

Sulfonyl Hydrazones: An Introduction and Applications in Total Synthesis

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2026. 06. 11



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何塞·巴伦加
(1940-2016)

- 1963 西班牙萨拉戈萨大学, 学士
- 1963–1967 西班牙萨拉戈萨大学, 博士
- 1967–1970 德国马克斯·普朗克煤炭研究所, 博士后 (导师: Heinz Hoberg)
- 1970–1972 萨拉戈萨国家研究委员会, 研究员
- 1972–1975 萨拉戈萨大学, 副教授
- 1975–2010 奥维耶多大学, 教授



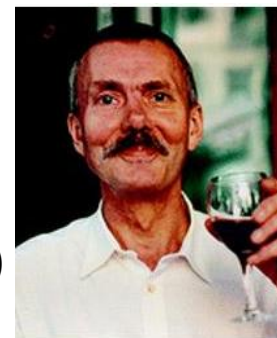
Carlos Valdés
卡洛斯·巴尔德斯

- 1992 奥维耶多大学, 博士 (导师: Fernando Aznar and José Barluenga)
- 1993–1995 MIT, 博士后 (导师: Julius Rebek, Jr.)
- 1995– 奥维耶多大学, 教授



Varinder K. Aggarwal

1980–1983 剑桥大学, 学士
1983–1986 剑桥大学, 博士 (导师: Stuart Warren)
1986–1988 哥伦比亚大学, 博士后 (导师: Gilbert Stork)
1988–1991 英国巴斯大学, 讲师
1991–1995 英国谢菲尔德大学, 讲师
1995–1997 英国谢菲尔德大学, 副教授
1997–2000 英国谢菲尔德大学, 教授
2000– 英国布里斯托大学, 教授



Phil S. Baran

1995–1997 New York University, **B.S.**, Advisor: D.I. Schuster
1997–2001 The Scripps Research Institute, **Ph.D.**, Advisor: K.C. Nicolaou
2001–2003 Harvard University, **Postdoctoral Associate**, Advisor: E.J. Corey
2003–2008 The Scripps Research Institute, Assistant Professor
2008– The Scripps Research Institute, Professor



王剑波

1979–1983 南京理工大学，学士

1984–1987 北海道大学，硕士（导师： Hiroshi Suginome）

1987–1990 北海道大学，博士（导师： Hiroshi Suginome）

1990–1993 日内瓦大学，博士后（导师： C. W. Jefford）

1993–1995 威斯康星大学麦迪逊分校，博士后（导师： H. E. Zimmerman 与 L. A. Fahien ）

1995–1999 北京大学，副教授

1999– 北京大学，教授



毕锡和

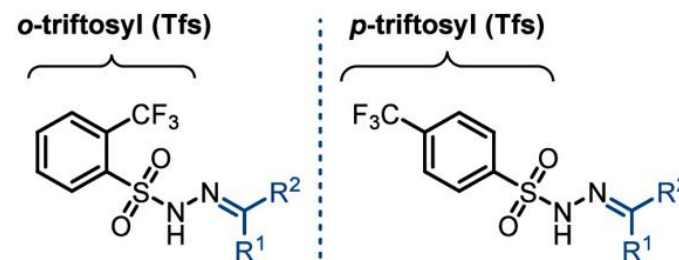
1996–2000 东北师范大学，学士

2000–2006 东北师范大学，博士（导师： 刘群）

2005–2008 东北师范大学，讲师

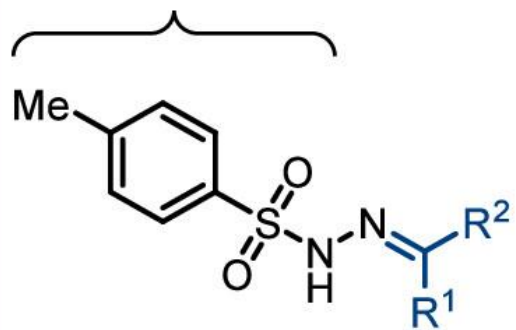
2006–2008 德国波恩大学凯库勒研究所，博士后（导师： Michael Famulok ）

2009– 副教授，教授



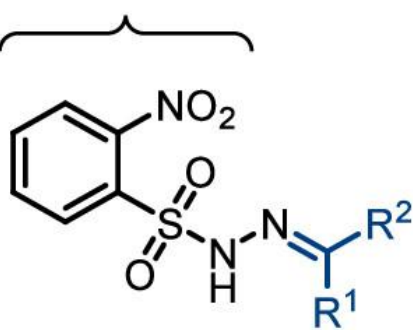
- 01** **The Bamford–Stevens and Shapiro Reactions**
- 02** **Carbene Chemistry of Sulfonyl Hydrazones**
- 03** **Radical Couplings of Sulfonyl Hydrazides**

tosyl (Ts)

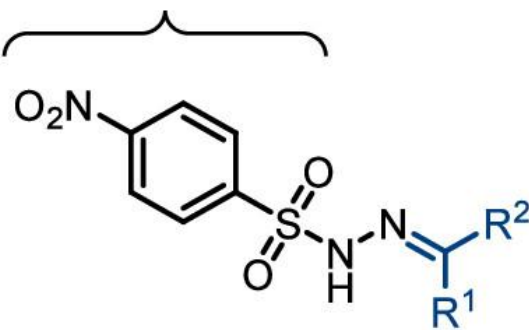


Blümmel (1924)

o-nosyl (Ns)

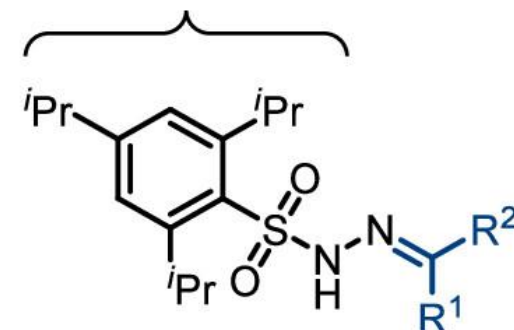


p-nosyl (Ns)



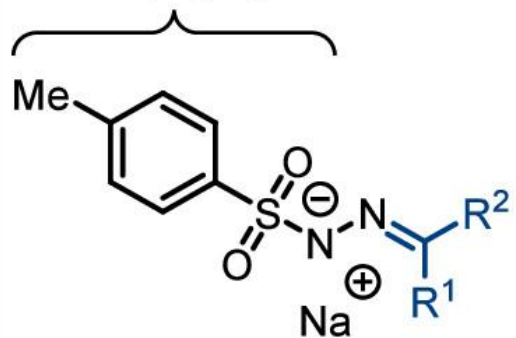
Storrie (1931)

trisyl (Tris)



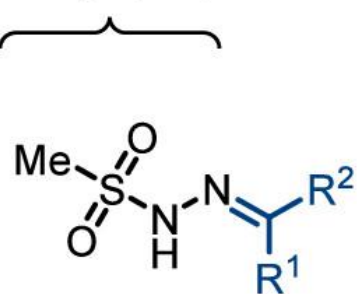
Rees (1982)

tosyl (Ts)



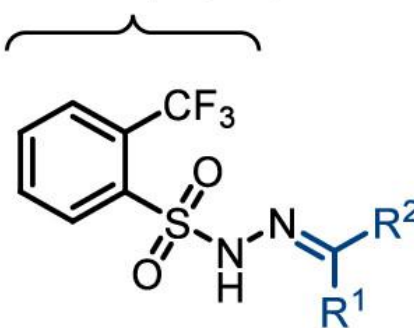
Creary (1986)

mesyl (Ms)

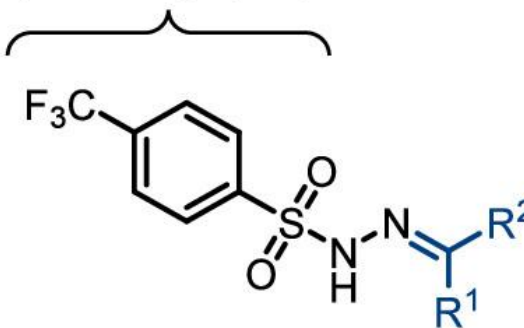


Harada (1998)

o-triftosyl (Tfs)

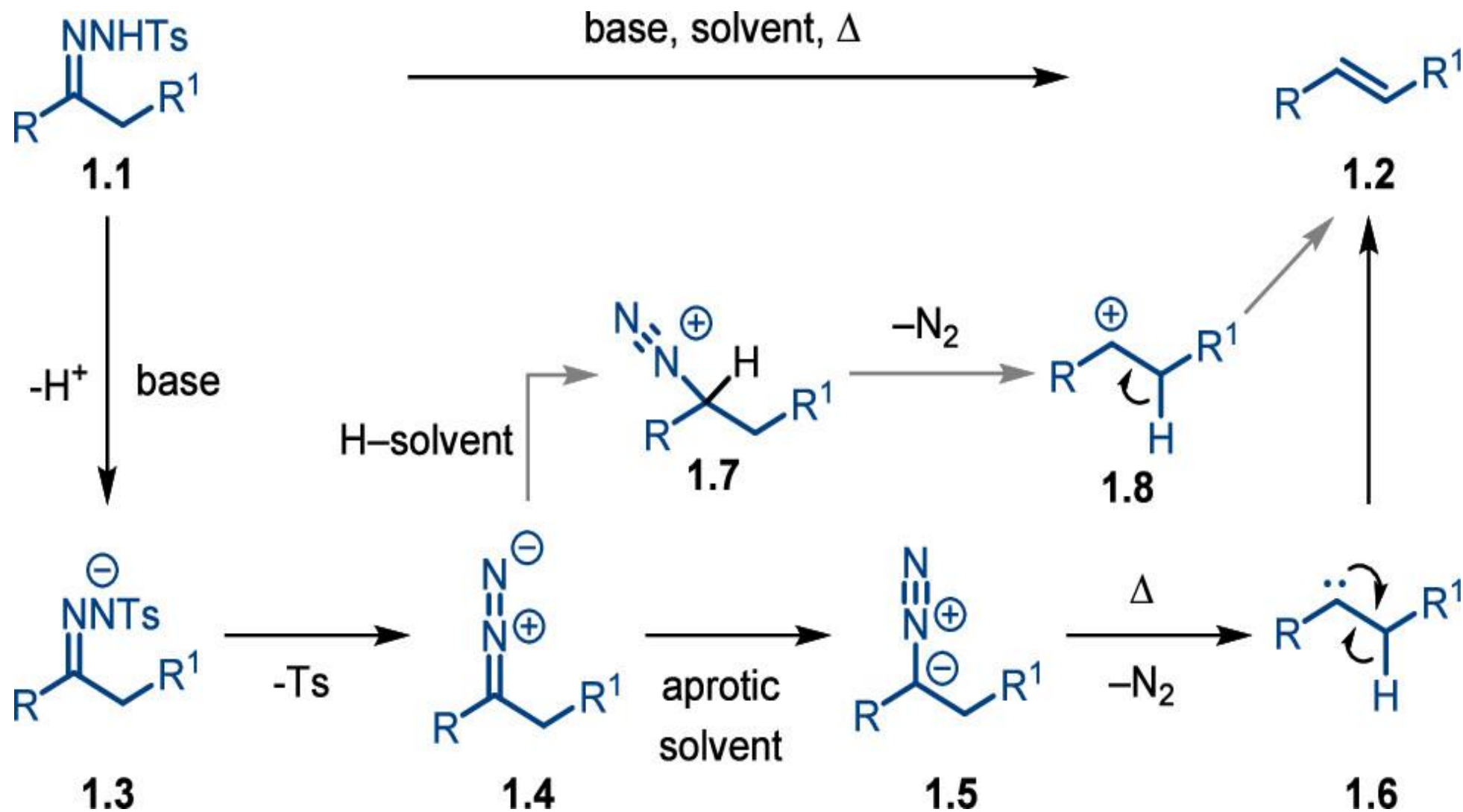


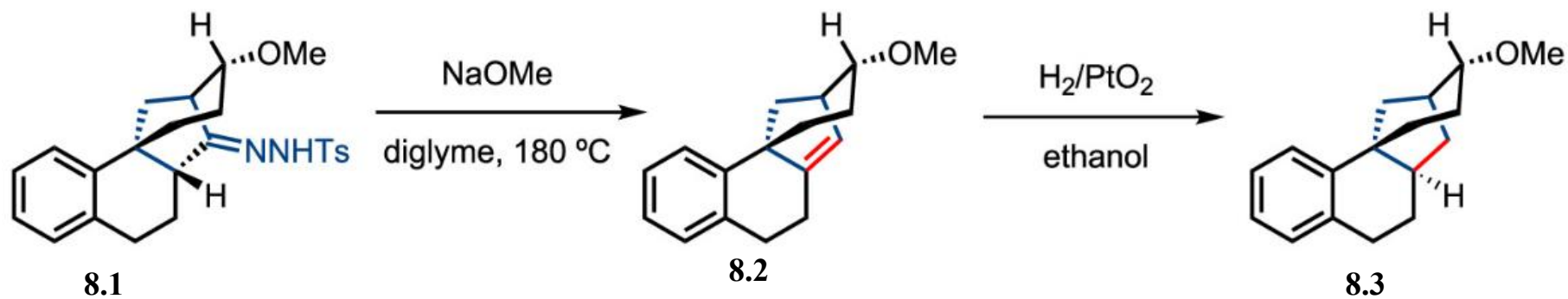
p-triftosyl (Tfs)



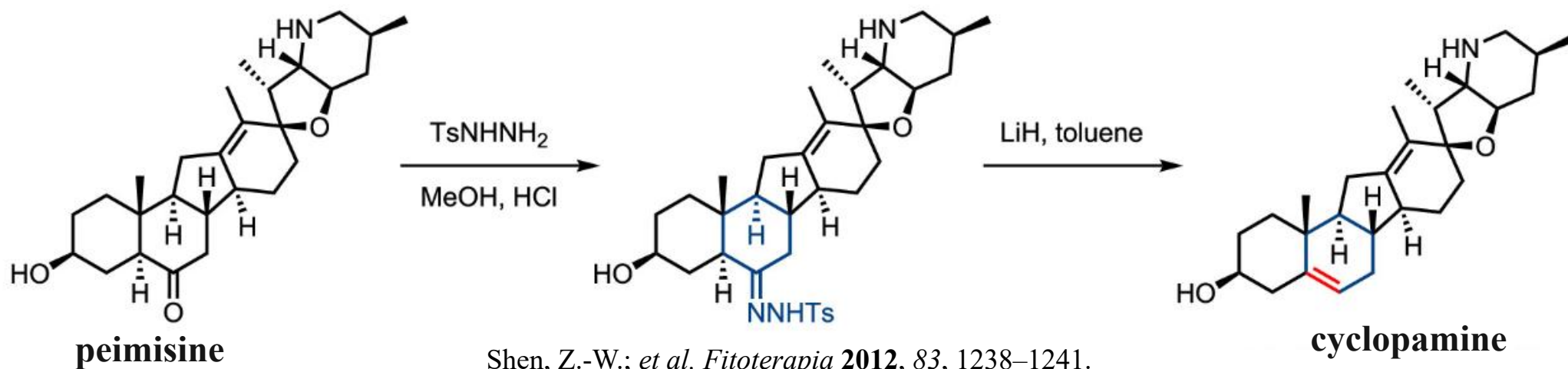
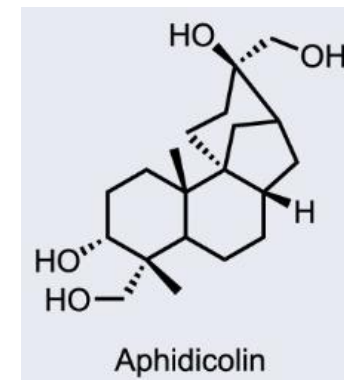
Bi (2018)

Bamford–Stevens Reaction (1952)

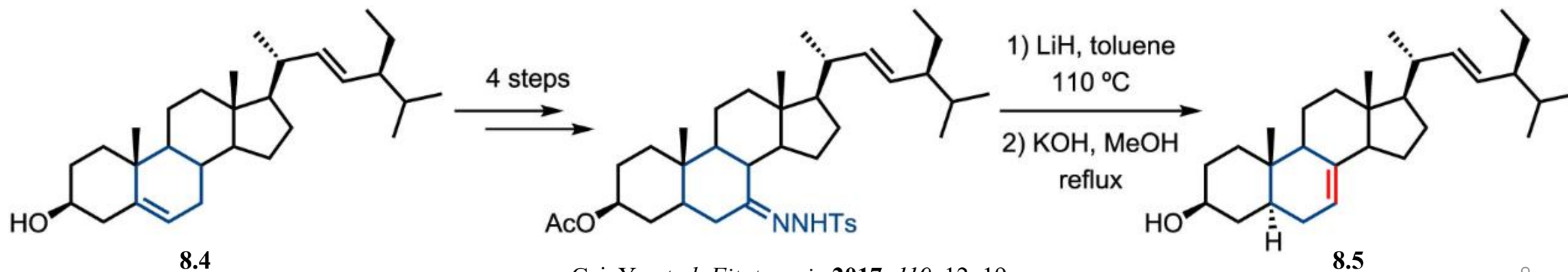




Mann, J.; *et al. Tetrahedron* **1995**, 51, 9079–9090.

