Silver (not proton) catalysis

General properties of silver

- ^{107}Ag (51.839%) and ^{109}Ag (48.161%) two stable isotopes
- Electron configuration: [Kr] $4d^{10}\ 5S^{1}$
- +1 most common oxidation state
- Highest electrical conductivity of all metals
- Highest thermal conductivity of all metals
- Among the highest optical reflectivities (silver mirror experiment)
- Silver bullets can kill werewolves and vampires

Silver salts of note

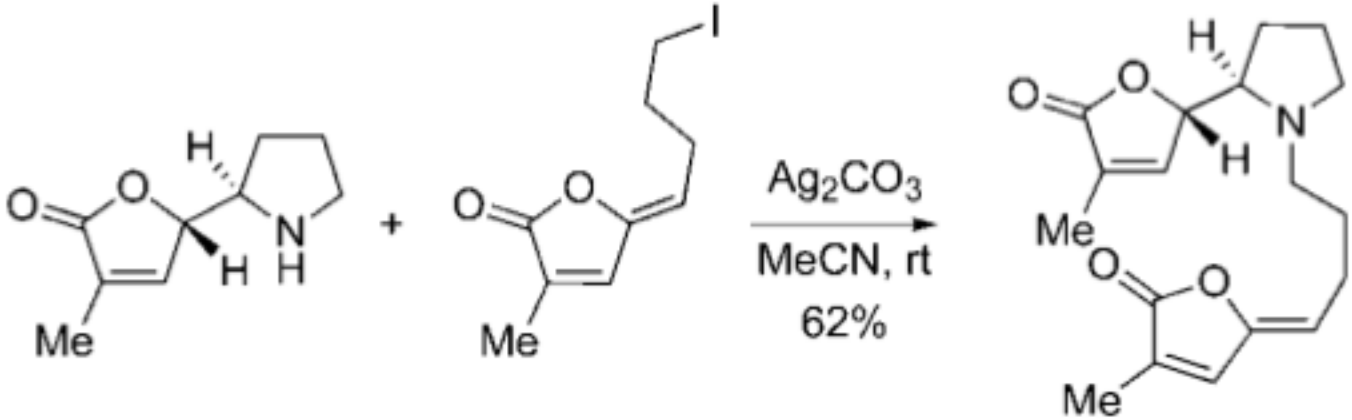
- Silver iodide
  - Used in cloud seeding and weather modification
  - Used in silver-based photography methods
- Silver nitrate
  - Used as an antiseptic
  - Yellow stain in stained glass
- Silver oxide
  - Used as anode in watch batteries

General modes of silver (I) reactivity

I. Ag halide abstraction
II. Ag catalyzed cross-coupling
III. Ag catalyzed cyclization (cycloisomerization)
IV. Ag acetylide formation
V. Ag (I) as either a σ-Lewis acid or π-Lewis acid
VI. Ag catalyzed radical generation with reoxidant

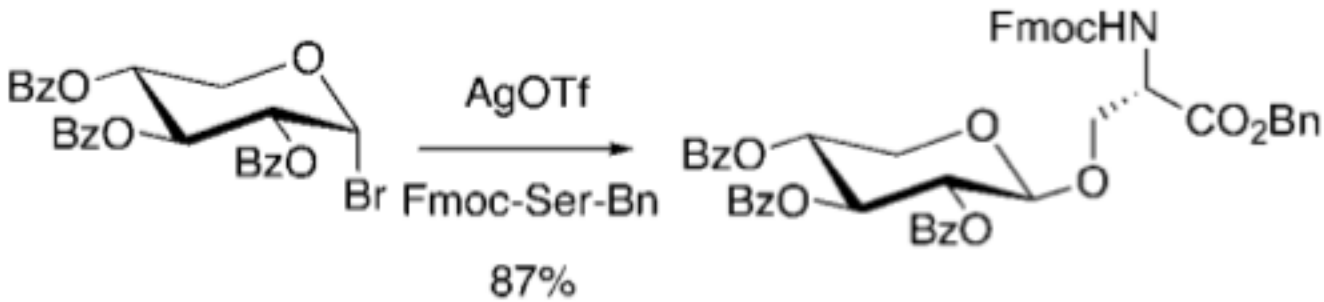
I. Ag halogenophilicity

S_N1



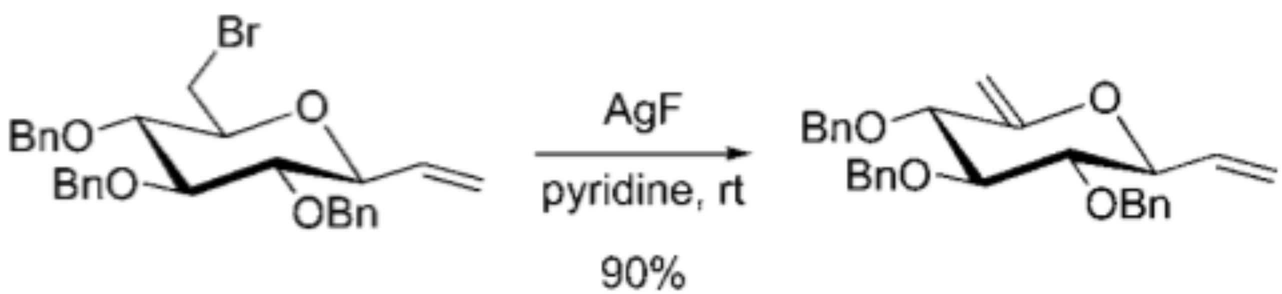
Honda, T.; Ushiwata, M.; Mizutani, H. *Tetrahedron Lett.* **2006**, *47*,6251–6254.

glycosylation



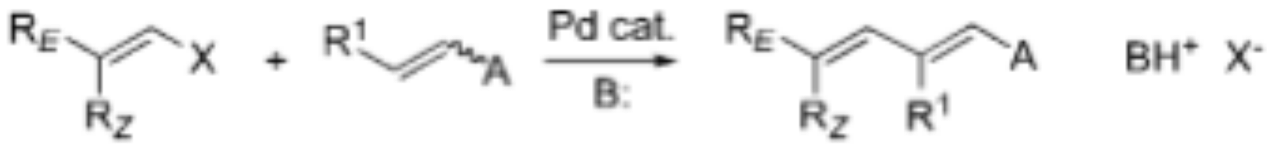
Schultheiss-Reimann, P.; Kunz, H. *Ang. Chem., Int. Ed.* **1983**, *22*,62–63.

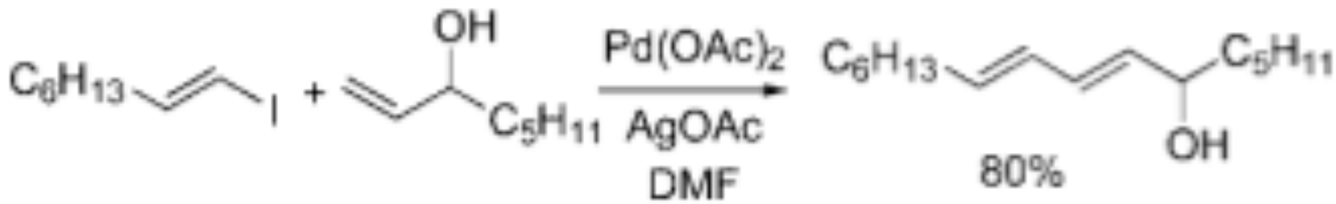
elimination

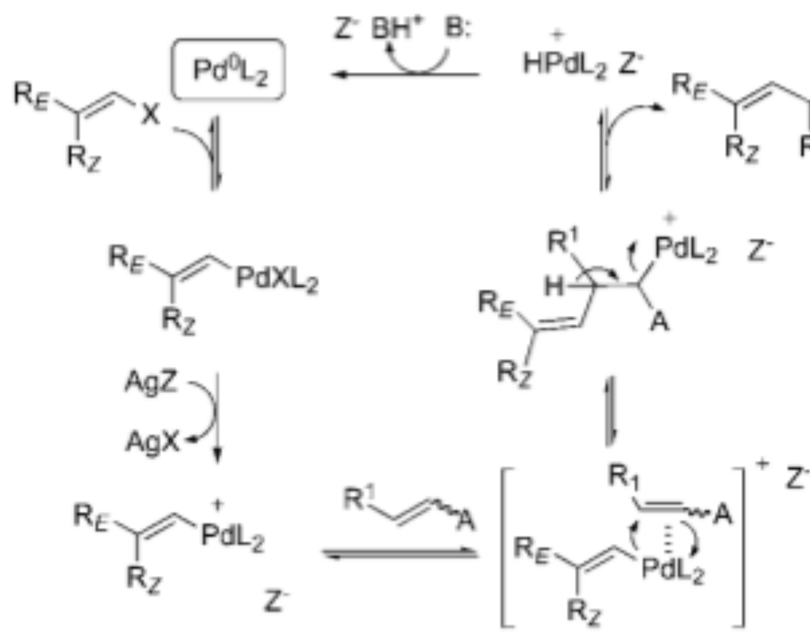


Jürs, S.; Werschkun, B.; Thiem, J. *Eur. J. Org. Chem.* **2006**, 4451-4462.

