# Preparation and Reactions of Masked Allylic Organozinc Reagents

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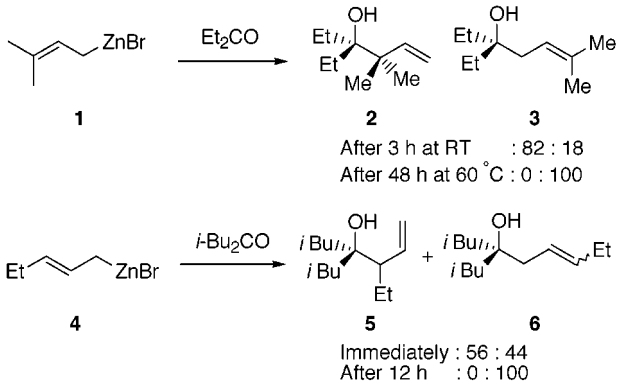
Allylic zinc reagents have been prepared from sterically hindered homoallylic alcohols **10** and **13**, using a novel fragmentation reaction of the corresponding zinc alkoxide, without any homocoupling products. These allylic zinc reagents react with a range of electrophiles in good to excellent yields. Substituted allylic zinc reagents have also been prepared in this manner. α-Substituted homoallylic alcohols **37**, **46**, and **51** give solely α-substituted products after the fragmentation−allylation sequence; these products are obtained not only regioselectively but also with extremely high anti diastereoselectivity. Likewise, γ-substituted homoallylic alcohols **57** and **58**, undergo the fragmentation−allylation reaction to give γ-substituted products. The reaction has also been demonstrated to be catalytic in zinc salts.

## Introduction

The use of organometallic reagents is today so commonplace that hardly any synthesis is now completed without the inclusion of at least one step involving an organometallic reagent, and often many more. One reaction of particular importance is the allylation of carbonyl compounds, and there has been extensive research in this area.[1] Despite notable successes, the use of crotylchromium reagents for highly antiselective additions to aldehydes,[2] the use of (*Z*)-crotylborates for the production of *syn*-homoallylic alcohols,[3] and the reaction of crotyltins promoted by Lewis acids to produce *syn*-homoallylic alcohols,[4] there remains several notable problems associated with these reagents. The classical method for the generation of allylic organometallics involves the reaction of an allyl halide with a metal; this method, due to the high reactivity of the resulting organometallic, results in a high proportion of the Wurtz homocoupling product. Second, to date, most reactions involving allylic organometallics are stoichiometric and generate at least 1 equiv of inorganic salts and waste. On a small scale this is irrelevant; however, on an industrial scale it becomes a major consideration.

We became aware of several reports in the literature whereby the addition of allylic metals to electrophiles is documented as being reversible.[5−7] Two papers by Miginiac in particular fascinated us.[7a,b] In the first,[7a] it was reported how the addition of prenylzinc bromide **1** to 3-pentanone gave after 3 h at room temperature initially the α-disubstituted product **2** in 82% together with 18% of the γ-disubstituted product **3** (Scheme 1); however, on warming the reaction to 60 °C for 2 days, the reaction mixture isomerized entirely to the γ-disubstituted product **3**, which was isolated in 50% yield. In the second paper, the addition of 2-pentenylzinc bromide **4** to 2,6-dimethylheptan-4-one gave immediately the 56:44 mixture of two homoallylic alcohols, **5** and **6**,[7b] with the major being the α-substituted; however, upon being stirred for 12 h, the mixture gave, after hydrolysis, 80% yield of solely the γ-substituted isomer **6**.

**Scheme 1**




We hypothesised that due to the reversibility of these reactions if we prepared a sterically hindered tertiary homoallylic alcohol **7**, upon generation of a zinc alkoxide **8** we could initiate a fragmentation reaction to generate an allylic zinc regent **9**, which in the presence of a suitable electrophile could result in further synthetically useful reactions (Scheme 2).[8]

## Results and Discussion

Accordingly, a pair of homoallylic alcohols, **10** and **13**, with increasing steric hindrance were prepared and

(1) (a) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Heathcock, C. H., Eds.; Pergamon: Oxford, 1991; Vol. 2, pp 1−53. (b) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207−2293.

(2) Buse, C. T.; Heathcock, C. H. *Tetrahedron Lett.* **1978**, 1685−1688.

(3) Hoffmann, R. W.; Zei*β*, H.-J. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 306.

(4) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107−7109.

(5) For reaction of Grignard reagents, see: (a) Bensker, R. A.; Siklosi, M. P. *J. Org. Chem.* **1976**, *41*, 3212−3213. (b) Bensker, R. A.; Siklosi, M. P.; Mozdzen, E. C. *J. Am. Chem. Soc.* **1978**, *100*, 2134−2139. (c) Bensker, R. A.; Young, W. G.; Broxterman, W. E.; Jones, D. A.; Piaseczynski, S. J. *J. Am. Chem. Soc.* **1969**, *91*, 132−137. (d) Barbot, F.; Miginiac, P. *Bull. Chim. Soc. Fr.* **1977**, 113−116.

(6) For reaction of organolithiums, see: (a) Gerard, F.; Miginiac, P. *Bull. Chim. Soc. Fr.* **1974**, 2527−2533; Gerard, F.; Miginiac, P. *Bull. Chim. Soc. Fr.* **1974**, 1924−1930.

(7) For reaction of organozincs, see: (a) Barbot, F.; Miginiac, P. *Tetrahedron Lett.* **1975**, 3829−3832. (b) Miginiac, P.; Bouchoule, C. *Bull. Chim. Soc. Fr.* **1968**, 4675−4676. (c) Barbot, F.; Miginiac, P. *J. Organomet. Chem.* **1977**, *132*, 445−454. (d) Bocoum, A.; Savoia, D.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1542−1544.

(8) For a preliminary communication of this work, see: (a) Jones, P.; Millot, N.; Knochel, P. *J. Chem. Soc., Chem. Commun.* **1998**, 2405−2406. (b) Jones, P.; Knochel, P *J. Chem. Soc., Chem. Commun.* **1998**, 2407−2408.

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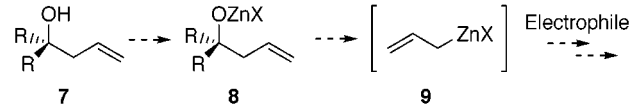
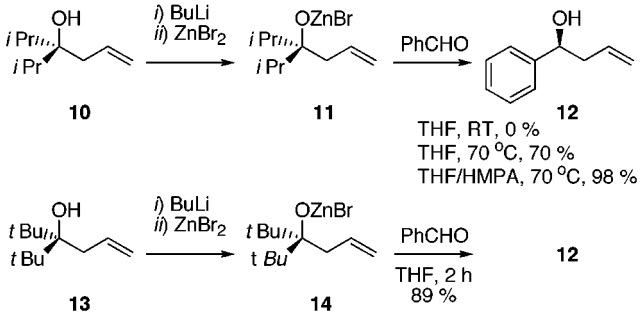
**Scheme 2**




**Scheme 3**

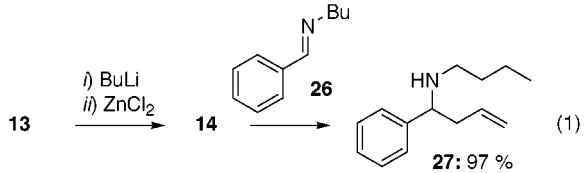



treated first with BuLi to form the lithium alkoxide, and then $ZnBr_2$ was added to give the zinc alkoxide (Scheme 3). The bis(isopropyl) alkoxide **11** was stable at room temperature; however, at 70 °C, this species fragmented to give an allylic zinc reagent in situ, which in the presence of benzaldehyde gave the benzylic alcohol **12** in 70% yield. The reaction could be improved by the addition of a cosolvent. In the presence of HMPA, the reaction was complete within 6 h to give 98% isolated yield of the benzylic alcohol **12**. However, we were delighted to find that the reaction using the bis(*tert*-butyl) alcohol **13** was far superior, with the fragmentation occurring in minutes at room temperature in only THF to give the benzylic alcohol **12** in 89% yield after 2 h. In both cases, no migration was observed using the corresponding lithium or magnesium alkoxides.

Inspired by this reaction, the scope of this procedure was investigated with a series of aldehydes and ketones (Table 1). Aromatic aldehydes, as well as aliphatic aldehydes, reacted well. The reaction with heptanal gives the homoallylic alcohol **15** in 83% yield (entry 1). Likewise, α,β-unsaturated aldehydes were tolerated, giving solely the product of 1,2-addition, **16** (entry 2). α-Substituted aldehydes caused no problems, with cyclohexanecarboxaldehyde and 2-phenylpropionaldehyde both giving the desired homoallylic alcohols, **17** and **18**, in good yields (entries 3 and 4). The reaction also proceeded well with ketones; however, a slightly longer reaction time, 2−4 h, was required to ensure the reaction went to completion. Treatment of cyclohexanone gave the tertiary alcohol **19** in 82% (entry 5), while 3-methylcyclohex-2-en-1-one gave the allylic alcohol **20** in 74% yield (entry 6). Benzylidene acetone and α-tetralone also gave good yields of the desired products (entries 7 and 8).

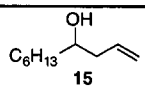
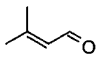
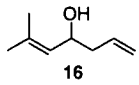
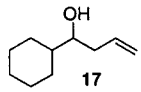
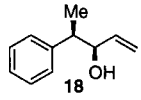
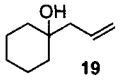
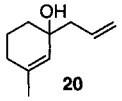
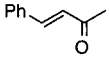
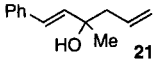
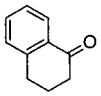
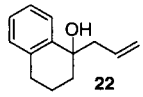
Having established the principle of retro-allylation/allylation from the sterically hindered zinc alkoxide **14**, we can consider this alkoxide as being a masked allylzinc reagent. We have now studied the scope of the reactivity of **14** and have examined if it would behave as a typical allylzinc reagent and undergo similar reactions.[9] Consequently, the homoallylic alcohol **13** was transformed to its zinc alkoxide **14** and reacted with benzonitrile; the appearance of bis(*tert*-butyl)ketone revealed the desired fragmentation had occurred, and we were delighted to find, upon mild acid work up, that the β,γ-unsaturated ketone **23** had been obtained in 73% yield (Scheme 4). Further reactions with 4-bromobenzonitrile and 4-chlorobutyronitrile gave the desired ketones **24** and **25** in 74% and 62% yields, respectively.

