Chapter-2

Visible light-induced cu-catalyzed synthesis of schiff's base of 2-amino benzonitrile derivatives and acetophenones

2.1 Introduction

At present, the use of visible light is a growing, powerful strategy for the paradigm shift in organic synthesis. This developing area aims to improve efficiency and synthetic utility and to recognize the long-term goal of gaining mechanistic new insight into chemical reactions. The wide use of universal visible light can be attributed to the fact that it is a pure, inexpensive, simple, sustainable, and eco-friendly energy source [1-8]. Inevitably, visible light-initiated chemical reactions have emerged as an influential tool in synthetic chemistry for improving the synthetic efficiency as well as developing mechanistically interesting novel synthetic routes to target molecules.

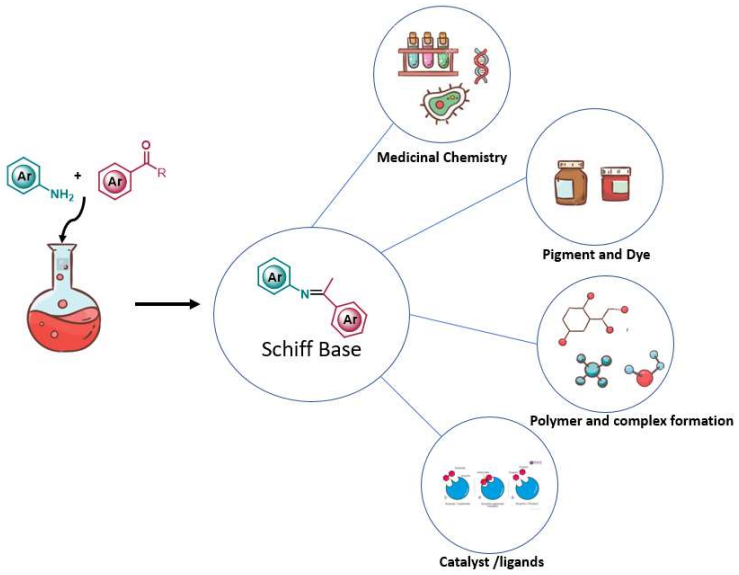


Figure 2.1 Applications of Schiff's base in various Fields

The development of novel and highly efficient strategies for forming azomethine chromophores is fundamentally important in synthesizing most of the N-containing

heterocyclic molecules and pharmaceutical drugs [9]. Schiff's bases have attracted much attention due to their important biological activities such as analgesic [11-14], anti-inflammatory [10-15], antimicrobial [15,16], anticancer [19,20], anticonvulsant [17], anthelmintic[22], antitubercular [18], and antioxidant, so forth (Figure 2.1). Besides biological activities, Schiff's base and its derivatives are also used as catalysts and intermediates in organic synthesis, pigments, dyes, corrosion inhibitors [21], and polymer stabilizers [25] (Figure 2.1).

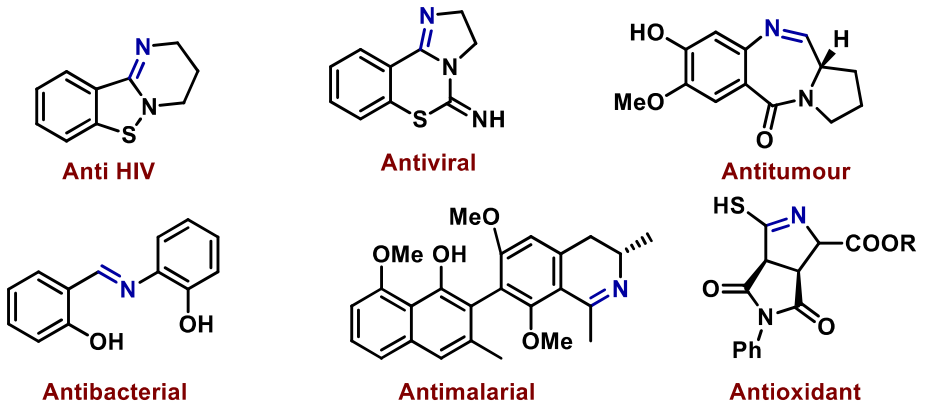
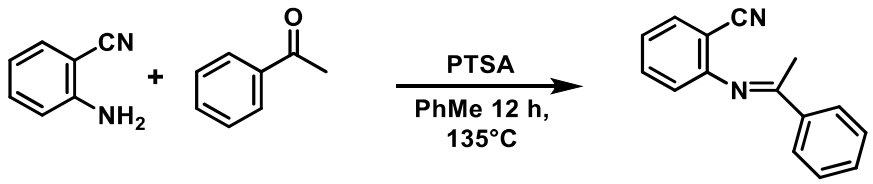


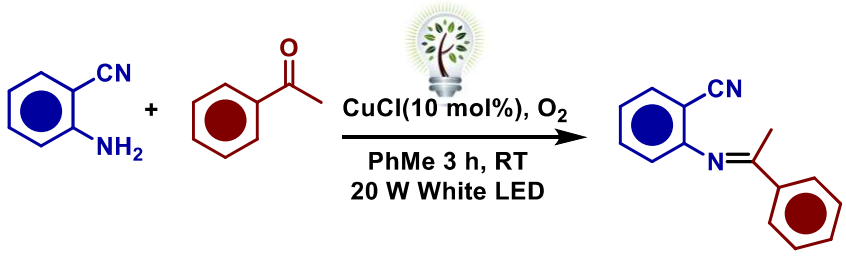
Figure 2.2 Structures of some bioactive Schiff's base

Several methods for synthesizing Schiff's base were reported [23-29]. However, these previous methods suffer from the following factors: (a) long reaction time, (b) high temperature or thermal conditions, and (c) acidic conditions or moisture-sensitive catalysts. Recently, the photoredox Cu-Based complex has been established as an inexpensive catalyst system, and importantly, no exogenous photosensitizer is required to promote these photocatalytic transformations [33-40] (Scheme 2.1).



