2.1 Introduction

Recently, the visible light-initiated reaction is a flourishing, potent approach for the synthesis of bioactive organic compounds and is an emerging area of research to increase efficacy and synthetic utility. The visible light-initiated organic reaction has received great devotion because visible light is a pure, inexpensive, benign, easily operational, inexhaustible, and eco-friendly fresh energy source[1–14]. Additionally, Photoinduced reactions are relatively accelerated because the reaction vessel catches light from all directions.

Now a day, photoredox catalyst has been developed as an easy and powerful tool for activating organic molecules in visible light and has been used for many unique and valuable chemical reactions[15–17]. In many cases, visible-light-driven synthetic transformation usually focuses on the excited condition of photocatalysts as they are more reducing and oxidizing than their ground states. The visible light, with or without photocatalysts has established unbelievable revolutions in this 21st century and allowed various useful synthetic transformations, which were not approachable by traditional methods.[18–26] The substrate could be activated by an excited photocatalyst by single electron transfer (SET) or through the transfer of energy, leading to several competent synthetic conversions.[27–34]

Along with the above approach, a hydrogen-atom transfer (HAT) path is another photoactivation mode.[35,36] In photocatalysis, there are usually three modes of the HAT process. The activated photocatalyst abstracts a hydrogen atom from the substrate in the first mode. The catalytic cycle is then turned over to a newly produced intermediate via a reverse

HAT (RHAT).[37–41] Second, the excited photocatalyst activated one more catalyst. After activation, this catalyst stimulates the reaction through the Hydrogen atom transfer pathway.[42,43] The subsequent (3rd) path is the proton-coupled electron transfer (PCET) process, which involves coordinating an electron transfer and proton transfer from the reagent. This mode generates a radical that might be engaged in many transformations.[44,45] Meanwhile, the indirect Hydrogen atom transfer and proton-coupled electron transfer paths are possible in the presence of some additional reagents; direct Hydrogen atom transfer catalysis among all these paths is the utmost proficient and economical procedure. Though, the main restriction in place of the wide exploitation of the Hydrogen atom transfer process is insufficient for recognized photocatalysts, for example, uranyl cations, polyoxometalates[46], and aromatic ketone. Additionally, the photocatalyst above requires extra additives associated with unwanted side reactions. Hence, metal-free and sustainable catalysts that could support direct hydrogen atom transfer routes are needed.

Due to its low cost, easy handling, and environmentally friendly nature, Eosin Y has been used as an economically and ecologically superior photocatalyst alternative to transition metal complexes in organic photochemistry.

Recently, Eosin Y as a HAT photocatalyst has been exposed[47] for C-H functionalization. Based on reported works, we proposed that Eosin Y possibly will be the best HAT photocatalyst and may abstract a proton from benzylic C-H from benzylamine. (**Figure 2.1**)

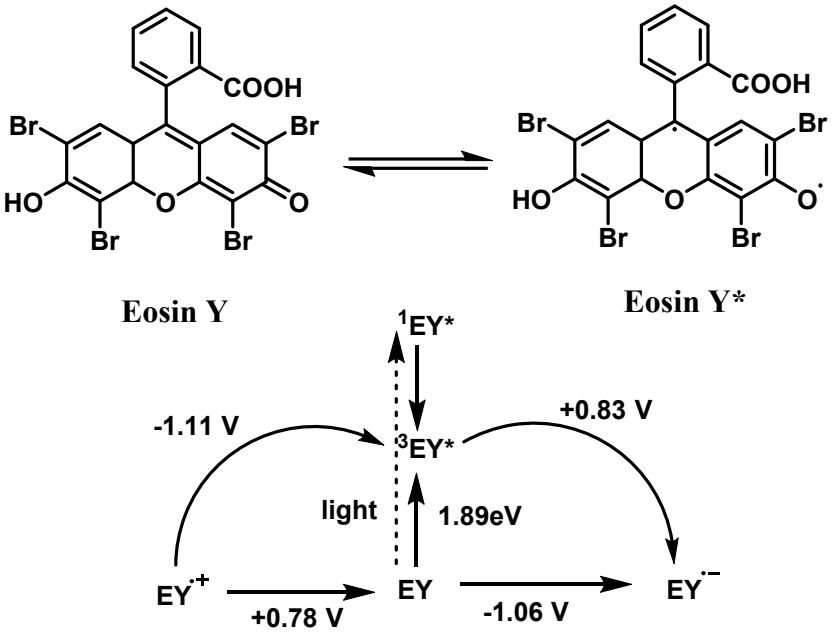


Figure 2.1 Photochemical and Electrochemical properties of Eosin Y

Among the biologically active N-containing heterocyclic moieties, imidazo[1,2-a]pyridines attribute substantial devotion to pharmacological manufacturing because of their extensive bioactivity antifungal[48,49], antiviral[50,51], antitumor, antiprotozoal, antibacterial[52], antiinflammatory[53], antipyretic, analgesic, antiapoptotic, enantioselective and hypnoselective, activities[54]. These compounds are not only of pharmaceutical importance, but they also have significant importance in material science. In recent times, imidazo [1,2-a]pyridine moiety was joined with some commercially available drugs[55,56] and used for the treatment of insomnia[57] (zolpidem), anxiolytic agent (alpidem), an agent for the treatment of peptic ulcer[58] (zolimidine) (**Figure 2.2**). As a result, hard work carries on just before the development of new approaches for the preparation of imidazo[1,2-a] pyridines. Several approaches were established to synthesize imidazo[1,2-a]pyridine, such as condensation[59],

oxidative coupling reaction[60], multicomponent reaction[61], aminooxygenation[62], hydroamination reaction[63], and tandem reaction.[64]

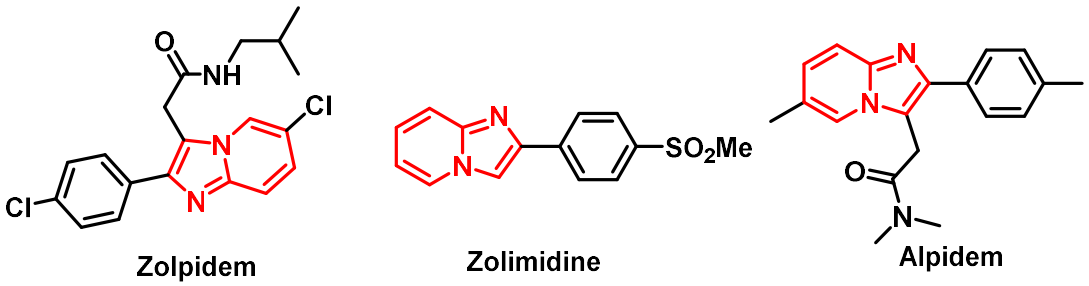
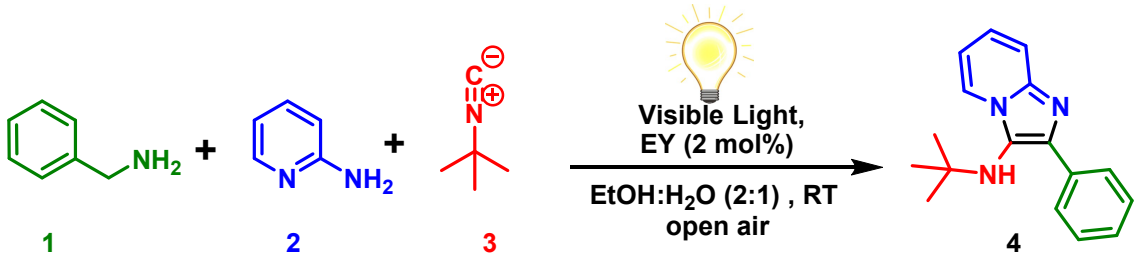


Figure 2.2 Some of the biologically active compounds containing imidazo[1,2-a]pyridine framework.

Despite the above methods, there is a need for the buildout of effective and viable visible-light-prompted preparation of imidazo[1,2-a] pyridines using photoinitiator Eosin Y. As far as we are aware, the preparation of imidazo[1,2-a]pyridines from a multicomponent reaction of benzylamine, 2-aminopyridine, and *t*-butylisocyanide via photocatalysis has not been reported yet. In view of the above, and as a part of our continuing research interest in the establishment of green and sustainable approaches for the production of biologically active compounds[65,66] herein, we report for the first time a visible light-promoted preparation of 3-aminoimidazo [1,2-a]pyridines via one-pot multicomponent reaction of benzylamine (**1**), 2-aminopyridine (**2**) and *t*-butylisocyanide (**3**) (**Scheme 2.1**).



Scheme 2.1 Synthesis of 3-aminoimidazo[1,2-a]pyridines via one-pot multicomponent reaction

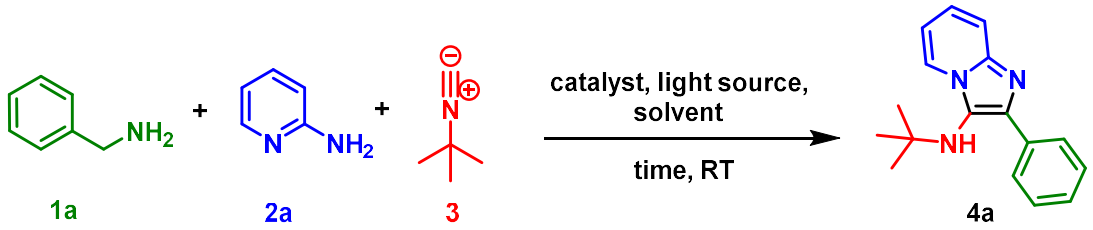
2.2 Results and Discussion

We started our observations using a visible-light-initiated multicomponent reaction of 2-aminopyridine (**2a**), benzylamine (**1a**), and tertiary butylisonitrile (**3**) as a model substrate under various reaction conditions. First of all, various solvents (green as well as conventional solvents), were examined for model reaction with 22 W white LED (light-emitting diode) under visible light in the presence of Eosin Y (2 mol %). Only a trace amount of product was obtained when the reaction was carried out with dichloromethane, CH_3CN, DMF, and DMSO solvent for 12 h at RT(room temperature) in the presence of photocatalyst Eosin Y (Table 2.1, entries 1−4). Pleasingly, the desired product **4a** was obtained in 45% and 51% yields with MeOH and EtOH, respectively (Table 2.1, entries 5 and 6). When the reaction was carried out in a mixture of a solvent such as EtOH/H_2O (1:1) and MeOH/H_2O (1:1), it led to a marginal increase in yield (81% and 63%, respectively) as well as the reduction in reaction time (6 h) (Table 2.1, entries 11 and 12). At this juncture, we thought of carrying out this reaction under the various ratio of ethanol and water solvent mixture. To our surprise, this led to a noticeable increase in yield (95%) when the ratio (EtOH: H_2O) is 2:1 (Table 2.1,

entry 13). The control examination showed that the dye is inevitable for this transformation (Table 2.1, entry 10).

Various organic photocatalysts such as rhodamine B, acridine red, and rose Bengal were screened, but none of them would match the catalytic efficacy of Eosin Y (Table 2.1, entries 7–9). The desired product was not obtained when the reaction was carried out at room temperature in the dark (Table 2.1, entry 19). This result indicates that visible light is a critical feature for this transformation. The energy source and intensities of visible light for the reaction were also optimized, and it was concluded that blue and green light could not give the product's desired yield (Table 2.1, entries 15-18).

