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The Palladium-Catalyzed Intermolecular C−H Chalcogenation of Arenes

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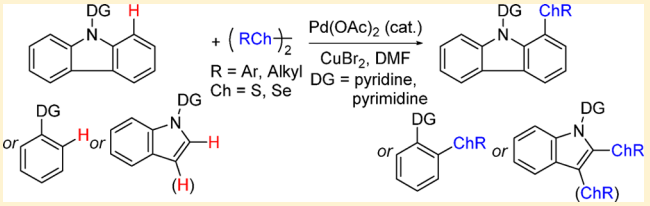
Supporting Information

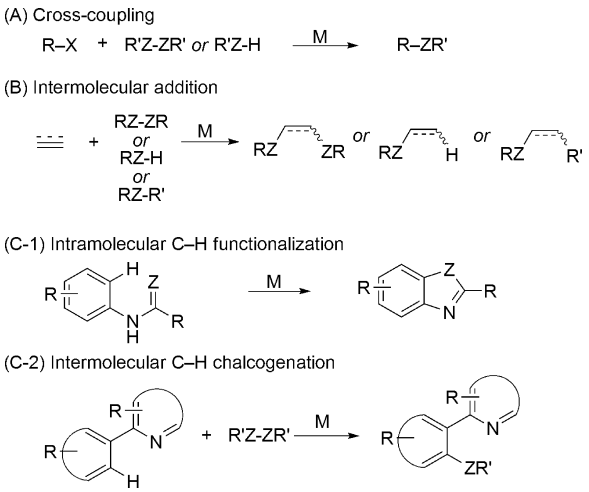
ABSTRACT: Palladium catalyzes the intermolecular chalcogenation of carbazole, 2-phenylpyridine, benzo[*h*]quinolone, and indole derivatives with disulfides and diselenides via selective C−H bond cleavage, providing a convenient route to thio and selenoethers.



INTRODUCTION

A great demand exists in general organic synthesis as well as in the pharmaceutical industry and in material science applications for useful methods of C−S and C−Se bond formation.[1] Transition metal catalysts provide promising tools for this purpose, and the reactions developed thus far can be classified into three general methods. The first method is based on the widely recognized cross-coupling reaction of organo halides with RZH or R_2Z_2 (Z = S, Se) (Scheme 1(A)), which provides reliable routes to the formation of C−Z bonds.[2] Another important approach to the formation of C−Z bonds involves the addition of Z−Z or Z−H or even C−Z bonds across unsaturated C−C bonds of alkynes or alkenes (Scheme 1(B)).[3] The third method is C−H bond functionalization (Scheme 1(C)).[4−8] In comparison with the first two well-established methods, C−S bond formation via C−H bond cleavage has not yet been well developed. *Intramolecular cyclization* reactions, as depicted in Scheme 1(C-1),[4,5] could be performed with[4a] or without[4b,c,5] metal catalysts and the more general *intermolecular* C−S bond formation is known to be catalyzed by Pd,[6] Cu,[7a−g] Ag,[7h] and Rh[8] (Scheme 1(C-2)).

Scheme 1. Transition-Metal-Catalyzed Carbon−Chalcogen Bond Formation (Z = S, Se)



Here, we report on our progress in achieving direct Pd-catalyzed intermolecular C−S bond formation via C−H cleavage[9,10] assisted by a directing group, as shown in Scheme 1(C-2), because a similar transformation has recently been reported.[6a,c] The present C−H sulfenylation reaction is compatible with pyridine and the easily removable pyrimidine as directing groups and readily tolerates various synthetically useful functionalized arenes and heteroarenes, including carbazole, 2-phenylpyridine, benzo[*h*]quinolone, and indole derivatives. In this reaction, indoles afforded mono- or dithioethers selectively depending on the structures of the substrates employed. Furthermore, this method can be easily extended to intermolecular C−Se bond formation.

RESULTS AND DISCUSSION

We first examined the reaction of carbazole **1** with diphenyl disulfide (**2a**) using $Pd(OAc)_2$ as catalyst and 2 equiv of various oxidants in DMF at 140 °C (Table 1, entries 1−5) and found that often used oxidants such as Cu salts as well as an Ag salt showed insignificant or almost no additive effects except for $CuBr_2$, which largely improved yield of desired sulfenylated product **3a** to 94%. In the absence of any oxidants, 95% of carbazole **1** was recovered (entry 6). Although 74% of **1** was consumed with 2 equiv of $CuBr_2$, no sulfenylated product **3a** was obtained in the absence of Pd catalyst (entry 7). Interestingly, the combination of $PdBr_2$ and $Cu(OAc)_2$ as well as $PdBr_2$ and $CuBr_2$ was not effective for the sulfenylation (entries 8 and 9). Although $Cu(OAc)_2$ is known to promote the sulfenylation of aromatic rings with disulfides via

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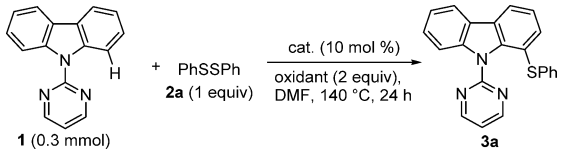
Table 1. Optimization of Reaction Conditions of the Sulfenylation of Carbazole 1 with PhSSPh[a]



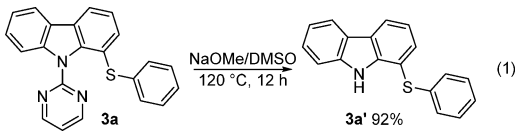
1 (0.3 mmol) 3a

entry	catalyst	oxidant	conv. 1 (%)[b]	yield 3a (%)
1	$Pd(OAc)_2$	$Cu(OAc)_2$	24	23
2	$Pd(OAc)_2$	CuF_2	23	21
3	$Pd(OAc)_2$	$CuCl_2$	19	18
4	$Pd(OAc)_2$	$CuBr_2$	95	94
5	$Pd(OAc)_2$	AgOAc	3	trace
6	$Pd(OAc)_2$		5	trace
7		$CuBr_2$	74	n.d.
8	$PdBr_2$	$Cu(OAc)_2$	38	27
9	$PdBr_2$	$CuBr_2$	14	13
10		$Cu(OAc)_2$	35	30

[a]Reaction conditions: catalyst (10 mol %), carbazole **1** (0.3 mmol), PhSSPh (0.3 mmol), oxidant (0.6 mmol), and solvent (1 mL) at 140 °C for 24 h. [b]Determined by GC.

Ar−H bond cleavage,[7a,c,e] only 30% of **3a** was produced under the conditions (entry 10).[7a,c]

