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tert-Butyl Nitrite Promoted Oxidative Intermolecular Sulfonamination of Alkynes to Synthesize Substituted Sulfonyl Pyrroles from the Alkynylamines and Sulfinic Acids

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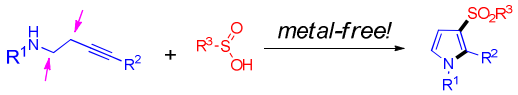
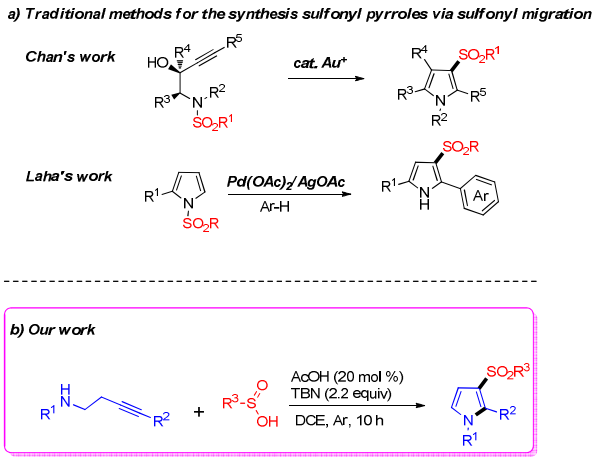


Abstract: *tert*-Butyl nitrite (TBN) promoted oxidative intermolecular sulfonamination of alkynes to synthesize substituted sulfonyl pyrroles from the alkynylamines and sulfinic acids via tandem addition/cyclization has been developed. This reaction is performed well by employing *tert*-butyl nitrite as the oxidant, and various substituted sulfonyl pyrroles are formed in moderate to good yields with no requirement of metal catalysis.

The reaction of radical-based tandem cyclization offers a strategic platform for the construction of polysubstituted heterocyclic structures in convergent manners through orchestrated multiple C−C/C−X bonds

formation. Sulfonyl radical, as intriguing sulfur-centered radical, which can be initiated from the common sulfinic acid, has received tremendous attentions in radical-based reactions due to its greater synthetic value.[1] In recent years, the pioneering studies about sulfonylation reactions using sulfinic acids as sulfonylating agents, mainly focus on direct sulfonylation of olefins or alkynes and decarboxylative sulfonylation of α,β-unsaturated carboxylic acids.[2] Despite the reactions of direct sulfonylation have been well exploited so far, the sulfonylation and cyclization to generate heterocyclic compound with benzenesulfinic acid through radical tandem reaction are very rare. Efforts from the Han[3] and Zhu[4] groups have demonstrated sulfonamination of alkynes to construct 3-sulfonylindoles and sulfone-containing 4-quinolones with sulfinic acids through radical tandem cyclization. Recently, the group of Wang provides a direct method for the preparation of 3-sulfonated coumarins with sulfinic acids and phenyl propiolates by visible-light initiated oxidative cyclization under metal-free conditions.[5] Notwithstanding the impressive advances, the obvious drawback of these approaches is only generation the sulfonyl benzo-heterocyclic compounds. Therefore, the formation of sulfonyl pyrroles from sulfinic acid in facial and mild strategy manner is still highly desirable.

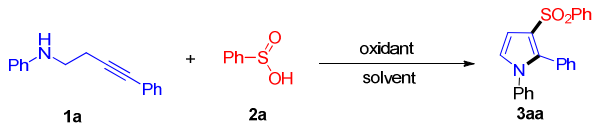
The substituted pyrroles are privileged heterocyclic scaffold prevalent in many different fields, incorporating smart materials, pharmaceuticals,



Scheme 1. Reactions for the Synthesis of Sulfonyl Pyrroles

and natural products.[6] Moreover, the sulfonyl substituted pyrroles play significant influence in organic synthesis and medicinal chemistry.[7] While the research on the synthesis of sulfonyl substituted pyrroles is limited to only a few reports.[8] These methods for the synthesis sulfonyl pyrroles are mainly based on sulfonyl migration. The group of Chan develops gold(I)-catalyzed cycloisomerization of *N*-substituted *N*-sulfonyl-aminobut-3-yn-2-ols through regioselectivity migration of the sulfonyl group to synthesize 3-sulfonyl-[*NH*]-pyrroles.[9] Recently, a one-pot synthesis of sulfonyl pyrroles is reported by Laha's group via sulfonyl migration and oxidative arylation.[10] But these methods still suffer from harsh reaction conditions, multi-step synthesis of precursors, expensive transition metal catalysts.[11] Inspired by recent studies in construction heterocyclic scaffolds and C-S bond formation,[12] herein, we disclose a direct method to synthesize 3-sulfonyl pyrroles from alkynylamines and sulfinic acids via sulfonamination of alkyne and

Table 1. Optimization of Reaction Condition[a]



Entry	Solvent	Oxidant	Acid (%)	Yield (%)[b]
1	THF	DTBP	-	54
2	DCE	DTBP	-	62
3	DMSO	DTBP	-	0
4	DMF	DTBP	-	trace
5	MeCN	DTBP	-	46
6[c]	DCE	DTBP	-	57
7[d]	DCE	DTBP	-	58
8	DCE	TBN	-	67
9	DCE	$K_2S_2O_8$	-	21
10	DCE	TBHP	-	45
11	DCE	BQ	-	0
12	DCE	DDQ	-	0
13	DCE	PIDA	-	33
14	DCE	TBN	CF_3SO_3H	60
15	DCE	TBN	CF_3COOH	65
16	DCE	TBN	$BF_3 \cdot OEt_2$	57
17	DCE	TBN	AcOH	73
18	**DCE**	**TBN**	**AcOH (20)**	**88**
19	DCE	TBN	AcOH (40)	64

[a] All reactions were carried out in argon atmosphere using **1a** (0.30 mmol), **2a** (0.60 mmol), oxidant (2.2 equiv.), acid (10 mol %) at 100 °C in 2 mL solvent for 10 h. [b] Isolated yield. [c] 80 °C. [d] 120 °C.

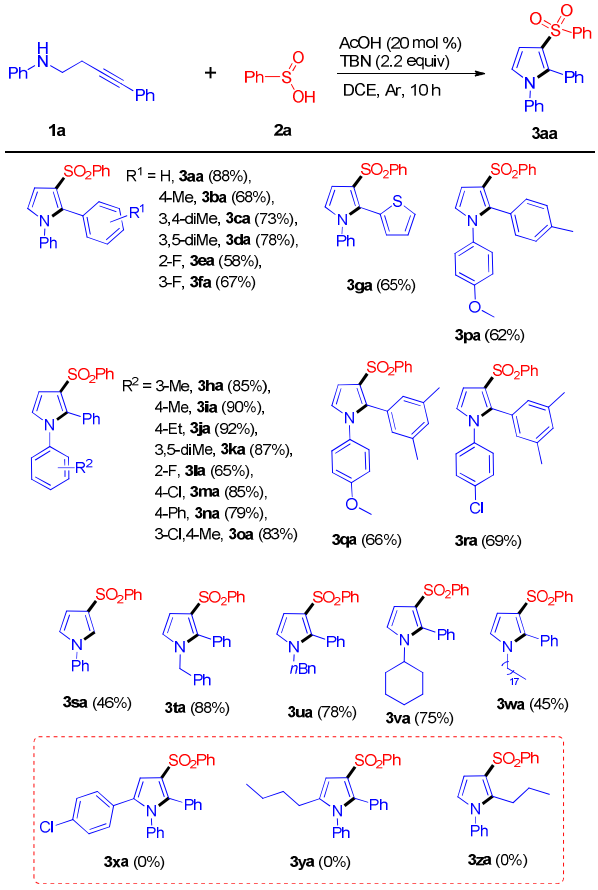
tandem oxidation/cyclization. (Scheme 1).

Initially, the substrates *N*-(4-phenylbut-3-yn-1-yl) aniline (**1a**) and benzenesulfinic acid (**2a**) were selected as the model for this reaction. Treating the substrate **1a** and **2a** with DTBP (di-*tert*-butyl peroxide) in THF at 100 °C under argon, the desired

1,2-diphenyl-3-(phenylsulfonyl)-1*H*-pyrrole (**3aa**) was obtained in 54% yield (Table 1, entry 1). The absolute stereochemistries of the product was determined by X-ray analysis of a single crystal of **3ab**[13] (in the Supporting Information). The DCE (1,2-dichloroethane) as solvent gave a higher yield than DMSO (dimethyl sulfoxide), DMF (dimethylformamide), MeCN and THF (entries 1-5). Changing the reaction temperature did not increase the yield of product **3aa** (entries 6-7). Then various oxidants were examined for this reaction, TBN (*tert*-butyl nitrite) showed better efficiency for this process and gave the desired product **3aa** in 67% (entry 2, entries 8-13). Meanwhile, it was found that the acid significantly influenced the reaction and the yield was increased to 73% when 10 mmol % AcOH was introduced (Table 1, entries 14-17). Luckily, increasing the AcOH loading to 20 mol %, the yield was improved to 88%. (Table 1, entries 17-19). So the optimized reaction system was established as Table 1, entry 18.

