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Indirect regioselective heteroarylation of indoles through a Friedel–Crafts reaction with (*E*)-1,4-diaryl-2-buten-1,4-diones

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ABSTRACT

A two-step synthesis of 3-heteroaryl indoles has been developed. The first step of the sequence involves a Friedel–Crafts alkylation of indoles with 1,4-diaryl-2-buten-1,4-diones to give the corresponding indoles bearing a 1,4-dicarbonyl moiety. The reaction is catalyzed by $InCl_3$ and takes place with good yields. Cyclization of the diones under different Paal–Knorr conditions allows to prepare indoles substituted at the C3 position with 3-furanyl, 3-pyrrolyl- and 3-thienyl moieties.

1. Introduction

Biaryls are common moieties present in high value molecules such as organic dyes, conducting polymers, asymmetric ligands or pharmaceuticals.[1] Therefore, the development of efficient methods to connect two arene nuclei has been a topic of great relevance in organic synthesis.[2] Three general procedures have been used to carry out the formation of these carbon–carbon biaryl linkage.[3] The most widely known and used procedure is the cross-coupling reaction of a nucleophilic unit Ar–Y (Y=BR_2, SnR_3, MgX, ZnX corresponding to the Suzuki–Miyaura,[4] Stille,[5] Kumada[6] and Negishi[7] reactions, respectively) with an electrophilic aryl reagent Ar–X (X=halogen or sulfonate). In fact, an impressive progress in the development of efficient catalytic systems to achieve this kind of reactions has been made in the last years. Besides the already classical procedures mentioned above, recent advances include the use of aryl carbinols and nitriles,[8] carboxylic acids (or their salts)[9] and silanolates[10] as valid replacements for aryl boronic acids and organometallic compounds as nucleophilic components of the cross-coupling reaction. Despite the success of these reactions, some drawbacks still remain. For instance, the overall process includes the prefunctionalization of the substrates as nucleophilic and electrophilic reagents; besides, although simple aryl halides and aryl boronic acids are successful coupling partners, reactions involving their heteroaryl analogues are less straightforward,[11] especially when both partners are heterocycles.[12] Thus, although the preparation of indolyl boronic acids and boronate esters has been carried out by several groups,[13] only few efficient procedures for the Suzuki–Miyaura cross-coupling involving the indole nucleus have been reported.[13h,i,14]

A second general method involves a direct arylation reaction in which an aryl boronic acid is replaced by a simple unfunctionalized arene. Although a variety of electron-rich heterocycles have been arylated using this methodology,[15] the reaction with indoles is limited to the use of homoaryl halides as electrophilic component; furthermore the regioselectivity of the arylation depends on the protecting group of the indole nitrogen atom.

The third general method is the cross-coupling reaction of two simple unactivated arenes. Fagnou and co-workers[3] have recently discovered the arylation of indoles with excess arenes under Pd(II) catalysis, and DeBoef and co-workers[16] have also described the arylation of indoles and benzofuranes. However, in both cases the reaction is limited to coupling with homoarenes and, besides, the arylation of unprotected (N–H) indoles has not been resolved. The best results were obtained with *N*-acetylindoles although the yields and regioselectivities were moderate.

According to these antecedents and despite the recent advances, the access to biheteroaryl compounds, especially those bearing two linked electron-rich heterocycles; i.e., a five-membered heterocycle linked to the heterocyclic ring of indole, remains very limited. Therefore the development of synthetic procedures addressed to

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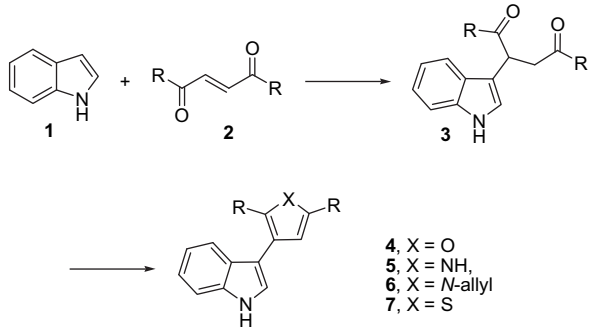
this kind of compounds constitutes an interesting challenge to organic chemists. In this paper we present a novel two-step synthesis of 3-heteroaryl indoles.

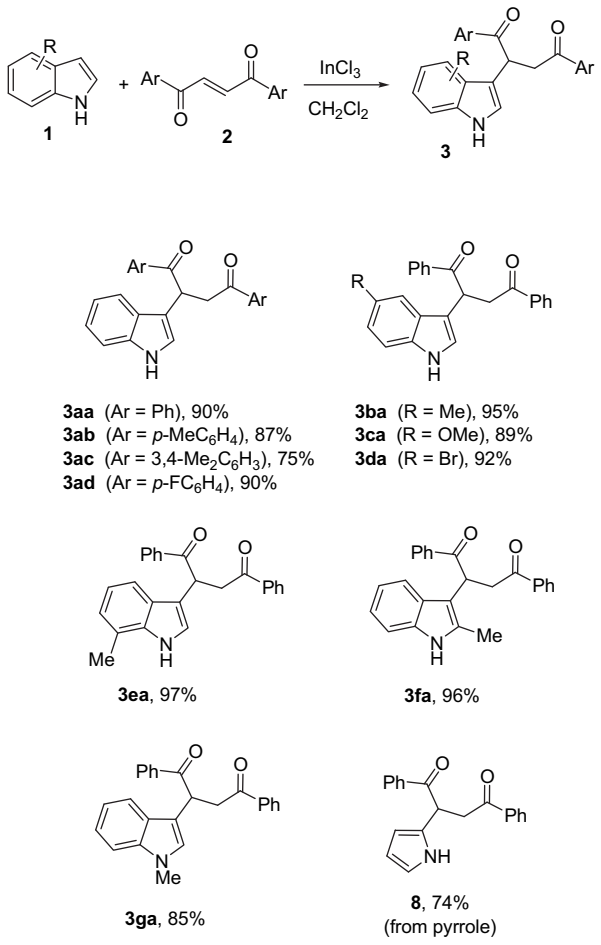
2. Results and discussion

Taking into consideration that 1,4-dicarbonyl compounds are the most important starting materials for the preparation of furans, pyrroles and thiophenes (Paal–Knorr synthesis) we envisioned the procedure for the synthesis of 3-heteroaryl substituted indoles outlined in Scheme 1. The procedure involves the introduction in a first step of a 1,4-dicarbonyl moiety on the indole framework via a Friedel–Crafts alkylation with (*E*)-1,4-diaryl-2-buten-1,4-diones. In a second step the 1,4-dicarbonyl moiety would be transformed into furan, pyrrole or thiophene rings via a Paal–Knorr cyclization under different conditions.



