OL | Organic Letters

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

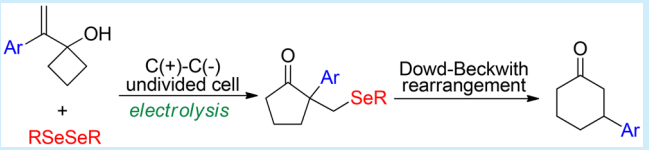
Electrochemical Radical Selenylation/1,2-Carbon Migration and Dowd−Beckwith-Type Ring-Expansion Sequences of Alkenylcyclobutanols

Yeon Joo Kim and Dae Young Kim*

Department of Chemistry, Soonchunhyang University, Asan, Chungnam 31538, Republic of Korea

Supporting Information

ABSTRACT: Electrochemical oxidative radical selenylation/1,2-carbon migration and Dowd−Beckwith-type ring-expansion sequences of alkenylcyclobutanols were developed in this study. This approach is environmentally benign and uses shelf-stable diselenides as selenium radical precursors and electrons as oxidizing reagents. The present protocol offers a facile way to prepare β-selenated cyclic ketone derivatives. Under Dowd−Beckwith-type rearrangement, it can afford the corresponding one-carbon ring-expanded ketones.



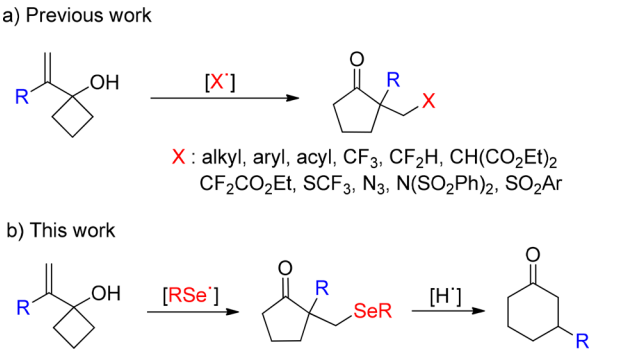
Selenium-containing organic compounds are of great importance in medicinal chemistry and material science because of their biological and chemical properties.[1] They can also be used as chemical intermediates for organic and inorganic synthesis.[2] Owing to the wide applications of these compounds, intensive efforts have been made to develop novel and practical synthetic methods as well as new organoselenium compounds.[3] Diselenides are easily accessible and shelf-stable reagents. They have emerged as valuable selenating agents for the synthesis of organoselenium compounds. The reaction of diselenides with various substrates such as alkenes, boronic acids, aromatics, and diazonium salts has been used to furnish diverse selenium-containing organic compounds.[4]

The radical-mediated difunctionalization of alkenes provided a practical approach for the difunctionalization of unactivated alkenes with high chemo- and regioselectivity.[5,6] Recently, several groups have reported the synthesis of β-funtionalized ketones via radical-addition and 1,2-rearrangement sequences of allylic alcohol derivatives with various radicals including alkyl, aryl, acyl, difluoromethyl, trifluoromethyl, azido, amine, and phenylsulfonyl radicals (Scheme 1a).[7]

In the past few years, electrochemistry has emerged as an attractive approach for organic chemists to introduce chemical functionality into organic molecules due to its environmentally benign and practical nature. Synthetic electrochemistry could achieve redox reactions without needing transition-metal catalysts or toxic reagents due to use of electrons as oxidizing or reducing reagents.[8]

To the best of our knowledge, electrochemical oxidative selenylation and ring-expansion sequences of alkenylcyclobutanols have not been reported yet. We envisioned transformation of alkenylcyclobutanols to β-selenated cyclopentanones by an electrochemical-catalyzed oxidative selenylation/semipinacol rearrangement sequence with diselenides as selenium radical precursors. In addition, β-selenated cyclic ketone derivatives under radical-initiated Dowd−Beckwith-type rearrangement could give the corresponding one-carbon ring-expanded ketones (Scheme 1b). Recently, application of a one-carbon ring-expansion reaction for the synthesis of cyclic ketones has gained increasing interest in organic chemistry due to the availability of substrates as building blocks for bioactive compounds.[9]

Scheme 1. Stratergy for Radical Selenation/1,2-Carbon Migration and Dowd−Beckwith-Type Ring-Expansion Sequences



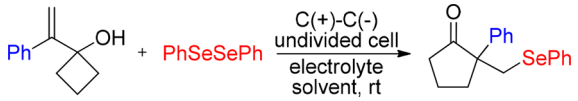
As part of our research program related to redox reaction and cyclization sequences, we recently reported intramolecular redox,[10] radical-addition, and ring-expansion reactions of alkenes with several radical sources under redox conditions.[7c−h] In this paper, we report electrochemical-catalyzed oxidative selenylation and semipinacol rearrangement sequences via 1,2-alkyl migration of alkenylcyclobutanol derivatives and Dowd−Beckwith-type rearrangement of β-selenyl-substituted cyclopentanones to afford cyclohexanone derivatives.

