The preparation of *N*-acylbenzotriazoles from aldehydes

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Dedicated to our good friend Branko Stanovnik on his 65th birthday

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Abstract

N-Acyl- (**3a–g**) and *N*-alkyl-benzotriazoles (**10a–c**) were prepared from the corresponding aldehydes or alkanes, respectively, using a slight excess of *N*-chlorobenzotriazole in the presence of AIBN (2,2'-azobisisobutyronitrile) as an initiator.

Keywords: *N*-Chlorobenzotriazole, *N*-acylbenzotriazole, *N*-alkylbenzotriazole, AIBN

Introduction

N-Acylbenzotriazoles are versatile N- and C- acylating agents[1-3] for the preparation of primary, secondary and tertiary amides[2] including formamides[4] and oxamides,[5] cinnamoyl hydrazides,[6] enaminones[3] and for the conversion of ketone enolates into β-diketones.[7]

Literature syntheses of *N*-acylbenzotriazoles (i) react acid chlorides with 1-(trimethylsilyl)benzotriazole,[8] the sodium salt of benzotriazole,[9] or benzotriazole[10, 11]; (ii) react carboxylic acids with 1-(methanesulfonyl)benzotriazole;[6] or (iii) employ palladium catalyzed carbonylation of diaryliodonium salts in the presence of benzotriazole.[12]

In cases where the aldehyde is more readily available than the corresponding carboxylic acid, it is convenient to carry out the conversion of aldehyde RCHO into an acylating agent RCOX. Indeed, a number of methods are available for the direct conversion of aldehydes to the corresponding acid halides: (i) by the treatment of aromatic aldehydes with SO_2Cl_2 in the presence of a phosphonium catalyst;[13] (ii) use of *N*-chlorosuccinimide;[14,15] (iii) carbon tetrahalides at high temperatures;[16] (iv) vapor phase photochemical halogenation;[17] and (v) iodobenzene dichloride.[18]

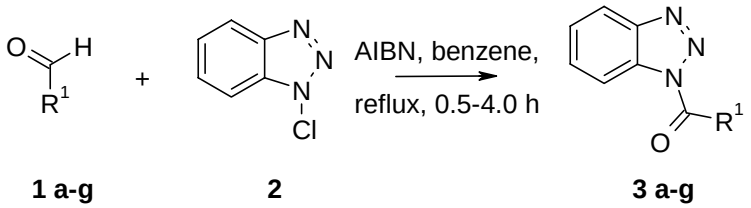
N-Chlorobenzotriazole has been widely used as (i) a mild oxidant[19, 20] for the preparation of aldehydes, ketones,[21] azo-compounds,[21] sulphoxides,[20] sulfonimidoyl chlorides,[22] nitrile oxides;[23] (ii) a chlorinating agent[24, 25] and (iii) for addition reactions to olefins[26-28] and

isonitriles.[29] Rees and Storr showed that the reactions of *N*-chlorobenzotriazole as an oxidant are radical in nature.[26]

We now show that *N*-chlorobenzotriazole (**2)** conveniently converts aldehydes **1a–g** into the corresponding *N*-acylbenzotriazoles **3a–g** (Scheme 1). Alcohols **8a** and **8h** are also converted into acylbenzotriazoles (Scheme 4), while substituted toluenes give the corresponding *N*-alkylbenzotriazoles **10a–c**. All these reactions take place in the presence of AIBN[15] as a radical initiator.

Results and Discussion

Preparation of *N*-acylbenzotriazoles 3a–g. Refluxing aldehydes **1a–g** with *N*-chlorobenzotriazole (**2**) in benzene for 0.5–4h in the presence of catalytic AIBN led to the *N*-acylbenzotriazole; yields in 53–83 % except for the furyl derivative **3g**. (Scheme 1) This resembles the known reaction of aldehydes with *N*-bromosuccinimide to give the corresponding acid bromides using catalytic amount of AIBN as a radical initiator.[15] Results are shown in Table 1. Known products were identified by m.p. and direct comparison of the NMR spectra. Compound **3e** is novel and its structure is supported by elemental analysis and its spectra.



