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Regioselective deoxygenative chalcogenation of 7-azindole *N*-oxides promoted by I_2/PEG-200†

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We developed a general and sustainable approach for the regioselective deoxygenative chalcogenation of 7-azindole *N*-oxides; the combination of an internal oxidant and a green solvent has been used successfully for the synthesis of mono- and dichalcogenyl 7-azaindoles which are of pharmaceutical interest. The regioselectivity is tunable by the variation of the reaction conditions. I_2/PEG was established as an efficient and reusable catalytic system for C–H chalcogenation. This developed methodology has great potential for practical utility, with a broad substrate scope, green reaction conditions, and operational simplicity.

Introduction

7-Azaindoles, as bioisosteres for indoles, are privileged scaffolds in drug discovery and exhibit significant biological activities.[1] Indeed, several 7-azaindole-containing drugs such as vemurafenib (Zelboraf™), Venetoclax, and GSK1070916 are in various stages of clinical development.[2,3] In particular, their corresponding sulfides and selenides have been established as 5-HT6 receptor agonists,[4] MKK4 kinase inhibitors,[5] and BRD4 inhibitors,[6] respectively (Fig. 1). Accordingly, methods for the synthesis of chalcogenyl 7-azindoles and their derivatives have attracted continuous interest over the past decades.[7]

The direct chalcogenation of the indole ring has been widely explored towards the synthesis of mono- or dichalcogenyl compounds and includes two typical strategies: (a) transition metal-catalyzed chalcogenylation through C–H metalation[8] and (b) aromatic chalcogenylation *via* SEAr by using *in situ* generated electrophilic chalcogenyl species[9–12] (Scheme 1). Molecular iodine has emerged as an ideal catalytic oxidant for the chalcogenation of indoles due to its commercial availability, low toxicity, and transition-metal free features.[9a,b,d–j,m–o] Pioneering studies using molecular iodine in green reaction media such as water,[9d] ethanol,[9a,m,n] dimethyl carbonate (DMC),[9g] polyethylene glycol (PEG),[9h] and glycerol[9j] were carried out by Barman,[9h] Tian,[9a] Sinha,[9d] Lenardão[9j] *etc.* However, in the presence of an additional nitrogen atom in the 7-azaindole ring system, when compared to indole, the reactivity reduces in terms of aromatic substitution owing to the fused electron-deficient pyridine ring. On the other hand, the metal catalyzed reaction would be prohibited due to the coordination of the substrate to metal catalyst. Therefore the modification of 7-azaindoles remains a chal-

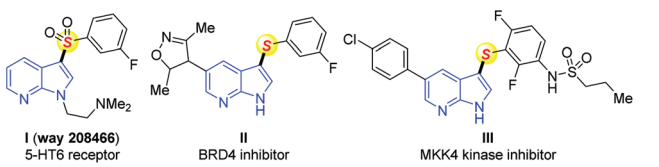
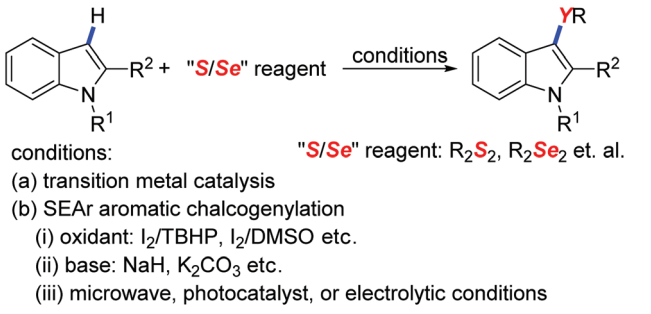


Fig. 1 Representative examples of biologically active C3 chalcogenyl 7-azaindoles.



Scheme 1 Previous strategies for C(sp^2)–H chalcogenation.

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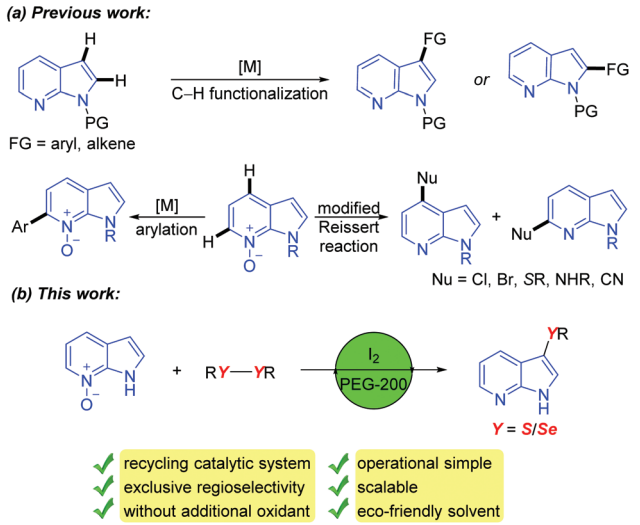
†Electronic supplementary information (ESI) available: All chiral HPLC chromatogram data and spectra for phospha-Michael addition products and copies of NMR spectra for new compounds. CCDC 1954603. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ob02044f



Scheme 2 General procedures for the C–H functionalization of 7-azaindoles.

lenge. In the past few years, C–H functionalization of 7-azaindoles has been accomplished either by transition metal catalysis[13] or by a modified Reissert–Henze type reaction[14] (Scheme 2a). To date, only sporadic examples associated with the chalcogenation of 7-azaindoles have been documented. The direct chalcogenation through C(sp^2)–H bond cleavage involves both the copper catalyzed process[15] and the electrophilic aromatic chalcogenation which can be achieved under mild conditions using base,[16] iodine,[17] bifunctional catalyst,[18] photocatalyst,[19] electrochemical process[11b] or ionic liquids.[20] Despite these achievements, the current methods generally provide a sole example of 7-azaindoles, which required a special reaction set-up, a superstoichiometric amount of external oxidant or toxic organic solvents. In terms of the synthetic simplicity as well as the environmentally benign and sustainable process, exploration of a green, efficient and recyclable catalytic system for selective chalcogenation of 7-indoles is highly desirable.

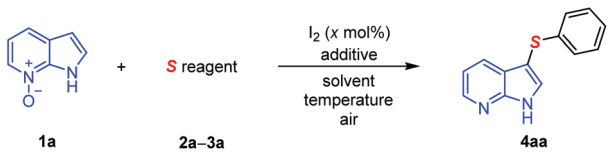
It has been shown that quinoline *N*-oxides serve as an oxidizing directing group for the alkenylation and additional oxidants were avoided.[21] Inspired by this, we assume that 7-azaindole *N*-oxides could also be employed as internal oxidants. Besides, by using the *N*-oxides to activate the aromatic system, both electrophilic and nucleophilic attack would be easier due to the σ-electron-withdrawing and π-back-donating character of the *N*-oxide moiety.[22] Moreover, the *N*-oxide moiety will increase the solubility of the substrate in nontoxic polar solvents. Recently, polyethylene glycol (PEG) has been shown to be a useful solvent due to its non-toxicity, cost effectiveness and reusability.[23] Herein, we developed a general method for the regioselective deoxygenative chalcogenation of 7-azaindole *N*-oxides. The combination of an internal oxidant and a green solvent has emerged as an eco-friendly and sustainable alternative protocol for the synthesis of diversely substituted mono- and bis-arylchalcogen-7-azaindole derivatives. The regioselectivity is tunable in different conditions.

Results and discussion

Initially, the stable and commercially available thiophenols and diaryl disulfides were employed as sulfenyl sources for the screening of reaction conditions. As outlined in Table 1, the mono-and di-sulfenylated products were observed in most cases. Thiophenol was outperformed by diaryl disulfides to deliver the C3 sulfenylation product in 54% yield (entries 1 and 2). Furthermore, the influence of solvents on the reaction system was assessed. The desired product **4aa** in CH_3CN and DMSO was obtained in small amounts (entries 3 and 4). Surprisingly, the reaction could proceed in water giving 37% yield. Various surfactants were subsequently employed to improve the yield; 59% yield was obtained when DDBAC was added while other surfactants were ineffective (entries 5–9). It was found that alcohol could improve the yield dramatically, when tested using methanol, ethanol, and *n*-butanol, and the desired sulfide **4aa** was obtained in 68%, 72%, and 78% yields, respectively (entries 10–12). Since ethanol had to be heated above its atmospheric boiling point, we switched to using PEG-200, which is a solvent with a higher boiling point. Indeed, this change increased the yield remarkably (entry 13). A significant effort has been made to further improve the yield by varying other reaction parameters. A detrimental effect was observed in the presence of water due to the poor solubility of diphenyl disulfide in this solvent (entries 14 and 15). In addition, the temperature screening revealed that the best efficiency was obtained at 110 °C (entry 16). To our delight, lowering the catalyst loading and sulfide had a much more pronounced effect, probably due to the inhibition of the competitive 2,3-disubstitution reaction in this case. Gratifyingly, 0.6 equiv. of diphenyl disulfide is sufficient for this transformation. The results revealed that 10 mol% iodine was necessary to obtain high yields (entries 17–19). Hence the optimal result obtained through the variations of the reaction conditions is indicated in entry 17 of Table 1.

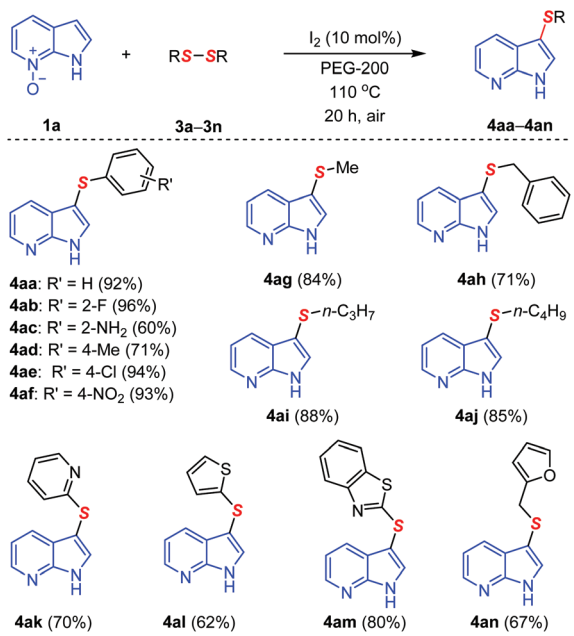
To probe the scope of the reaction, we applied the optimization conditions to a variety of diorgano disulfides as outlined in Scheme 3. It was satisfying to find that sulfides bearing either aromatic or heteroaromatic substitution underwent C3 sulfenylation smoothly. The reaction tolerated a range of functional groups, such as halogen, amino, and nitro groups. Notably, the reaction was sensitive to the electronic properties of the substituents on the aryls. The electron-withdrawing substituents showed superiority over electron-donating substituents to furnish the products in higher yields. The observed substitution effects on the yields were consistent with the electrophilic aromatic substitution mechanism. In previous reports, the sulfenylation of dialkyl disulfides was normally promoted by a higher catalyst loading or a relatively higher reaction temperature,[24] owing to the more difficult formation of electrophilic alkylthiolate counterions compared to arylthiolate counterions. Gratifyingly, good yield was achieved by employing the benzyl and alkyl thios under our optimal reaction conditions, which shows the efficiency and broad generality of our methodology.

