# Regio- and Stereoselective Additions of Diphenyldithiophosphinic Acid to *N*-(1-Alkynyl)amides and 1-Alkynyl Sulfides

**Shigenari Kanemura, Azusa Kondoh, Hiroto Yasui, Hideki Yorimitsu,* and Koichiro Oshima***

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510

Received December 12, 2007; E-mail: yori@orgrxn.mbox.media.kyoto-u.ac.jp

Treatment of *N*-(1-alkynyl)amides and 1-alkynyl sulfides with diphenyldithiophosphinic acid affords (*E*)-ketene *N*,*S*-acetals and *S*,*S*-acetals, respectively. The addition reactions proceed in *syn* fashions, which consist of protonation of the electron-rich alkynes and the following nucleophilic addition of diphenyldithiophosphinate anion to the resulting cationic intermediates.

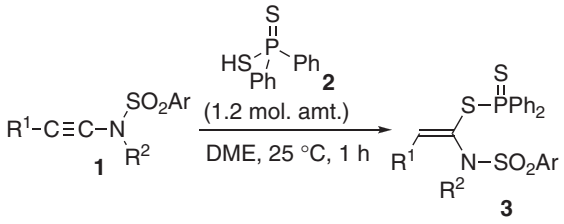
Addition of a hydrogen–sulfur bond across a carbon–carbon triple bond, hydrothiolation of alkyne, is useful for the synthesis of 1-alkenyl sulfide.[1] Hydrothiolation of alkyne under acidic conditions is interesting because of the characteristic Markovnikov regioselectivity. Here, we report hydrothiolation reactions of electron-rich alkynes, *N*-(1-alkynyl)amides[2,3] and 1-alkynyl sulfides,[4,5] with diphenyldithiophosphinic acid. The reactions under acidic conditions afford ketene *N*,*S*-acetals (=1-amino-1-thio-1-alkenes) and *S*,*S*-acetals (1,1-dithio-1-alkenes), which are useful building blocks for organic synthesis.[6]

## Results and Discussion

**Addition to *N*-(1-Alkynyl)amides.**[7] *N*-Phenylethynyl-*N*-methyl-*p*-toluenesulfonamide (**1a**) was treated with diphenyldithiophosphinic acid (**2**) in 1,2-dimethoxyethane (DME) at room temperature for 1 h to provide (*E*)-1-[methyl(*p*-tolylsulfonyl)amino]-2-phenylethenyl diphenyldithiophosphinate (**3a**) in 87% yield as the sole product (Table 1, Entry 1). The reaction proceeded in a *syn* fashion with perfect regio- and stereoselectivity.[8] A variety of ynamides underwent the hydrothiolation. The reaction of *N*-1-propynylamide **1b** yielded **3b** in good yield (Entry 2). The stereochemistry of the reaction was confirmed by analyzing nuclear Overhauser effect. Irradiation of the methyl group on the nitrogen of **3b** enhanced the intensity of the signal for the methyl group of the propenyl moiety (12%). The steric as well as electronic factors of the aryl groups attached to the carbon–carbon triple bonds were moderate (Entries 3–6). The reactions of trimethylsilyl-substituted ynamide **1g** and terminal alkyne **1h** also furnished the desired products **3g** and **3h** (Entries 7 and 8). Not only *p*-toluenesulfonamides but also *p*-nitrobenzenesulfonamide **1j** reacted with **2** smoothly to afford the corresponding product **3j** in 97% isolated yield (Entry 10). The choice of the solvent is not an important factor. For instance, the reaction of **1a** with **2** proceeded in DME, ethanol, dichloromethane, and hexane to afford **3a** in 98%, 97%, 91%, and 95% NMR yields, respectively.

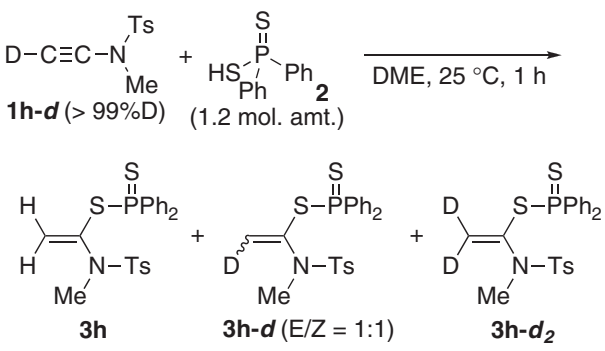
The reaction of deuterium-labeled ynamide **1h-*d*** yielded a mixture of adducts **3h**, **3h-*d***, and **3h-$d_2$** in 93% combined yield in a ratio of 18:75:7 (Scheme 1). Monodeuterated **3h-*d*** was

**Table 1.** Hydrothiolation Reactions of Ynamides **1** with Diphenyldithiophosphinic Acid (**2**)



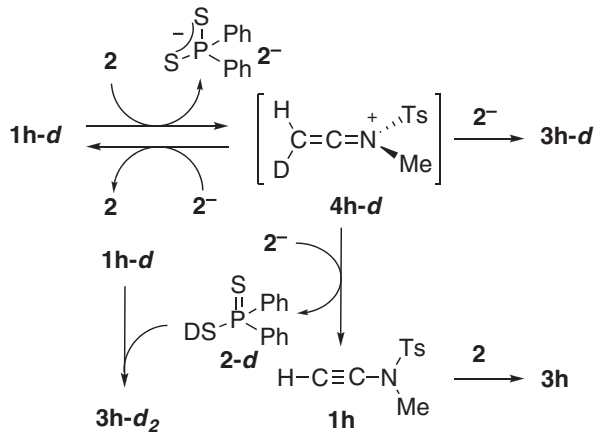

| Entry | 1 | $R^1$ | $R^2$ | Ar | 3 | Yield/%[a] |
|---|---|---|---|---|---|---|
| 1 | **1a** | Ph | Me | *p*-$MeC_6H_4$ | **3a** | 87 (98)[b] |
| 2 | **1b** | Me | Me | *p*-$MeC_6H_4$ | **3b** | 76 |
| 3 | **1c** | *p*-$MeC_6H_4$ | Me | *p*-$MeC_6H_4$ | **3c** | 91 |
| 4 | **1d** | *o*-$MeC_6H_4$ | Me | *p*-$MeC_6H_4$ | **3d** | 97 |
| 5 | **1e** | *p*-$ClC_6H_4$ | Me | *p*-$MeC_6H_4$ | **3e** | 88 |
| 6 | **1f** | *p*-$AcC_6H_4$ | Me | *p*-$MeC_6H_4$ | **3f** | 97 |
| 7 | **1g** | $Me_3Si$ | Me | *p*-$MeC_6H_4$ | **3g** | 63[c] |
| 8 | **1h** | H | Me | *p*-$MeC_6H_4$ | **3h** | 86 |
| 9 | **1i** | Ph | $CH_2$=$CHCH_2$ | *p*-$MeC_6H_4$ | **3i** | 95 |
| 10 | **1j** | Ph | Me | *p*-$NO_2C_6H_4$ | **3j** | 97 |

a) Isolated yields by silica gel column chromatography unless otherwise specified. b) NMR yield based on $^{31}P$ NMR analysis. c) Isolated yield after recrystallization.




**Scheme 1.** Reaction of deuterated ynamide.

Published on the web April 10, 2008; doi:10.1246/bcsj.81.506




**Scheme 2.** Plausible reaction mechanism for hydrothiolation.

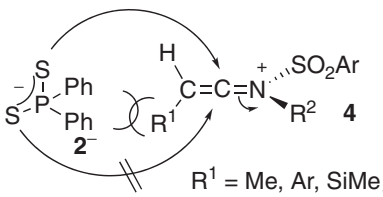
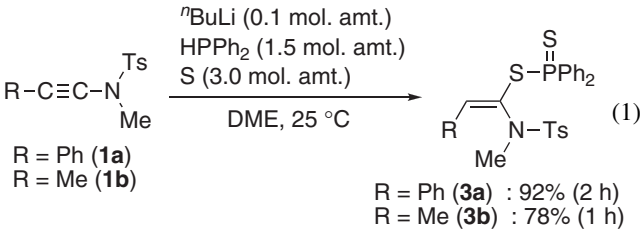



**Figure 1.** Stereoselective addition of $\mathbf{2}^-$ to ketene iminium intermediate.

obtained as a 1:1 mixture of the E and Z isomers, which suggests a stepwise mechanism for the hydrothiolation as outlined in Scheme 2. Protonation of **1h-*d*** with **2** would generate a ketene iminium intermediate **4h-*d*** and diphenyldithiophosphinate anion $\mathbf{2}^-$. The anion $\mathbf{2}^-$ would then attack the intermediate **4h-*d*** to afford (*E*)- and (*Z*)-**3h-*d***. Instead of the addition of $\mathbf{2}^-$ to **4h-*d***, abstraction of the deuterium in **4h-*d*** by $\mathbf{2}^-$ would generate **1h** and **2-*d***. The generation of **1h** and **2-*d*** resulted in the formations of unlabeled **3h** and **3h-$d_2$**, respectively.

The selective formation of E isomers from **1a**–**1g**, **1i**, and **1j** is rationalized as shown in Figure 1. Dithiophosphinate anion $\mathbf{2}^-$ would approach a ketene iminium intermediate **4** from the same side of the olefinic hydrogen to avoid steric repulsion between $R^1$ and $\mathbf{2}^-$.

