Alkoxydienylstannanes *via* metalation of α,β-unsaturated and α-phenyl acetals: preparation and synthetic uses in the Stille cross-coupling reaction

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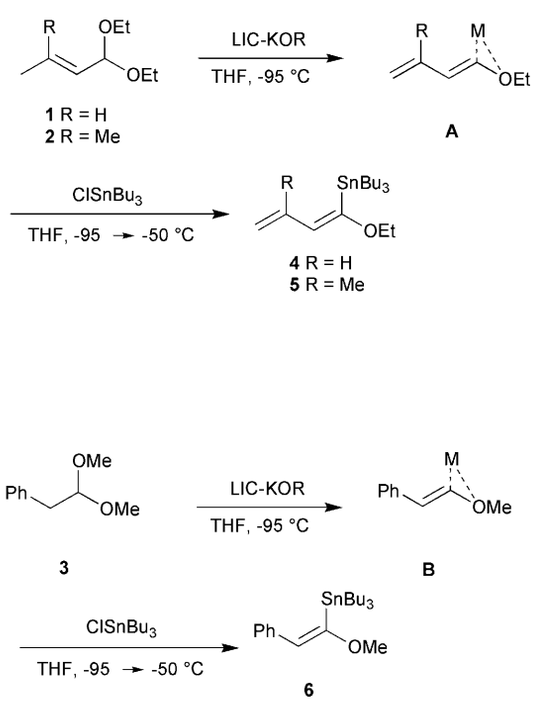
Treatment of α,β-unsaturated (**1** and **2**) and α-phenyl (**3**) acetals with an equimolar mixture of butyllithium and potassium *tert*-butoxide (Schlosser's reagent LIC–KOR) gives α-metalated 1,3-dienes and vinyl ethers that readily react with chlorotributyltin affording (*Z*)-functionalized alkoxyvinylstannanes **4**–**6**. Stille cross-coupling reaction between these reactants and allyl bromide, iodobenzene, or benzoyl chloride produces derivatives **7**–**13** that can be moreover converted into carbonyl compounds **14**–**19** according to an umpolung approach.

The palladium(0)-catalysed coupling reaction between an organotin reagent and an organic electrophile (Stille cross-coupling reaction)[1] is a powerful method for the formation of carbon–carbon bonds.[2] The synthetic utility of the Stille reaction owes a great deal to the mildness of the reaction conditions, which are compatible with many types of functional groups, and to the ease with which the organostannanes can be prepared. In particular, alk-1-enylstannanes are prepared *via* the hydrostannylation of alk-1-yne precursors in the presence of a radical initiator such as 2,2-azobis(isobutyronitrile).[3] Under standard experimental conditions the reaction usually affords the (*Z*) and (*E*) isomers as a thermodynamic mixture. Using this method almost pure (*E*)-vinyltins can be prepared as the thermodynamically stable product,[4] whereas the (*Z*)-vinyltin isomer is more difficult to obtain.[5] Careful control of the temperature in the initial step of the reaction is necessary in order to avoid isomerization to the more stable (*E*) derivative. New syntheses have been proposed to prepare (*E*) isomers, *e.g.* by hydrometallation,[6] carbometallation[7] and stannylmetallation[8] of alkynes. Alternative routes to (*Z*)-vinyltins have been carbometalation[9] or stannylmetalation[10] of alkynes. Isomerization is a major limitation. Titanation of alkynyltin acetals has been used to give the corresponding (*Z*)-disubstituted vinyltin derivatives as single geometrical isomers.[11] Moreover, stereodefined dienyltin derivatives are important intermediates for the preparation of polyenic building blocks that are of great importance not only for the synthesis of bioactive compounds,[12] but also useful chemicals in the production of new materials with non-linear optical properties[13] or high conductivity[14] and in the perfume industry.[15]

Results and discussion

During the past few years we have developed a facile synthesis of α-functionalized conjugate 1-alkoxy-1,3-dienes[16] and β-phenyl enol ethers.[17] The method has been set up exploiting the reactivity of α,β-unsaturated and α-phenyl acetals in the presence of the Schlosser's mixed superbase LIC–KOR (LIC = butyllithium and KOR = potassium *tert*-butoxide).[18] In this paper we provide the details of our work on the reaction of α-metalated intermediates with chlorotributylstannane in order to readily prepare dienyltin derivatives useful for Stille cross-coupling reactions. Experimental procedures are also given for the conversion of the Stille cross-coupling products into the corresponding carbonyl compounds. As shown in Scheme 1, in



