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Synthesis of dispiropyrrolidines from chromone-3-carbaldehyde using sarcosine and ninhydrin as the source of an azomethine ylide

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ABSTRACT

An efficient one-pot synthesis of several novel dispirochromanopyrrolidines has been accomplished by the reaction of chromone-3-carbaldehyde, sarcosine and ninhydrin. The structures were confirmed by single crystal X-ray diffraction studies.

Spiropyrans have drawn attention over the last two decades for their pharmaceutical importance and their attractive photochemical behaviour. Spirobenzopyranocyclopropanes act as cytochrome P 450 RAI inhibitors,[1] spirobenzopyrano[2,4′]-piperidines act as carbonic anhydrase inhibitors[2] and spirobenzopyranoimidazoles act as aldose reductase[3] and 5-lipoxygenase inhibitors.[4] They have been used for the treatment of hypertension, hair loss, erectile dysfunction[5] and lipoxygenase-mediated diseases.[4] Spiropyrans are a known family of photochromic compounds and have potential applications as optical switches and memory storage devices.[6] They are also used for manufacturing photochromic plastic lenses.[7] Some naturally occurring spiropyrans have insecticidal properties.[8] Spirobenzopyrans bearing suitable substituents are capable of exhibiting complexation properties with different metal ions.[9] The synthesis of pyrrolidine moieties in the fused form or in spiro-form with different heterocycles has drawn much interest because of their pharmaceutical activities.[10] 1,3-Dipolar cycloaddition of an azomethine ylide to a suitably disposed olefin is an attractive route for the synthesis of the pyrrolidine moiety. Reactions of azomethine ylides (derived from the reaction of ninhydrin or isatin with sarcosine, proline or thiazolidine-4-carboxylic acid) with activated olefins (generated by aldol condensation or by Baylis–Hillman reaction) have been reported.[11] 3-Arylidene-4-chromanone has been employed for the generation of chromone-based dispiro compounds.[12] Furthermore, chromone-3-carbaldehyde **1** has been used for in situ formation of azomethine ylide **7** (Scheme 1). Treatment of **1** with sarcosine (**2**) in boiling toluene in the presence[13] or absence[14] of *p*-toluenesulfonic acid produces *N*-methyl-3-salicyloylpyrrole **4** as the major product. A very small amount of **5** was obtained from the latter reaction.[14] Formation of dihydropyrrole **6**, a pyran ring-opened tautomer of **5**, has been reported from our laboratory using DMF as solvent.[15] Compound **4** was generated from the intramolecular reaction of azomethine ylide **7**, whereas compounds **5** and **6** arise from the intermolecular [3+2] cyclization reaction of **7** and **1**. The ylide **7** has been trapped using selective dienophiles.[14,16]

With the intention of using the C2–C3 double bond of **1** as a 1,3-dipolarophile in the presence of a suitable azomethine ylide, we considered ninhydrin **3** and sarcosine **2** as the precursors of the azomethine ylide. The choice of ninhydrin is due to its higher carbonyl group reactivity than **1** towards nucleophiles. The results of the reactions of **1**, **2** and **3** in boiling alcohol are reported herein.

Heating an equimolar mixture of **1**, **2** and **3** in methanol under reflux for 7 h followed by work-up and chromatographic separation yielded two products **8** and **9** (Scheme 2) in 15–26% and 14–17% yields, respectively (Table 1, entries 1–3). The ^{1}H NMR spectrum of **8b**[17b] showed the presence of seven aromatic protons, three protons as separate multiplets centred at δ 2.08, δ 2.87 and δ 3.48 and two singlets for six protons at δ 2.22 and for one proton at δ 5.28. Another resonance, which appeared to be a singlet at δ 3.28 integrated for four protons. The ^{1}H NMR spectrum of **8a**[17a] also contained a 3H singlet at δ 2.22. Compared with the ^{1}H