We also predicted that homoallylic amines could be prepared upon reaction with imines. Indeed, the zinc alkoxide **14** was treated with benzylidenebutylamine **26**, and after 2 h, the benzylamine **27** was obtained in 97% isolated yield (eq 1).



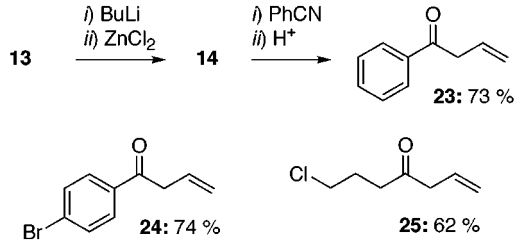
(1)

**Table 1. Reaction of 13 with Carbonyl Compounds**

| Entry | Aldehyde or Ketone | Product | Yield (%)[a] |
|---|---|---|---|
| 1 |  |  15 | 83 |
| 2 |  |  16 | 84 |
| 3 |  |  17 | 82 |
| 4 |  |  18 | 85[b] |
| 5 |  |  19 | 82 |
| 6 |  |  20 | 74 |
| 7 |  |  21 | 73 |
| 8 |  |  22 | 99 |

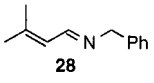
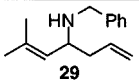
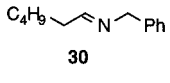
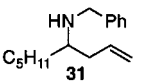
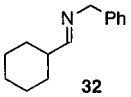
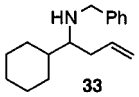
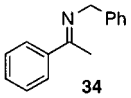
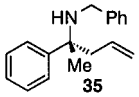
[a] Isolated yield of analytically pure products. [b] Isolated as a 3:1 mixture syn/anti.

**Scheme 4**




(9) For further reactions of allylzinc reagents, see: (a) Knochel, P.; Almena Perea, J. J.; Jones, P. *Tetrahedron* **1998**, *54*, 8275−8319. (b) Knochel, P.; Singer, R. D. *Chem. Rev.* **1993**, *93*, 2117−2188. (c) Knochel, P.; Normant, J. F. *J. Organomet. Chem.* **1986**, *309*, 1−23.

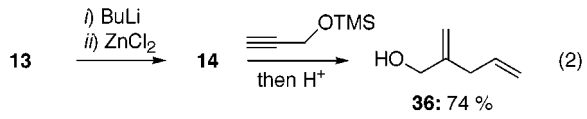
**Table 2: Reaction of 13 with Imines**

| Entry | Imine | Product | Yield (%)[a] |
|---|---|---|---|
| 1 |  **28** |  **29** | 90 |
| 2 |  **30** |  **31** | 63 |
| 3 |  **32** |  **33** | 63 |
| 4 |  **34** |  **35** | 67 |

[a] Isolated yield of analytically pure products.

Further reactions with α,β-unsaturate imines **28** (Table 2, entry 1) also proceeded well giving the 1,5-dienylamine **29** in 90% yield. Enolizable imines, **30** and **32**, reacted in moderate yield to give the benzylamines **31** and **33**, both in 63% isolated yield (entries 2 and 3). The reaction also proceeded with an imine of a ketone; reaction with benzyl(1-phenylethylidene)amine **34** gave the secondary amine **35** in 67% yield.

Another reaction of considerable synthetic importance is the carbozincation of carbon−carbon multiple bonds;[9c] we have examined if the masked zinc reagent **14** could add to an alkyne. In turn, the tertiary alcohol **13** was treated with BuLi, then $ZnCl_2$, and finally trimethylsilyl-protected propargyl alcohol (eq 2). Upon hydrolysis the 1,4-dienol, **36** was isolated in 74% yield, further demonstrating the synthetic utility of this approach.



(2)

Having developed this mild and clean method for the introduction of allylic groups into a range of molecules, we have examined the effect of substituents on the allyl group. We hoped that the study would give us some mechanistic insight into this reaction. Substituted allylzinc reagents had previously been prepared by Tamura from allyl benzoates.[10] We hoped that our mild method would give improved selectivities.

Accordingly, the tertiary homoallylic alcohol **37** bearing a methyl in the α-position was prepared and treated with *n*-BuLi at room temperature. However, we were disappointed to find that a rapid isomerization occurred to give the γ-substituted isomer **38** (Scheme 5). Undeterred, the deprotonation was attempted at −78 °C, and using these conditions, no isomerization was observed. Addition of benzaldehyde followed by a solution of zinc chloride gave, within 1 h at −78 °C, the benzylic alcohol **39** in 83% isolated yield. More interestingly, the product was isolated as a 94:6 mixture of anti/syn diastereomers.[11] This

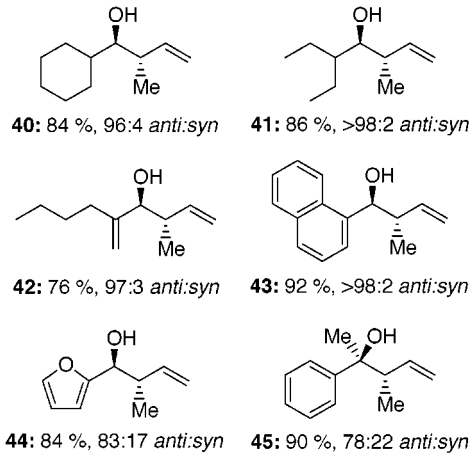
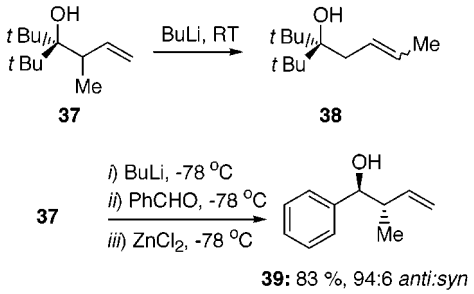



**Figure 1.**

**Scheme 5**




is in strong contrast to the addition of crotylzinc bromide to an aldehyde, which occurs with essentially no diastereoselectivity.[12]

Pleased by this finding, further synthetic investigations were carried out using a range of aldehydes and ketones (Figure 1). Saturated aldehydes, cyclohexanecarboxaldehyde and 2-ethylbutyraldehyde were excellent substrates giving the desired homoallylic alcohols **40** and **41** in good yields and excellent selectivities, 96:4 and >98:2, respectively. While 2-butylacrolein also reacted cleanly giving the 1,5-dien-3-ol **42** in 76% yield and a 97:3 diastereomeric excess. Aromatic aldehydes also provided the desired products, and the reaction with 1-naphthylaldehyde and furfural gave the desired alcohols **43** and **44** in good yields. Similarly, the reaction with acetophenone proceeded in good yield (90%) to give the tertiary alcohol **45**, but in moderate selectivity, 78:22 syn/anti. In all cases, none of the γ-substituted isomer was detected.

Following the success with the α-methyl-substituted reagent, we were interested to find whether other substitutes could be tolerated in the α-position. Therefore, the α-ethyl isomer **46** was prepared (Scheme 6) and treated with *n*-BuLi, benzaldehyde, and zinc chloride. As in the case of the α-methyl isomer **37**, the desired alcohol **47** was isolated in good yield starting from α-ethyl homallylic alcohol **46**, 91% yield as a 91:9 mixture of anti/syn diastereomers. Further reactions with cyclohexanecarboxaldehyde and 2-ethyl butyraldehyde gave rise to the homoallylic alcohols **48** and **49** in 83% and 81% yields, respectively; in both cases only the *anti*-diastereomer was detected.

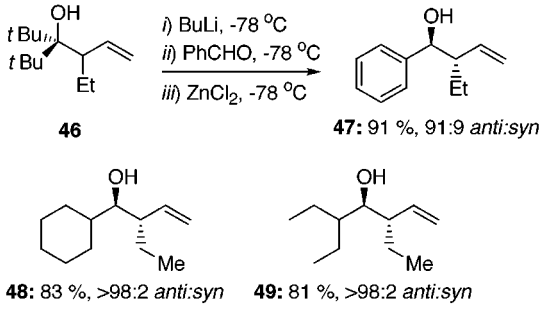
Further synthetic investigations also revealed that a substituent could easily be incorporated into the α-posi-

(10) Shimizu, M.; Kimura, M.; Tanaka, S.; Tamura, Y. *Tetrahedron Lett.* **1998**, *39*, 609−612.

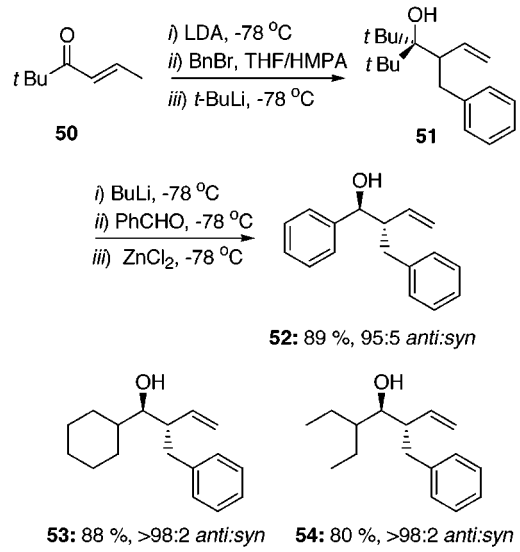
(11) Diastereomeric excesses were determined by $^1$H NMR.

(12) Wilson, S. R.; Guazzaroni, M. E. *J. Org. Chem.* **1989**, *54*, 3087−3091.

