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Rearrangement of Quinoxalin-2-ones When Exposed to Enamines Generated in Situ from Ketones and Ammonium Acetate: Method for the Synthesis of 1-(Pyrrolyl)benzimidazolones

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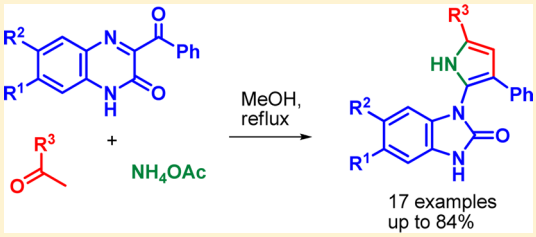
Supporting Information

ABSTRACT: The reaction of 3-benzoylquinoxalin-2(1*H*)-ones with enamines (generated in situ from ammonium acetate and the corresponding methylaryl(hetaryl)ketones) proceeds smoothly to give the corresponding substituted 1-(pyrrolyl)benzimidazolone derivatives in moderate yields through the novel rearrangement of 3-benzoylquinoxalin-2(1*H*)-ones involving a dual cleavage of the C3═N4 and C2-C3 bonds under mild conditions.



INTRODUCTION

3-Functionally substituted quinoxalinones (3-FSQs) are very important compounds due to their wide spectrum of biological activities.[1] Besides these, they are known as versatile building blocks[2] and reagents for transannulation processes[3] in organic synthesis. The direct connection of a functional group to the imine bond in quinoxalin-2(1*H*)-one with the intramolecular amide functionality endows this molecule with extra reactivity.[2a−d] 3-FSQs undergo a variety of annulation/ring-opening/ring-closure reactions with the contraction reactions in the presence of nucleophilic reagents because the combination of various functional groups provides a powerful thermodynamic driving force.[3d,4,5] In 2011, our group reported annulation/ring-opening/ring-closure reactions of 3-FSQs promoted by arylmethanediamines (*N,N*-1,3-binucleophilic reagents generated in situ from ammonium acetate and corresponding aldehyde) in which structurally different imidazole derivatives could be obtained in high yields (Scheme 1).[4c]

During our studies on the ring-opening/ring-closing reactions of 3-benzoylquinoxalin-2(1*H*)-ones (3-BQs),[3d,4a−e] we attempted to use enamines (generated in situ from ammonium acetate and corresponding methylaryl(hetaryl)ketones) as an alternative source of the *N,C*-1,3-binucleophilic reagents. Interestingly, we found that 1-[(3,5-diphenyl)pyrrol-2-yl)]benzimidazol-2(3*H*)-one **3a** was formed rather than the desired expected product(s) when the reaction of 3-benzoylquinoxalin-2(1*H*)-one **1a** with enamine as the *N,C*-1,3-binucleophilic reagent was conducted in refluxing MeOH as solvent. Apparently, as a result, there appeared a product with two newly formed heterocyclic systems. Herein, we report this novel enamine-mediated rearrangement of 3-BQs in MeOH, which proceeds through the ring-closure/ring-opening/ring-closure dual cleavage of the C3═N4 and C2-C3 bonds.

RESULTS AND DISCUSSION

We have examined in detail the reaction conditions for the 3-BQ **1a** and acetophenones **2b,d** with NH_4OAc in MeOH, and the results are shown in Table 1. When 3-BQ **1a** (1 equiv), 4-bromoacetophenone **2b** (1 or 2 equiv), and NH_4OAc (10 equiv) were used as reagents, product **3b** was afforded in low yields (entries 1−5) regardless of the reaction time (5, 7, or 14 h). The yield of **3b** was achieved with a maximum (81%) when the reaction was carried out with the use of reagents **1a**/**2b**/NH_4OAc in a ratio of 1:2:15 in boiling MeOH for 14 h (entry 6). The last portion of the 5 equiv of NH_4OAc (entry 6) was added to the reaction mixture after 8 h of boiling. Under similar conditions, the yield of **3d** was only 25% when 2-bromoacetophenone **2d** was used instead of 4-bromoacetophenone **2b** in the reaction considered (entry 7). Raising the ratio of NH_4OAc to 20 equiv and increasing the reaction time to 20 h afforded **3d** in a 62% yield (entry 9). In this case, the last two portions of 5 equiv of NH_4OAc in the reaction mixture were added after boiling for 8 and 14 h.

When regardless of the experimental conditions NH_4OH and $NH_2C(O)NH_2$ were used instead of NH_4OAc as suppliers of the nitrogen atom, the reaction did not occur at all, and the quinoxalin-2(1*H*)-one **1a** remained in the reaction mixture in unchanged form.

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Scheme 1. Our Previous Work and This Work

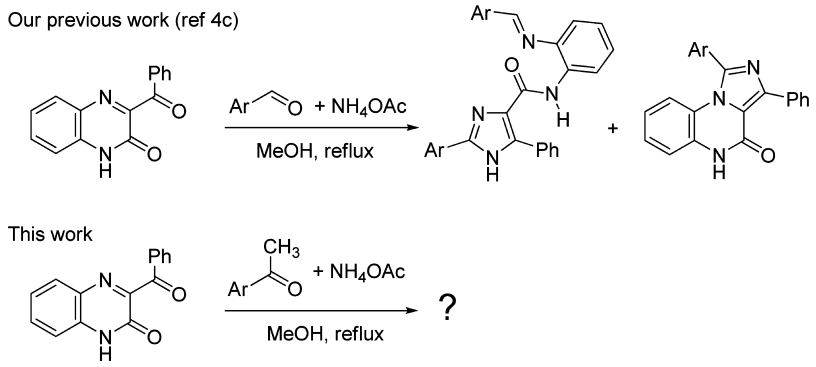
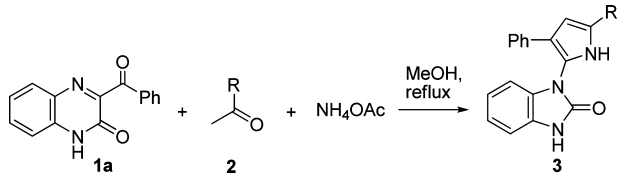


Table 1. Optimization of the Reaction Conditions



1a 2 3

entry	ketone **2**	ratio of **1**/**2**/NH_4OAc	time (h)	yield (%)
1	R = C_6H_4Br-4 (**2b**)	1/1/10	5	**3b** (24)
2	**2b**	1/1/10	7	**3b** (23)
3	**2b**	1/2/10	5	**3b** (43)
4	**2b**	1/2/10	7	**3b** (46)
5	**2b**	1/2/10	14	**3b** (46)
6	**2b**	1/2/15	14	**3b** (81)
7	R = C_6H_4Br-2 (**2d**)	1/2/15	14	**3d** (25)
8	**2d**	1/2/20	14	**3d** (47)
9	**2d**	1/2/20	20	**3d** (62)

With the optimized conditions in hand, we evaluated the generality of the reaction. A range of substrates with varying substituents were synthesized and investigated under standard conditions.

As can be seen from Table 2, the result does not depend on the nature of the substituent in acetophenones no matter whether it is a donor or an acceptor group. For acetophenones with electron-withdrawing halogen atoms at the *para*- and *metha*-positions of the benzene ring and even strongly a electron-withdrawing nitro group as well as an electron-donating methoxy group, the reaction proceeded smoothly and resulted in the desired products **3b**,**c**,**e**,**g**,**h** in high (entries 2, 5, and 8) and moderate (entries 3 and 7) yields. However, it should be pointed out that in the case of **2h** with a strongly electron-donating methoxy group, the regioisomeric product **4h** is formed along with the main product of the reaction **3h** as well, in a percentage ratio of 63:37 in favor of the former (entry 8). This is due to the occurrence of the competing direction of the processes with the benzoyl carbonyl group at the initial stage of the reaction (pathway II, in Scheme 3). When the electron-withdrawing halogen atoms (Cl or Br) were located at one *ortho*-position of the benzene ring, the desired products **3d** and **3f** were obtained in good yields (entries 4 and 6). This is apparently not due to the electronic effects of these groups but to the spacing effect, as in the cases of the reactions 2-, 3-, and 4-acetylpiridines. Regardless of the position of the nitrogen atom in the pyridine ring the yields of the desired products are higher (entries 9−11).

Table 2 reports the structural variations which are tolerated by this new multicomponent reaction (MCR). Acetophenones (electron-withdrawing and electron-donating substituents) and heteroaromatic ketones have given the corresponding products in good to excellent yields. The same is true for the different 3-BQs with various substituents (entries 12−15) involving functional CO_2H (entries 12 and 13) and 6,7-dimethyl (entry 15) groups with the exception of PhC(O) group (entry 14) in a benzene ring of the quinoxalin-2(1*H*)-one system.

The structures of compounds **3a**−**o** were established by a variety of 1D/2D NMR correlation experiments.[6,7] For example, benzimidazole (BI), phenyl (Ph), and R^3 fragments are revealed practically "directly" from $^1H-^1H$ COSY/TOCSY and $^1H-^{15}N/^1H-^{13}C$ HSQC/HMBC connectivities (see the SI). Then these moieties can be "linked" to pyrrole (P) ring by NMR heteronuclear connectivity's (e.g., for **3a** see Figure 1). Finally, key NOEs between Ph and H7-BI, Ph and H4-P, NH-P and H7-BI, and no NOE between NH-P and Ar protons in **3** (e.g., for **3a** see Figure 1) strongly support our conclusions about the regioisomeric structure of these compounds.

The structures of **3a** and **3k** were further confirmed by single-crystal X-ray analysis (Figure 2a,b).

Having developed this novel methodology for the diversification of the method and having displayed its general applicability we provided a benzimidazol-2-one and pyrrole heterocyclic cores in one concise straightforward step. Our next goal was to build the complexity of final products and gain access to more elaborated molecular scaffolds. Consequently, our studies were directed to an additional transformation capable of assembling a nitrogen-containing ring (Scheme 2). According to our synthetic plan (Scheme 2), the replacement of the commercially available acetophenones **2a**−**h** with 1,3-diacetylbenzene **5**, bearing an additional acetyl group, would allow the anticipated cascade process with two MCR modifications in one pot. The reaction would proceed with the formation of an unprecedented compound **7**, with two 1-(pyrrol-2-yl)benzimidazolone cores in the benzene ring as a major product which precipitated from the reaction mixture and compound **6** as a minor product with one 1-(pyrrol-2-yl)benzimidazolone core. It has been shown that acetophenone **6** can also be transformed into **7**. The reaction of acetophenone **6** with 3-BQ **1a** in the presence of NH_4OAc (the ratio of reagents is given in Scheme 2) proceeds with the formation of compound **7** with a 30% yield. For the complete transformation of compound **7** in the reaction mixture it was necessary to perform procedures of allocation and its transformation in into **7** three times (Scheme 2). The structure of this compound was unequivocally established in the same way as for the above compounds. First, the BI, Ph, and Ar moieties were revealed from NMR correlations. Then they were "bind" to the pyrrole ring according to the NMR heteronuclear connectivities.

