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# Palladium-catalysed Heck reaction on 1,2-dien-1-ols: a stereoselective synthesis of α-arylated α,β-unsaturated aldehydes

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ABSTRACT

A new methodology for preparing α-arylated α,β-unsaturated aldehydes is reported. The starting materials are all commercially available alkyn-1-ols (**1a**–**c**) that have been easily isomerised to the corresponding allenes (**2a**–**c**). The key step is the Heck coupling of the 1,2-dien-1-ols with a series of iodo- and bromoarene. The products have been synthesised in good yields, and the reactions were carried out under very mild conditions.



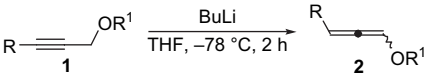
## 1. Introduction

α-Arylated α,β-unsaturated aldehydes are widely diffused in nature,[1] and constitute interesting building blocks for the synthesis of various natural products and their analogues.[2,3] Previously they have been prepared by the reaction of phenylacetaldehyde with acetaldehyde,[3] from the corresponding β,γ-unsaturated acetals heated in the presence of formic acid,[4] by the arylation of α,β-unsaturated aldehydes with triaryl bismuth dichlorides(V),[5] and by the dehydration of secondary diols.[6] Other methods exploit the treatment of allylic nitro compounds with alkaline alcoxides,[7] the hydroformylation of internal acetylenes by $PdCl_2(PCy_3)_2$[8] and the thermolysis of the suitable adduct of piridinium salts with allylic alcohol.[9] To our knowledge, no general methods for the stereoselective preparation of α-arylated α,β-unsaturated aldehydes have been proposed in the literature. In previous years we have developed the synthesis of functionalised 1-ethoxybuta-1,3-dienes starting from α,β-unsaturated acetals in the presence of the mixed lithium–potassium Schlosser's superbase LIC-KOR,[10,11] and more recently we have exploited the reactivity of these derivatives as valuable substrates for the Heck reaction,[12] in order to prepare γ-arylated α,β-unsaturated carbonyl compounds in a regio- and stereoselective manner.[13] We are, at the present time, interested in developing a new method for the synthesis of the α-arylated regioisomers exploiting the Heck reaction. It is known that the arylation of α,β-unsaturated aldehydes mainly produces the β-arylated isomer, in competition with the conjugate addition adducts.[14] Moreover, the palladium-catalysed α-arylation of carbonyl compounds cannot be applied to conjugated unsaturated derivatives, because dienolates are less nucleophilic than enolates, and more prone to self-condensation through a Michael reaction.[15] Furthermore, different methods have been developed to control the regioselectivity in the arylation or vinylation at the γ-position of β,γ-unsaturated ketones, in the α-alkylation of lithium carboxylic acids dienediolates with tosylates derived from both primary and secondary alcohols and in the γ-alkylation of copper dienolates.[16]

We decided to exploit the reactivity of allenes in Heck coupling; these substrates easily undergo carbopalladation and are extensively used for synthetic purposes.[17,18] The pathway of this catalytic process generally involves the attack of the aryl group at the central sp-carbon of the allene skeleton to give a π-allylpalladium complex intermediate. Then the attack of a nucleophile, mainly on the less substituted terminus, yields the corresponding alkene. In the absence of nucleophiles, β-H elimination occurs, and gives 2-substituted-1,3-dienes.[19]

## 2. Results and discussion

In this paper, we wish to report the results obtained from studies on the Heck cross-coupling arylation of protected 1,2-dienes-1-ols. The dienols were synthesised by the reaction of the protected alkynes **1a**–**c** with 3 equiv of BuLi, as shown in Scheme 1. As expected, when the reaction is carried out on internal alkynes it leads to an equilibrium mixture of propargyl and allenyl ethers.[20] Moreover, in the case of THP-protected allenols, the obtained




**1a**: R = Me, $R^1$ = THP **2a**: R = Me, $R^1$ = THP (60%)
**1b**: R = n-Pr, $R^1$ = THP **2b**: R = *n*-Pr, $R^1$ = THP (77%)
**1c**: R = Me, $R^1$ = $EtOCH_2$ **2c**: R = Me, $R^1$ = $EtOCH_2$ (66%)

**Scheme 1.** Isomerisation reaction of alkynes to allenes in presence of BuLi.

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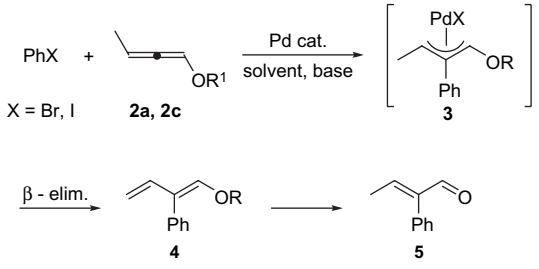
diastereoisomers were not separated and the mixture was used in the subsequent Heck coupling (Scheme 2). This is because the newly produced stereocenter does not affect the reaction outcome, and is lost in the formation of the cross-coupled product.




**Scheme 2.** Heck reaction of PhBr and PhI and allenols **2a** and **2c** to give (*E*)-2-phenylbut-2-enal (**5**).

In order to optimise the experimental conditions for the Heck cross-coupling, allenols **2a** and **2c** were reacted with iodo- or bromobenzene using different solvents and bases, altering the identity and the quantity of the catalyst, and finally exploiting different protecting groups for the hydroxyl function. The results are collected in Table 1.

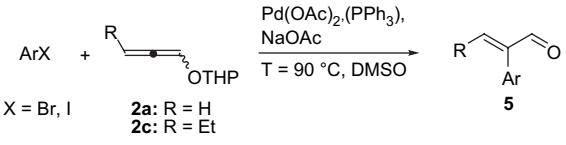
A possible reaction mechanism is proposed in Scheme 2, where the key step involves the addition of the phenyl group to the sp-carbon of the 1,2-diene **2** and affords the intermediate π-allylpalladium complex **3**. Subsequently the β-H elimination step leads to the conjugate diene **4** (not isolated) that undergoes hydrolysis affording the corresponding α-arylated α,β-unsaturated aldehyde **5**.

