CHAPTER-2

Electro-organic synthesis isatins and hydrazones through C-H cross-coupling C(SP^2)-H/C(SP^3)-H functionalization

2.1 Introduction

Isatin or indole-2,3-dione was initially created in 1840 by Erdmann and Laurent as a byproduct of the oxidation of the indigo dye by nitric acid and chromic acid, which produced the vivid orange monoclinic crystals known as isatin. The current form of isatin was established by Kekulé, whereas the chemistry of isatin was initially studied by Sumpter and then revisited by Popp, and Silva et al. refined Sumpter's first study on the chemistry of isatins [1]. Since then, isatin and its derivatives have been widely used for analytical and synthetic purposes. They form an important class of heterocyclic compounds which are used as precursors for the synthesis of drugs and bioactive molecules possessing significant biological activities, including anti-inflammatory, anticancer, antibacterial, anticonvulsant, anti-fungal, antioxidant properties, etc [2]. Therefore, researchers are focusing on devising new methods for the chemical synthesis of isatin derivatives. Recent research shows that C–H activation reactions on acetophenone with diverse nucleophiles is an effective technique in the chemical synthesis of heterocyclic compounds [3]. The process of synthesizing oxygen-containing subunits, which are found in a large number of natural products and physiologically active compounds, is most frequently carried out by selective oxidation [4].

The best and most accessible source of oxygen is molecular oxygen (O_2), which is also the purest natural oxidant [5]. The C–H activation of acetophenone, therefore, led to a large number of C–C bond-forming reactions [6]. Unfortunately, only a few techniques for utilizing transition metal catalysts to generate C–N bonds with C–H activation of 2-aminoacetophenones have been devised. Unfortunately, only a few techniques for utilizing transition metal catalysts to generate C–N bonds with C–H activation of 2-aminoacetophenones have been devised. These processes transform secondary amines into potential amides, suggesting that the amine group may also be crucial for such transformation [7,8]. Isatins using the above approach suffer from several drawbacks, including the employment of a costly or hazardous catalyst, a prolonged reaction time, laborious synthetic steps, a low product yield, etc. [9,10]. Therefore, there is a need to develop generic and straightforward methods for greener synthesis of isatins, particularly those that include a reaction without the need for metals. In this context, electrochemical synthesis proves to be a sustainable, greener and effective technology which has attracted special attention around the globe from the research community and industry [11]. for the synthesis of physiologically active natural products and functional materials. As a redox equivalent, electricity is used in the electrochemical process, which is a potent and sustainable method for the chemical transformation of organic molecules [12]. The utilization of electrons as a redox agent helps in achieving a cleaner metal-free method for the synthesis with reduced wastage and non-usage of toxic chemicals. The contemporary electrochemical organic synthesis renaissance is made possible by the culmination of the development of electrochemical techniques, methodologies, and equipment [13].

2.2 Results and Discussion

In our continuous effort towards the electro-organic synthesis of small molecules, [14] in this communication, we report a greener synthesis of isatins and their respective hydrazones in good to excellent yields using an electro-organic synthetic approach through C–N cross-coupling and C(sp^2)–H/C(sp^3)–H functionalization. In our initial studies, we took 2-aminoacetophenone **1a** as a model substrate to probe various reaction parameters in an undivided cell, as shown in **Table 2.1**.

We have chosen graphite electrodes for our study as graphite electrodes have advantages over other electrodes by offering excellent conductivity, homogeneity, stability, large surface area, versatility, chemical inertness and cost-effectiveness, all of which are crucial for the electrochemical process. We first evaluated the requirement of a promoter and the choice of solvent using ^{n}BuNBr as the electrolyte at a constant voltage of −0.2 V under ambient atmosphere for 2h in an undivided cell equipped with graphite carbon (2 cm^2) both as an anode and a cathode at room temperature (25°C). It was found that the desired product formed in 20% yield in the presence of molecule iodine (1.3 mmol) as a promoter and DMSO as a solvent (**Table 2.1, entry 3**). Different solvents such as 1,4-dioxane, DMF and DMSO were tested, and it was observed that the desired electro-organic transformation took place only in the presence of DMSO, which is a source of nascent oxygen for the newly formed carbonyl group in isatin product **2a** (**Table 2.2, entries 3–5**).

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Replacing $NaClO_4$ with other electrolytes results in a decrease in product yield to 13–23% (**Table 2.1**, **entries 3–8**). Atmospheric conditions also affected the product yield; upon changing from an ambient atmosphere to an inert atmosphere the yield decreased to 30% in 2 hour (**Table 2.1**, **entry 10**). It is worth mentioning here that under an inert atmosphere, the reaction proceeded slowly and requires more time for completion. The reaction yield was also decreased to 10% upon replacing the carbon graphite cathode with a platinum plate (**Table 2.1**, **entry 9**), indicating the importance of graphite electrodes in this electro- organic synthesis of isatins.

Further, it was observed that when keeping the voltage constant at -0.2 V, an excellent yield is produced, while a lower or higher current results in a decrease of product yield (**Table 2.4**). Finally, the reaction stopped under otherwise identical conditions when there was no electric current, supporting the initial hypothesis that current is extremely crucial (**Table 2.1**, **entry 2**). This implies that the envisioned conversion could be precisely controlled by switching the electric current on or off. Further, the discovered electro-organic synthesis also works well for the synthesis of isatin derivatives on the gram scale.

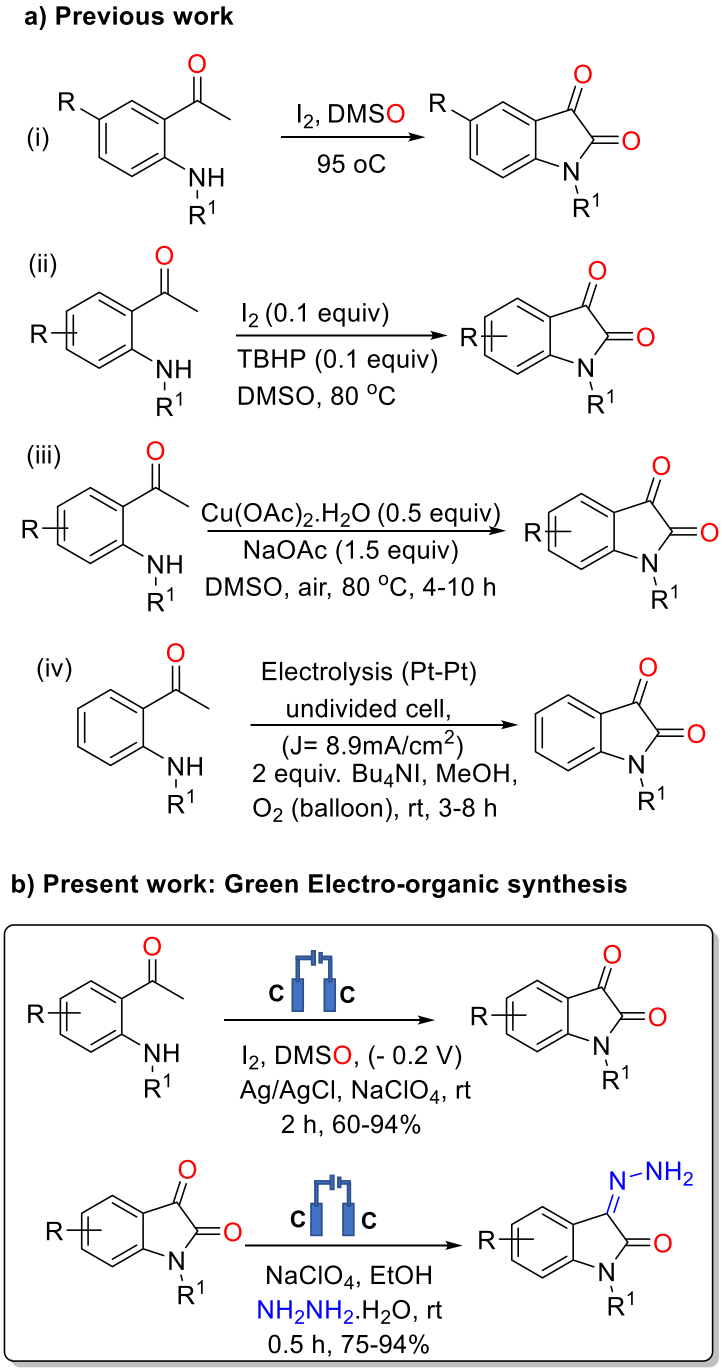
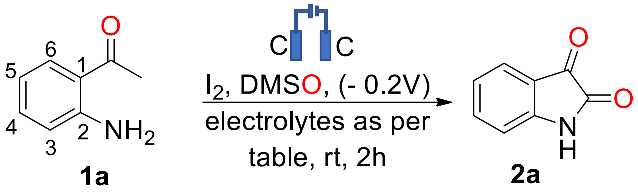

a) Previous work
(i)
R
O
NH
R1
I2, DMSO
95 oC
(ii)
I2 (0.1 equiv)
TBHP (0.1 equiv)
DMSO, 80 oC
(iii)
Cu(OAc)2.H2O (0.5 equiv)
NaOAc (1.5 equiv)
DMSO, air, 80 oC, 4-10 h
(iv)
Electrolysis (Pt-Pt)
undivided cell,
(J= 8.9mA/cm2)
2 equiv. Bu4NI, MeOH,
O2 (balloon), rt, 3-8 h
N
b) Present work: Green Electro-organic synthesis
C
C
I2, DMSO, (- 0.2 V)
Ag/AgCl, NaClO4, rt
2 h, 60-94%
NaClO4, EtOH
NH2NH2.H2O, rt
0.5 h, 75-94%
N-NH2

Table 2.1 Optimization of the reaction conditions.



Entry	Reaction conditions[a]	Yields (%)[b]
1	No electricity	0
2	No electrolyte	0
3	Electrolyte nBuNBr (0.1M)	20
4	Electrolyte KPF_6 (0.1M)	19
5	Electrolyte nBu_4NBF_4 (0.1M)	21
6	Electrolyte nBu_4PF_6, (0.1M)	17
7	Electrolyte nBu_4NaOAc (0.1M)	13
8	Electrolyte KBr (0.1M)	23
9	Electrolyte $NaClO_4$ (0.1M), Pt (cathode)	10
10	Electrolyte $NaClO_4$ (0.1M)/Ar	30
11	**Electrolyte $NaClO_4$ (0.1M)/ air O_2**	**94**
12	Electrolyte $NaClO_4$ (0.1M)/ air O_2/**TEMPO**	0

[a]Reaction condition: two graphite carbon electrode (Anode, 2 cm^2) and (cathode 2 cm^2), I_2 (1.3 equiv), reference electrode (Ag/AgCl), DMSO solvent (5 ml), at rt, 2 hour,[b] isolated yield.

After having the optimized reaction conditions in hand, the generality of the reaction protocol towards the synthesis of isatin was examined by investigating the substrate scope of 2-aminoacetophenones. The utilization of a variety of 2-amino acetophenones **1a–p**, formed by substitution on the aromatic ring with electron donating groups (EDG) and electron withdrawing groups (EWG) along with the substitution on the nitrogen atom of the amine group with alky and aryl groups [16], results in the formation of desired products **2a–p** in good to excellent yields (Scheme 1). Substitution of the amino group of 2-aminoacetophenone with a methyl group leads to the formation of the corresponding isatin derivative **2b** in 91%, while replacing this methyl group with the phenyl ring results in a decrease of product **2c** yield to 82%, which may be due to steric hindrance. There is a slight change in yields of the corresponding products **2d** and **2e** in the case of the 6-substituted aromatic ring with functional groups bromine and chlorine, respectively. In the case of the 5F-substituted precursor **1f**, the yield of the corresponding product **2f** was only 60%, while slight changes in yields, 89% and 87%, were observed when using the 5Cl-substituted precursor **1g** and the 5Br-substituted precursor **1h**, respectively, furnishing their corresponding chloro- and bromo-substituted products **2g** and **2h**. However, the 5-iodine substituted precursor **1i** results in a decrease of the yield to 80% of **2i** under identical reaction conditions. Substitution with a 5-methyl group in precursor **1j** leads to a decrease in the yield to 74% of **2j**, whereas the 5-methoxy substituted substrate **1k** furnished the product **2k** with a slight change in yield, 90% (**Scheme 2.1**). In the case of4Cl-substituted 2-aminoacetophenone **1l**, the yield of the corresponding isatin derivative **2l** decreased to 75%, while in the case of the 4-Br substituted precursor **1m** the product **2m** was produced with a slight change in yield (89%).

Interestingly, substitution of electron withdrawing groups (Cl, Br, I) at the 3-position of 2-aminoacetophone substrates **1n–p** leads to a decrease in the yield of isatin products **2n–p** to 74–78%, respectively (**Scheme 2.1**). One of the most effective uses of the electrochemical approach is the synthesis of C–N bonds, a group of significant chemical bonds that are typically present in bioactive chemicals, natural products, and functional materials [17,18]. For the purpose of synthesizing physiologically active natural products and functional materials, hydrazones, an important family of basic organic compounds with C–N linkages, are considered as essential building blocks.

Therefore, we planned to synthesize isatin hydrazones by electro-organic chemical synthesis. Due to their potential use in electrochemical processes, the attachment of hydrazone moieties to the isatin ring/aryl group has received much interest. Because of their immense relevance, numerous synthetic methods have been developed so far to synthesize these isatin hydrazones [19,20].

Thus, in our further efforts, we intended to synthesize the corresponding hydrazone **3a** of isatin **2a.** For this purpose, compounds **2a–p** were treated with hydrazine hydrate in an undivided cell equipped with graphite carbon (2 cm^2) both as an anode and a cathode at room temperature (25 °C), and a constant voltage of −0.2 V was applied under ambient atmosphere for 30 min.

