Tetrahedron 64 (2008) 10670–10675

Contents lists available at ScienceDirect

Tetrahedron

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

Hydrothiolation of terminal alkynes with diaryl disulfides and diphenyl diselenide: selective synthesis of (*Z*)-1-alkenyl sulfides and selenides

Zhang-Lin Wang [a], Ri-Yuan Tang [a,*], Pei-Song Luo [a], Chen-Liang Deng [b], Ping Zhong [a], Jin-Heng Li [a,b,*]

[a] College of Chemistry and Materials Science, Wenzhou University, Wenzhou 325035, China
[b] Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research (Ministry of Education), Hunan Normal University, Changsha 410081, China

ARTICLE INFO

Article history:
Received 25 June 2008
Received in revised form 31 August 2008
Accepted 5 September 2008
Available online 17 September 2008

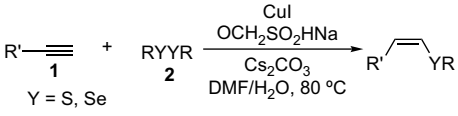
Keywords:
CuI
Rongalite
Hydrothiolation
Diaryl disulfide
Terminal alkyne
(*Z*)-1-Alkenyl sulfide

ABSTRACT

A simple, stereoselective and efficient method for the hydrothiolation of terminal alkynes with diaryl disulfides and diphenyl diselenide has been developed. In the presence of CuI, rongalite, and Cs_2CO_3, a variety of disulfides underwent the reaction of terminal alkynes stereoselectively to afford the corresponding (*Z*)-1-alkenyl sulfides in moderate to excellent yields. It is noteworthy that hydroselenations of 1,2-diphenyldiselane with alkynes are also conducted smoothly to afford (*Z*)-1-alkenyl selenides in good yields under the standard conditions.

1. Introduction

1-Alkenyl sulfides are significant synthetic intermediates as well as important structural units in many naturally occurring and biologically active compounds.[1] The majority of methods for the selective synthesis of 1-alkenyl sulfides are the hydrothiolations of alkynes with thiols.[2–4] Generally, hydrothiolations of alkynes with thiols include two transformations: (1) transition metal-catalyzed hyrothiolation[1f,g,2] and (2) radical hyrothiolation.[3] The former usually proceeds via *syn*-addition to afford anti-Markovnikov (*E*)-1-alkenyl sulfides or Markovnikov products, whereas the latter provides a mixture of anti-Markovnikov *E* and *Z* isomers. However, both are sometimes suffered from low regioselectivity besides stereoselectivity. As a result, some base-mediated hydrothiolations of alkynes have been described.[4] Truce and co-workers, for example, have reported a stereoselective method for the synthesis of (*Z*)-1-alkenyl sulfides by the reaction of an alkyne with a thiolate anion.[4a–c] Recently, cesium base-catalyzed stereoslective hydrothiolation of alkynes with alkanethiol has been developed to give (*Z*)-1-alkenyl sulfides.[4d] However, a radical inhibitor, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), was required. Moreover, the scope of thiols is limited to alkanethiol. Very recently, we reported sulfite-promoted one-pot synthesis of sulfides by the reaction of diaryl disulfides with alkyl halides.[5] In the presence of sulfite (in particular rongalite) and base (K_2CO_3), a variety of alkyl halides underwent the reaction with diaryl disulfides smoothly to afford the corresponding sulfides in good to excellent yields. As a continuing interest in the synthesis of sulfur-contianed compounds, we expected to apply the sulfite/base system in the hydrothiolations of alkynes. Although the reactions of alkynes with disulfides have been developed, the disulfidation products are generally obtained.[6] To the best of our knowledge, the reaction of an alkyne with a disulfide to prepare 1-alkenyl sulfides is still unexplored. Herein, we wish to report the hydrothiolations of alkynes with diaryl disulfides to stereoselectively afford (*Z*)-1-alkenyl sulfides in moderate to excellent yields using the CuI/rongalite/Cs_2CO_3 system (Eq. 1). Moreover, hydroselenations of 1,2-diphenyldiselane with terminal alkynes were also successful to afford (*Z*)-1-alkenyl selenides in good yields under the same conditions.



(1)

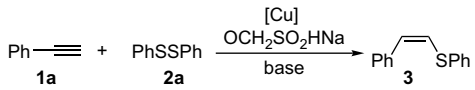
2. Results and discussion

As listed in Table 1, the reaction of phenylacetylene (**1a**) with diphenyl disulfide (**2a**) was conducted to screen the optimal

* Corresponding authors. Tel./fax: +86 577 8836 8607.
E-mail addresses: try@wzu.edu.cn (R.-Y. Tang), jhli@hunnu.edu.cn (J.-H. Li).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.09.022

Table 1
Screening conditions for hydrothiolation of phenylacetylene (**1a**) with 1,2-diphenyldisulfane (**2a**) in the presence of rongalite[a]



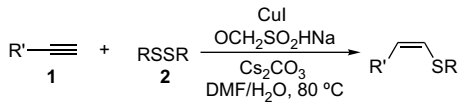
Entry	[Cu] (mol %)	Solvent	Base	Isolated yield (%)
1	—	DMF	K_2CO_3	59
2	—	DMF/H_2O (20/1)	K_2CO_3	66
3	—	DMF/H_2O (1/1)	K_2CO_3	46
4	—	EtOH/H_2O (20/1)	K_2CO_3	57
5	CuI (1)	DMF/H_2O (20/1)	K_2CO_3	73
6	CuI (2)	DMF/H_2O (20/1)	K_2CO_3	83
7	CuI (5)	DMF/H_2O (20/1)	K_2CO_3	87
8	CuI (10)	DMF/H_2O (20/1)	K_2CO_3	80
9	CuBr (5)	DMF/H_2O (20/1)	K_2CO_3	83
10	CuCl (5)	DMF/H_2O (20/1)	K_2CO_3	82
11	CuI (2)	DMF/H_2O (20/1)	—	Trace
12	CuI (2)	DMF/H_2O (20/1)	Et_3N	14
13	CuI (2)	DMF/H_2O (20/1)	Cs_2CO_3	95
14[b]	*CuI (2)*	*DMF/H₂O (20/1)*	*Cs_2CO_3*	*99*
15[c]	CuI (2)	DMF/H_2O (20/1)	Cs_2CO_3	33
16[b,d]	CuI (2)	DMF/H_2O (20/1)	Cs_2CO_3	90
17[b,e]	CuI (2)	DMF/H_2O (20/1)	Cs_2CO_3	NR
18[b]	—	DMF/H_2O (20/1)	Cs_2CO_3	69
19[b,f]	CuI (2)	DMF/H_2O (20/1)	Cs_2CO_3	12

