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Synthesis of Multisubstituted Pyrroles from Enolizable Aldehydes and Primary Amines Promoted by Iodine

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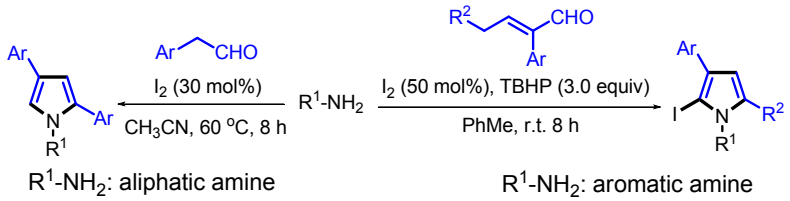


ABSTRACT: 1,2,4-Trisubstituted pyrroles were synthesized from enolizable aliphatic aldehydes and primary aliphatic amines by using iodine as dual Lewis acid/mild oxidant. In the presence of 3.0 equivalent of TBHP, enolizable α,β-unsaturated aldehyde, for example cocal, reacted with aromatic primary amines to form C2-iodized *N*-arylpyrroles. An acetal-containing pyrrole was successfully prepared from 4-aminobutyraldehyde diethyl acetal, which can be converted easily to 5,6,7,8-tetrahydroindolizine derivative.

Introduction

Pyrrole represents an important class of five-member nitrogen-containing naturally occurring heterocycle.[1] It is widely found in natural products,[2] pharmaceutical concerning drugs[3] and other

biologically active utilization ways.[4] Many pyrroles are also used in the synthesis of some functional materials.[5] The major route to access pyrroles relies heavily on chemical synthesis. Traditionally, synthesis of pyrrole can be generally catalogued as classical Knorr reaction,[6] Hantzsch reaction,[7] and Paal-Knorr reaction.[8] As pyrrole ring is an aromatic ring, some convergent reaction strategies were also used to synthesize pyrroles, such as multicomponent reactions,[9] tandem reactions,[10] and transition-metal-catalyzed cyclizations.[11] Recently, C-H bond activation strategy has also been prove to be a suitable choice to construct pyrrole scaffold.[12] Despite large number of efforts have been dedicated into the synthesis of pyrrole skeleton, a practical way that uses easily accessible starting materials, low-cost catalysts, and simple operation procedure is still appealingly needed.

Enolizable aliphatic aldehydes are easily available, and have often been used to construct pyrrole scaffolds.[13] Most of the synthetic protocols reported so far can be classified into the following two approaches:[14] (i) The aldehyde was used as 2C donor to construct pyrrole scaffold: many nitrogen-containing counter-reagents, such as α-amino carbonyl compounds,[15] secondary *N*-propargylamine,[16] vinyl azides,[17] cyclic 1,3-oxazolium-5-olates,[18] and tosylmethylisocyanide (TosMIC),[19] have been used to react with enolizable aliphatic aldehydes, providing various pyrrole derivatives; Some three-component reactions for synthesizing pyrroles were also developed by using a primary amine as nitrogen source and the aliphatic aldehyde as 2C donor;[20] (ii) The aldehyde was used as 4C donor to construct pyrrole scaffold: Scheidt *et al*[21] used hydrazine and some enolizable aliphatic aldehydes as precursors to synthesize *N*-acyl 3,4-disubstituted pyrroles *via* a Piloty-Robinson reaction; Jia *et al*[22] reported a AgOAc-mediated

oxidative coupling reaction of enolizable aliphatic aldehyde and primary amine, which produced 1,3,4-trisubstituted or 3,4-disubstituted pyrroles. While a diverse range of pyrrole derivatives were synthesized by using the aldehyde as 2C donor, the reported protocols to use the aldehyde as 4C donor produced only similar type of pyrrole products. However, the methods to construct pyrrole ring using an aldehyde as a 4C donor avoided the use of complex molecule as substrate, the operation procedure is also quite simple. To enrich the product diversity, a complementary method that can provide new type pyrroles meanwhile uses the aldehyde as 4C donor is therefore still needed. Herein, we report a new way for using the enolizable aliphatic aldehyde as 4C donor to synthesize pyrrole derivative. We found that, by using iodine as catalyst, the aldehyde reacted

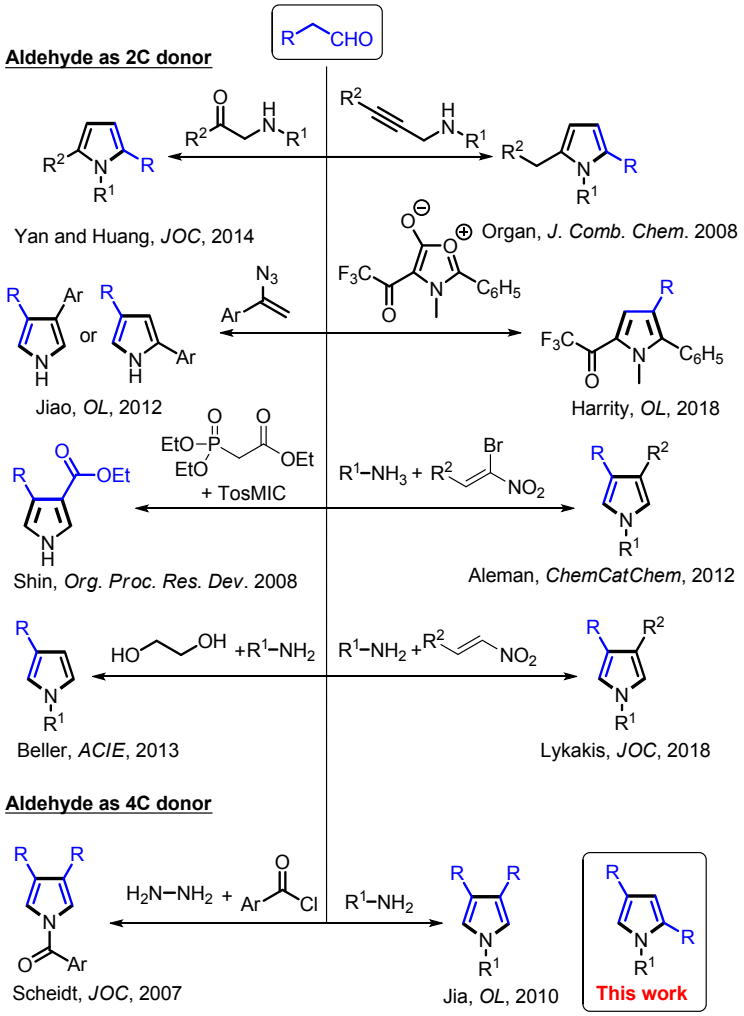


Fig. 1. Typical routes for pyrrole synthesis from enolizable aliphatic aldehydes.

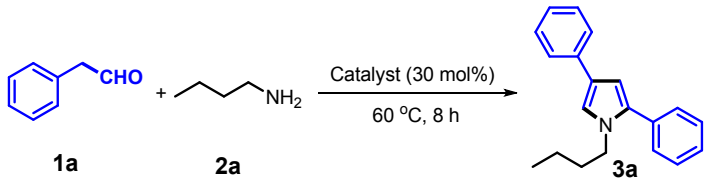
readily with primary aliphatic amine, producing exclusively 1,2,4-trisubstituted pyrroles in good to excellent yields. Iodine acted as dual catalyst/oxidant, and the primary aliphatic amine seemed also not innocent in the catalytic mechanism.

Results and discussion

Initially, 2-phenylacetaldehyde **1a** and *n*-butylamine **2a** were mixed together in a mole ratio of 2/1. The mixture was heated in acetonitrile at 60 °C. We expect that a *N*-butyldiphenylpyrrole can be formed. As shown in **Table 1**, no reaction occurred in the absence of catalyst (entry 1). Strong

Lewis acids, such as $AlCl_3$ and $Sc(OTf)_3$, were proven to be unsuitable for initiating the reaction as pyrrrole product can be hardly detected (entries 2 and 3). Attempts to use $LiBr.H_2O$, a weak Lewis acid, lead to recovery of unreacted starting materials (entry 4). *p*-Toluenesulfonic acid (PTSA), a strong Brönsted acid, cannot initiate this reaction either (entry 5). To our surprise, a 1,2,4-trisubstitued pyrrole derivative **3a** was isolated in 83% yield when 30 mol% of I_2 was used as catalyst (entry 6). It should be noted that such a reaction for converting enolizable aldehyde to 2,4-disubstituted pyrroles has not been reported before. Other iodine-containing species including (diacetoxyiodo)benzene and *N*-iodosuccinimide (NIS), were then screened. It was found that iodine was the best one for promoting the formation of **3a** (entries 7 to 9). Various solvents were then tested. Among the solvents used, CH_3CN clearly stood out because it delivered the desired product in the highest yield (entries 6, 10 to 13). In ethanol, the reaction proceeded also well. However, owing to the formation of diethyl acetal of **1a**, **3a** was only isolated in 78% yield (entry 10). Further investigations revealed that the reaction was also affected by temperature. And it was found that 60 ^oC was enough for ensuring a good yield of **3a** (entries 6 and 14). The reaction proceeded sluggishly when the amount of I_2 was decreased to 10 mol% (entry 15). When the reaction was performed in an inert atmosphere (with protection of argon), the yield reached only 9% (entry 16). This result implies that molecular oxygen was essential for ensuring completion of the reaction. Therefore, the optimal reaction conditions were confirmed to be the followings: **1a** (0.6 mmol), **2a** (0.3 mmol), acetonitrile as solvent (1 mL), 60 ^oC, and 8 h of reaction under air.

