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Regioselective, Solvent- and Metal-Free Chalcogenation of Imidazo[1,2-*a*]pyridines by Employing I_2/DMSO as Catalytic Oxidation System

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In memory of Dr. Syed H. Hussain who was killed by terrorists while protecting his students

Abstract: Highly efficient molecular-iodine-catalyzed chalcogenations (S and Se) of imidazo[1,2-*a*]pyridines were achieved by using diorganoyl dichalcogenides under solvent-free conditions. This approach afforded the desired products that had been chalcogenated regioselectively at the C3 position in up to 96% yield by using DMSO as an oxidant, in the absence of a metal catalyst, and under an inert atmosphere. This mild, green approach allowed the preparation of different types of chalcogenated imidazo[1,2-*a*]pyridines with structural diversity. Furthermore, the current protocol was also extended to other *N*-heterocyclic cores.

Introduction

The imidazo[1,2-*a*]pyridine (**IP**) core, found in many bioactive natural products and pharmaceuticals, represents an important "privileged scaffold".[1] Several commercially available drugs have the **IP** moiety in their core structure, e.g., alpidem, necopidem, saripidem (as anxiolytics), zolpidem (as a sedative), miroprofen (as an analgesic), and zolimidine (for the treatment of peptic ulcer) (Figure 1).[1a,2] Additionally, **IP** derivatives are

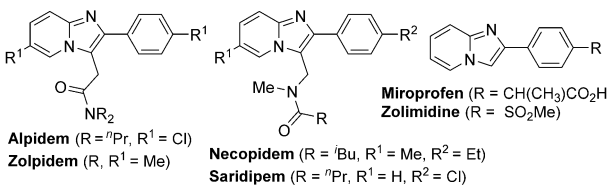

Figure 1. Imidazo[1,2-*a*]pyridine-based drug compounds.

useful in the field of optoelectronics and material sciences as charge transporters.[3] Therefore, the synthesis and functionalization of **IPs** has received considerable attention.[1a,4]

In recent decades, the biological and medicinal properties of organochalcogenides (S, Se) have gained increasing interest,[5] which is mainly due to their antioxidant, antitumor, anti-inflammatory, and antiviral activities.[5,6] In addition, these scaffolds are present in a wide range of molecules that have important applications in material sciences,[7] and they also play a fundamental role in modern organic synthesis and catalysis.[8,9] As a consequence, important advances are being made in the selective C–S/Se bond formation, and direct chalcogenation (S/Se) is an attractive approach.[5,8–10]

We have considered the biological relevance of organochalcogen compounds and the wide spectrum of therapeutic properties of **IPs**; however, few synthetic methods for the construction of 3-sulfenyl-imidazo[1,2-*a*]pyridines have been reported in the literature,[11] and even fewer studies have been carried out on the selenium counterpart.[11i,12] Furthermore, some of the methods suffer from limitations, such as the use of non-green solvents and prefunctionalized coupling partners, low atom economy, poor substrate scope, the requirement of metal catalysts, ligands, and bases, sensitivity to atmosphere, harsh reaction conditions, or elaborate multistep processes, and these issues reduce their synthetic utility.

In recent years, the I_2/DMSO oxidative system has been successfully applied in various types of organic transformations.[13] In this context, it would be advantageous and highly desirable to develop a ligand- and metal-free protocol that involves a solvent-free system for the preparation of chalcogenated **IPs**, which is applicable to various sources of stable organochalcogens. Thus, in relation to our continuing interest in the chalcogenation of heteroarenes and organochalcogen chemistry as well as the design of eco-friendly processes,[10a–c,14] we now report, for the first time, the use of the I_2/DMSO oxidant system in the chalcogenation (S, Se) of **IPs** at the C3 position. This new regioselective, scalable, and metal-free protocol proceeded smoothly with a half molar equivalent of different dichalcogenides and without the exclusion of air or moisture.

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Results and Discussion

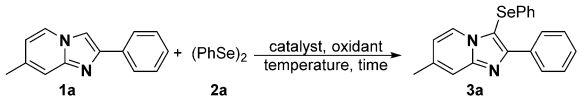
For the optimization of the selenylation reaction, 7-methyl-2-phenylimidazo[1,2-*a*]pyridine (**1a**) and diphenyl diselenide (**2a**) were selected as model substrates, and these were evaluated under various conditions (Table 1). The reaction was successful with I_2 (20 mol%) in the presence of 5 molar equivalents of DMSO (0.089 mL) at 110 °C for 18 h; this afforded the desired product **3a** in 69% yield (entry 1). There was no improvement in the yield when the reaction was conducted under inert atmosphere (entry 2), which shows that the reaction can be performed without the exclusion of air. The ideal reaction temperature was found to be 90 °C (entries 3–5). In relation to the source of iodine in the reaction system, a negative effect was observed when NaI and KI were used instead of I_2, and this resulted in 50 and 54% yields of the selenated product **3a**, respectively (entries 6 and 7). Lowering the catalyst loading to 5 and 2.5 mol% led to the desired product **3a** in lower yields (entries 9 and 10). The ideal reaction time was examined for this transformation and found to be 9 h (entries 11–13).

With regard to the influence of the oxidant on the selenylation of substrate **1a**, we found that the use of H_2O_2 or TBHP instead of DMSO resulted in a less efficient transformation (Table 1, entries 14–19). The use of DMSO (3 mL) as the solvent did not provide any further positive influence on the yield of **3a** (entry 16 vs. 12). Similarly, upon decreasing the amount of DMSO from 5 to 3 molar equivalents, we obtained the product **3a** in 89% yield (entry 17), whereas a further decrease in DMSO afforded a lower yield of **3a** (entries 18–19).

With the optimized reaction conditions in hand (Table 1, entry 17), we explored the generality and scope of this method, and the reaction demonstrated wide substrate scope in terms of the diorganyl diselenide substrates **2** (Table 2). Various diaryl diselenides with electron-donating (R = Me, OMe), electron-withdrawing (R = F, Cl, CF_3), and sterically bulky substituents (R = naphthyl) successfully reacted to afford the corresponding products in good to excellent yields (**3a–i**, 71–93%). We also observed that the C-2 heteroaryl diselenide gave the desired selenide **3j** in a similar high yield (82%). In general, electron-withdrawing groups afforded the best results (**3a–e** vs. **f–g**). Furthermore, steric hindrance of the *ortho*-substituent on the aryl unit of the diselenide substrate showed an unfavorable influence on the yields compared with the *para*-substituted counterparts (**3b–c** vs. **d–e**). However, a sterically bulkier aryl moiety on the diselenide substrate (R = 1-naphthyl) afforded the desired product **3i** in 71% yield. Finally, considering the importance of butylated organoselenides in cross-coupling reactions,[15] we were successful in using dibutyl diselenide **2k** to produce the corresponding product **3k** in good yield.