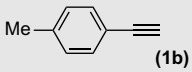
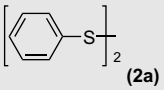
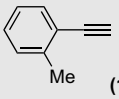
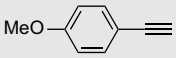
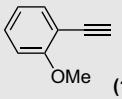
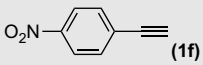
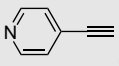
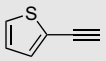
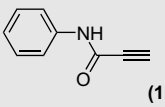
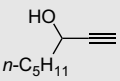
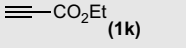
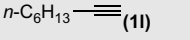
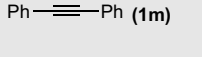
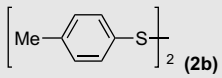
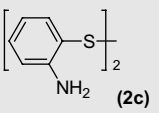
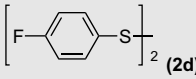
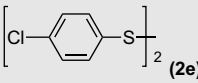
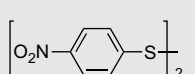
NR=No reaction.
[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), [Cu], OCH_2SO_2HNa (4 equiv), base (2 equiv), and solvent (1 mL) at 80 °C for 4 h.
[b] Cs_2CO_3 (1 equiv).
[c] Cs_2CO_3 (0.2 equiv).
[d] $HOCH_2SONa$ (3 equiv).
[e] Without $HOCH_2SONa$.
[f] At room temperature.

reaction conditions. Initially, effect of solvent was tested. We found that DMF combined with H_2O gave the best results and the amount of water affected the reaction to some extent (entries 1–4). While treatment of alkyne **1a** with **2a**, K_2CO_3, and rongalite (OCH_2SO_2HNa) in DMF selectively afforded the target product (*Z*)-**3** in a 59% yield (entry 1), the yield was enhanced to 66% in DMF/H_2O (20:1) (entry 2). However, DMF/H_2O (1:1) decreased the yield to 46%, and EtOH/H_2O (20:1) was also a less effective media (entries 3 and 4). To our delight, the presence of CuI was found to improve the reaction in view of yield (entries 5–8).[7] Therefore, the amount of CuI was then examined, and the highest yield was obtained in the presence of 5 mol % of CuI (entry 7). The results showed that the activities of both CuBr and CuCl were reduced slightly (entries 9 and 10). Subsequently, effect of bases was investigated. We found that trace amount of the product **3** was observed without bases (entry 11), and Et_3N provided only 14% yield of **3** (entry 12). Interestingly, quantitative yield of **3** was isolated in the presence of 1 equiv of Cs_2CO_3 (entry 14). However, the yield was decreased sharply using a catalytic amount of Cs_2CO_3 (entry 15). Note that rongalite plays a curial role in the reaction (entries 14, 16, and 17). The results indicated that the yield was decreased to some extent when 3 equiv of rongalite was added, and no reaction was observed in the absence of rongalite. We also found that without CuI the yield was reduced to some extent in the presence of OCH_2SO_2HNa, Cs_2CO_3, and DMF/H_2O (20:1) (entry 18). Finally, the reaction temperature was also evaluated, and only a low yield was isolated at room temperature (entry 19).

Scope of both disulfides and alkynes was explored under the optimal conditions, and the results are summarized in Table 2. Initially, a number of alkynes (**1**) were screened by reacting with 1,2-diphenyldisulfane (**2a**), CuI, rongalite, and Cs_2CO_3 (entries 1–11). The results showed that various alkynes **1b**–**j** underwent the reaction smoothly with disulfane **2a** in moderate to good yields.

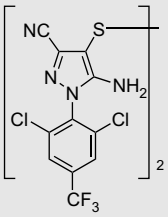
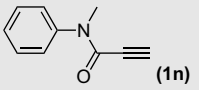
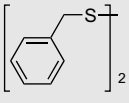
Table 2
Hydrothiolation of alkynes (**1**) with disulfanes (**2**) in the presence of CuI, rongalite and Cs_2CO_3[a]



Entry	Alkyne	RSSR	Time (h)	Yield[b] (%)
1	 **(1b)**	 **(2a)**	4	85 (**4**)
2	 **(1c)**	(**2a**)	22	70 (**5**)
3	 **(1d)**	(**2a**)	26	71 (**6**)
4	 **(1e)**	(**2a**)	24	89 (**7**)
5[c]	 **(1f)**	(**2a**)	4	74 (**8**)
6	 **(1g)**	(**2a**)	4	80 (**9**)
7	 **(1h)**	(**2a**)	4	62 (**10**)
8	 **(1i)**	(**2a**)	4	71 (**11**)
9	 **(1j)**	(**2a**)	4	90 (**12**)
10[d]	 **(1k)**	(**2a**)	4	63 (**13**)
11	 **(1l)**	(**2a**)	4	<5 (**14**)
12	 **(1m)**	(**2a**)	4	<5 (**15**)
13	(**1a**)	 **(2b)**	4	100 (**16**)
14	(**1a**)	 **(2c)**	4	56 (**17**)
15[e]	(**1f**)	(**2c**)	24	16 (**18**)
16	(**1g**)	(**2c**)	24	14 (**19**)
17[f]	(**1a**)	 **(2d)**	4	87 (**20**)
18	(**1a**)	 **(2e)**	4	98 (**21**)
19	(**1a**)	 **(2f)**	4	<5 (**22**)

