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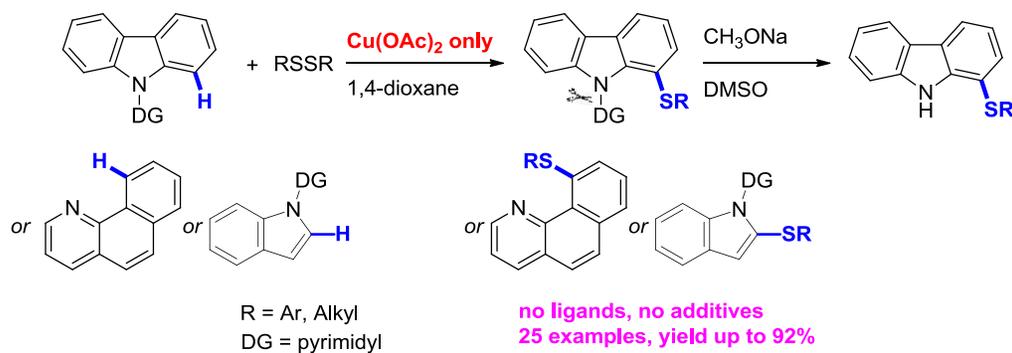
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TOC

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Copper-mediated thiolation of carbazole derivatives and related *N*-heterocycle compounds

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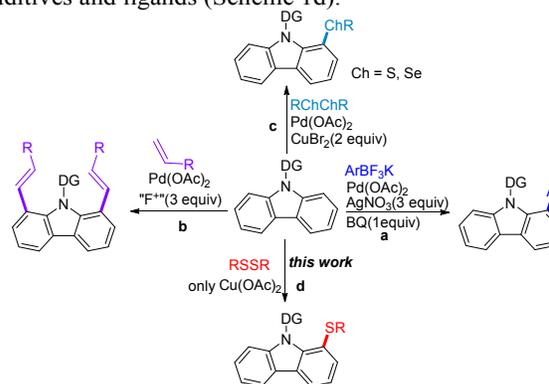
The copper-mediated direct thiolation of carbazole derivatives with disulfides via C(sp²)-H bond cleavage was developed for synthesizing diaryl and alkyl aryl sulfides. This reaction exhibits wide tolerance toward various functional groups giving the products in good yields without any additives or ligands, and can be easily extended to the synthesis of thioethers carrying a benzo[*h*]quinolone, 2-phenylquinoline, or indole moiety in satisfied yields.

Introduction

Among the various nitrogen-containing heterocycles that appear commonly in natural products, carbazole derivatives¹ have aroused considerable interest during the past decade, not only for their unique bioactivities² but also for their potential for use in practical applications in material science such as optoelectronics, functional polymers, or dyes etc.^{3,4} Despite the fact that many useful methods are available for preparing such a motif,^{1,4} site selective functionalization at the C1/C8 positions of carbazoles continues to pose a challenge due to the steric hindrance and lower electron density.⁵⁻⁷

By using directing group methodology, which has been widely employed for C-H bond functionalization,⁸ carbon-carbon bond formation at the C1/C8-positions of carbazoles was achieved without preliminary protection of the C3/C6 positions when a Pd catalyst is used.⁵ Wu and Chu *et al.*^{5a} reported on the Pd(II)-catalyzed direct *ortho*-arylation of carbazoles containing a pyridin-2-yl directing group (Scheme 1a). Carretero and co-workers^{5b} disclosed the Pd-catalyzed *ortho*-olefination of carbazoles by employing a (2-pyridyl)sulfonyl group (Scheme 1b). Given the importance of functionalized heterocycles in medicinal chemistry and the pharmaceutical industry,⁹ the introduction of aryl sulfide groups to an aromatic ring is a general and interesting way for their modification and has great practical value. Therefore various methods for the direct C-H thiolation of arenes have been reported.^{10,11} However, the syntheses of heteroatom-substituted carbazoles via C-H bond cleavage had never been disclosed until very recently.⁶ Patureau *et al.* recently reported on the oxidative dimerization of carbazoles with the concomitant direct C-H/N-H functionalization by the cooperative action of

Ru and Cu catalysts.^{6a} Our group recently reported on the Pd-catalyzed intermolecular C-H chalcogenation of arenes (Scheme 1c),^{6b} however, a drawback to this reaction is the use of the expensive Pd catalyst. Herein we report the first example of the copper(II)-mediated thiolation of the C1/C8 position of carbazole derivatives and related *N*-heterocycle compounds without the need for noble metal catalysts nor any additional additives and ligands (Scheme 1d).



Scheme 1. Direct functionalization of carbazoles at C1/C8-positions.

Results and discussion

Initially, 9-(pyrimidin-2-yl)-9*H*-carbazole (**1**) and diphenyl disulfide (**2a**) were chosen as the substrates to search for the optimal reaction conditions (Table 1). When the reaction was carried out using DMF as the solvent in the presence of a catalytic amount of Cu(OAc)₂ (10 mol%) at 140 °C for 24 h, only 18% of the product **3a** was obtained (entry 1). The use of CuCl₂ showed a similar reactivity, while Cu(I) and Cu(0) were

completely ineffective (entries 2-4). Although the addition of oxidants, $K_2S_8O_4$, DDQ, or molecular oxygen, did not improve the yield of **3a** (entries 5-7), the use of 2 equiv of $Cu(OAc)_2$ gave **3a** in 48% yield (entry 8). 1,4-Dioxane exhibited the best results among the solvents examined (entries 9-11). Prolonging the reaction time and elevating the reaction temperature, both increased the yield (entries 12-15). The addition of bipyridine or phenanthroline decreased the conversion and yield (entries 16 and 17). The fact that 99.999% pure $Cu(OAc)_2$ and the usual reagent grade $Cu(OAc)_2$ (97% purity) provided the same results (entries 15 and 18) eliminates the possibility that a trace amount of another metal(s) in the reagent played a crucial role in this reaction. Under the optimized conditions shown in entry 15, the carbazole (**1**) was found to react with PhSSPh to generate the arylthiolation product 1-(phenylthio)-9-(pyrimidin-2-yl)-9H-carbazole (**3a**) in 90% yield by the aid of 2 equiv of $Cu(OAc)_2$ without using any other additives.¹² When the reaction was performed using $CuBr_2$ without Pd under conditions that were identical to those for Pd-catalyzed reactions reported previously,^{6b} **3a** was not formed (entry 19). Use of 1,4-dioxane as the solvent and elevating the temperature did not improve the yield (entries 20 and 21). These results show that the use of $Cu(OAc)_2$ is a key to promoting the reaction in the absence of Pd. The structure of **3a** was characterized by X-ray crystallography (Figure 1).¹³