Table 2.1 Optimization of the Reaction Conditions[a]



1a 2a 3 4a

entry	catalyst (mol%)	light Source	solvent	time (h)	yield[b]
1	eosin Y (2)	White light	DCM	12	trace
2	eosin Y (2)	White light	DMSO	12	trace
3	eosin Y (2)	White light	CH_3CN	12	trace
4	eosin Y (2)	White light	DMF	12	trace
5	eosin Y (2)	White light	MeOH	8	45

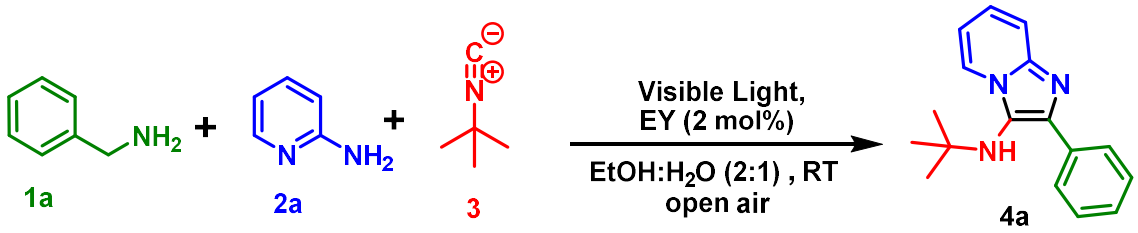
entry	catalyst (mol%)	light Source	solvent	time (h)	yield[b]
6	eosin Y (2)	White light	EtOH	6	51
7	rhodamine B (2)	White light	EtOH	12	32
8	rose bengal (2)	White light	EtOH	12	38
9	acridine red (2)	White light	EtOH	12	42
10	none	White light	EtOH	24	NR[c]
11	eosin Y (2)	White light	MeOH/H_2O (1:1)	6	63
12	eosin Y (2)	White light	EtOH/H_2O (1:1)	6	81
13	eosin Y (2)	White light	EtOH/H_2O (2:1)	3	95
14	eosin Y (2)	White light	EtOH/H_2O (5:1)	6	90
15[d]	eosin Y (2)	Blue light	EtOH/H_2O (1:1)	12	54
16	eosin Y (2)	Blue light	EtOH/H_2O (2:1)	6	56
17[e]	eosin Y (2)	Green light	EtOH/H_2O (1:1)	12	78
18	eosin Y (2)	Green light	EtOH/H_2O (2:1)	6	80
19	eosin Y (2)	dark	EtOH/H_2O (2:1)	12	trace
20[f]	eosin Y (2)	White light	EtOH/H_2O (2:1)	3	95

[a]Experimental condition: 2- Aminopyridine (1 mmol), Benzylamines (1 mmol), tertiary butyl isonitrile (1 mmol), solvent (3ml), room temperature, under visible light irradiation (22W, wavelength in range 380-780 nm) [b]Isolated yield [c]NR = no reaction [d]Blue light (455-660 nm) [e]Green light (520-525 nm) [f]The reaction was carried out in 10 mmol scale.

Additionally, to confirm the synthetic efficacy of the reaction, a gram scale reaction was carried out (10 mmol scales), and it was found that the reaction proceeded smoothly with the same efficiency, which emphasized the synthetic rewards of this procedure (Table 2.1, entry 20).

Now we carried out this experiment using light of different intensities (8W, 13W, 15W, 18W, 22W, and 32W) to find the optimal intensity of visible light needed for this reaction. It was observed that the yields and reaction times were the same when 22 W and 32 W white-light-emitting diodes (LED) were used. However, when LED of lower intensities was used, a marginal decrease in the yield and rate of the reaction was observed (Table 2.2, entries 1, 2, 3, and 4). On the other hand, using an LED of higher wattage (32 W) did not substantially increase the product yield or the reaction time (**Figure 2.3**).

Table 2.2: Effect of the visible light intensity on the reaction[a]



entry	visible light Intensity	time (h)	yield (%)[b]
1	8 W	8	75
2	13 W	6	82
3	15 W	4.5	85
4	18 W	4	89
5	22 W	3	95
6	32 W	3	95

[a]All reaction was carried out using **1** (1 mmol), **2** (1 mmol), and **3** (1 mmol) at room temperature under air. [b]Isolated yield

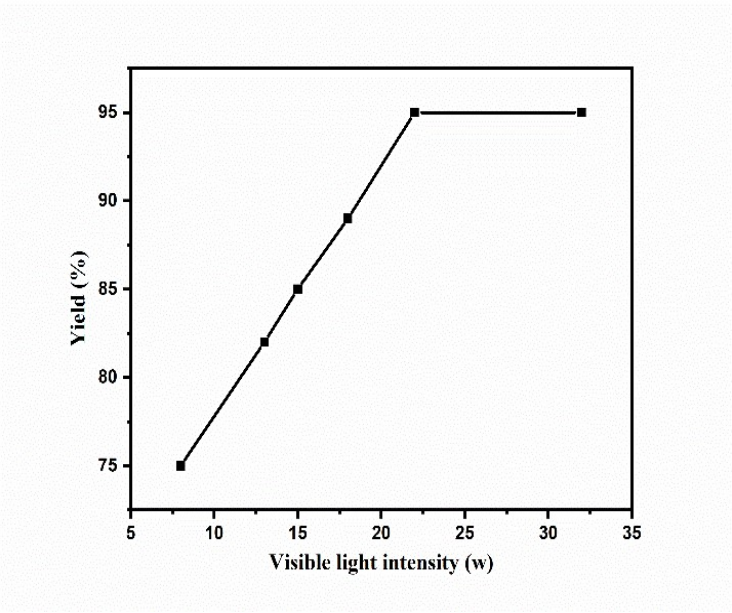
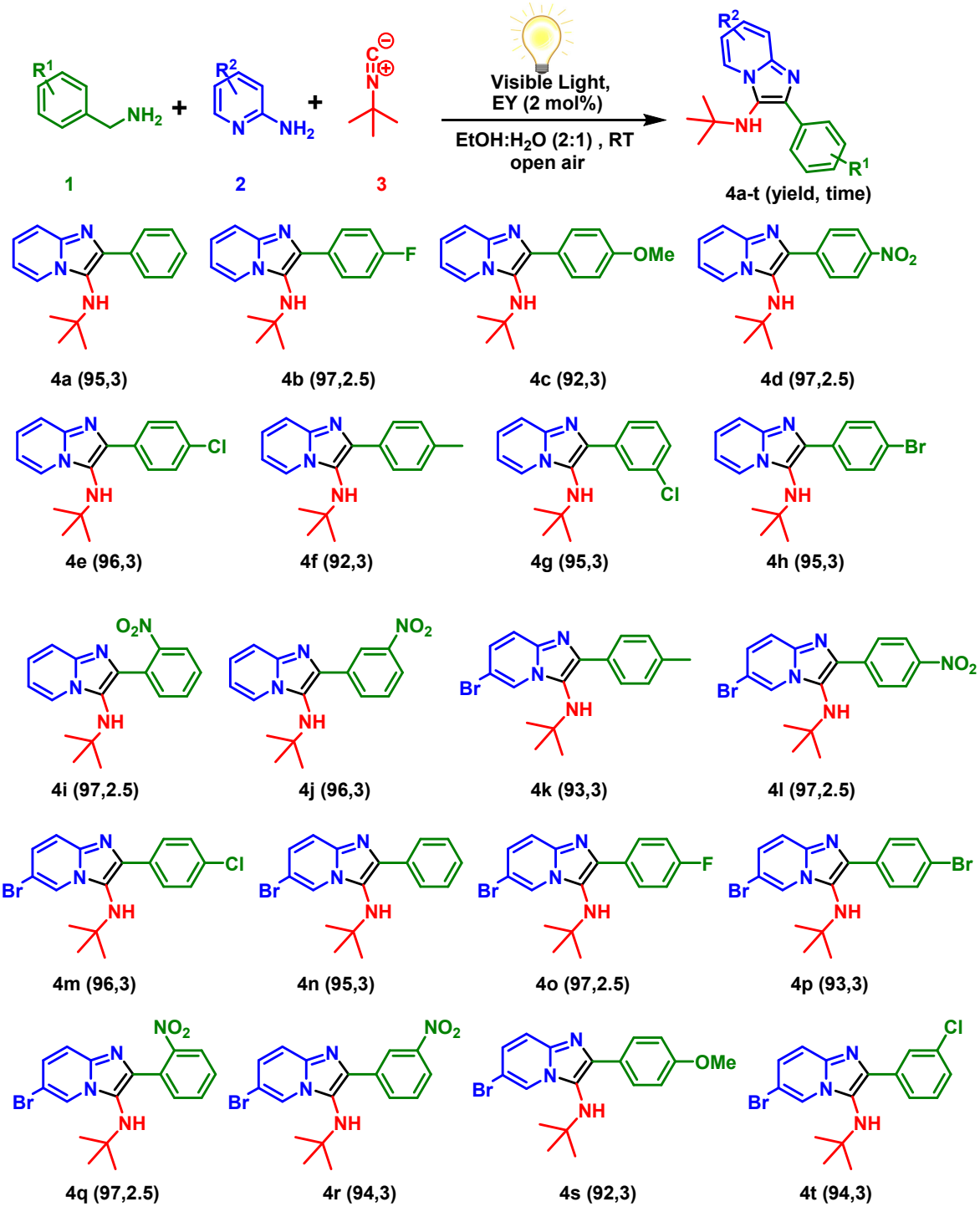


Figure 2.3. Yield (%) vs visible light intensity for the preparation of *N*-(tert-butyl)-2-phenylimidazo[1,2-a]pyridin-3-amine

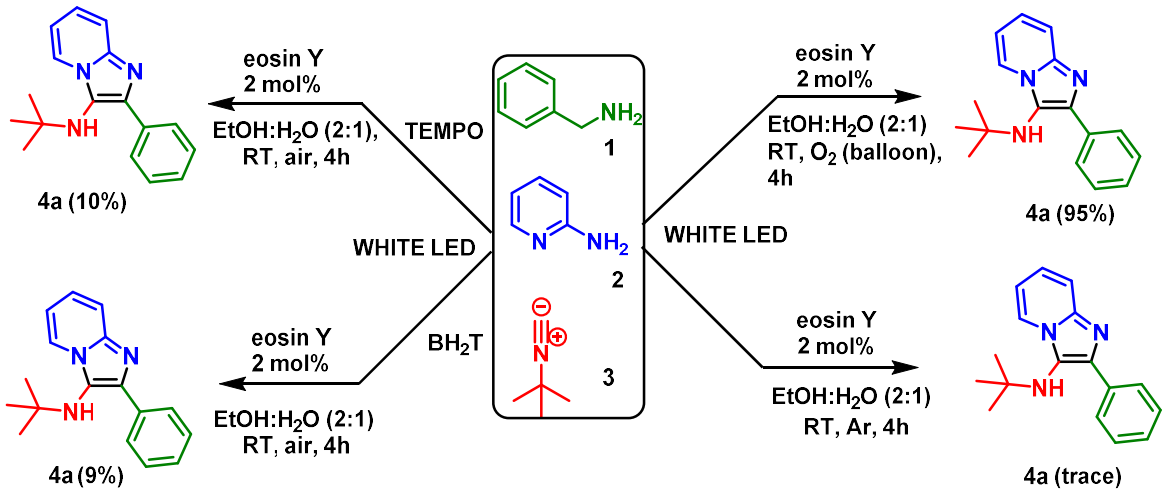
Once ideal conditions for carrying out this reaction had been identified, the scope and limitations of the developed synthetic strategy were explored for the preparation of various 3-Aminoimidazo-fused pyridines derivatives under the optimized condition by reacting a variety of benzylamine with 2-aminopyridine and 5-Bromo 2-aminopyridine and tertiary butyl isonitrile (Table 2.3). It has been indicated that the use of benzylamine containing an electron-withdrawing group (-NO_2 and -F) led to higher yields and faster reaction, while an electron-donating group (-Me and –OMe) on benzylamine slowed down the reaction and led to a reduction in the yield of the product.