(*continued on next page*)

Table 2 (*continued*)

Entry	Alkyne	RSSR	Time (h)	Yield[b] (%)
20[g]	(**1i**)	 (**2g**)	21	84 (**23**)
21	 (**1n**)	(**2g**)	21	68 (**24**)
22	(**1a**)	 (**2h**)	4	<5 (**25**)

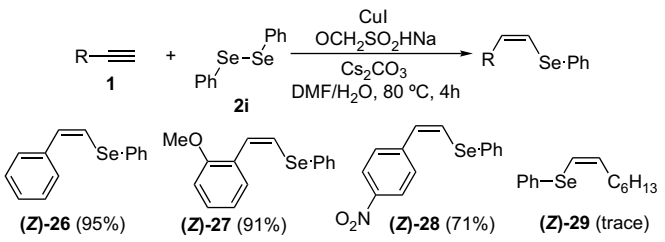
[a] Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), CuI (2 mol %), OCH_2SO_2HNa (4 equiv), Cs_2CO_3 (1 equiv) and DMF/H_2O (20:1; 1 mL) at 80 °C.
[b] Isolated yield.
[c] Ratio of *Z*/*E*-isomers is 1:1.5.
[d] Ratio of *Z*/*E*-isomers is 1:3.
[e] Ratio of *Z*/*E*-isomers is 1:1.
[f] Ratio of *Z*/*E*-isomers is 7.5:1.
[g] Ratio of *Z*/*E*-isomers is 3.3:1.

Note that a wide range of functional groups, including methyl, methoxy, nitro, amide, hydroxyl, and eater, on the alkyne moieties were tolerated well. The bulky 1-ethynyl-2-methoxybenzene (**1e**), for instance, was treated with **2a**, CuI, rongalite, and Cs_2CO_3 successfully in 89% yield under the standard conditions (entry 4). Gratifyingly, heteroaryl alkynes **1g** and **1h** were also suitable substrates under the same conditions (entries 6 and 7). We were happy to observe that good yields were still achieved from the reaction of disulfane **2a** with *N*-phenylpropiolamide (**1i**), oct-1-yn-3-ol (**1j**), or ethyl propiolate (**1k**) (entries 8–10). However, treatment of an aliphatic alkyne **1l** or an internal alkyne **1m** with substrate **2a** failed (entries 11 and 12).

Subsequently, a variety of disulfides were evaluated under the standard conditions. The results demonstrated that various diaryl disulfides were successful for reacting with alkynes, but both 1,2-bis(4-nitrophenyl)disulfane (**2f**) and 1,2-dibenzyldisulfane (**2h**) were unsuitable substrates. We found that diaryl disulfides **2b–e**, bearing electron-donating or electron-deficient substitutes, all work well with phenylacetylene (**1a**) in moderate to excellent yields (entries 13, 14, 17, and 18). Substrate **2c** bearing an NH_2 group on the aromatic ring, for instance, underwent the reaction with alkyne **1a** smoothly providing 56% yield (entry 14), but with alkynes **1f** or **1g** in low yields (entries 15 and 16). It is noteworthy that two new fipronil analogs **23** and **24** are synthesized under the standard conditions.[8] In the presence of CuI, rongalite, and Cs_2CO_3, dipyrazolyl disulfide **2g** underwent the reaction with alkynes **1i** or **1n** smoothly in good yields (entries 20 and 21). Unfortunately, attempt to addition of 1,2-dibenzyldisulfane (**2h**), a dialkyl disulfide, with phenylacetylene (**1a**) failed (entry 22).

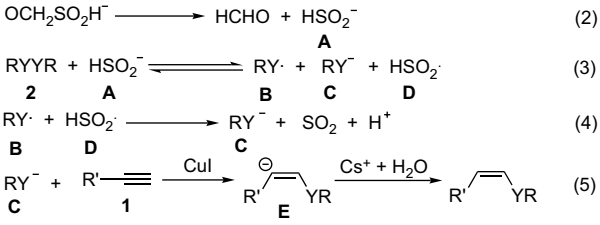
As listed in Scheme 1, hydroselenations of alkynes **1** with 1,2-diphenyl diselenide (**2i**) were also tested under the standard conditions.[9] In the presence of CuI, Rongalite, and Cs_2CO_3, three alkynes underwent the hydroselenation reaction with 1,2-diphenyl diselenide (**2i**) smoothly to afford the corresponding (*Z*)-1-alkenyl selenides in good yields. However, hydroselenation of octyne, an aliphatic alkyne, was still unsuccessful under the standard conditions.

Although base was required and *Z*-isomers were isolated as the major products, mechanism of the present reactions may be



Scheme 1. Hydroselenations of alkynes with 1,2-diphenyldiselenide (**2i**).

different from those of the base-mediated hydrothiolation reaction. In the base-mediated hydrothiolation reaction, a radical inhibitor was added, whereas the present reaction required a radical initiator. Thus, we have formulated a working mechanism as outlined in Scheme 2 based on the previous proposed mechanism.[1–7,10] Rongalite can be readily decomposed into HCHO and HSO_2^- anion (**A**).[10] Intermediate **A** then reacts with RYYR **2** to generate two radical intermediates (**B** and **D**) and an anion **C**. The radical **B** can also be converted into the anion **C** by reacting with intermediate **D**. Finally, the addition of the anion **C** with alkyne **1** affords the target product. We deduce that CuI can improve the generation of radical intermediate for the present reaction because CuI is a general radical catalyst,[11] and the Cs^+ ion favors both the generation of the anion **C** and the cis-addition with the C≡C bonds.[4] The electronic effect of substitutes on alkynes has a fundamental influence on stability of intermediate **E**. Thus, we deduced that arylalkynes display highly active for the hydrothiolation reaction due to the electron-withdrawing effect of aryl group, which can stabilize intermediate **E**. Whereas alkylalkynes bearing the electron-donating alkyl group disfavored the stability of intermediate **E** leading to less activity.



