CHEMISTRY
AN ASIAN JOURNAL
ACES
FULL PAPER

DOI: 10.1002/asia.201300882

Copper-Catalyzed C–H Bond Direct Chalcogenation of Aromatic Compounds Leading to Diaryl Sulfides, Selenides, and Diselenides by Using Elemental Sulfur and Selenium as Chalcogen Sources Under Oxidative Conditions

Fumitoshi Shibahara,*[a] Takafumi Kanai,[a] Eiji Yamaguchi,[a] Akika Kamei,[a] Takayuki Yamauchi,[a] and Toshiaki Murai*[a, b]

Abstract: The reactions of aromatic compounds and elemental chalcogens catalyzed by a copper salt with molecular oxygen as an oxidant were carried out. The reaction of 3-substituted imidazo[1,5-*a*]pyridines and elemental sulfur in the presence of CuTC (copper(I) thiophenecarboxylate) gave the corresponding bisimidazopyridyl sulfides in good to quantitative yields. The reaction proceeded even under aerobic oxidation conditions. The use of a polar solvent was crucial for the reaction, and DMSO (dimethyl sulfoxide) in particular stimulated the reaction. The reaction could be applied to common aromatic compounds, such as *N*-methyl indole and dialkyl anilines. The reaction of indole proceeded at the nucleophilic C3 position rather than at the acidic C2 position. In addition, the reaction of dialkyl anilines proceeded with an *ortho*, *para* orientation. The reactions of imidazopyridines and elemental selenium under similar conditions gave the corresponding bisimidazopyridyl diselenides along with bisimidazopyridyl monoselenides. The resulting diselenides were readily converted to the corresponding monoselenides with unreacted imidazopyridines under the same conditions. The reaction could be applied to the copolymerization of bifunctional bisimidazopyridines and elemental sulfur to give oligomeric copolymers in quantitative yield.

Keywords: C–H activation · chalcogens · copper · selenium · sulfur

Introduction

Diaryl chalcogenides and dichalcogenides are an important class of compounds. These motifs are frequently found in functional materials and pharmaceuticals.[1] Although a variety of methods for their syntheses have been reported,[2–6] these have generally used aryl chalcogenols and chalcogenolates in combination with aryl halides.[2–4] Alternatively, the oxidative cross-coupling reaction of aryl chalcogenols or chalcogenolates with aryl boronic acid is known as Chan–Lam coupling.[6a] It is important to develop a procedure for the direct use of elemental chalcogens as chemical resources and, in particular, methods for practical synthesis because they are readily available, involatile, and easy to handle. It would also be beneficial if chalcogenating reactions could be achieved by direct C–H bond functionalization reactions with elemental chalcogens through a simple operation. Although thermal reactions of arenes and elemental sulfur to give the corresponding symmetric diaryl sulfides are known, the sulfidation of arenes with elemental sulfur must be carried out at a very high temperature (230 °C) to give the desired products along with a stoichiometric amount of hydrogen sulfide.[7] Recently, a few methods for the synthesis of sulfides in combination with a formal nucleophile and electrophile with elemental sulfur have been reported.[6d]

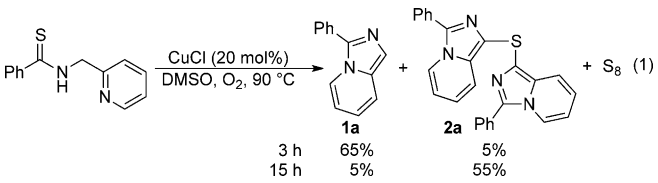
In our recent studies on thio- and selenocarbonyls,[8] we have reported the direct thionation and selenation of carbonyl compounds by means of the in situ reductive activation of elemental sulfur and selenium by hydrochlorosilanes, which formally leads to nucleophilic S^{2-} and Se^{2-} species.[8a] We envisioned that the oxidative activation of such elemental chalcogens would permit the direct C–H bond chalcogenation of aromatic compounds with in situ generated formal S^{2+} species through electrophilic substitution. In fact, we previously found that the copper-catalyzed oxidative desulfurization cyclization[9] of thioamides with an *N*-2-pyridylmethyl amino group, which leads to imidazo[1,5-*a*]pyridines **1**[10] under an oxygen atmosphere, gives significant amounts of bis(imidazo[1,5-*a*]pyridyl) sulfides **2** as well as elemental sulfur as side-products after a prolonged reaction time (see

[a] Prof. F. Shibahara, T. Kanai, E. Yamaguchi, A. Kamei, T. Yamauchi, Prof. T. Murai
Department of Chemistry and Biomolecular Science
Faculty of Engineering
Gifu University
Yanagido, Gifu 501-1193 (Japan)
Fax: (+81) 58-293-2794
E-mail: fshiba@gifu-u.ac.jp
mtoshi@gifu-u.ac.jp

[b] Prof. T. Murai
JST, ACT-C
Kawaguchi, Saitama 332-0012 (Japan)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201300882.

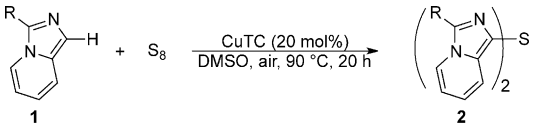
Equation (1): 3 vs. 15 h). These results suggested that sulfide **2** is likely generated through sulfidation of initially formed imidazopyridine **1** with elemental sulfur under oxidative conditions. Herein, we report the copper-catalyzed direct C–H bond chalcogenation of aromatic compounds with elemental sulfur and selenium to give diaryl chalcogenides and related compounds under aerobic oxidation conditions.



Results and Discussion

Initially, the sulfidation of 3-phenylimidazo[1,5-*a*]pyridine (**1a**) by using elemental sulfur was examined. As expected, the reaction with a catalytic amount of CuCl (20 mol%) under an oxygen atmosphere at 90°C gave corresponding sulfide **2a** in good yield (Table 1, entry 1). After screening metal catalysts,[11] we found that CuTC (copper(I) thiophenecarboxylate) facilitates the sulfidation even under air (Table 1, entry 2). The reaction gave sulfide **2a** in less than 20% yield in the absence of catalyst (Table 1, entry 4). This result clearly suggests that the catalyst is essential for the reaction to achieve efficient conversion under these conditions. The reaction also proceeded in dimethyl formamide (DMF; Table 1, entry 5), but was sluggish in less polar solvents, such as toluene (Table 1, entry 6). The reaction in DMF gave only a catalytic amount of **2a** under an argon atmosphere (Table 1, entry 8), but the reaction in DMSO proceeded significantly to give **2a** in 68% yield under identical conditions (Table 1, entry 7). The results suggest that DMSO also acts as a stoichiometric oxidant under these conditions along with air. With these conditions in hand, the scope of substrates was investigated. The reactions of both electron-deficient and -rich substrates proceeded with high efficiency (Table 1, entries 9–11). Notably, the use of an equivalent amount (based on the product) of elemental sulfur gave sulfides in yields of more than 50% (Table 1, entries 3 and 11). Also, hydrogen sulfide was not detected by a lead acetate test after the reaction. These results indicate that the reactions did not proceed by a formal disproportionation of elemental sulfur but rather by formal oxidation of the sulfur by an external oxidant, though the use of an excess amount of elemental sulfur usually gives the products in better yields (e.g., Table 1, entries 2 vs. 3). Imidazopyridines with heteroarenes (**1e** and **1f**) also selectively underwent sulfidation at C1 of the imidazopyridine to give sulfides **2e** and **2f** in quantitative yield and 85% yield, respectively (Table 1, entries 12 and 13). Furthermore, the reaction of highly electron-rich dimethylaminophenyl-substituted imidazopyridine **1g** gave corresponding sulfide **2g** in 63% yield (Table 1, entry 14). In addition, bromine on **1h** remained intact under the reaction conditions, and sulfide **2h** was obtained in 78% yield (Table 1, entry 15). The reaction of imidazopyridine **1i**, which has a readily oxidized cumene-like structure, also gave product **2i** as a major product in moderate yield (Table 1, entry 16).

Table 1. Scope of substrates for the sulfidation of imidazo[1,5-*a*]pyridines.