Scheme 2.1 Schiff's base under thermal condition

In this work, we further extended our methodologies [30-32] to catalyze the Schiff's base of 2-aminobenzonitrile with acetophenone, in the presence of air as an oxidant, at room temperature upon irradiation with white LED without the need of any exogenous photosensitizer (Scheme 2.2).

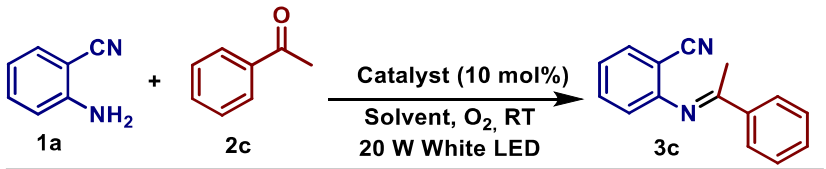


Scheme 2.2 Schiff's base under visible light irradiation.

2.2 Results and discussion

In order to optimize the experimental parameter, the reaction of 2-amino benzonitrile (**1a**) and acetophenone (**2c**) was chosen as the model reaction. Initially (Table 2.1), the reaction of 2-aminobenzonitrile (**1a**) (1mmol), acetophenone (**2c**) (1.2mmol), and CuCl (10 mol%) in ethanol in the presence of visible light under an open atmosphere led to the formation of the Schiff's base as a product (**3c**) in 60% yield (Table 2.1, entry 1). The use of toluene as a solvent dramatically improved the yield to 97% (Table 2.1, entry 2).

Table 2.1. Screening of catalyst and solvent [a]



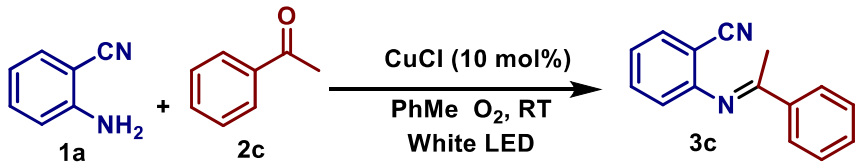
Entry	Catalyst	Solvent	Yield[b] %
1	CuCl	EtOH	60
2	CuCl	PhMe	97
3	$CuCl_2$	PhMe	Trace
4	CH_3COOH	PhMe	Trace
5	CF_3COOH	PhMe	Trace
6	Eosin Y	PhMe	nr
7	$FeCl_3$	PhMe	Trace
8	CuBr	PhMe	95
9	CuI	PhMe	95
10	CuCl	CH_3CN	70
11	CuCl	DCM	75
12	CuCl	DMF	11
13	CuCl	DMSO	Trace
14	CuCl	THF	10
15	CuCl	H_2O	nr
16	CuCl	neat	nr
17	neat	PhMe	Trace

[a]Reaction conditions: 1 mmol **(1a)** and 1.2 mmol **(2c),** 10 mol% catalysts in a solvent. The solution was irradiated with 20W LED for 3 h in the presence of 1 atm O_2 atmosphere. [b]Isolated yield.

In contrast to CuCl, $CuCl_2$ turns out to be ineffective in catalyzing product formation (Table 2.1, entry 3). Different types of a catalyst, such as acetic acid and trifluoroacetic acid,

provided low yields (Table 2.1, entries 4 and 5). When the common photocatalytic organic dye eosin Y was used, no product was detected (Table 2.1, entry 6). With $FeCl_3$ as a catalyst, only a trace amount of product was obtained (Table 2.1, entry 7). In contrast, the use of metal salt, CuX (X: Cl, Br, I) provided excellent yield (up to 95%) of the product (**3c**) (Table 2.1 entries 2, 8, 9). In the screening of solvent, when solvents, such as MeCN and DCM, were used, 70% and 75% yield of the product were obtained (Table1, entries 10,11) while other solvents like DMF, DMSO, and THF afforded low yield of product (Table 2.1, entries 12,13 and14). The aqueous solvent was ineffective in providing the product. (Table 2.1, entry 15). The product was not obtained in the absence of solvent (Table 2.1, entry 16), while a trace amount of product was obtained under catalyst-free conditions (Table 2.1, entry17).

