Benzotriazole- and 1,2,4-Triazole-Stabilized Allylic Anions: Applications in Syntheses of Functionalized α,β-Unsaturated Ketones, γ-Lactones, γ-Lactams, and β-Substituted Esters

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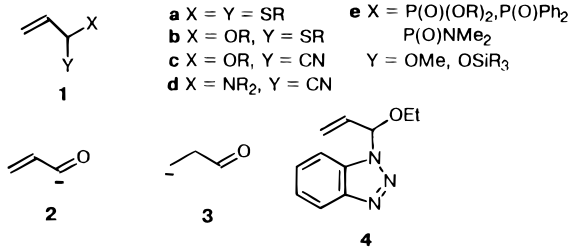
Deprotonated 1-(benzotriazol-1-yl)-1-ethoxy-2-hexene (**7**) reacted with alkyl halides, aldehydes, ketones, imines, and α,β-unsaturated esters to give exclusively the α-alkylated products **8a**−**c**, **10a**,**b**, **12**, **14**, **16**, and **18a**,**b**, respectively. Without isolation, these products were hydrolyzed under mild conditions to generate the corresponding simple or functionalized α,β-unsaturated ketones **9a**−**c**, **11a**,**b**, **13**, **15**, **17**, and **19a**,**b**. Similar reactions with the phenyl-substituted analog 3-(benzotriazol-1-yl)-3-ethoxy-1-phenyl-1-propene (**21**) also gave the analogous α-products, but they were accompanied by small amount of the γ-products in most cases. By contrast, deprotonation of the corresponding triazole derivative **29** with butyllithium followed by reactions with alkyl halides, aldehydes, ketones, or imines yielded exclusively γ-alkylated adducts **32**, **34**, **36**, **38**, **40**, and **42**. Intermediates **32**, **34**, **36**, **38**, **40**, and **42** were readily converted into β-substituted esters **33a**−**c**, γ-lactones **35a**,**b**, **39**, **41**, and **43**, and γ-lactams **37a**−**c** on hydrolysis.

Over recent decades, the chemistry of heteroatom-stabilized allylic anions has been intensively investigated and has led to the development of many new synthetically useful methods.[1−4] Deprotonated systems **1** provide the reversed polarity equivalents **2** and homoenolate anion synthon equivalents **3** through removal of the heteroatoms by hydrolysis. Among the most common precursors of 1,1-diheterostabilized allylic anions are α,β-unsaturated *S*,*S*-acetals **1a**,[5−8] α,β-Unsaturated *O*,*S*-acetals **1b**,[9] α,β-unsaturated *O*-alkyl- or *O*-(trimethylsilyl)-protected cyanohydrins **1c**,[10−15] 2-(dialkylamino)-3-butenenitriles **1d**,[16,17] and allylic phosphorus compounds **1e** (phosphites,[18] phosphonamides,[19] and phosphine oxides[20−22]). In most cases, these precursors are treated with butyllithium or LDA to generate the allylic anions, which are then reacted with an electrophile, such as an alkyl halide, an aldehyde, or a ketone. Their synthetic applications have been summarized in our recent publications.[23−25]



As discussed in our previous papers,[24,25] the synthetic utility of allylic anions **1** depends on (i) the degree of regioselectivity in their reactions with electrophiles, (ii) the availability of their precursors, and (iii) the ease of removal of the heteroatoms at the end of the reaction sequence. Among these, the regioselectivity is crucial to the practical application of the ambident anions **1**. Regioselectivity is influenced in a complicated manner by the substituents on the vinyl groups, the nature of the incoming electrophile, the nature of the hetero moiety (*i.e.*, X/Y groups in **1**), and the reaction.[3,4,15,21] There seems to be no known general rule for the prediction of the ratio of α-/γ-products: in rare cases α-attack is favored at low temperature under kinetic control and γ-attack at higher temperature under thermodynamic control.[14,15]

Recently we described the advantageous use of readily available *N*-(α-ethoxyallyl)benzotriazole (**4**) for the syntheses of functionalized vinyl ketones,[24] cyclopropanes,[25] γ-lactones,[25] β,γ-unsaturated carboxylic acids,[25] ketones,[26] 1,4-diketones,[26] 2-cyclopentenones,[26] and α-keto enamines.[26] Deprotonated **4** reacted with a variety of electrophiles (RX, RCHO, ketone and α,β-unsaturated esters)

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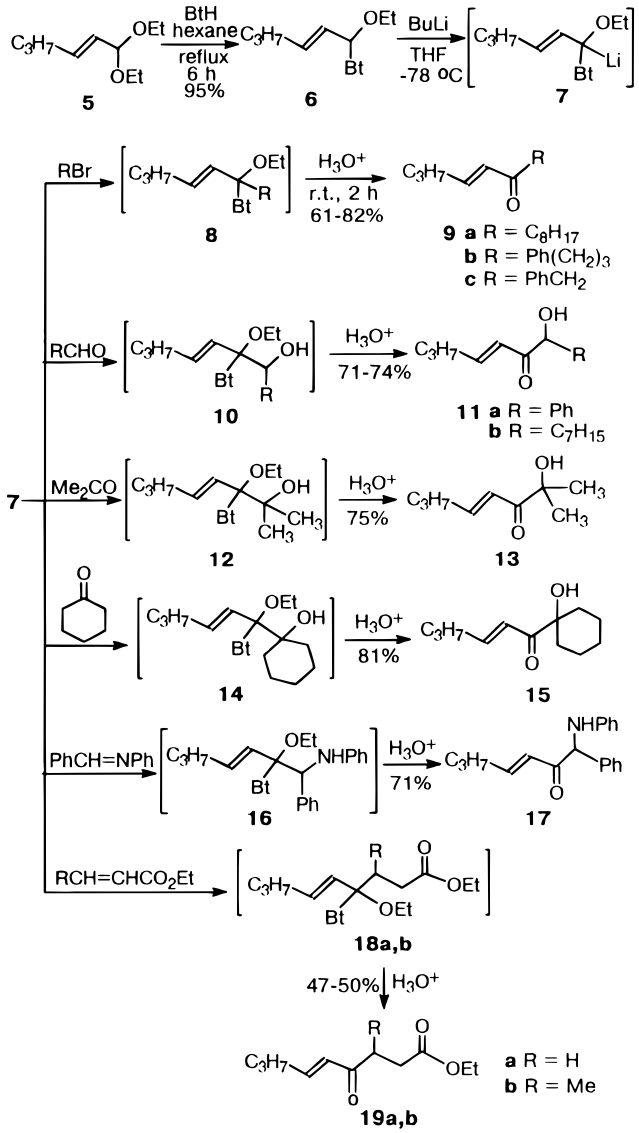
Scheme 1



to give either exclusive α-products (in most cases) or exclusive γ-alkylated products with sterically hindered electrophiles (bulky ketones). We have since studied the reactions of representative alkyl- (**6**) and aryl-substituted (**21**) analogs, investigated the reactions of anion **29** stabilized by a 1,2,4-triazolyl group instead of benzotriazole, and now disclose the details which are of synthetic and mechanistic interest.

Results and Discussion

Benzotriazole-Stabilized Allylic Anion 7 for the Synthesis of Simple and Functionalized α,β-Unsaturated Ketones. Heating acetal **5** with 1.3−1.5 equiv of benzotriazole in hexane for 6 h (or in benzene for 4 h) followed by normal workup (washing the excess benzotriazole with sodium carbonate solution and evaporation of the solvent) gave 1-(benzotriazol-1-yl)-1-ethoxy-2-hexene (**6**) and a very small proportion of benzotriazol-2-yl isomer (*ca.* 5−10%) in 95% total yield (Scheme 1). As the benzotriazol-2-yl isomer undergoes similar transformations, the crude mixture of the 1- and 2-isomers could be directly used in the subsequent reactions. An analytically pure sample of 1-isomer was obtained (85% yield) by column chromatography on silica gel and was fully characterized by NMR spectroscopy and by C,H,N analysis. ^{13}C NMR showed a chemical shift of 88.0 ppm for the methine carbon. Compound **6** is sensitive to acid but relatively stable in basic and neutral media, and can be stored at 0 °C for many days.

Treatment of **6** with 1 equiv of butyllithium at −78 °C results in formation of dark-blue intermediate **7**. Subsequent reaction with 3-phenylpropyl bromide for 2−5 min at the same temperature yielded regioselectively α-alkylated product **8b**, isolated in 41% yield for characterization purposes by column chromatography. No γ-product was observed from the crude NMR spectra. The relatively low yield is due to partial decomposition (hydrolysis) catalyzed by the weakly acidic silica gel. Treatment of pure **8b** with dilute HCl in ethanol at rt for 4 h gave the expected ketone **9b** in 98% yield. In practice, the intermediate **8b** was directly subjected to hydrolysis without isolation by adding H_2O−HCl into the reaction solutions to give, after keeping the solution at room temperature for 4 h, the expected α,β-unsaturated ketone **9b** in 61% overall yield. NMR spectra clearly showed a characteristic carbonyl signal at 202 ppm and absence of the benzotriazolyl and the ethoxy group. Compounds **9a** and **9c** were similarly prepared in 70−82% yields without isolation of the intermediates **8a** and **8c**. It is worth mentioning that previously α-alkylated **4** had to be hydrolzed by the weakly acidic H_2O−$H_2C_2O_4$−SiO_2 system to avoid the Michael addition reaction of the benzotriazole eliminated in the hydrolysis to the ketones obtained under the HCl hydrolysis conditions.[24] In the present cases, no such addition reactions occurred under HCl hydrolysis conditions, obviously due to the presence of the *n*-propyl group.

