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General and Efficient Insertion of Carbons Carrying Benzotriazole

Alan R. Katritzky,* Sergey Bobrov, Kostyantyn Kirichenko, and Yu Ji

Center for Heterocyclic Compounds, University of Florida, Department of Chemistry, Gainesville, Florida 32611-7200

katritzky@chem.ufl.edu

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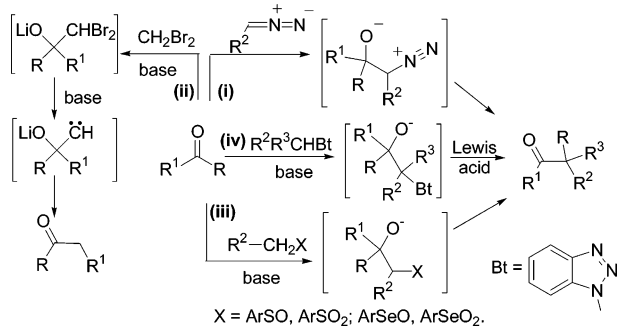
Anions formed from the lithiation of 1-(1-benzotriazolylalkyl)benzotriazoles (**1**, **6**) and 1-(1-methylthioalkyl)benzotriazoles (**10** and **10a**) with *n*-BuLi underwent additions to cyclic and acyclic ketones giving intermediates **3a**−**f**, **7b**−**f**, and **11b**−**d**, respectively, in excellent yields. Thermal rearrangements of intermediates **3a**,**b**,**d**−**f** and **7b**−**d**,**f** in the presence of zinc bromide provided one-carbon chain-extended or ring-expanded α-benzotriazolyl ketones **4a**,**b**,**d**−**f** and **8b**−**d**,**f** in moderate yields with excellent regioselectivity. By contrast, intermediates **11b**−**d** on treatment with zinc bromide loose a molecule of benzotriazole followed by intramolecular cyclization of the resulting intermediates **12b**−**d** to provide the 2,3- and 1,2,3-substituted indenes **13b**−**d** in good yields.

Introduction

The homologation of aldehydes and ketones is an important transformation in modern synthetic organic chemistry that has been extensively investigated. Published procedures for the insertions of a single carbon next to a carbonyl group have been summarized in several reviews[1] and in our recent publications.[2] These published results (Scheme 1) can be classified as follows: (i) insertion by diazo compounds;[1d−f,3] (ii) insertion via *β*-oxido carbenoid intermediates generated from dibromomethane[4] or dichloromethane;[5] (iii) insertions utilizing α-lithioalkyl sulfoxide,[6] selenoxide,[6,7] α-lithioalkyl sulfones,[8] or selenones;[9] (iv) rearrangement of a 2-benzotriazolylalkoxide.[2,10]

SCHEME 1



Recent work in our group achieved good regioselectivity in the simultaneous homologation and α-functionalization of ketones and aldehydes via benzotriazole intermediates.[2] In particular, various alkyl, aryl, heteroaryl, alkoxy, and aryloxy substituents were thus introduced.

The present manuscript deals with the insertions of carbon carrying a benzotriazolyl substituent to give α-benzotriazolyl ketones as products. Such ketones with an α-benzotriazolyl group are of significant synthetic utility for transformations to (i) diketones,[11] (ii) olefins,[12] (iii) for directed regioselective α-alkylation,[13] and (iv) heterocycle ring synthesis (Scheme 2).[14]

Our present investigations have led to regioselective α-carbon insertions into ketones **2a**−**f** (Schemes 3 and

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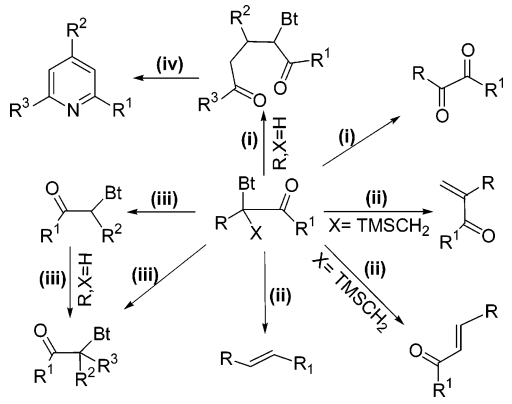
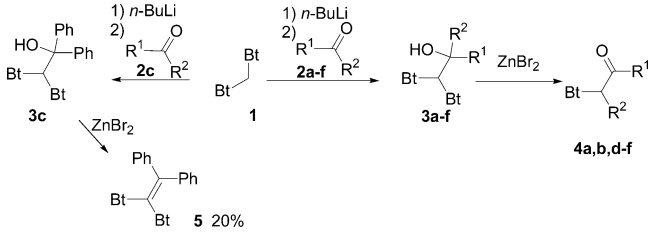
SCHEME 2

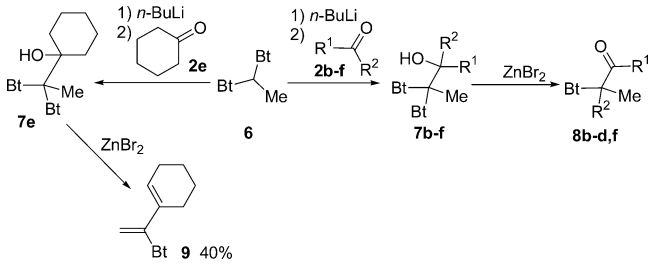


SCHEME 3[a]



[a] For designation of R^1–R^2 see Table 1.

SCHEME 4[a]



[a] For designation of R^1–R^2 see Table 2.

4) utilizing 1-(1-benzotriazolylalkyl)benzotriazoles **1** and **6**. In related work, the use of 1-(1-methylthioalkyl)-benzotriazoles **10** and **10a** led to the 2,3- and 1,2,3-substituted indenes **13b**–**d**.

Results and Discussion

We have examined the behavior of 1-(1-benzotriazolylalkyl)benzotriazoles **1** and **6** and 1-(1-methylthioalkyl)-benzotriazoles **10** and **10a** in the one-carbon homologation of ketones **2a**–**f** and found that reactivity of intermediates **3a**–**f**, **7b**–**f**, and **11b**–**d** varies with the degree and type of substitution at the α-carbon adjacent to the benzotriazole group.

