Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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

Victoria A. Vaillard, Roberto A. Rossi, Sandra E. Martín

Corrections

Following the study on the synthesis and derivatization of pyrrole and indole quinoxalinone, we tried to derivatize the pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**3a**) compound to obtain 4-chloropyrrolo[1,2-*a*]quinoxaline by methods described in the literature;[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 **3a**[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 *N*-(2-bromophenyl)-1*H*-pyrrole-2-carboxamide (**1a**) corresponds to 2-(1*H*-pyrrol-2-yl)benzo[*d*]oxazole. This conclusion can also be applied to all products derived from pyrrolo and indolo carboxamides **1b**, **1c**, **1d**, **1e**, **2a**, **2b**, **2c**. In view of this, we would need to correct and replace **3a**, **3b**,[3] **3c**, **3d**, **3e**, **5a**, **5b** and **5c** structures by the benzoxazole derivatives (**Figure 1**).

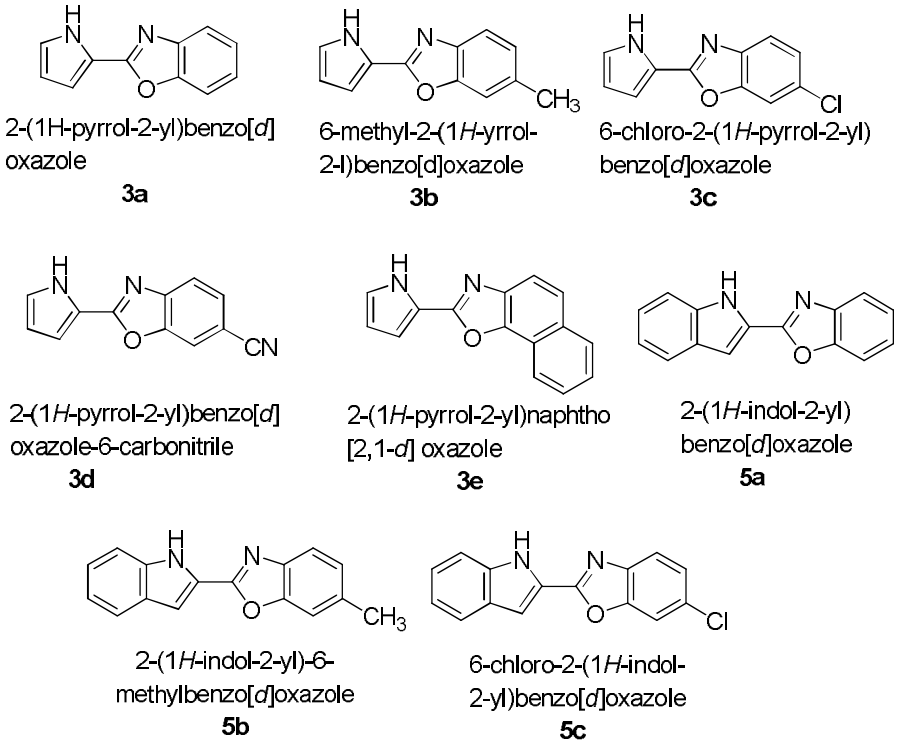


Figure 1: Benzoxazole ring obtained by intramolecular cooper-catalyzed reaction with carboxamides derived from pyrrole and indole.

