# Organic & Biomolecular Chemistry

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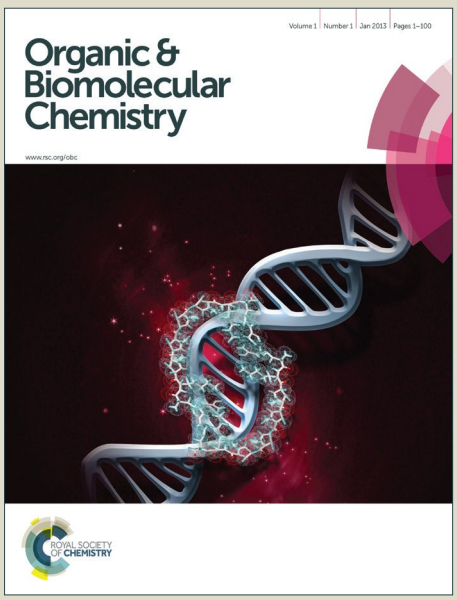





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ARTICLE

# Synthesis of two distinct pyrrole moiety-containing arenes from nitroanilines using Paal-Knorr followed by indium-mediated reaction

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Synthesis of arenes substituted with two different substituted-pyrrole moieties was investigated. A Paal-Knorr condensation reaction of nitroanilines with 1,4-diketone to nitrophenyl-1*H*-pyrroles followed by indium-mediated reduction-triggered coupling reaction with another kind of 1,4-diketone resulted in two distinct pyrrole-containing arenes, variously substituted 1-((1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrroles, in reasonable yield.

## Introduction

The pyrrole nucleus has received prominent attention as a key structural moiety because it is one of the most important heterocyclic units for medicinal and pharmaceutical chemistry, and pyrrole derivatives exhibit a broad spectrum of biological activity.[1] Moreover, pyrrole has also been applied in various areas; polypyrroles have been applied as conducting polymers,[2] while pyrrolic macrocycles, such as calix[4]pyrroles, have been used as anion receptors.[3] As pyrrole derivatives are used in a wide-range of applications, developing more efficient synthetic methods is still one of the main issues. However, the Paal-Knorr condensation remains as the most attractive and the easiest methods for the synthesis of pyrroles. Therefore, the use of 1,4-dicarbonyls has become one of the most versatile and widely applied methods among the many strategies that have been developed.[4] In addition to the Paal-Knorr reaction, various synthetic methods have been developed to synthesize pyrroles, including Hantzsch synthesis,[5] tandem reaction,[6] rearrangement of *o*-vinyl oximes,[7] [3+2] cycloaddition of 1,3-dipolar reagents with alkynes,[8] hydroamination of diynes,[9] and olefin cross-metathesis,[10] to mention a few.[11] Recently, we developed a new synthetic strategy of one-pot reductive condensation reactions using nitroarenes and 1,4-dicarbonyls that resulted in the efficient production of pyrroles,[12] which was an extension of our various indium-mediated reductive heterocyclizations via the reductive cyclization reaction of nitroarenes to nitrogen-containing heterocycles.[13] None of known methods involve this kind of one-pot reductive condensation reactions starting from nitroarenes and 1,4-dicarbonyls to pyrroles. With the success of new synthetic strategy, we could drive one step further to a more challenging synthesis for new and useful organic materials, which could not be prepared by Paal-Knorr reaction or any other methods.

There have been few reports for the synthesis and applications of bis-pyrrole-arenes.[14] Most of the known bis-pyrrole arenes consist of two identical pyrrole rings, undoubtedly because synthetic methods are not well developed other than the Paal-Knorr reaction of diaminobenzenes with 1,4-diketones. In addition to bis-pyrrole arene derivatives, there are structurally similar terphenyl compounds, some of which are used as organic scintillation materials for fast neutron detection in nuclear physics, medical, and other basic sciences.[15] *para*-Terphenyl, 1,4-diphenylbenzene, is a representative organic scintillator being used for scintillation detectors.[16] However, the number of scintillators which have proven practical is small because of the lack of useful, cheap, and a large volume synthetic methods.

With successful reductive condensation reactions of nitroarenes and 1,4-dicarbonyls toward pyrroles,[12] we became interested in the synthesis of *para*-terphenyl type heterocyclic compounds, ((1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrroles, which could potentially be useful organic materials as biologically active compounds and/or organic scintillation materials. Only a few of ((1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrroles are known because there are no production methods available other than the Paal-Knorr reaction starting from diaminoarenes.[16] However, if nitroanilines are used as substrates for the Paal-Knorr type condensation reaction, first with 1,4-dicarbonyls followed by our newly developed indium reduction-triggered intermolecular heterocyclization with other 1,4-dicarbonyls that are different from the first 1,4-dicarbonyls structurally, plenty of unsymmetrical bis-pyrrole arene derivatives, which are mostly unknown compounds, could be easily synthesized. In addition, nitroanilines are less expensive than diaminobenzenes or dinitrobenzenes, which will be one of the additional merits to access the reactions in the field of process chemistry.

In this study we report the development of a new synthetic strategy to terphenyl type heterocyclic compounds using Paal-Knorr condensation reaction followed by indium reduction-triggered intermolecular heterocyclization starting from nitroanilines with 1,4-dicarbonyls that could produce two distinct pyrrole moiety-containing arenes, with an aim at increasing the number of potential organic scintillators.

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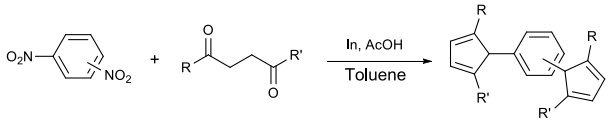
†Electronic Supplementary Information (ESI) available: Copies of NMR spectra of ((1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrrole compounds. See DOI: xxxxxx/xxxxxxxxxx

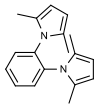
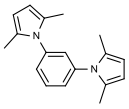
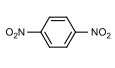
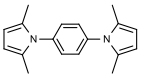
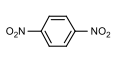
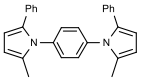
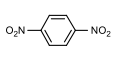
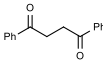
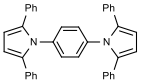
## Results and discussion

Prior to trying to develop the reaction of nitroanilines to produce two distinct pyrrole moiety-containing arenes, we examined the reductive coupling reactions of dinitrobenzenes with 1,4-diketones to produce a bis-pyrrole product using indium reduction-triggered intermolecular heterocyclization that was developed by us for one-pot pyrrole synthesis from nitroarenes;[12] *i.e.,* dinitrobenzene (1 equiv)/1,4-diketone (2 equiv)/indium (8 equiv)/acetic acid (20 equiv) in toluene (20 mL). In those reactions, the corresponding bis-pyrrole-arene product was obtained in reasonable yield except for 1,2-dinitrobenzene (Table 1). In the case of 1,2-dinitrobenzene, unexpectedly, 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)aniline was obtained as a major product after 2 hrs (68%) at 80 °C without any of the desired 1,1'-(1,3-phenylene)bis[2,5-dimethyl-1*H*-pyrrole]. Even with a prolonged reaction time of up to 24 hrs, the 1,1'-(1,3-phenylene)bis[2,5-dimethyl-1*H*-pyrrole] (**1**) was only obtained in 5% yield and 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)benzenamine (**1'**) remained as the major product (58%) (entry 1, Table 1). At reflux for 3 hrs, yield of **1** was improved to 15%, however, **1'** was the major product yet again (50%). It is believed that too much closely congested bis-pyrrole product formation may prevent the second pyrrole ring formation from reduced amino intermediate with 1,4-diketone and leave an amino group instead of one more heterocyclization. As proposed in our previous paper for pyrrole ring formation,[12] dinitrobenzene would be transformed into diaminobenzene intermediate, which would couple with 1,4-diketone to make a bis-pyrrole product except 1,2-dinitrobenzene. For the diketone part, phenyl-substituted diketones such as 1-phenyl-1,4-pentanedione (entry 4, Table 1) or 1,4-diphenyl-1,4-butanedione (entry 5, Table 1) was less reactive than 2,5-hexanedione (entries 1-3, Table 1) and required higher reaction temperature. As the use of 1,4-diphenyl-1,4-butanedione showed poor results as 1,2-dinitrobenzene, both may not be advantageous for synthetic application. Overall, except the reaction of sterically congested 1,2-dinitrobezene or 1,4-diphenyl-1,4-butanedione, our protocol could be used as an alternative method for the preparation of two identical pyrrole-substituted bis-pyrrole-arenes in addition to other well-known methods starting from diaminobenzenes.

