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Electrochemical Oxidative C–H Thiocyanation or Selenocyanation of Imidazopyridines and Arenes

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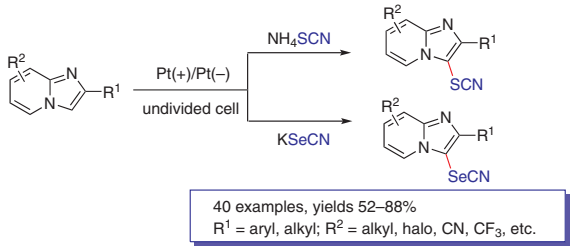

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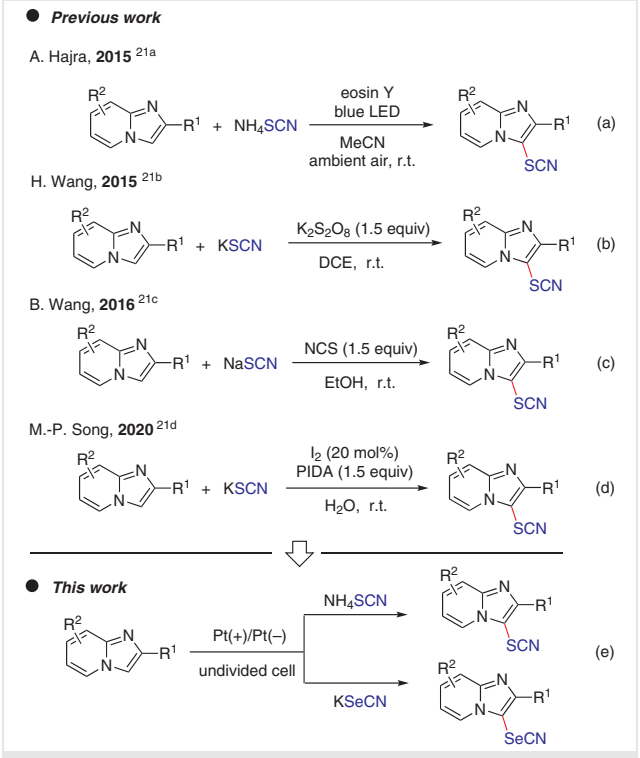
Abstract Regioselective electrochemical oxidative C–H thiocyanation or selenocyanation of imidazopyridines was achieved by using an undivided electrolytic cell. Transition-metal- and oxidant-free conditions are striking features of this protocol. A library of thiocyanated imidazopyridines with a broad range of functional groups were synthesized in high yields. This method was also applicable to the thiocyanation or selenocyanation of some electron-rich arenes.

Key words electrochemical oxidation, C–H functionalization, thiocyanation, selenocyanation, imidazopyridines, arenes

Organothiocyanates (RSCN) have been used as versatile synthetic precursors of sulfur-containing compounds, such as thiols,[1] thioethers,[2] vinyl sulfides,[3] disulfides,[4] phosphonothioates,[5] and sulfur-functionalized heterocycles.[6] SCN group-containing natural products, such as fasicularin and 9-thiocyanatopupukeanane have been isolated and their biological activities studied.[7] In addition, organothiocyanates are more stable than thiols and can serve as alternative precursors for gold thiolate assemblies in electrochemical analysis.[8] Consequently, increasing efforts have been devoted to developing new methods to introduce SCN groups onto organic molecules. A series of thiocyanating reagents,[9] including *N*-thiocyanatophthalimide,[10] *N*-thiocyanatosuccinimide,[11] *N*-thiocyanatosaccharin,[12] *N*-thiocyanatodibenzenesulfonimide,[13] aroyl isothiocyanates,[14] trimethylsilyl isothiocyanate,[15] and various thiocyanate salts (NH_4SCN, KSCN, NaSCN) have been used for this purpose. Among these reagents, the cheap and readily available thiocyanate salts have been favored in recent years.[16] However, many reactions of thiocyanate salts require the presence of stoichiometric oxidants [CAN,[17a] oxone,[17b] DDQ,[17c] $Mn(OAc)_3$,[17d] $K_2S_2O_8$,[17e,f] $(NH_4)_2S_2O_8$,[17g]] or other reagents (I_2,[18a] Selectfluor,[18b] NCS[18c]), in the generation of which waste is unavoidable. Therefore, the preparation of organothiocyanates by more environmentally friendly methods is still highly desirable.