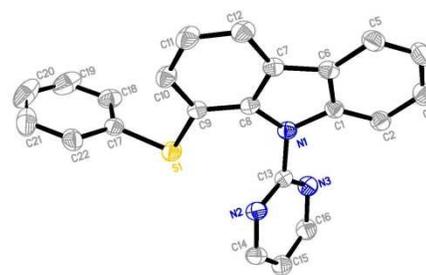


Figure 1. ORTEP drawing of **3a** with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity.

With the optimal reaction conditions for the present copper-mediated C-S bond-forming reaction in hand, the substrate scope with respect to disulfides was investigated (Table 2). The reaction proceeded smoothly with either electron rich or deficient diaryl disulfides in good to excellent yields. Chloro and bromo groups on the diphenyl disulfides were all tolerated (**3c**, 83% and **3d**, 76%). Diphenyl disulfides carrying a nitro group at the *ortho*, *meta*, or *para*-position all reacted efficiently (**3f-3h**). It is noteworthy that an alkyl ester group (**3i**, 39%) was compatible with this C-S bond-formation reaction.¹⁴ Disulfides having alkyl (**3i**, 65% and **3j**, 77%) or benzyl (**3k**, 30%) groups also afforded the corresponding thiolated products in reasonable yields, suggesting the wide compatibility of this catalytic system with respect to disulfides.

Table 1. Optimization of reaction conditions^a

Entry	Cu salt (equiv)	Solvent	Temp./Time	Conv. of 1 (%)	Yield of 3a (%)
1	$Cu(OAc)_2$ (0.1)	DMF	140 °C/24 h	22	18
2	$CuCl_2$ (0.1)	DMF	140 °C/24 h	19	16
3	CuI (0.1)	DMF	140 °C/24 h	NR	0
4	Cu powder(0.1)	DMF	140 °C/24 h	NR	0
5 ^b	$Cu(OAc)_2$ (0.1)	DMF	140 °C/24 h	79	28
6 ^c	$Cu(OAc)_2$ (0.1)	DMF	140 °C/24 h	83	26
7 ^d	$Cu(OAc)_2$ (0.1)	DMF	140 °C/24 h	99	40
8	$Cu(OAc)_2$ (2)	DMF	140 °C/24 h	52	48
9	$Cu(OAc)_2$ (2)	Toluene	140 °C/24 h	66	62
10	$Cu(OAc)_2$ (2)	1,4-Dioxane	140 °C/24 h	77	75
11	$CuOAc_2$ (2)	DMSO	140 °C/24 h	68	63
12	$Cu(OAc)_2$ (2)	1,4-Dioxane	150 °C/24 h	80	78
13	$Cu(OAc)_2$ (2)	1,4-Dioxane	160 °C/24 h	85	83
14	$Cu(OAc)_2$ (2)	1,4-Dioxane	160 °C/36 h	92	87
15	$Cu(OAc)_2$ (2)	1,4-Dioxane	160 °C/48 h	96	90
16 ^e	$Cu(OAc)_2$ (2)	1,4-Dioxane	160 °C/48 h	30	25
17 ^f	$Cu(OAc)_2$ (2)	1,4-Dioxane	160 °C/48 h	46	42
18 ^g	$Cu(OAc)_2$ (2)	1,4-Dioxane	160 °C/48 h	96	91
19	$CuBr_2$ (2)	DMF	140 °C/24 h	65	< 1%
20	$CuBr_2$ (2)	1,4-Dioxane	140 °C/24 h	68	< 1%
21	$CuBr_2$ (2)	1,4-Dioxane	160 °C/24 h	74	< 1%

Reaction conditions: ^a Cu salt (reagent grade 97% purity), carbazole (**1**) (0.25 mmol), PhSSPh (0.3 mmol), solvent (2 mL), isolated yield. ^b 2 equiv of $K_2S_8O_4$ was added. ^c 2 equiv of DDQ was added. ^d Under O_2 atmosphere. ^e 2 equiv of 2,2'-bipyridine was added. ^f 2 equiv of 1,10-phenanthroline monohydrate was added. ^g The purity of the $Cu(OAc)_2$ is 99.999%.

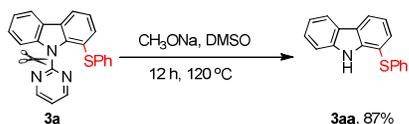
Table 2. Direct *ortho*-thiolation of carbazole (1**)^a**

Entry	Yield (%)
3a	90%
3b	92%
3c	83%
3d	76%
3e	78%
3f	72%
3g	82%
3h	73%
3i	65%
3j	77%
3k	30%
3l	39%

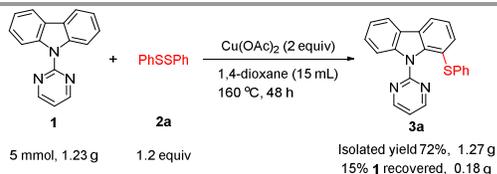
^a $Cu(OAc)_2$ (0.5 mmol), carbazole (**1**) (0.25 mmol), RSSR (0.3 mmol), 1,4-dioxane (2 mL) at 160 °C for 48 h.

The pyrimidyl directing group could be easily removed by treating the solution with CH_3ONa in DMSO as the solvent (Scheme 2).¹⁵

We next scaled-up the reaction as shown in Scheme 3. When a 20 fold increase in the substrate was used, the desired product **3a** was obtained in 72 % yield (1.27 g) after column chromatography on silica gel along with the recovery of 15% of the unreacted starting material **1** (0.18 g).