Scheme 2. A possible mechanism.

3. Conclusion

In summary, we have developed an efficient and stereoselective protocol for the hydrothiolation of terminal alkynes with diaryl disulfides and 1,2-diphenyl diselenide. In the presence of CuI, rongalite, and Cs_2CO_3, a number of disulfides stereoselectively underwent the reaction of various terminal alkynes to afford the corresponding (*Z*)-1-alkenyl sulfides in moderate to excellent yields. It is worth noting that two new fipronil analogs are synthesized in satisfactory yields. The hydroselenation of 1,2-diphenyldiselane with alkynes were also conducted smoothly to afford (*Z*)-1-alkenyl selenides in good yields under the standard conditions. Efforts to explore the detailed mechanism and extend the applications of the CuI/rongalite/Cs_2CO_3 system in other transformations using disulfide as a reaction partner are underway in our laboratory.

4. Experimental section

4.1. General

NMR spectroscopy was performed on both a Bruck-300 spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR)

and a Bruck-500 spectrometer operating at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). TMS (tetramethylsilane) was used as an internal standard and $CDCl_3$ was used as the solvent. Mass spectrometric analysis was performed on GC–MS analysis (SHIMADZU GCMS-QP2010).

4.2. Typical experimental procedure for the hydrothiolation of disulfides with terminal alkynes

A mixture of alkyne **1** (0.4 mmol), disulfide **2** (0.2 mmol), CuI (1.5 mg, 2 mol %), roganlite (189 mg, 4 equiv), and Cs_2CO_3 (130 mg, 1 equiv) in DMF/H_2O (20:1; 1 mL) was stirred at 80 °C under argon for the indicated time until complete consumption of starting material **1** as monitored by TLC. After the reaction was finished, diethyl ether was poured into the mixture, then washed with brine, extracted with diethyl ether, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by flash column chromatography (ethyl acetate or hexane/ethyl acetate) to afford the desired product.

4.2.1. (Z)-Phenyl(styryl)sulfane (**3**)[2a,4d]

Light-yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57 (d, J=7.3 Hz, 2H), 7.51 (d, J=7.1 Hz, 2H), 7.45–7.29 (m, 6H), 6.62 (d, J=10.7 Hz, 1H), 6.53 (d, J=10.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 136.5, 136.2, 130.1, 129.2, 128.7, 128.3, 127.3, 127.2, 127.1, 126.0; IR (KBr, cm^{-1}): 3057, 2922, 2860, 1586, 1481, 1441, 1355, 1082, 1024, 846, 739, 690; LRMS (EI, 70 eV) m/z (%): 212 (M^+, 100).

4.2.2. (Z)-(4-Methylstyryl)(phenyl)sulfane (**4**)[2c]

Yellow solid, mp 39.1–41.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51–7.39 (m, 4H), 7.35–7.18 (m, 5H), 6.57 (d, J=10.7 Hz, 1H), 6.43 (d, J=10.7 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.0, 136.4, 133.7, 130.0, 129.2, 129.0, 128.7, 127.3, 127.1, 124.8, 21.3; IR (KBr, cm^{-1}): 3047, 2920, 2859, 1581, 1470, 1352, 824, 737, 687; LRMS (EI, 70 eV) m/z (%): 226 (M^+, 100), 211 (–CH_3, 51).

4.2.3. (Z)-(2-Methylstyryl)(phenyl)sulfane (**5**)

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.54 (d, J=7.1 Hz, 1H), 7.42 (d, J=7.8 Hz, 2H), 7.43–7.19 (m, 6H), 6.71 (d, J=10.4 Hz, 1H), 6.54 (d, J=10.4 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 136.3, 135.2, 130.1, 129.8, 129.5, 129.1, 128.4, 127.6, 127.0, 126.4, 126.1, 125.6, 20.0; IR (KBr, cm^{-1}): 3053, 2925, 1584, 1470, 1360, 745, 691; LRMS (EI, 70 eV) m/z (%): 226 (M^+, 100), 211 (–CH_3, 30). HRMS (EI) for $C_{15}H_{14}S$ (M^+): calcd 226.0816, found 226.0816.

4.2.4. (Z)-(4-Methoxystyryl)(phenyl)sulfane (**6**)[2d]

Light-yellow solid, mp 51.2–52.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.52–7.45 (m, 4H), 7.37–7.27 (m, 3H), 6.94 (d, J=8.0 Hz, 2H), 6.57 (d, J=10.6 Hz, 1H), 6.38 (d, J=10.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.6, 136.4, 130.2, 129.9, 129.2, 129.1, 127.2, 127.1, 123.2, 113.7, 55.3; IR (KBr, cm^{-1}): 3050, 2953, 2836, 1598, 1503, 1462, 1249, 1175, 835, 738, 689; LRMS (EI, 70 eV) m/z (%): 242 (M^+, 100), 211 (–OCH_3, 23).

