A Convenient Synthesis of 2,3-Dihydro-4*H*-thiopyrano[2,3-*b*]-, -[2,3-*c*]-, or -[3,2-*c*]pyridin-4-ones by the Reaction of the Corresponding 1-(Chloropyridinyl)alk-2-en-1-ones with NaSH

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2,3-Dihydro-4*H*-thiopyrano[2,3-*b*]pyridin-4-ones **4** were prepared by a three-step sequence from commercially available 2-chloropyridine (**1**). Thus, successive treatment of **1** with $^{i}Pr_2NLi$ (LDA) and α,β-unsaturated aldehydes gave 1-(2-chloropyridin-3-yl)alk-2-en-1-ols **2**, which were oxidized with MnO_2 to 1-(2-chloropyridin-3-yl)alk-2-en-1-ones **3**. The reactions of **3** with $NaSH \cdot n\ H_2O$ proceeded smoothly at 0° in DMF to provide the desired thiopyranopyridinones. Similarly, 2,3-dihydro-4*H*-thiopyrano[2,3-*c*]pyridin-4-ones **8** and 2,3-dihydro-4*H*-thiopyrano[3,2-*c*]pyridin-4-ones **12** were obtained starting from 3-chloropyridine (**5**) and 4-chloropyridine (**9**), respectively.

Introduction. – Recently, significant attention has been focused on 2,3-dihydro-4*H*-thiopyrano[2,3-*b*]pyridin-4-one derivatives, as some of them have been used for the synthesis of more complex fused heterocycles [1], and a number of derivatives with this skeleton have been reported to exhibit biological activities [2]. *Da Settimo et al.* have demonstrated that 2,3-dihydro-4*H*-thiopyrano[2,3-*b*]pyridin-4-one can be prepared from 2-sulfanylpyridine-3-carboxylic acid and 3-bromopropanoic acid [3]. A similar synthesis of 2,3-dihydro-4*H*-thiopyrano[3,2-*c*]pyridin-4-one using 4-sulfanylpyridine-3-carboxylic acid has been also reported by *Gaillard et al.* [4]. However, there have been so far no reports on the general synthesis of these thiopyrano-pyridinone derivatives including 2,3-dihydro-4*H*-thiopyrano[2,3-*c*]pyridin-4-ones. Hence, we decided to develop a general method applicable to the preparation of these three thiopyranopyridinone derivatives starting with readily available compounds, and we report herein the results of our investigation, which provide facile entry to 2-substituted derivatives.

Results and Discussion. – The three-step preparation of 2,3-dihydro-4*H*-thiopyrano[2,3-*b*]pyridin-4-ones **4** was achieved according to the procedure outlined in *Scheme 1*. Commercially available 2-chloropyridine (**1**) was first lithiated with $^{i}Pr_2NLi$ (LDA) in THF at −78° as described by *Gribble* and *Saulnier* [5] to generate 2-chloro-3-lithiopyridine, which was then allowed to react with α,β-unsaturated aldehydes. The highly selective attack of the 2-chloropyridin-3-yl anion on the aldehyde in the 1,2-addition fashion proceeded cleanly, and 1-(2-chloropyridin-3-yl)alk-2-en-1-ols **2** were obtained in relatively good yields as compiled in *Table 1*. Subsequently, these alcohols were oxidized with MnO_2 to give the corresponding 1-(2-chloropyridin-3-yl)alk-2-en-1-

ones **3** in good-to-excellent yields. Finally, these ketones **3** were treated with NaSH · *n* H_2O in DMF at 0°. Substitution/ring-closing conjugate addition, or conjugate addition/ring closure *via* substitution proceeded smoothly even at this temperature, and TLC analyses confirmed that all starting materials had been consumed within 30 min. Usual aqueous workup, followed by column chromatography on SiO_2, provided good yields of 2-aryl-2,3-dihydro-4*H*-thiopyrano[2,3-*b*]pyridin-4-ones **4** (*Entries 1–4*), while the yields of the products derived from (*E*)-but-2-enal and 3-methylbut-2-enal, *i.e.* 2,3-dihydro-2-methyl-4*H*-thiopyrano[2,3-*b*]pyridin-4-one (**4e**) and 2,3-dihydro-2,2-dimethyl-4*H*-thiopyrano[2,3-*b*]pyridin-4-one (**4f**), were moderate (*Entries 5* and *6*, resp.). These results indicate that substitution of an aromatic group in *β*-position to the C=O group of **3** facilitates the cyclization. It should be noted that *trans*-2,3-dihydro-3-methyl-2-phenyl-4*H*-thiopyrano[2,3-*b*]pyridin-4-one (**4d**) was obtained almost exclusively; only a trace amount of its stereoisomer was detected by the ^{1}H-NMR spectrum of the crude product (*Entry 4*).

Scheme 1

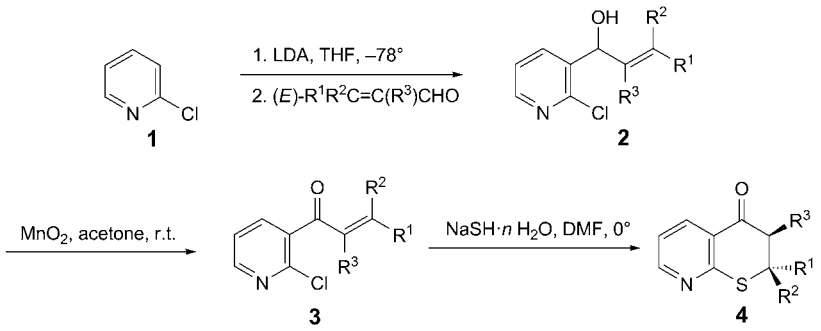


Table 1. *Preparation of 2,3-Dihydro-4*H*-thiopyrano[2,3-*b*]pyridin-4-ones* **4**

Entry	$R^1R^2C{=}C(R^3)CHO$	**2**	Yield[a])	**3**	Yield[a])	**4**	Yield[a])
1	R^1 = Ph, $R^2 = R^3$ = H	**2a**	77	**3a**	95	**4a**	80
2	R^1 = 4-Cl–C_6H_4, $R^2 = R^3$ = H	**2b**	71	**3b**	99	**4b**	78
3	R^1 = 4-MeO–C_6H_4, $R^2 = R^3$ = H	**2c**	71	**3c**	88	**4c**	78
4	R^1 = Ph, R^2 = H, R^3 = Me	**2d**	74	**3d**	95	**4d**	75
5	R^1 = Me, $R^2 = R^3$ = H	**2e**	52	**3e**	73	**4e**	54
6	$R^1 = R^2$ = Me, R^3 = H	**2f**	73	**3f**	67	**4f**	55

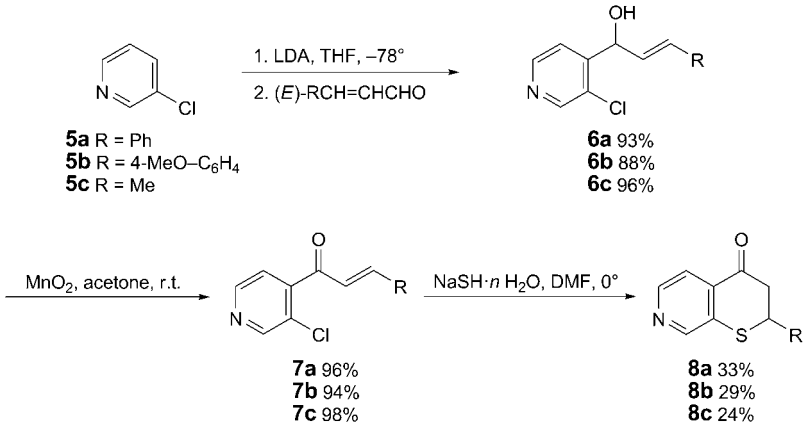
[a]) Yields of isolated products [%].