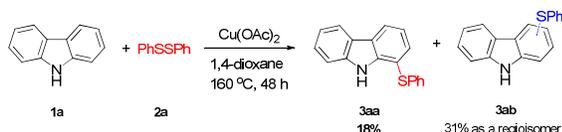


Scheme 2. Removal of the directing group. Conditions: **3a** (0.5 mmol), CH₃ONa (3 mmol), and DMSO (5 mL) were sealed in a Schlenk tube and heated for 12 h at 120 °C.



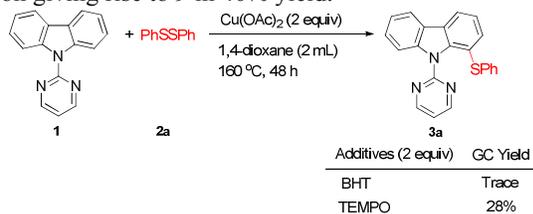
Scheme 3. Gram-scale synthesis of **3a**. Conditions: **1** (5 mmol), **2a** (6 mmol), and Cu(OAc)₂ (10 mmol) in 1,4-dioxane (15 mL).

In order to examine the effect of the pyrimidyl directing group, we conducted an experiment using the unsubstituted carbazole **1a** under the optimized conditions. As shown in Scheme 4, we obtained a mixture of products including the C1/C8-substituted product **3aa** as a minor component in 18% GC yield along with an unidentified product **3ab** having the same molecular weight as **3aa** by MS analysis as the major component in 31% yield estimated by GC as a regioisomer of **3aa**.¹⁶



Scheme 4. Reaction of carbazole under standard reaction conditions using **1a** (0.25 mmol), **2a** (0.3 mmol), Cu(OAc)₂ (0.5 mmol), 1,4-dioxane (2 mL).

We then applied this protocol to some related *N*-heterocycles, including benzo[*h*]quinolone (**4**), indole (**6**), and 2-phenylquinoline (**8**) derivatives (Table 3). The rigid tricyclic benzo[*h*]quinolone showed a high reactivity (**5a-5e**) and the reaction of bis(*p*-methoxyphenyl) disulfide gave **5d** in 90% yield. Indole derivatives were also found to be applicable to the present Cu-mediated thiolation reaction, affording the corresponding 2-sulfenylated indoles (**7a-7g**) in moderate yields. This is in sharp contrast to our previous report using a Pd catalyst, in which 2,3-disulfenylated products were produced.^{6b} Furthermore, 2-phenylquinoline (**8**) underwent this thiolation giving rise to **9** in 40% yield.

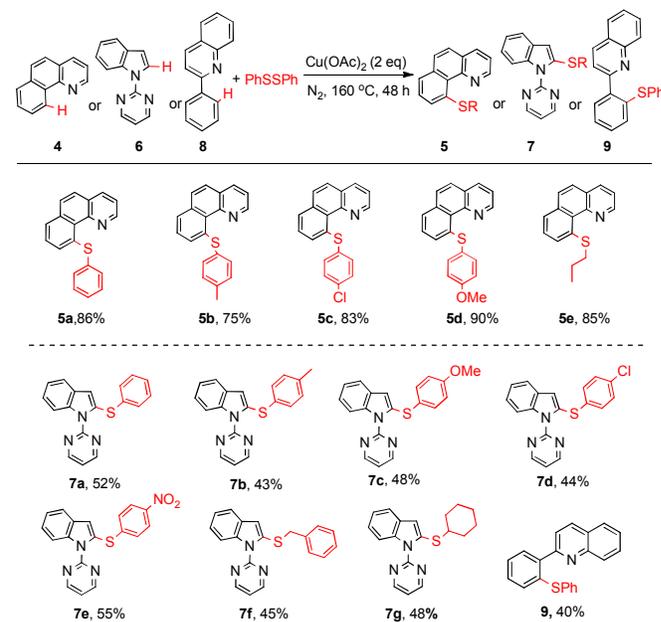


Scheme 5. Thiolation of **1** in the presence of a radical scavenger: Cu(OAc)₂ (0.5 mmol), carbazole (**1**, 0.25 mmol), PhSSPh (0.3 mmol), BHT (0.5 mmol) or TEMPO (0.5 mmol).

In order to examine the possible formation of radical intermediates, two separate reactions were carried out by adding 2 equiv of electron-transfer scavenger, BHT (2,6-di-*tert*-butyl-4-methylphenol) or the radical inhibitor TEMPO

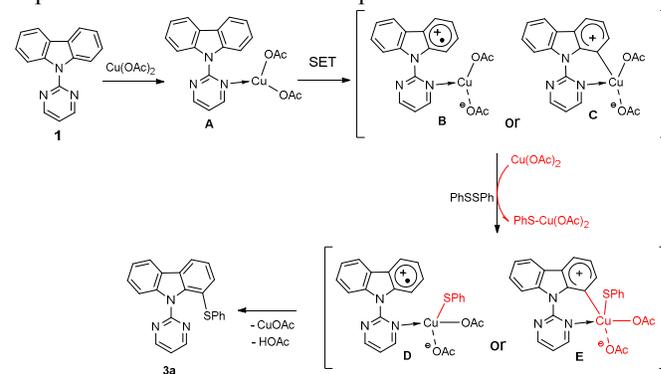
((2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl) (Scheme 5). The results showing that the yield of thiolated product **3a** decreased sharply suggest that a single-electron transfer (SET) process may be involved in this transformation.

Table 3. Direct *ortho*-thiolation of benzo[*h*]quinolone (**4**), indole (**6**), and 2-phenylquinoline (**8**)^a



^a Cu(OAc)₂ (0.5 mmol), arenes (**4**, **6**, **8**) (0.25 mmol), RSSR (0.3 mmol), 1,4-dioxane (2 mL) at 160 °C for 48 h.

On the basis of these results and previously reported studies,^{10a,17} we propose here a possible mechanism for this reaction (Scheme 6). Initially, the copper(II) is coordinated by the nitrogen atom of the pyrimidyl ring of **1** to yield the complex **A**,¹⁸ and an intramolecular one electron transfer generates a Cu(I) complex **B** or **C**, which readily reacts with PhSSPh and Cu(OAc)₂ to form complex **D** or **E**. As the final step, direct transfer of PhS group from Cu to the aryl group via **D**^{10a} or reductive-elimination via **E**¹⁷ with a concomitant deprotonation affords the desired product **3a**.