Table 2.2. Optimization of LED intensities

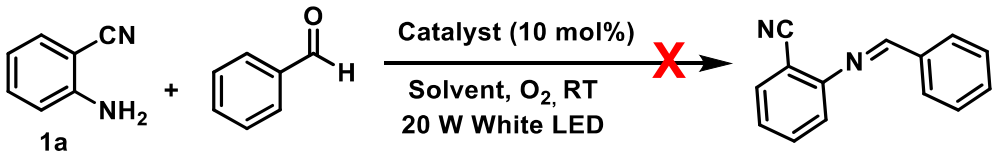


Entry	Reaction Condition and time	Yield[b](%)
1	Dark RT, 7h	Trace
2	LED(8W), RT,7h	44
3	LED(14W), RT 7h	81
4	LED(20W), RT 3h	97
5	LED(32W), RT 3h	95

[a]Reaction conditions: 1 mmol **(1a)** and 1.2 mmol **(2c)**, 10 mol% catalysts in the solvent. The solution was irradiated with 20W LED for 3 h in the presence of 1 atm O_2 atmosphere. A Reaction was conducted in the dark at RT. [b]Isolated yield.

After optimizing the reaction conditions, the actual role of the light source was determined. To understand the role of light in the reaction, some control experiments of the reaction of 2-aminobenzonitrile **(1a)** and acetophenone **(2c)** were carried out. The experiments showed that some trace amount of product was obtained under dark conditions (Table 2.2, entry 1). When the reaction was performed under different intensities (8W, 14W, 20W, and 32W)of light, we extracted some important results. With lower intensities 8W and 14 W white-light-emitting diode (LED) poor yield was obtained (Table 2.2, entries 2 and 3), but with higher intensities of LEDs (20W and 32 W), the yield was interestingly increased (Table 2.2, entry 4 and 5).

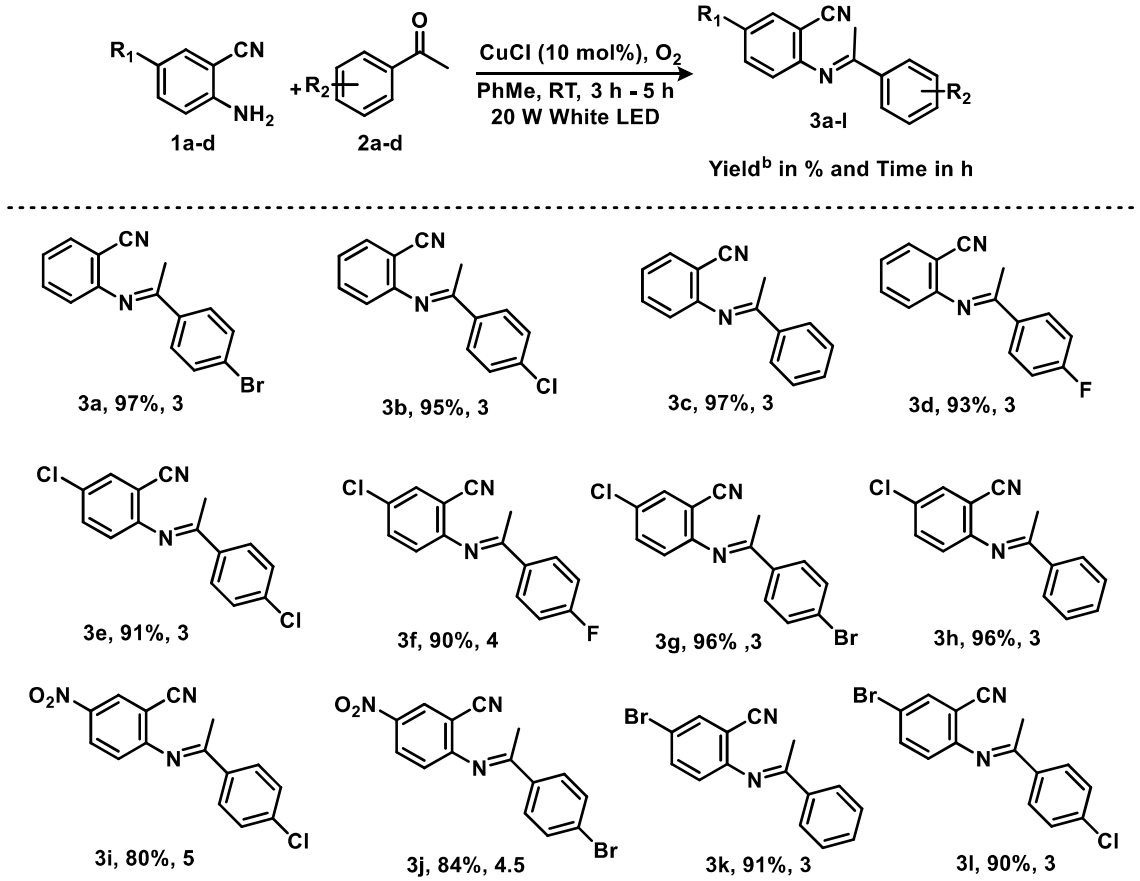
Finally, under the optimized condition, the scope and limitation of the reaction were examined. It was found that various 2-aminobenzonitrile react satisfactorily with several derivatives of acetophenone (Table 2.3). Afterward, this methodology was also examined with other carbonyl compounds (aldehyde). Unluckily, no desired products were obtained (Scheme 2.3).



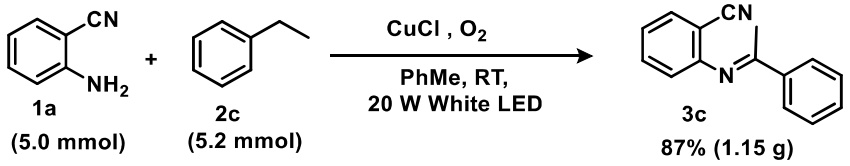
Scheme 2.3 Substrate Scope of the aldehyde with 2-aminobenzonitrile

Furthermore, we investigated whether gram-scale applications are feasible for the developed Schiff's base reaction or not. To our delight, the present reaction could afford 1.15 g of **3c** in the standard cases, with no significant loss of its efficiency (Scheme 2.4).