Table 1: Condition optimization for the model reaction.[a]



1a 2a 3a

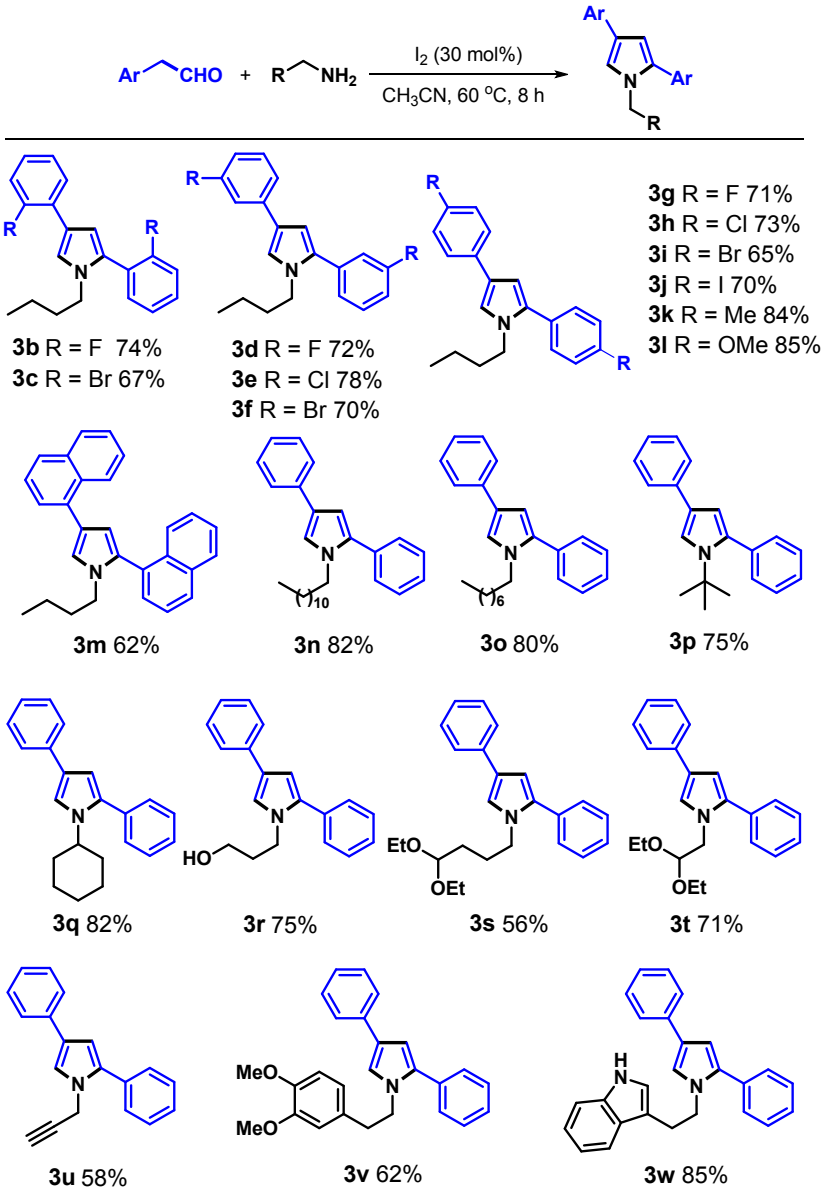
entry	catalyst	solvent	yield (%)
1	—	CH_3CN	0
2	$AlCl_3$	CH_3CN	Trace
3	$Sc(OTf)_3$	CH_3CN	Trace
4	$LiBr.H_2O$	CH_3CN	0
5	PTSA	CH_3CN	Trace
6	I_2	CH_3CN	83
7	KI	CH_3CN	20
8	$PhI(OAc)_2$	CH_3CN	Trace
9	NIS	CH_3CN	45
10	I_2	EtOH	78
11	I_2	Toluene	51
12	I_2	DCE	40
13	I_2	DMSO	31
14[b]	I_2	CH_3CN	36
15[c]	I_2	CH_3CN	39
16[d]	I_2	CH_3CN	9

[a] 1a (0.6 mmol), 2a (0.3 mmol), solvent (1 mL), 8 h, under air. [b] Reaction temperature: 40 °C. [c] Catalyst loading: 10 mol%. [d] The reaction was performed under inert atmosphere.

With the optimized reaction condition in hand, the scope of substrate with respect to the aldehyde component was screened. As evidenced in **Scheme 1**, 2-phenylacetaldehyde derivatives bearing *ortho*, *meta* or *para* substituent in the phenyl ring all participate in the reaction readily, affording the pyrrole products in good to excellent yields (**3b**–**3l**). Compared with the electron-deficient precursor, 2-phenylacetaldehyde possessing an electron-donating group in the phenyl ring produced pyrroles in relatively higher yield (**3k** and **3l**). Naphthalen-1-yl-acetaldehyde also worked well, producing the expected pyrrole **3m** in 62% yield. We also tried to use a linear

aliphatic aldehdye, *n*-butyraldehyde, but failed. Substrate scope with respect to amine component was then investigated. Primary aliphatic amines with long chain readily participated in the reaction (**3n** and **3o**). Aliphatic amines with a bulky group, for example *tert*-butylamine (**3p**) and cyclohexylamine (**3q**), were also able to take part in this reaction. 3-Aminopropanol was proven to be a viable substrate as well (**3r**). Aliphatic amines bearing an acetal group can also be used successfully. Interestingly, although the acetal fragment is known to be susceptible toward acid, it can be delivered into the product molecule without any structural damage (**3s** and **3t**). It should be noted that the presence of electrophilic acetal may facilitate the downstream conversions of the pyrrole products. A *N*-propargylpyrrole **3u** can be synthesized in 58% yield from propargylamine and phenylacetaldehyde. Notably, literature survey stated that this kind of *N*-propargylpyrrole derivative is useful intermediate for the synthesis of pyrrolo[1,2-α]azepine derivative.[23] To access these pyrroles, a three-step method was used by using phenylacetylene and α-aminoacetophenone hydrochloride as starting materials.[24] The present reaction offered thus a cost-effective and an straightforward way to synthesize *N*-propargylpyrroles. 2-(3,4-Dimethoxyphenyl)ethylamine and tryptamine were known to be able to react with an aldehyde to form Pictet-Spengler product.[25] But, under our conditions, these two amines can be converted to the corresponding pyrroles in 62% and 85% yields, respectively (**3v** and **3w**). During the reaction, no Pictet-Spengler reaction product or their downstream derivatives can be detected. We also attempted to use aniline in this pyrrole-forming reaction, but failed. The reasons will be given later.

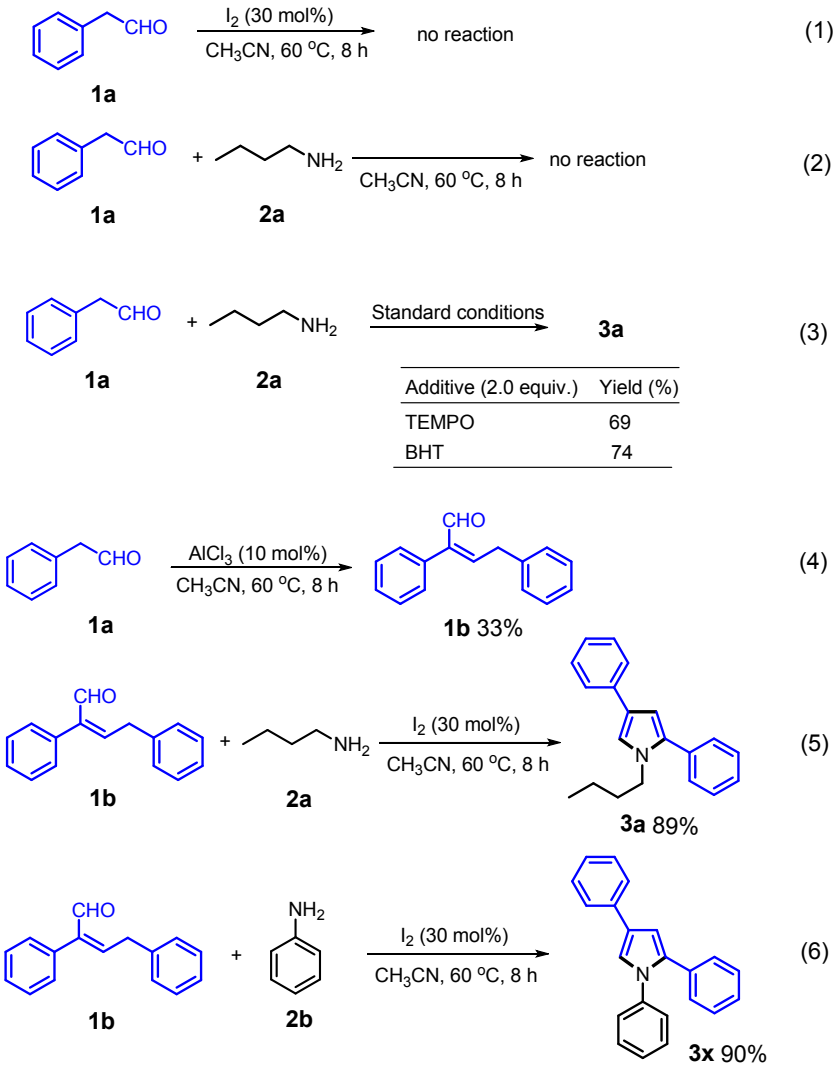
Scheme 1. Substrate scope of the pyrrole synthesis.



To gain insights into this reaction, some control experiments were carried out. Firstly, **1a** was treated with I_2 in the absence of amine. After 8 h of reaction at 60 °C, only unreacted starting material was recovered (**Scheme 2**, equation 1). Heating a mixture of **1a** and **2a** in the absence of I_2 gave no product (equation 2), When some radical scavengers, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 2.0 equiv.) or 2,6-di-*tert*-butyl-4-methylphenol (BHT, 2.0 equiv.), were added to the reaction system, the pyrrole product **3a** was obtained in 69% and 74% yields, respectively (equation 3). These results implies that this transformation may not

involve a radical mechanism. In literature, **1a** can be converted into an α,β-unsaturated aldehyde **1b** in the presence of a strong Lewis acid (e.g. $FeCl_3$)[26] or a strong organic base (e.g. pyrrolidine).[27] We also found that $AlCl_3$ can catalyze the formation of **1b** in the absence of **2a** (equation 4). But, I_2 alone cannot catalyze the self-condensation of **1a**. We also tried to isolate **1b**

Scheme 2. Some control experiments.

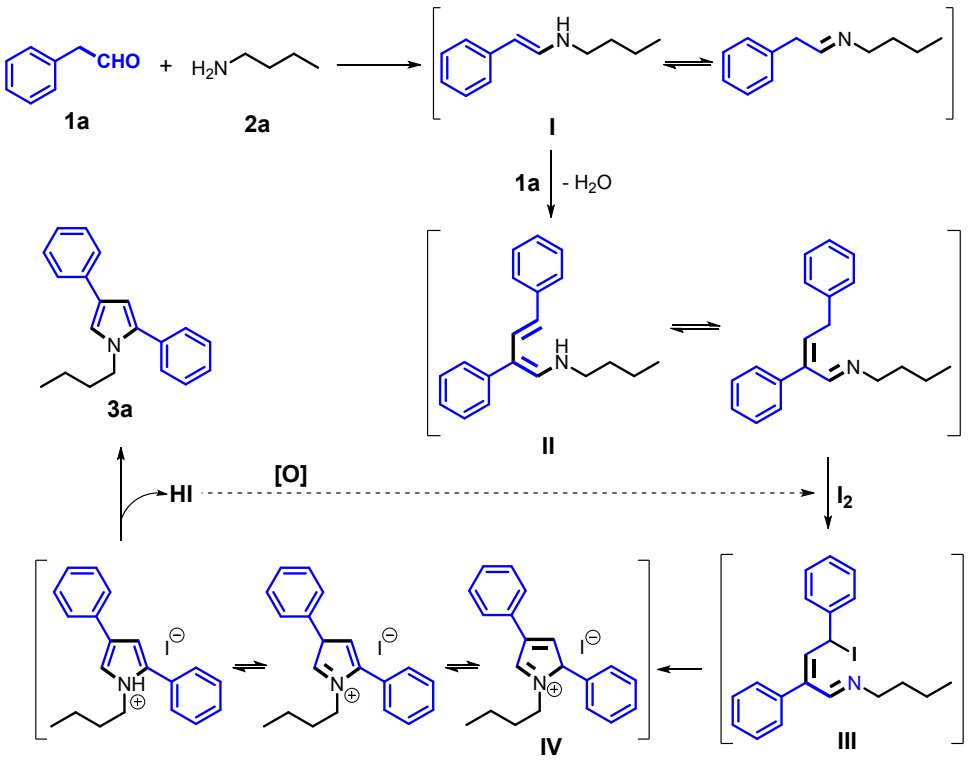


from the model reaction, but failed. However, we cannot totally exclude the possibility of forming **1b** in the model reaction. Therefore, other experiments were done in order for us to get some useful information. When **1b** was allowed to react with **2a** in the presence of 30 mol% of I_2 at 60

°C, **3a** was obtained in 89% yield (equation 5). Interestingly, under the identical conditions, a reaction between **1b** and aniline occurred smoothly, giving a 1,2,4-triphenylpyrrole **3x** in 90% yield (equation 6).

