Metal-free synthesis of 3-sulfenylindoles via an iodine-mediated electrophilic cyclisation of 2-alkynylanilines with disulfides

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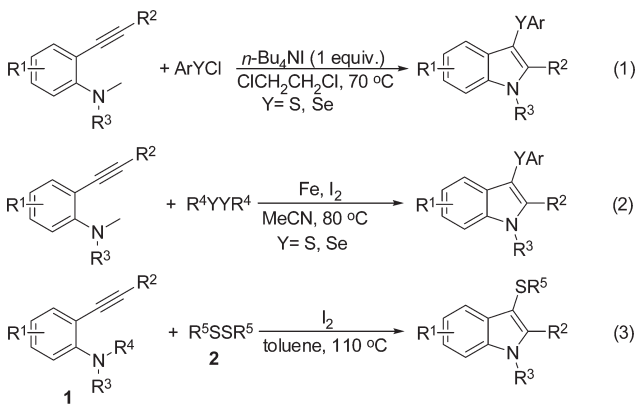
An efficient and metal-free method was developed to synthesise 3-sulfenylindoles via the iodine-mediated electrophilic cyclisation of 2-alkynylanilines with disulfides. In the presence of I_2, various 3-sulfenylindoles were obtained in moderate to high yields.

Keywords: metal-free, iodine, electrophilic cyclisation, 3-sulfenylindoles, 2-alkynylanilines, disulfides

The indole ring is a widespread heterocycle found in many natural products and pharmaceutical intermediates.[1–3] Among these indole derivatives, 3-sulfenylindoles are particularly attractive due to their therapeutic value in diseases such as cancers, HIV, obesity, heart disease, and allergies.[4–6] Although considerable efforts have been devoted to the development of efficient methods for 3-sulfenylindoles synthesis, the majority are focused on direct sulfenylation at the 3-position of the indole with thiols, disulfides, quinone mono-*O,S*-acetals, *N*-thioalkyl(aryl)-phthalimides, and ammonium thiocyanate.[7–13] Thus, the development of some novel alternative strategies for synthesising 3-sulfenylindoles remains a challenging area. Recently a few new efficient methods have been developed for this purpose *via* the electrophilic cyclisation of 2-(1-alkynyl)anilines. For example, Larock and co-workers have reported a novel synthetic approach to 3-sulfenylindoles by $(n\text{-Bu})_4$NI-induced electrophilic cyclisation of *N*,*N*-dialkyl-2-(1-alkynyl)anilines with an arylsulfenyl chloride or phenylselenenyl chloride [Eqn (1), Scheme 1].[14] Recently, Li and co-workers developed a simple and efficient transition metal-promoted electrophilic annulation method for the synthesis of 3-chalcogenoindoles [Eqn (2)].[15] However, transition metal-based protocols usually have inherent limitations, including moisture sensitivity, costly metal catalysts and environmental toxicity. Therefore, there is still a need for developing a direct and metal-free method to synthesise 3-sulfenylindoles. While studying the reaction of 2-(phenylethynyl)aniline (**1a**) with 1,2-diphenyl disulfide (**2a**), we serendipitously discovered that the annulation reaction can be accomplished in the presence of I_2 alone without the use of transition-metals. Here, we report the metal-free synthesis of 3-sulfenylindoles via an iodine-mediated electrophilic cyclisation of 2-alkynylanilines with disulfides [Eqn (3), Scheme 1].[15–17]



Scheme 1 Synthesis of 3-sulfenylindoles.

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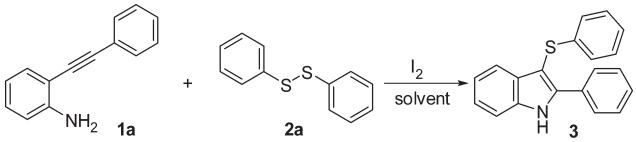
We chose the reaction of 2-(phenylethynyl)aniline (**1a**) with 1,2-diphenyl disulfide (**2a**) as a model system to determine the optimal reaction conditions, and the results are summarised in Table 1. Initially, the amount of I_2 was examined using DMSO as solvent at 80 °C, and it turned out that 1.0 equiv. I_2 was the most suitable for the reaction (entries 1 and 2). These results indicated that the solvent and temperature played important roles in the formation of **3** (entries 3–10). A series of solvents, such as MeOH, DMF, MeCN, THF, *m*-xylene and toluene, were firstly investigated. Screening revealed that toluene was the most effective solvent, increasing the yield to 81%. (entries 3–8). The effect of the reaction temperature was also examined. The reaction in toluene at 110 °C gave the highest yield (entries 9 and 10): the yield of **3** was enhanced to 93% at 110 °C. Notably, the amount of **2a** has no effect on the reaction (entry 11).

