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Green regioselective synthesis and theoretical insights into photo- and thermochromic spiro heterocycles: toward optical and thermal sensing applications

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Building on the significant potential of pyrimidine-based molecules for optoelectronic applications, we designed and synthesized a new series of spiro[indoline-pyrido-pyrimidine] derivatives with excellent selectivity. These compounds exhibit novel photochromic and thermochromic properties, addressing the growing need for diagnostic agents with minimal side effects. The regioisomers were identified using 1D, 2D homonuclear and heteronuclear correlation NMR spectroscopy, along with X-ray crystallography. Dynamic 1 H NMR (DNMR) studies revealed that the major isomer (4 sa) is more stable than the minor isomer (4 sb). Optical, electrochemical, and structural analyses of compounds 4aa, 4ab, 4 sa, and 4sb demonstrated the feasibility of chemical reactions converting closed-ring structures to open-ring structures, resulting in notable optical properties due to ring opening. To validate the experimental data, density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were conducted at the B3LYP/6-31G(d) level, offering insights into the electronic structure and absorption spectra. Additionally, Gibbs free energy (ΔG) calculations were performed to elucidate the proposed mechanism for open-ring compounds named 5 and 7. This work emphasizes employing the citric acid as a bio-organic catalyst in a green, multi-component domino reaction, underscoring its environmentally sustainable approach. These studies reveal the potential of these compounds for advanced optical and temperature sensing applications, aligning theoretical and experimental approaches to establish a robust foundation for future research.

Keywords Spiro[indoline-pyrido-pyrimidine], Regioselective synthesis, Photo and thermochromic compound, Green multicomponent reaction, Natural catalyst, Density functional theory

The initial step in disease management is diagnosis, which frequently involves the use of diagnostic agents that can potentially cause adverse effects, including allergic reactions. This highlights the urgent need to explore and develop novel molecules with photo- and thermochromic properties that exhibit minimal side effects^{1,2}. Among such promising candidates are spiro-heterocycles, known for their significant biological activity and therapeutic potential. Their unique conformational properties and structural influence on biological systems position them as key players in medicinal chemistry, with applications spanning anticancer, antimicrobial, and antidepressant therapies^{3–5}. One class of compounds mentioned is cyanine dyes, which, as fluorescent derivatives primarily based on indole as the most common skeleton, have found wide applications in various fields, including optical materials, biomolecular labelling, fluorescent imaging, photodynamic therapy, optical data storage, sensors, drug delivery systems, and dynamic materials^{6–10}. Within this class, the spiropyran family, as one of the first major groups of light-responsive colorants, has been extensively studied for its photochromic behavior¹¹.

These materials exhibit two principal isoforms: the closed hydrophobic (Spiropyran) and open hydrophilic (Merocyanine) forms, which are interconvertible under UV light irradiation. Upon UV excitation, colorless spiropyrans undergo photoexcitation, resulting in a ring-opened intermediate that quickly transitions through

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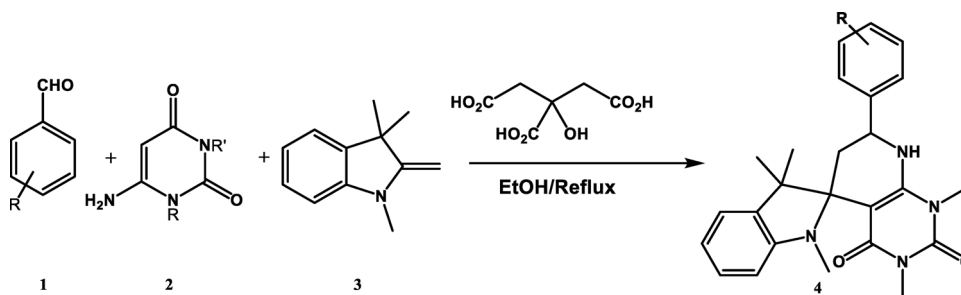
cis/trans isomerization of the benzopyran double bond to produce the highly colored merocyanine form. This reversible process can return to the initial state under thermal conditions or visible light irradiation. In addition to their light-responsive properties, spiropyrans demonstrate acidochromism, thermochromism, and pH-chromism, expanding their functional potential. While the early focus was on pyran-based systems, subsequent research explored other heterocyclic frameworks, particularly nitrogen-based systems, in the synthesis of spirocyanine dyes^{12,13}. Novel derivatives of these dyes, with enhanced photostability and broadened utility, have been developed for innovative optical and biomedical applications^{14,15}. These advancements, such as those highlighted by Guo et al. have expanded the relevance of spirocyanine dyes in areas like optical materials, drug delivery systems, and modern diagnostics, paving the way for novel applications^{16,17}.

Multi-component and domino reactions, as powerful platforms for medicinal, combinatorial, and organic chemists, are general ways for improving the synthetic efficiency of new biologically active compounds, pharmaceutical heterocycles, and functionalized organic compounds from three or more reactants. Compared to the conventional linear-type synthesis, these reactions offer important advantages including cost-effectiveness, high degree of atom economy, simple workup and purification routes, less time consuming due to flexible, convergent nature^{18–20}. Moreover, multi-component reactions are well-suited to the green chemistry fundamentals to facilitate the creation of complex products in a single step through environmentally considerate and innovative methods. The development of green catalysts, such as silica-supported ionic liquids and eutectic solvents has further refined these synthetic approaches, enabling efficient, reusable, and sustainable processes^{21–23}. Niu et al. enable the rapid synthesis of complex molecules, including biologically active compounds and pharmaceutical heterocycles, while minimizing environmental impact²⁴.

To date, various green catalysts have been employed in the fabrication of spirocyclic derivatives. For instance, ionic liquids serve as environmentally benign catalysts and reagents in the formation of diverse spiro-heterocycles²⁵. In an investigation, for obtaining spiro[indoline-3,4'-pyrano[2,3-c]pyrazoles], triethylammonium acetate was applied as an inexpensive and non-toxic catalyst²⁶. Many advantages of this study were high yield, very short times, and easy workup. In a separate study, Arya et al. described the catalyzed preparation of spiro[indole-pyrido[3,2-e]thiazine] by zeolite-supported ionic liquids²⁷. Besides, in similar work, brønsted acidic ionic liquids were employed as a benign catalyst for the making of fluorinated spiro-[indole-thiazinones]²⁸. Another green catalyst that has been used for the production of spiro-heterocycles is sodium chloride. In this regard, Dandia et al. designed spiro-heterocycles such as spiro[indoline-3,4'-pyrazolo[3,4-b]pyridines] with NaCl as a non-acidic green catalyst in water solvent under the sonication process^{29,30}. The gains of these methodologies were simplicity of the process, easy handling, environmentally benign character, and high yield. In addition to the stated cases, in recent years, other green materials have been used in this regard. Mondal et al.³¹ developed spiro-heterocyclics by employing an activated alumina ball catalyst. This work offered features such as high efficiency, no toxic by product formation, brief reaction time, straightforward workup, and excellent regioselectivity. Mohammadi et al.³² reported the use of alum as a heterogeneous green catalyst in the production of spiro-heterocycles through. Jazinizadeh et al.³³ utilized Na₂EDTA as a green and effective catalyst for synthesizing spiro-heterocyclic compounds under solvent-less conditions. Saluja et al.³⁴ reported employing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the catalyzed production of biologically and pharmacologically important spiropyranes in respectable yields.

Citric acid, a weak tricarboxylic acid abundantly present in several natural sources, is a biodegradable, safe, and reusable material. Its unique properties, such as physiological inertness, non-corrosive nature, economic viability, and ready availability, make it an ideal candidate for use as an eco-friendly catalyst. Despite its potential, its application in the preparation of heterocyclic derivatives has been limited^{35,36}. This study seeks to follow the principles of green chemistry and minimize the high costs associated with catalyst production by using citric acid as a bioorganic catalyst. We successfully synthesized novel photo- and thermochromic spiro-heterocyclic compounds *via* a multi-component domino reaction, utilizing aromatic aldehydes, 6-aminouracils, and 1,3,3-trimethyl-2-methyleneindoline (Fischer's base), Scheme 1.

In the following, the electronic and optical characteristics, conductivity, and voltammetric behaviour of the newly synthesized products are systematically examined. Additionally, a mechanism for the studied compounds is proposed. Through this study, we aspire to contribute to advancing the frontiers of photo- and thermochromic applications, organic synthesis, and the development of bioactive compounds with potential applications in modern medicine and pharmacology.



Scheme 1. Synthesis of novel optically active spiro indoline-pyrido-pyrimidines via a multicomponent domino reaction.

Experimental and theoretical approaches

Computational methodology

To further explore the molecular structures and stability of the systems under investigation, geometry optimizations were taken using density functional theory (DFT) with the B3LYP functional and the 6-31G(d) basis set^{37,38}. This level of theory was selected for its well-established accuracy and reliability in predicting molecular geometries and energies, as executed in the Gaussian 09 program package³⁹. The solvent effects were examined utilizing the conductor-like polarizable continuum model (C-PCM) with dichloromethane. Generally, including solvent effects enhances the accuracy of computational predictions, particularly when replicating experimental conditions⁴⁰.

To ensure that all optimized geometries correspond to energetic minima and to obtain Gibbs free energy for predicting reaction behavior, harmonic vibrational frequency calculations were performed^{37–42}. Moreover, time-dependent DFT (TD-DFT) calculations were conducted to work out electronic transitions and related orbital contributions, providing valuable insights into excited-state dynamics, including absorption and emission spectra.

Global reactivity descriptors were evaluated using highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies obtained from DFT calculations. These parameters play a significant role in predicting the stability, reactivity, and electron-donating or accepting nature of the synthesized compounds. The parameters are defined as: (a) chemical Hardness [$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2$], (b) global Softness [$S = 1/(2\eta)$], (c) chemical potential [$\mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2$], (d) electrophilicity index [$\omega = \mu^2/(2\eta)$].

These calculations are crucial for understanding the photochromic and thermochromic behavior as well as the optical properties of the synthesized spiro-heterocyclic compounds⁴³.

Materials and instrumentation

Chemicals were sourced from Merck, Aldrich, Fluka, and the solvents were distilled, dried, and purified according to standard procedures. The ¹H-, ¹³C-, and ¹³C *J*-modulated NMR spectra, along with 2D- NMR spectra such as COSY, ¹H-¹³C HSQC, ¹H-¹⁵N HSQC, ¹HMBC, TOCSY, ROESY and NOESY were documented using Bruker Avance DPX-400, and DPX-500 spectrometers. These measurements were performed in CDCl₃ and DMSO-*d*₆ to ensure accurate spectral data. Mass spectra were recorded via electron collision (EI) and adjustable in the range of 20–70 electron volts in the mass range of 10 to 800 dalton by model 5975 C (Agilent Technologies company) instrument. X-ray data were recorded on a Bruker D8 VENTURE diffractometer. The fluorescence spectrum of the as-prepared materials was run on a Perkin–Elmer spectrofluorometer (Model: LS45). The FT-IR spectrum was acquired on a Shimadzu FT-IR-8300 spectrometer, using a potassium bromide pellet, within the wavenumber range of 500 to 4000 cm^{−1}. Sample characterization was performed using a CHN analyzer (ECS 4010, Costech, Italy).

