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Tandem Double [3 + 2] Cycloaddition Reactions at Both C-1 and C-3 Atoms of *N*-Cyanomethylisoquinolinium Ylide

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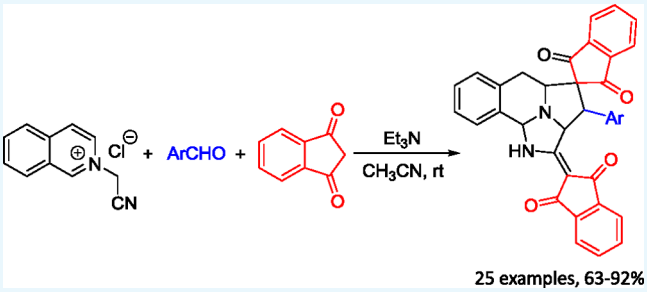
Supporting Information

ABSTRACT: The base-promoted cycloaddition reaction of *N*-cyanomethylisoquinolinium chloride with 2-arylidene-1,3-indanediones in dry tetrahydrofuran resulted in the expected spiro[indene-2,1′-pyrrolo[2,1-*a*]isoquinoline] derivatives. However, the triethylamine-promoted three-component reaction of *N*-cyanomethylisoquinolinium chloride, aromatic aldehydes, and two molecules of 1,3-indanediones in acetonitrile afforded unique spiro[benzo[*f*]imidazo[5,1,2-*cd*]-indolizine-4,2′-indene] derivatives in satisfactory yields through tandem double [3 + 2] cycloaddition reactions.



INTRODUCTION

As one of the reactive heteroaromatic *N*-ylides, isoquinolinium ylides have been attracting continuous attention due to their easy preparation and versatile reactivity and become one of the most valuable synthons for the construction of nitrogen-containing heterocyclic systems.[1,2] Isoquinolinium ylides can be conveniently generated in situ from deprotonation of the corresponding *N*-substituted methylisoquinolinium salts in basic media.[3] The most common reaction of isoquinolinium ylide is the [3 + 2] cycloaddition reaction with various 1,3-dipolarophiles to give pyrrolo[2,1-*a*]isoquinoline derivatives (eq 1 in Scheme 1).[4] By employing various substrates and adopting different reaction conditions, these kinds of reactions have resulted in many pyrrolo[2,1-*a*]isoquinoline derivatives and related spiro or polycyclic systems with valuable molecular diversity and regulated diastereoselectivity.[5] In recent years, new synthetic reaction patterns of isoquinolinium ylides have been successfully revealed, which indicated that there are many unknown characters in the chemistry of isoquinolinium ylides.[6] For examples, the base-promoted reaction of *N*-phenacylisoquinolinium ylides with arylidene Meldrum acid resulted in stable zwitterionic salts.[7a] More notably, the isoquinolinium zwitterionic salts with an unusual C-4 substitution pattern were also obtained from the reaction of *N*-benzylisoquinolinium ylides with aromatic aldehydes and cyclic 1,3-dicarbonyl compounds (eq 2 in Scheme 1).[7b] The base-mediated three-component reaction of *N*-alkoxycarbonylmethylisoquinolinium salts, aromatic aldehydes, and 1,3-indanedione afforded the unprecedented complex polycyclic compounds, in which the generated isoquinilonium ylide not only behaved as a reactive 1,3-dipole but also acted as a useful diene to accomplish sequential 1,3-dipolar cycloaddition and the Diels−Alder reaction (eq 3 in Scheme 1).[8] In continuation of our aim to exploit the potential synthetic applications of the heteroaromatic *N*-ylides,[8] herein, we wish to reveal the unprecedented reactions of *N*-cyanomethylisoquinolinium chloride with 2-arylidene-1,3-indanediones under different reaction conditions. The reaction not only gave the normal spiro[indene-2,1′-pyrrolo[2,1-*a*]isoquinoline] derivatives through the normal 1,3-dipolar cycloaddition reaction but also afforded unique spiro[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2′-indene] derivatives by the domino cyclization process (eq 4 in Scheme 1).

RESULTS AND DISCUSSION

Initially, the conditions for the reaction of *N*-cyanomethylisoquinolinium chloride with 2-benzylidene-1,3-indanedione were briefly examined on the basis of our previously established reaction conditions for the *N*-phenacyl and *N*-ethoxycarbonylmethylisoquinolinium salts.[8] When the reaction was carried out in the solvent of MeOH, EtOH, CH_3CN and dry tetrahydrofuran (THF) in the presence of triethylamine as base for about 10 h, the expected spiro[indene-2,1′-pyrrolo[2,1-*a*]isoquinoline], **1a**, was obtained in 47, 51, 56, and 81% yields. When 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and piperidine were used as base, the reaction in dry THF gave 45, 59, and 57% yields. When the triethylamine-promoted reaction was carried out in THF at about 50 °C for 5 h, the yield of product **1a** greatly decreased to 31%. Thus, in the presence of slight excess triethylamine, the reactions of *N*-cyanomethylisoquinolinium chloride with various 2-arylidene-1,3-indanediones in dry THF at room temperature (rt) for about 10 h afforded spiro[indene-2,1′-pyrrolo[2,1-*a*]isoquinolines] **1a−f** in good yields. The structures of spiro compounds were successfully characterized by IR, high-resolution mass spectrometry (HRMS), ^{1}H NMR, and ^{13}C NMR spectra. It should be pointed out that spiro

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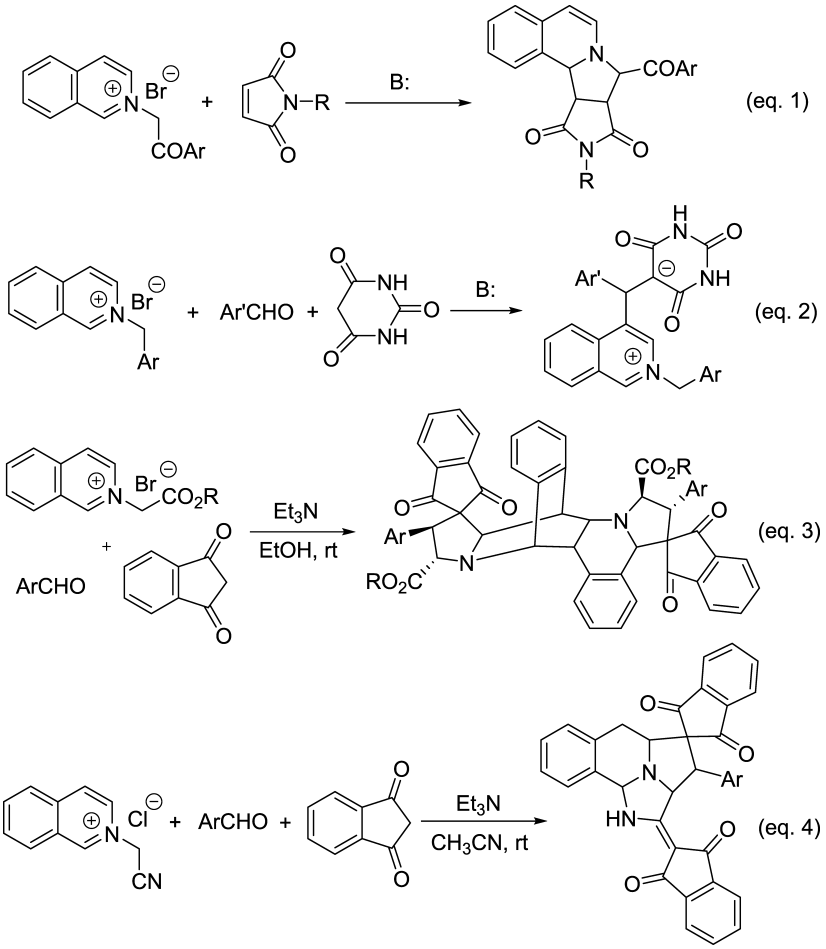
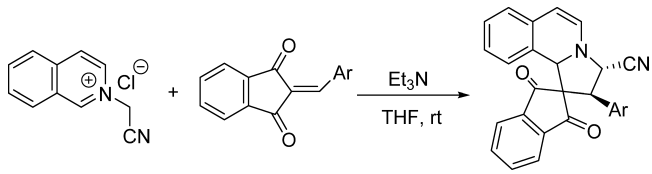
Scheme 1. Illustration of Typical Reaction Patterns of Isoquinolinium Ylides



compounds **1a–f** are not very stable in solution, especially in the protonic solvent or hydrous solvent. It must be quick to separate samples and record their ^{1}H and ^{13}C NMR spectra. The formation of spiro[indene-2,1′-pyrrolo[2,1-*a*]-isoquinolines] **1a–f** obviously took place from the normal [3 + 2] cycloaddition of the in situ-generated isoquinolinium ylide with 2-arylidene-1,3-indanediones. The ^{1}H NMR and ^{13}C NMR spectra clearly indicated that only one diastereoisomer exists in the obtained samples of the products. On the basis of NMR spectra and previously obtained results, we tentatively assigned the spiro compounds **1a–f** having trans-configuration.

