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Metal-Free Regioselective Direct Thiolation of 2-Pyridones

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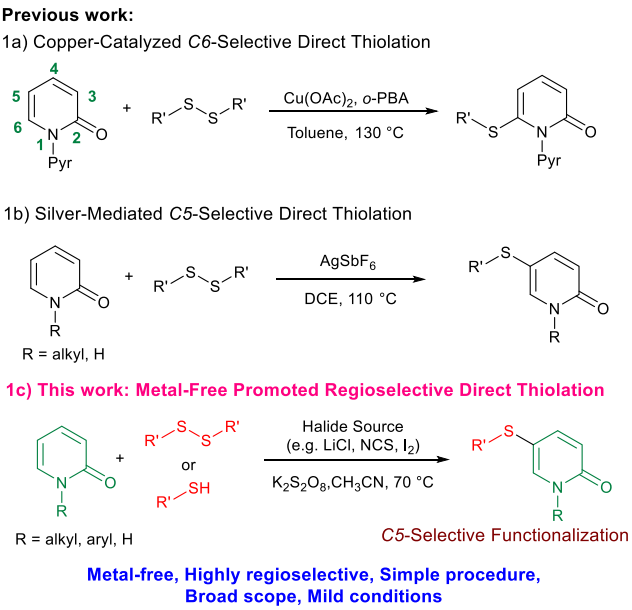
A highly regioselective metal-free direct C–H thiolation of 2-pyridones with disulfides or thiols has been developed. A combination of persulfate and a commercially available halide source such as LiCl, NCS or I_2 enables the successful direct incorporation of a sulfide moiety into the 5-position of pyridone under mild conditions, providing a useful and convenient approach for the preparation of a diverse array of 5-thio-substituted pyridones in moderate to excellent yields.

Introduction

Carbon–sulfur (C–S) bonds are widely distributed in a large number of naturally occurring compounds, bioactive molecules, pharmaceutical agents, and functional materials.[1] The thio-substituted scaffolds are also important building blocks in organic synthesis, material science, coordination chemistry and pharmaceutical research.[2] As the incorporation of sulfur moieties into organic molecules can partially modify the physical and biological properties of the molecules,[3] there has been a great effort to develop new and efficient methods for the construction of C–S bonds in the past few decades,[4] for instance, metal-catalyzed cross C–S bond coupling reactions,[5] nucleophilic addition reactions,[6] and electrophilic sulfenylation reactions.[7] These findings become highly efficient tools and have a great benefit to chemists and other researchers in both academia and industry.

Pyridone is considered as one of the privileged heteroaromatic skeletons found in several natural products, bioactive molecules, and pharmaceutical agents.[8] 2-Pyridones, in particular, exhibit remarkably interesting physical properties and chemical reactivities due to the presence of the amide group as well as the conjugated enone-like structure.[9] Many compounds in this class often display promising biological and pharmacological applications, such as antifungal, antibacterial, antiepileptic, and antitumor activities.[10] Therefore, the development of synthetic methods to rapidly access pyridones bearing substituents at specific positions is of great interest to synthetic, medicinal chemistry and other related research areas. To date, numerous synthetic methodologies have been developed for the above purpose. Among those strategies, direct carbon–hydrogen (C–H) bond functionalization,[11] which emerged as one of the most efficient transformations in modern synthetic chemistry as it bypasses the requirement for substrate prefunctionalization, has been mainly employed to manipulate 2-pyridone cores, particularly for the site-selective direct C–C bond coupling.[12] On the other hand, only a few examples exist in the literature for the regioselective direct carbon–heteroatom bond formation.[13] To date, the direct C–H thiolation of 2-pyridones has been disclosed by Jiang and Liu in 2016.[14] Under a catalytic amount of $Cu(OAc)_2$ and *o*-PBA, a successful direct *C6*-thiolation with disulfides was reported (Scheme 1a). In addition, Zhu and co-workers recently discovered a silver-mediated *C5*-selective thiolation of 2-pyridones and other related bicyclic compounds (Scheme 1b).[15]



Scheme 1 Direct C–H Thiolation 2-Pyridones.

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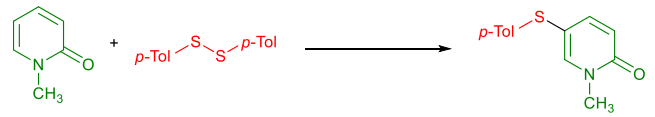
Based on our research interests in the oxidative C–H bond functionalization strategies to manipulate various *N*-containing compounds,[16] we recently reported useful and convenient protocols for direct C–H thiolation of *N*-heterocycles such as pyrazolones[17] and uracils[18] with disulfides as sulfur precursors. Herein, we report a straightforward approach for a highly regioselective direct C–H thiolation of 2-pyridones with disulfide or thiol precursors under metal-free conditions (Scheme 1c). This present strategy offers an alternative and expedient method for the direct installation of sulfur moiety into the *C5* position of pyridone substrates, resulting in 5-thiosubstituted derivatives in moderate to excellent yields under relatively mild conditions.

Results and discussion

We initiated our studies on a metal-free direct thiolation of 2-pyridones by examining a reaction between *N*-methyl-2-pyridone (**1a**) and *p*-tolyl disulfide (**2a**) under various conditions. To our delight, when employing molecular iodine (I_2) and potassium persulfate ($K_2S_2O_8$) in CH_3CN, a 5-thio-substituted product **3a** was obtained in 75% (Table 1, entry 1). No other regioisomers were observed. Meanwhile, testing reactions in other solvents resulted in much lower yields or no reaction (entries 2–5). Further screening of reaction conditions revealed that a halogen source played a role in this reaction, and lithium chloride (LiCl) and *N*-chlorosuccinimide (NCS) were found to be suitable in this transformation (entries 6–13). Noteworthy, 0.5 equivalent of LiCl or NCS was sufficient to give a very high quantity of the desired product (entries 14 and 15). Nonetheless, other persulfate oxidants (entries 16–17), as well as a change in reaction temperature, led to a decrease in yield. Lastly, only a trace amount or no reaction was observed in the absence of persulfate or halogen source (entries 18 and 19), which indicated a necessity of both reagents in this transformation.