The success in the iodine-catalyzed C–Se bond formation, through the C(sp^2)–H bond activation of biaryl substrate **1a**, prompted us to expand this method by using diorganyl disulfide substrates **4a–**

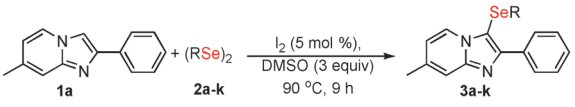
Table 1. Optimization of the reaction conditions.[a]

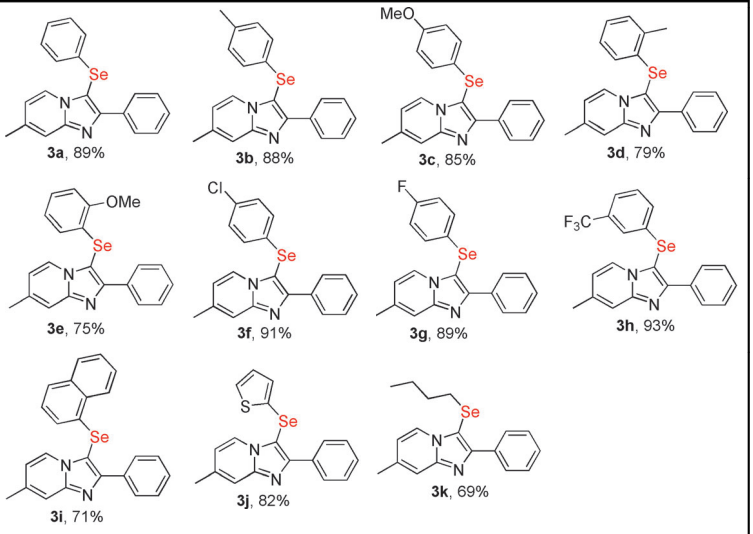


Entry	Catalyst [mol%]	Oxidant [equiv]	T [°C]	t [h]	Yield [%][b]
1	I_2 (20)	DMSO (5)	110	18	69
2[c]	I_2 (20)	DMSO (5)	110	18	67
3	I_2 (20)	DMSO (5)	100	18	83
4	I_2 (20)	DMSO (5)	90	18	87
5	I_2 (20)	DMSO (5)	80	18	78
6	NaI (20)	DMSO (5)	90	18	50
7	KI (20)	DMSO (5)	90	18	54
8	I_2 (10)	DMSO (5)	90	18	87
9	I_2 (5)	DMSO (5)	90	18	86
10	I_2 (2.5)	DMSO (5)	90	18	56
11	I_2 (5)	DMSO (5)	90	12	88
12	I_2 (5)	DMSO (5)	90	9	90
13	I_2 (5)	DMSO (5)	90	6	60
14	I_2 (5)	H_2O_2 (5)	90	9	57
15	I_2 (5)	TBHP (5)	90	9	12
16[d]	I_2 (5)	DMSO	90	9	91
17	**I_2 (5)**	**DMSO (3)**	**90**	**9**	**89**
18	I_2 (5)	DMSO (2)	90	9	77
19	I_2 (5)	DMSO (1)	90	9	44
20	–	DMSO (1)	90	9	–

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.125 mmol), catalyst (mol%), oxidant (molar equiv). [b] Yield of isolated poduct. [c] Reaction under argon atmosphere. [d] 2 mL DMSO.

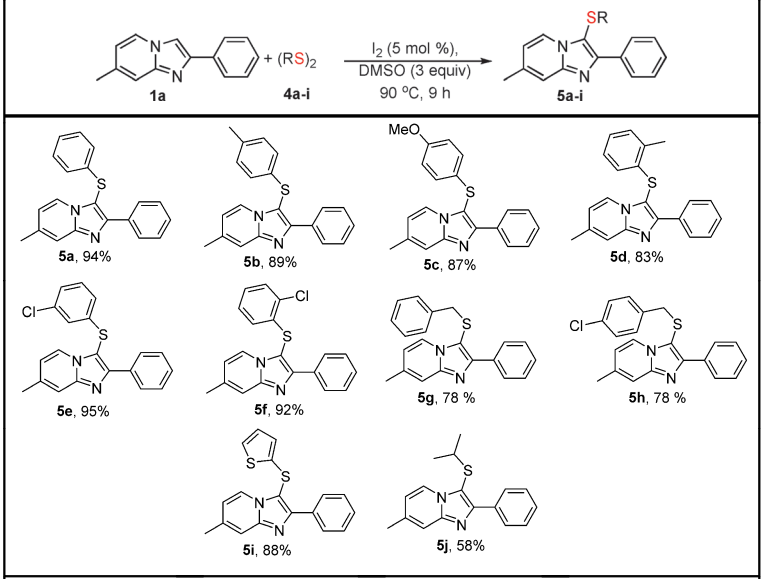
Table 2. Scope of diorganyl diselenide **2**.[a,b]





[a] Reaction conditions: **1a** (0.25 mmol), **2** (0.125 mmol), I_2 (5 mol%), DMSO (3 molar equiv, 0.054 mL), 90 °C, 9 h. [b] Yield of isolated product.

Table 3. Scope of diorganyl disulfides **5**.[a,b]

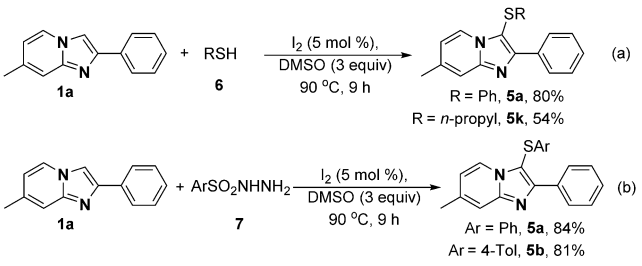


[a] Reaction conditions: **1a** (0.25 mmol), **4** (0.125 mmol), I_2 (5 mol%), DMSO (3 molar equiv, 0.054 mL), 90 °C, 9 h. [b] Yield of isolated product.

products **8a–i** and **aa–ai** were successfully obtained in 79–96% yield. In general, disulfide **4a** afforded the coupled products in better yields compared with the diselenide **2a. IP** substrates with substituents at C-6 or C-7, or without functionalization (at the pyridine ring) did not show any significant effects towards the yield. The system also tolerated changes in the electronic nature of the C-2 substituents of the phenyl group of the **IP** substrate; in this case, electron-withdrawing groups (Br, Cl, F, CN) showed superiority over an electron-donating group (OMe). Additionally, we extended the method to imidazo[1,2-*a*]pyrimidine, which furnished the corresponding chalcogenated products **8h** and **ah** in good yields. Notably, the method showed high regioselectivity because the **IP** substrate that had no substituent at the C-2 position was selectively chalcogenated at C-3 to exclusively give products **8i** and **ai** in 85 and 91% yield, respectively.

