Institut für Organische Chemie der Justus-Liebig-Universität

Recent Advances in Organoselenium Chemistry

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Giessen

Selenium Features

Discovery

Se Berzelius, 1817

First organoselenium compound

H_3C-CH_2-SeH Wöhler and Siemens, 1847

pure form Rathke, 1869

Applications

- in electronic devices as a photoconducting and semiconducting element,
- as a decolorizer of glass,
- in the pigments industry,
- in metallurgy,
- as an essential micronutrient.

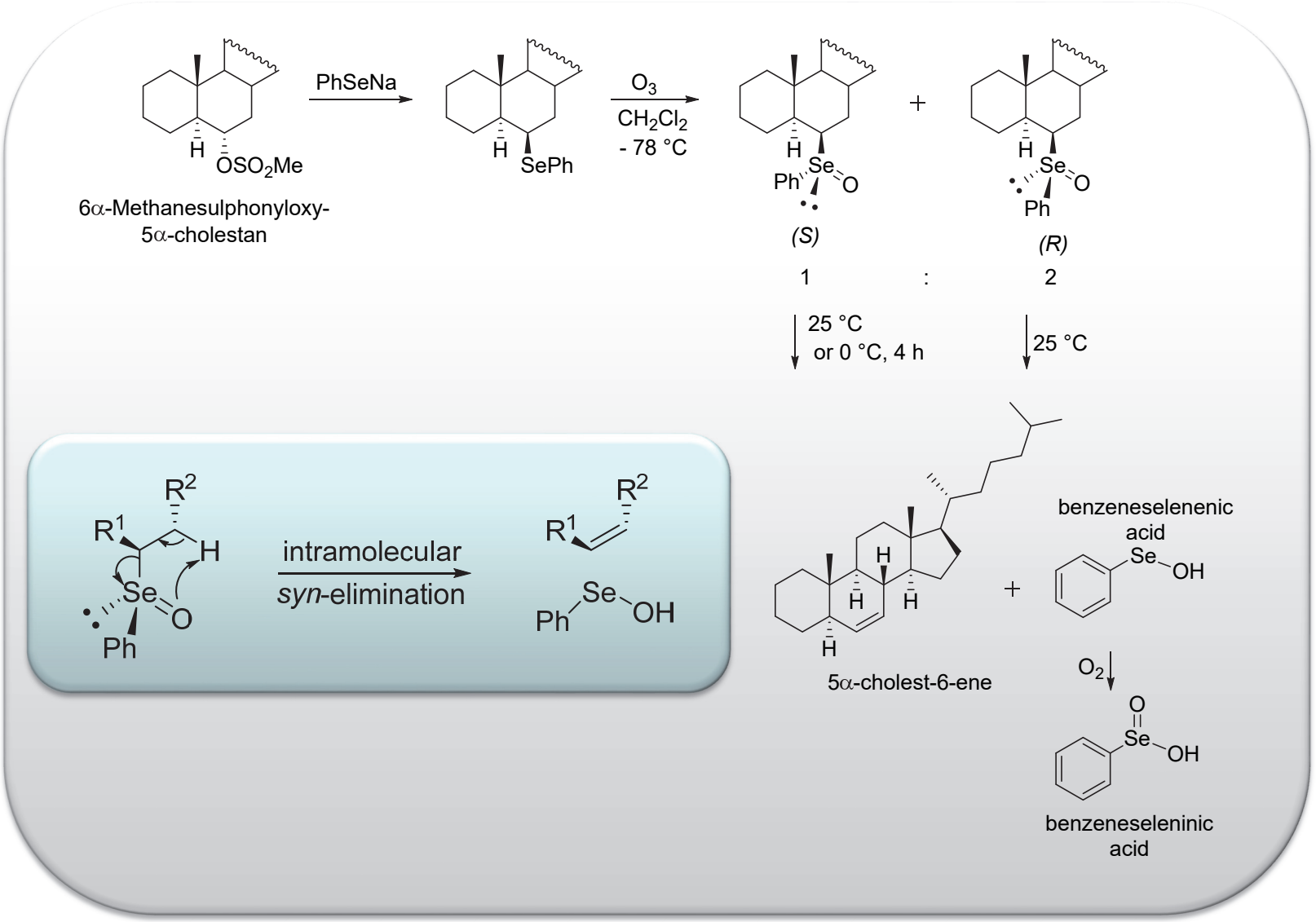
essential trace element
Schwarz and Foltz, 1957

First selenoenzyme

glutathione peroxidase
Rotruck, 1973

Berzelius, J. J. *Afhandl. Fys. Kemi Mineralogi* **1818**, *6*, 24;
Wöhler, F.; Siemens C. *Ann. Chem.* **1847**, *61*, 360; Rathke, B. *Ann. Chem.* **1869**, *152*, 211;
Schwarz, K.; Foltz, C. M. *J. Am. Chem. Soc.* **1957**, *79*, 3292; Rotruck, J. T.; Pope, A. L.; Ganther, H. E.; Swanson, A. B.; Hafeman, D. G.; Hoekstra, W. G. *Science* **1973**, *179*, 588.

Alkene Preparation Through Selenoxides Decomposition



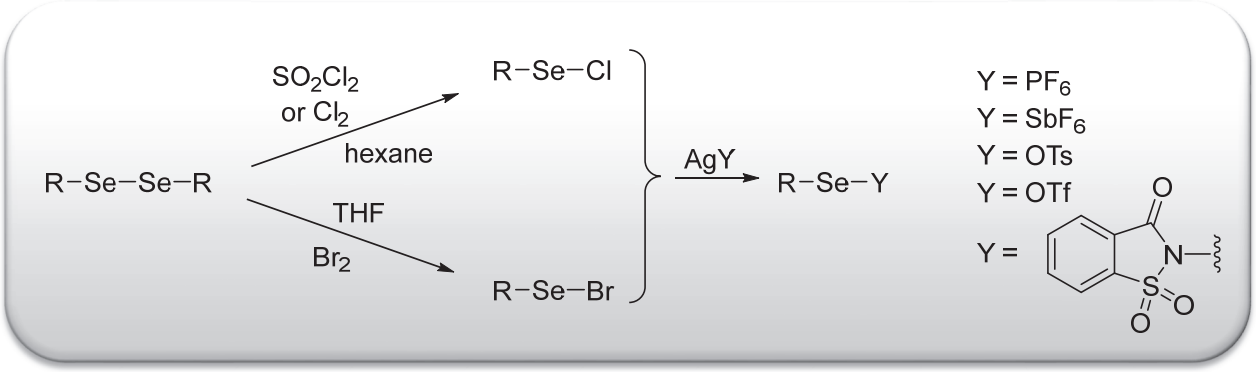
Jones, D. N.; Mundy, D.; Whitehouse, R. D. *J. Chem. Soc. D* **1970**, 86.

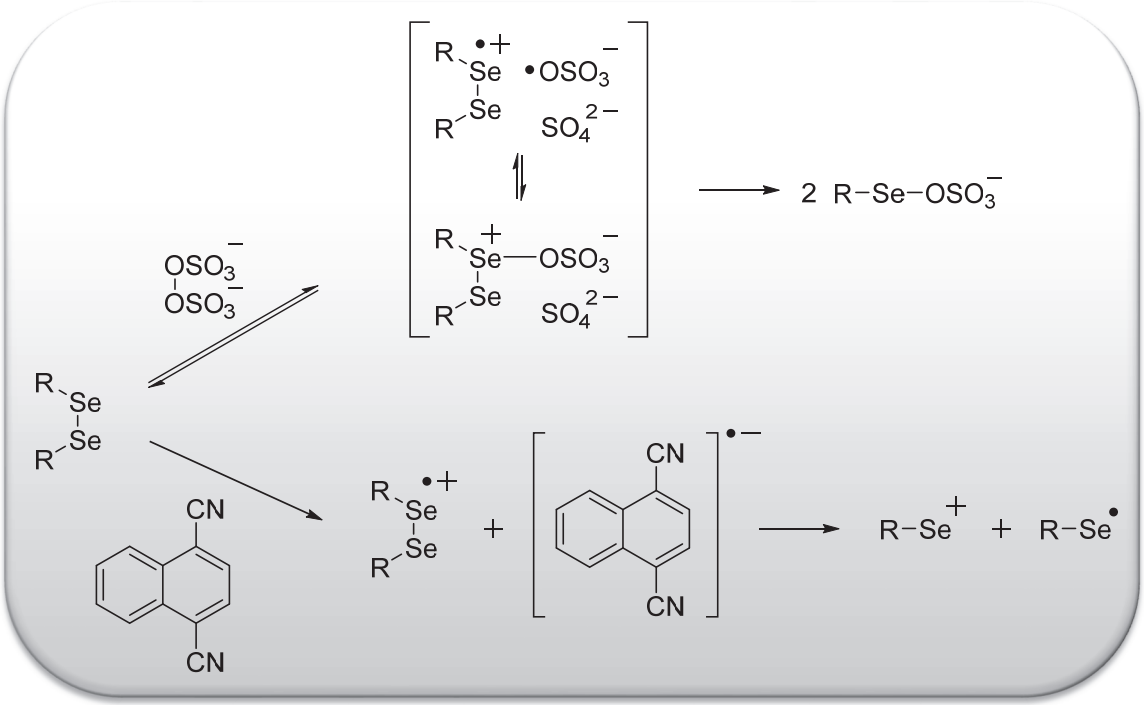
Comparison of Physical Constants of Main Group VI Elements