4.2.5. (Z)-(2-Methoxystyryl)(phenyl)sulfane (**7**)

Light-yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64 (d, J=7.5 Hz, 1H), 7.44 (d, J=7.5 Hz, 1H), 7.34–7.21 (m, 5H), 7.01 (t, J=7.5 Hz, 1H), 6.90 (d, J=10.7 Hz, 1H), 6.88 (d, J=7.9 Hz, 1H), 6.52 (d, J=10.7 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.6, 136.5, 134.2, 129.9, 129.3, 129.1, 128.7, 127.0, 125.7, 125.3, 122.6, 120.2, 110.4, 55.5; IR (KBr, cm^{-1}): 3287, 3045, 2936, 2835, 1587, 1464, 1250, 1171, 1033, 749, 682; LRMS (EI, 70 eV) m/z (%): 242 (M^+, 100), 211 (–OCH_3, 19); HRMS (EI) for $C_{15}H_{14}OS$ (M^+): calcd 242.0765, found 242.0765.

4.2.6. (4-Nitrostyryl)(phenyl)sulfane (**8**)

Z/E=1:1.5; yellow solid, mp 50.7–52.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.25 (d, J=8.7 Hz, 1H), 8.15 (d, J=8.7 Hz, 1H), 7.66 (d, J=8.7 Hz, 1H), 7.51–7.35 (m, 6H), 7.16 (d, J=15.6 Hz, 0.6H), 6.78 (d, J=10.6 Hz, 0.4H), 6.61–6.55 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 146.3, 142.9, 135.0, 133.0, 132.4, 131.4, 131.3, 130.6, 129.8, 129.5, 129.4, 129.1, 128.2, 128.0, 126.2, 126.0, 124.2, 123.7; IR (KBr, cm^{-1}): 3055, 2919, 1580, 1501, 1331, 1096, 846, 743, 683; LRMS (EI, 70 eV) m/z (%): 257 (M^+, 100); HRMS (EI) for $C_{14}H_{11}NO_2S$ (M^+): calcd 257.0511, found 257.0510.

4.2.7. (Z)-4-(2-(Phenylthio)vinyl)pyridine (**9**)

Light-yellow solid, mp 61.8–62.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.62 (d, J=5.4 Hz, 2H), 7.49 (d, J=5.4 Hz, 2H), 7.42–7.27 (m, 5H), 6.78 (d, J=10.9 Hz, 1H), 6.46 (d, J=10.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.8, 143.5, 135.2, 132.8, 130.5, 129.4, 127.9, 123.7, 122.9; IR (KBr, cm^{-1}) 3057, 2922, 2957, 1634, 1585, 1469, 1410, 824, 734, 685; LRMS (EI, 70 eV) m/z (%): 213 (M^+, 100). HRMS (EI) for $C_{13}H_{11}NS$ (M^+): calcd 213.0612, found 213.0612.

4.2.8. (Z)-2-(2-(Phenylthio)vinyl)thiophene (**10**)

Brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.45 (d, J=7.8 Hz, 2H), 7.36–7.25 (m, 4H), 7.16 (d, J=3.4 Hz, 1H), 7.05 (d, J=4.3 Hz, 1H), 6.82 (d, J=10.3 Hz, 1H), 6.38 (d, J=10.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 134.0, 135.8, 129.9, 129.2, 128.0, 127.2, 126.9, 126.2, 122.9, 121.5; IR (KBr, cm^{-1}): 3061, 2921, 2857, 1581, 1476, 1433, 1359, 1082, 1028, 739, 693; LRMS (EI, 70 eV) m/z (%): 218 (M^+, 100); HRMS (EI) for $C_{12}H_{10}S_2$ (M^+): calcd 218.0224, found 218.0224.

4.2.9. (Z)-N-Phenyl-3-(phenylthio)acrylamide (**11**)

Colorless solid, mp 151.3–152.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.63–7.47 (m, 5H), 7.36–7.27 (m, 5H), 7.19 (d, J=9.8 Hz, 1H), 7.22–7.06 (m, 1H), 6.04 (d, J=9.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.4, 147.3, 137.9, 137.0, 130.9, 129.3, 129.0, 128.0, 124.2, 119.7, 115.7; IR (KBr, cm^{-1}): 3433, 3307, 3048, 2925, 1637, 1574, 1521, 1434, 1299, 1245, 1172, 744, 690; LRMS (EI, 70 eV) m/z (%): 255 (M^+, 27), 163 (100); HRMS (EI) for $C_{15}H_{13}NOS$ (M^+): calcd 255.0718, found 255.0717.

4.2.10. (Z)-1-(Phenylthio)oct-1-en-3-ol (**12**)

Light-yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.38–7.24 (m, 5H), 6.32 (d, J=9.4 Hz, 1H), 5.81 (d, J=8.0 Hz, 1H), 4.65–4.63 (m, 1H), 2.19 (br s, 1H), 1.65–1.34 (m, 8H), 0.91 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 135.7, 129.8, 129.2, 126.8, 125.1, 124.2, 69.2, 38.9, 31.4, 24.9, 22.6, 14.0; IR (KBr, cm^{-1}): 3445, 3062, 2929, 2860, 1688, 1584, 1470, 1081, 741, 692; LRMS (EI, 70 eV) m/z (%): 236 (M^+, 12), 207 (–H_2O, 2), 110 (100); HRMS (EI) for $C_{14}H_{20}OS$ (M^+): calcd 236.1235, found 236.1233.

4.2.11. Ethyl-3-(phenylthio)acrylate (**13**)

Z/E=1:3; light-yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.78 (d, J=15.1 HZ, 0.25H), 7.51–7.46 (m, 2H), 7.41–7.35 (m, 3H), 7.27 (d, J=10.1 Hz, 0.75H), 5.91 (d, J=10.1 Hz, 0.75H), 5.65 (d, J=15.1 Hz, 0.25H), 4.29–4.22 (m, 1.5H), 4.18–4.14 (m, 0.5H), 1.33 (t, J=7.2 Hz, 2.3H), 1.26 (t, J=7.2 Hz, 0.7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.5, 165.2, 149.7, 146.8, 136.2, 133.0, 131.1, 130.4, 129.6, 129.3, 129.1, 128.2, 115.6, 113.3, 60.3, 14.3, 14.2; IR (KBr, cm^{-1}): 3059, 2981, 2927, 1701, 1574, 1475, 1369, 1215, 1164, 1031, 802, 745, 694; LRMS (EI, 70 eV) m/z (%): 208 (M^+, 64), 180 (2), 163 (53), 135 (100); HRMS (EI) for $C_{11}H_{12}O_2S$ (M^+): calcd 208.0558, found 208.0558.

