An Efficient General Synthesis of 1-(Benzotriazol-1-yl)alkyl Esters Alan R. Katritzky*, Alfredo Pastor and Michael V. Voronkov

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1-(Benzotriazol-1-yl)alkyl esters **2a-u** were obtained in yields averaging 86% by the direct reaction of various aldehydes with the corresponding *N*-acylbenzotriazoles in the presence of a catalytic amount of potassium carbonate (10-25 mole %). The procedure was optimized by evaluating the effects of solvent, catalyst, temperature and other parameters.

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Introduction.

Compounds containing the Bt-C-O functionality are versatile intermediates in organic synthesis [1]. Among such benzotriazole derivatives, 1-(benzotriazol-1-yl)alkyl ethers 1 have been widely used in the preparation of various heterocycles [2a-c], α-functionalized ketones [2c, 3a-c] and crown ethers [4]. While the corresponding 1-(benzotriazol-1-yl)alkyl esters 2 should offer similar synthetic opportunities, their applications are still relatively underdeveloped [5], largely because their accessibility has up until now been significantly limited (Figure 1) [5,6]. Direct treatment of 1H-benzotriazol-1-ylmethanol with benzoyl chloride or benzoic anhydride affords the corresponding benzoate in yields of only 27% and 24%, respectively [6]. Two alternative procedures for the preparation of 1-(benzotriazol-1-yl)alkyl esters, heating 1-(1-chloroalkyl)benzotriazoles with sodium carboxylates in dimethyl sulfoxide or by substitution of one acetoxy group in acylals with benzotriazole [5], proceed in good yields. However, these methods are limited to base or acid tolerant functionalities. To assist further development in this area, we now report a general, straightforward and efficient method to prepare a wide variety of 1-(benzotriazol-1-yl)alkyl esters 2.

Figure 1

Scheme 1

N=N N=N
$$K_2CO_3$$
 (cat)
R'CHO

R

2

Entry R R' T (°C) Time Yield (hours) (%) 29 C_6H_5 Et 20 100 [a] 2b 4-MeOC₆H₄ Pr 20 4 97 [a] ClCH₂ 2c 20 Pr 4 87 [a] 2d C_6H_5 t-Bu 20 24 93 [a] C₆H₅ 2e 2-furyl 70 6 78 2f C_6H_5 3-furyl 70 6 76 2g C₆H₅ 4-NO₂C₆H₄ 20 6 96 4-MeO₂CC₆H₄ 2h C₆H₅ 20 10 100 [a] 2i 4-NCC₆H₄ 20 16 98 C_6H_5 2j 4-MeOC₆H₄ 70 68 C_6H_5 6 2k 70 75 4-MeOC₆H₄ C_6H_5 6 21 70 70 4-MeOC₆H₄ 4-MeC₆H₄ 6 2m Cl(CH₂)₃ 70 86 4-MeC₆H₄ 6 2n 20 Me Et 4 100 [a] 20 Me t-Bu 20 24 96 [a] 2p Me C_6H_5 70 8 78

4-MeC₆H₄

4-MeO2CC6H4

4-NCC₆H₄

Εt

Et

70

20

20

20

8

16

24

4

72

82

74

99 [a]

100 [a]

Table 1

[a] Minor amount of Bt2 isomer was isolated.

Results and Discussion.

Me

Me

Me

t-Bu

2-furyl

2q

2r

2s

2t

2u

1-(Benzotriazol-1-yl)alkyl esters are now shown to result from the direct reaction of the corresponding N-acylbenzotriazole derivative 3 and an aldehyde in excellent yields (Scheme 1). The best results were obtained when the reaction was performed in acetonitrile at a 0.3 M concentration in the presence of a catalytic amount of base (Table 1). Aliphatic aldehydes were generally found to give almost quantitative yields at room temperature within four hours. On the other hand, aromatic aldehydes, unless electron deficient (entries 2g, 2h, 2i, 2r and 2s), required elevated temperature (70°) and prolonged reaction time to afford comparable yields. While most products were isolated as the Bt1 isomer only, some products contained small amounts (8-18%) of the Bt² isomer (the latter was separated by column chromatography on silica gel hexane/ethyl acetate and/or recrystallization). The method is tolerant to base sensitive moieties such as halo-substituents (entries 2c

and 2m), nitriles (entries 2i and 2s) and esters (entries 2h and 2r) and is able to provide products unobtainable from previously published methods. The presence of heteroaryl (entries 2e, 2f and 2u) or bulky substituents (entries 2d, 2o and 2t) did not affect the course of the reaction.

