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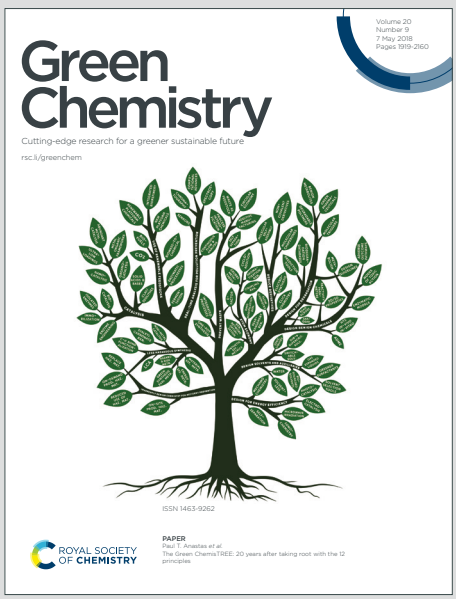

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COMMUNICATION

An Unconventional Sulfur-to-Selenium-to-Carbon Radical Transfer: Chemo-and Regioselective Cyclization of Yne-Ynamides

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An uncommon sulfur→selenium→carbon radical transfer process is employed to develop an unprecedented selenyl radical-mediated regioselective cyclization of yne-tethered-ynamides. Density functional theory studies and HRMS experiments are used to establish a reactivity scale between thiyl and selenyl radicals. The unique features of this transformation include, 1) the chemoselective reactivity of RSe• over RS•, 2) regioselective RSe• attack on alkyne over ynamide, 3) 5-*exo*-dig cyclization of yne-ynamide to unusual 4-selenyl-pyrroles, and 4) green synthetic method. The reaction of methyldiselenide with yne-ynamides to methylselenopyrroles is also described.

Selenium is a micronutrient essentially found in natural products, amino acids, and proteins.[1] Se-bearing heteroaryls are invaluable building blocks exhibiting distinct chemical, physical, and biological properties of pharmaceutical relevance.[2] Therefore, green synthetic methods that allow the rapid introduction of Se into heteroaromatic scaffolds are highly desirable. In this regard, binary chalcogens of type $(RS)_2$ and $(RSe)_2$ exhibit diverse synthetic applications, primarily including the homo-difunctionalization of unactivated olefins and alkynes.[3] Another notable application is the hetero-difunctionalization of olefins and alkynes involving the dominance of two reactive radical species, PhSe• and PhS•, through the sequential radical transfer: Se• →S• →C• , via the attack of PhS• to olefin or alkyne (Figure 1a).[4] These reactions are dependent on the preferential reactivity of PhS•, with the rate constant for the addition to the unsaturated system being 10–50 fold higher than that of PhSe•.[5] Surprisingly, a reverse S•

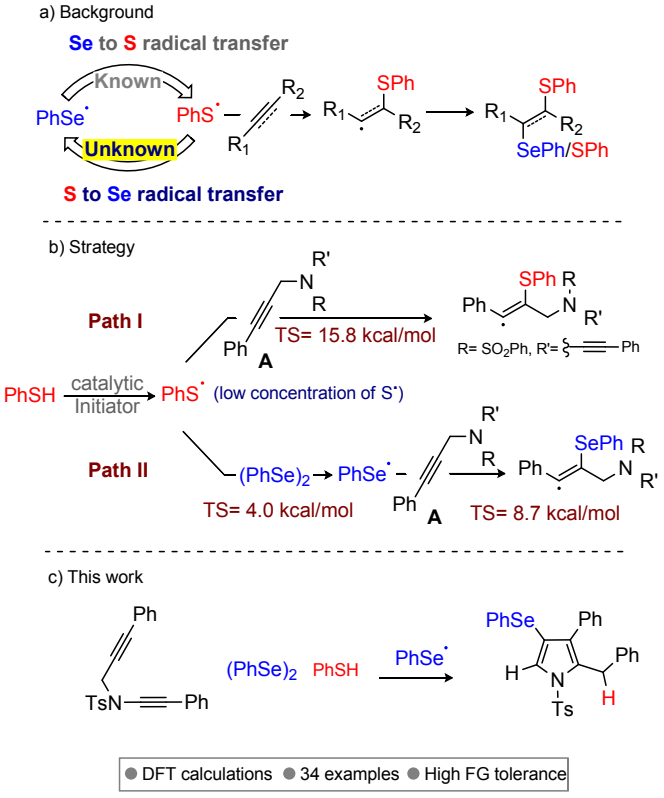

Figure 1. a) Background: Se to S radical transfer; b) Strategy: S to Se radical transfer; c) This work: chemo and regioselective selenyl radical attack to alkyne.