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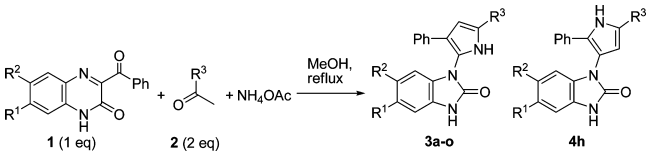
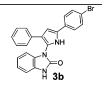
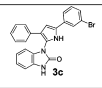
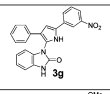
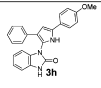
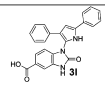
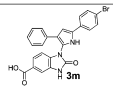
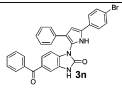
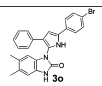
Table 2. Synthesis of 1-(Pyrrolyl)benzimidazolones



Entry	1	R^1/R^2	2	R^3	Time (h)/ NH_4OAc (eq)	Product	Yield (%)[a]
1	**1a**	H/H	**2a**	Ph	20/20	 **3a**	65
2	**1a**	H/H	**2b**	C_6H_4Br-4	14/15	 **3b**	81
3	**1a**	H/H	**2c**	C_6H_4Br-3	20/20	 **3c**	66
4	**1a**	H/H	**2d**	C_6H_4Br-2	20/20	 **3d**	62
5	**1a**	H/H	**2e**	C_6H_4Cl-4	14/15	 **3e**	79
6	**1a**	H/H	**2f**	C_6H_4Cl-2	20/20	 **3f**	63
7	**1a**	H/H	**2g**	$C_6H_4NO_2$-3	20/20	 **3g**	59
8	**1a**	H/H	**2h**	C_6H_4OMe-4	14/15	 **3h**	92[b,c]
9	**1a**	H/H	**2i**	Py-2	20/20	 **3i**	79
10	**1a**	H/H	**2j**	Py-3	20/20	 **3j**	73
11	**1a**	H/H	**2k**	Py-4	20/20	 **3k**	76
12	**1b**	CO_2H/H	**2a**	Ph	14/15	 **3l**	62
13	**1b**	CO_2H/H	**2b**	C_6H_4Br-4	14/15	 **3m**	84
14	**1c**	C(O)Ph/H	**2b**	C_6H_4Br-4	24/25	 **3n**	12[d]
15	**1d**	Me/Me	**2b**	C_6H_4Br-4	24/25	 **3o**	63

[a]Isolated yield. [b]Formed two isomers in a 63:37 percentage ratio (based on ^1H NMR). [c]Major isomer shown. [d]55% of **1c** was recovered.

Finally, stereospecific interresidual NOEs fully supported the regioisomeric structure of **7**.

Although the exact mechanism of this reaction is not very clear, a plausible reaction course is proposed on the basis of the known chemistry of ketones,[8] imines,[9] quinoxalines,[10] and enamines[11] in Scheme 3. The formation of the enamine intermediate **A** takes place at the initial stage of the reaction. Intermediate **A** reacts with the 3-BQ **1a** in two different ways (pathway I and pathway II) with the formation of an isomeric spiro[pyrrol-3,2′-quinoxalin]-3-one derivative **D** and spiro[pyrrol-2,2′-quinoxalin]-3-one derivative **F** through the intermediate **C** and **B**. The latter are formed by the initially attached enamine on the benzoyl carbonyl carbon atom (pathway I) and on the C3 atom of the quinoxalinone system (pathway II), correspondingly. Further, both pathway I and pathway II proceed by cascade reactions involving (a) the acid catalysis ring-closure of spiro-derivatives **D** and **F** with the formation of intermediates **E** and **G** with the aziridine ring system and (b) the acid catalysis ring-opening in intermediates **G** and **E** with the formation of the final 1-(pyrrol-2-yl)benzimidazolones **3** and 1-(pyrrol-3-yl)benzimidazolone derivative **4h**. Apparently, the formation of **4h** occurs due to the increase in the nucleophilic activity of the enamine **A** formed from acetophenone **2h** (1-(4-methoxyphenyl)ethanone). The strong electron-donating methoxy group reduces the regioselectivity of the process.

It can be assumed that as in cases of the quinoxalinone–benzimidazole rearrangement,[4d−f] the use of *N*-alkyl derivatives of quinoxalinone will provide the formation of *N*-alkylated derivatives of 1-(pyrrolyl)benzimidazolone under the studied conditions of rearrangement. However, the reaction of 3-benzoyl-1-octylquinoxalin-2-one **1e** with 4-bromoacetophenone **2b** and NH_4OAc proceeded with the formation of a spiro-derivative **8**-intermediate compound on the way to the product of rearrangement (Scheme 4). Changing the ratio of the reagents or the reaction time did not significantly influence the direction of the reaction. The product was identified as 5-(4-bromophenyl)-4′-octyl-2-phenyl-1′*H*-spiro[pyrrol-3,2′-quinoxalin]-3-one (**8**).

The structure of **8** was established by variety of NMR methods (some key correlations are shown in Figure 3). Thus, the whole structure of this compound was established practically "directly" upon NMR connectivity's. Reasonable agreement between calculated (GIAO DFT) and experimental $^{13}C/^{15}N$ chemical shifts (R^2 = 0.994, Supporting Information) strongly supports structure **8**.

Thus, there takes place the formation of only compound **8** but not the regioisomer 5-(4-bromophenyl)-4′-octyl-2-phenyl-1′*H*-spiro[pyrrol-3,2′-quinoxalin]-3′(4′*H*)-one (**8′**) (Scheme 4). In an attempt to carry out the rearrangement in boiling AcOH, compound **8** was converted to chalcone **9** with the extrusion of a nitrogen atom from the pyrrole ring. The analysis of crude products obtained from the reaction mixture after the evaporation of solvents by ^1H NMR spectroscopy reveals the presence of a spiro-compound **8** and a trace amount of unreacted starting compounds (**1e** and **2b**).

The structure of **9** was unequivocally established by combination of NMR methods. First, Q, Ph, and Ar moieties were established from NMR correlations (Supporting Information). The linkage to the acyclic fragment is almost direct from $^1H-^{13}C$ HMBC connectivities (Figure 4). The good correlation of GIAO DFT calculated with experimental $^{13}C/^{15}N$ chemical shifts (Supporting Information) additionally supports the structure of **9**.

The structure of **9** was further confirmed by single-crystal X-ray analysis (Figure 5).

The destruction of spiro-compounds takes place in the case of *N*-octyl derivative of spiro-quinoxalinone **8**, with the release of ammonia and the formation of the corresponding chalcone **9** under the rearrangement conditions (in boiling AcOH) (Scheme 5). It seems plausible that for the successful course of the rearrangement one of the necessary conditions is the presence of a hydrogen

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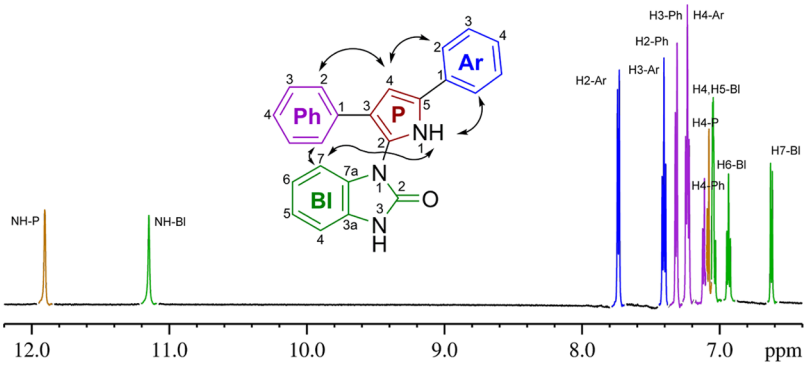
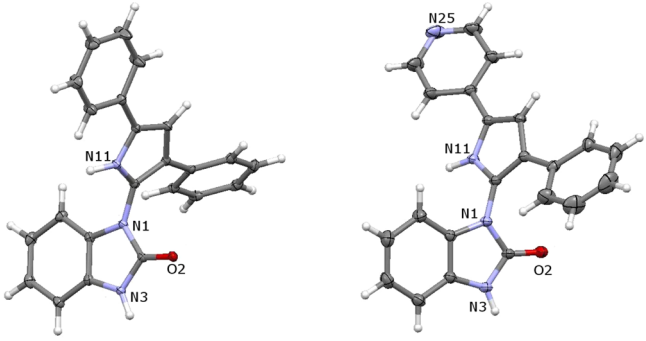


Figure 1. [1]H NMR spectra and structure of **3a** with key NOEs (black arrays).



(a) **(b)**

Figure 2. ORTEP plots of **3a** (a) and **3k** (b) with 30% probability displacement ellipsoids.

atom at the nitrogen atom. Taking this into account, it is possible to assume an alternative mechanism of the rearrangement in the new ring formation cascade reactions. The latter involve tautomerism (**8** to **L**) and subsequent ring opening (**L** to **M**) with the formation of the isocyanate derivative (**M**) and the ring closure (**M** to **3**) processes (Scheme 5). This type of ring closure is well precedented.[12]

It should be pointed out that the quinoxalin-2-one−quinoxalin-2-ol tautomerism like (**8** to **L**) when R = Alk is impossible ,and therefore, the isocyanate derivative responsible for the course of the rearrangement in the case of R = H cannot be formed (Scheme 5).

The formation of product **4h** can also be explained when the isocyanate mechanism is employed. This is similar to the formation of products **3**. But in this case, the isomeric spiro-quinoxalinone derivative **N** undergoes the rearrangement through the intermediates of **O** and **P** as shown in Scheme 6.

The formation of **9** from the spiro-quinoxalinone **8** can be presented with the AcOH as well, but in this case the pyrrole nitrogen atom of a molecule is released in the form of $AcNH_2$ (Scheme 7).

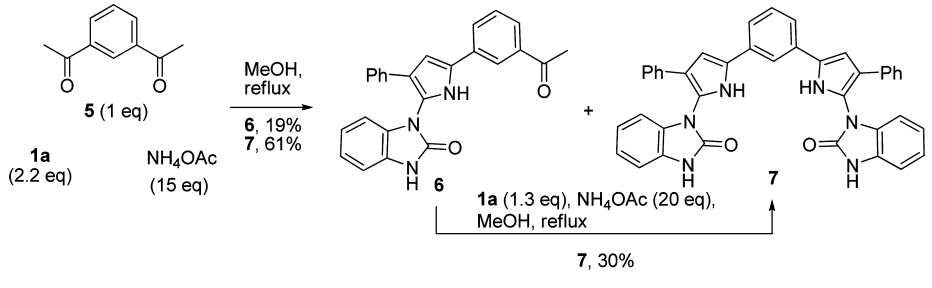
The formation of the benzimidazolone derivatives in the one-pot reactions of 3-BQs **1**, methylaryl(hetaryl)ketones, and ammonium acetate (NH_4OAc) in methanol at reflux conditions with good to excellent yields (Table 2, Scheme 2) makes it possible for us to propose a "new principle" that "any of the spiro-derivatives of 1,2,3,4-tetrahydroquinoxalin-3-one without any mobile hydrogen atom in their spiro-forming component are on their way to the benzimidazolone derivative with the spiro-forming component in position 1" (Scheme 8).

Benzimidazolones are important heterocycles that possess a variety of potential applications not only in medicinal aspects as antidiabetic,[13a] antiviral,[13b,c] and analgesic[13d] agents, p38 MAP kinase inhibitors,[13e] and progesterone receptor antagonists[13f] but also in the chemical fields as organic dyes[14a] and dye-sensitized solar cells.[14b] Many benzimidazolone derivatives have been successfully developed as clinical drugs such as antiemetic domperidone, antipsychotics pimozide and benperidol, analgesic bezitramide, and so on.[15] We fully expect that the methodology developed in this paper will have versatile applications in the practical syntheses of biologically important pharmaceutical and industrial interesting molecules with benzimidazolone and pyrrole moieties.

