A General and Highly Efficient Protocol for the Synthesis of Chalcogenoacetylenes by Copper(I)-Terpyridine Catalyst

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Abstract: A highly efficient copper-catalyzed C_{sp}–X (X = S, Se, Te) bond-forming reaction of terminal alkynes and diorganyl dichalcogenides has been developed. This transformation was realized through the use of copper(I) iodide as a catalyst, 4′-(4-methoxyphenyl)-2,2′:6′,2″-terpyridine as a ligand, and K_3PO_4 as a base. A variety of the functionalized substrates were found to react under these reaction conditions to provide products in good to excellent yields.

Key words: alkynyl chalcogenides, diorganyl dichalcogenides, terminal alkynes, terpyridines, copper-catalyzed reaction

Transition-metal catalysis of carbon–heteroatom bond formation are of great demand in general organic synthesis as well as the pharmaceutical industry and material science application.[1,2] In the last two decades, there has been a resurgence in interest in developing mild synthetic methods based on the copper-based catalysts as an alternative to other metal catalysts for the formation of C_{sp}–X (X = S, Se, Te) bonds.

Due to their fundamental roles in many organic transformations, many different classes of organochalcogenes have been prepared and studied to date.[3] Also, these classes of compounds are widely found in many biologically active and natural molecules like antioxidant, antitumor, antimicrobial, and antiviral.[4] In addition, organochalcogenes have been extensively used for technological purposes which is based on organic materials such as organic semiconductors and liquid crystals.[5] Among organochalcogenes, alkynyl chalcogenides can be employed as potent building blocks for a variety of chemical purposes.[6] For example, alkynyl selenides can be used in the synthesis of substituted olefins by hydroamination,[7] hydrohalogentation,[8] hydroboration,[9] hydrosulfonation,[10] hydrostannylation,[11] and hydrozirconation.[12] Furthermore, they are useful precursors in cycloaddition reactions, preparation of selenium salts,[13] and in the formation of selenol esters which are mild acyl-transferring agents.[14] Also, alkynyl sulfides can be utilized in cycloaddition and cross-coupling reactions.[15] However, there are limited reports of alkynyl tellurides' synthesis in the literature.[16a–f]

Alkynyl selenides are usually prepared by one of the five methods: (i) Coupling of terminal alkynes with diorganyl diselenides in the presence of a base;[17] (ii) the reaction of alkynyl bromides with a nucleophilic source of selenium;[16a] (iii) elimination of nitrogen by cleavage of selenodiazoles in the presence of an alkylating agent;[18] (iv) selenodecarboxylation of either arylpropiolic or cinnamic acid derivatives with diorganyl diselenide promoted by hypervalent iodine species such as iodosylbenzene (IB) and iodosobenzene diacetate (IBDA);[19] and (v) the reaction of metal alkynylide with elemental selenium,[20] or an appropriate electrophilic selenium agent, such as selenocyanates,[21] arylselenium halides,[22] or diaryl diselenides.[23] However, the commonly used method for the synthesis of alkynyl selenides is based on a copper-assisted cross-coupling reaction of terminal alkynes with a suitable source of electron-deficient selenium.[16d–h,24] Although synthetic routes based on organometallic species for the preparation of acetylenic selenides are widely used, these procedures suffer from several disadvantages such as using stoichiometric amount of toxic metal salts,[20] high temperatures,[16b,25] and performing anhydrous conditions.[26] Besides, similar reaction conditions applying for preparation of alkynyl sulfides and tellurides exhibit less acceptable results. Therefore, development of a new general approach for the synthesis of these types of organochalcogenes, especially for the efficient synthesis of alkynyl sulfides and tellurides, remains highly desirable. Because of the importance and current interest in C_{sp}–X coupling reactions, we decided to investigate the copper-catalyzed C–X bond formation between terminal alkynes and dichalcogenides (X = S, Se, Te) via the utilization of air-stable copper salt and a 4′-substituted terpyridine ligand.

