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Novel and Facile Syntheses of Alkenyl, Alkynyl, and Aryl 1,2-Diketones

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Novel and facile routes to alkenyl, alkynyl, and aryl 1,2-diketones utilize treatment of benzotriazole derivatives **1**, **7a**,**b**, and **15a**−**d** with butyllithium and subsequent reaction with esters or acid chlorides to yield the substituted intermediates **2a**−**d**, **8a**,**b**, and **16a**−**g**. Reactions of the deprotonated **1** and **7** with α,*β*-unsaturated aldehydes followed by oxidation also produces similar intermediates **5** and **11a**,**b**. Subsequent hydrolyses of the intermediates of type **2**, **5**, **8**, **11**, and **16** afford diverse 1,2-diketones in good yields.

Introduction

1,2-Diketones have found widespread applications in the synthesis of various heterocyclic compounds.[1] The synthesis of simple alkyl- and aryl-substituted 1,2-diketones has been extensively investigated, and many good methods are available through (i) oxidations,[2] (ii) use of masked acyl anion synthons,[3a−f] and (iii) other approaches.[4]

By contrast, relatively few examples are documented of the preparation of alkenyl- and alkynyl-substituted 1,2-diketones. Ahmad and Iqbal[5] reported the preparation of methyl alkenyl 1,2-diketones by cobalt(II) chloride catalyzed coupling of acetic anhydride with the corresponding α,*β*-unsaturated aldehydes. 1-Phenyl-1-pentyne-3,4-dione (an acetylenic 1,2-diketone) was previously prepared by reaction of the metal (Cd, Zn) acetylide with acyl chloride.[6] Leyendecker *et al.*[7] synthesized alkynyl 1,2-diketones in unspecified overall yields by a four-step conversion of α-amino acids *via* intermediate 2-(trifluoromethyl)-3-oxazolin-5-ones.

We have recently reported convenient benzotriazole acyl anion methodologies for the synthesis of a wide variety of simple and functionalized alkenyl,[8] alkynyl,[9] aryl/heteroaryl,[10] and alkyl[11] ketones and of alkenoyl-, alkynoyl-, aroyl-, and heteroaroylsilanes.[12] The benzotriazole-stabilized carbanions utilized share the following features: (i) ready availability of starting materials; (ii) adequate reactivity toward a diverse range of electrophiles including alkyl halides, aldehydes, ketones, and imines; and (iii) easy hydrolysis of the alkylated intermediates. Reactions with electrophiles are also regiospecific. We have reported the preparation of an acetylenic α-diketone (PhC≡CCOCOMe) by reaction of lithiated 1-(benzotriazol-1-yl)-3-phenylpropargyl ethyl ether with ethyl acetate followed by mild hydrolysis.[9] Faust and Weber[13] have recently utilized our methodology to synthesize 1-phenyl-1,5-hexadiyne-3,4-diones (PhC≡CCOCOC≡CR) which could not be prepared by conventional methods. We now report the successful extension of our benzotriazole acyl synthon methodology to reactions with acid chlorides, esters, or aldehydes followed by oxidation and demonstrate that these strategies provide facile and general routes to diverse alkenyl, alkynyl, and aryl 1,2-diketones.

Results and Discussion

Benzotriazole α,*β*-unsaturated acyl anion synthon **1** was prepared by reaction of the corresponding acetal with

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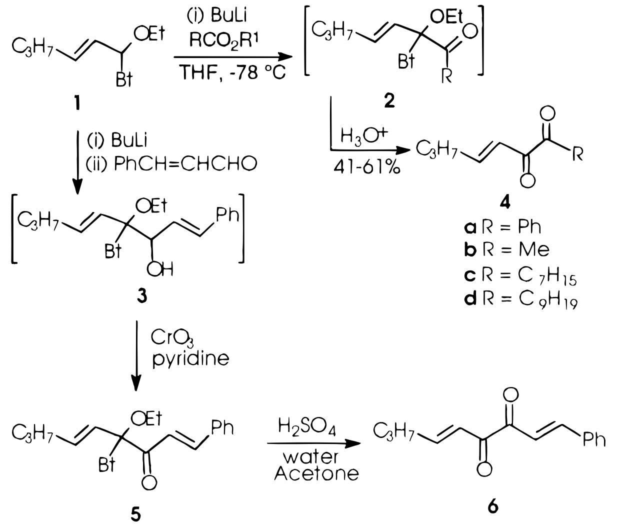
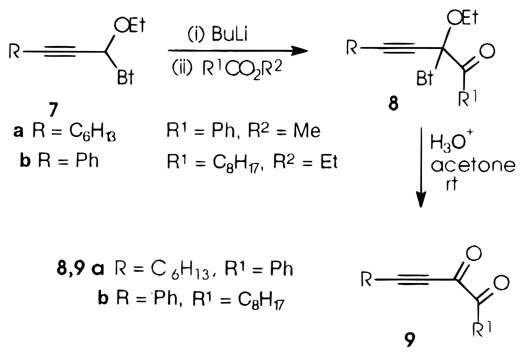
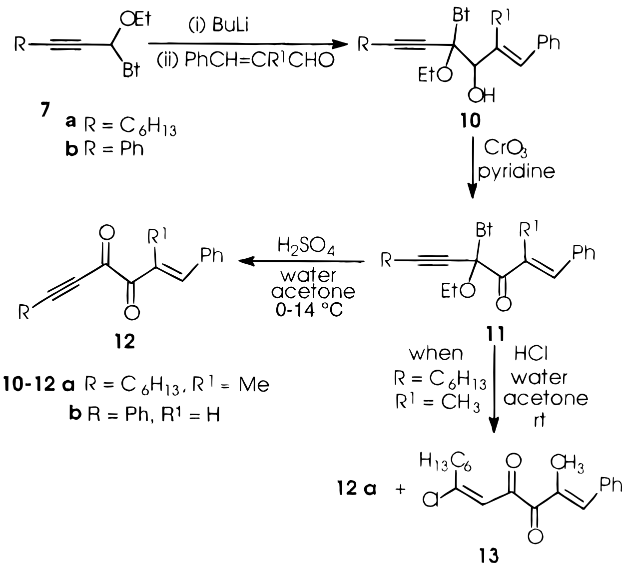
Scheme 1



Scheme 2



Scheme 3



benzotriazole, as previously reported.[8e] Treatment of **1** with BuLi and reaction with an ester followed by hydrolysis gave α-alkenyl-substituted 1,2-diketones **4a**–**d** in moderate overall yields (Scheme 1). Thus, treatment of **1** with BuLi at -78 °C in an oxygen free atmosphere for 5 min gave a deep blue-green solution, which was then reacted at -78 °C with methyl benzoate for 5 min. Subsequent quenching with water–HCl was followed by allowing the reaction mixture to warm to room temperature with stirring over 4 h. Final workup afforded **4a** in 41% yield. Compounds **4b**–**d** were similarly prepared in 54–61% yields. The use of an ester and not an acid chloride as the electrophile is critical to avoid a lower yield. The present results indicate that the reaction tolerates both alkyl- and aryl-substituted esters and allows the preparation of both alkyl alkenyl 1,2-diketones (**4b**–**d**) and aryl alkenyl 1,2-diketone (**4a**).

