Tetrahedron Letters 52 (2011) 1343–1347

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Copper-catalyzed chalcogenoamination of 2-alkynylanilines with dichalcogenides for one-step synthesis of 3-sulfenylindoles and 3-selenylindoles

Zhen Li[a], Longcheng Hong[a], Ruiting Liu[a], Jianzhong Shen[a], Xigeng Zhou[a,b,*]

[a] Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai 200032, China

ARTICLE INFO

Article history:
Received 9 November 2010
Revised 5 January 2011
Accepted 14 January 2011
Available online 20 January 2011

Keywords:
2-Alkynylaniline
Dichalcogenides
3-Chalcogenylindole
Copper(I) iodide

ABSTRACT

The copper-catalyzed chalcogenoamination of 2-alkynylanilines with dichalcogenides has been achieved under mild reaction conditions using the weak base Cs_2CO_3 in combination with air oxidant, providing a convenient and efficient method for synthesis of 3-sulfenylindoles and 3-selenylindoles, including complex products bearing two attached 3-sulfenylindole rings.

Substituted indole moiety is displayed in a wide range of natural products and synthetic materials that exhibit significant biological activities.[1] There has been a longstanding interest in the development of new indole-based structures and new methods for their construction because of the utility of these molecules as potential pharmaceuticals.[2] In addition, these derivatives are versatile building blocks in the synthesis of natural products[3] and useful ligands[4] for organometallic catalysts. Among a variety of indole derivatives, 3-chalcogenylindoles are currently attracting considerable attention due to their therapeutic value in diseases, such as HIV,[5] cancer,[6] obesity,[7] heart disease,[8] and allergies[9] as well as potential utility in organic synthesis, in particular the potential to access different oxidation states at chalcogen atom.[10] A number of different strategies have been devised for the synthesis of 3-chalcogenylindoles.[11] However, very few methods allow for the intermolecular formation of a carbon-chalcogen bond while simultaneously constructing the indole nucleus itself.[11a–c]

In recent years much effort has been devoted to the development of tandem or sequential reactions that effect the formation of several different bonds, and/or rings in one-pot transformations.[12] These types of reactions lead to the conversion of simple starting materials into relatively complex molecules in a rapid and efficient manner, and have considerable potential utility for the construction of diverse compounds. Very recently, one viable protocol for synthesis of 3-sulfenylindoles from the $PdCl_2$ catalyzed annulation reaction of disulfides with 2-alkynylanilines[11b] is reported. Since sulfur compounds are often considered to be incompatible with metal-catalyzed reactions,[13] the catalytic thiolation[14] and selenylation[15] reactions have been explored to a much lesser extent than amination,[16] alkoxylation,[17] and alkylation.[18] To the best of our knowledge, no example of metal-catalyzed selenoamination of C–C unsaturated substrates is known. In order to obtain further insight into the metal catalyzed sulfoamination and selenoamination of C–C unsaturated substrates and to develop a more diverse selection of catalyst and/or reaction systems, we herein describe a new, chemoselective, copper-catalyzed strategy to synthesize 3-chalcogenylindoles by reactions of 2-alkynylanilines with dichalcogenides, and present evidence that the transformation proceeds by a chemoselective chalcogenylation of alkynes and subsequent intramolecular amination, in which the formation and oxidation of intermediate PhSCu should be involved. Furthermore, the present procedure is also available for construction of complex products bearing two attached 3-chalcogenylindole rings.

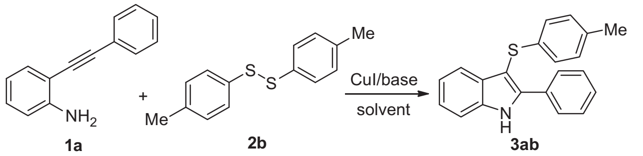
The study was initiated by the potential reaction of 2-(2-phenylethynyl)aniline (**1a**) with 1,2-di(*p*-tolyl)disulfane (**2b**) to form 2-phenyl-3-(*p*-tolylthio)-1*H*-indole **3ab**. Due to its cheapness, CuI was first used to test the feasibility of the chalcogenoamination. The results are summarized in Table 1. In contrast to the previously reported $PdCl_2$-catalyzed[11b] annulation of **1a** with **2b** to form **3ab**, no reaction was observed in the absence of base even at higher temperature for a longer reaction time (Table 1, entry 1). After

---

* Corresponding author. Tel./fax: +86 21 65643769.
E-mail address: xgzhou@fudan.edu.cn (X. Zhou).

