OL Organic Letters

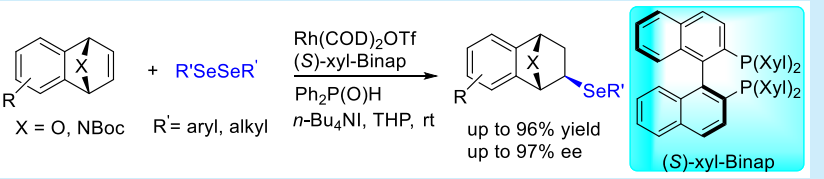
pubs.acs.org/OrgLett Letter

Rhodium-Catalyzed Enantioselective Hydroselenation of Heterobicyclic Alkenes

Sifeng Li, Qingjing Yang, Zhaoxiang Bian,* and Jun Wang*

Cite This: https://dx.doi.org/10.1021/acs.orglett.0c00762 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

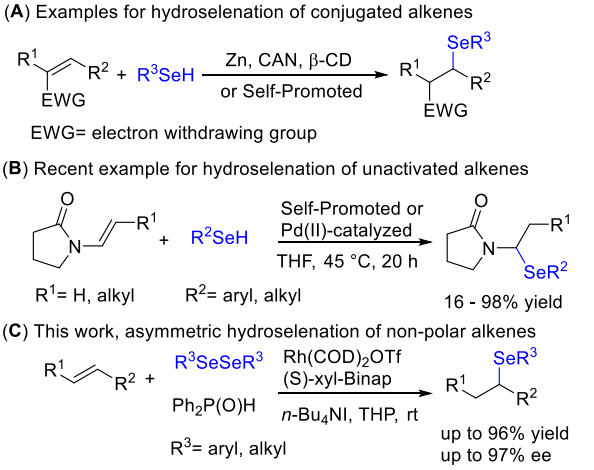


ABSTRACT: A highly efficient Rh(I)/(*S*)-xyl-Binap catalytic system is developed for the asymmetric hydroselenation of various nonpolar olefins with diselenides. Under these mild reaction conditions, a wide range of heterobicyclic alkenes give selenol-incorporated adducts in excellent enantioselectivities (up to 97%) along with high yields (up to 96%) by overcoming self-promoted racemic hydroselenation. The strategy is also applied for kinetic resolution of unsymmetric oxabenzonorbornadiene.

As an essential trace element for organisms, selenium was discovered over two hundred years ago.[1] Selenium plays an extremely important role in metabolism in the body[2] and disease chemoprevention and treatment.[3] From the investigations on numerous stable organoselenium compounds that were synthesized in recent decades, a large portion of them could be used as fluorescent probes,[4] antioxidants,[5] electrophiles,[6] organocatalysts,[7] which continually attracts interests from chemists. To date, the carbon−selenium bond is the most prevalent linkage in selenium-containing molecules. Among numerous approaches to construct C−Se bond, hydroselenation of unsaturated carbon−carbon double bonds provided the most efficient, atom-economic, and powerful approaches for the preparation of organoselenium compounds.

In 1988, Hevesi reported the first hydroselenation of conjugated enones in the presence of $ZnCl_2$,[8] although the desired adduct was controlled by the substrates used. Then the hydroselenation of α,β-unsaturated ketones was found to be catalyzed by ceric ammonium nitrate (CAN)[9] or β-cyclodextrin,[10] while the nitroalkenes[11] and vinylsulfonamide[12] were self-promoted in the absence of any catalyst (Scheme 1A). The substrates, such as those involving weakly activated or nonelectronically activated C=C bonds, were rarely reported. In 2016, Ogawa revealed the hydroselenation of *N*-vinyl lactams affording the corresponding N,Se-acetals as Markovnikov adducts (Scheme 1B).[13] The hydroselenation of terminal *N*-vinyl lactams was self-promoted, while Pd(II) catalyst was essential for the efficient hydroselenation of internal *N*-vinyl lactams. However, the direct asymmetric hydroselenation of alkenes has been seldom discovered, probably because of the high affinity of selenium with the transition metal. Furthermore, the selenols used in hydroselenation are odorous, poisonous, and easily oxidized in the air, which limited their utilization in organic synthesis. Interestingly, when diphenylphosphine oxide ($Ph_2P(O)H$) was served as a reductant in the selenation of unsaturated C−C bonds, the diaryl diselenides were preferentially converted to the corresponding selenols.[14] Herein, we present an example of asymmetric hydroselenation of various nonpolar alkenes under the presence of

