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Synthesis of highly substituted spiropyrrolidines *via* 1, 3-dipolar cycloaddition reaction of *N*-metalated azomethine ylides. A new access to spiropyrrolines derivatives

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Abstract: 1,3-dipolar cycloaddition of (*E*)-arylidene-(2*H*)-indanones **1** (Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$) and (*E*)-2-arylidene-(*2H*)-tetralones **2** (Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$) to *N*-metalated azomethine ylides **3** generated from methyl *N*-arylideneglycinate in the presence of silver acetate produces in good yields novel methyl 1-oxo-2',4'-diaryl-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylates **4** and methyl 1-oxo-2',4'-diaryl-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylates **5**. The cycloaddition proceeds in regio- and stereoselective manner (100%) at room temperature to afford respectively the *syn-endo* cycloadducts **4** and **5** *via* metallo-azomethine ylides. The regio- and stereochemistry of the spiranic adducts have been established on the basis of spectroscopic data and elemental analysis, corroborated by single-crystal X-ray crystallographic analysis of the heterocycles **4ci**, **4bg** and **5bi**. The *endo*-pyrrolidines **4** were brominated by *N*-bromosuccinimide to give finally the dehydrobrominated 3, 4-dihydro-2*H*-pyrrole derivatives **6**. The spiro-adducts **4** and their corresponding oxidation products **6** are fluorescent in solution.

Keywords: 1,3-dipolar cycloaddition; azomethine ylides; spiropyrrolidines; spiropyrrolines; luminescence.

Introduction

The 1,3-dipolar cycloaddition reaction is one of the best and most useful methods for the construction of five-membered rings in a convergent and stereocontrolled manner.[1] In particular, the [3+2] cycloaddition of azomethine ylides with alkenes constitutes a direct route to pyrrolidine derivatives[1-3], which are valuable substrates in synthetic organic chemistry[4, 5], pharmacology[6] and biology.[7-9]

Among the different versions of this reaction, one of most practical approach is the interaction between stabilized *N*-metalated azomethine ylides and electron-deficient alkenes[5, 9].

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This method allows the cycloaddition to proceed under mild reaction conditions with a high degree of diastereocontrol[10]. Silver salts are the most commonly used catalyst to facilitate the reaction along with an excess of base such as a tertiary amine[11].
Spiropyrrolidines have attracted much attention because of their antiproliferative[12] and anti-tuberculosis activities[13] , as well as potential antileukemic and anticonvulsant agents[14].

Moreover, many indanone and tetralone derivatives have been used as versatile intermediates for the synthesis of several natural and pharmaceutical products[15-17]. The combination of this chemical entity with a pyrrolidine unit might as well be envisioned to conceive heterocyclic compound with potentially interesting biological properties.

Recently, several reports have appeared on the synthesis of substituted spiropyrrolidines using azomethine ylides cycloaddition reactions[18]. For example, the work of Wang and co-workers[19] employing a silver acetate/(S)-TF-Biphamphos complex as catalyst afforded an elegant access to spiroheterocyclic compounds containing the pyrrolidine motif. Since several years, we have focused our studies on the reactivity of dipolarophiles bearing an exocyclic carbon-carbon double bond towards several 1,3-dipoles such as nitrones[20], nitrile oxides[21], diazoalkanes[22] and azomethine ylides[23]. We particularly paid attention to the role played by the substituents of the dipolarophile and dipole entities on chemical reactivity, regio- and stereoselectivity.

In continuation of our research interest in this field, we present in this contribution the synthesis of spiropyrrolidine derivatives through regio- and diastereoselective cycloaddition of (*E)*-2-arylidene-(2*H*)-indanones **1a-e** and *(E)*-2-arylidene-(2*H*)-tetralones **2a-e** with *N*-metalated azomethine ylides generated *in situ* by deprotonation of the corresponding iminoesters **3f-i** derived from glycine methyl ester. The reaction affords spiropyrrolidine derivatives **4af-ei** and **5af-ei**, respectively, with high regio- and stereoselectivity. In order to assess the impact of the substituent at the *p*-position of dipolarophiles and azomethine ylides on the outcome of the reaction, we examined the influence of the electronic and steric effects exerted by the aryl ring substituents. Furthermore, the products **4** were transformed by action of *NBS* to methyl 1-oxo-2',4'-diaryl-1,3,4',5'-tetrahydrospiro[indene-2,3'-pyrrole]-5'-carboxylate derivatives **6**. Finally, we report on the luminescence properties of some selected compounds.

