Benzotriazole-Mediated [2,3]-Wittig Rearrangement. General and Stereocontrolled Syntheses of Homoallyl Alcohols and β,γ-Unsaturated Ketones

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Readily accessible allyl 1-(benzotriazol-1-yl)alkyl ethers (**13** and **19**), upon treatment with 2.5 equiv of nucleophilic lithium reagents, give secondary and tertiary homoallyl alcohols (**16** and **21**), respectively, exclusively in the *E* configuration in excellent yields. This is achieved by deprotonation followed by [2,3]-Wittig rearrangement, departure of the benzotriazolyl group, and then nucleophilic addition to the resulting carbonyl compound. Following a similar protocol, primary *E*-homoallyl alcohols **18** are prepared in good yield by the reaction of ethers **13** with LDA in the presence of $NaBH_4$. Our approach complements the stereochemical *Z*-selective syntheses of primary homoallyl alcohols of Still and of Bruckner. Wittig rearrangement of the anions of **19** generated with LDA analogously furnishes *E*-β,γ-unsaturated ketones **20** in excellent yields.

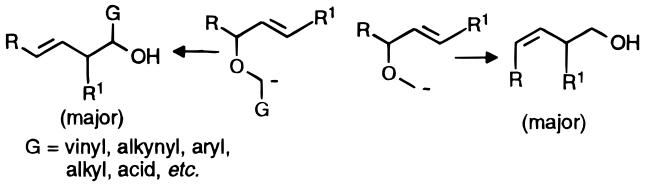
Introduction

[2,3]-Wittig rearrangement has become a powerful strategy in organic chemistry, as demonstrated by its numerous applications in natural product synthesis.[1,2] One of its attractive features is the stereoselective generation of a double bond due to a concerted, highly ordered transition state.[1,3,4] While the parent lithio methyl allyl ethers normally give, predominantly or exclusively, *Z*-homoallyl alcohols, analogs in which the methyl group carries a G substituent usually favor the formation of *E* isomers, especially when G is a "hydrocarbon" (vinyl, alkynyl, aryl, alkyl) (Scheme 1). These trends are accommodated by the favored transition state configurations.[1,4]

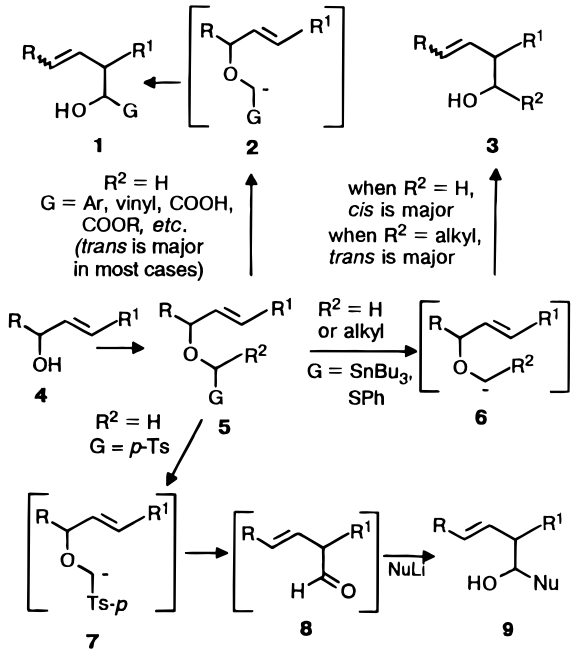
[2,3]-Wittig rearrangements of various allyl ethers **5** (Scheme 2) to provide a wide range of homoallyl alcohols have been reported.[1] The chemical and sterical outcomes of the rearrangements largely depend on the nature of the G substituent on the migrating terminus in **5** as shown by the following classification:

(i) G is an Electron-Withdrawing Group (e.g., COOH,[5] $CONR_2$,[6] propargyl[7] and Ar[8]). These groups facilitate the rearrangement by promoting the formation of the intermediate anions **2** to furnish α-G-substituted homoallyl alcohols **1**. However, since the G group remains in the molecule after the rearrangement, reactions of this type are restricted to the preparation of certain specific homoallyl alcohols.

Scheme 1



Scheme 2



(ii) G Can Be Exchanged for a Lithium Atom by the Action of BuLi (e.g., $SnBu_3$ and SPh). Still *et al.* reported a convenient *Z*-selective access to primary homoallyl alcohols **3** (R^2 = H) from stannylated ethers **5** (R^2 = H, G = $SnBu_3$) *via* tin/lithium exchange and rearrangement.[9,10] A similar transformation was achieved by Bruckner *et al. via* a reductive cleavage of allyl

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(1) For reviews, see: (a) Mikami, K.; Nakai, T. *Synthesis* **1991**, 594. (b) Nakai, T.; Mikami, K. *Chem. Rev.* **1986**, *86*, 885. (c) Marshall, J. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 3, p 975. (d) Bruckner, R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 6, p 873.

(2) For examples, see: (a) Sugimura, T.; Paquette, L. A. *J. Am. Chem. Soc.* **1987**, *109*, 3017. (b) Marshall, J. A.; Lebreton, J. *J. Am. Chem. Soc.* **1988**, *110*, 2925. (c) Bruckner, R. *Tetrahedron Lett.* **1988**, *29*, 5747.

(3) Wu, Y.-D.; Houk, K. N.; Marshall, J. A. *J. Org. Chem.* **1990**, *55*, 1421.