The treatment of compound **1** with *n*-BuLi (1 equiv) at −78 °C under nitrogen in THF for 1 h followed by reactions with ketones **2a**–**f** (1 equiv) at −78 °C for 1 h led to high isolated yields of the corresponding intermediates **3a**–**f** (Scheme 3, Table 1). Surprisingly, under the same reaction conditions, the lithium derivative of **6** reacted sluggishly and apparently reversibly with ketones **2b**–**f**: if the temperature of the reaction mixture rises to 20 °C prior to quenching with aqueous ammonium chloride, the starting compound **6** is recovered. However, keeping the reaction mixture at −78 °C for 12 h followed by quenching with aqueous ammonium chloride at the same temperature gave **7b**–**f** in high yields (Scheme 4, Table 2). The structures of compounds **3a**–**f** and **7b**–**f** were supported by their ^{1}H NMR and ^{13}C NMR spectra (see the Experimental Section).

TABLE 1. Preparation of Intermediates 3 and α-Benzotriazolyl Ketones 4

	2		yield, %/solvent/time, h	
	R^1	R^2	**3**	**4**
a	Bn	Bn	60/THF/2	54/$CHCl_2CHCl_2$/5
b	Me	Ph	90/THF/2	75/$CHCl_2CHCl_2$/5
c	Ph	Ph	85/THF/2	–
d	$-(CH_2)_4-$		60/THF/2	70/$CHCl_2CHCl_2$/5
e	$-(CH_2)_5-$		80/THF/2	41/$CHCl_2CHCl_2$/5
f	Me	*i*-Pr	90/THF/2	60/$CHCl_2CHCl_2$/5

TABLE 2. Preparation of Intermediates 7 and α-Benzotriazolyl Ketones 8

	2		yield, %/solvent/time, h	
	R^1	R^2	**7**	**8**
b	Me	Ph	90/THF/13	40/$CHCl_2CHCl_2$/0.25
c	Ph	Ph	70/THF/13	55/CH_2ClCH_2Cl/0.5
d	$-(CH_2)_4-$		50/THF/13	35/$CHCl_2CHCl_2$/0.25
e	$-(CH_2)_5-$		75/THF/13	*a*
f	Me	*i*-Pr	80/THF/13	20/CH_2ClCH_2Cl/4

[a] Product **9** was isolated in 40% yield.

The mechanism of transformation of **3** to **4** and **7** to **8** was explained in our previous publications.[2a,c,d] The present rearrangements proceed regioselectively: treating adducts **3a**,**b**,**d**–**f** and **7b**–**d**,**f** in 1,1,2,2-tetrachloroethane or 1,2-dichloroethane under reflux with a 5-fold excess of zinc bromide afforded the one carbon homologated ketones **4a**,**b**,**d**–**f** and **8b**–**d**,**f** respectively (Schemes 3 and 4, Tables 1 and 2). In each case, migration occurs of the carbon that can best stabilize an electron deficiency in the transition state. In the case of **4a**,**b**,**d**–**f**, the rearrangement could be completed in refluxing 1,1,2,2-tetrachloroethane for 5 h (Table 1). By contrast, adduct **3c** (Scheme 3) failed to undergo the zinc bromide-promoted rearrangement in the 1,1,2,2-tetrachloroethane under reflux for 64 h; under these reaction conditions (Scheme 3), only the dehydration product **5** was isolated in 20% yield.

We found that the rearrangements of the intermediates **7b**–**d**,**f** (Scheme 4, Table 2) required different reaction temperatures and reaction time to complete the formation of the corresponding ketones **8b**–**d**,**f**. Moreover, rearrangement of **7b**–**d**,**f** generally gave yields of **8b**–**d**,**f** around 20% less as compared to rearrangement of **3a**,**b**,**d**–**f** into **4a**,**b**,**d**–**f** probably due to the concurrent processes of dehydration and benzotriazole elimination, as in the case of the transformation of **7e** to **9** (Scheme 4). The structures of compounds **4a**,**b**,**d**–**f**, **5**, **8b**–**d**,**f**, and **9** were supported by their ^{1}H NMR and ^{13}C NMR spectra (see the Experimental Section).

We have previously demonstrated that 1-[(methylthio)-methyl]benzotriazole undergoes deprotonation with bu-

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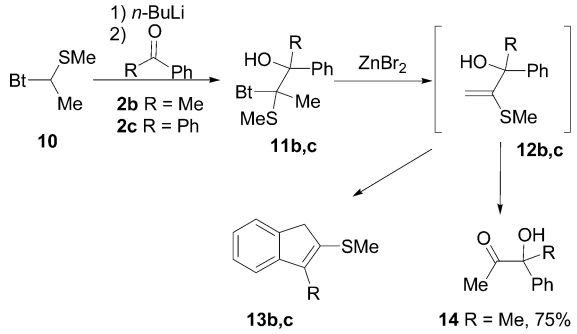
TABLE 3. Preparation of Intermediates 11b−d and 12c and Substituted Indenes 13b−d

	R	yield, %/solvent/time, h 11	12	13
b	Me	81/THF/2	*a*	30/CH_2ClCH_2Cl/0.1
c	Ph	98/THF/2	89/THF/0.25	70/CH_2ClCH_2Cl/0.1
d	Ph	96/THF/2	*a*	78/CH_2ClCH_2Cl/0.1

[a] Intermediate was not isolated.

