Synthesis of 4-Aryl-1,7-naphthyridine-2(1*H*)-thiones by the Electrocyclic Reaction of 4-(1-Arylalk-1-enyl)-3-isothiocyanatopyridines Generated *in situ* from the Corresponding Isocyanides

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A convenient synthis for 4-substituted and 3,4-disubstituted 1,7-naphthyridine-2(1*H*)-thiones **7** has been developed. The method is based on the electrocyclic reaction of 4-(1-arylalk-1-enyl)-3-isothiocyanatopyridines **6**, generated *in situ* by the treatment of the respective isocyanides **5** with S_8 in the presence of a catalytic amount of selenium. The isocyanides **5** can be easily prepared from commercially available pyridin-3-amine by conventional organic reactions.

Introduction. – We have previously reported the synthesis of 4-arylquinoline-2(1*H*)-thiones by the electrocyclic reaction of 1-(1-arylalk-1-enyl)-2-isothiocyanatobenzenes, generated *in situ* from the respective isocyanides [1]. Accordingly, we became interested in investigating the possibility of preparing 1,7-naphthyridine-2(1*H*)-thiones employing a similar sequence, and envisioned that 4-(1-arylalk-1-enyl)-3-isocyanopyridines **5** could be prepared from commercially available pyridin-3-amine, and they would give 4-aryl-1,7-naphthyridine-2(1*H*)-thiones **7** *via* the corresponding isothiocyanates **6**. A survey of the literature provided only one compound with the 1,7-naphthyridine-2(1*H*)-thione skeleton [2]. Here, we report the results of our investigation, which led to the first practical synthesis of 1,7-naphthyridine-2(1*H*)-thiones. This class of naphthyridines may be of biological interest, because some compounds with the 1,7-naphthyridin-2(1*H*)-one skeleton display biological activities [3].

Results and Discussion. – Our synthetic route to 1,7-naphthyridine-2(1*H*)-thiones **7** starting from 4-aroylpyridine-3-amines **1** is outlined in the *Scheme*. The preparation of 4-(1-arylalk-1-enyl)-3-isocyanopyridines **5**, precursors for the synthesis of **7**, was conducted in a four-step sequence from **1**. These amines **1** could be easily prepared from commercially available pyridin-3-amine according to the procedure described in [4], and they were reacted with alkylmagnesium bromides to give the corresponding amino alcohols **2**. Use of $SOCl_2$ as a dehydrating agent in THF in the presence of pyridine afforded 3-amino-4-(1-arylalk-1-enyl)pyridines **3**, which, by *N*-formylation with HCO_2H in the presence of Ac_2O, gave *N*-[4-(1-arylalk-1-enyl)pyridin-3-yl]formamides **4**. Subsequent dehydration of **4** with $POCl_3$ in the presence of Et_3N completed the synthesis of **5**. These conversions could be carried out generally with good yields as compiled in *Table 1*.

Scheme

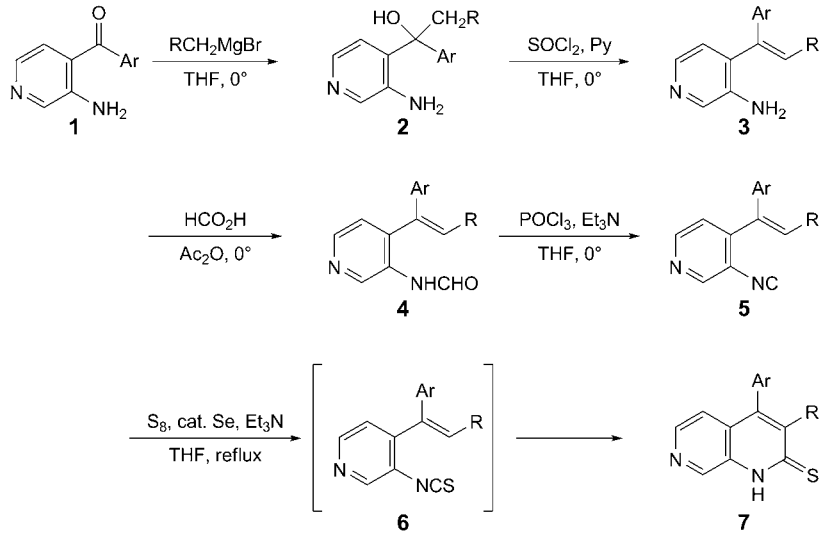

Table 1. *Preparation of 4-(1-Arylalk-1-enyl)-3-isocyanopyridines* **5**[a])

Entry	**1**	Ar	R	**2**	Yield	**3**	Yield	**4**	Yield	**5**	Yield
1	**1a**	Ph	H	**2a**	97	**3a**	67	**4a**	94	**5a**	94
2	**1b**	*m*-Tolyl	H	**2b**	98	**3b**	64	**4b**	79	**5b**	83
3	**1c**	*p*-Tolyl	H	**2c**	99	**3c**	64	**4c**	84	**5c**	86
4	**1d**	4-Cl–C_6H_4	H	**2d**	92	**3d**	58	**4d**	74	**5d**	91
5	**1e**	4-MeO–C_6H_4	H	**2e**	81	**3e**	63	**4e**	79	**5e**	85
6	**1f**	3,4-$(MeO)_2$–C_6H_3	H	**2f-i**	99	**3f-i**	68	**4f-i**	89	**5f-i**	87
7	**1f**	3,4-$(MeO)_2$–C_6H_3	Me	**2f-ii**	79	**3f-ii**	84	**4f-ii**	87	**5f-ii**	62
8	**1f**	3,4-$(MeO)_2$–C_6H_3	Et	**2f-iii**	74	**3f-iii**	91	**4f-iii**	76	**5f-iii**	57

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

The transformation of the obtained isocyano pyridines **5** into the desired 1,7-naphthyridine-2(1*H*)-thiones **7** was then performed by treating them with S_8 and a catalytic amount of Se in refluxing THF in the presence of Et_3N. These conditions are the same as described earlier by *Fujiwara et al.* for the conversion of isocyanides to the corresponding isothiocyanates [5]. First, conversion of 4-(1-arylalk-1-enyl)-3-isocyanopyridines **5a**–**5f-i** to 4-aryl-1,7-naphthyridine-2(1*H*)-thiones **7a**–**7f-i**, respectively, *via* **6a**–**6f-i**, was carried out. The desired products were obtained in good yields as collected in *Table 2* (*Entries 1–6*). The reactions were monitored by TLC (SiO_2) to evaluate their progress, revealing that the conversion of isocyanides **5** to isothiocyanate **6** proceeded immediately in all cases, but the rate of the conversion of **6** to the corresponding naphthyridin-2(1*H*)-thiones **7** were quite dependent on the substituents of the aryl groups of **5** or **6** (*cf. Table 2*, *Entries 1–6*). The cyclization of the substrates that carry one or two electron-donating MeO group(s) went to completion within 2.5 or 1 h, respectively, to give the corresponding products **7e** or **7f-i** (*Entries 5* or *6*, resp.).

