Synthesis of Novel *N*-Thiazolo-1,3-oxathiol-2-imines from α-Haloketones Using Potassium Thiocyanate–Silica Gel

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Abstract: Novel *N*-thiazolo-1,3-oxathiol-2-imines are synthesized by reaction of α-haloketones with potassium thiocyanate–silica gel. It is thought that the reaction occurs through conversion of the α-haloketone into the corresponding thiocyanate which then undergoes acid-catalyzed intramolecular cyclization to yield a cationic intermediate. Subsequent reaction of this intermediate with another molecule of the α-thiocyanatoketone and a second cyclization then gives the *N*-thiazolo-1,3-oxathiol-2-imine.

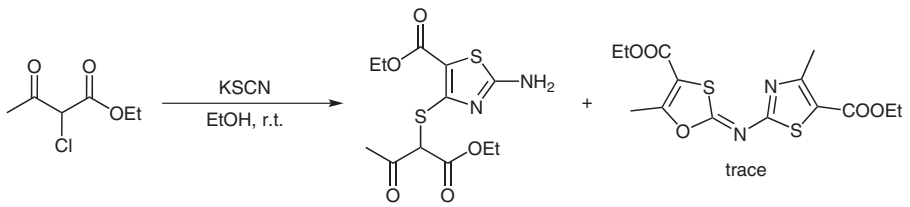
Key words: *N*-thiazolo-1,3-oxathiol-2-imines, potassium thiocyanate–silica gel, heterocycles

Prior to 1966, only a few simple 1,3-oxathioles were known.[1] Since, many different 1,3-oxathioles have been reported, however, compared to other heterocyclic compounds, they proved unsuitable as candidates in medicinal and agricultural fields. Recently, the synthesis of 2-imino-1,3-oxathioles has assumed importance due to the potent biological activities associated with compounds incorporating this heterocyclic system.[2] Hence, a number of synthetic procedures for 1,3-oxathiole derivatives have been reported. For example, 1,3-oxathiole derivatives can be prepared by the following methods: reaction of *O*-methyl benzoylcarbamothioate with an α-haloketone in the presence of sodium methoxide to give ethyl 2-(benzoylimino)-5-methyl-1,3-oxathiol-4-carboxylate,[3] rhodium(II) acetate catalyzed reactions of α-diazocarbonyl compounds with isothiocyanates,[4] chlorine–oxygen substitution and ring transformation of 5-chloro-1,2,4-thiadiazol-3(2*H*)-ones and active methylene ketones,[5] and via [4+1] cycloaddition of *o*-thioquinones with isocyanides.[6] Atkins et al. reported that a trace amount of ethyl *N*-[2-(4-methyl-5-carboxyethylthiazolo)]-5-methyl-1,3-oxathiol-2-imine-4-carboxylate was formed as a by-product in the reaction of ethyl 2-chloro-3-oxobutanoate and potassium thiocyanate in ethanol (Scheme 1).[7] To the best of our knowledge, there are no reports on the synthesis of *N*-thiazolo-1,3-oxathiol-2-imines, although a related compound, *N*-benzothioazolo-1,3-oxathiol-2-imine was described by Niki et al. as an agricultural and horticultural fungicide.[8]

We previously reported on the one-pot synthesis of aminothiazoles from α-haloketones using KSCN–SiO_2 and RNH_3OAc–Al_2O_3. A trace amount of *N*-[2-(4,5-diphenylthiazolo)]-4,5-diphenyl-1,3-oxathiol-2-imine (**3a**) was formed along with the expected 2-amino-4,5-diphenylthiazole during the reaction with 2-bromo-1,2-diphenylethanone (**1a**).[9]

In continuation of this work, we describe herein the development of a method for the synthesis of novel *N*-thiazolo-1,3-oxathiol-2-imine derivatives via reaction of α-haloketones with potassium thiocyanate–silica gel (KSCN–SiO_2).

