Chapter 2

A Novel Approach Towards Synthesis of Benzothiazole and Benzimidazole: Eosin Y Catalyzed Photo-Triggered C-S and C-N Bond Formation

2.1 Introduction

Green chemistry has become a contemporary research tool for designing proficient and environmentally compatible synthetic methods. The main objective of green chemistry is to pursue alternative reaction techniques to avoid using conventional organic solvents and thermal conditions with minimum waste generation [1, 2].

Currently, photocatalysts have been developed as simple and effective tools for activating organic molecules in visible light and have been used for many unique and valuable chemical processes [3]. Recent interest in catalytic organic synthesis reactions has focused on visible light as a rich, readily available, renewable, and clean energy source [4]. Compared with traditional synthetic methods, visible light-assisted reactions meet the requirements of mild reaction conditions [5], simple operation, and environmental friendliness [6]. However, most organic molecules cannot absorb visible light, and only selecting a suitable photocatalyst can promote the reaction. Photocatalysts such as ruthenium and iridium complexes are commonly used in organic reactions such as activating C-H bonds, direct arylation of C-H bonds, aerobic oxidation, and cyclizations [7-10].

These complexes have excellent catalytic properties but are expensive and potentially toxic. In both medicinal and industrial chemistry, nitrogen and sulfur-containing heterocycles such as benzothiazoles and benzimidazoles play an important role in human welfare [11].

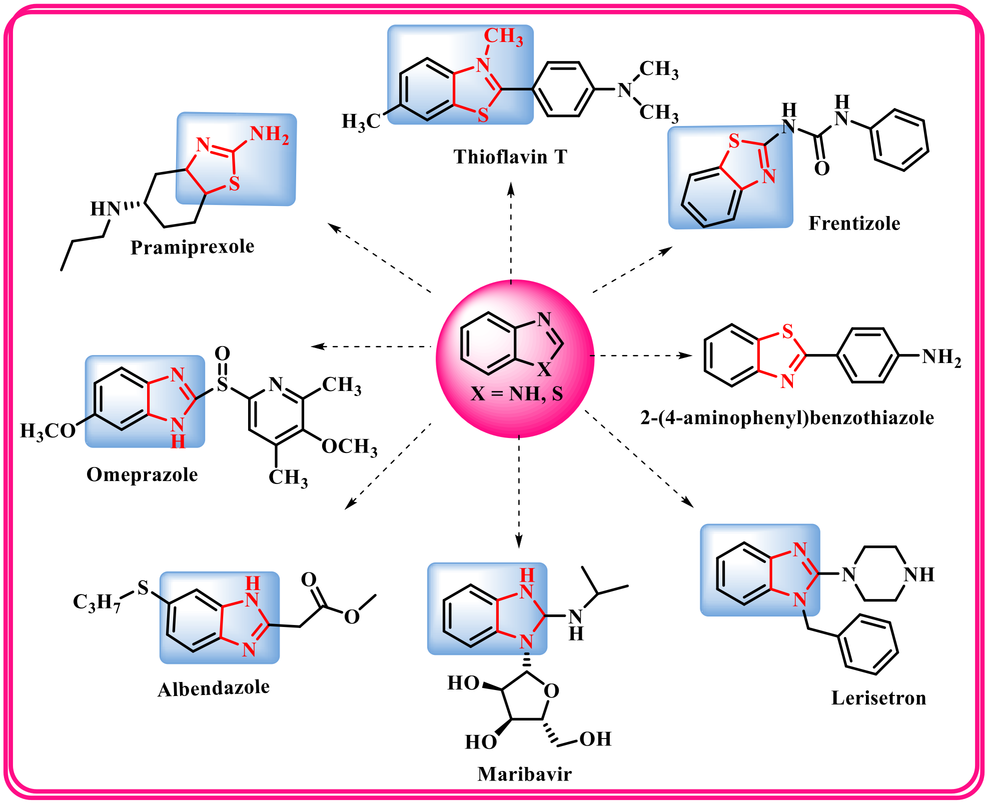
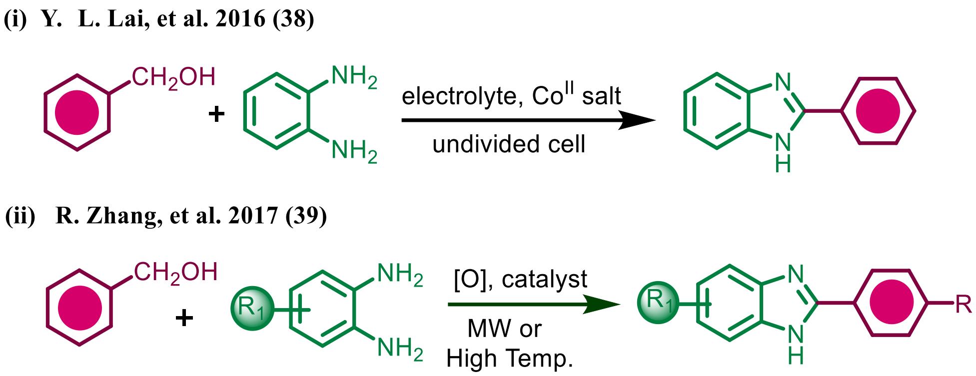


Figure 2.1 Some biologically active benzothiazoles and benzimidazoles.

These compounds play an important role in the metabolism of all living cells. Benzimidazole and benzothiazole derivatives exhibit numerous significant biological activities such as anticancer [12], antiallergic [13], antiulcer [14], antimicrobial [15], antihistaminic [16], antifungal [17], anti-inflammatory [18], antihypertensive [19], antidiabetic [20], antiviral [21], anti-HIV [22], antihepatitis-B virus [23], anti-convulsant [24], antioxidant [25], antitumor [26], and antitrichinellosis [27] activities (**Figure 2.1**).

Over the past 25 years, much effort has been devoted to preparing benzothiazoles; several synthetic methodologies have been developed [28]. In most cases, catalytic amounts of metal oxide nanocrystals like Fe_3O_4@SiO_2-dipyridine–Pd [29], cyanide [30], chlorobenzene [31], Cu/Al@SBA-15 [32], porous borocarbonitride (P-BCN) [33], or ZnO nanoparticles [34] and an excess of oxidants, such as $K_2S_2O_8$ [35], Bi_2O_3 [36], and H_2O_2 [37] are required. In 2016, Huang and co-workers presented an electrochemical method for synthesizing benzimidazole from alcohol and ortho-phenylenediamine, utilizing a CoII salt as a catalyst (**Scheme 2.1, i**) [38]. In 2017, Luo and co-workers synthesized benzimidazole from a primary amine with molecular oxygen as the oxidant (**Scheme 2.1, ii**) [39].


(i) Y. L. Lai, et al. 2016 (38)

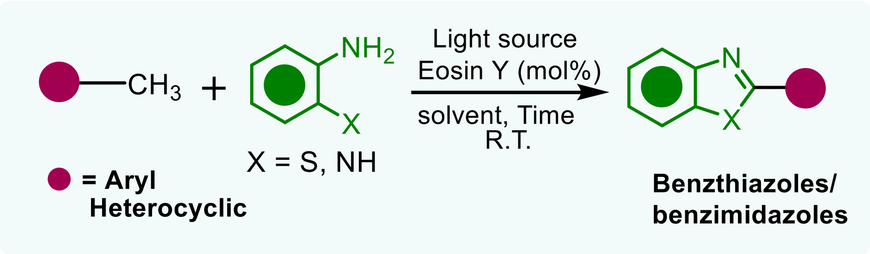
(ii) R. Zhang, et al. 2017 (39)

✓Metal catalyst ✓Long reaction time ✓High temperature ✓Additives

Scheme 2.1 Previous work for the synthesis of benzothiazole and benzimidazoles.

Moreover, the reaction suffered from bottlenecks such as toxic and expensive reagents or catalysts, long reaction times, harsh reaction conditions, side products, and low yields. Eosin-Y is a specific organic dye that triggers photoredox catalysis for organic transformations. It has drawn greater attention recently because of its easy handling, environmental friendliness, and significant potential for use in visible-light-mediated organic transformation [40]. Methyl arenes are the most affordable and naturally available substrates, obtained from crude oil and as a by-product in the production of gasoline and coke. The discerning and controlled oxidation of the benzylic carbon-hydrogen (C-H) bond of methylarene [41, 42] has emerged as an inspiring and demanding topic for a chemist. The conventional methods for getting benzaldehyde are non-selective, poisonous, tiresome, and operationally tricky [43].

In this perspective, the direct selective oxidation of methylarenes to benzaldehydes is of vital importance. Hence, simple, straightforward, green, waste-free, high-yielding, and environmentally friendly protocols using benign oxidants and high-atom economical pathways are needed. Therefore, establishing green, gentle, and effective protocols for visible light-induced C-N and C-S coupling using photoredox catalysis is quite exciting and appealing.



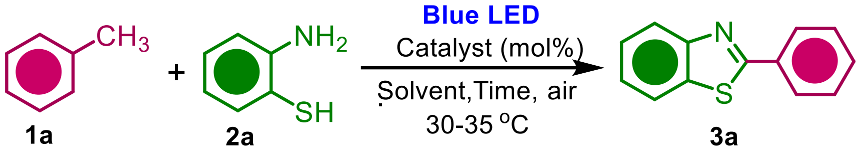
Scheme 2.2 This work: Eosin Y-catalyzed synthesis of benzothiazole and benzimidazole.

Herein, we explain the synthesis of benzothiazole derivatives via a reaction of o-aminothiophenol with different methylarenes catalyzed by Eosin Y in air. This method successfully combines C-H bond cleavage, dioxygen activation, and oxidative C-S, C-N bond functionalization with green chemistry and atom economy. We demonstrated that Eosin Y plays a significant role in aerobic oxidation (**Scheme 2.2**).

