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Allylic alkylation with function-bearing organozinc reagents

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Summary — The first palladium-catalysed alkylations of allylic acetates with organozinc reagents bearing functionality are reported. The reaction proceeds well from ethanoate, and propenoates, derived organozinc halides and provides a useful method for transferring these moieties to an allyl fragment. The reaction proceeds through a monophosphine complex; attempts to perform asymmetric syntheses are unsuccessful so far.

palladium / coupling / allylic substitution

Résumé — Alkylation allylique avec des réactifs organozinciques porteurs de fonctionnalités. Il a été rapporté les premières alkylations catalysées par le palladium, d'acétates allyliques avec des réactifs organozinciques porteurs de fonctionnalités. La réaction a lieu à partir d'éthanoate et de propénoates dérivés d'halogénures d'organozinc et fournit une méthode utile pour le transfert de ces «restes» au fragment allyle. Un complexe de monophosphine est l'intermédiaire de la réaction. Il n'a pas été possible d'effectuer des synthèses asymétriques.

palladium / couplage / substitution allylique

Introduction

In the development of palladium-catalysed C–C bond forming reactions, cross-coupling with organozinc halides has played an important role. Their use was pioneered by Negishi [1], who demonstrated successful cross-couplings and allylic alkylation. An interesting feature of the latter was that the stereochemical course of reaction was different for soft nucleophiles, exemplified by malonate ion, and hard nucleophiles exemplified by phenylzinc chloride [2]. For the organozinc reagent, this was interpreted in terms of a palladium-mediated reaction with the final C–C bond forming step being a reductive elimination of R– (arising from RZnX) and the allyl group; in contrast, malonate attacks palladium in an exometallic sense (fig 1).

Further significant extensions have come from the introduction of improved methods for the formation of functional organozinc reagents, prominently by Knochel and co-workers [3] which have been followed by a range of applications to cross-coupling. In this context the work of Jackson is notable providing access to many aromatic amino-acids through the zinc reagent derived from iodomethylglycine [4]. All the examples shown are formally cross- coupling chemistry. In the same time period, there have been significant advances in asymmetric allylic alkylation with soft nucleophiles, either through the application of novel heterotopic P–N ligands or new types of chelating biphosphine. In all of these reactions the palladium is thought to remain chelated during the course of substitution. Examples of successful asymmetric synthesis with hard nucleophiles are lacking. Part of the problem may be that the mechanism is significantly different, as indicated in figure 1. Kurosawa's work strongly indicates that the critical step is reductive elimination from a monophosphine η^1-alkyl η^3-allylpalladium intermediate [5]. This precludes the use of chelating ligands which will inhibit access to this structure, and provides a severe limitation to development of asymmetric synthesis. Further support for this reaction pathway comes from efforts to apply the Pd-catalysed phenylation of allylic acetates with PhZnCl in asymmetric synthesis. Low enantiomer excesses were obtained, and the only catalytically active ligands were monophosphines [6].

This lack of application of functional organozincs in allylic alkylation encouraged us to conduct a series of simple reactions, the scope of which is reported herein.

Fig 1. Exo- and endometallic transition states for nucleophilic substitution of Pd allyls.

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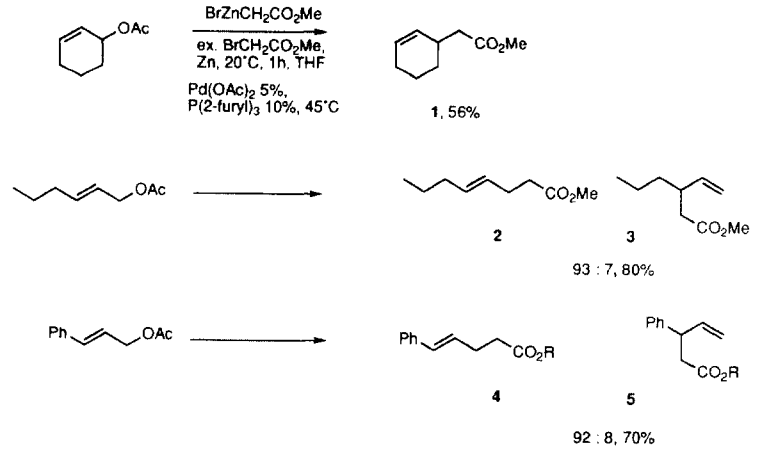


