JOC Article

Pd-Catalyzed Sulfinylzincation of Activated Alkynes with 1-Alkynyl Sulfoxides as a Sulfinyl Source

Naoyoshi Maezaki, Suguru Yagi, Ryoko Yoshigami, Jun Maeda, Tomoko Suzuki, Shizuka Ohsawa, Kouji Tsukamoto, and Tetsuaki Tanaka*

Graduate School of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565-0871, Japan

t-tanaka@phs.osaka-u.ac.jp

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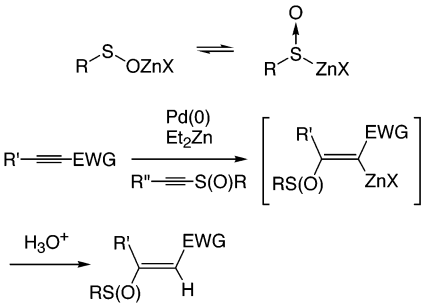
Unprecedented Pd-catalyzed sulfinylzincation with 1-alkynyl sulfoxide as a sulfinyl source was developed. Bis-sulfinyl alkenes were formed in good yields on treatment of 1-alkynyl sulfoxides with Et_2Zn in the presence of a Pd-catalyst, wherein zinc sulfenate (or sulfinylzinc) species would be generated in situ to undergo highly *syn*-selective conjugate addition to the 1-alkynyl sulfoxides. By using 3,3-dimethyl-1-butynyl sulfoxides, formation of the bis-sulfinyl alkenes was completely suppressed and the sulfinylzincation of activated alkynes was accomplished. The reaction tolerates various functionalities, and was promoted considerably by the neighboring group participation of the heteroatom at the δ-position in the alkynoates. Stereodivergent synthesis of two diastereomeric vinylic sulfoxides and reaction of the resulting vinylzinc species with electrophiles were also described.

Introduction

The chemistry of sulfenic acids has been extensively investigated to demonstrate the existence of the species as intermediates in biological processes, or to develop a convenient method for the synthesis of vinylic sulfoxides via addition to an unsaturated bond.[1] The species have also received considerable attention, since asymmetric addition of this species affords a novel method to synthesize versatile chiral vinylic sulfoxides by employing sulfenic acids with a chiral auxiliary.[2] Recent progress in this area is making this unstable species a useful tool in synthetic organic chemistry.

In contrast to the evolution of sulfenic acid chemistry, little attention has been paid to the use of the corresponding conjugate bases, sulfenate anions, for organic synthesis. This sulfenate anion is an ambident nucleophile bearing two nucleophilic sites at the sulfur and oxygen atoms, and presumably exists as an equilibrium between the sulfenate anion and the sulfinyl anion as shown in Scheme 1. The character of this species is not well-known so far, since they are very unstable for oxidation to sulfinates and self-condensation to thiosulfinates. There are few reports regarding sodium sulfenates, which are generated in situ from stable precursors, such as sulfenyl esters, sulfenyl halides, disulfides, and 2-sulfinylpyridine *N*-oxides, using strong alkaline conditions.[3] Furukawa and co-workers have, for the first time, isolated sodium sulfenates and proved the existence of the species.[4] However, reactions of the corresponding zinc salts have not hitherto been reported, to the best of our knowledge, although reactions of organozinc reagents are known to show high selectivity and tolerance to a variety of functionalities.[5]

SCHEME 1



Previously, we have accomplished Pd-catalyzed sulfinylzincation of activated alkynes using 1-alkynyl sulfoxides as a sulfinyl source, in which a zinc sulfenate species was suggested as a reaction intermediate (Scheme 1).[6] The zinc sulfenate species underwent addition to activated alkynes such as 1-alkynyl sulfoxides and alkynoates

(1) Review: (a) Hogg, D. R. In *The Chemistry of Sulfenic Acids and Their Derivatives*; Patai, S., Ed.; John Wiley & Sons: Chichester, UK, 1990; pp 361−402. (b) Van den Breok, L. A. G. M.; Delbressine, L. P. C.; Ottenheijm, H. C. J. In *The Chemistry of Sulfenic Acids and Their Derivatives*; Patai, S., Ed.; John Wiley & Sons: Chichester, UK, 1990; pp 701−721.

(2) Aversa, M. C.; Barattucci, A.; Bonaccorsi, P.; Giannetto, P.; Policicchio, M. *J. Org. Chem.* **2001**, *66*, 4845−4851.

(3) Hogg, D. R.; Stewart, J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 43−47. Danehy, J. P.; Parameswaran, K. N. *J. Org. Chem.* **1968**, *33*, 568−572.

(4) Furukawa, N.; Konno, Y.; Tsuruoka, M.; Fujihara, H.; Ogawa, S. *Chem. Lett.* **1989**, 1501−1504.

(5) For selected reviews, see: Boudier, A.; Bromm, L. O.; Lotz, M.; Knochel, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 4414−4435. Nakamura, M.; Nakamura, E. *J. Synth. Org. Chem. Jpn.* **1998**, *56*, 632−644. Knochel, P. *Synlett* **1995**, 393−403.

(6) Maezaki, N.; Yoshigami, R.; Maeda, J.; Tanaka, T. *Org. Lett.* **2001**, *3*, 3627−3629.

10.1021/jo034108j CCC: $25.00
Published on Web 06/17/2003

SCHEME 2

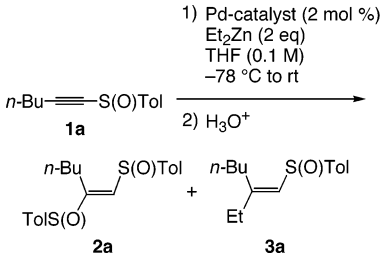


TABLE 1. Effect of Pd-Catalyst on Sulfinylzincation[a]

			yield (%)[c]	
entry	Pd-catalyst[b]	time (h)	**2a**[d]	**3a**
1	$PdCl_2$(dppf)	1	44	19
2	$PdCl_2$(dppe)	1	73	7
3	$PdCl_2(MeCN)_2$	1	86	trace
4	$PdCl_2(PPh_3)_2$	1	82	4
5	$Pd(PPh_3)_4$	1	88	trace
6	$Pd_2(dba)_3$·$CHCl_3$	1	95	trace
7	none	4	56	29

[a] All reactions were carried out with Et_2Zn (2 equiv) in THF (0.1 M) solution at −78 °C to room temperature. [b] 2 mol % of catalyst was used. [c] Isolated yield. [d] The yield is based on 50% of **1a** and the diastereomeric ratio is 1:1. dppf = 1,1′-bis(diphenylphosphino)ferrocene, dppe = 1,2-bis(diphenylphosphino)ethane.

at the sulfur atom rather than at the oxygen to give vinylic sulfoxides with high *syn*-selectivity under mild conditions. The resulting β-sulfinyl α,β-unsaturated esters are potentially useful building blocks with several reactive sites.[7]

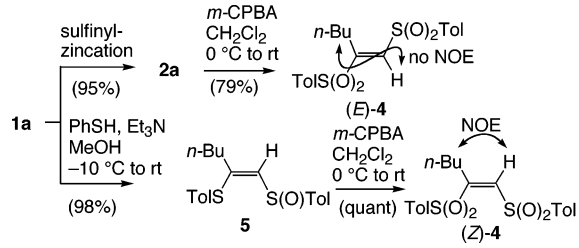
Herein, we will describe full details of the sulfinylzincation. We found that a heteroatom at the δ-position of alkynoates exhibits a neighboring effect and two Michael acceptors in a molecule were differentiated utilizing this effect. Influence of the reagent structure on the reactivity, stereodivergent synthesis of two geometric vinylic sulfoxides, and reaction of the resulting vinylzinc intermediate with electrophiles were also investigated.

Results and Discussion

Synthesis of Bis-sulfinyl Alkenes by Pd-Catalyzed Sulfinylzincation. During the course of our research regarding the reaction of 1-alkynyl sulfoxides and an organozinc reagent, we unexpectedly found that 1-hexynyl *p*-tolyl sulfoxide **1a** underwent an unusual sulfinylation on treatment with Et_2Zn in the presence of catalytic $PdCl_2$(dppf) (Scheme 2, entry 1 in Table 1). Bis-sulfinyl alkene **2a** was obtained in 44% yield as a 1:1 diastereomeric mixture based on sulfur stereogenic centers accompanied by a (*Z*)-isomer of ethylation product **3a** (19%). Both reactions proceeded in a highly *syn*-selective fashion, giving **2a** and **3a** exclusively.

We were interested in the unexpected product **2a** and investigated the reaction conditions to optimize the yield.

SCHEME 3



As a result, we found that the yield of **2a** was significantly affected by a ligand of the Pd-catalyst (Table 1). The yield was improved with replacement of the ligand from dppf to dppe, MeCN, or PPh_3 (entries 1−4). Pd(0)-catalysts [$Pd(PPh_3)_4$ and $Pd_2(dba)_3$·$CHCl_3$] yielded the bis-sulfinyl alkene **2a** in excellent yields (entries 5 and 6). Especially, the use of $Pd_2(dba)_3$·$CHCl_3$ afforded the best results, and the yield improved up to 95%[8] (entry 6). In each case, only 2 mol % of catalyst was sufficient to complete the reaction. Although the reaction provided **2a** even without a catalyst, longer reaction time was required for completion of the reaction, and both yield and selectivity were reduced (entry 7). Later, the reaction was found to proceed via a different reaction mechanism.

The reaction took place even in less polar toluene (70%) or more polar dioxane (69%) with $Pd_2(dba)_3$·$CHCl_3$. The yield of **2a** was almost unchanged over a range of concentrations (0.1−0.01 M) (81−95%), but was lowered by decreasing the amount of $Pd_2(dba)_3$·$CHCl_3$ [1 mol % (69%), 0.5 mol % (62%)] or Et_2Zn [1 equiv (61%)]. Sulfinylzincation with **1a** provided a 1:1 mixture of two isomers, even though the optically pure **1a** was used.[9] Since oxidation of **2a** with *m*-CPBA afforded a single bis-sulfonyl alkene (*E*)-**4**, these two compounds were confirmed not to be geometric isomers, but to be diastereomeric isomers arising from two sulfur stereogenic centers. The geometry of the double bond in **2a** was determined by comparing NOE between the olefinic proton and the allylic proton in (*E*)-**4** with that of the (*Z*)-isomer prepared via conjugated addition of TolSH to **1a** and subsequent oxidation to the bis-sulfonyl alkene. It should be noted that two geometric isomers could be synthesized stereodivergently in excellent yields and with high stereoselectivity by using two protocols (Scheme 3).