Received: December 18, 2018

DOI: 10.1021/acs.orglett.8b04041
Org. Lett. XXXX, XXX, XXX−XXX

To determine optimal reaction conditions for electrochemical radical selenylation/semipinacol rearrangement[11] sequences of alkenylcyclobutanol derivatives, we chose 1-(1-phenylvinyl) cyclobutanol (**1a**) and diphenyl diselenide (**2a**) as the model substrates. The reaction was conducted in an undivided cell with glassy carbon plate as electrodes under constant current. Initially, *n*-Bu_4NBF_4 was employed as the electrolyte and methanol as the solvent at a constant current of 3 mA. The radical-addition and ring-expansion product **3a** was obtained in 61% yield after the reaction proceeded at room temperature for 4 h (Table 1, entry 1). We then surveyed

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3a**

entry	solvent	current density (mA/cm^2)	electrolyte	time (h)	yield[b] (%)
1	MeOH	3	*n*-Bu_4NBF_4	4	61
2	DMSO	3	*n*-Bu_4NBF_4	4	32
3	THF	3	*n*-Bu_4NBF_4	4	trace
4	CH_3CN	3	*n*-Bu_4NBF_4	2	80
5	CH_3CN	3	*n*-Bu_4NPF_6	2	62
6	CH_3CN	3	*n*-Bu_4NClO_4	2	63
7	CH_3CN	3	$LiClO_4$	2	68
8	CH_3CN	3	KI	2	70
9[c]	CH_3CN	3	*n*-Bu_4NBF_4	1.5	80
10[d]	CH_3CN	3	*n*-Bu_4NBF_4	1.5	75
11[c]	CH_3CN	5	*n*-Bu_4NBF_4	1.5	82
12[c]	CH_3CN	7	*n*-Bu_4NBF_4	1	90
13[c,e]	CH_3CN	7	*n*-Bu_4NBF_4	1	81
14[f]	CH_3CN	0	*n*-Bu_4NBF_4	1	0

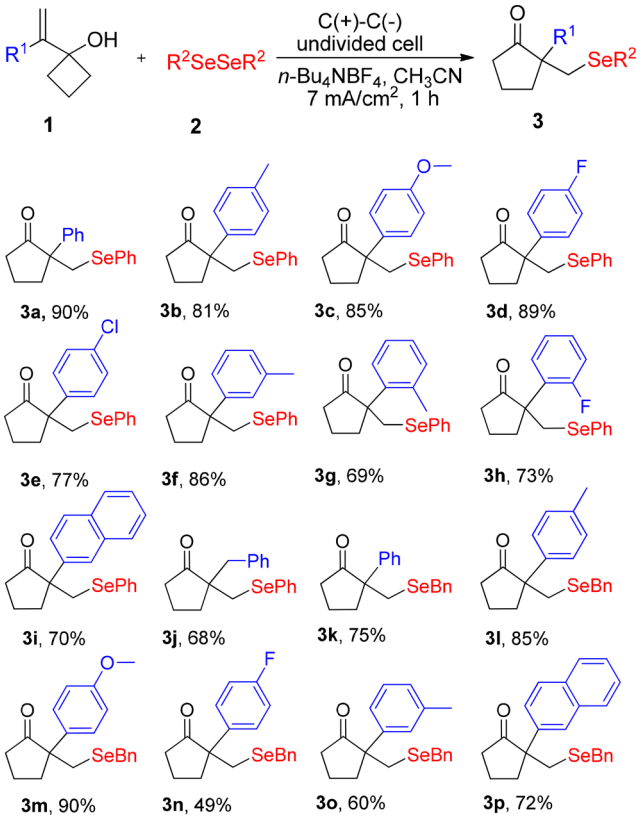
[a]Reaction conditions: glssy carbon anode, glssy carbon cathode, 1-(1-phenylvinyl)cyclobutanol **1a** (0.1 mmol), diphenyl diselenide **2a** (0.2 mmol), solvent (2.0 mL), electrolyte (0.4 mmol) at room temperature using ElectraSyn 2.0. [b]Isolated yield. [c]Electrolyte (0.2 mmol). [d]Electrolyte (0.1 mmol). [e]Pt(+)−Pt(−) instead of C(+)−C(−). [f]No electricity.

different kinds of common solvents, such as DMSO, THF, and acetonitrile (Table 1, entries 1−4). Of them, acetonitrile was found to be the best medium. Various supporting electrolytes such as *n*-Bu_4NBF_4, *n*-Bu_4NPF_6, *n*-Bu_4NClO_4, $LiClO_4$, and KI were screened (Table 1, entries 4−8). *n*-Bu_4NBF_4 was found to be the most efficient electrolyte for this transformation (Table 1, entry 4). The effect of the amount of supporting electrolyte (*n*-Bu_4NBF_4) was also investigated. The yield of **3a** was maintained when 2.0 equiv of *n*-Bu_4NBF_4 per 1-(1-phenylvinyl)cyclobutanol (**1a**) was used (Table 1, entries 4, 9, and 10). Current intensity was also examined, and 7 mA was found to be the optimum constant current for this reaction (Table 1, entries 4, 11, and 12). Using platinum plates to replace glassy carbon plates led to a slight decrease in reaction yields (Table 1, entry 13). Finally, no desired product was obtained without an electric current (Table 1, entry 14).