Table 1 Optimization of the reaction conditions[a]



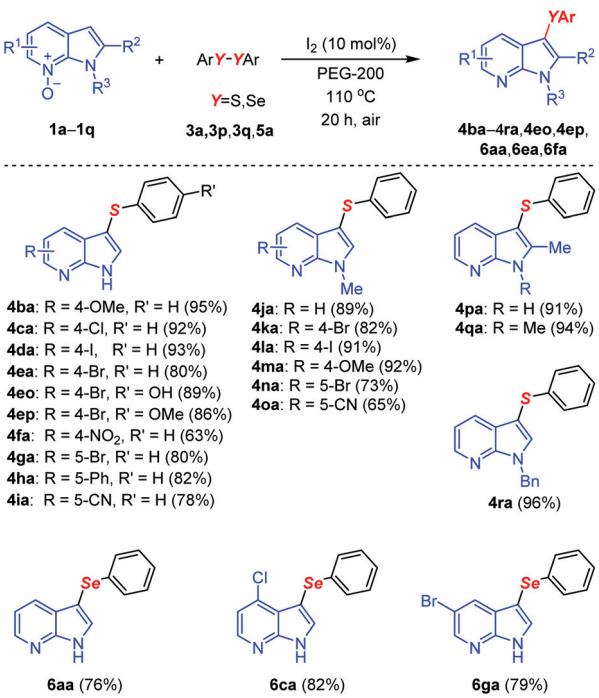
Entry	*S* reagent	I_2 (mol%)	Solvent	Additives	Temperature (°C)	Yield[b] (%)
1	PhSH (**2a**)	30	Toluene		100	54 (9)[c]
2	$(PhS)_2$ (**3a**)	30	Toluene		100	64 (12)[c]
3	$(PhS)_2$ (**3a**)	30	DMSO		100	45
4	$(PhS)_2$ (**3a**)	30	CH_3CN		100	39
5	$(PhS)_2$ (**3a**)	30	H_2O		100	37
6	$(PhS)_2$ (**3a**)	30	H_2O	DDBAC	100	59
7	$(PhS)_2$ (**3a**)	30	H_2O	SDBS	100	42
8	$(PhS)_2$ (**3a**)	30	H_2O	TBAB	100	45
9	$(PhS)_2$ (**3a**)	30	H_2O	DTAC	100	40
10	$(PhS)_2$ (**3a**)	30	Methanol		100	68 (8)[c]
11	$(PhS)_2$ (**3a**)	30	Butanol		100	72 (9)[c]
12	$(PhS)_2$ (**3a**)	30	Ethanol		100	78 (6)[c]
13	$(PhS)_2$ (**3a**)	30	PEG-200		100	86 (5)[c]
14	$(PhS)_2$ (**3a**)	30	PEG-800/H_2O[e]		100	79 (6)[c]
15	$(PhS)_2$ (**3a**)	30	PEG-200/H_2O[e]		100	81 (6)
16	$(PhS)_2$ (**3a**)	10	PEG-200		110	89
17[d]	$(PhS)_2$ (**3a**)	10	PEG-200		110	92
18[d]	$(PhS)_2$ (**3a**)	5	PEG-200		110	58
19[d]	$(PhS)_2$ (**3a**)	—	PEG-200		110	0

[a] Reactions were carried out using **1a** (0.4 mmol), **2a** (0.4 mmol), and solvent (2 mL) for 20 h under air. [b] Isolated yields. [c] Data in the parenthesis refer to the yield of 2,3-disulfenylation-7-azaindole product **4aa′**. [d] 0.6 equiv. of **2a** was used. [e] The volume ratio of PEG : H_2O = 1 : 1. DDBAC = benzyldodecyldimethyl ammonium chloride; SDBS = sodium dodecylbenzenesulfonate; TBAB = tetrabutylammonium bromide; DTAC = dodecyl trimethyl ammonium chloride.



Scheme 3 Variation of disulfides in the C3 sulfenylation.

Subsequently, a broad spectrum of 7-azaindole derivatives were subjected to chalcogenation (Scheme 4). As expected, all the reactions proceeded smoothly. Interestingly, the halogen moieties were intact under our conditions, providing the

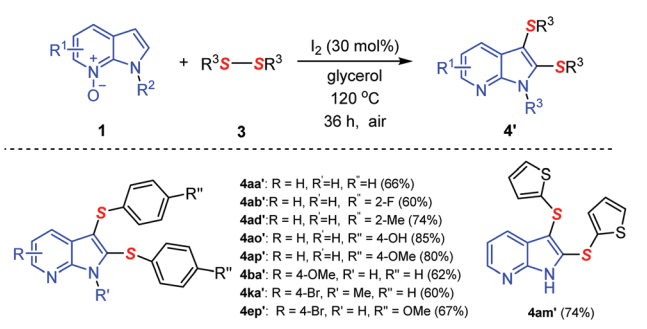


Scheme 4 Substrate scope of 7-azaindoles and organochalcogenating reagents.

desired products in excellent yields, amenable for further functionalization. The position of the substituents on 7-azaindole had a negligible effect on the reactivity, whereas a preference for electron-rich substituents was observed for this transformation, which provided the evidence for the SEAr pathway. To our delight, products **4ba** and **4qa** were obtained in nearly complete conversion. In addition, replacement of unsubstituted 7-azaindole with *N*-alkyl and *N*-benzyl 7-azaindoles led to slightly better results. It was rewarding to find that the present reaction system was applicable to C–H selenation, and structurally diverse 3-selenyl 7-indoles were formed in moderate to good yields. Notably, compound **4ga** is active on protein kinases and VPS34, which show potential for treating human diseases.[25] Our protocols allow access to a library of chalcogenated 7-azaindole derived bioactive compounds of pharmaceutical interest.

The C3-position is the most nucleophilic site of the 7-azaindole nucleus, and the presence of a sulfide group may sterically inhibit further sulfenylation. To test this hypothesis, an intensive screening was conducted (see the ESI† for details). The disulfenylation was established by using excess amounts of sulfenylating reagents in the presence of 30 mol% iodine in glycerol at 120 °C (Scheme 5). It is worth noting that the electron rich sulfenylating reagents **4ad′**–**4ap′** afforded the disulfenylated products in higher yields, whereas a reduced yield was observed in the case of electron poor sulfenylating reagent **4ab′** with a concomitant monosubstituted product. The reactivity pattern is contrary to the trend in terms of monosulfenylation. The data suggested that the migration was presumably involved in the second sulfenylation. Sulfide bearing electron rich substituents were preferred for the migration rather than electron-deficient substituted sulfide.

To further demonstrate the synthetic utility of this protocol, we studied the reusability of the catalytic system (Fig. 2) and gram scale experiments were carried out (Scheme 6). The recycling study of the catalytic system using a model substrate demonstrated that the catalytic system can be reused for up to three cycles without any notable loss in catalytic activity. The catalytic system could be reused due to the formation of a complex of iodine in polyethylene glycol.[26] Furthermore, scale-up reactions were carried out at 10 mmol and a compatible yield was obtained. The configuration of compound **4aa** is confirmed by X-ray diffraction. Next, we were pleased to find that halogen substituted 7-azaindoles were suitable building blocks for further elaboration. Gratifyingly, amino and pyridyl groups were installed at different positions through the palladium catalyzed coupling reaction.[25,28]



Scheme 5 Deoxygenative 2,3-disulfenylation of 7-azaindole *N*-oxides.

