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Dedicated to Professor Alexandru T. Balaban on the occasion of his 85th anniversary.
The authors acknowledge the pioneering and outstanding contributions of Prof. Balaban to several fields of chemistry, including the nitrogen-containing heterocycles

CONTRIBUTIONS TO SYNTHESES OF PYRROLO[1,2-*a*]BENZIMIDAZOLE DERIVATIVES *via* 1,3-DIPOLAR CYCLOADDITION REACTIONS

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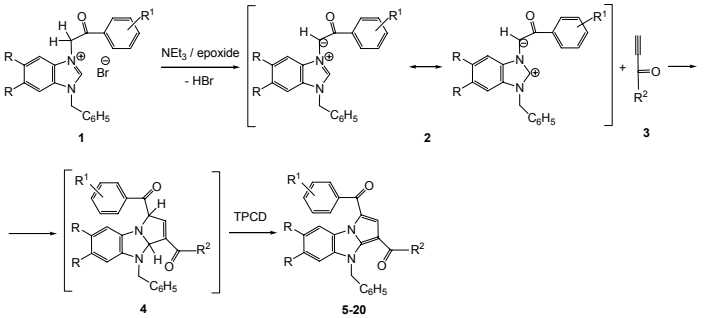
New pyrrolo[1,2-*a*]benzimidazoles were easily obtained in good yields *via* 1,3-dipolar cycloaddition reactions of benzimidazolium ylides with non-symmetrical electron-deficient alkynes in the presence of an oxidant such as tetrapyridinecobalt(II)dichromate using different acid acceptors to generate benzimidazolium ylides from the corresponding 3-phenacyl-benzimidazolium bromides. New synthesized pyrrolo[1,2-*a*]benzimidazoles were fully characterized by multinuclear NMR spectroscopy and X-Ray crystallography.



INTRODUCTION

Pyrrolo[1,2-*a*]benzimidazole, an interesting heterocyclic scaffold, was widely investigated due to its crucial role in biologically important molecules. Manny pyrrolo[1,2-*a*]benzimidazole compounds revealed remarkable biological and pharmacological properties, mainly as antitumor agents against various human cancer cells.[1-9] Several synthetic routes have been reported for the synthesis of pyrrolo[1,2-*a*]benzimidazole derivatives.[10,11] The classical multistep synthesis of pyrrolo[1,2-*a*]benzimidazoles *via* 1,3-dipolar cycloaddition reaction of benzimidazolium-ylides with electron-deficient alkynes or alkenes starts with the preparation of benzimidazolium salts followed by their *in situ* conversion into benzimidazolium-*N*-ylides in the presence of a

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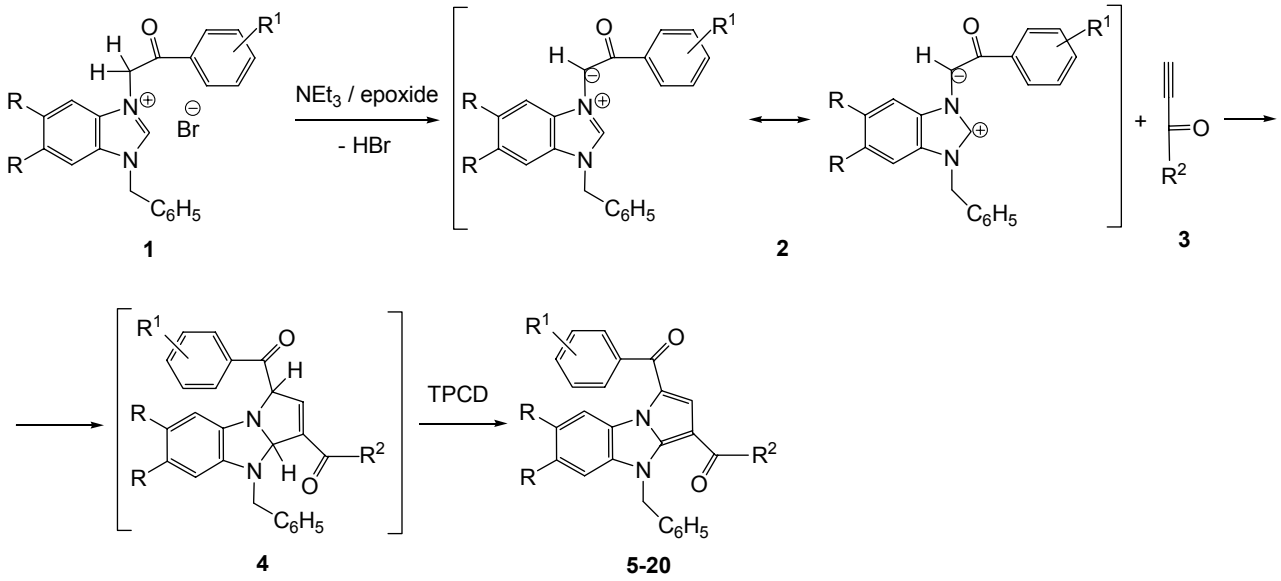
base and the dipolarophile, but the yields are small.[12-19] When needed, the benzimidazolium salts may be isolated for further properties and reactivity studies.[20]

Our group has developed a regiospecific, clean and simple one-pot, three component synthetic strategy towards pyrroloazines based on a consecutive quaternization, *in situ* generation of a heterocyclic *N*-ylide, 1,3-dipolar cycloaddition and aromatization sequence.[21-27] This synthetic route starts from *N*-heterocyclic compounds, α-bromocarbonyl derivatives and non-symmetrical activated alkynes in the presence of an epoxide which plays the role of both the reaction medium and acid scavenger. When we applied this synthetic strategy to obtain new pyrrolo[1,2-*a*]benzimidazole derivatives we obtained complex mixtures of pyrrolo[1,2-*a*]benzimidazoles along with various pyrrolo[1,2-*a*]quinoxaline derivatives.[28-30]

These results prompted us to further investigate the possibility to obtain variously substituted pyrrolo[1,2-*a*]benzimidazole derivatives by 1,3-dipolar cycloaddition reactions of benzimidazolium ylides to electron-deficient alkynes in the presence of an oxidant. Thus, we present here the syntheses of several new pyrrolo[1,2-*a*]benzimidazole compounds *via* 1,3-dipolar cycloaddition reactions of benzimidazolium ylides to non-symmetrical electron-deficient dipolarophiles in the presence of an oxidant such as tetrapyridinecobalt(II)dichromate (TPCD) and different acid acceptors able to generate benzimidazolium ylides from the corresponding 3-phenacylbenzimidazolium bromides.

RESULTS AND DISCUSSION

The classical multistep synthesis of pyrrolo[1,2-*a*]benzimidazoles *via* 1,3-dipolar cycloaddition reaction of benzimidazolium ylides with electron-deficient alkynes or alkenes starts with the preparation of benzimidazolium salts followed by their *in situ* conversion into benzimidazolium ylides in the presence of a base and dipolarophiles.[12-19] 3-Phenacylbenzimidazolium bromides **1** are easily obtained by the reactions of 1-benzylbenzimidazoles with phenacyl bromides. 1,3-Dipolar cycloaddition reactions of benzimidazolium ylides **2**, generated *in situ* from 3-phenacylbenzimidazolium bromides **1** in the presence of different acid acceptors and solvents, with non-symmetrical activated dipolarophiles lead to complex mixtures of reaction products containing pyrrolo[1,2-*a*]benzimidazoles and pyrrolo[1,2-*a*]quinoxaline derivatives from which pyrrolo[1,2-*a*]benzimidazoles were separated in small yields.[28,30] In order to obtain new pyrrolo[1,2-*a*]benzimidazoles in good yields, we carried out the 1,3-dipolar cycloaddition reactions of benzimidazolium ylides **2** with different non-symmetrical activated dipolarophile **3a-c** in the presence of an oxidant such as tetrapyridinecobalt(II)dichromate (TPCD) using 1,2-epoxybutane or triethylamine as acid acceptors in order to generate benzimidazolium ylides **2** from their corresponding quaternary salts **1**. Obviously, the synthetic pathway towards pyrrolo[1,2-*a*]benzimidazoles **5-20** involves the dehydrogenation of primary cycloadducts **4** in the presence of the oxidant complex TPCD (Scheme 1).