General procedure synthesis of pentamethyl-dihydro-1′H-spiro[indoline-2-pyrido[2,3-d]pyrimidine]–2′,4′(3′H,6′H)-diones

A mixture of aromatic aldehyde (**1**, 1.0 mmol), 6-aminouracil derivatives (**2**, 1.0 mmol), Fischer's base (**3**, 1.0 mmol), and citric acid (0.1 mmol) in 5 mL ethanol was refluxed for 1–2 h. Upon ending of the reaction, as traced by TLC, the produced precipitate was filtered, washed with water and ethanol to provide the pure product (**4a–u**).

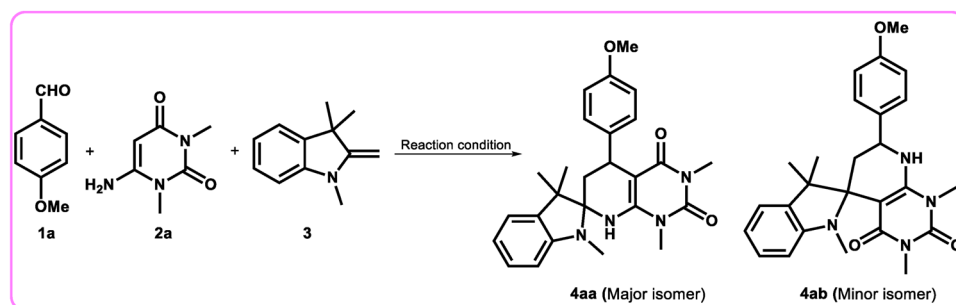
Results and discussion

Synthesis and characterization

To commence this study, a mixture of 4-methoxybenzaldehyde (**1a**, 1.0 mmol), 6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (**2a**, 1.0 mmol), Fischer's base (**3**, 1.0 mmol) in 5 mL ethanol was refluxed, as the prototype reaction, in the presence of citric acid (0.1 mmol) (Table 1, entry 1). After finishing of the reaction (determined by TLC), the filtered precipitate was washed with water and ethanol to give a white amorphous solid in 95% yield, which display an adduct ion at *m/z* 469.233 [*M* + Na]⁺ by HRESIMS corresponding to C₂₆H₃₀N₄O₃ (see Supplementary Figure S1).

The ¹H NMR spectrum of this white amorphous solid was acquired in CDCl₃, Fig. 1, and exhibited some duplicated signals evidently, which can be particularly assigned to regioselectivity of the reaction and the presence two regioisomers **4aa** and **4ab** in the white amorphous solid. Integration of these signals gave the ratio of 82:18 regioisomers. the ¹H NMR spectrum of the major isomer **4aa**, revealed a sharp singlet at δ 1.33 ppm corresponding to methyl group in indoline moiety. In addition, three different singlets at δ 2.77, 3.24, and 3.35 ppm were acquired assignable to N-methyl groups. Also, three protons of methoxy attached to aromatic ring appeared as a singlet at δ 3.81 ppm (both of isomers). The methylene group presented in the piperidine nucleus shown two mutually coupled doublet of doublets centered at δ 2.08 ppm (*J* = 13.5 Hz, *J* = 12.5 Hz), and 2.37 ppm (*J* = 13.5 Hz, *J* = 5.5 Hz). The one methine proton existing in this ring was revealed as a doublet of doublet, centered at δ 4.06 ppm (*J* = 12.0 Hz, *J* = 5.5 Hz). The amino NH proton was observed at δ 4.48 ppm. In the minor isomer **4ab**, these signals appeared at δ 1.08 and 1.25 (s, CH₃), 2.10 (m, CH₂), 2.53 (dd, *J* = 14.5 Hz, *J* = 7.5 Hz, CH₂), 2.84, 3.26 and 3.31 (s, N–CH₃), 3.81 (s, O–CH₃), 4.23–4.26 (m, CH), 4.71 (s, NH), respectively. The aromatic protons were distributed in the region δ 6.51–7.19 ppm.

The *J*-modulated ¹³C NMR of this product further supported the proposed structures, particularly allowing the identification of the spiro-carbon using this technique (see Supplementary Figure S4). The methyl carbons resonated in the region δ 22.30 (CH₃), 24.46 (CH₃), 27.85 (N–CH₃), 27.97 (N–CH₃), 28.58 (N–CH₃), 55.15 (O–CH₃) ppm. The peaks at δ 36.76, 36.81 and 49.10 ppm have been attributed to the methine, methylene and quaternary carbons, respectively. The spiro-center carbon and C_α (C–C=O) resonate most downfield (δ 85.17 and 87.49 ppm) among all the carbon atoms with chemical shifts in the aliphatic region. The HSQC spectrum



Entry	Catalyst (10 mol%)	pKa	Solvent (5mL)	Time (min)	Temperature (°C)	Yield ^a (%)
		3.128				
1	Citric acid	4.761	EtOH	60	80	95
		6.396				
2	Ascorbic acid	4.17	EtOH	60	80	70
		11.6				
3	Acetic acid	4.75	EtOH	60	80	50
		1.99				
4	L-Proline	10.60	EtOH	60	80	10
5	Amberlyst 15	-	EtOH	60	80	Trace
6	<i>p</i> -TSA	-2.8	EtOH	60	80	Trace
7	Citric acid		EtOH	15	80	30
8	Citric acid		EtOH	30	80	55
9	Citric acid		EtOH	45	80	75
10	Citric acid		EtOH	60	25	15
11	Citric acid		EtOH	60	45	35
12	Citric acid		EtOH	60	65	60
13	Citric acid		H ₂ O	60	80	0
14	Citric acid		CH ₂ Cl ₂	60	40	0
15	Citric acid		DCE	60	80	0
16	Citric acid		H ₂ O/EtOH	60	80	45
17	Citric acid		1,4-Dioxane	60	80	20

^a Total isolated yields

Table 1. Optimization of reaction conditions.

showed correlations to all expected carbon signals for protonated carbons, Figure S6 (in supplementary file), in agreement with their ¹H and ¹³C NMR spectra and supported the proposed structures as well (Fig. 2).

A careful structural study was required to determine the percentage of regioisomers for a credible structural assignment. The ¹H–¹H-COSY spectrum exhibits correlations between each of methylene protons (2.08, 2.37) and the methine proton (4.06) for the major isomer, similar correlation results were observed for the compounds **4ab** between hydrogens of CH₂ (2.08, 2.53) and the neighboring H (4.25) as shown in supplementary file (Figure S5). It was noted that the correlation between these protons from the both structures would have been absent,

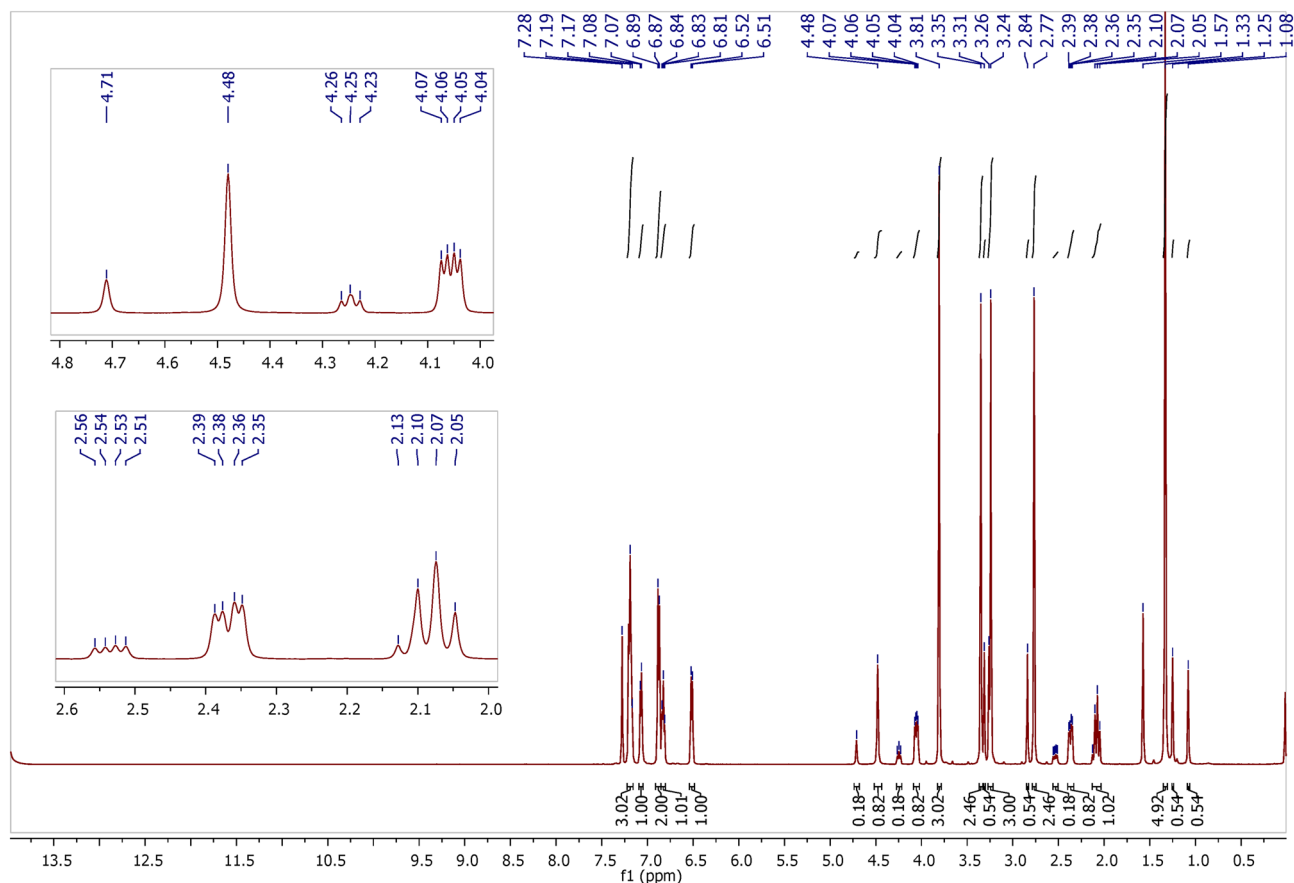


Fig. 1. ^1H NMR spectrum of the mixture of **4aa** and **4ab** in CDCl_3 .