Next, we surveyed a substrate scope of the metal-free direct thiolation of 2-pyridones under the established reaction conditions (LiCl or NCS 0.5 equiv., $K_2S_2O_8$ 3 equiv. in CH_3CN at 70 °C). In general, this method can accommodate a variety of *N*-protected pyridones and *NH*-pyridones, furnishing the corresponding 5-thio-substituted products in moderate to excellent yields. As illustrated in Table 3, many *N*-alkylated pyridone substrates can undergo direct thiolation smoothly with *p*-tolyldisulfide (**2a**), giving good quantities of products (**3a–3e**). The reaction of 2-pyridone (2-hydroxypyridine) also proceeded smoothly giving the desired product (**3f**) in a satisfactory amount. Other regioisomers or side reactions due to the presence of the *NH* group were not observed. Remarkably, the *N*-2-ethoxy-2-oxoethyl pyridone with an ester functionality was compatible and afforded the product **3g** in gratifying quantity. We also tested the reactions with *N*-arylated

Table 1 Optimization of Reaction Conditions[a]

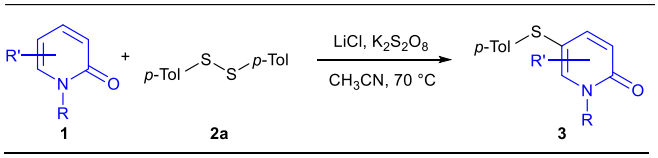


1a 2a 3a

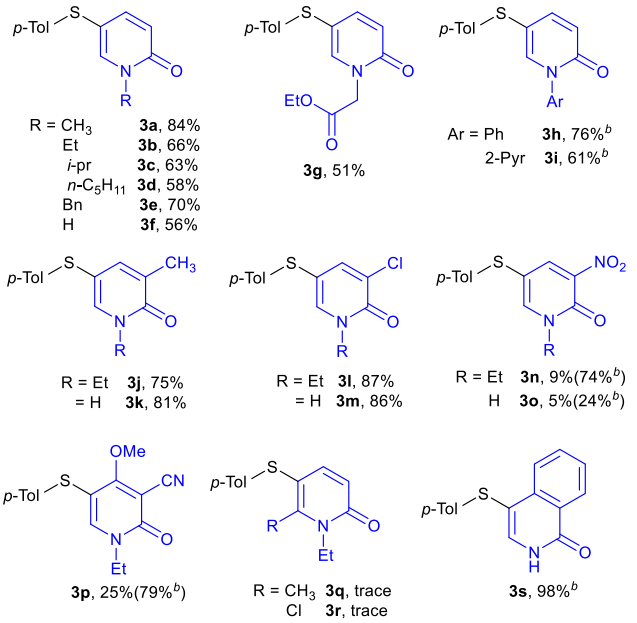
Entry	Reagent(equiv.)	Oxidant	Solvent	Yield(%)[b]
1	I_2 (1)	$K_2S_2O_8$	CH_3CN	75
2	I_2 (1)	$K_2S_2O_8$	Toluene	29
3	I_2 (1)	$K_2S_2O_8$	DMSO	2
4	I_2 (1)	$K_2S_2O_8$	MeOH	trace
5	I_2 (1)	$K_2S_2O_8$	H_2O	no reaction
6	$(^nBu)_4NI$ (1)	$K_2S_2O_8$	CH_3CN	30
7	KI (1)	$K_2S_2O_8$	CH_3CN	25
8	LiI (1)	$K_2S_2O_8$	CH_3CN	56
9	KBr (1)	$K_2S_2O_8$	CH_3CN	49
10	LiCl (1)	$K_2S_2O_8$	CH_3CN	78
11	NIS (1)	$K_2S_2O_8$	CH_3CN	64
12	NBS (1)	$K_2S_2O_8$	CH_3CN	39
13	NCS (1)	$K_2S_2O_8$	CH_3CN	80
14	NCS (0.5)	$K_2S_2O_8$	CH_3CN	82
15	LiCl (0.5)	$K_2S_2O_8$	CH_3CN	84(84[c])
16	LiCl (0.5)	$Na_2S_2O_8$	CH_3CN	30
17	LiCl (0.5)	$(NH_4)_2S_2O_8$	CH_3CN	31
18	LiCl (0.5)	-	CH_3CN	trace
19	-	$K_2S_2O_8$	CH_3CN	no reaction

[a] Conditions: pyridone **1a** (0.25 mmol, 1 equiv.), di-*p*-tolyl-disulfide **2a** (0.375 mmol, 1.5 equiv.), oxidant (0.75 mmol, 3 equiv.), solvent (0.5 mL), 70 °C, 16 h, under air atmosphere. [b] GC yield. [c] Isolated yield.

Table 2 Substrate Scope of 2-Pyridones[a]



1 2a 3



[a] Conditions: pyridone **1** (1 mmol, 1 equiv.), di-*p*-tolyl-disulfide **2a** (1.5 mmol, 1.5 equiv.), LiCl (0.5 mmol, 0.5 equiv.), $K_2S_2O_8$ (3 mmol, 3 equiv.), CH_3CN (2 ml), 70 °C, under air, 16–24 h as monitored by TLC. Isolated yields after chromatography purification. [b] Using NCS instead of LiCl.

