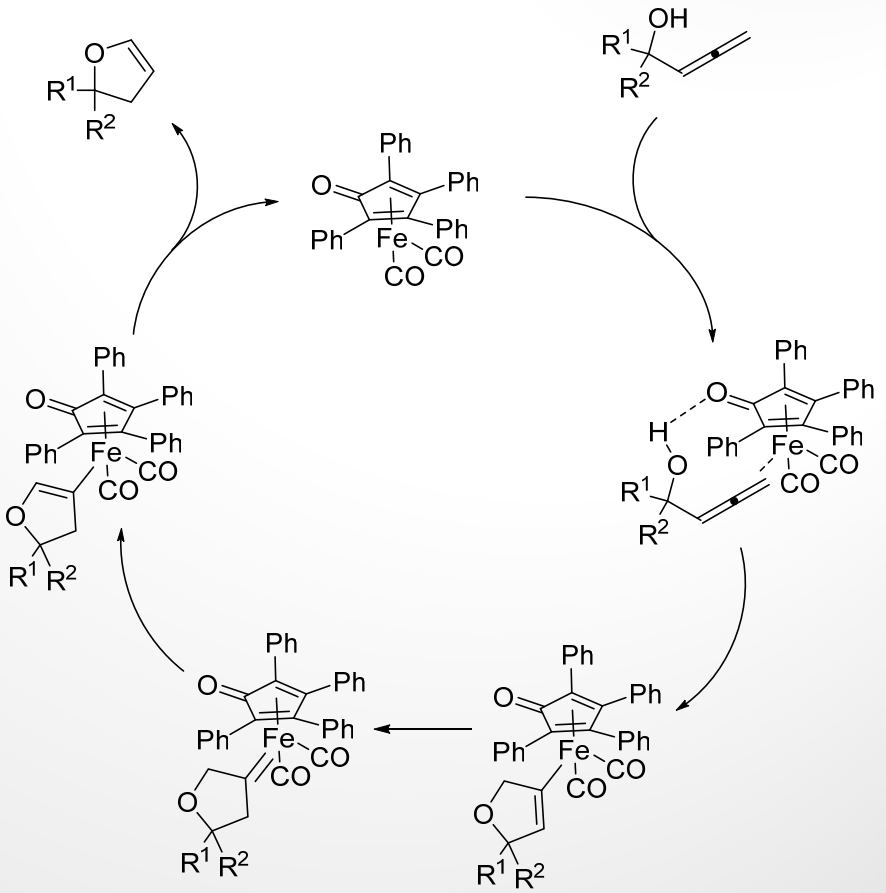


Guđmundsson, A.; Gustafson, K. P. J.; Mai, B. K.; Yang, B.; Himo, F.; Backvall. J. E. *ACS Catal*. **2018**, *8*, 12.

