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The First Aryne Evolution from the Reactions of Selenonium Salts with Aryllithiums

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Abstract—The first example of the benzyne generation was found in the reactions of alkynylselenonium salt **1a** with 1.0 equiv. of phenyllithium in THF at room temperature for 3 h. The formation of the aryne intermediate was confirmed in the reactions of alkynylselenonium salt **1b** and tri-*p*-tolylselenonium salt **6b** with tolyllithium, which gave a mixture of alkynylbiphenyl derivatives **18** and **19** in 19% yield (**18**:**19**=11:8) and a mixture of bitolyls **28** and **29** in 63% yield (**28**:**29**=2:1), respectively. The reaction mechanisms of these reactions are discussed.

Introduction

These days, numerous hypervalent chalcogen compounds, of which the chalcogen atom formally possesses more than eight valence electrons, have been synthesized.[1] Among them, sulfuranes and selenuranes with only carbon ligands can be prepared from the reactions of triarylsulfonium and selenonium salts with aryllithiums, respectively.[2] Reactions of triarylsulfonium salts with aryllithiums have been widely studied[3] and it is well-known that these reactions proceed via the hypervalent intermediate.[4] As a matter of fact, these reactions also form aryne intermediates because nucleophiles attack the *o*-proton of the aryl group of sulfonium salts. Khim and Oae reported that the reactions of tritolylsulfonium bromide with phenyllithium proceeded via the aryne formation as well as the nucleophilic attack of the phenyl anion on the sulfur.[4a] Andersen's group showed the formation of the benzyne intermediate from the reaction of tritolylsulfonium salt with *p*-tolyllithium.[5] On the other hand, few reports on the reactions of triarylselenonium salts with aryllithiums have been published till now.[2,6] Interestingly, there has been no report that aryne intermediates are generated from the reactions of selenonium salts with nucleophiles. In the course of our research on diphenylalkynylselenonium salts,[7] we have recently found the first formation of the benzyne intermediate from the reactions of alkynylselenonium salts with phenyllithium,[8] and here we wish to describe our extensive study on the preliminary result obtained.

Keywords: selenonium ions; arynes; hypervalent elements; lithium and compounds.

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Results and Discussion

First, we examined reactions of diphenyl(phenylethynyl)selenonium triflate **1a** with phenyllithium in THF (Scheme 1, Table 1). Reactions of the compound **1a** with 0.5–5 equiv. of phenyllithium at room temperature for 3 h gave complex mixtures in all cases. Yields of the products except for selenonium salts were analyzed by HPLC. Compound **7** was isolated and its structure was determined in comparison with its spectral data with those of compounds **7** and **8**. The authentic samples **7** and **8** were prepared by the method as shown in Scheme 2. Bromination of alkene **9**[9] followed by dehydrobromination with *t*-BuOK afforded 1-(*o*-biphenylyl)-2-phenylethyne **7** in 33% yield. 1-(*m*-Biphenylyl)-2-phenylethyne **8** was similarly prepared from alkene **10**[10] in 90% yield. The reactions shown in Scheme 1 and Table 1 revealed four interesting results: (1) when 0.5 equiv. of phenyllithium was used, the starting material **1a** was not recovered but triphenylselenonium triflate **6a** was obtained (entry 1); (2) 1,4-diphenylbutadiyne **5** was obtained in all cases; (3) alkynylbiphenyl **7** was given in low yields (entries 2–5); (4) when the quantity of phenyllithium was increased, the yields of diyne **5** and alkynylbiphenyl **7** were decreased and phenylethyne **2** was increased.

The result (1) implies that ligand exchange would occur in the first step of this reaction (Scheme 3). Therefore, we investigated the reaction of alkynylselenonium salt **1a** with 1 equiv. of phenyllithium in THF at −78°C for 3 h followed by quenching with aqueous TfOH at that temperature. Triphenylselenonium salt **6a** was obtained in 86% yield as the main product accompanied with the starting material, alkynylselenonium salt **1a** in 5% yield. The finding

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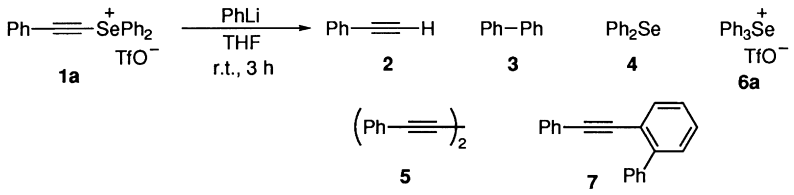
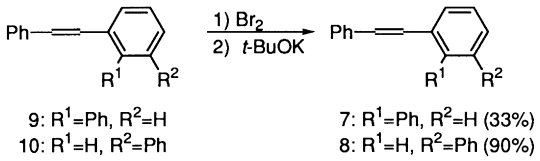


Scheme 1.

Table 1. Reactions of alkynylselenonium salt **1a** with phenyllithium

Entry	Phenyllithium (equiv.)	Products (% yield)[a]					
1	0.5	**2** (10)		**4** (56)	**5** (34)	**6a**[b] (18)	
2	1.0	**2** (14)	**3** (20)	**4** (92)	**5** (25)		**7** (15)
3	2.0	**2** (38)	**3**[c]	**4** (99)	**5** (13)		**7** (7)
4	3.0	**2** (51)	**3**[c]	**4** (100)	**5** (2)		**7** (5)
5	5.0	**2** (60)	**3**[c]	**4** (100)	**5** (2)		**7** (4)

[a] Determined by HPLC.
[b] Isolated yield.
[c] Biphenyl **3** was also obtained from the coupling of phenyllithium and, therefore, the yield of **3** is meaningless.

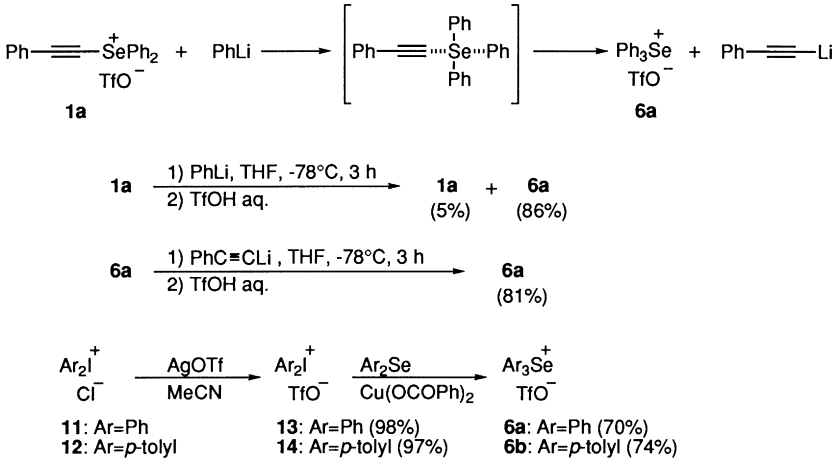


Scheme 2.