CONCLUSION

To summarize, we have developed an important three-component reaction of 3-benzoylquinoxalinones, various methylaryl(hetaryl)ketones, and ammonia. The method described in this paper allows the preparation of substituted 1-(pyrrolyl)benzimidazolone derivatives from easily available 3-benzoylquinoxalinone precursors under multicomponent reaction conditions in the presence of various methylaryl-(hetaryl)ketones and ammonia with good to excellent yields. Enamines could be generated in situ from ketones and ammonia and then smoothly react with 3-benzoylquinoxalinones

Scheme 2. Synthesis of Compounds with One and Two 1-(Pyrrol-2-yl)benzimidazolone Structural Blocks



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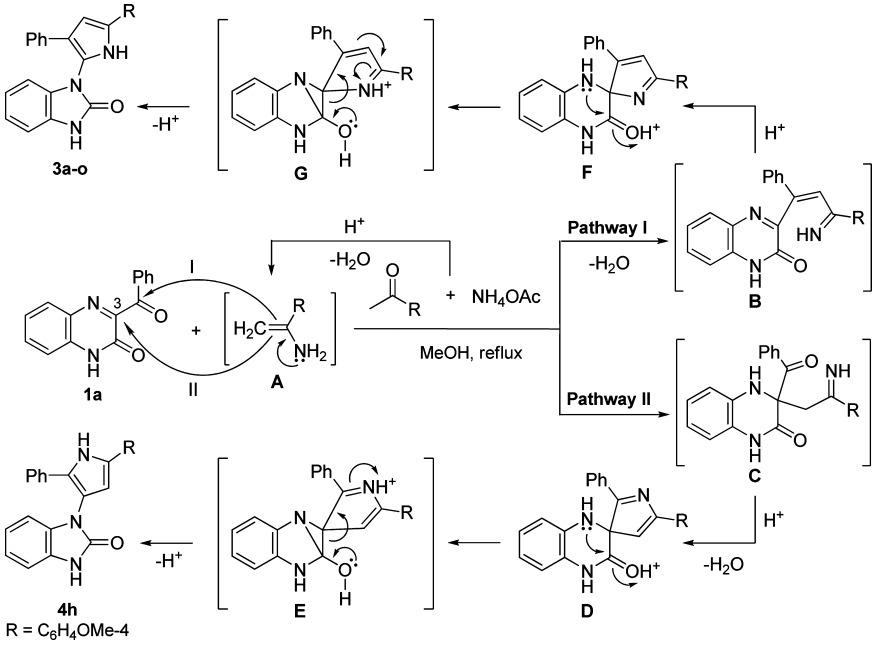
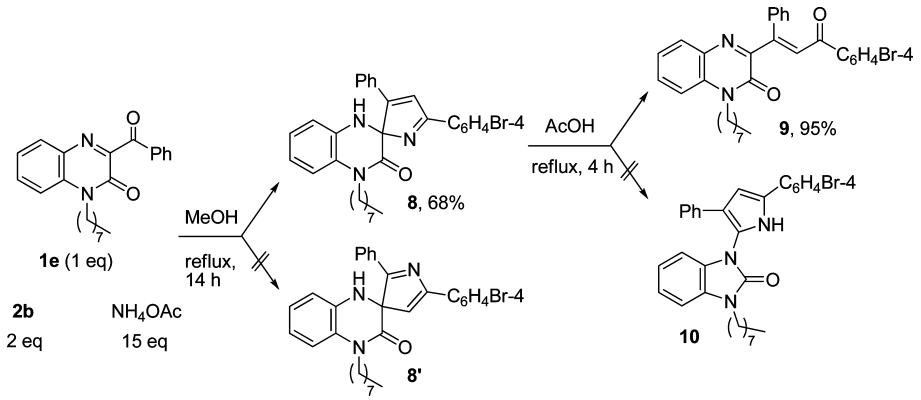
Scheme 3. Plausible Mechanism for the Formation of 1-(5-R-3-phenylpyrrol-2-yl)- (3a−o) and 1-(5-(4-Methoxyphenyl)-2-phenylpyrrol-3-yl)benzimidazol-2(3*H*)-ones (4h)



Scheme 4. Formation of 1′*H*-Spiro[pyrrol-3,2′-quinoxalin]-3-one 8 and Its Acid-Catalyzed Conversion to Chalcone 9



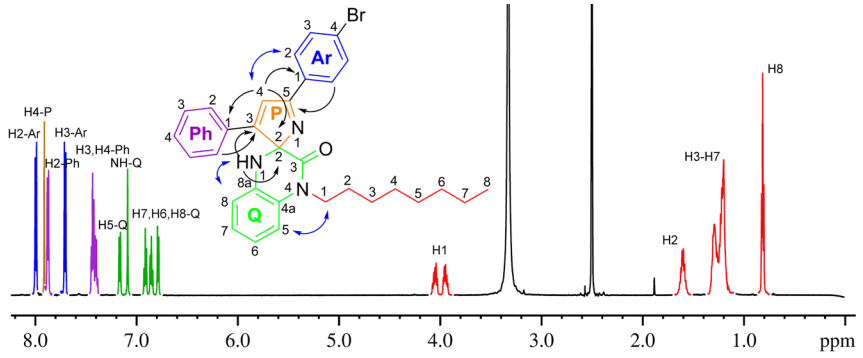


Figure 3. ^{1}H NMR spectra and structure of **8** with principal NMR correlations (^{1}H−^{13}C HMBC, black array; NOEs, blue array).

to produce 1-(pyrrolyl)benzimidazolone derivatives. Using this method, we were able to assemble a wide range of benzimidazolone derivatives. An important aspect of this protocol is that it can be adapted for the synthesis of a wide arrange of benzimidazolone derivatives, since various methylketones are commercially available and can easily be obtained through the acylation by the Friedel−Crafts reaction. The success of this methodology encourages future exploration of related reactions.

EXPERIMENTAL SECTION

General Methods. All NMR experiments were performed with a 600, 500, and 400 MHz (600, 500, and 400 MHz for ^{1}H NMR; 100 MHz for ^{13}C NMR; 60 MHz for ^{15}N NMR, respectively) spectrometers

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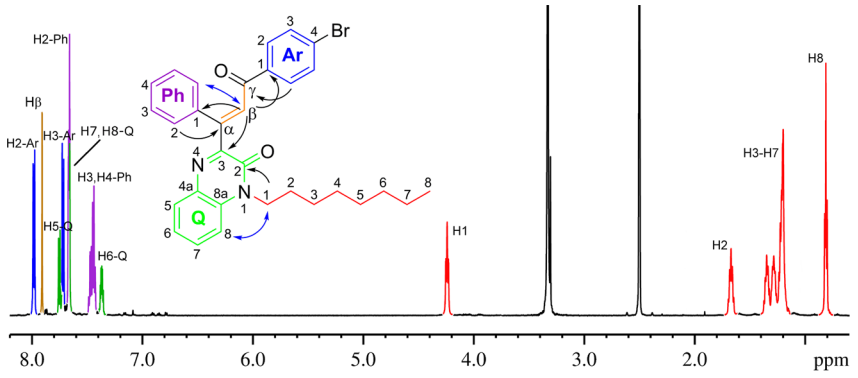


Figure 4. ^{1}H NMR spectra, structure of **9** with principal NMR correlations (^{1}H−^{13}C HMBC, black array; NOEs, blue array).

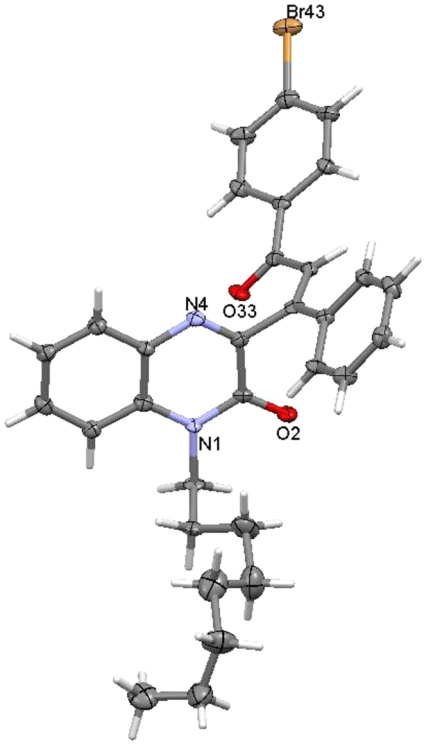
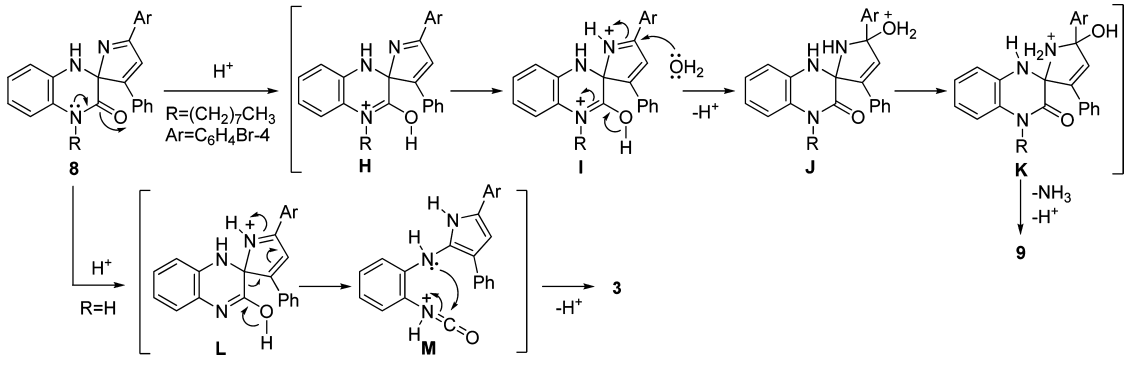


Figure 5. ORTEP plot of **9** with 30% probability displacement ellipsoids.

equipped with a 5 mm diameter gradient inverse broad band probehead and a pulsed gradient unit capable of producing magnetic field pulse gradients in the *z*-direction of 53.5 G·cm^{-1}. NMR experiments were carried out at 303 K. DPFGROE[7] and TOCSY spectra were obtained using a hermite-shaped pulse for selective excitation. Chemical shifts (δ in ppm) are referenced to the solvent DMSO-d_6 (δ = 2.49 ppm for ^{1}H and 39.5 ppm for ^{13}C NMR) to external CD_3NO_2 (380.2 ppm) for ^{15}N NMR spectra (conversion factor to NH_3: −380.2 ppm). The quantum chemical calculations were performed using a Gaussian 98w software package.[16] Full geometry optimizations have been carried out within the framework of the DFT (B3LYP) method using 6-31G(d) basis sets. Chemical shifts (CSs) were calculated by the GIAO method at the same level of theory.[17] All data were referred to TMS (^{13}C) and NH_3 (^{15}N) chemical shifts, which were calculated under the same conditions. Melting points were determined on a hot-stage apparatus. Infrared (IR) spectra were recorded on an FT-IR spectrometer. Silica gel column chromatography was performed using silica gel (0.060−0.200 mm, 40 Å). MALDI experiments (MALDI MS) were performed with a mass spectrometer equipped with a Nd:YAG laser. The mass spectra were measured in the positive-ion linear mode. Data were processed using the software FlexAnalysis 3.0 from Bruker Daltonics. The *p*-nitroaniline was used as the matrix. The dried-droplet spotting technique (matrix, analyte) was applied. For each sample, 0.5 μL of the analyte solution in dimethylformamide was spotted onto a target plate with matrix solution 10 mg/mL in acetonitrile MTP AnchorChip. HRMS spectra were obtained using the MALDI method (analyzer type: TOF-TOF reflectron).