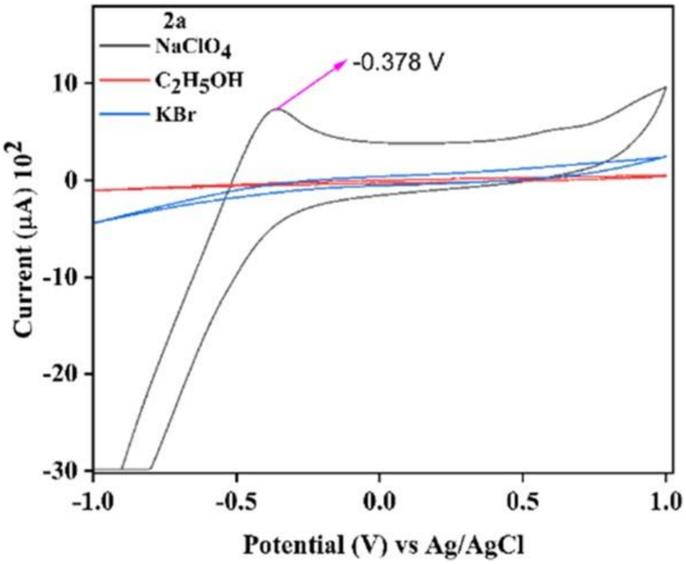


Figure 2.1 Cyclic voltammetry of **2a** at 0.02 mV s^{-1} at pH = 4.

It was found that the desired products **3a–p** were formed in good to excellent yields of 75–94% in the presence of ethanol as a solvent and $NaClO_4$ as an electrolyte [21,23] as shown in [**Scheme 2.2**].

The data for electro-organic synthesis of hydrazone derivatives **3a–p**, along with used potentials, are shown in **Table 2.2**. Further, to examine the spectrum of substrates for the synthesis of hydrazones electrochemically, the reactions of hydrazine hydrates with different acetophenone derivatives **4a–l** were also investigated, which produced the desired hydrazone derivatives of acetophenones **5a–l** in 80–95% yields under the optimized reaction conditions (**Scheme 2.3**) [24,25]. Various electron-donating groups (methoxy and methyl) were successfully tolerated in this transition, producing good to excellent yields (89–95%). The electron-withdrawing groups such as bromo and nitro also furnished good yields (80–89%) of the respective hydrazone compounds **5a–l** (**Scheme 2.3**)

To investigate the oxidation and reduction processes of the synthesized compounds, cyclic voltammetry (CV) experiments were performed in the potential range of −1.0 V to+1.0 V versus the Ag/AgCl electrode. The CV curves of substrate **2a** in $NaClO_4$ and other tested electrolytes, including KBr in C_2H_5OH, are shown in (**Figure 2.1**] [26,27].

It is clearly seen from the figure that compound **2a** in C_2H_5OH is inactive for oxidation in the absence of electrolyte $NaClO_4$. and reduction peaks were observed. However, when the $NaClO_4$ electrolyte was added to this reaction, a notable rise in the oxidation peak current was observed at −0.378 V, indicating that $NaClO_4$ is a suitable electrolyte for studying the electrochemical properties of compound **2a** (**Figure 2.1**). Further, when KBr and other tested electrolytes were added to this solution, no oxidation According to the CV graphs shown in [**Figure 2.2** and **2.3**], when the scan rate is increased, both the cathodic (reduction) peaks increase in magnitude.

This suggests that higher scan rates promote faster reaction rates. Additionally, the cathodic peak shifts towards more negative potentials as the scan rate increases. These potential shifts indicate that the reductionprocesses are influenced by the speed at which the potential changes. When the scan rate increased, the electrochemical current magnitude, proportional to the mass transport rate of compound **3a** towards the electrode, grew steadily and was more significant, as illustrated in [**Figure 2.2(a)** and **2. 3(a)**].

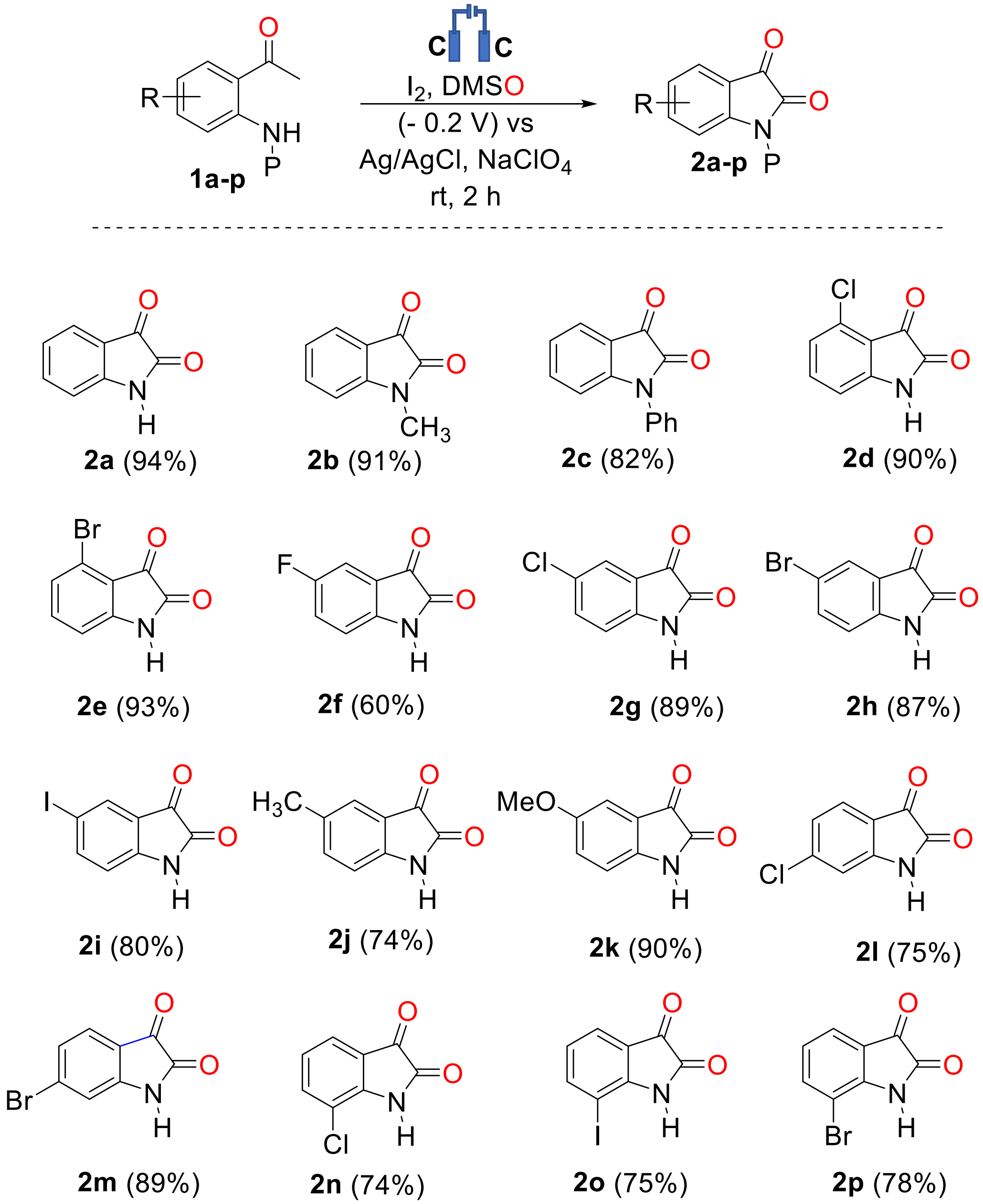
This implied that the rate of electrochemical kinetics in 0.1 M $NaClO_4$ was still not very effective in attaining equilibrium at the solution–electrode interface.

The linear relationship between the cathodic peak current and the square root of the scan rate seen in [**Figure 2.2(b)** and **2.3(b)**] points to a diffusion-con- trolled mechanism. We thought that enhancing the electro- chemical activity of **3a** may speed up the chemical reaction on its surface to improve the electrochemical kinetics of **3a** in 0.1 M $NaClO_4$ solution. the electrode, and thus the electrochemical current, decreases. However, the diffusion layer becomes thinner as the potential scan rate starts increasing which creates a larger concentration gradient and a higher mass flux of the target compound towards the electrode, resulting in a larger concentration gradient and a higher mass flux of the target compound towards the electrode, resulting in a larger electrochemical current.

At a faster scan rate which leads to larger peak currents, the electrochemical kinetics of **3a**, in an electrolyte, does not reach to equilibrium at the electrolyte-electrode interface. This means that the rate of the electrochemical reaction is primarily limited by the mass transport of **3a** to the electrode surface.

This has been achieved by enhancing the electrochemical activity of **3a** by accelerating the chemical reaction on the surface of the electrode. These improvements would aim to increase the efficiency of the electrochemical system and 7 shows faster reaction kinetics and higher cathodic peak current density than at pH = 4; achieve a faster equilibrium at the solution–electrode interface [30–32]. Compound **3a** at pH = this means that the rate of the electrochemical reaction is faster at pH = 7 at the electrode surface. From the above discussion, it can be concluded that compound **3a** is highly stable at pH = 7 (**Figure 2.2** and **2.3**) [33].

Scheme 2.1 Electro-organic synthesis of isatins **2a–p**.



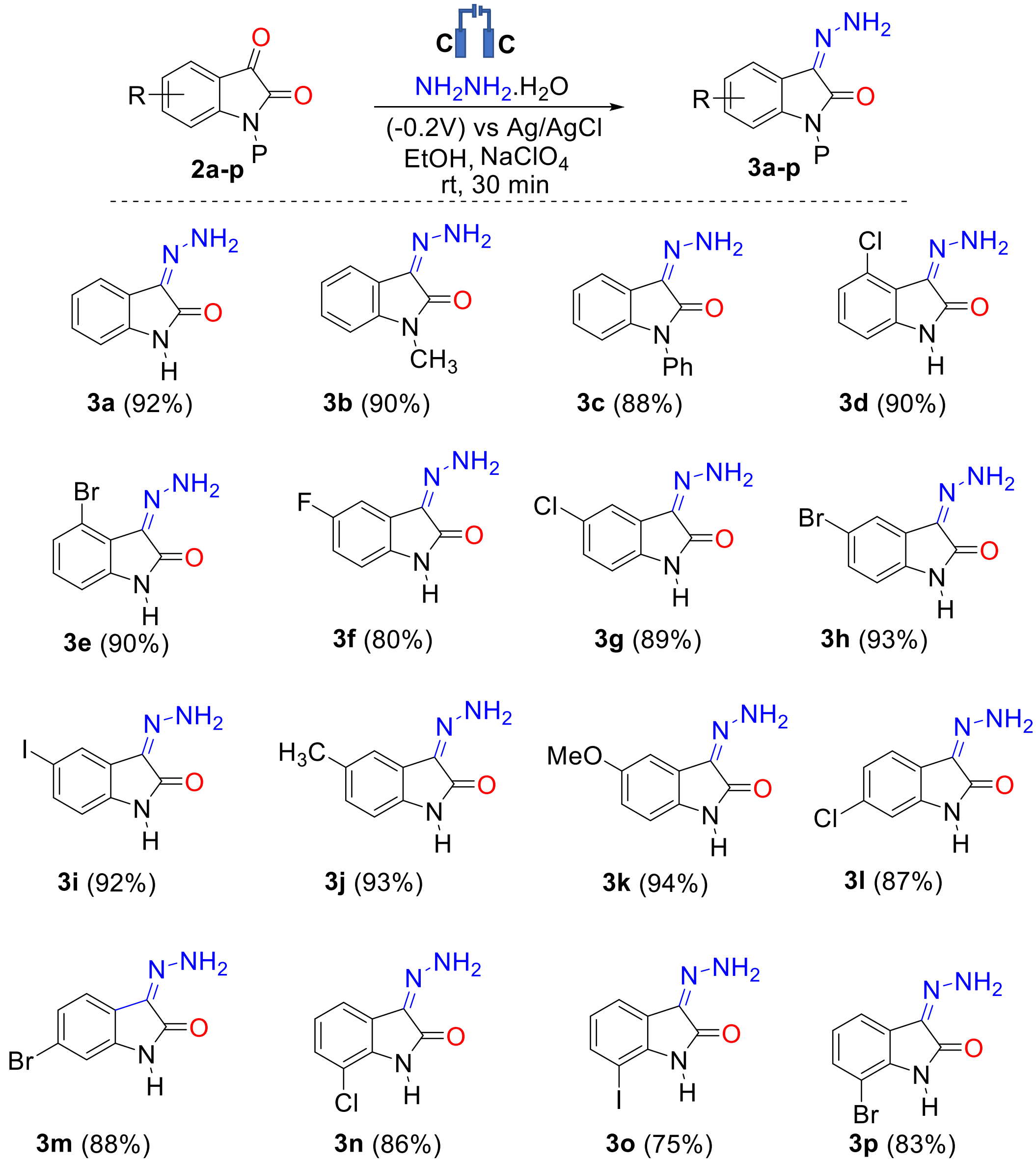
Reaction conditions: 2-aminoacetophenones **2a-2p** (1 equiv.), I_2 (1.3 equiv.), solvent DMSO (5 ml), two graphite electrodes (anode and cathode), and a reference electrode (Ag/AgCl) under open air at rt, 2 h.

Table 2.2 Data for Electro-organic synthesis of hydrazone derivatives (**3a-3p**) at rt and 1.8 × 10^3 sec.