applied to benzotriazole. The reaction is tolerant of a wide range of concentrations, and the yield is rather indifferent to the presence of water and/or phase transfer reagents which appear to be essential for the preparation of 1-cyanoalkyl esters by similar procedures [8a-c].

Table 2

Entry	Solvent	Base	Time (hours)	Yield (%)	2a/4a
1	acetonitrile	potassium carbonate	1	100	4:1
2	Hexanes	potassium carbonate	4	98	13:1
3	dicholoromethane	potassium carbonate	4	68	4.5:1
4	diethyl ether	potassium carbonate	4	18	4.6:1
5	tetrahydrofuran	potassium carbonate	. 4	12	3:1
6	acetonitrile	triethyl amine	5	86	10:1
7	acetonitrile	sodium bicarbonate	4	No reaction	
8	acetonitrile	potassium tert-butoxide	0.25	47	2.6:1
9	acetonitrile	potassium hydroxide	0.25	Dec	
10	acetonitrile	trisodium phosphate	24	31	4:1
11	acetonitrile	dipotassium kydrogenphosphate	24	No reaction	
12	Hexanes	triethyl amine	5	No reaction	
13	Hexanes	sodium bicarbonate	4	No reaction	
14	Hexanes	potassium hydroxide	0.25	Dec	
15	Neat	potassium carbonate	1.5	91	5.5:1

Although several studies of the optimum conditions for the preparation of alkyl esters containing α-functional groups have been reported, including halides [7a-d], cyanides [8a-c], triazoles [9] and pyridinium salts [10], we found that for our reaction the effects of solvent, catalyst, and nature of aldehyde did not parallel any of those previously reported. Solvents such as tetrahydrofuran and ether gave slightly lower yields than acetonitrile (entries 4 and 5 vs. 1). In hexanes (entry 2), or with no solvent (entry 15), aliphatic aldehydes produced excellent yields while aromatic aldehydes failed to react (for example, reaction with p-tolylaldehyde in refluxing hexanes for 20 hours did not afford the desired product). The presence of 10-25 mol% of potassium carbonate was essential for good yields; other bases, such as triethylamine (entry 6), potassium tert-butoxide (entry 8) or potassium hydroxide (entry 14) were less effective. Surprisingly, other inorganic bases failed, with the exception of sodium phosphate (entry 10), which yielded only 31% of the desired product. Lewis acid catalysis [11] resulted in the aldehyde bis-benzotriazole adducts as the major product, along with trace amounts of the desired product. The formation of the Bt² isomer was minimized by using hexanes as a solvent (entry 2) or triethylamine as a base (entry 6). Furthermore, aromatic aldehydes afforded only 45-50% of the desired product when a "one pot" procedure [9,10] was

In general, organic molecules containing benzotriazole as a leaving group are much more stable than the corresponding chloro analogues. Handling esters of 1-chloroalkanols is hindered by their low stability and sensitivity [12a-b]. The esters of 1-(benzotriazol-1-yl)alkanols described here could offer a synthetically useful alternative.

EXPERIMENTAL

Melting points were determined using a Thomas Hoover capillary Melting Point Apparatus and are not corrected. ¹H (300 MHz) and ¹³C (75 MHz) nmr spectra were recorded on a Varian Gemini-300 spectrometer using either deuteriochloroform or dimethyl-d₆ sulfoxide as solvent with tetramethylsilane as the internal reference for ¹H nmr and the central line of deuteriochloroform as the reference for ¹³C nmr. The gcms instrument used in the optimization of the procedure was a Hewlett Packard 5890 Series II Gas Chromatograph coupled to a Hewlett Packard 5972 Mass Selective Detector. Elemental analyses were performed on a Carlo Erba-1106 instrument. Column chromatography was carried out on MCB silica gel (230-400 mesh).