Cyclization reactions of 2,3-butadien-1-ol

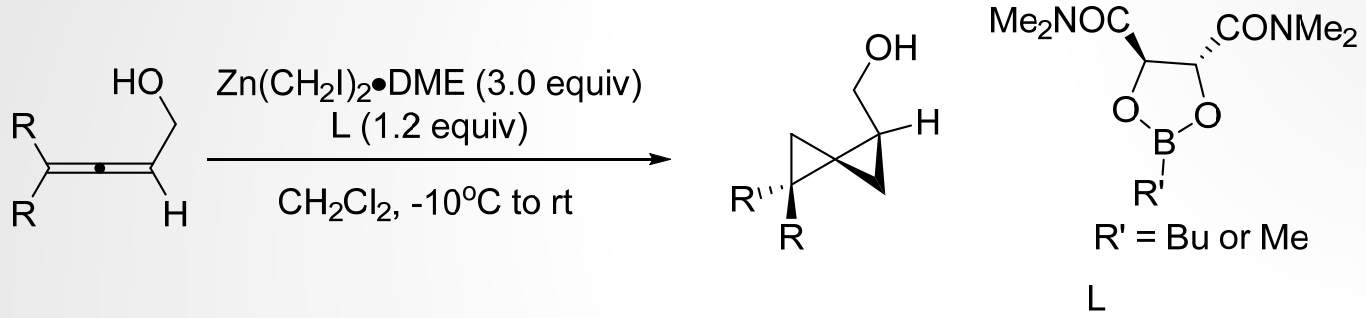


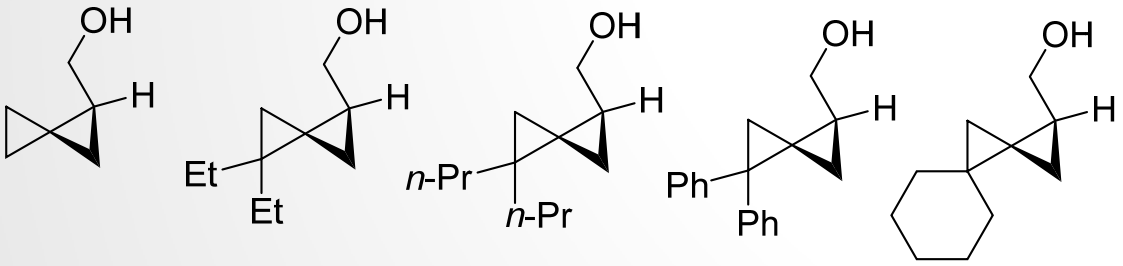




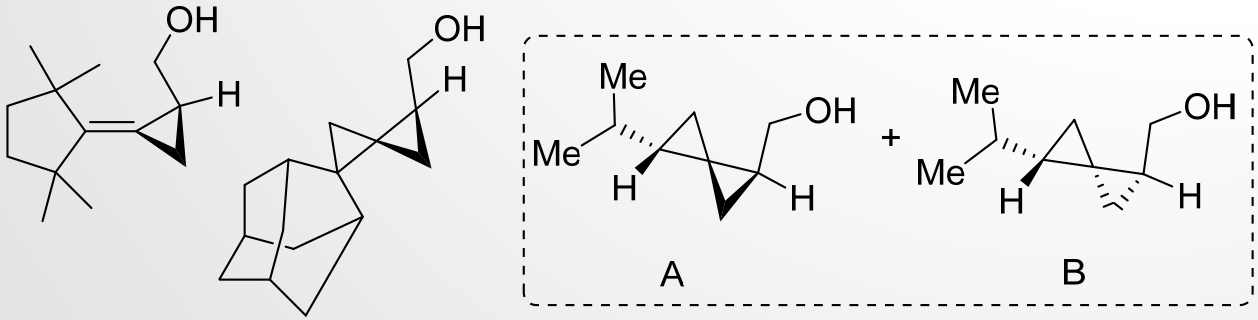
EI-Sepelgy, O.; Brzozowska, A.; Sklyaruk, J.; Jang, Y. K.; Zubar, V.; Rueping. M. *Org. Lett*. **2018**, *20*, 696.

Cyclization reactions of 2,3-butadien-1-ol





69% (86% ee) 70% (97% ee) 83% (94% ee) 7% (92% ee) 65% (96% ee)