Scheme 6. A plausible pathway.

Conclusions

In conclusion, we report herein on the development of a straightforward method for the direct thiolation of carbazole derivatives and related *N*-heterocycle compounds by using readily available disulfides as thiolating reagents with the aid of the monodentate pyrimidyl directing group. It should be noted that this method has a wide substrate scope covering dialkyl and diaryl disulfides possessing various functional groups including ester, nitroarene, and haloarene moieties etc. and carbazole, benzo[*h*]quinoline, 2-phenylquinoline, and indole derivatives. The present reaction proceeds site-selectively using less expensive Cu(OAc)₂ without the need for any expensive noble metal catalyst nor additives to give the corresponding sulfenylated products.

Experimental

General

All reactions were carried out under a N₂ atmosphere using standard Schlenk techniques. Glassware was dried in an oven (110 °C) and heated under reduced pressure before use. For thin layer chromatography (TLC) analyses and column chromatography were performed using Qingdao Haiyang silica gel (200-300) with distilled solvents. NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz (¹H NMR) and 100 MHz (¹³C NMR) in CDCl₃. All ¹H and ¹³C NMR chemical shifts were reported in ppm relative to internal references of (CH₃)₄Si at 0.00 and carbon resonance in chloroform-*d*₁ at 77.00, respectively.

Chemicals

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. All solvents were redistilled.

General method for the C-S Coupling Reaction

To a screw capped vial equipped with a magnetic stirring bar was added carbazole (**1**) / benzo[*h*]quinolone (**4**) / indole derivatives (**6**) / 2-phenylquinolin(**8**) (0.25 mmol), disulfide derivatives (**2**) (0.3 mmol), Cu(OAc)₂ (0.5 mmol), and dioxane (2.0 mL) under a N₂ atmosphere. The reaction mixture was placed in a pre-heated oil bath at 160 °C and vigorously stirred for 48 h. The reaction was cooled to ambient temperature, filtered through a plug of celite and then washed with ethyl acetate (3 x 5 mL). The solvents were removed under reduced pressure and the crude reaction mixture was purified by chromatography on silica gel (*n*-hexane/EtOAc) as an eluent to give the desired product. In some cases, the products were purified by the PTLC method.

Synthesis of starting materials 9-(pyrimidin-2-yl)-9*H*-carbazole (**1**) and 1-(pyrimidin-2-yl)-1*H*-indole (**6**)¹⁹

NaH (a 60% dispersion in mineral oil, 440 mg, 11.0 mmol) was added in portions at 0 °C to a stirred solution of carbazole (1.67 g, 10.0 mmol) or indole (1.17 g, 10.0 mmol) in DMF (40 mL). After stirring for 1 h at 0 °C, 2-chloropyrimidine (1.37 g, 12.0 mmol) was added and the mixture was stirred at 130 °C for an

additional 12 h. The reaction mixture was then cooled to ambient temperature, poured into H₂O (300 mL) and the resulting solution extracted with EtOAc (4 × 75 mL). The combined organic phase was dried over Na₂SO₄. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 40/1) to yield **1** (2.20 g, 90%) or **6** (1.65g, 85%) as a colorless solid.

Data of isolated products are as follows:

1-(Phenylthio)-9-(pyrimidin-2-yl)-9*H*-carbazole (**3a**)

The general method was followed using 9-(pyrimidin-2-yl)-9*H*-carbazole (**1**) (61.3 mg, 0.25 mmol) and diphenyl disulfide (**2a**) (65.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**3a**) in 90 % (79.4 mg) as a light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (d, *J* = 4.8 Hz, 2H), 8.04-7.99 (m, 3H), 7.43-7.39 (t, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.11-7.02 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 158.5, 158.3, 141.1, 140.1, 137.6, 132.9, 129.8, 128.8, 128.6, 126.9, 126.3, 124.8, 122.7, 122.1, 120.4, 120.0, 119.6, 118.2, 112.4. HRMS *m/z* (EI) calcd for [C₂₂H₁₅N₃S]: 353.0987, found: 353.0989. Crystal data : Formula, C₂₂H₁₅N₃S; Formula weight, 353.43; Crystal system, Orthorhombic; Space group, Pbc_a; *a* = 8.4993(5) Å, *b* = 17.7777(11) Å, *c* = 23.0409(15) Å; *V* = 3481.4(4) Å³; *Z* = 8, *D*_{calcd} = 1.349 g/cm³; μ = 0.196 mm⁻¹, *F*₍₀₀₀₎, 1472; Crystal size, mm, 0.28×0.25×0.21, θ range for data collection, 2.46-26.00 deg; Limiting indices, -9≤*h*≤10, -21≤*k*≤21, -17≤*l*≤28; Reflections collected/unique, 15000 / 3408 [R(int) = 0.0281] Final R indices [I>2σ(I)], *R*₁ = 0.0403, *wR*₂ = 0.1268; *R* indices (all data), *R*₁ = 0.0574, *wR*₂ = 0.1425; Goodness of fit on *F*₂, 1.097. Selected bond lengths [Å] and angles [°]: C(17)-S(1), 1.772(2); C(9)-S(1), 1.776(2); C(17)-S(1)-C(9), 102.84(9).

1-((4-Methylphenyl)thio)-9-(pyrimidin-2-yl)-9*H*-carbazole (**3b**)

The general method was followed using 9-(pyrimidin-2-yl)-9*H*-carbazole (**1**) (61.3 mg, 0.25 mmol) and 1,2-bis(4-methylphenyl)disulfane (**2b**) (73.9 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**3b**) in 92 % (84.5 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.80 (d, *J* = 4.7 Hz, 2H), 8.07 (t, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 8.1 Hz, 2H), 7.26-7.18 (m, 2H), 7.04-6.96 (m, 4H), 2.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 158.6, 158.4, 141.2, 139.8, 136.7, 133.7, 132.0, 131.0, 129.7, 126.9, 126.8, 125.0, 122.7, 122.2, 121.9, 120.0, 119.0, 118.1, 112.5, 21.0. HRMS *m/z* (EI) calcd for [C₂₂H₁₇N₃S]: 367.1143, found: 367.1142.