2.2 Results and Discussion

We started our observations using a visible-light photoredox reaction of methylarene **1a** with 2-aminothiophenol **2a**, which was selected as the model reaction to optimize the reaction conditions under blue LED irradiation in ambient air at room temperature (**Table 2.1**). Firstly, we investigated the role of various photocatalysts using ethanol as a solvent (**Table 2.1, entries 1-4**). Eosin Y was the most active catalyst, yielding product 3a in 52% (**Table 2.1, entry 4**). Next, different solvents were optimized (**Table 2.1, entries 5-11**), and water gave a good yield of 60% (**Table 2.1, entry 5**). It was observed that using water/ethanol in a 1:1 ratio led to a marginal increase of 70% in yield (**Table 2.1, entry 12**). Encouraged by the finding, a different ratio of ethanol and water (**Table 2.1, entries 12-15**) was tried. We got the best result (90%) using a mixture in the ratio of 1:2 (**Table 2.1, entry 14**). Further, we tried the reaction without blue LED but failed to give the desired product **3a** (**Table 2.1, entry 16**). Then, we varied the loading of Eosin Y from 3 mol% to 4 mol% (**Table 2.1, entries 17-18**) and found the exact yield on increasing the mol% of the photocatalyst. We tried extending the reaction time (**Table 2.1, entry 19**) but failed to get a better yield of product **3a**.

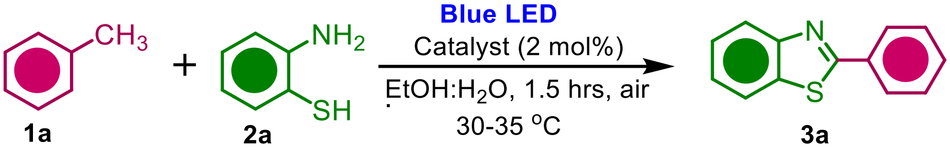
Table 2.1 Optimization of the Reaction Conditions for the Synthesis of Compound **3a**[a].



S.No	Light source	Catalyst (mol %)	Solvent	Time (h)	Yields[b] %
1	Blue LED	Rhodamine B (2)	EtOH	3	30
2	Blue LED	Rose Bengal (2)	EtOH	3	35
3	Blue LED	Acridine red (2)	EtOH	3	32
4	Blue LED	Esoin Y (2)	EtOH	3	52
5	Blue LED	Esoin Y (2)	H_2O	3	60
6	Blue LED	Esoin Y (2)	Methanol	3	35
7	Blue LED	Esoin Y (2)	DMF	3	20
8	Blue LED	Esoin Y (2)	Acetonitrile	3	25
9	Blue LED	Esoin Y (2)	DMSO	3	10
10	Blue LED	Esoin Y (2)	Toluene	3	30
11	Blue LED	Esoin Y (2)	THF	3	25
12	Blue LED	Esoin Y (2)	EtOH:H_2O (1:1)	1.5	70
13	Blue LED	Esoin Y (2)	EtOH:H_2O (2:1)	1.5	60
14	Blue LED	Esoin Y (2)	EtOH:H_2O (1:2)	1.5	90
15	Blue LED	Esoin Y (2)	EtOH:H_2O (1:4)	1.5	80
16	None	Esoin Y (2)	EtOH:H_2O (1:2)	1.5	NR
17	Blue LED	Esoin Y (3)	EtOH:H_2O (1:2)	1.5	91
18	Blue LED	Esoin Y (4)	EtOH:H_2O (1:2)	1.5	92
19	Blue LED	Esoin Y (3)	EtOH:H_2O (1:2)	4	90

(a)Reaction Condition: Methylarene **1a** (1.0 mmol), 2-aminothiophenol **2a** (1.2 mmol), catalyst (2 mol %), solvent (3 ml), blue LED (1.5 h) under open air at room temperature. [b]Isolated yield.

Table 2.2 Optimization of different colour LED**.**

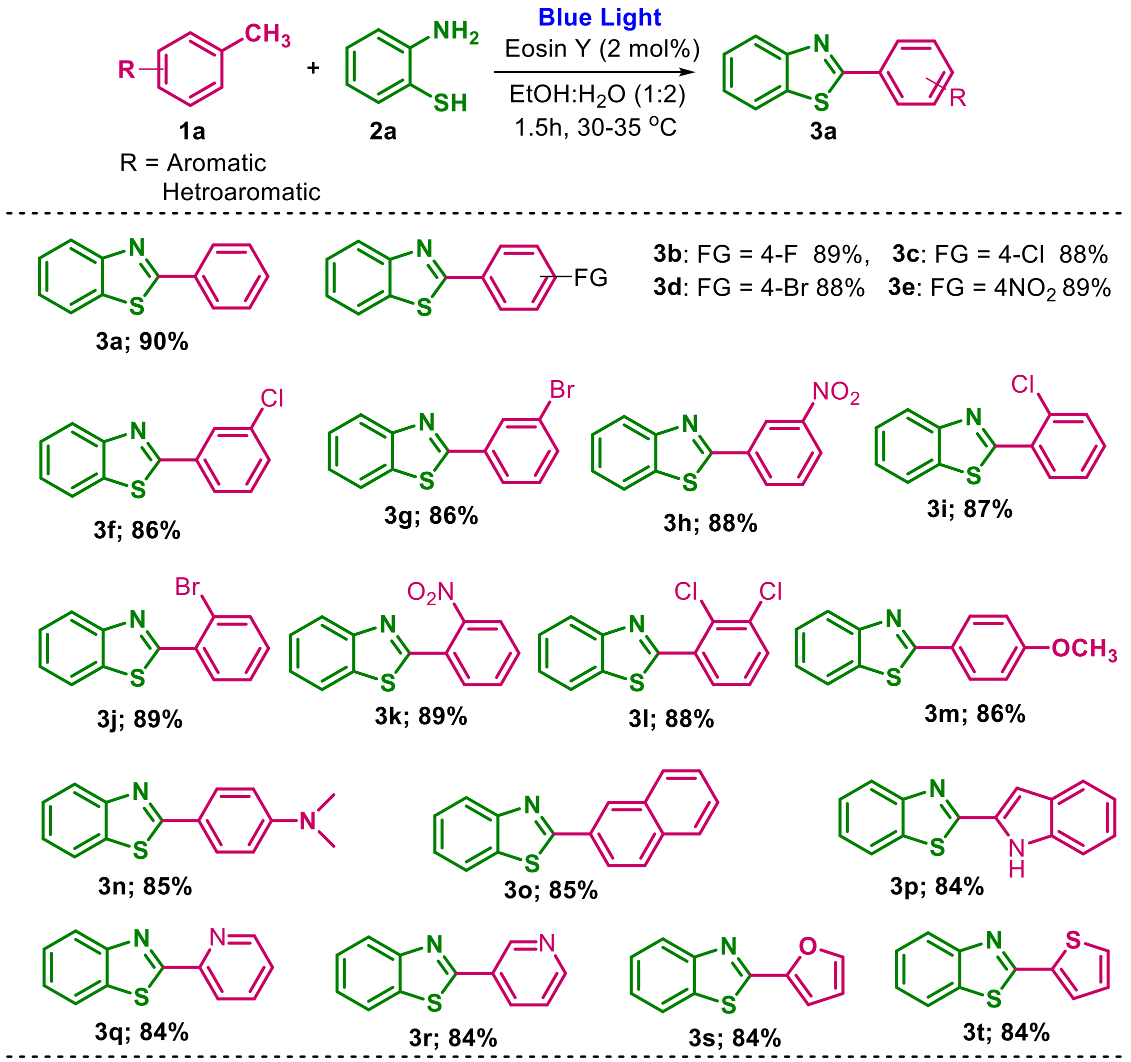


Entry	variations in the reaction conditions	Yield (%)[b]
1	in dark	nr
2	Green LEDs instead of blue LEDs	60
3	White LEDs instead of blue LEDs	65
4	Purple LEDs instead of blue LEDs	69
5	20W CFL instead of blue LEDs	65
6	Blue LEDs	90
7	under O_2 atmosphere	85

(a)Reaction Condition: Methyl arene (1.0 mmol), 2-aminothiophenol (1.2 mmol), catalyst (2 mol %), solvent (3 ml), blue LED (1.5 h) under open air at room temperature. [b]Isolated yield.

After that, under the same reaction condition, the influence of light on the reaction was investigated, and no product was formed in the absence of light (**Table 2.2, entry 1**), indicating the essential role of light irradiation. To further explore the impact of different light sources, purple, green, and white LED lights and a 20W CFL were used instead of the blue LED (**Table 2.2, entries 2-5**). The results showed that these light sources produced comparable yields of 65-69%. In addition, the effect of atmospheric air was examined, and the reaction under oxygen produced almost the exact yield as under air (**Table 2.2, entry 7**).

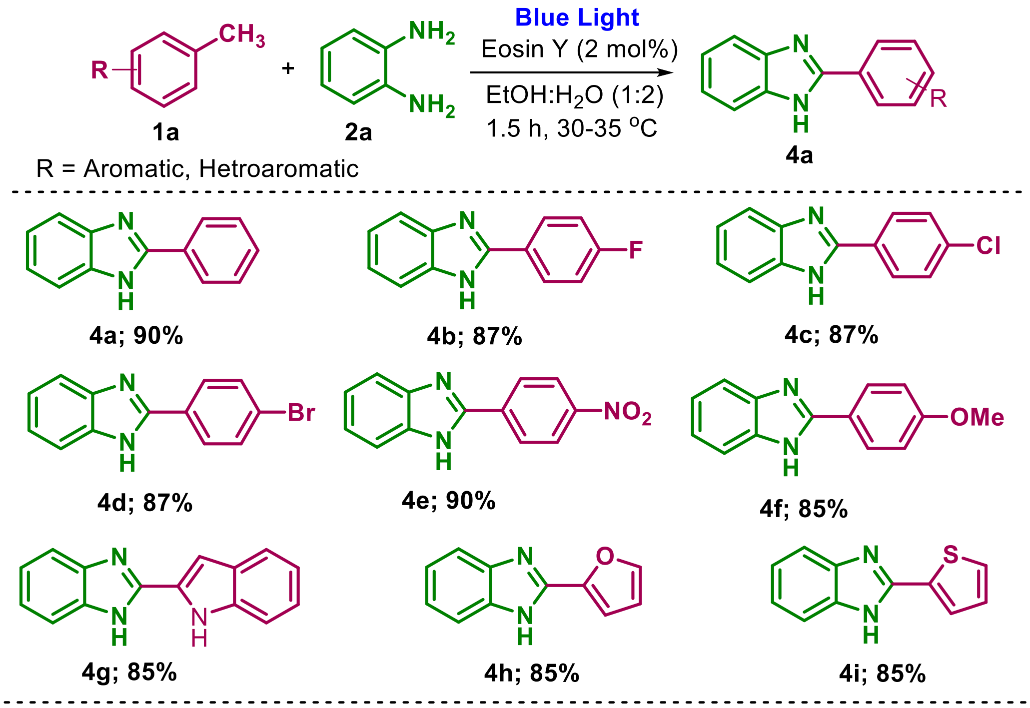
Scheme 2.3 Substrate scope of toluene for the synthesis of compound **3a-t**.