Table 2.3 Substrate scope and versatility of reaction



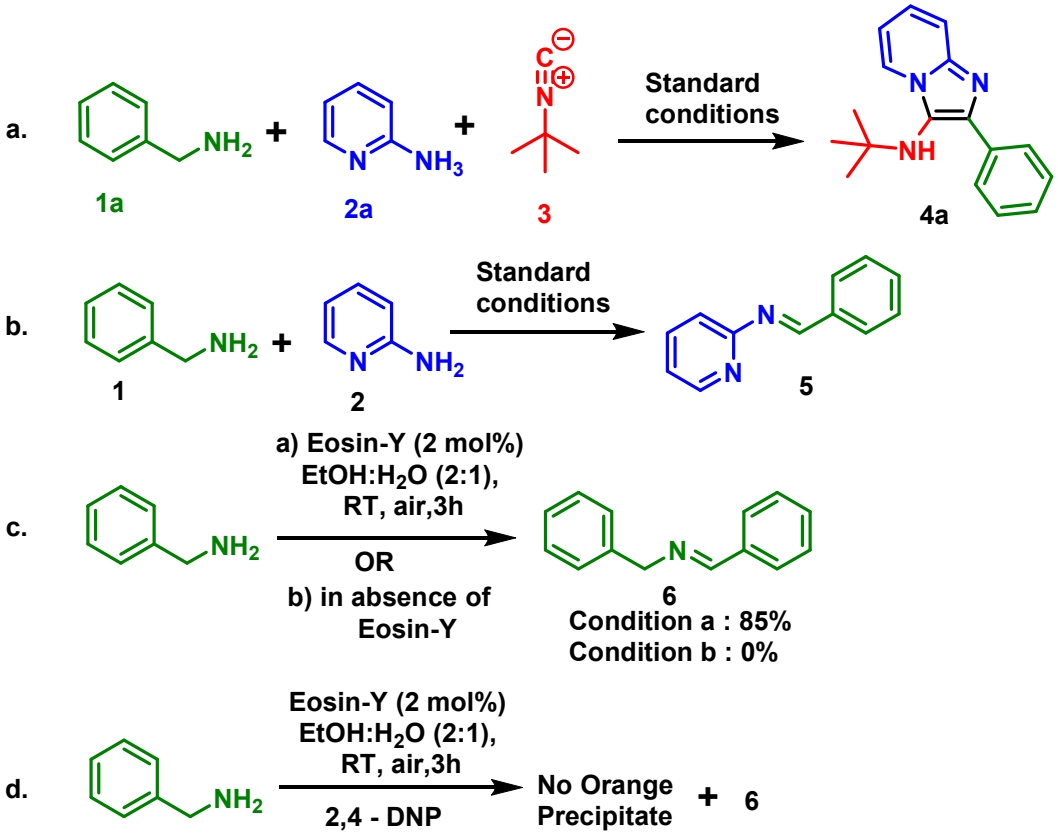
Experimental condition: 2- Aminopyridine (1 mmol), Benzylamines (1 mmol), tertiary butyl isonitrile (1 mmol), solvent (3ml), room temperature, under visible light irradiation (22W, wavelength in range 380-780 nm)

2.3 Control Experiment



Scheme 2.2 Control experiments

In order to recognize the mechanism, some control experiments were carried out with the help of radical scavenger TEMPO and BHT. **(Scheme 2.2)** There is an extreme reduction in the yield (9-11%) of the desired product **4a** in the presence of a radical scavenger**,** confirming the involvement of the radical mechanism. Further, to examine the effect of O_2 (oxygen), the reaction was carried out under an oxygen balloon. But there is no significant increase in the product yield, and a negligible amount of product was observed while the reaction was performed in the presence of argon, i.e., in the absence of oxygen. This result indicates that oxygen is necessary for this transformation.



Scheme 2.3 Control experiments

To support the path of the reaction, a couple of control experiment was carried out. **(Scheme 2.3)** Product **4a** was produced by the multicomponent reaction of benzylamine (1mmol), 2-aminopyridine (1mmol), and tertiary butyl isonitrile (1mmol) under standard reaction conditions (eq a). We suspected the intermediacy of imine; to confirm this, the reaction of 2-aminopyridine (1.0 equiv) with benzylamine (1.0 equiv) was carried out, which produces **5** **(Scheme 2.3, eq b)** under the optimized reaction conditions. This indicates imine to be a likely intermediate in the formation of product **4a**. To check the formation of imine intermediate in the reaction, the benzylamine was irradiated with visible light in EtOH: H_2O

(2:1) in the presence of EosinY at room temperature, which gave imine **6** in good yield. **(Scheme 2.3, eq c)** While a similar experiment was carried out under the same condition with 2,4-DNP, no orange precipitate was formed. **(Scheme 2.3, eq d)** This experiment omits the formation of benzaldehyde in the current procedure by using Eosin Y as photoredox catalyst.

2.3.1 UV-Vis absorption experiment

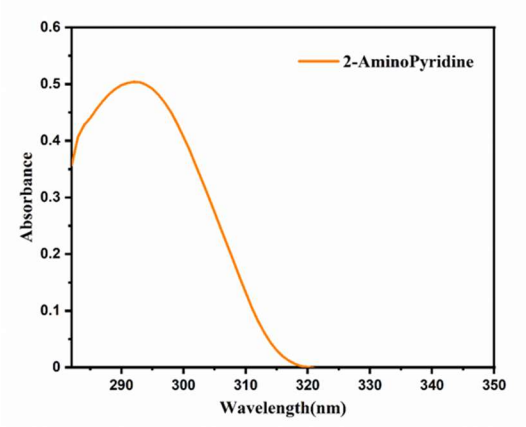


Figure 2.4 UV-Vis spectrum of 2-Amino Pyridine in chloroform (Conc. 1.0 x 10^{-4} mol/L)

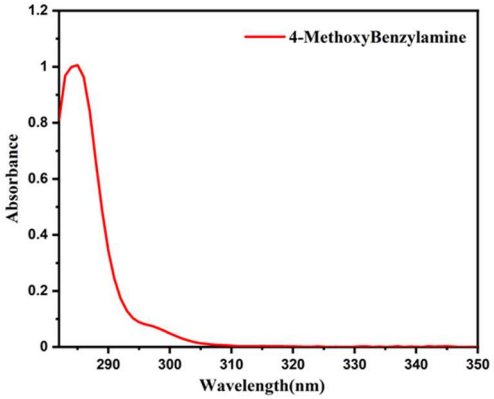
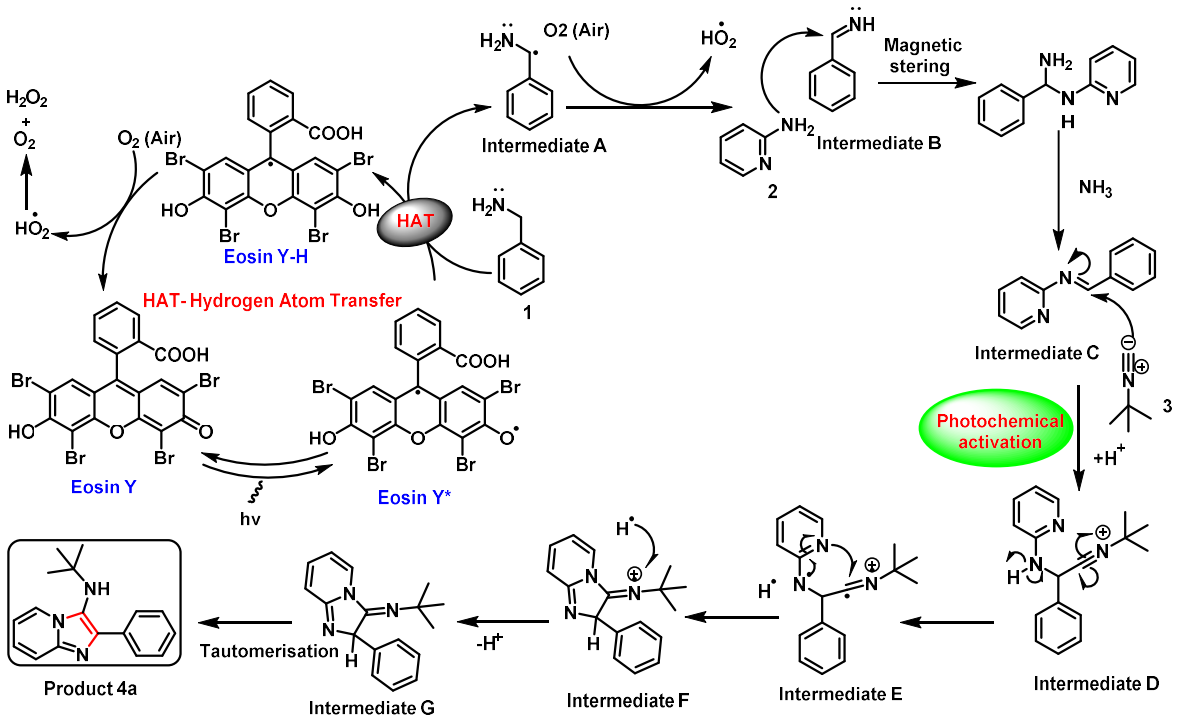


Figure 2.5 UV-Vis spectrum of 4-Methoxybenzyl amine in chloroform (Conc. 1.25 x 10^{-4} mol/L)

2.4 Proposed Mechanism

According to the previous reports[67–75] and based on control experiments, a possible pathway for the overall process was proposed. **(Scheme 2.5)** From the value of its redox potential, it is clear that Eosin Y is not responsible for the oxidation of benzylamine because the SET mode for this reaction was not valid. Initially, excited Eosin Y (EY*) was formed from Eosin Y (EY) through excitation with visible light, which extracts the hydrogen atom from benzylic amine to generate intermediate A. Subsequently, the oxidation of intermediate **A** gives benzylimine intermediate **B**. Reaction of benzylimine **B** with 2-aminopyridine **2** leads to the formation of imine intermediate **C** with the liberation of ammonia, which was afterward attacked by the isocyanide **3** to provide intermediate **D**. This intermediate **D** influenced by visible light radiation to generate free radical which was further cyclized followed by a 1,3-H shift to give the desired product.



Scheme 2.5 Plausible mechanism

2.5 Conclusions

In brief, an effective procedure to get various type of 3-aminoimidazo[1,2-a]pyridines through the visible-light-initiated multicomponent reaction of benzylamine, 2-aminopyridine, and *t*-butylisocyanide have been developed using an economical HAT photocatalyst Eosin Y dye at room temperature. Strangely, this approach is practically simple, profitable, environment-friendly, additive-/metal-free, and also shows outstanding compatibility with both electron-donating and the electron-withdrawing functional group containing benzylamine. This approach presents a promising alternative to the existing

method, accordingly extending the scope of photocatalyzed reaction, which overcomes the problem associated with the environmentally notorious metal-catalyzed reaction.