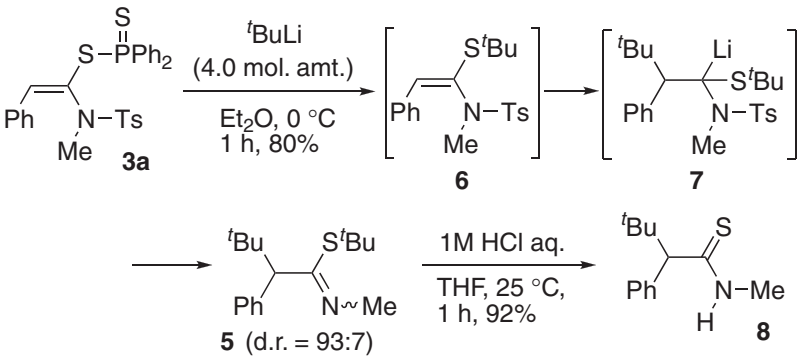
We found that the reaction of ynamide **1a** or **1b** with diphenylphosphine and sulfur in the presence of a catalytic amount of butyllithium in DME at 25 °C afforded **3a** or **3b**, respectively, in high yield (eq 1). Diphenyldithiophosphinic acid (**2**) would be generated in situ under the reaction conditions. It was reported that reaction of $Ph_2PH$ and 2 molar amount of sulfur in refluxing benzene afforded $Ph_2P(=S)SH$.[9] Catalytic amounts of butyllithium would accelerate the formation of $Ph_2P(=S)SH$ by generating $Ph_2PLi$ in situ. Indeed, treatment of diphenylphosphine with a catalytic amount of butyllithium in the presence of sulfur in DME at 25 °C for 1 h afforded diphenyldithiophosphinic acid (**2**) in 56% NMR yield ($^{31}$P NMR: $\delta$ 53.78 in $CDCl_3$), after acid–base extraction.



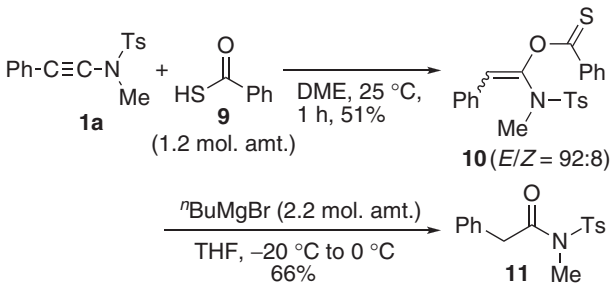

(1)

Transformation of the ketene *N*,*S*-acetals **3** was investigated to show the utility of **3**. The reaction of **3a** with 4.0 molar amount of *t*-butyllithium in ether at 0 °C provided thioimidate **5** in high yield (Scheme 3).[10] Attack of the sulfur atom attached to the olefinic carbon of **3a** by *t*-butyllithium could afford **6**.[11] An additional equivalent of *t*-butyllithium could then add to **6** to yield sulfur-stabilized anion **7**. Subsequent elimination of lithium *p*-toluenesulfinate would furnish thioimidate **5**. Hydrolysis of thioimidate **5** provided *t*-butyl-substituted thioamide **8** in 92% yield. Attempts to obtain **6** in high yield failed. For instance, treatment of **3c** with 1.2 molar amount of *t*-butyllithium in THF at −40 °C afforded **6** in only 34% NMR yield. Unfortunately, the use of other organolithium or -magnesium compounds instead of *t*-butyllithium gave complex mixtures.

When ynamide **1a** was treated with thiobenzoic acid (**9**) instead of **2** under conditions that were otherwise the same, ketene *N*,*O*-acetal **10** was obtained in 51% yield (Scheme 4). Reaction of **10** with butylmagnesium bromide in THF afforded amide **11**, which suggests that the adduct **10** was not *S*-alkenyl thioester but *O*-alkenyl thioester. On the other hand, treatment of ynamide **1a** with thiols such as benzenethiol and 1-dodecanethiol resulted in no hydrothiolation reactions, which clearly shows the importance of the acidity of the reagents.[12] Hydrothiolation with aromatic dithiocarboxylic acid could not be performed due to difficulty in preparing and purifying dithiocarboxylic acid.



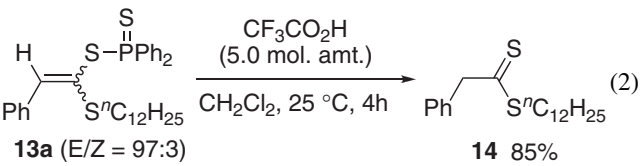

**Scheme 3.** Transformation of **3**.




**Scheme 4.** Addition of thiobenzoic acid to **1a**.

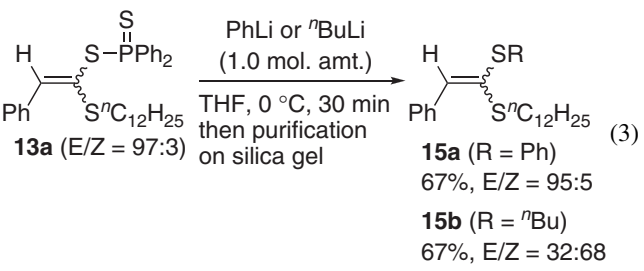
**Addition to 1-Alkynyl Sulfides.** The results of the hydrothiolation of 1-alkynyl sulfides **12** with **2** are summarized in Table 2. The scope of 1-alkynyl sulfides is wide enough to afford a variety of ketene *S*,*S*-acetals **13** in excellent yield. The syn addition predominated to yield E isomers as major products. The E configuration was assigned by X-ray crystallographic analysis of **13b**. However, the reactions of **12** showed poorer stereoselectivity than those of *N*-1-alkynylamide **1**. The $SR^2$ groups are sterically less hindered than the $NR^2(SO_2Ar)$ groups, which would partly allow dithiophosphinate anion $\mathbf{2}^-$ to attack the cationic thioketene intermediate from the same side of the $R^1$ group. The reaction of dodecyl ethynyl sulfide (**12j**) provided the corresponding product **13j** in 57% yield, along with dodecyl dithioacetate ($CH_3C(=S)S^nC_{12}H_{25}$, 29%), which would be formed by hydrolysis of **13j** (Entry 10). Solvent effect on the reaction is almost negligible, and the reaction proceeded as well in solvents such as DME and dichloromethane.

Treatment of **13a** with trifluoroacetic acid in dichloromethane afforded the corresponding dithioester **14** in high yield (eq 2).



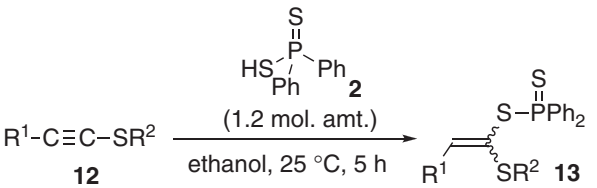

(2)

Organolithium reagents reacted with **13a** at the diphenylthiophosphinylated sulfur atom, leading to substitution reactions.[11] The reactions of **13a** with phenyllithium and butyllithium yielded **15a** and **15b**, respectively. Although the reactions proceeded with retention of configuration with **13a**, the products **15a** and **15b** readily underwent isomerization on silica gel upon chromatographic purification. To avoid the isomerization, **15a** was chromatographed on neutral silica gel with hexane/ethyl acetate/triethylamine = 93:2:5 as an eluent. The isomerization of **15b** was inevitable with various eluents tested.




(3)

**Table 2.** Hydrothiolation of 1-Alkynyl Sulfides **12** with Diphenyldithiophosphinic Acid (**2**)




| Entry | 12 | $R^1$ | $R^2$ | 13 | Yield/%[a] | E/Z |
|---|---|---|---|---|---|---|
| 1 | **12a** | Ph | $^nC_{12}H_{25}$ | **13a** | 96 | 97:3 |
| 2 | **12b** | Ph | *p*-$MeC_6H_4$ | **13b** | 85 | 100:0 |
| 3 | **12c** | $^nC_6H_{13}$ | $^nC_{12}H_{25}$ | **13c** | 92 | 83:17 |
| 4 | **12d** | $^nC_6H_{13}$ | *p*-$MeC_6H_4$ | **13d** | 86 | 97:3 |
| 5 | **12e** | *p*-$MeOC_6H_4$ | $^nC_{12}H_{25}$ | **13e** | 91 | 99:1 |
| 6 | **12f** | *o*-$MeOC_6H_4$ | $^nC_{12}H_{25}$ | **13f** | 83[b] | 98:2 |
| 7 | **12g** | *p*-$CF_3C_6H_4$ | $^nC_{12}H_{25}$ | **13g** | 86 | 95:5 |
| 8 | **12h** | $^cC_6H_{11}$ | $^nC_{12}H_{25}$ | **13h** | 92 | 94:6 |
| 9 | **12i** | $^tC_4H_9$ | $^nC_{12}H_{25}$ | **13i** | 97 | 97:3 |
| 10 | **12j** | H | $^nC_{12}H_{25}$ | **13j** | 57 | — |

a) Isolated yields by silica gel column chromatography unless otherwise noted. b) Isolated yield obtained by using gel permeation chromatography.

## Conclusion

We examined hydrothiolation reactions of ynamides and 1-alkynyl sulfides with diphenyldithiophosphinic acid. The reaction proved to proceed in *syn* fashions, yielding (*E*)-ketene *N*,*S*-acetals and *S*,*S*-acetals of synthetic use. The reactions begin with protonation of the electron-rich alkynes followed by nucleophilic addition of diphenyldithiophosphinate anion.