[a] **Reaction condition**: Methylarene (1.0 mmol), 2-aminothiophenol (1.2 mmol), catalyst (2 mol %), solvents (3 ml) at room temperature for 1.5 h, and irradiation under blue LED. [b] Isolated yield.

After determining the optimal reaction system, we further explored the range of photocatalytic condensation reactions of aromatic methyl arene with different substituents, and the results are summarized in (**Scheme 2.3, 2.4**). First, when there was no substituent on the methyl arene **1a**, the product **3a** and **4a** yield could reach 90%. When methyl arene has -F, -Cl, -Br, and -NO_2 in the p-position, it is found that the yields with electron-withdrawing groups are superior to those with electron-donating groups (**Scheme 2.3, 2.4**). The target product can be obtained in good yields when the substituent is in the m- and o-positions, giving 86% to 89% yields (**Scheme 2.3, 3f-3k**). In addition, methyl arene with multiple substituents gave an 88% yield (**Scheme 2.3, 3l**). We also tried to use heteroaromatic to react with methyl arene, and we found that the yields of (**3p, 3q, 3r, 3s, 3t, 4j, 4h, and 4i**) were good at 84% and 85%.

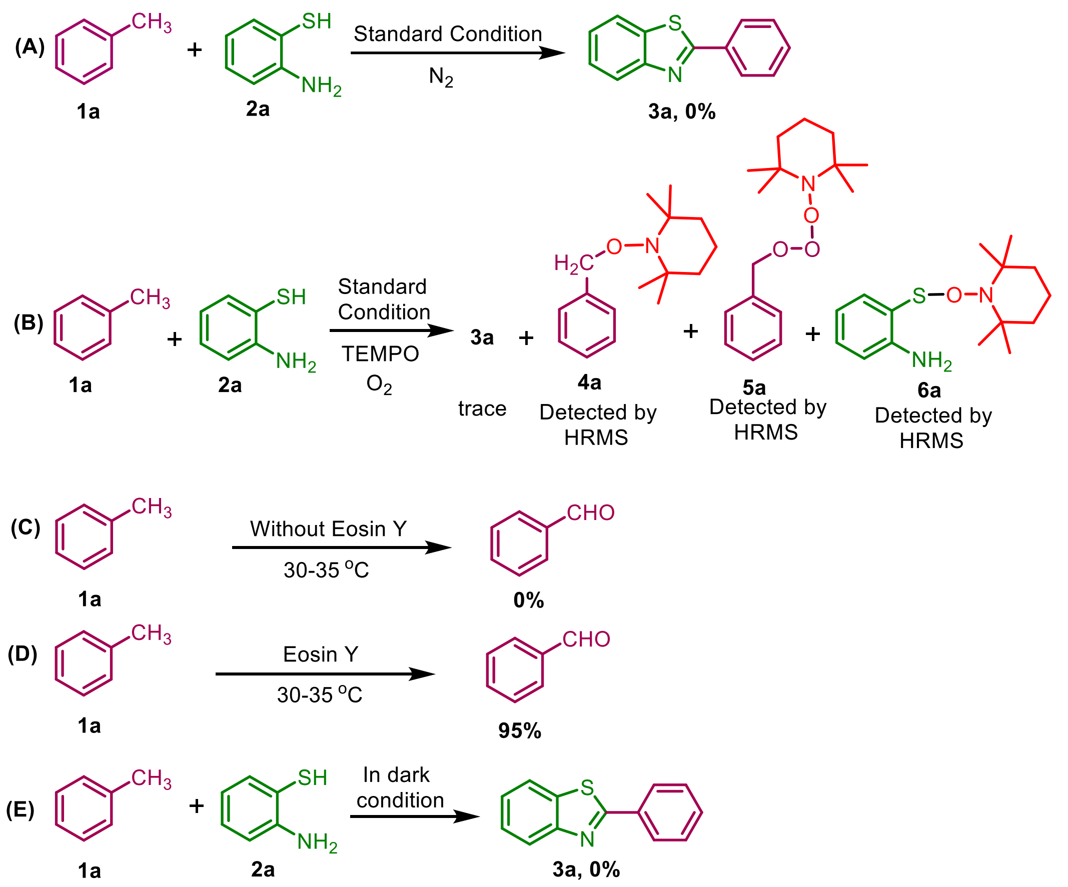
Scheme 2.4 Substrate scope of toluene for the synthesis of compound **4a-i**.



[a] **Reaction condition**: Methyl arene (1.0 mmol), o-phenylediamine (1.2 mmol), catalyst (2 mol %), solvents (3 ml) at room temperature for 1.5 h, and irradiation under blue LED.
[b] Isolated yield.

2.3 Optimized Experiments

Some optimized experiments were performed under optimized reaction conditions to establish the mechanism, as presented in (**Scheme 2.5**).



Scheme 2.5 optimized experiments for mechanistic investigation.

This result confirms the importance of visible light for this reaction. No product was obtained after the reaction was performed in N_2 atmosphere (**Scheme 2.5 A**). Herein, the reaction was performed in the presence of radical scavenger TEMPO (2,2,6,6-tetramethylpiperidin-1-yl) (2 equiv.) (**Scheme 2.5 B**) gave less than 10 % yield of the desired product, and TEMPO adduct are formed **4a**, **5a**, and **6a** (**Scheme 2.5 B**) which indicates that the formation of benzothiazole involves a radical mechanistic pathway.

Next, the optimized reaction was carried out between toluene and 2-aminothiolphenol without Eosin Y, which failed to give the product. This indicates that toluene is not oxidized to benzaldehyde without Eosin Y (**Scheme 2.5 C**), suggesting Eosin Y's necessity for the first step. After that, the control reaction was executed between methylarene, 2-aminothiophenol, and Eosin Y under optimized conditions; the reaction proceeded very well with a good yield of 95% (**Scheme 2.5 D**). This indicated that Eosin Y and air decomposition as an oxidant resulted in hydrogen peroxide and ½O_2, wherein hydrogen peroxide acted as an oxidizing agent for oxidizing toluene to benzaldehyde. Next, the control experiment was performed in dark conditions, and we didn't get any yield; this result suggests that visible light is necessary for our reaction (**Scheme 2.5 E**).

2.3.1 UV-Vis Absorption Experiment

After evaluating the sensitivity and reproducibility of the substrate scope, we moved our attention toward the mechanism of the reaction and conducted several mechanistic investigations.

The UV-visible spectra of reactants (**1a** and **2a**), reaction mixtures (**1a+2a**), and Eosin Y were observed (**Figure 2.2a, 2.2b**). The finding showed that, except for the reactants, the photocatalyst Eosin Y and the reaction mixture could absorb blue light.

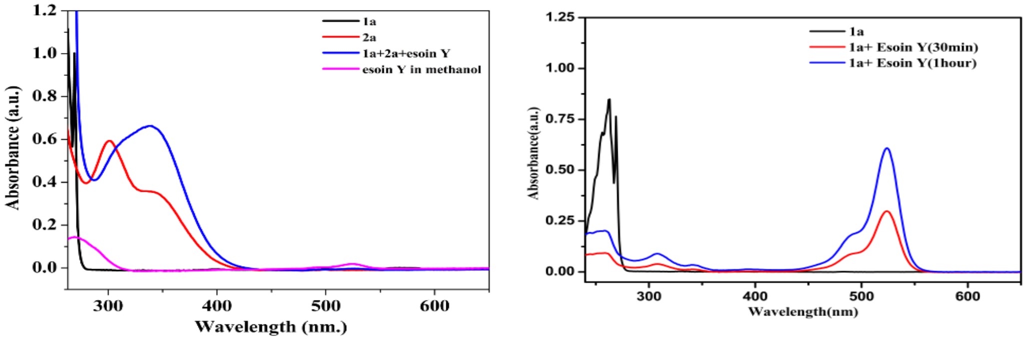


Figure 2.2a UV-vis absorption spectra of **1a, 2a, 2.2b** UV-vis absorption spectra of (1a+Eosin y)

2.3.2 Stern-Volmer Fluorescence Quenching Studies

Next, the results of subsequent Stern-Volmer experiments showed that excited **1a** was successfully quenched by **2a** (**Figure 2.3**). As seen in the figure, the quenching effect gets more pronounced as the concentration of **2a** rises.

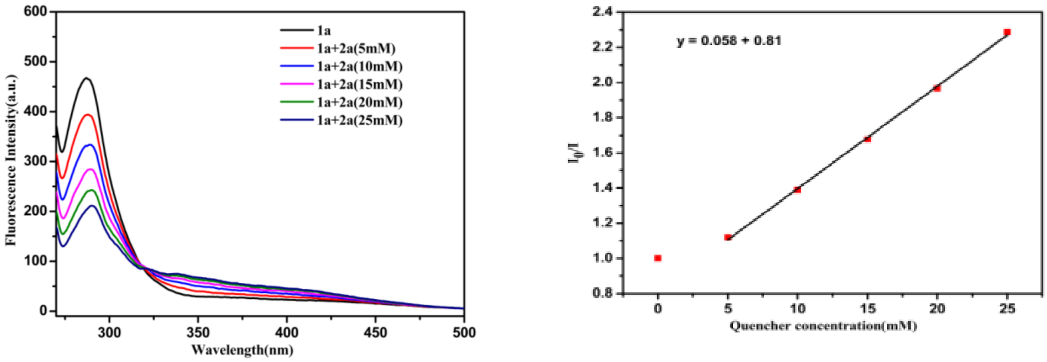


Figure 2.3. The fluorescence emission spectra of **1a** with different concentrations of quencher **2a**. **Figure 2.4** Stern-Volmer plot

It was discovered that there was a linear relationship between the concentration of **2a** and Io/I (Io and I are the fluorescence intensity prior to and following the addition of **2a**) (**Figure 2.4**). The outcomes showed that **2a** was an effective quencher for **1a**.