In addition to dinitroarene substrates, nitroaniline is a good alternative candidate as a starting substrate for the synthesis of bis-pyrrole-arene derivatives since nitroaniline would be transformed into diaminoarene by an in-situ indium-mediated reductive reaction that is an intermediate for the follow-up heterocyclization with 1,4-diketone in the reaction medium. Therefore, we examined several indium-mediated reductive reaction triggered heterocyclizations of 4-nitroaniline with representative 1,4-diketones that were used for reductive coupling reactions of dinitrobenzenes and summarized in Table 2. Those reactions of 4-nitroaniline with 1,4-diketones in the presence of indium (4 equiv) and acetic acid (10 equiv) in toluene presented similar trend to the experiments that were done with dinitrobenzenes with 1,4-diketones. Again, reaction using 1,4-diphenyl-1,4-dutadione was not very successful and produced a low yield contaminated with other by-products (entry 3, Table 2) while reactions using 2,5-hexanedione (entry 1) or 1-phenyl-1,4-hexanedione (entry 2) produced a desired bis-pyrrole product even with improved yield compared to reactions of dinitrobenzenes with 1,4-diketones. Those results gave us a useful clue for developing the synthesis of two distinct pyrrole moiety-containing arene derivatives.

**Table 1** Indium-mediated reductive heterocyclization of dinitrobenzene (1 mmol) with a 1,4-diketone compound (2 equiv) in the presence of indium (8 equiv)/acetic acid (20 equiv) toward ((1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrroles in toluene (20 mL)



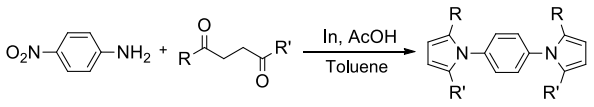

| Entry | Substrate | Diketone | Time (h) | Temp (°C) | Product | Yield[a] (%) |
|---|---|---|---|---|---|---|
| 1 |  |  | 24<br>(3) | 80<br>(reflux) |  | (**1**) 5<br>(15) |
| | | | | |  | (**1'**) 58<br>(50) |
| 2 |  |  | 5 | 80 |  | (**2**) 70 |
| 3 |  |  | 3 | 80 |  | (**3**) 62 |
| 4 |  |  | 12 | reflux |  | (**4**) 57 |
| 5 |  |  | 24 | reflux |  | (**5**) 19[b] |

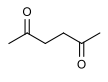
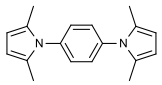
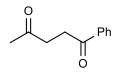
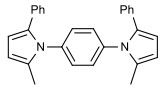
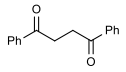
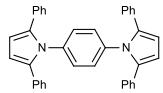
[a]Isolated yield.

[b]11% of 1-(4-aminophenyl)-2,5-diphenyl-1*H*-pyrrole was isolated.

Nitroaniline substrates can be used not only for the preparation of two identical pyrrole-substituted symmetrical bis-pyrrole arenes, but also for the preparation of its unsymmetrical analogs, in other words, two distinguishable pyrrole containing terphenyl type heterocyclic compounds with a simple synthetic strategy. Thus, we designed the two step synthesis with a combination of the Paal-Knorr reaction followed by an indium-mediated heterocyclization reaction starting from nitroanilines for the synthesis of more diverse bis-pyrrole substituted arenes. By applying the Paal-Knorr condensation reaction to nitroanilines with 1,4-diketones, the amino group of nitroanilines can be transformed into pyrrole moiety with an unreacted nitro group. Then indium-mediated heterocyclization reaction of this intermediate in the presence of another 1,4-diketone can introduce additional pyrrole moiety onto the nitro site of the intermediate, which resulted in unsymmetrical bis-pyrrole-arene molecule if the 1,4-diketones for each step are not identical. With this two-step synthesis, many new bis-pyrrole-arenes can be synthesized, which were not known because of the lack of applicable synthetic methods.

**Table 2** Indium-acetic acid-mediated reductive heterocyclization of nitroanilines (1 mmol) with a 1,4-diketone (2 equiv) in the presence of indium (4 equiv) and acetic acid (10 equiv) in toluene (5 mL)



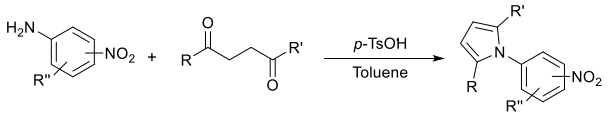

| Entry | Diketone | Time (h) | Temp (°C) | Product | Yield[a] (%) |
|---|---|---|---|---|---|
| 1 |  | 24 | 80 |  (**3**) | 87 |
| 2 |  | 24 | reflux |  (**4**) | 75 |
| 3 |  | 24 | reflux |  (**5**) | 23[b] |

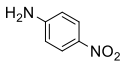
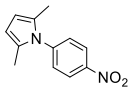
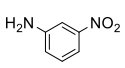
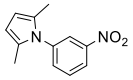
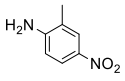
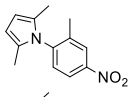
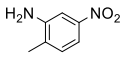
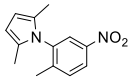
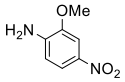
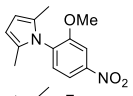
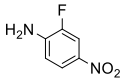
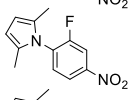
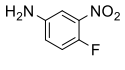
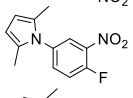
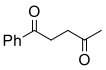
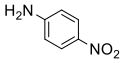
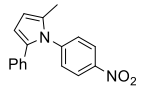
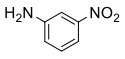
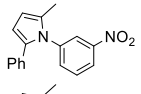
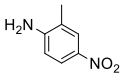
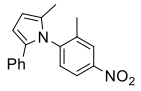
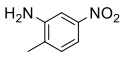
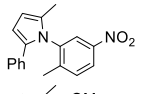
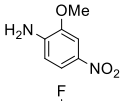
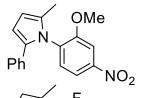
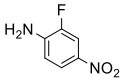
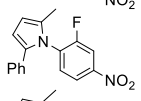
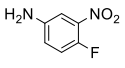
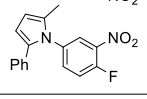
[a]Isolated yield.

[b]5% of 1-(4-aminophenyl)-2,5-diphenyl-1*H*-pyrrole was isolated.

First, we tried a one-batch reaction with stepwise adoption of two different reaction condition, *i.e.*, the Paal-Knorr and indium-mediated reaction, without isolation of the intermediate after the Paal-Knorr reaction since both the Paal-Knorr and indium-mediated reactions can be done in the same solvent and comparable acidic condition. Thus, the Paal-Knorr reaction of nitroaniline (1 mmol) with 2,5-hexanedione (1 equiv) in the presence of a catalytic amount of *p*-TsOH·$H_2O$ (0.02 equiv) in toluene at reflux was done for 1.5 hrs. For the dehydration of the reaction medium, the reaction was done with an excess amount of $MgSO_4$ (2-3 mmol) in the beginning. After cooling down the reaction mixture, indium (4 equiv), acetic acid (10 equiv) and 1-phenyl-1,4-pentanedione were added to the reaction mixture directly and refluxed again for 4 hrs. The reaction went well with a good yield (74%, NMR yield with an internal standard, 1,3,5-trimethoxybenzene), however, flash column chromatography purification from the small amount of undesired symmetrically substituted bis-pyrrole-benzene derivatives such as 2,5-dimethyl-1-(3-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrrole (**3**, ~3%) and 2,5-diphenyl-1-(3-(2,5-diphenyl-1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrrole (**4**, ~3%) was a problem because of $R_f$ value similarity to a desired product, 2,5-dimethyl-1-(4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrrole. Accordingly, we were obliged to change our strategy to the two step synthesis. Consequently, after completion of the Paal-Knorr reaction of nitroaniline under the above-mentioned conditions, the reaction mixture was worked up and purified with conventional methods. The isolated intermediate, 2,5-dimethyl-1-(3-nitrophenyl)-1*H*-pyrrole (**6**) (97% yield, Table 3, entry 1) was then reacted with 1-phenyl-1,4-pentanedione (1 equiv) in the presence of indium (4 equiv) and acetic acid (10 equiv) in toluene at reflux for 4 hrs. The desired product, 2,5-dimethyl-1-(4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrrole, was obtained in 92% yield without any problems. Technically the stepwise two step synthesis is better for purification than the one-batch reaction so the two step reaction was chosen for the two different pyrrole-substituted bis-pyrrole-arene derivative syntheses.