To elucidate the possible pathway for the formation of **4**, the reaction of (2-chloropyridin-3-yl)(phenyl)methanone [6] with NaSH · *n* H_2O under the above-mentioned conditions was carried out. It resulted in almost quantitative recovery of the starting materials. The substitution/ring-closing conjugate addition sequence may be excluded by this result, indicating that the conjugate addition/ring closure *via* substitution sequence is favored. Thus, conjugate addition of HS^- to the enone moiety of **3** is followed by intramolecular substitution of the resulting 3-(2-chlorophenyl)-3-

oxo-1-phenylpropane-1-thiolate to give **4**. The previous reports on the formation of 3-ethylsulfanyl-1,3-diphenylpropan-1-one by the reaction of 1,3-diphenylprop-2-en-1-one (chalcone) with EtSH in the presence of a base under mild conditions [7], and the formation of (2-ethylsulfanylpyridin-3-yl)phenylmethanone by the reaction of (2-chloropyridin-3-yl)phenylmethanone with EtSNa under mild conditions [6b] may support the latter sequence.

2,3-Dihydro-4*H*-thiopyrano[2,3-*c*]pyridin-4-ones **8** were prepared from 3-chloropyridine (**5**) and α,β-unsaturated aldehydes, *via* 1-(3-chloropyridin-4-yl)alk-2-en-1-ols **6** and 1-(3-chloropyridin-4-yl)alk-2-en-1-ones **7**, by a procedure analogous to that applied for the preparation of **4**, as shown in *Scheme 2*. The precursors **6** and **7** were obtained in excellent yields. Unfortunately, however, the expected cyclization of **7** with NaSH · *n* H_2O proceeded less smoothly (*ca.* 1.5 h for complete consumption of the starting materials) and less cleanly than that of **3**, and resulted in the formation of rather complicated mixtures of products, from which the desired products **8** were isolated in much lower yields than those of products **4**. This may be rationalized by considering the lower reactivity of the 3-chloro- compared to the 2-chloropyridine ring. The use of 2 equiv. NaSH · *n* H_2O did not improve the yields.

Scheme 2



By adapting the reaction conditions for the preparation of **4** and **8**, 2,3-dihydro-4*H*-thiopyrano[3,2-*c*]pyridin-4-ones **12** were also prepared starting with 4-chloropyridine (**9**) as depicted in *Scheme 3*. A similarly good performance of 1-(4-chloropyridin-3-yl)alk-2-en-1-ones **11**, obtained from the corresponding alcohols **10**, in the reaction with NaSH · *n* H_2O was observed as described for the conversion of **3** into **4**, and relatively good yields of the desired products **12** were accomplished as compiled in *Table 2*, indicating that both yields of compounds **10** and **11** are good as well. Again noted is that *trans*-2,3-dihydro-3-methyl-2-phenyl-4*H*-thiopyrano[3,2-*c*]pyridin-4-one (**12d**) was also obtained as the practically sole stereoisomer as stated above.

In summary, the methodology described in this work allows very easy access to substituted 2,3-dihydro-4*H*-thiopyrano[2,3-*b*]-, -[2,3-*c*]-, or -[3,2-*c*]pyridin-4-ones, which are difficult to prepare by previous methods, from 2-, 3- or 4-chloropyridines,

Scheme 3

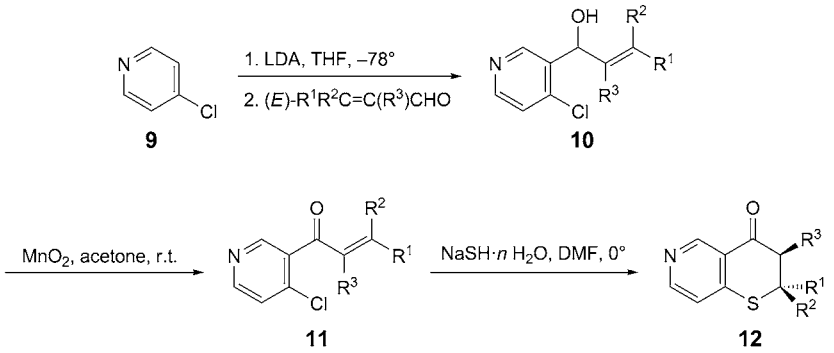


Table 2. *Preparation of 2,3-Dihydro-4*H*-thiopyrano[3,2-*c*]pyridin-4-ones* **12**

Entry	$R^1R^2C{=}C(R^3)CHO$	**10**	Yield[a])	**11**	Yield[a])	**12**	Yield[a])
1	$R^1 = Ph$, $R^2 = R^3 = H$	**10a**	77	**11a**	96	**12a**	78
2	$R^1 = 4\text{-Cl–}C_6H_4$, $R^2 = R^3 = H$	**10b**	75	**11b**	91	**12b**	75
3	$R^1 = 4\text{-MeO–}C_6H_4$, $R^2 = R^3 = H$	**10c**	79	**11c**	94	**12c**	78
4	$R^1 = Ph$, $R^2 = H$, $R^3 = Me$	**10d**	84	**11d**	99	**12d**	74
5	$R^1 = Me$, $R^2 = R^3 = H$	**10e**	71	**11e**	99	**12e**	52
6	$R^1 = R^2 = Me$, $R^3 = H$	**10f**	83	**11f**	91	**12f**	55

[a]) Yields of isolated products [%].

respectively. This method may also be of value in organic synthesis because of its simplicity as well as the ready availability of the starting materials.

Experimental Part

General. All of the org. solvents were dried over appropriate drying agents and distilled prior to use. BuLi was supplied by *Asia Lithium Corporation*. All chemicals were commercially available. TLC: *Merck* silica gel *60 PF_{254}*. Column chromatography (CC): *Wako Gel C-200E.* M.p.: *Laboratory Devices MEL-TEMP II* apparatus; uncorrected. IR: *Perkin–Elmer Spectrum 65 FT-IR* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR: in $CDCl_3$ with Me_4Si as an internal reference, with *JEOL ECP500* FT NMR or *JEOL LA400* FT NMR spectrometer (at 500 or 400 MHz (^{1}H) and at 125 or 100 MHz (^{13}C), resp.); δ in ppm, J in Hz. EI-MS (70 eV): with *JEOL JMS AX505 HA* spectrometer; *m/z* (rel. %).