Initially, we attempted to convert 2-oxo-1,2-diphenylethylthiocyanate (**2a**) into *N*-[2-(4,5-diphenylthiazolo)]-4,5-diphenyl-1,3-oxathiol-2-imine (**3a**) in order to confirm that **3a** was indeed formed from **1a** via thiocyanate **2a** (Table 1). Thus a solution of **2a** in toluene was stirred at 80 °C for six hours but no **3a** was formed (Table 1, entry 1). *N*-Thiazolo-1,3-oxathiol-2-imine **3a** was obtained in 24% yield when methanol was used as the solvent instead of toluene (Table 1, entry 2). The same reaction in the presence of silica gel as catalyst, in toluene or methanol, afforded **3a** in 20% and 26% yields, respectively (Table 1,



Scheme 1 Reaction of ethyl 2-chloro-3-oxobutanoate and potassium thiocyanate

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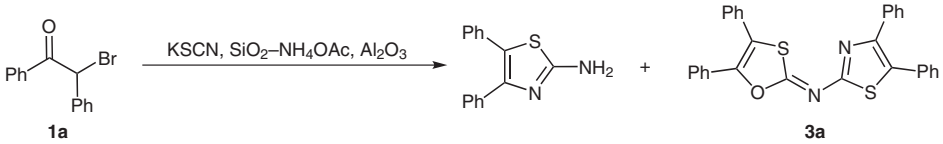
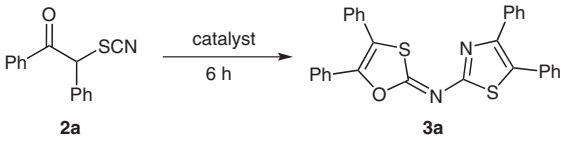


Scheme 2 Formation of *N*-thiazolo-1,3-oxathiol-2-imine **3a**

Table 1 Synthesis of *N*-Thiazolo-1,3-oxathiol-2-imine **3a** from Thiocyanate **2a**



Entry	Catalyst	Solvent	Temp (°C)	Yield (%)
1	none	toluene	80	0
2	none	MeOH	reflux	24
3	SiO_2	toluene	80	20
4	SiO_2	MeOH	reflux	26
5	KSCN	MeOH	reflux	27
6	KSCN	toluene	80	0
7	KSCN–SiO_2	toluene	80	58

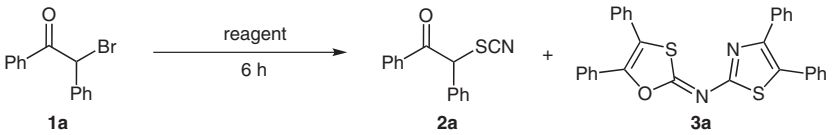
entries 3 and 4). The use of potassium thiocyanate as catalyst did not improve the yield of **3a**. However, the reaction using potassium thiocyanate–silica gel as catalyst afforded **3a** in a moderate yield of 58% (Table 1, entry 7).

It is well known that thiocyanates **2** can be easily prepared by reaction of an α-haloketone with potassium thiocyanate, therefore, we attempted to synthesize *N*-thiazolo-1,3-oxathiol-2-imines **3** directly from **1a** (Table 2). A mixture of **1a** (1 mmol) and potassium thiocyanate (5 mmol) in methanol was stirred for six hours at reflux to afford **3a** in 21% yield along with numerous by-products which were difficult to isolate (Table 2, entry 1). When the same reaction was carried out in the presence of silica gel, the desired product **3a** was obtained in 30% yield along with a 46% yield of 1,2-diphenylethanone as the major product (Table 2, entry 2). Compound **1a** did not react with finely ground potassium thiocyanate suspended in toluene (potassium thiocyanate is insoluble in non-polar solvents, Table 2, entry 3). In contrast, the same reaction using potassium thiocyanate–silica gel proceeded readily in toluene at 80 °C to afford **3a** in 64% yield after six hours (Table 2, entry 4). It is assumed that cationic intermediate **2′a**, which is formed by acid-catalyzed intramolecular cyclization of thiocyanate **2a**, reacts with another molecule of **2a** to afford intermediate **3′a**. Further cyclization and elimination of water then yields *N*-thiazolo-1,3-oxathiol-2-imine **3a** (Scheme 3).