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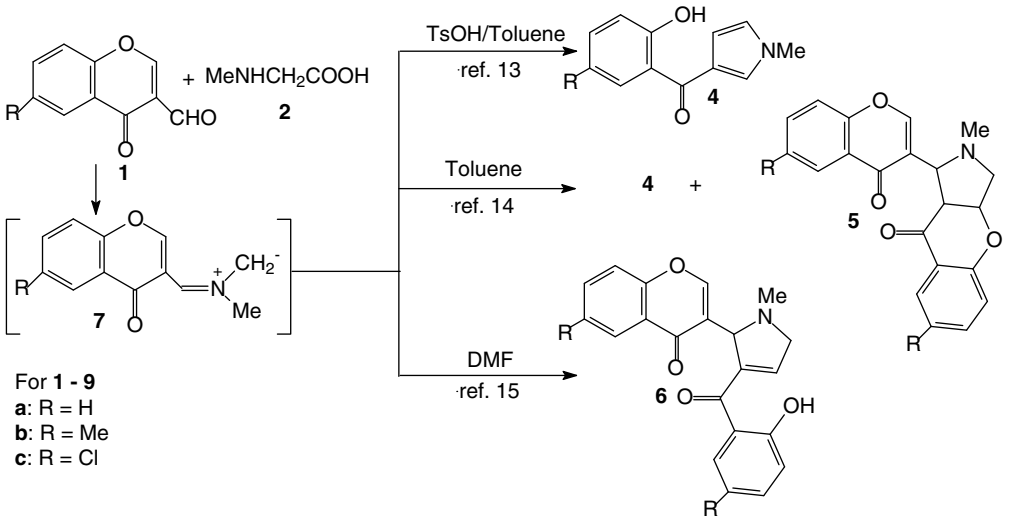
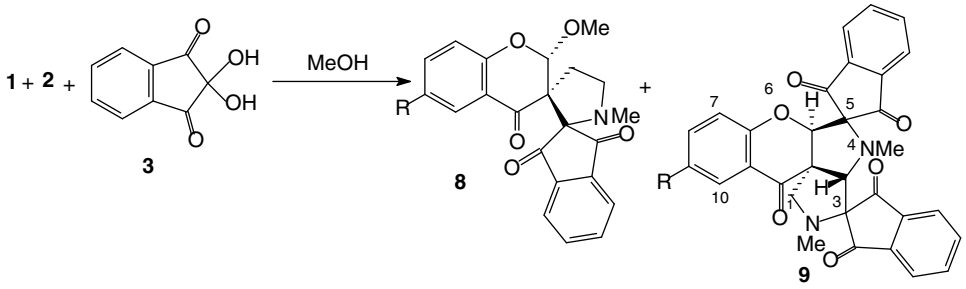


Scheme 1. Reaction between **1** and **2** under different conditions.[13–15]



Scheme 2. Synthesis of dispiropyrrolidines **8** and **9** by a one-pot multi-component reaction.

Table 1
Synthesis of dispiro compounds **8**, **9** and **14**, and their yields and melting points

Entry	R	Ratio of **1**:**2**:**3**	Additive	Time (h)	Yield (%)			Mps (°C)		
					8	**9**	**14**	**8**	**9**	**14**
1	H	1:1:1	—	7	22	15	—	186	204	—
2	Me	1:1:1	—	7	26	17	—	196–198	220–222	—
3	Cl	1:1:1	—	7	15	14	—	186–188	202	—
4	Me[a]	1:1:1	—	8	15	20	—	206[b]	220–222	—
5	Me	1:1:1	CH_2O	2	85	—	—	195–196	—	—
6	—	0:1:1	—	5	—	—	30	—	—	226–228
7	Me	1:2:2	—	2	—	65	10	—	218–219	226-228
8	Me	1:2:2	Argon	2	—	70	15	—	220–222	222–224

[a] EtOH was used as solvent in place of MeOH.
[b] OEt in place of OMe in **8b**.