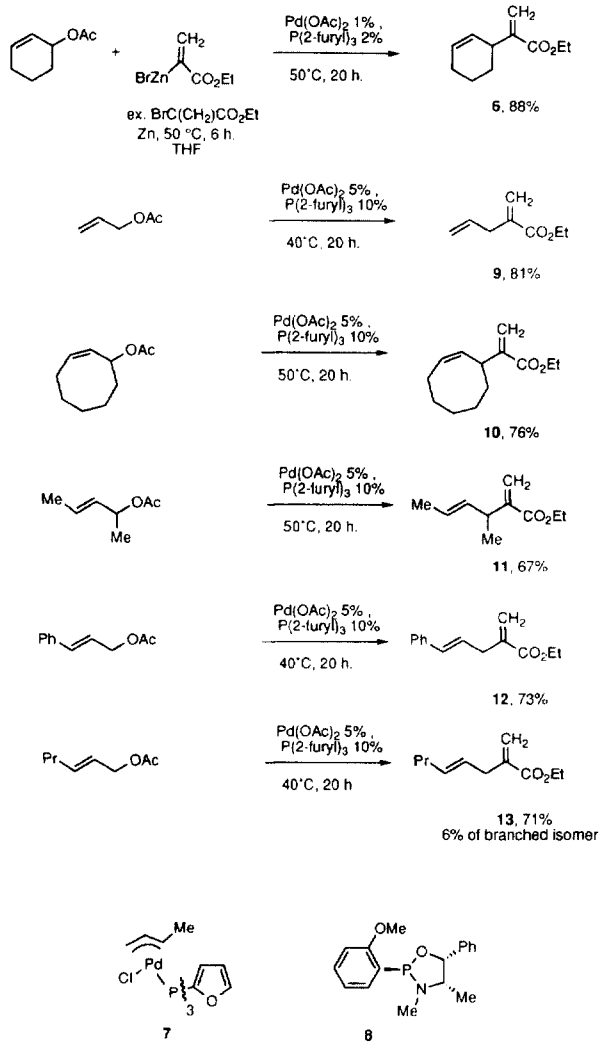
Scheme 1

Results and discussion

Ethyl or methyl 2-(bromozincato)ethanoate

Reactions of the simplest Reformatsky reagent $BrZnCH_2CO_2Et$ were carried out in THF solution. Because of the ready availability of this and also of cyclohex-2-enyl acetate, initial work proceeded to find the optimum reaction conditions. Just as in other Pd-catalysed reactions [7], the use of tris-2-furyl phosphine as ligand proved advantageous; the reactive complex was generated in situ according to scheme 1. The product ester **1** [8] was obtained in 56% yield with 5 mol% $Pd(OAc)_2$ and 10 mol% $P(C_4H_3O)_3$, conditions which would be expected to lead to the formation of a monophosphine complex with concomitant oxidation of a mole of the ligand [9]. Of a variety of related conditions tried with PPh_3 or $P(o\text{-tol})_3$ as ligand, none approached this in efficiency (<25%), and all reactions involving chelating diphosphine ligands were unsuccessful.

This encouraged us to try the other experiments reported in scheme 2. With *E*-hex-2-en-1-yl acetate the linear product **2** predominated strongly over the branched product **3**, as would be the case in allylic alkylation of a monosubstituted allylic acetate with soft nucleophiles [10]. Likewise with *E*-cinnamyl acetate, product **4** was obtained in 70% optimal yield and 90–92% regioselectivity. The preference for its formation over the branched ester **5** is consistent with the regiochemistry in allylic alkylation by soft nucleophiles, as in the monoalkylated case [11]. Very recently, Hayashi and co-workers have demonstrated reverse regioselectivity with bulky chiral monophosphines in the allylic substitution of arylallyl acetates by alkylmalonate anions [12]. In addition, tungsten-complex catalysed allylic alkylation of *E*-cinnamyl acetate gives the reverse regiochemistry with chelating diamine or phosphinamine ligands, although the mechanism of addition is distinct from the palladium case [13]. The contrast between the zincate case described here and the Hayashi case is not obviously explained, but indicates that there are factors other than the involvement of a monophosphine intermediate.