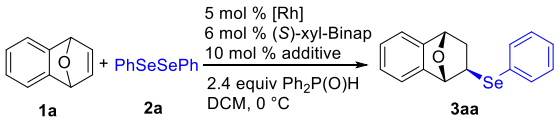
Scheme 1. Hydroselenation of Alkenes



Received: February 28, 2020

https://dx.doi.org/10.1021/acs.orglett.0c00762
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Initiation of Asymmetric Hydroselenation of Oxabenzonorbornadiene[a]



entry	[Rh]	additive	time (h)	yield[b] (%)	ee[c] (%)
1[d]			48	81	
2	$[Rh(COD)Cl]_2$	none	6	91	85
3	$[Rh(C_2H_4)Cl]_2$	none	8	70	82
4	$[Rh(NBD)Cl]_2$	none	36	80	80
5	$[Rh(coe)_2Cl]_2$	none	8	82	83
6	$[Rh(COD)OMe]_2$	none	48	90	86
7	$[Rh(COD)acac]_2$	none	8	89	86
8	$Rh(COD)_2BF_4$	none	4	77	87
9	$Rh(COD)_2OTf$	none	4	83	87
10	$Rh(COD)_2OTf$	n-Bu_4NBr	8	91	89
11	$Rh(COD)_2OTf$	n-Bu_4NI	0.3	92	94
12[e]	$Rh(COD)_2OTf$	n-Bu_4NI	0.5	97	94
13[e,f]	$Rh(COD)_2OTf$	n-Bu_4NI	3	91	95
14[e,f,g]	$Rh(COD)_2OTf$	n-Bu_4NI	4	91	87
15[e,f,h]	$Rh(COD)_2OTf$	n-Bu_4NI	30	82	68

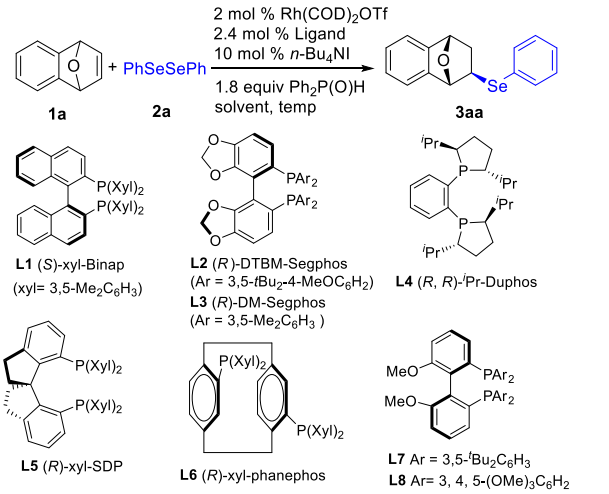
[a]Reaction conditions: Rh (5 mol %) and (*S*)-xyl-Binap (6 mol %) dissolved in DCM with stirring for 30 min under argon, then the additive (10 mol %, if applicable) was added and the mixture stirred for an additional 10 min. **1a** (0.2 mmol), **2a** (0.24 mmol), and $Ph_2P(O)H$ (2.4 equiv) were added into the mixture at 0 °C. [b]Isolated yields. [c]Determined by HPLC analysis. [d]No (*S*)-xyl-Binap was used. [e]1.8 equiv of $Ph_2P(O)H$ was used. [f]2 mol % of catalyst was used. [g]0.2 equiv of BHT was used. [h]1.0 equiv of BHT was used. DCM = dichloromethane. NaBArF = sodium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate. n-Bu_4NBr = tetrabutylammonium bromide. n-Bu_4NI = tetrabutylammonium iodide. BHT = 2,6-di-*tert*-butyl-4-methylphenol.

diphenylphosphine oxide and diselenides for generating the selenols in situ (Scheme 1C).

