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Stereoselective Synthesis of (1*Z*,3*E*)-2-Ethoxycarbonyl-Substituted 1,3-Dienes via Stille Coupling of (*E*)-α-Stannyl-α,β-Unsaturated Esters with Alkenyl Halides

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Abstract: Palladium-catalyzed hydrostannylation of alkynyl esters in benzene at room temperature gives stereoselectively (*E*)-α-stannyl-α,β-unsaturated esters **1** in good yields. (*E*)-α-Stannyl-α,β-unsaturated esters **1** are difunctional group reagents that undergo Stille coupling reactions with alkenyl halides **2** in the presence of $Pd(PPh_3)_4$ and CuI co-catalyst to afford stereoselectively (1*Z*,3*E*)-2-ethoxycarbonyl-substituted 1,3-dienes **3** in good yields.

Keywords: Alkynyl ester, functionalized 1,3-diene, hydrostannylation, (*E*)-α-stannyl-α,β-unsaturated ester, Stille coupling

INTRODUCTION

The stereocontrolled synthesis of conjugated dienes attracts considerable interest in organic chemistry because of their appearance in a wide variety of biologically active molecules and their key synthetic intermediates.[1] The synthesis of 1,3-dienes for use in the Diels–Alder reaction is still an important challenge in organic synthesis,[2] although other elegant uses of these compounds have been developed.[3] Conjugated dienes are usually prepared by utilizing either a Wittig-type approach[4] or the

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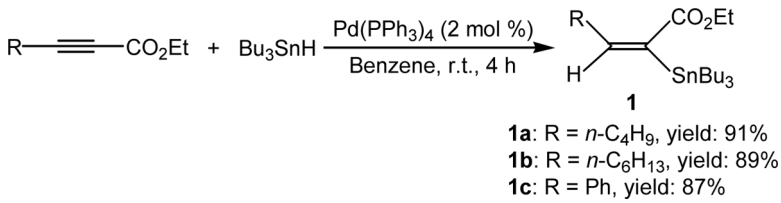
transition-metal-catalyzed coupling reactions of stereodefined vinyl halides with vinyl organometallic compounds.[5] Recently, Kasatkin and Whitby reported the insertion of 1-lithio-1-halobutadiene into organozirconocenes, providing a stereocontrolled synthesis of (1*E*,3*Z*)-1,3-dienes.[6] Molander and Yokoyama reported a one-pot stereoselective synthesis of trisubstituted 1,3-dienes via sequential Suzuki–Miyaura cross-coupling with alkenyl- and alkyltrifluoroborates.[7]

The stereoselective synthesis of functionalized 1,3-dienes is also of considerable interest in organic synthesis.[8] Heteroatom-substituted 1,3-dienes are also useful precursors for constructing highly functionalized ring systems in Diels–Alder reactions.[9] The stereoselective synthesis of 1,3-dienylsilanes,[10] 1,3-dienyl sulfides,[11] 1,3-dienyl selenides,[12] 1,3-dienyl sulfones,[13] and 1,3-dienylstannanes[14] has already been described in the literature. 2-Alkoxycarbonyl-substituted 1,3-dienes have been extensively studied in recent years as potential starting materials for organic synthesis, in particular for various [4 + 2] cycloadditions. A number of these compounds have proven to be valuable precursors for functionalized alkyl 1-cyclohexene-1-carboxylates,[15] naturally occurring cyclopentanoid terpenic acids,[16] and biologically important litsenolides.[17] Many methods for the synthesis of 2-alkoxycarbonyl-substituted 1,3-dienes have been developed, including aldol-type condensation of metalated alkene carboxylates,[16,17] Wittig olefination of aldehydes,[18] titanium(IV) chloride–catalyzed reaction of 1-ethoxy-3-trimethylsilyl-1-propyne with 1-haloketones,[19] Pd(0)-catalyzed coupling of lithium (α-alkoxycarbonyl)alkenyl cuprates with vinyl halides,[20] and the Horner–Emmons reaction of the allylphosphonates with aldehydes.[21] Very recently, Palmelund et al. have reported the synthesis of 2-ethoxycarbonyl-substituted 1,3-dienes from aldehydes and ethyl acrylate in the presence of a phosphine and a Lewis acid through a modification of the Morita reaction.[22] Despite considerable methodological differentiation, the majority of the reported procedures suffer from some drawbacks such as limited scope,[16,17] scarce availability of substrates,[19–21] moderate yields,[17,18] and poor stereoselectivity.[22] Herein, we report that (1*Z*,3*E*)-2-ethoxycarbonyl-substituted 1,3-dienes can be synthesized stereoselectively by palladium-catalyzed hydrostannylation of alkynyl esters, followed by Stille coupling reaction with alkenyl halides in the presence of $Pd(PPh_3)_4$ and CuI cocatalyst.