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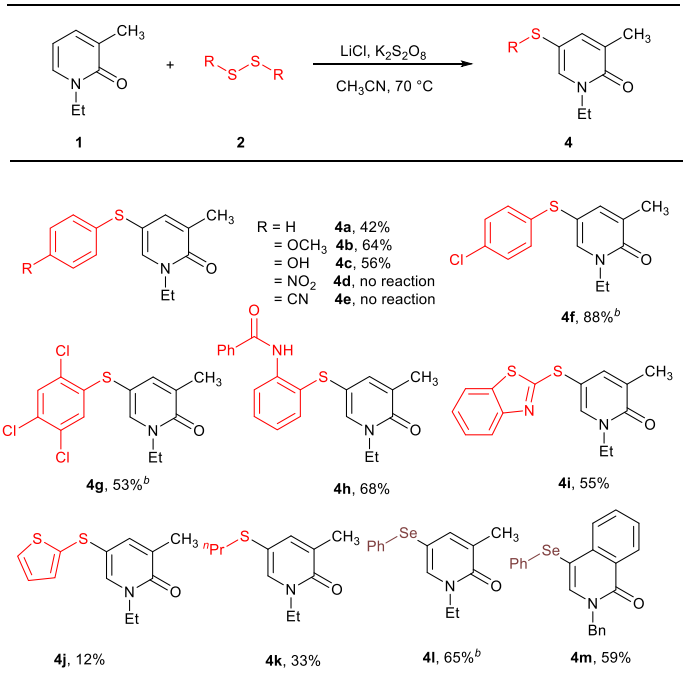
pyridones such as *N*-phenyl or *N*-pyridyl substrates (**3h** and **3i**), and we found that they underwent smooth transformations although using NCS as a halide source appeared to have somewhat better results than using LiCl. The effect of substituents on carbon atoms of pyridone rings was investigated, and the results revealed that both electronic and steric effects have an impact on the efficiency of the transformation. In the case of electron rich group or halogen substitution at *C3* position, very high yields of 5-thiosubstituted products were obtained (**3j**–**3m**). However, for the substrates with an electron withdrawing group such as NO_2 or cyano groups, significantly lower yields of products were isolated (**3n**–**3p**). The conversions to these products could be improved by using NCS instead of LiCl. Nonetheless, the pyridone substrates bearing substituents at *C6* position were incompatible with the thiolation reaction (**3q** and **3r**). These outcomes suggested that steric encumbrance at the *6* position could possibly impede the transformation. Interestingly, the carbostyril (2-quinolone), which is an important structural constituent frequently found in natural products, drugs and physiologically active substances, was found to exhibit a very good reactivity towards the direct thiolation, producing the excellent quantity of the product (**3s**).

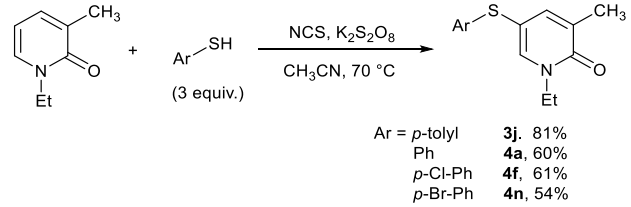
We also explored the effect of disulfide substrates toward the direct C–S bond construction, and results are shown in Table 3. A range of disulfides were viable in this metal-free direct thiolation reaction, providing fair to good yields of 5-thio-substituted pyridone compounds. Reactions of phenyl and electron rich arene disulfides proceeded without difficulty, affording products **4a** and **4b** in reasonable amounts. Surprisingly, the hydroxyl moiety was tolerated under the established conditions (**4c**). However, no reaction was detected in the case of diaryl disulfides bearing strong electron withdrawing groups (such as 4-nitro or 4-cyanophenyl disulfides, **4d** and **4e**), suggesting that the electronic contribution from disulfides is crucial for the efficiency of the transformation. Meanwhile, phenyl disulfide substrates with chloro substitutions were compatible, giving corresponding products, **4f** and **4g**, in good yields.[19] The direct thiolation reaction was also applicable to aryl disulfide bearing amide (CO-NH) functionality (**4h**). In addition, we examined the reactions with heteroaryl and dialkyl disulfides, unfortunately, only fair to modest yields of the corresponding 5-thiosubstituted products were obtained (**4i**–**4k**). These outcomes suggested that the sulfur species from heteroaryl or alkyl disulfides are somewhat less stable than those sulfur species from the diaryl disulfide sources. Finally, we further tested the reactions with diphenyl diselenide under the established conditions and the direct selenylation could be achieved in good yields (**4l** and **4m**).[19]

Apart from disulfides, the optimized reaction systems also proved applicable to arene thiols in the direct C–H thiolation. Comparable yields of *C5*-thiolated products were obtained in all cases (Scheme 2).[20]

Table 3 Scope of disulfides[a]



[a] Conditions: pyridone **1** (1 mmol, 1 equiv.), disulfide **2** (1.5 mmol, 1.5 equiv.), LiCl (0.50 mmol, 0.5 equiv.), $K_2S_2O_8$ (3 mmol, 3 equiv.), CH_3CN (2 ml), 70 °C, under air, 16–24 h as monitored by TLC. Isolated yields after chromatography purification. [b]Using I_2 instead of LiCl.



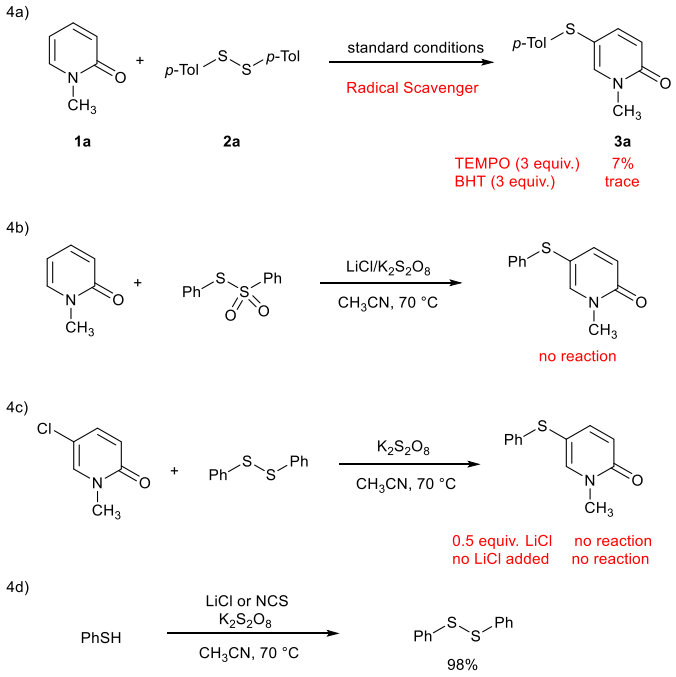
Scheme 2 Direct Thiolation with Arene Thiols.

