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Functionalization of Primary C–H Bonds in Picolines toward Pyridylthioamides

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Abstract

We report a method for coupling of nitroarenes, 2- or 4-methylazaarenes, and elemental sulfur to afford (2-pyridyl)aryl thioamides. Good tolerance of functionalities was observed, including primary and secondary amines, bromo, iodo, ester, and boronic ester groups. Thioamides derived from pyrazole, thiazole, quinoline, quinoxalines, and azoles were obtained in good yields, showing the compatibility of heterocycles. This appears to be a general method to obtain pyridyl thioamides in one step from commercial, simple substrates.

Keywords: Pyridylthioamide | Elemental sulfur | Picolines

1. Introduction

Activation of sp^3 C–H bonds in alkylazaarenes has been targeted over the last decades, since it is an atom-economical scheme to obtain complex heterocycles. Since a seminal report of Fagnou for directed C–H arylation of 2-methyl picoline *N*-oxides,[1a] many attempts have been devoted to broadening the substrate scope with regard to functionalization of primary C–H bonds. Charette described an *N*-pyridinium ylide-directed arylation of activated methyl groups with aryl chlorides.[1b] Synthesis of (2-pyridyl)aryl methanes via palladium-catalyzed decarboxylation or C–C cleavage was feasible.[1c,1d] The successes were dependent on the use of palladium catalysis and monodentate phosphine ligands. Xia and Huang reported a rare method for addition of C–H bonds in 2-methyl azaarenes to imines.[1e] One example of palladium-catalyzed, pyridine-directed coupling of methylene C–H bonds with aryl bromides was also presented.[1f] It should be noted that most of the known methods have suffered from the use of relatively scarce second-row transition metals. Only a couple of examples that allow for the metal-free, base-promoted activation of sp^3 C–H bonds in methylpyridines have been reported.[2] In 2011, Knochel developed a method for zincation of picolines with TMPZnCl.LiCl (TMP = 2,2,6,6-tetramethylpiperidyl).[2a] The benzylzinc intermediates were then used for coupling with aryl bromides. If electron-deficient nitroarenes were treated with strong bases such as *t*BuOK, arylation of activated methyl and methylene C–H bonds in substituted quinoxalines, quinolines, and azoles was obtained regioselectively.[2b] Yet those transformations are still far from practicality, since they often require extremely hygroscopic conditions.

The use of elemental sulfur as a metal-free representative in organic syntheses is emerging.[3a] In comparison with other

methods using strong bases, those promoted by elemental sulfur are much easier to handle under air. Nguyen reported early examples for sulfur-mediated synthesis of 2-heteroaryl benzothiazoles via functionalization of primary C–H bonds in picolines.[3b,3c] Using elemental sulfur in functionalization of activated sp^3 C–H bonds adjacent to ketone,[3d] carboxylic acid,[3e] and alcohol[3f] groups was known. Herein we report our attempts to afford (2-pyridyl)arylthioamides by coupling nitroarenes, 2-/4-picolines, and elemental sulfur. Although synthesis of *N*-arylthioamides is feasible,[4] the scope of the reactants has not been well established with heterocycles. Three examples of thiopicolinanilides were prepared by reactions of picolines, anilines, and elemental sulfur at elevated temperatures.[4a] Aromatic aldehydes, phenylacetic acids, and styrenes were also competent substrates to couple with anilines.[4b–4d] Pace and coworkers described a rare addition of aryllithium compounds to isothiocyanates to afford hindered thioamides.[4e] Given that *N*-arylpicolinamides are extensively used to stabilize high-valent metal complexes,[5] developing a method to obtain pyridylthioamides should be of interest. More importantly, uses of commercial, simple substrates such as nitroarenes, picolines, and elemental sulfur would increase the practicality of the method.

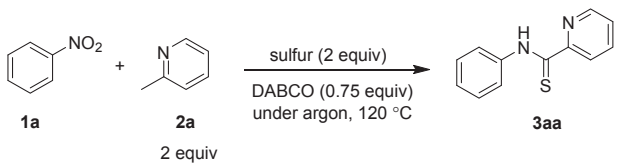
2. Results and Discussion

We firstly focused our attention on the reaction of nitrobenzene **1a**, 2-picoline **2a**, and elemental sulfur to afford picolinethioamide **3aa**. A few control experiments are shown in Table 1. An 87% yield of the product was obtained if DABCO base was used (Entry 1). The reaction was tolerant of other tertiary amines, albeit giving lower yields (Entries 2 and 3). Inorganic bases were inert to the transformation (Entry 4). Omitting DABCO caused the reaction yield to plummet, showing the crucial role of the amine (Entry 5). The transformation required the use of excess 2-picoline **2a** (Entry 6). Running the reaction at a temperature lower than 120 °C was not sufficient to obtain an affordable yield (Entry 7). Lastly, if the reaction was carried out under air, **3aa** was obtained in 68% yield (Entry 8).

Scope of the reaction with respect to nitroarenes is next investigated and presented in Scheme 1. In general, electron-rich (**3ad**, **3ae**, **3af**) and electron-poor (**3ag**, **3ah**) nitro compounds were all reactive. Hindered nitroarenes successfully yielded the pyridylthioamides (**3ab**, **3ac**), proving that steric effect somewhat does not affect the transformation. Functionalities such as primary amine (**3ae**), secondary amine (**3af**), ester (**3ag**), bromo (**3ah**), iodo (**3ai**), and boronic ester (**3aj**) groups were compatible with reaction conditions. Coupling of nitro-substituted heteroarenes such as that containing pyrazole (**3ak**), pyridine (**3al**), and benzothiazole (**3am**) afforded the thioamides in moderate to good yields.