Constants		O	S	Se	Te
Electronic configuration		$2s^2\ 2p^4$	$3s^2\ 3p^4$	$4s^2\ 3d^{10}\ 4p^4$	$5s^2\ 4d^{10}\ 5p^4$
Electronegativity (Pauling)		3.5	2.5	2.4	2.1
Ionization potential (V)		13.61	10.36	9.75	9.01
Bond energy (kcal/mol)	X–X	33	63	44	33
	X–H	111	88	67	57
	X–C	85	65	58	
pK_a aqueous XH_2		16	7.0	3.8	2.6
pK_a aqueous XH			12.9	11.0	11.0
Covalent radius (Å)		0.66	1.04	1.17	1.37
Bond length (Å)	C–X	1.41	1.81	1.98	
	C=X	1.22	1.54	1.67	

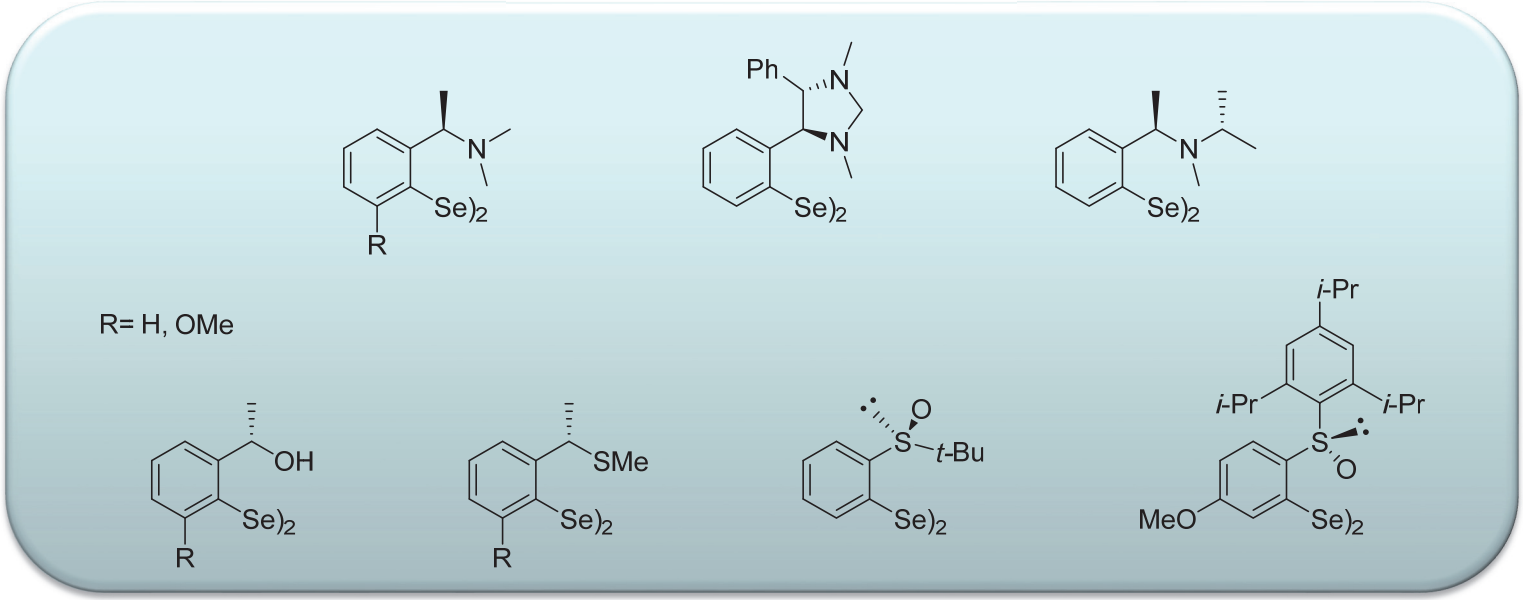
Paulmier, C.; Baldwin, J. E. *Selenium Reagents & Intermediates in Organic Synthesis*; Elsevier Science, 2013.