With the optimal reaction conditions in hand, we investigated the scope of substrates for the electrochemical radical selenylation/semipinacol rearrangement sequences of alkenylcyclobutanol derivatives **1** with diselenide **2**. As shown in Scheme 2, various alkenylcyclobutanols **1** with electron-donating or electron-withdrawing substituted-aryl and naphthyl groups furnished corresponding migration products with moderate to high yields (69−90%, Scheme 2, **3a**−**i**). Notably, this radical selenylation/semipinacol rearrangement reaction with alkyl-substituted vinylcyclobutanol, 1-(3-phenylprop-1-en-2-yl)cyclobutanol, gave 68% yield of desired product **3j** under the optimal reaction conditions. To further examine the scope of this reaction, a range of dibenzyl diselenides (**2b**) were exposed to the optimal reaction conditions to react with alkenylcyclobutanols **1**. Corresponding products **3k**−**p** were obtained in moderate to high yields (49−90%, Scheme 2). Furthermore, α,α-diphenyl allylic alcohol (**4**), 1-(3,4-dihydronaphthalen-1-yl)cyclobutanol (**6**), 9-(1-phenylvinyl)-9*H*-fluoren-9-ol (**8**), and 1-(1-phenylvinyl)cyclopentanol (**10**) derivatives were also used as substrates in these electrochemical radical selenylation/semipinacol rearrangement sequences. Corresponding products **5**, **7**, **9**, and **11** were obtained in 73%, 37% (5.5:1 dr), 45%, and 54% yields (Scheme 3). In order to demonstrate the practicability of this electrochemical selenylation and ring expansion, the gram-scale reaction was explored. As shown in Scheme 4, when 1-(1-phenylvinyl)-cyclobutanol (**1a**) with diphenyl diselenide (**2a**) was used under the optimum reaction conditions, the reaction proceeded to afford the desired phenylselenyl-substituted cyclopentanone **3a** on a gram scale with 83% yield.

To illustrate synthetic utility, we also carried radical ring expansion of selenyl-substituted cyclopentanones **3** through Dowd−Beckwith-type rearrangement to afford one-carbon ring-expanded cyclohexanone derivatives **12**.[9] By treating

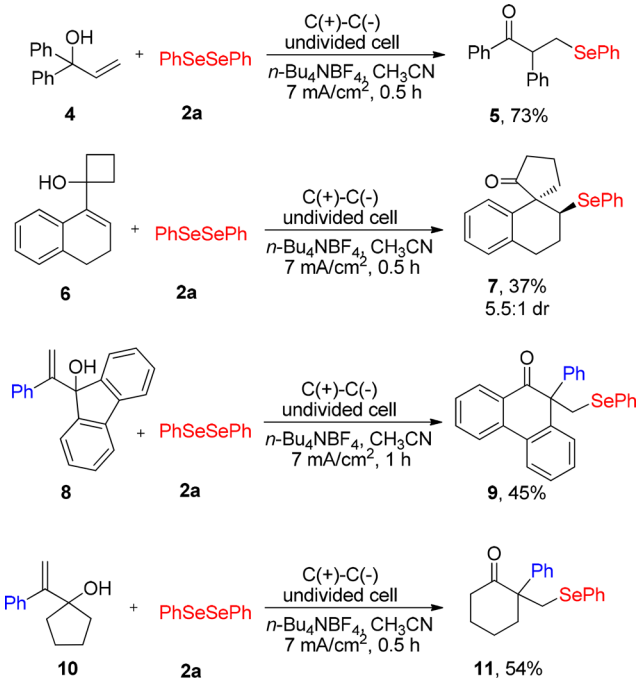
Scheme 2. Variation of Substrates.[a,b]



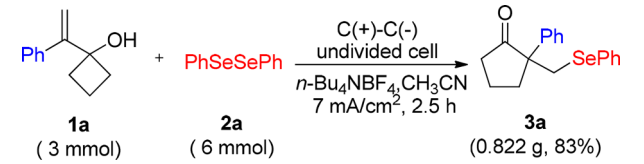
[a]Reaction conditions: glassy carbon anode, gassy carbon cathode, 1-(1-phenylvinyl)cyclobutanol (**1**, 0.1 mmol), R^2SeSeR^2 (**2**, 0.2 mmol), CH_3CN (2.0 mL), *n*-Bu_4NBF_4 (0.2 mmol), 7 mA/cm^2, 2.61 F/mol, at room temperature using ElectraSyn 2.0. [b]Isolated yield.