**Table 3** Paal-Knorr reaction of nitroanilines (1 mmol) with 1,4-diketones (1 mmol) toward variously substituted (1*H*-pyrrol-1-yl)nitroarenes under toluene (2.5 mL) reflux reaction conditions[a]




| Entry | Diketone | Substrate | Time (h) | Product | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 |  |  | 1.5 |  (**6**) | 97 |
| 2 | |  | 2 |  (**7**) | 93 |
| 3 | |  | 1 |  (**8**) | 99 |
| 4 | |  | 1.5 |  (**9**) | 96 |
| 5 | |  | 2.5 |  (**10**) | 94 |
| 6 | |  | 4 |  (**11**) | 87[c] |
| 7 | |  | 1.5 |  (**12**) | 94 |
| 8 |  |  | 3 |  (**13**) | 93 |
| 9 | |  | 8 |  (**14**) | 96 |
| 10 | |  | 4 |  (**15**) | 95 |
| 11 | |  | 8 |  (**16**) | 91 |
| 12 | |  | 3.5 |  (**17**) | 88 |
| 13 | |  | 2 |  (**18**) | 50[d] |
| 14 | |  | 2.5 |  (**19**) | 93 |

[a]0.02 mmol of *p*-TsOH·$H_2O$ was used with an excess amount of $MgSO_4$ (2-3 mmol) as a dehydrating reagent.

[b]Isolated yield.

[c]0.04 mmol of *p*-TsOH·$H_2O$ was used with an excess amount of $MgSO_4$ (2-3 mmol).

[d]Starting substrate still remained after 24 hrs.

Thus, the Paal-Knorr reaction of variously substituted nitroanilines (1 equiv) with 1,4-diketones (1 equiv) in the presence of catalytic amount of *p*-TsOH·$H_2O$ (0.02 equiv) with a dehydrating reagent ($MgSO_4$ (2-3 equiv)) was carried out under toluene reflux to obtain diverse (1*H*-pyrrol-1-

yl)nitroarenes. By applying this Paal-Knorr reaction, fourteen pyrrole-ring substituted nitrobenzene derivatives were prepared in high yields (Table 3). As the nitro group can be transformed into a pyrrole ring by our indium-mediated reductive cyclization reaction, these derivatives can be useful intermediates for the synthesis of two different interesting pyrrole-substituted bis-pyrrolearenes.

With the (1*H*-pyrrol-1-yl)nitroarene derivatives prepared, indium-mediated heterocyclizations for another pyrrole ring construction with 1,4-diketones, which are different from the first 1,4-diketones of the Paal-Knorr reaction, were completed in the presence of indium (4 equiv) and acetic acid (10 equiv) in toluene at reflux (1-phenyl-1,4-pentanedione) or at 80 °C (2,5-hexanedione) (Table 4). In most cases, heterocyclization for the second pyrrole ring formation was successful with reasonably good yield (70–92%). While the Paal-Knorr reactions of variously substituted nitroanilines with 1,4-diketones was not affected by electronic effect of the substitution, reductive heterocyclization reactions of substituted (1*H*-pyrrol-1-yl)nitroarene derivatives seemed to be affected by the substitution. Strong inductive effect of fluoro-substitution of the substrate slowed the reaction time and/or product yield (Table 4, entries 6, 7, 13, 14), which indicates that inductive effect may decrease the reactivity of the indium-mediated reductive reaction of nitro group to amino intermediate prior to heterocyclization reactions with 1,4-diketones.

Since the shape of terphenyl type bis-pyrrole-arene compounds is not well-documented and would be an important clue for its application, the exact structure of a representative compound, 2,5-dimethyl-1-[4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (**20**), was elucidated by X-ray crystallography.[17] The molecular structure with an atom-labeling scheme is shown in Fig. 1. The ORTEP plot of molecule **20** displays its structure, in which the 2-methyl-5-phenyl-substituted pyrrolyl ring (**A**) is twisted out of the plane of the central aryl ring (**B**) by dihedral angles of 72.11° and the 2,5-dimethyl-substituted pyrrolyl ring (**C**) is twisted out of the plane of the central aryl ring (**B**) by dihedral angles of -68.55° on its substituent. The dihedral angles of two pyrrole rings may change to some extent if there is an additional substituent on the aryl ring or two pyrrole rings are at different positions, like para- or meta-position, and will resulted in slight physical property changes, which will be of interest to material chemists for application.

## Conclusions

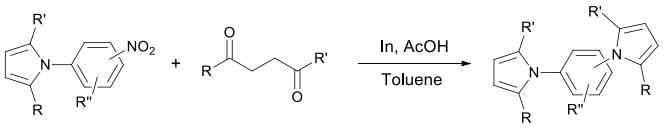
In conclusion, we developed a simple method for the synthesis of terphenyl type heterocyclic compounds, arene derivatives substituted with two different pyrrole moieties in a molecule, using the Paal-Knorr condensation reaction of nitroanilines with 1,4-dicarbonyls toward (1*H*-pyrrol-1-yl)nitroarenes followed by indium reduction-triggered intermolecular heterocyclization of the nitro group with another kind of 1,4-dicarbonyls that could produce two distinct pyrrole moiety-containing arenes. With this unique method many ((1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrrole derivatives, which up until now were mostly unknown compounds because of the lack of synthetic method or strategy for production, could be synthesized with ease.

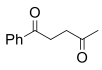
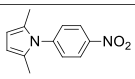
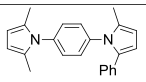
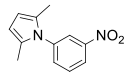
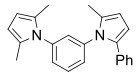
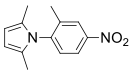
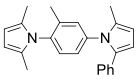
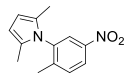
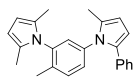
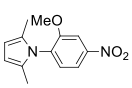
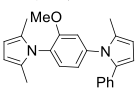
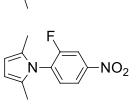
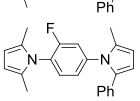
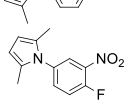
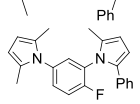
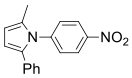
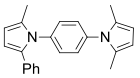
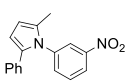
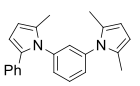
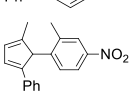
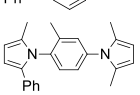
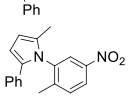
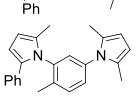
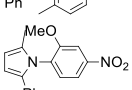
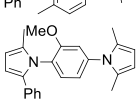
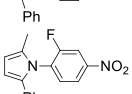
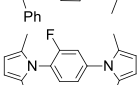
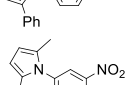
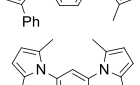
## Experimental

### General considerations

Most chemical reagents were purchased from Sigma-Aldrich Co. (St. Louis, Missouri, USA) and were used without further purification. Solvents were purchased and dried using standard methods. $^1$H and $^{13}$C NMR spectra were recorded at 400 and 100 MHz, respectively (JEOL, Tokyo, Japan). Chemical shifts are reported in parts per million relative to the residual solvent as an internal standard or a TMS. GC–MS spectra were recorded on an Agilent 6890N GC connected to an Agilent 5975 mass selective detector (Hewlett-

