Organic LETTERS

Letter

pubs.acs.org/OrgLett

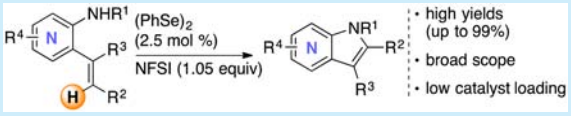
Selenium-Catalyzed Oxidative C(sp^2)−H Amination of Alkenes Exemplified in the Expedient Synthesis of (Aza-)Indoles

Stefan Ortgies and Alexander Breder*

Institut für Organische und Biomolekulare Chemie, Georg-August-Universität, Tammannstrasse 2, 37077 Göttingen, Germany

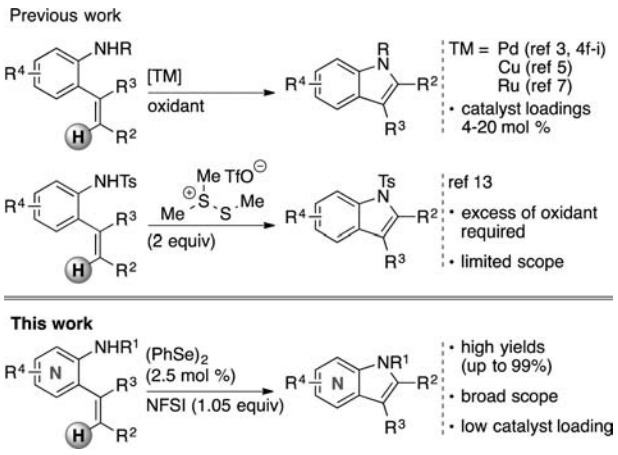
Supporting Information

ABSTRACT: A new selenium-catalyzed protocol for the direct, intramolecular amination of C(sp^2)−H bonds using *N*-fluorobenzenesulfonimide as the terminal oxidant is reported. This method enables the facile formation of a broad range of diversely functionalized indoles and azaindoles derived from easily accessible *ortho*-vinyl anilines and vinylated aminopyridines, respectively. The procedure exploits the pronounced carbophilicity of selenium electrophiles for the catalytic activation of alkenes and leads to the formation of C(sp^2)−N bonds in high yields and with excellent functional group tolerance.



Oxidative functionalization of C−H bonds constitutes a privileged and step-economic[1] strategy for the incorporation of heteroatoms into given hydrocarbon frameworks. In this direction, the oxidative C−H amination of nonactivated alkenes, arenes, and alkyl groups has evolved into a highly active area in contemporary chemical sciences.[2] For almost four decades, many research groups have devised elegant methods to address the challenging task of nitrogenating C(sp^2)−H bonds in a regio- and chemoselective manner. Large portions of these protocols use transition metal catalysts such as Pd,[3,4] Cu,[5] Rh,[6] and Ru complexes (Scheme 1).[2,7] Conversely, oxidative

Scheme 1. Indole Syntheses through C(sp^2)−H Amination



amination of nonactivated olefinic C−H bonds enabled by catalysts that possess nonmetallic main group elements as catalytically active species still constitutes a great challenge in current methodological research. Although significant and indicative progress has been made in the realm of iodine-mediated and, to some extent, -catalyzed C−H aminations of alkenes,[8] (hetero)arenes,[9] and dinitrogenations of olefins,[10] there is still a dearth of potent metal-free catalysis concepts for direct manipulation of olefinic carbon−hydrogen bonds. Seminal work by Engman[11] on the Se(IV)-mediated C−H chlorination of alkenes indicated that the carbon−halogen bond formation presumably occurs through the transient formation of a seleniranium species that subsequently undergoes ring opening by a chloride anion followed by dehydrodeselenation. A similar scenario for the initial electrophilic activation of the alkene moiety was recently suggested by Denmark and co-workers in the context of a *syn*-specific dichlorination of olefins by a selenium(IV) catalyst.[12] Other chalcogen-based electrophiles, such as sulfenium ions, were also shown to function as competent promoters for stoichiometric C−H amination reactions of alkenes (Scheme 1).[13]