Table 2 shows the sulfinylzincation of various 1-alkynyl sulfoxides **1b**−**f**.[10] Functional groups such as TBS, Ac, and I are compatible in this reaction (entries 1−3). The nucleophile-sensitive acetyl group was not affected under the reaction conditions and no iodine−zinc exchange reaction was observed.[11] However, the reaction of methyl propiolate **1e** (R = H) was sluggish and a 2:1 (*E*/*Z*)-

(7) For leading references for reaction of vinylic sulfoxides, see: Mase, N.; Watanabe, Y.; Toru, T.; Kakumoto, T.; Hagiwara, T. *J. Org. Chem.* **2000**, *65*, 7083−7090. Maezaki, N.; Izumi, M.; Yuyama, S.; Sawamoto, H.; Iwata, C.; Tanaka, T. *Tetrahedron* **2000**, *56*, 7927−7945. Abe, H.; Tsuchida, D.; Kashino, S.; Takeuchi, Y.; Harayama, T. *Chem. Pharm. Bull.* **1999**, *47*, 833−837. Midura, W. H.; Krysiak, J. A.; Mikolajczyk, M. *Tetrahedron* **1999**, *55*, 14791−14802. Priego, J.; Carretero, J. C. *Synlett* **1999**, 1603−1605. Buezo, N. D.; Alonso, I.; Carretero, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 7129−7130.

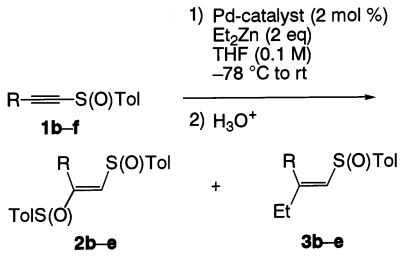
(8) Yields of the bis-sulfinyl alkenes were calculated based on the theoretical maximum 50% yield in this paper.

(9) The diastereomeric isomers were presumably produced by racemization of the introduced sulfoxide via sulfinyl−sulfenate tautomerization (see Scheme 1). However, it is possible to introduce optically pure sulfoxide by using an epimeric mixture of sulfoxide bearing a chiral auxiliary. We have already reported the preliminary results of the asymmetric sulfinylzincation in a recent report. Maezaki, N.; Yagi, S.; Ohsawa, S.; Ohishi, H.; Tanaka, T. *Tetrahedron*: *Asymmetry* **2002**, *13*, 1961−1964.

(10) Kosugi, H.; Kitaoka, M.; Tagami, K.; Takahashi, A.; Uda, H. *J. Org. Chem.* **1987**, *52*, 1078−1082.

(11) For palladium-catalyzed carbozincation with $PdCl_2$(dppf), see: Stadtmüller, H.; Vaupel, A.; Tucker, C. E.; Stüdemann, T.; Knochel, P. *Chem. Eur. J.* **1996**, *2*, 1204−1220.

TABLE 2. Pd-Catalyzed Sulfinylzincation of 1-Alkynyl *p*-Tolyl Sulfoxides 1b−f[a]



entry	substrate	R	time (h)	product (yield, %)[b]
1	**1b**	$TBSO(CH_2)_2$	1.5	**2b** (88); **3b** (0)
2	**1c**	$AcO(CH_2)_2$	1.5	**2c** (82); **3c** (0)
3	**1d**	$I(CH_2)_4$	1.5	**2d** (97); **3d** (0)
4	**1e**	H	0.5	**2e** (24);[c] **3e** (33)[d]
5	**1f**	*t*-Bu	12	complex mixture

[a] All reactions were carried out with $Pd_2(dba)_3$·$CHCl_3$ (2 mol %) and Et_2Zn (2 equiv) in THF solution at −78 °C to room temperature. [b] Isolated yield and the yields of **2** are based on 50% of **1**. The ratio of diastereomeric isomers is ca. 1:1 unless otherwise stated. [c] Single diastereomeric isomer. [d] The ratio of (*E*/*Z*)-isomers is 2:1.

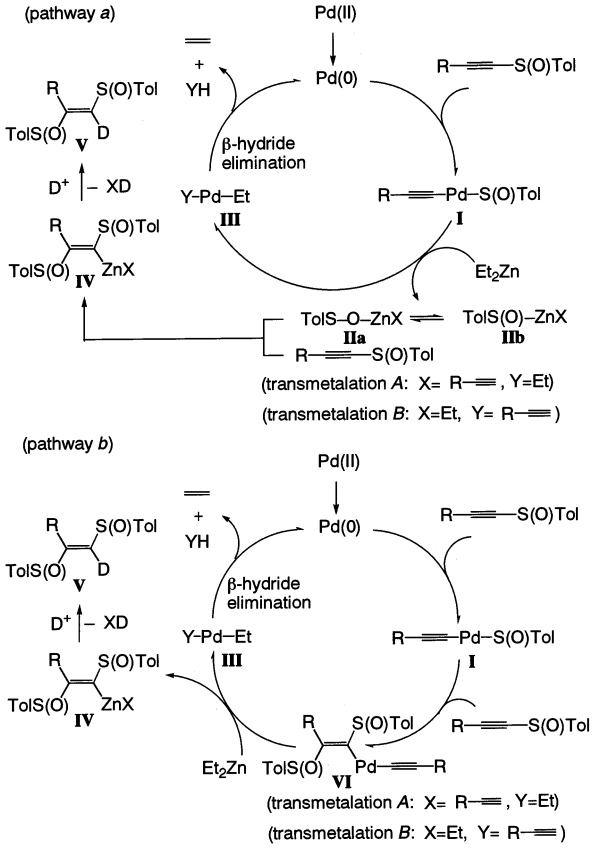
mixture of **3e**[12] was produced along with **2e** (entry 4). Compound **1f** bearing a bulky *tert*-butyl group afforded a complex mixture (entry 5).

Plausible Reaction Mechanism of Pd-Catalyzed Sulfinylzincation. We suggest the two reaction mechanisms of Pd-catalyzed sulfinylzincation as depicted in Scheme 4. The reaction would be initiated by oxidative addition of 1-alkynyl sulfoxides to a Pd(0) complex.[13] Then, sulfinylpalladium species **I** would be transmetalated with Et_2Zn, giving the zinc sulfenate species **IIa** presumably as a equilibrium mixture with sulfinylzinc species **IIb**. Subsequent addition of the zinc sulfenate to the 1-alkynyl sulfoxide would afford bis-sulfinyl vinylzinc species **IV**. On the other hand, the ethylpalladium intermediate **III** undergoes *β*-hydride elimination and regenerates the Pd(0)-catalyst (pathway *a*). A direct sulfinylpalladation to the 1-alkynyl sulfoxides (**I**→**VI**) is another possible reaction mechanism (pathway *b*). The resulting alkenylpalladium species **VI** was transmetalated to give the bis-sulfinyl vinylzinc species **IV**.

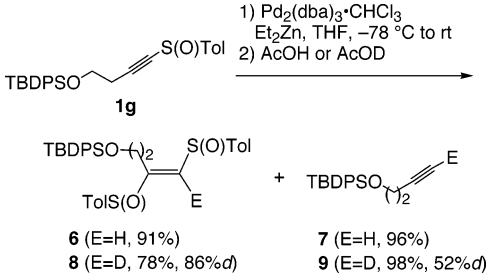
We cannot conclude which pathway is actual at the present time, but assume that pathway *a* would be more preferable than pathway *b* from the following: (1) Although insertion of alkyne into the C−Pd−X intermediate (X = halogen and triflate) regularly occurs at the C−Pd bond, no product arising from insertion of 1-alkynyl sulfoxide into the C−Pd bond of intermediate **I** was obtained. (2) Although Et_2Zn plays a role only to regenerate the Pd(0)-catalyst in pathway *b*, no bis-sulfinyl alkene was formed without Et_2Zn despite the use of a stoichiometric amount of $Pd_2(dba)_3$·$CHCl_3$ (0.5 equiv).

Next, we investigated the reaction of alkynyl sulfoxide **1g** bearing an alkyne moiety with low volatility to examine the reaction of the alkyne part in intermediate **I** (Scheme 5). Sulfinylzincation with **1g** and subsequent trapping of the resulting anion with AcOH provided two

SCHEME 4



SCHEME 5



compounds **6** and **7**[14] in 91% and 96% yield, respectively.[15] When the reaction was quenched with AcOD, the corresponding deuterated products **8** and **9** were produced in 78% and 98% yield, respectively.[15] In contrast to the 86% deuteration of the bis-sulfinyl alkene **8**, only 52% deuteration was observed in the alkyne **9**.

The results are rationalized as follows. As shown in Scheme 4, most of the *p*-tolylsulfinyl group of the oxidative adduct **I** in pathway *a* (or the alkenyl group of adduct **VI** in pathway *b*) would be transmetalated to zinc, giving the bis-sulfinyl alkene **V** (**8**, R = C≡C$(CH_2)_2$OTBDPS) after deuteration of **IV**. On the other hand, only half of the alkynyl group of **I** (or **VI**) would be converted by transmetalation *A* into the zinc salts **IV** (X = C≡C$(CH_2)_2$-OTBDPS), which led to the deuterated alkyne **9**. The other half of the alkynyl group of **I** (or **VI**) would be

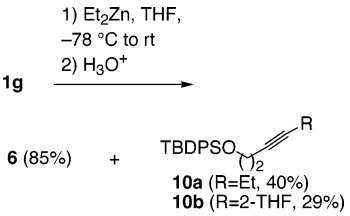
(12) Marsan, M.-P.; Warnock, W.; Muller, I.; Nakatani, Y.; Ourisson, G.; Milon, A. *J. Org. Chem.* **1996**, *61*, 4252−4257.