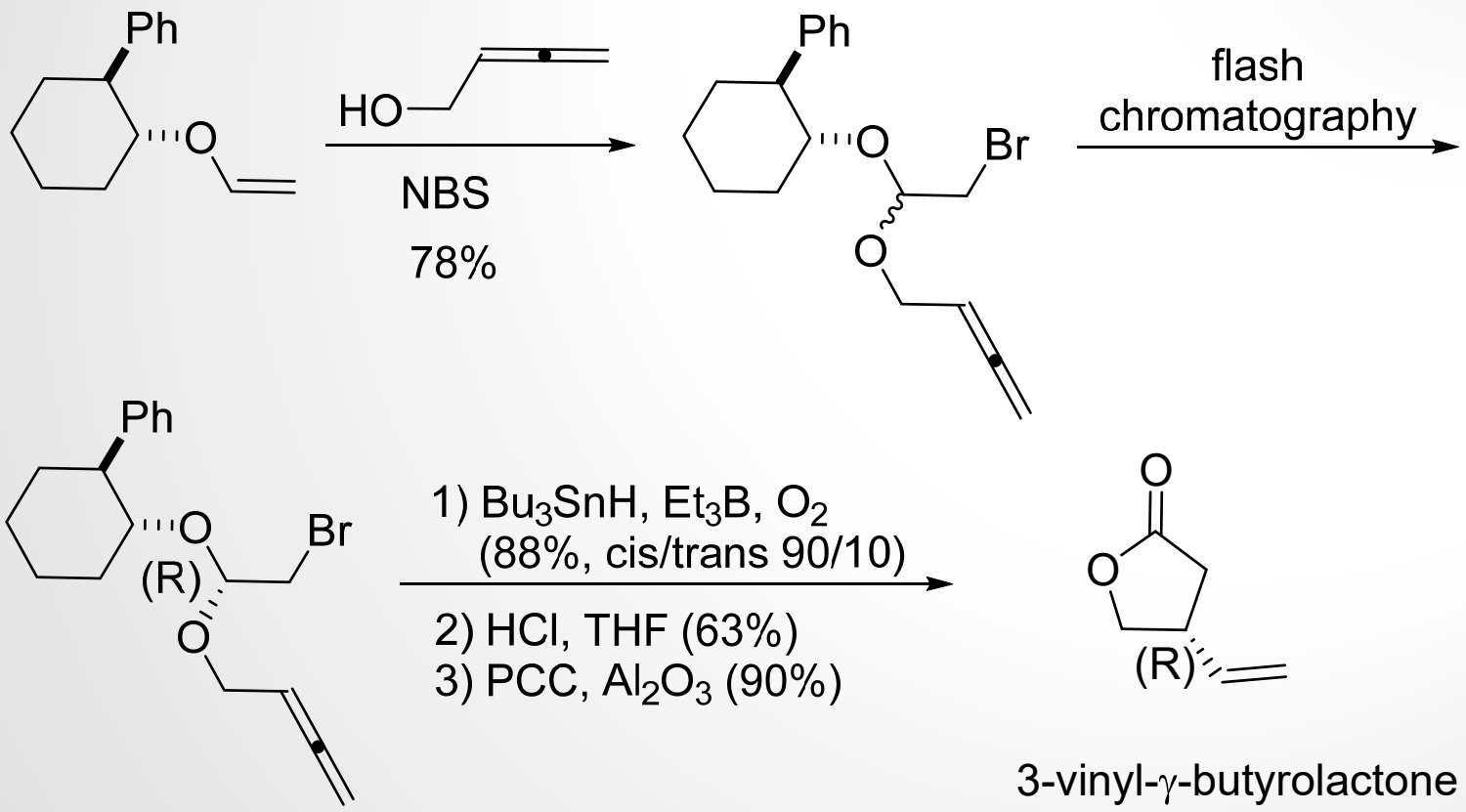


55% (95% ee) 91% (94% ee) 90% (A:B = 96:4)

Charette, A. B.; Jolicoeur, E.; Bydlinski, A. S. G. *Org. Lett.* **2001,** *21*, 3293

