Tributylstannyl Radical-Catalyzed Reaction of 1,2,3-Selenadiazoles with Olefins or Dienes

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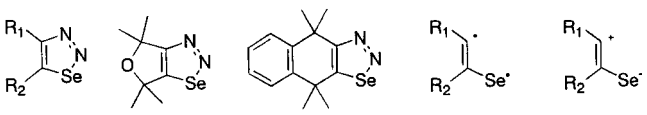
It was found that the reaction of 1,2,3-selenadiazoles derived from cyclic ketones with olefins or dienes was markedly promoted by a catalytic amount of tributylstannyl radical, which was generated in situ from tributylstannyl hydride or allyltributylstannane and AIBN, to give the corresponding dihydroselenophenes in moderate to good yields. In contrast, when 1,2,3-selenadiazoles prepared from linear and aromatic ketones were used as substrates, the same reaction did not take place, and alkynes were formed as the sole product.

Introduction

The radical reactions are one of the most popular and important types of reactions in organic synthesis. Various transformations such as reduction and inter- and intramolecular carbon−carbon bond formations have been developed using radical reactions.[1] In particular, the radical-mediated reactions employing a stoichiometric or an excess amount of tributylstannyl radical, which was generated in situ from the tributylstannyl hydride/AIBN or allyltributylstannane/AIBN system, have been widely utilized in organic synthesis.[2]

1,2,3-Selenadiazoles **1** are of recent interest as versatile intermediates for the preparation of alkynes, because compounds **1** are easily decomposed with the loss of a nitrogen molecule and selenium atom under light irradiation and thermal conditions.[3−5] Ando and Tokitoh et al. reported the reaction of sterically protected bicyclic 1,2,3-selenadiazoles **2** and **3** with various organic compounds during light irradiation ($h\nu$ > 365 and > 265 nm) and assumed the formation of biradical (**4**) and zwitterionic (**5**) intermediates.[6] We have recently examined the



1 **2** **3** **4** **5**

reaction of 1,2,3-selenadiazoles derived from cyclic ketones with olefins under thermal conditions and found that dihydroselenophenes were formed in moderate to good yields.[7] On the other hand, since a report by Clive,[8] the reaction of organoselenium compounds with organostannyl compounds such as R_3SnH, allyltributylstan-

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(1) For examples, see: (a) Giece, B. *Radical in Organic Synthesis: Formation of Carbon−Carbon Bonds*; Pergamon: New York, 1986. (b) Curran, D. P. *Synthesis* **1988**, 417. (c) Curran, D. P. *Synthesis* **1988**, 489. (d) Marthwell, W. B.; Crich, D. *Free Radical Chain Reactions in Organic Synthesis*; Academic: New York, 1992. (e) Fart, D. C. *Science* **1994**, *223*, 883. (f) Curran, D. P.; Porter, N. A.; Giece, B. *Stereochemistry of Radical Reactions*; VCH: New York, 1996. (g) *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, 2001. (h) McCarroll, A. J.; Walton, J. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2224.

(2) For reviews of the chemistry of organotin compounds, see: (a) Neumann, W. P. *Synthesis* **1987**, 665. (b) RajaBabu, T. V. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, T. A., Ed.; Wiley: New York, 1985. (c) Curran, D. P. *Synlett* **1991**, 63. (d) Curran, D. P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, p 779. (e) Ryu, I.; Sonoda, N.; Curran, D. P. *Chem. Rev.* **1996**, *96*, 177. (f) Ryu, I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1050. (g) Davies, A. G. *Organotin Chemistry*; VCH: New York, 1997.

(3) For recent reviews on the synthesis and the utilization of 1,2,3-selenadiazoles, see: (a) Ando, W.; Tokitoh, N. *Heteroat. Chem.* **1991**, 1. (b) Tanaka, R.; Shinkai, I. *Prog. Heterocycl. Chem.* **1992**, *4*, 123. (c) Reid, D. H. In *Comprehensive Heterocyclic Chemistry II: A Review of the Literature 1982−1995*; Torr, R. C. S., Ed.; Pergamon: Oxford, 1996; Vol. 4, p 743. (d) Regitz, M.; Krill, S. *Phosphorous, Sulfur Silicon Relat. Elem.* **1996**, *15*, 99. (e) Zmitrovich, N. I.; Petrov, M. L. *Zh. Org. Khim.* **1996**, *32*, 1870. (f) Padmavathi, V.; Sumathi, R. P.; Ramana, R. M. V.; Bhaskar, R. D. *Org. Prep. Proced. Int.* **1998**, *30*, 187 and references therein.

(4) Meier, H.; Menzel, I. *J. Chem. Soc., Chem. Commun.* **1971**, 1059. (b) Meier, H.; Hanold, N.; Kolshorn, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *21*, 66. (c) Larezari, I.; Shafiee, A. *J. Org. Chem.* **1971**, *36*, 2836. (d) Larezari, I.; Shafiee, A.; Rabest, F.; Yaplani, M. *J. Heterocycl. Chem.* **1972**, *9*, 141. (e) Meier, H.; Menzel, I. *Tetrehedron Lett.* **1972**, 445. (f) Meier, H.; Voigt, E. *Tetrahedron* **1972**, *28*, 1987. (g) Laureni, J.; Krantz, A.; Hanjdu, R. A. *J. Am. Chem. Soc.* **1976**, *98*, 7872. (h) Golgolab, H.; Layer, M.; Combrink, W.; Schniepp, S. *Chem. Ber.* **1976**, *109*, 1650. (i) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1977**, *99*, 4842. (j) Bak, B.; Nielsen, O.; Svanholt, H.; Holm, A. *Phys. Lett.* **1978**, *53*, 374. (k) Holm, A.; Berg, C.; Bjerre, C.; Bak, B.; Svanholt, *J. Chem. Soc., Chem. Commun.* **1979**, 99. (l) Bak, B.; Nielsen, O.; Svanholt, H. Holm, A.; Rosenkilde, S. *Chem. Phys. Lett.* **1981**, *78*, 301. (m) Meier, H.; Molz, T.; Merkle, U.; Echter, T.; Lorch, M. *Liebigs Ann. Chem.* **1982**, 914. (n) Peterso, H.; Meier, H. *Chem. Ber.* **1984**, *114*, 2382. (o) Narrit, N.; Rosenkilde, S.; Larsen, B. D.; Holm, A. *J. Chem. Soc., Perkin Trans. 1* **1985**, 907. (p) Gleiter, R.; Kratz, D.; Schafer, W.; Schehlmann, V. *J. Am. Chem. Soc.* **1991**, *113*, 9258. (q) Guziec, F. S., Jr.; SanFilippo, L. J. *J. Org. Chem.* **1991**, *56*, 3178.