## Experimental

**General.** $^1$H NMR (500 MHz) and $^{13}$C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. $^{31}$P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in $CDCl_3$ with 85% $H_3PO_4$ solution as an external standard. NMR yields were determined by fine $^{31}$P NMR spectra with $(MeO)_3P{=}O$ as an internal standard. The first delay of $^{31}$P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography unless otherwise noted. Purification of **15** was performed on Silica Gel 60 N (spherical, neutral), which is available from Kanto Chemical Co., Inc., by using hexane/ethyl acetate/triethylamine = 93:2:5 as an eluent. Gel permeation chromatography was performed by using LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, toluene, 3.8 mL min$^{-1}$, UV and RI detectors). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

**Material.** Materials obtained from commercial suppliers were used without further purification. Ynamide **1g** was prepared by a procedure described in the literature.[13] Ynamide **1h** and **1h-*d*** were prepared by treatment of **1g** with an excess amount of potassium carbonate in methanol or methanol-$d_1$. Preparation of other yna-

mides **1a**–**1f**, **1i**, and **1j** were performed according to the literature.[14] Diphenyldithiophosphinic acid (**2**) was easily prepared from benzene and $P_4S_{10}$ in the presence of $AlCl_3$.[15] 1-Alkynyl sulfides **12** were prepared according to the procedure described below. Butyllithium was purchased from Nacalai Tesque. Phenyllithium and *t*-butyllithium were obtained from Kanto Chemical.

**General Procedure for the Hydrothiolation Reactions of Ynamides with Diphenyldithiophosphinic Acid (Table 1).** Ynamide **1h** (0.11 g, 0.50 mmol) was placed in a 30-mL reaction flask under argon. A solution of **2** (0.15 g, 0.60 mmol in 5 mL of DME) was added to the reaction flask at room temperature. The mixture was stirred for 1 h at room temperature. The resulting mixture was concentrated in vacuo. $^{31}$P NMR analysis with trimethyl phosphate as an internal standard revealed formation of the corresponding product **3h** in 91% yield. Purification of the crude product by silica gel column chromatography provided **3h** (0.20 g, 0.43 mmol) in 86% yield as white crystal.

**Hydrothiolation of Ynamides with Diphenylphosphine and Sulfur in the Presence of a Catalytic Amount of Butyllithium (eq 1).** The reaction of ynamide **1b** is representative. DME (3 mL), butyllithium (1.6 mol L$^{-1}$, 31 μL, 0.050 mmol), and freshly distilled diphenylphosphine (0.13 mL, 0.75 mmol) were sequentially added to a 50-mL reaction flask under argon at room temperature. After the reaction mixture was stirred for 10 min at room temperature, $S_8$ (0.05 g) and ynamides **1b** (0.11 g, 0.5 mmol, dissolved in 3 mL of DME) were successively added. The resulting mixture was stirred at room temperature for 1 h, and saturated $NH_4Cl$ aq (2 mL) was added. The organic compounds were extracted with ethyl acetate twice. The combined organic part was washed with brine and dried over anhydrous sodium sulfate. After evaporation, the resulting residue was purified by silica gel column chromatography to afford **3b** (185 mg, 0.39 mmol) in 78% yield.

**Reaction of 3a with *t*-Butyllithium (Scheme 3).** Ketene *N*,*S*-acetal **3a** (0.16 g, 0.30 mmol) was placed in a 30-mL reaction flask under argon. Diethyl ether (5 mL) and *t*-butyllithium (1.58 mol L$^{-1}$, 0.76 mL, 1.2 mmol) were sequentially added at 0 °C. After being stirred for 1 h at 0 °C, water (5 mL) was added. The organic compounds were extracted with ethyl acetate twice. The combined organic part was washed with brine and dried over anhydrous sodium sulfate. After evaporation, the resulting residue was purified by silica gel column chromatography to afford thioimidate **5** (0.067 g, 0.24 mmol) in 80% yield.

**Hydrolysis of Thioimidate (Scheme 3).** Thioimidate **5** (0.065 g, 0.23 mmol) was placed in a 30-mL reaction flask under argon. THF (3 mL) and hydrochloric acid (1.0 mol L$^{-1}$, 3 mL) were sequentially added at ambient temperature. After the mixture was stirred for 1 h at ambient temperature, water (5 mL) was added. The organic compounds were extracted with ethyl acetate twice. The combined organic part was washed with brine and dried over anhydrous sodium sulfate. After evaporation, the resulting residue was purified by silica gel column chromatography to afford thioamide **8** (0.048 g, 0.22 mmol) in 92% yield.

**Synthesis of 1-Alkynyl Sulfides.** The synthesis of dodecyl phenylethynyl sulfide (**12a**) is representative. THF (15 mL) was placed in a 50-mL reaction flask under argon. At 0 °C, phenylacetylene (0.99 mL, 9.0 mmol) and butyllithium (1.6 mol L$^{-1}$ hexane solution, 5.2 mL, 8.5 mmol) were sequentially added. After the mixture was stirred for 30 min at 0 °C, didodecyl disulfide (3.2 g, 8.0 mmol) was added. The mixture was stirred for 1 h at room temperature. 2-Bromoethanol (0.71 mL, 10 mmol) was then added,[16] and the resulting mixture was stirred for 30 min. The mixture was poured into water (20 mL), and the product was extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Purification of the residual oil on silica gel afforded **12a** (1.8 g, 6.1 mmol, 76%) as a white solid.

**Hydrothiolation of 1-Alkynyl Sulfides 12 (Table 2).** The reaction of **12a** with **2** is representative. Ethanol (3.0 mL), **12a** (0.15 g, 0.50 mmol), and **2** (0.15 g, 0.60 mmol) were added to a 20-mL reaction flask under an argon atmosphere. The mixture was stirred for 5 h at 25 °C, and concentrated in vacuo. Silica gel column purification afforded **13a** (0.27 g, 0.48 mmol, 96%) as a pale yellow oil.

**Reaction of *S*,*S*-Acetal 13a with Trifluoroacetic Acid (eq 2).** Dichloromethane (2.0 mL), **13a** (0.11 g, 0.20 mmol), and trifluoroacetic acid (0.074 mL, 1.0 mmol) were added to a 20-mL reaction flask under an argon atmosphere. The mixture was stirred for 4 h at 25 °C, and concentrated in vacuo. Chromatographic purification on silica gel afforded **14** (0.058 g, 0.17 mmol, 85%) as a pale yellow oil.

**Reaction of 13a with Organolithium Reagent (eq 3).** Ketene *S*,*S*-acetal **13a** (0.28 g, 0.50 mmol) and THF (3.0 mL) were placed in a 20-mL reaction flask under argon. Phenyllithium (1.1 mol L$^{-1}$ hexane–cyclohexane solution, 0.44 mL, 0.50 mmol) was added to the solution at 0 °C. After being stirred at 0 °C for 30 min, the mixture was poured into water (10 mL). The product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate. After evaporation, the crude oil was purified by silica gel column chromatography to afford **15a** (0.14 g, 0.34 mmol) in 67% yield.

**Characterization Data.** The spectral data of **1g**,[13] **1i**,[14] **12b**,[17] and **12d**[18] are identical to those found in the literature.

***N*-Methyl-*N*-phenylethynyl-*p*-toluenesulfonamide (1a):** IR (nujol) 2924, 2233, 1595, 1365, 1164, 764, 676, 546 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.46 (s, 3H), 3.15 (s, 3H), 7.27–7.31 (m, 3H), 7.34–7.38 (m, 4H), 7.83–7.85 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.85, 39.49, 69.19, 84.11, 122.87, 128.02, 128.04, 128.44, 129.98, 131.57, 133.40, 144.97; Anal. Found: C, 67.07; H, 5.25%. Calcd for $C_{16}H_{15}NO_2S$: C, 67.34; H, 5.30%; mp 85–86 °C.

***N*-Methyl-*N*-1-propynyl-*p*-toluenesulfonamide (1b):** IR (nujol) 2924, 2855, 2265, 1456, 1355, 1168, 1158, 1042, 816, 677, 566, 545 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.88 (s, 3H), 2.46 (s, 3H), 3.01 (s, 3H), 7.34–7.39 (m, 2H), 7.76–7.81 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 3.39, 21.83, 39.43, 64.26, 73.90, 127.97, 129.87, 133.49, 144.64; Anal. Found: C, 59.16; H, 5.82%. Calcd for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87%; mp 99–100 °C.

***N*-Methyl-*N*-*p*-tolylethynyl-*p*-toluenesulfonamide (1c):** IR (nujol) 2922, 2854, 2232, 1366, 1166, 728, 664, 567, 543 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.35 (s, 3H), 2.48 (s, 3H), 3.16 (s, 3H), 7.11 (d, $J$ = 8.0 Hz, 2H), 7.24–7.32 (m, 2H), 7.38 (d, $J$ = 8.0 Hz, 2H), 7.85 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.60, 21.83, 39.53, 69.15, 83.39, 119.69, 128.05, 129.20, 129.94, 131.66, 133.40, 138.21, 144.90; Anal. Found: C, 68.20; H, 5.60%. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72%; mp 73–74 °C.

***N*-Methyl-*N*-*o*-tolylethynyl-*p*-toluenesulfonamide (1d):** IR (neat) 2923, 2235, 1597, 1457, 1367, 1189, 1169, 962, 811, 758, 735, 676, 547 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.37 (s, 3H), 2.46 (s, 3H), 3.18 (s, 3H), 7.08–7.14 (m, 1H), 7.17 (dd, $J$ = 5.0, 1.5 Hz, 2H), 7.31 (d, $J$ = 7.5 Hz, 1H), 7.34–7.38 (m, 2H), 7.82–7.87 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 20.88, 21.93, 39.64, 68.21, 87.91, 122.70, 125.66, 127.92, 128.02, 129.56, 129.99, 131.55, 133.59, 139.91, 144.95; HRMS(EI) Found: 299.0986. Calcd for $C_{17}H_{17}NO_2S$: 299.0980 [$M^+$].