Scheme 1 – The synthetic pathway towards pyrrolo[1,2-*a*]benzimidazoles.

Table 1

Newly synthesized pyrrolo[1,2-*a*]benzimidazoles **5-20**

Compound no.	R	R^1	R^2	mp (°C)	Yield (%)	
					(A)	(B)
5	H	4-F	CH_3	162-164	79	65
6	H	4-Br	CH_3	190-192	77	67
7	H	H	OCH_3	172-174	80	-
8	H	4-F	OCH_3	187-189	78	-
9	H	4-Cl	OCH_3	221-223	78	-
10	H	4-Br	OCH_3	224-225	75	-
11	H	3-NO_2	OCH_3	178-180	71	-
12	H	4-NO_2	OCH_3	235-236	74	-
13	H	4-Br	OC_2H_5	198-200	69	63
14	H	3-NO_2	OC_2H_5	175-177	77	-
15	H	4-OCH_3	OC_2H_5	196-197	72	-
16	CH_3	4-F	CH_3	281-283	79	64
17	CH_3	4-Cl	CH_3	276-278	81	69
18	CH_3	3-NO_2	CH_3	232-234	72	-
19	CH_3	4-F	OC_2H_5	208-210	82	-
20	CH_3	4-Cl	OC_2H_5	194-195	78	-

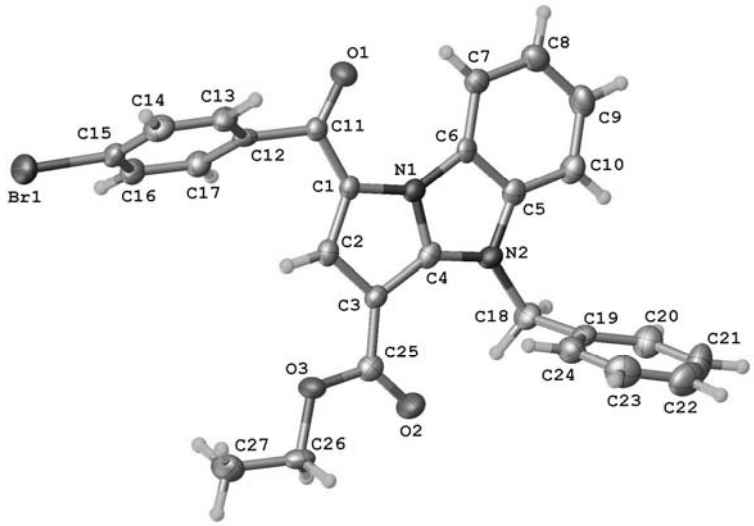


Fig. 1 – X-ray molecular structure of **13**. Only one of the three asymmetric molecules (**A**) is shown. Thermal ellipsoids are drawn at 50% probability level.

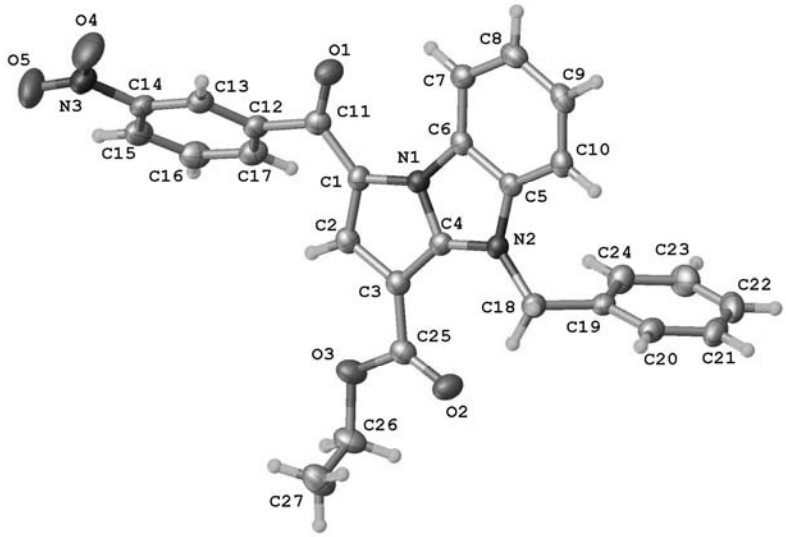


Fig. 2 – X-ray molecular structure of **14**. Thermal ellipsoids are drawn at 50% probability level.

In 1,3-dipolar cycloaddition reactions of benzimidazolium ylides **2** to non-symmetrical substituted dipolarophiles **3a-c**, carried out in the presence of TPCD using either triethylamine as acid acceptor in DMF as reaction solvent (procedure A) or in the presence of 1,2-epoxybutane as acid acceptor and reaction solvent (procedure B), new pyrrolo[1,2-*a*]benzimidazoles **5-20** were obtained in good yields. Better yields were obtained when 1,3-dipolar cycloaddition reactions were carried out in the presence of TPCD in DMF at 90ºC using triethylamine as acid acceptor (procedure A). Pyrrolo[1,2-*a*]benzimidazole derivatives **5-20** are easily separable from reaction mixture by crystallization (Table 1). All these 1,3-dipolar cycloaddition reactions, performed in the absence of TPCD, lead to mixtures of pyrrolo[1,2-*a*]quinoxaline and pyrrolo[1,2-*a*]benzimidazole derivatives.

The structures of new pyrrolo[1,2-*a*]benzimidazoles **5-20** were assigned by elemental analysis, IR and NMR spectroscopy. The ^{1}H, ^{13}C and ^{15}N NMR chemical shifts and structures have been unambiguously assigned based on 2D NMR experiments: H,H-COSY, H,C-HSQC, H,C-HMBC, H,N-HMBC, H,H-NOESY.

The single crystal X-ray studies confirm that compounds **13** and **14** have a molecular crystal structure consisting of the neutral molecules shown in Figs. 1 and 2. No co-crystallized solvent has been found in crystals of the studied compounds. The symmetric part of the unit cell in the crystal structure of **13** contains three chemically identical but crystallographically independent molecules. All the independent molecules (crystallographic forms **A**, **B** and **C**) exhibit very close geometric parameters (Experimental section). One of them differs by the opposite orientation of benzyl fragment with respect to the planar part of the molecule. Fig. 1 shows the structure of only one asymmetric component in the unit cell (crystallographic form **A**).

EXPERIMENTAL

General information. Melting points were measured on a Boëtius hot plate microscope and are uncorrected. IR spectra were recorded on a Nicolet Impact 410 spectrometer, in KBr pellets. Elemental analyses for C, H and N were obtained using a COSTECH Instruments EAS32. Satisfactory microanalyses for all new compounds were obtained.

The NMR spectra have been recorded on a Bruker Avance III 400 instrument operating at 400.1, 100.6 and 40.6 MHz for ^{1}H, ^{13}C, and ^{15}N nuclei respectively. Chemical shifts are reported in δ units (ppm) using internal TMS for ^{1}H chemical shifts, deuterated solvent for ^{13}C chemical shifts ($CDCl_3$ at 77.0 ppm), and referenced to liquid ammonia (0.0 ppm) using nitromethane (380.2 ppm) as external standard for ^{15}N chemical shifts. Unambiguous 1D NMR signal assignments were made based on 2D NMR homo- and heterocorrelation. H,H-COSY, H,C-HSQC and H,C-HMBC experiments were recorded using standard pulse sequences in the version with z-gradients, as delivered by Bruker with TopSpin 2.1 PL6 spectrometer control and processing software. The individual chemical shifts, multiplicities and coupling constants for overlapping signals have been obtained from undecoupled H,C-HSQC experiments recorded using the pulse sequence described by S. Simova.[31] The ^{15}N chemical shifts were obtained as projections from the 2D indirectly detected H,N-HMBC spectra, employing a standard pulse sequence in the version with z-gradients as delivered by Bruker (TopSpin 2.1 PL6).

