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Expedient Acylations of Primary and Secondary Alkyl Cyanides to α-Substituted β-Ketonitriles

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Primary and secondary cyanides are efficiently acylated with *N*-acylbenzotriazoles **3a**−**f** (derived from a variety of acids) to afford the corresponding α-substituted β-ketonitriles **5a**−**r** in 67−96% yields.

Introduction

β-Ketonitriles are an important class of difunctional intermediates for the synthesis of many heterocycles, including dihydropyrans and dihydrothiopyrans,[1] pyrazoles,[2] pyrimidines,[3] pyridones,[4] and quinolines.[5] Recent interest in β-ketonitriles has been focused on their bioreduction[6] and parallel kinetic resolution[7] for the preparation of enantiopure ketones and alcohols containing a quaternary stereocenter in line with the growing importance of optically active β-hydroxy nitriles as intermediates in the preparation of γ-amino alcohols (like the antidepressant fluoxetine).[8] In this respect, the diversity of the β-ketonitriles available significantly impacts the range of structures which can be accessed.

Classical and conventional methods for the syntheses of β-ketonitriles have been well documented.[9] Due to the acidity of protons adjacent to a nitrile group, a simple and direct preparation of β-ketonitriles is the acylation of acetonitriles. Early methods employing this route require harsh reaction conditions, e.g., sodium amide in liquid ammonia.[10] Recently the use of LDA or UDP systems (ultrasonic irradiation of a suspension of potassium in toluene) has been successful.[11] However, all these previous methods are apparently limited to the synthesis of β-ketonitriles unsubstituted at the α-position.[12] Additionally, the range of β-ketonitrile structures reported is quite limited: for example, ref 11b is confined to structures of types ArCOCH(Ph)CN and $ArCOCH_2CN$. All 18 β-ketonitriles reported in the present manuscript are novel.

Acylazoles are known as efficient acylating reagents.[13] We have recently used 1-(trifluoroacetyl)benzotriazole for trifluoroacetylation,[14] and 1-formylbenzotriazole for the formylation of amines and alcohols.[15] 1-Acylbenzotriazoles are good *C*-acylating reagents for ketones[16] and *O*-acylating reagents for aldehydes.[17] We now report an efficient and convenient procedure for the preparation of a variety of β-ketonitriles **5a**−**r** by the acylation of nitriles **4a**−**j** with *N*-acylbenzotriazoles **3a**−**f** in good to excellent yields.

Results and Discussion

N-Acylbenzotriazoles **3a**−**f** were prepared in excellent yields according to the literature procedure.[18] Treatment of acetonitriles **4a**−**j** with *n*-butyllithium in THF at −78 °C or *t*-BuOK in DMSO at 20 °C, followed by the addition of a solution of *N*-acylbenzotriazoles **3a**−**f** in the corresponding same solvent, provided the corresponding β-ketonitriles **5a**−**r**. The TLC and NMR of the crude products show that the reactions are very clean (usually benzotriazole is the only byproduct, but occasionally, small amounts of the unreacted starting *N*-acylbenzotriazoles **3** were detected). The pure aliphatic, aromatic, and heteroaromatic β-ketonitriles **5a**−**r** were isolated in 67−96% yields (Scheme 1 and Table 1).

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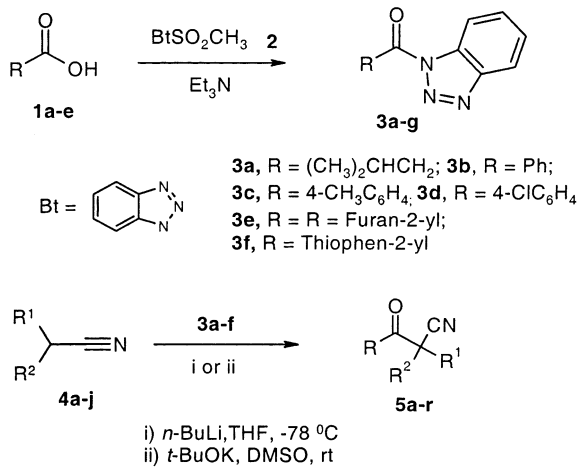
SCHEME 1



