Tetrahedron 65 (2009) 9316–9321

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of spiro[benzopyrazolonaphthyridine-indoline]-diones and spiro[chromenopyrazolopyridine-indoline]-diones by one-pot, three-component methods in water

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ARTICLE INFO

Article history:
Received 8 April 2009
Received in revised form 19 August 2009
Accepted 3 September 2009
Available online 9 September 2009

Keywords:
4-Hydroxy-1-methylquinolin-2(1*H*)-one
Coumarin
Isatin
Pyrazole
Spirooxindole

ABSTRACT

The synthesis of spiro[benzo[*h*]pyrazolo[3,4-*b*][1,6]naphthyridine-7,3′-indoline]-2′,6(5*H*)-diones and spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridine-7,3′-indoline]-2′,6(6a*H*,10*H*)-diones via a one-pot, three-component reaction of 4-hydroxycoumarin or 4-hydroxy-1-methylquinolin-2(1*H*)-one, isatins and 1*H*-pyrazol-5-amines in water is reported.

1. Introduction

The development of organic reactions in water has become highly desirable in recent years to meet environmental considerations.[1,2] The use of water as a sole medium for organic reactions would greatly contribute to the expansion of environmentally friendly processes. In this context, in recent years, much attention has been focused on organic reactions in water.

Multi-component reactions (MCRs), due to their productivity, simple procedures, convergence and facile execution, are one of the best tools in combinatorial chemistry.[3] Therefore, the design of novel MCRs has attracted great attention from research groups working in areas such as drug discovery, organic synthesis and materials science. As a result, the number of new MCRs in water has grown rapidly.[4–8]

Indole and indoline fragments are important moieties of a large number of natural products and medicinal agents,[9] and some indolines, spiro-annulated with heterocycles in the 3-position, have shown high biological activity.[10,11] The spirooxindole system is the core structure of many pharmacological agents and natural alkaloids.[12,13] Therefore, a number of methods have been reported for the preparation of spirooxindole fused heterocycles.[14–17]

Heterocycles containing the pyrazole ring are important targets in synthetic and medicinal chemistry because this fragment is a key moiety in numerous biologically active compounds,[18–20] among them such prominent drug molecules as Celecoxib and Pyrazofurine. On the other hand, benzonaphthyridine derivatives are compounds of current interest due to their diverse biological activities.[21] These compounds can also be considered as 'aza-analogues' of phenanthridine derivatives, which are widely studied in the field of medicinal chemistry.[22]

Chromenes are an important group of compounds; they widely exist in plants, including edible vegetables and fruits.[23] Synthetic analogues were developed over the years, some of them displaying remarkable effects as pharmaceuticals,[24,25] including antifungal[26] and antimicrobial activity.[27] Similarly, pyrazolopyridines are very interesting compounds and have received considerable attention as a result of their biological activity and structural relationship to indoles.[28–31]

As part of our continuing efforts on the development of new routes for the synthesis of biologically active heterocyclic compounds,[32–39] we have already reported some procedures for the synthesis of spiropyrimidoquinoline'pyrrolopyrimidines, spiroindoline-pyridodipyrimidines, spiroindoline-xanthen-triones and spirodibenzoxanthene-indoline-pentaones by the condensation reaction between amino-uraciles, dimedone or 2-hydroxynaphthalene-1,4-dione and isatins.[40–43] Herein, we report a simple and clean synthesis of spiro[benzo[*h*]pyrazolo[3,4-*b*][1,6]naphthyridine-7,3′-indoline]-2′,6(5*H*)-diones and spiro[chromeno[4,3-*b*]-pyrazolo[4,3-*e*]pyridine-7,3′-indoline]-2′,6(6a*H*,10*H*)-diones in water.

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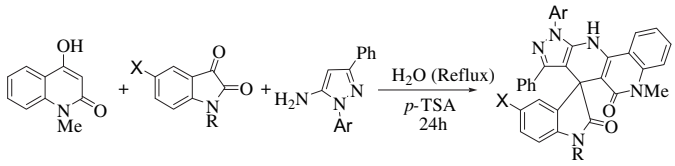
doi:10.1016/j.tet.2009.09.009

2. Results and discussion

The one-pot, three-component condensation reaction of 4-hydroxy-1-methylquinolin-2(1*H*)-one **1**, various isatins **2** and 1*H*-pyrazol-5-amines **3** in the presence of catalytic *p*-TSA proceeded rapidly in refluxing water and were complete after 24 h to afford 10,11-dihydrospiro[benzo[*h*]pyrazolo[3,4-*b*][1,6]naphthyridine-7,3′-indoline]-2′,6(5*H*)-diones **4**, in good yields (Scheme 1).

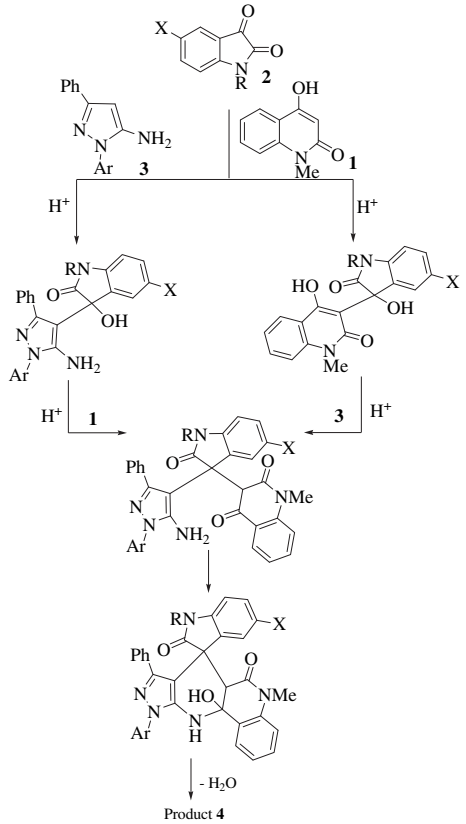


1 **2** **3** **4**

Product ***4***	*R*	*X*	*Ar*	*Yield (%)*[a]
a	H	H	C_6H_5	79
b	Me	H	C_6H_5	78
c	Et	H	C_6H_5	70
d	Br	H	C_6H_5	85
e	Br	Me	C_6H_5	83
f	Br	Et	C_6H_5	72
g	NO_2	H	C_6H_5	80
h	NO_2	Et	C_6H_5	68
i	H	H	4-NO_2-C_6H_4	77
j	Me	H	4-NO_2-C_6H_4	73
k	H	Br	4-NO_2-C_6H_4	65
l	H	NO_2	4-NO_2-C_6H_4	67

[a]Isolated yields

Scheme 1. Synthesis of spirobenzopyrazolonaphthyridine-indolines **4**.