X-Ray diffraction data were collected with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo*K*α radiation. Single crystals were positioned at 40 mm from the detector, and 390 and 214 frames were measured each of 60 and 10 s over 1º scan width for **13** and **14**, respectively. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.[32] Both structures were solved by direct methods using Olex2 software,[33] with the SHELXS structure solution program and refined by full-matrix least-squares on F^2 with SHELXL-97 (just modified the size).[34] Atomic displacements parameters for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms were placed in fixed, idealized positions and refined as rigidly bonded to the corresponding non-hydrogen atoms. The molecular plots were obtained using the Olex2 program. Supplementary crystallographic data for **13** (CCDC-1452892) and **14** (CCDC-1452893) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Benzimidazole, 5,6-dimethylbenzimidazole, methyl propiolate, ethyl propiolate, 3-butyn-2-one and phenacyl bromides were purchased from Aldrich and used without further purification. 1-Benzylbenzimidazole and 1-benzyl-5,6-dimethylbenzimidazole derivatives were obtained from corresponding benzimidazoles and benzyl chloride. 3-Phenacylbenzimidazolium bromides **3** were obtained from corresponding 1-substituted benzimidazole and phenacyl bromides **2** in acetone, according to previously reported methods.[13] Tetrapyridinecobalt(II)dichromate (TPCD) was obtained according to the previously reported method.[35]

General procedure A for synthesis of pyrrolo[1,2-*a*]benzimidazoles (5-20) To a solution of a 3-phenacylbenzimidazolium bromides **1** (2 mmol) in 20 mL of DMF, a non-symmetrical substituted dipolarophyle **3** (2.5 mmol), 0.8 g TPCD and 0.5 g (5 mmol) triethylamine were added. The reaction mixture was heated at 90 ºC for 4 hours, then cooled and poured under stirring over 30 mL solution of HCl 5 % in water and extracted with $CHCl_3$ (3x50mL). The combined extracts were dried on anhydrous $NaSO_4$ and the solvent was removed under vacuum. The solid was triturated with MeOH, the solid part was filtered and recrystallized from $CHCl_3$/MeOH to obtain the pyrrolo[1,2-*a*]benzimidazoles **5-20**.

General procedure B for synthesis of pyrrolo[1,2-*a*]benzimidazoles (5,6,13,16,17) To a suspension of a 3-phenacylbenzimidazolium bromides **1** (2 mmol) in 25 mL of

1,2-epoxybutane, a non-symmetrical substituted dipolarophyle **3** (2.5 mmol) and 0.8 g TPCD were added. The reaction mixture was heated at reflux temperature for 24 hours, then cooled and the solid was filtered and washed with 15 mL of $CHCl_3$. The filtrate was evaporated under vacuum, the residue was triturated with MeOH, the solid part was filtered and recristallyzed from $CHCl_3$/MeOH to obtain pyrrolo[1,2-*a*]benzimidazoles.

***1-(4-Fluorobenzoyl)-3-acetyl-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole* (5).** Pale yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 2.45 (3H, s, CH_3), 6.23 (2H, s, CH_2), 7.20-7.34 (10H, aromatic rings), 7.40 (1H, s, H-2), 7.93 (2H, dd, 8.8, 5.5 Hz, H-2'), 8.86 (1H, d, 7.6 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.20-7.34 multiplet were obtained from undecoupled HSQC as follows: 7.26 (2H, t, 8 Hz, H-3'), 7.26 (2H, d, 7.6 Hz, H-2"), 7.27 (1H, t, 7.6 Hz, H-4"), 7.31 (2H, t, 7.60 Hz, H-3"), 7.33 (1H, d, 8 Hz, H-5), 7.34 (1H, t, 8 Hz, H-6), 7.36 (1H, t, 8 Hz, H-7). **^{13}C NMR (**$CDCl_3$, δ ppm**):** δ 27.6 (CH_3), 49.3 (CH_2), 104.1 (C-3), 110.8 (C-5), 115.6 (d, 21.13 Hz, C-3'), 117.2 (C-8), 120.9 (C-1), 122.0 (C-7), 124.8 (C-6), 126.9 (C-2"), 127.2 (C-8a), 127.7 (C-4"), 128.8 (C-3"), 130.2 (C-2), 131.3 (d, 8.05 Hz, C-2'), 135.6 (d, 3 Hz, C-1'), 136.3 (C-4a), 136.9 (C-1"), 143.7 (C-3a), 164.9 (d, 252.5 Hz, C-4'), 181.9 (CO), 191.2 (CO-3). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 122.8 (N-4), 174.5 (N-9). **IR** (KBr): 1650, 1617, 1549, 1493, 1452, 1364, 1299, 1225, 1203, 1153, 1026 cm^{-1}. **Anal.** Calcd. for $C_{26}H_{19}FN_2O_2$ (410.45): C, 76.08; H, 4.67; N, 6.83. Found: C, 76.15; H, 4.71; N, 6.77.

***1-(4-Bromobenzoyl)-3-acetyl-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole* (6).** Pale yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 2.45 (3H, s, CH_3), 6.23 (2H, s, CH_2), 7.19-7.34 (8H, aromatic rings), 7.39 (1H, s, H-2), 7.67 (2H, d, 8.4 Hz, H-3'), 7.77 (2H, d, 8.8 Hz, H-2'), 8.88 (1H, d, 7.6 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.19-7.37 multiplet were obtained from undecoupled HSQC as follows: 7.20 (2H, d, 7.5 Hz, H-2"), 7.22 (1H, t, 7.3 Hz, H-4"), 7.26 (2H, t, 7.5 Hz, H-3"), 7.32 (1H, t, 8 Hz, H-7), 7.34 (1H, d, 8.1 Hz, H-5), 7.35 (1H, t, 8.0 Hz, H-6). **^{13}C NMR (**$CDCl_3$, δ ppm**):** 27.6 (CH_3), 49.3 (CH_2), 104.3 (C-3), 110.8 (C-5), 117.3 (C-8), 120.9 (C-1), 122.1 (C-7), 124.8 (C-6), 126.2 (C-4'), 126.9 (C-2"), 127.1 (C-8a), 127.7 (C-4"), 128.8 (C-3"), 130.4 (C-2), 130.5 (C-2'), 131.7 (C-3'), 136.3 (C-4a), 136.8 (C-1"), 138.2 (C-1'), 143.7 (C-3a), 181.9 (CO), 191.2 (CO-3). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 122.8 (N-4), 174.4 (N-9). **IR** (KBr): 1652, 1618, 1551, 1496, 1446, 1391, 1297, 1204, 1156, 1006 cm^{-1}. **Anal.** Calcd. for $C_{26}H_{19}BrN_2O_2$ (471.36): C, 66.25; H, 4.06; N, 5.94. Found: C, 66.18; H, 4.01; N, 5.97.

***Methyl 1-benzoyl-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate* (7).** Beige crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 3.78 (3H, s, CH_3), 6.12 (2H, s, CH_2), 7.23-7.35 (8H, aromatic rings), 7.52 (2H, t, 7.2 Hz, H-3'), 7.53 (1H, s, H-2), 7.58 (1H, t, 7.2 Hz, H-4'), 7.90 (2H, d, 7.6 Hz, H-2'), 8.93 (1H, d, 8 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.23-7.35 multiplet were obtained from undecoupled HSQC as follows: 7.24 (1H, t, 8 Hz, H-4"), 7.25 (2H, d, 8 Hz, H-2"), 7.28 (2H, t, 8 Hz, H-3"), 7.30 (1H, t, 8 Hz, H-7), 7.29 (1H, d, 8 Hz, H-5), 7.32 (1H, t, 8 Hz, H-6). **^{13}C NMR (**$CDCl_3$, δ ppm**):** 48.6 (CH_2), 51.3 (OCH_3), 93.0 (C-3), 110.4 (C-5), 117.2 (C-8), 121.5 (C-1), 121.7 (C-7), 124.5 (C-6), 126.8 (C-2"), 127.5 (C-8a), 127.7 (C-4"), 128.4 (C-3'), 128.8 (C-3"), 129.1 (C-2'), 130.5 (C-2), 131.4 (C-4'), 136.4 (C-4a), 136.7 (C-1"), 139.5 (C-1'), 144.0 (C-3a), 163.8 (COO), 183.4 (CO). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 117.7 (N-4), 172.9 (N-9). **IR** (KBr); 1693, 1619, 1576, 1498, 1453, 1394, 1305, 1234, 1205, 1155, 1114, 1083 cm^{-1}. **Anal**. Calcd. for $C_{26}H_{20}N_2O_3$ (408.46): C, 76.46; H, 4.94; N, 6.86. Found: 76.55; H, 5.02; N, 6.79.

