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Rh(III)-Catalyzed C7-Thiolation and Selenation of Indolines

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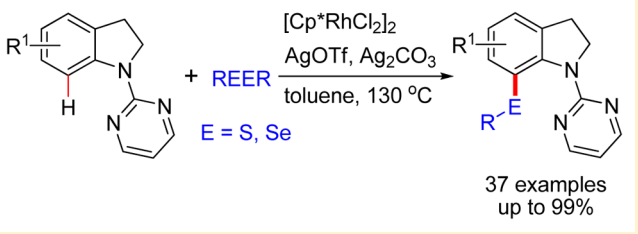
Supporting Information

ABSTRACT: The rhodium(III)-catalyzed intermolecular C7-thiolation and selenation of indolines with disulfides and diselenides were developed. This protocol relies on the use of a removable pyrimidyl directing group to access valuable C-7 functionalized indoline scaffolds with ample substrate scope and broad functional group tolerance.



INTRODUCTION

Indole and indoline scaffolds are ubiquitous structural motifs found in a multitude of biologically active natural products and pharmaceutical compounds as well as organic dyes.[1] In particular, 7-substituted indoles and indolines are particularly important as a result of their ubiquitous presence in numerous biologically active compounds.[2] Therefore, a method for a general, rapid, and regioselective preparation of 7-substituted indoles and indolines would be highly desirable.

Transition-metal-catalyzed C−H bond functionalization has emerged as a powerful tool due to its remarkable potential for step economy and environmental sustainability.[3] Given the significance of 7-substituted indolines, it would be highly desirable and attractive if we could directly functionalize the C−H bond at the C-7 position of an indoline by using a transition-metal-catalyzed C−H activation pathway. Recently, some examples of transition-metal-catalyzed chelation-assisted C7 C−H functionalization of indolines with various coupling partners have been disclosed by several groups,[4−11] e.g., arylation (Figure 1, 1.1a),[4] alkenylation (Figure 1, 1.1b),[5] alkynylation (Figure 1, 1.1c),[6] amination (Figure 1, 1.1d),[7] acylation (Figure 1, 1.1f),[8] allylation (Figure 1, 1.1g),[9] alkylation (Figure 1, 1.1h) of indolines,[10] and C−H functionalization/annulation to build 1,7-fused indolines (Figure 1, 1.1e).[11] However, these approaches are generally limited to C−C bond and C−N bond formation. To the best of our knowledge, there is no report on catalytic C-7 C−H thiolation or selenation of indolines, although C−S and C−Se bonds represent an important linkage in organic compounds and are widely found in biologically active natural products, pharmaceuticals, and functional materials.[12] While numerous approaches to C−N or C−C bond formation through direct C−H functionalization have been reported in recent years, reports of analogous C−S and C−Se bond formation through direct C−H thiolation and selenation by transition metals remain scarce.[13] Recently, Cu(II)-,[14] Pd(II)-,[15] Rh(III)-,[16] and

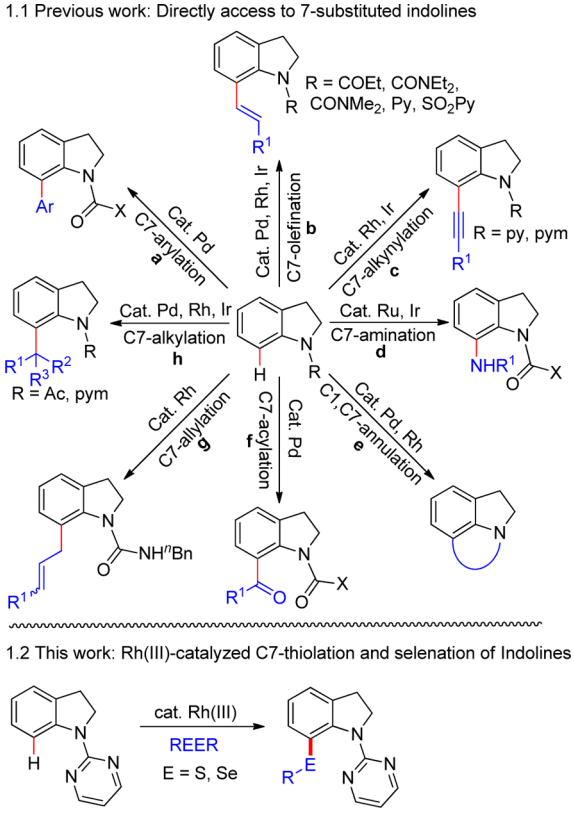


Figure 1. Transition-metal-catalyzed C7-selective C−H functionalization of indolines.

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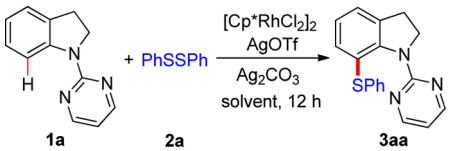
Ni(II)-catalyzed[17] chelate-assisted direct chalcogenations of inert C−H bonds with disulfides and diselenides have been reported by the groups of Yu, Daugulis, Nishihara, Kambe, Zhou and Li, Lu, Shi, Zhang, and Qiu. Inspired by these pioneering studies and our interest in the Rh(III)-catalyzed C−H bond functionalization,[18] herein, we report Rh(III)-catalyzed C7-thiolation and selenation of indolines by using a readily available and easily removable pyrimidyl group as a directing group (Figure 1, 1.2).

RESULTS AND DISCUSSION

Our effort was initially focused on the direct thiolation of 1-(pyrimidin-2-yl)indoline (**1a**) with diphenyl disulfide (**2a**) as a model reaction (for details of optimization studies of reaction, see the SI). As shown in Table 1, after treatment of **1a** (0.3 mmol) with **2a** (0.3 mmol, 1.0 equiv) in the presence of $[Cp^*RhCl_2]_2$ (5 mol %), AgOTf (20 mol %), and Ag_2CO_3 (1.0 equiv) in toluene at 110 °C for 12 h under air, the desired thiolated product 7-(phenylthio)-1-(pyrimidin-2-yl)indoline **3aa** was isolated in 89% yield (entry 1). The structure of **3aa** was confirmed by its ^1H and ^{13}C NMR spectra and high-resolution mass spectrometry. The reaction efficiency could be increased at higher temperature (130 °C), affording **3aa** in 95% yield (entry 2). Notably, when the reaction was carried out at 80 °C, only a trace amount of product was isolated (entry 3). Other representative solvents such as *t*-AmOH and MeCN resulted in a significant decrease of yields (entries 4−5). Ag_2CO_3 played an important role in the reaction. Decreasing the amount of Ag_2CO_3 to 50 mol % led to a decrease in yield, and only 7% yield was obtained without Ag_2CO_3 (entries 6−7). The control experiment suggested that AgOTf and $[Cp^*RhCl_2]_2$ were indispensable for the catalytic system (entries 8−9). Additionally, we also found that a related cationic Rh(III) catalyst $[Cp^*Rh(MeCN)_3](SbF_6)_2$ alone was ineffective for this catalytic reaction (entry 10).

