Novel stereoselective synthesis of (*Z*)-α,β-unsaturated esters by hydrostannylation-Stille tandem reaction of alkynyl esters with aryl iodides

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(*Z*)-α,β-Unsaturated esters can be stereoselectively synthesised in one pot under mild conditions and in good yields, by the hydrostannylation of alkynyl esters followed by Stille cross-coupling with aryl iodides.

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

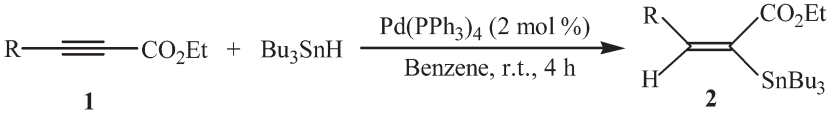
The synthesis of α,β-unsaturated esters has received considerable attention because they are essential intermediates in natural product synthesis.[1–4] The great synthetic value of these α,β-unsaturated esters derives from the fact that the positions α, β and γ to the ester groups can be activated and 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 still occupies a prominent position.[5–10] However, the reaction is limited frequently by the oxidation, decomposition, or polymerisation of the aldehydes employed. In order to avoid use of aldehydes as substrates, several methods for the one-pot oxidation-Wittig reaction of alcohols with phosphorus ylides have been devised.[11–15] Most of them, however, suffer from the use of hazardous oxidants and/or the requirement of an activation process. Recently, a one-pot alcohol oxidation-Wittig reaction catalysed by ruthenium using air or oxygen as oxidant has been reported.[16,17] Deng *et al.* reported that silyl ethers could be deprotected and oxidised with Dess-Martin periodinane, and the resulting aldehydes could be directly converted into the corresponding α,β-unsaturated esters in one pot with stabilised phosphoranes.[18] Concellon and Bardales described the synthesis of α,β-unsaturated esters by highly stereoselective β-elimination of 2,3-epoxy-esters promoted by SmI_2.[19] Despite considerable methodological differentiation the majority of the reported procedures suffer from some drawbacks such as significant by-product formation, the use of hazardous oxidants and moderate yields. Most of them are only suitable for the synthesis of disubstituted (*E*)-α,β-unsaturated esters. The stereoselective synthesis of trisubstituted α,β-unsaturated esters has received less attention. Therefore, there is still a need for the development of selective and better strategies for the one-pot synthesis of trisubstituted α,β-unsaturated esters.

The tandem reaction has recently been of interest in organic synthesis because it offers a convenient and economical method by which to prepare target organic molecules.[20–23] The palladium-catalysed hydrostannylation of alkynes and the Stille coupling reaction are acknowledged as useful tools for constructing complex organic molecules. 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 aryl iodides to date. Here we report that (*Z*)-α,β-unsaturated esters can be stereoselectively synthesised in one pot under mild conditions, and in good yields by the hydrostannylation of alkynyl esters followed by Stille cross-coupling with aryl iodides.

Palladium-catalysed hydrostannylation of alkynes provides a simple, general route for the synthesis of vinylstannanes.[24] Rossi *et al.*[25] 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 a better solvent than THF and that (*E*)-α-stannyl-α,β-unsaturated esters **2** were obtained with high regio- and stereoselectivity in high yields (Scheme 1).

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 compounds **2a** and **2b** splits characteristically into a triplet at $\delta = 6.04$ with coupling constant $J = 6.8$–7.2 Hz, which indicated that the hydrostannylation of 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–c** 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.[26]

(*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 the palladium-catalysed cross-coupling reaction with organic halides.[27,28] Considering the fact that both the hydrostannylation and Stille



1 **2**

2a: R = *n*-C_4H_9, Isolated yield: 91%
2b: R = *n*-C_6H_{13}, Isolated yield: 89%
2c: R = Ph, Isolated yield: 87%
2d: R = H, Isolated yield: 88%

Scheme 1

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reactions were catalysed by palladium complexes, we tried to combine the two reactions in one pot to synthesise stereoselectively (*Z*)-α,β-unsaturated esters (Scheme 2).

