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Synthesis of highly substituted spiropyrrolidines via 1,3-dipolar cycloaddition reaction of *N*-metalated azomethine ylides

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Abstract—3-Arylidene-4-chromanones undergo regioselective 1,3-dipolar cycloaddition reactions with *N*-metalated azomethine ylides derived from aromatic aldimines of glycine methyl ester in the presence of silver acetate and triethylamine to give spiropyrrolidine derivatives in good yield. X-Ray crystal structure analysis of one of the products confirms the structure and regiochemistry of the cycloadditions.

1. Introduction

The intermolecular 1,3-dipolar cycloaddition reaction of azomethine ylides with olefins represents an efficient and convergent method for the construction of the pyrrolidine structural unit.[1,2] Among the different versions of this reaction, the interaction between *N*-metalated azomethine ylides and π-deficient alkenes is especially interesting, since, in general, it allows the synthesis of pyrrolidine nuclei with good chemical yield.[3,4] It represents one of the most efficient and mild routes for the synthesis of polyfunctional pyrrolidine ring systems.[5]

Highly substituted pyrrolidines have attracted much interest in the past few years, since they constitute the main structural element of many alkaloids and pharmacologically active compounds.[6] 4-Chromanones are versatile intermediates for the synthesis of many natural products such as brazillin, hematoxylin, riparіochromene, clausenin, calonilide (A) and nophyllum (B).[7,8] Chromanone heterocycles have also drawn much attention due to their important pharmacological properties.[7] As a part of our ongoing research programme in the area of cycloaddition reactions,[9–12] we herein report the facile synthesis of spiropyrrolidine derivatives through regioselective cycloaddition of azomethine ylides with (*E*)-3-arylidene-chroman-4-ones.

2. Results and discussion

1,3-Dipolar cycloaddition of *N*-metalated azomethine ylides to (*E*)-3-arylidene-4-chromanones have results in the formation of novel spiropyrrolidine derivatives in good yield. The addition is highly regioselective and gives a single product in each of the cases that we have studied. The required dipolarophiles (*E*)-3-arylidene-4-chromanones chosen for our study were prepared by the acid catalyzed reaction of 4-chromanone with various benzaldehydes, and the products were assigned the *E* configuration on the basis of their NMR spectra, in accordance with prior literature.[13]

Reaction of (*E*)-3-arylidene-4-chromanones (**1a–e**) with *N*-metalated azomethine ylides derived from imines of glycine methyl ester with various aromatic aldehydes at ambient temperature gave a single cycloadduct in all cases, as evidenced by TLC and mass spectral studies (Scheme 1, Table 1). The reaction afforded a series of novel spiropyrrolidine derivatives through regioselective cycloaddition of azomethine ylides to the exocyclic double bond of the arylidenechromanones in all cases. The cycloaddition proceeded stereo- and regiospecifically in acetonitrile at room temperature to afford *syn–endo* cycloadduct (**3a–o**) via metallo-azomethine ylides. The stereochemistry of (**3a–o**) is based on the usual facial selectivity and *endo*-transition state observed for metalloazomethine ylide cycloadditions.[3] The structure and regiochemistry of the cycloadducts (**3a–o**) has been confirmed by spectroscopy data. Thus the keto carbonyl of **3e** exhibited a peak at 1683 cm^{-1} in the IR spectrum showing an increase of 19 cm^{-1} from the normal value observed for benzylidene chromanone, indicating loss of conjugation. The ^1H NMR spectrum of **3e** exhibited a doublet at 4.47 ppm and a singlet at 4.85 ppm due to two benzylic protons which clearly shows the regiochemistry of the cycloaddition reaction. Schiff bases formed from the reaction of glycine methyl ester with Ph ^{13}CHO showed singlet resonances for the imine carbon around 160–165 ppm which on cycloaddition were replaced by the resonance of C-5 of the pyrrolidine ring at ≈60–70 ppm. ^{13}C NMR spectra of the product showed peaks for six sp^3 carbons, two carbonyl carbons

Keywords: cycloadditions; ylides; spiro compounds.