Notes and References

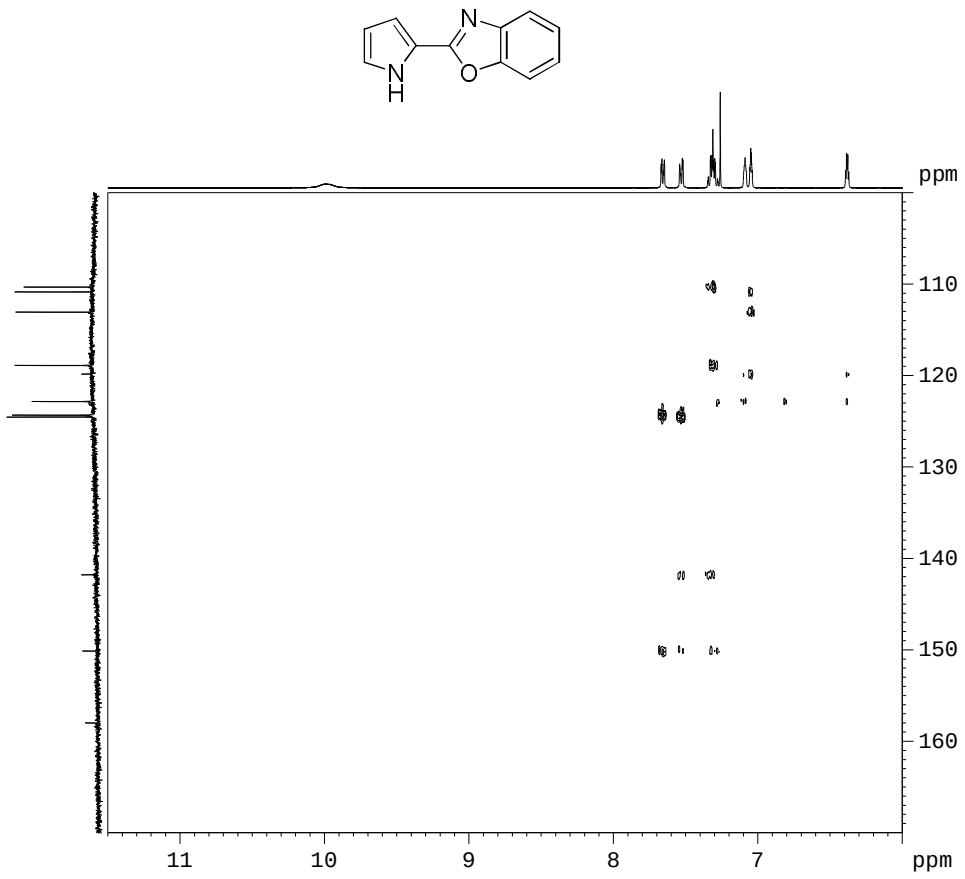
1 (a) Campiani,G., Cappelli,A., Nacci, V., Anzini, M ., Vomero,S., Hamon, M., Cagnotto, A., Fracasso, C., Uboldi, C., Caccia, S., Consolo, S., Mennini, T.; *J. Med. Chem*., 1997, **40**, 3670-3678. (b) Guillon, J., Grellier, P., Labaied, M., Sonnet, P., Léger, J-M-, Déprez-Poulain, R., Forfar-Bares, I., Dallemagne, P., Lemaître, N., Péhourcq, F., Rochette, J., Sergheraert, C., Jarry, C., *J. Med. Chem*. 2004, **47**, 1997-2009.

2 Spectroscopy data for **3a** compound from HMBC and NOESY experiments. HMBC (Heteronuclear Multiple Bond Correlation) in $CDCl_3$ ^{1}H-^{13}C δ_{H}-δ_{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) δ_{H}-δ_{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**.

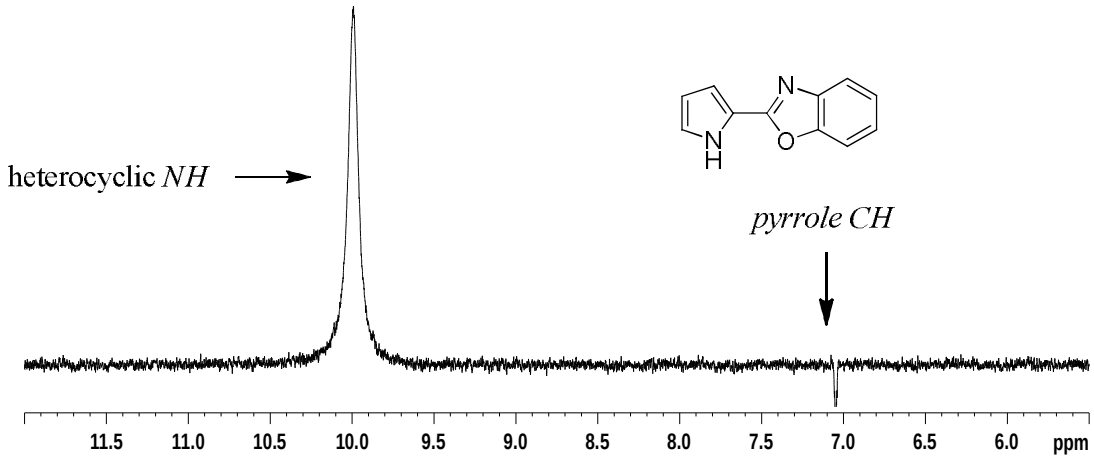
Additional spectra data for compounds 3a, 3b, 3c, 5a, 5b and 5c