***N*-*p*-Chlorophenylethynyl-*N*-methyl-*p*-toluenesulfonamide (1e):** IR (nujol) 2925, 2855, 2239, 1362, 1163, 1087, 960, 827, 691 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.46 (s, 3H), 3.15 (s, 3H), 7.24–7.30 (m, 4H), 7.36–7.40 (m, 2H), 7.80–7.85 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.83, 39.38, 68.28, 85.00, 121.41, 127.99, 128.76, 130.02, 132.73, 133.41, 133.96, 145.10; Anal. Found: C, 59.81; H, 4.45%. Calcd for $C_{16}H_{14}NO_2SCl$: C, 60.09; H, 4.41%; mp 95–97 °C.

***N*-*p*-Acetylphenylethynyl-*N*-methyl-*p*-toluenesulfonamide (1f):** IR (nujol) 2925, 2232, 1676, 1603, 1370, 1352, 1269, 1177, 1168, 714, 658 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.47 (s, 3H), 2.59 (s, 3H), 3.18 (s, 3H), 7.36–7.44 (m, 4H), 7.82–7.86 (m, 2H), 7.86–7.91 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.87, 26.75, 39.38, 69.33, 87.70, 128.00, 128.13, 128.44, 130.11, 130.96, 133.44, 135.81, 145.25, 197.44; Anal. Found: C, 65.87; H, 5.39%. Calcd for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23%; mp 131–133 °C.

***N*-Ethynyl-*N*-methyl-*p*-toluenesulfonamide (1h):** IR (nujol) 2923, 2360, 2137, 1597, 1359, 1172, 960, 691 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.46 (s, 3H), 2.68 (s, 1H), 3.06 (s, 3H), 7.37 (d, $J$ = 7.5 Hz, 2H), 7.80 (d, $J$ = 7.5 Hz, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.84, 39.01, 57.63, 77.76, 128.00, 130.01, 133.41, 145.09; Anal. Found: C, 57.35; H, 5.47%. Calcd for $C_{10}H_{11}NO_2S$: C, 57.40; H, 5.30%; mp 75–76 °C.

***N*-Methyl-*N*-phenylethynyl-*p*-nitrobenzenesulfonamide (1j):** IR (nujol) 2953, 2924, 2854, 2242, 1607, 1531, 1446, 1371, 1347, 1171, 769, 759, 598 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.23 (s, 3H), 7.28–7.40 (m, 5H), 8.15 (d, $J$ = 8.5 Hz, 2H), 8.44 (d, $J$ = 8.5 Hz, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 39.80, 69.99, 82.63, 122.04, 124.66, 128.62, 128.66, 129.22, 131.82, 141.82, 150.94; Anal. Found: C, 57.04; H, 3.88%. Calcd for $C_{15}H_{12}N_2O_4S$: C, 56.95; H, 3.82%; mp 150–153 °C.

***N*-Deuterioethynyl-*N*-methyl-*p*-toluenesulfonamide (1h-*d*):** IR (nujol) 2923, 2580, 2000, 1596, 1358, 1171, 955, 689, 544 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.45 (s, 3H), 3.05 (s, 3H), 7.34–7.49 (m, 2H), 7.78–7.82 (m, 2H); $^{13}C$ NMR ($CD_2Cl_2$) $\delta$ 21.94, 39.45, 57.48 (t, $J$ = 40.1 Hz), 77.74 (t, $J$ = 9.0 Hz), 128.30, 130.42, 133.65, 145.82; Anal. Found: C, 57.05; H + D, 5.61%. Calcd for $C_{10}H_{10}DNO_2S$: C, 57.12; H + D, 5.75%; mp 74–76 °C.

**(*E*)-1-[Methyl(*p*-tolylsulfonyl)amino]-2-phenylethenyl Diphenyldithiophosphinate (3a):** IR (nujol) 2924, 2855, 1437, 1351, 1163, 693, 654 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.44 (s, 3H), 2.56 (s, 3H), 6.80 (d, $J$ = 3.5 Hz, 1H), 7.22–7.54 (m, 13H), 7.69 (d, $J$ = 8.5 Hz, 2H), 7.73–7.89 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.77, 35.34, 125.73 (d, $J$ = 8.1 Hz), 128.44, 128.51, 128.62 (d, $J$ = 12.9 Hz), 129.31, 129.41 (d, $J$ = 0.9 Hz), 129.54, 131.75 (d, $J$ = 11.0 Hz), 132.11 (d, $J$ = 2.9 Hz), 133.91 (d, $J$ = 2.9 Hz), 134.19 (d, $J$ = 83.1 Hz), 135.09, 143.98, 146.65 (d, $J$ = 7.1 Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 65.09; Anal. Found: C, 62.78; H, 4.93%. Calcd for $C_{28}H_{26}NO_2PS_3$: C, 62.78; H, 4.89%; mp 128–129 °C.

**(*E*)-1-[Methyl(*p*-tolylsulfonyl)amino]-1-propenyl Diphenyldithiophosphinate (3b):** IR (neat) 3055, 2923, 1597, 1436, 1351, 1167, 1089, 957, 815, 720, 675, 654, 609 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.75 (dd, $J$ = 7.0, 4.5 Hz, 3H), 2.45 (s, 3H), 2.54 (s, 3H), 6.13 (dq, $J$ = 7.0, 3.5 Hz, 1H), 7.29–7.35 (m, 2H), 7.42 (br, 4H), 7.46–7.53 (m, 2H), 7.66–7.72 (m, 2H), 7.78–7.86 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 16.07 (d, $J$ = 2.4 Hz), 21.79, 35.78, 126.47 (d, $J$ = 7.6 Hz), 128.16, 128.69 (d, $J$ = 13.4 Hz), 129.77, 131.87 (br), 132.11 (d, $J$ = 3.4 Hz), 134.44 (d, $J$ = 84.5 Hz), 135.58, 143.91, 147.52 (d, $J$ = 7.1 Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 64.47; Anal. Found: C, 58.39; H, 5.12%. Calcd for $C_{23}H_{24}NO_2PS_3$: C, 58.33; H, 5.11%; mp 83–84 °C.

**(*E*)-1-[Methyl(*p*-tolylsulfonyl)amino]-2-*p*-tolylethenyl Diphenyldithiophosphinate (3c):** IR (nujol) 2923, 2854, 1433, 1335, 1160, 1095, 975, 815, 686 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.33 (s, 3H), 2.46 (s, 3H), 2.57 (s, 3H), 6.76 (d, $J$ = 3.5 Hz, 1H), 7.10 (d, $J$ = 8.5 Hz, 2H), 7.26–7.58 (m, 6H), 7.28 (d, $J$ = 8.0 Hz, 2H), 7.38 (d, $J$ = 8.0 Hz, 2H), 7.69–7.96 (m, 6H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.59, 21.79, 35.31, 124.52 (d, $J$ = 8.1 Hz), 128.58, 128.69 (d, $J$ = 13.4 Hz), 129.35, 129.57 (d, $J$ = 1.4 Hz), 129.60, 131.27 (d, $J$ = 2.9 Hz), 131.90 (d, $J$ = 11.0 Hz), 132.13 (d, $J$ = 3.4 Hz), 134.44 (d, $J$ = 83.1 Hz), 135.35, 139.74, 143.96, 147.02 (d, $J$ = 7.1 Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 64.87; Anal. Found: C, 63.19; H, 5.01%. Calcd for $C_{29}H_{28}NO_2PS_3$: C, 63.36; H, 5.13%; mp 144–146 °C.

**(*E*)-1-[Methyl(*p*-tolylsulfonyl)amino]-2-*o*-tolylethenyl Diphenyldithiophosphinate (3d):** IR (nujol) 2924, 2854, 1436, 1356, 1167, 1156, 1101, 723, 652 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.11 (s, 3H), 2.39 (s, 3H), 2.57 (s, 3H), 6.90 (s, 1H), 7.02–7.26 (m, 5H), 7.30–7.66 (m, 9H), 7.78–8.02 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 20.21, 21.68, 35.83, 125.97, 127.15, 128.33, 128.46 (d, $J$ = 1.4 Hz), 128.72 (d, $J$ = 12.9 Hz), 128.87, 129.43, 130.02, 131.90 (d, $J$ = 11.0 Hz), 132.16 (d, $J$ = 2.9 Hz), 133.42, 134.21 (d, $J$ = 83.5 Hz), 135.41, 137.09, 143.78, 143.84; $^{31}P$ NMR ($CDCl_3$) $\delta$ 64.35; Anal. Found: C, 63.54; H, 5.27%. Calcd for $C_{29}H_{28}NO_2PS_3$: C, 63.36; H, 5.13%; mp 165–167 °C.

**(*E*)-2-*p*-Chlorophenyl-1-[methyl(*p*-tolylsulfonyl)amino]ethenyl Diphenyldithiophosphinate (3e):** IR (nujol) 2924, 2855, 1437, 1351, 1162, 1090, 971, 815, 689 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.45 (s, 3H), 2.57 (s, 3H), 6.73 (d, $J$ = 3.0 Hz, 1H), 7.22–7.58 (m, 12H), 7.67 (d, $J$ = 8.5 Hz, 2H), 7.72–7.90 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.78, 35.33, 126.70 (d, $J$ = 8.6 Hz), 128.51, 128.70, 128.81, 128.83, 129.70, 130.75, 131.88 (d, $J$ = 10.9 Hz), 132.24 (d, $J$ = 3.4 Hz), 132.55 (d, $J$ = 2.9 Hz), 134.27 (d, $J$ = 83.1 Hz), 135.12, 144.22, 145.21 (d, $J$ = 7.1 Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 65.48; Anal. Found: C, 59.11; H, 4.43%. Calcd for $C_{28}H_{25}ClNO_2PS_3$: C, 58.99; H, 4.42%; mp 109–111 °C.