Next, a catalytic amount of aqueous hydrochloric acid or *p*-toluenesulfonic acid (PTSA) was added to the reaction mixture in an attempt to promote the formation of intermediate **2′a**. However, the yield of product **3a** decreased and thiocyanate **2a** was obtained as the major product (Table 2, entries 5 and 6).

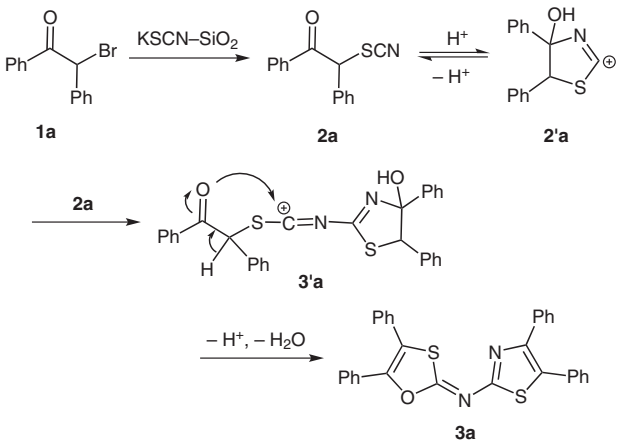
In order to determine the optimum reaction conditions for the synthesis of **3a** the reaction of **1a** and potassium thiocyanate–silica gel was investigated under various conditions (Table 3). *N*-Thiazolo-1,3-oxathiol-2-imine **3a** was obtained in 64% yield when a mixture of **1a** and potassium thiocyanate–silica gel in toluene (10 mL) was stirred at 80 °C for six hours (Table 3, entry 1). Decreasing the reaction temperature led to an increase in the yield of thiocyanate **2a** which was obtained in 69% yield as the major

Table 2 Direct Synthesis of *N*-Thiazolo-1,3-oxathiol-2-imine **3a** from α-Haloketone **1a**



Entry	Reagent	Solvent	Temp (°C)	Yield (%) **2a**	Yield (%) **3a**
1	KSCN	MeOH	reflux	11	21
2[a]	KSCN, SiO_2	MeOH	reflux	13	30
3	KSCN[b]	toluene	80	0	0
4	KSCN–SiO_2	toluene	80	4	64
5	KSCN–SiO_2, HCl	toluene	80	77	8
6	KSCN–SiO_2, PTSA	toluene	80	93	3

[a] A 46% yield of the debrominated starting material, 1,2-diphenylethanone, was obtained.
[b] No reaction using finely ground KSCN.