Entry	Substrate + $NH_2NH_2.H_2O$ + 0.1M $NaClO_4$, rt and 1.8 × 10^3 sec	Potential (in volts)	Products	Yield %
1.	**2a**	(-0.036 to 0.030)	**3a**	92
2.	**2b**	(0.099 to 0.090)	**3b**	90
3.	**2c**	(0.066 to 0.106)	**3c**	88
4.	**2d**	(-0.485 to - 0.535)	**3d**	90
5.	**2e**	(-0.432 to -0.495)	**3e**	90
6.	**2f**	(-0.463 to -0.490)	**3f**	80
7.	**2g**	(-0.383 to -0.389)	**3g**	89
8.	**2h**	(-0.402 to -0.415)	**3h**	93
9.	**2i**	(0.483 to – 0. 482)	**3i**	92
10.	**2j**	(-0.487 to -0.483)	**3j**	93
11.	**2k**	(-0.485 to -0.535)	**3k**	94
12.	**2l**	(-0.025 to 0.026)	**3l**	87
13.	**2m**	(-0.485 to -0.486)	**3m**	88
14.	**2n**	(0.033 to 0.330)	**3n**	86
15.	**2o**	(0.499 to 0.432)	**3o**	75
16.	**2p**	(-0.086 to -0.095)	**3p**	83

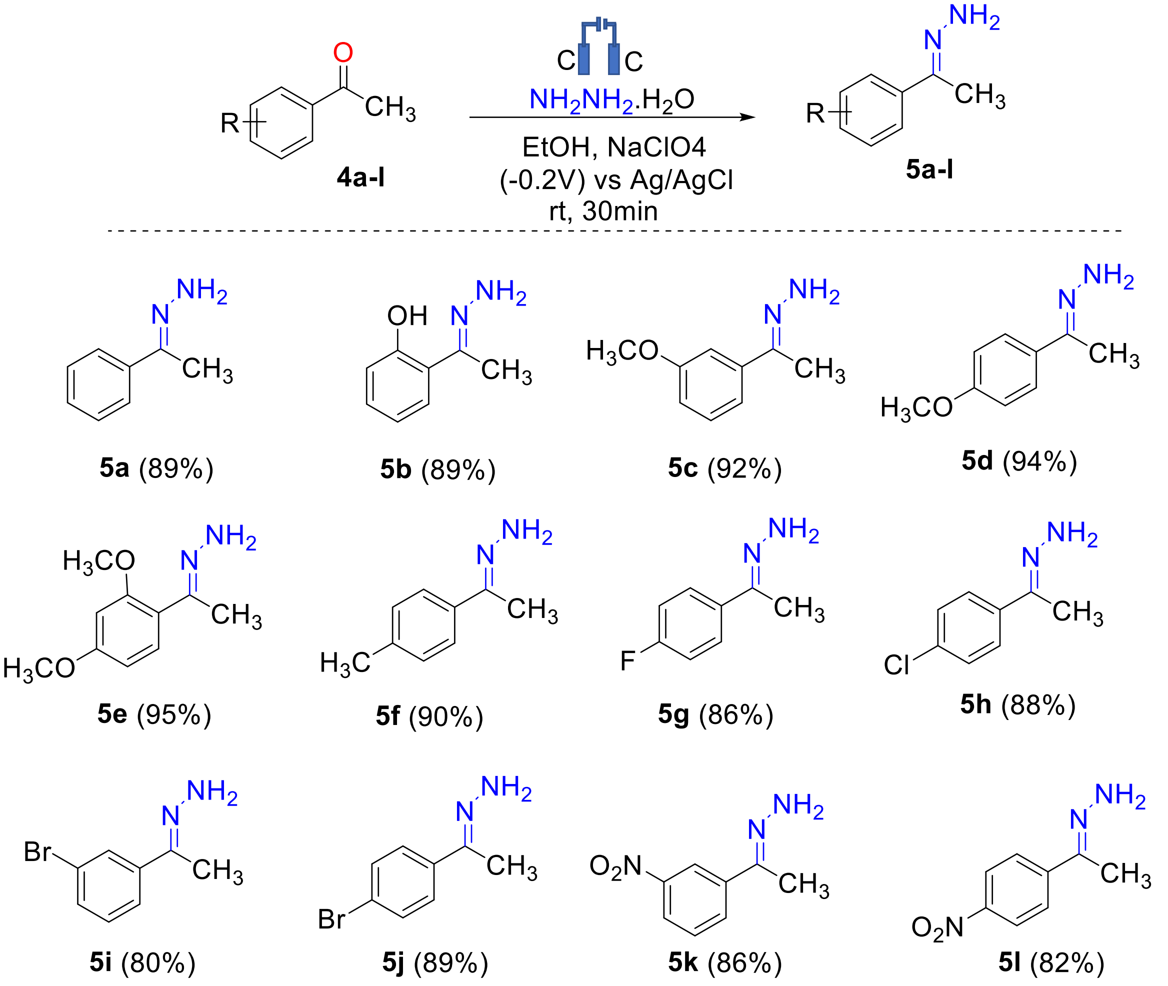
AC impedance measurements (electrochemical impedance spectroscopy – EIS) have also been carried out and Nyquist plots of **3a** and **5a** were recorded in a wide frequency range,0.01 Hz to 100 kHz at different potentials *viz.*, 0 V, −0.4 V and −0.9 V at pH 4.0 and 7.0 using C_2H_5OH with 0.1 M $NaClO_4$ as an electrolyte at room temperature. This study (**Figure 2.4, 2.5** and **Figure 2.8**) helped us to determine the charge transfer resistance offered by compounds **3a** and **5a** under the given reaction conditions. The study revealed that as the cathodic potential increases, the charge transfer resistance experienced by **3a** and **5a** at pH 4.0 and 7.0 decreases. showed that **3a** at pH 7.0 and −0.9 V *vs.* Ag/AgCl hasthe lowest charge transfer resistance which implies high conductivity of the compound.

Scheme 2.2 Electro-organic synthesis of hydrazones **3a–p**.



Reaction conditions: isatins (0.68 mmol), hydrazine hydrate (0.81 mmol), solvent (5 ml), at rt (25 °C), 30 min, a three-electrode system (two graphite electrodes and a reference electrode Ag/AgCl), an undivided cell, and $NaClO_4$ (0.1 M) as an electrolyte.

Scheme 2.3 Electro-organic synthesis of hydrazones **5a–l**.



Reaction conditions: acetophenones (0.68 mmol), hydrazine hydrate (0.81 mmol), solvent (5 ml), at rt (25 °C), 30 min, a three-electrode system (two graphite electrodes and a reference electrode Ag/AgCl), an undivided cell, and $NaClO_4$ (0.1 M) as an electrolyte.

Further C_{dl} values were calculated by plotting current density *vs.* scan rate. **Figure 2.6** show the C_{dl} value (1.8 µF cm^{-2}) at pH = 7 while [**Figure 2.7**] shows the C_{dl} value (2.67 µF cm^{-2}) at pH [37].

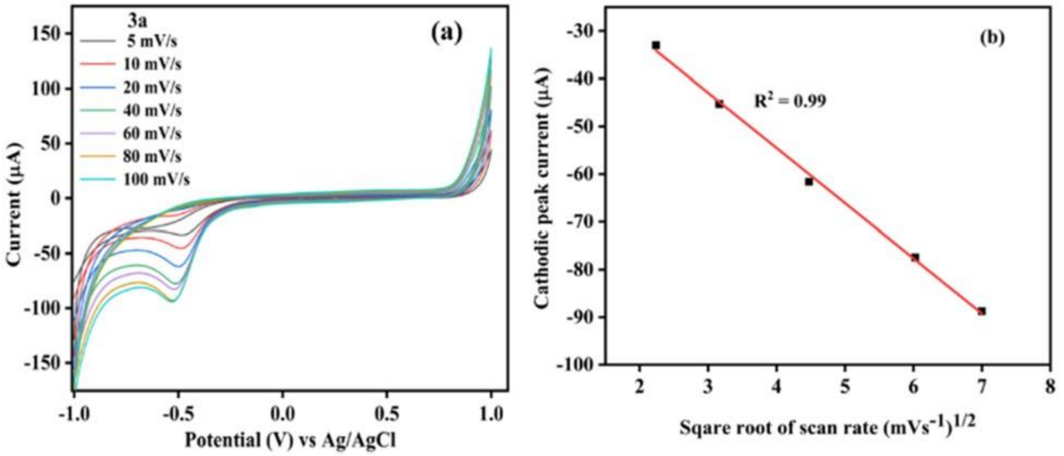


Figure 2.2 (a) Cyclic voltammograms of **3a** at pH = 7. (b) Plot for cathodic peak current vs. square root of scan rate for diffusion-controlled reaction of **3a** at pH = 7.

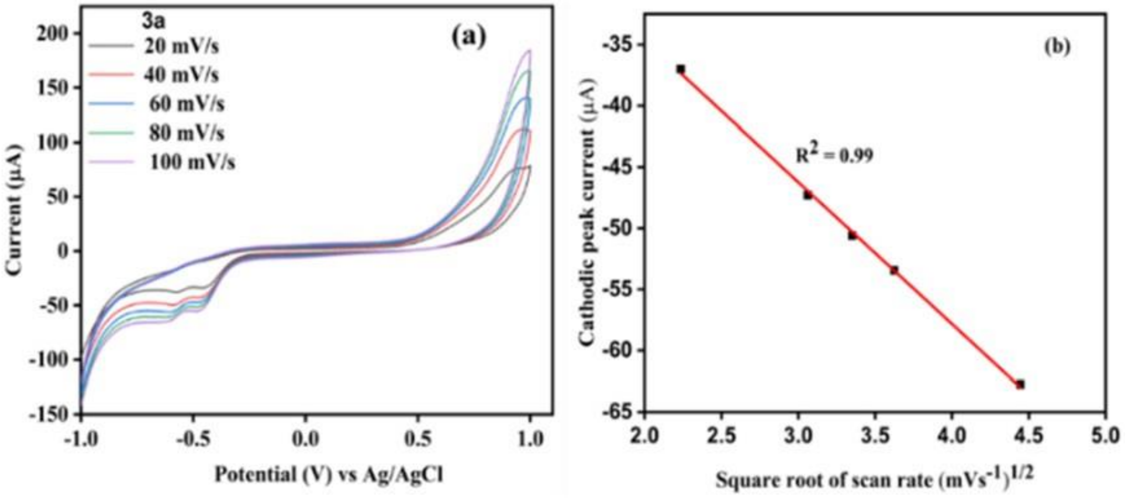


Figure 2.3 (a)Cyclic voltammograms of **3a** at pH = 4 (b) Plot for cathodic peak current vs square root of scan rate for diffusion-controlled reaction of **3a** at pH = 4

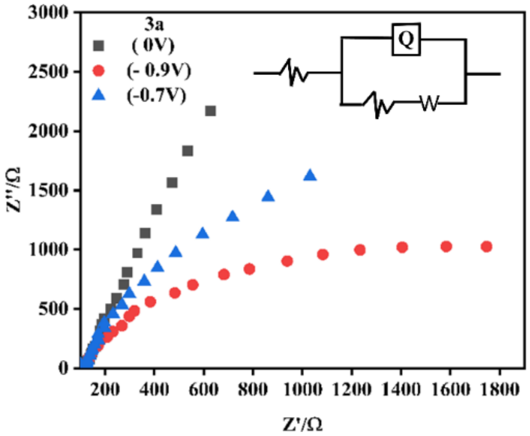


Figure 2.4 Electrochemical impedance spectroscopy (EIS) graph of **3a** at different potentials at pH = 4, and the fitted circuit plot corresponds the R(QR)W parameter.

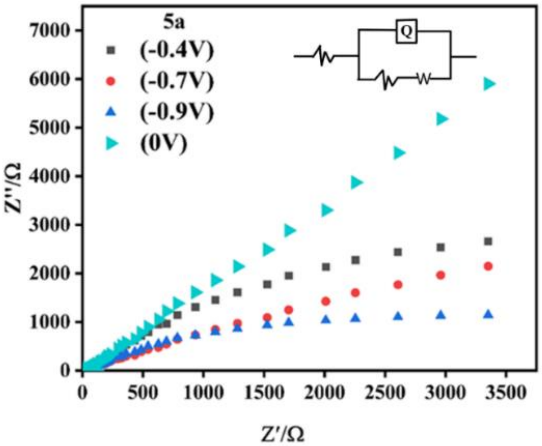


Figure 2.5 EIS graph of **5a** at different potentials at pH = 4, and the fittedcircuit plot corresponds to the R(QR)W parameter.

This shows that the Based on the experimental results and literature reports [16], a plausible mechanism is proposed in **Figure 2.6**.

To investigate the formation of free radical intermediates during the reaction, a parallel reaction of **1a** with the free radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) was performed under the optimal conditions [40,41].

It was observed that the desired product **2a** was not formed in the presence of TEMPO, molecular iodine alone could not promote the reaction in the absence of electricity (**Table 2.1, entry 1**). This shows that the iodine radical generated from the iodide anion by an electrochemical process was involved in the reaction process. This radical, when came into contact with compound **1a,** resulted in radicalization of the latter, giving intermediate **I** followed by the elimination of HI. Now, intermediate **I** reacts with DMSO and generates a new radical intermediate **II** with the formation of a new C–O bond in this transformation, the oxygen atom of DMSO bearing the free radical reacts with intermediate **I** having a methylene free radical.

In the next step, the formation of 2-(2-aminophenyl)-2-oxoacetaldehyde (**III**) takes place *via* the elimination of dimethyl sulphide (Kornblum oxidation). Intermediate **III** contains two carbonyl groups, and the newly formed carbonyl group contains the oxygen atom coming from DMSO. The nitrogen atom of the 2-amino group forms a C–N bond with the aldehydic carbon of **III**, followed by the attack of the O-atom on I_2, leading to the formation of intermediate **IV** with a five-membered N-heterocyclic ring fused with a benzene ring. In the final step, the formation of the desired compound isatin **2a** results *via the* liberation of HI [16]. The isatin **2a** at the cathode reacts with hydrazine hydrate under the standard reaction conditions and forms its respective hydrazone **3a** (**Figure 2.6**).