4.2.12. (Z)-Styryl(p-tolyl)sulfane (**16**)[2d,4b]

Light-yellow solid, mp 49.6–51.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58 (d, J=7.5 Hz, 2H), 7.47–7.41 (m, 4H), 7.30 (t, J=7.6 Hz, 1H), 7.20 (d, J=7.6 Hz, 1H), 6.60 (d, J=10.8 Hz, 10.8 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.4, 136.6, 132.7, 130.5, 129.9, 129.4,

128.7, 128.3, 127.1, 126.5, 21.1; IR (KBr, cm^{-1}): 3022, 2920, 2862, 1595, 1488, 1443, 806, 772, 687; LRMS (EI, 70 eV) *m*/*z* (%): 226 (M^+, 100), 211 (–CH_3, 47).

*4.2.13. (Z)-2-(Styrylthio)aniline (**17**)*

Yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.58 (d, *J*=7.8 Hz, 2H), 7.45–7.39 (m, 3H), 7.30–7.27 (m, 1H), 7.19 (t, *J*=7.6 Hz, 1H), 6.79–6.73 (m, 2H), 6.54 (d, *J*=10.7 Hz, 1H), 6.19 (d, *J*=10.7 Hz, 1H), 4.27 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.9, 135.3, 130.5, 128.8, 128.4, 127.7, 127.0, 126.2, 125.6, 121.9, 118.7, 115.3; IR (KBr, cm^{-1}): 3429, 3341, 1603, 1479, 1352, 751, 688; LRMS (EI, 70 eV) *m*/*z* (%): 227 (M^+, 100); HRMS (EI) for $C_{14}H_{13}NS$ (M^+): calcd 227.0769, found 227.0769.

*4.2.14. 2-(4-Nitrostyrylthio)aniline (**18**)*

Z/*E*=1:1; Rufous solid, mp 65.1–66.5 °C; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.23 (d, *J*=8.3 Hz, 1H), 8.08 (d, *J*=8.3 Hz, 1H), 7.66 (d, *J*=8.3 Hz, 1H), 7.41 (d, *J*=8.3 Hz, 1H), 7.32–7.18 (m, 2H), 6.86 (d, *J*=15.4 Hz, 0.5H), 6.80–6.74 (m, 2H), 6.51–6.49 (m, 1H), 6.20 (d, *J*=15.4 Hz, 0.5H), 4.31 (br s, 1H), 4.28 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.4, 147.7, 146.1, 145.8, 143.0, 142.9, 136.4, 135.3, 134.1, 131.5, 131.1, 130.6, 129.1, 125.9, 124.1, 123.7, 118.9, 118.8, 116.6, 115.6, 115.5, 112.6; IR (KBr, cm^{-1}): 3437, 2924, 2861, 1599, 1493, 1337, 1206, 1096, 746, 674; LRMS (EI, 70 eV) *m*/*z* (%): 278 (M^+, 20), 136 (100); HRMS (EI) for $C_{14}H_{12}N_2O_2S$ (M^+): calcd 272.0620, found 272.0619.

*4.2.15. (Z)-2-(2-(Pyridin-4-yl)vinylthio)aniline (**19**)*

Yellow solid, mp 121.9–122.8 °C; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.62 (d, *J*=6.1 Hz, 2H), 7.42 (d, *J*=6.1 Hz, 2H), 7.41 (d, 1H), 7.24–7.18 (m, 1H), 6.79–6.73 (m, 2H), 6.48 (dd, *J*=10.8 Hz, 10.8 Hz, 2H), 4.29 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.9, 147.7, 143.6, 135.3, 134.4, 130.9, 123.6, 122.9, 118.8, 116.7, 115.4; IR (KBr, cm^{-1}): 3435, 3296, 3023, 2923, 1589, 1474, 1409, 1310, 1240, 1153, 825, 744; LRMS (EI, 70 eV) *m*/*z* (%): 228 (M^+, 29), 195 (8), 136 (100); HRMS (EI) for $C_{13}H_{12}N_2S$ (M^+): calcd 228.0721, found 228.0721.

*4.2.16. (4-Fluorophenyl)(styryl)sulfane (**20**)*

Z/*E*=7.5:1; light-yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.58–7.34 (m, 7H), 7.36–7.30 (m, 2H), 7.09, 6.86 (dd, *J*=15.4 Hz, 15.4 Hz, 0.24H), 6.61, 6.44 (dd, *J*=10.8 Hz, 10.8 Hz, 1.76H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 1264.0, 160.7, 136.4, 136.3, 132.6, 132.5, 131.4, 131.3, 131.2, 130.0, 128.7 (2C), 128.4, 127.6, 127.2 (1C), 127.1, 126.5, 126.0, 123.9, 116.4 (d, *J*=21.9 Hz, 1C), 116.3 (d, *J*=21.9 Hz, 1C); IR (KBr, cm^{-1}): 3033, 1591, 1486, 945, 826; LRMS (EI, 70 eV) *m*/*z* (%): 230 (M^+, 100); HRMS (EI) for $C_{14}H_{11}FS$ (M^+): calcd 230.0566, found 230.0565.

