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Graphical Abstract

C-S and C-N Bond Formation via Mn-Promoted Oxidative Cascade Reaction: Synthesis of C3-Sulfenated Indoles

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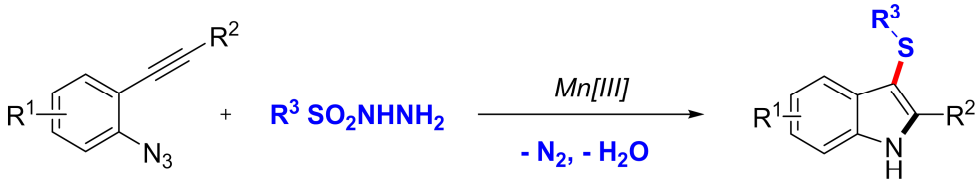

R^1, R^2 = Aryl, heterocryl, alkyl

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ABSTRACT

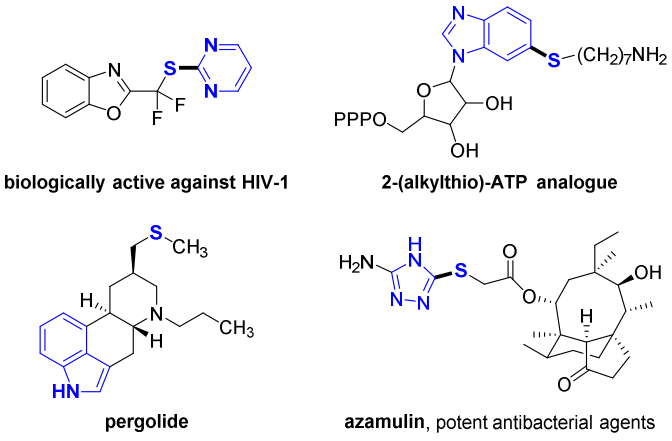
Thioethers are of synthetic value in pharmaceutical molecules and nature products, herein, we report an oxidative cascade reaction that delivers multiple substituted indole thioethers with great efficiency. This transformation utilized *ortho*-azido aromatic alkynes as the substrates, and sulfonyl hydrazides as the sulfenation reagent promoted by Mn(III) catalyst. Notably, great functional group tolerance, in combination with nitrogen and water as the byproducts, highlighted the sustainable chemistry of this protocol.

1. Introduction

To control the synthesis of architecturally complex molecules through catalysis is a key aspect in modern drug discovery.[1] Cascade reaction provides an efficient platform for the rapidly increase the molecular complexity of simple substrates via quick construction of multiple chemical bonds that delivers valuable molecules.[2,3] In this context, radical addition to unsaturated C-C bonds initiated cascade reactions[4] have received much attention due to their synthetic application in complex molecules. These transformations hold the advantages as follows: 1) multiple chemical bonds were formed in one-pot manner; 2) regio- and stereoselectivity were observed to highlight the synthetic potential for the rapid access to complex molecules, thus these concepts are accordance with requirments of green chemistry in modern organic chemistry.

The construction of C-S bond with great efficiency has been a long-standing endeavor of chemical community,[5] since thioether and their derived functionalities are of enormous utility in material science and drug discovery.[6] For instance, several drug candidates listed in **Scheme 1** contained thioether key moiety. For example, pergolide,[7] which has been showed activity against at the postsynaptic dopamine receptor and served as medicine to treat of Parkinson's disease, contained indole-derived thiother key structural moiety.

Despite the synthetic power of C-S bond in organic synthesis, due to the strong coordination ability of sulfur to metal center, the choice of metal catalysts in combination of sulfenation reagents is crucial to realize catalytic C-S bond formation.[8] C3-sulfenated indoles hold great synthetic utility in various areas across pharmaceutical, material area and serve as versatile building block in organic synthesis. Towards this goal, much efforts have been exploited in this research field toward expedient access to their derivatives. General methods[8] to afford these molecules include: 1) nucleophlic substitution of halogen derived indoles with aryl thiphenol derivatives; 2) transition-metal catalyzed cross-couplings as well as C-H bond fucntionalization of indoles with various sulfenation reagents.



Scheme 1. Thioether-containing bioactive molecules.

Considering the overall efficiency and sustainable chemistry of the transformations, great advancements have been achieved by using various types of sulfenation reagents,[9] such as aryl thiol, disulfide, 1-(thio)-1*H*-pyrrole-2,5-dione derivatives, sulfinic acid and its sodium salt, sulfonyl hydrazides, et. al. In combination of different types of radical acceptor, chemists have realized various structurally diverse sulfur-containing complex molecules.

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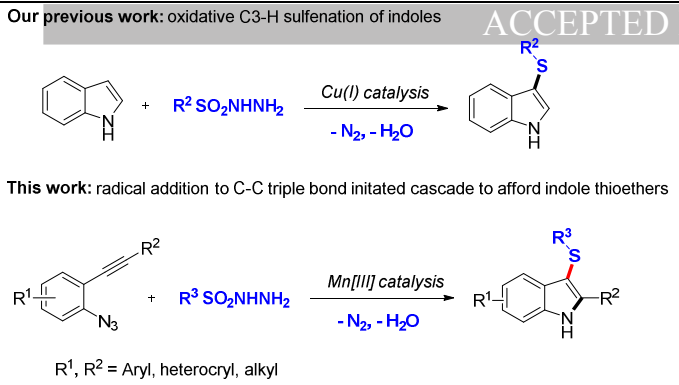


Scheme 2. Synthesis of C3-thioether with sulfonyl hydrazide via transition metal catalysis.

Recently, we have achieved copper-catalyzed direct oxidative functionalization of indoles with aryl sulfonyl hydrazines as the sulfenation reagent.[8e] In this reaction, cheap metal catalyst in combination with molecular oxygen as the green oxidant made this protocol applicable in direct synthesis as well as late-stage modification of sulfur-containing pharmaceuticals.