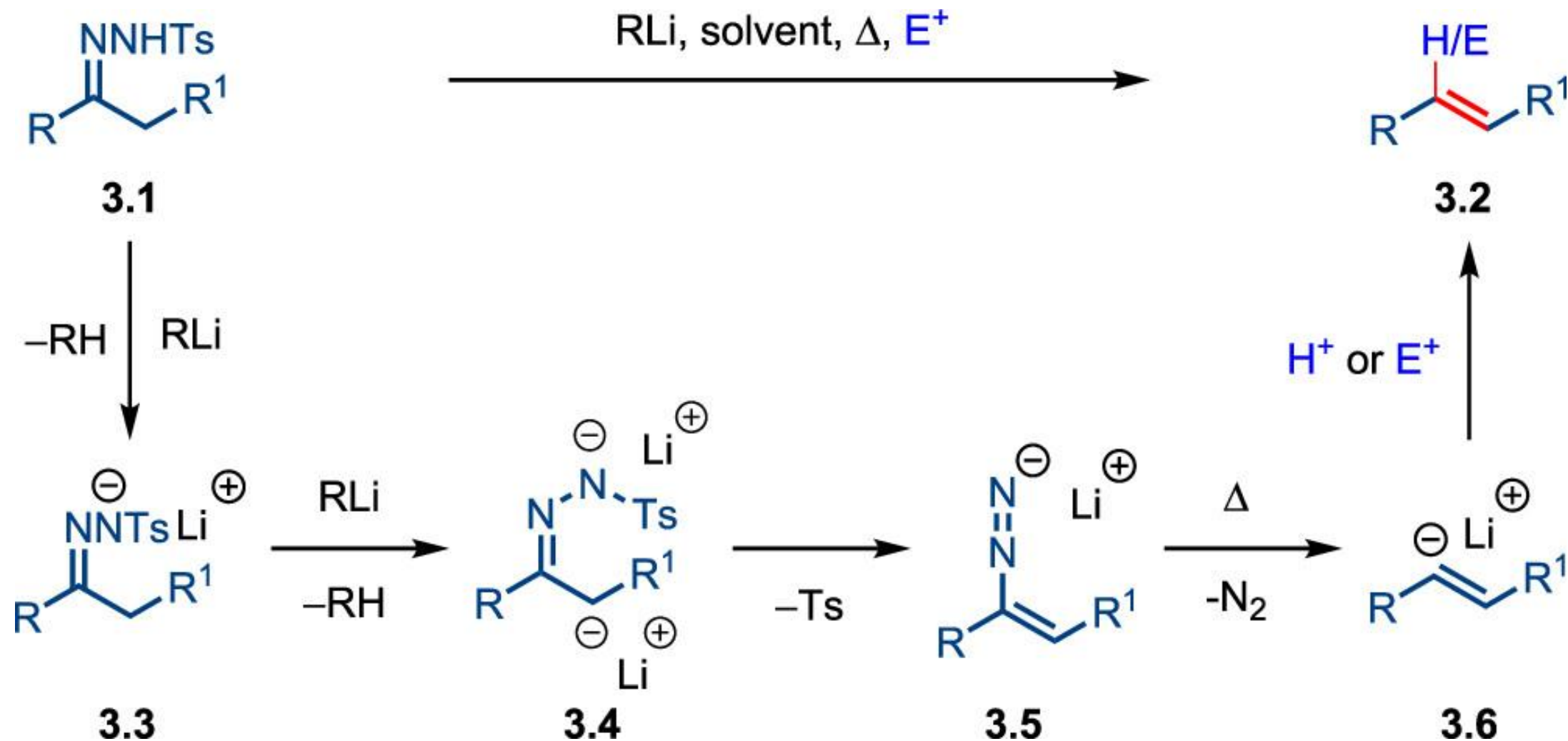


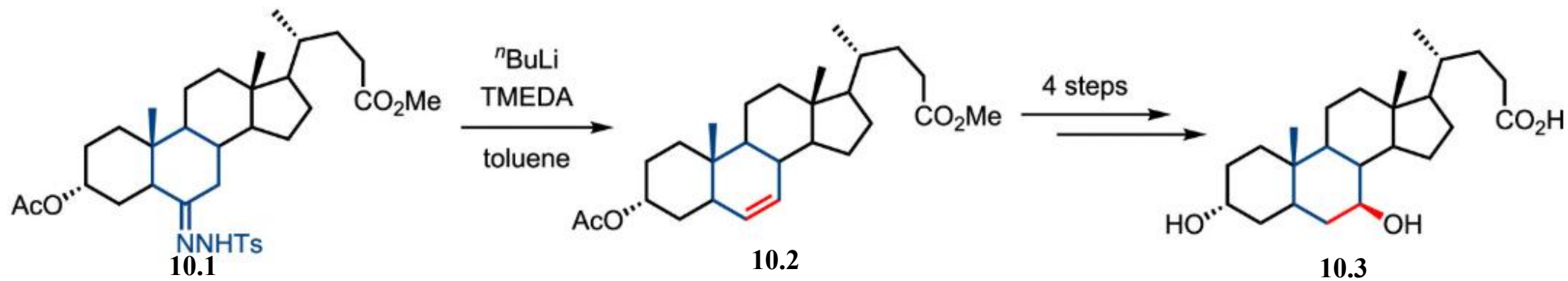
Shen, Z.-W.; *et al. Fitoterapia* **2012**, 83, 1238–1241.



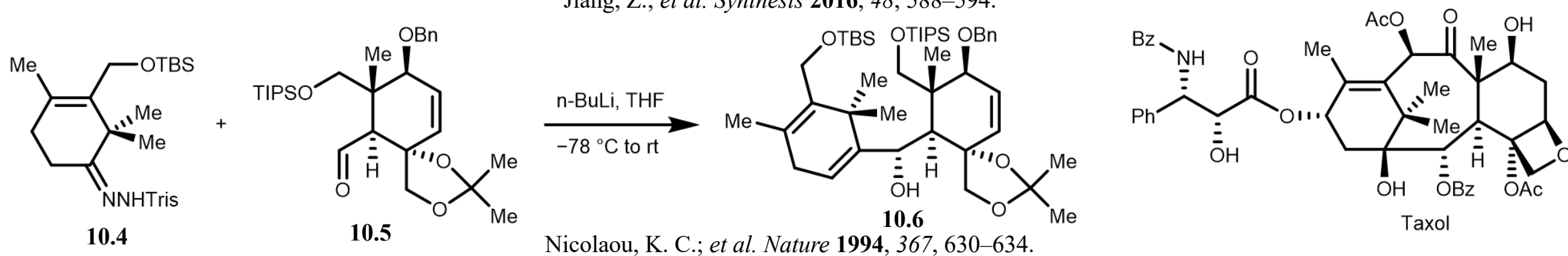
Cai, Y.; *et al. Fitoterapia* **2017**, 119, 12–19.

Shapiro Reaction (1967)

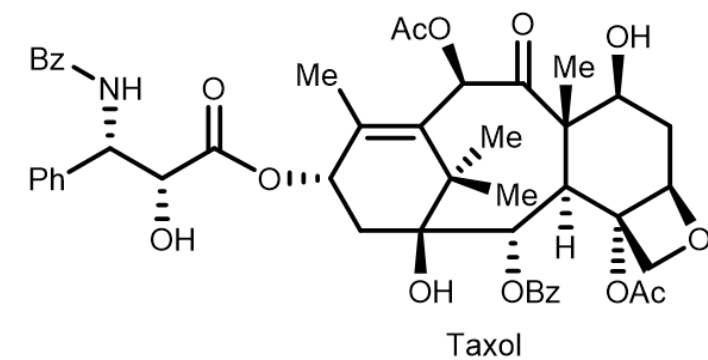




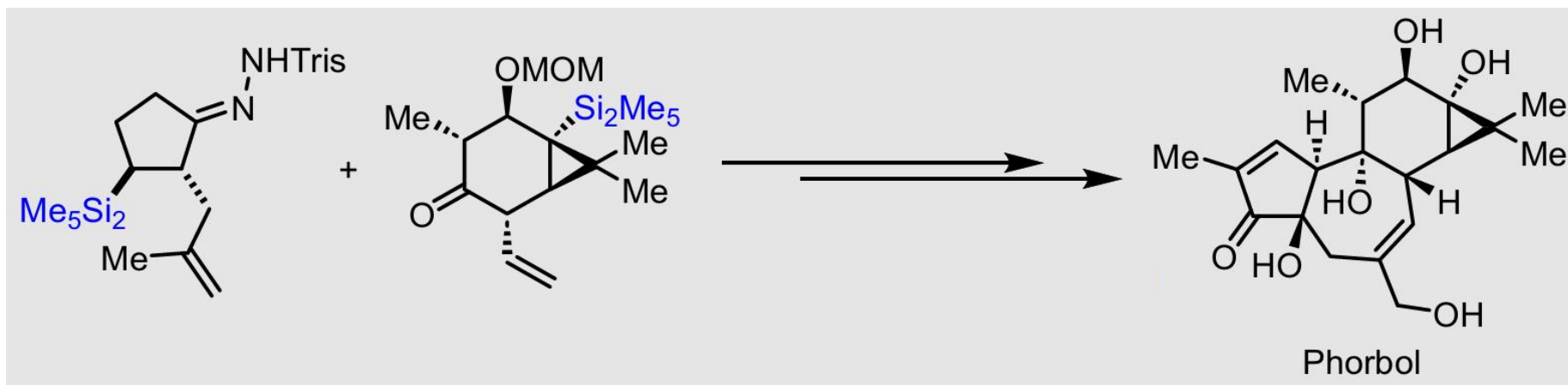
Jiang, Z.; *et al. Synthesis* **2016**, 48, 588–594.



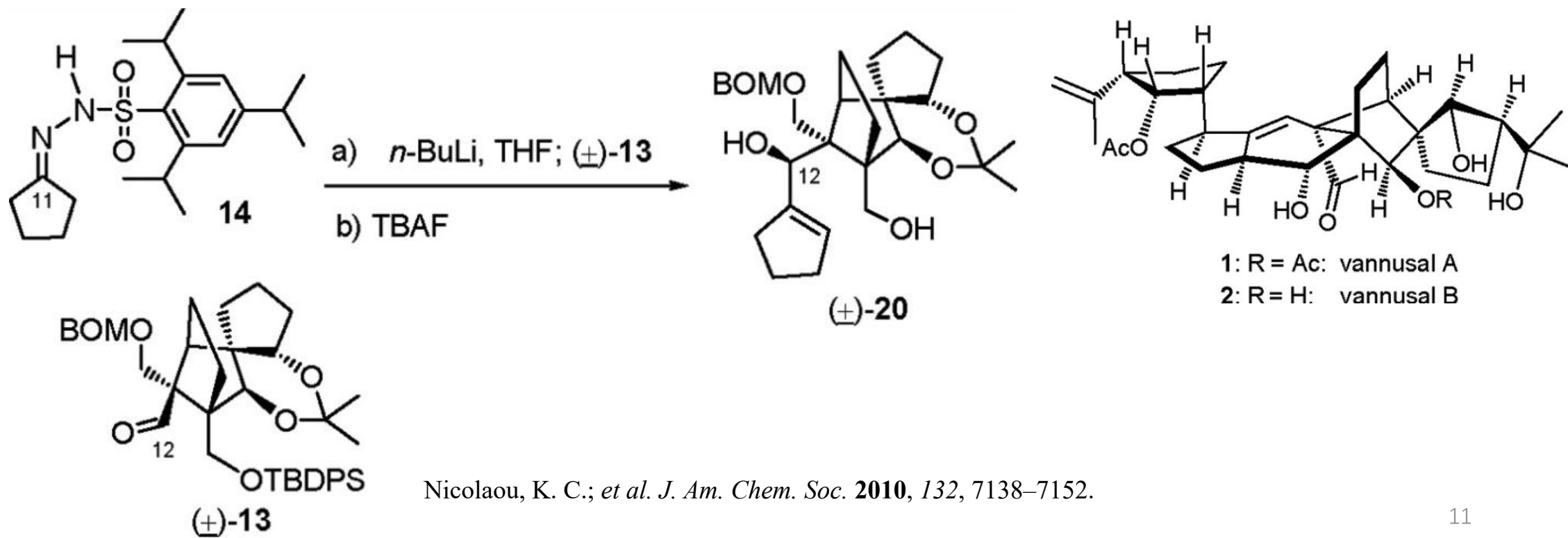
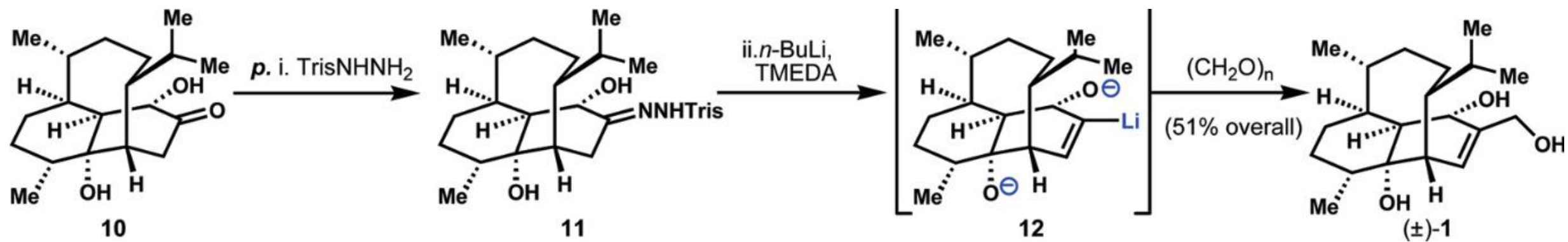
Nicolaou, K. C.; *et al. Nature* **1994**, 367, 630–634.

