# Benzotriazole-Mediated Conversions of Aromatic and Heteroaromatic Aldehydes to Functionalized Ketones

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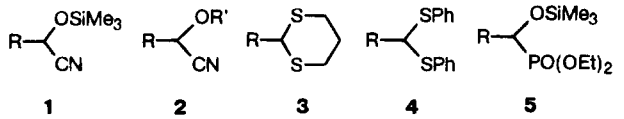
*Received May 9, 1995*[⊗]

Aromatic and heteroaromatic aldehydes reacted with benzotriazole and triethyl orthoformate in THF to give the corresponding α-(benzotriazol-1-yl)aryl ethyl ethers **7** in good yield. The novel acyl anion precursors **7** underwent smooth lithiation at the methine group followed by trapping with alkyl halides, aldehydes, ketones, and imines to yield the expected substituted intermediates of type **9**, which were hydrolyzed under mild conditions without isolation. Benzaldehyde, methyl-, chloro-, and methoxy-substituted benzaldehydes, 1-naphthalenecarboxaldehyde, 2- and 3-furaldehydes, 2- and 3-thiophenecarboxaldehydes, and 2-pyridinecarboxaldehyde were all transformed in this manner into a variety of aryl and heteroaryl ketones with alkyl (**10**), α-hydroxyalkyl (**12** and **13**), α-aminoalkyl (**14**) and acyl (**15**) substituents.

Over recent decades, the use of masked acyl anions has evolved as an important strategy in organic synthesis; they have been utilized frequently in the conversion of aldehydes to ketones. Such approaches normally involve a three-step procedure: (i) transformation of the aldehydes into substituted intermediates containing two heteroatoms, (ii) treatment of these intermediates with a strong base followed by reaction with an electrophile, and (iii) removal of the protective groups by hydrolysis to produce the ketones. Among the most common acyl anion equivalents are *O*-trimethylsilyl-protected cyanohydrins **1**, *O*-alkyl-protected cyanohydrins **2**, 1,3-dithianes **3**, bis(phenylthio)acetals **4**, and α-(silyloxy)alkylphosphonates **5**. Various aliphatic and aryl ketones have been prepared by this method, and several books and reviews have summarized the field.[1–4]




**1** **2** **3** **4** **5**

A variety of precursors with R = alkyl can be readily obtained for the preparation of aliphatic ketones, by alkylation of the corresponding formyl anion equivalents; recent examples and a literature survey have been reported.[5,6] However, when R = aryl, the precursors are almost invariably derived from aromatic or heteroaromatic aldehydes. Hünig *et al.*[7–12] reported that the condensation of aryl aldehydes with trimethylsilyl cyanide gives *O*-trimethylsilyl-protected cyanohydrins **1**, which are deprotonated by LDA and subsequently reacted with alkyl halides, aldehydes, or ketones to form the substituted derivatives. Subsequent successive two-step treatment with dilute HCl and NaOH gives the corresponding aryl ketones in high yield. However, this method requires the use of expensive trimethylsilyl cyanide and the need for special precautions due to the liberation of toxic HCN. *O*-Alkyl-protected cyanohydrins **2** (R = $CH(OEt)CH_3$), the addition products of cyanohydrins with vinyl ethers,[13] were reported to undergo similar reactions.[14] The need to prepare the cyanohydrins and to deal with HCN, however, has restricted their practical use.

1,3-Dithianes **3** with R = Ar, obtained by treatment of the aromatic aldehydes with 1,3-propanedithiol, are readily deprotonated and react with various electrophiles.[15–19] Unfortunately, the hydrolysis is difficult under acidic conditions, and only irreversible removal of the dithiol can drive the reaction to completion. Conversion to the carbonyl compounds requires complex formation with a heavy-metal cation (usually a mercury(II) salt).[16,18,20,21] The use of phenylthio **4** rather than alkylthio acetals, with attendant increase in anion stabilization, improves the performance of this system. Lithiations have been carried out with BuLi/TMEDA in hexane or THF with strict temperature control.[22–24] Hydrolysis requires trifluoroacetic acid to remove the phenylthio

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.

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group; when *p*-toluenesulfonic acid is used, α-(phenylthio)ketones are generated.[23,24]

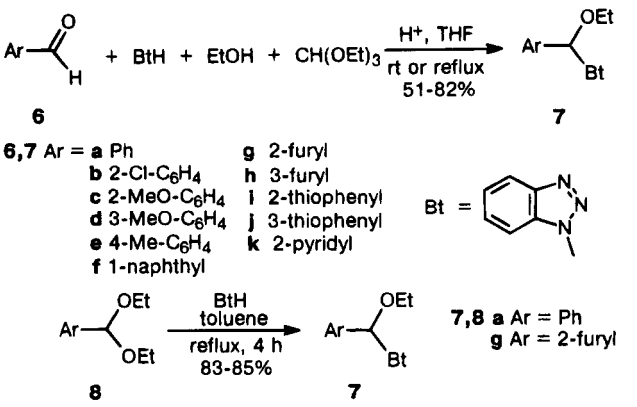
Zimmer[25,26] and Hata[27,28] separately reported that silyloxy phosphonates **5**, prepared from the reaction of aldehydes with triethyl phosphite and chlorotrimethylsilane or with diethyl trimethylsilyl phosphite, are good acyl anion equivalents. Deprotonation, reaction with an electrophile, and subsequent hydrolysis to the ketone all occur in high yield. However, while most of the examples presented deal with benzaldehyde, no other aromatic or heteroaromatic aldehydes were transformed.

Extensive investigations of the chemistry of benzotriazole-containing molecules in our group have revealed that the benzotriazole anion is a good activating and leaving group which can be used for many unique transformations.[29-31] Benzotriazole-assisted deprotonation of adjacent $CH_2$ or CH groups has led to a number of useful elaborations of anilines,[32] phenols,[33,34] amides,[35] and heterocycles.[36] In particular, recent work in this laboratory has shown that *N*-(α-alkoxyallyl)benzotriazole[37] and 1-(benzotriazol-1-yl)propargyl ethyl ethers,[38] readily obtained from reaction of the corresponding acetals with benzotriazole, are excellent acyl anion equivalents which can undergo facile lithiation and subsequent trapping with a diverse range of electrophiles to give substituted derivatives. We have now successfully extended this methodology to α-(benzotriazol-1-yl)aryl ethyl ethers **7**, which are easily prepared either from reactions of aromatic or heteroaromatic aldehydes with benzotriazole, ethanol, and triethyl orthoformate, or from the corresponding diethyl acetals with benzotriazole. Intermediates obtained after lithiation and reaction with electrophiles readily underwent hydrolysis during acidic workup to afford a wide variety of aryl ketones containing bromo, hydroxy, and amino substituents when dibromoalkanes, aldehydes, ketones, and imines, respectively, were used as the electrophiles. Further extension of this methodology to aliphatic aldehydes which requires modified conditions is still under investigation. **Note Added in Proof**: We have since demonstrated that compounds of type RCH(OPh)Bt allow such an extension to aliphatic aldehydes (manuscript in preparation).

