Oxidant Promoted 1,3-Dipolar Cycloaddition of Benzimidazolium Ylides to Alkenes for Preparation of 4*H*-Pyrrolo[1,2-*a*]benzimidazole

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An oxidant promoted 1,3-dipolar cycloaddition of benzimidazolium ylides to alkenes was developed for the preparation of 4*H*-pyrrolo[1,2-*a*]benzimidazole derivatives in moderate yields under mild conditions. In the presence of a suitable oxidant, the most commercially available "normal" alkenes, instead of alkynes or "abnormal" alkenes, could be used as dipolarophiles successfully. Moreover, CrO_3/Et_3N has been proved to be a more effective dehydrogenating reagent than MnO_2 or tetrakispyridine cobalt (II) dichromate (TPCD) in this procedure.

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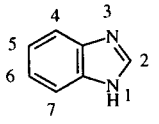
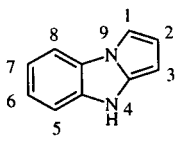
Due to their various practical utilities [1], many efforts have been made to develop methods for preparation of 4*H*-pyrrolo[1,2-*a*]benzimidazole derivatives (Chart 1) [2]. Among the published procedures, most require the use of 2-methyl or 2-methanobenzimidazoles as precursors. Although 1,3-dipolar cycloaddition of benzimidazolium *N*-ylides to electron-deficient alkynes or alkenes featured simple and convenient conditions, it was limited seriously to a very narrow range because of inaccessible dipolarophiles [3]. On the one hand, the most electron-deficient acetylenes are not easy to obtain except for dialkyl acetylenedicarboxylates [3a]. On the other hand, only few "abnormal" alkenes, which were attached by one or more leaving groups, could be used successfully for this purpose [3b]. The "normal" alkenes usually led to tetrahydro-adducts, which were generally unstable and could be reversibly converted back to the starting materials or to ring opened betaines [4].



Benzimidazole



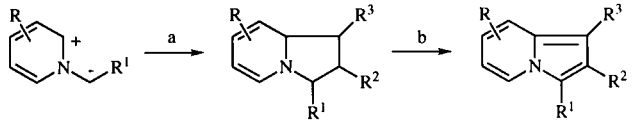
4*H*-Pyrrolo[1,2-*a*]benzimidazole

Chart 1.

In our previous works [5], a series of "oxidant promoted" 1,3-dipolar cycloaddition were reported, where many commercially available electron-deficient alkenes were used as dipolarophiles to react with heteroaromatic ylides successfully. The key of the strategy is dehydrogenation of unstable tetrahydro-adducts into their aromatic forms *in situ* by a suitable oxidant (Scheme 1). The method not only significantly extended the scope of 1,3-dipolar cycloadditions, but also made some "inhibited" reactions possible in moderate to good yields. Herein we report a convenient preparation of 4*H*-pyrrolo[1,2-*a*]benzimidazole using oxidant promoted 1,3-dipolar cycloaddition of heteroaromatic ylides to alkenes.

To a solution of 1-substituted benzimidazoles (**1a-b**) in ethyl acetate was added bromides (**2a-c**) to yield the corresponding benzimidazolium bromides (**3a-f**), the precursors of corresponding ylides, in 75-82% yields (Scheme 2, Table 1). Following the known procedure [5a], a mixture of 1-methyl-3-carbethoxymethylbenzimidazolium bromide (**3a**), methyl acrylate (**4a**) and triethylamine in DMF was treated with tetrakis-pyridine cobalt (II) dichromate [TPCD, $Py_4Co(HCrO_4)_2$] for 4 hours. Two white solids were isolated and, unfortunately, the major product in 23% yield was characterized as methyl ethyl indolizine-1,3-dicarboxylate (**5**) by its melting point (mp 123-125 °C, Lit. [6] mp 123-124 °C) and ^1H nmr spectra as well as ms. The expected product, ethyl methyl 4-methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-1,3-dicarboxylate (**6a**), was obtained only in 3% yield (mp 144-145 °C, Lit. [3b] mp 138 °C) (Scheme 3). Obviously, a salt exchange occurred between **3a** and pyridine, which came from TPCD, because pyridine is a stronger nucleophile than 1-methylbenzimidazoles (**1a**).

