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# Studies on Highly Stereoselective Addition−Elimination Reactions of 3-(Methoxycarbonyl)-1,2-allen-4-ols with MX. An Efficient Synthesis of 3-(Methoxycarbonyl)-2-halo-1,3(*Z*)-dienes

Youqian Deng, Xin Jin, and Shengming Ma*

*Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027, Zhejiang, People's Republic of China*

*masm@mail.sioc.ac.cn*

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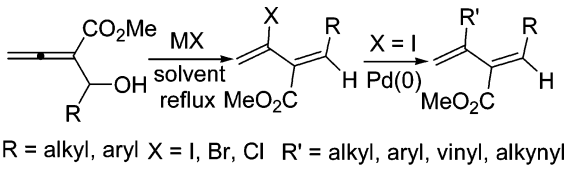
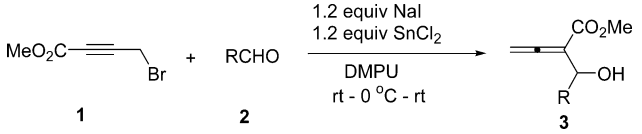



3-(Methoxycarbonyl)-2-halo-1,3(*Z*)-dienes were prepared highly stereoselectively via $S_N2'$-type addition−elimination reactions of 3-(methoxycarbonyl)-1,2-allen-4-ols with MX. These products may easily undergo Negishi or Sonogashira coupling reactions to yield a series of stereodefined polysubstituted (*E*)-1,3-dienes.

Stereoselective synthesis of conjugated 1,3-dienes is of current interest[1] since they are very important intermediates in organic synthesis.[2] It was observed that the reactions of the esters of 2,3-allenols in the presence of Pd(0) catalysts with hard carbonucleophiles such as Mg,[3a] Zn,[3b] and Cu[3b] reagents may afford 1,3-dienes with poor stereoselectivity. Recently, Bäckvall and Horváth reported a Pd-catalyzed reaction of α-allenic acetates with LiBr to afford (1*Z*,2*E*)-2-bromo-1,3-dienes[4] in good yields with good stereoselectivity (≥86). The carbonylation of allenyl methyl carbonates in $CH_3OH$ in the presence of Pd-$(PPh_3)_4$ may yield methyl 2-(methoxycarbonyl)-1,3-dienes in high yields with rather poor stereoselectivity.[5] The carbonylation of alka-2,3-dienylamines can afford 2-amido-1,3-dienes highly stereoselectively (≥95/5).[6] Hammond and Shen reported an efficient synthesis of 1,1-difluoro-2-aryl or vinyl-substituted 3-silyl-1,3-dienes[7] from 2,3-butadienyl bromides via palladium-catalyzed cross-coupling reactions with aryl halides or boronic acids and terminal alkynes. We also found a highly regio- and stereoselective protocol for the synthesis of 2(*E*),4-alkadienoates[1] via the Pd(0)-catalyzed reaction of aryl halides with 3,4-alkadienoates. 2,3-Allenylic trimethylsilyl ether can react with $TiCl_4$ forming 2-chloro-1,3-butadienes.[8] Rearrangement of tertiary α-allenic carbamates may afford 2-*O*-carbamoyl-4,4-disubstituted 1,3-dienes[9] with poor stereoselectivity. Recently, Alcaide et al. reported a novel stereoselective synthesis of 1,2,3-trisubstitued 1,3-dienes[10] through [3,3]-sigmatropic rearrangements in α-allenic methanesulfonates. The reactions of 2-(trimethylsilyl)-2,3-allenols with lithium aluminum hydride afforded 2-(trimethylsilyl)-1,3-butadienes[11] with rather poor stereoselectivity. We have observed that the reaction of 1-aryl-2,3-allenols with lithium halides in HOAc affords 1-aryl-3-halo-1,3-dienes[12] in the absence of any Pd catalyst; however, no reaction was observed with 1-alkyl or perfluoroalkyl-2,3-allenols. We wish to report here a highly stereoslective $S_N2'$-type addition−elimination reaction of MX and 3-(alkoxycarbonyl)-1,2-allen-4-ols with an alkyl or aryl group at the 4-position.

