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Ultrasound-assisted rapid and efficient one-pot synthesis of furanyl spirooxindolo and spiroquinoxalinopyrrolizidines by 1,3-dipolar cycloaddition: a green protocol

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Abstract Efficient synthesis of novel spirooxindolo and spiroquinoxalinopyrrolizidine derivatives was expediently accomplished with regioselectivity via one-pot, three-component 1,3-dipolar cycloaddition using ultrasonication. Chalcones derived from both heteroaryl methyl ketones and furfural were used as dipolarophiles in these reactions. The synthesized compounds were analyzed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR), mass spectrometry, and elemental (CHN) analysis. Single-crystal X-ray diffraction studies of one of the compounds (**11d**) proved the structure and regiochemistry of the cycloaddition. The ultrasound methodology is clearly advantageous, and the desired products were obtained in moderate to good yield in shorter reaction time compared with conventional heating and fusion methods.

Keywords Ultrasonication · 1,3-Dipolar cycloaddition · Azomethine ylide · Spirooxindolopyrrolizidines · Spiroquinoxalinopyrrolizidines · Dipolarophile

Introduction

Ultrasonication is an important technique that has been widely used recently in organic synthesis, having an immense impact on organic and parallel synthesis. This is due to the special sonochemical effects in liquids, which cause chemical reactions in either homo- or heterogeneous systems. As ultrasonic waves travel through a liquid, they form microbubbles or cavities which cause chemical reactions. These

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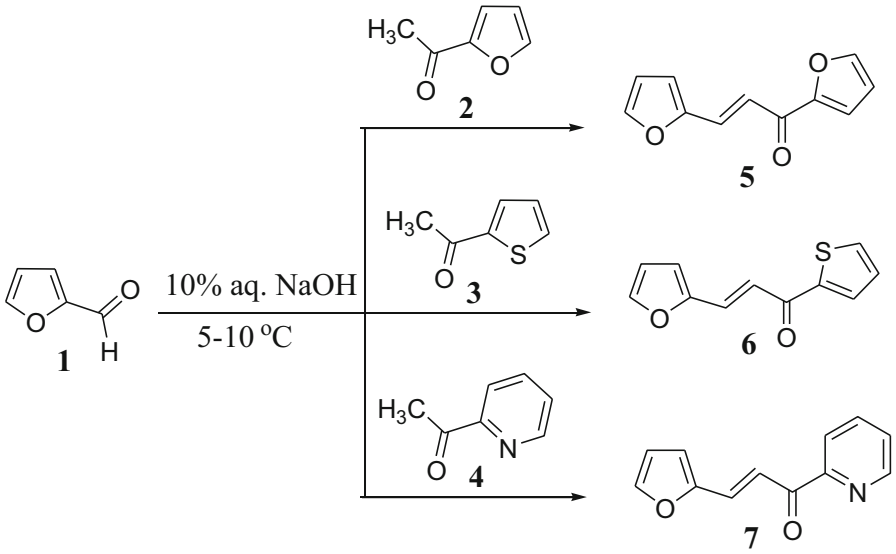
cavities produce high pressures and temperatures in their surroundings. Ultrasonic irradiation is very effective for a large number of organic reactions to obtain higher yield or reduce the reaction time, enabling use of milder conditions relative to traditional thermal heating [1]. Multicomponent reactions (MCRs) are one of the most important strategies for synthesis of heterocyclic compounds through formation of carbon–carbon and carbon–heteroatom bonds along with stereogenic carbon centers in one pot [2–4]. MCRs produce complex structures without isolation of reaction intermediates. Some of the advantages of MCRs are high reaction rate, high degree of atom economy, etc. [5, 6].

Over the last few decades, 1,3-dipolar cycloaddition reactions have been extensively studied due to their selectivity, which can be influenced by steric and electronic factors. The regio- and stereochemistry of such reactions can be controlled through use of a catalyst or suitable dipole or dipolarophile [7–11]. Several spiro compounds have been synthesized via multicomponent 1,3-dipolar cycloaddition under ultrasound irradiation [12–19]. Pyrrolizidines are important core structures of many natural products such as alkaloids, and also occur in synthetic compounds that exhibit a variety of remarkable bioactivities. In particular, multifunctional polycyclic spiropyrrolizidines exhibit versatile bioactivities, such as antimycobacterial, antitumor, antimicrobial, antibacterial, antifungal, and antiviral properties [20, 21]. Spiropyrrolizidines can be synthesized efficiently from azomethine ylide and electron-deficient alkenes and alkynes via 1,3-dipolar cycloaddition reaction [22–24]. Literature survey reveals that there are reports on regio- and stereoselective synthesis of spiropyrrolizidines using classical heating methods via 1,3-dipolar cycloaddition [25–32].

Among various methods, one-pot, three-component, 1,3-dipolar cycloaddition reaction of azomethine ylide with electron-deficient olefin is a convenient route for regio- and stereoselective synthesis of various spiropyrrolizidine derivatives [33, 34]. However, fewer reports are found on synthesis of spiropyrrolizidines using ultrasonication [35–38], and no reports on chalcones derived from heteroaryl methyl ketone and furfural as dipolarophiles. Hence, our aim in this work was to synthesize novel spirooxindolo and spiroquinoxalinopyrrolizidines with dipolarophiles having both heterocyclic rings using MCRs via 1,3-dipolar cycloaddition under environmentally benign conditions, i.e., using ultrasonication (method A). However, these reactions were also carried out using conventional heating (method B) and fusion (method C) methods.

Results and discussion

In the present study, three different dipolarophiles were synthesized via Claisen–Schmidt reaction from furfural (Scheme 1). Furfural (**1**, 1 mmol) reacts with 1 mmol of 2-acetylfuran (**2**)/2-acetylthiophene (**3**)/2-acetylpyridine (**4**) in presence of 10 % aq. NaOH solution at 5–10 °C to form corresponding dipolarophiles [39]. These three dipolarophiles, i.e., 1,3-di(furan-2-yl)prop-2-en-1-one (**5**), 3-(furan-2-yl)-1-(thiophen-2-yl)prop-2-en-1-one (**6**), and 3-(furan-2-yl)-1-(pyridin-2-yl)prop-2-en-1-one (**7**), were used to synthesize the novel spiropyrrolizidines.



Scheme 1 Synthesis of various dipolarophiles

Initially, during the synthesis of one of the target molecules (**10a**) under sonication, reflux, and fusion methods, higher yield and shorter reaction time were observed under sonication (method A). Hence, the reaction conditions were optimized using various solvents with the sonication method to synthesize **10a** (Table 1). Among all the solvents, use of methanol as solvent was prominent under these conditions.