Scheme 2

Ethyl 2-(bromozincato)propenoate

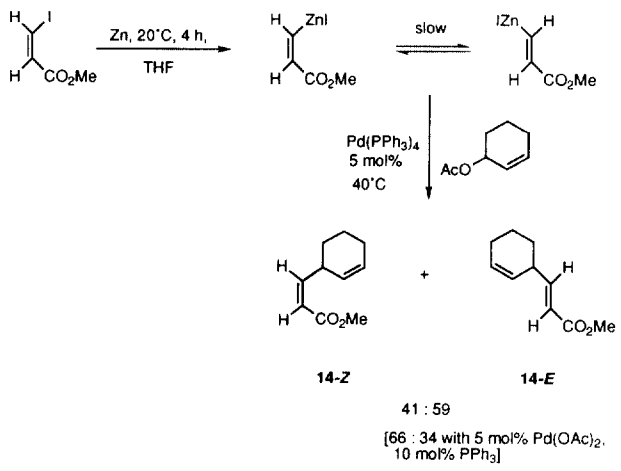
The zinc reagent is readily prepared in THF at 50 °C, and reacts well with cyclohex-2-enyl acetate under Pd catalysis. In this case $Pd(PPh_3)_4$ is an effective catalyst, although the combination of $Pd(OAc)_2$ and tris-

(2-furyl)phosphine operates at as low as 1% loading. A single product **6** [14] is formed in 88% yield from 3-acetoxycyclohexene (scheme 2). In order to underpin the presumed monophosphine route, the reaction was repeated with the isolated η^3-butenyl complex **7** as catalyst, and again a single product was isolated in 88% yield. But the phosphine is necessary, since $Pd(OAc)_2$ alone did not catalyse the reaction. The effects of enantiomerically pure phosphines were briefly investigated; yields were inferior and the enantiomer excess uniformly low, as typified by the use of oxazaphospholidine **8**.

Overall, the unsaturated organozincate is more reactive than the simple Reformatsky reagent, with a wider profile of reactivity. Allyl acetate reacts to form product **9** in 81% yield. Cyclooct-2-enyl acetate gives rise to the expected ester **10** in 76% yield. In particular, the formation of unsaturated ester **11** [15] in 67% yield indicates the enhanced reactivity, since its ester precursor pent-3-en-2-yl acetate does not react with $BrZnCH_2CO_2Et$ under the conditions of scheme 1. For this disubstituted linear allylic acetate 10 mol% catalyst is required for complete reaction, however. A similar set of observations was made to those for $BrZnCH_2CO_2R$ with the unsymmetrical cinnamyl [16] and hex-2-enyl acetates, the predominant products being the linear esters **12** and **13** with complete regioselectivity in the former and 94% regioselectivity in the latter case.

Ethyl 3-(iodozincato)propenoate

The reaction of *Z*-methyl 3-iodoacrylate with zinc dust is complete after 4 h at room temperature. The catalytic addition to cyclohexenyl acetate is very clean with $Pd(PPh_3)_4$ or $Pd(OAc)_2/2$ PPh_3 as catalysts (yield 82%), but a mixture of *Z* and *E* isomers of **14** is obtained (scheme 3) [17]. We have tried to identify at which stage the isomerisation takes place by quenching the reaction with MeOD. When the reaction of the haloester with zinc is quenched by addition of MeOD after 4 h, the proportions of *Z* and *E* isomers of ethyl 3-[^{2}H]-acrylate are 88:12. Quenching after 20 h (20 °C, 4 h; 40 °C, 16 h) the proportions are 70:30. This means that the *Z*-isomer of the organozinc substrate can be transformed into the *E*-isomer during the catalytic reaction, although the proportion of *E*-isomer is higher



Scheme 3

than would be expected on that basis alone. Since an excess of the zinc reagent is routinely used, the most likely explanation is that the *E*-iodozincate is more reactive than the *Z*-organozincate. Interestingly, reaction of the corresponding bromozincate with cyclohex-2-enyl acetate was also non-stereospecific but much less clean, giving a mixture of the expected unsaturated esters with three additional products.