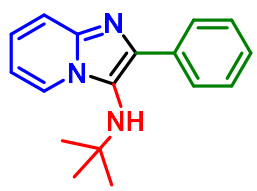
2.6 Experimental Procedures

2.6.1 General procedure for the preparation of compounds 4a-4t

Benzylamine **1** (1 mmol), 2-aminoheterocycle **2** (1 mmol), isocyanide **3** (1 mmol), and Eosin Y (2 mol%) were taken with 2:1 EtOH/H_2O (3 mL) in a 50 ml round bottom flask which was furnished with a magnetic stirrer bar. This mixture was agitated with 22 W white LEDs under visible light at room temperature. When the reaction was completed (monitored by TLC), water was added to stop the reaction. Subsequently, ethyl acetate was added to it to extract an aqueous layer. After that, it was dried over anhydrous $MgSO_4$. The crude product was obtained by evaporation of the solvent under reduced pressure. The crude product was purified using column chromatography over silica gel (100-200 mesh) (ethyl acetate/hexane:20/80) to provide pure product **4** in excellent yields.

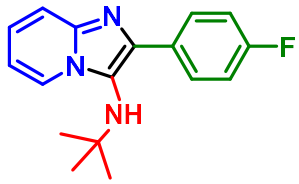
2.7 Characterization of products

N-(tert-butyl)-2-phenylimidazo[1,2-a]pyridin-3-amine (4a)



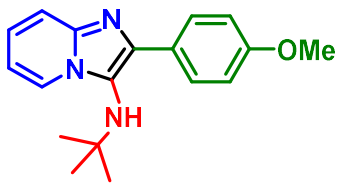
White solid (95%), mp 160– 162°C. IR (KBr, cm^{-1}): 3310 (NH), 2966 (sp^2-CH), 2934 (sp^3-CH), 1610, 1506, 1441, 1350, 1321, 1216, 1037, 756. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 6.9 Hz, 1H), 7.90 (d, *J* = 7.1 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 6.2 Hz, 1H), 7.16 – 7.09 (m, 1H), 6.77 (t, *J* = 6.8 Hz, 1H), 3.16 (s, 1H), 1.02 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.81, 139.13, 134.91, 129.74, 128.29, 128.18, 127.47, 124.32, 123.54, 117.14, 111.48, 56.44, 30.29. Anal. calcd for $C_{17}H_{19}N_3$: C, 76.95; H, 7.22; N, 15.84; found: C,76.93; H,7.20; N, 15.80

N-(tert-butyl)-2-(4-fluorophenyl)imidazo[1,2-a]pyridin-3-amine (4b)



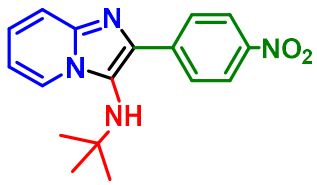
White solid (97%), mp 163-165°C. IR (KBr, cm^{-1}): 3296 (N-H), 2966 (sp^2-CH), 2934 (sp^3-CH), 1610, 1506, 1441, 1350, 1321, 1216, 1037, 756. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.9 Hz, 1H), 7.94 (dd, *J* = 8.3, 6.1 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.13 (t, *J* = 7.7 Hz, 2H), 6.84 – 6.79 (m, 1H), 3.12 (s, 1H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.25, 141.71, 138.12, 129.88, 129.82, 124.58, 123.42, 117.03, 115.34, 115.17, 111.71, 56.43, 30.35. Anal. Calcd for $C_{17}H_{18}FN_3$; C, 72.06; H, 6.40; N, 14.83 found: C, 72.03; H, 6.37; N, 14.80.

N-(tert-butyl)-2-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-amine (4c)



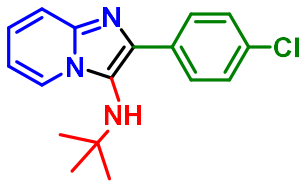
Off-white solid (92%), mp 142°C. IR (KBr, cm^{-1}): 3315 (NH), 2968 (sp^2-CH), 2925 (sp^3-CH), 1630, 1513, 1433, 1366, 1339, 1206, 1027, 716. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 6.9 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.15 – 7.10 (m, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.77 (t, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 3.12 (s, 1H), 1.05 (s, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 159.09, 141.77, 139.13, 129.35, 127.57, 124.04, 123.41, 122.91, 116.97, 113.70, 111.30, 56.30, 55.23, 30.34. Anal. Calcd for $C_{18}H_{21}N_3O$; C, 73.19; H, 7.17; N, 14.23 found: C, 73.16; H, 7.14; N, 14.21.

N-(tert-butyl)-2-(4-nitrophenyl)imidazo[1,2-a]pyridin-3-amine (4d)



Reddish brown solid (97%), mp 205°C. IR (KBr, cm^{-1}): 3303 (NH), 2935 (sp^2-CH), 2907 (sp^3-CH), 1584, 1476, 1424, 1343 (CN), 1315, 1191, 1007, 763. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 4H), 8.22 (d, *J* = 6.9 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.86 (t, *J* = 7.2 Hz, 1H), 3.15 (s, 1H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.74, 142.27, 141.48, 136.67, 128.46, 125.41, 124.92, 123.59, 123.49, 117.51, 112.26, 56.85, 30.50. Anal. Calcd for $C_{17}H_{18}N_4O_2$; C, 65.79; H, 5.85; N, 18.05 found: C, 65.77; H, 5.83; N, 18.03.

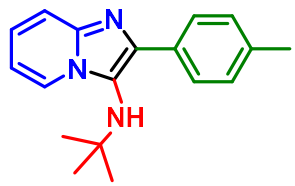
N-(tert-butyl)-2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-amine (4e)



Light orange solid (96%), mp 160-163°C. IR (KBr, cm^{-1}): 3320 (NH), 2962 (sp^2-CH), 2924 (sp^3-CH), 1600, 1506, 1441, 1360 (CN), 1331, 1206, 1027, 746. ^{1}H NMR (500 MHz, $CDCl_3$) δ

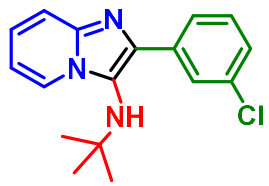
8.21 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 10.0 Hz, 1H), 7.39 (d, *J* = 11.2 Hz, 2H), 7.19 – 7.14 (m, 1H), 6.80 (t, *J* = 6.8 Hz, 1H), 3.10 (s, 1H), 1.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.89, 138.03, 133.42, 133.22, 131.05, 129.29, 129.04, 128.40, 124.59, 123.53, 123.45, 117.15, 111.67, 56.51, 30.28. Anal. Calcd for $C_{17}H_{18}ClN_3$; C, 68.11; H, 6.05; N, 14.02 found: C, 68.08; H, 6.01; N, 14.00.

N-(tert-butyl)-2-(p-tolyl)imidazo[1,2-a]pyridin-3-amine (4f)



White solid (92%), mp 170°C. IR (KBr, cm^{-1}): 3320 (NH), 2962 (sp^2-CH), 2924 (sp^3-CH), 1600, 1506, 1441, 1360 (CN), 1331, 1206, 1027, 746. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.25 (t, *J* = 14.3 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.75 (t, *J* = 6.7 Hz, 1H), 3.15 (s, 1H), 2.39 (s, 3H), 1.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.84, 139.35, 136.98, 132.16, 129.00, 127.99, 124.01, 123.47, 123.28, 117.09, 111.27, 56.19, 30.07, 21.43. Anal. Calcd for $C_{18}H_{21}N_3$; C, 77.38; H, 7.58; N, 15.04 found: C, 77.35; H, 7.55; N, 15.01.

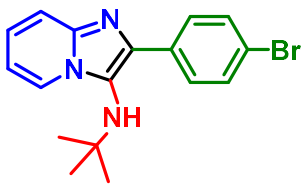
N-(tert-butyl)-2-(3-chlorophenyl)imidazo[1,2-a]pyridin-3-amine (4g)



Orange solid (95%), mp 148°C. IR (KBr, cm^{-1}): 3313 (NH), 2955 (sp^2-CH), 2917 (sp^3-CH), 1607, 1499, 1434, 1363 (CN), 1324, 1213, 1020, 752. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 6.9 Hz, 1H), 8.03 (t, *J* = 1.8 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.19 – 7.14 (m, 1H), 6.80 (t, *J* = 6.3 Hz, 1H), 2.98 (s, 1H), 1.07 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.01, 137.84, 136.84, 134.20, 129.51, 128.10,

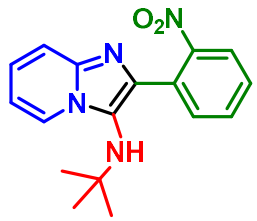
127.42, 126.12, 124.61, 123.46, 117.31, 111.70, 56.51, 30.42. Anal. Calcd for $C_{17}H_{18}ClN_3$; C, 68.11; H, 6.05; N, 14.02 found: C, 68.09; H, 6.02; N, 14.01.

2-(4-bromophenyl)-N-(tert-butyl)imidazo[1,2-a]pyridin-3-amine (4h)



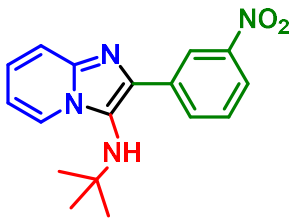
Yellow solid (95%), mp 143-148°C. IR (KBr, cm^{-1}): 3313 (NH), 2955 (sp^2-CH), 2924 (sp^3-CH), 1600, 1506, 1441, 1360 (CN), 1331, 1206, 1027, 746. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 6.9 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 3H), 7.19 – 7.13 (m, 1H), 6.80 (t, *J* = 7.2 Hz, 1H), 3.07 (s, 1H), 1.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.00, 138.17, 134.01, 131.40, 129.58, 124.52, 123.54, 123.44, 121.45, 117.25, 111.64, 55.91, 30.41. Anal. Calcd for $C_{17}H_{18}BrN_3$; C, 59.31; H, 5.27; N, 12.21 found: C, 59.28; H, 5.24; N, 12.18.

N-(tert-butyl)-2-(2-nitrophenyl)imidazo[1,2-a]pyridin-3-amine (4i)



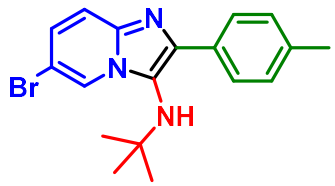
Brown solid (97%), mp 183-185°C. IR (KBr, cm^{-1}): 3312 (NH), 2954 (sp^2-CH), 2916 (sp^3-CH), 1592, 1498, 1449, 1352, 1323, 1199, 1019, 738. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 6.9 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.20 – 7.13 (m, 1H), 6.81 (t, *J* = 6.8 Hz, 1H), 2.75 (s, 1H), 0.95 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.46 (s), 142.40 (s), 136.16 (s), 132.82 (s), 130.21 (s), 128.40 (s), 124.67 (s), 124.34 (d, *J* = 17.5 Hz), 123.34 (s), 117.70 (s), 111.79 (s), 30.04 (s). Anal. Calcd for $C_{17}H_{18}N_4O_2$; C, 65.79; H, 5.85; N, 18.05 found: C, 65.76; H, 5.82; N, 18.02.

