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Novel 5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine derivatives

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Abstract: Starting with 4-piperidone, new 5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo [5,4-c]pyridines were synthesized. Structures of these compounds were confirmed by ^1H NMR, ^{13}C NMR, MS and elemental analysis.

Keywords: 4-piperidone; 5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo [5,4-c]pyridine; synthesis.

Introduction

Piperidine (hexahydropyridine) and imidazole are important nitrogen-containing heterocyclic compounds. Piperidine has good water solubility due to its basic group. The piperidine ring structure is often introduced into drug molecules, which can improve bioavailability and efficacy of the drugs [1]. Imidazole is widely present in natural products, and a variety of its derivatives have been developed to treat bacterial infection, cancer, inflammatory disease and low blood sugar among other things [2]. There are reports [3, 4] that tetrahydropyridine derivatives alter the Hedgehog signaling pathway and thus significantly inhibit the growth of prostate cancer, pancreatic cancer, breast cancer and some blood cancers. There are also reports [5–8] that imidazole compounds inhibit Met receptor tyrosine kinase, which indicates the potential therapeutic benefits of such compounds. Several new compounds containing tetrahydropyridine and imidazole, 4 and 5, were synthesized as part of this work (Scheme 1).

Results and discussion

The amino group of 4-piperidone (**1**) was first protected with a Boc group to give compound **2** which then was allowed

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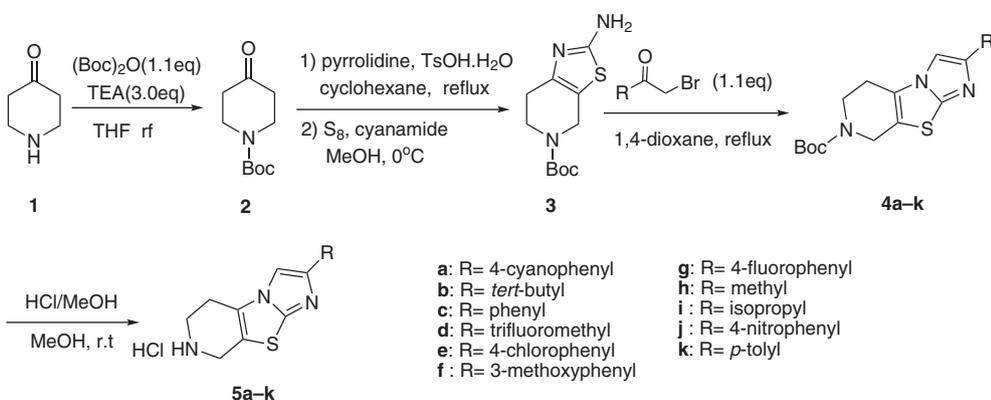
to react with elemental sulfur and cyanamide in the presence of *p*-toluenesulfonic acid to form *N*-Boc-2-amino-4,5,6,7-tetrahydrothiazolo[5,4-c]pyridine (**3**). Compound **3** was allowed to react with a variety of 3-bromoacetyl-bearing compounds to form cyclic products **4a–k**. These compounds were then deprotected to give compounds **5a–k**. The molecular structures of **5a–k** were analyzed using ^1H NMR, ^{13}C NMR, and elemental analysis. The presence of water in the reaction mixture leading to **3** greatly reduces the yield of compound **3**. Due to the fact that the catalyst *p*-toluenesulfonic acid is a monohydrate and water is also produced in the course of the reaction, the water must be constantly removed using a Dean-Stark apparatus. The yield of compound **3** increases with increasing temperature up to 90°C. A further increase in temperature lowers the yield due to formation of by-products. A catalyst is not required for the subsequent synthesis of **4a**. The reactions conducted in solvents of low polarity including 1,4-dioxane, benzene and toluene furnish higher yields of **4a** (76–82%) compared to the polar solvents such as methanol (34%), ethanol (51%) and acetonitrile (59%). The use of dichloromethane as a solvent gives product **4a** in a low yield of 23%, which indicates, as already mentioned, that low temperature is an adverse factor. Overall, 1,4-dioxane is a preferred solvent when compared with highly toxic benzene and toluene with high boiling point that makes it difficult to remove.

Conclusion

The reported synthesis of 5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridines (**5a–k**) is experimentally simple and highly efficient.