## Results and Discussion

Stirring a mixture of aldehyde **6a–k**, benzotriazole, absolute ethanol, triethyl orthoformate, and a catalytic amount of sulfonic acid in THF for the appropriate time gave the expected benzotriazole adducts **7a–k** in 51–82% yields (Scheme 1). The five-membered ring heterocyclic aldehydes **6g–j** were easily converted to the corresponding benzotriazole adducts **7g–j** at room temperature in 3 h. Compounds **7a–f** and **7k** obtained from benzaldehydes (**6a–e**), 1-naphthaldehyde (**6f**), and 2-pyridinecarboxaldehyde (**6k**) were prepared by carrying out the reaction at room temperature for 2–3 h followed by refluxing for 2–10 h. An alternative route for the preparation of compounds **7** involved direct reaction between the corresponding acetals **8** and benzotriazole in refluxing toluene. Thus, heating a mixture of **8a** and benzotriazole in toluene for 4 h afforded the expected **7a** in 85% yield. Compound **7g** was similarly prepared in 83% yield.

**Scheme 1**




Treatment of **7a–k** with 1 equiv of *n*-butyllithium in THF at −78 °C for a few seconds to 2 min gave the anions **11**. In the cases of **10a–o, 12a–f, 13a–c, 14a–c,** subsequent reaction with the appropriate electrophiles at this temperature for a few minutes followed by simultaneous hydrolysis with dilute HCl or $H_2SO_4$ during workup afforded the expected ketones in good yield (Scheme 2). In the case of **10p**, the reaction of anion **11k** (Ar = 2-pyridyl) with octyl bromide was accomplished at room temperature, and the hydrolysis was then carried out as usual. Reaction of anion **11k** (Ar = 2-pyridyl) with benzaldehyde was also performed at room temperature. Subsequent hydrolysis did not occur in a refluxing solution of equal amounts of THF and 1 N hydrochloric acid, and on refluxing in acetic acid, the α-hydroxy ketone formed was oxidized by air to give diketone **15** in 78% yield. This type of oxidation of benzoins to benzils is well known.[39-40] All of the reactions, including alkylation and hydrolysis, were monitored by TLC until the starting material was completely consumed.

With alkyl halides as electrophiles, various aromatic and heteroaromatic ketones **10a–p** were obtained in 65–99% yields (see Table 2). As can be seen from Table 2, when 1,3-dibromopropane and 1,4-dibromobutane were used as the electrophiles, the bromo-substituted ketones **10h** and **10i** were prepared in 71% and 95% yields, respectively. Ketone **10i** has previously been prepared by acylation of furan with δ-bromopentanoic acid under

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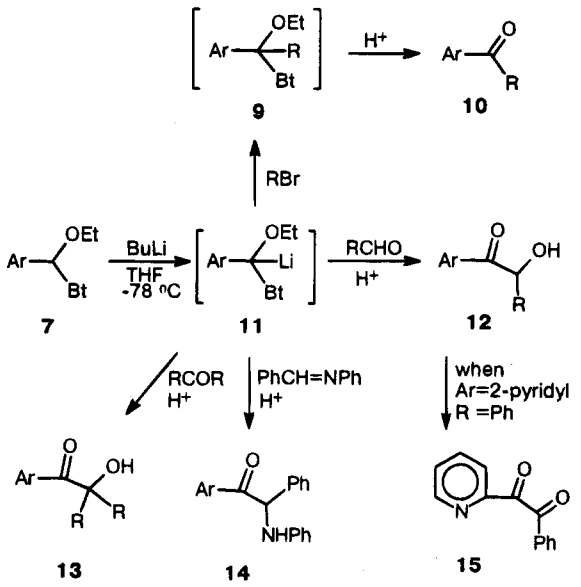
**Table 1. Preparative Data for Benzotriazole Adducts 7a–k**

| compd | Ar | yield (%) | mp (°C) | formula | CHN analysis (calcd/found) | | |
|---|---|---|---|---|---|---|---|
| | | | | | C | H | N |
| **7a** | Ph | 70 | 46–47 | $C_{15}H_{15}N_3O$ | 71.13/70.86 | 5.97/6.01 | 16.59/16.96 |
| **7b** | 2-Cl-$C_6H_4$ | 76 | 58–60 | $C_{15}H_{14}N_3OCl$ | 62.70/62.85 | 4.91/4.94 | 14.63/14.77 |
| **7c** | 2-MeO-$C_6H_4$ | 75 | 104–106 | $C_{16}H_{17}N_3O_2$ | 67.81/67.91 | 6.05/6.03 | 14.84/14.85 |
| **7d** | 3-MeO-$C_6H_4$ | 79 | oil | $C_{16}H_{17}N_3O_2$ | 67.81/67.86 | 6.05/6.12 | 14.84/14.88 |
| **7e** | 4-Me-$C_6H_4$ | 77 | oil | $C_{16}H_{17}N_3O$ | 71.87/72.09 | 6.41/6.49 | 15.73/15.73 |
| **7f** | 1-naphthyl | 71 | 138–140 | $C_{19}H_{17}N_3O$ | 75.23/75.29 | 5.65/5.61 | 13.85/13.82 |
| **7g** | 2-furyl | 57 | 59–60 | $C_{13}H_{13}N_3O_2$ | 64.17/63.83 | 5.39/5.38 | 17.28/17.62 |
| **7h** | 3-furyl | 71 | oil | $C_{13}H_{13}N_3O_2$ | 64.17/64.46 | 5.39/5.47 | 17.27/17.25 |
| **7i** | 2-thiophenyl | 58 | oil | $C_{13}H_{13}N_3OS$ | 60.21/60.12 | 5.05/5.09 | 16.20/16.30 |
| **7j** | 3-thiophenyl | 82 | oil | $C_{13}H_{13}N_3OS$ | 60.21/59.91 | 5.05/4.94 | 16.20/16.14 |
| **7k** | 2-pyridyl | 51 | 94–96 | $C_{14}H_{14}N_4O$ | 66.13/66.06 | 5.55/5.58 | 22.03/22.26 |

**Scheme 2**[a]




[a] For designation of Ar, see Scheme 1.

the catalysis of trifluoroacetic anhydride and a phosphonic resin[45,47] while **10h** is novel. In the cases of **10e** and **10j**, allyl aryl and allyl furyl ketones were generated when allyl bromide was used as the electrophile. For characterization purposes, intermediates **9a** (Ar = Ph, R = Et) and **9f** (Ar = 2-furyl, R = *n*-Bu) were isolated by column chromatography on silica gel without acidic treatment. The benzotriazole generated during the hydrolysis was easily removed by washing with a saturated sodium carbonate solution.

