One-Carbon Homologation of Carboxylic Acids via $BtCH_2TMS$: A Safe Alternative to the Arndt−Eistert Reaction

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Carboxylic acids are converted into the corresponding homologated acids or esters, using easily available 1-(trimethylsilylmethyl)benzotriazole (**1**) as a one-carbon synthon. The effectiveness of the reaction has been investigated on six aryl and seven alkyl carboxylic acids.

Introduction

Homologations of carbonyl compounds by a carbon−carbon coupling reaction[1] provide many attractive routes to higher analogue carbonyl compounds with one,[2] two,[3] three,[1] and four[1,4] additional carbon atoms. These techniques have enormously increased the synthetic utility of the carbonyl-containing compounds and have greatly diversified the nature of the chemical reactions available to a synthetic chemist for the construction of new carbon−carbon bonds. Since the synthetic exploitation of carbonyl-containing and particularly acyl functional groups plays a commanding role in the construction of a molecular backbone, reaction sequences that result in a carbon chain extension at a carbonyl group by one or more carbon atoms producing an aldehyde, ketone, or carboxylic acid are especially significant.

Among these reactions, one-carbon homologation of carbonyl compounds is the most important. Three general methods are available for the direct conversions of an acid or an acid derivative into a one-carbon higher homologated analogue: (1) The Arndt−Eistert reaction[5] (Scheme 1a) is the most important and most commonly used procedure for converting a carboxylic acid into its one-carbon higher homologue acid (or ester or amide derivative) with diazomethane; however, to achieve high overall yields, the intermediate diazo compounds often have to be recrystallized, and freshly prepared silver benzoate is required. The classical procedure also suffers from handling difficulties, hindering the large-scale preparations: for example, α-diazomethyl ketones are hazardous and strong skin irritant intermediates.[5j] Modified Arndt−Eistert procedures ease these only in part.[5i,k]

(2) Barton's radical homologation[6] gives good yields but employs the unstable intermediate *O*-acyl-*N*-hydroxylthiopyridone and two-carbon radical trap, phenyl vinyl sulfone, as a one-carbon synthon (Scheme 1b).

(3) Kowalski's ester homologation with CH_2Br_2 synthon[7] affords good yields using the modified procedure. A limitation is that a strong base is required (Scheme 1c).

In our preliminary communication,[8] we have reported that 1-(trimethylsilylmethyl)benzotriazole (**1**) reacts with acyl chlorides to give the corresponding one-carbon homologated acids or esters. In this paper, we describe in detail our study of a convenient, safe alternative for acid homologation with the one-carbon synthon 1-(trimethylsilylmethyl)benzotriazole (**1**), utilizing the anion-stabilizing and leaving-group properties of benzotriazole.[9]

Results and Discussion

Preparation of 1-(Trimethylsilylmethyl)benzotriazole (1) and *N*-Acylmethylbenzotriazoles 3a−m. 1-(Trimethylsilylmethyl)benzotriazole (**1**) and *N*-acylm-

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Scheme 1

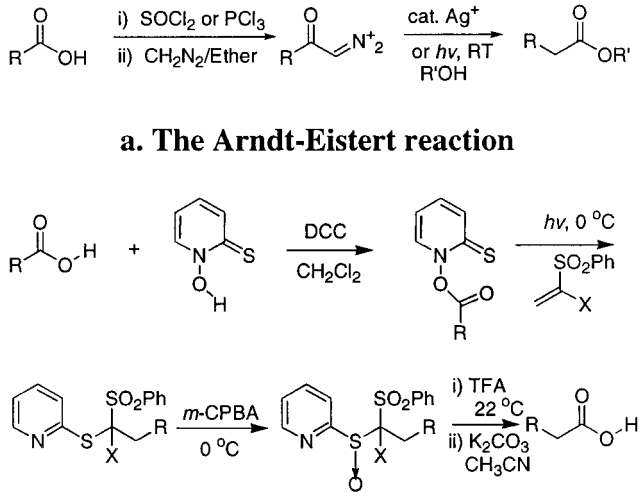

Table 1. One-Carbon Homologation of Carboxylic Acid Chlorides 2 to Derivatives 7

		isolated yields (%)			
2	R	**3**	**4**	**5**	**7**[a]
a	C_6H_5	85	95	98	89[b]
b	*p*-ClC_6H_4	90	95	97	98[c]
c	*p*-$CH_3OC_6H_4$	90	93	92	93[c]
d	*p*-$CH_3C_6H_4$	91	90	95	90[c]
e	*m*-$CH_3C_6H_4$	87	83	91	92[c]
f	*o*-$CH_3C_6H_4$	90	87	92	92[c]
g	$C_6H_5CH_2CH_2$	94	96	94	24[d]
h	CH_3	83	88	90	68[d]
i	$(CH_3)_3CCH_2$	95	95	98	62[d]
j	$(CH_3)_3CCH_2CH(CH_3)CH_2$	90	98	96	48[d]
k	$CH_3(CH_2)_4$	97	94	92	59[d]
l	*n*-$CH_3(CH_2)_6$	95	90	92	49[d]
m	*p*-$ClC_6H_4CH_2$	86	82		

[a] Isolated yield. [b] Methyl ester from **4** (Method A). [c] Ethyl ester from **4** in one-pot reaction (method A). [d] Acid from 8.

ethylbenzotriazoles **3a**−**m** (Table 1) were prepared according to the literature procedures in good yields (83−97%).[10]

Preparation of Enol Triflates 4a−m. *Z*-Enol triflates **4a**−**m** can be easily obtained stereoselectively from *N*-acylmethylbenzotriazoles **3a**−**m** (Scheme 2): treatment of **3a**−**m** with triflic anhydride (Tf_2O) in the presence of 2,6-lutidine at 0−20 °C for 2−12 h affords the corresponding enol triflates **4** in excellent isolated yields (82−98%) (see Table 1 and Scheme 2); no stereoisomers were isolated. The *Z*-configuration of the enol triflate **4j** was assigned on the basis of NOE experiments. On irradiation of the vinylic proton in **4j** at 7.42 ppm, NOE between the methylene group and this proton was

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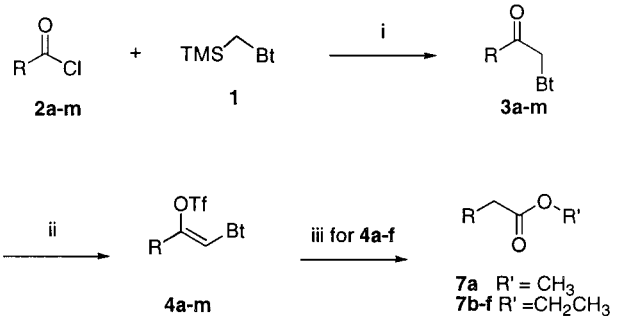
Scheme 2[a]



[a] Reagents and conditions: (i) THF, reflux; (ii) Tf_2O, 2,6-lutidine, CH_2Cl_2, 0−20 °C; (iii) (a) $NaOCH_3$, acetonitrile, 65 °C, 2 h, (b) concentrated HCl in an alcohol, reflux.

