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Microwave-Assisted Synthesis of Fluorescent Pyrido[2,3-*b*]indolizines from Alkylpyridinium Salts and Enaminones

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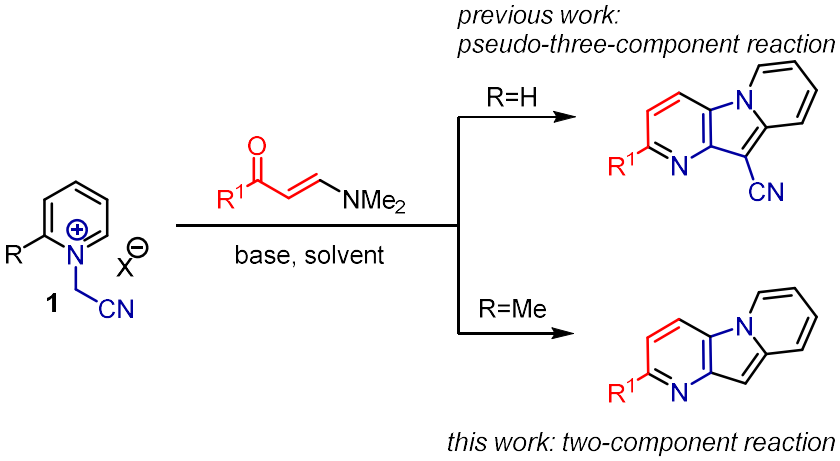
Abstract: Pyridinium ylides are well recognized as dipoles for cycloaddition reactions. In its turn, the microwave-assisted interaction of *N*-(cyanomethyl)-2-alkylpyridinium salts with enaminones unexpectedly proceeds as a domino sequence of cycloisomerization and cyclocondensation reactions, instead of a 1,3-dipolar cycloaddition. The reaction takes place in the presence of sodium acetate as base and employs benign solvents. The optical properties of the resulting pyrido[2,3-*b*]indolizines were studied, showing green light emission with high fluorescence quantum yields.

Keywords: pyridinium ylide; indolizine; domino reaction; fluorescence

1. Introduction

Indolizines, and in particular the annulated ones, are frequently found to exhibit useful biological [1–6] and optical properties [7–14]. The synthesis of indolizines usually relies on the reactivity of pyridinium ylides, which can undergo cycloaddition reactions with alkenes [15–18] or alkynes [19–23]. In some cases, interaction of ylides with alkenes or alkynes leads to a different outcome [24–26]. Another approach towards the indolizine scaffold is based on intramolecular cyclization of 2-alkylpyridinium ylides. For instance, Opatz et al. used 2-alkyl-1-(cyanomethyl)pyridinium salts to prepare aminoindolizines [27]. Following our interest in the chemistry of cyanomethylpyridinium salts [28–30], we recently showed that the interaction of *N*-(cyanomethyl)pyridinium chlorides with enaminones under basic conditions proceeds as a pseudo-three-component reaction, resulting in the formation of pyridoindolizine-10-carbonitriles [31].

In this work we discovered that the reactions of 2-alkyl-*N*-(cyanomethyl)pyridinium salts **1** with enaminones **2** proceed unexpectedly as a two-component domino sequence of cycloisomerization and cyclocondensation reactions, while cycloaddition processes were not observed (Scheme 1).

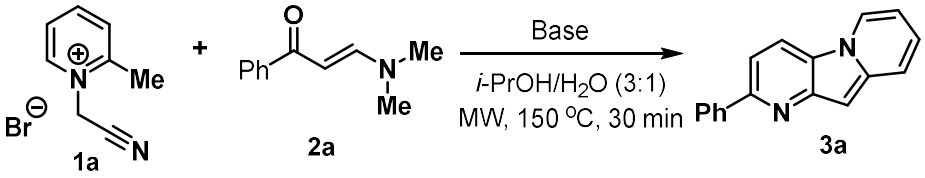


Scheme 1. General representation of the current work.

2. Results

Based on the previously investigated reaction [31], we started optimization of the conditions with the use of sodium acetate as base and an iso-propanol/water mixture as solvent (Table 1, entries 1–6). Varying the ratio of the starting materials and the base, the target compound **3a** was obtained with 50% yield (Table 1, entry 5). The use of other bases such as Et_3N, DIPEA, or NH_4OAc did not improve the yield (Table 1, entries 7–9). Inorganic bases did not ameliorate the process either (Table 1, entries 10 and 11). The variation of reaction time or temperature commonly led to diminished yields (Table 1, entries 12–14).

