

β -Acylvinyl Anion and Dianion Equivalents: Lithiation of 1-[(2*EZ*)-3-Chloroprop-2-enyl]-1*H*-1,2,3-benzotriazole: Preparation and Elaboration of 1-(2-Oxiranylviny)-1*H*-benzotriazoles

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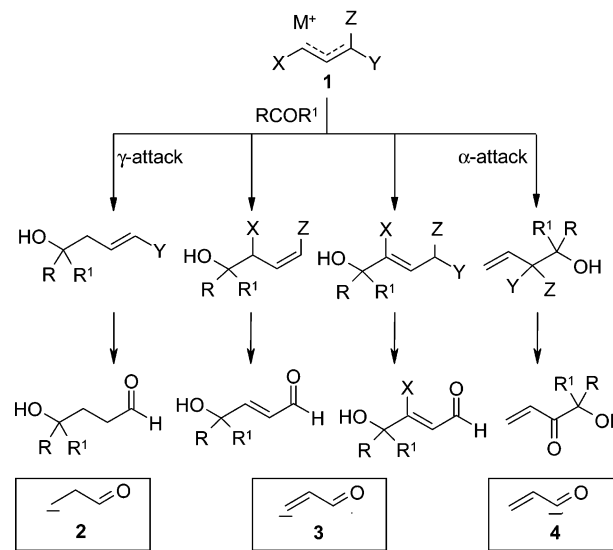
The allyllithium generated from 1-[(2*EZ*)-3-chloroprop-2-enyl]-1*H*-1,2,3-benzotriazole (**5**) and LDA, in the presence of HMPA, reacts with enolizable and nonenolizable carbonyls solely at the CCl terminus to give 1-(2-oxiranylviny)benzotriazoles **6a–g** in 61–82% yields. Allyllithiums generated from **6a,c** reacted exclusively at the CBt terminus to give **10a–d** in 68–88% yields. Acidic hydrolysis of (oxiranylviny)benzotriazoles **6a–g** and **10a–d** provided 4-hydroxyalk-2-en-1-one derivatives **12a,b,c,e,g**, **13a–d**, and furan **14** in 54–86% yields.

Introduction

Regiocontrol in the deprotonation-substitution of unsymmetrically substituted allylic systems is challenging. Heteroatom-stabilized allylic anions of type **1** are synthetically important as 3-carbon homologating agents.¹ Species **1** can act as diverse reversed-polarity equivalents: homoenolate anions **2**,² β -acylvinyl anions **3**,³ or α,β -unsaturated acyl anions **4**^{4a–c} (Scheme 1). The α/γ -regiochemistry of ambident allylic anions is controlled in a complex manner by several factors, such as the nature of the heteroatom(s), charge delocalization, steric effects, counteraction, type of electrophile, solvation, and additives.⁵ Allylic anions stabilized by a wide variety of heteroatoms including oxygen, sulfur, selenium, nitrogen, phosphorus, boron, silicon, and halogens have been examined.⁶

Prior to the advent of the in situ quench procedure (Barbier technique),⁷ 1-chloroallyllithiums were underuti-

SCHEME 1



X, Y, Z = O, S, Se, N, P, B, Si, X, H,.....

lized because of facile self-coupling. 1-Chloroallyllithiums preferentially react at the CH₂ terminus with carbonyl compounds and at the CCl terminus with aliphatic halides.^{8a–c} However, replacement of the lithium counterion with zinc results in a regioselective reaction at the CCl terminus with aldehydes as electrophiles.⁹ Chloroallyllithiums generated from *trans*-cinnamyl chloride and 2-[(1*E*)-3-chloroprop-1-enyl]-1,3-benzothiazole react with

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nonenolizable ketones and aromatic aldehydes at the CCl terminus exclusively.¹⁰