Scheme 2.

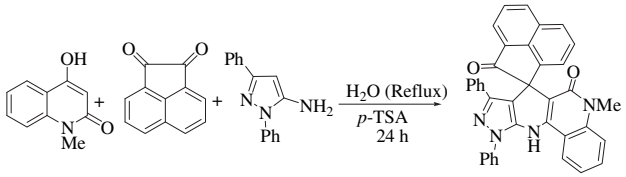
The elucidation of the structure of **4** using NMR spectroscopic data is discussed with **4a** as an example. The ^{1}H NMR spectrum of compound **4a** exhibited one singlet at δ=3.44 for the methyl group, a multiplet at δ=6.49–8.05 for the aromatic hydrogens and two singlets at δ 9.77 and 9.91 for the two NH groups. The generated spirocyclic carbon was assigned through ^{13}C NMR and DEPT experiments at 50.7 ppm. The ^{13}C NMR and DEPT spectrum of **4a** confirms the presence of one methyl group, ten quaternary carbons in the aromatic or alkenic region and two carbonyl groups. The mass spectrum shows the expected molecular ion peak.

The results were good in terms of yields and product purity in the presence of *p*-TSA, while without *p*-TSA the yields of products were trace even after 30 h.

To the best of our knowledge, this new procedure provides the first example of an efficient and three-component method for the synthesis of spiro[benzo[*h*]pyrazolo[3,4-*b*][1,6]naphthyridine-7,3′-indoline]-2′,6(5*H*)-diones. This method, based on three-component *p*-TSA-catalyzed reaction in water, is the most simple and convenient and would be applicable for the synthesis of different types of spirobenzopyrazolonaphthyridine-indolines.

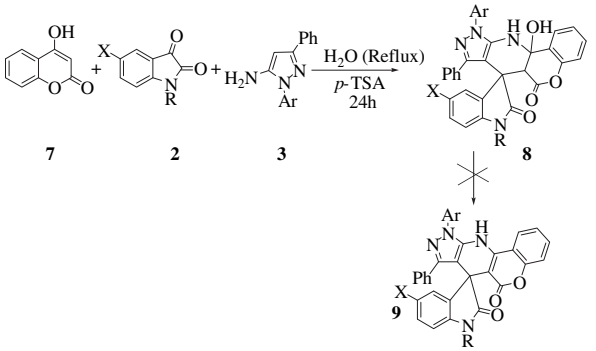
We have not established an exact mechanism for the formation of spirobenzopyrazolonaphthyridine-indolines **4**, however, a reasonable possibility is shown in Scheme 2.

To further explore the potential of this protocol for spiro-heterocycle synthesis, we investigated reaction of acenaphthylene-1,2-



1 **5** **3** **6**

Scheme 3.



7 **2** **3** **8** **9**

Product **8**	R	X	Ar	Yield (%)[a]
a	H	H	C_6H_5	72
b	Me	H	C_6H_5	70
c	Et	H	C_6H_5	69
d	H	NO_2	C_6H_5	75
e	Et	NO_2	C_6H_5	68
f	H	Br	C_6H_5	84
g	Me	Br	C_6H_5	88
h	H	H	4-NO_2- C_6H_4	86
i	Me	H	4-NO_2- C_6H_4	80
j	H	Br	4-NO_2- C_6H_4	70
k	H	NO_2	4-NO_2- C_6H_4	84

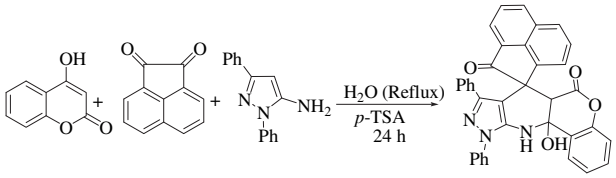
[a]Isolated yields

Scheme 4. Synthesis of spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridine-7,3′-indoline]-diones **8**.

dione **5** instead of isatin **2** and obtained 5′-methyl-8′,10′-diphenyl-10′,11′-dihydro-2*H*-spiro[acenaphthylene-1,7′-benzo[*h*]pyrazolo[3,4-*b*]-[1,6]naphthyridine]-2,6′(5′*H*)-dione **6** in 73% yield (Scheme 3).

When we introduced 4-hydroxycoumarin **7** into the described three-component condensation reaction instead of the 4-hydroxy-1-methylquinolin-2(1*H*)-one **1**, it was interesting that the desired products of **9** were not detected at all, while spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridine-7,3′-indoline]-2′,6(6a*H*,10*H*)-diones **8** were obtained in good yields under the same reaction conditions (Scheme 4).

As expected, when the isatin **2** was replaced by acenaphthylene-1,2-dione **5**, 11*a*′-hydroxy-8′,10′-diphenyl-11′,11*a*′-dihydro-2*H*,6′*H*-spiro[acenaphthylene-1,7′-chromeno[3,4-*e*]pyrazolo[3,4-*b*]pyridine]-2,6′(6*a*′*H*, 10′*H*)-dione **10** was obtained under the same reaction conditions (Scheme 5).



Scheme 5.

The nature of products **4**, **6**, **8** and **10** as 1:1:1 adducts was apparent from their mass spectra, which displayed, in each case, the molecular ion peak at appropriate *m*/*z* values. Compounds **4**, **6**, **8** and **10** are stable solids whose structures are fully supported by IR, ^{1}H and ^{13}C NMR spectroscopies, mass spectrometry and elemental analysis.