2.3.3 ON-OFF Experiments

The reaction between **1b** and **2a** was conducted under the standard conditions on a (1.0 mmol) scale.

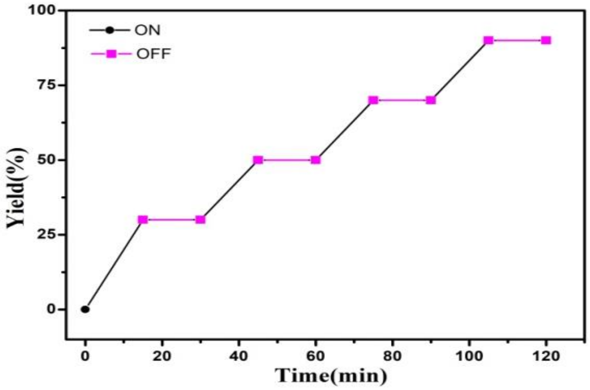


Figure 2.5 Light-dark cycle experiment

The reaction mixture was subjected to sequential periods of stirring under visible light irradiation (blue LED) followed by stirring in the absence of light. At each time point, one reaction system was suspended, which was then purified with column chromatography to give the corresponding products **3a**. The yield of **3a** was measured by weight of the product (**Figure 2.5**).

2.4 Proposed Mechanism

According to the literature and control experiment, [40] a possible mechanism for the Eosin Y-catalyzed oxidation reaction of methylarene was proposed **(Figure 2.6**). Under blue light, the Eosin Y photocatalyst is excited to its excited state (EY*), forming the highly reactive photooxidant EY*. This species undergoes a single electron transfer (SET) with methylarene **1a**, generating the radical cationic intermediate **A** and reducing EY to its ground state by transferring its electron to O_2, which is converted to a superoxide ion. The superoxide ion reacts with H_2O to produce hydrogen peroxide and an O_2 molecule, which increases the reaction yield. Intermediate **A** undergoes proton abstraction, producing benzylic radical **B**, which then reacts with oxygen to form peroxy-species **C**. After H-radical abstraction, result in benzyl hydroperoxide **D** is formed. This species leads to the formation of intermediate **E** after removing a water molecule, which reacts with 2-aminothiophenol to produce intermediate **F** and the desired product **3a** after the removal of another water molecule in a similar manner.

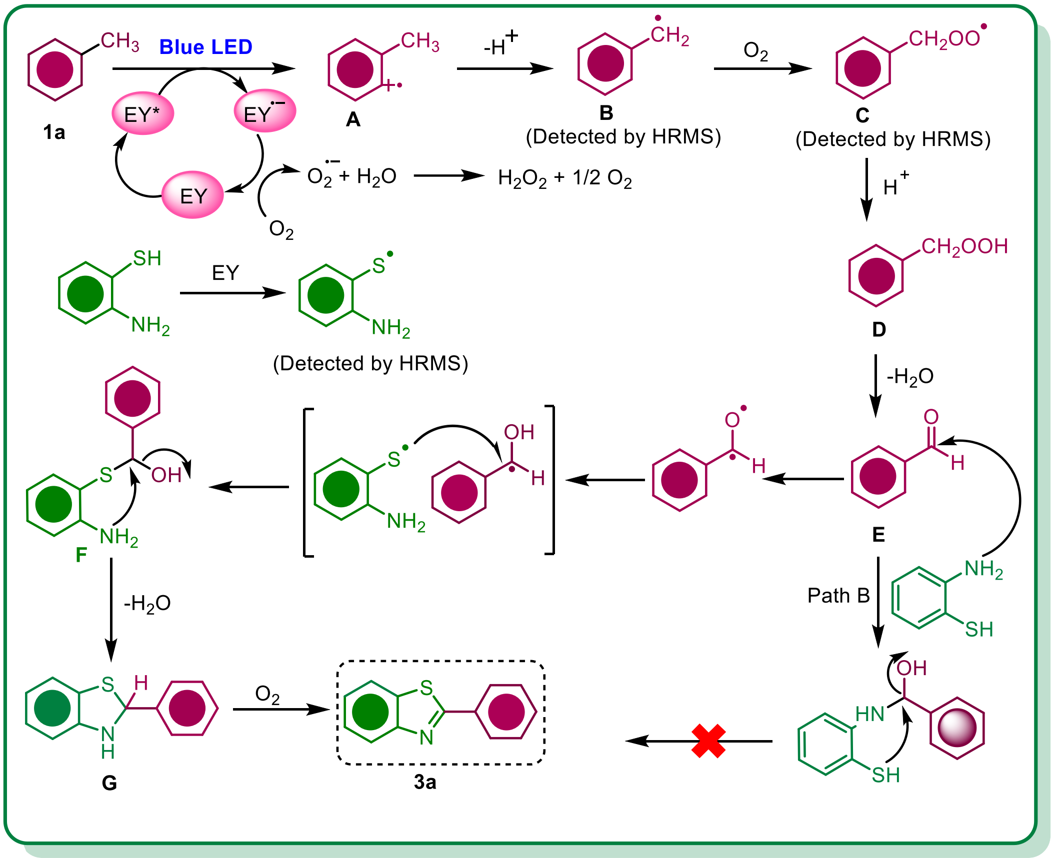


Figure 2.6 A plausible mechanism for the synthesis of benzothiazole.

2.5 Conclusion

In conclusion, an efficient catalytic method for the synthesis of benzothiazole, benzimidazole under visible-light-irradiation has been demonstrated from 2-aminothiophenol, o-phenylenediamine, and methylarene using of Eosin-Y as a photocatalyst, ethanol:water as green solvent and atmospheric air as oxidant at room temperature. All the reactions were carried out at room temperature in the presence of atmospheric oxygen as an oxidant. This methodology showed a broad substrate scope while the desired products were obtained in good to excellent yields.

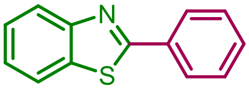
2.6 Experimental Procedure

2.6.1 General procedure for the synthesis of compound 3a-3t/4a-4i

A 25 ml RB flask equipped with a magnetic stirring bar was charged with methyl arene **1a** (1.0 mmol), 2-aminothiophenol **2a** (1.2 mmol), Eosin Y (2 mol %), and solvent (3 ml). The mixture was stirred at room temperature and irradiated with blue LEDs light strips for 1.5 h under the open air. The progress of the reaction was monitored via TLC. The precipitate obtained was filtered and washed with ethanol after the completion of the reaction. The desired product obtained good yields after recrystallization using ethanol.

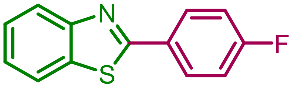
2.7 Analytical Data for [3a-3t, 4a-4i]

2-Phenylbenzothiazole (3a)



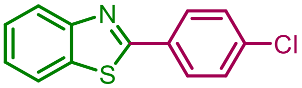
Yield 90%; Yellow solid; m.p. 115-116 °C; **^{1}H NMR** (500 MHz, DMSO-d$_6$); δ 8.18–8.15 (d, J = 8.0 Hz, 3H), 8.04-8.02 (m, 1H), 7.80-7.77 (m, 2H), 7.59-7.47 (d, J = 8.3, 1.2 Hz 3H) ppm. **^{13}C NMR** (125 MHz, DMSO-d$_6$) δ 166.6, 153.9, 135.0, 132.9, 132.5, 129.5, 127.3, 126.2, 125.4, 123.5, 122.9 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_9NS$ 212.0456, found: 212.0451.

2-(4-Flurophenyl)-benzothiazole (3b)



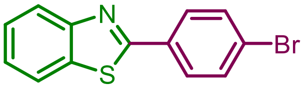
Yield 89%; Yellow solid; m.p. 101-102 °C; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 8.17-8.15 (m, 1H), 8.08-8.06 (d, J = 8.0 Hz, 1H), 7.57-7.56 (dd, J = 8.3, 1.2 Hz, 2H), 7.54-7.47 (m, 2H), 7.46–7.41 (m, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 166.6, 165.2, 163.4, 154.1, 134.9, 130.1, 127.2, 125.9, 123.5, 122.9, 117.0 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_8FNS$ 230.0361, found: 230.0350.

2-(4-Chlorophenyl)-benzothiazole (3c)



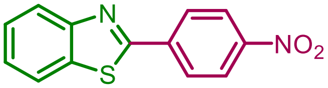
Yield 88%; Yellow solid; m.p. 111-112 °C; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 8.17-8.15 (d, J = 8.0 Hz, 2H), 8.08–8.06 (m, 1H), 7.57-7.56 (d, J = 7.56 Hz, 2H), 7.57-7.54 (dd, J = 8.3, 1.2 Hz, 1H), 7.49-7.41 (m, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 166.5, 163.3, 153.9, 135.0, 130.2, 127.2, 126.2, 123.3, 122.9, 117.0, 116.8 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_8ClNS$ 246.0066, found: 246.0069.

2-(4-Bromophenyl)-benzothiazole (3d)



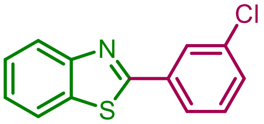
Yield 88%; Yellow powder; m.p. 132-133 °C; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 8.14-8.13 (m, 2H), 7.63-7.62 (d, J = 8.0 Hz, 1H), 7.51-7.49 (d, J = 7.56 Hz, 1H), 7.19-7.16 (m, 1H), 7.15-7.11 (d, J = 8.26 Hz, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 166.5, 163.2, 154.2, 135.2, 130.0, 127.2, 125.9, 123.4, 122.6, 117.2, 116.8 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_8BrNS$ 289.9561, found: 289.9553.

