CHAPTER-3

Synthesis of functionalized thioimidates from thioamides and arylboronic acids via copper-catalyzed cross-coupling reaction under mild conditions

3.1 Introduction

Sulfur-containing organic molecules are widespread in nature and have found applications in different fields, including pharmaceutics, agrochemicals, materials, etc., [1-6]. Among the different organosulfur compounds, thioamides play important roles in synthetic organic chemistry and medicinal chemistry. For instance, thioamide functional groups have been found in many natural products, bioactive molecules, and drugs [7-10] (**Figure 3.1**). On the other hand, thioamides undergo various types of reactions and provide biologically relevant molecules and heterocycles [7, 8, 11].

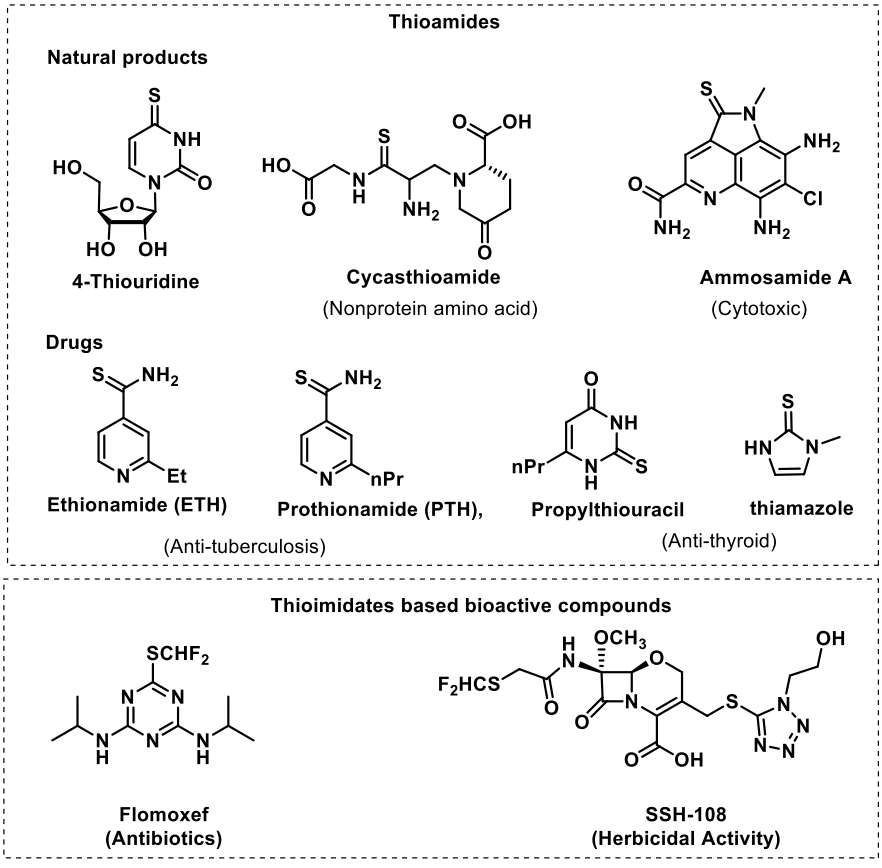
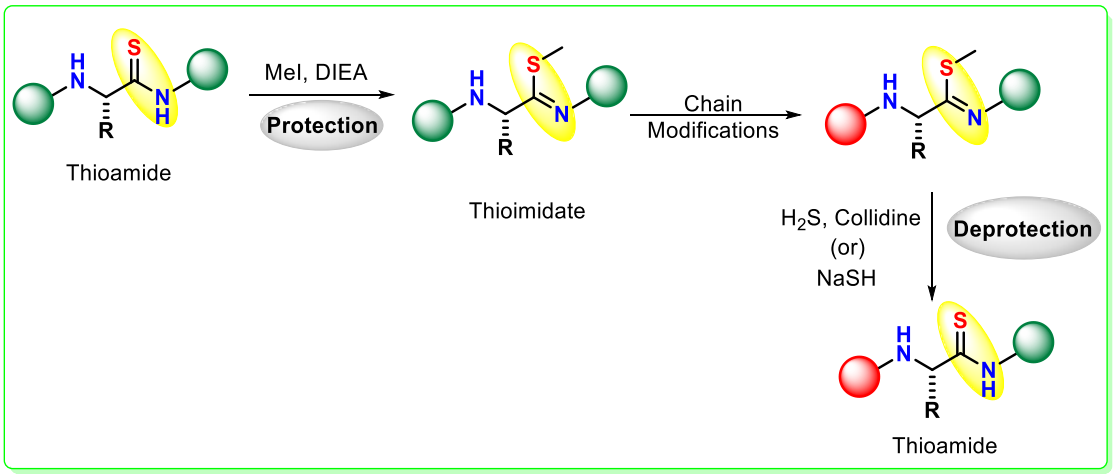


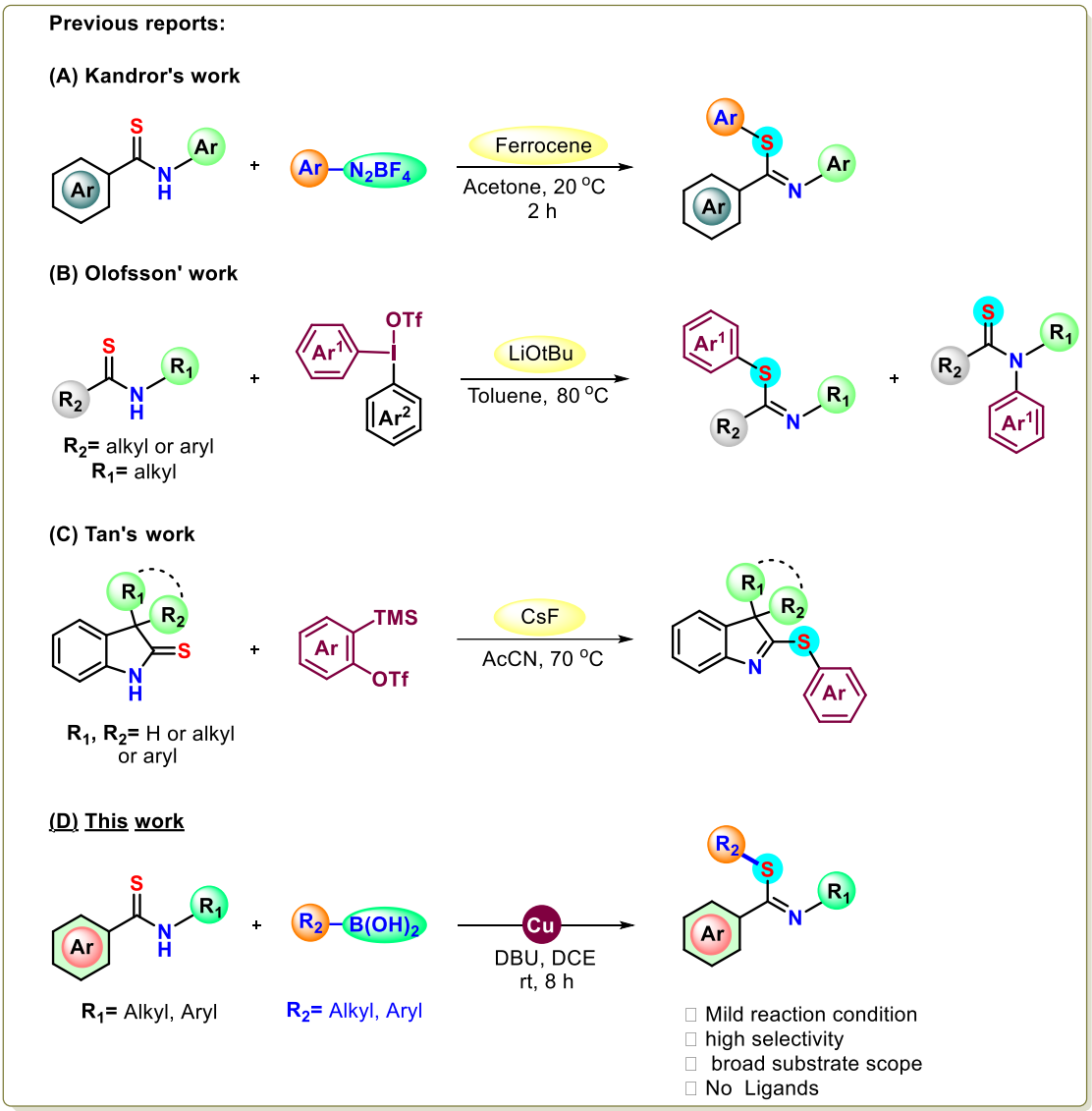
Figure 3.1 Thioamide and thioimidates based natural products and bioactive compounds.



Scheme 3.1: Protection of thioamides to thioimidates in the peptide synthesis.