3. Conclusion

In conclusion, we have described a facile, one-pot and three-component method for the synthesis of spiro[benzo[*h*]pyrazolo[3,4-*b*][1,6]naphthyridine-7,3′-indoline]-2′,6(5*H*)-diones and spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridine-7,3′-indoline]-diones in water. Prominent among the advantages of this new method are novelty, operational simplicity, good yields and easy work-up procedures employed.

4. Experimental

4.1. General

Melting points were measured on an Electrothermal 9100 apparatus. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. ^{1}H, ^{13}C NMR and DEPT spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz, respectively. ^{1}H and ^{13}C NMR spectra were obtained on solutions in CD_3SOCD_3 using TMS as internal standard. IR spectra were recorded using an FTIR apparatus. Elemental analyses were performed using a Heracus CHN-*O*-Rapid analyzer.

The chemicals used in this work were obtained from Fluka and Merck and were used without purification.

4.2. 5-Methyl-8,10-diphenyl-10,11-dihydrospiro [benzo[*h*]-pyrazolo[3,4-*b*][1,6]naphthyridine-7,3′-indoline]-2′,6(5*H*)-dione (4a)

A mixture of 4-hydroxy-1-methylquinolin-2(1*H*)-one (0.18 g, 1 mmol), isatin (0.15 g, 1 mmol), 1,3-diphenyl-1*H*-pyrazol-5-amine (0.24 g, 1 mmol) and *p*-TSA (0.1 g) in refluxing water (5 mL) was stirred for 24 h (the progress of the reaction was monitored by TLC). After completion, the reaction mixture was filtered and the precipitate washed with water (10 mL) and EtOH (10 mL) to afford the pure product **4a** as cream powder (0.41 g, 79%). Mp 290 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3363, 3198, 1725, 1632; ^{1}H NMR (300 MHz, DMSO-d_6) δ_H=3.44 (3H, s, CH_3), 6.49–8.05 (18H, m, H-Ar), 9.77 (1H, s, NH), 9.91 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=29.4 (NCH_3), 50.7 (C_{spiro}), 101.6 (C), 109.3 (CH), 114.0 (C), 115.1 (CH), 121.5 (CH), 121.8 (CH), 123.0 (CH), 123.6 (CH), 124.3 (CH), 127.4 (CH), 127.7 (CH), 128.0 (CH), 128.2 (CH), 129.1 (CH), 130.0 (CH), 131.6 (CH), 133.2 (C), 138.4 (C), 138.5 (C), 139.1 (C), 139.2 (C), 142.8 (C), 143.4 (C), 149.6 (C), 159.9 (CO), 179.6 (CO). MS (EI, 70 eV) *m*/*z*: 521 (M$^+$). Anal. Calcd for $C_{33}H_{23}N_5O_2$: C, 75.99; H, 4.44; N, 13.43%. Found: C, 75.78; H, 4.50; N, 13.49%.

*4.2.1. 1′,5-Dimethyl-8,10-diphenyl-10,11-dihydrospiro[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4b**).* Light brown powder (0.42 g, 78%); mp 300 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3419, 3055, 1723, 1610; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H=2.83 (3H, s, CH_3), 3.35 (3H, s, CH_3), 6.67–8.02 (18H, m, H-Ar), 9.75 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=27.0 (NCH_3), 49.0 (NCH_3), 49.4 (C_{spiro}), 95.9 (C), 97.4 (C), 109.1 (CH), 123.8 (CH), 124.3 (CH), 127.0 (CH), 127.2 (CH), 127.6 (CH), 127.7 (CH), 127.9 (CH), 128.8 (CH), 128.9 (CH), 129.6 (CH), 129.6 (CH), 132.2 (C), 134.7 (C), 135.2 (C), 138.7 (C), 139.0 (C), 142.7 (C), 145.9 (C), 146.6 (C), 150.4 (CO), 177.9 (CO). MS (EI, 70 eV) *m*/*z*: 535 (M$^+$). Anal. Calcd for $C_{34}H_{25}N_5O_2$. C, 76.24; H, 4.70; N, 13.08. Found: C, 76.13; H, 4.75; N, 13.01%.

*4.2.2. 1′-Ethyl-5-methyl-8,10-diphenyl-10,11-dihydrospiro[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4c**).* Yellow powder (0.38 g, 70%); mp 270 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3399, 3055, 1704, 1637; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H=0.77 (3H, t, CH_3, $^{3}J_{HH}$=6.6 Hz), 3.12–3.38 (2H, m, CH_2), 3.42 (3H, s, CH_3), 6.55–8.06 (18H, m, H-Ar), 9.84 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=12.0 (CH_3), 29.5 (NCH_3), 34.4 (CH_2), 50.1 (C_{spiro}), 101.5 (C), 107.3 (CH), 108.2 (CH), 114.0 (C), 115.1 (CH), 121.8 (CH), 122.1 (CH), 123.0 (CH), 123.6 (CH), 124.3 (CH), 127.4 (CH), 127.8 (CH), 128.3 (CH), 129.0 (CH), 130.0 (CH), 131.7 (CH), 133.2 (C), 137.7 (C), 138.6 (C), 139.1 (C), 142.9 (C), 143.8 (C), 149.6 (C), 160.0 (CO), 177.5 (CO). MS (EI, 70 eV) *m*/*z*: 549 (M$^+$). Anal. Calcd for $C_{35}H_{27}N_5O_2$. C, 76.48; H, 4.95; N, 12.74. Found: C, 76.39; H, 4.91; N, 12.69%.

*4.2.3. 5′-Bromo-5-methyl-8,10-diphenyl-10,11-dihydrospiro[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4d**).* White powder (0.51 g, 85%); mp 288 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3429, 3311, 1719, 1627; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H=3.49 (3H, s, CH_3), 6.41–8.06 (17H, m, H-Ar), 9.92 (1H, s, NH), 10.08 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=29.5 (NCH_3), 50.9 (C_{spiro}), 101.0 (C), 106.7 (CH), 111.2 (C), 113.0 (CH), 113.9 (C), 115.2 (CH), 123.2 (CH), 126.3 (CH), 127.5 (CH), 127.8 (CH), 128.4 (CH), 129.1 (CH), 129.9 (CH), 130.6 (CH), 131.8 (CH), 133.0 (C), 138.6 (C), 139.1 (C), 139.2 (C), 140.6 (C), 142.6 (C), 143.1 (C), 149.6 (C), 160.0 (CO), 179.3 (CO). MS (EI, 70 eV) *m*/*z*: 601 (M$^+$), 599 (M$^+$). Anal. Calcd for $C_{33}H_{22}BrN_5O_2$. C, 66.01; H, 3.69; N, 11.66. Found: C, 66.17; H, 3.60; N, 11.60%.

