# A facile one-pot stereoselective synthesis of (*Z*)-α-acyl-α,β-unsaturated esters from alkynyl esters and aryl acyl chlorides

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(*Z*)-α-Acyl-α,β-unsaturated esters can be stereoselectively synthesised in one pot under mild conditions and in good yields by the palladium-catalysed hydrostannylation of alkynyl esters in benzene, followed by the Stille cross-coupling with aryl acyl chlorides using CuI as co-catalyst.

**Keywords**: (*Z*)-α-acyl-α,β-unsaturated ester, hydrostannylation, alkynyl ester, Stille coupling, tandem reaction

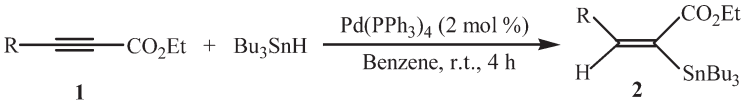
The synthesis of α,β-unsaturated esters has attracted considerable attention because they are important intermediates in natural product synthesis.[1–4] Their great synthetic value derives from the fact that the positions α,β and γ to the ester groups can be activated and functionalised by various means. A variety of methods for the synthesis of α,β-unsaturated esters have been developed. Of these methods, the Wittig reaction using aldehydes and phosphorus ylides is one of the most powerful and attractive methods and still occupies a prominent position.[5–10] Recently, the synthesis of α-functionalised α,β-unsaturated esters has also received considerable attention. For example, the synthesis of α-halo-α,β-unsaturated esters[11–13] and α-trifluoromethyl-α,β-unsaturated esters[14,15] has been described. α-Acyl-α,β-unsaturated esters are useful synthetic intermediates and have been widely used.[16–19] One general approach for the preparation of α-acyl-α,β-unsaturated esters is the Knoevenagel condensation of aromatic aldehydes with β-keto esters in the presence of a base or Lewis acid.[20–22] However, this methodology gives poor stereoselectivity and α-acyl-β-alkyl-α,β-unsaturated esters cannot be prepared by this method. Therefore, there is still a need for the development of selective and better strategies for the synthesis of α-acyl-α,β-unsaturated esters.

Tandem reactions have recently been of interest for organic synthesis because they offer convenient and economical methods with which to prepare target organic molecules.[23–26] The palladium-catalysed hydrostannylation of alkynes and the Stille coupling reaction are acknowledged as useful tools for constructing complex organic molecules. Recently, we reported the stereoselective synthesis of (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones by palladium-catalysed one-pot tandem hydrostannylation-Stille coupling reaction of tributyltin hydride with acetylenic sulfones and acyl chlorides.[27] However, to the best of our knowledge, there have been no reports on palladium-catalysed tandem hydrostannylation-Stille coupling reaction of tributyltin hydride with alkynyl esters and acyl chlorides to date. We report here that (*Z*)-α-acyl-α,β-unsaturated esters can be stereoselectively synthesised in one pot under mild conditions, in good yields, by the hydrostannylation of alkynyl esters, followed by the Stille cross-coupling with aryl acyl chlorides.

Palladium-catalysed hydrostannylation of alkynes provides a simple, general route for the stereoselective synthesis of vinylstannanes.[28] Rossi *et al.*[29] reported palladium-catalysed hydrostannylation of alkynyl esters in THF. In order to prepare highly selectively (*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 and (*E*)-α-stannyl-α,β-unsaturated esters **2** were obtained with high regio- and stereoselectivity in high yields (Scheme 1). The reaction did not occur in toluene.

Investigations of the crude products **2** by $^1$H NMR spectroscopy (400 MHz) showed isomeric purities of more than 98%. One olefinic proton signal of compound **2a** splits characteristically into a triplet at $\delta$ = 6.04 with coupling constant $J$ = 6.8 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 $^1$H NMR spectra of compounds **2a–b** 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.[30]

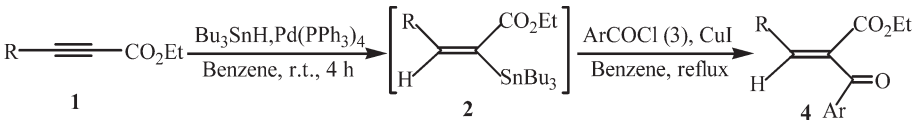
(*E*)-α-Stannyl-α,β-unsaturated esters **2** are difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and as α,β-unsaturated esters. It is well known that vinylstannanes can undergo palladium-catalysed cross-coupling with organic halides.[31,32] Considering the fact that both the hydrostannylation and Stille reactions were catalysed by palladium complexes, we tried to combine the two reactions, in one pot, to synthesise (*Z*)-α-acyl-α,β-unsaturated esters stereoselectively (Scheme 2).