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(7) Sayo, N.; Shirai, F.; Nakai, T. *Chem. Lett.* **1984**, 255.

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(9) Still, W. C.; Mitra, A. *J. Am. Chem. Soc.* **1978**, *100*, 1927.

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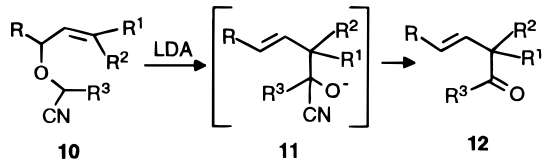
Scheme 3



(phenylthio)methyl ethers **5** (R^2 = H, G = SPh) and subsequent rearrangement.[11] This methodology has been further extended to the rearrangement of allyl (phenylthio)alkyl ethers **5** (R^2 = alkyl, G = SPh) to provide secondary homoallyl alcohols with *E* configuration.[4,12] However, tertiary homoallyl alcohols and primary homoallyl alcohols with *E* selectivity are not accessible by these approaches.

(iii) G Functions as Both an Electron-Withdrawing and a Leaving Group in the Rearrangement Process (e.g., sulfonyl group). The anions **7** of (allyloxy)methyl sulfones **5** (R_2 = H, G = *p*-Ts) undergo [2,3]-Wittig rearrangement followed by the departure of the sulfonyl group and the incorporation of an additional alkyl group into the molecule, to give secondary *E*-homoallyl alcohols **9**.[13] In this case, the sulfonyl group not only activates the α-CH_2 group toward proton loss but also departs to furnish a new functionality (a formyl group in **8**) which provides possibilities for further transformations. However, the reported examples of this method are limited to the synthesis of secondary alcohols.

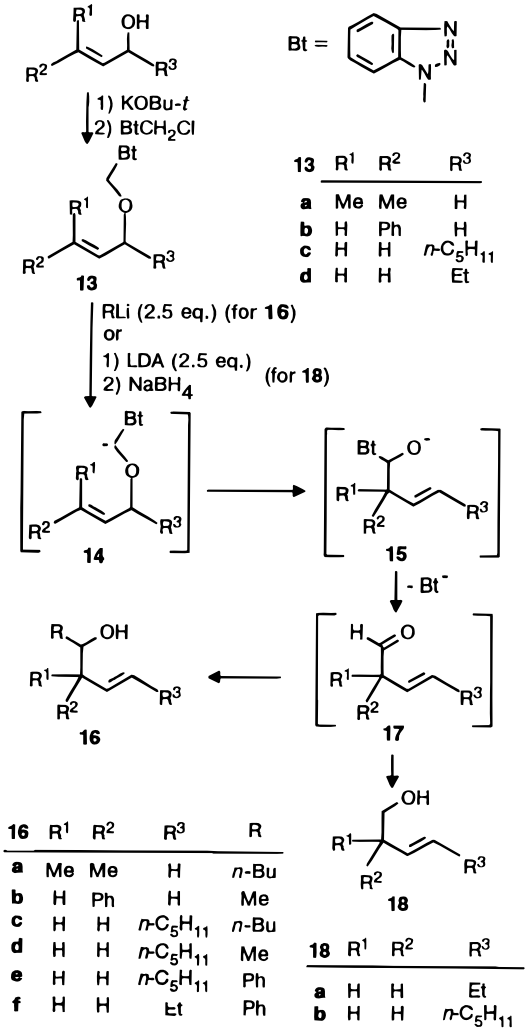
[2,3]-Wittig rearrangement has also been applied to the preparation of *β*,*γ*-unsaturated ketones (Scheme 3). Deprotonation of the allyl ethers of the cyanohydrins **10** effects the rearrangement to the transient *β*,*γ*-unsaturated cyanohydrins **11**, which are transformed to the ketones **12**.[14] However, syntheses of **10** suffer from low yields as well as the products **12** being contaminated with the corresponding α,*β*-unsaturated ketones when R^1 and/or R^2 is hydrogen.

In the course of our investigation on the use of benzotriazole derivatives in organic synthesis,[15] we found that the benzotriazolyl group is both a good anion-stabilizing group and a good leaving group. These properties coupled with the ready accessibility of such derivatives encouraged us to investigate benzotriazole-mediated [2,3]-Wittig rearrangements and their synthetic potential. We now report that the benzotriazole derivatives **13** and **19** can be readily lithiated and the resulting anions undergo facile [2,3]-Wittig rearrangement to provide, in excellent yields, primary (**18**), secondary (**16**), and tertiary (**21**) *E*-homoallyl alcohols and *E*-*β*,*γ*-unsaturated ketones (**20**), respectively, depending on the reaction conditions and reagents used.

Results and Discussion

Preparation of Allyl (Benzotriazol-1-yl)methyl Ethers 13 and Allyl 1-(Benzotriazol-1-yl)alkyl Ethers 19. When allylic alcohols were deprotonated with *t*-BuOK and alkylated with 1-(chloromethyl)benzotriazole in DMF at room temperature, the corresponding allyl (benzotriazol-1-yl)methyl ethers **13a**−**d** were produced in 63−83% yields (Scheme 4). Allyl 1-(benzotriazol-1-yl)benzyl ethers **19a**−**e** were prepared in 53−71% yields from the condensation reactions of benzotriazole, an allyl alcohol, and an aromatic aldehyde in the presence of molecular sieves and *p*-toluenesulfonic acid (Scheme 5). Ethers **19d** and **19e** were mixtures of diastereoisomers which did not need separating for the subsequent transformations. Compounds **13** and **19** were fully characterized by their NMR spectra and elemental analyses (or HRMS).