In method A, i.e., ultrasound irradiation, the starting materials were dissolved in methanol to prepare a homogeneous reaction medium. One-pot, three-component, 1,3-dipolar cycloaddition reaction of azomethine ylide generated in situ by reaction of isatin derivatives **8a–d** and L-proline (**9**) with dipolarophiles (**5**, **6**, and **7**) in methanol at room temperature yielded spirooxindolopyrrolizidine derivatives within short time (Table 2). The precipitated compounds were filtered and washed with

Table 1 Optimization of reaction conditions[a]

Entry	Solvent	Temp (°C)	Yield (%)	Time (min)
1	Methanol	RT	80	1
2	Ethanol	RT	79	1
3	Acetonitrile	RT	64	1
4	Tetrahydrofuran	RT	64	1
5	1,4-Dioxane	RT	73	1
6	Water:methanol	RT	69	1
7	Water	RT	No reaction	1

[a] The reaction was carried out with isatin (1.0 mmol), L-proline (1.0 mmol), and chalcone **5** (1.0 mmol) at room temperature in solvent (5 mL) under ultrasonic power of 250 W, irradiation frequency of 25 kHz. Isolated yield based on isatin

Table 2 Yield and time required for synthesis of spirooxindolopyrrolizidines **10a–d**, **11a–d**, and **12a**, **b**

S. no	Compound	Yield (%) and time					
		Method A	Time (s)	Method B	Time (h)	Method C	Time (min*)
1	**10a**	80	60	73	1	60	2
2	**10b**	82	50	74	2	61	2
3	**10c**	84	50	76	2	59	2
4	**10d**	78	73	71	3	57	2.5
5	**11a**	80	5	71	8	60	2
6	**11b**	82	7	72	6	58	2
7	**11c**	82	7	73	6	58	2
8	**11d**	77	15	69	8	56	2
9	**12a**	69	45	58	3	48	2
10	**12b**	64	45	52	4	45	2

Method A ultrasound irradiation in methanol at room temperature

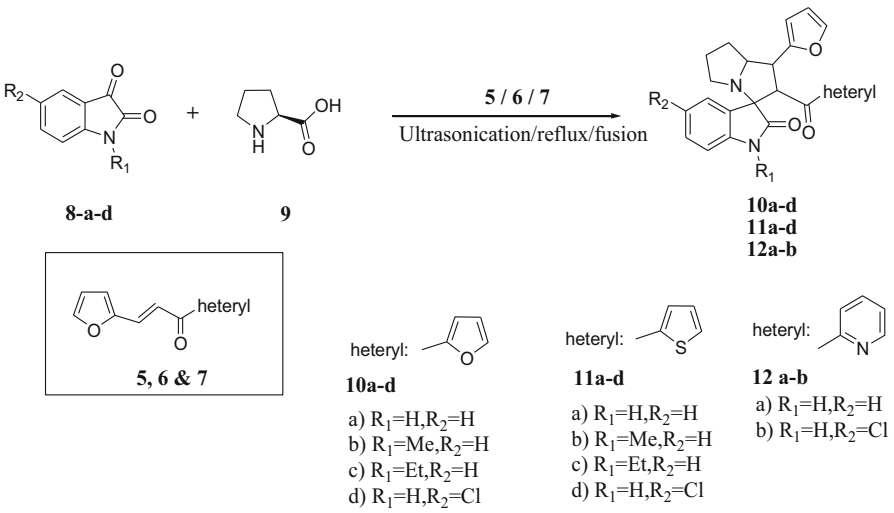
Method B conventional heating or refluxing in methanol (80–85 °C)

Method C fusion method

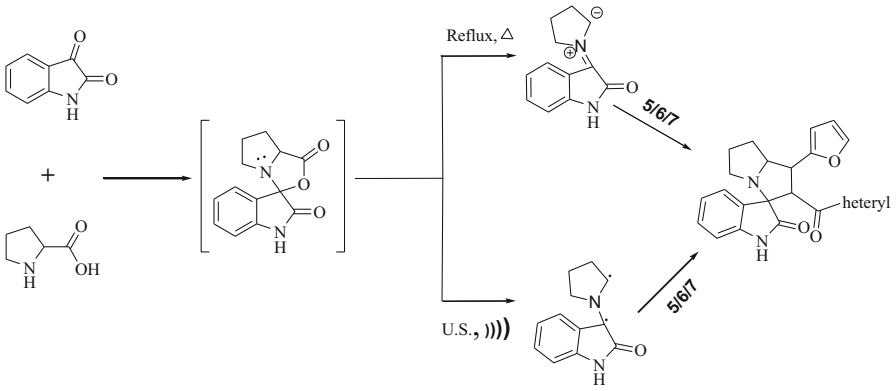
* Approximate time

methanol. Pure compounds were obtained without column chromatography (Scheme 2).

The same reactions were carried out using reflux (method B) and fusion (method C) methods. When using method B, i.e., under reflux conditions, among various solvents such as 1,4-dioxane, toluene, ethanol, acetonitrile, and methanol, it was observed that the yield was moderately enhanced for methanol. A significant temperature effect on the reaction in methanol was observed; at the particular reflux



Scheme 2 Synthesis of various spirooxindolopyrrolizidines

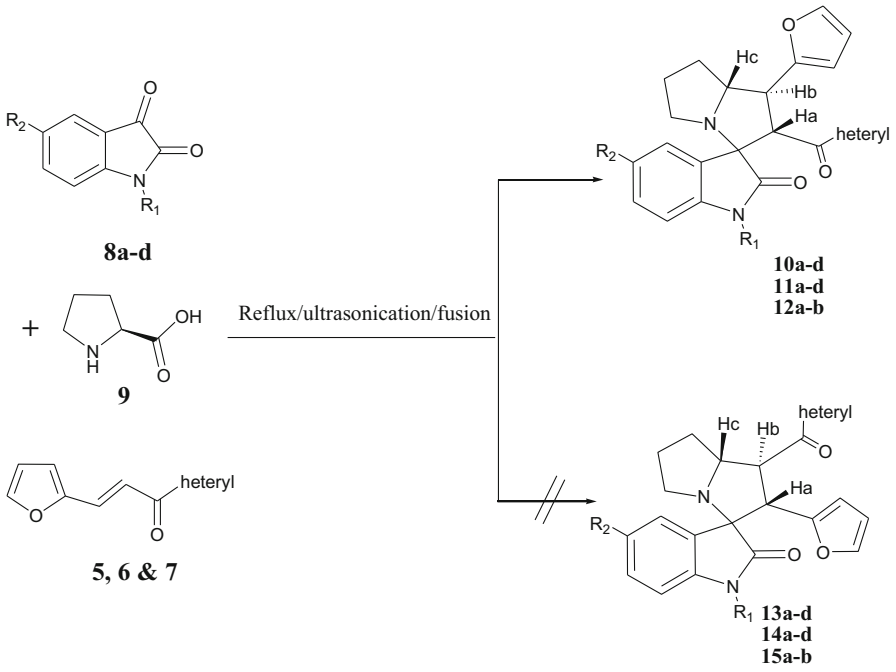


Scheme 3 Reaction pathway for 1,3-dipolar cycloaddition reaction

temperature, the reaction time was longer. This led us to elevate the temperature to 80–85 °C for methanol to obtain spirooxindolopyrrolizidines in 1–8 h. The crude products were purified by column chromatography. Further, method C, i.e., fusion was also applied as a benign method without solvent. The components were fused without solvent, and the products were formed in 2–3 min. Therefore, from the above results, it was found that higher yield and shorter reaction time were observed when using the sonication method. A plausible reaction pathway [40] for the above 1,3-dipolar cycloaddition reaction (under reflux and sonication conditions) is shown in Scheme 3. However, when these reactions were carried out at room temperature, no target compounds were obtained. Hence, sonication was found to be a better method for synthesis of the target molecules.

Spectral analysis

The synthesized compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectral analyses. The IR spectrum of **10a** showed peaks at 1731 and 1677 cm^{-1} due to oxindole ring carbonyl and heteroyl carbonyl group, respectively. In the ^{1}H NMR spectrum of **10a**, proton H_a appeared as a doublet at δ 4.72 (J = 11.6 Hz) and H_b appeared as a triplet at δ 4.04 (J = 10.0 Hz), clearly showing the regiochemistry of the cycloaddition reaction. If the other possible regioisomer **13a** had been formed (Scheme 4), the ^{1}H NMR spectrum would have shown a triplet for proton H_b at higher δ value (i.e., approximately δ 4.7). Literature [23, 32, 33] shows that the –CH– proton of –CH–CO–Ar/heteryl group shows a δ value ranging from ~4.7 to ~5.8. Therefore, the doublet for proton H_a appearing at δ 4.72 for **10a** indicates that the regioisomers formed are **10a–d**, **11a–d**, and **12a**, **b**. However, proton H_c appeared as a multiplet at δ 4.29–4.23, which is more deshielded than proton H_b. This is due to strong intramolecular C–H···O hydrogen bonding between proton H_c and furan ring O-atom. Later this was confirmed by single-crystal X-ray diffraction analysis. N–H protons of oxindole appeared as a singlet at δ 7.84.

