

A Novel Three-Component Coupling of Alkynes, Vinylcyclopropanes, and Diphenyl Diselenide under Visible-Light Irradiation

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The radical chemistry in organic synthesis has been growing in recent years, because of the development of highly selective radical reactions and the many synthetic applications of these reactions.¹ Among these useful radical reactions, the intramolecular sequential reaction between alkyne, alkene, and a radical precursor (tin hydride, thiol, sulfonyl chloride, etc.) is well-documented;² however, the corresponding intermolecular reaction, which attains both bond-connection between alkyne and alkene and introduction of heteroatom function from radical precursor into the carbon-carbon unsaturated bond, has remained largely unexplored.³

Difficulty in realizing this three-component coupling between alkyne, alkene, and radical precursor (X–Y) lies on the following (Scheme 1): (i) the addition step of heteroatom-centered radical (Y•) to alkyne (or alkene) is a reversible process, and the concentration of the vinylic radical (**1**) is generally very low; (ii) in the case of the lower carbon-radical capturing ability of radical precursor (X–Y), polymerization may occur in preference to the desired three-component coupling; (iii) in the case of the higher carbon-radical capturing ability of X–Y, the vinylic radical (**1**) may be quenched to give the vicinal addition product of alkyne. In our previous paper, we have examined the three-component coupling using several radical precursors such as ⁿBu₃SnH, (PhS)₂, (PhSe)₂, (PhTe)₂, etc., and found that just the right strength of carbon-radical trapping by diphenyl di-

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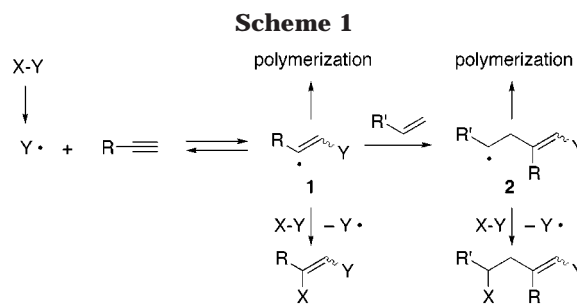
[‡] Osaka University.

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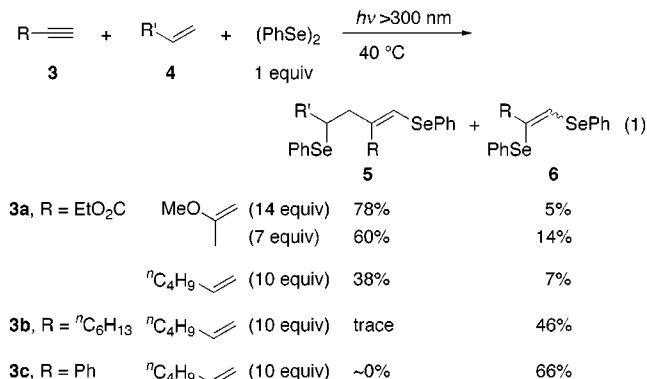
(1) (a) Curran, D. P.; Porter, N. A.; Giese, B. *Stereochemistry of Radical Reactions*; VCH: Weinheim, 1996. (b) Giese, B.; Kopping, B. Göbel, T.; Dickhaut, J.; Thoma, G.; Kulicke, K. J.; Trach, F. *Org. React.* **1996**, *48*, 301. (c) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Masson: Paris, 1995. (d) Curran, D. P. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, p 779. (e) Curran, D. P. *Synthesis* **1988**, 418 and 489. (f) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986.

(2) (a) Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1986**, 27, 4529. (b) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1987**, 109, 2829. (c) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, 109, 2547. (d) Broka, C. A.; Reichert, D. E. *C. Tetrahedron Lett.* **1987**, 28, 1503. (e) Ogawa, A.; Yokoyama, H.; Masawaki, T.; Yokoyama, K.; Sonoda, N. *Phosphorus Sulfur* **1992**, 67, 219. (f) Kataoka, T.; Yoshimatsu, M.; Noda, Y.; Sato, T.; Shimizu, H.; Hori, M. *J. Chem. Soc., Perkin Trans. I* **1993**, 121. (g) Brummell, J. E.; Simpkins, N. S.; Terrett, N. K. *Tetrahedron* **1994**, 50, 13533.