R = Ph (**1a**) 2-pyridyl (**1f**)
4-$F_3CC_6H_4$ (**1b**) 4-$Me_2NC_6H_4$ (**1g**)
4-MeC_6H_4 (**1c**) 4-BrC_6H_4 (**1h**)
4-$MeOC_6H_4$ (**1d**) *i*Pr (**1i**)
2-thienyl (**1e**)

Entry	Substrate	Scale [mmol]	S_8 [mmol]	*t* [h]	Yield of **2** [%][a]
1	**1a**	0.5	0.5	15	55
2	**1a**	0.5	0.5	20	quant.
3	**1a**	0.5	0.25	20	60
4[d]	**1a**	0.5	0.5	20	20
5[e]	**1a**	0.5	0.5	20	61 (39)
6[f]	**1a**	0.5	0.5	20	5 (95)
7[g]	**1a**	0.5	0.5	20	68 (32)
8[e,g]	**1a**	0.5	0.5	20	9 (91)
9	**1b**	0.5	1	20	98
10[b,c,h]	**1c**	1	1	6	quant.
11	**1d**	0.5	0.25	20	quant.
12	**1e**	5	10	48	quant.
13	**1f**	5	10	48	85
14[i]	**1g**	0.5	0.5	20	63
15	**1h**	0.5	1	20	78
16[b]	**1i**	5	10	3	54

[a] Isolated yield; quant. = quantitative. Yield of recovered starting **1** is shown in parentheses. [b] Reactions were carried out under an O_2 (1 atm) atmosphere. [c] CuCl (20 mol%) was used as a catalyst. [d] In the absence of copper salt. [e] DMF was used as a solvent. [f] Toluene was used as a solvent. [g] Under an Ar atmosphere. [h] 2,2′-Bipyridyl (20 mol%) was used as an additive. [i] The reaction was performed at 70°C.

The reaction could be applied to other electron-rich aromatic compounds. For instance, *N*-methylindole **3** underwent sulfidation to give sulfide **4** in good yield [Eq. (2)]. Importantly, the reaction proceeded not at the relatively acidic C2 position but rather selectively at the nucleophilic C3 position to give **4** as the sole product. The product was confirmed by X-ray analysis (Figure 1). Regarding the selectivity, the sulfidation of benzoxazole and -thiazole **5**, which have less nucleophilic and acidic C–H bonds at the C2 position, did not take place [Eq. (3)]. The results suggest that the reaction probably does not proceed by a deprotonation–cupration pathway that usually plays a role in copper-mediated C–H bond functionalization, such as the recently reported copper-catalyzed C–H bond functionalization of heteroarenes.[12] In contrast, electron-rich and nucleophilic aromatic compounds, such as *N*,*N*-dialkyl anilines **6**, also underwent a reaction [Eq. (4)]. In these cases, the reactions gave regioisomeric mixtures of sulfides in good yields, and bis(4-dialkylaminophenyl)sulfides **7** were isolated as major products in moderate yields.

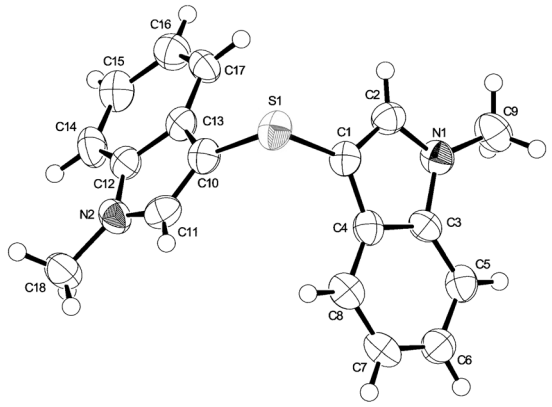
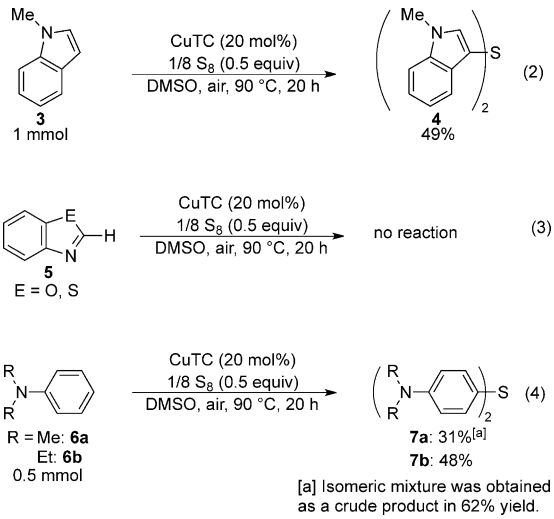


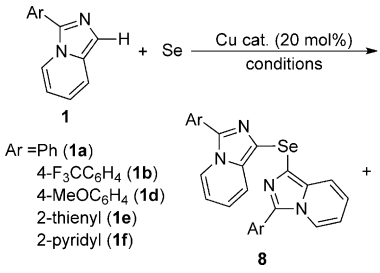
Figure 1. X-ray structure of bisindolyl sulfide **4**. Thermal ellipsoids were drawn at the 50 % probability level.



Next, we turned our attention to the selenidation of aromatic compounds with elemental selenium.[13] Initially, the reaction of **1a** (0.5 mmol) and selenium (0.5 mmol) with CuBr (20 mol %)[14] was carried out. As a result, diselenide **9a** was obtained in 45 % yield along with selenide **8a** in 45 % yield (Table 2, entry 1). Selenide **8a** was selectively obtained by decreasing the amount of selenium and extending the reaction time (Table 2, entry 2). The reaction proceeded for imidazopyridines with electron-donating and -withdrawing substituents (Table 2, entries 3 and 4). Heteroarene-substituted imidazopyridines were efficiently selenated by the use of CuCl as a catalyst under an oxygen atmosphere (Table 2, entries 5 and 6).

To gain insight into the mechanism, several control experiments were carried out. First, the pathways for the formation of selenides and diselenides were investigated. The reaction of selenide **8a** and elemental selenium under identical conditions did not give diselenide **9a** at all, and the reaction gave a complex mixture [Eq. (5)]. On the other hand, the reaction of **9a** and the parent imidazopyridine **1a** gave selenide **8a** in quantitative yield [Eq. (6)], and the coupling reaction did not occur at all in the absence of catalyst under

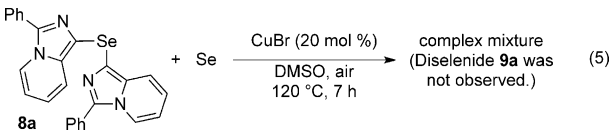
Table 2. Selenidation of imidazo[1,5-*a*]pyridines.[a]

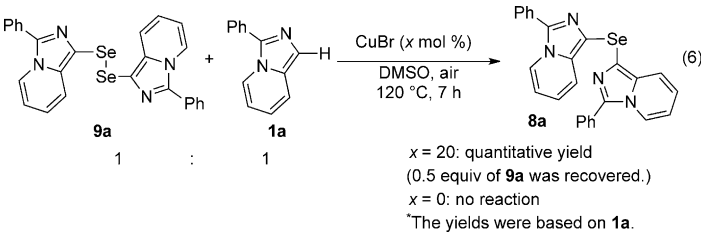


Entry	Ar	Cu cat.	Conditions	Yield [%][b]	
				8	**9**
1	Ph	CuBr	air, 20 h	n.d. (45)	n.d. (45)
2	Ph	CuBr	air, 30 h (Se 0.25 mmol)	80 (63)	– (–)
3	4-$F_3CC_6H_4$	CuBr	air, 20 h	50 (36)	20 (27)
4	4-$MeOC_6H_4$	CuBr	air, 20 h	54 (39)	44 (34)
5	2-thienyl	CuCl	O_2, 20 h	n.d. (22)	– (–)
6	2-pyridyl	CuCl	O_2, 20 h	40 (35)	– (–)