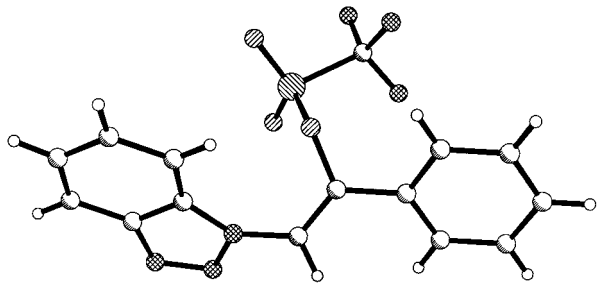


Figure 1. Perspective view of the X-ray crystal structure of **4a**.

observed, indicating that the alkyl and Bt groups in **4j** are mutually trans. For aromatic compounds **4a**−**f**, no obvious NOE were observed resulting from the rotation of the aryl group, which may be perpendicular to the olefin.

To clarify the stereochemistry of these compounds, an X-ray crystal structure determination was carried out on **4a**. Figure 1 shows a perspective view of the structure, which confirms unambiguously the *Z*-stereochemistry of the enol triflate. In the solid state, the planes of the phenyl and benzotriazole ring systems are inclined to the plane of the double bond at angles of 25.3(3) and 36.4(3)°, respectively.

Conversion of Aromatic Enol Triflates 4a−f into the Corresponding Esters. Treatment of aromatic enol triflates **4a**−**f** with 2.2 equiv of $NaOCH_3$ in acetonitrile at 65 °C for 2 h followed by hydrolysis with concentrated HCl in methanol or ethanol afforded the methyl or ethyl ester **7a**−**f** in good to excellent yield depending on the alcohol used (Table 1).

We postulate the reaction sequence outlined in Scheme 3. Enol triflate **4a** was treated with 2 N NaOH in THF at 20 °C for 30 min to afford 1-(2-phenylethynyl)-1*H*-1,2,3-benzotriazole (**5a**) (previously prepared in 56% yield using phenylethynyl phenyliodonium tosylate[11]) in quantitative yield. The effects of the base and solvent are small, using 2 N NaOH/THF or $NaOCH_3/CH_3CN$ gave similar results. Aromatic alkynylbenzotriazoles **5b**−**d**,[11] **e**, and **f** were obtained using the same procedure in excellent yields (Table 1).

Refluxing a reaction mixture of **5a** and $NaOCH_3$ in acetonitrile at 65 °C for 2 h afforded 1-[(*E*)-1-methoxy-

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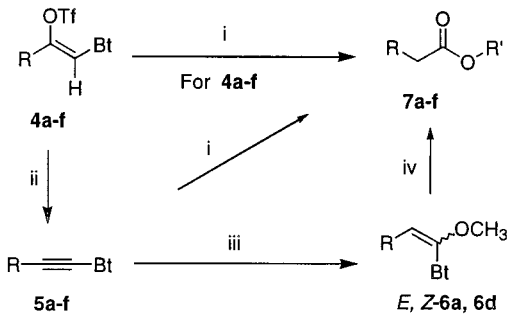
Scheme 3[a]



[a] Reagents and conditions: (i) (a) $NaOCH_3$ in CH_3CN, 65 °C, (b) concentrated HCl in an alcohol, 70 °C; (ii) $NaOCH_3$ in CH_3CN or NaOH in THF, 20 °C; (iii) $NaOCH_3$, acetonitrile, 65 °C, 2 h; (iv) concentrated HCl in an alcohol, 70 °C.

2-phenylethenyl]-1*H*-1,2,3-benzotriazole (*E*-**6a**)[12] as the major product together with 1-[(*Z*)-1-methoxy-2-phenylethenyl]-1*H*-1,2,3-benzotriazole (Z-**6a**)[12] as the minor product. No regioisomers were isolated. NOE experiments with *E*-**6a** displayed the interaction between OCH_3 group and the vinylic proton when the vinylic proton at 6.11 ppm was irradiated. The ratio of *E*/*Z*-**6a** is about 80:20 on the basis of ^{1}H NMR spectra of the crude product. Analogous intermediate *E*-**6d** can be isolated in 85% yield. The mixture of *E*-**6a** and *Z*-**6a** was hydrolyzed with concentrated HCl in methanol under reflux yielding the homologated methyl 2-phenylacetate **7a** in 96% yield.

Ethyl 2-(4-chlorophenyl)acetate **7b** was similarly obtained by treatment of **5b** with 1.0 equiv of $NaOCH_3$ in CH_3CN under reflux followed by hydrolysis with concentrated HCl in ethanol in 98% overall yield. Analogous two-step reactions from **4** gave **7c**−**f** in excellent yields (Table 1).

Conversion of Aliphatic Enol Triflates 4g−**l into the Corresponding Acids.** Applied to the aliphatic series, the above procedure gives different results. Allene compound **9i** (34%) and compound **10i** (27%) with the triple bond shifted were obtained when **4i** or **5i** was treated with $NaOCH_3$ in CH_3CN at 65 °C using the discussed procedure above (Scheme 4). No desired adducts were formed. Similar treatment of **4j** gave only triple bond shifted compound **10j** in 42% yield.

However, when aliphatic enol triflates **4g**−**m** were treated with 2.2 equiv of $NaOCH_3$/CH_3CN or 2 N NaOH/THF at room temperature for 1 h, aliphatic alkynylbenzotriazoles **5g**−**l** were obtained in good yields after workup (Table 1). Significantly, the only other known attempt to prepare similar compounds, using direct alkynylation of benzotriazole with alkynyliodonium salts, failed.[11] However, for **4m**, only allene compound **9m** was isolated in 75% yield even at 20 °C, which is not surprising because of the high acidity of benzylic and allylic protons compared to a sp^2 vinylic proton (Scheme 4).

Treatment of **5g**−**l** with *p*-toluenesulfonic acid monohydrate in acetonitrile at 65 °C for 2−12 h generated enol toluenesulfonates **8g**−**l** in good yields with a small amount of the regioisomers (about 10%) and small amount of hydrolyzed product **7g**−**l** (5%). For compound **5g**, the yield of **8g** is poor because cyclization product **11g** was isolated in 30% yield. The generation of **7g**−**l** was best carried out by the treatment of **8g**−**l** with 1 equiv of TBAF in THF at 70 °C. Direct treatment of **5l** with *p*-toluenesulfonic acid followed by the hydrolysis with TBAF in THF without the isolation of intermediate **8l** also generated **7l** in 49% GC yield (21% isolated yield). This one-pot procedure, though more convenient, affords a lower yield of the product. As shown in Table 2, various conditions for the hydrolysis of **8l** were investigated. The reaction conditions gave only moderate GC yield (10−34%).

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Conclusion

In summary, a concise and practical procedure for the transformation of both aromatic and aliphatic carboxylic acids into one-carbon homologated acid derivatives in good to excellent yields has been developed using readily available, versatile, and high-yielding reagent 1-(trimethylsilylmethyl)benzotriazole (**1**) as a one-carbon synthon. The mildness of the reaction conditions, good yields, and the simple workup procedure show the usefulness of this novel approach. 1-Alkynylbenzotriazoles **5a**−**l** greatly extends the scope of benzotriazole chemistry.

Experimental Section

General Methods. Melting points were determined on a MEL-TEMP capillary melting point apparatus equipped with a Fluke 51 digital thermometer. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H (300 MHz) and ^{13}C (75 MHz). THF was distilled from sodium/benzophenone under nitrogen immediately prior to use. All reactions with air-sensitive compounds were carried out under argon atmosphere. Column chromatography was conducted with silica gel (230−400 mesh).