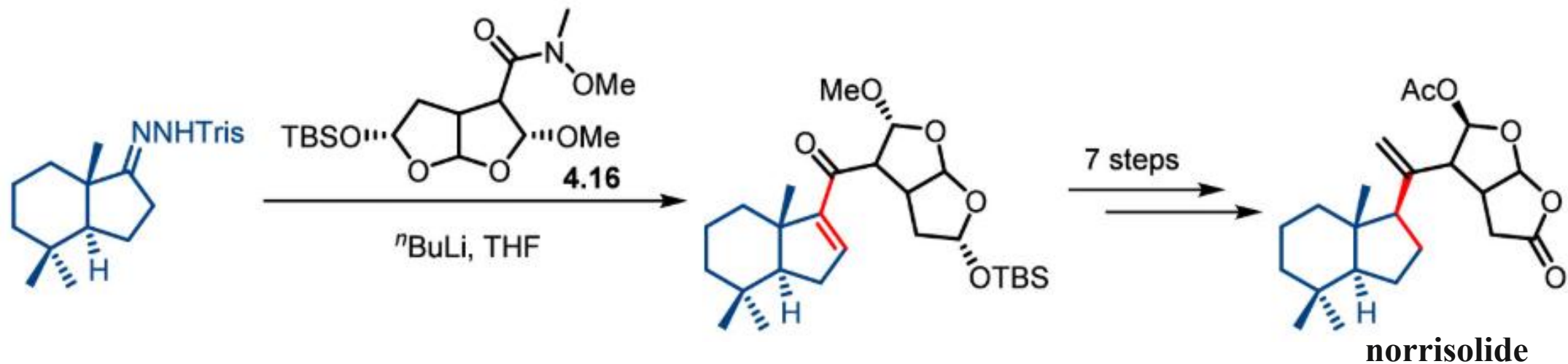


Taxol

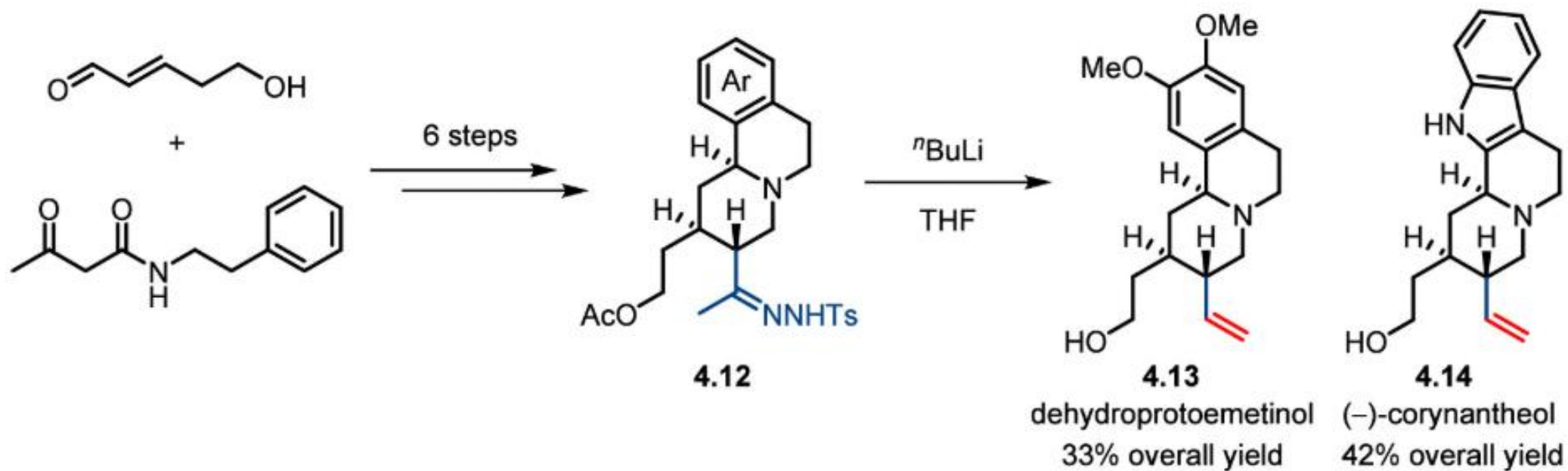


Jia, Y.; *et al. CCS Chem.* **2025**, 7, 375–380.

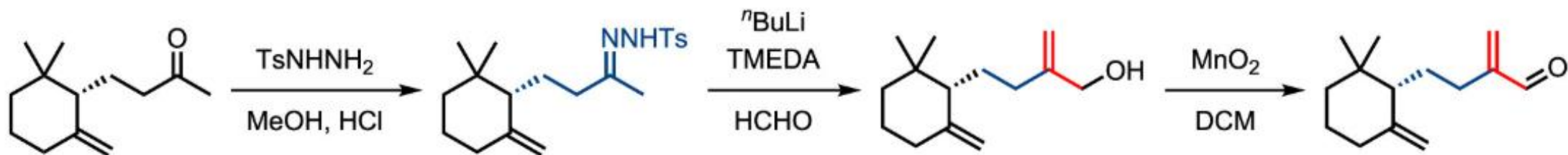




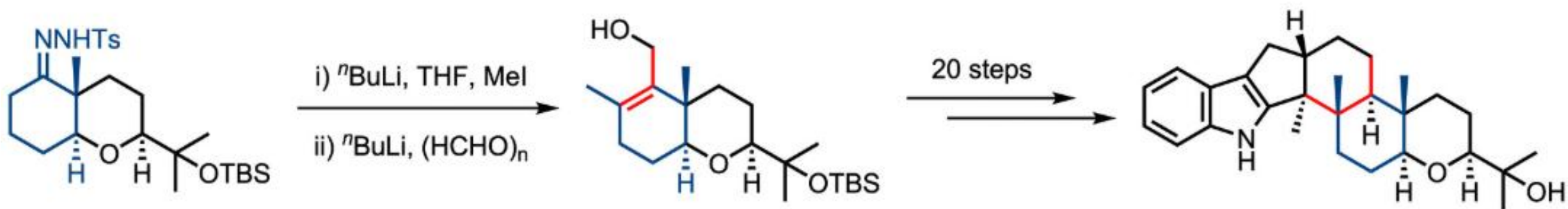
Snapper, M. L.; *et al. Eur. J. Org. Chem.* **2012**, 2012, 2308–2311.



Franzén, J.; *et al. Chem. Eur. J.* **2011**, 17, 13814–13824.

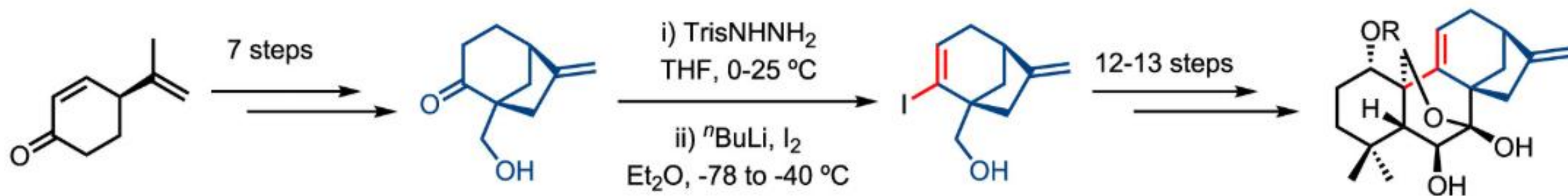


Serra, S. *Flavour Fragr. J.* **2013**, 28, 46–52.



Johnson, J. S.; *et al.* *J. Am. Chem. Soc.* **2015**, 137, 4968–4971.

Paspaline



5.14

5.15

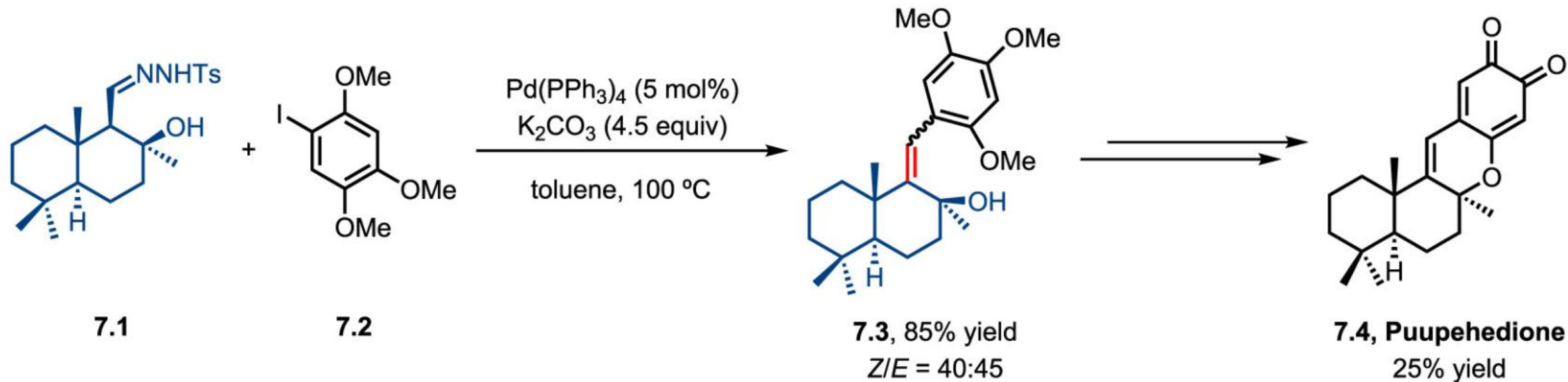
5.16, 50% (2 steps)

R = H; isorosthin L
R = Ac; isoadenolin I

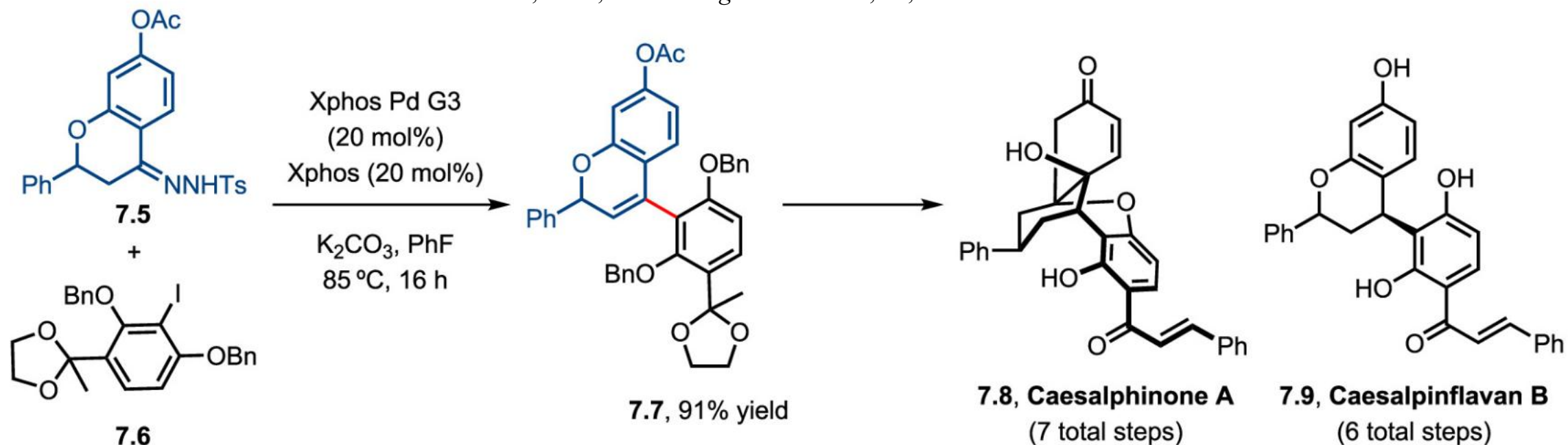
Liang, G.; *et al.* *Angew. Chem. Int. Ed.* **2022**, 61, e202114489.

- 01 The Bamford–Stevens and Shapiro Reactions
- 02 Carbene Chemistry of Sulfonyl Hydrazones**
- 03 Radical Couplings of Sulfonyl Hydrazides

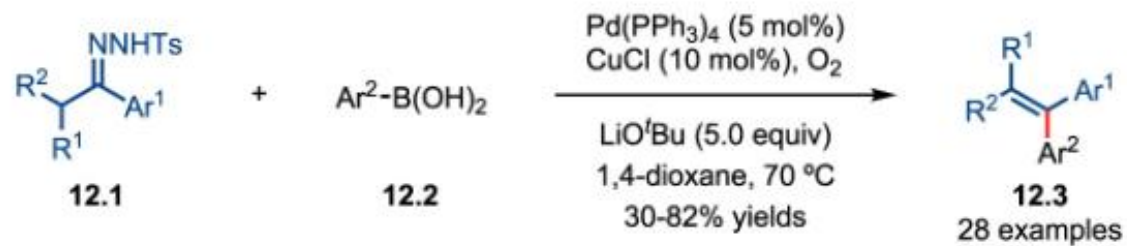
A portrait of a middle-aged man with short, graying hair and glasses. He is wearing a light blue collared shirt and a dark tie with a small, light-colored pattern. He has a serious expression and is looking directly at the camera. The background is a plain, light-colored wall.



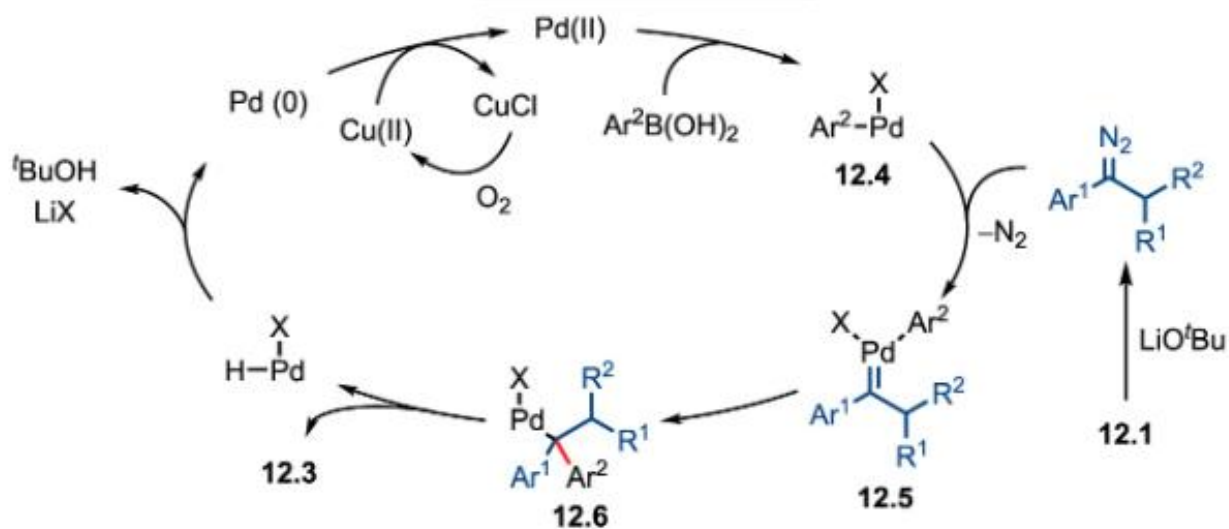
Wu, Y.-C.; *et al. J. Org. Chem.* **2017**, 82, 12914–12919.