SCHEME 5



tyllithium and that carbanion reacts readily with aliphatic and aromatic ketones followed by rearrangement of the resulting intermediates under zinc bromide catalysis to afford the one-carbon homologated α-(methylthio)methyl ketones.[2c] We now show that the 1-(1-methylthioalkyl)benzotriazoles **10** and **10a** similarly undergo smooth deprotonation with *n*-BuLi (1 equiv) at −78 °C under nitrogen in THF for 1 h and the resulting carbanions react cleanly with ketones **2b**,**c** (1 equiv) at −78 °C for 1 h giving excellent isolated yields of adducts (Schemes 5 and 6, Table 3). However, the adducts **11b−d** failed to undergo rearrangement to the α-carbon insertion products, instead the elimination of benzotriazole was observed and the 2,3- and 1,2,3-substituted indenes **13b−d** were isolated (Schemes 5 and 6, Table 3). In fact, the adducts **11b−d** react with 3-fold excess of zinc bromide for 15 min in 1,2-dichloromethane at 20 °C loosing a molecule of benzotriazole providing intermediates **12b−d** which, under reflux in the same solvent for 5 min undergo intramolecular cyclization to give **13b−d** in good yields (Schemes 5 and 6, Table 3). Formation of **12b−d** has been established by the isolation of **12c** in 89% yield, while **12b** was hydrolyzed after aqueous workup to give **14** in 75% yield.

In preceding papers,[2a,c,d] it was shown that monosubstituted benzotriazolylmethanes such as 1-(arylmethyl)-, 1-(heteroarylmethyl)-, 1-(alkenylmethyl)-, 1-(alkoxymethyl)-, and 1-[(phenylthio)methyl]benzotriazoles are excellent insertion reagents for the preparation of α-functionalized ketones. We have now found that (1*H*-benzotriazol-1-ylmethyl)-1*H*-benzotriazole **1** also behaves in the same manner undergoing α-carbon insertions into ketones **2**, while in the cases of disubstituted benzotriazolyl methane derivatives **6**, **10**, and **10a**, either poorer yields of inserted ketones **8b−d**,**f** were observed or a different reaction pathway was involved leading to the formation of indenes **13b−d**.

In summary, an efficient method for the α-carbon insertions of 1-(1-benzotriazolylalkyl)benzotriazoles into ketones has been demonstrated. The insertion reactions take place regioselectively with wide set of cyclic and acyclic ketones providing both one-carbon chain-extended and ring-expanded α-benzotriazolyl ketones. In certain cases, 1-(1-methylthioalkyl)benzotriazoles have been utilized as substrate for the synthesis of 2,3- and 1,2,3-substituted indenes.

Experimental Section

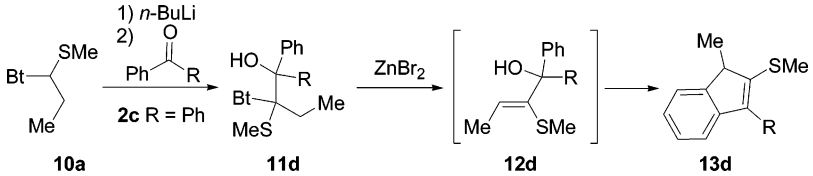
General Methods. Melting points were determined on a hot-stage apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$, acetone-d_6, or DMSO-d_6 with TMS as the internal standard for ^1H (300 MHz) or a solvent as the internal standard for ^{13}C (75 MHz). THF was dried over sodium/benzophenone and used freshly distilled. Column chromatography was conducted on silica gel 200−425 meshes. (1*H*-Benzotriazol-1-ylmethyl)-1*H*-benzotriazole **1**,[15] (1*H*-benzotriazol-1-ylethyl)-1*H*-benzotriazole **6**,[11a] and 1-(methylthio)-1-ethyl-1*H*-benzotriazole **10**[16] were prepared according to previously reported procedures.

General Procedure for the Preparation of Intermediates 3a−f. A solution of dibenzotriazol-1-ylmethane **1** (8.00 mmol) in THF (50 mL) was cooled to −78 °C, and a solution of *n*-BuLi (8.80 mmol, 1.58 M in hexane, 5.6 mL) was added dropwise. The reaction mixture was stirred at the same temperature for 1 h, and a solution of an appropriate ketone (8.80 mmol) in THF (15 mL) was added. The mixture was stirred for an additional 1 h at −78 °C. Then water was added (30 mL), and the reaction mixture was extracted with diethyl ether. The extract was dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **3a−f**.

1,1-Di(1,2,3-benzotriazol-1-yl)-2-benzyl-3-phenyl-2-propanol (3a): microcrystals from methanol (60%); mp 176−177 °C; ^1H NMR (DMSO-d_6) δ 8.11 (d, J = 8.1 Hz, 2H), 7.56−7.39 (m, 6H), 7.34 (s, 1H), 7.18−7.03 (m, 10H), 6.14 (s, 1H), 3.57 (d, J = 14.0 Hz, 2H), 3.16 (d, J = 14.0 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 144.8, 135.9, 132.9, 130.4, 128.5, 127.8, 126.4, 124.7, 119.5, 110.4, 77.8, 75.2, 42.7. Anal. Calcd for $C_{28}H_{24}N_6O$: C, 73.02; H, 5.25; N, 18.25. Found: C, 73.26; H, 5.32; N, 18.45.

(±)-1,1-Di(1,2,3-benzotriazol-1-yl)-2-phenyl-2-propanol (3b): microcrystals from methanol (90%); mp 181−182 °C; ^1H NMR (DMSO-d_6) δ 8.46 (s, 1H), 8.38 (d, J = 8.5 Hz, 1H), 8.30 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.80−7.68 (m, 2H), 7.68−7.50 (m, 2H), 7.50−7.27 (m, 2H), 7.27−7.04 (m, 3H), 6.49 (s, 1H), 1.81 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 144.8, 144.5, 143.7, 133.1, 132.9, 128.0, 127.7, 127.6, 127.1, 125.5, 124.5, 124.3, 119.1, 118.8, 112.7, 112.6, 77.2, 77.1, 27.5. Anal. Calcd for $C_{21}H_{18}N_6O$: C, 68.09; H, 4.90; N, 22.69. Found: C, 68.45; H, 5.10; N, 22.56.