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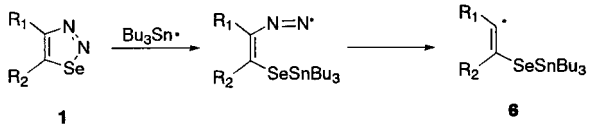
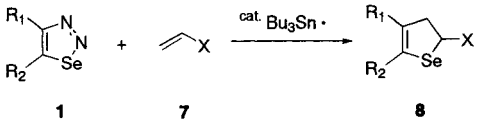
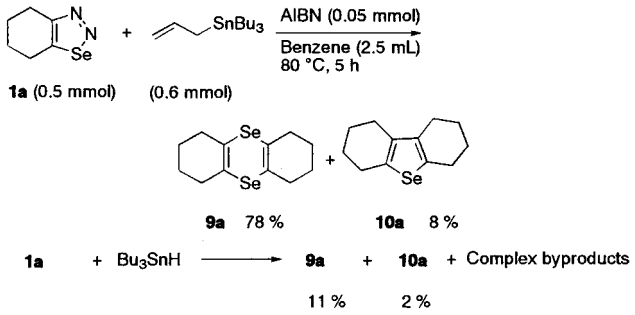
Scheme 1



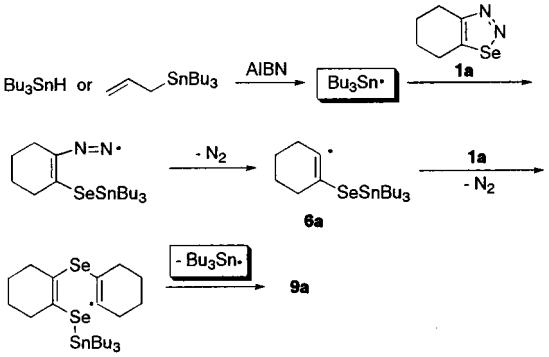
Scheme 2



Scheme 3



Scheme 4



nane, and $Bu_3SnSnBu_3$ under radical conditions has often been used as a method for the generation of carbon-centered radicals in organic synthesis.[9] On the basis of this information, it is expected that the reaction of **1** with the tributylstannyl radical should be an excellent method for the preparation of the vinyl radical intermediate **6** via the attack of the Bu_3Sn radical on the selenium atom of **1**, cleavage of the Se−N bond, and denitrogenation (Scheme 1).

We recently studied the treatment of the 1,2,3-selenadiazoles **1** with the tributylstannyl radical generated in situ from Bu_3SnH or allyltributylstannane and AIBN in the presence of olefins or dienes as a radical trapping agent and found that the reaction of 1,2,3-selenadiazoles with olefins or dienes **7** was markedly promoted by a catalytic amount of the tributylstannyl radical under mild conditions to give the corresponding dihydroselenophenes **8** in moderate to good yields (Scheme 2).[10]

In the stannyl radical-mediated reactions, the in situ generated organostannyl radical was converted into organostannyl compounds having stable Sn−X (X = halogen or heteroatom function) bonds via the abstraction of the halogen atom or heteroatom function from R−X by the stannyl radical. There are only a few examples of the catalytic use of organostannyl compounds due to the difficulty in the regeneration of organostannyl radical from organostannyl compounds having a high stability.[11,12] Some tributylstannyl hydride-catalyzed reactions have recently been disclosed: (i) the dehalogenation of organic halides,[13] (ii) the reduction of azides,[14] (iii) the reduction of α,β-unsaturated ketones,[15] (iv) the deoxygenation of alcohols,[16] (v) the reductive cyclization of enals and enones,[17] and (vi) the conversion of nitroalkanes to alkanes.[18] However, these transformations require the coexistence of a stoichiometric or excess amount of a secondary metal hydride such as $NaBH_3CN$, Ph_2SiH_2, or PMHS ($(TMSO)(SiHMe)_n(TMS)$) having the capability of regenerating Bu_3SnH. From this point of view, this catalytic reaction of 1,2,3-selenadiazoles with olefins or dienes using tributylstannyl radical is less common.[19] In this paper, the full results of the reaction of the 1,2,3-selenadiazoles with olefins or dienes in the presence of a catalytic amount of Bu_3SnH and AIBN are shown.

Results and Discussion

Dimerization of 1,2,3-Selenadiazoles in the Presence of a Catalytic Amount of Tributylstannyl Hydride or Allyltributylstannane and AIBN. When cyclohexeno-1,2,3-selenadiazole (**1a**) derived from cyclohexanone was allowed to react with a small excess amount of allyltributylstannane in the presence of a catalytic amount of AIBN at 80 °C for 5 h, the 1,4-diselenine derivative (**9a**) was formed in 78% yield (Scheme 3). When Bu_3SnH was employed in place of allyltributylstannane, the yield of **9a** was markedly decreased due to the formation of complex byproducts.[20,21] The reaction pathway shown in Scheme 4 is proposed to account for the formation of **9a**: (i) the attack of the

(9) See for examples: (a) Krief, A.; Hevesi, L. *Organoselenium Chemistry*; Springer-Verlag: Berlin, 1988; Vol. 1. (b) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, 1986. (c) Patai, S.; Rappoport, Z. *The Chemistry of Organic Selenium and Tellurium Compounds*, 1986; Vols. 1 and 2. (d) Krief, A. In *Comprehensive Organic Synthesis*; Trost, B. M., Eds.; Pergamon Press: Oxford, 1991; Vol. 3 and references therein.