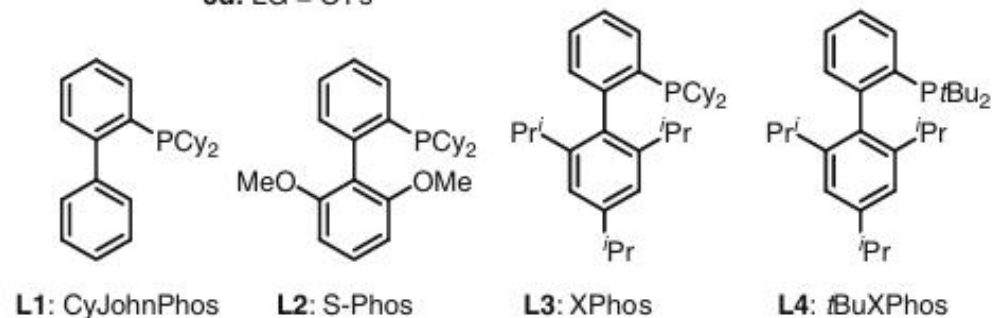
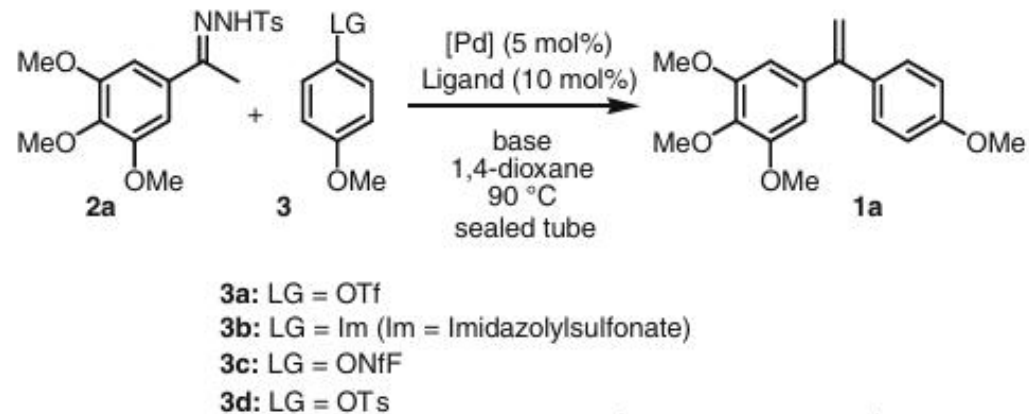
Wood, J. L.; *et al. J. Am. Chem. Soc.* **2019**, 141, 10082–10090.



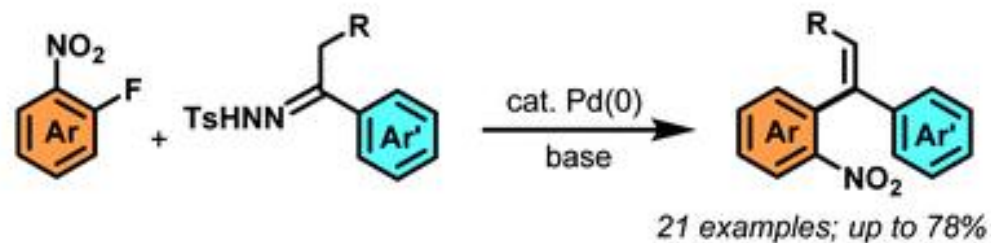
Proposed mechanism



Wang, J.; *et al. Chem. Commun.* **2010**, 46, 1724–1726.

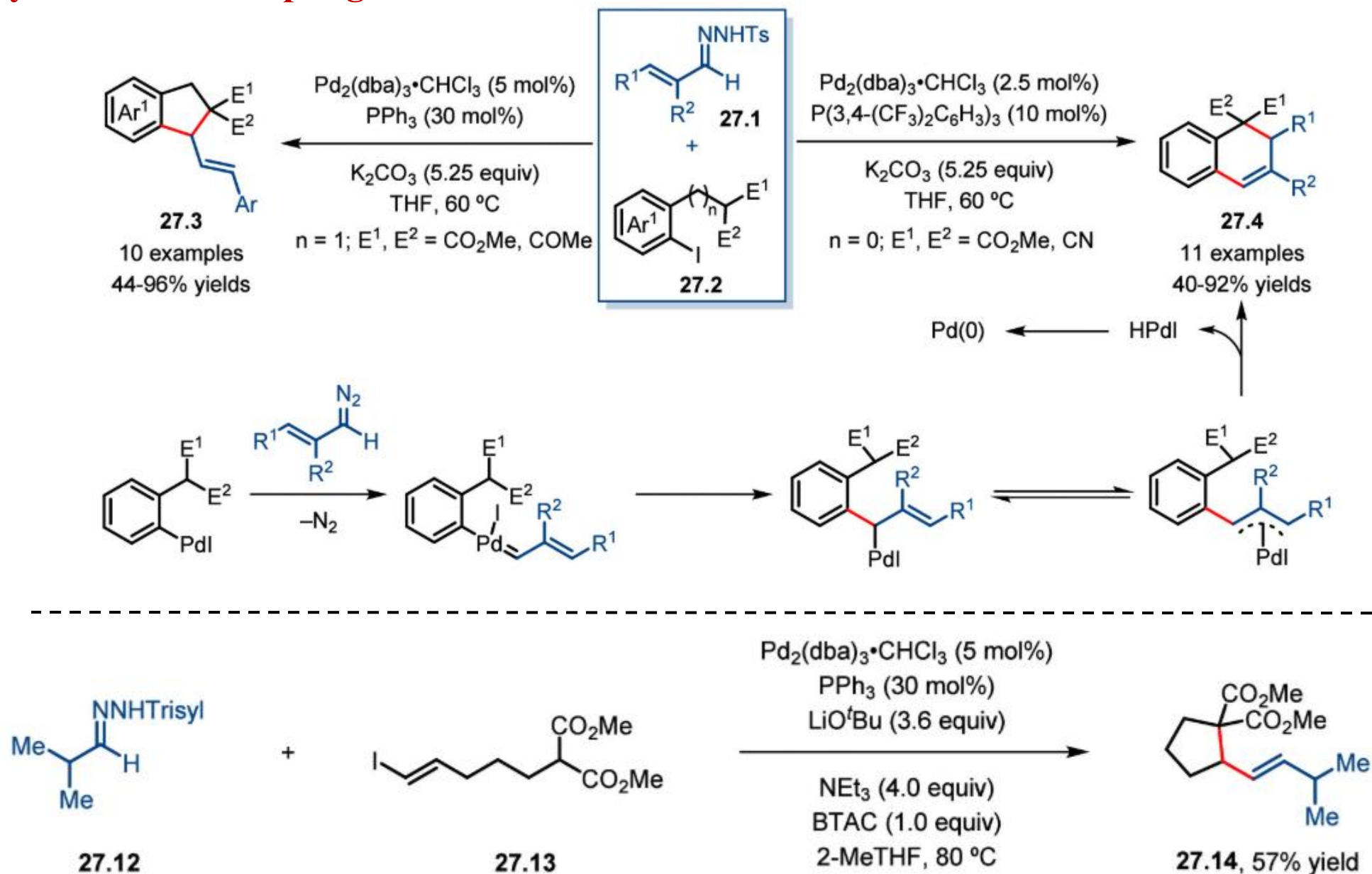


Barluenga, J.; *et al. Org. Lett.* **2011**, 13, 510–513.

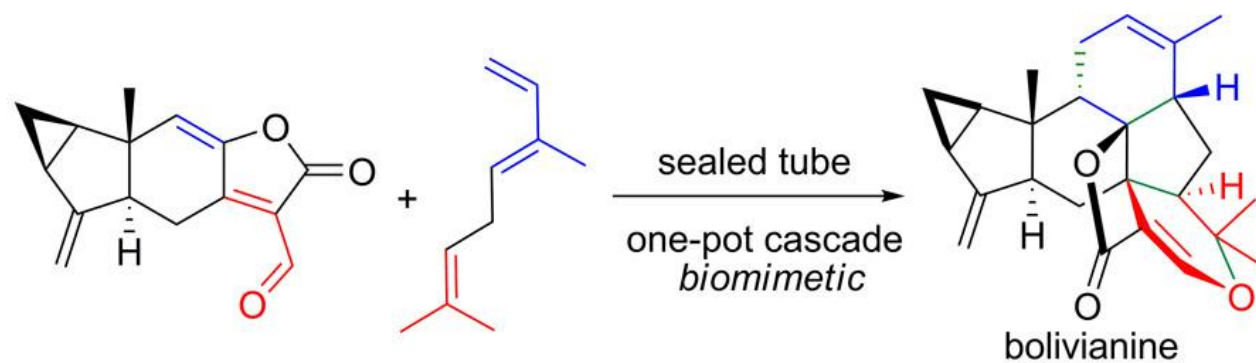
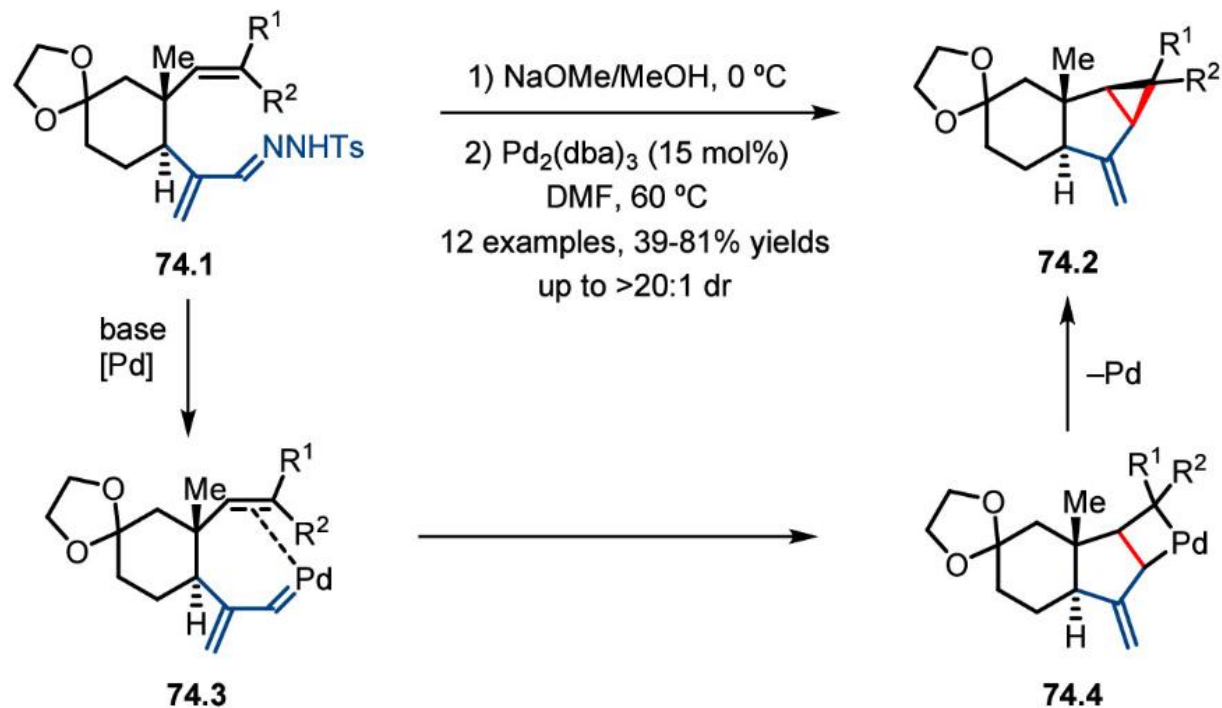


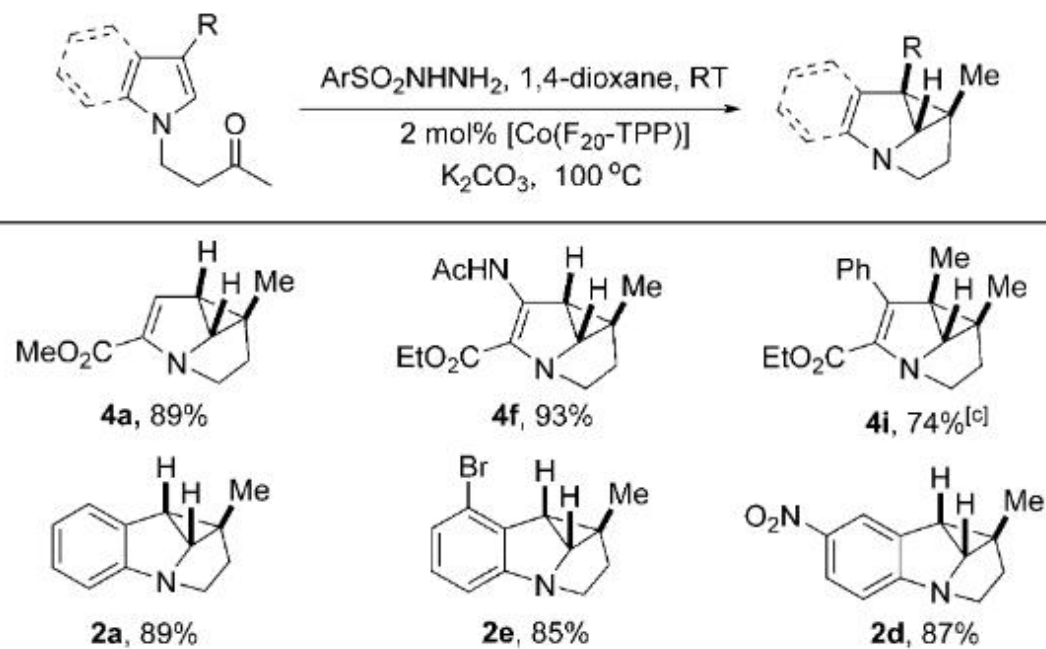
Wang, J.; *et al. Chem. Commun.* **2015**, 51, 13321–13323.

Pd-catalyzed cascade coupling

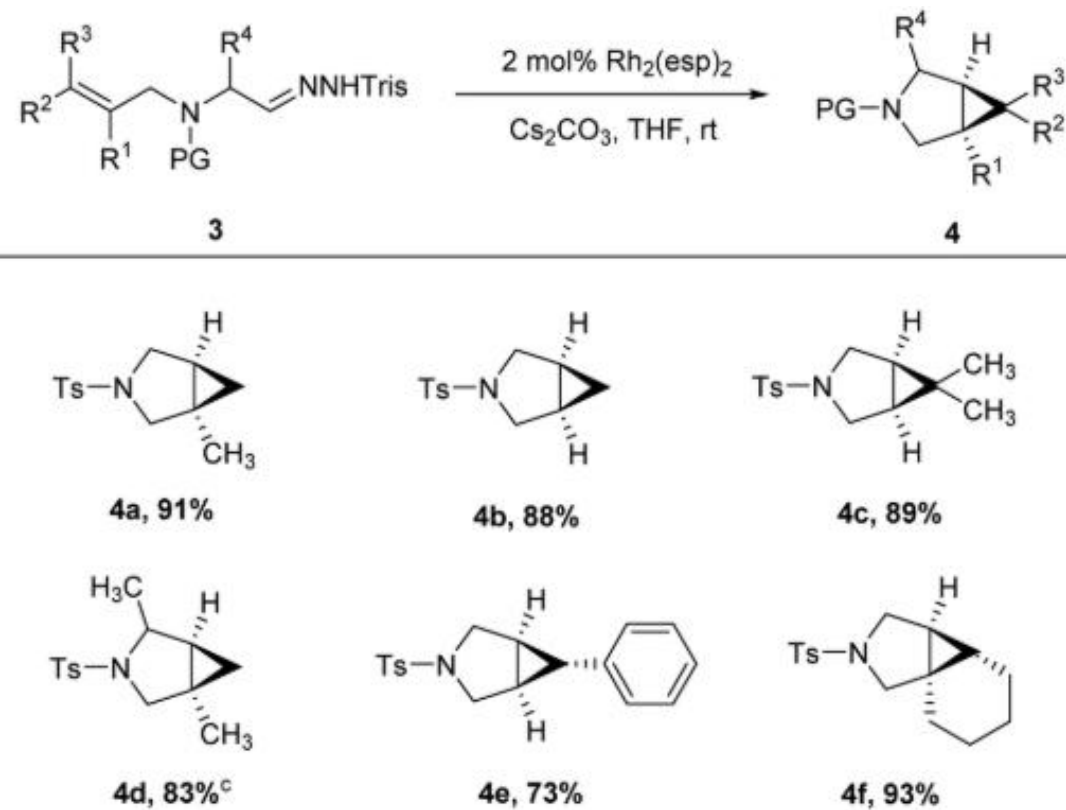


Intramolecular Cyclopropanation



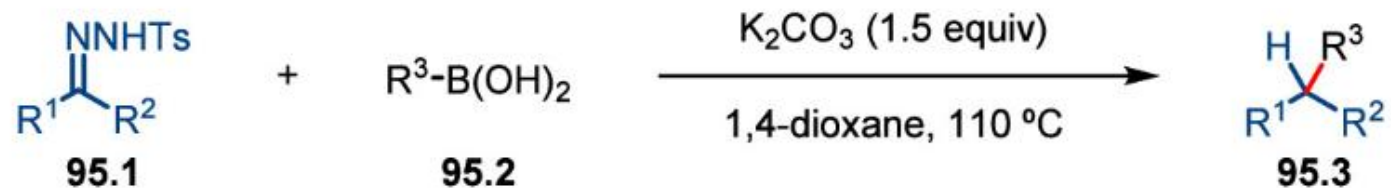


Che, C.; *et al. Angew. Chem., Int. Ed.* **2016**, 55, 1810–1815.