1 2

**2a**: R = n-$C_4H_9$, Isolated yield: 91%
**2b**: R = Ph, Isolated yield: 87%

**Scheme 1**




1 2 4

**Scheme 2**

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We found that, after the hydrostannylation reaction of alkynyl esters **1** with $Bu_3SnH$ using 2 mol% $Pd(PPh_3)_4$ in benzene at 25 °C for 4 h and aryl acyl chlorides **3** and 75 mol% CuI were added and the mixture was stirred at 80 °C for 10 h, (*Z*)-α-acyl-α,β-unsaturated esters **4** were obtained in good yields. The experimental results are summarised in Table 1. It was found that benzene was the best solvent among those tested, such as toluene, DMF, and THF for the Stille coupling of the intermediates **2** with aromatic acyl chlorides. As shown in Table 1, the hydrostannylation-Stille tandem reaction of $Bu_3SnH$ with a variety of alkynyl esters and aromatic acyl chlorides proceeded smoothly under mild conditions to afford stereoselectively the corresponding (*Z*)-α-acyl-α,β-unsaturated esters **4**. Various electron-donating and electron-withdrawing substituents such as methoxy, chloro, and nitro groups on aromatic acyl chlorides were well tolerated. However, the reactivity of 4-methoxybenzoyl chloride with its strong electron-donating group was lower than that of other aryl acyl chlorides. To broaden the scope of this methodology, we tried to use aliphatic acyl chlorides as substrates. However, the Stille coupling reaction of the intermediates **2** with aliphatic acyl chlorides did not occur under the same conditions.

It is well documented that the Stille cross-coupling reaction of vinylstannanes with organic halides in the presence of a palladium catalyst occurs with retention of configuration.[31,32] In addition, the (*Z*)-configuration of the compound **4d** was confirmed by the NOESY in the $^1$H NMR spectrum. An enhancement of the allylic protons was observed as the vinylic proton (δ = 6.34) of **4d** was irradiated. There was a correlation between the vinylic proton (δ = 6.34) and aromatic protons (δ = 7.48). Correlation between the allylic protons and aromatic protons (δ = 7.48) was not observed. The NOE results indicate that the compound **4d** has the expected (*Z*)-configuration and the palladium-catalysed cross-coupling reaction of (*E*)-α-stannyl-α,β-unsaturated esters **2** with aryl acyl chlorides occurs with the retention of the configuration of the starting intermediates **2**.

In summary, we have developed an efficient and stereoselective one-pot method for the synthesis of (*Z*)-α-acyl-α,β-unsaturated esters by the hydrostannylation–Stille coupling tandem reaction of alkynyl esters with aryl acyl chlorides. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, high stereoselectivity and good yields.

## Experimental

$^1$H NMR spectra were recorded on a Bruker Avance (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 Avance (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.

**Table 1** Synthesis of (*Z*)-α-acyl-α,β-unsaturated esters **4**

| Entry | R | Ar | Product | Yield/%[a] |
|---|---|---|---|---|
| 1 | *n*-$C_4H_9$ | Ph | **4a** | 79 |
| 2 | *n*-$C_4H_9$ | 4-$MeOC_6H_4$ | **4b** | 65 |
| 3 | *n*-$C_4H_9$ | 4-$ClC_6H_4$ | **4c** | 82 |
| 4 | *n*-$C_4H_9$ | 4-$O_2NC_6H_4$ | **4d** | 86 |
| 5 | Ph | Ph | **4e** | 84 |
| 6 | Ph | 4-$MeOC_6H_4$ | **4f** | 70 |
| 7 | Ph | 4-$ClC_6H_4$ | **4g** | 84 |
| 8 | Ph | 4-$O_2NC_6H_4$ | **4h** | 88 |

[a] Isolated yield based on the alkynyl esters **1** used.

*Synthesis of (E)-α-stannyl-α,β-unsaturated esters* **2a–b***; general procedure*

A 25 mL, two-necked, round-bottom flask equipped with a magnetic stirrer bar and with an argon atmosphere 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 reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: light petroleum ether/EtOAc, 19:1).

**2a**: 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, $^3J_{Sn\text{-}H}$ = 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; 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%.

**2b**: 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, $^3J_{Sn\text{-}H}$ = 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; 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%.

*Synthesis of (Z)-α-acyl-α,β-unsaturated esters* **4a–h***; general procedure*

A 25 mL, two-necked, round-bottom flask equipped with a magnetic stirrer bar and with an argon atmosphere was charged sequentially with alkynyl ester (1.0 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, then acyl chloride (1.1 mmol) and CuI (0.75 mmol) were added and the mixture was stirred for 10 h at 80 °C and monitored by TLC ($SiO_2$) for the disappearance of the intermediate **2**. 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/diethyl ether, 12:1).