(13) The oxidative addition of Pd(0) to the carbon−sulfur bond of the thioalkynes was reported, see: Savarin, C.; Srogel, J.; Liebeskind, L. S. *Org. Lett.* **2001**, *3*, 91−93.

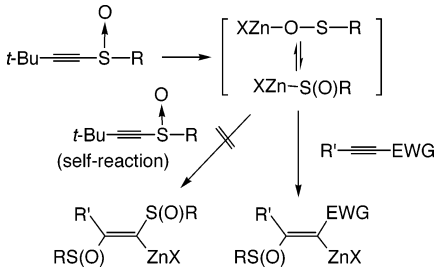
(14) Sinha, S. C.; Shinha, S. C.; Keinan, E. *J. Org. Chem.* **1999**, *64*, 7067−7073.

(15) These yields were calculated on the basis of a theoretical maximum 50% yield.

SCHEME 6



SCHEME 7



transformed into the ethylpalladium species **III** (Y = C≡C(CH$_2$)$_2$OTBDPS) by transmetalation *B*, giving the protonated alkyne **7** via subsequent *β*-hydride elimination. Accordingly, the ratio of deuteration was lower for the alkyne **9** than that for the bis-sulfinyl alkene **8**.

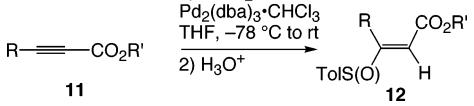
We also examined the sulfinylzincation without a Pd-catalyst as shown in entry 7 of Table 1 in detail. We assumed that there exists a different pathway to generate the zinc sulfenate species. When the reaction of **1g** was carried out in the absence of a Pd-catalyst, the bis-sulfinyl alkene **6** was produced via sulfinylzincation in 85% yield (Scheme 6). In sharp contrast to Pd-catalyzed sulfinylzincation, 3-hexyn-1-ol TBDPS ether (**10a**) and 4-(tetrahydrofuran-2-yl)-3-butyn-1-ol TBDPS ether (**10b**) were formed instead of **7** in 40% and 29% yield, respectively.[15] Obviously, the reaction mechanism was different from that of the Pd-catalyzed reaction. In this case, the zinc sulfenate species would be produced by the radical substitution reaction of the 1-alkynyl sulfoxides with the ethyl radical or the 2-tetrahydrofuranyl radical generated by radical transfer from the initially formed ethyl radical to the solvent.[16] A similar substitution reaction of acetylenic sulfones has been reported.[17]

Pd-Catalyzed Sulfinylzincation with 1-Alkynyl Sulfoxide Bearing a Bulky *β*-Substituent. If the self-reaction of the zinc sulfenate species with the 1-alkynyl sulfoxide could be suppressed, the species would be trapped with other activated alkynes as shown in Scheme 7. As mentioned above, we found that the reaction of 1-alkynyl sulfoxide **1f** was sluggish and did not undergo the self-reaction presumably due to steric bulkiness of the *tert*-butyl group (Table 2, entry 5). Therefore, we attempted the sulfinylzincation of alkynoates with the sulfinylating agent **1f**. Since chirality on the sulfur was lost during sulfinylzincation, the following experiments were conducted with racemic 1-alkynyl sulfoxides.

As we expected, the zinc sulfenate was trapped with alkynoates **11a** and **11b** (10 equiv) on treatment of **1f** (1 equiv) with Pd$_2$(dba)$_3$·CHCl$_3$ (2 mol %) and Et$_2$Zn (2 equiv) in THF (0.1 M) to furnish (*E*)-3-(*p*-tolylsulfinyl)-acrylate derivatives **12a** and **12b** in 87% and 62% yield, respectively (Table 3, entries 1 and 2). The reaction proceeded with high *syn*-selectivity, giving (*E*)-isomers as the sole geometric isomer.[18] Sulfinylzincation proceeded in alkynoates **11c**−**f** bearing functionalized substituents (entries 3−7). Substrate **11f** having a *β*-alkyl substituent exhibited reduced yield compared to the unsubstituted methyl propiolate **11a**. However, in the substrates **11c**−**e** bearing a *δ*-oxygen, the yields of adducts **12c**−**e** were dramatically improved. Comparing the yields of both **12c** (R = CH$_2$OBn) and **12f** (R = CH$_2$-CH$_2$Bn), it is obvious that the *δ*-oxygen plays some role to enhance the reaction. The effect was changed depending on the protecting group on the hydroxy group. Both the electron-withdrawing acetyl group and the sterically hindered TBS group slightly decreased the yields compared with the benzyl ether. The position of the oxygen atom also affected the yield (entries 3, 8, and 9). When the ether oxygen atom exists at the *δ*-position of the alkynoates, the reaction showed the best yield. The yield was reduced with increasing the distance of the oxygen from the reaction site. When the oxygen exists three carbons apart from the reaction site, the yield was the same as that of the methylene compound **12f** (entries 7 and 9). Enhancement of yields was observed in thioether **12i** and tertiary amine **12j** as well as in benzyl ether **12c**. The effect was reduced in the order of O > S > NMe (entries 3, 4, and 10−13). Obviously, the heteroatom at the *δ*-position exhibited a considerable neighboring effect, although the efficiency is different.

The observed activation of the sulfinylzincation by the neighboring heteroatom would be rationalized in that coordination of the heteroatom to the zinc cation would assist the sulfinylzincation by directing the sulfur atom to the reaction site (Figure 1). We demonstrated the

TABLE 3. Pd-Catalyzed Sulfinylzincation of 1-Alkynoates 11a−j with 1-Alkynyl Sulfoxide 1f



entry	substrate	R	R′	product (yield, %)[b]
1	**11a**	H	Me	**12a** (87)
2	**11b**	Me	Et	**12b** (62)
3	**11c**	CH$_2$OBn	Me	**12c** (100)
4	**11c**	CH$_2$OBn	Me	**12c** (92)[c]
5	**11d**	CH$_2$OAc	Me	**12d** (97)
6	**11e**	CH$_2$OTBS	Me	(*E*)-**12e** (93)
7	**11f**	CH$_2$CH$_2$Bn	Me	**12f** (48)
8	**11g**	(CH$_2$)$_2$OBn	Me	**12g** (57)
9	**11h**	(CH$_2$)$_3$OBn	Me	**12h** (48)
10	**11i**	CH$_2$SBn	Me	**12i** (98)
11	**11i**	CH$_2$SBn	Me	**12i** (83)[c]
12	**11j**	CH$_2$N(Me)Bn	Me	**12j** (98)
13	**11j**	CH$_2$N(Me)Bn	Me	**12j** (68)[c]

[a] All reactions were carried out with 1-alkynoate (10 equiv), Pd$_2$(dba)$_3$·CHCl$_3$ (2 mol %), and Et$_2$Zn (2 equiv) in THF solution at −78 °C to room temperature. [b] Isolated yield. [c] 2 equiv of 1-alkynoate was used.

(16) Yamamda, K.; Fujihara, H.; Yamamoto, Y.: Miwa, Y.: Taga, T.; Tomioka, K. *Org. Lett.* **2002**, *4*, 3509−3511. Gong, J.; Fuchs, P. L. *J. Am. Chem. Soc.* **1996**, *118*, 4486-4487.

(17) Back, T. G. *Tetrahedron* **2001**, *57*, 5263−5301 and references therein.

(18) All attempts to isolate zinc sulfenate species failed presumably due to its instability.

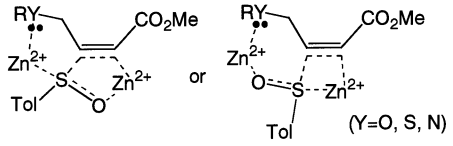


FIGURE 1.

SCHEME 8

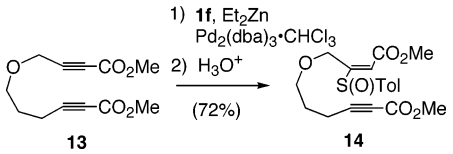
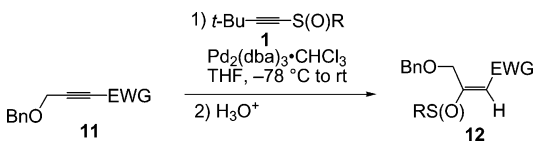


TABLE 4. Pd-Catalyzed Sulfinylzincation of Activated Alkynes with 1-Alkynyl Sulfoxides[a]



entry	activated alkyne	EWG	1-alkynyl sulfoxide	R	product (yield, %)[b]
1	**11c**	CO_2Me	**1f**	Tol (p-C_6H_4Me)	**12c** (92)
2	**11c**	CO_2Me	**1h**	p-C_6H_4OMe	**12k** (83)
3	**11c**	CO_2Me	**1i**	C_6H_5	**12l** (69)
4	**11c**	CO_2Me	**1i**	C_6H_5	**12l** (86)[c]
5	**11c**	CO_2Me	**1j**	p-C_6H_4Cl	**12m** (69)
6	**11c**	CO_2Me	**1j**	p-C_6H_4Cl	**12m** (82)[c]
7	**11c**	CO_2Me	**1k**	p-$C_6H_4NO_2$	**12n** (26)
8	**11c**	CO_2Me	**1*l***	Me	**12o** (73)
9	**11c**	CO_2Me	**1m**	$(CH_2)_3C{\equiv}CH$	**12p** (46)
10	**11k**	$CONMe_2$	**1f**	Tol	**12q** (59)
11	**11*l***	CN	**1f**	Tol	**12r** (27)

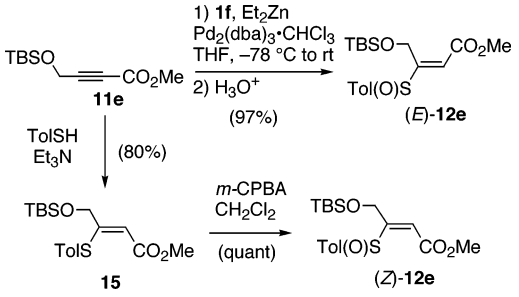
[a] All reactions were carried out with 1-alkynoate (2 equiv), $Pd_2(dba)_3$•$CHCl_3$ (2 mol %), and Et_2Zn (2 equiv) in THF solution at −78 °C to room temperature. [b] Isolated yield. [c] 5 equiv of 1-alkynoate was used.

selective sulfinylation of bis-alkynoate **13**. The sulfinylzincation absolutely proceeded to the alkynoate bearing a δ-oxygen to furnish **14** as the sole product (Scheme 8).