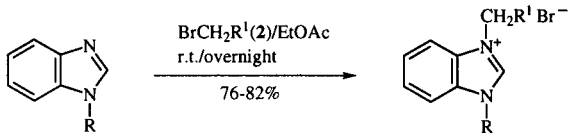
Scheme 1



tetrahydro-adduct

a: $R^2CH_2=CH_2R^3$; b: Dehydrogenation.

Scheme 2



1a R = CH_3
1b R = $C_6H_5CH_2$
2a R^1 = CO_2Et
2b R^1 = COMe
2c R^1 = COPh

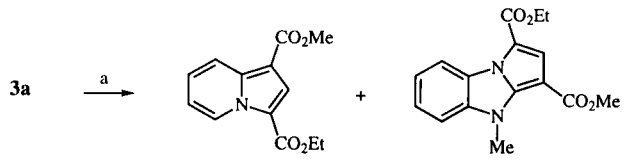
3

Table 1

Benzimidazolium Bromides (**3a-f**) Were Prepared

3	R	R^1	Yield (%)	MP (°C)	IR (ν_{max})
a	Me	CO_2Et	78	156-158	1730
b	Me	COMe	75	118-120	1725
c	Me	COPh	82	210-212 (205) [3a]	1680
d	CH_2Ph	CO_2Et	76	166-168	1740
e	CH_2Ph	COMe	81	128-130	1725
f	CH_2Ph	COPh	79	179-181	1685

Scheme 3



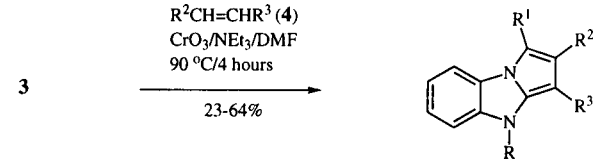
5 **6a**

a: CH_2=$CHCO_2Me$ (**4a**), TPCD, Et_3N, DMF, 90 °C, 4 hours.

MnO_2 used to be recommended as a valid alternative to TPCD as a solution to this problem [5d]. In this case, by-product was avoided by using MnO_2 as a dehydrogenation reagent and **6a** was obtained in 14% yield (DMF, 85 °C, 6 hours). To improve the yield several commercially available oxidants were tried on the same reaction and CrO_3 gave a positive result. It was interesting to note that the best result (31%) was obtained when four equivalents of Et_3N were used at elevated temperature (90 °C, 4 hours). The coordination of CrO_3 with excess Et_3N (one equivalent was consumed on the conversion of salt to corresponding ylide) decreased its ability as an oxidant and increased its ability as a dehydrogenation agent.

Under the same conditions, salts **3a-f** were subjected to reaction with dipolarophiles **4a-c** respectively. As shown in Scheme 4 and Table 2, a variety of 4*H*-pyrrolo[1,2-*a*]-benzimidazole derivatives (**6a-r**) were prepared in reasonable to moderate yields (23-65%). The results clearly showed that the steric factors in both salt **3** and dipolarophile **4** play major roles on the yields of products. For example, the smallest size salt **3b** (R = Me, R^1 = COMe) gave the products **6d-f** (52-64%) in the highest yields. In contrast, bulky salt **3d** gave the lowest yield (**6j-l**, 26-41%). Similarly, diethyl fumarate as a dipolarophile always gave the products in lowest yields (**6c**, **6f**, **6i**, **6l**, **6o**, **6r**).