→Se• cross-radical transfer to promote the addition of PhSe• radicals to unsaturated bonds remains unexplored (Figure 1). To address this challenge, the density functional theory (DFT) studies (detailed in Figure 2) were sought; the reaction between PhS• and alkyne (**A**) requires 15.8 kcal/mol (Path I, Figure 1b), whereas the PhS• with $(PhSe)_2$ needs 4.0 kcal/mol (Path II. Figure 1b). These valuable pieces of information can indeed be beneficial for circumventing the issue of the PhS• affinity for

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unsaturated bonds. Accordingly, the S• →Se• radical transfer was anticipated through the interaction of PhS• at a low concentration with $(PhSe)_2$ that requires 4.0 kcal/mol;

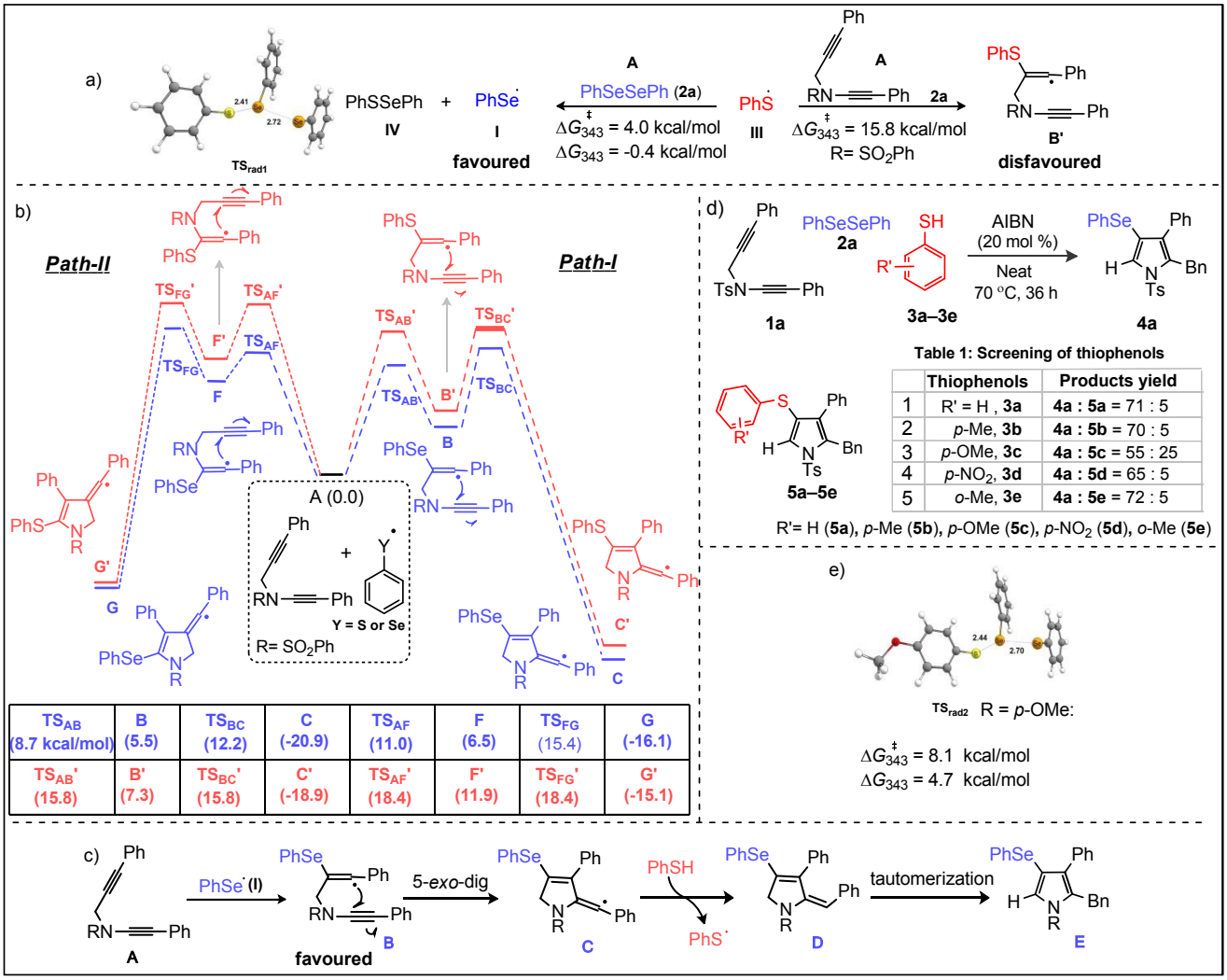


Figure 2. a) Energy comparison between formation of selenyl radical (**III**) and intermediate formation (**B'**); b) Energy comparison between various radical attacks and mode of cyclizations (R = SO_2Ph); c) Plausible mechanism; d) Screening of thiophenols; e) Energy calculation for *p*-OMe thiophenol.