Table 2.3 substrate scope

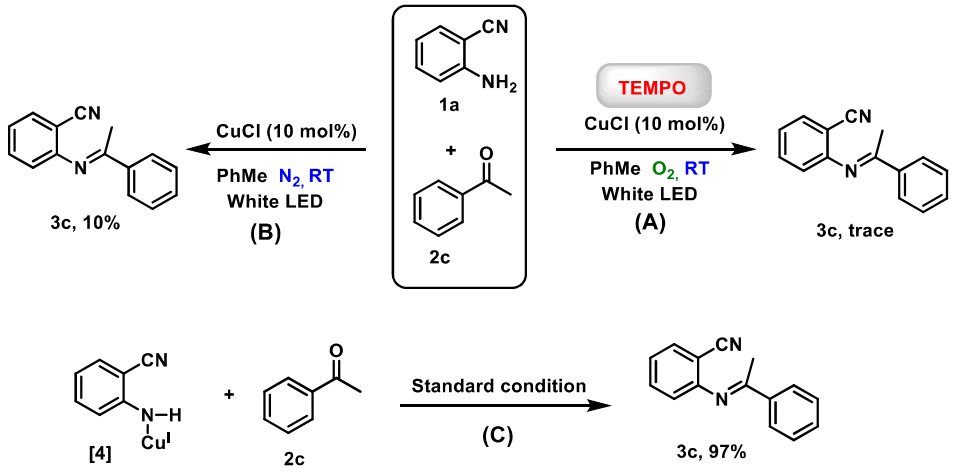


[a]Reaction conditions: 1 mmol **(1)** and 1.2 mmol **(2),** 10 mol% CuCl in PhMe solvent. The solution was irradiated with 20W LED for 3 h in the presence of 1 atm O_2 atmosphere [b]Isolated yield.



Scheme 2.4. Synthesis of **3c** product on gram-scale

In order to find out the mechanism, some control experiments were carried out. When the reaction of **1a** with **2c** was carried out in the presence of radical scavenger TEMPO (2,2,6,6, tetramethyl-1piperdenyl oxy, a popular radical-capturing species), the Schiff's base reaction was found to be suppressed **(A)**, indicating that a radical pathway might participate in the reaction. In addition, when the reaction was performed under a nitrogen atmosphere, only a 10% yield of the desired product was observed, highlighting oxygen's importance in the reaction **(B).** After that, we tried to add acetophenone in Cu-I amine complex **(4)** under standard conditions, and a 97% yield of product **3c** was observed **(C)**(Scheme 2.5). This confirms the intermediacy of Cu-I amine complex **(4)** in this reaction.



Scheme 2.5. Control experiments

We also evaluated the green chemistry metrics [38] for the synthesis of the Schiff's base **(3b)** of 2-aminobenzonitrile **(1a)** and 4-chloroacetophenone **(2b)** on a preparative scale (Table 2.4) with an *E* factor = 12.82, atom economy = 93%, 84.6% atom efficiency, carbon efficiency = 100% and, reaction mass efficiency = 90.6%. This indicated that the current

synthesis of the product is an eco-friendly, green, and simple process better than previously reported thermal methodologies [42-44].

Table 2.4 Evaluation of Green metrics of the current synthesis

Atom economy defined as "how much of the reactants remain in the final desired product"

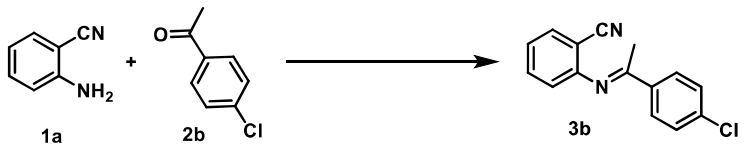
$$\text{Atom economy (AE)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100$$

"E-factor of a process is the ratio of the mass of waste per mass of product:"

$$\text{E-factor} = \frac{\text{mass of waste}}{\text{mass of desired product}}$$

Reaction mass efficiency (RME) defined as "the percentage of the mass of the reactants that remain in the product"

$$\text{Reaction mass efficiency (RME)} = \frac{\text{mass of desired product}}{\text{mass of all reactants}} \times 100$$



1a 2b 3b

Chemical Formula: $C_7H_6N_2$ Chemical Formula: C_8H_7ClO Chemical Formula: $C_{15}H_{11}ClN_2$

Mass: 118.5 Mass: 154.6 Mass: 254.06

Reactant A	2-aminobenzonitrile (1a)	0.7 g	0.005 mol	FW 118.5
Reactant B	p-chloroacetophenone(2b)	0.8 g	0.0055 mol	FW 154.6
Solvent	PhMe	17.3 g	—	—
Auxiliary	—	—	—	—
Product	2-((1-(4-chlorophenyl)ethylidene) amino)benzonitrile (3b)	1.36 g	0.0053 mol	FW 254.06