SCHEME 6



2,2-Di(1,2,3-benzotriazol-1-yl)-1,1-diphenyl-1-ethanol (3c): microcrystals from toluene (85%); mp 231−232 °C; ^{1}H NMR (DMSO-d_6) δ 9.30 (s, 1H), 8.04 (d, J = 8.5 Hz, 2H), 7.98 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 7.8 Hz, 4H), 7.50 (t, J = 7.1 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.25−7.10 (m, 6H), 7.01 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 144.6, 143.2, 132.6, 128.1, 127.9, 127.3, 125.8, 124.6, 119.2, 111.9, 81.3, 75.5. The spectral data of this compound is identical to that reported in the literature.[18]

1-[Di(1,2,3-benzotriazol-1-yl)methyl]cyclopentanol (3d): microcrystals from methanol (60%); mp 145−146 °C; ^{1}H NMR ($CDCl_3$) δ 8.05−8.01 (m, 2H), 7.54−7.49 (m, 3H), 7.40−7.26 (m, 4H), 4.64 (s, 1H), 2.10−1.75 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 145.8, 132.3, 128.7, 124.8, 120.0, 110.9, 85.4, 77.7, 38.7, 24.0. Anal. Calcd for $C_{18}H_{18}N_6O$: C, 64.66; H, 5.43; N, 25.13. Found: C, 65.03; H, 5.62; N, 25.49.

1-[Di(1,2,3-benzotriazol-1-yl)methyl]cyclohexanol (3e): microcrystals from acetone (83%); mp 191−192 °C; ^{1}H NMR ($CDCl_3$) δ 8.03 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.57 (s, 1H), 7.46−7.40 (m, 2H), 7.36−7.31 (m, 2H), 4.64 (s, 1H), 1.86−1.52 (m, 9H), 1.42−1.24 (m,1H); ^{13}C NMR ($CDCl_3$) δ 145.7, 132.5 128.7, 124.8, 120.0, 111.2, 77.4, 75.6, 34.8, 25.2, 21.2. Anal. Calcd for $C_{19}H_{20}N_6O$: C, 65.50; H, 5.79; N, 24.12. Found: C, 65.58; H, 5.69; N, 24.39.

(±)-1,1-Di(1,2,3-benzotriazol-1-yl)-2,3-dimethyl-2-butanol (3f): microcrystals from methanol (90%); mp 178−179 °C; ^{1}H NMR ($CDCl_3$) δ 8.06−7.99 (m, 2H), 7.85 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.75 (s, 1H), 7.50−7.26 (m, 4H), 4.77 (s,1H), 2.00−1.82 (m, 1H), 1.20 (s, 3H), 1.10 (d, J = 6.7 Hz, 3H), 1.04 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 146.1, 145.4, 132.6, 132.3, 129.0, 128.6, 125.0, 124.7, 120.1, 119.9, 111.9, 110.7, 79.6, 75.6, 34.8, 18.2, 18.0, 16.5. Anal. Calcd for $C_{18}H_{20}N_6O$: C, 64.27; H, 5.99; N, 24.98. Found: C, 64.72; H, 6.02; N, 25.43.

General Procedure for the Insertion into Ketones: Preparation of 4a,b,d−f. To a solution of an appropriate intermediate **3a**,**b**,**d**−**f** (3 mmol) in 1,1,2,2-tetrachloroethane (20 mL) under nitrogen was added zinc bromide (15 mmol), and the reaction mixture was refluxed for 5 h. The reaction mixture was poured into the 1 N aqueous hydrochloric acid and extracted by chloroform. The extract was washed with water, dried over potassium carbonate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **4a**,**b**,**d**−**f**.

(±)-3-(1,2,3-Benzotriazol-1-yl)-1,4-diphenyl-2-butanone (4a): microcrystals from acetone (54%); mp 106−107 °C; ^{1}H NMR ($CDCl_3$) δ 8.06−7.98 (m, 1H), 7.36−7.26 (m, 2H), 7.18−7.13 (m, 3H), 7.10−7.04 (m, 4H), 6.90−6.85 (m, 4H), 5.67 (dd, J = 9.8, 5.6 Hz, 1H), 3.72 (dd, J = 14.2, 5.6 Hz, 1H), 3.65 (d, J = 15.6 Hz, 1H), 3.55 (d, J = 15.6 Hz, 1H), 3.50 (dd, J = 14.2, 9.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 201.6, 145.9, 135.8, 133.0, 132.2, 129.1, 128.7, 128.6, 128.5, 127.7, 127.3, 127.0, 124.1, 120.0, 109.3, 67.5, 47.0, 36.1. Anal. Calcd for $C_{22}H_{19}N_3O$: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.06; H, 5.91; N, 12.35.

(±)-1-(1,2,3-Benzotriazol-1-yl)-1-phenylacetone (4b): microcrystals from ether (75%); mp 115−116 °C; ^{1}H NMR ($CDCl_3$) δ 8.06 (d, J = 7.3 Hz, 1H), 7.42−7.30 (m, 7H), 7.24−7.21 (m, 1H), 6.75 (s, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 200.5, 146.2, 132.9, 132.2, 129.5, 129.2, 128.9, 127.7, 124.0, 120.1, 110.4, 71.9, 28.1. Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 72.05; H, 5.13; N, 16.87.

(±)-2-(1,2,3-Benzotriazol-1-yl)cyclohexanone (4d): microcrystals from methanol (70%); mp 129−130 °C; ^{1}H NMR ($CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 1H), 7.47−7.32 (m, 3H), 5.58 (dd, J = 12.6, 6.3 Hz, 1H), 2.76−2.53 (m, 4H), 2.28−2.16 (m, 2H), 2.04−1.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 202.7, 146.1, 132.9, 127.2, 123.8, 120.1, 110.3, 66.6, 41.1, 32.9, 26.8, 24.5. Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 67.13; H, 6.17; N, 19.58. The spectral data of this compound is identical to that reported in the literature.[13]

(±)-2-(1,2,3-Benzotriazol-1-yl)cycloheptanone (4e): microcrystals from methanol (41%); mp 103−104 °C; ^{1}H NMR ($CDCl_3$) δ 8.05 (d, J = 8.3 Hz, 1H), 7.50−7.40 (m, 2H), 7.40−7.30 (m, 1H), 5.73 (dd, J = 10.3, 3.4 Hz, 1H), 2.85−2.35 (m, 4H), 2.25−1.70 (m, 5H), 1.65−1.50 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 205.8, 146.1, 132.9, 127.3, 123.8, 120.0, 110.4, 68.1, 41.5, 30.7, 29.3, 27.9, 23.6. Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 68.44; H, 6.61; N, 18.69.