Electrophilic Selenium Reagents

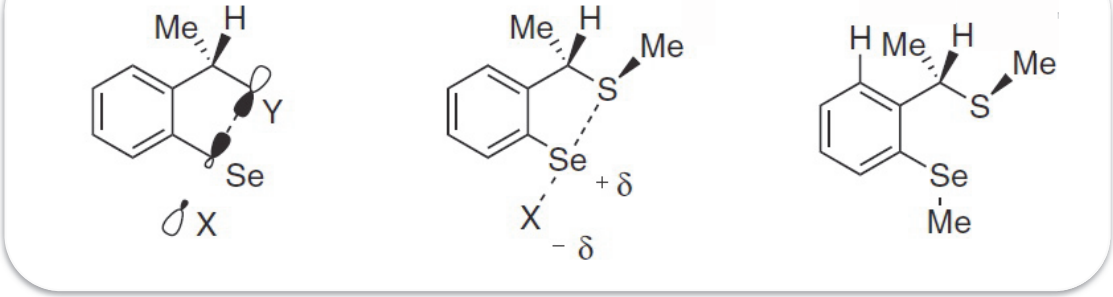




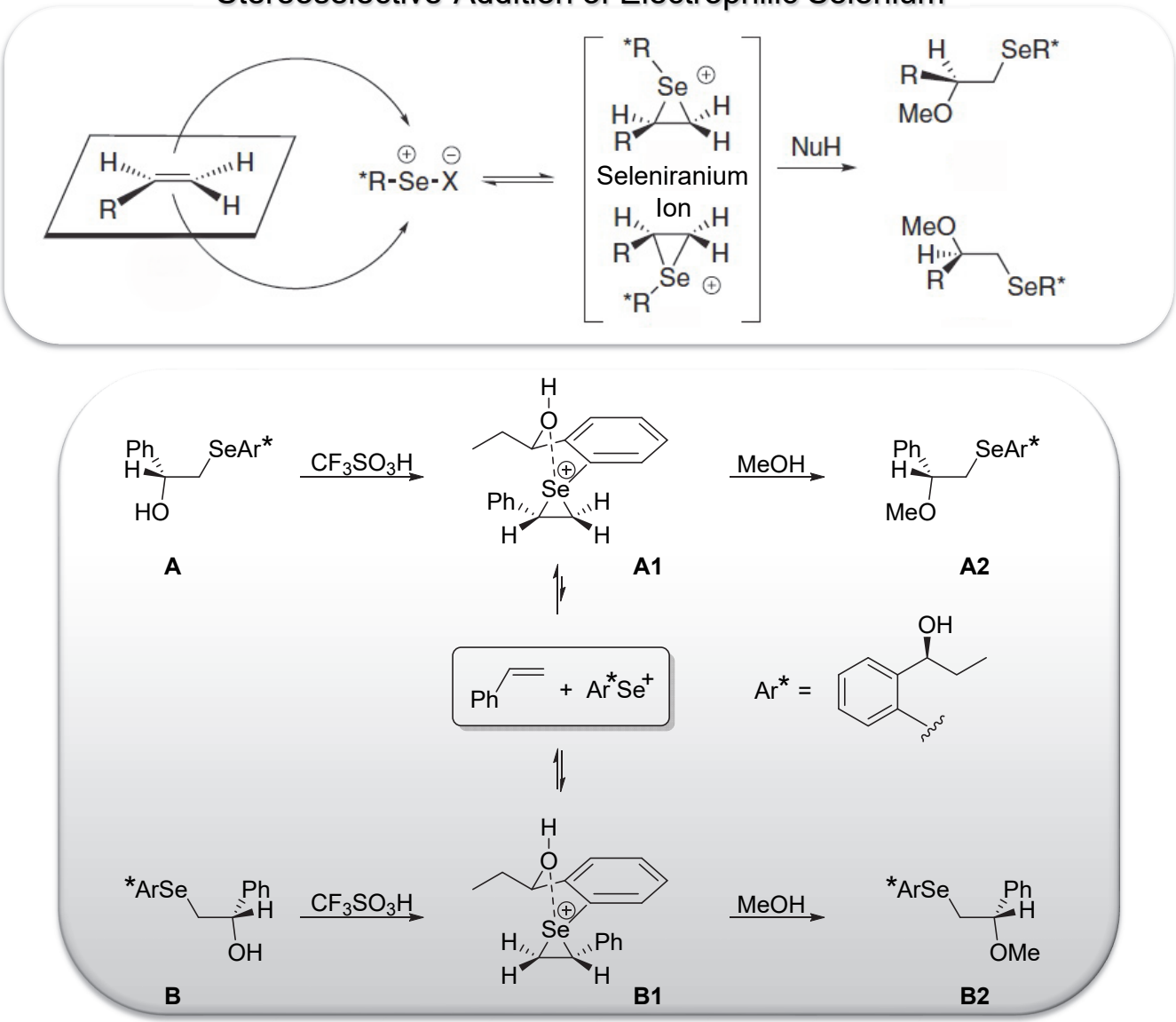
Aromatic Chiral Diselenides



Selenium–Heteroatom Nonbonding Interaction

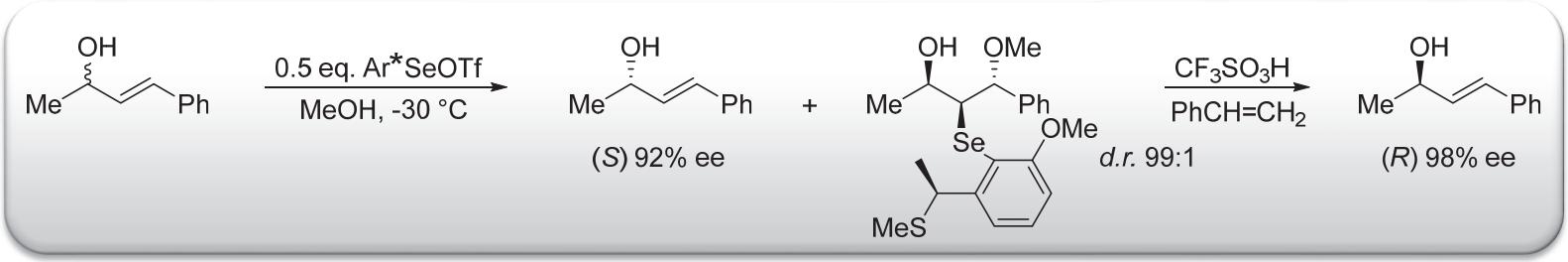


Stereoselective Addition of Electrophilic Selenium

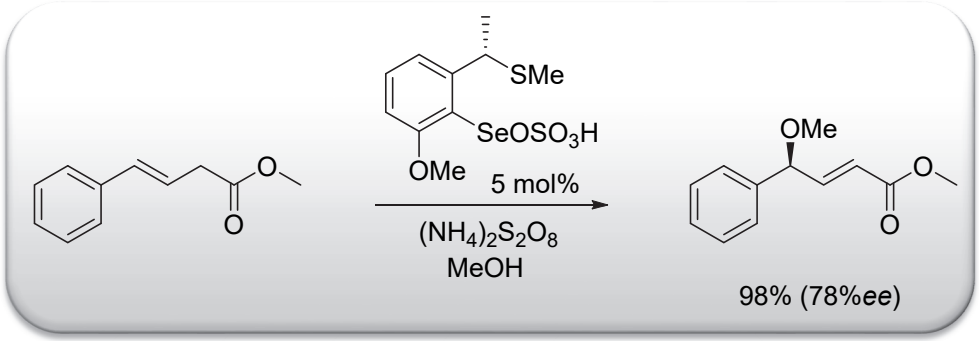


Wirth, T.; Fragale, G.; Spichty, M. *J. Am. Chem. Soc.* **1998**, *120*, 3376; Wang, X.; Houk, K. N.; Spichty, M.; Wirth, T. *J. Am. Chem. Soc.* **1999**, *121*, 8567.

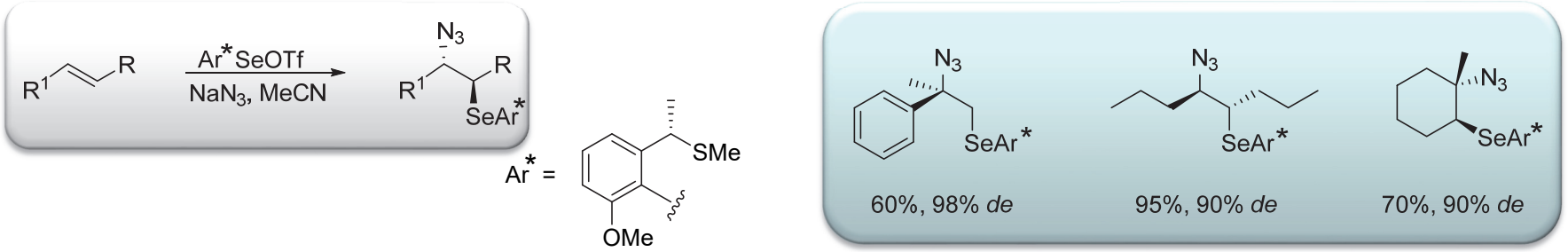
Kinetic Resolution of Allylic Alcohols



Asymmetric one-pot Methoxyselenenylation Deselenenylation Sequence

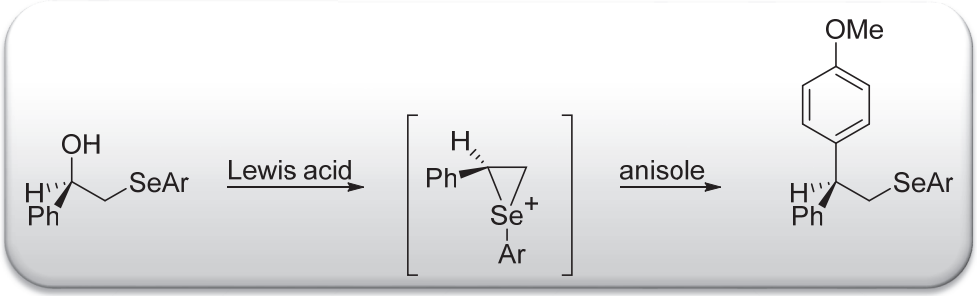


Asymmetric electrophilic azidoselenenylations



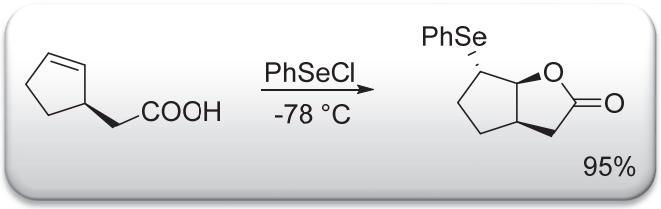
Tiecco, M.; Testaferri, L.; Santi, C.; Tomassini, C.; Bonini, R.; Marini, F.; Bagnoli, L.; Temperini, A. *Org. Lett.* **2004**, *6*, 4751;
Tiecco, M.; Testaferri, L.; Bagnoli, L.; Marini, F.; Temperini, A.; Tomassini, C.; Santi, C. *Tetrahedron Lett.* **2000**, *41*, 3241;
Tiecco, M.; Testaferri, L.; Santi, C.; Tomassini, C.; Marini, F.; Bagnoli, L.; Temperini, A. *Angew. Chem. Int. Ed.* **2003**, *42*, 3131.

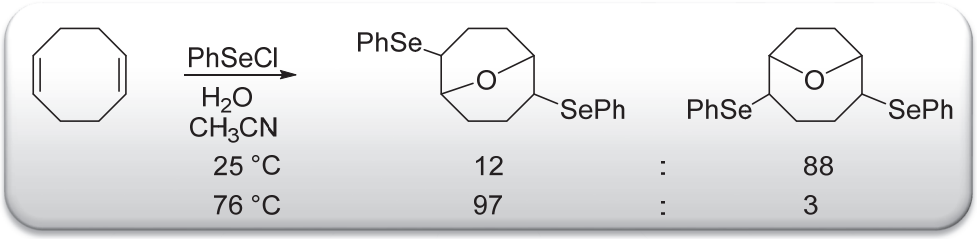
Addition of Aromatic Carbon-Centered Nucleophile



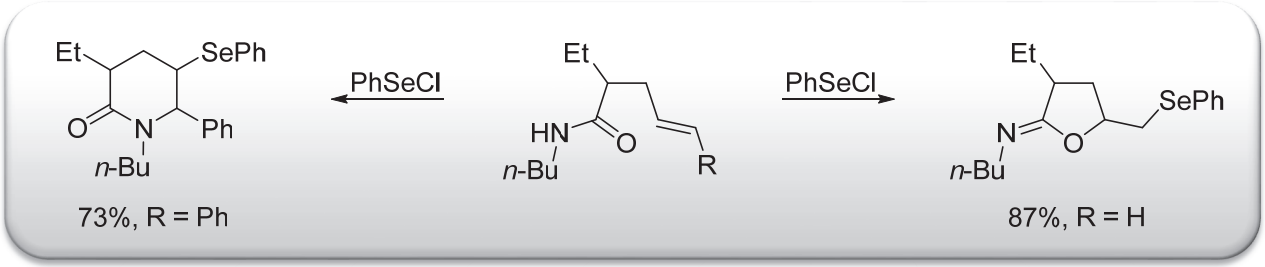
Ar = Ph 85%, 2% *ee*
Ar = 2-pyridyl 89%, 95% *ee*
Ar = 2,4,6-*t*-$Bu_3C_6H_2$ 85%, 98% *ee*

Selenolactonizations and Selenoetherifications





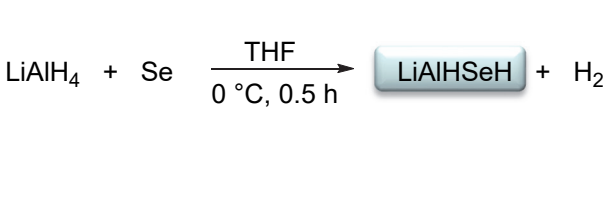
Competition between nitrogen and oxygen nucleophiles in selenocyclization

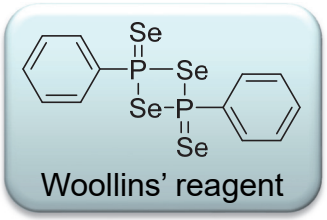


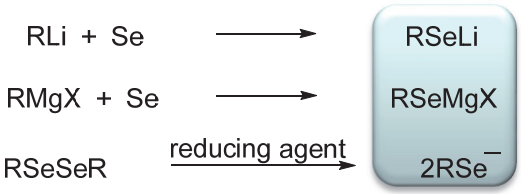
Okamoto, K.; Nishibayashi, Y.; Uemura, S.; Toshimitsu, A. *Tetrahedron Lett.* **2004**, *45*, 6137;
Nicolaou, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3884; Uemura, S.; Toshimitsu, A.; Aoai, T.; Okano, M. *Tetrahedron Lett.* **1980**, *21*, 1533;
Toshimitsu, A.; Terao, K.; Uemura, S. *J. Org. Chem.* **1987**, *52*, 2018.