The reaction of thioamides with carbon electrophiles provides thioimidates, one of the important scaffolds in organic synthesis and drug discovery [11, 12] (**Figure 3.1**). In peptide synthesis, thioimidates have been well explored as a protecting group for thioamides [13, 14] (**Scheme 3.1**). Synthesis of S-alkyl thioimidates is simple and can be achieved from thioamides and alkyl halides in the presence of a base [11]. However, the synthesis of S-aryl thioimidates is relatively difficult. Besides different approaches, the S-arylation of thioamides is considered as a straightforward approach for synthesizing S-aryl thioimidates [15-18]. In 1982, Kandror et al. reported the radical S-arylation of thioamides using aryl diazonium salts [15, 18] (**Scheme 3.2, A**). Later, in 2019, Olofsson group demonstrated the S-arylation of thioamides using diaryliodonium salts in the presence of LiO*t*Bu at 80^{o}C [17] (**Scheme 3.2, B**). Besides these reports, in 2020, Tan et al. reported a chemoselective S-arylation of thio-oxindoles with benzynes at 70 ^{o}C that affords 2-(arylthio)indolenines [16] (**Scheme 3.2, C**). Each of these methods has its own advantages

and disadvantages in terms of reaction conditions, substrate scope, safety, etc. Nevertheless, the synthesis of benzothiazoles, a class of biologically relevant cyclic thioimidates, has been achieved by different routes [19-22].



Scheme 3.2. Representative synthesis of S-arylated and s-alkylated products of thioamides.

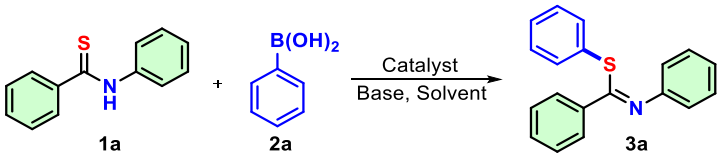
Aryl boronic acids are important precursors in organic synthesis and have been frequently employed in many cross-coupling reactions owing to their stability and eco-friendly nature [23, 24]. Although the arylation of thiols with arylboronic acids has been well explored, the S-arylation of thioamides is yet to be explored. Our group is focused on the development of new methods for the synthesis of biologically relevant molecules. In this context, we have recently reported different C-S bond formation reactions including S-arylation of 1-thiosugars, arylthiolation of indoles, multicomponent synthesis of S-benzyl thiocarbamates and S-insertion of diazo compounds [25-28]. In continuation of these reports, here we demonstrated the room-temperature S-arylation of thioamides using arylboronic acids in the presence of copper acetate and DBU (**Scheme 3.2, D**).

3.2 Results and Discussion

The reaction was optimized at the outset by choosing N-phenyl thiobenzamide (**1a**) and phenylboronic acid (**2a**) as the model substrates. Initially, the reaction was performed with different copper catalysts (10 mol%) in the presence of DBU for 12 h at room temperature. The reaction with copper (I) catalysts gave the desired coupling product **3a** in negligible yields, while reasonable yields were obtained with copper (II) catalysts. In particular, copper (II) acetate gave the desired product **3a** in 47 % yield. Further, it was observed that by increasing the amount of catalyst from 10 to 25 mol%, the desired product was obtained in 78% yield in 8 hours. However, with a further increase in catalyst loading (30 mol%), no significant change in the yield of the product was observed.

Further optimization was investigated by changing the base in the presence of 25 mol% copper (II) acetate. The organic bases, including pyridine, triethyl amine, and DABCO, gave the desired product in 45-61% yields, while 10-47% yields were obtained with inorganic bases such as potassium carbonate and potassium *tert*-butoxide. The reaction was further optimized with different solvents, including DCM, Toluene, acetonitrile, THF, and dioxane, and the desired product was obtained in 40 to 65% yields. Overall, this optimization study suggests that the use of 25 mol% copper (II) acetate in the presence of DBU base in DCE solvent at room temperature would be the optimal condition to obtain the desired product in good yields.

Table 3.1 Optimization of reaction condition[a, b]



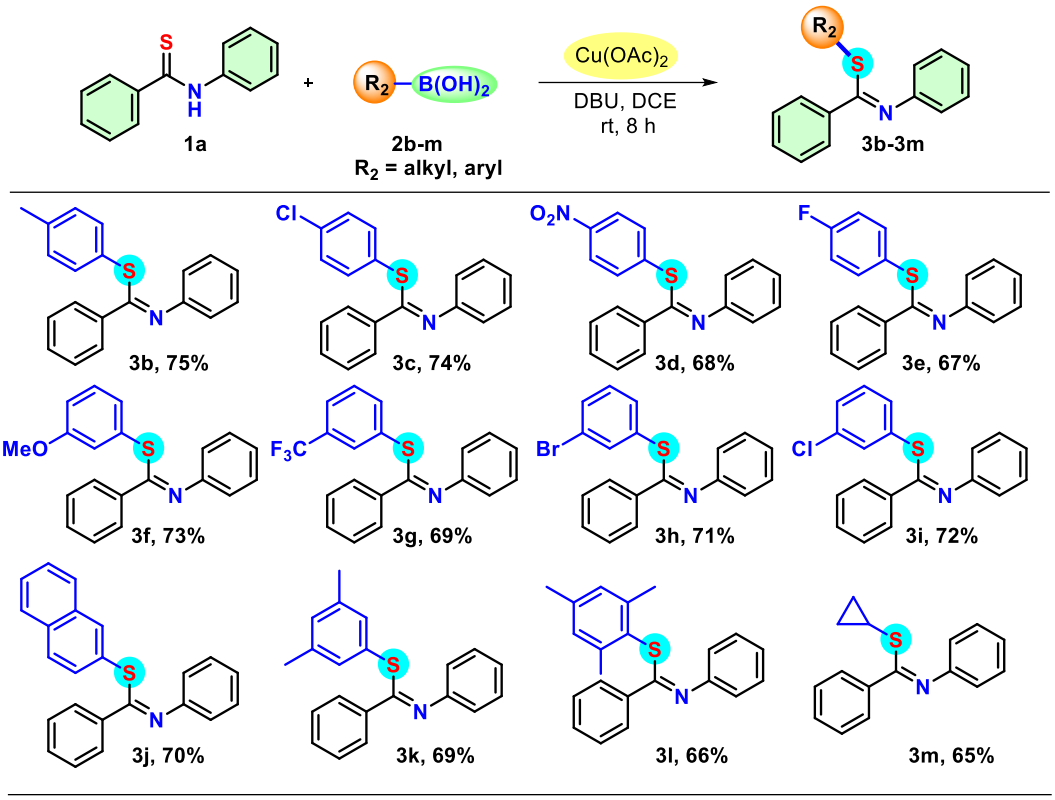
Entry	Catalyst	Mol %	Base (equiv)	Solvent (mL)	Time (h)	Yield (%)[b]
1	CuI	10	DBU	DCE	12	<10
2	CuCl	10	DBU	DCE	12	<10
3	CuTC	10	DBU	DCE	12	<5
4	Cu_2O	10	DBU	DCE	12	<5
5	$CuSO_4$	10	DBU	DCE	12	<10
6	$CuCl_2$	10	DBU	DCE	12	25
7	$Cu(OAc)_2$	10	DBU	DCE	12	47
8	$Cu(OAc)_2$	15	DBU	DCE	12	58
10	$Cu(OAc)_2$	20	DBU	DCE	12	71
11	$Cu(OAc)_2$	25	DBU	DCE	8	78
12	**$Cu(OAc)_2$**	**30**	**DBU**	**DCE**	**8**	**78**
13	$Cu(OAc)_2$	25	Pyridine	DCE	8	45
14	$Cu(OAc)_2$	25	NEt_3	DCE	8	50

15	$Cu(OAc)_2$	25	DABCO	DCE	8	61
16	$Cu(OAc)_2$	25	K_2CO_3	DCE	8	10
17	$Cu(OAc)_2$	25	t-BuOK	DCE	8	47
18	$Cu(OAc)_2$	25	DBU	DCM	8	65
19	$Cu(OAc)_2$	25	DBU	AcCN	8	55
20	$Cu(OAc)_2$	25	DBU	Toluene	8	40
21	$Cu(OAc)_2$	25	DBU	THF	8	45
22	$Cu(OAc)_2$	25	DBU	Dioxane	8	47

[a]**Reaction conditions:** Thioamide **1a** (64 mg, 0.3 mmol), boronic acid **2a** (54 mg, 0.45 mmol), DBU base (90 µL, 0.6 mmol) and catalyst (10-30 mol%) were stirred in a solvent (4 mL) for 8 h at room temperature. [b] Isolated yield.