RESULTS AND DISCUSSION

The Stille coupling reactions of vinylstannanes with alkenyl halides provide a convenient route to stereoselective synthesis of 1,3-dienes.[23]

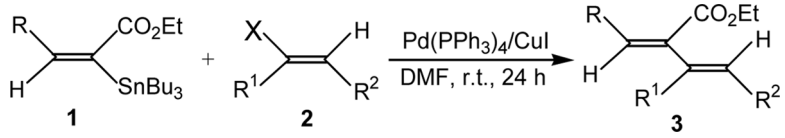


Scheme 1. Synthesis of (*E*)-α-stannyl-α,β-unsaturated esters.

The interesting point of the method is a high tolerance for functional groups such as allylic ether, vinylic thioethers, esters, ketones, or trimethylsilyl ether.[24] Palladium-catalyzed hydrostannylation of phenylthioalkynes,[25] alkynyl selenides,[26] and alkynyl sulfoxides[27] have been reported to be highly regio- and stereoselective, providing a direct route for the stereoselective synthesis of 1,1-difunctional group reagents containing heteroatom and tin. Rossi et al.[28] reported palladium-catalyzed hydrostannylation of alkynyl esters in tetrahydrofuran (THF). To prepare highly selectively (*E*)-α-stannyl-α,β-unsaturated esters, we investigated palladium-catalyzed hydrostannylation of alkynyl esters with Bu_3SnH in benzene at room temperature and found that benzene was a better solvent than THF. (*E*)-α-Stannyl-α,β-unsaturated esters **1** were obtained with good regio- and stereoselectivity in good yields (Scheme 1).

Investigations of the crude products **1** by ^1H NMR spectroscopy (400 MHz) showed their isomeric purities of more than 98%. One olefinic proton signal of compounds **1a** and **1b** splits characteristically into one triplet at $\delta = 6.04$ with coupling constant $J = 6.8$–7.2 Hz, which indicated that the hydrostannylation to the alkynyl esters had taken place with strong preference for the addition of the tin atom at the carbon adjacent to the ester group. The stereochemistry of the addition was readily apparent from the ^1H NMR spectra of compounds **1**, which showed a ($^3J_{Sn\text{-}H}$) coupling constant of 64 Hz, fully in accord with an *E* geometry and overall *cis* addition of tin hydride.[29]

(*E*)-α-Stannyl-α,β-unsaturated esters **1** are difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and as α,β-unsaturated esters. With a convenient route to the (*E*)-α-stannyl-α,β-unsaturated esters **1**, we decided to establish the feasibility of using **1** in cross-coupling reactions with alkenyl halides **2**. Gratifyingly, when the cross-coupling reactions of **1** with a variety of alkenyl iodides **2** were conducted in dimethylformamide (DMF) at room temperature using $Pd(PPh_3)_4$ and CuI as cocatalysts (Scheme 2), fairly rapid reactions



Scheme 2. Synthesis of (1*Z*,3*E*)-2-ethoxycarbonyl-substituted 1,3-dienes.

occurred, affording stereoselectively the desired coupling products **3** in good yields. The experimental results are summarized in Table 1. When alkenyl bromides were used as the electrophiles, the cross-coupling reactions of (*E*)-α-stannyl-α,β-unsaturated esters **1** also proceeded smoothly under the same conditions to give (1*Z*,3*E*)-2-ethoxycarbonyl-substituted 1,3-dienes **3** in good yields (entries 10–13).

