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Synthesis of Furans and Pyrroles from 2-Alkoxy-2,3-dihydrofurans Through a Nucleophilic Substitution-Triggered Heteroaromatization

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Abstract: An effective method to synthesize α-functionalized furan and pyrrole derivatives was developed using 2-alkoxy-2,3-dihydrofurans as modular precursors. This protocol featured a previously unreported tandem nucleophilic substitution/heteroaromatization reaction. Nucleophiles such as indole, α-oxoketene dithioacetal, trimethoxybenzene, and dimethoxynaphthalene can react readily with 2-alkoxy-2,3-dihydrofurans to afford α-functionalized five-membered ring heterocycles in the presence of acid catalysts, such as copper bromide and iron chloride. The mechanism of the reaction was also discussed, in which the first step, nucleophilic substitution, is the key in triggering the succeeding heteroaromatization. This method can also be extended to the synthesis of dihydrothiophenes.

Keywords: dihydrothiophenes; furans; heteroaromatization; indoles; pyrroles; α-oxoketene dithioacetal

Introduction

Furans, pyrroles, and thiophenes are naturally occurring heterocycles. Some of these functional groups are important biologically active pharmaceuticals.[1] Although myriad methods are known to accomplish the synthesis of these heterocycles, sustained efforts have been made to develop efficient synthetic methods under manageable conditions.[2] On the other hand, carbon–carbon bond formation through a nucleophilic substitution reaction is a fundamental pathway to construct complex organic molecules.[3] Tandem or cascade reactions, which are hot research topics of modern organic chemistry, often employ nucleophilic substitution as a key step because the conditions for implementing these reactions are compatible with many others.[4] By the rational design of organic substrates, many important heterocycles could be synthesized through nucleophilic substitution-triggered reaction sequences.[5] However, the potential capacity of this type of sequential reaction in creating molecular complexity and diversity has not been fully exploited, because most of the reported examples were established on the basis of an intramolecular condensation-pull reaction manner. Furthermore, redox reactions, which can enrich the product diversity significantly, have been rarely applied in the construction of a heterocyclic scaffold from nucleophilic substitution.[6]

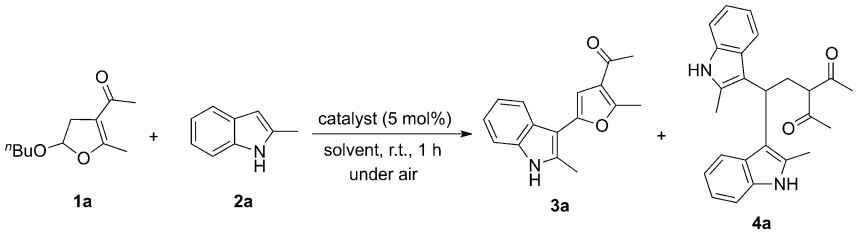
We reported a ring-opening reaction of 2-substituted 3,4-dihydropyrans with indoles, which provided a convenient method to synthesize 2-[3-(indol-3-yl)-propyl]-1,3-dicarbonyl compounds.[7] In continuation of our research to explore new reactions using cyclic acetals as building blocks, we recognized the value of investigating the reactions of 2-alkoxy-2,3-dihydrofurans.[8] Herein, we report, for the first time, a nucleophilic substitution-triggered heteroaromatization reaction of 2-alkoxy-2,3-dihydrofurans with aromatic nucleophiles that produces furan and pyrrole derivatives. Dihydrothiophenes could also be synthesized with a similar procedure.

Results and Discussion

Initially, a dihydrofuran derivative **1a** was treated with 2-methylindole **2a** (Table 1). The reaction was performed at room temperature in nitromethane. No product was formed in the absence of catalyst (entry 1). When $FeCl_3{\cdot}6H_2O$ was employed as catalyst, **1a** was consumed rapidly. However, the expected oxidative substitution product **3a** was obtained only at a 15% yield (entry 2). The formation of a ring-opening product **4a** was predominant. To improve the yield of **3a**, various Lewis acids were employed. Notably, when $CuBr_2$ was used, **3a** reached a 95% yield (entry 3). Many other copper salts were also screened. $CuCl_2$ and $Cu(OTf)_2$ were found to be less effective (entries 4 and 5), and **3a** was obtained at 55% and 23% yields, respectively. $CuSO_4{\cdot}5H_2O$ and CuBr cannot catalyze this reaction (entries 6 and 7). When strong acids, such as *para*-toluenesulfonic acid (PTSA), $AlCl_3$, $Sc(OTf)_3$, and I_2 were employed as catalysts, **1a** was consumed rapidly. However, **3a** was scarcely detected, and only **4a** was obtained (entries 8 to 11). A weak Lewis acid, $MnCl_2{\cdot}4H_2O$, was also employed, but only a trace amount of **3a** was formed (entry 12).

The effect of the solvent on the model reaction was then investigated. Nitromethane prominently cooperated with the $CuBr_2$ catalyst, followed by acetonitrile, 1,4-dioxane, and chlorobenzene to a distant second place (entries 13 to 15). By contrast, toluene, dichloromethane, and ethanol were found to be inappropriate for this reaction (entries 16 to 18). Further investigations revealed that the reaction was also affected significantly by the catalyst amount. When the amount of catalyst was increased, the maximum yield was reached sooner. With 20 mol% of catalyst, the reaction time was halved compared with that of the use of 5 mol% of $CuBr_2$ (entry 19). However, with a high catalyst loading, the reaction selectivity dropped slightly because of the formation of some inseparable products. Finally, the optimal reaction conditions were confirmed as the following: 5 mol% of $CuBr_2$ catalyst, nitromethane solvent, and 1 h reaction time at room temperature.

Table 1. Synthesis of **3a** from **1a** and **2a**.[a]

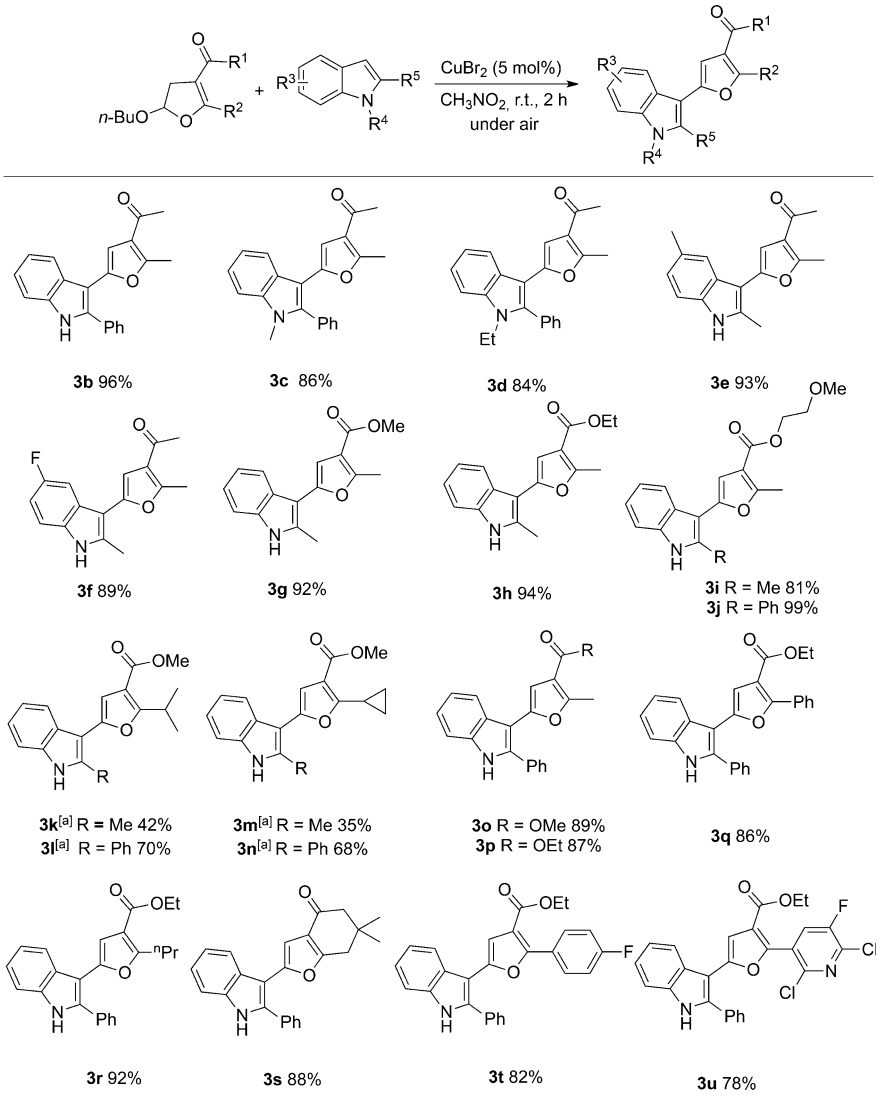


1a 2a 3a 4a

entry	catalyst (5 mol%)	solvent	Yield (%)	
			3a	**4a**
1	–	CH_3NO_2	0	0
2	$FeCl_3{\cdot}6H_2O$	CH_3NO_2	15	65
3	$CuBr_2$	CH_3NO_2	95 (92)[b]	–
4	$CuCl_2$	CH_3NO_2	55	22
5	$Cu(OTf)_2$	CH_3NO_2	23	52
6	$CuSO_4{\cdot}5H_2O$	CH_3NO_2	trace	trace
7	CuBr	CH_3NO_2	trace	trace
8	PTSA	CH_3NO_2	trace	68
9	$AlCl_3$	CH_3NO_2	trace	58
10	$Sc(OTf)_3$	CH_3NO_2	trace	45
11	I_2	CH_3NO_2	trace	53
12	$MnCl_2{\cdot}4H_2O$	CH_3NO_2	trace	10
13	$CuBr_2$	CH_3CN	65	15
14	$CuBr_2$	1,4-dioxane	59	13
15	$CuBr_2$	PhCl	55	24
16	$CuBr_2$	toluene	11	25
17	$CuBr_2$	DCM	trace	trace
18	$CuBr_2$	EtOH	trace	trace
19[c]	$CuBr_2$	CH_3NO_2	85	trace

[a] Conditions unless specified otherwise: **1a**, 0.2 mmol; **2a**, 0.2 mmol; catalyst, 0.01 mmol; solvent, 1 mL; room temperature, 1 h, under air.
[b] Reaction scale: 10 mmol.
[c] Catalyst amount, 20 mol%, 0.04 mmol, 30 min.

Under the optimized conditions, we probed the scope of the reaction with respect to both the dihydrofuran and the indole components. As demonstrated by the results in Figure 1, various indoles reacted with **1a** readily, affording the C3-furanyl substituted indole derivatives in good to excellent yields (**3b–f**). The presence of a phenyl group in the C2 position of the indole ring enabled more efficient reactions than the congeners with methyl group (**3j**, **3l**, **3n**). The scope of this oxidative substitution reaction with respect to the dihydrofuran component was next studied. Many 2-butoxy-2,3-dihydrofurans with ester or ether moieties were proven to be viable substrates (**3g–3u**). However, an unexpected subtle influence of a bulky group in the C2 position of the skeleton on the reactivity of the molecule was observed. 2-Isopropyl- or 2-cyclopropyl-substituted 2,3-dihydrofurans are rather reluctant to participate in the reaction, and moderate yields were obtained even though the reaction time was increased to 12 h (**3k** to **3n**). By sharp contrast, excellent yields were obtained when the dihydrofurans with phenyl or *n*-propyl group in C2 position were employed (**3n–3o**). The discrepancy between the reactivities is likely due to the possible steric hindrance associated with these groups. Despite obtaining only a 68% yield from the synthesis of **3k**, considering the fact that cyclopropane scaffold is amenable to many transformations,[9] the present reaction is quite interesting. This reaction enabled the synthesis of a C5-substituted fused furan **3s**, which has been proven to possess promising biological activity.[10] The catalytic activity of $CuBr_2$ was not affected by the existence of a pyridyl group in the skeleton of dihydrofuran. Owing to this unique ability of $CuBr_2$,



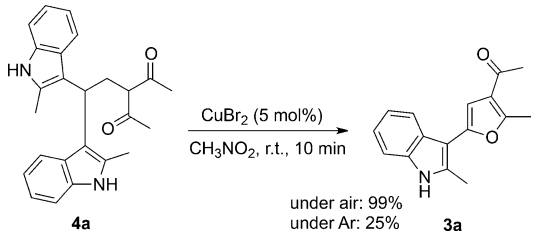
[a] Reaction time: 12 h.

Figure 1. Substrate scope of the reaction between 2-butoxy-2,3-dihydrofurans and indoles.

a tricyclic compound **3u** can be obtained at a 78% yield.

Notably, the product's skeleton contains an indole ring system, which has become an important structural component in many pharmaceutical agents.[11] Particularly, indoles substituted with aromatic heterocyclic rings at the C3 position have been found in a fascinating array of bioactive natural products and pharmaceutical compounds.[12] However, we found that the synthesis of these compounds is challenging because the reported arylation methods suffered from either insufficient reaction or the use of expensive reagents. For example, with the classical carbon–carbon cross-coupling strategy (Suzuki–Miyaura, Stille, Kumada, and Negishi reactions), the overall process includes the prefunctionalization of the substrates as nucleophilic and electrophilic reagents, which is generally less efficient with the heteroaryl analogues.[13] A direct arylation involving a C–H activation reaction allows the use of a simple unfunctionalized arene as substrate.[14] However, the reactions with indoles are limited to the use of homoaryl halides as the electrophilic component; furthermore, the regioselectivity of the arylation depends on the protecting group of the indole nitrogen atom.[15] The model reaction in Table 1 not only allowed the addition of a nucleophile moiety to the skeleton of a five-membered heterocycle in a convenient and efficient way, but also avoided the use of expensive catalysts and harsh reaction conditions. The reaction can also be scaled up effectively with similar efficiency. In particular, the reaction of **1a** (10 mmol) with **2a** (10 mmol) gave the corresponding product **3a** at a 92% yield (Table 1, entry 3).

To gain insight into this reaction, several controlled experiments were conducted. 2-Alkoxy-2,3-dihydrofurans are known to be rather susceptible to acidic conditions.[16] For instance, treating a dihydrofuran **1b** with PTSA in reflux benzene resulted in the formation of methyl 2-methyl-3-furancarboxylate. However, this compound was found to be highly stable in a cross-dehydrogenative coupling reaction (CDC) in the presence of 2-methylindole under previous reaction conditions (see the Supporting Information, Scheme S1). This precludes the possibility of forming **3a** through a CDC reaction. We then treated **4a** in the presence of $CuBr_2$. Intriguingly, **3a** was formed rapidly (Scheme 1). A low yield of 25% was obtained after inducing the same reaction under argon. This implies that molecular oxygen is important for rendering the reaction possible. On the basis of these results, we proposed a mechanism depicted in Figure 2. Initially, $CuBr_2$ may have activated the dihydrofuran **1a** through coordination with the ketone carbonyl. Then, 2-methylindole may have acted as a nucleophile to attack the anomeric carbon of **1a**. Both of the endocyclic C–O and exocyclic C–O bonds are fairly sensitive to acid; hence the nucleophilic substitution may have occurred twice, thereby forming **4a**. The good leaving ability of 2-methylindole **2a**[17] leads to the formation of the alkylideneindolenine intermediate (**I**).[11b,18] (**I**) may have instigated an intramolecular nucleophilic substitution, in which a OH group in the enol form of 1,3-dicarbonyl fragment of **4a** served as a nucleophile. An intermediate (**II**) was therefore



Scheme 1. Synthesis of **3a** from **4a**.