General Procedure for the Preparation of N-Acylbenzotriazoles 3.

To a solution of benzotriazole (11.9 g, 0.1 mole) in anhydrous dichloromethane (200 ml) at 0° under nitrogen was added dropwise triethylamine (17 ml, 0.12 mole), followed by addition of the corresponding acid chloride (0.11 mole). The resulting mixture was stirred at room temperature for 30 minutes. The reaction

was quenched at this temperature with hydrochloric acid (2 N, 100 ml), and the organic phase was separated and then washed with hydrochloric acid (2 N, 2 x 50 ml) and water (50 ml) successively. The organic extracts were dried over anhydrous magnesium sulfate, filtered and evaporated to dryness to give a white powdery solid which was purified by recrystallization.

1H-1,2,3-Benzotriazol-1-yl(phenyl)methanone (3a).

This compound was obtained as a white solid (98%), mp, 112-113° (lit [13] 112°); ${}^{1}H$ nmr (deuteriochloroform): δ 7.50-7.70 (m, 5H), 8.16 (d, J = 8.2 Hz, 1H), 8.21 (d, J = 7.3 Hz, 2H), 8.38 (d, J = 8.2 Hz, 1H); ${}^{13}C$ nmr (deuteriochloroform): δ 114.7, 120.1, 126.2, 128.3, 130.3, 131.4, 131.7, 132.3, 133.6, 145.7, 166.6.

1H-1,2,3-Benzotriazol-1-yl(4-methoxyphenyl)methanone (3b).

This compound was obtained as a white solid (97%), mp, $108-109^{\circ}$; ${}^{1}H$ nmr (deuteriochloroform): δ 3.32 (s, 3H), 7.05 (d, J = 8.8 Hz, 2H), 7.53 (t, J = 8.0 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.29 (d, J = 8.8 Hz, 2H), 8.36 (d, J = 8.0 Hz, 1H); ${}^{13}C$ nmr (deuteriochloroform): δ 55.6, 113.9, 114.8, 120.1, 123. 4, 126.1, 130.1, 132.6, 134.4, 145.6, 164.2, 165.6.

Anal. Calcd. for C₁₄H₁₁N₃O₂: (253.26) C, 66.38; H, 4.39; N, 16.59. Found: C, 65.98; H, 4.68; N, 16.42.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-ethanone (3c).

This compound was obtained as a white solid (95%), mp, $51-52^{\circ}$ (lit [13] $51-52^{\circ}$); ${}^{1}H$ nmr (deuteriochloroform): δ 3.00 (s, 3H), 7.50 (t, J = 7.5 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 8.10 (d, J = 7.5 Hz, 1H), 8.25 (d, J = 7.5 Hz, 1H); 1 C nmr (deuteriochloroform): δ 23.1, 114.3, 120.0, 126.0, 130.2, 130.9, 146.1, 169.4.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2,2-dimethyl-1-propanone (**3d**).

This compound was obtained as a white solid (94%), mp, 72-73°; 1H nmr (deuteriochloroform): δ 1.65 (s, 9H), 7.49 (t, J = 8.0 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 27.6, 42.5, 115.0, 119.8, 125.8, 130.1, 132.2, 144.8, 177.3.

Anal. Calcd. for C₁₁H₁₃N₃O (203.25): C, 65.00; H, 6.46; N, 20.68. Found: C, 65.14; H, 6.52; N, 20.77.

1H-1,2,3-Benzotriazol-1-yl(2-furyl)methanone (3e).

This compound was obtained as colorless needles (99%), mp, 165-166°; 1H nmr (deuteriochloroform): δ 6.70-6.80 (m, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 8.87 (s, 1H), 8.10-8.20 (m, 2H), 8.41 (d, J = 8.2 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 112.9, 114.6, 120.1, 124.7, 126.2, 130.4, 132.0, 144.5, 145.5, 148.9, 154.9.