For designation of R, R^1, R^2 in **5** see Table 1

TABLE 1. Preparation of β-Ketonitriles 5a−r via *C*-Acylation of Acetonitriles with *N*-Acylbenzotriazoles 3a−f

		from nitriles **4**			yield
entry	R of RCO	R^1	R^2	method	(%)
5a	$(CH_3)_2CHCH_2$	H	4-BrC_6H_4	B	95
5b	$(CH_3)_2CHCH_2$	H	benzotriazol-1-yl	A	83
5c	C_6H_5	H	4-$MeOC_6H_4$	A	93
5d	C_6H_5	H	4-MeC_6H_4	B	95
5e	C_6H_5	H	$CH_3(CH_2)_2CH_2$	A	74
5f	C_6H_5	CH_3	C_6H_5	A	79
5g	4-MeC_6H_4	H	H	A	88
5h	4-MeC_6H_4	H	$C_6H_5CH_2$	A	83
5i	4-MeC_6H_4	CH_3	C_6H_5	A	67
5j	4-ClC_6H_4	H	$CH_3(CH_2)_2CH_2$	A	71
5k	2-thienyl	H	4-BrC_6H_4	B	91
5l	2-thienyl	H	2,4-$Cl_2C_6H_3$	B	89
5m	2-thienyl	H	$C_6H_4CH_2$	A	85
5n	2-thienyl	CH3	C_6H_5	A	82
5o	2-thienyl	H	H	A	92
5p	2-furyl	H	2,4-$Cl_2C_6H_3$	B	94
5q	2-furyl	H	naphth-1-yl	B	92
5r	2-furyl	H	H	A	95

The structures of compounds **5a**−**r**, which are all novel, were supported by NMR spectroscopy and elemental analyses. For example, in the ^{1}H NMR spectrum of **5m**, a methine proton appears at 4.34 ppm as a doublet of doublets with coupling constants of 8.1and 6.5 Hz, and the diastereotopic protons of the methylene group displayed an AB type spectrum at δ 3.38 (dd, $^2J_{AB}$ = 13.9 Hz, ^3J = 6.2 Hz, 1H, A part of AB system) and 3.28 (dd, $^2J_{AB}$ = 13.7 Hz, ^3J = 8.7 Hz, 1H, B part of AB system). The signals that appear at δ 7.17 (t, J = 4.1 Hz, 1H), 7.28−7.34 (m, 5H), 7.78 (d, J = 4.8 Hz, 1H), and 7.81 (d, J = 3.7 Hz, 1H) were assigned to the protons from the phenyl and thienyl moieties. The carbonyl and methine groups appeared at δ 182.6 (CO) and 42.77 (CH), respectively, in the ^{13}C NMR spectrum.

This new synthetic procedure for the preparation of β-ketonitriles offers advantages over the literature procedures. It has demonstrated good generality: it can be used with aliphatic (to give **5a**,**b**), benzenoid (to give **5c**−**j**), and heterocyclic acylation reagents (thienyl to give **5k**−**o**, furyl to give **5p**−**r**). Primary alkyl-, aryl-, and heteroaryl-substituted nitriles can also be used. Significantly, our method provided a means to prepare β-ketonitriles **5f**,**i**,**n** derived from secondary nitriles, which are inaccessible by Claisen-type condensations.[10]

The present method is operationally simple and utilizes easily prepared, stable *N*-acylbenzotriazoles as acylating reagents, and the byproduct (benzotriazole) can be easily removed by simply washing with saturated aqueous Na_2CO_3. The current results represent the first example of the successful use of amides for the acylation of a nitrile.

In conclusion, we have developed a general, simple, and efficient method for the synthesis of aliphatic, aromatic, and heteroaromatic ketones bearing a cyano group at the α-position utilizing readily accessible *N*-acylbenzotriazoles. The high yields of ketones **5a**−**r** have proved *N*-acylbenzotriazoles **3** to be convenient and valuable alternative reagents for the *C*-acylation of nitriles.

