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A First Resource-Efficient and Highly Flexible Procedure for a Four-Component Synthesis of Dispiropyrrolidines

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Two series of dispiropyrrolidine derivatives were successfully synthesized by a tandem Knoevenagel–1,3-dipolar cycloaddition reaction sequence of isatin or acenaphthylene-1,2-dione, sarcosine, 1,3-indanedione, and an aldehyde without any catalyst. This strategy is not only suitable to aromatic aldehydes but aliphatic and heteroaromatic aldehydes as well. Moreover, this one-pot, four-component synthesis of dispiropyrrolidines is the first of its kind, as the dipole azomethine ylide and dipolarophile can be generated in situ. Such a strategy would provide access to a fast one-pot synthesis of dispiroheterocycles, which are otherwise accessible only through multistep synthesis.

Introduction

The rapid assembly of molecular diverse compounds is an important goal of synthetic organic chemistry and one of the key paradigms of modern drug discovery. One strategy that potentially meets the goals of synthesis and library production is multicomponent reactions (MCRs), in which three or more starting materials are brought together in a flexible, convergent, and atom-efficient approach to rapidly build up molecular structure and complexity.[1–3] They offer significant advantages over conventional linear step synthesis by reducing time and by saving money, energy, and raw materials, which thus results in both economical and environmental benefits. At the same time, diversity can be achieved from building up libraries by simply varying each component.

Tandem reactions are of paramount importance in the context of green chemistry, as they offer a convenient strategy for the rapid, elegant, and convergent construction of complex organic molecules without isolating and purifying the intermediates, which results in substantial minimization of waste, labor, time, and cost.[4]

The 1,3-dipolar cycloaddition, also known as the Huisgen cycloaddition, is a classical and fundamental reaction in organic chemistry, which consists of the reactions of azomethine ylides with olefinic or acetylenic dipolarophiles; this results in the production of various highly substituted five-membered heterocycles in a regio- and stereoselective manner.[5,6]

Some spiropyrrolidines are potential antileukemic and anticonvulsant agents[7] and possess antiviral[8] and local anaesthetic[9] activities. They are found in a number of biologically active compounds.[10] Isatin and its derivatives have interesting biological activities and are widely used as precursors for many natural products.[11] Especially, oxindole derivatives at C3 as spirocarbo- and heterocyclics highly enhance biological activity.[12] Spiropyrrolidinyloxindoles are also found in a number of alkaloids of biological importance.[13] For example, spirotryprostatin A, a natural alkaloid isolated from the fermentation broth of Aspergillus fumigatus, has been identified as a novel inhibitor of microtubule assembly, and pteropodine and isopteropodine have been shown to modulate the function of muscarinic serotonin receptors (Figure 1).

As a result of the vast utility of this kind of compound, a number of synthetic routes have been developed for the expedition of these structure frameworks,[14] and the 1,3-dipolar cycloaddition method was also widely employed.[15] All of these classical Huisgen 1,3-dipolar cycloaddition syntheses of spiropyrrolidines were performed by heating a mixture of the 1,3-dipole and dipolarophile. Some of them involved the use of a catalyst, such as K-10 montmorillonite[15c] and $ZrOCl_2 \cdot 8H_2O$-ball clay,[15b] and some were carried out under solvent-free and microwave-assisted conditions.[15d] However, all of these reactions have the same

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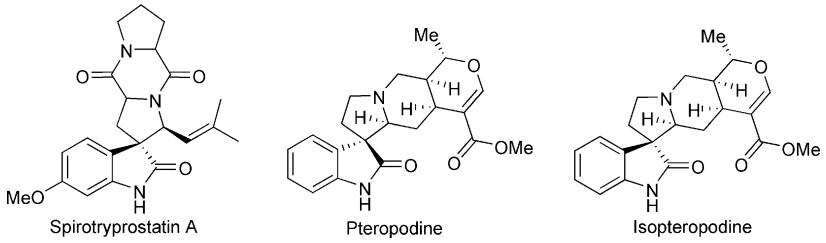
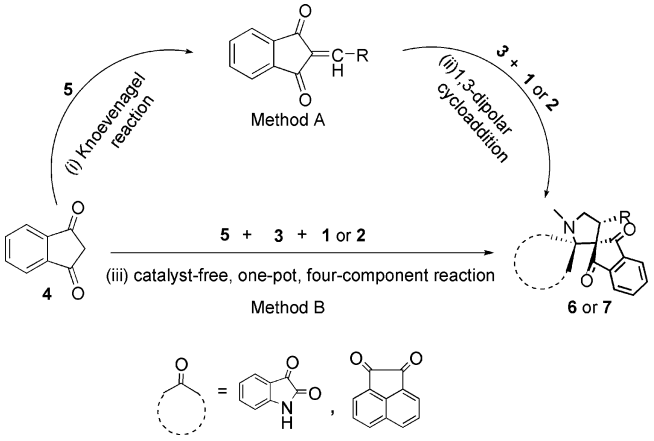


Figure 1. Representative spirooxindole-containing compounds.

limitation of preparation of dipolarophiles in advance. Therefore, it is worthwhile to develop a new, simple, and effective methodology.

In view of the advantages of MCRs and tandem reactions and prompted by our previous research on multicomponent reactions,[16] we wanted to develop a more convenient 1,3-dipolar cycloaddition synthesis of spiropyrrolidines. Herein we describe a rapid, mild, but effective extension of the Huisgen synthesis for dispiroheterocycles, which proceeds by a catalyst-free, four-component tandem Knoevenagel–1,3-dipolar cycloaddition reaction sequence of isatin (**1**) or acenaphthylene-1,2-dione (**2**), sarcosine (**3**), 1,3-indanedione (**4**), and aldehyde **5**, without the isolation of dipolarophiles (Scheme 1, Method B). Such a strategy would provide access to a fast, one-pot synthesis of dispiroheterocycles, which are otherwise accessible only through multistep synthesis.



Scheme 1. Our approach (Method B) compared with traditional synthetic route (Method A).

Results and Discussion

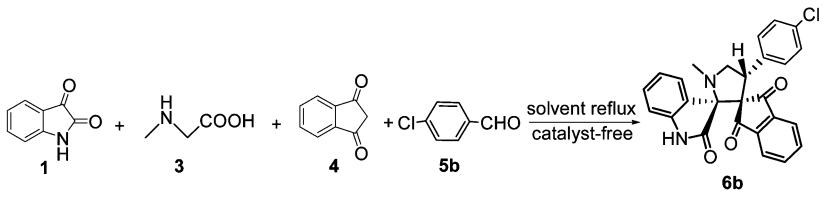
As we know, amino acids as effective catalysts are wildly used in organic synthesis[17] in reactions such as the aldol condensation and Mannich and Michael addition reactions. In our experiment, the Knoevenagel condensation reaction between 1,3-indanedione (**4**) and aldehyde **5b** cannot take place without sarcosine, even after heating at reflux in ethanol for 30 min. In the presence of sarcosine (20 mmol-%), however, the reaction can dramatically take place, and the reactants were completely converted only after heating at reflux for 5 min (monitored by TLC). This result indicates that sarcosine is an efficient catalyst for this Knoevenagel reaction. So, sarcosine, which was also a key substrate, plays a dual role in the tandem reaction.