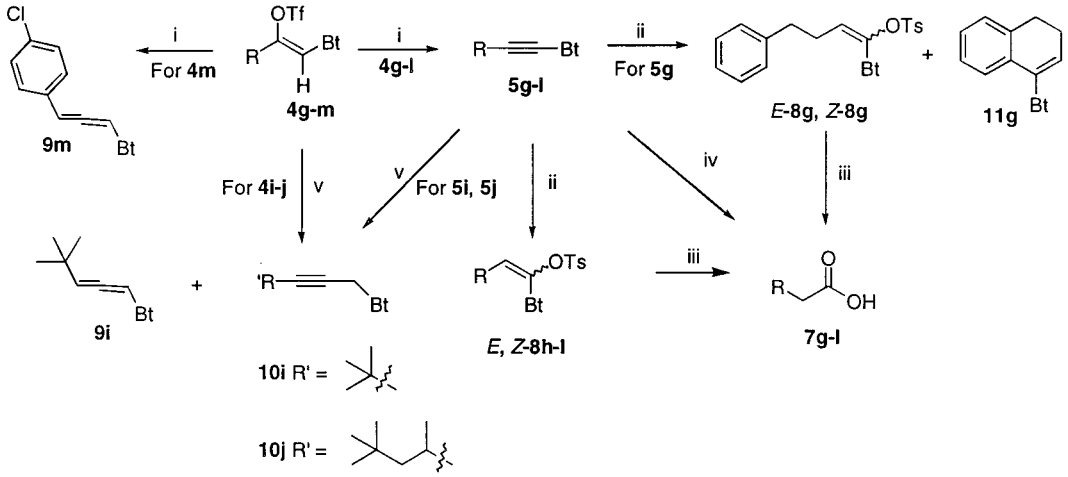
Typical Procedure for the Preparation of 4. To a cooled (0 °C) solution of **3a**−**m** (10 mmol) and 2,6-lutidine (3.47 mL, 20 mmol) in 20 mL of dry CH_2Cl_2 was added dropwise Tf_2O (3.36 mL, 14 mmol). After the mixture was stirred for 10 min, the ice bath was removed, and the reaction mixture was allowed to warm to 25 °C and stirred overnight. Hexane (20 mL) was added to the reaction mixture. The pyridinium salt was filtered off, and the precipitate was washed with ethyl acetate. The filtrate was washed with saturated NH_4Cl, brine, and H_2O, dried over $MgSO_4$, and concentrated in vacuo to dryness. The residue was recrystallized from hexanes−ethyl acetate to afford white crystals of **4a**−**m** in yields of 82−98%.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-phenylethenyl trifluoromethanesulfonate (4a): white needles; mp 98−99 °C (95%, hexane−ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (1H, dd, J = 8.3, 0.7 Hz, Bt), 7.70−7.75 (2H, m), 7.62−7.63 (2H, m), 7.60 (1H, s, CH=), 7.45−7.55 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3 (s), 142.3 (s), 132.4 (s), 131.0 (d), 129.6 (s), 129.2 (d, 2 × CH), 128.8 (d), 126.2 (d, 2 × CH), 124.9 (d), 120.5 (d), 118.2 (q, J = 319.0 Hz, CF_3), 113.8 (d), 109.9 (d). Anal. Calcd for $C_{15}H_{10}F_3N_3O_3S$: C, 48.78; H, 2.73; N, 11.38. Found: C, 48.89; H, 2.55; N, 11.33.

Crystal data for 4a: $C_{15}H_{10}F_3N_3O_3S$, MW 369.32, triclinic, space group *P*-1, a = 6.258(3) Å, b = 10.756(5) Å, c = 12.458(6) Å, α = 104.722(5)°, β = 93.709(6)°, γ = 96.542(6)°, V = 801.9(6) Å^3, $F(000)$ = 376, Z = 2, T = −100 °C, μ(Mo Kα) = 0.255 mm^{-1}, D_{calcd} = 1.530 g·cm^{-3}, $2\theta_{max}$ 50° (CCD area detector, Mo Kα radiation), GOF = 1.095, wR(F^2) = 0.1330 (all 2618 data), R = 0.0514 (2145 data with $I > 2\sigma I$).

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-chlorophenyl)-ethenyl trifluoromethanesulfonate (4b): white needles; mp 156−157 °C (95%, hexane−ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (1H, d, J = 8.3 Hz, Bt), 7.64−7.67 (5H, m), 7.51−7.17 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3 (s), 140.9 (s), 137.2 (s), 132.4 (s), 129.6 (s), 129.5 (d), 128.8 (d), 127.4 (d), 125.0 (d), 120.5 (d), 118.0 (q, J = 319.0 Hz, CF_3), 114 (d), 109.7

Scheme 4[a]



[a] Reagents and conditions: (i) $NaOCH_3$ in CH_3CN or NaOH in THF, 20 °C; (ii) *p*-TSA in CH_3CN, 65 °C, 2−12 h; (iii) TBAF in THF, 65 °C, 3−7 h; (iv) (a) *p*-TSA in CH_3CN, reflux, (b) 2 N NaOH in acetone or TBAF in THF, reflux; (v) $NaOCH_3$ in CH_3CN, 65 °C.

Table 2. Hydrolysis of 8l to 7l under Different Conditions

entry	reagent	solvent	time (h)	*T* (°C)	yield[a] (%)
1	concd HCl	EtOH	24	70	25
2	2 N NaOH	DMSO	4	20	34
3	2 N NaOH	acetone	2	20	28
4	2 N NaOH	EtOH		75	10

[a] GC results of crude product.