Experimental

Melting points were determined on a YUHUA X-3 melting point apparatus and are uncorrected. The ^1H NMR (400 MHz) and ^{13}C (100 MHz) spectra were recorded in CDCl_3 on a Bruker Avance 400 spectrometer. The electrospray ionization mass spectra (ESI-MS) were recorded on a Bruker Esquire 3000 instrument. Elemental analyses were conducted using an ELTRA analyzer. All reagents were obtained from commercial sources and used without further purification. All reactions were monitored by thin-layer chromatography



Scheme 1

(TLC). Compound **2** was synthesized by using previously published procedure [9, 10].

Synthesis of *tert*-butyl 2-amino-4,5,6,7-tetrahydrothiazolo[5,4-c]pyridine-5-carboxylate (**3**)

To a solution of compound **2** (30 g, 150 mmol) in cyclohexane (100 mL) were added pyrrolidine (13.2 mL, 158 mmol) and TsOH·H₂O (1.43 g, 7.53 mmol) and the mixture was heated under reflux for 3 h with constant removal of water using a Dean-Stark apparatus. After cooling to room temperature, the mixture was filtered and the filtrate was concentrated. The residue was dissolved in dry methanol (130 mL), and the solution was treated with elemental sulfur (S₈, 4.8 g, 151 mmol) followed by addition of a solution of cyanamide (6.34 g, 151 mmol) in dry methanol (20 mL) dropwise at 0°C. The mixture was stirred for 2 h at 90°C. After concentration, the residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate, 1:2, to give 22.8 g (59%) of compound **3** as a pale yellow solid; ¹H NMR: δ 4.26 (s, 2 H), 3.56 (t, *J*=5.7 Hz, 2 H), 2.42 (m, 2 H), 1.36 (s, 9 H); MS: *m/z* 256.3, [M+H]⁺.

General procedure for the preparation of **4a-k**

To a solution of compound **3** (50.3 g, 197 mmol) in 1,4-dioxane (1000 mL) was added R-C(O)CH₂Br (217 mmol, see Scheme 1 for R) in one portion. After stirring at room temperature for 1 h, the mixture was heated under reflux overnight. After concentration, the residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate, 2:1, to give compound **4a-k** as a pale yellow solid; yield 80%.

***tert*-Butyl 2-(4-cyanophenyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (**4a**)** Yield 80%; ¹H NMR: δ 7.89 (d, *J*=8.8 Hz, 2 H), 7.65 (m, 2 H), 7.37 (s, 1 H), 4.54 (s, 2 H), 3.86 (t, *J*=5.6 Hz, 2 H), 2.79–2.76 (m, 2 H), 1.49 (s, 9 H); MS: *m/z* 380.9, [M+H]⁺. Anal. Calcd for C₂₀H₂₀N₄O₂S: C, 63.14; H, 5.30; N, 14.73. Found: C, 63.17; H, 5.34; N, 14.75.

***tert*-Butyl 2-(*tert*-butyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (**4b**)** Yield 75%; ¹H NMR: δ

7.02 (s, 1 H), 4.49 (s, 2 H), 3.81 (t, *J*=5.2 Hz, 2 H), 2.71 (t, *J*=5.2 Hz, 2 H), 1.48 (s, 9 H), 1.33 (s, 9 H); MS: *m/z* 335.8, [M+H]⁺. Anal. Calcd for C₁₇H₂₅N₃O₂S: C, 60.87; H, 7.51; N, 12.53. Found: C, 60.79; H, 7.54; N, 12.55.

***tert*-Butyl 2-phenyl-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (**4c**)** Yield 72%; ¹H NMR: δ 7.94 (s, 1 H), 7.79 (d, *J*=7.6 Hz, 2 H), 7.40 (t, *J*=7.2 Hz, 2 H), 7.30 (t, *J*=7.2 Hz, 1 H), 4.58 (s, 2 H), 3.87 (t, *J*=6.0 Hz, 2 H), 2.85–2.82 (m, 2 H), 1.54 (s, 9 H); MS: *m/z* 356.2, [M+H]⁺. Anal. Calcd for C₁₉H₂₁N₃O₂S: C, 64.20; H, 5.95; N, 11.82. Found: C, 64.27; H, 5.94; N, 11.76.

***tert*-Butyl 2-(trifluoromethyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (**4d**)** Yield 70%; ¹H NMR: δ 7.63 (s, 1 H), 4.56 (s, 2 H), 3.86 (t, *J*=5.6 Hz, 2 H), 2.79 (m, 2 H), 1.48 (s, 9 H); MS: *m/z* 347.8, [M+H]⁺. Anal. Calcd for C₁₄H₁₆F₃N₃O₂S: C, 48.41; H, 4.64; N, 12.10. Found: C, 48.45; H, 4.65; N, 12.17.