Product Yield = 91%

$$\text{E- factor} = \frac{0.7\text{ g} + 0.8\text{ g} + 17.3\text{ g} - 1.36\text{ g}}{1.36\text{ g}} = 12.82 \text{ kg waste per kg product}$$

$$\text{Atom economy} = \frac{254}{272} \times 100 = 93\%$$

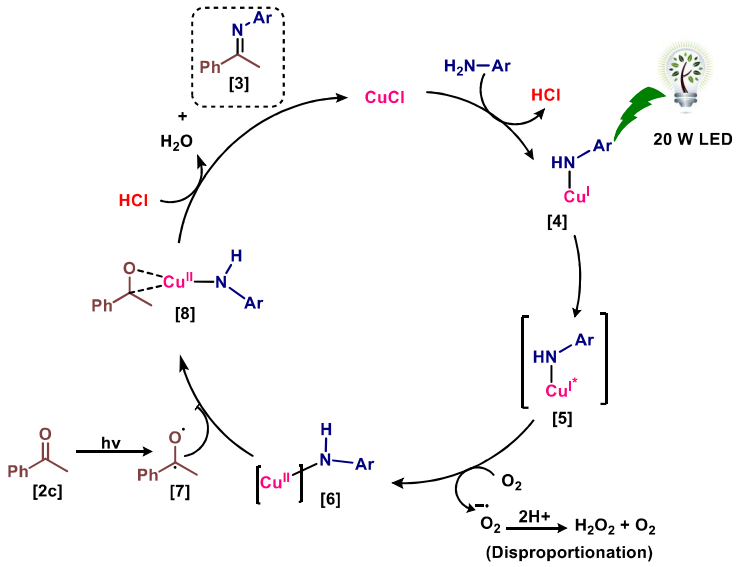
$$\text{Atom efficiency} = 91\% \times 93\% / 100 = 84.6\%$$

$$\text{Carbon efficiency} = \frac{15}{7+8} \times 100 = 100\%$$

$$\text{Reaction mass efficiency} = \frac{1.36\text{ g}}{0.7\text{ g} + 0.8\text{ g}} \times 100 = 90.6\%$$

2.3 Plausible Mechanism

Based on a literature survey[5], [33], [45]and control experiment, a plausible mechanism for the synthesis of copper-catalyzed Schiff's base was proposed (Scheme 2.6). The first step is the formation of Cu (I)-amine complex **[4].** Direct irradiation of the Cu (I) complex with the visible light (UV-visible absorption spectra Figure 2.4) resulted in the *in situ* formation of the excited complex with a partial positive charge on the ligand and partial negative charge on the metal center via the ligand to metal charge transfer (LMCT).



Scheme 2.6. Plausible mechanism

In the next step, the excited Cu complex **[5]** subsequently undergoes single electron transfer (SET) with molecular oxygen to furnish the Cu(II) complex**[6].** Next, the addition of the activated acetophenone **[7]** (via activation of acetophenone **(2c)** under visible light condition) to Cu (II) complex leads to the formation of intermediate, **[8]** which then leads to the formation of the Schiff's base as a product**[3]** by removal of water and regenerate the catalyst CuCl.

2.4 Conclusion

In conclusion, we have developed a simple, green eco-friendly, highly efficient, inexpensive process for Schiff's base using CuCl as a catalyst under visible light. This is the first example of using visible light to synthesize Schiff's base of 2-amino benzonitrile and acetophenone at room temperature using the CuCl catalyst. The inexpensive nature of the catalyst, no use of exogenous photosensitizer, and the energy efficiency under visible light irradiation make this process a green alternative to existing thermal methodologies.

2.5 Experimental section

2.5.1 General procedure for visible light-induced Schiff's base of 2-amino benzonitrile derivatives and acetophenones

A mixture of 2-aminobenzonitrile derivatives (**1**, 1 mmol), acetophenones (**2**, 1.2 mmol), a catalytic amount of CuCl in toluene as a solvent was stirred under an oxygen atmosphere and irradiation by commercially available 20 W LED for 3 hr. After the reaction was completed, the resulting product was washed with sodium bicarbonate solution followed by recrystallization of Schiff's base product **3** from ethanol.

2.5.2 Mechanistic Investigation with UV-Visible absorption spectra

UV-visible spectroscopy of the reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. The sample was prepared by mixing 2-aminobenzonitrile and CuCl with solvent (methanol) and a reaction mixture of 2-aminobenzonitrile, CuCl, and acetophenone in methanol solvent [Conc. 2-aminobenzonitrile = 1.0×10^{-4}mol/L,

Acetophenone = 1.25×10^{-4}mol/L] in a light path quartz UV cuvette. The UV-visible spectroscopy indicated that the maximum absorption wavelength of the reaction solution was found to be 324 nm.

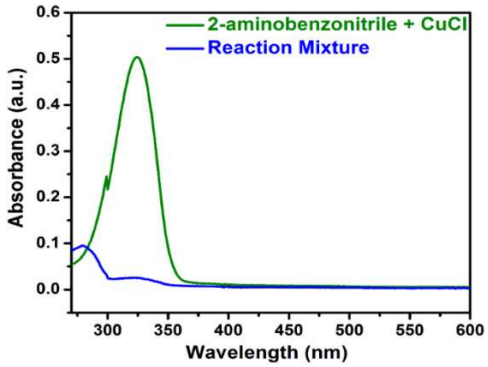
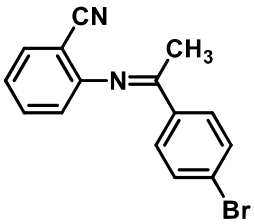


Figure 2.3 UV-visible absorption spectra of *in situ* generated Cu-(I) amine complex (green line), and the blue line indicates the reaction mixture of 2- amino benzonitrile, CuCl, and acetophenone.