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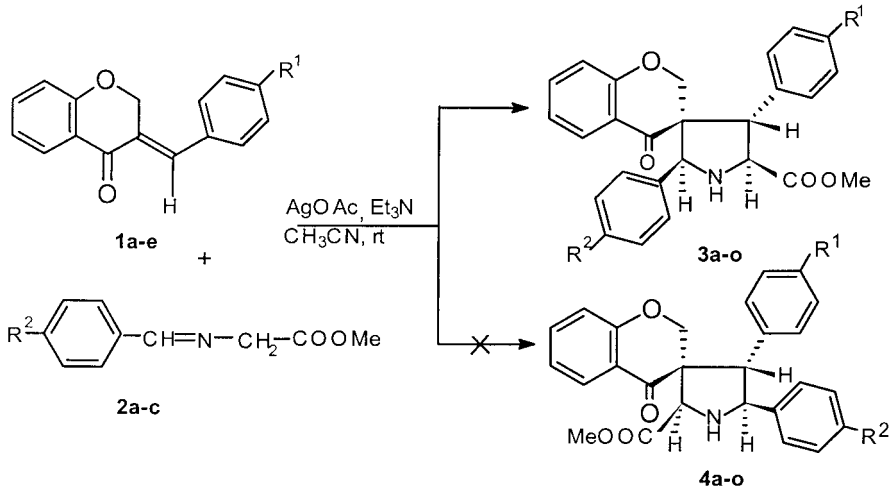

Scheme 1.

Table 1. 1,3-Dipolar cycloaddition reaction between benzylidenechromanones (**1a–e**) and *N*-metalated azomethine ylides derived from imines (**2a–c**) in the presence AgOAc

Entry	Product	R^1	R^2	Time (h)	Yield (%)
1	**3a**	H	H	2.5	72
2	**3b**	H	Cl	3	81
3	**3c**	H	OCH_3	2	78
4	**3d**	Cl	H	3.5	91
5	**3e**	Cl	Cl	2.5	69
6	**3f**	Cl	OCH_3	4	75
7	**3g**	OCH_3	H	2	68
8	**3h**	OCH_3	Cl	2	79
9	**3i**	OCH_3	OCH_3	2.5	82
10	**3j**	CH_3	H	3.5	85
11	**3k**	CH_3	Cl	3	74
12	**3l**	CH_3	OCH_3	2	68
13	**3m**	NO_2	H	4	77
14	**3n**	NO_2	Cl	3.5	69
15	**3o**	NO_2	OCH_3	3	79

and aromatic carbons that confirmed the proposed structure. No trace of the other regioisomer (**4a–o**) was detected.

Finally, X-ray analysis (Fig. 1) confirmed the structure of **3l** with the proposed regiochemistry. Identical results were obtained with other derivatives of benzylidene chromanone.

To the best of our knowledge to date there has been no report on cycloaddition reactions of *N*-metalated azomethine ylides derived from glycine methyl ester and aromatic aldehyde with exocyclic arylidenechromanones as dipolarophiles.

In conclusion, an efficient synthesis of a series of novel spiropyrrolidine derivatives has been achieved via the [3+2] cycloaddition reaction between *N*-metalated azomethine ylides and *E*-3-arylidene-4-chromanones.

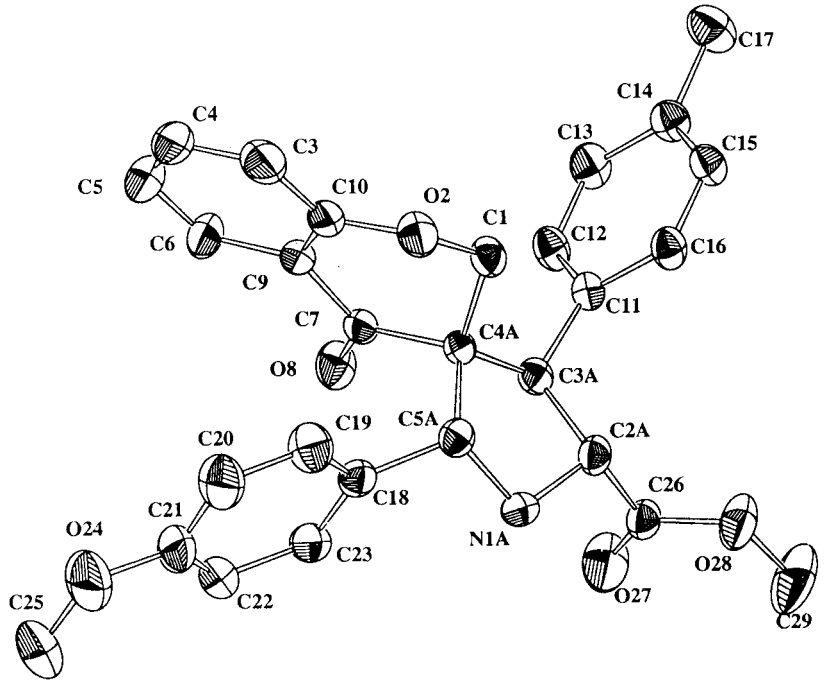

Figure 1. ORTEP diagram of **3l**.