Scheme 1

the presence of LIC–KOR superbase acetals **1**–**3** underwent 1,4- (**1** and **2**) or 1,2-elimination (**3**) reaction, affording unsaturated derivatives. Moreover, working with an excess of the base, elimination products were further metalated at the α-vinyl site affording intermediates **A** and **B**, which were functionalized with chlorotributyltin to give dienyl stannanes **4**–**5** and styrenyl stannane **6** as pure (*Z*) isomers. The configuration was deduced from the J_{trans} coupling constant between the α and β protons in the ^{1}H NMR spectrum of the corresponding derivatives obtained by quenching the reaction with H_2O instead of the

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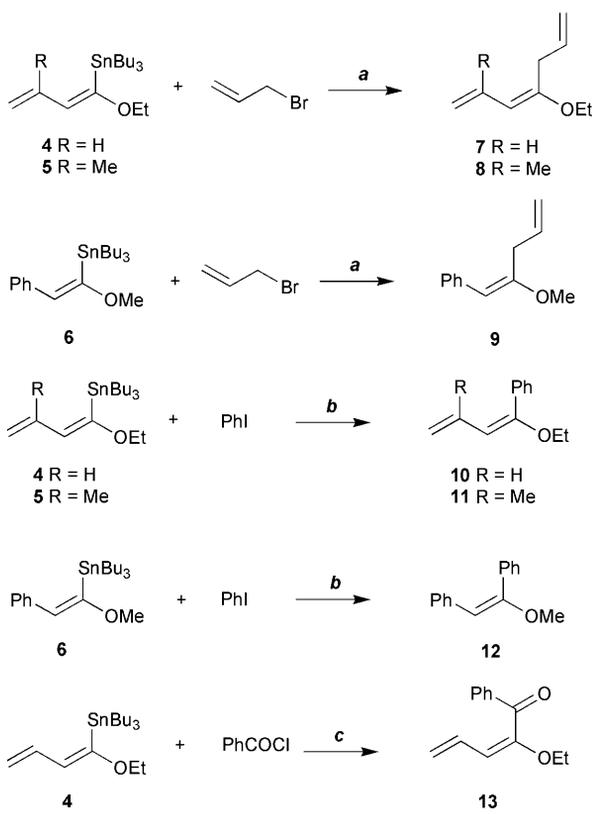
electrophile. Moreover, the (*Z*) configuration was confirmed through NOE experiments on stannane **6**: irradiation of the olefinic hydrogen gave rise to an Overhauser enhancement of the signals assigned to the phenyl and methoxy groups.‡

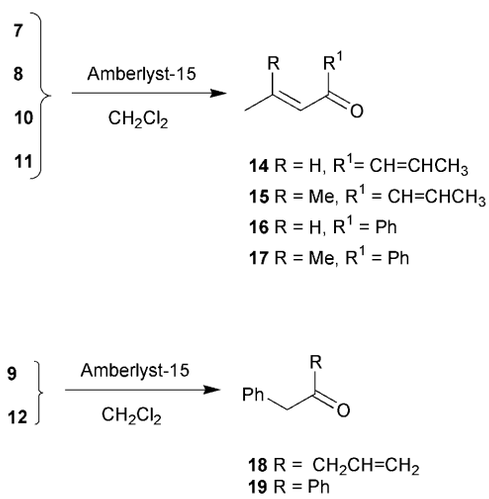
Stannanes **4**–**6** were coupled with allyl bromide, iodobenzene, and benzoyl chloride under different experimental conditions (Scheme 2), yielding derivatives **7**–**13**. The cross-coupling reactions afforded the stereochemically pure (*E*) isomers whose configuration was again deduced on the basis of NOE experiments. In particular, in the case of enol ether **12** irradiation of the olefinic hydrogen gave rise to an Overhauser enhancement of the signals assigned to the methoxy and to one of the phenyl groups.