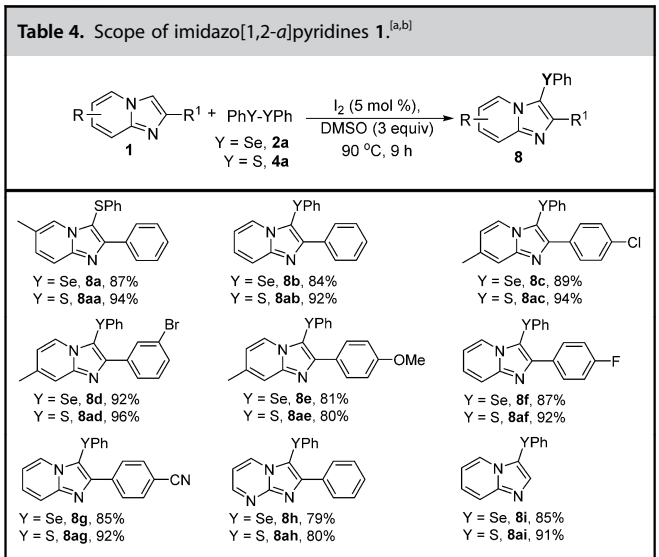
To demonstrate the synthetic utility of this new protocol, a series of reactions were carried out on different scales in a normal laboratory setup. Imidazo[1,2-*a*]pyridine **1a** efficiently reacted with diphenyl **i** as the coupling partner (Table 3). Accordingly, the thiolation of biaryl **1a** under the optimized reaction conditions that had been determined for selenylation afforded the corresponding sulfenylated products **5a–j** in 58 to 95% yield. The sulfenylation of **IP** was governed by similar electronic and steric effects that were observed in the selenylation reaction; furthermore, diorganyl disulfides **4** afforded the coupling products in better yields than the corresponding diorganyl diselenides **2**.

Other thiolating agents were tested under the optimized reaction conditions (Scheme 1). The reaction of thiols **6** proceed-



Scheme 1. Thiolation by using other sulfenylating agents.

Table 4. Scope of imidazo[1,2-*a*]pyridines **1**.[a,b]



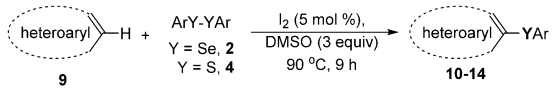
[a] Reaction conditions: **1a** (0.25 mmol), **2a** or **4a** (0.125 mmol), I_2 (5 mol%), DMSO (3 molar equiv, 0.054 mL), 90 °C, 9 h. [b] Yield of isolated product.

ed smoothly, and the corresponding coupled products **5a** and **k** were isolated in 80 and 54% yield, respectively (Scheme 1a). Similarly, when aryl sulfonyl hydrazide (**7**) was employed as the substrate, we obtained the desired products **5a** and **b** in 84 and 81% yield, respectively (Scheme 1b). However, the use of dichalcogenides as chalcogenylating agents appears to be a better synthetic option as they are odorless and inexpensive.

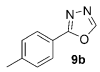
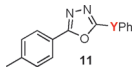
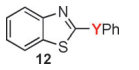
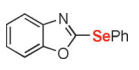
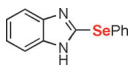
The reaction scope was further tested by using different **IP** cores **1** with diselenide **2a** and disulfide **4a** under the optimized conditions (Table 4). The corresponding chalcogenated diselenide **2a** under the optimized conditions up to a 10 mmol scale, which afforded product **3a** with no major decrease in yield (Figure 2). Therefore, this protocol represents a practical method for the synthesis of biologically relevant lead compounds.

Other *N*-heterocyclic cores were tested under the optimized conditions. Indazole **9a** furnished the corresponding C-3-selenylated products **10a–c** in good yields (Table 5, entries 1–3). On the other hand, 2-aryl 1,3,4-oxadiazole **9b** and benzothiazole **9c** afforded the corresponding selenylated and sulfenylat-

Table 5. Scope of *N*-heterocyclic core **9**.[a]



9 10-14

Entry	*N*-Heterocyclic core **9**	Product **10**–**14**		Yield [%][b]
1	 9a	 10	Ar = Ph, Y = Se, **10a**	81
2			Ar = 4-MeOPh, Y = Se **10b**	79
3			Ar = 4-ClPh, Y = Se, **10c**	85
4	 9b	 11	Ar = Ph, Y = Se, **11a**	39
5			Ar = Ph, Y = S, **11b**	33
6	 9c	 12	Ar = Ph, Y = Se, **12a**	22
7			Ar = Ph, Y = S, **12b**	19
8	 9d		**13**	–
9	 9e		**14**	–

[a] Reaction conditions: **9** (0.25 mmol), **2** or **4** (0.125 mmol), I_2 (5 mol%), DMSO (3 molar equiv, 0.054 mL), 90 °C, 9 h. [b] Yield of isolated product.

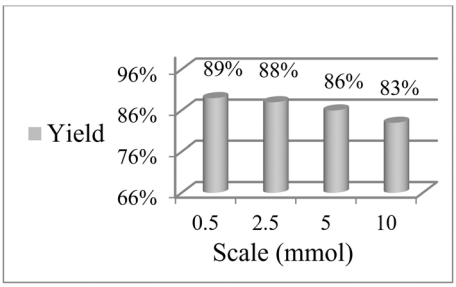


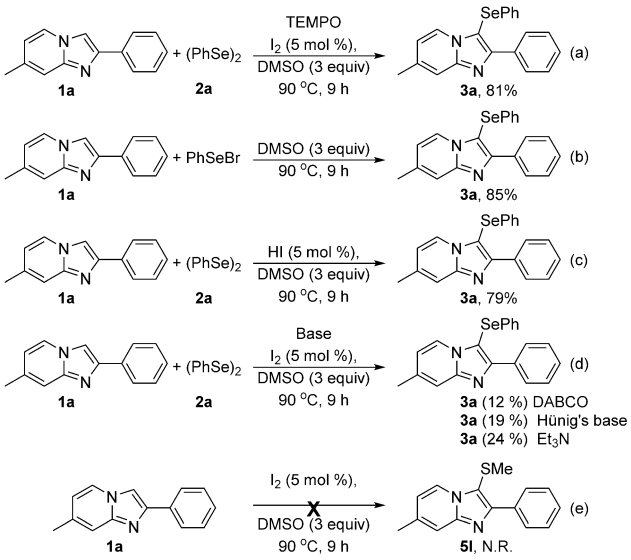
Figure 2. Results for the reaction on different scales.

ed products in low yields (entries 4–7), and benzoxazole **9d** and benzimidazole **9e** did not react under these conditions (entries 8–9).