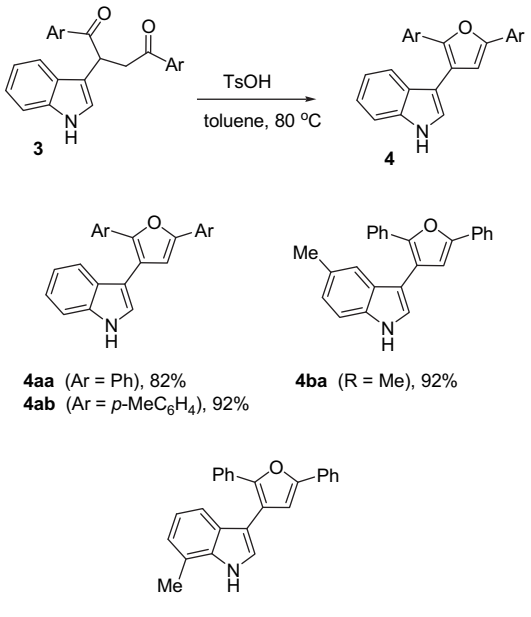
Scheme 1. Two-step synthetic sequence to 3-heteroaryl indoles.

The introduction of functionalized alkyl groups at the 3-position of indole by means of a Friedel–Crafts reaction using various electrophilic reagents constitutes a well established synthetic strategy.[17] However, there are no literature precedents on the Friedel–Crafts reaction of indoles **1** with (*E*)-1,4-diaryl-2-buten-1,4-diones **2** as electrophilic partners. Recently, indium trichloride has emerged as a mild, air stable and water tolerant Lewis acid in various organic transformations.[18] In particular it has been used to activate but-2-ene-1,4-diones as Michael acceptors against acetoacetates as nucleophiles.[19] Also, the tolerance of the indole framework to indium trichloride has been demonstrated in several catalytic reactions.[20] Accordingly, we anticipated that indium trichloride could be a suitable catalyst for the Friedel–Crafts alkylation of indoles. Thus, after some experimentation, we found that the reaction between indole (**1a**) and (*E*)-1,4-diphenyl-2-buten-1,4-dione (**2a**) proceeded smoothly in dichloromethane at room temperature in the presence of 10 mol % $InCl_3$ with complete substrate conversion after 3 h, providing the expected product **3aa** in 90% isolated yield. Under these conditions, several (*E*)-1,4-diaryl-2-buten-1,4-diones **2** containing either electron-donating (**2b–c**) or electron-withdrawing (**2d**) substituents on the phenyl ring reacted with indole (**1a**). In all cases the corresponding alkylated products **3aa–ad** were obtained in good yields (75–90%). The scope of the reaction with respect to the indole substrate was also explored. A number of C5, C7, C2 and N1-substituted indoles **2b–f** were reacted with (*E*)-1,4-diphenyl-2-buten-1,4-dione (**2a**). In general, the reaction time (3–4 h) and yield of products **3ba–fa** did not show a significant dependence with the electronic features of the substituent on the indole substrate. We also tested the reaction of pyrrole with compound **2a**. In this case 10 equiv of pyrrole was used to avoid double alkylation at the 2- and 5-positions of pyrrole. In this way the product of monoalkylation at the 2-position of pyrrole **8** was obtained in 74% yield after 0.5 h. The result of the $InCl_3$-catalyzed Friedel–Crafts alkylation is shown in Scheme 2.



Scheme 2. $InCl_3$-catalyzed Friedel–Crafts alkylation of indoles **1** and pyrrole with (*E*)-1,4-diaryl-2-buten-1,4-diones **2**.

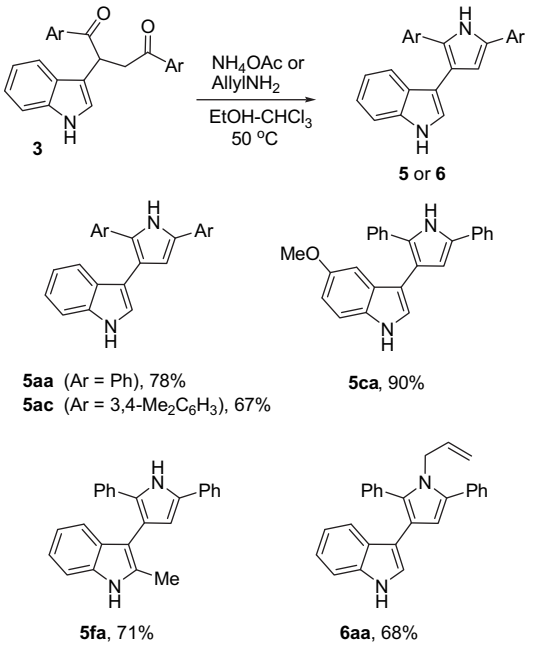
With the 1,4-dicarbonyl-functionalized indoles in our hands we proceeded to the construction of the five-membered heterocyclic ring via a Paal–Knorr strategy. First we studied the synthesis of furanyl indoles. Various dicarbonyl compounds **3** were subjected to de-



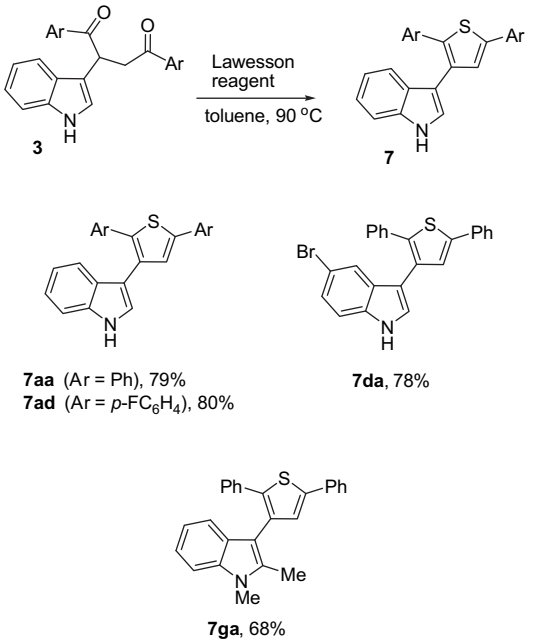
Scheme 3. Cyclization of dicarbonyl indoles **3** to furanyl indoles **4**.

hydration upon treatment with 10 mol % *p*-toluenesulfonic acid in toluene at 80 °C.[21] Cyclization of the 1,4-diketone moiety provided the corresponding furan derivatives **4** in good yields, from 82 to 93% (Scheme 3).

