A convenient synthesis of 3-arylideneindolin-2-ones and evaluation of their photoelectrochemical properties

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Abstract: An eco-friendly synthesis of 3-arylideneindolin-2-ones was achieved by reacting indolin-2-one with aryl aldehydes under acid catalyzed condition in ethanol medium. The (*E*)-isomers were obtained as the major products in a few minutes, at reflux temperature of the solvent. Examination of the synthesized compounds revealed interesting photoelectrochemical properties, and offered the possibility of developing them as molecular photoactive materials in photoconversion devices.
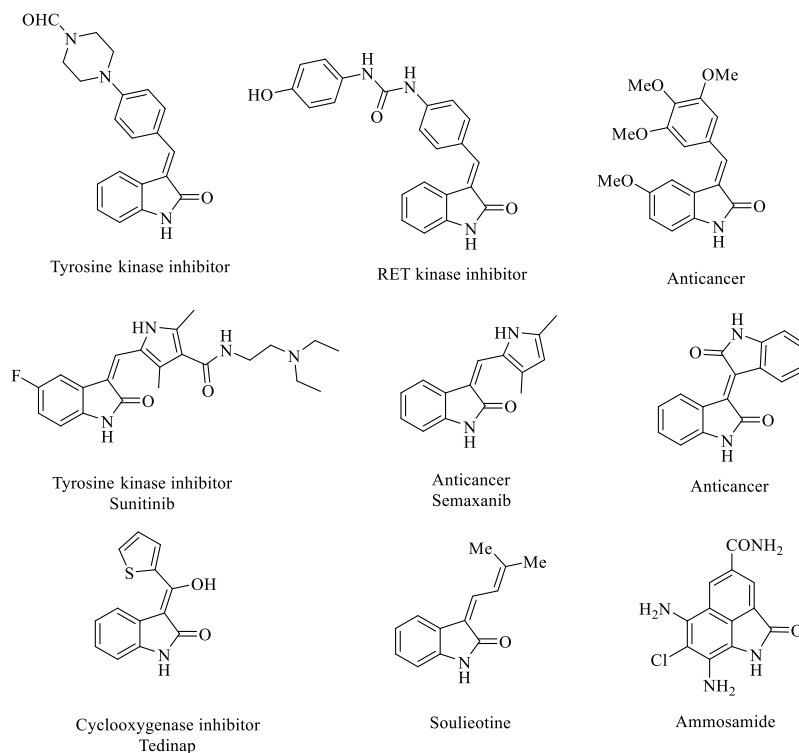
1. Introduction

Indolin-2-one fragments are found in many natural products, for instance Horsfiline was obtained from Horsfieldia superba[1], Soulieotine from Souliea vaginata[2] and Ammosamide from the marine-derived Streptomyces.[3] The indolin-2-one derivatives possess wide range of biological properties.[4] They are precursors to 3-arylideneindolin-2-ones whose skeleton is found in various potent molecules[5-7] (Figure 1), and marketed drugs such as Sunitinib[8], Semaxinib[9,10] and Nintedanib.[11] The configuration of the C=C bond in 3-arylideneindolin-2-ones was reported to influence the biological activities.[12,13] Various 3-substitutedindolin-2-ones have found use as antitumor agents.[14,15] The 3-arylideneindolin-2-ones find use in other ailments too, for example Tenidap, a cyclooxygenase inhibitor is employed for the treatment of rheumatoid arthritis and osteo-arthritis.[16]

The synthesis of 3-aryl/alkylideneindolin-2-ones from indoline-2-ones and aldehydes using piperidine in ethanol medium was reported to afford a mixture of [*E*]- and [*Z*]-isomers.[17,18] Since then several efforts had been made by different research groups for the stereoselective synthesis of these compounds from various starting materials. A stereoselective synthesis of 3-alkylideneindolin-2-ones was accomplished by rhodium-catalyzed reaction of 2-alkynylaryl isocyanates with aryl- and alkenylboronic acids.[19] The condensation of aldehydes and ketones with indolin-2-ones in the presence of potassium fluoride on alumina under microwave irradiation provides a convenient method for the preparation of 3-arylideneindolin-2-ones.[20] The *in situ* generated titanium enolate of indolin-2-one on reactions with carbonyl compounds afford 3-alkylideneindolin-2-ones stereoselectively.[21] To obtain stereodefined 3-alkylideneindolin-2-ones, cyclization reactions of 2-(alkynyl)aryl isocyanates with

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organoboron reagents was performed using palladium(0)/monophosphine catalyst.[22] The iron-catalyzed oxidative condensation of oxindoles with benzylamines formed (*E*)-3-alkylideneindolin-2-ones.[23] Hydrocarboxylation of 2-alkynylanilines was carried out with a bis(cycloocta-1,5-diene)nickel catalyst to obtain (*E*)-3-alkylideneindolin-2-ones, through the (*E*)-[2-(*o*-aminophenyl)]acrylic acid intermediates.[24] A Horner-Wadsworth-Emmons olefination and intramolecular Heck reaction provides rapid access to alkylideneindolin-2-ones from α-haloanilides.[25] The present work discusses a highly efficient synthesis of (*E*)-3-arylideneindolin-2-ones from indolin-2-ones and aldehydes by acid catalyzed reactions in ethanol medium, and evaluation of their photoelectrochemical properties.