Our group has recently reported the first Se-catalyzed C−H imidation of (hetero)cyclic alkenes and styrenes using *N*-fluorobenzenesulfonimide (NFSI) as both the terminal oxidant and nitrogen source.[14,15] On the basis of these initial investigations, we became interested in the design of a novel metal-free concept for the electrophilic activation of simple alkenes that would allow for the facile construction of C−N bonds from C(sp^2)−H entities. Since indoles and azainoldes represent structural motifs with important pharmaceutical, agrochemical, and material scientific applications,[16,17] we reasoned that such target structures would provide an ideal platform for the development of a Se-catalyzed C−H amination protocol. As a result, we present herein a useful and wide-ranging metal-free method for the synthesis of diversely functionalized indoles and azaindoles from *ortho*-vinylated anilines and aminopyridines, respectively, using $(PhSe)_2$ as a highly potent and cost-efficient catalyst.

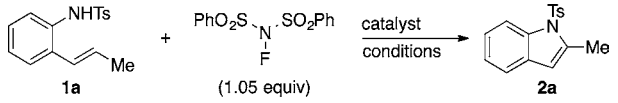
At the outset of our studies, we used anilide **1a** as the test substrate to determine optimal conditions for the title reaction. Treatment of compound **1a** with 1.05 equiv of NFSI in the

Received: April 21, 2015
Published: May 22, 2015

DOI: 10.1021/acs.orglett.5b01156
Org. Lett. 2015, 17, 2748−2751

presence of 10 mol % of $(PhSe)_2$ at ambient temperature in various solvents (Table 1, entries 1−12) revealed that the best result was obtained in toluene (0.1 M) with a yield of 47% for indole **2a**. At 100 °C, a catalyst loading of only 2.5 mol % led to a yield of 71% (entry 13). Next, we tested a number of other selenium catalysts, such as $(4\text{-anisylSe})_2$, $(BnSe)_2$, dibenzo[*c*,e][1,2]diselenine, and PhSeBr (entries 14−17), for their catalytic activity, but none of these species provided results superior to those of $(PhSe)_2$. At no instance during this study was the formation of fluorinated products detected. To exclude the possibility that the title reaction was actually catalyzed by traces of palladium or iron salts, which may have arisen from the substrate synthesis or the employed equipment, we also tested $PdCl_2$ and $FeCl_3$ (10 mol % each, entries 18 and 19) as potential catalysts. However, neither experiment resulted in detectable quantities of product **2a**. Treatment of anilide **1a** with NFSI at 100 °C in the absence of any catalyst led to product **2a** only in trace amounts (entry 20).

Table 1. Optimization of Reaction Conditions[a]