Results and Discussion

Synthesis of the spiroheterocycles

The *(E)*-2-arylidene-(2*H*)-indanones **1a-e** and *(E)*-2-arylidene-(2*H*)-tetralones **2a-e** employed as dipolarophiles have been prepared by the acid-catalyzed condensation of indanone and tetralone with various benzaldehydes. As confirmed by NMR spectroscopy, these starting materials display an *E*-configuration in accordance with our earlier studies and the literature[24].

The methyl *N*-arylideneglycinate were prepared by condensation of appropriately substituted aromatic aldehydes Ar'CHO with methyl glycine ester according to reported methods[25-27].

Initially, we studied the cycloaddition reaction without catalyst, choosing methyl *N*-chlorobenzylidene glycinate (Ar'= *p*-ClC_6H_4) **3i** and exocyclic enones **1a** and **2a** (Ar = Ph) as reagents. The outcome was however very unsatisfying. Whatever the solvent used, both at room temperature or under reflux during seven days, the obtained yields were always less than 10%. In order to optimize these conditions, we found that Ag_2CO_3, Ag_2O and AgOAc

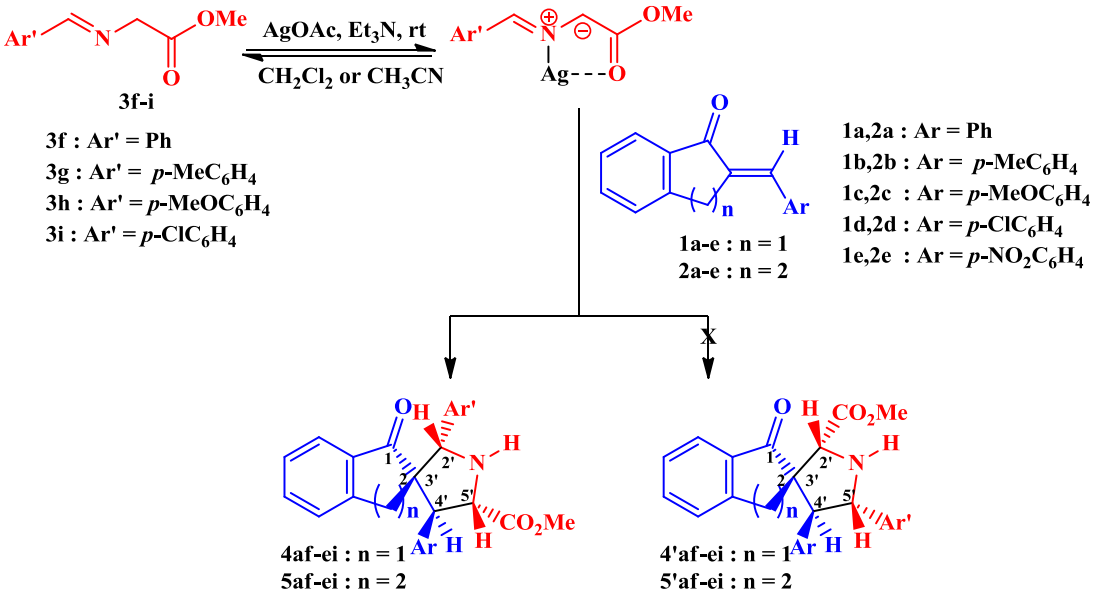
catalysed the 1, 3-dipolar cycloaddition reaction affording the desired spiropyrrolidine in 60%, 64%, and 70% yield, respectively (**Table 1**, entries 1-3) in toluene as solvent. Then, using AgOAc as catalyst, various solvents were screened, and it was found that CH_2Cl_2 and CH_3CN were the most appropriate solvents for the reaction with **1** and **2**, respectively (**Table 1**, entries 4-7).

