Novel and Efficient Insertions of Carbons Carrying O-, S-, and N-Linked Substituents: Synthesis of α-Alkoxyalkyl, α-(Alkylthio)alkyl, and α-(Carbazol-9-yl)alkyl Ketones

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A wide variety of benzotriazolyl-stabilized anions **2**, obtained by the lithiation of 1-(α-alkoxyalkyl)-, 1-[α-(alkylthio)alkyl]-, and 1-[α-(carbazol-9-yl)alkyl]benzotriazoles **1**, on reaction with aliphatic and aromatic aldehydes and ketones, followed by rearrangement induced by heating in the presence of zinc bromide, furnish one-carbon-homologated α-alkoxyalkyl, α-(alkylthio)alkyl, and α-(carbazol-9-yl)alkyl ketones **4** in simple one-pot operations in good yields with excellent regioselectivity. In several alkoxymethylene insertions, intermediate 2-alkoxyoxiranes were separated in good yields, demonstrating the epoxide mechanism for the rearrangements and providing a facile approach to polysubstituted 2-alkoxyoxiranes, another class of important compounds.

Introduction

Methods for the homologation of aldehydes and ketones by carbon-insertions α to the carbonyl group are of significant importance in organic synthesis as evidenced by the widespread and continuing interest in the development of new approaches.[1−12] As α-alkoxyalkyl and α-(alkylthio)alkyl ketones are important and versatile intermediates in organic synthesis,[13,14] approaches capable of inserting a heteroatom-substituted carbon such as −CR(OR′)− or −CR(SR′)− are especially desired. Most classical carbon insertion methods involve the use of diazo compounds $RCHN_2$,[1,8] which are unsuitable for large-scale work and often suffer from low regioselectivity, multiple homologation, and handling difficulties. Moreover, while diazo sulfones, diazophosphine oxides, and diazo phosphonates were described to add to aldehydes to yield β-keto sulfones, β-keto phosphine oxides, and β-keto phosphonates,[10] no successful alkoxymethylene and (alkylthio)methylene carbon insertions have been reported using diazo compounds.

Trost *et al.* introduced the first alkoxymethylene homologation methodology, which involves the addition of methoxymethyl phenyl sulfone anions to cyclic ketones, followed by a one-carbon ring expansion initiated by aluminum-based Lewis acids. The initial examples were limited to cyclobutanones and cyclopentanones in polycyclic systems,[2] but by using zirconium tetrachloride as the Lewis acid, the method was recently extended to monocyclic and acyclic ketones;[3] however, such insertions into aldehydes remain unreported. Recently, we described a facile conversion of aldehydes to α-acetoxymethyl ketones *via* reactions of aldehydes with (benzotriazolyl)phenoxy methyl anion, followed by the treatment of the resulting adducts with *p*-toluenesulfonic acid in acetic acid.[5] However, acetoxymethylene insertions of this type are restricted to aldehydes.

The lithium derivatives of bis(phenylthio)methane[4] and of (phenylthio)methyl phenyl sulfone[2] add to carbonyl compounds, and subsequent rearrangement of the adducts formed enables successful (phenylthio)methylene homologation of aldehydes and ketones. However, excess diethylaluminum chloride was needed to promote the addition reaction of (phenylthio)methyl phenyl sulfone anion to ketones. The yields were moderate, and all of these methods apparently require the isolation of the addition adducts. The successful bis(methylthio)methylene insertion developed by Knapp *et al.* to transform cyclic ketones to 1,2-keto thioketals *via* the reaction of $(MeS)_3CLi$ with ketones, followed by the ring expansion assisted by $CuBF_3$·4MeCN[15] as reported is limited to cyclic ketones. At the higher oxidation level, Yamakawa *et al.* have described an easy transformation of aldehydes[7d] and ketones[7c] to one-carbon-homologated α-sulfinylalkyl ketones *via* carbenoid intermediates using chloromethyl phenyl sulfoxide as the reagent.

In the course of our investigation on the use of benzotriazole derivatives in organic synthesis,[16] we found that the benzotriazolyl moiety is both a good anion-stabilizing group and a good leaving group. These properties, coupled with the ready availability of its derivatives, suggested its potential to provide general and

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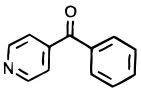
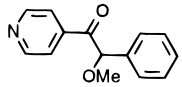
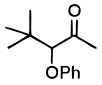
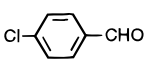
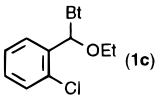
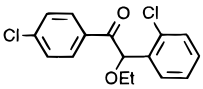
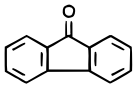
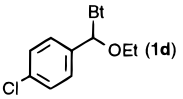
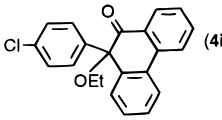
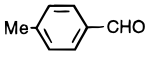
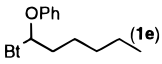
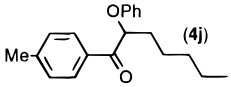
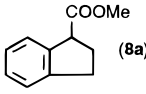
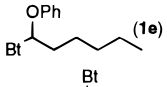
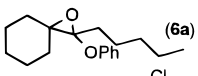
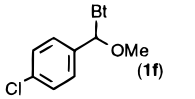
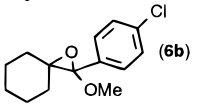
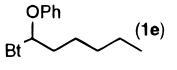
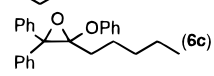
Table 1. Alkoxymethylene Insertion into Aldehydes and Ketones