(±)-3-(1,2,3-Benzotriazol-1-yl)-4-methyl-2-pentanone (4f): oil (60%); ^{1}H NMR ($CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 1H), 7.57−7.48 (m, 2H), 7.43−7.38 (m, 1H), 5.12 (d, J = 9.5 Hz, 1H), 3.20−2.98 (m, 1H), 2.10 (s, 3H), 1.12 (d, J = 6.7 Hz, 3H), 0.80 (d, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 202.5, 146.0, 132.9, 127.9, 124.3, 120.1, 109.9, 73.9, 28.5, 27.5, 19.8, 18.8. Anal. Calcd for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34. Found: C, 65.94; H, 7.14; N, 19.70.

1-[1-(1,2,3-Benzotriazol-1-yl)-2,2-diphenylvinyl]-1,2,3-benzotriazole (5). To a solution of 2,2-di(1,2,3-benzotriazol-1-yl)-1,1-diphenyl-1-ethanol **3c** (1 g, 2.3 mmol) in 1,1,2,2-tetrachloroethane (20 mL) under nitrogen was added zinc bromide (3.4 g, 11.6 mmol), and the reaction mixture was refluxed for 64 h. The reaction mixture was poured into the 1 N aqueous hydrochloric acid and extracted by chloroform. The chloroform solution was washed with water, dried over potassium carbonate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give the pure product **5** as microcrystals (20%): mp 229−230 °C; ^{1}H NMR ($CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.40−7.27 (m, 6H), 7.17−7.10 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 145.3, 142.1, 136.9, 132.7, 129.2, 129.1, 128.8, 128.5, 124.6, 122.0, 120.2, 109.7. Anal. Calcd for $C_{26}H_{18}N_6$: C, 75.35; H, 4.38; N, 20.28. Found: C, 75.22; H, 4.17; N, 20.40.

General Procedure for the Preparation of Intermediates 7b−f. A solution of 1-[1-(1,2,3-benzotriazol-1-yl)ethyl]-1,2,3-benzotriazole **6** (7.6 mmol) in THF (50 mL) was cooled to −78 °C, and a solution of *n*-BuLi (8.6 mmol, 1.58 M in hexane, 5.5 mL) was added dropwise. The reaction mixture was stirred at the same temperature for 1 h, and a solution of an appropriate ketone (8.3 mmol) in THF (15 mL) was added. The mixture was stirred for an additional 12 h at −78 °C. Then water was added (30 mL), and the reaction mixture was extracted with ether. The extract was dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **7b**−**f**.

(±)-3,3-Di(1,2,3-benzotriazol-1-yl)-2-phenyl-2-butanol (7b): microcrystals from methanol (90%); mp 211−212 °C; ^{1}H NMR ($CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.30−6.85 (m, 9H), 6.28 (d, J = 8.4 Hz, 1H), 6.04 (br s, 1H), 5.61 (s, 1H), 2.62 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 145.8, 1 45.7, 140.6, 133.0, 132.6, 128.5, 128.1, 127.6, 127.6, 126.4, 124.7, 124.3, 120.5, 119.9, 111.2, 111.2, 87.4, 81.7, 26.5, 24.2. Anal. Calcd for $C_{22}H_{20}N_6O$: C, 68.73; H, 5.24; N, 21.86. Found: C, 68.59; H, 5.36; N, 22.13.

2,2-Di(1,2,3-benzotriazol-1-yl)-1,1-diphenyl-1-propanol (7c): microcrystals from methanol (70%); mp 221−222 °C; ^{1}H NMR ($CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.30−7.00 (m, 14H), 6.42 (d, J = 6.6 Hz, 2H), 5.68 (s, 1H), 3.14 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 146.0, 143.0, 133.1, 129.4, 128.3, 127.9, 127.3, 124.4, 120.2, 111.4, 87.5, 87.1, 24.6. Anal. Calcd for $C_{27}H_{22}N_6O$: C, 72.63; H, 4.97; N, 18.82. Found: C, 72.52; H, 5.14; N, 18.76.

1-[1,1-Di(1,2,3-benzotriazol-1-yl)ethyl]cyclopentanol (7d): microcrystals from methanol (50%); mp 223−224 °C; ^{1}H NMR (DMSO-d_6) δ 8.08 (d, J = 8.3 Hz, 2H), 7.29−7.23 (m,

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2H), 7.15−7.10 (m, 2H), 6.24 (d, J = 8.4 Hz, 2H), 5.35 (s, 1H), 2.62 (s, 3H), 2.49−2.33 (m, 2H), 1.90−1.60 (m, 6H); ^{13}C NMR (DMSO-d_6) δ 145.3, 132.4, 127.6, 124.0, 119.4, 111.5, 87.4, 86.8, 37.2, 23.7, 23.6. Anal. Calcd for $C_{19}H_{20}N_6O$: C, 65.50; H, 5.79; N, 24.12. Found: C, 65.90; H, 6.03; N, 24.60.

1-[1,1-Di(1,2,3-benzotriazol-1-yl)ethyl]cyclohexanol (7e): microcrystals from methanol (75%); mp 249−250 °C; ^{1}H NMR (DMSO-d_6) δ 8.07 (d, J = 8.2 Hz, 2H), 7.28−7.23 (m, 2H), 7.16−7.10 (m, 2H), 6.26 (d, J = 8.4 Hz, 2H), 5.34 (s, 1H), 2.60 (s, 3H), 2.10 (br s, 2H), 1.85−1.48 (m, 7H), 1.35−1.05 (m, 1H); ^{13}C NMR (DMSO-d_6) δ 145.2, 132.7, 127.9, 124.3, 119.6, 111.9, 88.2, 78.3, 32.1, 24.9, 23.6, 21.2. Anal. Calcd for $C_{20}H_{22}N_6O$: C, 66.28; H, 6.12; N, 23.19. Found: C, 66.22; H, 6.58; N, 23.32.