The synthesis of indoles substituted with a pyrrole ring was examined next. Reaction of compounds **3** with excess of ammonium acetate in a mixture of EtOH–$CHCl_3$ (2:3) as the solvent at 50 °C afforded the trisubstituted pyrroles **5**, having an unsubstituted nitrogen atom in the pyrrole ring in good yields (67–90%). Compound **6aa**, bearing an *N*-allyl pyrrole ring, could also be obtained in 68% yield by using allylamine instead of ammonium acetate (Scheme 4).



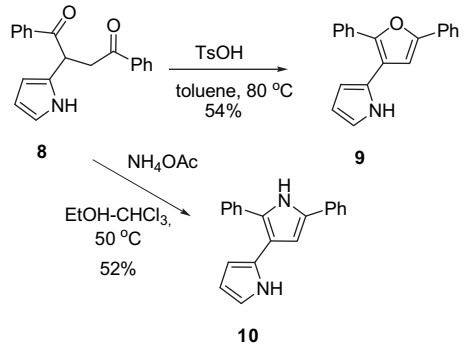
Scheme 4. Cyclization of dicarbonyl indoles **3** to pyrrolyl indoles **5** and **6**.



Scheme 5. Cyclization of dicarbonyl indoles **3** to thienyl indoles **7**.

Finally, we achieved the synthesis of indoles bearing a thiophene ring **7**.[22] The 1,4-diketones **3** were reacted with Lawesson's reagent in order to obtain the corresponding thiophenes **7**. Cyclization to furan took place in some extent as a side reaction. Different solvents and temperatures were studied in order to minimize the formation of the furan ring. The best results with compound **3aa** were obtained by heating at 90 °C in toluene as solvent during 30 min, in this way thiophene **7aa** was obtained in 79% yield together with furan **4aa** (20%). The results for the formation of several thiophenes are shown in Scheme 5.

We also have examined the application of this methodology to the synthesis of 2-heteroaryl pyrroles. Thus, compound **8** was transformed into furyl pyrrole **9** (54% yield) and bipyrrole **10** (52% yield) under the conditions developed for the synthesis of indole derivatives (Scheme 6).



Scheme 6. Cyclization of dicarbonyl pyrrole **8** to furyl pyrrole **9** and bipyrrole **10**.

3. Conclusion

In summary, we have developed a new strategy for the synthesis of biheteroaryl compounds that involves a Friedel–Crafts alkylation reaction of indoles (or pyrrole) with 2-buten-1,4-diones followed by a Paal–Knorr reaction of the 1,4-dicarbonyl moiety introduced in the first reaction. The overall sequence is an alternative to the cross-coupling between two electron-rich heterocycles, which is limited and troublesome. This strategy appears as a convenient method for the synthesis of highly substituted biheteroaryl compounds.

4. Experimental section

4.1. General

Commercial reagents were used as purchased. Dichloromethane and toluene were distilled from CaH_2 and stored over 4 Å molecular sieves. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040–0.063 mm. ^{1}H NMR were run at 300 MHz for ^{1}H and at 75 MHz for ^{13}C NMR, and referenced to the solvent as internal standard. MS(EI) were run at 70 eV. The starting 1,4-diketones were prepared by Friedel–Crafts acylation of aromatic compounds with fumaroyl chloride according to procedures reported in the literature.[23]

4.2. Experimental procedure for the Friedel–Crafts reaction

Endione **2a** (R=Ph, 118.0 mg, 0.5 mmol) was added to a solution of $InCl_3$ (11.1 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) under nitrogen. After stirring for 10 min, a solution of indole (**1a**, 42.2 mg, 0.6 mmol) in CH_2Cl_2 (2 mL) was added and the mixture was stirred at room temperature until completion (TLC). Water (5 mL) was then added and the mixture was extracted with diethyl ether (3×15 mL). The organic layer was washed with brine (15 mL) and dried over $MgSO_4$.

After filtration, the solvent was removed under reduced pressure and the mixture was chromatographed eluting with hexane–EtOAc mixtures (from 9:1 to 8:2) to give **3aa** (158.8 mg, 90%).

*4.2.1. 2-(1H-Indol-3-yl)-1,4-diphenylbutane-1,4-dione (**3aa**).* Reaction time: 3 h; (yield 90%); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (br s, 1H), 8.06 (dd, J=6.9, 1.5 Hz, 2H), 7.98 (dd, J=7.2, 1.2 Hz, 2H), 7.79 (dd, J=7.8, 1.8 Hz, 1H), 7.55 (tt, J=7.4, 1.5 Hz, 1H), 7.49–7.34 (m, 6H), 7.25–7.15 (m, 2H), 7.01 (d, J=2.4 Hz, 1H), 5.62 (dd, J=10.2, 3.6 Hz, 1H), 4.26 (dd, J=18.1, 10.2 Hz, 1H), 3.45 (dd, J=18.2, 3.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1 (C), 198.2 (C), 136.5 (C), 136.4 (C), 133.2 (CH), 132.7 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 126.0 (C), 122.8 (CH), 122.5 (CH), 120.0 (CH), 118.7 (CH), 113.2 (C), 111.4 (CH), 42.8 (CH_2), 39.6 (CH); MS(EI) m/z (%): 353 (M^+, 27), 335 (14), 248 (37), 105 (100), 77 (34); HRMS: 353.1414 (M^+), $C_{24}H_{19}NO_2$ requires 353.1416.

*4.2.2. 2-(1H-Indol-3-yl)-1,4-di-p-tolylbutane-1,4-dione (**3ab**).* Reaction time: 3 h; (yield 87%); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.97 (d, J=8.1 Hz, 2H), 7.88 (d, J=8.4 Hz, 2H), 7.79 (dd, J=7.7, 1.5 Hz, 1H), 7.34 (dd, J=7.8, 2.0 Hz, 1H), 7.14–7.24 (m, 6H), 7.00 (d, J=2.4 Hz, 1H), 5.59 (dd, J=10.2, 3.6 Hz, 1H), 4.22 (dd, J=18.0, 10.2 Hz, 1H), 3.40 (dd, J=18.0, 3.6 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.8 (C), 198.4 (C), 143.9 (C), 143.4 (C), 136.4 (C), 134.1 (C), 134.0 (C), 129.2 (CH), 129.1 (CH), 128.9 (CH), 128.3 (CH), 126.0 (C), 122.7 (CH), 122.4 (CH), 119.9 (CH), 118.7 (CH), 113.5 (C), 111.4 (CH), 42.7 (CH_2), 39.4 (CH), 21.6 (CH_3), 21.6 (CH_3); MS(EI) m/z (%): 381 (M^+, 28), 262 (26), 119 (100), 91 (24); HRMS: 381.1765 (M^+), $C_{26}H_{23}NO_2$ requires 381.1728.