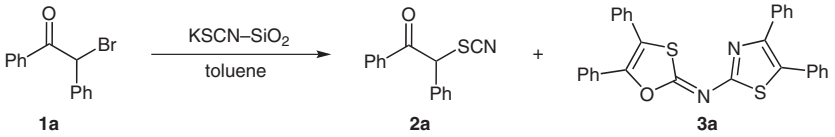


Scheme 3 A plausible mechanism for the synthesis of **3a**

product along with **3a** (3%) when the reaction was carried out at 40 °C (Table 3, entry 4), and at 25 °C, only **2a** was formed (Table 3, entry 5). A number of by-products were evident and the isolation of **3a** proved difficult when the reaction was carried out at 100 °C (Table 3, entry 2). A reduction in the volume of the solvent resulted in higher yields of **3a**; reaction using toluene (5 mL) gave products **3a** and **2a** in 74% and 24% yields, respectively; however, side reactions occurred when the quantity of solvent was decreased further (Table 3, entries 6 and 7). The amount of potassium thiocyanate–silica gel employed did not have a significant impact on the yield of **3a** (Table 3, entries 8–10). Reactions using potassium thiocyanate–silica gel (1.5 g) were carried out over longer periods in an effort to further improve the yield of **3a**, but unfortunately, the yield was not increased significantly (Table 3, entries 12 and 13). All further reactions were carried out using α-haloketone (1 mmol), potassium thiocyanate–silica gel (1.5 g, 5 mmol/g) and toluene (5 mL) as solvent, over six hours at a temperature of 80 °C.

In order to assess the scope of this procedure the reactions of various α-haloketones with potassium thiocyanate–silica gel were examined and the results are summarized in Table 4. Reaction of 2-bromo-1-(4-chlorophenyl)-2-phenylethanone (**1b**), which possesses an electron-withdrawing group, gave **3b** in a high 82% yield, whereas reactions using α-haloketones **1c** and **1d** possessing electron-donating groups gave products **3c** and **3d** in moderate yields (Table 4, entries 1–3). A possible explanation for the higher yield of **3b** compared to **3a**,**c**,**d** is as follows. The carbonyl carbon of **2b**, situated adjacent to the electron-withdrawing 4-chlorophenyl group, is more active toward nucleophilic attack by the thiocyanate N atom than that in **2a**,**c**,**d**, and therefore, conversion of **2b** into **2′b** occurs rapidly. The reaction using **1c** also gave debrominated 1-(4-methylphenyl)-2-phenylethanone in 36% yield along with products **2c** and **3c** (Table 4, entry 2). The structure of **3c** was confirmed by X-ray crystal structure analysis (Figure 1).

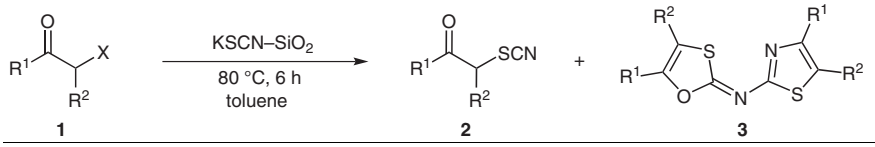
Table 3 Determination of the Optimum Reaction Conditions for the Synthesis of **3a**

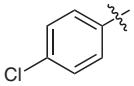
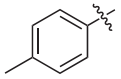
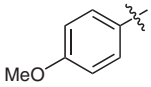
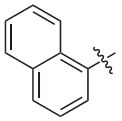
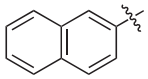


Entry	$KSCN–SiO_2$ (g)[a]	Solvent (mL)	Temp (°C)	Time (h)	Yield (%)[b] **2a**	Yield (%)[b] **3a**
1	1.0	10	80	6	4	64
2	1.0	10	100	6	8	68
3	1.0	10	60	6	11	54
4	1.0	10	40	6	69	3
5	1.0	10	25	6	quant.	0
6	1.0	5	80	6	24	74
7	1.0	3	80	6	0	70
8	0.5	5	80	6	5	71
9	1.5	5	80	6	12	76
10	2.0	5	80	6	7	78
11	1.5	5	80	4	18	71
12	1.5	5	80	12	9	77
13	1.5	5	80	24	6	80

[a] The loading ratio is 5.0 mmol/g.
[b] Yield of isolated product.