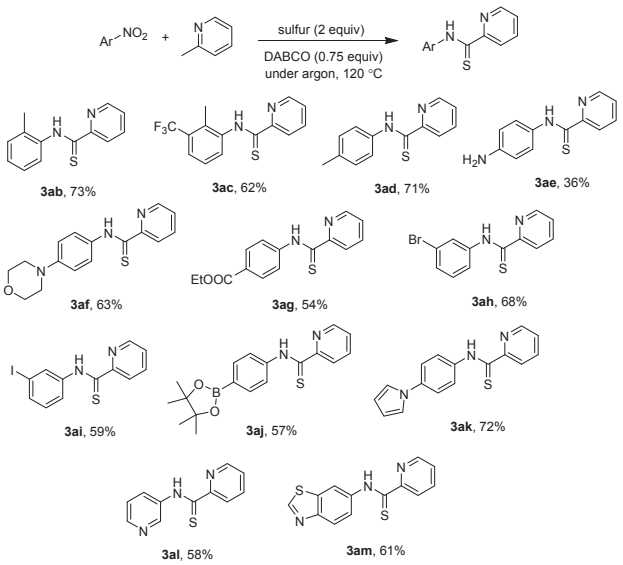
In some nitroarenes, 2-phenylbenzothiazoles were obtained, presumably after a sequence of thioamidation/cyclization (Scheme 2). It should be noted that such a sulfur-mediated cyclization often suffered from the use of prefunctionalized *ortho*-halo nitroarenes.[6] In our condition, the reaction of 3-methoxy nitrobenzene afforded a 2:1 ratio of the desired thioamide (**3am**) and a related 2-pyridyl benzothiazole (**4am**). Replacing the methoxy group with a more electron-donating group such as Me_2N gave selective cyclization products (**4an**, **4a′n**). Piperazine-derived nitrobenzene was also compatible with the conditions (**4ao**). The use of 6-nitroquinoline to couple with 2-picoline gave products (**3ap**, **4ap**) in low yields.

Table 1. Control experiments[a]

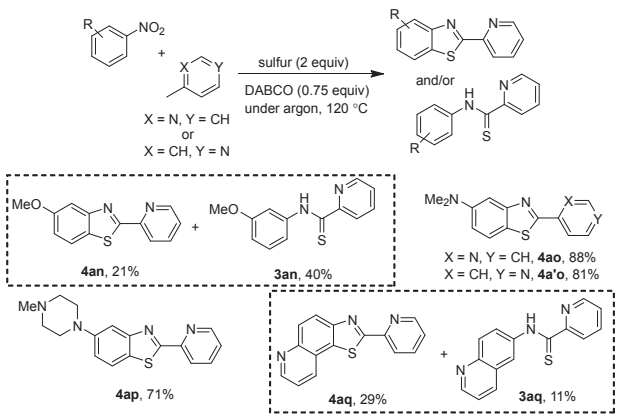


Entry	variation from standard conditions	yield of **3aa**, %
1	none	87, 85[b]
2	1-methylmorpholine instead of DABCO	28
3	1,4-dimethylpiperazine instead of DABCO	49
4	K_2CO_3 instead of DABCO	<5
5	no DABCO	18
6	1 equivalent of **2a** was used	35
7	100 °C instead of 120 °C	37
8	under air instead argon	68

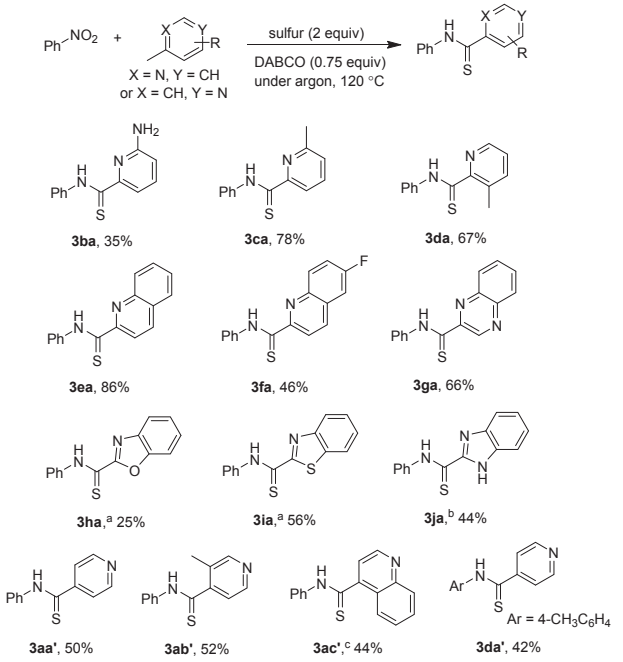
[a]Nitrobenzene (0.5 mmol), under argon for 16 h. Yields are GC yields using diphenyl ether internal standard. [b]Isolated yield.



Scheme 1. Scope of nitroarenes.



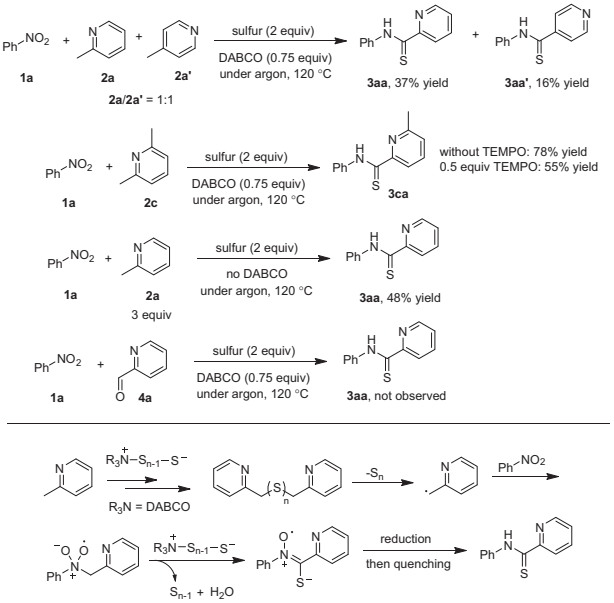
Scheme 2. Thioamidation/cyclization of nitroarenes.



Scheme 3. Scope of methylazaarenes. [a]4 equivalents of sulfur, 0.5 equivalent of pyridine. [b]CH_3CN (0.5 mL) was added. [c]CH_3CN (0.25 mL) was added.