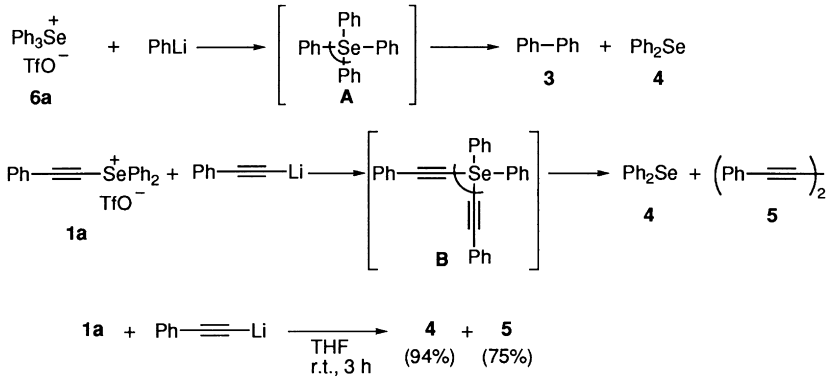
strongly supported our assumption that ligand exchange reaction occurred. On the other hand, the reaction of triphenylselenonium salt **6a** with phenylethynyllithium was also examined. Triphenylselenonium salt **6a** was prepared by the reaction of diphenyliodonium triflate **13**, derived from the corresponding chloride **11**[11,12] and silver triflate, with diphenyl selenide in the presence of copper(II) benzoate in 74% yield. The reaction of **6a** with the phenylethynyllithium did not proceed and the starting material **6a** was recovered (81%). This shows that the ligand exchange reaction was not an equilibrium reaction because phenyllithium is much more nucleophilic than phenylethynyllithium. Thus, the nucleophilic attack of phenyllithium at the selenium of **1a** gives rise to ligand exchange to form triphenylselenonium salt **6a** and phenylethynyllithium concertedly.

The selenonium salt **6a**, generated in situ, reacts with phenyllithium to form the selenurane A, which subsequently brings about the ligand coupling reaction to produce biphenyl **3** and selenide **4** (Scheme 4). On the other hand, the eliminated phenylethynyllithium reacts with unreacted alkynylselenonium salt **1a** to form selenurane intermediate B, whose two ethynyl ligands couple with each other to afford selenide **4** and diyne **5**. This route was experimentally supported by the result that the reaction of alkynylselenonium salt **1a** with phenylethynyllithium gave selenide **4** and diyne **5** in 94 and 75% yields, respectively. When the quantity of phenyllithium was increased, the yield of diyne **5** was decreased and phenylethyne **2** was increased (Table 1). This is attributed to the fact that alkynylselenonium salt **1a** reacts more rapidly with excess phenyllithium than with phenylethynyllithium.

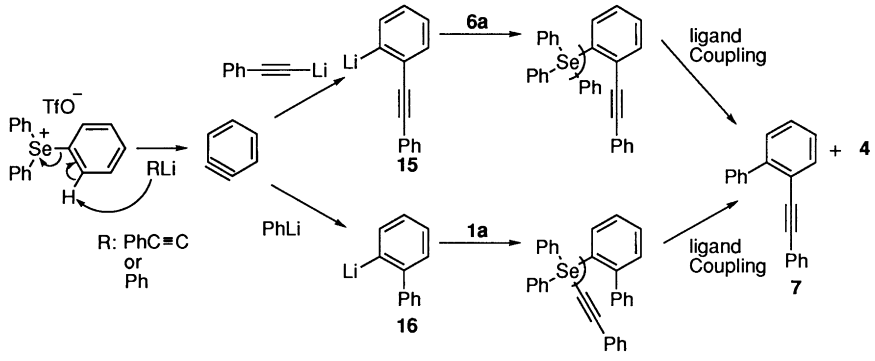
Alkynylbiphenyl **7** would be produced via benzyne. If phenyllithium abstracts the *o*-proton of the phenyl group



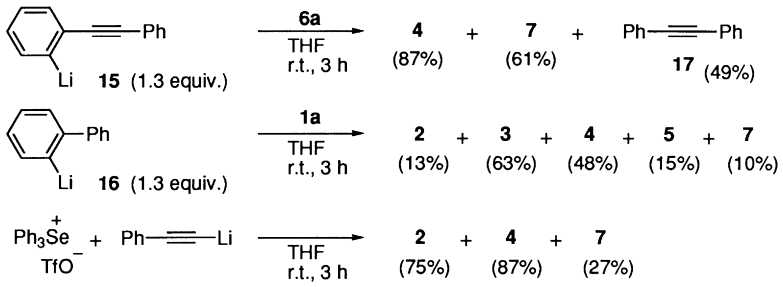
Scheme 3.



Scheme 4.

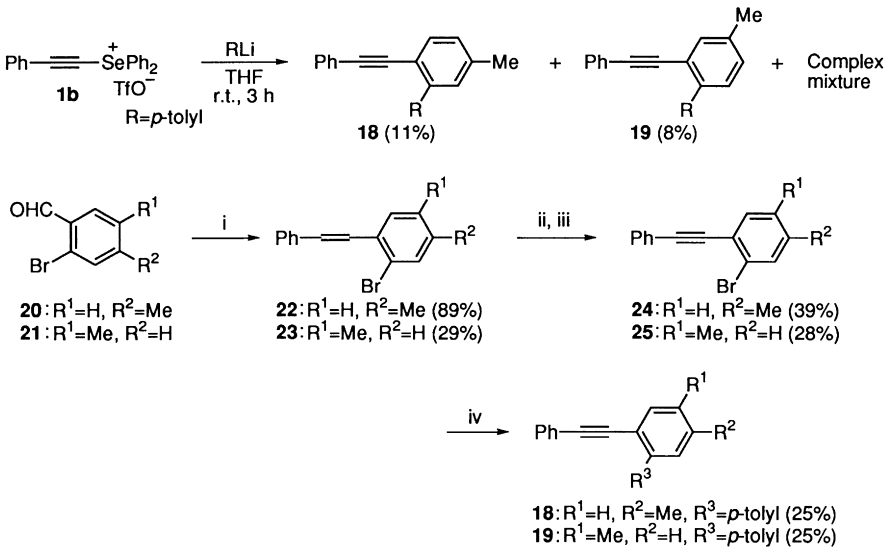


Scheme 5.



