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# Indium triflate catalyzed allylation of ketones with diallyldibutyltin

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**Abstract**—A series of ketones underwent an allylation reaction using diallyldibutyltin in the presence of a catalytic amount of $In(OTf)_3$. The method was found to be superior to most of the known methods. Thus, a new allyltin reagent $Bu_2Sn(allyl)_2/In(OTf)_3$ for ketones was developed.


## 1. Introduction

Allylation of carbonyl groups by various allylic metals is a highly efficient tool for the synthesis of homoallylic alcohols with the formation of a new carbon–carbon bond.[1] Among the various allylic metals, allyltin is an important reagent with its suitable activity, low cost and easily available. Diastereoselective and enantioselective allylation with different allyltin derivatives have been studied mostly for aldehydes[2] but rarely for ketones[3,4] since the lower reactivity of carbonyl group in ketones.

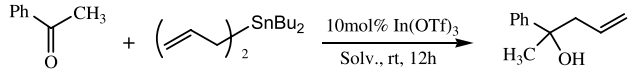
Recently, it was reported that a combination of zinc triflate and a base such as 2,6-lutidine or pyridine could catalyze the allylation of ketones with tetra-allyltin.[5] It was described that allylation of acetophenone with 1 equiv of different allylstannanes such as tetra-allylatin, diallyldibutyltin, and allyltributyltin gave 94, 59, and 19% yield of 1-phenyl-1-methylbut-3-en-1-ol (PMB), respectively, in the presence of 10 mol% $Zn(OTf)_2$ and 10 mol% pyridine. However, zinc triflate alone was ineffective as only a 16% yield of PMB was obtained in the case of acetophenone with tetra-allyltin. While working on the $In(OTf)_3$-catalyzed reactions, we observed that allylation of acetophenone with diallyldibutyltin afforded PMB in 95% yield. The reaction did not require any Lewis base as co-catalyst and it could be extended to the enantioselective version. Herein, we report a new allylation system for various ketones. Thus, it was extended to the other allyltin reagent for allylation of ketones compared to the previous only limited to tetra-allyltin.[6,7]

## 2. Results and discussion

Firstly, the effect of the solvents on the reaction of acetophenone (1 equiv) and diallyldibutyltin (1 equiv) in the presence of $In(OTf)_3$ (10 mol%) at room temperature was examined. The results in Table 1 showed that dichloromethane was a good choice over the other solvents such as MeCN, ether, THF, toluene, and DMSO.

Then different metal triflates (See Table 2) were examined and the indium triflate gave the best result. Furthermore, we also investigated the effect of the different amount of $In(OTf)_3$ on this reaction. The results showed that 10 mol% catalyst was the best choice for this reaction (Table 3).

**Table 1**. Effect of different solvents on allylation of acetophenone with diallyldibutyltin




| Entry | Solvent | Yield (%)[a] |
|---|---|---|
| **1** | **$CH_2Cl_2$** | **95** |
| 2 | MeCN | 37 |
| 3 | $Et_2O$ | 81 |
| 4 | THF | 72 |
| 5 | Toluene | 84 |
| 6 | DMSO | 61 |

[a] Isolated yields.

*Keywords*: Allylation; Ketone; Diallyldibutyltin; $In(OTf)_3$.
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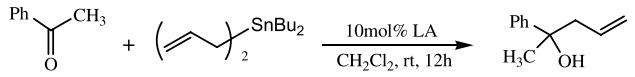
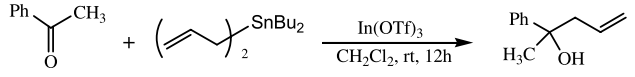
**Table 2**. Effect of different triflates' Lewis acids on allylation of acetophenone with diallyldibutyltin




| Entry | Lewis acid | Yield (%)[a] |
|---|---|---|
| 1 | — | 27 |
| **2** | **$In(OTf)_3$** | **95** |
| 3 | $Yb(OTf)_3$ | 74 |
| 4 | AgOTf | 71 |
| 5 | $Y(OTf)_3$ | 89 |
| 6 | $Cu(OTf)_2$ | 51 |
| 7 | $Zn(OTf)_2$ | 48 |

[a] Isolated yields.