(d). Anal. Calcd for $C_{15}H_9ClF_3N_3O_3S$: C, 44.62; H, 2.25; N, 10.14. Found: C, 44.49; H, 2.19; N, 10.22.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-methoxyphenyl)-ethenyl trifluoromethanesulfonate (4c): white needles; mp 113−114 °C (93%, hexane−ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (1H, d, J = 8.4 Hz), 7.66 (2H, d, J = 8.9 Hz), 7.59−7.61 (2H, d, J = 4.5 Hz), 7.49 (1H, s), 7.46 (1H, t, J = 4.6 Hz), 7.03 (2H, d, J = 8.9 Hz), 3.38 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8 (s), 145.2 (s), 143.0 (s), 132.5 (s), 128.6 (d), 127.9 (d, 2 × CH), 124.8 (d), 123.0 (s), 120.4 (d), 118.0 (q, J = 319.0 Hz, CF_3), 114.6 (d, 2 × CH), 112.2 (d), 109.9 (d), 55.5 (q). Anal. Calcd for $C_{16}H_{12}F_3N_3O_4S$: C, 48.12; H, 3.03; N, 10.52. Found: C, 48.12; H, 3.02; N, 10.38.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-methylphenyl)-ethenyl trifluoromethanesulfonate (4d): white needles; mp 147−148 °C (90%, hexane−ethyl acetate); ^{1}H NMR δ 8.10 (1H, dd, J = 8.3, 1.0 Hz, Bt), 7.59−7.62 (4H, m, Bt and aromatic proton), 7.56 (1H, s, CH ═), 7.42−7.48 (1H, m, Bt), 7.31 (2H, d, J = 8.1 Hz), 2.42 (3H, s, CH_3); ^{13}C NMR δ 145.2 (s), 142.8 (s), 141.5 (s), 132.5 (s), 129.9 (d, 2 × CH), 128.7 (d), 128.0 (s), 126.1 (d, 2 × CH), 124.8 (d), 120.3 (d), 118.0 (q, J = 319.6 Hz, CF_3), 113.0 (d), 109.9 (d), 21.4 (q). Anal. Calcd for $C_{16}H_{12}F_3N_3O_3S$: C, 50.13; H, 3.16; N, 10.96. Found: C, 50.19; H, 2.97; N, 10.92.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(3-methylphenyl)-ethenyl trifluoromethanesulfonate (4e): white microcrystals; mp 122 °C (83%, hexane−ethyl acetate); ^{1}H NMR δ 8.14 (1H, d, J = 8.4 Hz), 7.62 (2H, d, J = 3.8 Hz), 7.57 (1H, s), 7.54−7.35 (5H, m), 2.46 (3H, s); ^{13}C NMR δ 145.3 (s), 142.8 (s), 139.2 (s), 132.5 (s), 131.9 (d), 131.0 (s), 129.2 (d), 128.7 (d), 126.8 (d), 124.9 (d), 123.5 (d), 120.6 (d), 113.6 (d), 109.9 (d), 21.4 (q), missing CF_3.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(2-methylphenyl)-ethenyl trifluoromethanesulfonate (4f): white needles; mp 102 °C (87%, hexane−ethyl acetate); ^{1}H NMR δ 8.16 (1H, td, J = 8.2, 0.9 Hz), 7.63−7.57 (3H, m), 7.50−7.42 (2H, m), 7.35−7.33 (3H, m), 2.58 (3H, s); ^{13}C NMR δ 145.2 (s), 141.7 (s), 137.7 (s), 132.3 (s), 131.2 (d), 130.9 (d), 130.4 (d), 130.2 (s), 128.7 (d), 126.3 (d), 124.9 (d), 120.5 (d), 118.0 (q, J = 319 Hz, CF_3), 116.5 (d), 109.7 (d), 19.9 (q). Anal. Calcd for $C_{16}H_{12}F_3N_3O_3S$: C, 50.13; H, 3.16; N, 10.96. Found: C, 50.14; H, 3.04; N, 10.25.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-4-phenyl-1-butenyl trifluoromethanesulfonate (4g): white needles; mp 95−96 °C (87%, hexane−ethyl acetate); ^{1}H NMR δ 8.09 (1H, d, J = 8.2 Hz), 7.53 (1H, t, J = 7.7 Hz), 7.42 (1H, t, J = 7.8 Hz), 7.35 (1H, d, J = 7.1 Hz), 7.24−7.30 (4H, m), 6.98 (1H, s), 3.10 (2H, t, J = 7.0 Hz), 3.00 (2H, t, J = 7.0 Hz); ^{13}C NMR δ 145.2 (s), 144.7 (s), 138.6 (s), 132.3 (s), 128.9 (d, 2 × CH), 128.5 (d, 3 × CH), 127.0 (d), 124.6 (d), 120.3 (d), 114.8 (d), 109.8 (d), missing CF_3, 34.5 (t), 32.5 (t). Anal. Calcd for $C_{17}H_{14}F_3N_3O_3S$: C, 51.38; H, 3.55; N, 10.57. Found: C, 51.50; H, 3.57; N, 10.87.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-propenyl trifluoromethanesulfonate (4h): white microcrystals; mp 115−116 °C (88%, hexane−ethyl acetate); ^{1}H NMR δ 8.11 (1H, dd, J = 8.21, 0.9 Hz, Bt), 7.49−7.62 (2H, m), 7.41−7.47 (1H, m), 7.13 (1H, q, J = 1.2 Hz, CH ═), 2.43 (3H, d, J = 1.2 Hz, CH_3); ^{13}C NMR δ 145.2 (s), 142.4 (s), 132.3 (s), 128.6 (d), 124.7 (d), 120.3 (d), 118.5 (q, J = 319 Hz, CF_3), 114.1 (d), 109.8 (d), 18.8 (q). Anal. Calcd for $C_{10}H_8F_3N_3O_3S$: C, 39.09; H, 2.62; N, 13.68. Found: C, 39.49; H, 2.45; N, 13.59.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-4,4-dimethyl-1-pentenyl trifluoromethanesulfonate (4i): white needles; mp 97−99 °C (95%, hexanes−ethyl acetate); ^{1}H NMR δ 8.10 (1H, d, J = 8.3 Hz, Bt), 7.58 (1H, t, J = 8.3 Hz, Bt), 7.51 (1H, d, J = 8.2 Hz, Bt), 7.43 (1H, t, J = 8.2 Hz, Bt), 7.20 (1H, s, CH═), 2.55 (2H, s), 1.15 (9H, s); ^{13}C NMR δ 145.1 (s), 144.3 (s), 132.2 (s), 128.6 (d), 124.6 (d), 120.1 (d), 118.0 (q, J = 319 Hz, CF3), 116.0 (d), 109.9 (d), 46.2 (t), 31.7 (s), 29.3 (q, 3 × CH_3). Anal. Calcd for $C_{14}H_{16}F_3N_3O_3S$: C, 46.28; H, 4.44; N, 11.56. Found: C, 46.29; H, 4.14; N, 11.43.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-4,6,6-trimethyl-1-heptentyl trifluoromethanesulfonate (4j): white needles; mp 62−63 °C (94%, hexanes−ethyl acetate); ^{1}H NMR δ 8.27 (1H, d, J = 8.4 Hz), 7.75 (1H, t, J = 7.6 Hz), 7.64 (1H, d, J = 8.2 Hz), 7.60 (1H, t, J = 7.5 Hz), 7.42 (1H, s), 2.84 (1H, dd, J = 15.1, 6.1 Hz), 2.58 (1H, dd, J = 15.1, 8.6 Hz), 2.20−2.26 (1H, m), 1.55 (1H, dd, J = 14.0, 3.2 Hz), 1.42 (1H, dd, J = 14.0, 6.8 Hz), 1.32 (3H, d, J = 6.7 Hz), 1.14 (9H, s, 3 × CH_3); ^{13}C NMR δ 145.3 (s), 145.1 (s), 132.4 (s), 128.6 (d), 124.6 (d), 120.4 (d), 114.9 (d), 109.9 (d), 50.4 (t), 42.3 (d), 31.0 (s), 29.9 (q, 3 × CH_3), 27.0 (t), 22.0 (q). Anal. Calcd for $C_{17}H_{22}F_3N_3O_3S$: C, 50.36; H, 5.47; N, 10.36. Found: C, 50.25; H, 5.56; N, 9.70.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-heptenyl trifluoromethanesulfonate (4k): white needles; mp 84 °C (95%, hexane−ethyl acetate); ^{1}H NMR δ 8.10 (1H, d, J = 8.2 Hz), 7.57 (1H, t, J = 7.6 Hz), 7.50−7.40 (2H, m), 7.14 (1H, s), 2.67 (2H, t, J = 7.4 Hz), 1.74−1.82 (2H, m), 1.49−1.38 (4H, m), 0.96 (3H, t, J = 6.8 Hz); ^{13}C NMR δ 146.4 (s), 145.3 (s), 132.4 (s), 128.5 (d), 124.6 (d), 120.3 (d), 117.9 (q, J = 313.9 Hz, CF_3), 113.8 (d), 109.9 (d), 32.7 (t), 30.8 (t), 26.0 (t), 22.2 (t), 13.8 (q).