0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.01.052

Table 1
Optimization of reaction conditions for formation of 3-sulfenylindole[a]



Entry	Base (equiv)	Solvent	Temp (°C)	Time (h)	Yield[e] (%)
1	—	DMSO	100	24	NR
2	NEt_3 (1.0)	DMSO	80	6	8
3	K_2CO_3 (1.0)	DMSO	80	6	23
4	Cs_2CO_3 (1.0)	DMSO	80	6	75
5	K_3PO_4 (1.0)	DMSO	80	6	41
6	KOH (1.0)	DMSO	80	6	64
7	*t*-BuOK (1.0)	DMSO	80	6	56
8	Cs_2CO_3 (2.0)	DMSO	80	6	59
9	Cs_2CO_3 (0.5)	DMSO	80	4	56
10	Cs_2CO_3 (1.0)	DMSO	100	6	70
11	Cs_2CO_3 (1.0)	DMSO	25	24	NR
12	Cs_2CO_3 (1.0)	H_2O	80	24	NR
13	Cs_2CO_3 (1.0)	DCE	80	6	11
14	Cs_2CO_3 (1.0)	THF	80	24	NR
15	Cs_2CO_3 (1.0)	Toluene	80	6	NR
16	Cs_2CO_3 (1.0)	DMF	80	6	63
17	Cs_2CO_3 (1.0)	DMSO	80	4	78
18[b]	Cs_2CO_3 (1.0)	DMSO	80	4	65
19[c]	Cs_2CO_3 (1.0)	DMSO	80	6	37
20[d]	Cs_2CO_3 (1.0)	DMSO	80	4	64

[a] Reaction conditions: **1a** (0.2 mmol), **2b** (0.15 mmol), CuI (0.02 mmol, 10 mol %), base (1 equiv), solvent (2 mL), under air.
[b] 0.1 mmol **2b** was used.
[c] The reaction was carried out under N_2 atmosphere.
[d] 5 mol % CuI was added.
[e] Isolated yield.

some experimentation, we were delighted to find that **3ab** was obtained with the assistance of a base (Table 1, entries 2–7). Among the bases screened, Cs_2CO_3 gave the best result (Table 1, entry 4), indicating that the base additive plays a key role in determining the reaction. Furthermore, the ratio of substrate and base was found to be important for the reaction, and the best result was achieved in the molar ratio of **1a**:Cs_2CO_3 = 1:1 (Table 1, entries 4, 8, and 9). Heating the solution is essential, since at room temperature, no desired reaction occurred (Table 1, entries 4 and 11). During our optimization studies, other solvents, such as water, DCE, THF, toluene, and DMF, were also tested. DMF was efficient for this reaction (Table 1, entry 16), but H_2O, DCE, THF or toluene as a solvent proved to be fruitless (Table 1, entries 12–15). The result also indicated that decreasing amount of disulfide had effect on the yield to some extent (Table 1, entry 18). When reaction time was decreased to 4 h, a slight higher yield (78%) of **3ab** was obtained (Table 1, entry 17), which showed that lengthening the reaction was unnecessary and even adverse for this tandem reaction. It was noteworthy that air was also crucial for advancement of the reaction. If the reaction was carried out under N_2 atmosphere, only a low yield of **3ab** was obtained (Table 1, entry 19).