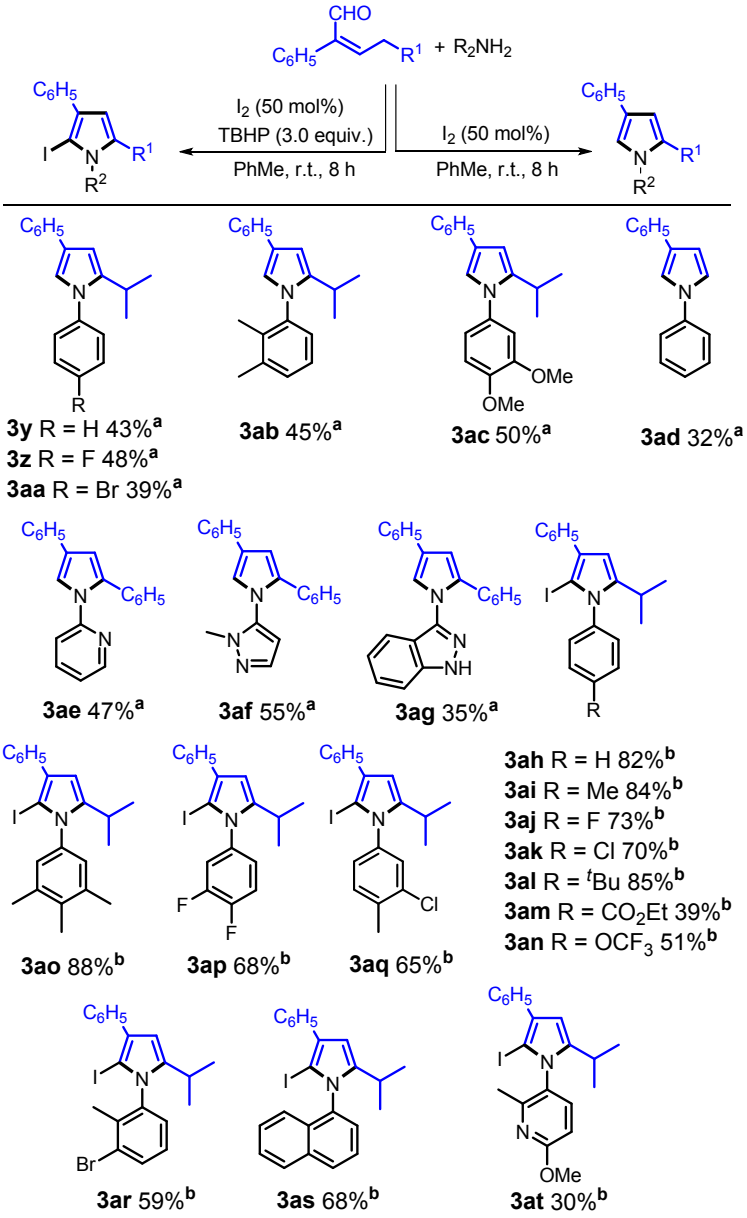
On the basis of the above-mentioned results and the previous literature's reports,[28] a plausible mechanism was proposed and depicted in **Scheme 3**. Initially, a reaction of **1a** and **2a** occurred, providing an imine intermediate **I**. The enamine form of **I** acted then as a nucleophile to react with another molecule of **1a** to generate an intermediate **II**.[29] The enamine of **II** tautomerized to the corresponding imine form. Hydrolysis of **II** may occur to form **1b** and **2a**. But, in the presence of I_2, the imine tautomer of **II** tended to be iodized to give an intermediate **III** *via* electrophilic substitution path.[30] Subsequently, **III** underwent an intramolecular quaternization and HI elimination to afford the final product **3a**.[31] It should be mentioned that iodine can be regenerated under an aerobic oxidative condition.[32] Therefore, oxygen is necessary in this reaction. We also suspected that a high nucleophilicity of the enamine form of the intermediate **I** should be the key to initiating the reaction. When aromatic amine **2b** was used, the generated intermediate may be less nucleophilic. As a result, the reaction of **1a** and **2b** hardly proceeded. In other words, the aliphatic amine played to some extent the role of a catalyst in the initial stage of the reaction, ensuring a C-C bond forming reaction between two molecules of **1a** proceeded. As both of the aromatic and aliphatic amines can be used as the counter-reagents of α,β-unsaturated aldehyde **1b** to synthesize pyrroles, we therefore deduced that the catalytic effect of amine ensured only the self-condensation of **1a** proceed well, but not critical for their downstream reactions.

Scheme 3. Proposed mechanism for pyrrole synthesis.



On the basis of these results, we also established a transformation of enolizable *α,β*-unsaturated aldehyde to a 1,2,4-trisubstituted pyrrole. Although some methods have been developed for pyrrole synthesis from *α,β,*-unsaturated aldehydes[33] or ketones,[34] transformation of an enolizable *α,β*-unsaturated aldehyde to 1,2,4-trisubstituted pyrrole has not been reported yet. We tried to use cocal, an easily available enolizable *α,β*-unsaturated aldehyde, to react with anilines. As shown in **Scheme 4**, in the presence of 0.5 equiv. of I_2, anilines with either electron-donating or moderately electron-withdrawing substituents reacted smoothly with cocal, providing the corresponding pyrroles in moderate yields (**3y**–**3ac**). A 1,3-diphenylpyrrole **3ad** can be synthesized in 32% yield from 2-phenyl-2-butenal. Amino-substituted heterocycles, such as 2-aminopyridine, 1-methyl-1*H*-pyrazol-5-ylamine and 3-amino-1*H*-indazole, can also be used in this reaction (**3ae**–**3ag**). But the reactions yields are less than 55%.

Scheme 4. Pyrrole synthesis from α,β,-unsaturated aldehydes and aromatic amines.



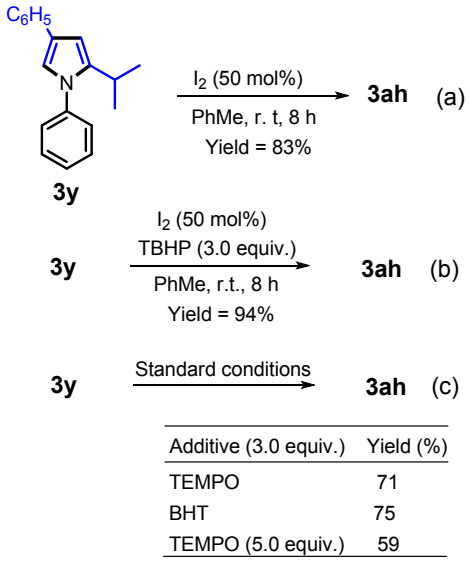
[a]: Reaction condition: I_2 (50 mol%), PhMe, r t, 8 h.
[b]: Reaction condition: I_2 (50 mol%), TBHP (3.0 equiv), PhMe, r t, 8 h.

Surprisingly, C2-iodized pyrrole was isolated when TBHP was added with the hope of enhancing the synthesis efficiency of pyrrole. Inspired by this observation, we added 3.0 equiv. of TBHP into the reaction system. This led us to develop an efficient method to synthesize C2-iodized *N*-arylpyrroles. All the electron-rich anilines worked well in this reaction. And the corresponding C2-iodized pyrroles can be obtained in up to 88% yield. But, electron-poor aniline,

for example, benzocaine, participated in the reaction reluctantly. The expected product **3am** was obtained only in 39% yield. 1-Aminonaphthalene can also be utilized successfully (**3as**). 3-Amino-6-methoxy-2-picoline can also be applied in this reaction, but the expected product can be isolated only in 30% yield. It should be noted that the iodized pyrroles are useful because the presence of iodo group offers a chance for further functionalization of the pyrrole ring.[35]

Several control experiments were conducted to further study the reaction mechanism to produce 2-iodine-substituted pyrrole derivative. In the absence of TBHP, the 2-iodine-substituted pyrrole product **3ah** could be formed in 83% yield *via* the reaction of **3y** with I_2 (**Scheme 5a**). In the presence of 3.0 equivalents of an oxidant TBHP, the yield of **3ah** could be improved to 94% (**Scheme 5b**). When radical scavengers, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 3.0 equiv.) or 2,6-di-*tert*-butyl-4-methylphenol (BHT, 3.0 equiv.), were added to the reaction system, **3ah** was obtained in 71% and 75% yields, respectively (**Scheme 5c**). The reaction proceeded even quite well in the presence of 5.0 equiv. of TEMPO. These results demonstrated that this transformation may not involve a radical pathway.

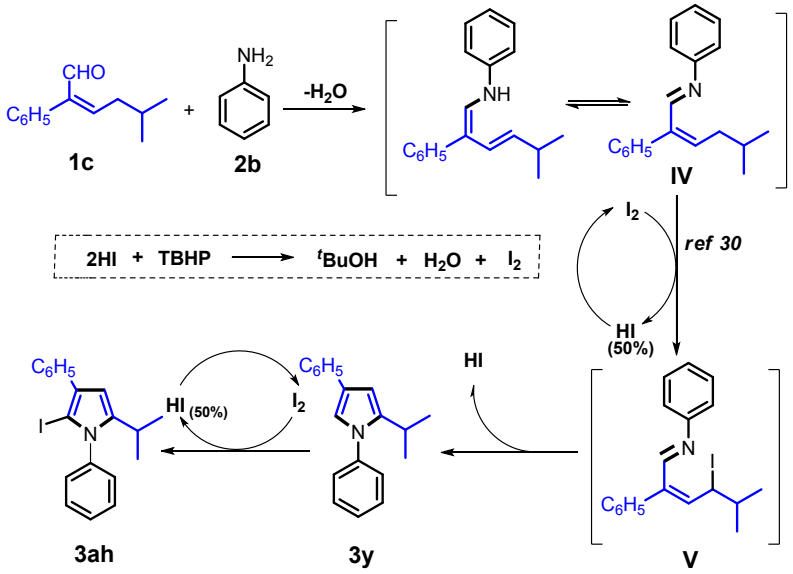
Scheme 5. Mechanistic investigation by control experiments.