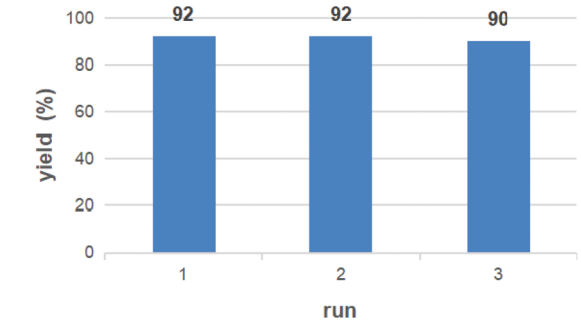
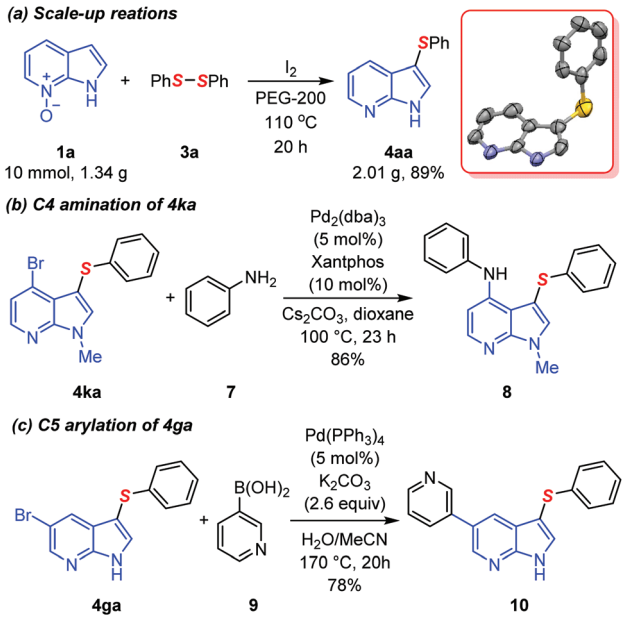
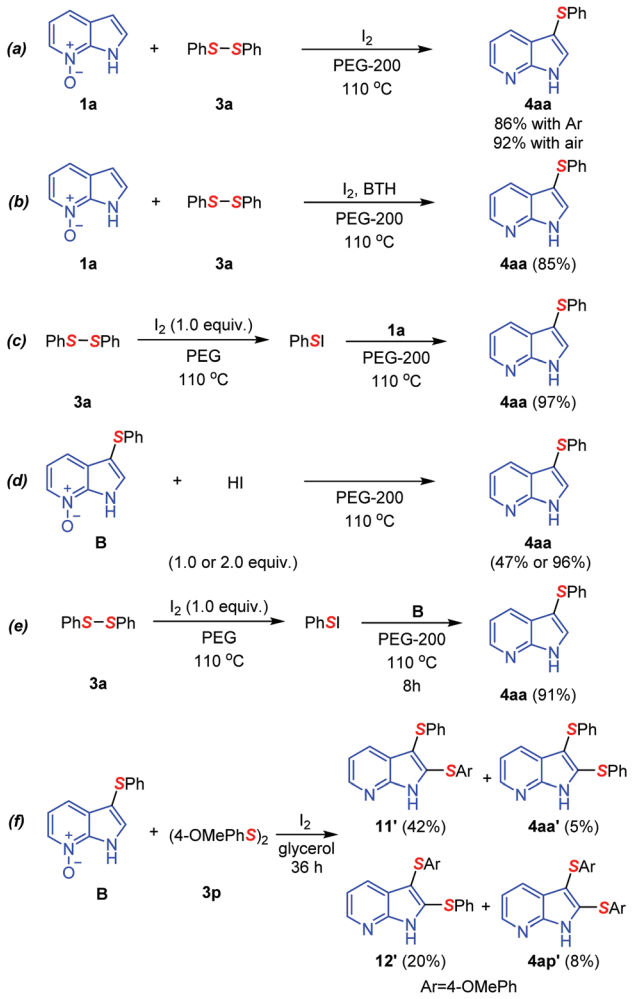


Fig. 2 Recyclability of I_2/PEG in the deoxygenative C–H sulfenylation between 7-azaindole *N*-oxide **1a** and diphenyl disulfide **2a**.

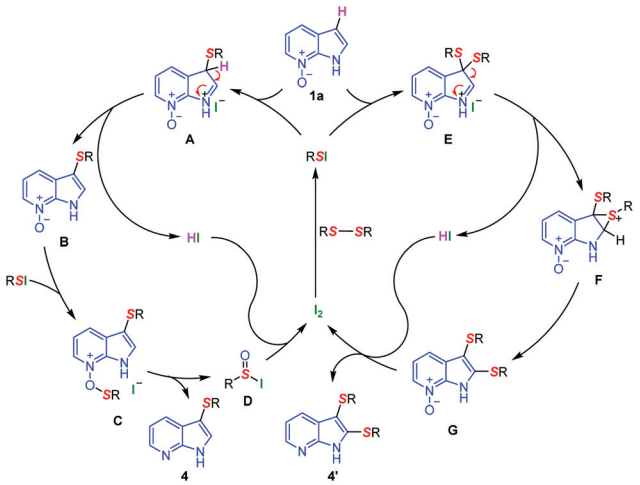


Scheme 6 The scale-up reaction and late-stage modification.

To elucidate the effect of *N*-oxides and air on the reaction, parallel experiments were carried out under air and argon, and similar high yields were obtained (Scheme 7a), which suggested that the *N*-oxides rather than air played a crucial role in ensuring the efficiency of the reaction. To gain insights into the reaction mechanism, control experiments were performed. The desired product was generated with a comparable yield in the presence of butylated hydroxytoluene (BHT) as a radical scavenger, which excluded the involvement of a free-radical pathway (Scheme 7b). I_2 and **3a** were heated to generate the *in situ* formed PhSI,[9b] then **1a** was added into the above solution, and **4aa** was delivered in 97% yield, which showed that the reaction would start from the formation of an electro-



Scheme 7 Mechanistic studies.



Scheme 8 Proposed mechanism.

philic sulfur species (Scheme 7c). In order to investigate the deoxygenation step, intermediate **B** was synthesized and subsequently subjected to the HI solution (Scheme 7d) and PhSI (Scheme 7e), respectively. The desired product **4aa** was formed in both cases, which revealed that the formation of **B** as the intermediate is involved in the reaction. When 1 equiv. of HI was used, a deoxygenative product was obtained in 47% yield (Scheme 7d), while 91% yield was observed by employing the *in situ* formed PhSI (Scheme 7e). These observations demonstrated that the deoxygenation step of the mono-sulfenylation occurred predominantly *via* the oxidation of PhSI. When excess HI was used, 96% yield was observed, which indicated that the HI generation in the disulfenylation step was probably sufficient to reduce the *N*-oxide.

Considering that migration would occur in the second sulfenylation, the reaction of 3-phenylthio-7-azaindole *N*-oxide and 4-methoxy substituted diphenyl disulfide was performed (Scheme 7f), and mixtures of mixed 2,3-bissulfides were obtained instead of a single isomer bearing the second sulfide group at the C2 position. This result indicated that the mechanism proceeded *via* an initial second sulfenylation at the C3 position followed by rearrangement. It was found that the major isomer was the sulfide bearing electron-rich group at the C2 position, and the electron rich substituted sulfide was favored in migration, offering a possible explanation in this regard.

Based on the above results and previous reports, a plausible pathway was proposed as depicted in Scheme 8. Initially, the electrophilic sulfur species PhSI was generated *in situ* from PhSSPh and I_2,[9b–d,f–h,j,n] which facilitated the electrophilic sulfenylation of 7-azaindole to form intermediate **A**. Then the deoxygenation took place by the attack of another PhSI to give the desired product **4** and compound **D**. Fortunately, **D** was detected by GC-MS. Subsequently, HI was oxidized by **D** to regenerate the catalyst I_2 and PhSOH, which would serve as the electrophilic sulfur source and involve in the next cycle. On the other hand, the second sulfenylation occurred by initial addition at the C3 position of the 7-azaindole ring, leading to 3,3′-disubstituted azaindolenine intermediate **E**, followed by the migration of one of the sulfide groups to the C2 position. Finally, two molecules of HI were oxidized by one molecule of intermediate **G** to deliver the disulfenylated product **4′** and reproduce the catalyst I_2.

Conclusions

In conclusion, we disclosed a novel and general approach for the chalcogenation of 7-azindole from the corresponding *N*-oxides. I_2/PEG was established as an efficient and reusable catalytic system for deoxygenative C–H chalcogenation. In this transformation, 7-azaindole *N*-oxides served both as substrates and as internal oxidants, leading to a wide spectrum of bioactive 7-azaindole derivatives bearing mono- and dichalcogenyl substituents. Alkyl, aryl, and heteroaryl chalcogenating reagents were compatible in our protocol, providing the corresponding products in excellent yields. The regioselectivity was modulated by variation of the reaction parameters, a reversed reactivity pattern for mono- and disulfenylation was observed,

and a possible mechanism was proposed to account for the observed results. This protocol represents an eco-friendly, scalable and sustainable process for the derivatization of 7-azaindole and has great potential in modern synthetic chemistry and the pharmaceutical industry.

Experimental

General remarks

All reactions were performed in flame-dried glassware with a magnetic stirring bar. Liquids and solutions were transferred with syringes. Solvents were purified and dried following the standard procedures. Technical grade solvents were used for extraction and chromatography (ethyl acetate, petroleum ether, and diethyl ether) and were distilled prior to use. Substrates **1a**, **1b**, **1e–1h**, **1j**, **1p**, and **1q** and chalcogenating reagents **2a** and **3a–3n** were purchased and used directly without purification. Analytical thin-layer chromatography (TLC) was performed on silica gel GF_{254} glass plates obtained from Qingdao Haiyang Chemical Co., Ltd. Flash column chromatography was performed on silica gel (300–400 mesh) obtained from Qingdao Haiyang Chemical Co., Ltd using the indicated solvents. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance III 400 MHz instrument. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H and $CDCl_3$: δ = 77.16 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectrometry (HRMS) analyses were performed on an Agilent 6460 instrument. Melting points were measured on SGW X-4B melting point apparatus and are uncorrected.

General procedure for the synthesis of 7-azaindole *N*-oxides (GP1)[2]

To a solution of 7-azaindole derivatives (2 mmol, 1 equiv.) in EtOAc (2 mL) was added *m*-CPBA (85 wt%, 1.30 equiv.) in portions below 20 °C. The resulting suspension was stirred at 25 °C for 12 h and filtered. The resulting solids were washed with EtOAc/petroleum ether (40/60, w/w, ×2) and dried at below 40 °C under reduced pressure to provide 7-azaindole *N*-oxide *m*-CPBA salts. Then 2 M aqueous K_3PO_4 solution and water were added to adjust the pH to 10 at 10–15 °C. The suspension was stirred at 0 °C for 1 h and filtered. The solid was washed with cold water and dried under reduced pressure. Purification by flash column chromatography on silica gel using mixtures of petroleum ether and ethyl acetate as eluents afforded the analytically pure product.

4-Chloro-7-azaindole-nitrogen oxide (1c)[27]

Pale solid (302 mg, 90%); **m.p.** = 222–223 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 14.03 (s, 1H), 8.19 (d, J = 6.7 Hz, 1H), 7.46 (d, J = 3.4 Hz, 1H), 7.10 (d, J = 6.7 Hz, 1H), 6.63 (d, J = 3.3 Hz, 1H) ppm.

4-Iodine-7-azaindole-nitrogen oxide (1d)

Pale solid (456 mg, 88%); **m.p.** = 214–215 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.88 (s, 1H), 7.95 (d, J = 6.4 Hz, 1H), 7.56 (d, J = 3.4 Hz, 1H), 7.47 (d, J = 6.5 Hz, 1H), 6.36 (d, J = 3.3 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 146.8, 143.1, 127.2, 125.7, 125.0, 103.0, 99.0 ppm; **HRMS** (ESI-TOF) exact mass for $[M + H]^+$ ($C_7H_6IN_2O$): calcd m/z 260.9519, found: 260.9518.