In conclusion, function-bearing organozincs are suitable nucleophiles for allylic coupling and perform as 'hard' nucleophiles in the same manner as PhZnCl. Our results support the intervention of a monophosphine palladium intermediate in the C–C coupling step. Extension to asymmetric synthesis is encouraged by these results, although the design of suitable enantiomerically pure monophosphine ligands is as yet an unsolved challenge.

Experimental section

All reactions were performed under argon. ^{1}H NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or a Bruker AM 500 (500 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Varian Gemini 200 (50.33 MHz) spectrometer. IR spectra were recorded as films on a Perkin-Elmer 1750 FT spectrometer. Mass spectra were recorded on an Varian MAT CH7, VG Mircomass 16F or ZAB-1H 16F spectrometer. Chiral capillary GC was carried out on a Fisons 8000 series machine, equipped with a FID and an HP Integrator, using a 25 m permethylated β-cyclodextrin in a BP10 stationary phase (Cydex-B^{TM}) column.

Starting materials

The α-haloacrylates [18], β-haloacrylates [19] and cyclooct-2-enol [20], were prepared by the appropriate literature methods. Allylic acetates were prepared by stirring in Ac_2O and pyridine for 1 d at RT, washed and distilled [21]. All the other compounds were obtained from commercial suppliers. Tetrahydrofuran (THF) was dried over sodium-benzophenone and distilled before use.

Preparation of alkenylzinc halides

General procedure [22]: a dry three-necked flask equipped with an argon inlet, a magnetic stirring bar and a thermometer was charged with zinc dust (Aldrich, < 10 μ, 95%) flushed with argon and heated at 120 °C for 10 min 3 mL of THF and 1,2-dibromoethane (60 μL) were added. The mixture was heated with a heat gun to ebullition, allowed to cool and heated again. This process was repeated thrice. Then Me_3SiCl (60 μL) was added and after 10 min of stirring a solution of the halide was added and stirred at the appropriate temperature. Methyl 3-bromoacrylate (0.35 g, 2 mmol) was heated at 40 °C for 4 h. Methyl 3-iodoacrylate (0.43 g, 2 mmol) was stirred at 20 °C during 4 h. Ethyl 2-bromoacrylate (0.35 g, 2 mmol) was heated at 50 °C during 6 h. Methyl bromoacetate (0.32 g, 2 mmol) was added slowly and stirred at 20 °C during 1 h. Ethyl bromoacetate (0.35 g, 2 mmol) was added slowly and stirred at 20 °C during 1 h. Ethyl iodoacetate (0.43 g, 2 mmol) was stirred at 20 °C during 1 h.

General procedure for Pd-catalysed substitutions with organozinc reagents

To a solution of RZnX in THF under argon, the allylic acetate and catalyst were added. The mixture was stirred at

the reported temperature (40–60 °C) for 20 h, then the mixture was filtered through a pad of silica using ether/pentane 1:10 as eluent. The filtrate was evaporated in vacuo and the residue was chromatographed on silica, or distilled.

• *Methyl 2-(cyclohex-2-enyl)ethanoate* **1**

To a solution of methyl 2-(bromozincato)ethanoate (4 mmol) in THF (5 mL), cyclohex-2-enyl acetate (0.140 g, 1 mmol), palladium acetate (12 mg, 5%) and tris-2-furylphosphine (24 mg, 10%) were added. The mixture was stirred at 40 °C. After filtration title compound **1** was purified by chromatography (ether/pentane 1:20) as a colourless oil (0.086 g, 56%).

IR (film): 2 959, 1 740, 1 632 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ 1.15–2.10 (m, 6H), 2.26 (dd, J = 15.0 and 8.2 Hz, 1H), 2.35 (dd, J = 15 and 6.9 Hz, 1H), 2.60 (m, 1H), 3.69 (s, 3H), 5.53 (dm, J = 9.9 Hz, 1H), 5.73 (dm, J = 9.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 20.8, 24.7, 28.6, 32.1, 40.5, 51.4, 128.3, 130.2, 173.6.

MS (Cl, NH_3): m/z 155 (M + 1).

Anal calc for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 70.53; H, 9.20.