α,β-Unsaturated ketones of type **9** were previously synthesized *via* (i) construction of the C=C double bond with Wittig−Hornes reactions[27] or Peterson reactions,[28] (ii) formation of the bond between C=C and C=O groups by reaction of vinyl metallic compounds with an acyl chloride or anhydride[29,30] or by palladium-catalyzed carbonylative coupling reaction of 1-halo-1-alkene with 9-alkyl-9-borabicyclo[3.3.1]nonanes,[31] or (iii) three-carbon homologation by oxidation of the corresponding hydroxy compounds[32,33] or by alkylation of an allenic anion followed by hydrolysis.[34] A closely related approach for the synthesis of α,β-unsaturated ketones of type **9** involves the use of alkenoyl anion equivalents of **1c** and **1d**.[13,15,16] However, the need to prepare the cyanohydrins and dealing with HCN during both stages of the preparation of the synthon equivalents and the hydrolysis are problematic on a large scale. The present three-carbon homologation combines simple procedure, readily accessible reagents, and mild hydrolysis conditions and compares favorably with the previous methodology.

When synthon **7** was reacted with benzaldehyde, octanal, acetone, cyclohexanone, and *N*-benzylideneaniline, as expected the corresponding hydroxy- and

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amino-functionalized α,*β*-substituted ketones **11a**,**b**, **13**, **15**, and **17** were prepared in isolated yields of 71−81% without separation of the intermediates **10a**,**b**, **12**, **14**, and **16**. The reactions all proceeded regioselectively, and no *γ*-products were observed in the NMR spectra of the crude product mixtures. The structures for compounds **11a**,**b**, **13**, **15**, and **17** were confirmed by ^{1}H and ^{13}C NMR spectroscopy and by elemental analysis or high-resolution mass spectroscopy. The characteristic ^{13}C carbonyl signals for the ketones **11a**,**b**, **13**, **15**, and **17** appear in the range 200−210 ppm. Interestingly, a similar procedure allows the convenient preparation of *β*-alkenoyl-substituted esters of type **19**. Only 1,4-addition was observed, as judged from the NMR spectra of the crude product. These results are similar to those obtained with the unsubstituted benzotriazole derivative **4**.[24]

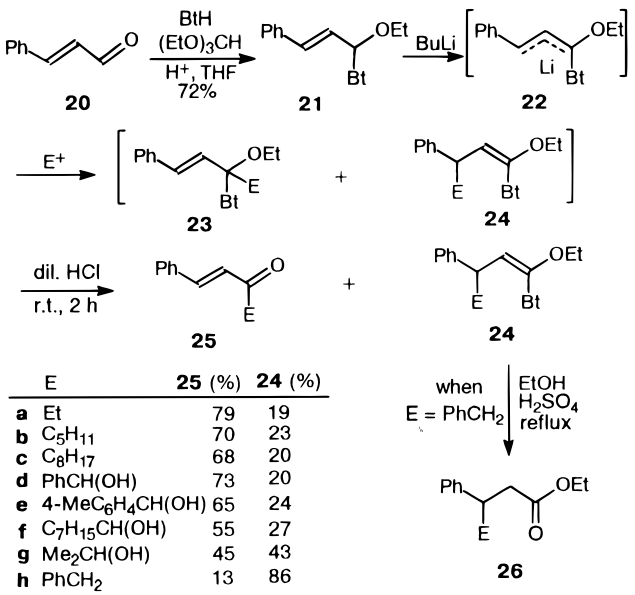
α′-Hydroxy-α,*β*-unsaturated ketones of types **11**, **13**, and **15** are useful intermediates for the cyclopentenone annelation[12,14,15] and for the synthesis of 3-tetrahydrofuranone.[15,35] Perhaps the most convenient previous synthesis is by using the ethyl vinyl ether protected cyanohydrin or trimethylsilyl-protected cyanohydrin **1c**. However, as mentioned earlier, this involves dealing with HCN.

Although imines have been employed as electrophiles in reactions with acyl anion equivalents for the synthesis of α-arylamino-substituted alkynyl, aryl, and dialkyl ketones in our recent publications,[36−38] no report has been found for the synthesis of α-arylamino-α,*β*-unsaturated ketones of type **17** using acyl anion equivalent methodology.

Syntheses of *δ*-ene *γ*-keto esters of type **19** were rarely reported. Ronald and Wheeler[39] prepared a *δ*-(triphenylphosphoranylidene)-*γ*-keto ester by condensation of methylenetriphenylphosphorane with 3-carbomethoxypropionyl chloride in THF or by condensation of triphenylphosphine with methyl 5-bromolevulinate in refluxing benzene followed by deprotonation. Subsequent Wittig reaction with an aldehyde formed the *δ*-ene double bond. However, this method is limited by the availability of the starting materials.

Reaction of Phenyl-Substituted Allylic Anion 22 with Electrophiles Leading to Both α-Alkylated and *γ*-Alkylated Products. Compound **21** was prepared in 72% yield from cinnamaldehyde (**20**) according to our previously developed procedure for the conversion of aldehydes to the corresponding benzotriazole derivatives.[37] Treatment of 3-(benzotriazol-1-yl)-3-ethoxy-1-phenyl-1-propene (**21**) with 1 equiv of BuLi at −78 °C for a few minutes followed by reaction with ethyl bromide afforded a mixture of **23a** and **24a** from NMR spectra in a ratio of *ca.* 4:1 (Scheme 2). TLC showed that these two compounds have similar retention times, which hinders separation by column chromatography. The mixture of **23a** and **24a** was treated with dilute hydrochloric acid in aqueous acetone at room temperature for 5 h to produce the hydrolyzed **25a** and unchanged **24a** in 79% and 19% yields, respectively. Compounds **25a** and **24a** were separated by column chromatography and fully characterized by NMR spectroscopy and elemental analyses. Compounds **25b**−**g** were similarly prepared in 45−73% isolated yields by this procedure. In the case of **25g**, the *γ*-alkylated product **24g** was also isolated and its structure confirmed by NMR spectra and elemental analysis. In the cases of **25b**−**f**, the amounts of the *γ*-byproducts **24b**−**f** were determined by NMR and GC of the crude product mixture.

Scheme 2



20 21 22 23 24 25 24 26

	E	**25** (%)	**24** (%)
a	Et	79	19
b	C_5H_{11}	70	23
c	C_8H_{17}	68	20
d	PhCH(OH)	73	20
e	4-MeC_6H_4CH(OH)	65	24
f	C_7H_{15}CH(OH)	55	27
g	Me_2CH(OH)	45	43
h	$PhCH_2$	13	86

When benzyl bromide was used as the electrophile, the *γ*-product **24h** was obtained predominantly (86%) along with minor α-product **25h** (13%). This is possibly controlled by the hard and soft acids and bases principle.[40] Benzyl bromide is softer than other alkyl bromides, and it appears that the α-position prefers hard electrophiles and the *γ*-position favors the soft electrophile. Consequently, benzyl bromide predominantly reacted at the *γ*-position. Murphy and Wattanasin[41] observed similar behavior when they reacted [2-((*E*)-α-styrenyl)-1,3-dithian-2-yl]lithium with alkyl halides and found that benzyl halides behave differently from normal halide compounds to give predominantly *γ*-products. The α:*γ* ratio has been correlated with the hardness of both the leaving group and the alkyl group of the alkylating agent. Compound **24h** was further hydrolyzed in refluxing EtOH−H_2O−H_2SO_4 to give ethyl 3,4-diphenylbutanoate (**26**).

As previously mentioned, the regioselectivity of the reactions of ambident allylic anions with electrophiles is strongly affected both by substrates and by the nature of the electrophile introduced. In the rare cases reported for *γ*-phenyl-substituted analogs **1**, alkylation of deprotonated **1d** (NR_2 = morpholino) bearing a *γ*-phenyl substituent with alkyl halides (MeI or EtBr) gave 75−80% of α-products along with 13−20% of *γ*-products[16] (when isopropyl bromide was used as the electrophile, 30% α-product and 30% *γ*-product were formed during the reaction[16]). Ahlbrecht and Vonderheid[11] studied similar systems and found that the regioselectivity also depended on the NR_2 group; however, when an aldehyde or ketone was used as the electrophile, it gave exclusively *γ*-products. Reactions of dithio-substituted cinnamyl-

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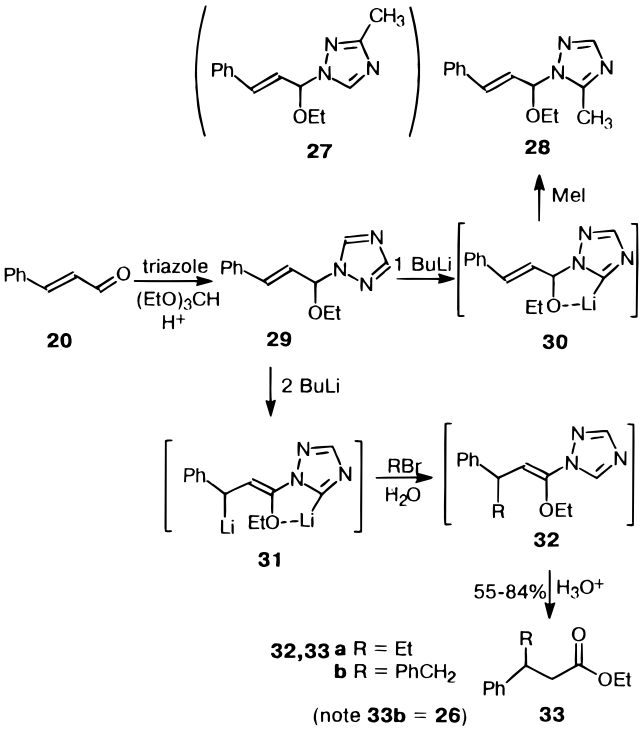
Scheme 3



lithium with carbonyl compounds have also been investigated.[6] Little regioselectivity was reported under normal lithiation conditions; while in the presence of $BF_3{\cdot}Et_2O$, the reaction occurred predominantly at the α-site.