General Procedure for the Synthesis of 1-(3-Phenyl-5-aryl(hetaryl)pyrrol-2-yl)benzimidazol-2(3*H*)-ones 3a−g,i−k and 3h/4h. The mixture of 3-benzoylquinoxalin-2(1*H*)-one **1a** (0.25 g, 1 mmol, 1 equiv), acetophenones **2a−h** (2 equiv) or acetylpyridines **2i−k** (2 equiv), and NH_4OAc (10 equiv) in MeOH (20 mL) was stirred under reflux for 8 h. Additional portions of NH_4OAc (5 equiv) were added either at one time (Table 2, entries 2, 5, 8, 12, and 13) or in two motions (2 × 5 equiv) over 8 and 14 h (Table 2, entries 1, 3, 4, 6, 7, 9−11). Stirring and reflux were continued. The overall reaction time was 14 h (in the first case) and 20 h (in the second case). The solvent was evaporated under reduced pressure on a third. The precipitate was collected by filtration, washed with ether (2 × 5 mL), and dried in air to

Scheme 5. Reasonable Mechanisms for the Formation of (*E*)-3-(3-(4-Bromophenyl)-3-oxo-1-phenylprop-1-enyl)-1-octylquinoxalin-2(1*H*)-one 9 and 1-(Pyrrol-2-yl)benzimidazolones 3



DOI: 10.1021/jo502135d
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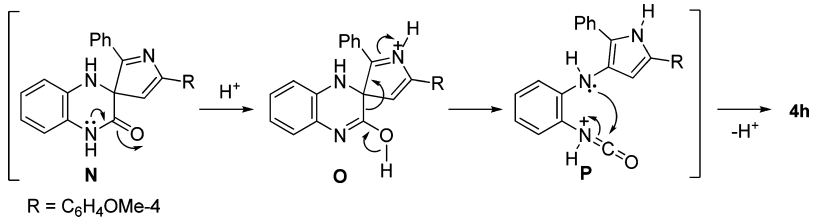
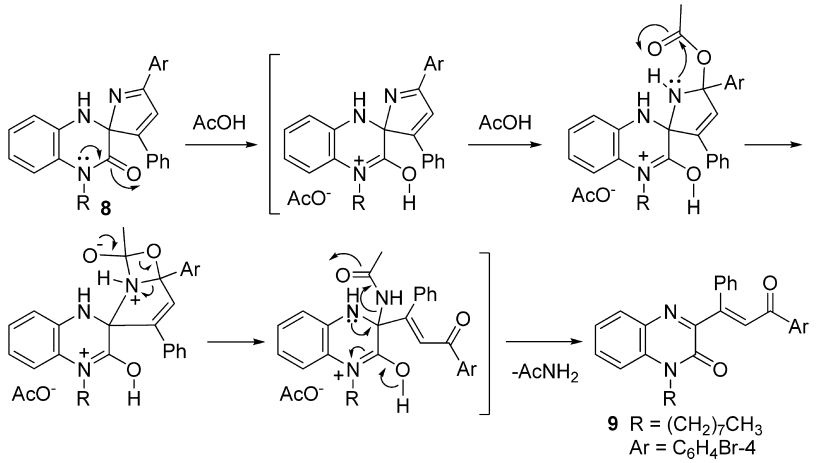
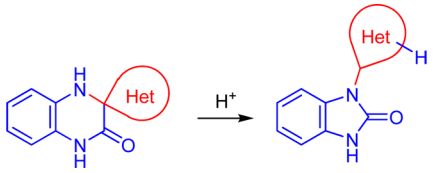
Scheme 6. Reasonable Mechanisms for the Formation of 1-[5-(4-Methoxyphenyl)-2-phenyl-pyrrol-3-yl]benzimidazol-2(3*H*)-one 4h through the Isocyanate Mechanism



Scheme 7. Plausible Mechanism for the Formation of 9

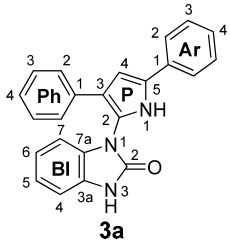


Scheme 8. Schematic Presentation of the Spiro-1,2,3,4-tetrahydroquinoxalin-3-one → Benzimidazolone Rearrangement



give an analytical sample of compounds **3a–g,i–k** and a mixture of isomers **3h/4h**.

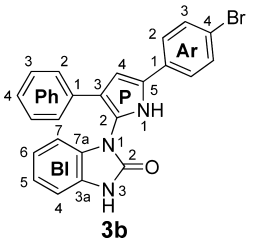
*1-[(3,5-Diphenyl)pyrrol-2-yl)]benzimidazol-2(3H)-one (**3a**).*



3a

Yield: 0.228 g (65%), white solid, mp 256–258 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.62 (d, J = 8.1 Hz, 1H, H7-BI), 6.93 (dd, J = 8.1, 7.6 Hz, 1H, H6-BI), 7.08 (d, J = 7.6 Hz, 1H, H4-BI), 7.02–7.06 (m, 2H, H5-BI, H4-P), 7.11 (dd, J = 7.6, 7.1 Hz, 1H, H4-Ph), 7.20–7.26 (m, 3H, H3,5-Ph, H4-Ar), 7.31 (d, J = 7.1 Hz, 2H, H2,6-Ph), 7.40 (dd, J = 8.1, 7.6 Hz, 2H, H3,5-Ar), 7.73 (d, J = 7.1 Hz, 2H, H2,6-Ar), 11.15 (br s, 1H, NH-BI), 11.90 (d, J = 1.4 Hz, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.0 (C2-BI), 134.2 (C1-Ph), 131.9 (C1-Ar), 131.4 (C7a-BI), 130.3 (C2-P), 128.7 (C3,5-Ar), 128.5 (C3,5-Ph, C3a-BI), 126.3 (C4-Ar), 125.7 (C4-Ph), 125.6 (C2,6-Ph), 123.5 (C2,6-Ar), 121.9 (C5-BI), 121.0 (C6-BI), 120.9 (C4-P), 118.1 (C5-P), 109.1 (C4-BI), 108.4 (C7-BI), 104.7 (C3-P). ^{15}N NMR (60 MHz, DMSO-d_6): δ 118.6 (N3-BI), 123.1 (N1-BI), 155.0 (N1-P). IR (Nujol): ν 3291, 3062, 1696, 1259, 753, 734, 700 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 352. HRMS (MALDI) m/z: [M]$^+$ calcd for $C_{23}H_{17}N_3O$ 351.1366, found 351.1341. Anal. Calcd for $C_{23}H_{17}N_3O$: C, 78.61; H, 4.88; N, 11.96. Found: C, 78.47; H, 4.80; N, 11.76.

*1-[5-(4-Bromophenyl)-3-phenylpyrrol-2-yl]benzimidazol-2(3H)-one (**3b**).*



Yield: 0.348 g (81%), white solid, mp 317–319 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.62 (d, J = 8.1 Hz, 1H, H7-BI), 6.93 (dd, J = 8.1, 7.6 Hz, 1H, H6-BI), 7.04 (dd, J = 8.1, 7.6 Hz, 1H, H5-BI), 7.08 (d, J = 7.6 Hz, 1H, H4-BI), 7.10 (d, J = 2.4 Hz, 1H, H4-P), 7.11 (dd, J = 7.6, 7.6 Hz, 1H, H4-Ph), 7.23 (dd, J = 7.6, 7.6 Hz, 2H, H3,5-Ph), 7.31 (d, J = 7.6 Hz, 2H, H2,6-Ph), 7.59 (d, J = 8.6 Hz, 2H, H3,5-Ar), 7.69 (d, J = 8.6 Hz, 2H, H2,6-Ar), 11.16 (s, 1H, NH-BI), 11.99 (s, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.9 (C2-BI), 134.00 (C1-Ph), 131.6 (C3,5-Ar), 131.3 (C7a-BI), 131.1 (C1-Ar), 129.1 (C2-P), 128.5 (C3,5-Ph), 128.4 (C3a-BI), 125.8 (C4-Ph), 125.6 (C2,6-Ph), 125.5 (C2,6-Ar), 121.9 (C5-BI), 121.1 (C6-BI, C4-P), 118.96 (C4-Ar), 118.53 (C5-P), 109.2 (C4-BI), 108.4 (C7-BI), 105.4 (C3-P). ^{15}N NMR (60 MHz, DMSO-d_6): δ 118.6 (N3-BI), 122.9 (N1-BI), 155.2 (N1-P). IR (Nujol): ν 3291, 3062, 1696, 1374, 753, 734, 700 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 430. HRMS (MALDI) m/z: [M]$^+$ calcd for $C_{23}H_{16}BrN_3O$ 429.0471, found 429.0438. Anal. Calcd for $C_{23}H_{16}BrN_3O$: C, 64.20; H, 3.75; N, 9.77. Found: C, 64.08; H, 3.79; N, 9.86.

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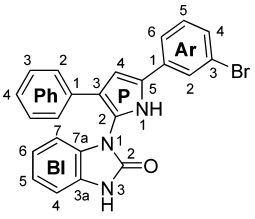
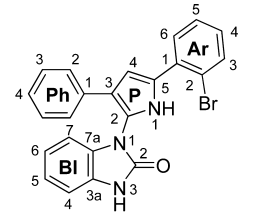
*1-[5-(3-Bromophenyl)-3-phenylpyrrol-2-yl]benzimidazol-2(3H)-one (**3c**).*



3c

Yield: 0.284 g (66%), white solid, mp 244−245 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.63 (d, J = 8.1 Hz, 1H, H7-BI), 6.94 (ddd, J = 8.1, 7.6, 1.0 Hz, 1H, H6-BI), 7.05 (ddd, J = 7.6, 7.6, 1.0 Hz, 1H, H5-BI), 7.09 (d, J = 7.6 Hz, 1H, H4-BI), 7.11 (br dd, J = 7.6, 7.1 Hz, 1H, H4-Ph), 7.18 (d, J = 2.4 Hz, 1H, H4-P), 7.24 (dd, J = 8.1, 7.6 Hz, 2H, H3,5-Ph), 7.32 (dd, J = 8.1, 1.4 Hz, 2H, H2,6-Ph), 7.36 (dd, J = 8.1, 7.6 Hz, 1H, H5-Ar), 7.40 (ddd, J = 8.1, 1.7, 1.4 Hz, 1H, H4-Ar), 7.75 (br d, J = 7.6 Hz, 1H, H6-Ar), 7.97 (dd, J = 1.7, 1.4 Hz, 1H, H2-Ar), 11.17 (br s, 1H, NH-BI), 12.03 (br s, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.9 (C2-BI), 134.2 (C1-Ar), 133.9 (C1-Ph), 131.3 (C7a-BI), 130.9 (C5-Ar), 128.7 (C4-Ar), 128.6 (C2-P), 128.5 (C3,5-Ph), 128.5 (C3a-BI), 125.9 (C2-Ar, C4-Ph), 125.6 (C2,6-Ph), 122.4 (C3-Ar, C6-Ar), 121.9 (C5-BI), 121.1 (C6-BI, C4-P), 118.8 (C5-P), 109.2 (C4-BI), 108.4 (C7-BI), 105.9 (C3-P). ^{15}N NMR (60 MHz, DMSO-d_6): δ 118.7 (N3), 122.8 (N1), 155.3 (N1-P). IR (Nujol): ν 3250, 3138, 3057, 1689, 1610, 1588, 1566, 1258, 756, 740 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 430. HRMS (MALDI) m/z: [M]$^+$ calcd for $C_{23}H_{16}BrN_3O$ 429.0471, found 429.0466. Anal. Calcd for $C_{23}H_{16}BrN_3O$: C, 64.20; H, 3.75; N, 9.77. Found: C, 64.14; H, 3.68; N, 9.67.