Total synthesis

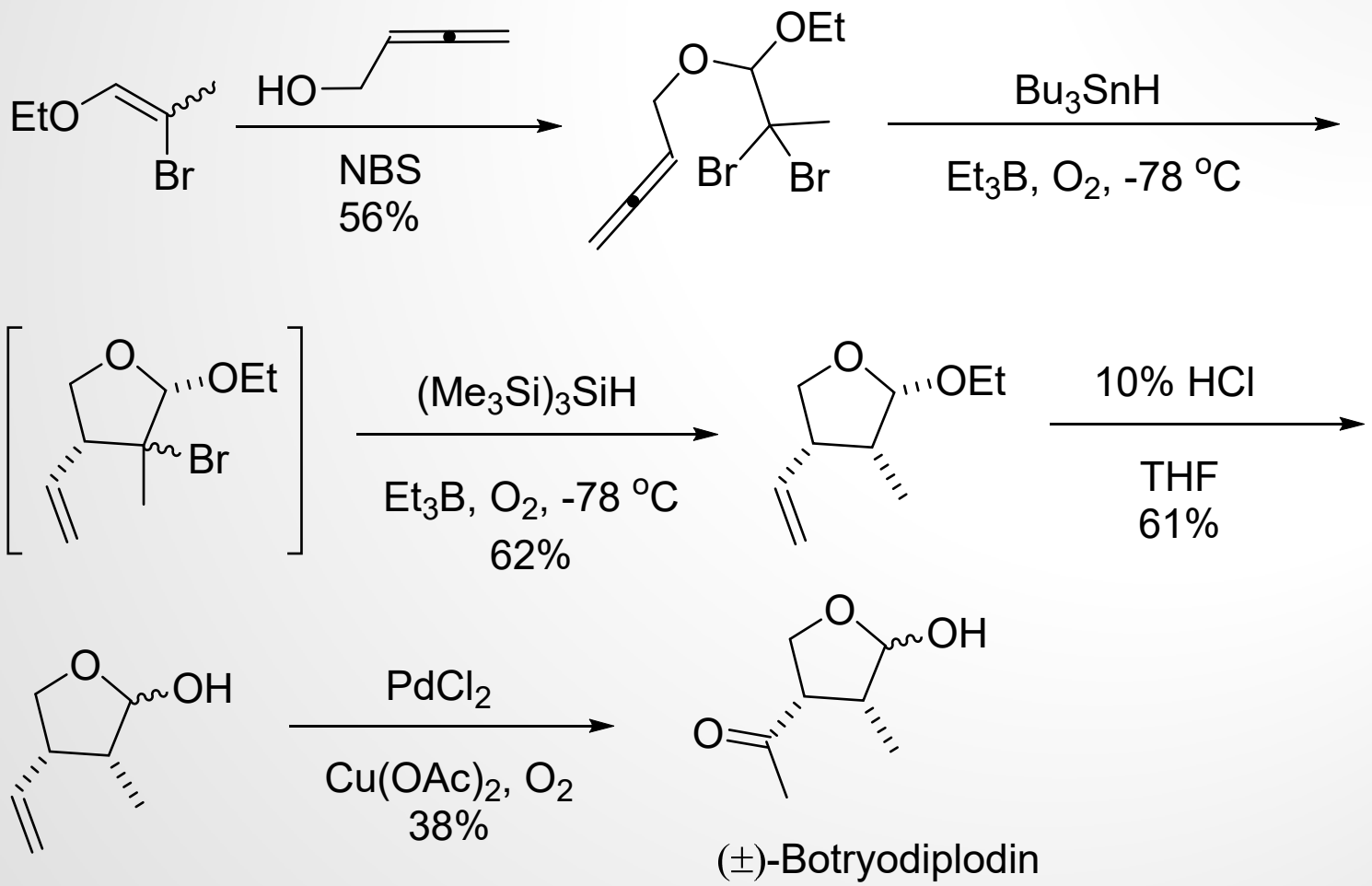
Synthesis of 3-vinyl-γ-butyrolactone



Villar, F.; Kolly-Kovac, T.; Equey, O.; Renaud, P. *Chem. Eur. J.* **2003**, *9*, 1566