After establishing the optimized conditions, the substrate scope of the reaction was investigated. Initially, the S-arylation of N-phenyl thiobenzamide was investigated with a wide range of aryl boronic acids under optimized conditions. Aryl boronic acids bearing electron-donating and withdrawing groups (e.g., methyl, halo, and nitro) at the para-position successfully underwent a coupling reaction with thiobenzamide smoothly. They gave the desired products **3b-3e** in 67-75% yields. Similarly, aryl boronic acids bearing electron-donating and withdrawing groups at the meta- and ortho-position gave the desired products **3f-3l** in 66-73% yields. In particular, the sterically hindered 2,4,6-trimethyl phenylboronic acid gave the product **3l** in a 66% yield. Moreover, to our delight, S-cyclopropanation of thiobenzamide with cyclopropyl boronic acid was also achieved in 65% yield.

Table 3.2: Scope of various boronic acids with N-phenylbenzothioamide.

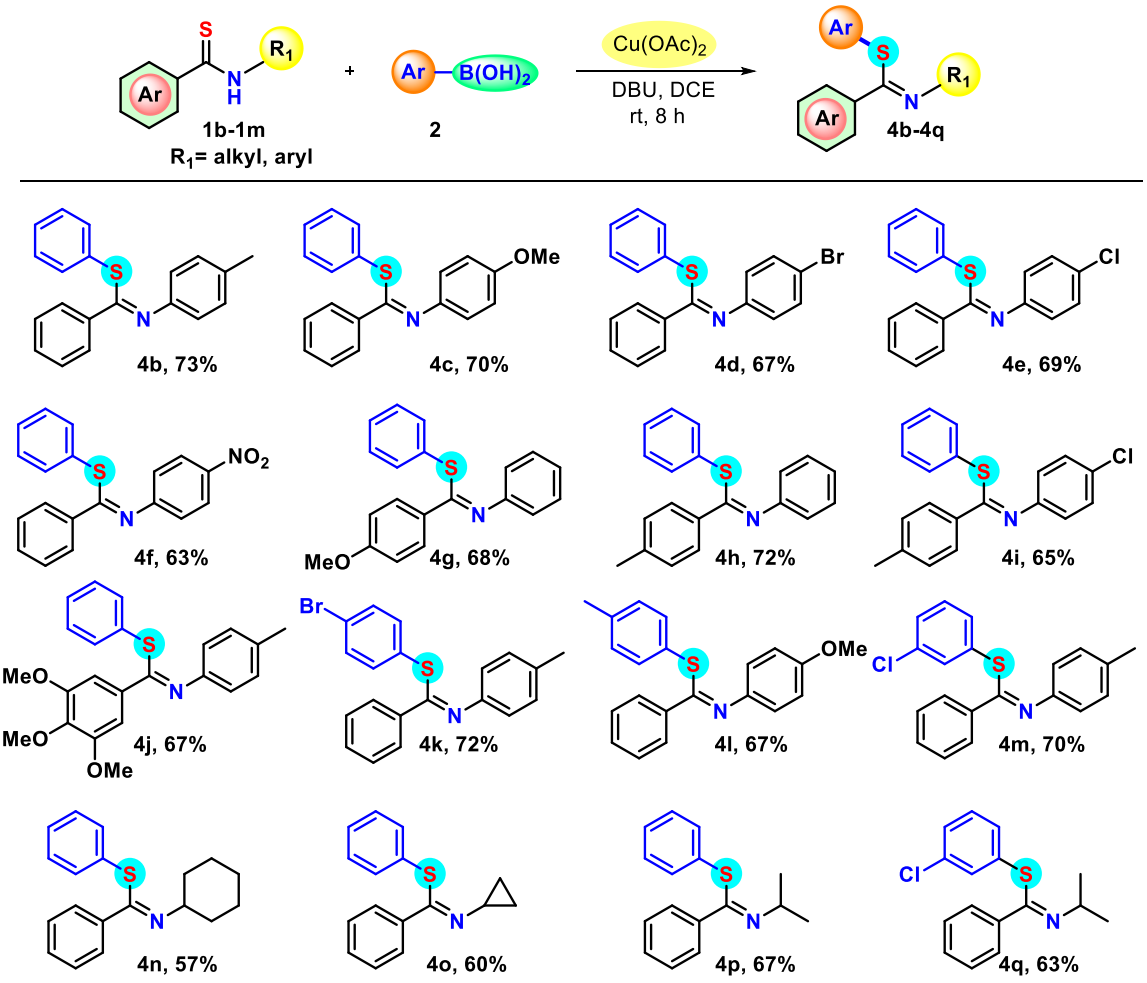


[a]**Reaction condition:** Thioamide **1a** (0.3 mmol), boronic acid **2b-m** (0.45 mmol), DBU (0.6 mmol) and catalyst (30 mol%) were stirred in a solvent (4 mL) for 8 h at room temperature. [b] Isolated yield.

After the investigation of the scope of aryl boronic acids, we studied the coupling reaction of arylboronic acids with thioamides bearing different functional groups. Initially, the coupling of phenylboronic acid with different N-aryl thiobenzamides was investigated. To our delight, electron-donating and withdrawing groups (e.g. Me, OMe, halo, nitro) containing thiobenzamides underwent coupling reactions smoothly with phenylboronic acid and gave the desired products **4j-4c** in 63-73% yields. Similarly, we have investigated the coupling reaction of randomly selected thiobenzamides with different arylboronic acids. These reactions gave the desired products **4b-4g** in good yields. Finally, we

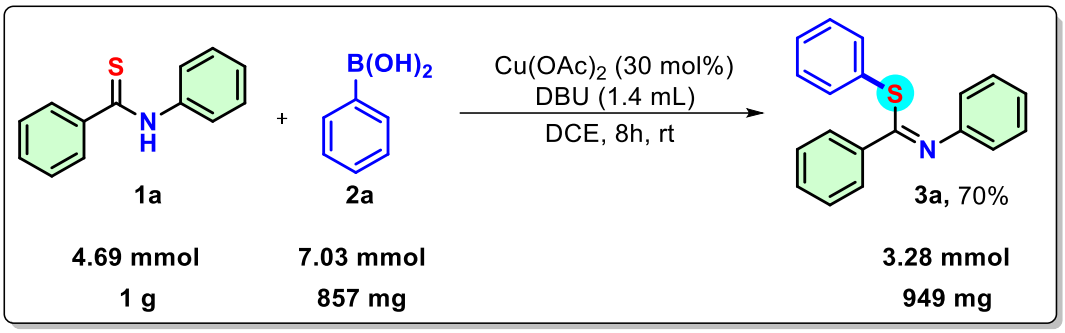
investigated the coupling of N-alkyl thiobenzamide with arylboronic acids, and that gave the desired N-alkyl S-aryl thioimidates in good yields.

Table 3.3: Scope of various thioamides with boronic acid.



[a]**Reaction condition:** Thioamide **1a-m** (0.3 mmol), boronic acid **2** (0.45 mmol), DBU (0.6 mmol) and catalyst (30 mol%) were stirred in a solvent (4 mL) for 8 h at room temperature. [b] Isolated yield.

To understand the general applicability of the method, we tried the model reaction in a gram scale. To our delight, we were able to achieve the desired product in 70% yield.



Scheme 3.3 Gram Scale synthesis reaction.

3.3 S-Arylation of Thioamides with Arynes

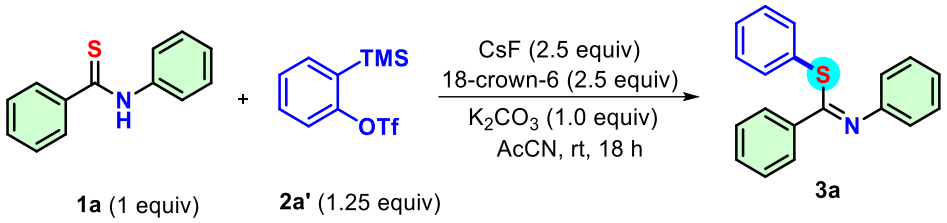
Arynes are important synthetic precursors in organic chemistry, and they have been well-explored in the synthesis of natural products, bioactive molecules, agrochemicals, and drugs. Arynes undergo a variety of reactions, including addition, insertion, substation reactions, etc.

Although the S-arylation of cyclic thioamides with benzynes was explored, the arylation of acyclic thioamides was not explored. In this context, we extended the S-aryl thioimidate synthesis using this approach under metal-free conditions. initially, the reaction condition was optimized using N-phenyl thiobenzamide and ortho-(trimethylsilyl)phenyl triflate.

The reaction was performed using cesium fluoride in the presence of 18-crown-6 and potassium carbonate in acetonitrile. The desired product **3a** was obtained at room temperature in 70% yield in 12h. The reaction condition was further optimized by changing the solvent and base. The use of THF instead of acetonitrile gave the desired product a low yield. Similarly, using cesium carbonate instead of potassium carbonate also gave the

product a low yield. On the other hand, the reaction proceeded faster at 70°C when compared to room temperature, although the yield of the reaction was relatively low. Later, we used other fluoride sources including potassium fluoride and TBAF. However, these reagents gave the desired products in low yield when compared with CsF.