**Scheme 6**



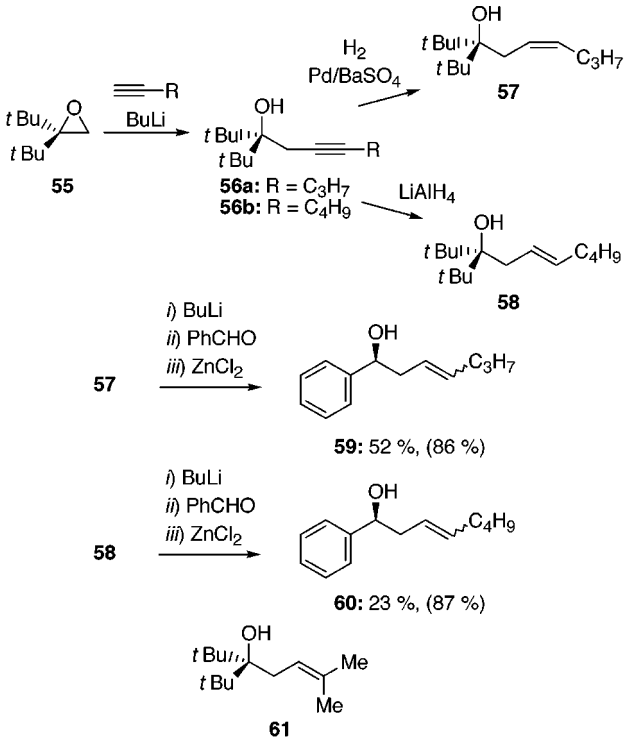

**Scheme 7**



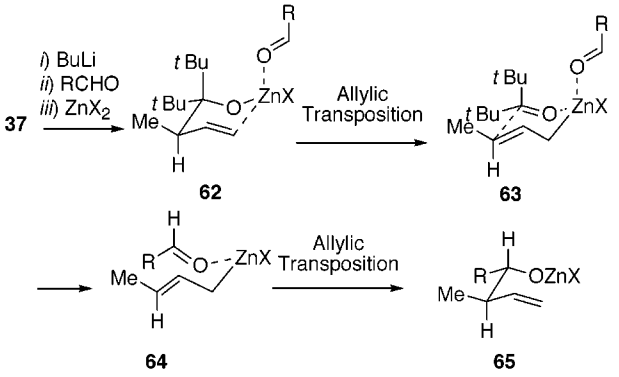

tion of the homoallylic alcohol using an alkylation sequence. 2,2-Dimethylhex-5-en-3-one **50** was readily deprotonated with LDA at −78 °C and subsequently alkylated in the α-position with benzyl bromide in THF/HMPA in 65% isolated yield. Subsequent reaction with *t*-BuLi gave the required homoallylic alcohol **51** in 85% yield. As in the previous cases, deprotonation, transmetalation, and reaction with benzaldehyde gave the desired benzylic alcohol **52** in 89% yield, again with excellent diastereoselectivity, 95:5. Other aldehydes also reacted well, giving the homoallylic alcohols **53** and **54** in 88% and 80% yields, respectively, both with excellent anti selectivity (Scheme 7).

Pleasantly surprised by these results, we were interested to investigate the outcome of placing substituents into the γ-position of the allylic system; however, a new preparation method was needed. Consequently, oxirane **55** was prepared and opened with a variety of lithium acetylides to give the propargyl alcohols **56a** and **56b** in reasonable yields, 84% and 65% (Scheme 8). Hydrogenation with palladium on barium sulfate gave the *Z* isomer **57** quantitatively, while treatment with $LiAlH_4$ gave the required *E* isomer **58**. We were now in a position to investigate the migration of these species. However, on generation of the zinc alkoxides, these species were found to be much less reactive. Whereas the α-substituted system migrated at −78 °C, these compounds were unreactive below room temperature. Using **57**, after 48 h at room temperature, migration had only occurred in 52% yield (86% based on recovered starting material) to give the desired homoallylic alcohol **59**, while the *E* isomer **58** gave the corresponding alcohol **60** in 23% yield

**Scheme 8**




**Scheme 9**

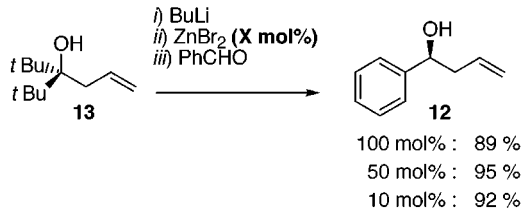



after 12 h (87% based on recovered starting material). In both cases, the products were isolated as 2:1 mixtures of E/Z isomers. The γ-disubstituted system **61** was also prepared, but the zinc alkoxide of this species was found to be inert and no migration was observed, even in refluxing THF.

On the basis of these observations, we feel that we can make a mechanistic proposal involving a double allylic transposition pathway (Scheme 9). Generation of the zinc alkoxide complexed by the aldehyde, RCHO, gives an intermediate **62**. Allylic transposition in a cyclic transition state gives rise to a crotyl zinc reagent **63** complexed to the parent bis(*tert*-butyl)ketone and the reaction partner, the crotylzinc bearing solely an (*E*) configuration. At −78 °C, this allylic species seems to be stable and undergoes no isomerization.[13] After reorganization of the ligand sphere leading to **64**, the second allylic transposition gives rise to the product **65**, predominately as the anti diastereomer. Compared to the standard nondias-

(13) Bis(3-methylallyl)zinc is known to be a rapid isomerizing system at room temperature, hence explaining the 1:1 anti/syn selectivity in additions to aldehydes. Benn, R.; Hoffmann, E. G.; Lehmkuhl, H.; Nehl, H. *J. Organomet. Chem.* **1978**, *146*, 103−112.

**Scheme 10**




tereoselective reaction of crotylzinc bromide with an aldehyde, this procedure appears to have the advantage of generating pure (*E*)-crotylzinc in the presence of the electrophile and therefore avoids an isomerization of the crotyl rest. This mechanism is supported by the unreactive nature of the $\gamma$-substituted homoallylic alcohols, whereby substitution on the $\gamma$-position prevents the first allylic transposition from occurring.

Despite the success of these reactions as a means of generating substituted allylic zinc reagents, one problem remained, that being the stoichiometric amount of zinc utilized in these reactions. We thought it may be possible to use catalytic quantities of zinc salts, as the zinc could shuttle between the sterically hindered zinc alkoxide, through the fragmentation, to give the allylic zinc reagent and then the subsequent product. This zinc alkoxide could then react with the lithium alkoxide of the tertiary alcohol completing the catalytic cycle. Indeed, when the reaction was carried out using 50 mol % of $ZnBr_2$, the benzylic alcohol **12** was isolated in 95% yield (Scheme 10). Further reductions in the zinc salts to 10 mol % gave the benzylic alcohol **12** in 92% yield. So far, we have been unable to make the reaction catalytic in a base, but further investigations are underway.

In summary, we have developed a novel fragmentation−allylation reaction of sterically hindered homoallylic alcohols to generate allylic zinc reagents in situ, without any Wurtz coupling products. The resulting allylic organozinc reagents react with a range of electrophiles to give the desired products in good to excellent yields. Substituted allylic organometallics can be prepared using this procedure, and they have been shown to be extremely regioselective. Excellent antidiastereoselectivities can be obtained in the fragmentation−allylation reaction from α-substituted homoallylic alcohols.[14,15]

## Experimental Section

Reactions were monitored by gas chromatography (GC) analysis of reaction aliquots. The ionization methods used for the performance of mass spectra were desorption chemical ionization (CI) and electron impact ionization (EI). THF was dried and freshly distilled over sodium/benzophenone, and HMPA was distilled from calcium hydride. Zinc chloride and zinc bromide were freshly dried before use for 2 h at 140 °C and less than 0.1 mmHg.

The following were prepared by known literature procedures: 3-isopropyl-2-methylhex-5-en-3-ol, **10**,[16] 3-*tert*-butyl-2,2-dimethylhex-5-en-3-ol, **13**,[16] benzylidenebutylamine, **26**,[17] benzyl(3-methylbut-2-enylidene)amine, **28**,[18] benzylhexylideneamine, **30**,[19] benzylcyclohexyl methyleneamine, **32**,[20] benzyl(1-phenylethylidene)amine, **34**,[21] crotonic acid chloride,[22] 2,2-di(*tert*-butyl)oxirane, **55**,[23] 2,2,6-trimethylhept-5-en-3-one.[24]

**Standard Preparation A, Addition of 13 to Carbonyl Compounds and Other Electrophiles. 1-Phenylbut-3-en-1-ol (12).** A solution of BuLi (2.71 mmol) in pentane (1.40 M, 1.94 mL) was added dropwise over 2 min to a stirred solution of **13** (500 mg, 2.71 mmol) in THF (4 mL) at 0 °C under argon. The resulting solution was then stirred for 15 min, and a solution of $ZnBr_2$ (610 mg, 2.71 mmol) in THF (2 mL) was added, followed by benzaldehyde (275 $\mu$L, 2.71 mmol). The reaction was allowed to warm to room temperature and stirred for 1 h. Saturated aqueous $NH_4Cl$ solution (15 mL) was added, and the reaction was worked up as usual. The crude residue was purified by column chromatography on silica using 15% $Et_2O$−hexanes as an eluent to give the alcohol[25] (356 mg, 89%) as a colorless oil: IR (film) 3391 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.35−7.12 (m, 5H), 5.85−5.61 (m, 1H), 5.15−5.01 (m, 2H), 4.64 (dd, $J$ = 7.0, 5.7 Hz, 1H), 2.47−2.37 (m, 2H), 2.04 (broad s, 1H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 143.82, 134.41, 128.36, 127.48, 125.77, 118.34, 73.25, 43.77; *m*/*z* (EI-MS) 107 ($M-C_3H_5^+$, 100%, $C_7H_7O$ requires 107). Anal. Calcd for $C_{10}H_{12}O$: C, 81.05; H, 8.16%. Found: C, 80.89; H, 8.13%.

**Dec-1-en-4-ol (15).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), heptanal (379 $\mu$L, 2.71 mmol), and $ZnBr_2$ (610 mg, 2.71 mmol) to give a crude residue, which was then purified by column chromatography on silica using 20% $Et_2O$−hexanes as an eluent to give the alcohol[12] (349 mg, 83%) as a colorless oil: IR (film) 3362 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 5.94−5.71 (m, 1H), 5.18−5.04 (m, 2H), 3.70−3.55 (m, 1H), 2.37−2.04 (m, 2H), 1.78−1.70 (m, 1H), 1.50−1.20 (m, 9H) 0.93−0.82 (m, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 134.91, 117.90, 70.63, 41.89, 36.77, 31.77, 29.28, 25.58, 22.56, 14.02; *m*/*z* (EI-MS) 115 ($M-C_3H_5^+$, 18%, $C_7H_{15}O$ requires 115), 55 (100%). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90%. Found: C, 76.52; H, 12.72%.