N-(tert-butyl)-2-(3-nitrophenyl)imidazo[1,2-a]pyridin-3-amine (4j)



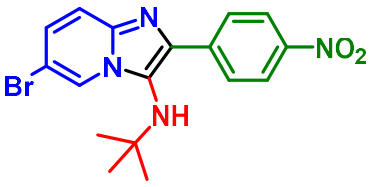
White solid (96%), mp 171°C. IR (KBr, cm^{-1}): 3311 (NH), 2953 (sp^2-CH), 2915 (sp^3-CH), 1591, 1506, 1441, 1360, 1331, 1206, 1018, 737. ^1H NMR (500 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.44 (d, *J* = 7.7 Hz, 1H), 8.20 (d, *J* = 6.9 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.58 (dd, *J* = 20.1, 8.6 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.83 (t, *J* = 6.5 Hz, 1H), 3.05 (s, 1H), 1.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.17 (s), 142.39 (s), 137.00 (d, *J* = 5.7 Hz), 133.75 (s), 129.20 (s), 124.85 (s), 124.07 (s), 123.37 (s), 122.63 (s), 121.95 (s), 117.62 (s), 111.94 (s), 30.56 (s). Anal. Calcd for $C_{17}H_{18}N_4O_2$; C, 65.79; H, 5.85; N, 18.05 found: C, 65.75; H, 5.81; N, 18.01.

6-bromo-N-(tert-butyl)-2-(p-tolyl)imidazo[1,2-a]pyridin-3-amine (4k)



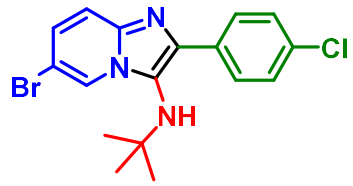
Off-white solid (93%), mp 128-130°C. IR (KBr, cm^{-1}): 3280 (N-H), 2946 (sp^2-CH), 2914 (sp^3-CH), 1610, 1501, 1461, 1363, 1341, 1231, 1067, 716. ^1H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 9.4 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 9.4 Hz, 1H), 3.15 (s, 1H), 2.39 (s, 3H), 1.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.44, 140.24, 137.44, 131.72, 129.08, 127.96, 127.29, 123.67, 123.63, 117.85, 106.23, 56.53, 30.31, 21.34. Anal. Calcd for $C_{18}H_{20}BrN_3$; C, 60.34; H, 5.63; N, 11.73 found: C, 60.32; H, 5.61; N, 11.71.

6-bromo-N-(tert-butyl)-2-(4-nitrophenyl)imidazo[1,2-a]pyridin-3-amine (4l)



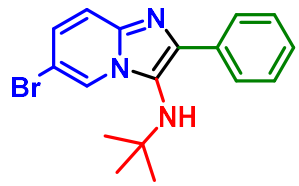
Brown solid (97%), mp 203°C. IR (KBr, cm^{-1}): 3300 (N-H), 3010 (sp^2-CH), 2990 (sp^3-CH), 1590, 1490, 1432, 1328, 1317, 1206, 1007, 766. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.29 (d, *J* = 8.9 Hz, 2H), 8.22 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 9.4 Hz, 1H), 7.26 (d, *J* = 9.4 Hz, 1H), 3.08 (s, 1H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.91, 141.28, 140.80, 140.71, 137.87, 128.57, 128.49, 125.03, 123.65, 118.37, 107.18, 56.77, 30.49. Anal. Calcd for $C_{17}H_{17}BrN_4O_2$; C, 52.46; H, 4.40; N, 14.39 found: C, 52.43; H, 4.37; N, 14.36.

6-bromo-N-(tert-butyl)-2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-amine (4m)



White solid (96%), mp 191°C. IR (KBr, cm^{-1}): 3301 (N-H), 3001 (sp^2-CH), 2984 (sp^3-CH), 1598, 1498, 1424, 1326, 1317, 1210, 1012, 748. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.37 (t, *J* = 9.0 Hz, 3H), 7.16 (d, *J* = 9.4 Hz, 1H), 3.07 (s, 1H), 1.02 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.33, 139.28, 133.31, 129.30, 128.49, 127.67, 123.82, 123.60, 117.95, 106.49, 56.49, 30.28. Anal. Calcd for $C_{17}H_{17}BrClN_3$; C, 53.92; H, 4.52; N, 11.10 found: C, 53.91; H, 4.51; N, 11.09.

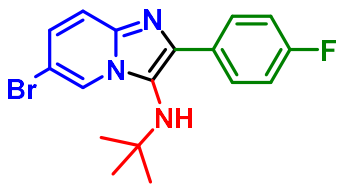
6-bromo-N-(tert-butyl)-2-phenylimidazo[1,2-a]pyridin-3-amine (4n)



White solid (95%), mp 230°C. IR (KBr, cm^{-1}): 3290 (N-H), 3052 (sp^2-CH), 2961 (sp^3-CH), 1601, 1506, 1436, 1357, 1321, 1226, 1037, 775. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.88 (d, *J* = 9.4 Hz, 2H), 7.47 – 7.42 (m, 3H), 7.34 (t, *J* = 6.8 Hz, 1H), 7.20 (dd, *J* = 9.4, 1.9 Hz, 1H),

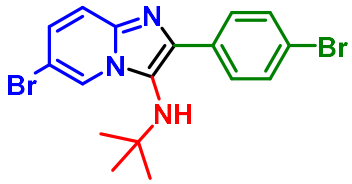
3.18 (s, 1H), 1.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.24, 134.53, 129.75, 128.39, 128.15, 127.76, 127.61, 127.45, 123.89, 123.75, 117.91, 56.58, 30.28. Anal. Calcd for $C_{17}H_{18}BrN_3$; C, 59.31; H, 5.27; N, 12.21 found: C, 59.29; H, 5.25; N, 12.19.

6-bromo-N-(tert-butyl)-2-(4-fluorophenyl)imidazo[1,2-a]pyridin-3-amine (4o)



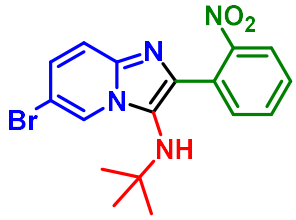
White solid (97%), mp 215°C. IR (KBr, cm^{-1}): 3280 (N-H), 2976 (sp^2-CH), 2940 (sp^3-CH), 1600, 1505, 1438, 1358, 1291, 1206, 1029, 776. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 2.4 Hz, 1H), 7.89 (dd, J = 8.8, 5.5 Hz, 2H), 7.44 (d, J = 9.8 Hz, 1H), 7.22 (d, J = 9.4 Hz, 1H), 7.13 (t, J = 8.7 Hz, 2H), 3.09 (s, 1H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.46, 140.21, 139.41, 129.82, 127.70, 123.67, 123.59, 117.85, 115.45, 115.28, 106.60, 56.54, 30.35. Anal. Calcd for $C_{17}H_{17}BrFN_3$; C, 56.37; H, 4.73; N, 11.60 found: C, 56.33; H, 4.69; N, 11.56.

6-bromo-2-(4-bromophenyl)-N-(tert-butyl)imidazo[1,2-a]pyridin-3-amine (4p)



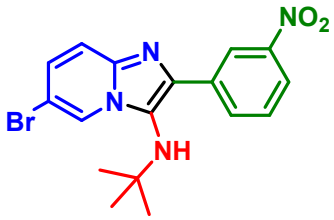
White solid (93%), mp 185°C. IR (KBr, cm^{-1}): 3313 (N-H), 2914 (sp^2-CH), 2910 (sp^3-CH), 1627, 1549, 1493, 1347, 1321, 1229, 1119, 753. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 9.4 Hz, 1H), 7.20 (d, J = 9.4 Hz, 1H), 3.04 (s, 1H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.46, 139.35, 133.71, 131.49, 129.62, 127.74, 123.81, 123.62, 121.75, 118.04, 106.55, 56.63, 30.40. Anal. Calcd for $C_{17}H_{17}Br_2N_3$; C, 48.25; H, 4.05; N, 9.93 found: C, 48.22; H, 4.02; N, 9.90.

6-bromo-N-(tert-butyl)-2-(2-nitrophenyl)imidazo[1,2-a]pyridin-3-amine (4q)



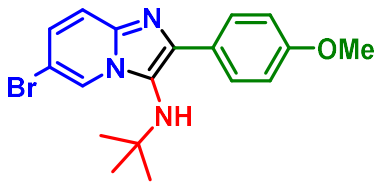
Brown solid (97%), mp 180°C. IR (KBr, cm^{-1}): 3290 (N-H), 2967 (sp^2-CH), 2930 (sp^3-CH), 1618, 1523, 1451, 1330, 1331, 1286, 1047, 760. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.1 Hz, 1H), 7.50 (t, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 9.4 Hz, 1H), 7.21 (d, *J* = 9.4 Hz, 1H), 2.75 (s, 1H), 0.94 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.37, 140.69, 137.08, 132.72, 132.54, 129.77, 128.73, 127.92, 125.03, 124.37, 123.58, 118.40, 106.95, 55.75, 30.04. Anal. Calcd for $C_{17}H_{17}BrN_4O_2$; C, 52.46; H, 4.40; N, 14.39 found: C, 52.42; H, 4.36; N, 14.35.

6-bromo-N-(tert-butyl)-2-(3-nitrophenyl)imidazo[1,2-a]pyridin-3-amine (4r)



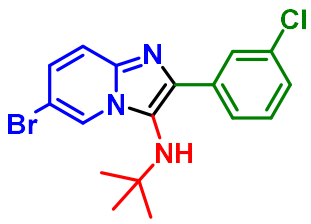
White solid (94%), mp 195°C. IR (KBr, cm^{-1}): 3310 (N-H), 2950 (sp^2-CH), 2890 (sp^3-CH), 1626, 1536, 1421, 1320, 1311, 1296, 1017, 756. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.8 Hz, 1H), 8.53 – 8.47 (m, 1H), 7.99 (d, *J* = 9.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 6.4 Hz, 1H), 3.23 (s, 1H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.40, 145.07, 141.06, 134.44, 131.09, 129.69, 128.79, 128.66, 128.42, 128.33, 127.90, 121.88, 107.85, 56.49, 30.28. Anal. Calcd for $C_{17}H_{17}BrN_4O_2$; C, 52.46; H, 4.40; N, 14.39 found: C, 52.45; H, 4.39; N, 14.38.

6-bromo-N-(tert-butyl)-2-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-amine (4s)



White solid (92%), mp 178°C. IR (KBr, cm^{-1}): 3321 (NH), 2961 (sp^2-CH), 2921 (sp^3-CH), 1601, 1501, 1441, 1351, 1311, 1201, 1021, 741. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.7 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 9.4 Hz, 1H), 7.13 (d, *J* = 9.4 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.09 (s, 1H), 1.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.16, 140.32, 140.20, 129.29, 127.22, 127.12, 123.54, 123.24, 117.69, 113.72, 106.09, 56.38, 55.21, 30.33. Anal. Calcd for $C_{18}H_{20}BrN_3O$; C, 57.76; H, 5.39; N, 11.23 found: C, 57.72; H, 5.34; N, 11.20.