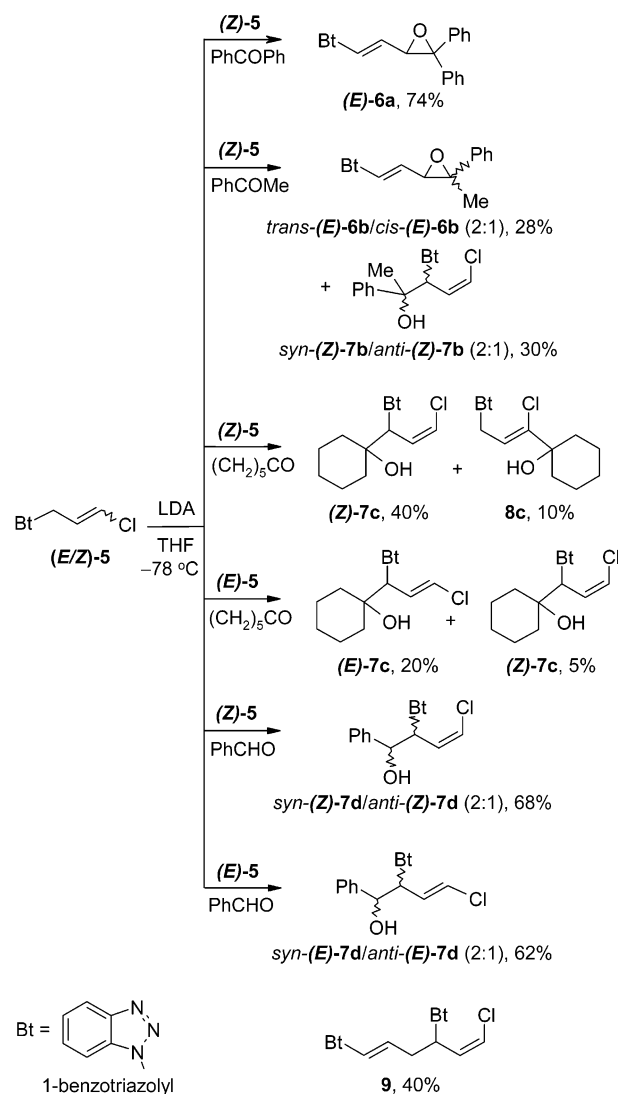
The regioselectivity of additions of 1,1-dichloroallyllithium to carbonyl compounds has been suggested to depend on electronic factors. Carbonyl compounds with electron-withdrawing substituents usually favor bond formation at the CH₂ terminus, and those with electron-releasing groups favor bond formation at the CCl₂ terminus.¹¹ The attack could be directed to the CCl₂ terminus exclusively by the presence of additives such as ^tBuOK¹² or cryptand[2.2.1].¹³

1-Chloro-(1-trimethylsilyl)allyllithium is less selective as compared to 1,1-dichloroallyllithium, and both α - and γ -adducts result from reactions with carbonyl compounds.¹⁴ The anion derived from (*E*)-3-chloro-1-phenylsulfonylethyl-1-ene reacts with aldehydes exclusively at the CCl terminus.¹⁵ Both (*E*)- and (*Z*)- γ -chloroallylphosphonamides react exclusively at the CCl terminus with α,β -unsaturated ketones to give the corresponding cyclopropanes.¹⁶

The synthetic utility of allyllithiums generated from 1-allylbenzotriazole,^{17a,b} 1-(1-ethoxyprop-2-enyl)-1*H*-1,2,3-benzotriazole,¹⁸ 3-(benzotriazol-1-yl)-1-ethoxyprop-1-ene,¹⁹ and 1-(3-morpholinoprop-2-enyl)benzotriazole²⁰ is well established. Anions generated from these *N*-allylbenzotriazoles react exclusively at the CBt terminus with aldehydes and nonhindered ketones. However, the regiochemistry is reversed to give γ -adducts when the intermediate 1-(benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxyprop-1-ene is first generated in situ from 1-(1-ethoxyprop-2-enyl)-1*H*-1,2,3-benzotriazole; deprotonation of the phosphoryl intermediate and subsequent reaction with carbonyl compounds now result in hydroxyalkylation exclusively at the CP terminus.²¹

We now report regiospecific lithiation-substitutions of 1-[(2*EZ*)-3-chloroprop-2-enyl]-1*H*-1,2,3-benzotriazole and its utilization as β -acylvinyl anion ([−]CH=CHCHO) or β -acylvinyl dianion ([−]COCH=CH[−]) equivalents.