Anal. Calcd. for $C_{11}H_7N_3O_2$ (213.20): C, 61.97; H, 3.32; N, 19.71. Found: C, 61.65; H, 3.19; N, 19.34.

1-(1H-1,2,3-Benzotriazol-1-yl)-2-chloro-1-ethanone (3f).

This compound was obtained as colorless needles (91%), mp, 45-46°; ¹H nmr (deuteriochloroform): δ 5.36 (s, 2H), 7.71 (t, J = 7.3 Hz, 1H), 7.85 (t, J = 7.3 Hz, 1H), 8.28 (d, J = 8.3 Hz, 1H), 8.36 (d, J = 8.3 Hz, 1H); ¹³C nmr (deuteriochloroform): δ 42.5, 113.8, 120.2, 126.5, 130.6, 130.8, 145.8, 164.8.

Anal. Calcd. for C₈H₆ClN₃O (195.61): C, 49.12; H, 3.10; N, 21.49. Found: C, 49.25; H, 3.01; N, 21.54.

1-(1H-1,2,3-Benzotriazol-1-yl)-4-chloro-1-butanone (3g).

This compound was obtained as white crystals (87%), mp, 33-35°; 1 H nmr (deuteriochloroform): δ 2.43-2.57 (m, 2H),

3.71-3.81 (m, 2H), 3.85-3.98 (m, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H); ¹³C nmr (deuteriochloroform): δ 26.6, 32.4, 43.7, 113.9, 119.8, 125.9, 130.1, 130.6, 145.7, 171.1.

Anal. Caled. for C₁₀H₁₀ClN₃O (223.66): C, 53.70; H, 4.52; N, 18.79. Found: C, 53.55; H, 4.30; N, 19.20.

General Procedure for the Preparation of 1-(Benzotriazol-1-yl)-alkyl Esters 2.

To a heterogeneous mixture consisting of acy1-benzotriazole (2 mmoles) and aldehyde (2.1 mmoles) in acetonitrile (6 ml) with vigorous stirring was added potassium carbonate (69 mg, 0.5 mmole), and the resulting mixture stirred at room temperature or heated at 70° (see Table 1). After the reaction was complete the potassium carbonate was filtered and washed with dichloromethane. Removal of the solvents under vacuum afforded the desired product. Purification was achieved by column chromatography on silica gel hexane/ethyl acetate (5:1) and/or recrystallization.

1-(1H-1,2,3-Benzotriazol-1-yl)propyl Benzoate (2a).

This compound was obtained as a white solid (100%), mp, 84-85°; 1 H nmr (deuteriochloroform): δ 1.04 (t, J = 7.4 Hz, 3H), 2.69 (m, 2H), 7.34-7.60 (m, 6H), 7.87 (d, J = 8.4 Hz, 1H), 7.98-8.10 (m, 3H); 13 C nmr (deuteriochloroform): δ 9.2, 26.6, 81.1, 110.2, 120.0, 124.3, 127.9, 128.4, 128.6, 129.9, 132.6, 133.7, 145.9, 165. 1.

Anal. Calcd. for C₁₆H₁₅N₃O₂ (281.32): C, 68.31; H, 5.39; N, 14.94. Found: C, 68.25; H, 5.40; N, 15.03.

1-(1*H*-1,2,3-Benzotriazol-1-yl)butyl 4-Methoxybenzoate (**2b**).

This compound was obtained as a colorless oil (97%); 1H nmr (deuteriochloroform): δ 1.00 (t, J = 7.4 Hz, 3H), 1.25-1.60 (m, 2H), 2.62 (q, J = 7.4 Hz, 2H), 3.81 (s, 3H), 6.88 (d, J = 8.8 Hz, 2H), 7.37 (t, J = 8.0 Hz, 1H), 7.46-7.58 (m, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.0 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 13.3, 17.9, 35.0, 55.3, 79.4, 110.2, 113.7, 119.8, 120.7, 124.2, 127.8, 131.9, 132.5, 145.8, 163.9, 164.7.