Table 1. Optimization of the reaction condition[a]

Entry	Dipolarophile	Product	Catalyst (10 mol %)	Solvent	Time (h)	Yields(%)[b]
1	1a	4ai	Ag_2CO_3	Toluene	48	60
2	1a	4ai	Ag_2O	Toluene	36	64
3	1a	4ai	AgOAc	Toluene	12	70
4	1a	4ai	AgOAc	CH_3CN	6	72
5	1a	4ai	AgOAc	CH_2Cl_2	2	80
6	2a	5ai	AgOAc	CH_3CN	4	77
7	2a	5ai	AgOAc	CH_2Cl_2	6	75

[a] All reactions were carried out in the absence of light in the presence of 15 mol % of Et_3N.
[b] Isolated yields after purification by column chromatography.

Having established suitable reaction conditions, we next explored the scope and generality of this methodology (**Scheme 1**). The AgOAc catalyzed [3+2] cycloadditions of *(E)*-2-arylidene-(2*H*)-indanones **1** and *(E)*-2-arylidene-(2*H*)-tetralones **2** with iminoesters **3** led to unique adducts corresponding to the expected novel spiropyrrolidine derivatives, the *syn-endo* methyl 1-oxo-2',4'-diaryl-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylates **4** and methyl 1-oxo-2',4'-diaryl-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylates **5**. The reactions proceed at room temperature with 100% regioselectivity.



Scheme 1. Reactions of enones **1** and **2** with methyl *N*-arylideneglycinate **3**

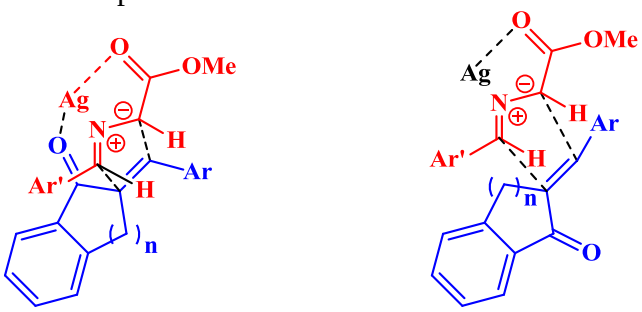
All results reported below proof that pyrrolidines were obtained with conservation of the stereochemistry of the starting alkenes. The structure and stereochemistry of the spiropyrrolidine resulting from the cycloaddition has been established on the basis of

elemental analyses, spectroscopic data and three X-ray structure determinations performed on cycloadducts **4ci**, **4bg** and **5bi**.

Spectroscopic characterisation

The IR spectra of the compounds **4** and **5** contain absorption bands at around 3447 cm^{-1}, 1723 cm^{-1}, and 1670 cm^{-1} due to NH, C=O ester and C=O ring stretching vibrations, respectively. In their ^{1}H NMR spectra, we observed a singlet at 4.23-4.62 ppm and a doublet in the range between 4.40-4.68 ppm due to benzylic hydrogens H-2' and H-4', respectively, which clearly ascertain the regiochemistry of the cycloaddition reaction in accordance with the literature.[9b, 28, 29] The two protons H-5' and H-4' couple with each other with *J* values ranging between 5.7 and 6.3 Hz in the case of compounds **4**, and between 6.9 and 8.7 Hz, for cycloadducts **5**, suggesting them to be on *trans* configuration. Another characteristic in products **4** and **5** is the presence of an N-H resonance between 2.49 and 3.55 ppm, exchangeable by D_2O.

The ^{1}H and ^{13}C NMR spectra of the spiro-adducts **4** and **5** exhibited only one set of signals, thereby confirming the formation of single diastereoisomer during the cycloaddition reactions. The stereochemistry of the cycloadducts **4** and **5** is based on the usual facial selectivity and *endo*-transition state observed. No cycloadduct corresponding to an *exo*-transition state has been evidenced. Thus in all the cases, the products **4** and **5** are formed *via* an *endo*-transition state involving *E, E*-(*syn*-dipole). This could be explained by the *endo*-transition state shown in **Figure 1**, where both the ylide and the dipolarophile coordinate to the Ag ion *via* two carbonyl Ag…O interactions and an Ag-N bond, whereas just one Ag…O and Ag-N interaction is present in the *exo*-transition state.