Additive (3.0 equiv.)	Yield (%)
TEMPO	71
BHT	75
TEMPO (5.0 equiv.)	59

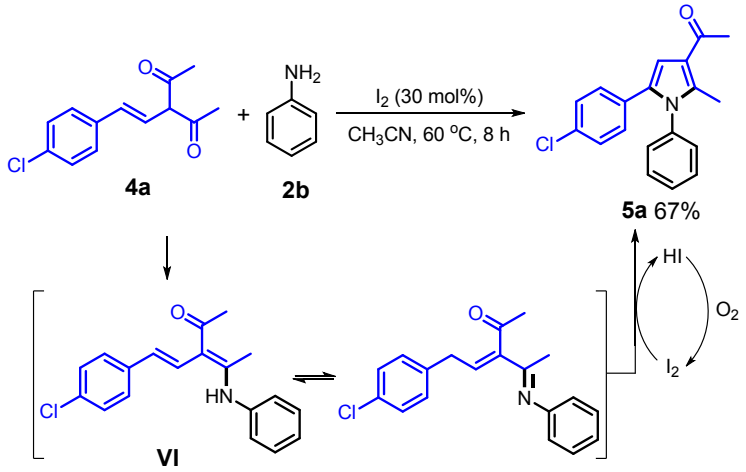
Based on our experimental results and the previous investigations, a plausible reaction mechanism of generating 2-iodine-substituted pyrrole was proposed in **Scheme 6**. Firstly, *α,β*-unsaturated aldehyde **1c** reacted with **2b**, providing an imine intermediate **IV**. Subsequently, the imine intermediate **IV** was iodized to give an intermediate **V** *via* an electrophilic substitution. Then, **3y** was formed *via* a reaction sequence including an intramolecular quaternization and HI elimination. Finally, the C-2 position of the pyrrole ring was iodized through electrophilic substitution to give 2-iodine-substituted pyrrole **3ah**. The eliminated HI was oxidized to I_2 in the presence of TBHP.

Scheme 6. A possible mechanism of this transformation



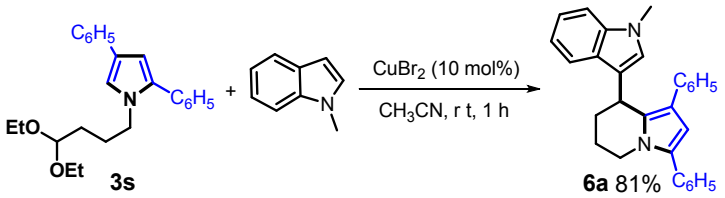
A Knoevenagel reaction product **4a**, formed from acetylacetone and 2-(*p*-chlorophenyl)acetaldehyde, was also proven to be capable of synthesizing a pyrrole derivative. As shown in **Scheme 7**, the reaction between **4a** and aniline occurred smoothly with the aid of 30 mol% of I_2, generating a pyrrole derivative **5a** in 67% yield. The formation of an intermediate **VI** may be involved in the reaction mechanism. We also tried to synthesize **5a** starting from enolizable aliphatic aldehyde, acetylacetone and aniline, but failed.

Scheme 7. Synthesis of pyrrole derivative **5a** from aniline and **4a**.



Pyrrole derivative **3s** contains both an electrophilic acetal moiety and a nucleophilic pyrrole fragment. We thus suspected that **3s** can be converted *via* an intramolecular reaction. As we expected, an indol-3-yl-substituted 5,6,7,8-tetrahydroindolizine derivative **6a** was obtained in 81% yield by treating **3s** with *N*-methylindole in the presence of 10 mol% of $CuBr_2$ (**Scheme 8**). It should be mentioned that indolizine was a privilege motif that widely existed in natural product and other biological molecular.[36]

Scheme 8. Synthesis of tetrahydroindolizine derivative from **3s**.



Conclusion

In summary, a range of 1,2,4-trisubstituted pyrrole derivatives were synthesized by using easily accessible enolizable aldehyde and aliphatic primary amines as starting materials by using I_2 as catalyst. The amine component not only played a role of nitrogen source, it can also be used as an activator to enhance the nucleophilicity of aldehyde by forming an enamine intermediate. With the aid of the similar catalytic system, enolizable α,β-unsaturated aldehydes reacted also smoothly with aromatic primary amines, generating C2-iodized *N*-arylpyrroles. This study offered a complementary method to the traditional protocols to construct pyrrole scaffolds using the aliphatic aldehyde as 4C donor, enriching thus the product diversity of the pyrrole derivatives.

Experimental Sections

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. The reactions were monitored by TLC with Haiyang GF-254 silica gel plates (Qingdao Haiyang chemical industry Co. Ltd, Qingdao, China) using UV light or $KMnO_4$ as visualizing agents as needed. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^1H NMR spectra and ^{13}C NMR spectra were respectively recorded on Brüker AV-400 spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard, and coupling constants (*J*) were reported in Hz. High-resolution mass spectra (HRMS) were obtained on Brüker Compass Data Analysis 4.0.

Typical procedure for the synthesis of pyrrole derivatives from phenylacetaldehyde and aliphatic amine. The reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, **1a** (0.60 mmol) was mixed with **2a** (0.30 mmol), I_2 (22.8 mg, 30 mol%) in acetonitrile (1.0 mL). The mixture was then stirred at 60 °C for 8 h. When the reactions were completed, the mixture was cooled to room temperature. Then, the mixture was washed with aqueous sodium thiosulfate, dried with sodium sulfate, and concentrated under reduced pressure. The product was obtained by isolation with silica column chromatography (eluting solution: petroleum ether / ethyl acetate = 40/1 (v/v)). Tests for substrate scope were all performed with an analogous procedure.

Typical procedure for the synthesis of pyrrole derivatives from 5-methyl-2-phenyl-2-hexenal and aromatic amine. The reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, 5-methyl-2-phenyl-2-hexenal (0.30 mmol) was mixed with aniline (0.36 mmol), I_2 (50 mol%) in toluene (1.0 mL). The mixture was then stirred at

room temperature for 8 h. When the reactions were completed, the mixture was washed with aqueous sodium thiosulfate, dried with sodium sulfate, and concentrated under reduced pressure. The organic residue was subjected to an isolation with silica column chromatography (eluting solution: petroleum ether / ethyl acetate = 50/1 (v/v)). Tests for substrate scope were all performed with an analogous procedure. In the synthesis procedure of **3ah** to **3at**, TPHP (3.0 equiv.) was added. All the other operation procedures are the same with the above reactions.

Procedure for large scale synthesis of 3ah. In a 50 mL of single-neck round bottom flask equipped with magnetic stirring, 5-methyl-2-phenyl-2-hexenal (1.88 g, 10.0 mmol) was mixed with aniline (1.12 g, 12.0 mmol), I_2 (2.03 g, 5.0 mmol) and TBHP (3.86 g, 30.0 mmol) in toluene (20.0 mL). The mixture was then stirred at room temperature for 8 h. When the reactions were completed, the mixture was washed with aqueous sodium thiosulfate and brine, and then extracted by ethyl acetate (20 mL × 3). The organic phase was combined and dried over anhydrous Na_2SO_4. After removing the volatile component, the residue mixture was subjected to an isolation with silica column chromatography (eluting solution: petroleum ether / ethyl acetate = 50/1 (v/v)). Product **3ah** was obtained in 71% yield (2.74 g).

Procedure for the synthesis of 1b. In a 50 mL of single-neck round bottom flask equipped with magnetic stirring, **1a** (2.40 g, 20.0 mmol) was mixed with $AlCl_3$ (267.0 mg, 2.0 mmol) in acetonitrile (30.0 mL). The mixture was then stirred at 60 ^oC for 8 h. After reaction, the mixture was cooled to room temperature, washed with brine (40 mL), and the aqueous phase was extracted by ethyl acetate (20 mL × 3). The organic phase was combined and dried over anhydrous Na_2SO_4. After removing the volatile component, the residue mixture was subjected to an isolation with

silica column chromatography (eluting solution: petroleum ether / ethyl acetate = 30/1 (v/v)). Product **1b** was obtained in 33% yield.

Procedure for the synthesis of 4b.[37] In a 10 mL roundbottom flask, 2-(4-chlorophenyl)acetaldehyde (154.0 mg, 1 mmol), acetyl acetone (100.0 mg, 1 mmol) and piperidinium acetate (29.0 mg, 0.2 mmol) were mixed, and reaction mixture was shaken under solvent-free conditions. The formation of aldehyde-acetyl acetone adduct was complete in about 10 min (monitored by TLC). The mixture was washed with brine (30 mL), and the aqueous phase was extracted by ethyl acetate (20 mL × 3). The organic phase was combined and dried over anhydrous Na_2SO_4. After removing the volatile component, the residue mixture was subjected to an isolation with silica column chromatography (eluting solution: petroleum ether / ethyl acetate = 20/1 (v/v)). Product **4a** was obtained in 65% yield.

Characterization data of compounds. *1-Butyl-2,4-diphenyl-1H-pyrrole (**3a**)*:[38] white solid, mp: 59–61 °C, 83% yield (68.4 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) $\boldsymbol{\delta}$ = 7.55 (d, J = 7.3 Hz, 2H), 7.44 (d, J = 4.3 Hz, 4H), 7.38 (d, J = 1.8 Hz, 1H), 7.31 (dd, J = 13.6, 6.1 Hz, 3H), 7.13 – 7.09 (m, 1H), 6.51 (d, J = 1.8 Hz, 1H), 3.96 (t, J = 7.2 Hz, 2H), 1.62 – 1.53 (m, 2H), 1.14 (dd, J = 14.7, 7.4 Hz, 2H), 0.76 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) $\boldsymbol{\delta}$ = 135.5, 134.5, 133.0, 128.6, 128.5, 128.3, 127.0, 125.0, 124.3, 123.0, 119.9, 106.3, 46.5, 32.8, 19.2, 13.4 ppm.

1-*Butyl-2,4-bis(2-fluorophenyl)-1H-pyrrole (**3b**)*: yellow oil, 74% yield (69.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.56–7.48 (m, 1H), 7.33–7.27 (m, 2H), 7.22 (s, 1H), 7.19 (s, 1H), 7.17–7.07 (m, 2H), 7.06–7.02 (m, 2H), 6.50 (s, 1H), 3.77 (t, J = 7.3 Hz, 2H), 1.57 (dt, J =

14.9, 7.5 Hz, 2H), 1.17–1.09 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 160.2 (d, *J* = 245.0 Hz), 159.7 (d, *J* = 245.0 Hz), 132.5 (d, *J* = 3.0 Hz), 129.8 (d, *J* = 8.1 Hz), 128.3, 127.5 (d, *J* = 5.0 Hz), 126.3 (d, *J* = 8.6 Hz), 124.3 (d, *J* = 4.0 Hz), 124.2 (d, *J* = 4.0 Hz), 123.4 (d, *J* = 13.0 Hz), 121.9 (d, *J* = 11.0 Hz), 121.3 (d, *J* = 15.0 Hz), 117.8, 116.0 (d, *J* = 22.0 Hz), 115.9 (d, *J* = 22.0 Hz), 108.8 (d, *J* = 1.5 Hz), 47.5, 33.4, 19.9, 13.7 ppm. ^{19}F NMR (377 MHz, $CDCl_3$, 25 °C) δ = -113.4, -115.2 ppm. IR (KBr) *v*: 2961, 2927, 2869, 1694, 1488, 1456, 1263, 1095, 1028, 800, 759 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}F_2N$, $[M + H]^+$ 312.1564, found 312.1562.