In the present approach, reactions with alkyl halides gave mainly the α-products in 68−79% yields, and reactions with aldehydes and ketones still generate the expected α-functionalized α,β-unsaturated ketones of types **25d**−**g** in reasonable to good yields. Considering the convenient availability of the starting materials, the simple manipulation required, and the easy separation of the products, this method is still useful in the synthesis of these types of compounds despite the absence of regiospecificity.

Triazole-Stabilized Homoenolate Anions for the Synthesis of β-Alkylated Esters. 3-Ethoxy-1-phenyl-3-(triazol-1-yl)-1-propene (**29**) was similarly prepared in 82% yield by reaction of *trans*-cinnamaldehyde (**20**) with 1,2,4-triazole and triethyl orthoformate in THF with sulfuric acid as a catalyst (Scheme 3).

Because of the presence of acidic protons on the triazole ring, treatment of compound **29** with 1 equiv of butyllithium followed by reaction with methyl iodide gave in quantitive yield a mixture of 5-methyl- (**28**) and 3-methyl-substituted (**27**) triazole products (ratio, 2.5:1 from NMR). ^{1}H NMR spectra of this mixture clearly showed two different ring proton signals at 7.82 (H-3) and 8.00 (H-5) ppm. However, we believe that the 3-methyl isomer **27** is not formed directly, but by isomerization of the 5-alkylated isomer **28**, and this is supported by the finding that keeping the original mixture for *ca.* 30 days resulted in the formation of equal amounts of the 3-methyl (**27**) and 5-methyl (**28**) isomers. 1-Substituted 1,2,4-triazoles have previously been shown to undergo easy lithiation at the 5-position of the triazole ring, and such isomerizations between the 3- and the 5-isomers has also been previously observed.[42,43]

Treatment of **29** with 2 equiv of butyllithium at −78 °C for a few minutes is believed to form dilithio derivative **31** or an isomer with Li attached to the α-rather than γ-position of the side chain. Subsequent reaction with 1 equiv of ethyl bromide at the same temperature for a few minutes afforded in 90% yield a mixture of two *cis*/*trans* isomers of the γ-alkylated product **32a** (*E* and *Z*; ratio *ca.* 1:1 by ^{1}H NMR). The structure of **32a** was determined by NMR spectroscopy. No α-product was observed from the NMR spectra of the crude product. The α-product ^{13}C NMR spectra would give a quaternary carbon signal in the range 88−100 ppm (the methine carbon of starting material **29** has a chemical shift of 88 ppm). Hydrolysis of **32a** in a HCl/ethanol/water solution under reflux for 3 h produced the expected β-alkylated ester **33a** in 84% yield. Ester **33b** was similarly prepared in 55% overall yield.

Even when we used 2 equiv of ethyl bromide in the reaction with **29**, only the monoalkylated product **32a** was generated and no dialkylated product (with γ-position and the triazole ring alkylating) was formed. This is consistent with that reported in the literature,[42,43] which indicated that the 5-lithiated 1-[(dialkylamino)-methyl]-1,2,4-triazole can only react with reactive electrophiles such as MeI, RCHO, or RCOR to generate the 5-alkyltriazoles.

Nucleophilic conjugated addition of organocopper reagents to unsaturated esters has been frequently used in the synthesis of β-alkylated esters **33**.[44,45] A different approach for the synthesis of these type of compounds is *via* reaction of homoenolate anions **3** with an electrophile, which has previously been realized by using allylic phosphorus compounds **1e**[18−22]). However, preparation of the phosphorus compounds requires relatively complicated manipulation and use of expensive reagents.[46] The present triazole-mediated transformation of cinnamaldehyde to β-alkylated esters of type **33** is a very convenient approach. Unfortunately, attempted extension of this methodology to other β-alkyl- substituted α,β-unsaturated aldehydes failed as a complex mixtures of several compounds was formed.

Triazole-Stabilized Homoenolate Anion 31 for the Synthesis of Lactones and Lactams. When aldehydes or ketones were used as electrophiles to react with dilithiated species **31** followed by hydrolysis, the expected γ-lactones **35a**,**b**, **39**, **41**, and **43** were easily prepared in 56%-90% yields (Scheme 4). Using imines as electrophiles similarly gave the lactams **37a**−**c** in 70−83% yields. A possible mechanistic rationalization is that under the acidic conditions the substituted triazole derivatives **34a**,**b**, **36a**−**c**, **38**, **40**, and **42** (initially formed after lithiation and reactions with the carbonyl compounds or imines) underwent hydrolysis to yield the γ-hydroxy- or γ-arylamino-substituted esters, which in turn spontaneously cyclized intramolecularly to furnish the five-membered cyclic products **35a**,**b**, **37a**−**c**, **39**, **41**, and **43**. Thus, treatment of compound **29** with 2 equiv

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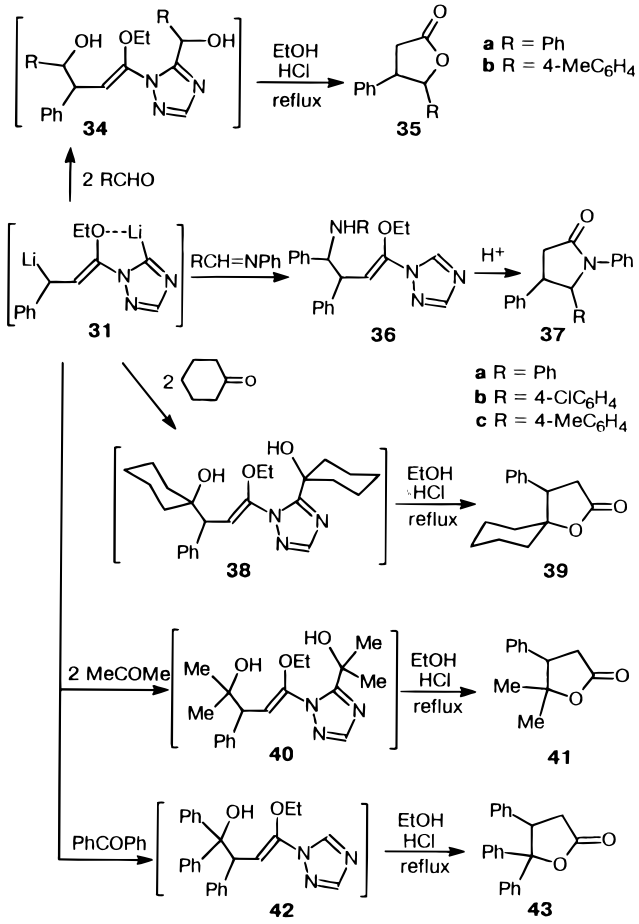
Scheme 4



of butyllithium at −78 °C for 5 min followed by reaction with 1 equiv of *N*-benzylideneaniline at this temperature for a few minutes generated the intermediate **36a** in 80% yield. Further acidic treatment of this intermediate in refluxing ethanol afforded lactam **37a** in 95% yield. The structures for intermediate **36a** and product **37a** were fully characterized by NMR spectroscopy and by C,H,N analyses. Compounds **35a**,**b**, **37b**,**c**, **39**, **41**, and **43** were similarly prepared by this procedure without isolation of the intermediates **34a**,**b**, **36b**,**c**, **38**, **40**, and **42**. These intermediates, **34a**,**b**, **36a**−**c**, **38**, **40** and **42**, would be mixtures of several isomers including regioisomers (*E* and *Z*) and diastereoisomers (three chiral centers), which would hinder their isolation and characterization.

In the preparations of **35a**,**b**, **39**, and **41**, 2 equiv of the appropriate electrophile was used. Otherwise, low yields were achieved. In the remaining cases (**37a**−**c**, **43**), only 1 equiv was consumed. This is because the triazole anions formed reacted only with the relatively reactive electrophiles (aldehydes or unhindered ketones) as mentioned before. Evidently benzophenone behaves as a hindered electrophile. Formation of the dialkylated **34a**,**b**, **38**, and **40** was determined by the crude NMR spectra, which indicated the disappearance of one triazole proton and the presence of two sets of signals from the substituents introduced.