Tyrosine kinase inhibitor

RET kinase inhibitor

Anticancer

Tyrosine kinase inhibitor
Sunitinib

Anticancer
Semaxanib

Anticancer

Cyclooxygenase inhibitor
Tedinap

Soulieotine

Ammosamide

Figure 1. A few 3-arylideneindolin-2-ones based biologically active molecules

2. Experimental

All the chemicals were purchased from commercial suppliers and used as received. The reactions were performed in oven-dried glasswares under appropriate atmosphere. The reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm Merck Silica gel 60 F254 plates using UV light for visualization. The column chromatography was performed with 100-200 mesh silica gel using hexane and ethyl acetate as the eluents. NMR spectra were recorded on a Jeol ECZ 400R Spectrometer (^{1}H at 400 MHz, ^{13}C at 100 MHz) using CDCl$_3$ as the solvent with TMS as the internal standard. Chemical shifts (δ) are reported relative to residual solvent signals (Chloroform-d, 7.26 ppm for ^{1}H NMR and triplet centered at 77.00 ppm for ^{13}C NMR). Melting points are uncorrected. Mass spectrometry was carried out in an ESI quadrupole time of flight Agilent mass spectrometer.

2.1. General Procedure for the Synthesis of 3-arylideneindolin-2-ones

To a solution of indolin-2-one (1 mmol) in ethanol (10 mL), hydrochloric acid (0.5 mL, 11.5 N) and aldehyde (1 mmol) were added and the reaction mixture was stirred at 80 °C for 15-25 minutes. The precipitate formed was filtered and purified by column chromatography using hexane-ethyl acetate (7:3) as the eluent. The pure product obtained was dried under reduced pressure, and the percentage yield was calculated. All the compounds were characterized by ^{1}H & ^{13}C NMR and mass spectrometric analysis. The analysis data has also been compared for those compounds reported in literature.[26, 27]

(E)-3-benzylideneindolin-2-one 3a: Yield = 80%; M.P. = 170 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.22 (s, 1H), 7.83 (s, 1H), 7.60 – 7.67 (m, 3H), 7.41 – 7.49 (m, 3H), 7.17 – 7.23 (m, 1H), 6.83 – 6.90 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.15, 141.69, 137.61, 134.99, 129.95, 129.72, 129.42, 129.40 129.37, 128.74, 127.56, 123.17, 121.95, 121.86, 110.17; MS (ESI): *m/z* calcd. for C$_{15}$H$_{11}$NO [M+H]$^+$: 221.0841, found: 222.0932.

(E)-3-(2-chlorobenzylidene)indolin-2-one 3b: Yield = 85%; M.P. = 156 °C; ^{1}H NMR (400 MHz,CDCl$_3$): δ NMR (400 MHz, CDCl$_3$): δ 8.41 (s, 1H), 7.86 (s, 1H), 7.71 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.29 – 7.41 (m, 3H), 7.18 – 7.23 (m, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.82 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.59, 141.83, 134.54, 133.91, 133.66, 130.79, 130.33, 130.22, 130.11, 129.14, 126.65, 123.29, 121.99, 121.52, 110.32; MS (ESI): *m/z* calcd. for C$_{15}$H$_{10}$ClNO [M+H]$^+$: 255.0451, found: 256.0544

(E)-3-(2,4-dichlorobenzylidene)indolin-2-one 3c: Yield = 80%; M.P. = 211 °C; ^{1}H NMR (400 MHz, CDCl$_3$): NMR δ 7.86 (s, 1H), 7.75 (s, 1H), 7.64 – 7.67 (m, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.31 – 7.35 (m, 1H), 7.27 – 7.30 (m, 1H), 7.20 – 7.24 (m, 1H), 6.82 – 6.88 (m, 2H); ^{13}C NMR (100 MHz,CDCl$_3$): 169.01, 141.81, 136.11, 135.41, 132.55, 132.14, 131.03, 130.60, 130.09, 129.39, 127.25, 123.38, 122.15, 121.34, 110.25; MS (ESI): *m/z* calcd. for C$_{15}$H$_9$C$_{12}$NO [M+H]$^+$: 289.0061, found: 290.0198.

(E)-3-(4-(trifluoromethoxy)benzylidene)indolin-2-one 3d: Yield = 75%; M.P. = 137 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.45 (s, 1H), 7.76 (s, 1H), 7.66 – 7.71 (m, 2H), 7.48 – 7.56 (m, 1H), 7.28 – 7.33 (m, 2H), 7.20 – 7.25 (m, 1H), 6.84 – 6.92 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.92, 149.92, 141.74, 135.58, 135.55, 133.70, 133.45, 130.98, 130.36, 128.32, 123.07, 122.11, 121.49, 121.03, 110.46, 109.75; MS (ESI): *m/z* calcd. for C$_{16}$H$_{10}$F$_3$NO$_2$ [M+H]$^+$: 305.2562, found: 306.0749.