Anal. Calcd. for C₁₈H₁₉N₃O₃ (325.37): C, 66.44; H, 5.90; N, 12.92. Found: C, 66.53; H, 6.07; N, 13.19.

1-(1H-1,2,3-Benzotriazol-1-yl)butyl 2-Chloroacetate (2c).

This compound was obtained as a colorless oil (85%); ¹H nmr (deuteriochloroform): δ 0.85 (t, 3H, J = 7.0 Hz), 1.22-1.44 (m, 2H), 2.34-2.51 (m, 2H), 3.98 (dd, J = 11.5, 14.0 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H); ¹³C nmr (deuteriochloroform): δ 13.5, 17.9, 35.6, 40.3, 80.7, 110.2, 119.6, 124.1, 128.4, 132.0, 145.9, 166.1.

Anal. Calcd. for C₁₂H₁₄CIN₃O₂ (267.72): C, 53.83; H, 5.28; N, 15.70. Found: C, 54.21; H, 5.43; N, 15.61.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2,2-dimethylpropyl Benzoate (2d).

This compound was obtained as a white solid (93%), mp, 128-129°; ¹H nmr (deuteriochloroform): δ 1.24 (s, 9H), 7.19 (s, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.40-7.66 (m, 4H), 7.80 (d, J = 8.4 Hz, 1H), 8.00-8.15 (m, 3H); ¹³C nmr (deuteriochloroform): δ 25.8, 37.4, 86.4, 110.6, 119.9, 124.0, 127.8, 128.5, 128.6, 129.9, 133.3, 133.8, 145.3, 164.8.

Anal. Calcd. for C₁₈H₁₉N₃O₂ (309.37): C, 69.88; H, 6.20; N, 13.59. Found: C, 69.89; H, 6.39; N, 13.61.

1H-1,2,3-Benzotriazol-1-yl(2-furyl)methyl Benzoate (2e).

This compound was obtained as colorless needles (78%), mp, 78-79°; 1 H nmr (deuteriochloroform): δ 6.45 (s, 1H), 6.71 (s, 1H), 7.35-7.60 (m, 6H), 7.78 (d, J = 8.3 Hz, 1H), 8.08 (d, J = 7.9 Hz, 3H), 8.72 (s, 1H); 13 C nmr (deuteriochloroform): δ 75.7, 110.6, 110.7, 111.0, 120.1, 124.4, 128.1, 128.2, 128.5, 130.0, 132.0, 134.0, 144.0, 146.2, 146.5, 164.1.

Anal. Calcd. for C₁₈H₁₃N₃O₃ (319.32): C, 67.70; H, 4.11; N, 13.16. Found: C, 67.74; H, 4.20; N, 13.40.

1H-1,2,3-Benzotriazol-1-yl(3-furyl)methyl Benzoate (2f).

This compound was obtained as colorless needles (76%), mp, 67-68°; 1 H nmr (deuteriochloroform): δ 6.53 (s, 1H), 7.35-7.80 (m, 8H), 8.00-8.10 (m, 3 H), 8.68 (s, 1H); 13 C nmr (deuteriochloroform): δ 75.8, 109.0, 110.5, 120.1, 120.7, 124.3, 128.0, 128.2, 128.4, 129.8, 131.9, 133.8, 141.1, 144.1, 146.1, 164.3.

Anal. Calcd. for C₁₈H₁₃N₃O₃ (319.32): C, 67.70; H, 4.11; N, 13.16. Found: C, 67.56; H, 4.08; N, 13.20.

1H-1,2,3-Benzotriazol-1-yl(4-nitrophenyl)methyl Benzoate (2g).

