A Novel Transformation of Esters to Alkynes with 1-Substituted Benzotriazoles

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Reactions of lithio benzotriazol-1-yl derivatives **2**, **11**, and **25** with aromatic and aliphatic esters **3**, **12**, and **26** gave α-(benzotriazol-1-yl) ketones **4**, **13**, and **27**, respectively, in high yields. Alternatively, α-(benzotriazol-1-yl) ketones **22** can be accessed by the reaction of α-(benzotriazol-1-yl) esters **20** with Grignard reagents. Condensation of **4**, **13**, **22**, and **27** with (*p*-toluenesulfonyl)-hydrazine provided *p*-tosylhydrazones **5**, **14**, **21**, and **28**. Treatment of hydrazones **5**, **21**, and **28** with *n*-butyllithium in diethyl ether resulted in the elimination of the tosyl group, dinitrogen, and benzotriazolyl group to afford the corresponding acetylenes **9**, **23**, and **29** in good yields. When α-(benzotriazol-1-yl) 1-α-phenoxy hydrazones **14** were treated with methyllithium, *n*-butyllithium, or phenyllithium, alkynes **18** were obtained, in which phenoxy groups were replaced by the lithium reagents.

Introduction

Alkyne preparations by the combination of two fragments with the formation of a triple bond are of considerable interest in organic synthesis.[1] However, the development of such transformations has received relatively little attention. In principle, such alkyne formation involves a nucleophilic species and an electrophilic species.[2,3] Among the electrophiles reported, carbonyl-containing compounds, especially aldehydes and ketones, are most widely used due to their great availability. Several efficient methods using this strategy have been documented: (i) Coupling of Wittig reagents bearing α-halogen (Cl, Br, or F) with aldehydes followed by base-assisted elimination is most frequently used in the synthesis of terminal alkynes.[3] (ii) Base-promoted reactions of dialkyl (diazomethyl)phosphonates or (diazomethyl)-trimethylsilane with aldehydes and aryl ketones lead directly to the corresponding homologous alkynes;[4−6] however, this method is not effective for the conversion of dialkyl ketones to alkynes. (iii) Double-elimination reaction of β-acetoxy or β-alkoxy sulfones prepared from α-sulfonyl carbanions and aldehydes affords the corresponding acetylenes,[7,8] but is applicable only when there are no allylic hydrogens in the vinyl sulfone intermediates.

Other carbonyl-containing compounds including carboxylic acids[9] and acyl halides[3] were less frequently employed in such alkynations due to handling difficulties. The transformation of esters, another class of widely available carbonyl-containing compounds, into alkynes is of significant interest, but few such methods have been reported. Kowalski and co-workers[10] treated esters with (dibromomethyl)lithium in the presence of tetramethylpiperidine to generate carbon−carbon triple bonds for siloxyalkyne derivatives. The most general and efficient acetylenation of esters was independently reported by Bartlett[11] and Lythgoe,[12,13] acylation of sulfonyl carbanions by esters led to β-keto sulfones, which were converted to enol phosphates by direct phosphorylation; reductive elimination of both the phosphate and the sulfonyl group resulted in the corresponding acetylenes. However, this method requires the use of (i) 2 equiv of the metalated sulfone to generate the α-keto sulfone, (ii) toxic diethyl phosphorochloridate, and (iii) harsh reductive elimination conditions such as sodium metal in liquid ammonia or sodium amalgam, which may lead to further reduction to alkenes.

We now report a novel and convenient alkyne synthesis from esters and benzotriazole derivatives *via* the formation of α-(benzotriazol-1-yl) ketones, subsequent treatment with (*p*-toluenesulfonyl)hydrazine, and base-assisted elimination of a tosyl group, dinitrogen, and benzotriazolyl group (Schemes 1−4).

Results and Discussion

1-Substituted benzotriazoles **1a**−**d** and **10** were readily prepared by our previously reported methods.[14−16] Treatment of 1-methylbenzotriazole (**1a**) with 1 equiv of *n*-butyllithium in THF at −78 °C for 2 h followed by addition of methyl decanoate, dropwise, gave the α-(benzotriazol-1-yl) ketone **4c** in a 40% yield along with unreacted **1a**. Rapid addition of the ester to a solution of α-lithio methylbenzotriazole **2a** at −78 °C improved the yield of the desired product **4c** to 88%, and no starting

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(1) Furber, M. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon Press: New York, 1995; Vol. 1, p 997.
(2) Ben-Efraim, D. A. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S. Ed.; John Wiley & Sons: NewYork, 1978; p 755.
(3) Larock, R. C. In *Comprehensive Organic Transformations*; VCH Publishers, Inc.: New York, 1989; p 289.
(4) Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 869.
(5) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1979**, *44*, 4997.
(6) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1982**, *47*, 1837.
(7) Mandai, T.; Yanagi, T.; Araki, K.; Morisaki, Y.; Kawada, M.; Otera, J. *J. Am. Chem. Soc.* **1984**, *106*, 3670.
(8) Otera, J.; Misawa, H.; Sugimoto, K. *J. Org. Chem.* **1986**, *51*, 3830.
(9) Kano, S.; Yokomatsu, T.; Shibuya, S. *J. Org. Chem.* **1978**, *43*, 4366.
(10) Kowalski, C. J.; Lal, G. S.; Haque, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 7127.
(11) Bartlett, P. A.; Green, F. R., III; Rose, E. H. *J. Am. Chem. Soc.* **1978**, *100*, 4852.
(12) Lythgoe, B.; Waterhouse, I. *Tetrahedron Lett.* **1978**, *1*, 2625.
(13) Lythgoe, B.; Waterhouse, I. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2429.
(14) Katritzky, A. R.; Rachwal, S.; Caster, K. C.; Mahni, F.; Law, K. W.; Rubio, O. *J. Chem. Soc., Perkin Trans. 1* **1987**, 781.
(15) Katritzky, A. R.; Drewniak-Deyrup, M.; Lan, X.; Brunner, F. *J. Heterocycl. Chem.* **1989**, *26*, 829.
(16) Katritzky, A. R.; Wu, J.; Kuzmierkiewicz, W.; Rachwal, S. *Liebigs Ann. Chem.* **1994**, 1.

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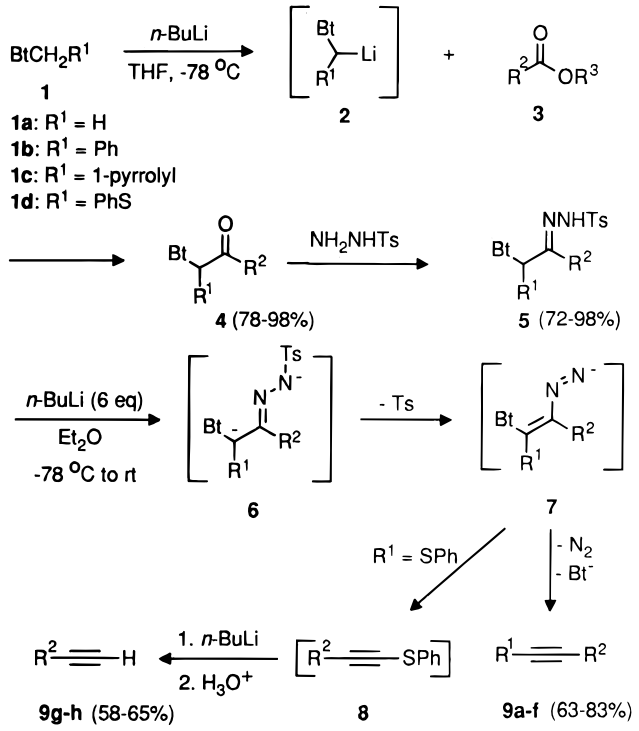
Table 1. Synthesis of Acetylenes 9 from Esters 3 and 1-Substituted Benzotriazoles 1 *via* α-(Benzotriazol-1-yl) Ketones 4