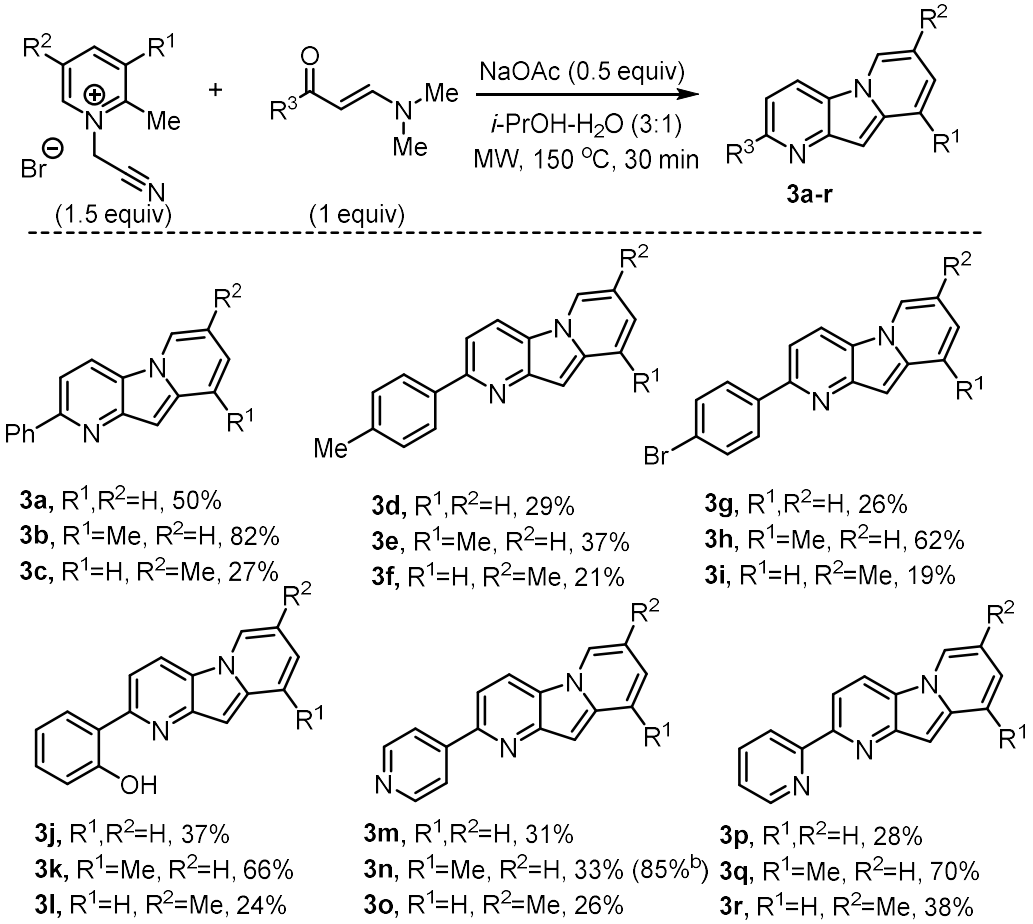
Table 1. Reaction conditions optimization.



Entry [a]	Base	1a: 2a: Base	Yield, % [b]
1	NaOAc	3: 1: 5	34
2		3: 1: 1	40
3		3: 1: 0.5	46
4		3: 1: 0.1	12
5		1.5: 1: 0.5	50
6		1: 1: 0.5	44
7	Et_3N	1.5: 1: 0.5	31
8	DIPEA	1.5: 1: 0.5	25
9	NH_4OAc	1.5: 1: 0.5	34
10	K_2CO_3	1.5: 1: 0.5	5
11	Cs_2CO_3	1.5: 1: 0.5	21
12 [c]	NaOAc	1.5: 1: 0.5	47
13 [d]	NaOAc	1.5: 1: 0.5	33
14 [e]	NaOAc	1.5: 1: 0.5	37

[a] A mixture of pyridinium salt **1** (0.591 mmol), enaminone **2** and the corresponding base in isopropyl alcohol (3 mL) and water (1 mL) was irradiated in a closed vessel in a microwave reactor Monowave 300 (Anton Paar GmbH) at 150 °C for 30 min. [b] Isolated yield. [c] The reaction time was prolonged from 30 to 60 min. [d] The reaction temperature was 120 °C. [e] The reaction temperature was 180 °C.

With the optimized conditions in hand, we went on to investigate the reaction scope. It turned out that the reaction of *N*-cyanomethyl-2,3-dimethylpyridinium salt with enaminone was more effective, and the target product **3b** was isolated with 82% yield (Scheme 2). On the contrary, the interaction of 2,5-dimethylpyridinium salt with the enaminone delivered product **3c** with 27% yield. When *p*-methylphenyl-substituted enaminone was used, the compounds **3d–f** were isolated with 21–37% yield. Bromo-substituted enaminones could be also used with various pyridinium salts to give indolizines **3g–i** with 19–62% yield. Pyridoindolizines **3j–l** with a phenol moiety were prepared with 24–66% yield. Moreover, we were pleased to find the pyridyl-containing enaminones to work successfully, producing the corresponding compounds **3m–r** with poor to moderate yields. It is worth noting that taking *N*-cyanomethyl-2,3-dimethylpyridinium bromide in a large excess increased the yield of the compound **3n** from 33% to 85%. Unfortunately, increasing the loading of the pyridinium salts in other cases did not result in yield improvement. The use of aliphatic enaminones (R^3 = Me or Et) in the reactions with *N*-cyanomethyl-2,3-dimethylpyridinium bromide generated complex mixtures, and no target product could be isolated. As a rule, the use of 2,3-dimethylpyridiniums resulted in greater yields of the target pyridoindolizines **3**. The scope of the enaminones included various aryl groups, even phenols and heterocycles, while the use of aliphatic enaminones was found to be a limitation of the method.



Scheme 2. The scope of the reaction between *N*-cyanomethyl-2-methylpyridinium bromides and various enaminones [a]. [a] General conditions: a mixture of pyridinium salt **1** (0.591 mmol), enaminone **2** (0.394 mmol), and sodium acetate (0.197 mmol) in isopropyl alcohol (3 mL) and water (1 mL) was placed into the microwave reactor and irradiated at 150 °C for 30 min. [b] The reaction was performed on 1.182 mmol scale of *N*-cyanomethyl-2,3-dimethylpyridinium salt.

The structure of pyridoindolizine **3b** was unambiguously determined by a single crystal X-ray diffraction study (Figure 1, CCDC 1922817).