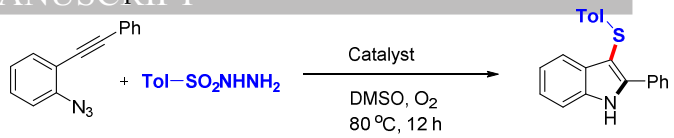
Nevertheless, the scope of thioether substrates was usually limited and the reaction conditions were relatively harsh. Therefore, the development of versatile and efficient methods for constructing different useful skeletons bearing thioether group under mild conditions is highly desirable. On our continuous research interest in the development of aerobic oxidative transformations[10] that enable quick access to valuable molecules, herein, we report a radical addition to C-C multiple bond initiated cascade reaction, delivering C3-sulfenated indole derivatives. Compared to our previous results, this oxidative difunctionalizations of alkynes[11] deliver highly substituted indole-substituted thioethers, and afford structurally divergent products from easily accessible starting materials. More significantly, this methodology builds fundament for the further research on intermolecular aminosulfenation of alkynes, of which, the obtained products are of great value as synthetic intermediates.

2. Results and Discussion

Reactions design. Considering the synthetic utilities of highly substituted sulfonated indoles, as well as the limited methods toward these molecules, efficient methodologies are highly desirable. Since *Ortho*-azido aromatic alkynes and alkenes serve as important synthetic intermediates for constructing important bioactive small molecules.[4b,12] We speculated that employing Ortho-azido aromatic alkynes to a catalytic system than enable the radical addition initiated the cascade reaction, the desired sulfenated indole products could be obtained under relative mild conditions.

To commence our research, we selected 1-azido-2-(phenyl-ethynyl)benzene (**1a**, 0.2 mmol) as the substrate, and 4-methylbenzenesulfonohydrazide **2a** as the sulfenation reagent under oxidation conditions. Previous work has demonstrated that azides might both act as precursors of metal carbenoids and nitrogen centered radical,[13] thus, the choice of metal catalyst might be crucial for these transformations. Moreover, due to the rich chemistry of C-C triple bond, et. al. while difunctionalization of alkynes with nucleophiles and electrophiles have been developed as state-of-art,[14] radical addition of C-C triple bonds initiated cascade reaction remained a hot topic arena for the rapid construction of multiple functionalized molecules.

Table 1. Optimization of reaction conditions. [a]



1a 2a 3a

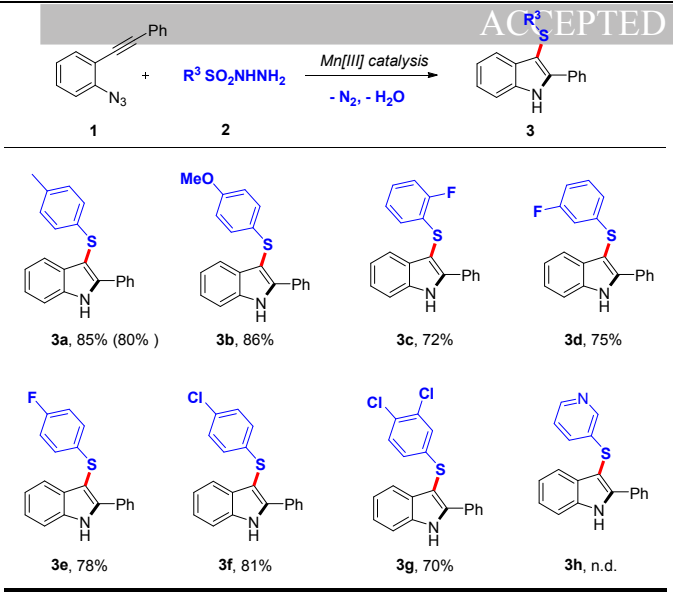
Entry	Catalyst	Additive	Ligand	Yield[b] (%)
1	CuI	-	-	20
2	$Cu(OAc)_2$	-	-	11
2	$FeCl_3$	-	-	26
3	$FeCl_2$	-	-	15
4	$Rh_2(OAc)_4$	-	-	n.d.
5	$Pd(OAc)_2$	-	-	n.d.
6	$AgNO_3$	-	-	n.d.
7	$Mn(OAc)_3$	-	-	44
8	$Mn(OAc)_3$	K_2CO_3	-	49
9	$Mn(OAc)_3$	LiBr	-	57
10	$Mn(OAc)_3$	K_3PO_4	-	52
11	$Mn(OAc)_3$	TBAF	-	31
12	$Mn(OAc)_3$	LiBr	-	64
13	$Mn(OAc)_3$	LiBr	DABCO	72
14	$Mn(OAc)_3$	LiBr	1,10-phen	87 (85)
15	$Mn(OAc)_3$	LiBr	Bpy	68
16	$Mn(OAc)_3$	LiBr	DBU	67
17[c]	$Mn(OAc)_3$	LiBr	1,10-phen	trace
18[d]	$Mn(OAc)_3$	LiBr	1,10-phen	35

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), catalyst (10 mol%) , additive (10 mol%), ligand (10 mol%) were stirred at 80 °C under oxygen atmosphere for 12 hours. [b] GC yield with biphenyl as the internal standard. Yield in the parenthesis was determined after flash column chromatography. [c] HOAc as the solvent. [d] DMF as the solvent.

Fig. 1 Optimization of reaction conditions. [a]

Quick solvent screening revealed that only solvents DMF or DMSO led to a noticeable conversion. As shown in Table 1, various metal catalysts were tested, $Mn(OAc)_3$ was identified to be the most efficient catalyst for the C3-sulfenation reaction, furnishing the desired C3-thioether indole **3a** in 44% yield. Other metal catalysts such as Ag(I), Fe(III), or Cu(II) complexes, which could work as one-electron oxidants,[15] were not viable for this transformation, the deleterious side reaction is indole product without sulfenation reaction. Further investigations of the reaction parameters indicated that both additive and solvent play critical roles in this transformation. Addition of base additive, such as K_2CO_3 was beneficial for this transformation, while LiBr additive led to practical yield, and the desired C3-thioether **3a** was obtained in 64% GC yield. Dinitrogens ligand were found to accelerate this reaction, and 1,10-phen was critical to maintaining high yields, as well as suppressing the decomposition of alkyne substrate **1a**.