**TABLE 1. Preparation of 3-(Methoxycarbonyl)-1,2-allen-4-ols**




| Entry | R | time (h) | yield of **3** (%) |
|---|---|---|---|
| 1 | $C_2H_5$ | 30 | 59 (**3a**) |
| 2 | *n*-$C_3H_7$ | 36 | 61 (**3b**) |
| 3 | *i*-$C_3H_7$ | 14 | 83 (**3c**) |
| 4 | *n*-$C_5H_{11}$ | 36 | 59 (**3d**) |
| 5 | Ph | 22 | 78 (**3e**) |
| 6 | *p*-$CH_3C_6H_4$ | 24 | 68 (**3f**) |

**Synthesis of Starting Materials.** 3-(Methoxycarbonyl)-1,2-allen-4-ols **3** are easily available from a modified one-step high-yielding reaction of 3-(methoxycarbonyl) propargyl bromide **1**,[13] aldehydes **2**, and $SnCl_2$/NaI[14] in DMPU[15] (Table 1).

**Addition−Elimination Reactions of 3-(Methoxycarbonyl)-1,2-allen-4-ols with MX.** Our initial work began with the reaction of 3-(methoxycarbonyl)-1,2-heptadien-4-ol **3b** with NaI.

* Corresponding author. Tel.: 86-21-549-25147; fax: 86-21-641-67510.

(1) For summary of some representative reports on the synthesis of 1,3-dienes, see the references cited in: Fu, C.; Ma, S. *Org. Lett.* **2005**, *7*, 1707.

(2) (a) Fringuelli, F.; Taticchi, A. *Dienes in the Diels−Alder Reaction*; John Wiley: New York, 1990. (b) Fringuelli, F.; Taticcchi, A. *Diels−Alder Reaction. Selected Practical Methods*; John Wiley: New York, 2002. (c) Wasserman, A. *Diels−Alder Reactions*; Elsevier: Amsterdam, 1965. (d) Wallweben, H. *Diels−Alder Reaction*; Thieme: Stuttgart, Germany, 1972. (e) Oppolzer, W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK **1991**, *Vol. 5*, Chapter 4.1, pp 315−400. (f) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, Ch. 4.4, pp 513−550. (g) Mehta, G.; Rao, S. P. In *The Chemistry of Dienes and Polyenes*; Rappoport, Z., Ed.; John Wiley: New York, 1997; Ch. 9, pp 361−467.

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(14) For the reactions of propargyl iodides with aldehydes in DMI, see: Mukaiyama, T.; Harada, T. *Chem. Lett.* **1981**, 621.

(15) For the reaction of 3-(methoxycarbonyl) propargyl iodide with aldehydes in DMPU, see: Winkler, J. D.; Quinn, K. J.; MacKinnon, C. H.; Hiscock, S. D.; McLaughlin, E. C. *Org. Lett.* **2003**, *5*, 1805.

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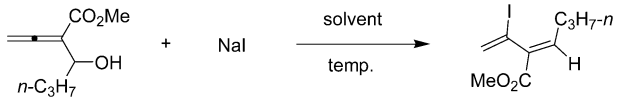
**TABLE 2. Reaction of 3-(Methoxycarbonyl)-1,2-heptadien-4-ol with NaI**

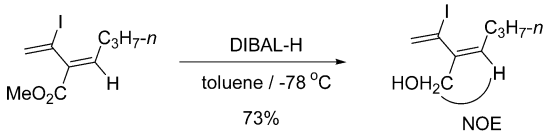



3b 4ba

| entry | solvent | NaI (equiv) | temp (°C) | time (h) | yield of **4ba** (%) |
|---|---|---|---|---|---|
| 1 | $CH_3COOH$ | 1.2 | reflux | 1 | trace |
| 2 | $Ac_2O$ | 1.2 | 110 | 1 | 41 |
| 3 | HI | | 80 | 3 | trace |
| 4 | TFA[a] | 1.2 | reflux | 1 | 61 |
| 5 | TFA | 2.0 | reflux | 1 | 73 |
| 6 | TFA | 4.0 | reflux | 1 | 68 |
| 7 | TFA | 2.0 | rt | 24 | 32 |

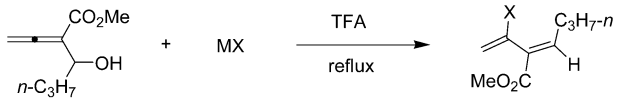
[a] TFA = $CF_3COOH$.