The hydrolysis reaction takes place during the aqueous work-up of the reaction mixture. As a matter of fact, the cross-coupling reaction was carried out under anhydrous conditions, and moreover, any attempt to isolate intermediate **4**, or to obtain the corresponding acetal derivative carrying out the reaction using anhydrous methanol as the solvent, was unsuccessful.

All the reactions were carried out in the presence of a 2:1 ratio of 1,2-allen-1-ol, with respect to the halobenzene, owing to its thermal and chemical instability. Among the bases that we tested, NaOAc gave the best results (entry 4), also anhydrous and aqueous $K_2CO_3$ and TBAA ($Bu_4N^+AcO^-$) afforded comparable yields (entries 2 and 6). In the presence of $Et_3N$ (entry 3), the coupling reaction was slower and the yield lower. DMSO gave better results in comparison to DMF (compare entry 4 with entry 6). The use of TBAB ($Bu_4N^+Br^-$) as an ionic liquid suppressed the reaction. Among the catalysts only $Pd(OAc)_2$ was efficacious, we decided to utilise a 2 mol % solution instead of a 5% one, also if in the latter case the yield was slightly better, in an attempt to lower the catalyst loading. On the other hand, the reaction also proceeded using 1% $Pd(OAc)_2$, but the outcome was less satisfactory. The identity of the protecting group did not affect the coupling result (compare entries 8 and 12).

The experimental conditions that were selected for PhI were modified in order to achieve satisfactory results using PhBr: only the use of $Pd(OAc)_2$ (5%) and $PPh_3$ (10%), in DMSO, in the presence of NaAcO as the base, ensured the formation of (*E*)-2-phenylbut-2-enal (**5a**) in good yield (compare entries 14, 15 and 17).

We applied the optimised reaction conditions to several aryl halides and 1,2-allenols. The coupling reaction is shown in Scheme 3 and the results are listed in Table 2.




**5a:** R = H, Ar = Ph
**5b:** R = Et, Ar = *p*-$MeOC_6H_4$
**5c:** R = Et, Ar = *p*-$MeCO_2C_6H_4$
**5d:** R = H, Ar = *m*-$MeC_6H_4$
**5e:** R = H, Ar = *o*-$MeC_6H_4$
**5f:** R = H, Ar = *p*-$MeOC_6H_4$
**5g:** R = H, Ar = *o*-$MeOC_6H_4$
**5h:** R = H, Ar = 1-Np
**5i:** R = H, Ar = *p*-$HOC_6H_4$
**5j:** R = Et, Ar = 3-Py
**5k:** R = H, Ar = *p*-$HCOC_6H_4$
**5l:** R = Et, Ar = *p*-$HCOC_6H_4$
**5m:** R = Et, Ar = *p*-$MeCOC_6H_4$
**5n:** R = Et, Ar = *m*-$MeC_6H_4$
**5o:** R = H, Ar = 2-Np
**5p:** R = Et, Ar = *p*-$MeC_6H_4$

**Scheme 3.** Heck couplings of aryl halides and allenols **2a** and **2c** to afford α-arylated α,β-unsaturated aldehydes (**5a–q**).

The cross-coupling reactions have been accomplished using various substituted iodo- and bromoarene that differ in the position and the electronic features of the substituents. The reactions proceed in a regio- and stereoselective way, and the (*E*) configuration of the newly formed carbon–carbon double bond was deduced, when possible, by a NOESY experiment in which a negative correlation spot between the aldehydic $H_b$ and the vinylic proton $H_a$, shown in Figure 1, is observed.

The outcome of the cross-coupling reactions turns out to be strongly influenced by steric effects, as observed in the case of *o*-halo derivatives that produce the corresponding α-arylated α,β-unsaturated aldehydes (**5f** and **5g**) in lower yields with respect to the corresponding *p*- and *m*-derivatives. Moreover, the electronic

**Table 1**
Heck reaction of PhX and allenols **2a** and **2c** to give (*E*)-2-phenylbut-2-enal (**5**)[a]

| Entry | PhX | Allen-1-ol | Base | Catalyst (%) | Solvent | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|---|---|
| 1 | PhI | **2a** | $K_2CO_3$ (anhydrous) | $Pd(OAc)_2$ (5) | DMSO | 0.5 | 70 |
| 2 | PhI | **2a** | $K_2CO_3$ (aqueous) | $Pd(OAc)_2$ (5) | DMSO | 0.5 | 72 |
| 3 | PhI | **2a** | $Et_3N$ | $Pd(OAc)_2$ (5) | DMSO | 3 | 55 |
| 4 | PhI | **2a** | NaAcO (anhydrous) | $Pd(OAc)_2$ (5) | DMSO | 0.5 | 80 |
| 5 | PhI | **2a** | NaAcO (anhydrous) | $Pd(OAc)_2$ (5) | TBAB | 16 | Trace |
| 6 | PhI | **2a** | NaAcO (anhydrous) | $Pd(OAc)_2$ (5) | DMF | 6 | 65 |
| 7 | PhI | **2a** | TBAA | $Pd(OAc)_2$ (5) | DMSO | 0.5 | 68 |
| 8 | PhI | **2a** | NaAcO (anhydrous) | $Pd(OAc)_2$ (2) | DMSO | 0.75 | 74 |
| 9 | PhI | **2a** | NaAcO (anhydrous) | $Pd(OAc)_2$ (1) | DMSO | 0.75 | 65 |
| 10 | PhI | **2a** | NaAcO (anhydrous) | $Pd(PPh_3)$ (1) | DMSO | 1 | 0[c] |
| 11 | PhI | **2a** | NaAcO (anhydrous) | $Pd(dba)_2$ (1) | DMSO | 0.75 | 0 |
| 12 | PhI | **2c** | NaAcO (anhydrous) | $Pd(OAc)_2$ (2) | DMSO | 1 | 75 |
| 13 | PhI | **2a** | NaAcO (anhydrous) | $Pd(OAc)_2$ (2) | DMSO | 1 | 72[d] |
| 14 | PhBr | **2a** | NaAcO (anhydrous) | $Pd(OAc)_2$ (2) | DMSO | 16 | Trace |
| 15 | PhBr | **2a** | NaAcO (anhydrous) | $Pd(OAc)_2$ (2)/$PPh_3$ (4) | DMSO | 16 | Trace |
| 16 | PhI | **2a** | NaAcO (anhydrous) | $Pd(OAc)_2$ (5) | DMSO | 16 | 30 |
| 17 | PhBr | **2a** | NaAcO (anhydrous) | $Pd(OAc)_2$ (5)/$PPh_3$ (10) | DMSO | 16 | 68 |