To test the practicality of the developed method, we conducted a gram scale reaction (10 mmol scale) under the optimal conditions and the pyridone products could be obtained with similar efficacy to small scale reactions (Scheme 3), suggesting a possibility of industrialized synthesis and potential utilization of this synthetic approach.

Scheme 3 Gram-Scale Reactions.

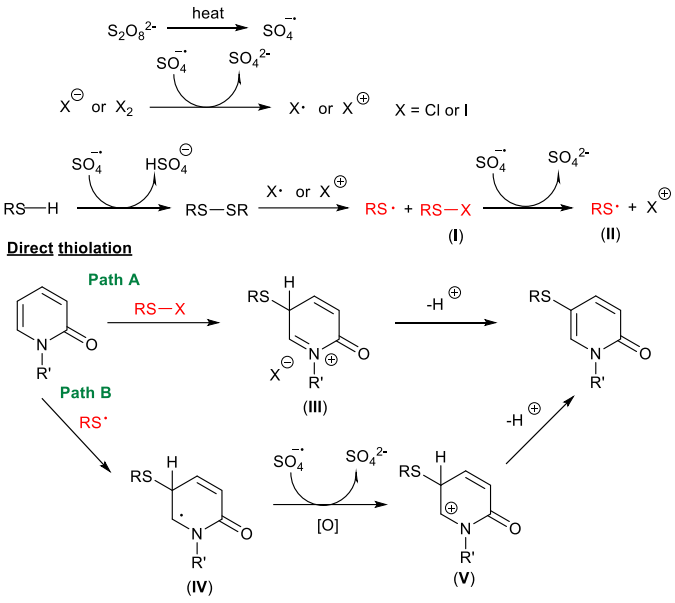
To gain insight into the reaction mechanism, we conducted some control experiments as shown in Scheme 4.[21] When a radical scavenger (such as TEMPO and BHT) was employed in the reaction, the direct thiolation was suppressed (Scheme 4a), suggesting that the reaction possibly involves a radical or single

electron transfer process. Given the possibility that aryl disulfides might be oxidized to thiosulfonate prior to reacting with pyridone substrate in the reaction, we subjected thiosulfonate to test the reactions under standard conditions, nonetheless, no product was obtained. Thus, this particular sulfur species might not be formed in the reaction (Scheme 4b). In addition, no reaction occurred when replacing 2-pyridone with 5-chloro 1-methylpyridone (Scheme 4c), indicating that this transformation takes place solely at the 5-position, and the 5-chloropyridone is not a likely intermediate in this reaction. Nevertheless, we found that the thiol precursor can be converted to a disulfide compound under the standard conditions (Scheme 4d).[22]



Scheme 4 Control Experiments.

Based on these preliminary mechanistic studies and relevant reports,[15,23] we proposed a reaction mechanism as depicted in Scheme 5. This transformation presumably involves an initial reaction of halide or halogen source with persulfate ($S_2O_8^{2-}$) or $SO_4^{\bullet-}$ to form an electrophilic halogen (X^+) or halogen radical ($X^\bullet$) species.[24] Next, the reaction of disulfide or thiol with these reactive halogen species would produce intermediate **I** (RS–X) or intermediate **II** ($RS^\bullet$).[25] Then, the corresponding 5-thiosubstituted product can be generated from two possible paths. In pathway A, pyridone substrate can directly react with RS–X (intermediate **I**), leading to a formation of iminium intermediate **III**. Finally, the final product can be obtained upon losing a proton. In pathway B, the $RS^\bullet$ (radical intermediate **II**) is captured by pyridone substrate to form the radical intermediate **IV**, which can be further oxidized by sulfate radical anion *via* a SET process to form cationic intermediate **V**. A subsequent elimination of a proton would furnish the final product. Considering the supportive evidence from the control studies, the latter pathway is more likely to proceed than the former. However, we still could not rule out the possibility of pathway **A** at this moment.



Scheme 5 Tentative Reaction Mechanism.

Conclusions

In summary, the metal-free approach for a highly regioselective direct C–H thiolation of 2-pyridones at the *C5* position with aromatic disulfides or arene thiols has been successfully accomplished. A combination of a simple halogen source such as LiCl, NCS or I_2, and $K_2S_2O_8$ enables the C–S bond formation to proceed smoothly, providing an effective and convenient method to access a series of 5-thiosubstituted pyridones in moderated to excellent quantities under relatively mild and easy-to-operate conditions. This method should find practical applications in the diversification of pyridones and other related nitrogen-containing compounds. Further mechanistic investigations, expansion of the synthetic application, and utilization of such compounds in organic synthesis and biological studies are currently ongoing in our laboratory.

Experimental section

General Information

Unless otherwise noted, all reagents were used as received from commercial suppliers. All experiments were carried out under air atmosphere, and oven-dried glasswares were used in all cases. Column chromatography was performed over silica gel (SiO_2; 60Å silica gel, 70–230 Mesh). GC experiments were carried out with a GC-FID on chromatograph equipped with HP-1 polydimethylsiloxane column (30.0 m × 0.25 mm ID × 0.25 µm). ^1H and ^{13}C NMR spectra

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were recorded on a Bruker-AV400 spectrometers in $CDCl_3$ or DMSO-d_6 solution, at 400 and 100 MHz, respectively. NMR chemical shifts are reported in ppm, and were measured relative to $CHCl_3$ (7.26 ppm for ^1H and 77.16 ppm for ^{13}C) or DMSO (2.50 ppm for ^1H and 39.52 ppm for ^{13}C). IR spectra were recorded on Bruker FT-IR Spectrometer Model ALPHA by neat method, and only partial data are listed. Melting points were determined on Buchi Melting Point M-565 apparatus. High-resolution mass spectroscopy (HRMS) data were analyzed by a high-resolution micrOTOF instrument with electrospray ionization (ESI). The structures of known compounds were corroborated by comparing their ^1H NMR and ^{13}C NMR data with those of literature.[12b,15]

Typical Procedure for a metal-free promoted direct thiolation of 2-pyridones: synthesis of compounds 3a–3s and 4a–4m. To a 2-dram vial equipped with a magnetic stir bar, pyridone **1** (1 mmol, 1 equiv.), disulfide **2** (1.5 mmol, 1.5 equiv.) or thiol (3 mmol, 3 equiv.), LiCl or *N*-chlorosuccinamide (NCS) (0.5 mmol, 0.5 equiv.), potassium persulfate ($K_2S_2O_8$) (3.0 mmol, 3.0 equiv.) and acetonitrile (CH_3CN) (2 mL) were added, respectively. The reaction mixture was stirred at 70 °C for 16−24 h. Upon completion (monitored by TLC), saturated $NaHCO_3$ (20 mL) was added, and the mixture was extracted with ethyl acetate (EtOAc) (2 × 40 mL). The combined organic layer was washed with distilled deionized H_2O, saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by SiO_2 column chromatography to afford the 5-thiolated pyridone products.