Scheme 2 *Reagents and conditions*: *a*: $[(C_6H_5)_3P]_4Pd$, $CHCl_3$, 60 °C; *b*: LiCl, $[(C_6H_5)_3P]_4Pd$, CuCl, DMSO, 25 °C; *c*: $[(C_6H_5)_3P]_4Pd$, toluene, 100 °C.

It is worth pointing out that both allyl bromide and benzoyl chloride failed to react with metalated intermediates **A** and **B** (Scheme 1). Therefore neither halide can be used as a quenching electrophile, and the direct functionalisation of the unsaturated intermediate was thus precluded.§ In the case of iodobenzene, we took advantage of the co-catalytic effect of copper(I), which was introduced by Liebeskind and Fengl,[19] and whose mechanistic bases were studied by Farina and Liebeskind,[20] since this reactant afforded no Stille product under standard conditions. In particular, we have used the protocol recently proposed by Corey, which involves the system $Pd(PPh_3)_4$–CuCl–LiCl.[21]

The synthesis of metallovinyl ethers (metal = Si, Ge, and Sn) *via* the transmetalation of lithium derivatives has been previously reported and the resulting compounds have been used for the preparation of the corresponding metalloidal ketones.[22] However, to our knowledge the present work reports a new application of α,β-unsaturated and α-phenyl acetals for the synthesis of dienylstannanes and their use in the Stille cross-coupling reaction. Moreover a method is described for the subsequent conversion of the coupling derivatives into carbonyl compounds, according to an umpolung procedure.[23] Products **7**–**12** like all enol ethers undergo acidic hydrolysis to afford enones **14**–**17** and benzyl ketones **18** and **19**. The hydrolysis was carried out in a dichloromethane suspension of Amberlyst-15[24] (Scheme 3).¶ In particular, enones **14** and **15** undergo a double bond shift, in order to extend conjugation, while on the other hand ketone **18** retains the terminal double bond.



Scheme 3

Experimental

Reactions were performed in flame-dried glassware under an argon atmosphere. The temperature of slush liquid nitrogen–acetone is indicated as −95 °C, that of an ice-bath as 0 °C, and "room temperature" as 25 °C. THF was distilled from benzophenone ketyl, anhydrous DMSO was purchased from Fluka. BuLi (Aldrich) was used as 1.6 M solution in hexanes. *t*-BuOK was sublimed *in vacuo* (0.1 mmHg). LiCl was dried at 120 °C under high vacuum (2×10^{-3} mm Hg) overnight, CuCl was dried under high vacuum for 15 h. All other commercially obtained reagents were used as received. Purification by column chromatography was performed on Merck silica gel 60 as stationary phase and Et_2O–light petroleum ether (distillation range 40–60 °C) as eluent. ^1H and ^{13}C NMR spectra were recorded at 400 and 100.4 MHz, respectively and were carried out at the Dipartimento IFM (Università di Torino). Coupling constants (*J*) are given in Hz. Mass spectra were obtained on a mass selective detector HP 5970 B instrument operating at an ionising voltage of 70 eV connected to a HP 5890 GC, cross linked methyl silicone capillary column (25 m × 0.2 mm × 0.33 mm film thickness).

‡ The assignment of the stereochemistry is based on the hypothesis that the mechanism of quenching the reaction with water will give the same stereochemistry as the stannylation reaction. In any case the results of NOE experiments on compound **6** seem to validate this assumption.

§ Experimental results obtained in our laboratory suggest that α-metalated intermediates **A** and **B** do not react by nucleophilic substitution with electrophiles that contain allylic hydrogens. For example, when 1-bromohexa-3,5-diene was treated with 1,1-diethoxybut-2-ene in the presence of the LIC–KOR base, the only isolated products were hexa-1,3,5-triene and 1-ethoxybuta-1,3-diene. On the other hand, *tert*-butyl benzoate was the main isolated product in the reaction between benzoyl chloride and 1,1-diethoxybut-2-ene under the same experimental conditions.

¶ Derivative **13** does not hydrolyze under these experimental conditions. This inertness can probably be ascribed to the presence of the carbonyl group which destabilizes the cationic intermediate that develops during the hydrolysis.