The tridentate 2,2′:6′,2″-terpyridines (tpys) have been of great interest over the last few years, mostly because of their ability to chelate transition metals.[27] Furthermore, they are widely used in various research fields, such as medicinal chemistry,[28] photochemistry,[29] organometallics,[30] and nanoscience.[31] Herein, we report a simple, inexpensive, and efficient catalytic system for the synthesis of alkynyl chalcogenides by using CuI and 4′-(4-methoxyphenyl)-2,2′:6′,2″-terpyridine (Mtpy)[32] under mild reaction conditions.

Phenylacetylene (**1a**) and diphenyl diselenide (**2a**) were used as substrates for the initial optimization of the reaction at 50 °C. The influences of the reaction parameters are summarized in Table 1. As expected, the model reaction did not occur in the absence of catalyst (Table 1, entry 1) while only a 64% yield was obtained after 18 hours in the absence of the ligand in DMSO (Table 1, entry 2).

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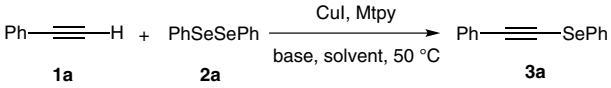
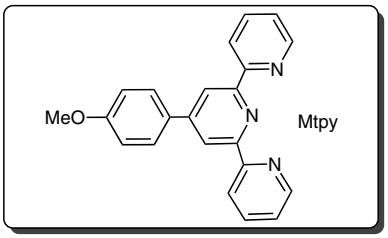
Among the screened copper(I) salts, copper(I) iodide resulted in the best performance (Table 1, entries 7–11).

Among the tested organic and inorganic bases, K_3PO_4 was found to be the most suitable base (Table 1, entries 12–17). For the solvent, DMSO resulted in the highest yield among the surveyed solvents (Table 1, entries 3–5). The solventless conditions were also studied, but compared to DMSO, it gave an inferior result (Table 1, entry 6). In addition, different copper (0.5 mol% and 1 mol%) and ligand (0.5 mol%, 1 mol%, and 2 mol%) concentrations were investigated (Table 1, entries 7 and 18–20); among them, 1 mol% of each were found to be the best (Table 1, entry 7). No significant change in the yield value of product was observed (96% isolated yield) when the reaction was conducted under inert (N_2) atmosphere. Lowering the temperature from 50 °C to 40 °C had a substantial reduction of the product yield (Table 1, entry 7). Therefore, the optimal reaction conditions were: diphenyl diselenide (1 equiv), phenylacetylene (2.0 equiv), CuI (1 mol%), Mtpy ligand (1 mol%), and K_3PO_4 (2 equiv) stirred in DMSO (4 mL) at 50 °C for five minutes in air.[33]

Table 1 Optimization of the Reaction Conditions[a]