**SCHEME 1**




4ba 5ba

**TABLE 3. Reaction of 3-(Methoxycarbonyl)-1,2-heptadien-4-ol with MX**



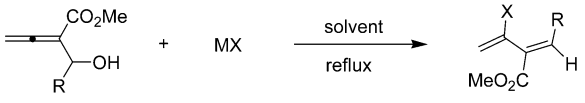

3b 4b

| Entry | MX (equiv) | time (h) | yield (%) |
|---|---|---|---|
| 1 | NaI (2.0) | 1 | 73 (**4ba**) |
| 2 | $LiI·3H_2O$ (2.0) | 1 | 58 (**4ba**) |
| 3 | KI (2.0) | 1 | 44 (**4ba**) |
| 4 | $LiBr·H_2O$ (2.0) | 2 | 76 (**4bb**) |
| 5 | KBr (2.0) | 3 | 58 (**4bb**) |
| 6 | $LiCl·H_2O$ (4.0) | 3 | 55 (**4bc**) |
| 7 | NaCl (4.0) | 14 | trace (**4bc**) |

Some typical results are summarized in Table 2. Among the solvents tested, TFA (Table 2, entry 4) is the best, while HOAc, $Ac_2O$, or HI (Table 2, entries 1−3) are all inferior. A higher-yielding reaction was observed when the reaction was conducted in TFA under reflux (compare Table 2, entries 5 and 7). Best results were obtained with the use of 2 equiv of NaI (compare Table 2, entries 4−6). In conclusion, the reaction may afford methyl 2-(1′-iodovinyl)hex-2(*Z*)-enoate **4ba** in 73% yield when the reaction was conducted with 2 equiv of NaI in TFA under reflux (Table 2, entry 5). $^1$H NMR spectra of the crude product indicated the formation of only one stereoisomer. The stereochemistry was established by the NOESY analysis of **5ba**, which was formed by the reduction of **4ba** with DIBAL-H in toluene in 73% yield (Scheme 1).

On the basis of these results, other $I^-$ sources were tested (Table 3). It was obvious that NaI afforded better results than $LiI·3H_2O$ and KI (Table 3, entries 1−3). As for $Br^-$ and $Cl^-$ sources, $LiBr·H_2O$ and $LiCl·H_2O$ are better (Table 3, entries 4−7). By applying the standard reaction conditions, the corresponding methyl 2-(1′-bromovinyl)hex-2(*Z*)-enoate **4bb** and methyl 2-(1′-chlorovinyl)hex-2(*Z*)-enoate **4bc** can be prepared in 76 and 55% yields, respectively (Table 3, entries 5 and 6).

**TABLE 4. Reactions of 3-(Methoxycarbonyl)-1,2-allen-4-ols with MX**




3 4

| entry | R | solvent | MX (equiv) | time (h) | yield of **4** (%) |
|---|---|---|---|---|---|
| 1 | $C_2H_5$ (**3a**) | TFA | NaI (2.0) | 1 | 50 (**4aa**) |
| 2 | $C_2H_5$ (**3a**) | TFA | $LiBr·H_2O$ (2.0) | 2 | 56 (**4ab**) |
| 3 | $C_2H_5$ (**3a**) | TFA | $LiCl·H_2O$ (4.0) | 3 | 39 (**4ac**) |
| 4 | *n*-$C_3H_7$ (**3b**) | TFA | NaI (2.0) | 1 | 73 (**4ba**) |
| 5 | *n*-$C_3H_7$ (**3b**) | TFA | $LiBr·H_2O$ (2.0) | 2 | 76 (**4bb**) |
| 6 | *n*-$C_3H_7$ (**3b**) | TFA | $LiCl·H_2O$ (4.0) | 6 | 55 (**4bc**) |
| 7 | *i*-$C_3H_7$ (**3c**) | TFA | NaI (2.0) | 2 | 53 (**4ca**) |
| 8 | *i*-$C_3H_7$ (**3c**) | TFA | $LiBr·H_2O$ (2.0) | 1 | 64 (**4cb**) |
| 9 | *i*-$C_3H_7$ (**3c**) | TFA | $LiCl·H_2O$ (4.0) | 2 | 39 (**4cc**) |
| 10 | *n*-$C_5H_{11}$ (**3d**) | TFA | NaI (2.0) | 1 | 75 (**4da**) |
| 11 | *n*-$C_5H_{11}$ (**3d**) | TFA | $LiBr·H_2O$ (2.0) | 3.5 | 67 (**4db**) |
| 12 | *n*-$C_5H_{11}$ (**3d**) | TFA | $LiCl·H_2O$ (4.0) | 4 | 47 (**4dc**) |
| 13 | Ph (**3e**) | TFA | NaI (2.0) | 1 | 0 (**4ea**)[a] |
| 14 | Ph (**3e**) | TFA | $LiBr·H_2O$ (2.0) | 1 | 44 (**4eb**) |
| 15 | Ph (**3e**) | TFA | $LiCl·H_2O$ (4.0) | 4 | 26 (**4ec**) |
| 16 | Ph (**3e**) | HOAc | NaI (2.0) | 2 | 40 (**4ea**) |
| 17 | Ph (**3e**) | HOAc | $LiBr·H_2O$ (2.0) | 3 | 44 (**4eb**) |
| 18 | Ph (**3e**) | HOAc | $LiCl·H_2O$ (4.0) | 4 | 30 (**4ec**) |
| 19 | *p*-$CH_3C_6H_4$ (**3f**) | HOAc | NaI (2.0) | 1 | 73 (**4fa**) |
| 20 | *p*-$CH_3C_6H_4$ (**3f**) | HOAc | $LiBr·H_2O$ (2.0) | 1 | 62 (**4fb**) |
| 21 | *p*-$CH_3C_6H_4$ (**3f**) | HOAc | $LiCl·H_2O$ (4.0) | 1 | 59 (**4fc**) |