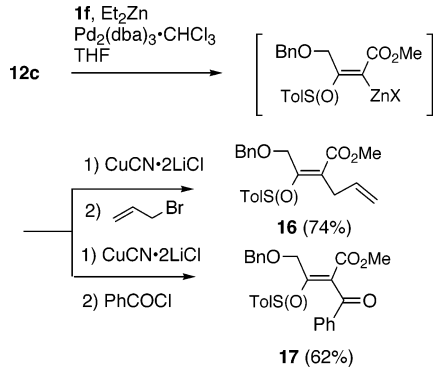
Next, we examined the influence of a para-substituent in the arylsulfinyl group on the yield of sulfinylzincation to **11c** using 1-alkynylsulfoxides **1f**,**h**−**k**. The results are shown in Table 4. Electron-withdrawing substituents led to a decrease in the yields presumably due to lowering nucleophilicity of the sulfenate anions. The order of yields is consistent with the order of the electron-donating nature of the para-substituents, i.e. NO_2 < Cl < H < Me. However, the most nucleophilic **1h** (R = OMe) rather showed lower yield than **1f** (R = Me) (entries 1−7). The reason has not been ascertained, but we assume that the decreased yield stems from the instability of the zinc sulfenate species, or was caused by effects on the oxidative addition and the transmetalation steps.

An alkylsulfinyl group could be transferred by this method. Sulfinylzincation of the alkynoates **11c** with **1*l*** and **1m** gave adducts **12o** and **12p**, respectively, in moderate yields (entries 8 and 9). Sulfinylzincation of other activated alkynes was also examined. Thus, alkynamide **11k** and alkynylnitrile **11*l*** were sulfinylated to give **12q** and **12r** in 59% and 27% yield, respectively (entries 10 and 11).

SCHEME 9



SCHEME 10



Since the Michael addition of thiolates to activated alkynes proceeds with *anti*-selectivity,[19] sulfinylzincation affords a complementary procedure to the *anti*-selective methodology. We demonstrated stereodivergent synthesis of (*E*)- and (*Z*)-β-sulfinyl enoates (*E*)- and (*Z*)-**12e** from the common alkynoate **11e**. Both geometric isomers were prepared in excellent yields and with high stereoselectivity (Scheme 9).

The vinylzinc species resulting from sulfinylzincation can be trapped with carbon electrophiles after transmetalation with CuCN•2LiCl. The reaction with allylbromide and benzoyl chloride afforded tetrasubstituted alkenes **16** and **17** in 74% and 62% yield, respectively (Scheme 10). It is noteworthy that no isomerization of the alkene stereochemistry occurred during these reactions and highly functionalized alkenes were formed stereoselectively.

Conclusion

In conclusion, we have developed novel Pd-catalyzed sulfinylzincation using 1-alkynyl sulfoxides as a sulfinyl source. The reaction is tolerant of a range of functional groups, and provides tri- and tetrasubstituted alkynes regio- and stereoselectively. In the substrates having a heteroatom at the δ-position, the yield was considerably increased presumably by coordination of a heteroatom in the substrate to the zinc sulfenate intermediate. This methodology also can be complementarily used in combination with conjugate addition of thiolate and subsequent oxidation, leading to an *anti*-adduct.

Experimental Section

All melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ solution at 500 or 300 MHz (^1H), and 125

(19) Perlmutter, P. In *Conjugate Addition Reactions in Organic Synthesis*; Baldwin, J. E., Magnus, P. D., Eds.; Pergamon Press: Oxford, UK, 1992; Vol. 9, pp 310−322 and references therein.

or 75 MHz (^{13}C). IR absorption spectra (FT: diffuse reflectance spectroscopy) were recorded with KBr powder, and only noteworthy absorptions (cm^{-1}) are listed. Column chromatography was carried out with Kanto Chemical silica gel 60 (63−210 μm). All air- or moisture-sensitive reactions were carried out in flame-dried glassware under an atmosphere of Ar. All solvents were dried and distilled according to standard procedures. All organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated with a rotary evaporator under reduced pressure.

General Procedure for the Synthesis of Bis-sulfinyl Alkenes by Sulfinylzincation (Table 1, entry 6). Et_2Zn (0.99 M in *n*-hexane) (0.36 mL, 0.354 mmol) was added slowly to a solution of 1-hexynyl *p*-tolyl sulfoxide (39.0 mg, 0.177 mmol) and $Pd_2(dba)_3$·$CHCl_3$ (3.7 mg, 0.00354 mmol) in THF (1.8 mL) with stirring at −78 °C. After 15 min, the dry ice bath was removed and the stirring was continued for 2 h. The reaction was quenched with saturated NH_4Cl and extracted with Et_2O. The organic layer was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane−AcOEt (3:1) to give **2a** (30.3 mg, 95%) as a colorless oil.

(*E*)-1,2-Bis(*p*-tolylsulfinyl)-1-hexene (2a): Colorless oil (1:1 diastereomeric mixture). ^{1}H NMR δ 0.87 (t, J = 7.3 Hz, 1.5H), 0.88 (t, J = 6.7 Hz, 1.5H), 1.35 (m, 2H), 1.44 (m, 1H), 1.59 (m, 1H), 2.03 (ddd, J = 14.6, 9.2, 5.5 Hz, 0.5H), 2.11 (ddd, J = 14.6, 9.2, 5.5 Hz, 0.5H), 2.43 (s, 3H), 2.43 (s, 1.5H), 2.44 (s, 1.5H), 2.69 (ddd, J = 14.6, 9.2, 6.7 Hz, 0.5H), 2.80 (ddd, J = 14.6, 9.2, 6.7 Hz, 0.5H), 7.07 (s, 0.5H), 7.12 (s, 0.5H), 7.27 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H). ^{13}C NMR δ 13.5, 21.4, 21.5, 22.4 (0.5C), 22.5 (0.5C), 26.5 (0.5C), 26.9 (0.5C), 31.7 (0.5C), 31.8 (0.5C), 124.2, 124.5, 125.9, 126.2, 130.2 (4C), 134.0 (0.5C), 134.8 (0.5C), 138.0 (0.5C), 138.5 (0.5C), 140.3 (0.5C), 140.4 (0.5C), 141.9 (0.5C), 142.1 (0.5C), 142.9 (0.5C), 143.1 (0.5C), 157.3 (0.5C), 158.0 (0.5C). IR 1051. MS (FAB) m/z 361 (MH$^+$). HRMS (FAB) calcd for $C_{20}H_{25}O_2S_2$ (MH$^+$) 361.1296, found 361.1291.

(*Z*,*R*s)-2-Ethylhex-1-enyl *p*-Tolyl Sulfoxide (3a): Yellow oil. $[\alpha]^{22}_D$ −181.0 (*c* 0.51, $CHCl_3$). ^{1}H NMR δ 0.96 (t, J = 7.2 Hz, 3H), 1.03 (t, J = 7.3 Hz, 3H), 1.25-1.48 (m, 2H), 1.49−1.63 (m, 2H), 2.19 (q, J = 7.3 Hz, 2H), 2.41 (s, 3H), 2.48−2.69 (m, 2H), 6.00 (s, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H). ^{13}C NMR δ 11.5, 13.8, 21.3, 22.7, 29.2, 31.0, 32.2, 124.1 (2C), 129.8 (2C), 130.7, 140.7, 141.8, 158.0. IR 1041. MS (FAB) m/z 251 (MH$^+$). HRMS (FAB) calcd for $C_{15}H_{23}OS$ (MH$^+$) 251.1470, found 251.1469.

(*E*)-1,2-Bis(*p*-tolylsulfonyl)-1-hexene [(*E*)-4]. *m*-CPBA (containing 30% water) (47.2 mg, 0.19 mmol) was added to a solution of **2a** (31.4 mg, 0.087 mmol) in CH_2Cl_2 (0.9 mL) with stirring at 0 °C, and the mixture was stirred at 0 °C. The stirring was continued at 0 °C for 15 min, and then at room temperature for 1 h. The mixture was quenched with saturated $NaHCO_3$, and extracted with $CHCl_3$. The organic layer was washed with brine prior to drying and solvent evaporation. The residue was purified by PTLC with $CHCl_3$ to give (*E*)-**4** (27.0 mg, 79%) as colorless columns. Mp 153.0−154.0 °C (AcOEt−hexane). ^{1}H NMR δ 0.83 (t, 3H, J = 7.3 Hz), 1.26−1.34 (m, 2H), 1.36−1.56 (m, 2H), 2.47 (s, 3H), 2.48 (s, 3H), 2.69 (t, 2H, J = 7.9 Hz), 7.33 (s, 1H), 7.37 (d, 2H, J = 7.9 Hz), 7.39 (d, 2H, J = 7.9 Hz), 7.71 (d, 2H, J = 7.9 Hz), 7.80 (d, 2H, J = 7.9 Hz). ^{13}C NMR δ 13.4, 21.7 (2C), 23.0, 26.6, 31.8, 127.9 (2C), 128.8 (2C), 130.2 (2C), 130.3 (2C), 134.2, 135.1, 136.8, 145.7, 145.8, 154.7. IR 1319, 1153. MS (FAB) m/z 393 (MH$^+$). HRMS (FAB) calcd for $C_{20}H_{25}O_4S_2$ (MH$^+$) 393.1194, found 393.1199.