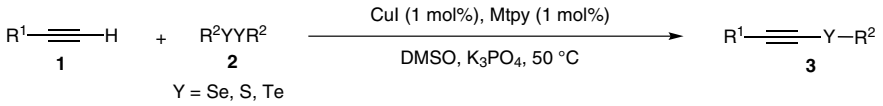


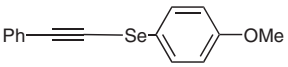
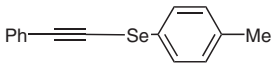
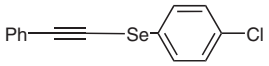
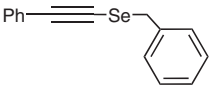
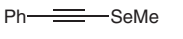
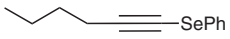
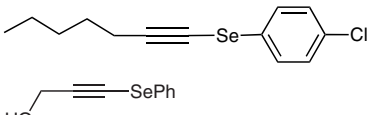
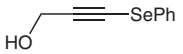
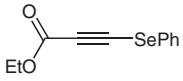
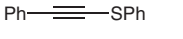
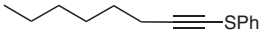
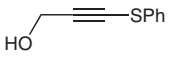
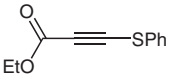
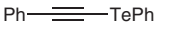
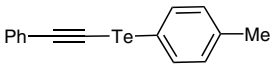
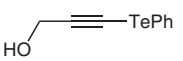
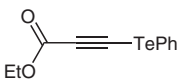
Entry	Catalyst (mol%)	Mtpy (mol%)	Base	Solvent	Time	Yield (%)[b]
1	–	1	K_3PO_4	DMSO	24 h	n.r.
2	CuI (1)	–	K_3PO_4	DMSO	18 h	64
3	CuI (1)	1	K_3PO_4	DMF	5 min	87
4	CuI (1)	1	K_3PO_4	EtOH	24 h	42
5	CuI (1)	1	K_3PO_4	$CHCl_3$	24 h	36
6	CuI (1)	1	K_3PO_4	–	24 h	35
7	CuI (1)	1	K_3PO_4	DMSO	5 min	97 (75)[c]
8	CuBr (1)	1	K_3PO_4	DMSO	5 min	12
9	CuCl (1)	1	K_3PO_4	DMSO	5 min	10
10	Cu_2O (1)	1	K_3PO_4	DMSO	5 min	16
11	CuOAc (1)	1	K_3PO_4	DMSO	5 min	25
12	CuI (1)	1	Cs_2CO_3	DMSO	10 min	84
13	CuI (1)	1	K_2CO_3	DMSO	10 min	93
14	CuI (1)	1	KOH	DMSO	10 min (90 min)	43 (78)
15	CuI (1)	1	DIPEA[d]	DMSO	10 min (12 h)	10 (45)
16	CuI (1)	1	Et_3N	DMSO	10 min (12 h)	15 (60)
17	CuI (1)	1	DABCO	DMSO	10 min (2 h)	31 (78)
18	CuI (0.5)	1	K_3PO_4	DMSO	2 h	72
19	CuI (1)	2	K_3PO_4	DMSO	5 min	94
20	CuI (1)	0.5	K_3PO_4	DMSO	2 h	84

[a] Reaction conditions: diphenyl diselenide (1 mmol), phenylacetylene (2.0 mmol), base (2.0 mmol), and solvent (4 mL) at 50 °C in air.
[b] Isolated yield.
[c] Reaction was performed at 40 °C.
[d] *N*,*N*-Diisopropylethylamine.

To determine the scope of the catalytic system, the present protocol was applied in the reactions of a range of terminal alkynes and diorganyl dichalcogenides (Table 2). First, a range of alkynyl selenides were synthesized by the reaction of diorganyl diselenides with different acetylenes. We found that this protocol was applicable to aromatic as well as aliphatic diselenides and alkynes. In terms of electronic effects, the reaction was not sensitive, since the treatment of phenylacetylene with diselenides containing either an electron-donating or -withdrawing group attached at the *para* position of the aromatic ring afforded the corresponding products in high yields (Table 2, entries 2–4). Interestingly, aryl- and nonaryl-substituted alkynes gave uniform results in terms of reaction time (0.1–2 h) and yield (72–97%). Reaction of ethyl propiolate proceeded at relatively higher rate compared with

Table 2 Copper-Catalyzed Synthesis of Alkynyl Chalcogenides[a]



Entry	R^1	R^2	Y	Product		Time (h)	Yield (%)[b]
1	Ph	Ph	Se		**3a**	0.1	97
2	Ph	4-$MeOC_6H_4$	Se		**3b**	0.25	90
3	Ph	4-MeC_6H_4	Se		**3c**	0.2	90
4	Ph	4-ClC_6H_4	Se		**3d**	0.1	92
5	Ph	$PhCH_2$	Se		**3e**	1	72
6	Ph	Me	Se		**3f**	1	85
7	*n*-Bu	Ph	Se		**3g**	1	84
8	*n*-C_5H_{11}	4-ClC_6H_4	Se		**3h**	0.5	90
9	CH_2OH	Ph	Se		**3i**	2	87
10	CO_2Et	Ph	Se		**3j**	0.5	97
11	Ph	Ph	S		**3k**	3	73
12	*n*-C_6H_{13}	Ph	S		**3l**	15	56
13	CH_2OH	Ph	S		**3m**	7	63
14	CO_2Et	Ph	S		**3n**	2	80
15	Ph	Ph	Te		**3o**	2	75
16	Ph	4-MeC_6H_4	Te		**3p**	2	87
17	CH_2OH	Ph	Te		**3q**	3	71
18	CO_2Et	Ph	Te		**3r**	1	82