• *Methyl E-oct-4-enoate* **2**

To a solution of methyl 2-(bromozincato)acetate (2 mmol) in THF (3 mL), *E*-hex-2-enyl acetate (0.071 g, 0.5 mmol), palladium acetate (6 mg, 5%) and tris-2-furylphosphine (12 mg, 10%) were added. The mixture was stirred at 50 °C. After filtration the product was purified by chromatography (ether/pentane 1:20) as a colourless oil. (0.063 g, 80%). The main component (93%) was methyl *E*-oct-4-enoate **2**, accompanied by 7% of (±)-methyl 3-ethenylhexanoate **3**.

IR (film): 2 958, 1 742, 1 633 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 0.88 (t, J = 7.2 Hz, 3H), 1.96 (dt, J = 6.7 and 6.1 Hz, 2H), 2.32 (dt, J = 6.7 and 6.1 Hz, 2H), 2.37 (t, J = 6.5 Hz, 2H), 3.67 (s, 3H), 5.40 (dt, J = 15.2 and 6.0 Hz, 1H), 5.46 (dt, J = 15.2 and 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 13.4, 22.4, 27.8, 34.0, 34.5, 51.4, 128.2, 131.8, 174.0.

MS (Cl, NH_3): m/z 157 (M + 1).

• *Methyl E-5-phenylpent-4-enoate* **4**

To a solution of methyl 2-(bromozincato)acetate (2 mmol) in THF (3 mL), *E*-3-phenylprop-2-enyl acetate (0.088 g, 0.5 mmol), palladium acetate (12 mg, 10%) and tris-2-furylphosphine (24 mg, 20%) were added. The mixture was stirred at 40 °C. After filtration the product was purified by chromatography (ether/pentane 1:20) as a colourless oil (0.067 g, 70%). The main component (92%) was methyl *E*-5-phenylpent-4-enoate **4**, accompanied by 8% of the branched isomer **5**.

IR (film): 2 952, 1 738, 1 600 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ 2.45–2.60 (m, 4H), 3.71 (s, 3H), 6.23 (dt, J = 15.8 and 6.4 Hz, 1H), 6.46 (d, J = 15.8 Hz, 1H), 7.15–7.45 (m, 5H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 28.1, 33.7, 51.6, 126.2, 127.3, 128.2, 128.6, 131.1, 137.5, 173.7.

MS (Cl, NH_3): m/z 190 (M^+).

• *Ethyl 2-(cyclohex-2-enyl)prop-2-enoate* **6**

To a solution of ethyl 2-(bromozincato)prop-2-enoate (2 mmol) in THF (3 mL), cyclohex-2-enyl acetate (0.070 g, 0.5 mmol), palladium acetate (1.2 mg, 1%) and tris-2-furylphosphine (2.4 mg, 2%) were added. The mixture was stirred at 60 °C. After filtration the product was purified by distillation (Kugelrohr) (175 °C, 20 mmHg) yielding **6** as a colourless oil (0.079 g, 88%).

IR (film): 2 932, 1 718, 1 625 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 1.32 (t, J = 7.1 Hz, 3H), 1.44 (m, 1H), 1.58 (m, 2H), 1.91 (m, 1H), 2.02 (m, 2H), 3.36 (m, 1H), 4.23 (q, J = 7.1 Hz, 2H), 5.53 (dm, J = 10.0 Hz, 1H), 5.54 (d, J = 1.5 Hz, 1H), 5.86 (dtd, J = 10.0, 3.8 and 2.1 Hz, 1H), 6.24 (d, J = 1.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 14.2, 19.2, 24.2, 28.1, 35.8, 60.1, 123.2, 128.0, 129.1, 144.2, 167.3.

MS (Cl, NH_3): m/z 181 (M + 1).

The corresponding *n*-propyl ester was similarly prepared in 80% yield:

IR (film): 2 936, 1 717, 1 626 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ 0.95 (t, J = 7.3 Hz, 3H), 1.30–2.05 (m, 8H), 3.35 (m, 1H), 4.10 (t, J = 6.7 Hz, 2H), 5.51 (dm, J = 10.1 Hz, 1H), 5.52 (d, J = 1.5 Hz, 1H), 5.84 (dtd, J = 10.1, 3.6 and 2.1 Hz, 1H), 6.24 (d, J = 1.5 Hz, 1H).