	substituents			4		5		6	
entry	R^1	R^2	R^3	yield (%)	mp (°C)	yield (%)	mp (°C)	yield (%)	mp (°C)
a	H	n-C_5H_{11}	CH_3CH_2	78	78−80	98[a]	139−141	73	oil
b	H	n-C_8H_{17}	CH_3CH_2	83	87−89	91[a]	136−138	75	oil
c	H	n-C_9H_{19}	CH_3	88	95−96	98[a]	140−142	82	oil
d	H	p-CH_3−C_6H_4	CH_3	88	137−138	72[b]	180−181	68	oil
e	Ph	Ph	CH_3	98	171−172	92[b]	174−175	85	59−60
f	1-pyrrolyl	n-$C_{16}H_{33}$	CH_3	78	79−80	95[a]	128−129	42	oil
g	PhS	p-CH_3−C_6H_4	CH_3	93	113−114	78[b]	166−167	65 (R^1 = H)	oil
h	PhS	n-$C_{17}H_{35}$	CH_3	81	82−83	91[a]	94−95	58 (R^1 = H)	36−38

[a] Without using Amberlyst-15. [b] In the presence of Amberlyst-15.

Scheme 1



material was detected by GCMS. Treatment of the other substituted benzotriazoles **2b**−**d** with 1 equiv of *n*-butyllithium at −78 °C, and subsequent reaction with an appropriate ester, provided α-(benzotriazol-1-yl) ketones **4a**,**b** and **4d**−**h** in good to excellent yields (Scheme 1 and Table 1).

Intermediates **4a**−**c**, **4f**, and **4h**, where R^2 was an aliphatic group, reacted readily with (*p*-toluenesulfonyl)-hydrazine in benzene under reflux using a Dean−Stark trap to give (*p*-toluenesulfonyl)hydrazones **5a**−**c**, **5f**, and **5h,** respectively, in good to excellent isolated yields. The aromatic ketones **4d**−**e** and **4g** (where R^2 was an aromatic group) required Amberlyst-15 as a catalyst and excess (*p*-toluenesulfonyl)hydrazine for conversion into the corresponding (*p*-toluenesulfonyl)hydrazones **5d**,**e** and **5g** in satisfactory yields as shown in Table 1. All of the ketones **4a**−**h** and the (*p*-toluenesulfonyl)hydrazones **5a**−**h** thus prepared were new, and the structures of the products were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses.

Treatment of the corresponding (*p*-toluenesulfonyl)-hydrazones **5a**−**f** with 6 equiv of *n*-butyllithium in diethyl ether at −78 °C under nitrogen for 2 h and then the solutions were kept at 20 °C for 2 days with stirring, resulted, after column chromatography, in the formation of the expected acetylenes **9a**−**f** in generally good yields. Significantly, the heterocyclic ynamine **9f**, which otherwise could be difficult to prepare,[17] is also accessible in moderate yield from the above transformation.

In the case of **5g**,**h**, lithiation of these compounds with 6 equiv of *n*-butyllithium failed to give the desired product 1-(phenylthio)acetylenes. Instead, terminal alkynes **9g**,**h** and 1-(phenylthio)butane were obtained. Presumably, 1-(phenylthio)acetylenes **8** formed first, which were attacked by *n*-butyllithium to generate the products **9g**,**h** and 1-(phenylthio)butane as in an analogous reaction shown by Comasseto and co-workers.[18] The formation of the acetylenes theoretically needs only 2 equiv of *n*-butyllithium. However, attempts to trap compound **9g** under the same reaction conditions using 2 equiv of *n*-butyllithium failed, either at room temperature or under reflux, and only starting material was recovered. When the above reaction was carried out in toluene under reflux, the starting material decomposed to give a complex mixture. It was found that 6 equiv of *n*-butyllithium gave the best yields (see Note at end).

(Phenoxymethyl)benzotriazole (**10**) behaved similarly in the transformations of **10** to ketones **13a**−**f** and hydrazones **14a**−**f** as illustrated in Scheme 2 and Table 2. Interestingly, the reactions of hydrazones **14a**,**b** with 6 equiv of *n*-butyllithium in diethyl ether afforded 1-(*p*-methylphenyl)-1-hexyne (**18a**) and 5-decyne (**18b**), respectively, in good yields after column chromatography. We envisaged that the reaction pathway for the formation of **18a**,**b** involved the 1,4-elimination of phenol from **14a**,**b** to generate intermediate azo-enes **16** which underwent nucleophilic addition with *n*-butyllithium and subsequent deprotonation to give dianions **7**. Intermediate **7** decomposed, affording alkynes **18a**,**b** as shown in Scheme 2. This reaction mechanism is supported by 1,4-elimination/addition reaction of α-(halotosyl)hydrazones.[19] Similarly, the reaction of hydrazones **14c**,**d** with methyllithium and phenyllithium afforded both aromatic and aliphatic acetylenes in good yields (Table 2). However, use of secondary and tertiary butyllithium resulted in complex mixtures. Nevertheless, the above transformation of esters and (phenoxymethyl)benzotriazole (**10**) to aliphatic acetylenes complemented the present methods for alkyne synthesis since the alkylation of 1-alkylbenzotriazoles with carbonyl-containing compounds failed to give the expected products[16] and no aliphatic alkyne could be obtained by the method of Scheme 1.

Alternatively, α-(benzotriazol-1-yl) ketones **22a**−**c** can be prepared, in moderate yields, from the reaction of Grignard reagents with α-(benzotriazol-1-yl) esters **20a**,**b**

(17) Booker-Milburn, K. I. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon Press: New York, 1995; Vol. 2, p 1039.

(18) Braga, A. L.; Comasseto, J. V.; Petragnani, N. *Tetrahedron Lett.* **1984**, *25*, 1111.

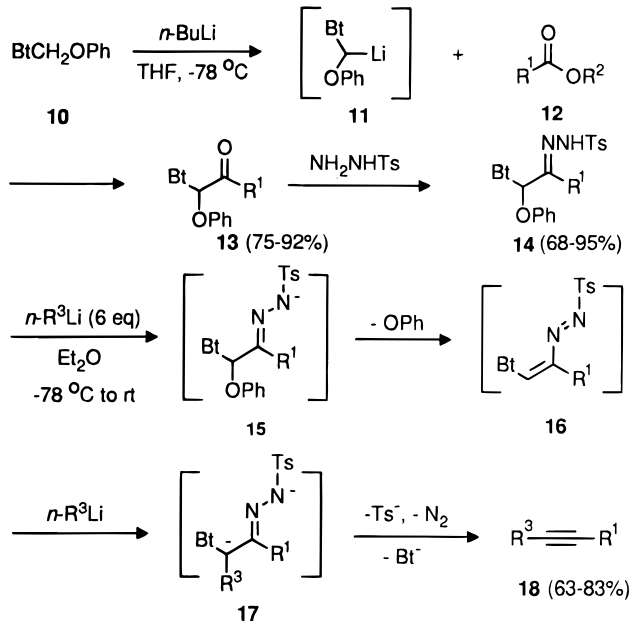
(19) Sacks, C. E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 7372.