***endo* transition state** ***exo* transition state**

Figure 1. Proposed transition states for the cycloaddition of enones **1** and **2** with azomethine ylide

Crystallographic characterisation.

The relative stereochemistry of the cycloadducts **4** and **5** was furthermore confirmed by X-ray crystal analysis of **4ci**, **4bg** and **5bi** (**Figures 2, 3** and **4**), showing that the ester carbonyl and aryl group stemming from the dipolarophile are in *trans* configuration. The crystal data collection and structure refinement of **4ci**, **4bg** and **5bi** are summarized in **Table 2**.

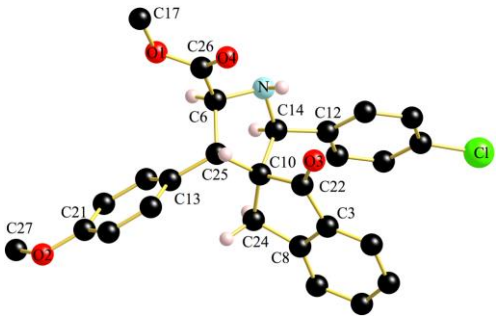


Figure 2. Molecular structure of spirocompound **4ci**. Selected bond lengths (Å) and angles (°). The aromatic hydrogen atoms have been omitted for clarity: C26–O4 1.202(3), N–C6 1.469(3), C6–C25 1.575(4), N–C14 1.462(3), C14–C10 1.596(4), C10–C25 1.563(3), C10–C22 1.529(3), O3–C22 1.222(3), C22–C3 1.466(4), C3–C8 1.395(4); C26–C6–N 109.6(2), C6–N–C14 101.9(2), N–C14–C10 115.1(2), N–C14–C12 114.9(2), N–C6–C25 106.4(2), C25–C10–C14 102.55(19), C25–C10–C24 119.6(2), C25–C10–C22 111.6(2), C24–C10–C22 104.3(2), C10–C22–O3 124.3(2), O3–C10–C3 127.6(2), C22–C3–C8 109.3(2), C3–C8–C24 111.0(2).

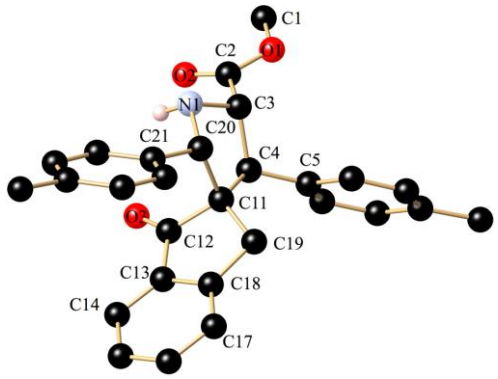


Figure 3. Molecular structure of spirocompound **4bg**. Selected bond lengths (Å) and angles (°): C1–O2 1.203(2), N–C3 1.465(2), C3–C4 1.570(2), N–C20 1.461(2), C20–C11 1.593(2), C11–C4 1.566(2), C11–C12 1.526(2), O2–C12 1.223(2); C2–C3–N 109.83(14), C3–N1–C20 102.33(13), N1–C20–C21 114.08(14), N1–C20–C11 105.09(13), C20–C11–C4 102.79(13), C20–C11–C12 106.28(13), C20–C11–C19 110.99(13), C11–C12–O3 124.89(15), O3–C12–C13 127.24(16), C12–C13–C18 108.93(15), C12–C11–C19 104.28(13).