Isosteres of 2-picolines successfully coupled with nitrobenzene. The scope of the reactants is presented in Scheme 3. An amino-substituted picoline afforded the thioamide in 35% yield (**3ba**). Only mono-functionalization of sp^3 C–H bonds occurred when 2,6-lutidine was used (**3ca**). The reaction of 2,3-lutidine gave a 67% yield of single regioisomer (**3da**). Activated primary C–H bonds in quinolines (**3ea**, **3fa**) and quinoxalines (**3ga**) were active, yielding synthetically useful bidentate ligands. 5,6-Bicyclic compounds could be used, affording the pyridylthioamides in low to moderate yields (**3ha**, **3ia**, **3ja**). It should be noted that such heterocycles were incompetent substrates in the presence of strong base.[3g] Methyl groups at C4 positions of pyridines were also compatible with reaction conditions, albeit giving the pyridylthioamides in much lower yields compared to those of 2-picolines (**3aa′**, **3ab′**, **3ac′**, **3da′**).

Some mechanistic experiments were next carried out. Some results are presented in Scheme 4. If a mixture of 2-picoline/4-picoline **2a**/**2a′** at a 1:1 molar ratio was used to couple with nitrobenzene **1a**, a 7:3 ratio of two pyridylthioamides **3aa**/**3aa′** were obtained in a combined 53% yield. Our result was consistent with that observed by Deng and co-workers, as 2-picoline was more reactive than 4-picoline in competitive reactions.[3g] The transformation was somewhat involved the formation of an active, unstable radical species, since the yield of the picoline thioamide was slightly decreased in the presence of the radical quencher TEMPO. Indeed, an EPR signal was detected when nitrobenzene **1a** reacted with 4-picoline **2a′** under standard conditions, presumably due to the formation of a trisulfide radical anion.[7,8] Picolines could be used to replace DABCO in the complexation step with elemental sulfur. Since reaction of 2-pyridinecarboxaldehyde **4a** failed to give the desired thioamide **3aa**, a simple oxidation of primary sp^3 C–H bonds into aldehyde was not likely involved in the mechanism. Similarly,



Scheme 4. Mechanistic considerations.

a simple reduction of nitrobenzene **1a** to afford aniline under the standard condition was not detected. Based on these results and that of previous reports,[3c,3g] a plausible mechanism was proposed (Scheme 4). Bis-pyridyl polysulfide was forged via the reaction of 2-picoline and the DABCO-sulfur adduct. Decomposition of the sulfide, possibly as a trisulfide radical anion, afforded the (2-pyridyl)methyl radical followed by its addition to nitrobenzene. The ensuing sequence of sulfuration, reduction, and quenching furnished the thioamide.

3. Conclusion

In conclusion, we have developed a method for coupling of nitroarenes, 2-/4-methylazaarenes, and elemental sulfur to afford (2-pyridyl)arylthioamides. Reactions proceeded in the presence of DABCO base. Functionalities such as primary and secondary amines, ester, bromo, iodo, and boronic ester groups were compatible with reaction conditions. The scope of 2-methylazaarenes included the feasible use of heterocycles including quinoline, quinoxaline, and azoles. Our method would offer a synthetically useful route to obtain pyridyl thioamides in one step.

4. Experimental

General. All reagents and starting materials were obtained from Sigma-Aldrich, Acros and Alfa, and were used as received without any further purification unless otherwise noted. Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The GC yield was calculated using diphenyl ether as the internal standard. GC-MS analyses were performed on a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). MS spectra were compared with the spectra gathered in the NIST library. The ^1H NMR and ^{13}C NMR were recorded on Bruker AV 500

spectrometers using residual solvent peak as a reference. Unless otherwise noted, chemical shifts are reported in ppm and referenced to the residual peak for $CDCl_3$ ($\delta = 7.26$ ppm for ^{1}H NMR and $\delta = 77.2$ ppm for ^{13}C NMR) or DMSO-d_6 ($\delta = 2.50$ ppm for ^{1}H NMR and $\delta = 39.5$ ppm for ^{13}C NMR). Splitting is reported with the following symbols: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, td = triplet of doublets, dd = doublet of doublets, ddd = doublet of doublets of doublets, and m = multiplet. Coupling constants (J) are reported in hertz. HR-MS spectra were recorded by an Agilent HPLC 1200 Series coupled to Bruker micrOTOF-QII.

General Procedure. In a typical experiment, a vial equipped with a magnetic stir bar was charged with nitroarene (0.5 mmol), 2- or 4-methylazaarene (1.0 mmol), sulfur (32 mg, 1.0 mmol, 32 mg/mmol), and DABCO (42 mg, 0.375 mmol). The vial was purged with argon for 1 min, placed on a preheated oil bath (120 °C), then stirred for 16 h. Upon the completion of the reaction, ethyl acetate (15 mL) was added to dilute the reaction mixture. The organic phase was washed with brine (3 × 5 mL) before being dried over anhydrous Na_2SO_4, filtered, and concentrated using a rotary evaporator. The resulting residue was purified by silica gel column chromatography using an appropriate ratio of hexanes/EtOAc mixture as eluent.

***N*-Phenylpyridine-2-carbothioamide (3aa):** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.06 (s, 1H), 8.81 (dt, $J = 8.0$, 1.0 Hz, 1H), 8.56 (ddd, $J = 4.7$, 1.7, 0.9 Hz, 1H), 8.10–8.07 (m, 2H), 7.89 (td, $J = 7.8$, 1.7 Hz, 1H), 7.49–7.45 (m, 3H), 7.32–7.28 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.0, 151.6, 146.7, 138.9, 137.6, 129.1, 126.7, 126.2, 125.0, 122.9. This compound is known.[4a]

