One-Pot Synthesis of Quinoline-2(1*H*)-thiones from 2-Isocyanostyrenes via Electrocyclic Reaction of the Corresponding 2-Isothiocyanatestyrenes

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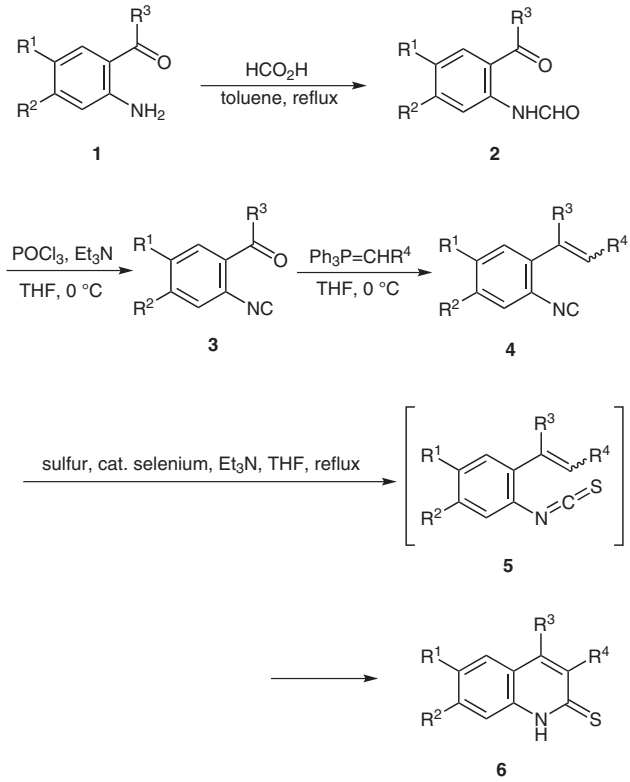
Abstract: The reaction of α-substituted 2-isocyanostyrenes, which could be readily prepared from commercially available 2-aminophenyl ketones or 2-aminobenzonitriles, with sulfur in the presence of a catalytic amount of selenium proceeded smoothly to give the corresponding 2-isothiocyanatestyrenes. The latter spontaneously underwent the electrocyclic reaction to afford 4-substituted quinoline-2(1*H*)-thiones in one-pot with isolated yields ranging from 37 to 91%.

Key words: quinoline-2(1*H*)-thiones, isocyanides, electrocyclic reaction, isothiocyanates, sulfur

We have previously reported that quinoline-2(1*H*)-ones can be readily prepared by reacting α-substituted 2-isocyanostyrenes with *m*-chloroperbenzoic acid (*m*CPBA).[1] The method involves oxidation of 2-isocyanostyrenes to the corresponding 2-isocyanatostyrenes, which spontaneously undergo the electrocyclic reaction to provide 4-substituted quinoline-2(1*H*)-ones. As an extension of this synthesis, we decided to develop a one-pot preparation of quinoline-2(1*H*)-thiones and found that treatment of 2-isocyanostyrenes with sulfur in the presence of a catalytic amount of selenium led to the formation of the desired products, via probably the electrocyclic reaction of the corresponding 2-isothiocyanatestyrenes. We wish to describe the results of our investigation which offer a new and facile method for the preparation of quinoline-2(1*H*)-thiones. Few methods for the preparation of this class of heterocycles have been reported, which are based on the reaction of 2-haloquinolines with thiourea[2a] or sodium sulfide,[2b] and the reaction of quinolin-2(1*H*)-ones with P_2S_5[3a] or Lawesson's reagent.[3b] However, these are of limited generality. Recently, Otani and Saito have reported a synthesis by an indium-promoted Friedel–Crafts alkenylation-cyclization of 2-alkynylphenyl isothiocyanates at higher temparature.[4] A report on the utilization of quinoline-2(1*H*)-thiones to the synthesis of more complex and important heterocycles has appeared.[5]

Our synthesis of 4-substituted quinoline-2(1*H*)-thiones **6** started mainly from 2-aminophenyl aryl ketones **1**, which are commercially available or readily obtained from the reaction of 2-aminobenzonitriles with arylmagnesium bromide followed by acid hydrolysis according to the procedure reported by Hanson et al.,[6] as illustrated in Scheme 1. Thus, treatment of **1** with formic acid in refluxing toluene afforded the corresponding *N*-(2-aroylphenyl)formamides **2**, which were then dehydrated with phosphoryl chloride in the presence of triethylamine in THF at 0 °C[7] to afford 2-isocyanophenyl ketones **3**. Wittig reaction between **3** and methylene- or ethylenetriphenylphosphoranes afforded α-substituted 2-isocyanostyrenes **4**.