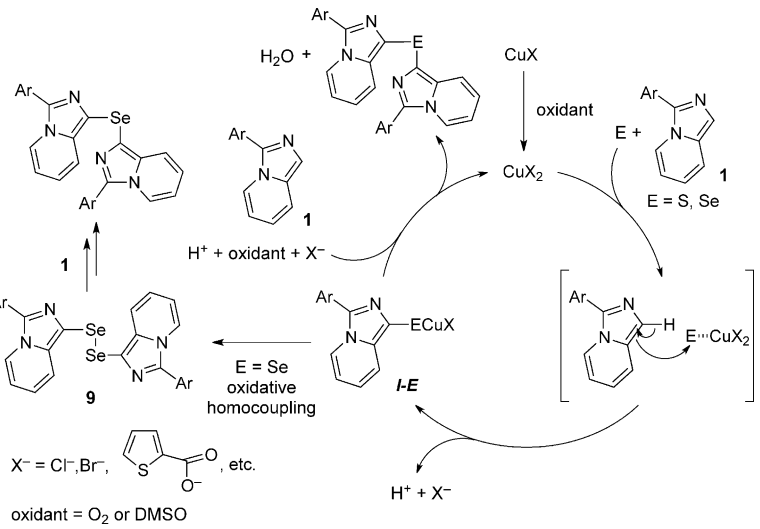
[a] Reactions were carried out with **1** (0.5 mmol) and Se (0.5 mmol) at 120 °C. Other conditions are indicated in the table. [b] The yields were determined by ^{1}H NMR spectroscopy by using 1,1,2,2-tetrachloroethane as an internal standard. Isolated yields are shown in parentheses. n.d. indicates not determined.

identical conditions. This result indicated that formed diselenide **9** reacted with unreacted imidazopyridine **1** to give selenide **8**. In contrast, the reaction of diphenyl disulfide and **1** did not occur at all under identical conditions.[15] Moreover, no disulfide was observed in the sulfidation reaction mixture. This result suggested that sulfidation did not take place by the formation of disulfides, and thus sulfidation and selenidation probably proceed through different reaction pathways. Furthermore, elemental chalcogens were intact under the reaction conditions in the absence of substrates and/or copper salts. Therefore, it is likely that the initial chalcogen-introduction step in these reactions proceeds by the concerted reaction of a substrate, an elemental chalcogen, and a copper salt.





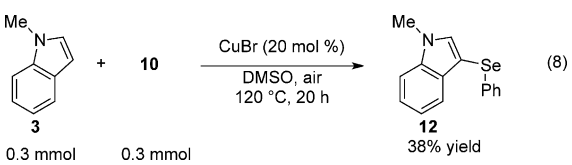
With this result in hand, plausible reaction pathways for sulfidation and selenidation are proposed in Scheme 1. Initially, the copper-mediated nucleophilic addition of arenes to elemental chalcogens takes place in both reactions to



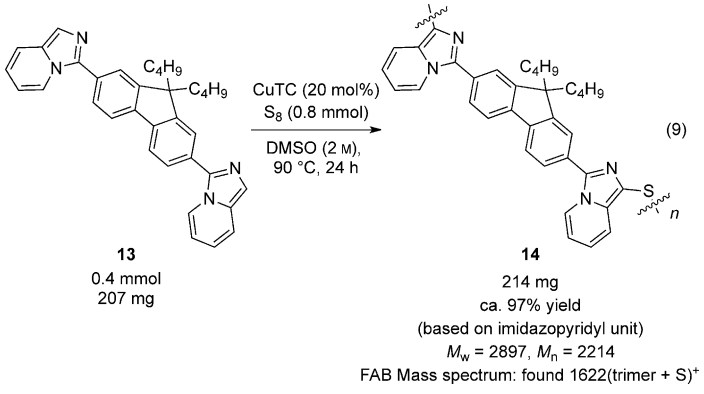
Scheme 1. Proposed reaction pathway for chalcogenidation of aromatic compounds.

give intermediate ***I-E*** (***E***=chalcogen). Next, in the case of sulfidation, an oxidation-assisted nucleophilic substitution of the parent arenes at the sulfur atom on ***I-S*** gives sulfides.[6,15] In contrast, oxidative homo-coupling of ***I-Se*** takes place to give diselenide **9** under selenidation conditions because the reaction rate of the oxidative homo-coupling of selenoates is usually faster than that of thionates. Therefore, the homo-coupling probably proceeded rather than nucleophilic substitution of the parent arenes at the selenium atom in ***I-Se***, though it is still possible. Diselenide **9** is then reacted with unreacted arenes catalyzed by copper salt under oxidative conditions to give the product selenides.[15]

Notably, the synthesis of unsymmetric diaryl selenides can be achieved by the reaction of diaryl diselenides and arenes with this reactivity. For example, the reaction of diphenyl diselenide (**10**) with **1d** gave phenylimidazopyridyl selenide **11** in quantitative yield even at 30°C [Eq. (7)]. Also, the reaction of diselenide **10** and *N*-methylindole **3** gave phenyl indolyl selenide **12** in moderate yield [Eq. (8)].



The sulfidation reaction could be applied to the synthesis of oligomeric sulfide by using bifunctional substrates. Oligomeric sulfide **14** was obtained by the reaction of bis-(imidazo[1,5-*a*]pyridyl)fluorene **13** in quantitative yield as a deep-greenish solid [Eq. (9)]. Size-exclusion chromatography based on polystyrene of the obtained material gave $M_w = 2897$ and $M_n = 2214$. These values correspond to tetra- and pentamers. In addition, the trimer ($M_w = 1622$) was detected as the largest fragment peak in FAB mass analysis.



Conclusion

We have developed a direct chalcogenation of aromatic compounds by using easy-to-handle elemental chalcogens as chalcogen sources. The reactions could be applied to electron-rich nucleophilic aromatic compounds, including *N*,*N*-dialkyl anilines and imidazo[1,5-*a*]pyridines.[10] With our previous report,[8] we identified a set of common protocols for using elemental sulfur and selenium as well-defined and unfunctionalized electrophilic and nucleophilic chalcogenating reagents by means of oxidative and reductive activations. This oxidative activation strategy with chalcogen-containing compounds for C–chalcogen bond formation should facilitate access to chalcogenides and related compounds. Further investigations of chalcogenating reactions with both oxidative and reductive activation strategies for several organic molecules are underway in our group.

Experimental Section

General procedure for sulfidation of imidazo[1,5-a]pyridines

A mixture of imidazo[1,5-*a*]pyridine **1** (0.5 mmol), S_8 (32 mg, 1.0 mmol), CuTC (0.018 g, 0.10 mmol, 20 mol%), and DMSO (0.5 mL) was stirred at

90 °C. The resulting solution was diluted with CH_2Cl_2 (3.0 mL) and to this was added aqueous ammonia. The organic layer was extracted with CH_2Cl_2 (3×10 mL), washed with saturated brine (5.0 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give corresponding bisimidazopyridyl sulfide **2**.

*Bis(3-phenylimidazo[1,5-a]pyridine-1-yl)sulfide (**2a**)[10x]*

^{1}H NMR ($CDCl_3$): δ=6.43 (dd, J=6.8, 7.8 Hz, 2H; Ar), 6.70 (dd, J=7.8, 9.3 Hz, 2H; Ar), 7.30 (d, J=7.3 Hz, 2H; Ar), 7.37 (t, J=7.3 Hz, 4H; Ar), 7.64 (d, J=7.3 Hz, 4H; Ar), 7.94 (d, J=9.3 Hz, 2H; Ar), 8.06 ppm (d, J=6.8 Hz, 2H; Ar).

*Bis(3-(4-trifluoromethylphenyl)imidazo[1,5-a]pyridine-1-yl)sulfide (**2b**)[10x]*

^{1}H NMR ($CDCl_3$): δ=3.77 (s, 3H; MeO), 6.56 (dd, J=6.8, 7.8 Hz, 2H; Ar), 6.79 (dd, J=7.8, 9.3 Hz, 2H; Ar), 7.63 (d, J=7.8 Hz, 4H; Ar), 7.80 (d, J=7.8 Hz, 4H; Ar), 7.96 (d, J=9.3 Hz, 2H; Ar), 8.11 (d, J=6.8 Hz, 2H; Ar), 8.11 ppm (d, J=7.1 Hz, 2H; Ar).

*Bis(3-(4-methylphenyl)imidazo[1,5-a]pyridine-1-yl)sulfide (**2c**)*

Yellow solid; m.p. 170 °C (decomp.); R_f=0.80 (hexane/AcOEt 1:2); ^{1}H NMR ($CDCl_3$): δ=2.41 (s, 6H; Me), 6.55 (dd, J=6.8, 7.1 Hz, 2H; Ar), 6.80 (dd, J=6.8, 9.2 Hz, 2H; Ar), 7.29 (d, J=8.1 Hz, 4H; Ar), 7.63 (d, J=8.1 Hz, 4H; Ar), 8.01 (d, J=9.2 Hz, 2H; Ar), 8.14 ppm (d, J=7.1 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ=21.4 (Me), 113.5, 119.4, 120.0, 121.6, 122.9, 127.0, 128.1, 129.6, 133.4, 138.0, 138.8 ppm (Ar); IR (KBr): $\tilde{\nu}$=3032, 1507, 1354, 1262, 828, 792 cm^{-1}; MS (EI): m/z: 446 $[M]^+$; HRMS: m/z calcd for $C_{28}H_{22}N_4S$: 446.1565; found: 446.1562.