2-(4-Nitrophenyl)-benzothiazole (3e)



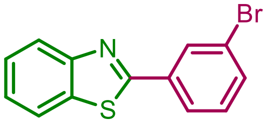
Yield 89%; Yellow powder; m.p. 230-231 °C; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.40 (m, 2H), 8.31-8.29 (m, 2H), 8.17-8.15 (d, J = 8.26 Hz, 1H), 8.00-7.98 (d, J = 8.12 Hz, 1H), 7.60-759 (m, 1H), 7.58-7.49 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$); δ 164.9, 153.7, 135.3, 133.0, 130.1, 126.8, 126.0, 125.2, 123.8, 122.4, 121.8 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_8N_2O_2S$ 257.0307, found: 257.0315.

2-(3-Chlorophenyl)-benzothiazole (3f)



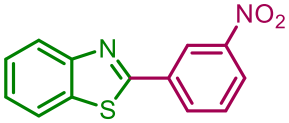
Yield 86%; White solid; m.p. 98-99 °C; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.13-8.12 (d, J = 1.6 Hz, 1H), 8.04-8.82 (s, 1H), 7.63-7.61 (d, J = 8.0 Hz, 2H), 7.47-7.44(m, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$); δ 164.6, 153.6, 135.4, 135.0, 133.1, 130.2, 126.9, 126.4, 125.9, 125.3, 123.8, 122.5, 121.8 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_9ClNS$ 246.0066, found: 246.0061.

2-(3-Bromophenyl)-benzothiazole (3g)



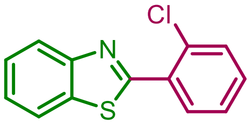
Yield 86%; White solid; m.p. 89-91 °C; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.13-8.04 (m, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.63-7.61 (d, J = 8.0 Hz, 2H), 7.47-7.44 (dd, J = 8.1 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$); δ 162.7, 152.4, 136.8, 136.2, 133.5, 132.3, 131.0, 130.5, 127.6, 126.6, 125.8, 123.7, 121.6 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_8BrNS$ 289.9561, found: 289.957.

2-(3-Nitrophenyl)-benzothiazole (3h)



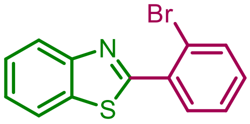
Yield 88%; White solid; m.p. 186-187 °C; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.40-8.31 (m, 1H), 8.17-8.15 (d, J = 8.26 Hz, 1H), 8.00-7.98 (d, J = 8.20 Hz, 1H), 7.59-7.57 (d, J = 8.0 Hz, 1H), 7.51 (d, 2H), 7.50-7-49 (d, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$); δ 164.9, 153.9, 135.3, 135.2, 133.0, 130.1, 126.8, 126.0, 125.5, 125.2, 123.8, 122.4, 121.8 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_8N_2O_2S$ 257.0307, found: 257.0330.

2-(2-chlorophenyl)-benzothiazole (3l)



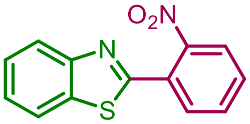
Yield 87%; White solid; m.p. 83-85 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.23-8.18 (m, 1H), 8.14 (d, J = 8.0, 1H), 7.93 (m, 1H), 7.57-7.48 (m, 2H), 7.44-7.35 (m, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$); δ 164.3, 152.6, 136.2, 132.8, 132.3, 131.8, 131.1, 130.9, 127.2, 126.5, 125.6, 123.4, 121.5 ppm. HRMS (ESI) $[M+H^+]$ calculated for $C_{13}H_9ClNS$ 246.0068, found: 246.0063.

2-(2-bromophenyl)-benzothiazole (3j)



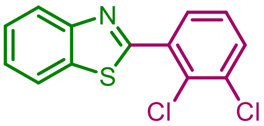
Yield 87%; White solid; m.p. 68-70 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.19 (d, J = 8.0 Hz, 1H), 8.04 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.48-7.43 (m, 2H), 7.37-7.28 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$); δ 161.9, 161.2, 161.0, 159.3, 152.6, 145.8, 132.2, 132.1, 129.9, 129.8, 126.5, 125.5, 124.8,124.6,123.4, 121.6, 116.6, 116.4 ppm. HRMS (ESI) $[M+H^+]$ calculated for $C_{13}H_8BrNS$ 289.9565, found: 289.9568

2-(2-Nitrophenyl)-benzothiazole (3k)



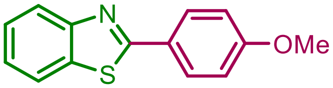
Yield 89%; White solid; m.p. 123-125 °C; ^{1}**H NMR** (500 MHz, CDCl$_3$); δ 8.12-8.10 (d, J = 1.6 Hz, 1H), 8.04-8.82 (s, 1H), 7.63-7.61 (d, J = 8.0 Hz, 2H), 7.47-7.44 (m, 4H) ppm. ^{13}**C NMR** (125 MHz, CDCl$_3$); δ 162.33, 153.60, 148.99, 135.84, 133.36, 131.82, 130.92, 128.16, 126.59, 125.88, 124.52, 123.98, 121.58 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_8N_2O_2S$ 257.0307, found: 257.0312.

2-(2,3-Dichlorophenyl)-benzothiazole (3l)



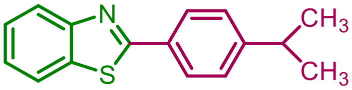
Yield 88%; White solid; m.p. 134-135 °C; ^{1}**H NMR** (500 MHz, CDCl$_3$); δ 8.26-8.24 (m, 1H), 8.16-8.14 (d, J = 8.1 Hz, 1H), 7.99-7.97 (d, J = 8.0 Hz, 1H), 7.59-7.55 (dd, J = 8.1 Hz, 2H), 7.48-7.42 (m, 2H) ppm. ^{13}**C NMR** (125 MHz, CDCl$_3$); δ 162.9, 152.6, 136.7, 136.2, 133.2, 132.3, 131.9, 130.4, 127.6, 126.7, 125.6, 123.6, 121.6 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_7Cl_2NS$ 279.9673, found: 279.9666.

2-(4-Methoxyphenyl)-benzothiazole (3m)



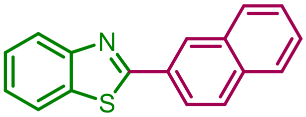
Yield 86%; Yellow solid; m.p. 125-127 °C; ^{1}**H NMR** (500 MHz, DMSO-d_6); δ 8.14–8.12 (m, 2H), 7.63-7.62 (dd, J = 8.0, 0.5 Hz, 1H), 7.51-7.49 (d, J = 8.3, 1.2 Hz, 2H), 7.19-7.16 (dd, J = 8.3, 1.2 Hz, 1H), 7.15–7.11 (m, 2H) ppm. ^{13}**C NMR** (100 MHz, DMSO-d_6); δ 160.8, 152.2, 144.4, 135.7, 128.6, 123.4, 122.3, 121.8, 118.8, 114.7, 111.7, 55.3 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{14}H_{11}NOS$ 242.0561, found: 242.0552.

2-(4-N,N-dimethyle)-benzothiazole (3n)



Yield 85%; Yellow powder; m.p. 170-171 °C; ^{1}**H NMR** (500 MHz, $CDCl_3$); δ 8.01-7.98 (d, 3H), 7.87-7.86 (d, J = 7.8, 1.2 Hz, 1H), 7.47-7.34 (d, 1H), 7.33-7.28 (d, 1H), 6.78-6.77 (m, 2H), 3.08 (s, 6H) ppm. ^{13}**C NMR** (125 MHz, $CDCl_3$); δ 168.8, 154.4, 152.2, 134.6, 128.9, 125.9, 124.2, 122.3, 121.4, 121.4, 111.7, 40.2 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{16}H_{15}NS$ 254.0925, found: 254.0436.

2-(Naphthalene-2-yl)-benzothiazole (3o)

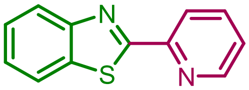


Yield 85%; White solid; m.p. 123-125 °C; ^{1}**H NMR** (500 MHz, $CDCl_3$); δ 8.60 (d, J = 1.0 Hz, 1H), 8.25-8.23 (dd, J = 8.6, 1.8 Hz, 1H), 8.16-8.14 (d, J = 8.1 Hz, 1H), 8.01-7.90 (m, 4H), 7.59-7.53 (m, 3H), 7.45-7.42 (dd, J = 8.1, 1.2 Hz, 1H) ppm. ^{13}**C NMR** (125 MHz, $CDCl_3$); δ 168.1, 154.5, 135.2, 134.5, 133.2, 131.0, 128.8, 127.9, 127.6, 127.5, 126.9, 126.4, 125.3, 124.3, 123.4, 121.7 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{17}H_{12}NS$ 263.0690, found: 263.0699.

2-(1H-Indol-2-yl)-benzothiazole (3p)

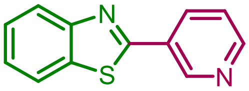
Yield 84%; Yellow solid; m.p. 146-148 °C; ^{1}**H NMR** (500 MHz, DMSO-d_6); δ 11.00 (s, 1H), 8.34-8.32 (d, J = 8.2 Hz1H), 7.88-7.87 (d, J = 8.0, 1.2 Hz, 1H), 7.70-7.68 (m, 1H), 7.57-7.49 (dd, 2H), 7.27-7.18 (m, 3H), 5.83 (s, 1H) ppm. ^{13}**C NMR** (125 MHz, DMSO-d_6); δ 150.0, 136.8, 136.5, 136.1, 126.9, 126.0, 123.9, 122.8, 121.9, 120.7, 119.3, 118.8, 112.3, 110.9, 105.5 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{15}H_{10}N_2S$ 251.0565, found: 250.0575.

2-(Pyridin-2-yl)-benzothiazole (3q)



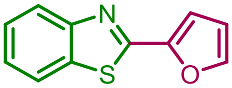
Yield 84%; Yellow powder; m.p. 133-135 °C; ^{1}H NMR (500 MHz, $CDCl_3$); δ 8.69 (d, = 7.8 Hz, 1H), 8.38 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 7.8, 1H), 7.52-7.49 (d, 1H), 7.43-7.41 (d, J = 8.0, Hz, 1H), 7.40 (d, J = 7.9, 1H), 7.38-7.35 (dd, J = 8.2, 7.7 Hz, 1H) ppm. ^{13}**C NMR** (125 MHz, $CDCl_3$); δ 169.4, 154.3, 151.4, 149.6, 136.9, 136.1, 126.3, 125.7, 125.3, 123.6, 122.0, 120.7 ppm. HRMS (ESI): m/z: [M+H$^+$] calculated for $C_{12}H_8N_2S$ 213.0408, found: 213.0420.