*4.2.4. 5′-Bromo-1′,5-dimethyl-8,10-diphenyl-10,11-dihydrospiro[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4e**).* Cream powder (0.51 g, 83%); mp 293 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3260, 3070, 1713, 1643; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H=2.67 (3H, s, CH_3), 3.43 (3H, s, CH_3), 6.56–8.08 (17H, m, H-Ar), 9.92 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=26.1 (CH_3), 29.5 (NCH_3), 50.2 (C_{spiro}), 101.0 (C), 106.3 (CH), 109.9 (C), 113.9 (C), 115.3 (CH), 121.9 (CH), 123.2 (CH), 124.4 (CH), 126.0 (CH), 127.5 (CH), 127.8 (CH), 128.4 (CH), 129.0 (CH), 129.9 (CH), 130.8 (CH), 131.9 (CH), 132.8

(C), 138.5 (C), 139.1 (C), 139.2 (C), 139.5 (C), 143.3 (C), 143.5 (C), 149.5 (C), 160.0 (CO), 177.6 (CO). MS (EI, 70 eV) *m/z*: 615 (M^+), 613 (M^+). Anal. Calcd for $C_{34}H_{24}BrN_5O_2$. C, 66.46; H, 3.94; N, 11.40. Found: C, 66.54; H, 3.98; N, 11.48%.

*4.2.5. 5′-Bromo-1′-ethyl-5-methyl-8,10-diphenyl-10,11-dihydrospiro-[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4f**).* Cream powder (0.45 g, 72%); mp >300 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3214, 3072, 1694, 1638; ^1H NMR (300 MHz, DMSO-d_6): δ_H=0.78 (3H, t, CH_3, $^3J_{HH}$=6 Hz), 3.08–3.35 (2H, m, CH_2), 3.42 (3H, s, CH_3), 6.61–8.07 (17H, m, H-Ar), 9.89 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=11.9 (CH_3), 29.6 (NCH_3), 34.5 (CH_2), 50.2 (C_{spiro}), 100.8 (C), 106.5 (CH), 110.1 (C), 113.7 (CH), 113.9 (C), 115.2 (CH), 121.9 (CH), 123.2 (CH), 124.4 (CH), 126.3 (CH), 127.5 (CH), 127.9 (CH), 128.4 (CH), 129.0 (CH), 129.9 (CH), 130.8 (C), 131.8 (CH), 133.1 (C), 138.6 (C), 139.1 (C), 139.2 (C), 139.9 (C), 143.1 (C), 149.4 (C), 160.0 (CO), 177.2 (CO). MS (EI, 70 eV) *m/z*: 629 (M^+), 627 (M^+). Anal. Calcd for $C_{35}H_{26}BrN_5O_2$. C, 66.88; H, 4.17; N, 11.14. Found: C, 66.75; H, 4.11; N, 11.20%.

*4.2.6. 5-Methyl-5′-nitro-8,10-diphenyl-10,11-dihydrospiro[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4g**).* Yellow powder (0.45 g, 80%); mp 275 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3409, 3224, 1744, 1626; ^1H NMR (300 MHz, DMSO-d_6): δ_H=3.46 (3H, s, CH_3), 6.61–8.09 (17H, m, H-Ar), 9.97 (1H, s, NH), 10.70 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=29.5 (NCH_3), 50.6 (C_{spiro}), 100.5 (C), 106.1 (CH), 113.9 (C), 115.3 (CH), 122.0 (CH), 123.3 (CH), 123.6 (CH), 124.4 (CH), 125.6 (CH), 127.6 (CH), 127.9 (CH), 128.5 (CH), 129.1 (CH), 129.5 (CH), 130.0 (CH), 132.0 (C), 132.8 (C), 138.6 (C), 139.0 (C), 139.2 (C), 142.3 (C), 143.5 (C), 149.6 (C), 149.8 (C), 160.1 (CO), 180.3 (CO). MS (EI, 70 eV) *m/z*: 566 (M^+). Anal. Calcd for $C_{33}H_{22}N_6O_4$. C, 69.96; H, 3.91; N, 14.83. Found: C, 69.88; H, 3.87; N, 14.76%.

*4.2.7. 1′-Ethyl-5-methyl-5′-nitro-8,10-diphenyl-10,11-dihydrospiro-[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4h**).* Yellow powder (0.40 g, 68%); mp 266 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3255, 3070, 1714, 1638; ^1H NMR (300 MHz, DMSO-d_6): δ_H=. 0.86 (3H, t, CH_3, $^3J_{HH}$=9 Hz), 3.18–3.52 (5H, m, CH_2 and CH_3), 6.65–8.16 (17H, m, H-Ar), 10.03 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=11.9 (CH3), 29.6 (NCH_3), 35.3 (CH_2), 50.0 (C_{spiro}), 100.3 (C), 106.0 (CH), 108.1 (CH), 113.8 (C), 115.4 (CH), 118.8 (CH), 122.0 (CH), 123.3 (CH), 124.5 (CH), 125.7 (CH), 127.6 (CH), 128.0 (CH), 129.0 (CH), 130.0 (CH), 132.0 (CH), 132.8 (C), 138.4 (C), 138.7 (C), 139.0 (C), 139.2 (C), 142.7 (C), 143.5 (C), 149.4 (C), 149.8 (C), 160.1 (CO), 178.4 (CO). MS (EI, 70 eV) *m/z*: 594 (M^+). Anal. Calcd for $C_{35}H_{26}N_6O_4$. C, 70.70; H, 4.41; N, 14.13. Found: C, 70.79; H, 4.47; N, 14.05%.