***Methyl 1-(4-fluorobenzoyl)-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate* (8).** Yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 3.79 (3H, s, CH_3), 6.10 (2H, s, CH_2), 7.19 (2H, t, 8.3 Hz, H-3'), 7.22-7.32 (8H, aromatic rings), 7.50 (1H, s, H-2), 7.93 (2H, dd, 8.8, 5.6 Hz, H-2'), 8.87 (1H, d, 7.92 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.22-7.32 multiplet were obtained from undecoupled HSQC as follows: 7.23 (2H, d, 7.84 Hz, H-2"), 7.24 (1H, t, 7.72 Hz, H-4"), 7.27 (1H, d, 8.48 Hz, H-5), 7.28 (2H, t, 7.8 Hz, H-3"), 7.29 (1H, t, 7.72 Hz, H-7), 7.32 (1H, t, 8.1 Hz, H-6). **^{13}C NMR (**$CDCl_3$, δ ppm**):** 48.5 (CH_2), 51.3 (CH_3), 93.1 (C-3), 110.4 (C-5), 115.4 (d, 22.1 Hz, C-3'), 117.1 (C-8), 121.1 (C-1), 121.7 (C-7), 124.6 (C-6), 126.7 (C-2"), 127.4 (C-8a), 127.7 (C-4"), 128.8 (C-3"), 130.3 (C-2), 131.4 (d, 9.05 Hz, C-2'), 135.6 (d, 4.0 Hz, C-1'), 136.4 (C-4a), 136.6 (C-1"), 143.9 (C-3a), 163.7 (COO), 164.8 (d, 251.8 Hz, C-4'), 181.8 (CO). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 119.1 (N-4), 173.9 (N-9). **IR** (KBr): 1693, 1619, 1595, 1571, 1496, 1452, 1391, 1306, 1227, 1201, 1152, 1117, 1082 cm^{-1}. Anal. Calcd. for $C_{26}H_{19}FN_2O_3$ (426.45): C, 73.23; H, 4.49; N, 6.57. Found: C, 73.19; H, 4.55; N, 6.63.

***Methyl 1-(4-chlorobenzoyl)-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate* (9).** Yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 3.79 (3H, s, CH_3), 6.11 (2H, s, CH_2), 7.22-7.35 (8H, aromatic rings), 7.49 (2H, d, 8.8 Hz, H-3'), 7.50 (1H, s, H-2), 7.84 (2H, d, 8.8 Hz, H-2'), 8.89 (1H, d, 8 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.22-7.35 multiplet were obtained from undecoupled HSQC as follows: 7.23 (2H, d, 7.5 Hz, H-2"), 7.25 (1H, t, 7.6 Hz, H-4"), 7.28 (1H, d, 8 Hz, H-5), 7.29 (2H, t, 7.5 Hz, H-3"), 7.30 (1H, t, 8.0 Hz, H-7), 7.33 (1H, t, 8.0 Hz, H-6). **^{13}C NMR (**$CDCl_3$, δ ppm**):** 48.6 (CH_2), 51.3 (CH_3), 93.3 (C-3), 110.4 (C-5), 117.1 (C-8), 121.1 (C-1), 121.8 (C-7), 124.6 (C-6), 126.7 (C-2"), 127.4 (C-8a), 127.7 (C-4"), 128.6 (C-3'), 128.8 (C-3"), 130.4 (C-2'), 130.5 (C-2), 136.3 (C-4a), 136.6 (C-1"), 137.6 (C-4'), 137.8 (C-1'), 143.9 (C-3a), 163.7 (COO), 181.8 (CO). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 119.3 (N-4), 173.8 (N-9). **IR** (KBr): 1693, 1618, 1573, 1499, 1452, 1392, 1306, 1233, 1201, 1152, 1117, 1086 cm^{-1}. **Anal**. Calcd. for $C_{26}H_{19}ClN_2O_3$ (442.91): C, 70.51; H, 4.32; N, 6.32. Found: C, 70.60; H, 4.36; N, 6.26.

***Methyl 1-(4-Bromobenzoyl)-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate* (10).** Yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 3.79 (3H, s, CH_3), 6.11 (2H, s, CH_2), 7.22-7.33 (8H, aromatic rings), 7.49 (1H, s, H-2), 7.65 (2H, d, 8.4 Hz, H-3'), 7.76 (2H, d, 8.4 Hz, H-2'), 8.89 (1H, d, 8.4 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.22-7.33 multiplet were obtained from undecoupled HSQC as follows: 7.23 (2H, d, 7.3 Hz, H-2"), 7.25 (1H, t, 7.5 Hz, H-4"), 7.28 (2H, t, 7.7 Hz, H-3"), 7.29 (1H, d, 8.1 Hz, H-5), 7.30 (1H, t, 8.0 Hz, H-7), 7.33 (1H, t, 7.9 Hz, H-6). **^{13}C NMR (**$CDCl_3$, δ ppm**):** 48.6 (CH_2), 51.3 (CH_3), 93.3 (C-3), 110.4 (C-5), 117.1 (C-8), 121.0 (C-1), 121.8 (C-7), 124.6 (C-6), 126.1 (C-4'), 126.7 (C-2"), 127.3 (C-8a), 127.7 (C-4"), 128.8 (C-3"), 130.5 (C-2), 130.6 (C-2'), 131.6 (C-3'), 136.2 (C-4a), 136.5 (C-1"), 138.2 (C-1'), 144.0 (C-3a), 163.7 (COO), 181.9 (CO). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 118.6 (N-4), 172.9 (N-9). **IR** (KBr): 1698, 1617, 1574, 1497, 1453, 1394, 1303, 1229, 1198, 1150, 1116, 1082 cm^{-1}. **Anal**. Calcd. for $C_{26}H_{19}BrN_2O_3$ (487.36): C, 64.08; H, 3.93; N, 5.75. Found: C, 64.15; H, 4.00; N, 5.69.

***Methyl 1-(3-nitrobenzoyl)-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate* (11).** Yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 3.80 (3H, s, CH_3), 6.14 (2H, s, CH_2), 7.24-7.38 (8H, aromatic rings), 7.49 (1H, s, H-2), 7.72 (1H, t, 8 Hz, H-5'), 8.20 (1H, dt, 7.7, 1.3 Hz, H-6'), 8.43 (1H, ddd, 8.2, 3.3, 1.1 Hz, H-4'), 8.72 (1H, t, 1.6 Hz, H-2'), 8.92 (1H, dd, 6.5, 1.8 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.24-7.38 multiplet were obtained from undecoupled HSQC as follows: 7.25 (2H, d, 7.6 Hz, H-2"), 7.27 (1H, t, 7.7 Hz, H-4"), 7.31 (2H, t, 7.8 Hz, H-3"), 7.33 (1H, d, 8 Hz, H-5), 7.35 (1H, t, 7.7 Hz, H-7), 7.37 (1H, t, 8 Hz, H-6). **^{13}C NMR (**$CDCl_3$, δ ppm**):** 48.7 (CH_2), 51.5 (CH_3), 94.1 (C-3), 110.6 (C-5), 117.1 (C-8), 120.6 (C-1), 122.0 (C-7), 123.8 (C-2'), 124.8 (C-6), 125.7 (C-4'), 126.8 (C-2"), 127.4 (C-8a), 127.8 (C-4"), 128.9 (C-3"), 129.6 (C-5'), 130.9 (C-2), 134.6 (C-6'), 136.3 (C-4a), 136.4 (C-1"), 144.1 (C-1'), 144.2 (C-3a), 148.1 (C-3'), 163.5 (COO), 180.1 (CO). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 119.1 (N-4), 172.9 (N-9), 367.2 (NO_2). **IR** (KBr): 1698, 1615, 1575, 1532, 1496, 1454, 1349, 1306, 1201, 1157, 1080 cm^{-1}. **Anal**. Calcd. for $C_{26}H_{19}N_3O_5$ (453.46): C, 68.87; H, 4.22; N, 9.27. Found: C, 68.79; H, 4.18; N, 9.33.