Imidazo[1,2-*a*]pyridine is recognized as an important structural motif in medicinal chemistry,[19] and the structural modification of this heterocycle by C–H functionalization



Scheme 1 C–H thiocyanation reactions of imidazopyridines

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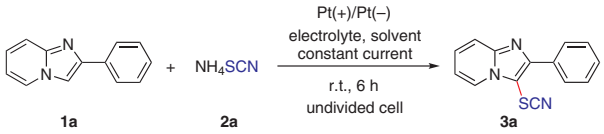
has received much attention in recent years.[20] The direct C–H thiocyanation of imidazo[1,2-*a*]pyridines has also been studied by several groups. In 2015, Hajra and co-workers developed a visible-light-induced C-3 thiocyanation of imidazo heterocycles with NH_4SCN under transition-metal-free conditions (Scheme 1a).[21a] Shortly after this work, an efficient method for this reaction was realized by Wang and co-workers using $K_2S_2O_8$ and KSCN (Scheme 1b).[21b] In 2016, the Wang group used a combination of NaSCN and NCS for the C-3 thiocyanation of imidazo heterocycles (Scheme 1c).[21c] More recently, Song and co-workers accomplished C–H thiocyanation and selenocyanation of imidazo heterocycles with I_2 and iodobenzene diacetate (PIDA) in aqueous media (Scheme 1d).[21d]

Electrochemical oxidation is a powerful and straightforward method in organic synthesis, because it provides access to C–H-functionalized products without the use of oxidants or other additives.[22] In 2019, Lei and co-workers demonstrated the feasibility of electrochemically induced C–H amination,[23a] phosphonylation,[23b] sulfenylation,[23c] and halogenation[23d] of imidazo heterocycles. In 2020, Yang, Wang, and co-workers successfully achieved C-3 thiomethylation of imidazopyridines by a three-component reaction under electrochemical conditions.[23e] For electrochemical C–H selenylation of imidazopyridines, two reports have been published by the groups of Kim and Xu.[23f,g] Recently, electrochemical oxidative C–H thiocyanations of ketones[24a] and of ketene dithioacetals[24b] were also reported by the Zeng and Wang groups, respectively. As part of our continuing efforts to develop new methods for the functionalization of imidazopyridines,[25] we describe electrochemical oxidative C–H thiocyanations or selenocyanations of imidazopyridines or electron-rich arenes (Scheme 1e).

We began our investigation by using 2-phenylimidazo[1,2-*a*]pyridine (**1a**; 0.2 mmol) as a model substrate and NH_4SCN (0.4 mmol, 2 equiv) as a thiocyanating agent in MeCN (Table 1). Initially, the electrolysis was conducted at a constant current (5 mA) in an undivided cell equipped with a platinum plate anode and cathode, and containing Bu_4NPF_6 (0.05 M) as an electrolyte under air. Gratifyingly, the desired product 2-phenylimidazo[1,2-*a*]pyridin-3-yl thiocyanate (**3a**) was obtained in 89% yield after six hours (Table 1, entry 1). Encouraged by this result, we conducted extensive investigations of the reaction conditions. The electrode materials were important for this transformation. Reactions carried out with a carbon rod as the anode or cathode were less efficient, affording the product **3a** in lower yields (60 and 54%; respectively) (entries 2 and 3). Replacement of the platinum plate cathode with a Ni or Fe electrode with a comparable surface area also gave inferior results (entries 4 and 5). The reaction did not proceed in the absence of an electric current (entry 6). The supporting electrolyte had an obvious influence on the reaction outcome. Replacement of Bu_4NPF_6 by Bu_4NBF_4 or $LiClO_4$ brought lower yields (entries 7 and 8). Further evaluations of 4:1 mixtures of MeCN with MeOH, DMF, or CH_2Cl_2 (10 mL) as solvents showed that pure MeCN was optimal (entries 1 and 9–11). Increasing the amount of NH_4SCN to five equivalents did not significantly raise the yield of **3a** (entry 12). Replacing NH_4SCN with KSCN slightly reduced the yield of **3a** (80%) (entry 13). In addition, when the reaction was performed under an Ar atmosphere, **3a** was obtained in a similar yield (82%) (entry 14).

