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# The reaction of triphenylstannylcobaloxime with enynes under photochemical and thermal conditions

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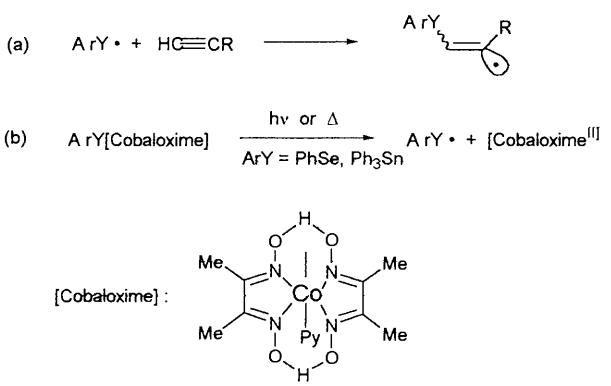
**Abstract**

Enynes having the 4-oxa-6-en-1-yne, 4-tosylaza-6-en-1-yne and 5-oxa-7-en-1-yne system, and 5,7-dioxa-1-octyne were reacted with triphenylstannylcobaloxime, which is a source of the triphenylstannyl radical and cobaloxime radical. The reaction pattern is different under photochemical and thermal conditions. Photochemical reaction gave the products formed by the addition of the triphenylstannyl radical to the acetylene group followed by the tandem addition of the intermediate vinyl radical to the intramolecular olefin. Thermal reaction gave triphenylstannyl-substitution products at the terminal position of the acetylene moiety. Thus, the photochemical reaction takes a free radical pathway, and the thermal reaction is proposed to take a single electron transfer mechanism. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Stannyl-cobalt complex; Enyne; Triphenylstannyl radical; Tandem cyclization; Triphenylstannyl-acetylide

## 1. Introduction

Heteroatom free radicals such as chalcogen [1–4] or stannyl radical [5–12] add to terminal acetylenes to yield vinyl-chalcogenides or vinylstannyl derivatives, respectively (Scheme 1(a)). Cyclization products are obtained from enynes such as hept-6-en-1-yne [13], 4-oxa-hept-6-en-1-yne [1c,5], 4-tosylaza-hept-6-en-1-yne [6], and diethyl 2-allyl-2-propynylmalonate [2,13b,14].




Scheme 1.

A heteroatom radical is usually generated from a dichalcogenide [14,15] or a distannane [16] and more conventionally by the combination of tributylstannane and AIBN. We have reported that arylselenocobaloxime [17] and triphenylstannylcobaloxime [18] (phenylseleno- and triphenylstannyl(pyridine)-bis-dimethylglyoximatocobalt(III)) are good sources of the arylseleno and arylstannyl radicals (Scheme 1(b)). Triphenylstannylcobaloxime is a unique complex which yields a pair of metal radicals of different character in the cleavage of the metal–metal bond. On reaction of the triphenylstannyl radical from triphenylstannylcobaloxime, the cobaloxime(II) species coexists in the reaction system and may affect the reaction process to give different products from those with stannanes.

In this paper, we compare the reactions between triphenylstannylcobaloxime and some enynes under photochemical and thermal conditions. Enynes **1**–**3** were selected because of the possible tandem cyclization of the intermediate vinyl radical, and homopropargyl ethers **4** and **5** were selected because of the possible 1,5-shift of the hydrogen activated by adjacent ether or vinyl functions.

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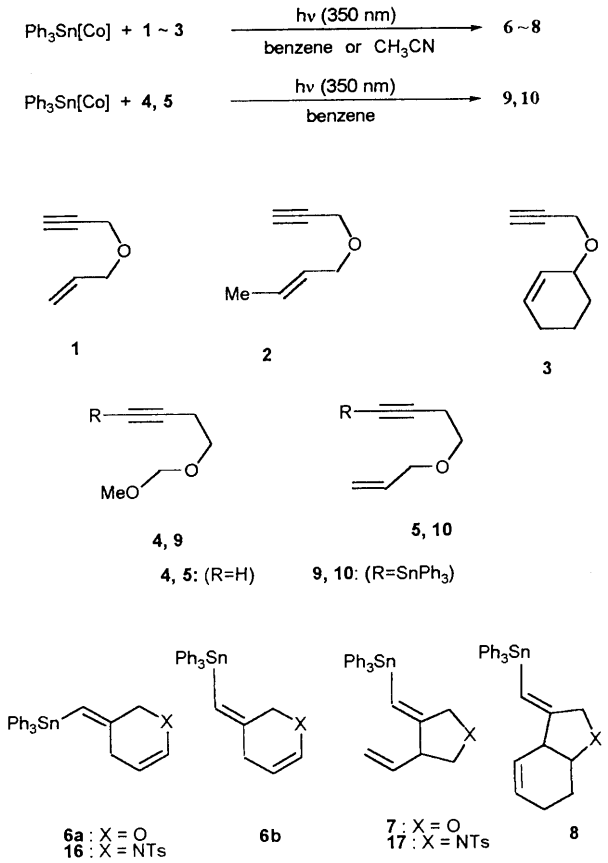