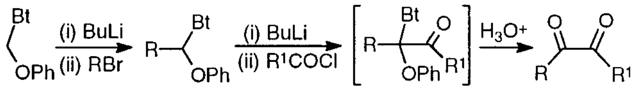
Our previous work has shown that use of α,*β*-unsaturated esters as electrophiles in the reactions with acyl anion synthon **1** leads regiospecifically to 1,4-addition products which eventually produce 1,4-dicarbonyl compounds after hydrolysis.[8e] We have now found an alternative procedure which readily provides the desired 1,2-diketone **6** in a reasonable yield. Thus, treatment of **1** with BuLi followed by reaction with cinnamaldehyde gave the crude intermediate **3**, which underwent oxidation to produce the benzotriazole derivative **5** in 47% overall yield based on **1.** Subsequent hydrolysis afforded the alkenyl-substituted 1,2-diketone **6** in 82% yield.

The method we previously used[9] to prepare the acetylenic α-diketone, 1-phenyl-1-pentyne-3,4-dione, by reaction of ethynyl-substituted acyl anion equivalent **7** with ethyl acetate has now been extended satisfactorily to other alkyl- and aryl-substituted esters. Treatment of **7a** with BuLi followed by reaction with methyl benzoate gave the intermediate **8a** in 63% yield (Scheme 2). Subsequent hydrolysis afforded the expected acetylenic 1,2-diketone **9a** in 84% yield. Compound **9b** was similarly prepared in 69% yield without isolation and characterization of the intermediate **8b**.

Attempted preparation of acetylenic 1,2-diketones of type **12** by using α,*β*-unsaturated esters and α,*β*-unsaturated acid chlorides as electrophiles in the reactions with synthon **7** failed: such reactions produced complicated mixtures as indicated by TLC and NMR spectra. However, a procedure similar to that applied above to the preparation of alkenyl-substituted 1,2-diketone **6** was successful in producing 1,2-diketones of type **12**. Thus, treatment of **7a** with 1 equiv of BuLi followed by quenching with α-methyl-*trans*-cinnamaldehyde gave intermdiate **10a** in 51% yield (Scheme 3). Subsequent application of Sarett's modification of Jones oxidation[14] yielded the benzotriazole derivative **11a** in 93% yield. Finally, hydrolysis with H_2SO_4–H_2O–acetone at 0–25 °C produced the expected 1,2-diketone **12a** in 83% yield. Compound **12b** was prepared by a similar sequence. The hydrolysis conditions have to be controlled carefully, otherwise side reaction can occur. We have found that hydrolysis of the intermediate **11a** with HCl–H_2O–acetone at 0–22 °C resulted in the formation of 37% diketone **13** along with the expected **12a**. It is believed that HCl partially added to the triple bond of the formed 1,2-diketone **12a**. Compounds of type **12** were previously unknown.

The versatility of this benzotriazole-assisted diketone synthesis has been further demonstrated by the convenient syntheses of aryl 1,2-diketones **17a**–**g**. 1-(Phenoxymethyl)benzotriazole (**14**) and its alkylated derivative (**15a**) were prepared according to our previously described procedure.[11] Treatment of compound **15d** with butyllithium at -78 °C for 5 min followed by addition of benzoyl chloride gave intermediate **16f** in 84% isolated yield. Further heating of **16f** in a mixture of AcOH–H_2SO_4–H_2O under reflux for 13.5 h afforded the desired 1,2-diketone **17f** in 92% yield. The structures of **16f** and **17f** were fully characterized by NMR spectroscopy and elemental analysis. Intermediate **16b** and diketone **17b**

Scheme 4



14 **15** **16** **17**

15 **a** R = C_5H_{11}
b R = C_6H_{13}
c R = $C_{10}H_{21}$
d R = $Ph(CH_2)_3$

16,17 **a** R = C_5H_{11}, R^1 = Ph
b R = C_6H_{13}, R^1 = *t*-Bu
c R = C_6H_{13}, R^1 = Naph
d R = $C_{10}H_{21}$, R^1 = 4-Cl-C_6H_4
e R = $C_{10}H_{21}$, R^1 = 2-Me-C_6H_4
f R = $Ph(CH_2)_3$, R^1 = Ph
g R = $Ph(CH_2)_3$, R^1 = 4-Cl-C_6H_4

were similarly prepared in 86% and 83% yields, respectively. Compounds **17a**,**c**,**e**,**g** were obtained in 52−72% overall yields directly from **15** without purification of the intermediates **16a**,**c**,**e**,**g**.

These sequences of type **15** → **17** were thus very effective, provided aroyl chlorides or aliphatic acid chlorides without an active α-proton were used as the electrophile indicated in Scheme 4. However, the attempted use of esters or of aliphatic acid chlorides containing α-hydrogen as electrophiles led to low yields or complicated mixtures. For the esters this may be due to the relatively low stability of the anion formed from **15** in the reaction with less reactive esters (compared with acid chlorides); by contrast, in the case of the synthesis of **4** and **9**, the benzotriazole-stabilized anions which are formed from the deprotonation of **1** and **7** are further stabilized by alkenyl and alkynyl groups. For normal aliphatic acid chlorides, failure to obtain the expected intermediates could be attributed to the kinetically controlled equilibrium leading to the deprotonation of the electrophiles at the α-position.

Hydrolysis of the intermediates **16** derived from other electrophiles (RX, RCHO, RCOR, *etc.*) was previously carried out in refluxing ethanol containing a small amount of H_2SO_4 for only 10−20 min.[11] The present relatively difficult hydrolysis of **16** derived from acid chlorides can be mainly attributed to the electron-withdrawing effect of the carbonyl group. However, compared with the commonly used acyl anion equivalent, 1,3-dithiane, which requires either the use of mercury salts (and still gave low yields)[15] or of the electrochemical anodic oxidation[3b] to deprotect the dithio groups in the preparation of 1,2-diketones (other available methods for deprotection of 1,3-dithiane[3c,16] did not mention the synthesis of 1,2-diketones), the present method, with readily available starting materials and a simple procedure, represents an optimal synthesis of 1,2-diketones of type **17**. Although a variety of approaches to the synthesis of 1,2-diketones have been developed,[17] most involve oxalic acid derivatives, and this often causes problems in obtaining unsymmetrical 1,2-diketones.[18] The present method can be used to obtain both symmetrically and unsymmetrically functionalized 1,2-diketones.

The structures for all new compounds are supported by ^1H and ^{13}C NMR spectroscopy and microanalyses. The data for known compounds are consistent with data reported in the literature. The ^{13}C NMR spectra showed the two characteristic carbonyl carbon signals in the range of 176−208 ppm.

In conclusion, novel and convenient routes to alkyl-, alkenyl-, alkynyl-, and aryl-substituted 1,2-diketones in good yields were developed from readily available starting materials, by utilizing simple methodology.