I. Ag in Pd catalyzed Heck reactions



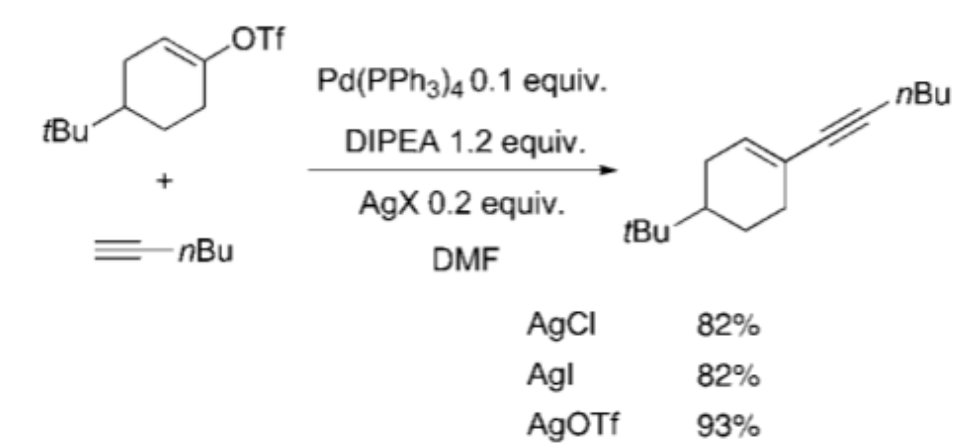


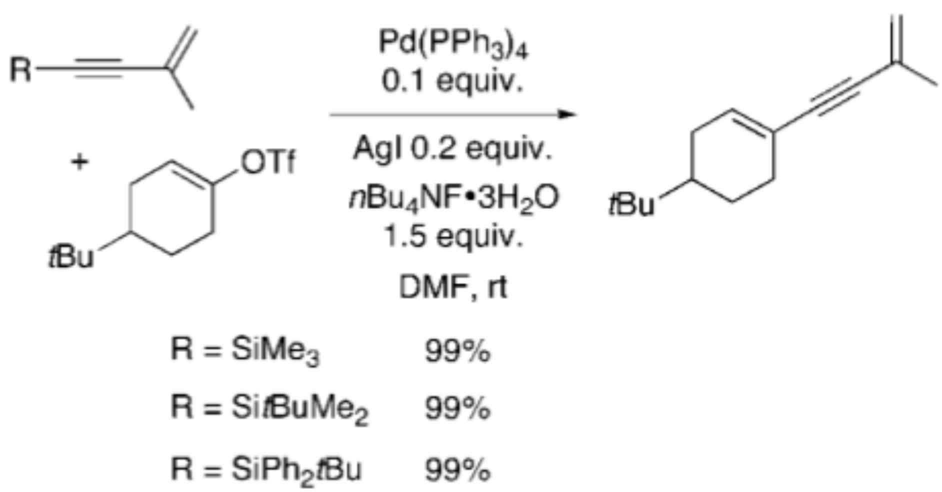


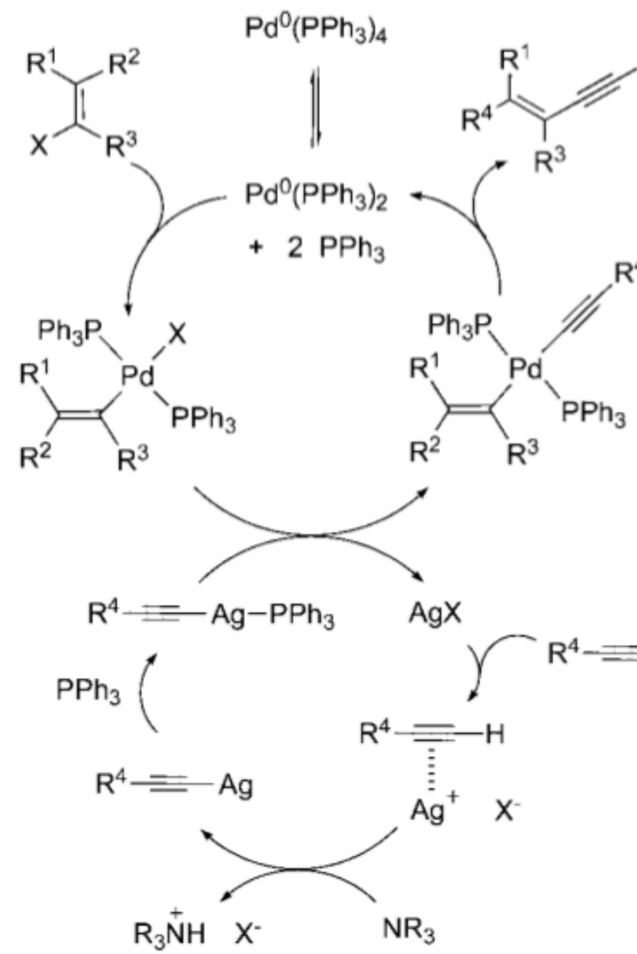
Chem. Rev. **2008,** 108, 3149–3173

Abelman, M. M.; Oh, T.; Overman, L. E. *J. Org. Chem.* **1987**, *52*, 4130–4133.

II. Ag catalyzed enyne synthesis







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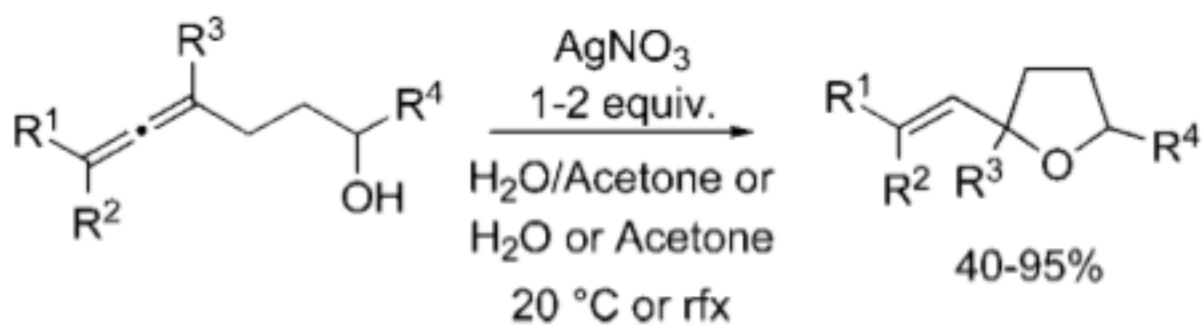
Halbes-Letinois, U.; Pale, P.; Berger, S. *J. Org. Chem.* **2005**, *70*, 9185–9190.

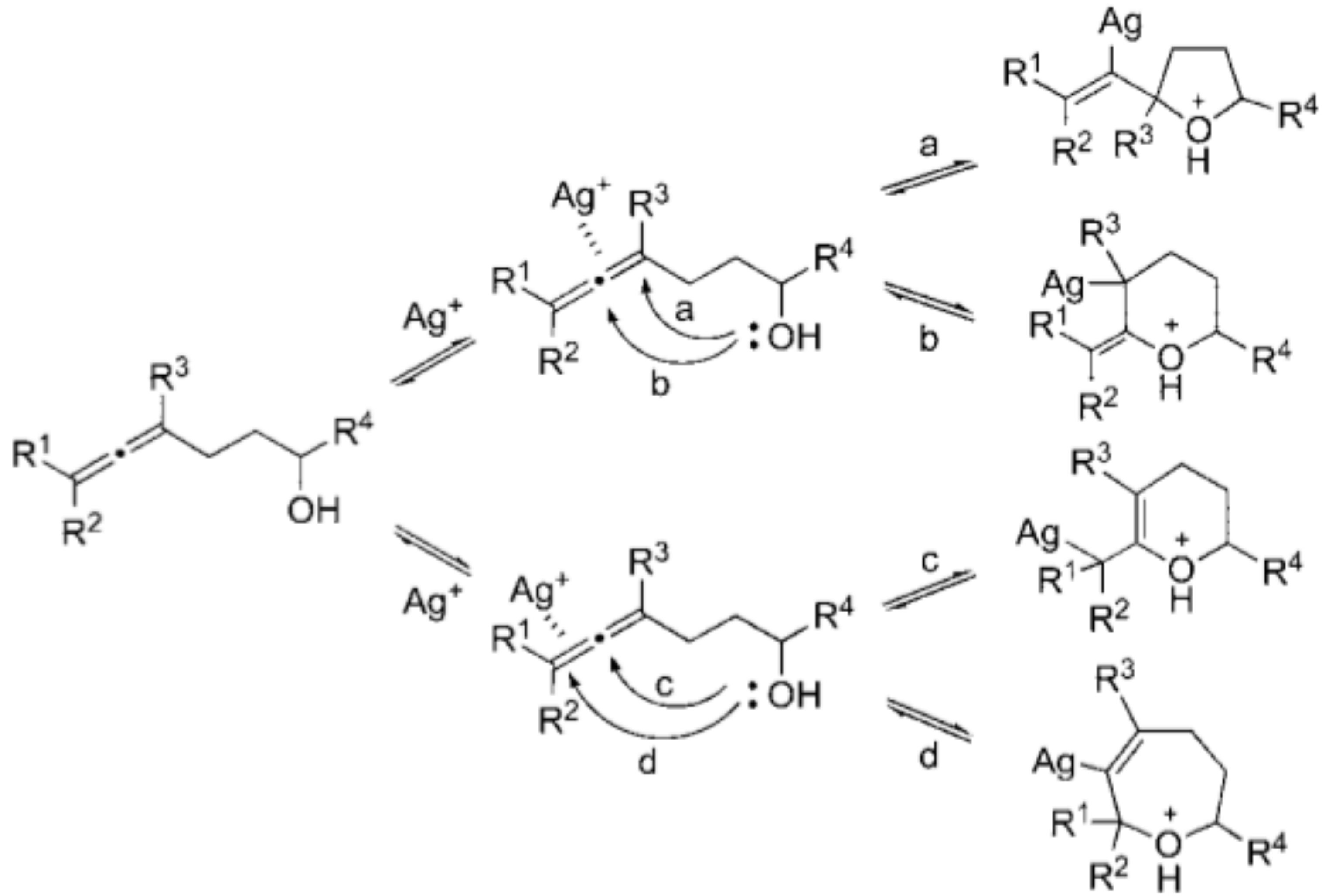
III. Intramolecular heterocyclization



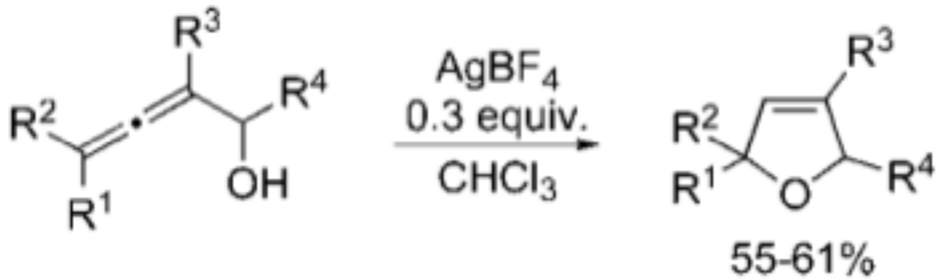
Balme, G. Ph.D. Thesis, University Claude Bernard, Lyon, 1979.

Audin, P.; Doutheau, A.; Ruest, L.; Goré, J. *Bull. Soc. Chim. Fr* **1981**, II-313–318.