**2-Methylhept-2,6-dien-4-ol (16).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), 3-methylbut-2-enal (261 $\mu$L, 2.71 mmol), and $ZnBr_2$ (610 mg, 2.71 mmol) to give a crude residue, which was then purified by column chromatography on silica using 15−25% $Et_2O$−hexanes as an eluent to give the alcohol[26] (286 mg, 84%) as a colorless oil: IR (film) 3353 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 5.80 (m, 1H), 5.23−5.05 (m, 3H), 4.39 (m, 1H), 2.32−2.20 (m, 2H), 1.73 (d, $J$ = 1.3 Hz, 3H), 1.68 (d, $J$ = 1.3 Hz, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 135.36, 134.53, 127.19, 117.78, 67.71, 42.15, 25.70, 18.21; *m*/*z* (EI-MS) 108.0943 ($M-H_2O^+$, 5%, $C_8H_{12}$ requires 109.0939), 93 (100%).

**1-Cyclohexylbut-3-en-1-ol (17).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), cyclohexanecarboxaldehyde (328 $\mu$L, 2.71 mmol), and $ZnBr_2$ (610 mg, 2.71 mmol) to give a crude residue, which was then purified by column chromatography on silica using 20% $Et_2O$−hexanes as an eluent to give the alcohol[27] (342 mg, 82%) as a colorless oil: IR (film) 3397 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 5.95−5.72 (m, 1H), 5.19−5.06 (m, 2H), 3.45−3.30 (m, 1H), 2.42−2.25 (m, 1H), 2.19−2.03 (m,

(14) A patent has been filed with Chemetall GmbH (Frankfurt).

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1H), 1.95−0.90 (m, 11H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 135.45, 117.83, 74.69, 43.02, 38.75, 29.03, 28.06, 26.46, 26.23, 26.08; *m*/*z* (EI-MS) 113 (M−$C_3H_5^+$, 23%, $C_7H_{13}O$ requires 113), 95 (100%). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76%. Found: C, 77.63; H, 11.84%.

***syn*-2-Phenylhex-5-en-3-ol and *anti*-2-Phenylhex-5-en-3-ol (18).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), 2-phenylpropionaldehyde (360 $\mu$L, 2.71 mmol), and $ZnBr_2$ (610 mg, 2.71 mmol) to give a crude residue, which was then purified by column chromatography on silica using 15% $Et_2O$−hexanes as an eluent to give the alcohol[28] (404 mg, 85%) as an inseparable mixture of diastereomers (syn/anti 3:1). IR (film) 3426 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.38−7.13 (m, 5H), 5.99−5.67 (m, 1H), 5.19−5.02 (m, 2H), 3.78−3.62 (m, 1H), 2.88−2.72 (m, 1H), 2.45−1.70 (m, 2H), 1.40−1.25 (m, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) (major diastereomer) $\delta$ 144.36, 135.04, 128.41, 127.72, 126.38, 117.99, 74.95, 45.32, 39.46, 16.34, (minor diastereomer) $\delta$ 143.23, 135.00, 128.13, 126.60, 117.60, 38.89, 17.66; *m*/*z* (EI-MS) 176 ($M^+$, 1%, $C_{12}H_{16}O$ requires 176), 106 (100%). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%. Found: C, 81.61; H, 8.92%.

**1-Allylcyclohexanol (19).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), cyclohexanone (280 $\mu$L, 2.71 mmol), and $ZnBr_2$ (610 mg, 2.71 mmol) over 4 h to give a crude residue, which was then purified by column chromatography on silica using 20% $Et_2O$−hexanes as an eluent to give the alcohol[12] (325 mg, 82%) as a colorless oil: IR (film) 3393 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 6.00−5.77 (m, 1H), 5.18−5.02 (m, 2H), 2.20 (dt, $J$ = 7.5, 1.2 Hz, 2H), 1.70−1.38 (m, 10H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 133.69, 118.54, 70.87, 46.65, 37.32, 25.71, 22.11; *m*/*z* (EI-MS) 99 (M−$C_3H_5^+$, 100%, $C_6H_{11}O$ requires 99). Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%. Found: C, 77.08; H, 11.23%.

**1-Allyl-3-methylcyclohex-2-enol (20).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), 3-methylcyclohex-2-en-1-one (307 $\mu$L, 2.71 mmol), and $ZnBr_2$ (610 mg, 2.71 mmol) over 4 h to give a crude residue, which was then purified by column chromatography on silica using 20% $Et_2O$−hexanes as an eluent to give the alcohol[29] (305 mg, 74%) as a colorless oil: IR (film) 3374 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.99−5.76 (m, 1H), 5.35 (broad s, 1H), 5.16−5.04 (m, 2H), 2.27 (dt, $J$ = 7.5, 1.0 Hz, 2H), 1.95−1.50 (m, 6H), 1.67 (s, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 138.15, 133.93, 126.72, 118.31, 69.67, 46.96, 35.14, 30.13, 23.68, 19.17; *m*/*z* (EI-MS) 134 (M−$H_2O^+$, 98%, $C_{10}H_{14}$ requires 134), 91 (100%). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59%. Found: C, 78.75; H, 10.82%.

**(*E*)-3-Methyl-1-phenylhex-1,5-dien-3-ol (21).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), benzylideneacetone (396 mg, 2.71 mmol), and $ZnBr_2$ (610 mg, 2.71 mmol) over 4 h to give a crude residue, which was then purified by column chromatography on silica using 20% $Et_2O$−hexanes as an eluent to give the alcohol[25] (373 mg, 73%) as a colorless oil: IR (film) 3409 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.48−7.15 (m, 5H), 6.60 (d, $J$ = 16.0 Hz, 1H), 6.28 (d, $J$ = 16.0 Hz, 1H), 5.94−5.72 (m, 1H), 5.22−5.06 (m, 2H), 2.39 (t, $J$ = 7.0 Hz, 2H), 2.00 (broad s, 1H), 1.37 (s, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 136.78, 136.10, 133.50, 128.46, 127.28, 126.32, 119.15, 72.26, 47.22, 27.81; *m*/*z* (EI-MS) 188 ($M^+$, 1%, $C_{13}H_{16}O$ requires 188), 147 (100%). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57%. Found: C, 82.85; H, 8.87%.

**1-Allyl-1,2,3,4-tetrahydronaphthalen-1-ol (22).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), α-tetralone (360 $\mu$L, 2.71 mmol), and $ZnBr_2$ (610 mg, 2.71 mmol) over 4 h to give a crude residue, which was then purified by column chromatography on silica using 20% $Et_2O$−hexanes as an eluent to give the alcohol[30] (500 mg, 99%) as a colorless oil: IR (film) 3416 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.60−7.50 (m, 1H), 7.27−7.03 (m, 3H), 5.91−5.70 (m, 1H), 5.18−5.04 (m, 2H), 2.84−2.72 (m, 2H), 2.59 (dt, $J$ = 7.3, 1.0 Hz, 2H), 2.12−1.70 (m, 4H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 141.81, 136.73, 133.99, 128.82, 127.10, 126.32, 126.19, 118.56, 71.89, 46.97, 36.03, 29.70, 19.65; *m*/*z* (EI-MS) 170.1095 (M−$H_2O^+$, 3%, $C_{13}H_{14}$ requires 170.1093), 147 (100%).

**Standard Procedure B, Addition of 13 to Nitriles. 1-Phenylbut-3-en-1-one (23).** A solution of BuLi (2.71 mmol) in pentane (1.40 M, 1.94 mL) was added dropwise over 2 min to a stirred solution of **13** (500 mg, 2.71 mmol) in THF (4 mL) at 0 °C under argon. The resulting solution was then stirred for 15 min, and then a solution $ZnCl_2$ (370 mg, 2.71 mmol) in THF (2 mL) was added, followed by benzonitrile (278 $\mu$L, 2.71 mmol). The reaction was allowed to warm to room temperature and stirred for 1 h. A solution of 0.25 N HCl (15 mL) and $Et_2O$ (30 mL) were added, and the resulting mixture was stirred vigorously for 10 min. The reaction was worked up as usual to give a crude residue, which was purified by column chromatography on silica using 5% $Et_2O$−hexanes as an eluent to give the ketone[31] (289 mg, 73%) as a colorless oil. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 8.05−7.90 (m, 2H), 7.68−7.42 (m, 3H), 6.20−5.98 (m, 1H), 5.27−5.15 (m, 2H), 3.76 (dt, $J$ = 6.8, 1.5 Hz, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 197.91, 136.47, 133.08, 130.97, 128.53, 128.19, 118.61, 43.34.

**1-(4-Bromophenyl)but-3-en-1-one (24).** The reaction was carried out according to standard procedure B using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), 4-bromobenzonitrile (493 mg, 2.71 mmol), and $ZnCl_2$ (370 mg, 2.71 mmol) to give a crude residue, which was then purified by column chromatography on silica using 5% $Et_2O$−hexanes as an eluent to give the ketone[32] (320 mg, 74%), which crystallized on standing: IR (film) 1687 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.83 (d, $J$ = 8 Hz, 2H), 7.60 (d, $J$ = 8 Hz, 2H), 6.06 (m, 1H), 5.29−5.16 (m, 2H), 3.72 (d, $J$ = 6.8 Hz, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 196.90, 135.18, 131.89, 130.59, 129.76, 128.31, 118.97, 43.32; *m*/*z* (EI-MS) 223.9837 ($M^+$, 7%, $C_{10}H_9BrO$ requires 223.9837), 69 (100).

**1-Chlorohept-6-en-4-one (25).** The reaction was carried out according to standard procedure B using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), 4-chlorobutyronitrile (242 $\mu$L, 2.71 mmol), and $ZnCl_2$ (370 mg, 2.71 mmol) to give a crude residue, which was then purified by column chromatography on silica using 5% $Et_2O$−hexanes as an eluent to give the ketone[33] (238 mg, 62%) as a colorless oil: IR (film) 1715 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 6.04−5.81 (m, 1H), 5.23−5.08 (m, 2H), 3.57 (t, $J$ = 6.3 Hz, 2H), 3.19 (dt, $J$ = 7.0, 1.0 Hz, 2H), 2.65 (t, $J$ = 7.0 Hz, 2H), 2.03 (app. quintet, $J$ = 6.5 Hz, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 207.41, 130.26, 119.02, 47.82, 44.33, 38.75, 26.13; *m*/*z* (EI-MS) 146 ($M^+$, 0.3%, $C_7H_{11}ClO$ requires 146), 41 (100).