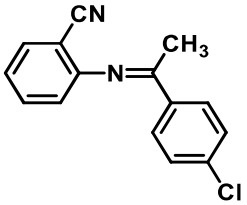
2.6 Characterization of product

2-((1-(4-Bromophenyl) ethylidene) amino) benzonitrile (3a)



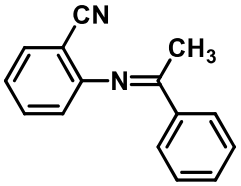
97% yield. White solid. m.p.: 165-167 °C ^{1}H NMR (500 MHz, DMSO) δ 7.54 – 7.46 (m, 2H), 7.41 – 7.26 (m, 2H), 7.14 (dd, J = 8.4, 0.6 Hz, 2H), 6.80 (dd, J = 8.4, 0.5 Hz, 1H), 6.66 – 6.53 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.79, 145.58, 138.46, 134.44, 132.91, 128.63, 125.96, 118.56, 116.55, 115.78, 94.03, 21.25. Anal. Calcd for $C_{15}H_{11}BrN_2$; C, 60.22; H, 3.71; N, 9.36 found: C, 60.20; H, 3.69; N, 9.34.

2-((1-(4-Chlorophenyl)ethylidene)amino)benzonitrile 3(b)



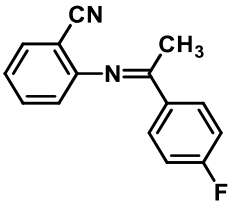
95% yield. White solid. m.p.: 163-165°C ^{1}H NMR (500 MHz, DMSO) δ 7.53 – 7.46 (m, 2H), 7.40 – 7.35 (m, 1H), 7.33 – 7.26 (m, 1H), 7.14 (dd, J = 8.4, 0.6 Hz, 2H), 6.80 (dd, J = 8.4, 0.5 Hz, 1H), 6.64 – 6.56 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.84, 145.63, 138.45, 134.44, 132.89, 128.63, 125.97, 116.56, 115.77, 94.05, 21.24. Anal. Calcd for $C_{15}H_{11}ClN_2$; C, 70.73; H, 4.35; N, 11.00 found: C, 70.70; H, 4.32; N, 10.98.

2-((1-Phenylethylidene)amino)benzonitrile 3(c)



97% yield. White solid. m.p.: 168-170 °C ^{1}H NMR (500 MHz, DMSO) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.38 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.17 – 7.10 (m, 2H), 6.85 – 6.77 (m, 1H), 6.64 – 6.56 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.79, 145.57, 138.42, 134.44, 132.91, 128.63, 125.96, 118.56, 116.52, 115.77, 94.02, 21.25. Anal. Calcd for $C_{15}H_{12}N_2$; C, 81.79; H, 5.49; N, 12.72 found: C, 81.75; H, 5.44; N, 12.69.

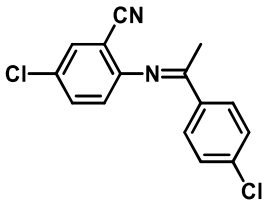
2-((1-(4-Fluorophenyl)ethylidene)amino)benzonitrile 3(d)



93% yield. White solid. m.p.: 162-165 °C ^{1}H NMR (500 MHz, DMSO) δ 7.54 – 7.48 (m, 2H), 7.38 (dd, J = 7.8, 1.3 Hz, 1H), 7.30 (ddd, J = 8.7, 7.2, 1.6 Hz, 1H), 7.15 (d, J = 7.8 Hz, 2H), 6.85 – 6.77 (m, 1H), 6.66 – 6.56 (m, 1H), 2.29 (s, 3H).^{13}C NMR (126 MHz, DMSO) δ 151.47, 145.17, 138.73, 134.45,

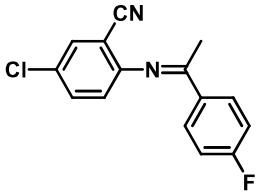
132.91, 128.72, 125.95, 118.50, 116.81, 115.96, 94.30, 21.25. Anal. Calcd for $C_{15}H_{11}FN_2$; C, 75.62; H, 4.65; N, 11.76 found C, 75.60; H, 4.63; N, 11.73.