Scheme 6.

of alkynylselenonium salt **1a**, benzyne and 1-phenyl-2-(phenylseleno)ethyne should be obtained. However, the selenide was not obtained from this reaction. Therefore, benzyne would be generated from the reaction of triphenylselenonium salt **6a** with phenyllithium or phenylethynyllithium (Scheme 5). Two pathways are possible for formation of alkynylbiphenyl **7**. One way goes through the intermediate **15** which was formed via the reaction of benzyne with phenylethynyllithium, and the other is a route via the intermediate **16** which is generated from the reaction with phenyllithium. In order to confirm these pathways, we conducted the reactions of selenonium salts **6a** and **1a** with *o*-(phenylethynyl)phenyllithium **15** and *o*-biphenylyllithium **16**, respectively. These aryllithiums were prepared from *n*-butyllithium and the corresponding aryl bromides in THF at room temperature for 3 h (Scheme 6). The former reaction afforded ligand coupling products **4** (87%) and **7** (61%), while the latter gave a small amount of **7** together with some other products **2**–**5**. This result showed that alkynylbiphenyl **7** would be mainly produced from the reaction of **6a** with **15**. However, the reasons why the selenurane which was formed from aryllithium **15** and selenonium salt **6a** underwent the selective ligand-coupling between the phenyl and the phenylethynylphenyl groups are not clear so far. When more than 2 equiv. of phenyllithium were used, excess phenyllithium, which is more nucleophilic than ethynyllithium, reacted with benzyne and then with triphenylselenonium salt **6a** faster than phenylethynyllithium, and consequently the yield of alkynylbiphenyl **7** was decreased. Although the reaction of triphenylselenonium salt **6a** with phenylethynyllithium at −78°C did not proceed as mentioned above, the reaction at room temperature afforded alkynylbiphenyl **7** in 27% yield. It is interesting that benzyne was even evolved from the reaction of triphenylselenonium salt **6a** with phenylethynyllithium, a much lower nucleophilic carbanion than phenyllithium.[13]

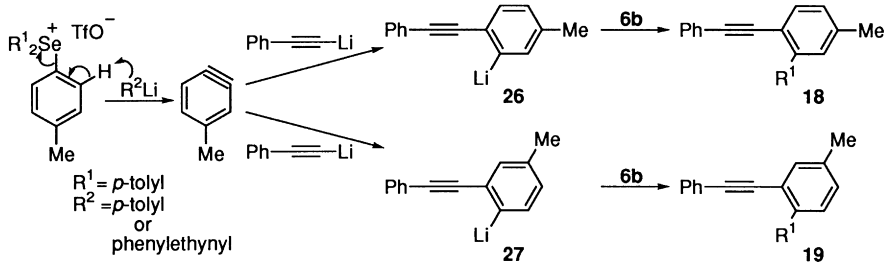


Scheme 7. *Reagents and conditions:* (i) $PhCH_2P^+Ph_3Br^-$, *n*-BuLi, THF, r.t.; (ii) Br_2, CH_2Cl_2, r.t.; (iii) *t*-BuOK, *t*-BuOH, reflux; (iv) *n*-BuLi, $(p\text{-tolyl})_3Se^+TfO^-$ **6b**, THF, r.t.

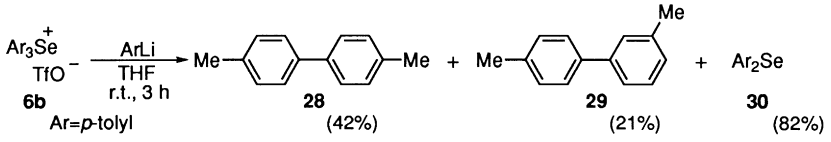
This result indicated that the acidity of the *o*-proton of the phenyl group in triphenylselenonium salt **6a** was fairly high.

In order to study the formation of an aryne more precisely, we planned to conduct the reaction of di-*p*-tolyl(phenylethynyl)selenonium triflate **1b**[7b] with *p*-tolyllithium in THF. If an unsymmetrical aryne, 4-methylbenzyne is formed, two types of alkynylbiphenyls **18** and **19** should be produced (Scheme 7). Actually, the reaction of alkynylselenonium salt **1b** with *p*-tolyllithium in THF at room temperature afforded a complex mixture and the products were separated by preparative TLC to give a mixture of alkynylbiphenyls **18** and **19** in 19% yield (**18**:**19**=11:8) as we had expected. These compounds were identical with authentic samples **18** and **19**. The authentic samples were prepared by an alternative method shown in Scheme 7. The Wittig reaction of aldehyde **20**[15] with benzylphosphorane gave olefin **22** and subsequent bromination and dehydrobromination with *t*-BuOK afforded *o*-bromoalkynylbenzene derivative **24** in 35% yield from **20**. The reaction of tri-*p*-tolylselenonium salt **6b** with an aryllithium derivative, which was derived from alkyne **24** and *n*-butyllithium, furnished the desired product 2-(phenylethynyl)-5,4′-dimethyl-1,1′-biphenyl **18** in 25% yield. 2-(Phenylethynyl)-4,4′-dimethyl-1,1′-biphenyl **19** was similarly prepared from aldehyde **21**.[16] Thus, 4-methylbenzyne is generated from **6b** with RLi, and reacts with phenylethynyllithium at both 3- and 4-positions to form the carbanions **26** and **27**, respectively (Scheme 8). These tolyllithiums **26** and **27** react with **6b** and afford the ligand coupling products **18** and **19**, respectively. More than 13% of the reaction went through aryne and the isomeric ratio of **18** and **19** (ca. 1:1) was faithfully similar to that of Oae's report.[4a]