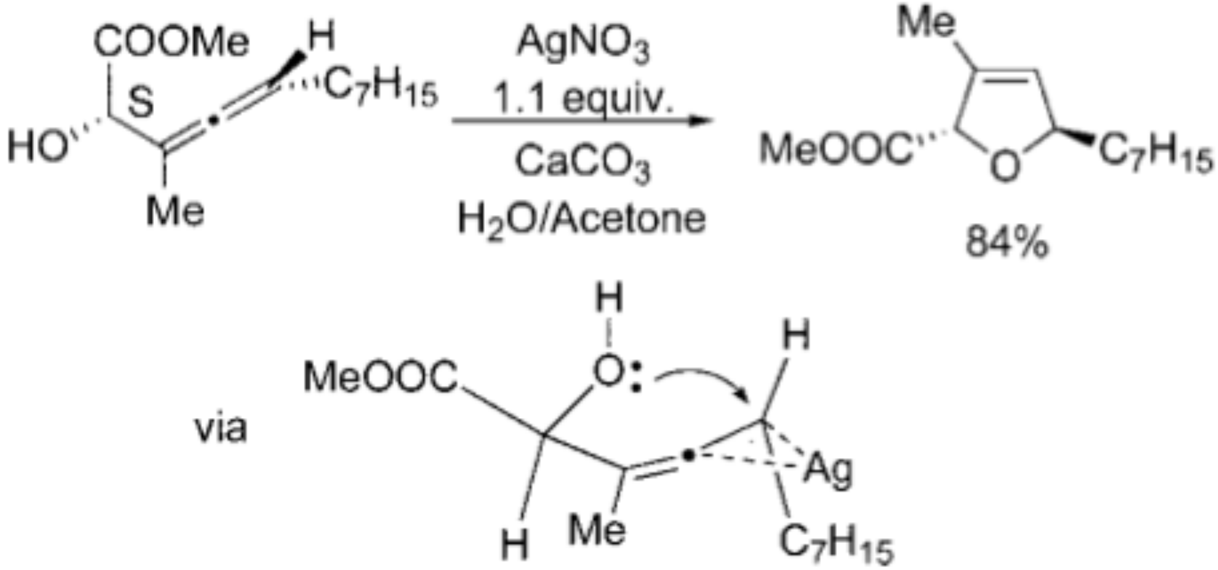
III. Intramolecular heterocyclization



III. Intramolecular heterocyclization

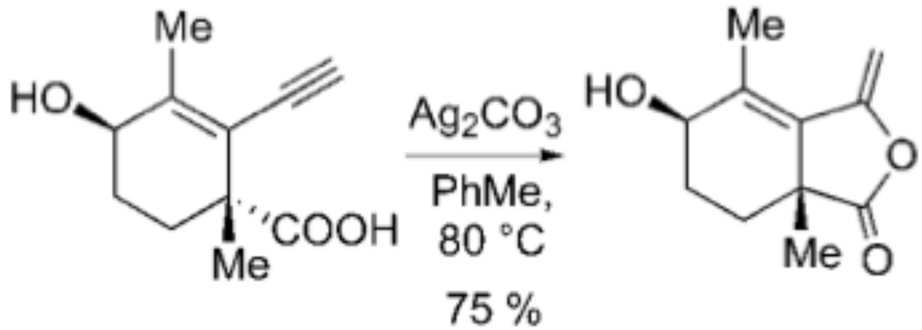


Olsson, L. I.; Claesson, A. *Synthesis* **1979**, 743–745.

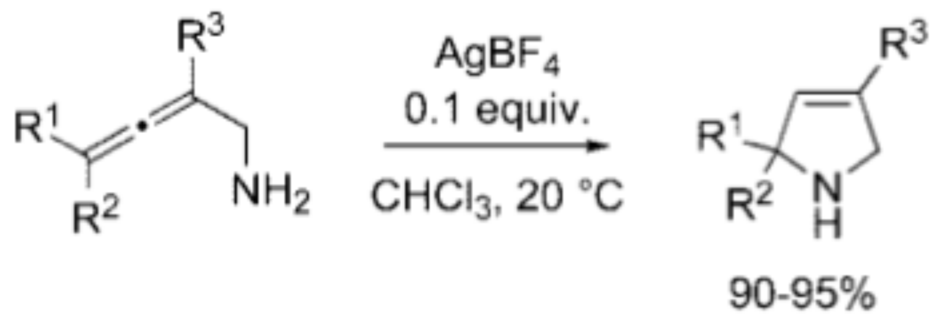


Marshall, J. A.; Pinney, K. G. *J. Org. Chem.* **1993**, *58*, 7180–7184.

III. Intramolecular heterocyclization

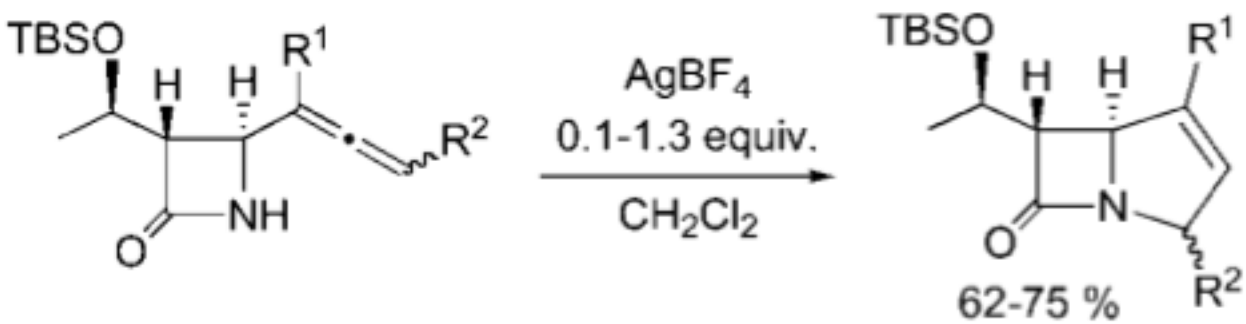


Huang, P. Q.; Zhou, W. S. *Tetrahedron: Asymmetry* **1991**, *2*, 875– 878.



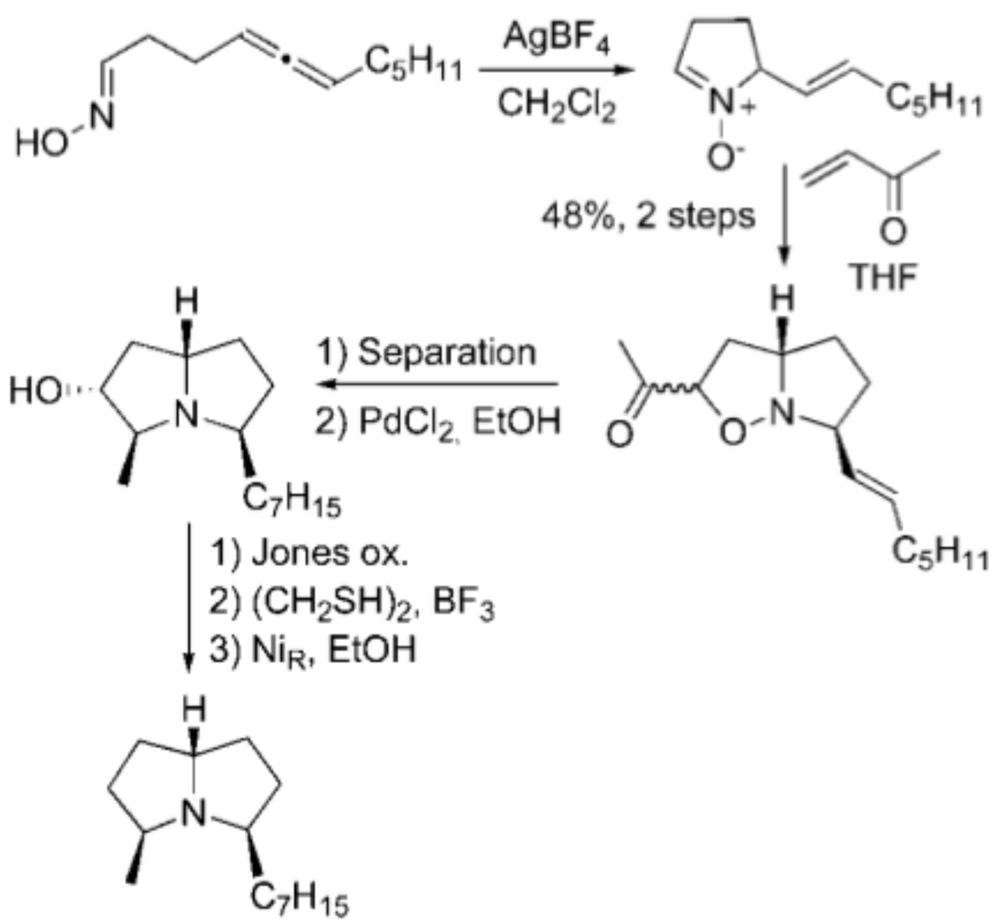
Claesson, A.; Sahlberg, C.; Luthma, K. *Acta Chem. Scand.* **1979**, *B-33*, 309–310.