2.3 Plausible mechanism

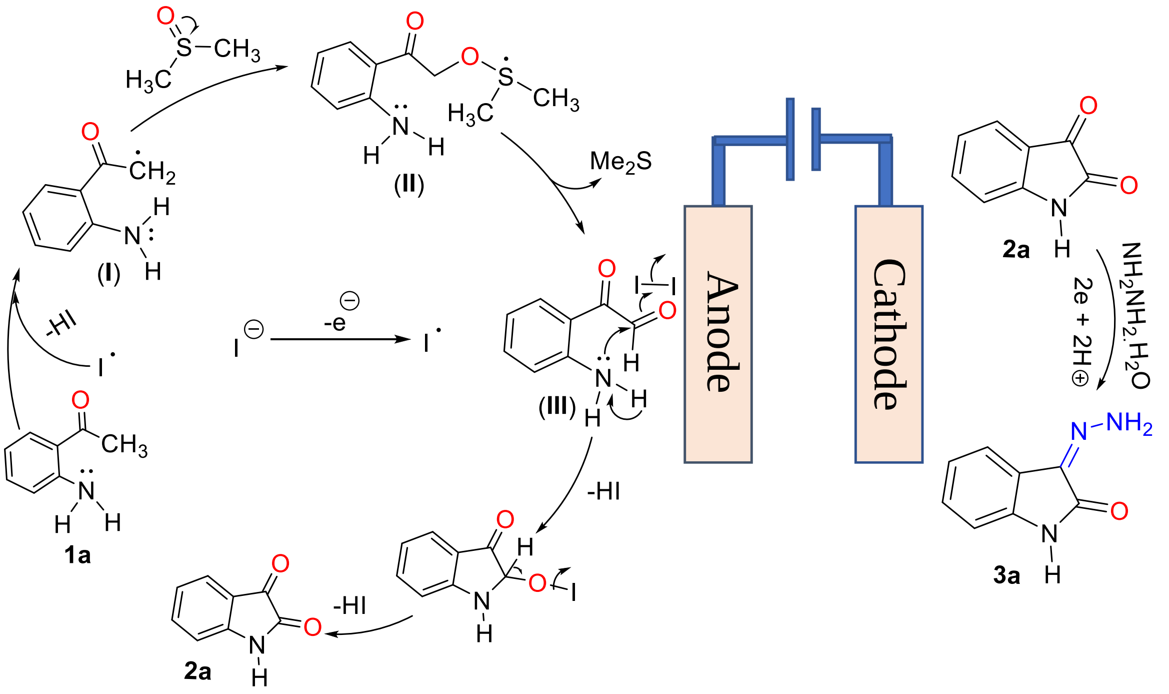


Figure 2.6 Plausible mechanism of the electro-organic synthesis of isatins and hydrazones.

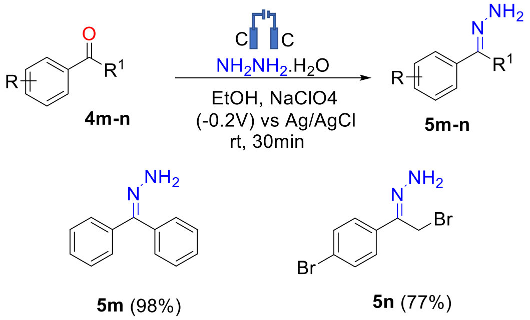
2.4 Conclusion

In summary, we have reported the efficient and greener method for the synthesis of isatin derivatives and their corresponding hydrazones. Electro-organic method promoted by iodine in DMSO solvent through C-N Cross-coupling and C(sp^2)-H/C(sp^3)-H functionalization was reported here to synthesize isatin derivatives via free radical mechanism in shorter reaction time. Corresponding hydrazone derivatives of isatins were prepared in the absence of iodine in ethanol. These transformations were well tolerated with EDG and EWG substituents on core molecules and furnished isatins and respective hydrazones in good to excellent yield. The optimized reaction protocol reported here works well on acetophenone derivatives bearing

EDG and EWG substituents to synthesize their corresponding hydrazones. Notably, our electro-organic method is free from use of transition metals. Importantly, this reaction is feasible on a gram scale to synthesize biologically relevant molecules for a larger production.

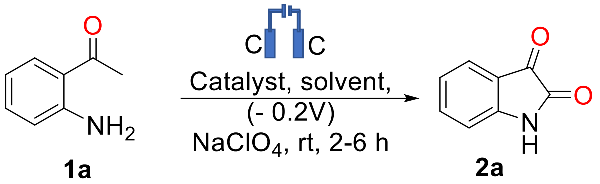
2.5 Experimental section

All reactions were performed in an Electrochemical cell at room temperature (~25-26 ^{o}C). Solvents and chemicals were purchased from Merck. Prior to usage, all glassware underwent an extended 110 °C oven drying period. All commercial materials and solvents were used without purification unless otherwise indicated. Anhydrous acetonitrile, Methanol, and Ethanol were purchased from Sigma-Aldrich. A CHI-608C Potentiostat/Galvanostat has been used for all electrochemical studies. All electrochemical experiments were performed in an undivided electrochemical cell using redried Glassware. Each electro organic synthesis was performed using two electrodes system viz., carbon cloth (2cm^2) as an anode and iron electrode (2cm^2) as a cathode. All electrodes were purchased from Sinsil International India (CH Instruments). Thin-layer chromatography was performed using pre-coated plates contained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV). The column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate and hexane as eluent. Melting points were recorded on a digital melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded in Bruker Avance 500 MHz NMR spectrophotometer with operating frequencies of 500 MHz (^{1}H) and 125 MHz (^{13}C), respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent ($CDCl_3$ and DMSO-d_6) signal. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet. The information for the 1H NMR spectra is given in the order, chemical shifts (multiplicity, coupling constants, and the number of hydrogen. All chemical shifts are reported relative to TMS. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz.



Scheme 2.3 The electro-organic synthesis of hydrazones **5m** and **5n**

Table 2.3 Optimization conditions for the solvent and promoter



Entry	Promoter	Solvents	Time (h)	Yield%
1	-	-	6	NR
2	-	DMSO	6	NR
3	I_2	Dioxane	6	NR
4	I_2	DMF	6	NR
5	I_2	DMSO	2	94

NR = No Reaction

Table 2.4. Optimization of the Potential

Potential	Yield%
(-0.2) V	94
(-0.3) V	60

Table 2.5 Compound (3-hydrazonoindolin-2-one) **3a** at pH=4

Entry	Potential (V vs Ag/AgCl)	R_{ct} (Ω/cm^2)
1	-0.9	3.48
2	-0.7	4.52
3	0	5.42

Table 2.5 shows the lowest charge transfer resistance for (3-hydrazonoindolin-2-one**)** compared **3a** at pH = 4 with -0.9V, -0.7 V and 0V (vs Ag/AgCl). At -0.9 V, the lowest charge transfer resistance (R_{ct}) value was calculated to be 3.48 Ω/cm^2, which was lower compared to -0.7 V (4.52 Ω/cm^2) and 0 V (5.42 Ω/cm^2). It has been observed that the charge transfer resistance value was decreased when potential was decreased from 0 V to -0.9 V.

Table 2.6 Compound (3-hydrazonoindolin-2-one) **3a** at pH= 7

Entry	Potential (V vs Ag/AgCl)	R_{ct} (Ω/ cm^2)
1	-0.9	3.25
2	-0.7	4.12
3	-0.4	4.67
4	0	5.36

Table 2.6 shows the lowest charge transfer resistance for (3-hydrazonoindolin-2-one) compared to **3a** at pH =7 with -0.9 V, -0.7 V and 0 V (vs Ag/AgCl). Similar to the previous calculation, the lowest charge transfer resistance (Rct) value was observed at -0.9 V (3.25 Ω/cm2) in contrast to -0.7 V (4.12 Ω/cm2), -0.4 V (4.67 Ω/cm2) and 0 V (5.42 Ω/cm2). The result has established that the increment in the potential leads to the lowering of the charge

transfer resistance. Therefore, enhancement in the charge transfer has been observed **Table 2.7** shows the lowest charge transfer resistance (Rct) value was determined for -0.9 V (3.89 Ω/cm2) compared to -0.7 V (3.95 Ω/cm2), -0.4 V (4.67 Ω/cm2), and 0 V (5.52 Ω/cm2.

Table 2.6 shows the lowest charge transfer resistance for (3-hydrazonoindolin-2-one) compared to **3a** at pH =7 with -0.9 V, -0.7 V and 0 V (vs Ag/AgCl). Similar to the previous calculation, the lowest charge transfer resistance (Rct) value was observed at -0.9 V (3.25 Ω/cm2) in contrast to -0.7 V (4.12 Ω/cm2), -0.4 V (4.67 Ω/cm2) and 0 V (5.42 Ω/cm2). Therefore, enhancement in the charge transfer has been observed **Table 2.7** shows the lowest charge transfer resistance (Rct) value was determined for -0.9 V (3.89 Ω/cm2) compared to -0.7 V (3.95 Ω/cm2), -0.4 V (4.67 Ω/cm2), and 0 V (5.52 Ω/cm2.

Table 2.7. Compound (1-phenylethylidene) hydrazine **5a** at pH=4

Entry	Potential (V vs Ag/ AgCl)	R_{ct} (Ω /cm^2)
1	-0.9	3.89
2	-0.7	3.95
3	-0.4	4.67
4	0	5.52

It can be concluded here that the charge transfer resistance (R_{ct}) value was decreased after increases in Voltage from 0 to -0.9 V (vs Ag/AgCl) when compared with the different potentials. In this way **Figure 2.7** shows that C_{dl} value (1.8μF/cm^2) at different scan rate pH=7. **Figure 2.8** shows that C_{dl} value (2.67 μF/cm^2) at different scan rate pH=4

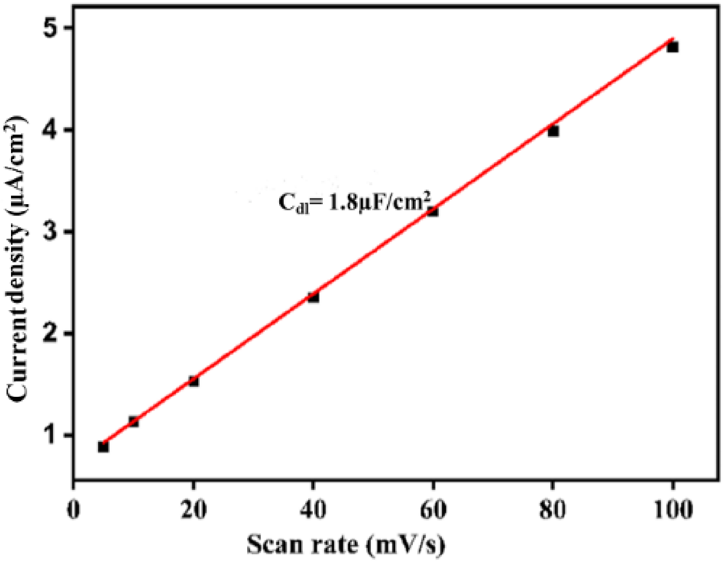


Figure 2.7 C_{dl} curve of **3a** different scan rate at pH =7

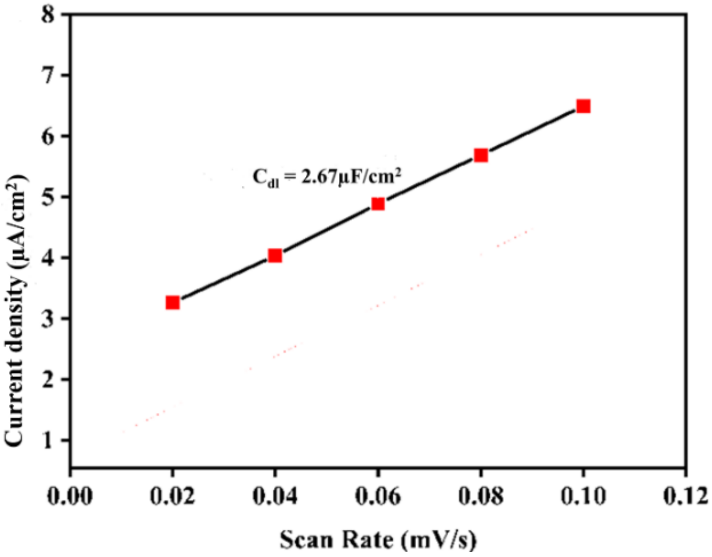


Figure 2.8 C_{dl} curve of **3a** different scan rate at pH =4

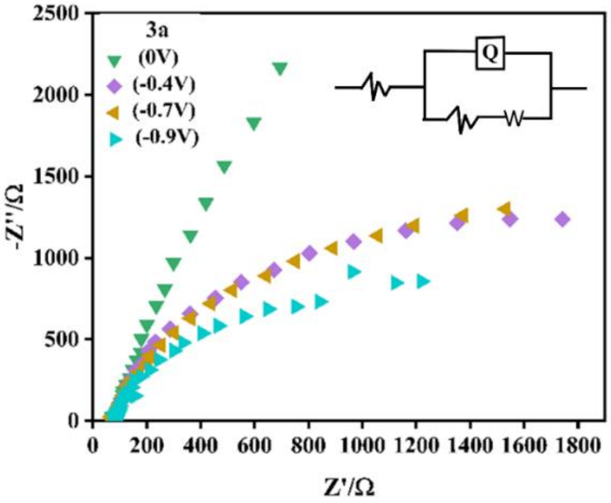


Figure 2.9 Shows the Electrochemical impedance Spectroscopy (EIS) graph of **3a** at different potentials (pH = 7), the fitted circuit plot corresponds to R(QR)W parameter.