This may be attributed to the higher electron density of the ethenyl moieties. On the other hand, the 4-Cl–C_6H_4 substrate required 20 h for the completion of the reaction, probably due to the lower electron density of the ethenyl moiety (*Entry 4*).

Table 2. *Preparation of 1,7-Naphthyridine-2(1*H*)-thiones* **7**

Entry	**5**	Time [h]	**7**	Ar	R	Yield[a])
1	**5a**	15	**7a**	Ph	H	81
2	**5b**	7	**7b**	*m*-Tolyl	H	82
3	**5c**	8	**7c**	*p*-Tolyl	H	80
4	**5d**	20	**7d**	4-Cl–C_6H_4	H	87
5	**5e**	2.5	**7e**	4-MeO–C_6H_4	H	96
6	**5f-i**	1	**7f-i**	3,4-$(MeO)_2$–C_6H_3	H	82
7	**5f-ii**	18	**7f-ii**	3,4-$(MeO)_2$–C_6H_3	Me	99
8	**5f-iii**	20	**7f-iii**	3,4-$(MeO)_2$–C_6H_3	Et	99

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

We next attempted to synthesize 3,4-disubstituted 1,7-naphthyridine-2(1*H*)-thiones **7f-ii** or **7f-iii** from the respective 4-(1-arylprop-1-enyl)- or 4-(1-arylbut-1-enyl)-3-isocyanopyridines **5f-ii** and **5f-iii**. When the latter were treated with S_8 in the presence of Se under the same conditions as described for the preparation of **5a**–**5f-i**, the isocyanides were also converted immediately to the corresponding isothiocyanates **6f-ii** and **6f-iii**, but prolonged reaction times were required for the complete consumption of the isothiocyanates. The sluggishness may be ascribed to the steric hindrance due to the Me or Et substituents. Fortunately, however, the electrocyclic reaction proceeded cleanly in each case and resulted in the formation of the desired products **7f-ii** and **7f-iii** in almost quantitative yields (*Table 2*, *Entries 7* and *8*).

In conclusion, an efficient route for the preparation of 1,7-naphthyridine-2(1*H*)-thiones **7** utilizing the electrocyclic reaction of the respective 4-(1-arylalk-1-enyl)-3-isothiocyanatopyridines **6** has been developed, which starts from commercially available pyridin-3-amine. This is the first practical method for preparing this type of naphthyridine derivatives, and it is valuable for organic synthesis, because it consists of simple procedures, and the starting materials are readily available.

Experimental Part

General. All org. solvents used in this study were dried over appropriate drying agents and distilled prior to use. TLC: *Merck* silica gel *60 PF_{254}*. Column chromatography (CC): *Wako Gel* C-200E. M.p.: *Laboratory Devices MEL-TEMP II* melting point apparatus; uncorrected. IR Spectra: *Shimadzu FTIR-8300* spectrophotometer. ^{1}H- and ^{13}C-NMR Spectra: with TMS as an internal reference with a *JEOL ECP500* FT NMR spectrometer, at 500 and 125 MHz, resp. LR-MS (EI, 70 eV): *JEOL JMS AX505 HA* spectrometer.

2,2-Dimethyl-N-*(pyridin-3-yl)propanamide* was prepared according to the procedure described in [6]. All of the other chemicals used in this study were commercially available.

(3-Aminopyridin-4-yl)arylmethanones **1**. These compounds were prepared by the successive treatment of 2,2-dimethyl-*N*-(pyridin-3-yl)propanamide with 2 equiv. of BuLi (*Asia Lithium Corporation*) and *N*-methoxy-*N*-methylbenzamides, followed by hydrolysis of the resulting *N*-(4-aroylpyridin-

3-yl)-2,2-dimethylpropanamides with 10% HCl under the conditions reported in [4]. Compounds **1a** [4], **1c** [4], **1d** [7], and **1e** [4] are known compounds, and the data for new compounds follow.

*2,2-Dimethyl-*N*-[4-(3-methylbenzoyl)pyridin-3-yl]propanamide.* Yield 57%. White solid. M.p. 84–86° (hexane/Et_2O). IR (KBr): 3327, 1661, 1603. ^{1}H-NMR ($CDCl_3$): 1.34 (*s*, 9 H); 2.44 (*s*, 3 H); 7.38 (*d*, *J* = 5.0, 1 H); 7.41 (*dd*, *J* = 7.8, 7.3, 1 H); 7.47 (*d*, *J* = 7.3, 1 H); 7.53 (*d*, *J* = 7.8, 1 H); 7.58 (*s*, 1 H); 8.46 (*d*, *J* = 5.0, 1 H); 9.92 (*s*, 1 H); 10.41 (br. *s*, 1 H). Anal. calc. for $C_{18}H_{20}N_2O_2$ (296.36): C 72.95, H 6.80, N 9.45; found: C 72.91, H 6.86, N 9.44.

(3-Aminopyridin-4-yl)(3-methylphenyl)methanone (**1b**). Yield 83%. Yellow solid. M.p. 105–107° (hexane/CH_2Cl_2). IR (KBr): 3445, 3316, 1647, 1605. ^{1}H-NMR ($CDCl_3$): 2.43 (*s*, 3 H); 5.79 (br. *s*, 2 H); 7.24 (*d*, *J* = 5.0, 1 H); 7.37 (*dd*, *J* = 7.8, 7.3, 1 H); 7.40 (*d*, *J* = 7.3, 1 H); 7.46 (*d*, *J* = 7.8, 1 H); 7.50 (*s*, 1 H); 7.94 (*d*, *J* = 5.0, 1 H); 8.28 (*s*, 1 H). Anal. calc. for $C_{13}H_{12}N_2O$ (212.25): C 73.56, H 5.70, N 13.20; found: C 73.36, H 5.78, N 13.02.