In the present cases, no matter whether the triazole is alkylated or not, the triazole moiety, as a leaving group in the present work, will finally be hydrolyzed off and can easily be removed from the reaction mixture by an aqueous washing.

Synthesis of γ-lactones was previously accomplished by cyclization of γ-hydroxy carboxylates in the presence of a mineral acid. Available methods for the generation of γ-hydroxy carboxylates include (i) reduction of γ-oxo-substituted esters,[47] (ii) Grignard reaction of γ-oxo-substituted esters,[48] (iii) reaction of β-zinc esters with an aldehyde,[49] (iv) reaction of manganic and other higher valent metal carboxylates with olefins and carbocylic acids,[50] and (v) direct lactonization of unsaturated carboxy acids.[51] Reaction of homoenolate anions of types **3** generated from **1a**,[52] **1c**,[15] **1d**,[11] or **1e**[19] with a carbonyl compound has also frequently been utilized for the synthesis of γ-lactones. However, each homoenolate anion only applies to the synthesis of certain substituted γ-lactones.

Major methods for γ-lactam syntheses are intramolecular acylation of a γ-amino-functionalized carboxylic acid or ester.[53] These amino acids or amino esters are frequently generated *in situ* by reactions such as reductive amination of keto acids,[54] aminolysis of lactones,[55] or reduction of nitro esters.[56] Takahata reported a novel synthesis of γ-lactams by a two-step conversion *via* γ-hydroxy amides.[57] Reactions of a homoenolate anion or equivalent with an imine analogous to the present approach for the preparation of γ-lactams were also previously reported.[58]

The structures for the final products and the isolated intermediates were confirmed by ^{1}H and ^{13}C NMR spectroscopy and by elemental analyses. The data for known compounds are consistent with those reported in literature.

Conclusions

Novel benzotriazole- and 1,2,4-triazole-stabilized allylic anions have been developed for the generation of α,β-unsaturated ketones, γ-lactones, γ-lactams, and β-substituted esters. The simplicity and convenient availability of the starting materials give these methods considerable potential importance in organic synthesis.

Experimental Section

General Comments. Melting points were determined on a hot stage apparatus without correction. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were in $CDCl_3$ with TMS or $CDCl_3$, respectively, as the internal reference. Elemental analyses and high-resolution mass spectra were performed within the department. Column chromatography was carried out on MCB silica gel (230−400 mesh). Tetrahydrofuran (THF) was freshly distilled from sodium−benzophenone. Lithiation reactions were carried out under the protection of dry nitrogen.

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Preparation of *trans*-1-(Benzotriazol-1yl)-1-ethoxy-2-hexene (6). A mixture of 2-hexenal diethyl acetal (**5**) (3.45 g, 20 mmol) and benzotriazole (3.57 g, 30 mmol) in hexane (40 mL) was heated under reflux for 6 h. Diethyl ether (300 mL) was then added. The resulting solution was washed with a saturated sodium carbonate solution (3 × 100 mL) and dried with anhydrous $MgSO_4$. Evaporation of the solvent gave 4.67 g of oil: yield 95% (contaning 5−10% 2-benzotriazole isomer). Further separation by column chromatography (hexane/ethyl acetate 17:1) gave analytically pure compound (4.2 g, 85%): ^{1}H NMR δ 0.86 (t, 3 H, J = 7.3 Hz), 1.15 (t, 3 H, J = 7.0 Hz), 1.42 (sixtet, 2 H, J = 7.4 Hz), 2.04−2.11 (m, 2 H), 3.28−3.38 (m, 1 H), 3.57−3.68 (m, 1 H), 5.85−6.08 (m, 2 H), 6.57−6.60 (m, 1 H), 7.39 (t, 1 H, J = 7.0 Hz), 7.48 (t, 1 H, J = 7.0 Hz), 7.77 (d, 1 H, J = 8.3 Hz), 8.09 (d, 1 H, J = 8.3 Hz); ^{13}C NMR δ 13.4, 14.5, 21.6, 33.8, 64.2, 89.1, 111.5, 119.8, 123.9, 124.8, 127.1, 131.1, 136.1, 146.7. Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.32; H, 7.87; N, 17.34.

Preparation of Intermediate 8b and Ketone 9b. To a solution of 1-(benzotriazol-1yl)-1-ethoxy-2-hexene (**6**) (1.23 g, 5 mmol) in THF (50 mL) at −78 °C was added *n*-butyllithium (2.0 M in cyclohexane, 3 mL, 6 mmol). The solution was stirred at this temperature for 5 min, and 3-phenyl-1-bromopropane (1.0 g, 5 mmol) was then added. After the solution was stirred at −78 °C for an additional 5 min, the reaction was quenched at this temperature with water (50 mL), extracted with diethyl ether (2 × 100 mL), and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue which was separated by column chromatography (hexane/ethyl acetate, 30:1) to give **8b**. Compound **8b** was disolved in EtOH (20 mL) and cooled to 0 °C. Water (10 mL) and hydrochloric acid (2 M, 5 mL) were added at this temperature, and the mixture was stirred at room temperature for 4 h. The resulting solution was extracted with diethyl ether (2 × 200 mL) and washed with saturated sodium carbonate solution (2 × 50 mL). The organic phase was separated and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue which was separated by column chromatography (hexane/ethyl acetate 100:1) to give ketone **9b**.

***trans*-4-(Benzotriazol-1-yl)-4-ethoxy-1-phenyl-5-nonene (8b):** obtained as a colorless oil; yield 41%; ^{1}H NMR δ 0.90 (t, 3 H, J = 7.4 Hz), 1.10−1.40 (m, 5 H), 1.55−1.84 (m, 2 H), 1.94−2.12 (m, 1 H), 2.13−2.37 (m, 3 H), 2.51 (t, 2 H, J = 7.4 Hz), 3.61−3.82 (m, 2 H), 4.92 (d, 1 H, J = 9.1 Hz), 5.47 (q, 1 H, J = 7.4 Hz), 7.08−7.49 (m, 8 H), 8.05 (d, 1 H, J = 8.3 Hz); ^{13}C NMR δ 13.4, 14.3, 19.4, 28.9, 30.3, 35.2, 38.7, 58.1, 62.4, 96.4, 109.9, 119.9, 123.5, 125.6, 126.6, 128.1, 128.2, 131.7, 141.8, 146.0, 160.4. Anal. Calcd for $C_{23}H_{29}N_3O$: C, 76.00; H, 8.04; N, 11.56. Found: C, 76.32; H, 8.29; N, 11.97.

***trans*-1-Phenyl-5-nonen-4-one (9b):** obtained as a colorless oil; yield 98%; ^{1}H NMR δ 0.92 (t, 3 H, J = 6.9 Hz), 1.47 (sixtet, 2 H, J = 7.3 Hz), 1,90−2.02 (m, 2 H), 2.12−2.22 (m, 2 H), 2.53 (t, 2 H, J = 7.3 Hz), 2.64 (t, 2 H, J = 7.4 Hz), 6.07 (d, 1 H, J = 15.1 Hz), 6.71−6.83 (m, 1 H), 7.15−7.35 (m, 5 H); ^{13}C NMR δ 13.5, 21.2, 25.5, 34.2, 35.0, 39.0, 125.7, 128.2, 128.3, 130.3, 141.6, 146.9, 200.0. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 82.86; H, 9.35.

General Procedure for the Preparation of 9a−c, 11a,b, 13, 15, 17, and 19a,b. To a solution of 1-(benzotriazol-1yl)-1-ethoxy-2-hexene (**6**) (1.23 g, 5 mmol) in THF (50 mL) at −78 °C was added *n*-butyllithium (2.0 M in cyclohexane, 2.5 mL, 5 mmol). The solution was stirred at this temperature for 5 min, and the appropriate electrophile ($C_8H_{17}Br$, $Ph(CH_2)_3Br$, $PhCH_2Br$, benzaldehyde, octanal, acetone, cyclohexanon, *N*-benzylideneaniline, methyl acrylate, or methyl crotonate; 5.5 mmol) was then added. After the solution was stirred at −78 °C for an additional 5 to 10 min, the reaction was quenched at this temperature with water (50 mL). Hydrochloric acid (2 M, 5 mL) was added at this temperature, and the mixture was stirred at room temperature for 4 h. The resulting solution was extracted with diethyl ether (2 × 100 mL) and washed with saturated sodium carbonate solution (2 × 100 mL). The organic phase was separated and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue which was separated by column chromatography (hexane/ethyl acetate 30:1). Compound **9b** was obtained by using the above procedure (yield, 61%).

***trans*-4-Tetradecen-5-one (9a):** obtained as a colorless oil; yield 70%; ^{1}H NMR δ 0.89 (t, 3 H, J = 7.2 Hz), 0.96 (t, 3 H, J = 7.2 Hz), 1.22−1.38 (m, 10 H), 1.45−1.70 (m, 4 H), 2.27−2.37 (m, 2 H), 2.54 (t, 2 H, J = 7.2 Hz), 6.11 (d, 1 H, J = 15.9 Hz), 6.79−6.90 (m, 1 H); ^{13}C NMR δ 13.6, 14.0, 21.3, 22.5, 24.2, 29.1, 29.2, 29.3, 31.7, 34.3, 40.0, 130.4, 146.8, 200.7; HRMS calcd for $C_{14}H_{26}O$ M^+ = 210.1983, found M = 210.1992.