[a] Reaction conditions: PhX, 0.5 mmol, **2a** or **2c** 1.0 mmol, solvent 3 mL, base 0.5 mmol, $T$=90 °C.
[b] Isolated products, purified by column chromatography.
[c] Only PhI was recovered.
[d] Reaction conditions: PhI, 0.5 mmol, diene 0.75 mmol, solvent 3 mL, base 0.5 mmol; unreacted PhI was recovered.

**Table 2**
Heck couplings of aryl halides and allenols **2a** and **2b** to afford α-arylated α,β-unsaturated aldehydes (**5a**–**q**)

| Entry | 1,2-Allen-1-ol | Aryl halide | Product | Time (h) | *E*/*Z*[c] | Yield[d] (%) |
|---|---|---|---|---|---|---|
| 1 | **2a** | PhI | **5a**[a] | 0.75 | 99:1 | 74 |
| 2 | **2b** | PhI | **5b**[a] | 1 | 99:1 | 80 |
| 3 | **2b** | *p*-$MeOC_6H_4I$ | **5c**[a] | 3 | 99:1 | 80 |
| 4 | **2a** | *p*-$MeO_2CC_6H_4I$ | **5d**[a] | 0.5 | 99:1 | 70 |
| 5 | **2a** | *m*-$MeC_6H_4I$ | **5e**[a] | 1 | 99:1 | 90 |
| 6 | **2a** | *o*-$MeC_6H_4I$ | **5f**[a] | 4 | 99:1 | 68 |
| 7 | **2a** | *o*-$MeOC_6H_4I$ | **5g**[a] | 4.5 | 99:1 | 48 |
| 8 | **2a** | 1-NpI | **5h**[a] | 1.5 | 99:1 | 51 |
| 9 | **2b** | *p*-$HOC_6H_4I$ | **5i**[a] | 2 | 99:1 | 55 |
| 10 | **2b** | 3-IPy | **5j**[a] | 1 | 99:1 | 78 |
| 11 | **2a** | PhBr | **5a**[b] | 16 | 99:1 | 68 |
| 12 | **2a** | *p*-$HCOC_6H_4Br$ | **5l**[b] | 4 | 99:1 | 78 |
| 13 | **2b** | *p*-$HCOC_6H_4Br$ | **5m**[b] | 4 | 99:1 | 83 |
| 14 | **2b** | *p*-$MeCOC_6H_4Br$ | **5n**[b] | 3 | 99:1 | 75 |
| 15 | **2b** | *m*-$MeOC_6H_4Br$ | **5o**[b] | 5 | 99:1 | 61 |
| 16 | **2a** | 2-NpBr | **5p**[b] | 8 | 99:1 | 83 |
| 17 | **2a** | *p*-$MeC_6H_4Br$ | **5q**[b] | 6 | 99:1 | 75 |

[a] Reaction conditions: PhI 0.5 mmol, **2a** or **2b** 1.0 mmol, DMSO 3 mL, NaOAc 0.5 mmol, *T*=90 °C, $Pd(OAc)_2$ 2 mol %.
[b] Reaction conditions: PhBr 0.5 mmol, **2a** or **2b** 1.0 mmol, DMSO 3 mL, NaOAc 0.5 mmol, *T*=90 °C, $Pd(OAc)_2$ 5 mol %, $PPh_3$ 10 mol %.
[c] Determined by $^1H$ NMR.
[d] Isolated products, purified by column chromatography.

effects of the substituents appear to be important when aryl bromides are used as the arylating agent, and electron withdrawing substituents increase the yield of the reaction (compare entries 11, 12 and 13).

## 3. Conclusions

In summary, we have developed a new synthetic route that allows the synthesis of a series of α-arylated α,β-unsaturated aldehydes starting from protected 1,2-diene-1-ols, exploiting a Pd(0)-catalysed cross-coupling reaction. The reaction is regio- and stereoselective, and moreover, experimental conditions turn out to be very mild: in the case of aryl iodides, phosphines are not required while with aryl bromides the cheap and easy available triphenylphosphine is indispensable.

## 4. Experimental

### 4.1. General

Flasks and all equipments used for the generation and reaction of moisture-sensitive compounds were dried by electric heat gun under Ar. THF and $CH_2Cl_2$ were distilled from sodium benzophenone ketyl and $CaH_2$, respectively. BuLi (1.6 M in hexanes) was obtained from Aldrich. All commercially obtained reagents and solvents were used as received. Products were purified by preparative column chromatography on Macherey Nagel silica-gel for flash chromatography, 0.04–0.063 mm/230–400 mesh.