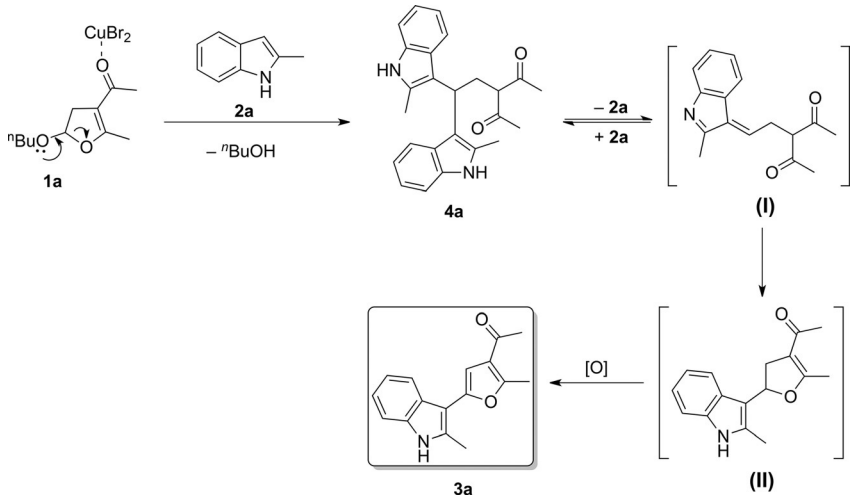
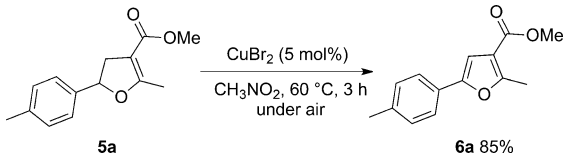


Figure 2. Proposed mechanism for the synthesis of furan derivatives.



Scheme 2. $CuBr_2$-catalyzed aromatization of **5a**.

generated. Finally, **3a** may have been formed through a $CuBr_2$-induced heteroaromatization.[19] All of our earlier attempts at isolating intermediate (**II**) from the reaction system failed. Hence, to verify the amenability of (**II**) for the heteroaromatization reaction, a similar C5-aryl-substituted 2,3-dihydrofuran **5a** was synthesized and subjected to the conditions of the model reaction (Scheme 2). As we expected, **5a** was easily converted to **6a** at 60 °C. These results suggest that the heteroaromatization of (**II**) may indeed be the last step of the mechanism. Interestingly, the formation of (**II**) starting from the dihydrofuran **1a** appears to involve a nucleophilic substitution, in which the butoxy group acted as the leaving group. The heteroaromatization step is rather fast; therefore, the formation rate of the final product **3a** should be under the control of this apparent nucleophilic substitution.

Considering the success of the earlier experiments, we were prompted to use other nucleophiles in this type of reaction. We found that α-oxoketene dithioacetals, which have recently emerged as important building blocks,[20] can react with our dihydrofurans easily in the presence of $CuBr_2$ catalyst at 60 °C. This result is reasonable because the α-carbon of the double bond that is close to the carbonyl group is fairly reactive because of the presence of electron-releasing alkylthiol groups (p-π conjugation). The substrate scope was also found to be excellent (Figure 3). Reasonable yields were obtained regardless of the nature of the substituent present on the α-oxoketene thioacetal (electron-donating or electron-withdrawing). Cyclopropyl, difluoromethyl, and double bonds in the substrates can all be delivered uneventfully into the structure of final products (**8f**, **8k**, and **8q**). The synthesis of **8a** and **8q** scaled up to 5 mmol provided uniform results.

Trimethoxybenzenes **9a**, **9b**, and dimethoxynaphthalene **11a** reacted readily with **1b** to form α-aryl-functionalized furan derivatives (Scheme 3). Particu-

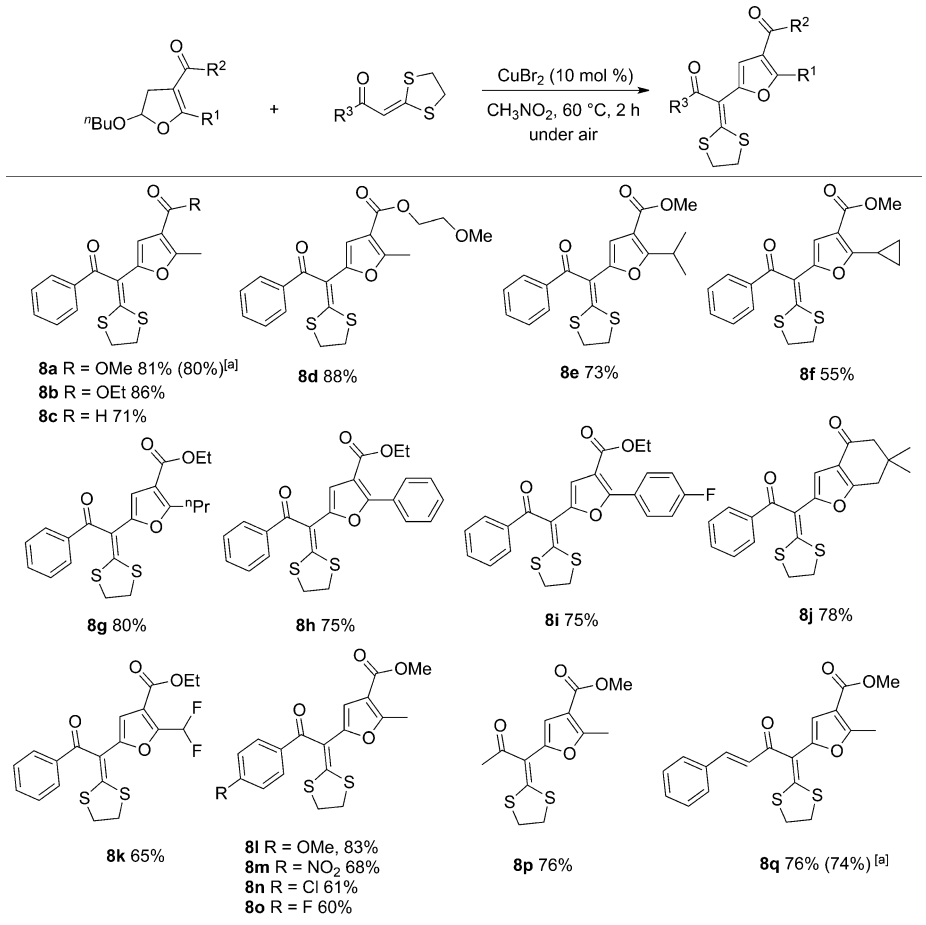
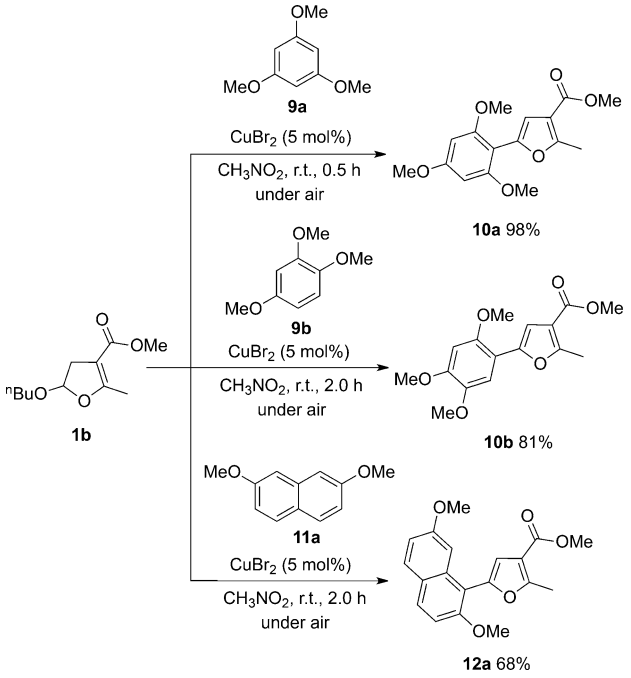


Figure 3. α-Ketene dithioacetal reactions with 2-alkoxy-2,3-dihydrofuran to produce corresponding furan derivatives.



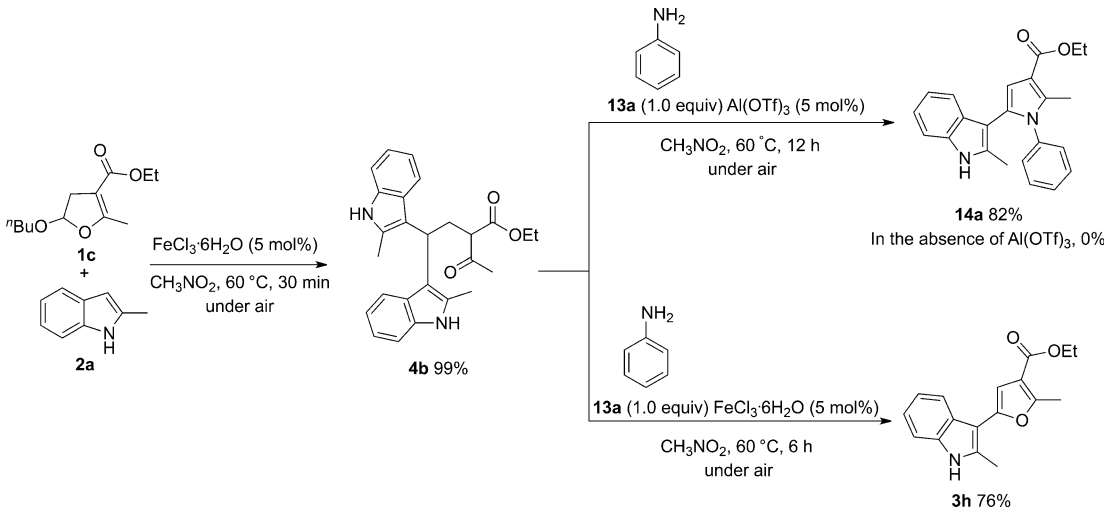
Scheme 3. Reactions of **1b** with **9a**, **9b** and **11a**.

larly, when 1,3,5-trimethoxybenzene **9a** was used as nucleophile, the desired product **10a** was obtained in an almost quantitative yield within 30 min. The inferior reaction yield of 1,2,4-trimethoxybenzene **9b** with respect to that of **9a** may be due to the low nucleophilicity in the former compound.

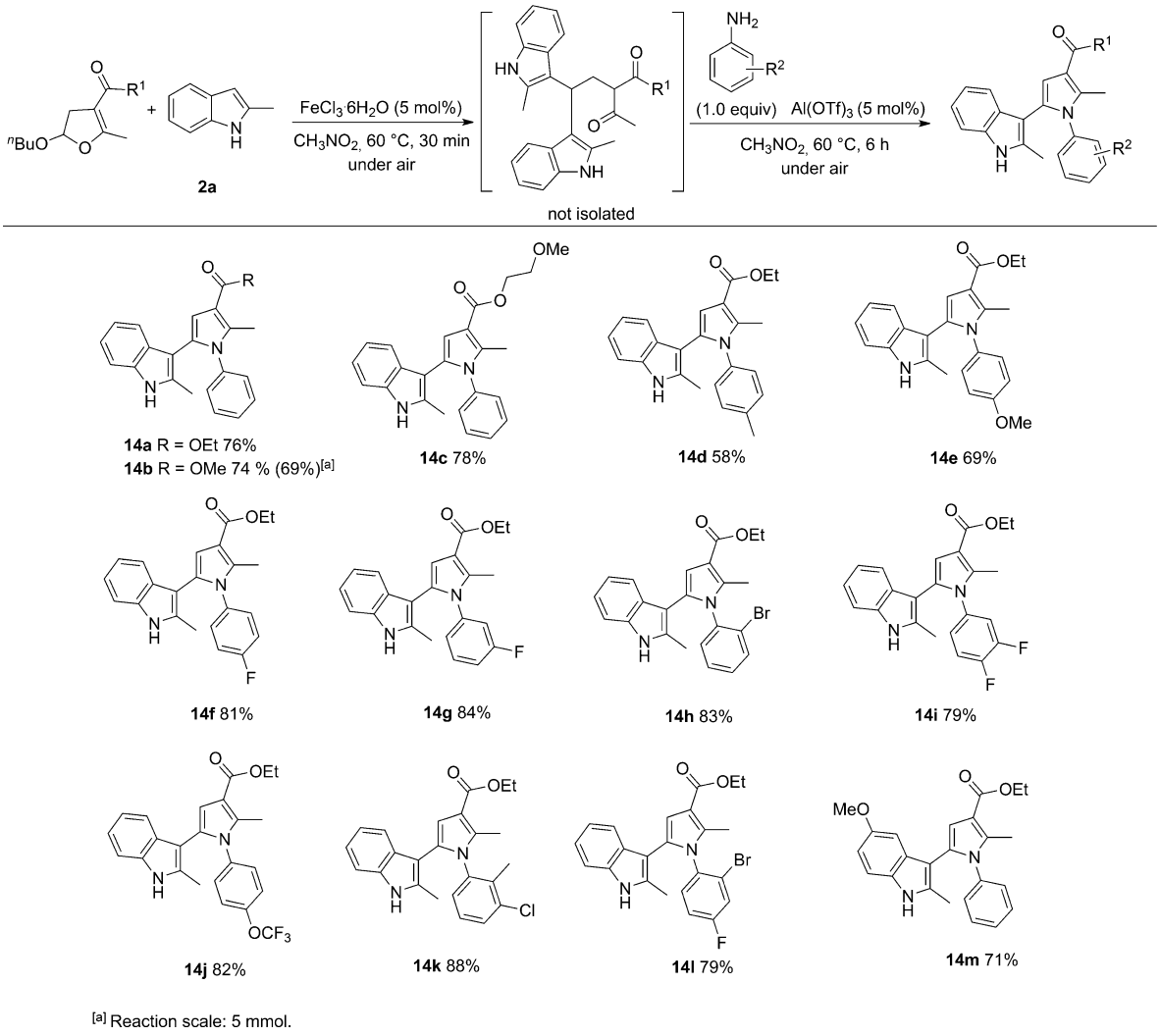
2-Alkoxy-2,3-dihydrofuran is well known to react with amines to generate pyrrole.[21] Thus, we established a three-component reaction of dihydrofuran **1c**, aniline **13a**, and **2a**, with which a pyrrole derivative is expected to be synthesized. Although **1c** was consumed in some cases, we failed to obtain the anticipated assembly product **14a**. Nevertheless, **14a** could be synthesized through an alternative two-step method as shown in Scheme 4. In the first step, **1c** reacts readily with 2.0 equivalents of **2a** with the aid of the catalyst $FeCl_3{\cdot}6H_2O$, affording a ring-opening product **4b** in almost quantitative yield. Treatment of **4b** with **13a** in the presence of $Al(OTf)_3$ catalyst produced **14a** in 82% yield. The addition of $Al(OTf)_3$ as catalyst in the second step is necessary because **14a** cannot be obtained in the absence of $Al(OTf)_3$ (Scheme 4). When $FeCl_3{\cdot}6H_2O$ was used instead of $Al(OTf)_3$, only **3h** was obtained, and aniline remained unchanged at the end of the reaction (Scheme 4).