Table 1 Optimization of the Reaction Conditions[a]



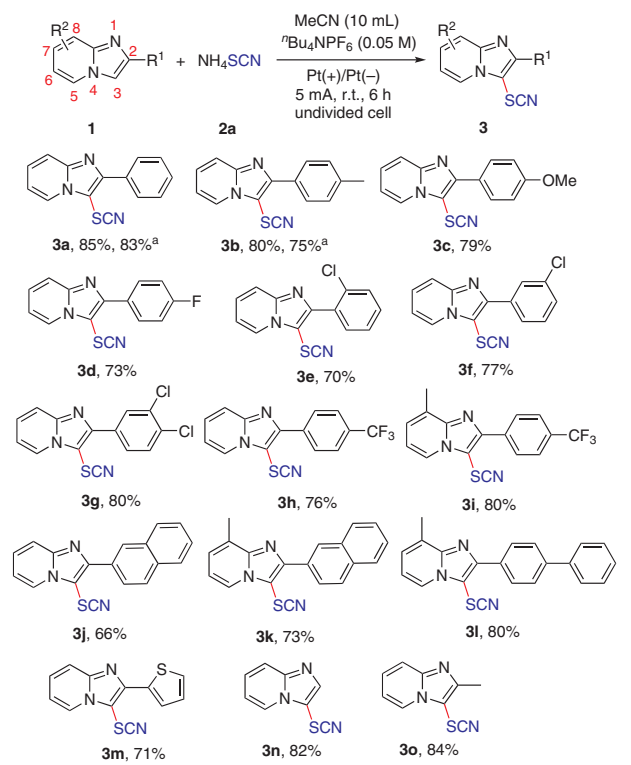
1a 2a 3a

Entry	Anode/Cathode	Solvent	Electrolyte	Yield[b] (%)
1	Pt(+)/Pt(–)	MeCN	Bu_4NPF_6	89
2	C(+)/Pt(–)	MeCN	Bu_4NPF_6	60
3	Pt(+)/C(–)	MeCN	Bu_4NPF_6	54
4	Pt(+)/Ni(–)	MeCN	Bu_4NPF_6	70
5	Pt(+)/Fe(–)	MeCN	Bu_4NPF_6	40
6[c]	Pt(+)/Pt(–)	MeCN	Bu_4NPF_6	0
7	Pt(+)/Pt(–)	MeCN	Bu_4NBF_4	78
8	Pt(+)/Pt(–)	MeCN	$LiClO_4$	60
9	Pt(+)/Pt(–)	MeCN–MeOH (4:1)	Bu_4NPF_6	80
10	Pt(+)/Pt(–)	MeCN–DMF (4:1)	Bu_4NPF_6	81
11	Pt(+)/Pt(–)	MeCN–DCM (4:1)	Bu_4NPF_6	70
12[d]	Pt(+)/Pt(–)	MeCN	Bu_4NPF_6	90
13[e]	Pt(+)/Pt(–)	MeCN	Bu_4NPF_6	80
14[f]	Pt(+)/Pt(–)	MeCN	Bu_4NPF_6	82

[a] Reaction conditions: Anode (10 × 10 mm), cathode (10 × 10 mm), constant current (5.0 mA), **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv), supporting electrolyte (0.05 M), MeCN (10 mL), under air, r.t., 6 h, undivided cell.
[b] Isolated yields based on **1a**.
[c] No electric current.
[d] NH_4SCN (1.0 mmol, 5 equiv).
[e] KSCN (0.4 mmol, 2.0 equiv).
[f] Under Ar.

With the optimized conditions in hand, we investigated the substrate scope and limitations of the C–H thiocyanation of imidazopyridines to study the generality of this method. Gratifyingly, a wide range of imidazo[1,2-*a*]pyridines were suitable for this transformation (Scheme 2). We first explored the effects of substituents on the C-2 position of the imidazo[1,2-*a*]pyridine. For 2-phenylimidazo[1,2-*a*]pyridines, an electron-donating methyl or methoxy group on the *para*-position of the benzene ring was well tolerated in the reaction, and the C-3 thiocyanated products **3b** and **3c** were produced in good yields (80 and 79%, respectively). The presence of electron-withdrawing substituents such as F, Cl, or CF_3 also had no obvious effect to the reaction, and satisfactory yields of 70–80% were obtained (**3d–i**). The re-