*Bis[3-(4-methoxyphenyl)imidazo[1,5-a]pyridine-1-yl]sulfide (**2d**)[10x]*

^{1}H NMR ($CDCl_3$): δ=3.77 (s, 3H; MeO), 6.55 (dd, J=6.8, 7.8 Hz, 2H; Ar), 6.70 (dd, J=7.8, 9.3 Hz, 2H; Ar), 6.92 (d, J=8.5 Hz, 4H; Ar), 7.58 (d, J=8.5 Hz, 4H; Ar), 7.92 (d, J=9.3 Hz, 2H; Ar), 7.94 (d, J=9.3 Hz, 2H; Ar), 8.11 ppm (d, J=7.1 Hz, 2H; Ar).

*Bis(3-(2-thienyl)imidazo[1,5-a]pyridine-1-yl)sulfide (**2e**)*

Yellow solid; m.p. 195–200 °C. R_f=0.40 (hexane/AcOEt 1:1); ^{1}H NMR ($CDCl_3$): δ=6.57 (dd, J=7.1, 6.5 Hz, 2H; Ar), 6.77 (dd, J=8.8, 6.5 Hz, 2H; Ar), 7.06 (dd, J=4.9, 3.6 Hz, 2H; Ar), 7.36 (d, J=4.9 Hz, 2H; Ar), 7.40 (d, J=3.6 Hz, 2H; Ar), 7.96 (d, J=8.8 Hz, 2H; Ar), 8.16 ppm (d, J=7.1 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ=114.2, 119.5, 120.2, 121.8, 123.3, 125.4, 126.2, 127.5, 131.8, 132.5, 133.7 ppm (Ar); IR (KBr): $\tilde{\nu}$=2360, 1630, 1500, 1406, 1364, 1304, 1011, 848, 742, 688 cm^{-1}; MS (EI): m/z: 430 $[M]^+$; HRMS (EI): m/z calcd for $C_{22}H_{14}N_4S_3$: 430.0381 $[M]^+$; found: 430.0374.

*Bis[3-(2-pyridyl)imidazo[1,5-a]pyridine-1-yl]sulfide (**2f**)[10x]*

^{1}H NMR ($CDCl_3$): δ=6.68 (dd, J=7.3, 6.3 Hz, 2H; Ar), 6.90 (dd, J=8.8, 6.3 Hz, 2H; Ar), 7.12 (dd, J=7.4, 4.9 Hz, 2H; Ar), 7.70 (dd, J=7.8, 7.4 Hz, 2H; Ar), 7.95 (d, J=8.8 Hz, 2H; Ar), 8.34 (d, J=7.8 Hz, 2H; Ar), 8.53 (d, J=4.9 Hz, 2H; Ar), 9.86 ppm (d, J=7.3 Hz, 2H; Ar).

*Bis(3-(4-N,N-dimethylaminophenyl)imidazo[1,5-a]pyridine-1-yl)sulfide (**2g**)*

Green solid; m.p. 197–199 °C; R_f=0.38 (hexane/AcOEt 1:4); ^{1}H NMR ($CDCl_3$): δ=3.01 (s, 12H; CH_3), 6.49 (dd, J=6.8, 7.3 Hz, 2H; Ar), 6.74 (dd, J=9.3, 6.8 Hz, 2H; Ar), 6.79 (d, J=8.6 Hz, 4H; Ar), 7.62 (d, J=8.6 Hz, 4H; Ar), 8.00 (d, J=9.3 Hz, 2H; Ar), 8.12 ppm (d, J=7.3 Hz, 2H; Ar);^{13}C NMR ($CDCl_3$): δ=40.3 (NCH_3), 112.0, 112.3, 113.0, 117.5, 119.4, 121.7, 122.5, 129.2, 133.0, 138.6, 150.5 ppm (Ar); IR (KBr): $\tilde{\nu}$=2358, 1611, 1538, 1481, 1442, 1360, 1200, 943, 820, 742 cm^{-1}; MS (EI): m/z: 504 $[M]^+$; HRMS (EI): m/z calcd for $C_{30}H_{28}N_6S$: 504.2096 $[M]^+$; found: 504.2111.

*Bis(3-(4-bromophenyl)imidazo[1,5-a]pyridine-1-yl)sulfide (**2h**)*

Yellow solid; m.p. 190 °C (decomp.); ^{1}H NMR ($CDCl_3$): δ=6.53 (dd, J=6.8, 7.3 Hz, 2H; Ar), 6.75 (dd, J=6.8, 9.0 Hz, 2H; Ar), 7.51–7.56 (m, 8H; Ar), 7.94 (d, J=9.0 Hz, 2H; Ar), 7.63 ppm (d, J=7.3 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ=114.0, 119.4, 120.3, 121.3, 122.8, 123.4, 128.8, 129.5, 132.1, 133.8, 136.7 ppm (Ar); IR (KBr): $\tilde{\nu}$=2912, 2361, 1631, 1511, 733 cm^{-1}; MS (EI): m/z: 272 $[M-C_{13}H_9BrN_2S]^+$ (50.0), 274 $[M-2-C_{13}H_9BrN_2S]^+$ (50.0); HRMS: m/z calcd for $C_{26}H_{16}{}^{80}Br_2N_4S$: 573.9262; found: 573.9483.

*Bis(3-(1-methylethyl)imidazo[1,5-a]pyridin-1-yl)sulfide (**2i**)*

Yellow green solid; m.p. 76–80 °C; ^{1}H NMR ($CDCl_3$): δ=1.39 (d, J=6.8 Hz, 12H; CH_3), 3.20 (sept., J=6.8 Hz, 2H; CH), 6.48 (t, J=6.3 Hz, 2H; Ar), 6.67 (t, J=7.8 Hz, 2H; Ar), 7.64(d, J=6.8 Hz, 2H; Ar), 7.87 ppm (d, J=9.3 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ=20.3 (CH_3), 26.0 (CH), 112.7, 118.6, 119.2, 120.6, 121.0, 132.0, 142.8 ppm (Ar); IR (KBr): $\tilde{\nu}$=2972, 2927, 2898, 2871, 1632, 1510, 1488, 1458, 1382, 1365, 1333, 1285, 1263, 1085, 1050, 978, 767, 750, 698, 485,4612, 529 cm^{-1}; MS (EI): m/z: 350 $[M]^+$; HRMS: m/z calcd for $C_{20}H_{22}N_4S$: 350.1565; found: 350.1537.

*Sulfidation of 1-methylindol (**3**)*

A mixture of 1-methylindole (**3**, 125 μL, 1.0 mmol), S_8 (32 mg, 1.0 mmol), CuTC (0.036 g, 0.20 mmol, 20 mol%), and DMSO (1.0 mL) was stirred at 90 °C for 20 h. The resulting solution was diluted with CH_2Cl_2 (3.0 mL) and to this was added aqueous ammonia. The organic layer was extracted with CH_2Cl_2 (3×10 mL), washed with saturated brine (5.0 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt 3:1) to give bis(1-methyl-1*H*-indol-3-yl)sulfide (**4**) as a yellow solid (0.11 g, 0.37 mmol, 75%). M.p. 131–133 °C; R_f=0.80 (hexane/AcOEt 1:1); ^{1}H NMR ($CDCl_3$): δ=3.68 (s, 6H; NMe), 7.15 (dd, J=8.1, 6.7 Hz, 2H; Ar), 7.19 (d, J=8.1 Hz, 2H; Ar). 7.22 (s, 2H; Ar), 7.23 (dd, J=7.6, 6.7 Hz, 2H; Ar) 7.86 ppm (d, J=7.6 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ=32.8 (NCH_3), 106.1, 109.4, 119.5, 119.8, 122.0, 129.3, 132.5, 137.0 ppm (Ar); IR (KBr): $\tilde{\nu}$=2359, 2341, 1506, 1459, 1334, 1240, 741 cm^{-1}; MS (EI): m/z: 292 $[M]^+$; HRMS (EI): m/z calcd for $C_{18}H_{16}N_2S$: 292.1034 $[M]^+$; found: 292.1027.