Table 1. Optimization of Reaction Conditions[a]



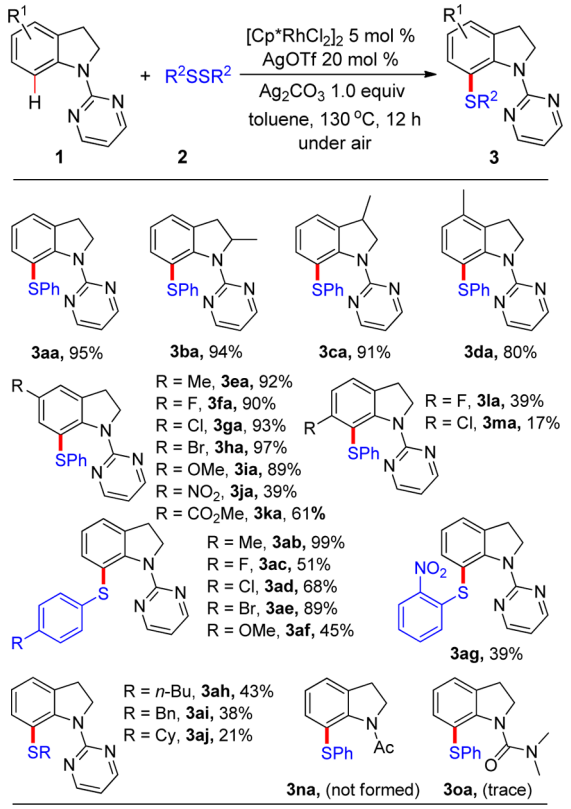
1a 2a 3aa

entry	Ag_2CO_3 (equiv)	solvent	temp (°C)	yields (%)
1	1	toluene	110	89
2	1	toluene	130	95
3	1	toluene	80	trace
4	1	*t*-AmOH	130	37
5	1	MeCN	130	52
6	0.5	toluene	130	83
7	none	toluene	130	7
8[b]	1	toluene	130	n.r.
9[c]	1	toluene	130	n.r.
10[b,d]	1	toluene	130	n.r.

[a]Conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (0.015 mmol, 5 mol %), AgOTf (0.06 mmol, 20 mol %), solvent (1.5 mL), heating in a sealed tube, under air; isolated yields are shown. [b]No AgOTf. [c]No $[Cp^*RhCl_2]_2$. [d]$[Cp^*Rh(MeCN)_3][SbF_6]_2$ instead of $[Cp^*RhCl_2]_2$.

With the optimal conditions in hand, the substrate scope was examined with respect to indolines (Table 2). The indolines bearing electron-donating or electron-withdrawing substituents at C2, C3, C4, or C5 positions (**3ba−ia**) participated well in coupling, providing the corresponding 7-substituted indolines in excellent yields. *N*-Pyrimidinyl indolines possessing halogen substituents at the C5 position were well-tolerated to afford the desired products (**3fa−ha**) in excellent yields, thus allowing for the possibility of further transformations. Indoline with a methyl moiety at the C4 position exhibited slightly decreased reactivity (80%, **3da**). Indoline with the strong electron-withdrawing group NO_2 at the C5 position afforded only 39% yield (**3ja**). It was found that substituents at the C6 position would decrease the yields dramatically (**3la, 3ma**), probably due to the steric congestion neighboring the reactive site. The substrate scope was further extended to disulfides. To our delight, various diaryl disulfides showed good reactivities. Different substituents on the phenyl ring of diaryl disulfides proceeded smoothly, providing the corresponding products in 39−99% yields (**3ab−ag**). Both of the strong electron-withdrawing (**2c**, **2d** and **2g**) and donating (**2f**) substituents in the arene ring of diaryl disulfides decreased the yields. The molecular structure of **3ag** was further confirmed by single-crystal X-ray diffraction analysis (Figure S1, Supporting Information). Fortunately, the alkyl and benzyl disulfides were also compatible with the conditions and afforded the corresponding thiolation products (**3ah−aj**), although in low to moderate yields, thus allowing for high diversity in the synthesis of aryl thioethers. Notably, the choice of the *N*-protecting group was found to be crucial for this reaction. The acetyl (**1n**) or *N*,*N*-dimethylcarbamoyl (**1o**) directing group did not deliver the corresponding product under the standard conditions.

Table 2. Substrate Scope of Rh(III)-Catalyzed C7-Thiolation of Indolines[a]



[a]Conditions: **1** (0.3 mmol), **2** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), AgOTf (20 mol %), Ag_2CO_3 (0.3 mmol), toluene (1.5 mL), 130 °C, 12 h, under air; isolated yields are shown.

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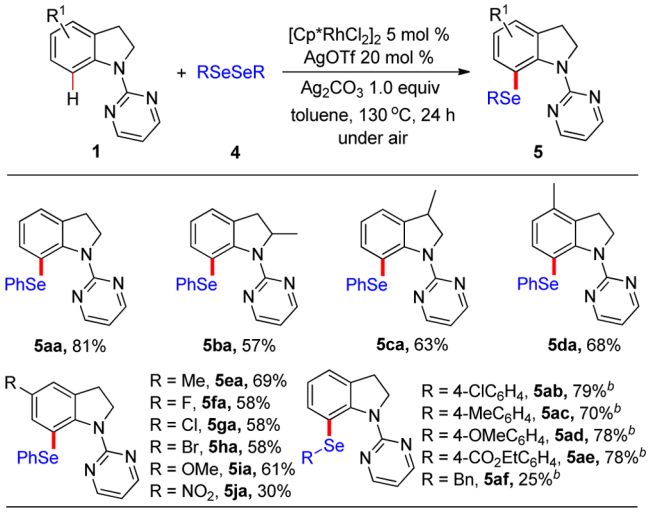
The successful results of direct thiolation led us to examine the related direct selenation of **1a** with diphenyl diselenides. Under similar conditions optimized for direct thiolation, the desired product **5aa** was obtained in 81% yield after 24 h (Table 3). Consequently, we explored the generality and

Table 3. Substrate Scope of Rh(III)-Catalyzed C7-Selenation of Indolines[a]



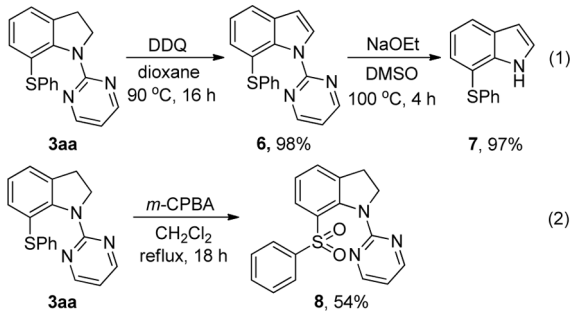
[a]Conditions: **1** (0.3 mmol), **4** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), AgOTf (20 mol %), Ag_2CO_3 (0.3 mmol), toluene (1.5 mL), 130 °C, 24 h, under air; isolated yields are shown. [b]**4** (0.45 mmol).

limitations of this selenation protocol under optimized conditions. The indolines with a methyl group at C2, C3, C4, or C5 positions were well tolerated, and the corresponding products were isolated in good yields (**5ba**–**ea**). The slightly electron-deficient (**5fa**–**ha**) and electron-rich (**5ea**, **5ia**) substrates were also selenylated under the standard conditions in good yields. Especially, the indolines bearing a chloro or bromo functional group (**5ga**, **5ha**) were also compatible with this catalytic system, thus offering the opportunity for further transformations. A relatively lower yield (30%) was obtained when a strong electron-withdrawing group (NO_2, **5ja**) was introduced into the C5 position of indoline. To demonstrate the scope of diselenide substrates, different readily synthesized diselenides were applied as substrates to couple with **1a**. Thus, symmetrical diselenides with a wide range of valuable functional groups such as methoxy (**4d**), chloro (**4b**), and ester (**4e**) groups in the arene ring of diaryl diselenides all reacted smoothly with good efficiency (**5ab**–**ae**).

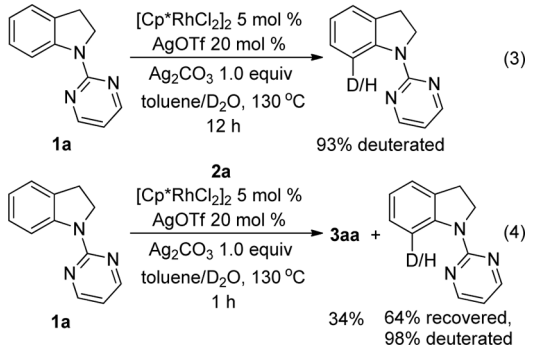
In addition, the utility of this C7-thiolation reaction was further highlighted by its successful conversion of indolines into indoles **6** in almost quantitative yield (Scheme 1, eq 1). Moreover, the pyrimidyl group can be successfully removed by reaction with NaOEt in DMSO at 100 °C for 4 h, affording 7-(phenylthio)-1*H*-indole **7** in 97% yield. Selective oxidation of **3aa** with *m*-CPBA furnished the sulfonyl indoline **8** in 54% yield (Scheme 1, eq 2).