5-Chloro-2-((1-(4-chlorophenyl)ethylidene)amino)benzonitrile 3(e)



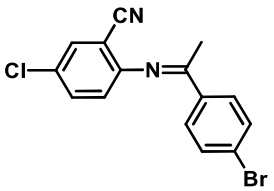
91% yield. White solid. m.p.: 164-166 ^oC ^1H NMR (500 MHz, DMSO) δ 7.49 (t, J = 5.4 Hz, 3H), 7.32 (dd, J = 9.0, 2.6 Hz, 1H), 7.13 (d, J = 8.3 Hz, 2H), 6.80 (d, J = 9.0 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.12, 145.66, 138.43, 134.54, 131.57, 128.63, 125.97, 119.01, 117.52, 117.34, 94.84, 21.25. Anal. Calcd for $C_{15}H_{10}Cl_2N_2$; C, 62.31; H, 3.49; N, 9.69 found C, 62.29; H, 3.47; N, 9.66

5-Chloro-2-((1-(4-fluorophenyl)ethylidene)amino)benzonitrile 3(f)



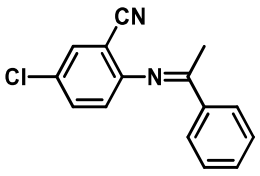
90% yield. White solid. m.p.: 172-175 ^oC ^1H NMR (500 MHz, DMSO) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 2.6 Hz, 1H), 7.32 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 1H), 2.29 (s, 3H).^{13}C NMR (126 MHz, DMSO) δ 151.09, 145.38, 138.61, 134.53, 131.56, 128.69, 125.97, 119.05, 117.55, 117.33, 94.87, 21.25. Anal. Calcd for $C_{15}H_{10}ClFN_2$; C, 66.07; H, 3.70; N, 10.27 found C, 66.05; H, 3.69; N, 10.25

2-((1-(4-Bromophenyl)ethylidene)amino)-5-chlorobenzonitrile 3(g)



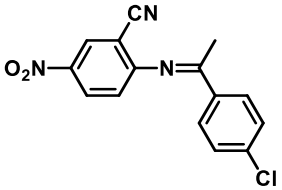
96% yield. White solid. m.p.: 164-166 ^{o}C ^{1}H NMR (500 MHz, DMSO) δ 7.53 – 7.46 (m, 3H), 7.32 (dd, J = 9.0, 2.6 Hz, 1H), 7.13 (dd, J = 7.9, 0.4 Hz, 2H), 6.80 (d, J = 9.0 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.13, 145.62, 138.45, 134.54, 131.58, 128.64, 125.97, 118.99, 117.52 , 117.35 , 94.82 , 21.25. Anal. Calcd for $C_{15}H_{10}BrClN_2$; C, 54.00; H, 3.02; N, 8.40 found C, 53.96 H, 3.00; N, 8.36

5-Chloro-2-((1-phenylethylidene)amino)benzonitrile 3(h)



96% yield. White solid. m.p.: 168-172 ^{o}C ^{1}H NMR (500 MHz, DMSO) δ 7.49 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.30 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 7.17 – 7.11 (m, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.63 – 6.56 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.47, 145.17, 138.73, 134.45, 132.91, 128.72, 125.95, 118.50, 116.81, 115.96, 94.30, 21.25. Anal. Calcd for $C_{15}H_{11}ClN_2$ C, 70.73; H, 4.35; N, 11.00. Found C, 70.70; H, 4.33; N, 10.98

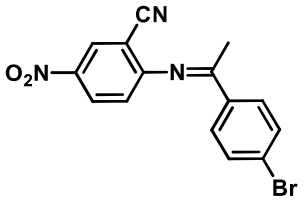
2-((1-(4-Chlorophenyl)ethylidene)amino)-5-nitrobenzonitrile 3(i)



80% yield. White solid. m.p.: 160-165 ^{o}C ^{1}H NMR (500 MHz, DMSO) δ 7.53 – 7.44 (m, 3H), 7.32 (dd, J = 9.0, 2.6 Hz, 1H), 7.14 (d, J = 7.8 Hz, 2H), 6.80 (d, J = 9.0 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.11, 145.59, 138.48, 134.54, 131.56, 128.64, 125.96, 119.04,

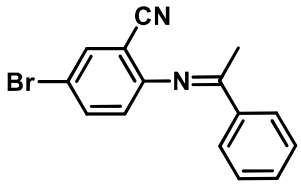
117.53, 117.33, 94.85, 21.24. Anal. Calcd for $C_{15}H_{10}ClN_3O_2$ C, 60.11; H, 3.36; N, 14.02. found C, 60.08; H, 3.34; N,14.00.

2-((1-(4-Bromophenyl)ethylidene)amino)-5-nitrobenzonitrile 3(j)



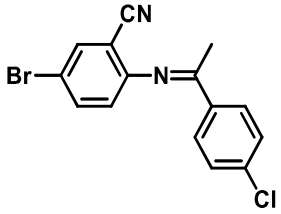
88% yield. White solid. m.p.: 163-168 °C ^{1}H NMR (500 MHz, DMSO) δ 7.52 – 7.47 (m, 3H), 7.32 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.13, 145.62, 138.45, 134.54, 131.58 , 128.64 , 125.97 , 118.99, 117.52, 117.35, 94.82, 21.25. Anal. Calcd for $C_{15}H_{10}BrN_3O_2$; C, 52.35; H, 2.93; N, 12.21 found C, 52.33; H, 2.90; N, 12.18

5-Bromo-2-((1-phenylethylidene)amino)benzonitrile 3(k)



91% yield. White solid. m.p.: 160-163 °C ^{1}H NMR (500 MHz, DMSO) δ 7.53 – 7.47 (m, 2H), 7.40 – 7.35 (m, 1H), 7.30 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.14 (dd, *J* = 8.4, 0.6 Hz, 2H), (s). 6.80 (dd, J = 8.4, 0.5 Hz, 1H), 6.64 – 6.54 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.41, 145.21, 138.72 , 134.45, 132.94, 128.73, 125.97 , 118.50 , 116.85, 116.02, 94.39, 21.26. Anal. Calcd for $C_{15}H_{11}BrN_2$; C, 60.22; H, 3.71; N, 9.36 found: C, 60.19; H, 3.69; N, 9.33.