3. Experimental

3.1. General

All melting points are uncorrected. IR spectra were recorded on a SHIMADZU FT-IR 8300 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a Bruker DPX200 at 200 and 50.3 MHz, respectively. Elemental analyses were carried out on a CEST 1106 instrument. MS spectra were recorded on a Finnigan MAT-8230 GC-Mass spectrometer.

Imines (**2a–c**)[5] and 3-arylidene-4-chromanones (**1a–e**)[13] were prepared by the literature procedures.

3.2. General procedure for the cycloaddition reaction between 3-arylidene4-chromanones (1a–e) and the imines (2a–c) in the presence of silver acetate as catalyst

To a solution of benzylideneglycine ester (1 mmol) in dry acetonitrile (10 ml), triethylamine (1 mmol), benzylidene-chromanone (1 mmol) and then AgOAc (0.15 equiv.) were added. After completion of the reaction as determined by TLC, the reaction mixture was filtered through a celite pad, washed with saturated aqueous solution of NH_4Cl and then extracted with CH_2Cl_2 (2×20 ml). The combined organic layers were washed with brine, dried ($MgSO_4$) filtered and the solvent evaporated in vacuo. The residue was purified by column chromatography on silica gel (100–200 mesh) with petroleum ether/ethylacetate (4:1) to afford the cycloadduct which was crystallized from EtOH.

3.2.1. Spiro[3,5-diphenyl-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3a). 0.3 g, 72%. Colourless crystals, mp: 182–184°C; IR (KBr): 1681, 1743 cm^{-1}; ^{1}H NMR: δ 2.81 (bs, 1H), 3.76 (s, 3H), 3.80 (d, J=11.9 Hz, 1H, OCH_2), 4.21 (d, J=11.9 Hz, 1H, OCH_2), 4.28 (d, J=9.0 Hz, 1H), 4.54 (d, J=9.0 Hz, 1H), 4.84 (s, 1H), 6.62–7.32 (m, 13H), 7.45 (dd, J=6.3, 1.6 Hz, 1H); ^{13}C NMR: 52.32, 52.46, 59.70, 64.38, 70.88, 73.30, 76.38, 77.02, 77.65, 116.94, 119.59, 120.97, 121.27, 127.19, 127.59, 127.73, 127.83, 128.60, 128.71, 135.35, 136.48, 137.98, 160.35, 173.30, 192.71; MS *m/z*: 413 (M^+); Anal. Calcd for $C_{26}H_{23}O_4N$: C, 75.5; H, 5.6; N, 3.4. Found: C, 75.5; H, 5.7; N, 3.4.

3.2.2. Spiro[3-phenyl-5-(4-chlorophenyl)-2-carbomethoxy-pyrrolidine-4,3′chroman-4′-one] (3b). 0.36 g, 81%. Colourless crystals, mp: 150–152°C; IR (KBr): 1680, 1743 cm^{-1}; ^{1}H NMR: δ 3.25 (bs, 1H), 3.74 (s, 3H), 3.78 (d, J=11.0 Hz, 1H, OCH_2), 4.18 (d, J=11.0 Hz, 1H, OCH_2), 4.32 (d, J=8.0 Hz, 1H), 4.53 (d, J=8.0 Hz, 1H), 4.84 (s, 1H), 6.55–7.25 (m, 12H), 7.46 (dd, J=6.3, 1.5 Hz, 1H); ^{13}C NMR: 51.83, 52.48, 59.56, 64.18, 69.81, 73.15, 76.36, 77.00, 77.63, 116.98 121.15, 121.25, 127.24, 127.66, 127.82, 128.56, 128.74, 129.20, 133.52, 135.62, 136.22, 136.84, 160.27, 173.25, 192.42; MS *m/z* 447 (M^+); Anal. Calcd for $C_{26}H_{22}O_4NCl$: C, 69.7; H, 4.95; N, 3.1. Found: C, 69.65; H, 5.2; N, 3.1.

