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Acid-Catalyzed Condensation of *o*-Phenylenediammines and *o*-Aminophenols with α-Oxodithioesters: A Divergent and Regioselective Synthesis of 2-Methylthio-3-aryl/Heteroarylquinoxalines and 2-Acylbenzoxazoles

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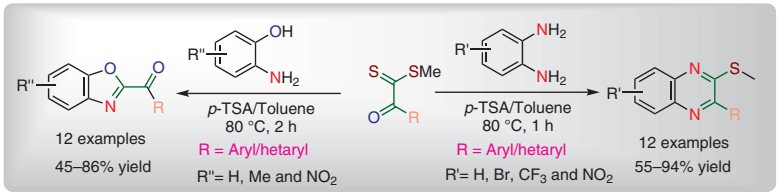

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Abstract *o*-Phenylenediammines and *o*-aminophenols were reacted with α-oxodithioesters in a highly regioselective fashion to give 2-methylthio-3-aryl/heteroarylquinoxalines and 2-acylbenzoxazoles in 55–94% and 45–86%, respectively, in the presence of *p*-toluene sulfonic acid catalyst. Control experiments involving reaction of aniline with a α-oxodithioester indicated that the thiocarbonyl group is more reactive than the carbonyl group. Based on this, probable mechanisms for the formation of quinoxalines and benzoxazoles are given. Biological targets of the quinoxalines and benzoxazoles were identified by bioinformatics. It was found that quinoxalines have good binding affinity with human dual-specificity tyrosine-phosphorylation-regulated kinase 1A and benzoxazoles with human carboxylesterase.

Key words α-oxodithioester, quinoxaline, benzoxazole, condensation, *p*-TSA

Quinoxalines and benzoxazoles are important members of the family of azaheterocycles. They display a broad range of biological activities,[1] which makes them privileged scaffolds in drug discovery.[2] They are present in many dyes and organic semiconductors.[3] As a consequence, increasing numbers of new methods are being reported for their synthesis. In particular, the challenging synthesis of functionalized azaheterocycles is a subject of great importance.

Quinoxalines can be synthesized by the reaction of *o*-phenylenediammine with 1,2-diketones,[4] α-hydroxyketones,[5] epoxides,[6] α-bromoketones,[7,4h] terminal alkynes,[8] aldehydes,[9] deoxybenzoins,[10] β-aryl amines,[11] and ynones.[12] Other approaches include, copper-catalyzed condensation of 2-iodoanilines, aryl acetaldehydes and sodium azide[13] and *N*-aryl ketimines with sodium azide,[14] reductive coupling of 2-nitroanilines with 1,2-diketones,[15] heteroannulation of nitro ketene *N*,*S*-arylaminoacetals with $POCl_3$,[16] nucleophilic substitution on *o*-nitrohalobenzene by aliphatic amine followed by reductive cyclization[17] and cyclization of α-aryliminophenylhydrazone[18] or oxime derivatives[19] of α-dicarbonyl compounds with anilines.

On the other hand, the benzoxazole skeleton can be constructed by the reaction of *o*-aminophenol with aldehydes,[20] aryl and vinyl bromides,[21] β-diketones,[22] orthoesters,[23] carboxylic acids,[24] ketones,[25] and isocyanides.[26] Other strategies include intramolecular cyclization of *o*-bromoaryl amides,[27] cyclization of *o*-hydroxyaryl *N*-*H* ketimines,[28] copper-catalyzed conversion of bisaryloxime ethers,[29] and oxidative cyclization of *o*-hydroxy-*N*-aryl-*N*,*N*-dialkylformamidines.[30]

In particular, reaction of *o*-phenylenediammines with pyruvates (Hinsberg and Körner synthesis)[31] gives 3-substituted quinoxalin-2(1*H*)-ones.[32] Our literature survey revealed that reaction of *o*-phenylenediammines with sulfur analogues of pyruvates (2-oxo-2-(het)arylethanedithioates) to give 2-methylthio-3-aryl/heteroarylquinoxalines, has not been reported. Other synthetic methods to access 2-acylbenzoxazoles are very limited. The available methods include transition-metal-catalyzed cyclization of 1,1-dibromoethenes[33] and alkynyl bromides[34] with 2-aminophenols, and oxidative cyclization of *N*-(2-hydroxyphenyl)-4-methyl-*N*-(phenacyl)benzene sulfonamides.[35] Preconstructed benzoxazole can also be functionalized to get 2-acylbenzoxazoles.[36] In general, many of these methods suffer from

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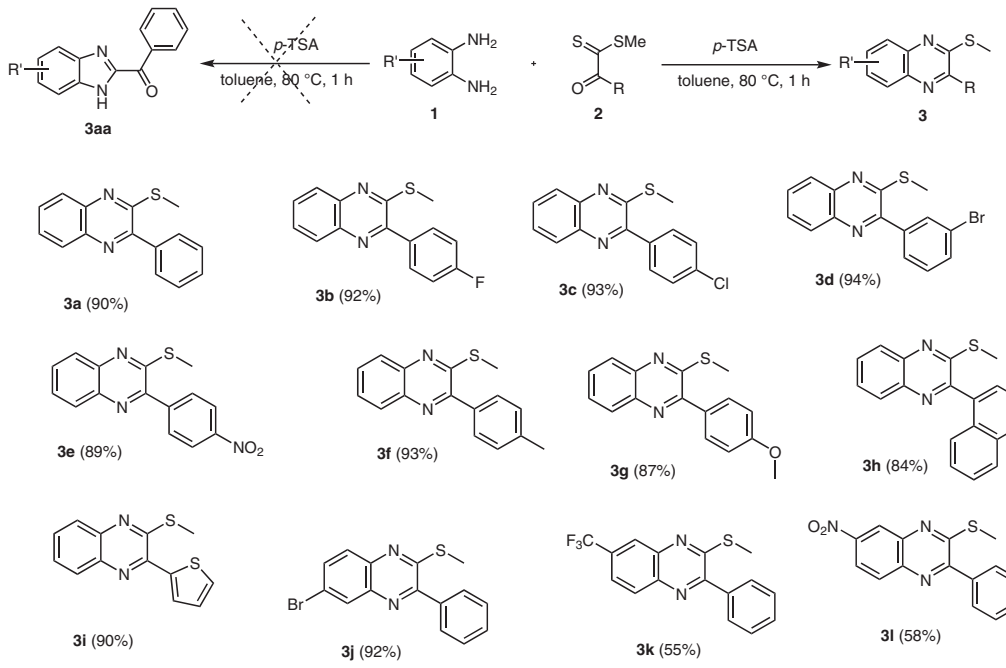
drawbacks such as the use of toxic/volatile organic solvents, transition-metal catalysts, long reaction times, poor yields, harsh reaction conditions and tedious work-up procedures. To our knowledge, the synthesis of 2-acylbenzoxazoles from activated dithioates has not been reported.