***tert*-Butyl 2-(4-chlorophenyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (**4e**)** Yield 61%; ¹H NMR: δ 7.74 (d, *J*=8.4 Hz, 2 H), 7.56 (s, 1 H), 7.35 (d, *J*=8.4 Hz, 2 H), 4.53 (m, 2 H), 3.86 (m, 2 H), 2.77 (m, 2 H), 1.49 (s, 9 H); MS: *m/z* 390.1, [M+H]⁺. Anal. Calcd for C₁₉H₂₀ClN₃O₂S: C, 58.53; H, 5.17; N, 10.78. Found: C, 58.51; H, 5.14; N, 10.72.

***tert*-Butyl 2-(3-methoxyphenyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (**4f**)** Yield 67%; ¹H NMR: δ 7.57 (s, 1 H), 7.42 (s, 1 H), 7.33 (d, *J*=7.6 Hz, 1 H), 7.27 (t, *J*=8.0 Hz, 1 H), 6.83 (d, *J*=8.0 Hz, 1 H), 4.54 (m, 2 H), 3.81 (m, 5 H), 2.77 (m, 2 H), 1.50 (s, 9 H); MS: *m/z* 386.2, [M+H]⁺. Anal. Calcd for C₂₀H₂₃N₃O₃S: C, 62.32; H, 6.01; N, 10.90. Found: C, 62.30; H, 6.05; N, 10.87.

***tert*-Butyl 2-(4-fluorophenyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (**4g**)** Yield 64%; ¹H NMR: δ 7.68 (d, *J*=8.4 Hz, 2 H), 7.55 (s, 1 H), 7.39 (d, *J*=8.4 Hz, 2 H), 4.41 (m, 2 H), 3.87 (m, 2 H), 2.74 (m, 2 H), 1.47 (s, 9 H); MS: *m/z* 374.5, [M+H]⁺. Anal. Calcd for C₁₉H₂₀FN₃O₂S: C, 61.11; H, 5.40; N, 11.25. Found: C, 61.17; H, 5.45; N, 11.21.

***tert*-Butyl 2-methyl-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (**4h**)** Yield 76%; ¹H NMR: δ 7.79 (s, 1 H), 4.71 (s, 2 H), 3.69 (t, *J*=5.6 Hz, 2 H), 2.87 (m, 2 H), 2.36 (s, 3 H), 1.45 (s, 9 H); MS: *m/z* 294.4, [M+H]⁺. Anal. Calcd for C₁₄H₁₉N₃O₂S: C, 57.31; H, 6.53; N, 14.32. Found: C, 57.36; H, 6.61; N, 14.33.

tert-Butyl 2-isopropyl-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (4i) Yield 73%; $^1\text{H NMR}$: δ 7.56 (s, 1 H), 4.93 (s, 2 H), 3.66 (t, $J=5.6$ Hz, 2 H), 3.17 (d, $J=8.0$ Hz, 1 H), 2.60 (m, 2 H), 1.65 (s, 9 H), 1.38 (s, 6 H); MS: m/z 322.5, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$: C, 59.78; H, 7.21; N, 13.07. Found: C, 59.76; H, 7.19; N, 13.03.

tert-Butyl 2-(4-nitrophenyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (4j) Yield 59%; $^1\text{H NMR}$: δ 7.97 (d, $J=8.4$ Hz, 2 H), 7.65 (s, 1 H), 7.48 (d, $J=8.4$ Hz, 2 H), 4.93 (m, 2 H), 3.76 (d, $J=8.4$ Hz, 2 H), 2.83 (m, 2 H), 1.43 (s, 9 H); MS: m/z 401.4, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_4\text{S}$: C, 56.99; H, 5.03; N, 13.99. Found: C, 56.96; H, 5.01; N, 13.93.

tert-Butyl 2-(*p*-tolyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-7-carboxylate (4k) Yield 54%; $^1\text{H NMR}$: δ 7.76 (d, $J=8.4$ Hz, 2 H), 7.67 (s, 1 H), 7.39 (d, $J=8.4$ Hz, 2 H), 4.81 (m, 2 H), 3.65 (d, $J=8.4$ Hz, 2 H), 2.75 (m, 2 H), 2.17 (s, 3 H), 1.43 (s, 9 H); MS: m/z 370.5, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$: C, 65.01; H, 6.27; N, 11.37. Found: C, 65.06; H, 6.32; N, 11.33.

General procedure for the preparation of 5a–k

To a solution of compound 4a–k (84.5 mmol) in methanol (350 mL) was added dropwise a solution of 4 M HCl in MeOH (300 mL) at 0°C. The mixture was stirred at room temperature for 0.5 h and then concentrated to afford compound 5a–k.