*4.2.3. 2-(1H-Indol-3-yl)-1,4-bis(3,4-dimethylphenyl)butane-1,4-dione (**3ac**).* Reaction time: 4 h; (yield 75%); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.86 (s, 1H), 7.79–7.82 (m, 2H), 7.75 (s, 1H), 7.72 (d, J=7.8 Hz, 1H), 7.34 (dd, J=6.9, 2.4 Hz, 1H), 7.15–7.24 (m, 3H), 7.10 (d, J=7.8 Hz, 1H), 7.01 (d, J=2.4 Hz, 1H), 5.59 (dd, J=10.2, 3.6 Hz, 1H), 4.21 (dd, J=18.0, 10.2 Hz, 1H), 3.42 (dd, J=18.0, 3.6 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1 (C), 198.6 (C), 142.6 (C), 142.2 (C), 136.7 (C), 136.6 (C), 136.4 (C), 134.5 (C), 134.4 (C), 129.8 (CH), 129.7 (CH), 129.6 (CH), 129.3 (CH), 126.5 (CH), 126.1 (C), 125.9 (CH), 122.7 (CH), 122.4 (CH), 119.9 (CH), 118.8 (CH), 113.7 (C), 111.4 (CH), 42.8 (CH_2), 39.4 (CH), 20.0 (CH_3), 19.9 (CH_3), 19.8 (CH_3), 19.7 (CH_3); MS(EI) m/z (%): 409 (M^+, 7), 133 (100), 105 (17); HRMS: 409.2035 (M^+), $C_{28}H_{27}NO_2$ requires 409.2042.

*4.2.4. 1,4-Bis(4-fluorophenyl)-2-(1H-indol-3-yl)butane-1,4-dione (**3ad**).* Reaction time: 3 h; (yield 90%); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (S, 1H), 8.07 (dd, J=8.7, 5.4 Hz, 2H), 8.00 (dd, J=8.7, 5.4 Hz, 2H), 7.76 (d, J=7.2 Hz, 1H), 7.37 (d, J=7.8 Hz, 1H), 7.24 (td, J=7.2, 2.0 Hz, 1H), 7.19 (td, J=7.4, 1.3 Hz, 1H), 7.10 (t, J=8.5 Hz, 2H), 6.98–7.06 (m, 3H), 5.54 (dd, J=10.2, 3.3 Hz, 1H), 4.22 (dd, J=18.0, 10.2 Hz, 1H), 3.83 (dd, J=18.0, 3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5 (C), 197.1 (C), 165.5 (d, J=253.5 Hz, C), 165.5 (d, J=252.6 Hz, C), 136.4 (C), 132.9 (d, J=3.0 Hz, C), 132.8 (d, J=3.0 Hz, C), 131.4 (d, J=9.2 Hz, CH), 130.8 (d, J=9.2 Hz, CH), 125.8 (C), 122.72 (CH), 122.68 (CH), 120.2 (CH), 118.5 (CH), 115.7 (d, J=21.8 Hz, CH), 115.5 (d, J=21.8 Hz, CH), 112.9 (C), 111.5 (CH), 42.7 (CH_2), 39.6 (CH); MS(EI) m/z (%): 389 (M^+, 3), 123 (100), 95 (23); HRMS: 389.1216 (M^+), $C_{24}H_{17}F_2NO_2$ requires 389.1227.

*4.2.5. 2-(5-Methyl-1H-indol-3-yl)-1,4-diphenylbutane-1,4-dione (**3ba**).* Reaction time: 3 h; (yield 95%); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04–8.07 (m, 3H), 7.99 (dd, J=8.3, 1.4 Hz, 2H), 7.58–7.52 (m, 2H), 7.44–7.50 (m, 3H), 7.36 (t, J=7.4 Hz, 2H), 7.25 (d, J=9.3, 1H), 7.05 (dd, J=8.4, 1.5, 1H), 6.96 (d, J=2.4, 1H), 5.58 (dd, J=10.5, 3.3 Hz, 1H), 4.25 (dd, J=18.2, 10.4 Hz, 1H), 3.42 (dd, J=18.0, 3.3 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2 (C), 198.8 (C), 136.5 (C), 134.8 (C), 133.2 (CH), 132.7 (CH), 129.4 (C), 128.8 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 126.2 (C), 124.2 (CH), 122.9 (CH), 118.2 (CH), 112.7 (C), 111.1 (CH), 42.8 (CH_2), 39.6 (CH), 21.55 (CH_3); MS(EI) m/z (%): 367 (M^+, 45), 263 (22), 262 (83), 106 (16), 105 (100), 77 (41); HRMS: 367.1579 (M^+), $C_{25}H_{21}NO_2$ requires 367.1572.

*4.2.6. 2-(5-Methoxy-1H-indol-3-yl)-1,4-diphenylbutane-1,4-dione (**3ca**).* Reaction time: 3 h; (yield 89%); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04–8.07 (m, 3H), 7.99 (dd, J=7.8, 1.5 Hz, 2H), 7.56 (tt, J=7.8, 1.6 Hz, 1H), 7.42–7.50 (m, 3H), 7.37 (t, J=7.5 Hz, 2H), 7.24 (d, J=8.7, 1H), 7.19 (d, J=2.4, 1H), 6.99 (d, J=2.4, 1H), 6.88 (dd, J=9, 2.4 Hz, 1H), 5.54 (dd, J=10.2, 3.6 Hz, 1H), 4.25 (dd, J=18.0, 10.2 Hz, 1H), 3.88 (s, 3H), 3.43 (dd, J=18.0, 3.45 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1 (C), 198.8 (C), 154.4 (C), 136.6 (C), 136.5 (C), 133.2 (CH), 132.7 (CH), 131.5 (C), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 126.4 (C), 123.5 (CH), 112.9 (C), 112.8 (CH), 112.2 (CH), 100.3 (CH), 56.0 (CH_3), 42.7 (CH_2), 39.7 (CH); MS(EI) m/z (%): 383 (M^+, 57), 279 (25), 278 (75), 106 (25), 105 (100), 77 (57); HRMS: 383.1526 (M^+), $C_{25}H_{21}NO_3$ requires 383.1521.