1 a-g **2** **3 a-g**

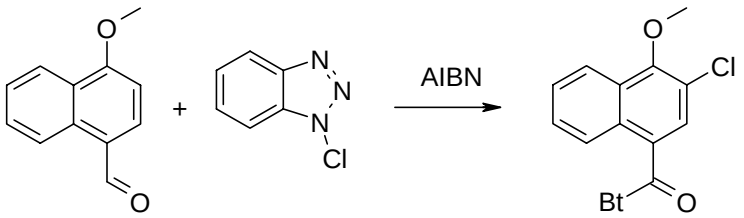
Scheme 1

Table 1. Preparation of N-acylbenzotriazoles **3a–g**

	R^1	Time (h)	Yield (%)	m.p. (^oC)	Lit. m.p. (^oC)
3a	Ph	1.2	63	112–113	112–113[30-31]
3b	C_2H_5	2.5	53[a]	77–78	80–82[31]
3c	4-ClC_6H_4	1.0	81	138–139	138–139[2]
3d	$C_6H_5(CH_2)_2$	2.0	62	62–64	63–64[2]
3e	3-thienyl	3.0	56	118–120	Novel
3f	$(CH_3)_3CCH_2$	1.5	83	56–57	56–57[7]
3g	2-furyl	4.0	38	165–167	165–167[30]

[a]heating at 50–55 ^{o}C.

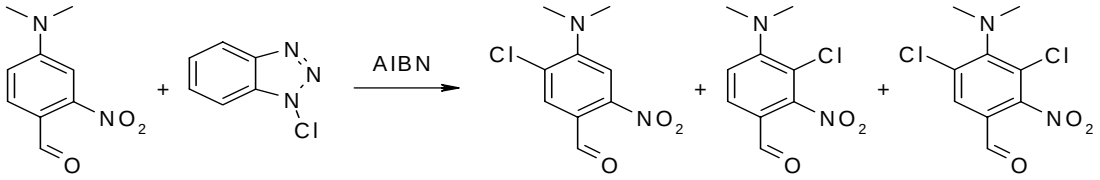
Treatment of 4-methoxynaphthaldehyde (**4**) using our standard conditions formed a mixture of two compounds, however using 2 equivalents of *N*-chlorobenzotriazole gave 1*H*-1,2,3-benzotriazol-1-yl-(3-chloro-4-methoxy-1-naphthyl)methanone (**5**). (Scheme 2) Boehlow et al. showed that ring halogenation takes place on the reaction of 4-methoxybenzaldehyde with *N*-bromosuccinimide.[32] Compound **5** was identified from its elemental analysis and spectral examination.



4 **2** **5**

Scheme 2

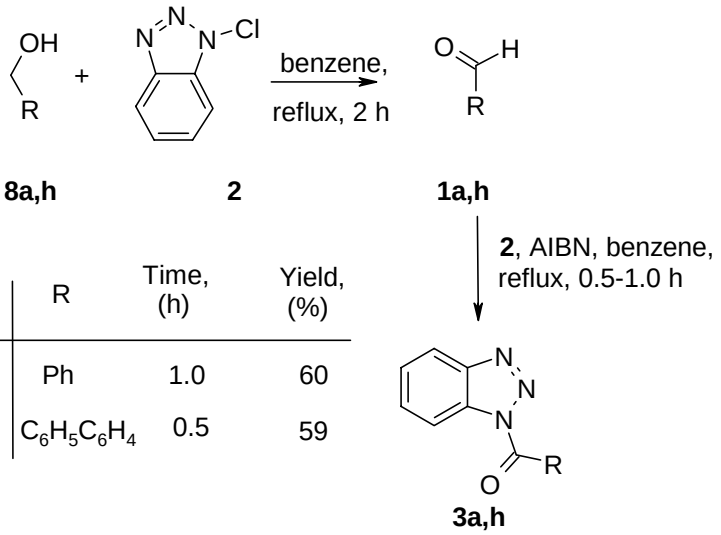
4-(Dimethylamino)-2-nitrobenzaldehyde (**6**), on treatment with 2 equiv of *N*-chlorobenzotriazole gave three ring halogenation products **7a–c** (Scheme 3), which were separated by column chromatography. The structures of **7a–c** were assigned on the basis of ^{1}H and ^{13}C NMR data and elemental analyses.