(E)-3-(4-methoxybenzylidene)indolin-2-one 3e: Yield = 75%; M.P. = 139 °C; ^{1}HNMR (400 MHz, CDCl$_3$): δ 8.33 – 8.40 (s, 1H), 7.78 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.64 – 7.69 (m, 2H), 7.19 (m, *J* = 7.7, 3.4, 1.1 Hz, 1H), 6.95 – 7.03 (m, 2H), 6.85 – 6.92 (m, 2H), 3.87 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.46, 161.05, 141.37, 137.82, 134.59, 132.63, 131.57, 129.49, 127.34, 125.70, 122.80, 122.14, 121.81, 114.21, 110.13, 55.47; MS (ESI): *m/z* calcd. for C$_{16}$H$_{13}$NO$_2$ [M+H]$^+$: 251.0946, found: 252.1049.

(E)-3-(4-nitrobenzylidene)indolin-2-one 3f: Yield = 87%; M.P. = 233 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.66 (s, 1H), 8.26 – 8.34 (m, 2H), 7.91 (m, 2H), 7.63 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.29 (m, 1H), 6.77 – 6.89 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.70, 148.02, 144.04, 142.02, 133.48, 132.99, 131.55, 130.95, 130.68, 124.44, 123.66, 123.40, 121.94, 120.79, 110.92; MS (ESI): *m/z* calcd. for C$_{15}$H$_{10}$N$_2$O$_3$ [M+H]$^+$: 266.0691, found: 267.0830

(E)-3-(4-chlorobenzylidene)indolin-2-one 3g: Yield = 82%; M.P. = 164 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.86 (s, 1H), 7.74 (s, 1H), 7.54 – 7.60 (m, 3H), 7.42 – 7.45 (m, 2H), 7.19 – 7.24 (m, 1H), 6.85 – 6.89 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 169.61, 141.59, 135.96, 135.94, 135.64, 133.40, 130.71, 130.22, 129.11, 129.08, 129.06, 127.94, 123.11, 122.03, 110.20; MS (ESI): *m/z* calcd. for C$_{15}$H$_{10}$ClNO [M+H]$^+$: 255.7010, found: 256.0532

(E)-3-((2-oxoindolin-3-ylidene)methyl)benzonitrile 3h: Yield = 85%; M.P. = 196 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 (s, 1H), 7.89 – 7.93 (m, 1H), 7.84 (dt, *J* = 1.9, 1.5 Hz, 1H), 7.69 – 7.73 (m, 2H), 7.56 – 7.62 (m, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 1.6 Hz, 1H), 6.85 – 6.90 (m, 2H); ^{13}C NMR (100MHz, CDCl$_3$): δ 169.21, 141.94, 136.45, 133.78, 133.35, 132.76, 132.40, 130.90, 129.81, 129.58, 123.12, 122.32, 121.05, 118.19, 119.33, 110.54; MS (ESI): *m/z* calcd. for C$_{16}$H$_{10}$N$_2$O [M+H]$^+$: 246.0793, found: 247.0880.

(E)-3-(2-bromobenzylidene)indolin-2-one **3i**: Yield = 84%; M.P. = 172 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.09 (s, 1H), 7.79 (s, 1H), 7.66 – 7.71 (m, 2H), 7.36 – 7.42 (m, 1H), 7.26 – 7.32 (m, 2H), 7.17 – 7.22 (m, 1H), 6.85 – 6.89 (m, 1H), 6.78 – 6.83 (m, 1H); ^{13}C NMR (100MHz, CDCl$_3$): 169.31, 141.69, 135.91, 135.57, 133.28, 130.88, 130.28, 128.74, 127.31, 124.28, 123.36, 122.20, 121.99, 121.50, 110.20; MS (ESI): *m/z* calcd. for C$_{15}$H$_{10}$BrNO [M+H]$^+$: 298.9946, found: 300.0034.

(E)-3-(2-hydroxybenzylidene)indolin-2-one **3j**: Yield = 86%; M.P. = 161 °C; ^{1}H NMR (400 MHz,CDCl$_3$): NMR δ 10.47 (s, 1H), 7.66 (s, 1H), 7.58 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.29 (m, 1H), 7.14 – 7.19 (m, 1H), 6.92 – 6.96 (m, 1H), 6.78 – 6.89 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): 169.40, 157.39, 143.17, 133.19, 132.10, 130.14, 130.06, 126.89, 122.84, 121.89, 121.87, 121.51, 119.16, 116.63, 110.49; MS (ESI): *m/z* calcd. for C$_{15}$H$_{11}$NO$_2$ [M+H]$^+$: 237.0790, found: 238.0874.

(E)-3-((E)-3-phenylallylidene)indolin-2-one **3k**: Yield = 88%; M.P. = 197 °C; ^{1}H NMR (400 MHz,CDCl$_3$): δ NMR (400 MHz,) δ7.97 (d, *J* = 0.5 Hz, 1H), 7.67 – 7.73 (m, 1H), 7.56 – 7.65 (m, 3H), 7.45 – 7.49 (m, 1H), 7.34 – 7.43 (m, 3H), 7.13 – 7.25 (m, 2H), 7.04 – 7.09 (m, 1H), 6.87 – 6.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.00, 144.56, 140.91, 136.15, 136.08, 129.79, 129.10, 129.08, 129.06, 127.80, 127.78, 125.68, 123.80, 123.48, 123.12, 122.23, 110.11; MS (ESI): *m/z* calcd. for C$_{17}$H$_{13}$NO [M+H]$^+$: 247.0997, found: 248.1077.