With the optimized conditions in hand, the scope and generality of this reaction were investigated, and the results were illustrated in Scheme 2. The optimized conditions were proved to be effective for the generation of sunfonyl pyrroles and various alkynylarylamines with electron-donating or withdrawing groups on benzene rings reacted with substrate **2a** smoothly, giving the desired sulfonyl pyrroles in moderate to excellent yields. Therefore, the results demonstrated that the reaction was

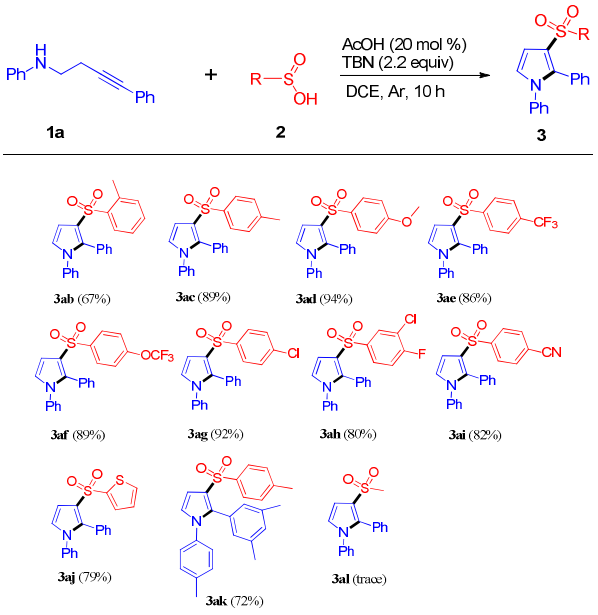
Scheme 2. Scope of Aminoalkynes[a]



[a] Reaction conditions: **1** (0.30 mmol), **2a** (0.60 mmol), AcOH (20 mol %) and TBN (0.66 mmol) in DCE (2.0 mL) at 100 °C under Ar.

sensitive to the steric effect of the *ortho*-position and the products **3ea** and **3la** were obtained only in 58% and 65% yields. The *N*-(4-(thiophen-2-yl)but-3-yn-1-yl)aniline **1g** was also tolerated in this reaction, producing the desired pyrrole **3ga** in 65% yield. The substrate **1s** of *N*-(but-3-yn-1-yl)aniline genenrated the corresponding product **3sa** in 46% yield under the standard conditions. Furthermore, homopropargylic amines with *N*-substituent as alkyl substituents also performed well and the desired products were isolated in ideal yields (**3ta-3wa**). In addition the alkynylarylamines with groups at 4-position or alkyl group at

Scheme 3. Scope of Sulfinic Acids[a]

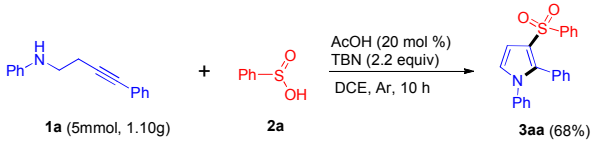


[a] Reaction conditions: **1a** (0.30 mmol), **2** (0.60 mmol), AcOH (20 mol %) and TBN (0.66 mmol) in DCE (2.0 mL) at 100 °C under Ar.

1-position performed unsuccessfully in this process and no products were detected (**3xa**-**3za**).

Having successfully achieved the cascade sequence with homopropargylic amines, we shifted our attention to explore the scope of sulfinic acids **2**. The reactions of a variety of sulfinic acids with **1a** were tested, and the results were illustrated in Scheme 3. Arylsulfinic acids bearing substituents such as *p*-Me, *p*-OMe, *p*-CF_3, *p*-OCF_3, *p*-Cl, *p*-F, *p*-CN (**2c**-**2i**) on the phenyl ring gave the corresponding sulfonyl substituted pyrroles in high yields. Obviously, 2-methylbenzenesulfinic acid reacted with **1a** to afford **3ab** in 67% yield, suggesting that the

Scheme 4. Scalable Experiment of Substituted Sulfonyl Pyrroles



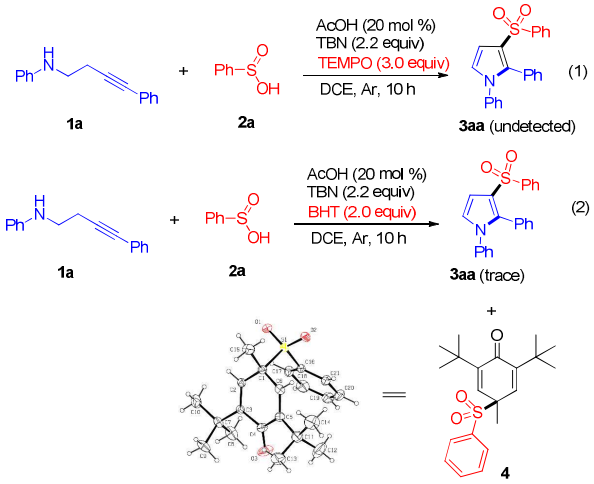
reaction was influenced by the steric effect. More challenging substrate **2j** was also tolerated well, generating the desired product in 79% yield. The methanesulfinic acid **2l** performed unsuccessfully in this process and only trace desired product was detected.

It was worth mention that scalable experiment of substituted sulfonyl pyrroles had been performed with optimized conditions and the desired product **3aa** was obtained in 68% when the amount of substrate **1a** was increased to 5mmol (1.10g) (Scheme 4).

In order to gain further insight into this reaction and verify the reaction mechanism, 3.0 equiv the radical scavenge of 2,2,6,6-tetramethyl-1-piperi dinyl-oxy (TEMPO) was added to the standard reaction system and no desired product **3aa** was detected. The result demonstrated that the reaction underwent radical pathway (Scheme 5, entry 1). When the radical scavenger of 2,6-di-tert-butyl-4-methyl-phenol (BHT) was used for this reaction, the product **3aa** was almost not detected and a product **4**[14] (in the Supporting Information), which was confirmed by NMR, HMRS and XRD spectroscopy, was isolated in 52% yield (Scheme 5, entry 2). This result suggested that sulfonyl radical should be the important radical intermediate for this transformation.

Based on the above control experiment and the literature,[2-5] a plausible mechanism is proposed in Scheme 6. Initially, sulfinic acids **2a** reacts with TBN to generate the corresponding radical **A**, which could

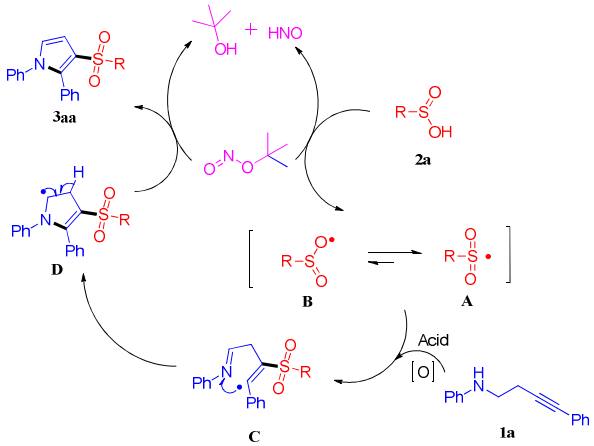
Scheme 5. Control Experiments



equilibrates to intermediate **B** under optimized conditions. Subsequently, the sulfonyl radical adds to the alkynyl moiety of substrate **1a** to afford the vinyl radical intermediate **C** under acidic and oxidative conditions. The intermediate **D** is easily gained from **C** via intramolecular radical addition and cyclization process. Finally, **D** is oxidized to give the desired product **3aa**.

In summary, we have demonstrated a metal-free and direct annulation method for the synthesis of 3-substituted pyrrole sulfones from

Scheme 6. Proposed Mechanism



alkynylarylamines and sulfinic acids via radical cascade sulfonation/cyclization process. This protocol not only provides a novel method for the efficient C-S bond formation but also provides a general approach for the synthesis of 3-sulfonylpyrrole frameworks. In addition, various substituted homopropargylic amines proceed smoothly with sulfinic acids and the desired products are obtained in moderate to good yields.