It is well documented that the cross-coupling reaction (Stille coupling) of vinylstannanes with organic halides in the presence of a palladium catalyst occurs with retention of configuration.[24] The 3*E*-configuration of the compounds **3a**–**h** has been proved by their ^{1}H NMR spectra, which show a doublet at $\delta = 6.00$–6.88 with a coupling constant of 15.6–16.4 Hz, and this is also the evidence of the retention of the *E*-configuration of the starting compounds **2**. In addition, the 1*Z*-configuration of the compound **3c** was confirmed by nuclear overhauser effect spectroscopy (NOESY) in the ^{1}H NMR spectrum. An enhancement of the allylic protons was observed as the vinylic proton ($\delta = 5.92$) of **3c** was irradiated. There was no correlation between the allylic protons

Table 1. Synthesis of (1*Z*,3*E*)-2-ethoxycarbonyl-substituted 1,3-dienes (**3a**—**i**)

Entry	R	R^1	R^2	X	Product	Yield[a] (%)
1	*n*-C_4H_9	H	*n*-C_4H_9	I	**3a**	81
2	*n*-C_4H_9	H	Ph	I	**3b**	86
3	*n*-C_4H_9	H	CH_3OCH_2	I	**3c**	78
4	*n*-C_4H_9	H	*n*-C_6H_{13}	I	**3d**	79
5	Ph	H	CH_3OCH_2	I	**3e**	75
6	Ph	H	Ph	I	**3f**	82
7	Ph	H	*n*-C_4H_9	I	**3g**	86
8	Ph	H	*n*-C_6H_{13}	I	**3h**	84
9	*n*-C_4H_9		$-(CH_2)_4-$	I	**3i**	80
10	*n*-C_4H_9	H	*n*-C_4H_9	Br	**3a**	78
11	*n*-C_4H_9	H	Ph	Br	**3b**	81
12	Ph	H	CH_3OCH_2	Br	**3e**	74
13	Ph	H	Ph	Br	**3f**	80

[a]Isolated yield based on (*E*)-α-stannyl-α,β-unsaturated ester **1**.

($\delta = 2.26$–2.32) and the vinylic proton ($\delta = 6.24$). The correlation between the vinylic proton ($\delta = 5.92$) and another vinylic proton ($\delta = 6.24$) was observed. The NOE results indicate that **3c** had the expected 1*Z*-configuration and that the cross-coupling reaction of (*E*)-α-stannyl-α,β-unsaturated esters with alkenyl halides occured with the configuration retention of both the starting compounds **1** and the compounds **2**.

EXPERIMENTAL

General

^{1}H NMR spectra were recorded on a Bruker AC-P400 (400-MHz) spectrometer with tetramethylsilane (TMS) as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR (100-MHz) spectra were recorded on a Bruker AC-P400 (400-MHz) spectrometer using $CDCl_3$ as the solvent. Infrared (IR) spectra were determined on an FTS-185 instrument as neat films. Mass spectra (MS) were obtained on a Finnigan 8239 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. All reactions were carried out in predried glassware (150°C, 4 h) and cooled under a stream of dry Ar. Benzene was distilled from sodium prior to use. DMF was dried by distillation over calcium hydride.

Synthesis of (*E*)-α-Stannyl-α,β-unsaturated Esters (1a–c)

General Procedure

A 25-mL, two-necked, round-bottomed flask equipped with a magnetic stir bar and argon was charged sequentially with alkynyl ester (1 mmol), benzene (4 mL), $Pd(PPh_3)_4$(0.02 mmol), and Bu_3SnH (1.05 mmol). The mixture was stirred at room temperature for 4 h. After removal of the solvent under reduced pressure, the residue was diluted with light petroleum ether (20 mL) and filtered to remove the palladium catalyst. The resulting solution was concentrated under vacuum, and the residue was purified by flash chromatography on silica gel (eluent: light petroleum ether/EtOAc, 19:1).