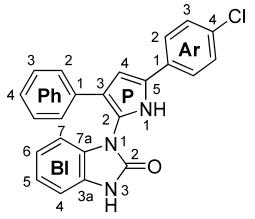
*1-[5-(2-Bromophenyl)-3-phenyl-pyrrol-2-yl]benzimidazol-2(3H)-one (**3d**).*



3d

Yield: 0.267 g (62%), white solid, mp 198−201 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.66 (d, J = 7.6 Hz, 1H, H7-BI), 6.95 (ddd, J = 7.6, 7.6, 1.4 Hz, 1H, H6-BI), 6.98 (d, J = 2.9 Hz, 1H, H4-P), 7.04 (dd, J = 7.6, 7.1 Hz, 1H, H5-BI), 7.08 (d, J = 7.1 Hz, 1H, H4-BI), 7.11 (dd, J = 7.1, 7.1 Hz, 1H, H4-Ph), 7.22−7.27 (m, 3H, H4-Ar, H3,5-Ph), 7.30 (dd, J = 8.6, 1.4 Hz, 2H, H2,6-Ph), 7.45 (ddd, J = 7.6, 7.6, 1.0 Hz, 1H, H5-Ar), 7.59 (dd, J = 7.6, 1.7 Hz, 1H, H6-Ar), 7.74 (dd, J = 8.1, 1.0 Hz, 1H, H3-Ar), 11.13 (s, 1H, NH-BI), 11.86 (br d, J = 2.4 Hz, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.9 (C2-BI), 134.1 (C1-Ph), 133.7 (C3-Ar), 132.7 (C1-Ar), 131.5 (C7a-BI), 130.2 (C6-Ar), 128.6 (C4-Ar), 128.5 (C3,5-Ph), 128.44 (C3a-BI), 128.39 (C2-P), 127.8 (C5-Ar), 125.76 (C4-Ph), 125.70 (C2,6-Ph), 121.8 (C5-BI), 121.0 (C6-BI), 120.6 (C2-Ar), 120.0 (C4-P), 118.1 (C5-P), 109.1 (C4-BI), 108.7 (C3-P), 108.4 (C7). IR (Nujol): ν 3444, 3214, 3057, 1681, 1257, 757, 705 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 430. HRMS (MALDI) m/z: [M]$^+$ calcd for $C_{23}H_{16}BrN_3O$ 429.0471, found 429.0499. Anal. Calcd for $C_{23}H_{16}BrN_3O$: C, 64.20; H, 3.75; N, 9.77. Found: C, 64.37; H, 3.62; N, 9.92.

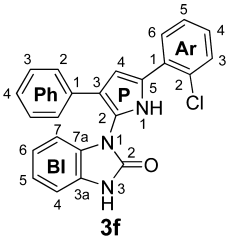
*1-[5-(4-Chlorophenyl)-3-phenylpyrrol-2-yl]benzimidazol-2(3H)-one (**3e**).*



3e

Yield: 0.305 g (79%), white solid, mp 298−300 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.62 (d, J = 8.1 Hz, 1H, H7-BI), 6.93 (dd, J = 8.1, 7.6 Hz, 1H, H6-BI), 7.04 (dd, J = 7.6, 7.6 Hz, 1H, H5-BI), 7.08 (d, J = 7.6 Hz, 1H, H4-BI), 7.09 (d, J = 2.9 Hz, 1H, H4-P), 7.11 (dd, J = 7.6, 7.6 Hz, 1H, H4-Ph), 7.24 (dd, J = 8.1, 7.6 Hz, 2H, H3,5-Ph), 7.31 (d, J = 8.1 Hz, 2H, H2,6-Ph), 7.46 (d, J = 8.6 Hz, 2H, H3,5-Ar), 7.75 (d, J = 8.6 Hz, 2H, H2,6-Ar), 11.16 (br s, 1H, NH-BI), 11.99 (br s, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.0 (C2-BI), 134.0 (C1-Ph), 131.3 (C7a-BI), 130.8 (C1-Ar), 130.5 (C4-Ar), 129.1 (C2-P), 128.7 (C3,5-Ar), 128.5 (C3,5-Ph), 128.4 (C3a-BI), 125.8 (C4-Ph), 125.6 (C2,6-Ph), 125.2 (C2,6-Ar), 121.9 (C5-BI), 121.07 (C6-BI), 121.04 (C4-P), 118.5 (C5-P), 109.2 (C4-BI), 108.4 (C7-BI), 105.4 (C3-P). ^{15}N NMR (60 MHz, DMSO-d_6): δ 118.6 (N3-BI), 122.9 (N1-BI), 155.2 (N1-P). IR (Nujol): ν 3298, 3192, 3067, 1696, 1257, 758, 740 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 386. HRMS (MALDI) m/z: [M]$^+$ calcd for $C_{23}H_{16}ClN_3O$ 385.0976, found 385.0995. Anal. Calcd for $C_{23}H_{16}ClN_3O$: C, 71.59; H, 4.18; N, 10.89. Found: C, 71.38; H, 4.10; N, 11.05%.

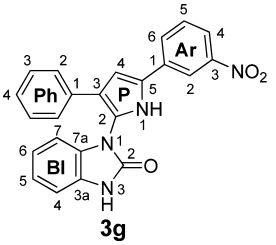
*1-[5-(2-Chlorophenyl)-3-phenylpyrrol-2-yl]benzimidazol-2(3H)-one (**3f**).*



3f

Yield: 0.243 g (63%), white powder, mp 215−216 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.64 (d, J = 7.6 Hz, 1H, H7-BI), 6.95 (ddd, J = 7.6, 7.3, 1.0 Hz, 1H, H6-BI), 7.03 (d, J = 2.9 Hz, 1H, H4-P), 7.04 (ddd, J = 7.6, 7.3, 1.0, 1H, H5-BI), 7.08 (d, J = 7.3 Hz, 1H, H4-BI), 7.11 (dd, J = 7.1, 7.1 Hz, 1H, H4-Ph), 7.23 (dd, J = 8.1, 7.1 Hz, 2H, H3,5-Ph), 7.30 (d, J = 8.1 Hz, 2H, H2,6-Ph), 7.31 (ddd, J = 7.6, 7.3, 1.0 Hz, 1H, H4-Ar), 7.41 (ddd, J = 8.1, 7.6, 1.4 Hz, 1H, H5-Ar), 7.56 (dd, J = 8.1, 1.4 Hz, 1H, H6-Ar), 7.65 (dd, J = Hz, 1H, H3-Ar), 11.13 (s, 1H, NH-BI), 11.89 (br s, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.9 (C2-BI), 134.0 (C1-Ph), 131.4 (C7a-BI), 130.5 (C3-Ar), 130.5 (C1-Ar), 130.1 (C2-Ar), 129.4 (C6-Ar), 128.5 (C3,5-Ph), 128.4 (C3a-BI), 128.1 (C4-Ar), 127.3 (C5-Ar), 126.9 (C2-P), 125.8 (C4-Ph), 125.7 (C2,6-Ph), 121.8 (C5-BI), 121.0 (C6-BI), 120.3 (C4-P), 118.4 (C5-P), 109.1 (C4-BI), 109.0 (C3-P), 108.4 (C7-BI). ^{15}N NMR (60 MHz, DMSO-d_6): δ 119.0 (N3-BI), 122.6 (N1-BI), 159.8 (N1-P). IR (Nujol): ν 3434, 3188, 3061, 1699, 1500, 754, 703 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 386. HRMS (MALDI) m/z [M]$^+$ calcd for $C_{23}H_{16}ClN_3O$ 385.0976, found 385.0984. Anal. Calcd for $C_{23}H_{16}ClN_3O$: C, 71.59; H, 4.18; N, 10.89. Found: C, 71.78; H, 4.23; N, 10.75.

*1-[5-(3-Nitrophenyl)-3-phenylpyrrol-2-yl)]benzimidazol-2(3H)-one (**3g**).*



3g

Yield: 0.234 g (59%), yellow solid, mp 261−262 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.64 (d, J = 7.8 Hz, 1H, H7-BI), 6.94 (ddd, J = 7.7, 7.7, 1.3 Hz, 1H, H6-BI), 7.05 (ddd, J = 7.6, 7.6, 1.1 Hz, 1H, H5-BI), 7.10 (br dd, J = 7.6, 1.1 Hz, 1H, H4-BI), 7.14 (dd, J = 7.3, 7.3 Hz, 1H, H4-Ph), 7.25 (dd, J = 7.6, 7.3 Hz, 2H, H3,5-Ph), 7.32−7.36 (m, 1H, 3H, H2,6-Ph, H4-P), 7.70 (dd, J = 8.1, 8.0 Hz, 1H, H5-Ar), 8.06 (dd, J = 8.0, 2.2 Hz, 1H, H4-Ar), 8.60 (br d, J = 8.1 Hz, 1H, H6-Ar), 7.84 (dd, J = 2.2, 2.2 Hz, 1H, H2-Ar), 11.20 (br s, 1H, NH-BI), 12.31 (d, J = 1.8 Hz, 1H, HN-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.9 (C2-BI), 148.6 (C3-Ar), 133.8 (C1-Ph), 133.5 (C1-Ar), 131.2 (C7a-BI), 130.3 (C5-Ar),

DOI: 10.1021/jo502135d
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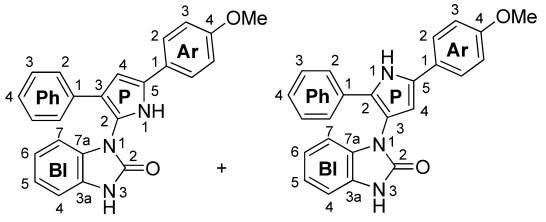
129.7 (C6-Ar), 128.5 (C3,5-Ph), 128.5 (C3a-BI), 128.0 (C2-P), 125.99 (C4-Ph), 125.69 (C2,6-Ph), 121.99 (C5-BI), 121.32 (C4-P), 121.12 (C6-BI), 120.5 (C4-Ar), 119.4 (C5-P), 117.5 (C2-Ar), 109.2 (C4-BI), 108.4 (C7-BI), 106.8 (C3-P). ^{15}N NMR (60 MHz, DMSO-d_6): δ 118.9 (N3-BI), 123.0 (N1-BI), 156.1 (N1-P), 371.5 (NO_2). IR (KBr): ν 3251, 3066, 1688, 1535, 1516, 1350, 737, 700 cm^{-1}. MALDI MS m/z: $(M + H)^+$ 397. HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{23}H_{16}N_4O_3$ 396.1217, found 396.1215. Anal. Calcd for $C_{23}H_{16}N_4O_3$: C, 69.69; H, 4.07; N, 14.13. Found: C, 69.78; H, 4.03; N, 14.09.