Scheme 4



13	R^1	R^2	R^3
a	Me	Me	H
b	H	Ph	H
c	H	H	n-C_5H_{11}
d	H	H	Et

16	R^1	R^2	R^3	R
a	Me	Me	H	n-Bu
b	H	Ph	H	Me
c	H	H	n-C_5H_{11}	n-Bu
d	H	H	n-C_5H_{11}	Me
e	H	H	n-C_5H_{11}	Ph
f	H	H	Et	Ph

18	R^1	R^2	R^3
a	H	H	Et
b	H	H	n-C_5H_{11}

Preparation of Secondary and Primary *E*-Homoallyl Alcohols. Treatment of compounds **13a**−**d** with 2.5 equiv of a nucleophilic alkyl- or aryllithium reagent at −78 °C provided secondary homoallyl alcohols **16a**−**f** in good yields (81−87%) (Scheme 4). These transformations are envisaged to proceed *via* deprotonation to **14** followed by [2,3]-Wittig rearrangement to form intermediates **15**, which undergo expulsion of the benzotriazolyl anion to form aldehydes **17** and subsequent *in situ* nucleophilic addition of a second molecule of the lithium reagent to give the desired products **16**. When secondary allyl ethers **13c**,**d** ($R^3 \neq$ H) were the substrates, the homoallyl alcohols thus produced (**16c**−**f**) existed exclusively in the *E* configuration as indicated by their olefinic coupling constants (*J ca.* 15 Hz). Also noteworthy is the fact that, in spite of the formation of a quarternary center

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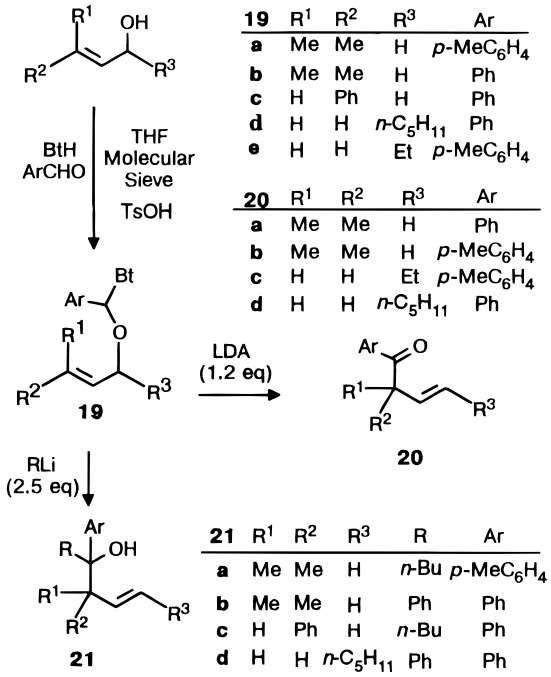
(11) Kruse, B.; Bruckner, R. *Chem. Ber.* **1989**, *122*, 2023.
(12) Broka, C. A.; Shen, T. *J. Am. Chem. Soc.* **1989**, *111*, 2981.
(13) Bruckner, R.; Peiseler, B. *Tetrahedron Lett.* **1988**, *29*, 5233.
(14) Cazes, B.; Julia, S. *Tetrahedron Lett.* **1974**, 2077.
(15) For reviews, see: (a) Katritzky, A. R.; Rachwal, S.; Hitchings, G. J. *Tetrahedron* **1991**, *47*, 2683. (b) Katritzky, A. R.; Yang, Z.; Cundy, D. J. *Aldrichimica Acta* **1994**, *27*, 31. (c) Katritzky, A. R.; Lan, X. *Chem. Soc. Rev.* **1994**, 363. (d) Katritzky, A. R.; Lan, X.; Fan, W.-Q. *Synthesis* **1994**, 445.

Scheme 5



in the rearrangement step, compound **16a** was readily produced in 87% yield when **13a** was treated with 2.5 equiv of *n*-BuLi.

Since the formation of secondary homoallyl alcohols **16** is rationalized by the addition of the lithium reagents to the aldehyde intermediates **17**, it followed that the presence of hydride instead of nucleophilic lithium reagents in the reaction mixtures should produce the corresponding primary homoallyl alcohols. In accordance with our expectations, when allyl ethers **13c**,**d** were treated with 1.2 equiv of LDA and *ca.* 3 equiv of sodium borohydride, primary homoallyl alcohols **18a**,**b** were formed in yields of 56 and 60% exclusively as the *E* isomers (Scheme 4). This approach thus constitutes the *E*-selective complement of the *Z*-selective primary homoallyl alcohol syntheses of Still[9] and of Bruckner[11] (*vide supra*).

Preparation of Tertiary *E*-Homoallyl Alcohols and *β,γ*-Unsaturated Ketones. In a manner similar to the reaction sequences **13** → **16**, treatment of **19a**−**d** with 2.5 equiv of *n*-butyllithium or phenyllithium at −78 °C resulted in the facile formation of tertiary homoallyl alcohols **21a**−**d** in yields of 72−89% (Scheme 5). Complete *E* stereocontrol was also achieved in this case, as exemplified by the formation of **21d** ($R^3 \neq H$). Significantly, tertiary homoallyl alcohols of type **21** were previously inaccessible by Wittig rearrangement methodology.