General procedure for the synthesis of stannanes (4–6)

To a cooled (−95 °C) solution of *t*-BuOK (1.4 g, 12.5 mmol) in anhydrous THF (10 cm^3), acetal (**1**–**3**, 5.0 mmol) and BuLi (7.8 cm^3, 12.5 mmol) were added dropwise. After a few seconds the solution turned purple and was stirred for 2 h at −95 °C, then $ClSnBu_3$ (1.62 g, 5.0 mmol) was added. After 2 h the reaction was quenched with a THF solution of H_2O (10 cm^3) and the colour was discharged. The two phases were separated and the aqueous one extracted with Et_2O (2 × 20 cm^3). The combined organic phases were washed with brine (2 × 15 cm^3), dried (Na_2SO_4) and concentrated to give crude products that were purified by chromatography.

(*Z*)-1-(Tri-*n*-butylstannyl)-1-ethoxybuta-1,3-diene (4). Purification by chromatography (2:98, Et_2O–light petroleum ether) gave **4** (1.23 g, 64%) as a yellow oil. δ_H (400 MHz; $CDCl_3$) 0. 89 (t, *J* = 7.3, 9 H), 0.92–1.01 (m, 6 H), 1.26–1.29 (t, *J* = 6.5, 3 H), 1.28–1.32 (sextet, *J* = 7.3, 6 H), 1.53–1.55 (m, 6 H), 3.77 (q, *J* = 6.5, 2 H), 4.81 (dd, *J* = 10.0, 1.0, 1 H), 4.97 (dd, *J* = 16.0, 1.0, 1 H), 6.08 (d, *J* = 10.0, 1 H), 6.22 (dt, *J* = 16.0, 10.0, 1 H); δ_C (100.4 MHz; $CDCl_3$) 10.4, 13.6, 14.5, 28.8, 29.0, 63.0, 110.4, 115.2, 135.6, 174.2; *m/z* (EI, 70 eV, rel. int.) 386 (M^+, 1), 365 (16), 361 (100), 358 (66), 304 (54), 245 (29), 41 (13) (Found: C, 55.64; H 9.56. Calc. for $C_{18}H_{36}OSn$: C, 55.84; H, 9.37%).

(*Z*)-1-(Tri-*n*-butylstannyl)-1-ethoxy-3-methylbuta-1,3-diene (5). Purification by chromatography (2:98, Et_2O–light petroleum ether) gave **5** (1.62 g, 81%) as a yellow oil. δ_H (400 MHz; $CDCl_3$) 0.89 (t, *J* = 7.3, 9 H), 0.92–1.01 (m, 6 H), 1.26–1.29 (t, *J* = 6.5, 3 H), 1.28–1.32 (sextet, *J* = 7.3, 6 H), 1.53–1.55 (m, 6 H), 1.79 (s, 3 H), 3.68 (q, *J* = 6.5, 2 H), 4.63 (q, *J* = 1.5, 1 H), 4.71 (q, *J* = 1.5, 1 H), 5.78 (s, 1 H); δ_C (100.4 MHz; $CDCl_3$) 11.2, 13.5, 14.6, 26.9, 28.8, 28.9, 63.0, 110.0, 116.2, 143.4, 167.9; *m/z* (EI, 70 eV, rel. int.) 313 (M^+ − 87, 100), 311 (58), 198 (25), 257 (32) (Found: C, 56.65; H 9.56. Calc. for $C_{19}H_{38}OSn$: C, 56.88; H, 9.55%).

1-(Tri-*n*-butylstannyl)-1-methoxy-2-phenylethene (6). Purification by chromatography (2:98, Et_2O–light petroleum ether) gave **6** (1.94 g, 92%) as a red oil. δ_H (400 MHz; $CDCl_3$) 0.96 (t, *J* = 7.3, 9 H), 0.98–1.03 (m, 6 H), 1.32–1.35 (m, 6 H), 1.35–1.41 (sextet, *J* = 7.3, 6 H), 3.69 (s, 3 H), 6.5 (s, 1 H), 7.17 (t, *J* = 7.2, 1 H), 7.25 (t, *J* = 7.2, 2 H), 7.30 (d, *J* = 7.2, 2 H); δ_C (100.4 MHz; $CDCl_3$) 10.1, 11.1, 27.1, 27.3, 56.5, 114.0, 125.7, 126.8, 128.2, 128.3, 142.0; *m/z* (EI, 70 eV, rel. int.) 371 (M^+ − 51), 365 (51), 151 (98), 91 (12), 41 (100) (Found: C, 59.50; H 8.43. Calc. for $C_{21}H_{36}OSn$: C, 59.60; H, 8.57%).