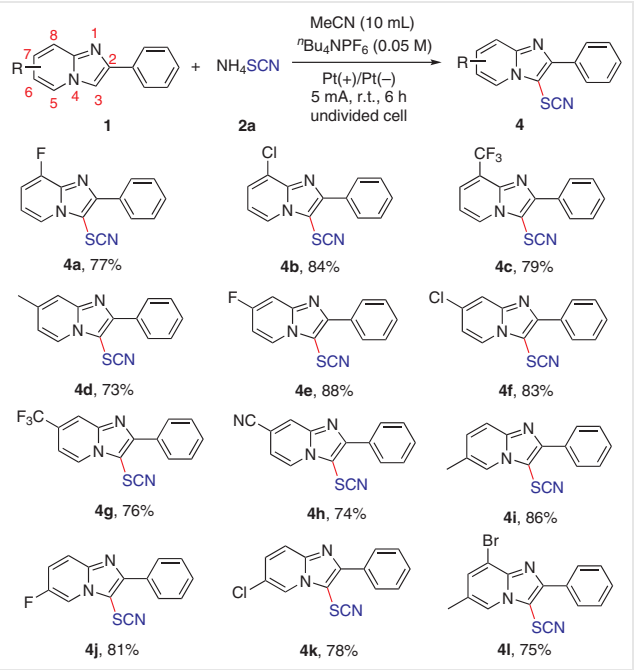
actions of imidazo[1,2-*a*]pyridines substituted with 2-naphthyl, biphenyl-4-yl-, and 2-thienyl groups proceeded well and gave the corresponding products **3j–m** in yields of 66–80%. Furthermore, unsubstituted imidazo[1,2-*a*]pyridine (**1n**) and 2-methylimidazo[1,2-*a*]pyridine (**1o**) were found to be suitable substrates, delivering the C-3 thiocyanated products **3n** and **3o**, respectively, in yields of 82 and 84%. In addition, for the reactants **1a** and **1b**, a chemical oxidation method[21d] gave comparable yields of 83 and 75%, respectively.



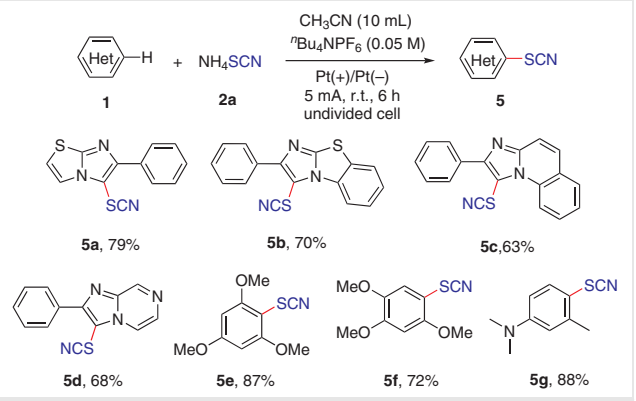
Scheme 2 Substrate scope of imidazopyridines. *Reagents and conditions*: platinum plate anode (10 × 10 mm), platinum plate cathode (10 × 10 mm), constant current (5 mA), Bu_4NPF_6 (0.05 M), **1** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), MeCN (10 mL), air, r.t., 6 h, undivided cell. [a] **1** (0.2 mmol), KSCN (0.3 mmol, 1.5 equiv), I_2 (20 mol%), PIDA (0.3 mmol, 1.5 equiv), H_2O (1 mL), air, r.t., 12 h.

Next, we turned our attention to imidazopyridines bearing substituents on the pyridine ring. Electronic effects of substituents on the pyridine ring had no obvious influence on the reaction outcome. As shown in Scheme 3, electron-donating (R = Me) or electron-withdrawing (R = F, Cl, Br, CF_3, CN) functional groups were well tolerated, providing the corresponding products **4a–l** in good yields (73–88%).

The present protocol was also applicable to some other imidazopyridines (Scheme 4). As expected, a similar process occurred with 4-phenylimidazo[2,1-*b*]thiazole and 2-phenylimidazo[2,1-*b*][1,3]benzothiazole, providing the desired products **5a** and **5b** in yields of 79 and 70%, respectively. The fused azaheterocycles imidazo[1,2-*a*]quinoline and imidazo[1,2-*a*]pyrazine were also found to be suitable substrates and gave the corresponding thiocyanated products **5c** and **5d** in yields of 63 and 68%, respectively. Although the thiocyanation of electron-rich arenes by electrochemical synthesis has been reported previously,[26] we wondered whether these substrates were suitable for our conditions. The results showed that arenes substituted with