Similarly, when aldehydes, ketones, and imines were used as electrophiles, a variety of α-hydroxy or amino substituted aryl ketones **12a–f**, **13a–c**, and **14a–c** were prepared in 54–93% yields. The aldehydes and ketones employed could be aliphatic (**12b,e, 13a–c**) or aromatic (**12a,c,d,f**). The imine used was aromatic. Although the acyl anion synthons of types **1**,[10] **3**,[15] **4**[23] and **5**[25-26] have been used in reactions with aldehydes and ketones, no reactions with imines have apparently been previously reported.

Due to the strong activation of the benzotriazole moiety, deprotonation of the methine group occurred immediately after the addition of *n*-butyllithium. The highly reactive species **11** are not indefinitely stable in solution, especially in the case of furan and thiophene systems, and therefore immediate quenching with electrophiles is necessary for satisfactory results. Prolonged lithiation times lead to partial decomposition of the resulting anion intermediates and subsequently to low yields. Two exceptions are the 2-pyridyl ketones **10p** and **15**: as described above, the precursor anion **11k** was stable even at room temperature. An alternative approach for the preparation of compounds **10a–d,f–i,k–p** was the "inverse addition procedure", i.e. BuLi was added to the mixture of bromides and substrates **7a–d,g–k**: this reverse approach assures the shortest existence of lithio intermediates **11**. In the case of **10j**, the reverse process led to lithium exchange with allyl bromide to give *n*-butyl bromide and subsequently 2-pentanoylfuran **10f** after workup. Such a reversed lithiation process is not applicable to the other cases (**10e**, **12a–f**, **13a–c**, **14a–c**, and **15**) due to expected preferential reactions of *n*-butyllithium with the electrophiles.

The structures of all products obtained were confirmed by $^1H$, $^{13}C$ NMR spectra, and elemental analysis or high resolution mass spectra. Data for known compounds has been compared with that reported in the literature.

In summary, a convenient two-step procedure has been developed for the conversion of aromatic and heteroaromatic aldehydes to a variety of simple and functionalized ketones. The present method meets the three requirements for practical utility: (i) easy conversions to species **7**; (ii) sufficient reactivity of acyl anions **11** toward various alkylating agents including alkyl halides, aldehydes, ketones, and imines; and (iii) facile removal of the protecting group during workup. Moreover, compared with previous methods, this approach utilizing inexpensive, nontoxic, and recyclable benzotriazole as an auxiliary is applicable to a diverse range of aromatic and heteroaromatic ketones and is very attractive for large-scale industrial use.

## Experimental Section

Melting points were determined on a hot stage apparatus without correction. $^1H$ (300 MHz) and $^{13}C$ NMR (75 MHz) spectra were recorded in $CDCl_3$ (otherwise stated) with TMS or $CDCl_3$, respectively, as the internal reference. Elemental analyses and high resolution mass measurements were performed within the department.

**Preparation of α-(Benzotriazol-1-yl)aryl Ethyl Ethers (7a–k). General Procedure.** A mixture of aryl aldehyde **6a–k** (20 mmol), benzotriazole (25 mmol), absolute ethanol (40 mmol), triethyl orthoformate (60 mmol), and a catalytic amount of sulfuric acid (6 drops) was stirred in THF (30 mL) for the appropriate time (for **7a–f**, room temperature for 2–3 h followed by refluxing for another 2–3 h; for **7g–j**, room temperature for 3 h; for **7k**, room temperature for 2–3 h followed by refluxing for 10 h). Ether (200 mL) was then

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**Table 2. Preparative Data for Ketones 10a–p, 12a–f, 13a–c, 14a–c, and 15**

| compd | Ar | R | yield (%) | mp (°C) | formula | CHN analysis (calcd/found) C | H | N |
|---|---|---|---|---|---|---|---|---|
| **10a** | Ph (**11a**) | Et | 94 | oil[a] | $C_9H_{10}O$ | Lit[41] | | |
| **10b** | 2-Cl-$C_6H_4$ (**11b**) | 3-Me-Bu | 84 | oil | $C_{12}H_{15}OCl$ | 68.54/68.33 | 7.20/7.27 | |
| **10c** | 2-MeO-$C_6H_4$ (**11c**) | *n*-Bu | 80 | oil[b] | $C_{12}H_{16}O_2$ | Lit[42] | | |
| **10d** | 3-MeO-$C_6H_4$ (**11d**) | *n*-$C_8H_{17}$ | 80 | oil | $C_{16}H_{24}O_2$ | 77.36/77.17 | 9.75/9.83 | |
| **10e** | 4-Me-$C_6H_4$ (**11e**) | allyl | 65 | oil | $C_{11}H_{12}O$ | 82.45/82.34 | 7.55/7.76 | |
| **10f** | 2-furyl (**11g**) | *n*-Bu | 94 | oil[c] | $C_9H_{12}O_2$ | 71.01/70.82 | 7.95/7.98 | |
| **10g** | 2-furyl (**11g**) | *n*-$C_8H_{17}$ | 96 | oil[d] | $C_{13}H_{20}O_2$ | 74.95/75.05 | 9.68/9.91 | |
| **10h** | 2-furyl (**11g**) | $Br(CH_2)_3$ | 71 | oil | $C_8H_9O_2Br$ | 44.45/44.14 | 4.20/4.18 | |
| **10i** | 2-furyl (**11g**) | $Br(CH_2)_4$ | 95 | 53–54[e] | $C_9H_{11}O_2Br$ | 46.96/46.99 | 4.82/4.79 | |
| **10j** | 2-furyl (**11g**) | allyl | 90 | oil | $C_8H_8O_2$ | 70.56/70.45 | 5.93/6.03 | |
| **10k** | 3-furyl (**11h**) | *n*-Bu | 84 | oil | $C_9H_{12}O_2$ | 71.03/70.62 | 7.95/7.95 | |
| **10l** | 3-furyl (**11h**) | 3-Me-Bu | 99 | oil | $C_{10}H_{14}O_2$ | 72.26/71.95 | 8.49/8.58 | |
| **10m** | 2-thiophene-yl (**11i**) | *n*-$C_8H_{17}$ | 90 | oil | $C_{13}H_{20}OS$ | 69.59/69.33 | 8.98/8.97 | |
| **10n** | 3-thiophene-yl (**11j**) | Et | 82 | oil | $C_7H_8OS$ | 59.99/59.84 | 5.76/5.79 | |
| **10o** | 3-thiophene-yl (**11j**) | *n*-Bu | 84 | oil | $C_9H_{12}OS$ | 64.26/64.20 | 7.20/7.18 | |
| **10p** | 2-pyridyl (**11k**) | *n*-$C_8H_{17}Br$ | 75 | oil | $C_{14}H_{21}NO$ | 76.67/76.31 | 9.65/9.72 | 6.39/6.36 |
| **12a** | Ph (**11a**) | 4-Me-$C_6H_4$ | 57 | 113–115 | $C_{15}H_{14}O_2$ | 79.61/79.71 | 6.24/6.31 | |
| **12b** | 1-naphthyl (**11f**) | *i*-Pr | 82 | oil | $C_{15}H_{16}O_2$ | 78.92/79.12 | 7.06/7.15 | |
| **12c** | 2-furyl (**11g**) | Ph | 55 | 147–148[f] | $C_{12}H_{10}O_3$ | 71.26/71.47 | 4.99/5.00 | |
| **12d** | 2-furyl (**11g**) | 4-Me$C_6H_4$ | 60 | 142–144 | $C_{13}H_{12}O_3$ | 72.20/71.82 | 5.60/5.50 | |
| **12e** | 2-furyl (**11g**) | *i*-Pr | 67 | oil | $C_9H_{12}O_3$ | 64.26/64.08 | 7.20/7.56 | |
| **12f** | 2-thiophene-yl (**11i**) | Ph | 93 | 145–146 | $C_{12}H_{10}O_2S$ | 66.03/65.83 | 4.62/4.64 | |
| **13a** | 1-naphthyl (**11f**) | Me | 81 | oil | $C_{14}H_{14}O_2$ | 78.48/78.28 | 6.59/6.64 | |
| **13b** | 2-furyl (11g) | Ph | 55 | oil | $C_{18}H_{14}O_3$ | 77.67/77.42 | 5.07/5.44 | |
| **13c** | 2-furyl (**11g**) | cyclopropyl | 65 | oil | $C_{12}H_{14}O_3$ | 69.87/69.71 | 6.85/7.06 | |
| **14a** | 2-Cl-$C_6H_4$ (**11b**) | – | 83 | 129–131 | $C_{20}H_{16}NOCl$ | 74.65/74.79 | 5.01/5.04 | 4.35/4.22 |
| **14b** | 4-Me-$C_6H_4$ (**11e**) | – | 61 | 138–139 | $C_{21}H_{19}NO$ | 83.68/83.66 | 6.36/6.44 | 4.65/4.60 |
| **14c** | 2-furyl (**11g**) | – | 54 | 123–124 | $C_{18}H_{15}O_2N$ | 77.95/77.75 | 5.46/5.39 | 5.05/4.97 |
| **15** | – | – | 78 | oil | $C_{13}H_9O_2N$ | 211.0633/211.0682[g] | | |