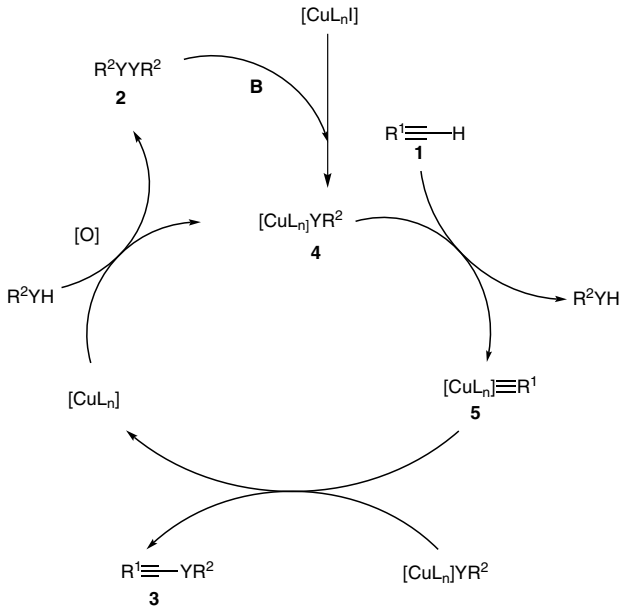
[a] Reaction conditions: diorganyl dichalcogenide (1.0 mmol), alkyne (2.0 mmol), K_3PO_4 (2.0 mmol), CuI (1 mol%), Mtpy (1 mol%), DMSO (4 mL) at 50 °C.
[b] Isolated yield.

those of other aliphatic alkynes, which can be attributed to facile deprotonation of this terminal alkyne (Table 2, entry 10).

Disulfides underwent similar reactions as diselenides, but in most cases longer reaction times and lower yields were observed compared to those of diselenides (Table 2, entries 11–14). Then, we examined the tellurylation reaction of various acetylenes (Table 2, entries 15–18). The reaction proceeded uniformly irrespective of the nature of terminal alkynes, and the corresponding products were obtained in relatively lower yields (71–87%) and in rather longer reaction times (1–3 h) than those of their diselenide counterparts.

In general, almost all chalcogenoacetylenes obtained smoothly, in high yields, and in short reaction times. Several functionalities, such as OH, CO_2Et, OMe, and Cl are well accepted in this reaction.

According to the above experimental results, we propose the mechanism as follows (Scheme 1). Initially, copper(I) intermediate **4** is quickly formed by dichalcogenide, CuI, Mtpy (L_n), and the strong inorganic base B (K_3PO_4). Then, intermediate **5** is formed from terminal acetylene, which in the presence of **4** gives the desired alkynyl chalcogenide (**3**). Finally, in the presence of diorganyl dichalcogenide, and [CuL_n], intermediate **4** would be regenerated, completing the cycle.



Scheme 1 Plausible reaction pathway

In summary, we have introduced a general and highly efficient copper-catalyzed procedure for the synthesis of alkynyl chalcogenides from terminal acetylenes and diorganyl dichalcogenides using K_3PO_4 as base and terpyridine Mtpy as ligand. A variety of functional groups are compatible with these reaction conditions. This new protocol should be added as a straightforward approach to preparing a variety of chalcogenoacetylenes in good to excellent yields in relatively short reaction times under mild and aerobic conditions.

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References and Notes

(1) (a) *Organoselenium Chemistry – Modern Developments in Organic Synthesis*, In *Topics in Current Chemistry*; Vol. 208; Wirth, T., Ed.; Springer Verlag: Berlin, **2000**. (b) McReynolds, M. D.; Dougherty, J. M.; Hanson, P. R. *Chem. Rev.* **2004**, *104*, 2239. (c) Zheng, B.; Gong, Y.; Xu, H.-J. *Tetrahedron* **2013**, *69*, 5342.