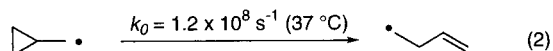
(3) Lee, E.; Hur, C. U. *Tetrahedron Lett.* **1991**, 32, 5101.



selenide facilitates its selective three-component coupling with an electron-poor alkyne and an electron-rich alkene (eq 1).^{4,5}



In this paper, we wish to describe a three-component coupling of alkynes, vinylcyclopropanes, and diphenyl diselenide under visible-light irradiation. Vinylcyclopropanes are expected to undergo addition of a radical species, generating the corresponding cyclopropylcarbinyl radical intermediates, the ring-opening of which is accepted as a very fast process, as indicated in eq 2.⁶ Accordingly, the influence of this fast process on the three-component coupling was investigated in detail.



Upon irradiation through Pyrex with a tungsten lamp (500 W) at 40 °C,⁷ the reaction of phenylacetylene (**3c**) with 1-cyclopropylstyrene (**7a**) and diphenyl diselenide provided the desired three-component coupling product (**8a**) along with the bisselelated adduct to **3c** in 23% and 52% yields, respectively (eq 3). The formation of **8a** may be explained by the following: (i) selective addition of



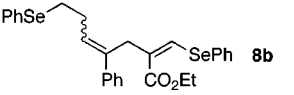


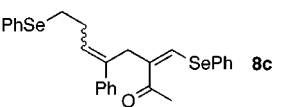


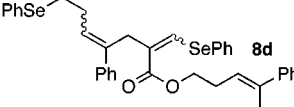
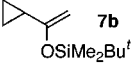

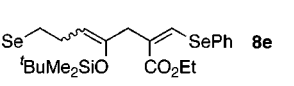


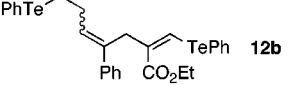
(4) The rate constants for the S_H2 reaction of 5-hexenyl radical with (PhSe)₂ are determined to be $1.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, see: (a) Russell, G. A.; Tsatshouh, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398. (b) Perkins, M. J.; Turner, E. S. *J. Chem. Soc., Chem. Commun.* **1981**, 139. (c) Russell, G. A.; Ngovivatchai, P.; Tsatshouh, H. I.; Pla-Dalmau, A.; Khanna, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 3530.

(5) Ogawa, A.; Doi, M.; Ogawa, I.; Hirao, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 2027.

(6) (a) Bowry, V. W.; Luszytyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687. (b) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5699. (c) Beckwith, A. L. J.; Bowry, V. W. *J. Am. Chem. Soc.* **1994**, *116*, 2710. (d) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

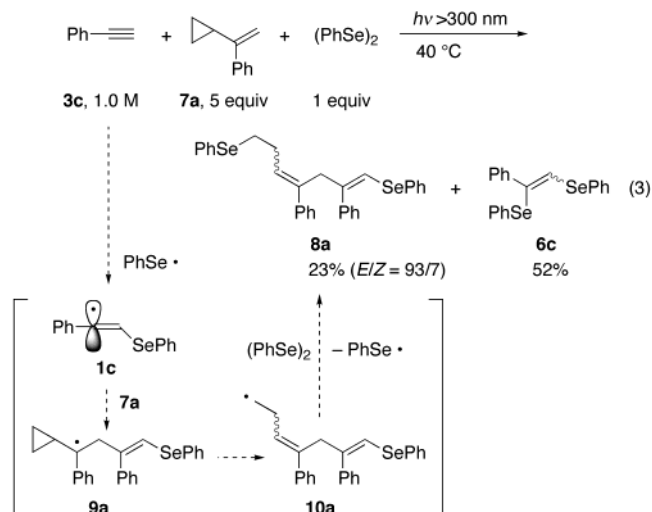
(7) The absorption maximum of diphenyl diselenide lies in the near-UV regions ($\lambda_{\text{max}} = 330 \text{ nm}$, $\epsilon_{\text{max}} = 1000$), and therefore, irradiation with the lights causes homolytic cleavage of the selenium-selenium bonds to generate the corresponding phenylseleno radical as a label species. See: Schmidt, U.; Müller, A.; Markau, K. *Chem. Ber.* **1964**, *97*, 405.