α-Oxodithioesters have been known from a long time[37] but their synthetic applications have not been extensively explored to date. In a few reports, they were used as dienophiles in thia-Diels–Alder reaction.[38] Furthermore, they reacted with diazomethane to give 1,3-oxathiole, which can react with maleic anhydride to give tetrahydrothiene.[39] The synthesis of both quinoxaline and benzoxazole from the same substrate with subtle variation in regioselectivity is not known. As a part of our work on the development of new synthetic methods[40] for biologically interesting heterocyclic compounds, we have designed new organosulfur building blocks and explored their applications.[41] In a continuation of these studies, we now disclose a highly regioselective cyclization of *o*-phenylenediammines and *o*-aminophenols with α-oxodithioesters to get quinoxalines and benzoxazoles, respectively.

We started our study with the cyclocondensation of *o*-phenylenediammine **1** with methyl 2-oxo-2-phenylethanedithioate **2a** in the presence of various acid catalysts such as *p*-toluenesulfonic acid (*p*-TSA), trifluoroacetic acid, acetic acid and methanesulfonic acid in toluene as a solvent at various temperatures (Table S1, entries 1–7; Supporting Information). The highest yield of 2-(methylthio)-3-phenylquinoxaline (**3a**; 90%) was obtained in the presence of *p*-TSA at 80 °C (Scheme 1, and Table S1, entry 6). Replacement of toluene with ethanol did not improve the yield (Table S1, entry 8). The reaction was successful even in the presence of base catalysts such as DBU and triethylamine, but yields were reduced (Table S1, entries 9 and 10). Surprisingly, the other possible product (1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanone (**3aa**; Scheme 1) was not observed. Thus, the product **3a** was formed in highly regioselective fashion.

With the optimized reaction conditions, the generality of the protocol was tested by conducting reactions with various α-oxodithioesters bearing halogens such as F, Cl, and Br at various positions, which yielded the respective 2-(methylthio)-3-arylquinoxalines **3b–d** in 92–94% yield (Scheme 1). α-Oxodithioesters with electron-withdrawing or electron-donating groups also furnished 2-(methylthio)-3-(aryl)quinoxalines **3e–g** in 87–93% yield. The 2-(methylthio)-3-(naphthalen-1-yl) quinoxaline (**3h**) was obtained in 84% yield from methyl-2-(naphthalen-1-yl)-2-oxoethanedithioate. The methyl 2-oxo-2-(thiophen-2-yl)ethanedithioate also afforded 2-(methylthio)-3-(thiophen-2-yl)quinoxaline (**3i**) in 90% yield upon condensation with **1**. Finally, 4-bromobenzene-1,2-diamine (with electron-donating bromo group) also gave the corresponding 6-bromo-2-(methylthio)-3-phenylquinoxaline (**3j**) in 92% yield. Similarly, 4-trifluromethyl/nitrobenzene-1,2-diamine furnished the respective 6-trifluoromethyl/nitro-2-(methylthio)-3-phenylquinoxaline **3k** and **3l** in 55% and 58% yield, which were less than for the unsubstituted and bromo-1,2-diam-

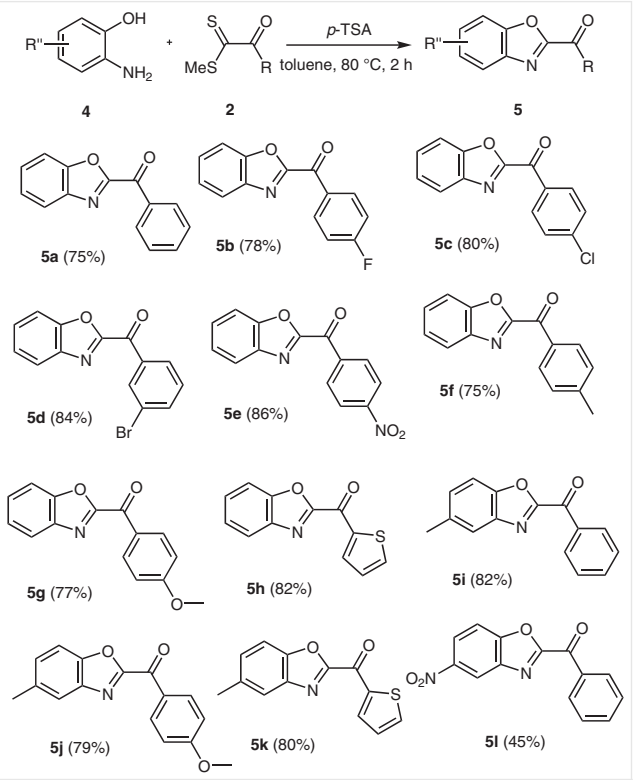


Scheme 1 Synthesis of 2-aryl-3-methylthioquinoxalines **3**. *Reagents and conditions*: **1** (1 mmol), **2** (1 mmol), *p*-TSA (0.1 mmol), toluene (3 mL), 80 °C, 1 h.

mine. In none of the examples the other possible isomer 3-acylbenzimidazole was observed, which indicates the high regioselectivity in the formation of 2-methylthio-3-aryl/heteroarylquinoxalines.