Reactions were monitored by TLC using silica-gel on TLC-PET foils Fluka, 2–25 μm, layer thickness 0.2 mm, medium pore diameter 60 Å. $^1H$ NMR spectra were recorded at 200 MHz, $^{13}C$ NMR spectra at 50.2 MHz, in $CDCl_3$. Data were reported as follows: chemical shifts in parts per million from $Me_4Si$ as an internal standard, integration, multiplicity, coupling constants (Hz) and assignment. $^{13}C$ NMR spectra were measured with complete proton decoupling. Chemical shifts were reported in parts per million from the residual pick solvent as an internal standard. GC–MS 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 with a cross-linked methyl silicone capillary column (25 m×0.2 mm×0.33 μm film thickness). IR spectra were recorded on a Perkin Elmer BX FT-IR.

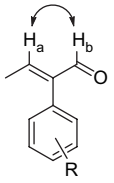



**Figure 1.**

### 4.2. Procedure for the tetrahydropyranylation of alkynols[21]

In a 100 mL three-necked round bottom flask, the alkynol (10.0 mmol) was dissolved in anhydrous $CH_2Cl_2$ (25 mL) at rt, then DHP (1.5 equiv, 15.0 mmol, 1.26 g) followed by PPTS (0.1 equiv, 1.0 mmol, 0.25 g) were added. The reaction mixture was stirred overnight at rt under Ar, then the solvent was partly evaporated. The mixture was diluted with $Et_2O$, then washed with brine (2×20 mL), dried over $K_2CO_3$, filtered and evaporated under reduced pressure, to give the crude reaction product that was used in the subsequent step without further purification.

#### *4.2.1. 2-(But-2-ynyloxy)tetrahydro-2H-pyran (**1a**)*

Pale yellow oil (1.43 g, 93%). Spectral data correspond to those reported in the literature.[22]

#### *4.2.2. 2-(Hex-2-ynyloxy)tetrahydro-2H-pyran (**1b**)*

Pale yellow oil (1.80 g, 99%) that was at once used for the following reactions. Found C, 72.65; H, 9.92%. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%. $\nu_{max}$ (neat)/$cm^{-1}$ 2943, 2250, 1728, 1054, 733. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 0.94 (3H, t, *J*=7.1 Hz, C$H_3$), 1.25–1.80 (8H, m, C$H_2$), 2.12–2.21 (2H, m, C$H_2$CC), 3.30–3.62 (1H, m, C$H_a$O), 3.72–3.95 (1H, m, C$H_b$O), 4.05–4.54 (2H, m, C$H_2$O), 4.74 (1H, br s, OC*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 13.12 (1×q), 18.80 (1×t), 20.46 (1×t), 21.74 (1×t), 25.13 (1×t), 29.98 (1×t), 54.18 (1×t), 61.50 (1×t), 75.60 (1×s), 86.01 (1×s), 96.13 (1×d). MS (EI, 70 eV): *m*/*z* (%)=153 (2) [$M^+-C_2H_5$], 85 (100), 79 (94), 67 (54), 55 (59).

#### *4.2.3. Synthesis of 1-(ethoxymethoxy)but-2-yne (**1c**)*

In a 100 mL three-necked round bottom flask, 2-butyn-1-ol (10.0 mmol, 0.71 g) was dissolved in anhydrous $CH_2Cl_2$ (25 mL) and cooled to 0 °C, then Et(*i*-Pr)$_2$N (2.0 equiv, 20.0 mmol, 3.48 mL) followed by $MeOCH_2Cl$ (1.9 equiv, 19.0 mmol, 1.77 mL) were added. The reaction mixture was stirred overnight at rt under Ar, then a 20 mL of a solution of aqueous $NaHCO_3$ (10%) was added. The mixture was extracted with $CH_2Cl_2$ (2×20 mL), then washed with aqueous HCl (5%, 1×20 mL) and $H_2O$ (1×20 mL), dried ($K_2CO_3$) and evaporated under reduced pressure, affording 1.16 g (90%) of a pale yellow oil. Found C, 65.78; H, 9.45%. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44%. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 1.20 (3H, m, $CH_2CH_3$), 1.84 (3H, m, CC$CH_3$), 3.59 (2H, m, CC$CH_2$O), 4.15 (2H, m, O$CH_2CH_3$), 4.73 (2H, m, O$CH_2$O$CH_2CH_2$); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 3.0 (1×q), 14.7 (1×q), 54.2 (1×t), 63.0 (1×t), 74.4 (1×t), 81.5 (1×s), 92.8 (1×s). MS (EI, 70 eV): *m*/*z* (%)=83 (16) [$M^+-C_2H_5O$], 69 (34), 59 (16), 54 (36), 53 (100).

### 4.3. General procedure for the isomerisation of alkynes to allenes

In a Schlenk vessel alkynol (10.0 mmol) was dissolved in anhydrous THF (20 mL) and cooled to −95 °C, then *n*-BuLi (3.0 equiv, 30.0 mmol, 18.7 mL) was added. The reaction mixture was stirred for 2 h at −95 °C, then a solution of THF/$H_2O$ was added (20 mL). The mixture was extracted with $Et_2O$ (2×20 mL), then washed with

brine (2×20 mL), dried ($K_2CO_3$), filtered and evaporated under reduced pressure.