Table 1. Selective Coupling of Vinylcyclopropanes with Alkynes and (PhSe)₂^a

| entry | vinylcyclopropane | alkyne | product | yield, % ^b | E/Z |
|-------|---|---|---|-----------------------|----------------|
| 1 |  7a |  3a |  8b | 72 | 82/18 |
| 2 |  7a |  3d |  8c | 45 | 94/6 |
| 3 |  7a |  3e |  8d | 33 | — ^c |
| 4 |  7b |  3a |  8e | 55 | 16/84 |
| 5 |  7a |  3a |  12b | 32 | 96/4 |

^a Reaction conditions: alkyne (0.3–1.0 mmol), vinylcyclopropane (5 equiv), (PhSe)₂ (1 equiv), added over 1.5 h in several portions, 40 °C, 24 h, *hν* > 300 nm (tungsten lamp 500 W, Pyrex). ^b Isolated yield. ^c The ratio of the isomers 82/9/6/3.

PhSe• to phenylacetylene to form the vinyl radical intermediate (**1c**),^{8–10} which then adds to the vinylcyclopropane; (ii) ring-opening of thus formed benzylic radical (**9a**) to the primary radical (**10a**), which undergoes S_H2 reaction with (PhSe)₂ to give **8a**.¹¹



In contrast, the attempted three-component coupling using 1-hexene in place of vinylcyclopropane (**7a**) resulted in the formation of only the bis-selenated adduct to **3c**, as can be seen from eq 1. When styrene was used in place of **7a**, a polymeric mixture was obtained most probably

due to the instability of the benzylic carbon–selenium bond of the desired coupling product (**5**, R = R' = Ph) under photoirradiation conditions.¹² These results indicate that the introduction of a cyclopropyl group to the α-position of styrene enables the desired three-component coupling by converting benzylic radical (**9a**) to a primary one (**10a**).

Table 1 represents the three-component coupling of alkynes with vinylcyclopropanes and diphenyl diselenide (or diphenyl ditelluride). Ethyl propiolate (**3a**) as an electron-poor alkyne underwent three-component coupling with vinylcyclopropane (**7a**) and (PhSe)₂ very smoothly to give 1,7-bis(phenylseleno)-1,4-heptadiene derivatives (**8b**) along with a small amount of the bis-selenation product (**6a**, R = EtO₂C) of ethyl propiolate, which could be easily separated by GPC (entry 1). Compared with the three-component coupling of **3a** with 1-hexene and (PhSe)₂ (eq 1), the higher yield of **8b** was observed despite diminishing the amount of alkene. Similar conditions can be employed with 1-butyne-3-one (**3d**), providing the corresponding three-component coupling product (**8c**) in moderate yield (entry 2). In the case of propionic acid (**3e**), the ring-opening reaction of vinylcyclopropane (**7a**) with **3e** took place in preference to the three-component coupling to produce 2-phenyl-3-pentenyl propiolate (**3f**),

(8) For the radical addition of (PhSe)₂ to alkynes, see: (a) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 2533. (b) Ogawa, A.; Yokoyama, H.; Yokoyama, K.; Masawaki, T.; Kambe, N.; Sonoda, N. *J. Org. Chem.* **1991**, *56*, 5721. (c) Ogawa, A.; Takami, N.; Sekiguchi, M.; Yokoyama, H.; Kuniyasu, H.; Ryu, I.; Sonoda, N. *Chem. Lett.* **1991**, 2241.

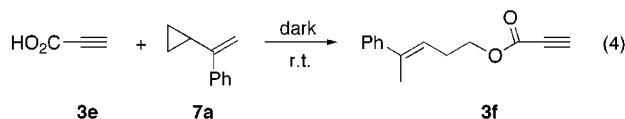
(9) The reaction of vinylcyclopropane (**7a**) with diphenyl diselenide did not proceed at all under similar photoirradiated conditions. See: Ogawa, A.; Ogawa, I.; Obayashi, R.; Umez, K.; Doi, M.; Hirao, T. *J. Org. Chem.* **1999**, *64*, 86.