SCHEME 2



Results and Discussion

Regioselectivity of Reactions of Lithiated (*E*)-5 and (*Z*)-5 with Carbonyl Compounds. 1-[(2*EZ*)-3-chloroprop-2-enyl]-1*H*-1,2,3-benzotriazole (**5**) was prepared by the reaction of BtNa and (1*EZ*)-1,3-dichloroprop-1-ene. (**Z**)-5 (47%) and (**E**)-5 (21%) were separated by silica gel column chromatography. Unlike (1*E*)-3-chloro-1-phenylsulfonylethyl-1-ene,¹⁵ no *E/Z*-isomerization was observed when a 1:1 mixture of (**E**)-5 and (**Z**)-5 was stirred with Et₃N in CHCl₃ at 20 °C for 3 h. Under Barbier conditions,⁷ lithiated (**E**)-5 or (**Z**)-5 reacted with various carbonyl compounds at the CBt terminus to give the corresponding homoallylic alcohols **7b–d** or at the CCl terminus to give either the corresponding (oxiran-2-yl)benzotriazoles **6a,b** or allylic alcohol **8c** (Scheme 2).

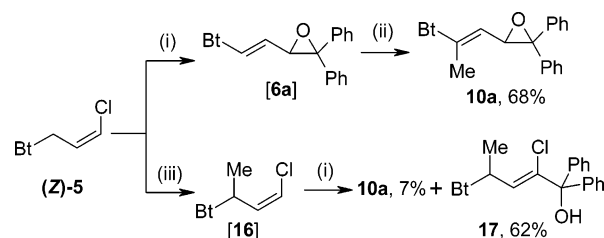
Lithiation of (**Z**)-5 with LDA at −78 °C and trapping with benzophenone gave vinyloxirane (**E**)-6a in 74% yield as the sole product (Scheme 2). However, reaction of benzophenone with lithiated (**E**)-5 provided a complex mixture of products having both (*Z*)- and (*E*)-configured double bonds as shown by the ¹H NMR spectrum.

Deprotonation of (**Z**)-5 and reaction with acetophenone at −78 °C gave products from attack at both the CBt and

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TABLE 2. Preparation of γ -Hydroxy- α,β -enones **13a–d** via (Oxiranylviny)benzotriazoles **10a–d**

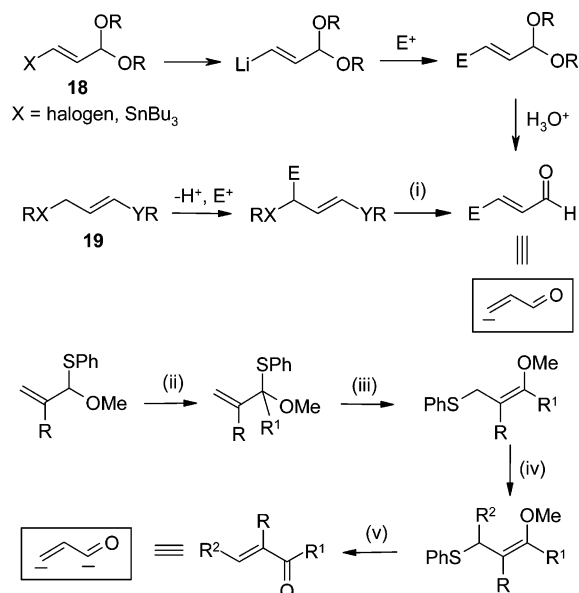
entry	R	R ¹	E	oxirane, yield ^a (%)	ketone, yield ^a (%)
1	Ph	Ph	Me	10a (88)	13a (76)
2	Ph	Ph	Et	10b (72)	13b (78)
3	Ph	Ph	Bu	10c (68)	13c (82)
4	(CH ₂) ₅		Me	10d (85)	13d (56)