To gain a mechanistic insight, H/D exchange experiments were performed (Scheme 2). Significant H-D scrambling was observed at the C7 position of indoline **1a** when toluene and D_2O were employed as a mixed solvent system (Scheme 2, eq 3). When the reaction was performed in the presence of **2a**, no deuterium incorporation of product **3aa** was observed except for significant deuteration (98% D) of recovered starting

Scheme 1. Derivatization Reactions



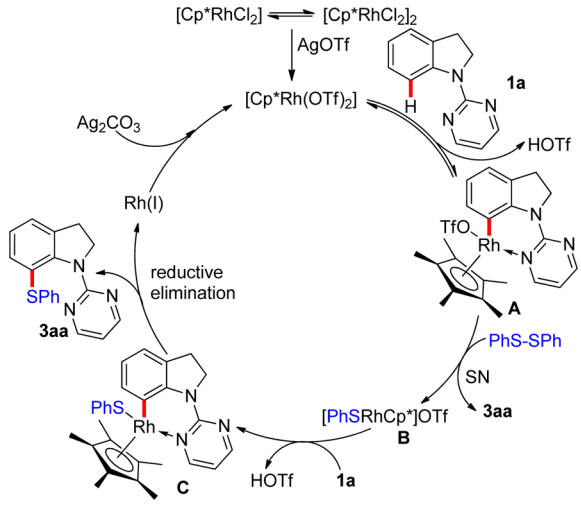
Scheme 2. Deuterium Exchange Reactions



material (Scheme 2, eq 4). Together, these results indicated the reversibility of the C–H activation.

A proposed mechanistic pathway for the Rh(III)-catalyzed thiolation of indolines with disulfide is depicted in Scheme 3.[16a]

Scheme 3. Mechanism Proposal



We hypothesize that a proposed catalytic cycle initiates with the formation of the rhodacycle intermediate **A** via Rh(III)-catalyzed C–H activation. Intermediate **A** can undergo nucleophilic substitution reaction with disulfide to afford the desired product **3aa** and Rh(III) species **B**. Reaction of Rh(III) complex **B** with **1a** forms the rhodacycle intermediate **C** via C–H activation, which would undergo reductive elimination to afford **3aa** together with a rhodium(I) species. Finally, Rh(I) is oxidized to Rh(III) by external oxidant Ag_2CO_3 to complete the catalytic cycle.

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CONCLUSION

In conclusion, we have disclosed a highly selective C7-thiolation and selenation of indolines with disulfides and diselenides through Rh(III)-catalyzed C−H bond activation. These transformations have been applied to a wide range of substrates and typically proceed with excellent levels of chemoselectivity as well as with high functional group tolerance. Synthetic utility of the current approach was demonstrated by the successful access to C-7 thiolated indoles and the removal of a pyrimidyl group. Considering the valuable structure of the products, we expect this regioselective thiolation and selenation reaction to gain broad synthetic utility. Detailed mechanistic studies and synthetic applications are underway.

EXPERIMENTAL SECTION

General Information. All the reactions were carried out under an argon atmosphere using the standard Schlenk technique. ^{1}H NMR (400 MHz), ^{19}F (376 M Hz), and ^{13}C NMR (100 MHz) were recorded on an NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H, ^{19}F, and ^{13}C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.00 ppm). All coupling constants (J values) were reported in hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200−300 mesh. IR spectra were recorded as KBr disks on an FT-IR spectrometer. High-resolution mass spectrometry (HRMS) was done on a FTICR-mass spectrometer. $[Cp^*RhCl_2]_2$ was prepared from $RhCl_3{\cdot}xH_2O$ following a literature procedure.[19] The substrates disulfides and diselenides,[20] and **1a**−**o**[6a] were prepared according to the literature. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available without any further purification.

General Procedure for the Preparation of 1-(Pyrimidin-2-yl)indolines 1.[6a,21] To a solution of an indole (5.0 mmol, 1.0 equiv) in AcOH (25 mL) at 0 °C was added $NaBH_3CN$ (1.26 g, 20.0 mmol, 4.0 equiv) in portions. The reaction was allowed to stir at room temperature until completion (typically 4 h). Water was then added, and the reaction mixture was basified with NaOH aqueous solution and extracted with EtOAc three times. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure to afford the corresponding crude indoline.

The crude indoline and 2-chloropyrimidine (0.57g, 5.0 mmol, 1.0 equiv) were dissolved in a mixture of EtOH (40 mL) and H_2O (10 mL). Concentrated hydrochloric acid (1 mL) was added to the mixture. Then, the resulting solution was refluxed overnight. EtOH was then removed under reduced pressure, and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/EtOAc (8:1−3:1).

General Procedure for Rh(III)-Catalyzed C7-Thiolation of Indolines. An oven-dried reaction vessel was charged with $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol), AgOTf (15.4 mg, 0.06 mmol), 1-(pyrimidin-2-yl)indoline (**1a**) (59.2 mg, 0.3 mmol), diphenyl disulfide (**2a**) (65.5 mg, 0.3 mmol), Ag_2CO_3 (82.7 mg, 0.3 mmol), and 1.5 mL of toluene under air. The vessel was sealed and heated at 130 °C (oil bath) for 12 h. The resulting mixture was cooled to room temperature, diluted with CH_2Cl_2, and transferred to a round-bottom flask. Silica was added to the flask, and volatiles were evaporated under reduced pressure. The purification was performed by column chromatography on silica gel with petroleum ether/EtOAc (8:1) to give product **3aa** (87.4 mg, 95%).

*7-(Phenylthio)-1-(pyrimidin-2-yl)indoline (**3aa**).* White solid (87.4 mg, 95%); Mp 133−134 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (d, J = 4.5 Hz, 2H), 7.41−7.09 (m, 7H), 6.96 (t, J = 7.5 Hz, 1H), 6.75 (t, J = 4.5 Hz, 1H), 4.51 (t, J = 7.8 Hz, 2H), 3.18 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.6, 157.1, 143.7, 138.1, 134.6, 131.4, 131.0, 128.6, 126.4, 125.9, 124.1, 122.9, 112.7, 52.2, 29.5; IR (cm^{-1}) ν 1576, 1552, 1455, 1426, 1382, 1278, 800, 770, 750, 694; HRMS (ESI) calcd for $C_{18}H_{16}N_3S$ $[M + H]^+$ 306.1065, found 306.1062.

*2-Methyl-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3ba**).* White solid (90.0 mg, 94%); mp 123−125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.43 (d, J = 4.5 Hz, 2H), 7.23−7.10 (m, 7H), 6.93 (t, J = 7.5 Hz, 1H), 6.71 (t, J = 4.5 Hz, 1H), 5.04−4.92 (m, 1H), 3.52 (dd, J = 15.4, 8.6 Hz, 1H), 2.58 (d, J = 15.5 Hz, 1H), 1.45 (d, J = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3, 157.3, 142.8, 138.6, 133.5, 132.1, 130.9 128.7, 126.3, 126.2, 124.2, 123.8, 112.8, 59.7, 36.9, 21.4; IR (cm^{-1}) ν 1576, 1551, 1462, 1435, 1222, 1056, 794, 765, 741, 686; HRMS (ESI) calcd for $C_{19}H_{18}N_3S$ $[M + H]^+$ 320.1221, found 320.1220.