(10) In general, vinyl radicals are believed to be a stereoisomeric mixture of *σ*-radicals and a fast equilibrium is present between the stereoisomers: (a) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147. Contrary to this, *α*-aryl-substituted vinyl radicals are assumed to be *π*-radicals: (b) Singer, L. A.; Chen, J. *Tetrahedron Lett.* **1969**, 4849. Ethyl propiolate is assumed to generate vinylic *π*-radical: (c) Galli, C.; Guarneri, A.; Koch, H.; Mencarelli, P.; Rappoport, Z. *J. Org. Chem.* **1997**, *62*, 4072. (d) Rubin, H.; Fischer, H. *Helv. Chim. Acta* **1996**, *79*, 1670. (e) Metzger, J. O.; Blumenstein, M. *Chem. Ber.* **1993**, *126*, 2493.

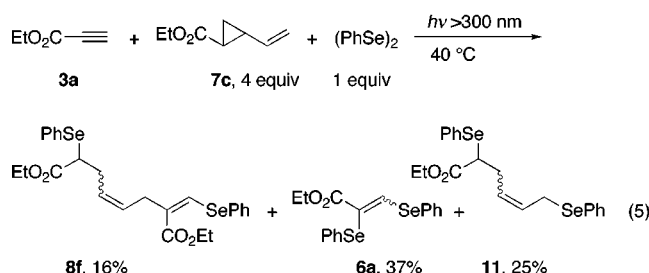
(11) Alternative pathway from **9a** to **8a** may involve the ring-opening of the cyclopropyl group of **9a** by the attack of PhSe•.

(12) For the photoinduced cleavage of benzylic selenides, see for example: (a) Chu, J. Y. C.; Marsh, D. G.; Günther, W. H. H. *J. Am. Chem. Soc.* **1975**, *97*, 4905. (b) Spencer, H. K.; Cava, M. P. *J. Org. Chem.* **1977**, *42*, 2937. (c) Stanley, W.; VanDeMark, M. R.; Kumler, P. L. *J. Chem. Soc., Chem. Commun.* **1974**, 4905.

which then reacted with (PhSe)₂ and **7a** via the radical process to give the three-component coupling product (**8d**) (entry 3). The reaction of **3e** with **7a** in the absence of (PhSe)₂ in the dark gave rise to **3f** in high yield (eq 4). This suggests that the formation of **3f** may proceed via ionic process.



The three-component coupling of cyclopropyl-substituted enol silyl ether (**7b**) with ethyl propiolate (**3a**) and (PhSe)₂ afforded the desired 1,7-bis(phenylseleno)-2-ethoxycarbonyl-4-(*tert*-butyldimethylsiloxy)-1,4-heptadiene (**8e**) in good yield (entry 4). On the other hand, the three-component coupling of ethoxycarbonyl-substituted vinylcyclopropane (**7c**) gave a mixture of the desired coupling product (**8f**) and the (PhSe)₂-adducts of **3a** (**6a**) and **7c** (**11**), as illustrated in eq 5.



We already reported that the attempted three-component coupling of ethyl propiolate with 1-hexyne using (PhTe)₂ instead of (PhSe)₂ resulted in the formation of only the (PhTe)₂-adduct to 1-hexyne,⁵ due to the excessive carbon radical capturing ability of (PhTe)₂.^{4a} In the case of 1-cyclopropylstyrene (**7a**), however, the corresponding three-component coupling product (**12b**) was obtained in 32% yield together with 44% of the (PhTe)₂-adduct to **3a**¹³ (entry 5).

In conclusion, a novel, three-component coupling of alkynes, vinylcyclopropanes, and diphenyl diselenide (or ditelluride) under visible-light irradiation has been developed. The fast rearrangement process of cyclopropyl-carbinyl radical intermediates contributes to the efficiency in the desired three-component coupling reaction, providing the corresponding ring-opened products. We are currently examining applicability of this methodology to a variety of different classes of substrates.

Experimental Section

General Comments.¹⁴ Unless otherwise noted, alkynes were used commercially and were purified by distillation. Vinylcyclopropanes were synthesized according to the literature.¹⁵ Diphenyl diselenide¹⁶ and diphenyl ditelluride¹⁷ were prepared according to the literature and were recrystallized from hexane.