*(2*E*)-1-(2-Chloropyridin-3-yl)-3-phenylprop-2-en-1-ol* (**2a**; *Representative Procedure*). To a stirred soln. of LDA (5.0 mmol), generated from ^{i}Pr$_2$NH and BuLi by the standard method, in THF (6 ml) at $-78°$ was added *2-chloropyridine* (**1**; 0.23 g, 2.0 mmol) dropwise [5]. After 1 h, (*E*)-3-phenylprop-2-enal (0.32 g, 2.4 mmol) was added, and stirring was continued for an additional 10 min before sat. aq. NH_4Cl (20 ml) was added. The mixture was warmed to r.t. and extracted with AcOEt (3×15 ml). The combined extracts were washed with brine (15 ml) and dried (Na_2SO_4). Evaporation of the solvent gave a residue, which was purified by CC (SiO_2) to give **2a** (0.38 g, 77%). Yellow oil. R_f (THF/hexane 1:5) 0.19. IR (neat): 3349, 1407. ^{1}H-NMR (500 MHz): 2.38 (*d*, $J = 3.4$, 1 H); 5.75 (*dd*, $J = 6.3, 3.4$, 1 H); 6.29 (*dd*, $J = 16.0, 6.3$, 1 H); 6.77 (*d*, $J = 16.0$, 1 H); 7.24–7.33 (*m*, 4 H); 7.39 (*d*, $J = 7.4$, 2 H); 8.01 (*dd*, $J = 8.0, 1.7$, 1 H); 8.33 (*dd*, $J = 4.6, 1.7$, 1 H). Anal. calc. for $C_{14}H_{12}ClNO$ (245.70): C 68.44, H 4.92, N 5.70; found: C 68.37, H 4.97, N 5.62.

(2E)-3-(4-Chlorophenyl)-1-(2-chloropyridin-3-yl)prop-2-en-1-ol (**2b**). Yellow oil. R_f (AcOEt/hexane 1:2) 0.19. IR (neat): 3317, 1407. ^{1}H-NMR (500 MHz): 2.32 (*s*, 1 H); 5.75 (*d*, *J* = 6.3, 1 H); 6.27 (*dd*, *J* = 16.0, 6.3, 1 H); 6,73 (*d*, *J* = 16.0, 1 H); 7.28 (*d*, *J* = 8.0, 2 H); 7.31 (*d*, *J* = 8.0, 2 H); 7.32 (*dd*, *J* = 7.4, 4.6, 1 H); 7.99 (*dd*, *J* = 7.4, 1.7, 1 H); 8.34 (*dd*, *J* = 4.6, 1.7, 1 H). Anal. calc. for $C_{14}H_{11}Cl_2NO$ (280.15): C 60.02, H 3.96, N 5.00; found: C 59.98, H 4.05, N 4.97.

(2E)-1-(2-Chloropyridin-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-ol (**2c**). Yellow oil. R_f (AcOEt/hexane 1:2) 0.23. IR (neat): 3342, 1607, 1512, 1407. ^{1}H-NMR (500 MHz): 2.29 (*s*, 1 H); 3.80 (*s*, 3 H); 5.72 (*d*, *J* = 6.3, 1 H); 6.14 (*dd*, *J* = 15.7, 6.3, 1 H); 6.70 (*d*, *J* = 15.7, 1 H); 6.85 (*d*, *J* = 8.0, 2 H); 7.31 – 7.32 (*m*, 3 H); 8.00 (*dd*, *J* = 7.4, 1.7, 1 H); 8.32 (*dd*, *J* = 4.6, 1.7, 1 H). Anal. calc. for $C_{15}H_{14}ClNO_2$ (275.73): C 65.34, H 5.12, N 5.08; found: C 65.25, H 5.15, N 5.06.

(2E)-1-(2-Chloropyridin-3-yl)-2-methyl-3-phenylprop-2-en-1-ol (**2d**). Yellow oil. R_f (THF/hexane 1:5) 0.19. IR (neat): 3339, 1407. ^{1}H-NMR (400 MHz): 1.78 (*d*, *J* = 1.0, 3 H); 2.26 (*d*, *J* = 3.9, 1 H); 5.63 (*d*, *J* = 3.9, 1 H); 6.77 (*s*, 1 H); 7.22 – 7.36 (*m*, 6 H); 8.00 (*dd*, *J* = 7.3, 2.0, 1 H); 8.35 (*dd*, *J* = 4.9, 2.0, 1 H). Anal. calc. for $C_{15}H_{14}ClNO$ (259.73): C 69.36, H 5.43, N 5.39; found: C 69.19, H 5.50, N 5.38.

(2E)-1-(2-Chloropyridin-3-yl)but-2-en-1-ol (**2e**). Yellow oil. R_f (AcOEt/hexane 1:3) 0.36. IR (neat): 3350, 1408. ^{1}H-NMR (500 MHz): 1.73 (*d*, *J* = 6.8, 3 H); 2.13 (*d*, *J* = 3.4, 1 H); 5.50 – 5.52 (*m*, 1 H); 5.60 (*ddd*, *J* = 14.9, 6.9, 1.7, 1 H); 5.85 (*dq*, *J* = 14.9, 6.9, 1 H); 7.28 (*dd*, *J* = 7.4, 4.6, 1 H); 7.94 (*dd*, *J* = 7.4, 1.7, 1 H); 8.30 (*d*, *J* = 4.6, 1.7, 1 H). Anal. calc. for $C_9H_{10}ClNO$ (183.63): C 58.86, H 5.49, N 7.63; found: C 58.80, H 5.67, N 7.49.

1-(2-Chloropyridin-3-yl)-3-methylbut-2-en-1-ol (**2f**). Yellow oil. R_f (AcOEt/hexane 1:3) 0.37. IR (neat): 3350, 1673, 1406. ^{1}H-NMR (500 MHz): 1.76 (*d*, *J* = 1.1, 3 H); 1.88 (*d*, *J* = 1.7, 3 H); 1.98 (*d*, *J* = 2.9, 1 H); 5.20 (*ddd*, *J* = 9.2, 1.7, 1.1, 1 H); 5.73 (*dd*, *J* = 9.2, 2.9, 1 H); 7.28 (*dd*, *J* = 7.4, 4.6, 1 H); 7.99 (*dd*, *J* = 7.4, 1.7, 1 H); 8.29 (*d*, *J* = 4.6, 1.7, 1 H). Anal. calc. for $C_{10}H_{12}ClNO$ (197.66): C 60.76, H 6.12, N 7.09; found: C 60.64, H 6.20, N 7.05.

(2E)-1-(3-Chloropyridin-4-yl)-3-phenylprop-2-en-1-ol (**6a**). White solid. M.p. 106 – 108° (hexane/Et_2O). IR (KBr): 3153, 1647, 1591. ^{1}H-NMR (500 MHz): 2.44 (*d*, *J* = 3.4, 1 H); 5.74 (*dd*, *J* = 6.3, 3.4, 1 H); 6.26 (*dd*, *J* = 16.0, 6.3, 1 H); 6.76 (*d*, *J* = 16.0, 1 H); 7.26 (*td*, *J* = 7.4, 1.1, 1 H); 7.31 (*t*, *J* = 7.4, 2 H); 7.38 (*dd*, *J* = 7.4, 1.1, 2 H); 7.61 (*d*, *J* = 4.6, 1 H); 8.52 (*d*, *J* = 4.6, 1 H); 8.54 (*s*, 1 H). Anal. calc. for $C_{14}H_{12}ClNO$ (245.70): C 68.44, H 4.92, N 5.70; found: C 68.38, H 5.16, N 5.67.