Heterobicyclic alkenes are ideal substrates to be activated by transition-metal complexes due to the angle strain and the proximal heteroatom coordination.[15] Recently, transition-metal-catalyzed hydrofunctionalization of aza/oxabenzonorborna dienes with heteronucleophiles, including hydroamination,[16] hydrothiolation,[17] hydrophosphination,[18] and hydroboration,[19] have been developed successfully. However, enantioselective hydroselenation for these bicyclic alkenes has not been involved. Selenols are more nucleophilic and acidic than thiols, thus providing distinct challenges and opportunities for hydrofunctionalization.

Based our previous experience on asymmetric hydrofunctionalization of aza/oxabenzonorbornadienes with heteronucleophiles,[17d,18b] we embarked on the asymmetric hydroselenation of nonpolar alkenes in the presence of rhodium precursor (5 mol %) and (*S*)-xyl-Binap (6 mol %) in dichloromethane at 0 °C by utilizing oxabicyclic alkenes **1a** and diphenyl diselenide **2a** as standard substrates and diphenylphosphine oxide as a reductant. It should be noted that the self-promoted hydroselenation of oxabicyclic alkenes **1a** was a competitive background reaction, and the racemic adduct was obtained in 81% yield without any catalyst (Table 1, entry 1). In the primal reaction for screening the rhodium precursors, a wide range of rhodium complexes including $[Rh(COD)Cl]_2$, $[Rh(C_2H_4)Cl]_2$, $[Rh(NBD)Cl]_2$, $[Rh(coe)_2Cl]_2$, $[Rh(COD)OMe]_2$, $[Rh(COD)acac]_2$, $Rh(COD)_2BF_4$, and $Rh(COD)_2OTf$ were investigated. Among them, $Rh(COD)_2OTf$ gave relatively better results, 83% yield and 87% enantioselectivity (Table 1, entry 9). An additional improvement to 94% ee could be achieved via a halide exchange protocol, where the initial OTf counterion was replaced by an iodide counterion (n-Bu_4NI) (Table 1, entry 11). The addition of n-Bu_4NI also greatly accelerated this process, reducing the reaction time to 20 min, and the yield and ee were obtained in 92% and 94%, respectively. Decreasing the amount of $Ph_2P(O)H$ to 1.8 equiv and lowering the catalyst loading to 2 mol % have no significant effect on the result, and the yield remained at 91% while the ee was retained at 95% (entry 13). The use of 0.2 equiv of radical inhibitor BHT did not obviously decrease the yield and enantioselectivity, but the reaction slowed down and the ee was dropped to 68% when 1 equiv of BHT was added (entries 14 and 15).

Table 2. Screening of Ligand, Solvent, and Temperature[a]



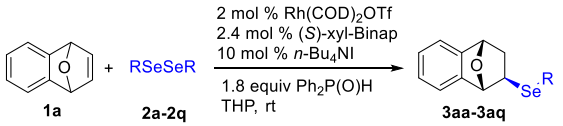
entry	ligand	solvent	time (h)	yield (%)[b]	ee (%)[c]
1	L1	DCM	3	91	95
2	L2	DCM	2	95	85
3	L3	DCM	12	86	93
4	L4	DCM	72	nr	
5	L5	DCM	72	trace	
6	L6	DCM	72	trace	
7	L7	DCM	4	83	84
8	L8	DCM	4	87	92
9	L1	THF	6	83	97
10	L1	DME	12	80	96
11	L1	DCE	48	60	84
12	L1	toluene	6	93	95
13	L1	dioxane	6	90	92
14	L1	DMF	72	nr	
15	L1	THP	6	86	97
16[d]	L1	THP	2	96	97

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $Rh(COD)_2OTf$ (2 mol %), ligand (2.4 mol %), n-Bu_4NI (10 mol %), and $Ph_2P(O)H$ (0.36 mmol) were added into a Schlenk tube with solvent (2 mL), and then the mixture was stirred at 0 °C for the indicated duration. [b]Isolated yields. [c]Determined by HPLC analysis. [d]The reaction was carried out at room temperature. THF = tetrahydrofuran. DME = dimethoxyethane. DCE = dichloroethane. DMF = *N*,*N*-dimethylformamide. THP = tetrahydropyran.