***Methyl 1-(4-nitrobenzoyl)-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate* (12).** Yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 3.80 (3H, s, CH_3), 6.14 (2H, s, CH_2), 7.23-7.38 (8H, aromatic rings), 7.47 (1H, s, H-2), 8.02 (2H, d, 8.7 Hz, H-2'), 8.37 (2H, d, 8.7 Hz, H-3'), 8.95 (1H, d, 6.5 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.23-7.38 multiplet were obtained from undecoupled HSQC as follows: 7.24 (2H, d, 7.3 Hz, H-2"), 7.26 (1H, t, 7.8 Hz, H-4"), 7.30 (2H, t, 7.3 Hz, H-3"), 7.32 (1H, d, 7.9 Hz, H-5), 7.34 (1H, t, 8.0 Hz, H-7), 7.37 (1H, t, 8.1 Hz, H-6). **^{13}C NMR (**$CDCl_3$, δ ppm**):** 48.7 (CH_2), 51.5 (CH_3), 94.2 (C-3), 110.6 (C-5), 117.2 (C-8), 120.8 (C-1), 122.0 (C-7), 123.6 (C-3'), 124.9 (C-6), 126.8 (C-2"), 127.4 (C-8a), 127.9 (C-4"), 128.9 (C-3"), 129.8 (C-2'), 131.2 (C-2), 136.3 (C-4a), 136.4 (C-1"), 144.2 (C-3a), 145.2 (C-1'), 149.4 (C-4'), 163.5 (COO), 180.6 (CO). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 119.3 (N-4), 172.8 (N-9), 367.1 (NO_2). **IR** (KBr): 1699, 1618, 1594, 1570, 1526, 1497, 1453, 1345, 1306, 1196, 1152, 1117, 1081 cm^{-1}. **Anal**. Calcd. for $C_{26}H_{19}N_3O_5$ (453.46): C, 68.87; H, 4.22; N, 9.27. Found: C, 68.81; H, 4.20; N, 9.22.

***Ethyl 1-(4-bromobenzoyl)-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate* (13).** White crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 1.29 (3H, t, 7.2 Hz, CH_3-Et), 4.27 (2H, q, 7.2 Hz, CH_2-Et), 6.12 (2H, s, CH_2), 7.22-7.35 (8H, aromatic rings), 7.50 (1H, s, H-2), 7.66 (2H, d, 8.4 Hz, H-3'), 7.78 (2H, d, 8.8 Hz, H-2'), 8.90 (1H, d, 7.6 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.23-7.38 multiplet were obtained from undecoupled HSQC as follows: 7.23 (2H, d, 7.1 Hz, H-2"), 7.24 (1H, t, 7.6 Hz, H-4"), 7.28 (1H, d, 7.9 Hz, H-5), 7.29 (2H, t, 7.2 Hz, H-3"), 7.30 (1H, t, 8.1 Hz, H-7), 7.33 (1H, t, 7.6 Hz, H-6). **^{13}C NMR** ($CDCl_3$, δ ppm): 14.4 (CH_3-Et), 48.6 (CH_2), 60.2 (CH_2-Et), 93.8 (C-3), 110.4 (C-5), 117.1 (C-8), 120.9 (C-1), 121.7 (C-7), 124.6 (C-6), 126.1 (C-4'), 126.8 (C-2"), 127.4 (C-8a), 127.7 (C-4"), 128.8 (C-3"), 130.5 (C-2), 130.6 (C-2'), 131.6 (C-3'), 136.3 (C-4a), 136.6 (C-1"), 138.3 (C-1'), 143.9 (C-3a), 163.3 (COO), 181.9 (CO). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 119.1 (N-4), 173.8 (N-9). **IR** (KBr): 1688, 1620, 1577, 1501, 1479, 1451, 1392, 1306, 1236, 1202, 1152, 1115, 1083 cm^{-1}. **Anal**. Calcd. for $C_{27}H_{21}BrN_2O_3$ (501.37): C, 64.68; H, 4.22; N, 5.59. Found: C, 64.60; H, 4.19; N, 5.64. **Single crystal X-ray (CCDC-1452892)**: $C_{81}H_{63}Br_3N_6O_9$ (M_r = 1504.10 g·mol^{-1}), triclinic, a = 10.753(5) Å, b = 11.668(5) Å, c = 27.063(5), α = 86.507(5)º, β = 79.208(5)º, γ = 86.377(5)º, V = 3325(2) Å^3, T = 200 K, space group $P\bar{1}$, Z = 2, 25411 coll. refl., 11736 indep. (R_{int} = 0.0992), Gof = 0.983, R_1 = 0.0526, w$R(F^2)$ = 0.0864. Bond lengths (Å) (Fig. 1) for crystallographic form **13A**: 1.900(4) (Br1-C15), 1.228(4) (O1-C11), 1.207(4) (O2-C25), 1.347(4) (O3-C25), 1.450(4) (O3-C26), 1.416(4) (N1-C1), 1.373(4) (N1-C4), 1.410(4) (N1-C6), 1.361(4) (N2-C4), 1.394(4) (N2-C5), 1.463(4) (N2-C18), 1.378(4) (C1-C2), 1.432(5) (C1-C11), 1.403(4) (C2-C3), 1.406(4) (C3-C4), 1.454(5) (C3-C25), 1.396(5) (C5-C6), 1.384(5) (C5-C10), 1.389(4) (C6-C7), 1.391(5) (C7-C8), 1.386(5) (C8-C9), 1.382(5) (C9-C10), 1.502(5) (C11-C12), 1.377(5) (C12-C13), 1.389(5) (C12-C17), 1.390(5) (C13-C14), 1.373(5) (C14-C15), 1.371(5) (C15-C16), 1.380(5) (C16-C17), 1.520(5) (C18-C19), 1.378(5) (C19-C20), 1.379(5) (C19-C24), 1.387(5) (C20-C21), 1.366(5) (C21-C22), 1.379(5) (C22-C23), 1.386(5) (C23-C24), 1.505(5) (C26-C27); Crystallographic form **13B**: 1.893(4) (Br1-C15), 1.233(4) (O1-C11), 1.210(4) (O2-C25), 1.343(4) (O3-C25), 1.448(4) (O3-C26), 1.409(4) (N1-C1), 1.368(4) (N1-C4), 1.411(4) (N1-C6), 1.364(4) (N2-C4), 1.393(4) (N2-C5), 1.459(4) (N2-C18), 1.369(4) (C1-C2), 1.437(5) (C1-C11), 1.409(4) (C2-C3), 1.405(4) (C3-C4), 1.451(4) (C3-C25), 1.395(5) (C5-C6), 1.382(4) (C5-C10), 1.383(4) (C6-C7), 1.386(5) (C7-C8), 1.387(5) (C8-C9), 1.382(5) (C9-C10), 1.495(5) (C11-C12), 1.387(5) (C12-C13), 1.383(5) (C12-C17), 1.387(5) (C13-C14), 1.377(5) (C14-C15), 1.376(5) (C15-C16), 1.382(5) (C16-C17), 1.518(5) (C18-C19), 1.385(5) (C19-C20), 1.377(5) (C19-C24), 1.386(5) (C20-C21), 1.364(6) (C21-C22), 1.379(5) (C22-C23), 1.390(5) (C23-C24), 1.487(5) (C26-C27);); Crystallographic form **13C**: 1.894(4) (Br1-C15), 1.232(4) (O1-C11), 1.211(4) (O2-C25), 1.348(4) (O3-C25), 1.451(4) (O3-C26), 1.410(4) (N1-C1), 1.383(4) (N1-C4), 1.409(4) (N1-C6), 1.360(4) (N2-C4), 1.395(4) (N2-C5), 1.458(4) (N2-C18), 1.388(4) (C1-C2), 1.435(4) (C1-C11), 1.403(4) (C2-C3), 1.403(4) (C3-C4), 1.453(5) (C3-C25), 1.385(5) (C5-C6), 1.389(5) (C5-C10), 1.389(4) (C6-C7), 1.388(5) (C7-C8), 1.385(5) (C8-C9), 1.375(5) (C9-C10), 1.493(5) (C11-C12), 1.391(4) (C12-C13), 1.386(4) (C12-C17), 1.379(5) (C13-C14), 1.388(5) (C14-C15), 1.379(5) (C15-C16), 1.383(5) (C16-C17), 1.517(5) (C18-C19), 1.377(5) (C19-C20), 1.372(5) (C19-C24), 1.396(5) (C20-C21), 1.372(6) (C21-C22), 1.372(5) (C22-C23), 1.383(5) (C23-C24), 1.485(5) (C26-C27).