*4.2.8. 5-Methyl-10-(4-nitrophenyl)-8-phenyl-10,11-dihydrospiro-[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4i**).* Yellow powder (0.44 g, 77%); mp >300 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3414, 3168, 1698, 1643; ^1H NMR (300 MHz, DMSO-d_6): δ_H=3.44 (3H, s, CH_3), 6.47–8.50 (17H, m, H-Ar), 9.97 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=29.4 (NCH_3), 50.6 (C_{spiro}), 102.7 (C), 107.8 (CH), 109.4 (CH), 113.9 (C), 115.1 (CH), 121.6 (CH), 121.9 (CH), 123.1 (CH), 123.7 (CH), 124.4 (CH), 125.6 (C), 127.8 (CH), 128.1 (CH), 128.6 (CH), 129.0 (CH), 131.8 (CH), 132.6 (C), 138.1 (C), 139.1 (C), 139.4 (C), 142.7 (C), 143.3 (C), 144.2 (C), 145.5 (C), 151.4 (C), 159.8 (CO), 179.4 (CO). MS (EI, 70 eV) *m/z*: 566 (M^+). Anal. Calcd for $C_{33}H_{22}N_6O_4$. C, 69.96; H, 3.91; N, 14.83. Found: C, 69.82; H, 3.84; N, 14.77%.

*4.2.9. 1′,5-Dimethyl-10-(4-nitrophenyl)-8-phenyl-10,11-dihydrospiro-[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4j**).* Yellow powder (0.42 g, 73%); mp >300 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3162, 3070, 1685, 1643; ^1H NMR (300 MHz, DMSO-d_6): δ_H=2.65 (3H, s, CH_3)=2.65 (3H, s, CH_3), 3.42 (3H, s, CH_3), 6.58–8.5 (17H, m, H-Ar), 10.04 (1H, s, NH). MS (EI, 70 eV) *m/z*: 580 (M^+). Anal. Calcd for $C_{34}H_{24}N_6O_4$. C, 70.34; H, 4.17; N, 14.47. Found: C, 70.19; H, 4.11; N, 14.40%.

Due to very low solubility of the product **4c**, we cannot report the ^{13}C NMR data for this product.

*4.2.10. 5′-Bromo-5-methyl-10-(4-nitrophenyl)-8-phenyl-10,11-dihydrospiro[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4k**).* Yellow powder (0.42 g, 65%); mp >300 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3424, 3193, 1712, 1647; ^1H NMR (300 MHz, DMSO-d_6): δ_H=3.45 (3H, s, CH_3), 6.42–8.51 (16H, m, H-Ar), 10.03 (1H, s, NH), 10.15 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=29.5 (NCH_3), 50.8 (C_{spiro}), 102.0 (C), 107.0 (CH), 111.2 (CH), 113.1 (CH), 113.8 (C), 115.2 (CH), 123.3 (CH), 124.5 (CH), 125.6 (C), 126.4 (CH), 127.9 (CH), 128.7 (CH), 129.0 (CH), 130.8 (CH), 131.9 (CH), 132.4 (C), 139.2 (C), 139.5 (C), 140.3 (C), 142.6 (C), 143.0 (C), 144.1 (C), 145.6 (C), 151.2 (C), 159.9 (CO), 179.1 (CO). MS (EI, 70 eV) *m/z*: 646 (M^+), 646 (M^+). Anal. Calcd for $C_{33}H_{21}BrN_6O_4$. C, 61.41; H, 3.28; N, 13.02. Found: C, 61.49; H, 3.22; N, 13.11%.

*4.2.11. 5-Methyl-5′-nitro-10-(4-nitrophenyl)-8-phenyl-10,11-dihydrospiro[benzo[h]pyrazolo[3,4-b][1,6]naphthyridine-7,3′-indoline]-2′,6(5H)-dione (**4l**).* Yellow powder (0.40 g, 65%); mp >300 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3394, 3203, 1717, 1637; ^1H NMR (300 MHz, DMSO-d_6): δ_H=3.45 (3H, s, CH_3), 6.61–8.51 (16H, m, H-Ar), 10.1 (1H, s, NH), 10.73 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=29.6 (NCH_3), 50.5 (C_{spiro}), 101.6 (C), 106.4 (CH), 109.2 (CH), 113.8 (C), 119.1 (CH), 122.1 (CH), 123.4 (CH), 124.5 (CH), 125.6 (C), 128.0 (CH), 128.8 (CH), 129.0 (CH), 132.1 (CH), 132.2 (CH), 138.6 (C), 139.2 (C), 139.6 (C), 142.3 (C), 143.4 (C), 144.1 (C), 145.7 (C), 149.7 (C), 151.2 (C), 160.0 (C), 166.7 (CO), 180.1 (CO). MS (EI, 70 eV) *m/z*: 611 (M^+). Anal. Calcd for $C_{33}H_{21}N_7O_6$. C, 64.81; H, 3.46; N, 16.03. Found: C, 64.92; H, 3.42; N, 15.97%.

4.3. 5′-Methyl-8′,10′-diphenyl-10′,11′-dihydro-2*H*-spiro[acenaphthylene-1,7′-benzo[*h*]pyrazol[3,4-*b*]-[1,6]naphthyridine]-2,6′(5′*H*)-dione (6)

Cream powder (0.41 g, 73%); mp 210 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3260, 3073, 1714, 1643; ^1H NMR (300 MHz, DMSO-d_6): δ_H=3.02 (3H, s, CH_3), 6.6 (20H, m, H-Ar), 8.77 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=28.4 (CH_3), 63.0 (C_{spiro}), 97.6 (CH), 111.4 (C), 111.7 (CH), 114.6 (C), 120.7 (CH), 121.0 (CH), 121.4 (C), 122.8 (CH), 123.3 (CH), 125.8 (CH), 126.6 (CH), 128.8 (CH), 129.1 (CH), 129.5 (CH), 131.2 (C), 131.4 (CH), 135.1 (C), 135.4 (CH), 140.4 (C), 141.8 (C), 142.0 (C), 144.5 (C), 153.1 (C), 158.7 (CO), 159.1 (CO). MS (EI, 70 eV) *m/z*: 556 (M^+). Anal. Calcd for $C_{37}H_{24}N_4O_2$. C, 79.84; H, 4.35; N, 10.07. Found: C, 79.71; H, 4.39; N, 10.02%.