III. Intramolecular amidation



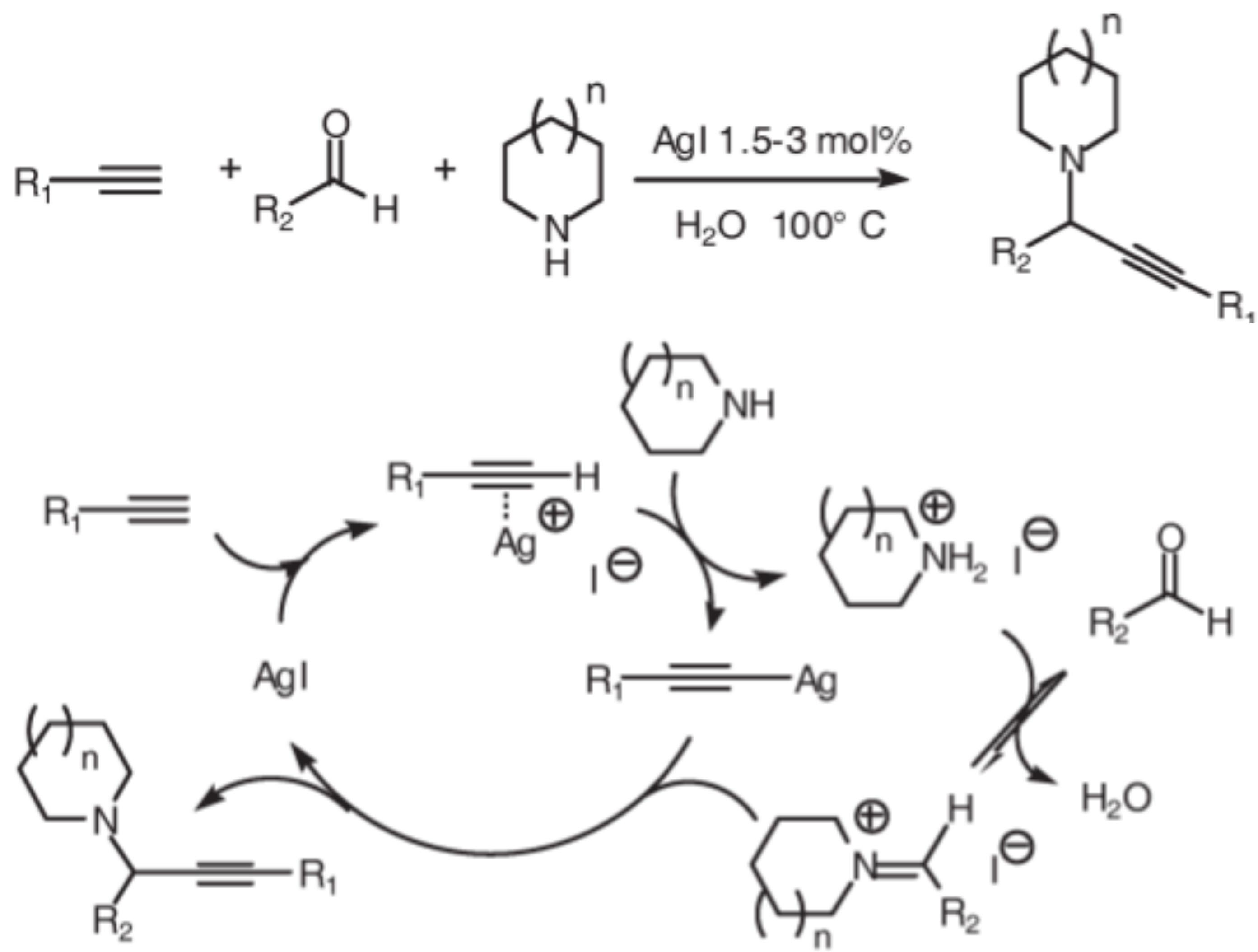
Prasad, J. S.; Liebeskind, L. S. *Tetrahedron Lett.* **1988**, *29*, 4253– 4256.

III. Application to a pyrrolizidine alkaloid



Lathbury, D. C.; Gallagher, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1017–1018.

IV. Three component coupling



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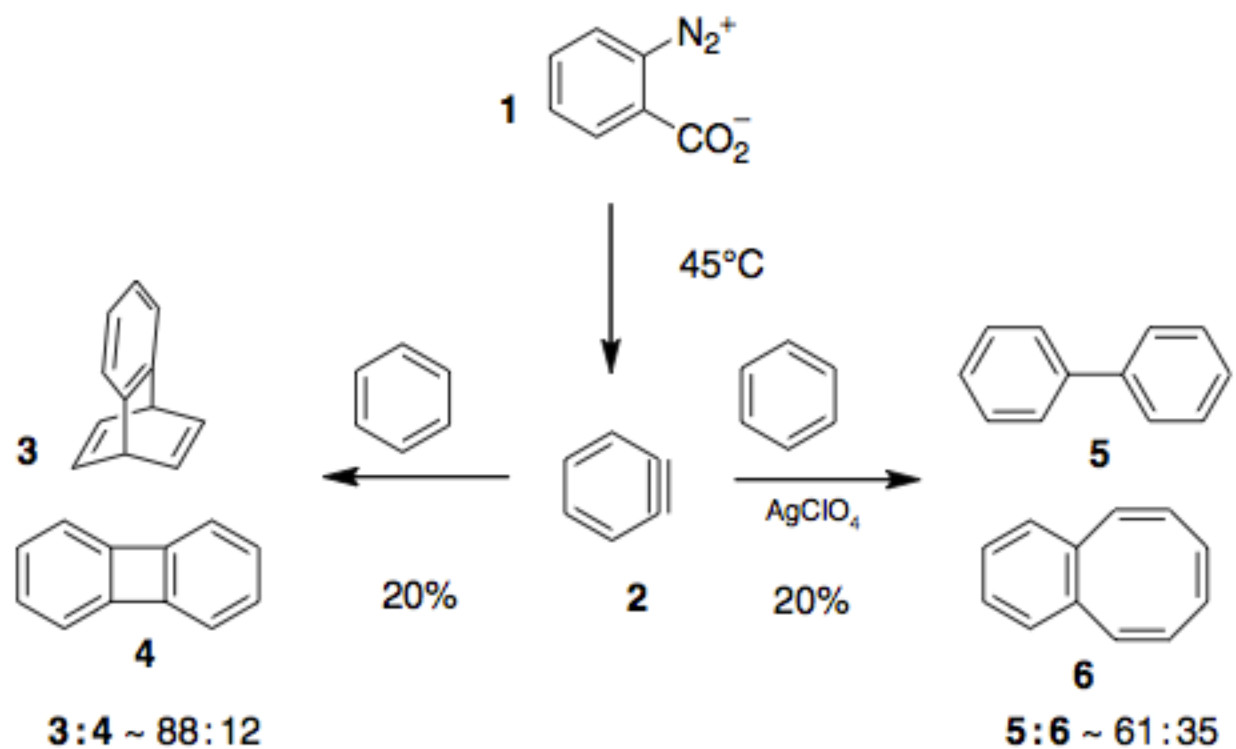
V. Ag cayalyzed cycloadditions



(a)Friedman,L.,*J.Am.Chem.Soc*.**1967**,89,3071–3073;(b)
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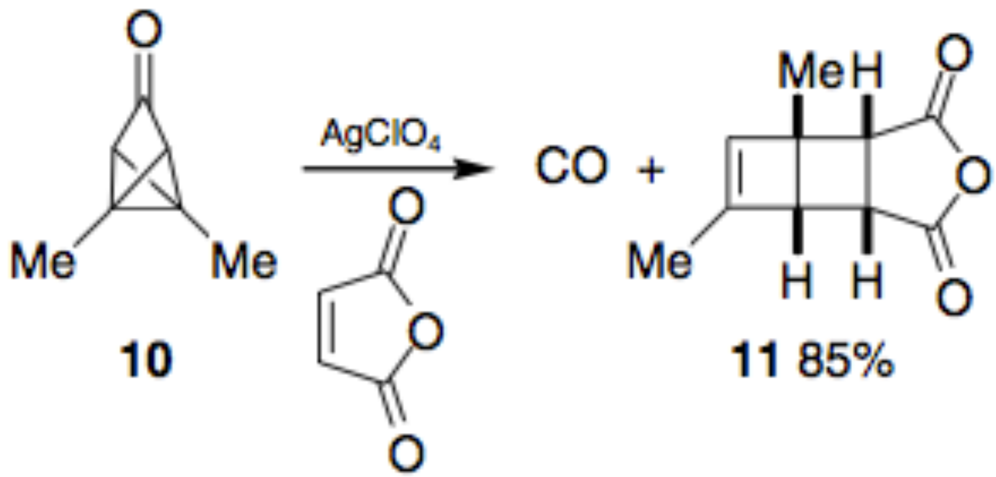
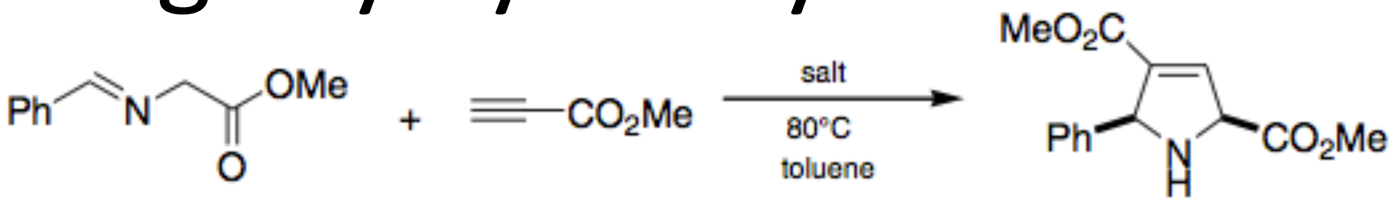
7. Paquette, L. A., *Chem. Commun*. **1971**, 1076–1077.

V. Ag cayalyzed cycloadditions

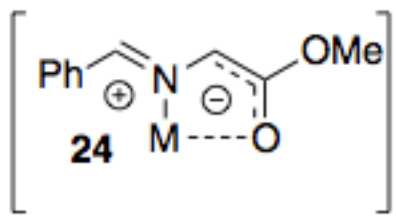


Ona, H.; Sakai, M.; Suda, M.; Masamune, S., *Chem. Commun*. **1973**, 45–46.