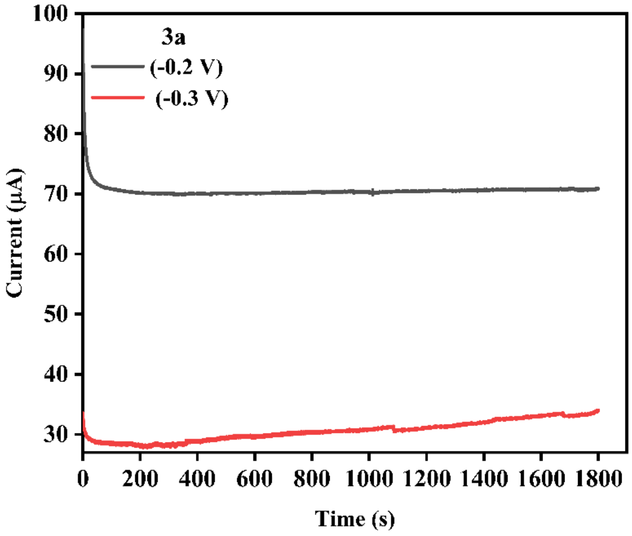


Figure 2.10. Chrono-amperometry graph for the synthesis of 3-hydrazonoindolin-2-one **3a.**

The chrono-amperometry graph of 3-hydrazonoindolin-2-one **3a** at (-0.2 V) exhibits a strong current of 80 microamperes at 1800 seconds, as shown in (**Figure 2.6**). Moreover, the current density of 30 microamperes was attained at -0.3 V in chrono-amperometry.

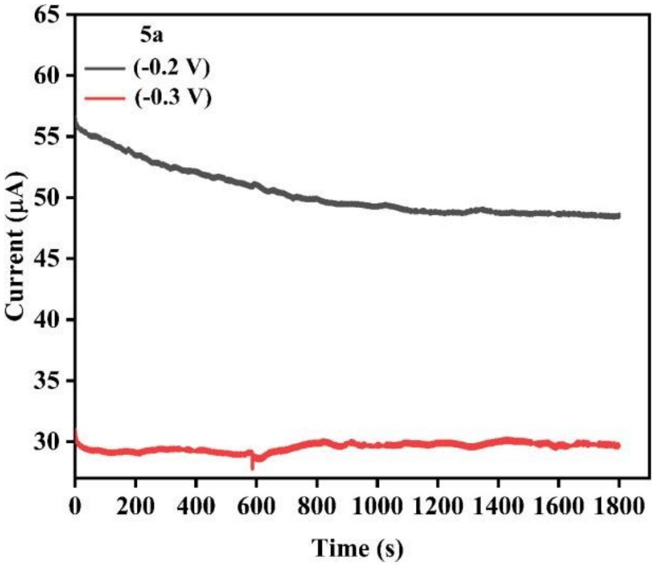


Figure 2.11 Chrono-amperometry graph for the synthesis (1-Phenylethylidene) hydrazine **5a.**

Table 2.8 OCP data for electro-organic synthesis of hydrazonoindolin derivatives **3a-3p**

Entry	Electrochemical reaction mixture reaction (substrate +$NH_2NH_2.H_2O$ + 0.1M $NaClO_4$)	Open circuit Potential OCP (in Volts)
1.	**2a**	-0.036
2.	**2b**	-0.023
3.	**2c**	-0.058
4.	**2d**	-0.136
5.	**2e**	-0.122
6.	**2f**	-0.280
7.	**2g**	-0.216
8.	**2h**	-0.180
9.	**2i**	-0.079
10	**2j**	-0.084
11	**2k**	-0.066
12	**2l**	-0.069
13	**2m**	-0.126
14	**2n**	-0.109
15	**2o**	-0.118
16.	**2p**	-0.111

The **Table 2.8** contains the OCP data for hydrazone formation from acetophenone. Compound **4i** (-0.485) and **4c** (-0.470) have a high reduction potential of the OCP, which indicates that the electrode has a strong tendency to accept electrons and undergo reduction. A high reduction potential facilitates electron transfer from the electrode to the organic substrate, promoting the reduction reaction. This enhanced reactivity can lead to faster reaction rates and short reaction times. Here**, 4g, 4j, 4k, 4b and 4m** have reduction potential of the OCP (-0.467, -0.432, -0.412, -0.278 and -0.275) can influence the selectivity of the reaction. Different functional groups within an organic molecule may have varying affinities for electrons, and a high reduction potential can favour the reduction of specific functional groups, while leaving others unaffected. This selectivity Control is valuable in organic synthesis, as it allows for the targeted formation of desired products.

In electro-organic synthesis, the OCP reduction potential of an electrode material can influence the selectivity of the desired electrochemical transformation. Different organic compounds have varying tendencies to be reduced at different potential, it is possible to promote the selective reduction of specific functional groups or bonds within a complex organic molecule.

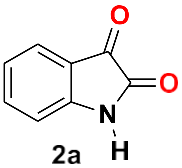
2.6 Detailed description of products

All reactions took place in an electrochemical cell outside at ambient temperature (about 25–26 °C). Sigma Aldrich was used to acquire chemicals and solvents. Using pre-coated E. Merck TLC silica gel 60 F254 plates, thin-layer chromatography was carried out. TLC plates were observed using ultraviolet (UV) light. On silica gel (100–200 mesh), the column chromatography was carried out with ethyl acetate and hexane as the eluent. ^{13}NMR spectra

Were reported, and the NMR spectra were obtained using a Bruker Avence 500 MHz NMR spectrometer

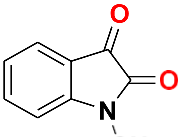
2.7 Experimental Procedure and Spectral data of all compound

2.7.1 Typical Experimental Procedure for synthesis of Indolin-2,3-diones (2a-2p). To a solution of 2-aminoacetophenone **1a** (1.0 mmol), in DMSO solvent (5 ml), I_2 (1.3mmol) and drops of $NaClO_4$ (0.1 M), with two graphite electrode (anode and cathode) and reference electrodeAg/AgCl, at room temperature (25 °C), electric current passes for 2 hour (7.2×10^3 sec). The progressof the reaction was monitored by TLC. After completion of the reaction (TLC), mixture was extracted with EtOAc (3 × 5 ml) and combined organic layer, dried over Na_2SO_4, filtered, and concentrated. The product was purified by silica gel column chromatography using hexane/ethyl acetate as solvent which furnished isatin product **2a** in 94% isolated yield. The similar reaction protocol was adopted for other 2- amino acetophenone derivatives (**1b-1p**) and the correspondingisatin products (**2b-2p**) were obtained in 60-94% yields.



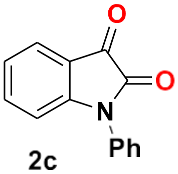
2a

Indolin-2,3-dione (2a). The Product was purified by silica column chromatography (Ethyl acetate:Hexane 1:2), Red Solid: m.p. (202-203 °C); Yield (94%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ =11.03 (s, 1H), 7.57 (d, *J* = 7.7, 1.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 184.2, 159.2, 150.5, 138.2, 124.5, 122.6, 117.6, 112.0 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_5NO_2$ $[M+H]^+$ 148.0399, found 148.0389.



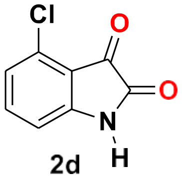
2b

1-methylindoline-2,3-dione (2b). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (129-130 °C); yield (91%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 7.67 (d, J = 7.5 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.12 (brt, J = 7.7 Hz, 2H), 3.13 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.4, 158.1, 151.3, 138.1, 124.2, 123.1, 117.3, 110.5, 26.0 ppm; HRMS (ESI) m/z: calcd for $C_9H_7NO_2$ [M+H]+ 162.0555, found 162.0572.

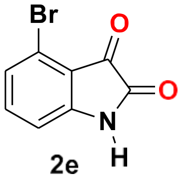


2c

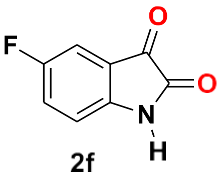
1-phenylindoline-2,3-dione (2c). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (137-138 °C); Yield (82%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 7.66-7.61 (m, 1H), 7.60 – 7.58 (m, 3H), 7.50 – 7.48 (m, 3H), 7.18 (d, J = 8.0 Hz,1H), 6.82 (d, J = 8.0 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 182.9, 157.5, 151.3, 138.1, 133.4, 129.8, 128.5, 126.6, 124.8, 123.7, 117.7, 110.8 ppm; HRMS (ESI) m/z: calcd for $C_{14}H_9NO_2$ $[M+H]^+$ 224.0712, found 224.0731.


2d

4-chloro-indolin-2,3-dione (2d). The Product was Purified by column chromatography (Ethyl acetate: Hexane 1:2), Orange Solid: m.p. (254-255 °C); Yield (90%),^{1}**H NMR** (500 MHz, DMSO- d_6) δ = 11.20 (s, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.83 (d, J = 7.4 Hz, 1H); ^{13}**C NMR** (125 MHz, DMSO-d_6) δ = 181.3, 158.8, 152.3, 139.1, 131.1, 123.7, 114.9, 111.0 ppm; HRMS (ESI) m/z: calcd for $C_8H_4ClNO_2$ $[M+H]^+$ 182.0009, found 182.0023.

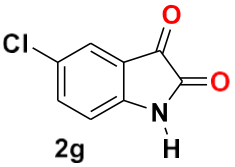

2e

4-bromo-indolin-2,3-dione (2e). The Product was Purified by column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (257-258 °C), Yield (93%); ^{1}**H NMR** (500 MHz, DMSO-d_6) δ = 11.18 (s, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.19 (d, J = 8.2 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H); ^{13}**C NMR** (125 MHz, DMSO-d_6) δ = 181.3, 158.2, 152.1, 138.4, 126.2, 119.0, 116.0, 110.9 ppm; HRMS (ESI) m/z: calcd for $C_8H_4BrNO_2$ $[M+H]^+$ 225.9504, found 225.9525.


2f

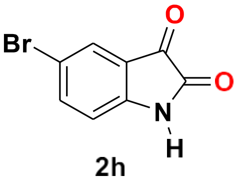
5-fluoro-indoline-2,3-dione (2f). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (221-222 °C); Yield (60%), ^{1}**H NMR** (500 MHz, DMSO-d_6) δ = 11.04 (s, 1H), 7.45-7.39 (m, 2H), 6.91 (d, J = 7.2 Hz, 1H); ^{13}**C NMR** (125

MHz, DMSO-d_6) δ = 184.2, 159.3, 157.4, 147.3, 124.7, 118.8, 113.8, 111.6 ppm; HRMS (ESI) m/z: calcd for $C_8H_4FNO_2$ $[M+H]^+$ 166.0304, found 166.0345.



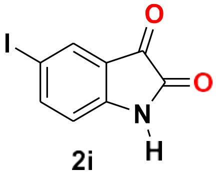
2g

5-Chloro-indolin-2,3-dione (2g). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (245-246 °C); Yield (89%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.12 (s, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.51 (s, 1H), 6.90 (d, J = 8.0 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.3, 159.1, 149.2, 137.2, 126.8, 124.1, 119.0, 113.8 ppm; HRMS (ESI) m/z: calcd for $C_8H_4ClNO_2$ $[M+H]^+$ 182.0009, found 182.0031.



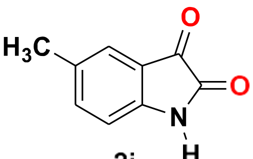
2h

5-Bromo-indolin-2,3-dione (2h). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Yellow solid: m.p. (254-256 °C); yield (87%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.13 (s, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.63 (s, 1H), 6.86 (d, J = 8.0 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 182.8, 158.6, 149.2, 139.6, 126.5, 124.3, 119.1, 113.9 ppm; HRMS (ESI) m/z: calcd for $C_8H_4BrNO_2$ $[M+H]^+$ 225.9504, found 225.9541.



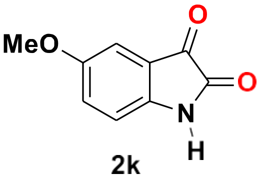
2i

5-iodo-indolin-2,3-dione (2i). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Orange Solid: m.p. (263-264 °C); Yield (80%), **^{1}H NMR** (500 MHz, DMSO- d_6) δ = 11.11 (s, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.75 (s, 1H), 6.75 (d, J = 8.2 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 182.7, 158.4, 149.6, 145.4, 132.1, 119.6, 114.3, 85.1 ppm; HRMS (ESI) m/z: calcd for $C_8H_4INO_2$ $[M+H]^+$ 273.9365, found 273.9381.



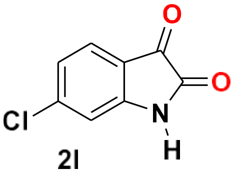
2j

5-methyl-indolin-2,3-dione (2j). The Product was purified by column chromatography (Ethyl acetate: Hexane 1:2), Orange Solid: m.p. (196-197 °C); Yield (74%),**^{1}H NMR** (500 MHz, DMSO- d_6) δ = 10.92 (s, 1H), 7.38 (d, J = 7.9 Hz, 1H), 7.30 (s, 1H), 6.79 (d, J = 7.9 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 184.3, 159.1, 148.2, 138.5, 131.7, 124.5, 117.4, 111.7, 19.8 ppm; HRMS (ESI) m/z: calcd for $C_9H_7NO_2$ $[M+H]^+$ 162.0555, found 162.0572.