With the tentative reaction conditions in hand, a batch of bulky bidentate phosphine ligands were tested for the better yields and enantioselectivities. In the presence of 2 mol % of

https://dx.doi.org/10.1021/acs.orglett.0c00762
Org. Lett. XXXX, XXX, XXX−XXX

Table 3. Scope of Diselenides for the Asymmetric Hydroselenation of Oxabenzonorbornadiene[a]



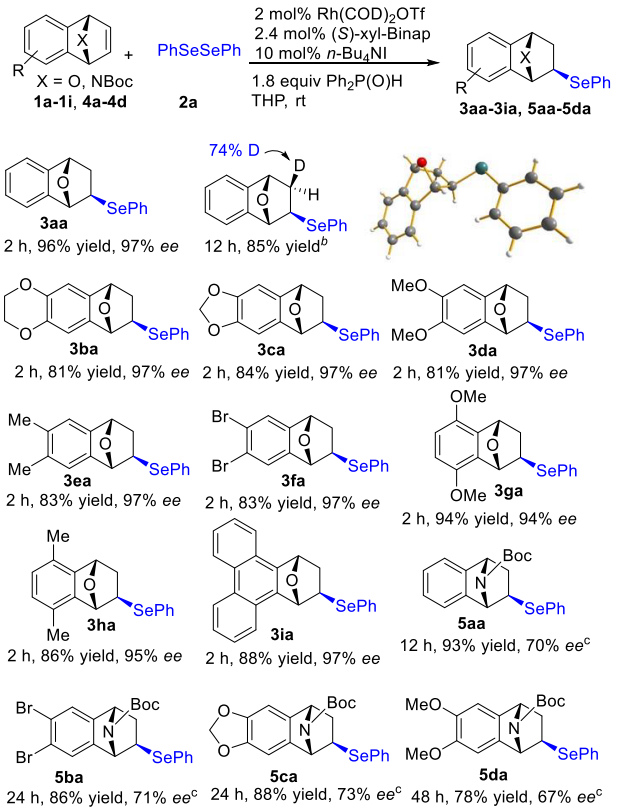
entry	R		time (h)	yield[b] (%)	ee[c] (%)
1	Ph	**2a**	2	96	97
2[d]	4-FC_6H_4	**2b**	8	91	93
3	4-ClC_6H_4	**2c**	6	93	91
4	4-BrC_6H_4	**2d**	10	96	95
5[d]	4-$CF_3C_6H_4$	**2e**	24	86	87
6[d]	4-OHC_6H_4	**2f**	12	63	60
7[d]	4-$OMeC_6H_4$	**2g**	2	97	95
8[d]	3-$OMeC_6H_4$	**2h**	24	82	87
9[d]	2-$OMeC_6H_4$	**2i**	36	79	87
10	4-$^tBuC_6H_4$	**2j**	8	91	96
11	4-*i*-PrC_6H_4	**2k**	4	96	95
12[d]	4-MeC_6H_4	**2l**	8	86	87
13[d]	3-MeC_6H_4	**2m**	10	83	92
14[d]	2-MeC_6H_4	**2n**	10	95	92
15[d]	4-PhC_6H_4	**2o**	8	76	88
17[d]	Bn	**2p**	8	92	75
18[d]	Me	**2q**	12	96	72

[a]Reaction conditions: **1a** (0.2 mmol), **2a**–**2q** (0.24 mmol), 2 mol % of $Rh(COD)_2OTf$, 2.4 mol % of (*S*)-xyl-Binap, 10 mol % of *n*-Bu_4NI, 2.4 equiv of $Ph_2P(O)H$, and THP (2 mL) were stirred at rt for the indicated duration. [b]Isolated yields. [c]Determined by HPLC analysis. [d]5 mol % of catalyst was used.