***trans*-1-Phenyl-3-hepten-2-one (9c):** obtained as a colorless oil; yield 82% (lit.[59] mp 76−79 °C/mmHg); ^{1}H NMR δ 0.90 (t, 3 H, J = 7.4 Hz), 1.46 (sixtet, 2 H, J = 7.3 Hz), 2.10−2.20 (m, 2 H), 3.81 (s, 2 H), 6.14 (d, 1 H, J = 15.8 Hz), 6.85−6.96 (m, 1 H), 7.17−7.35 (m, 5 H); ^{13}C NMR δ 13.5, 21.1, 34.3, 47.4, 126.6, 128.5, 129.3, 129.4, 134.5, 148.1, 197.2.

***trans*-1-Hydroxy-1-phenyl-3-hepten-2-one (11a):** obtained as a colorless oil; yield 74%; ^{1}H NMR δ 0.82 (t, 3 H, J = 7.4 Hz), 1.32−1.45 (m, 2 H), 2.04−2.15 (m, 2 H), 4.51 (br s, 1 H), 5.20 (s, 1 H), 6.11 (d, 1 H, J = 15.6 Hz), 6.95−7.10 (m, 1 H), 7.22−7.43 (m, 5 H); ^{13}C NMR δ 13.4, 21.0, 34.5, 78.4, 124.6, 127.6, 128.4, 128.8, 138.2, 150.4, 197.3. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.83; H, 8.30.

***trans*-7-Hydroxy-4-tetradecen-6-one (11b):** obtained as a colorless oil; yield 71%; ^{1}H NMR δ 0.87 (t, 3 H, J = 6.6 Hz), 0.95 (t, 3 H, J = 7.4 Hz), 1.20−1.60 (m, 13 H), 1.72−1.87 (m, 1 H), 2.20−2.29 (m, 2 H), 3.64 (d, 1 H, J = 5.4 Hz), 4.32−4.40 (m, 1 H), 6.24 (d, 1 H, J = 15.7 Hz), 6.96−7.10 (m, 1 H); ^{13}C NMR δ 13.5, 13.9, 21.1, 22.5, 24.7, 29.0, 29.3, 31.6, 34.3, 34.6, 75.0, 124.9, 149.6, 200.7; HRMS calcd for $C_{14}H_{26}O_2$ M^+ = 226.1932 11, found M = 226.1919.

***trans*-2-Hydroxy-2-methyl-4-octen-3-one (13):** obtained as a colorless oil; yield 75%; ^{1}H NMR δ 0.97 (t, 3 H, J = 7.4 Hz), 1.40 (s, 6 H), 1.54 (sixtet, 2 H, J = 7.4 Hz), 2.20−2.30 (m, 2 H), 4.09 (s, 1 H), 6.46 (d, 1 H, J = 15.4 Hz), 7.10−7.22 (m, 1 H); ^{13}C NMR δ 13.5, 21.1, 26.2, 34.6, 75.0, 122.3, 150.6, 202.2. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.34; H, 9.94.

***trans*-1-(1-Hydroxycyclohexyl)-2-hexen-1-one (15):** obtained as a colorless oil; yield 81%; ^{1}H NMR δ 0.96 (t, 3 H, J = 7.3 Hz), 1.21−1.38 (m, 1 H), 1.41−1.60 (m, 4 H), 1.61−1.81 (m, 7 H), 2.20−2.30 (m, 2 H), 3.88 (s, 1 H), 6.56 (d, 1 H, J = 15.2 Hz), 7.07−7.19 (m, 1 H); ^{13}C NMR δ 13.5, 20.9, 21.2, 25.2, 33.5, 34.6, 76.7, 122.6, 150.2, 202.3. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.31; H, 10.83.

***trans*-1-Phenyl-1-(phenylamino)-3-hepten-2-one (17):** yield 71%; mp 78−79 °C: ^{1}H NMR δ 0.82 (t, 3 H, J = 7.4 Hz), 1.32−1.42 (m, 2 H), 2.05 (q, 2 H, J = 7.1 Hz), 5.11 (s, 1 H), 5.56 (br s, 1 H), 6.23 (d, 1 H, J = 15.6 Hz), 6.55−6.67 (m, 3 H), 6.96−7.12 (m, 3 H), 7.17−7.35 (m, 3 H), 7.42 (d, 2 H, J = 7.1 Hz); ^{13}C NMR δ 13.4, 20.9, 34.3, 66.2, 113.2, 117.3, 125.7, 127.8, 127.9, 128.8, 128.9, 137.8, 146.0, 149.2, 194.4. Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.54; H, 7.80; N, 5.04.

Ethyl *trans*-4-oxa-5-nonenoate (19a): obtained as a colorless oil; yield 47%; ^{1}H NMR δ 0.96 (t, 3 H, J = 7.4 Hz), 1.27 (t, 3 H, J = 7.1 Hz), 1.47−1.60 (m, 2 H), 2.18−2.27 (m, 2 H), 2.63 (t, 2 H, J = 6.7 Hz), 2.90 (t, 2 H, J = 6.7 Hz), 4.15 (q, 2 H, J = 7.1 Hz), 6.14 (d, 1 H, J = 15.9 Hz), 6.85−6.96 (m, 1 H); ^{13}C NMR δ 13.4, 13.9, 21.1, 27.9, 34.2, 60.3, 129.9, 147.4, 172.7, 198.0. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.96; H, 9.46.

Ethyl *trans*-3-methyl-4-oxa-5-nonenoate (19b): obtained as a colorless oil; yield 50%; ^{1}H NMR δ 0.95 (t, 3 H, J = 7.4 Hz), 1.15 (d, 3 H, J = 7.2 Hz), 1.24 (t, 3 H, J = 7.1 Hz), 1.46−1.59 (m, 2 H), 2.18−2.25 (m, 2 H), 2.31 (dd, 1 H, J = 16.6 and 6.1 Hz), 2.79 (dd, 1 H, J = 16.6 and 8.2 Hz), 3.20−3.32 (m, 1 H), 4.11 (q, 2 H, J = 7.1 Hz), 6.19 (d, 1 H, J = 15.7 Hz), 6.87−6.98 (m, 1 H); ^{13}C NMR δ 13.5, 14.0, 17.0, 21.2, 34.4, 36.9, 39.6, 60.3, 128.5, 147.8, 172.2, 201.9. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.49; H, 9.94.

Preparation of Benzotriazole and Triazole Derivatives 21 and 29. A mixture of cinnamaldehyde (16.3 g, 120

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mmol), triazole or benzotriazole (240 mmol), ethanol (8.3 g, 180 mmol), triethyl orthoformate (53.6 g, 360 mmol), and concd sulfuric acid (0.68 g) in THF (100 mL) was heated under reflux for 4 h. After cooling, sodium carbonate (15 g) was added the solution was stirrred for 10 min. Diethyl ether (300 mL) was added, and the resulting solution was washed with water (2 × 100 mL) and dried with anhydrous magnesium sulfate. Evaporation of the solvent gave a residure, which was subjected to column chromatography (hexane/ethyl acetate, 20:1 for **21** and 1:1 for **29**).

***trans*-3-(Benzotriazol-1-yl)-3-ethoxy-1-phenyl-1-propene (21):** yield 72%; mp 75−77 °C: ^{1}H NMR δ 1.20 (t, 3 H, J = 7.0 Hz), 3.33−3.43 (m, 1 H), 3.61−3.71 (m, 1 H), 6.52 (dd, 1 H, J = 15.9 and 4.4 Hz), 6.78 (d, 1 H, J = 4.4 Hz), 6.93 (d, 1 H, J = 16.0 Hz), 7.20−7.48 (m, 7 H), 7.78 (d, 1 H, J = 8.1 Hz), 8.10 (d, 1 H, J = 8.2 Hz); ^{13}C NMR δ 14.5, 64.3, 88.7, 111.3, 119.7, 123.4, 124.0, 126.7, 127.3, 128.4, 128.5, 131.1, 133.8, 135.0, 146.6. Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.10; H, 6.13; N, 15.04. Found: C, 73.27; H, 6.22; N, 15.07.

***trans*-3-Ethoxy-1-phenyl-3-(triazol-1-yl)-1-propene (29):** yield 82%; mp 47−49 °C; ^{1}H NMR δ 1.25 (t, 3 H, J = 7.0 Hz), 3.50−3.70 (m, 2 H), 6.07 (d, 1 H, J = 5.2 Hz), 6.38 (dd, 1 H, J = 16.0 and 5.2 Hz), 6.83 (d, 1 H, J = 16.0 Hz), 7.23−7.55 (m, 5 H), 8.00 (s, 1 H), 8.32 (s, 1 H); ^{13}C NMR δ 14.7, 64.9, 88.6, 123.6, 126.8, 128.5, 128.6, 134.2, 135.0, 141.7, 151.5. Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 68.52; H, 6.93; N, 18.54.