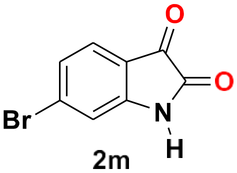
2k

5-methoxy-indolin-2,3-dione (2k). The Product was purified by column chromatography (Ethyl acetate: Hexane 1:2), Mustered yellow solid: m.p. (200-201 °C); Yield (90%), **^{1}H NMR** (500MHZ, DMSO-d_6) δ = 10.83 (s, 1H), 7.17 (d, J = 7.8 Hz, 1H), 7.06 (s, 1H), 6.83 (d, J = 8.1 Hz, 1H), 3.74 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 184.3, 159.2, 155.0, 144.3, 124.5, 117.8, 112.9, 108.5, 55.4 ppm; HRMS (ESI) m/z: calcd for $C_9H_7NO_3$ $[M+H]^+$ 178.0504, found 178.0532.



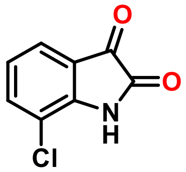
2l

6-chloro-indolin-2,3-dione (2l). The Product was purified by column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (254-255 °C); Yield (75%), **^{1}H NMR** (500 MHz, DMSO-d_6) $\delta = 11.14$ (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.08 (s, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) $\delta = 183.1$, 159.5, 151.9, 142.5, 126.4, 122.8, 116.9, 112.3 ppm; HRMS (ESI) m/z: calcd for $C_8H_4ClNO_2$ $[M+H]^+$ 182.0009, found 182.0042.

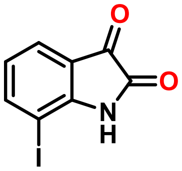


2m

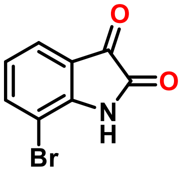
6-bromo-indolin-2,3-dione (2m). The Product was Purified by column chromatography (Ethyl acetate: Hexane 1:2) Red solid, m.p. (255-256 °C); yield (89%), **^{1}H NMR** (500 MHz, DMSO-d_6) $\delta = 11.15$ (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.08 (s, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) $\delta = 183.5$, 159.6, 152.0, 131.9, 126.5, 126.0, 117.4, 115.3 ppm; HRMS (ESI) m/z: calcd for $C_8H_4BrNO_2$ $[M+H]^+$ 225.9504, found 225.9534.



7-chloro-indolin-2,3-dione (2n). The Product was purified by column chromatography (Ethyl acetate: Hexane 1:2), Orange Solid: m.p. (181-182 °C); Yield (74%), **^{1}H NMR** (500 MHz, DMSO- d_6) δ = 11.16 (s, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.7, 159.9, 148.0, 137.6, 124.0, 123.4, 120.2, 116.4 ppm; HRMS (ESI) m/z: calcd for $C_8H_4ClNO_2$ $[M+H]^+$ 182.0009, found 182.0015.



7-iodo-indolin-2,3-dione (2o). The Product was purified by column chromatography (Ethyl acetate: Hexane 1:2), yellow solid: m.p. (202-203 °C); Yield (75%), **^{1}H NMR** (500 MHz, DMSO- d_6) δ = 11.31 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 7.1 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.5, 159.5, 149.2, 140.2, 124.0, 123.4, 119.9, 104.5 ppm; HRMS (ESI) m/z: calcd for $C_8H_4INO_2$ $[M+H]^+$ 273.9365, found 273.9375.

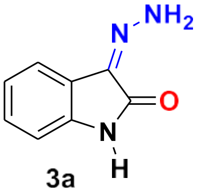


7-bromo-indolin-2,3-dione (2p). The Product was purified by column chromatography (Ethyl acetate:Hexane 1:2), Orange Solid: m.p. (208-209 °C); Yield (78%), **^{1}H NMR** (500 MHz, DMSO- d_6) δ = 10.62 (s, 1H), 7.33 (d, J = 8.5 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 6.88 (t, J = 7.7 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.9, 159.9, 149.6, 140.6, 124.4, 123.8, 120.4, 104.9 ppm; HRMS (ESI) m/z: calcd for $C_8H_4BrNO_2$ $[M+H]^+$ 225.9504, found 225.9541.

2.8 Typical Experimental Procedure for the synthesis of 3-hydrazonoindolin-2-ones (3a-3p).

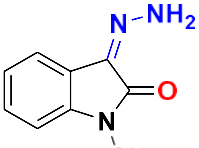
To a solution of isatin 2a (0.68 mmol), hydrazine hydrates (0.81 mmol) in C_2H_5OH solvent (5 ml) and drops of NaClO4 (0.1 M), with two graphite electrode (anode and cathode) and reference electrode Ag/AgCl, at room temperature (25 °C), electric current passes for 1800 sec (30 min). The progress of the reaction was monitored by TLC. After complete consumption of isatin **2a**, the reaction mixture was extracted with EtOAc (3 × 5 ml) and combined organic layer, dried over Na2SO4, filtered, and concentrated. The product was purified by silica gel column chromatography using hexane/ethyl acetate as solvent which furnished hydrazone product **3a** in 92% isolated yield. The similar reaction protocol was adopted for other isatin derivatives (**2b-2p**) and the corresponding products (**3b-3p**) were obtained in 75-94% yields.

2.8.1 Spectral data for few products



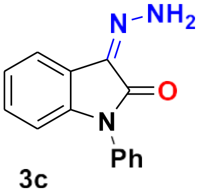
3a

3-hydrazonoindolin-2-one (3a). The Product was purified by silica gel column chromatography Ethyl Acetate: Hexane, 1:1), Orange Solid; m. p. (238-239 °C); Yield (92%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.36 (s, 1H, NH), 8.77 (s, 2H, NH_2), 7.91 (d, J = 7.5 Hz, 1H, ArH), 7.20 (t, 1H, J = 7.6 Hz, ArH), 6.96 (d, J = 7.6 Hz, 1H, ArH), 6.85 (t, J = 7.8 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO - d_6) δ = 162.5, 138.3, 126.7, 125.9, 121.9, 121.0, 117.1, 109.6 ppm; HRMS (ESI) m/z: calcd for $C_8H_7N_3O$ $[M+H]^+$ 162.0667, found 162.0671.



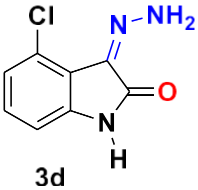
3b

1-Methyl-1H-indole-2,3-dione 3-hydrazone (3b). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane, 1:1), Orange Solid; m. p. (105-106°C); Yield (90%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.52 (d, J = 14.6 Hz, 1H, NH), 9.65 (d, J = 14.6 Hz, 1H), 7.38 (d, J = 7.5 Hz, 1H, ArH), 7.22 (t, J = 7.7 Hz, 1H, ArH), 7.04-6.99 (m, 2H, ArH), 3.18 (s, 3H, CH_3);**^{13}C NMR** (125 MHz, DMSO-d_6) δ = 160.6, 139.8, 126.8, 125.2, 121.7, 121.2, 117.0, 108.4, 24.9 ppm; HRMS (ESI) m/z: calcd for $C_9H_9N_3O$ $[M+H]^+$ 176.0824, found 176.0851.



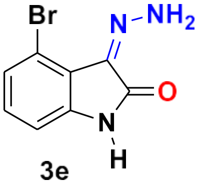
3c

1-Phenyl-1H-indole-2,3-dione 3-hydrazone (3c). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane, 1:1), Brown red Solid; m. p. (116-117°C); Yield (88%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 9.12 (brs, 2H, NH_2), 8.06 (d, J = 7.5 Hz, 1H, ArH), 7.56 (t, J = 7.6 Hz, 2H, ArH), 7.46 (t, J = 7.9 Hz, 1H, ArH), 7.43 (d, J = 7.5 Hz, 2H, ArH), 7.24 (t, J = 7.8 Hz, 1H, ArH), 7.09 (t, J = 7.6 Hz, 1H, ArH), 6.79 (d, J = 7.9 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 164.1, 141.4, 134.8, 129.8, 128.8, 128.0, 127.3, 127.0, 122.9, 122.5, 116.7, 109.0 ppm; HRMS (ESI) m/z: calcd for $C_{14}H_{11}N_3O$ $[M+H]^+$ 238.0980, found 238.0989.



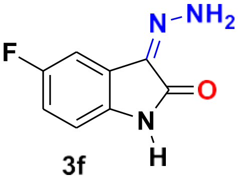
3d

4 – (Chloro-1H- indole-2,3- dione 3-hydrazone) (3d). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), mustard yellow solid: m.p. (236-236 °C); Yield (90%), ^{1}**H NMR** (500 MHz, DMSO - d_6) $\delta = 10.98$ (d, J = 13.5 Hz, 1H, NH), 10.92 (s, 1H, NH), 9.95 (d, J = 13.5 Hz, 1H, NH), 7.14 (d, J = 7.9 Hz, 1H, ArH), 7.05 (t, J = 7.9 Hz, 1H, ArH), 6.87 (d, J = 8.1 Hz, 1H, ArH); ^{13}**C NMR** (125 MHz, DMSO-d_6) $\delta = 162.6$, 140.1, 128.0, 125.8, 125.3, 120.4, 112.2, 109.3 ppm; HRMS (ESI) m/z: calcd for $C_8H_6ClN_3O$ $[M+H]^+$ 196.0278, found 196.0291.



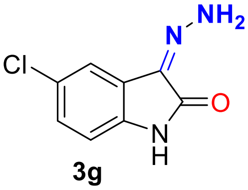
3e

4-(Bromo-1H-indole-2,3-dione 3-hydrazone) (3e). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), Brown red solid: m. p. (220-221 °C); Yield (90%), ^{1}**H NMR** (500 MHz, DMSO-d_6) $\delta = 10.99$ (d, J = 15.3 Hz, 1H, NH), 10.93 (s, 1H, NH), 9.98 (d, J = 15.4 Hz, 1H, NH), 7.16 (d, J = 8.0 Hz, 1H, ArH), 7.06 (t, J = 7.9 Hz, 1H, ArH), 6.89 (d, J = 7.8 Hz, 1H, ArH); ^{13}**C NMR** (125 MHz, DMSO-d_6) $\delta = 162.6$, 140.1, 128.0, 125.8, 125.3, 120.4, 112.2, 109.3 ppm; HRMS (ESI) m/z: calcd for $C_8H_6BrN_3O$ $[M+H]^+$ 239.9772, found 239.9782.



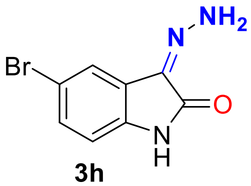
3f

5- Fluoro-1H-indole-2,3-dione 3-hydrazone (3f). The Product was purified by silica gel column chromatography (Ethyl Acetate: Hexane, 1:1), Orange Solid; m. p. (184-186 °C); Yield (80%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.71 (s, 1H, NH), 10.66 (d, J = 14.9 Hz, 1H, NH), 9.80 (d, J = 14.9 Hz, 1H, NH), 7.15 (d, J = 1.8 Hz, 1H, ArH), 6.98 (d, J = 8.0 Hz, 1H, ArH), 6.84 (d, J = 8.1 Hz, 1H, ArH); **^{13}CNMR** (125 MHz, DMSO-d_6) δ = 163.4, 159.4, 157.6, 135.1, 126.1, 113.4, 111.2, 104.9 ppm; HRMS (ESI) m/z: calcd for $C_8H_6FN_3O$ $[M+H]^+$ 180.0573, found 180.0591.



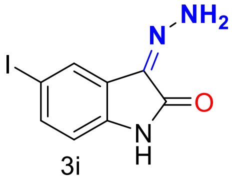
3g

Chloro-1H-indole-2,3-dione 3-hydrazone (3g). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane,1:1), Orange Solid; m. p. (176-177 °C); Yield (89%); **^{1}H NMR** (500 MHz, DMSO – d_6) δ = 10.82 (s, 1H, NH), 10.65 (d, J = 15.0 Hz, 1H, NH), 9.86 (d, J = 15.0 Hz, 1H, NH), 7.32 (d, J = 2.1 Hz, 1H, ArH), 7.16 (dd, J = 8.3, 2.2 Hz, 1H, ArH), 6.86 (d, J = 8.3 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO -d_6) δ = 162.4, 137.0, 126.1, 125.4, 124.8, 123.9,116.8, 111.2 ppm; HRMS (ESI) m/z: calcd for $C_8H_6ClN_3O$ $[M+H]^+$ 196.0278, found 196.0285.



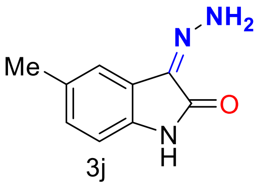
3h

5-Bromo-1H-indole-2,3-dione 3-hydrazone (3h). The Product was purified by silica gel column chromatography Ethyl Acetate: Hexane ,1:1), Yellow Solid; m. p. (167-168 °C); Yield (93%); **^{1}H NMR** (500 MHz, DMSO-d$_6$) δ = 10.80 (s, 1H, NH), 10.63 (d, J = 14.9 Hz, 1H, NH), 9.83 (d, J = 14.9 Hz, 1H, NH), 7.60 (d, J = 1.8 Hz, 1H, ArH), 7.44 (dd, J = 8.3, 1.8 Hz, 1H, ArH), 6.71 (d, J = 8.1 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d$_6$) δ = 162.5, 138.3, 135.3, 125.7, 125.2, 125.0, 112.7, 84.7 ppm; HRMS (ESI) m/z: calcd for $C_8H_6BrN_3O$ $[M+H]^+$ 239.9772, found 239.9791.