Zhou, C.-Y.; *et al. Org. Chem. Front.* **2023**, 10, 699–704.

Metal-Free Carbene Coupling Reactions

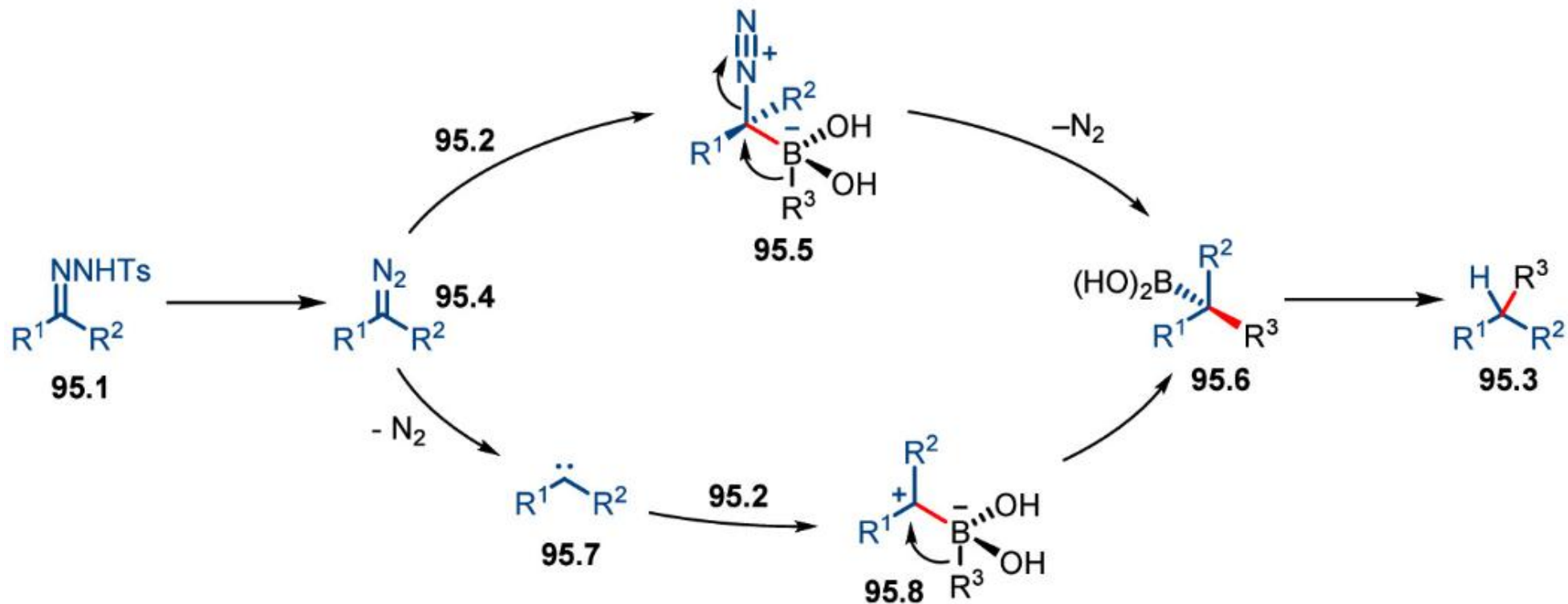


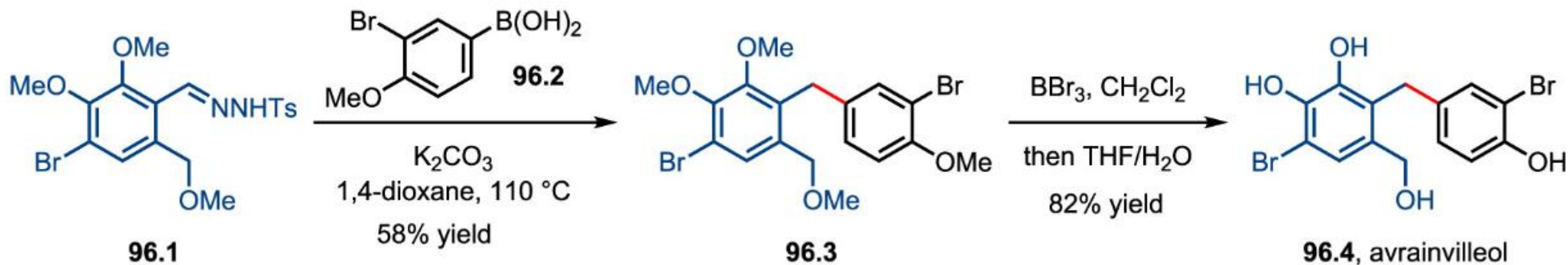
$\text{R}^1 = \text{H, alkyl}$

$\text{R}^2, \text{R}^3 = \text{aryl, heteroaryl or alkyl}$

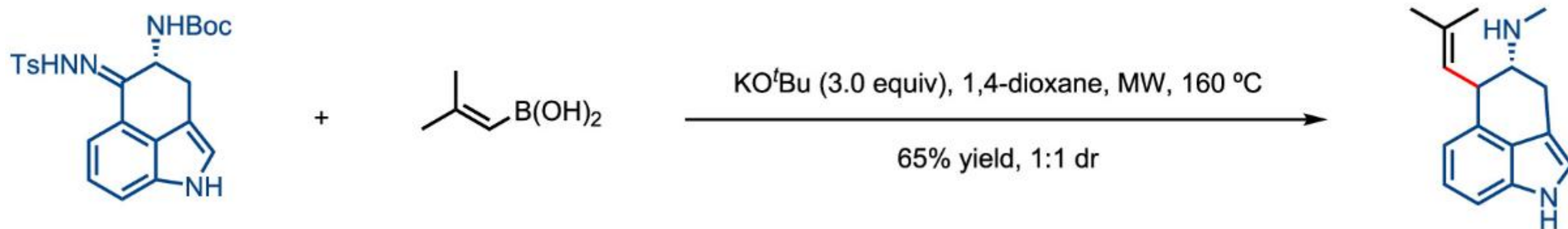
28 examples
30-82% yields

Proposed mechanism

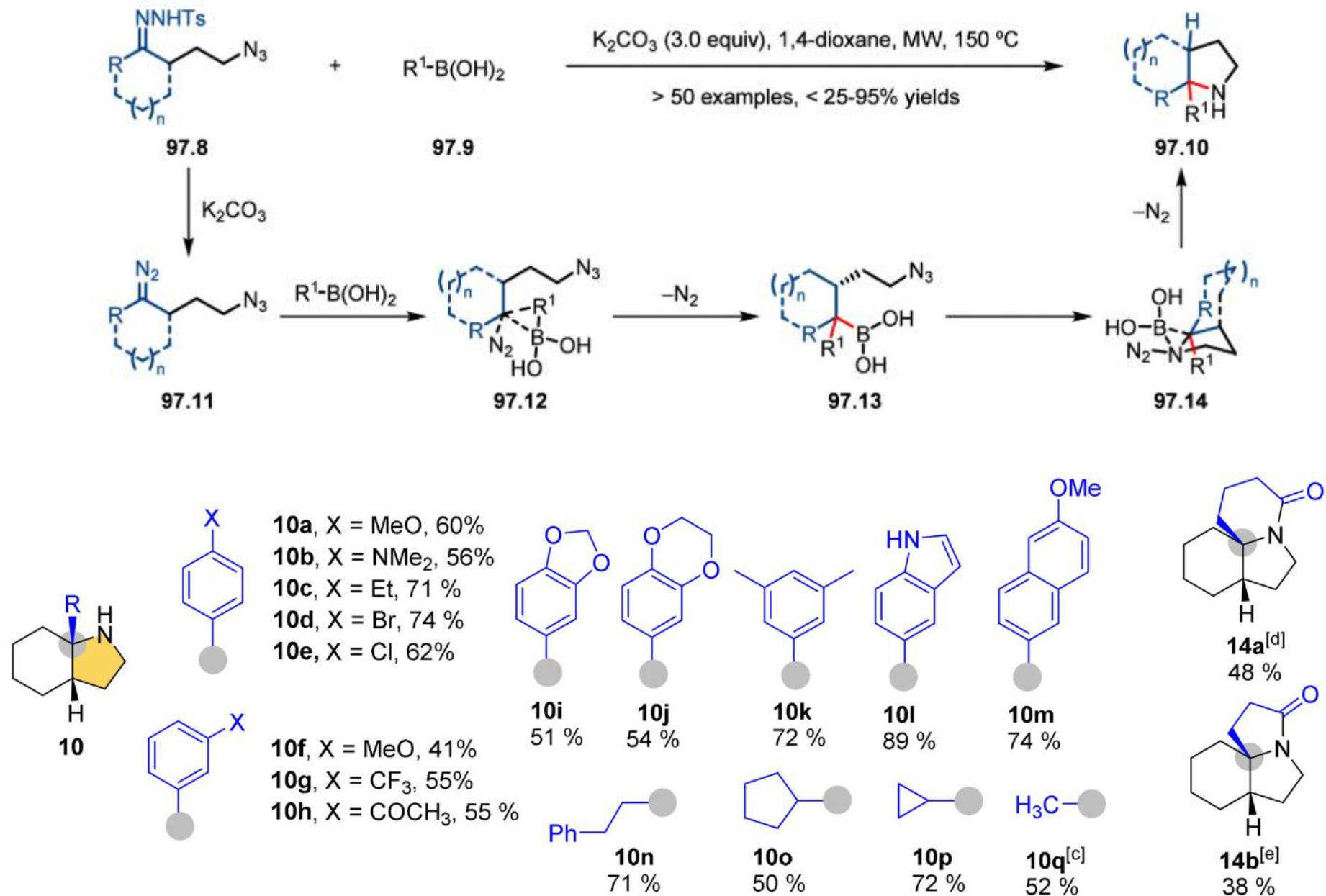




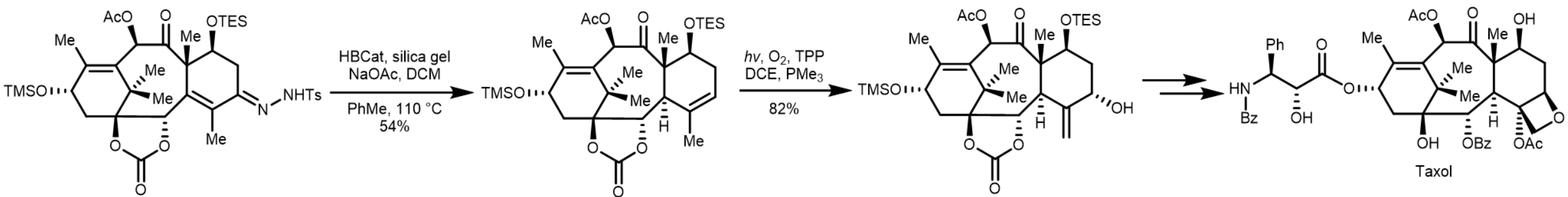
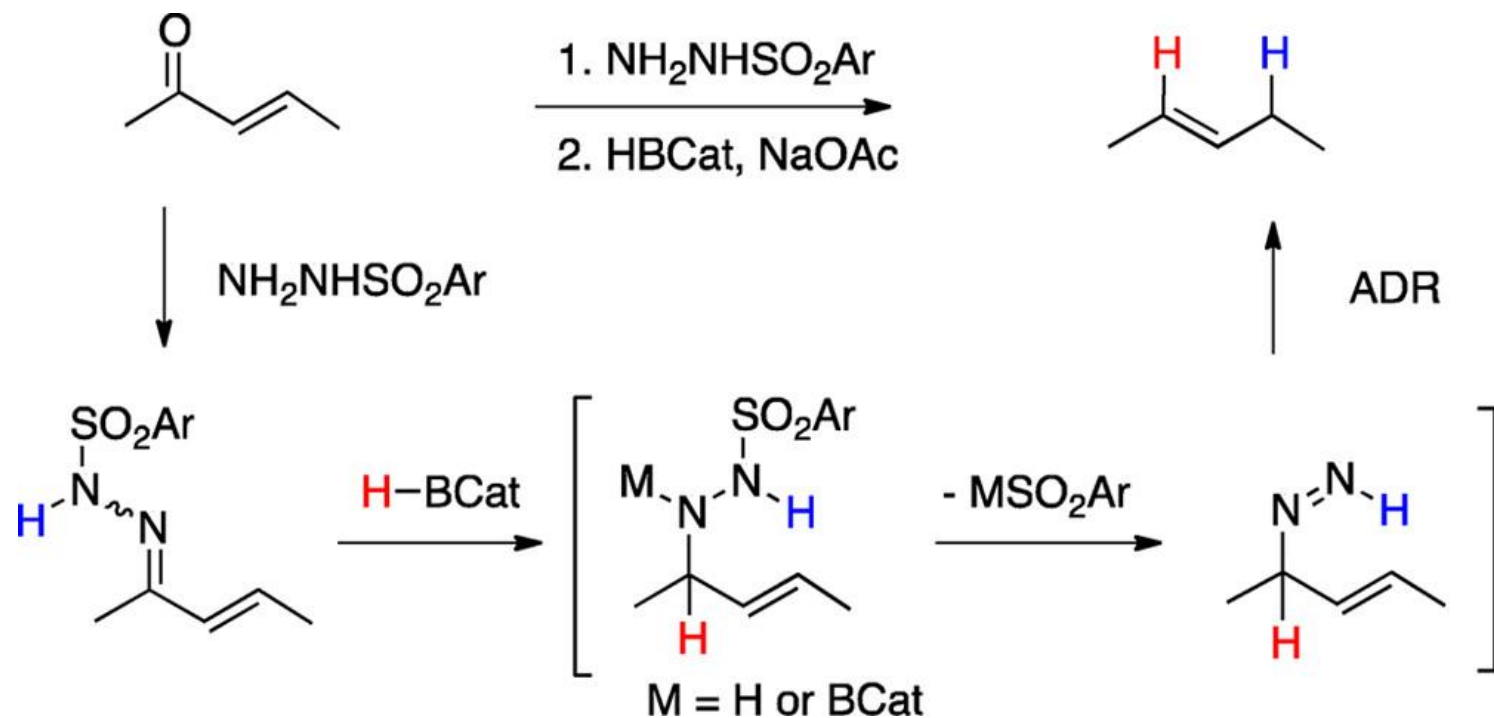
Miller, K. A.; *et al. J. Org. Chem.* **2017**, 82, 11655–11658.



Piersanti, G.; *et al. Eur. J. Org. Chem.* **2024**, 27, e202400035.