3. Results and Discussion

In spite of the advancements to access 3-arylideneindolin-2-ones, the synthesis from indolin-2-one still remains as an attractive choice due to operational simplicity (Scheme 1). One of the earlier reported procedures in this direction involves refluxing a mixture of indolin-2-one and aldehydes in ethanol medium in the presence of piperidine.[17,18] Upon removal of the solvent under reduced pressure and cooling the residue to room temperature, 3-arylideneindolin-2-ones were obtained as a mixture of (*E*)- and (*Z*)-isomers.
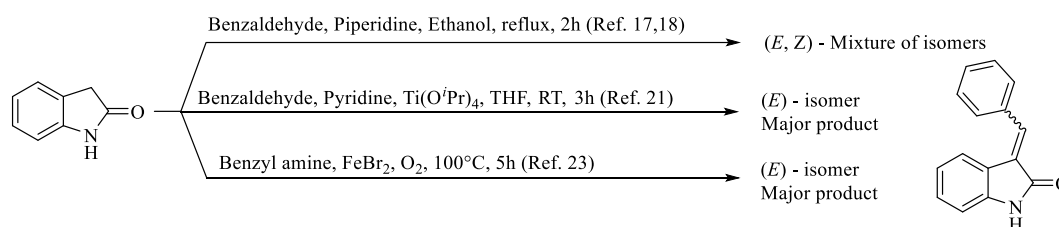

Scheme 1. Synthesis of 3-arylideneindolin-2-ones from indolin-2-ones

An improvisation of the reaction between these two reacting partners was made through metal enolates formed by dropwise addition of Ti(O^{i}Pr)$_4$ in THF to a solution of indolin-2-one and pyridine, followed by aldehyde in THF.[21] An aqueous extractive workup upon completion of the reaction, and column chromatographic purification afforded the (*E*)-isomer of 3-arylideneindolin-2-ones as the major product. However, the reaction took longer time and the stereochemical biasness towards the (*E*)-isomer was not fully reasoned. Another strategy to access the (*E*)-3-alkylideneindolin-2-ones from indolin-2-ones was by iron-catalyzed aerobic oxidative condensation with benzylamines.[23] The mechanistic investigations revealed that the reaction proceeded through C-H activation, amine self-condensation, nucleophilic addition and C-C double bond formation.
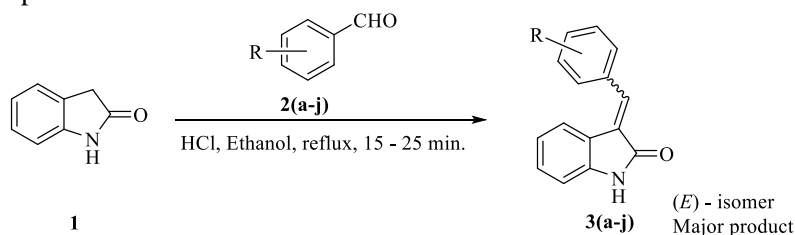
Scheme 2. Acid catalyzed synthesis of 3-arylideneindolin-2-ones from indolin-2-ones
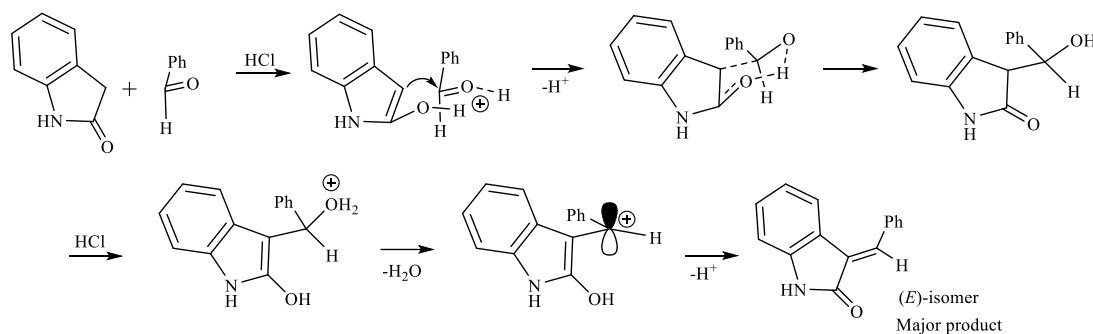
Scheme 3. Formation of (*E*)-3-arylideneindolin-2-ones as the major product under acid catalyzed condition

Table 1. Comparison of ^{1}H NMR chemical shift values of (*E*)- and (*Z*)-3-arylideneindolin-2-ones