Table 2. Synthesis of Acetylenes 18 from (Phenoxymethyl)benzotriazoles 10 and Esters 12

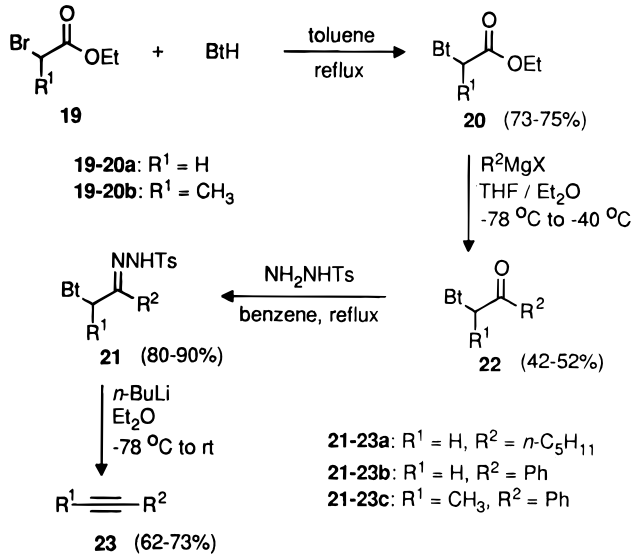
	substituents			13		14		18	
entry	R^1	R^2	R^3	yield (%)	mp (°C)	yield (%)	mp (°C)	yield (%)	mp (°C)
a	*p*-CH_3−C_6H_4	CH_3	*n*-C_4H_9	92	130−131	71[a]	162−163	63	oil
b	*n*-C_4H_9	CH_3CH_2	*n*-C_4H_9	75	oil	80[b]	129−130	72	oil
c	Ph	CH_3	CH_3	95	108−109	68[a]	138−139	74	oil
d	Ph	CH_3	Ph	95	108−109	68[a]	138−139	78	56−58
e	*n*-C_7H_{15}	CH_3CH_2	Ph	88	oil	95[b]	108−110	83	oil
f	*n*-C_7H_{15}	CH_3CH_2	CH_3	88	oil	95[b]	108−110	68	oil

[a] In the presence of Amberlyst-15. [b] Without using Amberlyst-15.

Scheme 2



Scheme 3

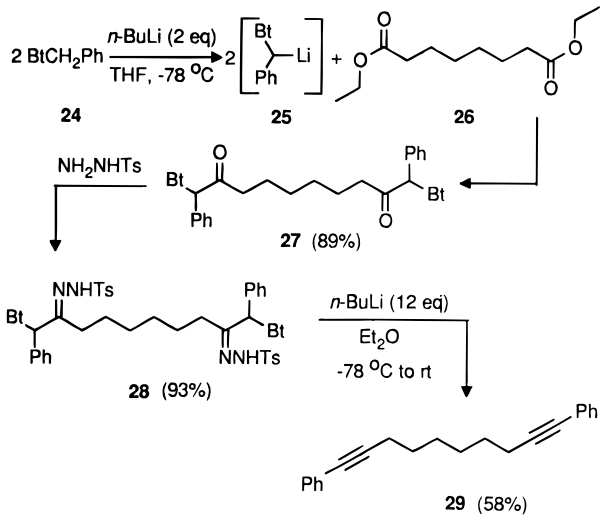


derived from α-bromo ketones **19a**,**b** and benzotriazole in high yields (Scheme 3).[20] Similarly, as in Scheme 1, compounds **22a**−**c** were converted to hydrazones **21a**−**c** and alkynes **23a**−**c** in satisfactory yields. Thus, α-(benzotriazol-1-yl) esters **20a**,**b** can be considered as the acetylenic cation synthons for the synthesis of various alkynes.

Analogous transformations can also be applied to the preparation of bifunctional acetylenes. Thus, diethyl

(20) Katritzky, A. R.; Wu, J. *Synthesis* **1994**, 597.

Scheme 4



suberate (**26**) reacted with 2 equiv of 1-(α-lithiobenzyl)-benzotriazole (**25**), generated from the reaction of *n*-butyllithium and 1-benzylbenzotriazole (**24**), to give the 1,10-bis(benzotriazol-1-yl)-1,10-diphenyl-2,9-decanedione (**27**) which was treated with (*p*-toluenesulfonyl)-hydrazine to afford 1,10-bis(benzotriazol-1-yl)-1,10-diphenyl-2,9-decanedione bis(*p*-tosylhydrazone) (**28**). The reaction of tosylhydrazone **28** with 12 equiv of *n*-butyllithium furnished the expected product 1,10-diphenyl-1,9-decadiyne (**29**) (Scheme 4).

In summary, we have developed a new, efficient, and convenient synthetic methodology for the preparation of various aromatic, aliphatic, and terminal acetylenes from both aromatic and aliphatic esters.

Experimental Section

General Comments. Melting points were determined on a hot stage apparatus without correction. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ or DMSO-d_6. Diethyl ether and THF were freshly distilled from sodium−benzophenone ketyl immediately before use. All lithiations were carried out in a nitrogen atmosphere.

Preparation of α-(Benzotriazol-1-yl) Ketones 4a−h and 13a−f. General Procedure. To a stirred solution of the corresponding 1-substituted benzotriazole **2** (10 mmol) (Schemes 1 and 2 and Tables 1 and 2) in THF was added *n*-butyllithium (4.5 mL, 10 mmol, 2.22 M in hexane) at −78 °C under nitrogen followed by the appropriate ester **3** or **12** (10 mmol) in THF (10 mL). The mixture was stirred for another 12 h while the temperature was allowed to rise to 20 °C. The reaction was quenched with water, extracted with ethyl acetate, and dried over anhydrous magnesium sulfate. Removal of the solvent *via* rotary evaporation gave a residue which was subjected to column chromatography or crystallization to provide the desired ketones **4** or **13** (Tables 1 and 2).

1-(Benzotriazol-1-yl)-2-heptanone (4a): purified by column chromatography using EtOAc/hexane (1:3) as the eluent;

^{1}H NMR δ 8.10 (d, J = 8.2 Hz, 1 H), 7.54−7.49 (m, 1 H), 7.40 (d, J = 7.8 Hz, 2 H), 5.44 (s, 2 H), 2.48 (t, J = 7.2 Hz, 2 H), 1.68−1.58 (m, 2 H), 1.37−1.23 (m, 4 H), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR δ 202.3, 145.9, 133.4, 127.8, 124.0, 120.1, 109.1, 56.2, 39.7, 31.0, 22.9, 22.2, 13.7. Anal. Calcd for $C_{13}H_{17}N_3O$: C, 67.51; H, 7.41; N, 18.17. Found: C, 67.61; H, 7.63; N, 18.21.

1-(Benzotriazol-1-yl)-2-decanone (4b): purified by column chromatography using EtOAc/hexane (1:3) as the eluent; ^{1}H NMR δ 8.06 (d, J = 8.9 Hz, 1 H), 7.52−7.44 (m, 1 H), 7.42−7.33 (m, 2 H), 5.42 (s, 2 H), 2.46 (t, J = 7.3 Hz, 2 H), 1.67−1.54 (m, 2 H), 1.35−1.17 (m, 10 H), 0.87 (t, J = 6.7 Hz, 3 H); ^{13}C NMR δ 202.2, 145.9, 133.4, 127.8, 124.0, 120.0, 109.1, 56.2, 39.7, 31.6, 29.1, 29.0, 28.0, 23.1, 22.5, 13.9. Anal. Calcd for $C_{16}H_{23}N_3O$: C, 70.30; H, 8.48; N, 15.37. Found: C, 70.12; H, 8.64; N, 15.30.

1-(Benzotriazol-1-yl)-2-undecanone (4c): purified by column chromatography using EtOAc/hexane (1:3) as the eluent; ^{1}H NMR δ 8.06 (d, J = 8.2 Hz, 1 H), 7.51−7.45 (m, 1 H), 7.40−7.34 (m, 2 H), 5.42 (s, 2 H), 2.46 (t, J = 7.3 Hz, 2 H), 1.67−1.53 (m, 2 H), 1.37−1.28 (m, 12 H), 0.87 (t, J = 6.6 Hz, 3 H); ^{13}C NMR δ 202.2, 145.8, 133.4, 127.8, 124.0, 120.0, 109.1, 56.1, 39.7, 31.7, 29.2, 29.1, 29.0, 28.9, 23.1, 22.5, 14.0. Anal. Calcd for $C_{17}H_{25}N_3O$: C, 71.05; H, 8.77; N, 14.62. Found: C, 70.81; H, 8.96; N, 14.64.