Table 3.4 Optimization of compound 3a in the case of aryne[a]

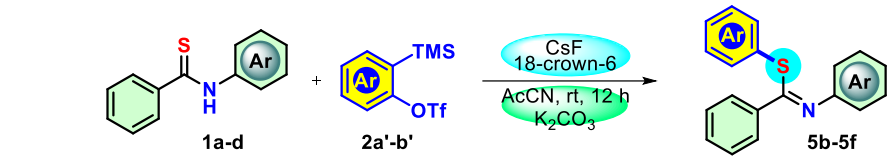


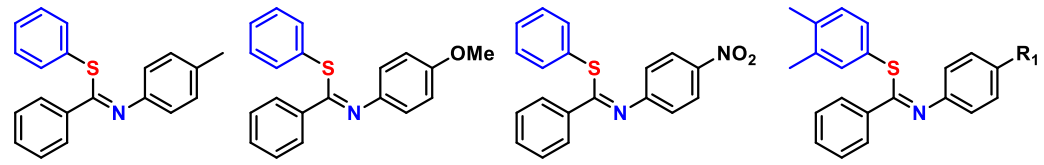
Entry	Deviation from the optimized condition	Time (h)	Yield (%)[b]
1	none	12	70
2[c]	THF instead of AcCN	12	62
3[d]	Cs_2CO_3 instead of K_2CO_3	12	57
4[e]	In the absence of K_2CO_3	24	40
5	At 70°C instead of RT	4	64[f]
6	KF	12	61
7	TBAF	12	65

[a]**Reaction conditions:** thioamide **1a** (0.3 mmol), **2a'** (0.375 mmol), CsF (0.75 mmol), 18-crown-6 (0.75 mmol) and Base (0.3 mmol) were stirred in a solvent (4 mL) for 12 h at room temperature. [b] Isolated yield. [c] THF used as solvent. [d] Cs_2CO_3 used in place of K_2CO_3. [e] Without any base. [f] Yield based on increasing of temperature from 25 °C to 70 °C.

After finding the optimized conditions, the substrate scope was investigated using different amides and arynes. One of the limitations of this method is that we observed a mixture of regioisomers and, in some cases, stereoisomers (E/Z).

Table 3.5 Substrate of various arynes with N-phenylbenzothioamide.



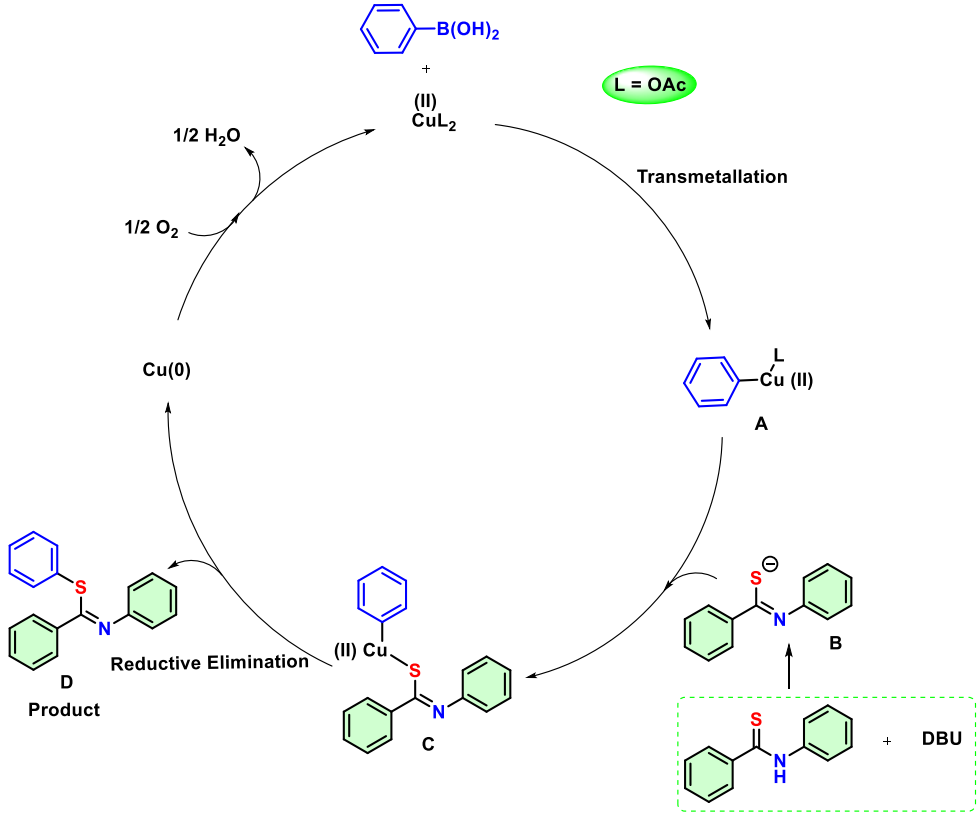


5b, 70% | **5c,** Z:E(85:15) 67% | **5d,** Z:E(60:40) 60% | **5e, R= H,** 65% **5f, R= Me**, 61%

[a]**Reaction condition:** thioamide **1** (0.3 mmol), **2'** (0.375 mmol), CsF (0.75 mmol), 18-crown-6 (0.75 mmol) and Base (0.3 mmol) were stirred in AcCN solvent (4 mL) for 12 h at room temperature. [b] Isolated yield.

3.4 Plausible Reaction Mechanism

The plausible reaction mechanism for the synthesis of thioimidates is depicted in (**Scheme 3.4**), based on the previously described methods [29-31]. Initially, the reaction involving boronic acid and copper(II) acetate resulted in the formation of intermediate **A** by transmetalation. Next, intermediate **A** undergoes the substitution reaction with the in situ-generated intermediate **B** formed from thioamide and DBU base to produce intermediate **C**. Subsequently, intermediate **C** facilitates the formation of desired product **D** by reductive elimination process along with the copper (0) species. Finally, Cu(II) is achieved by the process of aerobic oxidation of Cu(0) in order to complete the cycle. We believed Z-stereoisomer is more stable compare to E-stereoisomer. On the basis of previous reports and bond-pairs repulsion is more favourable than lone-pairs repulsion.



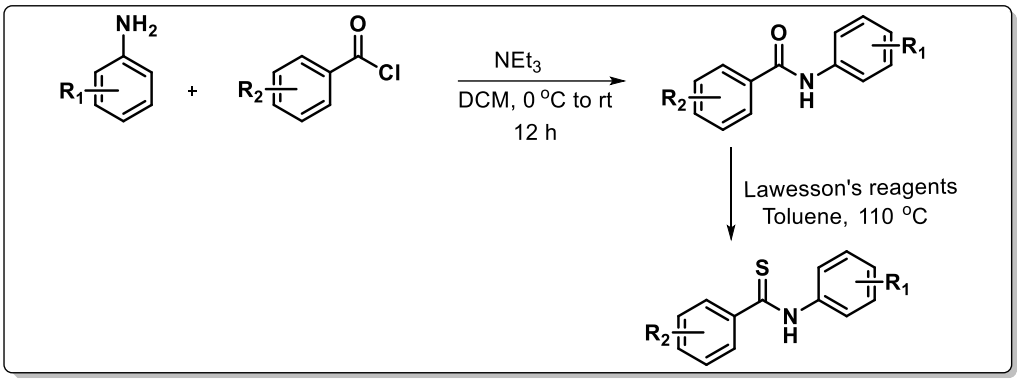
Scheme 3.4 Plausible reaction mechanism.

3.5 Conclusion

Concisely, we have developed a ligand-free copper-catalyzed method for synthesizing S-arylthioimidates by coupling of thioamides and boronic acids under mild conditions. The reaction occurs at room temperature and in an open-air atmosphere. Easy to use, chemoselectivity and a broad range of functional group tolerances are the important features of this method, affording the corresponding thioimidates in good yields. In addition, it can be efficiently scaled up to the gram level. The S-arylation of thioamides with benzynes was also preliminary explored.

3.6 Experimental Section

3.6.1 General Procedure for the Synthesis of Thioamides



Scheme 3.5 Synthesis of thioamides.

Thioamides **1a-1m** were synthesized following the previously described methods [32]. Obtained thioamides were confirmed after correlating with earlier reported analytical data [33].