**Butyl-(1-phenylbut-3-enyl)amine (27).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), benzylidenebutylamine **26** (436 mg, 2.71 mmol), and $ZnCl_2$ (370 mg, 2.71 mmol) to give a crude residue, which was then purified by removal of the bis-(*tert*-butyl)ketone under reduced pressure, <0.1 mm Hg for 3 h, to give the amine[34] (534 mg, 97%) as a colorless oil. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.42−7.18 (m, 5H), 5.84−5.60 (m, 1H), 5.15−4.98 (m, 2H), 3.63 (t, $J$ = 7.2 Hz, 2H), 2.47−2.36 (m, 2H), 1.60−1.25 (m, 4H), 0.87 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 144.13, 135.55, 128.26, 127.13, 126.87, 117.40, 62.66, 47.41, 43.03, 32.28, 20.44, 13.96; *m*/*z* (EI-MS) 162 (M−$C_3H_5^+$, 100%, $C_{11}H_{16}N$ requires 162).

**(1-Allyl-3-methylbut-2-enyl)benzylamine (29).** The reaction was carried out according to standard procedure A using

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**13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), benzyl-(3-methylbut-2-enylidene)amine **28** (468 mg, 2.71 mmol), and $ZnCl_2$ (370 mg, 2.71 mmol) to give a crude residue, which was then purified by column chromatography on silica using 25−100% $Et_2O$−hexanes as an eluent to give the amine[35] (522 mg, 90%) as a colorless oil. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.35−7.16 (m, 5H), 5.87−5.63 (m, 1H), 5.15−4.97 (m, 3H), 3.81 (d, $J$ = 13.3 Hz, 1H), 3.62 (d, $J$ = 13.3 Hz, 1H), 3.43−3.30 (m, 1H), 2.25−2.14 (m, 2H), 1.74 (d, $J$ = 1.2 Hz, 3H), 1.58 (d, $J$ = 1.5 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 140.75, 135.53, 133.82, 128.24, 128.06, 127.85, 126.66, 116.93, 54.53, 51.19, 40.57, 25.81, 18.33; *m*/*z* (EI-MS) 174 ($M-C_3H_5^+$, 68%, $C_{12}H_{16}N$ requires 174), 91 (100%).

**(1-Allylhexyl)benzylamine (31).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), benzylhexylideneamine **30** (512 mg, 2.71 mmol), and $ZnCl_2$ (370 mg, 2.71 mmol) to give a crude residue, which was then purified by column chromatography on silica using 20−35% $Et_2O$−hexanes as an eluent to give the amine[36] (393 mg, 63%) as a colorless oil: IR (film) 3442 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.36−7.15 (m, 5H), 5.90−5.65 (m, 1H), 5.16−5.02 (m, 2H), 3.77 (s, 2H), 2.67−2.54 (m, 1H), 2.35−2.06 (m, 2H), 1.53−1.20 (m, 8H), 0.88 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 140.82, 135.80, 128.30, 128.11, 126.76, 117.07, 56.14, 51.15, 38.33, 33.83, 32.06, 25.36, 22.63, 14.04; *m*/*z* (EI-MS) 190 ($M-C_3H_5^+$, 43%, $C_{13}H_{20}N$ requires 190), 91 (100%). Anal. Calcd for $C_{16}H_{25}N$: C, 83.06; H, 10.89; N, 6.05%. Found: C, 82.81; H, 11.04; N, 6.06%.

**Benzyl-(1-cyclohexylbut-3-enyl)amine (33).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), benzylcyclohexylmethyleneamine **32** (545 mg, 2.71 mmol), and $ZnCl_2$ (370 mg, 2.71 mmol) to give a crude residue, which was then purified by column chromatography on silica using 15−40% $Et_2O$−hexanes as an eluent to give the amine[37] (414 mg, 63%) as a colorless oil: IR (film) 3330 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.42−7.14 (m, 5H), 5.95−5.65 (m, 1H), 5.17−5.01 (m, 2H), 3.75 (s, 2H), 2.48−2.03 (m, 3H), 1.87−0.83 (m, 11H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 142.09, 136.66, 128.24, 128.14, 126.70, 116.76, 61.24, 51.90, 40.57, 35.28, 29.41, 28.83, 26.81, 26.69, 26.24; *m*/*z* (EI-MS) 202 ($M-C_3H_5^+$, 64%, $C_{14}H_{20}N$ requires 202), 91 (100%).

**Benzyl-(1-methyl-1-phenylbut-3-enyl)amine (35).** The reaction was carried out according to standard procedure A using **13** (500 mg, 2.71 mmol), BuLi (2.71 mmol), benzyl (1-phenylethylidene)amine **34** (567 mg, 2.71 mmol), and $ZnCl_2$ (370 mg, 2.71 mmol) to give a crude residue, which was then purified by column chromatography on silica using 15% $Et_2O$−hexanes as an eluent to give the amine[37] (458 mg, 67%) as a colorless oil. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.99−7.91 (m, 1H), 7.60−7.16 (m, 9H), 5.78−5.55 (m, 1H), 5.16−5.02 (m, 2H), 3.60−3.40 (m, 2H), 2.65−2.40 (m, 2H), 1.49 (s, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 146.57, 141.23, 134.21, 133.02, 128.51, 128.26, 128.12, 128.06, 126.68, 126.29, 118.15, 58.27, 47.38, 46.89, 25.59; *m*/*z* (EI-MS) 162 ($M-C_7H_5^+$, 100%, $C_{11}H_{16}N$ requires 162).

**2-Methylenepent-4-en-1-ol (36).** A solution of BuLi (5.4 mmol) in pentane (1.40 M, 3.9 mL) was added dropwise over 5 min to a stirred solution of **13** (1.0 g, 5.4 mmol) in THF (8 mL) at 0 °C under argon. The resulting solution was stirred for 15 min, and then a solution of $ZnCl_2$ (741 mg, 5.4 mmol) in THF (2 mL) was added, followed by trimethylprop-2-ynyloxysilane (347 mg, 2.71 mmol) in THF (1 mL). The reaction was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was poured into 2 N HCl solution (10 mL) and $Et_2O$ (10 mL) and stirred for 15 min, before being worked up as usual to give a crude residue, which was then purified by column chromatography on silica using 25% $Et_2O$−hexanes as an eluent to give the alcohol[38] (202 mg, 74%) as a colorless oil: IR (film) 3333 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.93−5.71 (m, 1H), 5.16−5.05 (m, 2H), 5.06−5.02 (m, 1H), 4.92 (d, $J$ = 1.2 Hz, 1H), 4.08 (s, 2H), 2.82 (d, $J$ = 7 Hz, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 147.22, 135.70, 116.49, 110.45, 65.59, 37.55.

**3-*tert*-Butyl-2,2,4-trimethylhex-5-en-3-ol (37).** Crotyl chloride (9.7 mL, 0.10 mol) in THF (10 mL) was added dropwise over 20 min to magnesium (2.48 g, 0.1 mol) in THF (50 mL) at 0 °C under argon. Upon complete addition, the reaction was stirred at 0 °C for 10 min and then warmed to room temperature and stirred for 30 min, before being cooled to 0 °C. Pivaldehyde (5.5 mL, 50 mmol) in THF (10 mL) was then added dropwise over 10 min, warmed to room temperature, and stirred for a further 30 min. The reaction was quenched cautiously with saturated aqueous $NH_4Cl$ solution (50 mL) and worked up as usual.

Chromic acid (prepared from $Na_2Cr_2O_7 \cdot 2H_2O$ (10 g, 33.5 mmol), concentrated $H_2SO_4$ (7.5 mL, 0.13 mol), and $H_2O$ (50 mL)) was added dropwise over 30 min to a stirred solution of the crude alcohol in $Et_2O$ (40 mL), maintaining the internal temperature below 30 °C. Upon complete addition, the reaction was stirred at room temperature for 2 h. The organic phase was extracted with $Et_2O$ (2 × 50 mL), and then combined and washed with $H_2O$ (50 mL) and brine (50 mL). The resulting solution was dried and then concentrated under reduced pressure to give the crude ketone.

The crude ketone in $Et_2O$ (10 mL) was added dropwise over 15 min to a stirred solution of *t*-BuLi (70 mmol) in pentane (1.48 M, 47.3 mL) at −78 °C under argon. The mixture was then stirred for 1.5 h at −78 °C and quenched by careful addition of $NH_4Cl$ solution (50 mL) at −78 °C. The mixture was warmed to room temperature and extracted with $Et_2O$ (3 × 50 mL), and the combined organic extracts were washed with brine (50 mL), dried, and concentrated under reduced pressure. The mixture was purified by distillation, 70−71 °C, 1 mmHg, to yield the alcohol[5b] (6.51 g, 65%) as a colorless oil: IR (film) 3578 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 6.20−6.01 (m, 1H), 5.13−4.98 (m, 2H), 3.08−2.91 (m, 1H), 1.37 (d, $J$ = 7.2 Hz, 3H), 1.16 (s, 9H), 1.14 (s, 9H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 143.88, 116.16, 80.33, 46.13, 43.46, 43.07, 30.11, 49.66, 19.67; *m*/*z* (EI-MS) 143 ($M-C_4H_7^+$, 3%, $C_9H_{19}O$ requires 143), 57 (100%). Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21%. Found: C, 78.82; H, 13.00%.

**Standard Procedure C, Addition of Substituted Allylic Zinc Reagents to Electrophiles. *anti*-2-Methyl-1-phenyl-3-buten-1-ol (39).** A solution of *n*-BuLi (2.52 mmol) in pentane (1.60 M, 1.58 mL) was added dropwise over 5 min to a stirred solution of **37** (500 mg, 2.52 mmol) in THF (4 mL) at −78 °C under argon. The resulting solution was stirred for 15 min, at which time PhCHO (256 $\mu$L, 2.52 mmol) was added, and stirred for a further 15 min. Finally, a solution of $ZnCl_2$ (343 mg, 2.52 mmol) in THF (2 mL) was added over 3 min. The reaction was stirred at −78 °C for 1 h then allowed to warm to room temperature. The reaction was worked up as described previously in standard procedure A to give a crude residue, which was then purified by column chromatography on silica using 10% $Et_2O$−hexanes as an eluent to give the alcohol[39] (341 mg, 83%) as a pale-yellow oil: IR (film) 3418 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.38−7.22 (m, 5H), 5.90−5.70 (m, 1H), 5.23−5.12 (m, 2H), 4.33 (dd, $J$ = 7.8, 2.5 Hz, 1H), 2.56−2.37 (m, 1H), 2.29 (broad s, 1H), 0.85 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 142.39, 140.58, 128.14, 127.53, 126.76, 116.66, 78.26, 46.66, 16.92; *m*/*z* (EI-MS) 162 ($M-OH^+$, 1%, $C_{11}H_{13}$ requires 145), 107 (100%). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%. Found: C, 81.35; H, 8.56%.