entry	carbonyl compound	Bt-reagent	temp, °C/ time, h [a] / solvent	product	yield [b] (%)
1	PhCHO	$BtCH_2OMe$ (**1a**)	140 / 1 / $CHCl_2CHCl_2$	$PhCOCH_2OMe$ (**4a**)	82
2	PhCOMe	$BtCH_2OMe$ (**1a**)	140 / 1 / $CHCl_2CHCl_2$	PhCH(OMe)COMe (**4b**)	60
3	PhCOPh	$BtCH_2OMe$ (**1a**)	140 / 0.5 / $CHCl_2CHCl_2$	PhCOCH(OMe)Ph (**4c**)	62
4		$BtCH_2OMe$ (**1a**)	140 / 14 / $CHCl_2CHCl_2$	 (**4d**)	78
5	$PhCH_2CH_2CHO$	$BtCH_2OMe$ (**1a**)	140 / 1 / $CHCl_2CHCl_2$	$PhCH_2CH_2COCH_2OMe$ (**4e**)	50
6	PhCOPh	$BtCH_2OPh$ (**1b**)	140 / 12 / $CHCl_2CHCl_2$	PhCH(OPh)COPh (**4f**)	53
7		$BtCH_2OPh$ (**1b**)	140 / 12 / $CHCl_2CHCl_2$	 (**4g**)	47
8		 (**1c**)	65 / 6 /THF	 (**4h**)	91
9		 (**1d**)	65 / 24 / THF	 (**4i**)	51
10		 (**1e**)	65 / 4.5 /THF	 (**4j**)	81
11		$BtCH_2OMe$ (**1a**)	140 / 1 / $CHCl_2CHCl_2$	 (**8a**)	36
12	PhCH=CHCHO	$BtCH_2OMe$ (**1a**)	140 / 1 / $CHCl_2CHCl_2$	$PhCH=CHCH_2COOMe$ (**8b**)	40
13 [c]		 (**1e**)	65 / 4.5 /THF	 (**6a**)	56
14 [c]		 (**1f**)	65 / 4.5 /THF	 (**6b**)	45
15	PhCOPh	 (**1e**)	65 / 4.5 /THF	 (**6c**)	71

[a] Conditions for the *in situ* rearrangement step. [b] Overall yield for the isolated pure product from carbonyl compound. [c] Heating the intermediate **3** in $CHCl_2CHCl_2$ at 140 °C gave a complex mixture. No desired ring expanded ketone **4** was obtained.

efficient carbon-insertion methodology. Since disclosure of our preliminary paper,[17] we have further developed and generalized the regioselective insertion approach to one-carbon-homologated α-alkoxyalkyl, α-(alkylthio)alkyl, and α-(carbazol-9-yl)alkyl ketones with many more examples and now provide full details of this work in this and the following paper.

Results and Discussion

Alkoxymethylene Insertion into Aldehydes and Ketones. 1-(Alkoxymethyl)benzotriazoles **1a**,[18] **1b**,[19] and **1c**[20] (Table 1) were prepared according to our previously reported procedures. 1-[Ethoxy(4-chlorophenyl)methyl]-benzotriazole (**1d**) and 1-[methoxy(4-chlorophenyl)methyl]benzotriazole (**1f**) were made by a procedure similar to that used for **1c**. 1-(1-Phenoxyhexyl)benzotriazole (**1e**) (Table 1) was made by the lithiation of 1-(phenoxymethyl)benzotriazole (**1b**), followed by the addition of pentyl iodide.[21] Compounds **1d** and **1f** were previously unknown and were characterized by their NMR spectra and CHN analyses.

Treatment of **1a**−**f** with *n*-butyllithium at −78 °C, under argon in THF, furnished deep green solutions of the corresponding anions **2**, which reacted smoothly with aliphatic and aromatic aldehydes and ketones (Scheme 1). Our previous work has shown that these reactions provided intermediates of type **3**, which upon hydrolysis or methanolysis furnished various α-hydroxy ketones[20,21] or methyl acetals[22] in sequences in which benzotriazole

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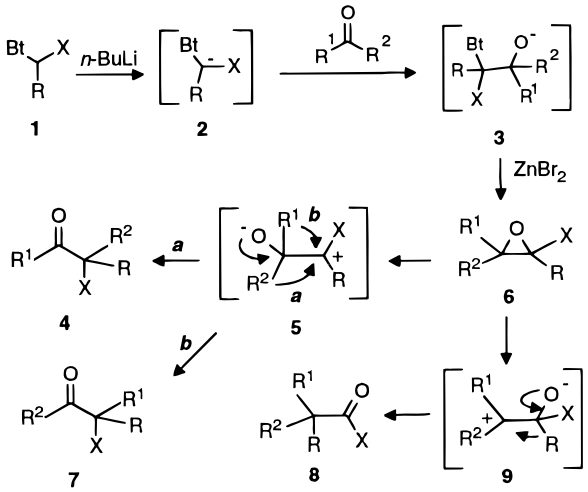
Scheme 1[a]



[a] Bt = benzotriazol-1-yl; X = R′O, R′S, or carbazol-9-yl; R = H, alkyl, or aryl (see Tables 1 and 2 for the designation of X, R^1, R^2, and R).

derivatives **1** functioned as useful heterocycle-stabilized acyl anion equivalents.

In the present work, the intermediates **3** thus produced were each shown to be capable of *in situ* rearrangement to afford one-carbon-homologated α-alkoxyalkyl ketones **4a**−**j** in good to excellent yields. The structures of products **4a**−**j** were proved by their NMR spectroscopy and elemental analysis data. Rearrangement was found to be promoted by a *ca.* 3-fold molar excess of zinc bromide and to occur upon heating. In accordance with previous observations,[16] zinc bromide played a vital role in assisting the departure of the benzotriazolyl group. As indicated in Table 1, the reaction temperatures necessary for rearrangement vary with the nature of the R group (Scheme 1). In the cases of **4a**−**g** (R = H), the required temperature for rearrangement was much higher than the boiling point of THF. Thus, after the reactions of anions **2** with aldehydes and ketones, the THF was distilled off, 1,1,2,2-tetrachloroethane was added, and the mixture was refluxed for the time required to complete rearrangement. In the cases of **4h**−**j** (R = aryl or alkyl groups), rearrangement can be completed in refluxing THF due to its facilitation by the aryl or alkyl groups which stabilize the transient cations **5** (Scheme 1).