2-(Pyridin-3-yl)-benzothiazole (3r)



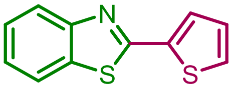
Yield 84%; Yellow powder; m.p. 133-135 °C; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 9.03 (d, = 7.8 Hz, 1H), 8.73 (d, J = 7.9 Hz, 1H), 8.41 (m, 1H), 8.12 (d, J = 7.8, 1H), 7.95 (d, 1H), 7.65-7.41 (m, 2H), 7.40 (d, J = 7.9, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$); δ 164.3, 153.7, 151.3, 148.3, 134.9, 134.1, 129.3, 126.7, 125.5, 123.6, 123.0, 121.7 ppm. HRMS (ESI): m/z: [M+H$^+$] calculated for $C_{12}H_8N_2S$ 213.0408, found: 213.0420.

2-(Furan-2-yl)-benzothiazole (3s)



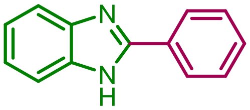
Yield 84%; Yellow solid; m.p. 104-106 °C; **^{1}H NMR** (500 MHz, DMSO-d_6);5 δ 8.16 (d, J = 8.2 Hz, 1H), 8.04-8.02 (d, J = 8.2 Hz, 2H), 7.46 (dd, J = 1.8, 0.5 Hz, 1H), 7.37 (ddd, J = 8.0, 1.2 Hz, 1H), 6.61 (ddd, J = 8.0, 1.2 Hz, 1H), 6.80 (dd, J = 3.5, 0.5 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 157.3, 153.8, 148.6, 146.6, 134.0, 127.3, 125.9, 123.1, 122.9, 113.5, 112.4 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{11}H_7NOS$ 202.0248, found: 202.0243.

2-(Thiophen-2-yl)-benzothiazole (3t)



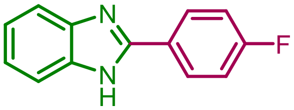
Yield 84%; White solid; m.p. 97-99 ºC; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 7.84 (dd, J = 8.0, 1.1 Hz, 1H), 7.73 (dd, J = 8.0, 1.1 Hz, 1H), 7.72 (dd, J = 3.7, 1.1 Hz, 1H), 7.62–7.51 (m, 1H), 7.50-7.22 (m, 3H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 147.5, 144.0, 135.0, 134.2, 129.2, 128.7, 127.1, 123.1, 122.2, 119.0, 111.7 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{11}H_7NS_2$ 218.0020, found: 218.0026.

2-Phenylbenzoimidazole (4a)



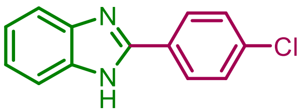
Yield 90%; Yellow powder; m.p. 293-294 ºC; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 12.91 (s, 1H), 8.20-8.18 (d, 2H), 7.68 (s, 1H), 7.58-7.55 (d, 3H), 7.50 (d, 1H), 7.49-7.18 (m, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 151.7, 144.3, 135.5, 130.6, 130.3, 129.4, 126.9, 122.9, 122.1, 119.3, 111.8 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_{10}N_2$ 195.0844, found: 195.0850.

2-(4-Fluorophenyl)-benzoimidazole (4b)



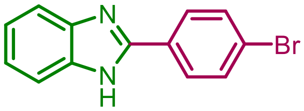
Yield 91%; Yellow powder; m.p. 256-258 °C; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 12.91 (s, 1H), 8.25-8.22 (d, J = 8.3 Hz, 2H), 7.67- 7.66 (d, J = 8.32 Hz, 2H), 7.43-7.42 (m, 2H), 7.39-7.21 (s, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 164.7, 162.9, 151.0, 144.3, 135.4, 129.0, 127.2, 123.0, 122.2, 119.5, 116.5, 111.6 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_9FN_2$ 213.0750, found: 213.0760.

2-(4-chlorophenyl)-benzoimidazole (4c)



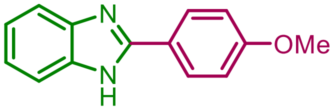
Yield 87%; White solid; m.p. 294-296 °C; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 13.10 (s, 1H), 8.16-8.11 (d, J = 8.3 Hz, 2H), 7.79-7.62 (m, 4H), 7.25-7.22 (d, J = 8.1Hz, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 150.8, 132.4, 129.9, 128.9, 123.8, 122.7 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_9ClN_2$ 229.0454, found: 229.0450.

2-(4-Bromophenyl)-benzoimidazole (4d)



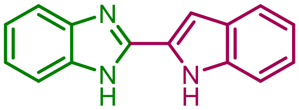
Yield 90%; White solid; m.p. 294-296 °C; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 13.01 (s, 1H), 8.14-8.12 (d, J = 8.3 Hz, 2H), 7.78-7.61 (m, 4H), 7.23-7.22 (d, J = 8.1Hz, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 150.7, 132.5, 129.9, 128.8, 123.7, 122.7 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{13}H_9BrN_2$ 272.9950, found: 272.9980.

2-(4-Methoxyphenyl)-benzimidazole (4f)



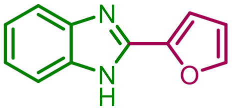
Yield 86%; White solid; m.p. 222-224 °C; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 12.72 (s, 1H), 8.14 (d, J = 8.0Hz, 2H), 7.63-7.61 (m, 2H), 7.18–7.15 (m, 4H), 7.22 (d, J = 7.6Hz, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 161.0, 151.8, 144.4, 135.4, 128.5, 123.2, 122.5, 121.9, 118.9, 114.8, 111.5, 55.8 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{14}H_{12}N_2O$ 225.0950, found: 225.0980.

2-(1H-Indol-2-yl)-benzimidazole (4g)



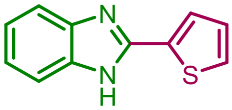
Yield 83%; Yellow solid; m.p. 160-161 °C; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 11.67 (s, 1H), 11.00 (s, 1H) 8.34-8.33 (dd, J = 2.8, 0.9 Hz, 1H), 7.88-7.87 (d, J = 5.0, 0.7 Hz, 1H), 7.57-7.56 (dd, J = 5.0, 2.9 Hz, 1H), 7.27-7.19 (m, 1H), 6.84-6.83 (m, 4H), 5.83 (s, 1H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 150.4, 136.9, 136.3, 127.3, 125.8, 124.3, 123.2, 121.7, 120.6, 119.1, 112.7, 111.4, 105.9 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{15}H_{11}N_3$ 234.0953, found: 234.0920.

2-(Furan-2-yl)-benzimidazole (4h)



Yield 84%; Yellow solid; m.p. 280 °C; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 12.92 (s, 1H), 7.95 (d, J = 1.0, Hz, 1H), 7.58 (s, 2H), 7.24-7.17 (m, 3H), 6.75 (m, 1H), ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 146.1, 145.2, 144.4, 134.2, 129.2, 128.6, 127.0, 123.0, 122.2, 112.9, 110.6 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{11}H_8N_2O$ 185.0637, found: 185.0632.

2-(Thiophen-2-yl)-benzimidazole (4i)



Yield 84%; White solid; m.p. 280 °C; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 12.81 (s, 1H), 7.84-7.83 (dd, J = 2.8, 0.9 Hz, 1H), 7.73-7.72 (dd, J = 5.0, 0.7 Hz, 1H), 7.62-7.51 (dd, J = 5.0, 2.9 Hz, 1H), 7.50 (s, 1H), 7.25-7.20 (m, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6); δ 147.4, 144.2, 135.4, 134.2, 129.2, 128.6, 127.0, 123.0, 122.2, 118.9, 111.6 ppm. HRMS (ESI) [M+H$^+$] calculated for $C_{11}H_8N_2S$ 201.0408, found: 201.0430.