Having established the optimal reaction conditions, we investigated the scope of both 2-alkynylanilines **1** and disulfides **2** for the annulation reaction (Table 2).[18] Initially, a number of 2-alkynylanilines **1a–1i** was tested in the reaction with 1,2-diphenyl disulfide (**2a**). We found that a series of functional groups at the terminal position of the alkyne moiety of 2-alkynylaniline were well-tolerated under the optimal conditions but steric hindrance disfavoured the reaction in terms of yields. For example, 2-bromophenyl and alkyl groups favoured the reactions providing moderate to good yields (entries 2–4), but 2-methoxyphenyl and 4- acetylphenyl groups gave low yields (entries 1 and 5). Substrates **1g**, having a methyl group on the corresponding aromatic ring of the aniline, also underwent the annulation reaction with disulfide **2a** smoothly in 72% yield (entry 6). Notably, N–Me substituted

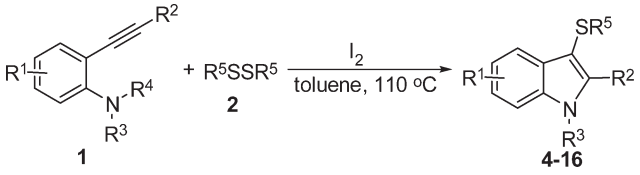
Table 1 Screening optimal conditions[a]



Entry	I_2 (equiv.)	Solvent	T/ °C	Isolated yields/%
1	0.5	DMSO	80	49
2	1.0	DMSO	80	68
3	1.0	MeOH	80	37
4	1.0	DMF	80	26
5	1.0	MeCN	80	72
6	1.0	THF	80	25
7	1.0	*m*-Xylene	80	61
8	1.0	Toluene	80	81
9	1.0	Toluene	100	88
10	1.0	Toluene	110	93
11[b]	1.0	Toluene	110	94

[a]Under otherwise indicated, the reaction conditions were as follows: **1a** (0.2 mmol), **2a** (0.1 mmol), I_2, solvent (2 mL) for 8 h under air atmosphere. [b]**2a** (0.2 mmol).

Table 2 I_2-Mediated annulation reactions of 2-alkynylanilines (**1**) with disulfides (**2**)[a]



Entry	2-Alkynylaniline **1**	Disulfide **2**	Time/h	Yield/%[b]
1	$R^1 = R^3 = R^4 = H$, R^2 =2-$MeOC_6H_4$ (**1b**)	R^5= Ph (**2a**)	8	44 (**4**)
2	$R^1 = R^3 = R^4 = H$, R^2 = 2-BrC_6H_4 (**1c**)	R^5= Ph (**2a**)	15	77 (**5**)
3	$R^1 = R^3 = R^4 = H$, R^2= n-C_6H_{13} (**1d**)	R^5= Ph (**2a**)	8	73 (**6**)
4	$R^1 = R^3 = R^4 = H$, R^2= t-C_4H_9 (**1e**)	R^5= Ph (**2a**)	15	87 (**7**)
5	$R^1 = R^3 = R^4 = H$, R^2= 4-$CH_3COC_6H_4$ (**1f**)	R^5= Ph (**2a**)	8	24 (**8**)
6	R^1 = 4-Me, R^2 = Ph, $R^3 = R^4 = H$ (**1g**)	R^5= Ph (**2a**)	8	72 (**9**)
7	$R^1 = R^4 = H$, R^2 = Ph, R^3 = Me (**1h**)	R^5= Ph (**2a**)	8	71 (**10**)
8	R^1 = H, R^2 = Ph, $R^3 = R^4$ = Me (**1i**)	R^5= Ph (**2a**)	8	81 (**10**)
9	$R^1 = R^3 = R^4 = H$, R^2 = Ph (**1a**)	R^5= 4-MeC_6H_4 (**2b**)	10	59 (**11**)
10	$R^1 = R^3 = R^4 = H$, R^2 = Ph (**1a**)	R^5= 4-$MeOC_6H_4$ (**2c**)	8	75 (**12**)
11	$R^1 = R^3 = R^4 = H$, R^2 = Ph (**1a**)	R^5= 4-ClC_6H_4 (**2d**)	8	95 (**13**)
12	$R^1 = R^3 = R^4 = H$, R^2 = Ph (**1a**)	R^5= 4-$NO_2C_6H_4$ (**2e**)	8	93 (**14**)
13	$R^1 = R^3 = R^4 = H$, R^2 = Ph (**1a**)	R^5= pyridin-2-yl (**2f**)	8	77 (**15**)
14	$R^1 = R^3 = R^4 = H$, R^2 = Ph (**1a**)	R^5 = Me (**2g**)	8	82 (**16**)