Scheme 2.

Table 1
Photoreaction of triphenylstannylcobaloxime with enynes

| Enyne | Solvent | Reaction time (h) | Product (yield/%) |
|---|---|---|---|
| **1** | Benzene [a] | 22 | **6a** [b] + **6b** [b] (38) |
| **1** | $CH_3CN$ [c] | 19 | Complex mixture |
| **2** | Benzene [a] | 17 | **7** (35) |
| **2** | $CH_3CN$ [c] | 21 | **7** (36) |
| **3** | Benzene [a] | 47 | **8** (41) |
| **3** | $CH_3CN$ [c] | 19 | **8** (48) |
| **4** | Benzene [a] | 94 | **9** (30) |
| **5** | Benzene [a] | 78 | **10** (40) |
| **14** | Benzene [d] | 120 | **16** (15) |
| **15** | Benzene [d] | 120 | **17** (19) |

[a] Enyne $1.0\times10^{-1}$ mol $l^{-1}$; $Ph_3Sn$(4-*t*-butylpyridine)[Co] $1.0\times10^{-2}$ mol $l^{-1}$.
[b] A 2:1 mixture of **6a** and **6b**.
[c] Enyne $5.0\times10^{-2}$ mol $l^{-1}$; $Ph_3Sn$(4-*t*-butylpyridine)[Co] $5.0\times10^{-3}$ mol $l^{-1}$.
[d] Enyne $1.0\times10^{-2}$ mol $l^{-1}$; $Ph_3Sn$(4-*t*-butylpyridine)[Co] $1.0\times10^{-2}$ mol $l^{-1}$.

## 2. Results and discussion

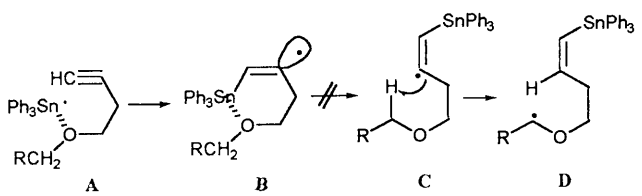
Photolysis of triphenylstannylcobaloxime has been known to generate a pair of triphenylstannyl and cobaloxime radicals [18,19], and the photolysis of a 1:10 mixture of triphenylstannylcobaloxime and enynes **1**–**3** in benzene or acetonitrile gave cyclized products **6**–**8** in moderate yields as shown in Scheme 2 and Table 1.

The reactions of homopropargyl derivatives **4** and **5** were expected to give the products derived from intramolecular 1,5-hydrogen transfer (Scheme 3). The photoreactions, however, gave only the substitution products **9** and **10** in poor yields after the prolonged irradiation (Scheme 2 and Table 1). Moderate or low yields of the addition products are mainly due to the formation of phenylcobaloxime and the insoluble polymers of diphenylstannylene units which show only the signals due to the phenyl group in the $^1$H-NMR spectrum.