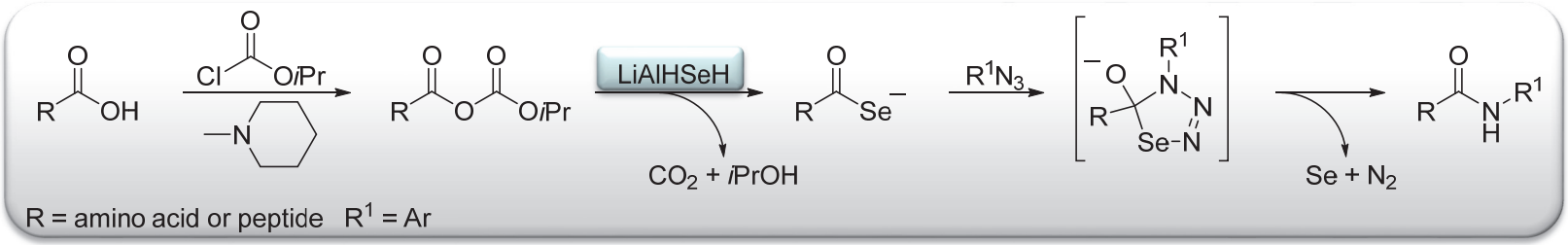
Nucleophilic Selenium Reagents

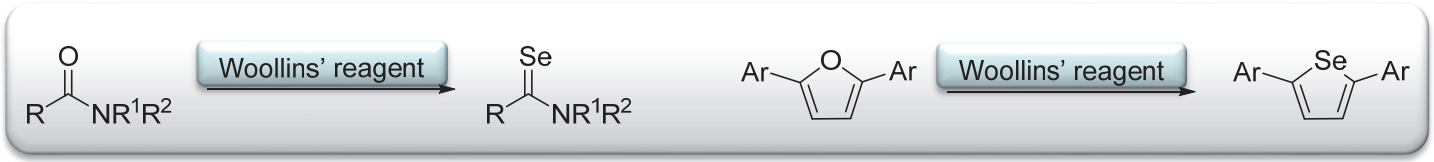
Li_2Se_2, NaHSe, Na_2Se, Na_2Se_2, KSeCN, $[Et_4N]_2WSe_4$, P_4Se_{10}



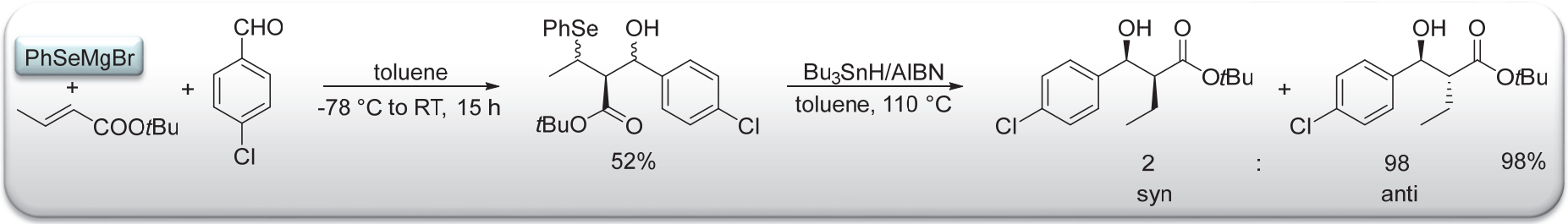






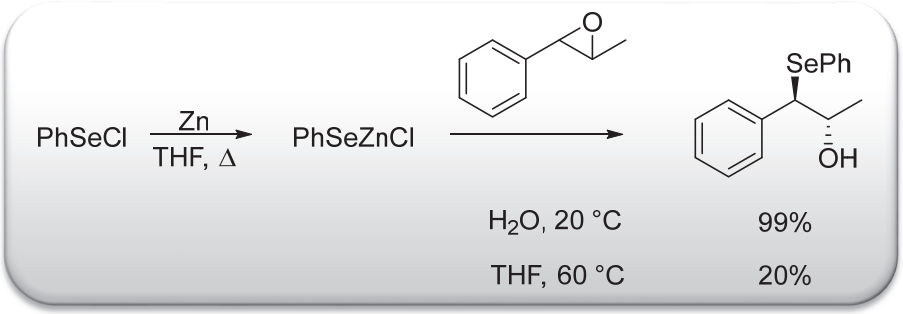


Michael/aldol tandem addition of magnesium selenolate

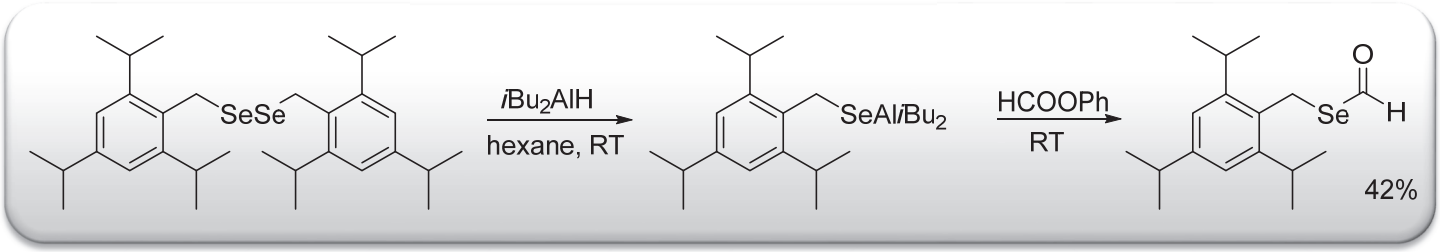


Iwaoka, M. In Organoselenium Chemistry; Wiley-VCH Verlag GmbH: **2011**, p 53;
Wu, X.; Hu, L. *J. Org. Chem.* **2007**, *72*, 765; Bethke, J.; Karaghiosoff, K.; Wessjohann, L. A. *Tetrahedron Lett.* **2003**, *44*, 6911;
Mohanakrishnan, A. K.; Amaladass, P. *Tetrahedron Lett.* **2005**, *46*, 7201; Kamimura, A.; Mitsudera, H.; Omata, Y.; Matsuura, K.; Shirai, M.; Kakehi, A. *Tetrahedron* **2002**, *58*, 9817.

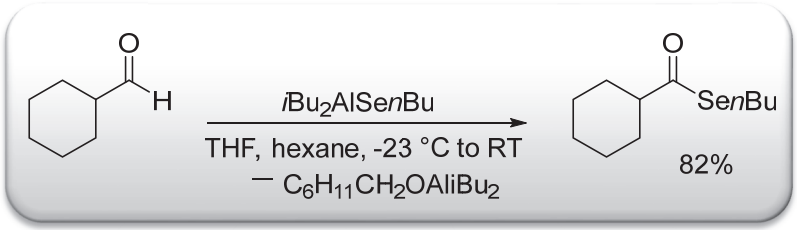
First Bench-Stable Phenyl Selenolate



Synthesis of Selenoformates

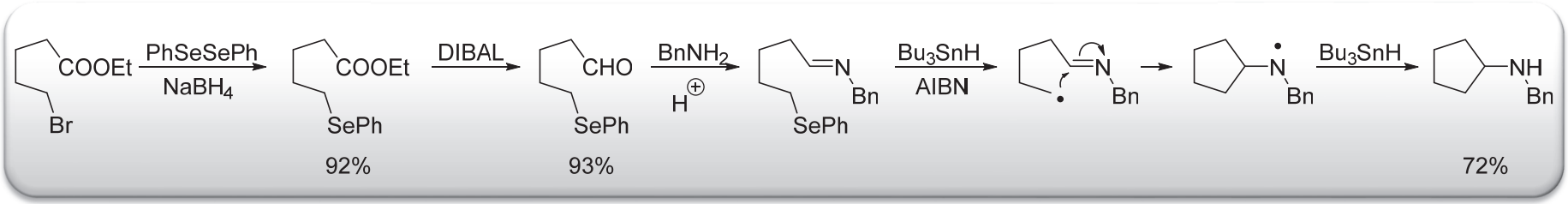


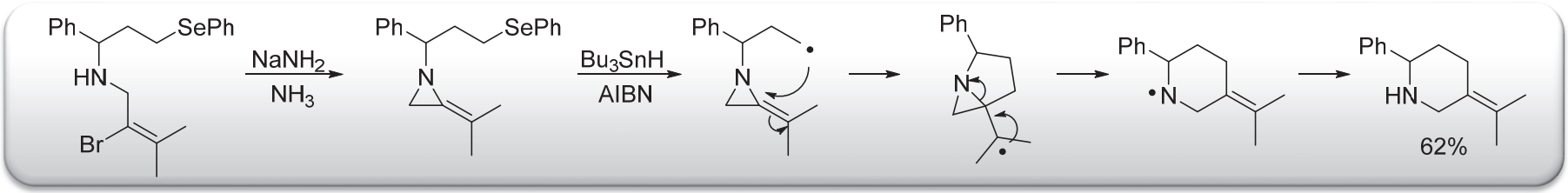
Selenol Esters from Aldehydes



Santi, C.; Santoro, S.; Battistelli, B.; Testaferri, L.; Tiecco, M. *Eur. J. Org. Chem.* **2008**, 5387;
Maeda, H.; Tanabe, T.; Hotta, K.; Mizuno, K. *Tetrahedron Lett.* **2005**, *46*, 2015; Inoue, T.;
Takeda, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 5824.