***N*-(*o*-Tolyl)pyridine-2-carbothioamide (3ab):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.14 (s, 1H), 8.68 (d, $J = 4.7$ Hz, 1H), 8.56 (d, $J = 8.0$ Hz, 1H), 8.03 (td, $J = 7.8$, 1.6 Hz, 1H), 7.68–7.63 (m, 1H), 7.49–7.44 (m, 1H), 7.33 (dd, $J = 6.6$, 1.9 Hz, 1H), 7.27 (ddd, $J = 12.2$, 5.9, 3.9 Hz, 2H), 2.23 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 191.4, 152.2, 147.5, 138.4, 137.7, 134.1, 130.5, 127.3, 126.7, 126.5, 126.3, 124.7, 17.6. This compound is known.[9]

***N*-(2-Methyl-3-(trifluoromethyl)phenyl)pyridine-2-carbothioamide (3ac):** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.80 (s, 1H), 8.80 (d, $J = 8.0$ Hz, 1H), 8.58 (d, $J = 4.5$ Hz, 1H), 8.08 (d, $J = 8.0$ Hz, 1H), 7.92 (td, $J = 7.8$, 1.5 Hz, 1H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.53 (dd, $J = 7.4$, 4.8 Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 2.45 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 190.6, 151.0, 146.7, 138.8, 137.7, 132.6, 129.8, 126.4, 126.2, 125.2, 125.0 (d, $J = 5.8$ Hz), 13.8 (d, $J = 2.3$ Hz). **HR-MS** (ESI) calcd. for $C_{14}H_{12}F_3N_2S^+$ $[M + H]^+$: 297.0668; found 297.0671.

***N*-(*p*-Tolyl)pyridine-2-carbothioamide (3ad):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.22 (s, 1H), 8.67 (d, $J = 4.4$ Hz, 1H), 8.53 (d, $J = 8.0$ Hz, 1H), 8.04 (t, $J = 7.7$ Hz, 1H), 7.84 (d, $J = 8.3$ Hz, 2H), 7.65 (dd, $J = 6.8$, 5.3 Hz, 1H), 7.26 (d, $J = 8.1$ Hz, 2H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 189.3, 152.7, 147.3, 137.8, 136.7, 135.8, 128.9, 126.3, 124.6, 123.8, 20.7. This compound is known.[9]

***N*-(4-Aminophenyl)pyridine-2-carbothioamide (3ae):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.49 (s, 1H), 9.43 (s, 1H), 8.84 (d, $J = 2.0$ Hz, 1H), 8.71 (d, $J = 4.6$ Hz, 1H), 8.56 (d, $J = 8.0$ Hz, 1H), 8.15 (d, $J = 8.7$ Hz, 1H), 8.07 (td, $J = 7.7$, 1.6 Hz, 1H), 7.96 (dd, $J = 8.8$, 2.0 Hz, 1H), 7.68 (dd, $J = 7.5$, 4.7 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 186.6, 153.3, 147.9, 147.7, 138.2, 128.4, 126.4, 125.0, 124.8, 113.6. This compound is known.[10]

***N*-(4-Morpholinophenyl)pyridine-2-carbothioamide (3af):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.13 (s, 1H), 8.68–8.65 (m, 1H), 8.53 (d, $J = 8.0$ Hz, 1H), 8.03 (td, $J = 7.8$, 1.7 Hz, 1H), 7.90 (d, $J = 9.0$ Hz, 2H), 7.63 (ddd, $J = 7.5$, 4.7, 1.0 Hz, 1H), 7.02–6.97 (m, 2H), 3.78–3.72 (m, 4H), 3.18–3.13 (m, 4H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 187.6, 152.7, 149.2, 147.2, 137.7, 130.8, 126.1, 124.45, 124.38, 114.3, 66.0, 48.1. This compound is known.[11]

Ethyl 4-(pyridine-2-carbothioamido)benzoate (3ag): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.25 (s, 1H), 8.78 (d, $J = 8.0$ Hz, 1H), 8.56 (d, $J = 4.1$ Hz, 1H), 8.25 (d, $J = 8.7$ Hz, 2H), 8.14 (d, $J = 8.7$ Hz, 2H), 7.90 (td, $J = 7.9$, 1.7 Hz, 1H), 7.49 (ddd, $J = 7.4$, 4.7, 0.9 Hz, 1H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.41 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.5, 166.0, 151.4, 146.7, 142.7, 137.8, 130.7, 128.1, 126.4, 125.0, 121.8, 61.2, 14.5. **HR-MS** (ESI) calcd. for $C_{15}H_{14}N_2O_2SNa^+$ $[M + Na]^+$: 309.0668; found 309.0671.

***N*-(3-Bromophenyl)pyridine-2-carbothioamide (3ah):** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.07 (s, 1H), 8.78 (d, $J = 8.0$ Hz, 1H), 8.55 (dd, $J = 4.7$, 0.6 Hz, 1H), 8.36 (t, $J = 1.9$ Hz, 1H), 8.03 (dd, $J = 8.0$, 1.4 Hz, 1H), 7.90 (td, $J = 7.8$, 1.7 Hz, 1H), 7.49 (ddd, $J = 7.5$, 4.7, 1.0 Hz, 1H), 7.44–7.40 (m, 1H), 7.32 (t, $J = 8.1$ Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.5, 151.4, 146.7, 140.1, 137.8, 130.3, 129.6, 126.4, 125.5, 125.0, 122.5, 121.3. **HR-MS** (ESI) calcd. for $C_{12}H_9{}^{79}BrN_2SNa^+$ $[M + Na]^+$: 316.1712; found 316.1713.

***N*-(3-Iodophenyl)pyridine-2-carbothioamide (3ai):** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.04 (s, 1H), 8.77 (d, $J = 8.0$ Hz, 1H), 8.54 (d, $J = 4.6$ Hz, 1H), 8.46 (s, 1H), 8.11 (dd, $J = 8.1$, 1.4 Hz, 1H), 7.90 (td, $J = 7.8$, 1.6 Hz, 1H), 7.61 (d, $J = 7.9$ Hz, 1H), 7.49 (dd, $J = 7.4$, 4.8 Hz, 1H), 7.18 (t, $J = 8.0$ Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.4, 151.3, 146.6, 140.0, 137.8, 135.6, 131.3, 130.4, 126.4, 125.0, 122.0, 93.8. **HR-MS** (ESI) calcd. for $C_{12}H_9IN_2SNa^+$ $[M + Na]^+$: 362.9423; found 362.9429.