2.8 Spectral Data of Few Products

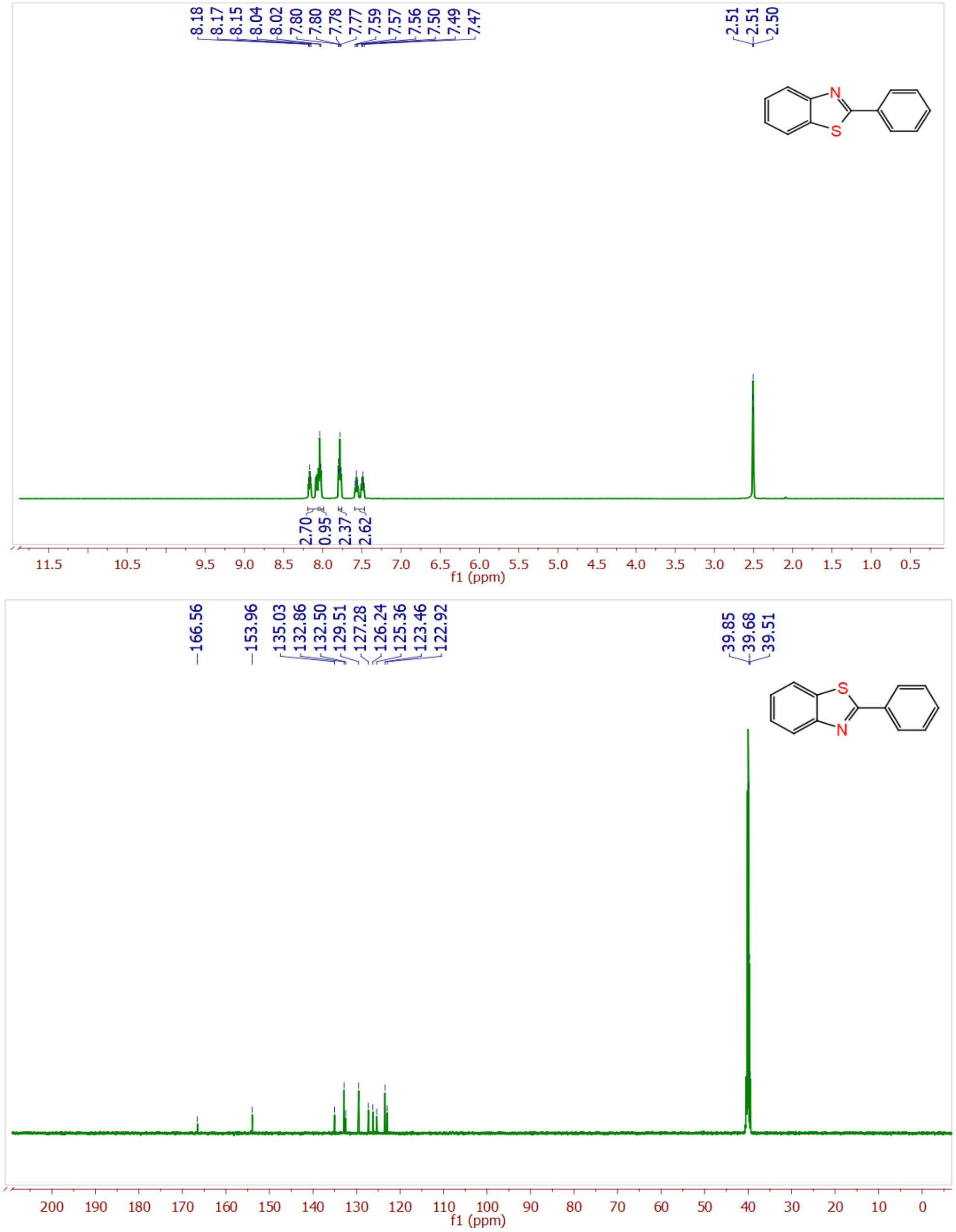
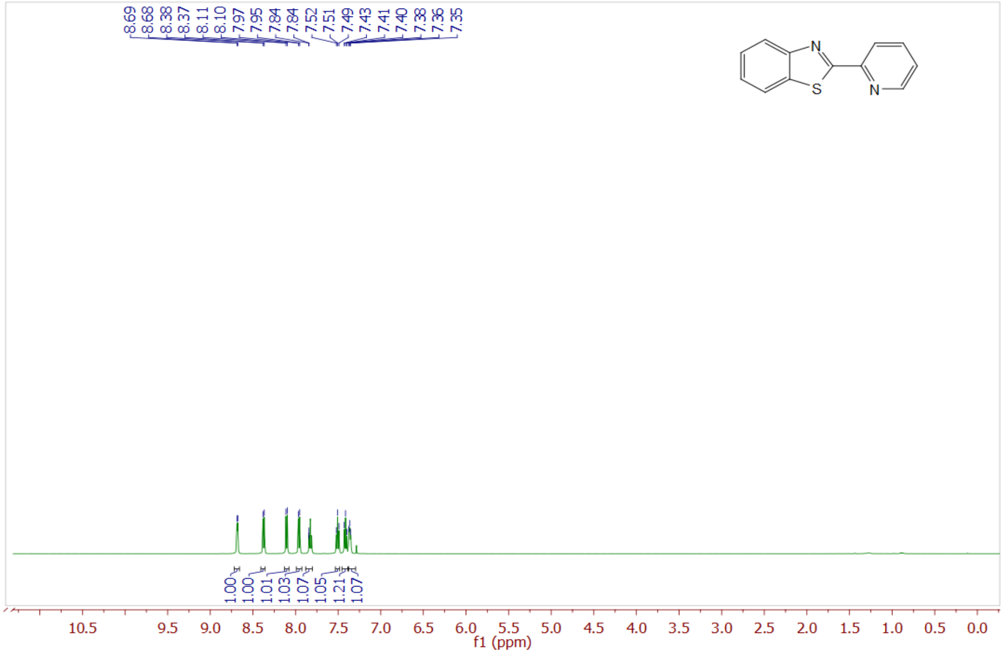