(2E)-1-(3-Chloropyridin-4-yl)-3-(4-methoxyphenyl)prop-2-en-1-ol (**6b**). Yellow solid. M.p. 123 – 125° (dec.; hexane/Et_2O). IR (KBr): 3450, 1607. ^{1}H-NMR (500 MHz): 2.32 (br. *s*, 1 H); 3.80 (*s*, 3 H); 5.70 (*d*, *J* = 6.9, 1 H), 6.11 (*dd*, *J* = 16.0, 6.9, 1 H); 6.69 (*d*, *J* = 16.0, 1 H); 6.85 (*d*, *J* = 8.6, 2 H); 7.31 (*d*, *J* = 8.6, 2 H); 7.61 (*d*, *J* = 5.2, 1 H); 8.52 (*d*, *J* = 5.2, 1 H); 8.54 (*s*, 1 H). Anal. calc. for $C_{15}H_{14}ClNO_2$ (275.73): C 65.34, H 5.12, N 5.08; found: C 65.09, H 5.14, N 5.03.

(2E)-1-(3-Chloropyridin-4-yl)but-2-en-1-ol (**6c**). White solid. M.p. 57 – 59° (hexane). IR (KBr): 3179, 1400. ^{1}H-NMR (500 MHz): 1.72 (*d*, *J* = 6.9, 3 H); 2.41 (*s*, 1 H); 5.50 (*d*, *J* = 6.9, 1 H); 5.57 (*ddd*, *J* = 14.7, 6.9, 1.1, 1 H); 5.85 (*dq*, *J* = 14.7, 6.9, 1 H); 7.54 (*d*, *J* = 4.6, 1 H); 8.48 (*d*, *J* = 4.6, 1 H); 8.50 (*s*, 1 H). Anal. calc. for $C_9H_{10}ClNO$ (183.63): C 58.86, H 5.49, N 7.63; found: C 58.69, H 5.61, N 7.52.

(2E)-1-(4-Chloropyridin-3-yl)-3-phenylprop-2-en-1-ol (**10a**). Yellow solid. M.p. 99 – 101° (hexane/Et_2O). IR (KBr): 3207, 1648, 1579. ^{1}H-NMR (500 MHz): 2.61 (*d*, *J* = 2.9, 1 H); 5.79 (*dd*, *J* = 6.3, 2.9, 1 H); 6.34 (*dd*, *J* = 16.0, 6.3, 1 H); 6.75 (*d*, *J* = 16.0, 1 H); 7.26 (*t*, *J* = 7.4, 2 H); 7.29 – 7.33 (*m*, 2 H); 7.38 (*dd*, *J* = 8.6, 1.7, 2 H); 8.43 (*d*, *J* = 5.2, 1 H); 8.83 (*s*, 1 H). Anal. calc. for $C_{14}H_{12}ClNO$ (245.70): C 68.44, H 4.92, N 5.70; found: C 68.37, H 5.04, N 5.68.

(2E)-3-(4-Chlorophenyl)-1-(4-chloropyridin-3-yl)prop-2-en-1-ol (**10b**). Pale-yellow solid. M.p. 114 – 116° (hexane/Et_2O). IR (KBr): 3390, 1652, 1579. ^{1}H-NMR (500 MHz): 2.52 (*d*, *J* = 3.4, 1 H); 5.80 (*dd*, *J* = 6.3, 3.4, 1 H); 6.32 (*dd*, *J* = 15.5, 6.3, 1 H); 6.71 (*d*, *J* = 15.5, 1 H); 7.28 (*d*, *J* = 8.6, 2 H); 7.30 (*d*, *J* = 5.7, 2 H); 7.31 (*d*, *J* = 8.6, 1 H); 8.44 (*d*, *J* = 5.7, 1 H); 8.82 (*s*, 1 H). Anal. calc. for $C_{14}H_{11}Cl_2NO$ (280.15): C 60.02, H 3.96, N 5.00; found: C 59.87, H 3.76, N 5.97.

(2E)-1-(4-Chloropyridin-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-ol (**10c**). Pale-yellow solid. M.p. 125 – 127° (hexane/Et_2O). IR (KBr): 3425, 1639, 1606. ^{1}H-NMR (500 MHz): 2.39 (*s*, 1 H); 3.80 (*s*, 3 H); 5.76 (*d*, *J* = 6.9, 1 H); 6.20 (*dd*, *J* = 16.0, 6.9, 1 H); 6.68 (*d*, *J* = 16.0, 1 H); 6.85 (*d*, *J* = 9.2, 2 H); 7.29 (*d*, *J* = 5.7, 1 H); 7.32 (*d*, *J* = 9.2, 2 H); 8.43 (*d*, *J* = 5.7, 1 H); 8.84 (*s*, 1 H). Anal. calc. for $C_{15}H_{14}ClNO_2$ (275.73): C 65.34, H 5.12, N 5.08; found: C 65.29, H 5.19, N 5.09.

*(2*E*)-1-(4-Chloropyridin-3-yl)-2-methyl-3-phenylprop-2-en-1-ol* (**10d**). Pale-yellow solid. M.p. 140–142° (hexane). IR (KBr): 3421, 1653, 1579. ^{1}H-NMR (500 MHz): 1.81 (*d*, *J* = 1.1, 3 H); 2.36 (*d*, *J* = 3.4, 1 H); 5.68 (*d*, *J* = 3.4, 1 H); 6.78 (*s*, 1 H); 7.22–7.36 (*m*, 6 H); 8.44 (*d*, *J* = 5.2, 1 H); 8.84 (*s*, 1 H). Anal. calc. for $C_{15}H_{14}ClNO$ (259.73): C 69.36, H 5.43, N 5.39; found: C 69.30, H 5.69, N 5.32.

*(2*E*)-1-(4-Chloropyridin-3-yl)but-2-en-1-ol* (**10e**). Pale-yellow oil. R_f (AcOEt/hexane 1:1) 0.38. IR (neat): 3233, 1671, 1579. ^{1}H-NMR (500 MHz): 1.73 (*dd*, *J* = 6.9, 1.7, 3 H); 2.29 (*d*, *J* = 3.4, 1 H); 5.56 (br. *d*, *J* = 6.9, 1 H); 5.67 (*ddd*, *J* = 15.5, 6.9, 1.7, 1 H); 5.84 (*dq*, *J* = 15.6, 6.9, 1 H); 7.28 (*d*, *J* = 5.7, 1 H); 8.40 (*d*, *J* = 5.7, 1 H); 8.76 (*s*, 1 H). Anal. calc. for $C_9H_{10}ClNO$ (183.63): C 58.86, H 5.49, N 7.63; found: C 58.63, H 5.33, N 7.41.

1-(4-Chloropyridin-3-yl)-3-methylbut-2-en-1-ol (**10f**). Yellow oil. R_f (AcOEt/hexane 1:2) 0.17. IR (neat): 3330, 1673, 1579. ^{1}H-NMR (500 MHz): 1.76 (*s*, 3 H); 1.85 (*s*, 3 H); 2.16 (*d*, *J* = 2.9, 1 H); 5.32 (*d*, *J* = 8.8, 1 H); 5.79 (*dd*, *J* = 8.8, 2.9, 1 H); 7.26 (*d*, *J* = 4.9, 1 H); 8.40 (*d*, *J* = 4.9, 1 H); 8.82 (*s*, 1 H). Anal. calc. for $C_{10}H_{12}ClNO$ (197.66): C 60.76, H 6.12, N 7.09; found: C 60.65, H 6.39, N 7.09.