*3-Methyl-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3ca**).* White solid (87.5 mg, 91%); mp 123−125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.41 (d, J = 4.7 Hz, 2H), 7.26 (d, J = 7.6 Hz, 2H), 7.22−7.12 (m, 3H), 7.09 (d, J = 7.9 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.67 (dd, J = 6.3, 3.1 Hz, 1H), 4.63 (t, J = 9.6 Hz, 1H), 3.99−3.91 (m, 1H), 3.44 (d, J = 7.1 Hz, 1H), 1.30 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8, 157.2, 143.4, 139.8, 138.0, 131.4, 131.1, 128.7, 126.5, 125.9, 124.3, 121.7, 112.7, 60.1, 36.2, 18.7; IR (cm^{-1}) ν 1576, 1552, 1423, 1279, 1054, 785, 749, 695; HRMS (ESI) calcd for $C_{19}H_{18}N_3S$ $[M + H]^+$ 320.1221, found 320.1222.

*4-Methyl-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3da**).* White solid (76.5 mg, 80%); mp 128−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (d, J = 4.5 Hz, 2H), 7.21−7.11 (m, 4H), 7.10−7.01 (m, 2H), 6.73 (d, J = 8.0 Hz, 1H), 6.65 (t, J = 4.4 Hz, 1H), 4.41 (t, J = 7.8 Hz, 2H), 3.00 (t, J = 7.7 Hz, 2H), 2.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8, 157.1, 143.8, 138.9, 133.2, 132.8, 132.1, 130.3, 128.5, 126.0, 125.5, 122.2, 112.7, 52.0, 28.3, 18.4; IR (cm^{-1}) ν 1575, 1556, 1453, 1402, 1274, 1207, 1059, 797, 743, 693; HRMS (ESI) calcd for $C_{19}H_{18}N_3S$ $[M + H]^+$ 320.1221, found 320.1222.

*5-Methyl-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3ea**).* White solid (88.2 mg, 92%); mp 137−139 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (d, J = 4.7 Hz, 2H), 7.28−7.06 (m, 5H), 6.90 (d, J = 5.8 Hz, 2H), 6.63 (t, J = 4.7 Hz, 1H), 4.40 (t, J = 7.8 Hz, 2H), 3.04 (t, J = 7.8 Hz, 3H), 2.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8, 157.1, 141.8, 138.4, 134.8, 134.0 131.7, 130.6, 128.6, 126.2, 125.2, 124.1, 112.5, 52.3, 29.6, 20.7; IR (cm^{-1}) ν 1575, 1552, 1458, 1402, 1274, 1208, 797, 748, 694; HRMS (ESI) calcd for $C_{19}H_{18}N_3S$ $[M + H]^+$ 320.1221, found 320.1221.

*5-Fluoro-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3fa**).* White solid (87.0 mg, 90%); mp 129−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.41 (d, J = 4.8 Hz, 2H), 7.35−7.27 (m, 2H), 7.27−7.16 (m, 3H), 6.81−6.74 (m, 1H), 6.69 (dd, J = 11.4, 6.9 Hz, 2H), 4.45 (t, J = 7.8 Hz, 2H), 3.07 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 159.4 (d, $J_{C\text{-}F}$ = 243.6 Hz) 157.3, 139.5, 136.7, 136.4 (d, $J_{C\text{-}F}$ = 8.9 Hz), 132.2, 129.0, 128.3 (d, $J_{C\text{-}F}$ = 8.4 Hz), 127.3, 116.4 (d, $J_{C\text{-}F}$ = 24.9 Hz), 112.7, 110.3 (d, $J_{C\text{-}F}$ = 24.1 Hz), 52.6, 29.8; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −119.1; IR (cm^{-1}) ν 1576, 1550, 1455, 1429, 1405, 1278, 1255, 1195, 864, 795, 748, 693; HRMS (ESI) calcd for $C_{18}H_{15}FN_3S$ $[M + H]^+$ 324.0971, found 324.0972.

*5-Chloro-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3ga**).* White solid (94.8 mg, 93%); mp 146−148 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.41 (d, J = 4.7 Hz, 2H), 7.31−7.24 (m, 2H), 7.24−7.15 (m, 3H), 7.00 (d, J = 6.2 Hz, 1H), 6.70 (t, J = 4.7 Hz, 1H), 4.42 (t, J = 7.8 Hz, 2H), 3.07 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.5, 157.2, 142.3, 136.9, 136.3, 131.7, 130.1, 128.9, 128.7, 127.8, 127.2, 123.0, 113.0, 52.4, 29.4; IR (cm^{-1}) ν 1576, 1553, 1443, 1403, 1188, 1149, 853, 799, 760, 697; HRMS (ESI) calcd for $C_{18}H_{15}ClN_3S$ $[M + H]^+$ 340.0675, found 340.0675.

*5-Bromo-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3ha**).* White solid (111.8 mg, 97%); mp 165−167 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.41 (d, J = 4.7 Hz, 2H), 7.30−7.13 (m, 7H), 6.71 (t, J = 4.7 Hz, 1H), 4.42 (t, J = 7.9 Hz, 2H), 3.08 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.5, 157.3, 142.8, 136.9, 136.7, 133.0, 131.6, 129.0, 128.2, 127.1, 125.8, 116.2, 113.1, 52.3, 29.3; IR (cm^{-1}) ν 1574,

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1552, 1460, 1394, 1275, 1207, 1152, 794, 744, 691; HRMS (ESI) calcd for $C_{18}H_{15}BrN_3S$ $[M + H]^+$ 384.0170, found 384.0166.

*5-Methoxy-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3ia**).* White solid (89.1 mg, 89%); mp 95−97 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, J = 4.7 Hz, 2H), 7.35−7.04 (m, 5H), 6.76−6.50 (m, 3H), 4.40 (t, J = 7.7 Hz, 2H), 3.56 (s, 3H), 3.03 (t, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.9, 157.2, 156.6, 137.6, 137.5, 136.1, 131.3, 128.7, 126.9, 126.6, 115.2, 112.3, 110.2, 55.5, 52.4, 30.0; IR (cm^{-1}) ν 1577, 1550, 1461, 1407, 1277, 1194, 1116, 1040, 796, 748, 693; HRMS (ESI) calcd for $C_{19}H_{18}N_3OS$ $[M + H]^+$ 336.1171, found 336.1171.

*5-Nitro-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3ja**).* Yellow solid (41.4 mg, 39%); mp 162−164 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.52 (d, J = 4.8 Hz, 2H), 7.96 (d, J = 1.8 Hz, 1H), 7.90 (s, 1H), 7.27 (m, 5H), 6.87 (t, J = 4.8 Hz, 1H), 4.52 (t, J = 8.2 Hz, 2H), 3.24 (t, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 157.5, 148.7, 143.8, 136.0, 135.4, 132.3, 129.3, 127.9, 127.7, 126.9, 118.0, 114.4, 52.8, 28.7; IR (cm^{-1}) ν 1568, 1506, 1428, 1317, 1286, 1077, 802, 751, 695, 634; HRMS (ESI) calcd for $C_{18}H_{15}N_4O_2S$ $[M + H]^+$ 351.0916, found 351.0913.

*Methyl 7-(Phenylthio)-1-(pyrimidin-2-yl)indoline-5-carboxylate (**3ka**).* Yellow solid (66.9 mg, 61%); mp 156−160 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.39 (s, 2H), 7.73 (d, J = 36.4 Hz, 2H), 7.13 (s, 5H), 6.72 (s, 1H), 4.39 (t, J = 7.4 Hz, 2H), 3.73 (s, 3H), 3.12 (t, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.4, 160.2, 157.3, 147.9, 137.5, 134.8, 134.4, 130.9, 128.9, 126.8, 125.8, 125.1, 124.2, 113.7, 52.6, 51.9, 28.9; IR (cm^{-1}) ν 1715, 1577, 1553, 1445, 1278, 1201, 1157, 908, 794, 769, 743, 689; HRMS (ESI) calcd for $C_{20}H_{18}N_3O_2S$ $[M + H]^+$ 364.1120, found 364.1119.