(±)-2,2-Di(1,2,3-benzotriazol-1-yl)-3,4-dimethyl-3-pentanol (7f): microcrystals from methanol (80%); mp 170−172 °C; ^{1}H NMR (DMSO-d_6) δ 8.06 (dd, J = 8.2, 2.9 Hz, 2H), 7.29−7.22 (m, 2H), 7.17−7.09 (m, 2H), 6.45 (d, J = 8.5 Hz, 1H), 6.24 (d, J = 8.1 Hz, 1H), 5.44 (s, 1H), 2.65 (s, 3H), 2.46−2.31 (m, 1H), 1.45 (s, 3H), 0.97 (d, J = 6.4 Hz, 3H), 0.82 (d, J = 6.7 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 145.3, 145.1, 132.7, 132.5, 127.9, 127.8, 124.3, 124.2, 119.5, 119.5, 112.1, 112.0, 89.0, 80.7, 33.9, 24.3, 20.4, 19.8, 18.7. Anal. Calcd for $C_{19}H_{22}N_6O$: C, 65.12; H, 6.33; N, 23.98. Found: C, 65.00; H, 6.53; N, 24.29.

(±)-3-(1,2,3-Benzotriazol-1-yl)-3-phenyl-2-butanone (8b). To a solution of 3,3-di(1,2,3-benzotriazol-1-yl)-2-phenyl-2-butanole **7b** (0.4 g, 1 mmol) in 1,1,2,2-tetrachloroethane (20 mL) under nitrogen was added zinc bromide (1.2 g, 5.3 mmol), and the reaction mixture was refluxed for 15 min. The reaction mixture was poured into the 1 N aqueous hydrochloric acid and extracted by chloroform. The chloroform solution was washed with water, dried over potassium carbonate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **8b** as an oil (40%): ^{1}H NMR ($CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 1H), 7.42−7.24 (m, 7H), 6.66 (d, J = 8.2 Hz, 1H), 2.27 (s, 3H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 202.1, 146.4, 137.0, 132.8, 129.0, 128.9, 127.3, 127.0, 123.9, 120.2, 112.0, 75.2, 26.4, 24.8. Anal. Calcd for $C_{16}H_{15}N_3O$: C, 72.43; H, 5.70; N, 15.84. Found: C, 72.70; H, 5.77; N, 15.96.

(±)-2-(1,2,3-Benzotriazol-1-yl)-1,2-diphenyl-1-propanone (8c). To a solution of 2,2-di(1,2,3-benzotriazol-1-yl)-1,1-diphenyl-1-propanole **7c** (0.3 g, 0.67 mmol) in 1,2-dichlorethane (20 mL) under nitrogen was added zinc bromide (1.2 g, 3.5 mmol), and the reaction mixture was refluxed for 30 min. The reaction mixture was poured into the 1 N aqueous hydrochloric acid and extracted by chloroform. The chloroform solution was washed with water, dried over potassium carbonate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **8c** as an oil (55%): ^{1}H NMR ($CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 1H), 7.56−7.53 (m, 2H), 7.43−7.20 (m, 10H), 6.74 (d, J = 8.2 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 196.5, 146.6, 138.4, 135.3, 133.5, 132.7, 129.4, 129.0, 128.8, 128.3, 127.9, 127.3, 123.8, 120.2, 111.9, 75.1, 27.6. Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.83. Found: C, 77.00; H, 5.27; N, 12.80.

(±)-2-(1,2,3-Benzotriazol-1-yl)-2-methylcyclohexanone (8d). To a solution of 1-[1,1-di(1,2,3-benzotriazol-1-yl)-ethyl]cyclopentanole **7d** (0.3 g, 0.86 mmol) in 1,1,2,2-tetrachloroethane (20 mL) under nitrogen was added zinc bromide (1 g, 4.4 mmol) and the reaction mixture was refluxed for 15 min. The reaction mixture was poured into the 1 N aqueous hydrochloric acid and extracted by chloroform. The chloroform solution was washed with water, dried over potassium carbonate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **8d** as an oil (35%): ^{1}H NMR ($CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 1H), 7.47−7.30 (m, 3H), 3.52−3.34 (m, 1H), 2.57−2.49 (m, 1H), 2.36−2.25 (m, 1H), 2.16−1.83 (m, 5H), 1.73 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 207.1, 146.6, 131.8, 127.5, 123.9, 120.2, 110.6, 70.0, 39.5, 39.1, 28.0, 23.0. 21.3. Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 67.85; H, 6.67; N, 18.50.

(±)-3-(1,2,3-Benzotriazol-1-yl)-3,4-dimethyl-2-pentanone (8f). To a solution of 2,2-di(1,2,3-benzotriazol-1-yl)-3,4-dimethyl-3-pentanole **7f** (0.4 g, 1.14 mmol) in 1,2-dichlorethane (20 mL) under nitrogen was added zinc bromide (1.3 g, 5.8 mmol), and the reaction mixture was refluxed for 4 h. The reaction mixture was poured into the 1 N aqueous hydrochloric acid and extracted by chloroform. The chloroform solution was washed with water, dried over potassium carbonate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **8f** as an oil (20%): ^{1}H NMR ($CDCl_3$) δ 8.12 (d, J = 7.1 Hz, 1H), 7.46−7.35 (m, 3H), 3.28 (q, J = 6.7 Hz, 1H), 1.98 (s, 3H), 1.86 (s, 3H), 1.09 (d, J = 7.7 Hz, 3H), 0.82 (d, J = 7.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 204.9, 146.7, 132.3, 127.6, 124.1, 120.3, 111.0, 75.4, 31.3, 24.4, 18.0, 17.3, 15.8. Anal. Calcd for $C_{13}H_{17}N_3O$: C, 67.51; H, 7.41; N, 18.17. Found: C, 67.87; H, 7.85; N, 18.33.