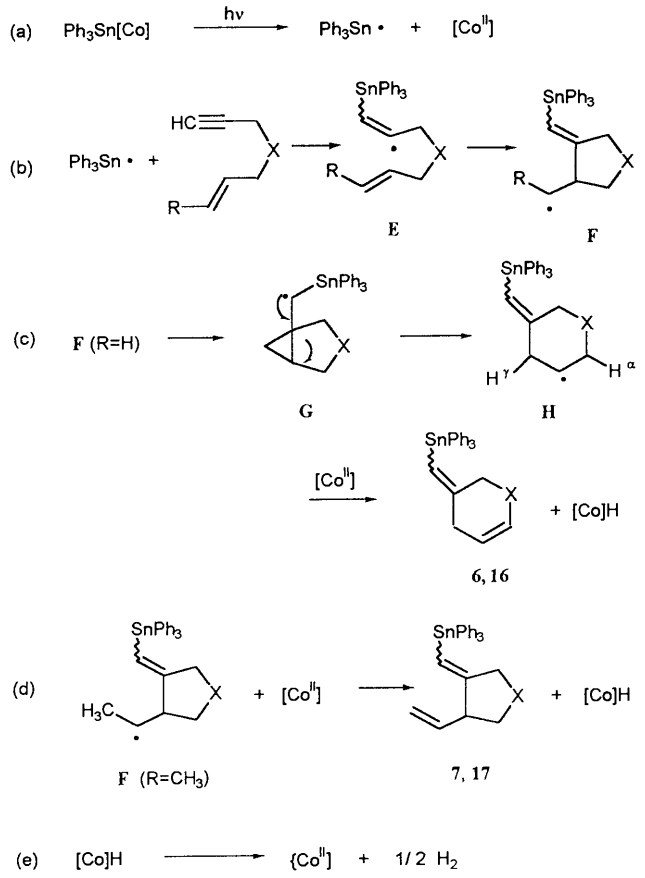
Product **6** (**6a**/**6b** = 2) shows twin peaks in the $^1$H-NMR for every proton. The spectrum is characterized by the double triplets ($J = 5.9$ and 3.7) at $\delta = 4.56$ and 4.67, and other double triplets ($J = 5.9$ and 2.4) at $\delta = 6.43$ and 6.30 due to the *endo*-cyclic olefin. Two ring methylenes give multiplets at $\delta = 2.74$ and 3.00 (next to the ring olefin) and singlets at $\delta = 4.39$ and 4.29 (next to the oxygen). Signal assignment was made by $^1$H-$^1$H COSY (500 MHz), and the *E*/*Z* ratio of **6a** and **6b** was based on the NOE observation (300 MHz) between the hydrogen of *exo*-cyclic olefin and the methylene next to the ring oxygen (*E*-isomer) or the methylene next to the ring olefin (*Z*-isomer).

Structure **7** was characterized by the typical pattern of vinyl signals (3H) at $\delta = 5.1$–5.7 region, the signals of *exo*-olefin at $\delta = 6.10$ (multiplet), and two ring methylene groups at $\delta = 3.56$, 4.05, 4.19 and 4.13. The signal assignment was done by $^1$H-$^1$H COSY and is shown in the Section 3. Structure **8** was deduced from the mechanistic similarity to the formation of **7** and the analysis of the $^1$H-NMR spectrum including $^1$H-$^1$H COSY. Signals due to the *endo*-cyclic olefin protons appear at $\delta = 5.67$ (double triplet) and 5.77 (multiplet), and the *exo*-cyclic olefin proton appears at $\delta = 6.15$ (double triplet). The methylene protons in the five-membered ring appear at $\delta = 4.10$ and 4.17 (double double doublet).

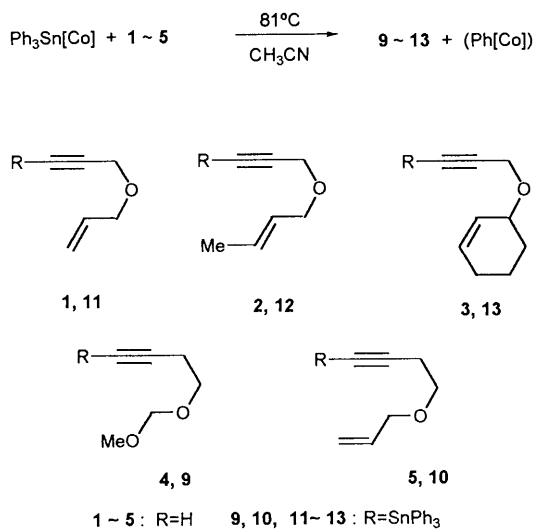
The formation processes of **6** and **7** are shown in Scheme 4. These tandem processes are analogous to the free radical cyclizations of enynes reported by Beckwith and O'Shea [13a], Stork and Mock [13b], and Malacria et al. [20]. The less hindered α-hydrogen ($H^{\alpha}$) in **H** is abstracted by the coexisting cobaloxime(II) species in preference to the sterically hindered γ-hydrogen ($H^{\gamma}$).