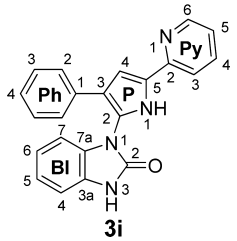
*1-[5-(4-Methoxyphenyl)-3-phenylpyrrol-2-yl]benzimidazol-2(3H)-one (**3h**) and 1-[5-(4-methoxyphenyl)-2-phenylpyrrol-3-yl]-benzimidazol-2(3H)-one (**4h**).*



3h **4h***

Yield: 0.351 g (92%), off-white powder, mp 220−222 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 3.79 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3*), 6.58 (d, J = 7.7 Hz, 1H, H7-BI*), 6.62 (d, J = 7.8 Hz, 1H, H7-BI), 6.90 (d, J = 3.0 Hz, 1H, H4-P), 6.91 (d, J = 3.0 Hz, 1H, H4-P*), 6.92 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H, H6-BI*), 6.93 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H, H6-BI), 6.98 (d, J = 8.9 Hz, 2H, H3,5-Ar), 6.99−7.12 (m, 8H, H5-BI, H5-BI*, H4-BI, H4-BI*, H4-Ph, H4-Ph*, H3,5-Ar*), 7.21−7.26 (m, 4H, H3,5-Ph, H3,5-Ph*), 7.29−7.32 (m, 4H, H2,6-Ph, H2,6-Ph*), 7.66 (d, J = 8.9 Hz, 2H, H2,6-Ar), 7.68−7.10 (m, 2H, H2,6-Ar*), 11.08 (s, 1H, NH-BI*), 11.13 (s, 1H, NH-BI), 11.51 (br s, 1H, NH-P*), 11.55 (br d, J = 2.8 Hz, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.9 (C4-Ar), 155.26 (C4-Ar*), 154.09 (C2-BI*), 154.06 (C2-BI), 134.41 (C1-Ph*), 134.32 (C1-Ph), 131.69 (C7a-BI*), 131.50 (C7a-BI), 130.34 (C2-P), 128.49 (C3a-BI*), 128.44 (C3a-BI, C3,5-Ph, C2,6-Ph*), 127.46 (C3,5-Ph*), 127.15 (5-P*), 126.18 (C2,6-Ar*), 125.66 (C4-Ph), 125.62 (C4-Ph*), 125.58 (C2,6-Ph), 124.91 (C2,6-Ar), 124.74 (C1-Ar), 121.80 (C5-BI), 121.64 (C5-BI*), 121.01 (C6-BI), 120.90 (C6-BI*), 120.63 (C4-P), 120.30 (C1-Ar*), 120.10 (C2-P*), 117.43 (C3-P*), 117.24 (C5-P), 114.20 (C3,5-Ar), 111.79 (C3,5-Ar*), 109.09 (C4-BI), 108.99 (C4-BI*), 108.40 (C7-BI), 108.36 (C7-BI*), 107.54 (C4-P*), 103.37 (C3-P), 55.35 (OCH_3*), 55.07 (OCH_3). ^{15}N NMR (60 MHz, DMSO-d_6): δ 118.8 (N3-BI, N3-BI*), 123.2 (N1-BI, N1-BI*), 154.4 (N1-P), 157.1 (N1-P*). IR (KBr): ν 1700, 1502, 1250, 1178, 1030, 758, 696 cm^{-1}. MALDI MS m/z: $(M + H)^+$ 382. HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{24}H_{19}N_3O_2$ 381.1472, found 381.1444. Anal. Calcd for $C_{24}H_{19}N_3O_2$: C, 75.57; H, 5.02; N, 11.02. Found: C, 75.28; H, 4.91; N, 11.18.

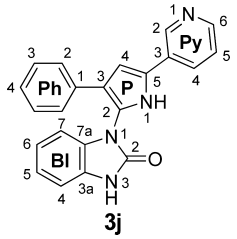
*1-[3-Phenyl-5-(pyridin-2-yl)-pyrrol-2-yl]benzimidazol-2(3H)-one (**3i**).*



3i

Yield: 0.278 g (79%), beige powder, mp 291−293 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.58 (d, J = 8.1 Hz, 1H, H7-BI), 6.91 (ddd, J = 8.1, 7.1, 1.0 Hz, 1H, H6-BI), 7.02 (dd, J = 7.6, 7.1 Hz, 1H, H5-BI), 7.06 (d, J = 7.6 Hz, 1H, H4-BI), 7.12 (dd, J = 7.6, 7.6 Hz, 1H, H4-Ph), 7.21 (ddd, J = 5.6, 4.8, 1.9 Hz, 1H, H5-Py), 7.24 (dd, J = 7.6, 7.1 Hz, 2H, H3,5-Ph), 7.27 (d, J = 2.9 Hz, 1H, H4-P), 7.33 (d, J = 7.1 Hz, 2H, H2,6-Ph), 7.79−7.84 (m, 2H, H4-Py, H3-Py), 8.53 (d, J = 4.8 Hz, 1H, H6-Py), 11.08 (s, 1H, NH-BI), 12.14 (br s, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.1 (C2-BI), 149.96 (C2-Py), 149.01 (C6-Py), 136.8 (C4-Py), 134.15 (C1-Ph), 131.5 (C7a-BI), 130.3 (C2-P), 128.6 (C3a-BI), 128.5 (C3,5-Ph), 125.84 (C4-Ph), 125.65 (C2,6-Ph), 121.69 (C5-BI), 121.13 (C5-Py), 121.10 (C4-P), 120.9 (C6-BI), 119.4 (C5-P), 118.0 (C3-Py), 109.0 (C4-BI), 108.3 (C7-BI), 106.7 (C3-P). ^{15}N NMR (60 MHz, DMSO-d_6): δ 118.9 (N3-BI), 122.6 (N1-BI), 156.4 (N1-P), 299.7 (N1-Py). IR (Nujol): ν 1694, 1591, 1254, 755, 695 cm^{-1}. MALDI MS m/z: $(M + H)^+$ 353. HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{22}H_{16}N_4O$ 352.1319, found 352.1257. Anal. Calcd for $C_{22}H_{16}N_4O$: C, 74.98; H, 4.58; N, 15.90. Found: C, 75.13; H, 4.51; N, 15.96.

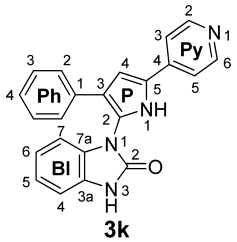
*1-[3-Phenyl-5-(pyridin-3-yl)pyrrol-2-yl]benzimidazol-2(3H)-one (**3j**).*



3j

Yield: 0.257 g (73%), off-white powder, mp 312−314 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.64 (d, J = 7.6 Hz, 1H, H7-BI), 6.94 (dd, J = 7.6, 7.6 Hz, 1H, H6-BI), 7.05 (dd, J = 7.6, 7.6 Hz, 1H, H5-BI), 7.09 (d, J = 7.6 Hz, 1H, H4-BI), 7.13 (ddd, J = 7.6, 7.1, 1.0 Hz, 1H, H4-Ph), 7.21 (d, J = 2.9 Hz, 1H, H4-P), 7.25 (dd, J = 8.6, 7.1 Hz, 2H, H3,5-Ph), 7.32 (d, J = 8.6 Hz, 2H, H2,6-Ph), 7.42 (dd, J = 8.1, 4.8 Hz, 1H, H5-Py), 8.08 (d, J = 8.1 Hz, 1H, H4-Py), 8.42 (d, J = 4.8 Hz, 1H, H6-Py), 8.99 (br s, 1H, H2-Py), 11.19 (s, 1H, NH-BI), 12.10 (br s, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.0 (C2-BI), 147.1 (C6-Py), 145.0 (C2-Py), 133.9 (C1-Ph), 131.3 (C7a-BI), 130.5 (C4-Py), 128.54 (C3,5-Ph), 128.47 (C3a-BI), 127.8 (C3-Py), 127.2 (C2-P), 126.0 (C4-Ph), 125.7 (C2,6-Ph), 123.8 (C5-Py), 122.0 (C5-BI), 121.2 (C4-P), 121.1 (C6-BI), 119.0 (C5-P), 109.2 (C4-BI), 108.5 (C7-BI), 105.9 (C3-P). ^{15}N NMR (60 MHz, DMSO-d_6): δ 118.9 (N3-BI), 122.8 (N1-BI), 155.2 (N1-P), 317.2 (N1-Py). IR (Nujol): ν 1687, 1608, 1570, 1503, 1260, 742, 696 cm^{-1}. MALDI MS m/z: $(M + H)^+$ 353. HRMS (MALDI) m/z: $[M + H]^+$ calcd for $C_{22}H_{16}N_4O$ 353.1397, found 353.1433. Anal. Calcd for $C_{22}H_{16}N_4O$: C, 74.98; H, 4.58; N, 15.90. Found: C, 75.06; H, 4.56; N, 15.85.

*1-[3-Phenyl-5-(pyridin-4-yl)-pyrrol-2-yl]benzimidazol-2(3H)-one (**3k**).*



3k

Yield: 0.268 g (76%), beige powder, mp 333−335 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.63 (d, J = 7.8 Hz, 1H, H7-BI), 6.94 (ddd, J = 7.8, 7.4, 1.4 Hz, 1H, H6-BI), 7.05 (dd, J = 7.4, 1.0 Hz, 1H, H5-BI), 7.10 (dd, 1H, J = 7.4, 1.0 Hz, 1H, H4-BI), 7.14 (ddd, J = 7.3, 7.3, 1.0 Hz, 1H, H4-Ph), 7.25 (dd, J = 7.9, 7.5 Hz, 2H, H3,5-Ph), 7.32 (dd, J = 7.9, 1.1 Hz, 2H, H2,6-Ph), 7.36 (d, J = 2.9 Hz, 1H, H4-P), 7.69 (d, J = 6.2 Hz, 2H, H3,5-Py), 8.54 (d, J = 6.2 Hz, 2H, H2,6-Py), 11.21 (s, 1H, NH-BI), 12.27 (d, J = 2.2 Hz, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.9 (C2-BI), 150.1 (C2,6-Py), 138.5 (C1-Py), 133.7 (C1-Ph), 131.1 (C7a-BI), 128.6 (C3,5-Ph), 128.5 (C3a-BI), 127.5 (C2-P), 126.1 (C4-Ph), 125.7 (C2,6-Ph), 122.1 (C5-BI), 121.6 (C4-P), 121.2 (C6-BI), 120.0 (C5-P), 117.6 (C3,5-Py), 109.3 (C4-BI), 108.4 (C7-BI), 107.8 (C3-P). IR (Nujol): ν 1707, 1597, 1196, 998, 755, 737, 695 cm^{-1}. MALDI MS m/z: $(M + H)^+$ 353. HRMS (MALDI) m/z: $[M + H]^+$ calcd for $C_{22}H_{16}N_4O$ 353.1397, found 353.1425. Anal. Calcd for $C_{22}H_{16}N_4O$: C, 74.98; H, 4.58; N, 15.90. Found: C, 74.87; H, 4.53; N, 15.81.

*Synthesis of 5/6-Substituted Derivatives of 1-[3-Phenyl-5-aryl-pyrrol-2-yl)]benzimidazol-2(3H)-ones **3l**−**o**.* Compounds **3l** and **3m** were synthesized using the same procedure as **3b**, except the reactions of 3-benzoylquinoxalin-2(1*H*)-one-7-carboxylic acid **1b** (0.30 g, 1.02 mmol)

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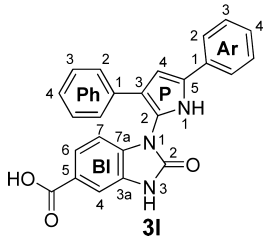
with acetophenones **2a** (0.25 g, 2.04 mmol) and **2b** (0.41 g, 2.04 mmol) were used, respectively.