1-(Benzotriazol-1-yl)-*p*-methylacetophenone (4d): purified by recrystallization from EtOAc/hexane (1:4); ^{1}H NMR δ 8.01 (d, J = 8.1 Hz, 1 H), 7.88 (d, J = 8.1 Hz, 2 H), 7.44−7.19 (m, 5 H), 6.02 (s, 2 H), 2.39 (s, 3 H); ^{13}C NMR δ 189.9, 145.8, 145.4, 133.7, 131.3, 129.6, 128.1, 127.5, 123.7, 119.7, 109.5, 53.6, 21.6. Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.55; H, 5.27; N, 16.85.

1-(Benzotriazol-1-yl)-1-phenylacetophenone (4e): purified by recrystallization from EtOAc/hexane (1:4); ^{1}H NMR δ 8.06−7.98 (m, 3 H), 7.89 (s, 1 H), 7.57−7.50 (m, 1 H), 7.43−7.20 (m, 10 H); ^{13}C NMR δ 192.6, 146.5, 134.4, 134.1, 133.1, 132.9, 129.4, 129.2, 129.1, 128.9, 128.8, 127.4, 123.8, 119.8, 111.3, 68.1. Anal. Calcd for $C_{20}H_{15}N_3O$: C, 76.66; H, 4.82; N, 13.41. Found: C, 76.78; H, 4.94; N, 13.31.

1-(Benzotriazol-1-yl)-1-pyrrolyl-2-octadecanone (4f): purified by column chromatography using EtOAc/hexane (1:3) as the eluent; ^{1}H NMR δ 8.06 (d, J = 8.3 Hz, 1 H), 7.48−7.26 (m, 4 H), 6.89 (t, J = 2.2 Hz, 2 H), 6.26 (t, J = 2.2 Hz, 2 H), 2.71−2.51 (m, 2 H), 1.72−1.60 (m, 2 H), 1.35−1.18 (m, 26 H), 0.87 (t, J = 6.7 Hz, 3 H); ^{13}C NMR δ 199.1, 146.1, 132.3, 128.4, 124.5, 120.8, 120.2, 110.8, 110.0, 75.2, 39.7, 31.9, 29.7, 29.6, 29.59, 29.55, 29.5, 29.3, 29.2, 28.8, 23.4, 22.6, 14.0. Anal. Calcd for $C_{28}H_{42}N_4O$: C, 74.62; H, 9.39; N, 12.43. Found: C, 75.03; H, 9.72; N, 12.38.

1-(Benzotriazol-1-yl)-1-(phenylthio)-*p*-methylacetophenone (4g): purified by recrystallization from EtOAc/hexane (1:4); ^{1}H NMR δ 8.05−7.95 (m, 4 H), 7.81 (s, 1 H), 7.54 (t, J = 7.8 Hz, 1 H), 7.39 (t, J = 7.7 Hz, 1 H), 7.30−7.22 (m, 3 H), 7.20 (t, J = 7.7 Hz, 2 H), 7.12 (d, J = 8.2 Hz, 2 H), 2.39 (s, 3 H); ^{13}C NMR δ 188.5, 146.9, 145.9, 133.5, 132.1, 130.7, 129.7, 129.4, 129.3, 127.7, 124.3, 120.0, 113.1, 71.2, 21.8. Anal. Calcd for $C_{21}H_{17}N_3OS$: C, 70.17; H, 4.77; N, 11.69. Found: C, 69.97; H, 4.77; N, 11.82.

1-(Benzotriazol-1-yl)-1-(phenylthio)-2-nonadecanone (4h): purified by column chromatography using EtOAc/hexane (1:3) as the eluent; ^{1}H NMR δ 8.06 (d, J = 8.4 Hz, 1 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.53 (t, J = 8.2 Hz, 1 H), 7.45 (t, J = 8.2 Hz, 1 H), 7.30−7.12 (m, 5 H), 6.97 (s, 1 H), 2.90−2.76 (m, 1 H), 2.67−2.55 (m, 1 H), 1.72−1.59 (m, 2 H), 1.38−1.20 (m, 28 H), 0.91 (t, J = 6.7 Hz, 3 H); ^{13}C NMR δ 199.5, 146.8, 133.3, 132.0, 130.5, 129.4, 129.2, 127.7, 124.3, 120.1, 112.3, 74.0, 39.8, 31.9, 29.6, 29.54, 29.47, 29.3, 29.1, 28.8, 23.6, 22.6, 14.0. Anal. Calcd for $C_{31}H_{45}N_3OS$: C, 73.33; H, 8.93; N, 8.28. Found: C, 73.48; H, 9.26; N, 8.36.

1-(Benzotriazol-1-yl)-1-phenoxy-*p*-methylacetophenone (13a): purified by recrystallization from EtOAc/hexane (1:4); ^{1}H NMR δ 8.06 (s, 1 H), 8.04−7.97 (m, 3 H), 7.76 (d, J = 9.1 Hz, 1 H), 7.47 (t, J = 7.7 Hz, 1 H), 7.34 (t, J = 7.7 Hz, 1 H), 7.28−7.23 (m, 4 H), 7.09 (d, J = 8.6 Hz, 2 H), 7.03 (t, J = 7.4 Hz, 1 H), 2.39 (s, 3 H); ^{13}C NMR δ 187.2, 155.5, 146.6, 145.9, 132.2, 130.6, 129.9, 129.7, 129.4, 128.3, 124.5, 123.6, 119.9, 116.2, 111.8, 85.4, 21.8. Anal. Calcd for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24. Found: C, 73.63; H, 4.98; N, 12.27.

1-(Benzotriazol-1-yl)-1-phenoxyhexan-2-one (13b): purified by column chromatography using EtOAc/hexane (1:3) as the eluent; ^{1}H NMR δ 8.03 (d, J = 8.4 Hz, 1 H), 7.62−7.54 (m, 1 H), 7.51−7.40 (m, 1 H), 7.39−7.30 (m, 1 H), 7.28 −7.14 (m, 3 H), 7.12−6.94 (m, 3 H), 3.01−2.88 (m, 1 H), 2.79−2.60 (m, 1 H), 1.78−1.50 (m, 2 H), 1.40−1.20 (m, 2 H), 0.87 (t, J = 6.7 Hz, 3 H); ^{13}C NMR δ 199.9, 156.0, 146.3, 131.7, 129.8, 128.3, 124.5, 123.6, 120.0, 116.2, 110.7, 87.6, 38.4, 25.1, 22.0, 13.6. Anal. Calcd for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58. Found: C, 69.49; H, 6.34; N, 13.85.

1-(Benzotriazol-1-yl)-1-phenoxyacetophenone (13c = 13d): purified by recrystallization from EtOAc/hexane (1:4); ^{1}H NMR δ 8.16−8.04 (m, 3 H), 8.02 (d, J = 8.1 Hz, 1 H), 7.73 (d, J = 8.3 Hz, 1 H), 7.64−7.53 (m, 1 H), 7.52−7.38 (m, 3 H), 7.37−7.16 (m, 3 H), 7.10 (d, J = 8.4 Hz, 2 H), 7.02 (t, J = 7.1 Hz, 1 H); ^{13}C NMR δ 187.6, 155.4, 146.5, 134.5, 133.0, 132.1, 129.9, 129.2, 128.9, 128.3, 124.5, 123.7, 119.9, 116.1, 111.7, 85.3. Anal. Calcd for $C_{20}H_{15}N_3O_2$: C, 72.94; H, 4.59; N, 12.76. Found: C, 72.70; H, 4.61; N, 12.98.