MS (Cl, NH_3): m/z 194 (M^+).

Anal calc for $C_{12}H_{18}O_2$: C, 74.22; H, 9.45. Found: C, 74.16; H, 9.28.

• *Ethyl 2-methylenepent-4-enoate* **9**

To a solution of ethyl 2-(bromozincato)prop-2-enoate (4 mmol) in THF (5 mL), allyl acetate (0.10 g, 1 mmol), palladium acetate (12 mg, 5%) and tris-2-furylphosphine (24 mg, 10%) were added. The mixture was stirred at 40 °C. After filtration the product was purified by chromatography (ether/pentane 1:20) as a colourless oil (0.114 g, 81%).

IR (film): 2 983, 1 719, 1 631 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ 1.29 (t, J = 7.1 Hz, 3H), 3.07 (d, J = 6.7 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 5.08 (d, J = 11.8 Hz, 1H), 5.11 (d, J = 15.5 Hz, 1H), 5.58 (d, J = 1.4 Hz, 1H), 5.88 (ddt, J = 11.8, 15.5 and 6.7 Hz, 1H), 6.20 (s, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 14.0, 35.8, 60.7, 116.9, 125.4, 135.4, 139.4, 167.3.

MS (Cl, NH_3): m/z 140 (M^+).

• *Ethyl 2-(cyclooct-2-enyl)prop-2-enoate* **10**

To a solution of ethyl 2-(bromozincato)prop-2-enoate (2 mmol) in THF (3 mL), cyclooct-2-enyl acetate (0.084 g, 0.5 mmol), palladium acetate (6 mg, 5%) and tris-2-furylphosphine (12 mg, 10%) were added. The mixture was stirred at 50 °C. After filtration the product was purified by chromatography (ether/pentane 1:20) as a colourless oil (0.079 g, 76%).

IR (film): 2 928, 1 718, 1 629 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 1.31 (t, J = 7.1 Hz, 3H), 1.33–1.80 (m, 8H), 2.11 (m, 1H), 2.36 (m, 1H), 3.72 (m, 1H), 4.22 (q, J = 7.1 Hz, 2H), 5.38 (dd, J = 9.0 and 10.4 Hz, 1H), 5.62 (s, 1H), 5.72 (dt, J = 8.3 and 10.4 Hz, 1H), 6.20 (s, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 14.0, 25.7, 26.3, 26.4, 29.5, 34.9, 37.1, 60.6, 122.8, 130.3, 132.2, 145.4, 167.7.

MS (Cl, NH_3): m/z 209 (M + 1).

• *Ethyl E-2-methylene-3-methylhex-4-enoate* **11**

To a solution of ethyl 2-(bromozincato)prop-2-enoate (2 mmol) in THF (3 mL), pent-3-en-2-yl acetate (0.064 g, 0.5 mmol), palladium acetate (12 mg, 10%) and tris-2-furylphosphine (24 mg, 20%) were added. The mixture was stirred at 50 °C for 20 h. After filtration the product was purified by chromatography (ether/pentane 1:40) as a colourless oil (0.056 g, 67%).

IR (film): 2 964, 1 717, 1 627 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.16 (d, J = 7.0 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.66 (d, J = 4.9 Hz, 3H), 3.35 (dq, J = 6.9 and 5.6 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 5.45 (dd, J = 15.3 and 5.4 Hz, 1H), 5.48 (dq, J = 15.3 and 5.3 Hz, 1H), 5.51 (d, J = 1.1 Hz, 1H), 6.13 (d, J = 1.1 Hz, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 14.0, 17.8, 19.4, 37.4, 60.5, 122.9, 124.8, 134.2, 145.6, 167.5.

MS (Cl, NH_3): m/z 169 ($M + 1$).

Anal calc for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 71.27; H, 9.84.

• *Ethyl E-2-methylene-5-phenylpent-4-enoate* **12**

To a solution of ethyl 2-(bromozincato)prop-2-enoate (2 mmol) in THF (3 mL), *trans*-3-phenylprop-2-enyl acetate (0.088 g, 0.5 mmol), tetrakis(triphenylphosphine) palladium (29 mg, 5%) were added. The mixture was stirred at 50 °C for 20 h. After filtration the product was purified by chromatography (ether/pentane 1:20) as a colourless oil (0.072 g, 67%).