5-Cyano-7-azaindole-nitrogen oxide (1i)[2]

Red solid (276.8 mg, 87%); **m.p.** = 116–117 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 13.17 (s, 1H), 8.76 (d, J = 1.3 Hz, 1H), 8.25 (d, J = 1.3 Hz, 1H), 7.65 (d, J = 3.3 Hz, 1H), 6.72 (d, J = 3.3 Hz, 1H) ppm.

N-Methyl-4-bromine-7-azaindole-nitrogen oxide (1k)

Brown solid (330 mg, 77%); **m.p.** = 94–95 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.96 (d, J = 6.5 Hz, 1H), 7.51 (d, J = 3.4 Hz, 1H), 7.26 (d, J = 6.5 Hz, 1H), 6.43 (d, J = 3.4 Hz, 1H), 4.27 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 136.5, 133.7, 133.1, 124.7, 123.8, 116.4, 99.4, 36.9 ppm; **HRMS** (ESI-TOF) exact mass for $[M + H]^+$ ($C_8H_8BrN_2O$): calcd m/z 226.9815, found: 226.9813.

N-Methyl-4-iodo-7-azaindole-nitrogen oxide (1l)

Yellow solid (394 mg, 72%); **m.p.** = 214–215 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.97 (s, 1H), 7.63 (s, 1H), 7.54 (s, 1H), 6.30 (s, 1H), 3.85 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 145.9, 142.9, 131.1, 125.9, 124.9, 101.9, 99.3, 31.8 ppm; **HRMS** (ESI-TOF) exact mass for $[M + H]^+$ ($C_8H_8IN_2O$): calcd m/z 274.9676, found: 274.9678.

N-Methyl-4-methoxy-7-azaindole-nitrogen oxide (1m)

White solid (281.5 mg, 79%); **m.p.** = 102–103 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.15 (dd, J = 5.5, 1.3 Hz, 1H), 7.33 (dd, J = 3.5, 1.3 Hz, 1H), 6.67 (dd, J = 5.5, 1.3 Hz, 1H), 6.45 (dd, J = 3.4, 1.4 Hz, 1H), 3.95 (d, J = 1.4 Hz, 3H), 3.79 (d, J = 1.4 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 159.6, 149.7, 144.9, 127.8, 110.2, 98.3, 96.5, 55.8, 31.4 ppm; **HRMS** (ESI-TOF) exact mass for $[M + H]^+$ ($C_9H_{11}N_2O_2$): calcd m/z 179.0815, found: 179.0816.

N-Methyl-5-bromine-7-azaindole-nitrogen oxide (1n)

Brown solid (354.1 mg, 78%); **m.p.** = 97–98 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.27 (d, J = 1.4 Hz, 1H), 7.84 (t, J = 1.3 Hz, 1H), 7.46 (dd, J = 3.4, 1.0 Hz, 1H), 6.50 (dd, J = 3.3, 1.1 Hz, 1H), 4.24 (d, J = 1.3 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 136.2, 133.7, 133.6, 126.1, 122.8, 108.2, 101.1, 36.6 ppm; **HRMS** (ESI-TOF) exact mass for $[M + H]^+$ ($C_8H_8BrN_2O$): calcd m/z 226.9815, found: 226.9817.

N-Methyl-5-cyano-7-azaindole-nitrogen oxide (1o)

Red solid (207.6 mg, 60%); **m.p.** = 116–117 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.60 (d, J = 1.3 Hz, 1H), 8.16 (d, J = 1.4 Hz, 1H), 7.59 (d, J = 3.4 Hz, 1H), 6.67 (d, J = 3.4 Hz, 1H), 4.29 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO): δ = 145.3, 138.4, 134.8, 125.2, 116.8, 102.9, 101.4, 37.0 ppm; **HRMS** (ESI-TOF) exact mass for $[M + H]^+$ ($C_9H_8N_3O$): calcd m/z 174.0662, found: 174.0661.

N-Benzyl-7-azaindole-nitrogen oxide (1r)

Light red solid (336 mg, 75%); **m.p.** = 104–105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 6.2 Hz, 1H), 7.55 (dd, J = 8.0, 1.0 Hz, 1H), 7.38–7.30 (m, 4H), 7.29 (s, 1H), 7.12 (t, J = 2.7 Hz, 1H), 6.98 (dd, J = 8.0, 6.2 Hz, 1H), 6.53 (t, J = 2.9 Hz, 1H), 6.17 (d, J = 1.7 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO: δ = 147.7, 143.0, 138.9, 129.4, 129.0, 128.9, 128.7, 127.7, 120.5, 116.2, 100.1, 47.6 ppm; **HRMS** (ESI-TOF) exact mass for $[M + H]^+$ ($C_{14}H_{13}N_2O$): calcd m/z 225.1022, found: 225.1021.

General procedure for the deoxygenative C3–H chalcogenation of 7-azaindole *N*-oxides (GP2)

A Teflon capped vial equipped with a magnetic stir bar was successively charged with 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide derivative (0.40 mmol, 1.0 equiv.), 1,2-diaryldisulfane or 1,2-diphenyldiselane (0.24 mmol, 0.6 equiv.), and I_2 (0.04 mmol, 10 mol%) in PEG-200 (2.0 mL) at room temperature. The reaction mixture was heated to 110 °C for an indicated time. The reaction was monitored by TLC. After completion, the reaction mixture was allowed to cool to room temperature and extracted with diethyl ether (Et_2O) at least three times. The combined mixture was concentrated under reduced pressure. Purification by flash column chromatography on silica gel using mixtures of petroleum ether and ethyl acetate as eluents afforded the analytically pure product.

3-(Phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4aa)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (83.3 mg, 92%) as a white solid; **m.p.** = 188–189 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.30 (s, 1H), 8.31 (dd, J = 4.7 Hz, J = 1.6 Hz, 1H), 7.94 (d, J = 2.3 Hz, 1H), 7.79 (dd, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.21 (dd, J = 8.3 Hz, J = 7.1 Hz, 2H), 7.15–7.01 (m, 4H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 148.9, 143.7, 138.6, 133.2, 128.9, 126.7, 125.5, 125.0, 120.9, 116.6, 98.5 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{11}N_2S$): calcd m/z 227.0737, found: 227.0635.

3-[(2-Fluorophenyl)thio]-1*H*-pyrrolo[2,3-*b*]pyridine (4ab)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-bis(2-fluorophenyl)disulfane (**3b**, 61.0 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (93.8 mg, 96%) as a pale solid; **m.p.** = 192–193 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.43 (s, 1H), 8.33 (dd, J = 4.6 Hz, J = 1.5 Hz, 1H), 8.00 (s, 1H), 7.81 (dd, J = 7.9 Hz, J = 1.5 Hz, 1H), 7.21–7.08 (m, 3H), 6.96 (t, J = 7.6 Hz, 1H), 6.68 (td, J = 7.9 Hz, J = 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 158.6 (J = 240 Hz), 149.3, 144.3, 134.4, 127.9 (J = 2.1 Hz), 127.3 (J = 7.3 Hz), 127.1, 126.2 (J = 16.5 Hz), 125.5 (J = 3.2 Hz), 121.5, 117.2, 115.8 (J = 21 Hz), 96.5 ppm; **^{19}F NMR** (377 MHz, DMSO-d_6): δ = −114.28; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}FN_2S$): calcd m/z 245.0543, found: 245.0540.

2-[(1*H*-Pyrrolo[2,3-*b*]pyridin-3-yl)thio]aniline (4ac)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 2,2′-disulfanediyldianiline (**3c**, 59.6 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (62.7 mg, 65%) as a brown solid; **m.p.** = 212–213 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.38 (s, 1H), 8.33 (dd, J = 4.6 Hz, J = 1.6 Hz, 1H), 7.98–7.90 (m, 2H), 7.74 (dd, J = 7.9 Hz, J = 1.5 Hz, 1H), 7.27 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.21–7.09 (m, 2H), 6.70 (d, J = 8.1 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 166.1, 149.6, 144.3, 143.6, 134.2, 133.1, 131.3, 127.2, 126.4, 124.6, 121.4, 117.2, 99.2 ppm; **HRMS** (ESI-TOF) exact mass for $[M + H]^+$ ($C_{13}H_{12}N_3S$): calcd m/z 242.0746, found: 242.0744.

3-(*p*-Tolylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ad)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-di-*p*-tolyldisulfane (**3d**, 59.1 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (68.2 mg, 71%) as a white solid; **m.p.** = 172–173 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.24 (s, 1H), 8.30 (d, J = 4.6 Hz, 1H), 7.91 (d, J = 2.3 Hz, 1H), 7.77 (dd, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.12 (dd, J = 7.9 Hz, J = 4.6 Hz, 1H), 7.06–6.93 (m, 4H), 2.20 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 148.9, 143.6, 134.8, 134.5, 132.8, 129.6, 126.7, 126.0, 120.9, 116.5, 99.3, 20.4 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{13}N_2S$): calcd m/z 241.0794, found: 241.0798.

3-[(4-Chlorophenyl)thio]-1*H*-pyrrolo[2,3-*b*]pyridine (4ae)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-bis(4-chlorophenyl)disulfane (**3e**, 68.9 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (98.0 mg, 94%) as a white solid; **m.p.** = 203–204 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.33 (s, 1H), 8.32 (dd, J = 4.7 Hz, J = 1.6 Hz, 1H), 7.96 (d, J = 2.3 Hz, 1H), 7.79 (dd, J = 7.9 Hz, J = 1.6 Hz, 1H), 7.32–7.23 (m, 2H), 7.15 (dd, J = 7.9 Hz, J = 4.7 Hz, 1H), 7.09–7.00 (m, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.6, 136.9, 132.0, 130.5, 130.4, 129.8, 129.4, 128.0, 127.7, 117.9, 39.9 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}ClN_2S$): calcd m/z 261.0248, found: 261.0246.