DOI: 10.1021/acs.orglett.8b04041
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 3. Electrochemical Radical Selenylation/1,2-Carbon Migration Sequences of 4, 6, 8, and 10



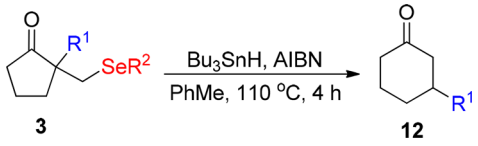
Scheme 4. Gram-Scale Synthesis of 3a



cyclopentanones **3** with tri-*n*-butyltin hydride and azobis(isobutyronitrile) (AIBN) in toluene at 110 °C for 4 h, the one-carbon ring-expanded cyclic ketones **12** could be furnished readily (Table 2). This is the first example of Dowd−Beckwith-type ring expansion with selenyl-substituted cyclopentanones **3**. It is noteworthy that *β*-substituted cyclohexanones can be prepared using a consecutive one-carbon ring-expansion sequence.

To gain mechanistic insights into this transformation, some preliminary experiments were performed. The reaction was shut down without an electric current (Table 1, entry 14). A trace or reduced yields of the product were detected in the presence of a radical scavengers, 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT), and 1,1-diphenylethene (Scheme 5). We also carried out cyclic voltammetry (CV) experiments to study the redox potential of substrates. An oxidation peak of 1-(1-phenylvinyl)cyclobutanol (**1a**) and diphenyl diselenide (**2a**) in acetonitrile were observed at 1.74 and 1.33 V, respectively (see the Supporting Information). We proposed the reaction mechanism as shown in Figure 1 based on our results and previously reported work.[11] Diphenyl diselenide (**2a**) is oxidized to generate cationic radical intermediate (**I**) which is decomposed to give phenylselenium radical **II** and phenyl selenium cation **III**.[11] This phenyl selenium radical **II** then reacts with 1-(1-arylvinyl)cyclobutanol **1**, yielding intermediate **IV** which is oxidized on anode to afford the cation **V**. 1,2-Carbon migration of cation **V** then leads to ring expansion that yields product **3a**

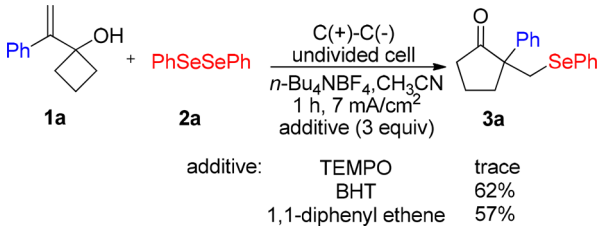
Table 2. Dowd−Beckwith Rearrangement in the One-Carbon Ring Expansion of 3[a]



entry	3, R^1, R^2	yield[b] (%)
1	**3a**, Ph, Ph	**12a**, 65
2	**3b**, 4-MeC_6H_4, Ph	**12b**, 77
3	**3c**, 4-$OMeC_6H_4$, Ph	**12c**, 73
4	**3d**, 4-FC_6H_4, Ph	**12d**, 67
5	**3e**, 4-ClC_6H_4, Ph	**12e**, 76
6	**3f**, 3-MeC_6H_4, Ph	**12f**, 62
7	**3g**, 2-MeC_6H_4, Ph	**12g**, 72
8	**3h**, 2-FC_6H_4, Ph	**12h**, 65
9	**3i**, 2-naphthyl, Ph	**12i**, 68
10	**3j**, benzyl, Ph	**12j**, 70
11	**3k**, Ph, benzyl	**12a**, 60
12	**3l**, 4-MeC_6H_4, Benzyl	**12b**, 70
13	**3m**, 4-$OMeC_6H_4$, Benzyl	**12c**, 81
14	**3n**, 4-FC_6H_4, Benzyl	**12d**, 72
15	**3o**, 3-MeC_6H_4, Benzyl	**12f**, 60

[a]Reaction conditions: 2-phenyl-2-((selanyl)methyl)cyclopentanone **3** (0.1 mmol), tributyltin hydride (0.3 mmol), AIBN (20 mol %), toluene (1 mL) at 110 °C. [b]Isolated yield.

Scheme 5. Control Experiments



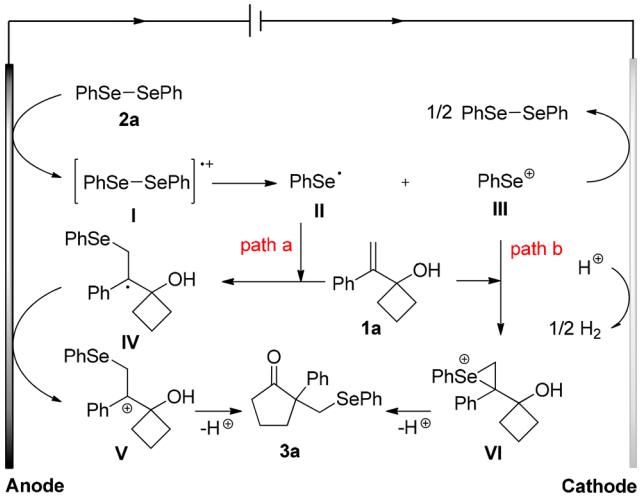


Figure 1. Proposed reaction mechanism.