	Experimental		Literature[26]			
	(*E*-isomer)		(*E* isomer)		(*Z* isomer)	
	H$_a$ (vinylic)	**H$_b$** (ortho)	**H$_a$** (vinylic)	**H$_b$** (ortho)	**H$_a$** (vinylic)	**H$_b$** (ortho)
3a R^1 = H	7.83	7.67	7.84	7.62	7.55	8.28
3e R^1 = OMe	7.78	7.69	7.79	7.66	7.50	8.35
3g R^1 = Cl	7.74	7.60	7.74	7.53	7.45	8.25
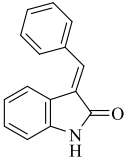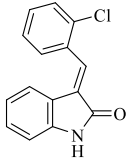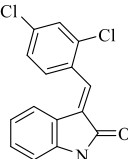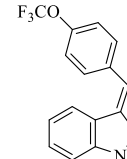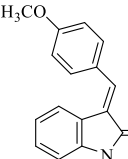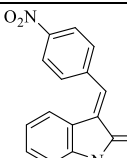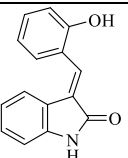
Table 2. Effect of reaction conditions on the synthesis of (*E*)-3-benzylideneindolin-2-one

S. No.	Solvent	Time	Quantity of HCl	Yield
1	DMSO	2 h	1 mL	50%
2	DMF	2 h	1 mL	45%
3	1,4-Dioxane	1 h	0.5 mL	60%
4	THF	1.5 h	0.5 mL	62%
5	CH$_3$CN	45 min.	0.5 mL	67%
6	EtOH	20 min.	0.5 mL	80%

Indolin-2-one: 1 mmol, Benzaldehyde: 1 mmol, Solvent: 10 mL, HCl conc.: 11.5 N

Intriguingly, the stereochemical outcome of the reactions of indolin-2-one with aldehydes under Bronsted acid conditions remained unexplored, and therefore became the subject of our investigations. We presumed that using a polar protic solvent under acidic condition would substantiate the formation of the thermodynamically favored isomer of the product (Scheme 2). Stabilization of the transition state by H-bonding interaction shall promote the intermolec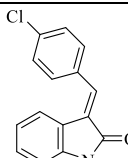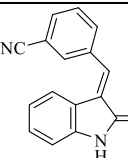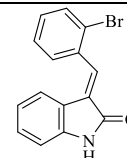ular reaction with the disposition of the phenyl group (Ph) in a pseudoequatorial position on the six membered cyclic transition state. This would direct the transition state to orient the phenyl group away from the carbonyl functionality of the indolin-2-one under equilibrating conditions. The secondary benzyl carbocation formed by the elimination of water would be stabilized by inductive and resonance effects, and will undergo a proton loss to afford (*E*)-isomer as the major product (Scheme 3).

Synthesis and photoelectrochemical properties of 3-arylideneindolin-2-ones

Table 3. (*E*)-3-Arylideneindolin-2-ones synthesized under acid catalyzed condition

(*E*)-3-benzylidene indolin-2-one **3a**	(*E*)-3-(2-chloro benzylidene) indolin-2-one **3b**	(*E*)-3-(2,4-dichloro benzylidene) indolin-2-one **3c**	(*E*)-3-(4-(trifluoro methoxy)benzylidene) indolin-2-one **3d**	(*E*)-3-(4-methoxy benzylidene) indolin-2-one **3e**
Time: 20 min. Yield: 80%	Time: 20 min. Yield: 85%	Time: 15 min. Yield: 78%	Time: 25 min. Yield: 73%	Time: 20 min. Yield: 87%
(*E*)-3-(4-nitro benzylidene) indolin-2-one **3f**	(*E*)-3-(4-chloro benzylidene) indolin-2-one **3g**	(*E*)-3-((2-oxoindolin -3-ylidene)methyl) benzonitrile **3h**	(*E*)-3-(2-bromo benzylidene) indolin-2-one **3i**	(*E*)-3-(2-hydroxy benzylidene) indolin-2-one **3j**
Time: 20 min. Yield: 82%	Time: 20 min. Yield: 85%	Time: 20 min. Yield: 84%	Time: 15 min. Yield: 86%	Time: 15 min. Yield: 80%

To achieve the conversion, a solution of indolin-2-one (1 mmol) in 10 mL ethanol was treated with 0.5 mL of hydrochloric acid (conc. 11.5 N), and to this reaction mixture benzaldehyde (1 mmol) was added and refluxed. The solid product obtained from the reaction mixture was purified, and characterized as 3-benzylideneindolin-2-one. The product was confirmed as the (*E*)-isomer by comparing the ^{1}H NMR chemical shift values of the vinylic proton and ortho protons of the arylidene moiety with the literature reported values[23] (Table 1). For instance, the protons at the ortho positions of the arylidene moiety for the (*E*)-isomer of 3-benzylideneindolin-2-one **3a** is distinctly conspicuous at 7.6 ppm, while the (*Z*)-isomer would indicate these protons' signal at 8.2 ppm. On the other hand, the vinylic proton signal of **3a** is observed at 7.8 ppm and 7.5 ppm for the (*E*) and (*Z*)-isomers, respectively. Similar observations were made with other (*E*)-3-arylideneindolin-2-ones also. The scope of the reaction was examined by employing aldehydes with electron donating and withdrawing groups. In all the cases 0.5 mL of HCl (conc. 11.5 N) was employed for 1 mmol of the indolin-2-one and the reaction was performed in the polar protic medium ethanol. Polar solvents facilitated the reaction as expected, by the nature of transition state that would be involved (Table 2). Aprotic solvents such as DMSO and DMF took longer time. Employing ethers as solvents assisted the reaction by reducing the time. Interestingly the reaction time was significantly reduced with the aprotic polar solvent acetonitrile when compared to DMSO. With the polar protic solvent ethanol, the reaction proceeds at a faster rate. Under the conditions employed, the preferential formation of the (*E*)-isomer as the major product in all the cases was encouraging. Invariably, the reactions were complete in 15-25 minutes and the isolated yields are compiled in Table 3.