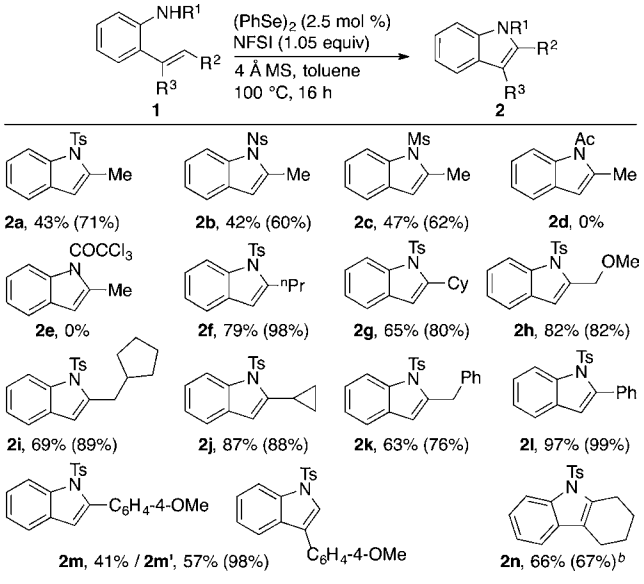


entry	catalyst (mol %)	solvent	temp (°C)	yield (%)[b]
1	$(PhSe)_2$ (10)	THF	22	14
2	$(PhSe)_2$ (10)	Et_2O	22	12
3	$(PhSe)_2$ (10)	1,4-dioxane	22	11
4	$(PhSe)_2$ (10)	MeCN	22	9
5	$(PhSe)_2$ (10)	$MeNO_2$	22	10
6	$(PhSe)_2$ (10)	DMF	22	0
7	$(PhSe)_2$ (10)	DMSO	22	0
8	$(PhSe)_2$ (10)	hexane	22	17
9	$(PhSe)_2$ (10)	benzene	22	46
10	$(PhSe)_2$ (10)	toluene	22	47
11	$(PhSe)_2$ (10)	DCM	22	43
12	$(PhSe)_2$ (10)	MeOH	22	0
13	$(PhSe)_2$ (2.5)	toluene	100	71
14	$(BnSe)_2$ (10)	toluene	100	37
15	$(4\text{-MeO-}C_6H_4Se)_2$ (10)	toluene	100	13
16	DBDS (10)	toluene	100	20
17	PhSeBr (2.5)	toluene	100	65
18	$PdCl_2$ (10)	toluene	100	0
19	$FeCl_3$ (10)	toluene	100	0
20	none	toluene	100	4

[a]Reactions were carried out on a 0.17 mmol scale in 1.5 mL of solvent with 1.05 equiv of NFSI and 4 Å molecular sieves for 16 h. [b]Yields were determined by ^1H NMR using 4-bromoanisole as an internal standard. DBDS = dibenzo[*c*,*e*][1,2]diselenine.

With optimized conditions in hand, investigations continued with the exploration of the scope and limitations of our amination protocol (Schemes 2 and 3). Initially, various substituents at the nitrogen atom (R^1) and the alkene (R^2 and R^3) were tested (Scheme 2). While tosyl, nosyl, and mesyl groups were compatible with the reaction conditions (**2a−c**, 42−47%), the corresponding carboxamide derivatives (**1d** and **1e**) did not participate in the reaction. These observations suggest that the pK_a of the N−H units plays an important role in the reaction turnover. Presumably, neither of the carboxamide groups is acidic enough to be deprotonated under the reaction conditions. This finding is congruent with reports by other research groups on related cyclization reactions.[13,18]

Scheme 2. Scope of the Se-Catalyzed C(sp^2)−H Amination with Varying R^1 and R^2 Substituents[a]



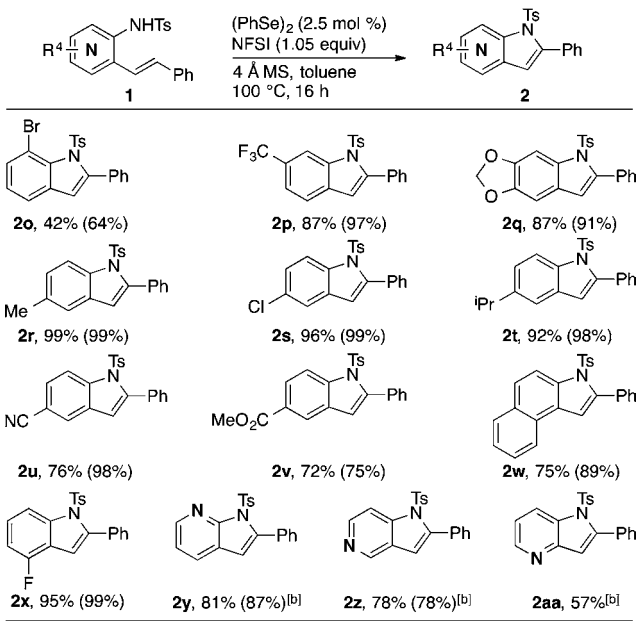
[a]Reactions were carried out on a 0.3 mmol scale in 5 mL of toluene with 1.05 equiv of NFSI, 2.5 mol % of $(PhSe)_2$, and 4 Å molecular sieves for 16 h. Yields refer to isolated compounds. Numbers in parentheses refer to yields determined by ^1H NMR using 4-bromoanisole as an internal standard. [b]5 mol % of $(PhSe)_2$ was used.