Scheme 3.




Scheme 4.




Scheme 5.

Similarly, the least hindered methyl hydrogen from the intermediate **F** ($R = CH_3$) is abstracted by cobaloxime(II) to give product **7** (Scheme 4(d)) [21,22]. The same type of reaction with a stannane terminates the tandem cyclization by the hydrogen abstraction by **H** to give a mono-ene product [13,14]. In contrast, the products from the reaction of triphenylstannyl-cobaloxime are dienes, 3-oxa-5-(2-triphenylstannylmethylen)-cyclohex-1-ene (6) (Scheme 4(c)).

Nativi and Taddei proposed the interaction between the triphenylstannyl radical and an ether function [23]. This interaction with a homopropargyl ether function in **4** and **5** (Scheme 3(**A** and **B**)) may prevent the conformation **C** for the 1,5-hydrogen transfer from the activated methylene to the vinyl radical as reported in a few cases [24–28]. One of the plausible accounts for the formation of **9** and **10** is that the addition of the triphenylstannyl radical to the acetylene group is reversible and that the intermediate **B** (Scheme 3) is a non-productive one. As a result only a slow thermal reaction (described later) takes place after the prolonged reaction period (Table 1). Thus the photoreactions of triphenylstannylcobaloxime are accounted for by the radical process triggered by the addition of the triphenylstannyl radical to the terminal acetylenes.

Next, triphenylstannylcobaloxime [18] was reacted with enynes **1**–**5** in boiling acetonitrile (81°C) to compare the reactivity under photochemical and thermal conditions, and triphenylstannyl-substituted products **11**–**13**, **9** and **10** were obtained as shown in Scheme 5 and Table 2. Similar thermal reactions in boiling benzene were extremely slow and gave complex mixtures. Structures **9**–**13** were unequivocally determined from the displacement of the $^1$H-NMR signal due to the terminal acetylenic hydrogen with the signals of the triphenylstannyl group.

Under the thermal conditions phenylcobalaoxime and a polymer of the diphenylstannyl residue were formed in considerable amounts, and the yields of **9**–**13** remained at moderate or low figures (Table 2). These by-products must originate from a process other than the triphenylstannyl substitution of acetylenes, and its mechanism is still ambiguous.

The photoreactions of enynes **14** and **15** (Fig. 1) having a tosylaza-bridge show a poor but similar type of photo-reaction with enynes **1**–**3**, and the products **16** and **17** were obtained in low yields after a prolonged irradiation in benzene (Scheme 2 and Table 1). In acetonitrile, however, those enynes having the *N*-tosyl

Table 2
Thermal reaction of triphenylstannylcobaloxime with enynes [a]

| Enyne | Reaction time (h) | Product (yield/%) |
|---|---|---|
| **1** | 22 | **11** (33) |
| **2** | 17 | **12** (23) |
| **3** | 17 | **13** (16) |
| **4** | 19 | **9** (46) |
| **5** | 18 | **10** (36) |

[a] Enyne $2.0 \times 10^{-1}$ mol $l^{-1}$; $Ph_3Sn$(4-*t*-butyl-pyridine)[Co] $2.0 \times 10^{-2}$ mol $l^{-1}$; solvent, dry acetonitrile.

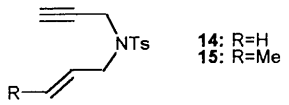
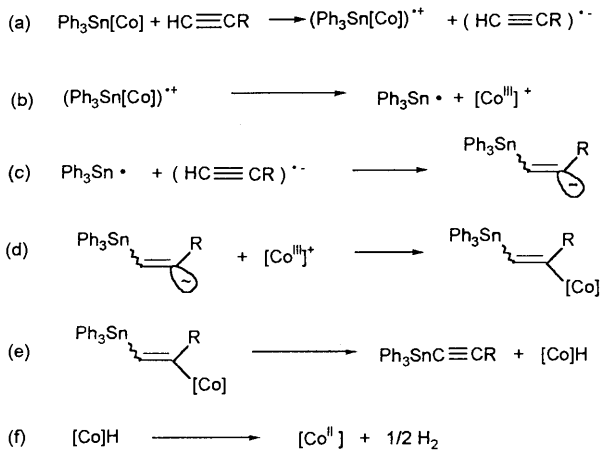
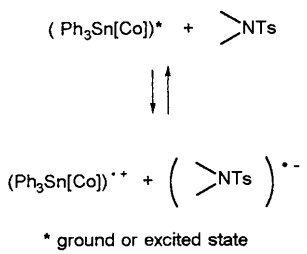



Fig. 1. Enynes **14** and **15**.