In these consecutive steps, the same solvent nitromethane was used. To simplify the operational procedure, we also attempted to perform the reaction in a one-pot stepwise manner. First, **1c** was treated with 2.0 equivalents of **2a** in the presence of $FeCl_3{\cdot}6H_2O$ in nitromethane. After 30 min of stirring at 60 °C, by monitoring the reaction with thin layer chromatography (TLC), we found that both **1c** and **2a** were completely consumed. Then, **13a** was added along with the $Al(OTf)_3$ catalyst. After 6 h of reaction, **14a** was obtained in 76% yield. With this procedure, various C3-pyrrolylated indoles could be obtained. Random combinations of the three starting substrates could provide final products with up to 88% yield (Figure 4). The reaction with the 5 mmol scale also proceeded successfully. Previous methods employed to access this kind of pyrrole/indole hybrid molecular scaffold were not easy and suffered from either the difficulty of preparing the starting substrate[22] or the use of harsh conditions.[23]

To understand the exact role of these two catalysts, several controlled experiments were performed (Scheme 5). In the skeleton of **4b**, two active sites that can potentially react with **13a**. The diketone moiety may react with **13a** to form an enamine. In its opposite side, a cleavage of a C–C bond may also



Scheme 4. Synthesis of **14a** *via* a two-step method.

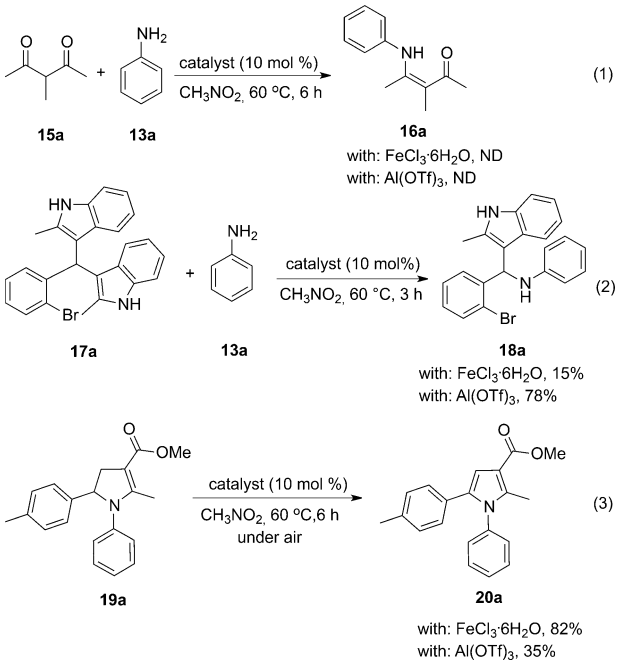


[a] Reaction scale: 5 mmol.

Figure 4. Scope of one-pot, stepwise, multicomponent reactions of indoles, 2-butoxy-2,3-dihydrofurans and anilines.

occur, enabling the formation of a nucleophilic substitution product with the removal of one molecule of **2a**. To determine the favorability of the reaction, 3-methyl-2,4-pentane **15a** was treated with **13a** under our conditions. However, no reaction occurred when $FeCl_3{\cdot}6H_2O$ or $Al(OTf)_3$ was used as catalyst. A combination of $FeCl_3{\cdot}6H_2O$ and $Al(OTf)_3$ also gave the same result. Afterward, a diindolylmethane derivative **17a** was subjected to our reaction conditions. An intermolecular nucleophilic substitution product **18a** was then generated in 78% yield when $Al(OTf)_3$ was used as catalyst. $FeCl_3{\cdot}6H_2O$ was demonstrated to be less efficient in this reaction, and the yield of **18a** in this case reached only 15% under identical conditions. These results imply that the initial step in the reaction of **4b** and **13a** might be a pseudo-nucleophilic substitution to form intermediate (**IV**). In this step, the $Al(OTf)_3$ catalyst plays an important role (Figure 5). Once (**IV**) is formed, it might be rapidly converted to a dihydropyrrole (**V**) through an intramolecular enamination. The following heteroaromatization of (**V**) would then result in the formation of **14a**. (**V**) is difficult to isolate from the reaction mixture; hence, to clarify the exact contribution of each component of the catalyst in the heteroaromatization reaction, a dihydropyrrole **19a** was used as an alternative model to (**V**) in the controlled experiments. The oxidation of **19a** proceeded favorably in the presence of $FeCl_3{\cdot}H_2O$, and the expected pyrrole derivative **20a** was obtained in 82% yield. By contrast, the reaction over $Al(OTf)_3$ proceeded sluggishly, and the yield of **20a** reached only 35% under identical conditions. These results led us to conclude that in the heteroaromatization step, the main driving force is the catalytic effect of the iron salt.

This one-pot stepwise method was also proven to be applicable in the synthesis of a dihydrothiophene derivative **21a** (Figure 6). After finishing the electrophilic ring-opening of **1b** with **2a**, P_2S_5 was added into the reaction system. Compound **21a** was obtained in



Scheme 5. Control experiments.

95% yield within 1 h of reaction at 60 °C. The resistance of the dihydrothiophene derivative against the heteroaromatization reaction may partially result from the existence of sulfur that significantly diminishes the catalytic ability of Fe^{3+} in promoting an oxidation reaction.[24] A reaction in the 5 mmol scale also proceeded successfully, indicating the usefulness of this reaction for practical synthesis. Notably, the methods to access C3-thiophenyl-substituted indole derivatives have been rarely reported,[25] although this scaffold has often been employed in the production of medicines and pesticides.[26]

Conclusions

A novel nucleophilic substitution-triggered heteroaromatization reaction of 2-butoxy-2,3-dihydrofuran was developed by using metal Lewis acids as catalysts. With this method, many nucleophiles that have conjugated systems, such as indole, α-oxoketene dithioacetal, trimethoxybenzene and dimethoxynaphthalene could be installed into C2 position of the furan skeleton with the aid of $CuBr_2$ catalyst. Thanks to the good leaving ability of 2-methylindole, stepwise approaches for the synthesis of pyrrole and dihydrothiophene derivatives were also developed. These reactions offered effective means to heteroarylate some commonly used nucleophiles. Given the large number of commercially available nucleophiles and the easy access to the dihydrofurans, the present method should be applicable to the synthesis of α-functionalized furans, pyrroles and dihydrothiophenes. Particularly, it should be useful for establishing some indole/five-membered heterocycle hybrid molecule libraries with high diversity.

Experimental Section

General

Melting points were determined by microscopic melting pointmeter and were uncorrected. IR spectra were recorded on a FT-IR Bruker (EQUINOX 55) using KBr pellets or neat liquid technology. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 or 600. Chemical shifts were expressed in ppm relative to Me_4Si in solvent. All chemicals used were of reagent grade and were used as received without further purification. 2-Alkoxy-2,3-dihydrofuran were prepared according to previously reported methods.[8] In the most cases, the reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring.

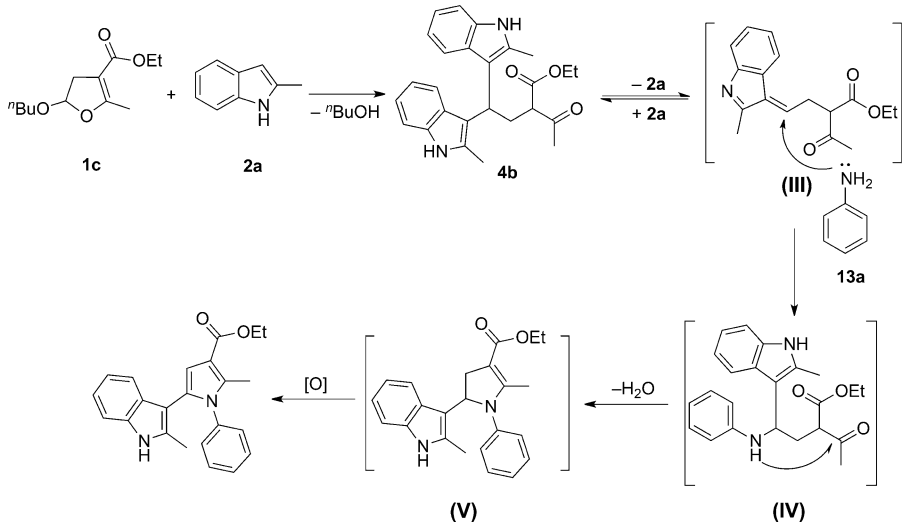
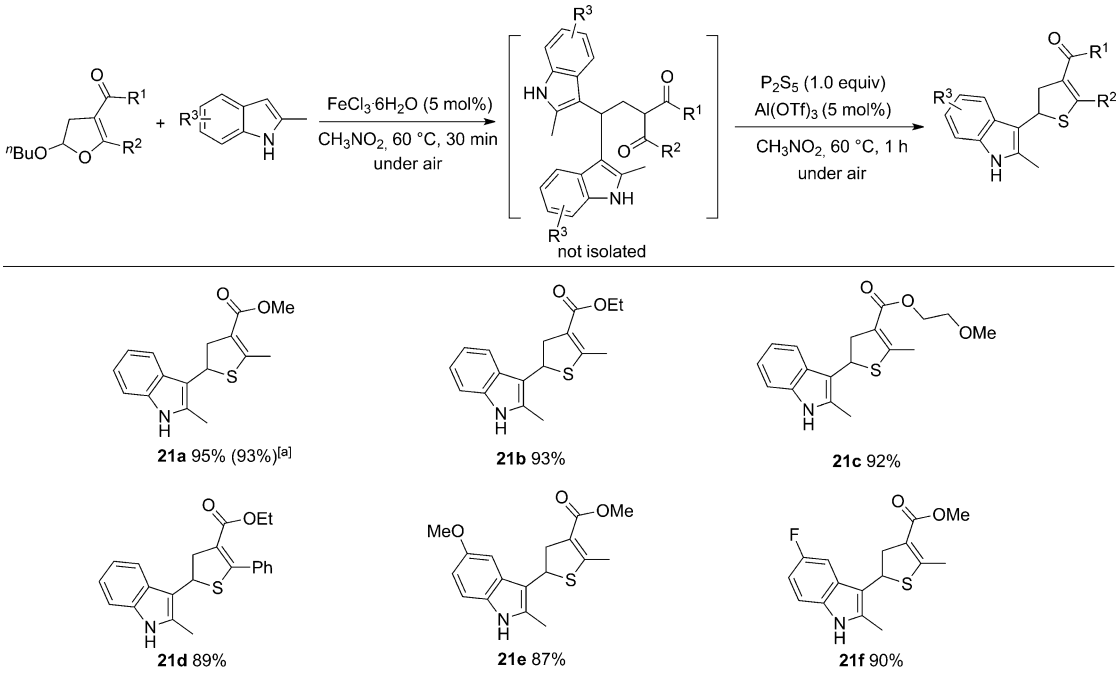


Figure 5. Proposed mechanism for the synthesis of pyrrole derivatives.



[a] Reaction scale: 5 mmol.

Figure 6. Synthesis of thiophene derivatives.

A typical procedure for the reaction of dihydrofuran and indole. In a typical reaction, **1a** (0.20 mmol) was mixed with **2a** (0.20 mmol) and $CuBr_2$ (5 mol%) in nitromethane (1.0 mL). The mixture was then stirred at room temperature for one hour. After reaction, the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether/ethyl acetate = 5:1 (v/v)). Tests for substrate scope were all performed with an analogous procedure. Compound **4a** was obtained in 65% yield by changing the catalyst to $FeCl_3{\cdot}6H_2O$ (5 mol%).

Large-scale synthesis of 4a. In a 100 mL of round-bottom flask, **1a** (10.0 mmol) was mixed with **2a** (10.0 mmol), and $CuBr_2$ (5 mol%) in nitromethane (30.0 mL). The mixture was then stirred at room temperature for one hour. After completion of the reaction, brine (30 mL) was added. And then the aqueous phase was extracted by ethyl acetate (30 mL × 3). The acquired organic phase was dried over anhydrous Na_2SO_4. After removing volatile components, the organic residue was submitted to an isolation with silica gel column chromatography (eluting solution: petroleum ether/ethyl acetate = 10:1 (v/v)).

Synthesis of 6a. Compound **5a** was synthesized from 4-methylstyrene and methyl acetylacetonate by using I_2 as catalyst and TBPB as oxidant.[27] **5a** (0.2 mmol, 46.4 mg) was mixed with $CuBr_2$ (0.01 mmol, 2.2 mg) in nitromethane (1 mL). The mixture was then stirred at 60 °C for 3 h. After reaction, the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether/ethyl acetate = 5:1 (v/v)) in 85% yield (0.17 mmol, 39.3 mg).

A typical procedure for the reaction of 2-butoxy-2,3-dihydrofuran and α-ketene dithioacetal. In a typical reaction, **1a** (0.20 mmol) was mixed with α-ketene dithioacetal (0.20 mmol), $CuBr_2$ (5 mol%) in nitromethane (1.0 mL). The mixture was then stirred at 60 °C for 2 h. After reaction, the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether/ethyl acetate = 5:1 (v/v)). Tests for substrate scope were all performed with an analogous procedure.

Large-scale synthesis of 8a and 8n. In a 100 mL of round-bottom flask, dihydrofuran **1b** (5.0 mmol) was mixed with α-oxoketene dithioacetal (5.0 mmol) and $CuBr_2$ (5 mol%) in nitromethane (20.0 mL). The mixture was then stirred at 60 °C for 2 h. After completion of the reaction, brine (20 mL) was added. And then, the aqueous phase was extracted by ethyl acetate (20 mL × 3). The acquired organic phase was dried over anhydrous Na_2SO_4. After removing volatile components, the organic residue was submitted to an isolation with silica gel column chromatography (eluting solution: petroleum ether/ethyl acetate = 10:1 (v/v)). Large scale synthesis of compound **8n** was implemented according to an analogous procedure.

Synthesis of 10a, 10b and 12a. Dihydrofuran **1b** (0.2 mmol, 42.8 mg) was mixed with 1,3,5-trimethoxybenzene **9a** (0.2 mmol, 33.6 mg) and $CuBr_2$ (0.01 mmol, 2.2 mg, 5 mol%) in nitromethane (1 mL). Then, the mixture was stirred at room temperature for 0.5 h. After reaction, **10a** was obtained by isolation with preparative TLC (eluting solution: petroleum ether/ethyl acetate = 5:1 (v/v)) in 98% yield (0.2 mmol, 60.0 mg). **10b** and **12a** were synthesized according to an analogous procedure.

Synthesis of 14a in a two-step method. Dihydrofuran **1c** (0.2 mmol, 45.6 mg) was mixed with **2a** (0.4 mmol, 52.4 mg) and $FeCl_3{\cdot}6H_2O$ (0.01 mol, 2.7 mg) in nitromethane (1 mL). The mixture was then stirred at 60 °C for 30 min. After reaction, the mixture was cooled to room temperature, and the product **4b** was obtained by isolation with preparative TLC (eluting solution: petroleum ether/ethyl acetate = 3:1 (v/v)) in 99% yield (0.2 mmol, 82.4 mg). Compound **4b** (0.2 mmol,

82.4 mg) was mixed with aniline (0.2 mmol, 18.6 mg) and $Al(OTf)_3$ (0.01 mmol, 4.7 mg) in nitromethane (1 mL). The mixture was then stirred at 60 °C for 12 h. After reaction, the mixture was cooled to room temperature, and the product **14a** was obtained by isolation with preparative TLC (eluting solution: petroleum ether/ethyl acetate = 5:1 (v/v)) in 82 % yield (0.16 mmol, 58.7 mg).

A typical procedure for the one-pot stepwise three-component reaction of dihydrofuran, indole and aniline. Dihydrofuran **1b** (0.2 mmol) was mixed with **2a** (0.4 mmol) and $FeCl_3{\cdot}6H_2O$ (5 mol %) in nitromethane (1 mL). The reaction was then stirred at 60 °C. After completion of the reaction monitored by TLC, aniline **13a** (0.2 mmol) and $Al(OTf)_3$ (5 mol %) were added to the flask. Then, the mixture submitted to the specified conditions of the second step. Finally the mixture was cooled to room temperature, and the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether/ethyl acetate = 5:1 (v/v)). Tests for substrate scope were all performed with an analogous procedure.