*4.2.17. (Z)-(4-Chlorophenyl)(styryl)sulfane (**21**)*

Colorless solid, mp 66.3–67.4 °C; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.51 (d, *J*=7.7 Hz, 2H), 7.42–7.25 (m, 7H), 6.63 (d, *J*=10.7 Hz, 1H), 6.42 (d, *J*=10.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 136.2, 134.7, 133.3, 131.2, 129.3, 128.7, 128.3, 128.0, 127.3, 125.1; IR (KBr, cm^{-1}): 3071, 2926, 1588, 1441, 1386, 1087, 821, 772, 676; LRMS (EI, 70 eV) *m*/*z* (%): 248 (M^++2, 36), 246 (M^+, 100), 211 (–Cl, 38); HRMS (EI) for $C_{14}H_{11}ClS$ (M^+): calcd 246.0270, found 246.0270.

*4.2.18. 3-(5-Amino-3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)-phenyl)-1H-pyrazol-4-ylthio)-N-phenylacrylamide (**23**)*

Z/*E*=3.3:1; colorless solid, mp 216.3–217.5 °C; ^1H NMR (300 MHz, CD_3COCD_3) δ: 9.39 (br s, 0.77H), 9.21 (br s, 0.23H), 8.13 (s, 1.54H), 8.08 (s, 0.46H), 7.75–7.65 (m, 2H), 7.35–7.28 (m, 2H), 7.10–7.03 (m, 1H), 6.88–6.83 (m 1H), 6.27–6.21 (m, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ: 168.7, 155.6, 152.2, 145.2, 143.8, 141.1, 138.3 (q, *J*=34.1 Hz, 1C), 135.3, 133.3, 131.0, 126.9 (q, *J*=271.0 Hz, 1C), 127.9, 123.5, 122.4, 117.3, 99.9; IR (KBr, cm^{-1}): 3405, 3323, 1613, 1538, 1499, 1443, 1391, 1316, 1172, 1139, 823, 756, 691, 626; LRMS (EI, 70 eV) *m*/*z* (%): 499 (2), 498 (M^++2, 3), 497 (10), 496 (M^+, 1), 407 (10), 405 (15), 257 (7), 255 (5), 93 (100); HRMS (EI) for $C_{20}H_{11}Cl_2F_3N_5OS$ (M^+): calcd 496.0014, found 496.0012.

*4.2.19. (Z)-3-(5-Amino-3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-1H-pyrazol-4-ylthio)-N-methyl-N-phenylacrylamide (**24**)*

Colorless solid, mp 233.9–234.8 °C; ^1H NMR (300 MHz, C_3D_6O) δ: 8.09 (s, 2H), 7.50–7.40 (m, 2H), 7.37–7.30 (m, 3H), 6.69 (d, *J*=9.4 Hz, 1H), 6.16 (br s, 2H), 5.84 (d, *J*=9.4 Hz, 1H), 3.30 (s, 3H); ^{13}C NMR (75 MHz, C_3D_6O) δ: 165.3, 151.1, 147.7, 143.9, 136.4, 133.5 (q, *J*=33.9 Hz, 1C), 130.8, 129.6, 127.4, 127.2, 126.4, 126.3, 122.4 (q, *J*=271.7 Hz, 1C), 115.0, 112.7, 95.7, 36.0; IR (KBr, cm^{-1}): 3456, 3341, 2930, 1629, 1573, 1495, 1387, 1315, 1140, 802, 698; LRMS (EI, 70 eV) *m*/*z* (%): 513 (5), 512 (M^++2, 3), 511 (6), 510 (M^+, 3), 407 (10), 405 (14), 353 (4), 351 (6), 257 (7), 255 (10), 191 (27), 107 (100); HRMS (EI) for $C_{22}H_{15}Cl_2F_3N_4OS$ (M^+): calcd 510.0296, found 510.0295.

*4.2.20. (Z)-Phenyl(styryl)selane (**26**)*[9]

Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.59 (d, *J*=8.0 Hz, 2H), 7.58–7.39 (m, 4H), 7.33–7.24 (m, 4H), 6.98 (d, *J*=10.0, 1H), 6.78 (d, *J*=10.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.3, 132.8, 131.7, 130.1, 129.4, 128.4, 128.3, 127.7, 127.3, 124.0; LRMS (EI, 70 eV) *m*/*z* (%): 262 (M^++2, 13), 260 (M^+, 67), 258 (35), 245 (8), 180 (77), 179 (75), 178 (43), 169 (24), 165 (29), 152 (6), 102 (37), 77 (100).

*4.2.21. (Z)-(2-Methoxystyryl)(phenyl)selane (**27**)*

Yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.55 (d, *J*=7.2 Hz, 2H), 7.40 (d, *J*=7.5 Hz, 1H), 7.28–7.23 (m, 4H), 7.19 (d, *J*=10.3, 1H), 6.99 (t, *J*=7.5 Hz, 1H), 6.87 (d, *J*=8.1 Hz, 1H), 6.78 (d, *J*=10.3 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.6, 132.6, 129.2, 128.9, 128.6, 127.4, 126.2, 125.8, 123.9, 120.5, 120.2, 110.6, 55.4; IR (KBr, cm^{-1}): 3049, 2939, 2840, 1691, 1586, 1464, 1250, 1033, 749, 682; LRMS (EI, 70 eV) *m*/*z* (%): 292 (M^++2, 13), 291 (11), 290 (M^+, 67), 289 (9), 288 (32), 287 (14), 286 (13), 259 (–OCH_3, 7), 211 (16), 210 (100); HRMS (EI) for $C_{15}H_{14}OSe$ (M^+): calcd 290.0210, found 290.0210.

*4.2.22. (Z)-(4-Nitrostyryl)(phenyl)selane (**28**)*[9]

Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.14 (d, *J*=7.5 Hz, 2H), 7.59 (d, *J*=7.0 Hz, 2H), 7.47 (d, *J*=16.0, 1H), 7.39–7.37 (m, 5H), 6.72 (d, *J*=16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.2, 133.9, 133.1, 129.9, 129.7, 128.8, 128.4, 127.8, 126.2, 124.2; LRMS (EI, 70 eV) *m*/*z* (%): 305 (M^++2, 65), 303 (M^+, 32), 288 (10), 259 (31), 258 (15), 257 (17), 225 (49), 214 (8), 195 (8), 179 (35), 178 (100).