*4.3.1. 2-(Buta-1,2-dienyloxy)tetrahydro-2H-pyran (**2a**)*

EP/EE 98:2, 1% $Et_3N$; diastereomeric mixture 60:40. Pale yellow oil (0.92 g, 60%). Found C, 69.91; H, 9.14%. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%. $\nu_{max}$ (neat)/$cm^{-1}$ 2945, 1961, 1730, 1119, 749. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 1.20–195 (9H, m, $(CH_2)_3CH_3$), 3.55 (1H, m, $CH_aO$), 3.95 (1H, m, $CH_bO$), 4.95 (1H, br s, OC*H*O), 5.65 (1H, m, $CH_3CHC$=CCH), 6.55 (1H, m, $CH_3CHC$=CC*H*); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 16.4 (1×q), 16.5 (1×q), 18.4 (2×t), 24.9 (2×t), 29.5 (2×t), 61.5 (2×t), 97.0 (2×d), 99.7 (1×d), 99.8 (1×d), 116.4 (1×d), 116.5 (1×d), 194.4 (1×s), 194.7 (1×s). MS (EI, 70 eV): *m*/*z* (%)=154 (2) [$M^+$], 85 (100), 67 (25), 57 (31), 55 (18); 154 (2) [$M^+$], 85 (100), 67 (30), 57 (32), 55 (20).

*4.3.2. 2-(Hexa-1,2-dienyloxy)tetrahydro-2H-pyran (**2b**)*

EP/EE 99:1, 1% $Et_3N$; diastereomeric mixture 55:45. Pale yellow oil (1.40 g, 77%). Found C, 72.49; H, 9.95%. Calcd for $C_{11}H_{18}O_2$: C, 72.27; H, 9.94%. $\nu_{max}$ (neat)/$cm^{-1}$ 2957, 2874, 1959, 1203. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 0.93 (3H, t, *J*=7.2, $CH_3$), 1.42–2.12 (10H, m, $(CH_2)_3$), 3.54 (1H, m, $CH_aO$), 3.85 (1H, m, $CH_bO$), 4.92 (1H, br s, OC*H*O), 5.79 (1H, sext, *J*=6.4, $CH_3CHC$=CCH), 6.55 (1H, m, $CH_3CHC$=CC*H*); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 13.4 (2×q), 18.5 (1×t), 18.6 (1×t), 21.4 (1×t), 21.5 (1×t), 25.0 (2×t), 29.6 (2×t), 32.7 (1×t), 32.7 (1×t), 61.5 (1×t), 61.6 (1×t), 96.9 (2×d), 104.9 (1×d), 105.0 (1×d), 117.1 (1×d), 117.2 (1×d), 193.5 (1×s), 193.8 (1×s). MS (EI, 70 eV): *m*/*z* (%)=182 (1) [$M^+$], 85 (100), 67 (22), 57 (24), 55 (15); 182 (1) [$M^+$], 85 (100), 67 (22), 57 (25), 55 (17).

*4.3.3. 1-(Ethoxymethoxy)buta-1,2-diene (**2c**)*

EP/EE 95:5, 1% $Et_3N$. Pale yellow oil (0.84 g, 66%). Found C, 65.73; H, 9.43%. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44%. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 1.20 (3H, m, $CH_2CH_3$), 1.76 (3H, m, $CH_3$), 3.63 (2H, m, $CH_2O$), 4.80 (2H, m, $OCH_2O$), 5.74 (1H, m, $CH_3CHC$=CCH), 6.53 (1H, m, $CH_3CHC$=CC*H*); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 14.8 (1×q), 16.6 (1×q), 63.9 (1×t), 93.3 (1×t), 100.5 (1×d), 117.0 (1×d), 194.0 (1×s). MS (EI, 70 eV): *m*/*z* (%)=128 (6) [$M^+$], 99 (34), 69 (38), 59 (100), 53 (38).

### 4.4. Typical procedure for the Heck couplings between protected allenols and iodoarenes

$Pd(OAc)_2$ (2 mol %, 0.010 mmol, 2.24 mg) was dissolved in anhydrous DMSO (3 mL) and the solution was degassed under Ar for 10 min at rt. Then NaAcO (0.5 mmol, 41 mg), iodoarene (0.5 mmol) and allenol (1.0 mmol) were subsequently added. The reaction mixture was stirred in a sealed tube at 90 °C until the disappearance of the allenol was observed by TLC and GC on a sample taken and partitioned between $Et_2O$ and $H_2O$. Then $H_2O$ was added and the mixture was extracted with $Et_2O$ (2×20 mL), then washed with brine (2×20 mL), dried ($K_2CO_3$), filtered and evaporated under reduced pressure.

*4.4.1. (E)-2-Phenylbut-2-enal (**5a**)*

EP/EE 90:10, 1% $Et_3N$. Pale yellow oil (54 mg, 74%). The spectral characterisation corresponded to those reported in the literature.[23]

*4.4.2. (E)-2-Phenylhex-2-enal (**5b**)*

EP/EE 90:10, 1% $Et_3N$. Pale yellow oil (70 mg, 80%). Found C, 82.47; H, 8.11%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%. $\nu_{max}$ (neat)/$cm^{-1}$ 3362, 3024, 1694, 728, 702. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 0.95 (3H, t, *J*=7.3, $CH_3$), 1.55 (2H, sext, *J*=7.4, $CH_3CH_2$), 2.38 (2H, q, *J*=7.5, $CH_2CH_2$), 6.74 (1H, t, *J*=7.5, C*H*=C), 7.18 (2H, m, Ar), 7.42 (3H, m, Ar), 9.63 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 13.6 (1×q), 21.9 (1×t), 31.5 (1×t), 127.7 (1×d), 128.0 (2×d), 129.2 (2×d), 132.5 (1×s), 143.9 (1×s), 156.3 (1×d), 194.0 (1×d). MS (EI, 70 eV): *m*/*z* (%)=174 (100) [$M^+$], 117 (62), 115 (65), 104 (61), 91 (60).