Having delineated the optimum reaction conditions for the chalcogenoamination of 2-alkynylanilines with disulfides, we then applied them to a variety of substrates to determine the scope and limitations of the method.[21] As shown in Table 2, the reactions of electron-rich, electron-neutral, and electron-deficient 2-alkynylaniline derivatives with a variety of disulfide coupling partners proceeded in good yields. In general, the disulfides bearing electron-withdrawing group were more reactive than those with electron-donating groups (Table 2, entries 2–4). Furthermore, slight better yields were also obtained when an electron-withdrawing substituent was introduced at the 4-position of the benzenamine substrates (Table 2, entries 14–18). However, the electronic effects of R^1 substituents seem to be contrary to the above observations, and the presence of an electron-rich substituent gave a higher yield (Table 2, entries 1 vs 9, and 4 vs 12). The structure of compound **3cb** has been determined by the X-ray diffraction analysis (Fig. 1). These exciting results prompted us to examine if 2-alkynylanilines could undergo selectively the selenoamination/cyclization with diselenides under the present conditions. Indeed, the reaction of 2-alkynylanilines with diselenide proceeded smoothly to give the desired 3-selenylindoles in satisfactory yields (Table 2, entries 5, 13, and 18).

Having demonstrated the viability of the one-pot mono-chalcogenoamination process catalyzed by copper, we set out to achieve the selectively double sulfoamination. Thus, the 1,4-di(2-aminophenylethynyl)benzene substrate **1f** was prepared in three steps from commercially available materials (Scheme 1):[19] (a) Sonogashira coupling of 2-iodoaniline with TMS-acetylene provided **4a** in almost quantitative yield; (b) deprotecting TMS group of **4a** with KF/MeOH gave **5a** in a quantitative yield; (c) Sonogashira coupling of **5a** with 1,4-diiodobenzene afforded **1f**. Then we turned our attention to evaluate the reactivity of **1f** under the optimal reaction condition. As shown in Scheme 1, we were gratified to find that the CuI-catalyzed reaction of **1f** with disulfides **2b**–**d** proceeded smoothly to generate the corresponding bicyclization products **3fb**–**fd** in moderate yields. These reactions effect the conversion of acyclic precursors into bicyclic products with formation of four bonds, and two rings in a single step.

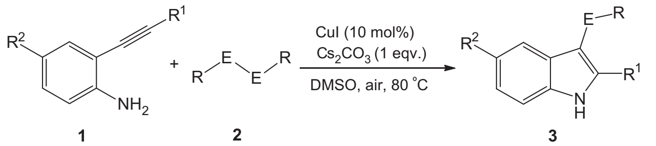
In order to obtain further insight into the chalcogenoamination process, we conducted the following experiments (Scheme 2). Firstly, the reactivity of PhSCu as an intermediate was examined. As expected, the reaction of **1a** with 1 equiv of phenylthiolate copper (PhSCu) in the presence of Cs_2CO_3 (1 equiv) and KI (0.2 equiv) in DMSO at 80 °C for 4 h under air, gave the corresponding 3-sulfenylindole **3aa** in 52% yield (*route a*). However, only trace amount of **3aa** was determined when the reaction was carried out under nitrogen (*route b*), indicating that PhSCu cannot carry out sulfenylation of 2-alkynylaniline by itself. In addition, we carried out the reaction of PhSCu with air in the presence of Cs_2CO_3 (1 equiv) and KI (0.2 equiv), PhSSPh (**2a**) was obtained in 34% (Eq. 1). These results suggest that the formation and oxidation of intermediate PhSCu should be involved in the reaction.