(2) (a) Gangjee, A.; Zeng, Y.; Tolreja, T.; McGuire, J. J.; Kisliuk, R. L.; Queener, S. F. *J. Med. Chem.* **2007**, *50*, 3046. (b) Faucher, A.-M.; White, P. W.; Brochu, C.; Maitre, C. G.; Rancourt, J.; Fazal, G. *J. Med. Chem.* **2004**, *47*, 18. (c) Lin, C.-H.; Wang, Y.-J.; Lee, C.-F. *Eur. J. Org. Chem.* **2010**, 4368.

(3) (a) *Organoselenium Chemistry*, In *Topics in Current Chemistry*; Wirth, T., Ed.; Springer: Heidelberg, **2000**, 208. (b) Taniguchi, N.; Onami, T. *J. Org. Chem.* **2004**, *69*, 915. (c) Zhang, S.; Qian, P.; Zhang, M.; Hu, M.; Cheng, J. *J. Org. Chem.* **2010**, *75*, 6732. (d) Freudendahl, D. M.; Santoro, S.; Shahzad, S. A.; Santi, C.; Wirth, T. *Angew. Chem. Int. Ed.* **2009**, *121*, 8409. (e) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596. (f) Magano, J.; Dunetz, J. R. *Chem. Rev.* **2011**, *111*, 2177. (g) Godoi, M.; Paixão, M. W.; Braga, A. L. *Dalton Trans.* **2011**, *40*, 11347.

(4) (a) Stadtman, T. C. *Annu. Rev. Biochem.* **1980**, *49*, 93. (b) Geiger, P. G.; Lin, F.; Girotti, A. W. *Free Radical Biol. Med.* **1993**, *14*, 251. (c) Krief, A. *Janssen Chim. Acta* **1993**, *11*, 10. (d) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255. (e) Mugesh, G.; du Mont, W. W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125. (f) Krehl, S.; Loewinger, M.; Florian, S.; Kipp, A. P.; Banning, A.; Wessjohann, L. A.; Brauer, M. N.; Iori, R.; Esworthy, R. S.; Chu, F.-F.; Brigelius-Flohé, R. *Carcinogenesis* **2012**, *33*, 620. (g) Wessjohann, L. A.; Schneider, A.; Abbas, M.; Brandt, W. *Biol. Chem.* **2007**, *388*, 997. (h) Mecklenburg, S.; Shaaban, S.; Ba, L. A.; Burkholz, T.; Schneider, T.; Diesel, B.; Kiemer, A. K.; Röseler, A.; Becker, K.; Reichrath, J.; Stark, A.; Tilgen, W.; Abbas, M.; Wessjohann, L. A.; Sasse, F.; Jacob, C. *Org. Biomol. Chem.* **2009**, *7*, 4753. (i) Roman, M.; Jitaru, P.; Barbante, C. *Metallomics* **2014**, *6*, 25.

(5) (a) Crouch, D. J.; Skabara, P. J.; Lohr, J. E.; McDouall, J. J. W.; Heeney, M.; McCulloch, I.; Sparrowe, D.; Shkunov, M.; Coles, S. J.; Horton, P. N.; Hursthouse, M. B. *Chem. Mater.* **2005**, *17*, 6567. (b) Petrov, V. F. *Mol. Cryst. Liq. Cryst.* **2005**, *442*, 51. (c) Tavares, A.; Schneider, P. H.; Merlo, A. A. *Eur. J. Org. Chem.* **2009**, 889. (d) Shimizu, Y.; Oikawa, K.; Nakayama, K. I.; Guillon, D. *J. Mater. Chem.* **2007**, *17*, 4223. (e) Passo, J. A.; Vilela, G. D.; Schneider, P. H.; Ritter, O. M. S.; Merlo, A. A. *Liq. Cryst.* **2008**, *35*, 833. (f) Lepeltier, M.; Hiltz, J.; Lockwood, T.; Belanger-Gariepy, F.; Perepichka, D. F. *J. Mater. Chem.* **2009**, *19*, 5167.