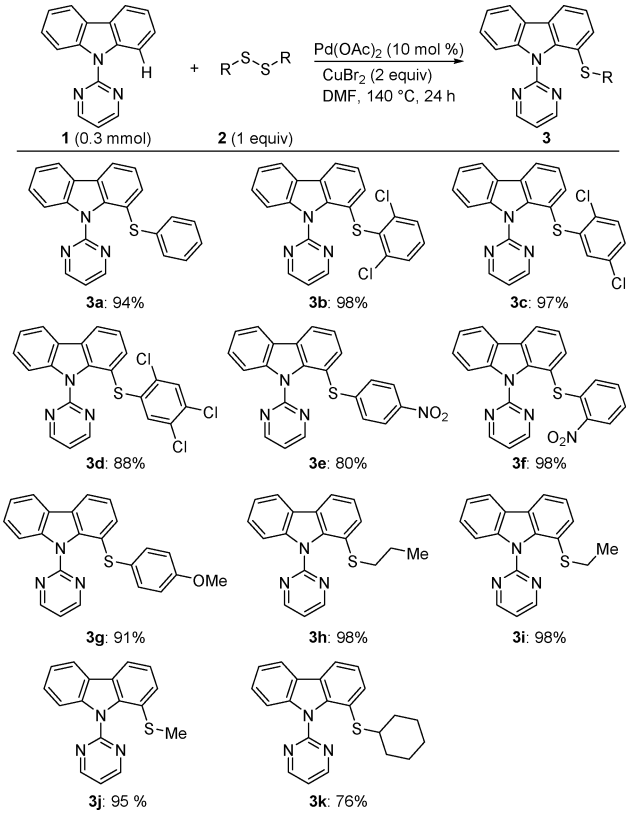
Several diaryl and dialkyl disulfides also were found to react with the carbazole in C−S cross-coupling reactions via *ortho*-C−H bond cleavage (Table 2). Electron-deficient diaryl disulfides bearing chloro groups were highly reactive, giving **3b**−**3d** in 88−98% yields without affecting the C−Cl bonds. Disulfides **2** having a nitro group at the *para*- or *ortho*-position afforded the corresponding products **3e**,**f** in good to nearly quantitative yields (80% and 98%, respectively). An electron-donating methoxy group at the *para*-position did not affect the reaction, and **3g** was produced in 91% yield. In a study reported by Nishihara, dialkyl disulfides were not employed, except for dimethyl disulfide, which inefficiently reacted to give the methylsulfenylated product in only 30% yield.[6a] Our catalytic system afforded the corresponding aryl alkyl sulfides in good to excellent yields (**3h**−**k**, 76−98%), when various primary and secondary alkyl disulfides were used. The pyrimidyl directing group employed here could easily be removed by treating with NaOMe in DMSO at 120 °C for 12 h (eq 1).[11]



Phenylpyridines **4**, benzo[*h*]quinoline **6**, and indoles **8** also reacted with disulfides to give the corresponding diaryl sulfides **5**, **7**, and **9**, respectively, and the results are summarized in Table 3. 2-Phenylpyridine and its methylated analogues showed high reactivities with **5a**−**c** being produced in 83−85% yields. *p*-Bromo- and 2,5-dichlorodiphenyl disulfides gave the expected products **5d** and **5e** in 65% and 72% yields, respectively. Benzo[*h*]quinoline **6** also underwent sulfenylation with diaryl disulfides having either electron-attracting or electron-donating substituents and with dipropyl disulfide to give the corresponding diaryl and aryl alkyl sulfides **7a**−**7d** in excellent yields. Under the same conditions, dimethyl disulfide afforded **7e** in moderate yield (64%). We next turned our attention to indoles, because the sulfenylation of *N*-heteroaromatic C−H bonds is quite limited; only one example of a pyrrole catalyzed by Rh[8] and a few examples of pyrrole and pyridine derivatives catalyzed by Cu[7c,e,g] have been reported, with moderate yields of products being achieved. Indole derivatives with a pyrimidine or a pyridine ring as a directing group were then subjected to the current catalytic system (Table 3, **9a**−**9f**). When bis(4-methoxyphenyl) disulfide was employed, sulfenylation took place selectively at the 2-position, and **9a** was selectively produced in 90% yield. Interestingly, a double sulfenylation proceeded at both the 2- and 3-positions of indoles to give 61−73% yields of **9b**−**9e**, when diphenyl or bis(2,5-dichlorophenyl) disulfides were used. These results along with a preliminary result using $(p\text{-}NO_2C_6H_4S)_2$ that the corresponding disulfenylated product was obtained as the major product in nearly 80% yield may suggest that this selectivity depends on the electronic property of disulfides and the electron-withdrawing group accelerates the second sulfenylation at the 3-position. When the reaction was conducted using 20 mol % of PPh_3, however, the selectivity of the monosulfenylated product did not improve. An indole bearing a methyl substituent at the 3-position underwent monosulfenylation on treatment with diphenyl disulfide to yield **9f** in 94% yield.

We next examined the use of diphenyl diselenide (**10**) (Table 4) in C−Se bond formation. After simple optimization of the reaction conditions, the expected selenylated carbazole derivative **11a** was obtained in 98% yield by heating the reaction mixture at 80 °C for 48 h. Under the same conditions, benzo[*h*]quinoline **6** also coupled with PhSeSePh to give the corresponding products **11c** in 82% yield, which could not be obtained when Nishihara's Pd catalytic system was used.[6c] 2-Phenylpyridine **4** and indole

Table 2. Pd-Catalyzed C−H Bond Sulfenylation of Carbazole 1 with RSSR[a]



[a]Reaction conditions: **1** (0.3 mmol), RSSR (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol), $CuBr_2$ (0.6 mmol), and DMF for 24 h at 140 °C in a sealed tube.

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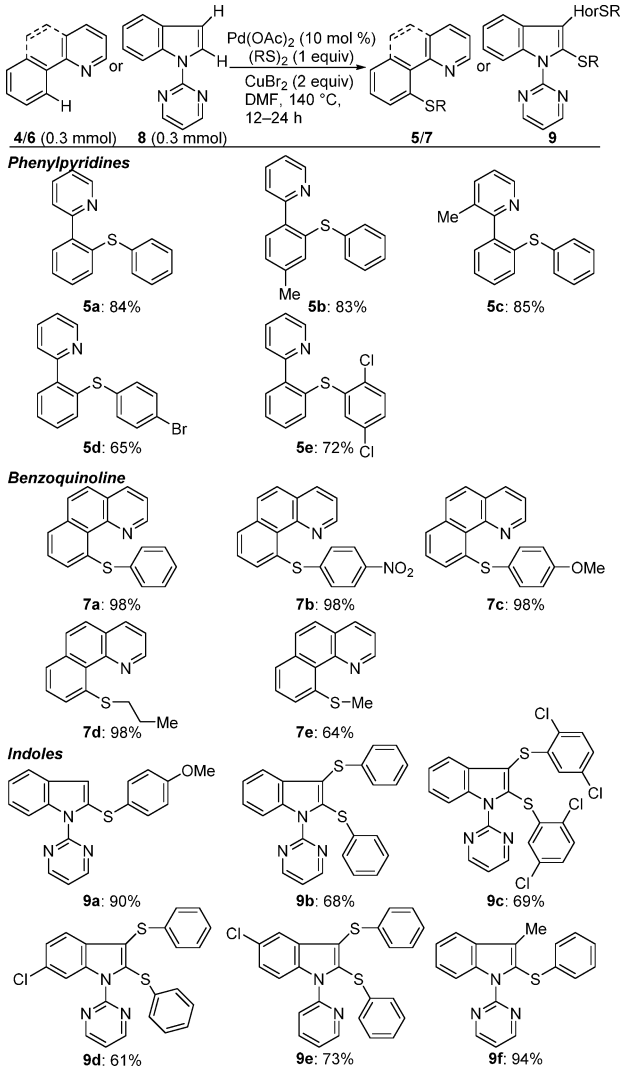
Table 3. C−S Cross-Coupling of Arenes with RSSR Catalyzed by $Pd(OAc)_2$[a]

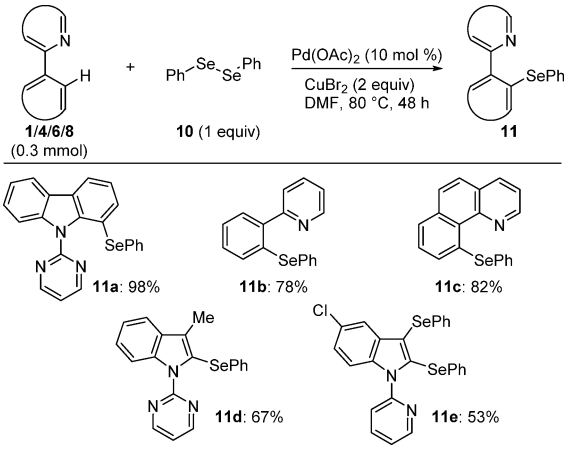


[a]Reaction conditions: **4**/**6**/**8** (0.3 mmol), RSSR (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol), $CuBr_2$ (0.6 mmol), and DMF for 12 h (for **4**) or 24 h (for **6** and **8**) at 140 °C in a sealed tube.

derivatives **8** underwent selenylation to afford **11b**,**d**,**e** in good yields.