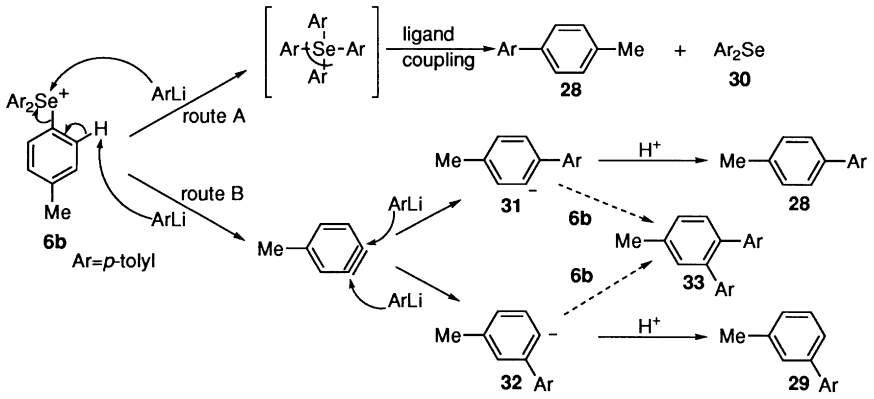
When the ligands on the selenonium salt and an aryl group of aryllithium are different, the reaction would be very complex and several products with similar polarity are produced and product separation is troublesome. Therefore, we planned to match effectively tri-*p*-tolylselenonium salt **6b** with *p*-tolyllithium. Tri-*p*-tolylselenonium triflate **6b**



Scheme 8.



Scheme 9.



Scheme 10.

was prepared from **12**[11] as shown in Scheme 3. The reaction of the selenonium salt **6b** with *p*-tolyllithium in THF at room temperature for 3 h was carried out and a mixture of bitolyls **28** and **29**[17] was isolated in 63% yield (**28**:**29**=2:1) besides selenide **30** (Scheme 9). Compounds **28** and **29** were determined by comparison of their ^{1}H NMR spectra with those of authentic samples. On the basis of the result that bitolyl **29** was obtained, the reaction mechanism involving an aryne intermediate is shown in Scheme 10. The nucleophilic attack of *p*-tolyllithium at the selenium atom of selenonium salt **6b** forms tetra-*p*-tolylselenurane intermediate. The ligand coupling reaction of the selenurane affords bitolyl **28** and selenide **30** (route A). On the other hand, *p*-tolyllithium as a base abstracts an *o*-aromatic proton of tri-*p*-tolylselenonium salt **6b** to generate 4-methylbenzyne. The aryne reacts with *p*-tolyllithium at both 3- and 4-positions to give carbanions **31** and **32**, respectively, and the protonation of them afforded bitolyls **28** and **29**. If the ratio of the *p*-tolyllithium attack at 3- or 4-position of 4-methylbenzyne was ca. 1:1, the same as that of reaction of **1b** with *p*-tolyllithium, more than 42% of the reaction would have proceeded via the aryne intermediate. We did not detect terphenyl derivative **33** which would be generated by ligand coupling reaction of a selenurane generated from carbanions **31** or **32** and tri-*p*-tolylselenonium salt **6b**. These results indicated that the reaction of tri-*p*-tolylselenonium salt **6b** with *p*-tolyllithium proceeded through both ligand coupling reaction and aryne formation. The reason why terphenyl derivative **33**, which was expected to be formed, was not obtained would be attributable to the steric hindrance of carbanions **31** and **32**.

Conclusion

The reaction of alkynylselenonium salt **1a** with phenyllithium produced characteristic compounds, diyne **5** and alkynylbiphenyl **7**, which could not be generated from only a ligand coupling reaction. The present investigation showed that this reaction proceeded through both ligand coupling reaction of a selenurane intermediate and aryne formation. The aryne formation was elucidated from the reactions of selenonium salts having tolyl groups. This is the first example of the aryne formation in the reactions of selenonium salts with nucleophiles. The *o*-proton of the aryl group of a selenonium salt was readily abstracted by phenylethynyllithium as well as phenyllithium. Treatment of a triarylselenonium salt with a base would lead to a new method for the easy formation of aryne.

Experimental

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (NaCl) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL GX-270 (270 MHz) or a JEOL EX-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR spectra were obtained on a JEOL EX-400 spectrometer. The *J* values are given in Hz. Mass spectra were recorded on a JEOL JMS-SX 102A spectrometer with a direct-insertion probe at 70 eV. Elemental analyses of new compounds were performed by a Yanaco CHN Corder MT-5. All chromatographic isolations were accomplished with either Kieselgel 60 (Merck) or BW-127ZH (Fuji Silysia) for column chromatography or Kieselgel 60 PF_{254} containing gypsum (Merck) for PTLC. HPLC analyses were carried out using a JASCO chromatography system (PU–986, UV–970) with monitoring of the 220 nm, DEVELOSIL 60-5 HPLC column with a flow rate of 1.0 cm^3 min^{-1} eluting hexane and their data were recorded with a System Instruments integrator (Chromatocorder 21J). Authentic pure samples of ethynylbenzene, biphenyl, diphenylselenide and diphenylethyne were commercially available.

Reactions of alkynylselenonium salt 1a with phenyllithium: general procedure

Phenyllithium in cyclohexane–ether was added dropwise to a THF solution (10 ml) of alkynylselenonium salt **1a**[7b] (290 mg, 0.6 mmol) at room temperature under argon. After being stirred magnetically for 3 h at ambient temperature, the reaction mixture was quenched with water (5 ml), and extracted with hexane. Reaction products were identified by comparison of the retention times with those of authentic samples except triphenylselenonium salt **6a**. Yields of the products estimated were determined by means of HPLC using *p*-iodoanisole as an internal standard and described on the basis of starting alkynylselenonium salt **1a**. Products and their yields were summarized in

Table 1. 1,4-Diphenyl-1,3-butadiyne **5** was prepared by the method of Hay.[18] Alkynylbiphenyl **7** was isolated by preparative TLC (hexane) and its structure was determined by comparison of the spectral data and the retention time with those of an authentic sample. In entry 1, the aqueous layer was extracted with $CHCl_3$ and the organic phase was dried over anhydrous $MgSO_4$. After the solvent was evaporated under reduced pressure, the precipitate was washed several times with ether to give triphenylselenonium salt **6a** (50 mg, 18%), which was identical with an authentic sample.