The reaction of isatin (**1**), sarcosine (**3**), 1,3-indanedione (**4**), and aldehyde **5b** was carried out in different solvents, and the mol ratio of reactants for this MCR was also investigated. The results are collected in Table 1. The reaction gave a low yield of 35% in toluene and took a long time (8 h; Table 1, Entry 2). When the reaction was carried out in acetonitrile, 1,4-dioxane, or methanol, spiropyrrolidine **6b** was obtained in moderate yields (Table 1, Entries 1, 3, 4). It was exciting that the reaction proceeded well in ethanol to give a good yield of 72% in a shorter time period (1 h; Table 1, Entry 5). To further improve the yield, the ratios of isatin (**1**), sarcosine (**3**), 1,3-indanedione (**4**), and benzaldehyde **5b** were examined (Table 1, Entries 6–9). The yield was remarkably improved from 72 to 81% when 1.2 equiv. of sarcosine was added (Table 1, Entry 6). When more sarcosine was added, the yield was not further improved (Table 1, Entry 7). To enhance the conversion of aldehyde **5b**, 1.2 equiv. of 1,3-indanedione (**4**) was employed, and the yield was slightly enhanced to 88% (Table 1, Entry 8) but not further improved when more 1,3-indanedione was added (Table 1, Entry 9). So, ethanol as solvent and the mol ratio of **1/3/4/5b** = 1:1.2:1.2:1 were deemed as the optimum reaction condition (Table 1, Entry 8).

To extend the scope of this new procedure for the synthesis of dispiropyrrolidines, a series of reactions were carried out under the optimal conditions. We were pleased to find that the reaction proceeded smoothly and desired products were afforded in excellent yields. Notably, the electronic effects of the substituent on the aromatic ring have no significant influence on the reaction yields.

The reaction is highly regio- and stereoselective. By using ketones **1** and **2**, sarcosine (**3**), and 1,3-indanedione (**4**) as model substrates, when 11 aromatic aldehydes bearing either electron-withdrawing or electron-donating substituents in the *meta* or *para* positions were employed, the reaction proceeded very efficiently in all cases and afforded only one diastereomer of dispiropyrrolidines **6a**–**k** and **7a**–**k**. However, for aromatic aldehydes with *ortho* substituents,

Table 1. Optimization of reaction conditions for the multicomponent reactions.



Entry	Solvent	**1**:**3**:**4**:**5b** (mol ratio)	Time [h]	Yield [%][a]
1	acetonitrile	1:1:1:1	5	60
2	toluene	1:1:1:1	8	35
3	methanol	1:1:1:1	3	65
4	dioxane	1:1:1:1	5	54
5	ethanol	1:1:1:1	1	72
6	ethanol	1:1.2:1:1	1	81
7	ethanol	1:1.4:1:1	1	81
8	ethanol	1:1.2:1.2:1	1	88
9	ethanol	1:1.2:1.4:1	1	87

[a] Isolated yields.

such as *o*-chloro- and *o*-fluorobenzaldehydes, the 1:0.38 and 1:0.13 (determined by ^{1}H NMR spectroscopy) mixture of two diastereomeric dispiropyrrolidines **6l** and **6m** were obtained, respectively. This can be ascribed to the severe steric interaction between the *ortho* substituents aromatic aldehydes and 1,3-indanedione. The structures of the dispiropyrrolidines were further confirmed by X-ray crystal analysis of two representative compounds, **6e** and **7e** (Figures 2 and 3),[18] and we can assign all products **6** (except **6l** and **6m**) with the *R* configuration and all products **7** with the *S* configuration.

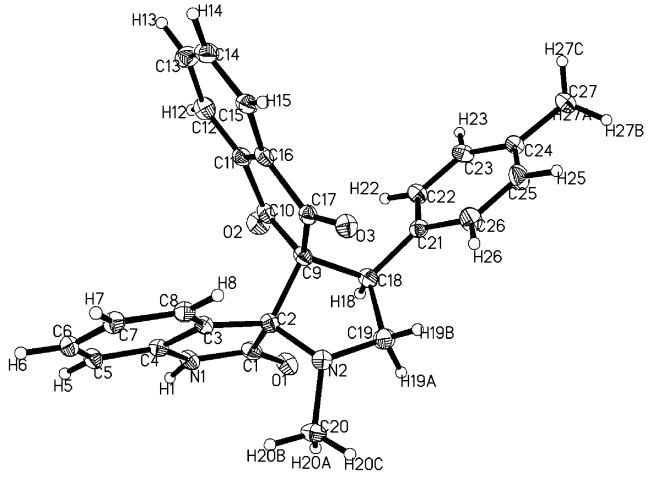


Figure 2. X-ray structure of **6e**.

Similarly, to our delight, aliphatic aldehydes such as butyraldehyde and acetaldehyde and heteroaromatic aldehyde such as furan-2-carbaldehyde were also successfully employed to produce the corresponding dispiropyrrolidines (Table 2, Entries 14–16). However, product **6o** showed lower

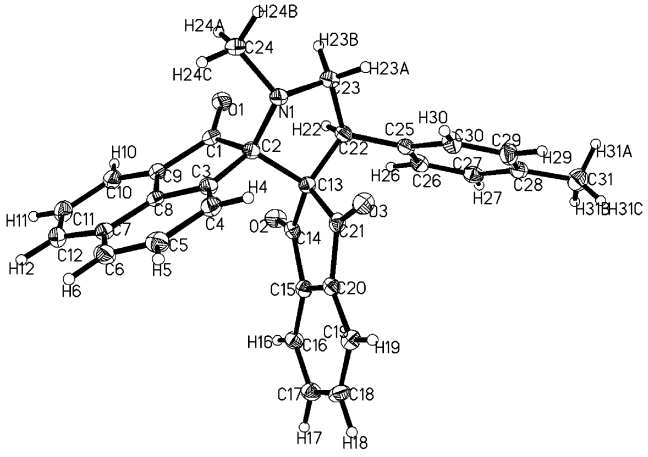
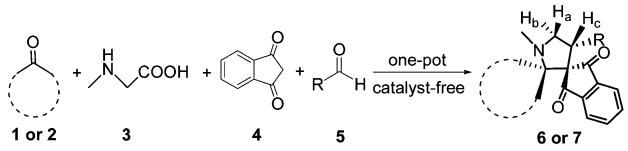


Figure 3. X-ray structure of **7e**.

yield when the aqueous solution of acetaldehyde was employed, which may be ascribed to two points: firstly, this domino reaction is a dehydration reaction; secondly, the solubility of reactants was lower in the presence of water. All the compounds were thoroughly characterized by spectroscopic methods (IR, ^{1}H and ^{13}C NMR), mass spectra, and elemental analysis. The results are summarized in Table 2.