*2,4-Bis(2-bromophenyl)-1-butyl-1H-pyrrole (**3c**)*: brown oil, 67% yield (86.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.68 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.51 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.41 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.27 (dd, *J* = 13.3, 6.2 Hz, 2H), 7.22 (d, *J* = 1.6 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.46 (d, *J* = 1.6 Hz, 1H), 3.76 (t, *J* = 7.2 Hz, 2H), 1.61 – 1.57 (m, 2H), 1.19 (dt, *J* = 14.7, 7.4 Hz, 2H), 0.81 (t, *J* = 7.3 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 136.7, 134.7, 133.8, 133.2, 133.0, 132.2, 130.6, 129.7, 127.4, 127.2, 126.8, 125.9, 122.2, 121.9, 121.0, 110.4, 47.3, 33.4, 19.9, 13.7 ppm. IR (KBr) *v*: 2958, 2928, 2869, 1702, 1463, 1434, 1024, 753 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}Br_2N$, $[M + H]^+$ 431.9962, 431.9945.

*1-Butyl-2,4-bis(3-fluorophenyl)-1H-pyrrole (**3d**)*: brown oil, 72% yield (67.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.37 (dd, *J* = 14.2, 7.8 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.19 (t, *J* = 9.5 Hz, 2H), 7.11 (d, *J* = 9.8 Hz, 1H), 7.07 – 7.05 (m, 1H), 7.04 – 6.99 (m, 1H), 6.87 – 6.82 (m, 1H), 6.47 (d, *J* = 1.1 Hz, 1H), 3.94 (t, *J* = 7.3 Hz, 2H), 1.66 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.24 (dt, *J* =

14.9, 7.3 Hz, 2H), 0.85 (t, *J* = 7.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 163.5 (d, *J* = 242.0 Hz), 162.9 (d, *J* = 245.0 Hz), 138.0 (d, *J* = 8.4 Hz), 135.4 (d, *J* = 8.1 Hz), 134.4, 129.7 (d, *J* = 9.0 Hz), 124.6 (d, *J* = 2.7 Hz), 120.6 (d, *J* = 2.5 Hz), 119.8, 115.8 (d, *J* = 22.0 Hz), 114.2 (d, *J* = 21.0 Hz), 112.2 (d, *J* = 21.0 Hz), 111.7 (d, *J* = 21.9 Hz), 107.4, 47.4, 33.6, 19.9, 13.7 ppm. ^{19}F NMR (377 MHz, $CDCl_3$, 25 °C) δ = -112.8, -113.8 ppm. IR (KBr) *v*: 3078, 2962, 2934, 2872, 1692, 1588, 1487, 1444, 1268, 789 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}F_2N$, $[M + H]^+$ 312.1564, found 312.1562.

*1-Butyl-2,4-bis(3-chlorophenyl)-1H-pyrrole (**3e**)*: brown oil, 78% yield (80.2 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.50 (s, 1H), 7.43 – 7.36 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 1.4 Hz, 1H), 6.46 (d, *J* = 1.5 Hz, 1H), 3.93 (t, *J* = 7.3 Hz, 2H), 1.67 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.25 (dt, *J* = 14.8, 7.5 Hz, 2H), 0.85 (t, *J* = 7.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 137.6, 135.1, 134.6, 134.5, 134.3, 130.0, 129.8, 128.9, 127.4, 127.0, 125.5, 125.0, 123.3, 123.1, 119.8, 107.4, 47.4, 33.6, 19.9, 13.7 ppm. IR (KBr) *v*: 3071, 2960, 2928, 2856, 1698, 1569, 1419, 1256, 1078, 792, 694 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}Cl_2N$, $[M + H]^+$ 344.0973, found 344.0973.

*2,4-Bis(3-bromophenyl)-1-butyl-1H-pyrrole (**3f**)*: brown oil, 70% yield (90.3 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.66 (s, 1H), 7.56 (s, 1H), 7.44 (dd, *J* = 11.1, 8.7 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.24 (m, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.06 (s, 1H), 6.45 (s, 1H), 3.92 (t, *J* = 7.3 Hz, 2H), 1.66 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.25 – 1.19 (dt, 2H), 0.85 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 137.8, 135.3, 134.1, 131.8, 130.3, 130.1, 128.4, 127.9, 127.4, 123.5, 123.1, 123.0, 122.6, 119.8, 107.4, 47.3, 33.6, 19.9, 13.7 ppm. IR (KBr) *v*:

3067, 2959, 2930, 2869, 1694, 1565, 1416, 1250, 1072, 789, 688 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}Br_2N$, $[M + H]^+$ 431.9962, found 431.9959.

*1-Butyl-2,4-bis(4-fluorophenyl)-1H-pyrrole (**3g**)*: yellow oil, 71% yield (66.2 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.47 (dd, J = 8.3, 5.5 Hz, 2H), 7.36 (dd, J = 8.2, 5.5 Hz, 2H), 7.11 (t, J = 8.5 Hz, 2H), 7.02 (dd, J = 14.9, 5.9 Hz, 3H), 6.38 (s, 1H), 3.89 (t, J = 7.4 Hz, 2H), 1.65 (dt, J = 14.9, 7.4 Hz, 2H), 1.26 – 1.21 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 134.4, 131.7, (d, J = 30.0 Hz), 130.8 (d, J = 7.9 Hz), 130.7 (d, J = 239.0 Hz), 126.4 (d, J = 7.7 Hz), 123.5, 118.4, 115.7 (d, J = 4.0 Hz), 115.4 (d, J = 3.0 Hz), 106.8, 47.2, 33.7, 20.0, 13.8 ppm. ^{19}F NMR (377 MHz, $CDCl_3$, 25 °C) δ =-114.67 – -114.93 (m), -117.89 – -118.15 (m) ppm. IR (KBr) v: 3077, 2960, 2931, 1693, 1603, 1508, 1232, 1159, 839 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}F_2N$, $[M + H]^+$ 312.1564, found 312.1561.

*1-Butyl-2,4-bis(4-chlorophenyl)-1H-pyrrole (**3h**)*: yellow solid, mp: 70–72 °C, 73% yield (75.1 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.37 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.26 (s, 1H), 7.21 (dd, J = 17.0, 8.6 Hz, 3H), 6.97 (d, J = 1.5 Hz, 1H), 6.34 (d, J = 1.5 Hz, 1H), 3.83 (t, J = 7.3 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.20 – 1.14 (m, 2H), 0.77 (t, J = 7.4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 134.5, 134.2, 133.3, 131.8, 131.0, 130.2, 129.7, 128.9, 126.2, 123.4, 119.2, 107.0, 47.3, 33.7, 20.0, 13.8 ppm. IR (KBr) v: 3093, 2960, 2929, 2869, 1689, 1593, 1490, 1402, 1093, 830 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}Cl_2N$, $[M + H]^+$ 344.0973, found 344.0972.

*2,4-Bis(4-bromophenyl)-1-butyl-1H-pyrrole (**3i**)*: white solid, mp: 78–80 °C, 65% yield (83.8 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.54 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.2 Hz,

2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.05 (s, 1H), 6.42 (s, 1H), 3.91 (t, *J* = 7.3 Hz, 2H), 1.71 – 1.59 (m, 2H), 1.24 (dd, *J* = 14.9, 7.1 Hz, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 134.5, 134.4, 132.1, 131.7, 131.6, 130.4, 126.4, 123.3, 121.4, 119.2, 118.9, 106.9, 47.2, 33.5, 19.8, 13.6 ppm. IR (KBr) *v*: 3085, 2958, 2927, 2869, 1685, 1485, 1398, 1072, 1010, 825 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}Br_2N$, $[M + H]^+$ 431.9962, found 431.9958.

*1-Butyl-2,4-bis(4-iodophenyl)-1H-pyrrole (**3j**)*: brown solid, mp: 75–77 °C, 70% yield (110.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.74 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.26 (d, J = 5.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 1.3 Hz, 1H), 6.42 (d, *J* = 1.4 Hz, 1H), 3.91 (t, *J* = 7.4 Hz, 2H), 1.69 – 1.61 (m, 2H), 1.25 – 1.19 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 137.8, 137.7, 135.2, 134.6, 132.8, 130.7, 126.9, 123.5, 119.5, 107.0, 92.9, 90.0, 47.4, 33.7, 20.0, 13.8 ppm. IR (KBr) *v*: 2957, 2924, 2854, 1680, 1461, 1378, 1059, 821 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}I_2N$, $[M + H]^+$ 527.9685, found 527.9687.

*1-Butyl-2,4-di-p-tolyl-1H-pyrrole (**3k**)*: yellow oil, 84% yield (76.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.43 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 7.01 (s, 1H), 6.42 (s, 1H), 3.91 (t, *J* = 7.4 Hz, 2H), 2.39 (s, 3H), 2.33 (s, 3H), 1.71 – 1.64 (m, 2H), 1.26 – 1.22 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 136.9, 135.4, 134.9, 133.1, 130.7, 129.4, 129.2, 129.0, 125.0, 124.2, 118.2, 106.4, 47.1, 33.7, 21.4, 21.2, 20.0, 13.8 ppm. IR (KBr) *v*: 3029, 2959, 2928, 2869, 1694, 1610, 1410, 1178, 820 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{22}H_{26}N$, $[M + H]^+$ 304.2065,

found 304.2063.

*1-Butyl-2,4-bis(4-methoxyphenyl)-1H-pyrrole (**3l**)*: yellow oil, 85% yield (85.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.45 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 7.4 Hz, 3H), 6.88 (d, J = 8.5 Hz, 2H), 6.35 (d, J = 1.5 Hz, 1H), 3.89 (t, J = 7.3 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 1.70 – 1.62 (m, 2H), 1.29 – 1.20 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ = 158.9, 157.7, 135.1, 130.4, 129.5, 128.9, 126.1, 123.9, 117.5, 114.2, 113.9, 106.1, 55.4, 47.0, 33.7, 20.0, 13.8 ppm. IR (KBr) v: 3075, 2959, 2932, 2870, 2839, 1688, 1606, 1511, 1254, 1175, 1032, 835 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{22}H_{26}NO_2$, [M + H]$^+$ 336.1964, found 336.1962.

*1-Butyl-2,4-di(naphthalen-1-yl)-1H-pyrrole (**3m**)*: yellow oil, 62% yield (69.7 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 8.54 (d, J = 8.5 Hz, 1H), 8.08 – 8.02 (m, 2H), 8.01 –7.96 (m, 1H), 7.91 – 7.82 (m, 2H), 7.68 –7.63 (m, 2H), 7.63 –7.53 (m, 6H), 7.39 (d, J = 1.6 Hz, 1H), 6.51 (d, J = 1.7 Hz, 1H), 3.81 (t, J = 7.3 H, 2H), 1.53 – 1.44 (m, 2H), 1.08 (m, 2H), 0.65 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 134.2, 133.8, 133.3, 132.6, 131.1, 131.0, 130.5, 128.7, 128.3, 126.6, 126.1, 126.0, 125.9, 125.8, 125.6, 125.5, 125.4, 121.5, 121.3, 111.1, 46.4, 32.7, 19.0, 13.2 ppm. IR (KBr) v: 3050, 2957, 2927, 2867, 1703, 1593, 1461, 1389, 1022, 798, 777 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{28}H_{26}N$, [M + H]$^+$ 376.2065, found 376.2067.