With regard to the substitution pattern on the alkene, both aromatic and aliphatic groups were tolerated under the reaction conditions. For instance, anilide **1f** was readily converted into corresponding indole **2f** in an isolated yield of 79%. It is noteworthy to point out that anilides homologous to structures **1a** and **1f** were shown to be unsuitable for cognate cyclizations under single-electron oxidation conditions.[19] Thus, our results underscore the high degree of chemoselectivity and functional group tolerance exerted by selenium catalysis. Furthermore, other aliphatic and alicyclic substituents, such as cyclohexyl (**2g**), methoxymethyl (**2h**), cyclopentylmethyl (**2i**), and cyclopropyl groups (**2j**), were tolerated in the C−H amination (65−87%). The conversion of substrate **1n** to tetrahydrocarbazole **2n** required an increased catalyst loading of 5 mol % and resulted in an isolated yield of 66%. Particularly good results were recorded for substrates with aromatic residues in the *β*-position of the alkene. Anilides **1l** and **1m** underwent oxidative cyclization with isolated yields of 97 and 98%, respectively. In the case of substrate **1m**, a 1:1.4 mixture of isomeric indoles **2m** (41%) and **2m′** (57%) was isolated. The formation of 3-arylated indole **2m′** is believed to involve a phenonium migration from the 2- into the 3-position.[7,19,20]

To further demonstrate the generality and utility of the Se-catalyzed C−H amination protocol, our efforts continued with the investigation of steric and electronic effects exerted by substituents within the anilide ring (Scheme 3). For this purpose, a series of anilide derivatives **1o−1x**, which possess electron-donating and electron-withdrawing groups in various positions, were synthesized. In general, the title transformation exhibited a broad functional group tolerance since halides, ethers, a nitrile, and an ester were compatible with the reaction conditions. Moreover, it was found that the electronic nature of the R^4 group did not have a significant impact on the yield. For example, trifluoromethylated compound **2p** and dioxoloindole **2q** were

DOI: 10.1021/acs.orglett.5b01156
Org. Lett. 2015, 17, 2748−2751

Scheme 3. Scope of the Se-Catalyzed C(sp^2)−H Amination with Varying R^4 Substituents and Aminopyridines[a]



[a]Reactions were carried out on a 0.3 mmol scale in 5 mL of toluene with 1.05 equiv of NFSI, 2.5 mol % of $(PhSe)_2$, and 4 Å molecular sieves for 16 h. Yields refer to isolated compounds. Numbers in parentheses refer to yields determined by ^{1}H NMR using 4-bromoanisole as an internal standard. [b]5 mol % of $(PhSe)_2$ was used.

isolated in 87% yield. Even better results were recorded for 5-methylated indole **2r** and 5-chlorinated indole **2s** with isolated yields of 99 and 96%, respectively. On the other hand, steric factors were found to have a more substantial impact on the yield. More precisely, 2-bromoanilide **1o** was converted into corresponding indole **2o** in a moderate yield of 42%. This result was rationalized by considering steric repulsions between the Br atom and the adjacent tosylamide group.

Given that the electronic nature of the R^4 group was virtually inconsequential with regard to the yields of products **2**, we surmised that other electron-deficient entities, such as pyridines, might also be tolerated under the title conditions. The use of vinylated aminopyridines as aza analogues of anilides **1a−1x** would provide a facile and expedient route toward azaindoles.[21] Thus, vinylated aminopyridines **1y−1aa** were tested in the Se-catalyzed C−H amination. From initial experiments, in which aminopyridine **1y** was used as the test substrate, we learned that an increased catalyst loading of 5 mol % under otherwise unchanged reaction conditions led to 7-azaindole **2y** in a satisfying yield of 81%. Application of the modified reaction parameters to aminopyridines **1z** and **1aa** provided access to azaindoles **2z** and **2aa** in isolated yields of 57 and 78%, respectively. The slightly diminished yield of azaindole **2z** was rationalized with the electronically deactivating effect of the endocyclic nitrogen atom in the 4-position on the adjacent alkene. Attempts to synthesize the 6-azaindole analogue failed, presumably due to insufficient solubility of the respective 3-aminopyridine substrate in toluene.