*4.2.7. 2-(5-Bromo-1H-indol-3-yl)-1,4-diphenylbutane-1,4-dione (**3da**).* Reaction time: 3 h; (yield 92%); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.04 (dd, J=7.9, 1.5 Hz, 2H), 7.98 (dd, J=7.9, 1.5 Hz, 2H), 7.90 (d, J=1.8 Hz, 1H), 7.56 (tt, J=7.4, 1.8 Hz, 1H), 7.42–7.51 (m, 3H), 7.38 (t, J=7.4, 2H), 7.29 (dd, J=8.7, 1.8 Hz, 1H), 7.20 (d, J=8.7 Hz, 1H), 7.02 (d, J=2.4 Hz, 1H), 5.54 (dd, J=10.2, 3.6 Hz, 1H), 4.22 (dd, J=10.2, 3.6 Hz, 1H), 3.41 (dd, J=18.0, 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9 (C), 198.5 (C), 136.7 (C), 136.3 (C), 135.0 (C), 133.3 (CH), 132.9 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 127.7 (C), 125.5 (CH), 124.0 (CH), 121.3 (CH), 113.4 (C), 112.9 (CH), 42.8 (CH_2), 39.4 (CH); MS(EI) m/z (%): 431 (M^+, 12), 105 (100), 77 (18); HRMS: 431.0536 (M^+), $C_{24}H_{18}BrNO_2$ requires 431.0521.

*4.2.8. 2-(7-Methyl-1H-indol-3-yl)-1,4-diphenylbutane-1,4-dione (**3ea**).* Reaction time: 3 h; (yield 97%); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.06 (dd, J=7.9, 1.5 Hz, 2H), 7.98 (dd, J=7.9, 1.5 Hz, 2H), 7.65 (d, J=7.8 Hz, 1H), 7.55 (tt, J=6.8, 1.7 Hz, 1H), 7.41–7.48 (m, 3H), 7.35 (t, J=7.5 Hz, 2H), 7.13 (t, J=7.5 Hz, 1H), 7.04 (d, J=8.1 Hz, 1H), 7.02 (d, J=2.4 Hz, 1H), 5.61 (dd, J=10.2, 3.3 Hz, 1H), 4.26 (dd, J=18.3, 10.2 Hz, 1H), 3.44 (dd, J=18.2, 3.5 Hz), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1 (C), 198.7 (C), 136.5 (c), 136.0 (C), 133.2 (CH), 132.7 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 125.5 (C), 123.0 (CH), 122.5 (CH), 120.7 (C), 120.3 (CH), 116.3 (CH), 113.1 (C), 42.9 (CH_2), 39.7 (CH), 16.5 (CH_3); MS(EI) m/z (%): 367 (M^+, 22), 262 (34), 105 (100), 77 (26); HRMS: 367.1577 (M^+), $C_{25}H_{21}NO_2$ requires 367.1572.

*4.2.9. 2-(2-Methyl-1H-indol-3-yl)-1,4-diphenylbutane-1,4-dione (**3fa**).* Reaction time: 3 h; (yield 96%); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97–8.01 (m, 4H), 7.88 (s, 1H), 7.68–7.73 (m, 1H), 7.54 (tt, J=7.4, 1.5 Hz, 1H), 7.40–7.46 (m, 3H), 7.32 (t, J=7.4 Hz, 2H), 7.19–7.23 (m, 1H), 7.08–7.13 (m, 2H), 5.53 (dd, J=9.3, 4.2 Hz, 1H), 4.37 (dd, J=9.3, 4.2 Hz, 1H), 3.28 (dd, J=18.0, 4.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9 (C), 198.9 (C), 136.8 (C), 136.7 (C), 135.2 (C), 133.1 (CH), 132.5 (CH), 132.0 (C), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.3 (C), 121.3 (CH), 119.8 (CH), 118.5 (CH), 110.3 (CH), 108.2 (C), 40.6 (CH_2), 40.1 (CH), 12.2 (CH_3); MS(EI) m/z (%): 367 (M^+, 40), 263 (19), 262 (95), 105 (100), 77 (18); HRMS: 367.1577 (M^+), $C_{25}H_{21}NO_2$ requires 367.1572.

*4.2.10. 2-(1-Methyl-1H-indol-3-yl)-1,4-diphenylbutane-1,4-dione (**3ga**).* Reaction time: 3 h; (yield 85%); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (dd, J=7.8, 1.5 Hz, 2H), 7.99 (dd, J=7.8, 1.5 Hz, 2H), 7.79 (d, J=7.8 Hz, 1H), 7.55 (tt, J=7.4, 2.1 Hz, 1H), 7.41–7.50 (m, 3H), 7.37 (t, J=7.5 Hz, 2H), 7.23–7.31 (m, 2H), 7.16–7.21 (m, 1H), 6.9 (s,

1H), 5.61 (dd, *J*=10.2, 3.6 Hz, 1H), 4.26 (dd, *J*=18.3, 10.2 Hz, 1H), 3.70 (s, 3H), 3.44 (dd, *J*=18.2, 3.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1 (C), 198.7 (C), 137.2 (C), 136.53 (C), 136.49 (C), 133.1 (C), 132.7 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 127.4 (CH), 126.4 (C), 112.0 (CH), 119.5 (CH), 118.7 (CH), 111.5 (C), 109.5 (CH), 43.2 (CH_2), 39.4 (CH), 32.8 (CH_3); MS(EI) *m*/*z* (%): 367 (M^+, 20), 262 (53), 105 (100), 77 (24); HRMS: 367.1575 (M^+), $C_{25}H_{21}NO_2$ requires 367.1572.

*4.2.11. 1,4-Diphenyl-2-(1H-pyrrol-2-yl)butane-1,4-dione (**8**).* Reaction time: 30 min; (yield 74%); mp 128–131 °C (CH_2Cl_2–hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (br s, 1H), 8.07 (dd, *J*=8.0, 1.5 Hz, 2H), 7.96 (dd, *J*=8.0, 1.5 Hz, 2H), 7.59–7.51 (m, 2H), 7.47–7.42 (m, 4H), 6.71–6.69 (m, 1H), 6.12–6.07 (m, 2H), 5.43 (dd, *J*=9.0, 4.5 Hz, 1H), 4.11 (dd, *J*=18.2, 9.2 Hz, 1H), 3.49 (dd, *J*=18.2, 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1 (C), 198.3 (C), 136.4 (C), 136.2 (C), 133.4 (CH), 133.2 (CH), 128.8 (CH), 128.6 (CH), 128.1 (CH), 127.4 (C), 118.3 (CH), 108.8 (CH), 107.2 (CH), 43.3 (CH_2), 41.3 (CH); MS(EI) *m*/*z* (%): 303 (M^+, 10), 198 (22), 105 (100), 77 (41); HRMS: 303.1283 (M^+), $C_{20}H_{17}NO_2$ requires 303.1259.

4.3. Experimental procedure for the cyclization of compounds 3 to furanyl indoles 4

A solution of **3aa** (88.2 mg, 0.25 mmol) and TsOH (4.8 mg, 0.025 mmol) in toluene (10 mL) was heated at 80 °C until completion (5 h, TLC). Then, the solvent was removed under reduced pressure and the concentrated chromatographed on silica gel eluting with hexane–diethyl ether (95:5) to give furanyl indole **4aa** (68.7 mg, 82%).