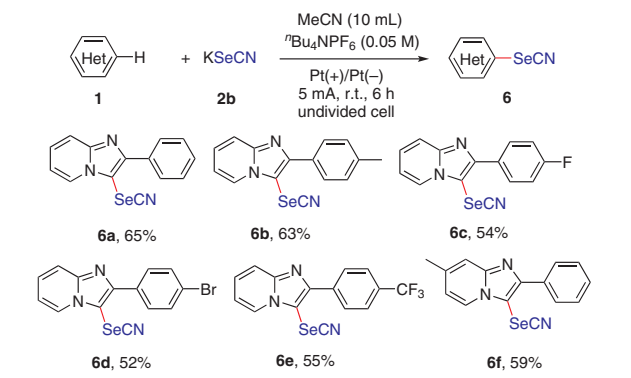
Scheme 3 Substrate scope of imidazopyridines. *Reagents and conditions*: platinum plate anode (10 × 10 mm), platinum plate cathode (10 × 10 mm), constant current (5 mA), Bu_4NPF_6 (0.05 M), **1** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), MeCN (10 mL), air, r.t., 6 h, undivided cell.



Scheme 4 Substrate scope of other imidazopyridines and arenes. *Reagents and conditions*: platinum plate anode (10 × 10 mm), platinum plate cathode (10 × 10 mm), constant current (5 mA), Bu_4NPF_6 (0.05 M), **1** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), MeCN (10 mL), air, r.t., 6 h, undivided cell.

strongly electron-donating groups, including 1,3,5-trimethoxybenzene, 1,3,4-trimethoxybenzene, and *N*,*N*,3-trimethylaniline, underwent electrochemical oxidative cross-coupling with NH_4SCN to give the corresponding products **5e–g** in high yields of 87, 72, and 88%, respectively.

Encouraged by the feasibility of electrochemical oxidative C–H thiocyanation, we further explored the C–H selenocyanation of imidazopyridines (Scheme 5). To our delight, various 2-phenylimidazo[1,2-*a*]pyridines reacted smoothly with KSeCN under the standard conditions to give the 3-selenocyanated products **6a–f** in acceptable yields (52–65%). The presence of methyl, halo (F or Br), or trifluoromethyl substituents on the benzene ring had no significant effect on the reaction.

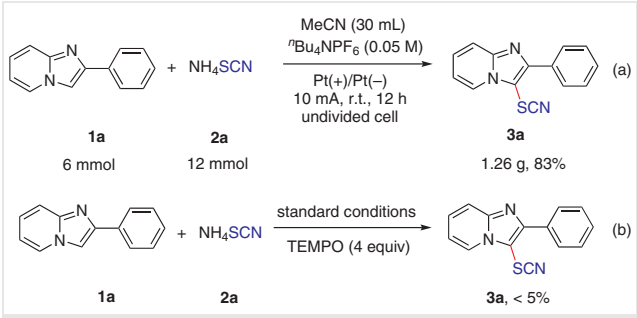


Scheme 5 Substrate scope for electrochemical oxidative C–H selenocyanation of imidazopyridines. *Reagents and conditions*: platinum plate anode (10 × 10 mm), platinum plate cathode (10 × 10 mm), constant current (5 mA), Bu_4NPF_6 (0.05 M), **1** (0.2 mmol), **2b** (0.4 mmol, 2 equiv), MeCN (10 mL), air, r.t., 6 h, undivided cell.

In addition, the reaction could be easily scaled up without the loss of reactivity (Scheme 6a). When the reaction was conducted with 6 mmol of **1a** and 12 mmol of **2a** by increasing the current to 10 mA and prolonging the reaction time to 12 hours, the thiocyanated product **3a** was obtained in 83% yield (5.0 mmol, 1.26 g). To investigate the mechanism, a control experiment was conducted involving the addition of the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO; 4 equiv) to the model reaction. The reaction was obviously suppressed, indicating that the reaction possibly proceeds by a radical pathway (Scheme 6b).

Next, cyclic voltammetry (CV) experiments were carried out to study the redox potential of the substrates (Figure 1). NH_4SCN (**2a**) had a lower oxidation potential (1.30 V vs. SCE) than 2-phenylimidazo[1,2-*a*]pyridine (**1a**, 1.70 V vs. SCE) in MeCN, indicating that the oxidation of NH_4SCN occurred prior to that of the imidazopyridine **1a** under the electrochemical reaction conditions.

Based on the above mechanistic studies and previous reports in the literature,[21,24b] we proposed a radical mechanism initiated by an electrochemical oxidation (Scheme 7).