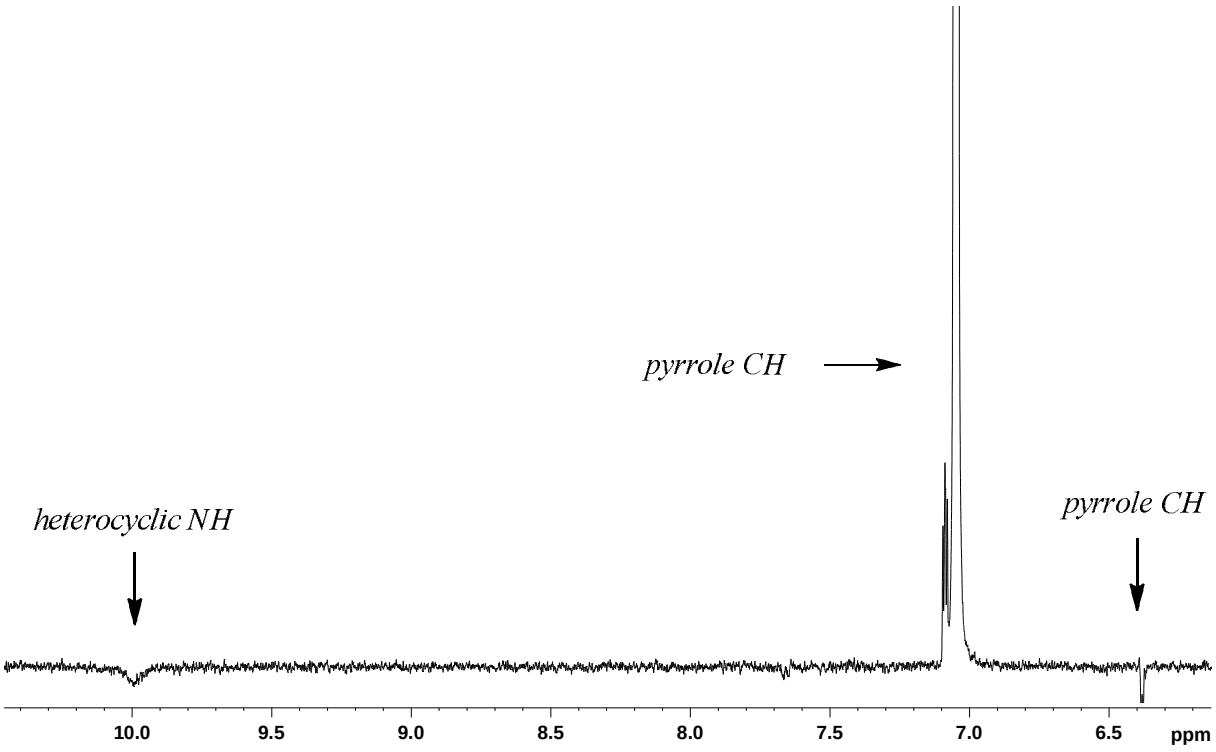
^{1}H-^{13}C HMBC 2-(1*H*-pyrrol-2-*yl*)benzo[d]oxazole ($CDCl_3$) **3a**



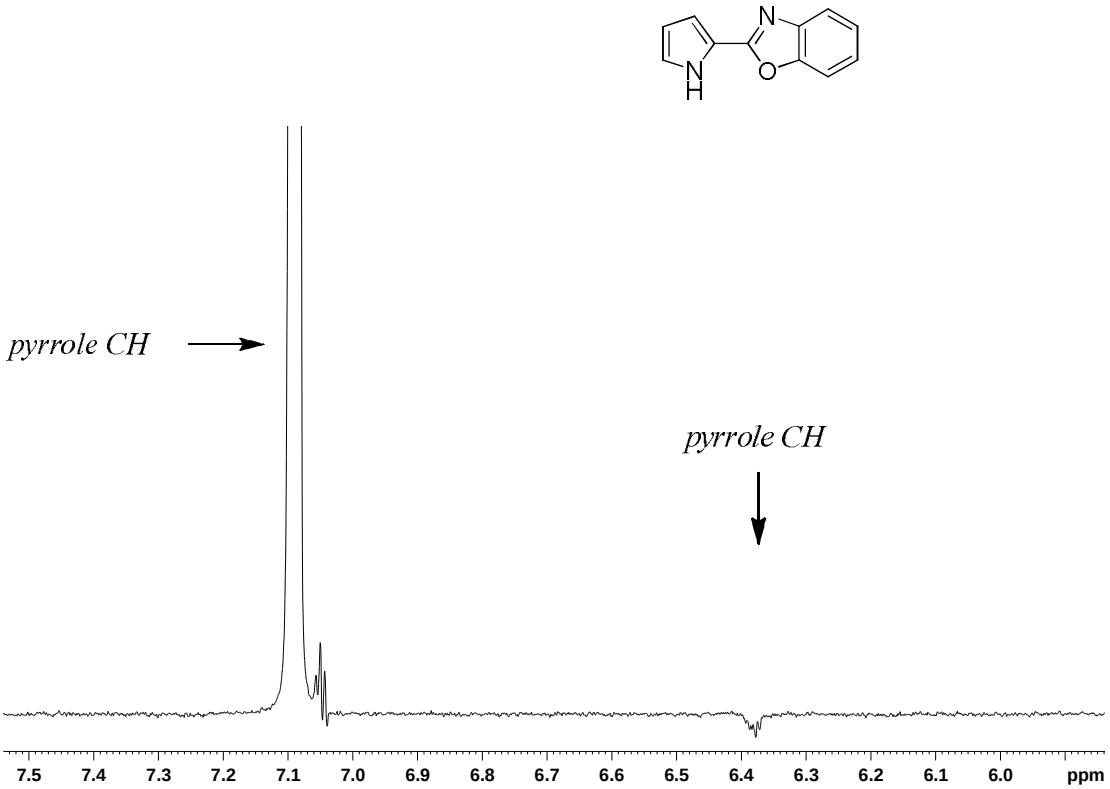
^{1}H-^{13}C HMBC NMR (CDCl3) δH/δC : 6.38/113.2, 6.38/119.8, 6.38/123.0, 7.05/110.8, 7.05/113.2, 7.10/119.8, 7.10/123.0, 7.32/118.8, 7.32/141.8, 7.32/150.4, 7.54/124.4, 7.54/124.6, 7.54/141.8, 7.54/150.2, 7.66/124.4, 7.66/124.5, 7.66/141.9, 7.66/150.2.