The formation of tertiary allyl alcohols **21** indicates ketones **20** as the intermediates. Accordingly, when allyl ethers **19** were treated with a nonnucleophilic base such as LDA, the corresponding *β,γ*-unsaturated ketones **20a**−**d** were isolated in yields of 86−92% *via* rearrangement and subsequent departure of the benzotriazolyl group (Scheme 5). This approach to *β,γ*-unsaturated ketones has two attractive features: (i) complete stereocontrol was accomplished as illustrated by the exclusive *E* configuration of **20c**,**d** and (ii) corresponding isomeric α,*β*-unsaturated ketones were not observed in the cases of **20c** and **20d** (R^1 or/and $R^2 \neq H$), although many previously reported syntheses of *β,γ*-unsaturated ketones are complicated by a tendency to undergo prototropic rearrangement.[16]

All compounds prepared showed the expected NMR spectra, and all new compounds were further characterized by elemental analyses or HRMS (see Experimental Section). The NMR results of the crude reaction mixtures and absence of signals for isomers for **16c**−**f**, **18a**,**b**, **20c**,**d** and **21** demonstrated at least 95% stereoselectivity. The olefinic coupling constants (*J* around 15 Hz) are indicative of the *E* configuration of **16c**−**f**, **18a**,**b**, **20c**,**d**, and **21d** (see Experimental Section). In the cases of **20c**,**d**, the signals for the olefinic protons were overlapped in $CDCl_3$. Thus, in order to measure the coupling constants, their ^1H NMR spectra were recorded in $CDCl_3$ and C_6D_6 and the olefinic coupling constants *J* are 15.4 and 15.5 Hz, respectively.

Conclusion

The presently reported facile [2,3]-Wittig rearrangements of allyl (benzotriazolyl)alkyl ethers **13** and **19** enable the easy preparation of primary, secondary, and tertiary homoallyl alcohols and of *β,γ*-unsaturated ketones in stereochemically pure form in excellent yields, all starting from readily available allylic alcohols. The methodology promises wide generality as well as considerable synthetic utility.

Experimental Section

General. Melting points were determined with a hot-stage apparatus and are uncorrected. NMR spectra were recorded using $CDCl_3$ as the solvent with tetramethylsilane as the internal standard for ^1H (300 MHz) or solvent as the internal standard for ^{13}C (75 MHz). Tetrahydrofuran was distilled under nitrogen immediately prior to use from sodium/benzophenone. All reactions with air-sensitive compounds were carried out under an argon atmosphere. Column chromatography was conducted with silica gel 230−400 mesh. 1-(Chloromethyl)benzotriazole was prepared according to our previously reported procedure.[15a]

General Procedure for the Preparation of Allyl (Benzotriazol-1-yl)methyl Ethers 13a−**d.** To a solution of the appropriate allyl alcohol (36 mmol) in DMF (60 mL) at room temperature was added *t*-BuOK (4.04 g, 36 mmol). After 2 h, 1-(chloromethyl)benzotriazole (6.02 g, 36 mmol) was added. The reaction mixture was stirred at room temperature overnight. Water (300 mL) was added, and the mixture was extracted with diethyl ether (4 × 100 mL). The combined organic extracts were washed with water (3 × 50 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was subjected to column chromatography (hexanes: ethyl acetate = 4:1) to give the pure product.

2-Methyl-4-((benzotriazol-1-yl)methoxy)-2-butene (13a): colorless oil, yield (7.8 g, 79%); ^1H NMR δ 1.58 (s, 3H), 1.72 (s, 3H), 4.00 (d, $J = 6.9$ Hz, 2H), 5.26 (t, $J = 7.1$ Hz, 1H), 6.01 (s, 2H), 7.39−7.44 (m, 1H), 7.51−7.56 (m, 1H), 7.71 (d, $J = 8.3$ Hz, 1H), 8.09 (d, $J = 8.3$ Hz, 1H); ^{13}C NMR δ 18.0, 25.7, 65.4, 76.1, 110.0, 119.0, 119.9, 124.2, 127.8, 132.8, 139.4, 146.4. Anal. Calcd for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.63; H, 7.03; N, 19.35.

1-Phenyl-3-((benzotriazol-1-yl)methoxy)-1-propene (13b): white prisms, mp 76−79 °C, yield (6.0 g, 63%); ^1H NMR δ 4.16 (d, $J = 6.3$ Hz, 2H), 6.06 (s, 2H), 6.15 (dt, $J = 15.9$ and 6.3 Hz, 1H), 6.60 (d, $J = 15.9$ Hz, 1H), 7.23−7.34 (m, 5H), 7.38−7.43 (m, 1H), 7.51−7.56 (m, 1H), 7.71 (d, $J = 8.3$ Hz, 1H), 8.08 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR δ 69.5, 75.9, 109.9, 120.1, 123.6, 124.3, 126.6, 127.9, 128.0, 128.5, 132.8, 134.3,

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136.2, 146.5. Anal. Calcd for $C_{16}H_{15}N_3O$: C, 72.43; H, 5.70; N, 15.84. Found: C, 72.09; H, 5.69; N, 15.96.