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(11) Tsai, Y.-M.; Chang, S.-Y. *J. Chem. Soc., Chem. Commun.* **1995**, 981.

(12) As another example of the catalytic use of tributyltin hydride, intramolecular cyclization of organotin compounds has been reported. See: (a) Kim, S.; Lee, S. *Tetrahedron Lett.* **1991**, *32*, 6575. (b) Spino, C.; Barriault, N. *J. Org. Chem.* **1999**, *64*, 5292.

(13) (a) Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1975**, *40*, 2554. (b) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1986**, *63*, 303.

(14) Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2796.

(15) Hays, D. S.; Scholl, M.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 6751.

(16) Lopez, R. M.; Hays, D. S.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 6949.

(17) (a) Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 4. (b) Hays, D. S.; Fu, G. C. *Tetrahedron* **1999**, *55*, 8815.

(18) Tormo, J.; Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 5296.

(19) More recently, R. E. Maleczka, Jr. showed a new approach for the catalytic use of organotin compounds. See: Terstige, I.; Maleczka, R. E., Jr. *J. Org. Chem.* **1999**, *64*, 342.

(20) We suggested that, in the reaction using a small excess amount of tributylstannyl hydride, the formation of vinyl selenide derivatives via the reaction of vinyl radical with Bu_3SnH and subsequent side reactions occurred under these reaction conditions to afford the unidentified byproducts.

(21) It has been reported that the rate constants of S_H2 reactions of alkyl radicals with tributylstannyl hydride[22] are known to be much larger than those with allyltributylstannane.[23]

(22) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

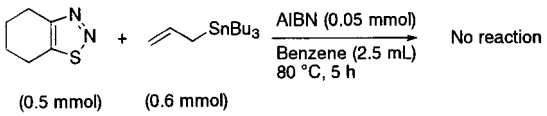
(23) Curran, D. P.; van Elburg, P. A.; Giese, B.; Gilges, S. *Tetrahedron Lett.* **1990**, *31*, 2861.

Table 1. Treatment of 1a with a Catalytic Amount of Organostannyl Compound and Radical Initiator[a]

entry	Bu_3SnR	initiator	yield (%)[b] 9a	10a
1	$Bu_3SnCH_2CH{=}CH_2$	AIBN	81	7
2	Bu_3SnH	AIBN	77	15
3[c]	Bu_3SnH	AMVN	80	6
4[d]	Bu_3SnH	Et_3B/O_2	71	5
5[e]	none	none	17	2

[a] Reaction conditions: **1a** (0.5 mmol), Bu_3SnR (0.025 mmol), radical initiator (0.0125 mmol), and benzene (2.5 mL) at 80 °C for 5 h. [b] GC yield. [c] At 60 °C. [d] At 25 °C. [e] **1a** (77%) was recovered.

Scheme 5



tributylstannyl radical generated in situ from Bu_3SnH/AIBN or allyltributylstannane/AIBN on the selenium atom of **1a**, followed by cleavage of the Se−N bond, (ii) denitrogenation to form the vinyl radical species **6a**, (iii) attack of the vinyl radical **6a** on the selenium atom of another molecule of **1a**, (iv) cleavage of the Se−N bond and elimination of the nitrogen molecule, and (v) intramolecular S_H2 reaction of vinyl radical to form **9a** and the regeneration of the tributylstannyl radical. From the result with the use of allyltributylstannane, the catalytic use of organostannyl compounds has been expected. In fact, when 1,2,3-selenadiazole **1a** derived from cyclohexanone was treated with a catalytic amount of allyltributylstannane (0.05 mol %) and AIBN (2.5 mol %) in benzene solvent at 80 °C for 5 h, the 1,4-diselenine derivative **9a** was formed in 81% yield along with a 7% yield of the selenophene derivative **10a** (entry 1 in Table 1). Table 1 shows the results of the treatment of **1a** with a catalytic amount of organostannyl compounds under various reaction conditions. In the absence of Bu_3SnH and AIBN at 80 °C for 5 h, the yield of **9a** was markedly decreased and **1a** (77%) was recovered (entry 5).[14] It is interesting to note that the catalytic use of tributylstannyl hydride instead of allyltributylstannane also led to the 77% yield of **9a** (entry 2). When diazavaleronitrile (AMVN) or Et_3B/O_2 was used instead of AIBN as the radical initiator, the reaction occurred at a lower reaction temperature, giving **9a** in 80% or 71% yield, respectively (entries 3 and 4). For cyclohexeno-1,2,3-thiadiazole, the similar reaction did not take place, and thiadiazole (98%) was recovered (Scheme 5).

Reaction of 1,2,3-Selenadiazoles with Various Olefins. On the basis of the proposed reaction pathway for the formation of **9a**, the synthesis of dihydroselenophene **8** by the addition of a vinyl radical species (**6a**) to the carbon−carbon double bond of olefins followed by intramolecular cyclization was examined (Scheme 6). When **1a** was allowed to react with an excess amount of ethyl acrylate (**7a**) (200 equiv) in the presence of Bu_3SnH/AIBN reagent at 80 °C for 5 h, the corresponding dihydroselenophene **8a**, the 1:1 addition product of **1a** and **7a**, was formed in 77% yield along with **9a** (8%) (entry 4 in Table 2). The decrease in the amount of **7a** led to a decrease in the yield of **8a** (entries 1−4). Also, the yield of **8a** was improved by the addition of a small amount of hydroquinone to prevent the oligomerization of **7a** (entry 6).[24] Table 3 shows the results of the reaction of **1a** with various olefins in the presence of a catalytic