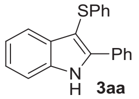
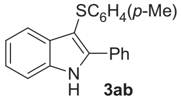
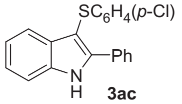
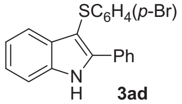
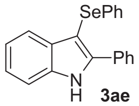
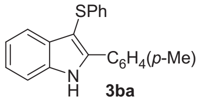
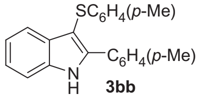
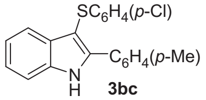
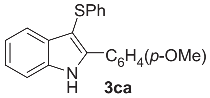
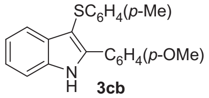
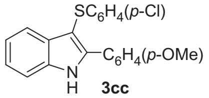
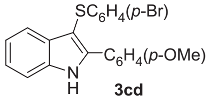
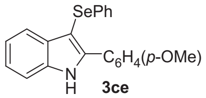
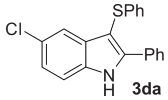
On the other hand, treatment of **1a** with CuI and Cs_2CO_3 in the absence of disulfide did not give the corresponding hydroamination product, 2-phenylindole, at 80 °C even with an increased catalyst loading of 20 mol % and a longer reaction time of 24 h (Scheme 2, *route c*). As already mentioned, treatment of **1a** with a lone Cs_2CO_3 under the same conditions did not form 2-phenylindole too (Scheme 2, *route d*). Then, we examined the direct thiolation of indole with disulfide (**2a**) under the present conditions, and only a low yield of **3aa** was obtained (Scheme 2, *route e*). These results indicate that the construction of the indole ring is not prior to the C–S bond formation. In addition, addition of 1,4-benzoquinone did not inhibit the chalcogenoamination, indicating that the reaction took place in a non-radical fashion.

On the basis of the above results, a plausible reaction mechanism for the copper-catalyzed chalcogenoamination of 2-alkynylanilines with dichalcogenides is outlined in Scheme 3. Initially, coordination of CuI to disulfide promotes the polarization of the RE–ER (E = S, Se) bond that may undergo heterolytic cleavage to form a RE^+ cation as observed previously.[20] Sequentially, RE^+ reacts with 2-alkynylaniline (**1**) to give a three-membered cyclic chalcogenonium cation (**III**) and PhECu (**II**) as reactive intermediates.[11a,20] Finally, the deprotonation of the NH_2 group of **III** with Cs_2CO_3 followed by an intramolecular attack to the sulfonium ion produces 3-sulfenylindole (**3**). At the same time, the oxidation of the

Table 2

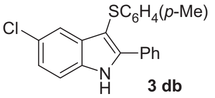
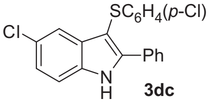
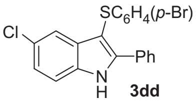
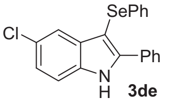
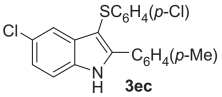
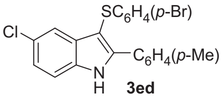
CuI catalyzed synthesis of 3-sulfenylindoles and 3-selenylindoles under the optimum conditions[a]



Entry	**1**: R^1; R^2	**2**: RE	Product	Yield[b] (%)
1	**1a**: Ph; H	**2a**: C_6H_5S	 **3aa**	72
2	**1a**	**2b**: *p*-MeC_6H_4S	 **3ab**	78
3	**1a**	**2c**: *p*-ClC_6H_4S	 **3ac**	82
4	**1a**	**2d**: *p*-BrC_6H_4S	 **3ad**	79
5	**1a**	**2e**: C_6H_5Se	 **3ae**	72
6	**1b**: *p*-MeC_6H_4; H	**2a**	 **3ba**	76
7	**1b**	**2b**	 **3bb**	81
8	**1b**	**2c**	 **3bc**	83
9	**1c**: *p*-$MeOC_6H_4$; H	**2a**	 **3ca**	77
10	**1c**	**2b**	 **3cb**	82
11	**1c**	**2c**	 **3cc**	85
12	**1c**	**2d**	 **3cd**	86
13	**1c**	**2e**	 **3ce**	77
14	**1d**: Ph; Cl	**2a**	 **3da**	81

(*continued on next page*)

Table 2 (*continued*)

Entry	**1**: R^1; R^2	**2**: RE	Product	Yield[b] (%)
15	**1d**	**2b**	 **3 db**	79
16	**1d**	**2c**	 **3dc**	87
17	**1d**	**2d**	 **3dd**	86
18	**1d**	**2e**	 **3de**	81
19	**1e**: p-MeC_6H_4; Cl	**2c**	 **3ec**	81
20	**1e**	**2d**	 **3ed**	83

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.15 mmol), CuI (0.02 mmol), Cs_2CO_3 (0.2 mmol), DMSO (2 mL), 80 °C, in air.