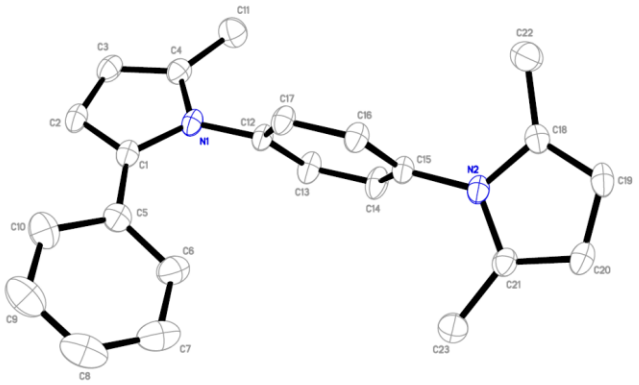
**Table 4** Indium-mediated heterocyclization of variously substituted (1*H*-pyrrol-1-yl)nitroarenes (1mmol) with 1,4-diketone(1 equiv) in the presence of indium (4 equiv) and acetic acid (10 equiv) in toluene (5 mL) at reflux (1-phenyl-1,4-pentanedione) or at 80 °C (2,5-hexanedione)




| Entry | Diketone | Substrate | | Time (h) | Product | | Yield[a] (%) |
|---|---|---|---|---|---|---|---|
| 1 |  |  | (**6**) | 4 |  | (**20**) | 92 |
| 2 | |  | (**7**) | 4 |  | (**21**) | 92 |
| 3 | |  | (**8**) | 8 |  | (**22**) | 85 |
| 4 | |  | (**9**) | 9 |  | (**23**) | 84 |
| 5 | |  | (**10**) | 8 |  | (**24**) | 70 |
| 6 | |  | (**11**) | 9 |  | (**25**) | 69 |
| 7 | |  | (**12**) | 12 |  | (**26**) | 71 |
| 8 |  |  | (**13**) | 8 |  | (**20**) | 79 |
| 9 | |  | (**14**) | 4 |  | (**21**) | 90 |
| 10 | |  | (**15**) | 2 |  | (**27**) | 81 |
| 11 | |  | (**16**) | 2 |  | (**28**) | 78 |
| 12 | |  | (**17**) | 5 |  | (**29**) | 77 |
| 13 | |  | (**18**) | 12 |  | (**30**) | 40[b] |
| 14 | |  | (**19**) | 12 |  | (**31**) | 55[b] |

[a]Isolated yield.

[b]Aniline derivative and several unidentified by-products were observed.




A B C

Fig. 1. Molecular structure of 2,5-dimethyl-1-[4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (**20**) with an atom-labeling scheme.

Packard Co., Palo Alto, California, USA). Infrared (IR) spectra were recorded using an MB104 FTIR (ABB Bomem, Inc., Zurich, Switzerland). The elemental analysis data were obtained by the Thermo Scientific Flash 2000 (Thermo Fisher Scientific, USA). Melting points were determined on an electrothermal apparatus and were uncorrected. All the major products were isolated by flash column chromatography on silica gel (230–400 mesh ATSM, Merck & Co., Inc., Whitehouse Station, New Jersey, USA) using a mixed solvent eluent (ethyl acetate/hexane). Analytical thin-layer chromatography (TLC) was performed using 0.25 mm silica gel $60F_{254}$ precoated-glass plate. For single-crystal X-ray structure determinations, data were collected at 50 KV, 30 mA using Bruker SMART Apex II X-ray Diffractometer (Bruker Nano Analytics, Berlin, Germany) equipped with Mo tube, graphite-monochromator, and CCD area-detector. Bruker SHELXTL software was used for structure analysis.

### General procedures

**General procedure for the indium-mediated reaction of dinitrobenzenes with 1,4-diketones to obtain ((1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrroles.** Dinitrobenzene derivative (1.0 mmol) and indium powder (920 mg, 8.0 mmol) was placed in toluene (20 mL), and was added acetic acid (1.144 mL, 20 mmol) and 1,4-diketone (2.0 mmol) in toluene (20 mL) to the mixture. The reaction mixture was stirred at 80 °C (2,5-hexanedione) or at reflux (1-phenyl-1,4-pentadione or 1,4-diphenyl-1,4-butanedione) under nitrogen. After the reaction was completed, the reaction mixture was diluted with ethyl acetate (30 mL) or dichloromethane (30 mL), filtered through Celite, poured into 10% aqueous $NaHCO_3$ solution (30 mL), and then the aqueous layer was extracted with ethyl acetate (30 mL × 3) or dichloromethane (30 mL × 3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The residue was eluted with ethyl acetate/hexane (v/v = 5/95) through a neutral silica gel column to give the corresponding pyrroles. The structures of the pyrroles were characterized by $^1$H NMR, $^{13}$C NMR, FTIR, and GC–MS and were mostly known compounds. For unknown compounds, HRMS data were additionally reported.

**2,5-Dimethyl-1-(2-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrrole (1).**[18,19] Yield 5%. White solid, mp 148–150 °C (lit.[18] mp 132 °C). TLC (30% ethyl acetate/hexane) $R_f$ 0.80; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42–7.37 (m, 2H), 7.25–7.18 (m, 2H), 5.75 (s, 4H), 1.81 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 135.6, 131.1, 129.0, 127.8, 106.9, 12.9; IR (NaCl) 3114, 3047, 2927, 2854, 1581, 1450, 1392 cm$^{-1}$; GC–MS *m/z* (rel intensity) 264 ($M^+$, 93), 249 (100), 233 (17), 296 (14), 168 (12), 154 (10).

**2-(2,5-dimethyl-1*H*-pyrrol-1-yl)benzeneamine (1').**[18] Yield 58%. Pale yellow solid, mp 63–64 °C (lit.[18] mp 75 °C). TLC (30% ethyl acetate/hexane) $R_f$ 0.67; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.20 (td, 1H, *J* = 7.8, 1.5 Hz), 7.05 (dd, 1H, *J* = 7.8, 1.5 Hz), 6.81–6.78 (m, 2H), 5.93 (s, 2H), 3.43 (s, 2H), 1.98 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.1, 129.32, 129.28, 128.4, 124.4, 118.2, 115.5, 105.8, 12.3; IR (NaCl) 3476, 3367, 3101, 2920, 1616, 1504, 1461, 1400 cm$^{-1}$; GC–MS *m/z* (rel intensity) 186 ($M^+$, 63), 171 (100), 156 (10), 144 (9), 92 (11), 65 (13), 51 ( 11).

**2,5-Dimethyl-1-(3-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrrole (2).**[19] Yield 70%. White solid, TLC (30% ethyl acetate/hexane) $R_f$ 0.80; mp 102–103 °C (lit.[19a] mp 99–100 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, 1H, *J* = 7.9 Hz), 7.26 (dd, 2H, *J* = 7.9, 1.8 Hz), 7.09 (t, 1H, *J* = 1.8 Hz), 5.91 (s, 4H), 2.07 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.6, 129.4, 128.6, 128.0, 127.4, 106.1, 13.0; IR (NaCl) 3105, 3055, 2923, 1600, 1523, 1492, 1454, 1396, 1311 cm$^{-1}$; GC–MS *m/z* (rel intensity) 264 ($M^+$, 100), 249 (20), 233 (9), 168 (10), 154 (12), 131 (16).

**2,5-Dimethyl-1-(4-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrrole (3).**[19] Yield 62%. White solid, TLC (20% ethyl acetate/hexane) $R_f$ 0.60; mp 250–251 °C (lit.[19a] mp 256–257 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 4H), 5.93 (s, 4H), 2.08 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.2, 128.78, 128.77, 106.0, 13.0; IR (KBr) 3109, 3033, 2987, 2923, 1515, 1406 cm$^{-1}$; GC–MS *m/z* (rel intensity) 264 ($M^+$, 100), 249 (10), 233 (5), 168 (10), 154 (15), 131 (20).

**1,1'-*p*-phenylenebis[2-methyl-5-phenylpyrrole] (4).** Yield 57%. White solid, TLC (20% ethyl acetate/hexane) $R_f$ 0.78; mp 237–238 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.19–7.05 (m, 14H), 6.36 (d, 2H, *J* = 3.2 Hz), 6.10 (d, 2H, *J* = 3.2 Hz), 2.15 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.4, 134.1, 133.2, 131.5, 128.9, 127.9, 127.7, 125.8, 108.9, 107.8, 13.2; IR (NaCl) 3051, 2974, 1596, 1512, 1446, 1392, 1216 cm$^{-1}$; GC–MS *m/z* (rel intensity) 388 ($M^+$, 100) , 373 (5), 230 (5), 194 (11), 115 (5); HRMS *m/z* calc. for $C_{28}H_{24}N_2$ 388.1939, found 388.1932.

**1,1'-*p*-phenylenebis[2,5-diphenylpyrrole] (5)**. Yield 19%. White solid, TLC (30% ethyl acetate/hexane) $R_f$ 0.73; mp 310–311 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.20–7.16 (m, 12H), 7.08–7.04 (m, 8H), 6.99 (bd s, 4H), 6.42 (bd s, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.8, 135.8, 133.0, 129.2, 128.7, 127.9, 126.3, 110.2; IR (KBr) 3066, 1600, 1515, 1485, 1388, 1330 cm$^{-1}$; HRMS *m/z* calc. for $C_{38}H_{28}N_2$ 512.2252, found 512.2247.