Anal. Calcd for $C_{14}H_{16}F_3N_3O_3S$: C, 46.28; H, 4.44; N, 11.56. Found: C, 46.44; H, 4.42; N, 11.51.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-nonenyl trifluoromethanesulfonate (4l): white needles; mp 77−78 °C (90%, hexanes−ethyl acetate); ^{1}H NMR δ 8.11 (1H, d, J = 8.3 Hz, Bt), 7.57 (1H, d, J = 8.3 Hz, Bt), 7.50 (1H, t, J = 8.3 Hz, Bt), 7.43 (1H, t, J = 8.2 Hz, Bt), 7.14 (1H, s, CH═), 2.67 (2H, t, J = 7.1 Hz), 1.78 (2H, m, CH_2), 1.33−1.48 (8H, m, 4 × CH_2), 0.91 (3H, t, J = 6.6 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6 (s), 145.5 (s), 132.6 (s), 128.8 (d), 124.9 (d), 120.6 (d), 118.0 (q, J = 319 Hz, CF_3), 114.1 (d), 110.2 (d), 32.9 (t), 31.8 (t), 29.0 (t), 28.9 (t), 26.6 (t), 22.8 (t), 14.3 (q). Anal. Calcd for $C_{15}H_{10}F_3N_3O_3S$: C, 49.10; H, 5.15; N, 10.74. Found: C, 48.98; H, 5.17; N, 10.17.

(*Z*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-3-(4-chlorophenyl)-1-propenyl trifluoromethanesulfonate (4m): white needles, mp 115−116 °C (82%, hexanes−ethyl acetate); ^{1}H NMR δ 8.07 (1H, dd, J = 8.3, 1.0 Hz, Bt), 7.52 (1H, t, J = 8.3 Hz, Bt), 7.51 (1H, d, J = 8.3 Hz), 7.43 (1H, t, J = 8.3 Hz, Bt), 7.05 (1H, s, CH═), 3.93 (3H, s); ^{13}C NMR δ 145.2 (s), 144.2 (s), 134.0 (s), 132.2 (s), 131.9 (s), 130.5 (d), 129.4 (d), 128.7 (d), 124.8 (d), 120.3 (d), 118.1 (q, CF_3), 115.6 (d), 109.8 (d), 38.3 (t). Anal. Calcd for $C_{16}H_{11}ClF_3N_3O_3S$: C, 46.00; H, 2.65; N, 10.06. Found: C, 46.14; H, 2.47; N, 10.00.

Typical Procedure for the Preparation of 5a−l. To a solution of **4a**−**l** (5 mmol) in 10 mL of THF was added 5 mL of 10% NaOH at room temperature. After being stirred for 30 min, the reaction mixture was diluted with Et_2O (60 mL), washed with brine and H_2O, dried over $MgSO_4$, and concentrated in vacuo to dryness. The residue was purified by column chromatography on silica gel using hexanes−ethyl acetate (10:1) to afford **5a**−**l** in the yields of 90−98%.

1-[2-(3-Methylphenyl)ethynyl]-1*H*-1,2,3-benzotriazole (5e): white microcrystals; mp 80−81 °C (91%, hexane−ethyl acetate); ^{1}H NMR δ 8.13 (1H, d, J = 8.2 Hz), 7.77 (1H, d, J = 8.2 Hz), 7.64 (1H, t, J = 7.1 Hz), 7.50−7.43 (3H, m), 7.31 (1H, t, J = 8.0 Hz), 7.26 (1H, d, J = 7.0 Hz), 2.40 (3H, s); ^{13}C NMR δ 143.9 (s), 138.4 (s), 134.3 (s), 132.4 (d), 130.4 (d), 129.3 (d), 128.9 (d), 128.5 (d), 125.2 (d), 120.6 (d), 120.0 (s), 110.2 (d), 80.0 (s), 75.5 (s), 21.2 (q). Anal. Calcd for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01. Found: C, 76.94; H, 4.71; N, 17.88.

1-[2-(2-Methylphenyl)ethynyl]-1*H*-1,2,3-benzotriazole (5f): white microcrystals; mp 79 °C (92%, hexane−ethyl acetate); ^{1}H NMR δ 8.14 (1H, dd, J = 8.4, 0.9 Hz), 7.74 (1H, dd, J = 8.2, 0.9 Hz), 7.65 (1H, t, J = 7.0 Hz), 7.62 (1H, d, J = 8.2 Hz), 7.49 (1H, t, J = 7.0 Hz), 7.36−7.23 (3H, m), 2.60 (3H, s); ^{13}C NMR δ 146.8 (s), 144.0 (s), 140.4 (s), 134.3 (s), 132.2 (d), 129.8 (d), 129.5 (d), 129.4 (d), 125.9 (d), 125.3 (d), 120.6 (d); 110.1 (d), 78.7 (s), 74.1 (s), 21.0 (q). Anal. Calcd for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01. Found: C, 77.24; H, 4.76; N, 17.90.

1-(4-Phenyl-1-butynyl)-1*H*-1,2,3-benzotriazole (5g): white needles; mp 72 °C (94%, hexane−ethyl acetate); ^{1}H NMR δ 8.08 (1H, d, J = 8.2 Hz), 7.54 (1H, t, J = 7.1 Hz), 7.49−7.34 (2H, m), 7.32−7.25 (5H, m), 3.03 (2H, t, J = 6.8 Hz), 2.91 (2H, t, J = 6.8 Hz); ^{13}C NMR δ 143.7 (s), 139.9 (s), 134.4 (s), 129.0 (d), 128.3 (d, 2 × CH), 128.1 (d, 2 × CH), 126.6 (d), 125.0 (d), 120.3 (d), 110.0 (d), 79.6 (s), 68.6 (s), 34.5 (t), 20.8 (t). Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.57; H, 5.56; N, 16.68.

1-(1-Propynyl)-1*H*-1,2,3-benzotriazole (5h): solid (90%); ^{1}H NMR δ 8.08 (1H, d, J = 8.3 Hz, Bt), 7.65 (1H, d, J = 8.3 Hz, Bt), 7.58 (1H, t, J = 8.3 Hz, Bt), 7.42 (1H, t, J = 8.3 Hz, Bt), 2.23 (3H, s); ^{13}C NMR δ 143.5 (s), 134.1 (s), 128.9 (d), 124.9 (d), 120.2 (d), 109.9 (d), 76.3 (s), 66.8 (s), 3.5 (q, CH_3). Anal. Calcd for $C_9H_7N_3$: C, 68.77; H, 4.49. Found: C, 69.10; H, 4.86.

1-(4,4-Dimethyl-1-pentynyl)-1*H*-1,2,3-benzotriazole (5i): solid (95%); ^{1}H NMR δ 8.08 (1H, d, J = 8.3 Hz, Bt), 7.62 (1H, d, J = 8.3 Hz, Bt), 7.58 (1H, t, J = 8.3 Hz, Bt), 7.42 (1H, t, J = 8.3 Hz, Bt), 2.48 (2H, s, CH_2), 1.13 (9H, s, 3 × CH_3); ^{13}C NMR δ 143.6 (s), 134.3 (s), 128.9 (d), 124.9 (d), 120.2 (d), 109.9 (d), 78.9 (s), 69.2 (s), 33.5 (t), 31.4 (s), 29.0 (q). Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.09; H, 6.97; N, 20.04.