[b] Isolated yield.

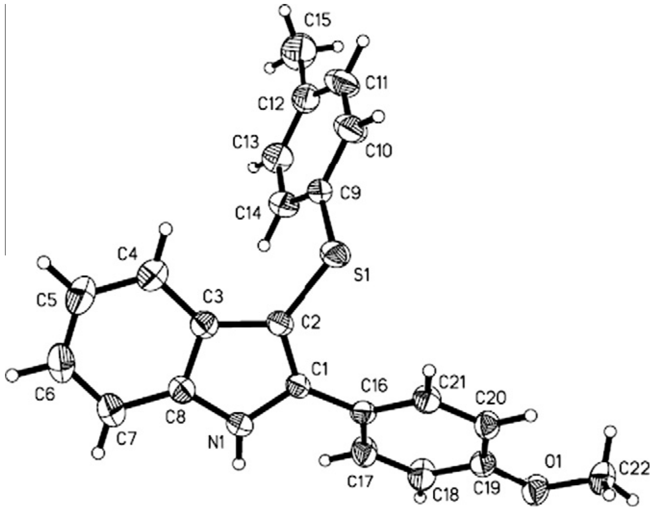
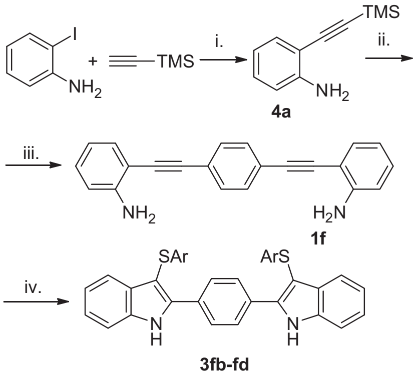


Figure 1. ORTEP diagram of **3cb** (30% probability level).

intermediate **II** with air reproduces disulfide **2a** and CuI in the presence of I^- ion. Consistent with this, when a stoichiometric amount of CuI was used, the reaction of **1a** with 1 equiv of **2a** in the presence of Cs_2CO_3 in DMSO at 80 °C smoothly proceeded under N_2 to give **3aa** in 40% (Scheme 2, *route f*).

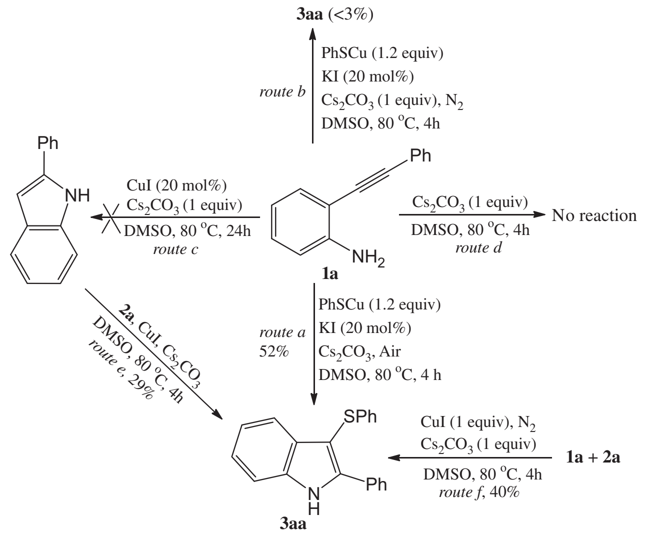
$$\mathrm{PhSCu + KI + Cs_2CO_3 \xrightarrow[80\ ^\circ C,\ air]{DMSO} \underset{34\%}{PhSSPh} + CuI} \tag{1}$$

In conclusion, a copper-catalyzed chalcogenoamination of 2-alkynylanilines with dichalcogenides has been established, which provides a convenient and efficient method for synthesis of 3-sulfenylindoles and 3-selenylindoles, including complex products bearing two attached 3-sulfenylindole rings. Moreover, the methodology proved to be efficient for construction of complex products bearing two attached 3-sulfenylindole rings in one-pot process. The simplicity, economy, high efficiency, and use of environmentally benign reagents render this method useful and competitive to the conventional approaches. The results described herein indicate that the chalcogenoamination involve three-membered cyclic chalcogenonium cation and PhECu as reactive intermediates, both dichalcogenide and the copper catalyst can be reproduced from PhECu(I) under the present conditions in the presence of air.