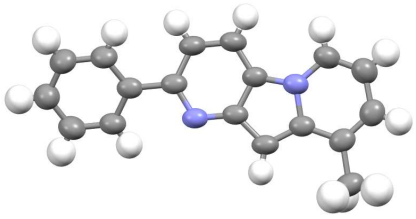
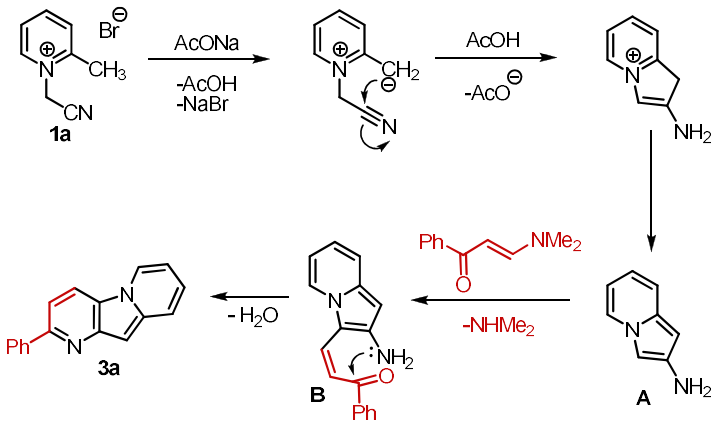


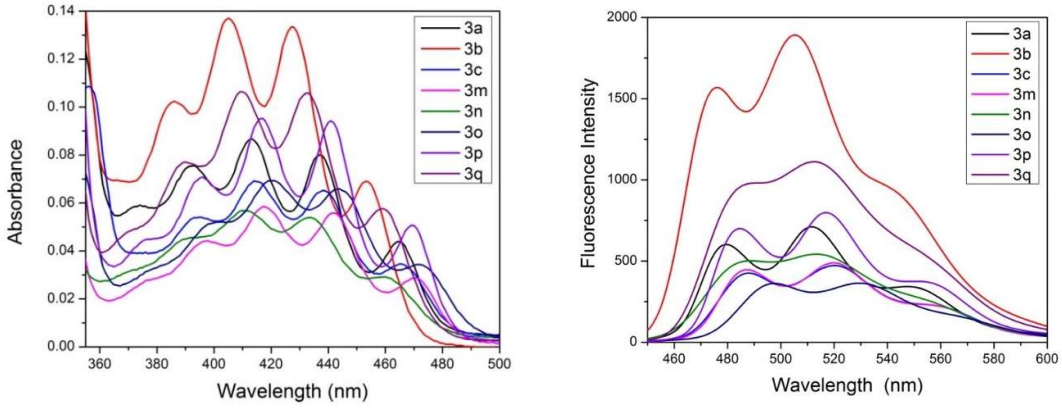
Figure 1. Crystal structure of **3b** (CCDC 1922817).

The reaction presumably starts with the intramolecular cyclization of a deprotonated α-methyl group on a nitrile moiety, eventually giving an aminoindolizine intermediate **A** [27] (Scheme 3). The interaction of the latter with enaminone produces an intermediate **B**. The cyclocondensation of **B** completes the reaction sequence, delivering pyridoindolizine **3a**. The intermediate **A** is evidently a highly nucleophilic species, containing a π-extensive pyrrole fragment combined with an amino group, readily reacting with the present electrophiles. Unfortunately, our attempts to isolate this intermediate failed. Even experiments in the absence of the enaminone generated multicomponent mixtures, pointing out the possibility for **A** to interact with the starting salt **1a**.



Scheme 3. Proposed mechanism for pyrido[2,3-*b*]indolizine formation.

The optical properties of the synthesized compounds were evaluated and all the spectra were measured in toluene solutions (Figure 2, Table 2, separate images are available in Supplementary Materials). Indolizines **3a–c**, **m–q** exhibited absorption peak maxima at 403–420 nm. The emission peak maxima lay in the green region 505–528 nm, and the largest Stokes shift 4950 cm^{-1} was registered for compound **3b**. The fluorescence quantum yields (FQYs) were determined using coumarin 153 as a standard [32]. The lowest FQY values of 55–63% were measured for 4-pyridyl-substituted pyridoindolizines **3m–o**, while the phenyl-substituted pyridoindolizine **3b** demonstrated the highest FQY, 82%. This optical behavior is in accordance with the literature. For instance, indolizines, condensed with isoindole [33], quinoline [34,35] or dihydropyrrole [36] cycles also emit in the blue to green region 410–556 nm with FQYs up to 77%.



(**a**) (**b**)

Figure 2. The absorbance (**a**) and emission (**b**) spectra of the above synthesized compounds in toluene.

Table 2. Photophysical properties of the synthesized compound.

Compound	Abs [a]	ε [b]	Emission [a]	FQY [c]	Stokes Shift
	[nm]	[(M cm)$^{-1}$ (10^9)]	[nm]	[%]	[cm^{-1}]
3a	413	1.652	511	77	4643
3b	404	1.616	505	82	4950
3c	414	1.656	520	64	4923
3m	418	1.672	519	57	4655
3n	410	1.640	513	63	4897
3o	420	1.680	528	55	4870
3p	416	1.664	516	64	4658
3q	409	1.636	512	77	4918

[a] Peak maximum. [b] Molar extinction coefficient. [c] Fluorescence quantum yield.

3. Materials and Methods

3.1. General Information

Starting reagents were purchased from commercial sources and were used without any additional purification. Enaminones **2** were prepared according to the literature procedures [37]. Microwave reactions were conducted in a Monowave 300 Microwave Reactor (Anton Paar GmbH, Graz, Austria). Column chromatography was performed using silica gel (230–400 mesh) and mixtures in different proportions of ethyl acetate with hexane as the mobile phase. Melting points were determined on a SMP-10 apparatus (Barloworld Scientific Limited, Stone, UK). ^{1}H NMR spectra were recorded on a 400 MHz spectrometer (Bruker, 100 MHz for ^{13}C NMR) and referenced to the residual signals of the solvent (for ^{1}H and ^{13}C). Chemical shifts are reported in parts per million (δ/ppm). Coupling constants are reported in Hertz (*J*/Hz). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; dd, doublet of doublets and td, triplet of doublets. Low resolution mass spectra were recorded with an LCMS-8040 triple quadrupole liquid chromatograph mass-spectrometer (Shimadzu corp., Tokyo, Japan). The reaction progress was monitored by TLC and the spots were visualized under UV light (254 or 365 nm). Elemental analysis was performed on a EuroVector EA-3000 instrument (EuroVector S.p.A., Milan, Italy).