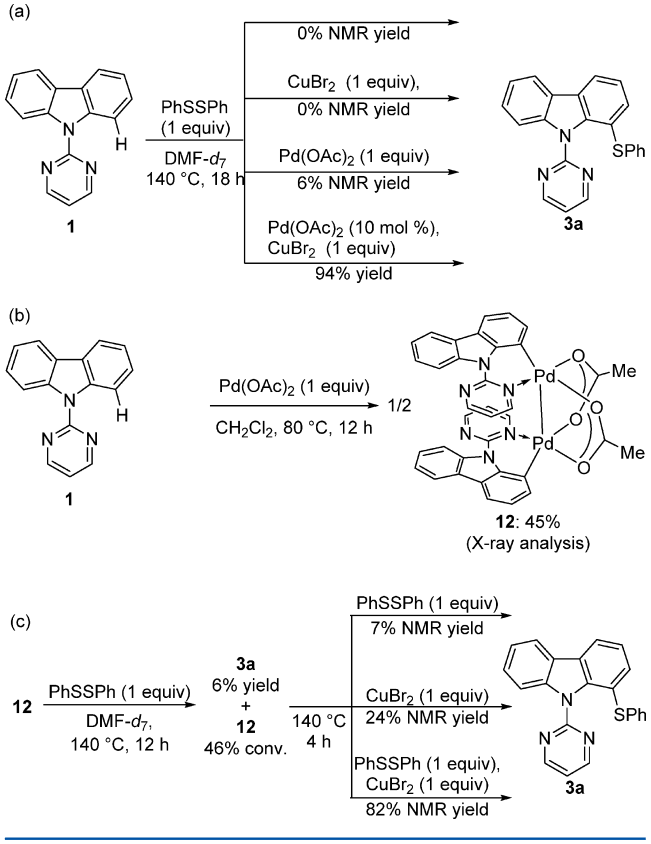
To shed light on the mechanisms responsible for this C−S cross-coupling reaction, we conducted some control experiments (Scheme 2). We conducted four reactions, as shown in Scheme 2a, in the absence and presence of metal catalysts, and the results indicated that both Pd and Cu were essential in the success of the present reaction. The reaction of stoichiometric amounts of carbazole **1** with $Pd(OAc)_2$ proceeded at 80 °C to form **12**[12] (Figure 1) as a dimer of ArPdOAc, generated formally via the metalation of carbazole **1** by Pd(II) (Scheme 2b). This reaction indicates that C−H bond cleavage proceeds readily in the catalytic cycle,[13] as reported for the formation of similar benzo[*h*]quinoline and phenylpyridine complexes.[14,15] When complex **12** was treated with 1 equiv of PhSSPh in DMF at 140 °C for 12 h, both the disulfide and complex **12** (46% conv.) were partially consumed, as evidenced by the ^{1}H NMR spectrum of the reaction mixture, but the expected coupling product **3a** was formed in only 6% yield (Scheme 2c). When an additional equivalent of the disulfide was added to the mixture, no change

Table 4. Selenylation of C−H Bond by PhSeSePh Catalyzed by $Pd(OAc)_2$[a]



[a]Reaction conditions: **1**/**4**/**6**/**8** (0.3 mmol), PhSeSePh (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol), $CuBr_2$ (0.6 mmol), and DMF for 48 h at 80 °C in a sealed tube.

Scheme 2. Control Experiments



was observed, but when an equimolar amount of $CuBr_2$ was added, the coupling product **3a** was formed in 24% yield. In contrast, when both the disulfide and $CuBr_2$ were added, sulfenylation did proceed, leading to the formation of the coupling product in 82% yield. These results indicate that Cu plays an important role in the conversion of C−Pd bonds into C−S bonds in the presence of disulfides. Although detailed reaction mechanisms are not currently clear, Cu may facilitate the transfer of the PhS group to Pd to form a thiolate complex, analogous to **15**, and/or possibly promote the oxidation of Pd to

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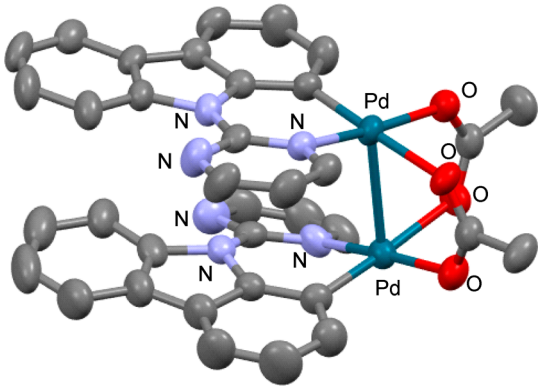
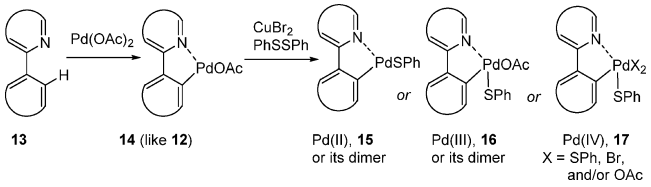


Figure 1. ORTEP drawing of complex **12** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and a solvent molecule ($CHCl_3$) are omitted for clarity.

generate Pd(III) or Pd(IV) complexes, such as **16** or **17** (Scheme 3). Pd thiolate complexes at higher oxidation states such as **16** or

Scheme 3. Possible Pd Species



17 as intermediates cannot be ruled out, because dinuclear Pd complexes such as **12** are known to form dinuclear Pd(III) complexes[14a,b] or mononuclear Pd(IV) complexes[14c] on reacting with suitable oxidizing reagents. The formed Pd complexes carrying the PhS ligand would then undergo reductive elimination to form the coupling products.

CONCLUSION

In conclusion, we report on the development of an efficient method for preparing diaryl or alkyl aryl sulfides and selenides via the *ortho*-C−H functionalization of carbazole, 2-phenylpyridine, benzo[*h*]quinoline, and indole derivatives with diaryl or dialkyl disulfides and diphenyl diselenide catalyzed by a $Pd(OAc)_2$/$CuBr_2$ system without the use of phosphine ligands or any other additives. It was confirmed by isolation of an ArPd(OAc) dimer from a direct reaction of $Pd(OAc)_2$ with Ar−H carrying a directing group that C−H bond cleavage is a facile process. Copper is essential for achieving C−S or C−Se bond formation from Ar−Pd(II) intermediates that are formed by the metalation of arenes carrying a pyrimidyl or pyridyl directing group. It was proposed that Cu might promote this process by transferring ArS and ArSe groups to Pd and/or by generating Pd intermediates with a higher oxidation state.

EXPERIMENTAL SECTION

All manipulations involving air- and moisture-sensitive compounds were carried out by the standard Schlenk techniques under an N_2 atmosphere. Nuclear magnetic resonance (^1H NMR and ^{13}C NMR) spectra were recorded at 400 MHz (^1H NMR) and 100 MHz (^{13}C NMR) in 5 mm NMR tubes. All ^1H NMR chemical shifts were reported in ppm relative to tetramethylsilane at δ 0.00 as an internal reference. All ^{13}C NMR chemical shifts were reported in ppm relative to carbon resonance in chloroform-d_1 at δ 77.00. EI and CI high-resolution mass spectra were recorded with a double-focusing magnetic sector mass instrument. X-ray crystallographic analysis was carried out using an imaging plate diffractometer (Mo−Kα). Preparative TLC (PTLC) was performed using Wakogel B-5F. All commercially available chemicals and dehydrated solvents were purchased and used as received.