which to our knowledge is revealed for the first time. Moreover, organic solvents and toxic transition-metals are being largely used in the synthetic transformations, which ultimately poses serious concern to the environment as well as the human body; thus, the development of organic reactions in the absence of these reagents have aroused intensive interest.[6] As the current transformation does not primarily require transition metal catalyst and solvent; thus, synthesis of 4-selenylated pyrroles through selenyl radical mediated cyclization of yne-ynamide is truly green. Thus, a reverse S• →Se• cross-radical transfer and chemo- and regioselective cyclization of yne-tethered ynamides, which have been used for diverse cyclization/cycloisomerization processes to construct complex N-heterocycles,[7-9] is envisioned.

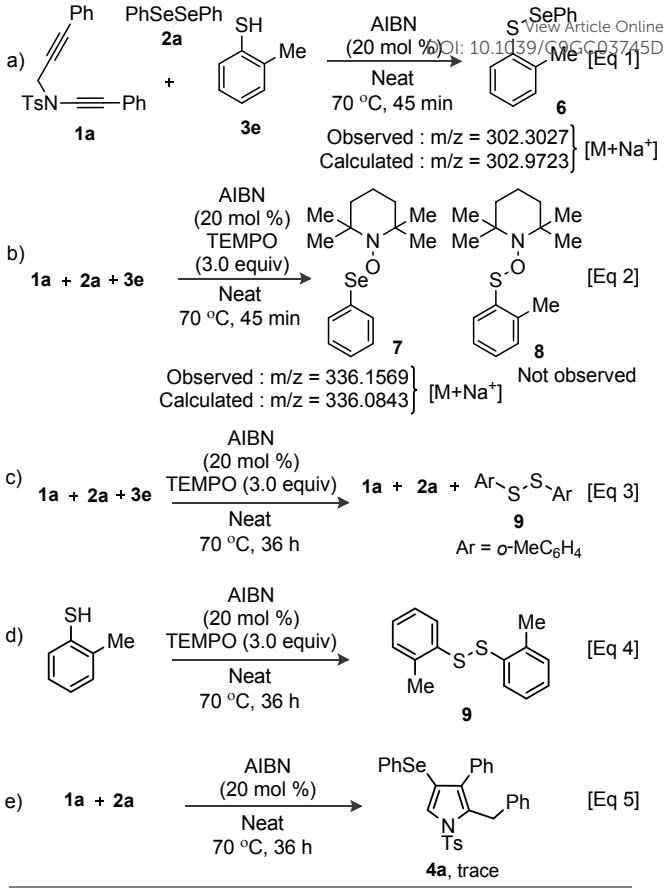
As part of our earlier investigations, we reported the ArS• radical-triggered cyclization of yne-ynamides to 4-sulfinylated pyrroles.[10] The development of a novel synthetic method for the construction of unusual 4-selenylated pyrroles is important, but as explained above, it is challenging. The envisaged synthetic plan to reach 4-selenylated pyrroles is outlined in Figure 2b. It relies on the following hypotheses: *i*) S• →Se• cross-radical transfer; *ii*) chemoselective trapping of RSe• over RS•, *iii*) regioselective RSe• attack to alkyne over ynamide, *iv*) 5-*exo*-dig cyclization, *v*) trapping of the cyclic vinyl radical with H-atom of PhSH.

DFT computations were carried out to validate the possibility of PhSe• formation by sulfur-to-selenium radical transfer from PhS• and PhSeSePh (see the Supporting Information for details). The transition state (TS_{rad1}) for the addition of PhS• (**III**) to PhSeSePh (**2a**) lies 4.0 kcal/mol above the reactants and the step is exergonic by 0.4 kcal/mol (Figure 2a). On the other hand, the reaction of PhS• to yne-ynamide **A** requires 15.8 kcal/mol of free energy of activation. Thus, attack of PhS• to PhSeSePh seems feasible, even in the presence of the yne-ynamide.