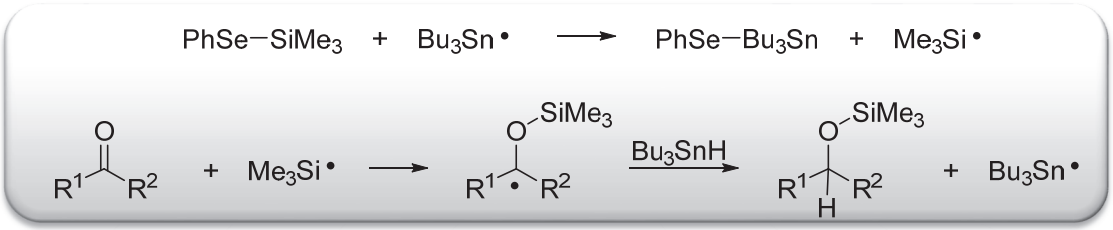
Selenium Compounds in Radical Reactions



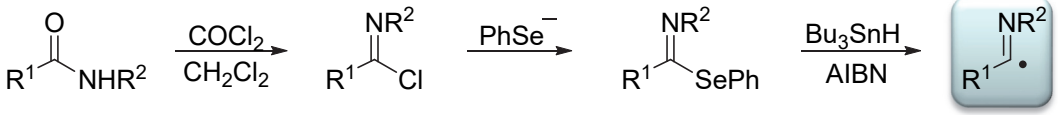


Acyl Radicals from Acyl Selenides

Trimethylsilyl Radicals Generation

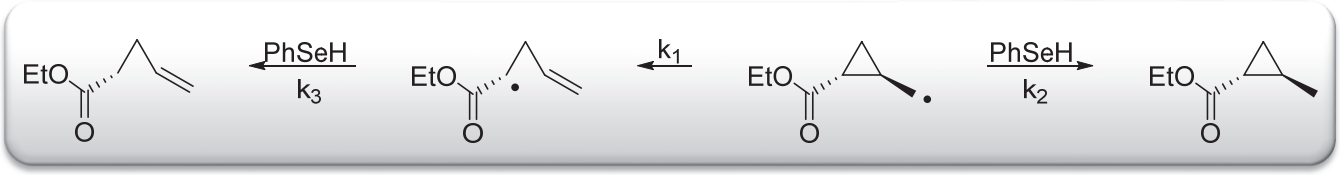


Imidoyl Radicals from Imidoyl Selenides

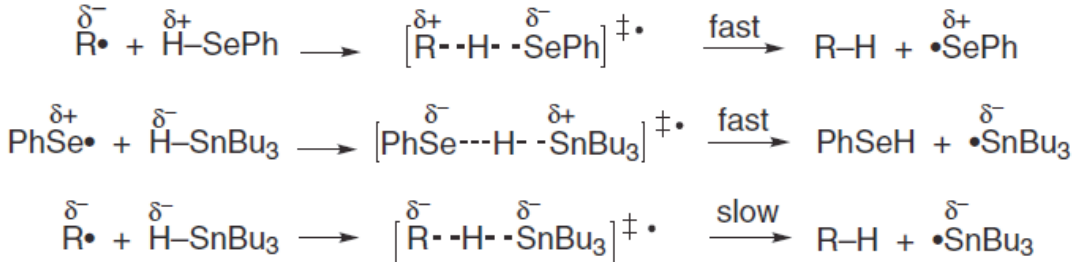


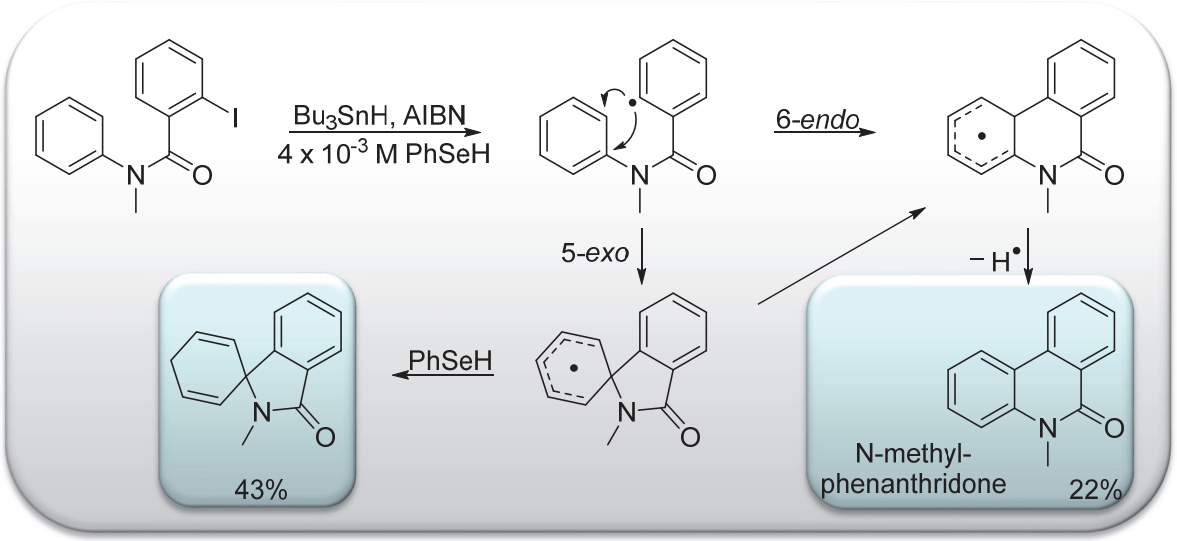
Bowman, W. R.; Stephenson, P. T.; Terrett, N. K.; Young, A. R. *Tetrahedron Lett.* **1994**, *35*, 6369;
Prévost, N.; Shipman, M. *Tetrahedron* **2002**, *58*, 7165;
Nishiyama, Y.; Kajimoto, H.; Kotani, K.; Sonoda, N. *Org. Lett.* **2001**, *3*, 3087.