Experimental Section

General remarks. ^{1}H NMR and ^{13}C NMR spectra of materials and products were respectively recorded on 300MHz and 75MHz (VARIAN 300M), 400MHz and 100MHz (BRUKER 400M or JNM-ECS 400M) in $CDCl_3$. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; HRMS was performed on an FT-ICRMS mass instrument and measured with electrospray ionization (ESI). Copies of their ^{1}H NMR and ^{13}C NMR spectra are provided in Supporting Information. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. Unless otherwise noted, commercially available reagents and solvents were used without further purification. In addition, it is important to note that *tert*-butyl nitrite (TBN) is toxic and easily to decompose.

General procedure for the synthesis of aminoalkynes 1a-1w and 1z[15-17]. For the reaction scheme, see Scheme S1 in the Supporting Information.

To a suspension of $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol), CuI (5.7 mg, 0.03 mmol) in Et_3N (1.5 mL) was added a solution of R^2I (1.2 eq) and but-3-yn-1-ol (210 mg, 3.0 mmol, 1.0 eq) in Et_3N (15 mL). The mixture was stirred at room temperature for 12 h and then was diluted with EtOAc (20 mL), filtered off and evaporated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/EtOAc = 15/1 to 5/1) to afford substituted $\mathbf{S_1}$ in 90% yields as yellow oil.

To a solution of $\mathbf{S_1}$ (3 mmol), triethylamine (0.52 mL, 3.6 mmol), and 4-(dimethylamino)pyridine (7.8 mg, 0.05 mmol) in DCM (18 mL) at 0 ^oC was added *p*-toluenesulfonyl chloride (0.6 g, 3.1 mmol) in three portions. The reaction mixture was brought to room temperature and stirred for 15 h. Aq. NaOH (1 N, 5.7 mL) was added, and the mixture was vigorously stirred for 15 min at rt. The usual workup (DCM, brine) gave *p*-toluenesulfonate derivatives $\mathbf{S_2}$ in 80% yields as yellowish oil.

To a solution of R^1NH_2 (3.0 mmol, 1.5 eq), the above obtained $\mathbf{S_2}$ (2.0 mmol, 1 eq) and KI (0.2 mmol, 0.1 eq) in DMF (4 mL) was added K_2CO_3 (6.0 mmol, 3 eq). The mixture was heated to 90 °C. After the complete consumption of $\mathbf{S_2}$ (TLC), the reaction mixture was cooled to room

temperature, quenched with a saturated solution of NH_4Cl, extracted with AcOEt three times (3×20 mL), washed with small amounts of water (100 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed in vacuo to afford a residue. The residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (40:1) as eluent to provide the desired compounds **1a-1w** in 35%-80% yields as a yellow oil.

***N*-(3-phenylprop-2-yn-1-yl)aniline (1a).** Yellow oil (397.8 mg, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.42-7.39 (m, 2 H), 7.30-7.28 (m, 3 H), 7.22-7.18 (m, 2 H), 6.75-6.72 (m, 1 H), 6.68-6.66 (m, 2 H), 3.99 (s, 1 H), 3.42-3.38 (m, 2 H), 2.75-2.71 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.7, 131.6, 129.3, 128.3, 127.9, 123.4, 117.8, 113.2, 87.2, 82.3, 42.8, 20.2.

***N*-(4-(*p*-tolyl)but-3-yn-1-yl)aniline (1b).** Yellow oil (458.2 mg, 65% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.31-7.28 (m, 2 H), 7.19-7.15 (m, 2 H), 7.07-7.06 (m, 2 H), 6.73-7.69 (m, 1 H), 6.62-6.60 (m, 2 H), 3.92 (s, 1 H), 3.34-3.30 (m, 2 H), 2.67-2.63 (m, 2 H), 2.30 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.5, 137.8, 131.4, 129.2, 128.9, 120.2, 117.6, 113.0, 86.4, 82.2, 42.6, 21.3, 20.0.

***N*-(4-(3,4-dimethylphenyl)but-3-yn-1-yl)aniline (1c).** Yellow oil (410.9 mg, 55% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.20-7.13 (m, 4 H), 7.05-7.03 (m, 1 H), 6.74-6.70 (m, 1 H), 6.65-6.63 (m, 2 H), 3.96 (s, 1

H), 3.37-3.34 (m, 2 H), 2.70-2.67 (m, 2 H), 2.23 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.7, 136.7, 136.5, 132.6, 129.5, 129.3, 129.0, 120.6, 117.7, 113.1, 86.1, 82.3, 42.7, 20.1, 19.6, 19.5**.**

***N*-(4-(3,5-dimethylphenyl)but-3-yn-1-yl)aniline (1d).** Yellow oil (433.3 mg, 58% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.21-7.16 (m, 2 H), 7.04 (s, 2 H), 6.92 (s, 1 H), 6.75-6.71 (m, 1 H), 6.66-6.64 (d, *J* = 6.0 Hz, 2 H), 3.96 (s, 1 H), 3.37-3.34 (m, 2 H), 2.70-2.67 (m, 2 H), 2.27 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.7, 137.8, 129.8, 129.3, 123.0, 117.7, 113.1, 86.4, 82.5, 42.7, 21.1, 20.1.

***N*-(4-(2-fluorophenyl)but-3-yn-1-yl)aniline (1e).** Yellow oil (487.7 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.40-7.36 (m, 1 H), 7.26-7.17 (m, 3 H), 7.07-7.02 (m, 2 H), 6.75-6.70 (m, 1 H), 6.67-6.65 (m, 2 H), 4.02 (s, 1 H), 3.40-3.37 (m, 2 H), 2.75-2.72 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 162.9 (d, *J* = 249.0 Hz, 1 C), 147.6, 133.4, 129.5 (d, *J* = 8.0 Hz, 1 C), 129.3, 123.8 (d, *J* = 4.0 Hz, 1 C), 117.7, 115.3 (d, *J* = 19.0 Hz, 1 C), 113.1, 111.9 (d, *J* = 16.0 Hz, 1 C), 92.7, 75.6, 42.5, 20.2.

***N*-(4-(3-fluorophenyl)but-3-yn-1-yl)aniline (1f).** Yellow oil (430.2 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.25-7.16 (m, 4 H), 7.11-7.07 (m, 1 H), 7.01-6.96 (m, 1 H), 6.75-6.72 (m, 1 H), 6.66-6.64 (m, 2 H), 3.93 (s, 1 H), 3.39-3.36 (m, 2 H), 2.71-2.68 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 162.3 (d, *J* = 245.0 Hz, 1 C), 147.5, 129.8,

129.3, 127.8, 125.3 (d, J = 10.0 Hz, 1 C), 118.5 (d, J = 30.0 Hz, 1 C), 117.8, 115.2 (d, J = 22.0 Hz, 1 C), 113.1, 88.4, 81.1, 42.5, 20.1.

***N*-(4-(thiophen-2-yl)but-3-yn-1-yl)aniline (1g).** Yellow oil (306.5 mg, 45% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.23-7.16 (m, 4 H), 7.01 (m, 1 H), 6.77-6.58 (m, 3 H), 4.32-4.30 (m, 2 H), 3.93 (s, 1 H), 2.26-2.23 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.6, 132.0, 129.5, 127.8, 127.2, 122.5, 120.9, 113.6, 96.3, 84.0, 50.3, 18.9.

3-methyl-*N*-(4-phenylbut-3-yn-1-yl)aniline (1h). Yellow oil (444.2 mg, 63% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.42-7.39 (m, 2 H), 7.30-7.24 (m, 3 H), 7.11-7.06 (m, 1 H), 6.58-6.56 (d, J = 6.0 Hz, 1 H), 6.49-6.47 (d, J = 6.0 Hz, 2 H), 3.93 (s, 1 H), 3.41-3.36 (m, 2 H), 2.74-2.69 (m, 2 H), 2.29 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.7, 139.1, 131.6, 129.2, 128.2, 127.9, 123.4, 118.7, 113.9, 110.2, 87.2, 82.2, 42.7, 21.6, 20.2.

4-methyl-*N*-(4-phenylbut-3-yn-1-yl)aniline (1i). Yellow oil (472.4 mg, 67% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.42-7.39 (m, 2 H), 7.29-7.26 (m, 3 H), 7.01-6.99 (d, J = 6.0 Hz, 2 H), 6.60-6.57 (m, 2 H), 3.84 (s, 1 H), 3.37-3.33 (m, 2 H), 2.71-2.67 (m, 2 H), 2.24 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 145.3, 131.6, 129.8, 128.2, 127.8, 127.0, 123.4, 113.5, 87.3, 82.1, 43.0, 20.4, 20.1.