*Sulfidation of N,N-dimethylaniline (**6a**)*

A mixture of *N,N*-dimethylaniline (**6a**, 127 μL, 1.0 mmol), S_8 (32 mg, 1.0 mmol, 1 equiv), CuTC (39 mg, 0.20 mmol, 20 mol%), and DMSO (0.5 mL) was stirred at 90 °C for 24 h. The resulting solution was diluted with CH_2Cl_2 (3 mL). Aqueous ammonia was added and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was washed with saturated brine (5 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by gel permeation chromatography to give bis(*N,N*-dimethylanilin-4-yl)sulfide (**7a**) as a yellow solid (42 mg, 0.15 mmol, 31%). ^{1}H NMR ($CDCl_3$): δ=2.91 (s 12H; NMe), 6.64 (d, J=9.0 Hz, 4H; Ar), 7.24 ppm (d, J=9.0 Hz, 4H; Ar).

*Sulfidation of N,N-diethylaniline (**6b**)*

A mixture of diethylaniline (**6b**, 0.09 g, 1 mmol), S_8 (0.03 g, 1.0 mmol, 1 equiv), CuTC (0.04 g, 0.2 mmol, 20 mol%), and DMSO (0.25 mL) was stirred at 90 °C for 24 h under an O_2 atmosphere (balloon). The resulting solution was diluted with CH_2Cl_2 (3 mL). Aqueous ammonia was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with saturated brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1–4:1) to give bis(4-(diethylamino)phenyl)-sulfide (**7b**) as a yellow oil (0.056 g, 0.017 mmol, 34%). R_f=0.4 (hexane/EtOAc 1:1); ^{1}H NMR ($CDCl_3$): δ=1.04–1.09 (m, 12H; CH_3), 3.21–3.28 (m, 8H; CH_2), 6.51 (d, J=8.7 Hz, 4H; Ar), 7.15 ppm (d, J=8.7 Hz, 4H).

General procedure for selenidation of imidazo[1,5-a]pyridines

A mixture of imidazo[1,5-*a*]pyridine **1** (0.50 mmol), selenium (38 mg, 0.50 mmol), CuBr (14 mg, 0.10 mmol, 20 mol%), and DMSO (0.25 mL) was stirred at 120 °C for 30 h under air. The resulting solution was diluted

with CH_2Cl_2 (3 mL), and to this was added aqueous ammonia. The organic layer was extracted with CH_2Cl_2 (3×10 mL), washed with saturated brine (5 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give a mixture of bisimidazo[1,5-*a*]pyridylselenide (**8**) and bisimidazo[1,5-*a*]pyridyldiselenide (**9**). The ratio (selenide/diselenide) was estimated by ^{1}H NMR spectroscopic analysis. Further isolation was performed by preparative gel permeation chromatography to give analytically pure selenide and diselenide, respectively.

*Bis(3-phenylimidazo[1,5-a]pyridin-1-yl)selenide (**8a**)*

M.p. 168–170 °C; R_f = 0.63 (hexane/AcOEt 1:1); ^{1}H NMR ($CDCl_3$): δ = 6.53 (dd, J = 7.3, 6.3 Hz, 2H; Ar), 6.78 (dd, J = 9.3, 6.3 Hz, 2H; Ar), 7.39 (t, J = 7.3 Hz, 2H; Ar), 7.47 (t, J = 7.3 Hz, 4H; Ar), 7.74 (d, J = 7.3 Hz, 4H; Ar), 7.98 (d, J = 9.3 Hz, 2H; Ar), 8.15 ppm (d, J = 7.3 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 113.6, 118.3, 120.0, 120.1, 121.5, 128.2, 128.8, 128.9, 129.8, 134.6, 138.5 ppm (Ar); ^{77}Se NMR ($CDCl_3$): δ = 139.9 ppm; IR (KBr): $\tilde{\nu}$ = 3055, 2993, 2852, 1633, 1599, 1506, 1456, 1364, 1355, 1264, 1011, 776, 741, 702, 692 cm^{-1}; MS (FAB): m/z: 467 $[M+H^+]^+$; HRMS (FAB): m/z calcd for $C_{26}H_{19}N_4Se$: 467.0775 $[M+H^+]^+$; found: 467.0765.

*Bis(3-phenylimidazo[1,5-a]pyridin-1-yl)diselenide (**9a**)*

R_f = 0.63 (hexane:AcOEt 1:1). ^{1}H NMR ($CDCl_3$): δ = 6.53 (dd, J = 7.0, 5.8 Hz, 2H; Ar), 6.58 (dd, J = 8.8, 5.8 Hz, 2H; Ar), 7.09 (d, J = 8.8 Hz, 2H; Ar), 7.48 (t, J = 7.5 Hz, 2H; Ar), 7.54 (dd, J = 7.5, 6.8 Hz, 4H; Ar), 7.82 (d, J = 6.8 Hz, 4H; Ar), 8.19 ppm (d, J = 7.0 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 113.7, 119.1, 119.9, 120.1, 121.0, 121.5, 121.9, 128.2, 128.8, 128.95, 129.00 ppm (Ar); ^{77}Se NMR ($CDCl_3$): δ = 412.3 ppm; MS (FAB): m/z: 546 $[M+H^+]^+$; HRMS (FAB): m/z calcd for $C_{26}H_{19}N_4Se_2$: 546.9940 $[M+H^+]^+$; found: 546.9916.

*Bis(3-(4-trifluoromethylphenyl)imidazo[1,5-a]pyridin-1-yl)selenide (**8b**)*

M.p. 221–222 °C; R_f = 0.33 (hexane/AcOEt 3:1); ^{1}H NMR ($CDCl_3$): δ = 6.67 (dd, J = 7.3, 6.3 Hz, 2H; Ar), 6.90 (dd, J = 9.3, 6.3 Hz, 2H; Ar), 7.75 (d, J = 8.3 Hz, 4H; Ar), 7.91 (d, J = 8.3 Hz, 4H; Ar), 8.03 (d, J = 9.3 Hz, 2H; Ar), 8.22 ppm (d, J = 7.3 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 114.4, 119.0, 120.0, 120.7, 121.3 (Ar), 124.0 (q, J = 272.9 Hz, F_3C), 125.9 (q, J = 3.3 Hz, F_3C-C=*C*), 128.0 (Ar), 130.4 (q, J = 33.1 Hz, F_3C-*C*), 133.3, 135.2, 137.1 ppm (Ar); ^{19}F NMR ($CDCl_3$): δ = −62.6 ppm (CF_3); ^{77}Se NMR ($CDCl_3$): δ = 142.7 ppm; IR (KBr): $\tilde{\nu}$ = 2926, 1616, 1325, 1168, 1111, 1066, 1012, 845, 739 cm^{-1}; MS (FAB): m/z: 603 $[M+H^+]^+$; HRMS (FAB): m/z: calcd for $C_{28}H_{17}F_6N_4Se$: 603.0523 $[M+H^+]^+$; found: 603.0503.

*Bis(3-(4-trifluoromethylphenyl)imidazo[1,5-a]pyridin-1-yl)diselenide (**9b**; not isolated)*

R_f = 0.33 (hexane/AcOEt 3:1); ^{1}H NMR ($CDCl_3$): δ = 6.67 (t, J = 6.8 Hz, 2H; Ar), 6.71 (dd, J = 9.3, 6.8 Hz, 2H; Ar), 7.29 (d, J = 9.3 Hz, 2H; Ar), 7.77 (d, J = 8.3 Hz, 4H; Ar), 7.95 (d, J = 8.3 Hz, 4H; Ar), 8.25 ppm (d, J = 6.8 Hz, 2H; Ar); MS (FAB): m/z: 683 $[M+H^+]^+$; HRMS (FAB): m/z: calcd for $C_{28}H_{17}F_6N_4Se_2$: 682.9688 $[M+H^+]^+$; found: 682.9686.