*4.3.1. 3-(2,5-Diphenylfuran-3-yl)-1H-indole (**4aa**).* Reaction time: 5 h; (yield 82%); orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (br s, 1H), 7.81 (dd, *J*=8.0, 1.5 Hz, 2H), 7.70 (dd, *J*=8.4, 1.5 Hz, 2H), 7.50–7.41 (m, 4H), 7.32–7.18 (m, 6H), 7.11 (dd, *J*=7.5, 0.9 Hz, 1H), 6.90 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2 (C), 148.2 (C), 136.1 (C), 131.5 (C), 130.7 (C), 128.7 (CH), 128.3 (CH), 127.4 (CH), 127.0 (CH), 126.5 (C), 125.5 (CH), 123.8 (CH), 122.8 (CH), 122.4 (CH), 120.4 (CH), 120.0 (CH), 117.0 (C), 111.2 (CH), 110.7 (CH), 109.8 (C); MS(EI) *m*/*z* (%): 335 (M^+, 100), 306 (11), 230 (34); HRMS: 335.1301 (M^+), $C_{24}H_{17}NO$ requires 335.1310.

*4.3.2. 3-(2,5-Di-p-tolylfuran-3-yl)-1H-indole (**4ab**).* Reaction time: 20 h; (yield 92%); orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (br s, 1H), 7.69 (d, *J*=8.1 Hz, 2H), 7.58 (d, *J*=8.1 Hz, 2H), 7.50 (d, *J*=7.8 Hz, 1H), 7.44 (d, *J*=8.1 Hz, 1H), 7.27–7.22 (m, 4H), 7.13–7.05 (m, 3H), 6.82 (s, 1H), 2.40 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 152.1 (C), 148.1 (C), 137.1 (C), 136.7 (C), 136.1 (C), 129.4 (CH), 128.9 (CH), 128.1 (C), 126.6 (C), 125.4 (CH), 124.5 (C), 123.7 (CH), 123.6 (C), 122.8 (CH), 122.3 (CH), 120.4 (CH), 119.9 (CH), 116.2 (C), 111.2 (CH), 109.2 (CH), 21.3 (CH_3), 21.3 (CH_3); MS (EI) *m*/*z* (%): 363 (M^+, 100), 244 (14); HRMS: 363.1624 (M^+), $C_{26}H_{21}NO$ requires 363.1623.

*4.3.3. 3-(2,5-Diphenylfuran-3-yl)-7-methyl-1H-indole (**4ba**).* Reaction time: 5 h; (yield 92%); brown solid, mp 135–140 °C (CH_2Cl_2–hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (br s, 1H), 7.82 (dd, *J*=8.0, 1.5 Hz, 2H), 7.71 (dd, *J*=8.4, 1.2 Hz, 2H), 7.44 (dd, *J*=7.7 Hz, 2H), 7.36–7.17 (m, 8H), 7.10 (dd, *J*=8.25, 1.4 Hz, 2H), 6.90 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 152.2 (C), 148.2 (C), 134.5 (C), 131.5 (C), 130.7 (C), 129.4 (CH), 129.0 (CH), 128.7 (CH), 128.2 (CH), 127.3 (CH), 126.9 (CH), 125.5 (CH), 124.0 (CH), 123.8 (CH), 122.9 (CH), 119.8 (CH), 117.2 (C), 110.8 (CH), 110.7 (CH), 109.2 (C), 21.4 (CH_3); MS (EI) *m*/*z* (%): 349 (M^+, 100), 243 (19); HRMS: 349.1464 (M^+), $C_{25}H_{19}NO$ requires 349.1467.

*4.3.4. 3-(2,5-Diphenylfuran-3-yl)-7-methyl-1H-indole (**4ea**).* Reaction time: 7 h; (yield 93%); orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (br s, 1H), 7.81 (dd, *J*=7.8, 1.2 Hz, 2H), 7.71 (dd, *J*=8.4, 1.5 Hz, 2H), 7.44 (dd, *J*=7.7 Hz, 2H), 7.37–7.19 (m, 6H), 7.08–7.01 (m, 2H), 6.89 (s, 1H), 2.56 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 152.2 (C), 148.1 (C), 135.7 (C), 131.5 (C), 130.7 (C), 128.7 (CH), 128.3 (CH), 127.4 (CH), 127.0 (CH), 126.1 (C), 125.5 (CH), 123.8 (CH), 122.9 (CH), 122.5 (CH), 120.4 (C), 120.2 (CH), 118.1 (CH), 117.2 (C), 110.7 (CH), 110.3 (C), 16.6 (CH_3); MS (EI) *m*/*z* (%): 349 (M^+, 100), 244 (19); HRMS: 349.1467 (M^+), $C_{25}H_{19}NO$ requires 349.1467.

4.4. Experimental procedure for the cyclization of compounds 3 to pyrrolyl indoles 5

A solution of **3aa** (88.2 mg, 0.25 mmol) and ammonium acetate (385 mg, 5.0 mmol) in a mixture of EtOH (4 mL) and $CHCl_3$ (6 mL) was heated at 50 °C until completion (24 h, TLC). Then, the solvent was removed under reduced pressure and the concentrated chromatographed on silica gel eluting with hexane–diethyl ether (97:3) to give pyrrolyl indole **5aa** (65.2 mg, 78%).

*4.4.1. 3-(2,5-Diphenyl-1H-pyrrol-3-yl)-1H-indole (**5aa**).* Reaction time: 24 h; (yield 78%); yellow solid, mp 205–208 °C (ether–hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (br s, 1H), 8.00 (br s, 1H), 7.52–7.48 (m, 3H), 7.38–7.30 (m, 5H), 7.21–7.08 (m, 6H), 7.03 (d, *J*=2.4 Hz, 1H), 6.99 (td, *J*=7.5, 0.9 Hz, 1H), 6.72 (d, *J*=3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1 (C), 133.4 (C), 132.4 (C), 132.1 (C), 129.4 (C), 129.0 (CH), 128.6 (CH), 127.0 (CH), 126.7 (CH), 126.4 (CH), 123.8 (CH), 122.2 (CH), 122.0 (CH), 120.5 (CH), 119.6 (CH), 116.4 (C), 112.0 (C), 111.0 (CH), 109.7 (CH); MS(EI) *m*/*z* (%): 334 (M^+, 100), 333 (16); HRMS: 334.1464 (M^+), $C_{24}H_{18}N_2$ requires 334.1470.