(*Z*)-2-(*p*-Tolylthio)-1-hexenyl *p*-Tolyl Sulfoxide (5). A mixture of *p*-toluenethiol (55.4 mg, 0.446 mmol) and Et_3N (32 μL, 0.446 mmol) in MeOH (10 mL) was stirred at room temperature for 10 min. Then, a solution of **1a** (81.9 mg, 0.372 mmol) was added to the mixture at −10 °C. After 30 min, the temperature was raised to room temperature and the solution was stirred for 1 h. The mixture was extracted with AcOEt and washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane−AcOEt (3:1) to give **5** (125 mg, 98%) as a yellow oil. ^{1}H NMR δ 0.74 (t, 3H, J = 7.5 Hz), 1.04−1.19 (m, 2H), 1.31−1.43 (m, 2H), 2.12−2.17 (m, 2H), 2.37 (s, 3H), 2.42 (s, 3H), 6.30 (s, 1H), 7.17 (d, 2H, J = 8.0 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.58 (d, 2H, J = 8.0 Hz). ^{13}C NMR δ 13.6, 21.2, 21.4, 21.7, 30.1, 35.6, 124.1 (2C), 127.3, 129.9 (2C), 130.0 (2C), 133.6 (2C), 135.3, 139.0, 140.6, 141.8, 150.8. IR 1041. MS (FAB) m/z 345 (MH$^+$). HRMS (FAB) calcd for $C_{20}H_{25}OS_2$ (MH$^+$) 345.1347, found 345.1344.

(*Z*)-1,2-Bis(*p*-tolylsulfonyl)-1-hexene [(*Z*)-4]. By the same procedure as for (*E*)-**4** from **2a**, **5** (42.1 mg, 0.122 mmol) was converted into (*Z*)-**4** (73.5 mg, quant). Yellow oil. ^{1}H NMR δ 0.83 (t, J = 7.3 Hz, 3H), 1.26 (tq, J = 7.5, 7.3 Hz, 2H), 1.39 (tt, J = 7.5, 7.5 Hz, 2H), 2.39 (td, J = 7.5, 1.5 Hz, 2H), 2.46 (s, 6H), 6.72 (t, J = 1.5 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H). ^{13}C NMR δ 13.5, 21.66, 21.71, 21.9, 30.3, 33.2, 128.2 (2C), 129.0 (2C), 129.6 (2C), 129.9 (2C), 135.7, 138.3, 138.5, 144.8, 145.6, 153.9. IR 1159, 1081. MS (FAB) m/z 393 (MH$^+$). HRMS (FAB) calcd for $C_{20}H_{25}O_4S_2$ (MH$^+$) 393.1194, found 393.1188.

(*E*)-4-(*tert*-Butyldimethylsilyloxy)-1,2-bis(*p*-tolylsulfinyl)-1-butene (2b): Colorless oil (1:1 diastereomeric mixture). ^{1}H NMR δ 0.03−0.05 (m, 6H), 0.89 (s, 9H), 2.24 (dt, J = 14.5, 7.2 Hz, 0.5H), 2.31 (dt, J = 14.3, 7.2 Hz, 0.5H), 2.41 (s, 3H), 2.43 (s, 1.5H), 2.44 (s, 1.5H), 2.99 (dt, J = 14.3, 6.3 Hz, 0.5H), 3.08 (dt, J = 14.5, 6.3 Hz, 0.5H), 3.60−3.77 (m, 2H), 7.12 (s, 0.5H), 7.19 (s, 0.5H), 7.29 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 1H). ^{13}C NMR δ −5.5 (2C), 18.2, 21.3, 21.4, 25.8 (3C), 30.4 (0.5C), 30.7 (0.5C), 61.8 (0.5C), 62.3 (0.5C), 124.2, 124.5, 126.0, 126.3, 130.1 (2C), 130.2 (2C), 135.5 (0.5C), 135.9 (0.5C), 138.1 (0.5C), 138.5 (0.5C), 140.2 (0.5C), 140.4 (0.5C), 141.8 (0.5C), 141.9 (0.5C), 142.8 (0.5C), 143.0 (0.5C), 154.3 (0.5C), 155.1 (0.5C). IR 1051. MS (FAB) m/z 463 (MH$^+$). HRMS (FAB) calcd for $C_{24}H_{35}O_3S_2Si$ (MH$^+$) 463.1797, found 463.1815.

(*E*)-3,4-Bis(*p*-tolylsulfinyl)-3-butenyl acetate (2c): Colorless oil (1:1 diastereomeric mixture). ^{1}H NMR δ 2.06 (s, 1.5H), 2.07 (s, 1.5H), 2.39−2.49 (m, 7H), 3.16 (dt, J = 14.7, 6.7 Hz, 1H), 4.06−4.17 (m, 2H), 7.14 (s, 0.5H), 7.19 (s, 0.5H), 7.28−7.37 (m, 4H), 7.44−7.59 (m, 4H). ^{13}C NMR δ 20.78 (0.5C), 20.81 (0.5C), 21.4, 21.5, 25.9 (0.5C), 26.2 (0.5C), 62.1 (0.5C), 62.4 (0.5C), 124.2 (0.5C), 124.3, 124.5, 125.8, 126.1, 129.9 (0.5C), 130.31 (1.5C), 130.35, 133.4 (0.5C), 136.4, 136.8, 137.7 (0.5C), 138.0 (0.5C), 139.89 (0.5C), 139.94 (0.5C), 142.2 (0.5C), 142.3 (0.5C), 143.1 (0.5C), 143.3 (0.5C), 170.5 (0.5C), 170.6 (0.5C). IR 1741, 1047. MS (FAB) m/z 391 (MH$^+$). HRMS (FAB) calcd for $C_{20}H_{23}O_4S_2$ (MH$^+$) 391.1037, found 391.1035.

(*E*)-6-Iodo-1,2-bis(*p*-tolylsulfinyl)-1-hexene (2d): Colorless oil (1:1 diastereomeric mixture). ^{1}H NMR δ 1.43−1.57 (m, 2H), 1.78−1.83 (m, 2H), 2.09 (ddd, J = 14.7, 9.7, 5.5 Hz, 0.5H), 2.18 (ddd, J = 14.7, 9.7, 5.5 Hz, 0.5H), 2.42 (s, 3H), 2.44 (s, 1.5H), 2.50 (s, 1.5H), 2.71 (ddd, J = 14.7, 9.8, 6.1 Hz, 0.5H), 2.79 (ddd, J = 14.7, 9.8, 6.1 Hz, 0.5H), 3.04 (t, J = 6.7 Hz, 2H), 7.01 (s, 0.5H), 7.13 (s, 0.5H), 7.29 (d, J = 7.3 Hz, 1H), 7.31 (d, J = 7.3 Hz, 1H), 7.36 (d, J = 7.3 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H). ^{13}C NMR δ 5.2 (0.5C), 5.4 (0.5C), 21.5 (2C), 25.5 (0.5C), 25.9 (0.5C), 30.3 (0.5C), 30.5 (0.5C), 32.7, 124.3, 124.6, 125.9, 126.3, 130.3 (4C), 134.6 (0.5C), 135.2 (0.5C), 137.9 (0.5C), 138.3 (0.5C), 140.1, 142.1 (0.5C), 142.3 (0.5C), 143.1 (0.5C), 143.3 (0.5C), 156.4 (0.5C), 156.8 (0.5C). IR 1051. MS (FAB) m/z 487 (MH$^+$). HRMS (FAB) calcd for $C_{20}H_{24}IO_2S_2$ (MH$^+$) 487.0263, found 487.0287.

(*E*)-1,2-Bis(*p*-tolylsulfinyl)ethene (2e): Colorless needles. Mp 191.0−192.5 °C (hexane−AcOEt). $[\alpha]^{24}_D$ +807 (*c* 0.60, $CHCl_3$). ^{1}H NMR δ 2.43 (s, 6H), 7.21 (s, 2H), 7.31 (d, J = 8.3 Hz, 4H), 7.44 (d, J = 8.3 Hz, 4H). ^{13}C NMR δ 21.5 (2C), 125.1 (4C), 130.4 (4C), 139.0 (2C), 141.7 (2C), 142.7 (2C). IR 1051.

MS (FAB) *m/z* 305 (MH^+). HRMS (FAB) calcd for $C_{16}H_{17}O_2S_2$ (MH^+) 305.0670, found 305.0681.

(*E*)-4-(*tert*-Butyldiphenylsilyloxy)-1,2-bis(*p*-tolylsulfinyl)-1-butene (6): Yellow oil. ^{1}H NMR δ 1.05 (s, 9H), 2.19-2.25 (m, 0.5H), 2.31−2.42 (m, 6.5H), 3.02 (dt, J = 13.4, 7.3 Hz, 0.5H), 3.16 (dt, J = 13.4, 6.7 Hz, 0.5H), 3.63-3.87 (m, 2H), 7.10 (s, 0.5H), 7.16−7.66 (m, 18.5H). ^{13}C NMR δ 19.0, 21.4, 21.5, 26.8 (3C), 30.3 (0.5C), 30.6 (0.5C), 62.8 (0.5C), 63.1 (0.5C), 124.3, 124.6, 126.0, 126.4, 127.6, 127.8, 129.6, 129.8, 129.9, 130.17 (0.5C), 130.22 (0.5C), 130.24 (0.5C), 130.3 (0.5C), 133.00 (0.5C), 133.04 (0.5C), 133.1 (0.5C), 133.2 (0.5C), 135.5 (2C), 136.1, 138.1, 138.5, 140.1, 140.4, 141.9, 142.0, 142.8, 143.1, 153.7, 154.9. IR 1086. MS (FAB) *m/z* 587 (MH^+). HRMS (FAB) calcd for $C_{34}H_{39}O_3SiS_2$ (MH^+) 587.2110, found 587.2104.