1-((4-Chlorophenyl)thio)-9-(pyrimidin-2-yl)-9*H*-carbazole (**3c**)

The general method was followed using 9-(pyrimidin-2-yl)-9*H*-carbazole (**1**) (61.3 mg, 0.25 mmol) and 1,2-bis(4-chlorophenyl)disulfane (**2c**) (86.3 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**3c**) in

83 % (80.4 mg) as a white solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.74 (d, J = 2.5 Hz, 2H), 8.05 (t, J = 7.4 Hz, 3H), 7.43 (m, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.29-7.23 (m, 1H), 7.16 (s, 1H), 7.10 (d, J = 7.2 Hz, 2H), 6.96 (d, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 158.5, 158.3, 141.2, 140.2, 136.4, 133.0, 132.2, 130.8, 128.9, 127.1, 127.0, 124.8, 122.3, 120.1, 120.0, 119.9, 119.8, 118.3, 112.5. HRMS m/z (EI) calcd for $[\text{C}_{22}\text{H}_{14}\text{ClN}_3\text{S}]$: 387.0597, found: 387.0596.

1-((4-Bromophenyl)thio)-9-(pyrimidin-2-yl)-9H-carbazole (3d)

The general method was followed using 9-(pyrimidin-2-yl)-9H-carbazole (**1**) (61.3 mg, 0.25 mmol) and 1,2-bis(4-bromophenyl)disulfane (**2d**) (86.2 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**3d**) in 76 % (82.1 mg) as a white solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.77 (d, J = 4.8 Hz, 2H), 8.06 (m, 3H), 7.45 (m, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.27 (t, J = 3.1 Hz, 1H), 7.25 (d, J = 3.0 Hz, 1H), 7.22 (t, J = 4.8 Hz, 1H), 6.90 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 158.7, 158.4, 141.3, 140.4, 137.3, 133.3, 131.9, 131.7, 131.0, 128.8, 127.2, 127.1, 124.9, 122.9, 122.3, 120.1, 119.6, 118.4, 112.5. HRMS m/z (EI) calcd for $[\text{C}_{22}\text{H}_{14}\text{BrN}_3\text{S}]$: 431.0092, found: 431.0094.

1-((4-Methoxyphenyl)thio)-9-(pyrimidin-2-yl)-9H-carbazole (3e)

The general method was followed using 9-(pyrimidin-2-yl)-9H-carbazole (**1**) (61.3 mg, 0.25 mmol) and 1,2-bis(4-methoxyphenyl)disulfane (**2e**) (83.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**3e**) in 78% (74.7 mg) as a white solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.83 (d, J = 4.8 Hz, 2H), 8.13 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.27-7.15 (m, 5H), 6.74 (d, J = 8.7 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 159.3, 158.7, 158.5, 141.2, 139.2, 134.0, 130.7, 127.3, 126.9, 126.8, 125.2, 123.6, 122.7, 122.3, 120.1, 118.5, 118.1, 114.7, 112.7, 55.3. HRMS m/z (EI) calcd for $[\text{C}_{23}\text{H}_{17}\text{N}_3\text{OS}]$: 383.1092, found: 383.1093.

1-((2-Nitrophenyl)thio)-9-(pyrimidin-2-yl)-9H-carbazole (3f)

The general method was followed using 9-(pyrimidin-2-yl)-9H-carbazole (**1**) (61.3 mg, 0.25 mmol) and 1,2-bis(2-nitrophenyl)disulfane (**2f**) (92.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 30/1) yielded (**3f**) in 72 % (71.7 mg) as a yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.57 (d, J = 4.8 Hz, 2H), 8.25 (d, J = 7.7 Hz, 1H), 8.11-8.04 (m, 2H), 7.66 (t, J = 8.2 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.24 (t, J = 2.5 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 158.1, 157.8, 144.8, 141.2, 138.4, 136.2, 133.6, 133.4, 128.6, 128.5, 127.3, 127.2, 125.3, 124.9, 123.9, 122.4, 122.0, 120.1, 119.0, 114.7, 111.6. HRMS m/z (EI) calcd for $[\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}_2\text{S}]$: 398.0837 found: 398.0833.

1-((3-Nitrophenyl)thio)-9-(pyrimidin-2-yl)-9H-carbazole (3g)

The general method was followed using 9-(pyrimidin-2-yl)-9H-carbazole (**1**) (61.3 mg, 0.25 mmol) and 1,2-bis(3-nitrophenyl)disulfane (**2g**) (92.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 30/1) yielded (**3g**) in 82 % (81.7 mg) as a yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.72 (d, J = 4.7 Hz, 2H), 8.14 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.82 (s, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.37 (dd, J = 14.0, 7.1 Hz, 2H), 7.22-7.12 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 158.4, 158.2, 148.2, 141.2, 141.1, 140.6, 134.1, 133.7, 129.3, 127.5, 127.2, 124.5, 122.9, 122.5, 122.3, 121.1, 120.5, 120.1, 118.5, 117.1, 112.4. HRMS m/z (EI) calcd for $[\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}_2\text{S}]$: 398.0837, found: 398.0841.

1-((4-Nitrophenyl)thio)-9-(pyrimidin-2-yl)-9H-carbazole (3h)

The general method was followed using 9-(pyrimidin-2-yl)-9H-carbazole (**1**) (61.3 mg, 0.25 mmol) and 1,2-bis(4-nitrophenyl)disulfane (**2h**) (92.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 30/1) yielded (**3h**) in 73 % (72.7 mg) as a yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.67 (d, J = 4.8 Hz, 2H), 8.19 (d, J = 7.1 Hz, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.94 (t, J = 8.0 Hz, 3H), 7.56 (d, J = 7.1 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.40-7.35 (m, 2H), 7.18 (t, J = 4.8 Hz, 1H), 6.93 (d, J = 8.9 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 158.34, 158.26, 148.7, 145.1, 141.2, 141.1, 135.0, 127.6, 127.3, 126.5, 124.4, 123.7, 122.9, 122.4, 121.8, 120.1, 118.6, 115.3, 112.3. HRMS m/z (EI) calcd for $[\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}_2\text{S}]$: 398.0837, found: 398.0840.