The mechanism of this novel domino reaction has not been unequivocally established, but one reasonable mechanism for the reaction is outlined in Scheme 2.[19] The initial condensation between 1,3-indanedione (**4**) and aldehydes **5** gives dipolarophiles **10** catalyzed by sarcosine; at the same time, sarcosine reacts with ketone **1** or **2** to form dipole azomethine ylide **11**. Upon 1,3-dipolar cycloaddition of dipole **11** and dipolarophiles **10**, products **6** or **7** can be formed.

Table 2. One-pot, four-component synthesis of dispiropyrrolidines **6** and **7** without catalyst.

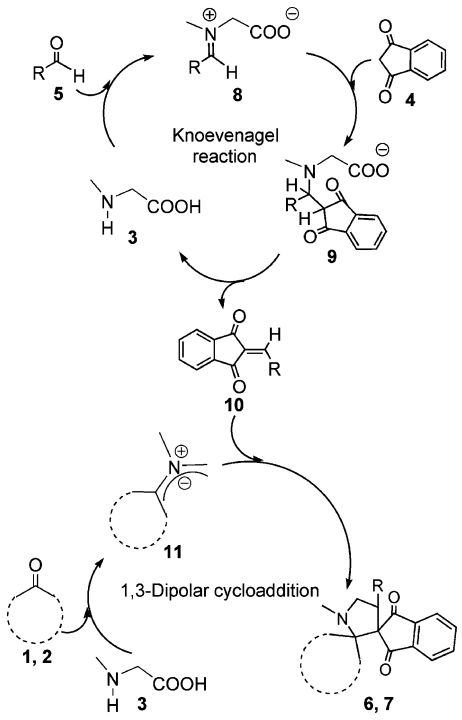


Entry	R	Product 6,7	Time [h]	Yield [%][a]
1	C_6H_5	**6a**	1.5	84
2	4-ClC_6H_4	**6b**	1.0	88
3	4-BrC_6H_4	**6c**	1.0	87
4	4-OHC_6H_4	**6d**	1.5	82
5	4-$CH_3C_6H_4$	**6e**	1.5	90
6	4-$OCH_3C_6H_4$	**6f**	2.0	84
7	3-$NO_2C_6H_4$	**6g**	1.0	87
8	3-FC_6H_4	**6h**	1.5	83
9	3-OHC_6H_4	**6i**	2.0	85
10	3,4-$(OCH_3)_2C_6H_3$	**6j**	1.5	86
11	3,4-$(OCH_2O)C_6H_3$	**6k**	2.5	82
12	2-ClC_6H_4	**6l**	1.5	85
				(*R*/*S*, 1:0.38)[b]
13	2-FC_6H_4	**6m**	1.5	83
				(*R*/*S*, 1:0.13)[b]
14	$CH_3CH_2CH_2$	**6n**	2.0	80
15	CH_3[c]	**6o**	2.0	63
16		**6p**	2.0	85
17	C_6H_5	**7a**	1.5	86
18	4-ClC_6H_4	**7b**	1.0	91
19	4-BrC_6H_4	**7c**	1.5	87
20	4-OHC_6H_4	**7d**	1.5	85
21	4-$CH_3C_6H_4$	**7e**	1.0	90
22	4-$OCH_3C_6H_4$	**7f**	1.5	87
23	3-$NO_2C_6H_4$	**7g**	1.0	92
24	3-FC_6H_4	**7h**	1.5	85
25	3-OHC_6H_4	**7i**	1.5	83
26	3,4-$(OCH_3)_2C_6H_3$	**7j**	2.0	85
27	3,4-$(OCH_2O)C_6H_3$	**7k**	2.0	83

[a] Isolated yields. [b] Determined by ^{1}H NMR spectroscopy. [c] Acetaldehyde was used as an aqueous solution.

Conclusions

We successfully designed a facile and direct entry into two series of interesting novel dispiropyrrolidines in good yields by a tandem Knoevenagel–1,3-dipolar cycloaddition reaction. Sarcosine plays a dual role and served as a key substrate as well as an efficient catalyst in this reaction. This one-pot, four-component synthetic method is the first of its kind, as dispiropyrrolidines allows 1,3-dipole azomethine ylide and dipolarophile to be generated in situ, which make this novel annulation strategy both practical and attractive. The direct use of commercially available and inexpensive reagents, simple experimental and work-up procedures, short reaction times, and mild reaction conditions is complementary to the classical Huisgen synthesis, in that it could be suited to the preparation of dispiroheterocyclic compounds such as alkaloids. Further studies and applications on this domino reaction are ongoing in our laboratory and will be published in due course.



Scheme 2. A reasonable mechanism for synthesis of dispiropyrrolidines.

Experimental Section

General: The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV-500 spectrometer. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS) or the residual proton resonances in the deuterated solvents: dimethyl sulfoxide (DMSO) or chloroform ($CDCl_3$). IR spectra were recorded with a Nicolet 510P FTIR spectrometer. Mass spectra were performed with a Bruker Esquire Hct and Ultima Global spectrometer with an ESI source. Elemental analyses were carried out with a Vario EL-Sh analyzer. The X-ray single-crystal diffraction was performed with a Rigaku Saturn instrument. Melting points were determined with a RY-1 microscopic melting apparatus and are uncorrected. TLC analysis was performed on 0.25 mm silica gel GF_{254} plates. All chemicals were purchased and used without further purification.

General Procedure for the Synthesis of Dispiropyrrolidines 6 and 7: A mixture of isatin (**1**; 0.147 g, 1.0 mmol) or acenaphthylene-1,2-dione (**2**; 0.182 g, 1.0 mmol), sarcosine (**3**; 0.107 g, 1.2 mmol), 1,3-indanedione (**4**; 0.175 g, 1.2 mmol), and aldehyde **5** (1.0 mmol) was heated at reflux in EtOH (10 mL). After completion of the reaction as indicated by TLC (petroleum ether/EtOAc, 4:1), the mixture was

cooled to room temperature, left overnight, and the solid product was filtered and recrystallized from CH_3CN to give the pure product.