1-Methyl-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3a).[15] White solid (194 mg, 84% yield); mp = 101.2–102.2 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 2.5 Hz, 1H), 7.35 (dd, *J* = 9.4, 2.6 Hz, 1H), 7.12−7.07 (m, 4H), 6.55 (d, *J* = 9.6 Hz, 1H), 3.54 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 145.2, 143.1, 136.7, 133.5, 130.1, 128.5, 121.5, 110.6, 37.9, 21.1; IR (neat, cm^{-1}): *v* = 3037, 2945, 2912, 1649, 1585, 1522, 1488, 1423, 1322, 927, 906, 827, 794, 665, 551; HRMS (ESI): calcd for $C_{13}H_{13}NOSNa$ $[M+Na]^+$ 254.0610, found 254.0609.

1-Ethyl-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3b). Brown solid (162 mg, 66% yield); mp = 78.0–79.0 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 2.5 Hz, 1H), 7.29 (d, *J* = 9.6 Hz, 1H), 7.09−7.04 (m, 4H), 6.51 (d, *J* = 9.6 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 144.8, 141.9, 136.5, 133.5, 130.0, 128.2, 121.7, 110.5, 45.1, 21.0, 14.7; IR (neat, cm^{-1}): *v* = 3031, 2976, 2930, 2871, 1710, 1648, 1583, 1490, 1397, 1263, 1160, 1082, 825, 797, 553; HRMS (ESI): calcd for $C_{14}H_{16}NOS$ $[M+H]^+$ 246.0947, found 246.0950.

1-Isopropyl-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3c). Brown oil (163 mg, 63% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 2.5 Hz, 1H), 7.29 (dd, *J* = 9.4, 2.6 Hz, 1H), 7.10−7.06 (m, 4H), 6.53 (d, *J* = 9.6 Hz, 1H), 5.23 (sep, *J* = 6.8 Hz, 1H), 2.30 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 144.2, 138.0, 136.5, 133.6, 130.1, 128.1, 121.6, 110.6, 46.9, 22.1, 21.1; IR (neat, cm^{-1}): *v* = 2975, 2921, 2870, 1648, 1582, 1592, 1490, 1418, 1256, 1180, 1148, 828, 802, 657, 556; HRMS (ESI): calcd for $C_{15}H_{17}NOSNa$ $[M+Na]^+$ 282.0923, found 282.0927.

1-Pentyl-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3d). Brown oil (166 mg, 58% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 2.5 Hz, 1H), 7.30 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.09−7.05 (m, 4H), 6.51 (d, *J* = 9.4 Hz, 1H), 3.89 (t, *J* = 7.5 Hz, 2H), 2.28 (s, 3H), 1.73 (quin, *J* = 7.3 Hz, 3H), 1.39 – 1.25 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 144.8, 142.4, 136.5, 133.6, 130.0, 128.3, 121.7, 110.3, 50.1, 28.9, 28.8, 22.3, 21.0, 14.0; IR (neat, cm^{-1}): *v* = 3043, 2954, 2926, 2858, 1651, 1586, 1523, 1490, 1435, 1380, 1157, 828, 802, 664, 554; HRMS (ESI): calcd for $C_{17}H_{21}NOSNa$ $[M+Na]^+$ 310.1236, found 310.1230.

1-Benzyl-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3e). Brown solid (214 mg, 70% yield); mp = 73.0–74.0 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 2.0 Hz, 1H), 7.38 – 7.30 (m, 6H), 7.09−7.06 (m, 4H), 6.58 (d, *J* = 9.5 Hz, 1H), 5.13 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 144.9, 141.8, 136.7, 136.0, 133.2, 130.1, 129.1, 128.5, 128.4, 128.3, 122.0, 111.0, 52.2, 21.0; IR (neat, cm^{-1}): *v* = 3056, 3028, 2917, 2851, 1655, 1582, 1521, 1489, 1245, 1160, 849, 797, 693, 665, 543; HRMS (ESI): calcd for $C_{19}H_{17}NOSNa$ $[M+Na]^+$ 330.0923, found 330.0925.

5-(*p*-Tolylthio)pyridin-2(1*H*)-one (3f).[15] Brown solid (122 mg, 56% yield); mp = 146.6–147.6 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 13.33 (s, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.48 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 9.4 Hz, 1H), 2.31 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 147.2, 139.1, 137.0, 132.9, 130.2, 129.2, 121.2, 112.9, 21.1; IR (neat, cm^{-1}): *v* = 3042, 2923, 2850, 1724, 1645, 1594, 1538, 1465, 1415, 1122, 895, 833, 800, 672, 528; HRMS (ESI): calcd for $C_{12}H_{11}NOSNa$ $[M+Na]^+$ 240.0454, found 240.0458.

Ethyl 2-(2-oxo-5-(*p*-tolylthio)pyridin-1(2*H*)-yl)acetate (3g). Brown oil (154 mg, 51% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 2.5 Hz, 1H), 7.34 (dd, *J* = 9.6, 2.0 Hz, 1H), 7.12 – 7.06 (m, 4H), 6.54 (d, *J* = 9.5 Hz, 1H), 4.61 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 161.6, 145.7, 142.6, 136.7, 133.1, 130.1, 128.6, 121.7, 111.0, 62.1, 50.5, 21.0, 14.2; IR (neat, cm^{-1}): *v* = 3050, 2980, 2922, 1744, 1656, 1587, 1524, 1374, 1208, 1190, 1170, 1017, 829, 803, 547; HRMS (ESI): calcd for $C_{16}H_{17}NO_3SNa$ $[M+Na]^+$ 326.0821, found 326.0821.

