Synthesis of pyrrole and indole quinoxalinone and oxazinone derivatives by intramolecular copper-catalyzed reactions

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Corrections

Following the study on the synthesis and derivatization of pyrrole and indole quinoxalinone, we tried to derivatize the pyrrolo[1,2-\textit{a}]quinoxaline-4(5\textit{H})-one (3\textit{a}) compound to obtain 4-chloropyrrolo[1,2-\textit{a}]quinoxaline by methods described in the literature\cite{1} however, it was not possible to carry out this reaction. These results led us to infer that the structures of the compounds reported in Org. Biomol. Chem., 2011, 9, 4927-4935 had not been properly characterized. We decided to reevaluate the spectroscopic data of compound 3\textit{a}\textsuperscript{2} for which experiments of Nuclear Magnetic Spectroscopy such as HMBC and NOESY were performed. Their detailed analysis allowed us to conclude that the product obtained in the intramolecular cooper-catalyzed reactions of \textit{N}-(2-bromophenyl)-1\textit{H}-pyrrole-2-carboxamide (1\textit{a}) corresponds to 2-(1\textit{H}-pyrrol-2-yl)benzo[d]oxazole. This conclusion can also be applied to all products derived from pyrrolo and indolo carboxamides 1\textit{b}, 1\textit{c}, 1\textit{d}, 1\textit{e}, 2\textit{a}, 2\textit{b}, 2\textit{c}. In view of this, we would need to correct and replace 3\textit{a}, 3\textit{b}\textsuperscript{3}, 3\textit{c}, 3\textit{d}, 3\textit{e}, 5\textit{a}, 5\textit{b} and 5\textit{c} structures by the benzoaxazole derivatives (Figure 1).

![Chemical structures](image)

**Figure 1**: Benzoaxazole ring obtained by intramolecular cooper-catalyzed reaction with carboxamides derived from pyrrole and indole.
Notes and References


2 Spectroscopy data for 3a compound from HMBC and NOESY experiments. HMBC (Heteronuclear Multiple Bond Correlation) in CDCl$_3$ $^1$H-$^{13}$C $\delta^H$-$\delta^C$: 6.38/119.8 (pyrrole proton/pyrrole quaternary carbon), 6.38/113.2 (pyrrole proton/pyrrole carbon), 6.38/123.0 (pyrrole proton/pyrrole carbon), 7.05/110.8 (pyrrole proton/pyrrole carbon), 7.05/113.2 (pyrrole proton/pyrrole carbon), 7.05/119.8 (pyrrole proton/pyrrole quaternary carbon), 7.10/119.8 (pyrrole proton/pyrrole quaternary carbon), 7.10/123.0 (pyrrole proton/pyrrole carbon), 7.32/110.4 (aromatic proton/aromatic carbon), 7.32/118.8 (aromatic proton/aromatic carbon), 7.32/141.8 (aromatic proton/aromatic quaternary carbon), 7.32/150.2 (aromatic proton/aromatic quaternary carbon), 7.54/124.4 (aromatic proton/aromatic carbon), 7.54/124.6 (aromatic proton/aromatic carbon), 7.54/141.8 (aromatic proton/aromatic quaternary carbon), 7.54/150.2 (aromatic proton/aromatic quaternary carbon), 7.66/124.4 (aromatic proton/aromatic carbon), 7.66/124.6 (aromatic proton/aromatic carbon), 7.66/150.2 (aromatic proton/aromatic quaternary carbon). NOESY (Proton-proton through-space interactions via NOE) $\delta^H$-$\delta^H$: 6.38/7.09, 7.05/6.38, 7.05/10.51 (pyrrole proton/pyrrole NH). This compound was previously described (C. Praveen, K. H. Kumar, D. Muralidharan and P. T., Perumal, Tetrahedron, 2008, 64, 2369-2374; K. G. Ozokan, M. K. Gumus and S. Kaban, J. Heterocycl. Chem., 2008, 45, 1831-1834), but data from 2D NMR experiments are not reported.

3 HMBC and NOESY experiments carried out with this compound allowed us to reach the same conclusion as 3a.
Additional spectra data for compounds 3a, 3b, 3c, 5a, 5b and 5c

$^1$H-$^{13}$C HMBC 2-(1H-pyrrol-2-yl)benzo[d]oxazole (CDCl$_3$) 3a

$^1$H-$^{13}$C HMBC NMR (CDCl$_3$) $\delta$H/$\delta$C: 6.38/113.2, 6.38/119.8, 6.38/123.0, 7.05/110.8, 7.05/113.2, 7.10/119.8, 7.10/123.0, 7.32/118.8, 7.32/141.8, 7.32/150.4, 7.54/124.4, 7.54/124.6, 7.54/141.8, 7.54/150.2, 7.66/124.4, 7.66/124.5, 7.66/141.9, 7.66/150.2.
$^1$H-$^1$H NOESY NMR 2-($1H$-pyrrol-2-yl)benzo[d]oxazole (CDCl$_3$) 3a.