(*E*)-1-Tributylstannyl-1-ethoxycarbonyl-1-hexene (**1a**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (t, $J = 6.8$ Hz, $^3J_{Sn\text{-}H} = 64$ Hz, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 2.44–2.40 (m, 2H), 1.58–1.26 (m, 19H),

0.95–0.84 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 153.6, 135.6, 59.9, 31.8, 31.4, 29.9, 27.3, 22.3, 14.4, 13.9, 13.7, 10.3; IR (neat): ν (cm^{-1}) 2958, 2929, 1709, 1603, 1464, 1182, 1038; MS (EI, 70 eV): m/z 446 (M^+, 2.3), 389 (69), 387 (48), 205 (50), 105 (100), 73 (75). Anal. calc. for $C_{21}H_{42}O_2Sn$: C, 56.64; H, 9.50. Found: C, 56.34; H, 9.25%.

(*E*)-1-Tributylstannyl-1-ethoxycarbonyl-1-octene (**1b**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (t, $J = 7.2$ Hz, $^3J_{Sn\text{-}H} = 64$ Hz, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 2.45–2.39 (m, 2H), 1.53–1.26 (m, 23H), 0.96–0.84 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 153.7, 135.5, 59.9, 32.1, 31.7, 29.2, 29.0, 28.9, 27.3, 22.6, 14.4, 14.1, 13.7, 10.3; IR (neat): ν (cm^{-1}) 2957, 2927, 1709, 1603, 1464, 1377, 1180; MS (EI, 70 eV): m/z 417 (M^+-Bu, 100), 371 (21), 291 (19), 235 (28), 179 (38). Anal. calc. for $C_{23}H_{46}O_2Sn$: C, 58.36; H, 9.79. Found: C, 58.08; H, 9.62%.

(*E*)-1-Tributylstannyl-1-ethoxycarbonyl-2-phenylethene (**1c**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.29 (m, 5H), 6.70 (s, $^3J_{Sn\text{-}H} = 64$ Hz, 1H), 4.17 (q, $J = 7.2$ Hz, 2H), 1.58–1.52 (m, 6H), 1.37–1.32 (m, 6H), 1.22 (t, $J = 7.2$ Hz, 3H), 1.07 (t, $J = 8.0$ Hz, 6H), 0.91 (t, $J = 7.2$ Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 142.1, 139.8, 137.0, 128.3, 128.1, 128.0, 60.3, 28.9, 27.3, 14.2, 13.7, 10.6; IR (neat): ν (cm^{-1}) 3059, 2958, 2923, 1700, 1596, 1463, 1183, 1034, 788, 695; MS (EI, 70 eV): m/z 466 (M^+, 1.5), 409 (100), 407 (87), 179 (54), 177 (46). Anal. calc. for $C_{23}H_{38}O_2Sn$: C, 59.37; H 8.23. Found: C, 59.57; H, 8.35%.

Synthesis of (1*Z*,3*E*)-2-Ethoxycarbonyl-substituted 1,3-Dienes (3a–i)

General Procedure

(*E*)-α-Stannyl-α,β-unsaturated ester **1** (1.0 mmol) and alkenyl halide **2** (1.1 mmol) were dissolved in DMF (8 mL) under Ar at room temperature. $Pd(PPh_3)_4$ (0.05 mmol) and CuI (0.75 mmol) were then added. The mixture was stirred for 20–24 h at room temperature and monitored by thin-layer chromatography (TLC) (SiO_2) for the disappearance of the starting (*E*)-α-stannyl-α,β-unsaturated ester **1**. The reaction mixture was diluted with diethyl ether (30 mL), filtered, and then treated with 20% aqueous KF (10 ml) for 30 min before being dried and concentrated. The residue was purified by column chromatography on silica gel (eluent: light petroleum ether/EtOAc, 19:1).

(5*Z*,7*E*)-6-(Ethoxycarbonyl)-5,7-dodecadiene (**3a**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.00 (d, $J = 15.6$ Hz, 1H), 5.75 (t, $J = 7.6$ Hz, 1H), 5.68 (dt, $J = 15.6$, 7.2 Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 2.25–2.20 (m, 2H), 2.10–2.06 (m, 2H), 1.43–1.25 (m, 11H), 0.92–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 136.2, 133.4, 131.8, 127.8, 60.5, 32.6, 31.4, 31.3, 29.3, 22.3, 22.2, 14.3, 13.9; IR (neat): ν (cm^{-1}) 2959, 2931, 2873, 1717, 1650, 1465, 1226, 1120, 696; MS (EI, 70 eV): *m*/*z* 238 (M^+, 6.4), 209 (22), 149 (100), 85 (61), 57 (82). Anal. calc. for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.31; H, 10.76%.