N-*[4-(3,4-Dimethoxybenzoyl)pyridin-3-yl]-2,2-dimethylpropanamide.* Yield 59%. White solid. M.p. 110–112° (hexane/Et_2O). IR (KBr) 3320, 1657. ^{1}H-NMR ($CDCl_3$): 1.33 (*s*, 9 H); 3.96 (*s*, 3 H); 3.99 (*s*, 3 H); 6.93 (*d*, *J* = 8.2, 1 H); 7.34 (*dd*, *J* = 8.2, 2.3, 1 H), 7.38 (*d*, *J* = 5.0, 1 H); 7.42 (*d*, *J* = 2.3, 1 H); 8.46 (*d*, *J* = 5.0, 1 H); 9.83 (*s*, 1 H); 10.07 (br. *s*, 1 H). Anal. calc. for $C_{19}H_{22}N_2O_4$ (342.39): C 66.65, H 6.48, N 8.18; found: C 66.62, H 6.57, N 8.17.

(3-Aminopyridin-4-yl)(3,4-dimethoxylphenyl)methanone (**1f**). Yield 87%. Yellow solid. M.p. 107–109° (hexane/CH_2Cl_2). IR (KBr): 3474, 3364, 1634, 1615. ^{1}H-NMR ($CDCl_3$): 3.94 (*s*, 3 H); 3.97 (*s*, 3 H); 5.48 (br. *s*, 2 H); 6.92 (*d*, *J* = 8.2, 1 H); 7.26 (*d*, *J* = 5.0, 1 H); 7.32 (*dd*, *J* = 8.2, 1.8, 1 H); 7.37 (*d*, *J* = 1.8, 1 H); 7.98 (*d*, *J* = 5.0, 1 H); 8.28 (*s*, 1 H). Anal. calc. for $C_{14}H_{14}N_2O_3$ (258.27): C 65.11, H 5.46, N 10.85; found: C 65.00, H 5.53, N 10.82.

1-(3-Aminopyridin-4-yl)-1-arylethanols **2**. These compounds were prepared by reacting **1** (3.0 mmol) with the respective alkylmagnesium bromide (12 mmol) in THF (15 ml) at 0° for 15 min.

1-(3-Aminopyridin-4-yl)-1-phenylethanol (**2a**). Pale-yellow solid. M.p. 184–186° (hexane/THF). IR (KBr) 3412, 3323, 3218, 1634. ^{1}H-NMR ($CDCl_3$): 1.90 (*s*, 3 H); 3.52 (br. *s*, 1 H); 3.86 (br. *s*, 2 H); 7.21 (*d*, *J* = 5.0, 1 H); 7.28 (*tt*, *J* = 7.3, 1.8, 1 H); 7.34 (*dd*, *J* = 7.8, 7.3, 2 H); 7.38 (*dd*, *J* = 7.8, 1.8, 2 H); 7.98 (*s*, 1 H); 8.06 (*d*, *J* = 5.0, 1 H). Anal. calc. for $C_{13}H_{14}N_2O$ (214.26): C 72.87, H 6.59, N 13.07; found: C 72.84, H 6.72, N 12.94.

1-(3-Aminopyridin-4-yl)-1-(3-methylphenyl)ethanol (**2b**). Pale-yellow solid. M.p. 151–153° (hexane/CH_2Cl_2). IR (KBr): 3424, 3331, 3235, 1638, 1609. ^{1}H-NMR ($CDCl_3$): 1.88 (*s*, 3 H); 2.33 (*s*, 3 H); 3.58 (br. *s*, 1 H); 3.86 (br. *s*, 2 H); 7.09 (*d*, *J* = 7.3, 1 H); 7.15–7.23 (*m*, 4 H); 7.96 (*s*, 1 H); 8.06 (*d*, *J* = 4.6, 1 H). Anal. calc. for $C_{14}H_{16}N_2O$ (228.29): C 73.66, H 7.06, N 12.27; found: C 73.59, H 7.18, N 12.08.

1-(3-Aminopyridin-4-yl)-1-(4-methylphenyl)ethanol (**2c**). Pale-yellow solid. M.p. 171–173° (hexane/THF). IR (KBr): 3410, 3337, 3220, 1627. ^{1}H-NMR ($CDCl_3$): 1.88 (*s*, 3 H); 2.33 (*s*, 3 H); 3.46 (br. *s*, 1 H); 3.89 (br. *s*, 2 H); 7.14 (*d*, *J* = 8.2, 2 H); 7.19 (*d*, *J* = 5.0, 1 H); 7.25 (*d*, *J* = 8.2, 2 H); 7.95 (*s*, 1 H); 8.04 (*d*, *J* = 5.0, 1 H). Anal. calc. for $C_{14}H_{16}N_2O$ (228.29): C 73.66, H 7.06, N 12.27; found: C 73.37, H 7.13, N 12.27.

1-(3-Aminopyridin-4-yl)-1-(4-chlorophenyl)ethanol (**2d**). Pale-yellow solid. M.p. 164–166° (hexane/CH_2Cl_2). IR (KBr): 3472, 3374, 3088, 1603. ^{1}H-NMR ($CDCl_3$): 1.88 (*s*, 3 H); 3.74 (br., 1 H); 3.96 (br. *s*, 2 H); 7.17 (*d*, *J* = 5.0, 1 H); 7.30 (*s*, 4 H); 7.95 (*s*, 1 H); 8.02 (*d*, *J* = 5.0, 1 H). Anal. calc. for $C_{13}H_{13}ClN_2O$ (248.71): C 62.78, H 5.27, N 11.26; found: C 62.59, H 5.40, N 11.19.

1-(3-Aminopyridin-4-yl)-1-(4-methoxyphenyl)ethanol (**2e**).White solid. M.p. 204–206° (THF). IR (KBr): 3414, 3325, 3240, 1627, 1610. ^{1}H-NMR ($CDCl_3$): 1.89 (*s*, 3 H); 3.30 (*s*, 1 H); 3.80 (*s*, 3 H); 3.88 (br. *s*, 2 H); 6.86 (*d*, *J* = 8.7, 2 H); 7.18 (*d*, *J* = 5.0, 1 H); 7.29 (*d*, *J* = 8.7, 2 H); 7.99 (*s*, 1 H); 8.06 (*d*, *J* = 5.0, 1 H). Anal. calc. for $C_{14}H_{16}N_2O_2$ (244.29): C 68.83, H 6.60, N 11.47; found: C 68.59, H 6.63, N 11.43.

1-(3-Aminopyridin-4-yl)-1-(3,4-dimethoxyphenyl)ethanol (**2f-i**). Yellow solid. M.p. 168–170° (THF). IR (KBr): 3451, 3352, 3158, 1614. ^{1}H-NMR ($CDCl_3$): 1.89 (*s*, 3 H); 3.54 (br. *s*, 1 H); 3.84 (*s*, 3 H); 3.87 (*s*, 3 H); 3.88 (br. *s*, 2 H); 6.79 (*d*, *J* = 8.7, 1 H); 6.82 (*dd*, *J* = 8.7, 1.4, 1 H); 7.00 (*d*, *J* = 1.4, 1 H); 7.19 (*d*, *J* = 5.0, 1 H); 8.00 (*s*, 1 H); 8.07 (*d*, *J* = 5.0, 1 H). Anal. calc. for $C_{15}H_{18}N_2O_3$ (274.32): C 65.63, H 6.61, N 10.21; found: C 65.41, H 6.61, N 10.10.