4-((5,6,7,8-Tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine-2-yl)benzotrile hydrochloride (5a) Yellow solid; yield 98%; mp 199–201°C; $^1\text{H NMR}$: δ 10.26 (s, 1 H), 8.52 (s, 1 H), 8.00 (d, $J=8.4$ Hz, 2 H), 7.86 (d, $J=8.4$ Hz, 2 H), 4.52 (s, 2 H), 3.78 (t, $J=6.0$ Hz, 2 H), 3.28 (m, 2 H); $^{13}\text{C NMR}$: δ 165.2, 153.1, 139.4, 138.6, 131.8, 127.9, 122.2, 107.1, 101.5, 59.8, 56.3, 47.3, 42.1; MS: m/z 281.2, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{ClN}_4\text{S}$: C, 56.87; H, 4.14; N, 17.68. Found: C, 56.89; H, 4.09; N, 17.65.

2-(tert-Butyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine hydrochloride (5b) Yellow solid, yield 98%; mp 142–144°C; $^1\text{H NMR}$: δ 10.14 (s, 1 H), 8.12 (s, 1 H), 4.67 (s, 2 H), 3.88 (t, $J=6.0$ Hz, 2 H), 3.41 (t, $J=6.0$ Hz, 2 H), 1.58 (s, 9 H); $^{13}\text{C NMR}$: δ 159.2, 131.4, 126.5, 122.3, 101.8, 59.1, 51.5, 42.3, 28.1, 23.6; MS: m/z 236.1, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{ClN}_3\text{S}$: C, 53.03; H, 6.77; N, 15.46. Found: C, 53.09; H, 6.74; N, 15.49.

2-Phenyl-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine hydrochloride (5c) White solid; yield 95%; mp 207–209°C; $^1\text{H NMR}$: δ 10.23 (s, 1 H), 8.19 (s, 1 H), 7.69 (m, 2 H), 7.54 (m, 3 H), 4.56 (s, 2 H), 3.76 (t, $J=5.6$ Hz, 2 H), 3.25 (t, $J=6.0$ Hz, 2 H); $^{13}\text{C NMR}$: δ 165.2, 153.3, 139.3, 138.6, 131.8, 127.9, 122.1, 101.5, 59.8, 56.3, 47.3, 41.9; MS: m/z 256.3, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{ClN}_3\text{S}$: C, 57.63; H, 4.84; N, 14.40. Found: C, 57.57; H, 4.89; N, 14.45.

2-(Trifluoromethyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine hydrochloride (5d) White solid; yield 91%; mp 191–193°C; $^1\text{H NMR}$: δ 10.12 (s, 1 H), 8.16 (s, 1 H), 3.95 (s, 2 H), 3.25 (t, $J=6.0$ Hz, 2 H), 2.81 (m, 2 H); $^{13}\text{C NMR}$: δ 161.4, 129.5, 122.5, 119.7, 101.4, 59.7, 52.1, 42.3, 27.3; MS: m/z 248.2, $[\text{M}+\text{H}]^+$. Anal. Calcd

for $\text{C}_9\text{H}_9\text{ClF}_3\text{N}_3\text{S}$: C, 38.10; H, 3.20; N, 14.81. Found: C, 38.16; H, 3.14; N, 14.85.

2-(4-Chlorophenyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine hydrochloride (5e) Yellow solid; yield 94%; mp 271–274°C; $^1\text{H NMR}$: δ 10.16 (s, 1 H), 8.51 (s, 1 H), 7.87 (d, $J=8.8$ Hz, 2 H), 7.52 (d, $J=8.8$ Hz, 2 H), 4.32 (m, 2 H), 3.54 (m, 2 H), 3.11 (m, 2 H); $^{13}\text{C NMR}$: δ 165.2, 153.3, 139.3, 138.6, 131.8, 129.3, 124.7, 104.1, 59.8, 56.3, 47.3, 41.9; MS: m/z 289.7, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{Cl}_2\text{N}_3\text{S}$: C, 51.54; H, 4.02; N, 12.88. Found: C, 51.49; H, 4.04; N, 12.85.

2-(3-Methoxyphenyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine hydrochloride (5f) Yellow solid; yield 96%; mp 174–177°C; $^1\text{H NMR}$: δ 10.13 (s, 1 H), 8.58 (s, 1 H), 7.44 (m, 2 H), 7.36 (t, $J=8.0$ Hz, 1 H), 6.91 (d, $J=8.0$ Hz, 1 H), 4.33 (m, 2 H), 3.81 (s, 3 H), 3.54 (m, 2 H), 3.10 (m, 2 H); $^{13}\text{C NMR}$: δ 165.3, 152.9, 139.4, 138.6, 131.8, 127.9, 122.2, 107.1, 101.5, 59.8, 52.9, 44.2, 39.5; MS: m/z 286.3, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{ClN}_3\text{OS}$: C, 55.98; H, 5.01; N, 13.06. Found: C, 55.92; H, 5.04; N, 13.05.