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), I_2 (1 equiv.), toluene (2 mL) at 110 °C under air atmosphere.
[b]Isolated yield.

substrates **1h** and **1i**, which had previously been reported as efficient substrates,[15,16] also displayed high reactivity under the metal-free conditions (entries 7 and 8).

Subsequently, we studied the reactions of disulfide **2a–g** with 2-(phenylethynyl)aniline (**1a**) under the optimal conditions. We were pleased to observe that several functional groups, such as methyl, methoxy, chloro, nitro and pyridine groups on the aromatic moiety of disulfides were perfectly tolerated, and disulfides having electron-deficient aryl groups gave the better results. Treatment of substrate **1a** with disulfide **2b–f**, afforded the corresponding products **11–15** in 59%, 75%, 95%, 93% and 77% yields, respectively (entries 9–13). Gratifyingly, an excellent yield was still achieved from the reaction of substrate **1a** with aliphatic disulfide **2g** in the presence of I_2 and toluene (entry 14).

A possible mechanism for the present transformation is outlined in Scheme 2.[14–17] Initially, the reaction of disulfide with I_2 would yield R_2SI **A** *in situ*.[15,16] Then, the electrophilic addition of R_2SI **A** with the 2-alkynylaniline would afford intermediate **B**. Annulation of intermediate B gives intermediate **C**, and then hydrogen can be removed from intermediate **C** with the aid of I^- to afford the target product.

In summary, we have developed a simple and metal-free protocol for the construction of 3-sulfenylindoles via the iodine-mediated electrophilic cyclisation of 2-alkynylanilines and disulfides. In the presence of I_2, a variety of 3-sulfenylindoles were synthesised from the reaction of 2-alkynylanilines derivatives with different disulfides in moderate to good yields. Importantly, these reactions were conducted under metal-free conditions.

Experimental

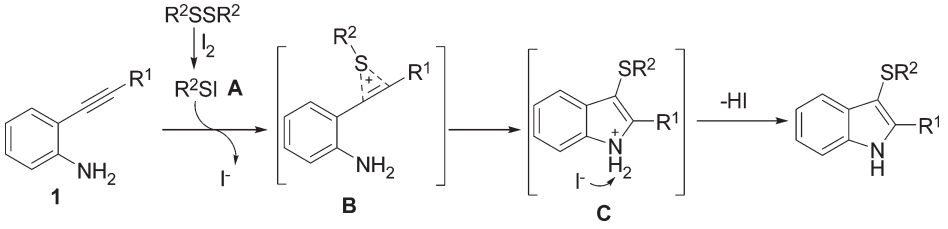
NMR spectroscopy was performed on a Bruker Avance spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR). TMS (tetramethylsilane) was used an internal standard and $CDCl_3$ was used as the solvent. Mass spectrometric analysis was performed on GC-MS analysis (Shimadzu GCMS-QP2010).

Iodine-mediated annulation of 2-alkynylanilines with disulfides; general procedure

2-Alkynylaniline derivative **1** (0.2 mmol), disulfide **2** (0.5 equiv), I_2 (1 equiv.) and toluene (2 mL) were added to a Schlenk tube. Then the tube was stirred at 80 °C in air for the indicated time until complete consumption of starting material was revealed as monitored by TLC or GC-MS analysis. After the reaction finished, the reaction mixture was filtered through a glass filter and washed with ethyl acetate. The solution was washed with saturated aqueous $Na_2S_2O_3$ (5×2 mL) and extracted with diethyl ether (3×5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under vacuum. The resulting residue was purified by column chromatography on silica gel (hexane/ethyl acetate) to afford the desired product.

2-Phenyl-3-(phenylthio)-1H-indole (**3**):[18] Pale yellow oil. ^{1}H NMR (300MHz, $CDCl_3$) δ: 8.57 (brs, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.49–7.42 (m, 4H), 7.30–7.27 (m, 1H), 7.22–7.12 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 139.3, 135.9, 131.4, 131.2, 128.9, 128.8, 128.7, 128.1, 125.6, 124.6, 123.4, 121.2, 120.0, 111.2, 99.4; LRMS (EI, 70 eV) *m/z* (%): 301 (M+, 100); HRMS *m/z* (ESI) Calcd for $C_{20}H_{16}NS$ ($[M+H]^+$) 302.0998; found 302.0993.