**Table 3**. Effect of different $In(OTf)_3$ amount on allylation of acetophenone with diallyldibutyltin




| Entry | Solvent | Temperature (°C) | Amount of $In(OTf)_3$ (mol%) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | Room temperature | 1 | 38 |
| 2 | $CH_2Cl_2$ | Room temperature | 5 | 68 |
| 3 | $CH_2Cl_2$ | Room temperature | 10 | 95 |

[a] Isolated yields.

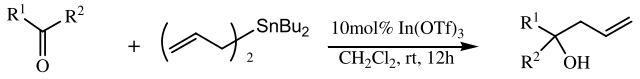
In order to ascertain whether both allyl groups could all be transferred, 1 and 0.5 equiv of diallyldibutyltin were used in two separate experiments by taking an example of the acetophenone. It was observed that on use of 0.5 equiv of the diallyldibutyltin, only 31% yield of the product was obtained even after 24 h at room temperature. Similar experiments were carried out with other ketones such as 4-bromo-acetophenone (entry 4) and cycloheptanone (entry 15). The yields of allylated products dropped from 86 to 35% for entry 4 and from 90 to 40% for entry 15, respectively. Thus, it was concluded that the second allyl group of diallyldibutyltin was uneasily transferred under the current reaction condition.

In a word, the optimized reaction condition was that ketones were treated with an equal mol of diallyldibutyltin in the presence of 10 mol% $In(OTf)_3$ in $CH_2Cl_2$ at room temperature for 12 h.

The extended investigation on different kinds of ketones with diallyldibutyltin was examined under the optimized conditions. High yields were obtained in most of the cases (Table 4).

Arylmethyl ketones bearing an electron-withdrawing group at the *para*-position of the aromatic ring gave the corresponding allylation products in high yields (entries 2–4). Arylmethyl ketones bearing an electron-donor group such as *p*-Me or *p*-MeO gave the products in moderate yields (entries 9 and 10). Moreover, the former proceeded much faster by TLC monitoring. Even after stirred for 12 h, the arylmethyl ketones bearing an EDG at the *para*-position could not react completely, as the starting material was recovered. The *p*-$NH_2$ substituted phenylmethyl ketone did

**Table 4**. Allylation of ketones with diallyldibutyltin catalyzed by $In(OTf)_3$



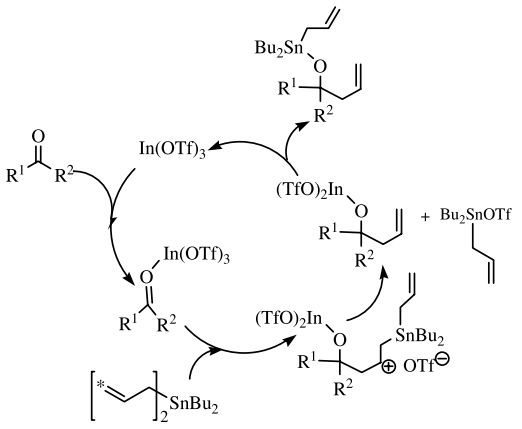

| Entry | $R^1$ | $R^2$ | Yield (%)[a] |
|---|---|---|---|
| 1 | Ph | $CH_3$ | 95 |
| 2 | *p*-$FC_6H_4$ | $CH_3$ | 81 |
| 3 | *p*-$ClC_6H_4$ | $CH_3$ | 75 |
| 4 | *p*-$BrC_6H_4$ | $CH_3$ | 86 |
| 5 | *p*-$NO_2C_6H_4$ | $CH_3$ | 66 |
| 6 | *m*-$NO_2C_6H_4$ | $CH_3$ | 71 |
| 7 | *m*-$BrC_6H_4$ | $CH_3$ | 93 |
| 8 | *m*-$CF_3C_6H_4$ | $CH_3$ | 90 |
| 9 | *p*-$MeC_6H_4$ | $CH_3$ | 58 |
| 10 | *p*-$MeOC_6H_4$ | $CH_3$ | 50 |
| 11 | *p*-$NH_2C_6H_5$ | $CH_3$ | — |
| 12 | Ph | Ph | 42 |
| 13 |  | | 78 |
| 14 |  | | 82 |
| 15 |  | | 90 |
| 16 | $CH_2CH_2CH_3$ | $CH_3$ | 45 |
| 17 | $CH_2CH(CH_3)_2$ | $CH_3$ | 27 |
| 18 | *p*-$MeOC_6H_4$ | H | 80 |