1-(3-Aminopyridin-4-yl)-1-(3,4-dimethoxyphenyl)propan-1-ol (**2f-ii**). Pale-yellow solid. M.p. 174–176° (hexane/THF). IR (KBr): 3476, 3364, 3111, 1618. ^{1}H-NMR ($CDCl_3$): 0.91 (*t*, *J* = 7.3, 3 H); 2.13–2.20 (*m*, 1 H); 2.29–2.36 (*m*, 1 H); 3.46 (br. *s*, 1 H); 3.82 (*s*, 3 H); 3.86 (*s*, 3 H); 3.93 (br. *s*, 2 H); 6.79

(*d*, *J* = 8.2, 1 H); 6.81 (*dd*, *J* = 8.2, 1.4, 1 H); 6.93 (*d*, *J* = 1.4, 1 H); 7.19 (*d*, *J* = 5.0, 1 H); 7.95 (*s*, 1 H); 8.04 (*d*, *J* = 5.0, 1 H). Anal. calc. for $C_{16}H_{20}N_2O_3$ (288.34): C 66.65, H 6.99, N 9.72; found: C 66.53, H 7.17, N 9.53.

1-(3-Aminopyridin-4-yl)-1-(3,4-dimethoxyphenyl)butan-1-ol (**2f-iii**). Pale-yellow solid. M.p. 178–180° (hexane/CH_2Cl_2). IR (KBr): 3451, 3358, 3206, 1626. ^{1}H-NMR ($CDCl_3$): 0.93 (*t*, *J* = 7.3, 3 H); 1.20–1.47 (*m*, 2 H); 2.06–2.13 (*m*, 1 H); 2.20–2.26 (*m*, 1 H); 3.63 (br. *s*, 1 H); 3.82 (*s*, 3 H); 3.86 (*s*, 3 H); 3.94 (br. *s*, 2 H); 6.78–6.81 (*m*, 2 H); 6.94 (*d*, *J* = 1.4, 1 H); 7.20 (*d*, *J* = 5.0, 1 H); 7.94 (*s*, 1 H); 8.02 (*d*, *J* = 5.0, 1 H). Anal. calc. for $C_{17}H_{22}N_2O_3$ (302.37): C 67.53, H 7.33, N 9.26; found: C 67.49, H 7.48, N 9.00.

4-(1-Arylethenyl)pyridin-3-amines **3**. These compounds were prepared by treating **2** (2.0 mmol) with $SOCl_2$ (8.0 mmol) in THF (10 ml) in the presence of pyridine (Py) (30 mmol) at 0° for 30 min.

4-(1-Phenylethenyl)pyridin-3-amine (**3a**). Yellow oil. R_f (hexane/THF 1:1) 0.35. IR (neat): 3462, 3306, 1624. ^{1}H-NMR ($CDCl_3$): 3.57 (br. *s*, 2 H); 5.41 (*d*, *J* = 0.9, 1 H); 5.86 (*d*, *J* = 0.9, 1 H); 7.02 (*d*, *J* = 5.0, 1 H); 7.34 (*dd*, *J* = 7.8, 7.3, 2 H); 7.38 (*dd*, *J* = 7.8, 0.9, 2 H); 7.68 (*td*, *J* = 7.3, 0.9, 1 H); 8.07 (*d*, *J* = 5.0, 1 H); 8.08 (*s*, 1 H). Anal. calc. for $C_{13}H_{12}N_2$ (196.25): C 79.56, H 6.16, N 14.27; found: C 79.43, H 6.34, N 14.08.

4-[1-(3-Methylphenyl)ethenyl]pyridin-3-amine (**3b**). Yellow oil. R_f (hexane/THF 1:1) 0.32. IR (neat): 3460, 3323, 1616. ^{1}H-NMR ($CDCl_3$): 2.33 (*s*, 3 H); 2.57 (br. *s*, 2 H); 5.38 (*s*, 1 H); 5.83 (*s*, 1 H); 7.02 (*d*, *J* = 4.6, 1 H); 7.12–7.15 (*m*, 3 H); 7.23 (*t*, *J* = 7.8, 1 H); 8.04 (*d*, *J* = 5.0, 1 H); 8.09 (*s*, 1 H). Anal. calc. for $C_{14}H_{14}N_2$ (210.27): C 79.97, H 6.71, N 13.32; found: C 79.96, H 6.76, N 13.20.

4-[1-(4-Methylphenyl)ethenyl]pyridin-3-amine (**3c**). Yellow oil. R_f (hexane/THF 1:1) 0.27. IR (neat): 3460, 3316, 1614. ^{1}H-NMR ($CDCl_3$): 2.36 (*s*, 3 H); 3.56 (br. *s*, 2 H); 5.34 (*s*, 1 H); 5.81 (*s*, 1 H); 7.02 (*d*, *J* = 5.0, 1 H); 7.15 (*d*, *J* = 8.2, 2 H); 7.23 (*d*, *J* = 8.2, 2 H); 8.04 (*d*, *J* = 5.0, 1 H); 8.08 (*s*, 1 H). Anal. calc. for $C_{14}H_{14}N_2$ (210.27): C 79.97, H 6.71, N 13.32; found: C 79.95, H 6.88, N 13.13.

4-[1-(4-Chlorophenyl)ethenyl]pyridin-3-amine (**3d**). Yellow oil. R_f (hexane/THF 1:2) 0.41. IR (neat): 3458, 3322, 3202, 1614. ^{1}H-NMR ($CDCl_3$): 3.57 (br. *s*, 2 H); 5.42 (*s*, 1 H); 5.85 (*s*, 1 H); 6.99 (*d*, *J* = 5.0, 1 H); 7.26 (*d*, *J* = 8.7, 2 H); 7.31 (*d*, *J* = 8.7, 2 H); 8.04 (*d*, *J* = 5.0, 1 H); 8.11 (*s*, 1 H). Anal. calc. for $C_{13}H_{11}ClN_2$ (230.69): C 67.68, H 4.81, N 12.14; found: C 67.63, H 5.05, N 12.12.