Later, we conducted cyclocondensation of *o*-aminophenol (**4**) with methyl 2-oxo-2-phenylethanedithioate (**2a**) in the presence of different acid catalysts such as *p*-TSA, trifluoroacetic acid, acetic acid and methane sulfonic acid in toluene as a solvent of choice at varying temperatures (Table S2, entries 1–8, Supporting Information). The highest yield of benzo[*d*]oxazol-2-yl(phenyl)methanone (**5a**) (75%; Scheme 2) was obtained in the presence of *p*-TSA at 80 °C (Table S2, entry 6). The desired product **5a** was obtained even in the presence of bases like triethylamine and DBU (Table S2, entry 9–10). Conducting the reaction in ethanol did not give the desired product (Table S2, entry 11).

The generality of cyclocondensation of *o*-aminophenol with α-oxodithioesters under the optimized reaction conditions to afford 2-acylbenzoxazoles was explored (Scheme 2). 2-Oxo-2-phenylethanedithioate furnished benzo[*d*]oxazol-2-yl(phenyl)methanone (**5a**) in 75% yield. Later, the versatility of the reaction was investigated with various α-oxodithioesters bearing halogens, which afforded the corresponding benzoxazoles **5b–d** in 78–84% yield. Furthermore, benzo[*d*]oxazol-2-yl(aryl)methanones **5e–g** were obtained in 75–86% yield. Various aryl and heteroaryl substituted α-oxodithioesters underwent condensation with *o*-aminophenol and substituted *o*-aminophenol (electron-donating methyl and electron-withdrawing nitro substituents) to give the respective benzoxazoles **5i–l** in 45–82% yield. The structure of benzoxazole **5i** was confirmed by X-ray diffraction studies, and its ORTEP diagram is given in Figure 1. These reactions reflect the change in regioselective cyclization on changing the bi-nucleophile from *o*-phenylenediammine to *o*-aminophenol.



Scheme 2 Synthesis of 2-acylbenzoxazoles **5**. *Reagents and conditions*: **4** (1 mmol), **2** (1 mmol), *p*-TSA (0.1 mmol), toluene (3 mL), 80 °C, 2 h.

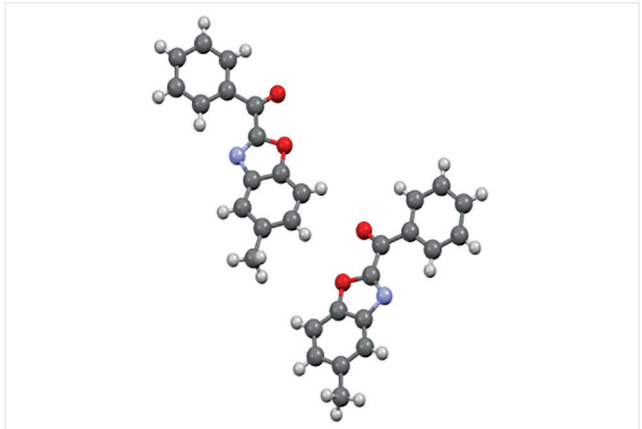
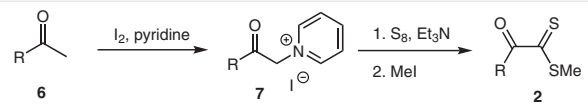


Figure 1 ORTEP diagram of (5-methylbenzo[*d*]oxazol-2-yl)(phenyl)methanone (**5i**)

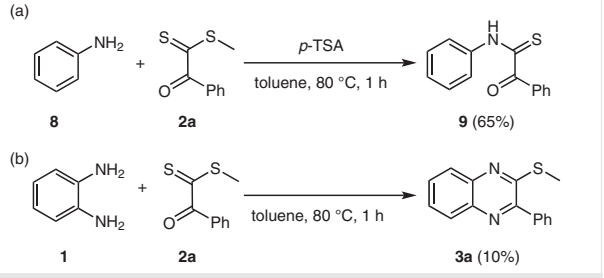
The required starting materials α-oxodithioesters **2** were synthesized according to the earlier reported protocol (Scheme 3).[37] Reaction of methyl ketones **6** with iodine in pyridine solvent gave pyridinium iodide **7** in quantitative yield. Further treatment with sulfur in the presence of trimethylamine followed by reaction with methyl iodide afforded α-oxodithioesters **2** in moderate to good yields (52–65%). In this way, various substrates **2a–j** were synthesized bearing phenyl, substituted phenyl (halogens, electron-donating groups and electron-withdrawing groups), naphthyl and thienyl groups. However, attempts to synthesize α-oxodithioesters with aliphatic substituents were unsuccessful. The characterization data are given in the Supporting Information.



Scheme 3 Synthesis of α-oxodithioesters **2**

To establish whether nucleophilic attack of the amine took place on the thiocarbonyl or carbonyl group, we conducted a control experiment involving the reaction of aniline **8** with methyl 2-oxo-2-phenylethanedithioate (**2a**), under the optimized reaction conditions. The reaction resulted in the formation of 2-oxo-*N*,2-diphenylethanethioamide (**9**) through the elimination of methane thiol, which indi-

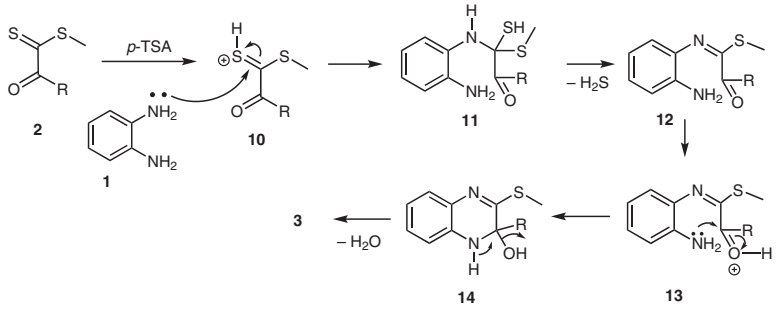
cates that the thiocarbonyl group is more reactive than the carbonyl group (Scheme 4a). When **1** was reacted with **2a** in the absence of catalyst *p*-TSA in toluene at 80 °C, the desired product **3a** was furnished in only 10% yield (Scheme 4b). Thus, this experiment indicates the requirement of catalyst *p*-TSA for the cyclocondensation.