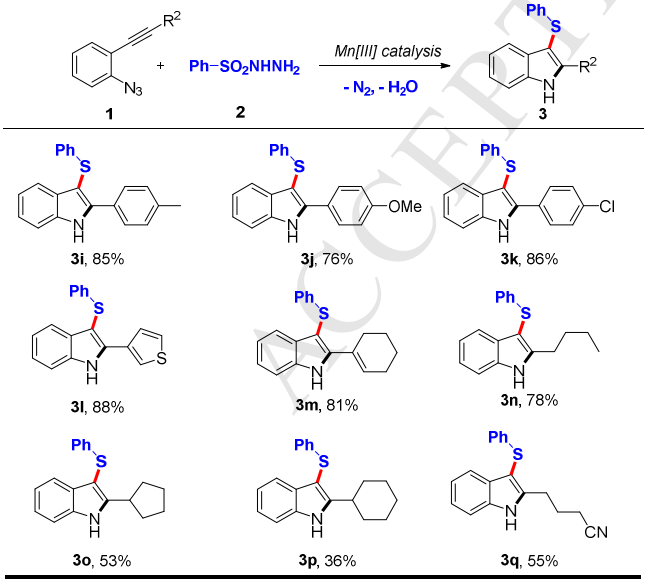
With the optimal condition in hand, we further explored the generality of this oxidative cascade reaction. Various substituted sulfonyl hydrazides were tested, as summarized in **Scheme 3**.



[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), $Mn(OAc)_3$ (10 mol%), LiBr (10 mol%), 1,10-phen (10 mol%) in DMSO under 1 atm oxygen atmosphere at 80 °C for 12 h. Yields referred to isolated yields. Yield in the parenthesis refers to 3 mmol scale transformation.

Scheme 3. Mn(III)-promoted thioamination of alkynes to C3-thioether indoles[a]

Electron-donating substituted **2** showed better performance than that of electron-withdrawing phenyl substrates. Fluoro and trifluoro methyl groups, which were widely used in medicinal and material functionality showed good reactivity in this transformation, delivering the desired C3-sulfenated indoles in good yields (**3c**, **3d**, **3e**). Steric demand aryl sulfonyl hydrazide led to the decreased yield (**3c**). Moreover, halogen functional groups were well tolerated (**3f**, **3g**), holding the synthetic potential for the further decoration via cross-coupling reactions. To our disappointment, nitrogen heterocycle, such as pyridine-derived sulfonyl hydrazide was not tolerated in this reaction.



Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), $Mn(OAc)_3$ (10 mol%), LiBr (10 mol%), 1,10-phen (10 mol%) in DMSO under 1 atm oxygen atmosphere at 80 °C for 12 h. Yields referred to isolated yields.

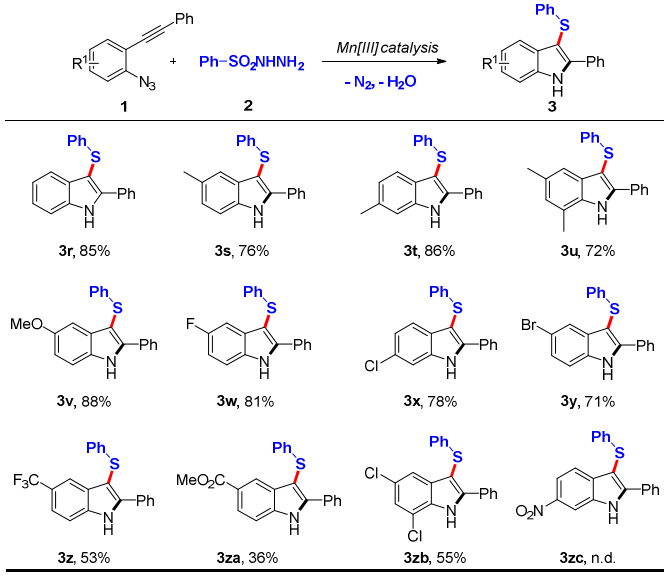
Scheme 4. Mn(III)-promoted thioamination of alkynes to C3-thioether indoles[a]

We next explored functional groups compatility towards *ortho* azido alkynes in this transformation, and the results were depicted in **Scheme 4**. Both aryl and aliphatic substituted phenyl alkynes exhibited good efficiency in this cascade reaction. Methyl, methoxyl and chloro-substituted diaryl alkynes (**3i**, **3j**, **3k**) were suitable platforms in this regioselective difucntionalization reaction. Moreover, heterocycles, such as thiophene-derived alkynes showed great practicality (**3l**).

Great chemoselectivity towards alkynes was also exhibited in this transformation, when both alkene and alkyne functionality existed in the substrate **1m**, and this reaction took place only at C-C triple bond with C-C double bond inert. Both linear and cyclic aliphatic alkyl-aryl alkynes gave the desired C3-thioether indoles in high yields (**3n**, **3o**, **3p**). Significantly, cyan-derived substrate **1q** could also give the desired thioether product with CN available for further modification.

To further demonstrate the synthetic generality of this reaction, we investigate the substrate generality as to substituents on aryl ring of alkynes. As summarized in **Scheme 5**, this reaction was not sensitive to steric hindance as well as electron effect. C5, C6-substituted as well as disubstituted methyl group was well tolerated (**3s**, **3t**, **3u**). Functional groups, such as methoxyl (**3v**), fluoro (**3w**), chloro (**3x**), bromo (**3y**) and trifluoromethyl (**3z**) showed good efficiency in delivering C3-thioether indoles. The compatibility of halogen functionality holds synthetic potential for further decoration for rapid access to complex molecules constructions. Ester group as a versatile functionality was also compatible (**3za**), leaving room for further modification to give more functionalized indole derivatives. However, no desired product was detected with nitro group on aryl ring (**3zc**).