*3.2. General Procedure for the Synthesis of Salts **1a–c***

Bromoacetonitrile (0.026 mol) was added to a stirred solution of corresponding pyridine (0.022 mol) in acetonitrile (10 mL). The reaction mixture was heated at reflux for 4 h. The precipitate was filtered, washed with acetonitrile, and dried in vacuum over P_2O_5.

N-(Cyanomethyl)-2-methylpyridinium bromide (**1a**). White powder; m.p. 195–196 °C (decomp.); yield, 3.56 g (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (1H, d, *J* = 6.1 Hz, H-6), 8.59–8.62 (1H, m, H-4), 8.16 (1H, d, *J* = 7.6 Hz, H-3), 8.06–8.08 (1H, m, H-5), 6.11 (2H, d, *J* = 1.5 Hz, CH_2-CN), 2.90 (3H, s, C_2-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 147.3, 146.1, 130.2, 126.1, 113.5, 45.1, 20.0. ESI MS: *m/z* 133 $[M]^+$. Elemental analysis calcd (%) for $C_8H_9BrN_2$: C 45.10; H 4.26; N 13.15; found: C 45.02; H 4.29; N 13.26.

N-(Cyanomethyl)-2,3-dimethylpyridinium bromide (**1b**). Light beige powder; m.p. 175–177 °C (decomp.); yield, 3.60 g (72%); IR (cm^{-1}): 2256 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (1H, d, *J* = 6.1 Hz, H-6), 8.53 (1H, d, *J* = 8.1 Hz, H-4), 7.98–8.01 (1H, m, H-5), 6.20 (2H, s, CH_2-CN), 2.83 (3H, s, C_2-CH_3), 2.52 (3H, s, C_3-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 147.3, 143.9, 139.2, 125.1, 113.7, 45.9, 19.3, 17.3. ESI MS: *m/z* 147 $[M]^+$. Elemental analysis calcd (%) for $C_9H_{11}BrN_2$: C 47.60; H 4.88; N 12.34; found: C 47.56; H 4.87; N 12.43.

N-(Cyanomethyl)-2,5-dimethylpyridinium bromide (**1c**). Light beige powder; m.p. 168–169 °C (decomp.); yield, 2.90 g (58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (1H, s, H-6), 8.49 (1H, d, *J* = 8.3 Hz, H-3), 8.08 (1H, d, *J* = 8.3 Hz, H-4), 6.07 (2H, s, CH_2-CN), 2.88 (3H, s, C_2-CH_3), 2.46 (3H, s, C_5-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 147.9, 145.3, 136.5, 129.5, 113.5, 44.9, 19.4, 17.4. ESI MS: *m/z* 147 $[M]^+$. Elemental analysis calcd (%) for $C_9H_{11}BrN_2$: C 47.60; H 4.88; N 12.34; found: C 47.57; H 4.91; N 12.45.

3.3. General Procedure for the Synthesis of Enaminones **2**

A mixture of dimethylformamide dimethylacetal (14.8 mmol) and methyl ketone (14.8 mmoL) was placed into the microwave reactor and irradiated at 150 °C for 15 min, then left to cool to room temperature. After cooling, the precipitate was filtered-off, washed twice with toluene and dried on air. *(E)-3-(Dimethylamino)-1-phenylprop-2-en-1-one* (**2a**). Yellow powder; m.p. 91–92 °C; yield, 1.17 g (45%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (2H, d, *J* = 6.9 Hz, Ph-H), 7.78 (1H, d, *J* = 12.4 Hz, CH=CH-NMe_2), 7.39–7.45 (3H, m, Ph-H), 5.70 (1H, d, *J* = 12.4 Hz, CH=CH-NMe_2), 3.11 (3H, s, N-CH_3), 2.90 (3H, s, N-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 154.4, 140.7, 131.0, 128.2 (2C), 127.6 (2C), 92.3, 45.1, 37.4. ESI MS: *m/z* 176 $[M + H]^+$.

(E)-3-(Dimethylamino)-1-(p-tolyl)prop-2-en-1-one (**2b**). Yellow powder; m.p. 88–89 °C; yield, 0.62 g (24%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (2H, d, *J* = 8.1 Hz, Ph-H), 7.77 (1H, d, *J* = 12.3 Hz, CH=CH-NMe_2), 7.19 (2H, d, *J* = 8.1 Hz, Ph-H), 5.70 (1H, d, *J* = 12.3 Hz, CH=CH-NMe_2), 3.09 (3H, s, N-CH_3), 2.89 (3H, s, N-CH_3), 2.37 (3H, s, Ph-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 153.9, 141.1, 137.7, 128.7 (2C), 127.5 (2C), 92.0, 44.8, 37.1, 21.3. ESI MS: *m/z* 190 $[M + H]^+$.

(E)-3-(Dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one (**2d**). Orange powder; m.p. 133–135 °C; yield, 1.58 g (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.98 (1H, s, C_2-OH), 7.87 (1H, d, *J* = 12.3 Hz, CH=CH-NMe_2), 7.69 (1H, dd, *J* = 8.1, 1.1 Hz, Ph-H), 7.35 (1H, m, Ph-H), 6.93 (1H, d, *J* = 8.1, Ph-H), 6.80 (1H, m, Ph-H), 5.77 (1H, d, *J* = 12.3 Hz, CH=CH-NMe_2), 3.18 (3H, s, N-CH_3), 2.96 (3H, s, N-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 163.0, 154.9, 134.0, 128.3, 120.4, 118.3, 118.1, 90.1, 45.5, 37.5. ESI MS: *m/z* 192 $[M + H]^+$.

(E)-3-(Dimethylamino)-1-(pyridin-4-yl)prop-2-en-1-one (**2e**). Yellow powder; m.p. 115–116 °C; yield, 0.886 g (34%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (2H, d, *J* = 5.6, Ar-H), 7.82 (1H, d, *J* = 11.9 Hz, CH=CH-NMe_2), 7.67 (2H, d, *J* = 5.6 Hz, Ar-H), 5.63 (1H, d, *J* = 11.9 Hz, CH=CH-NMe_2), 3.16 (3H, s, N-CH_3), 2.93 (3H, s, N-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 155.2, 149.9 (2C), 147.3, 121.2 (2C), 91.6, 45.2, 37.4. ESI MS: *m/z* 177 $[M + H]^+$.