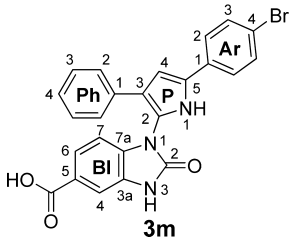
*1-[3,5-Diphenylpyrrol-2-yl)benzimidazol-2(3H)-one-5-carboxylic Acid (**3l**).*



3l

Yield: 0.250 g (62%), off-white solid, mp 334−336 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.71 (d, J = 8.6 Hz, 1H, H7-BI), 7.06 (d, J = 2.9 Hz, 1H, H4-P), 7.12 (dd, J = 7.6, 7.1 Hz, 1H, H4-Ph), 7.24 (dd, J = 7.6, 7.6 Hz, 1H, H4-Ar), 7.24 (dd, J = 7.6, 7.6 Hz, 2H, H3,5-Ph), 7.30 (d, J = 7.6 Hz, 2H, H2,6-Ph), 7.41 (dd, J = 7.6, 7.6 Hz, 2H, H3,5-Ar), 7.61−7.63 (m, 2H, H4-BI, H6-BI), 7.73 (d, J = 7.6 Hz, 2H, H2,6-Ar), 11.43 (s, 1H, NH-BI), 11.96 (d, J = 2.4 Hz, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 167.2 (C(O)OH), 154.2 (C2-BI), 135.0 (C7a-BI), 134.0 (C1-Ph), 131.8 (C1-Ar), 130.6 (C2-P), 128.8 (C3,5-Ar), 128.6 (C3,5-Ph), 128.3 (C3a-BI), 126.4 (C4-Ar), 125.9 (C4-Ph), 125.7 (C2,6-Ph), 124.5 (C5-BI), 123.6 (C2,6-Ar), 123.5 (C6-BI), 121.1 (C4-P), 117.4 (C5-P), 109.9 (C4-BI), 108.1 (C7-BI), 104.8 (C3-P). ^{15}N NMR (60 MHz, DMSO-d_6): δ 119.0 (N3-BI), 154.8 (N1-P), 126.1 (N1-BI). IR (Nujol): ν 1715, 1678, 1299, 754, 694 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 396. HRMS (MALDI) m/z: [M]$^+$ calcd for $C_{24}H_{17}N_3O_3$ 395.1264, found 395.1260. Anal. Calcd for $C_{24}H_{17}N_3O_3$: C, 72.90; H, 4.33; N, 10.63. Found: C, 72.76; H, 4.40; N, 10.77.

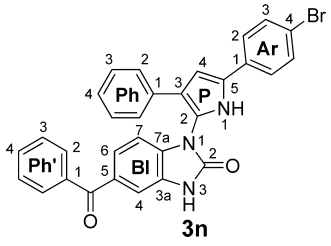
*1-[5-(4-Bromophenyl)-3-phenylpyrrol-2-yl)]benzimidazol-2(3H)-one-5-carboxylic Acid (**3m**).*



3m

Yield: 0.406 g (84%), off-white solid, mp 332−334 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.72 (d, J = 8.7 Hz, 1H, H7-BI), 7.11 (d, J = 3.1 Hz, 1H, H4-P), 7.12 (dd, J = 7.7, 7.7 Hz, 1H, H4-Ph), 7.24 (dd, J = 8.2, 7.7 Hz, 2H, H3,5-Ph), 7.29 (d, J = 8.2 Hz, 2H, H2,6-Ph), 7.58−7.62 (m, 4H, H4-BI, H6-BI, H3,5-Ar), 7.68 (d, J = 8.7 Hz, 2H, H2,6-Ar), 11.44 (s, 1H, NH-BI), 12.04 (d, J = 3.1 Hz, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 167.11 (C(O)OH), 154.08 (C2-BI), 134.84 (C7a-BI), 133.76 (C1-Ph), 131.67 (C3,5-Ar), 131.03 (C1-Ar), 129.38 (C2-P), 128.58 (C3,5-Ph), 128.31 (C3a-BI), 126.00 (C4-Ph), 125.66 (C2,6-Ph), 125.52 (C2,6-Ar), 124.55 (C5-BI), 123.49 (C6-BI), 121.26 (C4-P), 119.11 (C4-Ar), 117.85 (C5-P), 109.90 (C4-BI), 108.10 (C7-BI), 105.47 (C3-P). IR (Nujol): ν 3348, 1696, 1658, 1272, 1256, 763 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 474. HRMS (MALDI) m/z: [M]$^+$ calcd for $C_{24}H_{16}N_3O_3Br$ 473.0369, found 473.0358. Anal. Calcd for $C_{24}H_{16}BrN_3O_3$: C, 60.77; H, 3.40; N, 8.86. Found: C, 60.48; H, 3.29; N, 8.71.

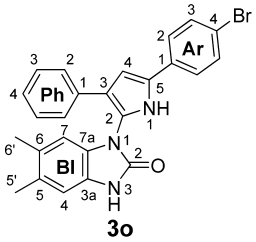
*5-Benzoyl-1-[5-(4-bromophenyl)-3-phenyl-pyrrol-2-yl]-benzimidazol-2(3H)-one (**3n**).*



3n

NH_4OAc (0.65 g, 8.46 mmol) was added to a suspension of 3-benzoylquinoxalin-2(1H)-one **1c** (0.30 g, 0.85 mmol) and 4-bromoacetophenone **2b** (0.34 g, 1.69 mmol) in MeOH (40 mL). The mixture was stirred under reflux for 8 h after other portions of NH_4OAc (0.65 g, 8.46 mmol) and (0.33 g, 4.23 mmol) were added in two portions in equal intervals of time (every 8 h). Stirring and refluxing were continued for 24 h. The cake of the unreacted starting compound **1c** 0.165 g (55%) was removed by filtration. The filtrate was evaporated under vacuum and the residue was treated with water (15 mL). The precipitate was filtered, washed with water (2 × 5 mL), dried in air, and purified by column chromatography on silica gel (eluent, hexane/EtOAc, 10:1 → 4:1) to afford **3n** as a beige powder. Yield: 54.3 mg (12%), mp 289−290 °C. R_f = 0.36 ($CHCl_3$/hexane/MeOH, 6:3:1). ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.77 (d, J = 8.2 Hz, 1H, H7-BI), 7.09 (d, J = 3.0 Hz, 1H, H4-P), 7.14 (ddd, J = 7.2, 7.2, 1.3 Hz, 1H, H4-Ph), 7.25 (dd, J = 8.1, 7.2 Hz, 2H, H3,5-Ph), 7.30 (br d, J = 8.1 Hz, 2H, H2,6-Ph), 7.40 (dd, J = 8.2, 1.7 Hz, 1H, H6-BI), 7.49 (d, J = 1.7 Hz, 1H, H4-BI), 7.53 (dd, J = 7.8, 1.6 Hz, 2H, H3,5-Ph′), 7.59 (d, J = 8.6 Hz, 2H, H3,5-Ar), 7.64 (ddd, J = 7.8, 7.5, 1.1 Hz, 1H, H4-Ph′), 7.66 (br d, J = 7.8 Hz, 2H, H2,6-Ph′), 7.67 (d, J = 8.6 Hz, 2H, H2,6-Ar), 11.51 (s, 1H, NH-BI), 12.07 (d, J = 2.5 Hz, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 195.2 (C(O)Ph′), 154.4 (C2-BI), 137.9 (C1-Ph′), 135.3 (C7a-BI), 133.9 (C1-Ph), 132.4 (C4-Ph′), 132.0 (C3,5-Ar), 131.20 (C1-Ar), 131.18 (C5-BI), 129.7 (C2-P), 129.4 (C2,6-Ph′), 128.9 (C3,5-Ph), 128.70 (C3a-BI), 128.65 (C3,5-Ph′), 126.4 (C4-Ph), 125.9 (C2,6-Ph), 125.8 (C2,6-Ar), 125.1 (C6-BI), 121. Seven (C4-P), 119.4 (C4-Ar), 117.9 (C5-P), 110.6 (C4-BI), 108.3 (C7-BI), 105.7 (C3-P). IR (KBr): ν 3262, 2925, 1717, 1684, 1303, 1280, 1262, 764, 700 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 534. HRMS (MALDI) m/z: [M]$^+$ calcd for $C_{30}H_{20}BrN_3O_2$ 533.0733, found 533.0718. Anal. Calcd for $C_{30}H_{20}BrN_3O_2$: C, 67.42; H, 3.77; N, 7.86. Found: C, 67.74; H, 3.88; N, 7.72.

*1-[5-(4-Bromophenyl)-3-phenylpyrrol-2-yl]-5,6-dimethylbenzimidazol-2(3H)-one (**3o**).*



3o

1-[5-(4-Bromophenyl)-3-phenyl-pyrrol-2-yl]-5,6-dimethylbenzimidazol-2(3H)-one **3o** was synthesized using the same procedure as **3n**, with the use of 3-benzoylquinoxalin-2(1H)-one **1d** (0.30 g, 1.08 mmol) instead of 3-benzoylquinoxalin-2(1H)-one **1c**. The solvent was evaporated under reduced pressure on a third. The precipitate was collected by filtration, washed with ether (2 × 5 mL), and dried in air to give 0.311 g (63%) of compound **3o** as a off-white powder, mp 280−282 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.10 (s, 3H, CH_3-6′), 2.20 (s, 3H, CH_3-5′), 6.44 (s, 1H, H7-BI), 6.87 (s, 1H, H4-BI), 7.10 (d, J = 2.9 Hz, 1H, H4-P), 7.11 (dd,, J = 7.6, 7.6 Hz, 1H, H4-Ph), 7.23 (dd, J = 7.6, 7.6 Hz, 2H, H3,5-Ph), 7.30 (d, J = 7.6 Hz, 2H, H2,6-Ph), 7.59 (d, J = 8.6 Hz, 2H, H3,5-Ar), 7.69 (d, J = 8.6 Hz, 2H, H2,6-Ar), 10.94 (s, 1H, NH-BI), 11.96 (d, J = 2.4 Hz, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.1 (C2-BI), 134.0 (C1-Ph), 131.6 (C3,5-Ar), 131.2 (C1-Ar), 129.56 (C7a-BI), 129.54 (C6-BI), 129.0 (C2-P), 128.7 (C5-BI), 128.5 (C3,5-Ph), 126.4 (C3a-BI), 125.8 (C4-Ph), 125.6 (C2,6-Ph), 125.4 (C2,6-Ar), 121.0 (C4-P), 118.9 (C4-Ar, C5-P), 110.2 (C4-BI), 109.3 (C7-BI), 105.3 (C3-P), 19.3 (CH_3-5′), 19.2 (CH_3-6′). ^{15}N NMR (60 MHz, DMSO-d_6): δ 117.2 (N3-BI), 121.5 (N1-BI), 155.6 (N1-P). IR (Nujol): ν 1693, 1616, 1497, 1256, 799, 759, 698 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 458. HRMS (MALDI) m/z: [M]$^+$ calcd for $C_{25}H_{20}BrN_3O$ 457.0784, found 457.0803. Anal. Calcd for $C_{25}H_{20}BrN_3O$: C, 65.51; H, 4.40; N, 9.17. Found: C, 65.40; H, 4.37; N, 9.10.