Notably, compared to our previous studies on Cu(I)-catalyzed oxidative functionalization of indoles, this cascade reaction has tremendously expanded the synthetic utility in delivering multiple functionalized thioether indole derivatives.



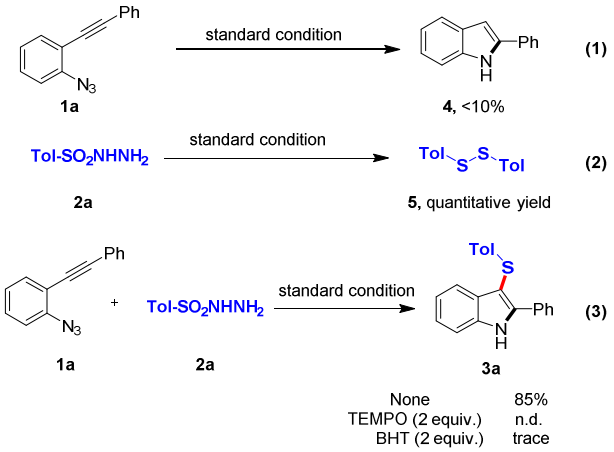
[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), $Mn(OAc)_3$ (10 mol%), LiBr (10 mol%), 1,10-phen (10 mol%) in DMSO under 1 atm oxygen atmosphere at 80 °C for 12 h. Reaction was monitored by TLC for the completion of the reaction. Yields referred to isolated yields.

Scheme 5. Mn(III)-promoted thioamination of alkynes to give C3-thioether indoles[a]

Plausible Reaction Mechanism. To gain more insight into the mechanism of this reaction, several control experiments were performed (Scheme 6). Exposure of **1a** alone to the standard

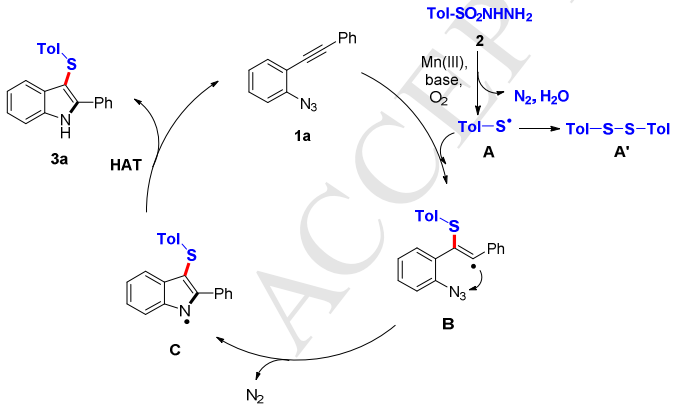
reaction condition, the cyclization product indole **4** could be obtained in low efficiency (eq. 1); Disulfide **5** was generated in quantitative yield with **2a** in this catalytic oxidative condition (eq. 2). These controlled experiments revealed that sulfenyl radical might be generated in this transformation. More significantly, sulfenyl radical addition to the C-C triple facilitated the subsequent cyclization reaction.

When the radical scavenger TEMPO (2 equiv) or BHT (2 equiv) was added under the standard conditions, the yield of product **3a** declined obviously, indicating the transformation should proceed via a free-radical pathway (eq. 3).



Scheme 6. Control experiments

On the basis of these results, a possible mechanism is proposed in **Scheme 7**.[16,17] In this scenario, one-electron oxidation of sulfonyl hydrazide **2** by higher-oxidation-state Mn^{III} catalyst with the assistance of base and molecular oxygen would provide the corresponding sulfide radical species **A**,[18] which may undergo addition to C-C triple bond, delivering the sulfide substituted alkenyl radical intermediate **B**. Subsequent release of N_2 of **B** with an azido moiety affords the *N*-centered radical species **C**, which further undergoes hydrogen-atom abstraction to deliver the desired product **3**. Notably, disulfide **A'**, which might be generated from the oxidative coupling of the sulfide radical **A**, was also detected as side product in this catalytic system.



Scheme 7 A plausible reaction mechanism

3. Conclusion

In summary, we have developed an efficient method of Mn(III)-catalyzed cascade reaction that affords multiple functionalized thioether indole derivatives. This transformation involved sulfide radical generation induced by Mn(III) catalyst and oxygen oxidant, addition to unsaturated C-C bond, nitrogen radical generation from the corresponding azido moiety and indole formation process. Notably, the features that nitrogen and water as the byproducts, mild conditions and great functional compatibility, which might find utility for further elaboration of medicinal molecules as well as natural products. Future work for the further development of radical initiated cascade reactions would be the central of our research topic.

4. Experimental Section

4.1. General Methods. Melting points were measured with a BÜCHI B-545 melting point instrument and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Elemental analyses were performed with a Vario EL elemental analyzer. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. High-resolution mass spectra were obtained with Shimadazu LCMS-IT-TOF mass spectrometer. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. Other reagents were purchased as reagent grade and used without further purification.

4.2. General Procedure for the Synthesis of C3-thioether indoles 3. A mixture of alkynes **1** (0.5 mmol), **2** (0.6 mmol), $Mn(OAc)_3$ (23 mg, 20 mol%), LiBr (10 mol%), 1,10-phen (10 mol%) in DMSO under 1 atm oxygen atmosphere in a test tube (15 mL) equipped with a magnetic stirring bar. The mixture was stirred at 80 ^{o}C for given time. After the reaction was completed, 10 mL ethyl acetate (3×10 mL) was added into the tube. The combined organic layers were washed with brine to neutral, dried over $MgSO_4$, and concentrated in vacuum. Purification of the residue on a preparative TLC afforded the desired products.