1-Phenyl-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3h). Yellow pale solid (222 mg, 76% yield); mp = 166.9–167.9 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.63−7.62 (m, 1H), 7.53 – 7.48 (m, 2H), 7.46 – 7.42 (m, 1H), 7.41 – 7.38 (m, 3H), 7.19 – 7.16 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.66 – 6.62 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 145.3, 142.2, 140.5, 137.0, 133.1, 130.2, 129.6, 129.0, 128.9, 126.6, 122.6, 111.2, 21.1; IR (neat, cm^{-1}): *v* = 3039, 2915, 2861, 1713, 1664, 1597, 1580, 1517, 1488, 1272, 1235, 830, 782, 694, 564; HRMS (ESI): calcd for $C_{18}H_{16}NOS$ $[M+H]^+$ 294.0947, found 294.0947.

5-(*p*-Tolylthio)-2*H*-[1,2'-bipyridin]-2-one (3i). Yellow solid (180 mg, 61% yield); mp = 100.5–101.5 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.58

(ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 8.18 (d, *J* = 2.0 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.85 (ddd, *J* = 8.7, 6.8, 1.9 Hz, 1H), 7.38 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.34 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 7.21 – 7.19 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 9.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 151.5, 149.1, 145.4, 140.2, 138.0, 136.9, 133.0, 130.14, 129.1, 123.5, 122.9, 121.4, 111.9, 21.1; IR (neat, cm^{-1}): *v* = 3096, 3053, 2918, 2850, 1657, 1591, 1463, 1431, 1268, 1237, 858, 808, 798, 763, 687; HRMS (ESI): calcd for $C_{17}H_{15}N_2OS$ $[M+H]^+$ 295.0900, found 295.0903.

1-Ethyl-3-methyl-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3j). Yellow oil (194 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 2.5 Hz, 1H), 7.20 (s, 1H), 7.10 – 7.06 (m, 4H), 3.98 (d, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 2.10 (s, 3H), 1.36 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1, 141.9, 139.4, 136.3, 133.9, 131.0, 130.0, 128.1, 109.7, 45.2, 21.0, 17.3, 14.7; IR (neat, cm^{-1}): *v* = 3019, 2975, 2918, 1642, 1596, 1547, 1490, 1439, 1394, 1376, 1225, 1205, 802, 768, 603; HRMS (ESI): calcd for $C_{15}H_{17}NOSNa$ $[M+Na]^+$ 282.0923, found 282.0925.

3-Methyl-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3k). White solid (188 mg, 81% yield); mp = 184.8–185.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.21 (s, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.36 (dd, *J* = 1.3, 1.0 Hz, 1H), 7.14–7.07 (m, 4H), 2.31 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 144.4, 136.8, 136.7, 133.5, 130.4, 130.1, 128.9, 112.1, 21.1, 16.7; IR (neat, cm^{-1}): *v* = 3291, 3135, 3068, 2847, 2686, 1884, 1641, 1607, 1477, 1252, 961, 878, 800, 657, 566; HRMS (ESI): calcd for $C_{13}H_{13}NOSNa$ $[M+Na]^+$ 254.0610, found 254.0610.

3-Chloro-1-ethyl-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3l). White solid (242 mg, 87% yield); mp = 87.5–88.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.52 (m, 2H), 7.13 – 7.09 (m, 4H), 4.03 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 142.3, 140.0, 137.2, 132.7, 130.2, 129.0, 127.1, 110.5, 46.4, 21.1, 14.6; IR (neat, cm^{-1}): *v* = 3067, 3052, 2973, 2929, 2868, 1704, 1643, 1591, 1488, 1378, 1249, 1149, 800, 764, 582; HRMS (ESI): calcd for $C_{14}H_{14}ClNOSNa$ $[M+Na]^+$ 302.0377, found 302.0376.

3-Chloro-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3m). White solid (216 mg, 86% yield); mp = 213.5–214.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.16 (br s, 1H), 7.68 (d, *J* = 2.4 Hz, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 144.5, 137.8, 136.8, 131.9, 130.4, 130.1, 126.4, 113.9, 21.2; IR (neat, cm^{-1}): *v* = 3256, 3162, 3128, 3044, 3000, 1642, 1603, 1518, 1115, 1051, 955, 878, 803, 646, 565; HRMS (ESI): calcd for $C_{12}H_{11}ClNOS$ $[M+H]^+$ 252.0244, found 252.0247.

1-Ethyl-3-nitro-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3n). Yellow solid (214 mg, 74% yield); mp = 125.6–126.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 2.6 Hz, 1H), 7.86 (d, *J* = 2.6 Hz, 1H), 7.19 – 7.17 (m, 2H), 7.15 – 7.13 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 146.8, 143.0, 138.2 (2C), 131.6, 130.6, 129.9, 110.2, 46.7, 21.2, 14.7; IR (neat, cm^{-1}): *v* = 3043, 2922, 2852, 1676, 1591, 1498, 1442, 1334, 1292, 1245, 986, 912, 814, 773, 568; HRMS (ESI): calcd for $C_{14}H_{14}N_2O_3SNa$ $[M+Na]^+$ 313.0617, found 313.0619.

3-Nitro-5-(*p*-tolylthio)pyridin-2(1*H*)-one (3o). Orange solid (63 mg, 24% yield); mp = 159.7–160.7 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 2.4 Hz, 1H), 8.01 (d, *J* = 2.4 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 146.5, 144.7, 138.5, 137.7, 131.0, 130.8, 130.6, 114.1, 21.2; IR (neat, cm^{-1}): *v* = 3468, 3101, 3055, 2946, 2916, 1708, 1648, 1584, 1527, 1515, 1490, 1381, 1277, 1205, 556; HRMS (ESI): calcd for $C_{12}H_{10}N_2O_3SNa$ $[M+Na]^+$ 285.0304, found 285.0305.