6 **2** **7a** **7b** **7c**

Scheme 3

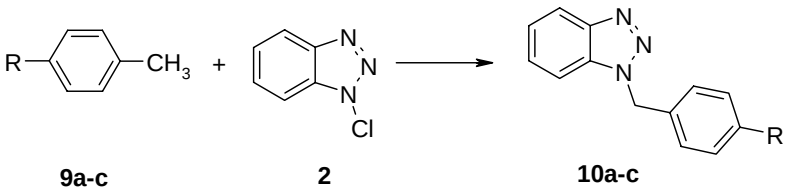
The oxidation of alcohols into the corresponding aldehydes by *N*-chlorobenzotriazole has been reported previously.[19] We now show that two equivalents of *N*-chlorobenzotriazole converted alcohols **8a,h** as expected into the corresponding *N*-acylbenzotriazoles **3a,h** (Scheme 4), which were purified by recrystallization. Known **3a** was identical with the authentic sample, novel **3h** was identified by elemental analysis and ^{1}H and ^{13}C NMR spectra.



	R	Time, (h)	Yield, (%)
3a	Ph	1.0	60
3h	$C_6H_5C_6H_4$	0.5	59

Scheme 4

Preparation of *N*-alkylbenzotriazoles 10a–c. Reactions of *N*-chlorobenzotriazole (**2**) with substituted toluenes **9a–c** in the presence of AIBN at 90–100 °C for 21–48 h led to the formation of corresponding *N*-alkylbenzotriazoles **10a–c**, similar to the radical bromination of the side chain of toluene previously observed by Slutter et al.[33] on reaction with *N*-bromosuccinimide.



	R	Time (h)	Yield (%)
10a	H	32	69
10b	Cl	21	55
10c	CN	48	64

Scheme 5

Compounds **10a** and **10b** had singlets at δ 5.84 and 5.82 identical with spectra previously published.[34] Novel compound **10c** was identified by elemental analysis and by its ^{1}H and ^{13}C NMR spectra.

N-Benzylbenzotriazoles are useful synthetically in many ways. Thus, lithiation with butyl lithium can be followed by the addition to aliphatic, aromatic, and α,β-unsaturated aldehydes;[35]

cyclic and acyclic ketones;[35, 36] carboxylic esters;[37] enamines[38, 39] and imides[40] and leading to the formation of trans-alkenes, dienes , trienes and alkynes. 2-(Benzotriazol-1-yl)enamines (obtained from lithiated 1-(arylmethyl)benzotriazoles and nitriles) undergo rearrangement to give 2,2-diarylquinazolines.[41] 1-Benzylbenzotriazoles act as a 1,3-dipole synthons in Michael addition–cyclization for the preparation of polysubstituted naphthalenes and phenanthrenes.[42] Annulation of benzylbenzotriazole with 2-bromoacetaldehyde diethyl acetal followed by the treatment with BuLi and *N*-benzylideneaniline leads to the formation of 1,2,3-triarylpyrroles in one pot.[43] [3+2] cycloaddition of benzyl benzotriazole with alkenes leads to the formation of functionalised indans.[44]

Literature methods to prepare *N*-benzylbenzotriazoles include reactions of the corresponding alkane or arene with 1-chloromethylbenzotriazole in the presence of aluminium halide;[45] or from the corresponding arylmethyl halide with benzotriazole.[42, 46]

To summarize, we have developed one pot syntheses of *N*-acyl- and *N*-alkyl-benzotriazoles from the corresponding aldehydes/alcohols or toluenes respectively, utilizing *N*-chlorobenzotriazole in the presence of a radical initiator.

Experimental Section

General Procedures. Melting points were determined on a hot-stage apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard for ^1H (300 MHz) or a solvent as the internal standard for ^{13}C (75 MHz). Micro elemental analyses were performed on a Carlo Erba EA-1108 elemental analyzer.

Materials. 1-Chlorobenzotriazole (**2**) was synthesized according to the previously published procedure[47]as white crystals mp 103–105 ^oC (103–105 ^oC[47]). 4-(Dimethylamino)-2-nitrobenzaoldehyde (**6**) was synthesized according to the published procedure by Baumann et al.[48] and was confirmed by the NMR data and CHN analysis.

General procedure for the synthesis of *N*-acylbenzotriazole from the corresponding aldehydes (3a–g)

The mixture of corresponding aldehyde (11 mmol), *N*-chlorobenzotriazole (2.70 g, 17.6 mmol) and AIBN (0.1 g, 0.6 mmol) in benzene (80 mL) were refluxed for the specified time (Scheme 1). To the cooled reaction mixture ethyl acetate was added, and the organic layer was washed with saturated aqueous Na_2CO_3, brine, and dried over $MgSO_4$. The solvent was evaporated to give the crude product, which was purified by recrystallisation from the appropriate solvent to afford the pure compound.