Experimental Section

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

General Procedure for the Preparation of 4a−d. To a solution of 1-(benzotriazol-1-yl)-1-ethoxy-2-hexene (**1**, 1.23 g, 5 mmol) in THF (50 mL) at −78 °C was added *n*-butyllithium (1.6 M in cyclohexane, 3.2 mL, 5.1 mmol). The solution was stirred at this temperature for 5 min and the appropriate electrophile (methyl benzoate, butyl acetate, ethyl octanoate, or methyl decanoate; 5 mmol) added. After the solution was stirred at −78 °C for an additional 5 to 10 min, it was quenched at this temperature with water (50 mL). A solution of hydrochloric acid (1 mL, 37%) in water (5 mL) was added at this temperature, and the mixture was stirred at room temperature for 4 h. The resulting solution was extracted with diethyl ether (2 × 50 mL) and washed with aqueous sodium hydroxide solution (0.5 N, 2 × 50 mL). The organic phase was separated and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue which was purified by column chromatography (hexane/ethyl acetate, 30:1).

***trans*-1-Phenyl-4-heptene-1,2-dione (4a):** obtained as a yellow oil, yield 41%; ^1H NMR δ 0.95 (t, 3 H, $J = 7.4$ Hz), 1.53 (sextet, 2 H, $J = 7.3$ Hz), 2.30 (q, 2 H, $J = 7.2$ Hz), 6.47 (dt, 1 H, $J = 16.2$, 1.5 Hz), 7.01 (dt, 1 H, $J = 16.2$, 6.9 Hz), 7.50 (t, 2 H, $J = 7.0$ Hz), 7.64 (t, 1 H, $J = 7.4$ Hz), 7.96 (d, 2 H, $J = 8.6$ Hz); ^{13}C NMR δ 13.6, 20.9, 35.1, 127.1, 128.8, 129.9, 132.8, 134.5, 155.4, 193.5, 193.6; HRMS (CI) calcd for $C_{13}H_{15}O_2$ ($M^+ + 1$) 203.1072, found 203.1106.

***trans*-4-Octene-2,3-dione (4b):** obtained as a yellow oil, yield 54%; ^1H NMR δ 0.96 (t, 3 H, $J = 7.3$ Hz), 1.54 (sextet, 2 H, $J = 7.3$ Hz), 2.29 (q, 2 H, $J = 7.2$ Hz), 2.39 (s, 2 H), 6.74 (dt, 1 H, $J = 15.9$, 1.4 Hz), 7.11−7.22 (m, 1 H); ^{13}C NMR δ 13.6, 21.1, 24.4, 35.2, 122.6, 154.0, 187.1, 199.2. Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.71; H 8.70.

***trans*-4-Tetradecene-6,7-dione (4c):** obtained as a yellow oil, yield 61%; ^1H NMR δ 0.80 −1.00 (m, 6 H), 1.20−1.40 (m, 8 H), 1.44−1.65 (m, 4 H), 2.28 (q, 2 H, $J = 7.2$ Hz), 2.78 (t, 2 H, $J = 7.4$ Hz), 6.69 (d, 1 H, $J = 15.9$ Hz), 7.14 (dt, 1 H, $J = 15.9$, 6.8 Hz); ^{13}C NMR δ 13.6, 13.9, 21.1, 22.5, 23.0, 28.9, 29.0, 31.6, 35.1, 36.8, 123.2, 153.7, 188.0, 201.7; HRMS (CI) calcd for $C_{14}H_{25}O_2$ ($M^+ + 1$) 225.1855, found 225.1854.

***trans*-4-Hexadecene-6,7-dione (4d):** obtained as a yellow oil, yield 60%; ^1H NMR δ 0.90 (t, 3 H, $J = 6.6$ Hz), 0.97 (t, 3 H, $J = 7.4$ Hz), 1.22−1.40 (m, 12 H), 1.50−1.68 (m, 4 H), 2.25−2.32 (m, 2 H), 2.80 (t, 2 H, $J = 7.4$ Hz), 6.71 (dt, 1 H, $J = 15.9$, 1.7 Hz), 7.15 (dt, 1 H, $J = 15.9$, 6.9 Hz); ^{13}C NMR δ 13.6, 14.0, 21.1, 22.6, 23.0, 29.1, 29.2, 29.3, 29.4, 31.8, 35.1, 36.9, 123.2, 153.7, 188.1, 201.7; HRMS (CI) calcd for $C_{16}H_{29}O_2$ ($M^+ + 1$) 253.2168, found 253.2165.

1-Phenyl-4-(benzotriazol-1-yl)-4-ethoxy-(*E*,*E*)-1,5-nonadien-3-one (5). To a solution of *trans*-1-(benzotriazol-1-yl)-1-ethoxy-2-hexene (**1**, 2.73 g, 11.1 mmol) in THF (40 mL) at −78 °C was added *n*-butyllithium (1.6 M in cyclohexane, 7.0 mL, 11.2 mmol) dropwise. The solution was stirred at this temperature for 2 min and *trans*-cinnamaldehyde (1.52 g, 11.2 mmol) added. After the solution was stirred at −78 °C for 5 min, it was quenched at this temperature with water (30 mL) and the mixture was extracted with ether (2 × 40 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent and purification of the residue by column chromatography (hexane/

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[18] Faust, R. *J. Prakt. Chem.* **1997**, *339*, 98.

ethyl acetate, 30:1) gave a mixture of two diastereoisomeric alcohols with unreacted aldehyde (2.82 g), which was used for the following reaction without further purification. To pyridine (54 mL) at 15−20 °C was added CrO_3 (5.4 g) in portions with stirring. The temperature should be kept below 30 °C during the addition. At the end of the addition a slurry of a complex in pyridine remained. A solution of the above impure alcohols in pyridine (54 mL) was combined with the slurry prepared above, and the contents were mixed thoroughly for 8 h at room temperature. The reaction mixture was poured into water and extracted with three portions of benzene−ether (1:1) using filtration through Celite 545 to break the emulsions. The combined organic solution was washed with water (30 mL), dried over anhydrous $MgSO_4$, and finally concentrated under high vacuum. The crude product was purified by column chromatography (hexane/ethyl acetate, 30:1) to give colorless prisms (1.96 g, 5.2 mmol), yield 47% and mp 108−110 °C: ^{1}H NMR δ 0.96 (t, 3 H, J = 7.4 Hz), 1.13 (t, 3 H, J = 7.1 Hz), 1.50−1.62 (m, 2 H), 2.24−2.38 (m, 2 H), 2.89−2.96 (m, 1 H), 3.60−3.70 (m, 1 H), 6.25−6.40 (m, 1 H), 6.67 (d, 1 H, J = 15.9 Hz), 7.12 (d, 1 H, J = 15.9 Hz), 7.35−7.50 (m, 5 H), 7.50−7.65 (m, 3 H), 7.84 (d, 1 H, J = 15.6 Hz), 8.12 (d, 1 H, J = 7.8 Hz); ^{13}C NMR δ 13.6, 15.0, 21.9, 34.5, 59.8, 95.6, 111.9, 119.5, 120.1, 122.9, 124.3, 127.8, 128.7, 128.9, 131.0, 132.3, 134.3, 138.6, 146.0, 146.5, 189.8. Anal. Calcd for $C_{23}H_{25}N_3O_2$: C, 73.58; H, 6.71; N, 11.19. Found: C, 73.41; H, 7.01; N, 11.05.