1′-Methyl-4′-phenyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6a): M.p. 212–213 °C. IR (KBr): $\tilde{\nu}$ = 3137, 3083, 2934, 1743, 1714, 1710, 1619, 1597, 1470, 1263, 754, 697 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.43 (s, 1 H, NH), 6.58–7.72 (m, 13 H, ArH), 5.03–5.07 (m, 1 H, H_c), 4.03–4.06 (m, 1 H, H_b), 3.57–3.61 (m, 1 H, H_a), 2.15 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 198.10, 197.10, 175.96, 143.14, 142.60, 141.36, 137.21, 136.79, 136.66, 130.41, 128.91, 128.77, 127.66, 125.66, 123.96, 123.09, 121.80, 110.28, 77.78, 69.97, 56.11, 46.02, 35.15 ppm. MS (ESI): *m*/*z* = 409.3 $[M + H]^+$. $C_{26}H_{20}N_2O_3$ (408.46): calcd. C 76.45, H 4.94, N 6.86; found C 76.61, H 4.91, N 6.84.

4′-(4-Chlorobenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6b): M.p. 242–243 °C. IR (KBr): $\tilde{\nu}$ = 3333, 3057, 2932, 1743, 1725, 1700, 1619, 1593, 1469, 1261, 854, 754 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.44 (s, 1 H, NH), 6.57–7.71 (m, 12 H, ArH), 5.00–5.06 (m, 1 H, H_c), 3.99–4.03 (m, 1 H, H_b), 3.57–3.62 (m, 1 H, H_a), 2.13 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 197.86, 196.99, 175.85, 143.09, 142.55, 142.22, 137.39, 136.84, 135.86, 132.27, 130.80, 130.49, 128.79, 123.89, 123.75, 123.20, 121.86, 110.34, 77.85, 69.88, 56.04, 45.22, 35.12 ppm. MS (ESI): *m*/*z* = 443.3 $[M + H]^+$. $C_{26}H_{19}ClN_2O_3$ (442.90): calcd. C 70.51, H 4.32, N 6.33; found C 70.77, H 4.29, N 6.31.

4′-(4-Bromobenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6c): M.p. 249–250 °C. IR (KBr): $\tilde{\nu}$ = 3335, 3057, 2932, 1740, 1724, 1700, 1619, 1469, 1261, 1009, 756 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.45 (s, 1 H, NH), 6.58–7.74 (m, 12 H, ArH), 5.00–5.03 (m, 1 H, H_c), 3.99–4.02 (m, 1 H, H_b), 3.58–3.62 (m, 1 H, H_a), 2.14 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 197.84, 196.98, 175.84, 143.09, 142.56, 141.31, 137.38, 136.83, 136.31, 131.71, 131.15, 130.49, 125.59, 123.74, 123.20, 121.85, 120.83, 110.33, 77.88, 69.81, 55.99, 45.23, 35.12 ppm. MS (ESI): *m*/*z* = 487.2 $[M + H]^+$. $C_{26}H_{19}BrN_2O_3$ (487.35): calcd. C 64.08, H 3.93, N 5.75; found C 64.32, H 3.91, N 5.73.

4′-(4-Hydroxybenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6d): M.p. 216–217 °C. IR (KBr): $\tilde{\nu}$ = 3315, 3054, 2941, 1745, 1714, 1707, 1618, 1519, 1469, 1261, 852, 758 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.39 (s, 1 H, NH), 9.22 (s, 1 H, OH), 6.47–7.72 (m, 12 H, ArH), 4.93–4.96 (m, 1 H, H_c), 3.93–3.97 (m, 1 H, H_b), 3.50–3.54 (m, 1 H, H_a), 2.14 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 198.22, 197.25, 175.95, 156.70, 143.09, 142.60, 141.43, 136.98, 136.43, 130.19, 129.92, 126.40, 125.62, 124.12, 122.90, 121.64, 115.42, 110.11, 77.58, 70.09, 56.45, 45.73, 35.04 ppm. MS (ESI): *m*/*z* = 425.4 $[M + H]^+$. $C_{26}H_{20}N_2O_4$ (424.46): calcd. C 73.57, H 4.75, N 6.60; found C 71.83, H 4.72, N 6.57.

1′-Methyl-4′-(4-methylbenzoyl)trispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6e): M.p. 232–233 °C. IR (KBr): $\tilde{\nu}$ = 3184, 3084, 2940, 1743, 1710, 1707, 1617, 1513, 1470, 1261, 782, 767 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.37 (s, 1 H, NH), 6.54–7.67 (m, 12 H, ArH), 4.95–4.99 (m, 1 H, H_c), 3.96–3.99 (m, 1 H, H_b), 3.50–3.54 (m, 1 H, H_a), 2.11 (s, 3 H, N-CH_3), 2.06 (s, 3 H, 4-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 198.17, 197.17, 175.96, 143.10, 142.63, 141.39, 137.20, 136.74, 136.66, 133.67, 130.39, 129.37, 128.81, 125.60, 123.98, 123.09, 121.78, 110.26, 77.81, 69.94, 56.22, 45.62, 35.14, 20.93 ppm. MS (ESI): *m*/*z* = 423.2 $[M + H]^+$. $C_{27}H_{22}N_2O_3$ (422.48): calcd. C 76.76, H 5.25, N 6.63; found C 76.95, H 5.21, N 6.61.

1′-Methyl-4′-(4-methoxybenzoyl)trispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6f): M.p. 199–200 °C. IR (KBr): $\tilde{\nu}$ = 3189, 3086, 2935, 1745, 1710, 1707, 1616, 1514, 1470, 1255, 828, 756 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.42 (s, 1 H, NH), 6.58–7.70 (m, 12 H, ArH), 4.97–5.01 (m, 1 H, H_c), 3.96–4.00 (m, 1 H, H_b), 3.54–3.60 (m, 1 H, H_a), 2.14 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 198.13, 197.22, 175.91, 158.57, 143.04, 142.56, 141.35, 137.11, 136.55, 130.28, 130.04, 128.23, 125.54, 123.98, 122.99, 121.70, 114.04, 110.17, 77.70, 69.97, 56.42, 55.24, 45.41, 35.06 ppm. MS (ESI): *m*/*z* = 439.2 $[M + H]^+$. $C_{27}H_{22}N_2O_4$ (438.48): calcd. C 73.96, H 5.06, N 6.39; found C 74.18, H 5.03, N 6.36.