3-[(4-Nitrophenyl)thio]-1*H*-pyrrolo[2,3-*b*]pyridine (4af)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-bis(4-nitrophenyl)disulfane (**3f**, 74.0 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (100.9 mg, 93%) as a yellow solid; **m.p.** = 222.4–224.6 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.53 (s, 1H), 8.37 (dd, J = 4.7 Hz, J = 1.6 Hz, 1H), 8.07 (td, J = 8.6 Hz, J = 2.6 Hz, 3H), 7.81 (dd, J = 7.9 Hz, J = 1.6 Hz, 1H), 7.19 (ddd, J = 11.2 Hz, J = 7.5 Hz, J = 3.3 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.7, 149.5, 145.0, 144.5, 134.6, 127.1, 125.5, 124.6, 121.0, 117.4, 96.4 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}N_3O_2S$): calcd m/z 272.0488, found: 272.0485.

3-(Methylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ag)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-dimethyldisulfane (**3g**, 21.2 μL, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (59.3 mg, 90%) as a yellow solid; **m.p.** = 184–185 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 11.94 (s, 1H), 8.27 (dd, J = 4.6 Hz, J = 1.6 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.64 (s, 1H), 7.13 (ddd, J = 7.4 Hz, J = 4.7 Hz, J = 2.4 Hz, 1H), 2.33 (d, J = 1.5 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.0, 143.7, 129.7, 127.2, 121.1, 116.3, 105.1, 20.0 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_8H_9N_2S$): calcd m/z 165.0481, found: 165.0477.

3-(Benzylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ah)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-dibenzyldisulfane (**3h**, 59.1 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (68.3 mg, 71%) as a white solid; **m.p.** = 172–173 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 11.89 (s, 1H), 8.24 (dd, J = 4.6 Hz, J = 1.5 Hz, 1H), 7.79 (dd, J = 7.8 Hz, J = 1.5 Hz, 1H), 7.43 (d, J = 2.2 Hz, 1H), 7.22–7.06 (m, 6H), 3.90 (s, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 148.9, 143.5, 139.2, 131.8, 129.3, 128.6, 127.2, 127.2, 121.8, 116.5, 102.4, 46.8 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{13}N_2S$): calcd m/z 241.0794, found: 241.0792.

3-(Propylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ai)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-dipropyldisulfane (**3i**, 36.1 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (67.7 mg, 88%) as a white solid; **m.p.** = 187–188 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 11.98 (s, 1H), 8.27 (dt, J = 4.8 Hz, J = 1.3 Hz, 1H), 7.97 (dt, J = 7.8 Hz, J = 1.3 Hz, 1H), 7.65 (s, 1H), 7.13 (dd, J = 7.9 Hz, J = 4.7 Hz, 1H), 2.60 (t, J = 7.2 Hz, 2H), 1.42 (q, J = 7.3 Hz, 2H), 0.88 (t, J = 7.3 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.1, 143.6, 131.5, 127.1, 121.9, 116.5, 102.7, 38.2, 23.0, 13.3 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{10}H_{13}N_2S$): calcd m/z 193.0794, found: 193.0790.

3-(Butylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4aj)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-dibutyldisulfane (**3j**, 42.8 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (70.1 mg, 85%) as a white solid; **m.p.** = 178–180 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 11.96 (s, 1H), 8.26 (dt, J = 4.6 Hz, J = 1.2 Hz, 1H), 7.97 (dt, J = 7.9 Hz, J = 1.1 Hz, 1H), 7.64 (d, J = 1.8 Hz, 1H), 7.13 (ddd, J = 7.8 Hz, J = 4.6 Hz, J = 0.8 Hz, 1H), 2.64 (t, J = 7.0 Hz, 2H), 1.43–1.29 (m, 4H), 0.79 (td, J = 7.2, 1.1 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.1, 143.6, 131.5, 127.1, 121.9, 116.5, 102.8, 35.9, 31.8, 21.4, 14.0 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{11}H_{15}N_2S$): calcd m/z 207.0950, found: 207.0948.

3-(Pyridin-2-ylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ak)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-di(pyridin-2-yl)disulfane (**3k**, 52.9 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (63.6 mg, 70%) as a white solid; **m.p.** = 183–185 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.39 (s, 1H), 8.35 (dd, J = 10.6, J = 4.5 Hz, 2H), 7.98 (d, J = 1.8 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.51 (dd, J = 7.6, J = 1.9 Hz, 1H), 7.12–7.09 (m, 2H), 6.68 (d, J = 8.1 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 162.0, 149.7, 149.5, 144.2, 137.6, 134.1, 127.2, 121.4, 120.2, 119.6, 117.2, 97.7 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{12}H_{10}N_3S$): calcd m/z 228.0590, found: 228.0587.

3-(Thiophen-2-ylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4al)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-di(thiophen-2-yl)disulfane (**3l**, 55.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (57.6 mg, 62%) as a pale solid; **m.p.** = 196–198 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.20 (s, 1H), 8.29 (dd, J = 4.7 Hz, J = 1.5 Hz, 1H), 8.01 (dd, J = 7.9 Hz, J = 1.5 Hz, 1H), 7.91 (d, J = 1.9 Hz, 1H), 7.44 (dd, J = 5.2 Hz, J = 1.1 Hz, 1H), 7.25–7.13 (m, 2H), 6.95 (dd, J = 5.3 Hz, J = 3.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 148.9, 144.1, 137.3, 132.1, 130.8, 129.0, 128.2, 127.2, 120.9, 117.0, 103.1 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{11}H_9N_2S_2$): calcd m/z 233.0202, found: 233.0199.

2-[(1*H*-Pyrrolo[2,3-*b*]pyridin-3-yl)thio]benzo[*d*]thiazole (4am)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-bis(benzo[*d*]thiazol-2-yl)disulfane (**3n**, 79.8 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (90.7 mg, 80%) as a yellow solid; **m.p.** = 202–203 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.68 (s, 1H), 8.39 (d, J = 4.6 Hz, 1H), 8.24 (s, 1H), 7.99 (d,

J = 7.8 Hz, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 7.7 Hz, 1H), 7.30–7.20 (m, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 173.0, 154.5, 149.3, 144.7, 135.4, 135.2, 127.2, 126.7, 124.5, 122.1, 121.6, 120.9, 117.7, 96.8 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{10}N_3S_2$): calcd m/z 284.0311, found: 284.0306.

3-[(Furan-2-ylmethyl)thio]-1*H*-pyrrolo[2,3-*b*]pyridine (4an)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-bis(furan-2-ylmethyl)disulfane (**3n**, 54.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (65.4 mg, 71%) as a brown solid; **m.p.** = 187.1–188.6 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 11.98 (s, 1H), 8.25 (dd, J = 4.7 Hz, J = 1.6 Hz, 1H), 7.78 (dd, J = 7.9 Hz, J = 1.6 Hz, 1H), 7.59–7.47 (m, 2H), 7.10 (dd, J = 7.9 Hz, J = 4.7 Hz, 1H), 6.28 (dd, J = 3.2 Hz, J = 1.9 Hz, 1H), 5.95 (d, J = 3.2 Hz, 1H), 3.92 (s, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 151.9, 148.9, 143.7, 142.8, 132.2, 127.1, 121.8, 116.5, 111.1, 108.3, 101.9, 33.4 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{12}H_{11}N_2OS$): calcd m/z 231.0587, found: 231.0585.

4-Methoxy-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ba)

Prepared from 4-methoxy-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1b**, 65.7 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 56.7 mg, 0.24 mmol, 0.65 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (100.4 mg, 98%) as a yellow solid; **m.p.** = 175–176 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.16 (s, 1H), 8.16 (d, J = 5.5 Hz, 1H), 7.63 (s, 1H), 7.20 (t, J = 7.6 Hz, 2H), 7.04 (d, J = 8.1 Hz, 3H), 6.67 (d, J = 5.5 Hz, 1H), 3.72 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 160.7, 151.2, 146.2, 140.9, 131.4, 129.1, 126.1, 125.1, 110.7, 99.4, 98.5, 55.9 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{13}N_2OS$): calcd m/z 257.0743, found: 257.0740.

4-Chloro-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ca)

Prepared from 4-chloro-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1c**, 67.4 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 56.7 mg, 0.24 mmol, 0.65 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (95.9 mg, 92%) as a light brown solid; **m.p.** = 198–199 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.67 (s, 1H), 8.24 (d, J = 5.1 Hz, 1H), 8.02 (d, J = 2.1 Hz, 1H), 7.21 (q, J = 6.2 Hz, J = 4.8 Hz, 3H), 7.08 (t, J = 7.3 Hz, 1H), 7.02 (d, J = 7.8 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 150.4, 144.7, 140.6, 135.9, 135.4, 129.4, 125.7, 125.3, 118.1, 118.0, 98.8 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}ClN_2S$): calcd m/z 261.0248, found: 261.0245.

4-Iodo-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4da)

Prepared from 4-iodo-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1d**, 104 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 56.7 mg, 0.24 mmol, 0.65 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (93.8 mg, 93%) as a brown solid; **m.p.** = 212–214 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.59 (s, 1H), 8.06 (d, J = 2.1 Hz, 1H), 7.92 (d, J = 4.9 Hz, 1H), 7.63 (d, J = 4.9 Hz, 1H), 7.21 (t, J = 7.6 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 7.00–6.94 (m, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 148.0, 144.1, 141.1, 136.7, 129.3, 128.3, 125.6, 125.2, 122.0, 100.7, 97.8 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}IN_2S$): calcd m/z 352.9604, found: 352.9601.

4-Bromo-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ea)

Prepared from 4-bromo-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1e**, 85.2 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (102.5 mg, 84%) as a light yellow solid; **m.p.** = 210–212 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.68 (s, 1H), 8.14 (d, J = 5.1 Hz, 1H), 8.05 (d, J = 2.4 Hz, 1H), 7.37 (d, J = 5.1 Hz, 1H), 7.22 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 7.8 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.7, 144.5, 140.8, 136.4, 129.4, 125.7, 125.3, 124.2, 121.4, 119.5, 99.6 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}BrN_2S$): calcd m/z 304.9743, found: 304.9741.