2-(2-Methoxyphenyl)-3-(phenylthio)-1H-indole (**4**):[16] Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.44 (brs, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.38–7.27 (m, 2H), 7.20–7.12 (m, 5H), 7.06–7.04 (m, 3H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7, 139.5, 139.4, 135.4, 131.8, 130.4, 130.0, 128.7, 125.5, 124.4, 123.0, 121.1, 120.7, 119.7, 111.5, 111.1, 99.3,



Scheme 2 Possible mechanism.

55.8; LRMS (EI, 70 eV) *m/z* (%): 331 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{21}H_{18}ONS$ ([M+H]$^+$) 332.1104; found 332.1109.

2-(2-Bromophenyl)-3-(phenylthio)-1H-indole (**5**):[19] Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (brs, 1H), 7.72–7.66 (m, 2H), 7.49–7.47 (m, 2H), 7.36–7.31 (m, 3H), 7.22–7.14 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 138.8, 135.7, 133.22, 133.16, 132.4, 130.5, 129.6, 128.7, 127.2, 125.8, 124.6, 123.5, 123.4, 121.1, 120.0, 111.4, 101.6; LRMS (EI, 70 eV) *m/z* (%): 381 (M^++2, 30), 379 (M^+, 31), 300 (100); HRMS *m/z* (ESI) Calcd for $C_{20}H_{15}BrNS$ ([M+H]$^+$) 382.0083; found 382.0085.

2-Hexyl-3-(phenylthio)-1H-indole (**6**):[19] Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (brs, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.28–7.14 (m, 4H), 7.09–7.04 (m, 3H), 2.94 (t, *J* = 7.6 Hz, 2H), 1.71–1.61 (m, 2H), 1.34–1.29 (m, 6H), 0.89 (q, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 139.5, 135.4, 130.3, 128.6, 125.4, 124.4, 122.1, 120.6, 119.0, 110.7, 98.9, 31.5, 29.7, 29.5, 28.9, 26.4, 22.5; LRMS (EI, 70 eV) *m/z* (%): 309 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{20}H_{24}NS$ ([M+H]$^+$) 310.1624; found 310.1627.

2-tert-Butyl-3-(phenylthio)-1H-indole (**7**): Pale yellow solid, m.p. 114.5–115.5 °C (uncorrected) (lit.[19] 115.0–115.6 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (brs, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.27–7.14 (m, 4H), 7.09–7.06 (m, 3H), 1.60 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 139.8, 133.9, 131.5, 128.5, 125.1, 124.1, 122.1, 120.7, 118.8, 96.7, 33.4, 29.8; LRMS (EI, 70 eV) *m/z* (%): 281 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{18}H_{20}NS$ ([M+H]$^+$) 282.1311; found 282.1317.

1-(4-(3-(Phenylthio)-1H-indol-2-yl) phenyl)ethanone (**8**): Yellow solid, m.p. 158.0–159.6 °C (uncorrected) (lit.[19] 158.2–160.3 °C). ^{1}H NMR (300 MHz, DMSO-D_6) δ 12.25 (brs, 1H), 8.06 (d, *J* = 9.4 Hz, 2H), 8.02 (d, *J* = 9.4 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.13–7.04 (m, 5H), 7.01–6.98 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (75 MHz, DMSO-D_6) δ: 197.9, 141.0, 138.9, 136.9, 136.6, 135.8, 131.0, 129.6, 128.9, 128.5, 125.5, 125.4, 123.8, 121.2, 119.3, 112.7, 98.6, 27.2; LRMS (EI, 70 eV) *m/z* (%): 343 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{22}H_{18}NOS$ ([M+H]$^+$) 344.1104; found 344.1108.

5-Methyl-2-phenyl-3-(phenylthio)-1H-indole (**9**): Pale yellow solid, m.p. 117.0–118.6 °C (uncorrected) (lit.[19] 117.5–118.2 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (brs, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.47–7.42 (m, 5H), 7.27–7.15 (m, 6H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 139.5, 134.1, 131.5, 130.7,128.8, 128.7, 128.6, 128.0, 125.4, 125.0, 124.5, 119.5, 115.0, 110.8, 98.6, 21.5; LRMS (EI, 70 eV) *m/z* (%): 315 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{21}H_{18}NS$([M+H]$^+$) 316.1154; found 316.1152.