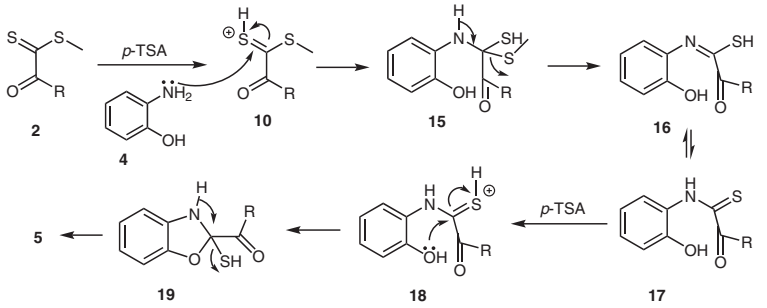
Scheme 4 Control experiments

Based on the results of the control experiments, a probable mechanism for the formation of quinoxaline is given in Scheme 5. The first step involves *p*-TSA catalyzed nucleophilic attack of *o*-phenylenediamine (**1**) with protonated **10** to give intermediate **11**. Elimination of hydrogen sulfide from **11** forms ketothioimidate **12**. In contrast to the result of the control experiment, H_2S is eliminated instead of methane thiol, probably for the formation of more stable aromatic quinoxaline ring. Further acid-catalyzed cyclization of **13** *via* intermediate **14** through dehydration finally furnishes quinoxalines **3**. On the other hand, acid-catalyzed condensation of *o*-aminophenol **4** with protonated α-oxodithioester **10** gives intermediate **15** (Scheme 6). Elimination of methane thiol from **15** furnished α-ketothioamide **17** *via* the thio-enol tautomer **16**. Further acid-catalyzed cyclocondensation of **18** gave benzoxazole **5** *via* intermediate **19** through the elimination of H_2S (Scheme 6). However, in reactions with *o*-phenylenediammine and *o*-aminophenol, intermediates **12**, **16**, and **17** were not detected, probably because they were short lived in the reaction. Nevertheless, we tried to identify the intermediates by controlling the temperature of the reaction, which directly furnished the final products in varying yields; however these intermediates were also unidentifiable (Table S1 and S2, Supporting Information).

The target prediction of quinoxalines and benzoxazoles was conducted based on well-established bioinformatics techniques.[42] The studies showed that quinoxalines have good binding affinity with human dual-specificity tyrosine-phosphorylation-regulated kinase 1A (PDB ID: 2WO6) and benzoxazoles with human carboxylesterase (PDB ID: 2H7C). Quinoxalines and benzoxazoles exhibited good docking scores in the range –6.706 to –5.414 and –6.316 to –4.92 respectively. The binding of quinoxalines **3h** and **3a**, and benzoxazoles **5c** and **5e**, with respective targets are given in Figure 2. The docking scores of all compounds are given in the Supporting Information.



Scheme 5 Probable mechanism for the formation of quinoxalines



Scheme 6 Probable mechanism for the formation of benzoxazoles

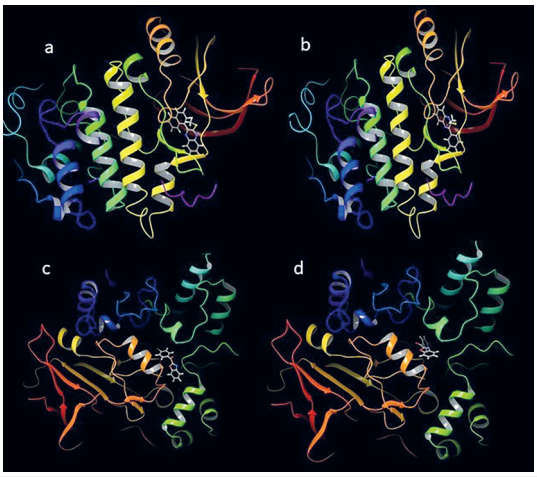


Figure 2 Binding of (a) **3h** with human dual-specificity tyrosine-phosphorylation-regulated kinase 1A; (b) **3a** with human dual-specificity tyrosine-phosphorylation-regulated kinase 1A; (c) **5c** with human carboxylesterase, and (d) **5e** with human carboxylesterase.

In summary, we have reported an acid-catalyzed highly regioselective cyclization of *o*-phenylenediammines and *o*-aminophenols with α-oxodithioesters to form 2-methylthio-3-aryl/heteroarylquinoxalines and 2-acylbenzoxazoles. In a control reaction, aniline reacted in a highly regioselectively manner with the thiocarbonyl group of α-oxodithioester. Probable mechanisms for the formation of quinoxalines and benzoxazoles are proposed. Furthermore, biological target prediction of the synthesized molecules indicated that quinoxalines have good binding affinity towards human dual-specificity tyrosine-phosphorylation-regulated kinase 1A and benzoxazoles with human carboxyl esterase.

All reagents were purchased from commercial suppliers and used without further purification. The reactions were monitored by thin-layer chromatography (TLC) using pre-coated sheets of silica gel (Merck 60F254, 0.25 mm thickness) and visualized under UV light. Melting points were determined with a Selaco melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained with a AGILENT NMR spectrometer. Chemical shifts (δ) are given in parts per million (ppm) using the residue solvent ($CDCl_3$) peak as reference relative to TMS. Coupling constants (*J*) are given in Hz. Mass spectral analysis was performed with a Water-Synapt G2 mass spectrometer. Single-crystal X-ray diffraction data of the compounds were generated with a Rigoku SMART Lab model, Japan; which uses Cu source and works at r.t. in a monochrome beam method. The structure was established by full matrix least square methods by using the SHELXS program.