**General procedure for the indium-mediated reaction of nitroanilines with 2,5-hexanedione or 1-phenyl-1,4-pantanedione to obtain ((1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrroles.** Nitroaniline derivative (1.0 mmol) and indium powder (460 mg, 4.0 mmol) in toluene (1 mL) was placed, and was added 1,4-diketone (1.0 mmol) and acetic acid (0.572 mL, 10 mmol) in toluene (4 mL) to the mixture. The reaction mixture was stirred at 80 °C or reflux under nitrogen. After the reaction was completed, the reaction mixture was diluted with ethyl acetate (30 mL) or dichloromethane (30 mL), filtered through Celite, poured into 10% $NaHCO_3$ (30 mL), and then

the aqueous layer was extracted with ethyl acetate (30 mL x 3) or dichloromethane (30 mL x 3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The residue was eluted with ethyl acetate/hexane (v/v = 5/95) for through a silica gel column to give the corresponding pyrroles (3, 87%; 4, 75%; 5, 23%).

**General procedure for the Paal-Knorr reaction of nitroanilines with 2,5-hexanedione or 1-phenyl-1,4-pantanedione to obtain (1*H*-pyrrol-1-yl)nitroarenes.** Nitroaniline derivative (1.0 mmol) was added to a mixture of catalytic amount of *p*-TsOH·$H_2O$ (0.02 equiv) and $MgSO_4$ (2-3 equiv) in toluene (1.5 mL), followed by the addition of 2,5-hexanedione or 1-phenyl-1,4-pentanedione (1.0 mmol) in toluene (1 mL). The reaction mixture was stirred at reflux under a nitrogen atmosphere. After the reaction was completed, the reaction mixture was diluted with ethyl acetate (30 mL) and was poured into 10% aqueous $NaHCO_3$ solution. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3) or dichloromethane (30 mL x 3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The residue was eluted with hexane for most derivatives or ethyl acetate/hexane (v/v = 5/95) for pyrrole-ring substituted nitrobenzene derivatives through a neutral silica gel column to give the corresponding pyrroles. The structures of the pyrroles were characterized by $^1$H NMR, $^{13}$C NMR, FTIR, and GC–MS. For unknown compounds, HRMS data were additionally reported.

**2,5-Dimethyl-1-(4-nitrophenyl)-1*H*-pyrrole (6).**[20, 21] Yield 97%. Yellow solid, mp 131–132 °C (lit.[20] mp 145 °C; lit.[21] mp 125-129 °C). TLC (30% ethyl acetate/hexane) $R_f$ 0.78; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, 1H, *J* = 9.0 Hz), 7.39 (d, 1H, *J* = 9.0 Hz), 5.96 (s, 1H), 2.07 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 146.8, 144.8, 128.8, 128.5, 124.5, 107.4, 13.0; IR (NaCl) 3105, 3074, 2923, 2854, 1593, 1519, 1492, 1396, 1338 cm$^{-1}$; GC–MS *m/z* (rel intensity) 216 ($M^+$, 100), 201 (5), 169 (46), 154 (30), 128 (9), 115 (5), 76 (1), 50 (11).

**2,5-Dimethyl-1-(3-nitrophenyl)-1*H*-pyrrole (7).**[22] Yield 93%. Yellow solid, mp 84–85 °C (lit.[22] mp 84–85 °C). TLC (30% ethyl acetate/hexane) $R_f$ 0.56; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22–8.18 (m, 1H), 8.04 (t, 1H, *J* = 1.8 Hz), 7.60 (t, 1H, *J* = 8.0 Hz), 7.52–7.48 (m, 1H), 5.87 (s, 2H), 1.98 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.6, 140.1, 134.2, 129.9, 128.6, 123.2, 122.4, 106.9, 13.0; IR (NaCl) 3097, 2927, 2854, 1535, 1485, 1350 cm$^{-1}$; GC–MS *m/z* (rel intensity) 216 ($M^+$,100), 201 (5), 169 (30), 154 (33), 128 (8), 77 (8).

**2,5-Dimethyl-1-(2-methyl-4-nitrophenyl)-1*H*-pyrrole (8).**[21] Yield 99%. Yellow solid, mp 51–52 °C (lit.[21] mp 101-103 °C). TLC (30% ethyl acetate/hexane) $R_f$ 0.78; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, 1H, *J* = 2.0 Hz). 8.09 (dd, 1H, *J* = 8.5, 2.0 Hz), 7.27 (d, 1H, *J* = 8.5 Hz), 5.88 (s, 2H), 1.98 (s, 3H), 1.84 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.5, 144.2, 139.3, 130.0, 127.8, 125.7, 121.9, 106.5, 17.2, 12.4; IR (NaCl) 3105, 2923, 1589, 1527, 1492, 1350 cm$^{-1}$; GC–MS *m/z* (rel intensity) 230 ($M^+$, 100), 215 (63), 198 (8), 183 (32), 169 (52), 154 (30); HRMS *m/z* calc. for $C_{13}H_{14}N_2O_2$ 230.1055, found 230.1035.

**2,5-Dimethyl-1-(2-methyl-5-nitrophenyl)-1*H*-pyrrole (9).**[22] Yield 96%. Yellow solid, mp 103–104 °C (lit.[22] mp 103–104 °C). TLC (30% ethyl acetate/hexane) $R_f$ 0.85; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, 1H, *J* = 8.5, 2.3 Hz), 8.08 (d, 1H, *J* = 2.3 Hz), 7.51 (d, 1H, *J* = 8.5 Hz), 5.95 (s, 2H), 2.05 (s, 3H), 1.92 (s, 6H); 7.49 (d, 1H, *J* = 8.3 Hz), 5.95 (s, 2H), 2.05 (s, 3H), 1.91 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 146.8, 145.5, 139.2, 131.3, 127.9, 124.2, 123.3, 106.5, 17.3, 12.4 ; IR (NaCl) 3109, 2985, 2912, 1589, 1523, 1492, 1342 cm$^{-1}$; GC–MS *m/z* (rel intensity) 230 ($M^+$, 100), 215 (56), 198 (14), 183 (24), 169 (40), 154 (26).

**1-(2-Methoxy-4-nitrophenyl)-2,5-dimethyl-1*H*-pyrrole (10).**[21] Yield 94%. Yellow solid, mp 99–100 °C (lit.[21] mp 68–70 °C). TLC (30% ethyl acetate/hexane) $R_f$ 0.75; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, 1H, *J* = 8.5, 2.2 Hz), 7.91 (d, 1H, *J* = 2.2 Hz), 7.33 (d, 1H, *J* = 8.5 Hz), 5.95 (s, 2H), 2.93 (s, 3H), 1.97 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.2, 148.2, 133.6, 130.6, 128.9, 115.9, 107.1, 106.3, 56.3, 12.4; IR (NaCl) 3109, 2927, 2854, 1589, 1527, 1458, 1346, 1235 cm$^{-1}$; GC–MS *m/z* (rel intensity) 246 ($M^+$, 100), 231 (54), 215 (8), 199 (27), 185 (21), 154 (14); HRMS *m/z* calc. for $C_{13}H_{14}N_2O_3$ 246.1004, found 246.1009.

**1-(2-Fluoro-4-nitrophenyl)-2,5-dimethyl-1*H*-pyrrole (11).** Yield 87%. Yellow solid, mp 78–79 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.79; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.19–8.13 (m, 2H), 7.48–7.43 (m, 1H), 5.98 (s, 2H), 2.04 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.7 (d, *J* = 255.7 Hz), 147.7 (d, *J* = 7.4 Hz), 133.0 (d, *J* = 13.2 Hz), 131.1, 128.9, 119.7 (d, *J* = 3.3 Hz), 112.7 (d, *J* = 25.7 Hz), 107.5, 12.4 (d, *J* = 1.7 Hz); IR (NaCl) 3058, 2989, 1608, 1539, 1500, 1454, 1350, 1218 cm$^{-1}$; GC–MS *m/z* (rel intensity) 234 ($M^+$, 93), 204 (100), 187 (65), 172 (22), 148 (31), 109 (18); HRMS *m/z* calc. for $C_{12}H_{11}FN_2O_2$ 234.0805, found 234.0788.