4-[1-(4-Methoxyphenyl)ethenyl]pyridin-3-amine (**3e**). Yellow oil. R_f (hexane/THF 1:2) 0.30. IR (neat): 3457, 3329, 1606. ^{1}H-NMR ($CDCl_3$): 3.58 (br. *s*, 2 H); 3.81 (*s*, 3 H); 5.28 (*s*, 1 H); 5.75 (*d*, *J* = 0.9, 1 H); 6.87 (*d*, *J* = 8.7, 2 H); 7.02 (*d*, *J* = 5.0, 1 H); 7.27 (*d*, *J* = 8.7, 2 H); 8.04 (*d*, *J* = 5.0, 1 H); 8.09 (*s*, 1 H). Anal. calc. for $C_{14}H_{14}N_2O$ (226.27): C 74.31, H 6.24, N 12.38; found: C 74.20, H 6.49, N 12.39.

4-[1-(3,4-Dimethoxyphenyl)ethenyl]pyridin-3-amine (**3f-i**). Yellow oil. R_f (hexane/THF 1:2) 0.29. IR (neat): 3445, 3382, 1614. ^{1}H-NMR ($CDCl_3$): 3.59 (br. *s*, 2 H); 3.85 (*s*, 3 H); 3.89 (*s*, 3 H); 5.31 (*s*, 1 H); 5.75 (*s*, 1 H); 6.81 (*d*, *J* = 8.2, 1 H); 6.84 (*dd*, *J* = 8.2, 1.8, 1 H); 6.90 (*d*, *J* = 1.8, 1 H); 7.03 (*d*, *J* = 4.6, 1 H); 8.05 (*d*, *J* = 4.6, 1 H); 8.09 (*s*, 1 H). Anal. calc. for $C_{15}H_{16}N_2O_2$ (256.30): C 70.29, H 6.29, N 10.93; found: C 70.21, H 6.45, N 10.89.

4-[(1E)-1-(3,4-Dimethoxyphenyl)prop-1-en-1-yl]pyridin-3-amine (**3f-ii**). Yellow oil. R_f (hexane/THF 1:2) 0.49. IR (neat): 3460, 3367, 1618. ^{1}H-NMR ($CDCl_3$): 1.69 (*d*, *J* = 6.9, 3 H); 3.61 (br. *s*, 2 H); 3.83 (*s*, 3 H); 3.86 (*s*, 3 H); 6.29 (*q*, *J* = 6.9, 1 H); 6.70 (*dd*, *J* = 8.2, 2.3, 1 H); 6.76 (*d*, *J* = 8.2, 1 H); 6.85 (*d*, *J* = 2.3, 1 H); 6.92 (*d*, *J* = 5.0, 1 H); 8.06 (*d*, *J* = 5.0, 1 H); 8.16 (*s*, 1 H). Anal. calc. for $C_{16}H_{18}N_2O_2$ (270.33): C 71.09, H 6.71, N 10.36; found: C 71.08, H 6.79, N 10.28.

4-[(1E)-1-(3,4-Dimethoxyphenyl)but-1-en-1-yl]pyridin-3-amine (**3f-iii**). Pale-yellow oil. R_f (hexane/THF 1:2) 0.50. IR (neat): 3460, 3368, 3203, 1622. ^{1}H-NMR ($CDCl_3$): 1.03 (*t*, *J* = 7.3, 3 H); 2.02 (*quint.*, *J* = 7.3, 2 H); 3.60 (br. *s*, 2 H); 3.84 (*s*, 3 H); 3.86 (*s*, 3 H); 6.20 (*t*, *J* = 7.3, 1 H); 6.71 (*dd*, *J* = 8.2, 1.8, 1 H); 6.77 (*d*, *J* = 8.2, 1 H); 6.85 (*d*, *J* = 1.8, 1 H); 6.92 (*d*, *J* = 4.6, 1 H); 8.05 (*d*, *J* = 4.6, 1 H); 8.14 (*s*, 1 H). Anal. calc. for $C_{17}H_{20}N_2O_2$ (284.35): C 71.81, H 7.09, N 9.85; found: C 71.54, H 7.23, N 9.55.

N-*[4-(1-Arylethenyl)pyridin-3-yl]formamides* **4**. These compounds were prepared by treating **3** (1.8 mmol) with HCO_2H (36 mmol) in the presence of Ac_2O (9.0 mmol) at 0° for 30 min [7].

N-*[4-(1-Phenylethenyl)pyridin-3-yl]formamide* (**4a**). White solid. M.p. 118–119° (hexane/AcOEt). IR (KBr): 3183, 1695. ^{1}H-NMR ($CDCl_3$): 5.40, 5.42 (2*s*, 1 H); 5.95, 6.00 (2*s*, 1 H); 6.98–9.54 (*m*, 10 H). Anal. calc. for $C_{14}H_{12}N_2O$ (224.26): C 74.98, H 5.39, N 12.49; found: C 74.90, H 5.40, N 12.48.

N-*[4-[1-(3-Methylphenyl)ethenyl]pyridin-3-yl]formamide* (**4b**). Pale-yellow solid. M.p. 112–114° (hexane/Et_2O). IR (KBr): 3231, 1695, 1668. ^{1}H-NMR ($CDCl_3$): 2.33 (*s*, 3 H); 5.37, 5.39 (2*s*, 1 H); 5.91,

5.97 (2*s*, 1 H); 6.98 – 9.54 (*m*, 9 H). Anal. calc. for $C_{15}H_{14}N_2O$ (238.28): C 75.61, H 5.92, N 11.76; found: C 75.54, H 5.96, N 11.78.

N-*{4-[1-(4-Methylphenyl)ethenyl]pyridin-3-yl}formamide* (**4c**). Pale-yellow solid. M.p. 110 – 111° (hexane/CH_2Cl_2). IR (KBr): 3180, 1691. ^{1}H-NMR ($CDCl_3$): 2.355, 2.362 (2*s*, 3 H); 5.33, 5.35 (2*s*, 1 H); 5.90, 5.95 (2*s*, 1 H); 7.00 – 9.55 (*m*, 9 H). Anal. calc. for $C_{15}H_{14}N_2O$ (238.28): C 75.61, H 5.92, N 11.76; found: C 75.58, H 5.95, N 11.60.

N-*{4-[1-(4-Chlorophenyl)ethenyl]pyridin-3-yl}formamide* (**4d**). Pale-yellow solid. M.p. 116 – 117° (hexane/Et_2O). IR (KBr): 3175, 1692. ^{1}H-NMR ($CDCl_3$): 5.41, 5.43 (2*s*, 1 H); 5.95, 6.00 (2*s*, 1 H); 6.97 – 9.52 (*m*, 9 H). Anal. calc. for $C_{14}H_{11}ClN_2O$ (258.70): C 65.00, H 4.29, N 10.83; found: C 64.70, H 4.44, N 10.75.