[a] Literature[41] oil. [b] Literature.[42] [c] Literature.[43] [d] Literature[44] oil. [e] Literature[45] 55 °C. [f] Literature[46] mp 141 °C. [g] HRMS.

added, and the solution was washed with saturated $Na_2CO_3$ solution (2 × 100 mL) and water (100 mL). Evaporation of the solvents gave a residue, which was chromatographed on silica gel (hexane/ethyl acetate = 30:1). Melting points, yields, and elemental analyses are given in Table 1.

**[(Benzotriazol-1-yl)ethoxymethyl]benzene (7a):** $^1$H NMR δ 1.25 (t, 3 H, *J* = 7.0 Hz), 3.42–3.52 (m, 1 H), 3.70–3.80 (m, 1 H), 7.23 (s, 1 H), 7.30–7.38 (m, 6 H), 7.44–7.47 (m, 2 H), 8.05–8.09 (m, 1 H); $^{13}$C NMR δ 14.5, 64.8, 89.4, 111.5, 119.7, 124.0, 125.7, 127.3, 128.4, 128.8, 130.9, 136.2, 146.8.

**2-Chloro-1-[(benzotriazol-1-yl)ethoxymethyl]benzene (7b):** $^1$H NMR δ 1.25 (t, 3 H, *J* = 7.0 Hz), 3.50–3.60 (m, 1 H), 3.75–3.85 (m, 1 H), 7.38–7.94 (m, 7 H), 8.00 (d, 1 H, *J* = 7.2 Hz), 8.05–8.10 (m, 1 H); $^{13}$C NMR δ 14.6, 65.1, 86.6, 110.7, 119.9, 123.9, 126.7, 127.4, 128.1, 130.0, 130.5, 131.6, 133.0, 133.5, 146.4.

**2-Methoxy-1-[(benzotriazol-1-yl)ethoxymethyl]benzene (7c):** $^1$H NMR δ 1.23 (t, 3 H, *J* = 7.0 Hz), 3.49–3.57 (m, 1 H), 3.59 (s, 3 H), 3.70–3.78 (m, 1 H), 6.79 (dd, 1 H, *J* = 8.3, 1.0 Hz), 7.08 (td, 1 H, *J* = 7.5, 1.0 Hz), 7.26–7.39 (m, 5 H), 7.96 (dd, 1 H, *J* = 7.7, 1.7 Hz), 8.01–8.04 (m, 1 H); $^{13}$C NMR δ 14.7, 55.3, 64.8, 85.2, 110.7, 111.1, 119.7, 120.2, 123.6, 124.3, 127.0, 130.4, 131.5, 146.4, 156.7.

**3-Methoxy-1-[(benzotriazol-1-yl)ethoxymethyl]benzene (7d):** $^1$H NMR δ 1.26 (t, 3 H, *J* = 7.1 Hz), 3.45–3.50 (m, 1 H), 3.71–3.79 (m, 4 H), 6.89 (dd, 1 H, *J* = 8.2, 2.6 Hz), 6.97 (dd, 1 H, *J* = 7.7, 1.6 Hz), 7.06 (s, 1 H), 7.19 (s, 1 H), 7.24–7.36 (m, 4 H), 8.05–8.09 (m, 1 H); $^{13}$C NMR δ 14.6, 55.2, 65.0, 89.3, 111.7, 114.3, 118.2, 119.8, 124.2, 127.4, 129.6, 131.1, 137.9, 146.9, 159.7.

**4-Methyl-1-[(benzotriazol-1-yl)ethoxymethyl]benzene (7e):** $^1$H NMR δ 1.23 (t, 3 H, *J* = 7.0 Hz), 2.31 (s, 3 H), 3.40–3.50 (m, 1 H), 3.69–3.79 (m, 1 H), 7.12–7.20 (m, 3 H), 7.26–7.35 (m, 5 H), 8.01–8.08 (m, 1 H); $^{13}$C NMR δ 14.6, 21.0, 64.8, 89.5, 111.6, 119.7, 124.0, 125.7, 127.2, 129.1, 131.0, 133.4, 138.7, 146.9.