4.5.2 Starting Materials Prepared

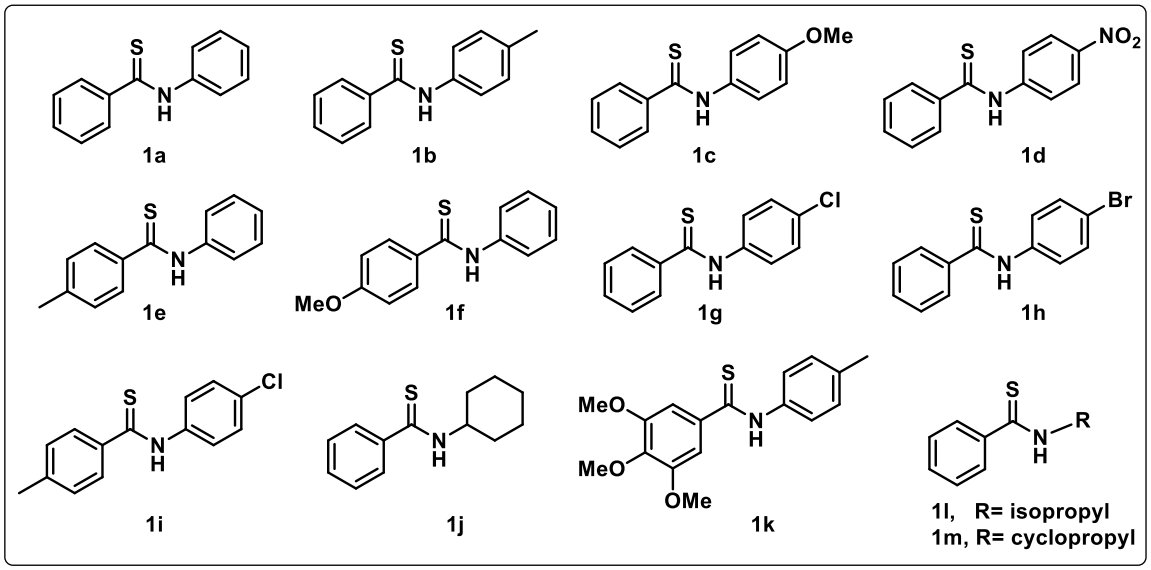


Figure 3.2 Prepared starting materials.

3.6.2 General Procedure for the Synthesis of Thioimidates from Thioamides and Boronic acids

A 100 mL oven-dried round-bottom flask was charged with the mixture of corresponding thioamide (0.3 mmol), boronic acid (0.45 mmol), DBU (0.6 mmol) and copper catalyst (30 mol%) dissolved in DCE (4 mL) in an open atmosphere. The resulting mixture was stirred continuously at room temperature for 8 h. Upon complete consumption of the starting materials, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (5 mL), extracted with CH_2Cl_2 (2× 30 mL), and washed with brine (2 × 15 mL), dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (230-400 mesh) using hexane/ethyl acetate as an eluent to afford the thioimidates.

3.6.3 General Procedure for the Synthesis of Thioimidates from Thioamide and Aryne Source

A 100 mL oven-dried round-bottom flask was charged with the mixture of corresponding thioamide (0.3 mmol), o-silyl triflate (0.375 mmol), K_2CO_3 (0.3 mmol), CsF (0.75 mmol) and 18-crown-6 (0.75 mmol) dissolved in AcCN (4 mL) under the argon atmosphere. The resulting reaction mixture was stirred continuously at room temperature for 12 h. After the complete consumption of the starting materials, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (5 mL), extracted with EtOAc (2× 30 mL), and washed with brine (2 × 15 mL), dried over anhydrous Na_2SO_4. The organic layer was

concentrated and purified by column chromatography on silica gel (230-400 mesh) using hexane/ethyl acetate as an eluent to afford the thioimidates.

3.7 Analytical Data of Synthesized Thioimidates

3.7.1 Phenyl (Z)-N-phenylbenzimidothioate (3a):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 70 ^{o}C. R_f (5 % ethyl acetate in hexane): 0.65. Yield 77% (66.86 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 2H), 7.38 (s, 2H), 7.30-7.28 (m, 1H), 7.26 (t, *J* = 3.7 Hz, 1H), 7.25-7.23 (m, 1H), 7.17 (s, 3H), 7.09 (s, 3H), 7.02 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.72, 150.28, 137.52, 133.28, 132.23, 129.98, 129.16, 128.81, 128.69, 127.91, 127.57, 124.31, 119.86. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{16}NS$: 290.1003; found: 290.1002.

3.7.2 p-tolyl (Z)-N-phenylbenzimidothioate (3b):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 75 ^{o}C. R_f (5 % ethyl acetate in hexane): 0.64. Yield 75% (68.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 2H), 7.41 (s, 2H), 7.30-7.27 (m, 3H), 7.18 (s, 1H), 7.07 (d, *J* = 10.8 Hz, 4H), 6.92 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.25, 150.30, 137.66, 137.55, 133.31, 129.81, 129.46, 129.09, 128.75, 128.46, 127.82, 124.19, 119.82, 20.98. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{18}NS$: 304.1160; found: 304.1137.

3.7.3 4-chlorophenyl (Z)-N-phenylbenzimidothioate (3c):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 85 ^{o}C. R_f (5 % ethyl acetate in hexane): 0.62. Yield 74% (72 mg). ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.72 (s, 2H), 7.38-7.33 (m, 3H), 7.29 (t, *J* = 7.2 Hz, 3H), 7.16 (s, 1H), 7.08 (d, *J* = 6.8 Hz, 3H), 7.00 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.66, 150.04, 137.26, 134.37, 133.84, 130.74, 130.27, 129.11, 128.86, 128.80, 128.07, 124.41, 119.77, 77.25. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{15}ClNS$: 324.0614; found: 324.0590

3.7.4 4-nitrophenyl(Z)-N-phenylbenzimidothioate (3d):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 89 ºC. R_f (5 % ethyl acetate in hexane): 0.57. Yield 68% (68.2 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.5 Hz, 2H), 7.82 (d, *J* = 4.7 Hz, 2H), 7.38-7.31 (m, 6H), 7.26 (s, 1H), 7.15 (s, 1H), 6.95 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.71, 149.85, 146.41, 141.96, 136.96, 132.18, 131.08, 129.34, 128.91, 128.45, 124.87, 123.59, 119.74. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{15}N_2O_2S$: 335.0854; found: 335.0830.

3.7.5 4-fluorophenyl (Z)-N-phenylbenzimidothioate (3e):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 94 ºC. R_f (5 % ethyl acetate in hexane): 0.61. Yield 67% (61.2 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.37-7.28 (m, 4H), 7.26-7.25 (m, 1H), 7.14 (s, 3H), 6.99 (s, 2H), 6.78 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.64, δ 162.32 (d, *J* = 251.5 Hz). 150.07, 137.35, 135.53 (d, *J* = 6.1 Hz), 130.10, 129.06, 128.84, 128.03, 127.29, 124.37, 119.81, 115.92 (d, *J* = 22.1 Hz). HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{15}FNS$: 308.0909; found: 308.0883.

3.7.6 3-methoxyphenyl (Z)-N-phenylbenzimidothioate (3f):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 115 ºC. R_f (5 % ethyl acetate in hexane): 0.6. Yield 73% (70 mg). ^1H NMR (600 MHz,

DMSO) δ 7.58 (s, 2H), 7.39 (s, 2H), 7.31-7.27 (m, 4H), 7.16 (s, 2H), 6.98 (d, *J* = 3.8 Hz, 2H), 6.72 (d, *J* = 4.9 Hz, 2H), 3.64 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 163.60, 159.21, 150.09, 137.01, 135.34, 129.86, 128.97, 128.86, 127.85, 124.13, 121.54, 119.49, 114.64, 55.14. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{18}NOS$: 320.1109; found: 320.1106.

3.7.7 3-(trifluoromethyl)phenyl (Z)-N-phenylbezimidothioate (3g):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 74 ^{o}C. R_f (5 % ethyl acetate in hexane): 0.58. Yield 69% (74 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.34-7.28 (m, 7H), 7.15 (d, *J* = 38.7 Hz, 3H), 6.96 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.88, 149.85, 137.25, 136.23, 133.67, 131.06 (dd, *J* = 65.4, 32.7 Hz), 130.50, 129.90, 129.11, 129.03 128.83, 128.21, 124.54, 124.27, 122.29, 119.80. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{15}F_3NS$: 358.0877; found: 358.0852.

3.7.8 3-bromophenyl (Z)-N-phenylbenzimidothioate (3h):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 85 ^{o}C. R_f (5 % ethyl acetate in hexane): 0.62. Yield 71% (78 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.35-7.26 (m, 6H), 7.21 (s, 1H), 7.13 (s, 1H), 7.07 (s, 1H), 6.96 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.10, 149.93, 137.27, 135.60, 134.34, 131.61, 130.60, 130.45, 129.89, 129.14, 128.79, 128.14, 124.48, 122.24, 119.79. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{15}BrNS$: 368.0109; found: 368.0081.