*4.4.3. (E)-2-(4-Methoxyphenyl)hex-2-enal (**5c**)*

EP/EE 90:10, 1% $Et_3N$. Pale yellow oil (90 mg, 88%). Found C, 76.20; H, 7.89%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%. $\nu_{max}$ (neat)/$cm^{-1}$ 3358, 3041, 1694, 1032, 805. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 0.94 (3H, t, *J*=7.6, $CH_3$), 1.56 (2H, sext, *J*=7.4, $CH_3CH_2$), 2.39 (2H, q, *J*=7.4, $CH_2CH_2$), 3.83 (3H, s, $OCH_3$), 6.69 (1H, t, *J*=7.4, C*H*=C), 6.94 (2H, d, *J*=8.8, Ar), 7.12 (2H, d, *J*=8.8, Ar), 9.64 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 13.6 (1×q), 22.0 (1×t), 31.6 (1×t), 55.0 (1×q), 113.5 (1×d), 124.5 (2×d), 130.5 (2×d), 143.3 (1×s), 156.0 (1×d), 159.0 (1×s), 194.0 (1×d). MS (EI, 70 eV): *m*/*z* (%)=204 (100) [$M^+$], 148 (75), 147 (70), 134 (51), 115 (62).

*4.4.4. (E)-Methyl 4-(1-oxobut-2-en-2-yl)benzoate (**5d**)*

EP/EE 70:30, 1% $Et_3N$. Pale yellow oil (71 mg, 70%). Found C, 70.80; H, 5.91%. Calcd for $C_{12}H_{12}O_3$: C, 70.60; H, 5.92%. $\nu_{max}$ (neat)/$cm^{-1}$ 3063, 2955, 1718, 1097. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 2.01 (3H, d, *J*=7.1, $CH_3$), 3.92 (3H, s, $OCH_3$), 6.91 (1H, q, *J*=7.1, C*H*=C), 7.25 (2H, d, *J*=8.1, Ar), 8.08 (2H, d, *J*=8.1, Ar), 9.61 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 15.8 (1×q), 52.0 (1×q), 129.3 (2×d, 1× s), 129.4 (2×d), 136.9 (1×d), 144.1 (1×s), 151.6 (1×d), 166.6 (1×s), 192.6 (1×d). MS (EI, 70 eV): *m*/*z* (%)=204 (85) [$M^+$], 145 (66), 117 (95), 116 (49), 115 (62).

*4.4.5. (E)-2-m-Tolylbut-2-enal (**5e**)*

EP/EE 95:5, 1% $Et_3N$. Pale yellow oil (72 mg, 90%). Found C, 82.44; H, 7.54%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%. $\nu_{max}$ (neat)/$cm^{-1}$ 2923, 1688, 1586, 791. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 2.01 (3H, d, *J*=7.1, $CH_3$), 2.38 (3H, s, Ar$CH_3$), 6.80 (1H, q, *J*=7.1, C*H*=C), 6.95–7.34 (4H, m, Ar), 9.61 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 15.8 (1×q), 21.3 (1×q), 126.3(1×d), 128.0 (1×d), 128.5 (1×d), 129.8 (1×d), 132.0 (1×s), 137.6 (1×s), 145.0 (1×s), 151.0 (1×d), 193.4 (1×d). MS (EI, 70 eV): *m*/*z* (%)=160 (100) [$M^+$], 117 (76), 116 (38), 115 (54), 91 (51).

*4.4.6. (E)-2-o-Tolylbut-2-enal (**5f**)*

EP/EE 95:5, 1% $Et_3N$. Pale yellow oil (54 mg, 68%). Found C, 82.45; H, 7.54%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%. $\nu_{max}$ (neat)/$cm^{-1}$ 3061, 2816, 1689, 1635, 735. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 1.85 (3H, d, *J*=7.0, $CH_3$), 2.23 (3H, s, Ar$CH_3$), 6.95 (2H, m, C*H*=C, Ar), 7.22 (3H, m, Ar), 9.62 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 15.6 (1×q), 19.4 (1×q), 125.5 (1×d), 128.0 (1×d), 129.3 (1×d), 129.9 (1×d), 132.3 (1×s), 136.2 (1×s), 145.7 (1×s), 151.3 (1×d), 191.0 (1×d). MS (EI, 70 eV): *m*/*z* (%)=160 (62) [$M^+$], 145 (70), 142 (55), 115 (90), 91 (100).

*4.4.7. (E)-2-(2-Methoxyphenyl)but-2-enal (**5g**)*

EP/EE 90:10, 1% $Et_3N$. Pale yellow oil (42 mg, 48%). Found C, 75.01; H, 6.85%. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86%. $\nu_{max}$ (neat)/$cm^{-1}$ 2940, 1687, 1492, 1246, 752. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 1.90 (3H, d, *J*=7.0, $CH_3$), 3.83 (3H, s, $OCH_3$), 6.87–6.39 (3H, m, *J*=7.1, C*H*=C, Ar), 7.45–8.85 (2H, m, Ar), 9.80 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 15.8 (1×q), 55.3 (1×q), 110.9 (1×d), 120.3 (1×d), 121.5 (1×s), 129.4 (1×d), 130.8 (1×d), 142.2 (1×s), 150.9 (1×s), 156.7 (1×d), 192.9 (1×d). MS (EI, 70 eV): *m*/*z* (%)=176 (100) [$M^+$], 131 (41), 119 (39), 115 (42), 91 (78).

*4.4.8. (E)-2-(Naphthalen-1-yl)but-2-enal (**5h**)*

EP/EE 80:20, 1% $Et_3N$. White solid (49 mg, 51%). Found C, 85.89; H, 6.15%. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16%. Mp 89–92 °C. $\nu_{max}$ (neat)/$cm^{-1}$ 3044, 1675, 1638, 779. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 1.83 (3H, d, *J*=7.0, $CH_3$), 7.19 (2H, m, C*H*=C, Ar), 7.53 (4H, m, Ar), 7.88 (2H, m, Ar), 9.60 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 16.0 (1×q), 124.8 (1×d), 125.2 (1×d), 125.7 (1×d), 126.1 (1×d), 127.2 (1×d), 128.4 (2×d), 130.4 (1×s), 131.2 (1×s), 133.5 (1×s), 144.3 (1×s), 152.5 (1×d), 193.2 (1×d). MS (EI, 70 eV): *m*/*z* (%)=196 (74) [$M^+$], 167 (96), 165 (100), 153 (83), 152 (98).