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, solvent removal under reduced pressure and stirring of the residue with DMF, aryl iodides **3** and 75 mol% CuI at room temperature for 8 h, (*Z*)-α,β-unsaturated esters **4** were obtained in good yields. The experimental results are summarised in Table 1. It was found that DMF was the best solvent among those tested, such as benzene and THF for the Stille coupling of the intermediates **2** with aryl iodides. As shown in Table 1, the hydrostannylation- Stille tandem reaction of Bu_3SnH with a variety of alkynyl esters and aryl iodides proceeded smoothly under mild conditions to afford stereoselectively the corresponding (*Z*)-α,β-unsaturated esters **4**. However, the Stille coupling reaction of the intermediates **2** with aryl bromides didn't 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.[27,28] In addition, the (*Z*)-configuration of the compound **4c** was confirmed by the NOESY in the ^1H NMR spectrum. An enhancement of the allylic protons was observed as the vinylic proton (δ = 6.08) of **4c** was irradiated. There was a correlation between the vinylic proton (δ = 6.08) and aromatic protons (δ = 7.24–7.26). A correlation between the allylic protons and aromatic protons (δ = 7.24–7.26) was not observed. The NOE results indicate that the compound **4c** has the expected (*Z*)-configuration and the palladium-catalysed cross-coupling reaction of (*E*)-α-stannyl-α,β-unsaturated esters **2** with aryl iodides occurs with the configuration retention of the starting intermediates **2**.

In summary, we have developed an efficient and stereoselective one-pot method for the synthesis of trisubstituted (*Z*)-α,β-unsaturated esters by the hydrostannylation-Stille coupling tandem reaction of alkynyl esters with aryl iodides. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields. The procedure should find wide application to the synthesis of a large array of naturally occurring substances having the trisubstituted (*Z*)-α,β-unsaturated ester system.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard 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.

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

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) in an argon atmosphere. 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).

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

Entry	R	Ar	Product	Yield/%[a]
1	*n*-C_4H_9	Ph	**4a**	76
2	*n*-C_4H_9	3-MeC_6H_4	**4b**	74
3	*n*-C_4H_9	4-$MeOC_6H_4$	**4c**	65
4	*n*-C_4H_9	2-Thienyl	**4d**	80
5	*n*-C_4H_9	4-$O_2NC_6H_4$	**4e**	79
6	*n*-C_4H_9	1-naphthyl	**4f**	75
7	Ph	Ph	**4g**	84
8	Ph	4-ClC_6H_4	**4h**	73
9	Ph	4-$MeOC_6H_4$	**4i**	71
10	Ph	1-naphthyl	**4j**	79
11	Ph	2-Thienyl	**4k**	74
12	H	3-MeC_6H_4	**4l**	83

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

2a: Oil. IR (film): ν (cm^{-1}) 2958, 2929, 1709, 1603, 1464, 1182, 1038; ^1H 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%.

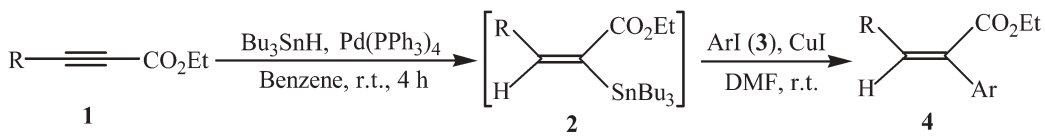
2b: Oil. IR (film): ν (cm^{-1}) 2957, 2927, 1709, 1603, 1464, 1377, 1180; ^1H NMR (400 MHz, $CDCl_3$): δ 6.04 (t, *J* = 7.2 Hz, $^3J_{Sn-H}$ = 64 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.45–2.39 (m, 2H), 1.53–1.26 (m, 23H), 0.96–0.84 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 153.7, 135.5, 59.9, 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%.

2c: Oil. IR (film): ν (cm^{-1}) 3059, 2958, 2923, 1700, 1596, 1463, 1183, 1034, 788, 695; ^1H 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%.

2d: Oil. IR (film): ν (cm^{-1}) 2958, 2929, 1709, 1603, 1464, 1182, 1038; ^1H NMR (400 MHz, $CDCl_3$): δ 6.91 (d, *J* = 2.4 Hz, $^3J_{Sn-H}$ = 116 Hz, 1H), 5.91 (d, *J* = 2.4 Hz, $^3J_{Sn-H}$ = 58 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.54–1.45 (m, 6H), 1.35–1.26 (m, 9H), 1.02–0.95 (m, 6H), 0.89 (t, *J* = 7.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 146.2, 139.8, 60.6, 28.9, 27.3, 14.3, 13.7, 10.1; MS (EI): *m/z* (%) 389 (M^+, 3.5), 332 (M^+-Bu, 100), 205 (50), 105 (97), 73 (75); Anal. Calcd for $C_{17}H_{34}O_2Sn$: C, 52.47; H, 8.81. Found: C, 52.18; H, 8.64%.