3-((Benzotriazol-1-yl)methoxy)-1-octene (13c): colorless oil, yield (7.3 g, 78%); ^{1}H NMR δ 0.72 (t, J = 7.3 Hz, 3H), 0.91−1.15 (m, 6H), 1.34−1.52 (m, 2H), 3.72−3.79 (m, 1H), 5.27−5.35 (m, 2H), 5.61−5.73 (m, 1H), 5.95 (d, J = 11.4 Hz, 1H), 6.06 (d, J = 11.4 Hz, 1H), 7.39−7.44 (m, 1H), 7.51−7.57 (m, 1H), 7.72 (d, J = 8.3 Hz, 1H), 8.09 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 13.8, 22.4, 24.6, 31.2, 34.9, 74.4, 79.2, 110.0, 118.9, 120.0, 124.2, 127.7, 132.9, 136.9, 146.4. Anal. Calcd for $C_{15}H_{21}N_3O$: C, 69.47; H, 8.16; N, 16.20. Found: C, 69.86; H, 8.24; N, 16.40.

3-((Benzotriazol-1-yl)methoxy)-1-pentene (13d): colorless oil, yield (6.5 g, 83%); ^{1}H NMR δ 0.68 (t, J = 7.4 Hz, 3H), 1.43−1.56 (m, 2H), 3.66−3.73 (m, 1H), 5.27−5.35 (m, 2H), 5.60−5.72 (m, 1H), 6.00 (d, J = 11.2 Hz, 1H), 6.04 (d, J = 11.2 Hz, 1H), 7.38−7.44 (m, 1H), 7.51−7.56 (m, 1H), 7.70−7.74 (m, 1H), 8.07−8.10 (m, 1H); ^{13}C NMR δ 9.3, 27.8, 74.3, 80.6, 109.9, 119.0, 119.8, 124.1, 127.6, 132.8, 136.5, 146.2; HRMS calcd for $C_{12}H_{15}N_3O$ 218.1293 (M + 1), found 218.1302.

General Procedure for the Preparation of Secondary Homoallyl Alcohols 16a−f. To a solution of the appropriate allyl (benzotriazol-1-yl)methyl ether **13** (1.7 mmol) in THF (100 mL) at −78 °C under argon was added *n*-BuLi (2.4 mL, 4.3 mmol, 1.8 M in cyclohexane). The mixture was stirred and allowed to warm to room temperature overnight. Water (50 mL) was added, and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was subjected to column chromatography (hexanes: ethyl acetate = 5:1) to give the pure product.

3,3-Dimethyl-1-octen-4-ol (16a): colorless oil, yield (0.23 g, 87%); ^{1}H NMR δ 0.92 (t, J = 7.0 Hz, 3H), 1.02 (s, 6H), 1.22−1.40 (m, 4H), 1.51−1.56 (m, 3H), 3.24−3.27 (m, 1H), 5.03−5.12 (m, 2H), 5.84 (dd, J = 17.4 and 11.0 Hz, 1H); ^{13}C NMR δ 14.0, 22.1, 22.7, 23.1, 29.2, 31.1, 41.6, 78.3, 113.1, 145.5; HRMS calcd for $C_{10}H_{20}O$ 157.1592 (M + 1), found 157.1636.

3-Phenyl-4-penten-2-ol (16b): colorless oil, a mixture of two diastereoisomers (78:22) (signals of minor isomer in brackets), yield (0.22 g, 81%); ^{1}H NMR δ 1.09 [1.26] (d, J = 6.2 Hz, 3H), 1.98 (d, J = 2.5 Hz, 1H), 3.16−3.29 (m, 1H), 3.97−4.04 (m, 1H), 5.12−5.28 (m, 2H), 6.00−6.20 (m, 1H), 7.19−7.39 (m, 5H); ^{13}C NMR δ 20.6 [20.7], 59.1 [58.9], 70.2 [70.4], 117.9 [116.8], 126.7 [126.9], 127.9 [128.4], 128.6 [128.8], 138.5 [138.4], 141.5 [140.9]; HRMS calcd for $C_{11}H_{14}O$ 163.1123 (M + 1), found 163.1162.

7-Tridecen-5-ol (16c): colorless oil, yield (0.28 g, 84%); ^{1}H NMR δ 0.87−0.94 (m, 6H), 1.23−1.46 (m, 12H), 1.69 (br s, 1H), 1.99−2.09 (m, 3H), 2.20−2.28 (m, 1H), 3.55−3.62 (m, 1H), 5.41 (dt, J = 15.5 and 6.8 Hz, 1H), 5.55 (dt, J = 15.5 and 6.4 Hz, 1H); ^{13}C NMR δ 14.0, 22.5, 22.7, 27.9, 29.1, 31.4, 32.6, 36.4, 40.7, 70.9, 125.8, 134.7. The spectral data for **16c** are in agreement with published[17] values.

4-Decen-2-ol (16d): colorless oil, yield (0.23 g, 86%); ^{1}H NMR δ 0.89 (t, J = 6.9 Hz, 3H), 1.18 (d, J = 6.2 Hz, 3H), 1.21−1.41 (m, 6H), 1.84 (s, 1H), 1.98−2.24 (m, 4H), 3.75−3.81 (m, 1H), 5.41 (dt, J = 15.3 and 6.4 Hz, 1H), 5.54 (dt, J = 15.3 and 6.4 Hz, 1H); ^{13}C NMR δ 14.0, 22.4, 22.5, 29.1, 31.3, 32.6, 42.5, 67.2, 125.7, 134.6. The spectral data for **16d** are in agreement with published[18] values.