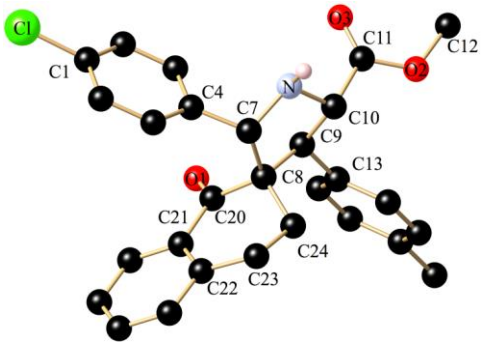


Figure 4. Molecular structure of spirocompound **5bi**. Selected bond lengths (Å) and angles (°): C11–O3 1.198(2), C11–C10 1.514(4), N–C10 1.455(3), N–C7 1.479(3), C7–C8 1.585(3), C8–C9 1.560(3), C11–C4 1.566(2), C9–C10 1.537(3), C8–C20 1.523(4), O1–C20 1.225(3), C21–C20 1.494(4); C4–C7–N 109.6(2), C7–N–C10 109.9(2), N–C10–C9 114.08(14), N–C7–C8 104.32(19), C7–C8–C9 102.3(2), C8–C9–C10 101.6(2), C7–C8–C20 111.6(2), C20–C8–C24 109.1(2), C8–C20–O1 121.5(2), O1–C20–C21 121.1(2), C24–C8–C9 112.5(2).

The three compounds studied by X-ray diffraction apparently don't need any further strong intermolecular interaction for stabilization of their crystal phases. One could expect the presence of intermolecular N–H…O (=C) hydrogen bonds. However, there is almost no

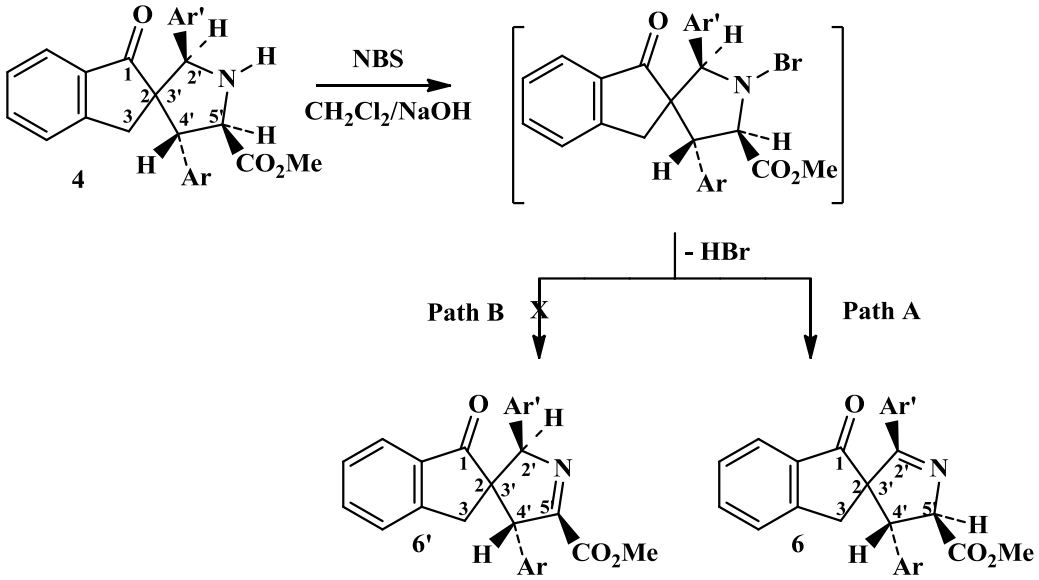
occurrence of this bonding interaction in the three compounds. It's only in **5bi**, where the electronegative atoms N, O and Cl are involved in a very weak and bifurcated "hydrogen bond" interaction (**Figure S1** in ESI). The N–H…O (ketone), C–H…O (ketone) and C–H…Cl interactions seem to be of similar strength therein. The crystal packing in **4bg** is assured only by a very weak C–H…C (different nature) interactions (**Figure S2** in ESI) and by the C–H…O (ketone and carboxylate) ones in **4ci** (**Figure S3** in ESI). In conclusion, the intermolecular contacts within these three crystal structures are mainly built from weak van der Waals interactions that are of different nature in each individual case.

Table 2. Crystal data collection and structure refinement of **4ci, 4bg** and **5bi**.