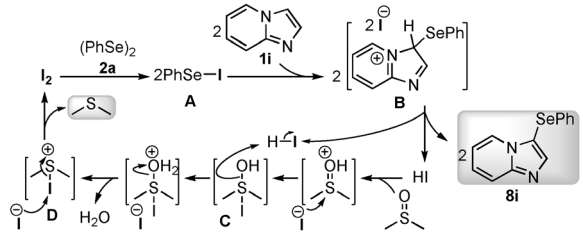
To elucidate the mechanism, we performed some control experiments (Scheme 2). Firstly, addition of a radical inhibitor (TEMPO) did not hamper the reaction, and the desired selenylated product **3a** was obtained in 81% yield (Scheme 2a); this excluded the possibility of a radical pathway. Secondly, when biaryl **1a** was treated with PhSeBr instead of diphenyl diselenide (**2a**), we isolated the product **3a** in 85% yield, which shows that the reaction goes through a phenylselenium cationic intermediate (Scheme 2b). Thirdly, the coupling reaction of biaryl **1a** with diselenide **2a** by using a catalytic amount of HI instead of iodine smoothly gave product **3a** in 82% yield (Scheme 2c), which demonstrates that HI is most likely one of the intermediates of this transformation.

To further develop our understanding of the reaction mechanism, we carried out the reaction in the presence of tertiary amines as the base (Scheme 2d). The use of DABCO, Hünig's base, and Et_3N resulted in an abrupt decrease in the yields. These results indicate that scavenging the generated HI terminates the catalytic cycle by inhibiting the DMSO activation. To exclude the unusual formation of C–I and C–S bonds with imidazo[1,2-*a*]-pyridines,[16] we carried out an experiment without diphenyl diselenide (**2a**). Interestingly, we did not observe these unusual products; we believe that this is the consequence of a low concentration of iodine and DMSO (Scheme 2e).

Based on the above results and on previous reports,[10a–b,11] a possible mechanism has been proposed with model substrates **1i** and **2a** (Scheme 3). An electrophilic species **A** (PhSeI) is most likely generated when the diphenyl diselenide (**2a**) is submitted to reaction with the catalyst (I_2). Next, the reactive intermediate **A** reacts regioselectively with imidazo[1,2-*a*]pyridine (**1i**) at the C-3 position to form species **B**. This species can undergo proton elimination to afford the desired selenylated product **8i**, with the concomitant formation of HI. Two molar equivalents of HI react with DMSO to afford the protonated sulfur species **C**, which with the elimination of water, results in the formation of iodine–dimethyl sulfide intermediate **D**.[17] Finally, the iodide species **D** eliminates Me_2S, which regenerates the catalyst in the reac-



Scheme 2. Investigation of the reaction mechanism.



Scheme 3. Proposed mechanism for the reaction.

tion medium. An important feature of this process is that the concentration of iodide in the reaction medium is low as it is continuously consumed by the mild oxidant (DMSO), which precludes competitive side reactions.

Conclusion

We have developed a green, iodine-catalyzed, regioselective, and efficient strategy for the preparation of 3-selenyl- and 3-sulfenyl-imidazo[1,2-*a*]pyridine derivatives. Under mild conditions, the reaction worked well in the presence of the I_2/DMSO oxidant system with a half molar equivalent of diorganyl dichalcogenides, an odorless source of chalcogens, without the exclusion of air and moisture, which afforded a wide range of chalcogenated imidazo[1,2-*a*]pyridines at the C3 position in good to excellent yields. Furthermore, thiols and sulfonyl hydrazides were also successfully applied as alternative sulfenylating agents. This reaction is robust, and no significant loss of yield is expected upon scale-up. Similarly, the current protocol was successfully extended to other *N*-heterocyclic cores.

Experimental Section

General

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 200 MHz on a Bruker AC-200 NMR spectrometer. Spectra were recorded in $CDCl_3$. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz, and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 50 MHz on a Bruker AC-200 NMR spectrometer. Spectra were recorded in $CDCl_3$. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), and m (multiplet). Selenium-77 nuclear magnetic resonance spectra (^{77}Se NMR) at 38.14 MHz on a Bruker AC-200 NMR spectrometer. Spectra were recorded in $CDCl_3$. Chemical shifts are reported in ppm, referenced to diphenyl diselenide as the external reference (463.15 ppm). High resolution mass spectra were recorded on a Bruker microTOF-Q II ESI mass spectrometer equipped with an automatic syringe pump for sample injection. Infrared spectra were recorded on a Bruker Optics Alpha benchtop FT-IR spectrometer and are reported in frequency of absorption (cm^{-1}). The melting points were determined in a Microquimica MQRPF-301 digital model equipment with heating plate. Column chromatography was performed on silica gel (230–400 mesh). Thin layer chromatography (TLC) was performed by using Merck silica gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light or stained with iodine vapor and acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material.

General procedure for the iodine-catalyzed chalcogenation of imidazo[1,2-*a*]pyridines 1 by using diorganyl chalcogenides 2 or 4

A mixture of the appropriate imidazo[1,2-*a*]pyridines **1** (0.25 mmol), diorganyl dichalcogenide **2** or **4** (0.125 mmol), iodine (5 mol%, 3.2 mg), and DMSO (3 equiv, 0.75 mmol, 59 mg) were charged in a Schlenk tube. The reaction was heated to 90 °C in an oil bath for 9 h. Then, the reaction mixture was dissolved in ethyl acetate (10 mL), and washed with 2×5 mL of an aqueous solution of 10% $Na_2S_2O_3$. The organic layer was separated, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (hexane or hexane/ethyl acetate, 8:2).

7-Methyl-2-phenyl-3-(p-tolylselanyl)imidazo[1,2-a]pyridine (3 b) (New compound)

Yield: 88% (83 mg); yellow solid; mp: 119–120 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.27–8.02 (m, 3H), 7.48–7.30 (m, 4H), 7.04–6.90 (m, 4H), 6.63 (dd, J = 7.0, 1.5 Hz, 1H), 2.40 (s, 3H), 2.23 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 151.5, 148.0, 137.5, 136.6, 134.0, 130.4, 128.7, 128.4, 128.3, 127.3, 124.8, 116.0, 115.5, 102.4, 21.4, 21.0 ppm; IR (KBr): 3068, 2922, 1652, 1558, 1456, 1350, 1236, 1154, 1032, 844, 770, 669 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{19}N_2Se$: 379.0709 $[M+H]^+$; found: 379.0707.

3-((4-Methoxyphenyl)selanyl)-7-methyl-2-phenylimidazo[1,2-a]pyridine (3 c) (New compound)

Yield: 85% (84 mg); yellow solid; mp: 100–101 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.28–8.08 (m, 3H), 7.52–7.28 (m, 4H), 7.08 (d, J = 8.8 Hz, 2H), 6.76–6.59 (m, 3H), 3.69 (s, 3H), 2.40 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.0, 151.1, 147.9, 137.5, 134.1, 130.6, 128.8, 128.3, 124.7, 120.9, 116.0, 115.5, 115.4, 103.2, 55.3, 21.4 ppm; IR (KBr): $\tilde{\nu}$ = 3047, 2924, 1652, 1558, 1458, 1340, 1227, 1064, 821, 736, 666 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{19}N_2OSe$: 395.0658 $[M+H]^+$; found: 395.0662.