*4.4.9. (E)-2-(4-Hydroxyphenyl)hex-2-enal (**5i**)*

EP/EE 50:50, 1% $Et_3N$. Pale yellow oil (45 mg, 55%). Found C, 75.85; H, 7.41%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%. $\nu_{max}$ (neat)/$cm^{-1}$ 3369, 1672, 1611, 1516, 838. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 0.93 (3H, t, *J*=7.3, C*H*$_3$), 1.53 (2H, sext, *J*=7.5, C*H*$_2$CH$_3$), 2.36 (2H, q, *J*=7.5, C*H*$_2$), 5.93 (1H, br s, O*H*), 6.72 (1H, t, *J*=7.5, C*H*=C), 6.81 (2H, d, *J*=8.6, Ar), 7.00 (2H, d, *J*=8.6, Ar), 9.58 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 13.6 (1×q), 21.9 (1×t), 31.7 (1×q), 115.2 (2×d), 123.9 (1×s), 130.5 (2×d), 143.5 (1×s), 155.7 (1×d), 157.2 (1×s), 194.9 (1×d). MS (EI, 70 eV): *m*/*z* (%)=190 (100) [$M^+$], 133 (44), 119 (44), 107 (32), 77 (34).

*4.4.10. (E)-2-(Pyridin-3-yl)hex-2-enal (**5j**)*

EE, 1% $Et_3N$. Pale yellow oil (68 mg, 78%). Found C, 75.62; H, 7.47; N, 7.97%. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99%. $\nu_{max}$ (neat)/$cm^{-1}$ 3031, 1686, 1024, 750, 717. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 0.93 (3H, t, *J*=7.4, C*H*$_3$), 1.55 (2H, sext, *J*=7.4, CH$_3$C*H*$_2$), 2.35 (2H, q, *J*=7.5, CH$_2$C*H*$_2$), 6.83 (1H, m, *J*=7.6, C*H*=C), 7.31 (1H, m, C*H*CHN), 7.52 (1H, dt, *J*=7.8, 1.9, C*H*CHCN), 8.40 (1H, dd, *J*=2.1, 0.8, CC*H*N), 8.57 (1H, dd, *J*=4.9, 1.6, CHC*H*N), 9.62 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 13.6 (1×q), 21.9 (1×t), 31.6 (1×t), 122.9 (1×d), 128.3 (1×s), 137.0 (1×d), 140.6 (1×d), 148.9 (1×d), 149.8 (1×s), 157.6 (1×d), 192.8 (1×d). MS (EI, 70 eV): *m*/*z* (%)=175 (100) [$M^+$], 118 (38), 117 (63), 105 (39), 104 (54).

### 4.5. Typical procedure for the Heck coupling between protected allenols and bromoarenes

$Pd(OAc)_2$ (5%, 0.025 mmol, 5.6 mg) and $PPh_3$ (10%, 0.05 mmol, 13 mg) were dissolved in anhydrous DMSO (3 mL) and degassed at rt under Ar until the solution turned to purple. Then NaAcO (0.5 mmol, 41 mg), the selected bromoarene (0.5 mmol) and the allenol (1.0 mmol) were added. The reaction mixture was stirred in a sealed tube at 90 °C until the disappearance of the allenol spot that was observed by TLC and GC on a sample taken and partitioned between $Et_2O$ and $H_2O$. $H_2O$ (5 mL) was added, and the mixture was extracted with $Et_2O$ (2×20 mL), then washed with brine (2×20 mL), dried ($K_2CO_3$), filtered and evaporated under reduced pressure.

*4.5.1. (E)-2-Phenylbut-2-enal (**5a**)*

EP/EE 90:10, 1% $Et_3N$. Pale yellow oil (50 mg, 68%). The spectral characterisation corresponded to those reported in the literature.[23]

*4.5.2. (E)-4-(1-Oxobut-2-en-2-yl)benzaldehyde (**5k**)*

EP/EE 70:30, 1% $Et_3N$. Pale yellow oil (68 mg, 78%). Found C, 75.65; H, 5.80%. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79%. $\nu_{max}$ (neat)/$cm^{-1}$ 3363, 2925, 1703, 1606, 842. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 2.03 (3H, d, *J*=7.1, C*H*$_3$), 6.95 (1H, m, *J*=7.1, C*H*=C), 7.31 (1H, m, C*H*CHN), 7.37 (2H, d, *J*=7.1, Ar), 7.93 (1H, d, *J*=7.1, Ar), 9.63 (1H, s, C*H*O), 10.03 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 15.9 (1×q), 129.4 (2×d), 130.1 (2×d), 135.5 (1×s), 138.9 (1×s), 143.0 (1×s), 157.3 (1×d), 191.7 (1×d), 192.7 (1×d). MS (EI, 70 eV): *m*/*z* (%)=174 (44) [$M^+$], 145 (27), 117 (63), 115 (100), 91 (43).

*4.5.3. (E)-4-(1-Oxohex-2-en-2-yl)benzaldehyde (**5l**)*

EP/EE 80:20, 1% $Et_3N$. Pale yellow oil (84 mg, 83%). Found C, 76.97; H, 6.98%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%. $\nu_{max}$ (neat)/$cm^{-1}$ 2959, 1687, 1027, 840, 716. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 0.93 (3H, t, *J*=7.3, C*H*$_3$), 1.55 (2H, sext, *J*=7.2, CH$_3$C*H*$_2$), 2.33 (2H, q, *J*=7.5, C*H*$_3$), 6.82 (1H, m, *J*=7.6, C*H*=C), 7.33 (2H, d, *J*=7.2, Ar), 7.91 (2H, d, *J*=7.4, Ar), 9.62 (1H, s, C*H*O), 10.03 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 13.6 (1×q), 21.8 (1×t), 31.6 (1×t), 129.3 (2×d), 130.5 (2×d), 135.5 (1×s), 138.9 (1×s), 143.0 (1×s), 157.3 (1×d), 191.7 (1×d), 192.7 (1×d). MS (EI, 70 eV): *m*/*z* (%)=202 (100) [$M^+$], 131 (40), 117 (48), 115 (71), 91 (52).