**(*E*)-2-*p*-Acetylphenyl-1-[methyl(*p*-tolylsulfonyl)amino]ethenyl Diphenyldithiophosphinate (3f):** IR (nujol) 2923, 2854, 1682, 1347, 1266, 1162, 973, 719, 682 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.45 (s, 3H), 2.58 (s, 3H), 2.60 (s, 3H), 6.80 (d, $J$ = 3.0 Hz, 1H), 7.24–7.30 (m, 2H), 7.32–7.60 (m, 8H), 7.66–7.70 (m, 2H), 7.74–7.92 (m, 6H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.81, 26.82, 35.44, 128.53, 128.62, 128.68, 128.81 (d, $J$ = 13.3 Hz), 129.56 (d, $J$ = 1.4 Hz), 129.74, 131.92 (d, $J$ = 11.0 Hz), 132.34 (d, $J$ = 2.9 Hz), 134.14 (d, $J$ = 83.5 Hz), 134.97, 137.10, 138.60 (d, $J$ = 2.9 Hz), 144.30, 144.91 (d, $J$ = 7.3 Hz), 197.60; $^{31}P$ NMR ($CDCl_3$) $\delta$ 65.70; Anal. Found: C, 62.25; H, 4.86%. Calcd for $C_{30}H_{28}NO_3PS_3$: C, 62.37; H, 4.89%; mp 132–134 °C.

**(*E*)-1-[Methyl(*p*-tolylsulfonyl)amino]-2-(trimethylsilyl)ethenyl Diphenyldithiophosphinate (3g):** Purification by recrystallization from a mixture of hexane and benzene was performed instead of silica gel column chromatography. IR (nujol) 2924, 2854, 1439, 1348, 1245, 1166, 1157, 1103, 966, 864, 847, 721, 610 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.15 (s, 9H), 2.44 (s, 3H), 2.70 (s, 3H), 6.05 (d, $J$ = 2.5 Hz, 1H), 7.31 (d, $J$ = 8.0 Hz, 2H), 7.35–7.55 (m, 6H), 7.66–7.71 (m, 2H), 7.74–7.85 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ −0.61, 21.80, 36.06, 128.52, 128.69 (d, $J$ = 13.3 Hz), 129.77, 132.01 (d, $J$ = 10.5 Hz), 132.13 (d, $J$ = 3.3 Hz), 134.15 (d, $J$ = 83.9 Hz), 134.93, 136.27 (d, $J$ = 6.4 Hz), 144.04, 151.42 (d, $J$ = 5.1 Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 64.19; Anal. Found: C, 56.20; H, 5.64%. Calcd for $C_{25}H_{30}NO_2SiPS_3$: C, 56.47; H, 5.69%; mp 160–162 °C.

**1-[Methyl(*p*-tolylsulfonyl)amino]ethenyl Diphenyldithiophosphinate (3h):** IR (nujol) 2925, 2855, 2360, 1601, 1345,

1152, 930, 718, 668 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.41 (s, 3H), 2.70 (s, 3H), 5.49 (dd, $J = 3.5$, 1.5 Hz, 1H), 5.55 (dd, $J = 3.5$, 1.5 Hz, 1H), 7.26–7.32 (m, 2H), 7.42–7.54 (m, 6H), 7.62–7.67 (m, 2H), 7.91–7.99 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.70, 37.08, 128.11, 128.36 (d, $J = 6.6$ Hz), 128.74 (d, $J = 13.4$ Hz), 129.70, 131.98 (d, $J = 11.0$ Hz), 132.28 (d, $J = 2.9$ Hz), 133.53 (d, $J = 84.0$ Hz), 134.10, 136.21 (d, $J = 7.3$ Hz), 144.11; $^{31}$P NMR ($CDCl_3$) $\delta$ 63.97; Anal. Found: C, 57.24; H, 4.92%. Calcd for $C_{22}H_{22}NO_2PS_3$: C, 57.49; H, 4.82%; mp 99–100 °C.

**(*E*)-2-Phenyl-1-[(2-propenyl)(*p*-tolylsulfonyl)amino]ethenyl Diphenyldithiophosphinate (3i):** IR (nujol) 2924, 2854, 1358, 1167, 1101, 723 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.40 (s, 3H), 3.72 (br, 2H), 4.85–4.92 (m, 1H), 4.94–5.02 (m, 1H), 5.64 (ddt, $J = 17.0$, 10.0, 7.0 Hz, 1H), 6.79 (d, $J = 2.5$ Hz, 1H), 7.17–7.27 (m, 5H), 7.30–7.54 (m, 8H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.76–7.94 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.73, 52.22, 118.83, 125.32 (d, $J = 8.1$ Hz), 128.30, 128.63, 128.75 (d, $J = 13.3$ Hz), 129.29, 129.57, 129.83 (d, $J = 1.0$ Hz), 131.95 (d, $J = 11.0$ Hz), 132.21 (d, $J = 3.3$ Hz), 132.98, 134.04, 134.30 (d, $J = 83.5$ Hz), 136.00, 144.09, 146.96 (d, $J = 6.8$ Hz); $^{31}$P NMR ($CDCl_3$) $\delta$ 64.31; Anal. Found: C, 64.12; H, 5.09%. Calcd for $C_{30}H_{28}NO_2PS_3$: C, 64.15; H, 5.02%; mp 132–134 °C.

**(*E*)-1-[Methyl(*p*-nitrophenylsulfonyl)amino]-2-phenylethenyl Diphenyldithiophosphinate (3j):** IR (nujol) 2923, 2854, 1524, 1434, 1350, 1335, 1160, 718, 635 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.76 (s, 3H), 6.75 (d, $J = 3.0$ Hz, 1H), 7.24–7.31 (m, 3H), 7.32–7.38 (m, 2H), 7.38–7.49 (m, 4H), 7.49–7.56 (m, 2H), 7.74–7.90 (m, 4H), 7.92–7.97 (m, 2H), 8.21–8.26 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 36.02, 124.11, 125.40 (d, $J = 8.1$ Hz), 128.78, 128.86 (d, $J = 13.4$ Hz), 129.31 (d, $J = 1.4$ Hz), 129.64, 129.72, 131.87 (d, $J = 10.5$ Hz), 132.44 (d, $J = 3.3$ Hz), 133.72 (d, $J = 2.9$ Hz), 134.03 (d, $J = 83.0$ Hz), 144.09, 147.10 (d, $J = 7.1$ Hz), 150.33; $^{31}$P NMR ($CDCl_3$) $\delta$ 65.13; Anal. Found: C, 57.42; H, 4.23%. Calcd for $C_{27}H_{23}N_2O_4PS_3$: C, 57.23; H, 4.09%; mp 126–127 °C.

***t*-Butyl *N*,3,3-Trimethyl-2-phenylbutanethioimidate (5, a 93:7 Mixture of Diastereomers):** IR (neat) 2957, 2905, 1629, 1452, 1392, 1364, 1163, 976, 725, 703 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.01 (s, 9 × 0.93H), 1.10 (s, 9 × 0.07H), 1.36 (s, 9 × 0.93H), 1.56 (s, 9 × 0.07H), 3.25 (s, 3 × 0.07H), 3.53 (s, 3 × 0.93H), 3.90 (s, 1 × 0.93H), 4.03 (s, 1 × 0.07H), 7.20–7.33 (m, 3H), 7.36–7.44 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ (major isomer) 28.66, 33.09, 36.60, 42.81, 49.02, 68.90, 126.53, 127.48, 131.32, 138.68, 162.42; Anal. Found: C, 73.47; H, 9.66%. Calcd for $C_{17}H_{27}NS$: C, 73.59; H, 9.81%.

***N*,3,3-Trimethyl-2-phenylbutanethioamide (8):** IR (nujol) 3370, 2925, 2867, 1520, 1365, 1297, 1098, 1053, 740, 711 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.11 (s, 9H), 3.10 (s, 1.5H), 3.11 (s, 1.5H), 3.60 (s, 1H), 7.24–7.32 (m, 3H), 7.44 (br, 1H), 7.62–7.66 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 28.72, 32.99, 35.67, 72.63, 127.40, 127.98, 130.39, 138.26, 206.07; Anal. Found: C, 70.62; H, 8.51%. Calcd for $C_{13}H_{19}NS$: C, 70.54; H, 8.65%; mp 141–142 °C.

***O*-{(*E*)-1-[Methyl(*p*-tolylsulfonyl)amino]-2-phenylethenyl} Thiobenzoate ((*E*)-10):** IR (nujol) 2924, 2854, 1349, 1264, 1162, 1048, 1027, 990, 686 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.28 (s, 3H), 3.10 (s, 3H), 6.26 (s, 1H), 7.02 (d, $J = 8.0$ Hz, 2H), 7.30–7.40 (m, 5H), 7.55–7.60 (m, 3H), 7.62–7.68 (m, 2H), 7.88–8.04 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.63, 37.51, 119.74, 127.77, 128.23, 128.60, 128.82, 128.85, 129.52, 129.61, 131.83, 133.58, 136.17, 137.30, 142.55, 143.99, 209.53; Anal. Found: C, 65.17; H, 5.15%. Calcd for $C_{23}H_{21}NO_3S_2$: C, 65.22; H, 5.00%; mp 138–140 °C.

***N*-Methyl-*N*-(*p*-tolylsulfonyl)phenylacetamide (11):** IR (neat) 3031, 1696, 1356, 1167, 1075, 673, 583 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.44 (s, 3H), 3.28 (s, 3H), 4.04 (s, 2H), 7.11–7.16 (m, 2H), 7.22–7.34 (m, 5H), 7.67–7.72 (m, 2H); $^{13}$C NMR ($CDCl_3$) 21.78, 33.43, 43.23, 127.33, 127.69, 128.75, 129.54, 130.04, 133.62, 136.20, 145.12, 171.44; Anal. Found: C, 63.05; H, 5.66%. Calcd for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.65%.