Scheme 6

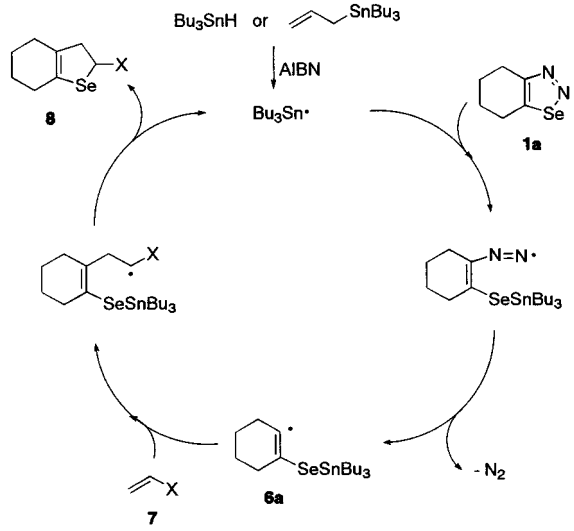
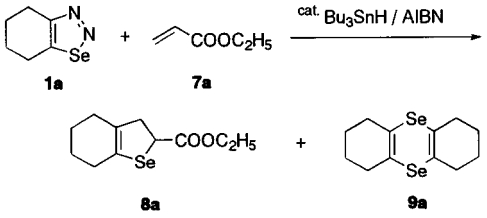


Table 2. Reaction of 1a with 7a[a]



entry	amt of **7a** (equiv)	yield (%)[b] 8a	9a
1	10	26	45
2	50	56	33
3	100	68	18
4	200	77	8
5[c]	200	72	15
6[d]	200	86 (75)	9

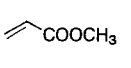
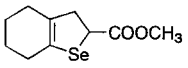
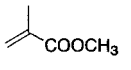
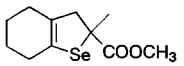
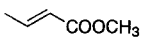
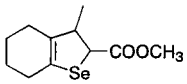
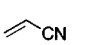
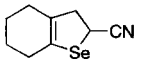
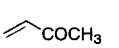
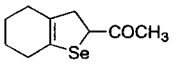
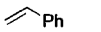
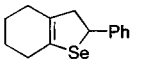
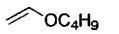
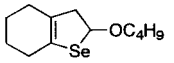
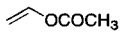
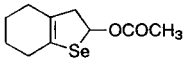
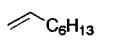
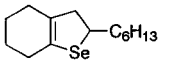
[a] Reaction conditions: **1a** (0.5 mmol), Bu_3SnH (0.025 mmol), radical initiator (0.0125 mmol), **7a**, and benzene (2.5 mL) at 80 °C for 5 h. [b] GC yield. The number in parentheses shows the isolated yield. [c] In the absence of benzene. [d] Hydroquinone (0.05 mmol) was added.

amount of Bu_3SnH/AIBN. For the reaction of methyl acrylate, acrylonitrile, and methyl vinyl ketone, the addition products were formed in 79%, 67%, and 74% yields, respectively (entries 1, 4, and 5). The use of α-methyl-substituted α,β-unsaturated esters such as methyl methacrylate also provided the corresponding dihydroselenophene in 51% yield (entry 2). In contrast to the reaction of methyl methacrylate, when methyl crotonate, in which the methyl group is substituted at the β-position, was used as an olefin, 1,4-diselenine **9a** was obtained as the main product (entry 3). Styrene also gave the corresponding addition product in 76% yield (entry 6). However, for butyl vinyl ether, vinyl acetate, and 1-octene, the yields of the addition products were very low due to the predominant formation of **9a** (entries 7−9).

Next, 1,2,3-selenadiazole **1a** was treated with dienes in the presence of a catalytic amount of the Bu_3Sn radical,

(24) We cannot explain in detail the reason for the improvement in the yields of addition products in the presence of hydroquinone. However, we suggest that the attack of the Bu_3Sn radical on 1,2,3-selenadiazole, the addition of the vinyl radical to the carbon−carbon double bond, and the intramolecular cyclization were faster than the reaction of the tributylstannyl radical with hydroquinone.

Table 3. Reaction of 1a with Olefins[a]

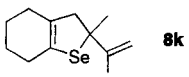
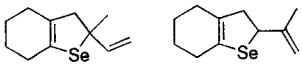
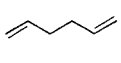
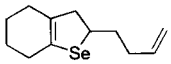
entry	olefin	product	yield (%)[b]
1	 **7b**	 **8b**	79 (71)
2	 **7c**	 **8c**	51 (43)
3	 **7d**	 **8d**	15 (9)[c,d]
4	 **7e**	 **8e**	67 (63)
5	 **7f**	 **8f**	74 (65)
6	 **7g**	 **8g**	76 (68)
7[d]	 **7h**	 **8h**	11 (7)[e]
8[e]	 **7i**	 **8i**	5 (4)[f]
9[f]	 **7j**	 **8j**	7 (5)[g]

[a] Reaction conditions: **1a** (0.5 mmol), Bu_3SnH (0.025 mmol), AIBN (0.0125 mmol), hydroquinone (0.05 mmol), olefin (100 mmol), and benzene (2.5 mL) at 80 °C for 5 h. [b] GC yield. The numbers in parentheses show the isolated yields. [c] **9a** (66%) was formed. [d] Mixture of stereoisomers (9:1). [e] **9a** (56%) was formed. [f] **9a** (67%) was formed. [g] **9a** (67%) was formed.

and these results are shown in Table 4. When **1a** was reacted with 2,3-dimethylbutadiene in the presence of a catalytic amount of Bu_3SnH and AIBN, the addition of the vinyl radical **6a** to the carbon−carbon double bond of the diene followed by cyclization proceeded to give the corresponding dihydroselenophene, the 1,2-addition product, in 58% yield (entry 1). In this reaction, when allyltributylstannane instead of Bu_3SnH was used as an organostannyl compound, the yield of the addition product was slightly increased (entry 2). For the reaction of isoprene, a mixture of 1,2-addition products was formed in 68% yield (entry 3). On the other hand, for 1,5-hexadiene, 1,4-diselenine was predominantly obtained (entry 4).