***Ethyl 1-(3-nitrobenzoyl)-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate* (14).** Pale yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 1.28 (3H, t, 6.8 Hz, CH_3-Et), 4.28 (2H, q, 7.2 Hz, CH_2-Et), 6.13 (2H, s, CH_2), 7.24-7.38 (8H, aromatic rings), 7.49 (1H, s, H-2), 7.72 (1H, t, 8 Hz, H-5'), 8.20 (1H, d, 7.6 Hz, H-6'), 8.42 (1H, dd, 8.2, 1.3 Hz, H-4'), 8.72 (1H, t, 2 Hz, H-2'), 8.92 (1H, d, 6.6 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.24-7.38 multiplet were obtained from undecoupled HSQC as follows: 7.25 (2H, d, 7.5 Hz, H-2"), 7.26 (1H, t, 7.4 Hz, H-4"), 7.30 (2H, t, 7.9 Hz, H-3"), 7.31 (1H, d, 8.1 Hz, H-5), 7.33 (1H, t, 7.8 Hz, H-7), 7.36 (1H, t, 7.9 Hz, H-6). **^{13}C NMR (**$CDCl_3$, δ ppm**):** 14.4 (CH_3-Et), 48.7 (CH_2), 60.4 (CH_2-Et), 94.6 (C-3), 110.6 (C-5), 117.1 (C-8), 120.5 (C-1), 121.9 (C-7), 123.8 (C-2'), 124.8 (C-6), 125.7 (C-4'), 126.8 (C-2"), 127.3 (C-8a), 127.8 (C-4"), 128.8 (C-3"), 129.6 (C-5'), 130.9 (C-2), 134.6 (C-6'), 136.3 (C-4a), 136.4 (C-1"), 141.1 (C-1'), 144.1 (C-3a), 148.1 (C-3'), 163.1 (COO), 180.0 (CO). **^{15}N NMR (**$CDCl_3$, δ

ppm)**:** 119.0 (N-4), 172.9 (N-9), 365.5 (NO_2). **IR** (KBr): 1696, 1627, 1574, 1534, 1501, 1451, 1349, 1304, 1231, 1204, 1157, 1080 cm^{-1}. **Anal**. Calcd. for $C_{27}H_{21}N_3O_5$ (467.47): C, 69.37; H, 4.53; N, 8.99. Found: C, 69.48; H, 4.58; N, 8.90. **Single crystal X-ray (CCDC-1452893)**: $C_{27}H_{21}N_3O_5$ (M_r = 467.47 g·mol^{-1}), monoclinic, a = 10.9068(4) Å, b = 11.108(3) Å, c = 18.6993(6) Å, β = 92.355(3)º, V = 2263.5(6) $Å^3$, T = 200 K, spce group $P2_1/n$ Z = 4, 9174 coll. refl., 3999 indep. (R_{int} = 0.0227), Gof = 1.021, R_1 = 0.0383, w$R(F^2)$ = 0.0960. Bond lengths (Å) (Fig. 2): 1.235(2) (O1-C11), 1.210(2) (O2-C25), 1.346(2) (O3-C25), 1.450(2) (O3-C26), 1.225(2) (O4-N3), 1.223(2) (O5-N3), 1.412(2) (N1-C1), 1.365(2) (N1-C4), 1.405(2) (N1-C6), 1.364(2) (N2-C4), 1.396(2) (N2-C5), 1.462(2) (N2-C18), 1.471(2) (N3-C14), 1.384(2) (C1-C2), 1.430(2) (C1-C11), 1.404(2) (C2-C3), 1.407(2) (C3-C4), 1.453(2) (C3-C25), 1.400(2) (C5-C6), 1.386(2) (C5-C10), 1.387(2) (C6-C7), 1.384(2) (C7-C8), 1.394(2) (C8-C9), 1.375(2) (C9-C10), 1.500(2) (C11-C12), 1.390(2) (C12-C13), 1.396(2) (C12-C17), 1.378(2) (C13-C14), 1.381(2) (C14-C15), 1.378(2) (C15-C16), 1.383(2) (C16-C17), 1.511(2) (C18-C19), 1.388(2) (C19-C20), 1.388(2) (C19-C24), 1.391(2) (C20-C21), 1.377(3) (C21-C22), 1.375(3) (C22-C23), 1.384(2) (C23-C24), 1.495(2) (C26-C27).

Ethyl 1-(4-methoxybenzoyl)-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate **(15).** White crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 1.33 (3H, t, 7.2 Hz, CH_3-Et), 3.96 (3H, s, OCH_3), 4.31 (2H, q, 7.2 Hz, CH_2-Et), 6.16 (2H, s, CH_2), 7.08 (2H, d, 8.8 Hz, H-3'), 7.28-7.36 (8H, aromatic rings), 7.59 (1H, s, H-2), 7.98 (2H, d, 8.8 Hz, H-3'), 7.78 (2H, d, 8.8 Hz, H-2'), 8.89 (1H, d, 8.0 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.28-7.36 multiplet were obtained from undecoupled HSQC as follows: 7.28 (1H, t, 8.3 Hz, H-4"), 7.29 (2H, d, 8.2 Hz, H-2"), 7.31 (1H, d, 9.4 Hz, H-5), 7.32 (1H, t, 8.3 Hz, H-7), 7.33 (2H, t, 7.8 Hz, H-3"), 7.35 (1H, t, 8.4 Hz, H-6). **^{13}C NMR** ($CDCl_3$, δ ppm): 14.4 (CH_3-Et), 48.6 (CH_2), 55.5 (OCH_3), 60.1 (CH_2-Et), 93.0 (C-3), 110.3 (C-5), 113.7 (C-3'), 117.1 (C-8), 121.3 (C-1), 121.6 (C-7), 124.4 (C-6), 126.8 (C-2"), 127.4 (C-8a), 127.7 (C-4"), 128.8 (C-3"), 129.7 (C-2), 131.2 (C-2'), 131.9 (C-1'), 136.4 (C-4a), 136.8 (C-1"), 143.8 (C-3a), 162.5 (C-4'), 163.5 (COO), 182.4 (CO). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 118.5 (N-4), 174.1 (N-9). **IR** (KBr): 1689, 1614, 1579, 1499, 1451, 1392, 1306, 1261, 1205, 1154, 1114, 1084 cm^{-1}. **Anal**. Calcd. for $C_{28}H_{24}N_2O_4$ (452.50): C, 74.32; H, 5.35; N, 6.19. Found: C, 74.27; H, 5.41; N, 6.23.