4-ethyl-*N*-(4-phenylbut-3-yn-1-yl)aniline (1j). Yellow oil (470.6 mg, 63% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.42-7.39 (m, 2 H),

7.29-7.26 (m, 3 H), 7.04-7.02 (m, 2 H), 6.61-6.59 (m, 2 H), 3.85 (s, 1 H), 3.37-3.33 (m, 2 H), 2.71-2.66 (m, 2 H), 2.58-2.50 (m, 2 H), 1.22-1.16 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 145.5, 133.6, 131.6, 128.6, 128.2, 127.8, 123.4, 113.3, 87.3, 82.1, 43.0, 27.9, 20.1, 16.0.

3,5-dimethyl-*N*-(4-phenylbut-3-yn-1-yl)aniline (1k). Yellow oil (515.4 mg, 69% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.42-7.39 (m, 2 H), 7.30-7.28 (m, 3 H), 6.40 (s, 1 H), 6.30 (s, 2 H), 3.87 (s, 1 H), 3.39-3.35 (m, 2 H), 2.73-2.68 (m, 2 H), 2.22 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.7, 139.0, 131.6, 128.2, 127.8, 123.4, 119.8, 111.1, 87.3, 82.1, 42.7, 21.5, 20.2.

2-fluoro-*N*-(4-phenylbut-3-yn-1-yl)aniline (1l). Yellow oil (351.3 mg, 49% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.42-7.40 (m, 2 H), 7.30-7.28 (m, 3 H), 7.01-6.96 (m, 2 H), 6.78-6.73 (m, 1 H), 6.67-6.62 (m, 1 H), 4.27 (s, 1 H), 3.45-3.41 (m, 2 H), 2.76-2.73 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 153.3 (J = 178.5 Hz, 1 C), 137.8 (d, J = 9.0 Hz, 1 C), 133.2, 129.8, 129.5, 126.1, 124.9, 118.6 (d, J = 6.8 Hz, 1 C), 116.2 (d, J = 13.5 Hz, 1 C), 113.9 (d, J = 3.0 Hz, 1 C), 88.3, 84.0, 43.9, 21.7.

4-chloro-*N*-(4-phenylbut-3-yn-1-yl)aniline (1m). Yellow oil (382.5 mg, 50% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.42-7.38 (m, 2 H), 7.31-7.28 (m, 3 H), 7.15-7.12 (m, 2 H), 6.60-6.55 (m, 2 H), 3.40 (s, 1 H), 3.37-3.33 (m, 2 H), 2.73-2.68 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm):

δ = 146.2, 131.6, 129.1, 128.3, 128.0, 123.3, 122.3, 114.2, 86.8, 82.4, 42.7, 20.0.

***N*-(4-phenylbut-3-yn-1-yl)-[1,1'-biphenyl]-4-amine (1n).** Yellow oil (356.4 mg, 40% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.54-7.52 (d, *J* = 6.0 Hz, 2 H), 7.46-7.36 (m, 6 H), 7.28-7.22 (m, 4 H), 6.71-6.69 (d, *J* = 6.0 Hz, 2 H), 4.03 (s, 1 H), 3.41-3.37 (m, 2 H), 2.72-2.69 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.1, 141.1, 131.6, 130.6, 128.6, 128.2, 127.9, 127.9, 126.2, 126.1, 123.4, 113.3, 87.1, 82.3, 42.7, 20.2.

3-chloro-4-methyl-*N*-(4-phenylbut-3-yn-1-yl)aniline (1o). Yellow oil (339.3 mg, 43% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.41-7.39 (m, 2 H), 7.30-7.28 (m, 3 H), 7.02-7.00 (d, *J* = 6.0 Hz, 1 H), 6.67 (d, *J* = 0.5 Hz, 1 H), 6.49-6.46 (m, 1 H), 3.91 (s, 1 H), 3.36-3.32 (m, 2 H), 2.72-2.68 (m, 2 H), 2.25 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 146.8, 134.9, 131.6, 131.3, 128.3, 127.9, 124.6, 123.3, 113.4, 112.0, 86.9, 82.3, 42.8, 20.1, 18.9.

2-methoxy-*N*-(4-(*p*-tolyl)but-3-yn-1-yl)aniline (1p). Yellow oil (349.8 mg, 44% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.31-7.29 (m, 2 H), 7.09-7.07 (d, *J* = 6.0 Hz, 2 H), 6.90-6.86 (m, 1 H), 6.77-6.75 (m, 1 H), 6.70-6.64 (m, 2 H), 4.57 (s, 1 H), 3.81 (s, 3 H), 3.40-3.37 (m, 2 H), 2.73-2.69 (m, 2 H), 2.32 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 146.9, 137.7, 137.6, 131.4, 128.9, 121.2, 120.4, 116.7, 109.9, 109.5, 86.5, 82.1, 55.3, 42.5, 21.3, 20.1.

***N*-(4-(3,5-dimethylphenyl)but-3-yn-1-yl)-2-methoxyaniline (1q).** Yellow oil (334.8 mg, 40% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.04 (s, 2 H), 6.90-6.86 (m, 2 H), 6.77-6.76 (d, *J* = 3.0 Hz, 1 H), 6.70-6.64 (m, 2 H), 4.57 (s, 1 H), 3.82 (s, 3 H), 3.40-3.37 (m, 2 H), 2.72-2.69 (m, 2 H), 2.26 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 146.9, 137.6, 137.6, 129.6, 129.2, 123.1, 121.2, 116.7, 109.9, 109.5, 86.5, 82.3, 55.3, 42.5, 21.0, 20.1.

4-chloro-*N*-(4-(3,5-dimethylphenyl)but-3-yn-1-yl)aniline (1r). Yellow oil (297.2 mg, 35% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.13-7.11 (m, 2 H), 7.03 (s, 2 H), 6.92 (s, 1 H), 6.56-6.54 (m, 2 H), 4.52 (s, 1 H), 3.33-3.29 (m, 2 H), 2.69-2.65 (m, 2 H), 2.27 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 146.3, 137.8, 129.8, 129.3, 129.0, 122.8, 122.1, 114.1, 86.1, 52.6, 42.7, 21.0, 20.0.

***N*-(but-3-yn-1-yl)aniline (1s).** Yellow oil (355.2 mg, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.18-7.14 (m, 2 H) , 6.73-6.69 (m, 1 H), 6.60-6.58 (m, 2 H), 3.88 (s, l H), 3.27 (m, 1 H), 2.45-2.41 (m, 2 H), 2.05-2.00 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.4, 129.2, 117.7, 113.0, 81.7, 70.0, 42.3, 19.0.

***N*-benzyl-4-phenylbut-3-yn-1-amine (1t).** Yellow oil (493.5 mg, 70% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.40-7.38 (m, 2 H), 7.36-7.31(m, 4 H), 7.29-7.25 (m, 4 H), 3.86 (s, 2 H), 2.89-2.86 (m, 2 H), 2.66-2.62 (m, 2 H), 2.09 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ =

140.0, 131.7, 131.4, 128.6, 128.3, 127.9, 127.5, 123.6, 87.8, 81.8, 53.3, 47.5, 20.5.

***N*-butyl-4-phenylbut-3-yn-1-amine (1u).** Yellow oil (434.2 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.41-7.39 (m, 2 H), 7.28-7.27 (m, 3 H), 2.87-2.84 (m, 2 H), 2.66-2.60 (m, 4 H), 1.71 (s, 1 H), 1.52-1.48 (m, 2 H), 1.39-1.35 (m, 2 H), 0.94-0.91 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 131.8, 128.5, 127.6, 123.8, 88.1, 81.8, 49.2, 48.7, 47.9, 32.3, 20.6, 14.1.

***N*-(4-phenylbut-3-yn-1-yl)cyclohexanamine (1v).** Yellow oil (469.9 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.41-7.38 (m, 2 H), 7.30-7.27 (m, 3 H), 2.90-2.85 (m, 2 H), 2.62-2.58 (m, 2 H), 2.53-2.46 (m, 1 H), 1.92-1.88 (d, *J* = 16.0 Hz, 2 H), 1.76-1.61 (m, 4 H), 1.33-1.07 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 131.5, 128.2, 127.6, 123.6, 88.0, 81.7, 56.2, 45.2, 33.56, 26.1, 25.0, 20.8.