1*H*-1,2,3-Benzotriazol-1-yl-(phenyl)methanone (3a). White needles from 2-propanol (63 %), mp 112–113 °C (112–113 °C[30, 31]); ^1H NMR δ 7.53–7.61 (m, 3H), 7.68–7.74 (m, 2H), 8.16–8.23 (m, 3H), 8.40 (d, J = 8.2 Hz, 1H) ; ^{13}C NMR δ 114.8, 120.2, 126.3, 128.4, 130.4, 131.5, 131.7, 132.3, 133.7, 145.7, 166.7.

1- (1*H*-1,2,3-Benzotriazol-1-yl)-1-propanone (3b). White prisms from 2-propanol (53 %), mp 77–78 °C (80– 82 °C[31]); ^{1}H NMR δ 1.43 (t, *J* = 7.3 Hz, 3H), 3.47 (q, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.1 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR δ 8.3, 29.1, 114.4, 120.1, 126.0, 130.3, 131.1, 146.1, 173.3. Anal. Calcd for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.77; H, 5.22; N, 24.12.

1*H*-1,2,3-Benzotriazol-1-yl-(4-chlorophenyl)methanone (3c). White needles from 2-propanol (81 %), mp 138–139 °C (138–139 °C[2]); ^{1}H NMR δ 7.54–7.59 (m, 3H), 7.72 (t, *J* = 8.1 Hz, 1H), 8.16–8.22 (m, 3H), 8.38 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR δ 114.8, 120.2, 126.5, 128.8, 129.7, 130.5, 132.2, 133.2, 140.4, 145.7, 165.6.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-3-phenyl-1-propanone (3d). White prisms from benzene at 5–10 °C overnight (62 %), mp 62– 64 °C (63– 64 °C[2]); ^{1}H NMR δ 3.23 (t, *J* = 7.8 Hz, 2H), 3.77 (t, *J* = 7.6 Hz, 2H), 7.19–7.32 (m, 5H), 7.47–7.52 (m, 1H), 7.61–7.67 (m, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR δ 30.1, 37.1, 114.4, 120.1, 126.1, 126.5, 128.4, 128.6, 130.3, 131.0, 139.8, 146.1, 171.6.

1*H*-1,2,3-Benzotriazol-1-yl(3-thienyl)methanone (3e). Brownish microcrystals from 2-propanol (56 %), mp 118–120 °C; ^{1}H NMR (DMSO) δ 7.65 (t, *J* = 7.7 Hz, 1H), 7.79–7.84 (m, 2H), 7.90 (d, *J* = 4.9 Hz,1H), 8.28–8.34 (m, 1H), 8.98 (br s, 1H); ^{13}C NMR (DMSO) δ 114.4, 120.0, 126.5, 127.3, 129.4, 130.7, 131.7, 132.5, 138.6, 145.0, 160.1. Anal. Calcd for $C_{11}H_7N_3OS$: C, 57.63; H, 3.08; N, 18.33. Found: C, 57.55; H, 2.92; N, 18.44.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-3,3-dimethyl-1-butanone (3f). White prisms from hexanes (83 %), mp 56–57 °C (56–57 °C[7]) ^{1}H NMR δ 1.17 (s, 9H), 3.36 (s, 2H), 7.48–7.54 (m, 1H), 7.63–7.68 (m, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR δ 29.8, 32.0, 47.1, 114.6, 120.1, 126.0, 130.2, 131.1, 146.2, 171.3.

1*H*-1,2,3-Benzotriazol-1-yl (2-furyl)methanone (3g). White microcrystals from 2-propanol (38 %); mp 165–167 °C (165–167 °C[30]); ^{1}H NMR δ 6.74 (dd, *J* = 3.7, 1.6 Hz, 1H), 7.52–7.57 (m, 1H), 7.67–7.73 (m, 1H), 7.88–7.88 (m, 1H), 8.15–8.18 (m, 2H), 8.42 (d, *J* = 8.4 Hz, 1H), ^{13}C NMR δ 113.0, 114.7, 120.2, 124.8, 126.3, 130.5, 132.2, 144.6, 145.6, 148.9, 155.1.