3.4. General Procedure for the Synthesis of Compounds ***3a–r***

Method A (for **3a–g**, **3i**, **3m–r**): A mixture of pyridinium salt **1** (0.591 mmol), enaminone **2** (0.394 mmol), and sodium acetate (0.197 mmol) in isopropyl alcohol (3 mL) and water (1 mL) was placed into the microwave reactor and irradiated at 150 °C for 30 min. After cooling to room temperature,

the solvent was then evaporated under reduced pressure. The products were isolated by column chromatography on silica gel, eluting with ethyl acetate-hexane mixture in different proportions.

Method B (for **3h**, **3k**): A mixture of pyridinium salt **1** (0.591 mmol), enaminone **2** (0.394 mmol), and sodium acetate (0.197 mmol) in isopropyl alcohol (3 mL) and water (1 mL) was placed into the microwave reactor and irradiated at 150 °C for 30 min and left to cool to room temperature. After cooling, the precipitate was filtered-off and washed with ethanol, water (2 times) and ethanol again, then dried in air.

Method C (for **3j**, **3l**): A mixture of pyridinium salt **1** (0.591 mmol), enaminone **2** (0.394 mmol), and sodium acetate (0.197 mmol) in isopropyl alcohol (3 mL) and water (1 mL) was placed into the microwave reactor and irradiated at 150 °C for 30 min and left to cool to room temperature. The reaction mixture was diluted with water (70 mL) and extracted with DCM. The combined organic layer was dried over Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure. The residue was recrystallized from the isopropyl alcohol-DCM 3-1 mixture. The precipitate was filtered-off and washed with isopropyl alcohol for 3 times, then dried in air.

2-Phenylpyrido[2,3-b]indolizine (**3a**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 10. Light brown powder; m.p. 178–180 °C (decomp.); yield, 48 mg (50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.1 Hz, 1H, H-6), 8.15 (d, *J* = 8.6 Hz, 1H, H-3), 8.11 (d, *J* = 7.6 Hz, 2H, Ph-H), 7.61 (d, *J* = 8.6 Hz, 1H, H-4), 7.50–7.52 (m, 3H, H-9, Ph-H), 7.42–7.44 (m, 1H, Ph-H), 6.95–6.98 (m, 1H, H-7), 6.90 (s, 1H, H-10), 6.53–6.55 (m, 1H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 146.3, 140.7, 139.2, 128.6 (2C), 128.4, 127.5 (2C), 124.6, 123.4, 121.7, 119.4, 118.0, 112.2, 108.7, 92.5. ESI MS: *m*/*z* 245 $[M + H]^+$. Elemental analysis calcd (%) for $C_{17}H_{12}N_2$: C 83.58; H 4.95; N 11.47; found: C 83.54; H 4.98; N 11.59.

9-Methyl-2-phenylpyrido[2,3-b]indolizine (**3b**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 5. Yellow powder; m.p. 143–146 °C (decomp.); yield, 83 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.20 (m, 2H, H-3, H-6), 8.12 (d, *J* = 7.6 Hz, 2H, Ph-H), 7.62 (d, *J* = 8.6 Hz, 1H, H-4), 7.50–7.53 (m, 2H, Ph-H), 7.41–7.44 (m, 1H, м, Ph-H), 6.88 (s, 1H, H-10), 6.80 (d, *J* = 6.1 Hz, 1H, H-8), 6.52–6.55 (m, 1H, H-7), 2.51 (s, 3H, C_9-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 146.2, 140.6 (2C), 128.7 (3C), 128.4, 127.5 (2C), 122.3 (2C), 122.0, 118.3, 112.2, 109.0, 91.1, 18.5. ESI MS: *m*/*z* 259 $[M + H]^+$. Elemental analysis calcd (%) for $C_{18}H_{14}N_2$: C 83.69; H 5.46; N 10.84; found: C 83.66; H 5.51; N 10.95.

7-Methyl-2-phenylpyrido[2,3-b]indolizine (**3c**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 5. Dark yellow powder; m.p. 175–176 °C (decomp.); yield, 27 mg (27%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.6 Hz, 1H, H-3), 8.10 (d, *J* = 7.6 Hz, 2H, Ph-H), 8.08 (s, 1H, H-6), 7.59 (d, *J* = 8.6 Hz, 1H, H-4), 7.49–7.52 (m, 2H, Ph-H), 7.41–7.46 (m, 2H, H-9, Ph-H), 6.86–6.87 (m, 2H, H-8, H-10), 2.31 (3H, c, C_7-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 146.0, 140.7, 138.3, 128.6 (2C), 128.3, 127.5 (2C), 127.1, 121.8, 121.6, 119.0, 118.1 (2C), 112.0, 91.9, 18.3. ESI MS: *m*/*z* 259 $[M + H]^+$. Elemental analysis calcd (%) for $C_{18}H_{14}N_2$: C 83.69; H 5.46; N 10.84; found: C 83.62; H 5.48; N 10.99.

2-(p-Tolyl)pyrido[2,3-b]indolizine (**3d**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 10. Bright yellow powder; m.p. 181–182 °C (decomp.); yield, 29 mg (29%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 7.1 Hz, 1H, H-6), 8.67 (d, *J* = 8.6 Hz, 1H, H-3), 8.09 (d, *J* = 8.1 Hz, 2H, Ph-H), 7.80 (d, *J* = 8.6 Hz, 1H, H-4), 7.61 (d, *J* = 9.6 Hz, 1H, H-9), 7.30 (d, *J* = 8.1 Hz, 2H, Ph-H), 7.09–7.11 (m, 1H, H-7), 6.78 (s, 1H, H-10), 6.68–6.70 (m, 1H, H-8), 2.37 (s, 3H, Ph-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 145.4, 138.7, 137.9, 137.2, 129.3 (2C), 126.8 (2C), 126.3, 124.1, 121.5, 119.6, 118.7, 111.3, 108.8, 91.5, 20.8. ESI MS: *m*/*z* 259 $[M + H]^+$. Elemental analysis calcd (%) for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84; found: C 83.65; H 5.49; N 10.96.