***N*-(4-phenylbut-3-yn-1-yl)octadecan-1-amine (1w).** Yellow oil (547.9 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.42-7.38 (m, 2 H), 7.29-7.26 (m, 3 H), 2.88-2.83 (m, 2 H), 2.68-2.60 (m, 4 H), 1.67 (s, 1 H), 1.51-1.49 (m, 2 H), 1.25 (m, 30 H), 0.89-0.88 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 131.6, 128.2, 127.7, 123.6, 87.9, 81.7, 49.4, 48.2, 31.9, 30.1, 29.7, 29.6, 29.4, 27.3, 22.7, 20.5, 14.1.

***N*-(hept-3-yn-1-yl)aniline (1z).** Yellow oil (415.1 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.19-7.14 (m, 2 H), 6.72-6.68 (m, 1

H), 6.62-6.60 (m, 2 H), 3.91 (s, 1 H), 3.32-3.20 (m, 2 H), 2.47-2.42 (m, 2 H), 2.16-2.11 (m, 2 H), 1.55-1.46 (m, 2 H), 0.99-0.95 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.8, 129.2, 117.5, 113.0, 82.0, 77.2, 42.9, 22.3, 20.7, 19.4, 13.4.

General procedure for the synthesis of 1x-1y[18-19]. For the reaction scheme, see Scheme S2 in the Supporting Information.

A dried round-bottom flask was charged with benzaldehyde (8.0 mmol), the aniline (8.0 mmol), molecular sieves 4Å (1mg /1.0 mmol aldehyde) and dichloromethane. The reaction mixture was stirred at room temperature and traced by TLC until the reaction finished. Then the mixture was filtered and the filtrate was concentrated under reduced pressure, gave the pure imines without additional purification.

An aluminum amalgam was prepared from aluminum powder (0.5 g, 18.0 mmol) and a catalytic amount of mercuric chloride (10 mg) in 7.5 mL anhydrous THF by vigorously stirring at room temperature for 1 h under a N_2 atmosphere. A solution of propargyl bromide (18.0 mmol) in 12.5 mL of anhydrous THF was then slowly added to the suspension at such a rate as to maintain the temperature between 30-40℃. After the addition, the reaction mixture was continued to stir until a dark grey solution was obtained. The generated propargyl aluminum sesquibromide solution was added to a solution of imine (6.0 mmol) in 20.0 mL of anhydrous THF at -78℃ under N_2 atmosphere. The reaction mixture was

stirred at -78℃ for about 1 h, then warmed to room temperature and continue to stir for additional 3-4 h (monitored by TLC). The mixture was quenched by adding saturated NH_4Cl (aq), and extracted with EtOAc (3 ×20 mL), and washed with brine, combined organic extracts, dried over $MgSO_4$, and concentrated in vacuo to give the residue. The residue was purified by flash chromatography over silica gel (gradient elution of EtOAc /petroleum ether, PE : EA = 50 : 1).

***N*-(1-(4-chlorophenyl)-4-phenylbut-3-yn-1-yl)aniline (1x).** Yellow oil (506.4mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.41-7.25 (m, 8 H), 7.14-7.08 (m, 2 H), 6.72-6.67 (m, 2 H), 6.55-6.52 (d, *J* = 12.0 Hz, 2 H), 4.61-4.55 (m, 1 H), 4.48 (s, 1 H), 3.00-2.81 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.8, 140.9, 133.1, 131.6, 129.2, 128.8, 128.3, 128.1, 127.8, 123.0, 118.0, 113.7, 85.1, 56.2, 29.2.

***N*-(1-phenyloct-1-yn-4-yl)aniline (1y).** Yellow solid (482.0 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.40-7.37 (m, 2 H), 7.28-7.25 (m, 3 H), 7.19-7.15 (m, 2 H), 6.71-6.67 (m, 1 H), 6.63-6.61 (m, 2 H), 3.71 (s, 1 H), 3.60-3.57 (m, 1 H), 1.81-1.77 (m, 1 H), 1.66-1.34 (m, 1 H), 1.46-1.34 (m, 4 H), 0.97-0.90 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.3, 131.6, 129.3, 128.2, 127.7, 123.6, 117.3, 113.4, 86.6, 82.7, 51.7, 34.0, 28.4, 24.7, 22.6, 14.0

General procedure for the synthesis of sulfinic acids[20]

Benzenesulfinic acid and *p*-toluenesulfinic acid were obtained by acidification of the commercially available sodium benzenesulfinate and sodium *p*-toluenesulfinate, then the mixture was extracted by Et_2O. After dried by Na_2SO_4, the solvent was removed under vacuum at 0 ^oC to provide pure product. Other arylsulfinic acids, heteroaromatic and aliphatic sulfinic acids were prepared by the following procedures: arylsulfonyl chloride (10 mmol) and anhydrous sodium sulfite (30 mmol) were added into 20 mL of water. The reaction mixture was kept at 70-80 ^oC for 5 h. After the reaction was complete, the mixture was washed with chloroform. The water phase was acidified with excess concentrated HCl solution at 0 ^oC, then extracted by Et_2O. After dried by Na_2SO_4, the organic solvent was removed under vacuum at 0 ^oC to provide pure products.

General procedure for synthesis of substituted sulfonyl pyrroles from alkynylanilines and sulfinic acids:

The alkynylamines **1** (1 equiv, 0.3 mmol), sulfinic acids **2** (2 equiv, 0.6 mmol), TBN (2.2 equiv, 0.66 mmol) (TBN is very toxic and dangerous. Caution!), AcOH (20 mol %, 0.06 mmol) were mixed in DCE (2 mL) were stirred at 100 ^oC under argon atmosphere for 10 h (TLC monitored). Then the reaction mixture was cooled to room temperature and the solvent was evaporated in vacuo, the crude product was purified by

column chromatography, eluting with petroleum ether/EtOAc (10:1) to afford the desired **3**.

1,2-diphenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3aa).

Yellow solid (94.8 mg, 88% yield), melting point: 94-96 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.52-7.50 (d, J = 8.0 Hz, 2 H), 7.41-7.38 (m, 1 H), 7.29-7.17 (m, 8 H), 7.09-7.07 (m, 2 H), 7.02-7.00 (m, 2 H), 6.91-6.89 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.1, 138.6, 135.5, 132.1, 131.4, 129.1, 129.0, 128.6, 128.4, 127.7, 127.6, 127.0, 125.8, 124.1, 122.4, 110.4; HRMS(ESI)*m/z* calcd for $C_{22}H_{18}NO_2S$ $[M+H]^+$ 360.1053; **found**: 360.1046.

1-phenyl-3-(phenylsulfonyl)-2-(*p*-tolyl)-1*H*-pyrrole (3ba).

Yellow solid (76.1 mg, 68% yield), melting point: 106-108 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.55-7.53 (d, J = 6.0 Hz, 2 H), 7.43-7.38 (m, 1 H), 7.30-7.21 (m, 6 H), 7.03-6.97 (m, 5 H), 6.87 (s, 2 H), 2.31 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 143.2, 138.7, 138.4, 135.7, 132.0, 131.4, 131.2, 128.9, 128.4, 127.6, 127.5, 126.9, 125.8, 123.7, 122.3, 110.4, 21.3; HRMS(ESI)*m/z* calcd for $C_{23}H_{20}NO_2S$ $[M+H]^+$ 374.1209; **found**: 374.1217.

2-(3,4-dimethylphenyl)-1-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3ca).

Yellow solid (84.8 mg, 73% yield), melting point: 120-122 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.58-7.55 (m, 2 H), 7.45-7.40 (m, 1 H), 7.32-7.22 (m, 6 H), 7.04-7.01 (m, 1 H), 6.95-6.92 (m, 1 H), 6.89-6.86 (m,

2 H), 6.80 (s, 1 H), 6.76-6.73 (d, J = 9.0 Hz, 1 H), 2.21 (s, 3 H), 2.11 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 143.3, 138.8, 137.1, 136.0, 135.7, 132.4, 132.0, 128.9, 128.7, 128.3, 127.6, 127.5, 127.1, 126.4, 125.9, 123.7, 122.1, 110.4, 19.6, 19.6; HRMS(ESI)*m/z* calcd for $C_{24}H_{22}NO_2S$ $[M+H]^+$ 388.1366; **found**: 388.1376.

2-(3,5-dimethylphenyl)-1-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3da). Yellow solid (90.6 mg, 78% yield), melting point: 123-125 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.57-7.54 (m, 2 H), 7.45-7.40 (m, 1 H), 7.32-7.22 (m, 6 H), 7.04-7.01 (m, 2 H), 6.91-6.86 (m, 3 H), 6.60 (s, 2 H), 2.15 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 143.2, 138.8, 137.0, 135.9, 132.0, 130.2, 129.0, 128.9, 128.3, 127.9, 127.5, 127.2, 125.8, 123.8, 122.0, 110.4, 21.1; HRMS(ESI)*m/z* calcd for $C_{24}H_{22}NO_2S$ $[M+H]^+$ 388.1366; **found**: 388.1360.