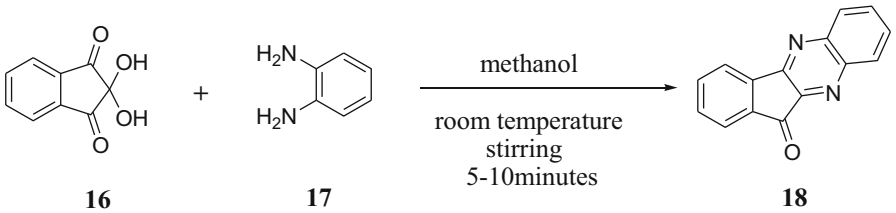


Scheme 4 Possible regioisomers during the synthesis of spirooxindolopyrrolizidines

The signal in the ^{13}C NMR spectrum of **10a** at δ 68.80 corresponds to the spiro carbon. The oxindole ring carbonyl and the heteroyl carbonyl resonated at δ 183.77 and 207.08, respectively. Moreover, the presence of a molecular ion peak at 389.10 (M^+) in the mass spectrum of **10a** confirmed the structure of the cycloadduct. The regiochemistry of the cycloaddition reaction and configurations at chiral centers of compound **11d** were determined unambiguously by single-crystal X-ray diffraction analysis.

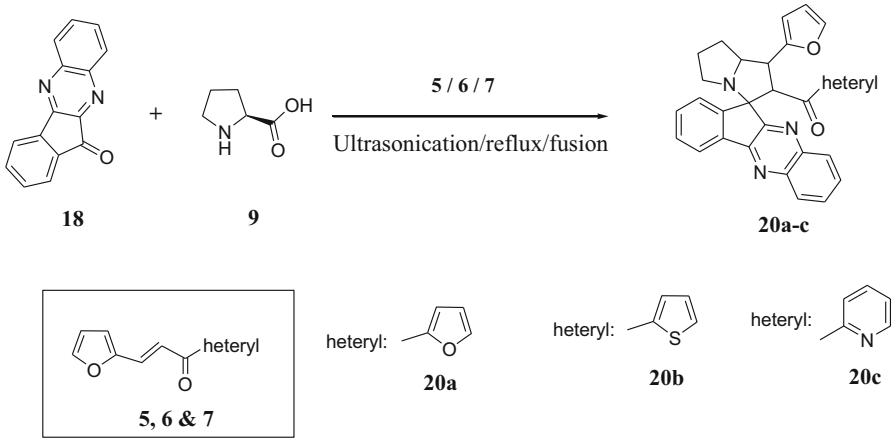
The above results encouraged us to extend this methodology to azomethine ylides generated from 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**18**) and L-proline (**9**) to synthesize spiroquinoxalinopyrrolizidines. Compounds **16** and **17** were stirred in methanol for 5–10 min to yield a yellow solid, 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**18**) (Scheme 5). To this compound, L-proline (**9**) and the three dipolarophiles (**5**, **6** or **7**) were added without decanting the methanol. The target molecules (**20a**–**c**) were synthesized by the above three methods (A, B, and C), as shown in Scheme 6. However, these experiments also proved that ultrasonication was a better method, as the yield improved from moderate to good. The reaction times and yields of the corresponding products formed using these three methods are presented in Table 3.

In the ^1H NMR spectrum of **20a**, the proton H_a appeared as a doublet at δ 4.87 ($J = 11.2$ Hz) and H_b appeared as a triplet at δ 4.33 ($J = 11.6$ Hz), which indicates the regiochemistry of the cycloaddition reaction. Similar to the molecule **10a**, if the other regioisomer **21a** had been formed, then the ^1H NMR spectrum would have shown a triplet for proton H_b at higher δ value (i.e., approximately δ 4.7)



16 **17** **18**

Scheme 5 Synthesis of 11*H*-indeno[1,2-*b*]quinoxalin-11-one



18 **9** **20a-c**

5, 6 & 7 **20a** **20b** **20c**

Scheme 6 Synthesis of spiroquinoxalinopyrrolizidines

Table 3 Yields and times required for synthesis of spiroquinoxalinopyrrolizidines **20a–c**

S. no.	Compound	Yield (%) and time					
		Method A	Time (min)	Method B	Time (h)	Method C	Time (min*)
1	**20a**	73	2	71	6	64	4
2	**20b**	78	3	68	6	59	4
3	**20c**	69	3	62	4	52	3

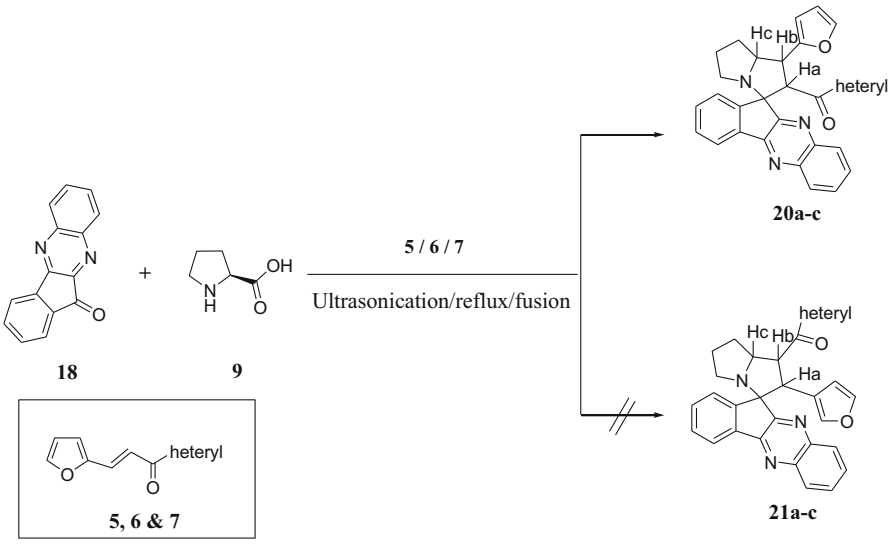
Method A ultrasound irradiation in methanol at room temperature

Method B conventional heating or refluxing in methanol (80–85 °C)

Method C fusion method

* Approximate time

(Scheme 7). The explanation for the formation of the above regioisomers (**10a–d**, **11a–d**, and **12a**, **b**) is also applicable to these **20a–c** isomers. However, the proton H_c appeared as a multiplet at δ 4.58–4.53, which is more deshielded than proton H_b. This may be due to strong intramolecular C–H···O hydrogen bonding between H_c proton and furan O-atom as in **11d**. The signal in the ^{13}C NMR spectrum of **20a** at δ 69.40 corresponds to the spiro carbon. The oxindole ring carbonyl and the heteroyl carbonyl resonated at δ 164.54 and 188.66, respectively.



Scheme 7 Possible regioisomers during the synthesis of spiroquinoxalinopyrrolizidines

Crystal structure analysis of 11d

Compound **11d** crystallizes in the centrosymmetric (racemate) monoclinic $P2_1/c$ space group with one molecule in the asymmetric unit. The furan moiety is located above the mean plane of the pyrrolizidine ring and displays conformational disorder (i.e., rotation through 90°), with site occupancy ratio of 0.529(4):0.471(4) as shown in Fig. 1. Crystal structure analysis revealed that the molecules form an elongated hexagonal network structure. The 2_1 screw axis-related molecules are connected by N–H group of isatin moiety and thiophene attached –C=O group via N–H···O [N(1)–H(1N)···O(2); $D = 2.928(3)$ Å; $\theta = 151°$] hydrogen bonds along the crystallographic c-axis. Three molecules from each 2_1 screw axis are connected with adjacent furan rings by C–H···O dimer synthons [C(23)–H(23)···O(3); $D = 2.945(13)$ Å, $\theta = 117°$] to form an elongated hexagonal network structure (Fig. 2). This hexagonal structure is extended along the crystallographic a-axis. Further, the crystal structure is stabilized by weak C–H···O hydrogen bonds. The relevant crystal data, collection parameters, and refinement results can be found in Table 4. The hydrogen bond parameters are given in Table 5.