***anti*-1-Cyclohexyl-2-methyl-3-buten-1-ol (40).** The reaction was carried out according to standard procedure C using **37** (500 mg, 2.52 mmol), BuLi (2.52 mmol), cyclohexane carboxaldehyde (304 $\mu$L, 2.52 mmol), and $ZnCl_2$ (343 mg, 2.52 mmol) to give a crude residue, which was then purified by column chromatography on silica using 15% $Et_2O$−hexanes

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as an eluent to give the alcohol[39] (356 mg, 84%) as a colorless oil: IR (film) 3396 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 5.88−5.68 (m, 1H), 5.15−5.02 (m, 2H), 3.10 (app. t, $J$ = 5.8 Hz, 1H), 2.46−2.26 (m, 1H), 1.90−1.10 (m, 11H), 1.02 (d, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 140.31, 115.97, 78.75, 40.44, 40.25, 29.89, 27.00, 26.42, 26.37, 26.06, 16.90.

***anti*-3-Methyl-5-ethyl-1-hepten-4-ol (41).** The reaction was carried out according to standard procedure C using **37** (500 mg, 2.52 mmol), BuLi (2.52 mmol), 2-ethylbutyraldehyde (310 $\mu$L, 2.52 mmol), and $ZnCl_2$ (343 mg, 2.52 mmol) to give a crude residue, which was then purified by column chromatography on silica using 8% $Et_2O$−hexanes as an eluent to give the alcohol[40] (340 mg, 86%) as a colorless oil: IR (film) 3458 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 5.87−5.67 (m, 1H), 5.19−5.06 (m, 2H), 3.36−3.27 (m, 1H), 2.36 (app. sextet, $J$ = 7 Hz, 1H), 1.65−1.15 (m, 5H), 1.00 (d, $J$ = 6.8 Hz, 3H), 0.96−0.84 (m, 6H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 141.03, 116.21, 75.42, 42.84, 41.40, 22.34, 20.27, 11.75, 11.32; *m*/*z* (EI-MS) 101 (M−$C_4H_7^+$, 40%, $C_6H_{13}O$ requires 101), 59 (100). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.99%. Found: C, 76.60; H, 12.97%.

***anti*-3-Methyl-5-methylenylnon-2-en-4-ol (42).** The reaction was carried out according to standard procedure C using **37** (500 mg, 2.52 mmol), BuLi (2.52 mmol), 2-butylacrolein (335 $\mu$L, 2.52 mmol), and $ZnCl_2$ (343 mg, 2.52 mmol) to give a crude residue, which was then purified by column chromatography on silica using 8% $Et_2O$−hexanes as an eluent to give the alcohol (321 mg, 76%) as a colorless oil: IR (film) 3441 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 5.88−5.63 (m, 1H), 5.21−4.87 (m, 4H), 3.79 (d, $J$ = 7.3 Hz, 1H), 2.48−2.28 (m, 1H), 2.25−1.85 (m, 2H), 1.79 (broad s, 1H), 1.56−1.28 (m, 4H), 1.04−0.86 (m, 6H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 149.68, 140.38, 116.41, 111.29, 79.18, 41.89, 30.45, 30.00, 22.66, 16.68, 13.98; *m*/*z* (EI-MS) 113 (M−$C_4H_7^+$, 20%, $C_7H_{13}O$ requires 113), 71 (100%). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%. Found: C, 78.55; H, 12.06%.

***anti*-2-Methyl-1-(1-naphthyl)-3-buten-1-ol (43).** The reaction was carried out according to standard procedure C using **37** (500 mg, 2.52 mmol), BuLi (2.52 mmol), 1-naphthylaldehyde (342 $\mu$L, 2.52 mmol), and $ZnCl_2$ (343 mg, 2.52 mmol) to give a crude residue, which was then purified by column chromatography on silica using 10% $Et_2O$−hexanes as an eluent to give the alcohol (490 mg, 92%) as a pale-yellow oil: IR (film) 3427 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 8.26−8.15 (m, 1H), 7.95−7.77 (m, 2H), 7.64−7.44 (m, 4H), 6.01−5.81 (m, 1H), 5.27−5.16 (m, 3H), 2.86 (app. sextet, $J$ = 7 Hz, 1H), 2.26 (broad s, 1H), 0.99 (d, $J$ = 6.7 Hz, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 140.16, 138.33, 133.81, 130.91, 128.86, 128.03, 125.79, 125.37, 125.19, 124.41, 123.51, 116.75, 74.67, 45.14, 17.09; *m*/*z* (EI-MS) 212 ($M^+$, 1%, $C_{15}H_{16}O$ requires 212), 157 (100%). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60%. Found: C, 84.68; H, 7.46%.

***anti*-1-(2-Furyl)-2-methyl-3-buten-1-ol (44).** The reaction was carried out according to standard procedure C using **37** (500 mg, 2.52 mmol), BuLi (2.52 mmol), furfural (209 $\mu$L, 2.52 mmol), and $ZnCl_2$ (343 mg, 2.52 mmol) to give a crude residue, which was then purified by column chromatography on silica using 20% $Et_2O$−hexanes as an eluent to give the alcohol[41] (320 mg, 84%) as a colorless oil: IR (film) 3431 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) (major diastereomer) $\delta$ 7.43−7.33 (m, 1H), 6.36−6.28 (m, 2H), 5.90−5.68 (m, 1H), 5.28−5.12 (m, 2H), 4.42 (d, $J$ = 7.6 Hz, 1H), 2.80−2.60 (m, 1H), 2.18 (broad s, 1H), 0.93 (d, $J$ = 6.7 Hz, 3H), (minor diastereomer) $\delta$ 7.28−7.24 (m, 1H), 5.10−5.02 (m, 2H), 4.55 (d, $J$ = 6.2 Hz, 1H), 1.06 (d, $J$ = 6.7 Hz, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) (major diastereomer) $\delta$ 154.96, 141.88, 139.93, 116.84, 110.01, 107.15, 71.28, 43.49, 16.14, (minor diastereomer) $\delta$ 155.29, 141.88, 139.93, 116.76, 109.96, 106.76, 71.28, 42.96, 14.99; *m*/*z* (EI-MS) 152 ($M^+$, 1%, $C_9H_{12}O_2$ requires 152), 97 (100).

***anti*-2-Phenyl-3-methyl-4-penten-2-ol (45).** The reaction was carried out according to standard procedure C using **37** (500 mg, 2.52 mmol), BuLi (2.52 mmol), acetophenone (293 $\mu$L, 2.52 mmol), and $ZnCl_2$ (343 mg, 2.52 mmol) to give a crude residue, which was then purified by column chromatography on silica using 20% $Et_2O$−hexanes as an eluent to give the alcohol[42] (397 mg, 90%) as a colorless oil: IR (film) 3468 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) (major diastereomer) $\delta$ 7.50−7.15 (m, 5H), 5.92−5.58 (m, 1H), 5.17−5.03 (m, 2H), 2.70−2.45 (m, 1H), 1.99 (broad s, 1H), 1.51 (s, 3H), 0.96 (d, $J$ = 6.8 Hz, 3H), (minor diastereomer) $\delta$ 0.86 (d, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) (major diastereomer) $\delta$ 146.99, 139.91, 127.83, 126.56, 125.43, 116.52, 75.63, 48.72, 25.83, 14.05, (minor diastereomer) $\delta$ 126.37, 125.15, 116.22, 51.39, 30.93, 17.23; *m*/*z* (EI-MS) 158 (M−$H_2O^+$, 1%, $C_{12}H_{14}$ requires 158), 43 (100). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%. Found: C, 81.56; H, 8.82%.

**3-*tert*-Butyl-2,2-dimethyl-4-ethylhex-5-en-3-ol (46).** This was prepared in a manner similar to that for **37** using 1-chloropent-2-ene (3.06 g, 29.3 mmol) and pivaldehyde (3.23 mL, 29.3 mmol). The crude residue was purified by column chromatography on silica using 2% $Et_2O$−hexanes as an eluent to give the alcohol (2.63 g, 74%) as a colorless oil: IR (film) 3578 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 5.95−5.74 (m, 1H), 5.24 (dd, $J$ = 10.0, 2.2 Hz, 1H), 5.05 (dd, $J$ = 17.0, 2.2 Hz, 1H), 2.63−2.49 (m, 1H), 2.18−1.98 (m, 1H), 1.70−1.43 (m, 1H), 1.16 (s, 9H), 1.13 (s, 9H), 0.85 (app. t, $J$ = 7 Hz, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 141.81, 119.51, 80.16, 56.16, 43.56, 43.04, 30.44, 29.63, 25.19, 14.22; *m*/*z* (EI-MS) 143 (M−$C_5H_9^+$, 1%, $C_9H_{19}O$ requires 143), 57 (100%). Anal. Calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29. Found: C, 79.14; H, 13.56%.

***anti*-2-Ethyl-1-phenyl-3-buten-1-ol (47).** The reaction was carried out according to standard procedure C using **46** (500 mg, 2.35 mmol), BuLi (2.35 mmol), PhCHO (239 $\mu$L, 2.35 mmol), and $ZnCl_2$ (321 mg, 2.35 mmol) to give a crude residue after stirring for 1 h at −78 °C and then warming to −50 °C. This residue was then purified by column chromatography on silica using 20% $Et_2O$−hexanes as an eluent to give the alcohol[43] (378 mg, 91%) as a colorless oil: IR (film) 3412 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) (major diastereomer) $\delta$ 7.40−7.21 (m, 5H), 5.75−5.55 (m, 1H), 5.30−5.12 (m, 2H), 4.38 (d, $J$ = 7.8 Hz, 1H), 2.38−2.10 (m, 1H), 1.85−1.05 (m, 2H), 0.78 (app. t, $J$ = 7.5 Hz, 3H), (minor diastereomer) $\delta$ 5.58−5.38 (m, 1H), 5.11−4.94 (m, 2H); $^{13}C$ NMR (50 MHz, $CDCl_3$) (major diastereomer) $\delta$ 142.54, 139.04, 128.15, 127.54, 126.89, 118.83, 76.66, 54.51, 23.32, 11.69, (minor diastereomer) $\delta$ 138.20, 117.38, 53.16, 22.54, 13.95; *m*/*z* (EI-MS) 107 (M−$C_5H_9^+$, 100%, $C_7H_7O$ requires 107), 79 (45%). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.72; H, 9.12%.