(1*E*,3*Z*)-1-Phenyl-3-(ethoxycarbonyl)-1,3-octadiene (**3b**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.20 (m, 5H), 6.74 (d, $J = 16.4$ Hz, 1H), 6.58 (d, $J = 16.4$ Hz, 1H), 6.02 (t, $J = 7.6$ Hz, 1H), 4.34 (q, $J = 7.2$ Hz, 2H), 2.35–2.29 (m, 2H), 1.49–1.22 (m, 7H), 0.92 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 135.4, 134.6, 132.7, 131.3, 129.0, 128.6, 128.2, 127.4, 60.5, 31.5, 29.2, 22.4, 14.3, 13.8; IR (neat): ν (cm^{-1}) 3131, 2958, 2929, 2871, 1718, 1619, 1452, 1227, 1096, 698; MS (EI, 70 eV): *m*/*z* 258 (M^+, 33), 229 (15), 201 (28), 105 (100), 77 (61). Anal. calc. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.85; H, 8.31%.

(2*E*,4*Z*)-1-Methoxy-4-(ethoxycarbonyl)-2,4-nonadiene (**3c**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24 (d, $J = 16.0$ Hz, 1H), 5.92 (t, $J = 7.6$ Hz, 1H), 5.80 (dt, $J = 16.0$, 5.2 Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 3.97 (d, $J = 5.2$ Hz, 2H), 3.34 (s, 3H), 2.32–2.26 (m, 2H), 1.43–1.25 (m, 7H), 0.92 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 139.7, 132.4, 130.3, 126.6, 72.8, 60.6, 58.0, 31.3, 29.4, 22.3, 14.3, 13.8; IR (neat): ν (cm^{-1}) 3064, 2929, 1713, 1450, 1402, 1198, 1095, 698; MS (EI, 70 eV): *m*/*z* 226 (M^+, 17), 197 (65), 73 (100), 57 (95). Anal. calc. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.71; H, 9.68%.

(5*Z*,7*E*)-6-(Ethoxycarbonyl)-5,7-tetradecadiene (**3d**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.02 (d, $J = 16.0$ Hz, 1H), 5.77 (t, $J = 7.6$ Hz, 1H), 5.69 (dt, $J = 16.0$, 7.6 Hz, 1H), 4.30 (q, $J = 7.2$ Hz, 2H), 2.27–2.20 (m, 2H), 2.13–2.06 (m, 2H), 1.45–1.21 (m, 15H), 0.91–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 136.1, 133.6, 131.9, 127.7, 60.5, 32.9, 31.7, 31.4, 29.3, 29.1, 28.9, 22.6, 22.3, 14.3, 14.1, 13.9;

IR (neat): ν (cm^{-1}) 2928, 1727, 1606, 1464, 1378, 1156, 962, 862; MS (EI, 70 eV): m/z 266 (M^+, 100), 221 (45), 177 (20). Anal. calc. for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.37; H, 11.09%.

(1*Z*,3*E*)-1-Phenyl-2-(ethoxycarbonyl)-5-methoxy-1,3-pentadiene (**3e**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.28 (m, 5H), 6.63 (s, 1H), 6.38 (d, $J = 16.0$ Hz, 1H), 5.86 (dt, $J = 16.0$, 5.6 Hz, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 4.04 (d, $J = 5.6$ Hz, 2H), 3.37 (s, 3H), 1.21 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 135.4, 133.5, 132.7, 130.5, 130.0, 128.8, 128.4, 128.2, 72.6, 61.3, 58.2, 13.9; IR (neat): ν (cm^{-1}) 3065, 2959, 2873, 1717, 1619, 1466, 1380, 1153, 1096, 965, 893, 792; MS (EI, 70 eV): m/z 246 (M^+, 12), 202 (48), 115 (64), 105 (100), 77 (63). Anal. calc. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.87; H, 7.22%.