Because 2-arylidene-1,3-indanediones were initially prepared from the base-catalyzed condensation of aromatic aldehydes with 1,3-indanedione, it is natural to test the possibility of converting the above reaction to a one-pot three-component reaction. When equal amounts of *N*-cyanomethylisoquinolinium chloride, benzaldehyde, and 1,3-indanedione were stirred in ethanol in the presence of triethylamine, instead of the formation of above spiro[indene-2,1′-pyrrolo[2,1-*a*]-isoquinoline], a unique spiro[benzo[*f*]imidazo[5,1,2-*cd*]-indolizine-4,2′-indene] **2a** was obtained in 31% yield, in which two scaffolds of 1,3-indanedione were eventually included in the molecule. When excess 1,3-indanedione was employed and triethylamine was used as the base, the reaction in MeOH, EtOH, and CH_3CN gave new product **2a** in 51, 67, and 83% yields, respectively. When other bases such as DABCO, DBU, and Na_2CO_3 were used as the base, the yield of the product did not increase. Prolonging reaction time or carrying out the reaction at an elevated temperature also caused a decrease in yield. Thus, the best conditions for this reaction are carrying out the reaction in acetonitrile at room temperature in the presence of triethylamine as the base promoter. Under these convenient reaction conditions, the reaction scope was investigated, and the obtained results are summarized in Tables 1 and 2. We were pleased to find that

Table 1. Synthesis of Spiro[indene-2,1′-pyrrolo[2,1-*a*]isoquinolines] 1a–f[a]



entry	compd	Ar	yield (%)[b]
1	**1a**	C_6H_5	81
2	**1b**	*o*-$CH_3OC_6H_4$	84
3	**1c**	*p*-$CH_3C_6H_4$	79
4	**1d**	*p*-BrC_6H_4	83
5	**1e**	*p*-ClC_6H_4	81
6	**1f**	*p*-(*t*-Bu)C_6H_4	61

[a]Reaction conditions: isoquinolinium salt (0.5 mmol), 2-arylidene-1,3-indanedione (0.5 mmol), Et_3N (0.6 mmol), THF (15.0 mL), rt, 10 h. [b]Isolated yields.

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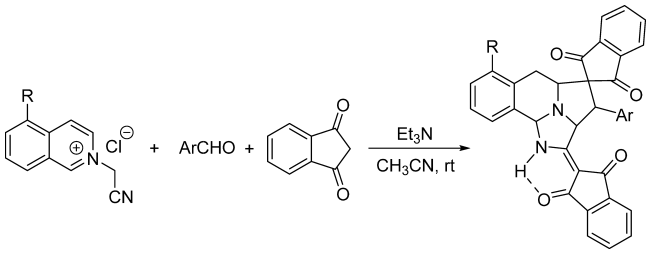
Table 2. Synthesis of Polycyclic Spiro Compounds 2a−u[a]



entry	compd	R	Ar	yield (%)[b]
1	**2a**	H	C_6H_5	83
2	**2b**	H	*o*-HOC_6H_4	78
3	**2c**	H	*o*-$CH_3OC_6H_4$	87
4	**2d**	H	*o*-ClC_6H_4	89
5	**2e**	H	*o*-BrC_6H_4	85
6	**2f**	H	*m*-$CH_3C_6H_4$	86
7	**2g**	H	*m*-FC_6H_4	81
8	**2h**	H	*m*-$NO_2C_6H_4$	82
9	**2i**	H	*p*-$CH_3C_6H_4$	92
10	**2j**	H	*p*-$(CH_3)_2NC_6H_4$	73
11	**2k**	H	*p*-BrC_6H_4	87
12	**2l**	H	*p*-ClC_6H_4	91
13	**2m**	H	*p*-*t*-$C(CH_3)_3C_6H_4$	81
14	**2n**	H	*p*-$NO_2C_6H_4$	79
15	**2o**	H	2-HO-4-ClC_6H_3	72
16	**2p**	H	2-furan	69
17	**2q**	H	2-thiophen	78
18	**2r**	H	2-Py	83
19	**2s**	H	3-Py	76
20	**2t**	H	4-Py	74
21	**2u**	H	benzoyl	85
22	**2v**	Br	*p*-ClC_6H_4	81
23	**2w**	Br	*p*-$NO_2C_6H_4$	83
24	**2x**	H	*n*-Hex	70
25	**2y**	Br	*n*-Hex	63

[a]Reaction conditions: isoquinolinium salt (0.5 mmol), aldehyde (0.5 mmol), 1,3-indanedione (1.1 mmol), Et_3N (1.2 mmol), CH_3CN (15.0 mL), rt, 8 h. [b]Isolated yields.

various aromatic aldehydes with different substituents reacted smoothly to give spiro polycyclic compounds **2a−o** in high yields. Some heterocylic substituted aldehydes, such as 2-furfural, 2-thiophenecarbaldehyde, picolinaldehyde, nicotinaldehyde, and isonicotinaldehyde, also gave desired products **2p−t** in good yields. *n*-Heptaldehyde was also successfully employed in the reaction to give spiro products **2x and 2y** in good yields. Phenylglyoxal also afforded benzoyl-substituted product **2y** in 85% yield. On the other hand, the reaction with substituted isoquinolines such as 5-bromoisoquinoline also resulted in spiro products **2v and 2w** in satisfactory yields. These results indicated that this reaction has a wide variety of substrates.

The structures of spiro compounds **2a−y** were successfully determined by various spectroscopy techniques. The single-crystal structures of two representative compounds **2i** and **2l** were successfully determined by the X-ray diffraction method (Figure 1). From Figures 1 and 2, it can be seen that both C-1 and C-3 atoms of isoquinolinium ylide took part in the reaction. Although the pyridinium salts sometimes undergo the double [3 + 2] cycloaddition reaction at both C-1 and C-6 atoms to give novel pyrrolo[2,1,5-*cd*]indolizine derivatives,[10] it is rare for isoquinolinium salts to undergo such double [3 + 2]

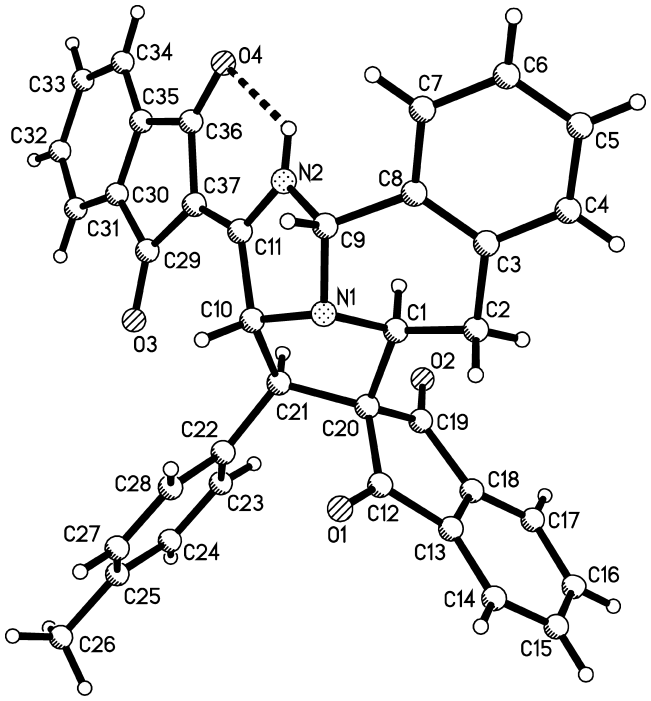


Figure 1. Single-crystal structure of compounds **2i**.

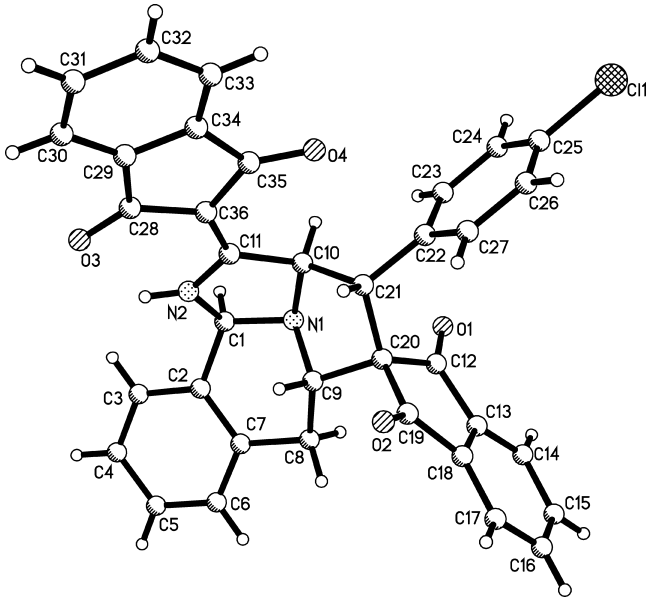


Figure 2. Single-crystal structure of compounds **2l**.

cycloaddition reactions at both C-1 and C-3 atoms of the isoquinoline ring. The only example is the early report about the formation of benzocyclo[3.2.2]azines in lower yield from the double [3 + 2] cycloaddition reaction of isoquinolinium ylide with *N*-methylmaleimide.[11a] Another related example is the NHC-catalyzed enantioselective dearomatizing double Mannich reaction at both C-1 and C-3 atoms of isoquinolinium salts to give 8-azabicyclo[3.2.1]octane derivatives.[11b] On the other hand, there are several reports about the cyano group to take part in the sequential cyclization process in the reactions of *N*-cyanomethylpyridinium salts and *N*-cyanomethylisoquinolinium salts.[12] Here, the normal [3 + 2] cycloaddition at 1,2-positions of isoquinolinium ylide was replaced by the abnormal