General Procedure for the Preparation of 24a,g,h and 25a−h. To a solution of 3-(benzotriazol-1-yl)-3-ethoxy-1-phenyl-1-propene (**21**) (1.40 g, 5 mmol) in THF (50 mL) at −78 °C was added *n*-butyllithium (2.5 M in cyclohexane, 2 mL, 5 mmol). The solution was stirred at this temperature for 5 min, and the appropriate electrophile (EtBr, $C_5H_{11}Br$, $C_8H_{17}Br$, benzaldehyde, 4-methylbenzaldehyde, octanal, acetone, or benzyl bromide; 5 mmol) was then added. After the solution was stirred at −78 °C for an additional 5 to 10 min, the reaction was quenched at this temperature with water (50 mL). The mixture was extracted with diethyl ether (3 × 100 mL). Evaporation of the solvent gave a residue, which was hydrolyzed in a mixture of acetone (15 mL), water (15 mL), and HCl (2 mL) at room temperature for 2 h. The resulting solution was extracted with diethyl ether (3 × 100 mL), washed with water (100 mL), and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue which was separated by column chromatography.

1-(Benzotriazol-1-yl)-1-ethoxy-3-phenyl-1-pentene (24a): obtained as a colorless oil; yield 19% (a mixture of *E* and *Z* isomers; ratio, *ca.* 4:1 as determined by ^{1}H NMR); ^{1}H NMR δ 0.76 (t, J = 7.2 Hz) and 1.00 (t, J = 7.4 Hz) (total 3 H), 1.23 (t, J = 7.1 Hz) and 1.32 (t, J = 7.1 Hz) (total 3 H), 1.70−1.95 (m, 2 H), 2.98−3.07 (m), 3.51−3.70 (m) and 3.82-4.03 (m) (total 3 H), 5.25 (d, J = 10.3 Hz) and 5.60 (d, J = 10.0 Hz) (total 1 H), 7.03−7.55 (m, 7 H), 7.65 (d, 1 H, J = 8.3 Hz), 8.05 (d, 1 H, J = 8.5 Hz); ^{13}C NMR δ (11.8, mi), 12.1, (14.1, mi), 14.6, 29.7, (29.8, mi), 43.3, (43.9, mi), (64.8, mi), 66.5, (106.9, mi), (110.5, mi), 110.8, 111.0, 113.4, (119.6, mi), 119.8, (124.0, mi), 124.2, (126.0, mi), 126.2, 127.0, 127.2, 127.9, 128.1, 128.2, 128.4, 132.2, (132.4, mi), 142.9, 144.3, 145.5. Anal. Calcd for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67. Found: C, 74.25; H, 7.06; N, 14.16.

1-(Benzotriazol-1-yl)-1-ethoxy-4-hydroxy-5-methyl-3-phenyl-1-pentene (24g): yield 43%; mp 118−120 °C (a mixture of *E* and *Z* isomers; ratio, *ca.* 1.8:1 as determined by ^{1}H NMR); ^{1}H NMR δ 1.03 (s), 1.26 (s) and 1.38 (s) (total 6 H), 1.15 (t, J = 7.1 Hz) and 1.35 (t, J = 7.1 Hz) (total 3 H), 2.56 (br s, 1 H), 3.15 (d, J = 10.7 Hz) and 4.01 (d, J = 10.4 Hz) (total 1 H), 3.40−3.51 (m, 1 H), 3.60−3.70 (m, 1 H), 4.01−4.13 (m, 1 H), 5.79 (d, J = 10.6 Hz) and 6.05 (d, J = 10.5 Hz) (total 1 H), 7.05−7.50 (m) and 7.66 (d, J = 8.3 Hz) (total 8 H), 8.04 (d, 1 H, J = 8.3 Hz); ^{13}C NMR δ 14.0, 14.5, 27.8, 27.9, 28.4, 52.4, 52.9, 64.8, 66.3, 72.1, 72.2, 102.3, 109.5, 110.5, 110.7, 119.3, 119.6, 124.0, 124.2, 126.3, 126.5, 127.7, 128.0, 128.1, 128.7, 129.0, 132.0, 132.5, 140.9, 141.0, 143.5, 144.4, 144.6, 145.2. Anal. Calcd for $C_{20}H_{23}N_3O_2$: C, 71.19; H, 6.87; N, 12.45. Found: C, 71.47; H, 7.04; N, 12.10.

1-(Benzotriazol-1-yl)-1-ethoxy-3,4-diphenyl-1-butene (24h): obtained as a colorless oil; yield 86% (a mixture of *E* and *Z* isomers; ratio, *ca.* 1.5:1 as determined by ^{1}H NMR); ^{1}H NMR δ 1.00 (t, J = 7.1 Hz) and 1.22 (t, J = 7.1 Hz) (total 3 H), 2.97−3.38(m), 3.51−3.63 (m), 3.78−3.90 (m) and 4.21−4.35 (m) (total 5 H), 5.24 (d, J = 10.2 Hz) and 5.60 (d, J = 10.2 Hz) (total 1 H), 6.80−7.48 (m, 13 H), 8.00 (d, 1 H, J = 8.2 Hz); ^{13}C NMR δ 13.9, 14.3, 43.1, 43.6, 44.1, 64.6, 66.1, 105.1, 110.5, 110.6, 111.9, 119.1, 119.5, 123.8, 124.0, 125.6, 125.9, 126.0, 126.2, 127.0, 127.1, 127.6, 127.7, 127.9, 128.1, 128.3, 128.7, 129.1, 132.0, 132.4, 138.9, 139.4, 142.8, 143.3, 143.5, 143.7, 144.8, 145.2; HRMS calcd for $C_{24}H_{23}N_3O$ M = 369.1763, found M = 369.1740.

***trans*-1-Phenyl-1-penten-3-one (25a):** yield 79%; mp 41−43 °C; ^{1}H NMR δ 1.17 (t, 3 H, J = 7.3 Hz), 2.68 (q, 2 H, J = 7.3 Hz), 6.74 (d, 1 H, J = 16.3 Hz), 7.33−7.42 (m, 3 H), 7.50−7.60 (m, 3 H); ^{13}C NMR δ 8.0, 33.8, 125.8, 128.0, 128.7, 130.1, 134.4, 141.9, 200.5. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.20; H, 7.76.

***trans*-1-Phenyl-1-octen-3-one (25b):** yield 70%; mp 44−45 °C; ^{1}H NMR δ 0.91 (t, 3 H, J = 6.7 Hz), 1.30−1.41 (m, 4 H), 1.62−1.74 (m, 2 H), 2.65 (t, 2 H, J = 7.5 Hz), 6.75 (d, 1 H, J = 16.2 Hz), 7.33−7.40 (m, 3 H), 7.50−7.59 (m, 3 H); ^{13}C NMR δ 13.8, 22.4, 24.0, 31.4, 40.8, 126.2, 128.1, 128.8, 130.2, 134.5, 142.1, 200.4. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.54; H, 9.28.

***trans*-1-Phenyl-1-undecen-3-one (25c):** yield 68%; mp 40−42 °C: ^{1}H NMR δ 0.89 (t, 3 H, J = 7.1 Hz), 1.20−1.43 (m, 10 H), 1.62−1.74 (m, 2 H), 2.65 (t, 2 H, J = 7.5 Hz), 6.74 (d, 1 H, J = 16.2 Hz), 7.35−7.42 (m, 3 H), 7.50−7.60 (m, 3 H); ^{13}C NMR δ 14.0, 22.6, 24.3, 29.1, 29.2, 29.3, 31.7, 40.9, 126.2, 128.1, 128.8, 130.2, 134.5, 142.1, 200.4. Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.57; H, 9.82.

***trans*-1-Phenyl-4-hydroxy-4-phenyl-1-buten-3-one (25d):** yield 73%; mp 106−108 °C; ^{1}H NMR δ 4.57 (d, 1 H, J = 4.6 Hz), 5.32 (d, 1 H, J = 4.5 Hz), 6.72 (d, 1 H, J = 15.9 Hz), 7.33−7.47 (m, 10 H), 7.75 (d, 1 H, J = 15.8 Hz); ^{13}C NMR δ 79.0, 120.3, 127.7, 128.6, 128.7, 128.9, 129.0, 131.0, 133.9, 138.0, 144.9, 197.3. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.80; H, 6.02.

***trans*-1-Phenyl-4-hydroxy-4-(4-methylphenyl)-1-buten-3-one (25e):** obtained as a colorless oil; yield 65%; ^{1}H NMR δ 2.29 (s, 3 H), 4.71 (br s, 1 H), 5.32 (s, 1 H), 6.75 (d, 1 H, J = 15.9 Hz), 7.16 (d, 2 H, J = 8.0 Hz), 7.21−7.35 (m, 5 H), 7.37−7.42 (m, 2 H), 7.75 (d, 1 H, J = 15.9 Hz); ^{13}C NMR δ 20.8, 78.5, 120.3, 127.4, 128.3, 128.5, 129.4, 130.6, 133.7, 134.9, 138.1, 144.3, 197.4. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.91; H, 6.66.