The regioselectivity of these insertions is remarkable. In all cases (Table 1, entries 1−10), single regioisomers **4a**−**j** were provided by migration of the group, which can best stabilize an electron deficiency in the transition state,[23] *i.e.*, H > Ar > alkyl; *tert*-alkyl > *sec*-alkyl > *n*-alkyl. No detectable amounts of the other possible regioisomers **7** (Scheme 1) were produced on the basis of GCMS examination of the crude product mixtures. Substituent effects on the relative migration rates are discussed in detail in the following paper.[24]

The generality of these insertions is also of special significance in regard to the structures of both benzotriazole adducts and of the carbonyl compounds that can be utilized. For benzotriazole reagents, X can be phenoxy and various alkoxy groups, while R can be hydrogen, alkyl, or aryl. As already mentioned, insertions of carbons carrying both an alkoxy group and an aryl or alkyl group into carbonyl compounds were previously unknown. As shown in Table 1, the present methodology is applicable to diverse aldehydes and ketones: while alkoxymethylene insertions into aliphatic and aromatic aldehydes and acyclic ketones gave chain-extended α-alkoxyalkyl ketones, similar insertions into aromatic cyclic ketones provided ring-expanded products. However, as discussed below, analogous insertions into aliphatic cyclic ketones failed to give ring-expanded products.

α-Alkoxyalkyl ketones have been previously prepared by many methods including the α-alkoxylation of ketones with hypervalent iodine reagents,[25] palladium-catalyzed coupling reaction of acyl chlorides with organotins of the type $MeOCH_2SnR_3$,[26] reactions of acyl chlorides or esters with diazomethane, followed by alcoholysis[27] and from acyl anion equivalents.[28] The present approach leading to one-carbon-homologated α-alkoxyalkyl ketones complements these methods and should be of substantial interest in organic synthesis.

Interestingly, when the anion of 1-(methoxymethyl)-benzotriazole (**1a**) reacted with 1-indanone and cinnamaldehyde after heating in the presence of zinc bromide, no expected methoxymethylene insertion products of type **4** were obtained. Instead, the corresponding one-carbon homologated esters, 1-(methoxycarbonyl)indan (**8a**) and methyl 4-phenyl-3-butenoate (**8b**) were separated in 36% and 40% yields, respectively. Structures of **8a** and **8b** were assigned on the basis of NMR spectra and elemental analyses. In their ^{13}C NMR spectra, signals typical for the ester groups appeared at 174.3 and 172.0 ppm. The formation of these esters **8a** and **8b** could be accounted for if epoxides **6** are the intermediates and if **6**, instead of giving oxygen-stabilized cations **5**, opened up from the other side to form cations **9**. Subsequent hydride migration furnished esters **8** (Scheme 1). Although the reasons for the migration in the alternative direction in these two cases are not yet clear, the stability of the cationic species **9** could play a major role.

The epoxide mechanism was further supported by the successful isolation of alkoxyoxiranes **6a**−**c** (Table 1, entries 13−15). When R ≠ H (see Scheme 1), the departure of the benzotriazol-1-yl group could be accomplished in refluxing THF. Under these conditions, the fully substituted epoxides of type **6** from **1** (R ≠ H) and ketones are stable enough to be separated. Accordingly, reactions of the anions of compounds **1e** and **1f** with ketones, followed by refluxing in THF in the presence of zinc bromide, with careful monitoring of the reaction by thin layer chromatography, provided epoxides **6a**−**c** in good yields. Compounds **6a**−**c** showed the expected NMR spectra and elemental analyses. The ^{13}C signals at *ca.* 91 and 70 ppm are characteristic for the two carbons on the oxirane ring. While these fully substituted alkoxyoxiranes **6a**−**c** partially decomposed on silica gel during column chromatography, they are stable to storage at 20 °C. 2-Alkoxyoxiranes have previ-

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ously been shown to be versatile building blocks for organic synthesis.[29] The following well-established methods for their preparation, (i) oxidation of vinyl ethers with peroxides[30,31] and (ii) reactions of α-halo ketones with dry alcohols under basic conditions,[29] are limited for the most part to rather structurally simple 2-alkoxyoxiranes due to the availability of the corresponding vinyl ethers and α-halo ketones. One successful approach for the preparation of 2-alkoxyoxiranes from ketones was previously available,[32] but it involves rather complex transformations: electrolytic oxidation of ketone *N*-acylhydrazones in methanolic sodium acetate, followed by thermal evolution of N_2 of the intermediates 2-methoxy-Δ^3-1,3,4-oxadiazolines. Our present method potentially enables the facile construction of a wide range of fully substituted α-alkoxyoxiranes in one-pot processes starting from ketones.

It was expected that epoxides **6a**−**c** would undergo further thermal rearrangement to furnish the corresponding ring-expanded or chain-extended α-alkoxyalkyl ketones of type **4**. Unfortunately, the attempted ring expansion of cyclohexanone in the cases of entries 13 and 14 (Table 1) failed. Thus, treatment of epoxides **6a** and **6b** with zinc bromide upon heating in 1,1,2,2-tetrachloroethane at 90 °C resulted in the recovery of the epoxides, while heating at 120 °C gave mixtures of starting epoxides together with small amounts of expected α-alkoxyalkyl ketones of type **4** and heating at 140 °C provided a complicated mixture based on GCMS analyses. Similar results were obtained when **1a** and **1b** reacted with cyclohexanone and cyclopentanone. We believe the ring-expansion did occur at high temperature (≥120 °C). However, the resultant α-alkoxyalkyl ketones with *β*-hydrogen were not stable under these vigorous conditions possibly because of elimination of ethanol or phenol to form the corresponding α,*β*-unsaturated ketones, which again under the reaction conditions led to other side products. When epoxide **6c** was treated with $ZnBr_2$ in 1,1,2,2-tetrachloroethane at 110 °C, rearrangement occurred immediately. However, instead of the chain-extended ketone of type **4**, the corresponding α,*β*-unsaturated ketone 1,2-diphenylhept-2-en-1-one [PhCOC(Ph)=CH$(CH_2)_3$Me] was obtained in good yield, evidently from the initially formed 2-phenoxyketone by elimination. Transformations of this type from carbonyl compounds into chain-extended α,*β*-unsaturated ketones are being actively explored and will be reported subsequently.