1-Phenyl-(*E*,*E*)-1,5-nonadiene-3,4-dione (6). To a solution of 1-phenyl-4-(benzotriazol-1-yl)-4-ethoxy-(*E*,*E*)-1,5-nonadien-3-one (**5**, 0.46 g, 1.23 mmol) in acetone at 5 °C was added a precooled H_2SO_4 aqueous solution (0.6 mL, 11%) in acetone (10 mL), and the solution was stirred at 12−14 °C for 1.5 h. Water (40 mL) was added to the solution, which was extracted with diethyl ether (3 × 50 mL), and the combined organic layers were washed with a 2 N Na_2CO_3 aqueous solution (3 × 60 mL) and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent the crude product was obtained as a yellow oil, which was purified by column chromatography (hexane/ethyl acetate, 250:1) to give a yellow oily product (0.23 g, 1 mmol), yield 82%: ^{1}H NMR δ 0.97 (t, 3 H, J = 7.4 Hz), 1.49−1.65 (m, 2 H), 2.25−2.60 (m, 2 H), 6.76 (d, 1H, J = 15.9 Hz), 7.19 (dt, 1 H, J = 15.9, 6.9 Hz), 7.35 (d, 1 H, J = 16.4 Hz), 7.41−7.55 (m, 3 H), 7.60−7.70 (m, 2 H), 7.79 (d, 1 H, J = 16.4 Hz); ^{13}C NMR δ 13.6, 21.0, 35.1, 120.0, 124.3, 128.8, 128.9, 131.2, 134.3, 147.5, 154.0, 189.5, 189.6. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.81; H, 7.35.

1-Phenyl-2-(benzotriazol-1-yl)-2-ethoxy-3-decyn-1-one (8a). To a solution of 1-(benzotriazol-1-yl)-3-hexylpropargyl ethyl ether (**7a**, 1 g, 3.5 mmol) in THF (40 mL) at −78 °C was added *n*-butyllithium (1.6 M in cyclohexane, 2.2 mL, 3.5 mmol) dropwise. The solution was stirred at −78 °C for 3 min, during which time the solution became dark blue. Methyl benzoate was added, and the solution was kept at −78 °C for an additional 35 min. After the reaction was quenched at −78 °C with water (40 mL), the mixture was extracted with ether (2 × 40 mL) and dried over $MgSO_4$. Evaporation of the solvent and purification by column chromatography (hexane/ethyl acetate, 30:1) gave colorless prisms (0.86 g, 2.2 mmol), yield 63% and mp 76−78 °C: ^{1}H NMR δ 0.87 (t, 3 H, J = 6.6 Hz), 1.15−1.45 (m, 9 H), 1.53−1.65 (m, 2 H), 2.44 (t, 2 H, J = 7.0 Hz), 3.25−3.38 (m, 1 H), 4.15−4.28 (m, 1 H), 7.34−7.50 (m, 4 H), 7.52−7.68 (m, 2 H), 8.10 (d, 1 H, J = 8.0 Hz), 8.22 (d, 2 H, J = 7.4 Hz); ^{13}C NMR δ 13.8, 14.7, 19.0, 22.3, 27.6, 28.3, 31.1, 61.5, 72.3, 90.2, 97.6, 111.9, 120.0, 124.1, 127.7, 128.0, 130.7, 132.2, 132.3, 133.5, 146.5, 186.9. Anal. Calcd for $C_{24}H_{27}N_3O_2$: C, 74.01; H, 6.99; N, 10.79. Found: C, 74.02; H, 7.03; N, 10.84.

1-Phenyl-3-Decyne-1,2-dione (9a). To a solution of 1-phenyl-2-(benzotriazol-1-yl)-2-ethoxy-3-decyn-1-one (**8a**, 0.71 g, 1.82 mmol) in acetone (37 mL) at 5 °C was added a precooled H_2SO_4 aqueous solution (3 mL, 11%) in acetone (10 mL), and the solution was stirred at room temperature for 19.5 h. Water (40 mL) was added to the solution, which was extracted with diethyl ether (3 × 40 mL), and the combined organic layers were washed with a 2 N Na_2CO_3 aqueous solution (3 × 50 mL) and dried over $MgSO_4$. After filtration and removal of the solvent, the crude product was obtained as a yellow oil, which was purified by column chromatography (hexane/ethyl acetate, 100:1) to give a yellow oil (0.37 g, 1.53 mmol), yield 84%: ^{1}H NMR δ 0.92 (t, 3 H, J = 6.7 Hz), 1.25−1.55 (m, 6 H), 1.60−1.75 (m, 2 H), 2.50 (t, 2 H, J = 7.1 Hz), 7.54 (t, 2 H, J = 7.7 Hz), 7.69 (t, 1 H, J = 7.4 Hz), 8.05 (d, 2 H, J = 8.0 Hz); ^{13}C NMR δ 13.8, 19.4, 22.3, 27.3, 28.4, 31.0, 79.6, 103.8, 128.7, 130.2, 131.5, 134.6, 178.8, 188.6. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.26; H, 7.79.

1-Phenyl-1-dodecyne-3,4-dione (9b). To a solution of 1-(benzotriazol-1-yl)-3-phenylpropargyl ethyl ether (**7b**, 1.0 g, 3.60 mmol) in THF (30 mL) at −78 °C was added *n*-butyllithium (1.6 M in cyclohexane, 2.25 mL, 3.6 mmol). The solution was stirred at −78 °C for 2 min, during which time the solution became dark blue. Ethyl nonanoate (0.68 g, 3.6 mmol) was added, and the solution was kept at −78 °C for an additional 2−5 min. The reaction was quenched at −78 °C with water (30 mL), extracted with diethyl ether (3 × 40 mL), and dried over $MgSO_4$. Evaporation of the solvent and purification by column chromatogaphy (hexane/ethyl acetate, 30:1) gave a slightly green oil, which was dissolved in acetone (15 mL) and cooled to 5 °C, and a cold hydrochloric acid solution (concd HCl (3 mL) in acetone (15 mL)) was added. The mixture was stirred at 5−20 °C for 15 min, and the solution was extracted with ether (3 × 40 mL), washed with a 2 N Na_2CO_3 aqueous solution (3 × 50 mL), and dried over $MgSO_4$. Evaporation of the solvent gave a yellow oil (0.67 g, 2.48 mmol), yield 69%: ^{1}H NMR δ 0.89 (t, 3 H, J = 7.2 Hz), 1.20−1.40 (m, 10 H), 1.60−1.72 (m, 2 H), 2.84 (t, 2 H, J = 7.2 Hz), 7.30−7.58 (m, 3 H), 7.68 (d, 2 H, 8.3 Hz); ^{13}C NMR δ 14.0, 22.6, 23.0, 29.0, 29.2, 31.7, 36.2, 86.0, 99.1, 119.4, 128.7, 131.5, 133.7, 176.2, 196.7; HRMS (FAB) calcd for $C_{18}H_{23}O_2$ (M^+ + 1) 271.1698, found 271.1702.