This compound was obtained as a white solid (96%), mp, 198-199°; ¹H nmr (dimethyl-d₆ sulfoxide): δ 7.40-7.80 (m, 5H), 7.90-8.00 (m, 3H), 8.05-8.15 (m, 3H), 8.32 (d, J = 8.6 Hz, 2H), 8.92 (s, 1H); ¹³C nmr (dimethyl-d₆ sulfoxide): δ 79.3, 111.1, 119.6, 123.9, 124.9, 127.7, 128.3, 128.7, 129.1, 129.7, 132.0, 134.5, 141.2, 145.1, 148.1, 163.9.

Anal. Calcd. for C₂₀H₁₄N₄O₄ (374.36): C, 64.16; H, 3.78; N, 14.97. Found: C, 63.91; H, 3.60; N, 14.91.

Methyl 4-[1*H*-1,2,3-Benzotriazol-1-yl(benzoyloxy)methyl]-benzoate (2h).

This compound was obtained as a white solid (100%), mp, 115-116°; 1H nmr (deuteriochloroform): δ 3.92 (s, 3H), 7.36-7.65 (m, 8H), 8.06-8.16 (m, 5H), 8.78 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 52.2, 80.1, 110.3, 120.3, 124.5, 126.3, 128.1, 128.3, 128.7, 130.0, 130.1, 131.4, 131.9, 134.1, 138.8, 146.3, 164.3, 166.1.

Anal. Calcd. for C₂₂H₁₇N₃O₄ (387.40): C, 68.20; H, 4.43; N, 10.85. Found: C, 68.17; H, 4.28; N, 10.87.

1H-1,2,3-Benzotriazol-1-yl(4-cyanophenyl)methyl Benzoate (2i).

This compound was obtained as a white solid (98%), mp, 153-154°; 1 H nmr (deuteriochloroform): δ 7.35-7.80 (m, 10H), 8.05-8.20 (m, 3H), 8.74 (s, 1H); 13 C nmr (deuteriochloroform): δ 79.4, 110.0, 113.7, 117.9, 120.4, 124.7, 127.2, 127.8, 128.5, 128.7, 130.0, 131.9, 132.7, 134.3, 139.1, 146.2, 164.2.

Anal. Calcd. for C₂₁H₁₄N₄O₂ (354.37): C, 71.17; H, 3.99; N, 15.81. Found: C, 70.90; H, 3.84; N, 15.66.

1*H*-1,2,3-Benzotriazol-1-yl(4-methoxyphenyl)methyl Benzoate (2j).

This compound was obtained as a colorless oil (68%); 1 H nmr (deuteriochloroform): δ 3.76 (s, 3H), 6.92 (d, J = 8.7 Hz, 2H), 7.30-7.60 (m, 8H), 8.00-8.20 (m, 3H), 8.71 (s, 1H); 13 C nmr (deuteriochloroform): δ 55.1, 80.7, 110.6, 114.1, 119.9, 124.2, 125.0, 127.6, 127.8, 128.4, 128.5, 129.8, 131.8, 133.7, 146.2, 160.3, 164.2.

Anal. Calcd. for C₂₁H₁₇N₃O₃ (359.39): C, 70.18; H, 4.78; N, 11.69. Found: C, 70.31; H, 5.05; N, 11. 52.

1H-1,2,3-Benzotriazol-1-yl(phenyl)methyl 4-Methoxybenzoate (2k).

This compound was obtained as a white solid (75%), mp, 98-99°; ¹H nmr (deuteriochloroform): δ 3.75 (s, 3H), 6.84 (d, J =

8.8 Hz, 2H), 7.45-7.20 (m, 8H), 8.10-7.95 (m, 3H), 8.64 (s, 1H); ¹³C nmr (deuteriochloroform): δ 55.4, 80.5, 110.6, 113.9, 120.1, 120.6, 124.3, 126.2, 128.0, 128.8, 129.5, 132.0, 132.2, 134.4, 146.4, 164.1, 164.2.

Anal. Calcd. for C₂₁H₁₇N₃O₃ (359.39): C, 70.18; H, 4.78; N, 11.69. Found: C, 70.00; H, 4.83; N, 11.77.

1*H*-1,2,3-Benzotriazol-1-yl(4-methylphenyl)methyl 4-Methoxybenzoate (2l).