Table 4 Synthesis of *N*-Thiazolo-1,3-oxathiol-2-imines from α-Haloketones in the Presence of Potassium Thiocyanate–Silica Gel



Entry	α-Haloketone	R^1	R^2	X	2	Yield (%)[a]	3	Yield (%)[a]
1	**1b**			Br	**2b**	6	**3b**	82
2[b]	**1c**			Br	**2c**	15	**3c**	47
3	**1d**			Br	**2d**	22	**3d**	47
4	**1e**			Br	**2e**	12	**3e**	77
5	**1f**			Br	**2f**	12	**3f**	76
6	**1g**			Br	**2g**	65	**3g**	27
7	**1h**	Me		Br	**2h**	27	**3h**	25
8	**1i**		H	Br	**2i**	65	**3i**	trace
9	**1j**		Me	Br	**2j**	67	**3j**	12
10[c]	**1k**			Br	**2k**	12	**3k**	0
11	**1l**	Me	Me	Cl	**2l**	95	**3l**	0

[a] Yield of isolated product.
[b] A 36% yield of 1-(4-methylphenyl)-2-phenylethanone was obtained.
[c] Starting material **1k** was recovered in 86% yield.

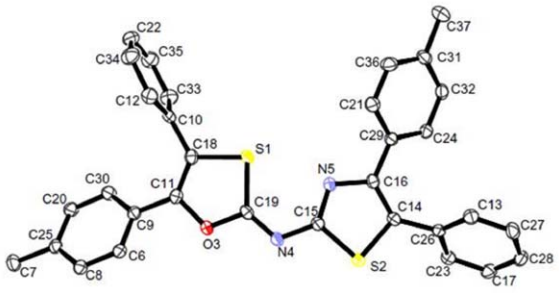


Figure 1 ORTEP representation of the crystal structure of **3c**

2-Bromo-1-(1-naphthyl)-2-phenylethanone (**1e**) and 2-bromo-1-(2-naphthyl)-2-phenylethanone (**1f**) reacted with potassium thiocyanate–silica gel to give compounds **3e** and **3f** in good yields (Table 4, entries 4 and 5). The α-haloketone **1g** which contains a thienyl group instead of a phenyl group gave thiocyanate **2g** as the major product and only a 27% yield of the desired product **3g** (Table 4, entry 6). 1-Bromo-1-phenylpropan-2-one (**1h**) was converted into compounds **2h** and **3h** in poor yields and the formation of numerous by-products was observed (Table 4, entry 7). The reactions of α-bromoacetophenone (**1i**) and α-bromopropiophenone (**1j**) gave thiocyanates **2i** and **2j** in 65% and 67% yields along with a trace amount of **3i** and 12% of **3j** (Table 4, entries 8 and 9). Reaction of

2-bromo-2-cyclohexyl-1-phenylethanone (**1k**) with potassium thiocyanate–silica gel afforded **2k** in 12% yield along with recovered starting material (86%). On the other hand, reaction of 3-chloro-2-butanone (**1l**) with potassium thiocyanate–silica gel gave thiocyanate **2l** in almost quantitative yield (Table 4, entries 10 and 11).

In conclusion, *N*-thiazolo-1,3-oxathiol-2-imines have been synthesized via reaction of various α-haloketones with potassium thiocyanate–silica gel in toluene at 80 °C. The heterocycles reported herein are important in the context of the potent biological activities typically associated with compounds incorporating this heterocyclic system.

Melting points were determined using a Yanako Micro melting point apparatus. IR spectra were obtained using a Thermo Electron Nicolet 380 spectrometer. NMR spectra were recorded using a JEOL JNM-GX400 or a JEOL JNM-ECX400 spectrometer [^{1}H NMR at 400 MHz using tetramethylsilane (δ = 0) as the internal standard and ^{13}C NMR at 100 MHz using $CDCl_3$ (δ = 77.0) as the internal standard]. High resolution TOF mass spectra were obtained using an Agilent G1969 LC/MDS TOF spectrometer. Elemental analysis data were recorded using a Yanako CHN corder MT-5. Column chromatography was carried out on silica gel 60N (40–50 μm) from Kanto Chemical Co. Inc.