^{1}H-^{1}H NOESY NMR 2-(1*H*-pyrrol-2-*yl*)benzo[d]oxazole ($CDCl_3$) **3a.**



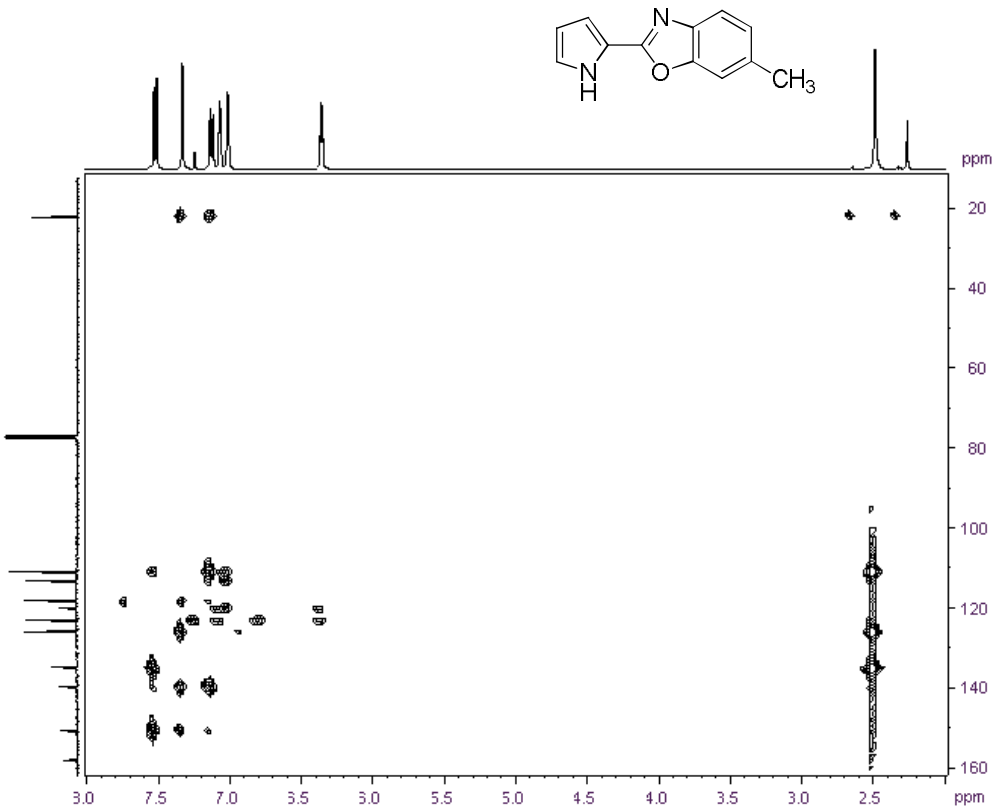


^{1}H-^{1}H NOESY NMR 2-(1*H*-pyrrol-2-*yl*)benzo[d]oxazole ($CDCl_3$) **3a.**



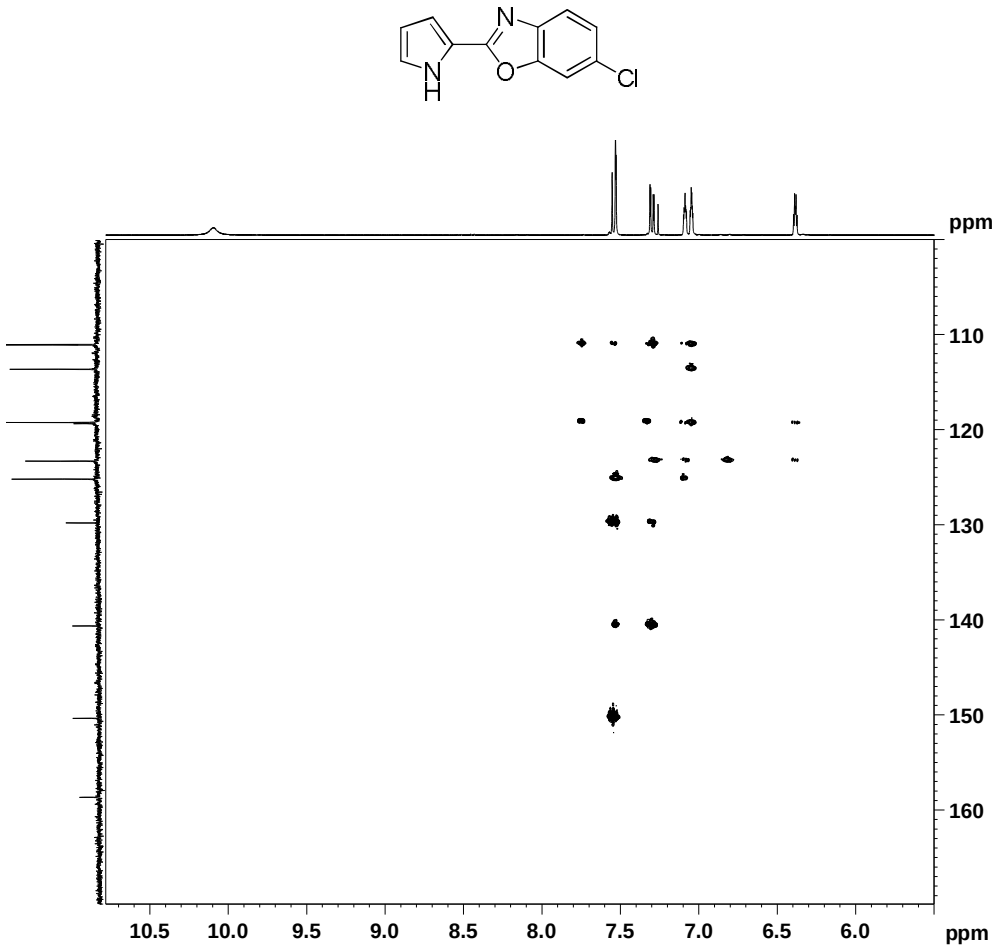
^{1}H-^{1}H NOESY NMR ($CDCl_3$) δH/δH: 6.38/7.09, 7.05/6.38, 7.05/10.51.

^{1}H-^{13}C HMBC NMR 6-methyl-2-(1*H*-pyrrol-2-yl)benzo[*d*]oxazole (acetone-*d6*)**3b.**