General Procedure for Synthesis of 1-(Pyrimidin-2-yl)-1*H*-indole (8a).[10b] NaH (60% dispersion in mineral oil, 440 mg, 11.0 mmol) was added in portions at 0 °C to a stirred solution of indole (1.17 g, 10.0 mmol) in DMF (25 mL). After stirring for 30 min at 0 °C, 2-chloropyrimidine (1.37 g, 12.0 mmol) was added and the mixture was stirred at 130 °C for 24 h. Then, the reaction mixture was cooled to ambient temperature, poured into H_2O (300 mL), and extracted with EtOAc (4 × 75 mL). The combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 4/1) to yield **8a** (1.80 g, 92%) as a colorless solid. Carbazole **1** and indole derivatives **8** were prepared in the same way.

*9-(Pyrimidin-2-yl)carbazole (**1**).*[10b] ^1H NMR (400 MHz, $CDCl_3$) δ 8.86−8.82 (m, 4H), 8.07 (d, J = 7.8 Hz, 2H), 7.52−7.48 (m, 2H), 7.39−7.35 (m, 2H), 7.12−7.10 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.1, 157.8, 139.1, 126.5, 125.7, 122.2, 119.5, 116.1, 115.9.

*1-(Pyrimidin-2-yl)indole (**8a**).*[10b] ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.7 Hz, 1H), 8.70−8.68 (m, 2H), 8.27 (d, J = 3.6 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.36−7.32 (m, 1H), 7.26−7.24 (m, 1H), 7.05−7.02 (m, 1H), 6.71 (d, J = 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.0, 157.7, 135.3, 131.2, 125.7, 123.5, 122.0, 120.7, 116.1, 116.0, 106.8.

*6-Chloro-1-(pyrimidin-2-yl)indole (**8b**).*[16] ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 5.2 Hz, 1H), 8.71 (t, J = 5.2 Hz, 2H), 8.26 (t, J = 4.0 Hz, 1H), 7.52 (t, J = 6.8 Hz, 1H), 7.26−7.21 (m, 1H), 7.08 (t, J = 5.2 Hz, 1H), 6.67 (d, J = 4.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.2, 135.6, 129.7, 129.4, 126.3, 122.6, 122.5, 121.4, 121.3, 116.5, 116.4, 106.6.

*5-Chloro-1-(pyridin-2-yl)indole (**8c**).*[17] ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.21−8.18 (m, 1H), 7.83 (d, J = 6.4 Hz, 1H), 7.71 (t, J = 3.6 Hz, 1H), 7.62 (s, 1H), 7.45 (t, J = 5.2 Hz, 1H), 7.30−7.17 (m, 2H), 6.65 (t, J = 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.9, 138.5, 133.4, 131.5, 127.0, 123.3, 120.4, 120.3, 114.3, 111.9, 105.0, 102.4.

*3-Methyl-1-(pyrimidin-2-yl)indole (**8d**).*[10b] ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.6 Hz, 1H), 8.63 (d, J = 5.0 Hz, 2H), 8.02 (s, 1H) 7.55 (d, J = 7.8 Hz, 1H), 7.36−7.30 (m, 1H), 7.27−7.23 (m, 1H), 6.94 (t, J = 5.0 Hz, 1H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 157.6, 135.5, 132.0, 123.6, 122.8, 121.6, 118.7, 116.1, 116.0, 115.4, 9.7.

General Procedure for Pd-Catalyzed C−S Cross-Coupling of (Hetero)arenes with Disulfides Using $CuBr_2$. To a screw-capped vial equipped with a magnetic stir bar were added carbazole **1**, 2-phenylpyridine **4a**−**4c**, benzo[*h*]quinoline **6**, or indole derivatives **8a**−**8d** (0.3 mmol), disulfide derivatives **2** (0.3 mmol), $Pd(OAc)_2$ (10 mol %), $CuBr_2$ (0.6 mmol), and DMF (1.0 mL) under air atmospheric conditions. The reaction mixture was stirred in a preheated oil bath at 140 °C for 24 h with vigorous stirring. The reaction was cooled to room temperature, filtered through a plug of Celite, and then washed with ethyl acetate (10 mL × 3). The solvents were removed under reduced pressure, and the crude reaction mixture was purified by PTLC on silica gel (*n*-hexane/EtOAc) as an eluent to give the desired product.

*1-(Phenylsulfanyl)-9-(pyrimidin-2-yl)carbazole (**3a**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and diphenyl disulfide (**2a**) (65.6 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **3a** in 94% (99 mg) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 5.0 Hz, 2H), 8.08 (q, J = 7.8 Hz, 3H), 7.49−7.45 (m, 2H), 7.38 (t, J = 6.9 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.21−7.14 (m, 4H), 7.10−7.08 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.5, 158.3, 141.1, 137.6, 132.9, 129.8, 128.7, 128.6, 126.9, 126.3, 124.8, 122.7, 122.2, 120.4, 120.0, 119.6, 118.2, 112.4; HRMS (EI) m/z [M^+] calcd for $C_{22}H_{15}N_3S$ 353.0987, found 353.0989.

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*1-(2,6-Dichlorophenylsulfanyl)-9-(pyrimidin-2-yl)carbazole (**3b**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and bis(2,6-dichlorophenyl) disulfide (**2b**) (107 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **3b** in 98% (123 mg) as a white powder: mp = 174−175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 4.6 Hz, 2H), 8.36 (d, J = 8.7 Hz, 1H), 8.05 (d, J = 7.4 Hz, 1H), 7.93 (d, J = 8.7 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.27 (t, J = 7.8 Hz, 2H), 7.22 (t, J = 5.0 Hz, 1H), 7.18−7.10 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.9, 158.5, 140.8, 139.5, 135.4, 129.8, 129.4, 128.6, 126.9, 126.6, 125.4, 123.0, 122.4, 122.3, 120.0, 118.6, 117.8, 113.2; HRMS (EI) m/z [M$^+$] calcd for $C_{22}H_{13}Cl_2N_3S$ 421.0207, found 421.0204.

*1-(2,5-Dichlorophenylsulfanyl)-9-(pyrimidin-2-yl)carbazole (**3c**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and bis(2,5-dichlorophenyl) disulfide (**2c**) (107 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **3c** in 97% (121 mg) as a yellow gel: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 4.6 Hz, 2H), 8.35 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.93 (dd, J = 7.8, 1.4 Hz, 1H), 7.50−7.46 (m, 1H), 7.39−7.35 (m, 1H), 7.29−7.22 (m, 3H), 7.18−7.09 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.4, 158.3, 141.31, 141.26, 139.7, 135.1, 133.0, 130.0, 129.6, 128.2, 127.5, 127.2, 126.4, 124.4, 122.8, 122.2, 121.7, 120.2, 118.7, 115.3, 112.2; HRMS (EI) m/z [M$^+$] calcd for $C_{22}H_{13}Cl_2N_3S$ 421.0207, found 421.0208.

*1-(2,4,5-Trichlorophenylsulfanyl)-9-(pyrimidin-2-yl)carbazole (**3d**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and bis(2,4,5-trichlorophenyl) disulfide (**2d**) (126 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 10/1) yielded the title compound **3d** in 88% (119 mg) as a yellow gel: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 9.2 Hz, 2H), 8.19 (d, J = 7.4 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.38 (q, J = 7.3 Hz, 2H), 7.33 (d, J = 4.1 Hz, 1H), 7.24 (dd, J = 8.7, 3.6 Hz, 1H), 6.81 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.4, 158.3, 141.2, 141.2, 138.2, 134.9, 131.4, 130.21, 130.18, 129.7, 129.6, 127.6, 127.3, 124.4, 122.9, 122.3, 121.8, 120.2, 118.7, 115.2, 112.2; HRMS (EI) m/z [M$^+$] calcd for $C_{22}H_{12}Cl_3N_3S$ 454.9818, found 454.9820.

*1-(4-Nitrophenylsulfanyl)-9-(pyrimidin-2-yl)carbazole (**3e**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and bis(4-nitrophenyl) disulfide (**2e**) (92 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **3e** in 80% (95 mg) as a yellow solid: mp = 107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.6 Hz, 2H), 8.21 (d, J = 7.8 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 8.7 Hz, 3H), 7.58 (d, J = 8.5 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.40 (q, J = 7.3 Hz, 2H), 7.23 (t, J = 4.6 Hz, 1H), 6.96 (d, J = 9.9 Hz, 2H); ^{13}C{^{1}H} 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 (EI) m/z [M$^+$] calcd for $C_{22}H_{14}N_4O_2S$ 398.0837, found 398.0840.