N-*{4-[1-(4-Methoxyphenyl)ethenyl]pyridin-3-yl}formamide* (**4e**). Yellow oil. R_f (hexane/THF 1:2) 0.38. IR (neat): 3259, 1694, 1604. ^{1}H-NMR ($CDCl_3$): 3.82 (*s*, 3 H); 5.27, 5.28 (2*s*, 1 H); 5.83, 5.89 (2*s*, 1 H); 6.87 – 9.56 (*m*, 9 H). Anal. calc. for $C_{15}H_{14}N_2O_2$ (254.28): C 70.85, H 5.55, N 11.02; found: C 70.82, H 5.60, N 10.91.

N-*{4-[1-(3,4-Dimethoxyphenyl)ethenyl]pyridin-3-yl}formamide* (**4f-i**). White solid. M.p. 161 – 163° (hexane/CH_2Cl_2). IR (KBr): 3235, 1699. ^{1}H-NMR ($CDCl_3$): 3.85 (*s*, 3 H); 3.887, 3.893 (2*s*, 3 H); 5.30, 5.32 (2*s*, 1 H); 5.84, 5.90 (2*s*, 1 H); 6.64 – 9.55 (*m*, 8 H). Anal. calc. for $C_{16}H_{16}N_2O_3$ (284.31): C 67.59, H 5.67, N 9.85; found: C 67.53, H 5.71, N 9.60.

N-*{4-[(1E)-1-(3,4-Dimethoxyphenyl)prop-1-en-1-yl]pyridin-3-yl}formamide* (**4f-ii**). Colorless crystals. M.p. 161 – 163° (hexane/CH_2Cl_2). IR (KBr) 3345, 1694. ^{1}H-NMR ($CDCl_3$): 1.65, 1.66 (2*d*, J = 6.9, 3 H); 3.83, 3.84 (2*s*, 3 H); 3.860, 3.864 (2*s*, 3 H); 6.37, 6.43 (2*q*, J = 6.9, 1 H); 6.52 – 9.68 (*m*, 8 H). Anal. calc. for $C_{17}H_{18}N_2O_3$ (298.34): C 68.44, H 6.08, N 9.39; found: C 68.39, H 6.06, N 9.34.

N-*{4-[(1E)-1-(3,4-Dimethoxyphenyl)but-1-en-1-yl]pyridin-3-yl}formamide* (**4f-iii**). White solid. M.p. 155 – 157° (hexane/CH_2Cl_2). IR (neat): 3345, 1697. ^{1}H-NMR ($CDCl_3$): 1.03 (*t*, J = 7.3, 3 H); 1.93 – 1.99 (*m*, 2 H), 3.84, 3.85, 3.87 (3*s*, 6 H); 6.27, 6.34 (2*t*, J = 7.8, 1 H); 6.52 – 9.66 (*m*, 8 H). Anal. calc. for $C_{18}H_{20}N_2O_3$ (312.36): C 69.21, H 6.45, N 8.97; found: C 68.97, H 6.58, N 8.97.

4-(1-Arylethenyl)-3-isocyanopyridines **5**. These compounds were prepared by treating **4** with $POCl_3$/Et_3N in THF at 0° [8].

3-Isocyano-4-(1-phenylethenyl)pyridine (**5a**). Pale-yellow solid. M.p. 51 – 53° (hexane). IR (KBr): 2122, 1614. ^{1}H-NMR ($CDCl_3$): 5.52 (*s*, 1 H); 5.96 (*s*, 1 H); 7.23 – 7.25 (*m*, 2 H); 7.30 (*d*, J = 5.0, 1 H); 7.35 – 7.37 (*m*, 3 H) 8.62 (*d*, J = 5.0, 1 H); 8.69 (*s*, 1 H). Anal. calc. for $C_{14}H_{10}N_2$ (206.24): C 81.53, H 4.89, N 13.58; found: C 81.26, H 4.98, N 13.30.

3-Isocyano-4-[1-(3-methylphenyl)ethenyl]pyridine (**5b**). Yellow oil. R_f (hexane/THF 3:1) 0.49. IR (neat): 2122. ^{1}H-NMR ($CDCl_3$): 2.34 (*s*, 3 H); 5.49 (*s*, 1 H); 5.94 (*s*, 1 H); 7.02 (*d*, J = 7.3, 1 H); 7.04 (*s*, 1 H); 7.16 (*d*, J = 7.3, 1 H); 7.24 (*t*, J = 7.3, 1 H); 7.29 (*d*, J = 5.0, 1 H); 8.61 (*d*, J = 5.0, 1 H); 8.69 (*s*, 1 H). Anal. calc. for $C_{15}H_{12}N_2$ (220.27): C 81.79, H 5.49, N 12.72; found: C 81.73, H 5.40, N 12.60.

3-Isocyano-4-[1-(4-methylphenyl)ethenyl]pyridine (**5c**). Pale-yellow solid. M.p. 71 – 73° (hexane). IR (KBr): 2122, 1609. ^{1}H-NMR ($CDCl_3$): 2.37 (*s*, 3 H); 5.45 (*s*, 1 H); 5.92 (*s*, 1 H); 7.12 (*d*, J = 8.2, 2 H); 7.16 (*d*, J = 8.2, 2 H); 7.29 (*d*, J = 5.0, 1 H); 8.61 (*d*, J = 5.0, 1 H); 8.68 (*s*, 1 H). Anal. calc. for $C_{15}H_{12}N_2$ (220.27): C 81.79, H 5.49, N 12.72; found: C 81.70, H 5.49, N 12.49.

4-[1-(4-Chlorophenyl)ethenyl]-3-isocyanopyridine (**5d**). Pale-yellow solid. M.p. 43 – 44° (hexane). IR (KBr): 2128, 1622. ^{1}H-NMR ($CDCl_3$): 5.54 (*s*, 1 H); 5.95 (*s*, 1 H); 7.17 (*d*, J = 8.7, 2 H); 7.29 (*d*, J = 5.0, 1 H); 7.33 (*d*, J = 8.7, 2 H); 8.64 (*d*, J = 5.0, 1 H); 8.70 (*s*, 1 H). Anal. calc. for $C_{14}H_9ClN_2$ (240.69): C 69.86, H 3.77, N 11.64; found: C 69.89, H 3.82, N 11.59.