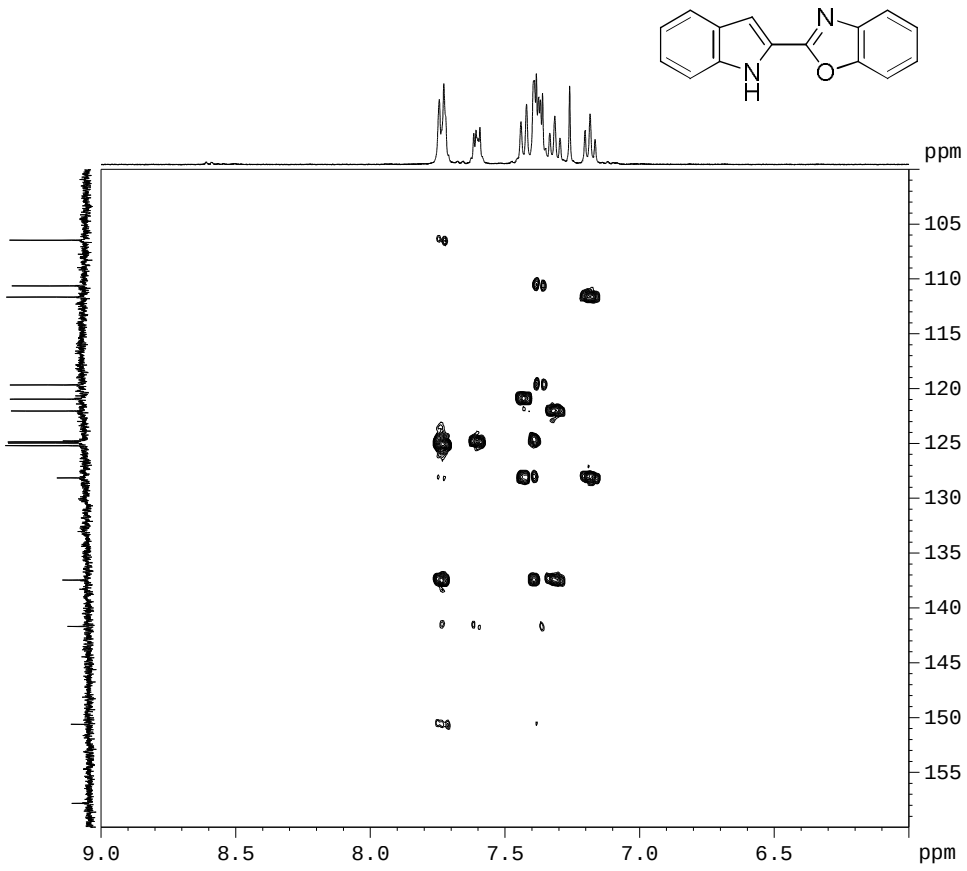
^{1}H-^{13}C HMBC NMR (CDCl3) δH/δC : 2.48/110.6, 2.48/125.7, 2.48/134.7, 6.35/119.9, 6.35/122.9, 7.01/110.6, 7.01/112.9, 7.01/119.9, 7.07/119.9, 7.07/122.9, 7.12/21.7, 7.12/110.7, 7.12/139.5, 7.33/21.7, 7.33/118.1, 7.33/125.7, 7.33/139.5, 7.33/150.4, 7.52/110.7, 7.52/134.7, 7.52/150.4.