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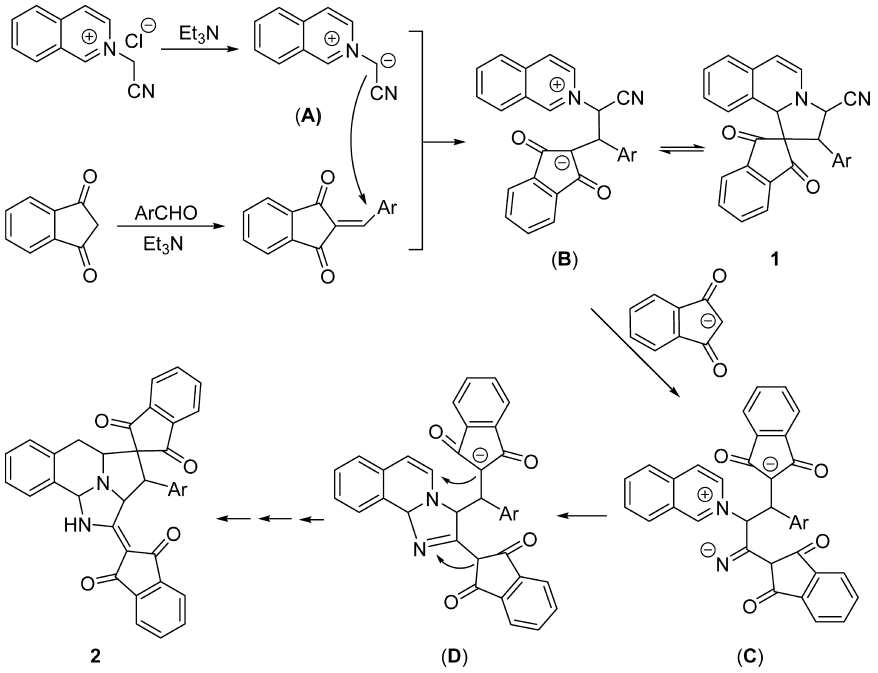
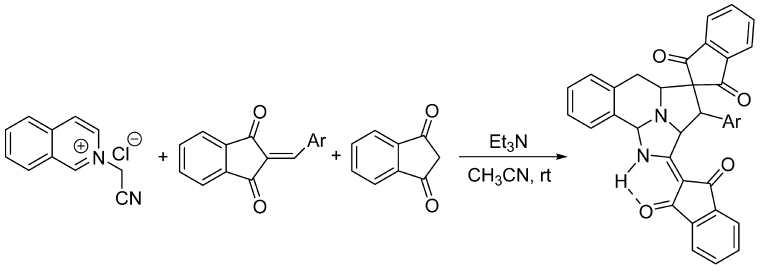
Scheme 2. Proposed Reaction Mechanism



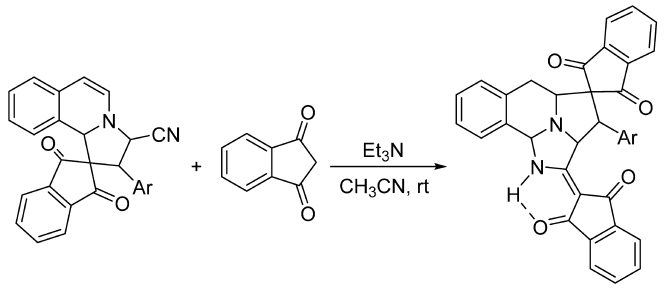
Scheme 3. Control Experiments



2a: Ar = C_6H_5, 90%

2f: Ar = *o*-$CH_3OC_6H_4$, 93%

2k: Ar = *p*-BrC_6H_4, 92%



2a: Ar = C_6H_5, 69%

2m: Ar = *p*-*t*-BuC_6H_4, 62%

[3 + 2] cycloaddition at 2,3-positions of isoquinolinium ylide and internal cyclization at the C-1 position. This kind of reaction pattern might be observed for the first time in the reactions of isoquinolinium ylides. It is also noticed that this reaction successfully provided a convenient dearomatizing method for the isoquinoline ring.

Although the exact mechanism is not completely understood at the present time, a plausible reaction mechanism is proposed on the basis of the above results and the previously reported reactions (Scheme 2).[9−12] First, an isoquinolinium ylide (**A**) was generated from deprotonation of *N*-cyanomethylisoquinolinium salt. In the meantime, 2-arylidene-1,3-indanedione was also formed from the Knoevenagel condensation of the

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respective aromatic aldehyde with 1,3-indanedione in the presence of triethylamine. Second, a Michael addition of a isoquinolinium ylide (**A**) to 2-arylidene-1,3-indanedione afforded a zwitterionic intermediate (**B**). Third, the intermolecular cyclization resulted in spiro compound **1** in dry THF. Spiro compound **1** is not very stable and is in equilibrium with the zwitterionic intermediate (**B**) in acetonitrile. Then, the nucleophilic addition of the carbanion of 1,3-indanedione to the cyano group generated an imine intermediate (**C**), which in turn added to the cyclic iminium ion to give a cyclic intermediate (**D**). Finally, the intermolecular nucleophilic addition of carbanion to enamine resulted in polycyclic product **2** with the corresponding protonation and proton immigration process. Here, the unique dual reactivities of the cyano group and 1,3-indanedione are the crucial factors for completing this reaction sequence.

To probe the credibility of our proposed mechanistic scheme and shed more light on the formation of polycyclic spiro compounds, further control experiments were carried out (Scheme 3). First, an equal combination of 1,3-indanedione and initially prepared 2-arylidene-1,3-indanedione was used in the three-component reaction, and corresponding spiro compounds **2a**, **2f**, and **2k** were obtained in very high yields, which clearly indicated that 2-arylidene-1,3-indanedione was the intermediate in the reaction. Second, the reaction of initially prepared spiro[indene-2,1′-pyrrolo[2,1-*a*]isoquinolines] **1** with 1,3-indandione in acetonitrile in the presence of triethylamine for overnight resulted in polycyclic spiro compounds **2a** and **2m** in moderate yields, which clearly showed that spiro[indene-2,1′-pyrrolo[2,1-*a*]isoquinolines] **1** decomposed to the zwitterionic intermediate (**B**) in the solution, which is the key intermediate in the above proposed mechanism.

CONCLUSIONS

In summary, we have successfully investigated the base-promoted cycloaddition reaction of *N*-cyanomethylisoquinolinium chloride with 2-arylidene-1,3-indanediones under different reaction conditions. The reaction not only gave the normal spiro[indene-2,1′-pyrrolo[2,1-*a*]isoquinoline] derivatives through the normal 1,3-dipolar cycloaddition reaction but also afforded unique spiro[benzo[*f*]imidazo[5,1,2-*cd*]-indolizine-4,2′-indene] derivatives via tandem double [3 + 2] cycloaddition reactions. The reaction originated from the versatile reactivity of the well-known heteroaromatic *N*-ylides and successfully revealed a new reaction pattern for isoquinolinium ylides in heterocyclic synthesis. The potential applications of this convenient synthetic protocol in organic and medicinal chemistry might be significant.

EXPERIMENTAL SECTION

General Procedure for the Preparation of Spiro-[indene-2,1′-pyrrolo[2,1-*a*]isoquinolines] 1a−f. A mixture of *N*-cyanomethylisoquinolinium chloride (0.5 mmol), 2-arylidene-1,3-indanedione (0.5 mmol), and triethylamine (0.6 mmol) in dry tetrahydrofuran (15.0 mL) was stirred at room temperature for 10 h. The solvent was removed at reduced pressure by rotatory evaporation. The residue was titrated with a mixture of light petroleum and methylene dichloride to give the pure solid.

*1,3-Dioxo-2′-phenyl-1,2′,3,3′-tetrahydro-10b′H-spiro-[indene-2,1′-pyrrolo[2,1-a]isoquinoline]-3′-carbonitrile (**1a**).* Yellow solid, 81%, mp 161−163 °C ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.78−7.76 (m, 4H, Ar H), 7.20−7.16 (m, 5H, Ar H), 6.94 (t, J = 7.2 Hz, 1H, Ar H), 6.85 (d, J = 7.6 Hz, 1H, Ar H), 6.59−6.35 (m, 2H, Ar H), 6.23 (d, J = 7.6 Hz, 1H, CH), 5.84 (s, 1H, CH), 5.68 (d, J = 10.0 Hz, 1H, CH), 5.36 (d, J = 7.6 Hz, 1H, CH), 4.29 (d, J = 10.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 198.1, 142.6, 137.0, 134.0, 132.5, 132.1, 129.3, 129.2, 129.0, 128.5, 125.7, 125.2, 125.1, 125.0, 123.2, 119.3, 100.3, 71.1, 71.0, 57.1, 53.9; IR (KBr) υ: 3061, 2924, 2860, 2238, 1810, 1696, 1592, 1491, 1420, 1244, 1033, 854, 760 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{19}N_2O_2$([M + H]$^+$): 403.1441, found: 403.1452.

*2′-(2-Methoxyphenyl)-1,3-dioxo-1,2′,3,3′-tetrahydro-10b′H-spiro[indene-2,1′-pyrrolo[2,1-a]isoquinoline]-3′-carbonitrile (**1b**).* Yellow solid, 84%, mp 162−164 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.79−7.71 (m, 4H, Ar H), 7.41 (d, J = 7.2 Hz, 1H, Ar H), 7.15 (t, J = 7.6 Hz, 1H, Ar H), 6.98−6.91 (m, 3H, Ar H), 6.65 (d, J = 7.6 Hz, 1H, CH), 6.61−6.56 (m, 2H, Ar H), 6.19 (d, J = 7.6 Hz, 1H, Ar H), 5.66 (d, J = 7.6 Hz, 1H, CH), 5.47−5.45 (m 2H, CH), 4.23−4.22 (m, 1H, CH), 3.12 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 198.1, 156.7, 142.2, 136.5, 132.6, 129.7, 128.9, 127.9, 125.6, 125.2, 124.9, 122.9, 120.8, 110.7, 69.8, 68.2, 56.0, 54.6, 49.4; IR (KBr) υ: 3031, 2928, 2269, 1738, 1704, 1593, 1548, 1540, 1359, 1262, 836, 813, 769, 675 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{21}N_2O_3$([M + H]$^+$): 433.1547, found: 433.1560.