(13) (a) Ogawa, A.; Yokoyama, K.; Yokoyama, H.; Obayashi, R.; Kambe, N.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1748. (b) Ogawa, A.; Yokoyama, K.; Obayashi, R.; Han, L.-B.; Kambe, N.; Sonoda, N. *Tetrahedron* **1993**, *49*, 1177.

(14) Ogawa, A.; Tanaka, H.; Yokoyama, H.; Obayashi, R.; Yokoyama, K.; Sonoda, N. *J. Org. Chem.* **1992**, *57*, 111.

(15) Teragi, T. *J. Chem. Soc., C* **1971**, 3252.

(16) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

(17) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.

General Procedure for the Three-Component Coupling of Alkynes, Vinylcyclopropanes, and Diphenyl Diselenide: Ethyl 2-[(phenylseleno)methylenyl]-4-phenyl-7-(phenylseleno)-4-heptenoate (**8b**). In a Pyrex glass tube (ϕ = 5 mm, length = 18 cm) under argon atmosphere were placed ethyl propiolate (0.6 mmol, 58.9 mg), 1-cyclopropylstyrene (2.4 mmol, 346.1 mg), and diphenyl diselenide (0.2 mmol, 62.4 mg). The mixture was irradiated with a tungsten lamp (500 W) at 40 °C for 14 h. Additionally, diphenyl diselenide (0.2 mmol, 62.4 mg) was added two times to the mixture, when the yellow color of the mixture turned pale yellow. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC) using CHCl₃ as an eluent, yielding 239.5 mg (72%) of ethyl 2-[(phenylseleno)methylenyl]-4-phenyl-7-(phenylseleno)-4-heptenoate (**8b**) obtained as a stereoisomeric mixture (*4E/4Z* = 82/18): a pale yellow oil; ¹H NMR (600 MHz, CDCl₃): (*4E*)-isomer: δ 1.35 (t, *J* = 7.2 Hz, 3 H), 2.57 (q like, *J* = 7.3 Hz, 2 H), 2.95 (t, *J* = 7.3 Hz, 2 H), 3.48 (s, 2 H), 4.28 (q, *J* = 7.2 Hz, 2 H), 5.87 (t, *J* = 7.3 Hz, 1 H), 7.20–7.30 (m, 14 H), 7.44–7.46 (m, 2 H). (*4Z*)-isomer: δ 1.32 (t, *J* = 7.2 Hz, 3 H), 2.39 (q like, *J* = 7.3 Hz, 2 H), 2.89 (t, *J* = 7.3 Hz, 2 H), 3.48 (s, 2 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 5.60 (t, *J* = 7.3 Hz, 1 H), 7.20–7.30 (m, 14 H), 7.44–7.46 (m, 2 H). The stereochemistry of the products were determined by NOE experiments: ¹³C NMR (100 MHz, CDCl₃): (*4E*)-isomer: δ 14.3, 27.0, 29.3, 32.9, 60.9, 125.0, 126.1, 126.7, 126.9, 127.5, 128.2, 128.9, 129.0, 129.9, 132.4, 132.5, 133.4, 137.2, 141.9, 143.8, 167.1. (*4Z*)-isomer: δ 14.1, 27.4, 30.0, 32.9, 60.7, 125.0, 126.2, 126.6, 126.7, 127.4, 127.7, 128.1, 128.8, 129.3, 130.3, 132.9, 133.0, 140.7, 142.1, 143.8, 167.1; IR (NaCl) 3055, 1688, 1578, 758, 737, 692 cm⁻¹; MS (EI), *m/z* = 556 (M⁺, 13.6); HRMS calcd for C₂₈H₂₈O₂Se₂: 556.0419, found: 556.0415; Anal. Calcd for C₂₈H₂₈O₂Se₂: C, 60.66; H, 5.09. Found: C, 60.85; H, 5.16.