4.4. Typical procedure for the preparation of 11*a*-hydroxy-8,10-diphenyl-11,11*a*-dihydro-6*H*-spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridine-7,3′-indoline]-2′,6(6a*H*,10*H*)-dione (8a)

A mixture of 4-hydroxycoumarin (0.16 g, 1 mmol), isatin (0.15 g, 1 mmol), 1,3-diphenyl-1*H*-pyrazol-5-amine (0.24 g, 1 mmol) and *p*-TSA (0.1 g) in refluxing water (5 mL) was stirred for 24 h (TLC). After completion, the reaction mixture was filtered and the precipitate washed with water (10 mL) and recrystallization from ethanol to afford the pure product **8a** as white powder (0.38 g, 72%). Mp 280 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3409, 3157, 3070, 1726, 1647; ^1H NMR (300 MHz, DMSO-d_6) δ_H=6.07 (1H, s, CH), 6.43–7.97 (18H, m, H-Ar), 10.66 (1H, s, NH), 11.22 (1H, s, NH), 11.31 (1H, br s, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=48.5 (C_{spiro}), 57.3 (CH), 102.6 (C), 109.8 (CH), 118.0 (CH), 119.7 (CH), 121.7 (CH), 122.1 (C), 123.7 (CH), 123.9 (CH), 127.8 (CH), 128.0 (CH), 128.2 (CH), 129.0 (CH), 129.8 (CH), 131.7 (CH), 132.5 (C), 136.8 (CH), 138.2 (C), 140.9 (C), 144.2 (C),

148.7 (C), 160.6 (C), 168.3 (C), 178.2 (CO), 199.2 (CO). MS (EI, 70 eV) *m*/*z*: 526 (M^+). Anal. Calcd for $C_{32}H_{22}N_4O_4$: C, 72.99; H, 4.21; N, 10.64%. Found: C, 72.80; H, 4.17; N, 10.58%.

*4.4.1. 11a-Hydroxy-1′-methyl-8,10-diphenyl-11,11a-dihydro-6H-spiro-[chromeno[4,3-b]pyrazolo[4,3-e]pyridine-7,3′-indoline]-2′,6(6aH,10H)-dione (**8b**).* White powder (0.38 g, 70%); mp 289 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3352, 1716, 1637; ^1H NMR (300 MHz, DMSO-d_6): δ_H=3.28 (3H, s, CH_3), 6.10 (1H, s, CH), 6.51–7.92 (18H, m, H-Ar), 11.23 (1H, s, NH), 11.29 (1H, br s, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=26.8 (CH_3), 47.9 (C_{spiro}), 57.6 (CH), 102.3 (C), 108.7 (CH), 118.0 (CH), 119.7 (CH), 122.2 (CH), 122.4 (C), 123.5 (CH), 123.7 (CH), 127.5 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 129.1 (CH), 129.8 (CH), 131.7 (CH), 132.4 (C), 136.7 (CH), 138.1 (C), 140.9 (C), 145.6 (C), 148.7 (C), 160.5 (C), 168.2 (C), 176.3 (CO), 198.8 (CO). MS (EI, 70 eV) *m*/*z* (%): 540 (M^+). MS (EI, 70 eV) *m*/*z*: 526 (M^+). Anal. Calcd for $C_{33}H_{24}N_4O_4$: C, 73.32; H, 4.48; N, 10.36%. Found: C, 73.17; H, 4.53; N, 10.44%.

*4.4.2. 1′-Ethyl-11a-hydroxy-8,10-diphenyl-11,11a-dihydro-6H-spiro-[chromeno[4,3-b]pyrazolo[4,3-e]pyridine-7,3′-indoline]-2′,6(6aH,10H)-dione (**8c**).* Yellow powder (0.38 g, 69%); mp 287 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3229, 1726, 1678; ^1H NMR (300 MHz, DMSO-d_6): δ_H=1.30 (3H, t, *J*=6.2 Hz, CH_3), 3.87 (2H, m, CH_2), 6.09 (1H, s, CH), 6.50–7.94 (18H, m, H-Ar), 11.26 (1H, s, NH), 11.29 (1H, br s, OH). MS (EI, 70 eV) *m*/*z* (%): 554 (M^+). MS (EI, 70 eV) *m*/*z*: 526 (M^+). Anal. Calcd for $C_{34}H_{26}N_4O_4$: C, 73.63; H, 4.73; N, 10.10%. Found: C, 73.70; H, 4.77; N, 10.16%.

Due to very low solubility of the product **4c**, we cannot report the ^{13}C NMR data for this product.

*4.4.3. 11a-Hydroxy-5′-nitro-8,10-diphenyl-11,11a-dihydro-6H-spiro[chromeno[4,3-b]pyrazolo[4,3-e]pyridine-7,3′-indoline]-2′,6(6aH,10H)-dione (**8d**).* Cream powder (0.43 g, 75%); mp 234 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3347, 1734, 1611; ^1H NMR (300 MHz, DMSO-d_6): δ_H=6.30 (1H, s, CH), 6.87–7.89 (17H, m, H-Ar), 11.15 (1H, s, NH), 11.32 (1H, s, NH), 11.40 (1H, br s, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=48.1 (C_{spiro}), 57.6 (CH), 101.6 (C), 110.0 (CH), 118.0 (CH), 119.7 (CH), 120.4 (CH), 122.2 (C), 123.7 (CH), 126.4 (CH), 127.9 (CH), 128.1 (CH), 128.2 (CH), 129.1 (CH), 129.8 (CH), 131.7 (CH), 132.5 (C), 136.9 (CH), 138.1 (C), 140.7 (C), 142.0 (C), 148.7 (C), 150.8 (C), 160.4 (C), 167.9 (C), 178.7 (CO), 198.8 (CO). MS (EI, 70 eV) *m*/*z*: 571 (M^+). Anal. Calcd for $C_{32}H_{21}N_5O_6$: C, 67.25; H, 3.70; N, 12.25%. Found: C, 67.39; H, 3.63; N, 12.17%.