*1,3-Dioxo-2′-(p-tolyl)-1,2′,3,3′-tetrahydro-10b′H-spiro-[indene-2,1′-pyrrolo[2,1-a]isoquinoline]-3′-carbonitrile (**1c**).* Yellow solid, 79%, mp 181−183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91−7.90 (m, 1H, Ar H), 7.73−7.69 (m, 1H, Ar H), 7.63−7.62 (m, 2H, Ar H), 7.06 (d, J = 8.0 Hz, 2H, Ar H), 6.97−6.92 (m, 3H, Ar H), 6.83 (d, J = 7.2 Hz, 1H, Ar H), 6.54 (d, J = 7.6 Hz, 1H, Ar H), 6.33 (d, J = 7.2 Hz, 1H, CH), 6.25 (d, J = 7.6 Hz, 1H, Ar H), 5.84 (s, 1H, CH), 5.39 (d, J = 7.2 Hz, 1H, CH), 5.16 (d, J = 10.4 Hz, 1H, CH), 4.29 (d, J = 10.8 Hz, 1H, CH), 2.18 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 198.2, 142.7, 138.4, 137.1, 134.1, 132.4, 129.7, 129.1, 128.9, 128.4, 125.6, 125.2, 125.1, 125.0, 123.2, 119.3, 100.1, 70.9, 69.4, 57.2, 53.7, 20.9; IR (KBr) υ: 3059, 2916, 2275, 1740, 1704, 1591, 1562, 1540, 1353, 878, 803, 772, 680 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{21}N_2O_2$([M + H]$^+$): 417.1598, found: 417.1611.

*2′-(4-Bromophenyl)-1,3-dioxo-1,2′,3,3′-tetrahydro-10b′H-spiro[indene-2,1′-pyrrolo[2,1-a]isoquinoline]-3′-carbonitrile (**1d**).* Yellow solid, 83%, mp 177−179 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.78−7.75 (m, 4H, Ar H), 7.41 (d, J = 8.0 Hz, 2H, Ar H), 7.16 (d, J = 8.0 Hz, 2H, Ar H), 6.98 (d, J = 7.2 Hz, 1H, Ar H), 76.89 (d, J = 7.6 Hz, 1H, Ar H), 6.64−6.60 (m, 2H, Ar H), 6.29 (d, J = 7.6 Hz, 1H, CH), 5.91 (s, 1H, CH), 5.73 (d, J = 10.0 Hz, 1H, CH), 5.44 (d, J = 7.6 Hz, 1H, CH), 4.31 (d, J = 10.4 Hz, 1H, CH),; ^{13}C NMR (100 MHz, DMSO-d_6) δ: 197.7, 142.5, 137.0, 133.9, 132.5, 132.1, 131.9, 130.8, 129.5, 125.9, 125.3, 125.3, 125.0, 123.1, 122.3, 119.0, 101.0, 71.7, 71.7, 57.2, 52.9; IR (KBr) υ: 3060, 2911, 2231, 1736, 1702, 1593, 1489, 1418, 1248, 766, 718 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{18}BrN_2O_2$([M + H]$^+$): 781.0546, found: 481.0542.

*2′-(4-Chlorophenyl)-1,3-dioxo-1,2′,3,3′-tetrahydro-10b′H-spiro[indene-2,1′-pyrrolo[2,1-a]isoquinoline]-3′-carbonitrile (**1e**).* Yellow solid, 81%, mp 180−183 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.91−7.90 (m, 1H, Ar H), 7.74−7.73 (m, 1H, Ar H), 7.67−7.62 (m, 2H, Ar H), 7.17−7.13 (m, 4H, Ar H), 6.93 (t, J = 7.2 Hz, 1H, Ar H), 6.84 (d, J = 7.2 Hz, 1H, Ar H), 6.54 (d, J = 7.2 Hz, 1H, Ar H), 6.32 (d, J = 6.6 Hz, 1H, CH), 6.24 (d, J = 7.8 Hz, 1H, Ar H), 5.81 (s, 1H, CH), 5.41 (d, J = 6.0 Hz, 1H, CH), 5.14 (d, J = 10.2 Hz, 1H, CH), 4.28 (d, J = 10.2 Hz,

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1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.1, 142.9, 136.0, 136.0, 134.8, 132.3, 131.8, 129.7, 129.6, 129.1, 128.7, 125.4, 125.3, 124.8, 124.8, 123.1, 109.9, 101.1, 70.1, 68.6, 57.7, 53.6; IR (KBr) υ: 3064, 2914, 2240, 1739, 1704, 1590, 1489, 1456, 1276, 1095, 849, 737 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{18}ClN_2O_2$([M + H]$^+$): 437.1051, found: 437.1045.

*2′-(4-(tert-Butyl)phenyl)-1,3-dioxo-1,2′,3,3′-tetrahydro-10b′H-spiro[indene-2,1′-pyrrolo[2,1-a]isoquinoline]-3′-carbonitrile (**1f**).* Yellow solid, 61%, mp 176−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91−7.90 (m, 1H, Ar H), 7.72−7.69 (m, 1H, Ar H), 7.63−7.62 (m, 2H, Ar H), 7.16 (d, J = 8.4 Hz, 2H, Ar H), 7.09 (d, J = 8.4 Hz, 2H, Ar H), 6.93 (t, J = 7.6 Hz, 1H, Ar H), 6.83 (d, J = 7.2 Hz, 1H, Ar H), 6.54 (t, J = 7.6 Hz, 1H, Ar H), 6.33 (d, J = 7.2 Hz, 1H, CH), 6.25 (d, J = 7.6 Hz, 1H, Ar H), 5.83 (s, 1H, CH), 5.39 (d, J = 6.8 Hz, 1H, CH), 5.16 (d, J = 10.4 Hz, 1H, CH), 4.30 (d, J = 10.8 Hz, 1H, CH), 1.16 (s, 9H, 3CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 198.1, 151.4, 142.7, 137.0, 134.2, 132.4, 129.2, 129.1, 128.3, 126.0, 125.6, 125.2, 125.1, 125.0, 123.2, 119.4, 100.2, 100.1, 71.1, 70.0, 57.4, 53.4, 34.6, 31.2; IR (KBr) υ: 3057, 2961, 2867, 2257, 1739, 1700, 1595, 1500, 1267, 1084, 951, 805, 762, 721 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{27}N_2O_2$([M + H]$^+$): 459.2067, found: 459.2081.

General Procedure for the Preparation of Spiro-[benzo[*f*]imidazo[5,1,2-*cd*]indolizine-4,2′-indenes] 2a−y. A mixture of *N*-cyanomethylisoquinolinium chloride (0.5 mmol), aromatic aldehyde (0.5 mmol), 1,3-indanedione (1.1 mmol), and triethylamine (1.2 mmol) in acetonitrile (15.0 mL) was stirred at room temperature for 8 h. The resulting precipitates were collected by filtration and washed with cold ethanol to give pure products **2a−v** for analysis. In the cases of reactions with n-heptanal, the crude products were subjected to column chromatography with a mixture of light petroleum and ethyl acetate (v/v = 2:1) as an eluent to give pure products **2x and 2y** for analysis.

*2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-phenyl-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2a**).* White solid, 83%, mp 249−251 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.29 (s, 1H, NH), 7.39 (d, J = 7.6 Hz, 1H, Ar H), 7.76 (t, J = 7.6 Hz, 1H, Ar H), 7.72−7.65 (m, 3H, Ar H), 7.61 (d, J = 6.8 Hz, 1H, Ar H), 7.57−7.51 (m, 2H, Ar H), 7.44 (d, J = 7.2 Hz, 1H, Ar H), 7.33 (t, J = 7.6 Hz, 1H, Ar H), 7.27 (t, J = 7.6 Hz, 1H, Ar H), 7.19−7.11 (m, 5H, Ar H), 7.01 (d, J = 7.2 Hz, 1H, Ar H), 5.99 (s, 1H, CH), 5.44 (d, J = 6.8 Hz, 1H, CH), 4.66−4.65 (m, 1H, CH), 3.54 (d, J = 10.4 Hz, 1H, CH), 2.93 (t, J = 12.4 Hz, 1H, CH), 2.41−2.36 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.7, 197.5, 194.0, 188.7, 165.7, 142.9, 141.5, 139.9, 139.7, 137.6, 136.1, 135.5, 134.8, 133.2, 132.8, 129.7, 129.1, 129.0, 128.0, 127.9, 127.3, 127.1, 123.1, 123.0, 122.0, 121.2, 100.9, 77.3, 74.5, 67.8, 62.4, 56.3, 30.1; IR (KBr) υ: 3276, 3026, 2916, 1738, 1703, 1570, 1457, 1273, 1087, 859, 739 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{25}N_2O_4$([M + H]$^+$): 549.1809, found: 549.1818.

*2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(2-hydroxyphenyl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]-imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2b**).* White solid, 78%, mp 247−249 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.43 (s, 1H, NH), 9.00 (s, 1H, OH), 7.91−7.88 (m, 3H, Ar H), 7.83−7.80 (m, 1H, Ar H), 7.66−7.60 (m, 4H, Ar H), 7.50−7.45 (m, 2H, Ar H), 7.34 (t, J = 7.6 Hz, 1H, Ar H), 7.29−7.26 (m, 1H, Ar H), 7.08 (d, J = 7.6 Hz, 1H, Ar H), 6.90−6.86 (m, 1H, Ar H), 6.74 (t, J = 7.2 Hz, 1H, Ar H), 6.38 (d, J = 8.0 Hz, 1H, Ar H), 5.95 (s, 1H, CH), 5.51−5.50 (m, 1H, CH), 4.64 (d, J = 3.6 Hz, 1H, CH), 3.21 (dd, J_1 = 11.6 Hz, J_2 = 2.4 Hz, 1H, CH), 2.62−2.55 (m, 1H, CH), 2.35 (dd, J_1 = 15.2 Hz, J_2 = 2.4 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.7, 197.4, 191.9, 188.2, 167.3, 154.3, 142.3, 141.4, 139.7, 139.5, 136.4, 136.2, 135.4, 133.8, 133.6, 130.4, 129.7, 129.3, 129.1, 128.5, 127.5, 127.2, 125.8, 123.2, 122.9, 121.6, 121.2, 118.7, 114.4, 100.0, 77.7, 73.7, 65.9, 63.4, 48.7, 29.9; IR (KBr) υ: 3265, 3069, 2910, 1745, 1707, 1566, 1457, 1206, 1139, 997, 862, 741, 694, 655 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{25}N_2O_5$([M + H]$^+$): 565.1758, found: 565.1757.