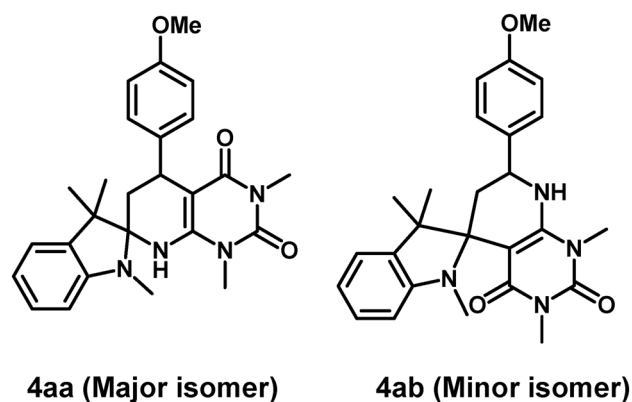


Fig. 2. The proposed structures of **4aa** and **4ab** regioisomers.

thus the interconversion between the major isomer (**4aa**) and the other isomer (**4ab**) does not occur. In the hypothetical case of the formation of the regioisomers **a** and **b**, the observation of the special discrepancies in the aliphatic region would be expected by applying standard 2D NMR techniques such as NOESY and ROESY. While 2D NOESY with zero-quantum suppression is commonly used, our focus on specific NOEs and the challenges of poorly separated peaks, significant distances between protons, and limited molecular rotation led us to opt for 2D ROESY. In the ROESY spectrum (Fig. 3), strong cross-peak correlations were observed between the NH proton (δ 4.48 ppm) and the C-CH₃ group, as well as the two N-CH₃ groups (δ 1.33, 2.77, and 3.35 ppm), indicating that these hydrogens are spatially close. Based on these results and the three-dimensional structure of the product, the major isomer was identified as **4aa**. Significant differences in the correlation patterns of the NH proton were noted between the two isomers. For the minor isomer, the NH proton (δ 4.71 ppm) showed correlations with the C-CH₃ group and only one N-CH₃ group (δ 1.25 and 3.31 ppm). This pattern confirmed

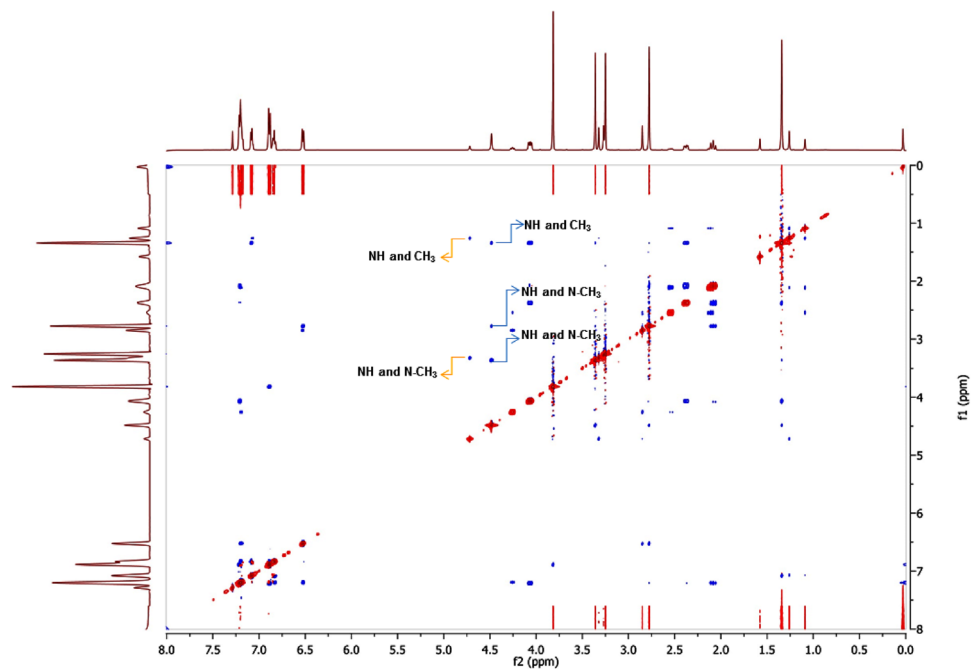


Fig. 3. ROSEY spectrum of the mixture of **4aa** and **4ab**.

the structure of **4ab**. These results provide a comprehensive determination of the chemical structures of the formed products and demonstrate the regioselectivity of the reaction, with the regioisomers present in an 82:18 ratio.

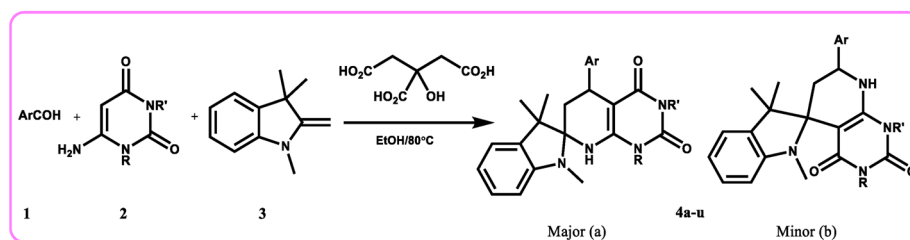
In continuing, for the optimization of reaction parameters, the model reaction was initially performed ascorbic acid in ethanol at 80 °C for 1 h. To our delight, the desired product **4a**, which is a mixture of **4aa** and **4ab**, were formed in 70% yield (Table 1, entry 2). To enhance the yield of **4a**, we conducted further screenings of various catalysts, solvents, reaction times, and temperatures. As reported in Table 1, the intend reaction was less efficient with both stronger and weaker acidic catalysts compared to citric acid, including amberlyst 15, *p*-TSA, and L-proline (Table 1, entries 2–6). The yield of **4a** was increased up to 95% when 10 mol% of citric acid was consumed (Table 1, entry 1). Thus, the reaction outcome is strongly dependent on the nature of the catalyst. The model reaction failed to obtain acceptable yield levels in lower reaction times and temperatures (Table 1, entries 7–12). The role of solvent was also investigated in the product formation next. The reaction failed in aprotic solvents such as CH₂Cl₂ and dichloroethane (DCE) as well as H₂O (Table 1, entries 13–15) and produced low yield of the desired product in 1,4-dioxane and the mixture of H₂O/EtOH (Table 1, entry 16 and 17). The maximum of efficiency was provided in EtOH as solvent (Table 1, entry 1).

Having optimized the reaction conditions, we then investigated a range of substrates (Table 2). The reaction proceeded efficiently with various substituted benzaldehydes, yielding products in high to excellent yields. Notably, functional groups such as nitro, tolyl, methoxy, hydroxy, chloro, and bromo were well tolerated (**4a-r**). Moreover, some bulky aromatic aldehyde such as 1-naphthaldehyde, and 9-phenanthrenecarboxaldehyde participated well in the MCRs to deliver the corresponding products **4s** and **4t** in good yields in up to 80:20 regioselectivity. Notably, when 6-amino-1-benzylpyrimidine-2,4(1*H*,3*H*)-dione was subjected to this process, desired product **4u** was formed with high regioselectivity (94:6), albeit in 93% yield.

To find deeper insights into the geometrical and electronic properties of the intended compounds, their stability and reactivity were analyzed. The relevant geometrical and energetic properties are listed in Table 3 and the ground state geometrical structures are presented in Fig. 4. Inspection of the total ground state energies in intermediate compounds indicates that the isomers **4aa** and **4sa** are 0.24 eV and 0.19 eV more stable than **4ab** and **4sb**, respectively. The observed stability trend aligns with previous experimental findings.

Additionally, the energy gap between HOMO and LUMO is directly related to the chemical hardness, with a larger gap indicating greater chemical hardness. The higher chemical hardness is also associated with the increased kinetic stability. Among the studied compounds, the HOMO–LUMO energy gaps of the major products **4aa** (5.11 eV) and **4sa** (4.29 eV) are larger than those of the minor products **4ab** (4.48 eV) and **4sb** (3.59 eV), suggesting that the **4aa** and **4sa** exhibit greater global hardness and, consequently, higher kinetic stability.

Since chemical hardness or its inverse, chemical softness, reflects the resistance of a compound to change in its electron density, a higher η indicates a more stable and reactive compound. Among the studied compounds, **4aa** has the highest chemical hardness ($\eta = 2.555$ eV), indicating its least reactivity and hence most stability. In contrast, **4sb** shows the lowest chemical hardness ($\eta = 1.795$ eV), suggesting that it is the most reactive and least stable. **4sa** and **4ab** lie in between ($\eta = 2.145$ eV and 2.240 eV, respectively), showing moderate reactivity and stability.



Entry	Ar	R, R'	Time (h)	Product (Yield) ^a	Isomers (Ratio) ^b	$[\alpha]_D^{22}$
1	4-MeO C ₆ H ₄	Me, Me	1	4a(95)	4aa, 4ab(82:18)	-80.5
2	3-MeO C ₆ H ₄	Me, Me	1.5	4b(91)	4ba, 4bb(91:9)	-47.1
3	2-MeO C ₆ H ₄	Me, Me	2	4c(90)	4ca, 4cb(78:22)	-11.6
4	3,4-(MeO) ₂ C ₆ H ₃	Me, Me	1	4d(96)	4da, 4db(96:4)	-46.4
5	4-N, N-Me ₂ NC ₆ H ₄	Me, Me	2	4e(95)	4ea, 4eb(94:6)	-42.1
6	4-HO C ₆ H ₄	Me, Me	1.5	4f(90)	4fa, 4fb(100:0)	-65.8
7	3-HO C ₆ H ₄	Me, Me	1	4g(88)	4ga, 4gb(100:0)	-57.1
8	2-HO C ₆ H ₄	Me, Me	1	4h(85)	4ha, 4hb(100:0)	-78.2
9	3-HO-4-MeO C ₆ H ₃	Me, Me	1	4i(97)	4ia, 4ib(95:5)	-47.0
10	4-Me C ₆ H ₄	Me, Me	1	4j(94)	4ja, 4jb(99:1)	-49.2
11	3-Me C ₆ H ₄	Me, Me	1	4k(90)	4ka, 4kb(100:0)	119.4
12	C ₆ H ₅	Me, Me	1	4l(94)	4la, 4lb(100:0)	-45.3
13	4-Cl C ₆ H ₄	Me, Me	1.5	4m(90)	4ma, 4mb(95:5)	-40.0
14	3-Cl C ₆ H ₄	Me, Me	1.5	4n(87)	4na, 4nb(100:0)	-45.2
15	2-Cl C ₆ H ₄	Me, Me	2	4o(85)	4oa, 4ob(92:8)	-39.3
16	4-O ₂ N C ₆ H ₄	Me, Me	2	4p(89)	4pa, 4pb(93:7)	-44.1
17	3-O ₂ N C ₆ H ₄	Me, Me	2	4q(86)	4qa, 4qb(98:2)	-46.4
18	2-O ₂ N C ₆ H ₄	Me, Me	2	4r(82)	4ra, 4rb(95:5)	-32.9
19	1-Naphthalen	Me, Me	1	4s(92)	4sa, 4sb(80:20)	-38.6
20	9-Phenanthren	Me, Me	1	4t(90)	4ta, 4tb(80:20)	-39.2
21	4-MeO C ₆ H ₄	Benzyl, H	1	4u(93)	4ua, 4ub(94:6)	-19.5

^a Isolated yield^b Determined by ¹HNMR analysis

Table 2. Scope of the synthesis of pentamethyl-dihydro-1'H-spiro[indoline-2-pyrido[2,3-d]pyrimidine]-2,4'(3'H,6'H)-diones.