2-(4-Fluorophenyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine hydrochloride (5g) Yellow solid; yield 89%; mp 217–219°C; $^1\text{H NMR}$: δ 10.21 (s, 1 H), 8.57 (s, 1 H), 7.69 (d, $J=8.8$ Hz, 2 H), 7.46 (d, $J=8.8$ Hz, 2 H), 4.27 (m, 2 H), 3.53 (m, 2 H), 3.08 (m, 2 H); $^{13}\text{C NMR}$: δ 164.7, 154.1, 139.3, 138.7, 132.2, 129.6, 124.5, 104.3, 59.8, 56.3, 47.5, 42.3; MS: m/z 274.4, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{ClFN}_3\text{S}$: C, 54.28; H, 4.23; N, 13.56. Found: C, 54.19; H, 4.34; N, 13.55.

2-Methyl-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine hydrochloride (5h) White solid; yield 97%; mp 167–169°C; $^1\text{H NMR}$: δ 10.17 (s, 1 H), 7.97 (s, 1 H), 4.11 (s, 2 H), 3.62 (t, $J=6.0$ Hz, 2 H), 2.83 (d, $J=6.0$ Hz, 2 H), 2.21 (s, 3 H); $^{13}\text{C NMR}$: δ 159.6, 131.4, 130.1, 117.6, 98.9, 59.3, 53.2, 44.6, 21.7; MS: m/z 248.2, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_9\text{H}_{12}\text{ClN}_3\text{S}$: C, 47.05; H, 5.27; N, 18.29. Found: C, 46.97; H, 5.34; N, 18.17.

2-Isopropyl-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine hydrochloride (5i) White solid; yield 94%; mp 203–205°C; $^1\text{H NMR}$: δ 10.11 (s, 1 H), 8.37 (s, 1 H), 4.33 (s, 2 H), 3.59 (t, $J=5.6$ Hz, 2 H), 3.21 (d, $J=8.0$ Hz, 1 H), 2.45 (m, 2 H), 1.25 (s, 6 H); $^{13}\text{C NMR}$: δ 160.4, 132.7, 128.9, 116.3, 100.6, 61.1, 54.8, 45.6, 32.6, 22.9; MS: m/z 222.3, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{ClN}_3\text{S}$: C, 51.25; H, 6.26; N, 16.30. Found: C, 51.31; H, 6.23; N, 16.37.

2-(4-Nitrophenyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine hydrochloride (5j) Yellow solid; yield 87%; mp 241–243°C; $^1\text{H NMR}$: δ 10.37 (s, 1 H), 8.49 (s, 1 H), 8.17 (d, $J=8.8$ Hz, 2 H), 7.97 (d, $J=8.8$ Hz, 2 H), 4.32 (m, 2 H), 3.36 (m, 2 H), 2.93 (m, 2 H); $^{13}\text{C NMR}$: δ 165.9, 156.4, 136.7, 131.5, 129.6, 127.7, 121.5, 102.6, 62.3, 55.4, 42.8, 41.3; MS: m/z 301.4, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{ClN}_4\text{O}_2\text{S}$: C, 49.93; H, 3.89; N, 16.64. Found: C, 49.99; H, 3.84; N, 16.65.

2-(*p*-Tolyl)-5,6,7,8-tetrahydroimidazo[2',1':2,3]thiazolo[5,4-c]pyridine hydrochloride (5k) White solid; yield 92%; mp 252–254°C; $^1\text{H NMR}$: δ 10.25 (s, 1 H), 8.81 (s, 1 H), 7.84 (d, $J=8.8$ Hz, 2 H), 7.47 (d, $J=8.8$ Hz, 2 H), 4.60 (m, 2 H), 3.32 (d, $J=8.0$ Hz, 2 H), 2.74 (m, 2 H), 2.21 (s, 3 H); $^{13}\text{C NMR}$: δ 160.3, 155.8, 136.7, 129.4, 127.6, 124.9, 118.1, 101.7, 65.3, 54.5, 42.2, 27.6; MS: m/z 270.4, $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{ClN}_3\text{S}$: C, 58.91; H, 5.27; N, 13.74. Found: C, 58.97; H, 5.24; N, 13.69.

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