General procedure for Stille cross-coupling reaction

Method A (allyl bromide and benzoyl chloride). A flame dried Schlenk tube was charged with $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol, 1% eq.,) in anhydrous $CHCl_3$ (1 cm^3), then allyl bromide (0.36 g, 3.0 mmol) and vinyltin compound (3.0 mmol) were added. The reaction was stirred for 2 h at 60 °C, and then was diluted with CH_2Cl_2 (5 cm^3) and H_2O (5 cm^3). The organic phase was washed with brine (2 × 10 cm^3), dried over Na_2SO_4 and concentrated to give a residue that was purified as stated below. The cross-coupling reaction of benzoyl chloride with organotin reagent **4** was carried out under the same experimental conditions, but using boiling toluene as the reaction solvent.

Method B (iodobenzene). A Schlenk vessel was charged with LiCl (0.21 g, 5.0 mmol), and flame dried under an inert atmosphere. Upon cooling, $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol) and CuCl (0.39 g, 4.0 mmol) were added. DMSO (8.0 cm^3) was introduced with stirring, followed by the addition of iodobenzene (0.16 g, 0.8 mmol,) and a vinyltin compound (1.0 mmol). The reaction mixture was stirred at 25 °C for 2 h. Completion of the coupling was monitored by GC. The reaction mixture was diluted with Et_2O (15 cm^3), and washed with brine (2 × 15 cm^3) and 5% aqueous NH_4OH (10 cm^3). The combined organic layers were washed with water (3 × 10 cm^3), then dried over Na_2SO_4 and concentrated to a residue that was purified as stated below.

(3*E*)-4-Ethoxyhepta-1,3,6-triene (7). Purification by chromatography (5:95, Et_2O–light petroleum ether) gave **7** (0.29 g, 70%) as a yellow oil. δ_H (400 MHz; $CDCl_3$) 1.29 (t, *J* = 6.5, 3 H), 3.01 (dt, *J* = 7.5, 1.5, 2 H), 3.75 (q, *J* = 6.5, 2 H), 4.81 (dd, *J* = 10, 1.5, 1 H), 4.97 (dd, *J* = 16.5, 1.5, 1 H), 5.04 (dq, *J* = 10.5, 1.5, 1 H), 5.10 (dq, *J* = 16.5, 1.5, 1 H), 5.31 (d, *J* = 10.5, 1 H), 5.80 (m, 1 H), 6.42 (dt, *J* = 16.5, 10.5, 1 H); δ_C (100 MHz; $CDCl_3$) 14.6, 35.6, 62.6, 101.2, 111.4, 116.0, 134.3, 134.5, 157.7; *m/z* (EI, 70 eV, rel. int.) 138 (M^+, 13), 110 (20), 68 (98), 41 (60), 39 (100) (Found: C, 78.65; H, 10.56. Calc. for $C_9H_{14}O$: C, 78.21; H, 10.21%).

(3*E*)-4-Ethoxy-2-methylhepta-1,3,6-triene (8). Purification by chromatography (5:95, Et_2O–light petroleum ether) gave **8** (0.30 g, 66%) as a yellow oil. δ_H (400 MHz; $CDCl_3$) 1.29 (t, *J* = 6.5, 3 H), 1.81 (s, 3 H), 3.07 (dt, *J* = 6.5, 1.5, 2 H), 3.75 (q, *J* = 6.5, 2 H), 4.73 (br s, 1 H), 4.81 (br s, 1 H), 5.01 (s, 1 H), 5.04 (dq, *J* = 10.5, 1.5, 1 H), 5.09 (dq, *J* = 16.5, 1.5, 1 H), 5.89 (ddt, *J* = 16.5, 10.5, 6.5, 1 H); δ_C (100 MHz; $CDCl_3$) 14.7, 24.7, 30.1, 62.4, 103.4, 111.1, 115.7, 135.6, 141.0, 155.9; *m/z* (EI, 70 eV, rel. int.) 152 (M^+, 14), 109 (100), 91 (27), 81 (23), 55 (44), 41 (34) (Found: C, 78.97; H 10.80. Calc. for $C_{10}H_{16}O$: C, 78.90; H, 10.59%).