*4.4.4. 1′-Ethyl-11a-hydroxy-5′-nitro-8,10-diphenyl-11,11a-dihydro-6H-spiro[chromeno[4,3-b]pyrazolo[4,3-e]pyridine-7,3′-indoline]-2′,6(6aH,10H)-dione (**8e**).* Cream powder (0.41 g, 68%); mp 224 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3445, 3394, 3234, 1725, 1673; ^1H NMR (300 MHz, DMSO-d_6): δ_H=1.36 (3H, br s, CH_3), 3.94 (2H, br s, CH_2), 6.34 (1H, s, CH), 6.83–7.90 (17H, m, H-Ar), 11.14 (1H, s, NH), 11.39 (1H, s, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=12.4 (CH_3), 35.3 (CH_3), 47.5 (C_{spiro}), 57.8 (CH), 101.2 (C), 109.1 (CH), 118.0 (CH), 119.8 (CH), 120.2 (CH), 122.1 (C), 123.7 (CH), 126.4 (CH), 127.9 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 129.8 (CH), 131.7 (CH), 132.4 (C), 136.9 (CH), 138.1 (C), 140.8 (C), 142.3 (C), 148.7 (C), 150.8 (C), 160.4 (C), 167.8 (C), 176.6 (CO), 198.7 (CO). MS (EI, 70 eV) *m*/*z*: 599 (M^+). Anal. Calcd for $C_{34}H_{25}N_5O_6$: C, 72.99; H, 4.21; N, 10.64%. Found: C, 72.78; H, 4.26; N, 10.58%.

*4.4.5. 5′-Bromo-11a-hydroxy-8,10-diphenyl-11,11a-dihydro-6H-spiro-[chromeno[4,3-b]pyrazolo[4,3-e]pyridine-7,3′-indoline]-2′,6(6aH,10H)-dione (**8f**).* Cream powder (0.51 g, 84%); mp 260 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3347, 3260, 3065, 1719, 1638; ^1H NMR (300 MHz, DMSO-d_6): δ_H=6.10 (1H, s, CH), 6.63–7.92 (17H, m, H-Ar), 10.79 (1H, s, NH), 11.24 (2H, br s, OH and NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=48.4 (C_{spiro}), 57.3 (CH), 102.2 (C), 111.7 (CH), 113.3 (C), 118.1 (CH), 119.8 (CH), 122.1 (C), 123.6 (CH), 127.1 (CH), 127.8 (CH), 128.0 (CH), 129.8 (CH), 130.4 (CH), 131.7 (CH), 132.5 (C), 136.8 (CH), 138.1 (C), 140.6 (C), 143.5 (C), 148.7 (C), 160.5 (C), 168.1 (C), 177.8 (CO), 199.0 (CO). MS (EI, 70 eV) *m*/*z*: 606 (M^+), 604 (M^+). Anal. Calcd for $C_{32}H_{21}BrN_4O_4$: C, 63.48; H, 3.50; N, 9.25%. Found: C, 63.34; H, 3.56; N, 9.17%.

*4.4.6. 5′-Bromo-11a-hydroxy-1′-methyl-8,10-diphenyl-11,11a-dihydro-6H-spiro[chromeno[4,3-b]pyrazolo[4,3-e]pyridine-7,3′-indoline]-2′,6(6aH,10H)-dione (**8g**).* White powder (0.54 g, 88%); mp 270 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3024, 1730, 1678; ^1H NMR (300 MHz, DMSO-d_6): δ_H=3.27 (3H, s, CH_3), 6.12 (1H, s, CH), 6.68–7.89 (17H, m, H-Ar), 11.17 (1H, s, NH), 11.30 (1H, s, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=26.9 (CH_3), 47.8 (C_{spiro}), 57.5 (CH), 101.8 (C), 110.7 (CH), 114.1 (C), 118.0 (CH), 119.6 (CH), 119.7 (CH), 122.1 (C), 123.6 (CH), 126.8 (CH), 128.0 (CH), 128.9 (CH), 129.5 (CH), 129.8 (CH), 131.3 (CH), 131.6 (CH), 132.3 (C), 136.4 (CH), 136.8 (C), 138.1 (C), 140.7 (C), 144.9 (C), 148.7 (C), 160.4 (C), 168.0 (C), 176.0 (CO), 198.5 (CO). MS (EI, 70 eV) *m*/*z*: 620 (M^+), 618 (M^+). Anal. Calcd for $C_{33}H_{23}BrN_4O_4$: C, 63.98; H, 3.74; N, 9.04%. Found: C, 64.09; H, 3.70; N, 9.10%.

*4.4.7. 11a-Hydroxy-10-(4-nitrophenyl)-8-phenyl-11,11a-dihydro-6H-spiro[chromeno[4,3-b]pyrazolo[4,3-e]pyridine-7,3′-indoline]-2′,6(6aH,10H)-dione (**8h**).* Brown powder (0.49 g, 86%); mp 285 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3413, 3193, 1730, 1724; ^1H NMR (300 MHz, DMSO-d_6): δ_H=6.12 (1H, s, CH), 6.44–8.45 (17H, m, H-Ar), 10.68 (1H, s, NH), 11.27 (1H, s, NH), 11.46 (1H, s, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=48.3 (C_{spiro}), 57.1 (CH), 104.0 (C), 109.9 (CH), 118.0 (CH), 119.8 (CH), 121.8 (CH), 122.0 (C), 123.7 (CH), 125.5 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 129.1 (CH), 131.6 (CH), 131.9 (C), 136.9 (CH), 141.5 (C), 143.1 (C), 144.2 (C), 146.0 (C), 150.2 (C), 160.5 (C), 168.4 (C), 178.0 (CO), 198.9 (CO). MS (EI, 70 eV) *m*/*z*: 571 (M^+). Anal. Calcd for $C_{32}H_{21}N_5O_6$: C, 67.25; H, 3.70; N, 12.25%. Found: C, 67.35; H, 3.76; N, 12.34%.