***trans*-4-Hydroxy-1-phenyl-1-undecen-3-one (25f):** obtained as a colorless oil; yield 55%; ^{1}H NMR δ 0.90 (t, 3 H, J = 6.2 Hz), 1.21−1.71 (m, 11 H), 1.84−1.99 (m, 1 H), 3.73 (d, 1 H, J = 5.3 Hz), 4.47−4.54 (m, 1 H), 6.90 (d, 1 H, J = 16.0 Hz), 7.40−7.50 (m, 3 H), 7.58−7.68 (m, 2 H), 7.78 (d, 1 H, J = 15.9 Hz); ^{13}C NMR δ 14.0, 22.5, 24.8, 29.0, 29.4, 31.7, 34.2, 75.7, 120.5, 128.5, 128.9, 130.9, 134.0, 144.4, 200.7. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.08; H, 8.90.

***trans*-4-Hydroxy-4-methyl-1-phenyl-1-penten-3-one (25g):** obtained as a colorless oil; yield 45% (lit.[35] mp 39−40 °C); ^{1}H NMR δ 1.50 (s, 6 H), 4.20 (br s, 1 H), 7.16 (d, 1 H, J = 15.7 Hz), 7.38−7.44 (m, 3 H), 7.58−7.62 (m, 2 H), 7.86 (d, 1 H, J = 15.7 Hz); ^{1}H NMR δ 26.2, 75.4, 118.4, 128.4, 128.7, 130.7, 134.1, 145.1, 202.3.

***trans*-1,4-Diphenyl-1-buten-3-one (25h):** yield 13%; mp 79−81 °C; ^{1}H NMR δ 3.94 (s, 2 H), 6.78 (d, 1 H, J = 16.1 Hz), 7.23−7.40 (m, 8 H), 7.48−7.54 (m, 2 H), 7.63 (d, 1 H, J = 16.0 Hz); ^{13}C NMR δ 48.3, 125.1, 126.9, 128.3, 128.6, 128.7, 128.9, 129.4, 130.5, 134.4, 143.3, 197.2. Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.63; H, 6.61.

Preparation of Ethyl 3,4-Diphenylbutanoate (26). A mixture of 1-(benzotriazol-1-yl)-1-ethoxy-3,4-diphenyl-1-butene (**24h**) (1.11 g, 3 mmol), ethanol (15 mL), water (15 mL), and HCl (2 mL) was heated under reflux for 3 h. The resulting solution was extracted with diethyl ether (3 × 100 mL), washed with a saturated Na_2CO_3 solution (2 × 100 mL), and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue which was separated by column chromatography

(hexane/ethyl acetate 60:1) to give 0.64 g of colorless oil: yield 80%; ^{1}H NMR δ 1.10 (t, 3 H, J = 7.1 Hz), 2.66−2.71 (m, 2 H), 2.91 (d, 2 H, J = 7.2 Hz), 3.37−3.49 (m, 1 H), 3.97 (q, 2 H, J = 7.1 Hz), 7.05 (d, 2 H, J = 8.0 Hz), 7.12−7.30 (m, 8 H); ^{13}C NMR δ 14.0, 40.2, 42.9, 43.9, 60.1, 126.0, 126.4, 127.4, 128.1, 128.2, 129.1, 139.4, 143.3, 172.1. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.72; H, 7.84.

Preparation of *trans*-1-Ethoxy-1-[5(3)-methyl(triazol-1-yl)]-3-phenyl-2-propene (28). To a solution of *trans*-3-ethoxy-1-phenyl-3-(triazol-1-yl)-1-propene (**29**) (1.15 g, 5 mmol) in THF (100 mL) at −78 °C was added *n*-butyllithium (2.5 M in cyclohexane, 2 mL, 5 mmol). The solution was stirred at this temperature for 5 min, and MeI (0.85 g, 6 mmol) was then added. After the solution was stirred at −78 °C for an additional 5 to 10 min, the reaction was quenched at this temperature with water (50 mL). The mixture was extracted with diethyl ether (2 × 100 mL). Evaporation of the solvent gave a residue, which was separated by column chromatography (hexane/ethyl acetate 500:3) to give a colorless oil: yield 81% (a mixture of 5-methyl- (**28**) and 3-methyl- (triazol-1-yl) (**27**) isomers); ratio, *ca*. 2:1; major, ma; minor, mi); ^{1}H NMR δ 1.17−1.28 (m, 3 H), 2.45 (s, 3 H), 3.40−3.69 (m, 2 H), 6.07 (d, mi, J = 5.2 Hz) and 6.13 (d, ma, J = 4.7 Hz) (total 1 H), 6.36 (dd, 1 H, J = 16.0, 4.7 Hz), 6.72 (d, ma, J = 15.9 Hz) and 6.82 (d, mi, J = 15.9 Hz) (total 1 H), 7.24−7.42 (m, 5 H), 7.83 (s, ma) and 8.00 (s, mi) (total 1 H); ^{13}C NMR δ 12.5, 14.5, (14.6, mi), 64.1, (64.7, mi), 88.3, (88.4, mi), (123.6, mi), 123.7, 126.7, (126.8, mi), (128.4, mi), 128.5, 133.4, 134.0, 135.1, 141.6, 150.0, 151.4, 152.1. Anal. Calcd for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27. Found: C, 68.65; H, 7.28; N, 17.33.

General Procedure for the Preparation of 32a, 33a,b, 35a,b, 37a−c, 39, 41, and 43. To a solution of 3-ethoxy-1-phenyl-3-(triazol-1-yl)-1-propene (**29**) (1.15 g, 5 mmol) in THF (100 mL) at −78 °C was added *n*-butyllithium (2.0 M in cyclohexane, 5 mL, 10 mmol). The solution was stirred at this temperature for 5 min, and the appropriate electrophile (EtBr, benzyl bromide, *N*-benzylidineaniline, *N*-(4-chlorophenylidine)-aniline, *N*-(4-methylphenylidine)aniline, or benzophenone: each 5.5 mmol; benzaldehyde, 4-methylbenzaldehyde, cyclohexanone, or acetone: each 11 mmol) was then added. After the solution was stirred at −78 °C for an additional 5 to 10 min, the reaction was quenched at this temperature with water (50 mL). The mixture was extracted with diethyl ether (2 × 100 mL). Evaporation of the solvent gave a residue (in the case of **32a**, it was isolated by column chromatography), which was heated under reflux in a mixture of ethanol (15 mL), water (15 mL), and HCl (2 mL) for the appropriate time (for **33a**,**b**, 3 h; **35a**,**b**, **39**, 8 h; **37a**−**c**, **43**, 6 h; **41**, 4 h). The resulting solution was extracted with diethyl ether (3 × 100 mL), washed with water (100 mL), and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue which was separated by column chromatography (hexane/ethyl acetate 25:1). Compound **33b** prepared is obtained in 55% yield and has identical spectral data to those of compound **26**.

1-Ethoxy-3-phenyl-1-(triazol-1-yl)-1-pentene (32a): obtained as a colorless oil; yield 90% (*E*/*Z* isomers, ratio, *ca*. 1:1). Isomer **I**: ^{1}H NMR δ 0.83 (t, 3 H, J = 7.4 Hz), 1.36 (t, 3 H, J = 7.0 Hz), 1.76−1.80 (m, 2 H), 3.18−3.28 (m, 1 H), 3.86−4.00 (m, 2 H), 4.93 (d, 1 H, J = 10.2 Hz), 7.11−7.22 (m, 3 H), 7.25−7.33 (m, 2 H), 8.06 (s, 1 H), 8.12 (s, 1 H); ^{13}C NMR δ 11.9, 14.2, 30.3, 43.6, 65.0, 103.3, 126.3, 127.0, 128.6, 143.8, 144.4 144.6, 151.9. Isomer **II**: ^{1}H NMR δ 0.94 (t, 3 H, J = 7.4 Hz), 1.33 (t, 3 H, J = 7.1 Hz), 1.72−1.80 (m, 2 H), 3.65−3.75 (m, 1 H), 3.77−3.90 (m, 2 H), 5.65 (d, 1 H, J = 10.3 Hz), 7.20−7.40 (m, 5 H), 8.00 (s, 1 H), 8.37 (s, 1 H); ^{13}C NMR δ 12.1, 15.0, 30.0, 43.1, 68.5, 109.5, 126.3, 127.2, 128.5, 141.5, 142.4, 144.2, 152.2.

Ethyl 3-phenylpentanoate (33a): obtained as a colorless oil; yield 84%; ^{1}H NMR δ 0.79 (t, 3 H, J = 7.4 Hz), 1.22 (t, 3 H, J = 7.1 Hz), 1.53−1.80 (m, 2 H), 2.50−2.68 (m, 2 H), 2.95−3.05 (m, 1 H), 4.01 (q, 2 H, J = 7.1 Hz), 7.13−7.21 (m, 3 H), 7.23−7.32 (m, 2 H); ^{13}C NMR δ 11.8, 14.0, 29.1, 41.4, 43.9, 60.1, 126.3, 127.5, 128.2, 143.8, 172.4. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.62; H, 9.01.