5-{(4-Bromo-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)thio}phenol (4eo)

Prepared from 4-bromo-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1e**, 85.2 mg, 0.4 mmol, 1.00 equiv.) and 4,4′-dihydroxyl-diphenyl disulfide (**3o**, 60 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (113.5 mg, 89%) as a brown solid; **m.p.** = 222–224 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.56–12.46 (m, 1H), 8.09 (d, J = 5.2 Hz, 1H), 7.92 (d, J = 2.2 Hz, 1H), 7.34 (d, J = 5.1 Hz, 1H), 6.99 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 156.2, 149.5, 144.3, 135.3, 129.3, 128.2, 124.2, 121.3, 119.3, 116.5, 102.5 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}BrN_2OS$): calcd m/z 320.9697, found: 320.9691.

4-Bromo-3-[(4-methoxyphenyl)thio]-1*H*-pyrrolo[2,3-*b*]pyridine (4ep)

Prepared from 4-bromo-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1e**, 85.2 mg, 0.4 mmol, 1.00 equiv.) and 4,4′-dimethoxyl-diphenyl disulfide (**3p**, 66.7 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (114.9 mg, 86%) as a light yellow solid; **m.p.** = 196–197 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.60 (s, 1H), 8.11 (d, J = 5.2 Hz, 1H), 8.00 (d, J = 2.3 Hz, 1H), 7.39–7.32 (m, 1H), 7.09–7.01 (m, 2H), 6.87–6.78 (m, 2H), 3.67 (d, J = 1.5 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 157.9, 149.6, 144.4, 135.7, 130.7, 128.5, 124.2, 121.3, 119.4, 115.1, 101.6, 55.5 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{12}BrN_2OS$): calcd m/z 334.9854, found: 334.9854.

4-Nitro-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4fa)

Prepared from 4-nitro-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1f**, 71.6 mg, 0.4 mmol, 1.00 equiv.) and 4,4′-dimethoxyl-diphenyl disulfide (**3a**, 87.2 mg, 0.24 mmol, 1 equiv.) according to **GP2**;

purification by flash column chromatography on silica gel afforded the analytically pure product (73.7 mg, 68%) as a red solid; **m.p.** = 191–192 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 13.15 (s, 1H), 8.57 (d, J = 5.1 Hz, 1H), 8.27 (s, 1H), 7.70 (d, J = 5.1 Hz, 1H), 7.23 (t, J = 7.7 Hz, 2H), 7.12 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 8.2 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 152.3, 148.4, 144.6, 139.3, 139.1, 129.4, 126.2, 125.7, 111.0, 110.6, 98.4 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}N_3O_2S$): calcd m/z 272.0494, found: 272.0496.

5-Bromo-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ga)

Prepared from 5-bromo-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1g**, 85.2 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3g**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (101.3 mg, 83%) as a white solid; **m.p.** = 238–240 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.59 (s, 1H), 8.39 (d, J = 2.2 Hz, 1H), 8.05 (s, 1H), 7.94 (d, J = 2.3 Hz, 1H), 7.23 (q, J = 8.1 Hz, 2H), 7.13–7.00 (m, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 147.8, 144.3, 138.5, 135.7, 129.6, 128.9, 126.1, 125.8, 123.3, 112.4, 99.0 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}BrN_2S$): calcd m/z 304.9743, found: 304.9740.

5-Phenyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ha)

Prepared from 5-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1h**, 84.1 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (99.1 mg, 82%) as a white solid; **m.p.** = 190–191 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.46–12.41 (m, 1H), 8.63 (t, J = 1.6 Hz, 1H), 8.01 (dd, J = 2.8 Hz, J = 1.2 Hz, 1H), 7.95 (t, J = 1.6 Hz, 1H), 7.65 (dt, J = 8.1 Hz, J = 1.3 Hz, 2H), 7.46–7.42 (m, 2H), 7.35 (dd, J = 7.3 Hz, J = 1.4 Hz, 1H), 7.24–7.19 (m, 2H), 7.10–7.05 (m, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.0., 143.2, 139.0, 138.9, 134.7, 129.8, 129.5, 129.5, 127.6, 127.5, 126.0, 125.6, 124.8, 121.5, 99.4 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{19}H_{15}N_2S$): calcd m/z 303.0950, found: 303.0947.

3-(Phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile (4ia)

Prepared from 5-cyano-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1i**, 63.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (78.4 mg, 78%) as a pale solid; **m.p.** = 234–236 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.96 (s, 1H), 8.71 (d, J = 1.9 Hz, 1H), 8.34 (d, J = 1.9 Hz, 1H), 8.21 (d, J = 2.6 Hz, 1H), 7.25 (t, J = 7.6 Hz, 2H), 7.12–7.09 (m, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 150.1, 146.9, 138.1, 136.6, 131.7, 129.6, 126.6, 126.0, 120.9, 118.9, 101.5, 101.2 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{10}N_3S$): calcd m/z 252.0590, found: 252.0594.

1-Methyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ja)

Prepared from 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1j**, 59.3 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (89.4 mg, 93%) as a light yellow solid; **m.p.** = 187–189 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.42 (dt, J = 4.7 Hz, J = 1.3 Hz, 1H), 7.89 (dt, J = 7.9 Hz, J = 1.3 Hz, 1H), 7.45 (d, J = 1.0 Hz, 1H), 7.19–7.14 (m, 2H), 7.12 (d, J = 1.3 Hz, 1H), 7.09 (dtd, J = 9.3 Hz, J = 3.2 Hz, J = 1.1 Hz, 3H), 3.93 (d, J = 1.2 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 148.4, 143.8, 139.0, 135.3, 128.8, 127.9, 125.9, 125.1, 122.2, 116.7, 99.6, 31.5 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{13}N_2S$): calcd m/z 241.0794, found: 241.0792.

4-Bromo-1-methyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ka)

Prepared from 4-bromo-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1k**, 90.8 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (109.8 mg, 86%) as a light yellow solid; **m.p.** = 209–210 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): 8.20 (d, J = 3.9 Hz, 1H), 8.06 (s, 1H), 7.41 (d, J = 3.8 Hz, 1H), 7.24 (d, J = 7.1 Hz, 2H), 7.15–7.03 (m, 3H), 3.92 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 148.5, 143.7, 140.5, 137.4, 128.8, 125.9, 125.4, 125.0, 121.3, 120.4, 100.5, 31.9 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{12}BrN_2S$): calcd m/z 318.9899, found: 318.9898.

4-Iodo-1-methyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4la)

Prepared from 4-iodo-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1l**, 109.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (132.8 mg, 91%) as a yellow solid; **m.p.** = 212–213 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.11 (s, 1H), 7.97 (d, J = 5.0 Hz, 1H), 7.67 (d, J = 4.9 Hz, 1H), 7.23 (t, J = 7.7 Hz, 2H), 7.12–7.07 (m, 1H), 7.00–6.96 (m, 2H), 3.88 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 147.0, 143.9, 140.9, 139.9, 129.3, 128.3, 125.6, 125.2, 122.2, 99.4, 98.1, 31.9 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{12}IN_2S$): calcd m/z 366.9760, found: 366.9761.

4-Methoxy-1-methyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ma)

Prepared from 4-methoxy-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1m**, 71.3 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (102.7 mg, 95%) as a yellow solid; **m.p.** = 201–203 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.26 (d, J = 5.6 Hz, 1H), 7.26 (s, 1H), 7.19–7.16 (m, 4H), 7.09 (d, J = 7.0 Hz, 1H), 6.54 (d, J = 5.6 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 161.0, 150.2, 145.7, 140.3, 133.1, 128.5, 126.4, 124.9, 111.4, 99.26, 98.72, 55.5,

31.7 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{15}H_{15}N_2OS$): calcd *m*/*z* 271.0900, found: 271.0897.

5-Bromo-1-methyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4na)

Prepared from 5-bromo-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1n**, 90.8 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (93.2 mg, 73%) as a brown solid; **m.p.** = 206–208 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.42 (d, *J* = 2.1 Hz, 1H), 8.08 (s, 1H), 7.95 (d, *J* = 2.1 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.14–7.03 (m, 3H), 3.88 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 146.9, 144.2, 139.0, 138.5, 129.6, 129.1, 126.2, 125.8, 123.5, 112.6, 97.8, 31.9 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{12}BrN_2S$): calcd *m*/*z* 318.9899, found: 318.9898.

1-Methyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine-5-carbonitrile (4oa)

Prepared from 5-cyano-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1o**, 69.3 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 87.1 mg, 0.24 mmol, 1 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (68.9 mg, 65%) as a brown solid; **m.p.** = 237–238 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.43 (d, *J* = 2.2 Hz, 1H), 8.09 (s, 1H), 7.96 (d, *J* = 2.3 Hz, 1H), 7.24–7.21 (m, 3H), 7.07 (d, *J* = 7.8 Hz, 2H), 3.89 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 146.9, 144.2, 139.0, 138.5, 129.6, 129.1, 126.2, 125.9, 123.5, 112.6, 99.9, 97.8, 31.9 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{15}H_{12}N_3S$): calcd *m*/*z* 266.0746, found: 266.0743.

2-Methyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4pa)

Prepared from 2-methyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1p**, 59.3 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (87.5 mg, 91%) as a light yellow solid; **m.p.** = 172–174 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.26 (s, 1H), 8.22 (dt, *J* = 4.7, 1.5 Hz, 1H), 7.70 (dt, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 7.19 (td, *J* = 7.7 Hz, *J* = 1.5 Hz, 2H), 7.06 (ddt, *J* = 7.6 Hz, *J* = 6.2 Hz, *J* = 3.0 Hz, 2H), 6.99–6.93 (m, 2H), 2.48 (d, *J* = 1.3 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 148.6, 144.0, 142.9, 139.0, 129.5, 126.1, 125.6, 125.3, 122.5, 116.9, 95.9, 12.2 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{14}H_{13}N_2S$): calcd *m*/*z* 241.0794, found: 241.0793.

1,2-Dimethyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4qa)

Prepared from 1,2-dimethyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1q**, 64.9 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 56.7 mg, 0.24 mmol, 0.65 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (99.7 mg, 98%) as a light yellow solid; **m.p.** = 191–193 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.28 (d, *J* = 4.7 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.15–7.06 (m, 2H), 6.99 (d, *J* = 7.7 Hz, 2H), 3.84 (s, 3H), 2.54 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 148.2, 145.4, 142.8, 138.9, 129.5, 126.3, 125.7, 125.4, 122.0, 117.1, 95.4, 29.0, 11.2 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{15}H_{15}N_2S$): calcd *m*/*z* 255.0950, found: 255.0945.