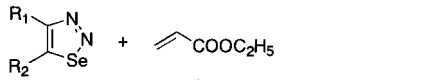
Reaction of Various 1,2,3-Selenadiazoles with Ethyl Acrylate. Various 1,2,3-selenadiazoles were reacted with ethyl acrylate (**7a**) (200 equiv) in the presence of a catalytic amount of Bu_3SnH and AIBN, and the results are shown in Table 5. When the 1,2,3-selenadiazoles prepared from 2-methyl- and 4-methylcyclohexanone were allowed to react with **7a**, the addition of vinyl radicals generated in situ from the 1,2,3-selenadiazoles to **7a** efficiently proceeded to afford the corresponding

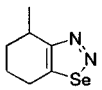
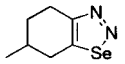
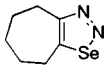
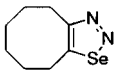
Table 4. Reaction of 1a with Dienes[a]

entry	diene	products, yield (%)[b]
1[c]	 **7k**	 **8k** 58
2	**7k**	**8k** 69
3	 **7l**	 **8l** 24 **8l'** 44
4	 **7m**	 **8m** trace

[a] Reaction conditions: **1a** (0.5 mmol), $Bu_3SnCH_2CH{=}CH_2$ (0.025 mmol), AIBN (0.0125 mmol), hydroquinone (0.05 mmol), diene (100 mmol), and benzene (2.5 mL) at 80 °C for 5 h. [b] Isolated yield. [c] Bu_3SnH was used.

Table 5. Reaction of Various 1,2,3-Selenadiazoles with Ethyl Acrylate[a]

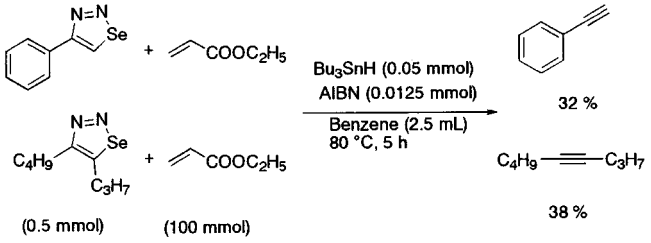


entry	1,2,3-selenadiazole	product, yield (%)[b]
1		**8n** 73 (68)[c]
2		**8o** 75 (72)[d]
3		**8p** 66 (62)
4		**8q** 26 (22)[e]
5		**8r** 5 (5)[f]

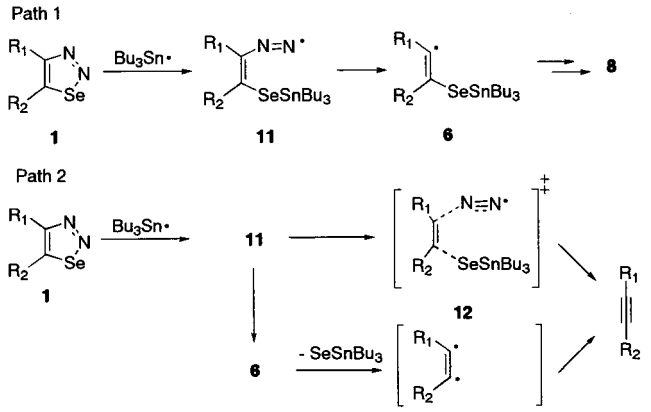
[a] Reaction conditions: 1,2,3-selenadiazole (0.5 mmol), Bu_3SnH (0.025 mmol), AIBN (0.0125 mmol), hydroquinone (0.05 mmol), ethyl acrylate (100 mmol), and benzene (2.5 mL) at 80 °C for 5 h. [b] GC yield. The numbers in parentheses show the isolated yields. [c] Mixture of stereoisomers (1:1). [d] Mixture of stereoisomes (3:2). [e] 1,2,3-Selenadiazole (40%) was recovered. Diselenine **9** was formed in 11% yield. [f] 1,2,3-Selenadiazole (52%) was recovered. Diselenine **9** was formed in 13% yield.

dihydroselenophenes in 73% and 75% yields, respectively (entries 1 and 2). Similarly, 1,2,3-selenadiazole derived from cyclopentanone gave the corresponding dihydroselenophene in 66% yield (entry 3). In the case of 1,2,3-selenadiazole prepared from cycloheptanone and cyclooctanone, the yields of the addition product were low (entries 4 and 5). For the reaction of 1,2,3-selenadiazole derived from acetophenone and dibutyl ketone, the corresponding dihydroselenophene and 1,4-diselenines were not isolated, and phenylacetylene and 4-nonyne were produced as the sole products (Scheme 7).

Scheme 7



Scheme 8. Plausible Reaction Paths



The different behaviors observed among the 1,2,3-selenadiazoles may be explained in terms of the difference in the geometry of the 1,2,3-selenadiazoles (Scheme 8). The attack of the tributylstannyl radical on the selenium atom of **1** and cleavage of the selenium−nitrogen bond successively occurred to generate the radical species **11**. In the case of 1,2,3-selenadiazoles derived from cyclic ketones, the denitrogenation from **11** to form the vinyl radical **6**, addition of **6** to the carbon−carbon double bond, and intramolecular cyclization smoothly proceeded to afford the corresponding dihydroselenophenes **8** (path 1). On the other hand, for the reaction of 1,2,3-selenadiazoles derived from linear and aromatic ketones, the fast β-fragmentation of Bu_3SnSe radical from **6** or the concerted elimination of the Bu_3SnSe radical and nitrogen molecule from **11** via the transition state **12** predominantly proceeded to give the corresponding alkynes (path 2).