(1*E*)-2-Methoxy-1-phenylpenta-1,4-diene (9). Purification by chromatography (5:95, Et_2O–light petroleum ether) gave **9** (0.45 g, 86%) as a yellow oil. δ_H (400 MHz; $CDCl_3$) 3.10 (dt, *J* = 7.5, 1.5, 2 H), 3.69 (s, 3 H), 5.14–5.19 (m, 2 H), 5.69 (s, 1 H), 5.94–5.98 (ddt, *J* = 16.5, 10.5, 7.5, 1 H), 7.21 (t, *J* = 7.2, 1 H), 7.25 (d, *J* = 7.2, 2 H), 7.31 (t, *J* = 7.2, 2 H); δ_C (100 MHz; $CDCl_3$) 35.5, 54.6, 100.3, 116.0, 125.3, 128.0, 128.4, 134.7, 137.2, 157.2; *m/z* (EI, 70 eV, rel. int.) 174 (M^+, 60), 141 (47), 115 (51), 91 (100), 89 (55), 41 (55) (Found: C, 82.95; H 8.45. Calc. for $C_{12}H_{14}O$: C, 82.72; H, 8.10%).

(1*E*)-1-Ethoxy-1-phenylbuta-1,3-diene (10). Purification by chromatography (5:95 Et_2O–light petroleum ether) gave **10** (0.10 g, 72%) as a yellow oil. δ_H (400 MHz; $CDCl_3$) 1.37 (t, *J* = 7.5, 3 H), 3.92 (q, *J* = 7.5, 2 H), 4.80 (dd, *J* = 10.5, 1.5, 1 H), 5.10 (dd, *J* = 16.5, 1.5, 1 H), 5.60 (d, *J* = 10.5, 1 H), 6.42 (dt, *J* = 16.5, 10.5, 1 H), 7.35 (t, *J* = 7.5, 1 H), 7.37 (t, *J* = 7.5, 2 H), 7.41 (d, *J* = 7.5, 2 H); δ_C (100 MHz; $CDCl_3$) 14.8, 63.6, 103.4, 112.3, 128.1, 128.6, 129.2, 133.9, 135.2, 158.2; *m/z* (EI, 70 eV, rel. int.) 174 (M^+, 50), 145 (100), 127 (41), 91 (23), 77 (79), 68 (24) (Found: C, 82.80; H 8.32. Calc. for $C_{12}H_{14}O$: C, 82.72; H, 8.10%).

(1*E*)-1-Ethoxy-3-methyl-1-phenylbuta-1,3-diene (11). Purification by chromatography (5:95, Et_2O–light petroleum ether) gave **11** (0.11 g, 75%) as a yellow oil. δ_H (400 MHz; $CDCl_3$) 1.26 (t, *J* = 6.5, 3 H), 1.79 (s, 3 H), 3.68 (q, *J* = 6.5, 2 H), 4.70 (br s, 2 H), 5.78 (s, 1 H), 7.32 (t, *J* = 7.5, 1 H), 7.35 (t, *J* = 7.5, 2 H), 7.40 (d, *J* = 7.5, 2 H); δ_C (100 MHz; $CDCl_3$) 14.9, 23.3, 63.6, 105.3, 114.1, 127.89, 129.4, 131.6, 133.7, 133.9, 157.6; *m/z* (EI, 70 eV, rel. int.) 188 (M^+, 34), 145 (35), 105 (32), 77 (100), 51 (56) (Found: C, 82.96; H 8.62. Calc. for $C_{13}H_{16}O$: C, 82.94; H, 8.57%).

1-Methoxy-1,2-diphenylethene (12). Purification by chromatography (5:95, Et_2O–light petroleum ether) gave **12** (0.13 g, 78%) as a yellow oil. δ_H (400 MHz; $CDCl_3$) 3.83 (s, 3 H), 5.85 (s, 1 H), 7.11 (t, *J* = 7.3, 2 H), 7.26 (t, *J* = 7.3, 4 H), 7.42 (d, *J* = 7.3, 4 H); δ_C (100 MHz; $CDCl_3$) 55.6, 101.6, 125.5, 128.1, 128.3, 128.7, 129.0, 129.4, 136.4, 137.0, 157.33; *m/z* (EI, 70 eV, rel. int.)