1-(Cyclohexylthio)-9-(pyrimidin-2-yl)-9H-carbazole (3i)

The general method was followed using 9-(pyrimidin-2-yl)-9H-carbazole (**1**) (61.3 mg, 0.25 mmol) and 1,2-bis(cyclohexyl)disulfane (**2i**) (69.1 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 40/1) yielded (**3i**) in 65% (58.4 mg) as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 8.83 (d, J = 4.8 Hz, 2H), 8.04 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.31 (dd, J = 15.5, 7.8 Hz, 2H), 7.24-7.17 (m, 1H), 2.90 (t, J = 9.7 Hz, 1H), 1.64-1.46 (m, 5H), 1.14-1.02 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3): δ = 159.1, 158.4, 141.8, 141.4, 132.9, 126.6, 126.3, 124.9, 122.1, 121.8, 120.0, 120.0, 119.3, 118.4, 111.8, 48.4, 33.0, 25.8, 25.6. HRMS m/z (EI) calcd for $[\text{C}_{22}\text{H}_{21}\text{N}_3\text{S}]$: 359.1456, found: 359.1454.

1-(Propylthio)-9-(pyrimidin-2-yl)-9H-carbazole (3j)

The general method was followed using 9-(pyrimidin-2-yl)-9H-carbazole (**1**) (61.3 mg, 0.25 mmol) and 1,2-bispropylthio disulfane (**2j**) (45.1 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 50/1) yielded (**3j**) in 77 % (61.5 mg) as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 8.827 (d, J = 4.9 Hz, 2H), 8.04 (dd, J = 11.9, 7.9 Hz, 2H), 7.97 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 7.4 Hz, 1H), 7.43 (dd, J = 11.7, 4.5 Hz, 1H),

7.36-7.31 (m, 2H), 7.24 (dd, $J = 10.0, 5.1$ Hz, 1H), 2.75 (t, $J = 7.3$ Hz, 2H), 1.45-1.36 (m, 2H), 0.84 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 159.0, 158.5, 141.4, 140.6, 130.2, 126.8, 126.5, 125.2, 122.5, 122.3, 122.1, 120.1, 118.5, 118.3, 112.3, 38.5, 22.6, 13.3$. HRMS m/z (EI) calcd for $[\text{C}_{19}\text{H}_{17}\text{N}_3\text{S}]$: 319.1143, found: 319.1142.

1-(Benzylthio)-9-(pyrimidin-2-yl)-9H-carbazole (3k)

The general method was followed using 9-(pyrimidin-2-yl)-9H-carbazole (**1**) (61.3 mg, 0.25 mmol) and 1,2-bisbenzylphenyl disulfane (**2k**) (73.9 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**3k**) in 30 % (27.6 mg) as a white solid. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.83$ (d, $J = 4.8$ Hz, 2H), 8.04–8.00 (m, 2H), 7.96 (dd, $J = 7.7, 1.0$ Hz, 1H), 7.47–7.41 (m, 2H), 7.33 (td, $J = 7.5, 0.9$ Hz, 1H), 7.26–7.24 (m, 1H), 7.21–7.17 (m, 4H), 7.11–7.09 (m, 2H), 3.94 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 158.9, 158.5, 141.4, 140.3, 137.4, 130.9, 129.0, 128.3, 127.0, 126.8, 126.7, 125.1, 122.5, 122.1, 121.9, 120.1, 119.0, 118.4, 112.4, 41.3$. HRMS m/z (EI) calcd for $[\text{C}_{23}\text{H}_{17}\text{N}_3\text{S}]$: 367.1143, found: 367.1141.

Methyl-3-((9-(pyrimidin-2-yl)-9H-carbazol-1-yl)thio)propano-ate (3l)

The general method was followed using 9-(pyrimidin-2-yl)-9H-carbazole (**1**) (61.3 mg, 0.25 mmol) and disulfanediybis(methylene) dipropionate (**2l**) (71.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 40/1) yielded (**3l**) in 39 % (35.4 mg) as a yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.85$ (d, $J = 4.8$ Hz, 2H), 8.06-7.99 (m, 3H), 7.57 (dd, $J = 7.6, 1.0$ Hz, 1H), 7.47-7.40 (m, 1H), 7.37-7.31 (m, 2H), 7.24 (t, $J = 4.9$ Hz, 1H), 3.56 (s, 3H), 3.00 (t, $J = 7.5$ Hz, 2H), 2.33 (t, $J = 7.5$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 172.2, 159.0, 158.5, 141.4, 141.0, 130.9, 126.9, 126.7, 125.0, 122.7, 122.2, 120.6, 120.2, 119.3, 118.4, 112.4, 51.7, 34.2, 31.4$. HRMS m/z (EI) calcd for $[\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_2\text{S}]$: 363.1041, found: 363.1034.

10-(Phenylthio)benzo[h]quinoline (5a)

The general method was followed using benzo[h]quinoline (**4**) (44.8 mg, 0.25 mmol) and diphenyl disulfide (**2a**) (65.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 10/1) yielded (**5a**) in 86% (61.8 mg) as a white thick oil. $^{10\text{h}}$ ^1H NMR (400 MHz, CDCl_3): $\delta = 9.14$ (dd, $J = 4.4, 1.8$ Hz, 1H), 8.12 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.74-7.69 (m, 3H), 7.62-7.57 (m, 2H), 7.50-7.41 (m, 4H), 7.35 (t, $J = 7.8$ Hz, 1H), 7.07 (dd, $J = 7.9, 1.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 147.4, 146.4, 140.7, 136.3, 135.3, 135.22, 135.16, 129.9, 129.1, 128.6, 127.44, 127.37, 127.2, 125.62, 125.56, 124.6, 121.0$. HRMS m/z (EI) calcd for $[\text{C}_{19}\text{H}_{13}\text{NS}]$: 287.0769, found: 287.0765.

10-((4-Methylphenyl)thio)benzo[h]quinoline (5b)

The general method was followed using benzo[h]quinoline (**4**) (44.8 mg, 0.25 mmol) and diphenyl 1,2-bis(4-methylphenyl)disulfane (**2b**) (73.9 mg, 0.30 mmol).

Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**5b**) in 75 % (56.5 mg) as a white solid. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.17$ (dd, $J = 4.3, 1.6$ Hz, 1H), 8.22 (d, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.71 (d, $J = 8.8$ Hz, 1H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.62-7.54 (m, 3H), 7.39 (t, $J = 7.8$ Hz, 1H), 7.30 (d, $J = 7.9$ Hz, 2H), 7.07 (dd, $J = 7.9, 1.0$ Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 147.5, 146.4, 141.0, 139.1, 136.3, 135.3, 135.1, 131.5, 130.6, 128.6, 127.4, 127.3, 127.2, 125.6, 125.4, 124.5, 121.0, 21.42$. HRMS m/z (EI) calcd for $[\text{C}_{20}\text{H}_{15}\text{NS}]$: 301.0925, found: 301.0920.

10-((4-Chlorophenyl)thio)benzo[h]quinoline (5c)

The general method was followed using benzo[h]quinoline (**4**) (44.8 mg, 0.25 mmol) and 1,2-bis(4-chlorophenyl)disulfane (**2c**) (86.3 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 10/1) yielded (**5c**) in 83% (66.8 mg) as a white solid. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.15$ (d, $J = 3.1$ Hz, 1H), 8.22 (d, $J = 7.8$ Hz, 1H), 7.81 (d, $J = 8.8$ Hz, 1H), 7.73–7.61 (m, 4H), 7.57 (dd, $J = 7.9, 4.2$ Hz, 1H), 7.46-7.40 (m, 3H), 7.05 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 147.3, 146.4, 140.0, 137.5, 135.3, 135.1, 133.9, 130.1, 130.0, 128.6, 127.4, 127.4, 127.2, 125.7, 125.5, 124.8, 121.1$. HRMS m/z (EI) calcd for $[\text{C}_{19}\text{H}_{12}\text{ClNS}]$: 321.0379, found: 321.0374.

10-((4-Methoxyphenyl)thio)benzo[h]quinoline (5d)

The general method was followed using benzo[h]quinoline (**4**) (44.8 mg, 0.25 mmol) and 1,2-bis(4-methoxyphenyl)disulfane (**2e**) (83.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**5d**) in 90 % (71.3 mg) as a yellow solid. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.16$ (dd, $J = 4.4, 1.8$ Hz, 1H), 8.16 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.62 (m, 4H), 7.51 (dd, $J = 8.0, 4.4$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 7.06 (dd, $J = 7.9, 0.8$ Hz, 1H), 7.00 (d, $J = 8.7$ Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 159.4, 146.4, 145.3, 140.4, 136.8, 134.1, 134.1, 127.5, 126.3, 126.2, 126.1, 124.7, 124.5, 124.1, 123.4, 119.9, 114.3, 54.3$. HRMS m/z (EI) calcd for $[\text{C}_{20}\text{H}_{15}\text{NOS}]$: 317.0874, found: 317.0870.

10-(Propylthio)benzo[h]quinoline (5e)

The general method was followed using benzo[h]quinoline (**4**) (44.8 mg, 0.25 mmol) and 1,2-bispropyl disulfane (**2j**) (45.1 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**5e**) in 85% (53.8 mg) as a yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.13$ (dd, $J = 4.4, 1.8$ Hz, 1H), 8.15 (d, $J = 7.9$ Hz, 1H), 7.78 (d, $J = 8.7$ Hz, 1H), 7.66 (dd, $J = 9.1, 5.1$ Hz, 2H), 7.61 (d, $J = 4.8$ Hz, 2H), 7.50 (dd, $J = 8.0, 4.4$ Hz, 1H), 3.02 (t, $J = 7.5, 2\text{H}$), 1.96-1.90 (m, 2H), 1.17 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 147.4, 146.3, 139.6, 135.2, 135.0, 128.6, 128.0, 127.3, 127.0, 125.6, 124.0, 123.0, 120.7, 35.6, 21.4, 14.3$. HRMS m/z (EI) calcd for $[\text{C}_{16}\text{H}_{15}\text{NS}]$: 253.0925 found: 253.0927.

2-(Phenylthio)-1-(pyrimidin-2-yl)-1H-indole (7a)

The general method was followed using 1-(pyrimidin-2-yl)-1H-indole (**6**) (48.8 mg, 0.25 mmol) and diphenyl disulfane (**2a**) (65.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-

hexane/EtOAc: 20/1) yielded (**7a**) in 52% (39.4 mg) as a light yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.83 (d, J = 8.4 Hz, 1H), 8.70 (d, J = 4.8 Hz, 2H), 8.58 (s, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.44-7.33 (m, 1H), 7.25-7.14 (m, 5H), 7.08 (dt, J = 9.5, 3.0 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 158.3, 157.3, 137.8, 136.1, 131.6, 131.5, 128.8, 126.8, 125.3, 124.6, 122.8, 119.8, 116.8, 116.6, 108.4. HRMS m/z (EI) calcd for $[\text{C}_{18}\text{H}_{13}\text{N}_3\text{S}]$: 303.0830, found: 303.0826.

2-((4-Methylphenyl)thio)-1-(pyrimidin-2-yl)-1H-indole (**7b**)

The general method was followed using 1-(pyrimidin-2-yl)-1H-indole (**6**) (48.8 mg, 0.25 mmol) and 1,2-bis(4-methylphenyl)disulfane (**2b**) (65.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**7b**) in 43 % (34.1 mg) as a light yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.81 (d, J = 4.8 Hz, 2H), 8.42 (d, J = 8.3 Hz, 1H), 7.48 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 7.7 Hz, 1H), 7.22-7.13 (m, 5H), 6.09 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 157.1, 156.8, 137.7, 136.1, 135.9, 132.8, 129.9, 129.2, 128.5, 121.7, 121.2, 118.1, 116.0, 113.3, 107.4, 20.3. HRMS m/z (EI) calcd for $[\text{C}_{19}\text{H}_{15}\text{N}_3\text{S}]$: 317.0987, found: 317.0984.