Synthesis of α-Oxodithioesters 2; General Procedure

The products α-oxodithioesters **2a–j** were prepared by a slight modification of the earlier reported protocol.[37] A solution of methyl ketone **6** (10 mmol) and iodine (10 mmol) in pyridine (5 mL) was heated at reflux for 12 h. The pyridinium iodide salt **7** formed was filtered, washed with hexane, and dried. Salt **7** (10 mmol) and sulfur (2.5 mmol) were stirred in a mixture of DMSO (50 mL) and DMF (20 mL). The reaction mixture was cooled to 0 °C and triethylamine (2.75 mL) was added slowly and stirring was continued for 45 min. Ice-cold water (50 mL) was added and the mixture was washed with diethyl ether (25 mL). Methyl iodide (1.25 mL) was added to the aqueous phase and stirring was continued for 10 min. The product was extracted with diethyl ether/cyclohexane (50 mL/50 mL, twice) and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the product was purified by column chromatography (hexane/EtOAc, 19:1).

Synthesis of Quinoxalines 3; General Procedure

A solution of *o*-phenyl diamine **1** (1 mmol), oxodithioester **2** (1 mmol) and *p*-TSA (0.1 mmol) in toluene (3 mL) was heated at 80 °C for 1 h and the progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to r.t., and the reaction was quenched with ice-cold water (25 mL). The mixture was extracted with EtOAc (3 × 25 mL) and the combined organic layer was washed with brine (25 mL), dried over anhydrous Na_2SO_4, and evaporated under vacuum to give the crude quinoxaline **3**, which was purified by column chromatography (hexane/EtOAc, 19:1).

Synthesis of Benzoxazoles 5; General Procedure

A solution of *o*-amino phenol **4** (1 mmol), oxodithioester **2** (1 mmol) and *p*-TSA (0.1 mmol) in toluene (3 mL) was heated at 80 °C for 2 h and the progress of the reaction was monitored by TLC. Soon after its completion, the mixture was cooled to r.t., ice-cold water (25 mL) was added, and the mixture was extracted with EtOAc (3 × 25 mL). The combined organic layer was washed with a saturated solution of NaCl (25 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give the crude benzoxazole **5**, which was purified by column chromatography (hexane/EtOAc, 19:1).

Synthesis of 2-Oxo-*N*,2-diphenylethanethioamide 9

A solution of aniline **8** (1 mmol), methyl 2-oxo-2-phenylethanedithioate **2a** (1 mmol) and *p*-TSA (0.1 mmol) in toluene (3 mL) was heated at 80 °C for 1 h and the progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to r.t., and the reaction was quenched with ice cold water (25 mL). The mixture was extracted with EtOAc (3 × 25 mL), and the combined organic layer was washed with brine (25 mL), dried over anhydrous Na_2SO_4 and evaporated under vacuum to give the crude 2-oxo-*N*,2-diphenylethanethioamide **9**, which was purified by column chromatography (hexane/EtOAc, 17:3).

Methyl 2-Oxo-2-phenylethanedithioate (2a)

Yield: 1294 mg (66%); red liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 1.2 Hz, 2 H, Ar-H), 7.60 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.45 (t, *J* = 8.0 Hz, 2 H, Ar-H), 2.82 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 231.5, 190.8, 134.3, 132.8, 130.4, 128.8, 18.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_9OS_2$: 197.0089; found: 197.0096.

Methyl 2-(4-Fluorophenyl)-2-oxoethanedithioate (2b)

Yield: 1278 mg (60%); red liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.96 (dd, *J* = 5.6, 3.2 Hz, 2 H, Ar-H), 7.11 (t, *J* = 8.1 Hz, 2 H, Ar-H), 2.81 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 230.7, 189.3, 167.7, 165.1 (d, *J* = 255.9 Hz), 133.3, 133.2 (d, *J* = 9.8 Hz), 129.2, 116.0, 115.7 (d, *J* = 22.4 Hz), 18.4.

^{19}F NMR (375 MHz, $CDCl_3$): δ = –102.4

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_8FOS_2$: 214.9995; found: 215.0001.

Methyl 2-(4-Chlorophenyl)-2-oxoethanedithioate (2c)

Yield: 1725 mg (75%); red liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 2.0 Hz, 2 H, Ar-H), 7.43 (d, *J* = 2.8 Hz, 2 H, Ar-H), 2.82 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 230.3, 189.4, 140.9, 131.8, 131.2, 129.2, 18.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_8ClOS_2$: 230.9700; found: 230.9709.

Methyl 2-(4-Bromophenyl)-2-oxoethanedithioate (2d)

Yield: 2137 mg (78%); red liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.24 (d, *J* = 8.4 Hz, 2 H, Ar-H), 2.81 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 231.7, 190.8, 145.6, 130.6, 130.2, 129.6, 18.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_7BrOS_2$: 274.9200; found: 274.9206.

Methyl 2-(3-Bromophenyl)-2-oxoethanedithioate (2e)

Yield: 1587 mg (69%); red liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 1 H, Ar-H), 7.86 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.71 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.33 (t, *J* = 8.0 Hz, 1 H, Ar-H), 2.83 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 229.7, 189.0, 137.0, 134.7, 133.0, 130.1, 128.9, 122.7, 18.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_8BrOS_2$: 274.9194; found: 274.9195.

Methyl 2-(4-Nitrophenyl)-2-oxoethanedithioate (2f)

Yield: 1373 mg (57%); reddish yellow solid; mp 55–57 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 2.0 Hz, 2 H, Ar-H), 8.10 (d, *J* = 2.0 Hz, 2 H, Ar-H), 2.85 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 228.6, 187.8, 150.7, 138.0, 131.3, 123.6, 18.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_8NO_3S_2$: 241.9940; found: 241.9936.