spectrum of **8b**, the six protons at δ 2.22 in **8b** are due to the $ArCH_3$ and N–CH_3 groups. The singlet at δ 3.28 in the spectrum of **8b** is broad and integrates for four protons. This indicated that it was a merged peak composed of a singlet for three protons and a one proton multiplet. Assuming the 3 H singlet at δ 3.28 to be due to OCH_3, we carried out the same reaction with **1b** in ethanol (Table 1, entry 4) and were able to confirm our assumption. The ^{1}H NMR spectrum of **8b** (OEt in place of OMe) demonstrated the expected signals,[17c] and showed a multiplet at around δ 3.50 due to the two protons of the CH_2 of the OEt group and a one proton multiplet due to one of the two *N*–CH_2 protons. The ^{1}H NMR signals of **8b**[17b] do not corroborate the structure of a compound produced by a (3+2) cyclization of the azomethine ylide (derived from **2** and **3**) with the 2,3-double bond of **1**. However, the IR spectrum of **8b** showed absorptions at 1699 and 1735 cm^{-1} corresponding to chromanone and indanone carbonyls, respectively. The dispiropyrrolidene structure for **8** was established on the basis of IR, ^{1}H NMR and mass spectral analysis. Single crystal X-ray analysis also corroborated the structure of **8a** (Fig. 1).[18] A proposed mechanism for the formation of **8** is depicted in Scheme 3. Reaction of **2** and **3** forms the azomethine ylide **10** by deprotonation of **18**. Hydrolysis of **18** produces **11** and formaldehyde. It should be mentioned here that the reaction of ninhydrin with an α-amino acid was used for the synthesis of an aldehyde having one carbon less than the starting amino acid.[19] Azomethine ylide **10** traps formaldehyde to form alcohol **12**, which is intercepted by **1** at C-3 using the enol ether moiety. A subsequent formyl-shift from C-3 of the pyran ring to the oxygen atom of the CH_2OH group and cyclization

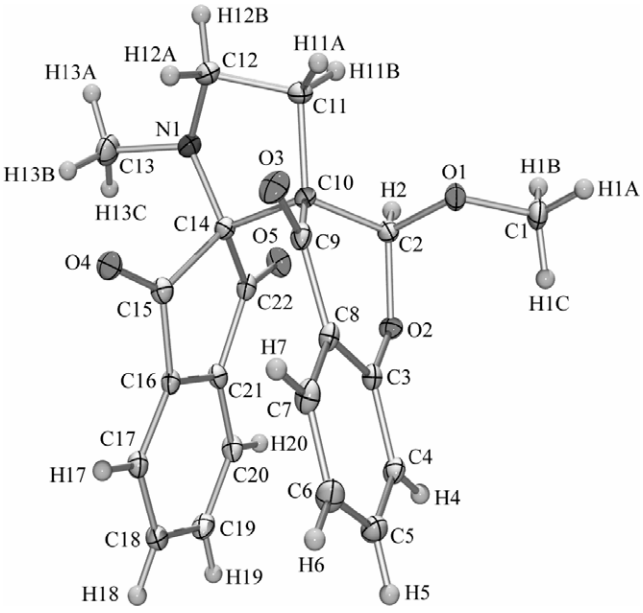
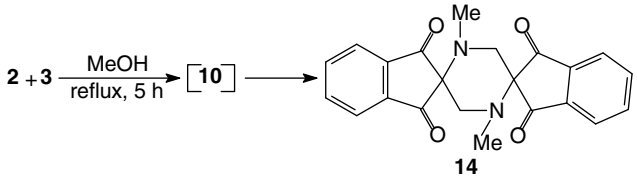


Figure 1. ORTEP diagram of **8a**.