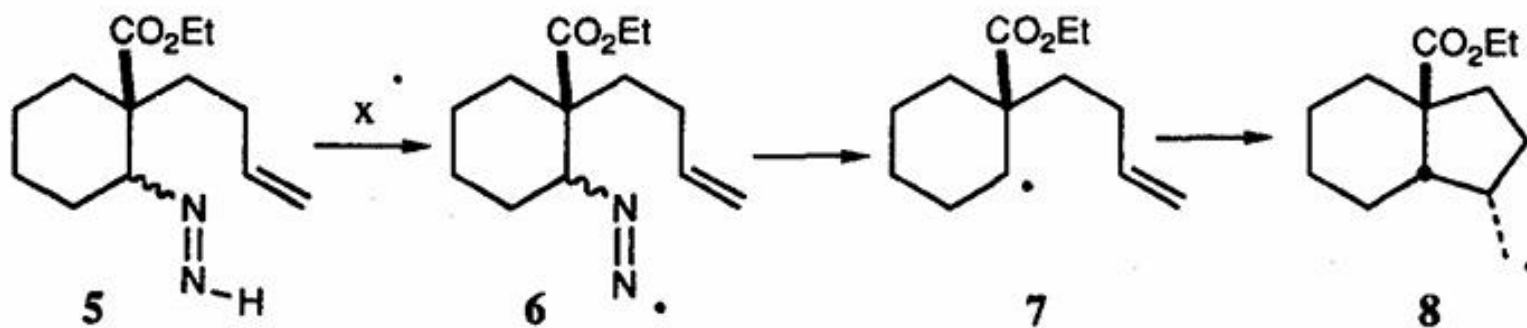
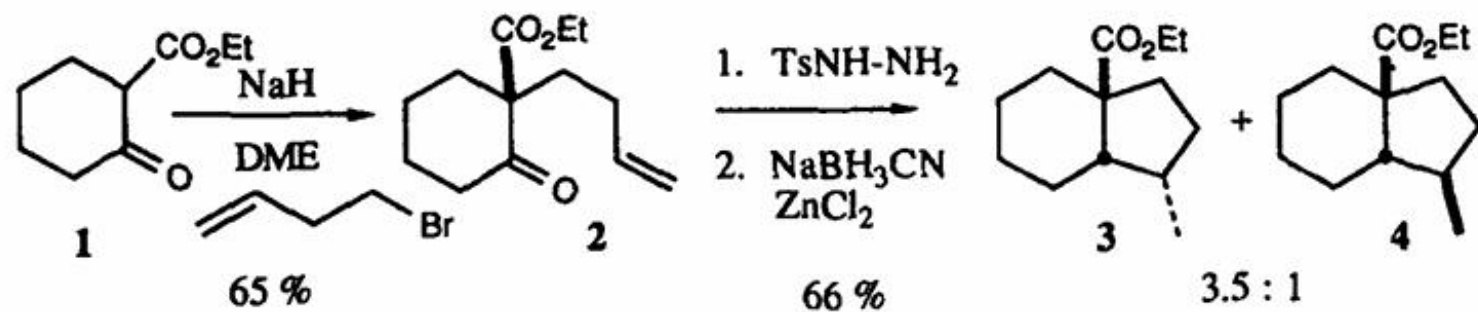


Diazeno rearrangement



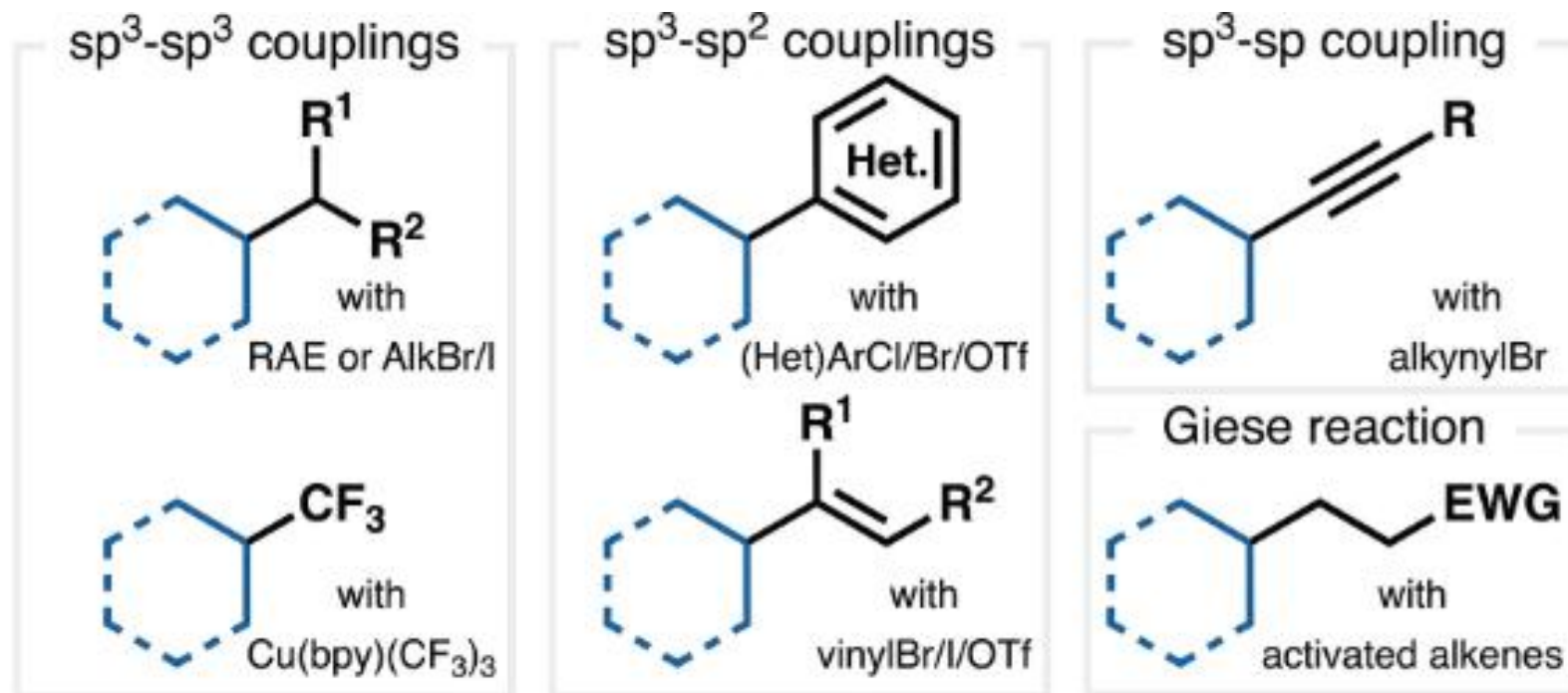
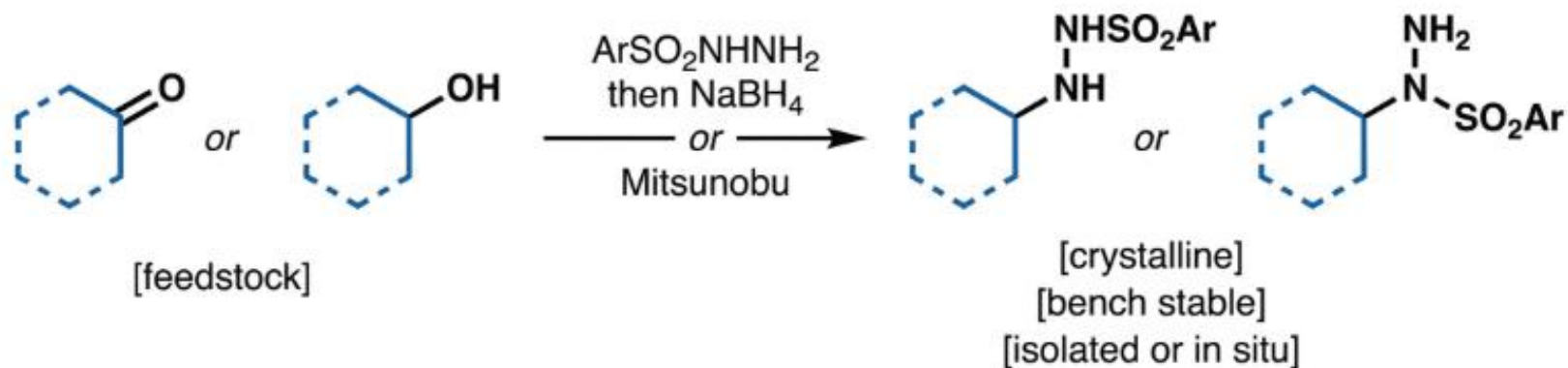
Li, C-C.; *et al. J. Am. Chem. Soc.* **2021**, *143*, 17862–17870.

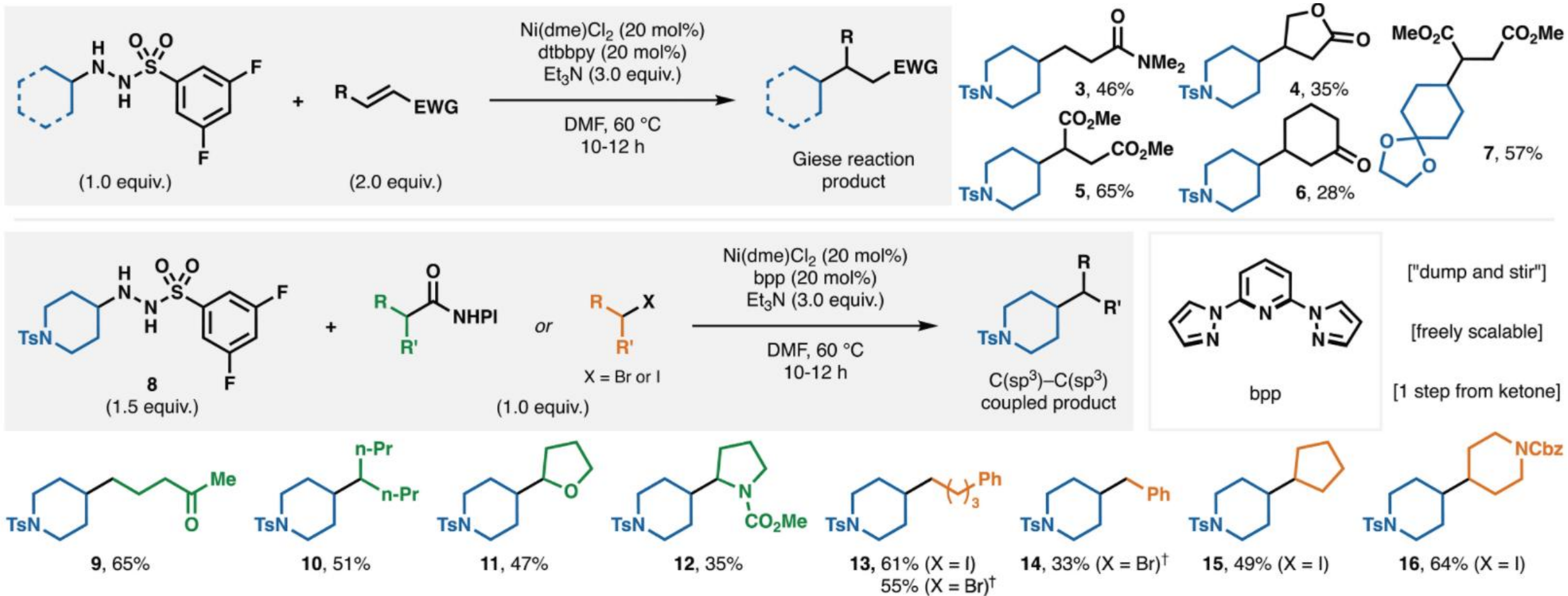
- 01 The Bamford–Stevens and Shapiro Reactions
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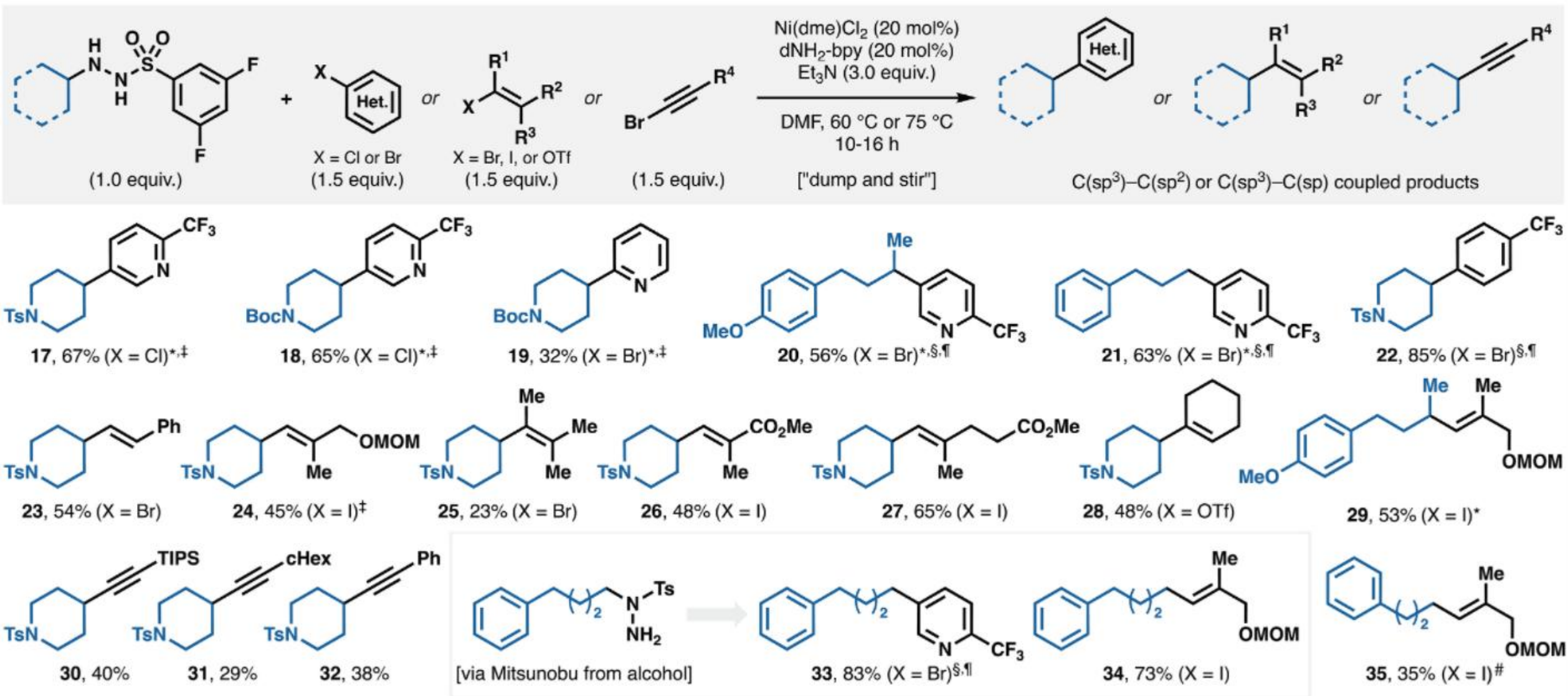