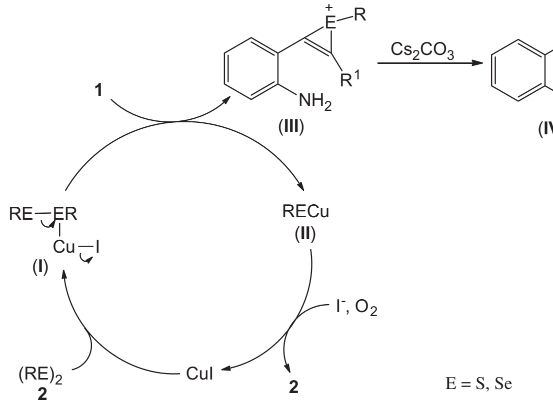


3fb: Ar = $C_6H_4(p\text{-Me})$, 58% yield;
3fc: Ar = $C_6H_4(p\text{-Cl})$, 72% yield;
3fd: Ar = $C_6H_4(p\text{-Br})$, 75% yield.

Scheme 1. Synthesis of 1,4-bis(3-(arylthio)-1*H*-indol-2-yl)benzenes. Reagents and conditions: (i) $Pd(PPh_3)_2Cl_2$ (1 mol %), CuI (2 mol %), NEt_3, (2 equiv), THF, rt, 97%; (ii) KF (3 equiv), MeOH, rt, 100%; (iii) 1,4-diiodobenzene, $Pd(PPh_3)_2Cl_2$ (2 mol %), CUI (4 mol %), NEt_3 (2 equiv), THF, reflux 4 h, 95%; (iv) dichalcogenides (2 equiv), CuI (10 mol %), Cs_2CO_3 (2 equiv), DMSO (2 mL), air, 80 °C, 12 h.



Scheme 2. Preliminary study on the formation pathway of **3**.



Scheme 3. Plausible mechanism for copper-catalyzed chalcogenoami-nation of 2-alkynylanilines with dichalcogenides.

Acknowledgments

We thank the NNSF of China, 973 Program (2009CB825300), Shanghai Science and Technology Committee (No. 08dj1400100), the Research Fund for the Doctoral Program of Higher Education of China, and Shanghai Leading Academic Discipline Project for financial support (B108).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.01.052.