*6-Fluoro-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3la**).* White solid (38.7 mg, 40%); mp 142−144 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38 (d, J = 3.7 Hz, 2H), 7.20−7.05 (m, 6H), 6.80−6.71 (m, 2H), 4.48 (t, J = 7.7 Hz, 2H), 3.12 (t, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.4 (d, $J_{C\text{-}F}$ = 122.5 Hz), 160.7, 160.5, 157.2, 147.2 (d, $J_{C\text{-}F}$ = 4.8 Hz), 137.5, 130.1 (d, $J_{C\text{-}F}$ = 2.6 Hz), 128.5, 127.9, 125.6, 124.7 (d, $J_{C\text{-}F}$ = 9.9 Hz), 113.4, 112.3 (d, $J_{C\text{-}F}$ = 22.2 Hz), 110.7 (d, $J_{C\text{-}F}$ = 24.6 Hz), 53.3, 29.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −107.9; IR (cm^{-1}) ν 1577, 1551, 1458, 1431, 1379, 1230, 1186, 795, 754, 691; HRMS (ESI) calcd for $C_{18}H_{15}FN_3S$ $[M + H]^+$ 324.0971, found 324.0971.

*6-Chloro-7-(phenylthio)-1-(pyrimidin-2-yl)indoline (**3ma**).* White solid (17.0 mg, 17%); mp 176−178 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (d, J = 4.8 Hz, 2H), 7.19−7.11 (m, 4H), 7.08 (d, J = 7.2 Hz, 1H), 6.96−6.91 (m, 2H), 6.75 (t, J = 4.8 Hz, 1H), 4.46 (t, J = 7.9 Hz, 2H), 3.14 (t, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 157.2, 148.3, 137.6, 133.8, 128.5, 127.5, 125.6, 125.4, 125.1, 122.4, 113.4, 53.2, 29.4; IR (cm^{-1}) ν 1571, 1551, 1426, 1106, 812, 741, 691; HRMS (ESI) calcd for $C_{18}H_{15}ClN_3S$ $[M + H]^+$ 340.0675, found 340.0669.

*1-(Pyrimidin-2-yl)-7-(p-tolylthio)indoline (**3ab**).* White solid (95.2 mg, 99%); mp 121−123 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.43 (d, J = 4.7 Hz, 2H), 7.19 (d, J = 7.5 Hz, 2H), 7.03 (t, J = 9.4 Hz, 2H), 6.86 (d, J = 7.4 Hz, 3H), 6.69 (t, J = 4.7 Hz, 1H), 4.44 (t, J = 7.8 Hz, 2H), 3.11 (t, J = 7.8 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 157.3, 143.3, 136.8, 134.5, 134.2, 132.0, 130.7, 129.6, 127.0, 124.1, 122.5, 112.7, 52.3, 29.6, 21.0; IR (cm^{-1}) ν 1573, 1550, 1489, 1454, 1426, 799, 761, 723; HRMS (ESI) calcd for $C_{19}H_{18}N_3S$ $[M + H]^+$ 320.1221, found 320.1222.

*7-(4-Fluorophenylthio)-1-(pyrimidin-2-yl)indoline (**3ac**).* White solid (49.5 mg, 51%); mp 130−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, J = 4.7 Hz, 2H), 7.24 (dd, J = 7.6, 5.3 Hz, 2H), 7.06 (d, J = 7.2 Hz, 1H), 6.97 (d, J = 7.9 Hz, 1H), 6.94−6.83 (m, 3H), 6.70 (t, J = 4.7 Hz, 1H), 4.43 (t, J = 7.9 Hz, 2H), 3.11 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.0 (d, $J_{C\text{-}F}$ = 247.3 Hz), 160.8, 160.7, 157.4, 143.4, 134.7, 133.9 (d, $J_{C\text{-}F}$ = 7.8 Hz), 133.1 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.8, 126.7, 124.3, 122.9, 115.9 (d, $J_{C\text{-}F}$ = 21.8 Hz), 112.8, 52.3, 29.6; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −114.8; IR (cm^{-1}) ν 1575, 1551, 1485, 1452, 1423, 836, 797, 769, 728; HRMS (ESI) calcd for $C_{18}H_{15}FN_3S$ $[M + H]^+$ 324.0971, found 324.0969.

*7-(4-Chlorophenylthio)-1-(pyrimidin-2-yl)indoline (**3ad**).* White solid (69.5 mg, 68%); mp 123−125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, J = 4.7 Hz, 2H), 7.17 (s, 4H), 7.09 (dd, J = 17.1, 7.5 Hz, 2H), 6.91 (t, J = 7.6 Hz, 1H), 6.71 (t, J = 4.7 Hz, 1H), 4.45 (t, J = 7.9 Hz, 2H), 3.13 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.6, 157.2, 144.0, 137.1, 134.8, 132.3, 132.1, 131.5, 128.8, 125.4, 124.3, 123.3, 112.8, 52.2, 29.5; IR (cm^{-1}) ν 1574, 1549, 1456, 1429, 1382, 1087, 801, 775; HRMS (ESI) calcd for $C_{18}H_{15}ClN_3S$ $[M + H]^+$ 340.0675, found 340.0672.

*7-(4-Bromophenylthio)-1-(pyrimidin-2-yl)indoline (**3ae**).* White solid (102.2 mg, 89%); mp 111−114 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, J = 4.7 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.16−7.05 (m, 4H), 6.91 (t, J = 7.6 Hz, 1H), 6.72 (t, J = 4.7 Hz, 1H), 4.46 (t, J = 7.9 Hz, 2H), 3.14 (t, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 157.2, 144.1, 137.9, 134.8, 132.3, 131.7, 131.6, 125.2, 124.3, 123.4, 120.2, 112.9, 52.2, 29.5; IR (cm^{-1}) ν 1574, 1549, 1456, 1430, 1381, 801, 774; HRMS (ESI) calcd for $C_{18}H_{15}BrN_3S$ $[M + H]^+$ 384.0170, found 384.0162.

*7-(4-Methoxyphenylthio)-1-(pyrimidin-2-yl)indoline (**3af**).* White solid (45.2 mg, 45%); mp 117−119 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.47 (d, J = 4.7 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 7.1 Hz, 1H), 6.95 (d, J = 7.9 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 8.5 Hz, 2H), 6.71 (t, J = 4.7 Hz, 1H), 4.46 (t, J = 7.8 Hz, 2H), 3.77 (s, 3H), 3.12 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 159.2, 157.3, 142.6, 134.7, 134.3, 129.9, 128.1, 127.8, 124.0, 122.1, 114.4, 112.6, 55.2, 52.3, 29.6; IR (cm^{-1}) ν 1579, 1550, 1488, 1455, 1376, 1291, 1243, 1168, 1033, 814, 787, 725; HRMS (ESI) calcd for $C_{19}H_{18}N_3OS$ $[M + H]^+$ 336.1171, found 336.1168.

*7-(2-Nitrophenylthio)-1-(pyrimidin-2-yl)indoline (**3ag**).* Yellow solid (41.1 mg, 39%); mp 178−180 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (d, J = 4.8 Hz, 2H), 8.06 (dd, J = 8.2, 1.2 Hz, 1H), 7.30 (m, 3H), 7.20−7.11 (m, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.98 (dd, J = 8.2, 0.9 Hz, 1H), 6.69 (t, J = 4.8 Hz, 1H), 4.42 (t, J = 7.9 Hz, 2H), 3.17 (t, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3, 157.1, 146.6, 146.0, 139.6, 136.0, 135.0, 132.7, 129.8, 125.7, 125.1, 124.7, 124.7, 121.4, 113.4, 52.4, 29.5; IR (cm^{-1}) ν 1576, 1552, 1510, 1455, 1427, 1344, 1303, 774, 733; HRMS (ESI) calcd for $C_{18}H_{15}N_4O_2S$ $[M + H]^+$ 351.0916, found 351.0912.