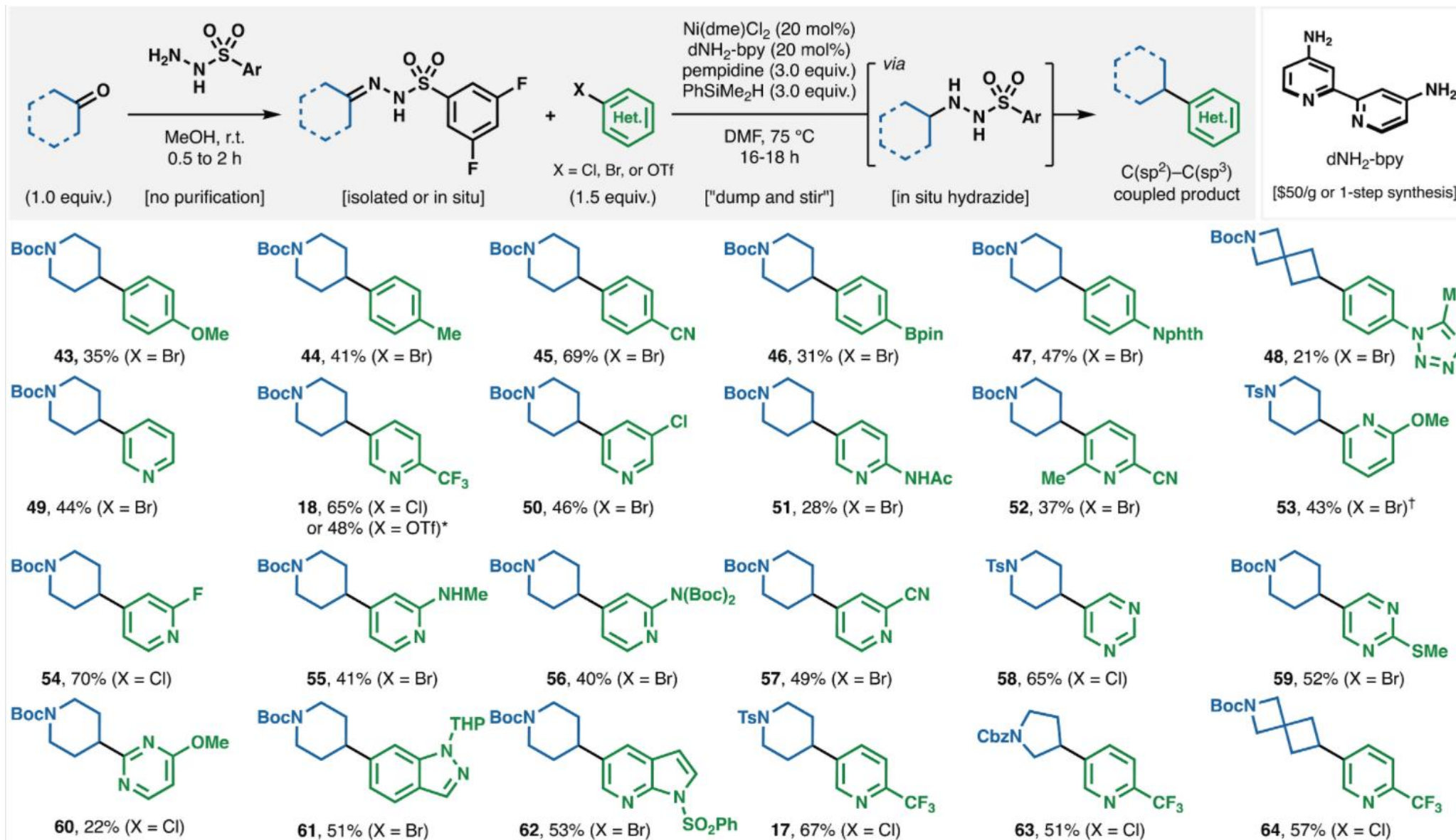
Taber, D.F.; *et al. Tetrahedron Lett.* **1993**, 34, 6209–6210.

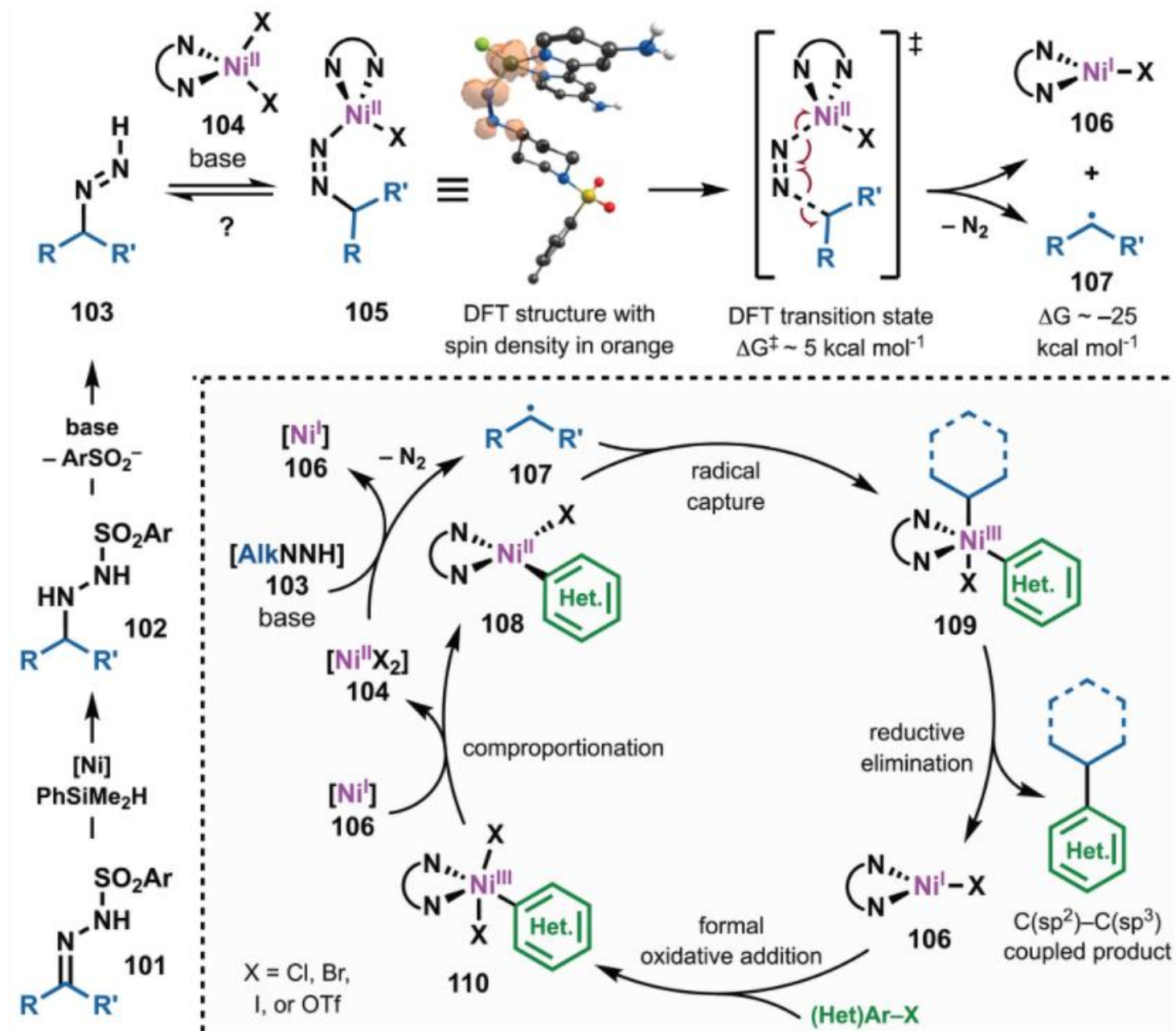
Sulfonyl hydrazides as a general redox-neutral platform for radical cross-coupling



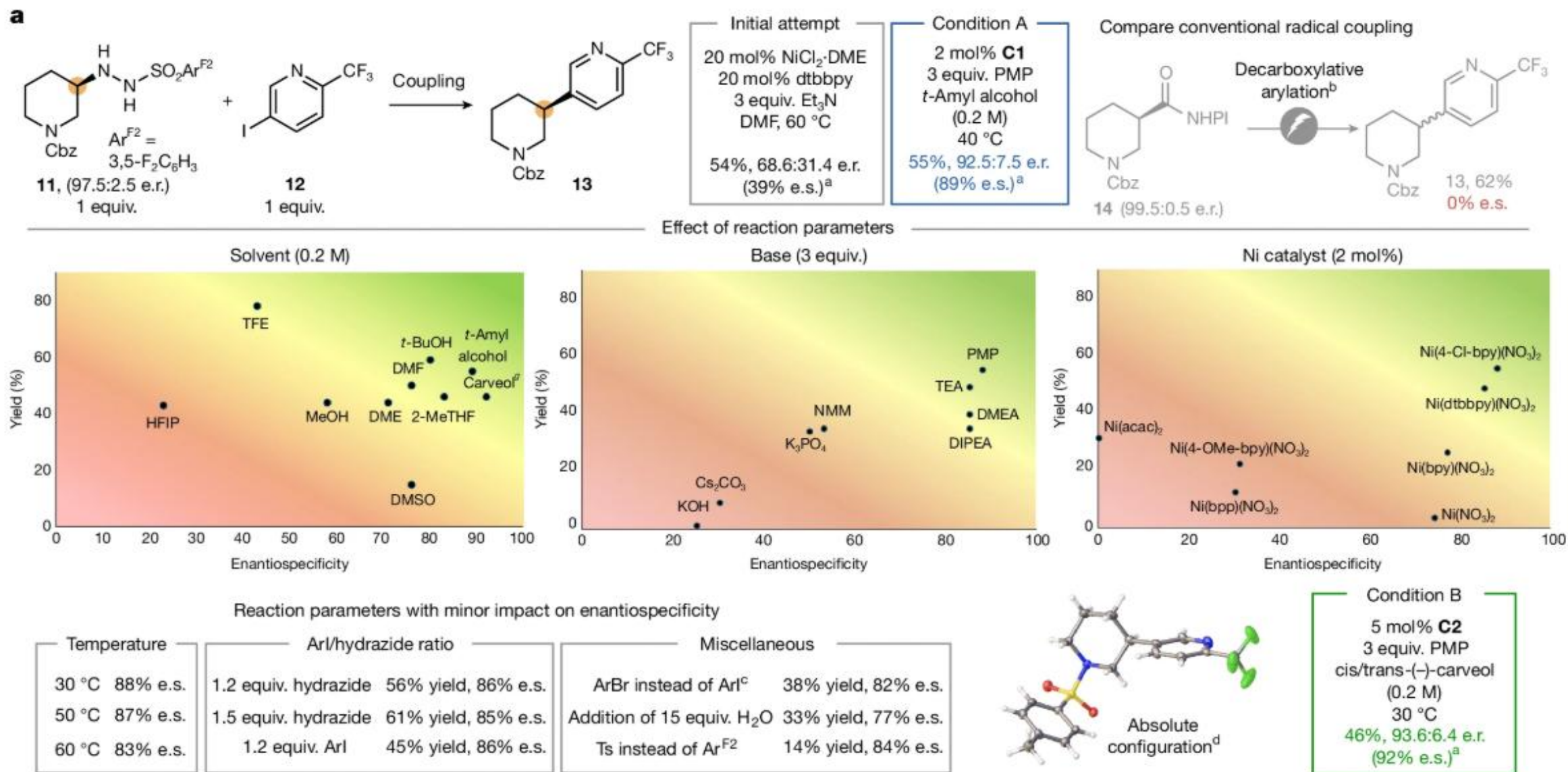


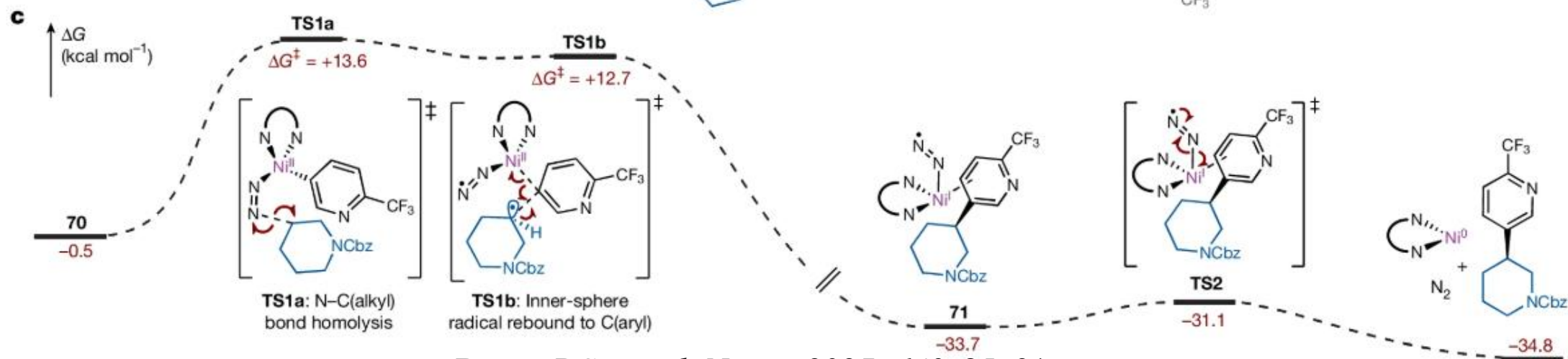
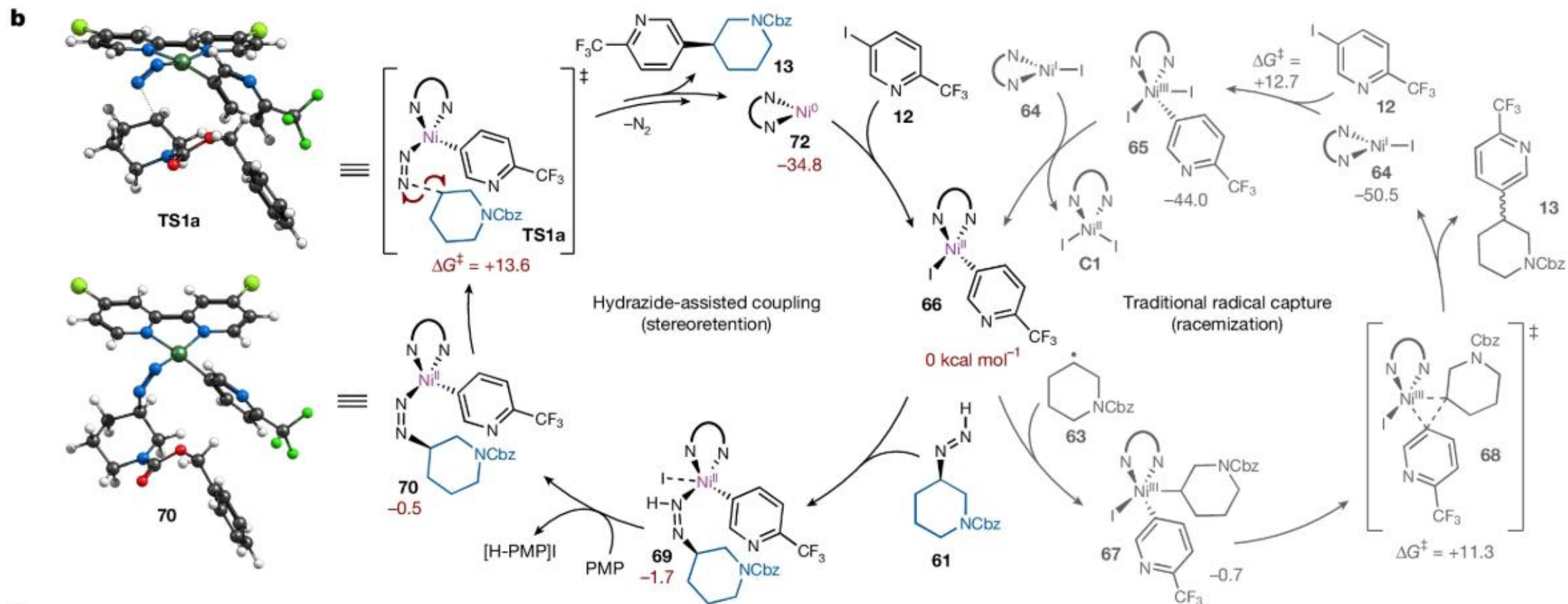