General Procedure for the Preparation of Compounds 10a,b. To a solution of 1-(benzotriazol-1-yl)-3-propargyl ethyl ether (**7**, 5.26 mmol) in THF (40 mL) at −78 °C was added *n*-butyllithium (1.6 M in cyclohexane, 3.3 mL, 5.28 mmol) dropwise. The solution was stirred at this temperature for 2 min, and the appropriate aldehyde (α-methyl-*trans*-cinnamaldehyde or *trans*-cinnamaldehyde, 5.26 mmol) was added and the solution stirred at −78 °C for an additional 2−5 min. The mixture was quenched at this temperature with water (20 mL), extracted with diethyl ether (2 × 30 mL), and dried over anhydrous $MgSO_4$. Evaporation of the solvent and purification of the residue by column chromatography (hexane/ethyl acetate, 200:1) gave the corresponding product.

***trans*-1-Phenyl-2-methyl-3-hydroxy-4-(benzotriazol-1-yl)-4-ethoxy-1-dodecen-5-yne (10a).** This compound was obtained as two diastereoisomers of *ca.* equal amount and overall yield is 51%. **Isomer 1**, less polar fraction: colorless prisms, mp 123−125 °C; ^{1}H NMR δ 0.87 (t, 3 H, J = 6.5 Hz), 1.20−1.58 (m, 9 H), 1.59−1.71 (m, 2 H), 1.75 (s, 3 H), 2.45 (t, 2 H, J = 7.1 Hz), 3.28 (br s, 1 H), 3.29−3.45 (m, 1 H), 4.00−4.15 (m, 1 H), 4.80 (d, 1 H, J = 3.3 Hz), 5.85 (s, 1 H), 6.85 (d, 2 H, J = 7.2 Hz), 7.07−7.25 (m, 3 H), 7.34 (t, 1 H, J = 7.5 Hz), 7.45 (t, 1 H, J = 7.4 Hz), 7.96 (d, 1 H, J = 8.1 Hz), 8.04 (d, 1 H, J = 8.4 Hz); ^{13}C NMR δ 13.8, 13.9, 14.6, 18.8, 22.3, 27.9, 28.5, 31.1, 61.4, 72.5, 82.2, 92.7, 93.9, 112.2, 119.9, 123.8, 126.3, 127.3, 127.6, 128.6, 129.9, 132.5, 133.4, 136.7, 146.3. Anal. Calcd for $C_{27}H_{33}N_3O_2$: C, 75.14; H, 7.71; N, 9.74. Found: C, 75.30; H, 7.88; N, 9.75. **Isomer 2**, more polar fraction: yellow oil: ^{1}H NMR δ 0.86 (t, 3 H, J = 6.6 Hz), 1.15−1.50 (m, 9 H), 1.52−1.70 (m, 2 H), 1.85 (s, 3 H), 2.44 (t, 2 H, J = 6.9 Hz), 3.21 (br s, 1 H), 3.22−3.41 (m, 1 H), 3.99−4.10 (m, 1 H), 4.86 (d, 1 H, J = 4.8 Hz), 6.42 (s, 1 H), 7.09 (d, 2 H, J = 7.2 Hz), 7.16−7.40 (m, 4 H), 7.43 (t, 1 H, J = 7.4 Hz), 7.96 (d, 1 H, J = 8.4 Hz), 8.01 (d, 1 H, J = 8.1 Hz); ^{13}C NMR δ 13.8, 14.5, 15.6, 18.7, 22.2, 27.9, 28.4, 31.1, 61.5, 73.2, 81.5, 93.1, 93.2, 112.6, 119.5, 123.6, 126.2, 127.1, 127.7, 128.8, 129.4, 132.6, 134.4, 137.1, 146.1. Anal. Calcd for $C_{27}H_{33}N_3O_2$: C, 75.14; H, 7.71; N, 9.74. Found: C, 75.31; H,7.99; N, 9.75.

***trans*-1,6-Diphenyl-3-hydroxy-4-(benzotriazol-1-yl)-4-ethoxy-1-hexen-5-yne (10b).** This compound was obtained as a mixture of two diastereoisomers (ratio = 1:1.5), the overall yield is 52%; yellow plates, mp 62−65 °C: ^{1}H NMR δ 1.10−1.45 (m, 3 H), 3.30−3.55 (m, 1 H), 4.02−4.22 (m, 1 H), 5.12 (d, 0.4 H, *J* = 6.3 Hz), 5.22 (d, 0.6 H, *J* = 5.4 Hz), 6.15−6.25 (m, 0.4 H), 6.45−6.62 (m, 1 H), 6.86 (d, 0.6 H, *J* = 15.9 Hz), 7.10−7.75 (m, 13 H), 7.92−8.20 (m, 2 H); ^{13}C NMR δ 14.7, 15.1, 61.9, 62.2, 77.3, 77.9, 81.1, 81.6, 91.3, 92.9, 93.2, 112.4, 112.5, 119.8, 119.9, 120.9, 124.0, 124.1, 124.3, 125.8, 126.5, 126.6, 127.5, 127.7, 127.8, 128.1, 128.2, 128.3, 128.4, 128.6, 129.5, 132.1, 132.6, 132.7, 133.4, 134.3, 136.2, 136.6, 146.2, 146.3. Anal. Calcd for $C_{26}H_{23}N_3O_2$: C, 76.26; H, 5.66; N, 10.26. Found: C, 75.97; H, 5.78; N, 10.18.

General Procedure for the Preparation of Compounds 11a,b. To pyridine (30 mL) at 15−20 °C was added CrO_3 (3 g) in portions with stirring. The temperature should be kept below 30 °C during the addition. At the end of the addition a slurry of a complex in pyridine remained. A solution of the alcohol **10** (2.67 mmol) in pyridine (30 mL) was combined with the slurry prepared above, and the contents were mixed thoroughly for 50 h with the reaction of **10a**, and 8 h with **10b**, at room temperature. The reaction mixture was poured into water and extracted with three portions of benzene/ether (1:1) using filtration through Celite 545 to break the emulsions. The combined organic solution was washed with water, dried over anhydrous $MgSO_4$, and finally concentrated under high vacuum. Purification of the residue by column chromatography (hexane/ethyl acetate, 30:1) gave the corresponding product.