***N*-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine-2-carbothioamide (3aj):** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.14 (s, 1H), 8.79 (d, $J = 8.0$ Hz, 1H), 8.55 (d, $J = 4.7$ Hz, 1H), 8.13 (d, $J = 8.4$ Hz, 2H), 7.92–7.87 (m, 3H), 7.49–7.46 (m, 1H), 1.36 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.9, 151.6, 146.5, 141.3, 137.8, 135.7, 126.2, 125.0, 121.6, 84.0, 25.0. **HR-MS** (ESI) calcd. for $C_{18}H_{22}BN_2O_2S$ $[M + H]^+$: 341.1490; found 341.1523.

***N*-(4-(1*H*-Pyrrol-1-yl)phenyl)pyridine-2-carbothioamide (3ak):** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.12 (s, 1H), 8.81 (d, $J = 8.0$ Hz, 1H), 8.57 (d, $J = 4.3$ Hz, 1H), 8.17 (d, $J = 8.8$ Hz, 2H), 7.91 (td, $J = 7.8$, 1.6 Hz, 1H), 7.51–7.46 (m, 3H), 7.12 (t, $J = 2.1$ Hz, 2H), 6.37 (t, $J = 2.1$ Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.8, 151.4, 146.6, 138.8, 137.9, 136.4, 126.3, 125.1, 124.0, 120.7, 119.4, 110.8. **HR-MS** (ESI) calcd. for $C_{16}H_{14}N_3S^+$ $[M + H]^+$: 280.0903; found 280.0938.

***N*-(Pyridin-3-yl)pyridine-2-carbothioamide (3al):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.44 (s, 1H), 8.96 (d, $J = 2.4$ Hz, 1H), 8.71 (d, $J = 4.6$ Hz, 1H), 8.54 (d, $J = 8.0$ Hz, 1H), 8.48 (dd, $J = 4.7$, 1.3 Hz, 1H), 8.36–8.31 (m, 1H), 8.06 (td, $J =$

7.8, 1.7 Hz, 1H), 7.71–7.67 (m, 1H), 7.50 (dd, $J = 8.2$, 4.7 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 191.8, 152.3, 147.5, 147.1, 146.0, 137.8, 136.0, 132.0, 126.7, 124.9, 123.3. **HR-MS** (ESI) calcd. for $C_{11}H_{10}N_3S^+$ $[M + H]^+$: 216.0590; found 216.0591.

***N*-(Benzo[*d*]thiazol-6-yl)pyridine-2-carbothioamide (3am):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.49 (s, 1H), 9.43 (s, 1H), 8.84 (d, $J = 2.0$ Hz, 1H), 8.71 (d, $J = 4.6$ Hz, 1H), 8.56 (d, $J = 8.0$ Hz, 1H), 8.15 (d, $J = 8.7$ Hz, 1H), 8.07 (td, $J = 7.7$, 1.6 Hz, 1H), 7.96 (dd, $J = 8.8$, 2.0 Hz, 1H), 7.68 (dd, $J = 7.5$, 4.7 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 190.6, 156.8, 152.6, 151.2, 147.4, 137.8, 136.7, 133.6, 126.5, 124.8, 123.6, 122.7, 117.7. **HR-MS** (ESI) calcd. for $C_{13}H_9N_3S_2^+$ $[M + H]^+$: 272.0311; found 272.0307.

***N*-(3-Methoxyphenyl)pyridine-2-carbothioamide (3an):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.25 (s, 1H), 8.68 (d, $J = 4.7$ Hz, 1H), 8.52 (d, $J = 8.0$ Hz, 1H), 8.08–8.02 (m, 1H), 7.73 (s, 1H), 7.66 (dd, $J = 7.4$, 4.8 Hz, 1H), 7.59 (d, $J = 7.9$ Hz, 1H), 7.36 (t, $J = 8.1$ Hz, 1H), 6.88 (dd, $J = 8.3$, 2.4 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 189.6, 159.2, 152.7, 147.3, 140.2, 137.8, 129.3, 126.4, 124.6, 115.9, 112.1, 109.3, 55.2. **HR-MS** (ESI) calcd. for $C_{13}H_{13}N_2OS^+$ $[M + H]^+$: 245.0743; found 245.0739.

5-Methoxy-2-(pyridin-2-yl)benzo[*d*]thiazole (4an): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.68 (d, $J = 3.0$ Hz, 1H), 8.37 (d, $J = 7.9$ Hz, 1H), 7.85 (td, $J = 7.8$, 1.5 Hz, 1H), 7.81 (d, $J = 8.8$ Hz, 1H), 7.59 (d, $J = 2.4$ Hz, 1H), 7.39 (dd, $J = 7.0$, 5.2 Hz, 1H), 7.08 (dd, $J = 8.8$, 2.4 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.6, 159.3, 155.5, 151.5, 149.8, 137.2, 128.2, 125.4, 122.4, 120.8, 116.4, 105.7, 55.8. **HR-MS** (ESI) calcd. for $C_{13}H_{11}N_2OS^+$ $[M + H]^+$: 243.0587; found 243.0586.

***N*,*N*-Dimethyl-2-(pyridin-2-yl)benzo[*d*]thiazol-5-amine (4ao):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.69 (d, $J = 4.5$ Hz, 1H), 8.27 (d, $J = 7.9$ Hz, 1H), 8.01 (td, $J = 7.7$, 1.6 Hz, 1H), 7.89 (d, $J = 8.9$ Hz, 1H), 7.60–7.51 (m, 1H), 7.31 (d, $J = 2.4$ Hz, 1H), 7.04 (dd, $J = 8.9$, 2.5 Hz, 1H), 2.99 (s, 6H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 168.9, 155.5, 150.7, 150.0, 149.8, 137.7, 125.7, 123.2, 122.1, 120.0, 113.9, 105.0, 40.5. **HR-MS** (ESI) calcd. for $C_{14}H_{14}N_3S^+$ $[M + H]^+$: 256.0903; found 256.0908.