^a Isolated yields.**SCHEME 4^a**^a (i) LDA, THF, PhCOPh, $-78\text{ }^{\circ}\text{C}$; (ii) BuLi, MeI, $-78\text{ }^{\circ}\text{C}$; (iii) LDA, THF, MeI, $-78\text{ }^{\circ}\text{C}$

Regiospecific Lithiation-Substitutions of (Oxiranylviny)benzotriazoles. Vinyloxiranes **6a,c** were further lithiated and reacted with alkyl halides to provide alkylation exclusively at the CBt terminus. Lithiation of **6a** with BuLi and trapping with various alkyl iodides at $-78\text{ }^{\circ}\text{C}$ gave the alkylated products **10a–c** in 68–88% yields (Scheme 3, Table 2). Interestingly, the *E*-stereochemistry of the double bond is retained, which is evident from the X-ray structure of **10a** and also by $J_{\text{allylic}} = 1\text{ Hz}$ between the methyl group and the allylic proton attached to the oxirane ring. Similarly, lithiation and subsequent methylation of **6c** provided vinyloxirane **10d** in 85% yield. However, the procedure was limited to the use of alkyl iodides as electrophiles; the use of 3-pentanone to trap lithiated **6a** resulted in the oxirane ring opening to give **11** in 75% yield. The structure for compound **11** was unambiguously determined by X-ray crystallography. Thus, both alkyl iodides and carbonyl compounds react at the CBt terminus of (oxiranylviny)benzotriazole.

Starting from (**Z**)-**5**, a one-pot, two-step procedure using the sequence (**Z**)-**5** \rightarrow **[6a]** \rightarrow **10a** gave **10a** in 68% yield (Scheme 4). However, changing the sequence to (**Z**)-**5** \rightarrow **[16]** \rightarrow **10a** resulted in a low yield of **10a** (7%) along with **17** in 62% yield. The regiochemistry of the addition of MeI to the lithiated (**Z**)-**5** has been assigned by analogy to the ^1H NMR spectra of 1-(1-methylprop-2-enyl)-1*H*-1,2,3-benzotriazole^{17b} and 3-chlorobut-1-ene.²³ The methine proton in 1-(1-methylprop-2-enyl)-1*H*-1,2,3-benzotriazole [$\text{CH}_2=\text{CH}-\text{CH}(\text{Me})\text{Bt}$] and in 3-chlorobut-1-ene [$\text{CH}_2=\text{CH}-\text{CH}(\text{Me})\text{Cl}$] appears at 5.57 and 4.34 ppm, respectively; the ^1H NMR spectrum of **16** showed the signal for the allylic methine proton at 5.95 ppm. Furthermore, no *Z* \rightarrow *E* isomerization was observed.

Acid-Catalyzed Hydrolysis of (Oxiranylviny)benzotriazoles: Preparation of α,β -Unsaturated Carbonyl Compounds. The synthetic utility of heteroatom-stabilized allylic systems as β -acylvinyl anion equivalents is well established.^{3a} A direct approach toward the

SCHEME 5^a^a X = Y = S, (i) HgCl₂; X = Y = Se, (i) H₂O₂; X = S, Y = O, (i) NaIO₄ or MoO₅; X = SO₂, Y = O, (i) DBU or SiO₂; X = Y = O, (i) 150 $^{\circ}\text{C}$, 72 h; (ii) LDA, R¹X, THF, $-78\text{ }^{\circ}\text{C}$; (iii) SiO₂, hexane, reflux, 4 h; (iv) BuLi, TMEDA, THF, 0 $^{\circ}\text{C}$, R²X; (v) NaIO₄, dioxane/H₂O.