Compound /Formula	**4bg** / $C_{28}H_{27}NO_3$	**4ci** / $C_{27}H_{24}ClNO_4$	**5bi** / $C_{28}H_{26}ClNO_3$
Formula weight	425.51	461.92	459.95
Temperature/K	115(2)	115(2)	115(2)
Wavelength/Å	0.71073	0.71073	0.71069
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	12.2869(3)	15.7976(4)	13.3588(5)
b/Å	11.7559(3)	6.4703(2)	12.4090(5)
c/Å	16.7554(4)	22.7657(8)	16.6956(6)
β	108.7240(10)	103.638(2)°	125.314(2
Volume/ Å^3	2292.12(10)	2261.39(12)	3627.3(2)
Z	4	4	4
Density (calculated) g/cm^3	1.233	1.357	1.353
Absorp. coefficient/mm^{-1}	0.080	0.204	0.201
F(000)	904	968	968
Crystal size/mm^3	0.40 x 0.40 x 0.40	0.12 x 0.07 x 0.02	0.20 x 0.10 x 0.10
Theta range for data collection/°	3.03 to 27.50	3.28 to 27.51	2.99 to 27.47
Index ranges	-15<=h<=15, -15<=k<=9, -21<=l<=21	-20<=h<=20, -8<=k<=8, -29<=l<=29	-17<=h<=17, -16<=k<=11, -21<=l<=21
Reflections collected	7848	9394	7276
Independent reflections	5215 [*R*(int) = 0.0177]	5127 [R(int) = 0.0568]	5084 [R(int) = 0.0280]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5215 / 1 / 295	5127 / 0 / 303	5084 / 0 / 300
Goodness-of-fit on F^2	1.029	1.111	1.108
Final *R* indices [*I*>2sigma(I)]	*R*1 = 0.0572, w*R*2 = 0.1218	*R*1 = 0.0659, w*R*2 = 0.1133	*R*1 = 0.0636, w*R*2 = 0.1161
R indices (all data)	*R*1 = 0.0714, w*R*2 = 0.1328	*R*1 = 0.0972, w*R*2 = 0.1274	*R*1 = 0.0917, w*R*2 = 0.1333
Largest diff. peak and hole/e. Å^{-3}	0.339 and -0.485	0.321 and -0.305	0.339 and -0.337

Treatment of 4 with *N*-bromosuccinimide (*NBS*)

The methyl 1-oxo-2',4'-diaryl-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylates **4ag**, **4ah** and **4df** were allowed to react at room temperature with *NBS* in CH_2Cl_2 for 1h30[30]. The formation of the single methyl 1-oxo-2',4'-diaryl-1,3,4',5'-tetrahydrospiro[indene-2,3'-pyrrole]-5'-carboxylate in each case suggests the reaction first involves the bromination of the amine followed by the spontaneous elimination of hydrogen bromide to afford the corresponding methyl 1-oxo-2',4'-diaryl-1,3,4',5'-tetrahydrospiro[indene-2,3'-pyrrole]-5'-carboxylates **6**. The elimination of the hydrogen bromide was facilitated by the highly conjugated nature of the newly formed double bond (**Scheme 2**). The structure of these compounds was established from elemental analyses and spectroscopic data. In the ^1H NMR spectra of compounds **6** appear two doublets between 4.10-4.30 ppm and 4.9-5.15 ppm corresponding to the H-4' and H-5' protons, respectively. This excludes the formation of other isomer **6'** bearing the imine function between the N-atom and C-5'. In this case, the protons H-2' and H-4' should appear as singlets. The ^{13}C NMR spectrum shows a signal at 139 ppm corresponding to the carbon atom of imine group. This was corroborated by the presence of a C=N vibration at 1640 cm^{-1} in the infrared spectra. These data are in favour of elimination of H-5 proton during the dehydrobromination of spiropyrrolidines **4**.