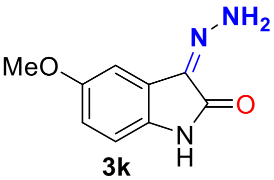
3i

5-Iodo-1H-indole-2,3-dione 3-hydrazone (3i). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane,1:1), Yellow Solid; m. p. (159-160 °C); Yield (92%); **^{1}H NMR** (500 MHz, DMSO-d$_6$) δ = 10.82 (s, 1H, NH), 10.65 (d, J = 14.9 Hz, 1H, NH), 9.85 (d, J = 14.9 Hz, 1H, NH), 7.32 (d, J = 1.7 Hz, 1H, ArH), 7.16 (dd, J = 8.1, 1.7 Hz, 1H, ArH), 6.86 (d, J = 8.2 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d$_6$) δ = 162.4, 137.0, 126.1, 125.4, 124.8, 123.9, 116.8, 111.2 ppm; HRMS (ESI) m/z: calcd for $C_8H_6IN_3O$ $[M+H]^+$ 287.9634, found 287.9651.



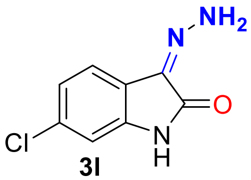
3j

5-Methyl-1H-indole-2,3-dione 3-hydrazone (3j). The Product was purified by silica gel column chromatography (Ethyl Acetate: Hexane, 1:1), light yellow Solid; m. p. (208-210 °C); Yield (93%); **^{1}H NMR** (500 MHz, DMSO-d$_6$) δ = 10.58 (s, 1H, NH), 10.52 (d, J = 14.6 Hz, 1H, NH),9.50 (d, J = 14.7 Hz, 1H, NH), 7.18 (d, J = 1.7 Hz, 1H, ArH), 6.96 (dd, J = 8.1, 1.7 Hz, 1H, ArH), 6.75 (d, J = 8.0 Hz, 1H, ArH), 2.27 (s, 3H, CH$_3$); **^{13}NMR** (125 MHz, DMSO-d$_6$) δ = 163.2, 136.8, 130.4, 127.9, 126.7, 122.6, 118.3, 110.0, 21.1 ppm; HRMS (ESI) m/z: calcd for $C_9H_9N_3O$ $[M+H]^+$176.0824, found 176.0852.



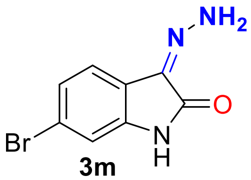
3k

5-(Methoxy-1H-indole-2,3-dione 3-hydrazone) (3k). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), Brown red solid: m. p. (187-189 °C); yield (94%). **^{1}H NMR** (500 MHz, DMSO-d$_6$) δ = 10.56 (d, J = 14.8 Hz, 1H, NH), 10.49 (s, 1H, NH), 9.53 (d, J = 14.8 Hz, 1H, NH), 6.93 (d, J = 1.8 Hz, 1H, ArH), 6.77 (d, J = 8.6 Hz, 1H, ArH), 6.73 (d, J = 8.6 Hz, 1H, ArH), 3.71 (s, 3H, OCH$_3$); **^{13}C NMR** (125 MHz, DMSO-d$_6$) δ = 162.9, 154.6, 132.3, 126.4, 123.0, 112.8, 110.4, 102.9, 55.2 ppm; HRMS (ESI) m/z: calcd for $C_9H_9N_3O_2$ $[M+H]^+$ 192.0773, found 192.0791.



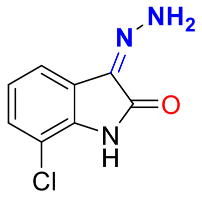
3l

6-(Chloro-1H-indole-2,3-dione 3-hydrazone) (3l). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), light yellow solid: m.p. (181-182 °C); Yield (87%), **^{1}H NMR** (500 MHz, DMSO-d$_6$) δ = 10.82 (s, 1H, NH), 10.58 (d, J = 14.8 Hz, 1H, NH), 9.75 (d, J = 14.8 Hz, 1H, NH), 7.28 (d, J = 8.1 Hz, 1H, ArH), 7.14 (dd, J = 8.0, 1.8 Hz, 1H, ArH), 7.02 (d, J = 1.7 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d$_6$) δ = 162.9, 140.2, 125.6, 124.4, 121.9, 119.6, 119.4, 113.1 ppm; HRMS (ESI) m/z: calcd for $C_8H_6ClN_3O$ $[M+H]^+$ 196.0278, found 196.0262.



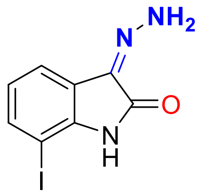
3m

6-(Bromo-1H-indole-2,3-dione 3-hydrazone) (3m). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), Brown red solid: m. p. (161-162 °C); Yield (88%), **^{1}H NMR** (500 MHz, DMSO-d$_6$) δ = 10.81 (s, 1H, NH), 10.59 (d, J = 14.8 Hz, 1H, NH), 9.77 (d, J = 14.8 Hz, 1H, NH), 7.28 (d, J = 7.8 Hz, 1H, ArH), 7.12 (d, J = 8.6 Hz, 1H, ArH), 7.00 (s, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d$_6$) δ = 162.3, 139.6, 124.9, 123.7, 121.4, 118.9, 118.8, 112.5 ppm; HRMS (ESI) m/z: calcd for $C_8H_6BrN_3O$ $[M+H]^+$ 239.9772, found 239.9761.



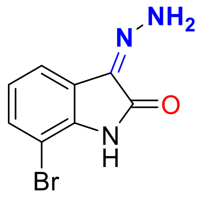
3n

7- Chloro-1H-indole-2,3-dione 3-hydrazone (3n). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane, 1:1), Orange Solid; m. p. (242-243 °C); Yield (86%); ^{1}**H NMR** (500 MHz, DMSO-d$_6$) δ = 11.12 (s, 1H, NH), 10.67 (d, J = 14.8 Hz, 1H, NH), 9.88 (d, J =14.8 Hz, 1H, NH), 7.32 (d, J = 8.0 Hz, 1H, ArH), 7.20 (dd, J = 8.1, 1.0 Hz, 1H, ArH), 6.99 (t, J = 7.9 Hz, 1H, ArH); ^{13}**C NMR** (125 MHz, DMSO-d$_6$) δ = 162.8, 135.8, 126.6, 125.5, 124.4, 122.7, 116.0, 114.4 ppm; HRMS (ESI) m/z: calcd for $C_8H_6ClN_3O$ $[M+H]^+$ 196.0278, found 196.0291.



3o

7-(Iodo-1H-indole-2,3-dione 3-hydrazone) (3o). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), brown red solid: m.p. (219-220 °C); yield (75%), ^{1}**H NMR** (500 MHz, DMSO-d$_6$) δ = 10.80 (s, 1H, NH), 10.62 (d, J = 14.8 Hz, 1H, NH), 9.83 (d, J = 14.8 Hz, 1H, NH), 7.60 (d, J = 7.9 Hz, 1H, ArH), 7.45 (t, J = 7.6 Hz, 1H, ArH), 6.72 (d, J = 8.0 Hz, 1H, ArH); ^{13}**C NMR** (125 MHz, DMSO-d$_6$) δ = 176.0, 142.7, 130.2, 127.5, 123.4, 122.8, 116.3, 101.2 ppm; HRMS (ESI) m/z: calcd for $C_8H_6IN_3O$ $[M+H]^+$ 287.9634, found 287.9674.

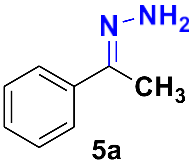


3p

(Bromo-1H-indole-2,3-dione 3-hydrazone) (3p). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), Yellow Solid: m. p. (227-228 °C); Yield (83%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.97 (s, 1H, NH), 10.63 (br, 2H, NH_2), 7.35 (d, J = 8.0 Hz, 1H, ArH), 7.18 (d, J = 7.9 Hz, 1H, ArH), 6.88 (t, J = 8.0 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO- d_6) δ = 175.6, 142.6, 129.9, 127.3, 123.1, 122.4, 115.9, 101.0 ppm; HRMS (ESI) m/z: calcd for $C_8H_6BrN_3O$ $[M+H]^+$ 239.9772, found 239.9779.

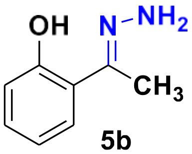
2.9 Typical Experimental Procedure for the synthesis of (1-Phenylethylidene) hydrazines (5a- 5n). To a solution of acetophenone 4a (0.83 mmol), hydrazine hydrates (0.99 mmol), in C_2H_5OH. solvent (5 ml) and drops of $NaClO_4$ (0.1 M), with two graphite electrode (anode and cathode) and reference electrode Ag/AgCl, at room temperature (25 °C), electric current passes for 1800 sec (30 min). The progress of the reaction was monitored by TLC. After completion of the reaction, mixture was extracted with EtOAc (3 × 5 ml) and combined organic layer, dried over Na_2SO_4, filtered, and concentrated. The product was purified by silica gel column chromatography using hexane/ethyl acetate as solvent which furnished hydrazone product 5a in 89% isolated yield. The similar reaction protocol was adopted for other acetophenone derivatives (4b-4m) and the corresponding hydrazone products (5b-5m) were obtained in 80-94% yields.

2.9.1 Spectral data for few products



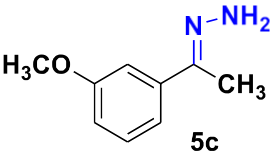
5a

(1-Phenylethylidene) hydrazone (5a). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), Colourless liquid, yield (89%), **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.92 (d, J = 7.8 Hz, 2H), 7.43-7.46 (m, 3H), 2.33 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.1, 138.8, 130.0, 128.7, 127.0, 15.4 ppm; HRMS (ESI) m/z: calcd for $C_8H_{10}N_2$ $[M+H]^+$ 135.0922, found 135.0942.



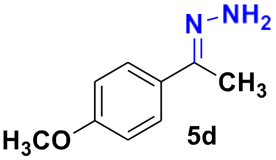
5b

1-(2-hydroxy phenyl) ethanone hydrazone (5b). The Product was Purified by silica gel column chromatography (Ethyl acetate: Hexane 1:9), Colourless liquid, Yield (89%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 12.93 (brs, 1H, OH), 7.37 (dd, J = 7.9, 1.5 Hz, 1H), 7.22 (dt, J = 8.5, 1.6 Hz, 1H), 6.97 (dd, J = 8.1, 1.4 Hz, 1H), 6.87 (dt, J = 7.7, 1.3 Hz, 1H), 5.30 (s, 2H, NH_2), 2.14 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.2, 152.2, 129.5, 126.3, 119.7, 118.1, 116.8, 10.3 ppm; HRMS (ESI) m/z: calcd for $C_8H_{10}N_2O$ $[M+H]^+$ 151.0871, found 151.0879.



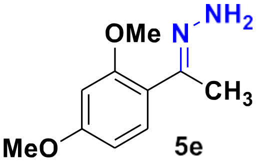
5c

1-(3-methoxy phenyl) ethanone hydrazone (5c). The Product was Purified by silica gel column chromatography (Ethyl acetate: Hexane 1:9), Colourless liquid, Yield (92%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.28-7.25 (m, 3H, ArH), 6.87-6.86 (m, 1H, ArH), 5.42 (s, 2H, NH_2), 3.81 (s, 3H, OCH_3), 2.08 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 159.7, 147.0, 140.9, 129.3, 118.2, 114.1, 110.7, 55.3, 11.7 ppm; HRMS (ESI) m/z: calcd for $C_9H_{12}N_2O$ $[M+H]^+$ 165.1028, found 165.1035.



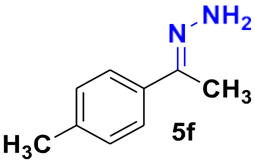
5d

1-(4-methoxy phenyl) ethanone hydrazone (5d). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), Colourless liquid, Yield (94%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.61 (d, J = 8.9 Hz, 2H, ArH), 6.90 (d, J = 8.9 Hz, 2H, ArH), 5.27 (s, 2H, NH_2), 3.84(s, 3H, OCH_3), 2.14 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 159.5, 147.3, 132.0, 126.6,113.5, 55.1, 1 ppm; HRMS (ESI) m/z: calcd for $C_9H_{12}N_2O$ $[M+H]^+$ 165.1028, found 165.1042.1**.**



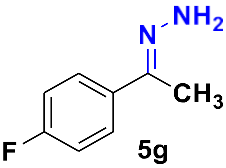
5e

(2,4-dimethoxy phenyl) ethanone hydrazone (5e). The Product was Purified by silica gel column chromatography (Ethyl acetate: Hexane 1:9), Colourless Solid; m. p. (122-123 °C); Yield (95%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.28 (d, J = 2.2 Hz, 1H, ArH), 7.00 (dd, J = 8.4, 2.0 Hz, 1H, ArH), 6.71 (d, J = 8.4 Hz, 1H, ArH), 5.25 (s, 2H, NH_2), 3.80 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 1.98 (s, 3H,CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.1, 148.7, 146.7, 132.3, 118.1, 110.4, 108.2, 55.8, 55.7, 11.3 ppm; HRMS (ESI) m/z: calcd for $C_{10}H_{14}N_2O_2$ $[M+H]^+$ 195.1134, found 195.1171.



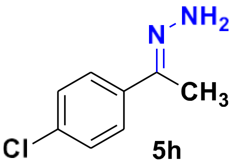
5f

1-(4-methyl phenyl) ethenone hydrazone (5f). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), colourless liquid; Yield (90%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.81 (d, J = 8.3 Hz, 2H, ArH), 7.24 (d, J = 8.0 Hz, 2H), 5.29 (s, 2H, NH_2), 2.31 (s, 3H, CH_3), 2.13 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 157.5, 139.5, 135.7, 128.9, 126.4, 21.2, 14.8 ppm; HRMS (ESI) m/z: calcd for $C_9H_{12}N_2$ $[M+H]^+$ 149.1079, found 149.1091.