Procedure for the synthesis of 1*H*-1,2,3-benzotriazol-1-yl (3-chloro-4-methoxy-1-naphthyl)methanone (5)

The mixture of 4-methoxy-1-naphthaldehyde (0.45 g, 2.4 mmol), *N*-chlorobenzotriazole (0.70 g, 4.6 mmol) and AIBN (0.1 g, 0.6 mmol) in benzene (80 mL) were refluxed for 4.0 h, then stirred at room temperature overnight. To the reaction mixture, ethyl acetate was added (50 ml), and the organic layer was washed with saturated aqueous Na_2CO_3, brine and dried over $MgSO_4$. The solvent was evaporated to give the crude product, which was purified by column chromatography (CH_2Cl_2: Hexanes = 1:1) to afford the pure product. White microcrystals (57%), mp 142–143 °C; ^{1}H NMR δ 4.14 (s, 3H), 7.56–7.67 (m, 3H), 7.74–7.80 (m, 1H), 7.96 (s, 1H), 8.13–8.17 (m, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.26–8.29 (m, 1H), 8.47 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR δ 61.7, 114.7, 120.4, 121.8, 122.6, 125.2, 126.2, 126.6, 127.5, 128.3, 129.4, 130.7,

131.4, 132.0, 132.4, 146.2, 155.7, 166.0. Anal. Calcd for $C_{18}H_{12}ClN_3O_2$: C, 64.01; H, 3.58; N, 12.44. Found: C, 64.30; H, 3.46; N, 12.42.

General procedure for the synthesis of substituted 4-(dimethylamino)-6-nitrobenzaldehyde (7a–c)

The mixture of 4-(dimethylamino)-2-nitrobenzaldehyde (0.97 g, 5.0 mmol), *N*-chlorobenzotriazole (1.44 g, 9.4 mmol) and AIBN (0.1 g, 0.6 mmol) in benzene (80 mL) were refluxed for 3.0 h, then stirred at room temperature overnight. To the reaction mixture, ethyl acetate was added, and the organic layer was washed with saturated aqueous Na_2CO_3, brine, and dried over $MgSO_4$. The solvent was evaporated to give the crude product, which was purified by column chromatography (CH_2Cl_2:Hexanes = 6:4) to give **7a–c**.

5-Chloro-4-(dimethylamino)-2-nitrobenzaldehyde (7a). Orange microcrystals (17 %), mp 92–94 °C; ^{1}H NMR δ 3.07 (s, 6H), 7.52 (s, 1H), 7.95 (s, 1H), 10.25 (s, 1H); ^{13}C NMR δ 42.8, 113.7, 122.5, 129.7, 132.4, 149.1, 154.1, 186.0. Anal. Calcd for $C_9H_9ClN_2O_3$: C, 47.28; H, 3.97; N, 12.25. Found: C, 47.23; H, 3.82; N, 12.49.

3-Chloro-4-(dimethylamino)-2-nitrobenzaldehyde (7b). Orange microcrystals (4%), mp 95–97 °C; ^{1}H NMR δ 3.07 (s, 6H), 7.09 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 9.72 (s, 1H); ^{13}C NMR δ 43.0, 116.0, 118.6, 119.8, 129.9, 130.3, 155.7, 184.8. Anal. Calcd for $C_9H_9ClN_2O_3$: C, 47.28; H, 3.97; N, 12.25. Found: C, 46.94; H, 3.77; N, 12.24.

3,5-Dichloro-4- (dimethylamino)-6-nitrobenzaldehyde (7c). Yellow needles (43%), mp 63–64 °C; ^{1}H NMR δ 3.07 (s, 6H), 7.83 (s, 1H), 9.73 (s, 1H); ^{13}C NMR δ 42.9, 100.2, 122.3, 124.3, 131.3, 134.0, 152.7, 183.9. Anal. Calcd for $C_9H_8Cl_2N_2O_3$: C, 41.09; H, 3.07; N, 10.65. Found: C, 41.17; H, 2.96; N, 10.47.