6-bromo-N-(tert-butyl)-2-(3-chlorophenyl)imidazo[1,2-a]pyridin-3-amine (4t)



White solid (94%), mp 197-199°C. IR (KBr, cm^{-1}): 3281 (N-H), 2951 (sp^2-CH), 2921 (sp^3-CH), 1609, 1491, 1431, 1341, 1311, 1209, 1037, 716. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 1.7 Hz, 1H), 7.99 (t, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 9.4 Hz, 1H), 7.40 – 7.26 (m, 2H), 7.22 (d, *J* = 9.4 Hz, 1H), 3.08 (s, 1H), 1.07 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.35, 138.85, 136.37, 134.30, 129.50, 128.08, 127.95, 127.72, 126.09, 124.04, 123.67, 118.05, 106.71, 56.63, 30.41. Anal. Calcd for $C_{17}H_{17}BrClN_3$; C, 53.92; H, 4.52; N, 11.10 found: C, 53.90; H, 4.50; N, 11.08.

2.8 Spectral Data of few products

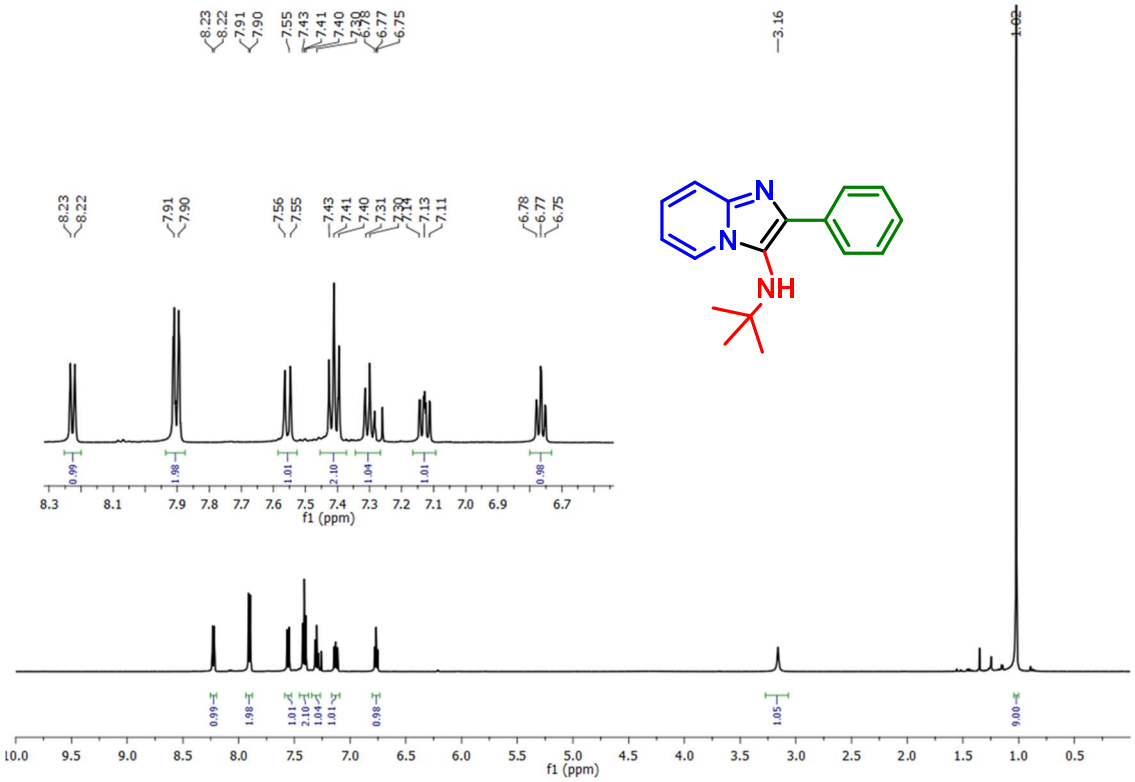


Figure 2.6 ^{1}H NMR of product **4a**

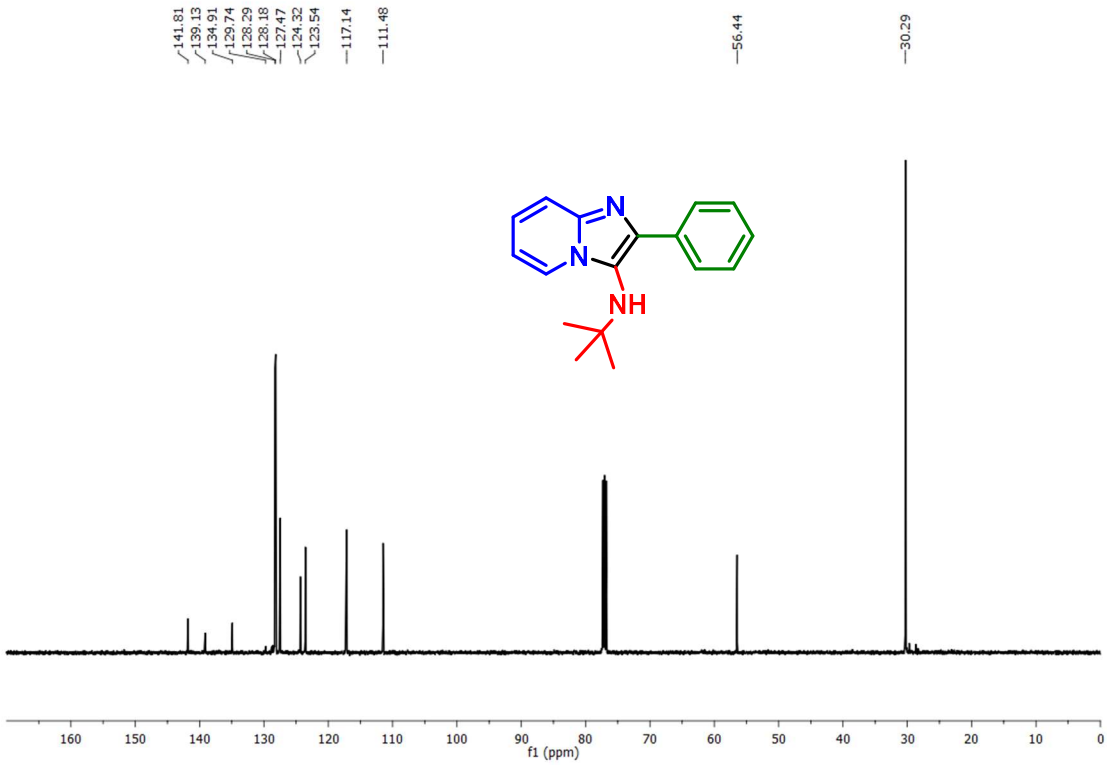


Figure 2.7 ^{13}C NMR of product **4a**

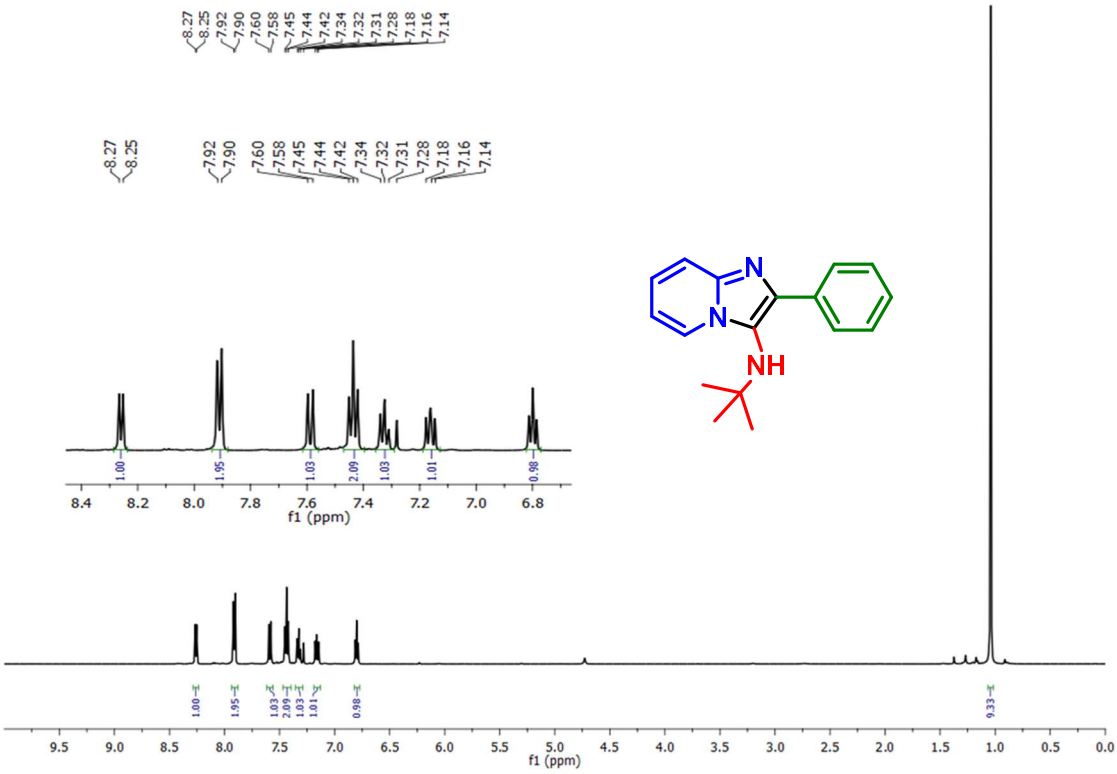


Figure 2.8 D_2O exchange ^1H NMR of product **4a**

2.9 FT-IR Spectra

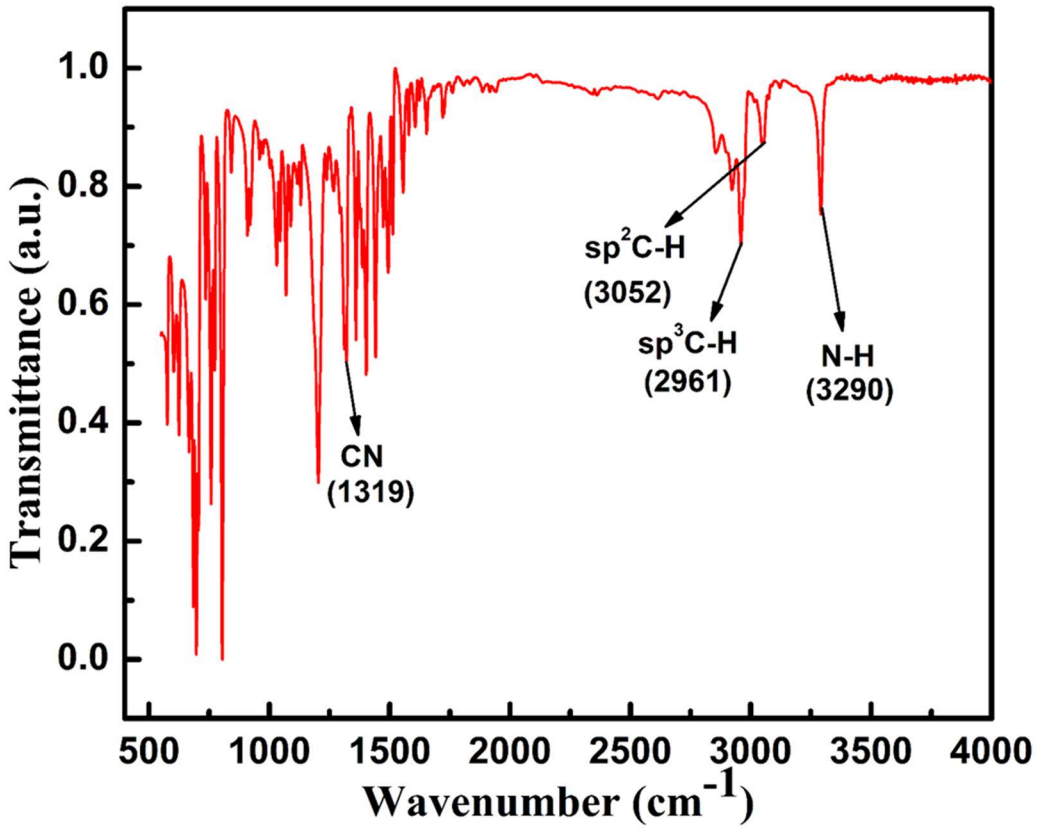


Figure 2.9 FT-IR spectrum of compound **4p**

2.10 References

(1) Choi, J.-H.; Park, C.-M. Three-Component Synthesis of Quinolines Based on Radical Cascade Visible-Light Photoredox Catalysis. *Adv. Synth. Catal.* **2018**, *360* (18), 3553–3562.
(2) Guillemard, L.; Colobert, F.; Wencel-Delord, J. Visible-Light-Triggered, Metal- and Photocatalyst-Free Acylation of N-Heterocycles. *Adv. Synth. Catal.* **2018**, *360* (21), 4184–4190.
(3) Hou, H.; Li, H.; Xu, Y.; Song, C.; Wang, C.; Shi, Y.; Han, Y.; Yan, C.; Zhu, S. Visible-Light-Mediated Chlorosulfonylative Cyclizations of 1, 6-Enynes. *Adv. Synth. Catal.* **2018**, *360* (22), 4325–4329.
(4) Li, R.; Chen, X.; Wei, S.; Sun, K.; Fan, L.; Liu, Y.; Qu, L.; Zhao, Y.; Yu, B. A Visible-Light-Promoted Metal-Free Strategy towards Arylphosphonates: Organic-Dye-Catalyzed Phosphorylation of Arylhydrazines with Trialkylphosphites. *Adv. Synth. Catal.* **2018**, *360* (24), 4807–4813.
(5) Revathi, L.; Ravindar, L.; Fang, W.-Y.; Rakesh, K. P.; Qin, H.-L. Visible Light-induced C− H Bond Functionalization: A Critical Review. *Adv. Synth. Catal.* **2018**, *360* (24), 4652–4698.
(6) Zhu, M.; Fu, W.; Guo, W.; Tian, Y.; Wang, Z.; Ji, B. Visible-Light-Induced Radical Trifluoromethylthiolation of N-(o-Cyanobiaryl) Acrylamides. *Org. Biomol. Chem.* **2019**, *17* (13), 3374–3380.
(7) Zhu, M.; Fu, W.; Wang, Z.; Xu, C.; Ji, B. Visible-Light-Mediated Direct Difluoromethylation of Alkynoates: Synthesis of 3-Difluoromethylated Coumarins. *Org. Biomol. Chem.* **2017**, *15* (43), 9057–9060.
(8) Zhu, M.; Han, X.; Fu, W.; Wang, Z.; Ji, B.; Hao, X.-Q.; Song, M.-P.; Xu, C. Regioselective 2, 2, 2-Trifluoroethylation of Imidazopyridines by Visible Light Photoredox Catalysis. *J. Org. Chem.* **2016**, *81* (16), 7282–7287.
(9) Fu, W.; Han, X.; Zhu, M.; Xu, C.; Wang, Z.; Ji, B.; Hao, X.-Q.; Song, M.-P. Visible-Light-Mediated Radical Oxydifluoromethylation of Olefinic Amides for the Synthesis of CF 2 H-Containing Heterocycles. *Chem. Commun.* **2016**, *52* (91), 13413–13416.
(10) Fu, W.; Zhu, M.; Zou, G.; Xu, C.; Wang, Z.; Ji, B. Visible-Light-Mediated Radical Aryldifluoroacetylation of Alkynes with Ethyl Bromodifluoroacetate for the Synthesis of 3-Difluoroacetylated Coumarins. *J. Org. Chem.* **2015**, *80* (9), 4766–4770.
(11) Tian, C.; Yang, L.-M.; Tian, H.-T.; An, G.-H.; Li, G.-M. C5-Selective Trifluoromethylation of 8-Amino Quinolines via Photoredox Catalysis. *J. Fluor. Chem.* **2019**, *219*, 23–28.
(12) Yang, H.; Tian, C.; Qiu, D.; Tian, H.; An, G.; Li, G. Organic Photoredox Catalytic Decarboxylative Cross-Coupling of Gem-Difluoroalkenes with Unactivated Carboxylic Acids. *Org. Chem. Front.* **2019**, *6* (14), 2365–2370.

(13) Zhang, M.; Yang, L.; Yang, H.; An, G.; Li, G. Visible Light Mediated C (Sp3)-H Alkenylation of Cyclic Ethers Enabled by Aryl Ketone. *ChemCatChem* **2019**, *11* (6), 1606–1609.
(14) Wei, Y.; Zhou, Q.-Q.; Tan, F.; Lu, L.-Q.; Xiao, W.-J. Visible-Light-Driven Organic Photochemical Reactions in the Absence of External Photocatalysts. *Synthesis* **2019**, *51* (16), 3021–3054.
(15) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113* (7), 5322–5363.
(16) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116* (17), 10075–10166.
(17) Xie, J.; Jin, H.; Hashmi, A. S. K. The Recent Achievements of Redox-Neutral Radical C–C Cross-Coupling Enabled by Visible-Light. *Chem. Soc. Rev.* **2017**, *46* (17), 5193–5203.
(18) Shaw, M. H.; Twilton, J.; MacMillan, D. W. Photoredox Catalysis in Organic Chemistry. *J. Org. Chem.* **2016**, *81* (16), 6898–6926.