*4.2.1. 2-Phenyl-3-(p-tolylthio)-1H-indole (**3a**):* Yield: 88% (55.4 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.73 (d, J = 7.6 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.46-7.32 (m, 4H), 7.24 (t, J = 7.6 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 6.97 (dd, J = 19.6, 8.0 Hz, 4H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 135.8, 135.6, 134.4, 131.5, 131.3, 129.7, 128.8, 128.7, 128.2, 125.8, 123.3, 121.2, 120.1, 111.2, 99.9, 20.9 ppm; ν_{max}(KBr)/cm^{-1} 3328, 2926, 1621, 1438, 1408, 686; MS (EI) m/z 121, 165, 223, 267, 283, 315; HRMS-ESI (m/z): calcd for $C_{21}H_{17}NNaS$, $[M+Na]^+$: 338.0974, found 338.0979.

*3-((4-Methoxyphenyl)thio)-2-phenyl-1H-indole (**3b**)*: Yield: 80% (53.0 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.75 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.49 - 7.33 (m, 4H), 7.23 (d, J = 6.4 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 141.6, 135.8, 131.6, 131.2, 129.8, 128.7, 128.6, 128.2, 127.8, 123.3, 121.1, 120.0, 114.6, 111.2, 100.9, 55.3 ppm; ν_{max}(KBr)/cm^{-1} 3335, 2906, 1628, 1429, 1405, 686; MS (EI) m/z 139, 155, 207, 281, 310, 331; HRMS-ESI (m/z): calcd for $C_{21}H_{17}NNaOS$, $[M+Na]^+$: 354.0923, found 354.0929.

*3-((2-Fluorophenyl)thio)-2-phenyl-1H-indole (**3c**):* Yield: 79% (50.4 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.70 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.37 (dt, J = 14.2, 7.2 Hz, 4H), 7.25 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.05 - 6.93 (m, 2H), 6.79 (dd, J = 9.6, 6.0 Hz, 1H), 6.71 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, J_{C-F} = 242.0 Hz), 142.6, 135.9, 131.2, 131.1, 128.9, 128.2, 127.4 (d, J_{C-F} = 2.5 Hz), 126.5, 126.4, 126.0 (d, J_{C-F} = 7.2 Hz), 124.5 (d, J_{C-F} = 3.2 Hz), 123.5, 121.3,

119.9, 115.1 (d, J_{C-F} = 20.8 Hz), 111.3, 97.1 ppm; ν_{max}(KBr)/cm^{-1} 3341, 2920, 1635, 1437, 1324, 689; MS (EI) m/z 121, 165, 196, 287, 319; HRMS-ESI (m/z): calcd for $C_{20}H_{14}FNNaS$, $[M+Na]^+$: 342.0723, found 342.0729.

*3-((3-Fluorophenyl)thio)-2-phenyl-1H-indole (**3d**):* Yield: 80% (51.0 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.48 - 7.32 (m, 4H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = 14.2, 7.6 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.72 (dd, J = 15.6, 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J_{C-F} = 245.8 Hz), 142.3, 142.0 (d, J_{C-F} = 7.3 Hz), 135.9, 131.2, 130.9, 130.1 (d, J_{C-F} = 8.5 Hz), 128.9, 128.8, 128.1, 123.6, 121.4, 121.1 (d, J_{C-F} = 2.8 Hz), 119.8, 112.4 (d, J_{C-F} = 23.9 Hz), 111.6 (d, J_{C-F} = 21.4 Hz), 111.3, 98.6 ppm; ν_{max}(KBr)/cm^{-1} 3336, 2934, 1627, 1442, 1324, 686; MS (EI) m/z 121, 165, 196, 242, 287, 319; HRMS-ESI (m/z): calcd for $C_{20}H_{14}FNNaS$, $[M+Na]^+$: 342.0723, found 342.0729.

*3-((4-Fluorophenyl)thio)-2-phenyl-1H-indole (**3e**):* Yield: 80% (51.0 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.39 (dq, *J* = 14.4, 7.2 Hz, 4H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.04 (dd, *J* = 8.8, 5.2 Hz, 2H), 6.84 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, J_{C-F} = 242.2 Hz), 141.9, 135.8, 134.1 (d, J_{C-F} = 3.0 Hz), 131.4, 131.0, 128.9, 128.8, 128.2, 127.5 (d, J_{C-F} = 7.7 Hz), 123.5, 121.3, 119.8, 116.6 (d, J_{C-F} = 21.9 Hz), 111.3, 99.9 ppm; ν_{max}(KBr)/cm^{-1} 3324, 2920, 1625, 1441, 1327, 686; MS (EI) m/z 121, 165, 196, 223, 287, 319; HRMS-ESI (m/z): calcd for $C_{20}H_{14}FNNaS$, $[M+Na]^+$: 342.0723, found 342.0726.

*3-((4-Chlorophenyl)thio)-2-phenyl-1H-indole (**3f**):* Yield: 73% (48.9 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.47 - 7.34 (m, 4H), 7.27 - 7.21 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 137.9, 135.9, 131.3, 130.9, 130.4, 128.9, 128.8, 128.6, 128.1, 126.8, 123.5, 121.4, 119.8, 111.3, 99.0 ppm; ν_{max}(KBr)/cm^{-1} 3327, 2930, 1625, 1446, 1321, 676; MS (EI) m/z 121, 150, 223, 267, 303, 335; HRMS-ESI (m/z): calcd for $C_{20}H_{14}ClNNaS$, $[M+Na]^+$: 358.0428, found 358.0432.