3.2.3. Spiro[3-phenyl-5-(4-methoxyphenyl)-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3c). 0.35 g, 78%. Colourless crystals, mp: 143–145°C; IR (KBr): 1681, 1737 cm^{-1}; ^{1}H NMR: δ 2.54 (bs, 1H), 3.63 (s, 3H), 3.76 (s, 3H), 3.86 (d, J=9.3 Hz, 1H, OCH_2), 4.16 (d, J=9.3 Hz, 1H, OCH_2), 4.34 (d, J=8.5 Hz, 1H), 4.53 (d, J=8.5 Hz, 1H), 4.81 (s, 1H), 6.43–7.33 (m, 12H), 7.46 (dd, J=6.3,1.6 Hz, 1H); ^{13}C NMR: 52.15, 52.38, 55.09, 59.42, 64.12, 70.14, 73.19, 76.37, 77.00, 77.64, 113.08, 116.89, 119.50, 120.92, 121.22, 127.13, 127.49, 128.52, 128.63, 128.86, 129.99, 135.26, 136.42, 159.00, 160.25, 170.31, 192.81; MS *m/z*: 443 (M^+); Anal. Calcd for $C_{27}H_{25}O_5N$: C, 73.1; H, 5.7; N, 3.2. Found: C, 73.2; H, 5.7; N, 3.1.

3.2.4. Spiro[3-(4-chlorophenyl)-5-phenyl-2-carbomethoxy-pyrrolidine-4,3′-chroman-4′-one] (3d). 0.41 g, 91%. Colourless crystals, mp: 140–141°C; IR (KBr): 1681,1739 cm^{-1}; ^{1}H NMR: δ 2.51 (bs, 1H), 3.76 (s, 3H),3.81 (d, J=12.0 Hz, 1H, OCH_2), 4.21 (d, J=12.0 Hz, 1H,OCH_2), 4.31 (d, J=9.0 Hz, 1H), 4.54 (d, J=9.0 Hz, 1H), 4.84 (s, 1H), 6.65–7.32 (m, 12H), 7.43 (dd, J=7.9, 1.6 Hz, 1H); ^{13}C NMR: 51.27, 52.50, 59.74, 63.94, 70.32, 72.98, 76.39, 77.03, 77.66, 116.97, 121.09, 121.17, 127.19, 127.78, 127.88, 128.87, 129.93, 133.50, 134.73, 135.49, 138.04, 160.29, 172.98, 192.26; MS *m/z*: 447 (M^+); Anal. Calcd for $C_{26}H_{22}O_4NCl$: C, 69.7, H, 4.95; N, 3.1. Found: C, 69.8; H, 5.0; N, 3.2.

3.2.5. Spiro[3,5-di(4-chlorophenyl)-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3e). 0.33 g, 69%. Colourless crystals, mp: 134–135°C; IR (KBr): 1683, 1739 cm^{-1}; ^{1}H NMR: δ 2.80 (bs, 1H), 3.74 (s, 3H), 3.81 (d, J=11.8 Hz, 1H, OCH_2), 4.17 (d, J=11.8 Hz, 1H, OCH_2), 4.35 (d, J=9.0 Hz, 1H), 4.47 (d, J=9.0 Hz, 1H), 4.85 (s, 1H), 6.61–7.28 (m, 11H), 7.42 (dd, J=7.5, 1.5 Hz, 1H); ^{13}C NMR: 51.53, 52.45, 59.64, 64.23, 69.78, 73.17, 76.36, 76.99, 77.63, 116.97, 121.20, 127.24, 127.80, 128.42, 129.18, 129.42, 133.04, 133.48, 135.57, 136.91, 137.35, 160.28, 173.32, 192.48; MS *m/z*: 481 (M^+); Anal. Calcd for $C_{26}H_{21}O_4NCl_2$: C, 64.7; H, 4.4; N, 2.9. Found: C, 64.8; H, 4.3; N, 3.0.