Scheme 4



4b R^2 = R, R^3 = CN
4c R^2 = R^3 = CO_2Et

6

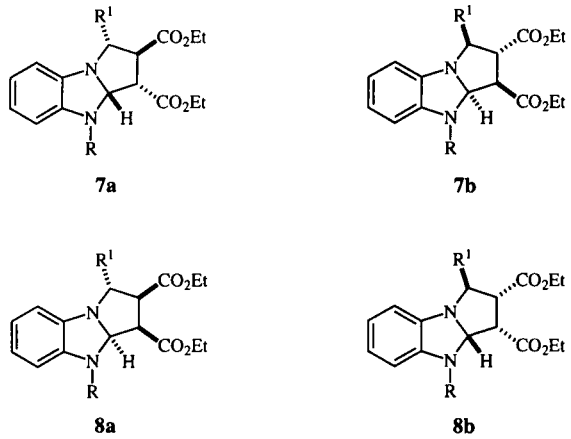
Table 2

4*H*-Pyrrolo[1,2-*a*]benzimidazole **6a-r** Prepared

6	R	R^1	R^2	R^3	Yield (%)
a	Me	CO_2Et	H	CO_2Me	31
b	Me	CO_2Et	H	CN	37
c	Me	CO_2Et	CO_2Et	CO_2Et	23
d	Me	COMe	H	CO_2Me	63
e	Me	COMe	H	CN	64
f	Me	COMe	CO_2Et	CO_2Et	52
g	Me	COPh	H	CO_2Me	65
h	Me	COPh	H	CN	62
i	Me	COPh	CO_2Et	CO_2Et	45
j	CH_2Ph	CO_2Et	H	CO_2Me	31
k	CH_2Ph	CO_2Et	H	CN	41
l	CH_2Ph	CO_2Et	CO_2Et	CO_2Et	26
m	CH_2Ph	COMe	H	CO_2Me	50
n	CH_2Ph	COMe	H	CN	54
o	CH_2Ph	COMe	CO_2Et	CO_2Et	47
p	CH_2PH	COPh	H	CO_2Me	64
q	CH_2Ph	COPh	H	CN	51
r	CH_2Ph	COPh	CO_2Et	CO_2Et	35

It was very interesting to observe that both diethyl maleate and diethyl fumarate can be used as dipolarophiles in the presence of TPCD, but diethyl maleate was inert to CrO_3/Et_3N. This phenomenon may result from the fact that 1,3-dipolar cycloaddition follows the rule of *syn*-addition. Since the initial step of oxidant promoted 1,3-dipolar cycloaddition gives tetrahydro-adducts as intermediates, diethyl fumarate as a dipolarophile should give the favored tetrahydro-adducts **7a** and **7b**.

However, **8a** and **8b** should be favored tetrahydro-adducts when diethyl maleate is used (Chart 2). Although **8a** and **8b** should be very unstable or may not be formed due to the steric hindrance of *syn*-2,3-dicarboxylates.



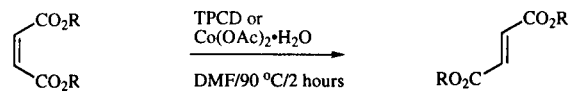
7a **7b**

8a **8b**

Chart 2.

The fact that diethyl maleate can be used as dipolarophile in TPCD promoted reactions suggests that TPCD can isomerize diethyl maleate into diethyl fumarate. The conversion of the maleate ester to fumarate ester is a classic isomerization transformation [7]. It could be achieved under free radical [7a-d], thermal [7e] and both acid- and base-catalyzed conditions [7f-g]. We also found that it can be achieved by cobalt (II) ion, a component of TPCD. Thus, by heating the mixture of dialkyl maleates (methyl or ethyl) and $Co(OAc)_2 \cdot H_2O$ in DMF at 80-85 °C for 1-2 hours, dialkyl fumarates were separated in 68-72% yield (Scheme 5). As expected, when the mixture of salt **3b**, diethyl maleate, CrO_3, Et_3N and $Co(OAc)_2 \cdot H_2O$ in DMF was warmed at 90 °C for 4 hours, **6f** was obtained smoothly in 50% yield. These results provide strong evidence in support of the above hypothesis.