*(2*E*)-1-(2-Chloropyridin-3-yl)-3-phenylprop-2-en-1-one* (**3a**; *Representative Procedure*). A soln. of **2a** (0.28 g, 1.1 mmol) in acetone (4 ml) containing MnO_2 (1.1 g, 13 mmol) was stirred for 30 min at r.t. The mixture was filtered, and the filtrate was concentrated by evaporation. The residue was purified by CC (SiO_2) to give **3a** (0.26 g, 95%). Pale-yellow oil. R_f (AcOEt/hexane 1:7) 0.13. IR (neat): 1651, 1617, 1397. ^{1}H-NMR (400 MHz): 7.18 (*d*, *J* = 15.6, 1 H); 7.37–7.50 (*m*, 4 H); 7.52 (*d*, 15.6, 1 H); 7.58 (*dd*, *J* = 7.8, 2.0, 2 H); 7.84 (*dd*, *J* = 7.8, 2.0, 1 H); 8.54 (*dd*, *J* = 4.9, 2.0, 1 H). Anal. calc. for $C_{14}H_{10}ClNO$ (243.69): C 69.00, H 4.14, N 5.75; found: C 69.01, H 4.15, N 5.65.

*(2*E*)-3-(4-Chlorophenyl)-1-(2-chloropyridin-3-yl)prop-2-en-1-one* (**3b**). Yellow solid. M.p. 149–151° (hexane). IR (KBr): 1668, 1603, 1390. ^{1}H-NMR (500 MHz): 7.15 (*d*, *J* = 16.0, 1 H); 7.38–7.41 (*m*, 3 H); 7.48 (*d*, 16.0, 1 H); 7.52 (*d*, *J* = 8.0, 2 H); 7.84 (*dd*, *J* = 7.4, 1.7, 1 H); 8.54 (*dd*, *J* = 4.7, 1.7, 1 H). Anal. calc. for $C_{14}H_9Cl_2NO$ (278.13): C 60.46, H 3.26, N 5.04; found: C 60.28, H 3.50, N 4.96.

*(2*E*)-1-(2-Chloropyridin-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-one* (**3c**). Yellow solid. M.p. 114–116° (hexane). IR (KBr): 1655, 1595, 1396. ^{1}H-NMR (500 MHz): 3.86 (*s*, 3 H); 6.93 (*d*, *J* = 9.2, 2 H); 7.04 (*d*, *J* = 16.0, 1 H); 7.37 (*dd*, *J* = 7.4, 5.2, 1 H); 7.45 (*d*, *J* = 16.0, 1 H); 7.54 (*d*, *J* = 9.2, 2 H); 7.82 (*dd*, *J* = 7.4, 1.7, 1 H); 8.52 (*dd*, *J* = 5.2, 1.7, 1 H). Anal. calc. for $C_{15}H_{12}ClNO_2$ (273.71): C 65.82, H 4.42, N 5.12; found: C 65.72, H 4.42, N 5.09.

*(2*E*)-1-(2-Chloropyridin-3-yl)-2-methyl-3-phenylprop-2-en-1-one* (**3d**). Pale-yellow solid. M.p. 120–122° (hexane). IR (KBr): 1646, 1619, 1396. ^{1}H-NMR (500 MHz): 2.27 (*d*, *J* = 1.1, 3 H); 7.09 (*q*, *J* = 1.1, 1 H); 7.35–7.43 (*m*, 6 H); 7.70 (*dd*, *J* = 7.4, 1.7, 1 H); 8.51 (*dd*, *J* = 5.1, 1.7, 1 H). Anal. calc. for $C_{15}H_{12}ClNO_2$ (257.71): C 69.91, H 4.69, N 5.43; found: C 69.66, H 4.70, N 5.46.

*(2*E*)-1-(2-Chloropyridin-3-yl)but-2-en-1-one* (**3e**). Pale-yellow oil. R_f (AcOEt/hexane 1:7) 0.23. IR (neat): 1660, 1622, 1397. ^{1}H-NMR (500 MHz): 1.99 (*dd*, *J* = 6.9, 1.7, 3 H); 6.53 (*dq*, *J* = 16.2, 1.7, 1 H); 6.78 (*dq*, *J* = 16.2, 6.9, 1 H); 7.33 (*dd*, *J* = 7.4, 5.2, 1 H); 7.71 (*dd*, *J* = 7.4, 1.7, 1 H); 8.49 (*dd*, *J* = 5.2, 1.7, 1 H). Anal. calc. for C_9H_8ClNO (181.62): C 59.52, H 4.44, N 7.71; found: C 59.48, H 4.48, N 7.47.

1-(2-Chloropyridin-3-yl)-3-methylbut-2-en-1-one (**3f**). Pale-yellow oil. R_f (AcOEt/hexane 1:3) 0.39. IR (neat): 1671, 1609, 1396. ^{1}H-NMR (400 MHz): 2.02 (*d*, *J* = 1.0, 3 H); 2.27 (*s*, 3 H); 6.48 (*q*, *J* = 1.0, 1 H); 7.32 (*dd*, *J* = 7.3, 4.9, 1 H); 7.79 (*dd*, *J* = 7.3, 2.0, 1 H); 8.46 (*dd*, *J* = 4.9, 2.0, 1 H). Anal. calc. for $C_{10}H_{10}ClNO$ (195.65): C 61.39, H 5.15, N 7.16; found: C 61.20, H 5.06, N 7.07.

*(2*E*)-1-(3-Chloropyridin-4-yl)-3-phenylprop-2-en-1-one* (**7a**). Pale-yellow solid. M.p. 96–98° (hexane). IR (KBr) 1651, 1619. ^{1}H-NMR (500 MHz): 7.07 (*d*, *J* = 16.0, 1 H); 7.35 (*d*, *J* = 4.6, 1 H); 7.41–7.46 (*m*, 4 H); 7.57 (*dd*, *J* = 7.4, 1.7, 2 H); 8.63 (*d*, *J* = 4.6, 1 H); 8.72 (*s*, 1 H). Anal. calc. for $C_{14}H_{10}ClNO$ (243.69): C 69.00, H 4.14, N 5.75; found: C 68.90, H 4.23, N 5.53.

*(2*E*)-1-(3-Chloropyridin-4-yl)-3-(4-methoxyphenyl)prop-2-en-1-one* (**7b**). Yellow solid. M.p. 109–111° (hexane). IR (KBr): 1634, 1623, 1603. ^{1}H-NMR (400 MHz): 3.86 (*s*, 3 H); 6.93 (*d*, *J* = 8.8, 2 H); 6.94 (*d*, *J* = 16.6, 1 H); 7.34 (*d*, *J* = 4.9, 1 H); 7.37 (*d*, *J* = 16.6, 1 H); 7.53 (*d*, *J* = 8.8, 2 H); 8.62 (*d*, *J* = 4.9, 1 H); 8.71 (*s*, 1 H). Anal. calc. for $C_{15}H_{12}ClNO_2$ (273.71): C 65.82, H 4.42, N 5.12; found: C 65.71, H 4.51, N 4.92.

*(2*E*)-1-(3-Chloropyridin-4-yl)but-2-en-1-one* (**7c**). Pale-yellow oil. R_f (AcOEt/hexane 1:3) 0.30. IR (neat): 1663, 1638, 1622. ^{1}H-NMR (500 MHz): 2.00 (*dd*, *J* = 6.9, 1.1, 3 H); 6.45 (*dd*, *J* = 15.5, 1.1, 1 H);

6.72 (*dq*, *J* = 15.5, 6.9, 1 H); 7.23 (*d*, *J* = 5.2, 1 H); 8.57 (*d*, *J* = 5.2, 1 H); 8.67 (*s*, 1 H). Anal. calc. for C_9H_8ClNO (181.62): C 59.52, H 4.44, N 7.71; found: C 59.43, H 4.49, N 7.60.