We next studied the reactivity and cyclization diversity of PhS• and/or PhSe• with the yne-ynamide. The addition of PhS• or

PhSe• to one or the other alkyne moiety of **A** would lead to vinyl radicals **B** (PhSe• attack to alkyne), **B′** (PhS• attack to alkyne) (Path-I, Figure 3b), or **F** (PhSe• attack to ynamide), **F′** (PhS• attack to ynamide) (Path-II, Figure 2b).[11] Next, intramolecular 5-*exo*-dig radical cyclization of **B/B′** and **F/F′** independently forms **C/C′** and **G/G′**, respectively. The formation of **B/B′** (Y = Se/S) is endergonic by 5.5/7.3 kcal/mol, while formation of **C/C′** is exergonic by 20.9/18.9 kcal/mol. The transition states $\mathbf{TS_{AB}}$ and $\mathbf{TS_{BC}}$ involved in PhSe• attack have free energies of 8.7 and 12.2 kcal/mol, respectively, whereas the identical PhS• attack requires free energies of 15.8 kcal/mol for both $\mathbf{TS_{AB}'}$ and $\mathbf{TS_{BC}'}$. Since $\mathbf{TS_{AB}'}$ and $\mathbf{TS_{BC}'}$ were located at much higher free energies than $\mathbf{TS_{AB}}$ and $\mathbf{TS_{BC}}$, formation of **C** (Y = Se) appears facile (Path I).[11] Indeed, $\mathbf{TS_{AF}}$ (11.0 kcal/mol) and $\mathbf{TS_{FG}}$ (15.4 kcal/mol) involved in the PhSe• attack to ynamide lie 2.3 and 3.2 kcal/mol higher on the free energy surface respective to $\mathbf{TS_{AB}}$ and $\mathbf{TS_{BC}}$. Moreover, **G** (Y = Se) is located at −16.1 kcal/mol and is less stable than **C** (Y = Se) by 3.8 kcal/mol. Likewise, the free energy of activation for the attack of PhS• to ynamide through $\mathbf{TS_{AF}'}$ (18.4 kcal/mol) or $\mathbf{TS_{FG}'}$ (18.4 kcal/mol) is higher. From these pieces of information, ***Path-I*** is found kinetically and thermodynamically favored over ***Path-II***, and the formation of **C** seems viable (Figure 2b).[11] Finally, quenching of **C** by PhSH provides **D** and subsequent tautomerization of **D** affords the desired 4-selenylated pyrrole **E** (Figure 2c). These steps, as well as other cyclization modes, were not computed. Considering our previous DFT analysis on the PhS• triggered cyclization of yne-ynamides,[10] other cyclization modes are actually very unlikely.

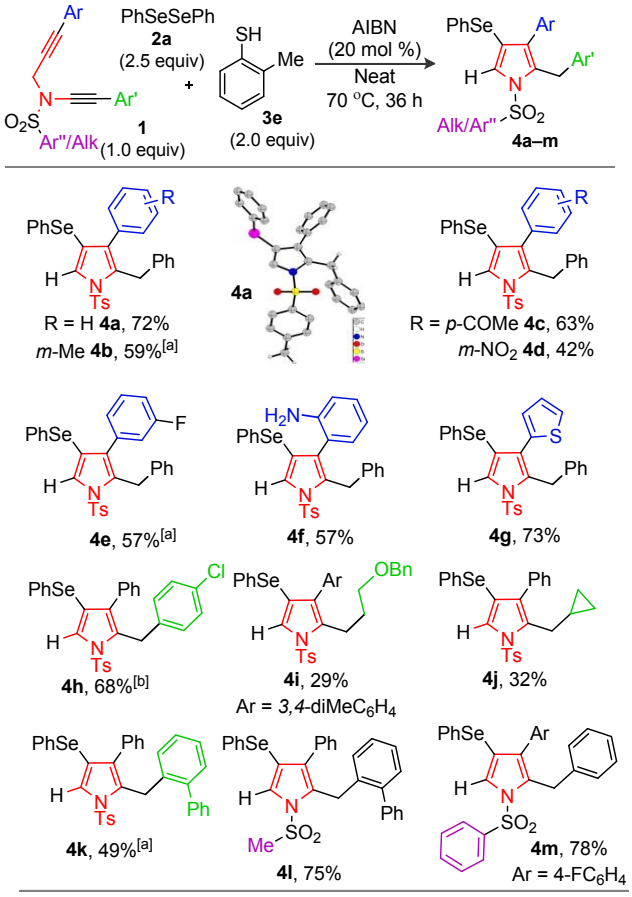
These results led us to examine the reaction between **1a** and PhSeSePh (**2a**) in the presence of phenylthiol (**3a**) and radical initiator (see Table S3 for the detailed optimization). Upon several trials, the expected 4-selenylated pyrrole **4a**[12] was obtained in 71% yield along with 4-thiyl pyrrole (**5a**; 5%) (entry 1, Figure 2d), when the reaction conducted with **1a** (1.0 equiv), **2a** (2.5 equiv), and **3a** (2.0 equiv) in the presence of 20 mol% AIBN under neat condition at 70 °C for 36 h. To increase the reaction selectivity and productivity, various substituted aryl thiols [*p*-MeC_6H_4SH (**3b**), *p*-$MeOC_6H_4SH$ (**3c**), *p*-$O_2NC_6H_4SH$ (**3d**), *o*-MeC_6H_4SH (**3e**) were screened (Figure 2d). Compound **4a** was isolated as major product in most cases, (entries 2, 4, and 5, Figure 1d). In contrast, the reaction in presence of **3c** delivered substantial amount of **5c** (4-thio-pyrrole, 25%) and **4a** (55%) (entry 3, Figure 2d). We believe that the radical transfer between *p*-$MeOC_6H_4S$• and PhSeSePh is inefficient and