Scheme 5



R = CH_3, 68%
R = C_2H_5, 72%

EXPERIMENTAL

All melting points were determined on a Yanaco melting point apparatus and are uncorrected. The ir spectra were recorded on a Nicolet FT-IR 5DX spectrometer with KBr pellets. The ^1H nmr spectra were recorded on a Bruker ACF-300 spectrometer in $CDCl_3$ with TMS as internal reference. The J values are given in Hz. The ms spectra were obtained on a ZAB-HS mass spectrometer with 70 eV. The elemental analyses were performed on a Perkin-Elmer 240C instrument.

General Procedure for Preparation of Benzimidazolium Bromides (**3a-f**).

A mixture of 1-substituted benzimidazole (**1**, 100 mmoles), bromide (**2**, 100 mmoles) in EtOAc (100 ml) was stirred at room temperature for 0.5 hour. After it stood for another 48 hours, the precipitated solid was collected and was rinsed with EtOAc (50 ml) to give salt **3** as white solid. It was used in the next step without any further purification and some physical data is shown in Table 1.

General Procedure for the Preparation of 4*H*-Pyrrolo[1,2-*a*]-benzimidazole (**6**).

A solution of benzimidazolium bromide (**3**, 5 mmoles), alkene (**4**), (20 mmoles), CrO_3 (0.7 g, 7 mmoles) and Et_3N (4.0 ml) in DMF (30 ml) was stirred at 90 °C for 4 hours (monitored by tlc). It was then cooled to room temperature and poured into 5% aqueous HCl (100 ml). The mixture was extracted with Et_2O (3 x 80 ml) and the combined extracts were washed with water (2 x 50 ml) and dried over Na_2SO_4. After the solvent was removed to give a solid, which was purified by chromatography [silica gel, 35% EtOAc in petroleum ether (60-90 °C)] to yield compound **6** (Table 2).

Ethyl Methyl 4-Methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-1,3-dicarboxylate (**6a**).

This compound was obtained as white crystals, mp 144-145 °C (from EtOH); ir: ν_{max} 3061, 2951, 3013, 1706, 1682, 1202, 1101, 752 cm^{-1}; ^1H nmr: δ 1.41 (t, 3H, J = 7.0 Hz, CH_3), 3.86 (s, 3H, NCH_3), 4.26 (s, 3H, $COOCH_3$), 4.38 (q, 2H, J = 7.0 Hz, OCH_2), 7.27-7.41 (m, 3H, ArH), 7.69 (s, 1H, ArH), 8.81 (d, 1H, J = 8.0 Hz, C8-H); ms: m/z (%) 300 (M^+, 100), 269 (10), 241 (46), 228 (46), 169 (9).

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 64.01; H, 5.17; N, 9.30

Ethyl 3-Cyano-4-methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-1-carboxylate (**6b**).

This compound was obtained as white crystals, mp 197-198 °C (from EtOH); ir: ν_{max} 3125, 2979, 1696, 1605, 1514, 1484, 1387, 1254, 1078, 1018, 848, 739 cm^{-1}; ^1H nmr: δ 1.41 (t, 3H, J = 7.0 Hz, CH_3), 3.82 (s, 3H, NCH_3), 4.36 (q, 2H, J = 7.0 Hz, OCH_2), 7.09-7.29 (m, 4H, ArH), 8.64 (m, 1H, C8-H); ms: m/z (%) 267 (M^+, 88), 239 (100), 222 (25), 195 (52), 180 (10), 168 (6), 102 (9), 76 (12).

Anal. Calcd. for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.71. Found: C, 67.61; H, 5.04; N, 15.68.

Triethyl 4-Methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-1,2,3-tricarboxylate (**6c**).