^{1}H-^{13}C HMBC NMR 6-chloro-2-(1*H*-pyrrol-2-yl)benzo[*d*]oxazole ($CDCl_3$) **3c.**



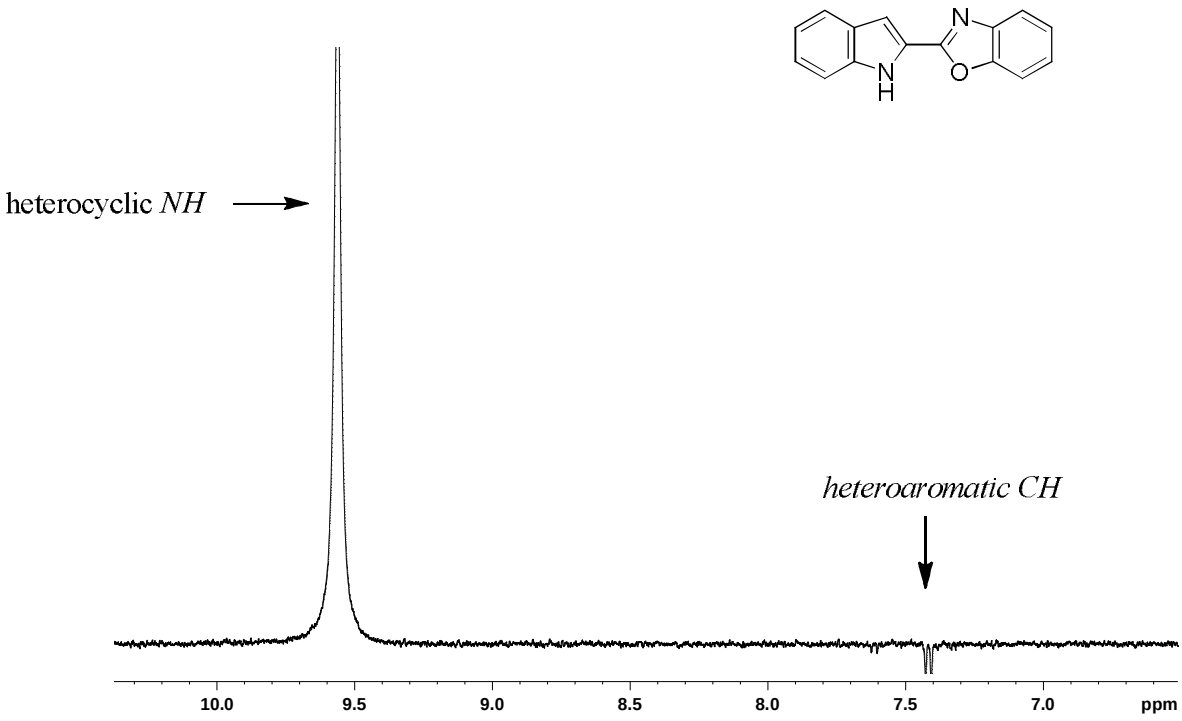
^{1}H-^{13}C HMBC NMR (CDCl3)δH/δC: 6.38/119.2, 6.38/123.3, 7.05/111.1, 7.05/113.6, 7.05/119.4, 7.05/123.3, 7.09/123.3, 7.09/125.2, 7.30/111.1, 7.30/123.3, 7.30/129.8, 7.30/140.6, 7.54/111.1, 7.54/119.4, 7.54/125.2, 7.54/129.8, 7.54/140.6, 7.54/150.5.