***β,γ*-Diphenylbutyrolactone (35a):** yield 90%; mp 89−102 °C (lit.[19] mp 97−106 °C) (a mixture of two diasteromers; ratio, *ca*. 1.7:1; major, ma; minor, mi); ^{1}H NMR δ 2.83−3.08 (m, 2 H), 3.57 (q, ma, J = 8.6 Hz) and 4.03 (q, mi, J = 8.0 Hz) (total 1 H), 5.40 (d, ma, J = 8.6 Hz) and 5.80 (d, mi, J = 6.9 Hz) (total 1 H), 6.79−6.90 (m) and 7.04−7.35 (m) (total 10 H); ^{13}C NMR δ (34.8, mi), 36.9, (46.6, mi), 50.3, (84.4, mi), 87.2, 125.5, 125.6, 127.1, 127.2, 127.5, 127.6, 127.7, 127.8, 128.0, 128.4, 128.9, 135.4, 136.6, 137.5, 137.8, 175.1, (176.6, mi). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.62; H, 5.98.

***γ*-(4-Methylphenyl)-*β*-phenylbutyrolactone (35b):** obtained as a colorless oil; yield 88% (a mixture of two diastereomers; ratio, *ca*. 1.6:1; major, ma; minor, mi): ^{1}H NMR δ 2.17 (s, mi) and 2.29 (s, ma) (total 3 H), 2.80−3.05 (m, 2 H), 3.57 (q, ma, J = 7.4 Hz) and 3.98 (q, mi, J = 7.4 Hz) (total 1 H), 5.34 (d, ma, J = 8.5 Hz) and 5.74 (d, mi, J = 6.9 Hz) (total 1 H), 6.73−6.92 (m, 2 H), 7.04−7.18 (m, 5 H), 7.20−7.33 (m, 2 H); ^{13}C NMR δ 20.8, 20.9, 34.7, 36.9, 46.5, 50.1, 84.4, 87.2, 125.5, 125.6, 127.0, 127.1, 127.5, 127.8, 128.3, 128.7, 129.0, 132.3, 134.4, 136.7, 137.2, 137.7, 138.2, 175.1, 176.6. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.41; H, 6.15.

***β,γ,N*-Triphenyl-*γ*-butyrolactam (37a):** yield 70%; mp 119−121 °C (a mixture of two diasteromers; ratio, *ca*. 3:1; major, ma; minor, mi); ^{1}H NMR δ 2.75−2.88 (m, 1 H), 3.10−3.21 (m, 1 H), 3.35−3.46 (m, ma) and 4.04−4.14 (m, mi) (total 1 H), 5.17 (d, ma, J = 5.0 Hz) and 5.35 (d, mi, J = 8.0 Hz) (total 1 H), 6.79−7.60 (m, 15 H); ^{13}C NMR δ (35.7, mi), 38.7, (44.7, mi), 47.8, (68.5, mi), 71.5, 121.1, 122.3, 124.5, 124.9, 125.9, 126.7, 126.8, 127.0, 127.3, 127.5, 127.7, 127.9, 128.1, 128.5, 128.8, 128.9, 136.1, 136.5, 137.9, 139.8, 141.6, 173.4, (173.7, mi). Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.40; H, 6.16; N, 4.41.

***β,N*-Diphenyl-*γ*-(4-chlorophenyl)-*γ*-butyrolactam (37b):** yield 70%; mp 139−140 °C (a mixture of two diasteromers; ratio, *ca*. 5:1; major, ma; minor, mi); ^{1}H NMR δ 2.86 (dd, 1 H, J = 17.2 and 7.5 Hz), 3.14 (dd, 1 H, J = 17.2 and 8.8 Hz), 3.32−3.40 (m, 1 H), 5.15 (d, ma, J = 5.8 Hz) and 5.33 (d, mi, J = 5.8 Hz) (total 1 H); 7.03−7.39 (m, 14 H); ^{13}C NMR δ (35.6, mi), 38.8, (44.7, mi), 48.2, (68.0, mi), 70.9, (121.2, mi), 122.5, (124.8, mi), 125.2, 127.0, 127.3, 127.5, 128.1, 128.2, 128.4, 128.7, 129.0, 133.6, 137.6, 138.3, 140.9, 173.3. Anal. Calcd for $C_{22}H_{18}NOCl$: C, 75.97; H, 5.22; N, 4.03. Found: C, 75.97; H, 5.22; N, 3.90.

***β,N*-Diphenyl-*γ*-(4-methylphenyl)-*γ*-butyrolactam (37c):** yield 83%; mp 154−156 °C (a mixture of two diasteromers; ratio, *ca*. 6:1; major, ma; minor, mi); ^{1}H NMR δ 2.19 (s, mi) and 2.26 (s, ma) (total 3 H), 2.80 (dd, 1 H, J = 17.2 and 6.6 Hz), 3.14 (dd, 1 H, J = 17.2 and 8.9 Hz), 3.35−3.48 (m, 1 H), 5.14 (d, ma, J = 5.0 Hz) and 5.32 (d, mi, J = 5.0 Hz) (total 1 H), 6.68−7.60 (m, 14 H); ^{13}C NMR δ (20.8, mi), 20.9 (35.8, mi), 38.7 (44.8, mi), 47.9, (68.4, mi), 71.3, 121.0, 122.3, 124.4, 124.8, 125.9, 126.6, 126.8, 126.9, 127.2, 127.9, 128.1, 128.2, 128.5, 128.8, 129.4, 133.0, 136.6, 136.8, 137.1, 137.4, 137.9, 141.8, 173.4, (173.7, mi). Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.33; H, 6.48; N, 4.23.

***β*-Phenyl-*γ,γ*-dimethylbutyrolactone (39):** yield 83%; mp 102−104 °C (lit.[19] mp 94−102 °C); ^{1}H NMR δ 0.89−1.12 (m, 2 H), 1.42−1.80 (m, 7 H), 1.88−1.98 (m, 1 H), 2.96 (d, 2 H, J = 9.0 Hz), 3.43 (t, 1 H, J = 8.9 Hz), 7.18−7.23 (m, 2 H), 7.28−7.40 (m, 3 H); ^{13}C NMR δ 21.5, 22.4, 24.8, 32.2, 34.6, 36.6, 51.0, 88.3, 127.5, 128.0, 128.4, 137.1, 175.5. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.21; H, 8.04.

***β*-Phenyl-*γ,γ*-dimethylbutyrolactone (41):** yield 56%; mp 94−95 °C; ^{1}H NMR δ 1.05 (s, 3 H), 1.56 (s, 3 H), 2.89 (dd, 1 H, J = 17.6 and 8.5 Hz), 3.02 (dd, 1 H, J = 17.6 and 10.2), 3.53 (dd, 1 H, J = 10.2 and 8.6 Hz), 7.20−7.27 (m, 2 H), 7.30−7.42 (m, 3 H); ^{13}C NMR δ 23.1, 27.6, 34.4, 51.1, 87.1, 127.6, 127.7, 128.6, 136.7, 175.2. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.96; H, 7.67.

***β,γ,γ*-Triphenylbutyrolactone (43):** yield 67%; mp 160−161 °C; ^{1}H NMR δ 2.79 (dd, 1 H, J = 17.5 and 4.7 Hz), 2.98 (dd, 1 H, J = 17.5 and 8.0 Hz), 4.50 (dd, 1 H, J = 8.0 and 4.7), 6.92−7.47 (m, 13 H), 7.66 (d, 2 H, J = 7.0 Hz); ^{13}C NMR δ 37.3, 50.9, 92.9, 126.0, 126.2, 127.1, 127.2, 127.6, 128.1, 128.3, 128.5, 128.6, 138.5, 139.9, 143.1, 175.6. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.96; H, 5.77.

Preparation of 1-Ethoxy-1-(triazol-1-yl)-3,4-diphenyl-4-(phenylamino)-1-butene (36a). To a solution of 3-ethoxy-1-phenyl-3-(triazol-1-yl)-1-propene (**29**) (1.15 g, 5 mmol) in THF (80 mL) at −78 °C was added *n*-butyllithium (2.0 M in cyclohexane, 5 mL, 10 mmol). The solution was stirred at this temperature for 5 min, and *N*-benzylidineaniline (0.91 g, 5 mmol) was added. After the solution was stirred at −78 °C for an additional 5 to 10 min, the reaction was quenched at this temperature with water (50 mL). The mixture was extracted with diethyl ether (2 × 100 mL). Evaporation of the solvent gave a residue, which was separated by column chromatography to give 1.65 g of product (80%): mp 127−130 °C; ^{1}H NMR δ 1.35 (t, 3 H, J = 7.0 Hz), 3.80−3.98 (m, 3 H), 4.54 (dd, 1 H, J = 9.1 and 6.0 Hz), 5.12 (d, 1 H, J = 11.0 Hz), 5.52 (d, 1 H, J = 6.0 Hz), 6.52−6.65 (m, 3 H), 6.88−6.95 (m, 2 H), 7.02−7.20 (m, 10 H), 8.08 (s, 1 H), 8.17 (s, 1 H); ^{13}C NMR δ 14.2, 49.8, 63.2, 65.2, 99.0, 113.1, 116.9, 126.8, 127.2, 127.9, 128.0, 128.4, 129.0, 140.8, 141.7, 143.6, 145.4, 147.3, 151.6. Anal. Calcd for $C_{26}H_{26}N_4O$: C, 76.07; H, 6.38; N, 13.65. Found: C, 76.34; H, 6.51; N, 13.76.

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