*(2*E*)-1-(4-Chloropyridin-3-yl)-3-phenylprop-2-en-1-one* (**11a**). This compound was rather unstable, so it had to be used in the next step as soon as possible after isolation. Pale-yellow oil. R_f (AcOEt/hexane 1:3) 0.40. IR (neat): 1642, 1620. ^{1}H-NMR (500 MHz): 7.15 (*d*, *J* = 16.0, 1 H); 7.42–7.45 (*m*, 4 H); 7.50 (*d*, *J* = 16.0, 1 H); 7.59 (*dd*, *J* = 8.0, 1.7, 2 H); 8.62 (*d*, *J* = 5.2, 1 H); 8.71 (*s*, 1 H).

*(2*E*)-3-(4-Chlorophenyl)-1-(4-chloropyridin-3-yl)prop-2-en-1-one* (**11b**). White solid. M.p. 114–116° (dec.; hexane/Et_2O). IR (KBr): 1670, 1630, 1605. ^{1}H-NMR (500 MHz): 7.13 (*d*, *J* = 16.0, 1 H); 7.40 (*d*, *J* = 8.6, 2 H); 7.44 (*d*, *J* = 5.2, 1 H); 7.48 (*d*, *J* = 16.0, 1 H); 7.52 (*d*, *J* = 8.6, 2 H); 8.62 (*d*, *J* = 5.2, 1 H); 8.70 (*s*, 1 H). Anal. calc. for $C_{14}H_9Cl_2NO$ (278.13): C 60.46, H 3.26, N 5.04; found: C 60.36, H 3.20, N 4.87.

*(2*E*)-1-(4-Chloropyridin-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-one* (**11c**). Pale-yellow solid. M.p. 114–116° (hexane). IR (KBr): 1655, 1594. ^{1}H-NMR (500 MHz): 3.86 (*s*, 3 H); 6.94 (*d*, *J* = 9.2, 2 H); 7.02 (*d*, *J* = 15.5, 1 H); 7.43 (*d*, *J* = 5.2, 1 H); 7.45 (*d*, *J* = 15.5, 1 H); 7.54 (*d*, *J* = 9.2, 2 H); 8.60 (*d*, *J* = 5.2, 1 H); 8.68 (*s*, 1 H). Anal. calc. for $C_{15}H_{12}ClNO_2$ (273.71): C 65.82, H 4.42, N 5.12; found: C 65.71, H 4.28, N 5.01.

*(2*E*)-1-(4-Chloropyridin-3-yl)-2-methyl-3-phenylprop-2-en-1-one* (**11d**). Pale-yellow oil. R_f (AcOEt/hexane 1:3) 0.33. IR (neat): 1658, 1619. ^{1}H-NMR (500 MHz): 2.27 (*d*, *J* = 1.1, 3 H); 7.11 (*q*, *J* = 1.1, 1 H); 7.35–7.43 (*m*, 6 H); 8.57 (*s*, 1 H); 8.60 (*d*, *J* = 5.2, 1 H). Anal. calc. for $C_{15}H_{12}ClNO$ (257.71): C 69.91, H 4.69, N 5.43; found: C 69.85, H 4.72, N 5.31.

*(2*E*)-1-(4-Chloropyridin-3-yl)but-2-en-1-one* (**11e**). Pale-yellow oil. R_f (AcOEt/hexane 1:2) 0.38. IR (neat): 1659, 1622. ^{1}H-NMR (500 MHz): 2.00 (*dd*, *J* = 6.9, 1.1, 3 H); 6.53 (*dq*, *J* = 15.5, 1.1, 1 H); 6.78 (*dq*, *J* = 15.5 6.9, 1 H); 7.39 (*d*, *J* = 5.2, 1 H); 8.57 (*d*, *J* = 5.2, 1 H); 8.58 (*s*, 1 H). Anal. calc. for C_9H_8ClNO (181.62): C 59.52, H 4.44, N 7.71; found: C 59.42, H 4.50, N 7.67.

1-(4-Chloropyridin-3-yl)-3-methylbut-2-en-1-one (**11f**). Pale-yellow oil. R_f (AcOEt/hexane 1:1) 0.40. IR (neat): 1669, 1610. ^{1}H-NMR (500 MHz): 2.03 (*s*, 3 H); 2.28 (*s*, 3 H); 6.47 (*s*, 1 H); 7.36 (*d*, *J* = 5.2, 1 H); 8.54 (*d*, *J* = 5.2, 1 H); 8.67 (*s*, 1 H). Anal. calc. for $C_{10}H_{10}ClNO$ (195.65): C 61.39, H 5.15, N 7.16; found: C 61.26, H 5.17, N 7.07.

*2,3-Dihydro-2-phenyl-4*H*-thiopyrano[2,3-*b*]pyridin-4-one* (**4a**; *Representative Procedure*). A mixture of **3a** (0.17 g, 0.70 mmol) in DMF (3 ml) containing NaSH·*n* H_2O (70% as NaSH; 62 mg, 0.77 mmol) was stirred at 0° until disappearance of the starting material had been confirmed by TLC analyses (SiO_2; within 30 min, *ca.* 1.5 h for **8**). Sat. aq. NH_4Cl (10 ml) was added, and the mixture was extracted with AcOEt (3 × 10 ml). The combined extracts were washed with brine (10 ml), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by CC (SiO_2) to give **4a** (0.13 g, 80%). Yellow oil. R_f (THF/hexane 1:5) 0.43. IR (neat): 1684, 1396. ^{1}H-NMR (500 MHz): 3.23 (*dd*, *J* = 16.0, 2.9, 1 H); 3.35 (*dd*, *J* = 16.0, 12.6, 1 H); 4.78 (*dd*, *J* = 12.6, 2.9, 1 H); 7.17 (*dd*, *J* = 7.4, 4.6, 1 H); 7.34–7.46 (*m*, 5 H); 8.35 (*dd*, *J* = 7.4, 1.7, 1 H); 8.58 (*dd*, *J* = 4.6, 1.7, 1 H). ^{13}C-NMR (100 MHz): 44.07; 45.77; 120.22; 126.88; 127.45; 128.61; 129.10; 136.55; 137.77; 153.88; 164.06; 193.95. EI-MS: 241 (100, M^+). Anal. calc. for $C_{14}H_{11}NOS$ (241.31): C 69.68, H 4.59, N 5.80; found: C 69.62, H 4.54, N 5.71.

*2-(4-Chlorophenyl)-2,3-dihydro-4*H*-thiopyrano[2,3-*b*]pyridin-4-one* (**4b**). Yellow solid. M.p. 108–110° (hexane). IR (KBr): 1683, 1396. ^{1}H-NMR (500 MHz): 3.21 (*dd*, *J* = 16.0, 2.9, 1 H); 3.30 (*dd*, *J* = 16.0, 12.6, 1 H); 4.75 (*dd*, *J* = 12.6, 2.9, 1 H); 7.17 (*dd*, *J* = 8.0, 4.6, 1 H); 7.37 (*d*, *J* = 9.2, 2 H); 7.38 (*d*, *J* = 9.2, 2 H); 8.34 (*dd*, *J* = 8.0, 2.3, 1 H); 8.58 (*dd*, *J* = 4.6, 2.3, 1 H). ^{13}C-NMR (100 MHz): 43.33; 45.59; 120.40; 126.85; 128.82; 129.31; 134.50; 136.26; 136.61; 153.96; 163.60; 193.56. EI-MS: 275 (100, M^+). Anal. calc. for $C_{14}H_{10}ClNOS$ (275.75): C 60.98, H 3.66, N 5.08; found: C 60.73, H 3.62, N 5.14.