1-Methyl-2-phenyl-3-(phenylthio)-1H-indole (**10**): Yellow solid, m.p. 93.5–95.0 °C (uncorrected) (lit.[15] 94.4–95.8 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.48–7.44 (m, 7H), 7.23–7.14 (m, 3H), 7.09–7.07 (m, 3H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.9, 139.9, 137.6, 130.6, 130.5, 129.8, 128.7, 128.6, 128.3, 125.5, 124.4, 122.8, 120.9, 119.8, 109.8, 99.6, 31.7; LRMS (EI, 70 eV) *m/z* (%): 315 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{21}H_{18}NS$ ([M+H]$^+$) 316.1154; found 316.1156.

2-Phenyl-3-(p-tolylthio)-1H-indole (**11**):[18] Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (brs, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.47–7.42 (m, 4H), 7.30–7.20 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9, 135.8, 135.6, 134.4, 131.5, 131.2, 129.6, 128.7, 128.6, 128.1, 125.7, 123.3, 121.1, 120.0, 111.1, 99.9, 20.9; LRMS (EI, 70 eV) *m/z* (%): 315 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{21}H_{18}NS$ ([M+H]$^+$) 316.1154; found 316.1158.

3-(4-Methoxyphenylthio)-2-phenyl-1H-indole (**12**):[20] Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (brs, 1H), 7.81–7.78 (m, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.49–7.40 (m, 4H), 7.31–7.20 (m, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 141.5, 135.8, 131.5, 131.1, 129.8, 128.7, 128.6, 128.1, 127.7, 123.2, 121.0, 119.9, 114.6, 111.1, 100.8, 55.3; LRMS (EI, 70 eV) *m/z* (%): 331 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{21}H_{18}NOS$ ([M+H]$^+$) 332.1104; found 332.1106.

3-(4-Chlorophenylthio)-2-phenyl-1H-indole (**13**):[18–20] Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (brs, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.45–7.40 (m, 4H), 7.28–7.18 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.2, 137.9, 135.9, 131.2, 130.9, 130.4, 129.3, 128.9, 128.8, 128.1, 126.8, 123.5, 121.3, 119.8, 111.3, 98.9; LRMS (EI, 70 eV) *m/z* (%): 337 (M^++2, 43), 335 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{20}H_{15}ClNS$ ([M+H]$^+$) 336.0608; found 336.0602.

3-(4-Nitrophenylthio)-2-phenyl-1H-indole (**14**):[19] Yellow solid, m.p. 155.9–157.5 °C (uncorrected) (lit.[19] 155.0–157.1 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.81 (brs, 1H), 8.01 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.56–7.43 (m, 5H), 7.34–7.22 (m, 2H), 7.16 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 144.9, 142.7, 135.9, 130.9, 130.4, 129.1, 128.9, 128.1, 125.1, 124.0, 123.8, 121.6, 119.4, 111.6; LRMS (EI, 70 eV) *m/z* (%): 346 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{20}H_{15}N_2O_2S$ ([M+H]$^+$) 347.0849; found 347.0847.

2-Phenyl-3-(pyridin-2-ylthio)-1H-indole (**15**): White solid, m.p. 184.5–186.0 °C (lit.[19] 185.4–185.7 °C) (uncorrected). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.40–8.38 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.65–7.63 (m, 1H), 7.47–7.18 (m, 7H), 6.95–6.91 (m, 1H), 6.97 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7, 149.3, 142.3, 136.8, 136.1, 131.3, 130.8, 128.7, 128.7, 128.2, 123.4, 121.2, 119.71, 119.7, 119.3, 111.5, 97.8; LRMS (EI, 70 eV) *m/z* (%): 302 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{19}H_{15}N_2S$ ([M+H]$^+$) 303.0950; found 303.0959.

3-(Methylthio)-2-phenyl-1H-indole (**16**):[21] Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (brs, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.69–7.67 (m, 1H), 7.47–7.40 (m, 2H), 7.53–7.50 (m, 2H), 7.30–7.27 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 135.6, 131.9, 128.6, 128.3, 127.7, 125.1, 123.0, 120.6, 120.2, 110.9, 99.9, 19.7; LRMS (EI, 70 eV) *m/z* (%): 239 (M^+, 100); HRMS *m/z* (ESI) Calcd for $C_{15}H_{14}NS$ ([M+H]$^+$) 240.0841; found 240.0847.

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