1′-Methyl-4′-(3-nitrobenzoyl)trispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6g): M.p. 223–224 °C. IR (KBr): $\tilde{\nu}$ = 3201, 3086, 2941, 1742, 1712, 1703, 1619, 1592, 1529, 1471, 1351, 771, 687 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.50 (s, 1 H, NH), 6.60–7.95 (m, 12 H, ArH), 5.13–5.18 (m, 1 H, H_c), 4.05–4.11 (m, 1 H, H_b), 3.68–3.73 (m, 1 H, H_a), 2.16 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 197.50, 196.86, 175.73, 147.92, 143.20, 142.53, 141.22, 139.30, 137.49, 136.96, 135.83, 130.60, 130.47, 125.56, 123.47, 123.25, 122.78, 121.99, 110.46, 78.23, 69.88, 53.99, 45.08, 35.09 ppm. MS (ESI): *m*/*z* = 454.2 $[M + H]^+$. $C_{26}H_{19}N_3O_5$ (453.45): calcd. C 68.87, H 4.22, N 9.27; found C 69.15, H 4.20, N 9.24.

4′-(3-Fluorobenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6h): M.p. 220–221 °C. IR (KBr): $\tilde{\nu}$ = 3249, 3087, 2938, 1742, 1722, 1716, 1619, 1589, 1471, 1265, 786, 754 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.46 (s, 1 H, NH), 6.59–7.73 (m, 12 H, ArH), 5.04–5.08 (m, 1 H, H_c), 4.01–4.04 (m, 1 H, H_b), 3.59–3.63 (m, 1 H, H_a), 2.15 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 197.79, 196.92, 175.84, 143.13, 142.57, 141.33, 139.89, 139.84, 137.31, 136.77, 130.74, 130.67, 130.46, 125.63, 125.06, 123.74, 123.14, 121.82, 115.70, 115.52, 114.63, 114.46, 110.31, 77.84, 69.90, 55.96, 45.44, 35.09 ppm. MS (ESI): *m*/*z* = 427.3 $[M + H]^+$. $C_{26}H_{19}FN_2O_3$ (426.45): calcd. C 73.23, H 4.49, N 6.57; found C 73.45, H 4.47, N 6.55.

4′-(3-Hydroxybenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6i): M.p. 215–216 °C. IR (KBr): $\tilde{\nu}$ = 3422, 3097, 2937, 1743, 1708, 1620, 1596, 1740, 1263, 787, 754 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.41 (s, 1 H, NH), 9.27 (s, 1 H, OH), 6.44–7.72 (m, 12 H, ArH), 4.95–4.98 (m, 1 H, H_c), 3.96–4.00 (m, 1 H, H_b), 3.53–3.56 (m, 1 H, H_a), 2.14 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 198.03, 196.94, 175.92, 157.44, 143.08, 142.63, 141.38, 137.18, 136.99, 136.43, 130.24, 129.54, 125.64, 123.95, 122.95, 121.64, 119.34, 115.80, 114.50, 110.13, 77.70, 69.80, 56.08, 45.75, 35.06 ppm. MS (ESI): *m*/*z* = 425.2 $[M + H]^+$. $C_{26}H_{20}N_2O_4$ (424.46): calcd. C 73.57, H 4.75, N 6.60; found C 73.84, H 4.74, N 6.57.

4′-(3,4-Dimethoxybenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6j): M.p. 209–210 °C. IR (KBr): $\tilde{\nu}$ = 3307, 3062, 2942, 1743, 1714, 1707, 1621, 1518, 1471, 1264, 769, 755 cm^{-1}. ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.38 (s, 1 H, NH), 6.55–7.68 (m, 11 H, ArH), 4.94–4.98 (m, 1 H, H_c), 3.95–3.98 (m, 1 H, H_b), 3.53–3.58 (m, 1 H, H_a), 3.54 (s, 3 H, OCH_3), 3.53 (s, 3 H, OCH_3), 2.11 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 198.33, 197.40, 176.00, 148.47, 148.20, 143.15, 142.68, 141.48, 137.21, 136.65, 130.37, 128.78, 125.67, 124.06, 123.10, 123.03, 121.79, 121.11, 112.50, 111.81, 110.26, 77.65, 70.02, 56.42, 55.68, 55.65, 46.03, 35.12 ppm. MS

(ESI): *m*/*z* = 469.2 [M + H]$^+$. $C_{28}H_{24}N_2O_5$ (468.51): calcd. C 71.78, H 5.16, N 5.98; found C 71.99, H 5.14, N 5.96.

4′-(Benzo[*d*][1,3]dioxole-5-benzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6k): M.p. 219–220 °C. IR (KBr): $\tilde{\nu}$ = 3433, 3188, 3086, 1743, 1712, 1619, 1505, 1489, 1471, 1261, 1234, 796, 766 cm^{-1}. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.41 (s, 1 H, NH), 6.50–7.75 (m, 11 H, ArH), 5.87 (d, *J* = 6.0 Hz, 2 H, OCH_2O), 4.95–4.99 (m, 1 H, H_c), 3.93–3.96 (m, 1 H, H_b), 3.52–3.56 (m, 1 H, H_a), 2.13 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 197.98, 197.16, 175.83, 147.39, 146.59, 143.03, 142.55, 141.33, 137.16, 136.62, 130.29, 130.19, 125.54, 123.86, 123.05, 123.01, 122.36, 121.69, 110.18, 109.05, 108.39, 101.30, 77.69, 69.94, 56.39, 45.74, 35.02 ppm. MS (ESI): *m*/*z* = 453.2 [M + H]$^+$. $C_{27}H_{20}N_2O_5$ (452.47): calcd. C 71.67, H 4.46, N 6.19; found C 71.89, H 4.44, N 6.15.