*7-(Butylthio)-1-(pyrimidin-2-yl)indoline (**3ah**).* White solid (37.1 mg, 43%); mp 76−78 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, J = 4.7 Hz, 2H), 7.19 (d, J = 7.3 Hz, 1H), 6.96 (dd, J = 21.4, 7.3 Hz, 2H), 6.63 (t, J = 4.7 Hz, 1H), 4.35 (t, J = 7.8 Hz, 2H), 3.02 (t, J = 7.7 Hz, 2H), 2.82−2.71 (m, 2H), 1.47−1.36 (m, 2H), 1.27 (dd, J = 14.7, 7.3 Hz, 2H), 0.77 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 157.3, 143.5, 134.4, 128.3, 127.4, 124.1, 121.9, 112.6, 52.6, 35.0, 31.3, 29.7, 22.0, 13.6; IR (cm^{-1}) ν 1577, 1550, 1461, 1434, 1385, 1276, 794, 769; HRMS (ESI) calcd for $C_{16}H_{20}N_3S$ $[M + H]^+$ 286.1378, found 286.1371.

*7-(Benzylthio)-1-(pyrimidin-2-yl)indoline (**3ai**).* Brown solid (36.8 mg, 38%); mp 158−159 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, J = 4.8 Hz, 2H), 7.33 (d, J = 7.8 Hz, 1H), 7.27−7.22 (m, 4H), 7.22−7.17 (m, 1H), 7.08 (d, J = 6.7 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.68 (t, J = 4.8 Hz, 1H), 4.37 (t, J = 7.9 Hz, 2H), 4.03 (s, 2H), 3.08 (t, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 157.3, 143.7, 137.7, 134.5, 129.2, 129.0, 128.2, 127.0, 126.9, 124.1, 122.5, 112.6, 52.3, 40.6, 29.7; IR (cm^{-1}) ν 1577, 1553, 1454, 1432, 1381, 796, 765, 702; HRMS (ESI) calcd for $C_{19}H_{18}N_3S$ $[M + H]^+$ 320.1221, found 320.1217.

*7-(Cyclohexylthio)-1-(pyrimidin-2-yl)indoline (**3aj**).* White solid (19.8 mg, 21%); mp 88−90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.43 (d, J = 4.7 Hz, 2H), 7.31 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 7.1 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 6.69 (t, J = 4.7 Hz, 1H), 4.41 (t, J = 7.8 Hz, 2H), 3.09 (t, J = 7.8 Hz, 3H), 1.83 (d, J = 8.3 Hz, 2H), 1.68 (d, J = 10.5 Hz, 2H), 1.56 (d, J = 10.6 Hz, 1H), 1.24−1.09 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.0, 157.3, 144.8, 134.5, 130.0, 125.8, 124.0, 122.4, 112.7, 52.6, 47.3, 33.3, 29.8, 26.2, 25.8; IR (cm^{-1}) ν 1575, 1549, 1450, 1423, 1377, 797, 773; HRMS (ESI) calcd for $C_{18}H_{22}N_3S$ $[M + H]^+$ 312.1534, found 312.1533.

General Procedure for Rhodium(III)-Catalyzed C7-Selective Selenation of Indolines. An oven-dried reaction vessel was charged

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with $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol), AgOTf (15.4 mg, 0.06 mmol), 1-(pyrimidin-2-yl)indoline (**1a**, 59.2 mg, 0.3 mmol), diphenyl diselenide (**4a**, 93.6 mg, 0.3 mmol, 1.0 equiv), Ag_2CO_3 (82.7 mg, 0.3 mmol), and 1.5 mL of toluene (0.2 m) under air. The vessel was sealed and heated at 130 °C (oil bath) for 24 h. The resulting mixture was cooled to room temperature, diluted with CH_2Cl_2, and transferred to a round-bottom flask. Silica was added to the flask, and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/EtOAc (10:1) to give products **5aa** (85.4 mg, 81%). **5ab**−**5ae** were prepared with 1.5 equiv of diselenides.

*7-(Phenylselanyl)-1-(pyrimidin-2-yl)indoline (**5aa**).* Brown solid (85.4 mg, 81%); mp 154−156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (d, J = 4.8 Hz, 2H), 7.53−7.45 (m, 2H), 7.25−7.19 (m, 3H), 7.13 (d, J = 7.9 Hz, 1H), 7.08 (dd, J = 7.2, 1.0 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.73 (t, J = 4.8 Hz, 1H), 4.49 (t, J = 8.0 Hz, 2H), 3.15 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.6, 157.4, 144.0, 134.7, 134.2, 134.1, 132.2, 129.0, 127.2, 124.3, 122.9, 122.7, 112.7, 51.4, 29.5; IR (cm^{-1}) ν 1573, 1550, 1455, 1427, 1378, 1278, 801, 789, 738, 690; HRMS (ESI) calcd for $C_{18}H_{16}N_3Se$ $[M + H]^+$ 354.0509, found 354.0506.

*2-Methyl-7-(phenylselanyl)-1-(pyrimidin-2-yl)indoline (**5ba**).* Brown solid (62.7 mg, 57%); mp 137−139 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (d, J = 4.7 Hz, 2H), 7.52−7.39 (m, 2H), 7.26−7.14 (m, 4H), 7.09 (d, J = 7.2 Hz, 1H), 6.83 (t, J = 7.6 Hz, 1H), 6.71 (t, J = 4.7 Hz, 1H), 5.09−4.99 (m, 1H), 3.51 (dd, J = 15.5, 8.7 Hz, 1H), 2.60 (d, J = 15.6 Hz, 1H), 1.47 (d, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3, 157.4, 142.8, 134.9, 133.9, 132.9, 132.5, 128.9, 127.0, 124.2, 123.5, 123.1, 112.7, 58.7, 36.8, 21.2; IR (cm^{-1}) ν 1574, 1551, 1453, 1427, 1378, 1277, 1210, 803, 765; HRMS (ESI) calcd for $C_{19}H_{18}N_3Se$ $[M + H]^+$ 368.0666, found 368.0663.

*3-Methyl-7-(phenylselanyl)-1-(pyrimidin-2-yl)indoline (**5ca**).* Brown solid (69.0 mg, 63%); mp 127−129 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (d, J = 4.8 Hz, 2H), 7.49 (dd, J = 6.7, 2.6 Hz, 2H), 7.22 (dd, J = 7.2, 3.7 Hz, 3H), 7.13 (d, J = 7.9 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.72 (t, J = 4.8 Hz, 1H), 4.68 (dd, J = 11.1, 8.4 Hz, 1H), 3.98 (dd, J = 11.2, 7.3 Hz, 1H), 3.46 (dd, J = 14.5, 7.2 Hz,1H), 1.33 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8, 157.3, 143.7, 139.4, 134.5, 134.2, 132.2, 128.9, 127.2, 124.0, 122.7, 121.7, 112.6, 59.3, 36.3, 18.9; IR (cm^{-1}) ν 1574, 1551, 1441, 1424, 1279, 801, 781, 740, 691; HRMS (ESI) calcd for $C_{19}H_{18}N_3Se$ $[M + H]^+$ 368.0666, found 368.0663.

*4-Methyl-7-(phenylselanyl)-1-(pyrimidin-2-yl)indoline (**5da**).* Brown oil (76.0 mg, 69%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (d, J = 4.7 Hz, 2H), 7.53−7.45 (m, 2H), 7.26−7.20 (m, 3H), 7.12 (d, J = 8.0 Hz, 1H), 6.73 (dd, J = 11.8, 6.6 Hz, 1H), 4.52 (t, J = 8.0 Hz, 2H), 3.08 (t, J = 7.9 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 157.3, 143.8, 135.0, 133.8, 133.6, 132.8, 132.4, 131.6, 129.0, 128.9, 128.8, 126.9, 125.5, 119.1, 112.6, 51.2, 28.2, 18.4; IR (cm^{-1}) ν 1575, 1550, 1443, 1279, 1224, 794, 739, 692; HRMS (ESI) calcd for $C_{19}H_{18}N_3Se$ $[M + H]^+$ 368.0666, found 368.0664.