Experimental

General considerations

All melting points were recorded using Stuart SMP30 melting point apparatus and are uncorrected. IR spectra were recorded on a PerkinElmer 100S series FTIR instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using tetramethylsilane (TMS) as internal standard on a Bruker Avance III HD 400 MHz instrument.

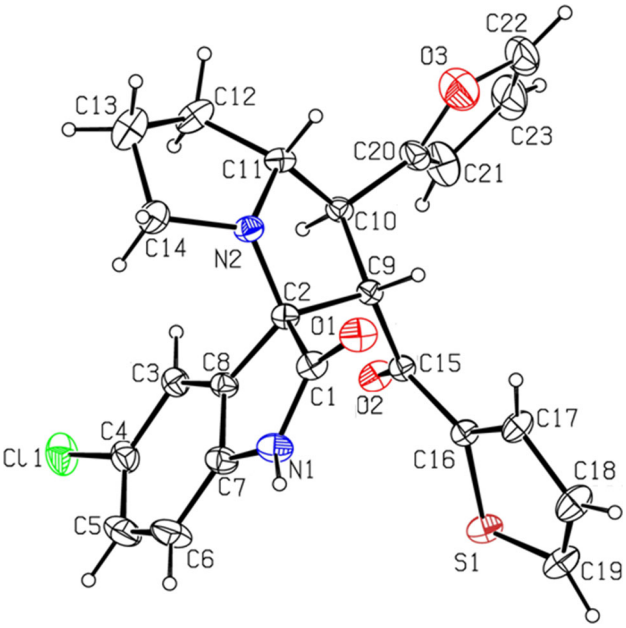


Fig. 1 ORTEP diagram of **11d** with the atom numbering scheme. Displacement ellipsoids are drawn at 20 % probability level, and H atoms are shown as *small spheres* of arbitrary radius. Only major component of the disordered furan ring atoms is shown for clarity. The configurations at chiral centers C2, C9, C10, and C11 are *R*, *S*, *S*, and *R*, respectively

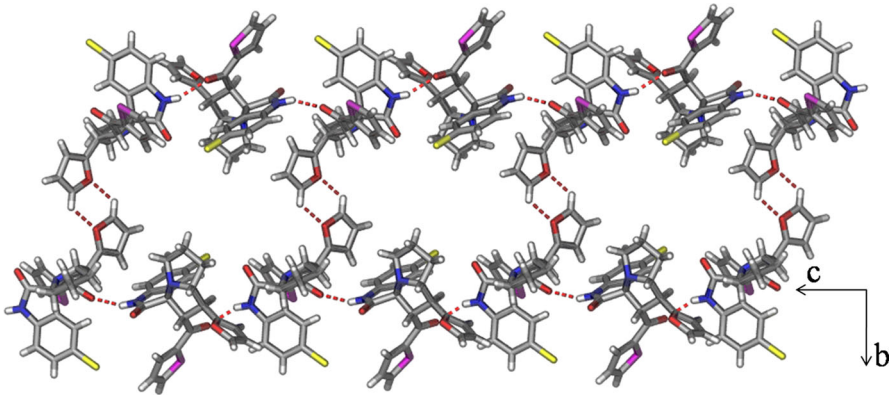


Fig. 2 Crystal structure packing diagram of **11d**. Notice the elongated hexagonal network structures formed by N–H···O hydrogen bonds and C–H···O dimer synthons

Mass spectra were recorded on Joel JMSD-300 spectrometer. Elemental analyses were performed on a Carlo-Erba model EA 1108 analytical unit (Triad, NJ, USA), and the values are within ±0.4 % of theoretical values. Column chromatography was performed on silica gel (100–120 mesh). Reaction progress and purity were monitored by thin-layer chromatography. Unless otherwise stated, all chemicals and solvents used were of high grade and purchased from Sigma Aldrich and

Table 4 Salient crystallographic data and structure refinement parameters of compound **11d**

	11d
Empirical formula	$C_{23}H_{19}ClN_2O_3S$
Formula weight	438.91
Crystal system	Monoclinic
Space group	$P2_1/c$
T (K)	293(2)
a (Å)	8.2305(6)
b (Å)	18.5917(13)
c (Å)	13.9102(10)
α (°)	90
β (°)	106.4740(10)
γ (°)	90
Z	4
V (Å^3)	2041.1(3)
D_{calc} (g/cm^3)	1.428
$F(000)$	912.0
μ (mm^{-1})	0.318
θ (°)	1.879–25.994
Index ranges	$-10 \leq h \leq 10$
	$-22 \leq k \leq 22$
	$-17 \leq l \leq 17$
N-total	21,054
N-independent	3996
N-observed	3593
Parameters	312
R_1 $[I > 2\sigma(I)]$	0.0651
wR_2 (all data)	0.1836
GOF	1.070
CCDC	1,470,017

Spectrochem. Ultrasonication was performed on PCi-Analytics-6.5L200H1DTC ultrasonic cleaner whose frequency is 25 kHz, input voltage range of 170–270 V_{AC} at 50 Hz, and output power is 250 W (Mumbai, India). The reaction flasks were immersed throughout the cleaner such that the surface of the reactants was slightly lower than the water in the cleaner.

Typical procedures for synthesis of spirooxindolopyrrolizidines and spiroquinoxalinopyrrolizidines

Ultrasound irradiation

A mixture of L-proline (1 mmol), isatin/11*H*-indeno[1,2-*b*]quinoxalin-11-one (1 mmol), and Claisen–Schmidt adducts **5**, **6**, **7** (1 mmol) in methanol was stirred

Table 5 Geometrical parameters of hydrogen bonds in compound **11d**

D–H···A[a]	D···A (Å)	H···A (Å)	D–H···A (°)	Symmetry code
N(1)–H(1 N)···O(2)	2.928(3)	2.00	151	$x, 1/2 - y, 1/2 + z$
C(3)–H(3)···O(1)	3.740(3)	2.70	160	$x, 1/2 - y, -1/2 + z$
Intra C(9)–H(9)···O(1)	3.116(3)	2.71	101	–
C(10)–H(10)···N(1)	3.710(3)	2.79	142	$x, 1/2 - y, -1/2 + z$
Intra C(11)–H(11)···O(3)	3.011(6)	2.54	105	–
C(13)–H(13A)···O(2)	3.539(6)	2.54	153	$-1 + x, y, z$
C(21)–H(21)···N(1)	3.182(8)	2.20	149	$x, 1/2 - y, -1/2 + z$
C(23)–H(23)···O(3)	2.945(13)	2.29	117	$1-x, 1-y, -z$

[a] All C–H and N–H distances are neutron normalized to 1.083 and 1.009 Å, respectively

for a few minutes. After obtaining a homogeneous solution, the mixture was irradiated in an ultrasonic bath for the appropriate time at room temperature (Tables 1, 2). Reaction progress was monitored by TLC. The precipitated compound was filtered and washed with methanol and dried.

Conventional heating

A mixture of L-proline (1 mmol), isatin/11*H*-indeno[1,2-*b*]quinoxalin-11-one (1 mmol), and Claisen–Schmidt adducts **5**, **6**, **7** (1 mmol) in methanol was refluxed vigorously (maintained 80–85 °C) for an appropriate time (Tables 1, 2). Reaction progress was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by column chromatography using petroleum ether:ethyl acetate (7:3) as eluent, followed by recrystallization from methanol.