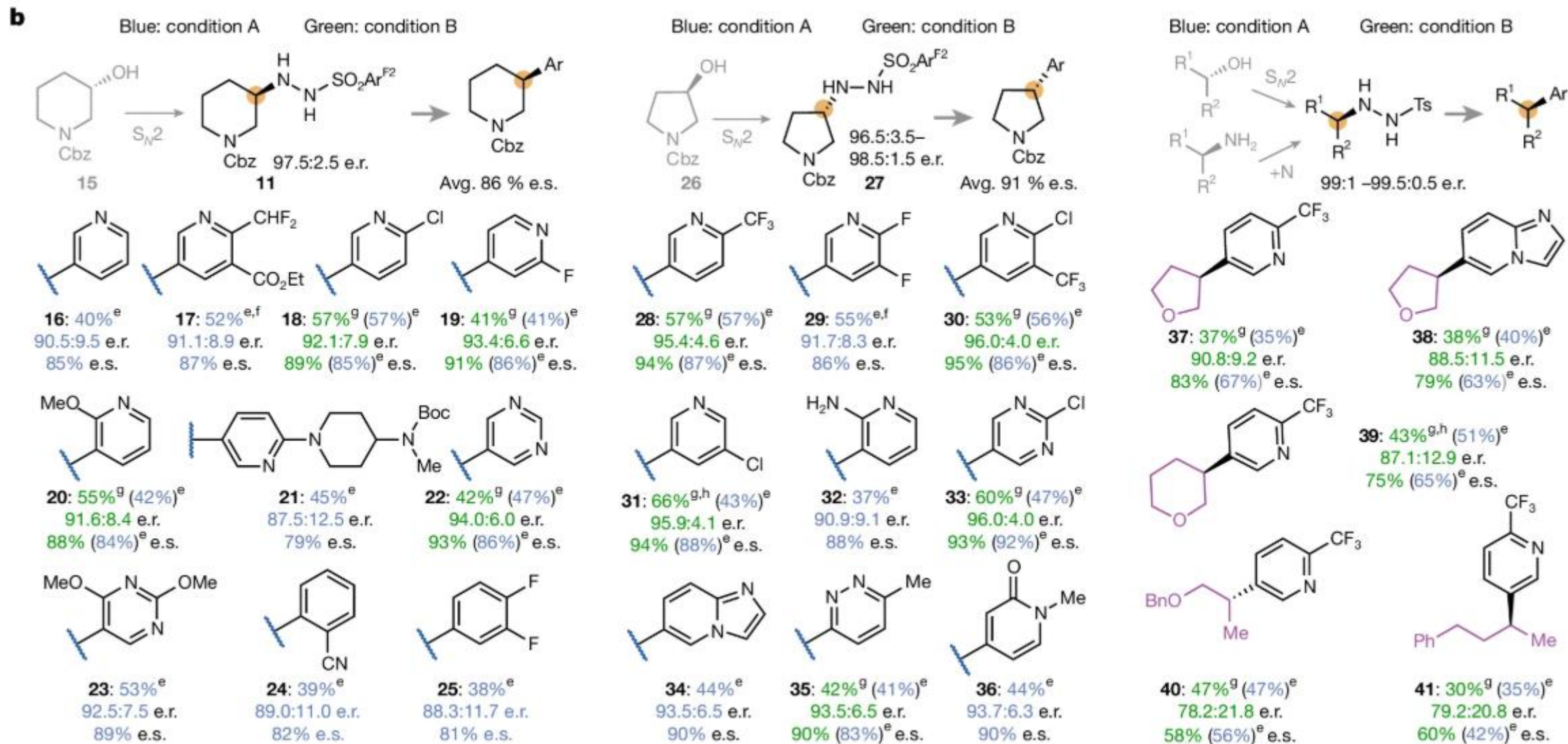


Stereoretentive radical cross-coupling

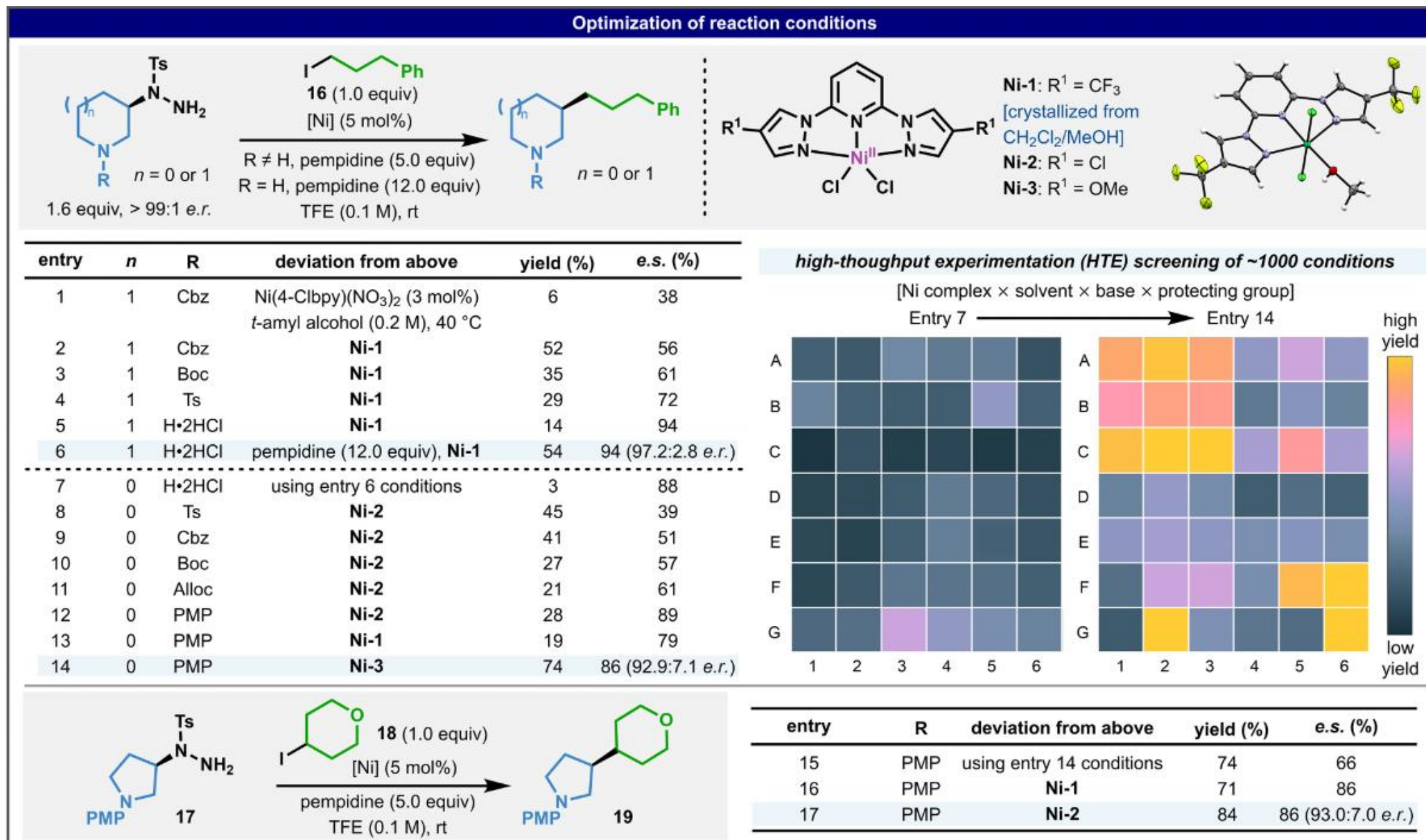


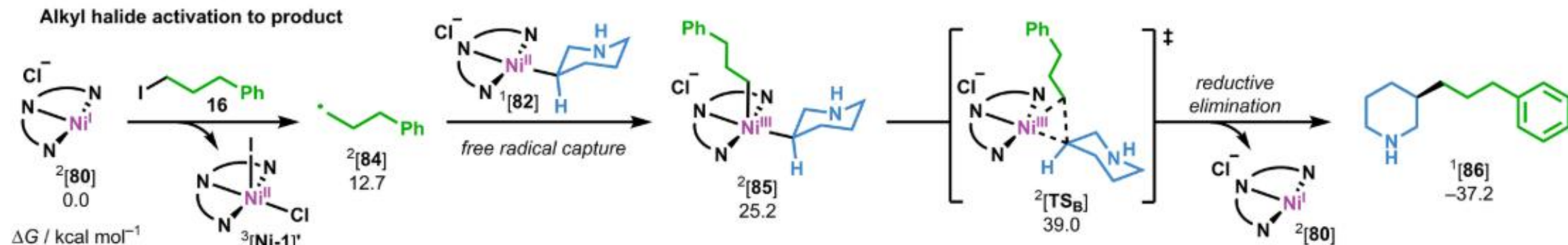


Baran, P.S.; *et al.* *Nature* **2025**, 642, 85–91.

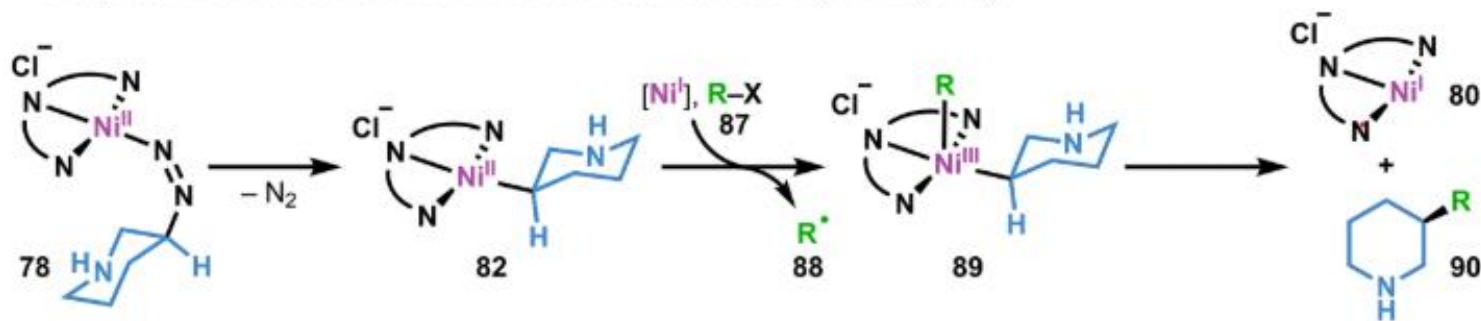


Stereoretentive radical-based alkyl-alkyl cross-coupling

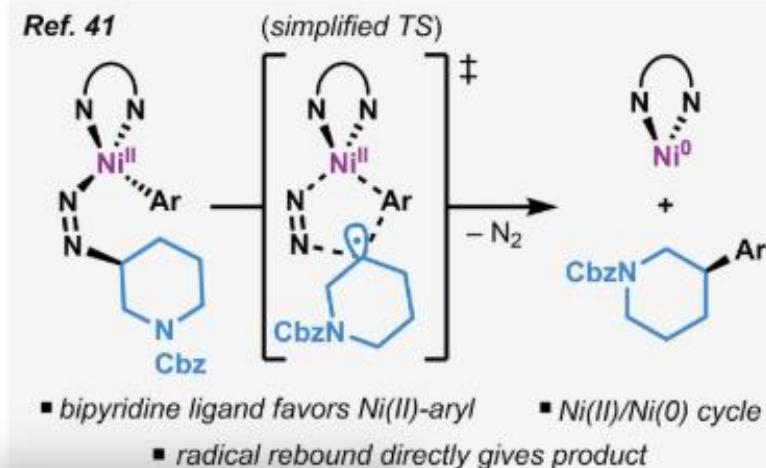


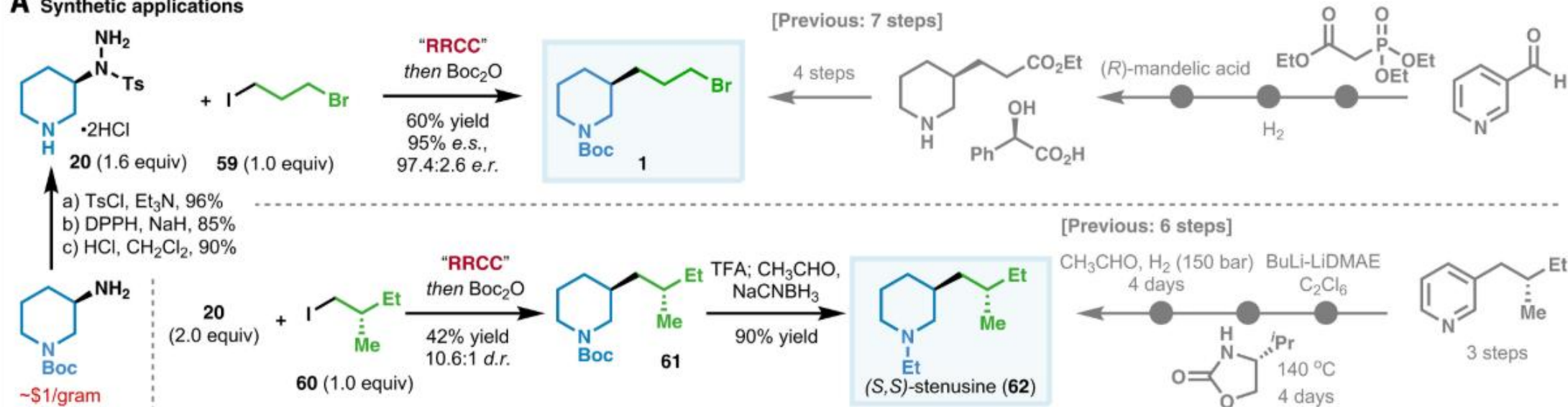
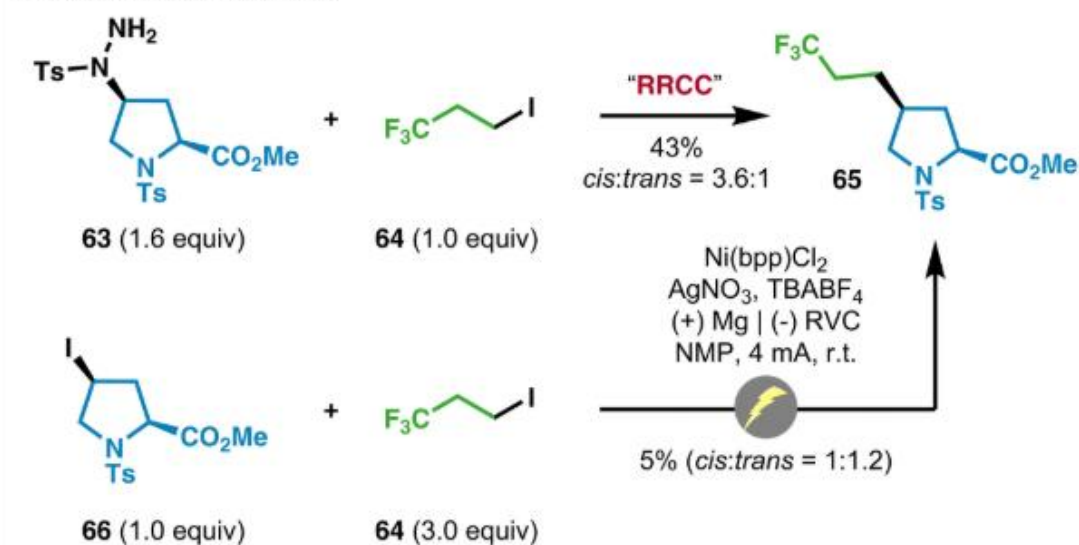


Comparison of stereoretentive RRCC to stereoretentive arylation (RCC)



- tridentate bpp ligand stabilizes Ni(II)-alkyl and promotes XAT
- radical rebound gives critical intermediate, but a second radical formation step (XAT) is still necessary
- productive Ni(I)/Ni(III) cycle



A Synthetic applications

B A diastereomeric case

C Gram-scale examples