Further it was decided to examine the optimum quantity of the Bronsted acid necessary for the reaction. Performed on 1 mmol of the substrate the reaction took much longer time to complete with 0.1 mL of HCl (conc. 11.5 N). Increasing the volume of HCl to 0.5 mL (conc. 11.5 N) increases the rate of the reaction by more than 20-fold. But further addition of the acid did not promote the reaction. It was interesting to note that the substitutions on the aldehyde did not significantly deter the time required for the conversion. The products precipitated subsequent to the complete consumption of the starting materials. This facilitated an easy isolation of the product from the solution, and the major isomer was purified by column chromatography. The highly convenient synthesis by this cost-effective protocol also prompted us to examine whether similar results could be obtained with α,β-unsaturated aldehyde. Thus the 1,2-addition of cinnamaldehyde followed by elimination afforded the (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one **3k** in 88% yield within 15 minutes.
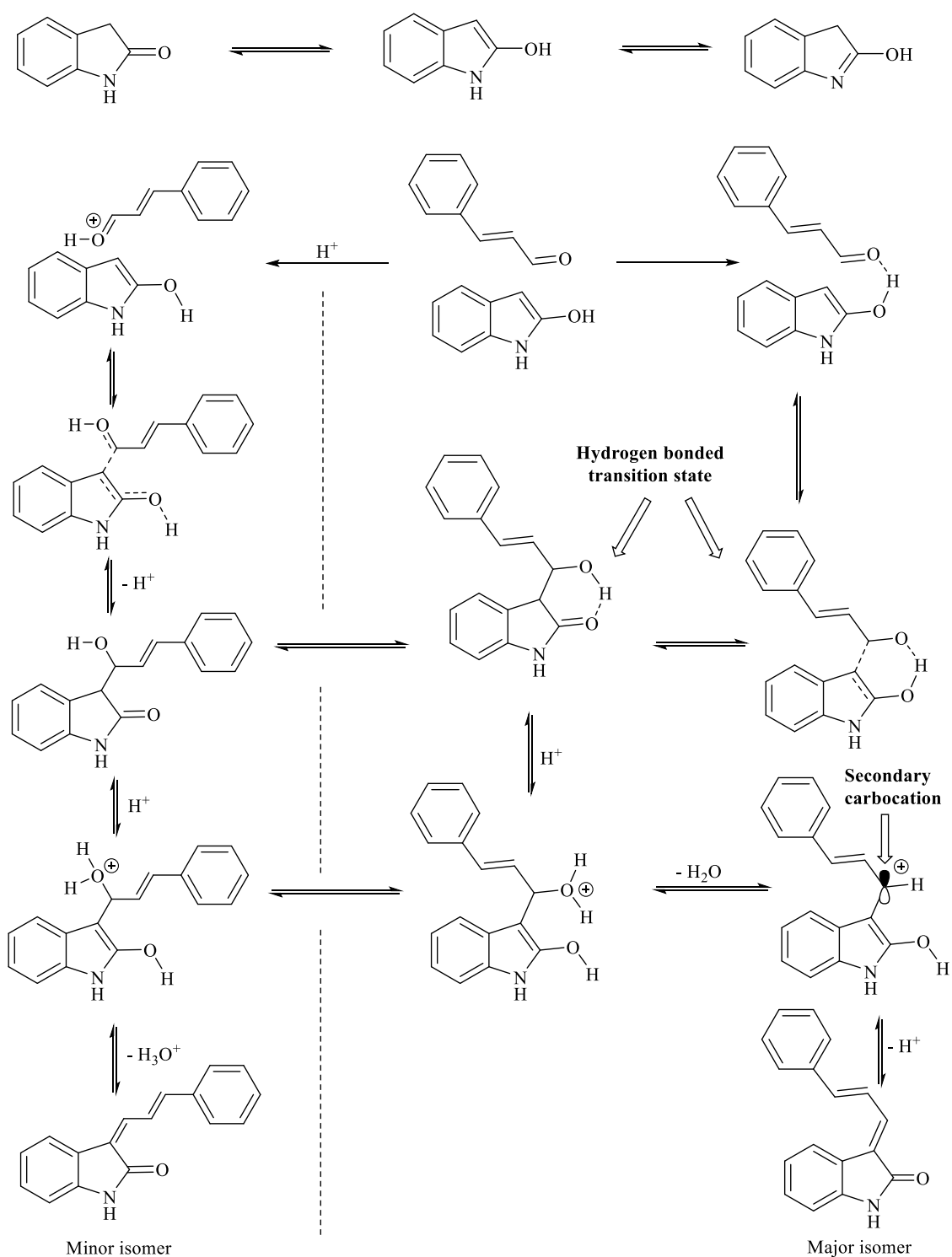
Figure 2. Plausible mechanisms for the formation of (*E*)- and (*Z*)-isomers of 3-arylideneindolin-2-ones