The chemical potential reflects the tendency of a compound to gain or lose electrons. A more negative chemical potential reflects a greater tendency to accept electrons. Among the compounds, **4 sb** shows the most negative μ , supporting its high electrophilicity and electron-accepting character. Among the compounds, **4 sb** has the most negative chemical potential ($\mu = -3.065$ eV), indicating it is the most stable. **4 sa** follows closely ($\mu = -3.265$ eV), suggesting it is slightly less stable than **4 sb**. **4 aa** ($\mu = -2.855$ eV) and **4 ab** ($\mu = -2.60$ eV) have fewer negative values, indicating moderate to lower stability.

Compounds	E_{Total} (ev)	E_{HOMO} (ev)	E_{LUMO} (ev)	E_{gap} (ev)	λ_{max} (nm)	Main contributions
4aa	-39554.45	-5.41	-0.30	5.11	251	H-2→L (67%)
4ab	-39554.21	-4.84	-0.36	4.48	238	H→L + 5 (84%)
4 sa	-40618.80	-5.41	-1.12	4.29	288	H-2→L (91%)
4 sb	-40618.61	-4.86	-1.27	3.59	286	H-2→L (94%)
5a	-39553.28	-4.50	-2.21	2.29	682	H→L (100%)
7a	-39553.26	-5.21	-2.03	3.18	268	H→L + 2 (58%)
5 s	-40617.42	-4.67	-2.23	2.44	652	H→L (100%)
7 s	-40617.80	-5.46	-1.99	3.47	288	H-1→L + 1 (95%)

Table 3. The ground state total electronic energy of all structures, main orbital contributions to the crucial transition worked out at the B3LYP/6-31G (d) level.

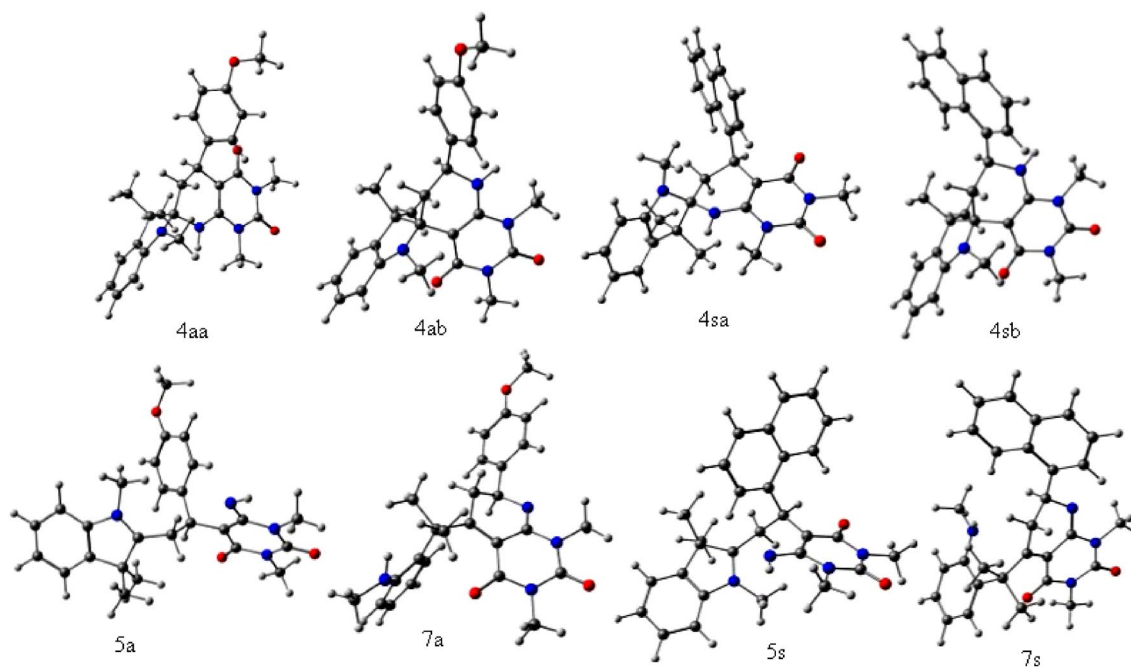


Fig. 4. Optimized ground state structures calculated at the B3LYP/6-31G (d) level.

The electrophilicity index measures how readily a compound can accept electrons, indicating its reactivity toward nucleophiles. Among the compounds, **4 sb** exhibits the highest electrophilicity ($\omega = 2.616$), suggesting it is the most reactive toward nucleophiles. This high reactivity indicates that **4 sb** is more prone to participate in electrophilic reactions. On the other hand, **4aa** shows the lowest electrophilicity ($\omega = 1.593$), meaning it is the least reactive and less likely to accept electrons from nucleophiles. **4 sa** and **4ab** have intermediate values ($\omega = 2.488$ and 1.510 , respectively), indicating moderate reactivity. The observed trend follows the order: **4 sb** > **4 sa** > **4aa** > **4a**.

In summary, **4 sb**, which stands out as the most electrophilic and softest compound, is the most reactive toward nucleophilic attack and **4aa**, which has the highest chemical hardness, is the most kinetically stable and least reactive. On the other hand, **4ab** appears to be the least stable, while **4 sa** shows intermediate behavior. Table 4 presents a comprehensive summary of all descriptors including (chemical hardness η , softness S , chemical potential μ , and electrophilicity index ω) for the studied compounds calculated based on HOMO and LUMO energies.

To further explore the relationship between structure and reactivity, the energy and spatial distribution of frontier molecular orbitals (FMOs) were examined and displayed in Fig. 5. It can be seen that the HOMOs of all close-ring molecules (**4aa**, **4ab**, **4 sa**, and **4 sb**) are almost delocalized throughout the molecule, while the LUMOs are mainly localized on the terminal anisole and naphthalene groups. The delocalization of HOMO might be helpful for intermolecular charge transfer giving rise to higher stability. The broken bond and ring opening alter the conjugation length within the molecule, with longer conjugation typically leading to lower-energy transitions and more delocalization π -electrons, which affect the energy levels.

This spiro indoline-pyrido-pyrimidine ring system has been found to be a dynamic system, due to the fact that, the indoline and pyridine have the basic nitrogen present and this can cause ring opening. The ^1H dynamic

Compounds	η (eV)	S (eV ⁻¹)	μ (eV)	ω (eV)
4aa	2.56	0.39	-2.86	1.59
4ab	2.24	0.45	-2.60	1.51
4 sa	2.15	0.47	-3.27	2.49
4 sb	1.80	0.56	-3.07	2.62

Table 4. Calculated global reactivity descriptors for the studied compounds based on HOMO and LUMO energies.

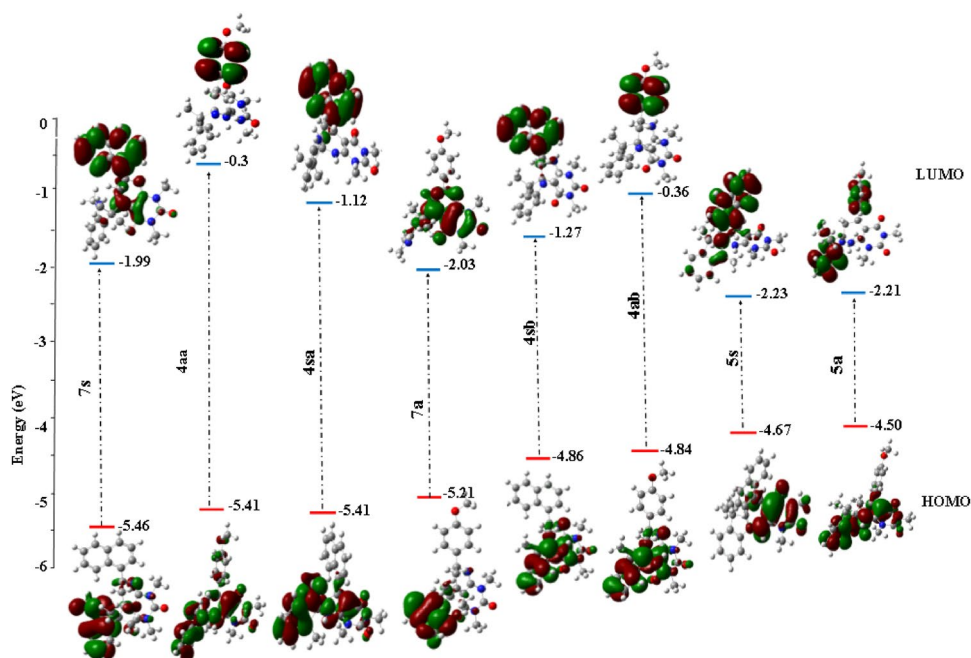


Fig. 5. Illustration of the frontier molecular orbitals (Contour plots) of all structures at the B3LYP/6-31G (d) level.

NMR (DNMR) study was performed at various temperatures in a 500 MHz instrument (Fig. 6). Interestingly, in the spectra of compounds **4 sa** and **4 sb**, it was observed that the major isomer is more stable than minor isomer. Notably, **4 sb** showed a singlet for NH at 4.92 ppm in 300 K, by heating the sample at 315 K hydrogen atom migrates between two nitrogen atoms (Scheme 2), so the corresponding broad singlet was converted into the peak with further coupling. In addition, when the ¹H NMR spectrum run at 340 K, the signal for methine proton (**4 sa**), which has been revealed as a doublet of doublets at 4.82 ppm in 300 K exhibited further broadening. The favored ring opening process for **4 sa** and **4 sb** respectively were proposed from the data of dynamic NMR spectroscopy. From the coalescence of the NH or methine proton and utilizing the expression $k = \pi\Delta\nu/1.42$, the first-order rate constants (k) were computed. Employment of the absolute rate theory with a transmission coefficient for **4 sa** a free energy of activation ($\Delta G^\ddagger$) was calculated as 17.8 kcal mol⁻¹. Alternatively, **4 sb** gives a free energy of activation ($\Delta G^\ddagger$) as 16.1 kcal mol⁻¹ with evaluation of all known sources of errors.