1-(4-Fluorobenzoyl)-3-acetyl-4-benzyl-5,6-dimethyl-4H-pyrrolo[1,2-a]benzimidazole **(16).** White crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 2.35 (3H, s, CH_3-6), 2.41 (3H, s, CH_3-7), 2.43 (3H, s, CH_3-3), 6.18 (2H, s, CH_2), 7.10 (1H, s, H-5), 7.18-7.29 (7H, aromatic rings), 7.35 (1H, s, H-2), 7.93 (2H, dd, 8.6, 5.5 Hz, H-2'), 8.62 (1H, s, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.18-7.29 multiplet were obtained from undecoupled HSQC as follows: 7.20 (2H, d, 7.5 Hz, H-2"), 7.23 (1H, t, 7.9 Hz, H-4"), 7.23 (2H, t, 8.1 Hz, H-3'), 7.28 (2H, t, 7.7 Hz, H-3"). **^{13}C NMR** ($CDCl_3$, δ ppm): 20.2 (CH_3-7), 20.5 (CH_3-6), 27.5 (CH_3-3), 49.1 (CH_2), 104.4 (C-3), 111.1 (C-5), 115.5 (d, 22 Hz, C-3'), 117.5 (C-8), 120.8 (C-1), 125.6 (C-8a), 126.7 (C-2"), 127.6 (C-4"), 128.7 (C-3"), 130.0 (C-2), 131.1 (C-7), 131.3 (d, 9 Hz, C-2'), 133.9 (C-6), 134.8 (C-4a), 135.7 (d, 4 Hz, C-1'), 137.2 (C-1"), 143.5 (C-3a), 164.8 (d, 251.5 Hz, C-4'), 181.8 (CO), 191.0 (CO-3). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 121.2 (N-4), 173.9 (N-9). **IR** (KBr): 2921, 1647, 1618, 1547, 1493, 1452, 1358, 1310, 1223, 1152 cm^{-1}. **Anal**. Calcd. for $C_{28}H_{23}FN_2O_2$ (438.51): C, 76.69; H, 5.29; N, 6.39. Found: C, 76.58; H, 5.33; N, 6.31.

1-(4-Chlorobenzoyl)-3-acetyl-4-benzyl-5,6-dimethyl-4H-pyrrolo[1,2-a]benzimidazole **(17).** Yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 2.35 (3H, s, CH_3-6), 2.41 (3H, s, CH_3-7), 2.43 (3H, s, CH_3-3), 6.18 (2H, s, CH_2), 7.10 (1H, s, H-5), 7.29 (2H, d, 8.2 Hz, H-2"), 7.22-7.29 (3H, aromatic rings), 7.35 (1H, s, H-2), 7.51 (2H, d, 8.4 Hz, H-2'), 7.85 (2H, d, 8.4 Hz, H-3'), 8.63 (1H, s, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.22-7.29 multiplet were obtained from undecoupled HSQC as follows: 7.22 (1H, t, 7.4 Hz, H-4"), 7.26 (2H, t, 7.3 Hz, H-3"). **^{13}C NMR** ($CDCl_3$, δ ppm): 20.2 (CH_3-7), 20.5 (CH_3-6), 27.5 (CH_3-3), 49.1 (CH_2), 104.5 (C-3), 111.1 (C-5), 117.4 (C-8), 120.7 (C-1), 125.6 (C-8a), 126.7 (C-2"), 127.5 (C-4"), 128.7 (C-2'), 128.8 (C-3"), 130.2 (C-2), 130.4 (C-3'), 131.1 (C-7), 134.0 (C-6), 134.7 (C-4a), 137.1 (C-1"), 137.7 (C-1'), 137.9 (C-4'), 143.5 (C-3a), 181.9 (CO), 191.0 (CO-3). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 121.1 (N-4), 173.0 (N-9). **IR** (KBr): 2921, 1646, 1612, 1545, 1496, 1451, 1358, 1311, 1222, 1169, 1088 cm^{-1}. **Anal**. Calcd. for $C_{28}H_{23}ClN_2O_2$ (454.96): C, 73.92; H, 5.10; N, 6.16. Found: C, 73.86; H, 5.14; N, 6.09.

1-(3-Nitrobenzoyl)-3-acetyl-4-benzyl-5,6-dimethyl-4H-pyrrolo[1,2-a]benzimidazole **(18).** Yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**):** 2.37 (3H, s, CH_3-6), 2.42 (3H, s, CH_3-7), 2.43 (3H, s, CH_3-3), 6.19 (2H, s, CH_2), 7.13 (1H, s, H-5), 7.20 (2H, d, 8.1 Hz, H-2"), 7.25 (1H, t, 6.9 Hz, H-4"), 7.28 (2H, t, 6.7 Hz, H-3"), 7.35 (1H, s, H-2), 7.74 (1H, t, 8 Hz, H-5'), 8.22 (1H, d, 7.6 Hz, H-6'), 8.45 (1H, ddd, 8.2, 3.2, 0.9 Hz, H-4'), 8.66 (1H, s, H-8), 8.74 (1H, t, 1.6 Hz, H-2'). **^{13}C NMR (**$CDCl_3$, δ ppm**):** 20.3 (CH_3-7), 20.6 (CH_3-6), 27.5 (CH_3-3), 49.1 (CH_2), 105.2 (C-3), 111.2 (C-5), 117.4 (C-8), 120.2 (C-1), 123.8 (C-2'), 125.5 (C-8a), 125.8 (C-4'), 126.7 (C-2"), 127.6 (C-4"), 128.8 (C-3"), 129.7 (C-5'), 130.6 (C-2), 131.4 (C-7), 134.3 (C-6), 134.6 (C-6'), 134.7 (C-4a), 136.9 (C-1"), 141.2 (C-1'), 143.7 (C-3a), 148.1 (C-3'), 180.0 (CO), 191.0 (CO-CH_3). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 121.4 (N-4), 172.9 (N-9). **IR** (KBr): 2924, 1666, 1621, 1527, 1497, 1451, 1349, 1313, 1248, 1225, 1094 cm^{-1}. **Anal**. Calcd. for $C_{28}H_{23}N_3O_4$ (465.51): C, 72.25; H, 4.98; N, 9.03. Found: C, 72.33; H, 5.04; N, 8.96.

Ethyl 1-(4-fluorobenzoyl)-4-benzyl-5,6-dimethyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate **(19).** Pale yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**)**: 1.27 (3H, t, 7.2 Hz, CH_3-Et), 2.33 (3H, s, CH_3-6), 2.40 (3H, s, CH_3-7), 4.25 (2H, q, 7.2 Hz, CH_2-Et), 6.06 (2H, s, CH_2), 7.10 (1H, s, H-5), 7.18-7.31 (7H, aromatic rings), 7.47 (1H, s, H-2), 7.93 (2H, dd, 8.7, 5.5 Hz, H-2'), 8.63 (1H, s, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.18-7.31 multiplet were obtained from undecoupled HSQC as follows: 7.21 (2H, t, 8.4 Hz, H-3'), 7.22 (2H, d, 7.4 Hz, H-2"), 7.25 (1H, t, 7.2 Hz, H-4"), 7.29 (2H, t, 7.6 Hz, H-3"). **^{13}C NMR** ($CDCl_3$, δ ppm): 14.4 (CH_3-Et), 20.2 (CH_3-7), 20.5 (CH_3-6), 48.4 (CH_2), 60.1 (CH_2-Et), 93.6 (C-3), 110.7 (C-5), 115.4 (d, 21 Hz, C-3'), 117.3 (C-8), 120.8 (C-1), 125.7 (C-8a), 126.6 (C-2"), 127.6 (C-4"), 128.7 (C-3"), 130.1 (C-2), 130.7 (C-7), 131.4 (d, 9 Hz, C-2'), 133.6 (C-6), 134.7 (C-4a), 135.7 (d, 3 Hz, C-1'), 136.9 (C-1"), 143.7 (C-3a), 164.8 (d, 252.5 Hz, C-4'), 163.4 (COO), 181.8 (CO). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 117.7 (N-4), 173.4 (N-9). **IR** (KBr): 2984, 1696, 1606, 1566, 1494, 1451, 1312, 1224, 1154, 1113, 1080 cm^{-1}. **Anal**. Calcd. for $C_{29}H_{25}FN_2O_3$ (468.52): C, 74.34; H, 5.38; N, 5.98. Found: C, 74.29; H, 5.41; N, 6.06.