*1-(2-Nitrophenylsulfanyl)-9-(pyrimidin-2-yl)carbazole (**3f**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and bis(2-nitrophenyl) disulfide (**2f**) (92 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc: 10/1) yielded the title compound **3f** in 98% (117 mg) as a yellow solid: mp = 120−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 4.6 Hz, 2H), 8.28 (dd, J = 7.8, 0.9 Hz, 1H), 8.12 (d, J = 7.3 Hz, 1H), 8.07 (dd, J = 8.2, 1.8 Hz, 1H), 7.69 (dd, J = 7.8, 1.4 Hz, 1H), 7.66 (d, J = 8.2 Hz, 1H), 7.46−7.34 (m, 3H), 7.23−7.12 (m, 3H), 6.73 (dd, J = 8.0, 1.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.1, 141.3 141.1, 138.5, 136.2, 133.7, 133.4, 128.6, 128.5, 127.4, 127.2, 125.5, 125.4, 124.9, 124.0, 122.5, 122.0, 120.2, 119.1, 114.7, 111.7; HRMS (EI) m/z [M$^+$] calcd for $C_{22}H_{14}N_4O_2S$ 398.0837, found 398.0833.

*1-(4-Methoxyphenylsulfanyl)-9-(pyrimidin-2-yl)carbazole (**3g**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and bis(4-methoxyphenyl) disulfide (**2g**) (83 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **3g** in 91% (104 mg) as a yellow solid: mp = 79−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84−8.76 (m, 4H), 8.03 (s, 1H), 7.98 (d, J = 7.3 Hz, 1H), 7.52−7.46 (m, 2H), 7.38−7.33 (m, 3H), 7.11 (t, J = 5.0 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 157.9, 139.4, 138.1, 133.0, 129.7, 129.6, 127.3, 127.0, 126.7, 125.0, 122.4, 122.2, 119.7, 117.0, 116.3, 116.1, 114.8, 55.4; HRMS (EI) m/z [M$^+$] calcd for $C_{23}H_{17}N_3OS$ 383.1092, found 383.1093.

*1-Propylsulfanyl-9-(pyrimidin-2-yl)carbazole (**3h**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and dipropyl disulfide (**2h**) (45 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **3h** in 98% (93 mg) as a yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 5.0 Hz, 2H), 8.03 (dd, J = 12.4, 7.8 Hz, 2H), 7.97 (d, J = 8.7 Hz, 1H), 7.55 (d, J = 7.4 Hz, 1H), 7.43 (t, J = 7.3 Hz, 1H), 7.36−7.29 (m, 2H), 7.26 (t, J = 3.6 Hz, 2H), 2.75 (t, J = 7.3 Hz, 2H), 1.44−1.35 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.9, 158.4, 141.3, 140.5, 130.1, 126.7, 126.5, 125.1, 122.5, 122.3, 120.1, 118.4, 118.2, 112.2, 38.5, 22.5, 13.3; HRMS (EI) m/z [M$^+$] calcd for $C_{19}H_{17}N_3S$ 319.1143, found 319.1142.

*1-Ethylsulfanyl-9-(pyrimidin-2-yl)carbazole (**3i**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and diethyl disulfide (**2i**) (37 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **3i** in 98% (89 mg) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 5.0 Hz, 2H), 8.04 (t, J = 8.7 Hz, 2H), 7.97 (dd, J = 7.4, 0.9 Hz, 1H), 7.54 (dd, J = 7.8, 0.9 Hz, 1H), 7.43 (td, J = 8.2, 1.4 Hz, 1H), 7.36−7.31 (m, 2H), 7.26 (t, J = 5.0 Hz, 1H), 2.80 (q, J = 7.4 Hz, 2H), 1.06 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.5, 141.3, 129.9, 126.8, 126.5, 125.1, 124.6, 124.4, 122.5, 122.1, 120.1, 118.5, 118.2, 112.3, 30.3. 14.3; HRMS (EI) m/z [M$^+$] calcd for $C_{18}H_{15}N_3S$ 305.0987, found 305.0988.

*1-(Methylthio)-9-(pyrimidin-2-yl)carbazole (**3j**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and dimethyl disulfide (**2j**) (28 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **3j** in 95% (82 mg) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, J = 7.2, 1.2 Hz, 2H), 8.11−8.04 (m, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.50−7.42 (m, 2H), 7.38−7.32 (m, 2H), 7.23 (td, J = 5.2, 1.2 Hz, 1H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.5, 141.3, 129.3, 127.6, 126.8, 126.4, 125.2, 124.4, 123.2, 122.7, 122.1, 120.1, 118.1, 117.8, 112.5, 19.1; HRMS (EI) m/z [M$^+$] calcd for $C_{17}H_{13}N_3S$ 291.0830, found 291.0830.

*1-(Cyclohexylthio)-9-(pyrimidin-2-yl)carbazole (**3k**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and dicyclohexyl disulfide (**2k**) (69 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **3k** in 76% (81 mg) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 5.0 Hz, 2H), 8.05 (d, J = 7.8 Hz, 1H), 8.01 (dd, J = 7.3, 1.4 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.58 (dd, J = 7.8, 1.3 Hz, 1H), 7.42 (td, J = 6.9, 1.4 Hz, 1H), 7.35−7.26 (m, 3H), 2.91 (td, J = 6.4, 3.6 Hz, 1H), 1.61 (t, J = 13.8 Hz, 5H), 1.19−1.03 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.5, 141.9, 141.4, 132.9, 126.7, 126.4, 125.0, 122.2, 121.9, 120.1, 120.0, 119.4, 118.5, 111.9, 110.8, 48.5, 33.1, 25.9, 25.7; HRMS (EI) m/z [M$^+$] calcd for $C_{22}H_{21}N_3S$ 359.1456, found 359.1454.

*2-(2-Phenylsulfanylphenyl)pyridine (**5a**).*[7a] The representative general procedure mentioned above was followed using 2-phenylpyridine (**4a**) (47.5 mg, 0.30 mmol) and diphenyl disulfide (**2a**) (65.6 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **5a** in 84% (66.3 mg) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.6 Hz, 1H), 7.73 (td, J = 7.8, 1.8 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.53 (dd, J = 7.3, 1.4 Hz, 1H), 7.33−7.21 (m, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.2, 149.0, 141.1, 135.9, 135.5, 135.4, 132.1, 131.3, 130.3, 129.2, 128.9, 127.3, 126.7, 124.2, 122.1; HRMS (EI) m/z [M$^+$] calcd for $C_{17}H_{13}NS$ 263.0769, found 263.0770.

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*2-(4-Methyl-2-(phenylsulfanyl)phenyl)pyridine (**5b**).* The representative general procedure mentioned above was followed using 2-(*p*-tolyl)pyridine (**4b**) (51 mg, 0.30 mmol) and diphenyl disulfide (**2a**) (65.4 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **5b** in 83% (68.9 mg) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 5.0 Hz, 2H), 8.09 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.26 (t, J = 6.8 Hz, 1H), 7.15−7.06 (m, 3H), 7.03 (t, J = 8.3 Hz, 3H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.0, 157.2, 137.9, 137.5, 129.2, 128.71, 128.65, 126.6, 125.2, 125.1, 124.9, 124.8, 121.7, 119.1, 117.5, 113.0, 10.1; HRMS (EI) m/z [M$^+$] calcd for $C_{18}H_{15}NS$ 277.0925, found 277.0923.