Methyl 2-Oxo-2-(*p*-tolyl)ethanedithioate (2g)

Yield: 1449 mg (69%); red liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.28 (d, *J* = 8.4 Hz, 2 H, Ar-H), 2.81 (s, 3 H, SMe), 2.42 (s. 3 H, Ar-Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 231.7, 190.8, 145.6, 130.6, 130.2, 129.3, 21.9, 18.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{11}OS_2$: 211.0246; found: 211.0240.

Methyl 2-(4-Methoxyphenyl)-2-oxoethanedithioate (2h)

Yield: 2169 mg (96%); red liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 6.8 Hz, 2 H, Ar-H), 6.91 (d, *J* = 9.2 Hz, 2 H, Ar-H), 3.86 (s, 3 H, OMe), 2.80 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 232.1, 190.0, 164.6, 132.9, 125.4, 113.9, 55.9, 18.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{11}O_2S_2$: 227.0195; found: 227.0189.

Methyl 2-(Naphthalen-2-yl)-2-oxoethanedithioate (2i)

Yield: 2017 mg (82%); red solid; mp 73–75 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1 H, Ar-H), 8.01 (dd, *J* = 6.8, 1.6 Hz, 1 H Ar-H), 7.92–7.85 (m, 3 H, Ar-H), 7.63–7.52 (m, 2 H, Ar-H), 2.87 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 231.4, 191.0, 136.1, 133.3, 132.1, 130.1, 129.8, 129.3, 128.5, 127.9, 127.0, 124.8, 18.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{11}OS_2$: 247.0246; found: 247.0243.

Methyl 2-Oxo-2-(thiophen-2-yl)ethanedithioate (2j)

Yield: 808 mg (40%); red liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 3.2 Hz, 1 H, Ar-H), 7.75 (d, *J* = 3.6 Hz, 1 H, Ar-H), 7.12 (t, *J* = 4.4 Hz, 1 H, Ar-H), 2.77 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 228.9, 182.5, 136.8, 132.4, 128.7, 128.4, 18.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_7H_7OS_3$: 202.9654; found: 202.9660.

2-(Methylthio)-3-phenylquinoxaline (3a)

Yield: 231 mg (65%); white solid; mp 165–167 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.98 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.79–7.77 (dd, *J* = 4.0, 2.0 Hz, 2 H, Ar-H), 7.67–7.60 (m, 2 H, Ar-H), 7.51 (t, *J* = 3.6 Hz, 3 H, Ar-H), 2.63 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 153.4, 141.6, 139.3, 137.4, 129.7, 129.7, 129.2, 128.9, 128.4, 128.1, 127.4, 13.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}N_2S$: 253.0794; found: 253.0798.

2-(4-Fluorophenyl)-3-(methylthio)quinoxaline (3b)

Yield; 232 mg (92%); pale-yellow solid; mp 160–162 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–7.96 (dd, *J* = 14.4, 8.0 Hz, 2 H, Ar-H), 7.68 (t, *J* = 7.2 Hz, 2 H, Ar-H), 7.70–7.59 (m, 2 H, Ar-H), 7.19 (t, *J* = 8.4 Hz, 2 H, Ar-H), 2.64 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 157.1, 150.3, 147.0 (d, *J* = 331.8 Hz), 136.3, 133.8, 128.1, 125.8, 125.7 (d, *J* = 7.8 Hz), 124.5, 123.8, 122.9, 122.1, 110.3, 110.1 (d, *J* = 21.4 Hz), 8.4.

^{19}F NMR (375 MHz, $CDCl_3$): δ = –110.9

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}FN_2S$: 271.0700; found: 271.0703.

2-(4-Chlorophenyl)-3-(methylthio)quinoxaline (3c)

Yield: 231 mg (93%); pale-yellow solid; mp 154–155 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.96 (dd, *J* = 12.8, 8.4 Hz, 2 H, Ar-H), 7.74–7.76 (m, 3 H, Ar-H), 7.63–7.59 (m, 1 H, Ar-H), 7.47 (d, *J* = 8.4 Hz, 2 H, Ar-H), 2.63 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2, 146.8, 136.3, 133.8, 130.6, 130.4, 125.1, 124.6, 123.8, 123.4, 122.9, 122.1, 8.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}ClN_2S$: 287.0404; found: 287.0400.

2-(3-Bromophenyl)-3-(methylthio)quinoxaline (3d)

Yield: 312 mg (94%); white solid; mp 161–168 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–7.97 (dd, *J* = 14.4, 8.0 Hz, 2 H, Ar-H), 7.92 (s, 1 H, Ar-H), 7.74–7.61 (m, 4 H, Ar-H), 7.38 (t, *J* = 8.0 Hz, 1 H, Ar-H), 2.64 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 151.8, 141.8, 139.3, 139.1, 132.7, 132.1, 130.1, 129.9, 129.2, 128.3, 127.6, 127.5, 122.6, 13.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}BrN_2S$: 330.9899; found: 330.9901.

2-(Methylthio)-3-(4-nitrophenyl)quinoxaline (3e)

Yield: 320 mg (89%); pale-yellow solid; mp 184–185 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.4 Hz, 2 H, Ar-H), 8.05–7.98 (m, 4 H, Ar-H), 7.76–7.64 (m, 2 H, Ar-H), 2.67 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9, 140.9, 138.4, 133.5, 131.8, 129.0, 120.6, 120.2, 119.2, 118.5, 117.5, 113.5, 7.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}N_3O_2S$: 298.0645; found: 298.0650.

2-(Methylthio)-3-(*p*-tolyl)quinoxaline (3f)

Yield: 369 mg (93%); white solid; mp 106–108 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–8.02 (dd, *J* = 7.2 Hz, 1.2 Hz, 2 H, Ar-H), 7.70–7.60 (m, 4 H, Ar-H), 7.31 (d, *J* = 7.6 Hz, 2 H, Ar-H), 2.62 (s, 3 H, SMe), 2.43 (s, 3 H, Ar-Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 148.2, 136.2, 134.5, 133.9, 129.2, 124.1, 123.8, 123.7, 123.5, 122.6, 122.1, 16.1, 8.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}N_2S$: 267.0950; found: 267.0955.