*2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(2-methoxyphenyl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]-imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2c**).* White solid, 87%, mp 266−268 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.45 (s, 1H, NH), 8.02 (d, J = 7.2 Hz, 1H, Ar H), 7.94−7.92 (m, 2H, Ar H), 7.85 (t, J = 7.2 Hz, 1H, Ar H), 7.68−7.60 (m, 5H, Ar H), 7.52 (d, J = 6.8 Hz, 1H, Ar H), 7.37 (t, J = 7.6 Hz, 1H, Ar H), 7.31 (t, J = 7.6 Hz, 1H, Ar H), 7.12−7.10 (m, 2H, Ar H), 6.97 (t, J = 7.6 Hz, 1H, Ar H), 6.58 (d, J = 8.0 Hz, 1H, Ar H), 6.00 (s, 1H, CH), 5.63 (s, 1H, CH), 4.67−4.66 (m, 1H, CH), 3.30−3.28 (m, 1H, CH), 2.95 (s, 3H, CH_3), 2.64 (t, J = 7.2 Hz, 1H, CH), 2.43 (d, J = 10.8 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.4, 197.2, 191.9, 188.4, 167.1, 155.5, 142.1, 141.1, 139.7, 139.5, 136.5, 136.3, 135.4, 133.8, 133.7, 130.4, 129.7, 129.3, 129.1, 128.1, 128.0, 127.4, 127.2, 123.1, 122.9, 121.6, 121.2, 120.5, 110.2, 100.0, 77.8, 73.0, 65.6, 63.1, 54.3, 49.1, 29.8; IR (KBr) υ: 3252, 3072, 2833, 1746, 1708, 1649, 1567, 1492, 1462, 1360, 1275, 1206, 1029, 933, 853, 697 cm^{-1}; HRMS (ESI) calcd for $C_{37}H_{27}N_2O_5$([M + H]$^+$): 579.1914, found: 579.1920.

*3-(2-Chlorophenyl)-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]-imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2d**).* White solid, 89%, mp 264−266 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.46 (s, 1H, NH), 7.98−7.92 (m, 3H, Ar H), 7.88 (t, J = 7.2 Hz, 1H, Ar H), 7.74 (d, J = 7.6 Hz, 1H, Ar H), 7.70−7.65 (m, 4H, Ar H), 7.56−7.55 (m, 1H, Ar H), 7.38−7.32 (m, 3H, Ar H), 7.17−7.12 (m, 3H, Ar H), 6.02 (s, 1H, CH), 5.46 (s, 1H, CH), 4.84−4.83 (m, 1H, CH), 3.37−3.34 (m, 1H, CH), 2.74 (t, J = 12.4 Hz, 1H, CH), 2.52−2.51 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.9, 196.9, 191.6, 188.5, 166.0, 141.9, 141.8, 139.7, 139.5, 137.3, 136.8, 136.7, 135.3, 133.9, 133.7, 133.4, 131.0, 130.3, 129.9, 129.3, 129.2, 129.0, 128.7, 127.2, 127.0, 123.6, 123.1, 121.6, 121.3, 99.9, 78.0, 76.1, 65.8, 63.4, 52.1, 29.7; IR (KBr) υ: 3279, 3069, 2907, 2836, 1746, 1709, 1659, 1572, 1461, 1436, 1205, 1036, 891, 850, 792, 685 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{24}ClN_2O_4$([M + H]$^+$): 583.1419, found: 583.1421.

*3-(2-Bromophenyl)-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]-imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2e**).* White solid, 85%, mp 270−272 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.21 (s, 1H, NH), 8.42−8.37 (m, 2H, Ar H), 7.97 (d, J = 7.2 Hz, 1H, Ar H), 7.83−7.73 (m, 5H, Ar H), 7.63−7.55 (m, 3H, Ar H), 7.46 (d, J = 7.8 Hz, 1H, Ar H), 7.36 (t, J = 7.8 Hz, 1H, Ar H), 7.30 (t, J = 7.2 Hz, 1H, Ar H), 7.26−7.24 (m, 1H, Ar H), 7.03 (d, J = 7.2 Hz, 1H, Ar H), 6.00 (s, 1H, CH), 5.39−5.38 (m, 1H, CH), 4.65−4.64 (m, 1H, CH), 3.56 (d, J = 12.0 Hz, 1H, CH), 2.91 (t, J = 13.2 Hz, 1H, CH), 2.40 (d, J = 15.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.0, 196.9, 191.5, 188.5, 165.9, 142.1, 141.9, 139.8, 139.6, 138.5, 137.2, 136.8, 135.4, 133.9, 133.7, 132.3, 131.4, 130.3, 129.9,

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129.3, 129.2, 128.9, 127.5, 127.2, 124.9, 123.7, 123.1, 121.6, 121.3, 100.0, 78.1, 76.8, 65.8, 63.3, 54.7, 29.7; IR (KBr) υ: 3278, 3066, 2914, 2836, 1741, 1703, 1584, 1464, 1431, 1265, 1132, 852, 746 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{24}BrN_2O_4([M + H]^+)$: 627.0914, found: 627.0900.

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(m-tolyl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2f**). White solid, 86%, mp 233−235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.23 (s, 1H, NH), 7.93 (d, J = 7.6 Hz, 1H, Ar H), 7.76 (t, J = 7.2 Hz, 1H, Ar H), 7.72−7.69 (m, 2H, Ar H), 7.66 (d, J = 8.0 Hz, 1H, Ar H), 7.62 (d, J = 6.8 Hz, 1H, Ar H), 7.57−7.50 (m, 1H, Ar H), 7.44 (d, J = 7.6 Hz, 1H, Ar H), 7.32 (t, J = 7.6 Hz, 1H, Ar H), 7.28−7.25 (m, 1H, Ar H), 7.04−7.00 (m, 3H, Ar H), 6.92−6.89 (m, 2H, Ar H), 6.00 (s, 1H, CH), 5.45 (d, J = 3.6 Hz, 1H, CH), 4.63 (d, J = 4.0 Hz, 1H, CH), 3.55−3.52 (m, 1H, CH), 2.99−2.92 (m, 1H, CH), 2.39 (dd, J_1 = 15.2 Hz, J_2 = 2.0 Hz, 1H, CH), 2.20 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.8, 197.5, 193.9, 188.7, 165.7, 143.0, 141.6, 139.9, 139.7, 137.5, 137.4, 136.0, 135.4, 134.9, 133.2, 132.8, 129.7, 129.1, 129.0, 128.5, 127.9, 127.8, 127.2, 125.1, 123.1, 123.0, 122.0, 121.2, 100.9, 77.3, 77.0, 76.7, 74.4, 67.8, 62.3, 56.3, 30.1, 21.4; IR (KBr) υ: 3273, 3099, 3018, 2918, 1741, 1706, 1570, 1489, 1461, 1365, 1278, 1137, 1062, 934, 868, 730, 700, 653 cm^{-1}; HRMS (ESI) calcd for $C_{37}H_{26}KN_2O_4([M + K]^+)$: 601.1524, found: 601.1527.

2-(1,3-Bioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(3-fluorophenyl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]-imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2g**). White solid, 81%, mp 259−261 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.24 (s, 1H, NH), 7.95 (d, J = 7.6 Hz, 1H, Ar H), 7.82−7.70 (m, 4H, Ar H), 7.63−7.61 (m, 1H, Ar H), 7.58−7.54 (m, 2H, Ar H), 7.44 (d, J = 7.6 Hz, 1H, Ar H), 7.33 (t, J = 7.6 Hz, 1H, Ar H), 7.29−7.25 (m, 1H, Ar H), 7.16−7.12 (m, 1H, Ar H), 7.02−6.93 (m, 3H, Ar H), 6.85−6.80 (m, 1H, Ar H), 5.98 (s, 1H, CH), 5.39 (d, J = 3.6 Hz, 1H, CH), 4.64 (d, J = 4.4 Hz, 1H, CH), 3.51 (dd, J_1 = 11.6 Hz, J_2 = 2.4 Hz, 1H, CH), 2.94−2.87 (m, 1H, CH), 2.37 (dd, J_1 = 15.2 Hz, J_2 = 2.8 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.4, 197.3, 193.8, 188.8, 165.3, 162.4 (d, J = 244.5 Hz), 142.8, 141.4, 140.4, 140.3, 139.9, 139.7, 134.6, 133.3, 133.0, 129.5, 129.5, 129.2, 129.1, 128.0, 127.3, 123.7, 123.3, 123.2, 121.9, 121.2, 115.2 (d, J = 22.6 Hz), 114.1 (d, J = 20.9 Hz), 109.9, 100.8, 77.2, 74.3, 67.6, 62.7, 55.6, 30.1; IR (KBr) υ: 3280, 3067, 3020, 2916, 2838, 1742, 1709, 1659, 1589, 1488, 1202, 1090, 959, 828, 739 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{24}FN_2O_4([M + H]^+)$: 567.1715, found: 567.1709.

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(3-nitrophenyl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]-imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2h**). White solid, 82%, mp 252−254 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.18 (s, 1H, NH), 8.16−8.15 (m, 1H, Ar H), 8.04−8.01 (m, 1H, Ar H), 7.97 (d, J = 7.6 Hz, 1H, Ar H), 7.84−7.80 (m, 1H, Ar H), 7.78−7.74 (m, 1H, Ar H), 7.72−7.71 (m, 1H, Ar H), 7.60−7.53 (m, 4H, Ar H), 7.45 (d, J = 7.2 Hz, 1H, Ar H), 7.41−7.33 (m, 2H, Ar H), 7.30−7.26 (m, 1H, Ar H), 7.01 (d, J = 7.6 Hz, 1H, Ar H), 5.99 (s, 1H, CH), 5.44 (d, J = 3.6 Hz, 1H, CH), 4.73 (d, J = 4.0 Hz, 1H, CH), 3.53 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H, CH), 2.91−4.84 (m, 1H, CH), 2.37 (dd, J_1 = 14.8 Hz, J_2 = 2.4 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.8, 197.2, 193.7, 189.0, 164.8, 147.8, 142.5, 141.3, 140.2, 139.8, 139.6, 136.6, 136.1, 134.4, 134.3, 133.4, 133.1, 129.4, 129.2, 129.0, 128.0, 127.4, 123.4, 123.3, 123.2, 122.2, 121.9, 121.3, 100.8, 77.2, 74.3, 67.6, 63.2, 55.0, 30.1; IR (KBr) υ: 3282, 3068, 2911, 2835, 1743, 1708, 1660, 1569, 1529, 1462, 1203, 994, 831, 737 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{24}N_3O_6([M + H]^+)$: 594.1660, found: 594.1651.