*5-Methyl-7-(phenylselanyl)-1-(pyrimidin-2-yl)indoline (**5ea**).* Brown solid (76.5 mg, 70%); mp 160−161 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (d, J = 4.7 Hz, 2H), 7.51−7.43 (m, 2H), 7.26−7.19 (m, 3H), 6.96 (s, 1H), 6.91 (s, 1H), 6.70 (t, J = 4.7 Hz, 1H), 4.47 (t, J = 7.9 Hz, 2H), 3.10 (t, J = 7.8 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8, 157.3, 142.0, 134.8, 134.3, 134.1, 133.8, 132.5, 128.9, 127.0, 124.0, 122.2, 112.4, 51.6, 29.6, 20.7; IR (cm^{-1}) ν 1579, 1547, 1459, 1433, 1402, 1374, 1276, 1221, 857, 796, 740, 690; HRMS (ESI) calcd for $C_{19}H_{18}N_3Se$ $[M + H]^+$ 368.0666, found 368.0659.

*5-Fluoro-7-(phenylselanyl)-1-(pyrimidin-2-yl)indoline (**5fa**).* Brown solid (64.2 mg, 58%); mp 132−135 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (d, J = 4.7 Hz, 2H), 7.55 (d, J = 7.0 Hz, 2H), 7.29 (d, J = 5.9 Hz, 3H), 6.82 (d, J = 8.5 Hz, 2H), 6.75 (t, J = 4.7 Hz, 1H), 4.53 (t, J = 7.9 Hz, 2H), 3.14 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.6, 159.3 (d, $J_{C\text{-}F}$ = 244.3 Hz), 157.4, 140.1, 135.9 (d, $J_{C\text{-}F}$ = 8.7 Hz), 134.7, 133.6, 129.2, 127.8, 124.4 (d, $J_{C\text{-}F}$ = 7.6 Hz), 117.6 (d, $J_{C\text{-}F}$ = 24.8 Hz), 112.7, 110.3 (d, $J_{C\text{-}F}$ = 24.0 Hz), 51.7, 29.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −119.5; IR (cm^{-1}) ν 1576, 1550, 1455, 1429, 1404, 1282, 865, 796, 738, 690; HRMS (ESI) calcd for $C_{18}H_{15}FN_3Se$ $[M + H]^+$ 372.0415, found 372.0409.

*5-Chloro-7-(phenylselanyl)-1-(pyrimidin-2-yl)indoline (**5ga**).* Brown solid (67.5 mg, 58%); mp 152−154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (d, J = 4.7 Hz, 2H), 7.57−7.44 (m, 2H), 7.27 (d, J = 4.2 Hz, 3H), 7.05 (d, J = 7.2 Hz, 2H), 6.75 (t, J = 4.7 Hz, 1H), 4.49 (t, J = 8.0 Hz, 2H), 3.12 (t, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.5, 157.4, 142.8, 135.8, 134.4, 133.7, 131.1, 129.2, 128.9, 127.8, 124.2, 123.0, 113.0, 51.6, 29.4; IR (cm^{-1}) ν 1576, 1552, 1447, 1401, 1278,1189, 1141, 858, 796, 750, 694; HRMS (ESI) calcd for $C_{18}H_{15}ClN_3Se$ $[M + H]^+$ 388.0120, found 388.0121.

*5-Bromo-7-(phenylselanyl)-1-(pyrimidin-2-yl)indoline (**5ha**).* Brown solid (74.6 mg, 58%); mp 153−156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.45 (d, J = 4.8 Hz, 2H), 7.53−7.43 (m, 2H), 7.32−7.14 (m, 5H), 6.74 (t, J = 4.8 Hz, 1H), 4.46 (t, J = 8.0 Hz, 2H), 3.11 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.5, 157.4, 143.3, 136.3, 134.3, 134.0, 133.8, 129.2, 127.7, 125.9, 124.6, 116.4, 113.0, 51.5, 29.3; IR (cm^{-1}) ν 1577, 1551, 1444, 1398, 1277, 1186, 1135, 853, 796, 749, 693; HRMS (ESI) calcd for $C_{18}H_{15}BrN_3Se$ $[M + H]^+$ 431.9615, found 431.9600.

*5-Methoxy-7-(phenylselanyl)-1-(pyrimidin-2-yl)indoline (**5ia**).* Brown solid (70.0 mg, 61%); mp 98−100 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.43 (d, J = 4.8 Hz, 2H), 7.52 (dd, J = 6.5, 2.9 Hz, 2H), 7.25−7.21 (m, 3H), 6.67 (dd, J = 8.7, 4.0 Hz, 3H), 4.47 (t, J = 7.9 Hz, 2H), 3.56 (s, 3H), 3.09 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 157.3, 156.4, 137.8, 135.5, 134.3, 128.9, 127.3, 123.5, 116.1, 112.2, 109.9, 55.5, 51.5, 29.8; IR (cm^{-1}) ν 1578, 1549, 1449, 1411, 1265, 1223, 1187, 1106, 1041, 846, 785, 747; HRMS (ESI) calcd for $C_{19}H_{18}N_3OSe$ $[M + H]^+$ 384.0615, found 384.0614.

*5-Nitro-7-(phenylselanyl)-1-(pyrimidin-2-yl)indoline (**5ja**).* Yellow solid (35.4 mg, 30%); mp 188−190 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54 (d, J = 4.8 Hz, 2H), 8.03 (d, J = 2.1 Hz, 1H), 7.93−7.87 (m, 1H), 7.51 (dd, J = 7.7, 1.6 Hz, 2H), 7.35−7.27 (m, 3H), 6.89 (t, J = 4.8 Hz, 1H), 4.55 (t, J = 8.3 Hz, 2H), 3.25 (t, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 157.6, 149.4, 143.6, 134.8, 133.0, 129.5, 128.7, 128.4, 122.7, 118.1, 114.3, 52.0, 28.5; IR (cm^{-1}) ν 1574, 1557, 1505, 1435, 1312, 1079, 993, 930, 891, 795, 752, 699, 626; HRMS (ESI) calcd for $C_{18}H_{15}N_4O_2Se$ $[M + H]^+$ 399.0360, found 399.0346.

*7-(4-Chlorophenylselanyl)-1-(pyrimidin-2-yl)indoline (**5ab**).* Brown solid (92.2 mg, 79%); mp 141−144 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (d, J = 4.8 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 7.13−7.06 (m, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.71 (t, J = 4.8 Hz, 1H), 4.48 (t, J = 8.0 Hz, 2H), 3.14 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.5, 157.3, 144.1, 135.2, 134.2, 133.3, 133.2, 132.1, 129.0, 124.3, 123.1, 122.3, 112.7, 51.2, 29.3; IR (cm^{-1}) ν 1574, 1548, 1455, 1379, 1278, 1082, 1007, 799, 771, 722; HRMS (ESI) calcd for $C_{18}H_{15}ClN_3Se$ $[M + H]^+$ 388.0120, found 388.0110.

*1-(Pyrimidin-2-yl)-7-(p-tolylselanyl)indoline (**5ac**).* Brown solid (76.8 mg, 70%); mp 120−122 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (d, J = 4.8 Hz, 2H), 7.40 (d, J = 7.9 Hz, 2H), 7.13−7.02 (m, 4H), 6.80 (t, J = 7.6 Hz, 1H), 6.72 (t, J = 4.8 Hz, 1H), 4.48 (t, J = 8.0 Hz, 2H), 3.14 (t, J = 7.9 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 157.4, 143.8, 137.3, 134.7, 134.1, 131.8, 130.7, 129.8, 124.2, 123.3, 122.7, 112.6, 51.4, 29.5, 21.1; IR (cm^{-1}) ν 1574, 1549, 1437, 1379, 1224, 1056, 793, 761, 732, 687; HRMS (ESI) calcd for $C_{19}H_{18}N_3Se$ $[M + H]^+$ 368.0666, found 368.0672.