Scheme 1 Preparation of quinoline-2(1*H*)-thiones

In general, the 2-isocyanostyrenes **4**, thus obtained, were allowed to react with 1.2 molar amounts of sulfur in THF in the presence of 2.4 molar amounts of triethylamine and 0.03 molar amount of selenium at reflux temperature.[8] The conversion of **4** into the corresponding isothiocyanates **5** and the subsequent electrocyclic reaction proceeded smoothly. Quinoline-2(1*H*)-thiones **6** were obtained by simply evaporating THF and triethylamine after cooling, and subsequently recrystallizing the residual solids from

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Table 1 Preparation of Quinoline-2(1*H*)-thiones **6** from 2-Isocyanostyrenes **4**

Entry	**4**	Conditions[a]	Time	**6** (Yield, %)[b]
1	**4a-i** ($R^1 = R^2 = R^4 = H$, $R^3 = Ph$)	A	20 min	**6a-i** (81)
2	**4a-ii** ($R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = Me$)	B	2.5 h	**6a-ii** (74)
3	**4b** ($R^1 = R^2 = R^4 = H$, $R^3 = p$-Tol)	A	1.5 h	**6b** (79)
4	**4c** ($R^1 = R^2 = R^4 = H$, $R^3 = 4\text{-MeOC}_6H_4$)	A	25 min	**6c** (89)
5	**4d** [$R^1 = R^2 = R^4 = H$, $R^3 = 3,4\text{-(MeO)}_2C_6H_3$]	A	40 min	**6d** (91)
6	**4e** ($R^1 = R^2 = R^4 = H$, $R^3 = Me$)	A	1.5 h	**6e** (37)
7	**4f** ($R^1 = Cl$, $R^2 = R^4 = H$, $R^3 = p$-Tol)	A	1.5 h	**6f** (45)
8	**4g** ($R^1 = R^2 = OMe$, $R^3 = Ph$, $R^4 = H$)	A	1.5 h	**6g** (58)

[a] A: THF, reflux; B: diglyme, 100 °C.
[b] Isolated yields.

appropriate solvents. The reaction conditions and results are summarized in Table 1, which indicates that the yields of the products were generally fair to good, while the substrates bearing chloro or methoxy substituents **4f** or **4g** afforded the desired products **6f** or **6g** in somewhat diminished yields (entries 7 or 8, respectively). The reduced yields of **6f** and **6g** may be attributable to the instability of the starting isocyanides **4f** and **4g**. The yield of 4-methylisoquinoline-2(1*H*)-thione (**6e**) was also rather low (entry 6). Probably, the high electron density of the vinyl moiety facilitates the electrocyclic reaction. Therefore, 1-ethenyl-2-isocyanobenzene ($R^3 = R^4 = H$ in **4**) would give the corresponding desired product in a much lower yield. 1-Isocyano-2-(1-phenylpropen-1-yl)benzene (**4a-ii**) was first treated with sulfur under the conditions mentioned above. However, no desired product, 3-methyl-4-phenylquinoline-2(1*H*)-thione (**6a-ii**), was produced, though TLC analyses for monitoring the progress of the reaction indicated that the starting isocyanide was consumed completely and that the corresponding isothiocyanate precursor **5a-ii** was produced almost quantitatively; the methyl substituent at the β-position of the styrene moiety may make the electrocyclic reaction difficult. Fortunately, the synthesis of **6a-ii** was accomplished by heating the reaction mixture in diethyleneglycol dimethyl ether (diglyme) at 100 °C in fair-to-good yield (entry 2).

In summary, the present work demonstrates that quinoline-2(1*H*)-thiones can be prepared by treating 2-isocyanostyrenes with sulfur in the presence of a catalytic amount of selenium. This method has advantages of simple manipulations as well as ready availability of the starting materials and may find some value in organic synthesis. Investigations on the possibility of the synthesis of derivatives related to quinoline-2(1*H*)-thiones by applying the present procedure are in progress in our laboratory.