In addition to the substrate scope, we also wanted to gain some insight into the mechanism of the title transformation. At the outset of this study, we wanted to exclude the possibility that the C−N bond formation may actually proceed by Brønsted acid catalyzed hydroamination[22] followed by oxidation of a transiently formed indoline intermediate. Thus, we synthesized *N*-tosylindoline and exposed it to 1.05 equiv of NFSI in toluene at 100 °C in both the absence and presence of $(PhSe)_2$. However, in neither case was the formation of the respective indole product detected, indicating that a hydroamination step is very unlikely.

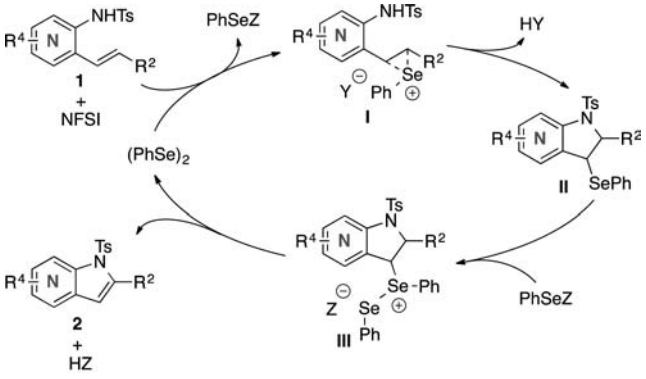
Next, we wanted to determine whether the C−H amination is catalyzed by $(PhSe)_2$ itself or by oxidized derivatives of it, such as PhSeF or $PhSeN(SO_2Ph)_2$. Hence, we initially examined the crude mixture of a completed reaction of substrate **1h** and NFSI under standard conditions. From this mixture, $(PhSe)_2$ was reisolated in 81% yield. To elucidate whether the diselane remains intact throughout the entire catalytic cycle or whether it undergoes a fragmentation/recombination sequence, we conducted a series of crossover experiments, in which substrate **1l** was initially converted with a 1:1 mixture of $(PhSe)_2$ and $(4\text{-tolylSe})_2$ (10 mol % each) in the presence of 1.05 equiv of NFSI. Analysis of the reisolated selenium catalysts by gas chromatography revealed no indication of the presence of a mixed diselane.[23] Ostensibly, this result was indicative of a mechanism in which the Se−Se bond may not undergo oxidative scission. To obtain a consistent picture of the catalytically active species, investigations continued with the analysis of arylselenyl halides as catalysts. Therefore, the cyclization of substrate **1p** was conducted with 10 mol % of PhSeBr to elucidate the fate of this catalyst upon completion of the reaction. Upon full conversion of the starting material, $(PhSe)_2$ was the only selenium species isolable (20%) from the reaction mixture. This finding proved that the recombination of the Se^{II} species to diselenides is possible under the title conditions.[24] Next, we performed another crossover experiment using PhSeBr and 4-tolylSeBr (10 mol % each) as catalysts under otherwise unaltered conditions. In contrast to our expectations, the gas chromatogram of the isolated selenium species displayed signals corresponding to only $(PhSe)_2$ and $(4\text{-tolylSe})_2$. This result implied that a recombination of diselenides via Se−Se bond homolysis under thermal conditions might be possible during the GC experiment, which potentially obviates the detection of a mixed diselane.[25] Eventually, we subjected the diselane samples from both crossover experiments to ^{77}Se NMR analysis ($CDCl_3$, cf. Supporting Information). The spectra exhibited resonances corresponding to $(PhSe)_2$ (462.2 ppm) and $(4\text{-tolylSe})_2$ (473.6 ppm). In addition, two resonances at 459.1 and 476.1 ppm were recorded, which could be assigned to the mixed diselane via 2D ^{77}Se,^{77}Se COSY experiments. From these data, it became evident that a mixed diselane was formed in both crossover experiments together with $(PhSe)_2$ and $(4\text{-tolylSe})_2$ in a statistical 2:1:1 ratio.

Consequently, we postulate the following catalytic cycle (Scheme 4). Following oxidative scission of the Se−Se bond through reaction of $(PhSe)_2$ with NFSI, the resulting selenium electrophiles presumably attack the alkene moiety to form seleniranium ion **I**. This, in turn, is then attacked by the adjacent sulfonamide group to furnish adduct **II**. Nucleofugic activation of the PhSe group within adduct **II** by another selenium electrophile initiates an elimination step, upon which the indole product and $(PhSe)_2$ are released.