In summary, we found that the reaction of 1,2,3-selenadiazoles with olefins and dienes was promoted by the catalytic amount of the tributylstannyl radical to give the corresponding dihydroselenophenes in moderate to good yields.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-400 (400 and 99.5 MHz) spectrometer using $CDCl_3$ as the solvent with tetramethylsilane as an internal standard. FT-IR spectra were obtained using a Perkin-Elmer model PARAGON 1000 spectrophotometer. Mass spectra were measured on a Shimadzu model QP-5050A instrument. Gas chromatography (GC) was carried out on a Shimadzu GC-14A instrument equipped with a flame ionizing detector and using a capillary column (Hicap-CBP-1-S25-0.25, 0.25 mm × 25 m). Selenium dioxide, ketones, aldehydes, semicarbazide hydrochloride, and acetic acid were commercially available high-grade products and were used without purification. 1,2,3-Selenadiazoles were prepared by the reaction of selenium dioxide with semicarbazones prepared by the reaction of semicarbazide hydrochloride with carbonyl compounds.[4c] The other reagents and solvents were purified by the usual methods before use.

General Procedure for the Dimerization of 1,2,3-Selenadiazoles in the Presence of a Catalytic Amount of Bu_3SnH and AIBN. 1,2,3-Selenadiazloles (0.5 mmol), Bu_3SnH (0.0025 mmol), AIBN (0.00125 mmol), and benzene (2.5 mL) were added to a 20 mL flask, and the mixture was stirred at 80 °C for 5 h under a nitrogen atmosphere. After the reaction was complete, benzene was removed under reduced pressure and purified by column chromatography on silica gel (n-C_6H_{14}:$CHCl_3$ = 7:1 as the eluent) to afford **2a** and **3a**. The products were characterized by comparison of their spectra with those of authentic samples. The structures of the products were assigned on the basis of the ^{1}H and ^{13}C NMR, IR, and GC−mass spectra.

Data for 9a: ^{1}H NMR ($CDCl_3$) δ 1.69−1.74 (m, 8H), 2.45−2.48 (m, 8H); ^{13}C NMR ($CDCL_3$) δ 23.7, 34.0, 129.7; IR (neat) 553, 762, 816, 846, 940, 1070, 1110, 1133, 1170, 1263, 1321, 1431, 1560, 2827, 2857, 2922 cm^{-1}.

Data for 10a: ^{1}H NMR ($CDCl_3$) δ 1.75−1.84 (m, 8H), 2.17−2.37 (m, 4H), 2.76−2.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 22.7, 24.2, 25.7, 27.6, 136.5, 137.3; IR (neat) 795, 1005, 1105, 1132, 1237, 1289, 1333, 1441, 1525, 2835, 2852, 2926 cm^{-1}.

General Procedure for the Reaction of 1,2,3-Selenadiazoles with Olefins or Dienes in the Presence of a Catalytic Amount of Bu_3SnH and AIBN. 1,2,3-Selenadiazole (0.5 mmol), olefin (100 mmol), Bu_3SnH (0.0025 mmol), AIBN (0.00125 mmol), hydroquinone (0.05 mmol), and benzene (2.5 mL) were added to a 20 mL flask, and the mixture was stirred at 80 °C for 5 h under a nitrogen atmosphere. After the reaction was complete, benzene and the volatile excess olefin were removed under reduced pressure and purified by column chromatography on silica gel (n-C_6H_{14}:$CHCl_3$ = 1:1 as the eluent) to afford the dihydroselenophene, 1,4-diselenine, and selenophene derivatives. The structures of the products were assigned on the basis of the ^{1}H and ^{13}C NMR, IR, and GC−mass spectra.

Data for 8a: ^{1}H NMR ($CDCl_3$) δ 1.26 (t, J = 7.3 Hz, 3H), 1.61−1.72 (m, 4H), 1.96−2.22 (m, 4H), 2.72−2.82 (m, 1H), 3.10−3.18 (m, 1H), 4.17 (d, J = 7.3 Hz, 1H), 4.18 (q, J = 7.3 Hz, 1H), 4.41 (dd, J = 5.9, 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.2, 23.5, 27.3, 27.7, 38.3, 43.1, 61.4, 125.2, 131.4, 174.0; IR (neat) 857, 1045, 1096, 1155, 1181, 1207, 1261, 1298, 1324, 1367, 1442, 1733, 2834, 2931, 2979 cm^{-1}.

Data for 8b: ^{1}H NMR ($CDCl_3$) δ 1.63−1.80 (m, 4H), 1.96−2.22 (m, 4H), 2.76−2.84 (m, 1H), 3.10−3.15 (m, 1H), 3.72 (s, 3H), 4.42 (dd, J = 5.9, 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.2, 23.5, 27.3, 27.7, 38.0, 43.2, 52.6, 125.3, 131.4, 174.5; IR (neat) 844, 983, 1055, 1155, 1172, 1209, 1262, 1293, 1329, 1435, 1737, 2835, 2855, 2930 cm^{-1}.

Data for 8c: ^{1}H NMR ($CDCl_3$) δ 1.62−1.72 (m, 4H), 1.82 (s, 3H), 1.98−2.09 (m, 4H), 2.11−2.22 (m, 2H), 2.41−2.46 (m, 1H), 3.35−3.41 (m, 1H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 22.3, 23.6, 27.5, 28.0, 28.2, 51.6, 52.3, 52.8, 125.8, 130.5, 175.9; IR (neat) 720, 767, 822, 995, 1063, 1097, 1136, 1154, 1211, 1239, 1260, 1274, 1307, 1349, 1436, 1732, 2856, 2928 cm^{-1}.

Data for 8d (mixture of stereoisomers): ^{1}H NMR ($CDCl_3$) δ 1.12 (d, J = 7.0 Hz, 2.7 H), 1.45 (d, J = 7.0 Hz, 0.3 H), 1.54−1.74 (m, 4H), 1.95−2.25 (m, 4H), 2.98−3.06 (m, 0.1 H), 3.20−3.28 (m, 0.9 H), 3.72 (s, 0.3 H), 3.73 (s, 2.7 H), 3.97 (d, J = 5.5 Hz, 0.9 H), 4.58 (d, J = 7.7 Hz, 0.1 H); ^{13}C NMR ($CDCl_3$) δ 17.7, 22.2, 22.3, 23.5, 23.6, 26.7, 27.5, 46.5, 49.5, 52.6, 124.4, 135.5, 174.2; IR (neat) 735, 780, 811, 911, 1019, 1064, 1145, 1175, 1199, 1272, 1341, 1434, 1736, 2835, 2929 cm^{-1}.