Scheme 1. a) & b) HRMS experiments, c) & d) TEMPO experiments e) Blank reaction (without **3e**).

responsible to this poor product selectivity. A high energy barrier $\mathbf{TS_{rad2}}$ (8.1 kcal/mol) is essential for the addition of *p*-$MeOC_6H_4S$• to **2a** (a consequence to the formation of electron-rich *p*-$MeOC_6H_4S$•), and the reaction is endergonic by 4.7 kcal/mol (Figure 2e). This large energy barrier necessary for the radical exchange of **3c** to PhSeSePh (8.1 kcal/mol) in comparison to **3a** (4.0 kcal/mol) validates the observation of entry 3, Figure 1d. The identical transformation in presence of **3e** afforded **4a** in 72% yield (entry 5, Figure 2d).

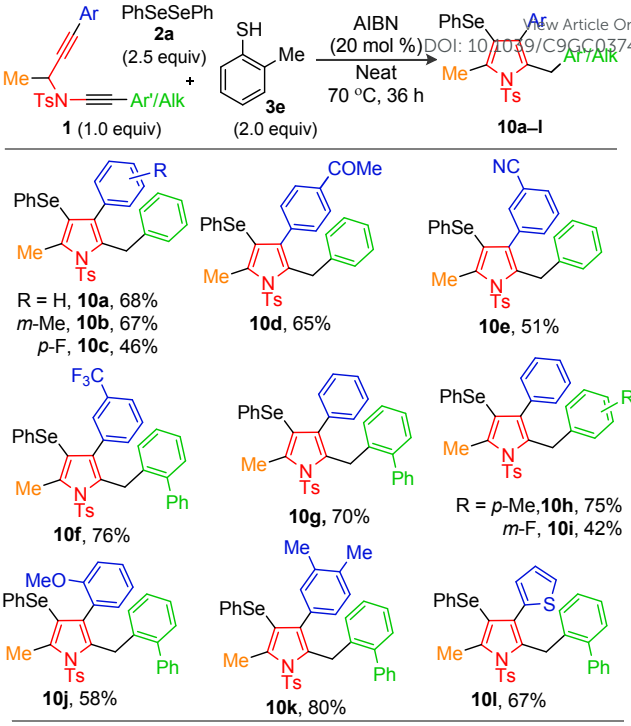
To further investigate the affinity of *o*-MeC_6H_4S• for **2a** to produce PhSe•, a few HRMS experiments were conducted. A mass peak at *m/z* 302.3027 [corresponding to (phenylselenyl)(*o*-tolyl)sulfane (**6**)] was detected from the reaction of **1a**, **2a**, and **3e** in presence of AIBN at 70 °C for 45 min [Eq 1, Scheme 1]; thus, affinity of *o*-MeC_6H_4S• for **2a** is higher than **1a**. Next, radical quenching experiment of **1a**, **2a**, **3e**, and TEMPO in presence of AIBN at 70 °C for 45 min produced TEMPO-SePh adduct **7** (*m/z* 336.1569) and not TEMPO-S-*o*-tolyl **8**; the Se• thus seems to be active (Eq 2, Scheme 1), whereas the same reaction after 36 h did not provide **7**/**4a** but rather the disulfide adduct **9** (Eq 3, Scheme 1). Moreover, exposing **3e** with AIBN in presence of TEMPO exclusively provided the disulfide adduct **9** (Eq 4, Scheme 1).The reaction in the absence of **3e** did not deliver **4a** (Eq 5, Scheme 1), thus *o*-MeC_6H_4S• is essential. However, we could not detect the radical through EPR, when the reaction



Scheme 2. Scope of yne-ynamides. [a] 50 °C, [b] 60 °C.