Total synthesis

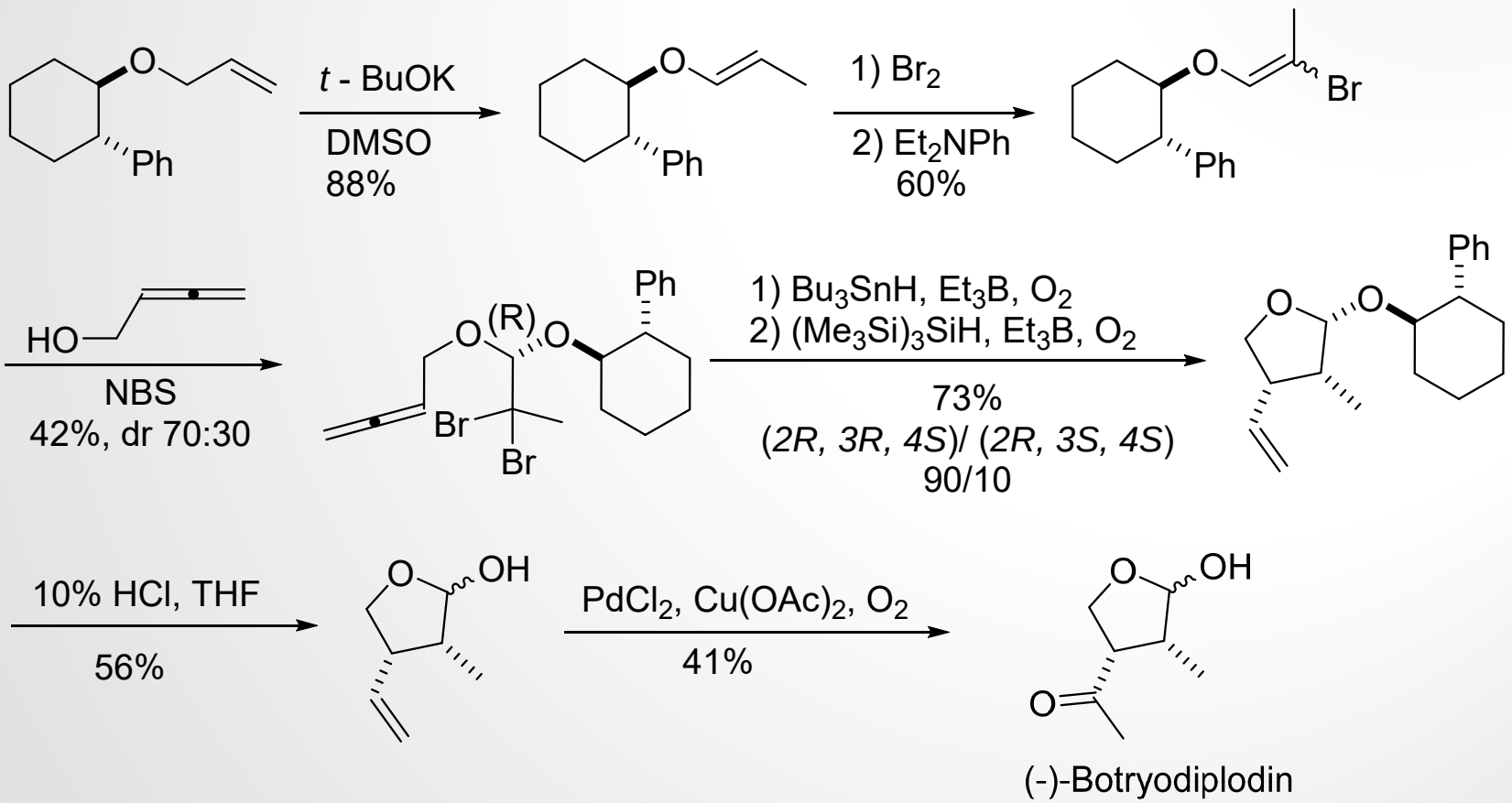
Synthesis of (±) and (−)-Botryodiplodin



Nouguier, R.; Gastaldi, S.; Stien, D.; Bertrand, M.; Villar, F.; Andrey, O.; Renaud, P. *Tetrahedron: Asymmetry.* **2003**, *14*, 3005

Total synthesis

Synthesis of (±) and (−)-Botryodiplodin



Nouguier, R.; Gastaldi, S.; Stien, D.; Bertrand, M.; Villar, F.; Andrey, O.; Renaud, P. *Tetrahedron: Asymmetry.* **2003**, *14*, 3005

Synthesis of 2,3-butadien-1-ol

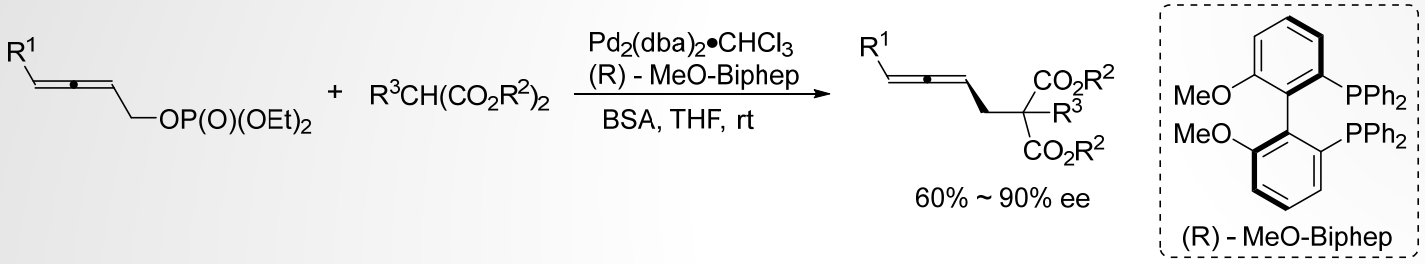
Transformation of 2,3-butadien-1-ol

- Coupling reactions of 2,3-butadien-1-ol
- Cyclization reactions of 2,3-butadien-1-ol
- Total synthesis