7-Methyl-2-phenyl-3-(o-tolylselanyl)imidazo[1,2-a]pyridine (3 d) (New compound)

Yield: 79% (74 mg); yellow solid; mp: 129–131 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.17–7.99 (m, 3H), 7.51–7.30 (m, 4H), 7.20–7.01 (m, 2H), 6.86 (t, J = 7.5 Hz, 1H), 6.65 (d, J = 7.0 Hz, 1H), 6.54 (d, J = 7.8 Hz, 1H), 2.45 (s, 3H), 2.42 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.3, 148.4, 137.7, 136.4, 134.0, 131.7, 130.6, 128.7, 128.4, 128.3, 127.2, 126.8, 126.4, 124.8, 116.1, 115.6, 100.9, 21.4, 21.1 ppm; IR (KBr): $\tilde{\nu}$ = 3059, 2922, 1652, 1558, 1458, 1348, 1230, 1032, 848, 770, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{19}N_2Se$: 379.0709 $[M+H]^+$; found: 379.0708.

3-((2-Methoxyphenyl)selanyl)-7-methyl-2-phenylimidazo[1,2-a]pyridine (3 e) (New compound)

Yield: 75% (74 mg); yellow solid; mp: 125–126 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.20–8.05 (m, 3H), 7.48–7.29 (m, 4H), 7.18–7.06 (m, 1H), 6.89–6.80 (m, 1H), 6.70–6.58 (m, 2H), 6.41 (dd, J = 7.7, 1.5 Hz, 1H), 3.91 (s, 3H), 2.41 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 156.6, 152.3, 148.4, 137.6, 134.0, 128.7, 128.2, 127.4, 127.2, 125.2, 122.0, 120.1, 116.0, 115.5, 110.6, 100.3, 55.9, 21.4 ppm; IR (KBr): $\tilde{\nu}$ = 3056, 2928, 1652, 1558, 1458, 1486, 1346, 1240, 1021, 856, 752, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{19}N_2OSe$: 395.0658 $[M+H]^+$; found: 395.0656.

3-((4-Chlorophenyl)selanyl)-7-methyl-2-phenylimidazo[1,2-a]pyridine (3 f) (New compound)

Yield: 91% (90 mg); yellow solid; mp: 144–146 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.18–8.04 (m, 3H), 7.52–7.34 (m, 4H), 7.12 (d,

J=8.4 Hz, 2H), 6.99 (d, J=8.5 Hz, 2H), 6.67 (dd, J=7.0, 1.4 Hz, 1H), 2.42 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=151.9, 148.2, 137.9, 133.8, 132.8, 129.8, 129.5, 128.7, 128.5, 128.3, 124.6, 116.2, 115.8, 101.5, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3066, 2922, 1652, 1558, 1472, 1350, 1087, 1053, 807, 786, 669 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{16}N_2ClSe$: 399.0160 $[M+H]^+$; found: 399.0154.

3-((4-Fluorophenyl)selanyl)-7-methyl-2-phenylimidazo[1,2-a]pyridine (3g) (New compound)

Yield: 89% (85 mg); yellow solid; mp: 147–148 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.25–8.09 (m, 3H), 7.48–7.34 (m, 4H), 7.13–7.03 (m, 2H), 6.87 (t, J=8.6 Hz, 2H), 6.67 (d, J=7.0 Hz, 1H), 2.42 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=162.0 (d, J_{C-F}=246.4 Hz), 151.6, 148.1, 137.7, 133.9, 130.3 (d, J_{C-F}=7.8 Hz), 128.7, 128.4, 128.3, 125.5 (d, J_{C-F}=3.2 Hz), 124.6, 117.1, 116.6, 115.9 (d, J_{C-F}=21.1 Hz), 102.3, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3066, 2924, 1652, 1558, 1456, 1337, 1021, 815, 736, 669 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{16}N_2FSe$: 383.0458 $[M+H]^+$; found: 383.0454.

7-Methyl-2-phenyl-3-((3-(trifluoromethyl)phenyl)selanyl)imidazo[1,2-a]pyridine (3h) (New compound)

Yield: 93% (100 mg); yellow solid; mp: 105–106 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.22–8.03 (m, 3H), 7.51–7.34 (m, 6H), 7.21 (t, J=7.7 Hz, 1H), 7.08 (d, J=7.8 Hz, 1H), 6.68 (d, J=7.0 Hz, 1H), 2.42 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=152.2, 148.3, 138.03, 133.6, 132.8, 131.8 (q, J_{C-F}=32.5 Hz), 131.03 (q, J_{C-F}=1.2 Hz), 129.9, 128.64, 128.5, 128.3, 126.2, 124.9, 124.7 (q, J_{C-F}=3.9 Hz), 123.5 (q, J_{C-F}=271.5 Hz), 123.4 (q, J_{C-F}=3.7 Hz), 116.2, 115.8, 100.8, 21.3 ppm; IR (KBr): $\tilde{\nu}$=3061, 2926, 1652, 1558, 1456, 1342, 1247, 1035, 844, 781, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{16}N_2F_3Se$: 433.0426 $[M+H]^+$; found: 433.0423.

7-Methyl-3-(naphthalen-1-ylselanyl)-2-phenylimidazo[1,2-a]pyridine (3i) (New compound)

Yield: 71% (73 mg); yellow solid; mp: 145–147 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.18–8.05 (m, 4H), 7.86–7.77 (m, 1H), 7.67–7.31 (m, 7H), 7.09 (t, J=7.7 Hz, 1H), 6.84 (d, J=7.3 Hz, 1H), 6.55 (d, J=7.0 Hz, 1H), 2.37 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=152.4, 148.4, 137.7, 134.3, 133.9, 132.2, 129.5, 128.8, 128.7, 128.4, 128.3, 127.1, 126.6, 126.4, 126.3, 125.4, 125.1, 124.8, 116.1, 115.6, 100.7, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3049, 2916, 1652, 1558, 1458, 1348, 1260, 1023, 956, 844, 766, 687 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{19}N_2Se$: 415.0709 $[M+H]^+$; found: 415.0711.

7-Methyl-2-phenyl-3-(thiophen-2-ylselanyl)imidazo[1,2-a]pyridine (3j) (New compound)

Yield: 82% (76 mg); yellow solid; mp: 89–91 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.40 (d, J=7.0 Hz, 1H), 8.23–8.10 (m, 2H), 7.57–7.35 (m, 4H), 7.26–7.19 (m, 1H), 7.14–7.09 (m, 1H), 6.92–6.81 (m, 1H), 6.72 (d, J=7.0 Hz, 1H), 2.40 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=150.7, 147.7, 137.5, 134.0, 132.5, 131.3, 129.6, 129.0, 128.3, 128.2, 128.0, 124.7, 116.1, 115.6, 104.2, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3060, 2924, 1652, 1558, 1472, 1346, 1229, 1023, 854, 742, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{15}N_2SeS$: 371.0116 $[M+H]^+$; found: 371.0113.