2-(2-fluorophenyl)-1-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3ea). Yellow solid (65.6 mg, 58% yield), melting point: 115-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.59-7.56 (m, 2 H), 7.46-7.44 (m, 1 H), 7.42-7.34 (m, 3 H), 7.31-7.23 (m, 4 H), 7.15-7.12 (m, 3 H), 7.10-7.05 (m, 2 H), 6.95-6.76 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.2 (d, J = 247.0 Hz, 1 C), 142.9, 138.5, 134.1, 132.3, 131.4 (d, J = 8.0 Hz, 1 C), 129.4, 129.0, 128.5, 128.0, 126.9, 125.4, 125.0, 123.6 (d, J = 3.0 Hz, 1 C), 123.1, 117.3 (d, J = 16.0 Hz, 1 C), 115.1 (d, J = 20.0 Hz, 1 C), 110.4;

HRMS(ESI)*m/z* calcd for $C_{22}H_{17}FNO_2S$ $[M+H]^+$ 378.0959; **found**: 378.0950.

2-(3-fluorophenyl)-1-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3fa).

Yellow solid (75.8 mg, 67% yield), melting point: 99-101 ^oC. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.58-7.55 (m, 2 H), 7.46-7.40 (m, 1 H), 7.33-7.20 (m, 5 H), 7.18-7.13 (m, 1 H), 7.03-6.94 (m, 3 H), 6.91-6.88 (m, 3 H), 6.79-6.75 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 163.3 (d, J = 327.0 Hz, 1 C), 142.8, 138.3, 133.6, 132.3, 131.1 (d, J = 11.0 Hz, 1 C), 129.2 (d, J = 5.0 Hz, 1 C), 128.5, 127.9, 127.4 (d, J = 4.0 Hz, 1 C), 126.9, 125.7, 124.5, 122.8, 118.5, 118.2, 115.6 (d, J = 7.0 Hz, 1 C), 110.5; HRMS(ESI)*m/z* calcd for $C_{22}H_{17}FNO_2S$ $[M+H]^+$ 378.0959; **found**: 378.0966.

1-phenyl-3-(phenylsulfonyl)-2-(thiophen-2-yl)-1*H*-pyrrole (3ga).

Yellow solid (71.2 mg, 65% yield), melting point: 114-116 ^oC. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.60-7.57 (m, 2 H), 7.46-7.41 (m, 1 H), 7.33-7.27 (m, 6 H), 7.16-7.09 (m, 3 H), 7.00-6.91 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.6, 138.5, 132.4, 132.3, 129.9, 129.0, 129.0, 128.8, 128.5, 128.1, 127.1, 126.6, 126.0, 125.8, 123.2, 110.7; HRMS(ESI)*m/z* calcd for $C_{20}H_{16}NO_2S_2$ $[M+H]^+$ 366.0617; **found**: 366.0623.

2-phenyl-3-(phenylsulfonyl)-1-(*m*-tolyl)-1*H*-pyrrole (3ha).

Yellow solid (95.1 mg, 85% yield), melting point: 114-116 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.52-7.49 (d, *J* = 9.0 Hz, 2 H), 7.42-7.27 (m, 1 H), 7.23-7.17 (m, 5 H), 7.09-7.00 (m, 4 H), 6.90-6.86 (m, 3 H), 6.77-6.75 (d, *J* = 6.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 143.1, 139.1, 138.5, 135.5, 132.1, 131.4, 129.2, 128.7, 128.5, 128.4, 127.9, 127.6, 127.0, 126.4, 123.9, 122.9, 122.3, 110.3, 21.1; HRMS(ESI)*m/z* calcd for $C_{23}H_{20}NO_2S$ $[M+H]^+$ 374.1209; **found**: 374.1213.

2-phenyl-3-(phenylsulfonyl)-1-(*p*-tolyl)-1*H*-pyrrole (3ia).

Yellow solid (100.7 mg, 90% yield), melting point: 116-118 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.52-7.49 (m, 2 H), 7.42-7.37 (m, 1 H), 7.29-7.17 (m, 5 H), 7.09-7.06 (m, 2 H), 7.03-7.00 (d, *J* = 9.0 Hz, 2 H) , 6.90-6.85 (m, 4 H), 2.27 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 142.9, 137.2, 135.5, 133.6, 132.2, 131.4, 129.2, 128.8, 128.4, 127.9, 127.0, 126.8, 124.6, 122.2, 110.7; HRMS(ESI)*m/z* calcd for $C_{23}H_{20}NO_2S$ $[M+H]^+$ 374.1209; **found**: 374.1206.

1-(4-ethylphenyl)-2-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3ja).

Yellow solid (106.8 mg, 92% yield), melting point: 123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.52-7.50 (d, *J* = 8.0 Hz, 2 H), 7.42-7.39 (m, 1 H), 7.29-7.17 (m, 6 H), 7.09-7.02 (m, 4 H), 6.93-6.86 (m, 4 H), 2.61-2.53 (m, 2 H), 1.19-1.14 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.8, 143.1, 136.3, 135.5, 132.1, 131.5, 129.3, 128.5, 128.4, 128.3, 127.6, 127.0, 125.7, 123.8, 122.4, 110.3, 28.2, 15.2;

HRMS(ESI)*m/z* calcd for $C_{24}H_{22}NO_2S$ $[M+H]^+$ 388.1366; **found**: 388.1375.

1-(3,5-dimethylphenyl)-2-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3ka). Yellow solid (101.0 mg, 87% yield), melting point: 131-133 ^oC. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.52-7.49 (m, 2 H), 7.41-7.36 (m, 1 H), 7.30-7.17 (m, 5 H), 7.09-7.06 (m, 2 H), 6.88-6.83 (m, 3 H), 6.61 (s, 2 H), 2.15 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 143.2, 138.7, 138.5, 135.5, 132.0, 131.4, 128.5, 128.3, 127.5, 127.0, 123.7, 123.6, 122.3, 110.2, 21.0; HRMS(ESI)*m/z* calcd for $C_{24}H_{22}NO_2S$ $[M+H]^+$ 388.1366; **found**: 388.1373.

1-(2-fluorophenyl)-2-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3la). Yellow solid (73.5 mg, 65% yield), melting point: 119-121 ^oC. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.01-7.98 (m, 2 H), 7.92-7.90 (m, 4 H), 7.78-7.68 (m, 3 H), 7.62-7.58 (m, 2 H), 7.55-7.51 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 160.2 (d, J = 186.0 Hz, 1 C), 142.9, 138.5, 134.1, 132.3, 131.4 (d, J = 6.8 Hz, 1 C), 129.4, 129.0, 128.5, 128.0, 126.9, 125.5, 125.0, 123.6 (d, J = 3.0 Hz, 1 C), 123.1, 117.3 (d, J = 11.3 Hz, 1 C), 115.1 (d, J = 16.5 Hz, 1 C), 110.4; HRMS(ESI)*m/z* calcd for $C_{22}H_{17}FNO_2S$ $[M+H]^+$ 378.0959; **found**: 378.0950.

1-(4-chlorophenyl)-2-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3ma). Yellow solid (100.2 mg, 85% yield), melting point: 135-137 ^oC. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.51-7.48 (m, 2 H), 7.43-7.38 (m, 1 H),

7.31-7.18 (m, 7 H), 7.08-7.05 (m, 2 H), 6.96-6.90 (m, 3 H), 6.87-6.86 (d, J = 3.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 142.9, 137.2, 135.5, 133.6, 132.2, 131.4, 129.2, 128.8, 128.4, 127.9, 127.0, 126.9, 126.8, 124.6, 122.2, 110.7; HRMS(ESI)*m/z* calcd for $C_{22}H_{17}ClNO_2S$ $[M+H]^+$ 394.0663; **found**: 394.0654.

1-([1,1'-biphenyl]-4-yl)-2-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3na).

Yellow solid (103.1 mg, 79% yield), melting point: 159-161 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.52-7.48 (m, 4 H), 7.45-7.38 (m, 5 H), 7.34-7.28 (m, 1 H), 7.27-7.19 (m, 5 H), 7.13-7.11 (m, 2 H), 7.07-7.05 (d, J = 8.0 Hz, 2 H), 6.93 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.0, 140.4, 139.5, 137.7, 135.4, 132.1, 131.5, 129.1, 128.8, 128.6, 128.4, 127.7, 127.5, 127.0, 126.9, 126.0, 124.2, 122.3, 110.5; HRMS(ESI)*m/z* calcd for $C_{28}H_{22}NO_2S$ $[M+H]^+$ 436.1366; **found**: 436.1374.