Potassium Thiocyanate–Silica Gel

Silica gel [25.70 g, Wakogel C-200 (Wako Pure Chemical Ind. Ltd.)] was added to a soln of KSCN (24.3 g, 250 mmol) in distilled H_2O and the mixture was stirred at r.t. for 0.5 h. The H_2O was evaporated under reduced pressure at a temperature below 80 °C, and the residue was dried in vacuo (10 mmHg) at r.t. for 2 h.

***N*-Thiazolo-1,3-oxathiol-2-imines; General Procedure**

A mixture of α-haloketone (1 mmol) and KSCN–SiO_2 (5 mmol) was stirred in toluene (5 mL) at 80 °C for 6 h, after which the supported reagent was removed by filtration. The filtrate was evaporated to leave a crude residue which was purified by column chromatography using hexane–EtOAc (4:1) as eluent.

***N*-[2-(4,5-Diphenylthiazolo)]-4,5-diphenyl-1,3-oxathiol-2-imine (3a)**

Yellow solid; mp 189–190 °C.

IR (neat): 3058, 1739, 1580, 1090, 1446, 763, 696 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.44 (16 H, m), 7.49–7.52 (2 H, m), 7.60–7.62 (2 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.4, 127.3, 127.6, 127.9, 128.2, 128.5, 128.7, 128.8, 129.1, 129.1, 129.2, 129.3, 129.4, 129.7, 129.8, 132.4, 134.9, 141.5, 146.0, 165.5, 166.0.

HRMS–TOF (CI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{21}N_2OS_2$: 489.1095; found: 489.1098.

Anal. Calcd for $C_{30}H_{20}N_2OS_2$: C, 73.74; H, 4.13; N, 5.73; S, 13.12. Found: C, 73.82; H, 4.13; N, 5.70; S, 13.03.

***N*-{2-[4-(4-Chlorophenyl)-5-phenylthiazolo]}-4-phenyl-5-(4-chlorophenyl)oxathiol-2-imine (3b)**

Yellow solid; mp 102 °C.

IR (neat): 3058, 2925, 1572, 1475, 1093 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (2 H, d, *J* = 8.7 Hz), 7.28 (2 H, d, *J* = 8.7 Hz), 7.33–7.39 (5 H, m), 7.43–7.46 (7 H, m), 7.53 (2 H, d, *J* = 8.7 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.0, 126.3, 128.2, 128.4, 128.6, 128.8, 128.9, 129.3, 129.4, 129.4, 129.5, 129.6, 130.1, 132.0, 133.3, 133.4, 135.3, 140.5, 144.8, 165.5, 165.7.

HRMS–TOF (CI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{19}N_2OS_2Cl_2$: 557.0315; found: 557.0314.

Anal. Calcd for $C_{30}H_{18}N_2OS_2Cl_2$: C, 64.63; H, 3.25; N, 5.02; S, 11.50. Found: C, 64.59; H, 3.24; N, 4.85; S, 11.46.

***N*-{2-[4-(4-methylphenyl)-5-phenylthiazolo]}-4-phenyl-5-(4-methylphenyl)oxathiol-2-imine (3c)**

Yellow solid; mp 114 °C.

IR (neat): 3029, 1558, 1078, 756, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (3 H, s), 2.34 (3 H, s), 7.04–7.15 (4 H, m), 7.28–7.46 (12 H, m), 7.48–7.54 (2 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 21.4, 116.5, 125.1, 127.3, 127.8, 128.4, 128.7, 128.7, 128.9, 129.0, 129.2, 129.2, 129.4, 129.7, 130.0, 132.1, 132.6, 137.4, 139.6, 141.8, 146.1, 165.5, 166.1.

HRMS–TOF (CI): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{25}N_2OS_2$: 517.1408; found: 517.1413.

Anal. Calcd for $C_{32}H_{24}N_2OS_2$: C, 74.39; H, 4.68; N, 5.42; S, 12.41. Found: C, 74.73; H, 4.60; N, 5.34; S, 12.53.