*3-Methyl-2-(2-phenylsulfanylphenyl)pyridine (**5c**).* The representative general procedure mentioned above was followed using 3-methyl-2-phenylpyridine (**4c**) (51 mg, 0.30 mmol) and diphenyl disulfide (**2a**) (74 mg, 0.75 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **5c** in 85% (70.6 mg) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, J = 4.6, 0.9 Hz, 1H), 7.56 (dd, J = 7.8, 0.9 Hz, 1H), 7.32−7.15 (m, 10H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.1, 146.6, 141.3, 137.7, 135.6, 134.9, 132.2, 131.9, 130.8, 129.4, 129.0, 128.6, 127.3, 126.7, 122.6, 19.1; HRMS (EI) m/z [M$^+$] calcd for $C_{18}H_{15}NS$ 277.0925, found 277.0924.

*2-(2-(4-Bromophenylsulfanyl)phenyl)pyridine (**5d**).* The representative general procedure mentioned above was followed using 2-phenylpyridine (**4a**) (51 mg, 0.30 mmol) and bis(4-bromophenyl) disulfide (**2l**) (112 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **5d** in 65% (64.5 mg) as a yellow powder: mp = 187−188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.6 Hz, 1H), 7.72 (td, J = 13.8, 5.8 Hz, 1H), 7.55 (d, J = 7.8 Hz, 2H), 7.38−7.24 (m, 6H), 7.13 (d, J = 8.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.8, 137.9, 137.1, 135.5, 133.9, 133.7, 133.5, 133.4, 130.7, 130.3, 128.6, 125.5, 125.3; HRMS (EI) m/z [M$^+$] calcd for $C_{17}H_{12}{}^{79}BrNS$ 340.9874, found 340.9875.

*2-(2-(2,5-Dichlorophenylsulfanyl)phenyl)pyridine (**5e**).* The representative general procedure mentioned above was followed using 2-phenylpyridine (**4a**) (43 mg, 0.25 mmol) and bis(2,5-dichlorophenyl) disulfide (**2c**) (106 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **5e** in 72% (71 mg) as a white solid: mp = 117−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 11.8 Hz, 1H), 7.70 (td, J = 9.2, 1.4 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.46 (quin, J = 8.7 Hz, 1H), 7.40 (t, J = 4.8 Hz, 2H), 7.22 (d, J = 12.8 Hz, 2H), 7.05 (dd, J = 8.2, 2.3 Hz, 1H), 7.00 (d, J = 2.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.8, 149.1, 138.2, 135.9, 133.9, 132.9, 132.0, 131.1, 130.9, 130.6, 130.5, 129.5, 128.6, 127.4, 124.0, 122.3; HRMS (CI) m/z [M + H$^+$] calcd for $C_{17}H_{12}Cl_2NS$ 332.0068, found 332.0062.

*10-(Phenylsulfanyl)benzo[h]quinoline (**7a**).* The representative general procedure mentioned above was followed using benzo[*h*]-quinoline (**6**) (53.7 mg, 0.30 mmol) and diphenyl disulfide (**2a**) (64.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **7a** in 98% (84 mg) as a white solid: mp = 77−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (dd, J = 4.6, 1.8 Hz, 1H), 8.19 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.7 Hz, 1H), 7.79−7.62 (m, 4H), 7.53 (dd, J = 12.4, 4.1 Hz, 1H), 7.51−7.45 (m, 3H), 7.37 (t, J = 3.6 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 146.4, 146.3, 140.5, 136.2, 135.2, 135.00, 134.97, 129.7, 128.9, 128.5, 127.2, 127.1, 125.5, 125.4, 124.5, 120.9; HRMS (EI) m/z [M$^+$] calcd for $C_{19}H_{13}NS$ 287.0769, found 287.0771.

*10-(4-Nitrophenylsulfanyl)benzo[h]quinoline (**7b**).* The representative general procedure mentioned above was followed using benzo[*h*]quinoline (**6**) (53.7 mg, 0.30 mmol) and bis(4-nitrophenyl) disulfide (**2e**) (92 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **7b** in 98% (97 mg) as a yellow solid: mp = 192−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (dd, J = 4.1, 1.4 Hz, 1H), 8.28−8.24 (m, 3H), 7.85−7.74 (m, 5H), 7.59 (dd, J = 8.2, 4.6 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.17 (dd, J = 8.3, 0.9 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.5, 146.8, 146.4, 145.6, 137.5, 135.3, 135.1, 131.1, 128.4, 127.9, 127.4, 127.2, 126.8, 125.9, 125.8, 124.5, 121.4; HRMS (EI) m/z [M$^+$] calcd for $C_{19}H_{12}N_2O_2S$ 332.0619, found 332.0621.

*10-(4-Methoxyphenylsulfanyl)benzo[h]quinoline (**7c**).* The representative general procedure mentioned above was followed using benzo[*h*]quinoline (**6**) (53.7 mg, 0.30 mmol) and bis(4-methoxyphenyl) disulfide (**2g**) (83 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **7c** in 98% (93 mg) as a white powder: mp = 77−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (ddd, J = 7.8, 1.8, 0.9 Hz, 1H), 9.00 (dd, J = 4.1, 1.8 Hz, 1H), 8.42 (d, J = 9.6 Hz, 1H), 8.20 (dd, J = 8.2, 1.8 Hz, 1H), 7.75 (d, J = 9.2 Hz, 1H), 7.64−7.54 (m, 3H), 7.33 (m, 2H), 6.87 (m, 2H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3, 149.0, 146.5, 135.8, 134.4, 133.4, 132.7, 132.4, 131.4, 127.0, 126.2, 125.9, 125.6, 124.4, 123.8, 122.1, 115.0, 55.3; HRMS (EI) m/z [M$^+$] calcd for $C_{20}H_{15}NOS$ 317.0874, found 317.0874.

*10-(Propylsulfanyl)benzo[h]quinoline (**7d**).* The representative general procedure mentioned above was followed using benzo[*h*]-quinoline (**6**) (53.7 mg, 0.30 mmol) and dipropyl disulfide (**2h**) (45 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **7d** in 75% (49.6 mg) as a white solid: mp = 77−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (dd, J = 4.6, 1.8 Hz, 1H), 8.19 (dd, J = 7.8, 1.8 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.69 (dd, J = 6.0, 2.8 Hz, 2H), 7.62 (t, J = 2.8 Hz, 2H), 7.53 (dd, J = 8.2, 4.6 Hz, 1H), 3.03 (t, J = 7.8 Hz, 2H), 1.97−1.88 (m, 2H), 1.18 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.5, 146.3, 139.6, 135.3, 135.1, 128.6, 128.0, 127.3, 127.1, 125.6, 124.0, 123.1, 120.8, 35.6, 21.5, 14.4; HRMS (EI) m/z [M$^+$] calcd for $C_{16}H_{15}NS$ 253.0925, found 253.0926.

*10-(Methylsulfanyl)benzo[h]quinoline (**7e**).*[7b] The representative general procedure mentioned above was followed using benzo[*h*]-quinoline (**6**) (53.7 mg, 0.30 mmol) and dimethyl disulfide (**2j**) (28 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **7e** in 64% (43 mg) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (dd, J = 4.1, 1.8 Hz, 1H), 8.20 (dd, J = 7.3, 5.5 Hz, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.72−7.64 (m, 3H), 7.58−7.51 (m, 2H), 2.59 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.5, 146.2, 140.1, 135.14, 135.08, 128.6, 128.0, 127.4, 127.0, 125.7, 124.1, 122.5, 120.8, 17.7; HRMS (EI) m/z [M$^+$] calcd for $C_{14}H_{11}NS$ 225.0612, found 225.0611.