[a] Isolated yields.

not afford the desired homoallylic alcohol but complicated products tracing by $^1H$ NMR (entry 11), the reason for which was not clear at present. Surprisingly, substituent in the *meta*-position of the aromatic ring underwent allylation in higher yield than the corresponding substituent in the *para*-position of the aromatic ring (entries 4 and 7, 5 and 6). In addition, aliphatic ketones afforded the allylation products in the moderate to good yields (entries 13–17). Furthermore, benzophenone could also react smoothly (entry 12) with a moderate yield. To confirm the reaction system could be applied in aldehyde too, *p*-anisaldehyde, which usually showed a relatively lower reactivity for allylation, was chosen to react with the diallyldibutyltin under the same conditions. And the homoallylic alcohol was obtained in 80% yield (entry 18).

The mechanism of this reaction was preliminarily studied. According to the previous reports, the Lewis acids catalyzed the allylation of carbonyl compounds with allylic metal reagents via an acyclic transition state.[8] Herein, we postulated a possible mechanism of this reaction according to the $^1H$ NMR tracing (Scheme 1). By using *p*-anisaldehyde as a representative substrate coordinated with 1 equiv $In(OTf)_3$, we found that the peak corresponding to this aldehyde proton in $^1H$ NMR showed a down-field shift ($\delta$ 9.732–9.872 ppm). This suggested some evidence of activation of aldehyde by $In(OTf)_3$.

In addition, we also selected several typical homoallylic alcohols to analyze their properties by ESI mass spectrometric analysis. As a result, we found that the molecular ion peaks of the general homoallylic alcohols were weak and easily decomposed by pulling off water to turn into the *tert*-carbonium ions, which were the highest response peak [(M+1)−18] except for *m*-trifluoromethyl acetophenone.



**Scheme 1.** Probable acyclic transition-state mechanism.

Since all the products were known compounds, only $^1$H NMR and selected $^{13}$C NMR and Mass spectra were determined for confirming the products. And all spectra were available in the supporting material.

## 3. Conclusion

In summary, we have found that diallyldibutyltin /$In(OTf)_3$ was a novel efficient system for the allylation of ketones under a mild condition. The reaction did not require any base as an additive and could be applied for various ketones with modest to high yields. Further investigation on diastereo- and enantio-selective allylation is currently in progress in our laboratory.

## 4. Experiment

### 4.1. General

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware. Commercial solvents and reagents were used without further purification except petroleum ether, dichloromethane, ether were fractionally distilled. Ketones were used without purification. Analytical thin-layer chromatography (TLC) was performed using Merck 60 $F_{254}$ precoated silica gel plate. Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with acidic solution of ceric molybdate, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on a Varian Mercury Plus 400 ($^1$H 400 MHz) ($CDCl_3$ as solvent). Chemical shifts for $^1$H NMR spectra are reported as $\delta$ in units of parts per million (ppm) downfield from $SiMe_4$ ($\delta$ 0.0) and relative to the signal of chloroform-*d* ($\delta$ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dddd (doublets of doublets of doublets of doublet); dt (doublets of triplet); or m (multiplets). The number of protons (*n*) for a given resonance is indicated by *n*H. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as $\delta$ in units of parts per million (ppm) downfield from $SiMe_4$ ($\delta$ 0.0) and relative to the signal of chloroform-*d* ($\delta$ 77.03, triplet). Mass spectrometric analysis was carried out on a ThermoFinnigan LCQ Advantage LC/MS with an electrospray ionization mode (ESI).

### 4.2. Synthesis

*Preparation of dibromodiallyltin ($(CH_2{=}CHCH_2)_2SnBr_2$).* To an oven dried 250 ml four-necked flask equipped with a magnetic stirring bar, a reflux condenser and a thermometer was added 150 ml toluene, tin powder (17.8 g, 0.15 mol) and $HgCl_2$ (0.5 g, 0.002 mol). The mixture was refluxed for 30 min, then cooled to room temperature, triethylamine (0.275 ml) was added and the mixture was heated until reflux, and 1-bromopropene (18.2 g, 0.15 mol) was added dropwise within 30 min. The reaction mixture was kept at reflux for 3 h and then cooled to room temperature, filtered, concentrated in vacuo. The residual crude product was distilled under reduced pressure and resulted in 19.5 g of a slightly yellow colored oil: bp 70–72 °C/0.5 mmHg, Yield 72%. The oil was analyzed by $^1$H NMR.