*4.4.2. 3-(2,5-Bis(3,4-dimethylphenyl)-1H-pyrrol-3-yl)-1H-indole (**5ac**).* Reaction time: 54 h; (yield 67%); orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (br s, 1H), 8.03 (br s, 1H), 7.63 (d, *J*=7.8 Hz, 1H), 7.37–7.34 (m, 2H), 7.30 (d, *J*=7.8 Hz, 1H), 7.24 (s, 1H), 7.21–7.05 (m, 6H), 6.97 (d, *J*=7.8 Hz, 1H), 6.73 (d, *J*=2.7 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H), 2.21 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 137.0 (C), 136.6 (C), 136.1 (C), 134.7 (C) 131.9 (C), 131.1 (C), 130.2 (C), 130.1 (CH), 129.7 (CH), 129.0 (C), 127.7 (CH), 127.1 (C), 125.1 (CH), 124.5 (CH), 122.2 (CH), 121.8 (CH), 121.2 (CH), 120.6 (CH), 119.4 (CH), 115.7 (C), 112.2 (C), 110.9 (CH), 108.9 (CH), 19.9 (CH_3), 19.8 (CH_3), 19.5 (CH_3), 19.5 (CH_3); MS (EI) *m*/*z* (%): 390 (M^+, 100), 389 (11), 388 (10); HRMS: 390.2104 (M^+), $C_{28}H_{26}N_2$ requires 390.2096.

*4.4.3. 3-(2,5-Diphenyl-1H-pyrrol-3-yl)-5-methoxy-1H-indole (**5ca**).* Reaction time: 48 h; (yield 90%); orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (br s, 1H), 8.08 (br s, 1H), 7.59 (d, *J*=7.5 Hz, 2H), 7.45–7.39 (m, 4H), 7.28–7.16 (m, 6H), 6.83–6.81 (m, 2H), 6.75 (d, *J*=2.7 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.6 (C), 133.6 (C), 132.5 (C), 131.2 (C), 129.1 (C), 128.8 (CH), 128.4 (CH), 126.8 (CH), 126.7 (C), 126.2 (CH), 123.8 (CH), 122.9 (CH), 116.5 (C), 116.5 (C), 112.2 (CH), 111.7 (C), 111.6 (CH), 111.6 (CH), 109.4 (CH), 101.9 (CH), 55.5 (CH_3); MS (EI) *m*/*z* (%): 364 (M^+, 100); HRMS: 364.1576 (M^+), $C_{25}H_{20}N_2O$ requires 364.1576.

*4.4.4. 3-(2,5-Diphenyl-1H-pyrrol-3-yl)-2-methyl-1H-indole (**5fa**).* Reaction time: 48 h; (yield 71%); violet oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (br s, 1H), 7.84 (br s, 1H), 7.58 (dd, *J*=8.0, 1.5 Hz, 2H), 7.52 (d, *J*=7.8 Hz, 1H), 7.40 (t, *J*=7.7 Hz, 2H), 7.36–7.29 (m, 3H), 7.25–7.19 (m, 3H), 7.16–7.10 (m, 2H), 7.05 (td, *J*=7.5, 1.1 Hz, 1H), 6.73 (d, *J*=3.0 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 135.5 (C), 133.7 (C), 132.4 (C), 132.0 (C), 131.6 (C), 129.9 (C), 128.9 (CH), 128.8 (C), 128.6 (CH), 126.3 (CH), 126.1 (CH), 125.7 (CH), 123.7 (CH), 121.1 (CH), 119.5 (CH), 119.4 (CH), 116.2 (C), 110.4 (CH), 110.0 (CH), 108.5 (C), 12.4 (CH_3);

MS (EI) *m*/*z* (%): 348 (M^+, 100), 347 (12); HRMS: 348.1625 (M^+), $C_{25}H_{20}N_2$ requires 348.1626.

4.5. Experimental procedure for the cyclization of compounds 3 to *N*-allyl pyrrolyl indoles 6

Allylamine (0.3 mL, 0.4 mmol) and acetic acid (0.23 mL) were added to a solution of compound **3aa** (70.1 mg, 0.2 mmol) in a mixture of EtOH (4 mL) and $CHCl_3$ (6 mL). The reaction mixture was heated at 50 °C until completion (20 h, TLC). The solvent was removed under reduced pressure and the concentrated chromatographed on silica gel eluting with hexane–diethyl ether (95:5) to give **6aa** (50.9 mg, 68%).

*4.5.1. 3-(1-Allyl-2,5-diphenyl-1H-pyrrol-3-yl)-1H-indole (**6aa**).* Brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.86 (br s, 1H), 7.57 (dd, *J*=7.8, 1.2 Hz, 2H), 7.50–7.42 (m, 3H), 7.38–7.30 (m, 6H), 7.03 (tt, *J*=7.5, 0.9 Hz, 1H), 6.89 (tt, *J*=7.4, 0.9 Hz, 1H), 6.79 (d, *J*=2.4 Hz, 1H), 6.57 (s, 1H), 5.64 (ddt, *J*=17.1, 10.5, 4.5 Hz, 1H), 4.94 (dd, *J*=10.8, 1.4 Hz, 1H), 4.59 (dd, *J*=17.1, 1.5 Hz, 1H), 4.54–4.52 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9 (C), 135.4 (CH), 134.1 (C), 133.23 (C), 133.21 (C), 131.2 (C), 130.9 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 127.4 (CH), 126.8 (CH), 126.3 (C), 122.1 (CH), 120.7 (CH), 119.4 (CH), 118.5 (CH), 116.5 (C), 115.5 (CH_2), 111.3 (CH), 110.2 (C), 109.6 (CH), 46.8 (CH_2); MS(EI) *m*/*z* (%): 374 (M^+, 100), 334 (18), 333 (60), 332 (26), 230 (20); HRMS: 374.1783 (M^+), $C_{27}H_{22}N_2$ requires 374.1783.

4.6. Experimental procedure for the cyclization of compounds 3 to thienyl indoles 7

A solution of Lawesson reagent (60 mg, 0.15 mmol) and compound **3aa** (44.2 mg, 0.125 mmol) in toluene (2 mL) was heated at 90 °C under nitrogen until completion (30 min, TLC). The solvent was removed under reduced pressure and the concentrated chromatographed on silica gel eluting with hexane–EtOAc (95:5) to give thienyl indole **7aa** (30.7 mg, 79%).