*2-(4-Methoxyphenylsulfanyl)-1-(pyrimidin-2-yl)indole (**9a**).* The representative general procedure mentioned above was followed using 1-(pyrimidin-2-yl)indole (**8a**) (58.5 mg, 0.30 mmol) and bis(4-methoxyphenyl) disulfide (**2g**) (83 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **9a** in 90% (90 mg) as a light yellow solid: mp = 109−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 8.2 Hz, 1H), 8.66 (d, J = 5.0 Hz, 2H), 8.50 (s, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.35 (t, J = 7.3 Hz, 1H), 7.24 (t, J = 8.7 Hz, 3H), 7.01 (t, J = 4.6 Hz, 1H), 6.75 (d, J = 11.9 Hz, 2H), 3.71 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.1, 157.2, 135.9, 131.4, 130.3, 129.8, 127.6, 124.4, 122.6, 119.7, 116.6, 116.4, 114.5, 110.4, 55.2; HRMS (EI) m/z [M$^+$] calcd for $C_{19}H_{15}N_3OS$ 333.0936, found 333.0938.

*2,3-Bis(phenylsulfanyl)-1-(pyrimidin-2-yl)indole (**9b**).* The representative general procedure mentioned above was followed using 1-(pyrimidin-2-yl)indole (**8a**) (58.5 mg, 0.30 mmol) and diphenyl disulfide (**2a**) (64.5 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **9b** in 68% (84 mg) as a yellow gel: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 5.0 Hz, 2H), 7.97 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.34 (t, J = 7.7 Hz, 1H), 7.24−7.18 (m, 2H), 7.13 (d, J = 4.1 Hz, 4H), 7.10−6.99 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 156.7, 137.7, 136.8, 136.4, 134.9, 129.5, 128.69, 128.66, 128.4, 127.1, 126.1, 125.24, 125.19, 122.6, 120.1, 118.6, 116.6, 112.8; HRMS (EI) m/z [M$^+$] calcd for $C_{24}H_{17}N_3S_2$ 411.0864, found 411.0865.

*2,3-Bis(2,5-dichlorophenylsulfanyl)-1-(pyrimidin-2-yl)indole (**9c**).* The representative general procedure mentioned above was followed using 1-(pyrimidin-2-yl)indole (**8a**) (58.5 mg, 0.30 mmol) and bis(2,5-dichlorophenyl) disulfide (**2c**) (107 mg, 0.30 mmol). Purification by PTLC on silica gel (*n*-hexane/EtOAc = 10/1) yielded the title compound **9c** in 69% (113 mg) as a yellow powder: mp = 90−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 5.0 Hz, 2H), 8.10 (d, J = 8.7 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.23−7.16 (m, 3H), 7.06 (d, J = 8.8 Hz, 1H), 6.94 (d, J = 8.7 Hz, 1H), 6.79 (dd, J =

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6.3, 2.3 Hz, 1H), 6.70 (dd, J = 8.7, 2.8 Hz, 1H), 6.33 (d, J = 2.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.2, 156.5, 137.34, 137.31, 135.6, 135.3, 132.90, 132.85, 132.4, 132.3, 130.1, 129.6, 128.7, 127.9, 125.8, 125.7, 125.6, 123.4, 119.4, 118.7, 113.5, 112.8; HRMS (EI) m/z [M^+] calcd for $C_{24}H_{13}Cl_4N_3S_2$ 546.9305, found 546.9309.

*6-Chloro-2,3-bis(phenylsulfanyl)-1-(pyrimidin-2-yl)indole (**9d**).* The representative general procedure mentioned above was followed using 6-chloro-1-(pyrimidin-2-yl)indole (**8b**) (69 mg, 0.30 mmol) and diphenyl disulfide (**2a**) (64.5 mg, 0.30 mmol). Purification by PTLC on silica gel (n-hexane/EtOAc = 10/1) yielded the title compound **9d** in 61% (81 mg) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 4.1 Hz, 1H), 7.70 (t, J = 7.4 Hz, 1H), 7.54 (s, 1H), 7.31–7.21 (m, 3H), 7.16 (d, J = 9.2 Hz, 1H), 7.10–6.96 (m, 7H), 6.84 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.5, 149.1, 138.3, 136.7, 136.5, 135.4, 134.5, 129.9, 128.9, 128.8, 128.0, 127.7, 126.4, 126.1, 125.2, 123.2, 122.4, 119.2, 113.0; HRMS (EI) m/z [M^+] calcd for $C_{24}H_{16}ClN_3S_2$ 445.0474, found 445.0478.

*5-Chloro-2,3-bis(phenylsulfanyl)-1-(pyridin-2-yl)indole (**9e**).* The representative general procedure mentioned above was followed using 5-chloro-1-(pyridin-2-yl)indole (**8c**) (68 mg, 0.30 mmol) and diphenyl disulfide (**2a**) (64.5 mg, 0.30 mmol). Purification by PTLC on silica gel (n-hexane/EtOAc = 10/1) yielded the title compound **9e** in 73% (97 mg) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 5.0 Hz, 2H), 8.01 (d, J = 1.8 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.24–7.02 (m, 13H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.4, 156.4, 137.9, 136.4, 136.1, 135.8, 131.2, 128.8, 128.7, 128.1, 127.2, 126.3, 125.5, 123.4, 121.0, 118.8, 116.7, 113.1; HRMS (EI) m/z [M^+] calcd for $C_{25}H_{17}ClN_2S_2$ 444.0522, found 444.0524.

*3-Methyl-2-(phenylsulfanyl)-1-(pyrimidin-2-yl)indole (**9f**).* The representative general procedure mentioned above was followed using 3-methyl-1-(pyrimidin-2-yl)indole (**8d**) (63 mg, 0.30 mmol) and diphenyl disulfide (**2a**) (64.5 mg, 0.30 mmol). Purification by PTLC on silica gel (n-hexane/EtOAc = 10/1) yielded the title compound **9f** in 94% (89 mg) as a yellow gel: ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 5.0 Hz, 2H), 8.11 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.26 (t, J = 6.4 Hz, 1H), 7.15–7.09 (m, 3H), 7.03 (t, J = 3.0 Hz, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.0, 157.2, 137.9, 137.5, 129.2, 128.7, 126.6, 125.24, 125.20, 124.9, 124.8, 121.7, 119.1, 117.5, 113.0, 10.1; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{15}N_3S$ 317.0987, found 317.0985.

General Procedure for Pd-Catalyzed C–Se Cross-Coupling of (Hetero)arenes with PhSeSePh by Using $CuBr_2$. To a screw-capped vial equipped with a magnetic stir bar was added carbazole **1**, 2-phenylpyridine **4a**, benzo[h]quinolone **6**, or indole derivatives **8c**, **8d** (0.3 mmol), PhSeSePh (0.3 mmol), $Pd(OAc)_2$ (10 mol %), $CuBr_2$ (0.6 mmol), and DMF (1.0 mL) under air atmospheric conditions. The reaction mixture was stirred in a preheated oil bath at 80 °C for 48 h with vigorous stirring. The reaction was cooled to room temperature, filtered through a plug of Celite, and then washed with ethyl acetate (10 mL × 3). 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 or PTLC method to give desired selenylated product.

*1-(Phenylselanyl)-9-(pyrimidin-2-yl)carbazole (**11a**).* The representative general procedure mentioned above was followed using 9-(pyrimidin-2-yl)carbazole (**1**) (73.5 mg, 0.30 mmol) and diphenyl diselenide (**10**) (93.6 mg, 0.30 mmol). Purification by PTLC on silica gel (n-hexane/EtOAc = 10/1) yielded the title compound **11a** in 98% (117 mg) as a yellow solid: mp = 131–132 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.85–8.78 (m, 4H), 8.31 (d, J = 1.4 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.70 (dd, J = 8.7, 1.8 Hz, 1H), 7.51 (dt, J = 7.3, 1.4 Hz, 1H), 7.41–7.34 (m, 3H), 7.24–7.18 (m, 3H), 7.11 (t, J = 4.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.9, 157.9, 139.3, 138.8, 133.34, 133.30, 130.9, 129.2, 127.1, 127.0, 126.42, 126.37, 124.9, 122.5, 122.1, 119.7, 117.2, 116.3, 116.2; HRMS (EI) m/z [M^+] calcd for $C_{22}H_{15}N_3Se$ 401.0431, found 401.0432.