***N*,*N*-Dimethyl-2-(pyridin-4-yl)benzo[*d*]thiazol-5-amine (4a′o):** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.74 (d, $J = 3.8$ Hz, 2H), 7.91 (d, $J = 5.8$ Hz, 2H), 7.72 (d, $J = 8.9$ Hz, 1H), 7.39 (d, $J = 2.4$ Hz, 1H), 6.99 (dd, $J = 8.9$, 2.4 Hz, 1H), 3.04 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.5, 155.9, 150.59, 150.53, 141.1, 123.5, 121.8, 121.2, 114.4, 105.8, 41.1. **HR-MS** (ESI) calcd. for $C_{14}H_{14}N_3S^+$ $[M + H]^+$: 256.0903; found 256.0924.

5-(4-Methylpiperazin-1-yl)-2-(pyridin-2-yl)benzo[*d*]thiazole (4ap): **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.70 (d, $J = 4.3$ Hz, 1H), 8.27 (d, $J = 7.9$ Hz, 1H), 8.02 (td, $J = 7.7$, 1.6 Hz, 1H), 7.93 (d, $J = 8.9$ Hz, 1H), 7.58–7.54 (m, 1H), 7.52 (d, $J = 2.2$ Hz, 1H), 7.24 (dd, $J = 8.9$, 2.3 Hz, 1H), 3.25–3.20 (m, 4H), 2.52–2.46 (m, 4H, overlapping with solvent peaks), 2.24 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 169.2, 155.3, 150.7, 150.6, 149.9, 137.8, 125.8, 125.8, 122.2, 120.0, 116.9, 108.1, 54.6, 48.6, 45.7. **HR-MS** (ESI) calcd. for $C_{17}H_{19}N_4S^+$ $[M + H]$: 311.1325; found 311.1351.

***N*-(Quinolin-6-yl)pyridine-2-carbothioamide (3aq):** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.36 (s, 1H), 9.24 (d, $J = 2.0$ Hz, 1H), 8.91 (d, $J = 3.0$ Hz, 1H), 8.81 (d, $J = 8.0$ Hz, 1H), 8.59 (d, $J = 4.5$ Hz, 1H), 8.27 (d, $J = 8.2$ Hz, 1H), 8.23 (d, $J = 9.0$ Hz, 1H), 8.03 (dd, $J = 9.0$, 2.3 Hz, 1H), 7.92 (td, $J = 7.8$, 1.5 Hz, 1H), 7.51 (dd, $J = 7.2$, 4.9 Hz, 1H), 7.47 (dd, $J = 8.3$, 4.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.3, 151.5, 149.9, 146.8, 146.0, 137.8, 137.03, 136.97, 130.0, 128.6, 126.4, 126.0, 124.9, 121.9, 119.1. One carbon signal could not be located. **HR-MS** (ESI) calcd. for $C_{15}H_{12}N_3S$ $[M + H]^+$: 266.0746; found 266.0754.

2-(Pyridin-2-yl)thiazolo[5,4-*f*]quinoline (4aq): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.67 (s, 1H), 8.37 (dd, $J = 15.3$, 8.0 Hz, 2H), 8.30 (d, $J = 9.0$ Hz, 1H), 8.14 (d, $J = 9.0$ Hz, 1H), 7.85 (t, $J = 7.6$ Hz, 1H), 7.51 (dd, $J = 7.9$, 3.9 Hz, 1H), 7.44–7.33 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.7, 152.6, 151.2, 150.0, 149.8, 146.7, 137.3, 133.6, 133.3, 129.0, 125.55, 125.46, 123.8, 121.7, 120.7. **HR-MS** (ESI) calcd. for $C_{15}H_{10}N_3S^+$ $[M + H]^+$: 266.0590; found 264.0607.

6-Amino-*N*-phenylpyridine-2-carbothioamide (3ba): **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.17 (s, 1H), 8.03 (d, $J = 7.7$ Hz, 2H), 7.68 (d, $J = 7.1$ Hz, 1H), 7.60 (t, $J = 7.8$ Hz, 1H), 7.47 (t, $J = 7.9$ Hz, 2H), 7.29 (t, $J = 7.4$ Hz, 1H), 6.72 (d, $J = 8.0$ Hz, 1H), 6.34 (bs, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 189.2, 157.5, 150.1, 138.9, 138.4, 128.7, 126.2, 122.8, 112.6, 111.6. **HR-MS** (ESI) calcd. for $C_{12}H_{12}N_3S^+$ $[M + H]^+$: 230.0746; found 230.0759.

6-Methyl-*N*-phenylpyridine-2-carbothioamide (3ca): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.13 (s, 1H), 8.61 (d, $J = 7.8$ Hz, 1H), 8.06 (d, $J = 7.7$ Hz, 2H), 7.76 (t, $J = 7.8$ Hz, 1H), 7.47 (t, $J = 7.9$, 2H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.29 (t, $J = 7.4$ Hz, 1H), 2.64 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.4, 155.8, 150.9, 138.9, 137.8, 129.0, 126.7, 125.9, 123.0, 122.1, 24.4. **HR-MS** (ESI) calcd. for $C_{13}H_{13}N_2S^+$ $[M + H]^+$: 229.0794; found 229.0795.

3-Methyl-*N*-phenylpyridine-2-carbothioamide (3da): **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.09 (s, 1H), 8.40 (d, $J = 4.3$ Hz, 1H), 7.97 (d, $J = 7.8$ Hz, 2H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.46 (t, $J = 7.9$ Hz, 2H), 7.35 (dd, $J = 7.7$, 4.8 Hz, 1H), 7.30 (t, $J = 7.4$ Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 196.2, 158.8, 145.9, 139.2, 138.7, 128.6, 128.5, 126.4, 123.5, 122.9, 18.0. **HR-MS** (ESI) calcd. for $C_{13}H_{13}N_2S^+$ $[M + H]^+$: 229.0794; found 229.0807.