***trans*-1-Phenyl-2-methyl-4-(benzotriazol-1-yl)-4-ethoxy-1-dodecen-5-yn-3-one (11a):** yield 93%; yellow prisms, mp 68−70 °C; ^{1}H NMR δ 0.83 (t, 3 H, *J* = 6.3 Hz), 1.14−1.52 (m, 9 H), 1.53−1.72 (m, 2 H), 2.14 (s, 3 H), 2.47 (t, 3 H, *J* = 6.9 Hz), 3.24−3.42 (m, 1 H), 4.11−4.30 (m, 1 H), 7.30−7.59 (m, 7 H), 7.64 (d, 1 H, *J* = 8.4 Hz), 8.08 (d, 1 H, *J* = 8.4 Hz), 8.14 (s, 1 H); ^{13}C NMR δ 13.7, 14.2, 14.6, 18.9, 22.2, 27.6, 28.3, 30.9, 61.3, 72.5, 90.2, 96.6, 111.8, 119.8, 123.9, 127.5, 128.2, 128.7, 129.7, 131.6, 132.1, 135.3, 143.1, 146.4, 188.9. Anal. Calcd for $C_{27}H_{31}N_3O_2$: C, 75.49; H, 7.27; N, 9.78. Found: C, 75.62; H, 7.60; N, 9.72.

***trans*-1,6-Diphenyl-4-(benzotriazol-1-yl)-4-ethoxy-1-hexen-5-yn-3-one (11b):** yield 92%; yellow prisms, mp 122−124 °C; ^{1}H NMR δ 1.29 (t, 3 H, *J* = 7.1 Hz), 3.35−3.50 (m, 1 H), 4.14−4.28 (m, 1 H), 7.30−7.70 (m, 13 H), 7.73 (d, 1 H, *J* = 8.4 Hz), 7.91 (d, 1 H, *J* = 15.9 Hz), 8.11 (d, 1 H, *J* = 8.4 Hz); ^{13}C NMR δ 14.6, 62.0, 79.8, 90.3, 93.0, 111.7, 118.7, 119.9, 120.4, 124.2, 127.8, 128.3, 128.6, 128.8, 129.7, 131.1, 131.9, 132.1, 133.9, 146.5, 147.0, 185.7. Anal. Calcd for $C_{26}H_{21}N_3O_2$: C, 76.64; H, 5.19; N, 10.31. Found: C, 76.38; H, 5.44; N 10.17.

General Procedure for the Preparation of Compounds 12a,b. To a solution of **11** (1.93 mmol) in acetone (40 mL) at 5 °C was added a precooled H_2SO_4 aqueous solution (3 mL, 11%) in acetone (10 mL), and the solution was stirred at room temperature for 20 h with the reaction of **11a** and 8 h with **11b**. Water (40 mL) was added to the solution, which was extracted with diethyl ether (3 × 40 mL), and the combined organic layers were washed with a 2 N Na_2CO_3 aqueous solution (3 × 50 mL) and dried over $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography (hexane/ethyl acetate, 100:1).

***trans*-1-Phenyl-2-methyl-1-dodecen-5-yne-3,4-dione (12a).** This compound was obtained as a yellow oil, yield 83%: ^{1}H NMR δ 0.89 (t, 3 H, *J* = 6.8 Hz), 1.20−1.52 (m, 6 H), 1.56−1.75(m, 2 H), 2.17 (d, 3 H, *J* = 0.95 Hz), 2.47 (t, 2 H, *J* = 7.1 Hz), 7.40−7.53 (m, 6 H); ^{13}C NMR δ 12.5, 13.9, 19.5, 22.4, 27.4, 28.5, 31.1, 79.8, 103.5, 128.6, 129.7, 130.2, 132.3, 134.9, 147.2, 180.8, 192.8. Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C,80.84; H, 8.23.

***trans*-1,6-Diphenyl-1-hexen-5-yne-3,4-dione (12b):** obtained as yellow needles, yield 85%, mp 103−105 °C; ^{1}H NMR δ 7.41−7.60 (m, 7 H), 7.62−7.82 (m, 4 H), 7.94 (d, 1 H, *J* = 16.2 Hz); ^{13}C NMR δ 86.6, 99.0, 118.0, 119.4, 128.7, 129.0, 131.5, 131.6, 133.7, 134.2, 148.5, 177.1, 184.5. Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.20; H, 4.64.

Preparation of 1-Phenyl-2-methyl-6-chloro-(*E*,*E*)-1,5-dodecadiene-3,4-dione (13) and 12a. To a solution of **11a** (0.83 g, 1.93 mmol) in acetone (40 mL) at 5 °C was added a precooled HCl aqueous solution (1 mL, 37%) in acetone (10 mL), and the solution was allowed to warm to room temperature over 30 min. Water (40 mL) was added to the solution, which was extracted with diethyl ether (3 × 40 mL), and the combined organic layers were washed with a 2 N Na_2CO_3 aqueous solution (3 × 50 mL) and dried over $MgSO_4$. After filtration and removal of the solvent, the oily residue was purified by column chromatography (hexane/ethyl acetate, 1000:1) to give the less polar fraction **12a** (0.2 g, 0.71 mmol), yield 37%, and more polar fraction **13** (0.23 g, 0.72 mmol) as a yellow oil, yield 37%: ^{1}H NMR δ 0.90 (t, 3 H, *J* = 6.4 Hz), 1.20−1.48 (m, 6 H), 1.60−1.75 (m, 2 H), 2.19 (d, 3 H, *J* = 1.0 Hz), 2.55 (t, 2 H, *J* = 7.4 Hz), 6.55 (s, 1 H), 7.37−7.60 (m, 6 H); ^{13}C NMR δ 12.6, 14.0, 22.4, 27.2, 28.3, 31.4, 41.6, 122.4, 128.6, 129.5, 130.2, 133.2, 135.1, 146.2, 154.1, 192.5, 196.0. Anal. Calcd for $C_{19}H_{23}O_2Cl$: C,71.67; H, 7.29. Found: C, 72.01; H, 7.61.

General Procedure for the Preparation of 15b−d. To a solution of 1-(phenoxymethyl)benzotriazole (**14**, 17.8 mmol) in THF (40 mL) at −78 °C was added *n*-butyllithium (1.6 M in cyclohexane, 11.3 mL, 18.1 mmol). The solution was stirred at this temperature for 5 min, and the appropriate electrophile (1-iodohexane, 1-iodododecane, or 1-bromo-3-phenylpropane, 11.8 mmol) was added. After the solution was stirred at −78 °C for an additional 5 min, it was allowed to warm to room temperature and quenched with water (20 mL). The mixture was extracted with diethyl ether (2 × 50 mL), and the combined organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue which was separated by column chromatography (hexane/ethyl acetate, 30:1).