3.2.6. Spiro[3-(4-chlorophenyl)-5-(4-methoxyphenyl)-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3f). 0.36 g, 75%. Colourless crystals, mp: 143–145°C; IR (KBr): 1681, 1739 cm^{-1}; ^{1}H NMR: δ 1.73 (bs, 1H), 3.65 (s, 3H), 3.76 (s, 3H), 3.80 (d, J=12.9 Hz, 1H, OCH_2), 4.20 (d, J=12.9 Hz, 1H, OCH_2), 4.29 (d, J=9.0 Hz, 1H), 4.52 (d, J=9.0 Hz, 1H), 4.81 (s, 1H), 6.52–7.33 (m, 11H), 7.44 (dd, J=6.3, 1.6 Hz, 1H); ^{13}C NMR: 51.10, 52.46, 55.22, 59.61, 64.22, 69.56, 73.10, 76.37, 77.00, 77.64, 114.12, 116.99, 121.22, 127.23, 127.82, 127.90, 129.16, 129.59, 133.48, 135.60, 136.99, 159.02, 160.30, 173.30, 192.45; MS *m/z* 477 (M^+); Anal. Calcd for $C_{27}H_{24}O_5NCl$: C, 67.85; H, 5.1; N, 2.9. Found: C, 67.8; H, 5.2; N, 2.9.

3.2.7. Spiro[3-(4-methoxyphenyl)-5-phenyl-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3g). 0.3 g, 68%. Colourless crystals, mp: 170–172°C; IR (KBr): 1685, 1735 cm^{-1}; ^{1}H NMR: δ 2.47 (bs, 1H), 3.77 (s, 3H), 3.78 (s, 3H), 3.84 (d, J=11.9 Hz, 1H, OCH_2), 4.2 (d, J=11.9 Hz, 1H, OCH_2), 4.32 (d, J=8.7 Hz, 1H), 4.50 (d, J=8.7 Hz, 1H), 4.83 (s, 1H), 6.63–7.34 (m, 11H), 7.43 (dd, J=6.3, 1.5 Hz, 1H); ^{13}C NMR: 51.54, 52.39, 55.18, 59.68, 64.37, 70.57, 73.21, 76.37, 77.00, 77.64, 114.04, 116.91, 120.90, 121.25, 127.12, 127.68, 127.75, 128.13, 129.57, 135.29, 138.07, 158.92, 160.33, 173.32, 192.70; MS *m/z*: 443

(M^+); Anal. Calcd for $C_{27}H_{25}O_5N$: C, 73.1; H, 5.7; N, 3.2. Found: C, 73.2; H, 5.6; N, 3.2.

3.2.8. Spiro[3-(4-methoxyphenyl)-5-(4-chlorophenyl)-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3h). 0.38 g, 79%. Colourless crystals, mp: 90–91°C; IR (KBr): 1683, 1739 cm^{-1}; ^1H NMR: δ 2.11 (bs, 1H), 3.77 (s, 3H), 3.78 (s, 3H), 3.85 (d, J=11.9 Hz, 1H, OCH_2), 4.19 (d, J=11.9 Hz, 1H, OCH_2), 4.32 (d, J=8.7 Hz, 1H), 4.49 (d, J=8.7 Hz, 1H), 4.81 (s, 1H), 6.65–7.26 (m, 11H), 7.46 (dd, J=6.3, 1.6 Hz, 1H); ^{13}C NMR: 51.10, 52.46, 55.22, 59.61, 64.22, 69.56, 73.10, 76.37, 77.00, 77.64, 114.12, 116.99, 121.22, 127.23, 127.82, 127.90, 129.16, 129.59, 133.48, 135.60, 136.99, 159.02, 160.30, 173.31, 192.45; MS m/z: 477 (M^+); Anal. Calcd for $C_{27}H_{24}O_5N_NCl$: C, 67.85; H, 5.1; N, 2.9. Found: C, 67.8; H, 5.0; N, 2.9.

3.2.9. Spiro[3,5-di(4-methoxyphenyl)-2-carbomethoxypyrolidine-4,3′-chroman-4′-one] (3i). 0.39 g, 82%. Colourless crystals, mp: 136–137°C; IR (KBr): 1679, 1741 cm^{-1}; ^1H NMR: δ 2.45 (bs, 1H), 3.64 (s, 3H), 3.76 (s, 3H), 3.79 (s,3H), 3.82 (d, J=9.2 Hz, 1H OCH_2), 4.20 (d, J=9.2 Hz, 1H, OCH_2), 4.29 (d, J=8.7 Hz, 1H), 4.48 (d, J=8.7 Hz, 1H), 4.79 (s, 1H), 6.51–7.26 (m, 11H), 7.45 (dd, J=6.3, 1.5 Hz, 1H); ^{13}C NMR: 51.48, 52.39, 55.11, 59.48, 64.22, 69.95, 73.18, 76.37, 77.01, 77.65, 113.10, 114.02, 116.92, 120.92, 121.29, 127.14, 128.17, 128.85, 129.55, 130.16, 135.27, 158.89, 158.99, 160.31, 173.39, 192.88; MS m/z: 473 (M^+); Anal. Calcd for $C_{28}H_{27}O_6N$: C, 71.0; H, 5.75; N, 3.0. Found: C, 71.0; H, 5.8; N, 3.05.