Experimental Section

General. Melting points were determined on a hot-stage apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as internal standard for ^{1}H (300 MHz) or solvent as the internal standard for ^{13}C (75 MHz). Anhydrous THF was obtained by distillation immediately prior to use. Column chromatography was conducted with silica gel 200−425 mesh. $BtSO_2CH_3$ (**1**) and *N*-acylbenzotriazoles **3a**−**f** were prepared according to literature procedures.[18]

General Procedures for the Preparation of β-Ketonitriles 5a−r. Method A: *n*-Butyllithium (1.6 mL of 1.55 M in hexane, 2.4 mmol) was added slowly with efficient stirring under nitrogen to a solution of acetonitrile **4** (2 mmol) in anhydrous THF (10 mL) at −78 °C. After 1 h, *N*-acylbenzotriazole **3** (2 mmol) was slowly added by syringe to minimize the temperature increase that results from the exothermic reaction. After the mixture was stirred for 2 h at −78 °C, the resultant solution was allowed to attain room temperature. Subsequently, the reaction mixture was poured into water (50 mL), acidified with 1 N HCl solution, and extracted with EtOAc. The organic layer was washed with NaCl solution and dried over $MgSO_4$. Then solvent was evaporated in vacuo, and the residue was subjected to column chromatography on silica gel and eluted with a mixture of EtOAc/hexanes (1:5, v/v) to give the desired product **5**.

Method B: A mixture of an acetonitrile **4** (2 mmol) and potassium *tert*-butoxide (2.2 mmol) in dimethyl sulfoxide (10 mL) was stirred while the temperature was maintained below 10 °C for 10 min. To the resulting solution was added *N*-acylbenzotriazole **3** (2 mmol) in dimethylsulfoxide (10 mL) dropwise, and the mixture was stirred at 25 °C for 12 h. The mixture was poured into water (40 mL), acidified with 1 N HCl, and then extracted with ethyl acetate (3 × 30 mL). The extracts were washed with water and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was placed in a silica gel column and eluted with a mixture of EtOAc/hexanes (1:5, v/v) to give the desired product **5**.

2-(4-Bromophenyl)-5-methyl-3-oxohexanenitrile (5a). Colorless microcrystals (95%), mp 76−78 °C. ^{1}H NMR δ 7.57 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 4.8 Hz, 2H), 4.61 (s, 1H), 2.56−2.39 (m, 2H), 2.14 (septet, J = 7.0 Hz, 1H), 0.86 (d, J = 4.5 Hz, 3H), 0.84 (d, J = 4.4 Hz, 3H). ^{13}C NMR δ 197.6, 132.7, 129.6, 128.6, 123.6, 115.9, 50.5, 48.50, 24.2, 22.1. Anal. Calcd for $C_{13}H_{14}BrNO$: C, 55.73; H, 5.04; N, 5.00. Found: C, 55.54; H, 5.07; N, 4.89.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-5-methyl-3-oxohexanenitrile (5b). Brown microcrystals (83%), mp 108−110 °C. ^{1}H NMR δ 7.86 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.55 (dd, J = 8.1, 6.9 Hz, 1H), 7.35−7.27 (m, 3H), 2.65 (d, J = 6.9 Hz, 2H), 2.35−2.28 (m, 1H), 1.14 (d, J = 6.0 Hz, 6H). ^{13}C NMR δ 170.9, 144.3, 131.7, 129.1, 125.6, 119.4, 114.7, 110.7, 88.2,

42.0, 27.2, 22.2. Anal. Calcd for $C_{13}H_{14}N_4O$: C, 64.45; H, 5.82. Found: C, 64.58; H, 6.04.

2-(4-Methoxyphenyl)-3-oxo-3-phenylpropanenitrile (5c). Yellow microcrystals (93%), mp 76−78 °C. ^{1}H NMR δ 7.93 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.57 (s, 1H), 3.78 (s, 3H). ^{13}C NMR δ 189.1, 160.1, 134.3, 133.6, 129.5, 129.2, 129.0, 122.1, 116.8, 115.0, 55.3, 45.9. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.15; H, 5.35; N, 5.47.