We reasoned that the (*E*)-selectivity originates from a cyclic transition state facilitated by hydrogen bonding. A reasonable mechanism as depicted in Figure 2 can be speculated. Under acidic conditions the reaction is expected to generate the enol tautomer which can form a H-bond with the carbonyl group of the aldehyde to set the stage for a cyclic six-membered transition state for an aldol type intermediate. The acid assisted elimination of water would then result in the formation of a carbocation which collapses to give the conjugated olefin with (*E*)-geometry. The orientation of the

arylidene moiety at position 3 with respect to the indolin-2-one is governed by an energetically favorable transition state. Therefore, it can be assumed that the geometry of the olefin is decided by a combination of factors such as the hydrogen bonding under acidic conditions, the cyclic transition state formed, spatial orientation of the intermediate β-hydroxyindolin-2-one, the stability of the carbocation formed by the elimination of the hydroxy group, and the subsequent loss of proton; making the reaction path catalytic in nature. The reaction when proceeds through the energetically unfavorable transition state shall form the (*Z*)-isomer as the minor product while the H-bonded cyclic transition state facilitates the formation of the (*E*)-isomer as the major product.
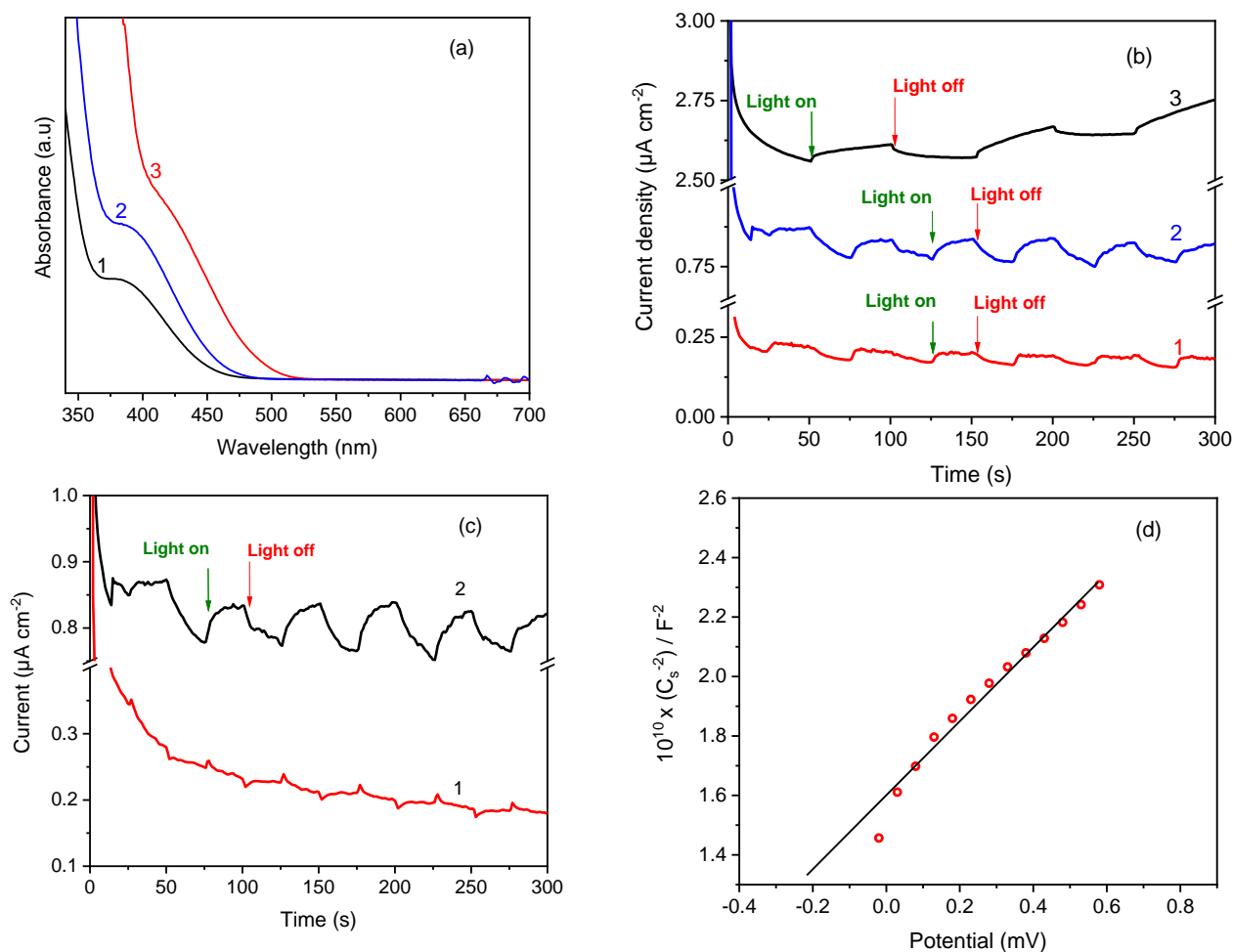
Figure 3. (**a**) UV-Visible absorption spectra of (1) (*E*)-3-benzylidineindolin-2-one, (2) (*E*)-3-(4-chlorobenzylidene)indolin-2-one and (3) (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one.