^{1}H-^{13}C HMBC NMR 2-(1*H*-indol-2-yl)benzo[*d*]oxazole ($CDCl_3$) **5a**.



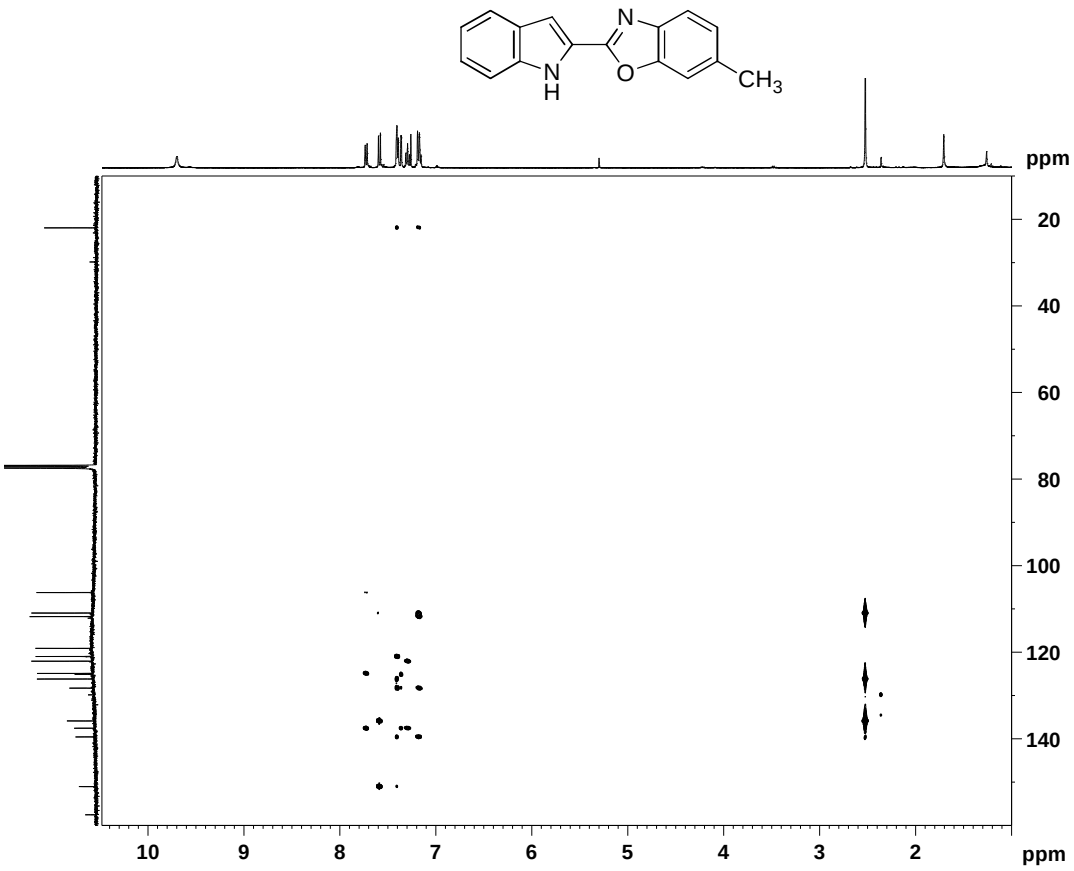
^{1}H-^{13}C HMBC NMR (CDCl3) δH/δC: 7.18/111.7, 7.18/128.1, 7.31/110.6, 7.31/122.0, 7.31/137.5, 7.37/119.6, 7.37/141.6, 7.41/120.9, 7.41/124.8, 7.41/128.1, 7.41/137.5, 7.61/124.9, 7.61/141.6, 7.73/106.5, 7.73/124.9, 7.73/137.5, 7.73/141.6, 7.73/150.6.