3-Isocyano-4-[1-(4-methoxyphenyl)ethenyl]pyridine (**5e**). Pale-yellow solid. M.p. 61 – 62° (hexane/Et_2O). IR (KBr): 2124, 1604. ^{1}H-NMR ($CDCl_3$): 3.82 (*s*, 3 H); 5.39 (*s*, 1 H); 3.86 (*s*, 1 H); 6.87 (*d*, J = 8.7, 2 H); 7.16 (*d*, J = 8.7, 2 H); 7.30 (*d*, J = 5.0, 1 H); 8.61 (*d*, J = 5.0, 1 H); 8.68 (*s*, 1 H). Anal. calc. for $C_{15}H_{12}N_2O$ (236.27): C 76.25, H 5.12, N 11.86; found: C 76.29, H 5.34, N 11.69.

4-[1-(3,4-Dimethoxyphenyl)ethenyl]-3-isocyanopyridine (**5f-i**). Pale-yellow solid. M.p. 97 – 100° (hexane/Et_2O). IR (KBr): 2126, 1614, 1603. ^{1}H-NMR ($CDCl_3$): 3.86 (*s*, 3 H); 3.89 (*s*, 3 H); 5.42 (*s*, 1 H); 5.87 (*s*, 1 H); 6.67 (*dd*, J = 8.2, 2.3, 1 H); 6.81 (*d*, J = 8.2, 1 H); 6.83 (*d*, J = 2.3, 1 H); 7.30 (*d*, J = 5.0, 1 H); 8.62 (*d*, J = 5.0, 1 H); 8.69 (*s*, 1 H). Anal. calc. for $C_{16}H_{14}N_2O_2$ (266.29): C 72.16, H 5.30, N 10.52; found: C 72.10, H 5.59, N 10.80.

*4-[(1*E*)-1-(3,4-Dimethoxyphenyl)prop-1-en-1-yl]-3-isocyanopyridine* (**5f-ii**). Pale-yellow solid. M.p. 111° (dec.; hexane/CH_2Cl_2). IR (KBr): 2126, 1601. ^{1}H-NMR ($CDCl_3$): 1.70 (*d*, *J* = 6.9, 3 H); 3.85 (*s*, 3 H); 3.86 (*s*, 3 H); 6.35 (*q*, *J* = 6.9, 1 H); 6.53 (*dd*, *J* = 8.2, 2.3, 1 H); 6.76 (*d*, *J* = 8.2, 1 H); 6.78 (*d*, *J* = 2.3, 1 H); 7.23 (*d*, *J* = 5.5, 1 H); 8.64 (*d*, *J* = 5.5, 1 H); 8.74 (*s*, 1 H). Anal. calc. for $C_{17}H_{16}N_2O_2$ (280.32): C 72.84, H 5.75, N 9.99; found: C 72.60, H 5.81, N 9.83.

*4-[(1*E*)-1-(3,4-Dimethoxyphenyl)but-1-en-1-yl]-3-isocyanopyridine* (**5f-iii**). Pale-yellow oil. R_f (hexane/THF 2:1) 0.66. IR (neat): 2124, 1601. ^{1}H-NMR ($CDCl_3$): 1.07 (*t*, *J* = 7.3, 3 H); 1.98 (*quint.*, *J* = 7.3, 2 H); 3.857 (*s*, 3 H); 3.863 (*s*, 3 H); 6.24 (*t*, *J* = 7.3, 1 H); 6.53 (*dd*, *J* = 8.2, 1.8, 1 H); 6.76 (*d*, *J* = 8.2, 1 H); 6.80 (*d*, *J* = 1.8, 1 H); 7.24 (*d*, *J* = 5.0, 1 H); 8.64 (*d*, *J* = 5.0, 1 H); 8.73 (*s*, 1 H). Anal. calc. for $C_{18}H_{18}N_2O_2$ (294.35): C 73.45, H 6.16, N 9.52; found: C 73.49, H 6.28, N 9.47.

*4-Phenyl-1,7-naphthyridine-2(1*H*)-thione* (**7a**; *Representative Procedure*). A soln. of **5** (0.21 g, 1.0 mmol), Et_3N (0.24 g, 2.4 mmol) in THF (6 ml) containing S_8 (39 mg, 1.2 mmol), and Se (3.9 mg, 0.050 mmol) was heated at reflux temp. for 15 h. After the mixture was cooled to r.t., it was concentrated by evaporation of the solvent. The residual solid was recrystallized from hexane/$CHCl_3$ to give **7a** (0.19 g, 81%). Yellow solid. M.p. 217–220°. IR (KBr): 3183, 1614, 1121. ^{1}H-NMR ((D_6)DMSO): 7.31 (*s*, 1 H); 7.40 (*d*, *J* = 5.5, 1 H); 7.52–7.57 (*m*, 5 H); 8.39 (*d*, *J* = 5.5, 1 H); 8.98 (*s*, 1 H); 13.99 (br. *s*, 1 H). ^{13}C-NMR ((D_6)DMSO): 118.5; 125.4; 128.9; 129.0; 129.5; 134.5; 134.7; 135.0; 139.8; 143.4; 143.7; 181.5. MS: 238 (100, M^+). Anal. calc. for $C_{14}H_{10}N_2S$ (238.31): C 70.56, H 4.23, N 11.76; found: C 70.51, H 4.23, N 11.89.

*4-(3-Methylphenyl)-1,7-naphthyridine-2(1*H*)-thione* (**7b**). Yellow solid. M.p. 232–234° (hexane/THF). IR (KBr): 3190, 1620, 1125. ^{1}H-NMR ((D_6)DMSO): 2.40 (*s*, 3 H); 7.31 (*s*, 1 H); 7.33 (*d*, *J* = 7.9, 1 H); 7.36 (*s*, 1 H); 7.37 (*d*, *J* = 7.3, 1 H); 7.44 (*d*, *J* = 5.5, 1 H); 7.45 (*dd*, *J* = 7.9, 7.3, 1 H); 8.40 (*d*, *J* = 5.5, 1 H); 8.98 (*s*, 1 H); 13.97 (br. *s*, 1 H). ^{13}C-NMR ((D_6)DMSO): 20.9; 118.5; 125.4; 126.0; 128.8; 129.3; 130.1; 134.5; 134.7; 135.0; 138.4; 139.7; 143.4; 143.8; 181.5. MS: 252 (100, M^+). Anal. calc. for $C_{15}H_{12}N_2S$ (252.33): C 71.40, H 4.79, N 11.10; found: C 71.47, H 4.85, N 11.07.