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(p-tolyl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2i**). White solid, 92%, mp 233−235 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.48 (s, 1H, NH), 7.97−7.95 (m, 1H, Ar H), 7.92−7.86 (m, 3H, Ar H), 7.68−7.62 (m, 4H, Ar H), 7.50 (d, J = 6.4 Hz, 1H, Ar H), 7.34 (t, J = 7.2 Hz, 1H, Ar H), 7.27 (t, J = 6.4 Hz, 1H, Ar H), 7.07 (d, J = 7.2 Hz, 1H, Ar H), 6.92−6.90 (m, 3H, Ar H), 5.96−5.95 (m, 1H, CH), 5.47−5.45 (m, 1H, CH), 4.37 (d, J = 4.0 Hz, 1H, CH), 3.18 (dd, J_1 = 12.0 Hz, J_2 = 2.4 Hz, 1H, CH), 2.64−2.57 (m, 1H, CH), 2.45−2.42 (m, 1H, CH), 2.16 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.5, 196.9, 192.0, 188.3, 166.7, 142.7, 141.3, 139.6, 139.5, 137.5, 136.7, 135.9, 135.7, 135.1, 133.9, 133.7, 130.3, 129.6, 129.4, 129.2, 128.7, 128.0, 127.3, 123.7, 123.3, 121.7, 121.2, 100.0, 77.3, 74.6, 67.6, 63.0, 55.4, 29.8, 21.0; IR (KBr) υ: 3275, 3018, 2918, 1738, 1704, 1569, 1459, 1357, 1274, 1135, 861, 740 cm^{-1}; HRMS (ESI) calcd for $C_{37}H_{27}N_2O_4([M + H]^+)$: 563.1965, found: 563.1979.

3-(4-(Bimethylamino)phenyl)-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2H-spiro-[benzo[f]imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2j**). White solid, 73%, mp 262−264 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.35 (s, 1H, NH), 7.92−7.91 (m, 1H, Ar H), 7.74−7.69 (m, 4H, Ar H), 7.62−7.61 (m, 1H, Ar H), 7.53−7.52 (m, 2H, Ar H), 7.43−7.41 (m, 1H, Ar H), 7.32−7.30 (m, 2H, Ar H), 7.04−7.01 (m, 3H, Ar H), 6.54−6.51 (m, 2H, Ar H), 5.98 (s, 1H, CH), 5.34 (s, 1H, CH), 4.60 (s, 1H, CH), 3.51 (d, J = 12.4 Hz, 1H, CH), 2.96 (t, J = 10.4 Hz, 1H, CH), 2.84 (s, 6H, $2CH_3$), 2.37 (d, J = 13.2 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.1, 197.9, 194.1, 188.6, 166.0, 149.2, 143.1, 141.7, 139.9, 139.7, 135.9, 135.2, 135.0, 133.1, 132.7, 129.8, 129.1, 129.0, 128.8, 127.9, 127.2, 125.3, 123.2, 122.9, 122.0, 121.1, 112.1, 101.0, 77.1, 75.2, 68.0, 62.1, 56.0, 40.4, 30.2; IR (KBr) υ: 3270, 3071, 2903, 2832, 1744, 1708, 1665, 1568, 1520, 1459, 1362, 1340, 1246, 1058, 858, 743, 693 cm^{-1}; HRMS (ESI) calcd for $C_{38}H_{29}N_3NaO_4([M + Na]^+)$: 614.2050, found: 614.2041.

3-(4-Bromophenyl)-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]-imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2k**). White solid, 81%, mp 278−281 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.46 (s, 1H, NH), 7.98−7.89 (m, 4H, Ar H), 7.73−7.71 (m, 1H, Ar H), 7.62−7.57 (m, 4H, Ar H), 7.36−7.30 (m, 3H, Ar H), 7.28 (t, J = 7.6 Hz, 1H, Ar H), 7.08−6.95 (m, 3H, Ar H), 5.93 (s, 1H, CH), 5.48 (s, 1H, CH), 4.36−4.35 (m, 1H, CH), 3.19 (d, J = 10.4 Hz, 1H, CH), 2.58 (t, J = 12.4 Hz, 1H, CH), 2.45−2.43 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.0, 196.9, 191.9, 191.9, 191.9, 188.5, 188.4, 188.4, 166.3, 142.6, 141.3, 138.4, 137.6, 136.9, 135.0, 133.9, 133.9, 133.8, 133.8, 133.8, 131.0, 130.4, 130.3, 129.7, 129.4, 129.2, 127.3, 123.8, 123.3, 120.0, 100.0, 77.4, 74.3, 67.5, 63.2, 54.9, 40.4, 40.2, 39.9, 29.9; IR (KBr) υ: 3279, 3066, 2902, 1738, 1704, 1569, 1488, 1279, 1137, 1003, 934, 862, 744 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{23}BrKN_2O_4([M + K]^+)$: 665.0473, found: 665.0460.

3-(4-Chlorophenyl)-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]-imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2l**). White solid, 91%, mp 269−272 °C; ^{1}H NMR (400 MHz,

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DMSO-d_6) δ: 10.50 (s, 1H, NH), 8.02−8.00 (m, 2H, Ar H), 7.97−7.94 (m, 2H, Ar H), 7.75 (d, J = 7.2 Hz, 1H, Ar H), 7.70−7.68 (m, 2H, Ar H), 7.54 (d, J = 6.8 Hz, 1H, Ar H), 7.42−7.40 (m, 1H, Ar H), 7.33−7.29 (m, 2H, Ar H), 7.24−7.22 (m, 3H, Ar H), 7.12−7.08 (m, 2H, Ar H), 5.98 (s, 1H, CH), 5.54−5.50 (m, 1H, CH), 4.42−4.41 (m, 1H, CH), 3.24 (d, J = 10.8 Hz, 1H, CH), 2.64 (t, J = 12.4 Hz, 1H, CH), 2.49−2.47 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.0, 196.9, 191.9, 188.4, 166.3, 142.6, 141.3, 139.7, 139.5, 138.0, 137.6, 136.9, 135.0, 133.9, 133.7, 131.4, 130.3, 130.1, 129.7, 129.3, 129.2, 128.1, 127.3, 123.8, 123.3, 121.7, 121.3, 100.0, 77.4, 74.4, 67.6, 63.2, 54.9, 29.9; IR (KBr) υ: 3287, 3042, 2938, 1739, 1704, 1661, 1568, 1487, 1283, 1141, 1020, 936, 897, 732 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{24}ClN_2O_4$([M + H]$^+$): 583.1419, found: 583.1421.

3-(4-(tert-Butyl)phenyl)-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2m**). White solid, 81%, mp 255−257 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.35 (s, 1H, NH), 7.92 (d, J = 7.6 Hz, 1H, Ar H), 7.76−7.73 (m, 1H, Ar H), 7.71−7.65 (m, 2H, Ar H), 7.63−7.61 (m, 1H, Ar H), 7.58−7.56 (m, 1H, Ar H), 7.55−7.50 (m, 2H, Ar H), 7.44 (d, J = 7.2 Hz, 1H, Ar H), 7.33 (t, J = 7.2 Hz, 1H, Ar H), 7.29−7.25 (m, 1H, Ar H), 7.15−7.06 (m, 4H, Ar H), 7.03 (d, J = 7.6 Hz, 1H, Ar H), 6.01 (s, 1H, CH), 5.40−5.38 (m, 1H, CH), 4.63 (d, J = 4.0 Hz, 1H, CH), 3.55 (dd, J_1 = 12.0 Hz, J_2 = 2.4 Hz, 1H, CH), 3.03−2.96 (m, 1H, CH), 2.40 (dd, J_1 = 15.6 Hz, J_2 = 2.4 Hz, 1H, CH), 1.20 (s, 9H, 3CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.7, 197.6, 197.6, 194.0, 188.8, 165.7, 149.5, 143.1, 141.6, 139.9, 139.6, 135.8, 135.3, 135.0, 134.4, 133.1, 132.8, 129.7, 129.2, 129.0, 127.9, 127.7, 127.2, 124.9, 122.9, 122.0, 121.2, 100.9, 77.3, 74.7, 68.0, 61.8, 56.4, 34.3, 31.2, 30.1; IR (KBr) υ: 3280, 3063, 3019, 2960, 2872, 1741, 1703, 1569, 1461, 1356, 1274, 1136, 931, 824, 742 cm^{-1}; HRMS (ESI) calcd for $C_{40}H_{33}N_2O_4$([M + H]$^+$): 605.2435, found: 605.2432.