In summary, we have delineated a novel Se-catalyzed C(sp^2)−H amination protocol via electrophilic activation of simple alkenes. Both *ortho*-aminostyrenes and vinylated aminopyridines have been successfully employed as substrates to access a broad range of indoles and azaindoles, respectively, in good to excellent yields. In general, the title reaction exhibits an excellent functional group tolerance and allows for a facile route to diverse substitution patterns around the (aza)indole core.

DOI: 10.1021/acs.orglett.5b01156
Org. Lett. 2015, 17, 2748−2751

Scheme 4. Mechanistic Hypothesis for the Intramolecular Se-Catalyzed Amination of C(sp^2)−H Bonds



Y = $N(SO_2Ph)_2$ if Z = F or vice versa.

Consequently, we expect our method to expediently complement current methodology in the area of catalytic, metal-free C−H aminations. Efforts toward the synthesis of other heterocycles are currently ongoing in our group.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and compound characterization data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01156.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: abreder@gwdg.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Fonds der Chemischen Industrie (FCI, Liebig-Fellowship to A.B., and Chemiefonds Fellowship to S.O.) and the Deutsche Forschungsgemeinschaft (DFG, Emmy Noether Fellowship to A.B.). We thank Prof. Dr. Lutz Ackermann (University of Göttingen, Germany) for generous support of our work. Dr. Michael John (University of Göttingen, Germany) is acknowledged for assistance during the ^{77}Se NMR studies.

■ REFERENCES

(1) Wender, P. A.; Verma, V. A.; Paxton, T. J.; Pillow, T. H. *Acc. Chem. Res.* **2008**, *41*, 40.

(2) (a) Liu, X.-Y.; Gao, P.; Shen, Y.-W.; Liang, Y.-M. *Org. Lett.* **2011**, *13*, 4196. (b) Yoo, E. J.; Ma, S.; Mei, T.-S. L.; Chan, K. S.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 7652. (c) Pan, J.; Su, M.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 8647. (d) Tan, Y.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 3676. (e) Neumann, J.; Rakshit, S.; Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 6892. (f) Tsang, W. C.; Zheng, N.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 14560.

(3) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800.

(4) (a) Iglesias, Á.; Álvarez, R.; de Lera, Á. R.; Muñiz, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 2225. (b) Xiao, B.; Gong, T.-J.; Xu, J.; Liu, Z.-J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133*, 1466. (c) Sun, K.; Li, Y.; Xiong, T.; Zhang, J.; Zhang, Q. *J. Am. Chem. Soc.* **2011**, *133*, 1694. (d) Xiong, T.; Lin, Y.; Lu, Y.; Zhang, Q. *Chem. Commun.* **2010**, *46*, 6831. (e) Wang, X.; Yu, J.-Q. *J. Am. Chem. Soc.* **2009**, *131*, 10806. (f) Youn, S. W.; Bihn, J. H.; Kim, B. S. *Org. Lett.* **2011**, *13*, 3738. (g) Tsvelikhovsky, D.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 14048. (h) Larock, R. C.; Hightower, T. R.; Hasvold, L. A.; Peterson, K. P. *J. Org. Chem.* **1996**, *61*, 3584. (i) Krolski, M. E.; Renaldo, A. F.; Rudisill, D. E.; Stille, J. K. *J. Org. Chem.* **1988**, *53*, 1170.

(5) (a) Liwosz, T. W.; Chemler, S. R. *Synlett* **2014**, *26*, 335. (b) Liwosz, T. W.; Chemler, S. R. *Chem.—Eur. J.* **2013**, *19*, 12771. (c) Ni, Z.; Zhang, Q.; Xiong, T.; Zheng, Y.; Li, Y.; Zhang, H.; Zhang, J.; Liu, Q. *Angew. Chem., Int. Ed.* **2012**, *51*, 1244.

(6) Tang, R.-J.; Luo, C.-R.; Yang, L.; Li, C.-J. *Adv. Synth. Catal.* **2013**, *355*, 869.