***anti*-1-Cyclohexyl-2-ethyl-3-buten-1-ol (48).** The reaction was carried out according to standard procedure C using **46** (500 mg, 2.35 mmol), BuLi (2.35 mmol), cyclohexane carboxaldehyde (286 $\mu$L, 2.35 mmol), and $ZnCl_2$ (321 mg, 2.35 mmol) to give a crude residue after stirring for 2 h at −78 °C and then slowly warming to −30 °C. The crude residue was then purified by column chromatography on silica using 15−20% $Et_2O$−hexanes as an eluent to give the alcohol[43] (355 mg, 83%) as a colorless oil: IR (film) 3394 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) 5.77−5.56 (m, 1H), 5.23−5.03 (m, 2H), 3.19 (app. t, $J$ = 5.5 Hz, 1H), 2.18−1.99 (m, 1H), 1.95−0.95 (m, 13H), 0.87 (t, $J$ = 7.4 Hz, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 138.59, 117.48, 77.41, 48.45, 40.46, 29.68, 27.61, 26.48, 26.33, 26.06, 23.92, 11.84; *m*/*z* (EI-MS) 113 (M−$C_5H_9^+$, 19%, $C_7H_{13}O$ requires 113), 95 (100%). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.88; H, 12.38%.

***anti*-3,5-Diethyl-1-hepten-4-ol (49).** The reaction was carried out according to standard procedure C using **46** (500 mg, 2.35 mmol), BuLi (2.35 mmol), 2-ethylbutyraldehyde (290 $\mu$L, 2.35 mmol), and $ZnCl_2$ (321 mg, 2.35 mmol) to give a crude residue after 3 h at −78 °C, which was then purified by column chromatography on silica using 15% $Et_2O$−hexanes as an eluent to give the alcohol (325 mg, 81%) as a colorless oil: IR

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(film) 3427 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 5.77−5.55 (m, 1H), 5.24−5.06 (m, 2H), 3.40 (dd, $J$ = 6.2, 4.7 Hz, 1H), 2.17−2.00 (m, 1H), 1.65−1.15 (m, 7H), 0.96−0.83 (m, 9H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 139.19, 117.84, 73.95, 49.25, 42.88, 23.81, 22.01, 20.33, 11.75, 11.55, 11.07; *m/z* (EI-MS) 101 ($M-C_5H_9^+$, 61%, $C_6H_{13}O$ requires 101), 59 (100%). Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.76; H, 12.91%.

**(*E*)-2,2-Dimethylhex-4-en-3-one (50).** *t*-BuMgCl (0.201 mol) in THF (1.7 M, 118 mL) was added dropwise over 1 h to a stirred solution of CuBr (28.8 g, 0.20 mol) and crotonic acid chloride (21.0 g, 0.20 mol) in THF (150 mL) at −10 °C under argon. Upon complete addition, the reaction was warmed slowly to room temperature and stirred for 15 min. The reaction mixture was poured onto ice (200 mL) and acidified with concentrated HCl. The mixture was diluted with $Et_2O$ (200 mL) and filtered. The organic layer was separated, and the aqueous layer was extracted with $Et_2O$ (2 × 100 mL). The combined organic extracts were washed with $H_2O$ (200 mL) and brine (150 mL), and then dried and concentrated under reduced pressure. The crude material was then distilled, 45−50 °C, 10 mmHg, to yield the ketone[44] (10.95 g, 43%) as a colorless oil: IR (film) 1691, 1629 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 6.94 (dq, $J$ = 15.3, 7.0 Hz, 1H), 6.51 (dq, $J$ = 15.3, 1.5 Hz, 1H), 1.88 (dd, $J$ = 7.0, 1.5 Hz, 3H), 1.13 (s, 9H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 204.17, 142.62, 125.76, 42.70, 26.13, 18.18.

**4-Benzyl-2,2-dimethyl-5-hexen-3-one (66).** *n*-BuLi (21. 8 mmol) in pentane (1.5 M, 14.6 mL) was added dropwise over 20 min to a stirred solution of *i*-$Pr_2NH$ (3.08 mL, 21.8 mmol) in THF (20 mL) and HMPA (10 mL) at −78 °C under argon. Upon complete addition, the reaction was stirred for 15 min. A solution of the ketone **50** (2.5 g, 19.8 mmol) in THF (4 mL) was added dropwise over 10 min, and then the solution was stirred for 15 min. Benzyl bromide (2.83 mL, 23.8 mmol) was then added dropwise over 2 min, and the reaction was stirred for a further 3 h. $NH_4Cl$ solution (20 mL) was then added, and the reaction mixture was warmed to room temperature. The organics were extracted with $Et_2O$ (2 × 40 mL), and the combined organic extracts were washed with $H_2O$ (2 × 50 mL) and brine (30 mL), dried, and then concentrated under reduced pressure. The crude residue was then purified by column chromatography on silica using 1−1.5% $Et_2O$−hexanes as an eluent to give the ketone (2.80 g, 65%) as a colorless oil: IR (film) 1704 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.30−7.07 (m, 5H), 5.87−5.67 (m, 1H), 5.10−4.97 (m, 2H), 3.94−3.79 (m, 1H), 3.03 (dd, $J$ = 13.3, 8.2 Hz, 1H), 2.71 (dd, $J$ = 13.3, 6.5 Hz, 1H), 0.93 (s, 9H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 214.99, 139.40, 137.41, 129.32, 128.17, 126.21, 117.10, 53.63, 44.97, 39.54, 25.71; *m/z* (EI-MS) 216.1513 ($M^+$, 7%, $C_{15}H_{20}O$ requires 216.1511), 57 (100%).

**4-Benzyl-3-(*tert*-butyl)-2,2-dimethyl-5-hexen-3-ol (51).** A solution of ketone **66** (2.43 g, 11.3 mmol) in $Et_2O$ (5 mL) was added dropwise over 15 min to a stirred solution of *tert*-BuLi (22.5 mmol) in pentane (1.5 M, 15 mL) at −78 °C under argon. The mixture was then stirred for 2 h at −78 °C and worked up as described for **37**. The crude residue was then purified by column chromatography on silica using 1% $Et_2O$−hexanes as an eluent to give the alcohol (2.63 g, 85%) as a colorless oil: IR (film) 3568 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.30−7.08 (m, 5H), 6.12−5.85 (m, 1H), 5.02 (dd, $J$ = 10.0, 2.0 Hz, 1H), 4.72 (dd, $J$ = 17.0, 2.0 Hz, 1H), 3.50 (dd, $J$ = 13.3, 2.0 Hz, 1H), 3.16−3.01 (m, 1H), 2.80 (dd, $J$ = 13.3, 11.3 Hz, 1H), 1.24 (s, 9H), 1.21 (s, 9H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 142.16, 140.93, 128.98, 128.10, 125.76, 119.31, 80.52, 55.12, 43.65, 43.40, 38.70, 30.40, 30.00; *m/z* (EI-MS) 143 ($M-C_{10}H_{11}^+$, 10%, $C_9H_{19}O$ requires 143), 57 (100%). Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.01. Found: C, 83.05; H, 11.08%.

***anti*-1-Phenyl-2-(phenylmethyl)-3-buten-1-ol (52).** The reaction was carried out according to standard procedure C using **51** (500 mg, 1.82 mmol), BuLi (1.82 mmol), PhCHO (185 $\mu$L, 1.82 mmol), and $ZnCl_2$ (249 mg, 1.82 mmol) to give a crude residue after stirring for 3 h at −78 °C. This residue was then purified by column chromatography on silica using 15% $Et_2O$−hexanes as an eluent to give the alcohol[45] (387 mg, 89%) as a colorless oil: IR (film) 3431 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.41−7.03 (m, 10H), 5.82−5.58 (m, 1H), 5.12 (d, $J$ = 10.3 Hz, 1H), 4.96 (d, $J$ = 17.0 Hz, 1H), 4.53 (d, $J$ = 5.5 Hz, 1H), 2.80−2.03 (m, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 142.51, 139.92, 137.67, 129.08, 128.22, 128.10, 127.55, 126.64, 125.86, 118.81, 75.44, 53.73, 37.17; *m/z* (EI-MS) 132 ($M-C_7H_6O^+$, 31%, $C_{10}H_{12}$ requires 132), 107 (100%). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.72; H, 7.81%.

***anti*-1-Cyclohexyl-2-(phenylmethyl)-3-buten-1-ol (53).** The reaction was carried out according to standard procedure C using **51** (500 mg, 1.82 mmol), BuLi (1.82 mmol), cyclohexanecarboxaldehyde (221 $\mu$L, 1.82 mmol), and $ZnCl_2$ (249 mg, 1.82 mmol) to give a crude residue after stirring for 4 h at −78 °C. The crude residue was then purified by column chromatography on silica using 15% $Et_2O$−hexanes as an eluent to give the alcohol (394 mg, 88%) as a colorless oil: IR (film) 3437 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.33−7.12 (m, 5H), 5.90−5.70 (m, 1H), 5.12 (dd, $J$ = 10.5, 2.0 Hz, 1H), 4.99 (dd, $J$ = 17.3, 2.0 Hz, 1H), 3.14 (dd, $J$ = 7.8, 3.8 Hz, 1H), 2.93−2.49 (m, 3H), 1.98−0.85 (m, 11H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 140.33, 137.46, 129.17, 128.15, 125.82, 117.61, 76.52, 47.54, 40.89, 37.89, 29.17, 28.49, 26.37, 26.09, 25.93; *m/z* (EI-MS) 132 ($M-C_7H_{12}O^+$, 99%, $C_{10}H_{12}$ requires 132), 95 (100%). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.49; H, 9.65%.