Scheme 6.




Scheme 7.

group show no reactivity toward triphenystannylcobaloxime under both photochemical and thermal conditions.

Tosylate **14** is not only inert to triphenylstannylcobaloxime but also inhibits the reaction of enyne **4** with the stannylcobaloxime in acetonitrile. The ene and yne part of **14** is unrelated to this inhibition because the addition of a molar equivalent of *N*,*N*-diethyl-*p*-toluenesulfonamide to the thermal reaction system of **4** (0.20 mol $l^{-1}$) reduced the yield of **9** from 46% to 7.1% under the same conditions. These findings prompt us to speculate the single electron transfer mechanism depicted in Scheme 6 as one of the most probable reaction mechanisms.

Processes (a)–(c) in Scheme 6 can take place in the single solvent-cage formed partly from the acetylenes, and the triphenylstannyl radical formed in step (b) dissipates by an in-cage coupling (c) before the diffusion from the solvent cage for the addition to untouched enynes. The coupling of the resulting vinyl anion and cobaloxime(III) cation gives a (*β*-triphenylstannyl)vinylcobaloxime (d) which decomposes into a triphenylstannyl-acetylene and hydrocobaloxime (e). This elimination step must be irreversible due to the loss of hydridocobaloxime by the decomposition into hydrogen and cobaloxime(II) (f) [29,30]. If the thermal reaction involves (triphenylstannyl)vinyl radical as an intermediate, it is difficult to explain the lack of tendem addition products **6**–**8** from enynes **1**–**3**, the solvent effect, and the inhibitory effect by tosylamides.

The intermediate (β-triphenylstannyl)vinylcobaloxime ((d) in Scheme 6) was not proven in the present case but (β-phenylseleno)vinylcobaloxime is a major product of the reaction of (phenylseleno)cobaloxime with acetylenes [17]. We have no definite explanation of this difference in the stability of the two kinds of vinylcobaloximes. If the reactive species is a triphenylstannyl cation other than the radical, the olefinic part of the enyne is more susceptible to the stannyl cation to give a different type of product.

There must be an efficient scavenging process in the photochemical and thermal reactions between *N*-tosylates (**14** and **15**) and the stannylcobaloxime in acetonitrile, a polar solvent. One of the reasonable accounts is a preferential single electron transfer between triphenylstannylcobaloxime and an *N*-tosyl group (Scheme 7). Triphenylstannylcobaloxime seems to be a good electron donor, and an excited triphenylstannylcobaloxime seems an even better electron donor in acetonitrile.

In conclusion, triphenystannylcobaloxime shows different reactivities toward the enynes under photochemical and thermal conditions. The reaction accompanies the thermal decomposition of triphenylstannylcobaloxime to give phenylcobaloxime and the formation of a polymer from diphenylstannylene units, and the moderate yields of the products limit the synthetic utilities of the present reactions. Nevertheless, it is noteworthy that triphenylstannylcobaloxime can provide both stannyl and cobalt free radicals in the photoreaction. The photoreaction proceeds by the addition of a triphenylstannyl radical to the terminal acetylene followed by the tandem addition of the vinyl radical to an intramolecular olefin and the termination by the hydrogen elimination by the coexisting cobaloxime(II) radical. When the intramolecular olefinic group is not located in the proper position to cause *exo*-5-*trig* cyclization, the tandem addition does not take place and the slow thermal decomposition produces acetylene-substituted products. On the other hand, the thermal reaction of triphenylstannylcobaloxime with enynes yields triphenylstannyl-acetylenes and can be accounted for by a single electron transfer mechanism. No free radical mechanism takes place under the thermal conditions as seen in the case of the reactions of phenylselenocobaloxime or tributylstannane with acetylenes.