Large scale synthesis of 14b. In a 100 mL of round-bottom flask, **1b** (5 mmol) was mixed with **2a** (10 mmol) and $FeCl_3{\cdot}6H_2O$ (0.25 mmol) in nitromethane (20 mL), the mixture was allowed to stir at 60 °C for 30 min. Then, aniline (465.0 mg, 5 mmol) and $Al(OTf)_3$ (0.25 mmol) were added to the reaction system. The mixture was stirred at 60 °C again for 6 h. After completion of the reaction, brine (20 mL) was added. And then, the aqueous phase was extracted by ethyl acetate (20 mL × 3). The acquired organic phase was dried over anhydrous Na_2SO_4. After removing volatile components, the organic residue was submitted to an isolation with silica gel column chromatography (eluting solution: petroleum ether/ethyl acetate = 10:1 (v/v)). Compound **14b** was obtained in 69 % yield.

Synthesis of 18a. Compound **17a** was synthesized according to a literature method (se the Supporting Information).[28]. Compound **17a** (0.2 mmol, 85.6 mg) was mixed with aniline **13a** (0.2 mmmol, 18.6 mg) and $Al(OTf)_3$ (0.02 mmol, 9.5 mg) in nitromethane (1 mL). The mixture was stirred at 60 °C for 3 h. After reaction, the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether/ethyl acetate = 5:1 (v/v)) in 78 % yield (0.16 mmol, 60.8 mg).

Synthesis of 20a. Compound **19a** was synthesized according to a literature method.[29] Compound **19a** (0.2 mmol, 61.4 mg) was mixed with $FeCl_3{\cdot}6H_2O$ (54.0 mg, 0.2 mmol) in nitromethane (1 mL). The mixture was stirred at 60 °C for 6 h. After reaction, the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether/ethyl acetate = 5:1 (v/v)) in 82 % yield (0.16 mmol, 50.0 mg).

A typical procedure for the synthesis of dihydrothiophene derivatives. Dihydrofuran **1b** (0.2 mmol) was mixed with **2a** (0.4 mmol) and $FeCl_3{\cdot}6H_2O$ (0.01 mmol, 5 mol %). The mixture was stirred at 60 °C for 0.5 h. Then, P_2S_5 (0.2 mmol, 44.4 mg) and $Al(OTf)_3$ (0.01 mmol, 5 mmol %) were added to the flask. The mixture was submitted to one hour of stirring at 60 °C. The product was obtained by isolation with preparative TLC (eluting solution: petroleum ether/ethyl acetate = 5:1 (v/v)). Tests for substrate scope were all performed with an analogous procedure.

Large scale synthesis of 15a. In a 100 mL of round-bottom flask, **1b** (5 mmol) was mixed with **2a** (10 mmol) and $FeCl_3{\cdot}6H_2O$ (0.25 mmol) in nitromethane (20 mL). The mixture stirred at 60 °C for 30 min. Then, P_2S_5 (1.11 g, 5 mmol) and $Al(OTf)_3$ (118.5 mg, 0.25 mmol) were added to the reaction system. The mixture was stirred at 60 °C for one hour. After completion of the reaction, brine (20 mL) was added. And then, the aqueous phase was extracted by ethyl acetate (20 mL × 3). The acquired organic phase was dried over anhydrous Na_2SO_4. After removing volatile components, the organic residue was submitted to an isolation with silica gel column chromatography (eluting solution: petroleum ether/ethyl acetate = 10/1 (v/v)). Compound **15a** was obtained in 93 % yield.

All spectroscopic data of obtained compounds

1-(2-Methyl-5-(2-methyl-1*H*-indol-3-yl)furan-3-yl)ethanone (**3a**) (0.19 mmol, 48.1 mg, 95 %): brown oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.36 (s, 1H), 7.81 (d, J = 7.1 Hz, 1H), 7.33 (d, J = 7.1 Hz, 1H), 7.12–7.04 (m, 2H), 6.76 (s, 1H), 2.63 (s, 3H), 2.57 (s, 3H), 2.46 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 199.2, 160.0, 154.3, 140.2, 138.9, 130.6, 127.8, 126.3, 124.9, 124.1, 116.1, 108.8, 107.5, 34.5, 19.3, 18.3 ppm; IR (KBr) ν: 3396, 2927, 2859, 1699, 1459, 1226, 742 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{16}H_{16}NO_2$, $[M+H]^+$ 254.1181, found 254.1183.

1-(2-Methyl-5-(2-phenyl-1*H*-indol-3-yl)furan-3-yl)ethanone (**3b**) (0.19 mmol, 60.5 mg, 96 %): light yellow solid, mp: 155–157 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 12.53 (s, 1H), 8.24 (d, J = 7.5 Hz, 1H), 7.73–7.67 (m, 2H), 7.66–7.60 (m, 3H), 7.50 (d, J = 7.6 Hz, 1H), 7.33–7.24 (m, 2H), 6.79 (s, 1H), 2.28 (s, 3H), 1.79 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 202.9, 197.9, 185.1, 147.6, 147.6, 136.4, 135.8, 132.3, 130.9, 130.6, 129.2, 127.5, 124.3, 123.1, 122.0, 115.1, 112.5, 31.3, 26.3 ppm; IR (KBr) ν: 3293, 2956, 2925, 2855, 1658, 1568, 1453, 1234, 950, 744 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{21}H_{18}NO_2$, $[M+H]^+$ 316.1338, found: 316.1352.

1-(2-Methyl-5-(1-methyl-2-phenyl-1*H*-indol-3-yl)furan-3-yl)ethanone (**3c)** (0.17 mmol, 56.6 mg, 86 %): brown oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 7.96 (d, J = 7.9 Hz, 1H), 7.57–7.52 (m, 4H), 7.48 (dd, J = 6.8, 2.8 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 6.20 (s, 1H), 3.57 (s, 3H), 2.48 (s, 3H), 2.28 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 198.6, 160.4, 153.4, 143.1, 141.8, 136.3, 135.8, 134.2, 133.8, 129.8, 127.8, 127.6, 125.8, 125.2, 115.6, 109.5, 108.8, 35.9, 34.2, 19.3 ppm; IR (KBr) ν: 3054, 2926, 2854, 1674, 1572, 1467, 1227, 1093, 948, 744, 702 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{22}H_{20}NO_2$, $[M+H]^+$ 330.1494, found: 330.1503.

1-(5-(1-Ethyl-2-phenyl-1*H*-indol-3-yl)-2-methylfuran-3-yl)ethanone (**3d**) (0.17 mmol, 57.6 mg, 84 %): light yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 8.32 (d, J = 7.7 Hz, 1H), 7.74–7.61 (m, 6H), 7.39 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 6.56 (s, 1H), 4.05 (q, J = 7.1 Hz, 2H), 2.21 (s, 3H), 1.70 (s, 3H), 1.19 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 202.7, 198.0, 184.7, 148.3, 147.5, 136.1, 135.5, 131.2, 131.1, 130.9, 129.6, 126.8, 124.6, 123.7, 122.3, 116.0, 111.6, 31.2, 26.1, 15.3 ppm; IR (KBr) ν: 3053, 2929, 2868, 1674, 1672, 1462, 1226, 1098, 744, 703 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{23}H_{22}NO_2$, $[M+H]^+$ 344.1651, found: 344.1659.

1-(5-(2,5-Dimethyl-1*H*-indol-3-yl)-2-methylfuran-3-yl)-ethanone (**3e**) (0.18 mmol, 49.7 mg, 93%): light yellow solid, mp: 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.05 (s, 1H), 7.61 (s, 1H), 7.19 (d, J = 8.2 Hz, 1H), 7.01 (dd, J = 8.2, 1.1 Hz, 1H), 6.59 (s, 1H), 2.69 (d, J = 6.6 Hz, 3H), 2.59 (s, 3H), 2.50 (s, 3H), 2.48 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 194.6, 156.2, 149.1, 133.3, 133.0, 129.8, 126.4, 123.4, 122.9, 119.1, 110.1, 104.3, 103.6, 29.3, 21.7, 14.6, 13.2 ppm; IR (KBr) ν: 3224, 2918, 2850, 1653, 1570, 1233, 1014, 908, 796, 725, 628 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{17}H_{18}NO_2$, $[M+H]^+$ 268.1338, found: 268.1339.

1-(5-(5-Fluoro-2-methyl-1*H*-indol-3-yl)-2-methylfuran-3-yl)ethanone (**3f**) (0.18 mmol, 48.2 mg, 89%): brown solid, mp: 178–180 °C, ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.13 (s, 1H), 7.77 (dd, J = 8.6, 5.3 Hz, 1H), 7.00 (dd, J = 9.3, 1.9 Hz, 1H), 6.94 (td, J = 9.3, 2.0 Hz, 1H), 6.59 (s, 1H), 2.70 (s, 3H), 2.59 (s, 3H), 2.49 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 199.2, 162.7 (d, J = 230.0 Hz), 160.1, 153.7, 141.0, 136.9, 133.4, 132.6, 131.0, 130.9, 130.8, 127.8, 117.1 (d, J = 10.0 Hz), 114.2 (d, J = 26.0 Hz), 109.1 (d, J = 24.0 Hz), 108.91, 108.0 (d, J = 4.0 Hz), 34.5, 19.2, 18.4 ppm. ^{19}F NMR (377 MHz, $CDCl_3$, TMS, 25 °C) δ = −121.1 ppm; IR (KBr) ν: 3240, 2955, 2923, 2853, 1659, 1570, 1464, 1240, 1138, 958, 776 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{16}H_{15}FNO_2$, $[M+H]^+$ 272.1087, found: 272.1102.

Methyl 2-methyl-5-(2-methyl-1*H*-indol-3-yl)furan-3-carboxylate (**3g**) (0.18 mmol, 49.5 mg, 92%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.37 (s, 1H), 7.76 (d, J = 7.2 Hz, 1H), 7.33 (d, J = 7.1 Hz, 1H), 7.13–7.02 (m, 2H), 6.56 (s, 1H), 3.79 (s, 2H), 2.63 (s, 3H), 2.55 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 164.3, 156.5, 150.0, 135.5, 134.3, 125.8, 121.6, 120.2, 119.3, 114.4, 111.4, 103.5, 102.7, 51.7, 13.9, 13.5 ppm; IR (KBr) ν: 3317, 2954, 2924, 2853, 1692, 1591, 1444, 1255, 1095, 1041, 761 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{16}H_{15}NNaO_3$, $[M+Na]^+$ 292.0950, found 292.0959.

Ethyl 2-methyl-5-(2-methyl-1*H*-indol-3-yl)furan-3-carboxylate (**3h**) (0.19 mmol, 53.2 mg, 94%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.38 (s, 1H), 7.76 (d, J = 7.2 Hz, 1H), 7.34 (d, J = 7.1 Hz, 1H), 7.13–7.03 (m, 2H), 6.55 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.63 (s, 3H), 2.55 (s, 3H), 1.31 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 163.9, 156.4, 149.9, 135.5, 134.3, 125.9, 121.6, 120.2, 119.3, 114.7, 111.4, 103.5, 102.1, 60.3, 14.7, 14.0, 13.5 ppm; IR (KBr) ν: 3319, 2925, 2854, 1961, 1590, 1460, 1233, 1095, 1038, 743 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{17}H_{17}NNaO_3$, $[M+Na]^+$ 306.1106, found 306.1109.

2-Methoxyethyl 2-methyl-5-(2-methyl-1*H*-indol-3-yl)furan-3-carboxylate (**3i**) (0.16 mmol, 50.7 mg, 81%), light yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.38 (s, 1H), 7.76 (d, J = 7.1 Hz, 1H), 7.34 (d, J = 7.1 Hz, 1H), 7.14–7.03 (m, 2H), 6.54 (s, 1H), 4.40–4.29 (m, 2H), 3.69–3.60 (m, 2H), 3.31 (s, 3H), 2.64 (s, 3H), 2.55 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 163.3, 156.1, 149.6, 135.0, 133.8, 125.4, 121.1, 119.8, 118.8, 114.0, 110.9, 103.0, 102.2, 69.9, 62.9, 58.1, 13.5, 13.1 ppm; IR(KBr) ν: 3350, 2926, 1712, 1459, 1230, 1090, 1035, 744 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{18}H_{19}NNaO_4$, $[M+Na]^+$ 336.1212, found 336.1219.

2-Methoxyethyl 2-methyl-5-(2-phenyl-1*H*-indol-3-yl)furan-3-carboxylate (**3j**) (0.20 mmol, 74.3 mg, 99%): yellowish oil; ^{1}H NMR (400 MHz, CD_3Cl, TMS, 25 °C) δ = 8.47 (s, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.53 (dd, J = 8.0, 1.5 Hz, 2H), 7.43–7.32 (m, 4H), 7.29–7.15 (m, 2H), 6.57 (s, 1H), 4.41–4.35 (m, 2H), 3.71–3.64 (m, 2H), 3.40 (s, 3H), 2.57 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 164.3, 157.9, 147.9, 135.7, 135.6, 132.4, 128.65, 128.5, 128.4, 127.3, 123.0, 120.9, 120.3, 114.5, 111.0, 106.8, 104.2, 70.7, 63.2, 59.0, 13.9 ppm; IR (KBr) ν: 3350, 2926, 1712, 1459, 1230, 1090, 1035, 744 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{23}H_{21}NNaO_4$, $[M+Na]^+$ 398.1368, found398.1365.

Methyl 2-isopropyl-5-(2-methyl-1*H*-indol-3-yl)furan-3-carboxylate (**3k**) (0.08 mmol, 24.9 mg, 42%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.38 (s, 1H), 7.74 (dd, J = 6.0, 2.3 Hz, 1H), 7.34 (dd, J = 6.1, 2.5 Hz, 1H), 7.12–7.04 (m, 2H), 3.79 (s, 4H), 3.78–3.72 (m, 1H), 2.56 (s, 3H), 1.32 ppm (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 164.2, 164.1, 149.8, 135.5, 134.3, 125.8, 121.6, 120.3, 119.1, 112.6, 111.5, 103.2, 102.9, 51.8, 27.10, 21.3, 13.6 ppm; IR (KBr) ν: 3399, 2969, 2932, 2873, 1716, 1587, 1461, 1230, 1064, 743 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{18}H_{19}NNaO_3$, $[M+Na]^+$ 320.1263, found 320.1268.

Methyl 2-isopropyl-5-(2-phenyl-1*H*-indol-3-yl)furan-3-carboxylate (**3l**) (0.14 mmol, 50.3 mg, 70%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.78 (s, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.58 (d, J = 7.0 Hz, 2H), 7.52–7.40 (m, 4H), 7.24–7.17 (m, 1H), 7.18–7.10 (m, 1H), 6.55 (s, 1H), 3.76 (s, 3H), 3.74–3.64 (m, 1H), 1.14 ppm (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 165.0, 164.0, 148.2, 136.5, 136.4, 132.7, 129.1, 128.9, 128.7, 126.8, 122.8, 120.8, 119.7, 112.6, 112.1, 105.7, 102.9, 51.8, 27.0, 21.2 ppm; IR (KBr) ν: 3399, 2969, 2932, 2873, 1716, 1587, 1461, 1230, 1064, 743 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{23}H_{21}NNaO_3$, $[M+Na]^+$ 382.1419, found 382.1413.