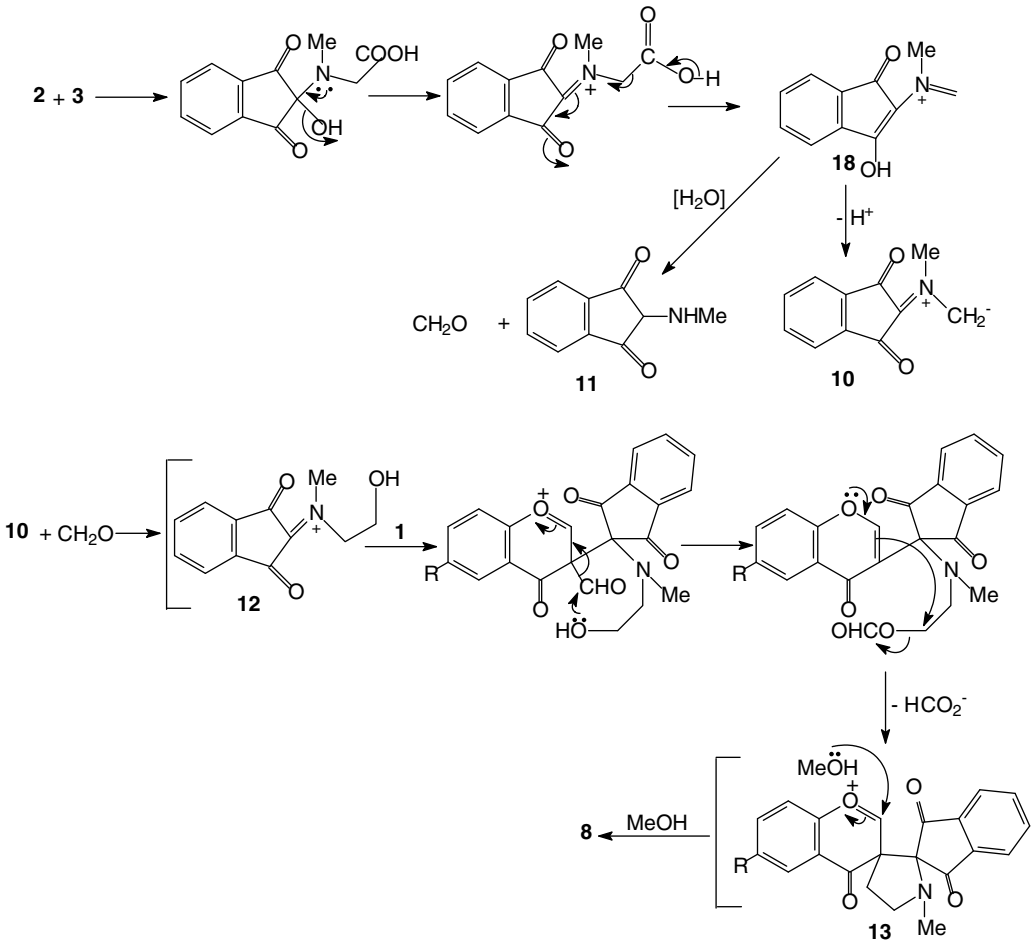
at C-3 of the pyran ring leads to the formation of spiro cation **13**, which readily forms the acetal **8** in the presence of alcohol. To verify the involvement of formaldehyde in this reaction, a mixture of **1b** (1 mmol), **2** (1 mmol), **3** (1 mmol) and 37% aqueous formaldehyde solution (0.2 ml) was heated in methanol under reflux. After heating for 2 h, aldehyde **1b** was found to be absent (TLC). On concentration and cooling, an orange yellow compound **8b** was obtained in good yield (Table 1, entry 5). Compound **9b** was not isolated from the reaction mixture.

