

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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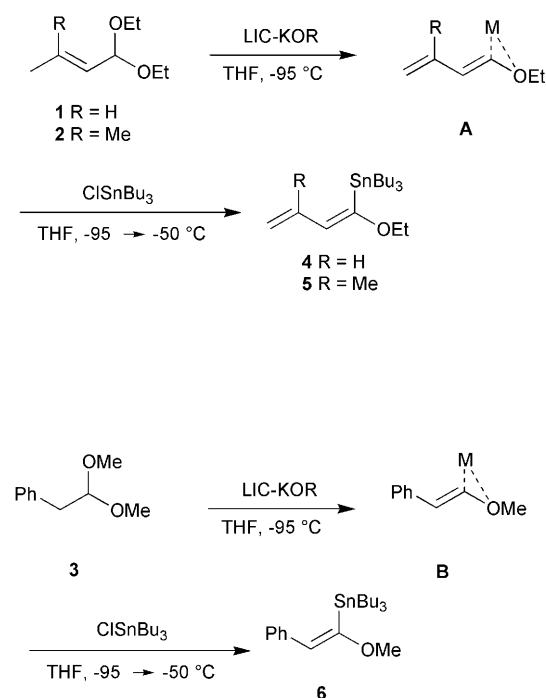
Treatment of α,β -unsaturated (**1** and **2**) and α -phenyl (**3**) acetals with an equimolar mixture of butyllithium and potassium *tert*-butoxide (Schlosser's reagent LIC–KOR) gives α -metalated 1,3-dienes and vinyl ethers that readily react with chlorotributyltin affording (*Z*)-functionalized alkoxyvinylstannanes **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 carbometallation⁷ and stannylation⁸ of alkynes. Alternative routes to (*Z*)-vinyltins have been carbometallation⁹ or stannylation¹⁰ 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, stereo-defined 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 properties¹³ or high conductivity¹⁴ 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-dienes¹⁶ 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

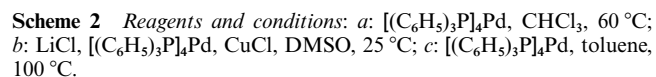


Scheme 1

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 ¹H NMR spectrum of the corresponding derivatives obtained by quenching the reaction with H₂O instead of the

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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 reac-



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

§ 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.

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 metalloid 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 dienylistannanes 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-15²⁴ (Scheme 3).[¶] In particular, enones **14** and



Experimental

¶ 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 ($-95\text{ }^{\circ}\text{C}$) solution of *t*-BuOK (1.4 g, 12.5 mmol) in anhydrous THF (10 cm³), acetal (**1–3**, 5.0 mmol) and BuLi (7.8 cm³, 12.5 mmol) were added dropwise. After a few seconds the solution turned purple and was stirred for 2 h at $-95\text{ }^{\circ}\text{C}$, then ClSnBu₃ (1.62 g, 5.0 mmol) was added. After 2 h the reaction was quenched with a THF solution of H₂O (10 cm³) and the colour was discharged. The two phases were separated and the aqueous one extracted with Et₂O ($2 \times 20\text{ cm}^3$). The combined organic phases were washed with brine ($2 \times 15\text{ cm}^3$), dried (Na₂SO₄) 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, Et₂O–light petroleum ether) gave **4** (1.23 g, 64%) as a yellow oil. δ_{H} (400 MHz; CDCl₃) 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; CDCl₃) 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 C₁₈H₃₆OSn: C, 55.84; H, 9.37%).

(Z)-1-(Tri-*n*-butylstannyl)-1-ethoxy-3-methylbuta-1,3-diene (5). Purification by chromatography (2:98, Et₂O–light petroleum ether) gave **5** (1.62 g, 81%) as a yellow oil. δ_{H} (400 MHz; CDCl₃) 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; CDCl₃) 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 ($\text{M}^+ - 87$, 100), 311 (58), 198 (25), 257 (32) (Found: C, 56.65; H 9.56. Calc. for C₁₉H₃₈OSn: C, 56.88; H, 9.55%).