Methyl 2-cyclopropyl-5-(2-methyl-1*H*-indol-3-yl)furan-3-carboxylate (**3m**) (0.07 mmol, 20.7 mg, 35%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.36 (s, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.32 (d, J = 6.9 Hz, 1H), 7.13–7.01 (m, 2H), 6.54 (s, 1H), 3.81 (s, 3H), 2.83–2.74 (m, 1H), 2.51 (s, 3H), 1.17–1.06 ppm (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 164.0, 159.7, 148.5, 135.0, 133.8, 125.3, 121.1, 119.9, 118.5, 113.5, 111.0, 103.0, 102.2, 51.3, 13.1, 9.0, 8.3 ppm; IR (KBr) ν: 3324, 2925, 2854, 1694, 1591, 1459, 1236, 1072, 741 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{18}H_{17}NNaO_3$, $[M+Na]^+$ 318.1106, found 318.1101.

Methyl 2-cyclopropyl-5-(2-phenyl-1*H*-indol-3-yl)furan-3-carboxylate (**3n**) (0.14 mmol, 48.6 mg, 68%): yellowsih oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.75 (s, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.57–7.52 (m, 2H), 7.49 (t, J = 7.3 Hz, 2H), 7.46–7.41 (m, 2H), 7.20 (t, J = 7.0 Hz, 1H), 7.13 (t, J = 7.0 Hz, 1H), 6.56 (s, 1H), 3.78 (s, 3H), 2.76–2.64 (m, 1H), 0.98 (dt, J = 6.4, 3.9 Hz, 2H), 0.77–0.67 ppm (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 164.4, 161.1, 147.3, 136.4, 132.7, 129.1, 128.9, 128.7, 126.6, 122.8, 120.8, 119.6, 114.0, 112.1, 105.9, 102.7, 51.7, 9.4, 9.0 ppm; IR (KBr) ν: 3324, 2925, 2854, 1694, 1591, 1459, 1236, 1072, 741 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{23}H_{19}NNaO_3$, $[M+Na]^+$ 380.1263, found 380.1261.

Methyl 2-methyl-5-(2-phenyl-1*H*-indol-3-yl)furan-3-carboxylate (**3o**) (0.18 mmol, 58.9 mg, 89%) : yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.33 (s, 1H),

7.89 (d, J=7.7 Hz, 1H), 7.56 (d, J=6.8 Hz, 2H), 7.46–7.38 (m, 4H), 7.30–7.18 (m, 2H), 6.58 (s, 1H), 3.82 (s, 3H), 2.59 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ=164.9, 157.7, 147.9, 135.7, 135.5, 132.4, 128.7, 128.5, 128.4, 127.3, 123.0, 120.9, 120.4, 114.5, 111.0, 106.7, 104.3, 51.3, 13.8 ppm; IR (KBr) ν: 3395, 2928, 2862, 1695, 1459, 1234, 742 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{21}H_{17}NNaO_3$, $[M+Na]^+$ 354.1106, found 354.1116.

Ethyl 2-methyl-5-(2-phenyl-1*H*-indol-3-yl)furan-3-carboxylate (**3p**) (0.17 mmol, 60.0 mg, 87%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ=11.78 (s, 1H), 7.73 (d, J=7.9 Hz, 1H), 7.60 (d, J=7.1 Hz, 2H), 7.53–7.39 (m, 4H), 7.20 (t, J=7.0 Hz, 1H), 7.12 (t, J=7.0 Hz, 1H), 6.48 (s, 1H), 4.22 (q, J=7.1 Hz, 2H), 2.55 (s, 3H), 1.27 ppm (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ=163.7, 157.3, 148.5, 136.4, 132.5, 129.0, 128.9, 128.8, 127.1, 122.8, 120.8, 119.9, 114.7, 112.1, 106.3, 102.7, 60.3, 14.7, 14.0 ppm; IR (KBr) ν: 3393, 2922, 2864, 1699, 1459, 1234, 742 cm^{-1}.HRMS (TOF, ESI): (m/z) calcd for $C_{22}H_{19}NNaO_3$, $[M+Na]^+$ 368.1263, found 368.1256.

Ethyl 2-phenyl-5-(2-phenyl-1*H*-indol-3-yl)furan-3-carboxylate (**3q**) (0.18 mmol, 70.0 mg, 86%): light yellow solid, mp: 168–170 °C, ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ=11.89 (s, 1H), 7.85 (d, J=7.7 Hz, 1H), 7.78 (dd, J=7.8, 1.8 Hz, 2H), 7.66 (d, J=6.8 Hz, 2H), 7.51 (dt, J=20.5, 7.3 Hz, 4H), 7.45–7.38 (m, 3H), 7.28–7.16 (m, 2H), 6.77 (s, 1H), 4.25 (q, J=7.1 Hz, 2H), 1.26 ppm (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ=163.4, 154.3, 149.7, 137.1, 136.5, 132.7, 129.8, 129.6, 129.3, 129.1, 129.0, 128.7, 128.1, 126.5, 123.0, 121.1, 119.7, 115.5, 112.3, 108.1, 102.5, 60.8, 14.5 ppm; IR (KBr) ν: 3406, 3058, 2980, 1714, 1489, 1452, 1235, 1091, 1033, 744 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{27}H_{21}NNaO_3$, $[M+Na]^+$ 430.1419, found 430.1415.

Ethyl 5-(2-phenyl-1*H*-indol-3-yl)-2-propylfuran-3-carboxylate (**3r**) (0.18 mmol, 68.6 mg, 92%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ=11.79 (s, 1H), 7.71 (d, J=7.9 Hz, 1H), 7.58 (d, J=7.0 Hz, 2H), 7.50–7.39 (m, 4H), 7.20 (t, J=7.6 Hz, 1H), 7.13 (t, J=7.9 Hz, 1H), 6.54 (s, 1H), 4.23 (q, J=7.1 Hz, 2H), 2.92 (t, J=7.3 Hz, 2H), 1.65–1.53 (m, 2H), 1.27 (t, J=7.1 Hz, 3H), 0.87 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ=163.6, 160.8, 148.4, 136.4, 132.6, 129.0, 128.9, 128.7, 128.2, 127.1, 122.8, 120.8, 119.7, 114.7, 112.1, 106.2, 102.8, 60.3, 29.3, 21.6, 14.7, 13.9 ppm; IR (KBr) ν: 3398, 3344, 2963, 2931, 1712, 1691, 1453, 1230, 1050, 743 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{24}H_{23}NNaO_3$, $[M+Na]^+$ 396.1576, found 396.1578.

6,6-Dimethyl-2-(2-phenyl-1*H*-indol-3-yl)-6,7-dihydrobenzofuran-4(5H)-one (**3s**) (0.18 mmol, 62.5 mg, 88%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ=11.82 (s, 1H), 7.76 (d, J=7.9 Hz, 1H), 7.59 (d, J=7.0 Hz, 2H), 7.54–7.42 (m, 4H), 7.21 (t, J=7.0 Hz, 1H), 7.13 (t, J=7.5 Hz, 1H), 6.45 (s, 1H), 2.79 (s, 2H), 2.35 (s, 2H), 1.08 ppm (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ=193.5, 165.3, 151.0, 136.7, 136.4, 132.5, 129.0, 129.0, 128.9, 127.0, 122.9, 120.9, 120.8, 120.0, 112.1, 102.7, 101.5, 51.9, 36.9, 35.4, 28.5 ppm; IR (KBr) ν: 3311, 2958, 2871, 1661, 1583, 1451, 1327, 1220, 1114,1032, 744 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{24}H_{21}NNaO_2$, $[M+Na]^+$ 378.1470, found 378.1474.

Ethyl 2-(4-fluorophenyl)-5-(2-phenyl-1*H*-indol-3-yl)furan-3-carboxylate (**3t**) (0.16 mmol, 69.7 mg, 82%): ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ=11.89 (s, 1H), 7.84 (dd, J=8.8, 5.4 Hz, 3H), 7.66 (d, J=6.8 Hz, 2H), 7.56–7.46 (m, 4H), 7.26 (t, J=9.0 Hz, 3H), 7.22–7.17 (m, 1H), 6.76 (s, 1H), 4.24 (q, J=7.1 Hz, 2H), 1.26 ppm (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ=163.3, 162.6 (d, J=246.0 Hz), 153.5, 149.8, 137.1, 136.5, 132.7, 130.5, 130.4, 129.3, 129.1, 129.0, 126.5, 126.3, 123.0, 121.1, 119.7, 115.7 (d, J=21.7 Hz), 115.3, 112.3, 108.0, 102.5, 60.8, 14.5 ppm; ^{19}F NMR (377 MHz, DMSO-d_6, 25 °C) δ=−111.4 ppm; IR (KBr) ν: 3331, 2980, 2932, 1071, 1598, 1502, 1454, 1234, 1092, 1028, 840, 744 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{27}H_{20}FNNaO_3$, $[M+Na]^+$ 448.1325, found 448.1327.

Ethyl 2-(2,6-dichloro-5-fluoropyridin-3-yl)-5-(2-phenyl-1*H*-indol-3-yl)furan-3-carboxylate (**3u**) (0.16 mmol, 77.1 mg, 78%); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ=11.95 (s, 1H), 8.41 (d, J=8.3 Hz, 1H), 7.84 (d, J=7.9 Hz, 1H), 7.65 (d, J=7.1 Hz, 2H), 7.57–7.43 (m, J=15.9, 7.4 Hz, 4H), 7.23 (t, J=7.1 Hz, 1H), 7.16 (t, J=7.3 Hz, 1H), 6.74 (s, 1H), 4.16 (q, J=7.1 Hz, 2H), 1.13 ppm (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ=162.2, 153.5 (d, J=258.0 Hz), 152.3, 147.9, 143.2, 137.6, 137.3, 136.4, 132.3, 131.1 (d, J=22.0 Hz), 129.2 (d, J=12.0 Hz), 127.3 (d, J=4.0 Hz), 126.7, 123.1, 121.1, 119.9 (d, J=16.0 Hz), 112.3, 106.8, 102.0, 61.0, 14.2 ppm; ^{19}F NMR (377 MHz, DMSO-d_6, 25 °C) δ=−122.7, −122.8 ppm; IR (KBr) ν: 3395, 3334, 2962, 2928, 1708, 1696, 1453, 1230, 1048, 743 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{26}H_{17}Cl_2FN_2NaO_3$, $[M+Na]^+$ 517.0498, found 517.0494.

3-(2,2-Bis(2-methyl-1*H*-indol-3-yl)ethyl)pentane-2,4-dione (mixture of enol and ketone, the ratio approximately : enol/ketone=3/2) (**4a**) (0.13 mmol, 50.2 mg, 65%): brown oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ=17.03 (s, 0.57H), 10.72 (d, J=12.0 Hz, 2H), 7.53 (d, J=8.0 Hz, 0.82H), 7.44 (d, J=8.0 Hz, 1.17H), 7.23 (dd, J=8.0, 4.0 Hz, 2H), 6.98–6.94 (m, 2H), 6.87 (t, J=8.0 Hz, 0.87H),6.81 (t, J=8.0 Hz, 1.22H), 4.31–4.27 (m, 1H), 3.71 (t, J=6.9 Hz, 0.43H), 3.32 (d, J=8.0 Hz, 1.22H), 2.84 (t, J=8.0 Hz, 0.8H), 2.31 (s, 6H), 1.98 (s, 3H), 1.65 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ=204.7, 191.9, 135.1, 131.5, 128.2, 120.8, 120.7, 119.4, 119.3, 119.3, 119.1, 113.0, 110.4, 67.5, 32.8, 29.1, 22.6, 12.7, 12.4 ppm; IR (KBr) ν: 3240, 2956, 2923, 2853, 1707, 1658, 1570, 1460, 1248, 939, 736, 636 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{25}H_{26}N_2NaO_2$, $[M+Na]^+$ 409.1892, found 409.1904.

Ethyl 2-acetyl-4,4-bis(2-methyl-1*H*-indol-3-yl)butanoate (**4b**) (0.20 mmol, 82.4 mg, 99%): brown oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ=7.70 (s, 1H), 7.68 (s, 1H), 7.65–7.59 (m, 2H), 7.15 (d, J=9.5 Hz, 2H), 7.01 (dt, J=16.1, 7.4 Hz, 4H), 4.44 (t, J=8.3 Hz, 1H), 4.16–4.02 (m, 2H), 3.52 (t, J=7.0 Hz, 1H), 3.04–2.91 (m, 2H), 2.18 (s, 3H), 2.15 (s, 3H), 2.04 (s, 3H), 1.19 ppm (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ=203.7, 170.1, 135.2, 135.1, 131.6, 131.4, 128.2, 128.1, 120.6, 120.6, 119.3, 119.3, 119.2, 113.1, 113.0, 110.4, 110.3, 61.3, 58.5, 32.7, 32.6, 29.1, 14.0, 12.6, 12.4 ppm; IR (KBr) ν: 3394, 2935, 2864, 1705, 1616, 1460, 1305, 1224, 911, 747 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{26}H_{28}N_2NaO_3$, $[M+Na]^+$ 439.1998, found 439.1998.

Methyl 2-methyl-5-(p-tolyl)-4,5-dihydrofuran-3-carboxylate (**5a**) (7.5 mmol, 1.74 g, 75%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ=7.22 (d, J=8.1 Hz, 2H), 7.17 (d, J=8.1 Hz, 2H), 5.55 (dd, J=10.6, 8.4 Hz, 1H), 3.71 (s, 3H), 3.29 (ddd, J=14.4, 10.7, 1.6 Hz, 1H), 2.91 (ddd, J=

14.5, 8.3, 1.6 Hz, 1H), 2.35 (s, 3H), 2.27 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ 168.0, 166.5, 138.4, 138.0, 129.4, 125.8, 101.5, 83.3, 50.8, 37.8, 21.2, 14.1 ppm; IR (KBr) ν: 2953, 2925, 2855, 1705, 1649, 1438, 1382, 1224, 1088, 984, 763 cm^{-1}; IR (KBr) ν: 3009, 2952, 2862, 1708, 1564, 1511, 1437, 1325, 1211, 1122, 826, 731 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{14}H_{16}NaO_3$, $[M+Na]^+$ 255.0997, found 255.1020.

Methyl 2-methyl-5-(p-tolyl)furan-3-carboxylate (**6a**) (0.17 mmol, 39.3 mg, 85%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.53 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.81 (s, 1H), 3.85 (s, 3H), 2.64 (s, 3H), 2.36 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 164.6, 158.4, 152.0, 137.6, 129.4, 127.4, 123.6, 115.0, 104.4, 51.4, 21.3, 13.9 ppm; IR (KBr) ν: 3012, 2932, 2862, 1708, 1568, 1437, 1325, 1122, 826, 731 cm^{-1}.HRMS (TOF, ESI): m/z calcd for $C_{14}H_{15}O_3$, $[M+H]^+$ 231.1021, found 231.1028.

Methyl 5-(1-(1,3-dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-2-methylfuran-3-carboxylate (**8a**) (0.16 mmol, 58.3 mg, 81%): yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.47 (d, J = 7.1 Hz, 2H), 7.37 (t, J = 6.8 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 6.59 (s, 1H), 3.80 (s, 3H), 3.53–3.46 (m, 2H), 3.42–3.35 (m, 2H), 2.39 ppm (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 189.5, 169.4, 164.3, 158.3, 149.4, 139.2, 131.2, 128.4, 127.9, 115.2, 114.4, 111.2, 51.4, 39.3, 35.9, 13.6 ppm; IR (KBr) ν: 2949, 2925, 1716, 1618, 1446, 1274, 1228, 1105, 775, 697 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{18}H_{16}NaO_4S_2$, $[M+Na]^+$ 383.0388, found 383.0390.