All melting points were obtained on a Laboratory Devices MEL-TEMP II and are uncorrected. IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H NMR spectra recorded in $CDCl_3$ using TMS as an internal reference on a JEOL ECP500 FT NMR spectrometer operating at 500 MHz or a JEOL LA400 FT NMR spectrometer operating at 400 MHz. The ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal reference on a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low- and high-resolution MS spectra (EI, 70 eV) were recorded on a JEOL JMS AX505 HA spectrometer. TLC was carried out on a Merck Kieselgel 60 PF_{254}. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All organic solvents used in this study were dried over appropriate drying agents and distilled prior to use. (2-Amininophenyl)phenylmethanone (**1a**) was commercially available. (2-Aminophenyl)(4-methylphenyl)methanone (**1b**) was prepared according to the procedure reported by Hanson et al.[6] (2-Isocyanophenyl)phenylmethanone (**3a**) was prepared from **1a** via *N*-(2-benzoylphenyl)formamide (**2a**) as described previously.[9] 1-Isocyano-2-(1-methylethenyl)benzene (**4e**) was prepared from 2-(1-methylethenyl)benzenamine by the procedure reported previously by us.[10] All other chemicals used in this study were commercially available.

Aryl(2-aminophenyl)methanones 1

These compounds, except for **1a** and **1e**, were prepared by treating 2-aminobenzonitriles with arylmagnesium bromides, followed by acidic hydrolysis, according to the procedure reported by Hanson et al.[6]

(2-Aminophenyl)(4-methoxyphenyl)methanone (1c)[11]

Yield: 88%; yellow solid; mp 75–76 °C (hexane–Et_2O) (Lit.[11] mp 76 °C).

IR (KBr): 3470, 3358, 1614 cm^{-1}.

^{1}H NMR (500 MHz): δ = 3.88 (s, 3 H), 5.85 (br s, 2 H), 6.63 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 1 H), 6.74 (d, *J* = 7.8 Hz, 1 H), 6.95 (d, *J* = 8.7 Hz, 2 H), 7.28 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.46 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.68 (d, *J* = 8.7 Hz, 2 H).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.85; H, 5.75; N, 6.04.

(2-Aminophenyl)(3,4-dimethoxyphenyl)methanone (1d)[12]

Yield: 89%; yellow solid; mp 79–81 °C (hexane) (Lit.[12] mp 78–80 °C).

The spectral (IR and ^{1}H NMR) data of this product were identical to those reported previously.[12]

(2-Amino-4-chlorophenyl)(4-methylphenyl)methanone (1f)

Yield: 76%; yellow solid; mp 115–116 °C (hexane).

IR (KBr): 3452, 3344, 1634, 1605 cm^{-1}.

^1H NMR (500 MHz): δ = 2.43 (s, 3 H), 6.10 (br s, 2 H), 6.57 (dd, *J* = 8.7, 1.8 Hz, 1 H), 6.73 (d, *J* = 1.8 Hz, 1 H), 7.26 (d, *J* = 7.8 Hz, 2 H), 7.39 (d, *J* = 8.7 Hz, 1 H), 7.53 (d, *J* = 7.8 Hz, 2 H).

Anal. Calcd for $C_{14}H_{12}ClNO$: C, 68.44; H, 4.92; N, 5.70. Found: C, 68.17; H, 4.98; N, 5.40.

(2-Amino-4,5-dimethoxyphenyl)phenylmethanone (1g)[12]
Yield: 72%; yellow oil; R_f = 0.47 (2:3 THF–hexane).

The spectral (IR and ^1H NMR) data for this compound were identical to those reported previously.[12]

***N*-(2-Aroylphenyl)formamides 2**
These compounds, except for **2e**, were prepared by treating **1** with HCO_2H in refluxing toluene under azeotropic conditions as described prepviously.[9] Data for new compounds follow.

***N*-[2-(4-Methylbenzoyl)phenyl]formamide (2b)**
Yield: 85%; white solid; mp 68–70 °C (hexane).

IR (KBr): 3300, 3277, 1703, 1618, 1603 cm^{-1}.

^1H NMR (500 MHz): δ = 2.46 (s, 3 H), 7.13 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 1 H), 7.29 (d, *J* = 7.8 Hz, 2 H), 7.56–7.59 (m, 2 H), 7.63 (d, *J* = 7.8 Hz, 2 H), 8.48 (d, *J* = 1.4 Hz, 1 H), 8.64 (d, *J* = 8.2 Hz, 1 H), 10.62 (br s, 1 H).