Radical Clock Reactions



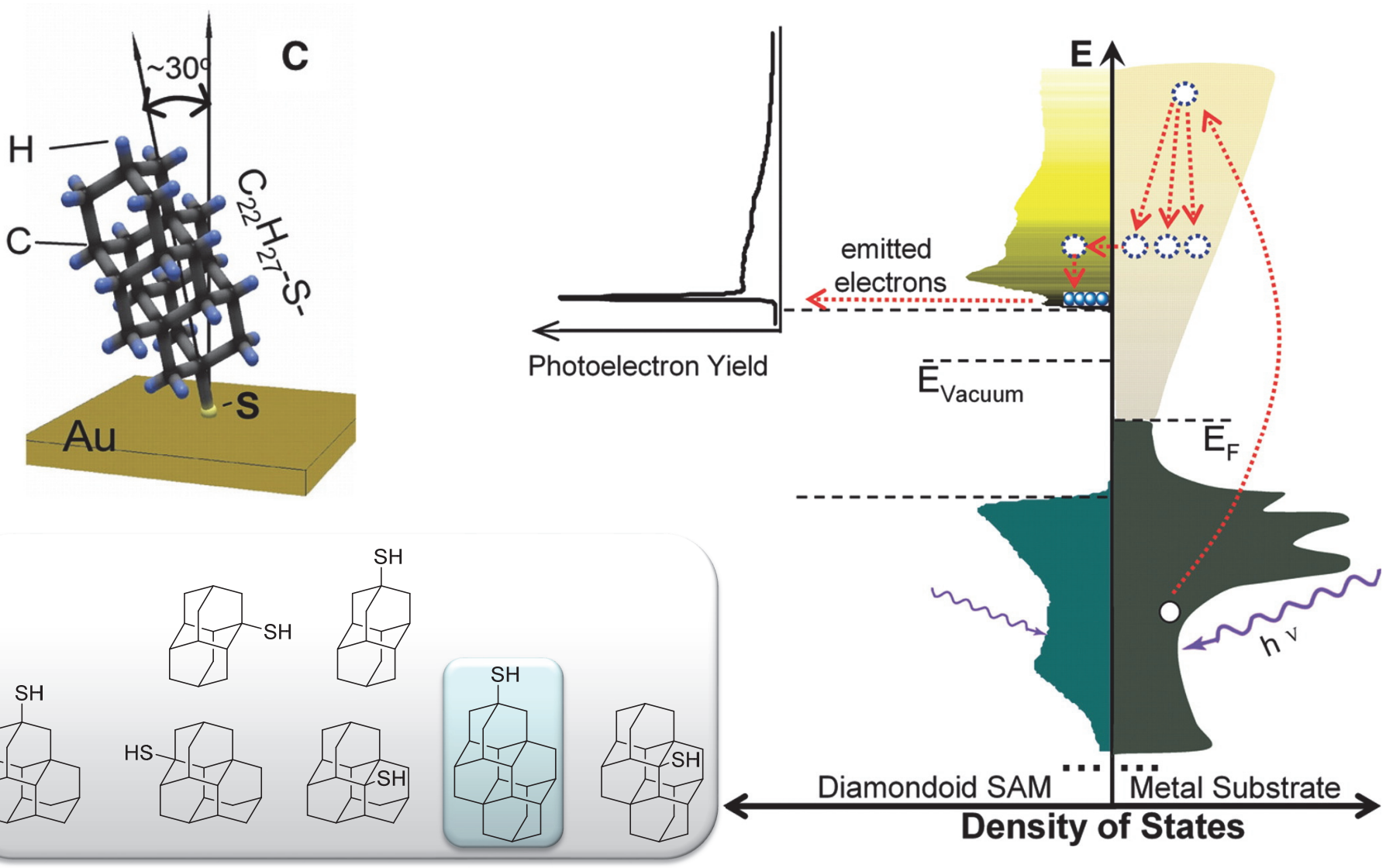
Evidence for Mechanistic Proposals





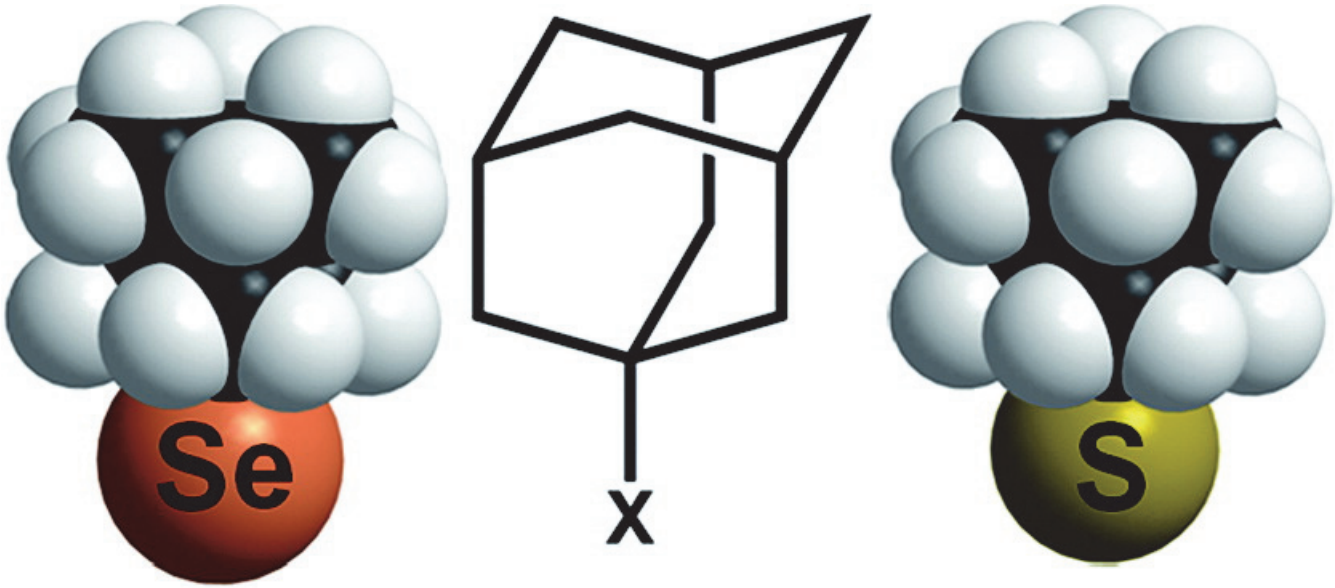
Newcomb, M. *Tetrahedron* **1993**, *49*, 1151;
Crich, D.; Hwang, J.-T. *J. Org. Chem.* **1998**, *63*, 2765.

Monochromatic Electron Photoemission from Diamondoid Monolayers



Yang, W. L.; Fabbri, J. D.; Willey, T. M.; Lee, J. R. I.; Dahl, J. E.; Carlson, R. M. K.; Schreiner, P. R.; Fokin, A. A.; Tkachenko, B. A.; Fokina, N. A.; Meevasana, W.; Mannella, N.; Tanaka, K.; Zhou, X. J.; van Buuren, T.; Kelly, M. A.; Hussain, Z.; Melosh, N. A.; Shen, Z.-X. *Science* **2007**, *316*, 1460.

AdSe and AdS Substrates for SAM Preparation



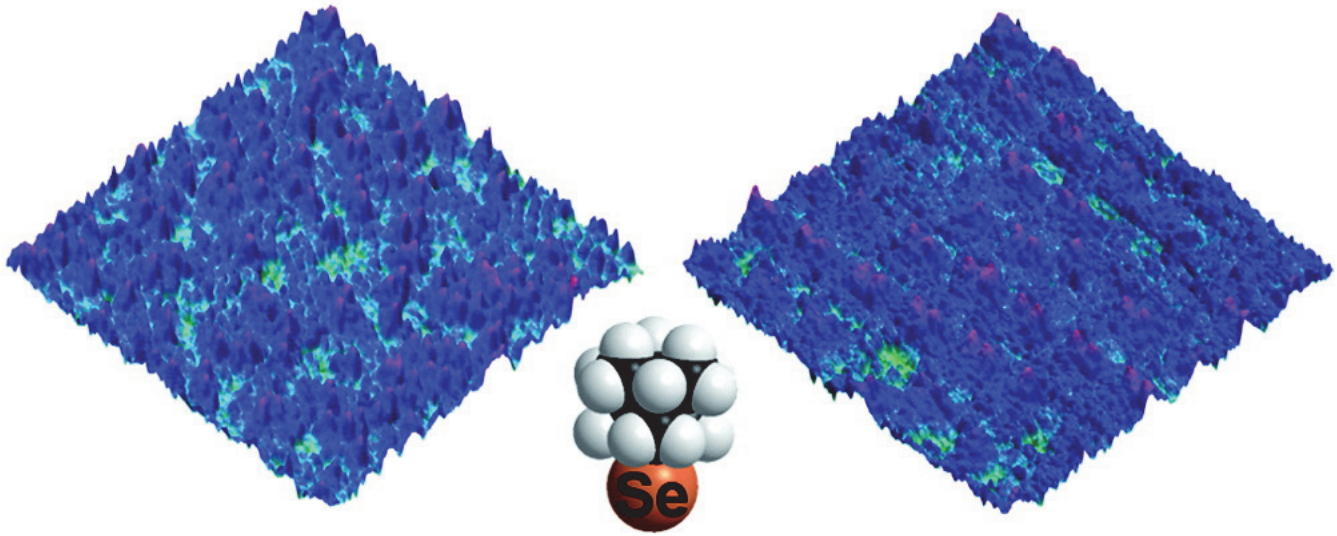
X = S, Se

Hohman, J. N.; Kim, M.; Schüpbach, B.; Kind, M.; Thomas, J. C.; Terfort, A.; Weiss, P. S. *J. Am. Chem. Soc.* **2011**, *133*, 19422.

Modes of AdSe SAM on Au{111} Lattice

High- and low-conductance modes mixed randomly

High-conductive dimer structure

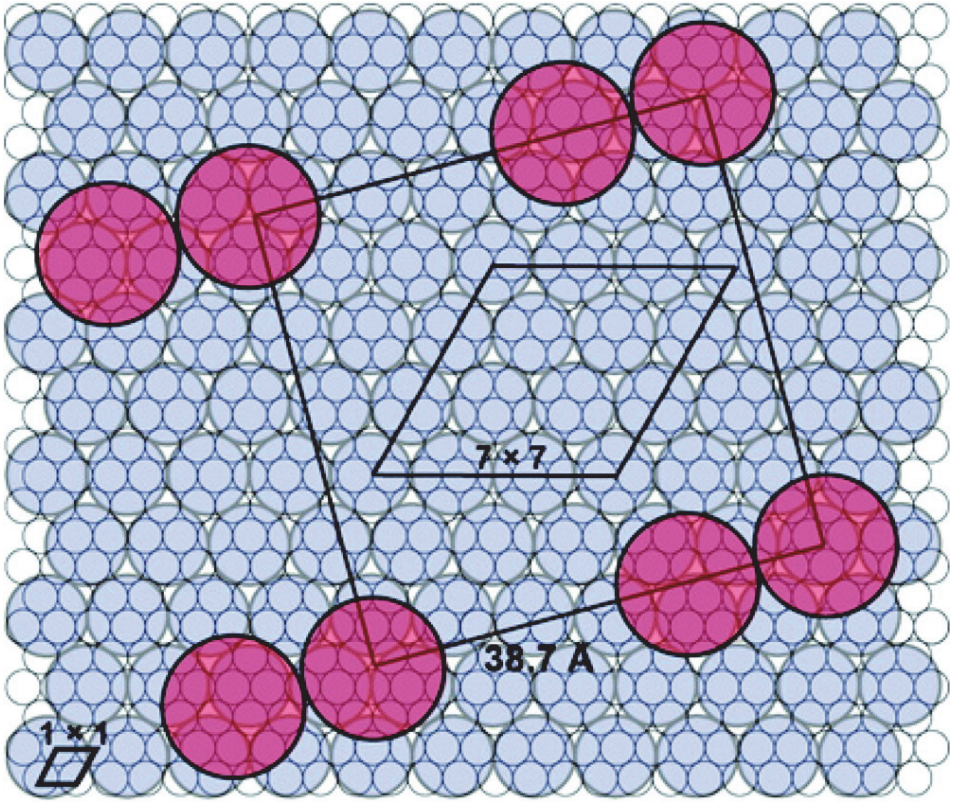


Deposition from ethanolic solution at room temperature)

dry-annealed (70 °C in air for 18 h)

Hohman, J. N.; Kim, M.; Schüpbach, B.; Kind, M.; Thomas, J. C.; Terfort, A.; Weiss, P. S. *J. Am. Chem. Soc.* **2011**, *133*, 19422.