***N*-{2-[4-(4-Methoxyphenyl)-5-phenylthiazolo]}-4-phenyl-5-(4-methoxyphenyl)oxathiol-2-imine (3d)**

Yellow solid; mp 211–212 °C.

IR (neat): 2931, 1610, 1539, 1254, 1031, 834 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (3 H, s), 3.81 (3 H, s), 6.80–6.84 (4 H, m), 7.30–7.37 (3 H, m), 7.39–7.45 (9 H, m), 7.53–7.57 (2 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2, 55.3, 113.6, 113.9, 115.2, 120.4, 127.5, 127.6, 127.7, 128.7, 128.9, 128.9, 129.2, 129.4, 129.7, 130.1, 132.7, 141.6, 145.8, 159.0, 160.2, 165.4, 166.0.

HRMS–TOF (CI): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{25}N_2O_3S_2$: 549.1306; found: 549.1302.

Anal. Calcd for $C_{32}H_{24}N_2O_3S_2$: C, 70.05; H, 4.41; N, 5.11; S, 11.69. Found: C, 70.08; H, 4.23; N, 5.25; S, 11.72.

***N*-{2-[4-(1-Naphthyl)-5-phenylthiazolo]}-5-(1-naphthyl)-4-phenyl-1,3-oxathiol-2-imine (3e)**

Yellow solid; mp 186–187 °C.

IR (neat): 3054, 2927, 1723, 1558, 1446, 1116, 773, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.03–7.16 (10 H, m), 7.41–7.56 (8 H, m), 7.89–7.97 (5 H, m), 8.13 (1 H, d, *J* = 8.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.2, 125.2, 125.3, 125.4, 125.8, 125.9, 126.0, 126.5, 126.6, 127.2, 127.3, 128.0, 128.2, 128.4, 128.4, 128.5, 128.6, 128.6, 128.7, 128.8, 129.3, 129.6, 130.8, 131.4, 131.8, 132.1, 132.2, 133.2, 133.7, 133.9, 141.4, 145.9, 165.4, 166.4.

HRMS–TOF (CI): *m*/*z* [M + H]$^+$ calcd for $C_{38}H_{25}N_2OS_2$: 589.1408; found: 589.1413.

Anal. Calcd for $C_{38}H_{24}N_2OS_2$: C, 77.52; H, 4.11; N, 4.76; S, 10.89. Found: C, 77.21; H, 4.24; N, 4.75; S, 10.94.

***N*-{2-[4-(2-Naphthyl)-5-phenylthiazolo]}-5-(2-naphthyl)-4-phenyl-1,3-oxathiol-2-imine (3f)**

Yellow solid; mp 206 °C.

IR (neat): 3052, 1561, 746, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.34 (3 H, m), 7.42–7.45 (8 H, m), 7.48–7.52 (4 H, m), 7.68–7.82 (7 H, m), 8.12 (1 H, s), 8.18 (1 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.8, 124.1, 125.2, 125.9, 126.1, 126.7, 126.8, 127.2, 127.4, 127.5, 127.6, 128.0, 128.1, 128.4, 128.5, 128.7, 129.3, 129.5, 129.5, 129.7, 129.8, 132.4, 132.4, 132.7, 132.9, 133.2, 133.3, 141.6, 146.0, 165.6, 166.0.

HRMS–TOF (CI): *m*/*z* [M + H]$^+$ calcd for $C_{38}H_{25}N_2OS_2$: 589.1408; found: 589.1417.

Anal. Calcd for $C_{38}H_{24}N_2OS_2$: C, 77.52; H, 4.11; N, 4.76; S, 10.89. Found: C, 77.62; H, 3.87; N, 4.77; S, 11.12.