Fusion method

A mixture of L-proline (1 mmol), isatin/11*H*-indeno[1,2-*b*]quinoxalin-11-one (1 mmol), and Claisen–Schmidt adducts **5**, **6**, **7** (1 mmol) was fused directly without solvent for the appropriate time (Tables 1, 2). Reaction progress was monitored by TLC.

Spectral data for all synthesized compounds

*11H-Indeno[1,2-b]quinoxalin-11-one (**18**)*

Color: yellow; M.p. 217–219 °C. IR (KBr, cm^{-1}): 1724, 1616, 1570. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (d, 1H, $J = 9.2$ Hz), 8.14–8.11 (m, 2H), 7.94 (d, 1H, $J = 7.6$ Hz), 7.86–7.75 (m, 3H), 7.62 (t, 1H, $J = 7.2$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.94, 156.63, 149.28, 143.14, 142.65, 141.56, 136.84, 136.68, 132.53, 132.47, 131.62, 130.30, 129.68, 124.79, 122.53. ESI mass spectrum (*m*/*z*): calcd. for [$C_{15}H_8N_2O$]: 232.24 (M^+), obsd.: 233.10.

2′-(Furan-2-carbonyl)-1′-(furan-2-yl)-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indoline-3-3′-pyrrolizin]-2-one (**10a**) Color: white. M.p. 215–217 °C. IR (KBr, cm^{-1}): 3335, 3123, 2871, 1731, 1677, 1393, 768. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (s, 1H), 7.39 (d, 1H, $J = 2.4$ Hz), 7.31 (d, 1H, $J = 2.8$ Hz), 7.24 (d, 1H, $J = 7.6$ Hz), 7.14 (t, 1H, $J = 7.6$ Hz), 7.06 (d, 1H, $J = 3.2$ Hz), 7.00 (t, 1H, $J = 7.6$ Hz), 6.69 (d, 1H, $J = 7.6$ Hz), 6.33–6.32 (dd, 1H, $J_{1,2} = J_{3,4} = 1.6$ Hz), 6.26–6.25 (dd, 1H, $J_{1,2} = J_{3,4} = 1.6$ Hz), 6.16 (d, 1H, $J = 3.6$ Hz), 4.72 (d, 1H, $J = 11.6$ Hz), 4.29–4.23 (m, 1H), 4.04 (t, 1H, $J = 10$ Hz), 2.70–2.57 (m, 2H), 2.15–1.79 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 207.08, 183.77, 180.50, 153.02, 147.05, 141.78, 140.38, 129.56, 127.70, 124.81, 122.42, 118.65, 112.24, 110.18, 106.17, 73.54, 68.80, 61.49, 48.13, 45.52, 30.96, 30.59, 27.15. ESI mass spectrum (*m/z*): calcd. for [$C_{23}H_{20}N_2O_4$]: 389.10 (M^+), obsd.: 388.42; Anal. calcd. for $C_{23}H_{20}N_2O_4$: C, 71.12; H, 5.19; N, 7.21; found: C, 70.94; H, 5.42; N, 7.49.

2′-(Furan-2-carbonyl)-1′-(furan-2-yl)-1-methyl-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indoline-3-3′-pyrrolizin]-2-one (**10b**) Color: white. M.p. 184–186 °C. IR (KBr, cm^{-1}): 3319, 3111, 2872, 1727, 1668, 1372, 757. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, 1H, $J = 2.4$ Hz), 7.30 (d, 1H, $J = 2.8$ Hz), 7.24–7.18 (m, 2H), 7.03–6.97 (m, 2H), 6.61 (d, 1H, $J = 7.6$ Hz), 6.33–6.31 (dd, 1H, $J_{1,2} = J_{3,4} = 2.0$ Hz), 6.26–6.25 (dd, 1H, $J_{1,2} = J_{3,4} = 1.6$ Hz), 6.15 (d, 1H, $J = 3.2$ Hz), 4.68 (d, 1H, $J = 11.6$ Hz), 4.32–4.26 (m, 1H), 4.02 (t, 1H, $J = 10$ Hz), 3.06 (s, 3H), 2.70–2.54 (m, 2H), 2.15–1.81 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.38, 178.72, 153.02, 143.96, 143.10, 141.78, 134.46, 132.31, 129.56, 127.66, 124.37, 122.51, 110.20, 108.14, 106.18, 73.89, 69.03, 62.99, 50.82, 48.33, 45.66, 30.88, 27.34, 26.24. ESI mass spectrum (*m/z*): calcd. for [$C_{24}H_{22}N_2O_4$]: 403.15 (M^+), obsd.: 402.44; Anal. calcd. for $C_{24}H_{22}N_2O_4$: C, 71.63; H, 5.51; N, 6.96; found: C, 71.35; H, 5.79; N, 6.73.

1-Ethyl-2′-(furan-2-carbonyl)-1′-(furan-2-yl)-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indoline-3-3′-pyrrolizin]-2-one (**10c**) Color: white. M.p. 193–195 °C. IR (KBr, cm^{-1}): 3315, 3130, 2870, 1720, 1667, 1371, 757. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, 1H, $J = 1.2$ Hz), 7.30 (d, 1H, $J = 2.0$ Hz), 7.26–7.18 (m, 2H), 7.06–6.99 (m, 2H), 6.65 (d, 1H, $J = 7.6$ Hz), 6.33–6.32 (dd, 1H, $J_{1,2} = J_{3,4} = 1.6$ Hz), 6.26–6.25 (dd, 1H, $J_{1,2} = J_{3,4} = 2.0$ Hz), 6.15 (d, 1H, $J = 3.2$ Hz), 4.71 (d, 1H, $J = 11.6$ Hz), 4.30–4.25 (m, 1H), 4.04 (t, 1H, $J = 10$ Hz), 3.76–3.54 (m, 2H), 2.64–2.53 (m, 2H), 2.14–1.79 (m, 4H), 1.06 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 183.77, 178.08, 153.10, 152.05, 147.05, 142.40, 141.79, 129.54, 127.54, 124.59, 122.18, 119.01, 112.07, 110.17, 108.31, 106.12, 73.39, 68.84, 61.48, 48.16, 45.44, 34.84, 30.58, 27.17, 12.43. ESI mass spectrum (*m/z*): calcd. for [$C_{25}H_{24}N_2O_4$]: 417.20 (M^+), obsd.:416.47; Anal. calcd. for $C_{25}H_{24}N_2O_4$: C, 72.10; H, 5.81; N, 6.73; found: C, 72.31; H, 5.55; N, 6.49.

5-Chloro-2′-(furan-2-carbonyl)-1′-(furan-2-yl)-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indoline-3-3′-pyrrolizin]-2-one (**10d**) Color: white. M.p. 212–214 °C. IR (KBr, cm^{-1}): 3280, 3107, 2863, 1729, 1651, 1393, 781. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (s, 1H), 7.42 (d, 1H, $J = 2.4$ Hz), 7.30 (d, 1H, $J = 2.4$ Hz), 7.22 (d, 1H, $J = 2.0$ Hz), 7.15–7.12 (dd, 1H, $J_{1,2} = J_{3,4} = 2.0$ Hz), 7.09 (d, 1H, $J = 3.2$ Hz),

6.65 (d, 1H, $J = 8.4$ Hz), 6.36–6.35 (dd, 1H, $J_{1,2} = J_{3,4} = 1.6$ Hz), 6.27–6.25 (dd, 1H, $J_{1,2} = J_{3,4} = 2.0$ Hz), 6.16 (d, 1H, $J = 3.2$ Hz), 4.72 (d, 1H, $J = 11.6$ Hz), 4.28–4.22 (m, 1H), 4.00 (t, 1H, $J = 10$ Hz), 2.64–2.61 (m, 2H), 2.16–1.75 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.07, 183.39, 180.51, 152.62, 152.05, 147.18, 141.89, 138.98, 129.68, 127.98, 127.82, 126.68, 118.79, 112.41, 111.08, 110.24, 106.36, 73.67, 68.85, 61.54, 48.00, 45.54, 30.65, 27.40. ESI mass spectrum (*m/z*): calcd. for [$C_{23}H_{19}N_2O_4Cl$]: 423.10 (M^+), obsd.: 422.86; Anal. calcd. For $C_{23}H_{19}N_2O_4Cl$: C, 65.33; H, 4.53; N, 6.62; found; C, 65.61; H, 4.29; N, 6.36.