1-(*o*-Biphenylyl)-2-phenylethyne 7. To a stirred solution of **9**[9] (*E*:*Z*=1:1) (400 mg, 1.6 mmol) in CH_2Cl_2 (20 ml) was added Br_2 (0.1 ml, 1.9 mmol) at 0°C under argon. After the reaction mixture was stirred for 2 h, sat. $Na_2S_2O_3$ (aq.) was added to it, and the whole was extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane) to give 1-(*o*-biphenylyl)-1,2-dibromo-2-phenylethane (221 mg, 46%) as a mixture of diastereomers (erythro:threo=1:1), δ_H(400 MHz; $CDCl_3$) 5.45 (1 H, d, *J*=10.3, CH), 5.53 (1 H, d, *J*=11.7, CH), 5.62 (1 H, d, *J*=10.3, CH), 5.69 (1 H, d, *J*=11.7, CH), 6.84 (2 H, d, *J*=7.8, ArH), 6.95 (1 H, d, *J*=7.6, ArH), 7.01–7.09 (3 H, m, ArH), 7.12 (1 H, t, *J*=7.6, ArH), 7.25–7.30 (8 H, m, ArH), 7.35–7.51 (11 H, m, ArH), 7.60 (1 H, d, *J*=7.6, ArH), 7.75 (1 H, d, *J*=7.8, ArH); δ_C(100 MHz; $CDCl_3$) 52.2, 56.08, 56.12, 59.7, 126.9, 127.53, 127.59, 127.68, 127.75, 127.79, 128.12, 128.17, 128.30, 128.39, 128.43, 128.48, 128.6, 128.8, 129.2, 130.0, 130.2, 136.3, 137.5, 138.3, 139.7, 139.8, 140.0, 140.7, 141.6; *m*/*z* (EI) 418 (1%, M^++4), 416 (2%, M^++2), 414 (1%, M^+), 255 (100). To a stirred solution of this compound (75 mg, 0.2 mmol) in *t*-BuOH (5 ml), 90% *t*-BuOK (60 mg, 0.5 mmol) was added at room temperature. The mixture was refluxed for 6 h, then quenched with water and extracted with hexane. The organic phase was dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by preparative TLC (hexane) to give **7** (45 mg, 98%) as yellow oil, (Found: C, 94.2; H, 5.67; $C_{20}H_{14}$ requires C, 94.45; H, 5.55%); ν_{max}(film)/cm^{-1} 2253; δ_H(400 MHz; $CDCl_3$) 7.25–7.33 (6 H, m, ArH), 7.35–7.46 (5 H, m, ArH), 7.63–7.67 (3 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 89.4, 92.2, 121.6, 123.5, 127.0, 127.5, 127.9, 128.1, 128.2, 128.5, 129.4, 129.5, 131.3, 132.8, 140.6, 143.9; *m*/*z* (EI) 254 (M^+, 88%), 253(100), 252 (65).

1-(*m*-Biphenylyl)-2-phenylethyne 8. A solution of (*Z*)-**10**[10] (200 mg, 0.8 mmol) in CH_2Cl_2 (5 ml) was similarly treated with Br_2 (0.1 ml, 1.9 mmol) at 0°C under argon. The raw product was purified by preparative TLC (hexane) to give 1-(*m*-biphenylyl)-1,2-dibromo-2-phenylethane (292 mg, 90%) as a single product detected by ^1H, ^{13}C NMR and mass spectra, δ_H(400 MHz; $CDCl_3$) 5.51 (1 H, d, *J*=8.0, CH), 5.54 (1 H, d, *J*=8.0, CH), 7.16–7.26 (7 H, m, ArH), 7.32–7.43 (7 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 59.0, 127.1, 127.4, 127.5, 127.6, 128.2, 128.5, 128.6, 128.7, 137.6, 138.1, 140.4, 141.1; *m*/*z* (EI) 418 (3%, M^++4), 416 (6%, M^++2), 414 (3%, M^+), 256 (100). The dibromo compound (292 mg, 0.7 mmol) was similarly dehydrobrominated with 90% *t*-BuOK (216 mg, 1.7 mmol). Compound **8** (179 mg, 100%) was obtained as a colorless solid, mp 39–41°C; ν_{max}(film)/cm^{-1} 2222; δ_H(400 MHz; $CDCl_3$) 7.32–7.37 (4 H, m, ArH), 7.39–7.45 (3 H, m, ArH), 7.51–7.60 (6 H, m, ArH), 7.77 (1 H, s, ArH); δ_C(100 MHz; $CDCl_3$) 89.4, 89.5, 123.2, 123.7, 127.1, 127.6, 128.28, 128.33, 128.8, 130.3, 131.6, 140.3, 141.4; *m*/*z* (EI) 254 (M^+, 100%), 252(25); HRMS: *m*/*z* For $C_{20}H_{14}$ (Calc.: *M*, 254.1095. Found: M^+, 254.1105).

Reaction of alkynylselenonium salt 1a with phenyllithium at −78°C

Phenyllithium in cyclohexane–ether (0.75 ml, 0.6 mmol) was added dropwise to a THF solution (10 ml) of alkynylselenonium salt **1a** (290 mg, 0.6 mmol) at −78°C under argon. After being stirred magnetically for 3 h at −78°C, the reaction mixture was quenched with TfOH (aq.) (5 ml), and extracted with $CHCl_3$ and the organic phase was dried over anhydrous $MgSO_4$. After the solvent was evaporated under reduced pressure, the precipitate was washed several times with ether to give the mixture of triphenylselenonium salt **6a** and **1a** (252 mg) as a colorless oil. The ratio of these compounds was determined by ^1H NMR spectrum (**6a**:236 mg, 86%, **1a**:16 mg, 5%).

Reaction of triphenylselenonium salt 6a with phenylethynyllithium at −78°C

n-Butyllithium in hexane (0.42 ml, 0.66 mmol) was added dropwise to a THF solution (5 ml) of ethynylbenzene (67 mg, 0.66 mmol) at −78°C under argon. After being stirred magnetically for 30 min at −78°C, the solution of phenylethynyllithium thus prepared was added dropwise to a THF solution (5 ml) of triphenylselenonium salt **6a** (276 mg, 0.60 mmol) at −78°C under argon with a cannula. After being stirred magnetically for 3 h at −78°C, the reaction mixture was quenched with TfOH (aq.) (5 ml), and extracted with $CHCl_3$. The organic phase was dried over anhydrous $MgSO_4$. After the solvent was evaporated under reduced pressure, the precipitate was washed several times with ether to give starting material **6a** (252 mg) as a colorless solid.