(1*Z*,3*E*)-1,4-Diphenyl-2-(ethoxycarbonyl)-1,3-butadiene (**3f**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.24 (m, 10H), 6.88 (d, $J = 16.4$ Hz, 1H), 6.75 (s, 1H), 6.64 (d, $J = 16.4$ Hz, 1H), 4.34 (q, $J = 7.2$ Hz, 2H), 1.25 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 135.6, 134.5, 134.3, 132.7, 131.1, 130.4, 128.9, 128.7, 128.5, 128.0, 127.4, 121.7, 61.1, 14.0; IR (neat): ν (cm^{-1}) 3073, 2934, 2863, 1721, 1565, 1201, 1095, 967, 804; MS (EI, 70 eV): m/z 278 (M^+, 24), 205 (100), 202 (37), 105 (82), 77 (25). Anal. calc. for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.72; H, 6.38%.

(1*Z*,3*E*)-1-Phenyl-2-(ethoxycarbonyl)-1,3-octadiene (**3g**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.22 (m, 5H), 6.51 (s, 1H), 6.16 (d, $J = 16.0$ Hz, 1H), 5.80 (dt, $J = 16.0$, 7.2 Hz, 1H), 4.26 (q, $J = 7.2$ Hz, 2H), 2.20–2.13 (m, 2H), 1.45–1.25 (m, 4H), 1.23 (t, $J = 7.2$ Hz, 3H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 135.7, 134.5, 134.2, 130.1, 128.7, 128.4, 128.1, 127.9, 61.2, 32.7, 31.2, 22.3, 14.0, 13.9; IR (neat): ν (cm^{-1}) 3067, 2927, 2854, 1716, 1494, 1451, 1094, 1027, 963, 756, 697; MS (EI, 70 eV): m/z 258 (M^+, 2.4), 229 (15), 205 (35), 105 (100), 77 (44). Anal. calc. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.26; H, 8.35%.

(1*Z*,3*E*)-1-Phenyl-2-(ethoxycarbonyl)-1,3-decadiene (**3h**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.23 (m, 5H), 6.51 (s, 1H), 6.16 (d, $J = 15.6$ Hz, 1H), 5.80 (dt, $J = 15.6$, 7.2 Hz, 1H), 4.26 (q, $J = 7.2$ Hz,

2H), 2.18–2.12 (m, 2H), 1.44–1.38 (m, 2H), 1.33–1.25 (m, 6H), 1.21 (t, $J = 7.2$ Hz, 3H), 0.89 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 135.7, 134.5, 134.3, 130.1, 128.7, 128.4, 128.1, 127.9, 61.1, 33.0, 31.7, 29.0, 28.9, 22.6, 14.1, 13.9; IR (neat): ν (cm^{-1}) 3059, 2924, 1728, 1637, 1598, 1574, 1447, 1149, 1022, 960, 696; MS (EI, 70 eV): m/z 286 (M^+, 100), 241 (43), 159 (46), 143 (82), 129 (97). Anal. calc. for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.40; H, 9.29%.

(*Z*)-1-(Ethoxycarbonyl)-1-(1-cyclohexenyl)-1-hexene (**3i**)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65–5.60 (m, 2H), 4.28 (q, $J = 7.2$ Hz, 2H), 2.14–2.02 (m, 6H), 1.69–1.56 (m, 4H), 1.42–1.25 (m, 7H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 137.7, 133.0, 128.4, 126.6, 60.6, 31.6, 29.5, 25.8, 25.2, 22.5, 22.3, 22.1, 14.4, 13.9; IR (neat): ν (cm^{-1}) 2958, 2931, 2873, 1715, 1617, 1453, 1379, 1228, 1096, 1023; MS (EI, 70 eV): m/z 236 (M^+, 14), 207 (61), 165 (97), 149 (92), 91 (93), 79 (83), 55 (100). Anal. calc. for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.11; H, 10.32%.

CONCLUSION

A convenient synthetic method for (1*Z*,3*E*)-2-ethoxycarbonyl-substituted 1,3-dienes has been developed by the palladium-catalyzed hydrostannylation of alkynyl esters, followed by a Stille coupling reaction with alkenyl halides. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, high stereoselectivity, and good yields.

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