[a] No **4ea** was formed when the reaction was conducted in TFA.

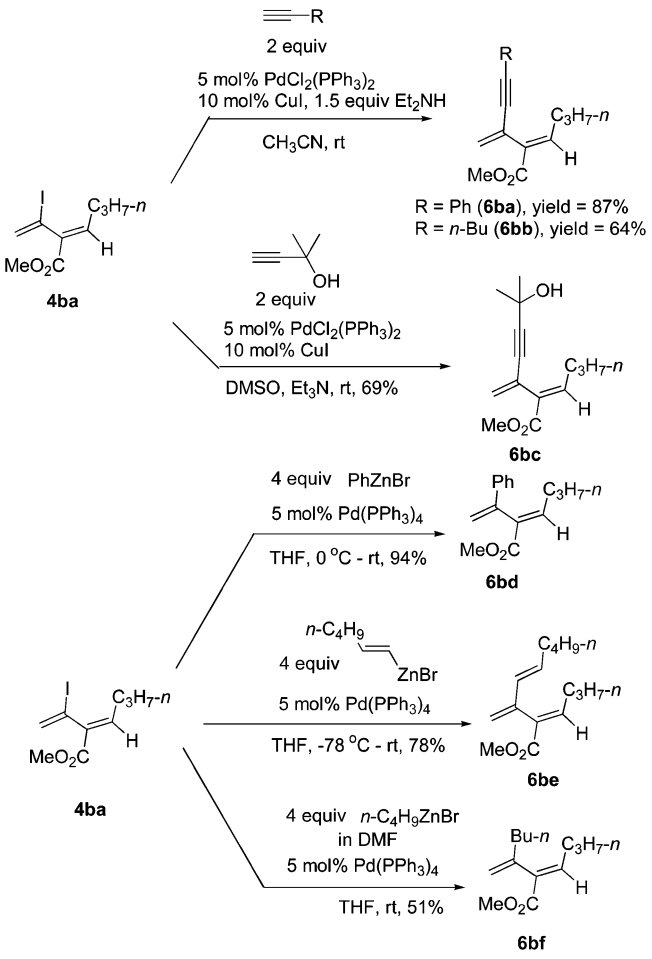
With the optimized conditions in hand, the scope of this reaction was explored with some of the typical results being summarized in Table 4. It may be concluded from Table 4 that R can be not only an aryl group but also an alkyl group, which was different from our previous report.[12] When R is an alkyl group, the reaction can occur smoothly to afford the products in moderate to good yields in TFA (Table 4, entries 1−12); it should be noted that when R is the phenyl group, the product **4ea** cannot be afforded in TFA (Table 4, entry 13). After some screening, it was found that when HOAc was used, **4ea** was produced in 40% yield (entry 16, Table 4). HOAc is also suitable for other similar reactions (Table 4, entries 16−21). It was obvious that the aryl group bearing an electron-donating group afforded the products in higher yields (compare Table 4, entries 16−21).