1-(Benzotriazol-1-yl)-1-phenoxy-2-nonanone (13e = 13f): purified by column chromatography using EtOAc/hexane (1:3) as the eluent; ^{1}H NMR δ 8.05 (d, J = 9.3 Hz, 1 H), 7.58 (d, J = 9.3 Hz, 1 H), 7.48 (t, J = 8.1 Hz, 1 H), 7.38 (t, J = 8.1 Hz, 1 H), 7.25 (t, J = 8.1 Hz, 2 H), 7.15 (s, 1 H), 7.10−7.00 (m, 3 H), 3.01−2.89 (m, 1 H), 2.78−2.62 (m, 1 H), 1.78−1.60 (m, 2 H), 1.40−1.20 (m, 8 H), 0.89 (t, J = 6.7 Hz, 3 H); ^{13}C NMR δ 199.9, 155.7, 146.4, 131.8, 129.9, 128.3, 124.6, 123.8, 120.2, 116.3, 110.8, 87.7, 38.8, 31.5, 28.9, 28.8, 23.2, 22.5, 14.0. Anal. Calcd for $C_{21}H_{25}N_3O_2$: C, 71.77; H, 7.17; N, 11.96. Found: C, 71.81; H, 7.17; N, 12.23.

Preparation of *p*-Tosylhydrazones 5a−h, 14a−f, and 21a−c. General Procedure. A mixture of (*p*-toluenesulfonyl)hydrazine (5 mmol) and the appropriate α-(benzotriazol-1-yl) ketone **4a**, **4c**−**e**, **4h**, or **22a**−**c** (5 mmol) in benzene (50 mL) (for the preparation of compound **5d**, **5e**, **5g**, **14a**, **14c**,**d**, and **21c**, a catalytic amount of Amberlyst-15 was needed) was refluxed, using a Dean−Stark trap, for 12 h. Removal of the solvent *via* rotary evaporation gave a residue which was recrystallized from a mixture of ethyl acetate and hexane to provide the expected product **5a**−**h**, **14a**−**f**, or **21a**−**c** (Tables 1−3).

1-(Benzotriazol-1-yl)-2-heptanone *p*-Tosylhydrazone (5a = 21a): ^{1}H NMR δ 8.35 (s, 1 H), 8.00 (d, J = 8.4 Hz, 1 H), 7.74 (d, J = 8.2 Hz, 2 H), 7.37−7.21 (m, 4 H), 7.09 (d, J = 8.2 Hz, 1 H), 5.32 (s, 2 H), 2.48 (s, 3 H), 2.09−2.03 (m, 2 H), 1.37−1.22 (m, 2 H), 1.20−1.05 (m, 4 H), 0.75 (t, J = 6.7 Hz, 3 H); ^{13}C NMR δ 153.1, 146.1, 144.3, 134.9, 133.0, 129.7, 128.0, 127.5, 124.0, 119.9, 109.9, 53.4, 31.4, 27.3, 24.2, 22.1, 21.6, 13.6. Anal. Calcd for $C_{20}H_{25}N_5O_2S$: C, 60.13; H, 6.31; N, 17.53. Found: C, 60.39; H, 6.33; N, 17.65.

1-(Benzotriazol-1-yl)-2-decanone *p*-Tosylhydrazone (5b): ^{1}H NMR δ 8.46 (s, 1 H), 8.00 (d, J = 8.3 Hz, 1 H), 7.72 (d, J = 8.3 Hz, 2 H), 7.35−7.19 (m, 4 H), 7.08 (d, J = 8.2 Hz, 1 H), 5.30 (s, 2 H), 2.47 (s, 3 H), 2.06 (t, J = 7.4 Hz, 2 H), 1.35−1.03 (m, 12 H), 0.85 (t, J = 7.0 Hz, 3 H); ^{13}C NMR δ 153.1, 146.1, 144.2, 134.9, 133.0, 129.6, 127.9, 127.4, 124.0, 119.8, 109.9, 53.4, 31.6, 29.4, 29.0, 28.9, 27.3, 24.5, 22.5, 21.6, 14.0. Anal. Calcd for $C_{23}H_{31}N_5O_2S$: C, 62.56; H, 7.08; N, 15.86. Found: C, 62.56; H, 7.26; N, 15.87.

1-(Benzotriazol-1-yl)-2-undecanone *p*-Tosylhydrazone (5c): ^{1}H NMR δ 8.47 (s, 1 H), 8.00 (d, J = 8.5 Hz, 1 H), 7.72 (d, J = 8.2 Hz, 2 H), 7.36−7.19 (m, 4 H), 7.07 (d, J = 8.2 Hz, 1 H), 5.30 (s, 2 H), 2.47 (s, 3 H), 2.11−2.00 (m, 2 H), 1.37−0.98 (m, 14 H), 0.87 (t, J = 7.0 Hz, 3 H); ^{13}C NMR δ 153.1, 146.1, 144.2, 134.9, 133.0, 129.6, 127.9, 127.4, 124.0, 119.8, 109.9, 53.4, 31.7, 29.4, 29.2, 29.1, 29.0, 27.4, 24.6, 22.5, 21.6, 14.0. Anal. Calcd for $C_{24}H_{33}N_5O_2S$: C, 63.27; H, 7.30; N, 15.37. Found: C, 62.99; H, 7.51; N, 15.24.

1-(Benzotriazol-1-yl)-2-(*p*-tolyl)ethan-2-one *p*-Tosylhydrazone (5d): ^{1}H NMR δ 8.06−7.98 (m, 1 H), 7.75 (s, 1 H), 7.65 (d, J = 8.3 Hz, 2 H), 7.41−7.32 (m, 3 H), 7.28 (d, J = 8.3 Hz, 2 H), 7.13 (d, J = 7.9 Hz, 2 H), 6.84 (d, J = 7.9 Hz, 2 H), 5.60 (s, 2 H), 2.47 (s, 3 H), 2.30 (s, 3 H); ^{13}C NMR δ 149.7, 146.1, 144.4, 141.2, 135.0, 133.1, 130.5, 129.7, 127.9, 127.6,

126.8, 126.0, 124.0, 119.9, 109.9, 54.0, 21.7, 21.3. Anal. Calcd for $C_{22}H_{21}N_5O_2S$: C, 62.99; H, 5.05; N, 16.69. Found: C, 62.94; H, 5.07; N, 16.79.

2-(Benzotriazol-1-yl)-2-phenylacetophenone *p*-Tosylhydrazone (5e): ^{1}H NMR δ 8.08−8.02 (m, 1 H), 7.70 (br s, 1 H), 7.40−7.30 (m, 11 H), 7.24−7.18 (m, 3 H), 7.14 (d, J = 14.9 Hz, 2 H), 7.04 (d, J = 8.5 Hz, 2 H), 2.39 (s, 3 H); ^{13}C NMR δ 151.3, 144.2, 143.0, 134.2, 133.7, 133.0, 130.7, 130.0, 129.8, 129.4, 129.0, 128.8, 127.6, 127.4, 123.9, 119.7, 111.9, 68.2, 21.6. Anal. Calcd for $C_{27}H_{23}N_5O_2S$: C, 67.34; H, 4.81; N, 14.54. Found: C, 67.01; H, 4.79; N, 14.36.