Figure 2.7 ^{1}H & ^{13}C NMR Spectrum of compound **3a**



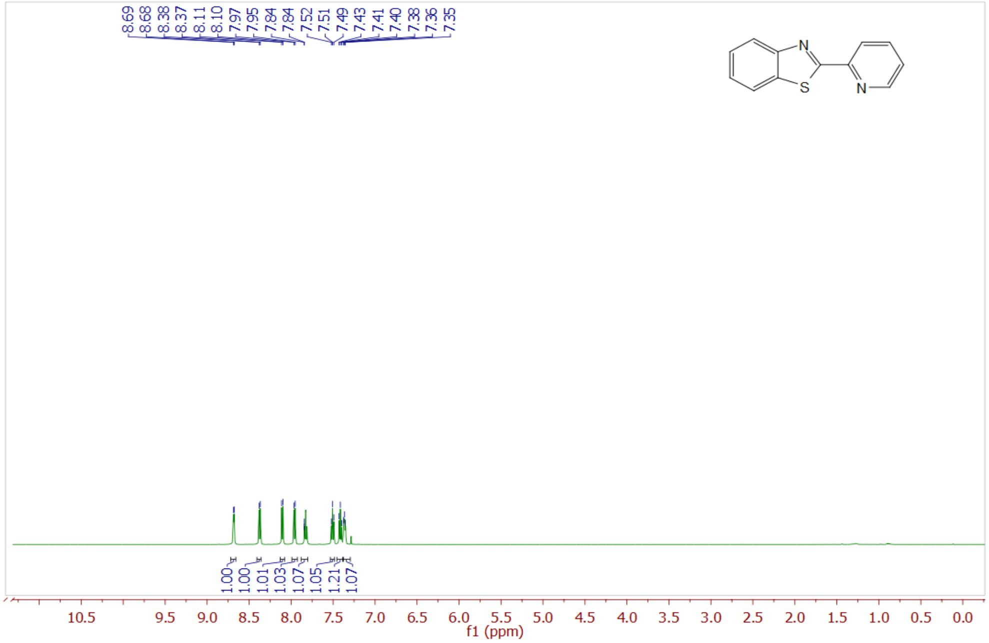


Figure 2.8 ^{1}H & ^{13}C NMR Spectrum of compound **3q**

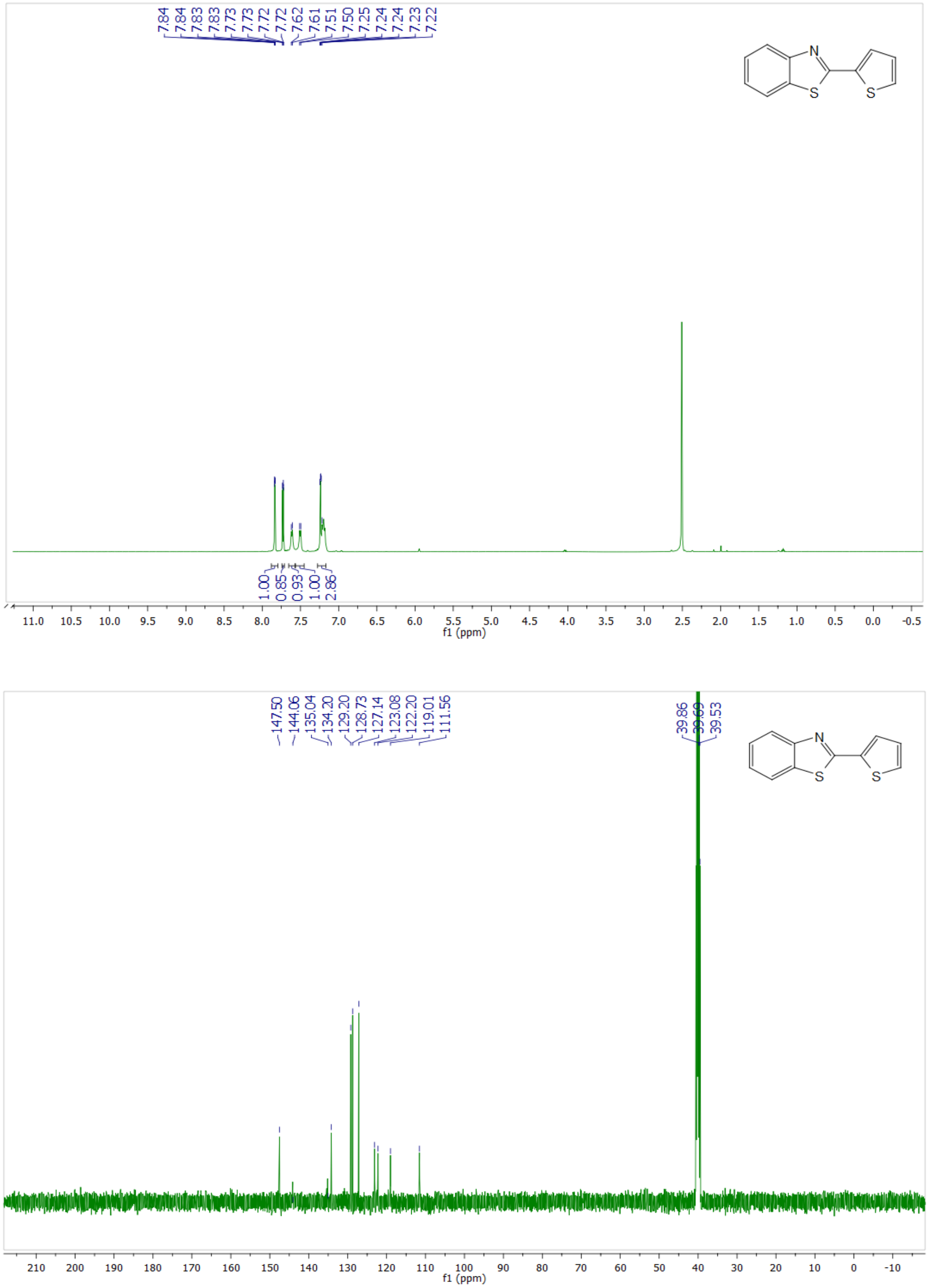


Figure 2.9 ^{1}H & ^{13}C NMR Spectrum of compound **3t**

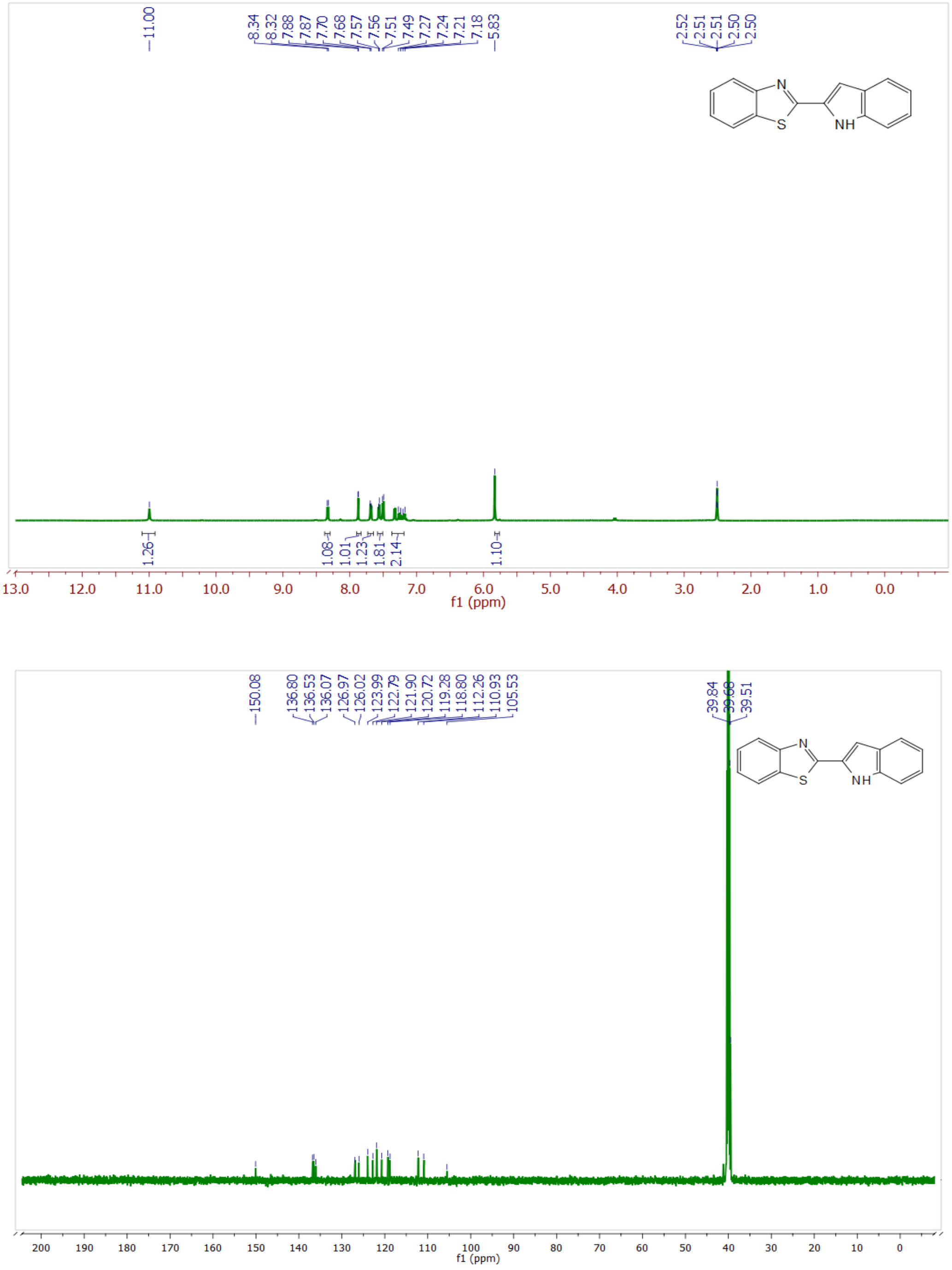


Figure 2.10 ^{1}H & ^{13}C NMR Spectrum of compound **3p**

2.8 HRMS Spectra

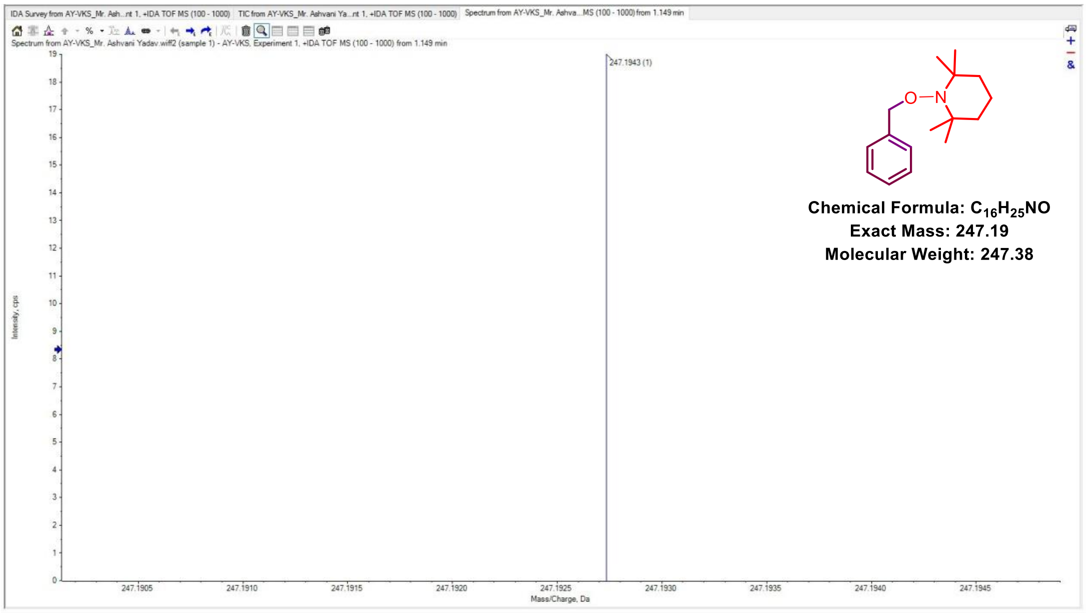


Figure 2.11 HRMS spectra of **5a**

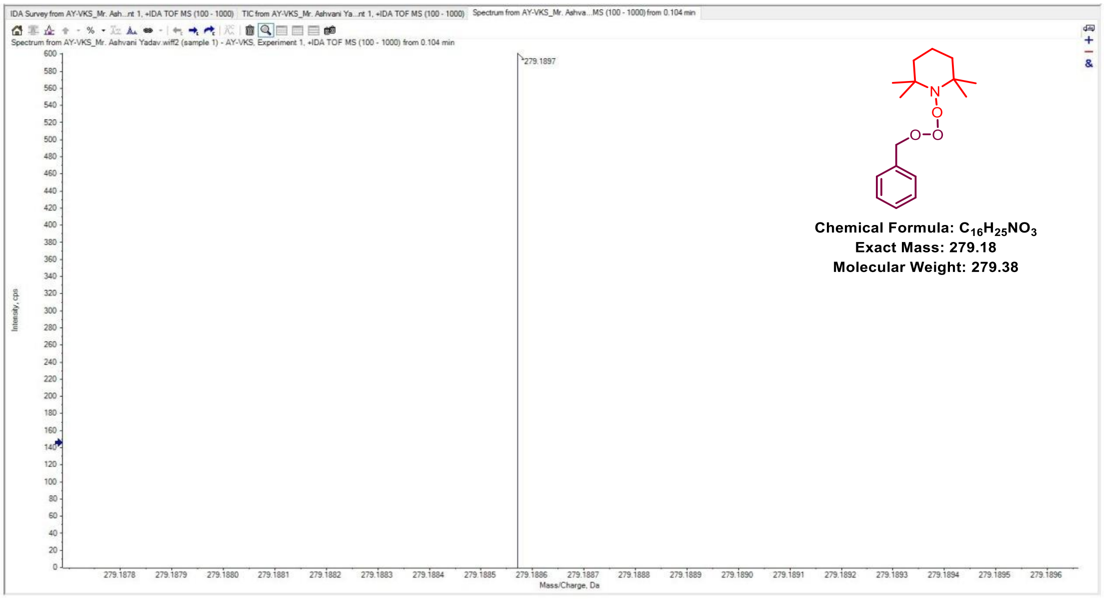


Figure 2.12 HRMS spectra of **6a**

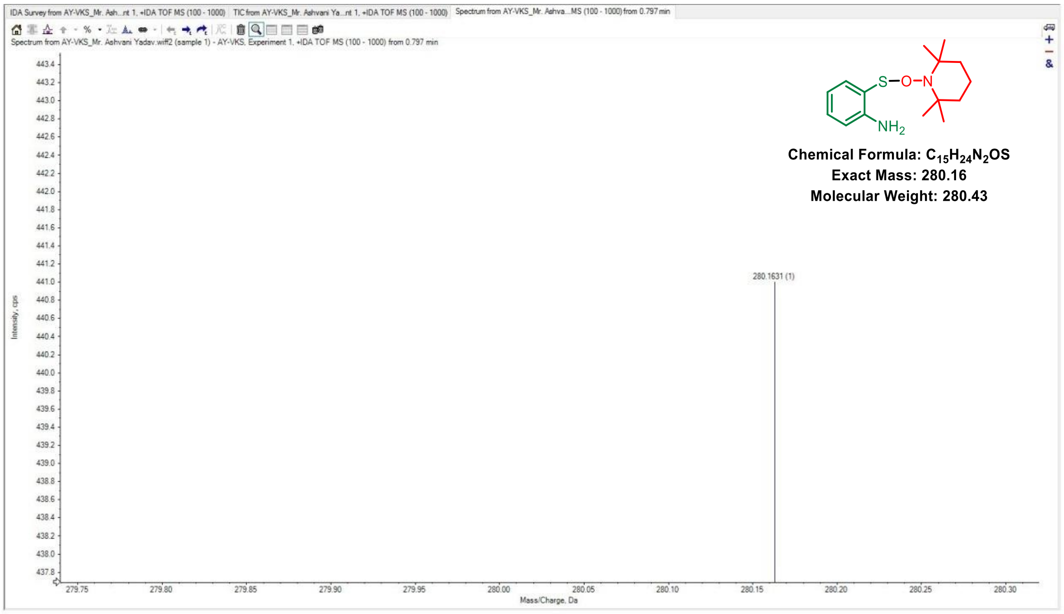


Figure 2.13 HRMS spectra of **7a**

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