*7-(4-Methoxyphenylselanyl)-1-(pyrimidin-2-yl)indoline (**5ad**).* Brown solid (88.9 mg, 78%); mp 105−108 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (d, J = 4.7 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.07 (t, J = 7.3 Hz, 2H), 6.82 (d, J = 8.2 Hz, 3H), 6.74 (t, J = 4.7 Hz, 1H), 4.50 (t, J = 8.0 Hz, 2H), 3.80 (s, 3H), 3.15 (t, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.6, 159.4, 157.4, 143.4, 136.7, 133.9, 131.2, 124.3, 124.0, 123.8, 122.4, 114.6, 112.5, 55.1, 51.3, 29.4; IR (cm^{-1}) ν 1574, 1550, 1485, 1450, 1377, 1280, 1244, 1176, 1027, 824, 793, 771; HRMS (ESI) calcd for $C_{19}H_{18}N_3OSe$ $[M + H]^+$ 384.0615, found 384.0619.

*Ethyl 4-(1-(Pyrimidin-2-yl)indolin-7-ylselanyl)benzoate (**5ae**).* Brown solid (99.6 mg, 78%); mp 125−127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, J = 4.8 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 7.41

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(d, J = 8.2 Hz, 2H), 7.17 (d, J = 7.9 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 6.84 (t, J = 7.6 Hz, 1H), 6.71 (t, J = 4.8 Hz, 1H), 4.47 (t, J = 8.0 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.14 (t, J = 7.9 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 160.5, 157.2, 144.7, 142.4, 134.4, 132.9, 132.0, 129.8, 129.7, 128.5, 124.4, 123.6, 121.1, 112.8, 60.7, 51.2, 29.3, 14.2; IR (cm^{-1}) ν 1703, 1577, 1551, 1458, 1390, 1272, 1170, 1102, 1014, 758; HRMS (ESI) calcd for $C_{21}H_{20}N_3O_2Se$ $[M + H]^+$ 426.0721, found 426.0720.

*7-(Benzylselanyl)-1-(pyrimidin-2-yl)indoline (**5af**).* Yellow solid (27.6 mg, 25%); mp 141−143 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38 (d, J = 4.8 Hz, 2H), 7.45 (d, J = 7.8 Hz, 1H), 7.26−7.10 (m, 6H), 6.99 (t, J = 7.6 Hz, 1H), 6.66 (t, J = 4.8 Hz, 1H), 4.41 (t, J = 8.0 Hz, 2H), 4.01 (s, 2H), 3.12 (t, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3, 157.3, 144.2, 138.5, 134.2, 130.8, 129.0, 128.4, 126.6, 124.2, 122.9, 112.5, 51.4, 33.4, 29.5; IR (cm^{-1}) ν 1575, 1548, 1490, 1458, 1431, 1378, 1274, 796, 765, 695; HRMS (ESI) calcd for $C_{19}H_{18}N_3Se$ $[M + H]^+$ 368.0666, found 368.0668.

Derivatization Reaction of 3aa (eq 1).[6a] To a solution of **3aa** (91.5 mg, 0.3 mmol) in 1,4-dioxane (3 mL) was added DDQ (136.2 mg, 0.6 mmol). The mixture was stirred at 90 °C for 12 h. After removal of solvent, the residue was absorbed to small amounts of silica. The product was purified by flash column chromatography with petroleum ether/EtOAc (8:1) to give product **6** (89.3 mg, 98%).

Under Ar, **6** (73.7 mg, 0.24 mmol) was dissolved in dry DMSO (4 mL), and EtONa (50 mg) in EtOH (0.4 mL) was added. The mixture was stirred at 100 °C for 4 h and then cooled, and HCl (2 M) was added. The mixture was diluted with EtOAc and washed with brine. The combined organic phase was dried (Na_2SO_4). After evaporation of the solvents under reduced pressure, the crude product was purified on a silica gel column with petroleum ether/EtOAc (4:1) to afford product 7 (52.5 mg, 97%).

*7-(Phenylthio)-1-(pyrimidin-2-yl)-1H-indole (**6**).* White solid (89.3 mg, 99%); mp 62−64 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.68 (d, J = 4.8 Hz, 2H), 7.81 (d, J = 3.5 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.28−7.23 (m, 1H), 7.14 (m, 7H), 6.75 (d, J = 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.0, 157.7, 137.7, 134.9, 132.1, 130.4, 129.9, 129.4, 128.7, 126.4, 122.7, 121.4, 120.3, 117.8, 106.7; IR (cm^{-1}) ν 1567, 1426, 1192, 1134, 1063, 786, 744, 715, 689, 475; HRMS (ESI) calcd for $C_{18}H_{14}N_3S$ $[M + H]^+$ 304.0908, found 304.0909.

*7-(Phenylthio)-1H-indole (**7**).* Brown oil (52.5 mg, 97%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.39 (s, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 7.3 Hz, 1H), 7.24−7.18 (m, 3H), 7.14 (t, J = 7.2 Hz, 4H), 6.64 (d, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.4, 136.8, 129.1, 129.0, 128.3, 126.9, 125.6, 124.5, 122.3, 120.5, 113.1, 103.3; IR (cm^{-1}) ν 3419, 1579, 1478, 1431, 1327, 1095, 1065, 791, 731, 691, 471; HRMS (ESI) calcd for $C_{14}H_{12}NS$ $[M + H]^+$ 226.0690, found 226.0683.

Derivatization Reaction of 3aa (eq 2).[22] *m*-CPBA (≤77%) (67.3 mg, 0.39 mmol) was added to a solution of **3aa** (61.1 mg, 0.2 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred under reflux for 18 h and then quenched with aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, the combined organic extracts were dried with $MgSO_4$ and filtered, and the solvent was removed in reduced pressure. The crude product was purified by column chromatography with petroleum ether/EtOAc (2:1) to give **8** (36.3 mg, 54%) as a brown solid. Mp 218−221 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, J = 4.8 Hz, 2H), 7.79 (dd, J = 5.3, 3.3 Hz, 2H), 7.64 (d, J = 8.1 Hz, 1H), 7.56−7.44 (m, 3H), 7.41 (dd, J = 7.3, 1.1 Hz, 1H), 7.12−7.04 (m, 1H), 6.67 (t, J = 4.8 Hz, 1H), 4.46 (t, J = 8.1 Hz, 2H), 3.13 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 157.1, 144.0, 142.4, 137.0, 131.9, 129.8, 129.3, 128.6, 128.1, 126.1, 123.0, 114.0, 52.6, 28.8; IR (cm^{-1}) ν 1572, 1455, 1420, 1297, 11521127, 1075, 807, 762, 731, 689, 580, 478; HRMS (ESI) calcd for $C_{18}H_{16}N_3O_2S$ $[M + H]^+$ 338.0963, found 338.0965.

H/D Exchange Reaction without Diphenyl Disulfide (eq 3). An oven-dried reaction vessel was charged with $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol), AgOTf (15.4 mg, 0.06 mmol), 1-(pyrimidin-2-yl)indoline (**1a**) (59.2 mg, 0.3 mmol), Ag_2CO_3 (82.7 mg, 0.3 mmol), toluene (1.3 mL), and D_2O (0.2 mL) under air. The vessel was sealed and heated at 130 °C (oil bath) for 12 h. After removal of solvents, the residue was purified by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:20).

H/D Exchange Reaction in the Presence of Diphenyl Disulfide (eq 4). An oven-dried reaction vessel was charged with $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol), AgOTf (15.4 mg, 0.06 mmol), 1-(pyrimidin-2-yl)indoline (**1a**) (59.2 mg, 0.3 mmol), diphenyl disulfide (**2a**) (65.5 mg, 0.3 mmol), Ag_2CO_3 (82.7 mg, 0.3 mmol), toluene (1.3 mL), and D_2O (0.2 mL) under air. The vessel was sealed and heated at 130 °C (oil bath) for 1 h. After removal of solvents, the residue was purified by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:20).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01943.

X-ray structural information for **3aj** (CIF)

Details of optimization studies of reaction and full spectroscopic data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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