3.2.10. Spiro[3-(4-methoxyphenyl)-5-phenyl-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3j). 0.36 g, 85%. Colourless crystals, mp: 160–162°C; IR (KBr): 1685, 1737 cm^{-1}; ^1H NMR: δ 2.32 (bs, 1H), 2.32 (s, 3H), 3.77 (s, 3H), 3.84 (d, J=11.9 Hz, 1H, OCH_2), 4.00 (d, J=11.9 Hz, 1H, OCH_2), 4.51 (d, J=8.5 Hz, 1H), 4.34 (d, J=8.5 Hz, 1H), 4.83 (s, 1H), 6.65–7.25 (m, 12H), 7.44 (dd, J=6.3, 1.6 Hz, 1H); ^{13}C NMR: 21.00, 51.99, 52.41, 59.66, 64.40, 70.81, 73.29, 76.38, 77.01, 77.64, 116.92, 120.91, 121.28, 127.16, 127.69, 127.80, 128.44, 129.37, 133.29, 135.29, 137.23, 138.08, 160.36, 173.34, 192.75; MS m/z: 427 (M^+); Anal. Calcd for $C_{27}H_{25}O_4N$: C, 75.9; H, 5.9; N, 3.3. Found: C, 75.9; H, 5.8; N, 3.3.

3.2.11. Spiro[3-(4-methylphenyl)-5-(4-chlorophenyl)-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3k). 0.34 g, 74%. Colourless crystals, mp: 110–111°C; IR (KBr): 1683,1739 cm^{-1}; ^1H NMR: δ 2.00 (bs, 1H), 2.32 (s, 3H), 3.77 (s, 3H), 3.84 (d, J=11.9 Hz, 1H, OCH_2), 4.17 (d, J=11.9 Hz, 1H, OCH_2), 4.34 (d, J=8.5 Hz, 1H), 4.50 (d, J=8.5 Hz, 1H), 4.81 (s, 1H), 6.63–7.29 (m, 11H), 7.47 (dd, J=6.2, 1.6 Hz, 1H); ^{13}C NMR: 21.00, 51.52, 52.46, 59.56, 64.22, 69.77, 73.16, 76.36, 76.99, 77.63, 116.98, 121.20, 127.23, 127.80, 128.42, 129.18, 129.42, 133.04, 133.48, 135.57, 136.90, 137.34, 160.30, 173.30, 192.48; MS m/z: 461 (M^+); Anal. Calcd for $C_{27}H_{24}O_4NCl$: C,70.2; H, 5.2; N, 3.0. Found: C, 70.3; H, 5.4; N, 3.1.

3.2.12. Spiro[3-(4-methylphenyl)-5-(4-methoxyphenyl)-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3l). 0.31 g, 68%. Colourless crystals, mp: 152–153°C; IR (KBr): 1678, 1739 cm^{-1}; ^1H NMR: δ 2.28 (bs, 1H), 2.31 (s, 3H), 3.64 (s, 3H), 3.77 (s, 3H), 3.82 (d, J=11.9 Hz, 1H, OCH_2), 4.17 (d, J=11.9 Hz, 1H, OCH_2), 4.32 (d, J=8.5 Hz, 1H), 4.49 (d, J=8.5 Hz, 1H), 4.79 (s, 1H), 6.51–7.26 (m, 11H), 7.46 (dd, J=6.3, 1.6 Hz, 1H); ^{13}C NMR: 21.09, 51.94, 52.42, 55.15, 59.46, 64.25, 70.19, 73.27, 76.38, 77.02, 77.65, 113.12, 116.93, 120.94, 121.32, 127.18, 128.43, 128.90, 129.36, 130.09, 133.32, 135.28, 159.04, 173.42, 192.94; MS m/z: 457 (M^+); Anal. Calcd for $C_{28}H_{27}O_5N$: C, 73.5; H, 5.95; N, 3.1. Found: C, 73.5; H, 6.0; N, 3.1.