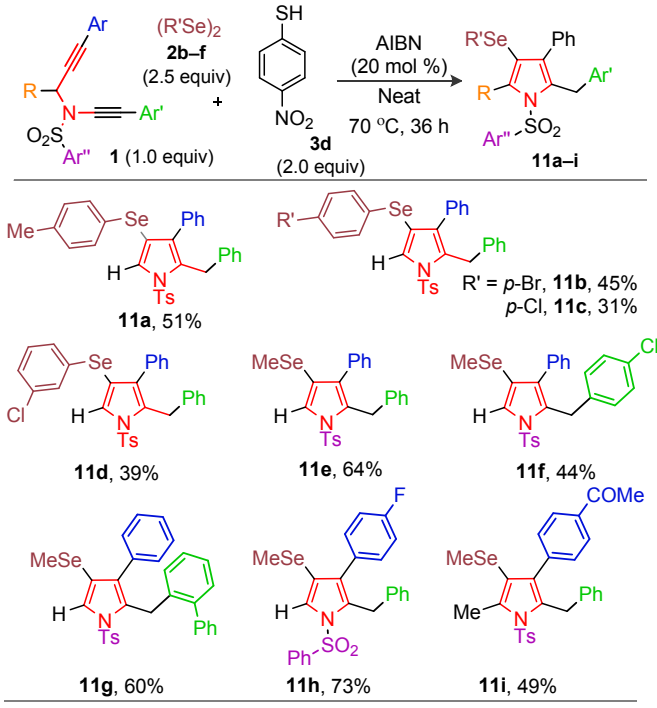
conducted at room temperature.[13]

We then examined the scope of Se• triggered cyclization of yne-ynamides under the established conditions (entry 5, Figure 1d) for the construction of unusual peripheral substituted 4-selenylated pyrroles (Schemes 2–4). To start with, the yne-ynamides having aryl substitutions at the propargyl terminus [electron-neutral phenyl, electron-rich (*m*-Me), and electron-poor (*p*-COMe, *m*-NO_2, *m*-F)] provided the desired products **4a–4e** (42–72%; Scheme 2). An aniline substituted product **4f** was obtained from **1f**; the free NH_2 group did not actually obstruct the reaction. Likewise, thienyl-substituted pyrrole **4g** was synthesized in 73% yield. The electron distribution via inherent *N*-lone pair polarization of the ynamide could possibly affect the reaction outcome. Thus, the Se• triggered cyclization of yne-ynamides having electronic variation of substituents at the ynamide terminus was next investigated (Scheme 2). The 4-selenylated pyrrole **4h** was fabricated from **1h** having aryl substitutions (*p*-Cl). The cyclization of **1i** with a O-benzyl protected flexible alkyl group at the ynamide terminus afforded **4i**, albeit in only 29% yield. A noteworthy observation is the synthesis of N-Ts-protected pyrrole **4j** (32%) with a cyclopropyl motif on the skeleton; cyclopropyl rings are prone to radical clock reactions when located adjacent to a radical (Scheme 2).The *ortho*-biphenyl substituted yne-ynamide **1k** provided **4k** in moderate yield. To evaluate the electronic properties of N-protecting groups in this cyclization, various N-



Scheme 3. Scope of tetra-substituted 4-selenylated pyrroles.

sulfonyl protected yne-ynamides **1l** and **1m** having different aryl groups at the alkyne terminus (C_6H_5, *p*-FC_6H_4) and at the ynamide terminus (*o*-PhC_6H_4 or C_6H_5,) were subjected to the standard conditions to yield the desired highly substituted 4-selenyl-N-sulfonyl pyrrole derivatives *N*-Ms (**4l**), *N*-SO_2Ph (**4m**), as shown in Scheme 2.



Scheme 4. Scope of diselenides.

The PhSe• mediated intramolecular 5-*exo*-trig cyclization of yne-ynamides having a methyl substitution at the propargyl position could furnish fully substituted pyrroles (Scheme 3). Hence, the α-methyl substituted propargyl tethered yne-ynamides **1n**–**1y** directly led to peripherally substituted selenylated pyrroles **10a**–**l** (42–80%). The steric and electronic effects of the aryl substituents both at the propargyl and ynamide terminus did not prevent the reaction outcome (Scheme 3).

The effect of other diaryl diselenides **2b**–**2e** was next scrutinized (Scheme-4). The reaction of **1a** and **2b** (*p*-$MeC_6H_4Se)_2$ in presence of **3e** led to **11a** (27%); however, the identical transformation with *p*-$O_2NC_6H_4SH$ (**3d**) proved more efficient, delivering **11a** in 51% yield. Likewise, the reaction of several diaryl diselenides {[(*p*-$BrC_6H_4Se)_2$ (2c)], [(*p*-$ClC_6H_4Se)_2$ (2d)], [(*m*-$ClC_6H_4Se)_2$ (2e)]} with 1a in the presence of 3d yielded the respective products 11b–d. Interestingly, the cyclization was compatible with $(MeSe)_2$ to provide 4-methylselenopyrroles 11e–i, and is remarkable (Scheme 4); as the identical reaction with aliphatic thiyl radicals was not viable. The MeSe• mediated intramolecular 5-*exo*-trig cyclization of yne-ynamides having various substitutions both at the propargyl and ynamide terminus furnished the respective 4-methylselenopyrroles 11e–g in moderate to good yield. Other than N-Ts-protected ynamides, the N-benzene sulfonyl protected 4-methylselenopyrrole 11h was constructed in good yield. The fully peripheral substituted selenopyrrole 11i was also synthesized (Scheme 4).