1-[1-(1-Cyclohexen-1-yl)vinyl]-1,2,3-benzotriazole (9). To a solution of 1-[1,1-di(1,2,3-benzotriazol-1-yl)ethyl]cyclohexanole **7e** (0.3 g, 0.83 mmol) in 1,1,2,2-tetrachloroethane (20 mL) under nitrogen was added zinc bromide (0.95 g, 4.2 mmol) and the reaction mixture was refluxed for 5 min. The reaction mixture was poured into the 1 N aqueous hydrochloric acid and extracted by chloroform. The chloroform solution was washed with water, dried over potassium carbonate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **9** as an oil (35%): ^{1}H NMR ($CDCl_3$) δ 8.08 (dd, J = 8.2, 0.8 Hz, 1H), 7.49−7.47 (m, 2H), 7.41−7.35 (m, 1H), 5.57 (s, 1H), 5.46 (t, J = 4.1 Hz, 1H), 5.35 (s, 1H), 2.35−2.30 (m, 2H), 2.12−2.03 (m, 2H), 1.81−1.73 (m, 2H), 1.67−1.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 145.4, 143.7, 133.6, 131.9, 129.9, 127.7, 123.9, 119.8, 110.6, 110.2, 25.5, 25.4, 22.2, 21.6. Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.60; H, 7.01; N, 18.53.

(±)-1-(1,2,3-Benzotriazol-1-yl)propyl Methyl Sulfide (10a). The solution of 1-(1,2,3-benzotriazol-1-yl)methyl methyl sulfide (2 g, 11.20 mmol) in THF (60 mL) was cooled to −78 °C, and the solution of *n*-BuLi (12.3 mmol, 1.58 M in hexane, 7.9 mL) was added dropwise. The reaction mixture was stirred at the same temperature for 1 h, and the solution of ethyl iodide (1.92 g, 12.3 mmol) in THF (15 mL) was added. The mixture was stirred for an additional 1 h at −78 °C. Then water was added (30 mL), and the product was extracted with ether. The residue was purified by gradient column chromatography using the mixture of hexanes/EtOAc (9:1−3:1) to give **10a** as an oil (82%): ^{1}H NMR ($CDCl_3$) δ 8.09 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.52−7.46 (m, 1H), 7.44−7.36 (m, 1H), 5.85 (dd, J = 8.8, 6.6 Hz, 1H), 2.50−2.26 (m, 2H), 1.89 (s, 3H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 147.0, 131.1, 127.1, 124.1, 120.2, 111.3, 67.6, 27.6, 13.7, 11.3. Anal. Calcd for $C_{19}H_{22}N_6O$: C, 57.94; H, 6.32; N, 20.27. Found: C, 57.97; H, 6.36; N, 20.65.

General Procedure for the Preparation of Intermediates (11b,c). The solution of 1-(1-methylthioethyl)-1,2,3-benzotriazole **10** (1 g, 5.18 mmol) in THF (50 mL) was cooled to −78 °C, and the solution of *n*-BuLi (5.70 mmol, 1.58 M in hexane, 3.7 mL) was added dropwise. The reaction mixture was stirred at the same temperature for 1 h, and the solution of corresponding ketones (5.70 mmol) in THF (15 mL) was added. The mixture was stirred for an additional 1 h at −78 °C. Then water was added (30 mL), and the product was extracted with ether. The rescue was purified by crystalization from ether to give **11b**,**c**.

(±)-3-(1,2,3-Benzotriazol-1-yl)-3-(methylthio)-2-phenyl-2-butanol (mixture of two diastereoisomers) (11b): microcrystals from acetone (81%); mp 116−117 °C; ^{1}H NMR ($CDCl_3$) δ 8.35 (d, J = 8.2 Hz, 1H), 8.30 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.50−7.20 (m, 10H), 7.20−7.00 (m, 2H), 6.97−6.85 (m, 2H), 2.98 (s, 1H), 2.88 (s, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.92 (s, 3H), 1.72 (s, 3H), 1.66 (s, 3H), 1.53 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 146.2, 146.1, 142.7, 141.8, 134.5, 134.1, 127.8, 127.7, 127.4, 127.2, 126.6, 126.5, 126.4, 126.4, 123.7, 123.5, 119.3, 119.2, 116.0, 115.9,

81.0, 80.8, 80.3, 80.2, 26.4, 25.8, 24.7, 24.5, 11.7, 11.5. Anal. Calcd for $C_{17}H_{19}N_3OS$: C, 65.15; H, 6.11; N, 13.41. Found: C, 64.49; H, 6.25; N, 12.83.

(±)-2-(1,2,3-Benzotriazol-1-yl)-2-(methylthio)-1,1-diphenyl-1-propanol (11c): microcrystals from acetone (98%); mp 139−140 °C; ^{1}H NMR ($CDCl_3$) δ 8.00−7.84 (m, 2H), 7.58−7.47 (m, 2H), 7.42−7.10 (m, 10H), 4.19 (s, 1H), 2.46 (s, 3H), 1.71 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 146.1, 143.0, 142.9, 134.0, 129.0, 128.3, 127.7, 127.5, 127.4, 127.3, 126.6, 123.6, 119.5, 115.4, 85.2, 80.6, 25.3, 12.7. Anal. Calcd for $C_{22}H_{21}N_3OS$: C, 70.37; H, 5.64; N, 11.19. Found: C, 70.62; H, 5.82; N, 10.95.