(19) Ravelli, D.; Protti, S.; Fagnoni, M. Carbon–Carbon Bond Forming Reactions via Photogenerated Intermediates. *Chem. Rev.* **2016**, *116* (17), 9850–9913.
(20) Douglas, J. J.; Sevrin, M. J.; Stephenson, C. R. Visible Light Photocatalysis: Applications and New Disconnections in the Synthesis of Pharmaceutical Agents. *Org. Process Res. Dev.* **2016**, *20* (7), 1134–1147.
(21) Teegardin, K.; Day, J. I.; Chan, J.; Weaver, J. Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations. *Org. Process Res. Dev.* **2016**, *20* (7), 1156–1163.
(22) Schultz, D. M.; Yoon, T. P. Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* **2014**, *343* (6174), 1239176.
(23) Marzo, L.; Pagire, S. K.; Reiser, O.; König, B. Visible-light Photocatalysis: Does It Make a Difference in Organic Synthesis? *Angew. Chem. Int. Ed.* **2018**, *57* (32), 10034–10072.
(24) Skubi, K. L.; Blum, T. R.; Yoon, T. P. Dual Catalysis Strategies in Photochemical Synthesis. *Chem. Rev.* **2016**, *116* (17), 10035–10074.
(25) Karkas, M. D. Photochemical Generation of Nitrogen-Centered Amidyl, Hydrazonyl, and Imidyl Radicals: Methodology Developments and Catalytic Applications. *ACS Catal.* **2017**, *7* (8), 4999–5022.
(26) Chen, J.-R.; Yan, D.-M.; Wei, Q.; Xiao, W.-J. Photocascade Catalysis: A New Strategy for Cascade Reactions. *ChemPhotoChem* **2017**, *1* (5), 148–158.
(27) Farney, E. P.; Yoon, T. P. Visible-Light Sensitization of Vinyl Azides by Transition-Metal Photocatalysis. *Angew. Chem. Int. Ed.* **2014**, *53* (3), 793–797.
(28) Brachet, E.; Ghosh, T.; Ghosh, I.; König, B. Visible Light C–H Amidation of Heteroarenes with Benzoyl Azides. *Chem. Sci.* **2015**, *6* (2), 987–992.
(29) Heitz, D. R.; Tellis, J. C.; Molander, G. A. Photochemical Nickel-Catalyzed C–H Arylation: Synthetic Scope and Mechanistic Investigations. *J. Am. Chem. Soc.* **2016**, *138* (39), 12715–12718.

(30) Welin, E. R.; Le, C.; Arias-Rotondo, D. M.; McCusker, J. K.; MacMillan, D. W. Photosensitized, Energy Transfer-Mediated Organometallic Catalysis through Electronically Excited Nickel (II). *Science* **2017**, *355* (6323), 380–385.
(31) Bagal, D. B.; Kachkovskyi, G.; Knorn, M.; Rawner, T.; Bhanage, B. M.; Reiser, O. Trifluoromethylchlorosulfonylation of Alkenes: Evidence for an Inner-sphere Mechanism by a Copper Phenanthroline Photoredox Catalyst. *Angew. Chem. Int. Ed.* **2015**, *54* (24), 6999–7002.
(32) Ghosh, I.; König, B. Chromoselective Photocatalysis: Controlled Bond Activation through Light-color Regulation of Redox Potentials. *Angew. Chem. Int. Ed.* **2016**, *55* (27), 7676–7679.
(33) Pandey, G.; Laha, R.; Singh, D. Benzylic $C_{(Sp^3)}$–H Functionalization for C–N and C–O Bond Formation via Visible Light Photoredox Catalysis. *J. Org. Chem.* **2016**, *81* (16), 7161–7171.
(34) Lenhart, D.; Bauer, A.; Pöthig, A.; Bach, T. Enantioselective Visible-light-induced Radical-addition Reactions to 3-alkylidene Indolin-2-ones. *Chem. Eur. J.* **2016**, *22* (19), 6519–6523.
(35) Capaldo, L.; Ravelli, D. Hydrogen Atom Transfer (HAT): A Versatile Strategy for Substrate Activation in Photocatalyzed Organic Synthesis. *Eur. J. Org. Chem.* **2017**, *2017* (15), 2056–2071.
(36) Ravelli, D.; Dondi, D.; Fagnoni, M.; Albini, A. Photocatalysis. A Multi-Faceted Concept for Green Chemistry. *Chem. Soc. Rev.* **2009**, *38* (7), 1999–2011.
(37) Waele, V. D.; Poizat, O.; Fagnoni, M.; Bagno, A.; Ravelli, D. Unraveling the Key Features of the Reactive State of Decatungstate Anion in Hydrogen Atom Transfer (HAT) Photocatalysis. *ACS Catal.* **2016**, *6* (10), 7174–7182.
(38) Kamijo, S.; Takao, G.; Kamijo, K.; Hirota, M.; Tao, K.; Murafuji, T. Photo-induced Substitutive Introduction of the Aldoxime Functional Group to Carbon Chains: A Formal Formylation of Non-acidic $C_{(Sp^3)}$− H Bonds. *Angew. Chem. Int. Ed.* **2016**, *55* (33), 9695–9699.
(39) Murphy, J. J.; Bastida, D.; Paria, S.; Fagnoni, M.; Melchiorre, P. Asymmetric Catalytic Formation of Quaternary Carbons by Iminium Ion Trapping of Radicals. *Nature* **2016**, *532* (7598), 218–222.
(40) Kamijo, S.; Takao, G.; Kamijo, K.; Tsuno, T.; Ishiguro, K.; Murafuji, T. Alkylation of Nonacidic C (Sp3)–H Bonds by Photoinduced Catalytic Michael-Type Radical Addition. *Org. Lett.* **2016**, *18* (19), 4912–4915.
(41) West, J. G.; Bedell, T. A.; Sorensen, E. J. The Uranyl Cation as a Visible-Light Photocatalyst for C (Sp3)− H Fluorination. *Angew. Chem. Int. Ed.* **2016**, *55* (31), 8923–8927.
(42) Shaw, M. H.; Shurtleff, V. W.; Terrett, J. A.; Cuthbertson, J. D.; MacMillan, D. W. Native Functionality in Triple Catalytic Cross-Coupling: Sp^3 C–H Bonds as Latent Nucleophiles. *Science* **2016**, *352* (6291), 1304–1308.