***N*-Phenylquinoline-2-carbothioamide (3ea):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.47 (s, 1H), 8.59 (q, $J = 8.6$ Hz, 2H), 8.23 (d, $J = 8.4$ Hz, 1H), 8.09 (d, $J = 8.1$ Hz, 1H), 8.03 (d, $J = 7.8$ Hz, 2H), 7.90 (t, $J = 7.5$ Hz, 1H), 7.74 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 2H), 7.33 (t, $J = 7.2$ Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 190.5, 152.5, 145.0, 139.2, 137.4, 130.7, 129.5, 128.6, 128.5, 128.3, 128.0, 126.6, 123.8, 121.0. This compound is known.[12]

6-Fluoro-*N*-phenylquinoline-2-carbothioamide (3fa): **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.44 (s, 1H), 8.58 (dd, $J = 33.4$, 8.7 Hz, 2H), 8.29 (dd, $J = 9.2$, 5.5 Hz, 1H), 8.02 (d, $J = 7.7$ Hz, 2H), 7.92 (dd, $J = 9.3$, 2.7 Hz, 1H), 7.82 (td, $J = 8.9$, 2.8 Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 190.3, 161.7, 159.7, 152.3, 152.2, 142.2, 139.2, 136.9, 136.9, 132.5, 132.5, 129.4, 129.3, 128.6, 126.6, 123.8, 121.8, 121.1, 120.9, 111.2, 111.1. **HR-MS** (ESI) calcd. for $C_{16}H_{12}FN_2S^+$ $[M + H]^+$: 283.0700; found 283.0699.

***N*-Phenylquinoxaline-2-carbothioamide (3ga):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.50 (s, 1H), 9.77 (s, 1H), 8.26 (dd, $J = 6.2$, 3.5 Hz, 1H), 8.19 (dd, $J = 6.3$, 3.4 Hz, 1H), 8.03–7.94 (m, 4H), 7.51 (t, $J = 7.8$ Hz, 2H), 7.35 (t, $J = 7.4$ Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 189.55, 148.0, 145.5, 142.1, 139.1, 138.7, 131.8, 131.5, 129.7, 128.9, 128.7, 126.8, 123.9. **HR-MS** (ESI) calcd. for $C_{15}H_{12}N_3S^+$ $[M + H]^+$: 266.0746; found 266.0744.

***N*-Phenylbenzo[*d*]oxazole-2-carbothioamide (3ha):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.61 (s, 1H), 7.96 (d, $J =$ 7.8 Hz, 1H), 7.91 (dd, $J = 12.5$, 4.9 Hz, 3H), 7.63–7.57 (m, 1H), 7.56–7.51 (m, 1H), 7.50–7.45 (m, 2H), 7.33 (dd, $J = 10.6$, 4.2 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 178.0, 158.0, 150.7, 140.1, 138.6, 128.6, 127.5, 126.9, 125.8, 124.0, 121.2, 111.7. **HR-MS** (ESI) calcd. for $C_{14}H_{11}N_2OS^+$ $[M + H]^+$: 255.0587; found 255.0595.

***N*-Phenylbenzo[*d*]thiazole-2-carbothioamide (3ia):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.48 (s, 1H), 8.19 (dd, $J =$ 8.5, 1.2 Hz, 2H), 7.92–7.90 (m, 2H), 7.63 (td, $J = 7.8$, 1.5 Hz, 1H), 7.58 (td, $J = 7.8$, 1.5 Hz, 1H), 7.47 (tt, $J = 8$, 2 Hz, 2H), 7.33 (tt, $J = 7.5$, 1 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 182.8, 169.9, 152.9, 138.7, 138.5, 128.5, 127.2, 126.8, 124.6, 124.4, 122.4. One carbon signal could not be located. **HR-MS** (ESI) calcd. for $C_{14}H_{11}N_2S_2^+$ $[M + H]^+$: 271.0358; found 271.0344.

***N*-Phenyl-1*H*-benzo[*d*]imidazole-2-carbothioamide (3ja):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 13.02 (s, 1H), 12.30 (s, 1H), 7.96 (dd, $J = 8.5$, 1 Hz, 2H), 7.80 (d, $J = 8$ Hz, 1H), 7.63 (d, $J = 8$ Hz, 1H), 7.458 (t, $J = 7.5$ Hz, 2H), 7.38–7.29 (m, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 181.3, 149.1, 142.1, 138.8, 135.5, 128.4, 126.5, 124.5, 124.2, 123.0, 120.3, 112.8. **HR-MS** (ESI) calcd. for $C_{14}H_{12}N_3S^+$ $[M + H]^+$: 254.0746; found 254.0747.

***N*-Phenylpyridine-4-carbothioamide (3aa′):** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.59 (s, 2H), 7.79 (d, $J =$ 7.8 Hz, 2H), 7.63 (d, $J = 4.8$ Hz, 2H), 7.46 (t, $J = 7.7$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.5, 150.2, 138.9, 129.3, 127.5, 123.6, 120.9. This compound is known.[4a]

3-Methyl-*N*-phenylpyridine-4-carbothioamide (3ab′): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.08 (s, 1H), 8.20 (d, $J = 4.7$ Hz, 1H), 8.16 (s, 1H), 7.89 (d, $J = 7.6$ Hz, 2H), 7.44 (t, $J = 7.9$ Hz, 2H), 7.31 (t, $J = 7.4$ Hz, 1H), 7.23 (d, $J = 5.0$ Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.7, 151.8, 150.7, 146.7, 138.8, 129.2, 127.3, 122.9, 120.8, 16.2. **HR-MS** (ESI) calcd. for $C_{13}H_{13}N_2S^+$ $[M + H]^+$: 229.0794; found 229.0828.