**1-(4-Fluoro-3-nitrophenyl)-2,5-dimethyl-1*H*-pyrrole (12).** Yield 94%. Yellow solid, mp 107–108 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.75; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, 1H, *J* = 6.6, 2.6 Hz), 7.53–7.48 (m, 1H), 7.45–7.37 (m, 1H), 5.93 (s, 2H), 2.05 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.4 (d, *J* = 265.7 Hz), 135.4 (d, *J* = 4.1 Hz), 135.2 (d, *J* = 8.3 Hz), 128.6, 125.6 (d, *J* = 2.5 Hz), 119.1 (d, *J* = 21.5 Hz), 119.0, 107.0, 12.9; IR (NaCl) 3082, 2923, 1593, 1542, 1446, 1353 cm$^{-1}$; GC–MS *m/z* (rel intensity) 234 ($M^+$,100), 188 (55), 172 (28), 94 (16), 51 (12); HRMS *m/z* calc. for $C_{12}H_{11}FN_2O_2$ 234.0805, found 234.0789.

**2-Methyl-1-(4-nitrophenyl)-5-phenyl-1*H*-pyrrole (13).** Yield 93%. Yellow solid, mp 102–103 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.71; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, 2H, *J* = 8.8 Hz), 7.29 (d, 2H, *J* = 8.8 Hz), 7.18–7.13 (m, 3H), 7.02 (d, 2H, *J* = 7.1 Hz), 6.37 (d, 1H *J* = 3.4 Hz), 6.14 (d, 1H, *J* = 3.4 Hz), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 146.4, 145.1, 134.4, 132.8, 131.3, 128.9, 128.2, 128.0, 126.3, 124.3, 110.2, 109.1, 13.4; IR (NaCl) 3073, 2923, 1596, 1519, 1496, 1346 cm$^{-1}$; GC–MS *m/z* (rel intensity) 278 ($M^+$, 100), 232 (84), 217 (29), 204 (14), 189 (13), 115 (17), 76 (11); HRMS *m/z* calc. for $C_{17}H_{14}N_2O_2$ 278.1055, found 278.1042.

**2-Methyl-1-(3-nitrophenyl)-5-phenyl-1*H*-pyrrole (14).** Yield 96%. Yellow solid, mp 91–92 °C. TLC (20% ethyl acetate/hexane) $R_f$ 0.70; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.18 (dt, 1H, *J* = 8.0, 1.3 Hz), 8.07 (t, 1H, *J* = 1.3 Hz), 7.51 (t, 1H, *J* = 8.0 Hz), 7.42 (dt, 1H, *J* = 8.0, 1.3 Hz), 7.18–7.09 (m, 3H), 7.02 (dd, 2H, *J* = 8.0, 1.2 Hz), 6.37 (d, 1H, *J* = 3.4 Hz), 6.14 (d, 1H, *J* = 3.4 Hz), 2.18 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.4, 140.5, 134.5, 134.4, 132.7, 131.4, 129.7, 128.2, 128.0, 126.2, 123.1, 122.1, 109.7, 108.6, 13.3; IR (NaCl) 3089, 2923, 1600, 1535, 1481, 1353 cm$^{-1}$; GC–MS *m/z* (rel intensity) 278 ($M^+$, 100), 232 (51), 217 (55), 189 (11), 154 (9), 115 (18), 76 (12); HRMS *m/z* calc. for $C_{17}H_{14}N_2O_2$ 278.1055, found 278.1038.

**2-Methyl-1-(2-methyl-4-nitrophenyl)-5-phenyl-1*H*-pyrrole (15).** Yield 95%. Yellow solid, mp 94–95 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.73; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, 1H, *J* = 8.4, 2.4 Hz), 8.09 (d, 1H, *J* = 2.4 Hz),

7.45 (d, 1H, *J* = 8.5 Hz), 7.14–7.09 (m, 3H), 7.03 (d, 2H, *J* = 7.6 Hz), 6.40 (d, 1H, *J* = 3.4 Hz), 6.15 (d, 1H, *J* = 3.4 Hz), 2.01 (s, 3H), 1.94 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.2, 144.7, 139.0, 134.3, 132.9, 130.7, 130.3, 128.2, 127.0, 126.2, 125.8, 121.7, 109.0, 108.4, 17.5, 12.7; IR (NaCl) 3074, 2923, 1600, 1527, 1446, 1350 cm$^{-1}$; GC–MS *m/z* (rel intensity) 292 ($M^+$,100), 277 (16), 246 (15), 230 (22), 115 (9), 89 (7); HRMS *m/z* calc. for $C_{18}H_{16}N_2O_2$ 292.1212, found 292.1248.

**2-Methyl-1-(6-methyl-3-nitrophenyl)-5-phenyl-1*H*-pyrrole (16).** Yield 91%. Yellow solid, mp 134–135 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.75; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, 1H, *J* = 2.2 Hz), 8.15 (dd, 1H, *J* = 8.3, 2.2 Hz), 7.36 (d, 1H, *J* = 8.3 Hz), 7.16–7.08 (m, 3H), 7.06–7.02 (m, 2H) 6.39 (s, 1H, *J* = 3.4 Hz), 6.15 (s, 1H, *J* = 3.4 Hz), 2.02 (s, 3H), 1.92 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 146.5, 145.2, 139.6, 134.4, 132.9, 131.5, 130.8, 128.2, 127.1, 126.2, 124.4, 123.1, 108.9, 108.3, 17.7, 12.8; IR (NaCl) 3070, 2927, 2854, 1600, 1523, 1442, 1350 cm$^{-1}$; GC–MS *m/z* (rel intensity) 292 ($M^+$, 100), 277 (17), 246 (11), 230 (25), 115 (11), 89 (6); HRMS *m/z* calc. for $C_{18}H_{16}N_2O_2$ 292.1212 found 292.1215.

**1-(2-Methoxy-4-nitrophenyl)-2-methyl-5-phenyl-1*H*-pyrrole (17).** Yield 88%. Yellow solid, mp 119–120 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.70; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85–7.81 (m, 2H), 7.24–7.06 (m, 4H), 7.02 (d, 2H, *J* = 6.8 Hz), 6.37 (d, 1H, *J* = 3.2 Hz), 6.14 (d, 1H, *J* = 3.2 Hz), 3.76 (s, 1H), 2.08 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.8, 147.9, 134.7, 134.3, 133.1, 131.6, 130.6, 128.0, 127.2, 126.1, 115.9, 108.9, 108.1, 107.1, 56.1, 12.5; IR (NaCl) 3093, 2939, 1600, 1527, 1450, 1346, 1257 cm$^{-1}$; GC–MS *m/z* (rel intensity) 308 ($M^+$,100), 293 (12), 262 (16), 231 (11), 115 (7); HRMS *m/z* calc. for $C_{18}H_{16}N_2O_3$ 308.1161 found 308.1147.

**1-(2-Fluoro-4-nitrophenyl)-2-methyl-5-phenyl-1*H*-pyrrole (18).** Yield 50%. Orange solid, mp 101–102 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.71; $^1$H NMR (400 MHz, $CDCl_3$) $^1$H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, 1H, *J* = 9.1, 2.3 Hz), 8.02 (dd, 1H, *J* = 8.5, 2.3 Hz), 7.31–7.25 (m, 1H), 7.19–7.12 (m, 3H), 7.06–7.03 (m, 2H), 6.40 (d, 1H *J* = 3.4 Hz), 6.18 (d, 1H *J* = 3.4 Hz), 2.15 (s, 3H); δ 7.99 (dd, 1H, *J* = 9.1, 2.3 Hz), 7.94 (dd, 1H, *J* = 8.7, 2.3 Hz), 7.21 (t, 1H, *J* = 8.0Hz), 7.12-6.95 (m, 5H), 6.32 (d, 1H *J* = 3.4 Hz), 6.09 (d, 1H *J* = 3.4 Hz), 2.06 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.4 (d, 1H, *J* = 255.7 Hz), 147.4 (d, 1H, *J* = 9.1 Hz), 134.9, 133.6 (d, 1H, *J* = 13.2 Hz), 132.5, 131.4, 128.3, 127.5, 126.6, 119.6 (d, 1H, *J* = 3.3 Hz), 112.6 (d, 1H *J* = 24.8 Hz), 110.0, 109.0, 12.5; IR (NaCl) 3090, 2923, 1604, 1531, 1504, 1350 cm$^{-1}$ GC–MS *m/z* (rel intensity) 296($M^+$, 100), 250 (46), 235 (7), 115 (6), 94 (6); HRMS *m/z* calc. for $C_{17}H_{13}FN_2O_2$ 296.0961 found 296.0961.