*4.4.8. 11a-Hydroxy-1′-methyl-10-(4-nitrophenyl)-8-phenyl-11,11a-dihydro-6H-spiro[chromeno[4,3-b]pyrazolo[4,3-e]pyridine-7,3′-indoline]-2′,6(6aH,10H)-dione (**8i**).* Brown powder (0.47 g, 80%); mp 276 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3625, 3183, 1728, 1685, 1642; ^1H NMR (300 MHz, DMSO-d_6): δ_H=3.28 (3H, s, CH_3), 6.15 (1H, s, CH), 6.50–8.48 (17H, m, H-Ar), 11.2 (1H, s, NH), 11.54 (1H, s, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=26.8 (CH_3), 47.8 (C_{spiro}), 57.4 (CH), 103.7 (C), 108.8 (CH), 118.0 (CH), 119.7 (CH), 122.1 (C), 122.4 (CH), 123.5 (CH), 123.7 (CH), 125.5 (C), 127.1 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 129.3 (CH), 131.6 (CH), 131.8 (C), 141.6 (C), 143.1 (C), 145.6 (C), 146.1 (C), 150.2 (C), 160.5 (C), 168.4 (C), 176.2 (CO), 198.5 (CO). MS (EI, 70 eV) *m*/*z*: 585 (M^+). Anal. Calcd for $C_{33}H_{23}N_5O_6$: C, 67.69; H, 3.96; N, 11.96%. Found: C, 67.69; H, 4.04; N, 11.89%.

*4.4.9. 5′-Bromo-11a-hydroxy-10-(4-nitrophenyl)-8-phenyl-11,11a-dihydro-6H-spiro[chromeno[4,3-b]pyrazolo[4,3-e]pyridine-7,3′-indoline]-2′,6(6aH,10H)-dione (**8j**).* Brown powder (0.55 g, 70%); mp 285 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3394, 3219, 1740, 1688, 1638; ^1H NMR (300 MHz, DMSO-d_6): δ_H=6.18 (1H, s, CH), 6.64–8.45 (16H, m, H-Ar), 10.89 (1H, s, NH), 11.24 (1H, s, NH), 11.53 (1H, br s, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=48.4 (C_{spiro}), 57.2 (CH), 103.6 (C), 111.8 (CH), 113.4 (C), 118.1 (CH), 119.8 (CH), 122.1 (C), 123.7 (CH), 125.5 (CH), 127.2 (C), 127.9 (CH), 128.1 (CH), 128.3 (CH), 130.1 (CH), 131.6 (CH), 131.8 (CH), 131.9 (C), 136.9 (CH), 141.3 (C), 143.1 (C), 143.6 (C), 146.1 (C), 150.3 (C), 160.5 (C), 168.3 (C), 177.7 (CO), 198.6 (CO). MS (EI, 70 eV) *m*/*z*: 651 (M^+), 649 (M^+). Anal. Calcd for $C_{32}H_{20}BrN_5O_6$: C, 59.09; H, 3.10; N, 10.77%. Found: C, 59.19; H, 3.14; N, 10.71%.

*4.4.10. 11a-Hydroxy-5′-nitro-10-(4-nitrophenyl)-8-phenyl-11,11a-dihydro-6H-spiro[chromeno[4,3-b]pyrazolo[4,3-e]pyridine-7,3′-indoline]-2′,6(6aH,10H)-dione (**8k**).* Brown powder (0.52 g, 84%); mp

287 °C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3383, 3224, 1744, 1690, 1628; ^1H NMR (300 MHz, DMSO-d_6): δ_H=6.14 (1H, s, CH), 6.65–8.43 (16H, m, H-Ar), 10.88 (1H, s, NH), 11.25 (1H, s, NH), 11.56 (1H, br s, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=48.1 (C_{spiro}), 57.5 (CH), 102.9 (C), 110.2 (CH), 118.1 (CH), 119.8 (CH), 120.4 (CH), 122.2 (C), 123.7 (CH), 125.5 (CH), 126.5 (CH), 128.1 (CH), 128.3 (CH), 128.8 (CH), 131.6 (CH), 131.9 (C), 136.9 (CH), 141.4 (C), 142.1 (C), 143.0 (C), 146.2 (C), 150.2 (C), 150.8 (C), 160.4 (C), 168.1 (C), 178.7 (CO), 198.5 (CO). MS (EI, 70 eV) *m*/*z*: 616 (M^+). Anal. Calcd for $C_{32}H_{20}N_6O_8$: C, 62.34; H, 3.27; N, 13.63%. Found: C, 62.23; H, 3.22; N, 13.54%.

4.5. 11*a*′-Hydroxy-8′,10′-diphenyl-11′,11*a*′-dihydro-2*H*,6′*H*-spiro[acenaphthylene-1,7′-chromeno[3,4-*e*]pyrazolo[3,4-*b*]-pyridine]-2,6′(6*a*′*H*,10′*H*)-dione (10)

Whit powder (0.39 g, 70%); mp 241 °C dec; IR (KBr) (ν_{max}, cm^{-1}): 3316, 3044, 1721, 1632; ^1H NMR (300 MHz, DMSO-d_6): δ_H=6.31 (1H, s, CH), 6.33–8.16 (20H, m, H-Ar), 10.98 (1H, s, NH), 11.37 (1H, s, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C=52.8 (C_{spiro}), 59.18 (CH), 103.4 (C), 118.0 (CH), 119.8 (CH), 121.0 (CH), 122.0 (C), 122.2 (CH), 123.6 (CH), 125.1 (CH), 127.2 (CH), 127.7 (CH), 128.0 (CH), 128.7 (CH), 129.1 (CH), 129.8 (CH), 130.5 (C), 131.7 (CH), 132.3 (C), 132.8 (C), 136.8 (CH), 137.5 (C), 138.1 (C), 140.5 (C), 142.5 (C), 149.1 (C), 160.4 (C), 168.5 (C), 198.6 (CO), 202.8 (CO). MS (EI, 70 eV) *m*/*z*: 561 (M^+). Anal. Calcd for $C_{36}H_{23}N_3O_4$. C, 76.99; H, 4.13; N, 7.48. Found: C, 76.90; H, 4.17; N, 7.41%.

Acknowledgements

We gratefully acknowledge financial support from the Research Council of Shahid Beheshti University, G.C.

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