Acknowledgements

We thank the Zhejiang Provincial Natural Science Foundation of China (Y407116) and National Natural Science Foundation of China (No 20572020) for financial support.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.09.022.

References and notes

1. (a) Ager, D. J. *Chem. Soc. Rev.* **1982**, *11*, 493; (b) Metzner, P.; Thuillier, A. *Sulfur Reagents in Organic Synthesis*; Academic: London, 1994; (c) Fernndez, F.; Khiar, N. *Chem. Rev.* **2003**, *103*, 3651; (d) Dubbaka, S. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7674; (e) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205; (f) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079; (g) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368.
2. Rh: (a) Cao, C.; Fraser, L. R.; Love, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 17614; (b) Shoai, S.; Bichler, P.; Kang, B.; Buckley, H.; Love, J. A. *Organometallics* **2007**, *26*, 5778; Rh or Pd: (c) Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108; Pd: (d) Kondoh, A.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2007**, *9*,

1383; Ni: (e) Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P. *Organometallics* **2006**, *25*, 1970; (f) Malyshev, D. A.; Scott, N. M.; Marion, N.; Stevens, E. D.; Ananikov, V. P.; Beletskaya, I. P.; Nolan, S. P. *Organometallics* **2006**, *25*, 4462; (g) Ananikov, V. P.; Malyshev, D. A.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *Adv. Synth. Catal.* **2005**, *347*, 1993; Sm: (h) Zheng, X.-L.; Xu, X.-L.; Zhang, Y.-M. *Chin. J. Chem.* **2004**, *22*, 958; In: (i) Yadav, J. S.; Reddy, B. V. S.; Raju, A.; Ravindar, K.; Baishya, G. *Chem. Lett.* **2007**, *36*, 1474.

3. (a) Griesbaum, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 273; (b) Ichinose, Y.; Wakamatsu, K.; Nozaki, K.; Birbaum, J.-L.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1987**, 1647; (c) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1035.
4. (a) Truce, W. E.; Simms, J. A.; Boudakian, M. M. *J. Am. Soc. Chem.* **1956**, *78*, 695; (b) Truce, W. E.; Simms, J. A. *J. Am. Soc. Chem.* **1956**, *78*, 2756; (c) Truce, W. E.; Tichenor, G. J. W. *J. Org. Chem.* **1972**, *37*, 2391; (d) Kondoh, A.; Takami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2005**, *70*, 6468; (e) Silva, M. S.; Lara, R. G.; Marczewski, J. M.; Jacob, R. G.; Lenardão, E. J.; Perin, G. *Tetrahedron Lett.* **2008**, *49*, 1927.
5. (a) Tang, R.-Y.; Zhong, P.; Lin, Q.-L. *J. Fluorine Chem.* **2006**, *127*, 948; (b) Tang, R.-Y.; Zhong, P.; Lin, Q.-L. *Synthesis* **2007**, 85.
6. (a) Ananikov, V. P.; Kabeshov, M. A.; Beletskaya, I. P.; Khrustalev, V. N.; Antipin, M. Yu. *Organometallics* **2005**, *24*, 1275; (b) Usugi, S.-i.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 601.
7. For papers on CuI-catalyzed additions of alkenes and alkynes with disulfide and HOAc or *n*-Bu_4NX (X=I, Br, Cl), see: (a) Taniguchi, N. *J. Org. Chem.* **2006**, *71*, 7874; (b) Taniguchi, N. *Synlett* **2008**, 849.
8. Fipronil displays highly birological activities including a highly efficient inselecticide, see: (a) Buntain, I. G.; Hatton, L. R.; Hawkins, D. W.; Pearson, C. J.; Roberts, D. A. Eur. Pat. Appl. 295,117 A1, 1988; *Chem. Abstr.* **1990**, *112*, 35845n; (b) Wu, T.-T. U.S. Patent 5,814,652, 1998; *Chem. Abstr.* **1998**, *129*, 256473; (c) Caboni, P.; Sammelson, R. E.; Casida, J. E. *J. Agric. Food Chem.* **2003**, *24*, 7055.
9. For papers on the hydroselenation of alkynes, see: (a) Comasseto, J. V. *J. Organomet. Chem.* **1983**, *253*, 131; (b) Renard, M.; Hevesi, L. *Tetrahedron* **1985**, *41*, 5939; (c) Comasseto, J. V.; Brandt, C. A. *Synthesis* **1987**, 146; (d) Ogawa, A.; Obayashi, R.; Sekiguchi, M.; Masawaki, T.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1992**, *33*, 1329; (e) Kamiya, I.; Nishinaka, E.; Ogawa, A. *J. Org. Chem.* **2005**, *70*, 696; (f) Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P. *Organometallics* **2007**, *26*, 740.
10. (a) William, R. D.; Maurice, M.; Samia, A. M. *Tetrahedron Lett.* **2001**, *42*, 4811; (b) Huang, B. N.; Liu, J. T.; Huang, W. Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 101; (c) Hodgson, W. G.; Neaves, A.; Parl, C. A. *Nature (London)* **1956**, *178*, 489.
11. For selective papers, see: (a) Richardson, H. W. *Handbook of Copper Compounds and Applications*; Marcel Dekker: New York, NY, 1997; (b) Javed, I.; Beena, B.; Naresh, K. N. *Chem. Rev.* **1994**, *94*, 519; (c) Krause, N. *Modern Organocopper Chemistry*; Wiley-VCH: Weinheim, 2002; (d) Niu, M.; Yin, Z.; Fu, H.; Jiang, Y.; Zhao, Y. *J. Org. Chem.* **2008**, *73*, 3961; (e) Shao, L.-X.; Shi, M. *Tetrahedron* **2007**, *63*, 11938.