**1-(4-Fluoro-3-nitrophenyl)-2-methyl--5-phenyl-1*H*-pyrrole (19).** Yield 93%. Yellow Solid, mp 108–109 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.63; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, 1H, *J* = 6.3, 2.0 Hz), 7.36–7.34 (m, 1H), 7.26–7.11 (m, 6H), 7.03 (d, 2H, *J* = 7.3 Hz), 6.35 (d, 1H, *J* = 2.9 Hz), 6.13 (d, 1H, *J* = 2.9 Hz), 2.18 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.1 (d, *J* = 266.5 Hz), 135.8 (d, *J* = 4.1 Hz), 135.3 (d, *J* = 9.1 Hz), 134.4, 132.5, 131.3, 128.3, 128.1, 126.4, 125.4 (d, *J* = 2.5 Hz), 119.0, 118.8, 109.8, 108.7, 13.3; IR (NaCl) 3093, 2943, 1600, 1531, 1450, 1346 cm$^{-1}$; GC–MS *m/z* (rel intensity) 296 ($M^+$, 100), 250 (48), 235 (45), 207 (7), 115 (11), 94 (11), 63 (5); HRMS *m/z* calc. for $C_{17}H_{13}FN_2O_2$ 296.0961 found 296.0949.

**General procedure for the indium-mediated reaction of (1*H*-pyrrol-1-yl)nitroarenes with 2,5-hexanedione or 1-phenyl-1,4-pantanedione to obtain unsymmetrical ((1*H*-pyrrol-1-yl)phenyl)-1*H*-pyrroles.** Nitrobenzene derivative (1.0 mmol) and indium powder (460 mg, 4.0 mmol) was placed in toluene (2 mL), and was added acetic acid (0.572 mL, 10 mmol) and 2,5-hexanedione (or 1-phenyl-1,4-pentanedione, 1.0 mmol) in toluene (3 mL) to the mixture. The reaction mixture was stirred at 80 °C for 2,5-hexanedione (or reflux for 1-phenyl-1,4-pentanedione) under nitrogen. After the reaction was completed, the reaction mixture was diluted with ethyl acetate (30 mL), filtered through Celite, poured into 10% aqueous $NaHCO_3$ solution (30 mL), and then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The residue was eluted with hexane for most derivatives or ethyl acetate/hexane (v/v = 5/95) for benzonitrile derivatives through a neutral silica gel column to give the corresponding pyrroles. As all of the final products were unknown compounds, the structures of the pyrroles were fully characterized by $^1$H NMR, $^{13}$C NMR, FTIR, GC–MS and HRMS data.

**2,5-Dimethyl-1-[4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (20).** Yield 92% (Table 4, entry1), 79% (entry 8). White solid, mp 161–162 °C. TLC (20% ethyl acetate/hexane) $R_f$ 0.66; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25–7.03 (m, 9H), 6.39 (d, 1H, *J* = 3.4 Hz), 6.14 (d, 1H, *J* = 3.4 Hz), 5.92 (s, 2H), 2.23 (s, 3H), 2.04 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.7, 137.9, 134.2, 133.2, 131.4, 129.1, 128.7, 128.6, 127.8, 127.7, 125.8, 108.8, 107.8, 105.9, 13.3, 12.8; IR (NaCl) 3105, 3058, 2977, 2920, 1600, 1512, 1442, 1392 cm$^{-1}$; GC–MS *m/z* (rel intensity) 326 ($M^+$, 100), 311 (24), 230 (12), 162 (36), 115 (10); HRMS *m/z* calc. for $C_{23}H_{22}N_2$ 326.1783, found 326.1770.

**2,5-Dimethyl-1-[3-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (21).** Yield 92% (Table 4, entry 2), 90% (entry 9). White solid, mp 87–88 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.83; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, 1H, *J* = 7.9 Hz), 7.28 (dt, 1H, *J* = 7.9, 2.0 Hz), 7.16–7.14 (m, 3H), 7.07 (t, 3H, *J* = 2.0 Hz), 6.94 (t, 1H, *J* = 2.0 Hz), 6.34 (d, 1H, *J* = 3.4 Hz), 6.10 (d, 1H, *J* = 3.4 Hz), 5.83 (s, 2H), 2.19 (s, 3H), 1.86 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.1, 139.5, 134.3, 133.3, 131.4, 129.4, 128.68, 128.61, 128.0, 127.9, 127.5, 127.2, 125.8, 108.9, 107.8, 105.8, 13.3, 12.7; IR (NaCl) 3101, 3062, 2974, 2920, 1604, 1492, 1392 cm$^{-1}$; GC–MS *m/z* (rel intensity) 326 ($M^+$,100), 311 (11), 295 (5), 230 (5), 162 (11); HRMS *m/z* calc. for $C_{23}H_{22}N_2$ 326.1783, found 326.1759.

**2,5-Dimethyl-1-[2-methyl-4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (22).** Yield 85%. White solid, mp 127–129 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.84; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.13–7.07 (m, 8H), 6.38 (d, 1H, *J* = 3.4 Hz), 6.11 (d, 1H, *J* = 3.4 Hz), 5.92 (s, 2H), 2.22 (s, 3H), 1.93 (s, 6H), 1.87 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.4, 138.2, 137.3, 134.2, 133.4, 131.4, 130.6, 129.4, 128.0, 127.8, 127.7, 126.8, 125.7, 108.8, 107.7, 105.7, 17.0, 13.2, 12.3; IR (NaCl) 3101, 3058, 2977, 2920, 1604, 1513, 1442, 1419, 1388 cm$^{-1}$; GC–MS *m/z* (rel intensity) 340 ($M^+$,100), 325 (86), 310 (14), 230 (13), 169 (30), 154 (13), 115 (11); HRMS *m/z* calc. for $C_{24}H_{24}N_2$ 340.1939, found 340.1918.

**2,5-Dimethyl-1-[2-methyl-5-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (23).** Yield 84%. yellow oily liquid. TLC (30% ethyl acetate/hexane) $R_f$ 0.83; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, 1H, *J* = 8.0 Hz), 7.21 (dd, 1H, *J* = 8.0, 2.0 Hz), 7.15–7.05 (m, 5H), 6.89 (d, 1H, *J* = 2.0 Hz), 6.32 (d, 1H, *J* = 3.4 Hz), 6.09 (d, 1H, *J* = 3.4 Hz), 5.84 (s, 2H), 2.18 (s, 3H), 1.93 (s, 3H), 1.77 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.8, 136.4, 134.2, 133.4, 131.4, 130.9, 129.0, 128.2, 128.1, 128.0, 127.9, 125.7, 108.7, 107.7, 105.4, 16.7, 13.3, 12.3; IR (NaCl) 3055, 2923, 1612, 1508, 1442, 1392 cm$^{-1}$; GC–MS *m/z* (rel intensity)

340 ($M^+$,100), 325 (96), 309 (22), 230 (14), 169 (27), 154 (15), 115 (11); HRMS *m/z* calc. for $C_{24}H_{24}N_2$ 340.1939, found 340.1939.

**2,5-Dimethyl-1-[2-methoxy-4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl] -1*H*-pyrrole (24).** Yield 70%. Colorless oily liquid. TLC (30% ethyl acetate/hexane) $R_f$ 0.68; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.17–7.06 (m, 6H), 6.90 (dd, 1H, *J* = 8.0, 2.2 Hz) , 6.70 (d, 1H, *J* = 2.2 Hz), 6.39 (d, 1H, *J* = 3.4 Hz), 6.13 (d, 1H, *J* = 3.4 Hz), 3.54 (s, 3H), 2.27 (s, 3H), 1.97 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.0, 140.1, 134.2, 133.3, 131.3, 130.1, 128.9, 127.8, 127.7, 126.5, 125.8, 120.4, 112.8, 108.7, 107.7, 105.3, 55.8, 13.3, 12.3; IR (NaCl) 3070, 2923, 1604, 1519, 1454, 1388 $cm^{-1}$; GC–MS *m/z* (rel intensity) 356 ($M^+$,100), 341 (34), 325 (8), 178 (10), 158 (6), 115 (5), 77 (4); HRMS *m/z* calc. for $C_{24}H_{24}N_2O$ 356.1889, found 340.1884.