(Alkylthio)methylene Insertions into Aldehydes and Ketones. [1-(Phenylthio)alkyl]benzotriazoles **1g**,[19] **1j**,[19] and **1i**[33] were prepared as previously described (Table 2). 1-[(Methylthio)methyl]benzotriazole (**1h**) was made from benzotriazole and dimethyl sulfoxide in acetic anhydride in 60% yield and was characterized by NMR spectra and CHN analysis. We have previously demonstrated that 1-[(phenylthio)methyl]benzotriazole (**1g**) underwent deprotonation with butyllithium and the resulting carbanion reacted readily with aldehydes and ketones.[19] In the present work, 1-[(phenylthio)alkyl]- and 1-[(methylthio)alkyl]benzotriazoles **1g**−**j** all underwent deprotonation easily with *n*-butyllithium in THF at −78 °C. Similar to the alkoxymethylene insertions, the lithio derivatives of **1g**−**j** reacted with aliphatic and aromatic aldehydes and ketones and subsequent treatment of the intermediates with a 3-fold molar excess of zinc bromide provided upon heating the corresponding one-carbon-homologated α-(phenylthio)alkyl ketones **4k**−**s** in good yields. The migration aptitude followed the same general trend that hydrogen migrates faster than aryl and aryl faster than alkyl. However, as an exception, a benzyl group migrates preferentially compared to a phenyl group, as demonstrated by the reaction of 1-[(methylthio)-methyl]benzotriazole (**1h**) and desoxybenzoin (entry 7, Table 2), indicating the stronger cation-stabilizing ability of benzyl over phenyl. Each case, except for entry 7, afforded a single regioisomer of type **4**. For desoxybenzoin (entry 7, Table 2), both regioisomers **4q** and **7q** were produced in 55% and 30% GC yields, respectively. While **4q** was separated in 50% yield, **7q** remained together with a small amount of desoxybenzoin as an inseparable mixture. Noteworthy is the fact that disubstituted methylene groups carrying both a phenylthio group and an aryl or alkyl group were again successfully inserted into a carbonyl compound. Compounds **4k**−**s** were all characterized by ^{1}H and ^{13}C NMR, and novel compounds were further confirmed by CHN analyses.

The main methods reported previously for the preparation of α-(phenylthio)alkyl ketones are based on the reaction of regiospecifically generated enolate anions or silyl enol ethers with various species containing an electrophilic sulfur atom.[14,34,35] They often suffer from side reactions such as bissulfenylation. Our procedure to one-carbon-homologated α-(phenylthio)alkyl ketones from readily available starting materials should find use in synthesis.

Carbazolylmethylene Insertions into Aldehydes and Ketones. A potential advantage of the present methodology is its extension to introduction of other heteroatoms concomitant with carbon insertions. Nitrogen is the most important of these, and we have done some preliminary work in this area. As examples, 1-(carbazol-9-ylalkyl)benzotriazole **1k** and **1l** were used successfully in the insertions. 1-(Carbazol-9-ylmethyl)-benzotriazole (**1k**)[36] and 1-(1-carbazol-9-ylethyl)benzotriazole (**1l**)[37] were made by previous procedures. By employing one-pot insertion procedures analogous to those described above, one-carbon homologated α-(carbazol-9-yl)alkyl ketones **4t**−**w** were obtained in 36−73% yields and were all characterized by ^{1}H and ^{13}C NMR and elemental analyses.

Conclusion

We have shown that 1-(α-alkoxyalkyl)-, 1-[α-(alkylthio)alkyl]-, and 1-[α-(carbazol-9-yl)alkyl]benzotriazoles are readily available, versatile, and high-yielding reagents for the transformations of aldehydes and ketones into one-carbon-homologated α-alkoxyalkyl, α-(alkylthio)alkyl, and α-(carbazol-9-yl)alkyl ketones. Significant advantages of the present one-pot methodology include its excellent regioselectivity, the readily available starting

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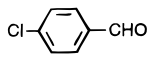
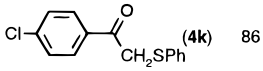
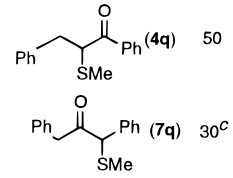
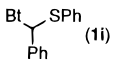
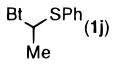
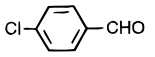
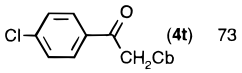
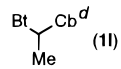
Table 2. (Alkylthio)methylene and Carbazolylmethylene Insertions into Aldehydes and Ketones

entry	carbonyl compound	Bt-reagent	temp, °C/ time, h [a] / solvent	product	yield [b] (%)
1		$BtCH_2SPh$ (**1g**)	140 / 10 / $CHCl_2CHCl_2$	 (**4k**)	86
2	PhCHO	$BtCH_2SPh$ (**1g**)	140 / 10 / $CHCl_2CHCl_2$	$PhSCH_2COPh$ (**4l**)	70
3	$PhCH_2CH_2CHO$	$BtCH_2SPh$ (**1g**)	65 / 5 / THF	$PhSCH_2COCH_2CH_2Ph$ (**4m**)	65
4	PhCOMe	$BtCH_2SPh$ (**1g**)	140 / 10 / $CHCl_2CHCl_2$	PhCH(SPh)COMe (**4n**)	65
5	PhCOPh	$BtCH_2SPh$ (**1g**)	140 / 10 / $CHCl_2CHCl_2$	PhCH(SPh)COPh (**4o**)	78
6	PhCHO	$BtCH_2SMe$ (**1h**)	120 / 10 / $CH_2ClCHCl_2$	$PhCOCH_2SMe$ (**4p**)	84
7	$PhCOCH_2Ph$	$BtCH_2SMe$ (**1h**)	120 / 10 / $CH_2ClCHCl_2$	 (**4q**) (**7q**)	50 [c] 30 [c]
8	PhCHO	 (**1i**)	65 / 10 / THF	PhCH(SPh)COPh (**4r**)	56
9	PhCHO	 (**1j**)	140 / 6 / $CHCl_2CHCl_2$	PhCOCH(SPh)Me (**4s**)	84
10		$BtCH_2Cb$ [d] (**1k**)	140 / 1 / $CHCl_2CHCl_2$	 (**4t**)	73
11	PhCHO	$BtCH_2Cb$ [d] (**1k**)	140 / 1 / $CHCl_2CHCl_2$	$PhCOCH_2Cb$ (**4u**)	70
12	PhCOMe	$BtCH_2Cb$ [d] (**1k**)	120 / 10 / $CH_2ClCHCl_2$	PhCH(Cb)COMe (**4v**)	36
13	PhCHO	 (**1l**)	120 / 10 / $CH_2ClCHCl_2$	PhCOCH(Cb)Me (**4w**)	56

[a] Conditions for the *in situ* rearrangement step. [b] Overall yield for the isolated pure product from carbonyl compound. [c] GC yield. [d] Cb represents carbazol-9-yl.

materials, and simple procedures. However, aliphatic cyclic ketones failed to undergo clean ring expansions, thus demonstrating a limitation to this approach.