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.29; H, 5.78; N, 5.83.

***N*-[2-(4-Methoxybenzoyl)phenyl]formamide (2c)**
Yield: 77%; yellow oil; R_f = 0.43 (1:2 EtOAc–hexane).

IR (neat): 3317, 1693, 1634 cm^{-1}.

^1H NMR (500 MHz): δ = 3.90 (s, 3 H), 6.98 (d, *J* = 8.7 Hz, 2 H), 7.15 (dd, *J* = 7.8, 7.3 Hz, 1 H), 7.55–7.58 (m, 2 H), 7.75 (d, *J* = 8.7 Hz, 2 H), 8.46 (s, 1 H), 8.60 (d, *J* = 7.8 Hz, 1 H), 10.42 (br s, 1 H).

Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.53; H, 5.18; N, 5.40.

***N*-[2-(3,4-Dimethoxybenzoyl)phenyl]formamide (2d)**
Yield: 68%; white solid; mp 139–141 °C (hexane–THF).

IR (KBr): 3377, 1697, 1638 cm^{-1}.

^1H NMR (500 MHz): δ = 3.94 (s, 3 H), 3.98 (s, 3 H), 6.91 (d, *J* = 8.7 Hz, 1 H), 7.16 (dd, *J* = 7.8, 7.3 Hz, 1 H), 7.32 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.39 (d, *J* = 1.8 Hz, 1 H), 7.56–7.59 (m, 2 H), 8.46 (d, *J* = 1.4 Hz, 1 H), 8.59 (d, *J* = 7.8 Hz, 1 H), 10.34 (br s, 1 H).

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.31; H, 5.32; N, 4.88.

***N*-[5-Chloro-2-(4-Methylbenzoyl)phenyl]formamide (2f)**
Yield: 90%; yellow solid; mp 123–125 °C (hexane–Et_2O).

IR (KBr): 3227, 1699, 1624 cm^{-1}.

^1H NMR (500 MHz): δ = 2.46 (s, 3 H), 7.11 (dd, *J* = 8.5, 1.6 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.53 (d, *J* = 8.5 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 8.48 (s, 1 H), 8.77 (d, *J* = 1.6 Hz, 1 H), 10.78 (br s, 1 H).

Anal. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.89; H, 4.45; N, 5.02.

***N*-(4,5-Dimethoxy-2-benzoylphenyl)formamide (2g)**
Yield: 84%; yellow solid; mp 119–121 °C (hexane–THF).

IR (KBr): 3227, 1684, 1616 cm^{-1}.

^1H NMR (500 MHz): δ = 3.73 (s, 3 H), 4.02 (s, 3 H), 7.06 (s, 1 H), 7.50 (dd, *J* = 7.8, 7.3 Hz, 2 H), 7.59 (t, *J* = 7.3 Hz, 1 H), 7.67 (d, *J* = 7.8 Hz, 2 H), 8.46 (s, 1 H), 8.49 (d, *J* = 1.4 Hz, 1 H), 11.28 (br s, 1 H).

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.36; H, 5.51; N, 4.69.

2-Isocyanophenyl Ketones 3
These compounds, except for **3e**, were prepared by treating **2** with $POCl_3$–Et_3N in THF at 0 °C under the conditions described previously.[7] Data for new compounds follow.

(2-Isocyanophenyl)(4-methylphenyl)methanone (3b)
Yield: 79%; yellow needle; mp 116–117 °C (hexane–Et_2O).

IR (KBr): 2124, 1655 cm^{-1}.

^1H NMR (500 MHz): δ = 2.44 (s, 3 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.49–7.57 (m, 4 H), 7.72 (d, *J* = 8.2 Hz, 2 H).

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.27; H, 5.16; N, 6.17.

(2-Isocyanophenyl)(4-methoxyphenyl)methanone (3c)
Yield: 84%; yellow oil; R_f = 0.54 (1:2 EtOAc–hexane).

IR (neat): 2124, 1661 cm^{-1}.

^1H NMR (500 MHz): δ = 3.89 (s, 3 H), 6.97 (d, *J* = 8.9 Hz, 2 H), 7.49–7.56 (m, 4 H), 7.80 (d, *J* = 8.9 Hz, 2 H).

Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 76.04; H, 4.92; N, 5.64.

(2-Isocyanophenyl)(3,4-dimethoxyphenyl)methanone (3d)
Yield: 78%; yellow solid; mp 126–128 °C (dec.) (hexane–THF).

IR (KBr): 2129, 1643 cm^{-1}.

^1H NMR (400 MHz): δ = 3.96 (s, 6 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 7.22 (dd, *J* = 8.4, 1.8 Hz, 1 H), 7.48–7.57 (m, 4 H), 7.58 (d, *J* = 1.8 Hz, 1 H).

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.64; H, 4.94; N, 5.34.

(4-Chloro-2-isocyanophenyl)(4-methylphenyl)methanone (3f)
Yield: 92%; yellow oil; R_f = 0.70 (1:5 EtOAc–hexane).

IR (neat): 2124, 1668, 1605 cm^{-1}.

^1H NMR (500 MHz): δ = 2.45 (s, 3 H), 7.30 (d, *J* = 7.8 Hz, 2 H), 7.46 (d, *J* = 8.7 Hz, 1 H), 7.50 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.51 (s, 1 H), 7.69 (d, *J* = 7.8 Hz, 2 H).

This compound was rather unstable and decomposed during the isolation procedure (distillation and chromatography on silica gel), so it was used in the next step after workup without any purification.

(2-Isocyano-4,5-dimethoxyphenyl)(4-methylphenyl)methanone (3g)
Yield: 72%; yellow solid; mp 122–124 °C (hexane–Et_2O).

IR (KBr): 2127, 1652 cm^{-1}.

^1H NMR (500 MHz): δ = 3.91 (s, 3 H), 3.97 (s, 3 H), 6.93 (s, 1 H), 7.01 (s, 1H), 7.50 (dd, *J* = 7.8, 7.3 Hz, 2 H), 7.63 (tt, *J* = 7.3, 1.4 Hz, 1 H), 7.81 (dd, *J* = 7.8, 1.4 Hz, 2 H).

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.72; H, 5.12; N, 5.23.

2-Isocyanostyrenes 4
These compounds, except for **4e**, were prepared by treating **3** (30 mmol) with methylenetriphenylphosphorane or ethylenetriphenylphosphorane (4.5 mmol) in THF (10 mmol) at 0 °C. Workup (Et_2O/H_2O) and subsequent purification by recrystallization or column chromatography on silica gel gave the products.

1-Isocyano-2-(1-phenylethenyl)benzene (4a-i)[10]
Yield: 74%; yellow oil; R_f = 0.66 (1:4 Et_2O–hexane).

The spectral (IR and ^1H NMR) data for this product were identical to those reported previously.[10]

1-Isocyano-2-(1-phenylprop-1-enyl)benzene (4a-ii)[1]
Yield: 68%; a mixture of stereoisomers (*E*/*Z* = ca. 8:2); yellow oil; R_f = 0.67 (1:3 Et_2O–hexane).

IR (neat): 2122 cm^{-1}.

^1H NMR (500 MHz): δ = 1.69 (d, *J* = 7.3 Hz, 2.4 H), 1.93 (d, *J* = 6.9 Hz, 0.6 H), 6.02 (q, *J* = 6.9 Hz, 0.2 H), 6.39 (q, *J* = 7.3 Hz, 0.8 H), 7.16–7.47 (m, 9 H).

1-Isocyano-2-[1-(4-methylphenyl)ethenyl]benzene (4b)[13]
Yield: 76%; pale-yellow oil; R_f = 0.55 (1:9 Et_2O–hexane).

IR (neat): 2122, 1618 cm^{-1}.

^1H NMR (500 MHz): δ = 2.35 (s, 3 H), 5.34 (s, 1 H), 5.84 (s, 1 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 7.15 (d, *J* = 8.2 Hz, 2 H), 7.34–7.37 (m, 2 H), 7.39–7.42 (m, 2 H).

1-Isocyano-2-[1-(4-methoxyphenyl)ethenyl]benzene (4c)[10]
Yield: 61%; yellow oil; R_f = 0.64 (1:2 Et_2O–hexane).

The spectral (IR and ^1H NMR) data for this product were identical to those reported previously.[10]

1-Isocyano-2-[1-(3,4-dimethoxyphenyl)ethenyl]benzene (4d)[10]
Yield: 50%; yellow oil; R_f = 0.50 (1:2 Et_2O–hexane).