Diphenyliodonium trifluoromethanesulfonate 13. Diphenyliodonium chloride **11**[11,12] (1.26 g, 4.0 mmol) was dissolved in MeCN (200 ml) with heating. Silver trifluoromethanesulfonate (977 mg, 3.8 mmol) was added to the solution at room temperature. After the mixture was stirred magnetically for 2 h at ambient temperature, the precipitate was filtered and washed with MeCN. The filtrate and washings were combined and the solvent was removed under reduced pressure. The residual solid was recrystallized from MeOH to give **13** (1.66 g, 98%) as a colorless solid, mp 177–180°C (Found: C, 36.46; H, 2.50; $C_{13}H_{10}F_3IO_3S$ requires C, 36.30; H, 2.34%); ν_{max}(film)/cm^{-1} 3047, 1465, 1442, 1240, 1150; δ_H(400 MHz; $CDCl_3$) 7.40 (4 H, t, *J*=7.8, ArH), 7.55 (2 H, t, *J*=7.8, ArH), 7.99 (4 H, d, *J*=7.8, ArH); δ_C(100 MHz; CD_3OD) 115.9, 121,8, 133.2, 133.6, 136.4; *m*/*z* (FAB) 281 ([M−TfO]$^+$, 55%).

Di-*p*-tolyliodonium trifluoromethanesulfonate 14. Di-*p*-tolyliodonium chloride **12**[11] (1.0 g, 2.9 mmol) was similarly treated with silver trifluoromethanesulfonate (745 mg,

2.9 mmol) and gave **14** (1.24 g, 97%) as a colorless solid, mp 153–155°C (Found: C, 39.15; H, 3.10; $C_{15}H_{14}F_3IO_3S$ requires C, 39.32; H, 3.08%); ν_{max}(film)/cm^{-1} 3053, 1482, 1264, 1165; δ_H(400 MHz; $CDCl_3$) 2.45 (9 H, s, Me), 7.41 (6 H, d, *J*=8.3, ArH), 7.41 (6 H, d, *J*=8.3, ArH); δ_C(100 MHz; $CDCl_3$) 21.3, 110.0, 120.3, 132.9, 135.0, 143.4; *m*/*z* (FAB) 309 ([M−TfO]$^+$, 10%).

Triphenylselenonium trifluoromethanesulfonate 6a. Diphenyliodonium trifluoromethanesulfonate **13** (2.0 g, 4.65 mmol) was added to a mixture of diphenyl selenide (1.5 g, 6.44 mmol) and copper benzoate (20 mg, 0.07 mmol) at room temperature under argon. After the mixture was stirred magnetically for 3 h at 120°C, the precipitate was washed several times with ether, and recrystallized from CH_2Cl_2–ether to give **6a** (1.5 g, 70%) as a colorless solid, mp 87–89°C (Found: C, 49.40; H, 3.46; $C_{19}H_{15}F_3O_3SSe$ requires C, 49.68; H, 3.29%); ν_{max}(KBr)/cm^{-1} 3091, 1475, 1445, 1248, 1140; δ_H(400 MHz; $CDCl_3$) 7.59–7.66 (12 H, m, ArH), 7.70–7.73 (3 H, m, ArH), 7.63–7.67 (3 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 120.5, 126.4, 131.2, 131.7, 133.7; *m*/*z* (FAB) 311 ([M−TfO]$^+$, 45%).

Tri-*p*-tolylselenonium trifluoromethanesulfonate 6b. Di-*p*-tolyliodonium trifluoromethanesulfonate **14** (1.0 g, 2.2 mmol) was similarly treated with di-*p*-tolyl selenide (0.57 g, 2.2 mmol) and copper benzoate (12 mg, 0.04 mmol) and gave **6b** (0.8 g, 74%) as a colorless solid, mp 124–126°C (Found: C, 52.71; H, 4.12; $C_{22}H_{21}F_3O_3SSe$ requires C, 52.70; H, 4.22%); ν_{max}(film)/cm^{-1} 3045, 1488, 1259, 1158; δ_H(400 MHz; $CDCl_3$) 2.45 (9 H, s, Me), 7.41 (6 H, d, *J*=8.3, ArH), 7.41 (6 H, d, *J*=8.3, ArH); δ_C(100 MHz; $CDCl_3$) 21.5, 120.6, 123.2, 130.8, 132.2, 144.7; *m*/*z* (FAB) 353 ([M−TfO]$^+$, 95%).

Reaction of alkynylselenonium salt 1a with phenylethynyllithium

A THF solution (5 ml) of alkynylselenonium salt **1a** (290 mg, 0.60 mmol) was treated with phenylethynyllithium, which was prepared in a similar way as mentioned above. Reaction products were analyzed by HPLC in the same manner as described in the reaction of alkynylselenonium salt **1a** with phenyllithium. 1,3-Diphenylbutadiyne **5** (75%) and diphenyl selenide **4** (94%) were obtained.

Reaction of triphenylselenonium salt 6a with 2-(phenylethynyl)phenyllithium 15

A THF solution (5 ml) of 1-bromo-2-(phenylethynyl)-benzene[19] (200 mg, 0.78 mmol) was treated with *n*-butyllithium in hexane (0.49 ml, 0.78 mmol) at −78°C under argon. After the mixture was stirred magnetically for 30 min at −78°C, the solution of 2-(phenylethynyl)phenyllithium **15** thus prepared was added dropwise to a THF solution (5 ml) of triphenylselenonium salt **6a** (276 mg, 0.60 mmol) at room temperature with a cannula. After being stirred magnetically for 3 h at ambient temperature, the reaction mixture was quenched with water (5 ml), and extracted with hexane. Reaction products were analyzed by HPLC as mentioned above. Diphenyl selenide **4** (87%) and 1-(*o*-biphenylyl)-2-phenylethyne **7** (61%) were obtained.

Reaction of alkynylselenonium salt 1a with *o*-biphenylyllithium 16

o-Biphenylyllithium **16** was prepared from *n*-butyllithium in hexane (0.49 ml, 0.78 mmol) and a THF solution (5 ml) of 2-bromobiphenyl (181 mg, 0.78 mmol) in a similar way as for phenylethynyllithium, and added dropwise to a THF solution (5 ml) of alkynylselenonium salt **1a** (290 mg, 0.60 mmol) at room temperature. After the mixture was treated as mentioned above and reaction products were analyzed by HPLC, ethynylbenzene **2** (13%), biphenyl **3** (63%), diphenyl selenide **4** (48%), 1,3-diphenylbutadiyne **5** (15%) and 1-(*o*-biphenylyl)-2-phenylethyne **7** (10%) were obtained.