The formation of azomethine ylide **10** was also evident from the formation of **14**, a dimer of **10** during the reaction of **2** and **3** (Scheme 4). On heating an equimolar mixture of **2** and **3** under reflux in methanol for 5 h and then cooling the reaction mixture, a fine crystalline yellow solid was obtained and identified as **14** (Table 1, entry 6).[20]

The structure of compound **9** was established on the basis of IR, ^{1}H NMR and mass spectral analysis[21] and finally confirmed by single crystal X-ray diffraction studies (Fig. 2).[22] Some notable features in the ^{1}H NMR spectrum of **9b** are as follows: (a) the 3 H singlet at δ 1.54 corresponds to one of the two *N*-methyl groups. The upfield shift of the methyl group is due to the shielding by the



Scheme 4. Dimerization of the azomethine ylide derived from **2** and **3**.



Scheme 3. Mechanism for the formation of **8**.

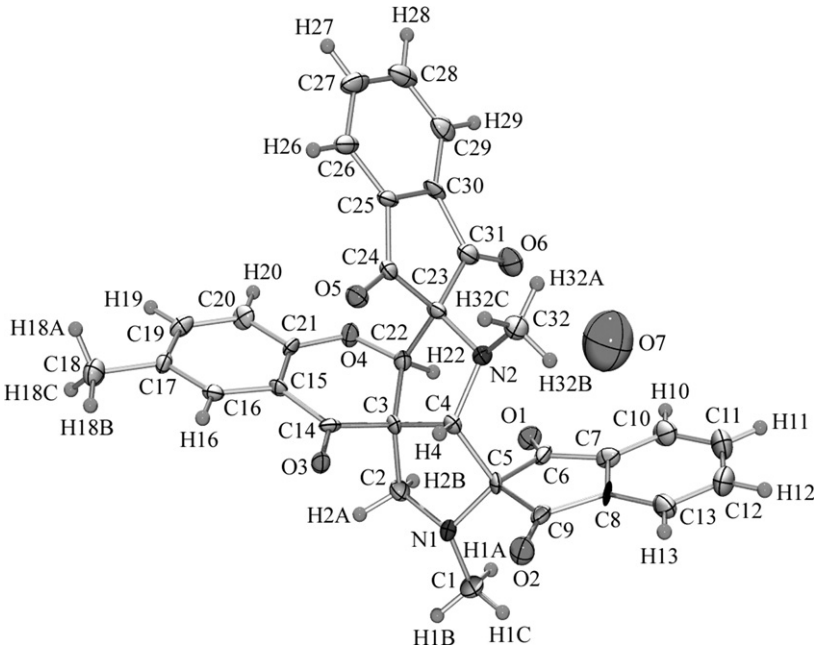


Figure 2. ORTEP diagram of **9b**.

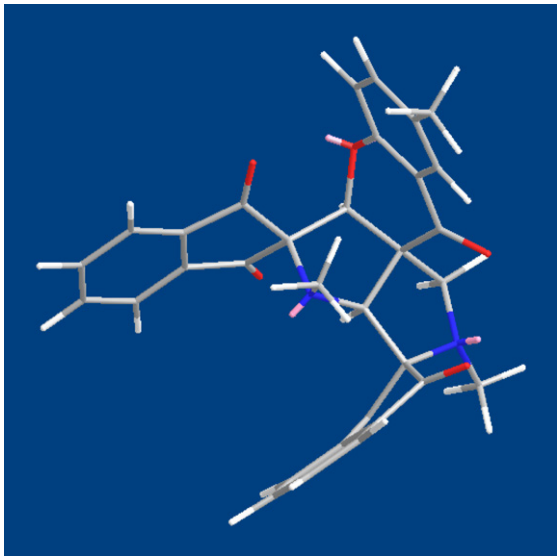


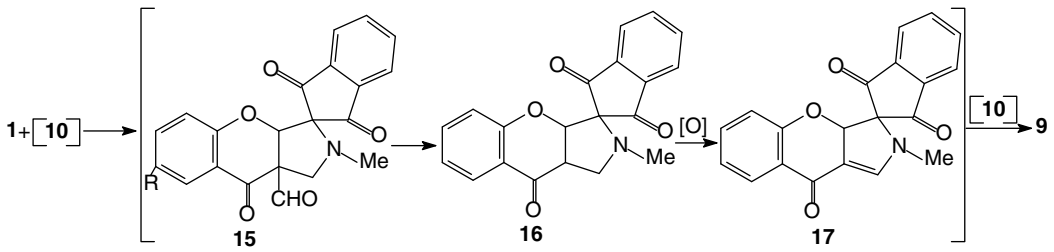
Figure 3. Energy minimized structure of **9b**.