$Rh(COD)_2OTf$, $Ph_2P(O)H$ (1.8 equiv) and *n*-Bu_4NI (10 mol %), **L2** (*R*)-DTBM-Segphos, **L3** (*R*)-DM-Segphos, and Biphep type ligands **L7** and **L8** all worked well, leading to a slightly decreased enantioselective control (84–93%) compared to (*S*)-xyl-Binap (Table 2, entries 1–3, 7, and 8), while the use of **L4** (*R*,*R*)-^{i}Pr-Duphos, **L5** (*R*)-xyl-SDP, and **L6** (*R*)-xyl-phanephos blocked the hydroselenation at 0 °C (entries 4–6). To further optimize the reaction, a series of solvents were tested. To our delight, except for DMF, the reaction proceeded well with the rest of the solvents employed (DCM, THF, DME, DCE, toluene, dioxane, and THP (entries 9–13 and 15) to give the yields in a range of 60–93% and the ee's in a range of 84–97%. THP was found to be the best solvent; when the reaction was performed at room temperature, the yield was increased from 92% to 96% and the enantioselectivity was kept at 97% (entry 16). Thus, the optimal reaction conditions were established under the presence of $Rh(COD)_2OTf$ (2 mol %), (*S*)- xyl-Binap (2.4 mol %), and *n*-Bu_4NI (10 mol %), and oxabenzonorbornadiene reacted with diselenide (1.2 equiv) and $Ph_2P(O)H$ (1.8 equiv) in THP at room temperature.

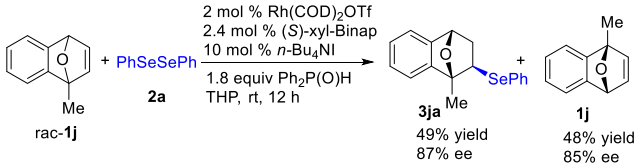
To test the compatibility of the optimized catalytic system, various diselenides were used as a selenium resource in the enantioselective hydroselenation of oxabenzonorbornadiene **1a**. The aryl diselenides substituted with MeO or Me at the *ortho*-, *meta*- or *para*-position were all well-tolerated and gave satisfactory results as well (Table 3, entries 7–9 and 12–14). The reaction protocol displayed a good functional group tolerance in most cases, and both the electron-donating groups (MeO, Me, *i*-Pr, *t*-Bu) (**2g**–**2n**) and the electron-withdrawing groups (Cl, F, Br, CF_3) (**2b**–**2e**) were found to be compatible under these conditions, affording good yields (79–97%) and high ee's (87–95%). To our delight, the naked hydroxyl group

Scheme 2. Scope of Alkenes[a]

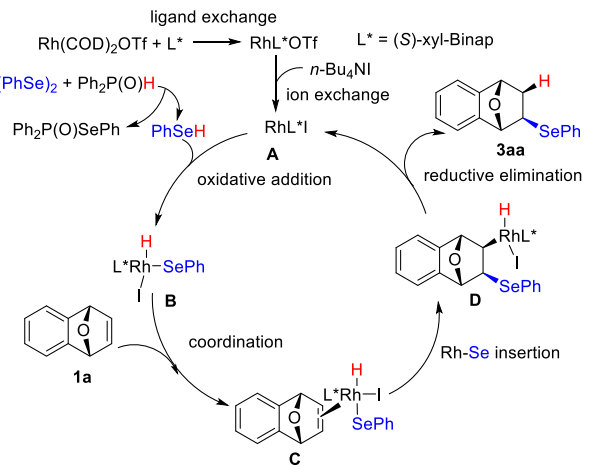


[a]Reaction conditions: oxabenzonorbornadienes **1a**–**1i** or azabenzonorbornadienes **4a**–**4d** (0.2 mmol), **2a** (0.24 mmol), $Rh(COD)_2OTf$ (2 mol %), (*S*)-xyl-Binap (2.4 mol %), *n*-Bu_4NI (10 mol %), $Ph_2P(O)H$ (2.4 equiv), and THP (2 mL) were stirred at rt for the indicated duration. Isolated yields and determined ees were indicated. [b]D_2O (20 equiv) was used. [c]5 mol % of catalyst was used.