(path a). As another possibility, the pathway in which phenyl selenium cation **III** was nucleophilically attacked by 1-(1-arylvinyl)cyclobutanol **1** and 1,2-carbon migration to form the desired product, could not be completely ruled out (path b).

DOI: 10.1021/acs.orglett.8b04041
Org. Lett. XXXX, XXX, XXX−XXX

In conclusion, we have developed a new and efficient strategy for the synthesis of cyclohexanone derivatives via electrochemically oxidative selenylation/1,2-carbon migration and Dowd−Beckwith-type rearrangement sequences of alkenylcyclobutanol derivatives **1** with diselenides **2**. This approach is environmentally benign by using shelf-stable diselenides as selenium radical precursors and electrons as oxidizing reagents. The present protocol is an efficient option for synthesizing β-selenated cyclic ketone and one-carbon expanded cyclic ketone derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b04041.

Experimental procedures and characterization data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dyoung@sch.ac.kr.

ORCID

Dae Young Kim: 0000-0002-6337-7505

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by Soonchunhyang University Research Fund and Basic Science Research Program through the National Research Foundation of Korea (NRF-2016R1D1A1B03933723).

■ REFERENCES

(1) (a) Mugesh, G.; Singh, H. B. *Acc. Chem. Res.* **2002**, *35*, 226. (b) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255. (c) Kumar, S.; Johansson, H.; Kanda, T.; Engman, L.; Müller, T.; Bergenudd, H.; Jonsson, M.; Pedulli, G. F.; Amorati, R.; Valgimigli, L. *J. Org. Chem.* **2010**, *75*, 716. (d) Sarma, B. K.; Manna, D.; Minoura, M.; Mugesh, G. *J. Am. Chem. Soc.* **2010**, *132*, 5364. (e) Santi, C. In *Organoselenium Chemistry Between Synthesis and Biochemistry*; Bentham Books, 2014. (f) Sancineto, L.; Mariotti, A.; Bagnoli, L.; Marini, F.; Desantis, J.; Iraci, N.; Santi, C.; Pannecouque, C.; Tabarrini, O. *J. Med. Chem.* **2015**, *58*, 9601. (g) Mondal, S.; Manna, D.; Mugesh, G. *Angew. Chem., Int. Ed.* **2015**, *54*, 9298. (h) Pang, Y.; An, B.; Lou, L.; Zhang, J.; Yan, J.; Huang, L.; Li, X.; Yin, S. *J. Med. Chem.* **2017**, *60*, 7300. (i) Kibriya, G.; Samanta, S.; Singsardar, M.; Jana, S.; Hajra, A. *Eur. J. Org. Chem.* **2017**, *2017*, 3055. (j) Jain, V. K., Priyadarsini, K. I., Eds. *Organoselenium Compounds in Biology and Medicine*; RSC: Cambridge, 2017.

(2) (a) Silveira, C. C.; Braga, A. L.; Vieira, A. S.; Zeni, G. *J. Org. Chem.* **2003**, *68*, 662. (b) Kundu, D.; Ahammed, S.; Ranu, B. C. *Org. Lett.* **2014**, *16*, 1814. (c) Luo, J.; Zhu, Z.; Liu, Y.; Zhao, X. *Org. Lett.* **2015**, *17*, 3620. (d) Verma, A.; Jana, S.; Prasad, C. D.; Yadav, A.; Kumar, S. *Chem. Commun.* **2016**, *52*, 4179.

(3) (a) Zeni, G.; Ludtke, D. S.; Panatieri, R. B.; Braga, A. L. *Chem. Rev.* **2006**, *106*, 1032. (b) Perin, G.; Lenardao, E. J.; Jacob, R. G.; Panatieri, R. B. *Chem. Rev.* **2009**, *109*, 1277. (c) Freudendahl, D. M.; Santoro, S.; Shahzad, S. A.; Santi, C.; Wirth, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 8409. (d) Abdo, M.; Zhang, Y.; Schramm, V. L.; Knapp, S. *Org. Lett.* **2010**, *12*, 2982. (e) Rafique, J.; Saba, S.; Rosario, A. R.; Braga, A. L. *Chem. - Eur. J.* **2016**, *22*, 11854. (f) Shu, S.; Fan, Z.; Yao, Q.; Zhang, A. *J. Org. Chem.* **2016**, *81*, 5263. (g) Sun, K.; Wang, X.; Lv, Y.; Li, G.; Jiao, H.; Dai, C.; Li, Y.; Zhang, C.; Liu, L. *Chem. Commun.* **2016**, *52*, 8471.