*4.6.1. 3-(2,5-Diphenylthiophen-3-yl)-1H-indole (**7aa**).* Reaction time: 30 min; (yield 79%); yellow solid, mp 133–137 °C (CH_2Cl_2–hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (br s, 1H), 7.68 (d, *J*=7.8 Hz, 2H), 7.55 (d, *J*=8.1 Hz, 1H), 7.53 (s, 1H), 7.44–7.39 (m, 5H), 7.32 (d, *J*=7.5 Hz, 1H), 7.28–7.20 (m, 4H), 7.09 (t, *J*=7.5 Hz, 1H), 7.04 (d, *J*=2.4 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 142.3 (C), 137.5 (C), 136.0 (C), 134.9 (C), 134.3 (C), 132.0 (C), 128.9 (CH), 128.8 (CH), 128.4 (CH), 127.5 (CH), 127.2 (CH), 126.9 (CH), 126.5 (C), 125.6 (CH), 123.2 (CH), 122.3 (CH), 120.3 (CH), 120.0 (CH), 112.6 (C), 111.1 (CH); MS(EI) *m*/*z* (%): 351 (M^+, 100), 350 (29), 349 (26); HRMS: 351.1087 (M^+), $C_{24}H_{17}NS$ requires 351.1082.

*4.6.2. 3-(2,5-Bis(4-fluorophenyl)thiophen-3-yl)-1H-indole (**7ad**).* Reaction time: 30 min; (yield 80%); orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (br s, 1H), 7.68 (dd, *J*=8.9, 5.3 Hz, 2H), 7.51 (d, *J*=8.1 Hz, 1H), 7.43 (s, 1H), 7.42–7.18 (m, 4H), 7.11 (t, *J*=8.7 Hz, 2H), 7.10 (tt, *J*=7.0, 0.9 Hz, 1H), 7.03 (d, *J*=2.4 Hz, 1H), 6.93 (t, *J*=8.9 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F}=246.0 Hz, C), 162.0 (d, J_{C-F}=245.7 Hz, C), 141.2 (C), 135.9 (C), 132.1 (C), 130.8 (d, J_{C-F}=3.8 Hz, C), 130.46 (d, J_{C-F}=7.5 Hz, CH), 130.45 (d, J_{C-F}=3.0 Hz, C), 128.2 (CH), 127.3 (d, J_{C-F}=8.3 Hz, C), 126.8 (CH), 126.3 (C), 125.3 (C), 123.2 (CH), 122.4 (CH), 120.1 (CH), 115.9 (d, J_{C-F}=21.8 Hz, CH), 115.4 (d, J_{C-F}=21.0 Hz, CH), 112.3 (C), 111.2 (CH); MS (EI) *m*/*z* (%): 387 (M^+, 100), 386 (19); HRMS: 387.0917 (M^+), $C_{24}H_{15}F_2NS$ requires 387.089.

*4.6.3. 5-Bromo-3-(2,5-diphenylthiophen-3-yl)-1H-indole (**7da**).* Reaction time: 30 min; (yield 78%); brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (br s, 1H), 7.68 (d, *J*=8.7, 1.5 Hz, 2H), 7.62–7.61 (m, 1H), 7.46 (s, 1H), 7.44–7.23 (m, 10H), 7.03 (d, *J*=2.7 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 142.6 (C), 137.9 (C), 134.6 (C), 134.5 (C), 134.1 (C), 131.2 (C), 129.0 (CH), 128.9 (CH), 128.4 (CH), 128.3 (C), 127.6 (CH), 127.4 (CH), 126.5 (CH), 125.7 (CH), 125.2 (CH), 124.3 (CH), 122.8 (CH), 113.4 (C), 112.5 (CH), 112.3 (C); MS (EI) *m*/*z* (%): 431 (M+2, 100), 429 (M^+, 96), 350 (16), 349 (50); HRMS: 429.0189 (M^+), $C_{24}H_{16}BrNS$ requires 429.0187.

*4.6.4. 3-(2,5-Diphenylthiophen-3-yl)-1-methyl-1H-indole (**7ga**).* Reaction time: 30 min; (yield 68%); orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J*=7.7, 1.5 Hz, 2H), 7.50 (d, *J*=8.1 Hz, 1H), 7.50 (s, 1H), 7.46–7.39 (m, 5H), 7.33 (t, *J*=7.9 Hz, 2H), 7.27–7.21 (m, 3H), 7.07 (td, *J*=7.5, 1.2 Hz, 1H), 6.92 (d, *J*=2.4 Hz, 1H), 3.76 (3H, s); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 142.2 (C), 137.0 (C), 136.8 (C), 135.0 (C), 134.3 (C), 132.1 (C), 128.9 (CH), 128.8 (CH), 128.4 (CH), 127.8 (CH), 127.5 (CH), 127.11 (CH), 127.08 (CH), 126.9 (C), 125.6 (CH), 121.7 (CH), 120.4 (CH), 119.5 (CH), 111.0 (C), 109.2 (C), 32.8 (CH_3); MS (EI) *m*/*z* (%): 365 (M^+, 100), 349 (14); HRMS: 365.1239 (M^+), $C_{25}H_{19}NS$ requires 365.1238.

*4.6.5. 2-(2,5-Diphenylfuran-3-yl)-1H-pyrrole (**9**).* Reaction time: 30 min; (yield 54%); violet oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (br s, 1H), 7.75 (dd, *J*=7.2, 1.5 Hz, 2H), 7.69 (dd, *J*=7.2, 1.5 Hz, 2H), 7.44–7.38 (m, 4H), 7.34–7.28 (m, 2H), 6.83 (s, 1H), 6.80–6.78 (m, 1H), 6.41–6.39 (m, 1H), 6.31 (q, *J*=2.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 152.8 (C), 147.0 (C), 131.2 (C), 130.4 (C), 128.7 (CH), 128.7 (CH), 127.8 (CH), 127.6 (CH), 126.1 (CH), 124.2 (C), 123.8 (CH), 117.9 (CH), 116.5 (C), 109.4 (CH), 108.2 (CH), 107.9 (CH); MS (EI) *m*/*z* (%): 285 (M^+, 100), 284 (26), 256 (10), 180 (18); HRMS: 285.1159 (M^+), $C_{20}H_{15}NO$ requires 285.1154.

*4.6.6. 2,5-Diphenyl-3-(1H-pyrrol-2-yl)-1H-pyrrole (**10**).* Reaction time: 30 min; (yield 52%); blue oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (br s, 1H), 7.67 (br s, 1H), 7.50 (dd, *J*=8.8, 1.1 Hz, 2H), 7.40–7.18 (m, 9H), 6.60 (d, *J*=3.0 Hz, 1H), 6.09 (t, *J*=3.0 Hz, 1H), 5.89 (t, *J*=3.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 138.3 (C), 132.8 (C), 132.3 (C), 132.1 (C), 128.9 (CH), 128.9 (CH), 127.7 (C), 127.2 (CH), 127.2 (CH), 126.5 (CH), 126.4 (CH), 123.8 (CH), 116.1 (C), 106.9 (CH), 105.3 (CH), 104.1 (CH); MS (EI) *m*/*z* (%): 284 (M^+, 89), 283 (45), 282 (15); HRMS: 284.1309 (M^+), $C_{20}H_{16}N_2$ requires 284.1313.

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