*Bis(3-(4-methoxyphenyl)imidazo[1,5-a]pyridin-1-yl)selenide (**8d**)*

M.p. 206–208 °C; R_f = 0.50 (hexane/AcOEt 1:1); ^{1}H NMR ($CDCl_3$): δ = 3.84 (s, 6H; OMe), 6.50 (t, J = 6.8 Hz, 2H; Ar), 6.75 (dd, J = 8.8, 6.8 Hz, 2H; Ar), 6.99 (d, J = 8.6 Hz, 4H; Ar), 7.65 (d, J = 8.6 Hz, 4H; Ar), 7.94 (d, J = 9.3 Hz, 2H; Ar), 8.08 ppm (d, J = 6.8 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 55.4 (MeO), 113.4, 114.3, 117.8, 119.8, 119.9, 121.4, 122.2, 129.6, 134.3, 138.5, 160.0 ppm (Ar); ^{77}Se NMR ($CDCl_3$): δ = 135.9 ppm (C-Se-C); IR (KBr): $\tilde{\nu}$ = 2936, 2835, 2358, 1608, 1523, 1457, 1432, 1353, 1252, 1187, 1173, 1010, 838, 742 cm^{-1}; MS (FAB): m/z: 527 $[M+H^+]^+$; HRMS (FAB): m/z: calcd for $C_{28}H_{23}N_4O_2Se$: 527.0986 $[M+H^+]^+$; found: 527.0969.

*Bis(3-(4-methoxyphenyl)imidazo[1,5-a]pyridin-1-yl)diselenide (**9d**; not isolated)*

R_f = 0.50 (hexane/AcOEt 1:1); ^{1}H NMR ($CDCl_3$): δ = 3.90 (s, 6H; OMe), 6.49 (dd, J = 8.1, 6.5 Hz, 2H; Ar), 6.52 (dd, J = 8.8, 6.5 Hz, 2H; Ar), 7.05 (d, J = 8.8 Hz, 4H; Ar), 7.70 (d, J = 8.8 Hz, 2H; Ar), 7.73 (d, J = 8.8 Hz, 4H; Ar), 8.10 ppm (d, J = 8.1 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 55.3 (MeO), 113.3, 114.3, 117.6, 118.9, 120.5, 121.7, 122.0, 129.6, 136.4, 139.8, 160.2 ppm (Ar); ^{77}Se NMR ($CDCl_3$): δ = 412.4 ppm (C-SeSe-C); MS (FAB): m/z: 607 $[M+H^+]^+$; HRMS (FAB): m/z: calcd for $C_{28}H_{23}N_4O_2Se_2$: 607.0151 $[M+H^+]^+$; found: 607.0178.

*Bis(3-(2-thienyl)imidazo[1,5-a]pyridin-1-yl)selenide (**8e**)*

M.p. 200–202 °C; R_f = 0.48 (hexane/AcOEt 1:1); ^{1}H NMR ($CDCl_3$): δ = 6.44 (dd, J = 7.4, 6.3 Hz, 2H; Ar), 6.82 (dd, J = 9.0, 6.3 Hz, 2H; Ar), 7.14 (dd, J = 5.0, 3.7 Hz, 2H; Ar), 7.39 (d, J = 5.0 Hz, 2H; Ar), 7.47 (d, J = 3.7 Hz, 2H; Ar), 7.98 (d, J = 9.0 Hz, 2H; Ar), 8.24 ppm (d, J = 7.4 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 114.2, 118.6, 119.2, 120.1, 121.8, 125.3, 125.7, 126.2, 127.6, 131.9, 134.8 ppm (Ar); ^{77}Se NMR ($CDCl_3$): δ = 144.1 ppm (C-Se-C); IR (KBr): $\tilde{\nu}$ = 2925, 2360, 2341, 1628, 1499, 1403, 1362, 1004, 911, 849, 739, 691 cm^{-1}; MS (FAB): m/z: 479 $[M+H^+]^+$; HRMS (FAB): m/z: calcd for $C_{22}H_{15}N_4S_2Se$: 478.9903 $[M+H^+]^+$; found: 478.9922.

*Bis(3-(2-pyridyl)imidazo[1,5-a]pyridin-1-yl)selenide (**8f**)*

M.p. 188–189 °C; R_f = 0.55 (hexane/AcOEt 1:1); ^{1}H NMR ($CDCl_3$): δ = 6.74 (dd, J = 7.3, 6.3 Hz, 2H; Ar), 6.94 (dd, J = 9.3, 6.3 Hz, 2H; Ar), 7.18 (dd, J = 7.0, 4.6 Hz, 2H; Ar), 7.76 (dd, J = 8.3, 7.0 Hz, 2H; Ar), 7.97 (d, J = 9.3 Hz, 2H; Ar), 8.42 (d, J = 8.3 Hz, 2H; Ar), 8.59 (d, J = 4.6 Hz, 2H; Ar), 9.91 ppm (d, J = 7.3 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 114.4, 119.1, 121.8, 122.0, 122.4, 122.4, 126.2, 135.7, 136.5, 136.6, 148.0, 148.1 ppm (Ar); ^{77}Se NMR ($CDCl_3$): δ = 144.2 ppm (C-Se-C); IR (KBr): $\tilde{\nu}$ = 3106, 2360, 1587, 1496, 1420, 1358, 1018, 784, 751, 685 cm^{-1}; MS (FAB): m/z: 469 $[M+H^+]^+$; HRMS (FAB): m/z: calcd for $C_{22}H_{17}N_6Se$: 469.0680 $[M+H^+]^+$; found: 469.0665.

*Reaction of diphenyl diselenide (10) and 3-(4-methoxyphenyl)imidazo[1,5-a]pyridine (**1d**)*

A mixture of 3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine (**1d**, 0.11 g, 0.50 mmol), diphenyldiselenide (**10**, 0.16 g, 0.50 mmol), CuBr (14 mg, 0.10 mmol, 20 mol%), and DMSO (1 mL) was stirred at 120 °C for 20 h. The resulting solution was diluted with CH_2Cl_2 (3 mL) and then aqueous ammonia was added. The organic layer was extracted with CH_2Cl_2 (3× 10 mL), washed with saturated brine (5 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt 4:1) to give phenyl-[3-(4-methoxyphenyl)imidazo[1,5-*a*]pyrid-1-yl]selenide (**11**) as a light green solid (0.18 g, 0.46 mmol, 93%). M.p. 88–89 °C; R_f = 0.70 (hexane/AcOEt 1:1); ^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 3H; OMe), 6.65 (dd, J = 7.2, 6.3 Hz, 1H; Ar), 6.84 (dd, J = 9.4, 6.3 Hz, 1H; Ar), 7.06 (d, J = 8.5 Hz, 2H; Ar), 7.17 (m, 3H; Ar), 7.37 (d, J = 8.1 Hz, 2H; Ar), 763 (d, J = 9.4 Hz, 1H; Ar), 7.77 (d, J = 8.5 Hz, 2H; Ar), 8.25 ppm (d, J = 7.2 Hz, 1H; Ar); ^{13}C NMR ($CDCl_3$): δ = 55.4 (OMe), 113.6, 114.4, 115.9, 119.1, 120.6, 121.9, 126.1, 129.0, 129.7, 129.8 (two carbon atoms were overlapped), 133.3, 135.4, 139.7 ppm (Ar); ^{77}Se NMR ($CDCl_3$): δ = 258.8 ppm; IR (KBr): $\tilde{\nu}$ = 1608, 1577, 1524, 1476, 1458, 1254, 1183, 1024, 1012, 835, 740, 691 cm^{-1}; MS (FAB): m/z: 381 $[M+H^+]^+$; HRMS (FAB): m/z: calcd for $C_{20}H_{17}N_2OSe$: 381.0506 $[M+H^+]^+$; found: 381.0511.