*3-((3,4-Dichlorophenyl)thio)-2-phenyl-1H-indole (**3g**):* Yield: 71% (52.4 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.50 - 7.36 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.24 - 7.19 (m, 1H), 7.02 (s, 1H), 6.92 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.6, 135.9, 135.3, 131.0, 130.7, 129.1, 128.9, 128.1, 124.9, 123.7, 123.4, 121.6, 119.6, 111.4, 97.4 ppm; ν_{max}(KBr)/cm^{-1} 3324, 2926, 1621, 1436, 1324, 679; MS (EI) m/z 107, 142, 177, 286, 321, 369; HRMS-ESI (m/z): calcd for $C_{20}H_{13}Cl_2NNaS$, $[M+Na]^+$: 392.0038, found 392.0042.

*3-(Phenylthio)-2-(p-tolyl)-1H-indole (**3i**):* Yield: 89% (56.1 mg) , yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.61 (d, *J* = 7.2 Hz, 3H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 9.2 Hz, 3H), 7.16 - 7.06 (m, 5H), 7.01 (t, *J* = 6.4 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 139.4, 138.8, 135.8, 131.3, 129.5, 128.8, 128.6, 128.0, 125.6, 124.6, 123.2, 121.1, 119.9, 111.1, 99.0, 21.4 ppm; ν_{max}(KBr)/cm^{-1} 3033, 2931, 1620, 1460, 1406, 1014, 689; MS (EI) m/z 121, 150, 204, 238, 267, 283, 315; HRMS-ESI (m/z): calcd for $C_{21}H_{17}NNaS$, $[M+Na]^+$: 338.0974, found 338.0973.

*2-(4-Methoxyphenyl)-3-(phenylthio)-1H-indole (**3j**):* Yield: 83% (54.9 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.71 - 7.56 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.19 - 7.04 (m, 5H), 7.02 (t, *J* = 6.8 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 142.2, 139.5, 135.8, 131.4, 129.5, 128.9, 125.6, 124.6, 123.9, 123.1, 121.1, 119.8, 114.3, 111.1, 98.4, 55.4 ppm; ν_{max}(KBr)/cm^{-1} 3031, 2925, 1628, 1435, 1021, 686; MS (EI) m/z 120, 165, 223, 254, 299, 316, 331; HRMS-ESI (m/z): calcd for $C_{21}H_{17}NNaOS$, $[M+Na]^+$: 354.0923, found 354.0926.

*2-(4-Chlorophenyl)-3-(phenylthio)-1H-indole (**3k**):* Yield: 80% (53.6 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.64 (dd, *J* = 15.2, 7.6 Hz, 3H), 7.40 (dd, *J* = 17.0, 8.0 Hz, 3H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 14.2, 7.2 Hz, 3H), 7.05 (dd, *J* = 14.8, 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 138.9, 135.9, 134.8, 131.2, 129.9, 129.3, 129.0, 128.9, 125.6, 124.8, 123.7, 121.4, 120.1, 111.2, 100.2 ppm; ν_{max}(KBr)/cm^{-1} 3327, 2923, 1624, 1448, 1320, 688; MS (EI) m/z 121, 150, 190, 223, 267, 303, 335; HRMS-ESI (m/z): calcd for $C_{20}H_{14}ClNNaS$, $[M+Na]^+$: 358.0428, found 358.0434.

3-(Phenylthio)-2-(thiophen-3-yl)-1*H*-indole (**3l**): Yield: 63% (47.5 mg), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.76 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 4.8 Hz, 1H), 7.44 - 7.29 (m, 2H), 7.24 - 7.19 (m, 1H), 7.12 (dt, *J* = 14.8, 7.6 Hz, 5H), 7.02 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.8, 135.6, 132.1, 131.3, 128.9, 126.5, 126.3, 125.7, 124.8, 123.8, 123.4, 121.3, 119.8, 111.1, 99.1 ppm; ν_{max}(KBr)/cm^{-1} 3344, 2935, 1627, 1438, 1401, 686; MS (EI) m/z 120, 136, 186, 229, 274, 307; HRMS-ESI (m/z): calcd for $C_{18}H_{13}NNaS_2$, $[M+Na]^+$: 330.0382, found 330.0389.

*2-(Cyclohex-1-en-1-yl)-3-(phenylthio)-1H-indole (**3m**):* Yield: 71% (47.5 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.24 - 6.92 (m, 8H), 6.35 (s, 1H), 2.61 - 2.52 (m, 2H), 2.24-2.17 (m, 2H), 1.77-1.70 (m, 2H), 1.68-1.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 139.7, 135.0, 131.3, 130.2, 129.3, 128.7, 125.5, 124.4, 122.7, 120.8, 119.5, 110.8, 97.8, 27.4, 25.7, 22.6, 21.8 ppm; ν_{max}(KBr)/cm^{-1} 3424, 2938, 1630, 1601, 1445, 1321, 684; MS (EI) m/z 115, 154, 195, 228, 272, 305; HRMS-ESI (m/z): calcd for $C_{20}H_{19}NNaS$, $[M+Na]^+$: 328.1130, found 328.1134.

*2-Butyl-3-(phenylthio)-1H-indole (**3n**):* Yield: 87% (48.9 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.11 (q, *J* = 6.8 Hz, 3H), 7.02 (dd, *J* = 12.8, 7.2 Hz, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 1.84-1.41 (m, 2H), 1.33 (dq, *J* = 14.2, 7.2 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 139.6, 135.5, 130.3, 128.7, 125.5, 124.5, 122.2, 120.7, 119.1, 110.8, 98.9, 31.7, 26.2, 22.4, 13.8 ppm; ν_{max}(KBr)/cm^{-1} 3361, 2923, 2847, 1632, 1316, 686; MS (EI) m/z 130, 172, 206, 238, 281; HRMS-ESI (m/z): calcd for $C_{18}H_{19}NNaS$, $[M+Na]^+$: 304.1130, found 304.1126.