1-Benzyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ra)

Prepared from 1-benzyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1r**, 89.7 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (121.6 mg, 96%) as a light yellow solid; **m.p.** = 193–194 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.38 (dd, *J* = 4.8 Hz, *J* = 1.6 Hz, 1H), 8.17 (s, 1H), 7.83 (dd, *J* = 7.9 Hz, *J* = 1.6 Hz, 1H), 7.36–7.15 (m, 8H), 7.07 (t, *J* = 8.8 Hz, 3H), 5.58 (s, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 148.1, 144.3, 138.8, 138.3, 136.3, 129.5, 129.1, 128.0, 127.9, 127.7, 126.0, 125.7, 121.8, 117.5, 99.0, 48.0 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{20}H_{17}N_2S$): calcd *m*/*z* 317.1107, found: 317.1103.

3-(Phenylselanyl)-1*H*-pyrrolo[2,3-*b*]pyridine (6aa)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldiselane (**5a**, 74.9 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (83.1 mg, 76%) as a white solid; **m.p.** = 173–174 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.32 (s, 1H), 8.30 (d, *J* = 4.6 Hz, 1H), 7.92 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.20–7.10 (m, 6H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.4, 144.1, 134.1, 133.7, 129.7, 128.7, 127.8, 126.3, 122.3, 117.1, 94.4 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{11}N_2Se$): calcd *m*/*z* 275.0082, found: 275.0080.

4-Chloro-3-(phenylselanyl)-1*H*-pyrrolo[2,3-*b*]pyridine (6ca)

Prepared from 4-chloro-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1c**, 67.4 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldiselane (**5a**, 74.9 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (100.9 mg, 82%) as a light yellow solid; **m.p.** = 120–121 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.67 (s, 1H), 8.24 (d, *J* = 5.1 Hz, 1H), 8.02 (s, 1H), 7.21 (q, *J* = 6.2 Hz, *J* = 4.8 Hz, 3H), 7.05 (dd, *J* = 25.5 Hz, *J* = 7.6 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 150.4, 144.7, 140.5, 135.9, 135.4, 129.4, 125.8, 125.4, 118.1, 118.0, 98.8 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}ClN_2Se$): calcd *m*/*z* 308.9692, found: 308.9692.

5-Bromo-3-(phenylselanyl)-1*H*-pyrrolo[2,3-*b*]pyridine (6ga)

Prepared from 5-bromo-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1g**, 85.2 mg, 0.4 mmol, 1.00 equiv.) and 1,2-diphenyldiselane (**5a**, 74.9 mg, 0.24 mmol, 0.60 equiv.) according to **GP2**; purification by flash column chromatography on silica gel afforded the analytically pure product (116.5 mg, 83%) as a light yellow solid; **m.p.** = 191–192 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.61 (s, 1H), 8.41 (d, *J* = 17.6 Hz, 1H), 8.01 (dd, *J* = 37.3 Hz, *J* =

16.8 Hz, 2H), 7.24 (d, J = 18.2 Hz, 5H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 147.7, 144.1, 135.8, 133.1, 129.7, 129.5, 128.9, 126.5, 124.2, 112.3, 94.3 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{13}H_{10}BrN_2Se$): calcd m/z 352.9187, found: 352.9185.

General procedure for the deoxygenative C2–H/C3–H dichalcogenation of 7-azaindole *N*-oxides (GP3)

A Teflon capped vial equipped with a magnetic stir bar was successively charged with 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide derivative (0.25 mmol, 1.0 equiv.), 1,2-diaryldisulfane or 1,2-diphenyldiselane (0.50 mmol, 2.0 equiv.), and I_2 (0.075 mmol, 30 mol%) in glycerol (2.0 mL) at room temperature. The reaction mixture was heated to 120 °C. After 36 h, the reaction mixture was allowed to cool to room temperature, diluted with water and ethyl acetate, and extracted with diethyl ether (Et_2O) at least three times. The combined extract was concentrated under reduced pressure. Purification by flash column chromatography on silica gel using mixtures of petroleum ether and ethyl acetate as eluents afforded the analytically pure product.

2,3-Bis(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4aa′)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 33.5 mg, 0.25 mmol, 1.0 equiv.) and 1,2-diphenyldisulfane (**3a**, 109.2 mg, 0.50 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (55.2 mg, 66%) as a white solid; **m.p.** = 126–127 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.88 (s, 1H), 8.37 (dd, J = 4.7 Hz, J = 1.6 Hz, 1H), 7.80 (dd, J = 7.9 Hz, J = 1.6 Hz, 1H), 7.30 (dd, J = 8.0 Hz, J = 6.8 Hz, 2H), 7.24–7.16 (m, 6H), 7.11 (d, J = 7.3 Hz, 1H), 7.06–7.00 (m, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.7, 145.7, 137.9, 135.4, 134.4, 129.9, 129.5, 128.6, 127.7, 127.2, 126.5, 125.9, 122.1, 117.7, 107.5 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{19}H_{15}N_2S_2$): calcd m/z 335.0671, found: 335.0668.

2,3-Bis[(2-fluorophenyl)thio]-1*H*-pyrrolo[2,3-*b*]pyridine (4ab′)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 33.5 mg, 0.25 mmol, 1.0 equiv.) and 1,2-bis(2-fluorophenyl)disulfane (**3b**, 127 mg, 0.50 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (55.6 mg, 60%) as a white solid; **m.p.** = 197–199 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 13.03 (s, 1H), 8.38 (d, J = 4.7 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.32–7.12 (m, 5H), 7.06 (dt, J = 19.7 Hz, J = 7.8 Hz, 2H), 6.94 (t, J = 6.9 Hz, 1H), 6.65 (t, J = 7.9 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 159.6 (J = 243 Hz), 158.9 (J = 241 Hz), 149.7, 145.8, 133.7, 131.1, 129.7 (J = 7.1 Hz), 128.4, 127.9 (J = 7.5 Hz), 127.6, 125.9 (J = 3.3 Hz), 125.5 (J = 3.2 Hz), 124.6 (J = 16.7 Hz), 122.2, 121.6 (J = 16.8 Hz), 117.9, 116.4 (J = 2.1 Hz), 115.9 (J = 2.1 Hz), 104.8 ppm; **^{19}F NMR** (377 MHz, DMSO-d_6): δ = −111.49, −113.63 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{19}H_{13}F_2N_2S_2$): calcd m/z 371.0483, found: 371.0480.

2,3-Bis(*p*-tolylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ad′)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 33.5 mg, 0.25 mmol, 1.0 equiv.) and 1,2-di-*p*-tolyldisulfane (**3d**, 123 mg, 0.50 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (70.5 mg, 78%) as a white solid; **m.p.** = 82–83 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.78 (s, 1H), 8.34 (d, J = 4.3 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.18–7.07 (m, 5H), 7.01 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 8.1 Hz, 2H), 2.25 (s, 3H), 2.20 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.6, 145.4, 137.0, 135.3, 135.0, 134.2, 131.6, 130.5, 130.1, 129.4, 127.6, 127.0, 122.0, 117.6, 107.6, 21.0, 20.9 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{21}H_{19}N_2S_2$): calcd m/z 363.0984, found: 363.0980.

4,4′-{(1*H*-Pyrrolo[2,3-*b*]pyridine-2,3-diyl}bis(sulfanediyl)) diphenol (4ao′)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 33.5 mg, 0.25 mmol, 1.0 equiv.) and 4,4′-disulfanediyldiphenol (**3o**, 125 mg, 0.50 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (80.6 mg, 88%) as a light yellow solid; **m.p.** = 246–248 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.48 (s, 1H), 9.71 (s, 1H), 9.47 (s, 1H), 8.27 (d, J = 4.7 Hz, 1H), 7.76 (d, J = 9.4 Hz, 1H), 7.22 (d, J = 8.6 Hz, 2H), 7.11 (d, J = 12.6 Hz, 1H), 7.01 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 158.6, 156.7, 149.4, 144.9, 136.4, 133.4, 130.6, 129.9, 127.4, 125.8, 122.5, 122.1, 116.9, 116.6, 108.2 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{19}H_{15}N_2O_2S_2$): calcd m/z 367.0569, found: 367.0571.

2,3-Bis[(4-methoxyphenyl)thio]-1*H*-pyrrolo[2,3-*b*]pyridine (4ap′)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 33.5 mg, 0.25 mmol, 1.0 equiv.) and 1,2-bis(4-methoxyphenyl)disulfane (**3p**, 139 mg, 0.50 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (82.8 mg, 84%) as an orange solid; **m.p.** = 187.1–188.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.57 (s, 1H), 8.16 (dd, J = 4.9 Hz, J = 1.6 Hz, 1H), 7.89 (dd, J = 7.9 Hz, J = 1.6 Hz, 1H), 7.41 (dd, J = 5.7 Hz, J = 3.5 Hz, 2H), 7.17–7.05 (m, 3H), 6.81–6.68 (m, 4H), 3.73 (d, J = 6.5 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 159.8, 158.1, 148.7, 142.6, 137.8, 133.5, 132.7, 129.5, 129.0, 128.2, 123.3, 116.9, 115.1, 114.5, 106.5, 55.6, 55.4 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{21}H_{19}N_2O_2S_2$): calcd m/z 395.0882, found: 395.0880.

2,3-Bis(thiophen-2-ylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4am′)

Prepared from 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 33.5 mg, 0.25 mmol, 1.0 equiv.) and 1,2-di(thiophen-2-yl)disulfane (**3m**, 116 mg, 0.50 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (69.3 mg, 80%) as a pale solid; **m.p.** = 200–202 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.75 (s, 1H), 8.31

(d, J = 4.7 Hz, 1H), 8.04 (dd, J = 7.9 Hz, J = 1.4 Hz, 1H), 7.42–7.34 (m, 2H), 7.25–7.18 (m, 2H), 7.16 (dd, J = 7.9 Hz, J = 4.7 Hz, 1H), 7.00 (dd, J = 5.3 Hz, J = 3.6 Hz, 1H), 6.93 (dd, J = 5.3 Hz, J = 3.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 148.4, 143.5, 136.5, 136.0, 135.3, 131.2, 131.1, 129.4, 128.1, 128.0, 127.9, 127.3, 122.8, 117.2, 107.5 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{15}H_{11}N_2S_4$): calcd m/z 346.9800, found: 346.9797.