Scheme 3. Strategy for Kinetic Resolution



Scheme 4. Proposed Mechanism



https://dx.doi.org/10.1021/acs.orglett.0c00762
Org. Lett. XXXX, XXX, XXX–XXX

(entry 6) was also tolerated in this system, and 63% yield and 60% ee were obtained within 12 h. Apart from aromatic diselenides, the aliphatic diselenides also proceeded well in this catalyst system with 5 mol % of Rh, affording good ee's (75% ee and 72% ee) with excellent yields (entries 17 and 18).

To further investigate the substrate scope, a broad range of heterobicyclic olefins were tested (Scheme 2). Delightedfully, all of the phenyl-functionalized oxabenzonorbornadienes were well compatible with standard conditions, maintaining good yields (81−96%) and high enantioselectivities (94% to 97%) (**3aa**−**3ia**). Furthermore, the azabenzonorbornadienes also tolerated the the rhodium system, yielding high yields (78−93%) and good enantioselectivities (67−73% ee) by using 5 mol % of catalyst (**5aa**−**5da**). When the deuterated water (20 equiv) was added to the standard system, 74% of deuteration on the vertical position was detected by NOESY. The *exo*-configuration of the exclusive addition product **3aa** was further confirmed by X-ray crystal structure analysis. To demonstrate the practicability of our method, the scaled-up reaction was conducted by using 1.2 mmol of oxabenzonorbornadiene **1a**. The reaction was completed in 6 h under the standard reaction conditions, and the product **3aa** was obtained in 91% yield (328 mg) without any loss of enantioselectivity.

When the C−O bridge monomethylated oxabenzonorbornadiene **1j** was subjected to $Rh(COD)_2OTf$/(*S*)-xyl-Binap conditions, kinetic resolution occurred (Scheme 3). Intriguingly, the newly formed selenol attacked the C−C double bond closer to the substituent group to form product **3ja** in 49% yield and 87% ee after 12 h, while the substrate **1j** was recovered in 84% ee with 48% yield (*s* factor is 38). This result indicated that the reaction condition could be applied to the kinetic resolution of unsymmetric oxabenzonorbornadienes.

On the basis of previous study for Rh(I)-catalyzed hydrothiolation,[20] a possible pathway for this hydroselenation is shown in Scheme 4. Chiral Rh(I) complex **A** is formed by the ligand and ion exchange of $Rh(COD)_2OTf$ with (*S*)-xyl-Binap and *n*-Bu_4NI. Oxidative addition of selenol with Rh(I) complex **A** provides intermediate **B**. The substrate **1a** coordinates to intermediate **B** to form the less sterically encumbered intermediate coordinated Rh complex **C**, and then the insertion of the C═C into the Rh−Se bond provides the intermediate **D**. Reductive elimination affords the product **3aa** and regenerates the active Rh complex **A**. The catalytic cycle consists of oxidative addition, coordination, *syn*-selenometalation, and reductive elimination.

In summary, a rhodium catalytic system consisting of $Rh(COD)_2OTf$/(*S*)-xyl-Binap and *n*-Bu_4NI was successfully established in the mild conditions for the highly enantioselective hydroselenation of heterobicyclic alkenes, which overcame the presumed poison of selenium to rhodium and the competition of the self-promoted hydroselenation. Meanwhile, this system could be well applied to the kinetic resolution of the bridge mono methylated oxabenzonorbornadiene. This methodology unlocked the asymmetric hydroselenation of nonpolar olefins. We believe this study will have versatile applications in the synthesis of bioactive organoselenium compounds.

■ ASSOCIATED CONTENT

Supporting Information

TThe Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00762.