generation of β -acylvinyl anion equivalents involves the use of protected carbonyl systems **18**, which can undergo halogen^{3b–d} or tin^{3e,f}–lithium exchange (Scheme 5). An alternative route involves the use of heteroallylic systems of type **19**, which carry the carbonyl group in the heterovinyl mask.^{5,6} Deprotonation-electrophilic substitution followed by unmasking provides an easy introduction of the β -acylvinyl moiety to the electrophilic reagent. The thio (X = Y = SR and X = SR, Y = OR)^{3g,h,24} and seleno (X = Y = Se)³ⁱ analogues of **19** have been used extensively; however, these systems require oxidative unmasking in the presence of reagents such as HgCl₂, H₂O₂, NaIO₄, or MoO₅. In the case of allylic sulfones,^{3j,k} often DBU is required for the final elimination of the sulfonyl group, and 4*H*-1,3-dioxin (RX, YR = $^-\text{OCH}_2\text{O}^-$ in **19**) requires prolonged thermolysis at 150 $^{\circ}\text{C}$ for 72 h for deprotection.^{3l}

Although systems of type **19** have been widely utilized as β -acylvinyl anion equivalents, reports on their use as β -acylvinyl dianion equivalents are rare. Mandai et al. introduced α -methoxyallyl sulfides as β -acylvinyl dianion equivalents; electrophilic substitution (α - to SPh) followed by silica-gel-promoted thioallylic rearrangement facilitated the second electrophilic substitution at the other end of the allylic system. Furthermore, oxidative removal of the heteroatoms provided α,β -unsaturated carbonyl compounds (Scheme 5).²⁴

Starting from (**EZ**)-**5**, we have successfully carried out two successive lithiation-electrophilic substitutions to get (oxiranylviny)benzotriazoles **6a–g** and **10a–d**. Furthermore, hydrolysis of (oxiranylviny)benzotriazoles under mild conditions provided the corresponding α,β -unsaturated carbonyl derivatives. Thus, the treatment of

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6a,b,c,e,g with *p*-TsOH (10 mol %) in THF at reflux for 30 min resulted in the formation of γ -hydroxy- α,β -enals **12a,b,c,e,g** in 54–86% yields (Scheme 3, Table 1). Under identical conditions, the hydrolysis of **6d** resulted in the formation of 2-phenylfuran (**14**) in 61% yield. However, the hydrolysis of **6f** resulted in the formation of **12f** in low yield (ca. 10%) along with other benzotriazole-containing byproducts as shown by the ^1H NMR spectrum of the crude material. Similarly, acidic hydrolysis of alkylated (oxiranylviny)benzotriazoles **10a–d** provided γ -hydroxy- α,β -enones **13a–d** in 56–82% yields (Scheme 3, Table 2). Thus, **5** functions as a synthetic equivalent for both β -formylvinyl anion **3** and β -acylvinyl dianion **15**.

Conclusions

In summary, we have shown that 3-chloroallylbenzotriazole (**5**), in the presence of HMPA, undergoes a regioselective lithiation-substitution at the CCl terminus to give (oxiranylviny)benzotriazoles **6a–g**. Furthermore, lithiation-alkylation of **6a,c** takes place exclusively at the CBt terminus to give **10a–d** in good yields. Acidic hydrolysis of **6a–g** and **10a–d** provided the corresponding 4-hydroxyalk-2-en-1-one derivatives **12a,b,c,e,g** and **13a–d**, respectively, establishing the utility of **5** as a β -acylvinyl anion and dianion equivalent. Furthermore, our procedure requires only a catalytic amount of acid for unmasking, which is milder than the oxidative unmasking procedures used for other β -acylvinyl anion equivalents.