1′-(Furan-2-yl)-2′-(thiophene-2-carbonyl)-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indoline-3-3′-pyrrolizin]-2-one (**11a**) Color: white. M.p. 231–232 °C. IR (KBr, cm^{-1}): 3300, 3063, 2874, 1730, 1660, 1325, 751. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, 1H, $J = 3.6$ Hz), 7.48 (d, 1H, $J = 4.0$ Hz), 7.31 (d, 1H,$J = 1.6$ Hz), 7.16–6.96 (m, 4H), 6.61 (d, 1H, $J = 7.6$ Hz), 6.26–6.25 (dd, 1H, $J_{1,2} = J_{3,4} = 1.6$ Hz), 6.15 (d, 1H, $J = 3.2$ Hz), 4.83 (d, 1H, $J = 11.6$ Hz), 4.30–4.24 (m, 1H),4.02 (t, 1H, $J = 7.2$ Hz), 2.68–2.58 (m, 2H), 2.17–1.79 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ: 188.55, 179.74, 153.72, 143.99, 142.65, 136.38, 133.30, 129.81, 129.01, 127.99, 124.91, 121.66, 110.90, 110.11, 106.38, 73.19, 69.06, 61.84, 47.91, 45.91, 31.17, 30.27, 27.18. ESI mass spectrum (*m/z*): calcd. for [$C_{23}H_{20}N_2O_3S$]: 405.10 (M^+), obsd.: 404.48; Anal. calcd. For $C_{23}H_{20}N_2O_3S$: C, 68.30; H, 4.98; N, 6.93; found: C, 68.07; H, 5.76; N, 6.69.

1′-(Furan-2-yl)-1-methyl-2′-(thiophene-2-carbonyl)-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indoline-3-3′-pyrrolizin]-2-one (**11b**) Color: white. M.p. 191–193 °C. IR (KBr, cm^{-1}): 3280, 3111, 2872, 1717, 1650, 1416, 755. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.5 (d, 1H, $J = 2.8$ Hz), 7.44 (d, 1H, $J = 4.0$ Hz), 7.31 (d, 1H, $J = 2.4$ Hz), 7.24–7.17 (m, 2H), 7.04 (t, 1H, $J = 7.6$ Hz), 6.95 (t, 1H, $J = 4.0$ Hz), 6.54 (d, 1H, $J = 7.6$ Hz), 6.26–6.25 (dd, 1H, $J_{1,2} = J_{3,4} = 2.0$ Hz), 6.16 (d, 1H, $J = 3.2$ Hz), 4.78 (d, 1H, $J = 11.6$ Hz), 4.31–4.26 (m, 1H), 4.0 (t, 1H, $J = 11.2$ Hz), 2.95 (s, 3H), 2.68–2.55 (m, 2H), 2.17–1.81 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 183.82, 178.66, 153.09, 152.07, 146.84, 143.27, 141.76, 129.58, 127.19, 124.34, 122.41, 118.41, 112.03, 110.18, 108.10, 106.14, 73.45, 68.84, 61.92, 48.31, 45.30, 30.56, 27.11, 26.37. ESI mass spectrum (*m/z*): calcd. for [$C_{24}H_{22}N_2O_3S$]: 419.10 (M^+), obsd.: 418.51; Anal. calcd. For $C_{24}H_{22}N_2O_3S$: C, 68.88; H, 5.30; N, 6.69; found: C, 68.64; H, 5.53; N, 6.93.

1-Ethyl-1′-(furan-2-yl)-2′-(thiophene-2-carbonyl)-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indoline-3-3′-pyrrolizin]-2-one (**11c**) Color: white. M.p. 198–200 °C. IR (KBr, cm^{-1}): 3276, 3112, 2869, 1716, 1650, 1354, 754. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, 1H, $J = 3.6$ Hz), 7.44 (d, 1H, $J = 4.8$ Hz), 7.31–7.18 (m, 3H), 7.04 (t, 1H, $J = 7.6$ Hz), 6.94 (t, 1H, $J = 4.4$ Hz), 6.6 (d, 1H, $J = 8$ Hz), 6.25 (s, 1H), 6.15 (d, 1H, $J = 2.8$ Hz), 4.84 (d, 1H, $J = 11.6$ Hz), 4.30–4.24 (m, 1H), 4.03 (t, 1H, $J = 10.4$ Hz), 3.67–3.45 (m, 2H), 2.64–2.54 (m, 2H), 2.15–1.78 (m, 4H), 0.95 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.40, 178.10, 153.07, 144.12, 142.28, 141.80, 134.53, 132.74, 129.49, 127.90, 124.61, 122.23, 110.18, 108.32, 106.12, 73.69, 69.02, 62.35, 50.86, 48.17, 45.84, 34.83, 30.86, 27.36, 12.08. ESI mass spectrum (*m/z*): calcd. for [$C_{25}H_{24}N_2O_3S$]: 433.15 (M^+), obsd.: 432.53; Anal.

calcd. For $C_{25}H_{24}N_2O_3S$: C, 69.42; H, 5.59; N, 6.48; found: C, 69.69; H, 5.85; N, 6.19.

5-Chloro-1′-(furan-2-yl)-2′-(thiophene-2-carbonyl)-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indoline-3-3′-pyrrolizin]-2-one (**11d**) Color: white. M.p. 220–222 °C. IR (KBr, cm^{-1}): 3296, 3107, 2857, 1729, 1635, 1408, 738. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, 1H, $J = 4.0$ Hz), 7.51 (d, 1H, $J = 4.0$ Hz), 7.44 (s, 1H), 7.31 (d, 1H, $J = 1.2$ Hz), 7.24 (dd, 1H, $J = 1.0$ Hz), 7.15–7.13 (dd, 1H, $J_{1,2} = J_{3,4} = 2.0$ Hz), 6.98–6.96 (dd, 1H, $J_{1,2} = J_{3,4} = 4.0$ Hz), 6.58 (d, 1H, $J = 8.4$ Hz), 6.26–6.25 (dd, 1H, $J_{1,2} = J_{3,4} = 2.0$ Hz), 6.16 (d, 1H, $J = 3.2$ Hz), 4.83 (d, 1H, $J = 11.6$ Hz), 4.29–4.23 (m, 1H), 3.99 (t, 1H, $J = 10$ Hz), 2.64–2.61 (m, 2H), 2.18–1.75 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 207.11, 187.90, 180.16, 152.61, 144.08, 141.90, 138.82, 134.93, 132.64, 129.61, 128.06, 127.97, 126.73, 110.97, 110.23, 106.33, 73.95, 68.96, 62.38, 47.99, 46.03, 30.96, 27.55. ESI mass spectrum (*m*/*z*): calcd. for [$C_{23}H_{19}N_2O_3ClS$]: 439.05 (M^+), obsd.: 438.93; Anal. calcd. for $C_{23}H_{19}N_2O_3ClS$: C, 62.94; H, 4.36; N, 6.38; found: C, 62.68; H, 4.57; N, 6.67.