*1-Dodecyl-2,4-diphenyl-1H-pyrrole (**3n**)*: yellow oil, 82% yield (95.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.54 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 4.0 Hz, 3H), 7.33 (t, J = 7.4 Hz, 3H), 7.25 (d, J = 7.0 Hz, 1H), 7.16 (t, J = 7.0 Hz, 1H), 7.07 (s, 1H), 6.48 (s, 1H), 3.92 (t, J = 7.4

Hz, 2H), 1.68 (d, *J* = 6.4 Hz, 2H), 1.24 – 1.20(m, 18H), 0.88 (t, *J* = 6.5 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 135.8, 135.4, 133.5, 129.0, 128.6, 128.4, 128.1, 127.1, 125.4, 124.9, 118.7, 106.7, 47.4, 31.9, 31.5, 29.6, 29.5, 29.4, 29.3, 29.1, 26.6, 22.7, 14.2 ppm. IR (KBr) *v*: 3063, 2925, 2854, 1683, 1579, 1451, 1411, 764, 697 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{28}H_{38}N$, $[M + H]^+$ 388.3004, found 388.3002.

*1-Octyl-2,4-diphenyl-1H-pyrrole (**3o**)*: yellow oil, 80% yield (79.4 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.55 (d, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 4.3 Hz, 4H), 7.36 (d, *J* = 1.4 Hz, 1H), 7.31 (dd, *J* = 14.8, 7.4 Hz, 3H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 1.5 Hz, 1H), 3.94 (t, *J* = 7.1 Hz, 2H), 1.60 –1.50 (m, 2H), 1.22 – 1.09 (m, 10H), 0.80 (t, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 135.5, 134.5, 133.1, 128.6, 128.5, 128.3, 126.9, 125.0, 124.3, 123.0, 119.9, 106.3, 46.7, 31.1, 30.6, 28.5, 28.3, 25.8, 22.0, 13.9 ppm. IR (KBr) *v*: 3063, 2955, 2926, 2855, 1694, 1450, 1409, 1261, 763, 697 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{24}H_{30}N$, $[M + H]^+$ 332.2378, found 332.2377.

*1-(tert-Butyl)-2,4-diphenyl-1H-pyrrole (**3p**)*:[39] White solid , mp: 101–103 °C, 75% yield (61.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.52 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 3.3 Hz, 2H), 7.37 – 7.27 (m, 5H), 7.21 (d, *J* = 0.8 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.34 (s, 1H), 1.46 (s, 9H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 137.1, 136.0, 135.2, 131.9, 128.7, 128.5, 127.8, 127.6, 125.3, 124.9, 115.8, 110.0, 57.6, 32.0 ppm.

*1-Cyclohexyl-2,4-diphenyl-1H-pyrrole (**3q**)*:[39] White solid, mp: 83–85 °C, 82% yield (74.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.54 (d, *J* = 7.4 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.32 (t, *J* = 6.9 Hz, 3H), 7.19 – 7.10 (m, 2H), 6.44 (s, 1H), 4.01 (t, *J* = 11.6 Hz, 1H), 2.03 (d, *J* = 11.6

Hz, 2H), 1.83 (d, *J* = 11.1 Hz, 2H), 1.70 (d, *J* = 10.3 Hz, 2H), 1.33 – 1.17 (m, 4H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 135.9, 135.0, 133.6, 129.2, 128.6, 128.5, 127.1, 125.3, 124.9, 124.3, 115.1, 106.3, 55.5, 35.0, 25.9, 25.5 ppm.

*1-3-(2,4-Diphenyl-1H-pyrrol-1-yl)propan-1-ol (**3r**)*: yellow oil, 75% yield (62.3 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.61 (d, *J* = 7.6 Hz, 2H), 7.50 (q, *J* = 7.8 Hz, 4H), 7.44 (d, *J* = 1.5 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 3H), 7.17 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 1.3 Hz, 1H), 4.60 (t, *J* = 4.8 Hz, 1H), 4.09 (t, *J* = 7.2 Hz, 2H), 3.39 – 3.38 (m, 2H), 1.87 – 1.79 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 136.0, 135.0, 133.4, 129.0, 128.7, 127.4, 125.5, 124.8, 123.5, 120.4, 106.9, 58.2, 44.5, 34.3 ppm. IR (KBr) *v*: 3390, 3061, 2930, 2874, 1699, 1450, 1401, 1052, 763, 699 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{19}H_{20}NO$, $[M + H]^+$ 278.1545, found 278.1543.

*1-(4,4-Diethoxybutyl)-2,4-diphenyl-1H-pyrrole (**3s**)*: yellow oil, 56% yield (60.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.54 (d, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 3.7 Hz, 4H), 7.33 (t, *J* = 7.1 Hz, 3H), 7.16 (t, *J* = 6.9 Hz, 1H), 7.07 (s, 1H), 6.48 (s, 1H), 4.35 (t, *J* = 5.3 Hz, 1H), 3.98 (t, *J* = 7.2 Hz, 2H), 3.60 – 3.51 (m, 2H), 3.44 – 3.35 (m, 2H), 1.81 – 1.71 (m, 2H), 1.56 – 1.49 (m, 2H), 1.15 (t, *J* = 6.9 Hz, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 135.8, 135.5, 133.5, 129.1, 128.7, 128.6, 127.3, 125.5, 125.1, 124.4, 118.8, 107.0, 102.5, 61.3, 47.3, 30.8, 26.8, 15.4 ppm. IR (KBr) *v*: 3063, 2974, 2928, 2878, 1696, 1449, 1375, 1125, 1062, 698 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{24}H_{30}NO_2$, $[M + H]^+$ 364.2277, found 364.2260.

*(2,2-Diethoxyethyl)-2,4-diphenyl-1H-pyrrole (**3t**)*: yellow oil, 71% yield (71.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.54 (d, *J* = 7.4 Hz, 2H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.43 – 7.39

(m, 2H), 7.36 – 7.32 (m, 3H), 7.20 – 7.15 (m, 2H), 6.50 (d, J = 1.3 Hz, 1H), 4.52 (t, J = 5.2 Hz, 1H), 4.06 (d, J = 5.2 Hz, 2H), 3.59 (td, J = 14.2, 7.0 Hz, 2H), 3.34 (td, J = 14.1, 7.0 Hz, 2H), 1.13 (t, J = 7.0 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 135.9, 135.8, 133.2, 129.3, 128.8, 128.6, 127.4, 125.6, 125.1, 124.5, 120.0, 107.2, 102.5, 63.6, 50.5, 15.3 ppm. IR (KBr) v: 3058, 2969, 2928, 2871, 1674, 1463, 778, 695 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{22}H_{26}NO_2$, $[M + H]^+$ 336.1964, found 336.1948.

*2,4-Diphenyl-1-(prop-2-yn-1-yl)-1H-pyrrole (**3u**):*[40] yellow oil, 58% yield (44.7 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.55 (d, J = 7.7 Hz, 2H), 7.50 (d, J = 7.4 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.6 Hz, 3H), 7.25 (s, 1H), 7.19 (t, J = 7.2 Hz, 1H), 6.53 (s, 1H), 4.69 (d, J = 2.1 Hz, 2H), 2.45 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 135.1, 134.5, 132., 128.7, 128.6, 128.0, 127.2, 125.4, 124.4, 123.7, 120.2, 106.8, 79.9, 76.0, 36.8 ppm.

*1-(3,4-Dimethoxyphenethyl)-2,4-diphenyl-1H-pyrrole (**3v**)*: yellow oil, 62% yield (71.2 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.51 (d, J = 7.6 Hz, 2H), 7.40 – 7.30 (m, 5H), 7.27 (d, J = 7.4 Hz, 2H), 7.17 (t, J = 7.1 Hz, 1H), 7.02 (s, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.51 (d, J = 7.9 Hz, 1H), 6.46 (s, 1H), 6.34 (s, 1H), 4.15 (t, J = 7.1 Hz, 2H), 3.83 (s, 3H), 3.71 (s, 3H), 2.85 (t, J = 7.0 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 149.0, 147.9, 135.8, 135.7, 133.4, 130.9, 129.2, 128.8, 128.5, 127.3, 125.6, 125.1, 124.5, 120.8, 118.8, 112.0, 111.4, 107.0, 56.1, 55.8, 49.2, 37.7 ppm. IR (KBr) v: 3060, 2931, 2836, 1692, 1600, 1515, 1452, 1262, 1236, 1028, 760, 731 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{26}H_{26}NO_2$, $[M + H]^+$ 384.1964, found 384.1963.

*3-(2-(2,4-Diphenyl-1H-pyrrol-1-yl)ethyl)-1H-indole (**3w**)*: yellow oil, 85% yield (92.3 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.93 (s, 1H), 7.53 (d, J = 7.4 Hz, 2H), 7.41 – 7.30 (m,

9H), 7.17 (dd, *J* = 12.5, 6.4 Hz, 2H), 7.07 (s, 2H), 6.81 (s, 1H), 6.50 (s, 1H), 4.23 (t, *J* = 7.5 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 136.2, 135.8, 135.4, 133.3, 129.1, 128.7, 128.6, 128.5, 127.2, 127.1, 125.4, 124.9, 124.2, 122.1, 119.5, 118.8, 118.5, 112.3, 111.1, 106.9, 48.0, 27.6 ppm. IR (KBr) *v*: 3421, 3056, 2925, 2853, 1675, 1602, 1454, 1195, 744, 698 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{26}H_{23}N_2$, $[M + H]^+$ 363.1861, found 363.1862.

*(Z)-2,4-diphenylbut-2-enal (**1b**):*[41] yellow oil, 33% yield (732.6 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 9.66 (s, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.23 (dd, *J* = 16.4, 7.3 Hz, 5H), 7.08 (t, *J* = 7.6 Hz, 1H), 3.65 (d, *J* = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 194.1, 154.1, 143.4, 138.2, 132.4, 129.4, 128.8, 128.5, 128.2, 127.9, 126.6, 35.1 ppm.

*1,2,4-Triphenyl-1H-pyrrole (**3x**):*[42] White solid, 150–152 °C, 90% yield (79.6 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.67 (d, *J* = 7.5 Hz, 2H), 7.59 (s, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.35 (dd, *J* = 9.2, 5.3 Hz, 3H), 7.24 (td, *J* = 14.2, 9.4 Hz, 5H), 7.16 (t, *J* = 7.7 Hz, 3H), 6.88 (s, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 140.3, 135.3, 134.4, 132.8, 129.7, 129.1, 128.7, 128.3, 127.5, 127.0, 126.1,126.0, 125.2, 125.1, 122.2, 109.1 ppm.

*2-Isopropyl-1,4-diphenyl-1H-pyrrole (**3y**)*: colourless oil, 43% yield (33.6 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.56 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 8.3 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 1.3 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.44 (s, 1H), 2.92 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.09 (d, *J* = 6.7 Hz, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 141.1, 139.8, 135.4, 129.4, 128.6, 127.5, 126.1, 125.1, 124.4, 123.2, 118.6, 102.5, 24.9,

23.0 ppm. IR (KBr) *v*: 3064, 2964, 2929, 2872, 1716, 1598, 1496, 1385, 1027, 753, 696 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{19}H_{20}N$, $[M + H]^+$ 262.1596, found 262.1593.