(*E*)-4-(*tert*-Butyldiphenylsilyloxy)-1-deuterio-1,2-bis(*p*-tolylsulfinyl)-1-butene (8) and 4-Deuterio-3-butyn-1-ol *tert*-Butyldiphenylsilyl Ether (9). The reaction was carried out according to the general procedure for synthesis of the bis-sulfinyl alkenes, but quenching with AcOD instead of NH_4Cl. **8**: Yellow oil. ^{1}H NMR δ 1.05 (s, 9H), 2.19−2.25 (m, 0.5H), 2.31−2.42 (m, 6.5H), 3.02 (dt, J = 13.4, 7.3 Hz, 0.5H), 3.16 (dt, J = 13.4, 7.3 Hz, 0.5H), 3.63-3.87 (m, 2H), 7.10 (s, 0.07H), 7.16−7.66 (m, 18.07H). ^{13}C NMR δ 19.1, 21.4, 21.5, 26.8 (3C), 30.2 (0.5C), 30.6 (0.5C), 62.9 (0.5C), 63.1 (0.5C), 124.3, 124.6, 126.0, 126.4, 127.77, 127.81, 129.80, 129.84, 129.9, 130.17 (0.5C), 130.22 (0.5C), 130.24 (0.5C), 130.3 (0.5C), 133.00 (0.5C), 133.04 (0.5C), 133.1 (0.5C), 133.2 (0.5C), 135.5 (2C), 136.1, 138.1, 138.5, 140.1, 140.4, 141.9, 142.0, 142.8, 143.1, 153.68 (0.5C), 153.78 (0.5C), 154.87 (0.5C), 154.93 (0.5C). IR 1595, 1086. MS (FAB) *m/z* 610 (MNa^+). HRMS (FAB) calcd for $C_{34}H_{37}DO_3SiS_2Na$ (MNa^+) 610.1992, found 610.1990. **9**: Yellow oil. ^{1}H NMR δ 1.06 (s, 9H), 1.94 (t, J = 2.5 Hz, 0.47H), 2.45 (td, J = 7.0, 2.5 Hz, 1H), 3.78 (t, J = 7.0 Hz, 2H), 7.36−7.68 (m, 10H). ^{13}C NMR δ 19.2, 22.6, 26.8 (3C), 62.3, 69.3, 81.5, 127.7 (4C), 129.7 (2C), 133.6 (2C), 135.6 (4C). IR 2121. MS (FAB) *m/z* 316 (MLi^+). HRMS (FAB) calcd for $C_{20}H_{23}DOSiNa$ (MNa^+) 332.1557, found 332.1559.

3-Hexyn-1-ol *tert*-Butyldiphenylsilyl Ether (10a) and 4-(Tetrahydrofuran-2-yl)-3-butyn-1-ol *tert*-Butyldiphenylsilyl Ether (10b). The reaction was carried out according to the general procedure for the synthesis of the bis-sulfinyl alkenes, but without Pd-catalyst. **10a**: Yellow oil. ^{1}H NMR δ 1.05 (s, 9H), 1.09 (t, J = 7.5 Hz, 2H), 2.13 (qt, J = 7.5, 2.4 Hz, 2H), 2.42 (tt, J = 7.1, 2.4 Hz, 2H), 3.74 (t, J = 7.1 Hz, 2H), 7.34−7.71 (m, 10H). ^{13}C NMR δ 12.4, 14.2, 19.2, 22.9, 26.8 (3C), 62.9, 76.3, 82.8, 127.6 (4C), 129.6(2C), 133.8 (2C), 135.6 (4C). IR 1589. MS (FAB) *m/z* 359 (MNa^+). HRMS (FAB) calcd for $C_{22}H_{28}OSiNa$ (MNa^+) 359.1807, found 359.1803. **10b**: Colorless oil. ^{1}H NMR δ 1.05 (s, 9H), 1.81−2.17 (m, 4H), 2.48 (td, J = 7.3, 1.8 Hz, 2H), 3.76 (t, J = 7.3 Hz, 2H), 3.76 (m, 1H), 3.89−3.94 (m, 1H), 4.52-4.55 (m, 1H), 7.36−7.44 (m, 6H), 7.66−7.68 (m, 4H). ^{13}C NMR δ 19.2, 22.9, 25.4, 26.8 (3C), 33.4, 62.4, 67.7, 68.3, 81.1, 82.0, 127.7 (4C), 129.6 (2C), 133.6 (2C), 135.5 (4C). IR 2237. MS (FAB) *m/z* 379 (MH^+). HRMS (FAB) calcd for $C_{24}H_{31}O_2Si$ (MH^+) 379.2093, found 379.2095.

General Procedute for Sulfinylzincation of Alkynoates. Et_2Zn (0.99 M in *n*-hexane) (0.31 mL, 0.307 mmol) was added slowly to a solution of **1f** (33.8 mg, 0.153 mmol), **11c** (62.6 mg, 0.307 mmol), and $Pd_2(dba)_3{\cdot}CHCl_3$ (3.2 mg, 0.00307 mmol) in THF (0.15 mL) with stirring at −78 °C. After 15 min, the dry ice bath was removed and the stirring was continued for 4 h. The reaction was quenched with saturated NH_4Cl and extracted with AcOEt. The organic layer was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane−AcOEt (3:1) to give **12c** (48.6 mg, 92%) as a yellow oil.

Methyl (*E*)-3-(*p*-tolylsulfinyl)propenoate (12a): Yellow oil. ^{1}H NMR δ 2.38 (s, 3H), 3.74 (s, 3H), 6.70 (d, J = 14.6 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 14.6 Hz, 1H), 7.49 (d, J = 7.9 Hz, 2H). ^{13}C NMR δ 21.4, 52.2, 123.5, 125.0 (2C), 130.4 (2C), 138.3, 142.6, 151.5, 164.4. IR 1728, 1086. MS (FAB) *m/z* 225 (MH^+). HRMS (FAB) calcd for $C_{11}H_{13}O_3S$ 225.0585, found 225.0580.

Ethyl (*E*)-3-(*p*-tolylsulfinyl)-2-butenoate (12b): Yellow oil. ^{1}H NMR δ 1.32 (t, J = 7.0 Hz, 3H), 2.04 (d, J = 1.5 Hz, 3H), 2.41 (s, 3H), 4.42 (q, J = 7.0 Hz, 2H), 6.74 (q, J = 1.5 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H). ^{13}C NMR δ 12.5, 14.1, 21.4, 60.7, 118.7, 126.0 (2C), 130.2 (2C), 138.2, 142.7, 160.9, 164.7. IR 1716, 1059. MS (EI) *m/z* 252 (M^+). HRMS (EI) calcd for $C_{13}H_{16}O_3S$ (M^+) 252.0820, found 252.0825.

Methyl (*E*)-4-benzyloxy-3-(*p*-tolylsulfinyl)-2-butenoate (12c): Yellow oil. ^{1}H NMR δ 2.39 (s, 3H), 3.76 (s, 3H), 4.06 (dd, J = 15.0, 2.0 Hz, 1H), 4.33 (d, J = 11.5 Hz, 1H), 4.49 (d, J = 11.5 Hz, 1H), 5.10 (dd, J = 15.0, 2.0 Hz, 1H), 6.83 (t, J = 2.0 Hz, 1H), 7.23−7.36 (m, 7H), 7.52 (d, J = 8.5 Hz, 2H). ^{13}C NMR δ 21.4, 51.9, 65.2, 73.1, 118.1, 126.1 (2C), 127.8 (2C), 127.9, 128.4 (2C), 130.0 (2C), 136.9, 139.0, 142.4, 163.9, 164.9. IR 1720, 1049. MS (FAB) *m/z* 345 (MH^+). HRMS (FAB) calcd for $C_{19}H_{21}O_4S$ (MH^+) 345.1160, found 345.1162.

Methyl (*E*)-4-acetoxy-3-(*p*-tolylsulfinyl)-2-butenoate (12d): Yellow oil. ^{1}H NMR δ 1.97 (s, 3H), 2.41 (s, 3H), 3.81 (s, 3H), 4.63 (d, J = 14.5 Hz, 1H), 5.48 (d, J = 14.5 Hz, 1H), 6.91 (s, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H). ^{13}C NMR δ 20.4, 21.5, 52.2, 58.4, 120.7, 126.3 (2C), 130.3 (2C), 138.1, 143.2, 159.5, 164.4, 169.7. IR 1747, 1720, 1435, 1041. MS (FAB) *m/z* 297 (MH^+). HRMS (FAB) calcd for $C_{14}H_{17}O_5S$ (MH^+) 297.0797, found 297.0797.

Methyl (*E*)-4-(*tert*-butyldimethylsilyloxy)-3-(*p*-tolylsulfinyl)-2-butenoate [(*E*)-12e]: Yellow oil. ^{1}H NMR δ −0.03 (s, 3H), 0.02 (s, 3H), 0.86 (s, 9H), 2.38 (s, 3H), 3.75 (s, 3H), 4.21 (dd, J = 16.0, 2.5, Hz, 1H), 5.32 (dd, J = 16.0, 2.5 Hz, 1H), 6.69 (dd, J = 2.5, 2.5 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H). ^{13}C NMR δ −5.7, −5.6, 18.2, 21.4, 25.7 (3C), 51.8, 59.9, 116.2, 126.2 (2C), 130.0 (2C), 139.3, 142.2, 165.0, 166.8. IR 1718, 1097. MS (FAB) *m/z* 369 (MH^+). HRMS (FAB) calcd for $C_{18}H_{29}O_4SSi$ (MH^+) 369.1556, found 369.1559.

Methyl (*E*)-6-phenyl-3-(*p*-tolylsulfinyl)-2-hexenoate (12f): Yellow oil. ^{1}H NMR δ 1.43−1.67 (m, 1H), 1.69−1.80 (m, 1H), 2.14 (ddd, J = 13.8, 10.5, 4.8 Hz, 1H), 2.40 (s, 3H), 2.49−2.62 (m, 2H), 2.73 (ddd, J = 13.8, 10.5, 5.7 Hz, 1H), 3.75 (s, 3H), 6.74 (s, 1H), 7.04−7.42 (m, 9H). ^{13}C NMR δ 21.5, 26.8, 30.3, 35.6, 51.7, 117.7, 125.9, 126.2 (2C), 128.3 (2C), 128.4 (2C), 130.2 (2C), 138.2, 141.2, 142.8, 165.0, 165.7. IR 1720, 1090. MS (FAB) *m/z* 343 (MH^+). HRMS (FAB) calcd for $C_{20}H_{23}O_3S$ (MH^+) 343.1368, found 343.1374.