4′-(2-Chlorobenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6l): 1:0.38 mixture of diastereomers A (*R*, major) and B (*S*, minor). M.p. 213–214 °C. IR (KBr): $\tilde{\nu}$ = 3334, 2938, 1743, 1728, 1707, 1619, 1595, 1468, 1259, 759 cm^{-1}. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.45 (s, 1 H, NH, A), 10.24 (s, 1 H, NH, B), 6.44–8.02 (m, 12 H, ArH, A + B), 5.49–5.53 (m, 1 H, H_c, A), 4.55–4.58 (m, 1 H, H_c, B), 4.39–4.43 (m, 1 H, H_b, B), 3.72–3.82 (m, 2 H, H_b + H_a, A), 3.53–3.56 (m, 1 H, H_a, B), 2.13 (s, 3 H, N-CH_3, A), 2.07 (s, 3 H, N-CH_3, B) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 199.18 (B), 196.95 (A), 196.78 (A), 194.41 (B), 175.69 (A), 175.34 (B), 143.62 (A), 143.12 (B), 141.97 (A), 141.45 (B), 141.33 (A), 141.03 (B), 136.91 (A), 136.67 (A), 136.46 (B), 136.24 (B), 135.86 (B), 134.43 (A), 134.28 (A), 134.22 (B), 131.77 (B), 131.65 (A), 130.34 (A), 130.21 (B), 129.56 (A), 129.17 (A), 128.91 (B), 128.69 (B), 127.25 (A), 127.09 (B), 126.65 (B), 126.27 (A), 123.73 (A), 123.25 (B), 123.14 (B), 123.03 (A), 122.90 (A), 122.61 (B), 121.67 (A), 121.58 (B), 110.14 (A), 109.83 (B), 78.02 (B), 77.45 (A), 69.37 (A), 68.62 (B), 57.70 (A), 56.73 (B), 43.11 (A, B), 34.81 (A), 34.68 (B) ppm. MS (ESI): *m*/*z* = 443.2 [M + H]$^+$. $C_{26}H_{19}ClN_2O_3$ (442.90): calcd. C 70.51, H 4.32, N 6.33; found C 70.78, H 4.28, N 6.30.

4′-(2-Fluorobenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6m): 1:0.13 mixture of diastereomers A (*R*, major) and B (*S*, minor). M.p. 218–219 °C. IR (KBr): $\tilde{\nu}$ = 3331, 2944, 2858, 1745, 1724, 1708, 1614, 1594, 1466, 1258, 757 cm^{-1}. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.43 (s, 1 H, NH, A), 10.23 (s, 1 H, NH, B), 6.44–7.72 (m, 12 H, ArH, A + B), 5.24–5.28 (m, 1 H, H_c, A), 4.48–4.52 (m, 1 H, H_c, B), 4.34–4.38 (m, 1 H, H_b, B), 3.94–3.98 (m, 1 H, H_b, A), 3.65–3.68 (m, 1 H, H_a, A), 3.53–3.57 (m, 1 H, H_a, B), 2.13 (s, 3 H, N-CH_3, A), 1.98 (s, 3 H, N-CH_3, B) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 198.38 (B), 197.07 (A), 196.92 (A), 194.46 (B), 175.81 (A), 175.18 (B), 161.66 (B), 159.72 (A), 143.41 (A), 142.96 (B), 142.07 (A), 141.54 (B), 141.30 (A), 137.09 (A), 136.77 (A), 136.49 (B), 136.43 (B), 130.94 (B), 130.48 (A), 129.60 (A), 129.53 (B), 125.88 (A), 124.70 (B), 123.75 (A), 123.11 (B), 123.05 (B), 121.82 (A), 115.50 (A), 115.32 (B), 110.29 (A), 109.84 (B), 78.31 (B), 77.61 (A), 69.11 (B), 68.93 (A), 55.94 (A), 55.69 (B), 39.04 (B), 38.77 (A), 34.96 (A, B) ppm. MS (ESI): *m*/*z* = 427.3 [M + H]$^+$. $C_{26}H_{19}FN_2O_3$ (426.45): calcd. C 73.23, H 4.49, N 6.57; found C 73.43, H 4.46, N 6.54.

1′-Methyl-4′-propyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6n): M.p. 202–203 °C. IR (KBr): $\tilde{\nu}$ = 3211, 2960, 2928, 1742, 1712, 1709, 1614, 1591, 1471, 1263, 759 cm^{-1}. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.29 (s, 1 H, NH), 6.55–7.87 (m, 8 H, ArH), 3.64–3.67 (m, 1 H, H_c), 3.34–3.39 (m, 1 H, H_b), 3.22–3.25 (m, 1 H, H_a), 2.19 (s, 3 H, N-CH_3), 0.89–1.32 (m, 4 H, $CH_2CH_2CH_3$), 0.69 (dd, *J* = 6.0, 3.5 Hz, 3 H, $CH_2CH_2CH_3$) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 198.47, 198.07, 175.92, 143.13, 142.51, 141.49, 137.21, 136.71, 130.26, 125.44, 124.04, 123.16, 121.66, 110.16, 77.70, 68.20, 58.29, 40.79, 35.09, 31.98, 21.97, 14.44 ppm. MS (ESI): *m*/*z* = 375.2 [M + H]$^+$. $C_{23}H_{22}N_2O_3$ (374.44): calcd. C 73.78, H 5.92, N 7.48; found C 74.05, H 5.90, N 7.46.

1′-Methyl-4′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6o): M.p. 193–194 °C. IR (KBr): $\tilde{\nu}$ = 3193, 3091, 2866, 1743, 1720, 1707, 1619, 1595, 1470, 1266, 762 cm^{-1}. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.29 (s, 1 H, NH), 6.55–7.91 (m, 8 H, ArH), 3.70–3.74 (m, 1 H, H_c), 3.36–3.40 (m, 1 H, H_b), 3.18–3.22 (m, 1 H, H_a), 2.04 (s, 3 H, N-CH_3), 0.75 (d, *J* = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 198.36, 198.05, 175.93, 143.11, 142.64, 141.79, 137.26, 136.71, 130.22, 125.44, 124.33, 123.15, 121.66, 110.13, 77.49, 68.89, 59.28, 35.57, 35.03, 13.52 ppm. MS (ESI): *m*/*z* = 347.2 [M + H]$^+$. $C_{21}H_{18}N_2O_3$ (346.39): calcd. C 72.82, H 5.24, N 8.09; found C 73.09, H 5.22, N 8.06.

4′-(Furan-2-yl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,3′′-indole]-1,3,2′′-trione (6p): M.p. 212–213 °C. IR (KBr): $\tilde{\nu}$ = 3297, 2853, 1745, 1733, 1702, 1617, 1593, 1469, 1264, 1185, 788, 754 cm^{-1}. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.44 (s, 1 H, NH), 6.15–7.80 (m, 11 H, ArH), 4.95–4.98 (m, 1 H, H_c), 3.86–3.89 (m, 1 H, H_b), 3.60–3.63 (m, 1 H, H_a), 2.11 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 197.21, 196.56, 175.84, 151.84, 143.17, 142.48, 142.27, 141.26, 137.14, 136.63, 130.50, 125.57, 123.48, 123.26, 123.12, 121.87, 110.90, 110.36, 107.52, 77.30, 67.78, 56.54, 55.14, 34.99 ppm. MS (ESI): *m*/*z* = 399.2 [M + H]$^+$. $C_{24}H_{18}N_2O_4$ (398.42): calcd. C 72.35, H 4.55, N 7.03; found C 72.55, H 4.53, N 7.01.