210 (M^+, 100), 167 (75), 165 (88), 105 (74), 91 (87), 77 (50) (Found: C, 85.76; H 6.75. Calc. for $C_{15}H_{14}O$: C, 85.68; H, 6.71%).

(2*E*)-2-Ethoxy-1-phenylpenta-2,4-dien-1-one (13). Purification by chromatography (10:90 Et_2O–light petroleum ether) gave **13** (0.41, 86%) as a yellow oil. δ_H (400 MHz; $CDCl_3$) 1.31 (t, J = 6.4, 3 H), 3.90 (q, J = 6.4, 2 H), 4.92 (dd, J = 10.0, 1.5, 1 H), 5.2 (dd, J = 16.4, 1.5, 1 H), 5.8 (d, J = 10.0, 1 H), 6.64 (dt, J = 16.4, 10.0, 1 H), 7.40 (t, J = 6.6, 2 H), 7.62 (t, J = 6.6, 1 H), 7.9 (d, J = 6.6, 2 H); δ_C (100.4 MHz; $CDCl_3$) 14.8, 60.42, 106.8, 116.3, 129.0, 129.71, 134.3, 136.8, 137.0, 156.7, 191.6; *m/z* (EI, 70 eV, rel. int.) 202 (M^+, 20), 182 (10), 105 (100), 77 (53), 55 (37) (Found: C, 77.75; H 6.86. Calc. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%).

Synthesis of ketones 14–19

To a solution of cross-coupling products (**7**–**12**, 3.0 mmol) in CH_2Cl_2 (5.0 cm^3) Amberlyst-15 (0.03 g) was added. The reaction was monitored by GC. After 1 h at 25 °C, the Amberlyst was filtered off and the organic layer was washed with $NaHCO_3$ 5% (2 × 5 cm^3), with brine (2 × 5 cm^3) and dried over $NaSO_4$. Evaporation of the solvent gives crude products that were purified by chromatography. Ketones **14**–**19** could be obtained directly in one step, diluting the cross-coupling reaction mixture with CH_2Cl_2 and adding Amberlyst (2% by weight) to the solution.

(2*E*,5*E*)-Hepta-2,5-dien-4-one (14). Purification by chromatography (10:90, Et_2O–light petroleum ether) gave **14** (0.26 g, 80%) as a yellow oil. ν_{max}(film)/cm^{-1} 1668; δ_H (400 MHz; $CDCl_3$) 1.87 (dd, J = 7.10, 1.5, 6 H), 6.34 (dq, J = 15.7, 1.5, 2 H), 6.88 (dq, J = 15.7, 6.4, 2 H); δ_C (100 MHz; $CDCl_3$) 18.2, 129.9, 142.9, 189.2; *m/z* (EI, 70 eV, rel. int.) 110 (M^+, 12), 69 (100), 67 (10), 41 (99), 39 (90) (Found: C, 76.45; H 9.34. Calc. for $C_7H_{10}O$: C, 76.33; H, 9.15%).

(5*E*)-2-Methylhepta-2,5-dien-4-one (15). Purification by chromatography (10:90, ethyl ether–light petroleum ether) gave **15** (0.29 g, 78%) as a yellow oil. ν_{max}(film)/cm^{-1} 1634; δ_H (400 MHz; $CDCl_3$) 1.83 (dd, J = 6.5, 1.5, 3 H), 1.86 (br s, 3 H), 2.09 (br s, 3 H), 6.11 (dq, J = 15, 1.5, 1 H), 6.15 (br s, 1 H), 6.78 (dq, J = 15, 6.5, 2 H); δ_C (100 MHz; $CDCl_3$) 17.3, 20.6, 27.5, 122.6, 133.3, 141.4, 155.2, 190.1; *m/z* (EI, 70 eV, rel. int.) 124 (M^+, 5), 109 (63), 83 (31), 55 (51), 39 (100) (Found: C, 77.43; H 9.34. Calc. for $C_8H_{12}O$: C, 77.38; H, 9.74%).