*2-Cyclopentyl-3-(phenylthio)-1H-indole (**3o**):* Yield: 85% (49.8 mg), yellow solid; mp = 73.4-74.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.18 - 7.07 (m, 4H), 7.06-6.94 (m, 3H), 3.57 (dd, *J* = 16.4, 8.0 Hz, 1H), 2.15-1.98 (m, 2H), 1.87-1.74 (m, 2H), 1.70-1.56 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 139.8, 135.5, 130.5, 128.7, 125.5, 124.5, 122.2, 120.8, 119.0, 110.9, 98.4, 37.3, 33.4, 25.8 ppm; ν_{max}(KBr)/cm^{-1} 3365, 2923, 1627, 1444, 1329, 684; MS (EI) m/z 108, 130, 155, 225, 260, 293; HRMS-ESI (m/z): calcd for $C_{19}H_{19}NNaS$, $[M+Na]^+$: 316.1130, found 316.1132.

*2-(Cyclohexylmethyl)-3-(phenylthio)-1H-indole (**3p**):* Yield: 75% (48.2 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.10 (q, *J* = 6.8 Hz, 3H), 7.01 (dd, *J* = 14.0, 7.2 Hz, 3H), 2.75 (d, *J* = 6.8 Hz, 2H), 1.70-1.53 (m, 7H), 1.16-1.06 (m, 3H), 1.01-0.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 139.6, 135.5, 130.3, 128.7, 125.6, 124.5, 122.2, 120.7, 119.2, 110.8, 99.7, 38.6, 34.3, 33.2, 26.3, 26.1 ppm; ν_{max}(KBr)/cm^{-1} 3344, 2930, 1622, 1435, 687; MS (EI) m/z 130, 178, 204, 238, 288, 321; HRMS-ESI (m/z): calcd for $C_{21}H_{23}NNaS$, $[M+Na]^+$: 344.1443, found 344.1448.

*4-(3-(Phenylthio)-1H-indol-2-yl)butanenitrile (**3q**):* Yield: 79% (47.5 mg) , yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 5.6 Hz, 1H),

7.14 (t, *J* = 7.6 Hz, 3H), 7.03 (t, *J* = 9.0 Hz, 3H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.28 (t, *J* = 6.8 Hz, 2H), 2.12-1.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.1, 135.6, 130.2, 128.8, 125.1, 124.8, 122.8, 121.1, 119.4, 119.2, 111.1, 100.2, 25.5, 25.4, 16.5 ppm; ν_{max}(KBr)/cm^{-1} 3412, 2938, 1716, 1442, 685; MS (EI) m/z 130, 205, 238, 259, 292; HRMS-ESI (m/z): calcd for $C_{18}H_{16}N_2NaS$, $[M+Na]^+$: 315.0926, found 315.0929.

*2-Phenyl-3-(phenylthio)-1H-indole (**3r**):* Yield: 90% (54.2 mg) , yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.37 (dt, *J* = 21.2, 6.8 Hz, 4H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.13 (dt, *J* = 15.6, 7.2 Hz, 5H), 7.03 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 139.3, 135.9, 131.5, 131.2, 128.8, 128.8, 128.7, 128.2, 125.6, 124.7, 123.4, 121.2, 120.0, 111.2, 99.5 ppm; ν_{max}(KBr)/cm^{-1} 3024, 2931, 1622, 1436, 1025, 687; MS (EI) m/z 121, 165, 197, 223, 268, 301.

*5-Methyl-2-phenyl-3-(phenylthio)-1H-indole (**3s**):* Yield: 87% (54.8 mg), yellow solid; mp = 116.8 - 118.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.45-7.32 (m, 4H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.11-7.00 (m, 4H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.6, 134.2, 131.6, 130.7, 128.9, 128.8, 128.6, 128.1, 125.5, 125.1, 124.6, 119.5, 110.9, 98.7, 21.5 ppm; ν_{max}(KBr)/cm^{-1} 3036, 2938, 1626, 1449, 1415, 689; MS (EI) m/z 121, 165, 204, 223, 238, 267, 282, 315; HRMS-ESI (m/z): calcd for $C_{21}H_{17}NNaS$, $[M+Na]^+$: 338.0974, found 338.0969.

*6-Methyl-2-phenyl-3-(phenylthio)-1H-indole (**3t**):* Yield: 89% (56.1 mg), yellow solid; mp = 129.7-130.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.46-7.32 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 7.11-6.99 (m, 5H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.6, 134.2, 131.6, 130.7, 128.8, 128.8, 128.6, 128.1, 125.5, 125.1, 124.6, 119.5, 110.9, 98.6, 21.5 ppm; ν_{max}(KBr)/cm^{-1} 3365, 2934, 1612, 1438, 1401, 675; MS (EI) m/z 128, 151, 178, 242, 257, 315; HRMS-ESI (m/z): calcd for $C_{21}H_{17}NNaS$, $[M+Na]^+$: 338.0974, found 338.0980.

*5,7-Dimethyl-2-phenyl-3-(phenylthio)-1H-indole (**3u**):* Yield: 83% (54.6 mg), yellow solid; mp = 156.1 - 157.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.27 (s, 1H), 7.17-7.08 (m, 4H), 7.03 (t, *J* = 6.8 Hz, 1H), 6.90 (s, 1H), 2.50 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ142.0, 139.6, 133.7, 131.7, 131.2, 130.9, 128.8, 128.7, 128.6, 128.2, 125.8, 125.5, 124.5, 120.0, 117.2, 99.2, 21.5, 16.4 ppm; ν_{max}(KBr)/cm^{-1} 3354, 2930, 1638, 1330, 683; MS (EI) m/z 115, 150, 237, 281, 296, 313, 329; HRMS-ESI (m/z): calcd for $C_{22}H_{19}NNaS$, $[M+Na]^+$: 352.1130, found 352.1137.