3.7.9 3-chlorophenyl (Z)-N-phenylbenzimidothioate (3i):

The title of the compound is obtaine as a yellowish solid using the general procedure. M.p 80 ^{o}C. R_f (5 % ethyl acetate in hexane): 0.61. Yield 72% (70 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.37-7.32 (m, 5H), 7.18 (s, 2H), 7.06-7.04 (m, 2H), 7.01 (d, *J* = 4.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.07, 149.92, 137.24, 134.16, 134.06, 132.67,

131.10, 130.40, 129.59, 129.11, 128.76, 128.09, 127.68, 124.44, 119.73. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{15}ClNS$: 324.0614; found: 324.0591.

3.7.10 naphthalen-2-yl (Z)-N-phenylbenzimidothioate (3j):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 90 ^oC. R_f 5 % ethyl acetate in hexane): 0.55. Yield 70% (71 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 2H), 7.74 (s, 1H), 7.67 (d, *J* = 13.6 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 3.4 Hz, 2H), 7.36 (s, 2H), 7.24-7.21 (m, 4H), 7.18-7.13 (m, 2H), 7.06 (d, *J* = 6.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.37, 150.25, 137.60, 133.23, 132.36, 132.10, 130.12, 129.99, 129.65, 129.17, 128.79, 128.27, 127.99, 127.58, 127.40, 126.50, 126.44, 124.37, 119.87. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{23}H_{18}NS$: 340.1160; found: 340.1140.

3.7.11 3,5-dimethylphenyl (Z)-N-phenylbenzimidothioate (3k):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 110 ^oC. R_f (5 % ethyl acetate in hexane): 0.6. Yield 69% (65 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.37 (s, 2H), 7.33-7.26 (m, 3H), 7.14 (s, 1H), 7.02 (s, 2H), 6.80 (s, 2H), 6.72 (s, 1H), 2.15 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.87, 150.25, 138.13, 137.77, 131.35, 130.91, 129.95, 129.30, 129.03, 128.63, 127.79, 124.04, 119.80, 20.86. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{21}H_{20}NS$: 318.1316; found: 318.1294.

3.7.12 mesityl (Z)-N-phenylbenzimidothioate (3l):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 120 ^oC. R_f (5 % ethyl acetate in hexane): 0.58. Yield 66% (66.5 mg). ^1H NMR (500 MHz, DMSO) δ 7.54 (d, *J* = 5.4 Hz, 2H), 7.36- 7.26 (m, 6H), 7.10 (s, 1H), 6.93 (d, *J* = 5.8 Hz,

2H), 6.73 (s, 1H), 2.27 (s, 6H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 163.11, 150.06, 140.73, 138.31, 137.27, 130.20, 128.92, 127.92, 127.77, 126.66, 123.97, 118.81, 21.55, 20.41. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{22}H_{22}NS$: 332.1473; found: 332.1447.

3.7.13 cyclopropyl (Z)-N-phenylbenzimidothioate (3m):

The title of the compound is obtained as a yellow oil using the general procedure. R_f (5 % ethyl acetate in hexane): 0.55. Yield 65% (49 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 2H), 7.45 (s, 3H), 7.35 (s, 2H), 7.11 (s, 1H), 6.99 (s, 2H), 1.68 (s, 1H), 0.63 (s, 2H), 0.49 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.97, 150.39, 139.29, 129.96, 128.24, 128.19, 123.94, 119.83, 13.72, 10.13. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{16}NS$: 254.1003; found: 254.0981.

3.7.14 phenyl (Z)-N-(p-tolyl)benzimidothioate (4b):

The title of the compound is obtained as a yellow oil using the general procedure. R_f (5 % ethyl acetate in hexane): 0.51. Yield 73% (66.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.9 Hz, 2H), 7.31- 7.27 (m, 2H), 7.26-7.20 (m, 5H), 7.10 (s, 3H), 6.99 (d, *J* = 7.7 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.36, 147.70, 137.50, 133.90, 133.15, 132.34, 129.78, 129.38, 129.12, 128.59, 127.80, 127.43, 119.83, 20.93. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{18}NS$: 304.1160; found: 304.1134.

3.7.15 phenyl (Z)-N-(4-methoxyphenyl)benzimidothioate (4c):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 92 ^{o}C. R_f (5 % ethyl acetate in hexane): 0.51. Yield 78% (67 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.0 Hz, 2H), 7.25-7.21 (m, 3H), 7.16-7.15 (m, 2H), 7.08 -7.07 (m,

3H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.12, 156.76, 143.40, 137.72, 133.18, 132.43, 129.82, 129.18, 128.65, 127.86, 127.49, 121.45, 114.04, 77.25, 77.00, 76.75, 55.40. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{18}NOS$: 320.1109; found: 320.1083.

3.7.16 phenyl (Z)-N-(4-bromophenyl)benzimidothioate (4d):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 83 ºC. R_f (5 % ethyl acetate in hexane): 0.58. Yield 67% (74.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.47-7.43 (m, 2H), 7.32-7.30 (m, 1H), 7.27-7.25 (m, 2H), 7.15-7.10 (m, 5H), 6.86 (d, *J* = 4.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.57, 149.15, 137.37, 133.40, 131.81, 130.30, 129.11, 128.79, 128.02, 127.83, 121.69, 117.31. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{15}BrNS$: 368.0109; found: 368.0073.

3.7.17 phenyl (Z)-N-(4-chlorophenyl)benzimidothioate (4e):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 70 ºC. R_f (5 % ethyl acetate in hexane): 0.59. Yield 69% (67.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 2H), 7.31-7.26 (m, 5H), 7.25 (d, *J* = 1.6 Hz, 1H), 7.16-7.10 (m, 4H), 6.93 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.56, 148.66, 137.40, 133.37, 131.82, 130.27, 129.53, 129.11, 128.86, 128.78, 128.01, 127.80, 121.30. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{15}ClNS$: 324.0614; found: 324.0585.

3.7.18 phenyl (Z)-N-(4-nitrophenyl)benzimidothioate (4f):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 90 ºC. R_f (5 % ethyl acetate in hexane): 0.56. Yield 63% (63.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 6.8 Hz, 2H), 7.40-7.37 (m, 1H), 7.32 (t, *J* =

7.5 Hz, 2H), 7.23 (d, *J* = 6.5 Hz, 2H), 7.17-7.13 (m, 3H), 6.93 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.86, 143.74, 136.55, 130.97, 130.58, 128.94, 128.46, 128.25, 124.70, 120.21. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{15}N_2O_2S$: 335.0854; found: 335.0827.

3.7.19 Phenyl (Z)-4-methoxy-N-phenylbenzimidothioat (4g):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 86 ^oC. R_f 5 % ethyl acetate in hexane): 0.57. Yield 68% (65.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 6.0 Hz, 2H), 7.33 (s, 2H), 7.16 (s, 2H), 7.10 (s, 4H), 6.96 (d, *J* = 5.3 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.19, 161.21, 150.51, 132.73, 131.00, 130.16, 128.71, 127.28, 124.03, 119.95, 113.31, 55.24. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{18}NOS$: 320.1109; found: 320.1079.

3.7.20 phenyl (Z)-4-methyl-N-phenylbenzimidothioate (4h):

The title of the compound is obtained as a yellow oil using the general procedure. R_f (5 % ethyl acetate in hexane): 0.5. Yield 72% (65.3 mg). ^{1}H NMR (500 MHz, DMSO) δ 7.57 (s, 2H), 7.38 (s, 2H), 7.21-7.16 (m, 6H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 3.7 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 161.65, 150.20, 140.09, 134.25, 132.64, 131.90, 129.06, 128.90, 128.58, 127.73, 124.13, 119.52, 20.81. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{18}NS$: 304.1160; found: 304.1148.

3.7.21 phenyl (Z)-N-(4-chlorophenyl)-4-methylbenzimidothioate (4i):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 75 ^oC. R_f (5 % ethyl acetate in hexane): 0.54. Yield 65% (66.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.26 (s, 2H), 7.14-7.07 (m, 7H), 6.88 (s, 2H), 2.31 (s, 3H). ^{13}C NMR

(126 MHz, $CDCl_3$) δ 164.03, 148.83, 140.82, 134.75, 133.09, 132.15, 129.16, 128.78, 127.62, 121.33, 21.33. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{17}ClNS$: 338.0770; found: 338.0741

3.7.22 phenyl (Z)-3,4,5-trimethoxy-N-(p-tolyl)benzimidothioate (4j):

The title of the compound is obtained as a yellow oil using the general procedure. R_f (5 % ethyl acetate in hexane): 0.48. Yield 67% (79.7 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.19-7.17 (m, 4H), 7.12-7.11 (m, 3H), 6.94 (s, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 3.75 (s, 6H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.64, 152.50, 147.71, 139.58, 133.93, 132.84, 132.75, 132.45, 129.43, 128.77, 127.54, 119.76, 106.83, 60.74, 55.92, 20.98. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{23}H_{24}NO_3S$: 394.1477; found: 394.1448.