Scheme 2. Dehydrobromination of spiropyrrolidines **4** with *NBS*

UV-vis spectra and luminescence properties

The electronic absorption and emission spectra of compounds **4**, **5** and **6** have been recorded at 298 K using CH_2Cl_2 as solvent. **Figures 5** and **6** show representative spectra of compounds **4bg** and **6ag**, respectively. The absorption and emission data obtained from all compounds are summarized in **Table 3**. The electronic absorption spectra of these compounds in general exhibit a strong band with a maximum between 230 and 280 nm attributed to π,π* transitions and a low-intensity band in the spectral range from 280 to 380 nm assigned to a n,π* transition. After excitation at 270 nm, compounds **4** exhibit emission maxima around 370 nm. However, no emission is observed for compounds **5**. Compounds **6** show the emission maxima in the similar spectral rang as observed for compounds **4** and other spiropyrrolidines published in the literature. [31] This study revealed that this emission bands are independent of the excitation wavelength. These fluorescence bands can be assigned to the

lowest energy singlet state $S_1 \rightarrow S_0$ transition. The only exception is observed for compound **4ef** which features two emission bands with maxima centred at 371 and 435 nm. We attribute this lowest energy to a charge transfer band due to the high sensitivity of emission wavelength to the solvent polarity λ_{max} = 398 (C_6H_{12}), 406 (EtOH) and 557 nm (MeCN). Fluorescence quantum yields $Ø_F$ of compounds **4** and **6** were determined using cresyl violet as a fluorescence quantum yield standard[32]. All in all, these values are lower compared to spiro-based anthracenone compounds[33a], but they exhibit quantum yields relatively similar to those of the family of isatin-based spiro compounds reported in the literature[33b].

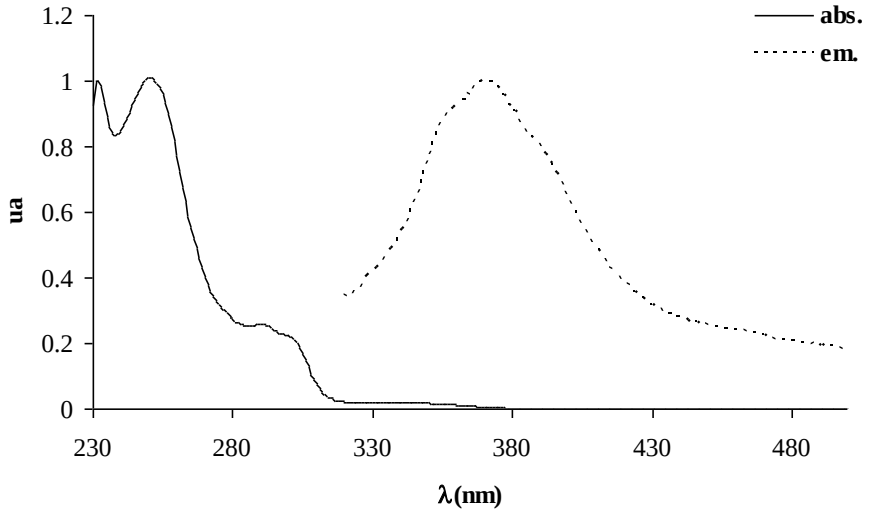


Figure 5. Normalized absorption (solid curve), and emission (dashed curve) spectra recorded for **4bg** in CH_2Cl_2 at 293 K.