References and notes

1. For reviews on indole chemistry, see: (a) Sundberg, R. L. *Indoles*; Academic: London, 1996; (b) Katritzky, A. R.; Pozharskii, A. F. *Handbook of Heterocyclic Chemistry*; Pergamon: Oxford, 2000; (c) Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2005**, *105*, 2873; (d) Humphrey, G. R.; Kuethe, J. T. *Chem. Rev.* **2006**, *106*, 2875; (e) Van, Z.; C, M.; Jones, M. L.; Gunn, D. E.; Geraci, L. S.; Jones, J. H.; Sawicki, D. R.; Sredy, J.; Jacot, J. L.; Dicioccio, A. T.; Petrova, T.; Mischler, A.; Podjarny, A. D. *J. Med. Chem.* **2005**, *48*, 3141; (f) Gribble, G. W. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1045; (g) Kim, K. S.; Zhang, L.; Schmidt, R.; Cai, Z. W.; Wei, D.; Williams, D. K.; Lombardo, L. J.; Trainor, G. L.; Xie, D.; Zhang, Y.; An, Y.; Sack, J. S.; Tokarski, J. S.; Darienzo, C.; Kamath, A.; Marathe, P.; Zhang, Y.; Lippy, J.; Jeyaseelan, S.; Wautlet, B.; Henley, B.; Brown, J. G.; Manne, V.; Hunt, J. T.; Fargnoli, J.; Borzilleri, R. M. *J. Med. Chem.* **2008**, *51*, 5330.
2. (a) Weng, J. R.; Tsai, C. H.; Kulp, S. K.; Chen, C. S. *Cancer Lett.* **2008**, *262*, 1533; (b) Rieck, G. C.; Fiander, A. N. *Mol. Nutr. Food Res.* **2008**, *52*, 105.
3. (a) Carroll, A. R.; Avery, V. M. *J. Nat. Prod.* **2009**, *72*, 696; (b) Lim, S. H.; Sim, K. M.; Abdullah, Z.; Hiraku, O.; Hayashi, M.; Komiyama, K.; Kam, T. S. *J. Nat. Prod.* **2007**, *70*, 1380; (c) Anna, K. K.; Mark, H. *Chem. Rev.* **2010**, *110*, 4489.
4. (a) McCormick, T. M.; Liu, Q. D.; Wang, S. N. *Org. Lett.* **2007**, *9*, 4087; (b) Chen, S.; Noll, B. C.; Peslherbe, L.; DuBois, M. R. *Organometallics* **1997**, *16*, 1089; (c) Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1994**, *13*, 3182.
5. Ragno, R.; Coluccia, A.; Regina, G. L.; Martino, G. D.; Piscitelli, F.; Lavecchia, A.; Novellino, E.; Bergamini, A.; Ciaprini, C.; Sinistro, A.; Maga, G.; Crespan, E.; Artico, M.; Silvestri, R. *J. Med. Chem.* **2006**, *49*, 3172.
6. Regina, G. L.; Edler, M. C.; Brancale, A.; Kandil, S.; Coluccia, A.; Piscitelli, F.; Hamel, E.; Martino, G. D.; Matesanz, R.; Díaz, J. F.; Scovassi, A. I.; Prosperi, E.; Lavecchia, A.; Novellino, E.; Artico, M.; Silvestri, R. *J. Med. Chem.* **2007**, *50*, 2865.
7. Ramakrishna, V. S. N.; Shirsath, V. S.; Kambhampati, R. S.; Vishwakarma, S.; Kandikere, N. V.; Kota, S.; Jasti. V. PCT Int. Appl. WO 2007020653, 2007.
8. Funk, C. D. *Nat. Rev. Drug Disc.* **2005**, *4*, 664.
9. Armer, R. E.; Wynne, G. M. PCT Int. Appl. WO 2008012511, 2008.
10. (a) Williams, T. M.; Ciccarone, T. M.; MacTough, S. C.; Rooney, C. S.; Balani, S. K.; Condra, J. H.; Emini, E. A.; Goldman, M. E.; Greenlee, W. J.; Kauffman, L. R.; O'Brien, J. A.; Sardana, V. V.; Schleif, W. A.; Theoharides, A. D.; Anderson, P. S. *J. Med. Chem.* **1993**, *36*, 12914; (b) Chen, Y.; Cho, C. H.; Shi, F.; Larock, R. C. *J. Org. Chem.* **2009**, *74*, 6802.