To complement the experimental findings, the reaction Gibbs free energies for the conversion of closed-ring to open-ring structures were evaluated theoretically. The relevant ΔG for converting closed-ring molecules **4aa**, **4ab**, **4 sa**, and **4 sb** into the open-ring molecules **5a**, **7a**, **5 s**, and **7 s** counterparts at $T = 300$ K were calculated to be 23.91, 18.33, 29.25, and 16.95 kcal mol⁻¹, respectively. Although all the conversions are endothermic due to positive ΔG , however, turning the **4 sa** into **5 s** has greater ΔG thus requiring higher temperature to perform. This theoretical result aligns with experimental observations, as stated above.

Altogether, the ring opening temperatures and the theoretical calculations predict that the major isomers **4aa** and **4 sa** are both thermodynamically and kinetically more stable than the minor isomers (**4ab** and **4 sb**).

X-ray crystal analysis

The region and the stereochemical result of the cyclization were furthermore established by X-ray analysis of the crystal structure of the isomer **4aa** (see Supplementary Table S1), whose ORTEP presentations are shown in Fig. 7. The absolute chirality of the stereogenic centers is RR for two central chiral carbons and also for the other conformer is SS. (CCDC:2208236).

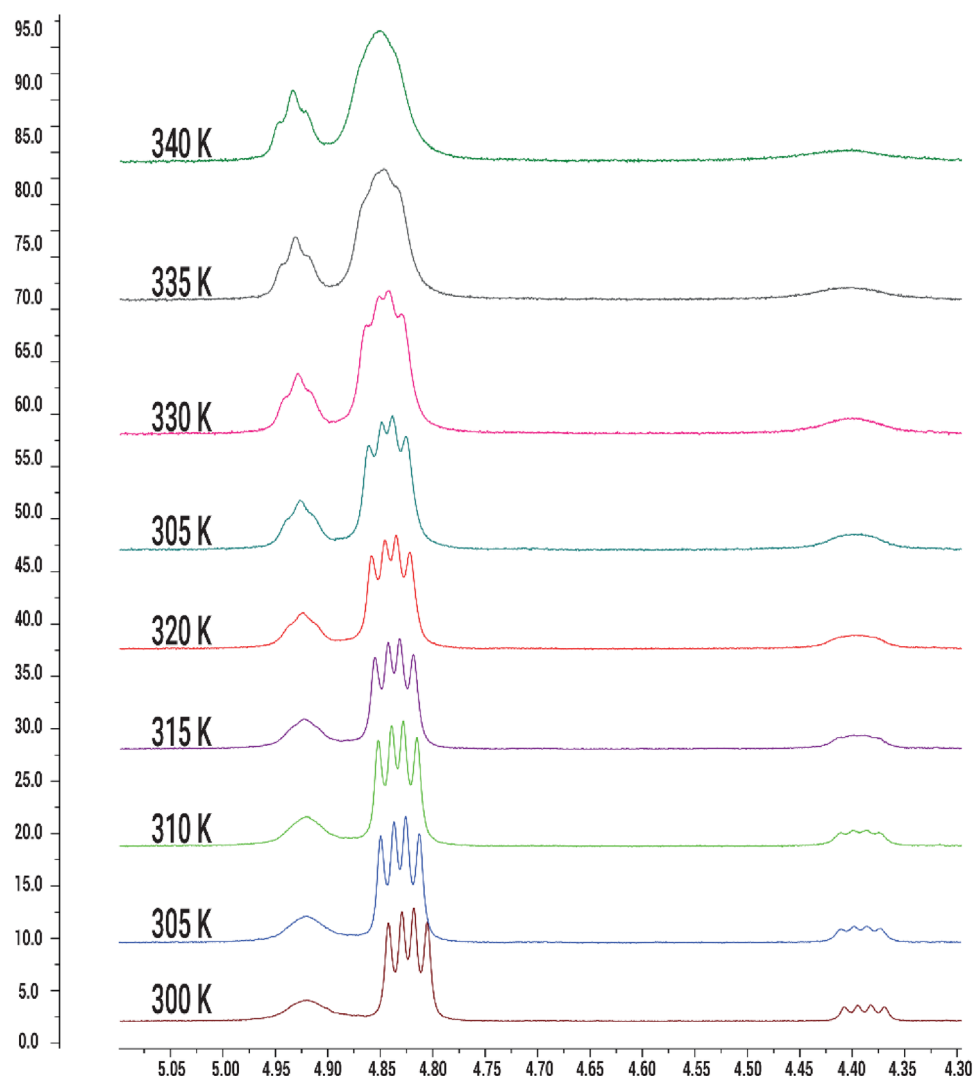


Fig. 6. The ^1H NMR spectra of **4 sa** and **4 sb** in $\text{DMSO}-d_6$ at the different temperature.

Proposed mechanism

Based on the experimental results, two different sequence of events portraying rationally mechanisms for different domino reactions are depicted in Scheme 3. At the initial stage aminouracil **2** reacted with the protonated carbonyl group in two different reversible reactions to afford Knoevenagel product **II** and iminum **II'**, which is the key step in both reaction pathways. **II** and **II'** undergone tandem reaction to obtain different isomeric products. This step is occurred by condensation of Fischer's base (**3**) and **II** or **II'** to form intermediates **III** and **III'**, which underwent intermolecular cyclization and deprotonation to furnish the major and minor products respectively.

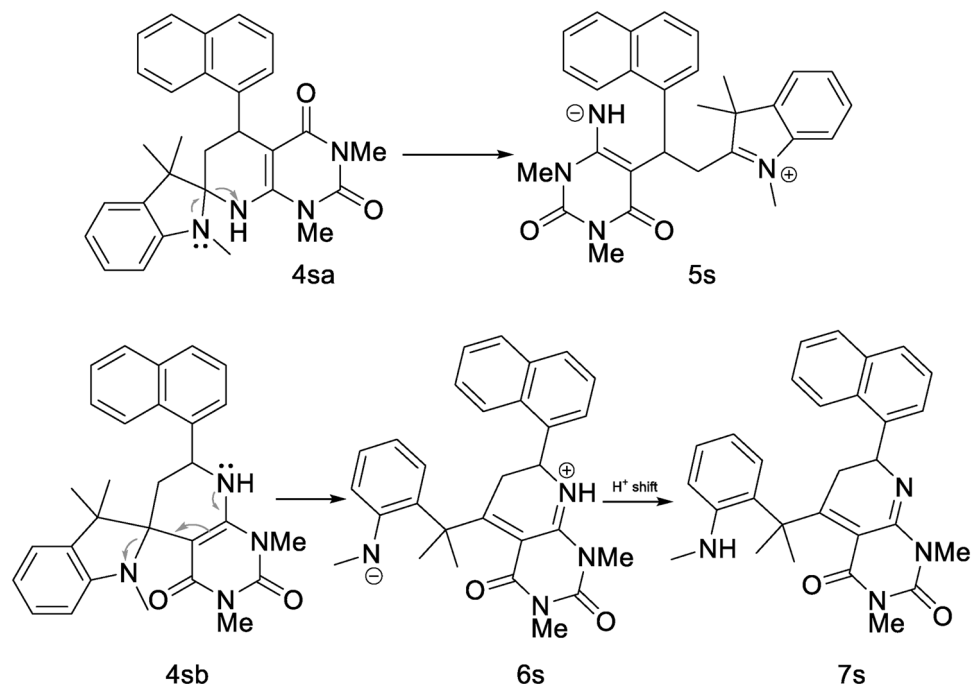
Absorption properties of compound **4a** and **4s**

To better understand the characteristics of the synthesized compounds, both experimental optical absorption spectra and theoretical calculations were employed for a comprehensive analysis.

Experimental study of optical absorption

The optical absorption property of the compounds **4aa**, **4ab**, **4 sa** and **4 sb** were studied by UV-Vis spectroscopy using dichloromethane as solvent. All of the derivatives, in general, displayed electronic transition bands in the UV area. These bands are related to certain types of transitions such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ type, which are characteristic for their aromatic function and heterocycle backbone as explained in the literature⁴⁴.

The UV-Vis spectra of these compounds was exhibited in Fig. 8a,b. As shown in Fig. 8a, two absorption peaks at 258 nm, and 309 nm were observed for the **4aa** and **4ab** compound. The UV-Vis spectra of compound **4 sa** and **4 sb**, shows an absorption peak over 224–335 nm with maximum absorption peaks at 254 nm and 312 nm. The peaks at 309–312 nm were contributed to the absorption of aromatic rings⁴⁵.



Scheme 2. Proposed ring opening of **4 sa** and **4 sb**.

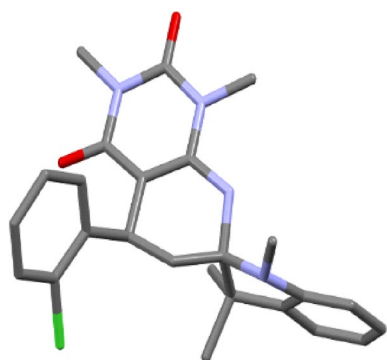
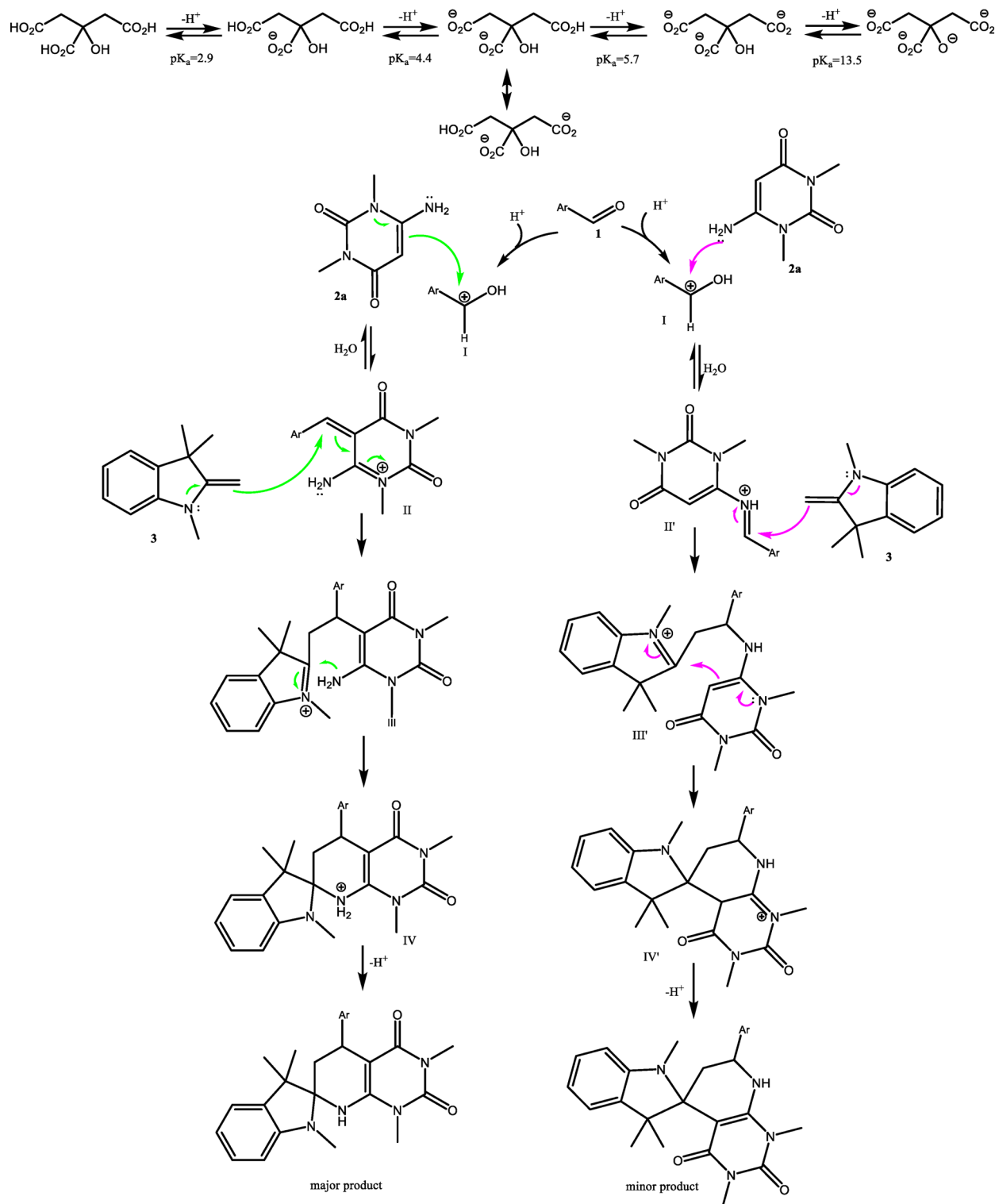