1-Phenyl-3-nonen-1-ol (16e): colorless oil, yield (0.31 g, 84%); ^{1}H NMR δ 0.88 (t, J = 6.9 Hz, 3H), 1.21−1.40 (m, 6H), 1.98−2.05 (m, 2H), 2.10 (d, J = 3.2 Hz, 1H), 2.35−2.50 (m, 2H), 4.65−4.70 (m, 1H), 5.39 (dt, J = 15.3 and 6.7 Hz, 1H), 5.57 (dt, J = 15.3 and 6.7 Hz, 1H), 7.23−7.36 (m, 5H); ^{13}C NMR δ 14.0, 22.5, 29.1, 31.3, 32.6, 42.8, 73.5, 125.4, 125.8, 127.4, 128.3, 135.2, 144.1; HRMS calcd for $C_{15}H_{22}O$: 219.1748 (M + 1), found 219.1727.

1-Phenyl-3-hexen-1-ol (16f): colorless oil, yield (0.25 g, 85%); ^{1}H NMR δ 0.97 (t, J = 7.4 Hz, 3H), 1.99−2.08 (m, 2H), 2.20 (br s, 1H), 2.37−2.46 (m, 2H), 4.63−4.68 (m, 1H), 5.39 (dt, J = 15.4 and 6.4 Hz, 1H), 5.61 (dt, J = 15.4 and 6.3 Hz, 1H), 7.24−7.34 (m, 5H); ^{13}C NMR δ 13.7, 25.6, 42.7, 73.5, 124.5, 125.8, 127.3, 128.3, 136.5, 144.1; HRMS calcd for $C_{12}H_{16}O$ 175.1123 (M − 1), found 175.1162.

General Procedure for the Preparation of Primary Homoallyl Alcohols 18a,b. To a solution of the appropriate allyl (benzotriazol-1-yl)methyl ether **13** (4 mmol) and $NaBH_4$ (0.3 g, 8 mmol) in THF (100 mL) at −78 °C under argon was added LDA (6.7 mL, 10 mmol, 1.5 M in cyclohexane). The mixture was stirred and allowed to warm to room temperature overnight. Water (50 mL) was added, and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was subjected to column chromatography (hexanes:ethyl acetate = 4:1) to give the pure product.

3-Hexen-1-ol (18a): colorless oil, yield (0.22 g, 56%); ^{1}H NMR δ 0.99 (t, J = 7.5 Hz, 3H), 1.68 (br s, 1H), 1.99−2.09 (m, 2H), 2.23−2.30 (m, 2H), 3.63 (t, J = 6.3 Hz, 2H), 5.39 (dt, J = 15.3 and 8.0 Hz, 1H), 5.61 (dt, J =15.3 and 6.2 Hz, 1H); ^{13}C NMR 13.7, 25.6, 35.9, 62.0, 124.8, 135.7. The spectral data for **18a** are in agreement with published[19] values.

3-Nonen-1-ol (18b): colorless oil, yield (0.34 g, 60%); ^{1}H NMR δ 0.89 (t, J = 6.7 Hz, 3H), 1.25−1.41 (m, 6H), 1.67 (br s, 1H), 2.00−2.05 (m, 2H), 2.26 (q, J = 6.6 Hz, 2H), 3.62 (t, J = 6.0 Hz, 2H), 5.38 (dt, J = 15.3 and 6.8 Hz, 1H), 5.56 (dt, J = 15.3 and 6.6 Hz, 1H); ^{13}C NMR δ 14.0, 22.5, 29.1, 31.4, 32.6, 36.0, 62.0, 125.7, 134.2. The spectral data for **18b** are in agreement with published[20] values.

General Procedure for the Preparation of Allyl 1-(Benzotriazol-1-yl)alkyl Ethers 19a−e. To a solution of an allyl alcohol (20 mmol), an aldehyde (20 mmol), and benzotriazole (2.6 g, 21.8 mmol) in CH_2Cl_2 (60 mL) at room temperature were added *p*-toluenesulfonic acid (1.9 g, 10 mmol) and molecular sieves (4 Å, 30 g). After the mixture was stirred at room temperature for 2 days, the molecular sieves were removed by filtration and the solvent was evaporated. The residue was dissolved in diethyl ether (100 mL), and the solution was washed with an aqueous NaOH solution (60 mL, 5 N). The aqueous layer was extracted with diethyl ether (3 × 50 mL), and the combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was subjected to column chromatography (hexanes:ethyl acetate = 20:1) to give the pure product.

1-((Benzotriazol-1-yl)(4-methylphenyl)methoxy)-3-methyl-2-butene (19a): colorless oil, yield (4.1 g, 67%); ^{1}H NMR δ 1.54 (s, 3H), 1.70 (s, 3H), 2.31 (s, 3H), 3.97−4.03 (m, 1H), 4.07−4.14 (m, 1H), 5.30−5.35 (m, 1H), 7.13 (d, J = 8.2 Hz, 2H), 7.21 (s, 1H), 7.26−7.36 (m, 5H), 8.03−8.06 (m, 1H); ^{13}C NMR δ 18.0, 21.1, 25.7, 65.3, 88.4, 111.8, 119.0, 119.7, 124.0, 125.8, 127.2, 129.1, 131.2, 133.6, 138.7, 139.3, 146.9. Anal. Calcd for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67. Found: C, 74.09; H, 6.91; N, 14.06.