Ethyl 5-(1-(1,3-dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-2-methylfuran-3-carboxylate (**8b**) (0.17 mmol, 64.3 mg, 86%): yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.51–7.45 (m, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 6.60 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.49 (t, J = 6.3 Hz, 2H), 3.38 (t, J = 6.2 Hz, 2H), 2.39 (s, 3H), 1.33 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 189.5, 169.3, 163.9, 158.1, 149.3, 139.2, 131.2, 128.4, 127.9, 115.3, 114.7, 111.3, 60.2, 39.3, 35.9, 14.3, 13.6 ppm; IR (KBr) ν: 2979, 2927, 1712, 1617, 1572, 1449, 1273, 1227, 1103, 1066, 696 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{19}H_{18}NaO_4S_2$, $[M+Na]^+$ 397.0544, found 397.0532.

2-(4-Acetyl-5-methylfuran-2-yl)-2-(1,3-dithiolan-2-ylidene)-1-phenylethanone (**8c**) (0.14 mmol, 48.8 mg, 71%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 7.42 (dt, J = 13.5, 4.3 Hz, 3H), 7.37–7.30 (m, 2H), 6.74 (s, 1H), 3.59–3.54 (m, J = 7.1, 4.8 Hz, 2H), 3.50–3.46 (m, 2H), 2.34 (s, 3H), 2.34 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 198.7, 193.7, 175.6, 161.7, 154.2, 144.2, 136.5, 133.3, 133.1, 127.7, 119.1, 116.2, 41.1, 34.3, 19.0 ppm; IR (KBr) ν: 2973, 2931, 2870, 1715, 1623, 1569, 1464, 1270, 1227, 1063, 695 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{18}H_{16}NaO_3S_2$, $[M+Na]^+$ 367.0439, found 367.0433.

2-(1,3-Dithiolan-2-ylidene)-2-(4-(2-(2-methoxyethoxy)acetyl)-5-methylfuran-2-yl)-1-phenylethanone (**8d**) (0.18 mmol, 73.6 mg, 88%): yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.48 (d, J = 7.1 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 6.62 (s, 1H), 4.40–4.33 (m, 2H), 3.70–3.63 (m, 2H), 3.49 (dd, J = 11.8, 4.9 Hz, 2H), 3.43–3.35 (m, 5H), 2.40 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 189.5, 169.4, 163.8, 158.5, 149.4, 139.2, 131.2, 128.4, 127.9, 115.2, 114.4, 111.3, 70.5, 63.3, 59.0, 39.3, 35.9, 13.7 ppm; IR (KBr) ν: 3059, 2926, 1715, 1624, 1571, 1448, 1273, 1226, 1103, 1027, 696 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{21}H_{22}NaO_5S_2$, $[M+Na]^+$ 441.0806, found 441.0821.

Methyl 5-(1-(1,3-dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-2-isopropylfuran-3-carboxylate (**8e**) (0.15 mmol, 56.6 mg, 73%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 7.44–7.39 (m, 1H), 7.37–7.30 (m, 4H), 6.61 (s, 1H), 3.73 (s, 3H), 3.61–3.54 (m, 2H), 3.51–3.47 (m, 3H), 0.84 (s, 3H), 0.82 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 189.2, 170.4, 165.6, 163.6, 149.5, 140.1, 131.4, 128.6, 127.9, 114.3, 112.4, 110.7, 51.9, 36.3, 26.8, 24.6, 20.7 ppm; IR (KBr) ν: 2970, 2929, 2871, 1715, 1623, 1569, 1448, 1272, 1227, 1063, 699 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{20}H_{20}NaO_4S_2$, $[M+Na]^+$ 411.0701, found 411.0691.

Methyl 5-(1-(1,3-dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-2-cyclopropylfuran-3-carboxylate (**8f**) (0.11 mmol, 42.5 mg, 55%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 7.44 (t, J = 6.9 Hz, 1H), 7.38–7.31 (m, 4H), 6.65 (s, 1H), 3.74 (s, 3H), 3.62–3.54 (m, 2H), 3.52–3.45 (m, 2H), 3.14 (t, J = 6.7 Hz, 2H), 2.90 (t, J = 7.1 Hz, 2H), 1.74–1.64 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 188.9, 171.4, 163.5, 159.9, 150.3, 139.8, 131.7, 128.6, 128.0, 114.7, 114.1, 111.1, 52.0, 36.3, 33.7, 30.9, 25.8 ppm; IR (KBr) ν: 2926, 2854, 1712, 1625, 1571, 1447, 1272, 1230, 1096, 803, 698 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{20}H_{18}NaO_4S_2$, $[M+Na]^+$ 409.0544, found 409.0534.

Ethyl 5-(1-(1,3-dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-2-propylfuran-3-carboxylate (**8g**) (0.16 mmol, 64.3 mg, 80%): yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.50–7.43 (m, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 6.63 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.54–3.48 (m, 2H), 3.40 (t, J = 6.3 Hz, 2H), 2.79 (t, J = 7.3 Hz, 2H), 1.35–1.30 (m, 5H), 0.72 ppm (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 189.7, 169.1, 163.9, 162.0, 149.3, 139.5, 131.0, 128.5, 128.3, 127.9, 127.9, 114.5, 111.2, 108.3, 60.2, 39.2, 35.9, 29.2, 21.2, 14.3, 13.5 ppm; IR (KBr) ν: 2964, 2929, 2872, 1712, 1623, 1570, 1452, 1274, 1226, 1109, 1050, 803, 697 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{21}H_{22}NaO_4S_2$, $[M+Na]^+$ 425.0857, found 425.0865.

Ethyl 5-(1-(1,3-dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-2-phenylfuran-3-carboxylate (**8h**) (0.15 mmol, 65.4 mg, 75%): yellow solid, mp: 99–101 °C, ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.54 (t, J = 7.3 Hz, 4H), 7.39 (t, J = 7.3 Hz, 1H), 7.34–7.27 (m, 5H), 6.81 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.54–3.48 (m, 2H), 3.45–3.40 (m, 2H), 1.32 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 189.8, 168.7, 163.4, 156.0, 150.0, 139.5, 131.3, 129.4, 129.2, 128.4, 128.3, 128.1, 127.9, 115.1, 114.9, 113.2, 60.6, 39.2, 36.1, 14.2 ppm; IR (KBr) ν: 3059, 2978, 2927, 1716, 1623, 1487, 1449, 1270, 1242, 1103, 1023, 764, 694 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{24}H_{20}NaO_4S_2$, $[M+Na]^+$ 459.0701, found 459.0691.

Ethyl 5-(1-(1,3-dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-2-(4-fluorophenyl)furan-3-carboxylate (**8i**) (0.15 mmol, 68.1 mg, 75%): yellow solid, mp: 131–132 °C, ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 7.53 (dd, J = 8.0, 6.4 Hz, 4H), 7.40 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 6.97 (t, J = 8.8 Hz, 2H), 4.28 (q, J = 7.1 Hz, 1H), 3.55–3.50 (m, 2H), 3.46–3.42 (m, 2H), 1.33 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 189.8, 168.6, 163.1 (d, J = 248.0 Hz), 163.4, 155.1, 145.0, 139.6, 131.3, 130.4, 130.3,

128.4, 128.1, 125.6, 125.6, 115.0 (d, $J=22.0$ Hz), 114.9 (d, $J=37.0$ Hz), 113.2, 60.7, 39.2, 36.2, 14.2 ppm; IR (KBr) ν: 3059, 2978, 2927, 1714, 1623, 1486, 1448, 1271, 1232, 1113, 1023, 764, 697 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{24}H_{19}FNaO_4S_2$, $[M+Na]^+$ 477.0606, found 477.0596.

2-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (**8j**) (0.16 mmol, 59.9 mg, 78%): yellowsih oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) $\delta=7.46$ (d, $J=7.3$ Hz, 2H), 7.36 (t, $J=7.4$ Hz, 1H), 7.24 (t, $J=7.6$ Hz, 2H), 6.67 (s, 1H), 3.52 (t, $J=6.3$ Hz, 2H), 3.40 (t, $J=6.3$ Hz, 2H), 2.50 (s, 2H), 2.35 (s, 2H), 1.06 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) $\delta=193.8$, 189.3, 170.1, 165.4, 152.2, 139.4, 131.1, 128.3, 127.8, 120.9, 115.0, 106.8, 51.9, 39.3, 37.2, 35.9, 35.3, 28.4 ppm; IR (KBr) ν: 2958, 2929, 2870, 1675, 1626, 1447, 1274, 1217, 1114, 1029, 802, 729 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{21}H_{20}NaO_3S_2$, $[M+Na]^+$ 407.0752, found 407.0749.

Ethyl 5-(1-(1,3-dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-2-(difluoromethyl)furan-3-carboxylate (**8k**) (0.13 mmol, 53.3 mg, 65%): yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) $\delta=7.47$–7.42 (m, 2H), 7.38 (t, $J=7.4$ Hz, 1H), 7.28 (t, $J=7.5$ Hz, 2H), 7.21 (s, 0.25H), 7.08 (s, 0.5H), 6.95 (s, 0.25H), 6.61 (s, 1H), 4.31 (q, $J=7.1$ Hz, 2H), 3.55–3.49 (m, 2H), 3.46–3.40 (m, 2H), 1.35 ppm (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) $\delta=184.6$, 167.5, 157.0, 148.4, 143.0 (t, $J=23.0$ Hz), 134.2, 126.6, 123.4, 123.3, 115.5, 109.3, 106.3, 104.0, 101.7, 99.3, 56.6, 34.5, 31.5, 9.4 ppm; ^{19}F NMR (377 MHz, $CDCl_3$, TMS, 25°C) $\delta=-121.8$, -122.0 ppm.IR (KBr) ν: 2951, 2926, 2853, 1717, 1597, 1445, 1272, 1229, 1104, 1065, 851, 775 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{19}H_{16}F_2NaO_4S_2$, $[M+Na]^+$ 433.0356, found 433.0349.

Methyl 5-(1-(1,3-dithiolan-2-ylidene)-2-(4-methoxyphenyl)-2-oxoethyl)-2-methylfuran-3-carboxylate (**8l**) (0.17 mmol, 64.7 mg, 83%): yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) $\delta=7.51$ (d, $J=8.9$ Hz, 2H), 6.77 (d, $J=8.9$ Hz, 2H), 6.59 (s, 1H), 3.81 (d, $J=2.3$ Hz, 6H), 3.50–3.44 (m, 2H), 3.42–3.36 (m, 2H), 2.45 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) $\delta=183.7$, 161.5, 159.6, 157.6, 153.6, 144.9, 126.7, 126.3, 110.7, 109.7, 108.5, 106.1, 50.6, 46.6, 34.3, 31.4, 8.9 ppm; IR (KBr) ν: 2951, 2927, 2841, 1716, 1599, 1443, 1308, 1253, 1171, 1104, 1028, 846, 774 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{19}H_{18}NaO_5S_2$, $[M+Na]^+$ 413.0493, found 413.0482.

Methyl 5-(1-(1,3-dithiolan-2-ylidene)-2-(4-nitrophenyl)-2-oxoethyl)-2-methylfuran-3-carboxylate (**8m**) (0.14 mmol, 55.1 mg, 68%): deep yellow solid, mp: 156–158°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) $\delta=8.12$ (d, $J=8.3$ Hz, 2H), 7.58 (d, $J=8.4$ Hz, 2H), 6.61 (s, 1H), 3.81 (s, 3H), 3.58 (t, $J=6.5$ Hz, 2H), 3.43 (t, $J=6.5$ Hz, 2H), 2.39 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) $\delta=182.3$, 169.6, 159.3, 153.8, 144.0, 143.8, 140.4, 124.3, 118.4, 109.9, 109.5, 107.3, 46.7, 34.9, 31.2, 8.9 ppm; IR (KBr) ν: 2952, 2926, 2853, 1716, 1597, 1521, 1442, 1347, 1275, 1228, 1105, 1066, 865, 754 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{18}H_{15}NNaO_6S_2$, $[M+Na]^+$ 428.0238, found 428.0245.

Methyl 5-(2-(4-chlorophenyl)-1-(1,3-dithiolan-2-ylidene)-2-oxoethyl)-2-methylfuran-3-carboxylate (**8n**) (0.12 mmol, 48.1 mg, 61%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25°C) $\delta=7.39$ (s, 4H), 6.60 (s, 1H), 3.73 (s, 3H), 3.59–3.55 (m, 2H), 3.50–3.46 (m, 2H), 2.35 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25°C) $\delta=187.0$, 172.3, 163.3, 157.8, 149.2, 137.8, 136.0, 129.7, 128.2, 113.9, 113.3, 111.0, 51.4, 35.9, 13.2 ppm; IR (KBr) ν: 2952, 2926, 2854, 1717, 1616, 1587, 1443, 1274, 1229, 1104, 1013, 775 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{18}H_{15}ClNaO_4S_2$, $[M+Na]^+$ 416.9998, found 416.9986.

Methyl 5-(1-(1,3-dithiolan-2-ylidene)-2-(4-fluorophenyl)-2-oxoethyl)-2-methylfuran-3-carboxylate (**8o**) (0.12 mmol, 45.4 mg, 60%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25°C) $\delta=7.46$ (dd, $J=8.8$, 5.6 Hz, 2H), 7.17 (t, $J=8.9$ Hz, 2H), 6.61 (s, 1H), 3.74 (s, 3H), 3.58–3.54 (m, 2H), 3.50–3.45 (m, 2H), 2.35 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25°C) $\delta=186.9$, 171.2, 163.6, 163.3 (d, $J=249.0$ Hz), 157.7, 149.3, 135.5, 135.5, 130.6 (d, $J=9.0$ Hz), 115.1 (d, $J=21.0$ Hz), 113.9, 113.5, 110.8, 51.4, 35.9, 13.2 ppm; ^{19}F NMR (377 MHz, DMSO-d_6, 25°C) $\delta=-108.2$ ppm; IR (KBr) ν: 2951, 2926, 2853, 1717, 1597, 1445, 1272, 1229, 1104, 1065, 851, 775 cm-1; HRMS (TOF, ESI): m/z calcd for $C_{18}H_{15}FNaO_4S_2$, $[M+Na]^+$ 401.0293, found 401.0312.

Methyl 5-(1-(1,3-dithiolan-2-ylidene)-2-oxopropyl)-2-methylfuran-3-carboxylate (**8p**) (0.15 mmol, 45.3 mg, 76%): yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) $\delta=6.66$ (s, 1H), 3.85 (s, 3H), 3.49 (t, $J=6.4$ Hz, 2H), 3.29 (t, $J=6.4$ Hz, 2H), 2.62 (s, 3H), 2.11 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) $\delta=188.4$, 165.9, 159.5, 154.2, 144.8, 111.1, 109.6, 106.9, 46.7, 35.0, 30.6, 23.2, 9.1 ppm; IR (KBr) ν: 2952, 2854, 1717, 1616, 1587, 1443, 1274, 1229, 1104, 1013, 775 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{13}H_{14}NaO_4S_2$, $[M+Na]^+$ 321.0231, found 321.0229.

(*E*)-Methyl 5-(1-(1,3-dithiolan-2-ylidene)-2-oxo-4-phenylbut-3-en-1-yl)-2-methylfuran-3-carboxylate (**8q**) (0.15 mmol, 58.7 mg, 76%): yellow solid, mp: 117–119°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) $\delta=7.71$ (d, $J=15.6$ Hz, 1H), 7.44 (dd, $J=6.3$, 3.0 Hz, 2H), 7.38–7.31 (m, 3H), 6.69 (d, $J=16.8$ Hz, 2H), 3.86 (s, 3H), 3.54–3.49 (m, 2H), 3.36–3.30 (m, 2H), 2.65 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) $\delta=183.9$, 164.4, 159.3, 148.9, 143.0, 135.2, 130.1, 128.8, 128.3, 123.2, 116.5, 114.5, 112.2, 51.5, 39.7, 35.6, 13.9 ppm; IR (KBr) ν: 2951, 2925, 1716, 1642, 1588, 1448, 1332, 1279, 1233, 1092, 979, 772, 717 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{20}H_{18}NaO_4S_2$, $[M+Na]^+$ 409.0544, found 409.0546.