3.7.23 4-bromophenyl (Z)-N-(p-tolyl)benzimidothioate (4k):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 70 ^oC. R_f (5 % ethyl acetate in hexane): 0.57. Yield 72% (82.3 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.0 Hz, 2H), 7.32-7.26 (m, 3H), 7.20 (s, 4H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.10, 147.47, 137.27, 134.46, 131.73, 131.58, 130.16, 129.40, 129.13, 128.04, 121.85, 119.79, 20.95. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{17}BrNS$: 382.0265; found: 382.0256.

3.7.24 p-tolyl (Z)-N-(4-methoxyphenyl)benzimidothioate (4l):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 115 ^oC. R_f (5 % ethyl acetate in hexane): 0.56. Yield 67% (67.8 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.9 Hz, 2H), 7.26-7.24 (m, 2H), 7.23 (s, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 3.83 (s,

3H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.67, 156.71, 143.45, 137.83, 137.61, 133.27, 129.67, 129.44, 129.13, 128.71, 127.80, 121.44, 114.02, 55.38, 21.00. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{21}H_{20}NOS$: 334.1266; found: 334.1261.

3.7.25 3-chlorophenyl (Z)-N-(p-tolyl)benzimidothioate (4m):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 80 ^oC. R_f (5 % ethyl acetate in hexane): 0.55. Yield 70% (71.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 6.6 Hz, 2H), 7.33- 7.26 (m, 4H), 7.18-7.14 (m, 3H), 7.04-6.99 (m, 3H), 6.89 (d, *J* = 7.3 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.83, 147.49, 137.38, 134.28, 134.19, 132.76, 131.14, 130.30, 129.58, 129.41, 129.16, 128.09, 127.62, 119.80, 20.96. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{17}ClNS$: 338.0770; found: 326.0741.

3.7.26 phenyl (Z)-N-cyclohexylbenzimidothioate (4n):

The title of the compound is obtained as a yellow oil using the general procedure. R_f (5 % ethyl acetate in hexane): 0.59. Yield 57% (50.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.20 – 7.13 (m, 5H), 7.13 – 7.06 (m, 3H), 3.97 (tt, *J* = 10.5, 3.8 Hz, 1H), 1.88 – 1.83 (m, 3H), 1.72 – 1.62 (m, 3H), 1.47-1.40 (m, 2H), 1.31 (ddd, *J* = 12.4, 7.8, 3.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.36, 138.17, 132.88, 132.66, 129.07, 129.01, 128.69, 127.74, 127.10, 77.25, 77.00, 76.75, 63.56, 33.32, 25.67, 24.72. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{22}NS$: 296.1473; found: 296.1440.

3.7.27 phenyl (Z)-N-cyclopropylbenzimidothioate (4o):

The title of the compound is obtained as a yellow oil using the general procedure. R_f (5 % ethyl acetate in hexane): 0.55. Yield 60% (46.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-

7.69 (m, 2H), 7.27 (t, *J* = 1.8 Hz, 1H), 7.26-7.21 (m, 4H), 7.19-7.12 (m, 3H), 3.66-3.62 (m, 1H), 1.08-1.04 (m, 2H), 1.01-0.98 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.55, 138.44, 133.20, 131.46, 129.27, 128.77, 128.66, 127.86, 126.78, 37.70, 9.63. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{16}NS$: 254.1003; found: 254.0900.

3.7.28 phenyl (Z)-N-isopropylbenzimidothioate (4p):

The title of the compound is obtained as a yellow oil using the general procedure. R_f (5 % ethyl acetate in hexane): 0.58. Yield 67% (51.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.20-7.19 (m, 1H), 7.18 (d, *J* = 1.5 Hz, 1H), 7.16 -7.15 (m, 1H), 7.15 (s, 1H), 7.12-7.07 (m, 3H), 4.32 (hept, *J* = 6.2 Hz, 1H), 1.34 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.32, 138.17, 134.87, 132.73, 129.03, 128.93, 128.67, 127.72, 127.13, 55.10, 23.33. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{18}NS$: 256.1160; found: 256.1128.

3.7.29 3-chlorophenyl (Z)-N-isopropylbenzimidothioate (4q):

The title of the compound is obtained as a yellow oil using the general procedure. R_f (5 % ethyl acetate in hexane): 0.57. Yield 63% (55 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.21-7.17 (m, 4H), 7.06-7.01 (m, 3H), 4.30-7.23 (m, 1H), 1.32 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.02, 137.76, 134.82, 134.23, 132.04, 130.50, 129.65, 129.40, 128.90, 127.92, 127.26, 55.50, 23.38. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{17}ClNS$: 290.0770; found: 290.741.

3.7.30 phenyl (Z)-N-(4-methoxyphenyl)benzimidothioate (5c):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 92 ^{o}C. R_f (5 % ethyl acetate in hexane): 0.51. Yield 67% (64 mg), *Z: E* ratio 85:15. ***(Z)***

ismomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.33 (s, 2H), 7.18-7.09 (m, 6H), 6.96-6.90 (m, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.30, 150.59, 132.82, 131.08, 128.79, 120.04, 113.40, 55.32. Distinguishing signals of the ***(E)*** **isomer: ^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.85 (s, 3H, N-Para-OCH3). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.29, 131.99, 130.93, 130.38, 129.81, 129.16, 128.30, 127.51, 127.35, 126.12, 124.11, 120.72, 113.74, 55.41, HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{18}NOS$: 320.1109; found: 320.1107.

3.7.31 phenyl (Z)-N-(4-nitrophenyl)benzimidothioate (5d):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 92 ^{o}C. R_f (5 % ethyl acetate in hexane): 0.51. Yield 60% (60 mg), Z: E ratio 60:40. ***(Z)*** **ismomer: ^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 4.9 Hz, 2H), 7.42-7.38 (m, 2H), 7.30-7.28 (m, 2H), 7.25-7.22 (m, 2H), 7.18-7.15 (m, 3H), 7.09 (s, 2H), 7.02 (d, *J* = 5.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.85, 150.35, 133.36, 131.94, 130.06, 129.25, 128.89, 128.76, 128.38, 128.34, 127.99, 120.54, 119.93. Distinguishing signals of the ***(E)*** **isomer: ^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 2H, N-meta-protons), **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.00, 151.02, 138.82, 137.62, 135.37, 134.68, 131.13, 130.83, 128.62, 127.53, 126.22, 124.40, 123.47. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{20}H_{18}NOS$: 320.1109; found: 320.1083.

3.7.32 3,4-dimethylphenyl (Z)-N-phenylbenzimidothioate (5e):

The title of the compound is obtained as a yellow oil using the general procedure. R_f (5 % ethyl acetate in hexane): 0.55. Yield 65% (62 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s,

2H), 7.36 (s, 2H), 7.29- 7.25 (m, 3H), 7.13 (s, 1H), 7.01-6.85 (m, 5H), 2.12 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.32, 150.35, 137.79, 137.06, 136.37, 134.50, 130.90, 129.94, 129.85, 129.07, 128.69, 127.83, 124.08, 119.86, 77.25, 77.00, 76.75, 19.39, 19.33. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{21}H_{20}NS$: 318.1316; found: 318.1283.

3.7.33 3,4-dimethylphenyl (Z)-N-(p-tolyl)benzimidothioate (5f):

The title of the compound is obtained as a yellowish solid using the general procedure. M.p 110 ^oC. R_f (5 % ethyl acetate in hexane): 0.52. Yield 61% (61.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 6.5 Hz, 2H), 7.28-7.26 (m, 1H), 7.25-7.23 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 6.95-6.91 (m, 4H), 6.84 (d, *J* = 7.5 Hz, 1H), 2.38 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.01, 147.78, 137.84, 136.99, 136.25, 134.44, 133.70, 130.84, 129.88, 129.69, 129.32, 129.07, 128.65, 127.75, 119.86, 20.95, 19.36, 19.30. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{15}N_2O_2S$: 335.0854; found: 335.0827.