(4) Reviews for reactions with diselenides, see: (a) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596. (b) Ivanova, A.; Arsenyan, P. *Coord. Chem. Rev.* **2018**, *370*, 55. For selected examples for the reaction of diselenides with various substrates, see: (c) Zheng, Y.; He, Y.; Rong, G.; Zhang, X.; Weng, Y.; Dong, K.; Xu, X.; Mao, J. *Org. Lett.* **2015**, *17*, 5444. (d) Sun, J.; Zhang-Negrerie, D.; Du, Y. *Adv. Synth. Catal.* **2016**, *358*, 2035. (e) Qiu, J.-K.; Shan, C.; Wang, D.-C.; Wei, P.; Jiang, B.; Tu, S.-J.; Li, G.; Guo, K. *Adv. Synth. Catal.* **2017**, *359*, 4332. (f) Zhu, Y.-Q.; He, J.-L.; Niu, Y.-X.; Kang, H.-Y.; Han, T.-F.; Li, H.-Y. *J. Org. Chem.* **2018**, *83*, 9958. (g) Liu, Y.; Li, C.; Mu, S.; Li, Y.; Feng, R.; Sun, K. *Asian J. Org. Chem.* **2018**, *7*, 720. (h) Yu, J.-M.; Cai, C. *Org. Biomol. Chem.* **2018**, *16*, 490. (i) Zhao, F.; Sun, T.; Liu, Z.; Sun, K.; Zhang, C.; Wang, X. *Curr. Org. Chem.* **2018**, *22*, 613. (j) Wu, P.; Wu, K.; Wang, L.; Yu, Z. *Org. Lett.* **2017**, *19*, 5450. (k) Ricordi, V. G.; Freitas, C. S.; Perin, G.; Lenardão, E. J.; Jacob, R. G.; Savegnago, L.; Alves, D. *Green Chem.* **2012**, *14*, 1030. (l) Zheng, B.; Gong, Y.; Xu, H.-J. *Tetrahedron* **2013**, *69*, 5342. (m) Kumar, A.; Kumar, S. *Tetrahedron* **2014**, *70*, 1763. (n) Jana, S.; Chakraborty, A.; Mondal, S.; Hajra, A. *RSC Adv.* **2015**, *5*, 77534. (o) Ricordi, V. G.; Thurow, S.; Penteado, F.; Schumacher, R. F.; Perin, G.; Lenardão, E. J.; Alves, D. *Adv. Synth. Catal.* **2015**, *357*, 933. (p) Yu, S.; Wan, B.; Li, X. *Org. Lett.* **2015**, *17*, 58. (q) Ferreira, N. L.; Azeredo, J. B.; Fiorentin, B. L.; Braga, A. L. *Eur. J. Org. Chem.* **2015**, *2015*, 5070. (r) Mandal, A.; Sahoo, H.; Baidya, M. *Org. Lett.* **2016**, *18*, 3202. (s) Sahoo, H.; Mandal, A.; Selvakumar, J.; Baidya, M. *Eur. J. Org. Chem.* **2016**, *2016*, 4321. (t) Gandeepan, P.; Koeller, J.; Ackermann, L. *ACS Catal.* **2017**, *7*, 1030. (u) Kibriya, G.; Samanta, S.; Singsardar, M.; Jana, S.; Hajra, A. *Eur. J. Org. Chem.* **2017**, *2017*, 3055. (v) Zhang, Q.-B.; Ban, Y.-L.; Yuan, P.-F.; Peng, S.-J.; Fang, J.-G.; Liu, L.-Z. W. Q. *Green Chem.* **2017**, *19*, 5559. (w) Saba, S.; Rafique, J.; Franco, M. S.; Schneider, A. R.; Espíndola, L.; Silva, D. O.; Braga, A. L. *Org. Biomol. Chem.* **2018**, *16*, 880. (x) Kumaraswamy, G.; Ramesh, V.; Gangadhar, M.; Vijaykumar, S. *Asian J. Org. Chem.* **2018**, *7*, 1689. (y) Mukherjee, N.; Chatterjee, T.; Ranu, B. C. *J. Org. Chem.* **2013**, *78*, 11110. (z) Kundu, D.; Ahammed, S.; Ranu, B. C. *Org. Lett.* **2014**, *16*, 1814.