1,7-Bis(phenylseleno)-2,4-diphenyl-1,4-heptadiene (8a): a pale yellow oil (obtained as a stereoisomeric mixture (*4E/4Z* = 93/7)); ¹H NMR (400 MHz, CDCl₃): (*4E*)-isomer: δ 2.52 (q like, *J* = 7.3 Hz, 2 H), 2.85 (t, *J* = 7.3 Hz, 2 H), 3.59 (s, 2 H), 5.88 (t, *J* = 7.3 Hz, 1 H), 6.36 (s, 1 H), 7.15–7.48 (m, 20 H); ¹³C NMR (100 MHz, CDCl₃): (*4E*)-isomer: δ 26.9, 29.7, 39.6, 118.9, 126.4, 126.5, 126.8, 127.0, 127.5, 127.6, 128.3, 129.0, 129.1, 129.9, 130.1, 131.2, 132.0, 132.7, 137.3, 141.2, 141.3, 142.3; IR (NaCl) 3054, 3020, 2925, 1578, 999, 805, 759, 736, 691, 670 cm⁻¹; MS (EI), *m/z* = 560 (M⁺, 36.8); HRMS calcd for C₃₁H₂₈Se₂: 560.0521, found: 560.0510. Anal. Calcd for C₃₁H₂₈Se₂: C, 66.67; H, 5.05. Found: C, 66.62; H, 5.14.

1,7-Bis(phenylseleno)-2-methylcarbonyl-4-phenyl-1,4-heptadiene (8c): a pale yellow oil (obtained as a stereoisomeric mixture (*4E/4Z* = 94/6)); ¹H NMR (400 MHz, CDCl₃): (*4E*)-isomer: δ 2.28 (s, 3 H), 2.53 (q like, *J* = 7.3 Hz, 2 H), 2.93 (t, *J* = 7.3 Hz, 2 H), 3.50 (s, 2 H), 5.90 (t, *J* = 7.3 Hz, 1 H), 7.39 (s, 1 H), 7.15–7.47 (m, 15 H); ¹³C NMR (100 MHz, CDCl₃): (*4E*)-isomer: δ 26.8, 27.5, 29.4, 34.3, 126.1, 126.9, 127.2, 127.6, 128.4, 129.0, 130.1, 130.9, 132.3, 132.6, 135.0, 137.1, 141.8, 145.4, 198.0; IR (NaCl) 3055, 1652, 1578, 1531, 739, 692, 669 cm⁻¹; MS (EI), *m/z* = 526 (M⁺, 16.6); HRMS calcd for C₂₇H₂₆OSe₂: 526.0313, found: 526.0327. Anal. Calcd for C₂₇H₂₆OSe₂: C, 61.84; H, 5.00. Found: C, 61.77; H, 5.03.

4-Phenyl-3-pentenyl 2-[(phenylseleno)methylenyl]-4-phenyl-7-(phenylseleno)-4-heptenoate (8d): a pale yellow oil (obtained as a stereoisomeric mixture (the ratio was 82/9/6/3); the major isomer bears (*E*)-structure concerning the unsaturated bond at 4-position and (*Z*)-structure concerning the (phenylseleno)methylenyl group); ¹H NMR (400 MHz, CDCl₃): the major isomer: δ 2.08 (s, 3 H), 2.55 (q like, *J* = 7.3 Hz, 2 H), 2.63 (q like, *J* = 6.8 Hz, 2 H), 2.93 (t, *J* = 7.3 Hz, 2 H), 3.48 (s, 2 H), 4.33 (t, *J* = 6.8 Hz, 2 H), 5.79 (t, *J* = 6.8 Hz, 1 H), 5.87 (t, *J* = 7.3 Hz, 1 H), 7.20–7.54 (m, 21 H); ¹³C NMR (100 MHz, CDCl₃): the major isomer: δ 16.1, 27.1, 28.4, 29.4, 33.0, 64.3, 122.9, 125.0, 125.7, 126.2, 126.8, 126.9, 127.1, 127.7, 128.2, 128.3, 129.0, 129.2, 130.2, 132.6, 132.7, 133.5, 137.2, 137.7, 142.0, 143.5, 144.3, 167.3; IR (NaCl) 3054, 2952, 1694, 1577, 758, 737, 692 cm⁻¹; MS (EI), *m/z* = 672 (M⁺, 3.96); HRMS calcd for C₃₇H₃₆O₂Se₂: 672.1045, found: 672.1048. Anal. Calcd for C₃₇H₃₆O₂Se₂: C, 66.27; H, 5.41. Found: C, 65.98; H, 5.41.