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

A 25 mL, two-necked, round-bottom flask equipped with a magnetic stir bar and argon 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) in an argon atmosphere. The mixture was stirred at room temperature for 4 h. Then the solvent was removed under reduced pressure and the residue was dissolved in DMF (8 mL). Aryl iodide (1.1 mmol) and CuI (0.75 mmol) were added and the mixture



Scheme 2

was stirred for 8 h at 25 °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 washed with 20% aqueous KF (10 mL) for 30 min before the organic layer was separated, dried and concentrated. The concentrate was purified by column chromatography on silica gel, eluting with a mixture of diethyl ether and light petroleum ether.

4a: Oil. IR (film): ν (cm^{-1}) 2958, 2928, 2857, 1717, 1464, 1371, 1195, 1036, 758, 697; ^{1}H NMR ($CDCl_3$): δ 7.33–7.27 (m, 5H), 6.16 (t, *J* = 7.8 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.45–2.39 (m, 2H), 1.50–1.46 (m, 2H), 1.41–1.36 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 168.4, 139.6, 137.9, 134.7, 128.3, 127.4, 127.1, 60.7, 31.5, 29.8, 22.4, 14.3, 13.9; MS (EI): *m/z* 232 (M^+, 55), 203 (54), 157 (55), 129 (57), 115 (100); Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.28; H, 8.47%.

4b: Oil. IR (film): ν (cm^{-1}) 2958, 2928, 2859, 1723, 1605, 1465, 1370, 1205, 1175, 1036, 786, 701; ^{1}H NMR ($CDCl_3$): δ 7.26–7.07 (m, 5H), 6.14 (t, *J* = 7.8 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.42–2.36 (m, 2H), 2.34 (s, 3H), 1.50–1.45 (m, 2H), 1.42–1.36 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 168.5, 139.0, 137.9, 137.8, 134.8, 128.3, 128.2, 127.7, 124.1, 60.7, 31.5, 29.8, 22.4, 21.4, 14.3, 13.9; MS (EI): *m/z* 246 (M^+, 97), 171 (100), 143 (45), 129 (68), 115 (47); Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.18; H, 8.86%.

4c: Oil. IR (film): ν (cm^{-1}) 2927, 2857, 1722, 1609, 1512, 1465, 1371, 1249, 1196, 1037, 830; ^{1}H NMR ($CDCl_3$): δ 7.26–7.24 (m, 2H), 6.86–6.84 (m, 2H), 6.08 (t, *J* = 7.8 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.42–2.36 (m, 2H), 1.50–1.46 (m, 2H), 1.41–1.35 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 168.6, 159.1, 137.9, 134.1, 130.5, 128.2, 113.7, 60.7, 55.3, 31.6, 29.8, 22.4, 14.3, 13.9; MS (EI): *m/z* 262 (M^+, 100), 187 (69), 145 (52); Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.47; H, 8.21%.

4d: Oil. IR (film): ν (cm^{-1}) 2958, 2930, 2860, 1723, 1465, 1375, 1262, 1183, 1025, 696; ^{1}H NMR ($CDCl_3$): δ 7.26–7.17 (m, 1H), 7.03–6.94 (m, 2H), 6.29 (t, *J* = 7.8 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.43–2.37 (m, 2H), 1.50–1.44 (m, 2H), 1.40–1.34 (m, 5H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 167.1, 140.6, 138.7, 128.4, 127.2, 124.9, 124.6, 61.1, 31.4, 29.8, 22.5, 14.3, 14.0; MS (EI): *m/z* 238 (M^+, 56), 192 (51), 182 (87), 163 (100); Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.22; H, 7.51%.

4e: Oil. IR (film): ν (cm^{-1}) 2960, 2932, 2861, 1722, 1629, 1597, 1520, 1345, 1199, 1110, 1037, 855; ^{1}H NMR ($CDCl_3$): δ 8.19–8.16 (m, 2H), 7.50–7.47 (m, 2H), 6.34 (t, *J* = 7.8 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.55–2.49 (m, 2H), 1.54–1.35 (m, 7H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 167.1, 146.9, 144.7, 144.5, 132.9, 128.1, 123.5, 61.2, 31.2, 30.1, 22.5, 14.2, 13.9; MS (EI): *m/z* 277 (M^+, 100), 194 (36), 115 (45); Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91. Found: C, 64.68; H, 6.67%.