**1-[(Benzotriazol-1-yl)ethoxymethyl]naphthalene (7f):** $^1$H NMR δ 1.30 (t, 3 H, *J* = 6.9 Hz), 3.54–3.64 (m, 1 H), 3.86–3.95 (m, 1 H), 7.23–7.33 (m, 3 H), 7.41–7.46 (m, 2 H), 7.61 (t, 1 H, *J* = 7.8 Hz), 7.83 (s, 1 H), 7.84–7.86 (m, 1 H), 7.92 (d, 1 H, *J* = 8.4 Hz), 8.00–8.06 (m, 2 H), 8.20 (d, 1 H, *J* = 7.2 Hz); $^{13}$C NMR δ 14.8, 65.1, 87.5, 111.6, 119.9, 122.6, 124.0, 124.4, 124.8, 125.9, 127.0, 127.4, 128.8, 130.2, 130.9, 131.4, 133.7, 146.9.

**2-[(Benzotriazol-1-yl)ethoxymethyl]furan (7g):** $^1$H NMR δ 1.23 (t, 3 H, *J* = 7.1 Hz), 3.45–3.55 (m, 1 H), 3.70–3.80 (m, 1 H), 6.41 (dd, 1 H, *J* = 3.4, 1.8 Hz), 6.58 (dd, 1 H, *J* = 3.4, 0.9 Hz), 7.22 (s, 1 H), 7.35–7.50 (m, 3 H), 7.59–7.62 (m, 1 H), 8.11 (d, 1 H, *J* = 8.4 Hz); $^{13}$C NMR δ 14.5, 65.0, 84.7, 109.1, 110.3, 111.4, 119.7, 124.2, 127.5, 131.4, 143.2, 146.6, 148.5.

**3-[(Benzotriazol-1-yl)ethoxymethyl]furan (7h):** $^1$H NMR δ 1.20 (t, 3 H, *J* = 7.1 Hz), 3.35–3.49 (m, 1 H), 3.65–3.78 (m, 1 H), 6.22 (d, 1 H, *J* = 1.8 Hz), 7.15 (s, 1 H), 7.35–7.48 (m, 3 H), 7.49–7.56 (m, 1 H), 7.57 (s, 1 H), 8.09 (d, 1 H, *J* = 6.9 Hz); $^{13}$C NMR δ 14.5, 64.6, 85.3, 108.4, 111.5, 119.8, 122.8, 124.1, 127.3, 131.0, 140.5, 143.7, 146.8.

**2-[(Benzotriazol-1-yl)ethoxymethyl]thiophene (7i):** $^1$H NMR δ 1.22 (t, 3 H, *J* = 7.0 Hz), 3.40–3.50 (m, 1 H), 3.70–3.80 (m, 1 H), 6.84–6.86 (m, 1 H), 6.92–6.95 (m, 1 H), 7.31–7.41 (m, 4 H), 7.43–7.51 (m, 1 H), 8.04–8.08 (m, 1 H); $^{13}$C NMR δ 14.5, 65.1, 87.1, 111.7, 119.9, 124.2, 125.7, 126.3, 127.0, 127.5, 130.9, 139.5, 146.8.

**3-[(Benzotriazol-1-yl)ethoxymethyl]thiophene (7j):** $^1$H NMR δ 1.23 (t, 3 H, *J* = 7.1 Hz), 3.40–3.50 (m, 1 H), 3.70–3.80 (m, 1 H), 6.91 (d, 1 H, *J* = 5.1 Hz), 7.20–7.40 (m, 5 H), 7.46 (s, 1 H), 8.07 (d, 1 H, *J* = 3.8 Hz); $^{13}$C NMR δ 14.6, 64.8, 87.2, 111.5, 119.7, 123.3, 124.1, 125.4, 126.6, 127.4, 131.1, 137.9, 146.8.

**2-[(Benzotriazol-1-yl)ethoxymethyl]pyridine (7k):** $^1$H NMR δ 1.26 (t, 3 H, *J* = 7.2 Hz), 3.52–3.58 (m, 1 H), 3.75–3.83 (m, 1 H), 7.20–7.40 (m, 5 H), 7.76–7.90 (m, 2 H), 8.05 (d, 1 H, *J* = 8.6 Hz), 8.50 (d, 1 H, *J* = 4.8 Hz); $^{13}$C NMR δ 14.5, 65.0, 89.7, 111.0, 119.8, 121.0, 123.7, 123.9, 127.3, 131.4, 136.7, 146.6, 149.4, 154.9.

**Preparation of Compounds 7a and 7g from the Corresponding Diethyl Acetals.** Diethyl acetal **8a** or **8g** (50 mmol) and benzotriazole (75 mmol) were heated under reflux in toluene (40 mL) for 4 h. Diethyl ether (200 mL) was added, and the solution washed with saturated $Na_2CO_3$ (2 × 100 mL) and water (100 mL). Evaporation of the solvent gave a residual oil. Hexane (*ca.* 10 mL) was added and the solution placed in a refrigerator for 2 h, during which time a white

solid crystallized **7a**: yield 85%. **7g**: yield 83%. The analytical data is consistent with the compounds obtained by the condensation method.

**Lithiation of Compounds 7a–k for the Preparation of Intermediates 9a,f and Ketones 10a–p, 12a–f, 13a–c, 14a–c, and 15. General Procedure.** To a solution of α-(benzotriazol-1-yl)aryl ethyl ether (**7a–k**) (5 mmol) in THF (70 mL) was added *n*-butyllithium (2 M in cyclohexane, 2.5 mL, 5 mmol) at −78 °C. The solution was stirred at this temperature for 15–120 s, and then the appropriate electrophile (6 mmol; in the cases of **10i,j** 30 mmol) was added (in the cases of **9a,f, 10a–d,f–i,k–p**, the electrophiles were added before the BuLi). The solution was kept at this temperature for 1–2 min (in the cases of **10p** and **15**, the reaction mixture was warmed to 20 °C and kept at this temperature for 30 min). The mixture was quenched at this temperature with water (30 mL), dilute HCl (4 mL concd HCl or $H_2SO_4$ in 10 mL water) was added, and the solution was stirred at room temperature for 30–60 min (in the cases of **9a** and **9f**, no acid was added; in the case of **15**, hydrolysis was carried out in refluxing acetic acid for 30 min). The solution was then extracted with diethyl ether (150 mL), washed with saturated $Na_2CO_3$ solution (2 × 100 mL) and water (100 mL), and dried over $MgSO_4$. Evaporation of the solvent gave a residue. In the cases of **10g,h**, pure compounds were afforded. In the remaining cases, pure compounds were obtained following column chromatography on silica gel (hexane/ethyl acetate = 30:1 except for **9a,f**, hexane/ethyl acetate = 10:1). Melting points, yields, elemental analyses, and high resolution mass measurements for **10a–p, 12a–f, 13a–c, 14a–c,** and **15** are given in Table 2.