Scheme 6 Gram-scale reaction and control experiment

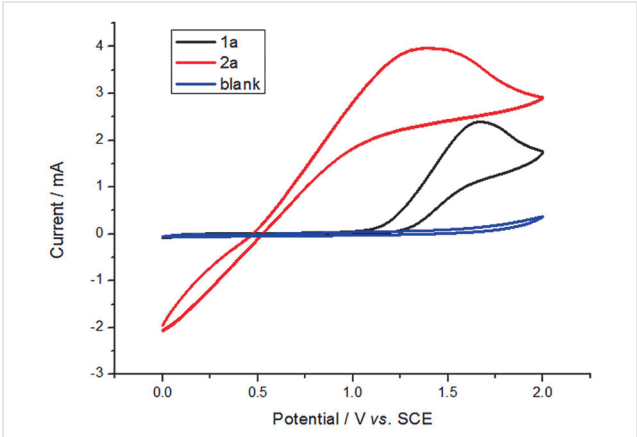
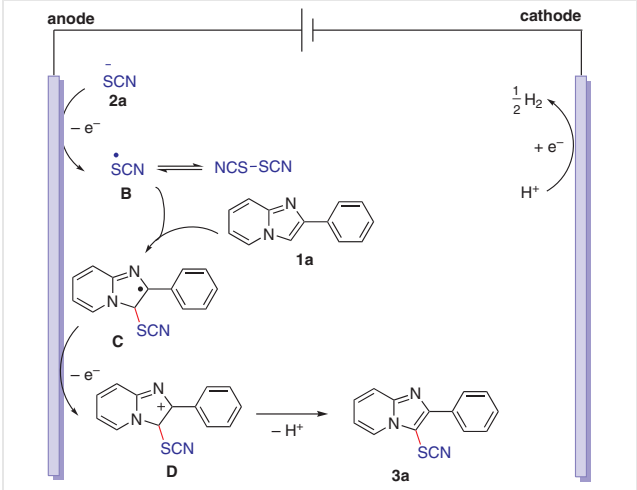


Figure 1 CV scans (scan rate: 100 mV·s^{-1}) of substrate **1a** (0.01 M) or **2a** (0.01 M) in MeCN containing Bu_4NPF_6 (0.02 M) at a platinum-wire electrode under air

First, a thiocyanate radical intermediate **B** is formed by anodic oxidation of the thiocyanate anion.[24b] Radical **B** is trapped by imidazopyridine **1a** to produce the radical intermediate **C**,[21] which is oxidized at the anode by single-elec-



Scheme 7 Proposed mechanism

tron transfer to form the cation intermediate **D**. Finally, deprotonation of cation **D** gives the desired product **3a**.

In summary, we have developed a protocol for the electrochemical oxidative C–H thiocyanation or selenocyanation of imidazopyridines and electron-rich arenes.[27] Cheap and readily available NH_4SCN and KSeCN are used as sources of SCN and SeCN, respectively. A broad scope of substrates and a variety of functional groups are well tolerated to give the thiocyanated or selenocyanated products in moderate to excellent yields. This convenient method for the synthesis of thiocyanated imidazopyridines might be applicable in the field of pharmaceutical synthesis.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-1299-3009.

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(27) **2-Phenylimidazo[1,2-*a*]pyridin-3-yl Thiocyanate (3a):[21a] Typical Procedure**

An undivided 25 mL three-necked flask was charged with 2-phenylimidazo[1,2-*a*]pyridine (**1a**, 38.8 mg, 0.2 mmol), NH_4SCN (**2a**, 30.5 mg, 0.4 mmol, 2 equiv), Bu_4NPF_6 (194 mg, 0.5 mmol, 2.5 equiv), and MeCN (10 mL). The flask was equipped with two platinum plate electrodes (10 × 10 mm) as the anode and cathode, respectively. The reaction mixture was electrolyzed and stirred at a constant current (5 mA) under air at r.t. for 6 h. When the reaction was complete, the mixture was diluted with H_2O (30 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated in vacuo. The resulting crude product was purified by chromatography [silica gel, PE–EtOAc (5:1)] to give a white solid; yield: 42.7 mg (85%); mp 115–117 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 6.6 Hz, 1 H), 8.08 (d, *J* = 7.3 Hz, 2 H), 7.80 (d, *J* = 8.9 Hz, 1 H), 7.58–7.48 (m, 4 H), 7.16 (t, *J* = 6.7 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 147.9, 131.9, 129.5, 128.8, 128.8, 128.1, 124.4, 118.3, 114.5, 108.2, 94.7.