1-((Benzotriazol-1-yl)phenylmethoxy)-3-methyl-2-butene (19b): colorless oil, yield (3.6 g, 61%); ^{1}H NMR δ 1.56 (s, 3H), 1.72 (s, 3H), 4.04−4.12 (m, 2H), 5.32−5.35 (m, 1H), 7.25−7.44 (m, 9H), 8.05−8.09 (m, 1H); ^{13}C NMR δ 18.0, 25.8, 65.4, 88.4, 111.8, 119.0, 119.8, 124.1, 126.0, 127.3, 128.5, 128.9, 129.0, 131.2, 136.6, 147.0. Anal. Calcd for $C_{18}H_{19}N_3O$: C, 73.70; H, 6.53; N, 14.32. Found: C, 73.81; H, 6.93; N, 14.28.

1-Phenyl-3-((benzotriazol-1-yl)phenylmethoxy)-1-propene (19c): white solid, mp 74−75 °C, yield (3.5 g, 53%); ^{1}H NMR δ 4.22−4.25 (m, 2H), 6.23 (dt, J = 15.9 and 6.0 Hz, 1H), 6.61 (d, J = 15.9 Hz, 1H), 7.22−7.36 (m, 12H), 7.44−7.48 (m, 2H), 8.04−8.08 (m, 1H); ^{13}C NMR δ 69.4, 88.3, 111.5, 119.8, 123.4, 124.1, 125.9, 126.5, 127.4, 127.9, 128.4, 128.5, 128.9, 131.1, 134.3, 136.0, 136.1, 146.9. Anal. Calcd for $C_{22}H_{19}N_3O$: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.26; H, 5.63; N, 12.27.

3-((Benzotriazol-1-yl)phenylmethoxy)-1-octene (19d): colorless oil, a mixture of two diastereoisomers (1:1) (signals of the other isomer in brackets), yield (4.7 g, 71%); ^{1}H NMR δ

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0.59−1.58 (m, 11H), 3.59−3.67 [4.08−4.12] (m, 1H), 5.01−5.40 (m, 2H), 5.67−5.89 (m, 1H), 7.20−7.46 (m, 8H), 7.79−8.02 (m, 2H); ^{13}C NMR δ 13.7 [13.9], 22.2 [22.5], 24.6 [24.9], 31.1 [31.6], 34.9 [37.0], 73.3 [78.9], 86.2, 111.8, 114.5, 119.6 [119.7], 124.3, 125.9, 127.3, 128.5, 128.8, 128.9, 136.5, 141.1, 146.7. Anal. Calcd for $C_{21}H_{25}N_3O$: C, 75.19; H, 7.51; N, 12.53. Found: C, 75.04; H, 7.68; N, 12.36.

3-((Benzotriazol-1-yl)(4-methylphenyl)methoxy)-1-pentene (19e): colorless oil, a mixture of two diastereomers (5:1) (signals of minor isomer in brackets), yield (3.7 g, 60%); ^{1}H NMR δ 0.68 [0.99] (t, J = 7.4 Hz, 3H), 1.49−1.64 (m, 2H), 2.32 (s, 3H), 3.59−3.66 (m, 1H) [4.02−4.10], 5.36−5.43 (m, 2H), 5.74−5.86 (m, 1H), 7.13−7.30 (m, 2H), 7.31−7.37 (m, 6H), 8.04−8.08 (m, 1H); ^{13}C NMR δ 9.47, 21.1, 28.0 [27.6], 80.2 [82.5], 86.1 [88.6], 111.8, 116.4, 119.7 [119.9], 124.0, 125.8, 127.0 [127.1], 129.1 [129.2], 131.2, 133.7, 136.3 [136.8], 138.6, 146.9. Anal. Calcd for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67. Found: C, 74.37; H, 7.05; N, 13.41.

General Procedure for the Preparation of β,γ-Unsaturated Ketones 20a−d. To a solution of the appropriate allyl 1-(benzotriazol-1-yl)alkyl ether **19** (2.6 mmol) in THF (100 mL) at −78 °C under argon was added LDA (2.1 mL, 3.1 mmol, 1.5 M in cyclohexane). The mixture was stirred and allowed to warm to room temperature overnight. Water (50 mL) was added, and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was subjected to column chromatography (hexanes:ethyl acetate = 10:1) to give the pure product.

1-Phenyl-2,2-dimethyl-3-buten-1-one (20a): colorless oil, yield (0.41 g, 91%); ^{1}H NMR δ 1.40 (s, 6H), 5.22 (d, J = 10.6 Hz, 1H), 5.24 (d, J = 17.6 Hz, 1H), 6.20 (dd, J = 17.6 and 10.7 Hz, 1H), 7.35−7.47 (m, 3H), 7.87−7.90 (m, 2H); ^{13}C NMR δ 26.0, 50.1, 114.0, 127.9, 129.2, 131.6, 137.1, 143.8, 204.6. The spectral data for **20a** are in agreement with published[16] values.

1-(4-Methylphenyl)-2,2-dimethyl-3-buten-1-one (20b): colorless oil, yield (0.42 g, 86%); ^{1}H NMR δ 1.40 (s, 6H), 2.38 (s, 3H), 5.18 (d, J = 10.7 Hz, 1H), 5.21 (d, J = 17.6 Hz, 1H), 6.20 (dd, J = 17.6 and 10.6 Hz, 1H), 7.18 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H); ^{13}C NMR δ 21.4, 26.1, 50.0, 113.7, 128.5, 129.6, 134.1, 142.2, 144.1, 203.8. The spectral data for **20b** are in agreement with published[21] values.