3-(Butylselanyl)-7-methyl-2-phenylimidazo[1,2-a]pyridine (3k) (New compound)

Yield: 69% (59 mg); yellow liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.40 (d, J=7.0 Hz, 1H), 8.28–8.16 (m, 2H), 7.60–7.26 (m, 4H), 6.72 (d, J=7.0 Hz, 1H), 2.64 (t, J=6.7 Hz, 2H), 2.43 (s, 3H), 1.54–1.38 (m, 2H), 1.35–1.19 (m, 2H), 0.75 ppm (t, J=7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=150.1, 147.6, 136.8, 134.4, 128.7, 128.1, 128.0, 124.8, 115.9, 115.2, 103.5, 32.1, 29.3, 22.7, 21.3, 13.5 ppm; IR (KBr): $\tilde{\nu}$=3045, 2927, 1652, 1558, 1474, 1352, 1227, 862, 751, 668 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{21}N_2Se$: 345.0865 $[M+H]^+$; found: 345.0870.

3-((4-Methoxyphenyl)thio)-7-methyl-2-phenylimidazo[1,2-a]pyridine (5c) (New compound)

Yield: 87% (75 mg); white solid; mp: 110–112 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.28–8.10 (m, 3H), 7.49–7.30 (m, 4H), 6.97 (d, J=8.6 Hz, 2H), 6.77–6.62 (m, 3H), 3.69 (s, 3H), 2.40 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=158.5, 150.7, 147.3, 137.7, 133.6, 128.4, 128.3, 127.8, 125.8, 123.6, 116.1, 115.6, 115.1, 106.9, 55.3, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3059, 2923, 1652, 1558, 1458, 1337, 1231, 1025, 854, 746, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{19}N_2SO$: 347.1213 $[M+H]^+$; found: 347.1214.

7-Methyl-2-phenyl-3-(o-tolylthio)imidazo[1,2-a]pyridine (5d) (New compound)

Yield: 83% (68 mg); white solid; mp: 156–157 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.14 (dd, J=8.0, 1.6 Hz, 2H), 8.02 (d, J=7.0 Hz, 1H), 7.49–7.32 (m, 4H), 7.17 (d, J=7.3 Hz, 1H), 7.02 (td, J=7.3, 1.1 Hz, 1H), 6.89 (t, J=6.9 Hz, 1H), 6.64 (dd, J=7.0, 1.5 Hz, 1H), 6.41 (d, J=7.7 Hz, 1H), 2.50 (s, 3H), 2.41 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=151.6, 147.7, 137.8, 134.9, 134.4, 133.5, 130.7, 128.4, 128.3, 126.9, 125.6, 124.1, 123.7, 116.2, 115.6, 104.7, 21.4, 19.8 ppm; IR (KBr): $\tilde{\nu}$=3066, 2921, 1652, 1558, 1458, 1340, 1244, 1025, 803, 744, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{19}N_2S$: 331.1263 $[M+H]^+$; found: 331.1265.

3-((3-Chlorophenyl)thio)-7-methyl-2-phenylimidazo[1,2-a]pyridine (5e) (New compound)

Yield: 95% (83 mg); white solid; mp: 101–103 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.19–8.05 (m, 3H), 7.55–7.34 (m, 4H), 7.12–7.04 (m, 2H), 6.99 (s, 1H), 6.84–6.76 (m, 1H), 6.69 (dd, J=7.0, 1.4 Hz, 1H), 2.42 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=151.7, 147.7, 138.2, 137.8, 135.4, 133.3, 130.4, 128.7, 128.4, 128.3, 126.2, 125.1, 123.5, 123.4, 116.3, 115.9, 104.3, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3067, 2924, 1652, 1558, 1458, 1342, 1264, 1070, 824, 734, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{16}N_2SCl$: 351.0717 $[M+H]^+$; found: 351.0723.

3-((2-Chlorophenyl)thio)-7-methyl-2-phenylimidazo[1,2-a]pyridine (5f) (New compound)

Yield: 92% (81 mg); white solid; mp: 148–149 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.17–8.05 (m, 3H), 7.52–7.34 (m, 5H), 7.11–6.89 (m, 2H), 6.70 (dd, J=6.9, 1.5 Hz, 1H), 6.39 (dd, J=7.8, 1.6 Hz, 1H), 2.44 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=152.1, 147.9, 138.3, 134.7, 133.3, 131.1, 130.1, 128.5, 128.3, 127.6, 126.8, 125.6, 123.7, 116.4, 115.9, 103.8, 21.5 ppm; IR (KBr): $\tilde{\nu}$=3048, 2922, 1652, 1558, 1456, 1356, 1238, 1030, 851, 724, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{16}N_2SCl$: 351.0717 $[M+H]^+$; found: 351.0718.

3-(Benzylthio)-7-methyl-2-phenylimidazo[1,2-a]pyridine (5g) (New compound)

Yield: 78% (72 mg); white solid; mp: 114–115 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.20 (dd, J=8.1, 1.4 Hz, 2H), 7.94 (d, J=

7.0 Hz, 1H), 7.50–7.32 (m, 4H), 7.15–7.01 (m, 3H), 6.98–6.85 (m, 2H), 6.50 (dd, J=7.0, 1.3 Hz, 1H), 3.79 (s, 2H), 2.37 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=150.1, 146.9, 137.3, 137.1, 134.0, 128.8, 128.5, 128.3, 128.1, 127.3, 126.1, 123.4, 115.9, 114.9, 108.7, 40.7, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3064, 2926, 1652, 1558, 1458, 1340, 1209, 1019, 770, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{19}N_2S$: 331.1263 $[M+H]^+$; found: 331.1258.

3-((4-Chlorobenzyl)thio)-7-methyl-2-phenylimidazo[1,2-a]pyridine (5h) (New compound)

Yield: 81% (74 mg); white solid; mp: 137–140 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.16–8.07 (m, 2H), 7.97 (d, J=7.0 Hz, 1H), 7.48–7.32 (m, 4H), 6.95 (d, J=8.4 Hz, 2H), 6.73 (d, J=8.2 Hz, 2H), 6.55 (d, J=7.0 Hz, 1H), 3.69 (s, 2H), 2.38 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=150.5, 146.9, 137.3, 135.7, 133.7, 133.2, 130.0, 128.4, 128.3, 128.2, 128.1, 123.2, 115.9, 115.1, 108.0, 39.8, 21.3 ppm; IR (KBr): $\tilde{\nu}$=3065, 2924, 1652, 1558, 1458, 1348, 1058, 774, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{18}N_2SCl$: 365.0874 $[M+H]^+$; found: 365.0872.

7-Methyl-2-phenyl-3-(thiophen-2-ylthio)imidazo[1,2-a]pyridine (5i) (New compound)

Yield: 88% (71 mg); light yellow solid; mp: 110–111 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.38–8.22 (m, 3H), 7.53–7.36 (m, 4H), 7.19–7.08 (m, 1H), 7.04–6.95 (m, 1H), 6.89–6.79 (m, 1H), 6.72 (dd, J=7.0, 1.4 Hz, 1H), 2.39 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=150.0, 147.0, 137.8, 134.0, 133.6, 129.7, 128.6, 128.5, 128.4, 127.7, 127.5, 123.5, 116.2, 115.6, 108.3, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3054, 2928, 1658, 1558, 1456, 1345, 1056, 845, 779, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{15}N_2S$: 323.0671 $[M+H]^+$; found: 323.0673.