Fig. 7. ORTEP14 representation of the crystal structure of product **4oa**.

Compounds **4a** and **4s** as spectrophotometric probes

Due to the temperature dependent absorption behaviour of compounds **4aa**, **4ab**, **4 sa** and **4 sb**, the potential of these compounds was checked as spectrophotometric temperature sensors. Therefore, the temperature effect was explored on the absorption behaviour of **4aa**, **4ab**, **4 sa** and **4 sb** over 27–65 °C in DMSO (Figs. 9a and 10a). It was found that their absorption was increased directly by raising the temperature. However, when the temperature adjusted to 50 °C and 65 °C for **4aa**, **4ab**, **4 sa** and **4 sb** respectively, this variation is higher than the other temperatures due to the conformational change of the compound (Figs. 9b and 10b) and their conversion to the corresponding open ring structures. At high temperature, a much more intense absorption band was noted, which is a consequence of the variation in dipole moment due to the conversion of ring structures, as confirmed by dynamic NMR data.

The calibration plot for spectrophotometric detection of temperature changes was constructed by plotting A/A_0 versus temperature variations where A_0 is the absorption (550 nm) at physiological temperature (37 °C) for **4aa** and **4ab** and the absorption (417 nm) at 35 °C for **4 sa** and **4 sb** respectively, and A is the absorption at a certain temperature. The results were displayed in Fig. 11a, b. As shown in Fig. 11a, compounds **4aa** and **4ab** exhibited a linear relationship between the absorption ratio at 550 nm and temperature variations over the range of 37°–60 °C, with an R^2 value of 0.9622. A calibration sensitivity of 0.0039 1/°C was determined from this evaluation. Similarly, as depicted in Fig. 11b, compounds **4 sa** and **4 sb** demonstrated a linear relationship between the absorption ratio at 550 nm and temperature variations over the range of 35°–65 °C, achieving an R^2 value of 0.9749. Notably, a calibration sensitivity of 0.0137 1/°C was obtained for this evaluation. Hence, we strongly proposed that the compounds **4aa**, **4ab**, **4 sa** and **4 sb** can be candidate for construction a temperature



Scheme 3. Proposed mechanism for the preparation of pentamethyl-dihydro-1'H-spiro[indoline-2-pyrido[2,3-d]pyrimidine]-2,4'(3'H,6'H)-diones.

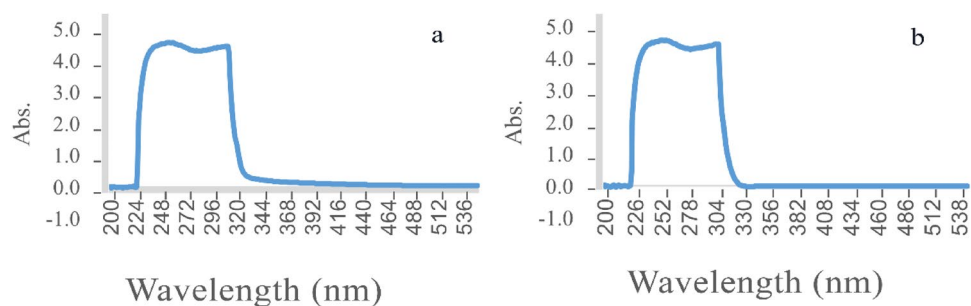


Fig. 8. UV-Vis spectra of (a) **4aa** and **4ab**, and (b) **4sa** and **4sb** in CH_2Cl_2 .

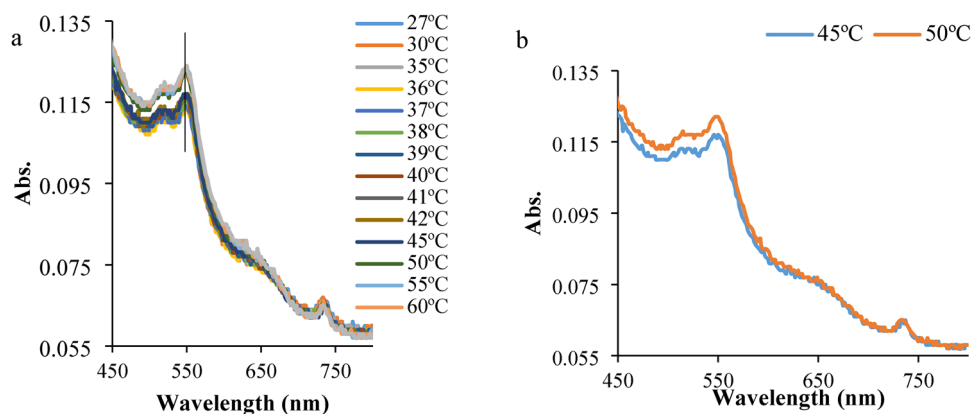


Fig. 9. (a) UV-Vis spectra of **4aa** and **4ab** at different temperatures over 27°–65 °C, and (b) temperature dependent of absorption behaviour of **4aa** and **4ab** at 45° and 50 °C.

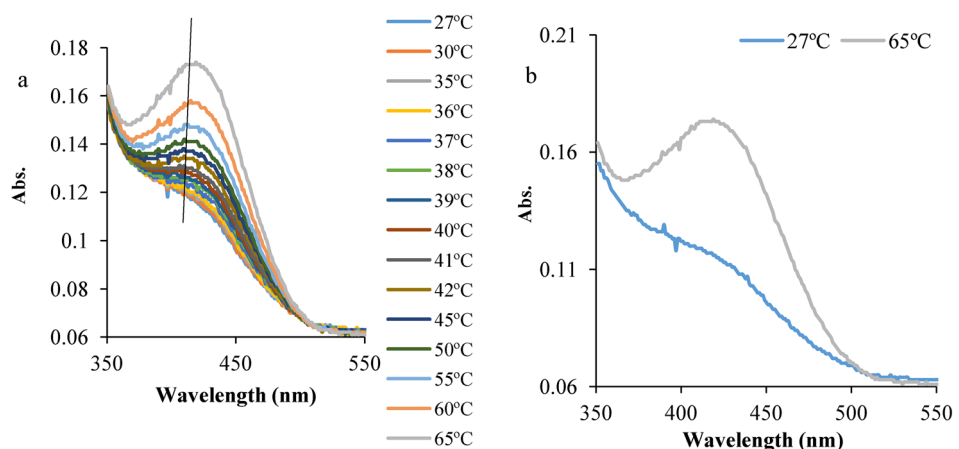


Fig. 10. (a) UV-Vis spectra of **4sa** and **4sb** at different temperatures over 27°–65 °C, and (b) temperature dependent absorption behaviour of **4sa** and **4sb** at 27° and 65 °C.

sensor. It should be mentioned that the compounds **4sa** and **4sb** are more suitable than compounds **4aa** and **4ab** for application as the spectrophotometric analytical probe toward temperature sensing due to its very higher calibration sensitivity (8.2-fold higher) than compounds **4aa** and **4ab** and its wider dynamic range.

Fluorescence (FL) behavior

Regarding the FL behaviour of compounds **4aa** and **4ab**, the fluorescence spectrum was recorded over the range of 250–700 nm with a maximum excitation wavelength of 330 nm. Figure 12a depicts the both excitation and emission spectra of compounds **4aa** and **4ab**. These compounds exhibit an emission spectrum with a maximum emission wavelength at 500 nm. It should be noted that the FL spectra of compounds **4aa** and **4ab** under visible

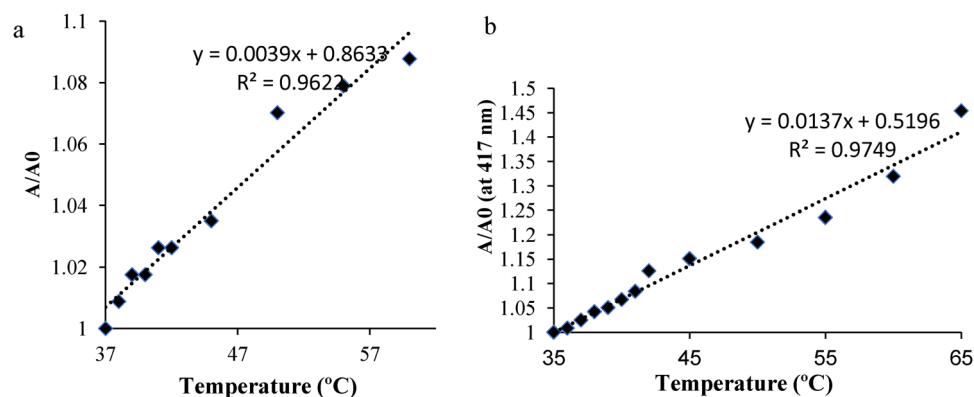


Fig. 11. Calibration plot for spectrophotometric temperature sensing of (a) **4aa** and **4ab**, and (b) **4sa** and **4sb**.