*2,3-Dihydro-2-(4-methoxyphenyl)-4*H*-thiopyrano[2,3-*b*]pyridin-4-one* (**4c**). Yellow solid. M.p. 104–106° (hexane/Et_2O). IR (KBr): 1683, 1395. ^{1}H-NMR (500 MHz): 3.20 (*dd*, *J* = 16.0, 2.9, 1 H); 3.31 (*dd*, *J* = 16.0, 13.2, 1 H); 3.82 (*s*, 3 H); 4.73 (*dd*, *J* = 13.2, 2.9, 1 H); 6.92 (*d*, *J* = 9.2, 2 H); 7.15 (*dd*, *J* = 8.0, 5.2, 1 H); 7.36 (*d*, *J* = 9.2, 2 H); 8.33 (*dd*, *J* = 8.0, 2.3, 1 H); 8.57 (*dd*, *J* = 5.2, 2.3, 1 H). ^{13}C-NMR (100 MHz): 43.50; 45.99; 55.30; 114.42; 120.15; 128.64; 129.66; 136.54; 136.57; 153.86; 159.68; 164.20; 194.18. EI-MS: 271 (100, M^+). Anal. calc. for $C_{15}H_{13}NO_2S$ (271.33): C 66.40, H 4.83, N 5.16; found: C 66.34, H 4.85, N 5.03.

trans-*2,3-Dihydro-3-methyl-2-phenyl-4*H*-thiopyrano[2,3-*b*]pyridin-4-one* (**4d**). Pale-yellow oil. R_f (AcOEt/hexane 1:5) 0.34. IR (neat): 1683, 1398. ^{1}H-NMR (500 MHz): 1.12 (*d*, *J* = 6.9, 3 H); 3.24–

3.31 (*m*, 1 H); 4.42 (*d*, *J* = 12.0, 1 H); 7.15 (*dd*, *J* = 8.0, 4.6, 1 H); 7.33 – 7.44 (*m*, 5 H); 8.30 (*dd*, *J* = 8.0, 1.7, 1 H); 8.56 (*dd*, *J* = 4.6, 1.7, 1 H). ^{13}C-NMR (100 MHz): 12.86; 47.65; 50.34; 120.10; 126.67; 128.24; 128.55; 129.05; 136.96; 137.32; 153.70; 163.03; 196.14. EI-MS: 255 (100, M^+). Anal. calc. for $C_{15}H_{13}NOS$ (255.33): C 70.56, H 5.13, N 5.49; found: C 70.39, H 5.27, N 5.26.

*2,3-Dihydro-2-methyl-4*H-*thiopyrano[2,3-*b*]pyridin-4-one* (**4e**). White solid. M.p. 64 – 66° (hexane). IR (KBr): 1683, 1399. ^{1}H-NMR (500 MHz): 1.49 (*d*, *J* = 6.9, 3 H); 2.81 (*dd*, *J* = 16.0, 11.5, 1 H); 3.05 (*dd*, *J* = 16.0, 3.4, 1 H); 3.65 – 3.72 (*m*, 1 H); 7.13 (*dd*, *J* = 8.0, 4.6, 1 H); 8.29 (*dd*, *J* = 8.0, 2.3, 1 H); 8.55 (*dd*, *J* = 4.6, 2.3, 1 H). ^{13}C-NMR (125 MHz): 20.38; 35.02; 46.68; 119.97; 126.84; 136.32; 153.75; 163.90; 194.33. EI-MS: 179 (100, M^+). Anal. calc. for C_9H_9NOS (179.24): C 60.31, H 5.06, N 7.81; found: C 60.05, H 4.94, N 7.85.

*2,3-Dihydro-2,2-dimethyl-4*H-*thiopyrano[2,3-*b*]pyridin-4-one* (**4f**). White solid. M.p. 76 – 79° (hexane). IR (KBr): 1685, 1396. ^{1}H-NMR (500 MHz): 1.51 (*s*, 6 H); 2.91 (*s*, 2 H); 7.13 (*dd*, *J* = 8.0, 4.6, 1 H); 8.30 (*dd*, *J* = 8.0, 1.7, 1 H); 8.57 (*dd*, *J* = 4.6, 1.7, 1 H). ^{13}C-NMR (125 MHz): 28.74; 43.73; 52.96; 119.78; 126.16; 136.10; 154.00; 163.79; 194.66. EI-MS: 193 (100, M^+). Anal. calc. for $C_{10}H_{11}NOS$ (193.27): C 62.15, H 5.74, N 7.25; found: C 61.95, H 5.74, N 7.04.

*2,3-Dihydro-2-phenyl-4*H-*thiopyrano[2,3-*c*]pyridin-4-one* (**8a**). Yellow solid. M.p. 155 – 156° (hexane/Et_2O). IR (KBr): 1688. ^{1}H-NMR (500 MHz): 3.26 (*dd*, *J* = 16.6, 2.9, 1 H); 3.36 (*dd*, *J* = 16.6, 13.1, 1 H); 4.75 (*dd*, *J* = 13.1, 2.9, 1 H); 7.35 – 7.44 (*m*, 5 H); 7.86 (*d*, *J* = 5.2, 1 H); 8.49 (*d*, *J* = 5.2, 1 H); 8.65 (*s*, 1 H). ^{13}C-NMR (125 MHz): 45.54; 46.46; 120.68; 127.36; 128.80; 129.13; 135.05; 137.20; 137.63; 146.37; 149.31; 193.80. EI-MS: 241 (100, M^+). Anal. calc. for $C_{14}H_{11}NOS$ (241.31): C 69.68, H 4.59, N 5.80; found: C 69.68, H 4.75, N 5.78.

*2,3-Dihydro-2-(4-methoxyphenyl)-4*H-*thiopyrano[2,3-*c*]pyridin-4-one* (**8b**). Yellow solid. M.p. 131 – 133° (hexane). IR (KBr): 1685, 1613. ^{1}H-NMR (400 MHz): 3.23 (*dd*, *J* = 16.6, 2.9, 1 H); 3.33 (*dd*, *J* = 16.6, 13.2, 1 H); 3.82 (*s*, 3 H); 4.71 (*dd*, *J* = 13.2, 2.9, 1 H); 6.92 (*d*, *J* = 8.3, 2 H); 7.35 (*d*, *J* = 8.3, 2 H); 7.86 (*d*, *J* = 4.9, 1 H); 8.48 (*d*, *J* = 4.9, 1 H); 8.64 (*s*, 1 H). ^{13}C-NMR (125 MHz): 45.01; 46.68; 55.32; 114.43; 120.67; 128.56; 129.59; 135.05; 137.38; 146.29; 149.29; 159.80; 194.01. EI-MS: 271 (100, M^+). Anal. calc. for $C_{15}H_{13}NO_2S$ (271.33): C 66.40, H 4.83, N 5.16; found: C 66.30, H 5.05, N 5.10.