1-(4,6,6-Trimethyl-1-heptynyl)-1*H*-1,2,3-benzotriazole (5j): oil (90%); ^{1}H NMR δ 8.07 (1H, d, J = 8.2 Hz), 7.64 (1H, d, J = 8.2 Hz), 7.58 (1H, td, J = 8.1, 0.6 Hz), 7.41 (1H, td, J = 8.1, 1.2 Hz), 2.57 (1H, dd, J = 16.6, 5.76 Hz), 2.47 (1H, dd, J = 16.6, 6.8 Hz), 1.99−1.89 (1H, m), 1.47 (1H, dd, J = 14.0, 4.2 Hz), 1.22 (1H, dd, J = 14.1, 6.2 Hz), 1.16 (3H, d, J = 6.6 Hz, CH_3), 0.95 (9H, s, 3 × CH_3); ^{13}C NMR δ 143.6 (s), 134.2 (s), 128.8 (d), 124.8 (d), 120.1 (d), 109.8 (d), 79.5 (s), 68.4 (s), 49.9 (t), 30.8 (s), 29.7 (q, 3 × CH_3), 28.9 (t), 28.0 (d), 22.0 (q). Anal. Calcd for $C_{16}H_{21}N_3$: C, 75.26; H, 8.29; N, 16.45. Found: C, 75.25; H, 8.55; N, 16.82.

1-(1-Heptynyl)-1*H*-1,2,3-benzotriazole (5k): oil (92%); ^{1}H NMR δ 8.00 (1H, d, J = 8.4 Hz), 7.57 (1H, d, J = 8.1 Hz), 7.52 (1H, t, J = 6.7 Hz), 7.35 (1H, t, J = 8.0 Hz), 2.53 (2H, t, J = 7.1 Hz), 1.69−1.59 (2H, m), 1.48−1.28 (4H, m), 0.88 (3H, t, J = 7.1 Hz); ^{13}C NMR δ 143.4 (s), 134.1 (s), 128.8 (d), 124.7 (d), 120.0 (d), 109.8 (d), 80.3 (s), 67.6 (s), 30.8 (t), 27.8 (t), 21.9 (t), 18.3 (t), 13.7 (q). Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 72.82; H, 7.13; N, 19.98.

1-(1-Nonynyl)-1*H*-1,2,3-benzotriazole (5l): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (1H, d, J = 8.3 Hz, Bt), 7.64 (1H, d, J = 8.3 Hz, Bt), 7.58 (1H, t, J = 8.3 Hz, Bt), 7.45 (1H, t, J = 8.3 Hz, Bt), 2.59 (2H, t, J = 7.1 Hz, CH_2), 1.70 (2H, m, CH_2), 1.50 (2H, m, CH_2), 1.13 (6H, m), 0.89 (3H, t, J = 6.6 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6 (s), 134.3 (s), 128.9 (d), 124.9 (d), 120.2 (d), 109.9 (d), 80.5 (s), 67.8 (s), 31.6 (t), 28.8 (t), 28.7 (t), 28.2 (t), 22.5 (t), 18.5 (t), 14.0 (q). Anal. Calcd for $C_{15}H_{19}N_3$: C, 74.65; H, 7.94; N, 17.41. Found: C, 74.42; H, 8.19; N, 17.66.

Typical Procedure for the Preparation of 6a,[12] 6d. Method A. To a solution of **4a** or **4d** (1 mmol) in acetonitrile was added solid $NaOCH_3$ (2 mmol) at room temperature. The reaction mixture was heated under reflux for 2 h and then cooled to room temperature. The reaction mixture was diluted with Et_2O, washed with brine and H_2O, dried over $MgSO_4$, and evaporated in vacuo to dryness. Purification by flash column chromatography on silica gel using hexane−ethyl acetate (10:1) gave *Z*-**6a** and *E*-**6a** (or **6d**) as a colorless oil in good yields (>80%).

Method B. To a solution of **5a** (219 mg, 1 mmol) in acetonitrile was added solid $NaOCH_3$ (1.1 mmol, 59.4 mg) at room temperature. The reaction mixture was heated under reflux for 2 h and then cooled to room temperature. The reaction mixture was diluted with Et_2O, washed with brine and H_2O, dried over $MgSO_4$, and evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel using hexane−ethyl acetate (10:1) to give *Z*-**6a** and *E*-**6a** as a colorless oil (total yield 98%).

1-[(*Z*)-1-Methoxy-2-phenylethenyl]-1*H*-1,2,3-benzotriazole (Z-6a):[12] colorless oil (18%); ^{1}H NMR δ 8.14 (1H, dd, J = 1.0, 7.6 Hz), 7.78 (1H, dd, J = 1.0, 7.6 Hz), 7.72 (2H, d, J = 7.3 Hz), 7.58 (1H, ddd, J = 1.0, 7.6, 7.6 Hz), 7.39−7.47 (3H, m), 7.30 (1H, ddd, J = 1.0, 7.6, 7.6 Hz), 6.29 (1H, s), 3.65 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.0 (s), 144.7 (s), 133.5 (s), 132.6 (s), 129.0 (d, 3 × CH), 128.9 (d, 2 × CH), 128.0 (d), 124.9 (d), 120.5 (d), 111.4 (d), 108.3 (d), 58.2 (q).

1-[(*E*)-1-Methoxy-2-phenylethenyl]-1*H*-1,2,3-benzotriazole (*E*-6a).[12] colorless oil (78%); ^{1}H NMR δ 8.07 (1H, dd, J = 1.6, 8.6 Hz), 7.33−7.38 (2H, m), 7.20−7.26 (1H, m), 6.99−7.03 (3H, m), 6.62−6.68 (2H, m), 6.11 (1H, s), 3.98 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.4 (s), 145.1 (s), 132.7 (s), 132.2 (s), 128.4 (d, 2 × CH), 128.3 (d), 127.5 (d, 2 × CH), 126.8 (d), 124.3 (d), 120.0 (d), 110.4 (d), 101.1 (d), 56.9 (q).

1-[(*E*)-1-Methoxy-2-(4-methylphenyl)ethenyl]-1*H*-1,2,3-benzotriazole (*E*-6d): colorless oil (85%); ^{1}H NMR δ 8.12 (1H, dd, J = 0.9, 8.3 Hz), 7.78 (1H, dd, J = 1.0, 7.6 Hz), 7.62 (2H, d, J = 8.1 Hz), 7.57 (1H, ddd, J = 0.9, 7.6, 7.8 Hz), 7.44 (1H, ddd, J = 0.9, 7.6, 8.4 Hz), 7.22 (2H, d, J = 8.1 Hz), 6.27 (1H, s), 3.64 (3H, s), 2.39 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7 (s), 143.9 (s), 137.3 (s), 132.3 (s), 130.3 (s), 129.3 (d, 3 × CH), 128.6 (d, 3 × CH), 124.6 (d), 120.2 (d), 111.1 (d), 108.1 (d), 57.8 (q), 21.3 (q); HRMS(EI) $[M + H]^+$ calcd for $C_{16}H_{15}N_3O$ 266.1293, found 266.1293.

Typical Procedure for the Preparation of 7a−f. Method A from 4a−f. To a cooled (0 °C) solution of enol triflates **4a**−**f**

(7 mmol) in CH_3CN (100 mL) was added $NaOCH_3$ (15 mmol). The reaction mixture was stirred for 2 h and then heated under reflux for additional 2 h. After the solvent was removed in vacuo, 50 mL of methanol or ethanol and 1 mL of concentrated HCl was added, and the reaction mixture was heated under reflux for 1−2 h. Methanol or ethanol was removed, and the crude product was dissolved in diethyl ether , washed with saturated Na_2CO_3 and H_2O, and dried over $MgSO_4$. The crude ester was purified by column chromatograph with hexane/ethyl acetate mixture (20:1) to provide the corresponding esters in good yields.