three phenyl rings. The energy minimized structure of **9b** (Fig. 3) looks like a flower having three petals (one chromanone and two indandione rings).

(b) The signal of the two protons singlet at δ 7.36 disappeared when the spectrum was recorded in $CDCl_3$–D_2O and corresponds to one molecule of H_2O. X-ray crystallography also indicated the presence of one O atom outside the molecule. The formation of **9** can be rationalized by considering the [3+2] cyclization of **1** and azomethine ylide **10** to form **15**, which undergoes deformylation (→**16**) and oxidation to form **17**. A second molecule of azomethine ylide **10** reacts with **17** to form **9** (Scheme 5). Both 1,3-dipolar cycloaddition steps are regioselective and the selectivities are in accordance with earlier reports.[11c]

This proposed mechanism requires the molar ratios of **1**, **2** and **3** to be 1:2:2. Indeed, the reaction was complete within 2 h of heating in methanol when carried out with **1b** in the above mentioned molar ratio. The reaction mixture on concentration and cooling yielded a yellow solid, which on chromatographic separation produced **9b** and **14** in a 6.5:1 ratio (Table 1, entry 7). The oxidation step leading to **17** from **16** is not a result of aerial oxidation, as the same product mixture of **9b** and **14** was obtained when the reaction was carried out under an argon atmosphere (Table 1, entry 8). The oxidation may take place by the imino compounds formed during the formation of **8** but this could not be ascertained.

In conclusion, the dual character of non-stabilized azomethine ylide **10** derived from ninhydrin and sarcosine has been described. The azomethine ylide undergoes a regioselective 1,3-dipolar cycloaddition reaction with chromone-3-carbaldehyde to produce dispirochromanopyrrolidine **9** via a one-pot three component reaction, whereas the same azomethine ylide reacts with chromone-3-



Scheme 5. Mechanism for the formation of **9**.

carbaldehyde in the presence of formaldehyde in methanol to give dispirochromanoindanopyrrolidine **8** in a one-pot five-component reaction.