(5) Reviews for difunctionalization of alkenes: (a) Chen, Z.-M.; Zhang, X.-M.; Tu, Y.-Q. *Chem. Soc. Rev.* **2015**, *44*, 5220. (b) Courant, T.; Masson, G. *J. Org. Chem.* **2016**, *81*, 6945. (c) Studer, A.; Curran, D. P. *Angew. Chem., Int. Ed.* **2016**, *55*, 58. (d) Tian, Y.; Chen, S.; Gu, Q.-S.; Lin, J.-S.; Liu, X.-Y. *Tetrahedron Lett.* **2018**, *59*, 203. Selected reports: (e) Chen, Y.; Duan, W.-L. *J. Am. Chem. Soc.* **2013**, *135*, 16754. (f) Unoh, Y.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 12975. (g) Gao, P.; Shen, Y.-W.; Fang, R.; Hao, X.-H.; Qiu, Z.-H.; Yang, F.; Yan, X.-B.; Wang, Q.; Gong, X.-J.; Liu, X.-Y.; Liang, Y.-M. *Angew. Chem., Int. Ed.* **2014**, *53*, 7629. (h) Douglas, J. J.; Albright, H.; Sevrin, M. J.; Cole, K. P.; Stephenson, C. R. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 14898. (i) Zhou, T.; Luo, F.-X.; Yang, M.-Y.; Shi, Z.-J. *J. Am. Chem. Soc.* **2015**, *137*, 14586. (j) Zhang, Y.-X.; Jin, R.-X.; Yin, H.; Li, Y.; Wang, X.-S. *Org. Lett.* **2018**, *20*, 7283. (k) Nakafuku, K. M.; Fosu, S. C.; Nagib, D. A. *J. Am. Chem. Soc.* **2018**, *140*, 11202.

(6) Review for aryl migration reaction: (a) Zeng, Y.; Ni, C.; Hu, J. *Chem. - Eur. J.* **2016**, *22*, 3210. Selected reports: (b) Thaharn, W.; Soorukram, D.; Kuhakarn, C.; Tuchinda, P.; Reutrakul, V.; Pohmakotr, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 2212. (c) Li, L.; Li, Z.-L.; Wang, F.-L.; Guo, Z.; Cheng, Y.-F.; Wang, N.; Dong, X.-W.; Fang, C.; Liu, J.; Hou, C.; Tan, B.; Liu, X.-Y. *Nat. Commun.* **2016**, *7*, 13852. (d) Li, L.; Gu, Q.-S.; Wang, N.; Song, P.; Li, Z.-L.; Li, X.-H.; Wang, F.-L.; Liu, X.-Y. *Chem. Commun.* **2017**, *53*, 4038. (e) Wang, N.; Gu, Q.-S.; Li, Z.-L.; Guo, Y.-L.; Kiu, X.-Y. *Angew. Chem., Int. Ed.* **2018**, *57*, 14225.

(7) (a) Shu, X.-Z.; Zhang, M.; He, Y.; Frei, H.; Toste, F. D. *J. Am. Chem. Soc.* **2014**, *136*, 5844. (b) Sahoo, B.; Li, J.-L.; Glorius, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 11577. (c) Suh, C. W.; Kim, D. Y. *Tetrahedron Lett.* **2015**, *56*, 5661. (d) Woo, S. B.; Kim, D. Y. *J. Fluorine Chem.* **2015**, *178*, 214. (e) Kwon, S. J.; Kim, Y. J.; Kim, D. Y. *Tetrahedron Lett.* **2016**, *57*, 4371. (f) Kwon, S. J.; Kim, D. Y. *Org. Lett.*

DOI: 10.1021/acs.orglett.8b04041
Org. Lett. XXXX, XXX, XXX−XXX

2016, *18*, 4562. (g) Kim, Y. J.; Kim, D. Y. *J. Fluorine Chem.* **2018**, *211*, 119. (h) Kim, Y. J.; Choo, M. H.; Kim, D. Y. *Tetrahedron Lett.* **2018**, *59*, 3863. (i) Honeker, R.; Garza-Sanchez, R. A.; Hopkinson, M. N.; Glorius, F. *Chem. - Eur. J.* **2016**, *22*, 4395. (j) Bergonzini, G.; Cassani, C.; Olsson, H. L.; Hörberg, J.; Wallentin, C.-J. *Chem. - Eur. J.* **2016**, *22*, 3292. (k) Weng, W.-Z.; Sun, J.-G.; Li, P.; Zhang, B. *Chem. - Eur. J.* **2017**, *23*, 9752. (l) Zhang, J.-J. *Chin. J. Chem.* **2017**, *35*, 311. (m) Wu, H.; Wang, Q.; Zhu, J. *Chem. - Eur. J.* **2017**, *23*, 13037. (n) Yao, S.; Zhang, K.; Zhou, Q.-Q.; Zhao, Y.; Shi, D.-Q.; Xiao, W.-J. *Chem. Commun.* **2018**, *54*, 8096.