*1-(4-Fluorophenyl)-2-isopropyl-4-phenyl-1H-pyrrole (**3z**)*: colourless oil, 48% yield (40.1 mg); ^1H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.56 (d, J = 7.6 Hz, 2H), 7.48 (dd, J = 8.5, 5.0 Hz, 2H), 7.36 (t, J = 8.7 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 1.2 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H), 6.43 (s, 1H), 2.86 (dt, J = 13.5, 6.7 Hz, 1H), 1.09 (d, J = 6.8 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 161.1 (d, J = 243.0 Hz), 141.2, 136.1 (d, J = 3.0 Hz), 135.4, 128.6, 128.4 (d, J = 8.0 Hz), 125.2, 124.4, 123.2, 118.8, 116.1 (d, J = 22.0 Hz), 102.4, 24.9, 23.0 ppm. ^{19}F NMR (377 MHz, DMSO-d_6, 25 °C, 25 °C) δ = -114.49 – -114.72 (m). IR (KBr) *v*: 2965, 2929, 2872, 1716, 1511, 1223, 1025, 799 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{19}H_{19}FN$, $[M + H]^+$ 280.1502, found 280.1498.

*1-(4-Bromophenyl)-2-isopropyl-4-phenyl-1H-pyrrole (**3aa**)*: yellow oil, 39% yield (39.6 mg); ^1H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.72 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.27 (s, 1H), 7.13 (t, J = 7.3 Hz, 1H), 6.46 (s, 1H), 2.92 (dt, J = 13.4, 6.6 Hz, 1H), 1.10 (d, J = 6.7 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 141.1, 139.0, 135.2, 132.4, 128.6, 128.2, 125.3, 124.5, 123.6, 120.3, 118.6, 102.9, 24.9, 23.0 ppm. IR (KBr) *v*: 3082, 2964, 2929, 2871, 1717, 1491, 1383, 1071, 798 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{19}H_{19}BrN$, $[M + H]^+$ 340.0701, found 340.0702.

*1-1-(2,3-Dimethylphenyl)-2-isopropyl-4-phenyl-1H-pyrrole (**3ab**)*: brown oil, 45% yield (39.0 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.54 (d, J = 7.8 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.19 – 7.10 (m, 3H), 6.86 (s, 1H), 6.38 (s, 1H), 2.53 (dt, J = 13.5, 6.7 Hz,

1H), 2.34 (s, 3H), 1.92 (s, 3H), 1.12 (dd, J = 6.6, 2.5 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 142.4, 139.2, 138.2, 135.9, 135.1, 129.8, 128.6, 126.0, 125.7, 125.2, 124.8, 123.8, 117.9, 101.2, 25.8, 23.8, 22.7, 20.4, 14.0 ppm. IR (KBr) v: 3030, 2961, 2926, 2869, 1714, 1602, 1472, 1382, 792, 764 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{21}H_{24}N$, $[M + H]^+$ 290.1909, found 290.1903.

*1-(3,4-Dimethoxyphenyl)-2-isopropyl-4-phenyl-1H-pyrrole (**3ac**)*: yellow oil, 50% yield (48.1 mg); ^1H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.55 (d, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.20 (s, 1H), 7.11 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 8.3 Hz, 1H), 6.99 (d, J = 1.1 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.39 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.91 (dt, J = 13.4, 6.6 Hz, 1H), 1.11 (d, J = 6.7 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 149.0, 148.1, 141.3, 135.6, 132.8, 128.6, 125.1, 124.4, 122.9, 118.8, 118.2, 111.7, 110.5, 101.9, 55.8, 55.7, 25.0, 23.1 ppm. IR (KBr) v: 3065, 2963, 2931, 2852, 1714, 1514, 1453, 1258, 1135, 1026, 792 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{21}H_{24}NO_2$, $[M + H]^+$ 322.1807, found 322.1808.

*1,3-Diphenyl-1H-pyrrole (**3ad**)*:[43] yellow solid, mp: 83−85 °C, 32% yield (21.0 mg); ^1H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.90 (s, 1H), 7.65 (d, J = 3.7 Hz, 4H), 7.47 (dd, J = 14.7, 5.2 Hz, 3H), 7.35 (t, J = 7.5 Hz, 2H), 7.27 (t, J = 7.3 Hz, 1H), 7.17 (t, J = 7.3 Hz, 1H), 6.71 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 139.7, 135.0, 129.7, 128.6, 125.9, 125.6, 125.4, 124.7, 120.2, 119.2, 115.8, 108.5 ppm.

*2-(2,4-Diphenyl-1H-pyrrol-1-yl)pyridine (**3ae**)*: yellow oil, 47% yield (41.7 mg); ^1H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 8.50 (d, J = 3.9 Hz, 1H), 7.83 (t, J = 7.6 Hz, 1H), 7.79 (s, 1H), 7.69 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 3H), 7.33 – 7.29 (m, 2H), 7.23 – 7.18 (m, 2H), 7.16 (d, J = 7.2

Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 152.0, 149.4, 139.0, 135.0, 134.3, 133.0, 129.2, 128.8, 128.3, 127.2, 126.3, 125.4, 125.3, 122.8, 121.0, 119.6, 110.3 ppm. IR (KBr) *v*: 3063, 2960, 2927, 2857, 1714, 1598, 1094, 1027 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{21}H_{17}N_2$, $[M + H]^+$ 297.1392, found 297.1393.

*5-(2,4-Diphenyl-1H-pyrrol-1-yl)-1-methyl-1H-pyrazole (**3af**)*: colourless oil, 55% yield (49.3 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.69 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 10.2 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.24 (dd, *J* = 13.9, 7.1 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.04 (s, 1H), 6.44 (s, 1H), 3.37 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 138.7, 138.4, 135.9, 134.7, 131.9, 129.2, 129.0, 127.6, 127.1, 126.5, 126.0, 125.3, 122.6, 108.3, 103.9, 35.6 ppm. IR (KBr) *v*: 3064, 2960, 2928, 2856, 1717, 1491, 1026 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{18}N_3$, $[M + H]^+$ 300.1501, found 300.1500.

*3-(2,4-Diphenyl-1H-pyrrol-1-yl)-1H-indazole (**3ag**)*: colourless oil, 35% yield (35.1 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 13.20 (s, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.66 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 3H), 7.23 (dd, *J* = 15.1, 7.8 Hz, 2H), 7.15 (d, *J* = 16.5 Hz, 5H), 7.07 – 7.01 (m, 1H), 7.00 (s, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 141.5, 141.3, 135.5, 135.1, 132.8, 129.2, 128.7, 127.5, 127.4, 127.1, 126.3, 125.5, 125.3, 122.3, 121.7, 119.5, 117.4, 111.2, 108.5 ppm. IR (KBr) *v*: 3405, 3060, 2927, 2855, 1719, 1520, 1490, 1025, 753, 696 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{23}H_{18}N_3$, $[M + H]^+$ 336.1501, found 336.1497.

*2-Iodo-5-isopropyl-1,3-diphenyl-1H-pyrrole (**3ah**)*: colourless oil, 82% yield (95.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.63 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 6.3 Hz, 3H), 7.40

(dd, J = 13.7, 5.8 Hz, 3H), 7.29 (d, J = 7.6 Hz, 2H), 6.34 (s, 1H), 2.74 (dt, J = 13.5, 6.8 Hz, 1H), 1.11 (d, J = 6.8 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 146.0, 140.3, 136.5, 129.7, 129.0, 128.7, 128.2, 128.1, 126.3, 119.9, 106.2, 70.3, 27.1, 23.1 ppm. IR (KBr) v: 3065, 2966, 2928, 2873, 1695, 1208 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{19}H_{19}IN$, $[M + H]^+$ 388.0562, found 388.0558.

*2-Iodo-5-isopropyl-3-phenyl-1-(p-tolyl)-1H-pyrrole (**3ai**)*: colourless oil, 84% yield (101.1 mg); ^1H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.58 (d, J = 7.3 Hz, 2H), 7.38 (dd, J = 14.8, 7.5 Hz, 4H), 7.25 (t, J = 7.4 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 6.34 (s, 1H), 2.64 (dt, J = 13.5, 6.7 Hz, 1H), 2.41 (s, 3H), 1.05 (d, J = 6.8 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 145.3, 138.4, 137.1, 136.3, 129.7, 129.2, 128.5, 128.2, 127.6, 126.0, 105.7, 72.5, 26.5, 22.9, 20.8 ppm. IR (KBr) v: 3033, 2962, 2928, 2871, 1714, 1515, 1386, 1286 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{21}IN$, $[M + H]^+$ 402.0719, found 402.0721.

*1-(4-Fluorophenyl)-2-iodo-5-isopropyl-3-phenyl-1H-pyrrole (**3aj**)*: yellow oil, 73% yield (88.7 mg); ^1H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.57 (d, J = 7.6 Hz, 2H), 7.44 – 7.36 (m, 6H), 7.25 (t, J = 7.3 Hz, 1H), 6.36 (s, 1H), 2.63 (dt, J = 13.4, 6.7 Hz, 1H), 1.06 (d, J = 6.8 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 161.8 (d, J = 244.0 Hz), 145.4, 136.2, 136.0 (d, J = 3.0 Hz),, 131.7 (d, J = 9.0 Hz), 129.7, 128.2, 127.6, 126.1, 116.0 (d, J = 23 Hz), 105.9, 72.7, 26.5, 22.8 ppm. ^{19}F NMR (377 MHz, DMSO-d_6, 25 °C, 25 °C) δ = -112.64 (dt, J = 13.3, 6.7 Hz) ppm. IR (KBr) v: 3071, 2964, 2928, 2870, 1717, 1602, 1511, 1026, 843, 764 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{19}H_{18}FIN$, $[M + H]^+$ 406.0468, found 406.0472.

*1-(4-Chlorophenyl)-2-iodo-5-isopropyl-3-phenyl-1H-pyrrole (**3ak**)*: yellow oil, 70% yield (88.4

mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.63 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.42 – 7.36 (m, 4H), 7.25 (t, J = 7.2 Hz, 1H), 6.37 (s, 1H), 2.64 (dt, J = 13.5, 6.7 Hz, 1H), 1.05 (d, J = 6.7 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 145.3, 138.6, 136.1, 133.5, 131.4, 129.3, 128.9, 128.2, 127.6, 126.2, 106.1, 72.4, 26.5, 22.8 ppm. IR (KBr) v: 3064, 2965, 2928, 2871, 1699, 1495, 1092, 696 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{19}H_{18}ClIN$, $[M + H]^+$ 422.0172, found 422.0172.

*1-(4-(tert-Butyl)phenyl)-2-iodo-5-isopropyl-3-phenyl-1H-pyrrole (**3al**)*: yellow oil, 85% yield (112.9 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.64 (d, J = 7.5 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.27 –7.22 (m, 1H), 7.19 (d, J = 8.2 Hz, 2H), 6.32 (s, 1H), 2.74 (dt, J = 13.5, 6.7 Hz, 1H), 1.39 (s, 9H), 1.11 (d, J = 6.8 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 151.8, 146.1, 137.5, 136.7, 129.6, 129.0, 128.2, 128.1, 126.2, 125.8, 106.0, 70.6, 34.8, 31.5, 27.1, 23.2 ppm. IR (KBr) v: 3059, 2962, 2927, 2869, 1664, 1603, 1514, 1106, 761, 696 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{23}H_{27}IN$, $[M + H]^+$ 444.1188, found 444.1195.