## 3. Experimental

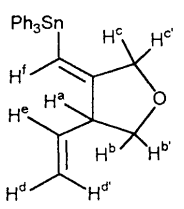
### 3.1. General

$^1$H-NMR spectra were recorded on a JEOL Al-300 (300 MHz), and $^1$H-$^1$H COSY and NOE measurement were done using a JEOL JMN-500 (500 MHz) spectrometer. The measurements were done in deuteriochloroform solutions containing TMS as an internal standard, and chemical shifts and coupling constants are recorded in $\delta$-values and Hertz, respectively. IR spectra were recorded on a Horiba FT-710 spectrometer in chloroform solution. FAB-mass spectra were recorded on a JEOL DX-300 spectrometer using *meta*-nitrobenzylalcohol or glycerol as a matrix medium. All the spectra and elemental analyses were performed using the facilities of the Materials Characterization Central Laboratory of Waseda University. Photo-irradiations were done using a Rayonet RPR-100 photoreactor equipped with 350 nm lamps. Dry benzene free of thiophene and acetonitrile were dried over phosphorous pentoxide followed by calcium hydride for the thermal and photochemical reactions. Preparative TLC was performed using $20 \times 20 \times 0.2$ cm plates of silica gel (Merck 60, PF254).

### 3.2. Starting materials

Enynes **1**–**5** [1c, 31–33] and **14** [34] were prepared by the reported methods and all the spectral data coincided with the reported ones. Enyne **15** was prepared by the same procedure for the preparation of enyne **14** starting from propargyl bromide and *N*-crotyl-*p*-toluenesulfonamide.

**15**: m.p. 63.0–64.0. $^1$H-NMR (300 MHz): 1.69 (3H, d, $J = 6.4$), 1.99 (1H, t, $J = 2.2$), 2.42 (3H, s), 3.75 (2H, d, $J = 6.6$), 4.08 (2H, d, $J = 2.2$), 5.36 (1H, dq, $J = 15.1$ and 6.4), 5.70 (1H, dt, $J = 15.1$ and 6.6), 7.29 (2H, d, $J = 8.1$), 7.72 (2H, d, $J = 8.1$). EI-mass(70 eV): $m/z =$ 263($M^+$, 23%). IR ($cm^{-1}$): 3307, 1559, 1436, 1347, 1162, 1092. Anal. Found: C, 63.80; H, 6.39; N, 5.40. Calc. for $C_{14}H_{17}NO_2Sn$: C, 63.85; H, 6.51; N, 5.32%.




7 (NMR assignment)

Fig. 2. The NMR assignment of **7**.

### 3.3. General procedure for the photoreaction of triphenylstannylcobaloxime with enynes

A mixture of triphenylstannylcobaloxime ($2.0 \times 10^{-4}$ moles) and one of the enynes ($4.0 \times 10^{-3}$ moles) in 20 ml of dry benzene was placed in two Pyrex reaction vessels and deaerated in an ultrasonic bath with introduction of argon. The photoreactions were monitored by TLC analyses of aliquots of the reaction mixtures. In the case of the photoreaction in acetonitrile, a mixture of triphenylstannylcobaloxime ($1.0 \times 10^{-4}$ moles) and one of the enynes ($1.0 \times 10^{-3}$ moles) in 20 ml of dry acetonitrile was used due to the low solubility of triphenylstannylcobaloxime at ambient temperature.

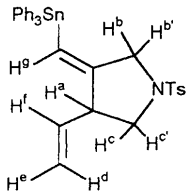
After irradiation for the period cited in Table 1, the reaction mixtures were condensed in vacuo and the residues were passed through a short column of Florisil using dichloromethane to remove polar degradation products. The eluates were subjected to preparative TLC using the mixed solvent of hexane–ethyl acetate. For the TLC separation of product **16** and **17**, chloroform and the mixture of hexane–ethyl acetate (15:1) were, respectively, used. Product **6** is an inseparable 2:1 mixture of the *E*- (**6a**) and **Z**-isomers (**6b**). All the $^1$H-NMR signals appear as a twin in 2:1 ratio. IR and mass measurements were done with this mixture.