5g

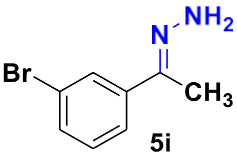
1-(4-Fluoro Phenyl) ethanone hydrazone (5g). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), Yellow Solid; Yield (86%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.58 (d, J = 8.2 Hz, 2H, ArH), 7.00 (d, J = 8.4 Hz, 2H, ArH), 5.34 (s, 2H, NH_2), 2.08 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 166.5, 164.5, 133.4, 130.7, 115.3, 26.2 ppm; HRMS (ESI) m/z: calcd for $C_8H_9FN_2$ $[M+H]^+$ 153.0828, found 153.0852.



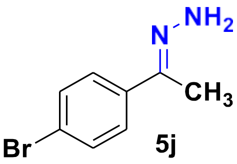
5h

1-(4-Chloro phenyl) ethanone hydrazone (5h). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), Colourless liquid; yield (88%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.51 (d, J = 8.7 Hz, 2H, ArH), 7.46 (d, J = 8.6 Hz, 2H, ArH), 5.38 (s, 2H,

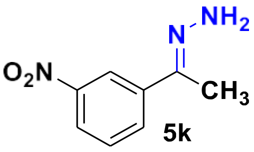
NH_2), 2.10 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 145.7, 138.1, 131.2, 128.0, 126.9, 121.9, 11.2 ppm; HRMS (ESI) m/z: calcd for $C_8H_9ClN_2$ $[M+H]^+$ 169.0533, found 169.0563.


5i

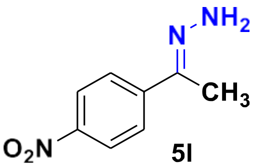
1-(3-Bromo phenyl) ethanone hydrazone (5i). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), Brown sticky solid; Yield (80%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.80 (s, 1H, ArH), 7.54 (d, J = 7.9 Hz, 1H, ArH), 7.40 (d, J = 8.9 Hz, 1H, ArH), 7.19 (t, J = 7.9 Hz, 1H, ArH), 5.42 (s, 2H, NH_2), 2.08 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 145.4, 141.4, 130.9, 129.8, 128.6, 124.0, 122.6, 11.5 ppm; HRMS (ESI) m/z: calcd for $C_8H_9BrN_2$ $[M+H]^+$ 213.0027, found 213.0065.


5j

1-(4-Bromo phenyl) ethanone hydrazone (5j). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), Brown solid; m. p. (164-165 °C); yield (89%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.51 (d, J = 8.7 Hz, 2H, ArH), 7.46 (d, J = 8.8 Hz, 2H, ArH), 5.38 (s, 2H, NH_2), 2.10 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 146.3, 138.6, 131.7, 127.4, 122.5, 11.7 ppm; HRMS (ESI) m/z: calcd for $C_8H_9BrN_2$ $[M+H]^+$ 213.0027, found 213.0052.

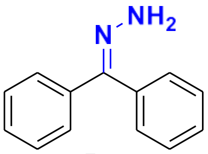

5k

1-(3-Nitro phenyl) ethanone hydrazone (5k). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), yellow Solid; m. p. (78-79 °C); Yield (86%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.47 (d, J = 2.0 Hz, 1H, ArH), 8.12 (dd, J = 8.1, 2.3 Hz, 1H, ArH), 7.99 (dd, J = 7.9, 1.8 Hz, 1H, ArH), 7.48 (t, J = 8.0 Hz, 1H, ArH), 5.56 (s, 2H, NH_2), 2.16 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.8, 144.1, 141.3, 131.4, 129.5, 122.8, 120.6, 11.6 ppm; HRMS (ESI) m/z: calcd for $C_8H_9N_3O_2$ $[M+H]^+$ 180.0773, found 180.0791.



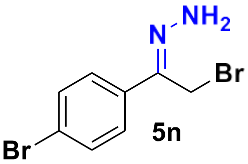
5l

1-(4-Nitro Phenyl) ethenone hydrazone (5l). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:9), yellow Solid: m. p. (148-149 °C); Yield (82%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.19 (d, J = 9.0 Hz, 2H), 7.80 (d, J = 9.0 Hz, 2H), 5.70 (s, 2H), 2.16 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 147.1, 145.4, 143.6, 125.9, 123.6, 11.2 ppm; HRMS (ESI) m/z: calcd for $C_8H_9N_3O_2$ $[M+H]^+$ 180.0773, found 180.0752.



5m

(diphenyl methylene) hydrazone (5m). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), White solid; m. p. (98-99 °C); Yield (98%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.58 – 7.54 (m, 2H, ArH), 7.52 – 7.47 (m, 3H, ArH), 7.32-7.30 (m, 5H, ArH), 5.46 (s, 2H, NH_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.5, 138.8, 133.3, 129.7, 129.1, 128.4, 126.8 ppm; HRMS (ESI) m/z: calcd for $C_{13}H_{12}N_2$ $[M+H]^+$ 197.1079, found 197.1032.



5n

2- bromo-1-(4-bromophenyl) ethylidene) hydrazine (5n). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), brown solid; m. p. (107-108 °C); Yield (77%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.38 (d, J = 7.9 Hz, 2H, ArH), 7.27 (d, J = 8.0 Hz, 2H, ArH), 5.41 (s, 2H, NH_2), 2.12 (s, 2H, CH_2Br); **13C NMR** (125 MHz, $CDCl_3$) δ = 146.6, 138.2, 134.1, 132.8, 130.8, 129.4, 127.0, 15.3 ppm; HRMS (ESI) m/z: calcd for $C_8H_8Br_2N_2$ $[M+H]^+$ 290.9132, found 290.9172.

^{1}H NMR (500MHz, DMSO-d$_6$) and ^{13}C NMR (125 MHz, DMSO-d$_6$) 2a

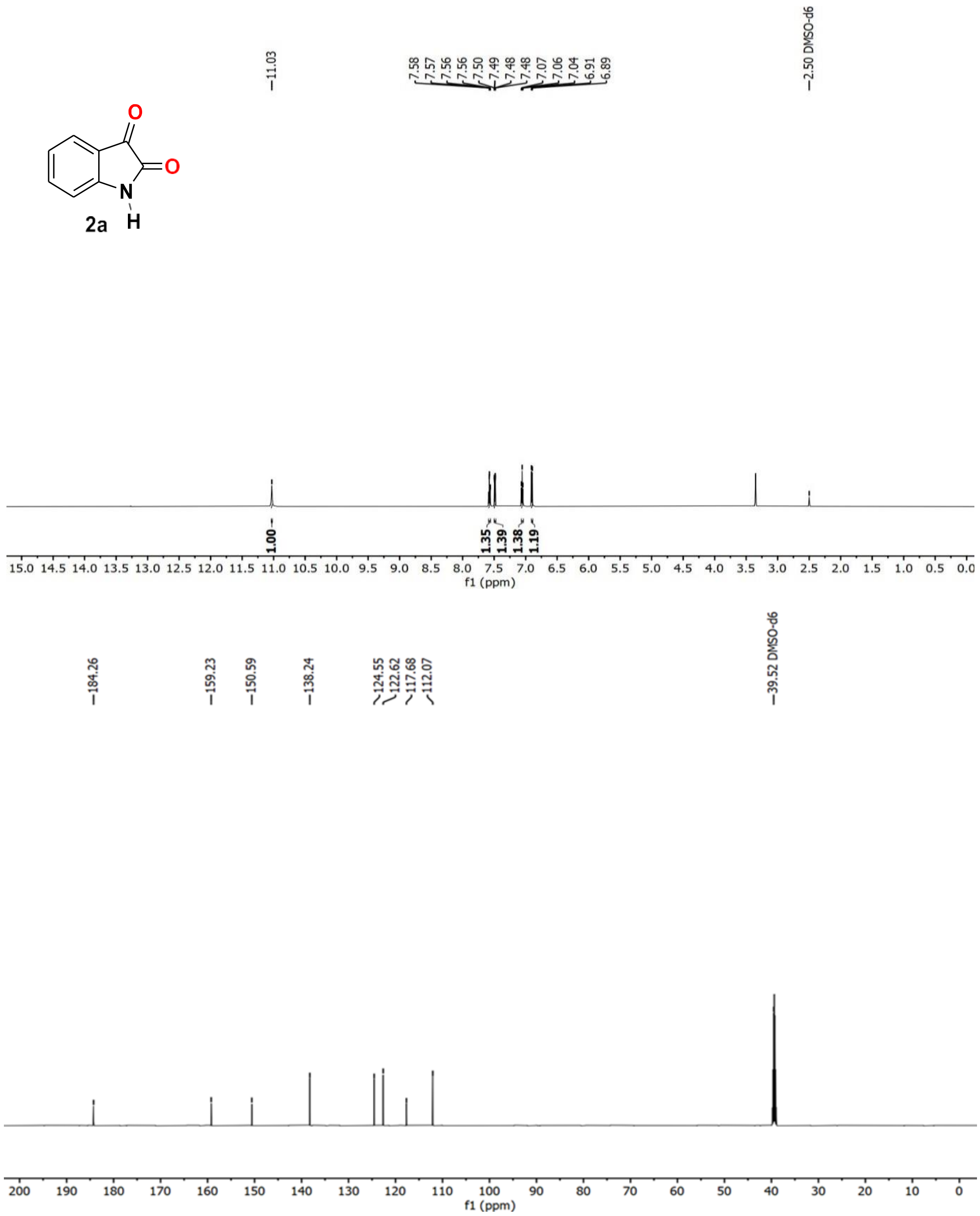


Figure 2.12 ^{1}H NMR ^{13}C NMR spectra of compound 2a in DMSO

^{1}H NMR (500MHz, DMSO-d$_6$) and ^{13}C NMR (125 MHz, DMSO-d$_6$) 3a

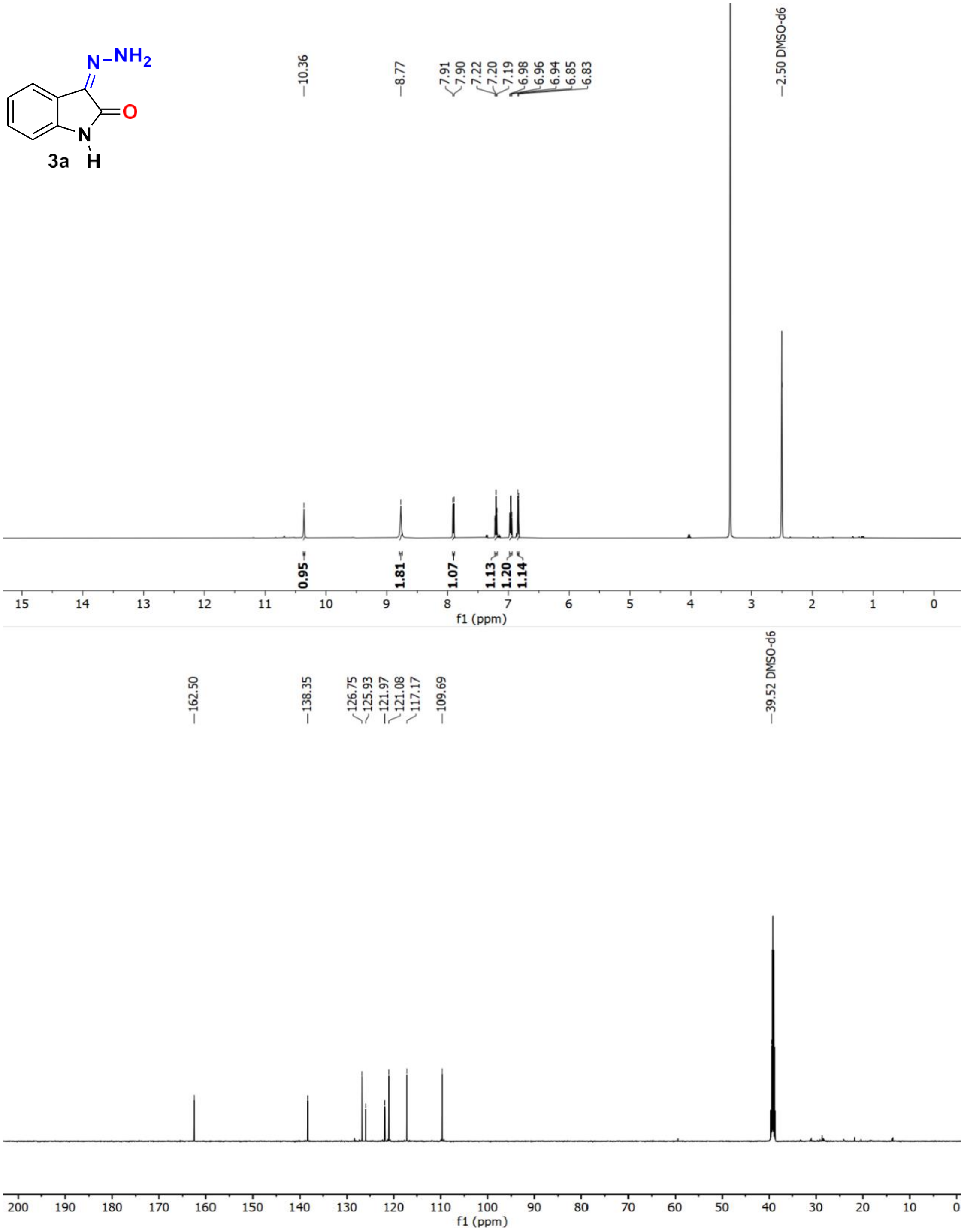


Figure 2.13 ^{1}H NMR ^{13}C NMR spectra of compound 3a in DMSO

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