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(4-nitrophenyl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2n**). White solid, 79%, mp 265−267 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.48 (s, 1H, NH), 8.12−8.00 (m, 4H, Ar H), 7.98−7.92 (m, 3H, Ar H), 7.74 (d, J = 7.6 Hz, 1H, Ar H), 7.70−7.65 (m, 3H, Ar H), 7.52 (d, J = 6.8 Hz, 1H, Ar H), 7.44−7.43 (m, 1H, Ar H), 7.38 (t, J = 7.2 Hz, 1H, Ar H), 7.32 (t, J = 7.6 Hz, 1H, Ar H), 7.11 (d, J = 7.6 Hz, 1H, Ar H), 6.00 (s, 1H, CH), 5.66 (s, 1H, CH), 4.56 (d, J = 3.6 Hz, 1H, CH), 3.26−3.25 (m, 1H, CH), 2.62 (t, J = 12.0 Hz, 1H, CH), 2.52−2.51 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.4, 196.7, 191.8, 188.6, 166.0, 147.0, 146.5, 142.4, 141.2, 139.6, 139.5, 137.8, 137.1, 134.9, 133.9, 133.8, 130.2, 129.7, 129.5, 129.4, 129.2, 127.3, 124.0, 123.4, 123.3, 121.7, 121.3, 99.9, 77.4, 74.0, 67.7, 63.6, 54.7, 29.9; IR (KBr) υ: 3245, 3017, 2900, 2832, 1741, 1704, 1571, 1571, 1460, 1206, 1050, 896, 789, 698 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{23}KN_3O_4$([M + K]$^+$): 632.1218, found: 632.1216.

3-(4-Chloro-2-hydroxyphenyl)-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2o**). White solid, 72%, mp 240−242 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.45 (s, 1H, NH), 9.44 (s, 1H, OH), 7.98−7.92 (m, 3H, Ar H), 7.88 (t, J = 7.2 Hz, 1H, Ar H), 7.75−7.73 (m, 1H, Ar H), 7.69−7.66 (m, 3H, Ar H), 7.55−7.54 (m, 2H, Ar H), 7.37 (t, J = 7.6 Hz, 1H, Ar H), 7.31 (t, J = 7.6 Hz, 1H, Ar H), 7.11 (d, J = 7.6 Hz, 1H, Ar H), 7.00−6.97 (m, 1H, Ar H), 6.45 (d, J = 8.8 Hz, 1H, Ar H), 5.98 (s, 1H, CH), 5.59 (s, 1H, CH), 4.61 (d, J = 3.6 Hz, 1H, CH), 3.24−3.21 (m, 1H, CH), 2.63−2.56 (m, 1H, CH), 2.40−2.37 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.4, 197.5, 191.8, 188.5, 167.0, 153.3, 142.2, 141.3, 139.7, 136.6, 136.5, 135.2, 133.7, 130.4, 129.8, 129.3, 129.2, 128.3, 127.3, 127.2, 123.3, 123.1, 122.6, 121.6, 115.9, 100.0, 77.8, 73.4, 65.7, 63.7, 48.3, 29.9; IR (KBr) υ: 3351, 3304, 3058, 2926, 1741, 1705, 1667, 1570, 1490, 1462, 1203, 1033, 928, 869, 787, 740, 700, 659 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{24}ClN_2O_5$([M + H]$^+$): 599.1368, found: 599.1364.

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(furan-2-yl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo-[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2p**). White solid, 69%, mp 221−223 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.54 (s, 1H, NH), 8.08−8.04 (m, 3H, Ar H), 7.96−7.92 (m, 2H, Ar H), 7.75−7.71 (m, 3H, Ar H), 7.62−7.60 (m, 1H, Ar H), 7.39−7.34 (m, 2H, Ar H), 7.26−7.25 (m, 1H, Ar H), 7.12−7.11 (m, 1H, Ar H), 6.38−6.34 (m, 2H, Ar H), 5.97 (s, 1H, CH), 5.56 (s, 1H, CH), 4.50−4.48 (m, 1H, CH), 3.16−3.10 (m, 1H, CH), 2.60−2.58 (m, 1H, CH), 2.50−2.46 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.3, 195.7, 191.5, 188.2, 165.4, 152.3, 142.0, 141.2, 140.6, 139.2, 139.0, 137.2, 136.4, 134.3, 133.6, 133.4, 129.8, 129.2, 129.0, 128.8, 126.9, 123.5, 122.9, 121.3, 120.9, 110.5, 106.4, 99.6, 76.6, 72.5, 65.6, 62.7, 47.7, 39.5, 29.2; IR (KBr) υ: 3278, 3069, 2913, 2831, 1744, 1707, 1680, 1593, 1564, 1462, 1244, 1135, 888, 697 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{23}N_2O_5$([M + H]$^+$): 539.1601, found: 539.1620.

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(thiophen-2-yl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]-imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2q**). White solid, 78%, mp 233−235 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.55 (s, 1H, NH), 8.06−8.04 (m, 1H, Ar H), 7.99−7.97 (m, 2H, Ar H), 7.94 (d, J = 8.0 Hz, 1H, Ar H), 7.82 (d, J = 8.0 Hz, 1H, Ar H), 7.69−7.67 (m, 3H, Ar H), 7.59−7.57 (m, 3H, Ar H), 7.37 (t, J = 8.0 Hz, 1H, Ar H), 7.32 (t, J = 7.6 Hz, 1H, Ar H), 7.21 (d, J = 4.4 Hz, 1H, Ar H), 7.11 (d, J = 7.6 Hz, 1H, Ar H), 6.87−6.86 (m, 2H, Ar H), 5.99 (s, 1H, CH), 5.53 (s, 1H, CH), 4.67 (d, J = 4.0 Hz, 1H, CH), 3.21−3.18 (m, 1H, CH), 2.62−2.59 (m, 1H, CH), 2.50−2.48 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.0, 196.2, 192.0, 188.3, 165.8, 142.8, 142.0, 141.4, 139.6, 139.5, 137.6, 136.8, 134.8, 134.0, 133.8, 130.2, 129.6, 129.4, 129.2, 127.3, 126.9, 125.5, 124.1, 123.8, 123.3, 121.7, 121.3, 100.1, 77.1, 75.6, 67.6, 63.0, 50.3, 29.8; IR (KBr) υ: 3277, 3068, 2915, 2836, 1742, 1705, 1568, 1462, 1245, 1203, 1060, 892, 738, 692 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{23}N_3O_2S$ ([M + H]$^+$): 555.1373, found: 555.1383.

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(pyridin-2-yl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo-[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2r**). White solid, 83%, mp 270−272 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.55 (s, 1H, NH), 8.07 (d, J = 7.6 Hz, 1H, Ar H), 8.01−7.94 (m, 4H, Ar H), 7.89 (d, J = 6.8 Hz, 1H, Ar H), 7.75 (d, J = 7.6 Hz, 1H, Ar H), 7.70−7.64 (m, 4H, Ar H), 7.55 (d, J = 6.8 Hz, 1H, Ar H), 7.37 (t, J = 7.6 Hz, 1H, Ar H), 7.30 (t, J = 7.6 Hz, 1H, Ar H), 7.13−7.09 (m, 2H, Ar H), 5.97 (s, 1H, CH), 5.91 (s, 1H, CH), 4.73 (d, J = 4.0 Hz, 1H, CH), 3.15−3.11 (m, 1H, CH), 2.48−2.45 (m, 1H, CH), 2.42−2.38 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.7, 197.7, 192.0, 188.7, 167.0, 158.6, 147.9, 147.9, 142.8, 141.4, 139.6, 139.5, 137.0,

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136.5, 136.4, 134.7, 134.0, 133.8, 130.3, 129.6, 129.4, 129.2, 127.3, 123.9, 122.9, 122.4, 121.9, 121.7, 121.3, 100.0, 77.0, 77.0, 71.4, 67.5, 63.1, 55.8, 55.7, 29.8, 29.8; IR (KBr) υ: 3271, 3062, 2925, 1745, 1710, 1648, 1568, 1466, 1338, 1212, 935, 682 cm^{-1}; HRMS (ESI) calcd for $C_{35}H_{24}N_3O_4$ ($[M + H]^+$): 550.1761, found: 550.1769.

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(pyridin-3-yl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo-[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2s**). White solid, 76%, mp 255−257 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.50 (s, 1H, NH), 8.33−8.32 (m, 1H, Ar H), 8.25−8.24 (m, 1H, Ar H), 8.02 (d, J = 7.2 Hz, 1H, Ar H), 7.99−7.92 (m, 3H, Ar H), 7.74−7.68 (m, 5H, Ar H), 7.55−7.53 (m, 1H, Ar H), 7.38 (t, J = 7.6 Hz, 1H, Ar H), 7.32 (t, J = 7.2 Hz, 1H, Ar H), 7.26−7.24 (m, 1H, Ar H), 7.12 (d, J = 7.6 Hz, 1H, Ar H), 5.99 (s, 1H, CH), 5.58 (s, 1H, CH), 4.43 (d, J = 3.2 Hz, 1H, CH), 3.28 (d, J = 12.0 Hz, 1H, CH), 2.66 (t, J = 12.0 Hz, 1H, CH), 2.54−2.51 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.7, 197.0, 191.8, 188.5, 166.1, 149.4, 148.1, 142.5, 141.3, 139.7, 139.5, 137.7, 137.1, 135.8, 135.0, 134.6, 133.9, 133.8, 130.2, 129.7, 129.4, 129.2, 127.3, 123.9, 123.3, 123.2, 121.7, 121.3, 99.9, 77.4, 74.2, 67.5, 63.3, 53.1, 29.8; IR (KBr) υ: 3284, 3070, 2969, 2916, 1741, 1704, 1571, 1484, 1202, 1089, 932, 713, 682, 618 cm^{-1}; HRMS (ESI) calcd for $C_{35}H_{24}N_3O_4$($[M + H]^+$): 550.1761, found: 550.1783.