Experimental Section

1-[(E)-2-(3,3-Diphenyloxiran-2-yl)viny]l-1H-1,2,3-benzotriazole (6a). White needles (from CH_2Cl_2 /hexanes); yield, 78%; mp 122–125 °C. ^1H NMR δ : 8.04 (d, $J = 8.2$ Hz, 1H), 7.63 (d, $J = 14.5$ Hz, 1H), 7.51 (d, $J = 7.5$ Hz, 2H), 7.47–7.31 (m, 10H), 7.29–7.24 (m, 1H), 5.99 (dd, $J = 14.5, 8.0$ Hz, 1H), 4.06 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR δ : 146.4, 140.1, 136.5, 131.4, 128.7, 128.6, 128.4, 128.3, 127.4, 126.8, 124.9, 120.6, 116.3, 110.1, 68.3, 64.9. Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}$: C, 77.86; H, 5.05; N, 12.38. Found: C, 77.46; H, 4.95; N, 12.49.

(4Z)-3-(1H-1,2,3-Benzotriazol-1-yl)-5-chloro-2-phenylpent-4-en-2-ol (7b). White needles (from EtOAc/hexanes); yield, 30%; major diastereomer: mp 132–133 °C. ^1H NMR δ : 7.89 (d, $J = 8.4$ Hz, 1H), 7.46–7.28 (m, 5H), 7.11–7.06 (m, 2H), 7.00–6.97 (m, 1H), 6.70 (dd, $J = 9.6, 7.3$ Hz, 1H), 6.47 (d, $J = 7.3$ Hz, 1H), 6.15 (d, $J = 9.6$ Hz, 1H), 4.81 (s, 1H), 1.73 (s, 3H). ^{13}C NMR δ : 144.5, 144.3, 133.0, 128.2, 127.7, 127.1, 126.6, 124.1, 123.8, 119.8, 109.3, 77.4, 63.0, 27.0. Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{ClN}_3\text{O}$: C, 65.07; H, 5.14; N, 13.39. Found: C, 65.32; H, 5.10; N, 13.32.

1-[3-(1H-1,2,3-Benzotriazol-1-yl)-1-chloroprop-1-enyl]-cyclohexanol (8c). White needles (from EtOAc/hexanes); yield, 10%; mp 113–114 °C. ^1H NMR δ : 8.03 (d, $J = 8.2$ Hz, 1H), 7.54–7.44 (m, 2H), 7.38–7.33 (m, 1H), 6.21 (t, $J = 6.5$ Hz, 1H), 5.46 (d, $J = 6.5$ Hz, 2H), 2.42 (s, 1H), 1.87–1.56 (m, 9H), 1.25–1.18 (m, 1H). ^{13}C NMR δ : 146.3, 146.2, 132.9, 127.7, 124.3, 120.2, 117.8, 109.7, 74.8, 47.0, 35.6, 25.4, 21.7. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{ClN}_3\text{O}$: C, 61.75; H, 6.22; N, 14.40. Found: C, 62.05; H, 6.27; N, 14.46.

1-[4-(1H-1,2,3-Benzotriazol-1-yl)-6-chloro-1,5-hexadienyl]-1H-1,2,3-benzotriazole (9). White needles (from EtOAc/hexanes); yield, 40%; mp 156–157 °C. ^1H NMR δ : 8.09–8.02 (m, 2H), 7.62 (d, $J = 8.2$ Hz, 1H), 7.53–7.35 (m, 6H), 6.48–6.37 (m, 3H), 6.04–5.97 (m, 1H), 3.51–3.41 (m, 1H), 3.29–3.19 (m, 1H). ^{13}C NMR δ : 146.1, 145.9, 132.9, 131.3, 128.9,

128.3, 127.8, 126.4, 124.5, 124.3, 122.6, 120.3, 120.2, 115.5, 109.9, 109.4, 55.8, 34.9. Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{ClN}_6$: C, 61.63; H, 4.31; N, 23.96. Found: C, 61.91; H, 4.23; N, 24.38.