(43) Mukherjee, S.; Maji, B.; Tlahuext-Aca, A.; Glorius, F. Visible-Light-Promoted Activation of Unactivated $C_{(Sp^3)}$–H Bonds and Their Selective Trifluoromethylthiolation. *J. Am. Chem. Soc.* **2016**, *138* (50), 16200–16203.
(44) Choi, G. J.; Zhu, Q.; Miller, D. C.; Gu, C. J.; Knowles, R. R. Catalytic Alkylation of Remote C–H Bonds Enabled by Proton-Coupled Electron Transfer. *Nature* **2016**, *539* (7628), 268–271.
(45) Chu, J. C.; Rovis, T. Amide-Directed Photoredox-Catalysed C–C Bond Formation at Unactivated Sp 3 C–H Bonds. *Nature* **2016**, *539* (7628), 272–275.
(46) Ravelli, D.; Protti, S.; Fagnoni, M. Decatungstate Anion for Photocatalyzed "Window Ledge" Reactions. *Acc. Chem. Res.* **2016**, *49* (10), 2232–2242.
(47) Fan, X.-Z.; Rong, J.-W.; Wu, H.-L.; Zhou, Q.; Deng, H.-P.; Tan, J. D.; Xue, C.-W.; Wu, L.-Z.; Tao, H.-R.; Wu, J. Eosin Y as a Direct Hydrogen-Atom Transfer Photocatalyst for the Functionalization of C− H Bonds. *Angew. Chem.* **2018**, *130* (28), 8650–8654.
(48) Fisher, M. H.; Lusi, A. Imidazo [1, 2-a] Pyridine Anthelmintic and Antifungal Agents. *J. Med. Chem.* **1972**, *15* (9), 982–985.
(49) Rival, Y.; Grassy, G.; Taudou, A.; Ecalle, R. Antifungal Activity in Vitro of Some Imidazo [1, 2-a] Pyrimidine Derivatives. *Eur. J. Med. Chem.* **1991**, *26* (1), 13–18.
(50) Hamdouchi, C.; de Blas, J.; del Prado, M.; Gruber, J.; Heinz, B. A.; Vance, L. 2-Amino-3-Substituted-6-[(E)-1-Phenyl-2-(N-Methylcarbamoyl) Vinyl] Imidazo [1, 2-a] Pyridines as a Novel Class of Inhibitors of Human Rhinovirus: Stereospecific Synthesis and Antiviral Activity. *J. Med. Chem.* **1999**, *42* (1), 50–59.
(51) Lhassani, M.; Chavignon, O.; Chezal, J.-M.; Teulade, J.-C.; Chapat, J.-P.; Snoeck, R.; Andrei, G.; Balzarini, J.; De Clercq, E.; Gueiffier, A. Synthesis and Antiviral Activity of Imidazo [1, 2-a] Pyridines. *Eur. J. Med. Chem.* **1999**, *34* (3), 271–274.
(52) Rival, Y.; GRASSY, G.; MICHEL, G. Synthesis and Antibacterial Activity of Some Imidazo [1, 2-α] Pyrimidine Derivatives. *Chem. Pharm. Bull. (Tokyo)* **1992**, *40* (5), 1170–1176.
(53) Rupert, K. C.; Henry, J. R.; Dodd, J. H.; Wadsworth, S. A.; Cavender, D. E.; Olini, G. C.; Fahmy, B.; Siekierka, J. J. Imidazopyrimidines, Potent Inhibitors of P38 MAP Kinase. *Bioorg. Med. Chem. Lett.* **2003**, *13* (3), 347–350.
(54) Bagdi, A. K.; Santra, S.; Monir, K.; Hajra, A. Synthesis of Imidazo [1, 2-a] Pyridines: A Decade Update. *Chem. Commun.* **2015**, *51* (9), 1555–1575.
(55) Almirante, L.; Polo, L.; Mugnaini, A.; Provinciali, E.; Rugarli, P.; Biancotti, A.; Gamba, A.; Murmann, W. Derivatives of Imidazole. I. Synthesis and Reactions of Imidazo [1, 2-α] Pyridines with Analgesic, Antiinflammatory, Antipyretic, and Anticonvulsant Activity. *J. Med. Chem.* **1965**, *8* (3), 305–312.
(56) Katritzky, A. R.; Xu, Y.-J.; Tu, H. Regiospecific Synthesis of 3-Substituted Imidazo [1, 2-a] Pyridines, Imidazo [1, 2-a] Pyrimidines, and Imidazo [1, 2-c] Pyrimidine. *J. Org. Chem.* **2003**, *68* (12), 4935–4937.
(57) Langer, S. Z.; Arbilla, S.; Benavides, J.; Scatton, B. Zolpidem and Alpidem: Two Imidazopyridines with Selectivity for Omega 1-and Omega 3-Receptor Subtypes. *Adv. Biochem. Psychopharmacol.* **1990**, *46*, 61–72.

(58) Almirante, L.; Polo, L.; Mugnaini, A.; Provinciali, E.; Rugarli, P.; Biancotti, A.; Gamba, A.; Murmann, W. Derivatives of Imidazole. I. Synthesis and Reactions of Imidazo [1, 2-α] Pyridines with Analgesic, Antiinflammatory, Antipyretic, and Anticonvulsant Activity. *J. Med. Chem.* **1965**, *8* (3), 305–312.
(59) Zhu, D.-J.; Chen, J.-X.; Liu, M.-C.; Ding, J.-C.; Wu, H.-Y. Catalyst: And Solvent-Free Synthesis of Imidazo [1, 2-a] Pyridines. *J. Braz. Chem. Soc.* **2009**, *20*, 482–487.
(60) He, C.; Hao, J.; Xu, H.; Mo, Y.; Liu, H.; Han, J.; Lei, A. Heteroaromatic Imidazo [1, 2-a] Pyridines Synthesis from C–H/N–H Oxidative Cross-Coupling/Cyclization. *Chem. Commun.* **2012**, *48* (90), 11073–11075.
(61) Chernyak, N.; Gevorgyan, V. General and Efficient Copper-Catalyzed Three-Component Coupling Reaction towards Imidazoheterocycles: One-Pot Synthesis of Alpidem and Zolpidem. *Angew. Chem.* **2010**, *122* (15), 2803–2806.
(62) Wang, H.; Wang, Y.; Liang, D.; Liu, L.; Zhang, J.; Zhu, Q. Copper-Catalyzed Intramolecular Dehydrogenative Aminooxygenation: Direct Access to Formyl-Substituted Aromatic N-Heterocycles. *Angew. Chem.* **2011**, *123* (25), 5796–5799.
(63) Chandra Mohan, D.; Nageswara Rao, S.; Adimurthy, S. Synthesis of Imidazo [1, 2-a] Pyridines:"Water-Mediated" Hydroamination and Silver-Catalyzed Aminooxygenation. *J. Org. Chem.* **2013**, *78* (3), 1266–1272.
(64) Santra, S.; Bagdi, A. K.; Majee, A.; Hajra, A. Iron (III)-Catalyzed Cascade Reaction between Nitroolefins and 2-Aminopyridines: Synthesis of Imidazo [1, 2-a] Pyridines and Easy Access towards Zolimidine. *Adv. Synth. Catal.* **2013**, *355* (6), 1065–1070.
(65) Kumari, S.; Kumar, D.; Gajaganti, S.; Srivastava, V.; Singh, S. Sc (OTf) 3 Catalysed Multicomponent Synthesis of Chromeno [2, 3-d] Pyrimidinetriones under Solvent-Free Condition. *Synth. Commun.* **2019**, *49* (3), 431–443.
(66) Maury, S. K.; Kumar, D.; Kamal, A.; Singh, H. K.; Kumari, S.; Singh, S. A Facile and Efficient Multicomponent Ultrasound-Assisted "on Water" Synthesis of Benzodiazepine Ring. *Mol. Divers.* **2021**, *25*, 131–142.
(67) Xiong, T.; Zhang, Q. New Amination Strategies Based on Nitrogen-Centered Radical Chemistry. *Chem. Soc. Rev.* **2016**, *45* (11), 3069–3087.
(68) Wang, Y.; Ren, P.; Gu, X.; Wen, X.; Wang, Y.; Guo, X.; Waclawik, E. R.; Zhu, H.; Zheng, Z. Probing the Mechanism of Benzaldehyde Reduction to Chiral Hydrobenzoin on the CNT Surface under Near-UV Light Irradiation. *Green Chem.* **2016**, *18* (6), 1482–1487.
(69) Mishra, A.; Srivastava, M.; Rai, P.; Yadav, S.; Tripathi, B. P.; Singh, J.; Singh, J. Visible Light Triggered, Catalyst Free Approach for the Synthesis of Thiazoles and Imidazo [2, 1-b] Thiazoles in EtOH: H_2O Green Medium. *RSC Adv.* **2016**, *6* (54), 49164–49172.
(70) Zhang, M.; Fu, Q.-Y.; Gao, G.; He, H.-Y.; Zhang, Y.; Wu, Y.-S.; Zhang, Z.-H. Catalyst-Free, Visible-Light Promoted One-Pot Synthesis of Spirooxindole-Pyran Derivatives in Aqueous Ethyl Lactate. *ACS Sustain. Chem. Eng.* **2017**, *5* (7), 6175–6182.

(71) Yadav, N.; Sagir, H.; Ansari, M. D.; Siddiqui, I. R. Visible-Light-Mediated Synthesis of 4 H-Benzo [1, 4] Thiazin-2-Amines and 3, 4-Dihydroquinoxalin-2-Amines: An Efficient and Metal Free Route to C–S, C–N Bond Formation. *Catal. Lett.* **2018**, *148*, 1676–1685.
(72) Kaur, T.; Wadhwa, P.; Bagchi, S.; Sharma, A. Isocyanide Based [4+1] Cycloaddition Reactions: An Indispensable Tool in Multi-Component Reactions (MCRs). *Chem. Commun.* **2016**, *52* (43), 6958–6976.
(73) Shivhare, K. N.; Jaiswal, M. K.; Srivastava, A.; Tiwari, S. K.; Siddiqui, I. R. Visible-Light-Activated C–C and C–N Bond Formation in the Synthesis of Imidazo [1, 2-a] Pyridines and Imidazo [2, 1-b] Thiazoles under Catalyst and Solvent-Free Conditions. *New J. Chem.* **2018**, *42* (20), 16591–16601.
(74) Rohokale, R. S.; Koenig, B.; Dhavale, D. D. Synthesis of 2, 4, 6-Trisubstituted Pyridines by Oxidative Eosin Y Photoredox Catalysis. *J. Org. Chem.* **2016**, *81* (16), 7121–7126.
(75) Ansari, M. A.; Yadav, D.; Soni, S.; Srivastava, A.; Singh, M. S. Visible-Light-Mediated Synthesis of 1, 2, 4-Dithiazolidines from β-Ketothioamides through a Hydrogen-Atom-Transfer Photocatalytic Approach of Eosin Y. *J. Org. Chem.* **2019**, *84* (9), 5404–5412.