Experimental Section

General Procedures. Melting points were determined with a hot-stage apparatus and are uncorrected. NMR spectra were taken in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H (300 MHz) or solvent as the internal standard for ^{13}C (75 MHz). Tetrahydrofuran was distilled under nitrogen immediately prior to use from sodium/benzophenone. All reactions with air-sensitive compounds were carried out under an argon atmosphere. Column chromatography was conducted with silica gel 230−400 mesh. 1-(Methoxymethyl)benzotriazole (**1a**),[18] 1-(phenoxymethyl)benzotriazole (**1b**),[19] 1-[ethoxy-(2-chlorophenyl)methyl]benzotriazole (**1c**),[20] 1-(1-phenoxyhexyl)-benzotriazole (**1e**),[21] 1-[(phenylthio)methyl]benzotriazole (**1g**),[19] 1-[(phenylthio)phenylmethyl]benzotriazole (**1i**),[33] 1-[1-(phenylthio)ethyl]benzotriazole (**1j**),[19] 1-[(carbazol-9-yl)methyl]benzotriazole (**1k**),[36] and 1-[1-(carbazol-9-yl)ethyl]benzotriazole (**1l**)[37] were prepared according to reported procedures.

1-[Ethoxy(4-chlorophenyl)methyl]benzotriazole (1d). This compound was prepared by the same procedure as for **1c**[20] as a colorless oil (60%): ^1H NMR δ 1.26 (t, J = 7.1 Hz, 3 H), 3.43−3.52 (m, 1 H), 3.73−3.82 (m, 1 H), 7.18 (s, 1 H), 7.27−7.40 (m, 7 H), 8.06−8.10 (m, 1 H); ^{13}C NMR δ 14.6, 65.0, 88.8, 111.4, 120.0, 124.3, 127.4, 127.6, 128.8, 130.9, 134.9 (2 C), 147.0. Anal. Calcd for $C_{15}H_{14}N_3OCl$: C, 62.61; H, 4.90; N, 14.60. Found: C, 62.42; H, 4.69; N, 14.69.

1-[Methoxy(4-chlorophenyl)methyl]benzotriazole (1f). This compound was prepared by the same procedure as for **1c**[20] as a colorless oil (50%): ^1H NMR δ 3.44 (s, 3H), 7.07 (s, 1H), 7.22−7.25 (m, 1H), 7.30−7.38 (m, 6H), 8.06−8.10 (m, 1H); ^{13}C NMR δ 56.7, 90.3, 111.2, 120.0, 124.3, 127.3, 127.6, 128.7, 130.7, 134.5, 134.9, 146.9. Anal. Calcd for $C_{14}H_{12}N_3OCl$: C, 61.43; H, 4.42; N, 15.35. Found: C, 61.47; H, 4.46; N, 15.60.

1-[(Methylthio)methyl]benzotriazole (1h). A mixture of benzotriazole (2.4 g, 20 mmol), dimethyl sulfoxide (20 mL), and acetic anhydride (13 mL) was stirred at 100 °C for 3 days. The reaction mixture was poured into saturated sodium bicarbonate aqueous solution (100 mL). To this solution were then added sodium hydroxide (6 g) and diethyl ether (100 mL), and the mixture was stirred overnight. The organic layer was separated and the aqueous layer extracted with diethyl ether (100 mL). The combined organic extracts were dried (Na_2SO_4), and solvent was evaporated to give a colorless oil, which was separated by column chromatography (hexane: Et_2O = 2:1) to give the pure product **1h** as colorless plates (60%): ^1H NMR δ 2.15 (s, 3H), 5.72 (s, 2H), 7.43 (t, J = 8.2 Hz, 1H), 7.55 (t, J = 8.2 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 8.1 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 14.7, 50.7, 110.1, 120.0, 124.1, 127.4, 131.8, 146.4. Anal. Calcd for $C_8H_9N_3S$: C, 53.62; H, 5.02; N, 23.50. Found: C, 53.36; H, 5.14; H, 23.26.

General Procedure for the Insertions into Aldehydes and Ketones; Preparation of α-Alkoxyalkyl Ketones 4a−j, α-(Alkylthio)alkyl Ketones 4k−s and 7q, α-(Carbazol-9-yl)alkyl Ketones (4t−w), 2-Alkoxyoxiranes 6a−c, and Esters 8a,b. To a solution of an appropriate benzotriazole derivative (5 mmol) in THF (50 mL) at −78 °C under argon was added *n*-BuLi (2*M*, 2.8 mL, 5.5 mmol). After 1 h (5 min in the cases of **1c**−**f** as the starting materials), a solution of an appropriate aldehyde or ketone (5.5 mmol) in THF (10 mL) was added. The mixture was stirred at −78 °C for an additional 4 h and allowed to warm to room temperature overnight. A solution of zinc bromide (15 mmol) in THF (15 mL) was then added. As indicated in Tables 1and 2, (i) the mixture was refluxed in THF (for **4h**−**j**, **6a**−**c**, **4m,** and **4r**) or (ii) the THF was removed, 1,1,2-trichloroethane (for **4p**, **4q**, **7q**, **4v**, and **4w**) or 1,1,2,2-tetrachloroethane (for **4a**−**g**, **7a**, **7b**, **4k**, **4l**, **4n**, **4o**, and **4s**−**u**) (15 mL) added, and the mixture refluxed. Ethyl acetate (150 mL) and diethyl ether (100 mL) were added to the residue, and the mixture was stirred for 1 h at room temperature. The solid was filtered off, and the solution was washed with water (2 × 100 mL) and dried ($MgSO_4$). After the solvent was removed, the residue was subjected to column chromatography to give the pure product.