High- and Low-conductance Modes of AdSe SAM on Au{111} Lattice



Two different binding modes for selenols on gold:

Low conducting

- blue circles
- (7 × 7) unit cell
- bind at bridge sites of Au{111} lattice
- similar to the analogous AdS monolayers

High conducting

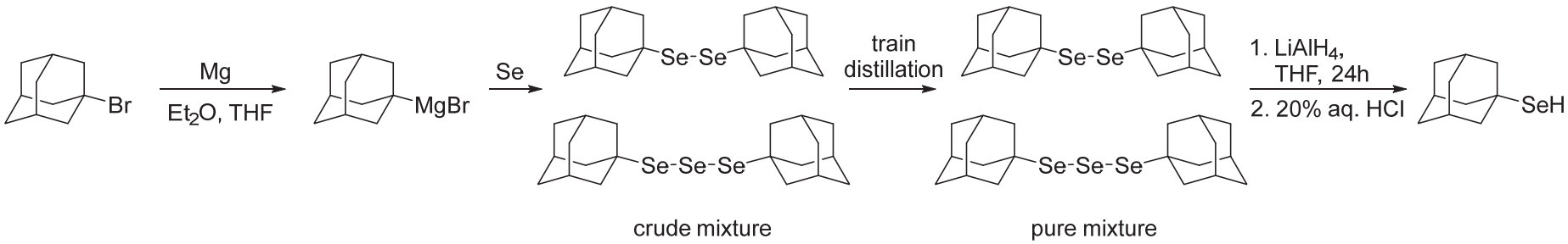
- molecules in dimer pairs (red circles)
- $(6\sqrt{5} \times 6\sqrt{5})R15°$ unit cell
- bind at three-fold hollow sites of Au{111} lattice

Dynamic monolayer, molecules switching reversibly between the two sitedependent conductance states.

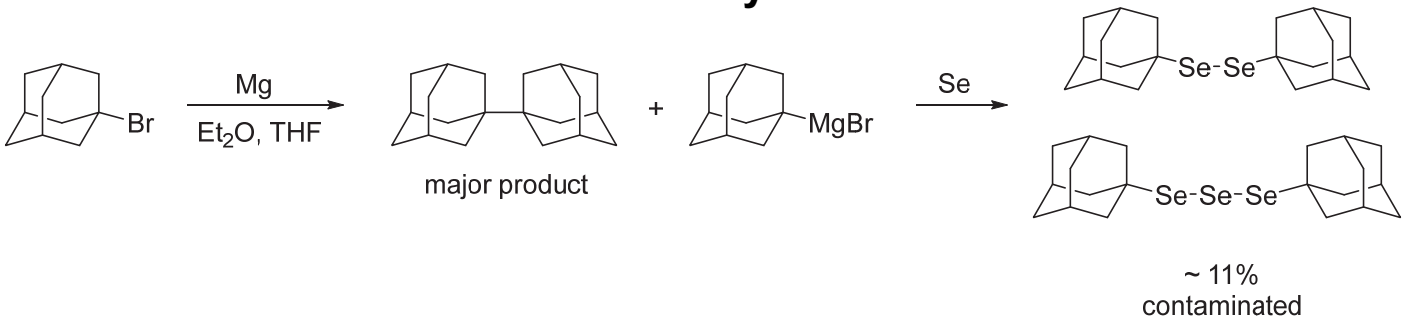
Hohman, J. N.; Kim, M.; Schüpbach, B.; Kind, M.; Thomas, J. C.; Terfort, A.; Weiss, P. S. *J. Am. Chem. Soc.* **2011**, *133*, 19422.

Known Preparation of Adamantylselenol

Promices

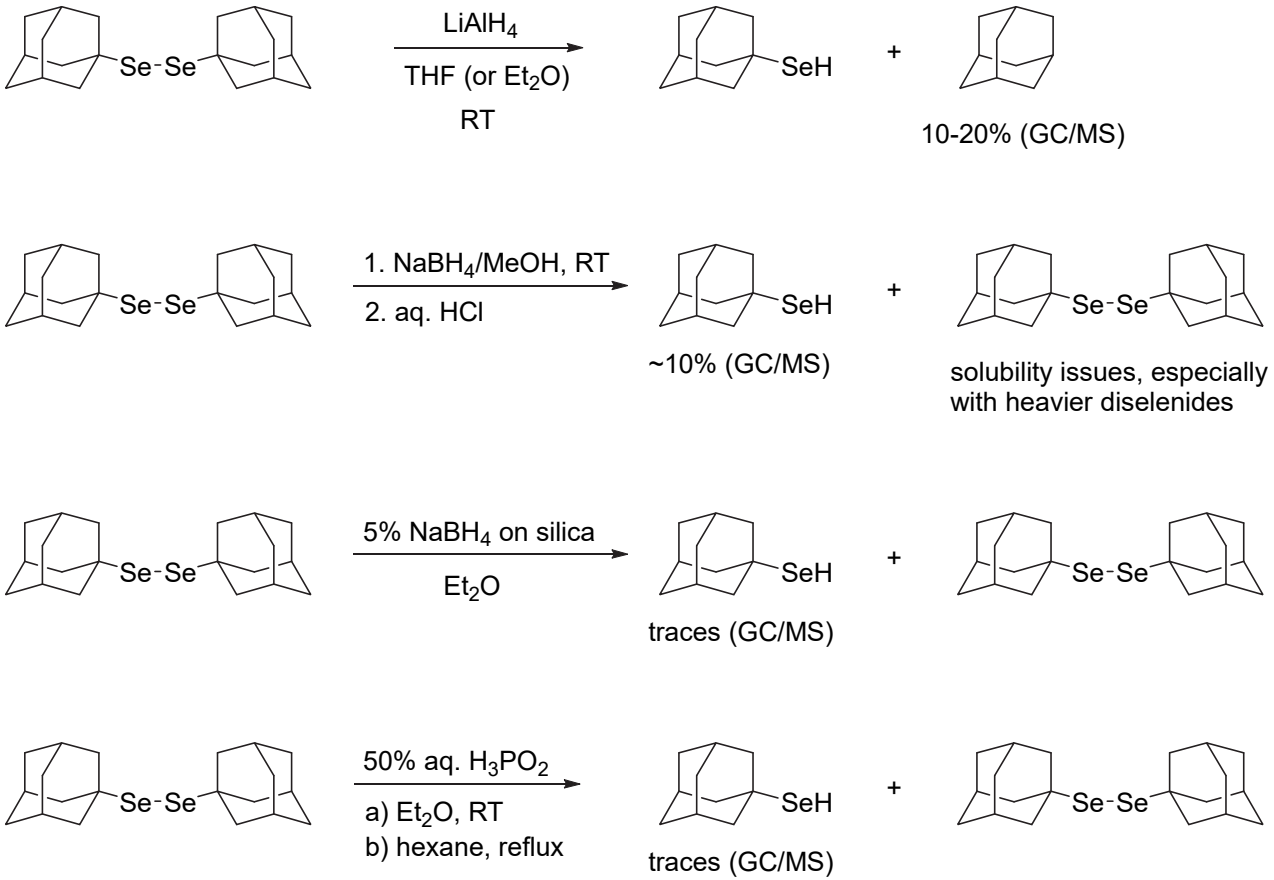


Reality



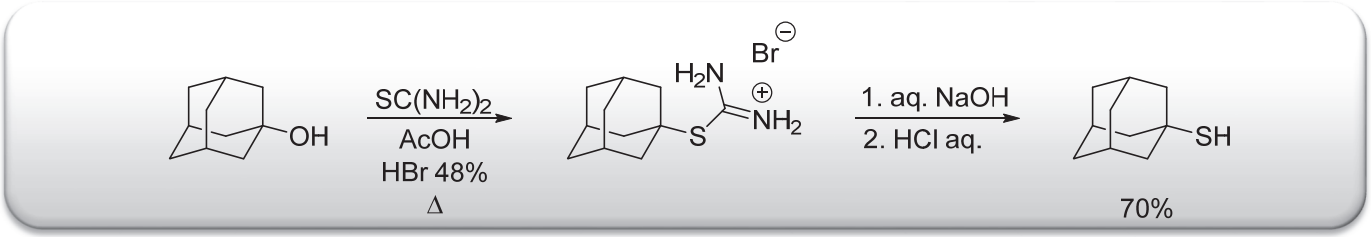
Hohman, J. N.; Kim, M.; Schüpbach, B.; Kind, M.; Thomas, J. C.; Terfort, A.; Weiss, P. S. *J. Am. Chem. Soc.* **2011**, *133*, 19422.