(7) Maity, S.; Zheng, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 9562.

(8) Fra, L.; Millán, A.; Souto, J. A.; Muñiz, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 7349.

(9) (a) Li, Y. X.; Wang, H. X.; Ali, S.; Xia, X. F.; Liang, Y. M. *Chem. Commun.* **2012**, *48*, 2343. (b) Kim, H. J.; Kim, J.; Cho, S. H.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 16382. (c) Kantak, A. A.; Potavathri, S.; Barham, R. A.; Romano, K. M.; DeBoef, B. *J. Am. Chem. Soc.* **2011**, *133*, 19960. (d) Antonchick, A. P.; Samanta, R.; Kulikov, K.; Lategahn, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 8605. (e) Cho, S. H.; Yoo, J.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 5996. (f) Samanta, R.; Lategahn, J.; Antonchick, A. P. *Chem. Commun.* **2012**, *48*, 3194.

(10) (a) Röben, C.; Souto, J. A.; González, Y.; Lishchynskyi, A.; Muñiz, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 9478. (b) Souto, J. A.; González, Y.; Iglesias, A.; Zian, D.; Lishchynskyi, A.; Muñiz, K. *Chem.—Asian J.* **2012**, *7*, 1103.

(11) Engman, L. *J. Org. Chem.* **1987**, *52*, 4086.

(12) Cresswell, A. J.; Eey, S. T.-C.; Denmark, S. E. *Nat. Chem.* **2015**, *7*, 148.

(13) (a) Samanta, R.; Matcha, K.; Antonchick, A. P. *Eur. J. Org. Chem.* **2013**, 5769. (b) Okuma, K.; Yasuda, T.; Takeshita, I.; Shiojia, K.; Yokomori, Y. *Tetrahedron* **2007**, *63*, 8250. (c) Okuma, K.; Takeshita, I.; Yasuda, T.; Shioji, K. *Chem. Lett.* **2006**, *35*, 1122. (d) Izumi, T.; Sugano, M.; Konno, T. *J. Heterocycl. Chem.* **1992**, *29*, 899.

(14) Trenner, J.; Depken, C.; Weber, T.; Breder, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 8952.

(15) Deng, Z.; Wei, J.; Liao, L.; Huang, H.; Zhao, X. *Org. Lett.* **2015**, *17*, 1834.

(16) (a) Lamberth, C.; Dinges, J. *Bioactive Heterocyclic Compound Classes*; Wiley-VCH: Weinheim, Germany, 2012; Vol. *1*. (b) Power, D. P.; Lozach, O.; Meijer, L.; Grayson, D. H.; Connon, S. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 4940.

(17) Wu, Q.; Estaghamatian, M.; Hu, N.-X.; Popovic, Z.; Enright, G.; Breeze, S. R.; Wang, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 985.

(18) Hegedus, L. S.; McKearin, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 2444.

(19) Jang, Y. H.; Youn, S. W. *Org. Lett.* **2014**, *16*, 3720.

(20) For further examples of related rearrangements, please refer to ref 7 within ref 19.

(21) (a) Frischmuth, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2013**, *52*, 10084. (b) Barl, N. M.; Sansiaume-Dagousset, E.; Karaghiosoff, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2013**, *52*, 10093. (c) Mérour, J.-Y.; Routier, S.; Suzenet, F.; Joseph, B. *Tetrahedron* **2013**, *69*, 4767.

(22) Schlummer, B.; Hartwig, J. F. *Org. Lett.* **2002**, *4*, 1471.

(23) ^{1}H NMR spectroscopic analysis of the catalyst mixture provided signals that could be assigned to $(PhSe)_2$ and $(4\text{-tolylSe})_2$.

(24) Tiecco, M.; Testaferri, L.; Santi, C.; Tomassini, C.; Marini, F.; Bagnoli, L.; Temperini, A. *Tetrahedron: Asymmetry* **2002**, *13*, 429.

(25) Chu, J. Y. C.; Lewicki, J. W. *J. Org. Chem.* **1977**, *42*, 2491.

DOI: 10.1021/acs.orglett.5b01156
Org. Lett. 2015, 17, 2748−2751