2-(4-Methylphenyl)-3-oxo-3-phenylpropanenitrile (5d). Colorless plates (95%), mp 69−71 °C. ^{1}H NMR δ 7.94 (d, J = 7.6 Hz, 2H), 7.59−7.43 (m, 3H), 7.32 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.7 Hz, 2H), 5.57 (s, 1H), 2.33 (s, 3H). ^{13}C NMR δ 189.0, 139.2, 134.3, 133.6, 130.3, 129.2, 129.0, 128.1, 127.3, 116.7, 46.4, 21.1. Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.61; H, 5.35; N, 5.94.

2-Benzoylhexanenitrile (5e). Pale yellow oil (74%). ^{1}H NMR δ 7.96 (d, J = 7.4 Hz, 2H), 7.68−7.63 (m, 1H), 7.55−7.50 (m, 2H), 4.37 (t, J = 7.1 Hz, 1H), 2.04−1.96 (m, 2H), 1.58−1.35 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR δ 190.9, 134.4, 133.9, 129.0, 128.7, 117.4, 40.0, 29.6, 29.1, 22.0, 13.6. Anal. Calcd for $C_{13}H_{15}NO$: N, 6.96. Found: N, 6.67.

2-Methyl-3-oxo-2,3-diphenylpropanenitrile (5f). Colorless oil (79%). ^{1}H NMR δ 7.87 (d, J = 7.4 Hz, 2H), 7.49−7.29 (m, 8H), 1.91 (s, 3H). ^{13}C NMR δ 191.0, 137.3, 133.6, 133.3, 130.0, 129.7, 128.5, 128.4, 125.3, 120.4, 51.5, 27.3. Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.36; H, 5.95; N, 5.92.

3-(4-Methylphenyl)-3-oxopropanenitrile (5g). Colorless plates (88%), mp 94−96 °C (lit.[11b] mp 175−176 °C). ^{1}H NMR δ 7.82 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.06 (s, 2H), 2.44 (s, 3H). ^{13}C NMR δ 186.6, 145.9, 131.8, 129.8, 128.5, 113.9, 29.2, 21.8. Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.09; H, 5.86; N, 8.77.

2-Benzyl-3-(4-methylphenyl)-3-oxopropanenitrile (5h). Colorless plates (83%), mp 65−67 °C. ^{1}H NMR δ 7.85 (d, J = 8.1 Hz, 2H), 7.35−7.25 (m, 7H), 4.50 (dd, J = 5.8, 5.9 Hz, 1H), [3.34 (dd, $^2J_{AB}$ = 13.9 Hz, ^3J = 5.6 Hz, 1H, A part of AB system), 3.22 (dd, $^2J_{AB}$ = 13.7 Hz, ^3J = 8.8 Hz, 1H, B part of AB system)], 2.43 (s, 3H). ^{13}C NMR δ 189.5, 145.8, 136.0, 131.5, 129.8, 129.0, 128.9, 128.8, 127.6, 117.1, 41.6, 35.5, 21.8. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.82; H, 6.35; N, 5.59.

2-Methyl-3-(4-methylphenyl)-3-oxo-2-phenylpropanenitrile (5i). Colorless oil (67%). ^{1}H NMR δ 7.78 (d, J = 8.2 Hz, 2H), 7.48−7.33 (m, 5H), 7.13 (d, J = 8.1 Hz, 2H), 2.32 (s, 3H), 1.91 (s, 3H). ^{13}C NMR δ 190.6, 144.8, 137.7, 130.8, 130.4, 129.8, 129.2, 128.5, 125.5, 120.7, 51.5, 27.5, 217. Anal. Calcd for $C_{17}H_{15}NO$: N, 5.62. Found: N, 5.54.