***anti*-5-Ethyl-3-(phenylmethyl)-1-hepten-4-ol (54).** The reaction was carried out according to standard procedure C using **51** (500 mg, 1.82 mmol), BuLi (1.82 mmol), 2-ethylbutyraldehyde (225 $\mu$L, 1.82 mmol), and $ZnCl_2$ (249 mg, 1.82 mmol) to give a crude residue after 4 h at −78 °C, which was then purified by column chromatography on silica using 15% $Et_2O$−hexanes as an eluent to give the alcohol (340 mg, 80%) as a colorless oil: IR (film) 3477 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.34−7.11 (m, 5H), 5.80−5.67 (m, 1H), 5.13 (dd, $J$ = 10.5, 2.0 Hz, 1H), 5.00 (dd, $J$ = 17.3, 2.0 Hz, 1H), 3.44−3.33 (m, 1H), 2.92−2.48 (m, 3H), 1.75−1.15 (m, 5H), 0.94−0.75 (m, 6H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 140.24, 137.96, 129.18, 128.15, 125.87, 117.96, 73.39, 48.37, 43.16, 37.93, 21.42, 20.48, 11.22, 10.43; *m/z* (EI-MS) 143 ($M-C_7H_5^+$, 2%, $C_9H_{19}O$ requires 143), 132 (100%). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.54; H, 10.68%.

**3-*tert*-Butyl-2, 2,-dimethylnon-5-yn-3-ol (56a).** 1-Pentyne (1.26 mL, 12.8 mmol) was added dropwise over 5 min to a stirred solution of BuLi (12.8 mmol) in pentane (1.6 M, 8.0 mL) at 0 °C under argon. The resulting mixture was stirred for 15 min, and then the solvents were removed under reduced pressure. HMPA (5 mL) was added followed by a solution of 2, 2-di(*tert*-butyl)oxirane **55** (1.0 g, 6.4 mmol) in HMPA (2 mL). The reaction was stirred at room temperature for 20 h and then quenched with saturated aqueous $NH_4Cl$ solution (20 mL). This was extracted with $Et_2O$ (3 × 30 mL), and the combined organic extracts were washed with $H_2O$ (2 × 20 mL) and then brine (20 mL), dried, and concentrated under reduced pressure. The crude residue was then purified by column chromatography on silica using 2% $Et_2O$−hexanes as an eluent to give the alcohol (1.21 g, 84%) as a colorless oil: IR (film) 3544 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 2.57 (t, $J$ = 2.5 Hz, 2H), 2.42 (s, 1H), 2.21−2.10 (m, 2H), 1.52 (app. sextet, $J$ = 7 Hz, 2H), 1.09 (s, 18H), 0.97 (t, $J$ = 7.5 Hz, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 85.54, 77.84, 77.25, 43.30, 28.78, 25.63, 22.30, 20.86, 13.53; *m/z* (EI-MS) 224 ($M^+$, 1%, $C_{15}H_{28}O$ requires 224), 57 (100%).

**3-*tert*-Butyl-2,2,-dimethyldec-5-yn-3-ol (56b).** The reaction was carried out as described for **56a** using 1-hexyne (2.94 mL, 25.6 mmol) and 2,2-di(*tert*-butyl)oxirane **55** (2.1 g, 12.8 mmol) to give a crude residue, which was purified by column chromatography on silica using 2% $Et_2O$−hexanes as an eluent to give the alcohol (2.17 g, 65%) as a colorless oil: IR (film) 3544 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 2.56 (t, $J$ = 2.5 Hz, 2H), 2.31 (s, 1H), 2.23−2.12 (m, 2H), 1.56−1.30 (m, 4H), 1.08

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(s, 18H), 0.90 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 85.65, 77.63, 77.25, 42.29, 30.94, 28.78, 25.62, 21.97, 18.52, 13.56; *m/z* (EI-MS) 181 ($M-C_4H_7^+$, 2%, $C_{12}H_{21}O$ requires 181), 57 (100%). Anal. Calcd for $C_{16}H_{30}O$: C, 80.60; H, 12.68%. Found: C, 80.40; H, 13.05%.

**(*Z*)-3-*tert*-Butyl-2, 2,-dimethylnon-5-en-3-ol (57).** 5% palladium on $BaSO_4$ (50 mg) was added in one portion to a stirred solution of **56a** (500 mg, 2.23 mmol) in pyridine (5 mL). The resulting mixture was degassed 3 times, and then an atmosphere of $H_2$ was introduced. The reaction was stirred overnight and then diluted with pentane (100 mL) and filtered through a plug of silica. The silica plug was washed with $Et_2O$ (100 mL). The combined organic fractions were washed with aqueous $CuSO_4$ solution (5 × 100 mL), $H_2O$ (100 mL), and brine (50 mL) and then dried and concentrated under reduced pressure to give the homoallylic alcohol (503 mg, 99%) as a colorless oil: IR (film) 3565 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.68−5.41 (m, 2H), 2.46 (d, $J$ = 6.5 Hz, 2H), 2.07 (app. q, $J$ = 7 Hz, 2H), 1.60 (s, 1H), 1.50−1.30 (m, 2H), 1.08 (s, 18H), 0.93 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 132.39, 127.19, 79.64, 42.45, 31.59, 29.55, 28.95, 22.69, 13.89; *m/z* (EI-MS) 169 ($M-C_4H_9^+$, 5%, $C_{11}H_{21}O$ requires 169), 57 (100%). Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36%. Found: C, 79.33; H, 13.27%.

**(*E*)-3-*tert*-Butyl-2, 2,-dimethyldec-5-en-3-ol (58).** A solution of **56b** (325 mg, 1.36 mmol) in THF (3 mL) was added dropwise over 5 min to a stirred mixture of $LiAlH_4$ (207 mg, 5.4 mmol) in THF (8 mL) at room temperature under argon. Upon complete addition, the reaction was heated at reflux for 24 h and then cooled to room temperature. The reaction was quenched by careful addition of EtOAc (5 mL) and then 10% HCl solution (25 mL) and stirred for 15 min. The organics were extracted with $Et_2O$ (3 × 30 mL), and then the combined extracts were washed with brine (20 mL), dried, and concentrated under reduced pressure. The crude residue was then purified by column chromatography on silica using 2% $Et_2O$−hexanes as an eluent to give the alcohol (313 mg, 96%) as a colorless oil: IR (film) 3556 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.58−5.45 (m, 2H), 2.46−2.36 (m, 2H), 2.12−1.98 (m, 2H), 1.68 (s, 1H), 1.43−1.20 (m, 4H), 1.08 (s, 18H), 0.90 (t, $J$ = 7 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 136.18, 127.89, 78.48, 42.28, 36.50, 32.49, 31.64, 28.81, 22.21, 13.91; *m/z* (EI-MS) 183 ($M-C_4H_9^+$, 6%, $C_{12}H_{23}O$ requires 183), 57 (100%). Anal. Calcd for $C_{16}H_{32}O$: C, 79.93; H, 13.41%. Found: C, 79.58; H, 13.36%.

**(*E*)- and (*Z*)-1-Phenyl-3-hepten-1-ol (59).** The reaction was carried out according to standard procedure C using **57** (452 mg, 2.0 mmol), BuLi (2.0 mmol), PhCHO (202 $\mu$L, 2.0 mmol), and $ZnCl_2$ (272 mg, 2.0 mmol). After warming to room temperature, the reaction was stirred for 80 h to give a crude residue, which was then purified by column chromatography on silica using 2−10% $Et_2O$−hexanes as an eluent to give first recovered starting material (180 mg, 40%) and then the alcohol[46] (197 mg, 52%) as a colorless oil. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.40−7.17 (m, 5H), 5.65−5.28 (m, 2H), 4.70−4.59 (m, 1H), 2.60−2.35 (m, 2H), 2.22 (broad s, 1H), 2.07−1.92 (m, 2H), 1.48−1.25 (m, 2H), 0.88 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) ((*Z*)isomer) $\delta$ 144.07, 133.40, 128.28, 127.39, 125.80, 124.79, 73.86, 37.23, 29.38, 22.64, 13.70, ((*E*)isomer) $\delta$ 143.99, 134.83, 127.30, 125.56, 73.44, 42.74, 34.65, 22.45, 13.58.

**(*E*)- and (*Z*)-1-Phenyl-3-octen-1-ol (60).** The reaction was carried out according to standard procedure C using **58** (265 mg, 1.1 mmol), BuLi (1.1 mmol), PhCHO (113 $\mu$L, 1.1 mmol), and $ZnCl_2$ (151 mg, 1.1 mmol). After warming to room temperature, the reaction was stirred for 12 h to give a crude residue, which was then purified by column chromatography on silica using 2−20% $Et_2O$−hexanes as an eluent to give first recovered starting material (195 mg, 74%) and then the alcohol[47] (52 mg, 23%) as a colorless oil. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.37−7.15 (m, 5H), 5.65−5.25 (m, 2H), 4.72−4.58 (m, 1H), 2.65−2.35 (m, 2H), 2.18−1.95 (m, 3H), 1.40−1.14 (m, 4H), 0.97−0.80 (m, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) ((*Z*)-isomer) $\delta$ 144.07, 133.67, 128.29, 127.41, 125.81, 124.56, 73.87, 37.23, 31.68, 27.07, 22.28, 13.91, ((*E*)-isomer) $\delta$ 143.99, 135.10, 128.27, 127.31, 125.77, 125.35, 73.42, 42.76, 32.26, 31.49, 22.12, 13.87.

**3-(*tert*-Butyl)-2, 2, 6-trimethyl-5-hepten-3-ol (61).** A solution of 2,2,6-trimethylhept-5-en-3-one (4.10 g, 26.6 mmol) in $Et_2O$ (10 mL) was added dropwise over 10 min to a stirred solution of *tert*-BuLi (40 mmol) in pentane (1.48 M, 27 mL) at −78 °C under argon. The mixture was then stirred for 1 h at −78 °C and worked up as described for **37**. The crude residue was then purified by column chromatography on silica using 2−5% $Et_2O$−hexanes as an eluent to give the alcohol (334 mg, 6%) as a colorless oil: IR (film) 3633 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.38−5.26 (m, 1H), 2.38 (d, $J$ = 7.3 Hz, 2H), 1.75 (s, 3H), 1.67 (s, 3H), 1.08 (s, 18H);$^{13}$C NMR (50 MHz, $CDCl_3$) 134.24, 121.94, 79.66, 42.37, 32.43, 28.99, 26.48, 18.05; *m/z* (EI-MS) 155 ($M-C_4H_9^+$, 7%, $C_{10}H_{11}O$ requires 155), 57 (100%).

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**Supporting Information Available:** Copies of $^1$H and $^{13}$C NMR spectra of compounds **42**, **43**, **46**, **49, 51, 53**, **54**, **56a**, **56b**, **57**, **58**, **61**, and **66** (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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