*Preparation of diallyldibutyltin ($(CH_2{=}CHCH_2)_2SnBu_2$).* Placed of dry magnesium turnings (5 g, 0.208 mol) and freshly distilled ether (25 ml) in a 250 ml four-necked flask equipped with a magnetic stirring bar, a reflux condenser with a drying tube, a dropping funnel charged with the solution of *n*-butyl chloride (19.3 g, 0.208 mol) and ether (10 ml). After addition of about one third of *n*-butyl chloride solution into the flask, a small iodine crystal was added to the mixture. The reaction started immediately and the color of iodine disappeared. The remaining *n*-butyl chloride solution was added slowly into the reaction mixture with gentle reflux (about 30 min). When all of the *n*-butyl chloride solution was dropped into the flask, the reaction was continued for an additional 30 min on a heated water bath until magnesium turning disappeared.

The resulting Grignard reagent was cooled to room temperature using a cold water bath. A solution of the freshly prepared dibromodiallyltin (27.0 g, 0.075 mol) in 10 ml dried ether was added dropwise. The dropping rate was controlled so that the mixture was refluxed gently. After the addition was finished, the reaction mixture was refluxed for further 30 min and then cooled in an ice-bath. Under constant stirring a solution of 1 N hydrochloride (about 80 ml) was added and the stirring was continued until the solid was dissolved. The organic layer was separated and the aqueous layer was extracted for three times with ether ($3\times$ 25 ml). The combined organic layers were dried with anhydrous sodium sulfate, filtered, concentrated in vacuo. The residual crude product was distilled under reduced pressure and resulted in 15.26 g of a colorless liquid, Yield 63%. The liquid was analyzed by $^1$H NMR.

**4.2.1. Preparation of 1-phenyl-1-methylbut-3-en-1-ol (1).** To an oven dried 10 ml tube equipped with a magnetic stirring bar was added acetophenone (60 mg, 0.5 mmol) and diallyldibutyltin (157 mg, 0.5 mmol), then added $In(OTf)_3$

(28 mg, 0.05 mmol) and dichloromethane (2 ml). The mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with 2 ml saturated aqueous $NaHCO_3$ solution, extracted with ether (3×10 ml), washed with brine, dried over $Na_2SO_4$, filtered and concentrated in vacuo. The residual crude product was purified via silica gel chromatography to afford the homoallylic alcohol as a colorless oil (95% yield). MS: $m/z=162.39$ ($M^+$), $m/z=145.49$ [(M+1)−18]; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.45–7.23 (m, 5H, Ar*H*), 5.66–5.58 (m, 1H, C*H*), 5.13 (t, $J=8$ Hz, 2H, CH=C$H_2$), 2.71–2.47 (m, 2H, C$H_2$), 2.09 (br, 1H, O*H*), 1.54 (s, 3H, C$H_3$); $^{13}$C NMR (400 MHz, $CDCl_3$): $\delta$ 30.0, 48.7, 73.9, 119.6, 125.0, 126.9, 128.4, 134.0, 148.0.

**4.2.2. 1-*p*-Fluorophenyl-methylbut-3-en-ol (2).** Homoallylic alcohol **2** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.41–7.30 (m, 2H, Ar*H*), 7.01 (t, $J=8$ Hz, 2H, Ar*H*), 5.63–5.55 (m, 1H, C*H*), 5.14 (d, $J=12$ Hz, 2H, CH=C$H_2$), 2.63–2.45 (m, 2H, C$H_2$), 2.07 (br, 1H, O*H*), 1.53 (s, 3H, C$H_3$).

**4.2.3. 1-*p*-Chlorophenyl-1-methylbut-3-en-1-ol (3).** Homoallylic alcohol **3** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.31–7.25 (m, 4H, Ar*H*), 5.53 (s, 1H, C*H*), 5.24–5.08 (m, 2H, CH=C$H_2$), 2.57–2.41 (m, 2H, C$H_2$), 2.02 (br, 1H, O*H*), 1.46 (t, $J=4$ Hz, 3H, C$H_3$).