**6**: oil (a 2:1 mixture of **6a** and **6b**). **6a**: $^1$H-NMR (300 MHz): 2.74 (2H, m), 4.39 (2H, s), 4.56 (1H, dt, $J = 5.9$ and 3.7), 6.08 (1H, s), 6.43 (1H, dt, $J = 5.9$ and 2.4), 7.30–7.42 (9H, m), 7.51–7.70 (6H, m). **6b**: $^1$H-NMR (300 MHz): 3.00 (2H, m), 4.29 (2H, s), 4.67 (1H, dt, $J = 5.9$ and 3.7), 6.09 (1H, s), 6.30 (1H, dt, $J = 5.9$ and 2.4), 7.30–7.42 (9H, m), 7.51–7.70 (6H, m). IR ($cm^{-1}$) (**6a** + **6b**): 1653, 1481, 1430, 1075. High-resolution mass (FAB): $m/z = 445.0651$. Calc. for $[C_{24}H_{22}O^{118}Sn + H^+]$: $m/z = 445.0614$.

**7**: oil. $^1$H-NMR (300 MHz): 3.43 (1H, dt, $J = 8.5$ and 8.5, Ha), 3.56 (1H, dd, $J = 8.5$ and 8.5, Hb), 4.05 (1H, ddd, $J = 14.0$, 2.4 and 2.4, Hc), 4.19 (1H, ddd, $J = 14.0$, 2.4 and 0.7, Hc), 5.15–5.18 (2H, m, Hdd′), 5.69 (1H, m, He), 6.10 (1H, dt, $J = 2.4$ and 2.4, Hf), 7.32–7.40 (9H, m), 7.50–7.58 (6H, m). IR ($cm^{-1}$): 1635, 1481, 1430, 1075. High-resolution mass (FAB): $m/z = 459.0793$. Calc. for $[C_{25}H_{24}O^{118}Sn + H^+]$: $m/z = 459.0791$ (the NMR assignment of **7** is shown in Fig. 2).

**8**: m.p. 109.0–110.0°C (hexane). $^1$H-NMR (300 MHz): 1.57–1.69 (2H, m), 1.78–1.99 (2H, m), 2.10–2.19 (1H, m), 4.10 (1H, ddd, $J = 14.0$, 2.6 and 0.9), 4.17 (1H, ddd, $J = 14.0$, 1.9 and 1.9), 4.23–4.29 (1H,dt, $J = 9.0$ and 3.0), 5.67 (1H, dt, $J = 9.9$ and 1.9), 5.77 (1H, m), 6.13–6.17 (1H, dt, $J = 2.5$ and 2.5), 7.32–7.40 (9H, m), 7.51–7.58 (6H, m). IR ($cm^{-1}$): 1624, 1481, 1430, 1075. Anal. Found: C, 66.72; H, 5.51. Calc. for $C_{27}H_{26}OSn$: C, 66.84; H, 5.40%.

**9**: oil. $^1$H-NMR (300 MHz): 2.67 (2H, t, $J = 7.0$), 3.34 (3H, s), 3.73 (2H, t, $J = 7.0$), 4.66 (2H, s), 7.32–




17 (NMR assignment)

Fig. 3. The NMR assignment of **17**.

7.49 (9H, m), 7.60–7.70 (6H, m). IR ($cm^{-1}$): 2120, 1643, 1481, 1431, 1257 1076. High-resolution mass (FAB): $m/z = 465.0877$. Calc. for $[C_{24}H_{24}O_2^{120}Sn + H^+]$: $m/z = 465.0832$.

**10**: oil. $^1$H-NMR (300 MHz): 2.66 (2H, t, $J = 7.2$), 3.65 (2H, t, $J = 7.2$), 4.03 (2H, ddd, $J = 5.7$, 1,7 and 1.7), 5.17 (1H, dtd, $J = 10.3$, 1.5 and 1.4), 5.29 (1H, dtd, $J = 17.2$, 1.5 and 1.4), 5.90 (1H, m), 7.31–7.44 (9H, m), 7.59–7.66 (6H, m). IR ($cm^{-1}$): 2157, 1646, 1482, 1431, 1097. FAB-mass: $m/z = 383$ and 381(17 and 10%, $M^+$–Ph), 351, 349(100 and 78%, $Ph_3Sn^+$), no molecular peak.