Data for 8e: ^{1}H NMR ($CDCl_3$) δ 1.61−1.79 (m, 4H), 1.98−2.32 (m, 4H), 2.91−3.07 (m, 2H), 4.24 (dd, J = 5.5, 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.0, 22.0, 23.4, 27.4, 27.6, 46.0, 121.6, 127.6, 129.8; IR (neat) 822, 997, 1062, 1156, 1200, 1262, 1307, 1350, 1437, 1655, 2231, 2834, 2855, 2928 cm^{-1}.

Data for 8f: ^{1}H NMR ($CDCl_3$) δ 1.61−1.73 (m, 4H), 1.95−2.23 (m, 4H), 2.26 (s, 3H), 2.64−2.75 (m, 1H), 3.05−3.11 (m, 1H), 4.40 (dd, J = 3.7, 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.2, 23.6, 27.2, 27.4, 27.8, 41.5, 47.6, 124.7, 132.3, 203.9; IR (neat)

827, 994, 1062, 1168, 1201, 1239, 1263, 1317, 1353, 1438, 1705, 2833, 2855, 2928 cm^{-1}.

Data for 8g: ^1H NMR ($CDCl_3$) δ 1.66−1.76 (m, 4H), 2.07−2.09 (m, 2H), 2.23−2.25 (m, 2H), 2.87−2.96 (m, 1H), 3.02−3.10 (m, 1H), 5.01 (dd, J = 7.3, 8.4 Hz, 1H), 7.18−7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 22.6, 23.8, 27.9, 28.0, 45.9, 49.9, 127.1, 127.2, 127.4, 128.7, 130.9, 144.9; IR (neat) 696, 761, 996, 1031, 1075, 1125, 1157, 1238, 1249. 1260, 1304, 1349, 1452, 1492, 1600, 1653, 2829, 2854, 2927, 3025, 3059 cm^{-1}.

Data for 8h: ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3H), 1.30−1.43 (m, 2H), 1.52−1.78 (m, 6H), 1.99−2.36 (m, 4H), 2.79−2.83 (m, 1H), 3.00−3.04 (m, 1H), 3.27 (dt, J = 6.6, 9.2 Hz, 1H), 3.58 (dt, J = 6.6, 9.2 Hz, 1H), 5.72 (dd, J = 1.5, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 19.6, 22.4, 23.8, 27.7, 28.2, 31.3, 50.2, 70.0, 86.4, 125.5, 130.2; IR (neat) 717, 827, 904, 1010, 1045, 1079, 1115, 1150, 1209, 1262, 1301, 1328, 1378, 1438, 1654, 1735, 2871, 2929 cm^{-1}.

Data for 8i: ^1H NMR ($CDCl_3$) δ 1.62−1.79 (m, 4H), 2.06 (s, 3H), 2.02−2.36 (m, 4H), 2.84 (td, J = 1.2, 13.2 Hz, 1H), 3.03−3.13 (m, 1H), 6.45 (dd, J = 1.1, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 22.3, 23.6, 27.5, 27.6, 48.1, 75.3, 126.6, 129.1, 170.6; IR (neat) 726, 826, 895, 976, 1014, 1111, 1131, 1149, 1201, 1231, 1304, 1371, 1439, 1742, 2855, 2928 cm^{-1}.

Data for 8j: ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20−1.40 (m, 10H), 1.47−1.69 (m, 4H), 1.98−2.03 (m, 2H), 2.18−2.22 (m, 2H), 2.39−2.43 (m, 1H), 2.78−2.80 (m, 1H), 3.88−3.90 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.3, 22.6, 22.8, 23.9, 28.0, 28.2, 29.2, 29.9, 32.0, 38.2, 45.2, 48.6, 126.4, 131.7; IR (neat) 724, 988, 1165, 1261, 1376, 1457, 1541, 1654, 1734, 2854, 2925 cm^{-1}.

Data for 8k: ^1H NMR ($CDCl_3$) δ 1.60−1.74 (m, 4H), 1.71 (t, J = 4.8 Hz, 3H), 1.94 (t, J = 0.8 Hz, 3H), 2.03−2.09 (m, 2H), 2.20−2.23 (m, 4H), 2.31−2.39 (m, 1H), 2.88−2.97 (m, 1H), 4.76 (dd, J = 0.8, 0.8 Hz, 1H), 4.84 (d, J = 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.9, 22.7, 23.9, 28.1. 29.2, 30.0, 53.6, 59.9, 109.5, 127.7, 131.0, 150.0; IR (neat) 890, 997, 1373, 1439, 1458, 2830, 2856, 2927, 3089 cm^{-1}.

Data for 8l (mixture of isomers): ^1H NMR ($CDCl_3$) δ1.56−1.74 (m, 6H), 1.84 (t, J = 0.8 Hz, 1.95H), 2.02−2.08 (m, 2H), 2.17−2.23 (m, 2H), 2.40−2.46 (m, 0.35H), 2.61−2.87 (m, 0.70H), 4.53 (t, J = 8.8 Hz, 0.65H), 4.71 (t, J = 1.6 Hz, 0.65H), 4.85 (d, J = 1.6 Hz, 0.65H), 4.91 (dd, J = 10.4, 0.8 Hz, 0.35H), 5.02 (dd, J = 17.2, 0.8 Hz, 0.35H), 6.30 (dd, J = 10.4, 17.2 Hz, 0.35H); ^{13}C NMR ($CDCl_3$) δ 20.0, 22.5, 22.6, 23.8, 23.9, 27.5, 27.9, 28.0, 28.1, 28.2, 46.2, 48.9, 54.9, 55.4, 55.9, 110.2, 110.6, 127.9, 130.1, 131.5, 145.0; IR (neat) 897, 996, 1064, 1533, 1440, 2830, 2856, 2926, 3081 cm^{-1}.