1-(Benzotriazol-1-yl)-1-pyrrolyl-2-octadecanone *p*-Tosylhydrazone (5f): ^{1}H NMR δ 8.51 (s, 1 H), 7.97 (d, J = 8.9 Hz, 1 H), 7.38 (s, 1 H), 7.37−7.23 (m, 2 H), 7.20−7.10 (m, 3 H), 6.94 (d, J = 8.0 Hz, 2 H), 6.72 (t, J = 2.2 Hz, 2 H), 6.14 (t, J = 2.2 Hz, 2 H), 2.38−2.23 (m, 5 H), 1.32−0.95 (m, 28 H), 0.80 (t, J = 6.6 Hz, 3 H); ^{13}C NMR δ 151.2, 146.2, 144.3, 134.1, 132.4, 129.4, 128.0, 127.6, 124.3, 120.5, 119.6, 111.5, 110.5, 74.1, 31.9, 29.6, 29.54, 29.50, 29.4, 29.3, 29.2, 29.0, 28.4, 24.6, 22.6, 21.5, 14.1. Anal. Calcd for $C_{35}H_{50}N_6O_2S$: C, 67.93; H, 8.14; N, 13.58. Found: C, 68.25; H, 8.43; N, 13.65.

1-(Benzotriazol-1-yl)-1-(phenylthio)-*p*-methylacetophenone *p*-Tosylhydrazone (5g): ^{1}H NMR δ 7.98 (t, J = 8.5 Hz, 2 H), 7.82 (s, 1 H), 7.53−7.46 (m, 3 H), 7.41 (t, J = 10.8 Hz, 1 H), 7.23−7.13 (m, 5 H), 7.12−7.05 (m, 3 H), 7.02−6.96 (m, 4 H), 2.42 (s, 3 H), 2.31 (s, 3 H); ^{13}C NMR δ 148.9, 146.7, 144.3, 141.4, 134.6, 133.4, 131.9, 131.1, 130.5, 129.5, 129.1, 129.0, 127.8, 127.4, 127.1, 125.7, 124.2, 119.7, 113.3, 71.7, 21.6, 21.3. Anal. Calcd for $C_{28}H_{25}N_5O_2S_2$: C, 63.74; H, 4.78; N, 13.27. Found: C, 63.97; H, 4.65; N, 13.34.

1-(Benzotriazol-1-yl)-1-(phenylthio)-2-nonadecanone *p*-Tosylhydrazone (5h): ^{1}H NMR δ 8.10 (br s, 1 H), 8.06−7.96 (m, 1 H), 7.74−7.64 (m, 1 H), 7.61 (d, J = 8.2 Hz, 2 H), 7.42−7.32 (m, 3 H), 7.25−7.16 (m, 2 H), 7.11 (t, J = 7.4 Hz, 2 H), 7.00 (d, J = 7.1 Hz, 2 H), 6.78 (s, 1 H), 2.44 (s, 3 H), 2.32−2.20 (m, 1 H), 2.15−2.01 (m, 1 H), 1.40−1.00 (m, 30 H), 0.88 (t, J = 6.6 Hz, 3 H); ^{13}C NMR δ 152.0, 146.7, 144.3, 134.5, 133.4, 131.7, 129.5, 129.2, 129.0, 128.3, 128.0, 127.4, 124.2, 119.7, 113.2, 71.4, 31.9, 30.0, 29.7, 29.6, 29.57, 29.45, 29.31, 29.27, 29.0, 28.3, 24.8, 22.6, 21.6, 14.1. Anal. Calcd for $C_{38}H_{53}N_5O_2S_2$: C, 67.52; H, 7.90; N, 10.36. Found: C, 67.33; H, 8.16; N, 10.47.

1-(Benzotriazol-1-yl)-1-phenoxy-*p*-methylacetophenone *p*-Tosylhydrazone (14a): ^{1}H NMR δ 8.05−8.03 (m, 1 H), 7.78 (s, 1 H), 7.64−7.60 (m, 1 H), 7.49 (s, 1 H), 7.41−7.32 (m, 2 H), 7.30−7.22 (m, 4 H), 7.18- 7.06 (m, 6 H), 6.95 (t, J = 7.4 Hz, 1 H), 6.88 (d, J = 8.8 Hz, 2 H), 2.38 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR δ 155.9, 148.4, 146.3, 144.2, 141.3, 134.4, 132.3, 130.5, 129.7, 129.4, 127.8, 127.7, 127.66, 125.3, 124.3, 123.4, 119.6, 116.2, 112.4, 88.5, 21.5, 21.4. Anal. Calcd for $C_{28}H_{25}N_5O_3S$: C, 65.74; H, 4.93; N, 13.69. Found: C, 66.10; H, 5.03; N, 13.57.

1-(Benzotriazol-1-yl)-1-phenoxyhexan-2-one *p*-Tosylhydrazone (14b): ^{1}H NMR δ 8.47 (s, 1 H), 8.07−8.01 (m, 1 H), 7.60−7.48 (m, 1 H), 7.46−7.39 (m, 2 H), 7.38−7.14 (m, 5 H), 7.12−6.82 (m, 5 H), 2.72−2.25 (m, 2 H), 2.35 (s, 3 H), 1.62−1.41 (m, 2 H), 1.40−1.22 (m, 2 H), 0.82 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 155.9, 151.5, 146.2, 144.1, 134.9, 132.2, 129.8, 129.3, 127.8, 127.6, 124.2, 123.4, 119.6, 116.0, 112.0, 87.7, 27.0, 26.8, 22.8, 21.5, 13.6. Anal. Calcd for $C_{25}H_{27}N_5O_3S$: C, 62.87; H, 5.70; N, 14.66. Found: C, 63.14; H, 5.97; N, 14.81.

1-(Benzotriazol-1-yl)-1-phenoxy-2-phenylethan-2-one *p*-Tosylhydrazone (14c = 14d): ^{1}H NMR δ 8.10−8.01 (m, 1 H), 7.78−7.70 (m, 1 H), 7.62−7.56 (m, 1 H), 7.54−7.43 (m, 3 H), 7.42−7.06 (m, 11 H), 6.96 (t, J = 7.2 Hz, 1 H), 6.86 (d, J = 8.0 Hz, 2 H), 2.39 (s, 3 H); ^{13}C NMR δ 155.9, 148.2, 146.4, 144.4, 134.4, 132.3, 131.0, 129.9, 129.8, 129.5, 129.4, 127.9, 127.8, 127.7, 124.3, 123.5, 119.6, 116.2, 112.3, 88.6, 21.6. Anal. Calcd for $C_{27}H_{23}N_5O_3S$: C, 65.18; H, 4.66; N, 14.08. Found: C, 65.05; H, 4.66; N, 14.12.

1-(Benzotriazol-1-yl)-1-phenoxy-2-nonanone *p*-Tosylhydrazone (14e = 14f): ^{1}H NMR δ 8.94 (s, 1 H), 8.10−8.02 (m, 1 H), 7.64−7.56 (m, 1 H), 7.43−7.32 (m, 2 H), 7.30−7.23 (m, 3 H), 7.20−7.15 (m, 2 H), 7.04 (d, J = 8.1 Hz, 2 H), 7.00−6.91 (m, 3 H), 2.61−2.40 (m, 2 H), 2.35 (s, 3 H), 1.60−1.42 (m, 2 H), 1.30−1.00 (m, 8 H), 0.81 (t, J = 6.9 Hz, 3 H); ^{13}C NMR δ 155.9, 151.7, 146.1, 144.0, 134.3, 132.2, 129.8, 129.3, 127.8, 127.6, 124.2, 123.4, 119.6, 116.0, 112.0, 87.7, 31.4, 29.5, 28.7, 27.3, 24.8, 22.4, 21.5, 13.9. Anal. Calcd for $C_{28}H_{33}N_5O_3S$: C, 64.72; H, 6.40; N, 13.48. Found: C, 64.92; H, 6.62; N, 13.26.