V. Ag cayalyzed cycloadditions



21 **22** **23**



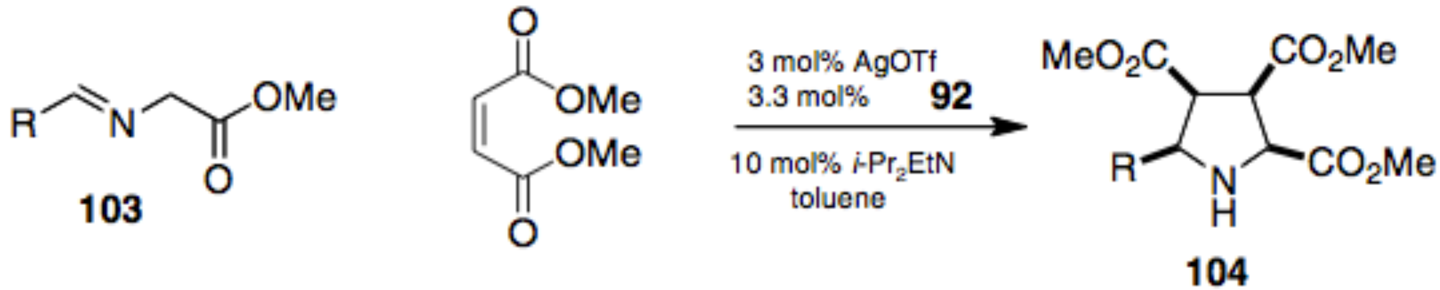
24

Entry	Lewis Acid[a]	$t_{1/2}$ of **21** (h)	Yield (%)[b]
1	None	38	94
2	CH_3COOH	1.8	0
3	AgOAc	3.25	95
4	$Zn(OAc)_2 \cdot 2H_2O$	3.0	88
5	$LiOAc \cdot 2H_2O$	5.5	93
6	$Mg(OAc)_2$	8.75	0

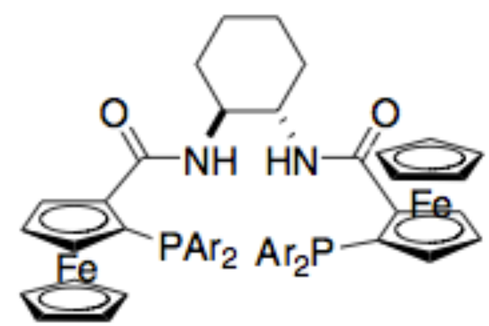
[a] Run with 1.5 equiv.
[b] Determined by NMR with hexamethyl benzene as internal standard.

11. Grigg, R.; Gunaratne, H. Q. N., *Chem. Commun*. **1982**, 384–386.

V. Asymmetric [3+2]



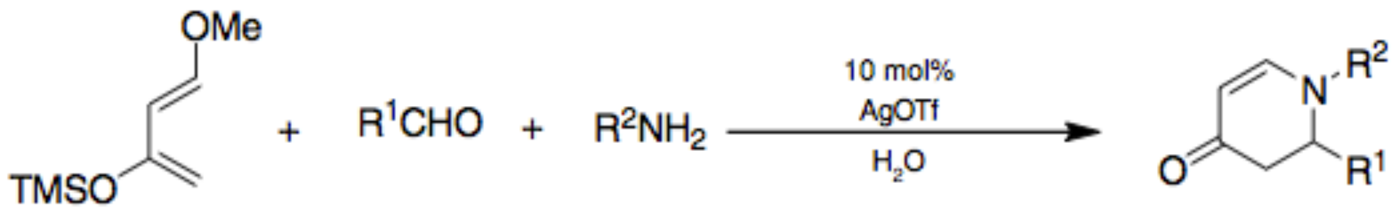
Entry	R	Yield (%)	ee (%)
1	Ph	87	87
2	*p*-Me-C_6H_4	93	88
3	*p*-MeOC_6H_4	98	92
4	*p*-Cl-C_6H_4	96	92
5	*p*-F-C_6H_4	96	90
6	*p*-CN-C_6H_4	90	96
7	*o*-Xl-C_6H_4	96	86
8	*o*-Me-C_6H_4	97	90
9	1-Naphthyl	73	85
10	2-Naphthyl	98	97
11	3-Pyridyl	98	84
12	*i*-Pr	82	70
13	*c*-Hex	82	81



(*S*, *S*, S_p)- FAP (**91**), Ar=Ph
(*S*, *S*, S_p)- xylyl-FAP (**92**)
Ar=3,5-dimethylphenyl

Longmire, J. M.; Wang, B.; Zhang, X., *Tetrahedron Lett*. **2000**, 41, 5435–5439;
You, S. -L.; Hou, X. -L.; Dai, L. -X; Gao, B. -X.; Sun, J., *Chem. Commun*. **2000**, 1933–1934.

V. [3+3] cycloaddition

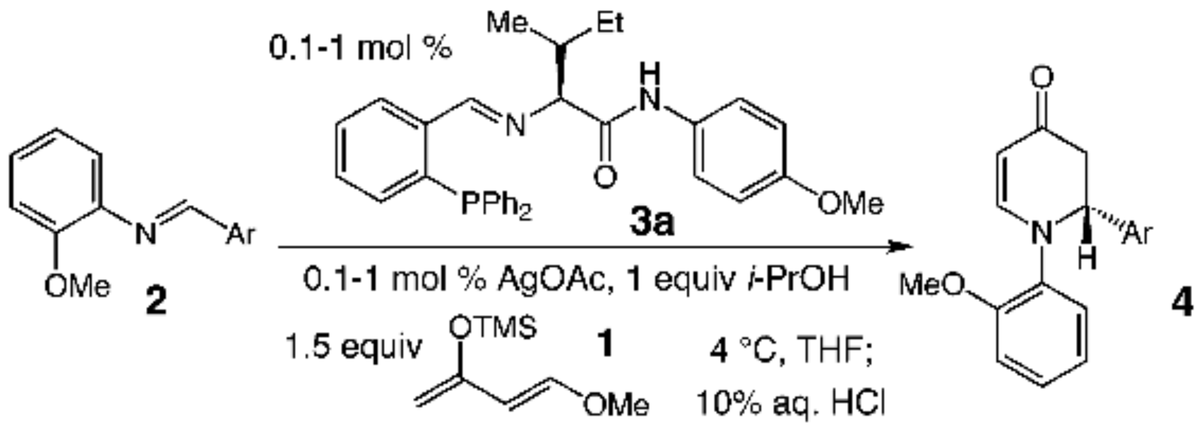


Entry	R^1	R^2	Yield (%)
1	Ph	Ph	63
2[b]	Ph	Ph	80
3[b,c]	Ph	*p*-BrC_6H_4	90
4[b]	Ph	*o*-$MeOC_6H_4$	56
5	*c*-C_6H_{12}	Ph	70
6[b]	*c*-C_6H_{12}	Ph	51
7[b]	$PhCH_2CH_2$	Ph	53
8	*i*-Pr-CH_2	Ph	72

[a] With 1.5 equiv of aldehyde and diene relative to amine.
[b] With 10 mol% Triton X-100 added.
[c] With 3 equiv diene.

Loncaric, C.; Manabe, K.; Kobayashi, S., *Adv. Synth. Catal*. **2003**, 345, 475–477.

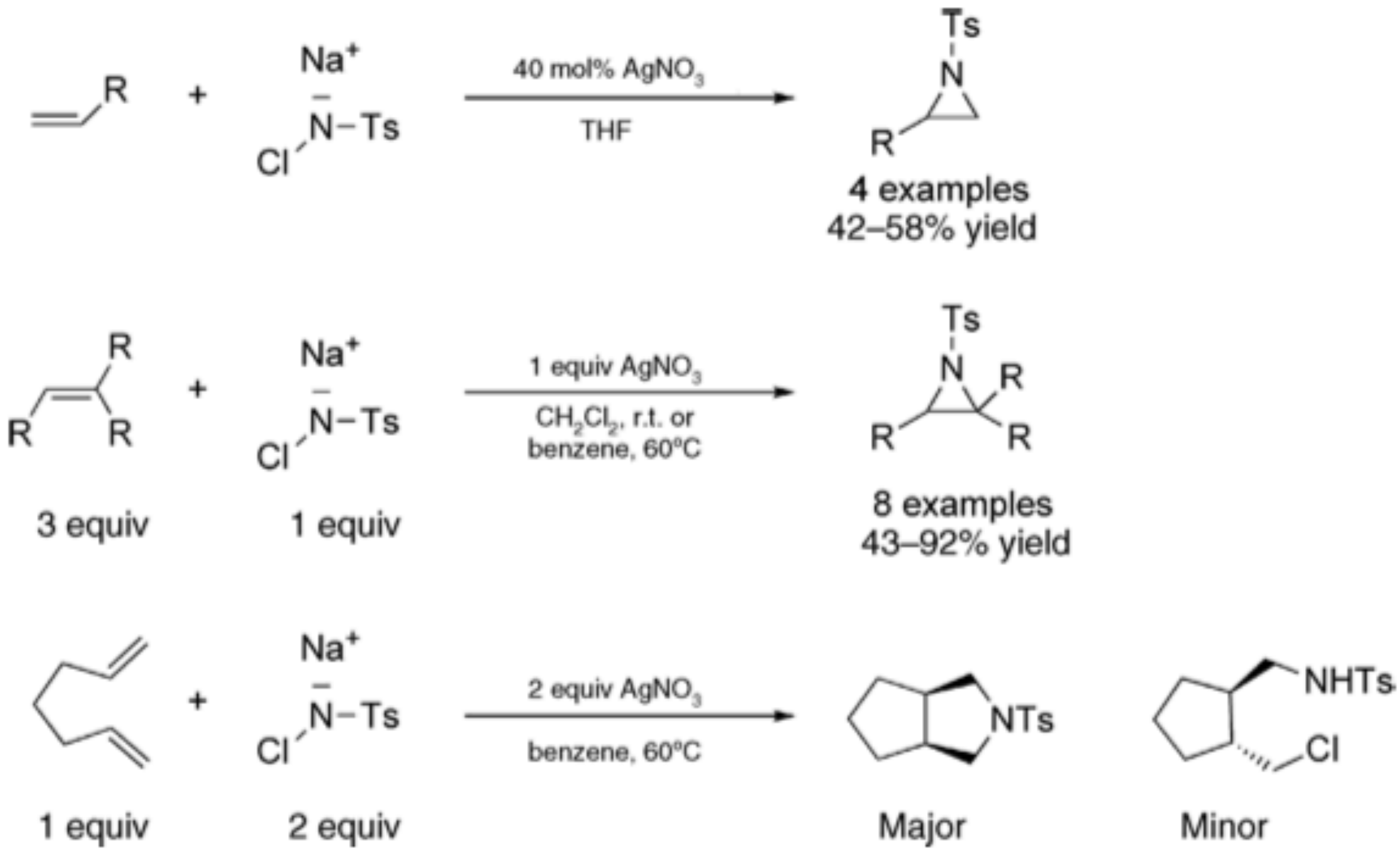
V. Asymmetric [3+3]



entry	Ar		3a, AgOAc (mol %)	yield (%)[b]	ee (%)[c]
1	Ph	**2a**	1.0	94	93
2	Ph	**2a**	0.5	92	92
3	Ph	**2a**	0.1	78	88
4	1-naphth	**2b**	1.0	94	90
5	2-naphth	**2c**	0.5	>98	95
6	*p*-OMe	**2d**	1.0	86	91
7	*p*-Cl	**2e**	1.0	98	90
8	*o*-Br	**2f**	1.0	91	89
9	*m*-NO_2	**2g**	1.0	92	91
10	*p*-NO_2	**2h**	1.0	>98	92
11	2-furyl	**2i**	1.0	89	92

Josephsohn, N. S.; Snapper, M. L.; Hoveyda, A. H., *J. Am. Chem. Soc*. **2003**, 125, 4018–4019.