**4.2.4. 1-*p*-Bromophenyl-1-methylbut-3-en-1-ol (4).** Homoallylic alcohol **4** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.46–7.29 (m, 4H, Ar*H*), 5.59–5.55 (m, 1H, C*H*), 5.14–5.11 (d, $J=12$ Hz, 2H, CH=C$H_2$), 2.66–2.44 (m, 2H, C$H_2$), 2.08 (br, 1H, O*H*), 1.51–1.49 (d, $J=10.8$ Hz, 3H, C$H_3$); $^{13}$C NMR (400 MHz, $CDCl_3$): $\delta$ 30.1, 48.5, 73.7, 120.1, 120.8, 127.0, 131.4, 133.4, 146.9.

**4.2.5. 1-*p*-Nitrophenyl-1-methylbut-3-en-1-ol (5).** Homoallylic alcohol **5** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.18–7.23 (m, 4H, Ar*H*), 5.57–5.55 (m, 1H, C*H*), 5.16–5.14 (t, $J=2.8$ Hz, 2H, CH=C$H_2$), 2.65–2.51 (m, 2H, C$H_2$), 2.14 (br, 1H, O*H*), 1.55–1.54 (d, $J=4$ Hz, 3H, C$H_3$).

**4.2.6. 1-*m*-Nitrophenyl-1-methylbut-3-en-1-ol (6).** Homoallylic alcohol **6** was obtained using the same procedure as **1**: slight yellow oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.32–7.26 (m, 4H, Ar*H*), 5.62–5.56 (m, 1H, C*H*), 5.17–5.13 (t, $J=7.6$ Hz, 2H, CH=C$H_2$), 2.70–2.51 (m, 2H, C$H_2$), 2.16 (br, 1H, O*H*), 1.58 (s, 3H, C$H_3$).

**4.2.7. 1-*m*-Bromophenyl-1-methylbut-3-en-1-ol (7).** Homoallylic alcohol **7** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.60–7.18 (m, 4H, Ar*H*), 5.60–5.56 (m, 1H, C*H*), 5.14–5.12 (d, $J=9.2$ Hz, 2H, CH=C$H_2$), 2.65–2.44 (m, 2H, C$H_2$), 2.08 (br, 1H, O*H*), 1.51–1.50 (d, $J=4.8$ Hz, 3H, C$H_3$).

**4.2.8. 1-*m*-Trifluoromethylphenyl-1-methylbut-3-en-1-ol (8).** Homoallylic alcohol **8** was obtained using the same procedure as **1**: colorless oil; MS: $m/z=230.35$ ($M^+$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.73–7.45 (m, 4H, Ar*H*), 5.63–5.55 (m, 1H, C*H*), 5.17–5.13 (m, 2H, CH=C$H_2$), 2.70–2.49 (m, 2H, C$H_2$), 2.17 (s, 1H, O*H*), 1.56 (s, 3H, C$H_3$).

**4.2.9. 1-*p*-Methylphenyl-1-methylbut-3-en-1-ol (9).** Homoallylic alcohol **9** was obtained using the same procedure as **1**: colorless oil; MS: $m/z=176.39$ ($M^+$), $m/z=159.58$ [(M+1)−18]; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.33–7.15 (m, 4H, Ar*H*), 5.69–5.59 (m, 1H, C*H*), 5.16–5.11 (m, 2H, CH=C$H_2$), 2.71–2.47 (m, 2H, C$H_2$), 2.35 (s, 3H, C$H_3$-Ar), 2.02 (br, 1H, O*H*), 1.54 (s, 3H, C$H_3$); $^{13}$C NMR (400 MHz, $CDCl_3$): $\delta$ 21.2, 30.1, 48.7, 73.8, 119.4, 125.0, 129.1, 134.1, 136.3, 145.0.

**4.2.10. 1-*p*-Methoxyphenyl-1-methylbut-3-en-1-ol (10).** Homoallylic alcohol **10** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.35–6.85 (m, 4H, Ar*H*), 5.64–5.58 (m, 1H, C*H*), 5.13–5.09 (t, $J=7.6$ Hz, 2H, CH=C$H_2$), 3.80 (s, 3H, C$H_3$O), 2.67–2.44 (m, 2H, C$H_2$), 1.98 (br, 1H, O*H*), 1.57 (s, 3H, C$H_3$).

**4.2.11. 1,1-Diphenyl-1-but-3-en-1-ol (12).** Homoallylic alcohol **12** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.40–7.18 (m, 10H, Ar*H*), 5.63–5.60 (m, 1H, C*H*), 5.23–5.12 (m, 2H, CH=C$H_2$), 3.03 (br, 1H, O*H*), 2.52–2.28 (m, 2H, C$H_2$).