**Synthetic Application.** The synthetic potentials of the addition−elimination products **4** are demonstrated by transformations of the representative product **4ba** (Scheme 2). Treatment of **4ba** with terminal alkynes gave corresponding Sonogashira coupling[16] products (i.e., the stereodefined conjugated dienynes **6ba** (87%), **6bb** (64%), and **6bc** (69%)). The Negishi coupling[17] reaction of **4ba** with phenyl, 1(*E*)-hexenyl, or *n*-butyl zinc

(16) For the seminal report of the Sonogashira coupling reaction, see: (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. For some the most recent examples, see: (b) Köllhofer, A.; Pullmann, T.; Plenio, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1056. (c) Tykwinski, R. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1566. (d) Gelman, D.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 5993. (e) Sakai, N.; Annaka, K.; Konakahara, T. *Org. Lett.* **2004**, *6*, 1527. (f) Ma, S.; Ren, H.; Wei, Q. *J. Am. Chem. Soc.* **2003**, *125*, 4817. (g) Lu, Z.; Ma, S. *J. Org. Chem.* **2006**, *71*, 2655.

(17) For the seminal report of Negishi coupling reactions, see: Negishi, E.; King, A. O.; Okudado, N. *J. Org. Chem.* **1977**, *42*, 1821. For a review, see: Negishi, E.; Liu, F. In *Metal-Catalyzed Cross-Coupling Reactions*; Stang, P., Diederich, F., Eds.; VCH: Weinheim, Germany, 1998; pp 1−47.

**SCHEME 2**




bromides gave the coupling products **6bd** (86%), **6be** (80%), and **6bf** (51%), respectively.

In conclusion, we have developed a $S_N2'$-type addition−elimination reaction of 3-(methoxycarbonyl)-1,2-allen-4-ols with MX forming 3-(methoxycarbonyl)-2-halo-1,3(*Z*)-dienes highly stereoselectively in moderate yields, providing an efficient route for the synthesis of a series of polysubstituted (*E*)-1,3-dienes. Further studies including the scope and synthetic application of this type of reaction are being carried out in our laboratory.

## Experimental Section

**Synthesis of 3-(Methoxycarbonyl)-1,2-allen-4-ols. 3-(Methoxycarbonyl)-1,2-hexadien-4-ol (3a). Typical Procedure.**[15] To a solution of 3-(methoxycarbonyl)propargyl bromide (3.4806 g, 19.7 mmol)[13] in 30 mL of DMPU were added $SnCl_2$ (4.6011 g, 24.2 mmol) and NaI (3.6107 g, 24.1 mmol) at room temperature. The resulting yellow slurry was stirred in the absence of light (the reaction tube was wrapped with a black plastic bag) for 6 h. A solution of propionaldehyde (0.9281 g, 16.0 mmol) in 10 mL of DMPU was then added dropwise over 15 min at 0 °C. The orange reaction mixture was allowed to warm up to room temperature and stirred in the dark for an additional 24 h. The reaction was cooled to 0 °C, diluted with $Et_2O$, and quenched with 30 mL of saturated aqueous $NH_4Cl$. The organic phase was separated, and the aqueous phase was extracted with $Et_2O$ (4 × 30 mL). The combined organic layer was washed with brine and dried over anhydrous $Na_2SO_4$. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) afforded **3a** (1.4606 g, 59%): liquid; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.20 (d, $J$ = 2.0 Hz, 2H), 4.32−4.24 (m, 1H), 3.70 (s, 3H), 3.20−2.94 (bs, 1H), 1.66−1.57 (m, 2H), 0.89 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 212.4, 167.3, 102.6, 80.5, 70.4, 52.1, 28.2, 10.0; MS (*m*/*z*): 156 ($M^+$, 0.12), 127 (100); IR (neat, $cm^{-1}$): 3490, 2965, 1964, 1935, 1713, 1266. HRMS calcd for $C_8H_{12}NaO_3$ ($M^+$ + Na): 179.0679, found: 179.0676.