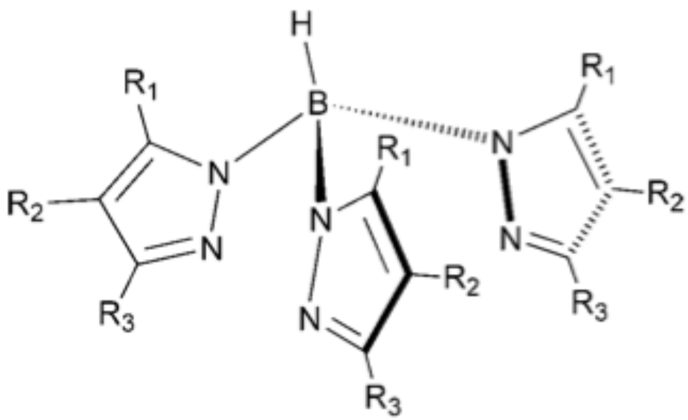
V. Ag catalyzed nitrene transfer



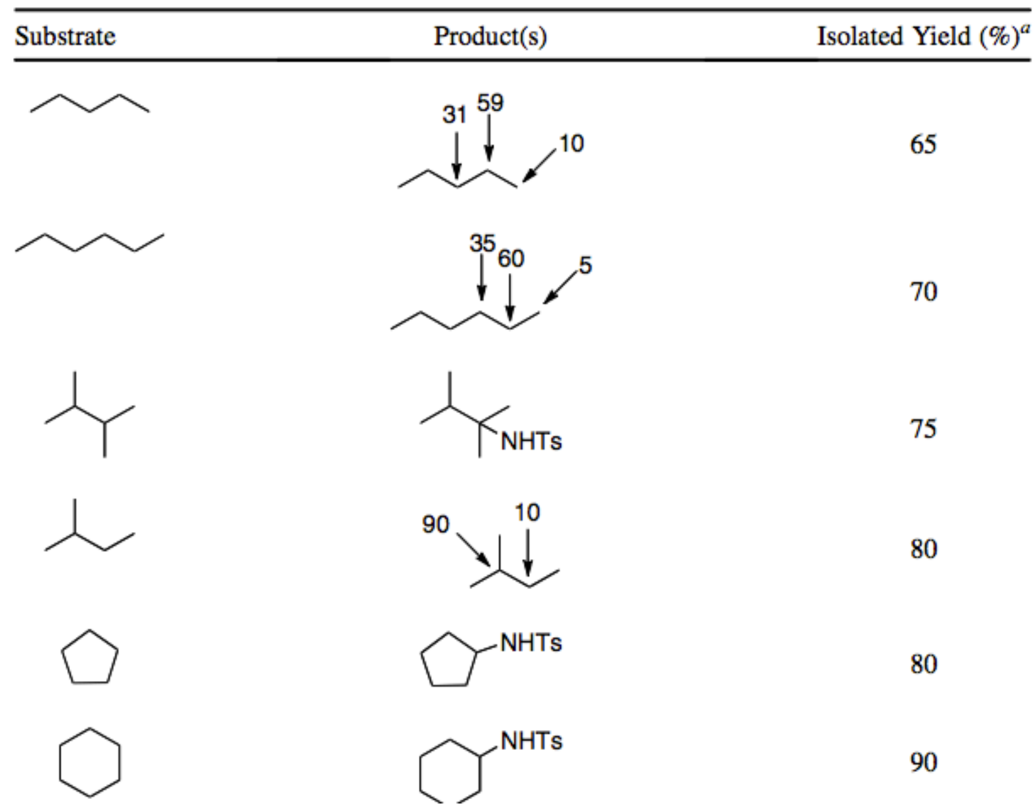
Kumar, K. A.; Rai, L. K. M.; Umesha, K. B., *Tetrahedron* **2001**, 57, 6993–6996. 15. Minakaa, S.; Kano, D.; Fukuoka, R.; Oderaotoshi, Y.; Komatsu, M., *Heterocycles* **2003**, 60, 289–298.

V. C-H amination

$$\text{R–H} + \text{PhI=NTs} \xrightarrow[\text{no solvent, 80°C, 16 h}]{\text{5 mol\% AgTp}^{*,\text{Br}}} \text{R–NHTs}$$



Tp^{type}	R_1	R_2	R_3
$Tp^{*,Br}$	Me	Br	Me



Gomez-Emeterio, B. P.; Urbano, J.; Diaz-Requejo, M. M.; Perez, P. J., *Organometallics* **2008**, 27, 4126–4130.

VI. Silver-Catalyzed Decarboxylative Chlorination

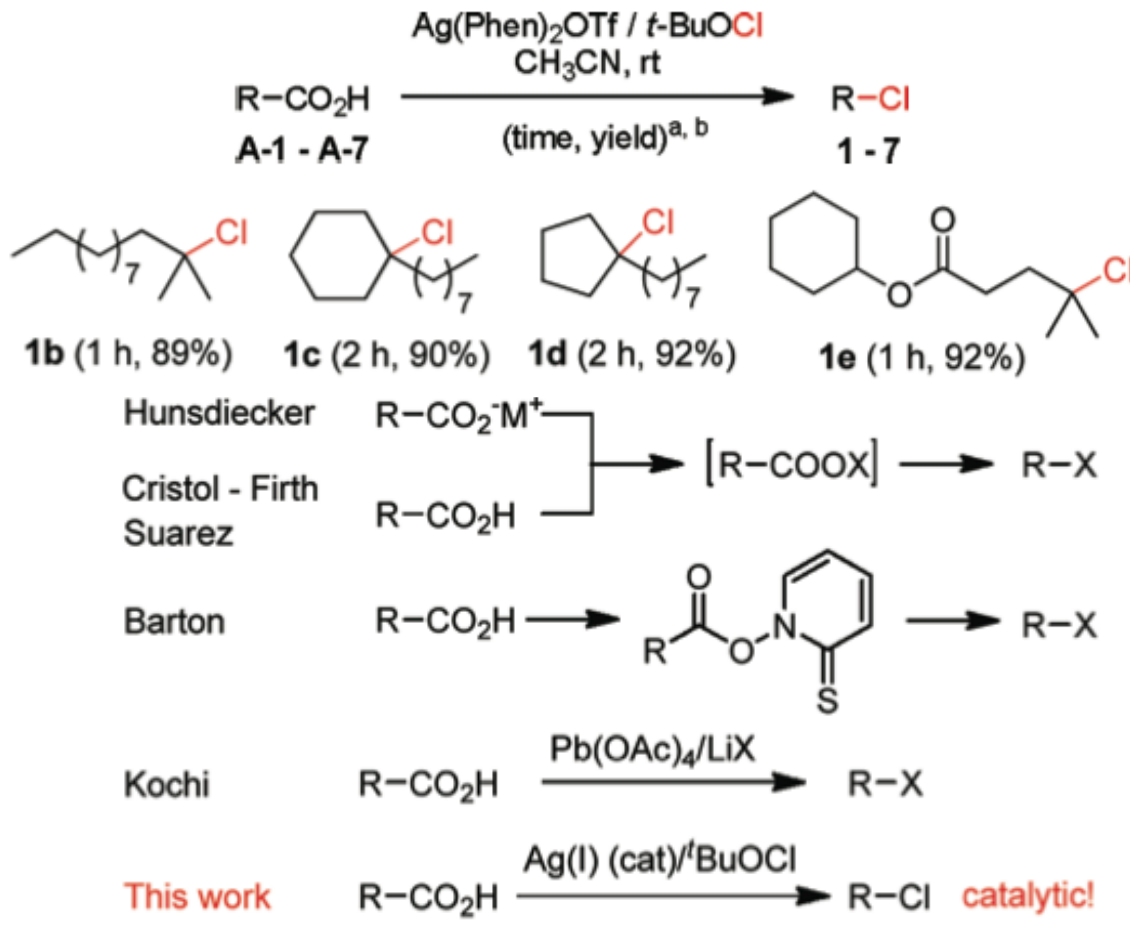


Figure 1. Overview of radical Hunsdiecker-type reactions.