***N*-Phenylquinoline-4-carbothioamide (3ac′):** **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.40 (s, 1H), 8.97 (d, $J = 4.4$ Hz, 1H), 8.10 (d, $J = 8.3$ Hz, 1H), 8.07 (d, $J = 7.9$ Hz, 1H), 8.01 (d, $J = 7.6$ Hz, 2H), 7.85–7.80 (m, 1H), 7.70–7.66 (m, 1H), 7.53 (d, $J = 4.4$ Hz, 1H), 7.50 (t, $J = 7.9$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 194.2, 150.3, 149.1, 147.9, 139.1, 129.8, 129.3, 128.8, 127.4, 126.7, 124.9, 123.4, 123.1, 117.7. **HR-MS** (ESI) calcd. for $C_{16}H_{13}N_2S^+$ $[M + H]^+$: 265.0794; found 265.0799.

***N*-(*p*-Tolyl)pyridine-4-carbothioamide (3da′):** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.60 (d, $J = 5.9$ Hz, 2H), 7.57 (dd, $J = 5.0$, 3.4 Hz, 4H), 7.19 (d, $J = 8.1$ Hz, 2H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.4, 150.5, 149.8, 137.7, 129.9, 123.7, 120.7, 21.4. **HR-MS** (ESI) calcd. for $C_{13}H_{13}N_2S^+$ $[M + H]^+$: 229.0794; found 229.0796.

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Supporting Information

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References

1 a) L.-C. Campeau, D. J. Schipper, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 3266. b) J. J. Mousseau, A. Larivée, A. B. Charette, *Org. Lett.* **2008**, *10*, 1641. c) T. Niwa, H. Yorimitsu, K. Oshima, *Angew. Chem., Int. Ed.* **2007**, *46*, 2643. d) R. Shang, Z.-W. Yang, Y. Wang, S.-L. Zhang, L. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 14391. e) B. Qian, S. Guo, J. Shao, Q. Zhu, L. Yang, C. Xia, H. Huang, *J. Am. Chem. Soc.* **2010**, *132*, 3650. f) B.-S. Kim, J. Jiménez, F. Gao, P. J. Walsh, *Org. Lett.* **2015**, *17*, 5788. g) J. H. Kim, S. Greßies, M. Boultadakis-Arapinis, C. Daniliuc, F. Glorius, *ACS Catal.* **2016**, *6*, 7652.

2 a) S. Duez, A. K. Steib, S. M. Manolikakes, P. Knochel, *Angew. Chem., Int. Ed.* **2011**, *50*, 7686. b) S.-S. Li, S. Fu, L. Wang, L. Xu, J. Xiao, *J. Org. Chem.* **2017**, *82*, 8703.

3 For reviews: a) T. B. Nguyen, *Adv. Synth. Catal.* **2017**, *359*, 1066. Examples: b) T. B. Nguyen, L. Ermolenko, A. Al-Mourabit, *J. Am. Chem. Soc.* **2013**, *135*, 118. c) T. B. Nguyen, L. Ermolenko, A. Al-Mourabit, *Org. Lett.* **2013**, *15*, 4218. d) H. Huang, Z. Xu, X. Ji, B. Li, G.-J. Deng, *Org. Lett.* **2018**, *20*, 4917. e) N. T. Do, K. M. Tran, H. T. Phan, T. A. To, T. T. Nguyen, N. T. S. Phan, *Org. Biomol. Chem.* **2019**, *17*, 8987. f) Q. Xing, Y. Ma, H. Xie, F. Xiao, F. Zhang, G.-J. Deng, *J. Org. Chem.* **2019**, *84*, 1238. g) H. Huang, Q. Wang, Z. Xu, G.-J. Deng, *Adv. Synth. Catal.* **2019**, *361*, 591.

4 a) H. D. Porter, *J. Am. Chem. Soc.* **1954**, *76*, 127. b) K. Okamoto, T. Yamamoto, T. Kanbara, *Synlett* **2007**, *17*, 2687. c) T. Guntreddi, R. Vanjari, K. N. Singh, *Org. Lett.* **2014**, *16*, 3624. d) P. Zhang, W. Chen, M. Liu, H. Wu, *J. Org. Chem.* **2018**, *83*, 14269. e) V. Pace, L. Castoldi, S. Monticelli, S. Safranek, A. Roller, T. Langer, W. Holzer, *Chem.—Eur. J.* **2015**, *21*, 18966.

5 Selected examples: a) E. T. Nadres, O. Daugulis, *J. Am. Chem. Soc.* **2012**, *134*, 7. b) R. Odani, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2013**, *78*, 11045. c) S. Rej, N. Chatani, *ACS Catal.* **2018**, *8*, 6699. d) Q. Li, S.-Y. Zhang, G. He, Z. Ai, W. A. Nack, G. Chen, *Org. Lett.* **2014**, *16*, 1764. e) S. Roy, S. Pradhan, T. Punniyamurthy, *Chem. Commun.* **2018**, *54*, 3899.

6 Selected examples: a) J. Jiang, G. Li, F. Zhang, H. Xie, G.-J. Deng, *Adv. Synth. Catal.* **2018**, *360*, 1622. b) X. Zhu, Y. Yang, G. Xiao, J. Song, Y. Liang, G. Deng, *Chem. Commun.* **2017**, *53*, 11917.

7 Please see the Supporting Information for details.

8 Selected examples for detection of trisulfur radical anion: a) T. Chivers, P. J. W. Elder, *Chem. Soc. Rev.* **2013**, *42*, 5996. b) G. Zhang, H. Yi, H. Chen, C. Bian, C. Liu, A. Lei, *Org. Lett.* **2014**, *16*, 6156.

9 R. R. Kumar, M. K. M. Subarkhan, R. Ramesh, *RSC Adv.* **2015**, *5*, 46760.

10 M. H. Klingele, S. Brooker, *Eur. J. Org. Chem.* **2004**, 3422.

11 S. M. Meier, M. Hanif, Z. Adhireksan, V. Pichler, M. Novak, E. Jirkovsky, M. A. Jakupec, V. B. Arion, C. A. Davey, B. K. Kepplera, C. G. Hartinger, *Chem. Sci.* **2013**, *4*, 1837.

12 F. M. Moghaddam, H. Z. Boinee, S. Taheri, *J. Sulfur Chem.* **2004**, *25*, 407.