^{1}H-^{1}H NOESY NMR 2-(1*H*-indol-2-yl)benzo[*d*]oxazole ($CDCl_3$) **5a**.



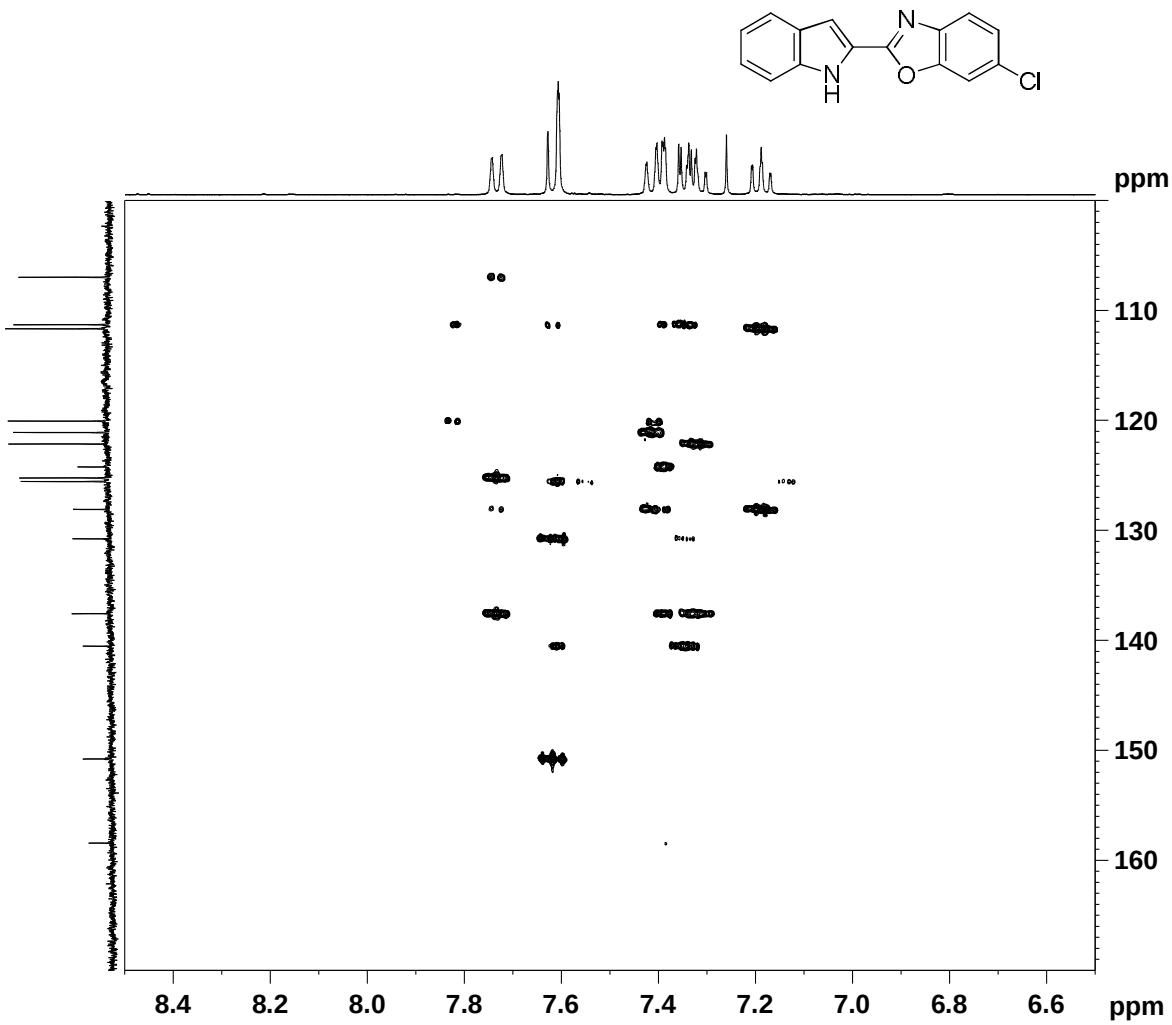
1H-1H NOESY NMR (CDCl3) δH/δH: 7.41/9.76.

^{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 (CDCl3) δH/δC: 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-(1*H*-indol-2-yl)benzo[*d*]oxazole ($CDCl_3$) **5c**.



^{1}H-^{13}C HMBC NMR (CDCl3) δH/δC: 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.