**Dodecyl Phenylethynyl Sulfide (12a):** IR (neat) 2925, 2854, 2168, 1596, 1488, 1466, 753, 690 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.89 (t, $J = 7.0$ Hz, 3H), 1.24–1.38 (m, 16H), 1.42–1.50 (m, 2H), 1.77–1.84 (m, 2H), 2.81 (t, $J = 7.5$ Hz, 2H), 7.27–7.34 (m, 3H), 7.39–7.44 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.10, 22.67, 28.26, 29.11, 29.32, 29.33, 29.48, 29.57, 29.61, 29.64, 31.90, 35.82, 79.71, 92.83, 123.60, 127.88, 128.22, 131.37. Anal. Found: C, 79.54; H, 10.24%. Calcd for $C_{20}H_{30}S$: C, 79.41; H, 9.99%.

**Dodecyl 1-Octynyl Sulfide (12c):** IR (neat) 2956, 2926, 2855, 1467, 1378, 722 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.88 (t, $J = 7.0$ Hz, 3H), 0.89 (t, $J = 7.5$ Hz, 3H), 1.20–1.34 (m, 20H), 1.35–1.44 (m, 4H), 1.47–1.54 (m, 2H), 1.68–1.75 (m, 2H), 2.29 (t, $J = 7.0$ Hz, 2H), 2.65 (t, $J = 7.5$ Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.02, 14.09, 20.12, 22.55, 22.68, 28.29, 28.51, 28.77, 29.15, 29.24, 29.34, 29.50, 29.59, 29.63, 29.65, 31.33, 31.91, 35.45, 68.31, 94.23. Anal. Found: C, 77.14; H, 12.58%. Calcd for $C_{20}H_{38}S$: C, 77.34; H, 12.33%.

**Dodecyl *p*-Methoxyphenylethynyl Sulfide (12e):** IR (neat) 2925, 2854, 1606, 1507, 1289, 1249, 1171, 1035, 830 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.89 (t, $J = 7.5$ Hz, 3H), 1.20–1.36 (m, 16H), 1.40–1.47 (m, 2H), 1.75–1.82 (m, 2H), 2.78 (t, $J = 7.0$ Hz, 2H), 3.80 (s, 3H), 6.82 (d, $J = 9.0$ Hz, 2H), 7.37 (d, $J = 9.0$ Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.09, 22.67, 28.28, 29.12, 29.30, 29.33, 29.48, 29.57, 29.61, 29.64, 31.89, 35.87, 55.23, 77.66, 92.54, 113.85, 115.69, 133.28, 159.49. Anal. Found: C, 75.91; H, 9.84%. Calcd for $C_{21}H_{32}OS$: C, 75.85; H, 9.70%.

**Dodecyl *o*-Methoxyphenylethynyl Sulfide (12f):** IR (neat) 2925, 2854, 2171, 1594, 1490, 1464, 1258, 1115, 1027, 749 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.88 (t, $J = 7.0$ Hz, 3H), 1.20–1.37 (m, 16H), 1.41–1.48 (m, 2H), 1.78–1.86 (m, 2H), 2.81 (t, $J = 7.5$ Hz, 2H), 3.86 (s, 3H), 6.83–6.90 (m, 2H), 7.22–7.27 (m, 1H), 7.35–7.39 (m, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.10, 22.66, 28.30, 29.16, 29.22, 29.33, 29.49, 29.59, 29.61, 29.64, 31.89, 35.95, 55.72, 83.51, 89.03, 110.54, 112.85, 120.34, 129.27, 133.28, 159.98. Anal. Found: C, 76.13; H, 9.64%. Calcd for $C_{21}H_{32}OS$: C, 75.85; H, 9.70%.

**Dodecyl *p*-(Trifluoromethyl)phenylethynyl Sulfide (12g):** IR (neat) 2926, 2855, 2166, 1614, 1323, 1168, 1130, 1067, 840 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.88 (t, $J = 7.0$ Hz, 3H), 1.20–1.38 (m, 16H), 1.40–1.50 (m, 2H), 1.77–1.84 (m, 2H), 2.83 (t, $J = 7.5$ Hz, 2H), 7.46–7.49 (m, 2H), 7.52–7.56 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.08, 22.68, 28.22, 29.10, 29.35 (×2), 29.48, 29.58, 29.63, 29.66, 31.92, 35.82, 83.41, 91.84, 123.95 (q, $J = 270.6$ Hz), 125.18 (q, $J = 3.9$ Hz), 127.42, 129.35 (q, $J = 32.4$ Hz), 131.16. Anal. Found: C, 68.34; H, 8.16%. Calcd for $C_{21}H_{29}F_3S$: C, 68.07; H, 7.89%.

**Cyclohexylethynyl Dodecyl Sulfide (12h):** IR (neat) 2927, 2854, 1448, 1361, 1296, 1232, 974, 888, 721 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.88 (t, $J = 7.0$ Hz, 3H), 1.20–1.52 (m, 24H), 1.64–1.83 (m, 6H), 2.45–2.55 (m, 1H), 2.66 (t, $J = 7.5$ Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.08, 22.66, 24.78, 25.86, 28.23, 29.10, 29.13, 29.33, 29.46, 29.57, 29.61, 29.64, 30.37, 31.90, 32.71, 35.51, 68.31, 98.15. Anal. Found: C, 77.85; H, 12.02%. Calcd for $C_{20}H_{36}S$: C, 77.85; H, 11.76%.

**Dodecyl 3,3-Dimethyl-1-butynyl Sulfide (12i):** IR (neat)

2967, 2926, 2855, 1458, 1362, 1252, 1203, 722 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.88 (t, $J = 7.0$ Hz, 3H), 1.22 (s, 9H), 1.23–1.33 (m, 16H), 1.34–1.44 (m, 2H), 1.70 (tt, $J = 7.0$, 7.5 Hz, 2H), 2.64 (t, $J = 7.5$ Hz, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.09, 22.67, 28.22, 28.69, 29.01, 29.14, 29.33, 29.46, 29.58, 29.62, 29.65, 31.00, 31.90, 35.49, 67.05, 102.08. Anal. Found: C, 76.54; H, 12.26%. Calcd for $C_{18}H_{34}S$: C, 76.52; H, 12.13%.

**Dodecyl Ethynyl Sulfide (12j):** IR (neat) 3309, 2925, 2854, 2044, 1466, 1061, 722, 666, 530 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.88 (t, $J = 7.0$ Hz, 3H), 1.20–1.35 (m, 16H), 1.36–1.44 (m, 2H), 1.74 (tt, $J = 7.0$, 7.5 Hz, 2H), 2.73 (t, $J = 7.5$ Hz, 2H), 2.74 (s, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.10, 22.68, 28.22, 29.07, 29.14, 29.33, 29.46, 29.56, 29.62, 29.63, 31.91, 35.11, 74.76, 81.69. Anal. Found: C, 74.21; H, 11.74%. Calcd for $C_{14}H_{26}S$: C, 74.26; H, 11.57%.

**(*E*)-1-Dodecylsulfanyl-2-phenylethenyl Diphenyldithiophosphinate (13a):** IR (neat) 3056, 2925, 2853, 1437, 1097, 925, 749, 721, 690, 655 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.90 (t, $J = 7.0$ Hz, 3H), 1.14–1.34 (m, 18H), 1.38–1.46 (m, 2H), 2.71 (t, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 3.5$ Hz, 1H), 7.23–7.27 (m, 1H), 7.29–7.34 (m, 2H), 7.45–7.56 (m, 8H), 8.00–8.07 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.10, 22.65, 28.63, 29.09, 29.31, 29.36, 29.41, 29.51, 29.59, 29.60, 31.88, 34.40, 125.02 (d, $J = 8.1$ Hz), 127.94, 128.07, 128.44 (d, $J = 13.4$ Hz), 129.61 (d, $J = 1.5$ Hz), 131.85 (d, $J = 10.9$ Hz), 131.91 (d, $J = 3.4$ Hz), 133.81 (d, $J = 83.0$ Hz), 135.84 (d, $J = 2.9$ Hz), 145.73 (d, $J = 7.6$ Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 63.45. Anal. Found: C, 69.64; H, 7.50%. Calcd for $C_{32}H_{41}PS_3$: C, 69.52; H, 7.47%.

**(*E*)-2-Phenyl-1-*p*-tolylsulfanylethenyl Diphenyldithiophosphinate (13b):** IR (nujol) 2924, 2855, 1458, 1437, 1377, 1095, 928, 898, 813, 718, 652 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.31 (s, 3H), 7.02 (d, $J = 8.0$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 7.22–7.34 (m, 3H), 7.36–7.42 (m, 4H), 7.46–7.52 (m, 3H), 7.57 (d, $J = 7.5$ Hz, 2H), 7.80–7.94 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.11, 123.39 (d, $J = 8.1$ Hz), 128.07, 128.35 (d, $J = 13.4$ Hz), 128.71, 129.60 (d, $J = 1.4$ Hz), 129.65, 130.43, 130.55, 131.80 (d, $J = 3.3$ Hz), 131.87 (d, $J = 10.9$ Hz), 133.67 (d, $J = 83.0$ Hz), 135.53 (d, $J = 2.4$ Hz), 137.06, 149.55 (d, $J = 7.1$ Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 64.81. Anal. Found: C, 68.03; H, 5.03%. Calcd for $C_{27}H_{23}PS_3$: C, 68.32; H, 4.88%. mp 87.5–88.0 °C. The crystal data have been deposited at CCDC, Cambridge, UK and given the reference number CCDC 670503. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

**(*E*)-1-Dodecylsulfanyl-1-octenyl Diphenyldithiophosphinate (13c):** IR (neat) 3056, 2924, 2854, 1457, 1437, 1097, 852, 748, 721, 690, 656 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.88 (t, $J = 7.0$ Hz, 6H), 1.18–1.45 (m, 28H), 2.25–2.33 (m, 2H), 2.60 (t, $J = 7.5$ Hz, 2H), 6.30 (dt, $J = 3.5$, 7.5 Hz, 1H), 7.42–7.53 (m, 6H), 7.95–8.20 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.08 (×2), 22.55, 22.65, 28.60, 28.77 (d, $J = 2.4$ Hz), 28.83, 29.17, 29.32, 29.49, 29.56 (×2), 29.61, 29.62, 31.61, 31.72 (d, $J = 1.9$ Hz), 31.88, 33.41, 122.64 (d, $J = 7.6$ Hz), 128.33 (d, $J = 13.4$ Hz), 131.80 (d, $J = 11.0$ Hz), 134.05 (d, $J = 83.1$ Hz), 148.04 (d, $J = 7.1$ Hz), 152.70 (d, $J = 7.8$ Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 62.34. Anal. Found: C, 68.73; H, 8.72%. Calcd for $C_{32}H_{49}PS_3$: C, 68.52; H, 8.80%.