1-Phenyl-2-methoxyethanone (4a). Hexanes:ethyl acetate (4:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 3.52 (s, 3H), 4.72 (s, 2H), 7.47 (t, J = 7.1 Hz, 2H), 7.59 (t, J = 7.1 Hz, 1H), 7.93 (dd, J = 7.1 and 1.8 Hz, 2H); ^{13}C NMR δ 59.3, 75.1, 127.7, 128.6, 133.4, 134.7, 196.0. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.94; H, 6.50.

1-Methoxy-1-phenyl-2-propanone (4b). Hexanes:ethyl acetate (5:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 2.11 (s, 3H), 3.38 (s, 3H), 4.66 (s, 1H), 7.33−7.39 (m, 5H); ^{13}C NMR δ 25.1, 57.1, 89.4, 126.9, 128.6, 128.8, 135.8, 206.6. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.86; H, 7.30.

1,2-Diphenyl-2-methoxyethanone (4c). Hexanes:ethyl acetate (7:1) was used as the eluent to give colorless powders: mp 46−47 °C; ^{1}H NMR δ 3.43 (s, 3H), 5.52 (s, 1H), 7.26−7.38 (m, 5H), 7.44−7.49 (m, 3H), 7.97 (dd, J = 7.4, 1.9 Hz, 2H); ^{13}C NMR δ 57.3, 86.5, 127.5, 128.4, 128.5, 128.7, 128.9, 133.1, 134.9, 136.0, 197.0. The mp as well as ^{1}H and ^{13}C NMR spectra of this material were identical with those of an authenic sample (Aldrich).

1-(4-Pyridinyl)-2-methoxy-2-phenylethanone (4d). Hexanes:ethyl acetate (1:1) was used as the eluent to give a yellow oil: ^{1}H NMR δ 3.46 (s, 3H), 5.43 (s, 1H), 7.32−7.46 (m, 5H), 7.73 (d, J = 6.2 Hz, 2H), 8.72 (d, J = 6.2 Hz, 2H); ^{13}C NMR δ 57.5, 87.1, 121.8, 127.3, 128.8, 129.0, 134.9, 140.8, 150.6, 196.8. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.98; H, 5.77; N, 6.17. Found: C, 74.29; H, 5.84; N, 6.10.

1-Methoxy-4-phenyl-2-butanone (4e). Hexanes:ethyl acetate (4:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 2.78 (t, J = 7.5 Hz, 2H), 2.93 (t, J = 7.5 Hz, 2H), 3.39 (s, 3H), 3.97 (s, 2H), 7.18−7.31 (m, 5H); ^{13}C NMR δ 29.3, 40.4, 59.3, 77.8, 126.2, 128.3, 128.5, 140.8, 207.9. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.96; H, 7.79.

1,2-Diphenyl-2-phenoxyethanone (4f). Hexanes:ethyl acetate (6:1) was used as the eluent to give colorless needles: mp 84−85 °C; ^{1}H NMR δ 6.37 (s, 1H), 6.92−6.97 (m, 3H), 7.21−7.26 (m, 2H), 7.31−7.42 (m, 5H), 7.48 (t, J = 7.4 Hz, 1H), 7.59 (d, J = 7.4 Hz, 2H), 8.04 (d, J = 7.2 Hz, 2H); ^{13}C NMR δ 82.8, 115.7, 121.7, 127.3, 128.5, 128.7, 128.9, 129.2, 129.6, 133.5, 134.6, 135.4, 157.6, 196.0. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.01; H, 5.52.

3-Phenoxy-4,4-dimethyl-2-pentanone (4g). Hexanes: ethyl acetate (10:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 1.02 (s, 9H), 2.02 (s, 3H), 4.00 (s, 1H), 6.76 (d, J = 8.8 Hz, 2H), 6.89 (t, J = 7.4 Hz, 1H), 7.18−7.23 (m, 2H); ^{13}C NMR δ 26.4, 27.5, 35.0, 90.2, 114.7, 121.4, 129.7, 158.3, 211.2. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.50; H, 8.96.

2-Ethoxy-1-(4-chlorophenyl)-2-(2-chlorophenyl)ethanone (4h). Hexanes:ethyl acetate (5:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 1.28 (t, J = 7.0 Hz, 3H), 3.57−3.73 (m, 2H), 6.10 (s, 1H), 7.23−7.26 (m, 2H), 7.36−7.44 (m, 4H), 7.90−7.94 (m, 2H); ^{13}C NMR δ 15.2, 65.8, 79.8, 127.5, 128.9, 129.3, 129.7, 129.9, 130.0, 133.6, 133.8, 134.2, 139.7, 194.7. Anal. Calcd for $C_{16}H_{14}O_2Cl$: C, 62.15; H, 4.56. Found: C, 62.13; H, 4.59.

10-Ethoxy-10-(4-chlorophenyl)-9(10*H*)-phenanthrenone (4i). Hexanes:ethyl acetate (8:1) was used as the eluent to give a white solid: mp 126−127 °C; ^{1}H NMR δ 1.33 (t, J = 7.0 Hz, 3H), 3.25−3.34 (m, 1H), 3.53−3.63 (m, 1H), 7.10−7.15 (m, 2H), 7.21−7.26 (m, 2H), 7.33−7.58 (m, 4H), 7.64−7.69 (m, 1H), 7.93 (dd, J = 7.8 and 1.4 Hz, 1H), 8.01−8.07 (m, 2H); ^{13}C NMR δ 15.6, 61.7, 85.5, 123.1, 123.7, 128.2 (2 C), 128.4 (2 C), 128.6, 128.9, 129.4, 129.7, 131.9, 134.1, 135.0, 136.8, 138.7, 139.4, 197.3. Anal. Calcd for $C_{22}H_{17}O_2Cl$: C, 75.75; H, 4.91. Found: C, 76.10; H, 4.91.

1-(4-Methylphenyl)-2-phenoxy-1-heptanone (4j). Hexanes:ethyl acetate (9:1) was used as the elute to give a colorless oil: ^{1}H NMR δ 0.87 (t, J = 6.8 Hz, 3H), 1.29−1.35 (m, 4H), 1.49−1.69 (m, 2H), 1.96−2.08 (m, 2H), 2.39 (s, 3H), 5.26 (dd, J = 8.2 and 4.7 Hz, 1H), 6.83−6.92 (m, 3H), 7.17 (d, J = 7.4 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 8.00 (d, J = 8.3 Hz, 2H); ^{13}C NMR δ 13.9, 21.6, 22.4, 25.4, 31.4, 33.4, 81.3, 115.1, 121.2, 128.9, 129.4, 129.5, 131.9, 144.5, 157.9, 198.6. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.36; H, 8.44.