(±)-2-(1,2,3-Benzotriazol-1-yl)-2-(methylthio)-1,1-diphenyl-1-butanol (11d). The solution of 1-(1,2,3-benzotriazol-1-yl)propyl methyl sulfide **10a** (1 g, 4.83 mmol) in THF (50 mL) was cooled to −78 °C, and the solution of *n*-BuLi (5.31 mmol, 1.58 M in hexane, 3.4 mL) was added dropwise. The reaction mixture was stirred at the same temperature for 1 h, and the solution of benzophenone (1 g, 5.31 mmol) in THF (15 mL) was added. The mixture was stirred for an additional 2 h at −78 °C. Then water was added (30 mL), and the product was extracted with ether. The rescue was purified by crystalization from acetone to give **11d** as microcrystals (96%): mp 123−124 °C; ^{1}H NMR ($CDCl_3$) δ 8.22 (d, J = 8.40 Hz, 1H), 8.00−7.92 (m, 1H), 7.60−7.50 (m, 2H), 7.50−7.41 (m, 2H), 7.40−7.27 (m, 2H), 7.23−7.14 (m, 3H), 7.14−7.06 (m, 3H), 5.25 (s, 1H), 3.21−3.08 (m, 1H), 2.60−2.46 (m, 1H), 1.48 (s, 3H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 145.4, 144.7, 142.3, 135.1, 129.5, 128.3, 127.5, 127.4, 127.1, 127.0 (2), 123.7, 119.9, 115.4, 86.2, 84.0, 29.4, 14.4, 9.5. Anal. Calcd for $C_{23}H_{23}N_3OS$: C, 70.92; H, 5.95; N, 10.79. Found: C, 70.76; H, 5.98; N, 10.81.

2-(Methylthio)-1,1-diphenyl-2-propen-1-ol (12c). To a solution of 2-(1,2,3-benzotriazol-1-yl)-2-(methylthio)-1,1-diphenyl-1-propanole **11c** (0.2 g, 0.53 mmol) in 1,2-dichlorethane (10 mL) under nitrogen was added zinc bromide (0.36 g, 1.6 mmol), and the reaction mixture was stirred at 25 °C for 15 min. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel using hexanes, to give **12c** as an oil (89%): ^{1}H NMR ($CDCl_3$) δ 7.42−7.36 (m, 4H), 7.35−7.27 (m, 6H), 5.12 (d, J = 1.1 Hz, 1H), 4.98 (d, J = 1.1 Hz, 1H), 3.29 (s, 1H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 153.9, 144.2, 127.8, 127.7, 127.5, 112.2, 82.7, 16.4. Anal. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29; N, 0. Found: C, 74.68; H, 6.30; N, 0.30.

2-(Methylthio)-3-methyl-1*H*-indene (13b). To a solution of 3-(1,2,3-benzotriazol-1-yl)-3-(methylthio)-2-phenyl-2-butanol **11b** (0.3 g, 1.60 mmol) in 1,2-dichlorethane (20 mL) under nitrogen was added zinc bromide (0.65 g, 2.87 mmol), and the reaction mixture was refluxed for 5 min. The solvent was evaporated under reduced pressure and residue was purified by column chromatography on silica gel using hexanes to give **13b** as an oil (30%): ^{1}H NMR ($CDCl_3$) δ 7.37 (d, J = 7.5 Hz, 1H), 7.32−7.17 (m, 2H), 7.16−7.09 (m, 1H), 3.52−3.47 (m, 2H), 2.41 (s, 3H), 2.12 (t, J = 2.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 146.3, 142.2, 136.0, 135.6, 126.5, 123.9, 122.9, 117.9, 40.7, 16.0, 11.1. Anal. Calcd for $C_{11}H_{12}S$: C, 74.95; H, 6.86; N, 0. Found: C, 74.94; H, 6.60; N, 0.06.

2-(Methylthio)-3-phenyl-1*H*-indene (13c). To a solution of 2-(1,2,3-benzotriazol-1-yl)-2-(methylthio)-1,1-diphenyl-1-propanole **11c** (0.5 g, 1.33 mmol) in 1,2-dichlorethane (20 mL) under nitrogen was added zinc bromide (0.9 g, 4 mmol), and the reaction mixture was refluxed for 5 min. The solvent was evaporated under reduced pressure, and residue was purified by column chromatography on silica gel using hexanes to give **13c** as plates (70%): mp 86−87 °C; ^{1}H NMR ($CDCl_3$) δ 7.52−7.38 (m, 5H), 7.36−7.19 (m, 3H), 7.16−7.08 (m, 1H), 3.63 (s, 2H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 145.4, 141.9, 138.6, 138.1, 134.5, 128.8, 128.3, 127.4, 126.5, 123.7, 123.1, 118.7, 41.0, 15.5. Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92; N, 0. Found: C, 80.94; H, 6.00; N, 0.

(±)-1-Methyl-2-(methylthio)-3-phenyl-1*H*-indene (13d). To a solution of 2-(1,2,3-benzotriazol-1-yl)-2-(methylthio)-1,1-diphenyl-1-butanole **11d** (0.5 g, 1.29 mmol) in 1,2-dichlorethane (20 mL) under nitrogen was added zinc bromide (0.87 g, 3.86 mmol), and the reaction mixture was refluxed for 5 min. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel using hexanes to give **13d** as plates (78%): mp 73−74 °C; ^{1}H NMR ($CDCl_3$) δ 7.52−7.30 (m, 6H), 7.28−7.12 (m, 3H), 3.69 (q, J = 7.4 Hz, 1H), 2.24 (s, 3H), 1.46 (d, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 148.3, 144.0, 143.7, 140.0, 134.5, 129.2, 128.2, 127.5, 126.6, 124.6, 122.5, 119.4, 46.0, 17.6, 16.7. Anal. Calcd for $C_{17}H_{16}S$: C, 80.90; H, 6.39; N, 0. Found: C, 80.65; H, 6.61; N, 0.

(±)-3-Hydroxy-3-phenyl-2-butanone (14). To a solution of 3-(1,2,3-benzotriazol-1-yl)-3-(methylthio)-2-phenyl-2-butanol **11b** (0.3 g, 0.96 mmol) in THF (20 mL) under nitrogen was added zinc bromide (0.65 g, 2.87 mmol), and the reaction mixture was stirred for 3 h. The solvent was evaporated under reduced pressure, and the residue was purified by gradient column chromatography using the mixture of hexanes/EtOAc (9:1−3:1) to give **14** as colorless liquid (75%): ^{1}H NMR ($CDCl_3$) δ 7.45−7.27 (m, 5H), 4.59 (s, 1H), 2.07 (s, 3H), 1.76 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.6, 141.3, 128.6, 127.9, 125.8, 79.8, 24.0, 23.4. The spectral data of this compound is identical to that reported in the literature.[17]

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