**Addition−Elimination Reactions of 3-(Methoxycarbonyl)-1,2-allen-4-ols with MX. Preparation of Methyl 2-(1′-Iodovinyl)-pent-2(*Z*)-enoate (4aa). Typical Procedure.** To a mixture of NaI (151.1 mg, 1.0 mmol) and **3a** (77.0 mg, 0.49 mmol) was added 1.0 mL of TFA at room temperature. After the addition, the reaction was refluxed at 80 °C with stirring for 1 h. After the reaction was complete as monitored by TLC, it was cooled to room temperature and slowly quenched by 10 mL of water followed by neutralization with $NaHCO_3$ until no gas was released. The mixture was extracted with diethyl ether (3 × 25 mL) and washed with a saturated aqueous solution of $Na_2S_2O_3$ and brine. The organic layer was dried over anhydrous $Na_2SO_4$. Evaporation and column chromatography on silica gel (30−60 °C petroleum ether/diethyl ether = 30:1) afforded **4aa** (65.4 mg, 50%): liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.75 (t, $J$ = 7.8 Hz, 1H), 6.08 (d, $J$ = 1.1 Hz, 1H), 6.03 (d, $J$ = 1.1 Hz, 1H), 3.77 (s, 3H), 2.29−2.18 (m, 2H), 1.06 (t, $J$ = 7.7 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 165.3, 146.6, 135.7, 131.2, 96.3, 52.1, 22.8, 12.3; MS (*m*/*z*): 267 ($M^+$ + 1, 100); IR (neat, $cm^{-1}$): 2962, 1722, 1603, 1434, 1243. HRMS calcd for $C_8H_{11}IO_2$ ($M^+$): 265.9798, found: 265.9790.

**Reduction of Methyl 2-(1′-Iodovinyl)hex-2(*Z*)-enoate (4ba).** DIBAL-H (1.4 mL, 1 M in toluene, 1.4 mmol) was added dropwise to a solution of **4ba** (180.0 mg, 0.64 mmol) in toluene (3 mL) at −78 °C. After complete conversion of the starting material as monitored by TLC, the reaction mixture was quenched with 2 mL of $CH_3OH$ and 5 mL of water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic layer was dried over $Na_2SO_4$. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) afforded 118.7 mg (73%) of **5ba**: liquid; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.03 (d, $J$ = 1.2 Hz, 1H), 5.99 (d, $J$ = 1.2 Hz, 1H), 5.53 (t, $J$ = 7.4 Hz, 1H), 4.15 (s, 2H), 2.13−2.00 (m, 3H), 1.45−1.34 (m, 2H), 0.90 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 142.4, 129.9, 129.8, 102.5, 64.9, 30.7, 22.0, 13.8; MS (*m*/*z*): 252 ($M^+$, 4.26), 79 (100); IR (neat, $cm^{-1}$): 3333, 2958, 2929, 2870, 1608, 1456, 1107, 900. HRMS calcd for $C_8H_{13}IO$ ($M^+$): 274.9903, found: 274.9914.

**Synthetic Application of Methyl 2-(1′-Iodovinyl)hex-2(*Z*)-enoate (4ba). Methyl 2-(4′-Phenylbut-1′-en-3′-yn-2′-yl)hex-2(*E*)-enoate (6ba).** A mixture of $Pd(PPh_3)_2Cl_2$ (6.8 mg, 5 mol %, 0.01 mmol), CuI (4.1 mg, 10 mol %, 0.02 mmol), $Et_2NH$ (22.2 mg, 0.30 mmol), phenylacetylene (41.6 mg, 0.41 mmol), and **4ba** (55.9 mg, 0.20 mmol) in $CH_3CN$ (2 mL) was stirred at room temperature over a period of 24 h under nitrogen. After complete conversion of the starting materials as monitored by TLC, the reaction mixture was diluted with 10 mL of $Et_2O$ and quenched with 5 mL of water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic layer was dried over $Na_2SO_4$. Evaporation and column chromatography on silica gel (petroleum ether/diethyl ether = 30:1) afforded **6ba** (44.1 mg, 87%): liquid; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.46−7.38 (m, 2H), 7.34−7.26 (m, 3H), 6.94 (t, $J$ = 7.6 Hz, 1H), 5.85 (s, 1H), 5.39 (s, 1H), 3.79 (s, 3H), 2.32 (q, $J$ = 7.3 Hz, 2H), 1.59−1.45 (m, 2H), 0.96 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 166.6, 145.8, 131.8, 131.6, 128.23, 128.18, 126.7, 125.1, 123.0, 89.1, 88.7, 52.0, 31.4, 21.9, 13.8; MS (*m*/*z*): 254 ($M^+$, 62.02), 165 (100); IR (neat, $cm^{-1}$): 2959, 1720, 1639, 1600, 1489, 1435, 1250, 1058. HRMS calcd for $C_{17}H_{18}NaO_2$ ($M^+$ + Na): 277.1199, found: 277.1196.

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**Supporting Information Available:** Complete set of experimental procedures and copies of $^{1}H$ and $^{13}C$ NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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