*4-(4-Methylphenyl)-1,7-naphthyridine-2(1*H*)-thione* (**7c**). Yellow solid. M.p. 238–241° (hexane/CH_2Cl_2). IR (KBr): 3177, 1611, 1127. ^{1}H-NMR ((D_6)DMSO): 2.32 (*s*, 3 H); 7.30 (*s*, 1 H); 7.37 (*d*, *J* = 8.0, 2 H); 7.43–7.45 (*m*, 3 H); 8.39 (*d*, *J* = 5.5, 1 H); 8.98 (*s*, 1 H); 13.94 (*s*, 1 H). ^{13}C-NMR ((D_6)DMSO): 20.9; 118.5; 125.4; 128.8; 129.5; 131.6; 134.5; 135.0; 139.2; 139.8; 143.3; 143.7; 181.5. MS: 252 (100, M^+). Anal. calc. for $C_{15}H_{12}N_2S$ (252.33): C 71.40, H 4.79, N 11.10; found: C 71.36, H 4.91, N 11.04.

*4-(4-Chlorophenyl)-1,7-naphthyridine-2(1*H*)-thione* (**7d**). Yellow solid. M.p. 250–252° (THF). IR (KBr): 3194, 1616, 1128. ^{1}H-NMR ((D_6)DMSO): 7.34 (*s*, 1 H); 7.40 (*d*, *J* = 5.5, 1 H); 7.58 (*d*, *J* = 8.6, 2 H); 7.63 (*d*, *J* = 8.6, 2 H); 8.40 (*d*, *J* = 5.5, 1 H); 8.98 (*s*, 1 H); 14.02 (br. *s*, 1 H). ^{13}C-NMR ((D_6)DMSO): 118.4; 125.3; 129.0; 130.8; 133.3; 134.4; 134.9; 135.0; 139.8; 142.5; 143.4; 181.5. MS: 272 (100, M^+). Anal. calc. for $C_{14}H_9ClN_2S$ (272.75): C 61.65, H 3.33, N 10.27; found: C 61.59, H 3.48, N 10.08.

*4-(4-Methoxyphenyl)-1,7-naphthyridine-2(1*H*)-thione* (**7e**). Yellow solid. M.p. 238–240° (hexane/CH_2Cl_2). IR (KBr): 3177, 1609, 1127. ^{1}H-NMR ((D_6)DMSO): 3.83 (*s*, 3 H); 7.10 (*d*, *J* = 9.2, 2 H); 7.28 (*s*, 1 H); 7.46 (*d*, *J* = 5.5, 1 H); 7.48 (*d*, *J* = 9.2, 2 H); 8.38 (*d*, *J* = 5.5, 1 H); 8.97 (*s*, 1 H); 13.91 (br. *s*, 1 H). ^{13}C-NMR ((D_6)DMSO): 55.3; 114.5; 118.6; 125.5; 126.6; 130.4; 134.3; 135.1; 139.8; 143.3; 143.5; 160.3; 181.4. MS: 268 (100, M^+). Anal. calc. for $C_{15}H_{12}N_2OS$ (268.33): C 67.14, H 4.51, N 10.44; found: C 66.87, H 4.56, N 10.46.

*4-(3,4-Dimethoxyphenyl)-1,7-naphthyridine-2(1*H*)-thione* (**7f-i**). Yellow solid. M.p. 267–269° (Me_2CO/MeOH). IR (KBr): 3192, 1618, 1601, 1129. ^{1}H-NMR ((D_6)DMSO): 3.81 (*s*, 3 H); 3.83 (*s*, 3 H); 7.09 (*dd*, *J* = 8.6, 1.8, 1 H); 7.13–7.14 (*m*, 2 H); 7.35 (*s*, 1 H); 7.56 (*d*, *J* = 5.5, 1 H); 8.41 (*d*, *J* = 5.5, 1 H); 8.98 (*s*, 1 H); 13.93 (br. *s*, 1 H). ^{13}C-NMR ((D_6)DMSO): 55.6; 55.7; 111.9; 112.4; 118.8; 121.7; 125.6; 126.8; 134.3; 135.1; 139.7; 143.3; 143.7; 149.0; 149.9; 181.4. MS: 298 (100, M^+). Anal. calc. for $C_{16}H_{14}N_2O_2S$ (298.36): C 64.41, H 4.73, N 9.39; found: C 64.25, H 4.77, N 9.26.

*4-(3,4-Dimethoxyphenyl)-3-methyl-1,7-naphthyridine-2(1*H*)-thione* (**7f-ii**). Pale-yellow solid. M.p. 252–254° (THF). IR (KBr): 3178, 1611, 1130. ^{1}H-NMR ((D_6)DMSO): 2.20 (*s*, 3 H); 3.74 (*s*, 3 H); 3.83 (*s*, 3 H); 6.82 (*dd*, *J* = 7.9, 1.2, 1 H); 6.91 (*d*, *J* = 1.2, 1 H); 6.97 (*dd*, *J* = 5.5, 1 H); 7.13 (*dd*, *J* = 7.9, 1 H); 8.31 (*d*, *J* = 5.5, 1 H); 8.98 (*s*, 1 H); 14.06 (br. *s*, 1 H). ^{13}C-NMR ((D_6)DMSO): 19.9; 55.5; 55.7; 112.0; 112.3; 119.0; 120.9; 127.1; 127.5; 133.2; 139.0; 139.2; 142.0; 143.0; 148.8; 149.0; 183.1. MS: 312 (100, M^+). Anal. calc. for $C_{17}H_{16}N_2O_2S$ (312.39): C 65.36, H 5.16, N 8.97; found: C 65.06, H 5.34, N 8.84.

*4-(3,4-Dimethoxyphenyl)-3-ethyl-1,7-naphthyridine-2(1*H*)-thione* (**7f-iii**). Yellow solid. M.p. 241–243° (hexane/THF). IR (KBr): 3275, 1607, 1142. ^{1}H-NMR ((D$_6$)DMSO): 1.02 (*t*, *J* = 7.3, 3 H); 2.68–2.80 (*m*, 2 H); 3.73 (*s*, 3 H); 3.83 (*s*, 3 H); 6.82 (*dd*, *J* = 7.9, 1.8, 1 H); 6.86 (*d*, *J* = 5.5, 1 H); 6.92 (*d*, *J* = 1.8, 1 H); 7.12 (*d*, *J* = 7.9, 1 H); 8.28 (*d*, *J* = 5.5, 1 H); 8.96 (*s*, 1 H); 14.01 (br. *s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 12.9; 25.2; 55.5; 55.7; 111.9; 112.0; 119.1; 120.6; 127.2; 127.6; 133.2; 138.9; 142.0; 143.0; 144.4; 148.7; 148.9; 182.4. MS: 326 (100, M^+). Anal. calc. for $C_{18}H_{18}N_2O_2S$ (326.41): C 66.23, H 5.56, N 8.58; found: C 66.20, H 5.65, N 8.39.

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