1-(4-Methylphenyl)-3-hexen-1-one (20c): colorless oil, yield (0.52 g, 89%); ^{1}H NMR δ 0.98 (t, J = 7.4 Hz, 3H), 2.04−2.09 (m, 2H), 2.39 (s, 3H), 3.64 (dd, J = 5.1 and 1.1 Hz, 2H), 5.63−5.67 (m, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 13.5, 21.6, 25.6, 42.4, 121.5, 128.4, 129.2, 134.2, 136.3, 143.7, 198.3; HRMS calcd for $C_{13}H_{16}O$ 189.1279 (M + 1), found 189.1276.

1-Phenyl-3-nonen-1-one (20d): colorless oil, yield (0.51 g, 92%); ^{1}H NMR δ 0.87 (t, J = 6.7 Hz, 3H), 1.23−1.39 (m, 6H), 2.01−2.08 (m, 2H), 3.68 (d, J = 5.3 Hz, 2H), 5.57−5.70 (m, 2H), 7.26−7.47 (m, 2H), 7.52−7.57 (m, 1H), 7.94−7.97 (m, 2H); ^{13}C NMR δ 14.0, 22.5, 28.9, 31.3, 32.6, 42.5, 122.1, 128.3, 128.5, 132.9, 135.1, 136.7, 198.6. The spectral data for **20d** are in agreement with published[22] values.

General Procedure for the Preparation of Tertiary Homoallyl Alcohols 21a−d. To a solution of the appropriate allyl 1-(benzotriazol-1-yl)alkyl ether **19** (2.2 mmol) in THF (100 mL) at −78 °C under argon was added *n*-BuLi (3.7 mL, 5.5 mmol, 1.5 M in cyclohexane). The mixture was stirred and allowed to warm to room temperature overnight. Water (50 mL) was added, and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was subjected to column chromatography (hexanes:ethyl acetate = 6:1) to give the pure product.

3,3-Dimethyl-4-(4-methylphenyl)-1-octen-4-ol (21a): colorless oil, yield (0.48 g, 89%); ^{1}H NMR δ 0.83 (t, J =7.1 Hz, 3H), 0.86−0.92 (m, 1H), 0.95 (s, 3H), 1.01 (s, 3H), 1.13−1.32 (m, 3H), 1.68−1.78 (m, 1H), 1.86 (s, 1H), 2.09−2.19 (m, 1H), 2.34 (s, 3H), 5.02 (d, J = 17.6 Hz, 1H), 5.09 (d, J = 11.0 Hz, 1H), 5.99 (dt, J = 17.6 and 11.0 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 14.1, 20.9, 22.7, 23.3, 26.0, 35.2, 44.9, 80.0, 113.6, 127.5, 127.8, 135.7, 139.6, 145.5; HRMS calcd for $C_{17}H_{26}O$ 247.2062 (M + 1), found 247.2079.

1,1-Diphenyl-2,2-dimethyl-3-buten-1-ol (21b): colorless oil, yield (0.40 g, 72%); ^{1}H NMR δ 1.20 (s, 6H), 2.48 (s, 1H), 5.15 (d, J = 17.6 Hz, 1H), 5.18 (d, J = 10.9 Hz, 1H), 6.20 (dd, J = 17.6 and 10.9 Hz, 1H), 7.18−7.29 (m, 6H), 7.54−7.58 (m, 4H); ^{13}C NMR δ 24.3, 45.4, 81.6, 112.6, 126.6, 127.2, 128.2, 128.4, 130.0, 132.4, 145.5, 146.3; HRMS calcd for $C_{18}H_{20}O$ 253.1592 (M + 1), found 253.1588.

3,4-Diphenyl-1-octen-4-ol (21c): colorless oil, yield (0.51 g, 83%); ^{1}H NMR δ 0.76 (t, J = 6.9 Hz, 3H), 0.85−0.88 (m, 1H), 1.15−1.25 (m, 3H), 1.86−1.91 (m, 2H), 2.05 (s, 1H), 3.56 (d, J = 9.9 Hz, 1H), 5.09−5.19 (m, 2H), 6.19−6.31 (m, 1H), 6.82−6.85 (m, 2H), 7.03−7.26 (m, 8H); ^{13}C NMR δ 14.0, 23.1, 25.7, 39.7, 62.2, 78.4, 117.9, 126.1, 126.2, 126.4, 127.4, 127.7, 129.3, 137.4, 140.1, 144.1. Anal. Calcd for $C_{20}H_{24}O$: C, 85.66; H, 8.63. Found: C, 85.56; H, 8.84.

1,1-Diphenyl-3-nonen-1-ol (21d): colorless oil, yield (0.56 g, 86%); ^{1}H NMR δ 0.79 (t, J = 6.8 Hz, 3H), 1.09−1.28 (m, 6H), 1.85−1.93 (m, 2H), 2.58 (s, 1H), 2.93 (d, J = 7.1 Hz, 2H), 5.18 (dt, J = 15.3 and 7.2 Hz, 1H), 5.59 (dt, J = 15.3 and 6.8 Hz, 1H), 7.11−7.26 (m, 6H), 7.35−7.39 (m, 4H); ^{13}C NMR δ 14.0, 22.4, 29.0, 31.3, 32.6, 45.6, 76.8, 124.2, 126.0, 126.7, 128.1, 137.6, 146.7. Anal. Calcd for $C_{21}H_{26}O$: C, 85.67; H, 8.90. Found: C, 85.42; H, 9.09.

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