*Ethyl 4-(2-iodo-5-isopropyl-3-phenyl-1H-pyrrol-1-yl)benzoate (**3am**)*: yellow oil, 39% yield (53.7 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 8.14 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 7.3 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 6.40 (s, 1H), 4.37 (q, J = 7.0 Hz, 2H), 2.67 (dt, J = 13.3, 6.6 Hz, 1H), 1.36 (t, J = 7.0 Hz, 3H), 1.05 (d, J = 6.7 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 165.5, 145.7, 144.1, 136.5, 130.6, 130.5, 130.4, 129.8, 128.7, 128.1, 126.7, 106.9, 72.3, 61.6, 26.9, 23.2, 14.6 ppm. IR (KBr) v: 3064, 2966, 2929, 2872, 1719, 1605, 1514, 1368, 1276, 1104, 700 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{22}H_{23}INO_2$, $[M + H]^+$ 460.0773, found 460.0778.

*2-Iodo-5-isopropyl-3-phenyl-1-(4-(trifluoromethoxy)phenyl)-1H-pyrrole (**3an**)*: yellow oil, 51% yield (72.1mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.61 – 7.55 (m, 4H), 7.52 (d, J = 8.8 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.3 Hz, 1H), 6.39 (s, 1H), 2.65 (dt, J = 13.4, 6.7 Hz, 1H), 1.06 (d, J = 6.7 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 ^{o}C) δ = 148.7, 145.8, 139.1, 136.5, 132.1, 130.3 (q, J = 280.0 Hz), 128.7, 128.1, 126.6, 122.1, 106.6, 73.0, 26.9, 23.2 ppm. ^{19}F NMR (377 MHz, DMSO-d_6, 25 °C, 25 ^{o}C) δ = -56.9 ppm. IR (KBr) v: 3065, 2968, 2930, 2874, 1674, 1511, 1261, 1210, 1172, 695 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{18}F_3INO$, $[M + H]^+$ 472.0385, found 472.0387.

*2-Iodo-5-isopropyl-3-phenyl-1-(3,4,5-trimethylphenyl)-1H-pyrrole (**3ao**)*: colourless oil, 88% yield (113.2 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.56 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 6.96 (s, 2H), 6.32 (s, 1H), 2.65 (dt, J = 13.6, 6.7 Hz, 1H), 2.31 (s, 6H), 2.20 (s, 3H), 1.06 (d, J = 6.8 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 ^{o}C) δ = 145.7, 137.4, 137.0, 136.9, 136.1, 128.7, 128.6, 128.4, 128.0, 126.4, 105.9, 73.0, 26.9, 23.5, 20.6, 15.5 ppm. IR (KBr) v: 2963, 2927, 2867, 1714, 1603, 1489, 1027, 798, 763, 697 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{22}H_{25}IN$, $[M + H]^+$ 430.1032, found 430.1033.

*(3,4-Difluorophenyl)-2-iodo-5-isopropyl-3-phenyl-1H-pyrrole (**3ap**)*: colourless oil, 68% yield (86.3 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.67 (dt, J = 19.5, 8.9 Hz, 2H), 7.58 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.3 Hz, 2H), 6.37 (s, 1H), 2.68 (dt, J = 13.5, 6.7 Hz, 1H), 1.08 (dd, J = 8.6, 7.2 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$, 25 ^{o}C) δ = 150.1 (dd, J = 247.0 Hz, 13.0 Hz), 149.5 (dd, J = 247.0 Hz, 14.0 Hz), 136.8 (dd, J = 8.5 Hz, 3.0 Hz), 136.5, 131.0, 129.4, 128.7, 128.1, 127.62 (dd, J = 7.0, 3.0 Hz), 126.7, 119.9 (d, J = 17.9 Hz),

118.2 (d, J = 17.9 Hz), 106.6, 73.0, 26.9, 23.3, 23.2 ppm. ^{19}F NMR (377 MHz, DMSO-d_6, 25 °C, 25 °C) δ = -136.15 – -136.47 (m), -137.25 – -137.58 (m) ppm. IR (KBr) v: 3064, 2966, 2929, 2872, 1693, 1517, 1215, 771 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{19}H_{17}F_2IN$, $[M + H]^+$ 424.0374, found 424.0376.

*1-(3-Chloro-2-methylphenyl)-2-iodo-5-isopropyl-3-phenyl-1H-pyrrole (**3aq**)*: yellow oil, 65% yield (84.8 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.63 (dd, J = 12.8, 7.8 Hz, 3H), 7.41 (dt, J = 15.1, 7.7 Hz, 3H), 7.33 (d, J = 7.6 Hz, 1H), 7.26 (t, J = 7.3 Hz, 1H), 6.41 (s, 1H), 2.43 (dt, J = 13.4, 6.7 Hz, 1H), 1.89 (s, 3H), 1.06 (dd, J = 10.2, 7.0 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 145.3, 140.7, 136.4, 136.0, 134.7, 130.5, 129.4, 129.3, 128.7, 128.2, 128.0, 126.6, 106.4, 72.1, 27.2, 23.9, 22.8, 15.5 ppm. IR (KBr) v: 3063, 2964, 2927, 2870, 1599, 1468, 1031, 764, 697 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}ClIN$, $[M + H]^+$ 436.0329, found 436.0327.

*1-(3-Bromo-4-methylphenyl)-2-iodo-5-isopropyl-3-phenyl-1H-pyrrole (**3ar**)*: yellow oil, 59% yield (84.6 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.60 (s, 1H), 7.55 (t, J = 9.3 Hz, 3H), 7.39 (t, J = 7.5 Hz, 2H), 7.30 – 7.23 (m, 2H), 6.35 (s, 1H), 2.65 (dt, J = 13.4, 6.7 Hz, 1H), 2.44 (s, 3H), 1.06 (t, J = 7.1 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 145.3, 138.6, 138.3, 136.1, 132.7, 131.3, 128.9, 128.8, 128.2, 127.6, 126.1, 123.8, 106.0, 72.5, 26.4, 22.8, 22.7, 22.2 ppm. IR (KBr) v: 3060, 2964, 2926, 2870, 1680, 1600, 1493, 1037, 821, 695 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}BrIN$, $[M + H]^+$ 479.9824, found 479.9828.

*2-iodo-5-isopropyl-1-(naphthalen-1-yl)-3-phenyl-1H-pyrrole (**3as**)*: colourless oil, 68% yield (89.1 mg); ^{1}H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 8.13 (d, J = 8.2 Hz, 1H), 8.08 (d, J = 7.7

Hz, 1H), 7.68 (dd, *J* = 15.8, 7.6 Hz, 3H), 7.58 (dd, *J* = 16.2, 7.8 Hz, 3H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.27 (m, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.50 (s, 1H), 2.35 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 146.3, 136.2, 136.1, 133.7, 131.5, 129.5, 128.6, 128.3, 128.2, 127.8, 127.6, 127.5, 126.8, 126.1, 125.6, 122.5, 105.8, 73.0, 26.9, 23.7, 22.6 ppm. IR (KBr) *v*: 3057, 2963, 2927, 2869, 1718, 1600, 1514, 1413, 1025, 803, 775 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{23}H_{21}IN$, $[M + H]^+$ 438.0719, found 438.0716.

*3-(2-Iodo-5-isopropyl-3-phenyl-1H-pyrrol-1-yl)-6-methoxy-2-methylpyridine (**3at**)*: colourless oil, 30% yield (38.8 mg); ^1H NMR: (400 MHz, DMSO-d_6, 25 °C) δ = 7.66 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.40 (s, 1H), 3.92 (s, 3H), 2.45 (dt, *J* = 13.5, 6.8 Hz, 1H), 2.00 (s, 3H), 1.11 – 1.03 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 163.2, 155.3, 145.5, 141.1, 136.5, 129.2, 129.0, 128.7, 127.9, 126.6, 108.9, 106.5, 73.0, 54.0, 27.2, 23.9, 22.7, 20.6 ppm. IR (KBr) *v*: 3061, 2964, 2928, 2870, 1599, 1481, 1308, 1036, 763 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{20}H_{22}IN_2O$, $[M + H]^+$ 433.0777, found 433.0772.

*(E)-3-((E)-4-chlorostyryl)-4-hydroxypent-3-en-2-one (**4a**)*:[44] yellow solid, mp: 70–72 °C, 65% yield (153.4 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 16.77 (s, 1H), 7.37 – 7.30 (m, 4H), 6.73 (d, *J* = 16.1 Hz, 1H), 6.36 (d, *J* = 16.1 Hz, 1H), 2.22 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 191.3, 135.7, 133.4, 132.9, 129.0, 127.4, 123.6, 111.3, 24.4 ppm.

*1-(5-(4-Chlorophenyl)-2-methyl-1-phenyl-1H-pyrrol-3-yl)ethanone (**5a**)*:[45] yellow oil, 67% yield (62.1 mg); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ =7.36 – 7.33 (m, 3H), 7.07 – 7.04 (m,

4H), 6.91 – 6.90 (m, 1H), 6.88 (t, *J* = 2.2 Hz, 1H), 6.65 (s, 1H), 2.43 (s, 3H), 2.35 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 194.2, 137.0, 136.9, 131.8, 131.3, 130.9, 129.6, 129.4, 128.8, 128.4, 128.2, 121.2, 111.1, 99.5, 28.7, 12.6 ppm.

3-(1,3-Diphenyl-5,6,7,8-tetrahydroindolizin-8-yl)-1-methyl-1H-indole ***(6a)***: yellow oil, 81% yield (97.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.61 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.4 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.31 (d, J = 7.6 Hz, 4H), 7.27 (s, 1H), 7.13 (dd, J = 10.7, 7.2 Hz, 3H), 7.02 (t, J = 7.1 Hz, 1H), 6.54 (d, J = 4.4 Hz, 2H), 4.86 (s, 1H), 4.25 (d, J = 11.7 Hz, 1H), 3.84 (dd, J = 14.9, 8.4 Hz, 1H), 3.66 (s, 3H), 2.31 (d, J = 10.0 Hz, 1H), 2.08 (dd, J = 27.3, 15.6 Hz, 2H), 1.74 (d, J = 12.3 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 137.7, 136.6, 133.8, 133.7, 130.1, 129.0, 128.7, 128.5, 128.3, 127.1, 126.8, 126.4, 124.9, 121.5, 120.4, 119.3, 118.9, 118.8, 109.5, 108.9, 45.4, 32.8, 31.1, 27.9, 19.4 ppm. IR (KBr) *v*: 3052, 2928, 2869, 1682, 1600, 1486, 1468, 1325, 1028, 760, 740, 699 cm^{-1}, HRMS (TOF, ESI): m/z calcd for $C_{29}H_{27}N_2$, $[M + H]^+$ 403.2174, found 403.2175.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR.

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Notes

The authors declare no competing financial interest.

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