11. (a) Chen, Y.; Cho, C. H.; Larock, R. C. *Org. Lett.* **2009**, *11*, 173; (b) Guo, Y. J.; Tang, R. Y.; Li, J. H.; Zhong, P.; Zhang, X. G. *Adv. Synth. Catal.* **2009**, *351*, 2615; (c) Montevecchi, P. C.; Navacchia, M. L.; Spagnolo, P. *Eur. J. Org. Chem.* **1998**, *6*, 1219; (d) Sanz, R.; Guilarte, V.; Castroviejo, M. P. *Synlett* **2008**, 3006; (e) Barraja, P.; Diana, P.; Carbone, A.; Cirrincione, G. *Tetrahedron* **2008**, *64*, 11625; (f) Matsugi, M.; Murata, K.; Gotanda, K.; Nambu, H.; Anilkumar, G.; Matsumoto, K.; Kita, Y. *J. Org. Chem.* **2001**, *66*, 2434; (g) Yadav, J. S.; Reddy, B. S.; Reddy, Y. J.; Praneeth, K. *Synthesis* **2009**, *9*, 1520; (h) Maeda, Y.; Koyabu, M.; Nishimura, T. *J. Org. Chem.* **2004**, *69*, 7688; (i) Tudge, M.; Tamiya, M.; Savarin, C.; Humphrey, G. *Org. Lett.* **2006**, *8*, 565; (j) Corrado, B.; Martino, C.; Marino, P. *Gazz. Chim. Ital.* **1986**, *116*, 181.
12. (a) Wasilke, J. C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001; (b) Chang, S.; Lee, M.; Jung, D. Y.; Yoo, E. J.; Cho, S. H.; Han, S. K. *J. Am. Chem. Soc.* **2006**, *128*, 12366; (c) John, J.; U, I.; Suresh, E.; Radhakrishnan, K. V. *J. Am. Chem. Soc.* **2009**, *131*, 5042; (d) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395.
13. Cao, C. S.; Fraser, L. R.; Love, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 17614.
14. (a) Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108; (b) Gareau, Y.; Tremblay, M.; Gauvreau, D.; Juteau, H. *Tetrahedron* **2001**, *57*, 5739; (c) Arisawa, M.; Yamaguchi, M. *Org. Lett.* **2001**, *3*, 763; (d) Usugi, S.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 601; (e) Yadav, L. D. S.; Awasthi, C. *Tetrahedron Lett.* **2009**, *50*, 3801.
15. (a) Stein, A. L.; Alves, D.; da Rocha, J. T.; Nogueira, C. W.; Zeni, G. *Org. Lett.* **2008**, *10*, 4983; (b) Bieber, L. W.; da Silva, M. F.; Menezes, P. H. *Tetrahedron Lett.* **2004**, *45*, 2735; (c) Yu, L.; Meng, J. D.; Xia, L.; Guo, R. *J. Org. Chem.* **2009**, *74*, 5087.
16. (a) Patil, N. T.; Kavthe, R. D.; Shinde, V. S.; Sridhar, B. *J. Org. Chem.* **2010**, *75*, 3371; (b) Figueiredo, D.; Marcia, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 1190; (c) Alexanian, E. J.; Lee, C.; Sorensen, E. J. *J. Am. Chem. Soc.* **2005**, *127*, 7690.
17. (a) Seo, S. Y.; Yu, X. H.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 263; (b) Miyabe, H.; Yoshida, K.; Yamauchi, M.; Takemoto, Y. *J. Org. Chem.* **2005**, *70*, 2148.
18. (a) Angelini, E.; Balsamini, C.; Bartoccini, F.; Lucarini, S.; Piersanti, G. *J. Org. Chem.* **2008**, *73*, 5654; (b) Hajra, S.; Maji, B.; Bar, S. *Org. Lett.* **2007**, *9*, 2783.
19. Yoo, E. J.; Chang, S. *Org. Lett.* **2008**, *10*, 1163.
20. (a) Taniguchi, N. *Tetrahedron* **2009**, *65*, 2782; (b) Taniguchi, N. *J. Org. Chem.* **2006**, *71*, 7874; (c) Takeuchi, H.; Hiyama, T.; Kamai, N.; Oya, H. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2301; (d) Taniguchi, N. *Synlett* **2006**, 1351.
21. *General procedure for synthesis of 3-chalcogenylindoles:* A mixture of 2-Alkynylaniline (0.2 mmol), dichalcogenide (0.15 mmol), CuI (0.02 mmol), and Cs_2CO_3 (0.2 mmol) in DMSO (2 mL) was stirred at 80 °C under an air atmosphere. After completion of the reaction that was monitored by GC–MS or TLC, 25 mL water was added, and the mixture was extracted with ethyl acetate, the combined organic layers were washed with water (10 mL × 3), dried over anhydrous Na_2SO_4. After filtration and removal of solvents in vacuum, the residue was purified by silica gel column chromatography to afford the corresponding products.