**(*E*)-1-*p*-Tolylsulfanyl-1-octenyl Diphenyldithiophosphinate (13d):** IR (neat) 2954, 2925, 2855, 2370, 1491, 1437, 1097, 805, 721 655 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.89 (t, $J = 7.0$ Hz, 3H), 1.20–1.36 (m, 6H), 1.40–1.48 (m, 2H), 2.33 (s, 3H), 2.39–2.46 (m, 2H), 6.65–6.71 (m, 1H), 7.00 (dd, $J = 2.0$, 7.5 Hz, 2H), 7.07 (d, $J = 7.5$ Hz, 2H), 7.37–7.43 (m, 4H), 7.45–7.51 (m, 2H), 7.84–7.90 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.06, 21.03, 22.53, 28.81, 28.85 (d, $J = 8.0$ Hz), 31.53, 32.12 (d, $J = 4.0$ Hz), 121.45 (d, $J = 7.1$ Hz), 121.47 (d, $J = 7.6$ Hz), 128.25 (d, $J = 13.4$ Hz), 129.56, 131.08, 131.65 (d, $J = 2.9$ Hz), 131.79 (d, $J = 11.0$ Hz), 133.78 (d, $J = 83.6$ Hz), 136.40, 156.27 (d, $J = 6.6$ Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 63.68. Anal. Found: C, 67.09; H, 6.43%. Calcd for $C_{27}H_{31}PS_3$: C, 67.18; H, 6.47%.

**(*E*)-1-Dodecylsulfanyl-2-*p*-methoxyphenylethenyl Diphenyldithiophosphinate (13e):** IR (neat) 2925, 2853, 1605, 1506, 1437, 1252, 1177, 1097, 1034, 722 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.90 (t, $J = 7.0$ Hz, 3H), 1.14–1.36 (m, 18H), 1.40–1.48 (m, 2H), 2.72 (t, $J = 7.5$ Hz, 2H), 3.80 (s, 3H), 6.85 (d, $J = 9.0$ Hz, 2H), 7.08 (d, $J = 3.5$ Hz, 1H), 7.44–7.54 (m, 8H), 8.00–8.06 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.06, 22.61, 28.61, 29.06, 29.27, 29.32, 29.38, 29.48, 29.55, 29.57, 31.83, 34.32, 55.15, 113.30, 121.79 (d, $J = 8.1$ Hz), 128.35 (d, $J = 13.4$ Hz), 128.60 (d, $J = 2.9$ Hz), 131.28 (d, $J = 1.4$ Hz), 131.80 (d, $J = 11.0$ Hz), 131.80 (d, $J = 3.3$ Hz), 133.86 (d, $J = 82.6$ Hz), 146.08 (d, $J = 7.6$ Hz), 159.37; $^{31}P$ NMR ($CDCl_3$) $\delta$ 63.40. Anal. Found: C, 67.81; H, 7.44%. Calcd for $C_{33}H_{43}OPS_3$: C, 68.00; H, 7.44%.

**(*E*)-1-Dodecylsulfanyl-2-*o*-methoxyphenylethenyl Diphenyldithiophosphinate (13f):** IR (neat) 3056, 2924, 2853, 1597, 1481, 1464, 1436, 1247, 1097, 748, 720, 690, 654 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.90 (t, $J = 7.0$ Hz, 3H), 1.14–1.32 (m, 18H), 1.36–1.44 (m, 2H), 2.67 (t, $J = 7.5$ Hz, 2H), 3.76 (s, 3H), 6.82 (d, $J = 7.5$ Hz, 1H), 6.91 (dd, $J = 7.5$, 7.5 Hz, 1H), 7.22–7.27 (m, 1H), 7.35 (d, $J = 4.0$ Hz, 1H), 7.44–7.54 (m, 6H), 7.60 (d, $J = 7.5$ Hz, 1H), 8.01–8.08 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.07, 22.63, 28.63, 29.09, 29.12, 29.29, 29.40, 29.51, 29.57, 29.59, 31.85, 34.19, 55.37, 110.16, 119.71, 124.77 (d, $J = 8.1$ Hz), 124.84 (d, $J = 2.4$ Hz), 128.35 (d, $J = 13.4$ Hz), 129.63, 130.66 (d, $J = 1.9$ Hz), 131.76 (d, $J = 2.9$ Hz), 131.86 (d, $J = 11.0$ Hz), 133.94 (d, $J = 83.0$ Hz), 141.30 (d, $J = 7.6$ Hz), 156.90 (d, $J = 0.9$ Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 63.16. Anal. Found: C, 68.03; H, 7.31%. Calcd for $C_{33}H_{43}OPS_3$: C, 68.00; H, 7.44%.

**(*E*)-1-Dodecylsulfanyl-2-*p*-(trifluoromethyl)phenylethenyl Diphenyldithiophosphinate (13g):** IR (neat) 2926, 2854, 1437, 1324, 1167, 1126, 1068, 908, 722 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.91 (t, $J = 7.5$ Hz, 3H), 1.16–1.36 (m, 18H), 1.42–1.50 (m, 2H), 2.75 (t, $J = 7.5$ Hz, 2H), 7.14 (d, $J = 3.0$ Hz, 1H), 7.44–7.62 (m, 10H), 8.00–8.08 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.04, 22.60, 28.54, 29.02, 29.26, 29.36 (×2), 29.46, 29.54, 29.55, 31.82, 34.48, 123.96 (q, $J = 270.5$ Hz), 124.83 (q, $J = 3.8$ Hz), 128.44 (d, $J = 4.8$ Hz), 128.49 (d, $J = 8.1$ Hz), 129.39 (d, $J = 32.5$ Hz), 129.65 (d, $J = 1.4$ Hz), 131.77 (d, $J = 10.9$ Hz), 132.00 (d, $J = 2.9$ Hz), 133.62 (d, $J = 83.5$ Hz), 139.15 (d, $J = 1.0$ Hz), 143.17 (d, $J = 7.6$ Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 63.87. Anal. Found: C, 63.71; H, 6.47%. Calcd for $C_{33}H_{40}F_3PS_3$: C, 63.84; H, 6.49%.

**(*E*)-2-Cyclohexyl-1-(dodecylsulfanyl)ethenyl Diphenyldithiophosphinate (13h):** IR (neat) 3056, 2925, 2852, 1956, 1899, 1810, 1437, 1097, 721, 690, 656 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.89 (t, $J = 7.5$ Hz, 3H), 1.00–1.34 (m, 23H), 1.36–1.46 (m, 2H), 1.56–1.70 (m, 5H), 2.56–2.66 (m, 3H), 6.17 (dd, $J = 3.5$, 10.0 Hz, 1H), 7.41–7.52 (m, 6H), 7.95–8.02 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.05, 22.60, 25.37, 25.76, 28.53, 29.13, 29.26, 29.43, 29.45, 29.51, 29.54, 29.57, 31.83, 32.14 (d, $J = 2.4$ Hz), 33.27, 40.70 (d, $J = 0.9$ Hz), 120.86 (d, $J = 7.6$ Hz), 128.26 (d, $J = 13.4$ Hz), 131.65 (d, $J = 2.9$ Hz), 131.76 (d, $J = 11.0$ Hz), 134.02 (d, $J = 83.0$ Hz), 157.86 (d, $J = 7.1$ Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 62.13.

Anal. Found: C, 68.71; H, 8.51%. Calcd for $C_{32}H_{47}PS_3$: C, 68.77; H, 8.48%.

**(*E*)-1-Dodecylsulfanyl-3,3-dimethyl-1-butenyl Diphenyldithiophosphinate (13i):** IR (neat) 2956, 2925, 2854, 2360, 1458, 1437, 1362, 1202, 1097, 721, 690, 655 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.89 (t, $J = 7.0$ Hz, 3H), 1.13 (s, 9H), 1.20–1.34 (m, 18H), 1.40–1.50 (m, 2H), 2.67 (t, $J = 8.0$ Hz, 2H), 6.28 (d, $J = 4.0$ Hz, 1H), 7.42–7.52 (m, 6H), 7.94–8.02 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.09, 22.64, 28.78, 29.15, 29.30, 29.47, 29.48, 29.54, 29.58, 29.60, 29.78 (d, $J = 1.9$ Hz), 31.87, 33.95, 35.22 (d, $J = 1.4$ Hz), 122.45 (d, $J = 7.3$ Hz), 128.30 (d, $J = 13.4$ Hz), 131.68 (d, $J = 2.9$ Hz), 131.84 (d, $J = 10.5$ Hz), 134.03 (d, $J = 83.0$ Hz), 161.41 (d, $J = 7.6$ Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 62.54. Anal. Found: C, 67.66; H, 8.39%. Calcd for $C_{30}H_{45}PS_3$: C, 67.62; H, 8.51%.