(6) (a) Magriotis, P. A.; Brown, J. T.; Scott, M. E. *Tetrahedron Lett.* **1991**, *32*, 5047. (b) Comasseto, J. V. *J. Organomet. Chem.* **1983**, *253*, 131. (c) Braga, A. L.; Reckziegel, A.; Silveira, C. C.; Comasseto, J. V. *Synth. Commun.* **1994**, *24*, 1165. (d) Braga, A. L.; Comasseto, J. V.; Petragnani, N. *Synthesis* **1984**, 240. (e) Ma, Y.; Qian, C. *Tetrahedron Lett.* **2000**, *41*, 945.
(7) (a) Petrov, M.; Radchenko, S. I.; Kupin, V. S.; Petrov, A. A. *J. Org. Chem. (USSR)* **1973**, *9*, 683. (b) Rampon, D. S.; Rodembusch, F. S.; Schneider, J. M. F. M.; Bechtold, I. H.; Gonçalves, P. F. B.; Merlo, A. A.; Schneider, P. H. *J. Mater. Chem.* **2010**, *20*, 715. (c) Rampon, D. S.; Rodembusch, F. S.; Lourega, R.; Gonçalves, P. F. B.; Merlo, A. A.; Schneider, P. H. *J. Braz. Chem. Soc.* **2010**, *21*, 2100.
(8) Comasseto, J. V.; Menezes, P. H.; Stefani, H. A.; Zeni, G.; Braga, A. L. *Tetrahedron* **1996**, *52*, 9687.
(9) Yang, D. Y.; Huang, X. J. *J. Organomet. Chem.* **1997**, *543*, 165.
(10) Tingolli, M.; Tiecco, M.; Testaferri, L.; Temperini, A.; Pelizzi, G.; Bacchi, A. *Tetrahedron* **1995**, *51*, 4691.
(11) Huang, X.; Ma, Y. *Synthesis* **1997**, 312.
(12) Zhu, L. S.; Huang, Z. Z.; Huang, X. J. *J. Chem. Res., Symop.* **1996**, 112.
(13) Kataoka, T.; Watanabe, S.; Yamamoto, K. *Tetrahedron Lett.* **1999**, *40*, 931.
(14) Tiecco, M.; Testaferri, L.; Temperini, A.; Bagnoli, L.; Marini, F.; Santi, C.; Terlizzi, R. *Eur. J. Org. Chem.* **2004**, 3447.
(15) (a) Bouillon, J. P.; Musyanovich, R.; Portella, C.; Shermolovich, Y. *Eur. J. Org. Chem.* **2001**, 3625. (b) Savarin, C.; Srogl, J.; Liebeskind, L. S. *Org. Lett.* **2001**, *3*, 91.
(16) (a) Ahammed, S.; Bhadra, S.; Kundu, D.; Sreedhar, B.; Ranu, B. C. *Tetrahedron* **2012**, *68*, 10542. (b) Sharma, A.; Schwab, R. S.; Braga, A. L.; Barcellos, T.; Paixão, M. W. *Tetrahedron Lett.* **2008**, *49*, 5172. (c) Godoi, M.; Liz, D. G.; Ricardo, E. W.; Rocha, M. S. T.; Azeredo, J. B.; Braga, A. L. *Tetrahedron* **2014**, *70*, 3349. (d) Braga, A. L.; Silveira, C. C.; Reckziegel, A.; Menezes, P. H. *Tetrahedron Lett.* **1993**, *34*, 8041. (e) Bieber, L. W.; da Silva, M. F.; Menezes, P. H. *Tetrahedron Lett.* **2004**, *45*, 2735. (f) Godoi, M.; Richardo, E. W.; Frizon, T. E.; Rocha, M. S. T.; Singh, D.; Paixão, M. W.; Braga, A. L. *Tetrahedron* **2012**, *68*, 10426. (g) Cohen, R. J.; Fox, D. L.; Salvatore, R. N. *J. Org. Chem.* **2004**, *69*, 4265. (h) Gendre, F.; Diaz, P. *Tetrahedron Lett.* **2000**, *41*, 5193.
(17) Movassagh, B.; Navidi, M. *Chin. Chem. Lett.* **2012**, *23*, 1035.
(18) Abramov, M. A.; Dehaen, W.; D'hooge, B.; Petrov, M. L.; Smeets, S.; Toppet, S.; Voets, M. *Tetrahedron* **2000**, *56*, 3933.
(19) Das, J. P.; Roy, U. K.; Roy, S. *Organometallics* **2005**, *24*, 6136.
(20) Takimiya, K.; Jigami, T.; Kawashima, M.; Kodani, M.; Aso, Y.; Otsubo, T. *J. Org. Chem.* **2002**, *67*, 4218.
(21) Werz, B. D.; Gleiter, R.; Rominger, F. *J. Org. Chem.* **2002**, *67*, 4290.
(22) (a) Back, T. G.; Bethell, R. J.; Parvez, M.; Wehrli, D. *J. Org. Chem.* **1998**, *63*, 7908. (b) Rampon, D. S.; Giovenardi, R.; Silva, T. L.; Rambo, R. S.; Merlo, A. A.; Schneider, P. H. *Eur. J. Org. Chem.* **2011**, 7066.
(23) Cook, D. J.; Hill, A. F.; Wilson, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1171.
(24) Mohammadi, E.; Movassagh, B. *Tetrahedron Lett.* **2014**, *55*, 1613.
(25) Lara, R. G.; Rosa, P. C.; Soares, L. K.; Silva, M. S.; Jacob, R. G.; Perin, G. *Tetrahedron* **2012**, *68*, 10414.