1-(4-Chlorophenyl)-2-(phenylthio)ethanone (4k). Hexanes:ethyl acetate (4:1) was used as the eluent to give a yellowish solid: mp 56−57 °C; ^{1}H NMR δ 4.22 (s, 2H), 7.24−7.32 (m, 2H), 7.37−7.40 (m, 3H), 7.42−7.45 (m, 2H), 7.86−7.89 (m, 2H); ^{13}C NMR δ 41.1, 127.3, 129.0, 129.1, 130.1, 130.7, 133.6, 134.3, 139.9, 192.9. Anal. Calcd for $C_{14}H_{11}OSCl$: C, 64.00; H, 4.22. Found: C, 63.99; H, 4.15.

1-Phenyl-2-(phenylthio)ethanone (4l). Hexanes:ethyl acetate (7:1) was used as the eluent to give a yellowish solid: mp 48−49 °C (lit.[38] mp 49−50 °C); ^{1}H NMR δ 4.27 (s, 2H), 7.21−7.46 (m, 7H), 7.55 (t, J = 6.4 Hz, 1H), 7.93 (d, J = 6.4 Hz, 2H); ^{13}C NMR δ 41.1, 127.0, 128.6, 129.0, 129.1, 129.2, 130.4, 132.8, 133.4, 194.0.

1-(Phenylthio)-4-phenyl-2-butanone (4m). Hexanes: ethyl acetate (10:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 2.84−2.91 (m, 4H), 3.61 (s, 2H), 7.11−7.30 (m, 10H); ^{13}C NMR δ 29.7, 41.9, 43.9, 126.1, 126.8, 128.2, 128.4, 129.0, 129.5, 134.6, 140.6, 204.1; HRMS calcd for $C_{16}H_{16}OS$ 256.0922, found 256.0935.

1-Phenyl-1-(phenylthio)-2-propenone (4n). Hexanes: ethyl acetate (7:1) was used as the eluent to give white needles: mp 67−68 °C (lit.[39] mp 70 °C); ^{1}H NMR δ 2.20 (s, 3H), 5.00 (s, 1H), 7.24−7.40 (m, 10H); ^{13}C NMR δ 27.2, 64.5, 127.8, 128.2, 128.5, 128.9, 129.0, 132.3, 133.7, 135.5, 202.9.

1,2-Diphenyl-2-(phenylthio)ethanone (4o). Hexanes: ethyl acetate (7:1) was used as the eluent to give yellowish needles: mp 72−73 °C; ^{1}H NMR δ 5.82 (s, 1H), 7.20−7.47 (m, 12H), 7.51 (t, J = 6.8 Hz, 1H), 7.93 (d, J = 7.6 Hz, 2H); ^{13}C NMR δ 60.3, 127.9, 128.0, 128.6, 128.7, 128.8, 128.9, 133.0, 133.3, 134.0, 135.5, 135.6, 136.5, 194.7. Anal. Calcd for $C_{20}H_{16}OS$: C, 78.92; H, 5.30. Found: C, 79.35; H, 4.97.

1-Phenyl-2-(methylthio)ethanone (4p). Hexanes:ethyl acetate (20:1) was used as the eluent to give an oil: bp 112−114 °C/0.5 mm (lit.[40] bp 94−96 °C/0.3 mm); ^{1}H NMR δ 2.49 (s, 3H), 3.78 (s, 2H), 7.48 (t, J = 7.2 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.99 (d, J = 7.2 Hz, 2H); ^{13}C NMR δ 15.9, 39.0, 128.6, 128.7, 133.3, 135.2, 194.0.

1,3-Diphenyl-2-(methylthio)-1-propanone (4q). Hexanes:ethyl acetate (20:1) was used as the eluent to give colorless plates: mp 57−58 °C; ^{1}H NMR δ 2.02 (s, 3H), 3.08 (dd, J = 14.0, 6.3 Hz, 1H), 3.46 (dd, J = 14.0, 8.4 Hz, 1H), 4.41 (dd, J = 6.3, 8.4 Hz, 1H), 7.18−7.29 (m, 5H), 7.43 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.94 (d, J = 7.2 Hz, 2H); ^{13}C NMR δ 11.4, 35.3, 47.6, 126.5, 128.3, 128.4, 128.5, 129.1, 133.0, 135.9, 138.8, 193.8. Anal. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29. Found: C, 75.21; H, 6.46.

1,2-Diphenyl-2-(phenylthio)ethanone (4r). Hexanes: ethyl acetate (5:1) was used as the eluent to give yellowish

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needles: mp 72−73 °C; ^{1}H NMR δ 5.86 (s, 1H), 7.20−7.46 (m, 12H), 7.52 (t, J = 6.8 Hz, 1H), 7.94 (d, J = 7.6 Hz, 2H); ^{13}C NMR δ 60.3, 127.9, 128.0, 128.5, 128.6, 128.7, 128.8, 128.9, 133.1, 133.3, 134.1, 135.7, 136.5, 194.7. Anal. Calcd for $C_{20}H_{16}OS$: C, 78.92; H, 5.30. Found: C, 79.36; H, 4.97.

1-Phenyl-2-(phenylthio)-1-propanone (4s). Chloroform was used as the eluent to give a colorless oil: ^{1}H NMR δ 1.50 (d, J = 6.8 Hz, 3H), 4.62 (q, J = 6.8 Hz, 1H), 7.22−7.29 (m, 3H), 7.33−7.36 (m, 2H), 7.40−7.45 (m, 2H), 7.51−7.57 (m, 1H), 7.94 (d, J = 7.1 Hz, 2H); ^{13}C NMR δ 17.0, 46.2, 127.9, 128.5, 128.6, 128.8, 129.0, 133.0, 134.4, 135.7, 196.2. The ^{1}H NMR spectrum is in agreement with the reported data.[41]

1-(4-Chlorophenyl)-2-(carbazol-9-yl)ethanone (4t). The crude material was recrystallized from hexane and ethyl acetate to give yellowish needles: mp 212−213 °C; ^{1}H NMR δ 6.20 (s, 2H), 7.29 (t, J = 8.4 Hz, 2H), 7.47 (t, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 8.23−8.28 (m, 4H); ^{13}C NMR δ 49.2, 109.3, 118.9, 120.0, 122.3, 125.5, 128.9, 130.1, 133.5, 138.9, 140.7, 193.2. Anal. Calcd for $C_{20}H_{14}NOCl$: C, 75.22; H, 4.42; N, 4.39. Found: C, 75.56; H, 4.46; N, 4.32.