9-Methyl-2-(p-tolyl)pyrido[2,3-b]indolizine (**3e**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 15. Yellow powder; m.p. 174 °C (decomp.); yield, 87 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 6.6 Hz, 1H, H-6), 8.66 (d, *J* = 8.6 Hz, 1H, H-3), 8.09 (d, *J* = 8.1 Hz, 2H, Ph-H), 7.80 (d, *J* = 8.6 Hz, 1H, H-4), 7.31 (d, *J* = 7.6 Hz, 2H, Ph-H), 6.93 (d, *J* = 6.1 Hz, 1H, H-8), 6.77 (s, 1H, H-10), 6.65–6.67 (m, 1H, H-7), 2.46 (s, 3H, C_9-CH_3), 2.37 (s, 3H, Ph-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1,

145.4, 139.7, 137.8, 137.2, 129.2 (2C), 127.2, 126.8 (2C), 123.9, 122.5, 122.1, 119.8, 111.4, 108.9, 90.3, 20.8, 18.0. ESI MS: *m*/*z* 273 $[M + H]^+$. Elemental analysis calcd (%) for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29; found: C 83.72; H 5.89; N 10.43.

7-Methyl-2-(p-tolyl)pyrido[2,3-b]indolizine (**3f**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 15. Dark yellow powder; m.p. 173–174 °C (decomp.); yield, 23 mg (21%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H, H-6), 8.60 (d, *J* = 8.6 Hz, 1H, H-3), 8.08 (d, *J* = 8.1 Hz, 2H, Ph-H), 7.77 (d, *J* = 8.6 Hz, 1H, H-4), 7.55 (d, *J* = 9.3, 1H, H-9), 7.30 (d, *J* = 7.6 Hz, 2H, Ph-H), 6.98 (d, *J* = 9.3 Hz, 1H, H-8), 6.73 (s, 1H, H-10), 2.37 (s, 3H, Ph-CH_3), 2.28 (s, 3H, C_7-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 145.3, 137.8, 137.6, 137.2, 129.2 (2C), 127.5, 126.7 (2C), 123.2, 121.3, 119.4, 118.3, 117.7, 111.1, 91.0, 20.8, 17.7. ESI MS: *m*/*z* 273 $[M + H]^+$. Elemental analysis calcd (%) for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29; found: C 83.84; H 5.90; N 10.33.

2-(4-Bromophenyl)pyrido[2,3-b]indolizine (**3g**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 15. Brown powder; m.p. 215–217 °C (decomp.); yield, 33 mg (26%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 7.1 Hz, 1H, H-6), 8.72 (d, *J* = 9.1 Hz, 1H, H-3), 8.15 (d, *J* = 8.6 Hz, 2H, Ph-H), 7.86 (d, *J* = 9.1 Hz, 1H, H-4), 7.69 (d, *J* = 8.6 Hz, 2H, Ph-H), 7.62 (d, *J* = 9.1 Hz, 1H, H-9), 7.11–7.14 (m, 1H, H-8), 6.80 (s, 1H, H-10), 6.70–6.73 (m, 1H, H-7). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 145.5, 139.1, 139.0, 131.6 (2C), 128.9 (2C), 126.4, 124.5, 122.1, 121.8, 119.9, 118.7, 111.3, 108.9, 91.6. ESI MS: *m*/*z* 324 $[M + H]^+$. Elemental analysis calcd (%) for $C_{17}H_{11}BrN_2$: C 63.18; H 3.43; N 8.67; found: C 63.25; H 3.40; N 8.63.

2-(4-Bromophenyl)-9-methylpyrido[2,3-b]indolizine (**3h**). Prepared according to the Method B. Gold powder; m.p. 192–193 °C (decomp.); yield, 82 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 7.1 Hz, 1H, H-6), 8.70 (d, *J* = 8.6 Hz, 1H, H-3), 8.16 (d, *J* = 8.3 Hz, 2H, Ph-H), 7.85 (d, *J* = 8.6 Hz, 1H, H-4), 7.69 (d, *J* = 8.3 Hz, 2H, Ph-H), 6.95 (d, *J* = 6.6 Hz, 1H, H-8), 6.79 (s, 1H, H-10), 6.66–6.69 (m, 1H, H-7), 2.46 (s, 3H, C_9-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 145.5, 140.0, 139.1, 131.5 (2C), 128.9 (2C), 127.2, 124.0, 122.7, 122.4, 122.0, 119.9, 111.4, 109.0, 90.4, 18.0. ESI MS: *m*/*z* 338 $[M + H]^+$. Elemental analysis calcd (%) for $C_{18}H_{13}BrN_2$: C 64.11; H 3.89; N 8.31; found: C 64.01; H 3.91; N 8.36.

2-(4-Bromophenyl)-7-methylpyrido[2,3-b]indolizine (**3i**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 15. Light brown powder; m.p. 177–178 °C (decomp.); yield, 25 mg (19%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H, H-6), 8.61 (d, *J* = 8.1 Hz, 1H, H-3), 8.14 (d, *J* = 7.6 Hz, 2H, Ph-H), 7.79 (d, *J* = 8.1 Hz, 1H, H-4), 7.67 (d, *J* = 7.6 Hz, 2H, Ph-H), 7.55 (d, *J* = 9.1 Hz, 1H, H-9), 6.99 (d, *J* = 9.1 Hz, 1H, H-8), 6.74 (s, 1H, H-10), 2.27 (s, 3H, C_7-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 145.3, 139.1, 137.9, 131.5 (2C), 128.9 (2C), 127.7, 123.2, 121.9, 121.5, 119.5, 118.3, 117.9, 111.1, 91.1, 17.7. ESI MS: *m*/*z* 338 $[M + H]^+$. Elemental analysis calcd (%) for $C_{18}H_{13}BrN_2$: C 64.11; H 3.89; N 8.31; found: C 64.17; H 3.92; N 8.34.