**4a**: Oil. IR (film): ν ($cm^{-1}$) 2959, 2931, 2873, 1723, 1676, 1642, 1598, 1449, 1366, 1232, 1070, 717, 690; $^1$H NMR ($CDCl_3$): δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.60–7.41 (m, 3H), 7.18 (t, *J* = 8.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.15–2.09 (m, 2H), 1.45–1.36 (m, 2H), 1.33–1.24 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$): δ 194.5, 164.6, 148.6, 136.9, 135.2, 133.7, 129.1, 128.9, 61.1, 30.5, 29.4, 22.3, 14.2, 13.7; Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.56; H, 7.51%.

**4b**: Oil. IR (film): ν ($cm^{-1}$) 3256, 2929, 2859, 1720, 1665, 1587, 1496, 1231, 1092, 848, 733; $^1$H NMR ($CDCl_3$): δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 2.12–2.07 (m, 2H), 1.45–1.37 (m, 2H), 1.32–1.23 (m, 2H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$): δ 193.1, 164.7, 163.5, 134.9, 133.8, 131.6, 131.5, 130.0, 61.1, 60.9, 30.5, 29.3, 22.3, 14.0, 13.8. Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.44; H, 7.45%.

**4c**: Oil. IR (film): ν ($cm^{-1}$) 2957, 2929, 2874, 1726, 1677, 1587, 1465, 1400, 1231, 1092, 848, 731; $^1$H NMR ($CDCl_3$): δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.13–2.08 (m, 2H), 1.44–1.38 (m, 2H), 1.32–1.23 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$): δ 193.3, 164.4, 149.2, 140.2, 135.2, 133.3, 130.5, 129.1, 61.2, 30.5, 29.7, 22.3, 14.1, 13.9. Anal. Calcd for $C_{16}H_{19}O_3Cl$: C, 65.18; H, 6.50. Found: C, 64.89; H, 6.33%.

**4d**: Oil. IR (film): ν ($cm^{-1}$) 2959, 2930, 2876, 1720, 1596, 1520, 1465, 1346, 1199, 1109, 855, 697; $^1$H NMR ($CDCl_3$): δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.34 (t, *J* = 7.6 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.55–2.49 (m, 2H), 1.54–1.48 (m, 2H), 1.43–1.37 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$): δ 194.6, 167.0, 147.0, 144.7, 144.4, 133.0, 128.1, 123.5, 61.1, 30.2, 29.9, 22.5, 14.3, 14.0. Anal. Calcd for $C_{16}H_{19}O_5N$: C, 62.94; H, 6.27. Found: C, 62.67; H, 6.05%.

**4e**: Oil. IR (film): ν ($cm^{-1}$) 2982, 1720, 1673, 1622, 1597, 1581, 1449, 1367, 1254, 1231, 1198, 1093, 734, 689; $^1$H NMR ($CDCl_3$): δ 7.96–7.94 (m, 3H), 7.57–7.21 (m, 8H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$): δ 195.6, 165.0, 142.6, 142.5, 136.1, 133.9, 132.8, 131.3, 130.2, 129.2, 129.1, 128.8, 61.5, 14.0. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.88; H, 5.47%.

**4f**: Oil. IR (film): ν ($cm^{-1}$) 2980, 2928, 1718, 1663, 1598, 1574, 1509, 1449, 1367, 1246, 1167, 1025; $^1$H NMR ($CDCl_3$): δ 7.93–7.88 (m, 3H), 7.39–7.14 (m, 5H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$): δ 194.1, 165.2, 164.2, 142.1, 142.0, 133.0, 131.6, 131.5, 130.3, 130.1, 129.4, 128.9, 61.5, 57.9, 14.1. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.26; H, 5.61%.

**4g**: Oil. IR (film): ν ($cm^{-1}$) 2956, 2927, 2873, 1720, 1674, 1586, 1464, 1406, 1197, 1091, 847, 730; $^1$H NMR ($CDCl_3$): δ 7.96 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.43–7.18 (m, 7H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$): δ 194.4 164.8, 142.9, 140.4, 134.5, 132.7, 130.8, 130.5, 130.4, 130.2, 129.3, 129.1, 61.7, 14.0. Anal. Calcd for $C_{18}H_{15}O_3Cl$: C, 68.67; H, 4.80. Found: C, 68.41; H, 4.57%.

**4h**: Oil. IR (film): ν ($cm^{-1}$) 2982, 2934, 2874, 1719, 1594, 1518, 1344, 1217, 1183, 851, 756; $^1$H NMR ($CDCl_3$): δ 8.23–8.20 (m, 2H), 7.65–7.62 (m, 2H), 7.42–7.33 (m, 5H), 7.18 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$): δ 194.8, 168.6, 147.4, 143.3, 134.9, 133.2, 128.6, 128.5, 128.4, 127.4, 127.2, 124.0, 61.8, 13.8. Anal. Calcd for $C_{18}H_{15}O_5N$: C, 66.46; H, 4.65. Found: C, 66.57; H, 4.43%.

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