Reaction of triphenylselenonium salt 6a with phenylethynyllithium at room temperature

A THF solution (2.5 ml) of triphenylselenonium salt **6a** (138 mg, 0.30 mmol) was allowed to react with phenylethynyllithium, prepared from *n*-butyllithium in hexane (0.21 ml, 0.33 mmol) and ethynylbenzene (34 mg, 0.33 mmol), at room temperature for 3 h under argon. After the reaction mixture was treated as mentioned above, reaction products were analyzed by HPLC. Ethynylbenzene **2** (75%), diphenyl selenide **4** (87%) and 1-(*o*-biphenylyl)-2-phenylethyne **7** (27%) were obtained.

Reaction of alkynylselenonium salt 1b with *p*-tolyllithium

p-Tolyllithium was prepared from a THF solution (5 ml) of *p*-bromotoluene (133 mg, 0.78 mmol) and *n*-butyllithium in hexane (0.49 ml, 0.78 mmol), and added dropwise to a THF solution (5 ml) of alkynylselenonium salt **1b** (290 mg, 0.6 mmol) at room temperature under argon. After being stirred magnetically for 3 h at ambient temperature, the reaction mixture was treated as mentioned above. The raw product was purified by preparative TLC (hexane) to give a mixture of **18** and **19** (32 mg, 19%) as a colorless oil and the ratio of these compounds was determined by HPLC (**18**: 19 mg, 11%, **19**: 13 mg, 8%).

1-Bromo-2-(phenylethynyl)-5-methylbenzene 22. *n*-Butyllithium in hexane (3.26 ml, 5.0 mmol) was added dropwise to a THF solution (20 ml) of benzyltriphenylphosphonium bromide (2.18 g, 5.0 mmol) at 0°C under argon. After the reaction mixture was stirred magnetically for 30 min at −78°C, 2-bromo-4-tolualdehyde **20**[15] (1.0 g, 5.0 mmol) was added to it. The whole was stirred for 2 h at room temperature, and extracted with hexane. The extracts were dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (hexane) to yield (*E*)-**22** (640 mg, 47%) and (*Z*)-**22** (574 mg, 42%) as yellow oils. (*E*)-**22**: ν_{max}(film)/cm^{-1} 3025, 1597, 1496, 1448, 1038; δ_H(400 MHz; $CDCl_3$) 2.29 (3 H, s, CH_3), 6.96 (1H, d, *J*=16.1, CH), 7.06 (1 H, d, *J*=7.8, ArH), 7.24 (1 H, t, *J*=7.6, ArH), 7.34 (2 H, t, *J*=7.6, ArH), 7.38 (1 H, s, ArH), 7.42 (1 H, s, *J*=16.1, CH), 7.49–7.53 (3 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 20.8, 123.9, 126.2, 126.7, 127.3, 127.8, 128.4, 128.7, 130.4, 133.4, 134.2, 137.2, 139.1; *m*/*z* (EI) 274 (M^++2, 42%), 272(M^+, 44%), 178

(100); HRMS: *m/z* For $C_{15}H_{13}Br$ (Calc.: *M*, 272.0401. Found: M^+, 272.0203). (*Z*)-**22**: ν_{max}(film)/cm^{-1} 3023, 1601, 1485, 1446, 1039; δ_H(400 MHz; $CDCl_3$) 2.27 (3 H, s, CH_3), 6.58 (1 H, d, *J*=12.0, CH), 6.63 (1 H, d, *J*=12.0, CH), 6.85 (1 H, d, *J*=7.8, ArH), 7.05 (1 H, d, *J*=7.8, ArH), 7.12–7.18 (5 H, m, ArH), 7.41 (1 H, s, ArH); δ_C(100 MHz; $CDCl_3$) 20.8, 123.8, 127.2, 127.9, 128.1, 128.9, 129.3, 130.4, 130.9, 133.0, 134.8, 136.5, 138.8; *m/z* (EI) 274 (M^++2, 52%), 272(M^+, 53%), 178 (100); HRMS: *m/z* For $C_{15}H_{13}Br$ (Calc.: *M*, 272.0401. Found: M^+, 272.0190).

1-Bromo-2-(phenylethynyl)-4-methylbenzene 23. A phosphorane was prepared from a THF solution (20 ml) of benzyltriphenylphosphonium bromide (1.95 g, 4.5 mmol) and *n*-butyllithium in hexane (2.8 ml, 4.5 mmol), and allowed to react with 2-bromo-5-tolualdehyde **21**[16] (900 mg, 4.5 mmol). The mixture was similarly treated as described above, and extracted with hexane. The extracts were dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (hexane) to yield (*E*)-**23** (350 mg, 29%) as a yellow oil, (Found: C, 65.80; H, 4.73; $C_{15}H_{13}Br$ requires C, 65.95; H, 4.80%); ν_{max}(film)/cm^{-1} 3058, 1599, 1495, 1470, 1025; δ_H(400 MHz; $CDCl_3$) 2.31 (3 H, s, CH_3), 6.91 (1 H, d, *J*=7.8, ArH), 7.00 (1 H, d, *J*=16.1, CH), 7.27 (1 H, t, *J*=7.3, ArH), 7.35 (2 H, t, *J*=7.3, ArH), 7.41–7.45 (3 H, m, ArH), 7.53 (2 H, d, *J*=7.3, ArH); δ_C(100 MHz; $CDCl_3$) 21.9, 120.9, 126.8, 127.3, 127.5, 128.0, 128.7, 129.8, 131.1, 132.7, 136.7, 137.1,137.3; *m/z* (EI) 274 (M^++2, 45%), 272(M^+, 48%), 178 (100).