1-(Benzotriazol-1-yl)-1-phenoxyheptane (15b): obtained as an oil; yield 86%; ^{1}H NMR δ 0.87 (t, 3 H, *J* = 6.8 Hz), 1.20−1.90 (m, 8 H), 2.25−2.40 (m, 1 H), 2.42−2.60 (m, 1 H), 6.85(t, 1 H, *J* = 6.8 Hz), 6.92−7.10 (m, 3 H), 7.19 (td, 2 H, *J* = 7.0, 1.9 Hz), 7.36 (td, 1 H, *J* = 8.2, 1.0 Hz), 7.47(td, 1 H, *J* = 8.2, 1.0 Hz), 7.83 (d, 1 H, *J* = 8.4 Hz), 8.05 (d, 1 H, *J* = 8.4 Hz); ^{13}C NMR δ 13.8, 22.3, 24.5, 28.4, 31.3, 34.6, 88.2, 111.0, 116.1, 119.9, 122.7, 124.1, 127.5, 129.5, 131.0, 146.6. 156.1. Anal. Calcd for $C_{19}H_{23}N_3O$: C, 73.76; H, 7.49; N, 13.58. Found: C, 73.87; H, 7.87; N, 13.91.

1-(Benzotriazol-1-yl)-1-phenoxyundecane (15c): obtained as an oil; yield 87%; ^{1}H NMR δ 0.89 (t, 3 H, *J* = 6.8 Hz), 1.15−1.65 (m, 16 H), 2.25−2.40 (m, 1 H), 2.42−2.60 (m, 1 H), 6.85 (t, 1 H, *J* = 6.8 Hz), 6.91−7.00 (m, 3 H), 7.19 (t, 2 H, *J* = 8.0 Hz), 7.34 (t, 1 H, *J* = 7.2 Hz), 7.46 (t, 1 H, *J* = 7.2 Hz), 7.83 (d, 1 H, *J* = 8.1 Hz), 8.05 (d, 1 H, *J* = 8.4 Hz); ^{13}C NMR δ 14.0, 22.6, 24.6, 28.8, 29.1, 29.2, 29.3, 29.4, 31.8, 34.7, 88.3, 111.1, 111.2, 116.1, 120.0, 122.8, 124.2, 127.6, 129.6, 131.1, 146.7, 156.1. Anal. Calcd for $C_{23}H_{31}N_3O$: C, 75.58; H, 8.55; N, 11.50. Found: C, 75.76; H, 8.83; N, 11.54.

1-(Benzotriazol-1-yl)-1-phenoxy-3-phenylpropane (15d): obtained as an oil; yield 71%; ^{1}H NMR δ 1.50−1.68 (m, 1 H), 1.77−1.98 (m, 1 H), 2.24−2.40 (m, 1 H), 2.43−2.60 (m, 1 H), 2.60−2.78 (m 2 H), 6.82 (t, 1 H, *J* = 6.9 Hz), 6.88−7.00 (m, 3 H), 7.09−7.38 (m, 8 H), 7.41 (t, 1 H, *J* = 7.7 Hz), 7.75 (d, 1 H, *J* = 8.4 Hz), 8.01 (d, 1 H, *J* = 7.5 Hz); ^{13}C NMR δ 26.2, 34.1, 34.9, 88.1, 111.0, 116.2, 120.0, 122.9, 124.2, 126.0, 127.6, 128.2, 128.3, 129.6, 131.1, 141.0, 146.6, 156.0. Anal. Calcd for $C_{22}H_{21}N_3O$: C, 76.94; H, 6.16; N, 12.24. Found: C, 77.19; H, 6.40; N, 12.19.

General Procedure for the Preparation of 16. To a solution of **15** (3.23 mmol) in THF (40 mL) at −78 °C was added *n*-butyllithium (1.6 M in cyclohexane, 3.39 mmol), with stirring, which was continued for 5 min before the appropriate acid chloride (benzoyl, trimethylacetyl, 2-naphthoyl, 4-chlorobenzoyl, 2-toluoyl, benzoyl, or 4-chlorobenzoyl chloride, 3.39 mmol) was added. After the solution was stirred at −78 °C for an additional 15 min, it was quenched at −78 °C with water (40 mL). The mixture was extracted with diethyl ether (3 × 40 mL), and the combined organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue which was separated by column chromatography (hexane/ethyl acetate, 30:1).

1-*tert*-Butyl-2-(benzotriazol-1-yl)-2-phenoxy-1-octanone (16b): obtained as an oil; yield 86%; ^{1}H NMR δ 0.85 (t, 3 H, *J* = 6.3 Hz), 1.05−1.46 (m 7 H), 1.52 (s, 9 H), 1.62−1.80 (m, 1 H), 2.42−2.58 (m, 1 H), 6.51 (d, 2 H, *J* = 7.8 Hz), 6.99 (t, 1 H, *J* = 7.2 Hz), 7.11 (t, 1 H, *J* = 7.7 Hz), 7.33 (t, 1 H, *J* = 7.5 Hz), 7.41 (t, 1 H, *J* = 7.7 Hz), 7.56 (d, 1 H, *J* = 8.4 Hz), 8.08 (d, 1 H, *J* = 8.1 Hz); ^{13}C NMR δ 13.8, 22.3, 24.5, 27.8, 29.1, 31.1, 34.1, 45.1, 99.8, 111.8, 119.9, 120.3, 124.0, 124.3, 127.6, 129.4, 132.5, 146.3, 152.3, 205.8. Anal. Calcd for $C_{24}H_{31}N_3O_2$: C, 73.25; H, 7.94; N, 10.68. Found: C, 72.87; H, 7.75; N, 10.98.

1-(4-Chlorophenyl)-2-(benzotriazol-1-yl)-2-phenoxy-1-dodecanone (16d): obtained as an oil; yield 85%; ^{1}H NMR δ 0.86 (t, 3 H, *J* = 6.9 Hz), 1.10−1.50 (m, 16 H), 2.80−2.92 (m, 1 H), 3.08−3.20 (m, 1 H), 6.55 (d, 2 H, *J* = 7.5 Hz), 7.03 (t, 1 H, *J* = 7.4 Hz), 7.14 (t, 2 H, *J* = 7.5 Hz), 7.34−7.48 (m, 4 H), 7.59 (d, 1 H, *J* = 7.5 Hz), 8.00 (d, 2 H, *J* = 8.7 Hz), 8.10 (d, 1 H, *J* = 7.2 Hz); ^{13}C NMR δ 14.1, 22.6, 23.2, 29.0, 29.2, 29.3, 29.4, 31.8, 34.3, 97.9, 112.0, 120.2, 120.5, 124.6, 124.7, 128.2, 129.0, 129.7, 131.3, 132.7, 140.3, 146.5, 152.3, 191.1. Anal. Calcd for $C_{30}H_{34}N_3O_2Cl$: C, 71.48; H, 6.80; N, 8.34. Found: C, 71.70; H, 6.92; N, 8.83.