2-(4-Chlorobenzoyl)hexanenitrile (5j). Pale yellow oil (71%). ^{1}H NMR δ 7.93 (br s, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.58−7.48 (m, 1H), 4.31 (t, J = 7.1 Hz, 1H), 2.01−1.98 (m, 2H), 1.58−1.38 (m, 4H), 0.94 (t, J = 7.1 Hz, 3H). ^{13}C NMR δ 189.8, 135.5, 135.5, 134.4, 130.4, 128.7, 126.7, 117.0, 40.1, 29.4, 29.0, 22.0, 13.6. Anal. Calcd for $C_{13}H_{15}NO$: N, 5.94. Found: N, 6.02.

2-(4-Bromophenyl)-3-oxo-3-(2-thienyl)propanenitrile (5k). Colorless needles (91%), mp 74−76 °C. ^{1}H NMR δ 7.88 (dd, J = 1.0, 3.9 Hz, 1H), 7.82 (dd, J = 1.1, 4.9, Hz, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8,7 Hz, 2H), 7.21 (dd, J = 1.0, 4.4 Hz, 1H), 5.45 (s, 1H). ^{13}C NMR δ 180.9, 139.8, 136.7, 134.4, 132.7, 129.8, 129.3, 128.8, 123.6, 115.8, 46.8. Anal. Calcd for $C_{13}H_8BrNOS$: C, 51.00; H, 2.63; N, 4.57. Found: C, 51.04; H, 2.53; N, 4.44.

2-(2,4-Dichlorophenyl)-3-oxo-3-(2-thienyl)propanenitrile (5l). Colorless plates (89%), mp 89−91 °C. ^{1}H NMR δ 7.90 (d, J = 3.9 Hz, 1H), 7.80 (d, J = 4.9 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.47 (br s, 1H), 7.36 (dd, J = 1.8, 8.2 Hz, 1H), 7.19 (t, J = 4.3 Hz, 1H), 5.92 (s, 1H). ^{13}C NMR δ 180.0, 140.1, 136.9, 136.3, 134.2, 133.8, 131.1, 129.9, 128.8, 128.3, 127.3, 115.1, 43.2. Anal. Calcd for $C_{13}H_7Cl_2NOS$: C, 52.72; H, 2.38; N, 4.73. Found: C, 53.08; H, 2.44; N, 4.51.

2-Benzyl-3-oxo-3-(2-thienyl)propanenitrile (5m). Colorless plates (85%), mp 72−74 °C. ^{1}H NMR δ 7.81 (d, J = 3.7 Hz, 1H), 7.78 (d, J = 4.8 Hz, 1H), 7.28−7.34 (m, 5H), 7.17 (dd, J = 4.1, 4.4 Hz, 1H), 4.34 (dd, J = 6.5, 8.1 Hz, 1H), [3.38 (dd, $^2J_{AB}$ = 13.9 Hz, ^3J = 6.2 Hz, 1H, A part of AB system), 3.28 (dd, $^2J_{AB}$ = 13.7 Hz, ^3J = 8.7 Hz, 1H, B part of AB system)]. ^{13}C NMR δ 182.6, 140.8, 136.3, 135.7, 133.8, 129.0, 128.9, 128.7, 127.7, 116.8, 42.8, 35.9. Anal. Calcd for $C_{14}H_{11}NOS$: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.37; H, 4.58; N, 5.75.

2-Methyl-3-oxo-2-phenyl-3-(thienyl)propanenitrile (5n). Colorless prisms (82%), mp 66−68 °C. ^{1}H NMR δ 7.64 (d, J = 4.0 Hz, 1H), 7.60 (d, J = 4.9 Hz, 1H), 7.51−7.35 (m, 5H), 6.98 (dd, J = 4.7, 4.3 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR δ 183.9, 139.6, 137.3, 135.2, 135.1, 129.6, 128.7, 128.3, 125.6, 120.4, 51.7, 26.5. Anal. Calcd for $C_{14}H_{11}NOS$: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.51; H, 4.80; N, 5.77.