***Ethyl 1-(4-chlorobenzoyl)-4-benzyl-5,6-dimethyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate* (20).** Pale yellow crystals. **^{1}H NMR (**$CDCl_3$**,** δ ppm**)**: 1. 27 (3H, t, 7.2 Hz, CH_3-Et), 2.33 (3H, s, CH_3-6), 2.40 (3H, s, CH_3-7), 4.25 (2H, q, 7.2 Hz, CH_2-Et), 6.05 (2H, s, CH_2), 7.04 (1H, s, H-5), 7.20-7.30 (5H, aromatic ring), 7.46 (1H, s, H-2), 7.50 (2H, d, 8.4 Hz, H-3'), 7.85 (2H, d, 8.0 Hz, H-2'), 8.64 (1H, s, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.20-7.30 multiplet were obtained from undecoupled HSQC as follows: 7.22 (2H, d, 7.7 Hz, H-2"), 7.26 (1H, t, 7.6 Hz, H-4"), 7.31 (2H, t, 7.7 Hz, H-3"). **^{13}C NMR** ($CDCl_3$, δ ppm): 14.4 (CH_3-Et), 20.2 (CH_3-7), 20.5 (CH_3-6), 48.4 (CH_2), 60.1 (CH_2-Et), 93.8 (C-3), 110.7 (C-5), 117.3 (C-8), 120.7 (C-1), 125.8 (C-8a), 126.6 (C-2"), 127.6 (C-4"), 128.6 (C-3'), 128.8 (C-3"), 130.2 (C-2), 130.5 (C-2'), 130.7 (C-7), 133.7 (C-6), 134.7 (C-4a), 136.8 (C-1"), 137.5 (C-4'), 137.9 (C-1'), 143.7 (C-3a), 163.3 (COO), 181.7 (CO). **^{15}N NMR (**$CDCl_3$, δ ppm**):** 117.7 (N-4), 173.1 (N-9). **IR** (KBr): 2920, 1688, 1620, 1572, 1489, 1451, 1392, 1308, 1222, 1168, 1117, 1080 cm^{-1}. **Anal**. Calcd. for $C_{29}H_{25}ClN_2O_3$ (484.97): C, 71.82; H, 5.19; N, 5.77. Found: C, 71.89; H, 5.26; N, 5.69.

CONCLUSIONS

We have described a simple way to obtain pyrrolo[1,2-*a*]benzimidazoles in good yields *via* 1,3-dipolar cycloaddition reactions of benzimidazolium ylides to non-symmetrical electron-deficient dipolarophiles in the presence of an oxidant such as tetrapyridinecobalt(II)dichromate using different acid acceptors to generate benzimidazolium ylides from the corresponding 3-phenacyl-benzimidazolium bromides. In the absence of the oxidant, 1,3-dipolar cycloaddition reactions of benzimidazolium ylides to non-symmetrical electron-deficient alkynes gave complex mixture of pyrrolo[1,2-*a*]benzimidazoles and pyrrolo[1,2-*a*]quinoxalines.

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REFERENCES

1. I. Islam, E. B. Skibo, R. T. Dorr and D. S. Alnerts, *J. Med. Chem.*, **1991**, *34*, 2954-2961.
2. E. B. Skibo and W. G. Schulz, *J. Med. Chem.*, **1993**, *36*, 3050-3055.
3. W. G. Schulz, I. Islam and E. B. Skibo, *J. Med. Chem.*, **1995**, *38*, 109-118.
4. W. G. Schulz, R. A. Nieman and E. B. Skibo, *Proc. Natl. Acad. Sci. USA*, **1995**, *92*, 11854-11858.
5. R. Zhou and E. B. Skibo, *J. Med. Chem.* **1996**, *39*, 4321-4331.
6. E. B. Skibo, S. Gordon, L. Bess, R. Boruah and M. J. J. Heileman, *J. Med. Chem.*, **1997**, *40*, 1327-1339.
7. W. A. Craigo, B. V. LeSueur and E. B. Skibo, *J. Med. Chem.*, **1999**, *42,* 3324-3333.
8. X. Huang, A. Suleman and E. B. Skibo, *Bioorg. Chem.*, **2000***, 28*, 324-337.
9. A. Suleman and E. B. Skibo, *J. Med. Chem*., **2002**, *45*, 1211-1220.
10. K. M. Dawood, N. M. Elwan, A. A. Farahat and B. F. Abdel-Wahab, *J. Heterocyclic Chem*., **2010**, *47*, 243-267.
11. K. M. Dawood, N. M. Elwan and B. F. Abdel-Wahab, *Arkivoc*, **2011**, 111-195.
12. H. Ogura and K. Kikuchi, *J. Org. Chem*., **1972**, *37*, 2679-2682.
13. I. Zugravescu, J. M. Herdan and I. Druta, *Rev. Roum. Chim*., **1974**, *19*, 649-658.
14. I. Zugravescu, J. M. Herdan and I. Druta, *Rev. Roum. Chim*., **1974**, *19*, 659-664.
15. O. Meth-Cohn, *Tetrahedron Lett*., **1975**, 413-416.
16 B. Wang, J. Hu, X. Zhang, Y. Hu and H. Hu, *J. Heterocycl. Chem.,* **2000**, *37*, 1533-1537.
17. E. Georgescu, F. Georgescu, C. Roibu, P. C. Iuhas, C. Draghici and M. T. Caproiu, *Rev. Roum. Chim*., **2002**, *47*, 885-891.
18. K. Wu and Q.-Y. Chen, *Synthesis,* **2003**, 35-40.
19. X. Fang, Y.-X. Wu, J. Deng and S.-W. Wang, *Tetrahedron,* **2004**, *60*, 5487-5493.
20. A. Nicolescu, M. Balan, E. Georgescu, F. Georgescu, L. Ursu, B. C. Simionescu, P. Filip and C. Deleanu, *Rev. Chim. (Bucharest)*, **2013**, *64*, 451-455.
21. E. Georgescu, M. R. Caira, F.Georgescu, C. Draghici, M. M. Popa and F. Dumitrascu, *Synlett*, **2009**, 1795-1799.
22. M. R. Caira, E. Georgescu, F. Georgescu, M. M. Popa and F. Dumitrascu, *Arkivoc*, **2009**, 242-253.
23. F. Dumitrascu, M. T. Caproiu, F. Georgescu, C. Draghici, M. M. Popa and E. Georgescu, *Synlett*, **2010**, 2407-2410.
24. F. Dumitrascu, M. M. Caira, E. Georgescu, F. Georgescu, C. Draghici and M. M. Popa, *Heteroatom Chem.,* **2011**, *22*, 723-729.
25. E. Georgescu, F. Georgescu, M. M. Popa, C. Draghici, L. Tarko and F. Dumitrascu, *ACS Comb. Sci*., **2012**, *14,* 101-107.
26. F. Dumitrascu, E. Georgescu, F. Georgescu, M. M. Popa and D. Dumitrescu, *Molecules*, **2013**, *18*, 2635-2645.
27. E. Georgescu, F. Dumitrascu, F. Georgescu, C. Draghici and L. Barbu, *J. Heterocyclic Chem*., **2013**, *50*, 78-82.
28. A. Nicolescu, C. Deleanu, E. Georgescu, F. Georgescu, A.-M. Iurascu, S. Shova and P. Filip, *Tetrahedron Lett*., **2013**, *54*, 1486-1488.
29. E. Georgescu, A. Nicolescu, F. Georgescu, F. Teodorescu, D. Marinescu, A.-M. Iurascu-Macsim and C. Deleanu, *Beilstein J. Org. Chem.*, **2014***, 10,* 2377-2387.
30. E. Georgescu, A. Nicolescu, F. Georgescu, F. Teodorescu, S. Shova, A.-M. Macsim and C. Deleanu, *Synthesis*, **2015**, *47*, 1443-1655.
31. S. Simova, *Magn. Reson. Chem*., **1998**, *36*, 505-510.
32. CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.34.76, 2003.
33. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*., **2009**, *42*, 339-341.
34. G. M. Sheldrick, *Acta Cryst. A*, **2008**, *64*, 112-122.
35. X. Wey, Z. Hu, T. Li and H. Hu, *J. Chem. Soc, Perkin Trans I*, **1993**, 2487-2489.