The spectral (IR and ^1H NMR) data for this product were identical to those reported previously.[10]

1-Chloro-3-isocyano-4-[1-(4-methylphenyl)ethenyl]benzene (4f)
Yield: 45%; yellow oil; R_f = 0.73 (1:9 Et_2O–hexane).

IR (neat): 2122 cm^{-1}.

^1H NMR (500 MHz): δ = 2.35 (s, 3 H), 5.34 (s, 1 H), 5.84 (s, 1 H), 7.13 (s, 4 H), 7.29 (d, *J* = 8.2 Hz, 1 H), 7.38 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.40 (d, *J* = 1.8 Hz, 1 H).

HRMS: *m*/*z* calcd for $C_{16}H_{12}ClN$ (M^+): 253.0658; found: 253.0678.

1-Isocyano-4,5-dimethoxy-2-[1-(4-methylphenyl)ethenyl]benzene (4g)
Yield: 60%; white solid; mp 99–100 °C (hexane).

IR (KBr): 2120, 1606 cm^{-1}.

^1H NMR (500 MHz): δ = 3.87 (s, 3 H), 3.91 (s, 3 H), 5.40 (s, 1 H), 5.86 (s, 1 H), 6.75 (s, 1 H), 6.89 (s, 1 H), 7.27–7.35 (m, 5 H).

HRMS: *m*/*z* calcd for $C_{17}H_{15}NO_2$ (M^+): 265.1103; found: 265.1084.

4-Phenylquinoline-2(1*H*)-thione (6a-i);[14] Typical Procedure
A solution of **4a** (0.21 g, 1.0 mmol) in THF (6 mL) containing Et_3N (0.24 g, 2.4 mmol), sulfur (powder; 39 mg, 1.2 mmol), and selenium (powder; 2.3 mg, 0.030 mmol) was heated at reflux temperature for 30 min. After cooling, THF and Et_3N were evaporated. The residual solid was recrystallized from hexane–THF to give **6a-i** as yellow needles; yield: 0.19 g (81%); mp 221–224 °C (dec.) (Lit.[4] mp 224–227 °C).

IR (KBr): 3445, 1620, 1117 cm^{-1}.

^1H NMR (500 MHz): δ = 7.30 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.47–7.48 (m, 3 H), 7.51–7.53 (m, 3 H), 7.57 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.61 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.66 (d, *J* = 7.8 Hz, 1 H), 12.15 (br s, 1 H).

3-Methyl-4-phenylquinoline-2(1*H*)-thione (6a-ii)
Yellow solid; mp 225–229 °C (dec.) (hexane–Et_2O).

IR (KBr): 3192, 1618, 1065 cm^{-1}.

^1H NMR (500 MHz): δ = 2.33 (s, 3 H), 7.13 (d, *J* = 7.8 Hz, 1 H), 7.21 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.23 (dd, *J* = 7.8, 1.4 Hz, 2 H), 7.49 (tt, *J* = 7.3, 1.4 Hz, 1 H), 7.53–7.56 (m, 4 H), 12.22 (br s, 1 H).

^{13}C NMR (125 MHz): δ = 19.65, 115.56, 124.02, 124.39, 127.21, 128.25, 128.56, 128.78, 130.14, 135.16, 136.81, 137.49, 145.67, 181.62.

MS: *m*/*z* (%) = 251 (66, [M^+]), 250 (100).

Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.40; H, 5.31; N, 5.67.

4-(4-Methylphenyl)quinoline-2(1*H*)-thione (6b)
Yellow solid; mp 229–230 °C (dec.) (hexane–THF).

IR (KBr): 3109, 1620, 1111 cm^{-1}.

^1H NMR (500 MHz): δ = 2.46 (s, 3 H), 7.29 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.33 (d, *J* = 7.8 Hz, 2 H), 7.37 (d, *J* = 7.8 Hz, 2 H), 7.45 (s, 1 H), 7.55 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.59 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.69 (d, *J* = 7.8 Hz, 1 H), 12.02 (br s, 1 H).

MS: *m*/*z* (%) = 251 (100, [M^+]).

Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.19; H, 5.29; N, 5.60.

4-(4-Methoxyphenyl)quinoline-2(1*H*)-thione (6c)
Yellow solid; mp 225–228 °C (dec.) (hexane–THF).