1-[(E)-2-(3,3-Diphenyloxiran-2-yl)-1-methylvinyl]-1H-1,2,3-benzotriazole (10a). Colorless cubes (from CH_2Cl_2 /hexanes); yield, 88%; mp 102–104 °C. ^1H NMR δ : 8.02–8.00 (m, 1H), 7.54–7.51 (m, 2H), 7.46–7.34 (m, 8H), 7.31–7.25 (m, 2H), 6.84–6.82 (m, 1H), 5.35 (dd, $J = 8.4, 1$ Hz, 1H), 4.28 (d, $J = 8.4$ Hz, 1H), 2.67 (d, $J = 1$ Hz, 3H). ^{13}C NMR δ : 146.4, 139.9, 138.1, 137.1, 131.8, 128.7, 128.5, 128.3, 128.0, 127.1, 124.5, 120.3, 117.8, 111.2, 67.9, 62.5, 16.9. Crystal data: triclinic, space group $P\bar{1}$, $a = 7.628(1)$ Å, $b = 9.693(1)$ Å, $c = 13.398(1)$ Å, $\alpha = 76.206(1)^\circ$, $\beta = 76.886(1)^\circ$, $\gamma = 72.791(1)^\circ$, $V = 905.8(1)$ Å³, $F(000) = 372$, $Z = 2$, $T = -110$ °C, μ (Mo K α) = 0.081 mm^{−1}, $D_{\text{calcd}} = 1.296$ g cm^{−3}, crystal size $0.39 \times 0.26 \times 0.18$ mm³, $2\theta_{\text{max}} = 45^\circ$ (CCD area detector, Mo K α radiation), 245 parameters, GOF = 1.17, $wR(F^2) = 0.1076$ (all 2370 data), $R = 0.0485$ (2145 data with $I > 2\sigma I$). Anal. Calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}$: C, 78.16; H, 5.42; N, 11.89. Found: C, 78.27; H, 5.51; N, 11.99.

2-[3-(1H-1,2,3-Benzotriazol-1-yl)-5,5-diethyl-2,5-dihydrofuran-2-yl](diphenyl)methanol (11). White pellets (from CH_2Cl_2 /hexanes); yield, 75%; mp 122–124 °C. ^1H NMR δ : 8.08 (d, $J = 8.2$ Hz, 1H), 7.64–7.61 (m, 2H), 7.57–7.50 (m, 4H), 7.44–7.35 (m, 5H), 7.30–7.25 (m, 2H), 5.99 (d, $J = 1.4$ Hz, 1H), 5.77 (d, $J = 1.4$ Hz, 1H), 3.19 (s, 1H), 2.26–2.07 (m, 2H), 2.01–1.81 (m, 2H), 1.08 (t, $J = 7.4$ Hz, 3H), 0.84 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR δ : 145.8, 145.5, 144.2, 139.7, 133.0, 128.7, 128.5, 128.3, 127.8, 127.5, 127.5, 126.2, 124.9, 120.5, 116.3, 111.1, 94.4, 88.5, 79.3, 31.4, 31.3, 8.8, 8.5. Crystal data: monoclinic, space group $P2_1/c$, $a = 14.113(4)$ Å, $b = 9.571(3)$ Å, $c = 17.403(5)$ Å, $\beta = 106.192(6)^\circ$, $V = 2257(1)$ Å³, $F(000) = 904$, $Z = 4$, $T = -105$ °C, μ (Mo K α) = 0.080 mm^{−1}, $D_{\text{calcd}} = 1.252$ g cm^{−3}, crystal size $0.54 \times 0.42 \times 0.21$ mm³, $2\theta_{\text{max}} = 50^\circ$ (CCD area detector, Mo K α radiation), 292 parameters, GOF = 0.90, $wR(F^2) = 0.0827$ (all 3935 data), $R = 0.0366$ (2459 data with $I > 2\sigma I$). Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}_2$: C, 76.21; H, 6.40; N, 9.87. Found: C, 75.97; H, 6.44; N, 9.86.

