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A facile stereoselective synthesis of (*Z*)-2-ethoxycarbonyl-substituted 1,3-enynes from (*E*)-α-stannyl-α,β-unsaturated esters and alkynyl bromides

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

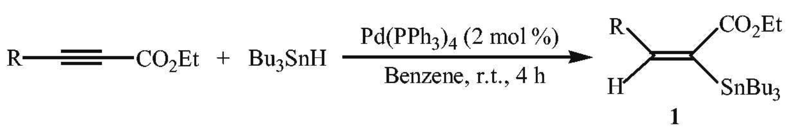
Keywords: alkynyl ester, hydrostannylation, (*E*)-α-stannyl-α,β-unsaturated ester, (*Z*)-2-ethoxycarbonyl-substituted 1,3-enyne, stereoselective synthesis

Enyne systems have attracted much attention from synthetic organic chemists as enynes show interesting chemical and biological reactivities.[1-3] Conjugated enynes are also important synthetic intermediates since the conjugated enyne moiety can be readily converted in a stereospecific manner into the corresponding diene system.[4-6] Recently, Takahashi *et al.*[7] described the formation of highly substituted enynes using a coupling reaction between alkenylzirconium compounds and alkynyl halides. Gimeno and coworkers[8] reported the stereoselective synthesis of chiral terminal (*E*)-1,3-enynes derived from optically active aldehydes. The synthesis of 1,3-enynes containing metal or heteroatom functional groups has also attracted considerable interest in organic syntheses because many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions. The stereoselective synthesis of 1,3-enynylsilanes,[9,10] 1,3-enynylsulfides,[11,12] 1,3-enynyltellurides,[13,14] 1,3-enynylselenides,[15-18] 1,3-enynylstannanes,[19,20] 1,3-enynylsulfones [21,22] and fluoro[23] or CF_3-substituted 1,3-enynes[24] have already been described in the literature. 1,3-Enynyl esters are important synthetic intermediates since the ester group both activates the adjacent multiple carbon–carbon bonds and provides a useful functional group for further transformation. 1-Alkoxycarbonyl-substituted 1,3-enynes can be conveniently prepared by palladium-catalysed cross-coupling reactions of terminal alkynes with β-halo-α,β-unsaturated esters.[25-27] However, the synthesis of 2-alkoxycarbonyl-substituted 1,3-enynes is limited.[28] We report here that (*Z*)-2-alkoxycarbonyl-substituted 1,3-enynes can be synthesised stereoselectively by palladium-catalysed hydrostannylation of alkynyl esters, followed by a cross-coupling reaction with alkynyl bromides in the presence of $Pd(PPh_3)_4$ and CuI co-catalyst.

Stille has reported[29] the use of organotin reagents to obtain enynes by cross-coupling reaction of vinyl triflates or vinyl iodides with alkynylstannanes in the presence of palladium catalysts.[29-31] Interest in the method is due to a high tolerance for functional groups such as allylic ether, vinylic thioethers, esters, ketones or trimethylsilyl ether.[32-34] However, the cross-coupling reaction of vinylstannanes with haloalkynes has rarely been reported.[35-37] Palladium-catalysed hydrostannylation of phenylthioalkynes,[38] alkynyl selenides,[39] and alkynyl sulfoxides[40] has been reported to be highly regio- and stereoselective, providing a direct route for the stereoselective synthesis of 1,1-difunctional group reagents containing heteroatoms and tin. Kazmaier *et al.*[41] reported that $Mo(CO)_3(NC\text{-}t\text{-}Bu)_3$ was an efficient catalyst for regioselective hydrostannylation of alkynes. Rossi *et al.*[42,43] reported palladium-catalysed hydrostannylation of alkynyl esters in THF. However, the hydrostannylation of ethyl 3-phenylpropiolate with Bu_3SnH gave the addition products with 90% α-regioselectivity in 71% yield. In order to prepare highly regioselectively (*E*)-α-stannyl-α,β-unsaturated esters, we investigated palladium-catalysed hydrostannylation of alkynyl esters with Bu_3SnH in benzene at room temperature and found that benzene was better solvent than THF or toluene and that (*E*)-α-stannyl-α,β-unsaturated esters **1** were obtained with high regio- and stereoselectivity in high yields (Scheme 1).