2-(4-Methoxyphenyl)-3-(methylthio)quinoxaline (3g)

Yield: 217 mg (87%); white solid; mp 135–137 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02–7.94 (dd, *J* = 20.0, 7.2 Hz, 2 H, Ar-H), 7.75–7.59 (m, 4 H, Ar-H), 7.02 (d, *J* = 6.8 Hz, 2 H, Ar-H), 3.86 (s, 3 H, OMe), 2.62 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 150.6, 147.8, 136.1, 133.9, 125.2, 124.4, 124.1, 123.7, 122.7, 122.0, 108.5, 50.0, 8.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}N_2OS$: 282.0827; found: 282.0830.

2-(Methylthio)-3-(naphthalen-1-yl)quinoxaline (3h)

Yield: 206 mg (84%); pale-yellow solid; mp 128–130 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.3 (s, 1 H, Ar-H), 8.09–7.85 (m, 6 H, Ar-H), 7.70 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.63 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.57–7.51 (m, 2 H, Ar-H), 2.65 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.7, 148.0, 136.3, 134.0, 129.4, 128.5, 127.6, 124.5, 123.9, 123.6, 123.3, 122.9, 122.8, 122.4, 122.1, 121.6, 121.1, 120.8, 8.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{15}N_2S$: 302.0878; found: 302.0880.

2-(Methylthio)-3-(thiophen-2-yl)quinoxaline (3i)

Yield: 230 mg (90%); pale-yellow solid; mp 145–147 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 4.0 Hz, 1 H, Ar-H), 7.99 (d, *J* = 6.4 Hz, 1 H, Ar-H), 7.17 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.63–7.52 (m, 3 H, Ar-H), 7.17 (t, *J* = 5.2 Hz, 1 H, Ar-H), 2.71 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 146.3, 141.3, 140.7, 138.8, 129.6, 129.5, 129.5, 128.8, 128.3, 127.8, 127.3, 13.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{11}N_2S_2$: 258.0285; found: 258.0284.

6-Bromo-2-(methylthio)-3-phenylquinoxaline (3j)

Yield: 310 mg (92%); white solid; mp 160–162 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 2.4 Hz, 1 H, Ar-H), 7.89 (d, *J* = 8.8 Hz, 1 H, Ar-H), 7.76–7.67 (m, 3 H, Ar-H), 7.51 (t, *J* = 3.2 Hz, 3 H, Ar-H), 2.60 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 148.4, 136.7, 132.6, 131.6, 126.1, 125.2, 124.6, 124.5, 123.5, 123.1, 118.3, 8.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}BrN_2S$: 329.9826; found: 329.9827.

3-(Methylthio)-2-phenyl-6-(trifluoromethyl)quinoxaline (3k)

Yield: 180 mg (55%); white solid; mp 126–128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1 H, Ar-H), 8.18 (d, *J* = 12.0 Hz, 1 H, Ar-H), 7.82 (d, *J* = *8* Hz, 3 H, Ar-H), 7.57 (s, 3 H, Ar-H), 2.68 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 155.4, 140.6, 140.4, 136.7, 130.3, 130.1, 128.9, 128.7, 128.5, [125.3, 125.3, 125.1 (multiplet)], 122.4, 13.9.

^{19}F NMR (375 MHz, $CDCl_3$): δ = –62.5

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}BrN_2S$: 321.0595; found: 321.0589.

(5-Nitrobenzo[*d*]oxazol-2-yl)(phenyl)methanone (3l)

Yield: 176 mg (58%); white solid; mp 188–190 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (s, 1 H, Ar-H), 8.19 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.85 (t, *J* = 4.0 Hz, 1 H, Ar-H), 7.58 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.57 (s, 3 H, Ar-H), 2.69 (s, 3 H, SMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 156.3, 147.7, 141.9, 140.4, 136.3, 130.6, 130.4, 129.0, 128.8, 123.6, 121.5, 14.05.

HRMS (ESI): *m*/*z* [M + H]$^+$ calc for $C_{15}H_{12}BrN_2S$: 298.3320; found: 298.3318.

Benzo[*d*]oxazol-2-yl(phenyl)methanone (5a)

Yield: 171 mg (75%); pale-yellow solid; mp 124–126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.94 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.71–7.66 (dd, *J* = 7.6, 7.2 Hz, 2 H, Ar-H), 7.58–7.44 (m, 4 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.6, 157.1, 150.4, 140.7, 135.0, 134.3, 131.0, 128.6, 128.4, 125.7, 122.4, 11.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}NO_2$: 223.0633; found: 223.0632.

Benzo[*d*]oxazol-2-yl(4-fluorophenyl)methanone (5b)

Yield: 176 mg (78%); pale-yellow solid; mp 116–118 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67–8.63 (dd, *J* = 5.2, 3.6 Hz, 2 H, Ar-H), 7.93 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.70 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.55 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.48 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.25–7.21 (dd, *J* = 5.6, 3.2 Hz, 2 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 162.5, 159.9 (d, *J* = 256.8 Hz), 151.5, 145.0, 135.3, 128.6, 128.5 (d, *J* = 9.7 Hz), 125.9, 123.2, 120.4, 117.0, 110.6, 110.4 (d, *J* = 22.3 Hz), 106.5.

^{19}F NMR (375 MHz, $CDCl_3$): δ = –102.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_9FNO_2$: 241.0539; found: 241.0543.

Benzo[*d*]oxazol-2-yl(4-chlorophenyl)methanone (5c)

Yield: 179 mg (80%); pale-yellow solid; mp 110–112 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.89 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.66 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.45–7.42 (m, 4 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.7, 151.4, 145.0, 135.7, 135.3, 127.8, 127.1, 123.6, 123.3, 120.5, 117.0, 106.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_9ClNO_2$: 258.0316; found: 258.0320.