1-(Benzotriazol-1-yl)-2-phenylethan-2-one *p*-Tosylhydrazone (21b): mp 158−160 °C; ^{1}H NMR δ 8.08−8.00 (m, 1 H), 7.84 (s, 1 H), 7.66 (d, J = 7.5 Hz, 2 H), 7.50−7.25 (m, 8 H), 7.01−6.90 (m, 2 H), 5.66 (s, 2 H), 2.50 (s, 3 H); ^{13}C NMR δ 149.4, 146.0, 144.4, 134.9, 133.1, 130.7, 129.8, 129.7, 129.1, 127.9, 127.6, 126.8, 124.0, 119.9, 109.8, 53.9, 21.6. Anal. Calcd for $C_{21}H_{19}N_5O_2S$: C, 62.21; H, 4.72; N, 17.27. Found: C, 62.15; H, 4.68; N, 17.31.

2-(Benzotriazol-1-yl)-3-phenylpropan-3-one *p*-Tosylhydrazone (21c): mp 179−180 °C; ^{1}H NMR δ 8.01 (d, J = 7.9 Hz, 1 H), 7.72 (d, J = 8.5 Hz, 2 H), 7.59 (s, 1 H), 7.40−7.24 (m, 8 H), 6.69 (d, J = 8.0 Hz, 2 H), 5.91 (q, J = 7.1 Hz, 1 H), 2.50 (s, 3 H), 1.92 (d, J = 7.2 Hz, 3 H); ^{13}C NMR δ 153.0, 146.4, 144.4, 135.1, 132.3, 130.6, 129.74, 129.71, 129.0, 127.9, 127.4, 126.8, 123.9, 120.1, 110.2, 60.6, 21.7, 16.8. Anal. Calcd for $C_{22}H_{21}N_5O_2S$: C, 62.99; H, 5.05; N, 16.69. Found: C, 62.59; H, 4.97; N, 16.62.

Preparation of Acetylenes 9a−h, 18a−f, and 23a−c. General Procedure. To a stirred suspension of the corresponding (*p*-toluenesulfonyl) hydrazone **5a−h**, **14a−f**, or **21a−c** (2 mmol) in diethyl ether (40 mL) was added the appropriate lithium reagent (6 equiv) (for compounds **9a−h** and **21a−c**, *n*-butyllithium was used and for compounds **18a−f**, see Scheme 2 and Table 2) at −78 °C. After the mixture was stirred for 0.5 h at −78 °C and 48 h at room temperature, the reaction was quenched with water, and the solution was extracted with diethyl ether and dried over anhydrous $MgSO_4$. Removal of the solvent *via* rotary evaporation gave a residue which was subjected to column chromatography using pentane or hexane as the eluent to provide the corresponding acetylene **9a−h**, **18a−f**, or **21a−c** (Tables 1 and 2, Scheme 3).

1-Heptyne (9a = 23a): oil (lit.[21] bp 99−100 °C); ^{1}H NMR δ 2.30−2.16 (m, 2 H), 1.93 (t, J = 2.3 Hz, 1 H), 1.65−1.28 (m, 6 H), 0.91 (t, J = 6.9 Hz, 3 H); ^{13}C NMR δ 84.7, 68.0, 30.9, 28.2, 22.1, 18.3, 13.9.

1-Decyne (9b): oil (lit.[22] bp 60−62 °C/0.8 mmHg); ^{1}H NMR δ 2.60−2.55 (m, 2 H), 2.32 (t, J = 2.3 Hz, 1 H), 1.95−1.68 (m, 12 H), 1.29 (t, J = 6.1 Hz, 3 H); ^{13}C NMR δ 84.5, 68.0, 31.8, 29.2, 29.1, 28.8, 28.5, 22.6, 18.4, 14.0.

1-Undecyne (9c): oil (lit.[23] bp 75−78 °C/10 mmHg); ^{1}H NMR δ 2.24−2.18 (m, 2 H), 1.96 (t, J = 2.6 Hz, 1 H), 1.62−1.49 (m, 2 H), 1.49−1.22 (m, 12 H), 0.91 (t, J = 6.7 Hz, 3 H); ^{13}C NMR δ 84.5, 68.0, 31.9, 29.5, 29.3, 29.1, 28.8, 28.5, 22.7, 18.4, 14.0.

Tolylacetylene (9d = 9g): oil (lit.[24] bp 64−66 °C); ^{1}H NMR δ 7.37 (d, J = 8.2 Hz, 2 H), 7.10 (d, J = 7.9 Hz, 2 H), 3.01 (s, 1 H), 2.33 (s, 3 H); ^{13}C NMR δ 138.9, 132.0, 129.0, 119.0, 83.8, 76.4, 21.4.

Diphenylacetylene (9e = 18d): mp 59−60 °C (lit.[8] mp 59−60 °C); ^{1}H NMR δ 7.53−7.50 (m, 4 H), 7.36−7.25 (m, 6 H); ^{13}C NMR δ 131.5, 128.3, 128.2, 123.2, 89.4.

1-Pyrrolyl-1-octadecyne (9f): ^{1}H NMR δ 6.83 (t, J = 2.2 Hz, 2 H), 6.15 (t, J = 2.2 Hz, 2 H), 2.34 (t, J = 7.0 Hz, 2 H), 1.62−1.24 (m, 28 H), 0.90 (t, J = 6.7 Hz, 3 H); ^{13}C NMR δ 124.5, 109.5, 74.3, 65.9, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 28.8, 22.7, 18.2, 14.1; HRMS ($M^+ + 1$) calcd for $C_{22}H_{38}N$ 316.3004, found 316.2993.

1-Nonadecyne (9h): mp 36−38 °C (lit.[25] mp 37−38 °C); ^{1}H NMR δ 2.22−2.15 (m, 2 H), 1.94 (t, J = 2.6 Hz, 1 H), 1.60−1.26 (m, 30 H), 0.89 (t, J = 6.8 Hz, 3 H); ^{13}C NMR δ 84.8, 68.0, 31.9, 29.7, 29.6, 29.5, 29.4, 29.1, 28.1.

1-(*p*-Methylphenyl)-1-hexyne (18a): ^{1}H NMR δ 7.30 (d, J = 8.0 Hz, 2 H), 7.09 (d, J = 8.0 Hz, 2 H), 2.41 (t, J = 7.0 Hz, 2 H), 2.34 (s, 3 H), 1.66−1.42 (m, 4 H), 0.96 (t, J = 7.3 Hz, 3

(21) Henne, A. L.; Greenlee, K. W. *J. Am. Chem. Soc.* **1945**, *67*, 484.
(22) Klein, J.; Gurfinkel, E. *Tetrahedron* **1970**, *26*, 2127.
(23) Epsztein, R.; Marszak, I. *Mem. services chim. état (Paris)* **1953**, *38*, 165; *Chem. Abstr.* **1956**, *50*, 2415b.
(24) Schlosser, M.; Ladenberger, V. *Chem. Ber.* **1967**, *100*, 3901.
(25) Coffman, D. D.; Tsao, J. C.-Y.; Schniepp, L. E.; Marvel, C. S. *J. Am. Chem. Soc.* **1933**, *55*, 3792.

H); ^{13}C NMR δ 137.3, 131.4, 128.9, 121.0, 89.5, 80.5, 30.9, 22.0, 21.4, 19.1, 13.6; HRMS (M^+) calcd for $C_{13}H_{16}$ 172.1252, found 172.1262.

5-Decyne (18b): oil (lit.[26] bp 172 °C/745 mmHg); ^{1}H NMR δ 2.14 (t, J = 3.0, 4 H), 1.46−1.36 (m, 8 H), 0.90 (t, J = 7.2 Hz, 6 H); ^{13}C NMR δ 80.0, 31.3, 21.9, 18.4, 13.5.