**[α-(Benzotriazol-1-yl)-α-ethoxypropyl]benzene (9a).** Obtained an an oil: yield 85%; $^1$H NMR δ 0.86 (t, 3 H, $J$ = 7.4 Hz), 1.14 (t, 3 H, $J$ = 7.0 Hz), 2.77–2.88 (m, 2 H), 3.13–3.21 (m, 1 H), 3.61–3.66 (m, 1 H), 7.20–7.36 (m, 8 H), 8.02 (d, 1 H, $J$ = 8.1 Hz); $^{13}$C NMR 7.0, 14.9, 29.2, 57.6, 95.7, 112.8, 119.5, 123.9, 125.9, 126.9, 128.1, 128.2, 132.2, 140.6, 146.6. Anal. Calcd for $C_{17}H_{19}N_3O$: C, 72.56; H, 6.81; N, 14.94. Found: C, 72.92; H, 6.96; N, 14.52.

**2-[α-(Benzotriazol-1-yl)-α-ethoxypentyl]furan (9f).** Obtained an an oil: yield 55%; $^1$H NMR δ 0.91 (t, 3 H, $J$ = 7.4 Hz), 1.10–1.20 (m, 4 H), 1.35–1.45 (m, 3 H), 2.90–3.10 (m, 3 H), 3.50–3.60 (m, 1 H), 6.38 (dd, 1 H, $J$ = 3.3, 0.8 Hz), 6.68 (dd, 1 H, $J$ = 3.4, 1.8 Hz), 7.25–7.35 (m, 3 H), 7.45–7.50 (m, 1 H), 8.00–8.05 (m, 1 H); $^{13}$C NMR δ 13.9, 14.8, 22.4, 25.0, 34.4, 58.1, 92.6, 109.3, 110.1, 112.4, 119.7, 123.8, 127.2, 132.4, 142.5, 146.5, 151.5. Anal. Calcd for $C_{17}H_{21}N_3O$: C, 68.19; H, 7.07; N, 14.04. Found: C, 68.38; H, 7.11; N, 14.09.

**Propiophenone (10a):** $^1$H NMR δ 1.44 (t, 3 H, $J$ = 7.2 Hz), 3.20 (q, 2 H, $J$ = 7.2 Hz), 7.65 (t, 2 H, $J$ = 7.3 Hz), 7.72–7.77 (m, 1 H), 8.17 (d, 2 H, $J$ = 7.35 Hz); $^{13}$C NMR δ 8.0, 31.5, 127.7, 128.3, 132.6, 136.7, 200.4.

**2-Chloro-(γ-methylpentanoyl)benzene (10b):** $^1$H NMR δ 0.92 (d, 6 H, $J$ = 5.4 Hz), 1.56–1.70 (m, 3 H), 2.93 (t, 2 H, $J$ = 7.1 Hz), 7.28–7.44 (m, 4 H); $^{13}$C NMR δ 22.3, 27.6, 32.7, 41.0, 126.8, 128.6, 130.3, 130.6, 131.3, 139.8, 203.8.

**2-Methoxypentanoylbenzene (10c):** $^1$H NMR δ 0.92 (t, 3 H, $J$ = 7.3 Hz), 1.33–1.41 (m, 2 H), 1.60–1.70 (m, 2 H), 2.96 (t, 2 H, $J$ = 7.4 Hz), 3.88 (s, 1 H), 6.93–7.00 (m, 2 H), 7.40–7.46 (m, 1 H), 7.63 (dd, 1 H, $J$ = 7.7, 1.8 Hz); $^{13}$C NMR δ 13.9, 22.4, 26.4, 43.4, 55.3, 111.4, 120.5, 128.7, 130.0, 132.9, 158.2, 203.2.

**3-Methoxynonanoylbenzene (10d):** $^1$H NMR δ 0.88 (t, 3 H, $J$ = 6.9 Hz), 1.27–1.36 (m, 10 H), 1.70–1.75 (m, 2 H), 2.93 (t, 2 H, $J$ = 7.4 Hz), 3.84 (s, 3 H), 7.06–7.10 (m, 1 H), 7.35 (t, 1 H, $J$ = 7.9 Hz), 7.48–7.54 (m, 2 H); $^{13}$C NMR δ 14.0, 22.6, 24.4, 29.1, 29.3, 29.4, 31.8, 38.6, 55.3, 112.2, 119.1, 120.6, 129.4, 138.4, 159.7, 200.2.

**4-Methylphenyl allyl ketone (10e):** $^1$H NMR δ 2.40 (s, 3 H), 3.73 (d, 2 H, $J$ = 6.7 Hz), 5.16–5.23 (m, 1 H), 5.23 (s, 1 H), 6.02–6.18 (m, 1 H), 7.25 (d, 2 H, $J$ = 8.1 Hz), 7.86 (d, 2 H, $J$ = 8.1 Hz); $^{13}$C NMR δ 21.6, 43.3, 118.5, 128.4, 129.3, 131.2, 134.1, 143.9, 197.6.

**2-Pentanoylfuran (10f):** $^1$H NMR δ 0.97 (t, 3 H, $J$ = 7.3 Hz), 1.35–1.50 (m, 2 H), 1.70–1.80 (m, 2 H), 2.85 (t, 2 H, $J$ = 7.5 Hz), 6.56 (dd, 1 H, $J$ = 3.6, 1.7 Hz), 7.21 (d, 1 H, $J$ = 3.6 Hz), 7.61 (d, 1 H, $J$ = 1.7 Hz); $^{13}$C NMR δ 13.7, 22.3, 26.3, 38.1, 112.0, 116.6, 146.0, 152.8, 189.6.

**2-Nonanoylfuran (10g):** $^1$H NMR δ 0.89 (t, 3 H, $J$ = 6.8 Hz), 1.20–1.40 (m, 10 H), 1.65–1.80 (m, 2 H), 2.82 (t, 2 H, $J$ = 7.5 Hz), 6.54 (dd, 1 H, $J$ = 3.5, 1.7 Hz), 7.18 (dd, 1 H, $J$ = 3.5, 1.7 Hz), 7.59 (dd, 1 H, $J$ = 1.7, 0.8 Hz); $^{13}$C NMR δ 13.9, 22.5, 24.2, 29.0, 29.1, 29.2, 31.7, 38.3, 111.9, 116.5, 145.9, 152.8, 189.5.

**2-Furyl 3-bromopropyl ketone (10h):** $^1$H NMR δ 2.25–2.35 (m, 2 H), 3.06 (t, 2 H, $J$ = 7.0 Hz), 3.54 (t, 2 H, $J$ = 6.4 Hz), 6.58 (dd, 1 H, $J$ = 3.5, 1.7 Hz), 7.25 (d, 1 H, $J$ = 3.5 Hz), 7.63 (s, 1 H); $^{13}$C NMR δ 26.6, 33.1, 36.2, 112.1, 117.0, 146.3, 152.3, 187.7.