Acknowledgements

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17. (a) *2′-Methoxychroman-4′-one-spiro[3′.3]-N-methylpyrrolidinespiro[2.2″]indan-1″,3″-dione* **8a**: Reddish crystalline solid, Anal. Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71. Found: C, 70.15; H, 4.85, N, 3.55; IR (KBr) ν_{max}: 2964, 2933, 2848, 1740, 1704 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.04–2.13 (1H, m, H-11A), 2.22 (3H, s, N–CH_3), 2.84–2.92 (1H, m, H-11B), 3.31 (4H, singlet with a broadened base, OCH_3 + H-12A), 3.47–3.52 (1H, m, H-12B), 5.32 (1H, s, H-2), 6.24 (1H, br d, J = 8.2 Hz, H-4), 6.92 (1H, br t, J = 7.5 Hz, H-6), 7.12–7.17 (1H, m, H-5), 7.39 (1H, br d, J = 7.5 Hz, H-20), 7.62 (1H, br t, J = 7.5 Hz, H-19), 7.71–7.92 (2H, m, H-7 + H-18) and 7.94 (1H, br d, J = 7.6 Hz, H-17); ^{13}C NMR ($CDCl_3$): δ 28.98, 35.59, 41.56, 54.20, 56.71, 64.87, 105.02, 116.91, 121.95, 122.21, 122.31, 122.56, 127.05, 135.57, 135.87, 135.90, 188.75, 200.08; mass m/z: 378 (M^++H), 400 (M^++Na).
(b) *2′-Methoxy-6′-methylchroman-4′-one-spiro[3′.3]-N-methylpyrrolidinespiro-[2.2″]indan-1″,3″-dione* **8b**: Reddish crystalline solid, Anal. Calcd for $C_{23}H_{21}NO_5$: C, 70.58; H, 5.41; N, 3.58. Found: C, 70.21; H, 5.65, N, 3.45; IR (KBr) ν_{max}: 2939, 2857, 1735, 1699 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.03–2.12 (1H, m, H-11A), 2.22 (6H, s, $ArCH_3$ + N–CH_3), 2.82–2.90 (1H, m, H-11B), 3.28 (4H, singlet with a broadened base, OCH_3 + H-12A), 3.44–3.52 (1H, m, H-12B), 5.28 (1H, s, H-2), 6.15 (1H, d, J = 8.3 Hz, H-4), 6.95 (1H, br d, J = 8.3 Hz, H-5), 7.42 (1H, br d, J = 7.6 Hz, H-20), 7.53 (1H, br s, H-7), 7.64 (1H, br t, J = 7.6 Hz, H-19), 7.78 (1H, br t, J = 7.3 Hz, H-18) and 7.93 (1H, br d, J = 7.3 Hz, H-17); ^{13}C NMR ($CDCl_3$): δ 20.34, 28.80, 35.50, 54.08, 56.49, 64.77, 104.82, 116.68, 121.46, 122.21, 122.46, 126.58, 131.62, 135.82, 136.44, 141.24, 152.85, 189.81, 198.99; mass m/z: 392 (M^++H), 414 (M^++Na).
(c) Compound **8b** (OEt in place of OMe): Reddish crystalline solid, Anal. Calcd for $C_{24}H_{23}NO_5$: C, 71.10; H, 5.72; N, 3.45. Found: C, 71.26; H, 5.55, N, 3.55; IR (KBr) ν_{max}: 2950, 2800, 1730, 1690 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.00 (3H, t, J = 7.2 Hz,CH_3–CH_2), 2.03–2.08 (1H, m, H-11A), 2.22 (6H, s, $ArCH_3$ + N–CH_3), 2.82–2.92 (1H, m, H-11B), 3.25–3.35 (1H, m, H-12A), 3.45–3.58 (3H, m, OCH_2CH_3 + H-12B), 5.39 (1H, s, H-2), 6.09 (1H, d, J = 8.4 Hz, H-4), 6.92 (1H, dd, J = 8.4, 1.8 Hz, H-5), 7.39 (1H, br d, J = 7.8 Hz, H-20), 7.51 (1H, d, J = 1.8 Hz, H-7), 7.61 (1H, dt, J = 7.5, 1.2 Hz, H-19), 7.75 (1H, dt, J = 7.5, 0.9 Hz, H-18) and 7.92 (1H, br d, J = 7.5 Hz, H-17); ^{13}C NMR ($CDCl_3$): δ 14.59, 20.36, 29.01, 35.54, 54.14, 64.98, 103.61, 116.66, 121.44, 122.18, 122.48, 126.59, 128.27, 131.41, 135.75, 136.41, 141.12, 153.18, 190.06, 199.11.