1-Ethyl-4-methoxy-2-oxo-5-(*p*-tolylthio)-1,2-dihydropyridine-3-carbonitrile (3p). White solid (238 mg, 79% yield); mp = 166.1–167.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.04 – 7.02 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 2.32 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 156.8, 152.1, 137.3, 132.2, 130.5, 128.5, 115.4, 110.5, 103.1, 42.3, 21.1, 18.9, 13.4; IR (neat, cm^{-1}): *v* = 3052, 2987, 2954, 2870, 2217, 1650, 1601, 1517, 1468, 1371, 1313, 1194, 1133, 799, 770; HRMS (ESI): calcd for $C_{16}H_{16}N_2O_2SNa$ $[M+Na]^+$ 323.0825, found 323.0829.

4-(*p*-Tolylthio)isoquinolin-1(2*H*)-one (3s).[15] White solid (262 mg, 98% yield); mp = 215.1–216.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.72 (d, *J* = 6.4 Hz, 1H), 8.24 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.71 (td, *J* = 7.0, 1.3 Hz, 1H), 7.68 (d, *J* = 6.1 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.08–7.04 (m, 4H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.8, 137.5, 137.3, 135.2, 133.4, 133.0, 129.9, 127.4, 127.1, 126.6, 126.5, 124.7, 104.7, 20.4; IR (neat, cm^{-1}): *v* = 3303, 3159, 3011, 2947, 2815, 1650, 1613, 1468, 1334, 874, 1019, 787, 768, 686, 515; HRMS (ESI): calcd for $C_{16}H_{14}NOS$ $[M+H]^+$ 268.0791, found 268.0788.

1-Ethyl-3-methyl-5-(phenylthio)pyridin-2(1*H*)-one (4a). White solid (103 mg, 42% yield); mp = 96.4–97.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 2.5 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.24 – 7.23 (m, 1H), 7.18 – 7.15 (m, 3H), 4.00 (q, *J* = 7.2 Hz, 2H), 2.12 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 142.1, 140.1, 137.9, 131.2, 129.3, 127.4, 126.2, 108.9, 45.3, 17.3, 14.8; IR (neat, cm^{-1}): *v* = 3052, 2980, 2931, 2852, 1638, 1590, 1578, 1547, 1474, 1229, 1209, 940, 739, 689, 586; HRMS (ESI): calcd for $C_{14}H_{16}NOS$ $[M+H]^+$ 246.0947, found 246.0947.

1-Ethyl-5-((4-methoxyphenyl)thio)-3-methylpyridin-2(1*H*)-one (4b). White solid (176 mg, 64% yield); mp = 95.8–96.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 2.5 Hz, 1H), 7.22 – 7.17 (m, 3H), 6.83 – 6.80 (m, 2H), 3.96 (q, *J* = 9.0 Hz, 2H), 3.77 (s, 3H), 2.08 (s, 3H), 1.34 (t, *J* = 9.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 159.0, 141.3, 138.3, 131.2, 130.8, 127.4, 115.0, 111.3, 55.5, 45.2, 17.3, 14.7; IR (neat, cm^{-1}): *v* = 3049, 2979, 2918, 2850, 1727, 1636, 1578, 1545, 1473, 1437, 1208, 770, 735, 688, 585; HRMS (ESI): calcd for $C_{15}H_{18}NO_2S$ $[M+H]^+$ 276.1053, found 276.1052.

1-Ethyl-5-((4-hydroxyphenyl)thio)-3-methylpyridin-2(1*H*)-one (4c). Brown oil (146 mg, 56% yield); mp = 63.6–64.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.62 (s, 1H), 7.89 (d, *J* = 2.4 Hz, 1H), 7.27 (dd, *J* = 2.5, 1.1 Hz, 1H), 7.15 – 7.13 (m, 2H), 6.74 – 6.72 (m, 2H), 3.94 – 3.89 (m, 2H), 1.95 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz DMSO-d_6): δ 160.9, 156.9, 141.1, 140.0, 131.3, 129.2, 124.8, 116.3, 109.6, 44.1, 16.7,

14.4; IR (neat, cm^{-1}): *v* = 3152, 2979, 2921, 1632, 1569, 1541, 1491, 1433, 1372, 1265, 1213, 1166, 826, 767, 541; HRMS (ESI): calcd for $C_{14}H_{16}NO_2S$ $[M+H]^+$ 262.0896, found 262.0897.

5-((4-Chlorophenyl)thio)-1-ethyl-3-methylpyridin-2(1*H*)-one (4f). Yellow oil (246 mg, 88% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 2.3 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.17 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.07 – 7.03 (m, 2H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.10 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 141.7, 140.2, 136.4, 132.0, 131.3, 129.3, 128.6, 108.3, 45.3, 17.3, 14.7; IR (neat, cm^{-1}): *v* = 3056, 2976, 2932, 1642, 1598, 1548, 1473, 1389, 1353, 1204, 1089, 1009, 812, 769, 538; HRMS (ESI): calcd for $C_{14}H_{15}ClNOS$ $[M+H]^+$ 280.0557, found 280.0557.

1-Ethyl-3-methyl-5-((2,4,5-trichlorophenyl)thio)pyridin-2(1*H*)-one (4g). White solid (184 mg, 53% yield); mp = 174.6–175.6 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.81 (d, *J* = 2.4 Hz, 1H), 7.50 (s, 1H), 7.12 (dd, *J* = 2.8, 1.2 Hz, 1H), 4.10–3.97 (m, 2H), 2.10 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 141.5, 137.5, 136.4, 133.5, 132.6, 131.8, 130.4, 129.0, 127.3, 119.2, 45.7, 17.5, 14.6; IR (neat, cm^{-1}): *v* = 3076, 3054, 2977, 2917, 1657, 1616, 1564, 1429, 1404, 1323, 1194, 1041, 857, 768, 557; HRMS (ESI): calcd for $C_{14}H_{12}Cl_3NOSNa$ $[M+Na]^+$ 369.9597, found 369.9590.