*4.5.4. (E)-2-(4-Acetylphenyl)hex-2-enal (**5m**)*

EP/EE 70:30, 1% $Et_3N$. Pale yellow oil (81 mg, 75%). Found C, 77.71; H, 7.45%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%. $\nu_{max}$ (neat)/$cm^{-1}$ 2960, 1682, 1605, 1264, 958, 834. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 0.93 (3H, t, *J*=7.4, C*H*$_3$), 1.55 (2H, sext, *J*=7.4, CH$_3$C*H*$_2$), 2.33 (2H, q, *J*=7.5, CH$_2$C*H*$_2$), 2.62 (3H, s, COC*H*$_3$), 6.80 (1H, t, *J*=7.6, C*H*=C), 7.26 (2H, d, *J*=8.3, Ar), 8.00 (2H, d, *J*=8.5, Ar), 9.62 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 13.6 (1×q), 21.8 (1×t), 26.4 (1×q), 31.6 (1×t), 128.0 (2×d), 129.6.1 (2×d), 136.2 (1×s), 137.5 (1×s), 143.0 (1×d), 157.1 (1×s), 192.8 (1×d), 197.6 (1×s). MS (EI, 70 eV): *m*/*z* (%)=216 (100) [$M^+$], 201 (57), 159 (86), 145 (32), 115 (54).

*4.5.5. (E)-2-(3-Methoxyphenyl)hex-2-enal (**5n**)*

EP/EE 70:30, 1% $Et_3N$. Pale yellow oil (62 mg, 61%). Found C, 76.61; H, 7.89%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%. $\nu_{max}$ (neat)/$cm^{-1}$ 2959, 1688, 1578, 1038, 788, 721. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 0.94 (3H, t, *J*=7.2, C*H*$_3$), 1.55 (2H, sext, *J*=7.4, CH$_3$C*H*$_2$), 2.33 (2H, q, *J*=7.4, CH$_2$C*H*$_2$), 3.81 (3H, s, OC*H*$_3$), 6.72 (4H, m, C*H*=C, Ar), 6.89 (1H, br d, *J*=8.0, Ar), 7.32 (1H, br t, *J*=8.0, Ar), 9.61 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 13.6 (1×q), 21.9 (1×t), 31.5 (1×t), 55.0 (1×q), 113.2 (1×d), 114.9 (1×d), 121.6 (1×d), 129.0 (1×d), 133.9 (1×s), 143.8 (1×s), 156.1 (1×d), 159.2 (1×s), 193.4 (1×d). MS (EI, 70 eV): *m*/*z* (%)=204 (100) [$M^+$], 148 (52), 147 (47), 115 (40), 91 (46).

*4.5.6. (E)-2-(Naphthalen-2-yl)but-2-enal (**5o**)*

EP/EE 90:10, 1% $Et_3N$. Yellow oil (81 mg, 83%). Found C, 85.93; H, 6.15%. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16%. $\nu_{max}$ (neat)/$cm^{-1}$ 3055, 2940, 1683, 1628, 1596, 749. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 2.06 (3H, d, *J*=7.1, C*H*$_3$), 6.94 (1H, q, *J*=7.2, C*H*=C), 7.28–7.92 (7H, m, Ar), 9.70 (1H, s, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 15.9 (1×q), 125.9 (1×d), 126.1 (1×d), 127.0 (1×d), 127.5 (1×d), 127.6 (1×d), 127.9 (1×d), 128.6 (1×d), 129.7 (1×s), 132.7 (1×s), 132.9 (1×s), 144.8 (1×s), 151.5 (1×d), 193.4 (1×d). MS (EI, 70 eV): *m*/*z* (%)=196 (100) [$M^+$], 168 (50), 167 (99), 165 (79), 152 (66).

*4.5.7. (E)-2-p-Tolylbut-2-enal[24] (**5p**)*

EP/EE 90:10, 1% $Et_3N$. Pale yellow oil (60 mg, 75%). Found C, 82.16; H, 7.56%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%. $\nu_{max}$ (neat)/$cm^{-1}$ 2921, 1685, 1632, 1514, 842, 818. $\delta_H$ (200 MHz; $CDCl_3$, $Me_4Si$) 2.06 (3H, dd, *J*=7.1, 1.4, C*H*$_3$), 2.39 (3H, s, C*H*$_3$), 6.83 (1H, qd, *J*=7.0, 1.1, C*H*=C), 7.08 (2H, d, *J*=7.1, Ar), 7.23 (2H, d, *J*=7.3, Ar), 9.62 (1H, br d, *J*=1.4, C*H*O); $\delta_C$ (50.2 MHz; $CDCl_3$, $Me_4Si$) 15.8 (1×q), 21.1 (1×q), 128.8 (2×d), 129.0 (1×s), 129.2 (2×d), 137.5 (1×s), 144.7 (1×s), 150.8 (1×d), 193.6 (1×d). MS (EI, 70 eV): *m*/*z* (%)=160 (100) [$M^+$], 131 (61), 117 (69), 115 (77), 91 (74).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## Supplementary data

$^1H$ and $^{13}C$ spectra of products **5a–q**. NOESY spectra of products **5f**, **5j**, **5o** and **5q**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.08.081.

## References and notes


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