heterocyclic $NH$ →

pyrrole $CH$

6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5 10.0 10.5 11.0 11.5 ppm

$^1$H-$^1$H NOESY NMR 2-($1H$-pyrrol-2-yl)benzo[d]oxazole (CDCl$_3$) 3a.

heterocyclic $NH$ →

pyrrole $CH$

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 ppm
$^{1}$H-$^{1}$H NOESY NMR  2-(1H-pyrrol-2-yl)benzo[d]oxazole (CDCl$_3$) 3a.

pyrrole CH

$^{1}$H-$^{1}$H NOESY NMR (CDCl$_3$) $\delta$/H/δH: 6.38/7.09, 7.05/6.38, 7.05/10.51.
$^1$H-$^{13}$C HMBC NMR 6-methyl-2-(1H-pyrrol-2-yl)benzo[d]oxazole (acetone-$d_6$)3b.

$^1$H-$^{13}$C HMBC NMR (CDCl$_3$) $\delta$H/$\delta$C: 2.48/110.6, 2.48/125.7, 2.48/134.7, 6.35/119.9, 6.35/122.9, 7.01/110.6, 7.01/112.9, 7.01/119.9, 7.07/119.9, 7.07/122.9, 7.12/21.7, 7.12/110.7, 7.12/139.5, 7.33/21.7, 7.33/118.1, 7.33/125.7, 7.33/139.5, 7.33/150.4, 7.52/110.7, 7.52/134.7, 7.52/150.4.
$^1$H-$^{13}$C HMBC NMR 6-chloro-2-($1H$-pyrrol-2-yl)benzo[$d$]oxazole (CDCl$_3$) 3c.

$^1$H-$^{13}$C HMBC NMR (CDCl$_3$) $\delta$H/$\delta$C: 6.38/119.2, 6.38/123.3, 7.05/111.1, 7.05/113.6, 7.05/119.4, 7.05/123.3, 7.09/123.3, 7.09/125.2, 7.30/111.1, 7.30/123.3, 7.30/129.8, 7.30/140.6, 7.54/111.1, 7.54/119.4, 7.54/125.2, 7.54/129.8, 7.54/140.6, 7.54/150.5.
$^1$H-$^{13}$C HMBC NMR 2-(1H-indol-2-yl)benzo[d]oxazole (CDCl$_3$) 5a.

$^1$H-$^{13}$C HMBC NMR (CDCl$_3$) $\delta$H/$\delta$C: 7.18/111.7, 7.18/128.1, 7.31/110.6, 7.31/122.0, 7.31/137.5, 7.37/119.6, 7.37/141.6, 7.41/120.9, 7.41/124.8, 7.41/128.1, 7.41/137.5, 7.61/124.9, 7.61/141.6, 7.73/106.5, 7.73/124.9, 7.73/137.5, 7.73/141.6, 7.73/150.6.
\(^1\text{H}-\text{H NOESY NMR}\) 2-(1H-indol-2-yl)benzo[d]oxazole (CDCl\(_3\)) 5a.

\[ \text{heterocyclic NH} \rightarrow \]

\[ \text{heteroaromatic CH} \]

\(1\text{H-1H NOESY NMR (CDCl3)} \delta H/\delta H: 7.41/9.76.\)
$^1$H-$^{13}$C HMBC NMR 2-($1$H-indol-2-yl)-6-methylbenzo[d]oxazole (CDCl$_3$) 5b

$^1$H-$^{13}$C HMBC NMR (CDCl$_3$) $\delta$H/$\delta$C: 2.52/110.9, 2.52/126.2, 2.52/135.9, 7.18/110.9, 7.18/128.3, 7.18/139.6, 7.29/122.1, 7.29/137.6, 7.36/122.1, 7.36/137.6, 7.40/121.0, 7.40/126.2, 7.40/128.3, 7.40/139.6, 7.59/135.9, 7.59/151.0.
$^1$H-$^{13}$C HMBC NMR 6-chloro-2-($H$-indol-2-yl)benzo[d]oxazole (CDCl$_3$) 5c.

$^1$H-$^{13}$C HMBC NMR (CDCl$_3$) $\delta$H/$\delta$C: 7.19/111.7, 7.19/128.1, 7.33/111.3, 7.33/122.1, 7.33/137.6, 7.33/140.5, 7.40/120.0, 7.40/111.3, 7.40/121.1, 7.40/124.2, 7.40/128.1, 7.40/137.6, 7.61/125.2, 7.61/130.8, 7.61/140.5, 7.61/150.8, 7.73/107.0, 7.73/125.2, 7.73/137.6.