*5-Methoxy-2-phenyl-3-(phenylthio)-1H-indole (**3v**):* Yield: 77% (50.9 mg), yellow solid; mp = 145.2 - 146.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.41 - 7.30 (m, 3H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.18 - 6.99 (m, 6H), 6.89 (d, *J* = 8.8 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 142.7, 139.3, 132.2, 131.5, 130.8, 128.9, 128.8, 128.6, 128.1, 125.5, 124.7, 113.8, 112.2, 101.2, 98.9, 55.8 ppm; ν_{max}(KBr)/cm^{-1} 3352, 2927, 1611, 1422, 676; MS (EI) m/z 107, 152, 183, 199, 277, 331; HRMS-ESI (m/z): calcd for $C_{21}H_{17}NNaOS$, $[M+Na]^+$: 354.0923, found 354.0928.

*5-Fluoro-2-phenyl-3-(phenylthio)-1H-indole (**3w**):* Yield: 81% (51.6 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.29 (dd, *J* = 16.0, 7.6 Hz, 3H), 7.24-7.14 (m, 2H), 7.06 (t, *J* = 7.2 Hz, 2H), 6.96 (dd, *J* = 14.8, 7.6 Hz, 3H), 6.88 (t, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8 (d, *J* = 235.7 Hz), 143.8, 138.8, 132.2 (d, *J* = 2.5 Hz), 132.1, 131.1, 129.0, 128.9, 128.8, 128.1, 125.7, 124.9, 112.1 (d, J_{C-F} = 9.4 Hz), 111.8 (d, J_{C-F} = 26.4 Hz), 105.0 (d, J_{C-F} = 24.1 Hz), 99.6 (d, J_{C-F} = 4.5 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3352, 2931, 1623, 1454, 689; MS (EI) m/z 139, 183, 215, 241, 285, 304, 319; HRMS-ESI (m/z): calcd for $C_{20}H_{14}FNNaS$, $[M+Na]^+$: 342.0723, found 342.0718.

*6-Chloro-2-phenyl-3-(phenylthio)-1H-indole (**3x**):* Yield: 84% (56.3 mg), yellow solid; mp = 114.7-115.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.46 - 7.32 (m, 4H), 7.17-7.10 (m, 3H), 7.08-7.01 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.8, 136.2, 131.0, 129.8, 129.2, 129.0, 128.9, 128.8, 128.1, 125.7, 124.9, 121.9, 120.9, 111.2, 99.9 ppm; ν_{max}(KBr)/cm^{-1} 3366, 2927, 1634, 1445, 686; MS (EI) m/z 121, 150, 223, 267, 300, 335; HRMS-ESI (m/z): calcd for $C_{20}H_{14}ClNNaS$, $[M+Na]^+$: 358.0428, found 358.0432.

*5-Bromo-2-phenyl-3-(phenylthio)-1H-indole (**3y**):* Yield: 80% (60.9 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.69 (s, 1H), 7.64 (d, *J* = 6.8 Hz, 2H), 7.32 (dd, *J* = 15.6, 7.2 Hz, 3H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.8, 134.5, 133.1, 130.9, 129.1, 128.9, 128.8, 128.1, 126.4, 125.6, 124.9, 122.5, 114.7, 112.7, 99.2 ppm; ν_{max}(KBr)/cm^{-1} 3412, 2946, 1630, 1439, 1343, 689; MS (EI) m/z 121, 150, 190, 223, 267, 300, 347, 381; HRMS-ESI (m/z): calcd for $C_{20}H_{14}BrNNaS$, $[M+Na]^+$: 401.9923, found 401.9927.

*2-Phenyl-3-(phenylthio)-5-(trifluoromethyl)-1H-indole (**3z**):* Yield: 70% (51.7 mg), yellow solid; mp = 247.4-248.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.94 (s, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.47 (s, 2H), 7.43-7.32 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.11-7.00 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 138.6, 137.2, 130.9, 130.7, 129.2, 129.0, 128.9, 128.2, 125.4 (q, J_{C-F} = 226.0 Hz), 123.7 (q, J_{C-F} = 63.0 Hz), 120.2 (q, J_{C-F} = 6.0 Hz), 111.7 (q, J_{C-F} = 8.0 Hz), 111.6, 100.7 ppm; ν_{max}(KBr)/cm^{-1} 3392, 2934, 1626, 1451, 684; MS (EI) m/z 121, 150, 188, 267, 337, 369; HRMS-ESI (m/z): calcd for $C_{21}H_{14}F_3NNaS$, $[M+Na]^+$: 392.0691, found 392.0697.

*Methyl 2-phenyl-3-(phenylthio)-1H-indole-5-carboxylate (**3za**):* Yield: 64% (45.9 mg), yellow solid; mp = 253.5-253.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.44 (dd, *J* = 19.6, 12.0 Hz, 4H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 143.5, 138.9, 138.4, 131.0, 130.9, 129.1, 128.9, 128.8, 128.1, 125.6, 124.9, 124.8, 123.5, 122.7, 110.9, 51.9 ppm; ν_{max}(KBr)/cm^{-1} 3363, 2940, 1634, 1440, 1326, 686; MS (EI) m/z 121, 163, 223, 267, 299, 327, 359; HRMS-ESI (m/z): calcd for $C_{22}H_{17}NNaO_2S$, $[M+Na]^+$: 382.0872, found 382.0872.

*5,7-Dichloro-2-phenyl-3-(phenylthio)-1H-indole (**3zb**):* Yield: 71% (52.4 mg), yellow solid; mp = 116.9-118.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.51 (s, 1H), 7.47 - 7.36 (m, 3H), 7.25 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 138.3, 133.2, 131.7, 130.5, 129.4, 129.0, 128.9, 128.2, 127.1, 125.7, 125.1, 122.9, 118.3, 117.0, 100.7 ppm; ν_{max}(KBr)/cm^{-1} 3326, 2941, 1633, 1438, 686; MS (EI) m/z 150, 257, 301, 337, 369; HRMS-ESI (m/z): calcd for $C_{20}H_{13}Cl_2NNaS$, $[M+Na]^+$: 392.0038, found 392.0037.

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