Known Preparation of Adamantylselenol



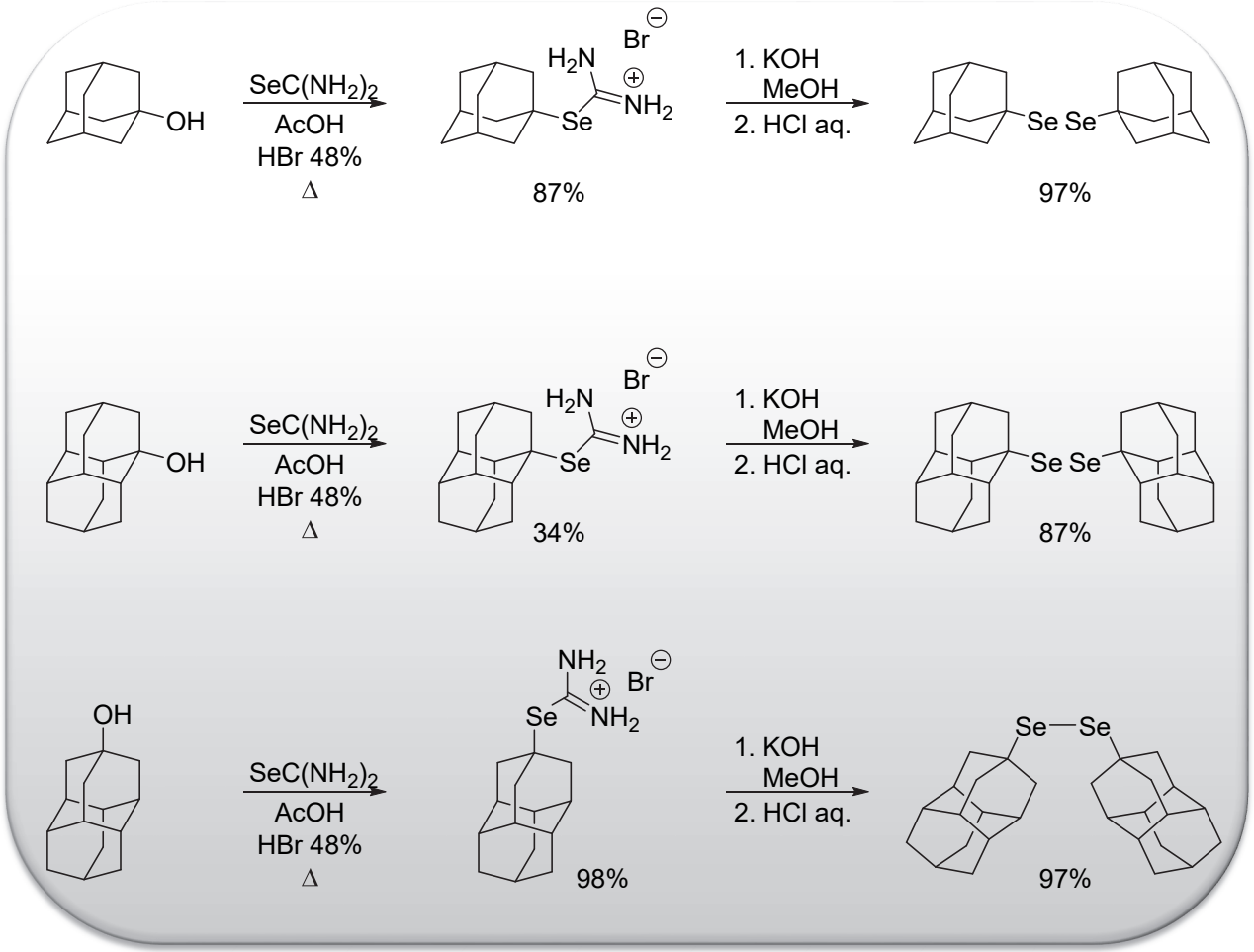
Hohman, J. N.; Kim, M.; Schüpbach, B.; Kind, M.; Thomas, J. C.; Terfort, A.; Weiss, P. S. *J. Am. Chem. Soc.* **2011**, *133*, 19422.

Preparation of Diamondoid Thiols



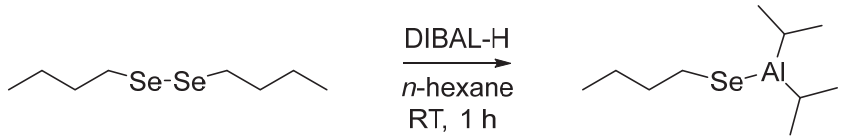
6-150 molar excess of $SC(NH_2)_2$ is required depending on diamondoid

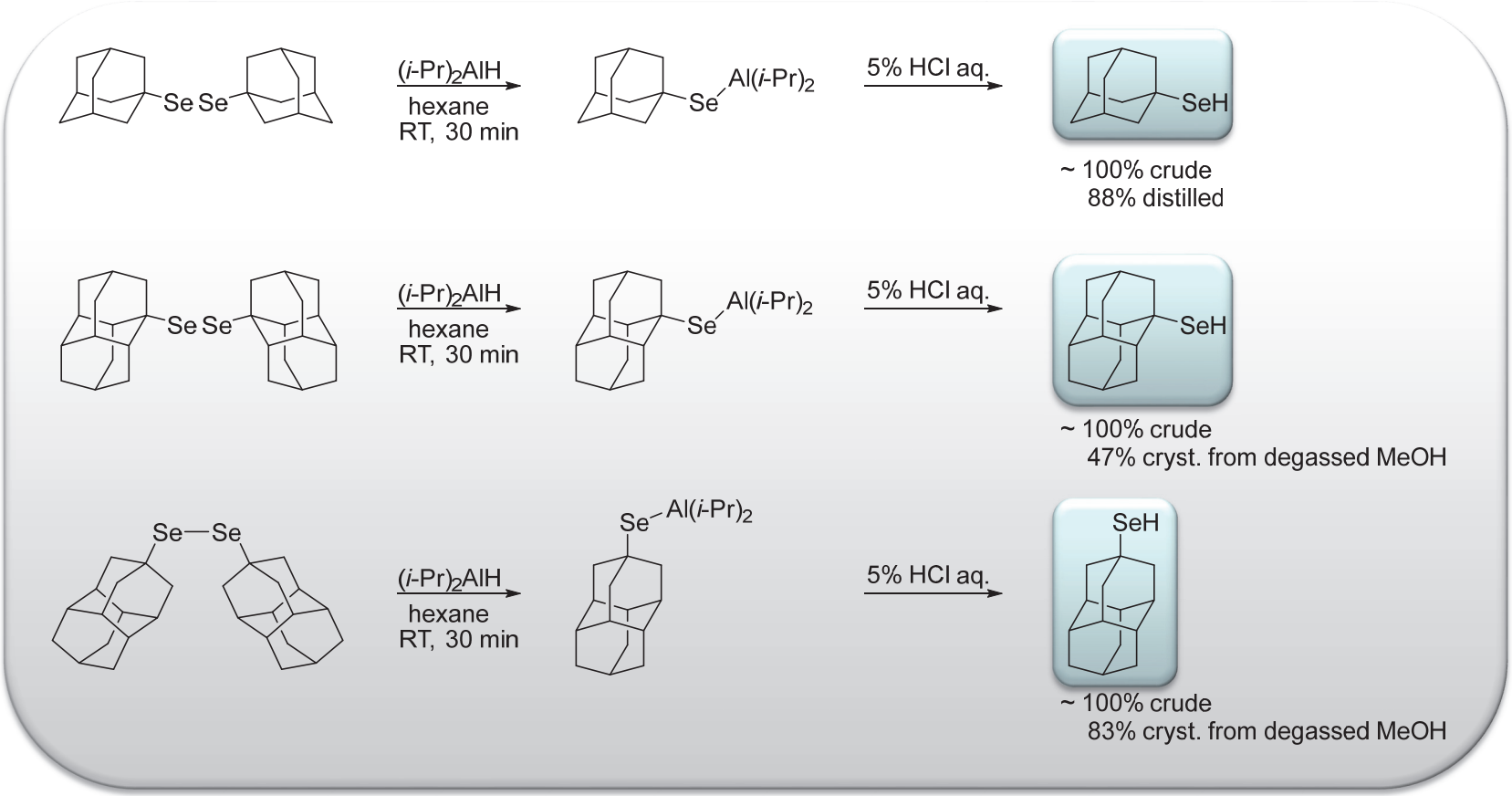
Diamantoiddiselenides Preparation



3 molar excess of $SeC(NH_2)_2$ is required

Diamantoidselenols Preparation





Takeda, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. J. Org. Chem. 1994, 59, 5824.

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Thank you for your attention!