Investigations of the crude products **1** by ^1H NMR spectroscopy (400 MHz) showed regioisomeric purities of more than 98%. One olefinic proton signal of compounds **1a** and **1b** splits characteristically into a 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.[44]

(*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. Palladium-catalysed cross-coupling reaction of vinylstannanes with alkynyl bromides has already been reported.[16,45] With a convenient route to the (*E*)-α-stannyl-α,β-unsaturated esters **1** we decided to establish the feasibility



1

1a: R = *n*-C_4H_9, Isolated yield: 91%
1b: R = *n*-C_6H_{13}, Isolated yield: 89%
1c: R = Ph, Isolated yield: 87%

Scheme 1

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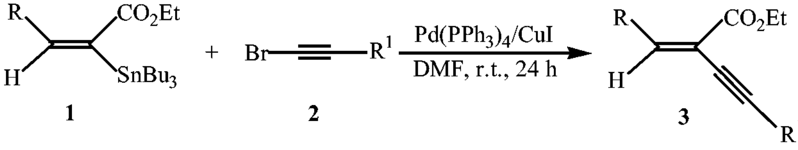

Scheme 2

of using **1** in cross-coupling reactions with alkynyl bromides **2**. Gratifyingly, when the cross-coupling reactions of **1** with a variety of alkynyl bromides **2** were conducted in DMF at room temperature using $Pd(PPh_3)_4$ and CuI as co-catalyst (Scheme 2), fairly rapid reactions occurred affording stereoselectively the desired coupling products **3** in good yields. The experimental results are summarised in Table 1. However, we found that when the cross-coupling reactions of (*E*)-α-stannyl-α,β-unsaturated esters **1** with alkynyl iodides were performed under the same conditions, only trace coupling products were obtained.

In summary, a convenient synthetic method for (*Z*)-2-ethoxycarbonyl-substituted 1,3-enynes has been developed by the palladium-catalysed hydrostannylation of alkynyl esters, followed by a cross-coupling reaction with alkynyl bromides in the presence of $Pd(PPh_3)_4$ and CuI. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with 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. IR spectra were determined on an FTS-185 instrument as neat films. Mass spectra were obtained on a Finnigan 8239 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser. All reactions were carried out in pre-dried 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.

General procedure for the synthesis of (E)-α-stannyl-α,β-unsaturated esters **1a–c**

CAUTION: Appropriate care was taken in handling benzene due to its carcinogenicity

A 25 mL, two-necked, round-bottom 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). If toluene in used instead of benzene the reactions occurred with low regioselectivity and low yields. 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 reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: light petroleum ether/EtOAc, 19:1).

1a: Oil. IR (film): ν (cm^{-1}) 2958, 2929, 1709, 1603, 1464, 1182, 1038; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (t, *J* = 6.8 Hz, $^3J_{Sn-H}$ = 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; MS (EI): *m/z* 446 (M$^+$, 2.3), 389 (69), 387 (48), 205 (50), 105 (100), 73 (75); Anal. Calcd for $C_{21}H_{42}O_2Sn$: C, 56.64; H, 9.50. Found: C, 56.34; H, 9.25%.

1b: Oil. IR (film): ν (cm^{-1}) 2957, 2927, 1709, 1603, 1464, 1377, 1180; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (t, *J* = 7.2 Hz, $^3J_{Sn-H}$ = 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; MS (EI): *m/z* 417 (M$^+$-Bu, 100), 371 (21), 291 (19), 235 (28), 179 (38); Anal. Calcd for $C_{23}H_{46}O_2Sn$: C, 58.36; H, 9.79. Found: C, 58.08; H, 9.62%.

Table 1 Synthesis of (*Z*)-2-ethoxycarbonyl-substituted 1,3-enynes **3a–h**

Entry	R	R^1	Product	Yield/%^{a}
1	*n*-C_4H_9	*n*-C_4H_9	**3a**	86
2	*n*-C_4H_9	Ph	**3b**	81
3	Ph	Ph	**3c**	73
4	Ph	*n*-C_6H_{13}	**3d**	78
5	Ph	CH_3OCH_2	**3e**	75
6	Ph	*n*-C_4H_9	**3f**	79
7	*n*-C_6H_{13}	Ph	**3g**	80
8	*n*-C_4H_9	*n*-C_6H_{13}	**3h**	82

^{a}Isolated yield based on the (*E*)-α-stannyl-α,β-unsaturated esters **1** used.

1c: Oil. IR (film): ν (cm^{-1}) 3059, 2958, 2923, 1700, 1596, 1463, 1183, 1034, 788, 695; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.29 (m, 5H), 6.70 (s, $^3J_{Sn-H}$ = 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; MS (EI): *m/z* 466 (M$^+$, 1.5), 409 (100), 407 (87), 179 (54), 177 (46); Anal. Calcd for $C_{23}H_{38}O_2Sn$: C, 59.37; H, 8.23. Found: C, 59.57; H, 8.35%.

General procedure for the synthesis of (Z)-2-ethoxycarbonyl-substituted 1,3-enynes **3a–h**

(*E*)-α-Stannyl-α,β-unsaturated ester **1** (1.0 mmol) and alkynyl bromide **2** (1.1 mmol) were dissolved in DMF (10 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 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).