Data for 8n (mixture of stereoisomers): ^1H NMR ($CDCl_3$) δ 0.97 (t, J = 7.2 Hz, 1.5H), 0.98 (t, J = 7.2 Hz, 1.5H), 1.26 (t, J = 7.2 Hz, 3H), 1.24−1.30 (m, 1H), 1.70−1.87 (m, 3H), 1.98−2.15 (m, 3H), 2.18−2.23 (m, 1H), 2.72−2.88 (m, 1H), 3.04−3.18 (m, 1H), 4.12−4.21 (m, 2H), 4.43 (dt, J = 4.0, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 21.4, 21.5, 27.5, 27.6, 29.9, 30.0, 30.5, 30.6, 35.4, 35.5, 38.6, 38.7, 42.7, 42.8, 61.4, 61.5, 124.9, 125.0, 131.1, 131.2, 174.0, 174.1; IR (neat) 1153, 1179, 1204, 1324, 1368, 1733, 2832, 2850, 2921, 2951 cm^{-1}.

Data for 8o (mixture of stereoisomers): ^1H NMR ($CDCl_3$) δ 1.03 (d, J = 7.2 Hz, 1.80H), 1.08 (d, J = 7.2 Hz, 1.20H), 1.25 (t, J = 7.2 Hz, 3H), 1.25−1.40 (m, 1H), 1.58−1.67 (m, 1H), 1.72−1.82 (m, 2H), 2.13−2.17 (m, 2H), 2.18−2.34 (m, 1H), 2.64−2.75 (m, 0.5 H), 2.92−3.12 (m, 1H), 3.24−3.35 (m, 0.5H), 4.15−4.21 (m, 2H), 4.37 (dd, J = 3.2, 7.2 Hz, 0.60H), 4.40 (dd, J = 3.2, 7.2 Hz, 0.40H); ^{13}C NMR ($CDCl_3$) δ 14.3, 19.9, 20.0, 21.4, 21.6, 27.7, 30.7, 30.8, 32.9, 33.0, 38.1, 38.5, 41.2, 41.3, 61.5, 125.7, 125.8, 135.8, 135.9, 174.1; IR (neat) 1180, 1209, 1318, 1322, 1732, 2852, 2927, 2957 cm^{-1}.

Data for 8p: ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 7.0 Hz, 3H), 2.19−2.34 (m, 4H), 2.35−2.45 (m, 4H), 2.62−2,67 (m, 1H), 2.95−3.01 (m, 1H), 4.18 (q, J = 7.0 Hz, 1H), 4.19 (q, J = 7.0 Hz, 1H), 4.91 (dd, J = 5.9, 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 28.0, 31.0, 31.7, 34.4, 46.8, 61.5, 132.0, 142.6, 173.7; IR (neat) 857, 1046, 1193, 1325, 1368, 1444, 1733, 2847, 2955 cm^{-1}.

Data for 9p: ^1H NMR ($CDCl_3$) δ 2.07−2.15 (m, 4H), 2.43 (t, J = 7.3 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 25.0, 37.2, 125.0; IR (neat) 865, 1024, 1108, 1201, 1238, 1305, 1442, 1597, 2840, 2903, 2950 cm^{-1}.

Data for 8q: ^1H NMR ($CDCl_3$) δ 1.26 (t, J = 7.3 Hz, 3H), 1.48−1.77 (m, 6H), 2.08−2.30 (m, 4H), 2.99 (dd, J = 9.5, 16.5 Hz, 1H), 3.28 (dd, J = 5.9, 16.5 Hz, 1H), 4.17 (q, J = 7.3 Hz, 1H), 4.18 (q, J = 7.3 Hz, 1H), 4.37 (dd, J = 5.9, 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 26.6, 27.0, 30.5, 30.9, 31.0, 39.0, 46.8, 61.4, 127.9, 135.2, 173.9; IR (neat) 755, 858, 969, 1023, 1097, 1178, 12,7, 1325, 1367, 1444, 1732, 2848, 2920, 2978 cm^{-1}.

Data for 9q: ^1H NMR ($CDCl_3$) δ 1.51−1.57 (m, 8H), 1.72−1.78 (m, 4H), 2.62−2.65 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 26.6, 31.9, 37.7, 135.1; IR (neat) 712, 766, 820, 970, 1075, 1124, 1214, 1274, 1358, 1431, 1587, 2829, 2844, 2873, 2922 cm^{-1}.

Data for 8r: ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 7.1 Hz, 3H), 1.35−1.59 (m, 3H), 2.11−2.38 (m, 4H), 2.92 (dd, J = 9.5, 16.1 Hz, 1H), 3.20 (dd, J = 4.8, 16.1 Hz, 1H), 4.17 (q, J = 7.1 Hz, 1H), 4.18 (q, J = 7.1 Hz, 1H), 4.34 (dd, J = 4.8, 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.3, 25.9, 26.4, 28.2, 28.6, 28.7, 29.2, 38.3, 43.6, 61.4, 127.7, 133.7, 174.2; IR (neat) 688, 736, 859, 1040, 1068, 1096, 1179, 1206, 1326, 1367, 1445, 1462, 1731, 2849, 2922. 2978 cm^{-1}.

Data for 9r: ^1H NMR ($CDCl_3$) δ 1.43−1.48 (m, 8H), 1.60−1.64 (m, 8H), 2.53−2.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 26.5, 30.0, 34.8, 133.1; IR (neat) 733, 779, 831, 879, 1017, 1126, 1253, 1308, 1322, 1353, 1439, 1458, 1592, 2844, 2907 cm^{-1}.

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Supporting Information Available: ^1H and ^{13}C NMR and IR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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