3.2.13. Spiro[3-(4-nitrophenyl)-5-phenyl-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3m). 0.35 g, 77%. Colourless crystals, mp: 115–116°C; IR (KBr): 1683, 1739 cm^{-1}; ^1H NMR: δ 1.81 (bs, 1H), 3.76 (s, 3H), 3.78 (d, J=11.5 Hz, 1H, OCH_2), 4.28 (d, J=11.5 Hz, 1H, OCH_2), 4.40 (d, J=9.4 Hz, 1H), 4.70 (d, J=9.4 Hz, 1H), 4.90 (s, 1H), 6.69–7.55 (m, 9H), 7.40 (dd, J=6.3, 1.4 Hz, 1H), 7.53 (d, J=8.7 Hz, 2H), 8.15 (d, J=8.7 Hz, 1H); ^{13}C NMR: 51.19, 52.62, 60.18, 63.55, 70.03, 72.68, 76.37, 77.00, 77.64, 117.03, 121.34, 123.81, 127.27, 127.77, 127.88, 128.05, 129.59, 135.73, 137.94, 143.69, 147.56, 160.33, 172.42, 191.67; MS m/z: 458 (M^+); Anal. Calcd for $C_{26}H_{22}O_6N_2$: C, 68.1; H, 4.8; N, 6.1. Found: C, 68.2; H, 4.8; N, 6.15.

3.2.14. Spiro[3-(4-nitrophenyl)-5-(4-chlorophenyl)-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3n). 0.34 g, 69%. Colourless crystals, mp:156–157°C; IR (KBr): 1687,1739 cm^{-1}; ^1H NMR: δ 2.68 (bs, 1H), 3.76 (s, 3H), 3.78 (d, J=11.0 Hz, 1H, OCH_2), 4.27 (d, J=11.0 Hz, 1H, OCH_2), 4.41 (d, J=9.4 Hz, 1H), 4.69 (d, J=9.4 Hz, 1H), 4.88 (s, 1H), 6.71–7.32(m, 7H), 7.42 (dd, J=6.3, 1.5 Hz, 1H), 7.51 (d, J=8.7 Hz, 2H), 8.20 (d, J=8.7 Hz, 2H); ^{13}C NMR: 50.65, 52.64, 60.00, 63.32, 68.93, 72.57, 76.38, 77.02, 77.65, 117.08, 120.97, 121.61, 123.84, 127.35, 127.98, 129.16, 129.59, 133.79, 136.01, 136.84, 143.66, 147.43, 160.17, 172.42, 191.40; MS m/z: 492 (M^+); Anal. Calcd for $C_{26}H_{21}O_6N_2Cl$: C, 63.35; H, 4.3; N, 5.7. Found: C, 63.4; H, 4.2; N, 5.6.

3.2.15. Spiro[3-(4-nitrophenyl)-5-(4-methoxyphenyl)-2-carbomethoxypyrrolidine-4,3′-chroman-4′-one] (3o). 0.39 g, 79%. Colourless crystals, mp: 104–106°C; IR (KBr): 1683, 1739 cm^{-1}; ^1H NMR: δ 2.07 (bs, 1H), 3.66 (s, 3H), 3.75 (s, 3H), 3.82 (d, J=11.6 Hz, 1H, OCH_2), 4.26 (d, J=11.6 Hz, 1H, OCH_2), 4.38 (d, J=9.4 Hz, 1H), 4.67 (d, J=9.4 Hz, 1H), 4.87 (s, 1H), 6.53–7.32 (m, 7H), 7.43 (dd, J=6.3, 1.6 Hz, 1H), 7.52 (d, J=8.7 Hz, 2H), 8.19 (d, J=8.7 Hz, 2H); ^{13}C NMR: 51.12, 52.38, 55.16, 60.02, 63.38, 68.94, 72.59, 76.38, 77.01, 77.66, 117.08, 120.94, 121.62, 123.84, 127.35, 127.99, 129.16, 129.58, 133.78, 136.02, 136.83, 143.65, 147.43, 160.17, 172.42, 192; MS m/z: 488 (M^+); Anal. Calcd for $C_{27}H_{24}O_7N_2$: C, 66.4; H, 4.95; N, 5.7. Found: C, 66.35; H, 5.1; N, 5.7.

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