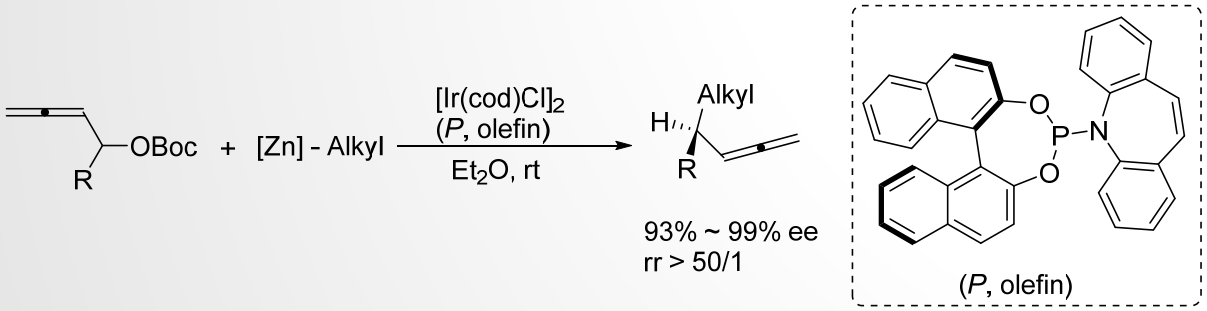
Transformation of 2,3-butadien-1-ol derivative

Conclusions and outlook

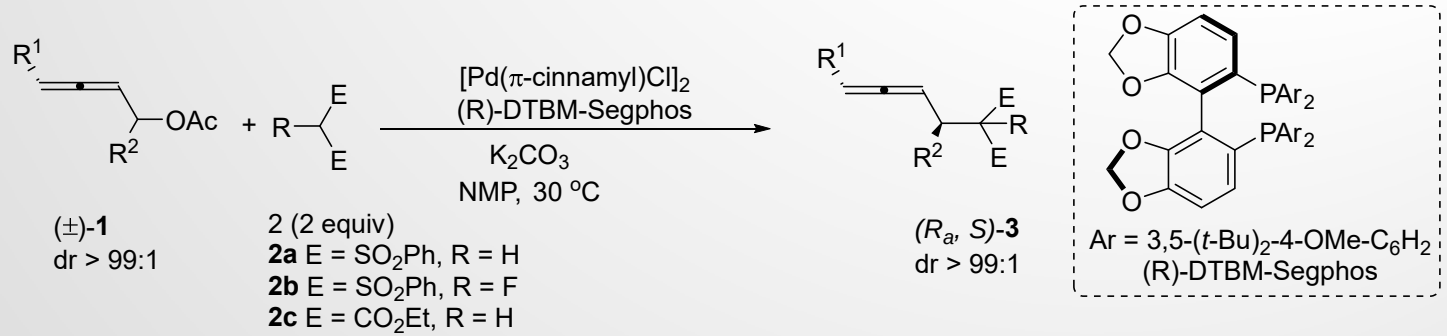
Applications of 2,3-butadien-1-ol derivative



Imada, Y.; Ueno, K.; Kutsuwa, K.; Murahashi, S. I. *Chem. Lett*. **2002**, 140.



Petrone, D. A.; Isomura, M.; Franzoni, I.; Rössler, S. L.; Carreira, E. M. *J. Am. Chem. Soc*., **2018**, *140* , 4697