*Reaction of diphenyl diselenide (**10**) and 1-methylindole (**3**)*

A mixture of 1-methylindole (**3**, 38 μL, 0.30 mmol), diphenyldiselenide (**10**, 94 mg, 0.30 mmol), CuBr (9 mg, 0.06 mmol, 20 mol%), and DMSO (0.6 mL) was stirred at 120 °C for 20 h. The resulting solution was diluted with CH_2Cl_2 (2 mL) and then aqueous ammonia was added. The organic layer was extracted with CH_2Cl_2 (3×7 mL), washed with saturated brine (3 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt 6:1) to give phenyl(1-methylindol-3-yl)selenide (**12**) as a light orange solid (33 mg, 0.12 mmol, 38%). M.p .59–61 °C; R_f = 0.85 (hexane/AcOEt 1:1); ^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 3H; Me), 7.11 (m, 3H; Ar), 7.17 (dd, J = 7.8, 6.8 Hz, 1H; Ar), 7.23 (d, J = 7.3 Hz, 2H; Ar), 7.29 (dd, J = 8.3, 6.8 Hz, 1H; Ar), 7.32 (s, 1H; Ar), 7.37 (d, J = 8.3 Hz, 1H; Ar), 7.63 ppm (d, J = 7.8 Hz, 1H; Ar); ^{13}C NMR ($CDCl_3$): δ = 33.1 (NMe), 95.9, 109.5, 120.39, 120.44, 122.4, 125.5, 128.5, 128.9, 130.7, 134.2, 135.6,

137.4 ppm (Ar); ^{77}Se NMR ($CDCl_3$): $\delta = 206.7$ ppm; IR (KBr): $\tilde{\nu} = 2360$, 1576, 1506, 1475, 1457, 1438, 1417, 1333, 1238, 742, 688 cm^{-1}; MS (EI): m/z: 287 $[M]^+$; HRMS (EI): m/z: calcd for $C_{15}H_{13}NSe$: 287.0213 $[M]^+$; found: 287.0195.

*Synthesis of 2,7-bis(imidazo[1,5-a]pyrid-3-yl)-9,9-dibutylfluorene (**13**)[10s,t]*

A solution of 2,7-diiodo-9,9-dibutylfluorene (0.27 g, 0.50 mmol), imidazo-[1,5-*a*]pyridine (0.12 g, 1.0 mmol), Cs_2CO_3 (0.33 g, 2.0 mmol), and [Pd-(phen)$_2$(PF_6)$_2$] (0.019 g, 0.025 mmol; phen = 1,10-phenanthroline) in DMA (dimethylacetamide) was stirred at 150 °C for 20 h. The resulting mixture was filtered through a Celite pad and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/AcOEt 2:1) to give the title compound as an orange solid (0.16 g, 63 %). M.p. 140–144 °C (decomp.); ^{1}H NMR ($CDCl_3$): $\delta =$ 0.66–0.73 (m, 10H), 1.08–1.16 (m, 4H), 2.07–2.12 (m, 4H), 6.62 (t, $J =$ 6.3 Hz, 2H; Ar), 6.76 (dd, $J = 9.2$, 6.3 Hz, 2H), 7.53 (d, $J = 9.2$ Hz, 2H), 7.62 (s, 2H), 7.80–7.84 (m, 4H), 7.90 (d, $J = 7.8$ Hz, 2H), 8.34 ppm (d, $J =$ 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 13.9$, 23.0, 36.1, 40.2, 55.6 (Bu), 113.2, 118.85, 118.93, 120.3, 120.6, 121.5, 122.8, 126.4, 129.2, 131.7, 138.7, 140.9, 152.0 ppm (Ar); IR (KBr): $\tilde{\nu} = 2954$, 2927, 2857, 1749, 1664, 1459, 1354, 1251, 1012, 829, 737, 695 cm^{-1}; MS (EI): m/z: 510 $[M]^+$; HRMS (EI): m/z: calcd for $C_{35}H_{34}N_4$: 510.2783 $[M]^+$; found: 510.2788.

X-ray structural analysis

X-ray data for compound **4** were recorded by using a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Reflection data were collected at 133–293 K by using a Rigaku XR-TCS-2-050 temperature controller. X-ray absorption was corrected by numerical methods based on the crystal shape.[16] An X-ray-quality crystal was obtained by the slow diffusion of hexane into a CH_2Cl_2 solution of the compounds at RT under air. The crystal was cut from the grown crystals and mounted on a MicroMount provided by MiTeGen. The structure was solved and refined by a direct method using SHELX-97[17] with the Yadokari-XG crystallographic software package from Molecular Structure Corporation.[18] Hydrogen atoms on C were placed in idealized positions and treated as riding atoms with C–H lengths of $\delta = 95$–100 pm. Crystal data and measurement descriptions are summarized in Table S4 in the Supporting Information. CCDC-943855 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This research was partly supported by Grants-in-Aid for Scientific Research on Innovative Areas "Molecular Activation Directed toward Straightforward Synthesis" (no. 2204), and "Stimuli-Responsive Chemical Species for the Creation of Functional Molecules" (no. 2408) from MEXT, and by the Asahi Glass Foundation. We also thank Prof. K. Nozaki and Prof. K. Nakano (U. of Tokyo) for permitting us to use their size-exclusion chromatography analysis.

[1] a) G. Liu, J. R. Huth, E. T. Olejniczak, R. Mendoza, P. DeVries, S. Leitza, E. B. Reilly, G. F. Okasinski, S. W. Fesik, T. W. von Geldern, *J. Med. Chem.* **2001**, *44*, 1202–1210; b) G. De Martino, M. C. Edler, G. LaRegina, A. Coluccia, M. C. Barbera, D. Barrow, R. I. Nicholson, G. Chiosis, A. Brancale, E. Hamel, M. Artico, R. Silvestri, *J. Med. Chem.* **2006**, *49*, 947–954; c) A. Gangjee, Y. Zeng, T. Talreja, J. J. McGuire, R. L. Kisliuk, S. F. Queener, *J. Med. Chem.* **2007**, *50*, 3046–3053.

[2] For recent examples of cross-coupling reactions of arylhalides and arylthiol, see: a) C.-M. Tan, G. S. Chen, C.-S. Chen, J.-W. Chern, *J. Chin. Chem. Soc.* **2011**, *58*, 94–100; b) H. Wang, L. Jiang, T. Chen, Y. Li, *Eur. J. Org. Chem.* **2010**, 2324–2329; c) Y. Feng, H. F. Wang, F. F. Sun, Y. M. Li, X. M. Fu, K. Jin, *Tetrahedron* **2009**, *65*, 9737–9741; d) H. Xu, X. Zhao, J. Deng, Y. Fu, Y. Feng, *Tetrahedron Lett.* **2009**, *50*, 434–437; e) S. L. Buchwald, C. Bolm, *Angew. Chem.* **2009**, *121*, 5694–5695; *Angew. Chem. Int. Ed.* **2009**, *48*, 5586–5587; f) F. Manarin, J. A. Roehrs, R. M. Gay, R. Brandão, P. H. Menezes, C. W. Nogueira, G. Zeni, *J. Org. Chem.* **2009**, *74*, 2153–2162; g) S. Jammi, P. Barua, L. Rout, P. Saha, *Tetrahedron Lett.* **2008**, *49*, 1484–1487; h) E. Sperotto, G. P. M. van Klink, J. G. de Vries, G. van Koten, *J. Org. Chem.* **2008**, *73*, 5625–5628; i) A. Correa, M. Carril, C. Bolm, *Angew. Chem.* **2008**, *120*, 2922–2925; *Angew. Chem. Int. Ed.* **2008**, *47*, 2880–2883.

[3] For examples of cross-coupling reactions of arylhalides and arylselenol, see: a) A. Dandapat, C. Korupalli, D. J. C. Prasad, R. Singh, G. Sekar, *Synthesis* **2011**, 2297–2302; b) P. Arsenyan, E. Paegle, S. Belyakov, I. Shestakova, E. Jaschenko, I. Domracheva, J. Popelis, *Eur. J. Med. Chem.* **2011**, *46*, 3434–3443; c) J.-H. Cho, F. V. Brown, K. H. Shaughnessy, *Main Group Chem.* **2007**, *6*, 201–214; d) W. Lin, F. Ilgen, P. Knochel, *Tetrahedron Lett.* **2006**, *47*, 1941–1944; e) G.-Y. Gao, A. J. Colvin, Y. Chen, X. P. Zhang, *J. Org. Chem.* **2004**, *69*, 8886–8892; f) R. K. Gujadhur, D. Venkataraman, *Tetrahedron Lett.* **2003**, *44*, 81–84; g) H. J. Cristau, B. Chabaud, R. Labaudiniere, H. Christol, *Organometallics* **1985**, *4*, 657–661; h) A. Osuka, N. Ohmasa, H. Suzuki, *Synthesis* **1982**, 857–858; i) H. Suzuki, H. Abe, A. Osuka, *Chem. Lett.* **1981**, 151–152.

[4] For an example of the decarbonylation of chalcogenoesters, see: T. Kato, H. Kuniyasu, T. Kajiura, Y. Minami, A. Ohtaka, M. Kinimoto, J. Terao, H. Kurosawa, N. Kambe, *Chem. Commun.* **2006**, 868–870.