(2*E*)-1-Phenylbut-2-en-1-one (16). Purification by chromatography (10:90, Et_2O–light petroleum ether) gave **16** (0.32 g, 74%) as a yellow oil. ν_{max}(film)/cm^{-1} 1624; δ_H (400 MHz; $CDCl_3$) 1.97 (dd, J = 6.5, 1.5, 3 H), 6.92 (dq, J = 15, 1.5, 1 H), 7.04 (dq, J = 15, 6.5, 1 H), 7.45 (t, J = 7.2, 2 H), 7.47 (t, J = 7.2, 1 H), 7.91 (d, J = 7.2, 2 H); δ_C (100 MHz; $CDCl_3$) 18.4, 127.3, 128.3, 132.4, 137.6, 144.6, 144.87, 190.1; *m/z* (EI, 70 eV, rel. int.) 146 (M^+, 48), 131 (42), 105 (100), 77 (97), 69 (77), 51 (66) (Found: C, 82.55; H 6.76. Calc. for $C_{10}H_{10}O$: C, 82.16; H, 6.89%).

1-Phenyl-3-methylbut-2-en-1-one (17). Purification by chromatography (10:90 Et_2O–light petroleum ether) gave **17** (0.41 g, 86%) as a yellow oil. ν_{max}(film)/cm^{-1} 1661; δ_H (400 MHz; $CDCl_3$) 2.00 (s, 3 H), 2.20 (s, 3 H), 6.74 (br s, 1 H), 7.43 (t, J = 7.2, 2 H), 7.51 (t, J = 7.2, 1 H), 7.92 (d, J = 7.2, 2 H); δ_C (100 MHz; $CDCl_3$) 21.2, 28.0, 121.2, 128.2, 128.5, 132.3, 139.3, 156.74, 191.5; *m/z* (EI, 70 eV, rel. int.) 160 (M^+, 39), 145 (43), 83 (45), 77 (88), 55 (68), 51 (100) (Found: C, 82.55; H 6.76. Calc. for $C_{11}H_{12}O$: C, 82.46; H, 7.55%).

1-Phenylpent-4-en-2-one (18). Purification by chromatography (10:90, Et_2O–light petroleum ether) gave **18** (0.35 g, 74% yield) as a yellow oil. ν_{max}(film)/cm^{-1} 1718; δ_H (400 MHz; $CDCl_3$) 3.20 (dt, J = 7.5, 1.5, 2 H), 3.7 (s, 2 H), 5.12 (dq, J = 16.0, 1.5, 1 H), 5.18 (dq, J = 10.0, 1.5, 1 H), 5.88 (ddt, J = 16.0, 10.0, 7.5, 1 H), 7.19 (d, J = 7.5, 2 H), 7.27 (t, J = 7.5, 1 H), 7.34 (t, J = 7.5, 2 H); δ_C (100 MHz; $CDCl_3$) 46.3, 49.4, 118.9, 126.9, 128.6, 129.3, 130.8, 133.8, 205.9; *m/z* (EI, 70 eV, rel. int.) 160 (M^+, 5), 119 (24), 91 (99), 65 (40), 41 (81) (Found: C, 82.55; H 7.56. Calc. for $C_{11}H_{12}O$: C, 82.46; H, 7.55%).

2-Phenylacetophenone (19). Purification by chromatography (10:90, Et_2O–light petroleum ether) gave **19** (0.52 g, 88%) as a yellow oil. ν_{max}(film)/cm^{-1} 1685; δ_H (400 MHz; $CDCl_3$) 4.32 (s, 2 H), 7.25 (m, 3 H), 7.33 (t, J = 7.2, 2 H), 7.46 (t, J = 7.2, 2 H), 7.55 (t, J = 7.2, 1 H), 8.02 (d, J = 7.2, 2 H); δ_C (100 MHz; $CDCl_3$) 45.3, 126.7, 128.4, 128.5, 128.6, 129.3, 133.1, 134.4, 136.4, 197.5; *m/z* (EI, 70 eV, rel. int.) 196 (M^+, 1), 105 (100), 91(6), 77 (47), 51 (66) (Found: C, 85.75; H 6.76. Calc. for $C_{14}H_{12}O$: C, 85.68; H, 6.16%).

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