J. Am. Chem. Soc. 2012, 134, 4258–4263

VI. Proposed mechanism

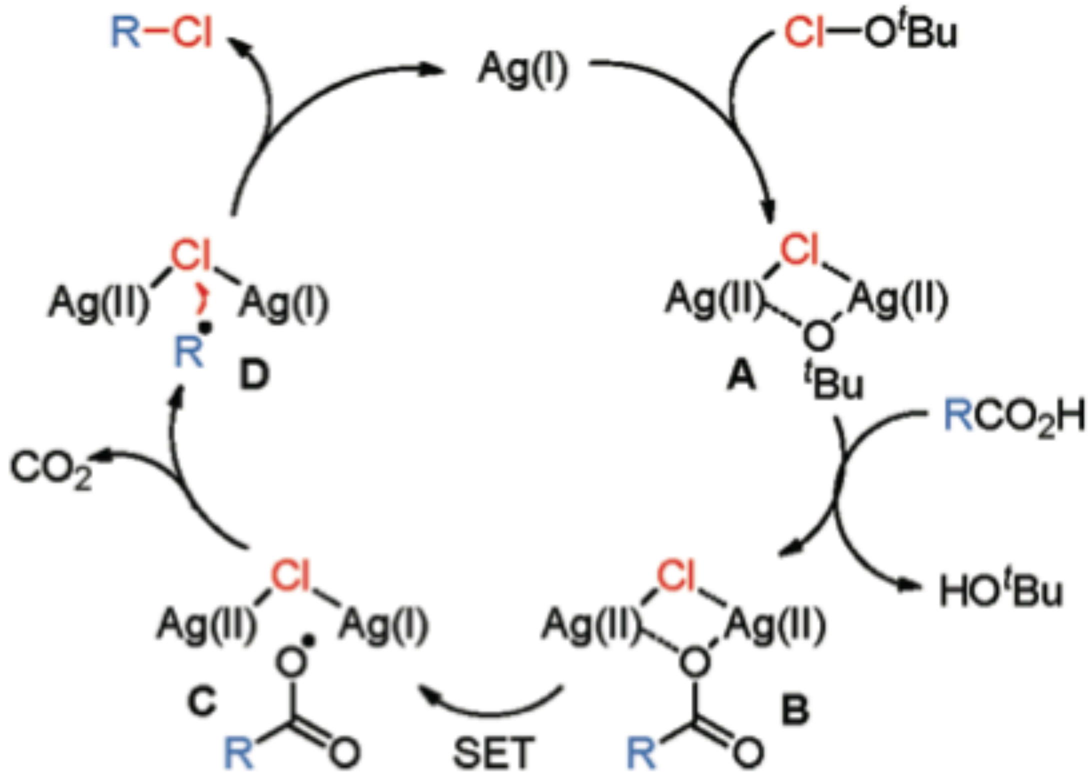
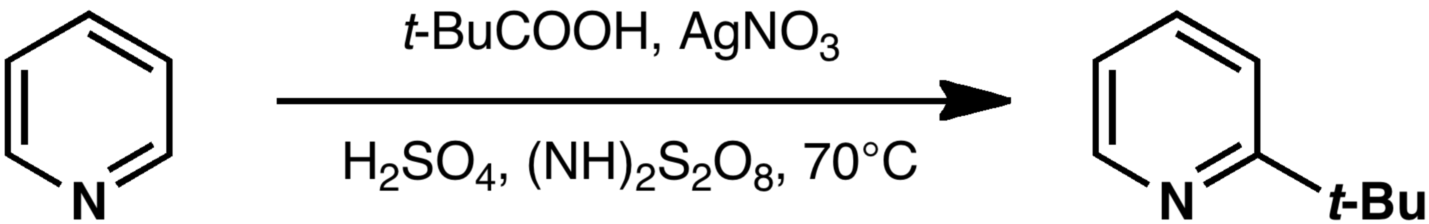


Figure 2. Proposed mechanism for Ag(I)-catalyzed decarboxylative chlorination.

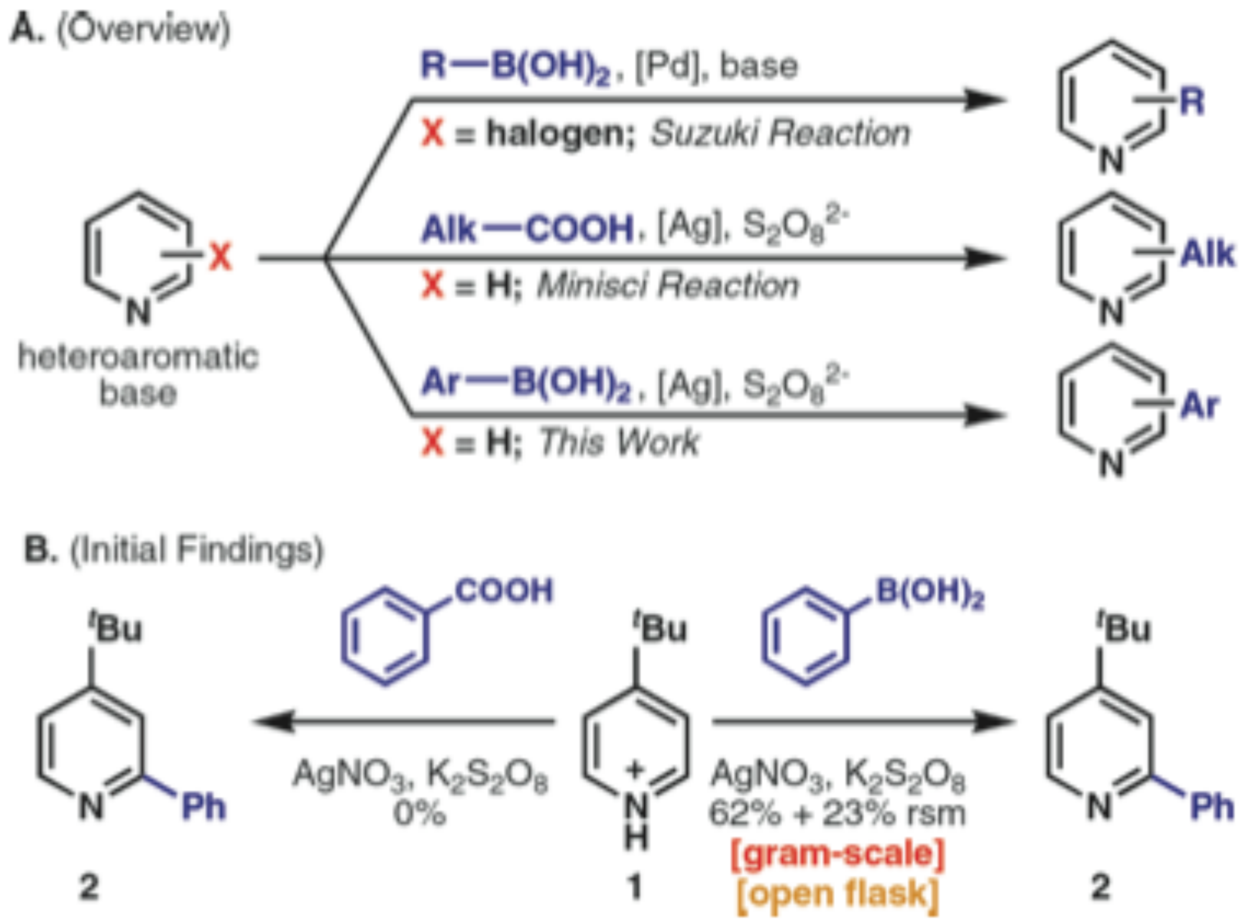
VI. Minisci reaction



$$2Ag^{+} + S_2O_8^{--} \rightarrow 2Ag^{++} + 2SO_4^{--}$$
$$R\text{—}COOH + Ag^{++} \rightarrow R\cdot + CO_2 + H^{+} + Ag^{+}$$

Tetrahedron. Vol. 27, pp. 3575 to 3579.

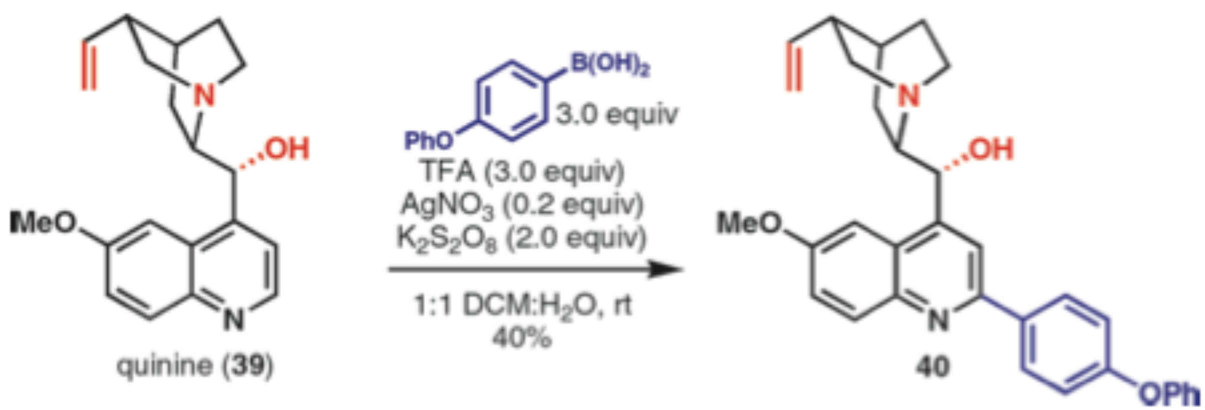
VI. Minisci reaction – Baran redux



Seiple,I.B.;Su,S.;Rodriguez,R.A.;Gianatassio,R.;Fujiwara,
Y.; Sobel, A. L.; Baran, P. S. *J. Am. Chem. Soc*. **2010**, *132*, 13194.

VI. Minisci reaction – Baran redux

Scheme 1. Direct Arylation of Quinine[a]