[5] For examples of the aromatic electrophilic substitution of sulfenyl chloride, see: a) W. Rudz, B. Gawdzik, *Int. J. Polym. Mater.* **2010**, *59*, 255–262; b) E. E. Glover, K. D. Vaughan, *J. Chem. Soc. Perkin Trans. 1* **1973**, 2595–2599.

[6] For examples of other coupling reactions that give chalcogenides, see reviews of Chan–Lam coupling and oxidative coupling of arylboronic acids and diaryldichalcogenides: a) K. S. Rao, T.-S. Wu, *Tetrahedron* **2012**, *68*, 7735–7754; also see: b) N. Taniguchi, *J. Org. Chem.* **2007**, *72*, 1241–1245; c) W. Ge, Y. Wei, *Green Chem.* **2012**, *14*, 2066–2070; d) X. Wang, Y. Li, Y. Yuan, *Synthesis* **2013**, 1247–1255.

[7] For examples of the thermal reactions of nucleophilic arenes and elemental sulfur, see: a) A. S. Hay, B. M. Boulette, *J. Org. Chem.* **1976**, *41*, 1710–1712; b) N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi, S. Miyano, *Tetrahedron* **2000**, *56*, 1437–1443.

[8] a) F. Shibahara, R. Sugiura, T. Murai, *Org. Lett.* **2009**, *11*, 3064–3067; b) T. Murai, T. Ohashi, F. Shibahara, *Chem. Lett.* **2011**, *40*, 70–71; c) T. Murai, Y. Mutoh, *Chem. Lett.* **2012**, *41*, 2–8; d) T. Murai, T. Nonoyama, *Tetrahedron* **2012**, *68*, 10489–10495; e) T. Murai, T. Ezaka, S. Kato, *Synthesis* **2012**, 3197–3201; f) F. Shibahara, S. Kobayashi, T. Maruyama, T. Murai, *Chem. Eur. J.* **2013**, *19*, 304–313.

[9] a) F. Shibahara, A. Yoshida, T. Murai, *Chem. Lett.* **2008**, *37*, 646–647; b) F. Shibahara, A. Suenami, A. Yoshida, T. Murai, *Chem. Commun.* **2007**, 2354–2356.

[10] Recently, imidazo[1,5-*a*]pyridine has attracted significant attention due to its potential applications in photofunctional and conductive materials, in bioactive compounds, and as a ligand for metals; for examples, see: a) A. Kamal, G. Ramakrishna, M. J. Ramaiah, A. Viswanath, A. V. S. Rao, C. Bagul, D. Mukhopadyay, S. N. C. V. L. Pushpavalli, M. Pal-Bhadra, *Med. Chem. Commun.* **2013**, *4*, 697–703; b) Y. Chen, L. Li, Y. Cao, J. Wu, Q. Gao, Y. Li, H. Hu, W. Liu, Y. Liu, Z. Kang, J. Li, *CrystEngComm* **2013**, *15*, 2675–2681; c) Y. Yan, Y. Zhang, Z. Zha, Z. Wang, *Org. Lett.* **2013**, *15*, 2274–2277; d) G. Pelletier, A. B. Charette, *Org. Lett.* **2013**, *15*, 2290–2293. Y. Prostota, O. D. Kachkovsky, L. V. Reis, P. F. Santos, *Dyes Pigm.* **2013**, *96*, 554–562; e) C. M. Álvarez, L. Álvarez-Miguel, R. Garcia-Rodríguez, D. Miguel, *Dalton Trans.* **2012**, *41*, 7041–7046; f) B. Jiang, J. Wang, Z.-g. Huang, *Org. Lett.* **2012**, *14*, 2070–2073; g) V. K. Fulwa, V. Manivannan, *Tetrahedron Lett.* **2012**, *53*, 3927–3931; h) V. K. Fulwa, V. Manivannan, *Tetrahedron Lett.* **2012**, *53*, 2420–2423; i) I. T. Raheem, M. J. Breslin, C. Fandozzi, J. Fuerst, N. Hill, S. Huszar, M. Kandebo, S. H. Kim, B. Ma, G. McGaughey, J. J. Renger, J. D. Schreier, S. Sharma, S. Smith, J. Uslaner, Y. Yan, P. J. Coleman,

C. D. Cox, *Bioorg. Med. Chem. Lett.* **2012**, *22*, 5903–5908; j) S. Roy, S. Javel, M. M. Olmstead, A. K. Patra, *Dalton Trans.* **2011**, *40*, 12866–12876; k) H.-R. Pan, X.-R. Wang, C.-X. Yan, Z.-X. Sun, Y. Cheng, *Org. Biomol. Chem.* **2011**, *9*, 2166–2174; l) J. T. Hutt, Z. D. Aron, *Org. Lett.* **2011**, *13*, 5256–5259; m) Y. Q. Ge, B. Q. Hao, G. Y. Duan, J. W. Wang, *J. Lumin.* **2011**, *131*, 1070–1076; n) C. Huang, A. Giokaris, V. Gevorgyan, *Chem. Lett.* **2011**, *40*, 939–940; for our recent studies on imidazo[1,5-*a*]pyridines, see: o) T. Murai, E. Nagaya, K. Miyahara, T. Maruyama, F. Shibahara, *Chem. Lett.* **2013**, *42*, 828–830; p) F. Shibahara, Y. Dohke, T. Murai, *J. Org. Chem.* **2012**, *77*, 5381–5388; q) T. Murai, E. Nagaya, F. Shibahara, T. Maruyama, *Org. Biomol. Chem.* **2012**, *10*, 4943–4953; r) E. Yamaguchi, F. Shibahara, T. Murai, *J. Org. Chem.* **2011**, *76*, 6146–6158; s) E. Yamaguchi, F. Shibahara, T. Murai, *Chem. Lett.* **2011**, *40*, 939–940; t) F. Shibahara, E. Yamaguchi, T. Murai, *Chem. Commun.* **2010**, *46*, 2471–2473; u) S. Tahara, F. Shibahara, T. Maruyama, T. Murai, *Chem. Commun.* **2009**, 7009–7011; v) F. Shibahara, E. Yamaguchi, A. Kitagawa, A. Imai, T. Murai, *Tetrahedron* **2009**, *65*, 5062–5073; w) F. Shibahara, R. Sugiura, E. Yamaguchi, A. Kitagawa, T. Murai, *J. Org. Chem.* **2009**, *74*, 3566–3568; x) F. Shibahara, A. Kitagawa, E. Yamaguchi, T. Murai, *Org. Lett.* **2006**, *8*, 5621–5624.

[11] For optimization of the reaction conditions, see the Supporting Information (Tables S1 and S2).

[12] For recent selected examples, see: a) N. Matsuda, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2011**, *13*, 2860–2863; b) L. Zhang, J. Cheng, T. Ohishi, Z. Hou, *Angew. Chem.* **2010**, *122*, 8852–8855; *Angew. Chem. Int. Ed.* **2010**, *49*, 8670–8673.

[13] Previously, a bis(imidazo[1,5-*a*]pyridyl) selenide and diselenide were synthesized by the reaction of picolyl amine and selenium dioxide, see: O. Niyomura, Y. Yamaguchi, S. Tamura, M. Minoura, Y, Okamoto, *Chem. Lett.* **2011**, *40*, 449–451.

[14] For initial screening of the reaction conditions, see the Supporting Information (Table S3).

[15] During our investigation, a similar copper-catalyzed oxidative coupling of disulfide or diselenide and heteroarenes was reported independently. Under our catalytic conditions, coupling with disulfide did not take place, see: Z. Li, J. Hong, X. Zhou, *Tetrahedron* **2011**, *67*, 3690–3697; ref. [2 f].

[16] T. Higashi, NUMABS, Numerical Absorption Correction. In Rigaku Corporation, Tokyo, Japan, **1999**.

[17] G. M. Sheldrick, SHELXL-97, A Program for the Refinement of Crystal Structures, University of Gottingen, Göttingen, Germany, **1997**.

[18] Yadokari-XG, Software for Crystal Structure Analyses, K. Wakita, **2001**; Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto, E. Kwon, *J. Cryst. Soc. Jpn.* **2009**, *51*, 218–224.

Received: July 4, 2013
Revised: September 25, 2013
Published online: November 4, 2013