IR (KBr): 3196, 1620, 1113 cm^{-1}.

^1H NMR (500 MHz): δ = 3.90 (s, 3 H), 7.05 (d, *J* = 8.7 Hz, 2 H), 7.30 (ddd, *J* = 8.2, 7.3, 1.8 Hz, 1 H), 7.42 (s, 1 H), 7.45 (d, *J* = 8.7 Hz, 2 H), 7.57–7.61 (m, 2 H), 7.72 (d, *J* = 8.2 Hz, 1 H), 12.14 (br s, 1 H).

^{13}C NMR (125 MHz): δ = 55.41, 114.22, 116.49, 122.51, 124.63, 126.86, 128.38, 130.43, 130.82, 131.24, 139.49, 147.78, 160.44, 179.70.

MS: *m*/*z* (%) = 267 (100, [M^+]).

Anal. Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24. Found: C, 71.75; H, 4.86; N, 5.14.

4-(3,4-Dimethoxyphenyl)quinoline-2(1*H*)-thione (6d)
Yellow solid; mp 195–199 °C (dec.) (hexane–THF).

IR (KBr): 3167, 1616, 1113 cm^{-1}.

^1H NMR (400 MHz): δ = 3.92 (s, 3 H), 3.97 (s, 3 H), 6.99 (d, *J* = 1.8 Hz, 1 H), 7.00 (d, *J* = 8.4 Hz, 1 H), 7.06 (dd, *J* = 8.4, 1.8 Hz, 1 H), 7.31 (ddd, *J* = 8.1, 7.3, 1.1 Hz, 1 H), 7.47 (s, 1 H), 7.53 (d, *J* = 8.1 Hz, 1 H), 7.60 (ddd, *J* = 8.1, 7.3, 1.1 Hz, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 11.83 (br s, 1 H).

^{13}C NMR (125 MHz): δ = 56.05, 56.13, 111.22, 112.14, 116.62, 121.94, 122.54, 124.74, 126.89, 128.67, 130.85, 131.32, 139.59, 147.93, 149.19, 149.95, 179.66.

MS: *m*/*z* (%) = 297 (100, [M^+]).

Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08; N, 4.71. Found: C, 68.52; H, 5.23; N, 4.47.

4-Methylquinoline-2(1*H*)-thione (6e)[2]
Yellow solid; mp 226–228 °C (dec.) [Lit.[2] mp 266 °C (dec.)].

IR (KBr): 3206, 1622, 1109 cm^{-1}.

^1H NMR (500 MHz): δ = 2.51 (s, 3 H), 7.37 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.39 (s, 1 H), 7.49 (d, *J* = 7.8 Hz, 1 H), 7.59 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.76 (dd, *J* = 7.8, 1.4 Hz, 1 H), 11.84 (br s, 1 H).

6-Chloro-4-(4-methylphenyl)quinoline-2(1*H*)-thione (6f)
Yellow solid; mp 240–243 °C (dec.) (hexane–THF).

IR (KBr): 3161, 1614, 1123 cm^{-1}.

^1H NMR (500 MHz): δ = 2.46 (s, 3 H), 7.23 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.34 (s, 4 H), 7.41 (s, 1 H), 7.48 (d, *J* = 1.8 Hz, 1 H), 7.61 (d, *J* = 8.7 Hz, 1 H), 11.64 (br s, 1 H).

MS: *m*/*z* (%) = 285 (100, $[M^+]$).

Anal. Calcd for $C_{16}H_{12}ClNS$: C, 67.24; H, 4.23; N, 4.90. Found: C, 67.15; H, 4.23; N, 4.60.

5,6-Dimethoxy-4-phenylquinoline-2(1*H*)-thione (6g)
Yellow solid; mp 214–217 °C (dec.) (hexane–THF).

IR (KBr): 3186, 1622, 1115 cm^{-1}.

^1H NMR (500 MHz): δ = 3.78 (s, 3 H), 4.04 (s, 3 H), 7.00 (s, 1 H), 7.25 (s, 1 H), 7.26 (s, 1 H), 7.41–7.56 (m, 5 H), 13.24 (br s, 1 H).

MS: *m*/*z* (%) = 297 (100, $[M^+]$).

Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08; N, 4.71. Found: C, 68.62; H, 5.10; N, 4.72.

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