(8) For selected reviews, see: (a) Roth, H. G.; Romero, N. A.; Nicewicz, D. A. *Synlett* **2016**, *27*, 714. (b) Yan, M.; Kawamata, Y.; Baran, P. S. *Chem. Rev.* **2017**, *117*, 13230. (c) Liu, K.; Song, C.; Lei, A. *Org. Biomol. Chem.* **2018**, *16*, 2375. (d) Yang, Q.-L.; Fang, P.; Mei, T.-S. *Chin. J. Chem.* **2018**, *36*, 338. (e) Möhle, S.; Zirbes, M.; Rodrigo, E.; Gieshoff, T.; Wiebe, A.; Waldvogel, S. R. *Angew. Chem., Int. Ed.* **2018**, *57*, 6018. (f) Wiebe, A.; Gieshoff, T.; Möhle, S.; Rodrigo, E.; Zirbes, M.; Waldvogel, S. R. *Angew. Chem., Int. Ed.* **2018**, *57*, 5594. (g) Moeller, K. D. *Chem. Rev.* **2018**, *118*, 4817. (h) Yoshida, J.-I.; Shimizu, A.; Hayashi, R. *Chem. Rev.* **2018**, *118*, 4702. (i) Zhao, Y.; Xia, W. *Chem. Soc. Rev.* **2018**, *47*, 2591. (j) Nutting, J. E.; Rafiee, M.; Stahl, S. S. *Chem. Rev.* **2018**, *118*, 4834. (k) Waldvogel, S. R.; Lips, S.; Selt, M.; Riehl, B.; Kampf, C. J. *Chem. Rev.* **2018**, *118*, 6706. (l) Sauermann, N.; Meyer, T. H.; Qiu, Y.; Ackermann, L. *ACS Catal.* **2018**, *8*, 7086. (m) Pletcher, D.; Green, R. A.; Brown, R. C. D. *Chem. Rev.* **2018**, *118*, 4573. (n) Kärkäs, M. D. *Chem. Soc. Rev.* **2018**, *47*, 5786. (o) Sauer, G. S.; Lin, S. *ACS Catal.* **2018**, *8*, 5175. Recent selected examples: (p) Du, K. S.; Huang, J.-M. *Org. Lett.* **2018**, *20*, 2911. (r) Zhang, X.; Wang, C.; Jiang, H.; Sun, L. *Chem. Commun.* **2018**, *54*, 8781.

(9) (a) Dowd, P.; Choi, S.-C. *J. Am. Chem. Soc.* **1987**, *109*, 3493. (b) Dowd, P.; Choi, S.-C. *J. Am. Chem. Soc.* **1987**, *109*, 6548. (c) Beckwith, A. L. J.; O'Shea, D. M.; Westwood, S. W. *J. Chem. Soc., Chem. Commun.* **1987**, 666. (d) Beckwith, A. L. J.; O'Shea, D. M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565. (e) Shono, T.; Kise, N.; Uematsu, N.; Morimoto, S.; Okazaki, E. *J. Org. Chem.* **1990**, *55*, 5037. (f) Dowd, P.; Zhang, W. *Chem. Rev.* **1993**, *93*, 2091. (g) Ardura, D.; Sordo, T. L. *Tetrahedron Lett.* **2004**, *45*, 8691. (h) Ardura, D.; Sordo, T. L. *J. Org. Chem.* **2005**, *70*, 9417. (i) Hasegawa, E.; Tateyama, M.; Hoshi, T.; Ohta, T.; Tayama, E.; Iwamoto, H.; Takizawa, S.-y.; Murata, S. *Tetrahedron* **2014**, *70*, 2776. (j) Hasegawa, E.; Mori, K.; Tsuji, S.; Nemoto, K.; Ohta, T.; Iwamoto, H. *Aust. J. Chem.* **2015**, *68*, 1648. (k) Hasegawa, E.; Ohta, T.; Tsuji, S.; Mori, K.; Uchida, K.; Miura, T.; Ikoma, T.; Tayama, E.; Iwamoto, H.; Takizawa, S.-y.; Murata, S. *Tetrahedron* **2015**, *71*, 5494. (l) Hasegawa, E.; Nemoto, K.; Nagumo, R.; Tayama, E.; Iwamoto, H. *J. Org. Chem.* **2016**, *81*, 2692. (m) Liu, Y.; Yeung, Y.-Y. *Org. Lett.* **2017**, *19*, 1422.

(10) For a selection of our recent works on C−H activation, see: (a) Kang, Y. K.; Kim, S. M.; Kim, D. Y. *J. Am. Chem. Soc.* **2010**, *132*, 11847. (b) Kang, Y. K.; Kim, D. Y. *Adv. Synth. Catal.* **2013**, *355*, 3131. (c) Suh, C. W.; Woo, S. B.; Kim, D. Y. *Asian J. Org. Chem.* **2014**, *3*, 399. (d) Kang, Y. K.; Kim, D. Y. *Chem. Commun.* **2014**, *50*, 222. (e) Suh, C. W.; Kim, D. Y. *Org. Lett.* **2014**, *16*, 5374. (f) Kwon, S. J.; Kim, D. Y. *Chem. Rec.* **2016**, *16*, 1191. (g) Suh, C. W.; Kwon, S. J.; Kim, D. Y. *Org. Lett.* **2017**, *19*, 1334. (h) Jeong, H. J.; Kim, D. Y. *Org. Lett.* **2018**, *20*, 2944.

(11) Kunai, A.; Harada, J.; Izumi, J.; Tachihara, H.; Sasaki, K. *Electrochim. Acta* **1983**, *28*, 1361.

DOI: 10.1021/acs.orglett.8b04041
Org. Lett. XXXX, XXX, XXX−XXX