Methyl 2-methyl-5-(2,4,6-trimethoxyphenyl)furan-3-carboxylate (**10a**) (0.2 mmol, 60.0 mg, 98%): light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) $\delta=6.65$ (s, 1H), 6.17 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.78 (s, 6H), 2.62 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) $\delta=164.9$, 161.9, 159.7, 158.4, 145.2, 114.1, 110.9, 101.8, 90.9, 56.0, 55.4, 51.2, 14.0 ppm; IR (KBr) ν: 2948, 2842, 1715, 1601, 1463, 1228, 1126, 1023, 950, 813, 799, 631 cm^{-1}; HRMS (TOF, ESI): (m/z) calcd for $C_{16}H_{18}NaO_6$, $[M+Na]^+$ 329.1001, found 329.1009.

Methyl 2-methyl-5-(2,4,5-trimethoxyphenyl)furan-3-carboxylate (**10b**) (0.16 mmol, 49.6 mg, 81%): light yellow solid, mp: 118–120°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) $\delta=7.32$ (s, 1H), 7.02 (s, 1H), 6.58 (s, 1H), 3.92 (s, 9H), 3.85 (s, 3H), 2.65 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) $\delta=164.8$, 157.3, 150.2, 149.1, 148.1, 143.1, 115.1, 111.1, 109.3, 108.6, 97.5, 56.6, 56.1, 51.3, 13.8 ppm; IR (KBr) ν: 2992, 2945, 2839, 1714, 1609, 1519, 1446, 1290, 1209, 1095, 1030, 818, 776 cm^{-1}; HRMS (TOF,

ESI): (*m*/*z*) calcd for $C_{16}H_{18}NaO_6$, $[M+Na]^+$ 329.1001, found 329.1009.

Methyl 5-(2,7-dimethoxynaphthalen-1-yl)-2-methylfuran-3-carboxylate (**12a**) (0.14 mmol, 44.3 mg, 68%): light yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 7.97 (d, J = 9.0 Hz, 1H), 7.84 (d, J = 8.6 Hz, 1H), 7.35 (d, J = 9.1 Hz, 1H), 7.09–7.03 (m, 2H), 6.78 (s, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.76 (s, 3H), 2.64 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 164.2, 158.8, 156.7, 147.2, 134.7, 131.6, 130.4, 128.6, 127.9, 126.2, 124.3, 116.4, 114.4, 111.7, 111.5, 111.4, 103.4, 56.9, 55.4, 51.8, 14.0 ppm; IR (KBr) ν: 3058, 2955, 1734, 1628, 1587, 1510, 1387, 1208, 1147, 818, 743 cm^{-1}; HRMS-ESI (*m*/*z*) calcd for $C_{19}H_{18}NaO_5$, $[M+Na]^+$ 349.1052, found 349.1043.

Ethyl 2-methyl-5-(2-methyl-1H-indol-3-yl)-1-phenyl-1H-pyrrole-3-carboxylate (**14a**) (0.16 mmol, 58.7 mg, 82%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 10.94 (s, 1H), 7.30–7.22 (m, 3H), 7.19–7.09 (m, 4H), 6.92 (t, J = 7.0 Hz, 1H), 6.82 (t, J = 7.9 Hz, 1H), 6.45 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 2.07 (s, 3H), 1.28 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 165.2, 138.1, 136.4, 135.5, 135.3, 129.1, 128.2, 127.5, 120.8, 119.3, 118.3, 112.3, 111.1, 110.9, 104.0, 59.3, 15.0, 13.0, 12.4 ppm; IR (KBr) ν: 3394, 3337, 2927, 2858, 1678, 1457, 1231, 1086, 745, 700 cm^{-1}; HRMS (TOF, ESI): *m*/*z* calcd for $C_{23}H_{22}N_2NaO_2$, $[M+Na]^+$ 381.1579, found 381.1581.

Methyl 2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1-phenyl-1*H*-pyrrole-3-carboxylate (**14b**) (0.15 mmol, 50.9 mg, 74%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 10.94 (s, 1H), 7.29–7.22 (m, 3H), 7.17–7.13 (m, 3H), 7.10 (d, J = 7.8 Hz, 1H), 6.92 (t, J = 8.0 Hz, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.46 (s, 1H), 3.75 (s, 3H), 2.36 (s, 1H), 2.07 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 165.6, 138.1, 136.5, 135.5, 135.3, 129.2, 129.1, 128.2, 127.6, 120.8, 119.3, 118.3, 111.9, 111.0, 110.9, 104.0, 51.1, 13.0, 12.4 ppm; IR (KBr) ν: 3396, 2925, 2854, 1701, 1548, 1443, 1233, 1092, 744, 701 cm^{-1}; HRMS (TOF, ESI): *m*/*z* calcd for $C_{22}H_{21}N_2O_2$, $[M+H]^+$ 345.1603, found 345.1603.

2-Methoxyethyl 2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1-phenyl-1*H*-pyrrole-3-carboxylate (**14c**) (0.16 mmol, 60.5 mg, 78%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 10.93 (s, 1H), 7.31–7.24 (m, 3H), 7.18–7.14 (m, 3H), 7.12 (d, J = 7.9 Hz, 1H), 6.95–6.90 (m, 1H), 6.82 (t, J = 7.8 Hz, 1H), 6.46 (s, 1H), 4.33–4.29 (m, 2H), 3.65–3.60 (m, 2H), 3.30 (s, 3H), 2.36 (s, 3H), 2.07 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 165.0, 138.1, 136.6, 135.5, 135.3, 129.2, 128.2, 127.6, 120.8, 119.3, 118.3, 112.0, 111.1, 110.9, 103.9, 70.7, 62.6, 58.6, 13.0, 12.4 ppm; IR (KBr) ν: 3397, 2927, 1698, 1497, 1458, 1227, 1082, 745, 701 cm^{-1}; HRMS (TOF, ESI): *m*/*z* calcd for $C_{24}H_{25}N_2O_3$, $[M+H]^+$ 389.1865, found 389.1870.

Ethyl 2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1-(*p*-tolyl)-1*H*-pyrrole-3-carboxylate (**14d**) (0.12 mmol, 43.2 mg, 58%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 10.95 (s, 1H), 7.17 (d, J = 7.8 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.93 (t, J = 7.5 Hz, 1H), 6.84 (t, J = 7.4 Hz, 1H), 6.44 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 2.20 (s, 3H), 2.07 (s, 3H), 1.28 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 169.9, 142.4, 141.3, 140.3, 140.2, 140.0, 134.4, 134.0, 132.7, 132.3, 125.5, 124.1, 123.1, 116.9, 115.8, 115.7, 108.8, 64.0, 25.7, 19.7, 17.8, 17.2 ppm; IR (KBr) ν: 3397, 2925, 2859, 1678, 1516, 1459, 1232, 1092, 744 cm^{-1}; HRMS (TOF, ESI): *m*/*z* calcd for $C_{24}H_{25}N_2O_2$, $[M+H]^+$ 373.1916, found 373.1941.

Ethyl 1-(4-methoxyphenyl)-2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1*H*-pyrrole-3-carboxylate (**14e**) (0.14 mmol, 53.5 mg, 69%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 10.94 (s, 1H), 7.17 (d, J = 7.9 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.07 (d, J = 8.7 Hz, 2H), 6.95–6.91 (m, 1H), 6.84 (d, J = 7.5 Hz, 1H), 6.80 (d, J = 8.9 Hz, 2H), 6.42 (s, 1H), 4.22 (q, J = 7.0 Hz, 2H), 3.67 (s, 3H), 2.34 (s, 3H), 2.09 (s, 3H), 1.28 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 165.2, 158.8, 136.7, 135.5, 135.3, 130.8, 129.3, 129.3, 127.7, 120.8, 119.3, 118.3, 114.3, 112.0, 110.9, 110.9, 104.1, 59.3, 55.6, 22.9, 15.0, 13.0, 12.5 ppm; IR (KBr) ν: 3396, 2927, 2855, 1697, 1678, 1513, 1243, 1090, 1070, 744 cm^{-1}; HRMS (TOF, ESI): *m*/*z* calcd for $C_{24}H_{25}N_2O_3$, $[M+H]^+$ 389.1865, found 389.1892.

Ethyl 1-(4-fluorophenyl)-2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1*H*-pyrrole-3-carboxylate (**14f**) (0.16 mmol, 60.9 mg, 81%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 10.98 (s, 1H), 7.21 (dd, J = 8.9, 5.1 Hz, 2H), 7.17 (d, J = 8.0 Hz, 1H), 7.11 (t, J = 8.9 Hz, 3H), 6.96–6.90 (m, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.45 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 2.11 (s, 3H), 1.29 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 165.1, 135.9 (d, J = 128.0 Hz), 135.60, 130.39, 130.30, 128.97, 127.66, 120.84, 119.32, 118.25, 116.12, 115.89, 112.30, 111.0 (d, J = 5.0 Hz), 103.80, 59.34, 14.97, 12.96, 12.42 ppm; ^{19}F NMR (377 MHz, DMSO-d_6, 25 °C) δ = −113.9, −114.0 ppm; IR (KBr) ν: 3397, 2927, 2855, 1698, 1679, 1511, 1422, 1221, 1091, 1016, 746 cm^{-1}; HRMS (TOF, ESI): *m*/*z* calcd for $C_{23}H_{22}FN_2O_2$, $[M+H]^+$ 377.1665, found 377.1689.

Ethyl 1-(3-fluorophenyl)-2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1*H*-pyrrole-3-carboxylate (**14g**) (0.17 mmol, 63.2 mg, 84%): yellowish oil; ^{1}H NMR (600 MHz, DMSO-d_6, 25 °C) δ = 11.00 (s, 1H), 7.30 (dd, J = 14.7, 8.1 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.13 (d, J = 9.8 Hz, 1H), 7.12–7.08 (m, 2H), 6.99 (d, J = 8.0 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.82 (t, J = 7.8 Hz, 1H), 6.46 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 2.12 (s, 3H), 1.29 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 165.1, 161.9 (d, J = 243.0 Hz), 139.6 (d, J = 10.0 Hz), 136.5, 135.6, 135.3, 130.7 (d, J = 9.0 Hz), 128.9, 127.6, 124.7, 120.9, 119.3, 118.2, 115.7 (d, J = 23.0 Hz), 115.3 (d, J = 21.0 Hz), 112.5, 111.1 (d, J = 23.0 Hz), 103.7, 59.4, 15.0, 13.0, 12.4 ppm; ^{19}F NMR (377 MHz, DMSO-d_6, 25 °C) δ = −112.2 ppm; IR (KBr) ν: 3398, 2926, 2855, 1676, 1606, 1456, 1240, 1178, 1085, 745 cm^{-1}; HRMS (TOF, ESI): *m*/*z* calcd for $C_{23}H_{22}FN_2O_2$, $[M+H]^+$ 377.1665, found 377.1682.

Ethyl 1-(2-bromophenyl)-2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1*H*-pyrrole-3-carboxylate (**14h**) (0.17 mmol, 73.2 mg, 83%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 10.98 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.34–7.24 (m, 2H), 7.20 (t, J = 7.0 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 6.91 (t, J = 7.0 Hz, 1H), 6.83 (t, J = 7.1 Hz, 1H), 6.45 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.24 (d, J = 4.0 Hz, 6H), 1.29 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 165.1, 137.4, 136.7, 136.2, 135.2, 133.4, 131.6, 131.0, 129.1, 128.7, 127.7, 123.3, 120.7, 119.1, 118.8, 112.4, 111.5, 110.9, 103.5, 59.4, 15.0, 12.8, 12.7 ppm; IR (KBr) ν: 3399, 3341, 2925, 1679, 1482, 1457, 1231, 1071,

744 cm^{-1}; HRMS (TOF, ESI): *m/z* calcd for $C_{23}H_{22}BrN_2O_2$, $[M+H]^+$ 437.0865, found 437.0877.

Ethyl 1-(3,4-difluorophenyl)-2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1*H*-pyrrole-3-carboxylate (**14i**) (0.16 mmol, 62.2 mg, 79%): yellowish oil; ^{1}H NMR (600 MHz, DMSO-d_6, 25°C) δ=11.03 (s, 1H), 7.50–7.44 (m, 1H), 7.34 (dd, *J*= 19.2, 9.0 Hz, 1H), 7.18 (d, *J*=8.0 Hz, 1H), 7.09 (d, *J*= 7.9 Hz, 1H), 7.01 (d, *J*=8.6 Hz, 1H), 6.94 (t, *J*=7.5 Hz, 1H), 6.83 (t, *J*=7.4 Hz, 1H), 6.45 (s, 1H), 4.23 (q, *J*= 7.1 Hz, 2H), 2.39 (s, 3H), 2.16 (s, 3H), 1.28 ppm (t, *J*= 7.1 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6, 25°C) δ= 165.0, 136.7–135.3 (m, 2C), 128.8, 127.7, 120.9, 119.4, 118.2 (d, *J*=32.7 Hz), 117.9, 112.5, 111.1 (d, *J*=17.6 Hz), 103.5, 59.4, 15.0, 12.9, 12.4 ppm; ^{19}F NMR (377 MHz, DMSO-d_6, 25°C) δ=−136.9, −137.0, −138.8, −138.9 ppm; IR (KBr) *v*: 3396, 2926, 1681, 1518, 1243, 1216, 1076, 745 cm^{-1}; HRMS (TOF, ESI): *m/z* calcd for $C_{23}H_{21}F_2N_2O_2$, $[M+H]^+$ 395.1571, found 395.1601.

Ethyl 2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1-(4-(trifluoromethoxy)phenyl)-1*H*-pyrrole-3-carboxylate (**14j**) (0.16 mmol, 72.5 mg, 82%): yellowish oil; ^{1}H NMR (600 MHz, DMSO-d_6, 25°C) δ=11.00 (s, 1H), 7.29 (q, *J*= 9.0 Hz, 4H), 7.17 (d, *J*=8.0 Hz, 1H), 7.08 (d, *J*=7.8 Hz, 1H), 6.93 (t, *J*=7.5 Hz, 1H), 6.82 (t, *J*=7.4 Hz, 1H), 6.47 (s, 1H), 4.23 (q, *J*=7.1 Hz, 2H), 2.39 (s, 3H), 2.08 (s, 3H), 1.29 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6, 25°C) δ=165.1, 147.7 (d, *J*=0.9 Hz), 137.1, 136.4, 135.5, 135.3, 130.3, 128.8, 127.6, 121.7, 120.9, 119.3, 118.2, 112.6, 111.1 (d, *J*=23.7 Hz), 103.6, 59.4, 15.0, 13.0, 12.4 ppm; ^{19}F NMR (377 MHz, DMSO-d_6, 25°C) δ=−57.0 ppm; IR (KBr) *v*: 3397, 2928, 1681, 1512, 1259, 1072, 746 cm^{-1}; HRMS (TOF, ESI): *m/z* calcd for $C_{24}H_{22}F_3N_2O_3$, $[M+H]^+$ 443.1583, found 443.1505.