Experimental procedures, characterization data, and copies of ^1H ^{13}C NMR, NOESY, and COSY spectra and HPLC charts (PDF)

Accession Codes

CCDC 1976783 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Zhaoxiang Bian − *School of Chinese Medicine, Hong Kong Baptist University, Kowloon, Hong Kong*; Email: bianzxiang@gmail.com

Jun Wang − *Shenzhen Grubbs Institute and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China*; orcid.org/0000-0001-9723-4054; Email: wang.j@sustech.edu.cn

Authors

Sifeng Li − *Shenzhen Grubbs Institute and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China; School of Chinese Medicine, Hong Kong Baptist University, Kowloon, Hong Kong*

Qingjing Yang − *Shenzhen Grubbs Institute and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c00762

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the National Natural Science Foundation of China (NSFC 21971102) and Shenzhen Basic Research Program (JCYJ20170817112532779).

■ REFERENCES

(1) *Organoselenium Chemistry: Synthesis and Reactions*; Wirth, T., Ed.; Wiley-VCH: Weinheim, 2012.

(2) (a) Weekley, C. M.; Harris, H. H. *Chem. Soc. Rev.* **2013**, *42*, 8870−8894. (b) Thiry, C.; Ruttens, A.; De Temmerman, L.; Schneider, Y.-J.; Pussemier, L. *Food Chem.* **2012**, *130*, 767−784.

(3) (a) Seng, H.-L.; Tiekink, E. R. T. *Appl. Organomet. Chem.* **2012**, *26*, 655−662. (b) Roy, G.; Mugesh, G. *Chem. Biodiversity* **2008**, *5*, 414−439. (c) Nogueira, C. W.; Zeni, G.; Rocha, J. B. *Chem. Rev.* **2004**, *104*, 6255−6285. (d) Ninomiya, M.; Garud, D. R.; Koketsu, M. *Coord. Chem. Rev.* **2011**, *255*, 2968−2990. (e) Soriano-Garcia, M. *Curr. Med. Chem.* **2004**, *11*, 1657−1669. (f) Cardoso, B. R.; Roberts, B. R.; Bush, A. I.; Hare, D. J. *Metallomics* **2015**, *7*, 1213−1228. (g) Roman, M.; Jitaru, P.; Barbante, C. *Metallomics* **2014**, *6*, 25−54.

(4) (a) Manjare, S. T.; Kim, Y.; Churchill, D. G. *Acc. Chem. Res.* **2014**, *47*, 2985−2998. (b) Panda, S.; Panda, A.; Zade, S. S. *Coord. Chem. Rev.* **2015**, *300*, 86−100.

(5) Mugesh, G.; Singh, H. B. *Chem. Soc. Rev.* **2000**, *29*, 347−357.

(6) (a) Browne, D. M.; Wirth, T. *Curr. Org. Chem.* **2006**, *10*, 1893−1903. (b) Mukherjee, A. J.; Zade, S. S.; Singh, H. B.; Sunoj, R. B. *Chem. Rev.* **2010**, *110*, 4357−4416.