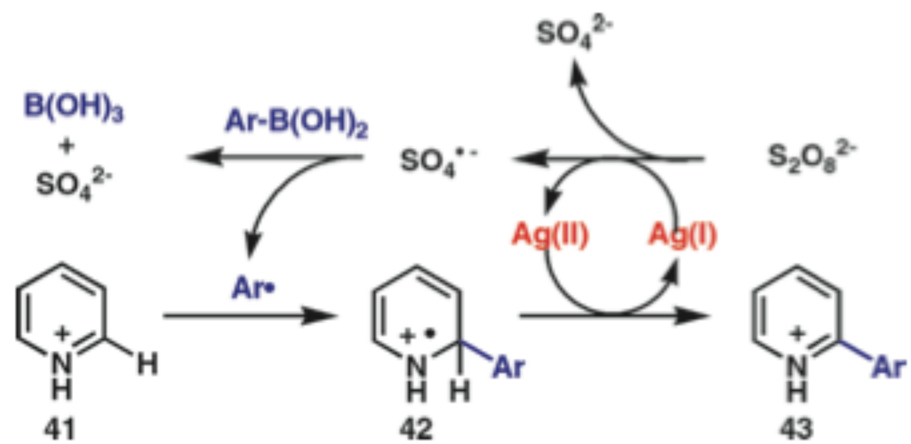
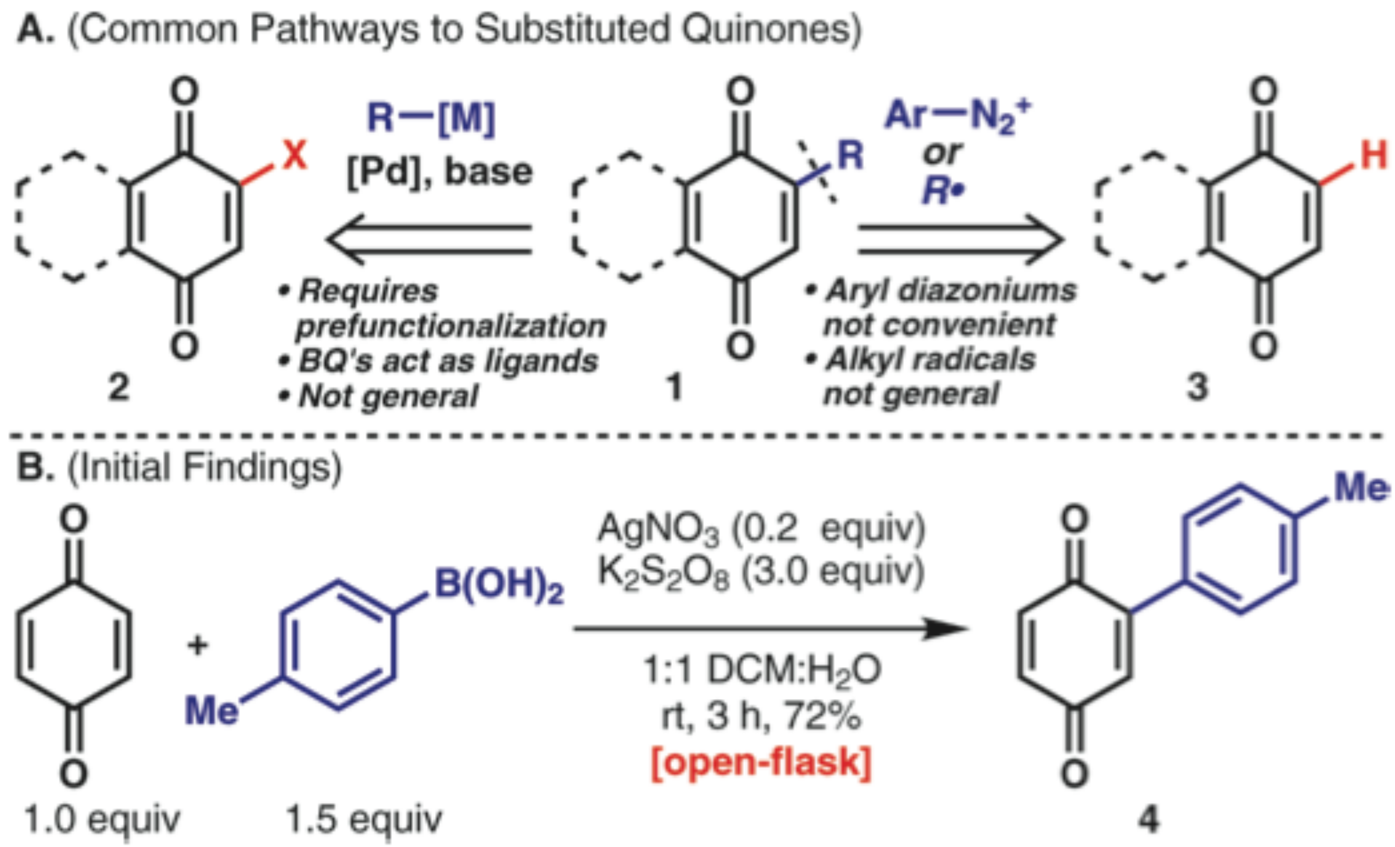


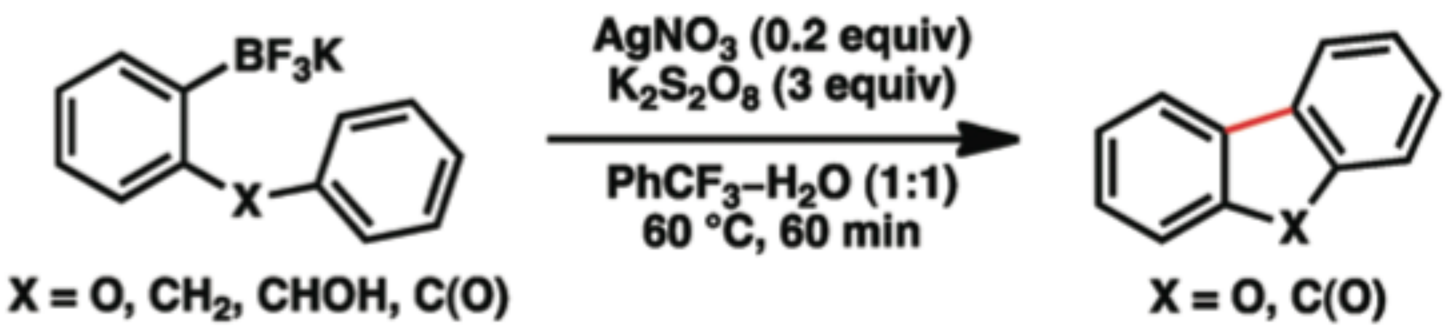
Figure 2. A mechanism consistent with previous studies by Minisci.

VI. Minisci reaction – Baran redux



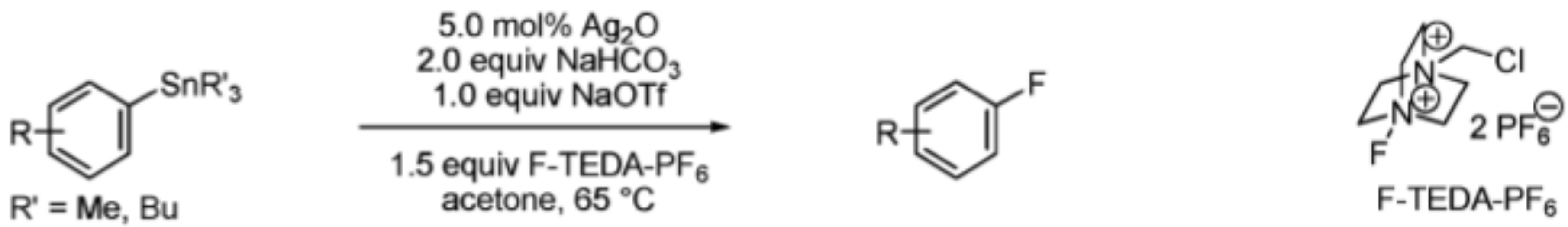
Fujiwara, Y.; Domingo, V.; Seiple, I.B.; Gianatassio, R.; Del Bel, M.; Baran, P.S. *J. Am. Chem. Soc.*, **2011**, 133, 3292-3295.

VI. Minisci reaction – Baran redux



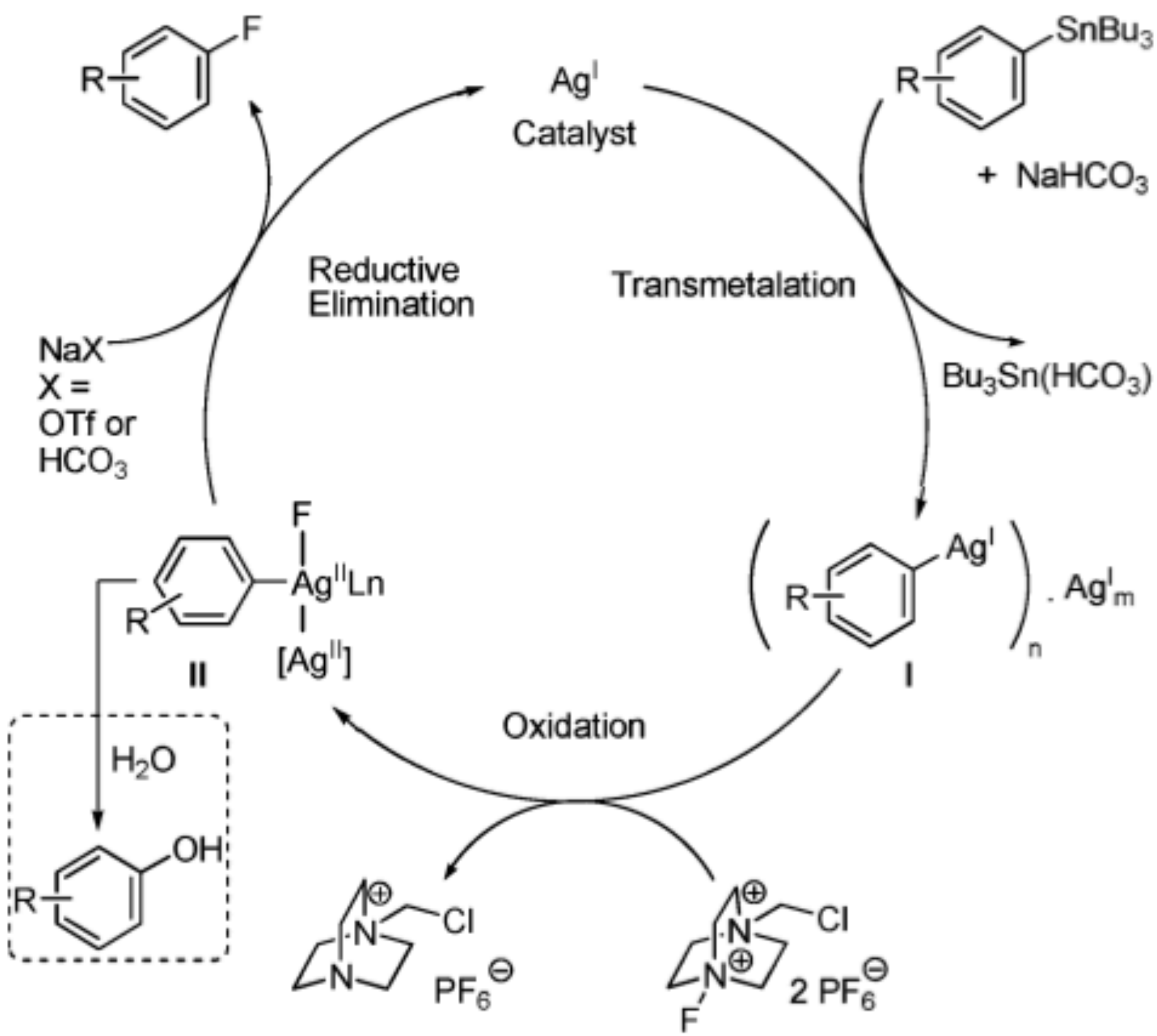
Lockner, J.W.; Dixon, D.D.; Risgaard, R.; Baran, P.S., *Org. Lett.*, **2011**, 13, 5628-5631.

Silver-catalyzed fluorination



Tang, P; Furuya, T; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 12150–12154

Scheme 2. Proposed Mechanism for Silver-Catalyzed Fluorination



Questions?