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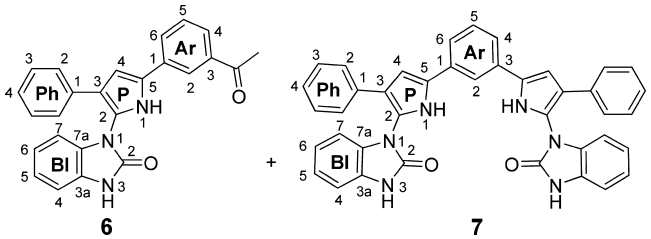
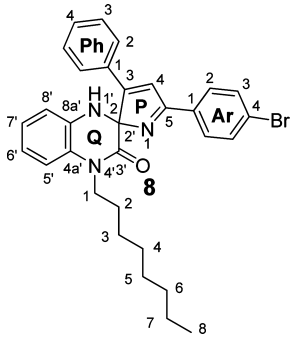
*Synthesis of 1-[5-(3-Acetylphenyl)-3-phenylpyrrol-2-yl]-benzimidazol-2(3H)-one (**6**) and 1,3-Bis[2-(benzimidazol-2-on-1-yl)-3-phenylpyrrol-5-yl]benzene (**7**).*



6 **7**

1,3-Diacetylbenzene **5** (0.1 mL, 0.62 mmol) was added to a suspension of 3-benzoylquinoxalin-2(1*H*)-one **1a** (0.34 g, 1.36 mmol) and NH_4OAc (0.47 g, 6.17 mmol) in MeOH (20 mL), and the mixture was stirred under reflux for 8 h. Another portion of NH_4OAc (0.24 g, 3.08 mmol) was added, and then stirring and reflux were continued for 14 h. The precipitate was removed by filtration, and the filtrate was washed with ether (3 × 1 mL) to give 0.235 g (61%) compound **7**. The filtrate was evaporated, and the remainder was treated with water (2 mL), dried in air, and purified by column chromatography on silica gel (eluent, EtOAc/hexane, 1:1 → 2:1) to afford the 46.2 mg (19%) of compound **6**. Data for **6**: yellow solid, mp 195−197 °C. R_f = 0.42 ($CHCl_3$/hexane/MeOH, 6:3:1). ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.64 (s, 3H, CH_3), 6.63 (d, J = 8.1 Hz, 1H, H7-BI), 6.94 (dd, J = 7.6, 7.6 Hz, 1H, H6-BI), 7.05 (dd, J = 8.1, 7.6 Hz, 1H, H5-BI), 7.10 (d, J = 7.6 Hz, 1H, H4-BI), 7.13 (dd, J = 8.1, 7.6 Hz, 1H, H4-Ph), 7.20 (d, J = 2.9 Hz, 1H, H4-P), 7.24 (dd, J = 8.1, 7.6 Hz, 2H, H3,5-Ph), 7.34 (d, J = 7.6 Hz, 2H, H2,6-Ph), 7.56 (dd, J = 8.1, 8.1 Hz, 1H, H5-Ar), 7.80 (d, J = 8.1 Hz, 1H, H4-Ar), 8.01 (d, J = 8.1 Hz, 1H, H6-Ar), 8.31 (br s, 1H, H2-Ar), 11.18 (s, 1H, NH-BI), 12.12 (d, J = 2.4 Hz, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 197.9 (*C*(O)CH_3), 154.0 (C2-BI), 137.4 (C3-Ar), 134.0 (C1-Ph), 132.3 (C1-Ar), 131.3 (C7a-BI), 129.3 (C2-P), 129.2 (C5-Ar), 128.49 (C3,5-Ph), 128.46 (C3a-BI), 128.0 (C6-Ar), 125.83 (C4-Ph), 125.76 (C4-Ar), 125.65 (C2,6-Ph), 123.0 (C2-Ar), 121.9 (C5-BI), 121.07 (C6-BI), 121.05 (C4-P), 118.6 (C5-P), 109.2 (C4-BI), 108.4 (C7-BI), 105.5 (C3-P), 26.8 (CH_3). IR (KBr): ν 1722, 1705, 1685, 1667, 1504, 1479, 1268, 1252, 764, 752, 698 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 394. HRMS (MALDI) m/z: [M + Na]$^+$ calcd for $C_{25}H_{19}N_3O_2$ 416.1369, found 416.1397. Anal. Calcd for $C_{25}H_{19}N_3O_2$: C, 76.32; H, 4.87; N, 10.68. Found: C, 76.07; H, 4.78; N, 10.56. Data for **7**: off-white powder, mp >350 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.65 (d, J = 7.7 Hz, 2H, 2 × H7-BI), 6.95 (dd, J = 8.2, 7.2 Hz, 2H, 2 × H6-BI), 7.05 (ddd, J = 8.2, 7.2, 1.0 Hz, 2H, 2 × H5-BI), 7.09 (d, J = 8.2 Hz, 2H, 2H, 2 × H4-BI), 7.13 (dd, J = 7.7, 7.7 Hz, 2H, 2 × H4-Ph), 7.15 (dd, J = 3.1 Hz, 2H, 2 × H4-P), 7.24 (dd, J = 7.7, 7.7 Hz, 4H, 2 × H3,5-Ph), 7.33 (d, J = 7.7 Hz, 4H, 2 × H2,6-Ph), 7.43 (dd, J = 8.2, 7.7 Hz, 1H, H5-Ar), 7.59 (dd, J = 8.2, 1.5 Hz, 2H, H4,6-Ar), 8.16 (br s, 1H, H2-Ar), 11.18 (s, 1H, NH-BI), 11.95 (d, J = 2.5 Hz, 1H, NH-P). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.0 (C2-BI), 134.2 (C1-Ph), 132.3 (C1-Ar, C3-Ar), 131.4 (C7a-BI), 130.2 (C2-P), 129.3 (C5-Ar), 128.48 (C3,5-Ph), 128.46 (C3a-BI), 125.8 (C4-Ph), 125.7 (C2,6-Ph), 121.9 (C5-BI), 121.3 (C4-Ar, C6-Ar), 121.1 (C6-BI), 120.9 (C4-P), 118.8 (C2-Ar), 118.1 (C5-P), 109.2 (C4-BI), 108.4 (C7-BI), 105.0 (C3-P). IR (Nujol): ν 3151, 1684, 1613, 1256, 757, 731, 659 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 625. HRMS (MALDI) m/z: [M]$^+$ calcd for $C_{40}H_{28}N_6O_2$ 624.2268, found 624.2284. Anal. Calcd for $C_{40}H_{28}N_6O_2$: C, 76.91; H, 4.52; N, 13.45. Found: C, 77.29; H, 4.41; N, 13.34.

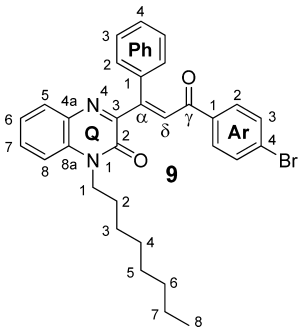
*5-(4-Bromophenyl)-4′-octyl-3-phenyl-1′H-spiro[pyrrol-2,2′-quinoxalin]-3′(4′H)-one (**8**).*



8

The mixture of 3-benzoylquinoxalin-2(1*H*)-one **1e** (0.35 g, 0.97 mmol), 4-bromoacetophenone **2b** (0.38 g, 1.93 mmol), and NH_4OAc (0.74 g, 9.66 mmol) in MeOH (20 mL) was stirred under reflux for 8 h. Another portion of NH_4OAc (0.37 g, 4.83 mmol) was added, and stirring and reflux were continued for 6 h. The precipitate was removed by filtration, and the filtrate was washed with ether (3 × 1 mL) to give 0.358 g (68%) of compound **8** as a yellow powder. Mp: 153−155 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 0.81 (dd, J = 6.9, 6.9 Hz, 3H, $CH_2CH_2(CH_2)_5CH_3$), 1.14−1.32 (m, 10H, $CH_2CH_2(CH_2)_5CH_3$), 1.54−1.65 (m, 2H, $CH_2CH_2(CH_2)_5CH_3$), 3.92−4.08 (m, 2H, $CH_2CH_2(CH_2)_5CH_3$), 6.78 (d, J = 7.6 Hz, 1H, H8′-Q), 6.85 (dd, J = 7.9, 7.6 Hz, 1H, H6′-Q), 6.91 (dd, J = 7.9, 7.6 Hz, 1H, H7′-Q), 7.08 (br s, 1H, NH′-Q), 7.16 (d, J = 7.9 Hz, 1H, H5′-Q), 7.39 (dd, J = 7.9, 6.9 Hz, 1H, H4-Ph), 7.43 (dd, J = 7.9, 6.9 Hz, 2H, H3,5-Ph), 7.70 (d, J = 8.6 Hz, 2H, H3,5-Ar), 7.87 (d, J = 7.9 Hz, 2H, H2,6-Ph), 7.91 (s, 1H, H4-P), 7.99 (d, J = 8.6 Hz, 2H, H2,6-Ar). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 170.8 (C5-P), 164.4 (C3-P), 162.4 (C3′-Q), 134.6 (C8a′-Q), 131.8 (C1-Ar, C3,5-Ar), 131.5 (C1-Ph), 129.9 (C2,6-Ar), 129.2 (C4-Ph), 128.3 (C3,5-Ph), 127.5 (C2,6-Ph), 126.7 (C4a′-Q), 125.2 (C4-Ar), 123.3 (C4-P), 123.0 (C7′-Q), 118.7 (C6′-Q), 114.7 (C5′-Q), 114.3 (C8′-Q), 92.1 (C2-P), 40.9 (C1-Alk), 31.1 (C6-Alk), 28.64 (C4-Alk), 28.62 (C5-Alk), 26.7 (C2-Alk), 26.1 (C3-Alk), 22.0 (C7-Alk), 13.8 (C8-Alk). ^{15}N NMR (60 MHz, DMSO-d_6): δ 73.0 (N1′-Q), 138.4 (N4′-Q), 327.0 (N1-P). IR (Nujol): ν 1662, 1459, 1391, 1098, 771, 753 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 542. HRMS (MALDI) m/z: [M + H]$^+$ calcd for $C_{31}H_{32}BrN_3O$ 542.1802, found 542.1868. Anal. Calcd for $C_{31}H_{32}BrN_3O$: C, 68.63; H, 5.95; N, 7.75. Found: C, 68.38; H, 5.86; N, 7.88.

*(E)-3-[3-(4-Bromophenyl)-3-oxo-1-phenylprop-1-enyl]-1-octylquinoxalin-2(1H)-one (**9**).*



9

A solution of spiro-compound **8** (0.20 g, 0.37 mmol) in AcOH (5 mL) was refluxed for 4 h. The solvent was evaporated under reduced pressure, and the residue was purified by recrystallization from *i*-PrOH (2 mL) to give 0.190 g (95%) of compound **9** as a black powder. Mp: 91−93 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 0.81 (dd, J = 7.0, 6.8 Hz, 3H, $CH_2CH_2(CH_2)_5CH_3$), 1.14−1.38 (m, 10H, $CH_2CH_2(CH_2)_5CH_3$), 1.62−1.70 (m, 2H, $CH_2CH_2(CH_2)_5CH_3$), 4.24 (t, J = 7.0 Hz, 2H, $CH_2CH_2(CH_2)_5CH_3$), 7.35−7.38 (m, 1H, H6-Q), 7.42−7.50 (m, 3H, H4-Ph, H3,5-Ph), 7.65−7.68 (m, 4H, H7-Q, H8-Q, H2,6-Ph), 7.72 (d, J = 8.5 Hz, 2H, H3,5-Ar), 7.75 (d, J = 7.9 Hz, 1H, H5-Q), 7.91 (s, 1H, H$^\delta$), 7.98 (d, J = 8.5 Hz, 2H, H2,6-Ar). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 188.3 (C$^\gamma$), 159.0 (C3-Q), 153.3 (C2-Q), 151.1 (C$^\alpha$), 136.9 (C1-Ph), 136.4 (C1-Ar), 132.5 (C4a-Q), 132.3 (C8a-Q), 131.7 (C3,5-Ar), 130.5 (C7-Q), 130.4 (C2,6-Ar), 130.2 (C4-Ph), 129.5 (C5-Q), 128.8 (C3,5-Ph), 127.7 (C2,6-Ph), 127.4 (C4-Ar), 123.3 (C6-Q), 122.9 (C$^\delta$), 114.7 (C8-Q), 41.3 (C1-Alk), 31.1 (C6-Alk), 28.6 (C4-Alk), 28.5 (C5-Alk), 26.9 (C2-Alk), 26.0 (C3-Alk), 22.0 (C7-Alk), 13.8 (C8-Alk). IR (Nujol): ν 1649, 1588, 1217, 1007, 766, 752 cm^{-1}. MALDI MS m/z: (M + H)$^+$ 543. HRMS (MALDI) m/z: [M + H]$^+$ calcd for $C_{31}H_{31}BrN_2O_2$ 543.1642, found 543.1696. Anal. Calcd for $C_{31}H_{31}BrN_2O_2$: C, 68.51; H, 5.75; N, 5.15. Found: C, 68.19; H, 5.62; N, 5.30.

■ ASSOCIATED CONTENT

Supporting Information

Related 1D/2D NMR and HRMS spectra for all new compounds; crystallographic data for **3a**, **3k**, and **9** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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