IR (film): 2 982, 1 717, 1 632 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.32 (t, J = 7.1 Hz, 3H), 3.22 (d, J = 6.7 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 5.64 (d, J = 1.3 Hz, 1H), 6.24 (d, J = 1.3 Hz, 1H), 6.28 (dt, J = 15.8 and 6.7 Hz, 1H), 6.47 (d, J = 15.8 Hz, 1H), 7.15–7.43 (m, 5H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 14.1, 35.0, 60.8, 125.6, 126.3, 127.0, 127.4, 128.7, 132.7, 137.5, 139.6, 167.2.

MS (Cl, NH_3): m/z 216 (M^+).

• *Ethyl E-2-methyleneoct-4-enoate* **13**

To a solution of ethyl 2-(bromozincato)prop-2-enoate (2 mmol) in THF (3 mL), *trans*-hex-2-enyl acetate (0.071 g, 0.5 mmol), palladium acetate (6 mg, 5%) and tris-2-furylphosphine (12 mg, 10%) were added. The mixture was stirred at 50 °C for 20 h. After filtration the product was purified by chromatography (ether/pentane 1:20) as a colourless oil (0.065 g, 71%). The main component (94%) was ethyl *E*-2-methyleneoct-4-enoate.

IR (film): 2 961, 1 719, 1 633 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.89 (t, J = 7.3 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.40 (m, 2H), 1.99 (dt, J = 5.7 and 7.5 Hz, 2H), 3.01 (d, J = 5.2 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 5.41 (dt, J = 15.7 and 5.2 Hz, 1H), 5.52 (dt, J = 15.7 and 5.7 Hz, 1H), 5.56 (d, J = 1.5 Hz, 1H), 6.16 (d, J = 1.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 13.5, 14.1, 22.4, 34.5, 34.6, 60.6, 124.8, 126.6, 133.2, 140.3, 167.5.

MS (Cl, NH_3): m/z 182 (M^+).

Anal calc for $C_{11}H_{18}O_2$: C, 72.53; H, 9.89. Found: C, 72.92; H, 10.03.

• *Z- and E-methyl 3-(cyclohex-2-enyl)propenoate* **14**

To a solution of methyl 3-(iodozincato)prop-2-enoate (2 mmol) in THF (3 mL), cyclohex-2-enyl acetate (0.070 g, 0.5 mmol), palladium acetate (6 mg, 5%) and triphenylphosphine (13 mg, 10%) were added. The mixture was stirred at 50 °C. After filtration the two isomers were separated by chromatography (ether/pentane 1:20), as colourless oils, (*E*: 0.043 g, *Z*: 0.022 g, 78%).

E-Isomer: IR (film): 2 932, 1 727, 1 654 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.45–1.65 (m, 2H), 1.72 (m, 1H), 1.86 (m, 1H), 2.02 (m, 2H), 2.96 (m, 1H), 3.74 (s, 3H), 5.51 (dm, J = 10.1 Hz, 1H), 5.56 (ddt, J = 10.0, 2.9 and 2.3 Hz, 1H), 5.83 (dd, J = 15.7 and 1.4 Hz, 1H), 5.85 (dm, J = 10.0 Hz, 1H), 6.94 (dd, J = 15.7 and 7.0 Hz, 1H).

MS (Cl, NH_3): m/z 166 (M^+).

Z-Isomer: IR (film): 2 931, 1 724, 1 637 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.48 (m, 1H), 1.60 (m, 1H), 1.73 (m, 1H), 1.86 (m, 1H), 2.02 (m, 2H), 3.72 (s, 3H), 4.09 (m, 1H), 5.49 (ddt, J = 10.0, 2.5 and 2.3 Hz, 1H), 5.74 (d, J = 11.4 Hz, 1H), 5.78 (dtd, J = 10.0, 3.7 and 2.3 Hz, 1H), 6.07 (dd, J = 11.4 and 10.1 Hz, 1H).

MS (Cl, NH_3): m/z 166 (M^+).

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