1′-(Furan-2-yl)-2′-picolinoyl-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indoline-3-3′-pyrrolizin]-2-one (**12a**) Color: white. M.p. 212–214 °C. IR (KBr, cm^{-1}): 3376, 3004, 2869, 1743, 1697, 1320, 760. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50–8.48 (m, 1H), 8.35 (s, 1H), 7.54–7.50 (m, 2H), 7.32 (d, 1H, $J = 2.0$ Hz), 7.22–7.24 (m, 1H), 7.03–6.94 (m, 2H), 6.80 (t, 1H, $J = 7.6$ Hz), 6.53 (d, 1H, $J = 7.6$ Hz), 6.28–6.27 (dd, 1H, $J_{1,2} = J_{3,4} = 1.6$ Hz), 6.21 (d, 1H, $J = 3.2$ Hz), 5.32 (d, 1H, $J = 11.2$ Hz), 4.35–4.29 (m, 1H), 3.98 (t, 1H, $J = 10.4$ Hz), 2.82–2.54 (m, 2H), 2.19–1.86 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.19, 182.03, 154.01, 152.48, 148.23, 141.59, 136.33, 129.13, 126.97, 126.90, 125.72, 121.49, 121.34, 110.15, 109.84, 105.86, 72.52, 68.59, 61.26, 48.70, 45.55, 29.79, 26.36. ESI mass spectrum (*m*/*z*): calcd. for [$C_{24}H_{21}N_3O_3$]: 399.44 (M^+), obsd.: 400.35; Anal. calcd. for $C_{24}H_{21}N_3O_3$: C, 72.16; H, 5.30; N, 10.52; found: C, 72.42; H, 5.49; N, 10.26.

5-Chloro-1′-(furan-2-yl)-2′-picolinoyl-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indoline-3-3′-pyrrolizin]-2-one (**12b**) Color: white. M.p. 209–211 °C. IR (KBr, cm^{-1}): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.44 (s, 1H), 8.49 (d, 1H, $J = 3.6$ Hz), 7.55–7.62 (m, 3H), 7.22–7.33 (m, 2H), 7.01–6.96 (m, 2H), 6.29 (d, 1H, $J = 3.2$ Hz), 6.22 (d, 1H, $J = 3.2$ Hz), 5.31(d, 1H, $J = 11.2$ Hz) 4.34–4.28 (m, 1H), 3.97 (t, 1H, $J = 10.4$ Hz), 2.57–2.79 (m, 2H), 2.18–1.84 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.80, 182.17, 153.66, 152.36, 148.27, 141.67, 140.37, 136.58, 129.16, 127.63, 127.17, 126.89, 121.57, 110.97, 110.20, 106.03, 72.54, 68.54, 61.31, 48.55, 45.46, 29.66, 26.50. ESI mass spectrum (*m*/*z*): calcd. for [$C_{24}H_{20}N_3O_3Cl$]: 434.10 (M^+), obsd.: 433.89; Anal. calcd. For $C_{24}H_{20}N_3O_3Cl$: C, 66.44; H, 4.65;N, 9.68; found: C, 66.17; H, 4.90; N, 9.43.

Furan-2-yl(1′-(furan-2-yl)-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indeno[1,2-*b*]quinoxaline-11,3′-pyrrolizin]-2′-yl)methanone (**20a**) Color: yellow. M.p. 181–183 °C. IR (KBr, cm^{-1}): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37–7.16 (m, 10H), 6.61–6.22 (m, 4H), 4.87 (d, 1H, $J = 11.2$ Hz), 4.58–4.53 (m, 1H), 4.33 (t, 1H, $J = 11.6$ Hz), 2.80–2.47 (m, 2H), 2.30–1.86 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.66, 164.54,

153.56, 153.03, 143.79, 143.46, 142.77, 142.12, 141.79, 137.28, 134.10, 132.03, 131.07, 129.82, 129.75, 128.97, 128.66, 128.24, 127.04, 122.14, 110.25, 109.70, 106.09, 75.47, 69.40, 65.50, 63.81, 47.82, 45.86, 31.34, 27.95. ESI mass spectrum (*m/z*): calcd. for [$C_{30}H_{23}N_3O_3$]: 473.17 (M^+), obsd.: 473.95. Anal. calcd. for $C_{30}H_{23}N_3O_3$: C, 76.09; H, 4.90; N, 8.87; found: C, 75.87; H, 4.65; N, 8.64.

(1′-(Furan-2-yl)-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indeno[1,2-*b*]quinoxaline-11,3′-pyrrolizin]-2′-yl)(thiopnen-2-yl)methanone (**20b**) Color: yellow. M.p. 192–194 °C. IR (KBr, cm^{-1}): 3103, 2942, 2853, 1657. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16–8.37 (m, 10H), 6.61–6.22 (m, 4H), 4.77 (d, 1H, $J = 11.2$ Hz), 4.59–4.52 (m, 1H), 4.32 (t, 1H,$J = 11.6$ Hz), 2.70–2.49 (m, 2H), 2.28–1.91 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.66, 164.54, 153.56, 153.03, 143.79, 143.46, 142.77, 142.12, 141.79, 137.28, 134.10, 132.03, 131.07, 129.82, 129.75, 128.97, 128.66, 128.24, 127.04, 122.14, 110.25, 109.70, 106.09, 75.47, 69.40, 65.50, 63.81, 47.82, 45.86, 31.34, 27.95. ESI mass spectrum (*m/z*): calcd. for [$C_{30}H_{23}N_3O_2S$]: 490.20 (M^+), obsd.: 489.59; Anal. calcd. for $C_{30}H_{23}N_3O_2S$: C, 73.60; H, 4.74; N, 8.58; found: C, 73.34; H, 4.44; N, 8.78.

(1′-(Furan-2-yl)-1′,2′,5′,6′,7′,7a′-hexahydrospiro[indeno[1,2-*b*]quinoxaline-11,3′-pyrrolizin]-2′-yl)(pyridin-2-yl)methanone (**20c**) Color: yellow. M.p. 193–195 °C. IR (KBr, cm^{-1}): 3113, 2942, 2883, 1692. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36–8.38 (m, 1H), 8.08–8.03 (m, 1H), 7.78–7.73 (m, 3H), 7.53–7.21 (m, 7H), 6.89–6.86 (m, 1H), 6.31–6.27 (m, 2H), 5.80 (d, 1H, $J = 3.6$ Hz), 4.66–4.60 (m, 1H), 4.24 (t, 1H, $J = 11.6$ Hz), 2.78–2.48 (m, 2H), 2.27–1.93 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.27, 165.84, 154.29, 152.75, 152.32, 147.22, 144.07, 142.59, 142.42, 141.58, 137.67, 136.23, 130.64, 130.16, 129.33, 129.19, 128.70, 128.63, 127.57, 126.47, 121.85, 121.44, 110.18, 105.85, 74.30, 69.37, 62.69, 47.83, 45.27, 30.56, 27.31. ESI mass spectrum (*m/z*): calcd. for [$C_{31}H_{24}N_4O_2$]: 485.20 (M^+), obsd.: 484.55; Anal. calcd. for $C_{31}H_{24}N_4O_2$: C, 76.84; H, 4.99; N, 11.56; found: C, 76.57; H, 4.71; N, 11.76.