(**b**) Photocurrent responses of (1) (*E*)-3-benzylidineindolin-2-one (2) (*E*)-3-(4-chlorobenzylidene)indolin-2-one and (3) (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one in 0.5 M KI at 0.4 V vs Ag/AgCl in sat. KCl.

(**c**) Comparison of photocurrent responses of (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one in (1) 0.5 M Na$_2$SO$_4$ and (2) 0.5 M KI.

(**d**) Representative Mott-Schottky plot of (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one in 0.5 M Na$_2$SO$_4$ at different potentials vs Ag/AgCl in sat. KCl.

Photoactive molecular organic compounds have established their sphere of influence in organic photovoltaics, photoelectrochemical interfaces, photodiagnostics and phototherapeutics.[28-32] Photoactive organic molecular and polymeric materials can perform as thin protective overlayer and improve the effective charge separation of photogenerated excitons and preferential charge transfer at the electrochemical interface. The indole compounds have been investigated for their interesting photophysical properties.[33] With this application in mind, we examined the photoelectrochemical activity of (*E*)-3-arylidineindolin-2-ones and the preliminary results are discussed herein. Furthermore, a comparison of the compound (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one **3k** with the other (*E*)-3-arylideneindolin-2-ones demonstrated the effect of conjugation in improving the photoelectrochemical properties. The initial evaluation of the compounds garnered the reasons to focus on the 3 compounds, (*E*)-3-benzylidineindolin-2-one,   (*E*)-3-(4-chlorobenzylidene)indolin-2-one   and   (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one. These representative molecules were dissolved in DCM and fabricated as thin film photoelectrodes on fluorine doped tin oxide (FTO) substrate without the use of any conductive binders. The photoelectrochemical measurements were performed in 0.5 M Na_2SO_4 and 0.5 M KI electrolytes. The photocurrent measurements were carried out at different applied bias potentials with repeated on-off cycles. Xe lamp source of 300 Watts was used for photoelectrochemical studies. The three electrodes photoelectrochemical cell setup consists of organic molecules coated FTO as working, Pt as counter and Ag/AgCl in saturated KCl as reference electrodes. Potential dependent impedance measurements were carried out at constant AC frequency (100 KHz) to obtain the Mott-Schottky plot and to understand the photoelectrode behaviour. The visible spectra of the representative compounds are shown in Figure 3(a). The absorption band edge position of (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one shows a significant bathochromic shift. This enhances the visible light absorption of the photoelectrodes due to the increase in conjugation of the (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one. The photoelectrochemical photovoltage measurements at the open circuit conditions exhibit the negative potential shift which suggest the *n*-type behaviour of all the three compounds. Figure 3(b) shows the photocurrent measurements with repeated on-off cycles in 0.5 M KI. The photocurrent values increase with anodic potential bias. The photocurrent measurements were done at different potentials (See Supporting Information). The overall increase in photocurrent was observed in KI electrolyte at higher anodic bias potentials. Here the photogenerated holes are used for the oxidation of iodide to triiodide at the *n*-type interface. The figure also displays the repeatable photocurrent values (200-300 nA cm^{-2}) observed with the three compounds. Figure 3(c) shows the comparative photocurrent responses in 0.5 M KI and in 0.5 M Na_2SO_4 electrolytes. The photocurrent observed in KI electrolyte is relatively higher than in Na_2SO_4. This is due to the photooxidation of iodide at higher potentials. Figure 3(d) shows the representative Mott-Schottky plot which further signifies the *n*-type behaviour of the (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one. The measurements carried out at the positive potentials to the open circuit potential (OCP) shows the positive slope values. The x-axis intercept indicates the flat band potential; and the small deviation from the linearity could be due to the surface roughness of the photoelectrode. These observations suggest the possible application of these molecular photoactive materials in photoconversion devices.

In conclusion, an environment friendly procedure was developed for 3-arylideneindolin-2-ones by reacting indolin-2-ones with aldehydes in ethanol medium under HCl catalyzed conditions. Upon refluxing, the reactions were complete in 15-25 minutes and preferentially gave the (*E*)-isomer as the major product. The photoelectrochemical properties of the synthesized compounds were examined, and preliminary investigations revealed appreciable photoactivity with (*E*)-3-benzylideneindolin-2-one,   (*E*)-3-(4-chlorobenzylidene)indolin-2-one   and   (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one. Further, the derivatives of (*E*)-3-((*E*)-3-phenylallylidene)indolin-2-one will be synthesized, and explored for possible application as molecular photoactive material in photoconversion devices.

Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Supporting information accompanies this paper on http://www.acgpubs.org/journal/organic-communications.

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