2-(Pyrido[2,3-b]indolizin-2-yl)phenol (**3j**). Prepared according to the Method C. Dark brown powder; m.p. 230–232 °C (decomp.); yield, 38 mg (37%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.09 (s, 1H, OH), 8.99 (d, *J* = 6.6 Hz, 1H, H-6), 8.85 (d, *J* = 8.9 Hz, 1H, H-3), 8.13 (d, *J* = 7.6 Hz, 1H, Ph-H), 8.06 (d, *J* = 8.9 Hz, 1H, H-4), 7.65 (d, *J* = 9.1 Hz, 1H, H-9), 7.29–7.31 (m, 1H, Ph-H), 7.18–7.20 (m, 1H, H-8), 6.92–6.96 (m, 2H, Ph-H), 6.84 (s, 1H, H-10), 6.78–6.80 (m, 1H, H-7). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 154.4, 141.6, 139.3, 130.8, 127.3, 126.3, 125.1, 121.6, 121.5, 119.7, 118.7, 118.6, 117.8, 110.2, 109.5, 90.3. ESI MS: *m*/*z* 261 $[M + H]^+$. Elemental analysis calcd (%) for $C_{17}H_{12}N_2O$: C 78.44; H 4.65; N 10.76; found: C 78.39; H 4.62; N 10.82.

2-(9-Methylpyrido[2,3-b]indolizin-2-yl)phenol (**3k**). Prepared according to the Method B. Gold powder; m.p. 179 °C (decomp.); yield, 71 mg (66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.10 (s, 1H, OH), 8.87 (d, *J* = 6.6 Hz, 1H, H-6), 8.84 (d, *J* = 8.6 Hz, 1H, H-3), 8.13 (d, *J* = 7.6 Hz, 1H, Ph-H), 8.06 (d, *J* = 8.6 Hz, 1H, H-4), 7.29–7.31 (m, 1H, Ph-H), 7.01 (d, *J* = 6.6 Hz, 1H, H-8), 6.92–6.96 (m, 2H, Ph-H), 6.84 (s, 1H, H-10), 6.73–6.76 (m, 1H, H-7), 2.47 (s, 3H, C_9-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 154.3, 141.5, 140.3, 130.8, 127.3, 127.2, 123.9, 123.4, 122.1, 121.6, 119.7, 118.6, 117.9, 110.3, 109.6, 89.2, 17.9. ESI MS: *m*/*z* 275

$[M + H]^+$. Elemental analysis calcd (%) for $C_{18}H_{14}N_2O$: C 78.81; H 5.14; N 10.21; found: C 78.77; H 5.16; N 10.30.

2-(7-Methylpyrido[2,3-b]indolizin-2-yl)phenol (**3l**). Prepared according to the Method C. Brown powder; m.p. 226–227 °C (decomp.); yield, 26 mg (24%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.13 (s, 1H, OH), 8.81 (s, 1H, H-6), 8.78 (d, *J* = 8.9 Hz, 1H, H-3), 8.11 (d, *J* = 7.1 Hz, 1H, Ph-H), 8.03 (d, *J* = 8.9 Hz, 1H, H-4), 7.60 (d, *J* = 9.1 Hz, 1H, H-9), 7.28–7.30 (m, 1H, Ph-H), 7.07 (d, *J* = 9.1 Hz, 1H, H-8), 6.91–6.95 (m, 2H, Ph-H), 6.78 (s, 1H, H-10), 2.30 (s, 3H, C_9-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 154.1, 141.4, 138.3, 130.7, 128.4, 127.2, 123.2, 121.3, 121.2, 119.7, 118.6 (2C), 118.3, 117.8, 110.0, 89.8, 17.7. ESI MS: *m*/*z* 275 $[M + H]^+$. Elemental analysis calcd (%) for $C_{18}H_{14}N_2O$: C 78.81; H 5.14; N 10.21; found: C 78.83; H 5.11; N 10.28.

2-(Pyridin-4-yl)pyrido[2,3-b]indolizine (**3m**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 5. Orange powder; m.p. 196–199 °C (decomp.); yield, 30 mg (31%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 5.9 Hz, 2H, Py-H), 8.29 (d, *J* = 6.6 Hz, 1H, H-6), 8.21 (d, *J* = 8.6 Hz, 1H, H-3), 8.01 (d, *J* = 5.9 Hz, 2H, Py-H), 7.66 (d, *J* = 8.6 Hz, 1H, H-4), 7.52 (d, *J* = 9.6 Hz, 1H, H-9), 7.00–7.03 (m, 1H, H-7), 6.90 (s, 1H, H-10), 6.58–6.60 (m, 1H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 150.2 (2C), 147.7, 146.5, 139.9, 124.7, 124.0, 122.4, 121.7 (2C), 119.6, 118.2, 111.8, 109.2, 92.7. ESI MS: *m*/*z* 246 $[M + H]^+$. Elemental analysis calcd (%) for $C_{16}H_{11}N_3$: C 78.35; H 4.52; N 17.13; found: C 78.31; H 4.55; N 17.20.

9-Methyl-2-(pyridin-4-yl)pyrido[2,3-b]indolizine (**3n**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 5. Light beige powder; m.p. 173–174 °C (decomp.); yield, 34 mg (33%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.8 Hz, 1H, Py-H), 8.18–8.20 (m, 2H, H-3, H-6), 8.01 (d, *J* = 5.8 Hz, 2H, Py-H), 7.65 (d, *J* = 8.6 Hz, 1H, H-4), 6.86 (s, 1H, H-10), 6.82 (d, *J* = 6.6 Hz, 1H, H-8), 6.54–6.56 (m, 1H, H-7), 3.18 (s, 3H, C_9-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 150.5, 150.2 (2C), 147.7, 141.1, 128.5, 123.6, 122.5, 122.3, 121.6 (2C), 118.3, 111.8, 109.3, 91.2, 18.5. ESI MS: *m*/*z* 260 $[M + H]^+$. Elemental analysis calcd (%) for $C_{17}H_{13}N_3$: C 78.74; H 5.05; N 16.20; found: C 78.71; H 5.09; N 16.29.