**2-Furyl 4-bromobutyl ketone (10i):** $^1$H NMR δ 1.80–2.00 (m, 4 H), 2.88 (t, 2 H, $J$ = 7.1 Hz), 3.45 (t, 2 H, $J$ = 6.4 Hz), 6.56 (dd, 1 H, $J$ = 3.5, 1.7 Hz), 7.23 (dd, 1 H, $J$ = 3.5, 0.7 Hz), 7.63 (dd, 1 H, $J$ = 1.7, 0.7 Hz); $^{13}$C NMR δ 22.3, 31.8, 33.0, 36.9, 111.9, 116.6, 146.0, 152.2, 188.3.

**2-Furyl allyl ketone (10j):** $^1$H NMR δ 3.62–3.65 (m, 2 H), 5.23 (s, 1 H), 5.26–5.29 (m, 1 H), 6.00–6.12 (m, 1 H), 6.57 (dd, 1 H, $J$ = 3.6, 1.7 Hz), 7.25 (dd, 1 H, $J$ = 3.6, 0.7 Hz), 7.63 (dd, 1 H, $J$ = 1.7, 0.7 Hz); $^{13}$C NMR δ 43.3, 112.2, 117.3, 118.9, 130.3, 146.4, 152.3, 186.8.

**3-Pentanoylfuran (10k):** $^1$H NMR δ 0.93 (t, 3 H, $J$ = 7.3 Hz), 1.32–1.44 (m, 2 H), 1.63–1.73 (m, 2 H), 2.73 (t, 2 H, $J$ = 7.4 Hz), 6.76 (d, 1 H, $J$ = 1.8 Hz), 7.43 (d, 1 H, $J$ = 1.8 Hz), 8.02 (s, 1 H); $^{13}$C NMR δ 13.8, 22.4, 26.5, 40.2, 108.6, 127.8, 144.1, 147.0, 195.3.

**3-(3-Methylpentanoyl)furan (10l):** $^1$H NMR δ 0.95 (d, 6 H, $J$ = 6.3 Hz), 1.59–1.65 (m, 3 H), 2.75 (t, 2 H, $J$ = 7.7 Hz), 6.78 (d, 1 H, $J$ = 1.9 Hz), 7.45 (d, 1 H, $J$ = 1.5 Hz), 8.05 (s, 1 H); $^{13}$C NMR δ 22.3, 27.7, 33.2, 38.4, 108.6, 127.7, 144.0, 146.9, 195.4.

**2-Nonanoylthiophene (10m):** $^1$H NMR δ 0.88 (t, 3 H, $J$ = 6.6 Hz), 1.21–1.42 (m, 10 H), 1.70–1.80 (m, 2 H), 2.89 (t, 2 H, $J$ = 7.3 Hz), 7.11 (t, 1 H, $J$ = 3.8 Hz), 7.60 (dd, 1 H, $J$ = 5.0, 1.0 Hz), 7.70 (dd, 1 H, $J$ = 3.7, 1.1 Hz); $^{13}$C NMR δ 13.9, 22.5, 24.6, 29.0, 29.2, 29.3, 31.7, 39.2, 127.9, 131.5, 133.1, 144.4, 193.2.

**3-Propionylthiophene (10n):** $^1$H NMR δ 1.21 (t, 3 H, $J$ = 7.4 Hz), 2.92 (q, 2 H, $J$ = 7.3 Hz), 7.31 (dd, 1 H, $J$ = 5.1, 3.0 Hz), 7.55 (dd, 1 H, $J$ = 5.1, 1.2 Hz), 8.05 (dd, 1 H, $J$ = 3.0, 1.2 Hz); $^{13}$C NMR δ 8.1, 32.9, 126.1, 126.8, 131.4, 142.1, 195.1.

**3-Pentanoylthiophene (10o):** $^1$H NMR δ 0.95 (t, 3 H, $J$ = 7.4 Hz), 1.34–1.46 (m, 2 H), 1.66–1.76 (m, 2 H), 2.88 (t, 2 H, $J$ = 7.4 Hz), 7.31 (dd, 1 H, $J$ = 5.1, 3.0 Hz), 7.55 (dd, 1 H, $J$ = 5.1, 1.2 Hz), 8.05 (dd, 1 H, $J$ = 2.9, 1.2 Hz); $^{13}$C NMR δ 13.9, 22.4, 26.5, 39.6, 126.2, 127.0, 131.6, 142.5, 194.9.

**2-Nonanoylpyridine (10p):** $^1$H NMR δ 0.89 (t, 3 H, $J$ = 6.8 Hz), 1.22–1.37 (m, 10 H), 1.70–1.80 (m, 2 H), 3.23 (t, 2 H, $J$ = 7.5 Hz), 7.44–7.50 (m, 1 H), 7.80–7.87 (m, 1 H), 8.05 (dd, 1 H, $J$ = 7.8, 1.2 Hz), 8.69 (dd, 1 H, $J$ = 4.7, 1.7 Hz); $^{13}$C NMR δ 14.0, 22.5, 23.9, 29.1, 29.2, 29.3, 31.7, 37.6, 121.6, 126.8, 136.6, 148.7, 153.5, 201.9.

**[Hydroxy(4-methylphenyl)acetyl]benzene (12a):** $^1$H NMR δ 2.17 (s, 3 H), 4.45 (d, 1 H, $J$ = 5.8 Hz), 5.82 (d, 1 H, $J$ = 5.8 Hz), 7.00 (d, 2 H, $J$ = 8.0 Hz), 7.12 (d, 2 H, $J$ = 8.0 Hz), 7.26 (t, 2 H, $J$ = 7.9 Hz), 7.38 (t, 1 H, $J$ = 7.6 Hz), 7.80 (d, 2 H, $J$ = 8.0 Hz); $^{13}$C NMR δ 21.0, 75.9, 127.6, 128.5, 129.0, 129.7, 133.7, 136.0, 138.3, 199.0.

**1-Hydroxy-2-methylpropyl 1-naphthyl ketone (12b):** $^1$H NMR δ 0.71 (d, 3 H, $J$ = 6.6 Hz), 1.11 (d, 3 H, $J$ = 6.9 Hz), 1.98–2.08 (m, 1 H), 3.91 (br s, 1 H), 5.08 (d, 1 H, $J$ = 2.5 Hz), 7.46–7.63 (m, 3 H), 7.77 (dd, 1 H, $J$ = 7.2, 1.2 Hz), 7.87 (dd, 1 H, $J$ = 7.8, 1.4 Hz), 8.00 (d, 1 H, $J$ = 8.3 Hz), 8.53 (d, 1 H, $J$ = 8.4 Hz); $^{13}$C NMR δ 15.0, 20.1, 32.5, 78.7, 124.2, 125.1, 126.6, 127.8, 128.2, 128.5, 130.2, 132.6, 133.3, 133.9, 205.5.