This compound was obtained as a white solid (70%), mp, 125-126°; ¹H nmr (deuteriochloroform): δ 2.36 (s, 3H), 3.84 (s, 3H), 6.92 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 7.4 Hz, 2H), 7.25-7.50 (m, 4H), 7.56 (d, J = 7.4 Hz, 1H), 8.00-8.10 (m, 3H), 8.69 (s, 1H); ¹³C nmr (deuteriochloroform): δ 21.2, 55.4, 80.6, 110.7, 113.9, 120.1, 120.7, 124.2, 126.1, 127.9, 129.5, 131.5, 132.0, 132.2, 139.5, 146.3, 164.1, 164.2.

Anal. Calcd. for C₂₂H₁₉N₃O₃ (373.42): C, 70.76; H, 5.14; N, 11.26. Found: C, 70.56; H, 5.35; N, 11.38.

1H-1,2,3-Benzotriazol-1-yl(4-methylphenyl)methyl 4-Chlorobutanoate (2m).

This compound was obtained as a colorless oil (86%); ¹H nmr (deuteriochloroform): δ 2.29-2.48 (m, 2H), 2.61 (s, 3H), 2.87-2.99 (m, 2H), 3.81 (t, J = 7.9 Hz, 2H), 7.45-7.64 (m, 7H), 8.31 (d, J = 7.9 Hz, 1H), 8.72 (s, 1H); ¹³C nmr (deuteriochloroform): δ 21.1, 27.1, 30.8, 43.6, 80.4, 110.5, 120.1, 121.3, 126.1, 127.9, 129.5, 130.8, 131.8, 133.7, 145.2, 170.5

HRMS Calcd. for $C_{18}H_{18}ClN_3O_2$: 344.1168 (M); observed: 344.1166

1-(1H-1,2,3-Benzotriazol-1-yl)propyl Acetate (2n).

This compound was obtained as a colorless oil (100%); ¹H nmr (deuteriochloroform): δ 0.96 (t, J = 7.4 Hz, 3H), 2.08 (s, 3H), 2.60-2.45 (m, 2H), 7.17 (t, J = 7.1 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1H), 8.08 (d, J = 7.7 Hz, 1H); ¹³C nmr (deuteriochloroform): δ 9.1, 20.6, 26.4, 80.6, 110.2, 120.0, 124.3, 127.9, 132.5, 145.9, 169.6.

Anal. Calcd. for C₁₁H₁₃N₃O₂ (219.25): C, 60.26; H, 5.99; N, 19.17. Found: C, 60.35; H, 6.09; N, 19.48.

1-(1H-1,2,3-Benzotriazol-1-yl)-2,2-dimethylpropyl Acetate (20).

This compound was obtained as colorless needles (96%), mp, 54-55°; 1 H nmr (deuteriochloroform): δ 1.13 (s, 9H), 2.14 (s, 3H), 6.96 (s, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1 H); 13 C nmr (deuteriochloroform): δ 20.3, 25.5, 36.8, 86.1, 110.6, 119.8, 123.9, 127.6, 133.1, 145.2, 169.2.

Anal. Calcd. for C₁₃H₁₇N₃O₂ (247.30): C, 63.13; H, 6.94; N, 17.00. Found: C, 62.97; H, 7.22; N, 17.02.

1H-1,2,3-Benzotriazol-1-yl(phenyl)methyl Acetate (2p).

This compound was obtained as a white solid (78%), mp, 85-86°; (lit [5] oil); 1 H nmr (deuteriochloroform): δ 2.21 (s, 3H), 7.30-7.50 (m, 8H), 8.07 (d, J = 8.0 Hz, 1H), 8.50 (s, 1H); 13 C nmr (deuteriochloroform): δ 20.5, 80.1, 110.5, 120.0, 124.2, 126.1, 127.9, 128.7, 129.5, 131.8, 133.9, 146.2, 168.7.

1H-1,2,3-Benzotriazol-1-yl(4-methylphenyl)methyl Acetate (2q).