Dai, J.; Duan, X.; Zhou, J.; Fu, C.; Ma, S. *Chin. J. Chem*. **2018**, *36*, 387

Synthesis of 2,3-butadien-1-ol

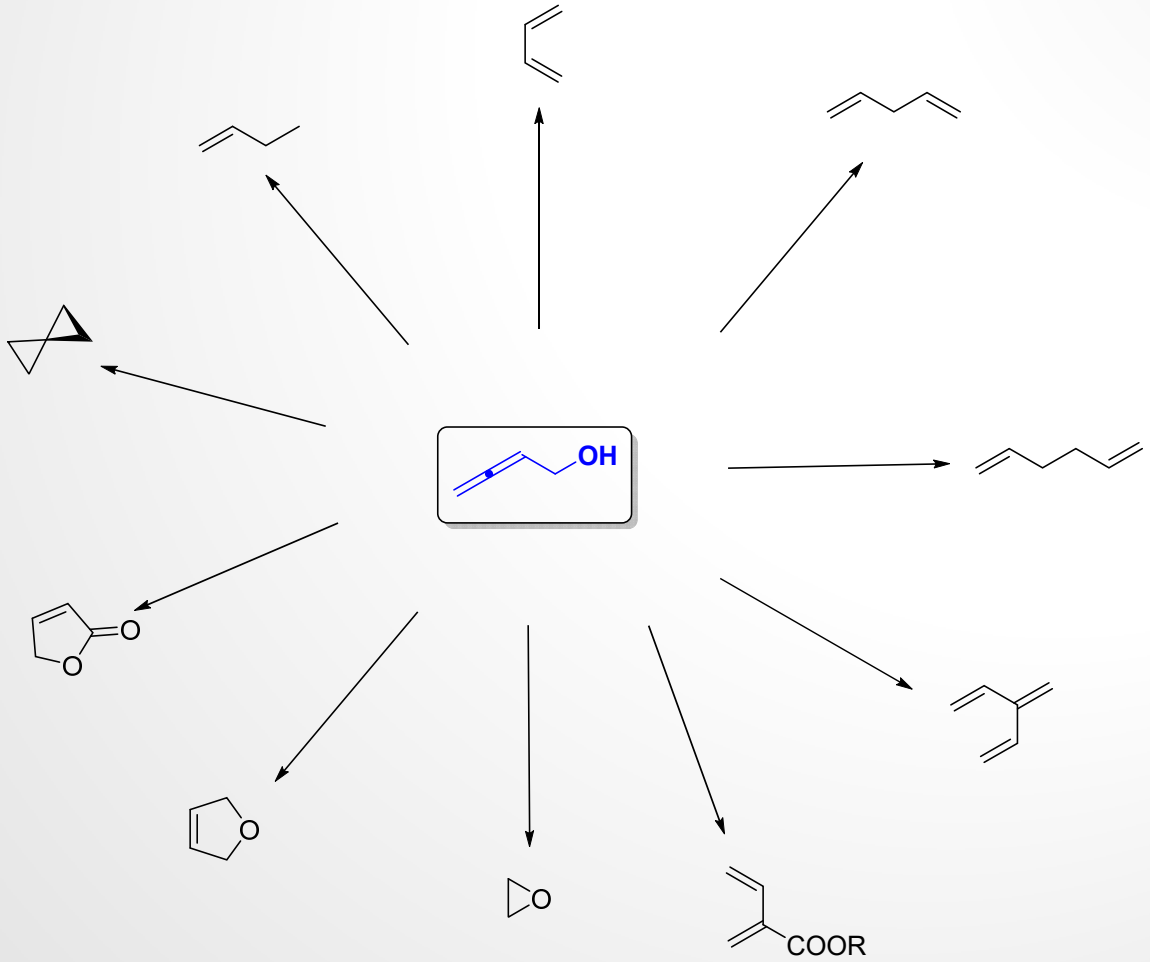
Transformation of 2,3-butadien-1-ol

- Coupling reactions of 2,3-butadien-1-ol
- Cyclization reactions of 2,3-butadien-1-ol
- Total synthesis

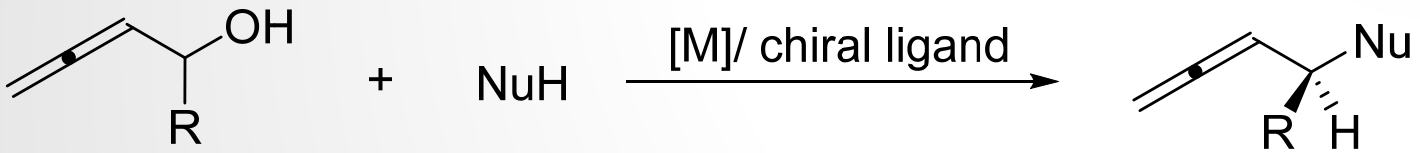
Transformation of 2,3-butadien-1-ol derivative

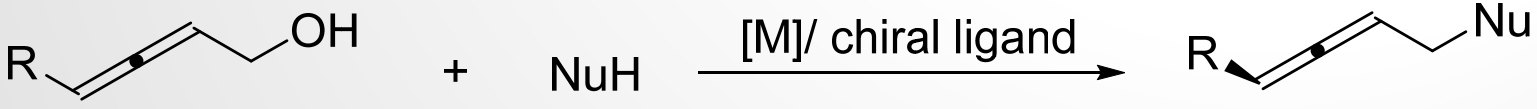
Conclusions and outlook

Conclusion and outlook



Conclusion and outlook





Thanks for your attention !