**16**: oil. $^1$H-NMR (300 MHz): 2.22 (3H, s), 2.58–2.65 (2H, m), 4.12 (2H, s), 4.89 (1H, dt, $J = 8.0$ and 3.6), 5.92 (1H, s), 6.66 (1H, dt, $J = 8.0$ and 2.0), 7.18 (2H, d, $J = 8.0$), 7.68 (2H, d, $J = 8.0$), 7.26–7.78 (15H, m). IR ($cm^{-1}$): 1652, 1645, 1446, 1429, 1164. High-resolution mass (FAB): $m/z = 600.1059$. Calc. for $[C_{31}H_{29}NO_2S^{-120}Sn + H^+]$: $m/z = 600.1019$.

**17**: powder. $^1$H-NMR (300 MHz): 2.42 (3H, s), 2.76 (1H, dd, $J = 9.2$ and 9.2, $H_a$), 3.41 (2H, m, $H_{bb'}$), 3.63 (1H, dd, $J = 9.2$ and 7.7, $H_c$), 3.76 (1H, m, $H_{c'}$), 5.16 (1H, dd, $J = 16.7$ and 0.7, $H_d$), 5.18 (1H, dd, $J = 10.3$ and 0.7, $H_e$), 5.52 (1H, ddd, $J = 16.7$, 10.3 and 9.2, $H_f$), 5.98–6.07 (1H, dt, $J = 2.7$ and 2.7, $H_g$), 7.18 (2H, d, $J = 8.1$), 7.33–7.75 (17H, m). IR ($cm^{-1}$): 1624, 1599, 1481, 1430, 1348, 1163. High-resolution mass (FAB): $m/z = 614.1135$. Calc. for $[C_{32}H_{31}NO_2S^{120}Sn + H^+]$: $m/z = 614.1176$ (the NMR assignment of **17** is shown in Fig. 3).

### *3.4. General procedure for the thermal reaction of triphenylstannylcobaloxime with enynes*

A mixture of triphenylstannylcobaloxime ($2.0 \times 10^{-4}$ moles) and one of the enynes ($2.0 \times 10^{-3}$ moles) in 10 ml of acetonitrile was refluxed for the period cited in Table 2 under an argon atmosphere. Acetonitrile was deaerated before use in an ultrasonic bath with bubbling argon. The reaction was monitored by TLC analysis of aliquots of the reaction mixture. After heating, the reaction mixture was condensed *in vacuo*, and the residue was passed through a short column of Florisil using dichloromethane to remove polar degradation products. The eluate was subjected to TLC separation using hexane-EtOAc (10:1) as a developing solvent.

**11**: oil. $^1$H-NMR (300 MHz): 4.14 (2H, diff.d, $J = 5.8$), 4.28 (2H, s), 5.22 (1H, diff.d, $J = 10.3$), 5.32 (1H, diff.d, $J = 17.2$), 5.91 (1H, ddt, $J = 17.2$, 10.3 and 5.8), 7.34–7.47 (9H, m), 7.58–7.68 (6H, m). IR ($cm^{-1}$): 2156, 1650, 1481, 1430, 1260, 1076. High-resolution mass (FAB): $m/z = 447.0744$. Calc. for $[C_{24}H_{22}O^{120}Sn + H^+]$: $m/z = 447.0771$.

**12**: oil. $^1$H-NMR (300 MHz): 1.71 (3H, br.d, $J = 6.4$), 4.06 (2H, d, $J = 6.3$), 4.25 (2H, s), 5.60 (1H, dt, $J = 15.2$ and 6.3), 5.76 (1H, dq, $J = 15.2$ and 6.4), 7.36–7.47 (9H, m), 7.57–7.70 (6H, m). IR ($cm^{-1}$): 2155, 1482, 1431, 1350, 1092. FAB-mass: $m/z = 382$ and 381(13 and 5.4%, $M^+$–Ph), 351 and 349(35 and 100%, $Ph_3Sn^+$), no molecular peak.

**13**: oil. $^1$H-NMR (300 MHz): 1.48–2.10 (6H, m), 4.15–4.25 (1H, m), 4.33 (2H, s), 5.83–5.92 (2H, m), 7.35–7.47 (9H, m), 7.75–7.70 (6H, m). IR ($cm^{-1}$): 2155, 1650, 1482, 1431, 1346, 1077. FAB-mass: $m/z = 487$ and 485 (1.0 and 2.1%, $[M + H^+]$), 351 and 349 (68 and 100%, $Ph_3Sn^+$), 197 and 195 (51 and 45%, $PhSn^+$), no molecular peak.

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