(26) Braga, A. L.; Reckziegel, A.; Menezes, P. H.; Stefani, H. A. *Tetrahedron Lett.* **1993**, *34*, 393.
(27) (a) Gong, H.; Gagné, M. R. *J. Am. Chem. Soc.* **2008**, *130*, 12177. (b) Joshi-Pangu, A.; Ganesh, M.; Biscoe, M. R. *Org. Lett.* **2011**, *13*, 1218. (c) Aoyama, N.; Hamada, T.; Manabe, K.; Kobayashi, S. *J. Org. Chem.* **2003**, *68*, 7329.
(28) Zhao, L. X.; Moon, Y. S.; Basnet, A.; Kim, E.-K.; Jahng, Y.; Park, J. G.; Jeong, T. C.; Cho, W.-J.; Choi, S.-U.; Lee, S.-Y.; Lee, C.-S.; Lee, E. S. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 1333.
(29) Park, J.; Pasupathy, A. N.; Goldsmith, J. I.; Chang, C.; Yaish, Y.; Petta, J. R.; Rinkoski, M.; Sethna, J. P.; Abruña, H. D.; McEuen, P. L.; Ralph, D. C. *Nature (London)* **2002**, *417*, 722.
(30) Wild, A.; Winter, A.; Schlütter, F.; Schubert, U. S. *Chem. Soc. Rev.* **2011**, *40*, 1459.
(31) Winter, A.; Hager, M. D.; Newkome, G. R.; Schubert, U. S. *Adv. Mater.* **2011**, *23*, 5728.
(32) Wang, J.; Hanan, G. S. *Synlett* **2005**, 1251.
(33) **General Procedure**
To the suspension of K_3PO_4 (2.0 mmol) in dry DMSO (4 mL) diorganyl dichalcogenide (1.0 mmol) and terminal acetylene (2.0 mmol) were added, and the mixture was stirred at 50 °C. Then, CuI (1.0 mol%) and Mtpy (1.0 mol%) were added to the above mixture, and the reaction mixture was stirred at that temperature under aerobic conditions. The progress of the reaction was monitored by TLC. When the reaction was complete, the mixture was poured into H_2O (15 mL) and extracted with EtOAc (2 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo to give the crude product which was further purified by preparative TLC (silica gel, *n*-hexane–EtOAc = 9:1). The identity and purity of the products were confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopic analysis.
Phenyl(2-phenylethynyl)selane (3a)
Yellow oil. IR (neat): ν = 2200 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 9 Hz, 2 H), 7.50–7.51 (m, 2 H), 7.32–7.37 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.7, 129.5, 129.0, 128.9, 128.6, 128.3, 127.1, 123.2, 102.9, 69.2.
(4-Methoxyphenyl)(2-phenylethynyl)selane (3b)
Yellow oil. IR (neat): ν = 2208 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.8 Hz, 2 H), 7.34–7.48 (m, 5 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 3.82 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7, 133.7, 131.9, 128.6, 128.1, 121.1, 120.2, 115.0, 101.1, 70.4, 55.3.
Benzyl(2-phenylethynyl)selane (3e)
Yellow oil. IR (neat): ν = 2156 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.42 (m, 10 H), 3.74 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.2, 137.5, 132.4, 131.4, 129.1, 128.2, 126.7, 123.5, 101.3, 68.1, 32.7.
Methyl(2-phenylethynyl)selane (3f)
Orange oil. IR (neat): ν = 2201 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.99 (m, 2 H), 7.86–7.89 (m, 3 H), 2.28 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.2, 129.99, 129.97, 125.1, 103.3, 73.2, 8.7.
(Hex-1-ynyl)(phenyl)selane (3g)
Yellow oil. IR (neat): ν = 2197 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.2 Hz, 2 H), 7.21–7.31 (m, 3 H), 2.47 (t, *J* = 6.9 Hz, 2 H), 1.61 (quin, *J* = 6.8 Hz, 2 H), 1.47 (sext, *J* = 7.2 Hz, 2 H), 0.94 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.0, 129.4, 128.6, 126.7, 104.7, 57.3, 30.8, 21.98, 20.3, 14.1, 13.6.
3-(Phenylselanyl)prop-2-yn-1-ol (3i)
Yellow oil. IR (neat): ν = 3339, 3059 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.63 (m, 2 H), 7.26–7.37 (m, 3 H), 4.15 (s, 2 H), 1.96 (br s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.3, 130.3, 129.4, 127.6, 101.5, 67.5, 64.9.