CONCLUSIONS

In summary, a chemo and regioselective RSe• radical mediated cyclization of yne-tethered ynamides to fully substituted 4-selenylated pyrroles has been developed. This reaction involves an uncommon S• →Se• radical transfer and is contrary to the well-explored radical dominance and reactivity of S• over Se•. This green synthetic method does not require transition metal catalyst and solvent and is general exhibiting a broad substrate scope and high functional group tolerance (the free NH_2 and the common radical trap electron-withdrawing groups did not affect the reaction outcome). Computational studies provided mechanistic insights for this transformation. Various control HRMS experiments validated the role of the arylthiol initiator for the in situ formation PhSe•. We believe these findings will open new avenues in trapping selenium radical for the construction of novel selenylated scaffolds.

Conflicts of interest

There are no conflicts to declare

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Notes and references

1 (a) U. Schmidt, A. Müller and K. Markau, *Chem. Ber,* 1964, **97**, 405; (b) J. K. Kochi, Free Radicals, *Wiley: New York,* 1973; Vol. II; (c) T. Torn, T. Seko and E. Maekawa, *Tetrahedron Lett.,* 1985, **26**, 3263; (d) Thomas G. Back and M. Vijaya Krishna, *J. Org. Chem.,* 1988, **53**, 2533; (e) A. Ogawa, K. Yokoyama, H. Yokoyama, M. Sekiguchi, N. Kambe and N. Sonoda, *Tetrahedron Lett*., 1990, **31**, 5931; (f) A. Ogawa, H. Yokoyama, K. Yokoyama, T. Masawaki, N. Kambe and N. Sonoda, *J. Org. Chem.,* 1991, **56**, 5721.

2 (a) A. Ogawa, H. Tanaka, H. Yokoyama, R. Obayashi, K.Yokoyama and N. Sonoda, *J. Org. Chem.,* 1992*,* **57***,* 111; (b) Akiya Ogawa, R. Obayashi, N. Sonoda and T. Hirao, *Tetrahedron Lett.,* 1998*,* **39***,* 1577; (c) A. Ogawa, R. Obayashi, H. Ine, Y. Tsuboi, N. Sonoda and T. Hirao, *J. Org. Chem*., 1998**,** **63***,* 881; d) K. Tsuchii, Y. Tsuboi, S.- i. Kawaguchi, J Takahashi, N Sonoda, A Nomoto and A. Ogawa, *J. Org. Chem.,* 2007**,** **72***,* 415.

3 (a) O. Ito, *J. Am. Chem. Soc.,* 1983, **105**, 850; (b) O. Ito and M. Matsuda, *J. Am. Chem. Soc.,* 1979, **101**, 1815; (c) O. Ito and M. Matsuda, *J. Org. Chem.,* 1984, **49**, 17; (d) O. Ito and M. Matsuda, *J. Am. Chem. Soc.,* 1981, **103**, 5871; (e) O. Ito and M. Matsuda, *J. Am. Chem. Soc.,* 1979, **101**, 5732; (f) O. Ito and M. Matsuda, *J. Am. Chem. Soc.,* 1982, **104**, 1701; (g) D. J. McPhee, M. Campredon, M. Lesage and D. Griller, *J. Am. Chem. Soc.,* 1989, **111**, 7563.

4 (a) K. Didehban, E. Vessally, A. Hosseinian, L. Edjlali and E. S. Khosroshahic, *RSC Adv*., 2018, **8**, 291; (b) G. Mugesh, W.-W. du Mont and H. Sies, *Chem. Rev.,* 2001**,** **101***,* 2125.

5 (a) S.H. Juang, C.C. Lung, P.C. Hsu, K.S. Hsu, Y.C. Li, P.C. Hong, H.S. Shiah, C.C. Kuo, C.W. Huang, Y.C. Wang, L. Huang, T.S. Chen, S.F. Chen, K.C. Fu, C.L. Hsu, M.J. Lin, C.J. Chang and C.L. Ashendel, T.C. Chan, K.M. Chou, J.Y. Chang. *Mol. Cancer Ther.,* 2007, **6**, 193. (b) P. Khalkar, J. Braude and A. P. Fernandes, *Free Radical Biology and Medicine,* 2018, **127**, 80.