**2,5-Dimethyl-1-[2-fluoro-4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (25).** Yield 69%. White solid, mp 158-159 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.79; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25–7.10 (m, 4H), 7.06–7.03 (m, 4H), 6.38 (d, 1H, *J* = 3.2 Hz), 6.13 (d, 1H, *J* = 3.2 Hz), 5.94 (s, 2H), 2.24 (s, 3H), 2.02 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.0 (d, *J* = 252.4 Hz), 140.4 (d, *J* = 9.1 Hz), 134.3, 132.9, 131.3, 130.6 (*J* = 1.7 Hz), 128.9, 128.0, 127.7, 126.1, 125.7 (d, *J* = 13.2 Hz), 124.7 (d, *J* = 3.3 Hz), 116.9 (d, *J* = 22.3 Hz), 109.2, 108.2, 106.3, 13.3, 12.3 ; IR (NaCl) 3051, 2920, 1600, 1519, 1442, 1388 $cm^{-1}$; GC–MS *m/z* (rel intensity) 344 ($M^+$, 100), 329 (7), 248 (4), 172 (14), 15 (4); HRMS *m/z* calc. for $C_{23}H_{21}FN_2$ 344.1689, found 344.1687.

**2,5-Dimethyl-1-[4-fluoro-3-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (26).** Yield 71%. White solid, mp 138–139 °C. TLC (20% ethyl acetate/hexane) $R_f$ 0.70; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, 1H, *J* = 8.8 Hz), 7.19–7.06 (m, 6H), 6.91 (dd, 1H, *J* = 6.8, 2.4 Hz), 6.35 (d, 1H, *J* = 3.4 Hz), 6.12 (d, 1H, *J* = 3.4 Hz), 5.81 (s, 2H), 2.17 (s, 3H), 1.80 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.4 (d, *J* = 251.6 Hz), 135.1 (d, *J* = 4.1 Hz), 134.7, 132.9, 132.1, 130.9, 129.2 (d, *J* = 8.3 Hz), 128.6, 128.1, 127.78 (d, *J* = 14.1 Hz), 127.74, 126.2, 116.8 (d, *J* = 22.3 Hz), 109.2, 108.0, 105.8, 12.6, 12.4 (d, *J* = 2.5 Hz); IR (NaCl) 3063, 2923, 1608, 1442, 1400, 1380 $cm^{-1}$; GC–MS *m/z* (rel intensity) 344 ($M^+$,100), 329 (5), 187 (4), 172 (13) 115 (4); HRMS *m/z* calc. for $C_{23}H_{21}FN_2$ 344.1689, found 344.1693.

**2,5-Dimethyl-1-[3-methyl-4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (27).** Yield 81%. Pale yellow solid, mp 88–89 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.82; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, 1H, *J* = 8.0 Hz), 7.03–6.99 (m, 7H), 6.35 (d, 1H, *J* = 3.4 Hz), 6.07 (d, 1H, *J* = 3.4 Hz), 5.83 (s, 2H), 2.01 (s, 3H), 1.96 (s, 6H). 1.79 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.1, 134.1, 133.5, 130.9, 130.5, 130.0, 128.5, 127.9, 126.9, 126.3, 125.8, 108.3, 107.6, 105.9, 17.3, 12.8, 12.7; IR (NaCl) 3101, 3055, 2977, 2920, 1604, 1512, 1442, 1415, 1384 $cm^{-1}$; GC–MS *m/z* (rel intensity) 340 ($M^+$,100), 325 (50), 309 (11), 263 (10), 230 (13), 170 (24), 154 (10), 115 (10); HRMS *m/z* calc. for $C_{24}H_{24}N_2$ 340.1939, found 340.1926.

**2,5-Dimethyl-1-[4-methyl-3-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (28).** Yield 78%. White solid, mp 148–149 °C. TLC (30% ethyl acetate/hexane) $R_f$ 0.88; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, 1H, *J* = 8.0 Hz), 7.14–7.06 (m, 7H), 6.38 (d, 1H, *J* = 3.4 Hz), 6.11 (d, 1H, *J* = 3.4 Hz), 5.87 (s, 2H), 2.05 (s, 3H), 1.97 (s, 6H), 1.93 (s, 3H); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, 1H, *J* = 7.8 Hz), 7.06-6.99 (m, 7H), 6.30 (d, 1H, *J* = 3.2 Hz), 6.03 (d, 1H, *J* = 3.2 Hz), 5.79 (s, 2H), 1.97 (s, 3H), 1.89 (s, 6H), 1.86 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.2, 137.3, 136.6, 134.2, 133.5,131.2, 130.9, 129.3, 128.6, 128.1, 128.0, 127.3, 125.8, 108.3, 107.6, 105.9, 16.9, 12.7, 12.6; IR (NaCl) 3062, 2923, 1611, 1508, 1446, 1400 $cm^{-1}$; GC–MS *m/z* (rel intensity) 340 ($M^+$, 100), 325 (60), 309 (12), 230 (16), 170 (2), 154 (10), 115 (10); HRMS *m/z* calc. for $C_{24}H_{24}N_2$ 340.1939, found 340.1929.

**2,5-Dimethyl-1-[3-methoxy-4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl] -1*H*-pyrrole (29).** Yield 77%. Colorless oily liquid. TLC (30% ethyl acetate/hexane) $R_f$ 0.67; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.16–7.04 (m, 6H), 6.80–6.77 (m, 2H), 6.79–6.78 (m, 2H), 6.39 (d, 1H, *J* = 3.4 Hz), 6.13 (d, 1H, *J* = 3.4 Hz), 5.92 (s, 2H), 3.62 (s, 3H), 2.15 (s, 6H), 2.06 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.0, 139.6, 134.5, 133.6, 131.7, 130.5, 128.6, 127.7, 127.6, 127.2, 125.7, 120.4, 112.2, 108.0, 107.2, 105.8, 55.8, 12.8, 12.6; IR (NaCl) 3062, 2922, 1604, 1519, 1454, 1388 $cm^{-1}$; GC–MS *m/z* (rel intensity) 356 ($M^+$, 100), 341 (12), 325 (5), 178 (8), 154(4), 115 (5), 77 (4); HRMS *m/z* calc. for $C_{24}H_{24}N_2O$ 356.1889, found 340.1874.

**2,5-Dimethyl-1-[3-fluoro-4-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (30).** Yield 40%. Orange oily liquid. TLC (30% ethyl acetate/hexane) $R_f$ 0.81; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.22–7.02 (m, 8H), 6.97 (dd, 1H, *J* = 8.4, 2.2 Hz), 6.40 (d, 1H, *J* = 3.4 Hz), 6.15 (d, 1H, *J* = 3.4 Hz), 5.91 (s, 1H), 2.19 (s, 3H), 2.04 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.0 (d, *J* = 252.4 Hz), 139.9 (d, *J* = 9.1 Hz), 134.7, 133.0, 131.9, 131.0 (d, *J* = 1.7 Hz), 128.5, 128.0, 127.4, 126.8 (d, *J* = 12.4 Hz), 126.2, 124.4 (d, *J* = 3.3 Hz), 116.6 (d, *J* = 20.7 Hz), 109.0, 108.0, 106.4, 12.8, 12.5 (d, *J* = 2.5 Hz); IR (NaCl) 3058, 2923, 1604, 1515, 1438, 1384 $cm^{-1}$; GC–MS *m/z* (rel intensity) 344 ($M^+$,100), 329 (6), 302 (4), 171 (10), 115 (4); HRMS *m/z* calc. for $C_{23}H_{21}FN_2$ 344.1689, found 344.1694.

**2,5-Dimethyl-1-[2-fluoro-5-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (31).** Yield 55%. Pale yellow solid, mp 142–143 °C. TLC (20% ethyl acetate/hexane) $R_f$ 0.65; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 2H), 7.18–7.05 (m, 5H), 6.97 (dd, 1H, *J* = 6.8, 2.0 Hz), 6.33 (d, 1H, *J* = 3.2 Hz), 6.10 (d, 1H, *J* = 3.2 Hz), 5.86 (s, 2H), 2.19 (s, 2H), 1.85 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.3 (d, *J* = 253.2 Hz), 135.7 (d, *J* = 3.3 Hz), 134.4, 133.1, 131.4, 130.8, 129.4 (d, *J* = 7.4 Hz), 128.9, 128.1, 128.0, 127.0 (d, *J* = 14.1 Hz), 126.0, 116.9, 116.7, 109.0, 107.9, 106.2, 13.2, 12.2 ; IR (NaCl) 3066, 2920, 1608, 1515, 1446, 1388, 1261 $cm^{-1}$; GC–MS *m/z* (rel intensity) 344 ($M^+$,100), 329 (7), 309 (5), 248(4), 172 (1), 115 (4); HRMS *m/z* calc. for $C_{23}H_{21}FN_2$ 344.1689, found 344.1697.

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