1′-Methyl-4′-phenyltrispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7a): M.p. 195–196 °C. IR (KBr): $\tilde{\nu}$ = 2932, 2864, 2793, 1793, 1722, 1704, 1598, 1493, 1264, 778, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.99–7.62 (m, 15 H, ArH), 5.13–5.17 (m, 1 H, H_c), 4.24–4.28 (m, 1 H, H_b), 3.87–3.92 (m, 1 H, H_a), 2.29 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 204.05, 198.64, 196.96, 142.94, 141.36, 140.93, 137.31, 136.59, 136.43, 134.05, 132.19, 131.55, 130.61, 129.20, 128.87, 128.83, 127.82, 126.31, 123.09, 123.06, 122.53, 121.32, 80.85, 71.45, 56.72, 47.50, 35.03 ppm. MS (ESI): *m*/*z* = 444.2 [M + H]$^+$. $C_{30}H_{21}NO_3$ (443.50): calcd. C 81.25, H 4.77, N 3.16; found C 81.49, H 4.75, N 3.14.

4′-(4-Chlorobenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7b): M.p. 231–233 °C. IR (KBr): $\tilde{\nu}$ = 2940, 2864, 2791, 1738, 1717, 1705, 1594, 1492, 1261, 831, 777 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.06–7.95 (m, 14 H, ArH), 5.11–5.15 (m, 1 H, H_c), 4.21–4.24 (m, 1 H, H_b), 3.89–3.93 (m, 1 H, H_a), 2.31 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 203.95, 198.40, 196.86, 142.86, 141.35, 140.85, 137.51, 136.79, 135.50, 133.82, 132.42, 132.30, 131.43, 130.60, 129.25, 128.86, 126.40, 123.18, 122.48, 121.42, 80.91, 71.27, 56.64, 46.62, 35.01 ppm. MS (ESI): *m*/*z* = 478.3 [M + H]$^+$. $C_{30}H_{20}ClNO_3$ (477.95): calcd. C 75.39, H 4.22, N 2.93; found C 75.56, H 4.20, N 2.91.

4′-(4-Bromobenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7c): M.p. 234–235 °C. IR (KBr): $\tilde{\nu}$ = 3426, 2970, 2925, 1738, 1716, 1705, 1652, 1624, 1262, 1051, 833, 777, 669 cm^{-1}. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 7.07–8.12 (m, 14 H, ArH), 4.94–4.98 (m, 1 H, H_c), 4.13–4.17 (m, 1 H, H_b), 3.75–3.79 (m, 1 H, H_a), 2.09 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 204.38, 198.28, 197.41, 143.01, 141.80, 141.32, 135.83, 135.19, 133.93, 131.72, 131.39, 131.32,

130.80, 130.55, 128.44, 128.29, 125.64, 122.85, 122.79, 122.54, 121.26, 121.07, 80.94, 71.41, 57.09, 47.47, 35.14 ppm. MS (ESI): m/z = 523.3 $[M + H]^+$. $C_{30}H_{20}BrNO_3$ (522.40): calcd. C 68.98, H 3.86, N 2.68; found C 69.20, H 3.84, N 2.66.

4′-(4-Hydroxybenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7d): M.p. 214–215 °C. IR (KBr): $\tilde{\nu}$ = 3468, 2979, 2941, 1737, 1722, 1705, 1615, 1593, 1516, 1260, 833, 780, 772 cm^{-1}. ^1H NMR (500 MHz, $[D_6]$DMSO, 25 °C): δ = 9.26 (s, 1 H, OH), 6.48–8.12 (m, 14 H, ArH), 4.87–4.91 (m, 1 H, H_c), 4.07–4.11 (m, 1 H, H_b), 3.66–3.70 (m, 1 H, H_a), 2.50 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, $[D_6]$DMSO, 25 °C): δ = 204.15, 198.94, 197.24, 156.91, 142.99, 141.32, 141.03, 137.28, 136.55, 134.28, 132.14, 131.60, 130.60, 130.00, 129.19, 128.86, 126.25, 126.05, 123.07, 123.01, 122.48, 121.27, 115.57, 100.03, 80.71, 71.63, 57.07, 47.37, 35.02 ppm. MS (ESI): m/z = 460.2 $[M + H]^+$. $C_{30}H_{21}NO_4$ (459.50): calcd. C 78.42, H 4.61, N 3.05; found C 78.69, H 4.59, N 3.03.

1′-Methyl-4′-(4-methylbenzoyl)trispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7e): M.p. 219–220 °C. IR (KBr): $\tilde{\nu}$ = 2930, 2866, 2792, 1738, 1720, 1704, 1593, 1514, 1462, 1259, 1158, 953, 830, 781, 764 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.92–8.12 (m, 14 H, ArH), 4.93–4.97 (m, 1 H, H_c), 4.14–4.17 (m, 1 H, H_b), 3.70–3.74 (m, 1 H, H_a), 2.15 (s, 3 H, N-CH_3), 2.09 (s, 3 H, 4-CH_3) ppm. ^{13}C NMR (125 MHz, $[D_6]$DMSO, 25 °C): δ = 204.02, 198.68, 197.01, 142.94, 141.30, 140.93, 137.28, 136.90, 136.57, 134.05, 133.30, 132.16, 131.51, 130.57, 129.40, 129.18, 128.80, 128.75, 126.26, 123.09, 123.03, 122.44, 121.29, 80.87, 71.37, 56.83, 47.07, 35.01, 20.91 ppm. MS (ESI): m/z = 458.2 $[M + H]^+$. $C_{31}H_{23}NO_3$ (457.53): calcd. C 81.38, H 5.07, N 3.06; found C 81.64, H 5.03, N 3.04.

1′-Methyl-4′-(4-methoxybenzoyl)trispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7f): M.p. 192–193 °C. IR (KBr): $\tilde{\nu}$ = 2948, 2862, 2790, 1740, 1714, 1702, 1604, 1512, 1260, 1182, 836, 780, 761 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.57–7.93 (m, 14 H, ArH), 5.08–5.12 (m, 1 H, H_c), 4.18–4.22 (m, 1 H, H_b), 3.84–3.88 (m, 1 H, H_a), 3.60 (s, 3 H, OCH_3), 2.29 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, $[D_6]$DMSO, 25 °C): δ = 204.07, 198.76, 197.16, 158.76, 142.98, 141.32, 140.98, 137.30, 136.57, 134.15, 132.17, 131.55, 130.60, 130.07, 129.19, 128.83, 127.95, 126.27, 123.10, 123.05, 122.46, 121.30, 114.19, 80.85, 71.52, 57.08, 55.34, 46.98, 35.02 ppm. MS (ESI): m/z = 474.2 $[M + H]^+$. $C_{31}H_{23}NO_4$ (473.53): calcd. C 78.63, H 4.90, N 2.96; found C 78.81, H 4.87, N 2.94.