4-Methoxy-2,3-bis(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ba′)

Prepared from 4-methoxy-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1b**, 41.1 mg, 0.25 mmol, 1.0 equiv.) and 1,2-diphenyldisulfane (**3a**, 109.2 mg, 0.50 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (63.9 mg, 70%) as a light yellow solid; **m.p.** = 183–185 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 5.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 7.5 Hz, 2H), 7.17 (dd, J = 13.3 Hz, J = 5.7 Hz, 5H), 7.08 (d, J = 7.0 Hz, 1H), 6.48 (d, J = 5.7 Hz, 1H), 3.82 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 160.8, 150.7, 145.3, 139.4, 135.1, 132.9, 129.3, 128.9, 128.5, 126.8, 126.7, 124.9, 112.5, 107.1, 98.9, 55.5 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{20}H_{17}N_2OS_2$): calcd m/z 365.0777, found: 365.0775.

4-Bromo-1-methyl-2,3-bis(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (4ka′)

Prepared from 4-bromo-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1k**, 56.8 0.25 mmol, 1.0 equiv.) and 1,2-diphenyldisulfane (**3a**, 109.2 mg, 0.50 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (69.5 mg, 65%) as a light yellow solid; **m.p.** = 213–214 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.19 (dd, J = 5.1 Hz, J = 1.3 Hz, 1H), 7.35 (dd, J = 5.2 Hz, J = 1.3 Hz, 1H), 7.23–7.08 (m, 10H), 3.89 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 149.2, 144.7, 139.8, 139.4, 134.3, 129.5, 128.8, 128.4, 126.9, 126.3, 125.9, 125.1, 122.3, 120.5, 109.6, 30.5 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{20}H_{16}BrN_2S_2$): calcd m/z 426.9933, found: 426.9929.

4-Bromo-2,3-bis[(4-methoxyphenyl)thio]-1*H*-pyrrolo[2,3-*b*]pyridine (4ep′)

Prepared from 4-bromo-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1e**, 53.2 mg, 0.25 mmol, 1.0 equiv.) and 1,2-bis(4-methoxyphenyl) disulfane (**3q**, 69.5 mg, 0.50 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (79.3 mg, 67%) as a light yellow solid; **m.p.** = 214–215 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.95 (s, 1H), 8.11 (d, J = 5.0 Hz, 1H), 7.37 (d, J = 5.0 Hz, 1H), 7.35–7.30 (m, 2H), 6.98–6.94 (m, 2H), 6.92–6.87 (m, 2H), 6.84–6.78 (m, 2H), 3.71 (s, 3H), 3.70 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 159.8, 157.9, 149.8, 144.9, 140.9, 133.6, 130.2, 128.3, 123.9, 123.5, 121.9, 120.2, 115.6, 115.2, 106.1, 55.7, 55.6 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{21}H_{18}BrN_2O_2S_2$): calcd m/z 472.9988, found: 472.9983.

Reuse of catalytic system study

The feasibility of recycling the catalyst system was studied under the optimized reaction conditions according to **GP2**. To a Teflon capped vial were added 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1a**, 53.6 mg, 0.4 mmol, 1.00 equiv.), 1,2-diphenyldisulfane (**3a**, 52.3 mg, 0.24 mmol, 0.60 equiv.), and I_2 (10 mg, 0.04 mmol, 10 mol%) in PEG-200 (2.0 mL). The resulting mixture was heated to 110 °C for 20 hours. After completion of the reaction, the product was separated by extraction with diethyl ether. The upper layer of diethyl ether contained a product mixture that was directly used for purification. The remaining mixture was subsequently subjected to vacuum to remove the rest of the solvents before it was reused in the next catalytic run. Purification by flash column chromatography afforded the pure product (83.3 mg, 92%), (83.1 mg, 92%), and (81.4 mg, 90%) in three cycles, respectively.

Preparation and characterization data of the C4-amination product 8 from 4ka under palladium catalysis: 1-methyl-*N*-phenyl-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine (8)[28]

A flame-dried Schlenk tube equipped with a magnetic stir bar was successively charged with **4ka** (0.30 mmol, 1.0 equiv.), aniline (**7**, 0.36 mmol, 1.2 equiv.), $Pd_2(dba)_3$ (0.015 mmol, 5 mol%), Xantphos (0.030 mmol, 10 mol%), and Cs_2CO_3 (0.6 mmol, 2.0 equiv.) in dioxane (2 mL) at room temperature. The reaction mixture was heated to 100 °C and monitored by TLC. After 23 h, the reaction mixture was allowed to cool to room temperature and diluted with ethyl acetate (15 mL). The crude reaction mixture was washed with 1% aq. HCl (5 mL) and H_2O (5 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using mixtures of petroleum ether and ethyl acetate as eluents afforded the analytically pure product (85.4 mg, 86%) as a light yellow oil; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.12–8.00 (m, 2H), 7.77 (s, 1H), 7.28 (dt, J = 15.8 Hz, J = 7.7 Hz, 4H), 7.15 (dd, J = 12.0 Hz, J = 7.6 Hz, 3H), 7.05 (dd, J = 15.9 Hz, J = 7.7 Hz, 3H), 6.78 (d, J = 5.5 Hz, 1H), 3.83 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.7, 145.6, 145.3, 140.1, 139.4, 135.1, 129.9, 129.8, 126.2, 126.1, 123.8, 121.2, 108.2, 99.5, 95.9, 31.8 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{20}H_{18}N_3S$): calcd m/z 332.1216, found: 332.1214.

Preparation and characterization data of the C5-heteroarylation product 10 from 4ga under palladium catalysis: 3-(phenylthio)-5-(pyridin-3-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (10)[25]

A flame-dried Schlenk tube equipped with a magnetic stir bar was successively charged with **4ga** (0.30 mmol, 1.0 equiv.), pyridin-3-ylboronic acid (**9**, 0.30 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (0.015 mmol, 5 mol%), and K_2CO_3 (0.78 mmol, 2.6 equiv.) in H_2O/MeCN mixed solvent (2.0 mL, v/v = 1/3) at room temperature. The reaction mixture was heated to 170 °C and monitored by TLC. After 20 h, the reaction mixture was allowed to cool to room temperature and diluted with ethyl acetate (15 mL). The

crude reaction mixture was washed with 1% aq. HCl (5 mL) and H_2O (5 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using mixtures of petroleum ether and ethyl acetate as eluents afforded the analytically pure product (71.1 mg, 78%) as a yellow oil; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.50 (s, 1H), 8.90 (s, 1H), 8.67 (s, 1H), 8.58 (s, 1H), 8.08 (dd, J = 25.6 Hz, J = 3.3 Hz, 3H), 7.47 (s, 1H), 7.28–7.19 (m, 2H), 7.09 (d, J = 8.2 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.1, 148.6, 148.0, 143.1, 138.7, 135.1, 134.9, 134.5, 129.5, 126.7, 126.2, 125.8, 125.3, 124.6, 121.6, 99.8 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{18}H_{15}N_3S$): calcd m/z 305.0981, found: 305.0978.

Synthesis of compound **B**: Prepared from 3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (**4aa**, 56.5 mg, 0.25 mmol,) and *m*-CPBA (56 mg, 1.3 equiv.) according to **GP1**; purification by flash column chromatography on silica gel afforded the analytically pure product (61.2 mg, 42%) as a white solid (54.4 mg, 90%); **m.p.** = 197–198 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.60 (s, 1H), 8.36 (s, 1H), 8.28 (d, J = 4.6 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.45 (d, J = 7.1 Hz, 1H), 7.02 (dd, J = 7.9 Hz, J = 4.7 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 149.5, 145.1, 144.8, 131.7, 130.6, 129.5, 127.9, 124.7, 117.4, 116.1, 115.9 ppm; **HRMS** (ESI-TOF) exact mass for $[M + H]^+$ ($C_{13}H_{11}N_2OS$): calcd m/z 243.0587, found: 243.0585.

2-[(4-Methoxyphenyl)thio]-3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (11′)

Prepared from 3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**11**, 24.2 mg, 0.1 mmol, 1.0 equiv.) and 1,2-bis(4-methoxyphenyl)disulfane (**3q**, 27.8 mg, 0.20 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (15 mg, 42%) as a light yellow solid; **m.p.** = 167–168 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.75 (s, 1H), 8.33 (d, J = 4.5 Hz, 1H), 7.75 (d, J = 6.5 Hz, 1H), 7.34–7.28 (m, 2H), 7.23–7.11 (m, 4H), 7.01–6.95 (m, 2H), 6.91–6.84 (m, 2H), 3.72 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 159.6, 149.6, 145.2, 138.1, 137.3, 133.1, 129.5, 127.4, 126.4, 125.8, 124.4, 122.2, 117.6, 115.5, 105.4, 55.8 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{20}H_{17}BrN_2OS_2$): calcd m/z 365.0777, found: 365.0776.

3-[(4-Methoxyphenyl)thio]-2-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (12′)

Prepared from 3-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine 7-oxidde (**11**, 24.2 mg, 0.1 mmol, 1.0 equiv.) and 1,2-bis(4-methoxyphenyl)disulfane (**3q**, 27.8 mg, 0.2 mmol, 2.0 equiv.) according to **GP3**; purification by flash column chromatography on silica gel afforded the analytically pure product (7.2 mg, 20%) as a light yellow solid; **m.p.** = 170–171 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.79 (s, 1H), 8.35 (d, J = 4.4 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 6.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 3H), 7.10 (d, J = 8.7 Hz, 2H), 6.81 (s, 2H), 3.68 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-d_6): δ = 159.6, 149.5, 145.2, 138.1, 137.3, 133.1, 129.5, 127.4, 126.4, 125.8, 124.4, 122.2, 117.9, 115.5, 105.4, 55.8 ppm; **HRMS** (APCI) exact mass for $[M + H]^+$ ($C_{20}H_{17}BrN_2OS_2$): calcd m/z 365.0777, found: 365.0775.

Conflicts of interest

There are no conflicts of interest to declare.

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