General procedure for the synthesis of *N*-acylbenzotriazole (3a, 3h) from the corresponding alcohols

The mixture of alcohol (8 mmol) and *N*-chlorobenzotriazole (1.78 g, 11.6 mmol) in benzene (100 mL) were refluxed for 2 h, then AIBN (0.1 g, 0.6 mmol) and the next portion of *N*-chlorobenzotriazole (1.70 g, 11.1 mmol) were added. The solution was kept at 80 ^{o}C for the specified time (Scheme 1), then stirred at room temperature overnight. To the reaction mixture, ethyl acetate was added and the organic layer was washed with saturated aqueous Na_2CO_3, brine and dried over anhyd. $MgSO_4$. The solvent was evaporated to give the crude product, which was purified by recrystallisation from the appropriate solvent to afford the pure compound.

1*H*-1,2,3-Benzotriazol-1-yl (phenyl)methanone (3a). White needles from 2-propanol (60 %), mp 112–113 °C (112–113 °C[30]). The spectrum is identical with that for compound **3a** prepared from benzaldehyde above.

1*H*-1,2,3-Benzotriazol-1-yl ([1,1'-biphenyl]-4-yl)methanone (3h). White prisms from 2-propanol (59 %), mp 165–167 °C; ^{1}H NMR (DMSO) δ 7.45–7.58 (m, 3H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.82–7.88 (m, 3H), 7.96 (d, *J* = 8.4 Hz, A part of AB system, 2H), 8.24 (d, *J* = 8.4 Hz, B part of AB system, 2H), 8.30–8.37 (m, 2H); ^{13}C NMR (DMSO) δ 114.5, 120.0, 126.5, 126.6,

127.1, 128.6, 129.1, 130.1, 130.7, 131.8, 132.2, 138.7, 145.0, 145.2, 166.2. Anal. Calcd for $C_{19}H_{13}N_3O$: C, 76.24; H, 4.38; N, 14.04. Found: C, 75.83; H, 4.24; N, 14.18.

General procedure for the synthesis of *N*-alkyl- and *N*-aryl- benzotriazoles (10a–c)

The a mixture of *N*-chlorobenzotriazole (2.30 g, 15.0 mmol) and AIBN (0.1 g, 0.6 mmol) in excess of corresponding toluene as a reagent as well as solvent (126.8 mmol) were heated at 105–110 ^oC for the specified time (Scheme 3). To the cooled reaction mixture, ethyl acetate was added, and the organic layer was washed with saturated aqueous Na_2CO_3, brine and dried over anhyd. $MgSO_4$. The solvent was evaporated under reduced pressure to give the crude product, which was purified by recrystallization from the appropriate solvent to give the pure compound.

1-Benzyl-1*H*-1,2,3-benzotriazole (10a). White microcrystals form 2-propanol (69 %), mp 115–116 °C (115–116 °C[34]); ^{1}H NMR δ 5.84 (s, 2H), 7.25–7.39 (m, 8H), 8.06 (d, *J* = 7.83 Hz, 1H); ^{13}C NMR δ 52.2, 109.7, 120.0, 123.8, 127.3, 127.5, 128.4, 128.9, 132.7, 134.7, 146.3.

1-(4-Chlorobenzyl)-1*H*-1,2,3-benzotriazole (10b). White microcrystals from 2-propanol (55 %), mp 98–99 °C (101–102 °C[49]); ^{1}H NMR δ 5.82 (s, 2H), 7.21 (d, *J* = 8.2 Hz, A part of the AB system, 2H), 7.29–7.46 (m, 5H), 8.08 (d, *J* = 8.8 Hz,1H); ^{13}C NMR δ 51.4, 109.4, 120.2, 124.0, 127.6, 128.9, 129.2, 132.6, 133.2, 134.4, 146.3. Anal. Calcd for $C_{13}H_{10}ClN_3$: C, 64.07; H, 4.14; N, 17.24. Found: C, 64.01; H, 3.95; N, 17.31.

4-(1*H*-1,2,3-Benzotriazol-1-ylmethyl)benzonitrile (10c). White prisms from 2-propanol (64 %), mp 164– 166 °C; ^{1}H NMR δ 5.91 (s, 2H), 7.33–7.49 (m, 5H), 7.63 (d, *J* = 8.4 Hz, A part of AB system, 2H), 8.10 (d, *J* = 8.2Hz, 1H); ^{13}C NMR δ 51.3, 109.1, 112.5, 118.1, 120.3, 124.2, 27.9, 128.0, 132.6, 132.7, 139.9, 146.2. Anal. Calcd for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.50; H, 4.30; N, 23.67.

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