Single-crystal X-ray diffraction study of 11d

X-ray data for the compound were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) with ω-scan method. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 5371 reflections. Integration and scaling of intensity data were accomplished using SAINT program [41]. The structure was solved by direct methods using SHELXS97, and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7 [42]. Anisotropic displacement parameters were included for all nonhydrogen atoms. H bound to N atom was located from the difference Fourier map. All other H atoms were positioned geometrically and treated as riding on their parent C atoms with C–H distances of 0.93–0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (C) or $1.5U_{eq}$ for methyl atoms. The furan ring atoms are found to be disordered over two sites, with 0.531(4) site occupancy for C22/C23/

C24/O3 atoms (representing the major component) and 0.469(4) site occupancy for C22D/C23D/C24D/O3D (minor component). PART and FVAR instructions were used for modeling the sulfur atom disorder, and DFIX instruction for restraining the C–C and C–O bond distance to their expected values. The anisotropic displacement parameters of the disordered atoms were restrained to be similar (SIMU instruction), and the direction of motion along the axis between these atoms was also restrained (DELU instruction) [43]. The software used to prepare material for publication was Mercury 2.3 (build RC4), ORTEP-3, and X-Seed [44–46].

Conclusions

Various spirooxindolopyrrolizidines and spiroquinoxalinopyrrolizidines were synthesized by 1,3-dipolar cycloaddition with isatin/11*H*-indeno[1,2-*b*]quinoxalin-11-one with L-proline and different dipolarophiles using ultrasonication, reflux, and fusion methods. The green, ultrasonication method was followed, obtaining moderate to good yield with reduced reaction time compared with the conventional heating and fusion methods. The synthesized compounds were analyzed by ^{1}H NMR, ^{13}C NMR, and mass spectrometric methods. Finally, the structure of compound **11d** was confirmed by single-crystal X-ray diffraction analysis.

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References

1. S.J. Tabatabaei Rezaei, M.R. Nabid, A. Yari, S.W.Ng, Ultrason. Sonochem. **18**, 49 (2011)
2. B.H. Rotstein, S. Zaretsky, V. Rai, A.K. Yudin, Chem. Rev. **114**, 8323 (2014)
3. F. Damkaci, A.J. Szymaniak, Chem. Educ. **91**, 943 (2014)
4. C.M.R. Volla, I. Atodiresei, M. Rueping, Chem. Rev. **114**, 2390 (2014)
5. J. Safari, Z. Zarnegar, Ultrason. Sonochem. **21**, 1132 (2014)
6. E. Pelit, Z. Turgut, Ultrason. Sonochem. **21**, 1600 (2014)
7. G. Bentabed-Ababsa, A. Derdour, T. Roisnel, J.A. Sáez, P. Pérez, E. Chamorro, L.R. Domingo, F.J. Mongin, Org. Chem. **74**, 2120 (2009)
8. W. Benchouk, S.M. Mekelleche, M.J. Aurell, L.R. Domingo, Tetrahedron, **65**, 4644 (2009)
9. A.K. Nacereddine, W. Yahia, S. Bouacha, A. Djerourou, Tetrahedron Lett. **51**, 2617 (2010)
10. K. Alimohammadi, Y. Sarrafi, M. Tajbakhsh, S. Yeganegi, M. Hamzehloueian, Tetrahedron **67**, 1589 (2011)
11. A. Bazgir, S. Ahadi, R. Ghahremanzadeh, H.R. Khavasi, P. Mirzaei, Ultrason. Sonochem. **17**, 447 (2010)
12. M. Dabiri, Z.N. Tisseh, M. Bahramnejad, A. Bazgir, Ultrason. Sonochem. **18**, 1153 (2011)
13. J. Feng, K. Ablajan, A. Sali, Tetrahedron **70**, 484 (2014)
14. A. Hasaninejad, S. Firoozi, F. Mandegani, Tetrahedron Lett. **54**, 2791 (2013)
15. T. Tsubogo, S. Saito, K. Seki, Y. Yamashita, S. Kobayashi, J. Am. Chem. Soc. **130**, 13321 (2008)
16. W. Li, M. Shi, J. Org. Chem. **73**, 4151 (2008)
17. X.X. Yan, Q. Peng, Y. Zhang, K. Zhang, W. Hong, X.L. Hou, Y.D. Wu, Angew. Chem., Int. Ed. **45**, 1979 (2006)
18. M. Ghandi, A. Yari, S.J.T. Rezaei, A. Taheri, Tetrahedron Lett. **50**, 4724 (2009)
19. Y. Yamashita, X. Guo, R. Takashita, J. Am. Chem. Soc. **132**, 3262 (2010)
20. S.Q. Ge, Y.Y. Hua, M. Xia, Ultrason. Sonochem. **16**, 232 (2009)

21. S. Haddad, S. Boudriga, F. Porzio, A. Soldera, M. Askri, M. Knorr, Y. Rousselin, M.M. Kubicki, C. Golz, C. Strohmann, J. Org. Chem. **80**, 9064 (2015)
22. E. Carlos, P. Galvis, V.V. Kouznetsov, Org. Biomol. Chem. 7372 (2013)
23. K. Revathy, A. Lalitha, RSC Adv. 279 (2014)
24. F. Yang, J. Sun, H. Gao, C.G.Yan, RSC Adv. **5**, 32786 (2015)
25. J. Častulík, J. Marek, C. Mazal, Tetrahedron **57**, 8339 (2001)
26. P. Shanmugam, B. Viswambharan, S. Madhavan, Org. Lett. **9**, 4095 (2007)
27. P. Shanmugam, B. Viswambharan, K. Selvakumar, S. Madhavan, Tetrahedron Lett. **49**, 2611 (2008)
28. G. Periyasami, R. Raghunathan, G. Surendiran, N. Mathivanan, Bioorg. Med. Chem. Lett. **18**, 2342 (2008)
29. R.R. Kumar, S. Perumal, P. Senthilkumar, P. Yogeeswari, D. Sriram, Tetrahedron **64**, 2962 (2008)
30. R. Ranjith-Kumar, S. Perumal, Tetrahedron **63**, 12220 (2007)
31. A.R.S. Babu, R. Raghunathan, Tetrahedron Lett. **49**, 4618 (2008)
32. J. Li, J. Wang, Z. Xu, S. Zhu. ACS Comb. Sci. **16**, 506 (2014)
33. A. Thangamani, Eur. J. Med. Chem. **45**, 6120 (2010)
34. R.J. Bridges, F.E. Lovering, J.M. Humphrey, M.S. Stanley, T.N. Blakely, Bioorg. Med. Chem. Lett. **3**, 115 (1993)
35. A.R.S. Babu, R. Raghunathan, Tetrahedron Lett. **48**, 6809 (2007)
36. K. Jadidi, R. Gharemanzadeh, M. Mehrdad, H.R. Darabi, H.R. Khavasi, D. Asgari, Ultrason. Sonochem. **15**, 124 (2008)
37. A.S. Konev, M.S. Novikov, A.F. Khlebnikov, Tetrahedron Lett. **46**, 8337 (2005)
38. E. Ramesh, R. Raghunathan, Tetrahedron Lett. **49**, 1125 (2008)
39. A.S. Amarasekara, T.B. Singh, E. Larkin, M.A. Hasan, H. Fan, Ind. Crop. Prod. **65**, 546 (2015)
40. Y. Hua, Y. Zou, H. Wu, D. Shi, Ultrason. Sonochem. **19**, 264 (2012)
41. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA (2001)
42. G.M. Sheldrick, SHELXS97 and SHELXL version 2014/7, http://shelx.uniac.gwdg.de/SHELX/index.php
43. P. Muller, R. Herbst-Imer, A.L. Spek, T.R. Schneider, M. R. Sawaya, in *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL*, ed. by P. Muller (Oxford University Press: Oxford, New York, 2006) pp. 57 + XXXV
44. C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. R-Monge, R. Taylor, J. Van de Streek, P.A. Wood, J. Appl. Cryst. **41**, 466 (2008)
45. L.J. Farrugia, J. Appl. Cryst. **30**, 565 (2008)
46. L.J. Barbour, J. Supramol. Chem. **1**, 189 (2001)