Methyl (*E*)-5-benzyloxy-3-(*p*-tolylsulfinyl)-2-pentenoate (12g): Yellow oil. ^{1}H NMR δ 2.31 (ddd, J = 14.0, 7.5, 7.5 Hz, 1H), 2.31 (s, 3H), 3.09 (ddd, J = 14.0, 7.0, 5.0 Hz, 1H), 3.32 (ddd, J = 9.0, 7.5, 5.0, 1H), 3.42 (ddd, J = 9.0, 7.5, 7.0 Hz, 1H), 3.67 (s, 3H), 4.35 (d, J = 14.0 Hz, 1H), 4.38 (d, J = 14.0 Hz, 1H), 6.75 (s, 1H), 7.18−7.28 (m, 7H), 7.45 (d, J = 8.0 Hz, 2H). ^{13}C NMR δ 21.5, 28.0, 51.8, 68.3, 72.8, 118.9, 126.5 (2C), 127.6 (2C), 128.3 (2C), 130.16 (2C), 130.18, 137.9, 138.1, 142.8, 162.8, 165.0. IR 1720, 1637, 1084. MS (FAB) *m/z* 359 (MH^+). HRMS (FAB) calcd for $C_{20}H_{23}O_4S$ (MH^+) 359.1317, found 359.1316.

Methyl (*E*)-6-benzyloxy-3-(*p*-tolylsulfinyl)-2-hexenoate (12h): Yellow oil. ^{1}H NMR δ 1.48−1.57 (m, 1H), 1.66 (m, 1H), 2.14 (ddd, J = 14.0, 10.0, 4.5 Hz, 1H), 2.32 (s, 3H), 2.77 (ddd, J = 14.0, 10.0, 5.5 Hz, 1H), 3.33−3.40 (m, 2H), 3.69 (s, 3H), 4.37 (d, J = 14.0 Hz, 1H), 4.39 (d, J = 14.0 Hz, 1H), 6.71 (s, 1H), 7.17−7.29 (m, 7H), 7.44 (d, J = 8.0 Hz, 2H). ^{13}C NMR δ 21.5, 24.2, 28.9, 51.7, 69.2, 72.6, 117.7, 126.4 (2C), 127.5, 127.6 (2C), 128.3 (2C), 130.1 (2C), 138.2, 138.3, 142.8, 165.0, 165.8. IR 1720, 1637, 1086. MS (FAB) *m/z* 373 (MH^+). HRMS (FAB) calcd for $C_{21}H_{25}O_4S$ (MH^+) 373.1474, found 373.1474.

Methyl (*E*)-4-benzylthio-3-(*p*-tolylsulfinyl)-2-butenoate (12i): Yellow oil. ^{1}H NMR δ 2.39 (s, 3H), 2.72 (d, J = 14.5 Hz, 1H), 3.72 (s, 2H), 3.74 (s, 3H), 4.38 (d, J = 14.5 Hz, 1H), 6.82 (s, 1H), 7.24−7.47 (m, 9H). ^{13}C NMR δ 21.5, 26.9, 36.6, 51.9, 118.8, 126.3 (2C), 127.3, 128.5 (2C), 129.0 (2C), 130.2 (2C), 137.1, 138.2, 142.9, 163.1, 164.9. IR 1720, 1105. MS (FAB) *m/z*

361 (MH^+). HRMS (FAB) calcd for $C_{19}H_{21}O_3S_2$ (MH^+) 361.0932, found 361.0935.

Methyl (*E*)-4-(*N*-benzyl-*N*-methylamino)-3-(*p*-tolylsulfinyl)-2-butenoate (12j): Yellow oil. ^{1}H NMR δ 2.03 (s, 3H), 2.38 (s, 3H), 2.88 (dd, J = 15.0, 2.5 Hz, 1H), 3.20 (d, J = 12.5 Hz, 1H), 3.72 (d, J = 12.5 Hz, 1H), 3.78 (s, 3H), 4.20 (d, J = 15.0 Hz, 1H), 6.89 (d, J = 2.5 Hz, 1H), 7.22−7.55 (m, 9H). ^{13}C NMR δ 21.5, 41.9, 51.9, 54.2, 61.5, 119.1, 126.2 (2C), 127.3, 128.3 (2C), 129.2 (2C), 129.9 (2C), 137.9, 139.5, 142.2, 165.3, 165.6. IR 1720, 1086. MS (FAB) *m*/*z* 358 (MH^+). HRMS (FAB) calcd for $C_{20}H_{24}NO_3S$ (MH^+) 358.1477, found 358.1480.

Methyl (*E*)-4-(5-Methoxycarbonyl-4-pentyloxy)-3-(*p*-tolylsulfinyl)-2-butenoate (14): Yellow oil. ^{1}H NMR δ 1.79 (tt, J = 6.7, 6.1 Hz, 2H), 2.35−2.39 (m, 2H), 2.40 (s, 3H), 3.36 (dt, J = 9.2, 6.1 Hz, 1H), 3.49 (dt, J = 9.2, 6.1 Hz, 1H), 3.77 (s, 3H), 3.78 (s, 3H), 4.02 (dd, J = 14.6, 1.8 Hz, 1H), 5.01 (dd, J = 14.6, 1.8 Hz, 1H), 6.81 (t, J = 1.8 Hz, 1H), 7.30 (d, J = 7.9 Hz, 2H), 7.55 (d, J = 7.9 Hz, 2H). ^{13}C NMR δ 15.4, 21.5, 27.4, 52.0, 52.6, 66.1, 69.1, 73.3, 88.5, 118.3, 126.1 (2C), 130.1 (2C), 139.0, 142.6, 154.1, 163.6, 164.9. IR 2237, 1716, 1643, 1084. MS (FAB) *m*/*z* 379 (MH^+). HRMS (FAB) calcd for $C_{19}H_{23}O_6S$ (MH^+) 379.1215, found 379.1228

Methyl (*E*)-4-benzyloxy-3-[(*p*-methoxyphenyl)sulfinyl]-2-butenoate (12k): Yellow oil. ^{1}H NMR δ 3.76 (s, 3H), 3.83 (s, 3H), 4.05 (dd, J = 15.3, 1.8 Hz, 1H), 4.32 (d, J = 11.6 Hz, 1H), 4.49 (d, J = 11.6 Hz, 1H), 5.09 (dd, J = 15.3, 1.2 Hz, 1H), 6.83 (dd, J = 1.8, 1.2 Hz, 1H), 6.91−6.94 (m, 2H), 7.22−7.24 (m, 2H), 7.29−7.36 (m, 3H), 7.53−7.56 (m, 2H). ^{13}C NMR δ 52.0, 55.5, 65.7, 73.1, 114.8 (2C), 118.1, 127.9 (2C), 128.0, 128.2 (2C), 128.4 (2C), 133.1, 136.9, 162.4, 163.9, 164.9. IR 1716, 1087. MS (EI) *m*/*z* 361 (MH^+). HRMS (EI) calcd for $C_{19}H_{21}O_5S$ (MH^+) 361.1110, found 361.1098.

Methyl (*E*)-4-benzyloxy-3-(phenylsulfinyl)-2-butenoate (12*l*): Yellow oil. ^{1}H NMR δ 3.76 (s, 3H), 4.07 (dd, J = 15.3, 1.8 Hz, 1H), 4.34 (d, J = 11.6 Hz, 1H), 4.50 (d, J = 11.6 Hz, 1H), 5.12 (dd, J = 15.3, 1.2 Hz, 1H), 6.84 (dd, J = 1.8, 1.2 Hz, 1H), 7.23−7.65 (m, 10H). ^{13}C NMR δ 52.0, 65.7, 73.1, 118.1, 126.0 (2C), 127.9 (2C), 128.0, 128.4 (2C), 129.3 (2C), 131.7, 136.9, 142.3, 163.9, 164.8. IR 1720, 1086. MS (FAB) *m*/*z* 331 (MH^+). HRMS (FAB) calcd for $C_{18}H_{19}O_4S$ (MH^+) 331.1011, found 331.1004.

Methyl (*E*)-4-benzyloxy-3-[(*p*-chlorophenyl)sulfinyl]-2-butenoate (12m): Yellow oil. ^{1}H NMR δ 3.76 (s, 3H), 4.14 (dd, J = 15.3, 1.8 Hz, 1H), 4.35 (d, J = 11.6 Hz, 1H), 4.52 (d, J = 11.6 Hz, 1H), 5.10 (dd, J = 15.3, 1.2 Hz, 1H), 6.80 (dd, J = 1.8, 1.2 Hz, 1H), 7.24−7.26 (m, 2H), 7.31−7.41 (m, 5H), 7.55−7.57 (m, 2H). ^{13}C NMR δ 52.1, 65.9, 73.3, 118.2, 127.4 (2C), 128.0 (2C), 128.2, 128.5 (2C), 129.5 (2C), 136.6, 137.9, 140.9, 163.7, 164.7. IR 1720, 1088. MS (FAB) *m*/*z* 365 (MH^+). HRMS (FAB) calcd for $C_{18}H_{18}ClO_4S$ (MH^+) 365.0615, found 365.0606.

Methyl (*E*)-4-benzyloxy-3-[(*p*-nitrophenyl)sulfinyl]-2-butenoate (12n): Yellow crystals. Mp 89.5−90.5 °C. ^{1}H NMR δ 3.77 (s, 3H), 4.26 (dd, J = 15.6, 2.4 Hz, 1H), 4.40 (d, J = 11.6 Hz, 1H), 4.57 (d, J = 11.6 Hz, 1H), 5.12 (dd, J = 15.6, 1.8 Hz, 1H), 6.81 (dd, J = 2.4, 1.8 Hz, 1H), 7.26−7.28 (m, 2H), 7.34−7.40 (m, 2H), 7.80−7.83 (m, 3H), 8.21−8.24 (m, 2H). ^{13}C NMR δ 52.2, 66.0, 73.5, 118.6, 124.2 (2C), 126.8 (2C), 128.1 (2C), 128.4, 128.6 (2C), 136.3, 149.5, 149.9, 163.2, 164.4. IR 1720, 1525, 1091. MS (FAB) *m*/*z* 376 (MH^+). HRMS (FAB) calcd for $C_{18}H_{18}NO_6S$ (MH^+) 376.0855, found 376.0851.