1,5-Diphenyl-2-(benzotriazol-1-yl)-2-phenoxy-5-pentanone (16f): obtained as an oil; yield 84%; ^{1}H NMR δ 1.72−1.95 (m, 2 H), 2.45−2.70 (m, 2 H), 2.90−3.05 (m, 1 H), 3.18−3.32 (m, 1 H), 6.52 (d, 2 H, *J* = 7.5 Hz), 7.00 (m, 3 H), 7.05−7.25 (m, 5 H), 7.28−7.48 (m, 4 H), 7.52 (t, 1 H, *J* = 7.4 Hz), 7.61 (d, 1 H, *J* = 8.1 Hz), 8.01 (d, 2 H, *J* = 7.8 Hz), 8.09 (d, 1 H, *J* = 7.5 Hz); ^{13}C NMR δ 24.6, 33.7, 35.1, 97.7, 112.0, 120.0, 120.5, 124.4, 124.5, 125.8, 128.1, 128.2, 128.5, 129.5, 129.7, 132.6, 133.5, 134.2, 140.6, 146.4, 152.2, 191.9. Anal. Calcd for $C_{29}H_{25}N_3O_2$: C, 77.83; H, 5.63; N, 9.39. Found: C, 77.54; H, 5.79; N, 9.26.

General Procedure for the Preparation of 17. To a solution of **16** (2.88 mmol) in acetic acid (22 mL) was added a solution of sulfuric acid (2.2 mL, 95−98%) in water (11 mL), and the solution was refluxed for 13.5 h under N_2. Water (30 mL) was added to the solution, which was extracted with diethyl ether (3 × 50 mL), and the combined organic layers were washed with a 2 N Na_2CO_3 aqueous solution (3 × 40 mL) and dried over $MgSO_4$. After filtration and removal of the solvent, the crude product was obtained as a yellow oil, which was purified by column chromatography (hexane/ethyl acetate, 30:1) to give the corresponding 1,2-diketone.

1-Phenyl-1,2-heptanedione (17a): obtained as a yellow oil; yield 56% based on **15a**; ^{1}H NMR δ 0.92 (t, 3 H, *J* = 7.1 Hz), 1.30−1.50 (m, 4 H), 1.64−1.80 (m, 2 H), 2.89 (t, 2 H, *J* = 7.4 Hz), 7.50 (t, 2 H, *J* = 7.5 Hz), 7.62 (t, 1 H, *J* = 7.4 Hz), 7.99 (d, 2 H, *J* = 8.4 Hz); ^{13}C NMR δ 13.8, 22.3, 22.5, 31.3, 38.7, 128.8, 130.1, 132.0, 134.5, 192.5, 203.4. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.07; H, 7.56.

1-*tert*-Butyl-1,2-octanedione (17b): obtained as a yellow oil; yield 83%; ^{1}H NMR δ 0.92 (t, 3 H, *J* = 6.5 Hz), 1.27 (s, 9 H), 1.28−1.50 (m, 6 H), 1.52−1.65 (m, 2 H), 2.68 (t, 2 H, *J* = 7.2 Hz); ^{13}C NMR δ 13.9, 22.4, 22.7, 26.0, 28.7, 31.5, 38.7, 42.0, 203.3, 207.9. Anal. Calcd for $C_{12}H_{22}O_2$: C,72.68; H, 11.18. Found: C, 72.68; H, 10.80.

1-(2-Naphthyl)-1,2-octanedione (17c): obtained as a yellow oil; yield 52% based on **15b**; ^{1}H NMR δ 0.89 (t, 3 H, *J* = 6.8 Hz), 1.15−1.55 (m, 6 H), 1.68−1.82 (m, 2 H), 2.94 (t, 2 H, *J* = 7.4 Hz), 7.52−7.70 (m, 2 H), 7.85−8.10 (m, 4 H), 8.52 (s, 1 H); ^{13}C NMR δ 14.0, 22.5, 22.9, 28.9, 31.5, 38.9, 124.2, 127.0, 127.9, 128.9, 129.3, 129.4, 130.0, 132.3, 133.5, 136.2, 192.5, 203.7. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.29; H, 7.55.

1-(4-Chlorophenyl)-1,2-dodecanedione (17d): obtained as yellow prisms, yield 91%, mp 45−47 °C; ^{1}H NMR δ 0.87 (t, 3 H, *J* = 6.6 Hz), 1.20−1.42 (m, 14 H), 1.60−1.75 (m, 2 H), 2.86 (t, 2 H, *J* = 7.2 Hz), 7.45 (d, 2 H, *J* = 8.4 Hz), 7.94 (d, 2 H, *J* = 8.4 Hz); ^{13}C NMR δ 14.1, 22.6, 22.9, 29.1, 29.3, 29.4, 29.5, 31.8, 38.6, 129.2, 130.5, 131.5, 141.2, 190.6. 202.7. Anal. Calcd for $C_{18}H_{25}O_2Cl$: C, 70.00; H, 8.16. Found: C, 69.98; H, 8.13.

1-(2-Methylphenyl)-1,2-dodecanedione (17e): obtained as a yellow oil; yield 72% based on **15c**; ^{1}H NMR δ 0.89 (t, 3 H, *J* = 6.6 Hz), 1.20−1.43 (m, 14 H), 1.65−1.78 (m, 2 H), 2.56 (s, 2 H, *J* = 7.4 Hz), 7.26−7.32 (m, 2 H), 7.44 (d, 1 H, *J* = 6.3 Hz), 7.58 (d, 1 H, *J* = 8.1 Hz); ^{13}C NMR δ 14.1, 21.4, 22.6, 22.9, 29.1, 29.2, 29.3, 29.4, 29.5, 31.9, 38.5, 125.7, 131.3, 132.0, 132.2, 133.1, 140.8. 195.6, 203.8; HRMS (EI) calcd for $C_{19}H_{28}O_2$ (M^+) 288.2089, found 288.2019.

1,5-Diphenyl-1,2-pentanedione (17f): obtained as a yellow oil; yield 92%; ^{1}H NMR δ 2.04 (quintet, 2 H, *J* = 7.5 Hz), 2.70 (t, 2 H, *J* = 7.5 Hz), 2.90 (t, 2 H, *J* = 7.5 Hz), 7.16−7.35 (m, 5 H), 7.47 (t, 2 H, *J* = 7.5 Hz), 7.62 (t, 1 H, *J* = 7.4 Hz), 7.95 (d, 2 H, *J* = 7.2 Hz); ^{13}C NMR δ 24.4, 35.1, 38.0, 126.1, 128.4, 128.8, 130.1, 131.9, 134.5, 141.1, 192.2, 202.9. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.49; H, 6.58.

1-(4-Chlorophenyl)-5-phenyl-1,2-pentanedione (17g): obtained as a yellow oil; yield 72% based on **15d**; ^{1}H NMR δ 2.03 (quintet, 2 H, *J* = 7.5 Hz), 2.70 (t, 2 H, *J* = 7.5 Hz), 2.89 (t, 2 H, *J* = 7.5 Hz), 7.12−7.35 (m, 5 H), 7.44 (d, 2 H, *J* = 8.7 Hz), 7.91 (d, 2 H, *J* = 9.0 Hz); ^{13}C NMR δ 24.4, 35.0, 37.8, 126.1, 128.5, 129.2, 130.3, 131.6, 141.0, 141.2, 190.4, 202.2. Anal. Calcd for $C_{17}H_{15}O_2Cl$: C, 71.21; H, 5.27. Found: C, 70.94; H, 5.34.

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