This compound was obtained as white crystals, mp 124-125 °C (from EtOH); ir: ν_{max} 2982, 2956, 1732, 1692, 1492, 1214,

1202, 750, 739, 722, 669 cm^{-1}; ^1H nmr: δ 1.36 (t, 3H, J = 7.0 Hz, CH_3), 1.40 (t, 3H, J = 7.0 Hz, CH_3), 1.43 (t, 3H, J = 7.0 Hz, CH_3), 4.23 (s, 3H, NCH_3), 4.29 (q, 2H, J = 7.0 Hz, OCH_2), 4.37 (q, 2H, J = 7.0 Hz, OCH_2), 4.42 (q, 2H, J = 7.0 Hz, OCH_2), 7.28-7.43 (m, 3H, ArH), 8.80 (d, 1H, J = 8.0 Hz, C8-H); ms: m/z (%) 386 (M^+, 100), 341 (18), 269 (24), 267 (21), 223 (25), 170 (19).

Anal. Calcd. for $C_{20}H_{22}N_2O_6$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.11; H, 5.76; N, 7.12.

Methyl 1-Acetyl-4-methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-3-carboxylate (**6d**).

This compound was obtained as yellowish crystals, mp 176-178 °C (from EtOH); ir: ν_{max} 3125, 2949, 1702, 1635, 1460, 1199, 1084, 945, 848, 769, 691; ^1H nmr: δ 2.48 (s, 3H, $COCH_3$), 3.85 (s, 3H, $COOCH_3$), 4.17 (s, 3H, NCH_3), 7.36-7.19 (m, 3H, ArH), 7.59 (s, 1H, C2-H), 8.91 (m, 1H, C8-H); ms: m/z (%) 270 (M^+, 100), 255 (79), 239 (27), 227 (36), 197 (8), 168 (10), 102 (8), 77 (3).

Anal. Calcd. for $C_{15}H_{14}N_2O_3$: C, 66.45; H, 5.22; N, 10.35. Found: C, 66.50; H, 5.31; N, 10.16.

1-Acetyl-4-methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-3-carbonitrile (**6e**).

This compound was obtained as white crystals, mp 224-225 °C (from EtOH); ir: ν_{max} 3113, 2210, 1647, 1599, 1478, 1290, 1181, 1066, 769, 739 cm^{-1}; ^1H nmr: δ 2.46 (s, 3H, $COCH_3$), 3.88 (s, 3H, NCH_3), 7.34-7.19 (m, 3H, ArH), 7.41 (s, 1H, C2-H), 8.83 (m, 1H, C8-H); ms: m/z (%) 237 (M^+, 96), 222 (100), 194 (71), 180 (5), 167 (3), 102 (8), 76 (10).

Anal. Calcd. for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.70. Found: C, 71.05; H, 4.72; N, 17.61.

Diethyl 1-Acetyl-4-methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-2,3-dicarboxylate (**6f**).

This compound was obtained as yellowish crystals, mp 118-119 °C (from EtOH); ir: ν_{max} 2925, 1741, 1697, 1638, 1575, 1484, 1378, 1187, 1069, 1028, 966, 772 cm^{-1}; ^1H nmr: δ 1.45 (m, 6H, $2CH_3$), 2.48 (s, 3H, $COCH_3$), 4.20 (s, 3H, NCH_3), 4.28-4.58 (m, 4H, $2OCH_2$), 7.34-7.60 (m, 3H, ArH), 8.89 (m, 1H, C8-H); ms: m/z (%) 356 (M^+, 100), 311 (16), 267 (22), 239 (29), 195 (13), 168 (13), 77 (6).

Anal. Calcd. for $C_{19}H_{20}N_2O_5$: C, 64.03; H, 5.65; N, 7.85. Found: C, 64.10; H, 5.64; N, 8.02.

Methyl 1-Benzoyl-4-methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-3-carboxylate (**6g**).