*2-(2-Phenylselanylphenyl)pyridine (**11b**).* The representative general procedure mentioned above was followed using 2-phenylpyridine (**4a**) (47.5 mg, 0.30 mmol) and diphenyl diselenide (**10**) (93.6 mg, 0.30 mmol). Purification by PTLC on silica gel (n-hexane/EtOAc = 10/1) yielded the title compound **11b** in 78% (72 mg) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.76–8.74 (m, 1H), 7.80 (td, J = 7.8, 1.8 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.60 (td, J = 7.3 Hz, 3H), 7.38–7.22 (m, 5H), 7.18–7.12 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.5, 148.2, 139.7, 136.5, 135.9, 134.4, 131.3, 131.2, 129.4, 129.2, 128.9, 128.2, 125.9, 122.7, 122.1; HRMS (EI) m/z [M^+] calcd for $C_{17}H_{13}NSe$ 311.0213, found 311.0210.

*10-(Phenylselanyl)benzo[h]quinolone (**11c**).* The representative general procedure mentioned above was followed using benzo[h]-quinoline (**6**) (53.7 mg, 0.30 mmol) and diphenyl diselenide (**10**) (93.6 mg, 0.30 mmol). Purification by PTLC on silica gel (n-hexane/EtOAc = 10/1) yielded the title compound **11c** in 82% (82 mg) as a yellow solid: mp = 128–129 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.14 (dd, J = 4.1, 1.4 Hz, 1H), 8.22 (dd, J = 8.2, 1.8 Hz, 1H), 7.85–7.80 (m, 3H), 7.70 (d, J = 8.7 Hz, 2H), 7.57 (dd, J = 8.2, 4.6 Hz, 1H), 7.49–7.44 (m, 3H), 7.37 (t, J = 7.8 Hz, 1H), 7.26–7.23 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.1, 145.8, 137.6, 137.4, 135.9, 135.2, 132.9, 130.9, 129.7, 129.3, 128.7, 128.6, 128.5, 127.7, 127.0, 125.3, 125.0, 121.1; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{13}NSe$ 335.0213, found 335.0210.

*3-Methyl-2-(phenylselanyl)-1-(pyrimidin-2-yl)indole (**11d**).* The representative general procedure mentioned above was followed using 3-methyl-1-(pyrimidin-2-yl)indole (**8d**) (63 mg, 0.30 mmol) and diphenyl diselenide (**10**) (93.6 mg, 0.30 mmol). Purification by PTLC on silica gel (n-hexane/EtOAc = 10/1) yielded the title compound **11d** in 75% (49.6 mg) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 5.0 Hz, 2H), 8.30 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 7.3 Hz, 1H), 7.31 (td, J = 8.7, 1.4 Hz, 1H), 7.26–7.22 (m, 3H), 7.17–7.11 (m, 4H), 2.12 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.7, 157.5, 137.7, 133.5, 130.24, 130.20, 129.0, 126.2, 124.2, 123.5, 123.4, 121.7, 118.6, 117.0, 113.2, 11.1; HRMS (EI) m/z [M^+] calcd for $C_{19}H_{15}N_3Se$ 365.0431, found 365.0433.

*5-Chloro-2,3-bis(phenylselanyl)-1-(pyridin-2-yl)indole (**11e**).* The representative general procedure mentioned above was followed using 5-chloro-1-(pyridin-2-yl)indole (**8c**) (69 mg, 0.30 mmol) and diphenyl diselenide (**10**) (93.6 mg, 0.30 mmol). Purification by PTLC on silica gel (n-hexane/EtOAc = 10/1) yielded the title compound **11e** in 53% (86 mg) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, J = 5.5, 1.8 Hz, 1H), 7.78 (td, J = 7.8, 2.3 Hz, 1H), 7.63 (d, J = 1.8 Hz, 1H), 7.33–7.28 (m, 2H), 7.26–7.24 (m, 3H), 7.19–7.13 (dd, J = 8.7, 1.8 Hz, 1H), 7.14–7.12 (m, 3H), 7.07–6.98 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.7, 149.2, 138.0, 137.5, 134.3, 132.3, 131.7, 131.2, 130.9, 129.6, 129.1, 127.7, 127.0, 126.1, 124.7, 123.1, 122.8, 120.4, 112.6, 111.4; HRMS (EI) m/z [M^+] calcd for $C_{25}H_{17}ClN_2Se_2$ 539.9411, found 539.9408.

Cleavage of Pyrimidine Directing Group.[11] To a solution of 1-(phenylsulfanyl)-9-(pyrimidin-2-yl)carbazole (**3a**) (105 mg, 0.30 mmol) in DMSO (1 mL) was added NaOMe (162 mg, 3.0 mmol), and the mixture was sealed in a tube. The resultant mixture was stirred at 120 °C for 12 h. The obtained mixture was diluted with EtOAc and washed with saturated $NaHCO_3$. The aqueous layer was extracted with EtOAc. The combined EtOAc solution was evaporated. Purification by column chromatograph on silica gel (n-hexane/EtOAc = 10/1) yielded the corresponding carbazole **3a'** in 92% (76 mg) as a white crystal: mp = 116–117 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H, NH), 8.05 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.56 (dd, J = 7.4, 0.9 Hz, 1H), 7.57–7.55 (m, 2H), 7.35–7.30 (m, 2H), 7.21–7.17 (m, 2H), 7.12–7.00 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 139.0, 136.7, 132.9, 129.1, 126.7, 126.3, 125.6, 123.8, 123.5, 121.8, 120.6, 120.1, 119.8, 112.3, 110.9; HRMS (EI) m/z [M^+] calcd for $C_{18}H_{13}NS$ 275.0769, found 275.0766.

Synthesis of Pd-Carbazole Complex.[14b] To a solution of **1** (245.3 mg, 1 mmol) in 10 mL of CH_2Cl_2 was added in $Pd(OAc)_2$ (223 mg, 1 mmol), the resultant mixture was stirred in a sealed tube at 80 °C for 12 h. After cooling to the room temperature, 1.0 mL of anhydrous n-hexane was added and the mixture was stored for 24 h at −20 °C in a refrigerator. Then, the brown crystal of complex **12** was precipitated and collected by filtration, yield 45% (183 mg): mp = 255–258 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, J = 6.0, 2.4 Hz, 2H), 8.00–7.98 (m, 4H), 7.82 (d, J = 7.6 Hz, 2H), 7.50 (dd, J = 4.8, 2.0 Hz, 2H), 7.27–7.23 (m, 2H), 7.06 (td, J = 8.4, 1.6 Hz, 2H), 6.98–6.92 (m, 4H), 6.33–6.28 (m,

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2H), 2.22 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 181.4, 159.1, 157.1, 149.8, 137.8, 135.8, 130.6, 127.4, 126.1, 123.2, 122.4, 122.2, 119.5, 118.7, 115.4, 114.0, 112.8, 24.8; Anal. Calcd for $C_{36}H_{26}N_6O_4Pd_2$: C, 52.76; H, 3.20; N, 10.26. Found: C, 52.67; H, 3.52; N, 10.14. Single crystals of **12**·$CHCl_3$ suitable for X-ray crystallography were obtained by recrystallization from $CHCl_3$. The structure was solved by direct method (SHELX-97[18]). The structure was refined on F^2 by full-matrix least-squares method using SHELXL-97. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. $C_{37}H_{27}Cl_3N_6O_4Pd_2$, T = 123(2) K, M = 938.82, monoclinic, $P2_1/c$, a = 15.7682(3) Å, b = 15.6424(3) Å, c = 16.4914(4) Å, β = 119.5469(7) °, V = 3538.62(13) Å^3, Z = 4, D_{calcd} = 1.762 g/cm^3, R_{int} = 0.032, R_1 = 0.029, wR_2 = 0.069 for $I > 2\sigma(I)$, R_1 = 0.032, wR_2 = 0.071 for all data. CCDC 948474.

■ ASSOCIATED CONTENT

Supporting Information

NMR charts of isolated compounds and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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