Phenyl(2-phenylethynyl)sulfane (3k)
Yellow oil. IR (neat): ν = 2215 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.64 (m, 2 H), 7.31–7.41 (m, 2 H), 7.18–7.29 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.7, 130.6, 129.37, 129.30, 129.1, 128.9, 126.7, 125.9, 98.5, 70.2.
(Oct-1-ynyl)(phenyl)sulfane (3l)
Yellow oil. IR (neat): ν = 2220 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.6 Hz, 2 H), 7.27–7.37 (m, 3 H), 2.26 (t, *J* = 7.2 Hz, 2 H), 1.51 (quin, *J* = 7.4 Hz, 2 H), 1.21–1.30 (m, 6 H), 0.86 (t, *J* = 6.5 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.5, 129.7, 129.1, 126.7, 106.1, 61.7, 37.1, 31.5, 28.5, 22.5, 14.1.
Ethyl 3-(Phenylthio)propiolate (3n)
Colorless oil. IR (neat): ν = 1678 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.38 (m, 3 H), 7.21–7.27 (m, 2 H), 4.55 (q, *J* = 6.9 Hz, 2 H), 1.54 (t, *J* = 6.9 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 130.4, 129.3, 128.1, 75.7, 74.1, 60.9, 15.1.
(2-Phenylethynyl)(*p*-tolyl)tellane (3p)
Orange oil. IR (neat): ν = 2210 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.59 (m, 9 H), 2.44 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.7, 129.5, 129.1, 128.8, 128.4, 128.2, 127.0, 123.1, 100.8, 64.3, 22.9.
Ethyl 3-(Phenyltellanyl)propiolate (3r)
Pale yellow oil. IR (neat): ν = 1674 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.36 (m, 5 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 1.33 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.9, 133.3, 129.3, 128.2, 74.1, 73.0, 60.5, 14.3.