Methyl (*E*)-4-benzyloxy-3-methylsulfinyl-2-butenoate (12o): Colorless oil. ^{1}H NMR δ 2.78 (s, 3H), 3.76 (s, 3H), 4.52 (d, J = 11.8 Hz, 1H), 4.60 (d, J = 11.8 Hz, 1H), 4.85 (dd, J = 15.8, 2.0 Hz, 1H), 4.98 (dd, J = 15.8, 2.0 Hz, 1H), 6.61 (t, J = 2.0 Hz, 1H), 7.26−7.40 (m, 5H). ^{13}C NMR δ 41.1, 52.0, 66.8, 73.8, 118.5, 127.9 (2C), 128.2, 128.6 (2C), 136.7, 164.5, 164.8. IR 1720, 1078. MS (FAB) *m*/*z* 269 (MH^+). HRMS (FAB) calcd for $C_{13}H_{17}O_4S$ (MH^+) 269.0848, found 269.0836.

Methyl (*E*)-4-(benzyloxy)-3-(4-pentynylsulfinyl)-2-butenoate (12p): Yellow oil. ^{1}H NMR δ 1.81−1.91 (m, 1H), 1.93 (t. J = 3.1 Hz, 1H), 2.05 (dddt, J = 13.4, 9.7, 6.4, 6.4 Hz, 1H), 2.32 (ddd, J = 9.7, 6.4, 3.1 Hz, 2H), 2.84 (ddd, J = 13.4, 9.7, 5.5 Hz, 1H), 3.29 (ddd, J = 13.4, 9.7, 6.4 Hz, 1H), 3.76 (s, 3H), 4.53 (d, J = 11.6 Hz, 1H), 4.60 (d, J = 11.6 Hz, 1H), 4.81 (dd, J = 15.9, 2.4 Hz, 1H), 4.98 (dd, J = 15.9, 1.8 Hz, 1H), 6.55 (dd, J = 2.4, 1.8 Hz, 1H), 7.30−7.38 (m, 5H). ^{13}C NMR δ 17.5, 21.0, 51.7, 51.9, 66.9, 69.7, 73.7, 82.5, 119.3, 127.9 (2C), 128.2, 128.6 (2C), 136.8, 162.7, 164.7. IR: 2118, 1716, 1092. MS (FAB) *m*/*z* 321 (MH^+). HRMS (FAB) calcd for $C_{17}H_{21}O_4S$ (MH^+) 321.1160, found 321.1154.

***N*,*N*-Dimethyl (*E*)-4-benzyloxy-3-(*p*-tolylsulfinyl)-2-butenamide (12q):** Pale yellow oil. ^{1}H NMR δ 2.39 (s, 3H), 2.98 (s, 3H), 3.12 (s, 3H), 3.98 (dd, J = 14.3, 1.8 Hz, 1H), 4.31 (d, J = 11.6 Hz, 1H), 4.46 (d, J = 11.6 Hz, 1H), 4.86 (dd, J = 14.3, 1.2 Hz, 1H), 7.15 (dd, J = 1.8, 1.2 Hz, 1H), 7.22−7.35 (m, 7H), 7.51 (d, J = 8.5 Hz, 2H). ^{13}C NMR δ 21.5, 35.1, 37.9, 65.9, 73.0, 120.7, 126.1 (2C), 127.8 (3C), 128.4 (2C), 130.0 (2C), 137.1, 138.9, 142.3, 156.5, 164.9. IR 1651, 1086. MS (FAB) *m*/*z* 358 (MH^+). HRMS (FAB) calcd for $C_{20}H_{24}NO_3S$ (MH^+) 358.1477, found 358.1474.

(*E*)-4-Benzyloxy-3-(*p*-tolylsulfinyl)-2-butenonitrile (12r): Yellow oil. ^{1}H NMR δ 2.43 (s, 3H), 3.86 (d, J = 14.0 Hz, 1H), 4.30 (d, J = 11.6 Hz, 1H), 4.43-4.46 (m, 2H), 7.15 (s, 1H), 7.17−7.42 (m, 9H). ^{13}C NMR δ 21.5, 65.9, 73.3, 100.0, 114.1, 125.9 (2C), 128.1 (2C), 128.3, 128.6 (2C), 130.4 (2C), 136.2, 137.4, 143.4, 169.1. IR 2224, 1099. MS (FAB) *m*/*z* 312 (MH^+). HRMS (FAB) calcd for $C_{18}H_{18}NO_2S$ (MH^+) 312.1058, found 312.1060.

Methyl (*Z*)-4-(*tert*-Butyldimethylsilyloxy)-3-(*p*-tolylthio)-2-butenoate (15). Following the same procedure for **5** from **1a**, **11e** (113 mg, 0.497 mmol) was converted into **15** (140 mg, 80%). Yellow oil. ^{1}H NMR δ −0.07 (s, 6H), 0.82 (s, 9H), 2.37 (s, 3H), 3.76 (s, 3H), 3.90 (s, 2H), 6.21 (s, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H). ^{13}C NMR δ −5.6 (2C), 18.2, 21.2, 25.7 (3C), 51.2, 64.8, 109.2, 125.1, 129.8 (2C), 135.8 (2C), 139.9, 158.9, 167.0. IR 1708. MS (FAB) *m*/*z* 353 (MH^+). HRMS (FAB) calcd for $C_{18}H_{29}O_3SSi$ (MH^+) 353.1606, found 353.1610.

Methyl (*Z*)-4-(*tert*-butyldimethylsilyloxy)-3-(*p*-tolylsulfinyl)-2-butenoate [(*Z*)-12e]: Colorless oil. ^{1}H NMR δ −0.03 (s, 3H), 0.01 (s, 3H), 0.85 (s, 9H), 2.39 (s, 3H), 3.82 (s, 3H), 4.35 (dd, J = 18.0, 2.2, Hz, 1H), 4.79 (dd, J = 18.0, 2.2 Hz, 1H), 6.46 (t, J = 2.2, Hz, 1H), 7.28 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H). ^{13}C NMR δ −5.6, −5.5, 18.2, 21.3, 25.7 (3C), 52.2, 57.7, 119.7, 124.5 (2C), 129.9 (2C), 140.3, 141.3, 164.6, 165.2. IR 1716, 1047. MS (FAB) *m*/*z* 369 (MH^+). HRMS (FAB) calcd for $C_{18}H_{29}O_4SSi$ (MH^+) 369.1556, found 369.1544.

Methyl (*E*)-2-Allyl-4-benzyloxy-3-(*p*-tolylsulfinyl)-2-butenoate (16). Et_2Zn (1.01 M in *n*-hexane) (0.44 mL, 0.449 mmol) was added slowly to a stirred solution of **11c** (91.7 mg, 0.449 mmol), **1f** (49.4 mg, 0.224 mmol), and $Pd_2(dba)_3{\cdot}CHCl_3$ (4.64 mg, 0.00449 mmol) in THF (0.22 mL) at −78 °C. After 15 min, the stirring was continued at room temperature for 5 h. Then, a solution of CuCN·2LiCl [prepared by drying a mixtute of CuCN (20.1 mg, 0.224 mmol) and LiCl (19.0 mg, 0.449 mmol) at 140 °C for 2 h in situ] in THF (0.22 mL) was added to the mixture. After the addition of allyl bromide (58 μL, 0.673 mmol), the reaction mixture was stirred at 0 °C for 1 h. The reaction was quenched with saturated NH_4Cl and extracted with Et_2O. The organic layer was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane−AcOEt (5:1) to give **16** (64.1 mg, 74%) as a yellow oil. ^{1}H NMR δ 2.40 (s, 3H), 3.63 (dd, J = 15.8, 6.7 Hz, 1H), 3.64 (s, 3H), 3.72 (dd, J = 15.8, 6.7 Hz, 1H), 4.17 (d, J = 11.6 Hz, 1H), 4.18 (d, J = 12.8, 1H), 4.22 (d, J = 11.6 Hz, 1H), 4.28 (d, J = 12.8, 1H), 5.19 (dd, J = 10.4, 1.5 Hz, 1H), 5.21 (dd, J = 17.1, 1.5 Hz, 1H), 5.85 (dddd, J = 17.1, 10.4, 6.7, 6.7 Hz, 1H), 7.12 (d, J = 8.5 Hz, 2H), 7.21−7.30 (m, 5H), 7.46 (d, J = 8.5 Hz, 2H). ^{13}C NMR δ 21.3, 34.8, 52.2, 61.1, 72.2, 118.4, 124.3 (2C), 127.4, 127.6 (2C), 128.1 (2C), 129.9 (2C), 132.7, 137.5, 138.2, 140.3, 141.2, 145.3, 167.5. IR 1732, 1051. MS (FAB) *m*/*z* 385 (MH^+). HRMS (FAB) calcd for $C_{22}H_{25}O_4S$ (MH^+) 385.1473, found 385.1459.

Methyl (*E*)-2-Benzoyl-4-benzyloxy-3-(*p*-tolylsulfinyl)-2-butenoate (17). Following the same procedure described for **16** but with the addition of benzoyl chloride (0.076 mL, 0.654 mmol), **11c** (89.1 mg, 0.436 mmol) and **1f** (48.0 mg, 0.218 mmol) were converted into **17** (61.1 mg, 62%). Yellow oil. ^{1}H NMR δ 2.40 (s, 3H), 3.63 (s, 3H), 4.28 (d, J = 11.6 Hz, 1H), 4.31 (d, J = 11.6 Hz, 1H), 4.35 (d, J = 13.4 Hz, 1H), 4.66 (d, J = 13.4 Hz, 1H), 7.14 (d, J = 6.7 Hz, 2H), 7.25−7.31 (m, 5H), 7.53 (t, J = 7.6 Hz, 2H), 7.62−7.67 (m, 3H), 8.02 (d, J = 7.3 Hz, 2H). ^{13}C NMR δ 21.4, 52.9, 61.4, 72.8, 125.4 (2C), 127.6 (2C), 127.7, 128.2 (2C), 128.9 (2C), 129.3 (2C), 130.0 (2C), 134.2, 135.9, 137.2, 137.4, 138.0, 141.8, 155.9, 163.4, 191.1. IR 1728, 1057. M/S (FAB) *m*/*z* 449 (MH^+). HRMS (FAB) calcd for $C_{26}H_{25}O_5S$ (MH^+) 449.1423, found 449.1439.

Supporting Information Available: The plots of yield vs equivalent of 1-alkynoate in sulfinylzication of 1-alkynoates; experimental procedure and characterization data for compounds **1b**−**d**, **1f**−**m**, **11f**, **11g**, **11i**−***l***, and **13**; ^{1}H NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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