Method B from 5a−f. Alkynylbenzotriazoles **5a−f** were treated with 1.0 equiv of $NaOCH_3$ in CH_3CN under reflux for 1−2 h followed by hydrolysis with concentrated HCl. The reaction mixture was worked up as in method A, affording desired esters in excellent yields.

Ethyl 2-(4-methoxyphenyl)acetate (7c):[13] oil (93%); ^{1}H NMR δ 7.19 (2H, d, J = 8.4 Hz), 6.84 (2H, d, J = 8.4 Hz), 4.12 (2H, q, J = 7.1 Hz, CH_2), 3.77 (3H, s, OCH_3), 3.54 (2H, s, CH_2), 1.48 (3H, t, J = 7.1 Hz, CH_3); ^{13}C NMR δ 171.8 (s, CO_2), 158.5 (s), 130.1(d, 2 × CH), 126.1 (s), 113.8 (d, 2 × CH), 60.6 (t), 55.1 (q), 40.3 (t), 14.0 (q).

Typical Procedure for the Preparation of 7g−l. Enol tosylates **8g−l** (1 mmol) were treated with 1.0 equiv of TBAF in THF (10 mL) under reflux for 3−48 h. The reaction mixtures were diluted and washed with 1 N HCl, saturated NaCl, and H_2O. The organic layers were dried over $MgSO_4$, and the solvent was evaporated in vacuo. Crude products were purified by flash chromatography to provide the desired acids in good yields.

4,4,6-Trimethylheptanoic acid (7j):[14] oil (62%); ^{1}H NMR δ 2.38−2.32 (2H, m), 1.69−1.61 (1H, m), 1.59−1.43 (2H, m), 1.25−1.18 (1H, dd, J = 3.3, 14.0 Hz), 1.15−1.10 (1H, dd, J = 5.8, 14.0 Hz), 0.93 (3H, d, J = 6.4 Hz), 0.89 (9H, s, 3 × CH_3), missing CO_2H; ^{13}C NMR δ 180.5 (s), 50.8 (t), 33.9 (t), 32.0 (t), 31.0 (s), 29.9 (q), 28.8 (d), 22.2 (q).

Typical Procedure for the Preparation of 8g−l. To a solution of **5g−l** (1 mmol) in acetonitrile 10 (mL) was added *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) at room temperature. The reaction mixture was stirred under reflux for 4 h until TLC showed no presence of the starting material. The resulting mixture was concentrated in vacuo to dryness, and the residue was purified by column chromatography on silica gel using hexanes−EtOAc (10:1) as an eluent to afford **8g−l** (yields of 65−85% except for 24% of **8g**).

1-(1*H*-1,2,3-Benzotriazol-1-yl)-4-phenyl-1-butenyl 4-methylbenzenesulfonate (8g): oil (24%); ^{1}H NMR δ 7.91 (1H, d, J = 8.8 Hz), 7.43−7.41 (3H, m), 7.34−7.29 (2H, m), 7.20−7.12 (3H, m), 7.02 (2H, d, J = 6.8 Hz), 5.96 (2H, d, J = 8.3 Hz), 5.93 (1H, t, J = 7.6 Hz), 2.73 (2H, t, J = 7.5 Hz), 2.34 (2H, dt, J = 7.5, 7.6 Hz), 2.25 (3H, s); ^{13}C NMR δ 145.5, 144.8, 139.9, 135.1, 132.0, 131.3, 129.2 (2 × CH), 128.5, 128.3 (2 × CH), 128.2 (2 × CH), 127.7 (2 × CH), 126.1, 124.4, 121.7, 119.6, 110.6, 34.8, 28.0, 21.4; HRMS (EI) $[M + H]^+$ calcd for $C_{23}H_{21}N_3O_3S$ 420.1382, found 420.1382. Anal. Calcd for $C_{23}H_{21}N_3O_3S$: C, 65.85; H, 5.05; N, 10.02. Found: C, 64.87; H, 4.87; N, 10.19.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-propenyl 4-methylbenzenesulfonate (8h): white needles; mp 78−80 °C (62%, hexanes−ethyl acetate); ^{1}H NMR δ 7.94 (1H, d, J = 8.2 Hz), 7.50−7.44 (2H, m), 7.43 (2H, d, J = 8.2 Hz), 7.33−7.39 (1H, m), 6.98 (2H, d, J = 8.2 Hz), 6.03 (1H, q, J = 7.3 Hz), 2.27 (3H, s), 1.69 (3H, d, J = 7.3 Hz); ^{13}C NMR δ 145.5 (s), 144.9 (s), 135.3 (s), 132.3 (s), 131.6 (s), 129.3 (d, 2 × CH), 128.6 (d), 127.8 (d, 2 × CH), 124.4 (d), 119.8 (d), 117.9 (d), 110.6 (d), 21.5 (q), 11.9 (q). Anal. Calcd for $C_{16}H_{15}N_3O_3S$: C, 58.34; H, 4.59; N, 12.76. Found: C, 58.44; H, 4.72; N, 12.68.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-4,4-dimethyl-1-pentenyl 4-methylbenzenesulfonate (8i): microcrystals; mp 56−59 °C (67%, hexanes−ethyl acetate); ^{1}H NMR δ 7.94 (1H, d, J = 8.3 Hz), 7.51−7.45 (4H, m), 7.38−7.33 (1H, m), 7.00 (2H, d, J = 7.8 Hz), 6.03 (1H, t, J = 7.4 Hz), 2.27 (3H, s), 1.91 (2H, d, J = 7.4 Hz), 0.84 (9H, s); ^{13}C NMR δ 145.4 (s), 144.7 (s), 135.1 (s), 132.2 (s), 131.5 (s), 129.2 (d, 2 × CH), 128.5 (d), 127.7 (d, 2 × CH), 124.3 (d), 120.9 (d), 119.6 (d), 110.4 (d), 39.8, 31.0, 28.9 (q, 3 × CH_3), 21.3 (q). Anal. Calcd for $C_{20}H_{23}N_3O_3S$: C, 62.32; H, 6.01; N, 10.90. Found: C, 62.68; H, 6.28; N, 11.05.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-4,6,6-trimethyl-1-heptenyl 4-methylbenzenesulfonate (8j): oil (77%); ^{1}H NMR δ 7.93 (1H, d, J = 7.4 Hz), 7.43−7.52 (4H, m), 7.32−7.38 (1H, m), 6.98 (2H, d, J = 8.1 Hz), 5.97 (1H, t, J = 7.9 Hz), 2.27 (3H, s), 1.95−2.00 (1H, m), 1.79−1.90 (1H, m), 1.58−1.68 (1H, m), 0.92−1.12 (2H, m), 0.86 (3H, d, J = 6.6 Hz), 0.79 (9H, s); ^{13}C NMR δ 145.5, 144.9, 135.1, 132.3, 131.6, 129.3, (2CH), 128.6, 127.8 (2CH), 124.34, 122.4, 119.8, 110.6, 50.2, 35.4, 30.9, 29.8 (3 × CH_3), 29.3, 22.4, 21.5; HRMS(EI) $[M + H]^+$ calcd for $C_{23}H_{29}N_3O_3S$ 428.2008, found 428.2008.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-heptenyl 4-methylbenzenesulfonate (8k): oil (82%); ^{1}H NMR δ 7.94 (1H, d, J = 7.4 Hz), 7.46−7.51 (4H, m), 7.33−7.38 (1H, m), 7.01 (2H, d, J = 8.1 Hz), 5.94 (1H, t, J = 7.9 Hz), 2.28 (3H, s), 1.99 (2H, dt, J = 7.5, 7.6 Hz), 1.38−1.43 (2H, m), 1.17−1.20 (4H, m), 0.82 (3H, t, J = 6.5 Hz); ^{13}C NMR δ 145.4, 144.7, 134.4, 132.2, 131.3, 129.2, (2CH), 128.4, 127.7 (2CH), 124.3, 123.1, 119.6, 110.4, 30.8, 28.4, 26.0, 22.0, 21.3, 13.6; HRMS(EI) $[M + H]^+$ calcd for $C_{20}H_{23}N_3O_3S$ 386.1538, found 386.1538.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-nonenyl 4-methylbenzenesulfonate (8l): pale yellow oil (75%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (1H, d, J = 8.2 Hz), 7.4−7.53 (4H, m), 7.38 (1H, m), 7.00 (2H, d, J = 8.2 Hz), 5.94 (1H, t, J = 8.0 Hz), 2.28 (3H, s), 1.99 (2H, dt, J = 8.0, 7.7 Hz), 1.40 (2H, m), 1.16−1.22 (8H, m), 0.82 (3H, t, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5 (s), 144.7 (s), 134.5 (s), 132.2 (s), 131.4 (s), 129.2 (d), 129.2 (d), 128.5 (d), 127.7 (d), 127.7 (d), 124.3 (d), 123.1 (d), 119.6 (d), 110.4 (d), 31.4 (t), 28.6 (t), 28.6 (t), 28.5 (t), 26.1 (t), 22.3 (t), 21.3 (q), 13.8 (q).