5-Bromo-2-((1-(4-chlorophenyl)ethylidene)amino)benzonitrile 3(l)



90% yield. Yellow solid. m.p.: 175-178 ^{o}C ^{1}H NMR (500 MHz, DMSO) δ 7.53 – 7.46 (m, 3H), 7.32 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.12, 145.66, 138.43, 134.54, 131.57 , 28.63 , 125.97, 119.01, 117.52, 117.34, 94.84, 21.25. Anal. Calcd for $C_{15}H_{10}BrClN_2$ C, 54.00; H, 3.02; N, 8.40 found: C, 53.98; H, 3.00; N, 8.37

2.7 Spectral Data of Product 3a

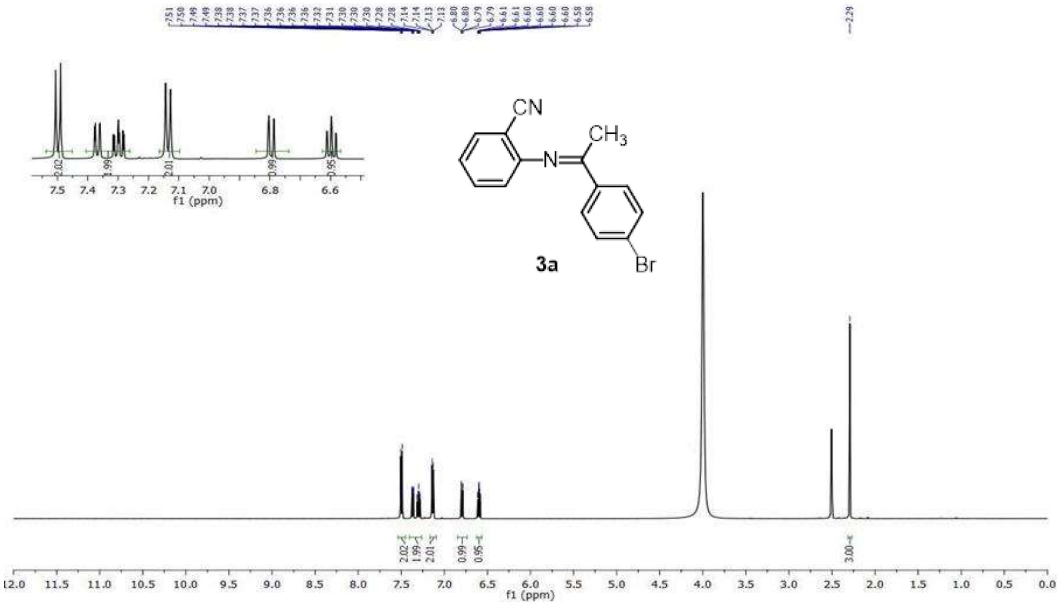


Figure 2.4 ^{1}H NMR spectrum of compound **3a**

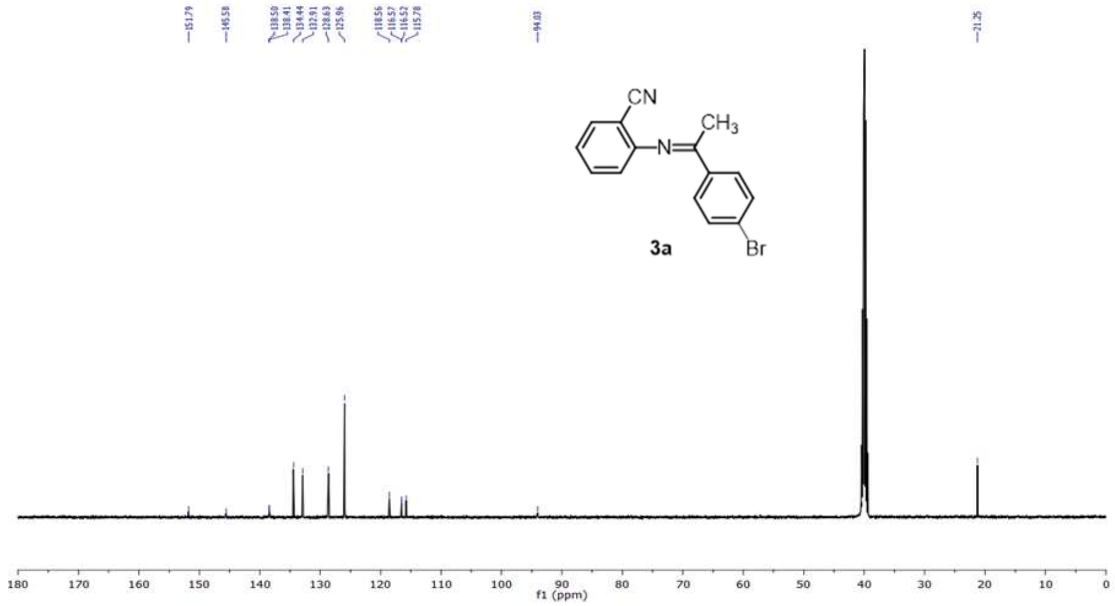


Figure 2.5 ^{13}C NMR spectrum of compound **3a**

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