3-Oxo-3-(2-thienyl)propanenitrile (5o). Colorless plates (92%), mp 124−126 °C. ^{1}H NMR δ 7.81−7.78 (m, 2H), 7.20 (dd, J = 1.0, 4.0 Hz, 1H), 4.02 (s, 2H). ^{13}C NMR δ 179.5, 140.8, 136.2, 133.7, 128.7, 113.4, 29.5. Anal. Calcd for C_7H_5NOS: C, 55.61; H, 3.33; N, 9.26. Found: C, 55.48; H, 3.28; N, 9.12.

2-(2,4-Dichlorophenyl)-3-(2-furyl)-3-oxopropanenitrile (5p). Colorless prisms (94%), mp 86−88 °C. ^{1}H NMR δ 7.70 (br s, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 2.1 Hz, 1H), 7.45 (d, J = 3.7 Hz, 1H), 7.36 (dd, J = 2.1, 8.4 Hz, 1H), 6.64 (dd, J = 1.5, 3.7 Hz, 1H), 5.93 (s, 1H). ^{13}C NMR δ 175.7, 149.7, 148.3, 136.1, 134.0, 131.2, 129.8, 128.2, 126.8, 120.6, 114.9, 113.4, 42.3. Anal. Calcd for $C_{13}H_7Cl_2NO_2$: C, 55.74; H, 2.52; N, 5.00. Found: C, 55.72; H, 2.47; N, 4.94.

3-(2-Furyl)-2-(1-naphthyl)-3-oxopropanenitrile (5q). Colorless plates (92%), mp 96−98 °C. ^{1}H NMR δ 8.08 (d, J = 8.4 Hz, 1H), 7.89−7.86 (m, 2H), 7.75 (d, J = 7.1 Hz, 1H), 7.62−7.46 (m, 4H), 7.30 (d, J = 3.7 Hz, 1H), 6.49 (dd, J = 1.7, 3.7 Hz, 1H), 6.10 (s, 1H). ^{13}C NMR δ 177.4, 149.9, 147.7, 134.0, 130.4, 130.1, 129.2, 128.0, 127.4, 126.4, 125.8, 125.4, 122.5, 120.3, 116.0, 113.2, 44.0. Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 78.49; H, 4.39; N, 5.22.

3-(2-Furyl)-3-oxopropanenitrile (5r). Colorless plates (95%), mp 66−68 °C (lit.[11b] mp 76−78 °C). ^{1}H NMR δ 7.68 (br s, 1H), 7.39 (d, J = 3.6 Hz, 1H), 6.65 (dd, J = 1.5, 1.4 Hz, 1H), 3.99 (s, 2H). ^{13}C NMR δ 175.7, 150.4, 147.8, 119.3, 113.3, 28.8. Anal. Calcd for $C_7H_5NO_2$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.23; H, 3.73; N, 10.37.

1-Isovaleroylbenzotriazole (3a). Pale yellow oil (95%). ^{1}H NMR δ 8.34 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 3.35 (d, J = 7.0 Hz, 2H), 2.53−2.44 (septet, J = 6.9 Hz, 1H), 1.25 (d, J = 6.6 Hz, 6H). ^{13}C NMR δ 172.0, 146.1, 131.0, 130.3, 126.0, 120.0, 114.4, 44.0, 25.6, 22.5. Anal. Calcd for $C_{11}H_{13}N_3O$: N, 20.67. Found: N, 20.53.

1-(2-Thienylcarbonyl)benzotriazole (3f). Colorless macrocrystals (93%), mp 166−168 °C. ^{1}H NMR δ 8.58 (d, J = 3.9 Hz, 1H), 8.40 (d, J = 5.2 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 5.0 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.28 (t, J = 3.5 Hz, 1H). ^{13}C NMR δ 159.2, 145.8, 138.5, 137.2, 133.5, 132.1, 130.5, 128.1, 126.3, 120.2, 114.8. Anal. Calcd for $C_{11}H_7N_3OS$: C, 57.63; H, 3.08; N, 18.33. Found: C, 57.64; H, 3.07; N, 18.24.

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Supporting Information Available: Characterization data for compounds **5a**−**r** and **3a**,**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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