Benzo[*d*]oxazol-2-yl(3-bromophenyl)methanone (5d)

Yield: 184 mg (84%); pale-yellow solid; mp 123–125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (s, 1 H, Ar-H), 8.53 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.96 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.79 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.70 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.55 (t, *J* = 7.6 Hz, 1 H,Ar-H), 7.49–7.41 (m, 2 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.6, 151.3, 145.1, 135.3, 131.7, 131.2, 128.4, 124.8, 124.3, 123.4, 120.5, 117.4, 117.2, 106.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_9BrNO_2$: 301.9811; found: 301.9805.

Benzo[*d*]oxazol-2-yl(4-nitrophenyl)methanone (5e)

Yield: 191 mg (86%); pale-yellow solid; mp 142–144 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 9.2 Hz, 2 H, Ar-H), 8.39 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.96 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.73 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.61–7.57 (m, 1 H, Ar-H), 7.50 (t, *J* = 7.2 Hz, 1 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.4, 151.1, 145.4, 145.2, 135.3, 134.1, 126.8, 123.9, 120.8, 118.3, 117.3, 106.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_9N_2O_4$: 269.0557; found: 269.0560.

Benzo[*d*]oxazol-2-yl(*p*-tolyl)methanone (5f)

Yield: 169 mg (75%); pale-yellow solid; mp 116–118 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.92 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.68 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.54–7.44 (m, 2 H, Ar-H), 7.34 (d, *J* = 8.4 Hz, 2 H, Ar-H), 2.45 (s, 3 H, Ar-Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.8, 151.9, 145.0, 140.2, 135.4, 127.1, 125.8, 124.0, 122.9, 120.3, 116.9, 106.5, 16.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}NO_2$: 238.2655; found: 238.2657.

Benzo[*d*]oxazol-2-yl(4-methoxyphenyl)methanone (5g)

Yield: 172 mg (77%); pale-yellow solid; mp 126–128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.91 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.68 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.53–7.42 (m, 2 H, Ar-H), 7.01 (d, *J* = 8.4 Hz, 2 H, Ar-H), 3.90 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.4, 159.3, 152.1, 145.0, 135.4, 128.2, 122.7, 122.6, 120.2, 116.8, 108.6, 106.4, 50.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}NO_3$: 254.0812; found: 254.0813.

Benzo[*d*]oxazol-2-yl(thiophen-2-yl)methanone (5h)

Yield: 186 mg (82%); yellow solid; mp 120–122 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 3.6 Hz, 1 H, Ar-H), 7.92 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.83 (d, *J* = 3.2 Hz, 1 H, Ar-H), 7.68 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.54–7.43 (m, 2 H, Ar-H), 7.24 (t, *J* = 4.4 Hz, 1 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 151.4, 145.2, 135.3, 135.2, 132.2, 131.7, 123.4, 123.0, 120.4, 116.9, 106.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_8NO_2S$: 230.0270; found: 230.0275.

(5-Methylbenzo[*d*]oxazol-2-yl)(phenyl)methanone (5i)

Yield: 198 mg (82%); pale-yellow solid; mp 126–128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.70–7.65 (m, 2 H, Ar-H), 7.58–7.53 (m, 3 H, Ar-H), 7.36–7.33 (dd, *J* = 7.2, 1.2 Hz, 1 H, Ar-H), 2.50 (s, 3 H. Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.6, 157.2, 148.7, 140.9, 135.8, 135.1, 134.2, 130.9, 129.9, 128.6, 121.9, 111.2, 21.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}NO_2$: 238.0863; found: 238.0861.

4-Methoxyphenyl(5-methylbenzo[*d*]oxazol-2-yl)methanone (5j)

Yield: 187 mg (79%); pale-yellow solid; mp 134–136 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, *J* = 9.2 Hz, 2 H, Ar-H), 7.69 (s, 1 H, Ar-H), 7.56 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.33 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.03 (d, *J* = 8.8 Hz, 2 H, Ar-H), 3.91 (s, 3 H, OMe), 2.51 (s, 3 H, Ar-Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.8, 164.6, 157.9, 148.4, 141.0, 135.6, 133.6, 129.5, 128.1, 121.7, 113.9, 111.1, 55.5, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}NO_3$: 268.0968; found: 268.0970.

(5-Methylbenzo[*d*]oxazol-2-yl)(thiophen-2-yl)methanone (5k)

Yield: 80%(192 mg); yellow solid; mp 132–135 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 3.6 Hz, 1 H, Ar-H), 7.80 (d, *J* = 4.8 Hz, 1 H, Ar-H), 7.66 (s, 1 H, Ar-H), 7.52 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.30 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.22 (t, *J* = 4.4 Hz, 1 H, Ar-H), 2.47 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 151.6, 143.5, 135.5, 135.3, 132.1, 131.5, 130.4, 124.4, 123.3, 116.5, 105.8, 16.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}NO_2S$: 244.0427; found: 244.0430.

(5-Nitrobenzo[*d*]oxazol-2-yl)(phenyl)methanone (5l)

Yield: 123 mg (45%); yellow solid; mp 138–140 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (s, 1 H, Ar-H), 8.59–8.51 (m, 3 H, Ar-H), 7.87 (d, *J* = 9.2 Hz, 1 H, Ar-H), 7.76 (t, *J* = 7.2 Hz, 1 H, Ar-H), 7.62 (t, *J* = 7.6 Hz, 2 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.8, 154.5, 148.8, 141.3, 136.2, 130.2, 129.6, 126.3, 124.1, 119.1, 114.1, 107.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_9N_2O_4$: 269.0485; found: 269.0490.

2-Oxo-*N*,2-diphenylethanethioamide (9)

Yield: 160 mg (65%); orange red solid; mp 140–142 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.80–10.60 (br s, 1 H, NH), 8.05–7.94 (m, 4 H, Ar-H), 7.58–7.19 (m, 6 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.7, 181.7, 132.5, 128.4, 125.5, 123.8, 123.4, 122.8, 121.9, 116.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{12}NOS$: 241.0561; found: 241.0568.

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Supporting Information

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