2-((4-Methoxyphenyl)thio)-1-(pyrimidin-2-yl)-1H-indole (**7c**)

The general method was followed using 1-(pyrimidin-2-yl)-1H-indole (**6**) (48.8 mg, 0.25 mmol) and 1,2-bis(4-methoxyphenyl)disulfane (**2e**) (83.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**7c**) in 48 % (40.0 mg) as a light yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 8.81 (d, J = 4.6 Hz, 2H), 8.47 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 7.4 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.2 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 5.96 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 160.4, 157.8, 157.6, 138.3, 137.2, 136.3, 129.7, 124.6, 122.5, 122.3, 119.0, 116.9, 115.1, 114.5, 107.3, 55.4. HRMS m/z (EI) calcd for $[\text{C}_{19}\text{H}_{15}\text{N}_3\text{OS}]$: 333.0936, found: 333.0938.

2-((4-Chlorophenyl)thio)-1-(pyrimidin-2-yl)-1H-indole (**7d**)

The general method was followed using 1-(pyrimidin-2-yl)-1H-indole (**6**) (48.8 mg, 0.25 mmol) and 1,2-bis(4-chlorophenyl)disulfane (**2c**) (86.3 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**7d**) in 44 % (37.2 mg) as a light yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.78 (d, J = 4.8 Hz, 2H), 8.39 (d, J = 8.2 Hz, 1H), 7.46-7.41 (m, 3H), 7.32-7.29 (m, 2H), 7.26 (d, J = 7.1 Hz, 1H), 7.20-7.13 (m, 2H), 6.25 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 157.9, 157.3, 137.3, 134.6, 134.2, 134.0, 133.8, 129.5, 129.2, 123.2, 122.3, 119.5, 117.2, 114.2, 110.1. HRMS m/z (EI) calcd for $[\text{C}_{18}\text{H}_{12}\text{ClN}_3\text{S}]$: 337.0440, found: 337.0442.

2-((4-Nitrophenyl)thio)-1-(pyrimidin-2-yl)-1H-indole (**7e**)

The general method was followed using 1-(pyrimidin-2-yl)-1H-indole (**6**) (48.8 mg, 0.25 mmol) and 1,2-bis(4-nitrophenyl)disulfane (**2h**) (92.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**7e**) in

55 % (47.9 mg) as a yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.72 (d, J = 4.8 Hz, 2H), 8.23 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 7.7 Hz, 1H), 7.37-7.31 (m, 3H), 7.24 (dd, J = 8.5, 6.5 Hz, 1H), 7.15 (t, J = 4.8 Hz, 1H), 6.90 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 158.1, 156.9, 147.7, 145.8, 137.9, 128.4, 128.0, 127.4, 124.8, 123.9, 122.5, 120.6, 117.9, 116.4, 113.9. HRMS m/z (EI) calcd for $[\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_2\text{S}]$: 348.0681, found: 348.0678.

2-((Benzyl)thio)-1-(pyrimidin-2-yl)-1H-indole (**7f**)

The general method was followed using 1-(pyrimidin-2-yl)-1H-indole (**6**) (48.8 mg, 0.25 mmol) and 1,2-bisbenzylphenyl disulfide (**2k**) (73.9 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**7f**) in 45 % (35.7 mg) as a yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.75 (d, J = 4.8 Hz, 2H), 8.43 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 7.0 Hz, 1H), 7.41 (d, J = 7.1 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.26 (dd, J = 4.0, 1.9 Hz, 1H), 7.22-7.20 (m, 1H), 7.19-7.17 (m, 1H), 7.09 (t, J = 4.8 Hz, 1H), 6.57 (s, 1H), 4.21 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 157.8, 157.5, 136.9, 136.5, 135.8, 129.8, 129.3, 128.7, 127.5, 122.8, 122.3, 119.1, 117.0, 114.4, 106.7, 40.2. HRMS m/z (EI) calcd for $[\text{C}_{19}\text{H}_{15}\text{N}_3\text{S}]$: 317.0987, found: 317.0978.

2-(Cyclohexylthio)-1-(pyrimidin-2-yl)-1H-indole (**7g**)

The general method was followed using 1-(pyrimidin-2-yl)-1H-indole (**6**) (48.8 mg, 0.25 mmol) and 1,2-bis(cyclohexyl)disulfane (**2i**) (69.1 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**7g**) in 48 % (37.1 mg) as a yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.81 (d, J = 4.8 Hz, 2H), 8.20 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.0 Hz, 1H), 7.22-7.15 (m, 3H), 6.68 (s, 1H), 3.24 (d, 3.5 Hz, 1H), 2.07 (t, J = 12.3 Hz, 2H), 1.76 (dd, J = 8.8, 3.3 Hz, 2H), 1.62 (d, J = 10.4 Hz, 1H), 1.41-1.23 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3): δ = 158.0, 157.5, 137.2, 133.6, 129.4, 122.9, 122.1, 119.3, 117.4, 113.5, 109.2, 47.5, 33.0, 26.2, 25.9. HRMS m/z (EI) calcd for $[\text{C}_{18}\text{H}_{19}\text{N}_3\text{S}]$: 309.1300, found: 309.1307.

2-(2-(Phenylthio)phenyl)quinoline (**9**)

The general method was followed using 2-phenyl quinoline (**8**) (51.3mg, 0.25 mmol) and diphenyl disulfide (**2a**) (65.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 20/1) yielded (**9**) in 40% (31.3 mg) as yellow oil. ^{10}H NMR (400 MHz, CDCl_3): δ = 8.15 (dd, J = 16.5, 8.4 Hz, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.74-7.61 (m, 3H), 7.51 (t, J = 7.1 Hz, 1H), 7.34-7.27 (m, 5H), 7.21 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 158.4, 147.6, 141.4, 135.8, 135.6, 132.1, 131.6, 130.4, 129.6, 129.5, 129.2, 129.1, 127.5, 127.3, 126.9, 126.8, 126.5, 122.2. HRMS m/z (EI) calcd for $[\text{C}_{21}\text{H}_{15}\text{NS}]$: 313.0925, found: 313.0925.

N-Phenyl carbazole (**1b**)

^1H NMR (400 MHz, CDCl_3): δ = 8.10 (d, J = 7.8 Hz, 2H), 7.52-7.47 (m, 4H), 7.39-7.33 (m, 5H), 7.26-7.22 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 140.8, 137.6, 129.8, 127.3, 127.0, 125.9, 123.3, 120.2, 119.9, 109.7.

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Notes and references

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