18. Crystal data for **8a**: $C_{22}H_{19}NO_5$, M = 377.38, triclinic, space group $P\bar{1}$, a = 7.9600(18), b = 15.677(15), c = 29.35(3) Å, α = 83.03(3)°, β = 87.97(2)°, γ = 80.53(4)°, U = 3585(5) $Å^3$, D_{calcd} = 1.398 g cm^{-3}, Z = 4, Mo K_α radiation (λ = 0.71073 Å), μ = 0.100 mm^{-1}, T = 150 K, 33,041 measured reflections, 17,564 observed reflections (R_{int} = 0.038), R_1 = 0.0618, wR_2 = 0.1883 (all data). The structure was solved and refined using the SHELXL-97 suite of programs.[23] Crystallographic data for this structure have been deposited at the Cambridge Crystallographic Data Centre and allocated deposition number CCDC 678464.
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20. *Spiro[2.2′]indan-1′,3′-dionespiro[5.2″]indan-1″,2″-dione-1,4-dimethylpiperazine* **14**: Fine crystalline yellow solid; Anal. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.35; H, 4.65, N, 7.57; IR (KBr) ν_{max}: 3060, 2947, 2856, 1737, 1704 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.32 (6H, s, 2 × N–CH_3), 3.47 (4H, s, 2 × CH_2), 7.89–7.93 (4H, m, ArH), 7.99–8.06 (4H, m, ArH). The coupling pattern of the aromatic protons is AA′BB′-type; ^{13}C NMR ($CDCl_3$): δ 40.19, 54.10, 69.66, 123.48, 136.28, 139.90, 200.27; Mass m/z: 397 (M^++Na).
21. Spiro[3.2‴]indan-1‴,3‴-dionespiro[5.2⁗]indan-1⁗,3⁗-dione-2,4-dimethyl-chromano[3′,2′-*c*]pyrrolidino[3″,4″-*b*]pyrrolidine **9b**: Yellow crystalline compound; Anal. Calcd for $C_{32}H_{24}N_2O_6$, H_2O: C, 69.81; H, 4.76; N, 5.09. Found: C, 69.74; H, 4.66, N, 4.96; IR (KBr) ν_{max}: 2809, 1743, 1712, 1610 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.54 (3H, s, N–CH_3), 2.21 (3H, s, $ArCH_3$), 2.30 (3H, s, N–CH_3), 3.31 (1H, d, J = 9.5 Hz, 1-H), 3.66 (1H, d, J = 9.5 Hz, 1-H), 4.80 (1H, s, 3a-H), 5.63 (1H, s, 5a-H), 6.23 (1H, d, J = 8.4 Hz, 7-H), 7.01 (1H, dd, J = 8.4, 2.4 Hz, 8-H), 7.36 (2H, s, exchangeable, H_2O), 7.47 (1H, br d, J = 7.5 Hz, ArH), 7.66–7.71 (2H, m, ArH), 7.75–7.85 (3H, m, ArH), 7.92 (1H, br d, J = 7.5 Hz, ArH), 7.97 (1H, br d, J = 7.2 Hz, ArH), 8.03 (1H, br d, J = 7.2 Hz, ArH); ^{13}C NMR ($CDCl_3$): δ 20.47, 35.91, 36.05, 58.71, 63.64, 80.17, 80.56, 81.85, 86.20, 116.76, 119.37, 123.26, 126.73, 131.43, 135.83, 135.88, 136.38, 141.39, 142,13, 142.14, 155.85, 188.77, 198.20, 199.94; Mass m/z: 533 (M^++H), 555 (M^++Na).
22. Crystal data for **9b**: $C_{32}H_{24}N_2O_6.O$, M = 548.53, orthorhombic, space group *Pbca*, a = 11.099(3), b = 13.014(3), c = 36.798(10) Å, U = 5315(2) $Å^3$, D_{calcd} = 1.371 g cm^{-3}, Z = 8, MoK_α radiation (λ = 0.71073 Å), μ = 0.098 mm^{-1}, T = 100 K, 18,943 measured reflections, 1528 observed reflections (R_{int} = 0.090), R_1 = 0.0469, wR_2 = 0.1417 (all data). The structure was solved and refined using the SHELXL-97 suite of programs.[23] Crystallographic data for this structure have been deposited at the Cambridge Crystallographic Data Centre and allocated deposition number CCDC 678465.
23. Sheldrick, G. M. SHELXL-*97, Program for Crystal Structure Refinement*; University of Gottingen, 1997.