**4.2.12. 1-Cyclopentyl-1-but-3-en-1-ol (13).** Homoallylic alcohol **13** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.94–5.84 (m, 1H, C*H*), 5.15–5.12 (m, 2H, CH=C$H_2$), 2.34–2.16 (t, $J=7.6$ Hz, 2H, C$H_2$), 1.79–1.24 (m, 8H, cyclopentyl).

**4.2.13. 1-Cyclohexyl-1-but-3-en-1-ol (14).** Homoallylic alcohol **14** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.93–5.84 (m, 1H, C*H*), 5.14–5.07 (t, $J=10.4$ Hz, 2H, CH=C$H_2$), 2.34–2.19 (t, $J=6.8$ Hz, 2H, C$H_2$), 1.70–1.24 (m, 10H, cyclohexyl).

**4.2.14. 1-Cycloheptyl-1-but-3-en-1-ol (15).** Homoallylic alcohol **15** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.89–5.85 (m, 1H, C*H*), 5.15–5.08 (t, $J=10.8$ Hz, 2H, CH=C$H_2$), 2.22–2.15 (t, $J=6.8$ Hz, 2H, C$H_2$), 1.63–1.37 (m, 12H, cycloheptyl); $^{13}$C NMR (400 MHz, $CDCl_3$): $\delta$ 22.6, 30.0, 41.3, 48.1, 75.1, 118.9, 134.3.

**4.2.15. 1-Methyl-1-propyl-1-but-3-en-1-ol (16).** Homoallylic alcohol **16** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.89–5.83 (m, 1H, C*H*), 5.15–5.09 (t, $J=8.4$ Hz, 2H, CH=C$H_2$), 2.22–2.20 (d, $J=7.6$ Hz, 2H, C$H_2$), 1.57–0.91 (m, 10H, C$H_3$, $C_3H_7$)

**4.2.16. 1-Methyl-1-isobutyl-1-but-3-en-1-ol (17).** Homoallylic alcohol **17** was obtained using the same procedure as **1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.88–5.82 (m, 1H, C*H*), 5.14–5.08 (t, $J=9.6$ Hz, 2H, CH=C$H_2$), 2.23 (m, 2H, C$H_2$), 1.82–0.95 (m, 12H, C$H_3$, *i*-$C_4H_9$).

**4.2.17. 1-*p*-Methoxylphenyl -1-but-3-en-1-ol (18).** Homoallylic alcohol **18** was obtained using the same procedure as

**1**: colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.31–7.28 (m, 2H, Ar*H*), 6.91–6.89 (m, 2H, Ar*H*), 5.88–5.75 (m, 1H, C*H*═$CH_2$), 5.20–5.13 (m, 2H, CH═C$H_2$), 4.72–4.68 (t, $J$=6.6 Hz, 1H, C*H*), 3.82 (s, 3H, C$H_3$O), 2.54–2.49 (m, 2H, C$H_2$), 2.18 (s, 1H, O*H*).

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.08.101

## References and notes

1. Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207–2293.
2. (a) Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357–386. (b) Hoffman, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555–566. (c) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243–249. (d) Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 4723–4724.
3. Hachiya, I.; Kobayashi, S. *J. Org. Chem.* **1993**, *58*, 6958–6960.
4. Kamble, R. M.; Singh, V. K. *Tetrahedron Lett.* **2001**, *42*, 7525–7526.
5. Hamasaki, R.; Chounan, Y.; Horino, H.; Yamamoto, Y. *Tetrahedron Lett.* **2000**, *41*, 9883–9887.
6. Kii, S.; Maruoka, K. *Chirality* **2003**, *15*, 68–70.
7. (a) Yasuda, M.; Kitahara, N.; Fujibayashi, T.; Baba, A. *Chem. Lett.* **1998**, *8*, 743–744. (b) Casolari, S.; Addario, D. D.; Tagliavini, E. *Org. Lett.* **1999**, *1*, 1061–1063. (c) Waltz, K. M.; Gavenonis, J.; Walsh, P. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3697–3699.
8. Denmark, S. E.; Fu, J. P. *Chem. Rev.* **2003**, *103*, 2763–2794.