*2,3-Dihydro-2-methyl-4*H-*thiopyrano[2,3-*c*]pyridin-4-one* (**8c**). Pale-yellow oil. R_f (AcOEt/hexane 1:3) 0.33. IR (neat): 1694. ^{1}H-NMR (500 MHz): 1.49 (*d*, *J* = 6.9, 3 H); 2.81 (*dd*, *J* = 16.6, 11.5, 1 H); 3.07 (*dd*, *J* = 16.6, 2.9, 1 H); 3.65 – 3.72 (*m*, 1 H); 7.80 (*d*, *J* = 5.2, 1 H); 8.44 (*d*, *J* = 5.2, 1 H); 8.62 (*s*, 1 H). ^{13}C-NMR (125 MHz): 20.38; 36.62; 47.51; 120.49; 134.97; 136.98; 146.05; 149.55; 193.96. EI-MS: 179 (100, M^+). Anal. calc. for C_9H_9NOS (179.24): C 60.31, H 5.06, N 7.81; found: C 60.22, H 5.10, N 7.75.

*2,3-Dihydro-2-phenyl-4*H-*thiopyrano[3,2-*c*]pyridin-4-one* (**12a**). Yellow oil. R_f (AcOEt/hexane, 1:3) 0.33. IR (neat): 1686. ^{1}H-NMR (500 MHz): 3.21 (*dd*, *J* = 16.6, 2.9, 1 H); 3.33 (*dd*, *J* = 16.6, 13.2, 1 H); 4.78 (*dd*, *J* = 13.2, 2.9, 1 H); 7.19 (*d*, *J* = 4.6, 1 H); 7.35 – 7.44 (*m*, 5 H); 8.46 (*d*, *J* = 4.6, 1 H); 9.18 (*s*, 1 H). ^{13}C-NMR (125 MHz): 45.33; 46.01; 121.28; 125.28; 127.38; 128.86; 129.18; 137.38; 150.39; 152.08; 152.27; 193.45. EI-MS: 241 (100, M^+). Anal. calc. for $C_{14}H_{11}NOS$ (241.31): C 69.68, H 4.59, N 5.80; found: C 69.43, H 4.83, N 5.81.

*2-(4-Chlorophenyl)-2,3-dihydro-4*H-*thiopyrano[3,2-*c*]pyridin-4-one* (**12b**). Yellow solid. M.p. 147 – 149° (hexane). IR (KBr): 1691. ^{1}H-NMR (500 MHz): 3.19 (*dd*, *J* = 16.0, 2.9, 1 H); 3.29 (*dd*, *J* = 16.0, 12.6, 1 H); 4.75 (*dd*, *J* = 12.6, 2.9, 1 H); 7.19 (*d*, *J* = 5.2, 1 H); 7.35 (*d*, *J* = 8.6, 2 H); 7.38 (*d*, *J* = 8.6, 2 H); 8.47 (*d*, *J* = 5.2, 1 H); 9.17 (*s*, 1 H). ^{13}C-NMR (125 MHz): 44.62; 45.86; 121.26; 125.19; 128.75; 129.40; 134.78; 135.89; 150.42; 151.78; 152.21; 193.01. EI-MS: 275 (100, M^+). Anal. calc. for $C_{14}H_{10}ClNOS$ (275.75): C 60.98, H 3.66, N 5.08; found: C 60.99, H 3.69, N 5.02.

*2,3-Dihydro-2-(4-methoxyphenyl)-4*H-*thiopyrano[3,2-*c*]pyridin-4-one* (**12c**). Yellow solid. M.p. 130 – 132° (hexane). IR (KBr): 1685, 1610. ^{1}H-NMR (400 MHz): 3.19 (*dd*, *J* = 16.0, 2.9, 1 H); 3.31 (*dd*, *J* = 16.0, 12.7, 1 H); 3.83 (*s*, 3 H); 4.74 (*dd*, *J* = 12.7, 2.9, 1 H); 6.92 (*d*, *J* = 8.8, 2 H); 7.18 (*d*, *J* = 5.4, 1 H); 7.33 (*d*, *J* = 8.8, 2 H); 8.46 (*d*, *J* = 5.4, 1 H); 9.17 (*s*, 1 H). ^{13}C-NMR (125 MHz): 44.78; 46.23; 55.30; 114.48; 121.22; 125.28; 128.59; 129.31; 150.37; 152.03; 152.43; 159.84; 193.67. EI-MS: 271 (100, M^+). Anal. calc. for $C_{15}H_{13}NO_2S$ (271.33): C 66.40, H 4.83, N 5.16; found: C 66.30, H 4.83, N 5.11.

trans-*2,3-Dihydro-3-methyl-2-phenyl-4*H-*thiopyrano[3,2-*c*]pyridin-4-one* (**12d**). Pale-yellow solid. M.p. 160 – 162° (hexane/Et_2O). IR (KBr): 1678. ^{1}H-NMR (500 MHz): 1.12 (*d*, *J* = 6.9, 3 H); 3.29 (*dq*, *J* = 12.0, 6.9, 1 H); 4.43 (*d*, *J* = 12.0, 1 H); 7.12 (*d*, *J* = 5.2, 1 H); 7.32 – 7.42 (*m*, 5 H); 8.44 (*d*, *J* = 5.2, 1 H); 9.13

(*s*, 1 H). ^{13}C-NMR (125 MHz): 12.62; 47.90; 51.38; 120.71; 125.12; 128.14; 128.78; 129.13; 137.00; 150.67; 151.34; 151.83; 195.66. EI-MS: 255 (100, M^+). Anal. calc. for $C_{15}H_{13}NOS$ (255.33): C 70.56, H 5.13, N 5.49; found: C 70.46, H 5.28, N 5.57.

*2,3-Dihydro-2-methyl-4*H-*thiopyrano[3,2-*c*]pyridin-4-one* (**12e**). Pale-yellow oil. R_f (AcOEt/hexane 1:2) 0.38. IR (neat): 1686. ^{1}H-NMR (500 MHz): 1.48 (*d*, *J* = 6.9, 3 H); 2.78 (*dd*, *J* = 16.0, 10.9, 1 H); 3.04 (*dd*, *J* = 16.0, 2.9, 1 H); 3.66–3.73 (*m*, 1 H); 7.16 (*d*, *J* = 5.2, 1 H); 8.42 (*d*, *J* = 5.2, 1 H); 9.11 (*s*, 1 H). ^{13}C-NMR (125 MHz): 20.36; 36.40; 46.94; 121.61; 125.25; 150.11; 151.87; 152.07; 193.63. EI-MS: 179 (100, M^+). Anal. calc. for C_9H_9NOS (179.24): C 60.31, H 5.06, N 7.81; found: C 60.15, H 5.05, N 7.73.

*2,3-Dihydro-2,2-dimethyl-4*H-*thiopyrano[3,2-*c*]pyridin-4-one* (**12f**). Pale-yellow oil. R_f (AcOEt/hexane 1:2) 0.30. IR (neat): 1686. ^{1}H-NMR (500 MHz): 1.50 (*s*, 6 H); 2.89 (*s*, 2 H); 7.14 (*d*, *J* = 5.2, 1 H); 8.44 (*d*, *J* = 5.2, 1 H); 9.13 (*s*, 1 H). ^{13}C-NMR (125 MHz): 28.61; 45.43; 53.15; 121.70; 124.56; 149.88; 151.70; 152.06; 194.03. EI-MS: 193 (100, M^+). Anal. calc. for $C_{10}H_{11}NOS$ (193.27): C 62.15, H 5.74, N 7.25; found: C 62.16, H 5.70, N 7.11.

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