7-Methyl-2-(pyridin-4-yl)pyrido[2,3-b]indolizine (**3o**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 5. Light beige powder; m.p. 223–225 °C (decomp.); yield, 27 mg (26%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 5.8 Hz, 2H, Py-H), 8.21 (d, *J* = 8.6 Hz, 1H, H-3), 8.11 (s, 1H, H-6), 8.03 (d, *J* = 5.8 Hz, 2H, Py-H), 7.66 (d, *J* = 8.6 Hz, 1H, H-4), 7.47 (d, *J* = 8.9 Hz, 1H, H-9), 6.90 (d, *J* = 8.9 Hz, 1H, H-8), 6.87 (s, 1H, H-10), 2.33 (s, 3H, C_7-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 150.1 (2C), 147.9, 146.4, 139.0, 127.6, 122.2, 121.9, 121.7 (2C), 119.1, 118.6, 118.1, 111.6, 92.2, 18.3. ESI MS: *m*/*z* 260 $[M + H]^+$. Elemental analysis calcd (%) for $C_{17}H_{13}N_3$: C 78.74; H 5.05; N 16.20; found: C 78.69; H 5.06; N 16.32.

2-(Pyridin-2-yl)pyrido[2,3-b]indolizine (**3p**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 10. Yellow powder; m.p. 159–162 °C (decomp.); yield, 27 mg (28%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.0 Hz, 1H, Pyr-H), 8.60 (d, *J* = 8.1 Hz, 1H, Py-H), 8.38 (d, *J* = 8.6 Hz, 1H, H-3), 8.33 (d, *J* = 7.1 Hz, 1H, H-6), 8.28 (d, *J* = 8.6 Hz, 1H, H-4), 7.86 (m, 1H, Py-H), 7.52 (d, *J* = 9.1 Hz, 1H, H-9), 7.31–7.33 (m, 1H, Py-H), 6.99–7.01 (m, 1H, H-7), 6.91 (s, 1H, H-10), 6.58–6.60 (1H, м, H-8), 6.58–6.60 (m, 1H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 153.4, 149.0, 145.9, 139.5, 136.9, 124.7, 123.6, 123.3, 122.8, 121.5, 119.5, 118.2, 112.5, 108.9, 92.5. ESI MS: *m*/*z* 246 $[M + H]^+$. Elemental analysis calcd (%) for $C_{16}H_{11}N_3$: C 78.35; H 4.52; N 17.13; found: C 78.32; H 4.57; N 17.14.

9-Methyl-2-(pyridin-2-yl)pyrido[2,3-b]indolizine (**3q**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 10. Lime-green powder; m.p. 124–127 °C (decomp.); yield, 71 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.0 Hz, 1H, Py-H), 8.61 (d, *J* = 7.6 Hz, 1H, Py-H), 8.37 (d, *J* = 8.6 Hz, 1H, H-3), 8.25 (d, *J* = 8.6 Hz, 1H, H-4), 8.22 (d, *J* = 7.1 Hz, 1H, H-6), 7.84–7.87 (m, 1H, Py-H), 7.30–7.32 (m, 1H, Py-H), 6.88 (s, 1H, H-10), 6.80 (d, *J* = 6.1 Hz, 1H, H-8), 6.53–6.55 (m, 1H, H-7), 2.51 (s, 3H, C_9-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 153.3, 149.0, 145.9, 140.7, 136.8, 128.4, 123.4, 123.2, 122.4, 122.1, 121.5, 118.3, 112.5, 109.1, 91.1, 18.5. ESI MS: *m*/*z* 260 $[M + H]^+$. Elemental analysis calcd (%) for $C_{17}H_{13}N_3$: C 78.74; H 5.05; N 16.20; found: C 78.70; H 5.07; N 16.25.

7-Methyl-2-(pyridin-4-yl)pyrido[2,3-b]indolizine (**3r**). Prepared according to the Method A. Eluent ethyl acetate-hexane 1: 7. Brown powder; m.p. 74–79 °C (decomp.); yield, 39 mg (38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.0 Hz, 1H, Py-H), 8.59 (d, *J* = 8.1 Hz, 1H, Py-H), 8.35 (d, *J* = 8.6 Hz, 1H, H-3), 8.25 (d, *J* = 8.6 Hz, 1H, H-4), 8.13 (s, 1H, H-6), 7.83–7.86 (m, 1H, Py-H), 7.47 (d, *J* = 9.1 Hz, 1H, H-9), 7.30–7.32 (m, 1H, Py-H), 6.86–6.89 (m, 2H, H-8, H-10), 2.33 (s, 3H, C_7-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 153.2, 149.0, 146.0, 138.5, 136.8, 127.1, 123.2, 122.6, 121.9, 121.5, 119.0, 118.2, 118.0, 112.3, 92.1, 18.3. ESI MS: *m*/*z* 260 $[M + H]^+$. Elemental analysis calcd (%) for $C_{17}H_{13}N_3$: C 78.74; H 5.05; N 16.20; found: C 78.71; H 5.09; N 16.33.

4. Conclusions

In conclusion, we discovered a novel domino route to condensed indolizines—pyrido[2,3-*b*] indolizines, containing various aromatic or heteroaromatic moieties at C(2) and alkyl groups at C(7) or C(9). The route is based on the interaction of 2-alkyl-*N*-(cyanomethyl)pyridinium salts with enaminones. The synthesized compounds are effective fluorophores, emitting green light with FQYs up to 82%.

Supplementary Materials: The supplementary materials are available online.

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