1-Phenyl-2-(carbazol-9-yl)ethanone (4u). Chloroform was used as the eluent to give yellowish needles: mp 210−212 °C; ^{1}H NMR δ 6.11 (s, 2H), 7.21 (t, J = 8.1 Hz, 2H), 7.39 (t, J = 8.1 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.59−7.64 (m, 2H), 7.73 (t, J = 7.6 Hz, 1H), 8.14−8.19 (m, 4H); ^{13}C NMR δ 49.2, 109.2, 118.8, 120.0, 122.3, 125.5, 128.1, 128.7, 133.7, 134.8, 140.7, 194.0; HRMS calcd for $C_{20}H_{15}NO$ 285.1154, found 285.1131.

1-(Carbazol-9-yl)-1-phenyl-2-propanone (4v). Hexanes:ethyl acetate (8:1) was used as the eluent to give colorless plates: mp 142−143 °C; ^{1}H NMR δ 2.04 (s, 3H), 6.38 (s, 1H), 7.15−7.42 (m, 11H), 8.16 (d, J = 7.5 Hz, 2H); ^{13}C NMR δ 28.0, 66.7, 109.7, 120.1, 120.6, 123.7, 126.2, 127.8, 128.1, 128.4, 133.5, 140.2, 203.4; HRMS calcd for $C_{21}H_{17}NO$ 300.1388 (M + 1), found 300.1392.

1-Phenyl-2-(carbazol-9-yl)-1-propanone (4w). Hexanes:ethyl acetate (4:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 1.78 (d, J = 6.8 Hz, 3H), 6.04 (q, J = 6.8 Hz, 1H), 7.14−7.26 (m, 4H), 7.31 (t, J = 7.1 Hz, 1H), 7.44−7.48 (m, 4H), 7.81 (d, J = 7.1 Hz, 2H), 8.06 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 14.1, 54.7, 109.1, 119.6, 120.5, 123.7, 126.1, 128.0, 128.5, 133.3, 135.3, 139.2, 198.0; HRMS calcd for $C_{21}H_{17}NO$ 300.1388 (M + 1), found 300.1362.

(1-Phenoxyhexylene)cyclohexane Epoxide (6a). Hexanes:ethyl acetate (5:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 0.82−0.90 (m, 3H), 1.22−1.31 (m, 4H), 1.44−1.79 (m, 13H), 2.07−2.17 (m, 1H), 6.95−7.04 (m, 3H), 7.23−7.30 (m, 2H); ^{13}C NMR δ 13.8, 22.4, 24.2, 24.4, 25.6, 28.7, 29.6, 30.2, 31.5, 67.3, 91.2, 117.6, 121.7, 129.3, 155.1; HRMS calcd for $C_{18}H_{26}O_2$ 275.2011 (M + 1), found 275.2018.

[**Methoxy(4-chlorophenyl)methylene]cyclohexane Epoxide (6b).** Hexanes:ethyl acetate (4:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 1.11−1.36 (m, 3H), 1.41−1.67 (m, 4H), 1.76−1.88 (m, 2H), 1.93−2.01 (m, 1H), 3.21 (s, 3H), 7.35−7.45 (m, 4H); ^{13}C NMR δ 24.6, 25.1, 25.6, 29.9, 30.1, 52.5, 71.5, 91.4, 128.3, 129.4, 133.3, 134.3. Anal. Calcd for $C_{14}H_{17}O_2Cl$: C, 66.53; H, 6.78. Found: C, 66.43; H, 6.85.

1,1-Diphenyl-2-phenoxyhept-1-ene Epoxide (6c). Hexanes:ethyl acetate (9:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 0.74 (t, J = 7.1 Hz, 3H), 1.02−1.12 (m, 4H), 1.43−1.53 (m, 3H), 2.03−2.10 (m, 1H), 6.97 (t, J = 7.3 Hz, 1H), 7.05 (d, J = 7.7 Hz, 2H), 7.20−7.40 (m, 8H), 7.49−7.53 (m, 4H); ^{13}C NMR δ 13.7, 22.1, 23.7, 29.6, 31.3, 70.4, 91.6, 118.3, 122.3, 127.2, 127.4, 127.7, 127.8, 127.9, 128.3, 129.2, 137.6, 138.1, 154.8. Anal. Calcd for $C_{25}H_{26}O_2$: C, 83.75; H, 7.53. Found: C, 83.81; H, 7.53.

1-(Methoxycarbonyl)indan (8a). Hexanes:ethyl acetate (5:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 2.27−2.51 (m, 2H), 2.87−2.97 (m, 1H), 3.06−3.16 (m, 1H), 3.73 (s, 3H), 4.06 (dd, J = 8.0, 7.7 Hz, 1H), 7.15−7.27 (m, 3H), 7.36−7.39 (m, 1H); ^{13}C NMR δ 28.7, 31.7, 50.1, 51.9, 124.6, 124.7, 126.4, 127.5, 140.6, 144.1, 174.3. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.96; H, 6.87. Found: C, 74.80; H, 6.49.

Methyl 4-Phenyl-3-butenoate (8b). Hexanes: methylene chloride (2:1) was used as the eluent to give a colorless oil: ^{1}H NMR δ 3.17 (dd, J = 7.0, 1.3 Hz, 2H), 3.64 (s, 3H), 6.62 (dt, J = 15.9, 7.0 Hz, 1H), 6.42 (d, J = 15.9 Hz, 1H), 7.15−7.31 (m, 5H); ^{13}C NMR δ 38.2, 51.9, 121.6, 126.3, 127.5, 128.5, 133.5, 136.8, 172.0. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.60; H, 6.82.

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