6 (a) M. B. Gawande, V. D. B. Bonifácio, R. Luque,P. S. Branco and R. S. Varma, *Chem. Soc. Rev*., 2013, **42**, 5522; (b) N. Isambert, M. del M. S. Duque, J.-C. Plaquevent,Y. Génisson, J. Rodriguez and T. Constantieux, *Chem. Soc. Rev.,* 2011, **40**, 1347. (c) S. K. R. Parumala and R. K. Peddinti *Green Chem*., 2015, **17**, 4068; (d) Z. L. Palchak, D. J. Lussier, C. J. Pierce and C. H. Larsen, *Green Chem.*, 2015, **17**,1802.

7 (a) K. A. DeKorver, H. Li, A. G. Lohse, R. Hayashi, Z. Lu, Y. Zhang and R. P. Hsung, *Chem. Rev.,* 2010, **110**, 5064; (b) G. Evano, A. Coste and K. Jouvin, *Angew. Chem. Int. Ed.,* 2010, **49**, 2840; (c) X.-N. Wang, H.-S. Yeom, L.-C. Fang, S. He, Z.-X. Ma, B. L. Kedrowski and R. P. Hsung, *Acc. Chem. Res.,* 2014, **47**, 560.

8 (a) J. R. Dunetz and R. L. Danheiser, *J. Am. Chem. Soc.,* 2005, **127**, 5776; (b) N. Ghosh, S. Nayak and A. K. Sahoo, *Chem. Eur. J*., 2013, **19**, 9428; (c) S. Y. Yun, K.-P. Wang, N.-k. Lee, P. Mamidipalli and D. Lee, *J. Am. Chem. Soc.,* 2013, **135**, 4668; (d) S. Nayak, N. Ghosh and A. K. Sahoo, *Org. Lett.,* 2014, **16**, 2996; (e) C. Theunissen, B. Metayer, N. Henry, G. Compain, J. Marrot, A. Martin-Mingot, S. Thibaudeau and G. Evano, *J. Am. Chem. Soc.,* 2014, **136**, 12528; (f) S. Nayak, N. Ghosh, B. Prabagar and A. K. Sahoo, *Org. Lett.,* 2015, **17**, 5662; (g) T. P. Willumstad, D. B. Paul and R. L. Danheiser, *J. Org. Chem.,* 2015, **80**, 11794; (h) B. Prabagar, S. Nayak, R. Prasad and A. K. Sahoo, *Org. Lett.,* 2016, **18**, 3066; (i) V. Chintalapudi, E. A. Galvin, R. L. Greenaway and E. A. Anderson, *Chem. Commun*.,

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DOI: 10.1039/C9GC03745D

2016, **52**, 693; (j) T. Wang and T. R. Hoye, *J. Am. Chem. Soc.,* 2016, **138**, 13870; (k) B. Prabagar, N. Ghosh and A. K. Sahoo, *Synlett,* 2017, **28**, 2539; (l) A. Mekareeya, P. R. Walker, A. Couce-Rios, C. D. Campbell, A. Steven, R. S. Paton and E. A. Anderson, *J. Am. Chem. Soc.,* 2017, **139**, 10104; (m) R. N. Straker, Q. Peng, A. Mekareeya, R. S. Paton and E. A. Anderson, *Nat. Commun.,* 2016, **7**, 10109.

9 (a) F. Marion, C. Courillon and M. Malacria, *Org. Lett*., 2003, **5**, 5095; (b) F. Denes, M. Pichowicz, G. Povie and P. Renaud, *Chem. Rev.,* 2004, **114**, 2587; (c) F. Marion, J. Coulomb, A. Servais, C. Courillon, L. Fensterbank and M. Malacria, *Tetrahedron,* 2006, **62**, 3856; (d) A. Sato, H. Yorimitsu and K. Oshma, *Synlett*, 2009, 28; (e) B. Banerjee, D. N. Litvinov, J. Kang, J. D. Bettale and S. L. Castle, *Org. Lett*., 2010, **12**, 2650; (f) S. Balieu, K. Toutah, L. Carro, L.-M. Chamoreau, H. Rousseliere and C. Courillon, *Tetrahedron Lett*., 2011, **52**, 2876.

10 S. Dutta, R. K. Mallick, R. Prasad, V. Gandon and A. K. Sahoo, *Angew. Chem. Int. Ed.,* 2019, **58**, 2289.

11 See the Supporting Information.

12 CCDC 1945002 contains the supplementary crystallographic data for compound **4a**.

13 Detection of selenyl radical cannot be completely ruled out at 70 °C. Due to inaccessibility of the EPR-probe at high temperature, such experiment was not possible.

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