Typical Procedure for the Preparation of 9i,m and 10i,j. Compounds **5i**,**j**, or **4i**,**j**,**m** (1 mmol) were treated with 2.0 equiv of $NaOCH_3$ in CH_3CN (10 mL) under reflux for 2 h. The solvent was removed in vacuo. The residue was dissolved in ethyl acetate and washed with brine and H_2O. The organic layer was dried over $MgSO_4$. Concentration in vacuo and purification by flash chromatography afforded **9i**,**j**,**m** and **10i**,**j**, respectively, in good yields.

1-(4,4-Dimethyl-1,2-pentadienyl)-1*H*-1,2,3-benzotriazole (9i): oil (94%); ^{1}H NMR δ 8.07 (1H, d, J = 8.2 Hz), 7.87 (1H, d, J = 6.2 Hz), 7.80 (1H, d, J = 8.3 Hz), 7.48 (1H, dt, J = 1.0, 8.1 Hz), 7.42 (1H, dt, J = 1.0, 8.1 Hz), 6.16 (1H, d, J = 6.2 Hz), 1.20 (9H, s); ^{13}C NMR δ 192.7 9s), 146.5 (s), 131.3 (s), 127.6 (d), 124.3 (d), 120.0 (d), 116.1 (d), 111.1 (d), 99.1 (d), 33.5 (s), 29.3 (q). Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 72.82; H, 7.14; N, 19.98.

1-[3-(4-Chlorophenyl)-1,2-propadienyl]-1*H*-1,2,3-benzotriazole (9m): oil (75%); ^{1}H NMR δ 8.23 (1H, d, J = 6.3 Hz), 8.10 (1H, d, J = 8.3 Hz), 7.68 (1H, d, J = 8.2 Hz), 7.44−7.35 (6H, m), 7.10 (1H, d, J = 6.3 Hz); ^{13}C NMR δ 197.3 (s), 146.6 (s), 134.9 (s), 131.4 (s), 130.8 (s), 129.3 (d, 2CH), 129.1 (d, 2CH), 128.3 (d), 124.7 (d), 120.3 (d), 110.9 (d), 106.0 (d), 101.1 (d); HRMS(EI) $[M + H]^+$ calcd for $C_{15}H_{10}ClN_3$ 268.0642, found 268.0642.

1-(4,4-Dimethyl-2-pentynyl)-1*H*-1,2,3-benzotriazole (10i): oil (94%); ^{1}H NMR δ 8.05 (1H, d, J = 8.3 Hz), 7.75 (1H, d, J = 8.3 Hz), 7.53 (1H, dt, J = 0.9, 8.3 Hz), 7.51 (1H, dt, J = 0.9, 8.3 Hz), 5.42 (2H, s), 1.20 (9H, s); ^{13}C NMR δ 146.29s), 132.4 (s), 127.2 (d), 123.9 (d), 119.9 (d), 110.1 (d), 95.3 (s), 70.1 (s), 38.7 (t), 32.3 (s), 30.5 (q). Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 72.82; H, 7.14; N, 19.98.

1-(4,6,6-Trimethyl-2-heptynyl)-1*H*-1,2,3-benzotriazole (10j): white microcrystals; mp 75 °C (94%, hexane); ^{1}H NMR δ 8.04 (1H, d, J = 8.4 Hz); 7.71 (1H, d, J = 8.4 Hz), 7.49 (1H, t, J = 7.3 Hz), 7.73 (1H, t, J = 7.3 Hz), 5.50 (2H, s), 2.44−2.50 (1H, m), 1.47 (1H, dd, J = 9.7, 13.5 Hz), 1.19 (1H, dd, J = 3.3, 13.3 Hz), 1.14 (3H, d, J = 7.0 Hz), 0.86 (9H, s); ^{13}C NMR δ 146.1 (s), 132.4 (s), 127.1 (d), 123.8 (d), 119.8 (d), 110.0 (d), 93.2 (s), 71.7 (s), 50.4 (t), 38.6 (q), 30.7 (s), 29.5 (q), 23.2 (t),

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21.9 (d). Anal. Calcd for $C_{16}H_{21}N_3$: C, 75.25; H, 8.29; N, 16.45. Found: C, 75.21; H, 8.55; N, 16.83.

1-(3,4-Dihydro-1-naphthalenyl)-1*H*-1,2,3-benzotriazole (11g): solid (30%); ^{1}H NMR δ 8.14 (1H, d, J = 7.5 Hz), 7.45−7.35 (3H, m), 7.28?7.21 (2H, m), 7.07 (1H, dd, J = 7.0, 7.8 Hz), 6.51 (1H, d, J = 7.8 Hz), 6.44 (1H, t, J = 4.8 Hz), 3.04 (2H, t, J = 8.0 Hz), 2.67 (2H, m); ^{13}C NMR δ 145.7 (s), 136.0 (s), 134.3 (s), 133.5 (s), 130.3 (s), 128.7 (d), 128.0 (d), 127.7 (d), 127.4 (d), 126.8 (d), 124.1 (d), 122.8 (d), 120.0 (d), 110.7 (d), 27.2 (t), 22.8 (t). Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.90; H, 5.63; N, 17.16.

Supporting Information Available: Experimental procedures and characterization for compounds **3a**−**l** and **5a**−**d**, **7b**,**d**−**f**,**i**; NMR spectra data for **4c**,**e**−**g**,**i**−**k**,**m**, **5e**−**k**, **6c**, **8g**−**j**, **9i**,**m**, **10i**,**j**, and **11g**; and details of the X-ray crystal structure of **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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