1-Bromo-2-(phenylethynyl)-5-methylbenzene 24. To a stirred solution of **22** (1458 mg, 1.68 mmol) in CH_2Cl_2 (50 ml) was added Br_2 (0.3 ml, 5.7 mmol) at 0°C under argon. After the reaction mixture was stirred for 2 h, sat. $Na_2S_2O_3$ (aq.) was added to it, and the whole was extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was dissolved in *t*-BuOH (25 ml) and treated with 90% *t*-BuOK (272 mg, 2.2 mmol) under reflux for 6 h. The mixture was quenched with water and extracted with hexane. The organic phase was dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by preparative TLC (hexane) to give **24** (178 mg, 39%) as white prisms, mp 48–50°C (Found: C, 66.68; H, 4.18; $C_{15}H_{11}Br$ requires C, 66.44; H, 4.09%); ν_{max}(film)/cm^{-1} 3060, 2221, 1596, 1498, 1442, 1041; δ_H(400 MHz; $CDCl_3$) 2.30 (3 H, s, CH_3), 7.07 (1 H, d, *J*=7.8, ArH), 7.33–7.36 (3 H, m, ArH), 7.43 (2 H, d, *J*=7.8, ArH), 7.55–7.58 (2 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 21.1, 88.2, 93.1, 122.4, 123.2, 125.4, 128.0, 128.4, 128.5, 131.6, 132.9, 133.0, 140.6; *m/z* (EI) 272 (M^++2, 98%), 270(M^+, 100%).

1-Bromo-2-(phenylethynyl)-4-methylbenzene 25. A solution of **23** (506 mg, 2.29 mmol) in CH_2Cl_2 (25 ml) was brominated with Br_2 (0.5 ml, 9.5 mmol) at 0°C under argon in a similar way as for compound **24**. The bromide thus prepared was dehydrobrominated with 90% *t*-BuOK (686 mg, 5.5 mmol) in *t*-BuOH (20 ml). The raw product was purified by preparative TLC (hexane) to give **25** (174 mg, 28%) as white prisms, mp 62–65°C (Found: C, 66.70; H, 4.10; $C_{15}H_{11}Br$ requires C, 66.44; H, 4.09%); ν_{max}(film)/cm^{-1} 3054, 2213, 1599, 1492, 1469, 1032; δ_H(400 MHz; $CDCl_3$) 2.29 (3 H, s, CH_3), 6.98 (1 H, dd, *J*=2.0 and 8.3, ArH), 7.34–7.37 (4 H, m, ArH), 7.47 (1 H, d, *J*=8.3, ArH), 7.56–7.58 (2 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 20.7, 88.2, 93.5, 122.3, 123.0, 125.0, 128.4, 128.6, 130.4, 131.7, 132.1, 133.8, 137.0; *m/z* (EI) 272 (M^++2, 99%), 270(M^+, 100%).

2-(Phenylethynyl)-5,4′-dimethyl-1,1′-biphenyl 18. *n*-Butyllithium in hexane (0.43 ml, 0.66 mmol) was added dropwise to a THF solution (5 ml) of **24** (178 mg, 0.66 mmol) at −78°C under argon. After being stirred magnetically for 30 min at −78°C, the reaction mixture was added dropwise to a THF solution (5 ml) of selenonium salt **6b** (300 mg, 0.60 mmol) at room temperature. The whole was stirred magnetically for 3 h at ambient temperature, quenched with water (5 ml), and extracted with hexane. The organic phase was dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude product was purified by preparative TLC (hexane) to give **18** (43 mg, 25%) as a yellow oil, (Found: C, 93.36; H, 6.60; $C_{22}H_{18}$ requires C, 93.58; H, 6.42%); ν_{max}(film)/cm^{-1} 3023, 2212, 1595, 1497; δ_H(400 MHz; $CDCl_3$) 2.40 (3 H, s, CH_3), 2.42 (3 H, s, CH_3), 7.10 (1 H, d, *J*=7.8, ArH), 7.22–7.27 (6 H, m, ArH), 7.32–7.35 (2 H, m, ArH), 7.52 (1 H, d, *J*=7.8, ArH), 7.56 (2 H, d, *J*=8.3, ArH); δ_C(100 MHz; $CDCl_3$) 21.2, 21.5, 89.7, 91.4, 118.5, 123.8, 127.6, 127.8, 128.2, 128.6, 129.2, 130.2, 131.3, 132.9, 137.1, 137.7, 138.6, 143.7; *m/z* (EI) 282 (M^+, 100%), 267 (40).

2-(Phenylethynyl)-4,4′-dimethyl-1,1′-biphenyl 19. 2-Phenylethynyl-4-tolyllithium was prepared from a THF solution (3 ml) of **25** (96 mg, 0.36 mmol) and *n*-butyllithium in hexane (0.23 ml, 0.36 mmol) at −78°C under argon and added dropwise to a THF solution (3 ml) of selenonium salt **6b** (162 mg, 0.32 mmol) at room temperature. The reaction mixture was treated in a similar way as for compound **18**. The crude product was purified by preparative TLC (hexane) to give **19** (25 mg, 25%) as a yellow oil; ν_{max}(film)/cm^{-1} 3022, 2211, 1604, 1492; δ_H(400 MHz; $CDCl_3$) 2.38 (3 H, s, CH_3), 2.41 (3 H, s, CH_3), 7.19 (1 H, d, *J*=7.8, ArH), 7.23–7.35 (8 H, m, ArH), 7.46 (1 H, s, ArH), 7.56 (2 H, d, *J*=8.3, ArH); δ_C(100 MHz; $CDCl_3$) 20.8, 21.2, 89.7, 91.7, 121.2, 123.7, 128.0, 128.2, 128.6, 129.2, 129.3, 129.5, 131.4, 133.4, 136.5, 136.9, 137.6, 141.0; *m/z* (EI) 282 (M^+, 100%), 267 (40); HRMS: *m/z* For $C_{22}H_{18}$ (Calc.: *M*, 282.1409. Found: M^+, 282.1403).

Reaction of tri-*p*-tolylselenonium salt 6b with *p*-tolyllithium

Tolyllithium in THF (1.0 ml, 0.20 mmol) was added dropwise to a THF solution (2.5 ml) of tri-*p*-tolylselenonium salt **6b** (100 mg, 0.62 mmol) at room temperature under argon. After being stirred magnetically for 3 h at ambient temperature, the reaction mixture was hydrolyzed with water (5 ml), and extracted with hexane. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane) to give di-*p*-tolyl selenide **30** (43 mg, 82%) and a mixture of **28** and **29**[17] (23 mg, 63%) as a yellow oil. The ratio of these compounds was determined in comparison with their methyl signals of

^{1}H NMR with authentic samples (**28**: 15 mg, 41%, **29**: 8 mg, 22%).

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