4f: Oil. IR (film): ν (cm^{-1}) 2958, 2929, 2859, 1714, 1508, 1465, 1370, 1203, 1174, 1034, 800; ^{1}H NMR ($CDCl_3$): δ 7.84–7.78 (m, 3H), 7.46–7.42 (m, 3H), 7.34 (d, *J* = 6.8 Hz, 1H), 6.23 (t, *J* = 7.4 Hz, 1H), 4.13 (q, *J* = 7.0 Hz, 2H), 2.74–2.69 (m, 2H), 1.58–1.38 (m, 4H), 1.13 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 167.8, 147.2, 137.6, 133.4, 132.8, 132.2, 128.3, 128.0, 127.1, 126.0, 125.7, 125.4, 125.3, 60.5, 31.6, 29.7, 22.6, 14.1, 14.0; MS (EI): *m/z* 282 (M^+, 88), 209 (33), 165 (100); Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 80.56; H, 7.57%.

4g: Oil. IR (film): ν (cm^{-1}) 3058, 3027, 2981, 1716, 1599, 1496, 1448, 1373, 1182, 1023, 768, 695; ^{1}H NMR ($CDCl_3$): δ 7.49–7.46 (m, 2H), 7.39–7.28 (m, 8H), 7.03 (s, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 169.6, 137.0, 135.8, 135.4, 131.2, 128.7, 128.5, 128.4, 128.3, 128.2, 126.4, 61.3, 13.9; MS (EI): *m/z* 252 (M^+, 98), 179 (100), 135 (65); Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.68; H, 6.44%.

4h: Oil. IR (film): ν (cm^{-1}) 3058, 3027, 2981, 2958, 1719, 1621, 1591, 1494, 1447, 1372, 1184, 1093, 820, 753, 695; ^{1}H NMR ($CDCl_3$): δ 7.40–7.26 (m, 9H), 7.00 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 169.2, 135.6, 135.5, 134.3, 134.2, 131.9, 128.9, 128.5, 128.3, 127.8, 61.5, 13.9; MS (EI): *m/z* 286 (M^+, ^{35}Cl, 9.8), 269 (100); Anal. Calcd for $C_{17}H_{15}ClO_2$: C, 71.19; H, 5.27. Found: C, 70.92; H, 5.43%.

4i: Oil. IR (film): ν (cm^{-1}) 2958, 2933, 1723, 1607, 1514, 1464, 1446, 1373, 1250, 1178, 1032, 826, 697; ^{1}H NMR ($CDCl_3$): δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.38–7.27 (m, 5H), 6.95 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 169.9, 159.8, 136.0, 134.8, 129.5, 129.4, 128.4, 128.2, 128.0, 127.7, 114.1, 61.3, 55.4, 13.9; MS (EI): *m/z* 282 (M^+, 54), 209 (100), 165 (49); Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.33; H, 6.15%.

4j: Oil. IR (film): ν (cm^{-1}) 3058, 2981, 2935, 1716, 1623, 1591, 1495, 1447, 1371, 1212, 1170, 1095, 1023, 797, 776, 696; ^{1}H NMR ($CDCl_3$): δ 8.12–8.10 (m, 1H), 7.87–7.83 (m, 2H), 7.55–7.44 (m, 6H), 7.39–7.32 (m, 3H), 6.97 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 169.1, 137.6, 136.6, 135.7, 134.1, 133.8, 131.9, 128.7, 128.6, 128.5, 128.4, 127.3, 126.4, 126.0, 125.4, 125.3, 61.2, 13.9; MS (EI): *m/z* 302 (M^+, 19), 229 (100); Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.15; H, 5.75%.

4k: Oil. IR (film): ν (cm^{-1}) 3073, 2981, 1724, 1611, 1447, 1377, 1219, 1182, 1022, 753, 696; ^{1}H NMR ($CDCl_3$): δ 7.37–7.28 (m, 5H), 7.24 (d, *J* = 5.6 Hz, 1H), 7.09 (d, *J* = 3.6 Hz, 1H), 7.07 (s, 1H), 7.02–7.00 (m, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 168.4, 140.7, 135.4, 129.5, 129.2, 128.5, 128.3, 128.2, 127.8, 125.8, 125.4, 61.6, 13.9; MS (EI): *m/z* 258 (M^+, 100), 184 (75), 135 (62); Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46. Found: C, 69.48; H, 5.71%.

4l: Oil. IR (film): ν (cm^{-1}) 2981, 2925, 1722, 1605, 1584, 1488, 1446, 1368, 1225, 1162, 1103, 792, 714; ^{1}H NMR ($CDCl_3$): δ 7.27–7.13 (m, 4H), 6.31 (s, 1H), 5.86 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 167.0, 141.7, 137.7, 136.7, 129.0, 128.9, 128.0, 126.2, 125.4, 61.1, 21.5, 14.2. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.48; H, 7.23%.

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