1′-Methyl-4′-(3-nitrobenzoyl)trispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7g): M.p. 213–214 °C. IR (KBr): $\tilde{\nu}$ = 2943, 2866, 2794, 1738, 1718, 1700, 1592, 1527, 1350, 1266, 834, 782, 688 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.24–7.87 (m, 14 H, ArH), 5.24–5.27 (m, 1 H, H_c), 4.28–4.31 (m, 1 H, H_b), 3.96–4.00 (m, 1 H, H_a), 2.30 (s, 3 H, N-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C): δ = 203.97, 197.63, 196.99, 148.05, 142.88, 141.80, 141.15, 138.62, 136.02, 135.40, 135.28, 133.29, 131.53, 131.50, 130.54, 129.27, 128.51, 128.30, 125.85, 124.05, 122.95, 122.90, 122.60, 122.42, 121.82, 81.08, 71.15, 56.96, 46.95, 35.18 ppm. MS (ESI): m/z = 489.3 $[M + H]^+$. $C_{30}H_{20}N_2O_5$ (488.50): calcd. C 73.76, H 4.13, N 5.73; found C 73.91, H 4.11, N 5.70.

4′-(3-Fluorobenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7h): M.p. 202–203 °C. IR (KBr): $\tilde{\nu}$ = 3424, 2936, 2862, 1739, 1721, 1704, 1613, 1589, 1263, 1229, 830, 785 cm^{-1}. ^1H NMR (500 MHz, $[D_6]$DMSO, 25 °C): δ = 6.87–8.12 (m, 14 H, ArH), 4.99–5.03 (m, 1 H, H_c), 4.15–4.18 (m, 1 H, H_b), 3.76–3.80 (m, 1 H, H_a), 2.15 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, $[D_6]$DMSO, 25 °C): δ = 203.86, 198.27, 196.37, 142.77, 141.28, 140.77, 139.39, 139.33, 137.39, 136.68, 133.71, 132.20, 131.36, 130.76, 130.70, 130.52, 129.15, 128.76, 126.31, 124.99, 123.09, 123.05, 122.42, 121.31, 80.79, 71.18, 56.44, 46.76, 34.90 ppm. MS (ESI): m/z = 462.2 $[M + H]^+$. $C_{30}H_{20}FNO_3$ (461.49): calcd. C 78.08, H 4.37, N 3.04; found C 78.32, H 4.35, N 3.02.

4′-(3-Hydroxybenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7i): M.p. 208–209 °C. IR (KBr): $\tilde{\nu}$ = 3422, 3280, 2863, 1740, 1699, 1599, 1457, 1264, 1222, 831, 785 cm^{-1}. ^1H NMR (500 MHz, $[D_6]$DMSO, 25 °C): δ = 9.28 (s, 1 H, OH), 6.45–8.10 (m, 14 H, ArH), 4.89–4.92 (m, 1 H, H_c), 4.10–4.13 (m, 1 H, H_b), 3.69–3.72 (m, 1 H, H_a), 2.15 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, $[D_6]$DMSO, 25 °C): δ = 204.12, 198.75, 196.96, 157.56, 143.00, 141.36, 140.97, 137.84, 137.30, 136.56, 134.08, 132.19, 131.54, 130.60, 129.79, 129.20, 128.84, 126.30, 123.13, 123.09, 122.53, 121.34, 119.43, 115.80, 114.77, 80.81, 71.27, 56.68, 47.33, 35.04 ppm. MS (ESI): m/z = 460.3 $[M + H]^+$. $C_{30}H_{21}NO_4$ (459.50): calcd. C 78.42, H 4.61, N 3.05; found C 78.65, H 4.59, N 3.03.

4′-(3,4-Dimethoxybenzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7j): M.p. 209–210 °C. IR (KBr): $\tilde{\nu}$ = 2934, 2857, 2788, 1739, 1722, 1707, 1589, 1518, 1461, 1257, 1160, 1033, 833, 788, 767 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.54–7.62 (m, 13 H, ArH), 5.08–5.11 (m, 1 H, H_c), 4.20–4.23 (m, 1 H, H_b), 3.86–3.90 (m, 1 H, H_a), 3.70 (s, 3 H, 4-OCH_3), 3.67 (s, 3 H, 3-OCH_3), 2.28 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 204.19, 198.81, 197.94, 148.31, 148.00, 143.12, 141.89, 141.53, 135.74, 135.11, 131.86, 131.31, 130.60, 128.46, 128.39, 125.63, 122.85, 122.65, 121.30, 121.02, 112.04, 110.72, 80.69, 77.41, 77.15, 76.90, 71.55, 57.46, 55.78, 55.69, 48.67, 35.30 ppm. MS (ESI): m/z = 504.2 $[M + H]^+$. $C_{32}H_{25}NO_5$ (503.55): calcd. C 76.33, H 5.00, N 2.78; found C 76.58, H 4.97, N 2.76.

4′-(Benzo[*d*][1,3]dioxole-5-benzoyl)-1′-methyltrispiro[indane-2,3′-pyrrolidine-2′,2′′-acenaphthene]-1,3,1′′-trione (7k): M.p. 194–195 °C. IR (KBr): $\tilde{\nu}$ = 3417, 3056, 2885, 1737, 1716, 1701, 1600, 1490, 1442, 1258, 1044, 830, 783, 769 cm^{-1}. ^1H NMR (500 MHz, $[D_6]$DMSO, 25 °C): δ = 6.52–8.12 (m, 14 H, ArH), 5.88 (d, J = 7.5 Hz, 2 H, OCH_2O), 4.90–4.94 (m, 1 H, H_c), 4.08–4.11 (m, 1 H, H_b), 3.69–3.73 (m, 1 H, H_a), 2.15 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, $[D_6]$DMSO, 25 °C): δ = 204.04, 198.65, 197.15, 147.54, 146.81, 142.97, 141.33, 140.97, 137.42, 136.71, 134.03, 132.24, 131.51, 130.61, 129.90, 129.24, 128.86, 126.33, 123.21, 123.10, 122.48, 121.35, 109.10, 108.56, 101.46, 80.85, 71.47, 57.06, 47.31, 35.02 ppm. MS (ESI): m/z = 488.2 $[M + H]^+$. $C_{31}H_{21}NO_5$ (487.51): calcd. C 76.38, H 4.34, N 2.87; found C 76.61, H 4.32, N 2.85.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures; copies of the spectra for all new compounds.

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