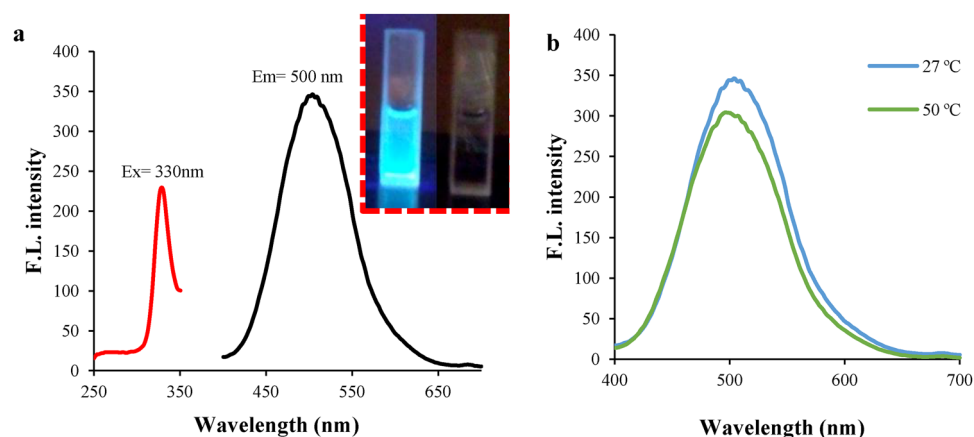


Fig. 12. (a) Emission and excitation spectra and (b) temperature dependent of FL behaviour of **4aa** and **4ab**.

light and UV excitation (365 nm) are shown in the inset of Fig. 12a. As depicted, compounds **4aa** and **4ab** emit a light blue cyan color upon excitation at 365 nm, which contributes to their high fluorescence intensity at 500 nm. It was also found that the fluorescence intensity was quenched by raising the temperature from 27 °C to 50 °C (Fig. 12b). Additionally, as the temperature increased, a blue-shifted emission was observed for compounds **4aa** and **4ab**, with electron withdrawal from the spiro derivatives⁴⁶.

Compound 4aa and 4ab as a fluorescence analytical probe for temperature sensing

Due to the temperature-dependent fluorescence properties of compounds **4aa** and **4ab**, their potential application as fluorescence analytical probes for temperature sensing was evaluated. To evaluate this, the influence of temperature on the fluorescence features of compounds **4aa** and **4ab** was investigated across a temperature range of 27°–60 °C (Fig. 13a). It was observed that the fluorescence intensity of the probes was quenched with increasing temperature. However, at 50 °C, the fluorescence intensity showed a more significant decrease compared to other temperatures, likely due to the conformational change of the compounds and their conversion to the corresponding open-ring structure. The calibration plot for spectrofluorometric detection of temperature changes was constructed by plotting fluorescence intensity versus temperature variations. As illustrated in Fig. 13b, a strong linear correlation ($R^2 = 0.997$) was noted between the fluorescence intensity at 500 nm and the temperature variations within the 27°–60 °C range. Furthermore, a calibration sensitivity of 1.7576 1/°C was obtained during this evaluation. Thus, we strongly propose that compounds **4aa** and **4ab** can be employed for constructing a fluorescence-based temperature sensor, following optimization of the sensor and its analytical validation. The observed decline in fluorescence intensity with raising temperature is likely due to enhanced internal conversion, where electronic energy is transferred to vibrational modes, a process that reduces emission efficiency. To further investigate this phenomenon, it is essential to explore various energy dissipation methods that do not generate light, such as transitions from higher to lower energy states, electron transfer from the reagent to solvent molecules, proton relocation, or electron transfer to a quenching group. These processes can occur if the excited state shifts to a nearby non-radiative state that does not emit light⁴⁷. Normally, the solute molecule's lowest excited state is the (n^*) state, but the presence of substituents can cause a reordering of states, making the ($*$) state the lowest energy state.

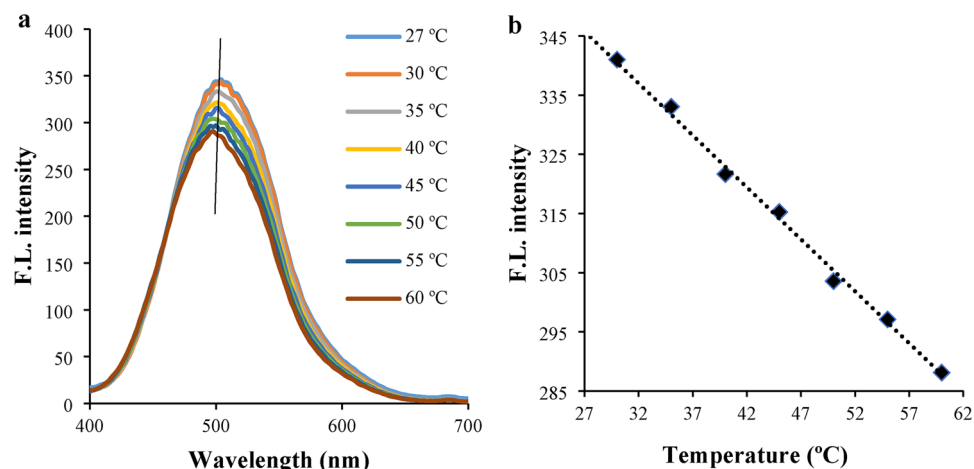


Fig. 13. (a) FL spectra of **4aa** and **4ab** at different temperatures over 27°–60 °C, and (b) Calibration plot for spectrofluorometric temperature sensing.

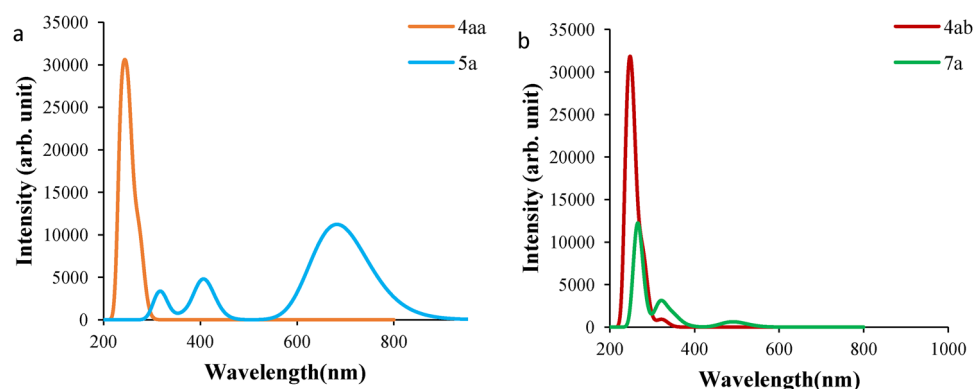


Fig. 14. (a) Calculated absorption spectra of **4aa** and **5a**, and (b) **4ab** and **7a** compounds at the B3LYP/6-31G (d) level.

Theoretical study of optical absorption

To achieve a comprehensive understanding of the electronic transitions in the synthesized compounds, the UV-Vis absorption spectra were theoretically modeled based on their optimized geometries in the ground state. The simulations were performed using time-dependent density functional theory at B3LYP/6-31G(d) level, incorporating dichloromethane as the solvent to account for environmental effects. The resulting absorption spectra are presented in Figs. 14 and 15, with comprehensive data, including the wavelength of maximum absorbance (λ_{max}) and the primary orbital contributions to the transition states, summarized in Table 3.

For the close-ring isomers **4aa**, **4ab**, **4 sa**, and **4 sb**, the maximum absorption wavelengths were observed at 251 nm, 238 nm, 288 nm, and 286 nm, respectively, falling within the UV region. Following the ring-opening conversions, the corresponding open-ring products **5a**, **7a**, **5 s**, and **7 s** displayed a maximum absorption at 682, 268, 652, and 288 nm, respectively. This significant bathochromic shift observed in the open-ring isomers, particularly for **5a** and **5 s**, reflects the extended conjugation and increased delocalization of π -electrons in these structures. In compound **5a**, two additional absorption peaks emerged at 320 nm and 695 nm, attributed to the formation of aminophenol or pyrimidine amide and the light-induced opening of the pyrrole or tetrahydropyridine rings, leading to the formation of opened ring isomers, respectively⁴². Notably, in the case of **7a** and **7 s**, the major electronic transitions H-1→L + 1 (95%) for **7a** and H→L + 2 (58%) for **7 s** indicate a shift to higher energy orbitals, which could contribute to the absorption of higher-energy photons and result in a near blue shift in absorption towards shorter wavelengths.

The numerical results for the electronic transitions in Table 3 revealed that the HOMO-to-LUMO transitions in **5a** and **5 s** occurred at lower excitation energies compared to other transitions in the system. This efficiency in electronic excitation is representative of enhanced charge transfer characteristics, aligning with their extended conjugation.

As a result, the synthesized compounds **4aa**, **4ab**, **4 sa** and **4 sb** demonstrate promising applications as spectrophotometric and fluorescence-based temperature sensors due to their temperature-dependent optical properties. Spectrophotometric evaluation revealed that the both compounds exhibit increased absorption with

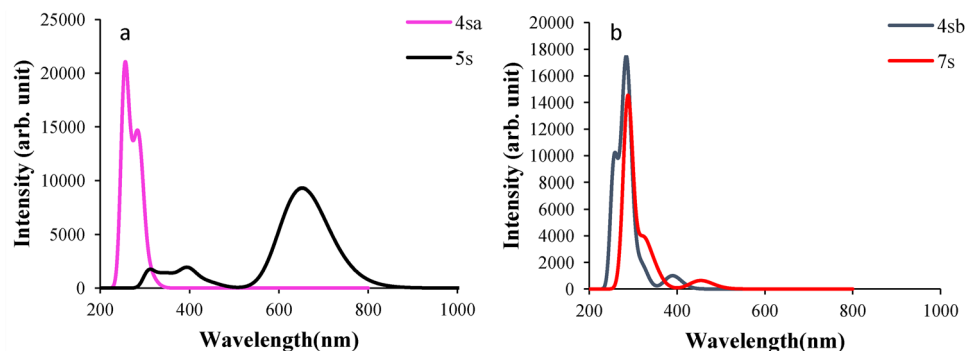


Fig. 15. The calculated absorption spectra of (a) the **4 sa** and **5 s**, and (b) **4 sb** and **7 s** at the B3LYP/6-31G (d) level in CH_2Cl_2 .

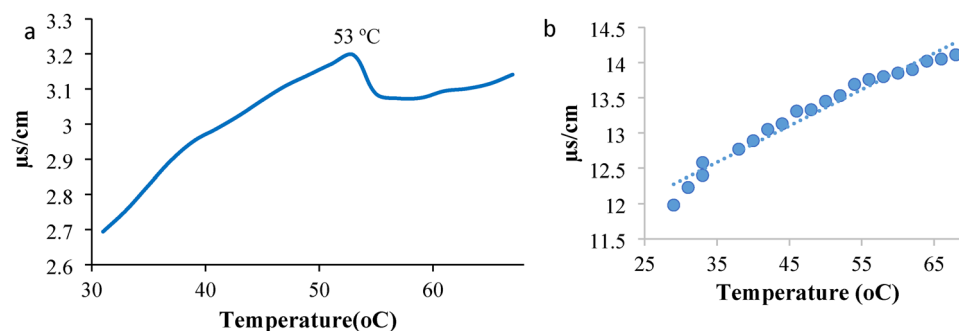


Fig. 16. (a) The plot of conductivity versus temperature for **4aa** and **4ab**, and (b) the calibration plot for **4 sa** and **4 sb** as electrochemical probe for temperature.

rising temperature, with significant conformational changes and open-ring structure transitions observed at higher temperatures (50 °C for **4aa** and **4ab** and 65 °C for **4 sa** and **4 sb**). Theoretical investigations into the optical absorption behaviour of these compounds confirm the experimental results.