3-(Isopropylthio)-7-methyl-2-phenylimidazo[1,2-a]pyridine (5j) (New compound)

Yield: 58% (41 mg); yellow liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.46–8.29 (m, 3H), 7.52–7.34 (m, 4H), 6.72 (dd, J=7.0, 1.6 Hz, 1H), 3.13 (hept, J=6.7 Hz, 1H), 2.43 (s, 3H), 1.14 ppm (d, J=6.7 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=149.9, 146.9, 137.1, 134.3, 128.4, 128.3, 128.1, 123.8, 116.1, 115.2, 109.5, 40.8, 23.2, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3056, 2920, 1652, 1558, 1456, 1352, 1227, 1054, 848, 795, 669 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{19}N_2S$: 283.1263 $[M+H]^+$; found: 283.1259.

7-Methyl-2-phenyl-3-(propylthio)imidazo[1,2-a]pyridine (5k) (New compound)

Yield: 54% (38 mg); yellow liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 8.45–8.22 (m, 2H), 7.53–7.34 (m, 2H), 6.82–6.68 (m, 1H), 2.61 (t, J= 7.6 Hz, 1H), 2.44 (s, 3H), 1.55–1.37 (m, 2H), 0.88 ppm (t, J=7.3 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=149.4, 146.8, 137.1, 134.1, 128.4, 128.3, 128.1, 123.7, 116.2, 115.3, 109.7, 38.0, 23.1, 21.4, 13.3 ppm; IR (KBr): $\tilde{\nu}$=3057, 2924, 1652, 1558, 1456, 1340, 1228, 1054, 838, 797, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{19}N_2S$: 283.1263 $[M+H]^+$; found: 283.1266.

6-Methyl-2-phenyl-3-(phenylselanyl)imidazo[1,2-a]pyridine (8a) (New compound)

Yield: 87% (78 mg); yellow solid; mp: 109–111 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.18–8.08 (m, 3H), 7.61 (d, J=9.1 Hz, 1H), 7.46–7.33 (m, 3H), 7.19–7.05 (m, 6H), 2.28 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=151.7, 146.8, 133.9, 131.3, 129.7, 129.6, 128.7, 128.4, 128.3, 128.2, 128.1, 126.6, 123.3, 122.8, 116.9, 102.3, 18.4 ppm; HRMS (ESI): *m/z* calcd for $C_{20}H_{17}N_2Se$: 365.0552 $[M+H]^+$; found: 365.0556.

2-(4-Chlorophenyl)-7-methyl-3-(phenylselanyl)imidazo[1,2-a]pyridine (8c) (New compound)

Yield: 89% (88 mg); yellow solid; mp: 113–115 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.63–8.44 (m, 3H), 7.88 (s, 1H), 7.77 (d, J= 8.6 Hz, 2H), 7.67–7.50 (m, 3H), 7.40–7.32 (m, 2H), 7.09 (d, J= 7.0 Hz, 1H), 2.82 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=149.8, 147.3, 138.4, 135.1, 134.5, 131.8, 129.5, 128.6, 126.2, 125.6, 123.7, 116.1, 116.0, 105.8, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3069, 2912, 2669, 1644. 1558, 1458, 1346, 1091, 834, 736 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{16}N_2SeCl$: 399.0160 $[M+H]^+$; found: 399.0163.

2-(3-Bromophenyl)-7-methyl-3-(phenylselanyl)imidazo[1,2-a]pyridine (8d) (New compound)

Yield: 92% (102 mg); yellow solid; mp: 103–105 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.35–8.28 (m, 1H), 8.22 (d, J=7.0 Hz, 1H), 8.10 (dt, J=7.7, 1.2 Hz, 1H), 7.55–7.43 (m, 2H), 7.33–7.22 (m, 1H), 7.20–7.05 (m, 5H), 6.72 (dd, J=7.0, 1.6 Hz, 1H), 2.43 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=149.2, 147.6, 138.7, 135.4, 131.6, 131.5, 130.6, 129.9, 129.8, 128.5, 127.2, 127.0, 124.9, 122.5, 116.3, 115.9, 103.0, 21.5 ppm; IR (KBr): $\tilde{\nu}$=3049, 2905, 1652 1558, 1458, 1350, 1233, 1150, 1066, 732, 667 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{16}N_2SeCl$: 399.0160 $[M+H]^+$; found: 399.0163.

2-(3-Bromophenyl)-7-methyl-3-(phenylthio)imidazo[1,2-a]pyridine (8ad) (New compound)

Yield: 96% (95 mg); white solid; mp: 120–121 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.38 (s, 1H), 8.22–8.09 (m, 2H), 7.56–7.42 (m, 2H), 7.31–7.10 (m, 4H), 7.01–6.93 (m, 2H), 6.72 (d, J=7.0 Hz, 1H), 2.42 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=158.1, 148.6, 146.8, 138.9, 134.6, 131.5, 131.1, 129.9, 129.4, 126.7, 126.3, 125.7, 123.6, 122.5, 116.3, 115.9, 106.5, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3048, 2912, 1658, 1558, 1456, 1337, 1070, 848, 779, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{16}N_2SBr$: 397.0192 $[M+H]^+$; found: 397.0190.

2-(4-Methoxyphenyl)-7-methyl-3-(phenylselanyl)imidazo[1,2-a]pyridine (8e) (New compound)

Yield: 81% (79 mg); yellow solid; mp: 104–105 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.20–8.05 (m, 3H), 7.44 (s, 1H), 7.19–7.05 (m, 5H), 7.00–6.91 (m, 2H), 6.64 (dd, J=7.0, 1.6 Hz, 1H), 3.82 (s, 3H), 2.41 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=159.9, 151.6, 148.1, 137.5, 131.4, 130.0, 129.7, 128.1, 126.6, 124.7, 115.9, 115.4, 113.8, 101.1, 55.3, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3066, 2924, 1652, 1553, 1456, 1248, 1142, 1021, 872, 736, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{19}N_2SeO$: 395.0658 $[M+H]^+$; found: 395.0659.

2-(4-Methoxyphenyl)-7-methyl-3-(phenylthio)imidazo[1,2-a]pyridine (8ae) (New compound)

Yield: 80% (69 mg); white solid; mp: 110–109 °C ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.20–8.01 (m, 3H), 7.45 (s, 1H), 7.25–7.07 (m, 3H), 7.04–6.89 (m, 4H), 6.64 (d, J=6.9 Hz, 1H), 3.80 (s, 3H), 2.40 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=159.9, 151.2, 147.5, 137.8, 135.7, 129.6, 129.4, 126.1, 125.9, 125.4, 123.6, 116.0, 115.5, 113.8, 104.5, 55.3, 21.4 ppm; IR (KBr): $\tilde{\nu}$=3063, 2961, 1652, 1558, 1458, 1248, 1172, 1032, 840, 734, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{19}N_2SO$: 347.1213 $[M+H]^+$; found: 347.1217.