***N*-[2-(5-Phenyl-4-thienylthiazolo)]-5-thienyl-4-phenyl-1,3-oxathiol-2-imine (3g)**
Yellow solid; mp 172 °C.

IR (neat): 1626, 1561, 853, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.88 (1 H, dd, *J* = 5.0, 3.7 Hz), 6.98 (1 H, dd, *J* = 5.1, 3.7 Hz), 7.06 (1 H, dd, *J* = 3.7, 1.4 Hz), 7.17 (1 H, dd, *J* = 5.0, 0.9 Hz), 7.27 (1 H, dd, *J* = 5.1, 1.4 Hz), 7.29 (1 H, dd, *J* = 3.7, 0.9 Hz), 7.41–7.47 (3 H, m), 7.49–7.58 (7 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.9, 125.3, 127.1, 127.2, 127.3, 127.4, 128.7, 128.8, 129.0, 129.4, 129.4, 129.7, 130.0, 130.3, 131.7, 137.7, 138.2, 140.4, 165.4, 166.2.

HRMS–TOF (CI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{17}N_2OS_4$: 501.0223; found: 501.0228.

Anal. Calcd for $C_{26}H_{16}N_2OS_4$: C, 62.37; H, 3.22; N, 5.60; S, 25.62. Found: C, 62.48; H, 3.14; N, 5.65; S, 25.31.

***N*-[2-(4-Methyl-5-phenylthiazolo)]-5-methyl-4-phenyl-1,3-oxathiol-2-imine (3h)**
Yellow solid; mp 123 °C.

IR (neat): 2920, 1661, 1568, 762, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (3 H, s), 2.49 (3 H, s), 7.25–7.46 (10 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8, 16.4, 116.0, 127.2, 128.0, 128.4, 128.5, 128.6, 129.0, 129.0, 129.8, 132.6, 141.0, 144.3, 165.2, 166.1.

HRMS–TOF (CI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}N_2OS_2$: 365.0782; found: 365.0789.

Anal. Calcd for $C_{20}H_{16}N_2OS_2$: C, 65.91; H, 4.42; N, 7.69; S, 17.59. Found: C, 65.86; H, 4.41; N, 7.23; S, 17.64.

***N*-[2-(4-Phenylthiazolo)]-5-phenyl-1,3-oxathiol-2-imine (3i)**
White solid; mp 173–174 °C.

IR (neat): 3073, 1579, 1558, 1480, 1445, 1128, 815, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.71 (1 H, s), 7.24 (1 H, s), 7.31–7.46 (6 H, m), 7.70 (2 H, d, *J* = 7.7 Hz), 7.95 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 99.6, 109.1, 124.8, 126.0, 127.6, 128.0, 128.7, 128.9, 129.6, 134.4, 148.0, 151.5, 167.7, 168.1.

HRMS–TOF (CI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{13}N_2OS_2$: 337.0469; found: 337.0480.

Anal. Calcd for $C_{18}H_{12}N_2OS_2$: C, 64.26; H, 3.60; N, 8.33; S, 19.06. Found: C, 64.11; H, 3.42; N, 8.40; S, 19.10.

***N*-[2-(5-Methyl-4-phenylthiazolo)]-4-methyl-5-phenyl-1,3-oxathiol-2-imine (3j)**
Yellow solid; mp 133 °C.

IR (neat): 2963, 2923, 1744, 1576, 1564, 1492, 884, 767, 693, 671 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (3 H, s), 2.56 (3 H, s), 7.34–7.49 (6 H, m), 7.62 (2 H, d, *J* = 7.3 Hz), 7.78 (2 H, d, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.2, 13.0, 112.5, 124.4, 127.2, 127.2, 128.3, 128.3, 128.7, 128.9, 135.3, 141.9, 146.7, 163.9, 165.7.

HRMS–TOF (CI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}N_2OS_2$: 365.0782; found: 365.0789.

Anal. Calcd for $C_{20}H_{16}N_2OS_2$: C, 65.91; H, 4.42; N, 7.69; S, 17.59. Found: C, 66.05; H, 4.41; N, 7.69; S, 17.35.

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