Ethyl 1-(3-chloro-2-methylphenyl)-2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1*H*-pyrrole-3-carboxylate (**14k**) (0.18 mmol, 71.4 mg, 88%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25°C) δ=11.00 (s, 1H), 7.38 (dd, *J*=12.3, 8.0 Hz, 2H), 7.23–7.13 (m, 3H), 6.93 (t, *J*=7.5 Hz, 1H), 6.85 (t, *J*= 7.4 Hz, 1H), 6.48 (s, 1H), 4.23 (q, *J*=7.1 Hz, 2H), 2.22 (s, 3H), 2.16 (s, 3H), 1.79 (s, 3H), 1.29 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25°C) δ=165.1, 138.7, 136.7, 135.8, 135.2, 134.9, 134.2, 129.9, 129.0, 128.8, 127.8, 127.6, 120.9, 119.3, 118.4, 112.4, 111.4, 111.0, 103.5, 59.4, 15.5, 14.9, 12.6, 12.5 ppm; IR (KBr) *v*: 3335, 2926, 1696, 1679, 1463, 1237, 1073, 1029, 745 cm^{-1}; HRMS (TOF, ESI): *m/z* calcd for $C_{24}H_{24}ClN_2O_2$, $[M+H]^+$ 407.1526, found 407.1544.

Ethyl 1-(2-bromo-4-fluorophenyl)-2-methyl-5-(2-methyl-1*H*-indol-3-yl)-1*H*-pyrrole-3-carboxylate (**14l**) (0.16 mmol, 71.7 mg, 79%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25°C) δ=11.03 (s, 1H), 7.66–7.53 (m, 2H), 7.26 (d, *J*= 7.9 Hz, 1H), 7.24–7.18 (m, 1H), 7.16 (d, *J*=8.0 Hz, 1H), 6.93 (t, *J*=7.0 Hz, 1H), 6.84 (t, *J*=7.9 Hz, 1H), 6.45 (s, 1H), 4.23 (q, *J*=7.1 Hz, 2H), 2.26 (s, 6H), 1.29 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6, TMS, 25°C) δ=165.1, 161.6 (d, *J*=249.0 Hz), 136.9, 136.3, 135.2, 134.2, 132.9 (d, *J*=9.0 Hz), 129.0, 127.9, 124.2 (d, *J*=10.0 Hz), 120.8, 120.5 (d, *J*=26.0 Hz), 119.2, 118.7, 115.7 (d, *J*=22.0 Hz), 112.5, 111.5, 110.6, 103.3, 59.5, 14.9, 12.8, 12.6 ppm; ^{19}F NMR (377 MHz, DMSO-d_6, 25°C) δ=−110.5 ppm; IR (KBr) *v*: 3396, 2926, 1695, 1675, 1484, 1227, 1085, 1030, 774 cm^{-1}; HRMS (TOF, ESI): *m/z* calcd for $C_{23}H_{20}BrFN_2NaO_2$, $[M+Na]^+$ 477.0590, found 477.0587.

Ethyl 5-(5-methoxy-2-methyl-1*H*-indol-3-yl)-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (**14m**) (0.14 mmol, 55.1 mg, 71%): yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25°C) δ=10.80 (s, 1H), 7.30–7.23 (m, 3H), 7.19 (d, *J*= 7.1 Hz, 2H), 7.03 (d, *J*=9.4 Hz, 1H), 6.54–6.50 (m, 2H), 6.44 (s, 1H), 4.23 (q, *J*=7.1 Hz, 2H), 3.62 (s, 3H), 2.37 (s, 3H), 2.11 (s, 3H), 1.29 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (1–0 MHz, DMSO-d_6, 25°C) δ=165.2, 153.7, 138.2, 136.3, 136.1, 130.2, 129.3, 129.1, 128.3, 127.8, 112.3, 111.5, 110.9, 110.7, 104.0, 100.3, 59.3, 55.6, 15.0, 13.1, 12.5 ppm; IR (KBr) *v*: 3396, 2926, 1695, 1675, 1484, 1227, 1085, 1030, 774 cm^{-1}; HRMS (TOF, ESI): *m/z* calcd for $C_{24}H_{25}N_2O_3$, $[M+H]^+$ 389.1865, found 389.1884.

3,3′-((2-bromophenyl)methylene)bis(2-methyl-1*H*-indole) (**17a**)[27] (0.95 mmol, 406.6 mg, 95%): white solid, mp: 140–142°C, ^{1}H NMR (400 MHz, DMSO-d_6, 25°C) δ=10.80 (s, 2H), 7.61 (d, *J*=7.8 Hz, 1H), 7.32–7.21 (m, 4H), 7.19–7.14 (m, 1H), 6.91 (t, *J*=7.3 Hz, 2H), 6.79 (d, *J*=7.7 Hz, 2H), 6.70 (t, *J*=7.3 Hz, 2H), 6.06 (s, 1H), 2.02 ppm (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6, 25°C) δ=143.7, 135.5, 133.1, 132.8, 131.5, 128.9, 128.7, 127.7, 125.1, 120.1, 118.6, 118.4, 111.1, 110.9, 12.2 ppm.

N-((2-bromophenyl)(2-methyl-1*H*-indol-3-yl)methyl)aniline (**18a**) (0.16 mmol, 60.8 mg, 78%), white solid, mp: 149–151°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ=7.89 (dd, *J*=7.8, 1.5 Hz, 1H), 7.73 (s, 1H), 7.52 (dd, *J*=7.9, 1.1 Hz, 1H), 7.36 (d, *J*=7.9 Hz, 1H), 7.28 (td, *J*=7.6, 1.0 Hz, 1H), 7.21 (d, *J*=8.2 Hz, 1H), 7.14–7.04 (m, 4H), 6.95 (t, *J*=8.0 Hz, 1H), 6.69 (t, *J*=7.3 Hz, 1H), 6.46 (d, *J*= 7.7 Hz, 2H), 5.87 (s, 1H), 4.29 (s, 1H), 2.27 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ=147.4, 140.5, 135.1, 133.4, 133.2, 129.5, 129.3, 128.7, 127.4, 127.3, 123.7, 121.3, 119.7, 118.8, 117.5, 113.2, 110.9, 110.4, 55.5, 12.7 ppm; IR (KBr) *v*: 3394, 3348, 2949, 2921, 1691, 1454, 1438, 1244, 1063, 608 cm^{-1}; HRMS (TOF, ESI): *m/z* calcd for $C_{22}H_{19}BrN_2Na$, $[M+Na]^+$ 413.0629, found 413.0622.

Methyl 2-methyl-1-phenyl-5-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**19a**) colorless oil; (0.85 mmol, 261.0 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ=7.24–7.17 (m, 2H), 7.14 (d, *J*=8.1 Hz, 2H), 7.08 (t, *J*=7.8 Hz, 3H), 6.94–6.87 (m, 2H), 5.01 (dd, *J*=11.3, 8.3 Hz, 1H), 3.69 (s, 2H), 3.36 (ddd, *J*=14.7, 11.4, 1.2 Hz, 1H), 2.78 (ddd, *J*= 14.8, 8.3, 1.4 Hz, 1H), 2.29 (s, 2H), 2.24 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ=204.3, 167.5, 159.0, 141.5, 139.9, 137.1, 129.3, 128.9, 126.8, 125.8, 125.6, 120.2, 98.6, 69.0, 50.4, 38.3, 21.1, 14.2 ppm; IR (KBr) *v*: 2961, 2922, 1699, 1597, 1458, 1435, 1243, 1063, 742 cm^{-1}; HRMS (TOF, ESI): *m/z* calcd for $C_{20}H_{21}NNaO_2$, $[M+Na]^+$ 330.1470, found 330.1463.

Methyl 2-methyl-1-phenyl-5-(*p*-tolyl)-1*H*-pyrrole-3-carboxylate (**20a**) colorless oil; (0.16 mmol, 50.0 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ=7.43–7.35 (m, 3H), 7.17–7.10 (m, 2H), 6.98–6.90 (m, 4H), 6.74 (s, 1H), 3.85 (s, 3H), 2.39 (s, 3H), 2.25 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ=166.1, 138.2, 138.0, 136.3, 134.1, 129.5, 129.2, 128.8, 128.5, 128.2, 128.0, 112.4, 109.5, 50.9, 21.1, 12.5 ppm; IR (KBr) *v*: 2961, 2922, 2911, 1703, 1597, 1452, 1439, 1240, 1061, 742 cm^{-1}; HRMS (TOF, ESI): *m/z* calcd for $C_{20}H_{19}NNaO_2$, $[M+Na]^+$ 328.1313, found 328.1301.

Methyl 2-methyl-5-(2-methyl-1*H*-indol-3-yl)-4,5-dihydrothiophene-3-carboxylate (**21a**) (0.19 mmol, 54.2 mg, 95%): brown oil; ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C) δ = 10.96 (s, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 7.9 Hz, 1H), 7.02 (t, J = 7.0 Hz, 1H), 6.95 (t, J = 7.0 Hz, 1H), 5.39 (t, J = 9.8 Hz, 1H), 3.65 (s, 3H), 3.41–3.34 (m, 2H), 2.36 ppm (s, 6H); ^{13}C NMR (100 MHz, DMSO-d$_6$, 25 °C) δ = 164.2, 157.0, 136.0, 133.4, 126.7, 120.9, 119.2, 119.1, 118.9, 111.3, 109.9, 51.4, 43.9, 43.7, 16.6, 11.9 ppm; IR (KBr) v: 3394, 3348, 2949, 2924, 1699, 1597, 1458, 1435, 1244, 1063, 742 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{16}H_{18}NO_2S$, $[M+H]^+$ 288.1058, found 288.1030.

Ethyl 2-methyl-5-(2-methyl-1*H*-indol-3-yl)-4,5-dihydrothiophene-3-carboxylate (**21b**) (0.19 mmol, 56.0 mmol, 93%), light yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C) δ = 7.97 (s, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 7.16–7.04 (m, 2H), 5.27 (t, J = 10.1 Hz, 1H), 4.18 (qd, J = 7.1, 1.3 Hz, 2H), 3.55 (ddd, J = 16.1, 10.1, 1.9 Hz, 1H), 3.43 (ddd, J = 16.2, 10.2, 1.4 Hz, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 1.26 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, TMS, 25 °C) δ = 164.4, 157.5, 135.5, 132.1, 126.8, 121.4, 119.7, 119.4, 119.4, 110.7, 110.6, 59.9, 43.9, 43.9, 16.6, 14.4, 12.0 ppm; IR (KBr) v: 3392, 3351, 2939, 2922, 1699, 1596, 1455, 1436, 1242, 1066, 742 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{17}H_{20}NO_2S$, $[M+H]^+$ 302.1215, found 302.1203.

2-Methoxyethyl 2-methyl-5-(2-methyl-1*H*-indol-3-yl)-4,5-dihydrothiophene-3-carboxylate (**21c**) (0.18 mmol, 60.9 mg, 92%), light yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C) δ = 7.93 (s, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.26 (d, J = 7.3 Hz, 1H), 7.11 (dtd, J = 15.9, 7.1, 1.0 Hz, 2H), 5.27 (t, J = 10.2 Hz, 1H), 4.34–4.22 (m, 2H), 3.61 (t, J = 4.8 Hz, 2H), 3.59–3.51 (m, 1H), 3.49–3.41 (m, 1H), 3.37 (s, 3H), 2.42 (s, 2H), 2.37 ppm (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, TMS, 25 °C) δ = 164.1, 158.4, 135.5, 132.0, 126.8, 121.4, 119.7, 119.5, 119.0, 110.6, 110.5, 70.7, 63.0, 59.0, 44.1, 43.7, 16.6, 12.0 ppm; IR (KBr) v: 3392, 3351, 2948, 2921, 1701, 1598, 1456, 1431, 1249, 1061, 742 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{18}H_{22}NO_3S$, $[M+H]^+$ 332.1320, found 332.1304.

Ethyl 5-(2-methyl-1*H*-indol-3-yl)-2-phenyl-4,5-dihydrothiophene-3-carboxylate (**21d**) (0.18 mmol, 64.6 mg, 89%), light yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C) δ = 7.92 (s, 1H), 7.89–7.84 (m, 1H), 7.47 (dd, J = 6.5, 3.1 Hz, 2H), 7.34 (dd, J = 5.0, 1.9 Hz, 3H), 7.26–7.21 (m, 1H), 7.16–7.09 (m, 2H), 5.42 (t, J = 10.2 Hz, 1H), 4.04 (qd, J = 7.1, 2.7 Hz, 2H), 3.77 (dd, J = 16.5, 10.3 Hz, 1H), 3.61 (dd, J = 16.5, 10.1 Hz, 1H), 2.38 (s, 3H), 1.05 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, TMS, 25 °C) δ = 159.1, 152.7, 130.8, 129.6, 127.5, 124.2, 123.8, 123.1, 122.1, 116.7, 115.3, 115.0, 114.8, 105.9, 105.8, 55.3, 40.2, 39.8, 9.2, 7.4 ppm; IR (KBr) v: 3395, 3341, 2944, 2928, 1699, 1596, 1457, 1435, 1398, 1240, 1061, 742 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{22}H_{22}NO_2S$, $[M+H]^+$ 364.1371, found 364.1360.

Methyl 5-(5-methoxy-2-methyl-1*H*-indol-3-yl)-2-methyl-4,5-dihydrothiophene-3-carboxylate (**21e**) (87%, 0.17 mmol, 55.2 mg), light yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25 °C) δ = 7.88 (s, 1H), 7.15 (d, J = 2.3 Hz, 1H), 7.12 (d, J = 8.7 Hz, 1H), 6.77 (dd, J = 8.7, 2.4 Hz, 1H), 5.21 (t, J = 9.6 Hz, 1H), 3.81 (s, 3H), 3.71 (s, 3H), 3.53–3.40 (m, 2H), 2.42 (s, 3H), 2.34 ppm (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$. TMS, 25 °C) δ = 164.73, 157.89, 153.73, 132.78, 130.57, 127.10, 119.06, 111.23, 111.04, 110.90, 102.20, 55.87, 51.10, 43.86, 43.56, 16.58, 12.10 ppm; IR (KBr) v: 3394, 3348, 2949, 2921, 1699, 1597, 1458, 1438, 1244, 1063, 608, 744 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{17}H_{20}NO_3S$, $[M+H]^+$ 318.1164, found 318.1161.

Methyl 5-(5-fluoro-2-methyl-1*H*-indol-3-yl)-2-methyl-4,5-dihydrothiophene-3-carboxylate (**21f**) (90%, 0.18 mmol, 57.1 mg), light yellow oil; ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C) δ = 11.09 (s, 1H), 7.26 (dd, J = 8.7, 4.7 Hz, 1H), 7.19 (dd, J = 10.3, 2.4 Hz, 1H), 6.85 (td, J = 9.3, 2.5 Hz, 1H), 5.35 (t, J = 9.7 Hz, 1H), 3.65 (s, 3H), 3.42–3.35 (m, 1H), 3.28 (ddd, J = 16.0, 9.2, 1.9 Hz, 1H), 2.35 ppm (d, J = 3.5 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d$_6$, 25 °C) δ = 164.1, 156.9 (d, J = 229.0 Hz), 156.8, 135.8, 132.6, 126.9 (d, J = 10.0 Hz), 119.1, 112.1 (d, J = 10.0 Hz), 110.4 (d, J = 4.0 Hz), 108.6 (d, J = 25.0 Hz), 103.9 (d, J = 23.0 Hz), 51.4, 43.8, 43.3, 16.6, 12.0 ppm; ^{19}F NMR (377 MHz, DMSO-d$_6$, 25 °C) δ = −124.7 ppm.IR (KBr) v: 3394, 3348, 2951, 2920, 1702, 1592, 1458, 1435, 1244, 1063, 742 cm^{-1}; HRMS (TOF, ESI): m/z calcd for $C_{16}H_{17}FNO_2S$, $[M+H]^+$ 306.0964, found 306.0961.

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