This compound was obtained as yellowish crystals, mp 183-184 °C (from EtOH); ir: ν_{max} 3052, 2949, 1708, 1617, 1502, 1393, 1308, 1205, 1012, 903, 767, 691 cm^{-1}; ^1H nmr: δ 3.82 (s, 3H, OCH_3), 4.25 (s, 3H, NCH_3), 7.29-7.92 (m, 8H, ArH), 7.47 (s, 1H, C2-H), 8.89 (m, 1H, C8-H); ms: m/z (%) 332 (M^+, 100), 301 (23), 255 (14), 227 (8), 105 (13), 77 (22).

Anal. Calcd. for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.42. Found: C, 72.58; H, 4.87; N, 8.67.

1-Benzoyl-4-methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-3-carbonitrile (**6h**).

This compound was obtained as white crystals, mp 262-264 °C (from EtOH); ir: ν_{max} 3113, 3056, 2213, 1619, 1503, 1447, 1391, 1303, 1194, 1163, 913, 750 cm^{-1}; ^1H nmr: δ 3.98 (s, 3H, NCH_3), 7.21-7.88 (m, 9H, ArH), 8.85 (m, 1H, C8-H); ms: m/z (%) 299 (M^+, 100), 270 (21), 222 (30), 194 (29), 167 (2), 105 (13), 77 (36).

Anal. Calcd. for $C_{19}H_{13}N_3O$: C, 76.24; H, 4.37; N, 14.03. Found: C, 76.20; H, 4.54; N, 13.88.

Diethyl 1-Benzoyl-4-methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-2,3-carboxylate (**6i**).

This compound was obtained as yellowish crystals, mp 138-139 °C (from EtOH); ir: ν_{max} 2985, 2934, 1727, 1699, 1614, 1571, 1459, 1378, 1202, 1122, 1073, 953, 778 cm^{-1}; ^1H nmr: δ 1.04 (t, 3H, J = 7.0 Hz, CH_3), 1.29 (t, 3H, J = 7.0 Hz, CH_3), 3.62 (s, 3H, NCH_3), 4.20 (q, 2H, J = 7.0 Hz, OCH_2), 4.27 (q, 2H, J = 7.0 Hz, OCH_2), 7.28-7.83 (m, 8H, ArH), 8.46 (m, 1H, C8-H); ms: m/z (%) 418 (M^+, 100), 373 (10), 346 (12), 301 (25), 273 (18), 241 (10), 105 (11), 77 (15).

Anal. Calcd. for $C_{24}H_{22}N_2O_5$: C, 68.89; H, 5.09; N, 6.69. Found: C, 69.25; H, 5.31; N, 6.65.

Ethyl Methyl 4-Benzyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-1,3-dicarboxylate (**6j**).

This compound was obtained as white crystals, mp 140-142 °C (from EtOH); ir: ν_{max} 3030, 2979, 2954, 1685, 1579,1512, 1454, 1189, 1107, 1074, 745, 700 cm^{-1}; ^1H nmr: δ 1.42 (t, 3H, J = 7.0 Hz, CH_3), 3.81 (s, 3H, OCH_3), 4.40 (q, 2H, J = 7.0 Hz, OCH_2), 6.09 (s, 2H, NCH_2), 7.21-7.29 (m, 8H, ArH), 7.72 (s, 1H, ArH), 8.83 (d, 1H, J = 8.0 Hz, C8-H); ms: m/z (%) 376 (M^+, 51), 331 (3), 285 (15), 227 (7), 91 (100).

Anal. Calcd. for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 70.26; H, 5.41; N, 7.46.

Ethyl 4-Benzyl-3-cyano-4*H*-pyrrolo[1,2-*a*]benzimidazole-1-carboxylate (**6k**).

This compound was obtained as white crystals, mp 176-178 °C (from EtOH); ir: ν_{max} 3030, 2984, 2209, 1698, 1592, 1507, 1452, 1074, 743, 704 cm^{-1}; ^1H nmr: δ 1.41 (t, 3H, J = 7.0 Hz, CH_3), 4.39 (q, 2H, J = 7.0 Hz, OCH_2), 5.52 (s, 2H, NCH_2), 7.25-7.37 (m, 7H, ArH), 7.45 (m, 2H, ArH), 8.79 (d, 1H, J = 8.0 Hz, C8-H); ms: m/z (%) 343 (M^+, 23), 298 (2), 224 (3), 168 (2), 91 (100).