(2E)-4-Hydroxy-4,4-diphenylbut-2-enal (12a). Yellow needles (from Et₂O/hexanes); yield, 73%; mp 119–120 °C. ^1H NMR δ : 9.69 (d, $J = 7.8$ Hz, 1H), 7.38–7.32 (m, 10H), 7.28 (d, $J = 15.6$ Hz, 1H), 6.51 (dd, $J = 15.6, 7.9$ Hz, 1H), 2.48 (s, 1H). ^{13}C NMR δ : 193.6, 160.3, 144.0, 130.1, 128.9, 128.4, 127.1, 79.5. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2$: C, 80.65; H, 5.92. Found: C, 80.57; H, 5.89.

(3E)-5-Hydroxy-5,5-diphenylpent-3-en-2-one (13a). Colorless needles (from CH_2Cl_2 /hexanes); yield, 76%; mp 152–154 °C. ^1H NMR δ : 7.35–7.25 (m, 11H), 6.48 (d, $J = 15.6$ Hz, 1H), 2.52 (s, 1H), 2.29 (s, 3H). ^{13}C NMR δ : 198.6, 150.6, 144.6, 128.7, 128.1, 127.1, 79.2, 28.4. Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$: C, 80.92; H, 6.39. Found: C, 80.50; H, 6.18.

2-Phenylfuran (14).²⁵ Yellow oil; yield, 61%. ^1H NMR δ : 7.69–7.66 (m, 2H), 7.46–7.35 (m, 3H), 7.28–7.22 (m, 1H), 6.64 (d, $J = 3.3$ Hz, 1H), 6.46 (dd, $J = 3.3, 1.8$ Hz, 1H). ^{13}C NMR δ : 154.2, 142.3, 131.1, 128.9, 127.5, 124.0, 111.8, 105.1.

1-(1-Methylprop-2-enyl)-1H-1,2,3-benzotriazole (16). Yellow oil; not isolated. ^1H NMR δ : 8.06 (d, $J = 8.2$ Hz, 1H), 7.60 (d, $J = 8.2$ Hz, 1H), 7.51–7.46 (m, 1H), 7.39–7.34 (m, 1H), 6.28–6.22 (m, 2H), 5.95 (dq, $J = 6.9, 5.9$ Hz, 1H), 1.92 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR δ : 146.2, 132.5, 130.9, 127.4, 124.1, 121.0, 120.1, 109.7, 52.1, 19.9.

4-(1H-1,2,3-Benzotriazol-1-yl)-2-chloro-1,1-diphenylpent-2-en-1-ol (17). White needles (from Et₂O/hexanes); yield, 62%; mp 102–104 °C. ^1H NMR δ : 8.05 (d, $J = 8.4$ Hz, 1H), 7.54–7.45 (m, 2H), 7.41–7.36 (m, 1H), 7.32–7.26 (m, 10H), 5.98–5.89 (m, 2H), 3.26 (s, 1H), 1.87 (d, $J = 6.3$ Hz). ^{13}C NMR δ : 146.2, 142.5, 132.6, 129.7, 128.5, 128.4, 128.4, 127.9, 127.7, 127.4, 124.3, 120.3, 109.8, 82.9, 54.2, 20.1. Anal. Calcd for

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C₂₃H₂₀ClN₃O: C, 70.85; H, 5.17; N, 10.78. Found: C, 71.27; H, 5.24; N, 10.73.

Supporting Information Available: General experimental methods and procedures, characterization data for compounds **6b–g**, **7c,d**, **8d,e**, **10b–d**, **12b,c,e,g**, **13b–d**, ¹H and

¹³C NMR spectra for the compounds with HRMS (**12e,g**), and X-ray structures for **trans-6b**, **syn-(Z)-7d**, **syn-(E)-7d**, **8d**, **10a**, and **11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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