2-(4-Fluorophenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (8af) (New compound)

Yield: 92% (73 mg); white solid; mp: 125 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.00–7.83 (m, 3H), 7.46–7.35 (m, 1H), 7.09–6.77 (m, 6H), 6.74–6.65 (m, 2H), 6.61–6.51 ppm (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.1 (d, J_{C-F} = 248.4 Hz), 150.5, 147.1, 135.0, 130.2 (d, J_{C-F} = 8.1 Hz), 129.6, 129.5, 126.8, 126.2, 125.6, 124.5, 117.6, 115.4 (d, J_{C-F} = 21.5 Hz), 113.2, 106.1 ppm; IR (KBr): $\tilde{\nu}$ = 3040, 2935, 1650, 1539, 1456, 1397, 1264, 1154, 1075, 830, 732, 669 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{14}N_2SF$: 321.0856 $[M+H]^+$; found: 321.0854.

2-(4-Cyanophenyl)-3-(phenylselanyl)imidazo[1,2-a]pyridine (8g) (New compound)

Yield: 85% (79 mg); yellow solid mp: 97–98 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.44–8.25 (m, 3H), 7.78–7.62 (m, 3H), 7.41–7.30 (m, 1H), 7.24–7.05 (m, 4H), 6.90 ppm (t, J = 6.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.3, 147.9, 138.3, 132.1, 130.2, 129.9, 129.1, 128.3, 127.2, 127.1, 125.7, 119.0, 117.8, 113.6, 111.7, 104.3 ppm; IR (KBr): $\tilde{\nu}$ = 2962, 2924, 1655, 1558, 1459, 1340, 1265, 1070, 803, 742, 668 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{14}N_3Se$: 376.0348 $[M+H]^+$; found: 376.0352.

General Procedure for the iodine-catalyzed reactions of thiols 6 with 7-methyl-2-phenylimidazo[1,2-*a*]pyridine (1a)

A mixture of 7-methyl-2-phenylimidazo[1,2-*a*]pyridine **1a** (0.25 mmol, 52 mg) and the appropriate thiol **6** (0.25 mmol) were used under standard conditions.

General Procedure for the iodine-catalyzed reactions of arylsulfonyl hydrazides 7 with 7-methyl-2-phenylimidazo[1,2-*a*]pyridine (1a)

A mixture of 7-methyl-2-phenylimidazo[1,2-*a*]pyridine **1a** (0.25 mmol, 52 mg) and the appropriate arylsulfonyl hydrazide **7** (0.25 mmol) were used under standard conditions.

General Procedure for the iodine-catalyzed reactions of diaryl dichalcogenides 2 or 4 with *N*-heterocyclic core 9

A mixture of the appropriate *N*-heterocyclic core **9** (0.25 mmol), diorganyl dichalcogenide **2** or **4** (0.125 mmol), iodine (5 mol%, 3.2 mg), and DMSO (3 equiv, 0.75 mmol, 59 mg) were charged into a Schlenk tube. Indazole **9a**, 2-(4-methylphenyl)-1,3,4-oxadiazole **9b**, benzothiazole **9c**, benzoxazole **9d**, and benzimidazole **9e** were used as *N*-heterocyclic cores **9**. The reaction was heated to 90 °C in an oil bath for 9 h. After this, the reaction mixture was dissolved in ethyl acetate (10 mL) and washed with an aqueous solution of 10% $Na_2S_2O_3$ (2×5 mL). The organic layers were separated, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (hexane or hexane/ethyl acetate, 8:2).

3-(phenylselanyl)-1H-indazole (10a) (New compound)

Yield: 81% (54 mg); yellow solid; mp: 91–92 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 12.78 (s, 1H), 7.74–7.62 (m, 2H), 7.45–7.34 (m, 3H), 7.19–7.11 ppm (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.4, 133.3, 131.1, 130.8, 129.3, 127.4, 127.0, 126.4, 121.8, 121.1, 110.9 ppm; IR (KBr): $\tilde{\nu}$ = 3405, 3068, 3021, 1649, 1542, 1450, 1352, 1239, 1147, 1027, 846, 772, 680 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}N_2Se$: 275.0082 $[M+H]^+$; found: 275.0080.

3-((4-methoxyphenyl)selanyl)-1H-indazole (10b) (New compound)

Yield: 79% (60 mg); yellow solid; mp: 99–101 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 12.50 (s, 1H), 7.79–7.61 (m, 2H), 7.52–7.30 (m, 3H), 7.19–7.10 (m, 1H), 6.72 (d, J = 8.8 Hz, 2H), 3.70 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.3, 141.3, 134.4, 134.2, 127.3, 126.0, 121.5, 121.1, 120.0, 115.0, 110.8, 55.3 ppm; IR (KBr): $\tilde{\nu}$ = 3402, 3050, 3027, 2990, 1655, 1548, 1450, 1360, 1231, 1142, 1031, 846, 775, 678 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}N_2OSe$: 305.0186 $[M+H]^+$; found: 305.0193.

3-((4-chlorophenyl)selanyl)-1H-indazole (10c) (New compound)

Yield: 85% (65 mg); white solid; mp: 105–107 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 12.38 (s, 1H), 7.75–7.58 (m, 2H), 7.47–7.29 (m, 3H), 7.25–7.09 ppm (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.3, 133.2, 132.5, 129.5, 128.9, 127.6, 126.2, 122.0, 121.0, 110.8 ppm; IR (KBr): $\tilde{\nu}$ = 3400, 3062, 3020, 1645, 1548, 1455, 1357, 1234, 1147, 1026, 844, 770, 681 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{10}N_2ClSe$: 308.9690 $[M+H]^+$; found: 308.9691.

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[17] A controlled experiment has been performed under the optimized conditions with some modifications to trap the formed DMS. By using cannula needle, it was possible to collect the formed gas directly in an NMR tube (placed in ice-cold water) that contained $CDCl_3$. The captured DMS was analyzed by using NMR (see the Supporting Information, S71).

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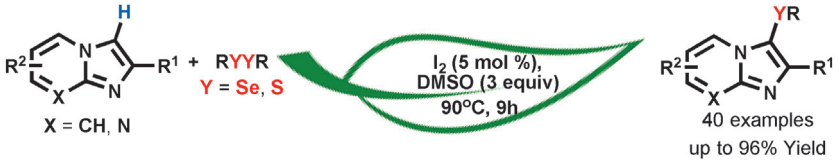

Regioselective, Solvent- and Metal-Free Chalcogenation of Imidazo[1,2-*a*]pyridines by Employing I_2/DMSO as Catalytic Oxidation System

Chalcogenation of *N*-heterocycles: Highly efficient molecular-iodine-catalyzed chalcogenations (S and Se) of imidazo[1,2-*a*]pyridines are achieved by using diorganoyl dichalcogenides under solvent-free conditions.