Anal. Calcd. for $C_{21}H_{17}N_3O_2$: C, 73.46; H, 4.99; N, 12.24. Found: C, 73.45; H, 5.19; N, 12.05.

Triethyl 4-Benzyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-1,2,3-tricarboxylate (**6l**).

This compound was obtained as white crystals, mp 120-122 °C (from EtOH); ir: ν_{max} 3030, 2983, 1729, 1706, 1687, 1615, 1514, 1456, 1220, 1181, 752 cm^{-1}; ^1H nmr: δ 1.26 (t, 3H, J = 7.0 Hz, CH_3), 1.40 (t, 3H, J = 7.0 Hz, CH_3), 1.44 (t, 3H, J = 7.0 Hz, CH_3), 4.24 (q, 2H, J = 7.0 Hz, OCH_2), 4.38 (q, 2H, J = 7.0 Hz, OCH_2), 4.43 (q, 2H, J = 7.0 Hz, OCH_2), 6.07 (s, 2H, NCH_2), 7.18-7.33 (m, 8H, ArH), 8.82 (d, 1H, J = 8.0 Hz, C8-H); ms: m/z (%) 462 (M^+, 84), 417 (34), 387 (31), 299 (13), 91 (100).

Anal. Calcd. for $C_{26}H_{26}N_2O_6$: C, 67.52; H, 5.67; N, 6.02. Found: C, 67.61; H, 5.88; N, 6.12.

Methyl 1-Acetyl-4-benzyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-3-carboxylate (**6m**).

This compound was obtained as yellowish crystals, mp 168-169 °C (from EtOH); ir: ν_{max} 3131, 2955, 1694, 1575, 1506, 1453, 1394, 1306, 1234, 1181, 1100, 1006, 941, 747 cm^{-1}; ^1H nmr: δ 2.50 (s, 3H, $COCH_3$), 3.80 (s, 3H, $COOCH_3$), 6.01 (s, 2H,

NCH_2), 7.16-7.30 (m, 8H, ArH), 7.66 (s, 1H, C2-H), 8.94 (m, 1H, C8-H); ms: m/z (%) 346 (M^+, 100), 272 (17), 255 (15), 224 (7), 168 (2), 91 (72), 77 (2).

Anal. Calcd. for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.23; N, 8.08. Found: C, 72.95; H, 5.28; N, 8.06.

1-Acetyl-4-benzyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-3-carbonitrile (**6n**).

This compound was obtained as red crystals, mp 183-185 °C (from EtOH); ir: ν_{max} 3119, 2210, 1647, 1591, 1502, 1472, 1394, 1291, 1066, 947, 856, 744, 706 cm^{-1}; ^1H nmr: δ 2.46 (s, 3H, $COCH_3$), 5.46 (s, 2H, NCH_2), 7.24-7.29 (m, 8H, ArH), 7.37 (s, 1H, C2-H), 8.93 (m, 1H, C8-H); ms: m/z (%) 313 (M^+, 24), 271 (2), 222 (2), 180 (3), 91 (100), 77 (3).

Anal. Calcd. for $C_{20}H_{15}N_3O$: C, 76.66; H, 4.83; N, 13.40. Found: C, 76.79; H, 4.82; N, 13.24.

Diethyl 1-Acetyl-4-benzyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-2,3-dicarboxylate (**6o**).