***N*-(2-((1-Ethyl-5-methyl-6-oxo-1,6-dihydropyridin-3-yl)thio)phenyl)benzamide (4h).** White solid (247 mg, 68% yield); mp = 136.6–137.6 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.90 (m, 2H), 7.61 – 7.57 (m, 1H), 7.54 – 7.50 (m, 2H), 7.46 – 7.39 (m, 2H), 7.13 (td, *J* = 7.6, 1.4 Hz, 1H), 7.06 (dd, *J* = 2.5, 1.1 Hz, 1H), 3.85 (q, *J* = 7.2 Hz, 2H), 2.04 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 161.8, 139.5, 138.3, 137.2, 134.9, 133.5, 132.3, 131.6, 130.0, 129.1, 127.2, 125.1, 124.1, 121.8, 109.7, 45.3, 17.4, 14.6; IR (neat, cm^{-1}): *v* = 3208, 3061, 3020, 2954, 1725, 1649, 1633, 1603, 1576, 1513, 1468, 1294, 1201, 743, 711; HRMS (ESI): calcd for $C_{21}H_{21}N_2O_2S$ $[M+H]^+$ 365.1318, found 365.1328.

5-(Benzo[d]thiazol-2-ylthio)-1-ethyl-3-methylpyridin-2(1*H*)-one (4i). Colorless solid (166 mg, 55% yield); mp = 121.4–122.4 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 2.5 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.32 – 7.28 (m, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 2.19 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 162.2, 154.4, 142.3, 141.8 135.6, 131.7, 126.5, 124.6, 122.2, 121.1, 105.7, 45.6, 17.4, 14.8; IR (neat, cm^{-1}): *v* = 3051, 2977, 2934, 1642, 1597, 1546, 1453, 1421, 1232, 1200, 1006, 935, 753, 725, 570; HRMS (ESI): calcd for $C_{15}H_{15}N_2OS_2$ $[M+H]^+$ 303.0620, found 303.0618.

1-Ethyl-3-methyl-5-(thiophen-2-ylthio)pyridin-2(1*H*)-one (4j). Colorless solid (30 mg, 12% yield); mp = 150.0–151.0 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 2.6 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.47 (dd, *J* = 2.5, 1.2 Hz, 1H), 7.11 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1, 143.0, 138.3, 133.9, 133.3, 132.2, 131.1, 128.1, 120.4, 46.2, 17.5, 14.6; IR (neat, cm^{-1}): *v* = 3078, 2922, 2851, 1646, 1612, 1561, 1317, 1146, 1129, 1014, 713, 666, 606, 585, 520; HRMS (ESI): calcd for $C_{12}H_{13}NOS_2Na$ $[M+Na]^+$ 274.0331, found 274.0335.

1-Ethyl-3-methyl-5-(propylthio)pyridin-2(1*H*)-one (4k). Yellow oil (70 mg, 33% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 2.4 Hz, 1H), 7.25 – 7.24 (m, 1H), 3.94 (qd, *J* = 7.2, 0.7 Hz, 2H), 2.62 (td, *J* = 7.2, 1.0 Hz, 2H), 2.10 (s, 3H), 1.58 – 1.49 (m, 2H), 1.31 (td, *J* = 7.2, 1.0 Hz, 3H), 0.95 (td, *J* = 7.3, 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 141.9, 138.6, 130.2, 111.1, 45.1, 38.7, 22.7, 17.3, 14.7, 13.2; IR (neat, cm^{-1}): *v* = 3057, 2961, 2931, 2871, 1640, 1595, 1546, 1439, 1376, 1224, 1206, 937, 733, 573, 551; HRMS (ESI): calcd for $C_{11}H_{18}NOSH$ $[M+H]^+$ 212.1104, found 212.1105.

1-Ethyl-3-methyl-5-(phenylselanyl)pyridin-2(1*H*)-one (4l). Brown oil (190 mg, 65% yield); mp = 78.4–79.8 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 2.4 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.27 – 7.19 (m, 3H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.12 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1, 143.3, 140.7, 132.5, 131.1, 130.2, 129.5, 126.9, 104.0, 45.2, 17.3, 14.8; IR (neat, cm^{-1}): *v* = 3049, 2981, 2957, 2916, 1633, 1586, 1573, 1542, 1473, 1437, 1208, 1048, 907, 735, 689; HRMS (ESI): calcd for $C_{14}H_{15}NOSeNa$ $[M+Na]^+$ 316.0211, found 316.0214.

2-Benzyl-4-(phenylselanyl)isoquinolin-1(2*H*)-one (4m). Yellow solid (231 mg, 59% yield); mp = 115.7–116.7.6 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.49 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.71 (s, 1H), 7.65 – 7.61 (m, 1H), 7.53 – 7.49 (m, 1H), 7.36 – 7.29 (m, 5H), 7.24 – 7.20 (m, 2H), 7.19 – 7.14 (m, 3H), 5.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4, 139.9, 137.8, 136.6, 133.1, 132.2, 129.4, 129.3, 129.1, 128.6, 128.2, 128.1, 127.7, 127.5, 126.8, 126.5, 104.9, 52.0; IR (neat, cm^{-1}): *v* = 3056, 2947, 2850, 1741, 1646, 1607, 1476, 1365, 763, 738, 702, 693, 611, 509, 469; HRMS (ESI): calcd for $C_{22}H_{18}NOSe$ $[M+H]^+$ 392.0548, found 392.0545.

5-((4-Bromophenyl)thio)-1-ethyl-3-methylpyridin-2(1*H*)-one (4n). Brown oil (174 mg, 54% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 2.4 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.20 (dd, *J* = 2.5, 1.2 Hz, 1H), 7.03 – 7.00 (m, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 2.12 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1, 141.9, 140.3, 137.2, 132.3, 131.5, 128.9, 119.9, 108.3, 45.4, 17.4, 14.8; IR (neat, cm^{-1}): *v* = 3056, 2961, 2928, 2870, 1645, 1601, 1547, 1469, 1377, 1198, 1083, 1002, 805, 765, 580; HRMS (ESI): calcd for $C_{14}H_{14}BrNOSNa$ $[M+Na]^+$ 347.9851, found 347.9844.

Conflicts of interest

There are no conflicts to declare.

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