Ethyl 2-[(Phenylseleno)methylenyl]-4-*t*-butyldimethylsiloxy-7-(phenylseleno)-4-heptenoate (8e): a pale yellow oil (obtained as a stereoisomeric mixture (4*E*/4*Z* = 16/84)); ¹H NMR (400 MHz, CDCl₃): (4*E*)-isomer: δ 0.05 (s, 6 H), 0.82 (s, 9 H), 1.32 (t, *J* = 7.3 Hz, 3 H), 2.38 (q like, *J* = 7.3 Hz, 2 H), 2.87 (t, *J* = 7.3 Hz, 2 H), 3.03 (s, 2 H), 4.24 (q, *J* = 7.3 Hz, 2 H), 4.67 (t, *J* = 7.3 Hz, 1 H), 7.20–7.34 (m, 6 H), 7.41–7.47 (m, 2 H), 7.50 (s, 1 H), 7.56–7.60 (m, 2 H). (4*Z*)-isomer: δ 0.07 (s, 6 H), 0.86 (s, 9 H), 1.32 (t, *J* = 7.3 Hz, 3 H), 2.38 (q like, *J* = 7.3 Hz, 2 H), 2.80 (t, *J* = 7.3 Hz, 2 H), 3.03 (s, 2 H), 4.27 (q, *J* = 7.3 Hz, 2 H), 4.47 (t, *J* = 7.3 Hz, 1 H), 7.20–7.34 (m, 6 H), 7.41–7.47 (m, 2 H), 7.50 (s, 1 H), 7.56–7.60 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃): (4*E*)-isomer: δ -4.6, 14.4, 17.9, 25.8, 26.3, 28.4, 34.9, 60.9, 107.0, 124.1, 126.6, 128.1, 128.9, 129.1, 132.4, 133.3, 145.6, 149.3, 167.3. (4*Z*)-isomer: δ -4.0, 14.4, 18.1, 25.7, 26.1, 27.6, 39.5, 60.9, 108.7, 124.4, 126.6, 127.9, 128.9, 129.2, 132.7, 133.2, 145.7, 148.8, 167.3; IR (NaCl) 2930, 2857, 1689, 1579, 838, 780, 737, 692 cm⁻¹; MS (EI), *m/z* = 610 (M⁺, 10.9); HRMS calcd for C₂₈H₃₈O₃SiSe₂: 610.0920, found: 610.0939. Anal. Calcd for C₂₈H₃₈O₃SiSe₂: C, 55.26; H, 6.29. Found: C, 54.97; H, 6.30.

Ethyl 2-[(Phenyltelluro)methylenyl]-4-phenyl-7-(phenyltelluro)-4-heptenoate (12b): an orange oil (obtained as a

stereoisomeric mixture (4*E*/4*Z* = 96/4)); ¹H NMR (400 MHz, CDCl₃): (4*E*)-isomer: δ 1.33 (t, *J* = 7.2 Hz, 3 H), 2.66 (q like, *J* = 7.3 Hz, 2 H), 2.91 (t, *J* = 7.3 Hz, 2 H), 3.50 (s, 2 H), 4.28 (q, *J* = 7.2 Hz, 2 H), 5.82 (t, *J* = 7.3 Hz, 1 H), 7.11–7.29 (m, 11 H), 7.52 (d, *J* = 6.8 Hz, 2 H), 7.67 (d, *J* = 6.8 Hz, 2 H), 7.85 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃): (4*E*)-isomer: δ 7.3, 14.3, 30.9, 34.0, 61.5, 111.5, 121.0, 126.2, 126.9, 127.5, 127.7, 128.3, 129.1, 129.1, 130.4, 131.9, 133.9, 137.0, 137.4, 138.4, 142.2, 168.6; IR (NaCl) 3052, 2979, 2930, 1702, 1670, 1574, 998, 732, 693 cm⁻¹; MS (EI), *m/z* = 652 (M⁺, 21.8); HRMS calcd for C₂₈H₂₈O₂Te₂: 656.0213, found: 656.0215. Anal. Calcd for C₂₈H₂₈O₂Te₂: C, 51.60; H, 4.33. Found: C, 52.02; H, 4.45.

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