This compound was obtained as yellowish crystals, mp 153-155 °C (from EtOH); ir: ν_{max} 2985, 2901, 1750, 1694, 1641, 1571, 1500, 1388, 1269, 1110, 1038, 1009, 966, 872, 750 cm^{-1}; ^1H nmr: δ 1.24 (t, 3H, J = 7.0 Hz, CH_3), 1.44 (t, 3H, J = 7.0 Hz, CH_3), 2.51 (s, 3H, $COCH_3$), 4.25 (q, 2H, J = 7.0 Hz, OCH_2), 4.47 (q, 2H, J = 7.0 Hz, OCH_2), 6.01 (s, 2H, NCH_2), 7.10-7.33 (m, 8H, ArH), 8.91 (m, 1H, C8-H); ms: m/z (%) 432 (M^+, 11), 387 (4), 357 (3), 168 (15), 91 (100), 77 (3).

Anal. Calcd. for $C_{25}H_{24}N_2O_5$: C, 69.43; H, 5.59; N, 6.47. Found: C, 69.20; H, 5.57; N, 6.63.

Methyl 1-Benzoyl-4-benzyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-3-carboxylate (**6p**).

This compound was obtained as white crystals, mp 173-174 °C (from EtOH); ir: ν_{max} 3031, 2987, 1693, 1620, 1502, 1206, 1115, 903, 721, 696 cm^{-1}; ^1H nmr: δ 3.79 (s, 3H, OCH_3), 6.13 (s, 2H, NCH_2), 7.24-7.35 (m, 8H, ArH), 7.51-7.60 (m, 4H, ArH), 7.89 (d, 2H, J = 7.5 Hz, ArH), 8.93 (d, 1H, J = 8.0 Hz, C8-H); ms: m/z (%) 408 (M^+, 85), 377 (3), 317 (31), 289 (12), 105 (68), 91 (100).

Anal. Calcd. for $C_{26}H_{20}N_2O_3$: C, 76.46; H, 4.94; N, 6.86. Found: C, 76.50; H, 4.91; N, 7.02.

1-Benzoyl-4-benzyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-3-carbonitrile (**6q**).

This compound was obtained as white crystals, mp 186-188 °C (from EtOH); ir: ν_{max} 3112, 3028, 2210, 1632, 1590, 1504, 910, 705 cm^{-1}; ^1H nmr: δ 5.59 (s, 2H, NCH_2), 7.31-7.61 (m, 12H, ArH), 7.86 (d, 2H, J = 8.0 Hz, ArH), 8.92 (d, 1H, J = 8.0 Hz, C8-H); ms: m/z (%) 375 (M^+, 24), 285 (3), 208 (2), 105 (16), 91 (100), 77 (9).

Anal. Calcd. for $C_{25}H_{17}N_3O$: C, 79.98; H, 4.56; N, 11.19. Found: C, 80.05; H, 4.73; N, 11.35.

Diethyl 1-Benzoyl-4-benzyl-4*H*-pyrrolo[1,2-*a*]benzimidazole-2,3-dicarboxylate (**6r**).

This compound was obtained as yellowish crystals, mp 197-198 °C (from EtOH); ir: ν_{max} 3030, 2982, 2939, 1738, 1717, 1688, 1616, 1520, 1457, 1183, 1071, 772, 746 cm^{-1}; ^1H nmr: δ 1.05 (t, 3H, J = 7.0 Hz, CH_3), 1.19 (t, 3H, J = 7.0 Hz, CH_3), 3.60 (q, 2H, J = 7.0 Hz, OCH_2), 4.21 (q, 2H, J = 7.0 Hz, OCH_2), 6.09 (s, 2H, NCH_2), 7.23-7.36 (m, 8H, ArH), 7.47 (m, 2H, ArH), 7.56 (m, 1H, ArH), 7.81 (d, 2H, J = 8.0 Hz, ArH), 8.5 (d, 1H, J = 8.0 Hz, C8-H); ms: m/z (%) 494 (M^+, 39), 448 (21), 420 (5), 419 (12), 333 (7), 331 (6), 105 (52), 91 (100).

Anal. Calcd. for $C_{30}H_{26}N_2O_5$: C, 72.86; H, 5.30; N, 5.66. Found: C, 72.81; H, 5.39; N, 5.87.

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