**1-Dodecylsulfanylethenyl Diphenyldithiophosphinate (13j):** IR (neat) 2924, 2853, 1576, 1436, 1309, 1096, 723, 690 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.88 (t, $J = 7.0$ Hz, 3H), 1.18–1.38 (m, 18H), 1.42–1.47 (m, 2H), 2.64 (t, $J = 7.5$ Hz, 2H), 5.56 (dd, $J = 1.5$, 3.5 Hz, 1H), 5.69 (dd, $J = 1.5$, 3.5 Hz, 1H), 7.38–7.58 (m, 6H), 7.96–8.02 (m, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.09, 22.65, 27.99, 28.78, 29.07, 29.31, 29.43, 29.53, 29.59, 29.61, 31.88, 34.15, 123.66 (d, $J = 7.3$ Hz), 128.42 (d, $J = 13.4$ Hz), 131.87 (d, $J = 11.0$ Hz), 131.93 (d, $J = 2.4$ Hz), 133.06 (d, $J = 6.8$ Hz), 133.68 (d, $J = 84.0$ Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ 62.81. Anal. Found: C, 65.64; H, 7.90%. Calcd for $C_{26}H_{37}PS_3$: C, 65.50; H, 7.82%.

**Dodecyl Phenylethanedithioate (14):** IR (neat) 2925, 2854, 2370, 1453, 1219, 1131, 991, 858, 697 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.89 (t, $J = 7.0$ Hz, 3H), 1.22–1.33 (m, 16H), 1.34–1.41 (m, 2H), 1.61–1.69 (m, 2H), 3.18 (t, $J = 7.5$ Hz, 2H), 4.31 (s, 2H), 7.25–7.38 (m, 5H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.10, 22.67, 27.12, 29.04, 29.09, 29.32, 29.40, 29.52, 29.60, 29.61, 31.89, 37.03, 58.13, 127.17, 128.49, 129.03, 137.09, 235.81. Anal. Found: C, 71.65; H, 9.62%. Calcd for $C_{20}H_{32}S_2$: C, 71.37; H, 9.58%.

**Dodecyl (*E*)-2-Phenyl-1-(phenylsulfanyl)ethenyl Sulfide (15a):** IR (neat) 3068, 2925, 2853, 2360, 1950, 1582, 1440, 1024, 739, 690 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.88 (t, $J = 7.0$ Hz, 3H), 1.14–1.40 (m, 18H), 1.48–1.55 (m, 2H), 2.79 (t, $J = 7.5$ Hz, 2H), 7.11 (s, 1H), 7.22–7.38 (m, 6H), 7.41–7.46 (m, 2H), 7.62–7.66 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.10, 22.68, 28.64, 29.07, 29.34, 29.44, 29.54, 29.62, 29.63, 29.65, 31.91, 33.80, 127.01, 127.58, 128.07, 129.02, 129.52, 130.15, 131.71, 135.20, 136.20, 137.51. Anal. Found: C, 75.63; H, 8.96%. Calcd for $C_{26}H_{36}S_2$: C, 75.67; H, 8.79%.

**(*Z*)-1-Butylsulfanyl-2-phenylethenyl Dodecyl Sulfide (15b):** IR (neat) 2956, 2925, 2854, 1560, 1491, 1466, 928, 750, 691 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.89 (t, $J = 7.0$ Hz, 3H), 0.95 (t, $J = 7.0$ Hz, 3H), 1.18–1.51 (m, 20H), 1.52–1.59 (m, 2H), 1.60–1.69 (m, 2H), 2.82 (t, $J = 6.0$ Hz, 2H), 2.83 (t, $J = 7.0$ Hz, 2H), 6.99 (s, 1H), 7.21–7.60 (m, 1H), 7.31–7.36 (m, 2H), 7.60–7.65 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.70, 14.10, 21.93, 22.68, 28.69, 29.14, 29.34 (×2), 29.47, 29.55, 29.63, 29.69, 31.16, 31.90, 33.28, 33.87, 127.12, 127.98, 129.31, 132.97, 134.32, 136.56. Anal. Found: C, 73.55; H, 10.44%. Calcd for $C_{24}H_{40}S_2$: C, 73.40; H, 10.27%.

This work was supported by Grants-in-Aid for Scientific Research and COE Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. A.K. acknowledges JSPS for financial support. We thank Prof. Masaki Shimizu (Kyoto University) for helping with the X-ray crystallographic analysis.

## References

1 a) H. Kuniyasu, in *Catalytic Heterofunctionalization*, ed. by A. Togni, H. Grützmacher, Wiley-VCH, Weinheim, **2001**, Chap. 7. b) F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* **2004**, *104*, 3079. c) C. Cao, L. R. Fraser, J. A. Love, *J. Am. Chem. Soc.* **2005**, *127*, 17614, and references cited therein.

2 Reviews on the chemistry of *N*-(1-alkynyl)amides, so-called ynamides: a) C. A. Zificsak, J. A. Mulder, R. P. Hsung, C. Rameshkumar, L.-L. Wei, *Tetrahedron* **2001**, *57*, 7575. b) J. A. Mulder, K. C. M. Kurtz, R. P. Hsung, *Synlett* **2003**, 1379. c) B. Witulski, C. Alayrac, in *Science of Synthesis*, ed. by A. de Meijere, Thieme, Stuttgart, **2005**, Vol. 24, Chap. 24.4.4.2.

3 Brønsted acid-catalyzed addition reaction of allyl or propargyl alcohol followed by Claisen rearrangement: a) J. A. Mulder, R. P. Hsung, M. O. Frederick, M. R. Tracey, C. A. Zificsak, *Org. Lett.* **2002**, *4*, 1383. b) M. O. Frederick, R. P. Hsung, R. H. Lambeth, J. A. Mulder, M. P. Tracey, *Org. Lett.* **2003**, *5*, 2663. Hydrohalogenation: c) J. A. Mulder, K. C. M. Kurtz, R. P. Hsung, H. Coverdale, M. O. Frederick, L. Shen, C. A. Zificsak, *Org. Lett.* **2003**, *5*, 1547. Brønsted acid-catalyzed hydroarylation: d) Y. Zhang, *Tetrahedron Lett.* **2005**, *46*, 6483. e) Y. Zhang, R. P. Hsung, X. Zhang, J. Huang, B. W. Slafer, A. Davis, *Org. Lett.* **2005**, *7*, 1047. Lewis acid-catalyzed reaction with carbonyl compounds: f) K. C. M. Kurtz, R. P. Hsung, Y. Zhang, *Org. Lett.* **2006**, *8*, 231. g) L. You, Z. F. Al-Rashid, R. Figueroa, S. K. Ghosh, G. Li, T. Lu, R. P. Hsung, *Synlett* **2007**, 1656.

4 A review on the chemistry of 1-alkynyl sulfides: V. A. Potapov, B. A. Trofimov, in *Science of Synthesis*, ed. by A. de Meijere, Thieme, Stuttgart, **2005**, Vol. 24, Chap. 24.4.3.

5 Addition to 1-alkynyl sulfides under acidic conditions: a) F. Manarin, J. A. Roehrs, M. Prigol, D. Alves, C. W. Nogueira, G. Zeni, *Tetrahedron Lett.* **2007**, *48*, 4805. b) A. L. Braga, D. J. Emmerich, C. C. Silveira, T. L. C. Martins, O. E. D. Rodrigues, *Synlett* **2001**, 371.

6 W. Dölling, in *Science of Synthesis*, ed. by A. de Meijere, Thieme, Stuttgart, **2005**, Vol. 24, Chap. 24.2.11; **2005**, Vol. 24, Chap. 24.2.13.

7 This work was communicated: H. Yasui, H. Yorimitsu, K. Oshima, *Chem. Lett.* **2008**, *37*, 40.

8 Syn addition to ynamides under Brønsted acid catalysis was reported in Ref. 3d.

9 G. Peters, *J. Org. Chem.* **1962**, *27*, 2198.

10 Treatment of **3a** with 2.2 molar amount of $^t$BuLi under similar conditions provided **8** in 44% $^1H$ NMR yield along with the recovery of **3c** in 33% $^{31}P$ NMR yield. The reason why 4.0 molar amount of $^t$BuLi was needed is not clear.

11 a) K. Goda, N. Inamoto, *Chem. Lett.* **1975**, 1009. b) K. Goda, R. Okazaki, K. Akiba, N. Inamoto, *Tetrahedron Lett.* **1976**, *17*, 181. c) K. Goda, R. Okazaki, K. Akiba, N. Inamoto, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 260. d) K. Goda, F. Hanafusa, N. Inamoto, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 818.

12 p$K_a$ ($Ph_2P(=S)SH$, in 80% alcohol) = 2.6: a) M. I. Kabachnik, T. A. Mastrukova, A. E. Shipov, T. A. Melentyeva, *Tetrahedron* **1960**, *9*, 10. p$K_a$ (PhC(=O)SH, in DMSO) = 5.2, p$K_a$ (PhSH, in DMSO) = 9.8: b) J. Courtot-Coupez, M. Le Démézet, *Bull. Soc. Chim. Fr.* **1969**, 1033.

13 T. B. Clark, K. A. Woerpel, *Organometallics* **2005**, *24*, 6212.

14 Y. Zhang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz, E. L. Vera, *Org. Lett.* **2004**, *6*, 1151.

15 W. A. Higgins, P. W. Vogel, W. G. Craig, *J. Am. Chem. Soc.* **1955**, *77*, 1864.

16 This operation converted dodecylthiolithium to 2-dodecylthioethanol. Without this, separation of the product **12** and dodecanethiol was difficult.

17 N. Riddel, W. Tam, *J. Org. Chem.* **2006**, *71*, 1934.

18 P. Zhong, M.-P. Guo, N.-P. Huang, *Synth. Commun.* **2002**, *32*, 175.