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(pyridin-4-yl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo-[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2t**). White solid, 74%, mp 265−267 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.50 (s, 1H, NH), 8.37−8.36 (m, 2H, Ar H), 8.05 (d, J = 6.8 Hz, 1H, Ar H), 8.01−7.95 (m, 3H, Ar H), 7.75 (t, J = 7.2 Hz, 1H, Ar H), 7.69−7.66 (m, 3H, Ar H), 7.55−7.53 (m, 1H, Ar H), 7.38 (t, J = 7.2 Hz, 1H, Ar H), 7.32 (t, J = 7.2 Hz, 1H, Ar H), 7.12−7.10 (m, 3H, Ar H), 5.98 (s, 1H, CH), 5.66 (s, 1H, CH), 4.41 (d, J = 3.2 Hz, 1H, CH), 3.24 (d, J = 11.2 Hz, 1H, CH), 2.59 (t, J = 11.6 Hz, 1H, CH), 2.49−2.48 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.5, 196.6, 191.8, 188.6, 166.1, 149.6, 147.8, 142.5, 141.2, 139.6, 137.8, 137.1, 134.9, 133.9, 133.8, 130.2, 129.7, 129.4, 129.2, 127.3, 124.0, 123.4, 123.2, 121.7, 121.3, 99.9, 77.3, 73.0, 67.4, 63.4, 54.2, 29.8; IR (KBr) υ: 3293, 3071, 3038, 2901, 2834, 1742, 1705, 1668, 1567, 1461, 1203, 1140, 1054, 892, 815, 740, 680 cm^{-1}; HRMS (ESI) calcd for $C_{35}H_{24}N_3O_4$ ($[M + H]^+$): 550.1761, found: 550.1783.

3-Benzoyl-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2u**). White solid, 85%, mp 284−286 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.68 (s, 1H, NH), 8.18 (d, J = 7.6 Hz, 1H, Ar H), 8.10−8.05 (m, 3H, Ar H), 7.99−7.91 (m, 4H, Ar H), 7.82 (d, J = 6.4 Hz, 1H, Ar H), 7.63−7.58 (m, 6H, Ar H), 7.52 (t, J = 7.2 Hz, 2H, Ar H), 7.41 (t, J = 7.2 Hz, 2H, Ar H), 7.30 (d, J = 7.6 Hz, 1H, Ar H), 6.26 (s, 1H, CH), 6.10 (s, 1H, CH), 5.27 (d, J = 3.6 Hz, 1H, CH), 3.40−3.37 (m, 1H, CH), 2.68−2.65 (m, 1H, CH), 2.61−2.57 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.5, 196.7, 193.8, 191.8, 189.4, 166.4, 141.5, 140.8, 139.8, 139.4, 137.5, 136.9, 136.5, 134.6, 134.0, 133.9, 133.3, 130.2, 129.8, 129.4, 129.1, 128.8, 128.2, 127.3, 123.6, 123.2, 121.8, 121.3, 99.7, 77.6, 69.7, 64.9, 64.7, 55.8, 29.6; IR (KBr) υ: 3239, 3065, 2913, 2828, 1739, 1708, 1653, 1580, 1461, 1266, 1144, 792, 704, 637 cm^{-1}; HRMS (ESI) calcd for $C_{37}H_{25}N_2O_5$ ($[M + H]^+$): 577.1758, found: 577.1765.

6-Bromo-3-(4-chlorophenyl)-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo-[f]imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2v**). White solid, 81%, mp 266−268 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.56 (s, 1H, NH), 8.04 (d, J = 7.8 Hz, 1H, Ar H), 8.01 (d, J = 7.8 Hz, 1H, Ar H), 7.97 (d, J = 7.8 Hz, 1H, Ar H), 7.93 (d, J = 7.2 Hz, 1H, Ar H), 7.73 (d, J = 7.8 Hz, 1H, Ar H), 7.71−7.67 (m, 4H, Ar H), 7.56 (d, J = 7.2 Hz, 1H, Ar H), 7.38 (t, J = 7.8 Hz, 1H, Ar H), 7.24−7.23 (m, 2H, Ar H), 7.12−7.11 (m, 1H, Ar H), 6.00 (s, 1H, CH), 5.51 (s, 1H, CH), 4.40 (d, J = 3.6 Hz, 1H, CH), 3.29 (dd, J_1 = 11.4 Hz, J_2 = 2.4 Hz, 1H, CH), 2.61−2.58 (m, 1H, CH), 2.53−2.52 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.5, 196.8, 191.6, 188.4, 165.9, 134.6, 132.8, 131.4, 130.1, 129.6, 128.9, 127.9, 124.3, 123.8, 123.2, 100.0, 77.0, 74.5, 67.1, 62.2, 55.4, 30.9; IR (KBr) υ: 3288, 3066, 2927, 1738, 1702, 1652, 1571, 1492, 1452, 1280, 1136, 1012, 892, 819, 779, 698 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{22}BrClN_2NaO_4$ ($[M + Na]^+$): 683.0344, found: 683.0351.

6-Bromo-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-(4-nitrophenyl)-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]-imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2w**). White solid, 83%, mp 275−277 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.59 (s, 1H, NH), 8.08−8.03 (m, 4H, Ar H), 7.99 (t, J = 7.2 Hz, 1H, Ar H), 7.93 (t, J = 7.2 Hz, 1H, Ar H), 7.74 (d, J = 7.6 Hz, 1H, Ar H), 7.67−7.65 (m, 3H, Ar H), 7.61−7.60 (m, 2H, Ar H), 7.40−7.35 (m, 3H, Ar H), 5.99 (s, 1H, CH), 5.62 (s, 1H, CH), 4.53 (d, J = 3.6 Hz, 1H, CH), 3.31 (dd, J_1 = 11.2 Hz, J_2 = 2.4 Hz, 1H, CH), 2.61−2.58 (m, 1H, CH), 2.48−2.44 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 199.2, 196.8, 165.8, 147.0, 146.5, 142.4, 141.2, 139.7, 137.8, 137.2, 134.6, 133.7, 133.0, 129.7, 129.7, 129.1, 124.4, 124.1, 123.4, 123.3, 121.3, 100.1, 78.0, 77.9, 77.9, 74.5, 67.5, 62.7, 55.4, 31.1; IR (KBr) υ: 3288, 3074, 2912, 1744, 1704, 1658, 1578, 1518, 1421, 1214, 1011, 942, 839, 706, 690 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{22}BrKN_3O_6$ ($[M + K]^+$): 710.0324, found: 710.0319.

2-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-hexyl-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2x**). White solid, 70%, mp 275−277 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.52 (s, 1H, NH), 8.10−8.03 (m, 4H, Ar H), 7.86 (t, J = 8.0 Hz, 1H, Ar H), 7.71−7.70 (m, 4H, Ar H), 7.35 (t, J = 7.6 Hz, 1H, Ar H), 7.28 (d, J = 7.2 Hz, 1H, Ar H), 7.08 (d, J = 7.2 Hz, 1H, Ar H), 5.86(s, 1H, CH), 4.70 (s, 1H, CH), 3.19 (d, J = 12.0 Hz, 1H, CH), 2.97 (d, J = 11.6 Hz, 1H, CH), 2.70−2.69 (m, 1H, CH), 2.49−2.46 (m, 1H, CH), 2.37 (d, J = 10.8 Hz, 1H, CH), 1.99−1.91 (m, 1H, CH), 1.10−1.05 (m, 2H, CH), 0.96−0.94 (m, 4H, CH), 0.79−0.78 (m, 1H, CH), 0.69 (t, J = 5.6 Hz, 3H, CH_3), 0.51−0.50 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.8, 198.3, 192.3, 188.9, 167.1, 142.3, 140.3, 139.7, 139.3, 137.6, 137.1, 134.7, 134.0, 133.8, 130.2, 129.4, 129.1, 127.3, 123.9, 123.3, 121.7, 121.3, 100.2, 76.9, 76.7, 65.0, 64.3, 49.3, 31.1, 31.0, 29.6, 28.4, 28.1, 21.8, 14.1; IR (KBr) υ: 3237, 3071, 2952, 2849, 1741, 1703, 1647, 1593, 1493, 1359, 1334, 1273, 1203, 1002, 897, 785, 737, 685 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{32}N_2NaO_4$($[M + Na]^+$): 579.2254, found: 579.2254.

6-Bromo-2-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-3-hexyl-1,2a,3,4a,5,9b-hexahydro-2H-spiro[benzo[f]imidazo-[5,1,2-cd]indolizine-4,2′-indene]-1′,3′-dione (**2y**). White solid, 63%, mp 251−253 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.54 (s, 1H, NH), 8.12−8.04 (m, 4H, Ar H), 7.95 (t, J = 7.2 Hz, 1H, Ar H), 7.72−7.70 (m, 4H, Ar H), 7.62 (d, J = 7.6 Hz, 1H, Ar H), 7.33 (t, J = 7.2 Hz, 1H, Ar H), 5.86(s, 1H, CH),

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4.71 (s, 1H, CH), 3.21 (d, J = 11.6 Hz, 1H, CH), 3.01 (d, J = 11.2 Hz, 1H, CH), 2.68−2.66 (m, 1H, CH), 2.41 (d, J = 15.0 Hz, 1H, CH), 2.33 (d, J = 12.4 Hz, 1H, CH), 1.98−1.95 (m, 1H, CH), 1.09−1.06 (m, 2H, CH), 0.96−0.92 (m, 4H, CH), 0.80−0.78 (m, 1H, CH), 0.70 (t, J = 5.6 Hz, 3H, CH_3), 0.52−0.50 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.6, 198.2, 192.2, 188.9, 166.9, 142.2, 140.4, 139.7, 139.3, 137.7, 137.2, 134.2, 134.0, 133.8, 133.0, 132.9, 129.4, 129.1, 124.5, 124.0, 123.3, 121.7, 121.3, 100.4, 76.7, 64.8, 63.8, 49.7, 31.1, 31.0, 30.8, 28.4, 28.1, 21.8, 14.1; IR (KBr) υ: 3247, 3071, 2925, 2853, 1742, 1707, 1669, 1569, 1451, 1359, 1276, 1215, 1090, 953, 833, 777, 696, 652 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{32}BrN_2NaO_4$([M + H]$^+$): 635.1540, found: 635.1544.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01391.

^{1}H and ^{13}C NMR spectra for all pure products (PDF)

X-ray crystal data for 2i (CCDC 1552741) and X-ray crystal data for **2l** (CCDC 1552742) (CIF)

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Notes

The authors declare no competing financial interest.

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