1-Phenylpropyne (18c = 23c): oil (lit.[27] bp 113 °C/84 mmHg); ^{1}H NMR δ 7.76−7.66 (m, 2 H), 7.64−7.54 (m, 3 H), 2.33 (s, 3 H); ^{13}C NMR δ 131.4, 128.1, 127.4, 124.0, 85.7, 79.7, 4.2.

1-Phenyl-1-nonyne (18e): oil; ^{1}H NMR δ 7.43−7.35 (m, 2 H), 7.30−7.23 (m, 3 H), 2.40 (t, J = 7.1 Hz, 2 H), 1.66−1.54 (m, 2 H), 1.50−1.40 (m, 2 H), 1.39−1.20 (m, 6 H), 0.90 (t, J = 6.7 Hz, 3 H); ^{13}C NMR δ 131.5, 128.1, 127.4, 124.1, 90.5, 80.6, 31.8, 28.9, 28.84, 28.79, 22.6, 19.4, 14.1; HRMS (M^+) calcd for $C_{15}H_{20}$ 200.1565, found 200.1567.

2-Decyne (18f): oil (lit.[22] bp 61 °C/0.8 mmHg); ^{1}H NMR δ 2.16−2.06 (m, 2 H), 1.77 (t, J = 2.5 Hz, 3 H), 1.52−1.20 (m, 10 H), 0.88 (t, J = 6.7 Hz, 3 H); ^{13}C NMR δ 79.3, 75.2, 31.8, 29.1, 28.9, 22.6, 18.7, 14.0, 3.4.

Phenylene (23b): oil (lit.[28] bp 73−74 °C/80 mmHg); ^{1}H NMR δ 7.62−7.46 (m, 2 H), 7.42−7.28 (m, 3 H), 3.07 (s, 1 H); ^{13}C NMR δ 132.1, 128.7, 128.3, 122.1, 83.6, 77.1.

Preparation of α-(Benzotriazol-1-yl) Ketones 22a−c from α-(Benzotriazol-1-yl) Esters 20a,b. An α-(benzotriazol-1-yl) ester **20a** or **20b** (10 mmol) was dissolved in dry THF/diethyl ether (100 mL, 1:1) and cooled to −78 °C. Grignard reagent (pentylmagnesium iodide or phenylmagnesium bromide) (15 mmol) in diethyl ether (15 mL) was slowly added with stirring. The mixture was allowed to warm to −40 °C, stirred overnight at −40 °C, and then poured into a saturated ammonium chloride solution followed by extraction with diethyl ether (3 × 25 mL). The combined organic extracts were washed with saturated brine (2 × 60 mL), dried with $MgSO_4$, and filtered. Removal of the solvent gave the residue, which was chromatographed on silica, using ethyl acetate/hexane (1:4) as the eluent, to afford the corresponding ketone (**20a−c**).

1-(Benzotriazol-1-yl)acetophenone (22b): mp 112−113 °C (lit.[29] mp 109−111 °C); ^{1}H NMR δ 8.11−7.97 (m, 3 H), 7.68−7.25 (m, 6 H), 6.06 (s, 2 H); ^{13}C NMR δ 190.4, 145.8, 134.3, 133.8, 133.7, 128.9, 128.1, 127.6, 123.8, 119.8, 109.4, 53.7.

1-Phenyl-2-(1-benzotriazol-1-yl)propanone (22c): mp 159−161 °C; ^{1}H NMR δ 8.06−7.96 (m, 2 H), 7.69−7.25 (m, 7 H), 6.72 (q, J = 7.2 Hz, 1 H), 1.96 (d, J = 7.2 Hz, 3 H); ^{13}C NMR δ 193.7, 146.2, 133.9, 133.8, 131.9, 128.7, 128.4, 127.4, 123.8, 119.8, 110.1, 59.1, 16.1. Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.67; H, 5.35; N, 16.85.

Preparation of Bifunctional Ketone 27, Hydrazone 28, and Acetylene 29. The procedures were the same as for the preparation of monofunctional ketones, hydrazones, and acetylenes as described above, except that 2 equiv of lithium reagent **25**, tosylhydrazine, and *n*-butyllithium were used.

1,10-Bis(benzotriazol-1-yl)-1,10-diphenyl-2,9-decanedione (27): purified by column chromatography using EtOAc/hexane (1:2) as the eluent; mp 63-65 °C; ^{1}H NMR δ 8.06−8.03 (m, 2 H), 7.43−7.29 (m, 14 H), 7.26−6.89 (m, 2 H), 6.74 (s, 2 H), 2.59 (t, J = 7.3 Hz, 4 H), 1.69−1.54 (m, 4 H), 1.30−1.18 (m, 4 H); ^{13}C NMR δ 202.9, 146.3, 133.0, 132.4, 129.5, 129.2, 128.9, 127.6, 124.0, 120.1, 110.6, 71.3, 40.5, 28.4, 23.2. Anal. Calcd for $C_{34}H_{32}N_6O_2$: C, 73.36; H, 5.79; N, 15.10. Found: C, 73.14; H, 5.63; N, 15.39.

1,10-Bis(benzotriazol-1-yl)-1,10-diphenyl-2,9-decanedione bis-*p*-tosylhydrazone (28): purified by recrystallization from acetone/hexane; mp 190−191 °C; ^{1}H NMR δ 10.50 (s, 2 H), 7.98 (d, J = 7.7 Hz, 2 H), 7.38−7.26 (m, 14 H), 7.20−7.14 (m, 6 H), 7.10 (d, J = 8.0 Hz, 4 H), 6.83 (s, 2 H), 2.38 (s, 6 H), 2.33−2.22 (m, 4 H), 1.36−1.03 (m, 8 H); ^{13}C NMR δ 154.5, 145.3, 142.6, 135.2, 134.2, 132.5, 128.6, 128.1, 128.0, 127.1, 126.7, 123.3, 118.8, 111.0, 66.3, 28.7, 28.3, 23.8, 20.9. Anal. Calcd for $C_{48}H_{48}N_{10}O_4S_2$: C, 64.55; H, 5.42; N, 15.68. Found: C, 64.93; H, 5.53; N, 15.49.

1,10-Diphenyl-1,9-decadiyne (29): purified by column chromatography using pentane as the eluent; oil; ^{1}H NMR δ 7.43−7.35 (m, 4 H), 7.31−7.21 (m, 6 H), 2.42 (t, J = 6.9 Hz, 4 H), 1.70−1.48 (m, 8 H); ^{13}C NMR δ 131.5, 128.1, 127.4, 126.9, 90.2, 80.7, 28.6, 28.4, 19.4; Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.06; H, 7.55.

Note Added in Proof. It is likely that the large excess of BuLi required is due to ring lithiation of the tosyl group and that a stoichiometric amount of BuLi could be used if $MeC_6H_4SO_2NHNH_2$ was replaced by the (2,4,6-triisopropylphenyl)sulfonyl analog (cf. Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147). We thank Dr. Rob Adlington (Oxford) for calling our attention to this point.

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Supporting Information Available: HRMS and NMR spectra of compounds **9f**, **18a**, and **18e** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(26) Vaughn, T. H.; Hennion, G. F.; Vogt, R. R.; Nieuwland, J. A. *J. Org. Chem.* **1937**, *2*, 17.
(27) Campbell, K. N.; O'Connor, M. J. *J. Am. Chem. Soc.* **1939**, *61*, 2897.
(28) Campbell, K. N.; Campbell, B. K. *Organic Syntheses*; John Wiley & Sons: New York, 1963; Collect. Vol. 4, p 763.
(29) Katritzky, A. R.; Wrobel, L.; Savage, G. P.; Deyrup-Drewniak, M. *Aust. J. Chem.* **1990**, *43*, 133.