3.8 Spectra of Few Synthesized Compounds

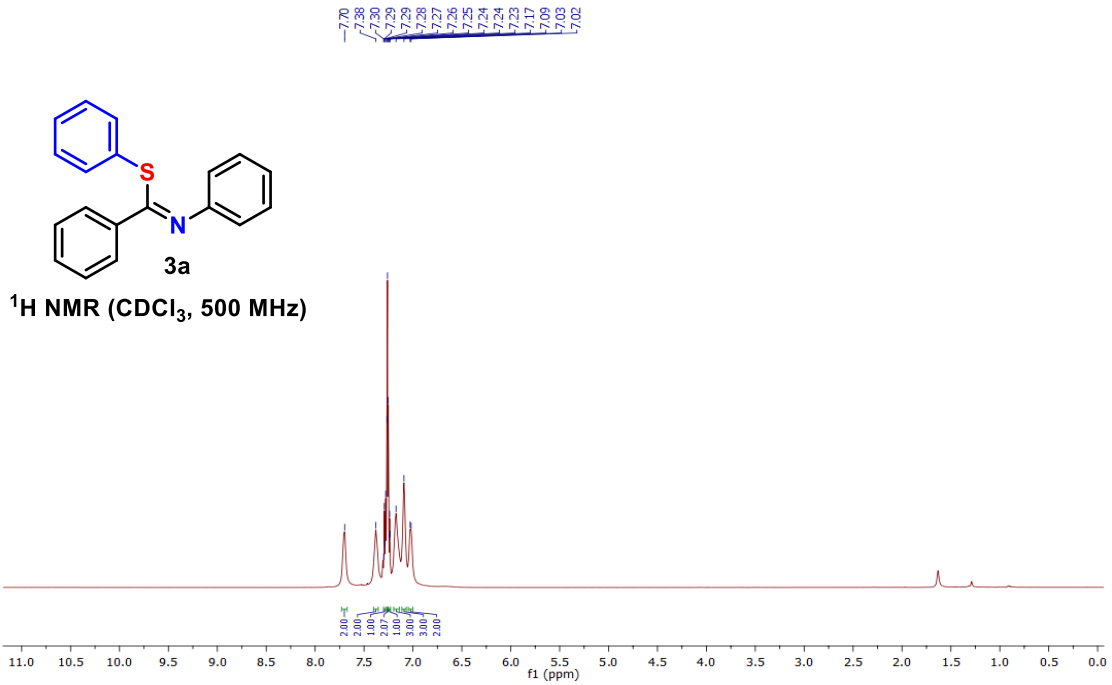


Figure 3.3 ^{1}H NMR Spectra of product 3a in CDCl$_3$

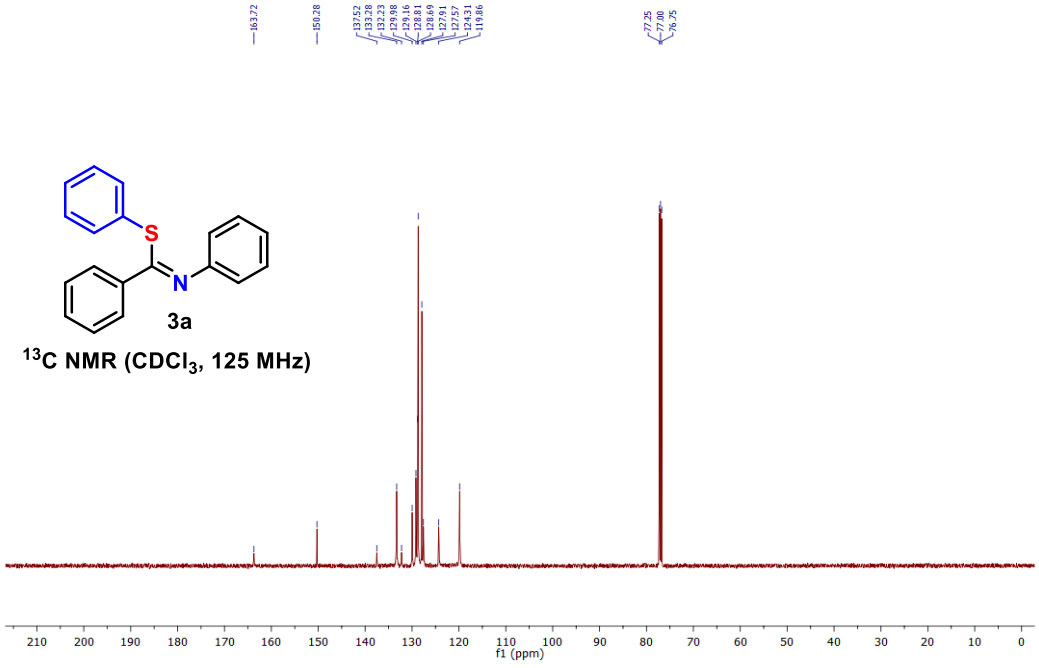


Figure 3.4 ^{13}C NMR Spectra of product 3a in CDCl$_3$

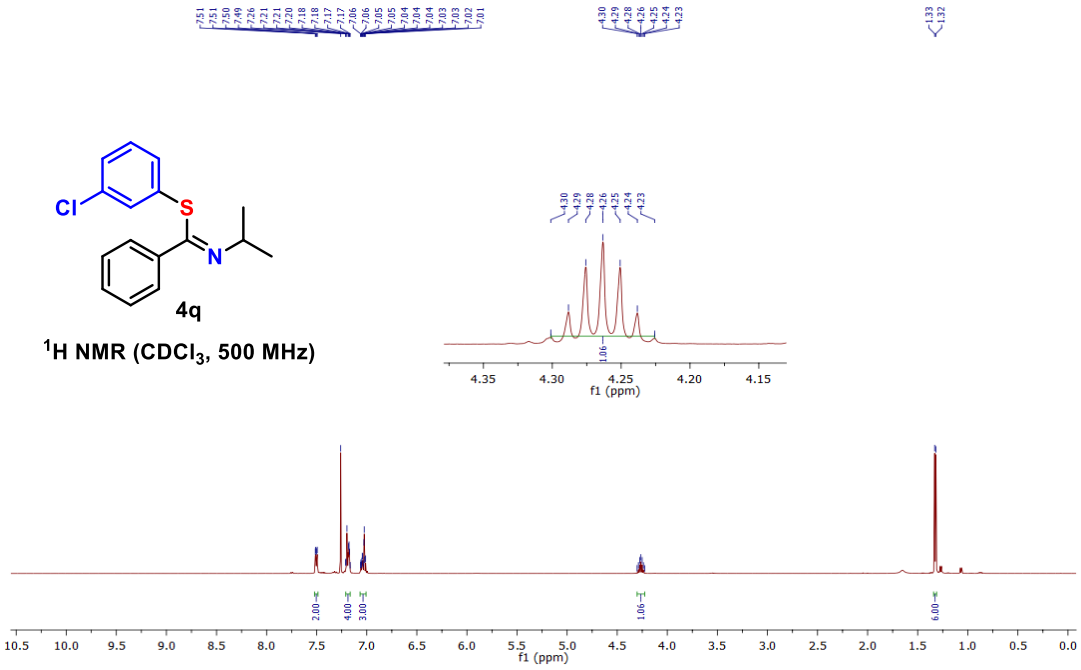


Figure 3.5 ^{1}H NMR Spectra of product 4q in CDCl$_3$

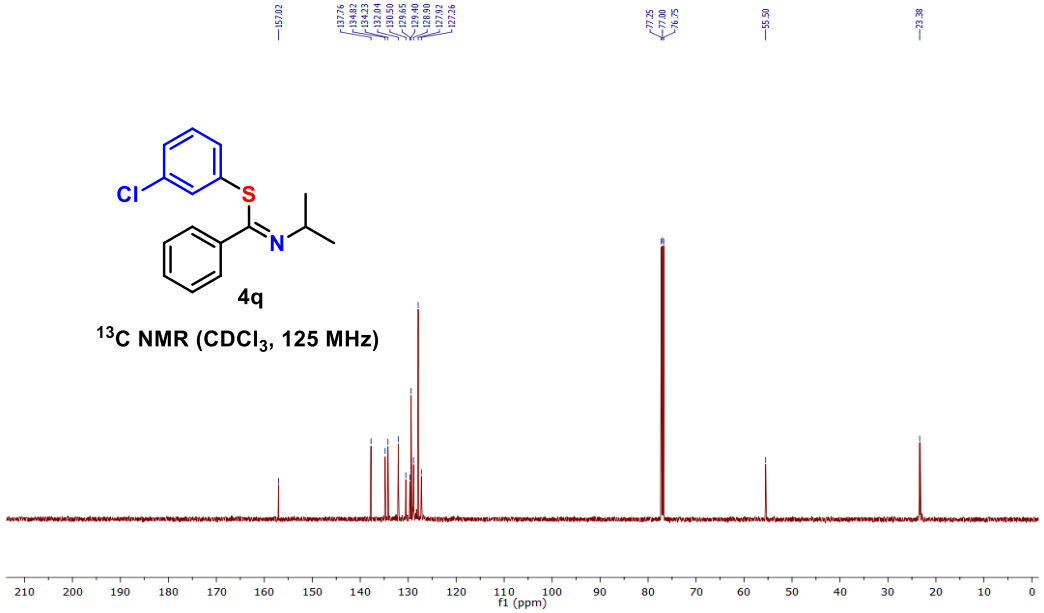


Figure 3.6 ^{13}C NMR Spectra of product 4q in CDCl$_3$

3.9 Reference

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