1-(3-chloro-4-methylphenyl)-2-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3oa).

Yellow solid (101.3 mg, 83% yield), melting point: 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.50-7.48 (m, 2 H), 7.42-7.38 (m, 1 H), 7.32-7.21 (m, 6 H), 7.09-7.07 (m, 3 H), 7.04-7.02 (d, J = 8.0 Hz, 1 H), 6.90-6.89 (m, 1 H), 6.86-6.85 (m, 1 H), 6.75-6.72 (m, 1 H), 2.28 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.0, 137.3, 135.8, 135.5, 134.5, 132.2, 131.4, 131.0, 128.8, 128.4, 127.8, 127.0, 126.2, 124.4, 124.1,

122.2, 110.6, 19.6; HRMS(ESI)*m/z* calcd for $C_{23}H_{19}ClNO_2S$ $[M+H]^+$ 408.0820; **found**: 408.0811.

1-(2-methoxyphenyl)-3-(phenylsulfonyl)-2-(*p*-tolyl)-1*H*-pyrrole (3pa). Yellow solid (75.0 mg, 62% yield), melting point: 160-162 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.58-7.55 (m, 2 H), 7.42-7.39 (m, 1 H), 7.31-7.19 (m, 4 H), 7.06-7.03 (m, 1 H), 6.95 (s, 3 H), 6.85-6.82 (m, 2 H), 6.80-6.73 (m, 2 H), 3.55 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 154.2, 143.5, 137.4, 136.4, 131.9, 129.9, 129.7, 129.2, 128.8, 128.6, 128.2, 127.6, 127.2, 122.6, 122.4, 120.2, 111.6, 109.8, 55.2, 21.1; HRMS(ESI)*m/z* calcd for $C_{24}H_{22}NO_3S$ $[M+H]^+$ 404.1315; **found**: 404.1307.

2-(3,5-dimethylphenyl)-1-(2-methoxyphenyl)-3-(phenylsulfonyl)-1*H*-pyrrole (3qa). Yellow solid (82.6 mg, 66% yield), melting point: 168-169 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.61-7.58 (m, 2 H), 7.43-7.41 (m, 1 H), 7.37-7.24 (m, 2 H), 7.21-7.19 (d, J = 9.0 Hz, 1 H), 7.04-7.01 (d, J = 6.0 Hz, 1 H), 6.88-6.81 (m, 5 H), 6.79-6.58 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 154.2, 143.5, 137.4, 136.3, 131.9, 129.9, 129.7, 129.2, 128.8, 128.6, 128.2, 127.6, 127.2, 122.6, 122.4, 120.2, 111.6, 109.8, 55.2, 21.1; HRMS(ESI)*m/z* calcd for $C_{25}H_{24}NO_3S$ $[M+H]^+$ 418.1472; **found**: 418.1478.

1-(4-chlorophenyl)-2-(3,5-dimethylphenyl)-3-(phenylsulfonyl)-1*H*-pyrrole (3ra).

Yellow solid (87.1 mg, 69% yield), melting point: 165-167 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.55-7.52 (m, 2 H), 7.46-7.41 (m, 1 H), 7.32-7.30 (m, 2 H), 7.22-7.19 (m, 2 H), 6.98-6.95 (d, *J* = 12.0 Hz, 2 H), 6.91-6.90 (d, *J* = 4.0 Hz, 2 H), 6.84 (s, 1 H), 6.59 (s, 2 H), 2.17 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.1, 137.2, 135.9, 133.6, 132.1, 130.5, 130.2, 129.1, 129.0, 128.3, 127.2, 127.0, 124.3, 121.9, 116.5, 110.6, 21.1; HRMS(ESI)m/z calcd for $C_{24}H_{21}ClNO_2S$ $[M+H]^+$ 422.0976; **found**: 422.0981.

1-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3sa).

Yellow solid (39.1 mg, 46% yield), melting point: 86-88 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.52-7.50 (m, 2 H), 7.41-7.38 (m, 1 H), 7.29-7.24 (m, 1 H), 7.22-7.17 (m, 4 H), 7.09-7.07 (m, d, *J* = 8.0 Hz, 2 H), 7.02-7.00 (m, 1 H), 6.91-6.89 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.1, 138.7, 132.1, 131.5, 129.0, 128.6, 128.4, 127.7, 127.0, 125.9, 124.2, 122.4, 110.5; HRMS(ESI)m/z calcd for $C_{16}H_{14}NO_2S$ $[M+H]^+$ 284.0740; **found**: 284.0736.

1-benzyl-2-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3ta).

Yellow solid (98.5 mg, 88% yield), melting point: 92-94 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.51-7.48 (d, *J* = 9.0 Hz, 2 H), 7.43-7.34 (m, 2 H), 7.32-7.24 (m, 8 H), 7.12-7.09 (d, *J* = 9.0 Hz, 2 H), 6.89-6.87 (m, 2

H), 6.80-6.79 (d, J = 3.0 Hz, 1 H), 6.69-6.68 (d, J = 3.0 Hz, 1 H), 4.81 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 143.5, 136.5, 136.2, 131.2, 129.2, 129.0, 128.7, 128.4, 128.0, 127.9, 127.0, 126.9, 121.0, 110.0, 51.1; HRMS(ESI)m/z calcd for $C_{23}H_{20}NO_2S$ $[M+H]^+$ 374.1209; **found**: 374.1200.

1-butyl-2-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3ua).

Yellow solid (79.3 mg, 78% yield), melting point: 87-89 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.47-7.45 (m, 2 H), 7.43-7.35 (m, 4 H), 7.29-7.25 (m, 2 H), 7.16-7.13 (m, 2 H), 6.76 (d, J = 3.2 Hz, 1 H), 6.70-6.69 (d, J = 4.0 Hz, 1 H), 3.64-3.60 (m, 2 H), 1.53-1.47 (m, 2 H), 1.15-1.12 (m, 2 H), 0.78-0.74 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.5, 135.7, 131.9, 131.2, 129.3, 129.0, 128.4, 128.0, 126.9, 122.1, 120.3, 109.6, 47.1, 33.0, 19.5, 13.4; HRMS(ESI)m/z calcd for $C_{20}H_{22}NO_2S$ $[M+H]^+$ 340.1366; **found**: 340.1374.

1-cyclohexyl-2-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3va)

Yellow solid (82.1 mg, 75% yield) , melting point: 91-92 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.47-7.44 (m, 3 H), 7.42-7.35 (m, 3 H), 7.29-7.25 (m, 2 H), 7.13-7.10 (m, 2 H), 6.77 (s, 2 H), 3.56-3.50 (m, 1 H), 1.85-1.74 (m, 4 H) , 1.61-1.54 (m, 4 H), 1.13-1.11 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 143.5, 135.1, 131.9, 131.0, 129.5, 129.0, 128.3, 128.0, 126.9, 121.6, 116.9, 109.6, 56.0, 34.4, 25.5, 25.0; HRMS(ESI)m/z calcd for $C_{22}H_{24}NO_2S$ $[M+H]^+$ 366.1522; **found**: 366.1518.

1-octadecyl--2-phenyl-3-(phenylsulfonyl)-1*H*-pyrrole (3wa).

Yellow solid (72.4 mg, 45% yield) , melting point: 143-145 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.48-7.34 (m, 6 H), 7.29-7.24 (m, 2 H), 7.16-7.12 (m, 2 H), 6.76-6.68 (m, 2 H), 3.63-3.58 (m, 2 H), 1.54-1.49 (m, 2 H), 1.26-1.10 (m, 30 H), 0.90-0.86 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 143.5, 135.7, 131.9, 131.2, 129.3, 129.0, 138.3, 128.0, 126.9, 122.1, 120.3, 109.5, 47.3, 31.9, 30.9, 30.5, 29.7, 29.5, 29.4, 29.3, 29.2, 28.9, 28.3, 26.3, 22.7, 14.1, 1.0; HRMS(ESI)m/z calcd for $C_{34}H_{50}NO_2S$ $[M+H]^+$ 536.3557; **found**: 536.3560.

1,2-diphenyl-3-(*o*-tolylsulfonyl)-1*H*-pyrrole (3ab).