1-(Tri-*n*-butylstannyl)-1-methoxy-2-phenylethene (6). Purification by chromatography (2:98, Et₂O–light petroleum ether) gave **6** (1.94 g, 92%) as a red oil. δ_{H} (400 MHz; CDCl₃) 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; CDCl₃) 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 ($\text{M}^+ - 51$), 365 (51), 151 (98), 91 (12), 41 (100) (Found: C, 59.50; H 8.43. Calc. for C₂₁H₃₆OSn: 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(PPh₃)₄ (0.035 g, 0.03 mmol, 1% eq.) in anhydrous CHCl₃ (1 cm³), 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 $60\text{ }^{\circ}\text{C}$, and then was diluted with CH₂Cl₂ (5 cm³) and H₂O (5 cm³). The organic phase was washed with brine ($2 \times 10\text{ cm}^3$), dried over Na₂SO₄ 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(PPh₃)₄ (0.06 g, 0.05 mmol) and CuCl (0.39 g, 4.0 mmol) were added. DMSO (8.0 cm³) 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 $25\text{ }^{\circ}\text{C}$ for 2 h. Completion of the coupling was monitored by GC. The reaction mixture was

diluted with Et₂O (15 cm³), and washed with brine ($2 \times 15\text{ cm}^3$) and 5% aqueous NH₄OH (10 cm³). The combined organic layers were washed with water ($3 \times 10\text{ cm}^3$), then dried over Na₂SO₄ and concentrated to a residue that was purified as stated below.

(3E)-4-Ethoxyhepta-1,3,6-triene (7). Purification by chromatography (5:95, Et₂O–light petroleum ether) gave **7** (0.29 g, 70%) as a yellow oil. δ_{H} (400 MHz; CDCl₃) 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; CDCl₃) 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 C₉H₁₄O: C, 78.21; H, 10.21%).

(3E)-4-Ethoxy-2-methylhepta-1,3,6-triene (8). Purification by chromatography (5:95, Et₂O–light petroleum ether) gave **8** (0.30 g, 66%) as a yellow oil. δ_{H} (400 MHz; CDCl₃) 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; CDCl₃) 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 C₁₀H₁₆O: C, 78.90; H, 10.59%).

(1E)-2-Methoxy-1-phenylpenta-1,4-diene (9). Purification by chromatography (5:95, Et₂O–light petroleum ether) gave **9** (0.45 g, 86%) as a yellow oil. δ_{H} (400 MHz; CDCl₃) 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; CDCl₃) 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 C₁₂H₁₄O: C, 82.72; H, 8.10%).

(1E)-1-Ethoxy-1-phenylbuta-1,3-diene (10). Purification by chromatography (5:95, Et₂O–light petroleum ether) gave **10** (0.10 g, 72%) as a yellow oil. δ_{H} (400 MHz; CDCl₃) 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; CDCl₃) 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 C₁₂H₁₄O: C, 82.72; H, 8.10%).

(1E)-1-Ethoxy-3-methyl-1-phenylbuta-1,3-diene (11). Purification by chromatography (5:95, Et₂O–light petroleum ether) gave **11** (0.11 g, 75%) as a yellow oil. δ_{H} (400 MHz; CDCl₃) 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; CDCl₃) 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 C₁₃H₁₆O: C, 82.94; H, 8.57%).

1-Methoxy-1,2-diphenylethene (12). Purification by chromatography (5:95, Et₂O–light petroleum ether) gave **12** (0.13 g, 78%) as a yellow oil. δ_{H} (400 MHz; CDCl₃) 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; CDCl₃) 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%).

(2E)-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% ($2 \times 5 cm^3$), with brine ($2 \times 5 cm^3$) 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.

(2E,5E)-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. $\nu_{max}(\text{film})/cm^{-1}$ 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%).

(5E)-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. $\nu_{max}(\text{film})/cm^{-1}$ 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%).

(2E)-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. $\nu_{max}(\text{film})/cm^{-1}$ 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. $\nu_{max}(\text{film})/cm^{-1}$ 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. $\nu_{max}(\text{film})/cm^{-1}$ 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. $\nu_{max}(\text{film})/cm^{-1}$ 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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