**2-(Hydroxyphenylacetyl)furan (12c):** $^1$H NMR δ 4.39 (d, 1 H, $J$ = 6.1 Hz), 5.75 (d, 1 H, $J$ = 6.1 Hz), 6.49 (dd, 1 H, $J$ = 3.7, 1.7 Hz), 7.20 (dd, 1 H, $J$ = 3.7, 3.7 Hz), 7.25–7.45 (m, 5 H), 7.57 (d, 1 H, $J$ = 1.6 Hz); $^{13}$C NMR δ 76.1, 112.5, 120.0, 127.7, 128.6, 128.8, 138.7, 147.3, 150.0, 187.4.

**2-[Hydroxy(4-methyphenyl)acetyl]furan (12d):** $^1$H NMR δ 2.32 (s, 3 H), 4.38 (d, 1 H, $J$ = 5.2 Hz), 5.74 (d, 1 H, $J$ = 4.6 Hz), 6.48 (dd, 1 H, $J$ = 3.7, 1.7 Hz), 7.12–7.21 (m, 3 H), 7.29

(d, 2 H, $J$ = 8.1 Hz), 7.57 (d, 1 H, $J$ = 1.0 Hz); $^{13}$C NMR $\delta$ 21.1, 75.9, 112.5, 119.9, 127.6, 129.5, 135.7, 138.5, 147.3, 150.0, 187.5.

**2-Furyl 1-hydroxy-2-methylethyl ketone (12e):** $^1$H NMR $\delta$ 0.76 (d, 3 H, $J$ = 6.8 Hz), 1.16 (d, 3 H, $J$ = 6.8 Hz), 2.20–2.30 (m, 1 H), 3.45 (d, 1 H, $J$ = 6.9 Hz), 4.73 (dd, 1 H, $J$ = 6.9, 2.9 Hz), 6.60 (dd, 1 H, $J$ = 3.6, 1.8 Hz), 7.33 (dd, 1 H, $J$ = 3.6, 0.8 Hz), 7.65 (d, 1 H, $J$ = 1.8 Hz); $^{13}$C NMR $\delta$ 14.8, 19.9, 32.6, 77.6, 112.4, 118.7, 146.9, 150.6, 190.5.

**2-(Hydroxyphenylacetyl)thiophene (12f):** $^1$H NMR (DMSO-$d_6$) $\delta$ 5.81 (d, 1 H, $J$ = 4.8 Hz), 6.35 (d, 1 H, $J$ = 5.1 Hz), 7.20–7.42 (m, 4 H), 7.52 (d, 2 H, $J$ = 6.9 Hz), 8.00 (d, 1 H, $J$ = 5.1 Hz), 8.13 (d, 1 H, $J$ = 3.8 Hz); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 76.7, 126.9, 127.7, 128.3, 128.5, 134.3, 135.3, 139.7, 140.5, 192.4.

**1-Hydroxy-1-methylethyl 1-naphthyl ketone (13a):** $^1$H NMR $\delta$ 1.53 (s, 6 H), 3.97 (s, 1 H), 7.41–7.58 (m, 4 H), 7.76–7.91 (m, 3 H); $^{13}$C NMR $\delta$ 27.1, 77.8, 124.0, 125.1, 126.3, 127.2, 128.4, 130.0, 130.4, 133.5, 135.4, 210.8.

**2-(Diphenylhydroxyacetyl)furan (13b):** $^1$H NMR $\delta$ 4.99 (s, 1 H), 6.34 (dd, 1 H, $J$ = 3.6, 1.7 Hz), 6.92 (dd, 1 H, $J$ = 3.6, 1.7 Hz), 7.27–7.32 (m, 6 H), 7.37–7.44 (m, 5 H); $^{13}$C NMR $\delta$ 84.0, 112.2, 122.3, 127.9, 128.0, 128.1, 141.6, 147.1, 150.2, 188.5.

**2-(Dicyclopropylhydroxyacetyl)furan (13c):** $^1$H NMR $\delta$ 0.15–0.30 (m, 4 H), 0.40–0.50 (m, 2 H), 0.68–0.78 (m, 2 H), 1.50–1.60 (m, 2 H), 3.57 (s, 1 H), 6.62 (dd, 1 H, $J$ = 3.6, 1.6 Hz), 7.48 (d, 1 H, $J$ = 3.6 Hz), 7.68 (d, 1 H, $J$ = 1.6 Hz); $^{13}$C NMR $\delta$ −1.1, 17.2, 75.0, 112.3, 120.3, 146.7, 150.3, 191.7.

**2-Chlorophenyl α-(phenylamino)benzyl ketone (14a):** $^1$H NMR $\delta$ 5.61 (br s, 1 H), 5.85 (s, 1 H), 6.61–6.71 (m, 3 H), 7.03–7.33 (m, 11 H); $^{13}$C NMR $\delta$ 66.6, 113.4, 117.7, 126.4, 127.9, 128.2, 128.8, 128.9, 129.1, 130.0, 130.7, 131.6, 136.3, 137.2, 145.7, 199.0.

**4-Methylphenyl α-(phenylamino)benzyl ketone (14b):** $^1$H NMR $\delta$ 2.32 (s, 3 H), 5.44 (d, 1 H, $J$ = 6.4 Hz), 6.00 (d, 1 H, $J$ = 6.8 Hz), 6.62–6.70 (m, 3 H), 7.08–7.28 (m, 7 H), 7.44 (d, 2 H, $J$ = 7.0 Hz), 7.88 (d, 2 H, $J$ = 8.2 Hz); $^{13}$C NMR $\delta$ 21.6, 62.4, 113.4, 117.7, 127.9, 128.0, 128.9, 129.1, 129.3, 132.4, 137.9, 144.4, 146.1, 196.5.

**2-Furyl (α-phenylamino)benzyl ketone (14c):** $^1$H NMR $\delta$ 5.37 (d, 1 H, $J$ = 6.7 Hz), 5.83 (d, 1 H, $J$ = 6.7 Hz), 6.43 (dd, 1 H, $J$ = 3.7, 1.7 Hz), 6.62–6.69 (m, 3 H), 7.10 (t, 2 H, $J$ = 7.4 Hz), 7.19–7.30 (m, 4 H), 7.50–7.55 (m, 3 H); $^{13}$C NMR $\delta$ 62.8, 112.6, 113.5, 117.8, 119.0, 128.0, 128.1, 128.8, 129.1, 137.5, 145.9, 146.8, 150.8, 185.5.

**1-(Pyrid-2-yl)-2-phenyl-1,2-ethanedione (15):** $^1$H NMR $\delta$ 7.46–7.54 (m, 3 H), 7.60–7.64 (m, 1 H), 7.90–7.97 (m, 3 H), 8.18–8.21 (m, 1 H), 8.64–8.66 (m, 1 H); $^{13}$C NMR $\delta$ 123.1, 128.1, 128.8, 129.5, 133.1, 134.5, 137.2, 149.7, 151.6, 195.1, 196.1.

JO9508661