This compound was obtained as a colorless oil (72%); 1 H nmr (deuteriochloroform): δ 2.20 (s, 3H), 2.35 (s, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.30-7.45 (m, 5H), 8.07 (d, J = 8.0 Hz, 1H), 8.45 (s,

1H); 13 C nmr (deuteriochloroform): δ 20.6, 21.1, 80.3, 110.6, 120.1, 124.2, 126.1, 127.8, 129.5, 131.0, 131.8, 139.6, 146.3, 168.8.

Anal. Calcd. for $C_{16}H_{15}N_3O_2$ (281.32): C, 68.31; H, 5.39; N, 14.94. Found: C, 68.17; H, 5.59; N, 15.3 1.

Methyl 4-[(Acetyloxy)(1*H*-1,2,3-benzotriazol-1-yl)methyl]benzoate (**2r**).

This compound was obtained as a colorless oil (82%); 1 H nmr (deuteriochloroform): δ 2.24 (s, 3H), 3.91 (s, 3H), 7.30-7.50 (m, 3H), 7.54 (d, J = 8.2 Hz, 2H), 8.08 (d, J = 8.2 Hz, 3H), 8.53 (s, 1H); 13 C nmr (deuteriochloroform): δ 20.4, 52.1, 79.4, 110.2, 120.0, 124.3, 126.2, 128.0, 129.9, 131.2, 131.7, 138.5, 146.1, 165.9, 168.5.

Anal. Calcd. for C₁₇H₁₅N₃O₄ (325.33): C, 62.76; H, 4.66; N, 12.92. Found: C, 62.78; H, 4.79; N, 13.15.

1H-1,2,3-Benzotriazol-1-yl(4-cyanophenyl)methyl Acetate (2s).

This compound was obtained as a colorless oil (74%); 1 H nmr (deuteriochloroform): δ 2.25 (s, 3H), 7.35-7.55 (m, 3H), 7.61 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.5 Hz, 2H), 8.09 (d, J = 8.0 Hz, 1H), 8.48 (s, 1H); 13 C nmr (deuteriochloroform): δ 20.4, 78.8, 110.0, 113.6, 117.8, 120.2, 124.6, 127.1, 128.4, 131.7, 132.5, 138.8, 146.1, 168.5.

Anal. Calcd. for $C_{16}H_{12}N_4O_2$ (292.30): C, 65.74; H, 4.15. Found: C, 65.58; H, 4.31.

1-(1*H*-1,2,3-Benzotriazol-1-yl)propyl Pivalate (2t).

This compound was obtained as a white solid (99%); mp, 55-56°; 1H nmr (deuteriochloroform): δ 0.98 (t, J = 7.4 Hz, 3H), 1.16 (s, 9H), 2.51 (c, J = 7.4 Hz, 2H), 7.18 (t, J = 7.1 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 9.06, 26.4, 26.7, 38.7, 80.8, 110.1, 119.9, 124.1, 127.7, 132.2, 145.8, 176.9.

Anal. Calcd. for $C_{14}H_{19}N_3O_2$ (261.33): C, 64.34; H, 7.34; N, 16.08. Found: C, 64.40; H, 7.42; N, 15.81.

1-(1*H*-1,2,3-Benzotriazol-1-yl)propyl 2-Furoate (2u).

This compound was obtained as a colorless oil (100%); 1H nmr (deuteriochloroform): δ 1.03 (t, J = 7.4 Hz, 3H), 2.67 (q, J = 7.4 Hz, 2H), 6.48-6.50 (m, 1H), 7.24 (d, J = 3.4 Hz, 1H), 7.39 (t, J = 7.4 Hz, 2H), 7.50-7.70 (m, 2H), 7.86 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 9.1, 26.4,

80.8, 110.2, 112.0, 119.6, 119.9, 124.3, 128.0, 132.5, 143.0, 145.8, 147.3, 157.0.

Anal. Calcd. for C₁₄H₁₃N₃O₃ (271.28): C, 61.98; H, 4.84; N, 15.49. Found: C, 61.91; H, 4.79; N, 15.72.

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