Yellow solid (75.0 mg, 67% yield). melting point: 115-117 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.48-7.46 (d, J = 6.0 Hz, 1 H), 7.24-7.15 (m, 5 H), 7.10-7.00 (m, 5 H), 6.97-6.90 (m, 5 H), 2.45 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 140.2, 138.6, 137.3, 135.3, 132.3, 131.8, 131.2, 129.0, 128.4, 127.6, 127.5, 125.8, 125.3, 123.8, 121.9, 111.1, 20.1; HRMS(ESI)m/z calcd for $C_{23}H_{20}NO_2S$ $[M+H]^+$ 374.1209; **found**: 374.1205.

1,2-diphenyl-3-tosyl-1*H*-pyrrole (3ac).

Yellow solid (99.6 mg, 89% yield), melting point: 161-163 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.40-7.38 (d, J = 8.0 Hz, 2 H), 7.30-7.26 (m, 1 H), 7.22-7.18 (m, 5 H), 7.11-7.06 (m, 4 H), 7.01-6.99 (m, 2 H), 6.88 (s, 2 H), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.8, 140.3,

138.7, 135.3, 131.5, 129.2, 129.0, 129.0, 128.5, 127.6, 127.6, 127.0, 125.9, 124.5, 122.3, 110.4, 21.4; HRMS(ESI)m/z calcd for $C_{23}H_{20}NO_2S$ $[M+H]^+$ 374.1209; **found**: 374.1216.

3-((4-methoxyphenyl)sulfonyl)-1,2-diphenyl-1*H*-pyrrole (3ad).

Yellow solid (109.7mg, 94% yield), melting point: 149-151 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.45-7.43 (m, 2 H), 7.42-7.40 (m, 1 H), 7.25-7.20 (m, 4 H), 7.12-7.08 (m, 2 H), 7.02-6.99 (m, 2 H), 6.88 (s, 2 H), 6.75-6.70 (m, 2 H), 3.77 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 162.4, 138.7, 135.0, 134.9, 131.5, 129.2, 129.1, 128.9, 128.5, 127.6, 127.6, 125.8, 124.8, 122.2, 113.5, 110.2, 55.5; HRMS(ESI)m/z calcd for $C_{23}H_{20}NO_3S$ $[M+H]^+$ 390.1159; **found**: 390.1168.

1,2-diphenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)-1*H*-pyrrole (3ae).

Yellow solid (110.2 mg, 86% yield). melting point: 105-107 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.45-7.41 (m, 1 H), 7.37-7.32 (m, 2 H), 7.28-7.24 (m, 6 H), 7.12-6.98 (m, 5 H), 6.93-6.90 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 161.8, 158.5, 139.9, 139.9, 138.4, 135.7, 131.4, 130.1, 129.1, 129.0, 127.9, 127.8, 127.4, 125.8, 122.5, 116.7-116.3 (d, J = 3.0 Hz, 1 C), 110.3; HRMS(ESI)m/z calcd for $C_{23}H_{17}F_3NO_2S$ $[M+H]^+$ 428.0927; **found**: 428.0920.

1,2-diphenyl-3-((4-(trifluoromethoxy)phenyl)sulfonyl)-1*H*-pyrrole (3af).

Yellow solid (106.3 mg, 80% yield). melting point: 291-292 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.51-7.48 (d, *J* = 9.0 Hz, 2 H), 7.24-7.17 (m, 6 H), 7.07-7.01 (m, 6 H), 6.92 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 151.7, 141.3, 138.5, 135.6, 131.4, 129.3, 129.2, 129.0, 129.0, 128.8, 127.8, 125.8, 123.8, 122.5, 120.3, 110.3, 77.2; HRMS(ESI)m/z calcd for $C_{23}H_{17}F_3NO_3S$ $[M+H]^+$ 444.0876; **found**: 444.0878.

3-((4-chlorophenyl)sulfonyl)-1,2-diphenyl-1*H*-pyrrole (3ag).

Yellow solid (108.5 mg, 92% yield). melting point: 144-146 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.41-7.38 (m, *J* = 9.0 Hz, 2 H), 7.33-7.20 (m, 8 H), 7.19 (m, 2 H), 7.10-7.00 (m, 2 H), 6.90 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 141.6, 138.6, 138.6, 135.6, 131.5, 129.0, 128.8, 128.6, 128.5, 127.8, 125.8, 123.8, 122.5, 110.4; HRMS(ESI)m/z calcd for $C_{22}H_{17}ClNO_2S$ $[M+H]^+$ 394.0663; **found**: 394.0669.

3-((3-chloro-4-fluorophenyl)sulfonyl)-1,2-diphenyl-1*H*-pyrrole (3ah).

Yellow solid (98.6 mg, 80% yield). melting point: 131-133 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.60-7.57 (d, *J* = 9.0 Hz, 2 H), 7.52-7.49 (d, *J* = 9.0 Hz, 2 H), 7.33-7.30 (m, 1 H), 7.24-7.21 (m, 4 H), 7.08-7.00 (m, 4 H), 6.92 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 146.4, 138.4, 136.0, 133.9, 133.5, 131.4, 129.1, 128.9, 128.5, 127.8, 127.5, 125.8, 125.5, 125.4, 123.2, 122.7, 110.5; HRMS(ESI)m/z calcd for $C_{22}H_{16}ClFNO_2S$ $[M+H]^+$ 412.0569; **found**: 412.0565.

4-((1,2-diphenyl-1*H*-pyrrol-3-yl)sulfonyl)benzonitrile (3ai).

Yellow solid (94.5 mg, 82% yield). melting point: 172-174 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.53 (m, 3 H), 7.34-7.29 (m, 1 H), 7.25-7.19 (m, 5 H), 7.07-7.00 (m, 4 H), 6.94-6.91 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 147.0, 138.3, 136.12, 132.2, 131.4, 129.3, 129.1, 129.0, 127.9, 127.9, 127.6, 125.8, 122.9, 117.4, 115.7, 110.5; HRMS(ESI)m/z calcd for $C_{23}H_{17}N_2O_2S$ $[M+H]^+$ 385.1005; **found**: 385.1010.

1,2-diphenyl-3-(thiophen-2-ylsulfonyl)-1*H*-pyrrole (3aj).

Yellow solid (86.5 mg, 79% yield). melting point: 106-108 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.44-7.41 (m, 1 H), 7.30-7.25 (m, 6 H), 7.24-7.21 (m, 1 H), 7.21-7.20 (d, *J* = 3.0 Hz, 2 H), 7.18-7.13 (m, 2 H), 7.05-7.02 (m, 2 H), 6.90-6.83 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 144.9. 138.6, 135.5, 132.1, 131.9, 131.5, 129.0, 128.7, 127.8, 127.7, 126.9, 125.9, 124.5, 122.4, 110.2; HRMS(ESI)m/z calcd for $C_{20}H_{16}NO_2S_2$ $[M+H]^+$ 366.0617; **found**: 366.0620.

2-(3,5-dimethylphenyl)-1-(*p*-tolyl)-3-tosyl-1*H*-pyrrole (3ak).

Yellow solid (89.6 mg, 72% yield). melting point: 189-190 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.44-7.42 (d, *J* = 8.0 Hz, 2 H), 7.10-7.08 (d, *J* = 8.0 Hz, 2 H), 7.02-7.00 (d, *J* = 8.0 Hz, 2 H), 6.90-6.85 (m, 4 H), 6.81 (m, 1 H), 6.60 (s, 2 H), 2.34 (s, 3 H), 2.27 (s, 3 H), 2.16 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.6, 140.6, 137.4, 136.9, 136.4, 135.8, 130.1, 129.4, 129.1, 128.9, 127.3, 125.6, 124.0, 122.0, 110.1, 21.4,

21.1, 20.9; HRMS(ESI)m/z calcd for $C_{26}H_{26}NO_2S$ $[M+H]^+$ 416.1679; **found**: 416.1670.

2,6-di-*tert*-butyl-4-methyl-4-(phenylsulfonyl)cyclohexa-2,5-dienone (4).

White solid (62.6 mg, 58% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.66-7.64 (d, J = 6.0 Hz, 2 H), 7.57-7.55 (d, J = 6.0 Hz, 1 H), 7.43-7.38 (m, 2 H), 6.66 (s, 2 H), 1.83 (s, 3 H), 1.10 (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 183.6, 151.3, 135.5, 134.1, 133.4, 130.2, 128.2, 65.8, 35.2, 28.9, 18.4; HRMS(ESI)m/z calcd for $C_{21}H_{29}O_3S$ $[M+H]^+$ 361.1832; **found**: 361.1825.

Supporting Information The X-ray data for **3ab**, **4** (CIF) and NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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