Temperature-dependent conductivity

Due to the fact that rigid compounds show lower conductivity than more flexible ones, the conductivity of compounds **4aa**, **4ab**, **4 sa**, and **4 sb** was examined to highlight the temperature-dependent behaviour of these compounds, which can result from their conformational changes with temperature. The plots of conductivity versus temperature variations for these compounds are presented in Fig. 16a and b. As demonstrated, the conductivity of compounds **4aa**, **4ab**, **4 sa**, and **4 sb** increased with rising temperature, reaching a maximum at 53 °C. This increase is attributed to the conversion of compounds **4aa** and **4ab** to their open-ring structures, consistent with the previously mentioned results. The plot of conductivity versus temperature for compounds **4 sa** and **4 sb**, presented in Fig. 16b, shows that, unlike compounds **4aa** and **4ab**, the conductivity of compounds **4 sa** and **4 sb** increased linearly with temperature, with an R^2 of 0.9651 and a calibration sensitivity of 0.0515 1/°C. It is noteworthy that a linear range from 29 °C to 68 °C was observed for temperature sensing. Therefore, we strongly recommend that compounds **4aa**, **4ab**, **4 sa**, and **4 sb** can be employed in the construction of a temperature sensor, following optimization and analytical validation.

Moreover, the conductivity of compounds **4aa**, **4ab**, **4 sa**, and **4 sb** was measured upon excitation under UV light at 254 nm and 366 nm for different time intervals ranging from 0 to 15 min. As shown in Fig. 17a,b, the conductivity of compounds **4aa** and **4ab** increased with longer incubation times under UV light, suggesting that conformational changes occurred in the structures of these compounds when exposed to UV light. However, the increase in conductivity was more pronounced when excited at 254 nm compared to 366 nm. This behaviour is attributed to the conversion of compounds **4aa** and **4ab** to their open-ring structures under high-energy UV light, consistent with their fluorescence behaviour. In contrast, the conductivity of compounds **4 sa** and **4 sb** decreased with increasing incubation time under UV light (Fig. 17b), indicating that conformational changes occurred in their structures as well. The decrease in conductivity was more significant when excited at 254 nm compared to 366 nm.

Voltammetric characteristics

The electrochemical behavior of compounds **4aa**, **4ab**, **4 sa**, and **4 sb** was investigated *via* voltammetric analysis using square wave voltammetry (SWV), which is recognized as one of the most sensitive and accurate electrochemical methods. The voltammograms were taken in a potential range of −0.5 to 1.0 V, and each

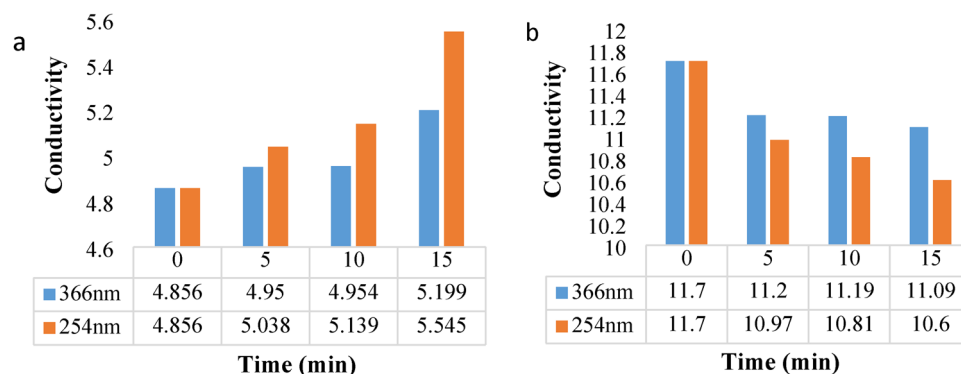


Fig. 17. Conductivity of (a) **4aa** and **4ab** and (b) **4sa** and **4sb** upon their excitation under UV light at 254 and 366 nm for different time intervals.

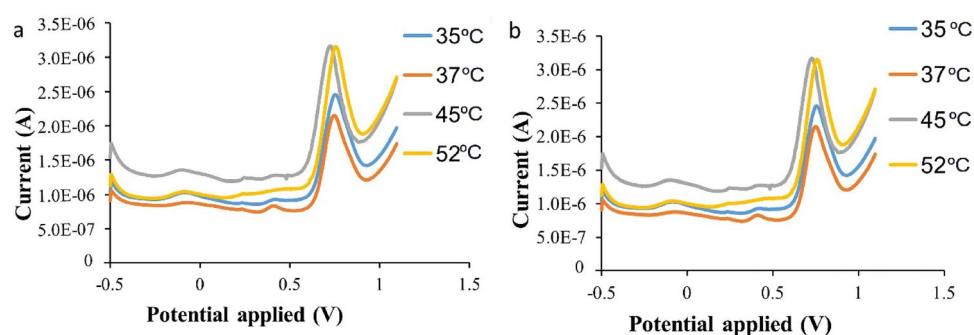


Fig. 18. SWV voltammograms of (a) **4aa** and **4ab**, and (b) **4sa** and **4sb** over 35°–52° C.

measurement was repeated three times to ensure the most accurate results. Additionally, the effect of temperature on the peak current was examined over the temperature ranges of 35°–52 °C and 19°–55 °C for compounds **4aa**, **4ab**, **4sa**, and **4sb**, respectively. The results are presented in Fig. 18a,b. As shown, compounds **4aa** and **4ab** exhibit an intense peak at approximately 0.75 V, indicating that these compounds participate in the redox process with good electroactivity. With respect to the temperature effect, the results indicate that the peak current intensity increased with rising temperature, while the voltage shift (0.70 V) remained negligible. This increase in peak current is likely attributed to the predominance of the open-ring structure at elevated temperatures, which more readily participates in the redox reaction compared to the closed-ring form.

The electrochemical behaviour of compounds **4aa**, **4ab**, **4sa**, and **4sb** was further examined using square wave voltammetry, as mentioned earlier. The voltammograms were conducted in a potential range from –0.5 to 1.0 V, with triplicate runs performed to ensure reliable data. The impact of temperature on the peak current was analysed across the 35°–52 °C range. As presented in Fig. 18a,b, compounds **4aa**, **4ab**, **4sa**, and **4sb** exhibited distinct peaks near 0.75 V and 0.76 V, respectively, underscoring their notable electrochemical activity. These prominent peaks reflect the compounds' capacity for effective electron transfer under the applied conditions. Temperature-induced changes showed that the peak current increased with temperature, with only a slight shift in voltage (0.70 V), which was not significant. This increase in peak current is likely attributed to the conversion of the compounds to their open-ring structures at higher temperatures, enabling easier participation in the redox reaction. The initial electron transfer that occurs at lower temperatures is related to $n \rightarrow \pi^*$ transitions, which require less energy. At higher temperatures, $\pi \rightarrow \pi^*$ transitions occur, requiring more energy to conduct electricity⁴⁸. The conductivity of a substance is determined by the mobility of its π -electrons. Some electrons remain localized and require energy to move, with π -electrons transferring to nearby molecules through a tunnelling effect. As temperature increases, the bonds weaken, allowing the conductivity to increase.

Conclusion

In the present study, a novel series of spiro[indoline-pyrido-pyrimidine] derivatives were successfully prepared efficiently with excellent regioselectivity. This developed methodology provided access to spiroheterocyclic compounds exhibiting photochromic and thermochromic properties, utilizing readily available substrates under mild reaction conditions with excellent yields. This approach represents a significant advancement in synthetic chemistry by offering a reliable and efficient regioselective route to these complex molecules. Employing citric acid as a bio-organic catalyst in a green, multi-component reaction underscores the environmentally friendly and sustainable nature of the synthesis, in agreement to the green chemistry fundamentals. The structural elucidation of the major isomer was achieved through single-crystal X-ray diffraction, complemented by

spectroscopic techniques for characterizing both isomers. Furthermore, theoretical studies, including Density Functional Theory (DFT) and TD-DFT calculations, supported the experimental findings by validating the geometric and energetic properties of the synthesized compounds.

The absorption properties of compounds **4aa**, **4ab**, **4sa** and **4sb** were thoroughly characterized using UV-Vis spectroscopy, revealing distinct electronic transition bands. Compound **4aa** and **4ab** displayed absorption peaks at 258 nm and 309 nm, while compound **4sa** and **4sb** exhibited broader absorption, peaking at 254 nm and 312 nm. Temperature-dependent spectrophotometric studies demonstrated their potential as temperature sensors, with calibration sensitivities of 0.0039 1/°C for **4aa** and **4ab** and 0.0137 1/°C for **4sa** and **4sb**. Furthermore, square wave voltammetry confirmed their electrochemical activity, highlighting their ability to engage in redox processes. Compound **4aa** and **4ab** exhibited fluorescence quenching with increasing temperature, further supporting its applicability as a fluorescence-based temperature sensor. Compound **4sa** and **4sb**, with its superior sensitivity and broader dynamic range, emerged as a particularly promising candidate for advanced temperature sensing applications.

The stability and optical properties arising from the ring-opening mechanism, validated through both experimental and computational studies, demonstrate the potential of these compounds for advanced optical and temperature sensing technologies. Compared to classical spiropyran-based systems, which undergo reversible transformations between hydrophobic (spiropyran) and hydrophilic (merocyanine) forms upon UV or thermal stimuli, our synthesized spiro[indoline-pyrido-pyrimidine] derivatives display broader absorption ranges and higher thermal sensitivities. This highlights their enhanced responsiveness and superior potential for integration into cutting-edge optoelectronic systems, making them promising alternatives to the previously reported photo- and thermochromic materials, which have been mentioned in the introduction part of this study.

Data availability

Data is provided within the manuscript or supplementary information files.

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M.J.: Data curation, Formal analysis, Investigation, Methodology; Software: Validation: Visualization: Writing – original draft; A.R.S.: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing; F.R.: Data curation; Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft; A.M.: Formal analysis, Methodology, Software, Validation, Visualization; M.M.G.: Formal analysis; G.B.: Formal analysis.

Declarations

Competing interests

The authors declare no competing interests.

Ethical approval

This declaration is “not applicable”.

Additional information

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