3a: Oil. IR (film): ν (cm^{-1}) 2958, 2931, 2872, 2220, 1728, 1447, 1374, 1211, 1174, 1024; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.48 (t, *J* = 7.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.59–2.53 (m, 2H), 2.33 (t, *J* = 6.8 Hz, 2H), 1.55–1.28 (m, 11H), 0.96–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 152.8, 116.6, 89.8, 77.8, 60.9, 31.1, 30.7, 29.6, 22.4, 21.9, 19.0, 14.1, 13.9, 13.6; MS (EI): *m/z* 236 (M$^+$, 15), 207 (41), 167 (50), 115 (100); Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.05; H, 10.32%.

3b: Oil. IR (film): ν (cm^{-1}) 2958, 2928, 2856, 2216, 1722, 1597, 1490, 1443, 1371, 1210, 1138, 756, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.44 (m, 2H), 7.33–7.30 (m, 3H), 6.68 (t, *J* = 7.6 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.68–2.63 (m, 2H), 1.49–1.34 (m, 7H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 154.6, 131.6, 128.4, 128.3, 123.2, 116.4, 88.8, 86.8, 61.1, 31.1, 29.8, 22.5, 14.2, 13.9; MS (EI): *m/z* 256 (M$^+$, 5.1), 129 (30), 115 (41), 105 (100); Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.38; H, 7.64%.

3c: Oil. IR (film): ν (cm^{-1}) 3062, 2957, 2226, 1726, 1595, 1490, 1215, 1094, 755, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.49 (m, 2H), 7.39–7.33 (m, 8H), 7.27 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 143.2, 134.7, 131.7, 129.2, 128.8, 128.6, 128.4, 128.3, 122.8, 116.9, 91.7, 87.0, 61.7, 13.9; MS (EI): *m/z* 276 (M$^+$, 89), 231 (54), 203 (100), 105 (90); Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.32; H, 5.61%.

3d: Oil. IR (film): ν (cm^{-1}) 3025, 2930, 2218, 1728, 1598, 1493, 1447, 1373, 1211, 1174, 1024, 753, 694; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.29 (m, 5H), 7.10 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 1.45–1.25 (m, 8H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 141.8, 134.9, 128.7, 128.5, 128.2, 117.4, 93.4, 78.1, 61.5, 31.4, 28.6, 28.5, 22.6, 19.6, 14.1, 13.8; MS (EI): *m/z* 284 (M^+, 100), 241 (43), 159 (46), 143 (82), 129 (97); Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 79.98; H, 8.54%.

3e: Oil. IR (film): ν (cm^{-1}) 3062, 2932, 2217, 1727, 1599, 1493, 1214, 1175, 1100, 1023, 753, 696; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.30 (m, 5H), 7.23 (s, 1H), 4.30 (s, 2H), 4.22 (q, J = 7.2 Hz, 2H), 3.44 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 144.4, 134.5, 129.2, 128.8, 128.3, 116.2, 87.3, 83.9, 61.7, 60.4, 57.8, 13.8; MS (EI): *m/z* 244 (M^+, 13), 199 (24), 149 (100), 141 (87), 115 (95), 105 (97); Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.48; H, 6.35%.

3f: Oil. IR (film): ν (cm^{-1}) 3060, 3025, 2930, 2858, 2218, 1729, 1598, 1492, 1447, 1373, 1211, 1174, 753, 694; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.26 (m, 5H), 7.10 (s, 1H), 4.21 (q, J = 7.2 Hz, 2H), 2.39 (t, J = 7.2 Hz, 2H), 1.38–1.22 (m, 4H), 1.20 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 141.8, 135.0, 128.7, 128.5, 128.2, 117.4, 93.3, 78.1, 61.5, 30.6, 22.0, 19.3, 13.8, 13.6; MS (EI): *m/z* 256 (M^+, 81), 211 (100), 141 (83); Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.41; H, 7.73%.

3g: Oil. IR (film): ν (cm^{-1}) 2928, 2857, 2215, 1722, 1597, 1490, 1443, 1372, 1210, 1137, 1027, 756, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.46 (m, 2H), 7.34–7.32 (m, 3H), 6.69 (t, J = 7.6 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 2.71–2.65 (m, 2H), 1.53–1.28 (m, 11H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 154.6, 131.6, 128.3, 128.2, 123.2, 116.4, 88.8, 86.8, 61.0, 31.6, 30.1, 29.1, 29.0, 22.6, 14.2, 14.1; MS (EI): *m/z* 284 (M^+, 34), 141 (36), 115 (40), 105 (100); Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.02; H, 8.69%.

3h: Oil. IR (film): ν (cm^{-1}) 2957, 2930, 2858, 2212, 1722, 1466, 1369, 1248, 1182; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.47 (t, J = 7.6 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 2.61–2.53 (m, 2H), 2.32 (t, J = 7.2 Hz, 2H), 1.59–1.26 (m, 15H), 0.92–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 152.7, 116.6, 89.9, 77.8, 60.8, 31.4, 31.1, 29.7, 28.6, 28.5, 22.6, 22.5, 19.4, 14.2, 14.1, 13.8; MS (EI): *m/z* 264 (M^+, 11), 219 (28), 165 (45), 113 (100); Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.42; H, 10.84%.

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