(7) Selected examples: (a) Denmark, S. E.; Hartmann, E.; Kornfilt, D. J. P.; Wang, H. *Nat. Chem.* **2014**, *6*, 1056−1064. (b) Liu, X.; Liang, Y.; Ji, J.; Luo, J.; Zhao, X. *J. Am. Chem. Soc.* **2018**, *140*, 4782−4786. (c) Xu, J.; Zhang, Y.; Qin, T.; Zhao, X. *Org. Lett.* **2018**, *20*, 6384−6388. (d) Luo, J.; Cao, Q.; Cao, X.; Zhao, X. *Nat. Commun.* **2018**, *9*, 527−535. (e) Chen, F.; Tan, C. K.; Yeung, Y.-Y. *J. Am. Chem. Soc.* **2013**, *135*, 1232−1235.
(8) Dieden, R.; Hevesi, L. *Synthesis* **1988**, *1988*, 616−619.
(9) Chu, C.-M.; Gao, S.; Sastry, M. N. V.; Kuo, C.-W.; Lu, C.; Liu, J.-T.; Yao, C.-F. *Tetrahedron* **2007**, *63*, 1863−1871.
(10) Srinivas, B.; Kumar, V. P.; Sridhar, R.; Reddy, V. P.; Nageswar, Y. V. D.; Rao, K. R. *Helv. Chim. Acta* **2009**, *92*, 1080−1084.
(11) Denmark, S. E.; Montgomery, J. I. *J. Org. Chem.* **2006**, *71*, 6211−6220.
(12) Kihara, N.; Mitsuhashi, Y.; Sato, M.; Hirose, S.-i.; Goudo, E.; Uzawa, Y.; Shirai, N.; Hamamoto, S.; Iwasaki, R.; Fujioka, A. *Tetrahedron Lett.* **2016**, *57*, 2563−2566.
(13) Tamai, T.; Yoshikawa, M.; Higashimae, S.; Nomoto, A.; Ogawa, A. *J. Org. Chem.* **2016**, *81*, 324−329.
(14) (a) Kawaguchi, S.; Kotani, M.; Atobe, S.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Organometallics* **2011**, *30*, 6766−6769. (b) Kobiki, Y.; Kawaguchi, S.; Ogawa, A. *Tetrahedron Lett.* **2013**, *54*, 5453−5456.
(15) For selected reviews, see: (a) Lautens, M.; Fagnou, K.; Hiebert, S. *Acc. Chem. Res.* **2003**, *36*, 48−58. (b) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169−196. (c) Rayabarapu, D. K.; Cheng, C.-H. *Acc. Chem. Res.* **2007**, *40*, 971−983. (d) Yang, D.; Han, Y. *Chin. J. Org. Chem.* **2006**, *26*, 1613−1622. (e) Cheng, H.; Liang, X.; li, X.; Long, Y.; Yang, D. *Youji Huaxue* **2012**, *32*, 433−443. (f) Wu, R.; Yang, W.; Cheng, G.; Li, Y.; Yang, D. *Youji Huaxue* **2016**, *36*, 2368−2379.
(16) Miki, Y.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2014**, *16*, 1498−1501.
(17) (a) Hodgson, D. M.; Bebbington, M. W. P.; Willis, P. *Org. Biomol. Chem.* **2003**, *1*, 3787−3798. (b) Leong, P.; Lautens, M. *J. Org. Chem.* **2004**, *69*, 2194−2196. (c) Yang, D.; Xia, J.; Long, Y.; Zeng, Z.; Zuo, X.; Wang, S.; Li, C. *Org. Biomol. Chem.* **2013**, *11*, 4871−4881. (d) Li, S.; Lu, Z.; Meng, L.; Wang, J. *Org. Lett.* **2016**, *18*, 5276−5279.
(18) (a) Sadeer, A.; Ong, Y. J.; Kojima, T.; Foo, C. Q.; Li, Y.; Pullarkat, S. A.; Leung, P. H. *Chem. - Asian J.* **2018**, *13*, 2829−2833. (b) Lu, Z.; Zhang, H.; Yang, Z.; Ding, N.; Meng, L.; Wang, J. *ACS Catal.* **2019**, *9*, 1457−1463.
(19) Lee, H.; Lee, B. Y.; Yun, J. *Org. Lett.* **2015**, *17*, 764−766.
(20) (a) Yang, X.-H.; Davison, R.; Nie, S.-Z.; Cruz, F. A.; McGinnis, T. M.; Dong, V. M. *J. Am. Chem. Soc.* **2019**, *141*, 3006−3013. (b) Yang, X.-H.; Davison, R.; Dong, V. M. *J. Am. Chem. Soc.* **2018**, *140*, 10443−10446. (c) Kennemur, J. L.; Kortman, G. D.; Hull, K. L. *J. Am. Chem. Soc.* **2016**, *138*, 11914−11919. (d) Pritzius, A. B.; Breit, B. *Angew. Chem., Int. Ed.* **2015**, *54*, 15818−15822.

https://dx.doi.org/10.1021/acs.orglett.0c00762
Org. Lett. XXXX, XXX, XXX−XXX