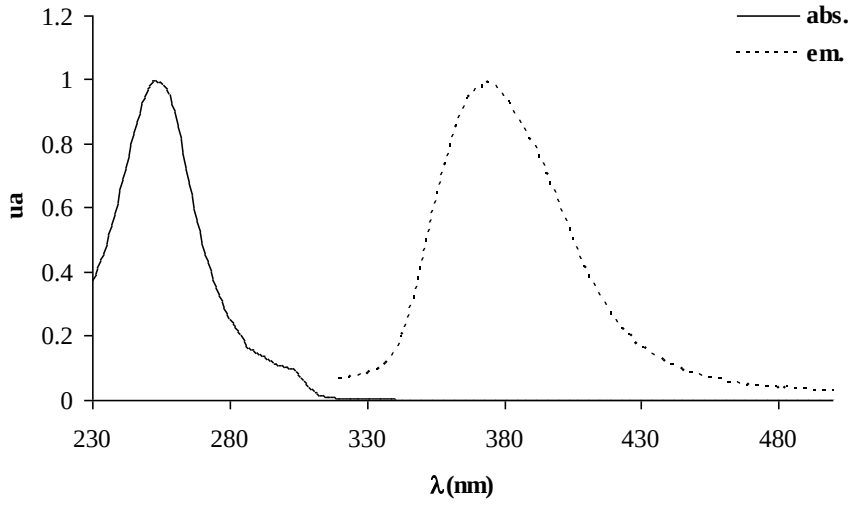


Figure 6. Normalized absorption (solid curve), and emission (dashed curve) spectra recorded for **6ag** in CH_2Cl_2 at 293 K.

Table 3. Absorption and emission data of compounds **4**, **5** and **6**. a) Values of absorption maxima ($\lambda_{abs.}$) and their associated molar extinction coefficient (ε); b) $\lambda_{excit.}$: Excitation wavelength; c) $\lambda_{em.}$: Emission wavelength; d) ϕ: Fluorescence quantum yield (± 8%).

Compound	Absorption	Emission	
	CH_2Cl_2 at 298 K λ_{abs} (nm) [ε ($M^{-1}cm^{-1}$)]	CH_2Cl_2 at 298 K λ_{em} (nm) [λ_{excit} =270 nm]	$Ø_F$
4ai	230 [9890], 254 [8040], 294 sh [1700]	370	0.4
4bg	232 [9770], 253 [9680], 294 sh [2400], 346 [190]	370	0.5
4ef	257 [10180], 284 [10400], 345 sh [1700]	371, 435	0.7
5ag	232 [9790], 253 [9700], 294 sh [2420], 346 [210]	*	*
5bi	234 [10700], 256 [13000], 296 sh [1950]	*	*
5dg	231 [10250], 257 [6950], 296 sh [1320]	*	*
6ag	253 [14150], 304 sh [1260]	373	0.8
6ah	235 sh [10000], 253 [13000], 292 sh [1950], 304 sh [1200]	369	0.6

*No emission

Conclusion

In conclusion, we have shown that the cycloaddition reaction of enones (**1a-e**) and (**2a-e**) with azomethine ylides **3f-i** leads straightforwardly to novel spiropyrrolidines in a regio- and diastereoselective manner (100%). The regiochemistry of the reaction is not influenced by the electronic nature of the substituents at the *para*-position on the dipolarophile as well as on the dipole. The cycloadducts **4** and **5** are formed exclusively *via* an *endo*-transition state involving *E,E*-(*syn*-dipole). Spiropyrrolidines **4** reacts under mild condition with *NBS* in CH_2Cl_2 to afford the corresponding methyl 1-oxo-2',4'-diaryl-1,3,4',5'-tetrahydrospiro[indene-2,3'-pyrrole]-5'-carboxylates **6.** Finally, the study of the luminescence properties of some compounds revealed that spiro-adducts **4** and their corresponding oxidation products **6** are fluorescent in solution at room temperature.

Experimental Section

Reactions were carried out under an atmosphere of dry N_2. Solvents were purified by standard methods and freshly distilled under nitrogen and dried before use. Melting points were determined on a Kofler bank. Materials: thin-layer chromatography (TLC): TLC plates (Merck, silica gel 60 F_{254} 0.2 mm 200×200 nm); substances were detected using UV light at 254 nm. ^1H, ^{13}C NMR spectra were recorded on a Bruker 300 MHz instrument in $CDCl_3$ using TMS as an internal standard. Chemical shifts are given in parts per million (d-scale) and the coupling constants are given in Hertz. IR spectra were recorded on a JASCOFT IR instrument (KBr pellet in case of solids). UV-vis spectra were measured in CH_2Cl_2 (c~10^{-5} M) at room temperature with a VARIAN-Cary 100 spectrophotometer. Emission spectra were

recorded in CH_2Cl_2 (c~10^{-6} M) at room temperature on a Jobin-Yvon FluoroLog 3.2.2 apparatus using a 1 cm width quartz cell with a scan speed of 1 nm/s and a slit width of 5. The enones **(1a-e)** and **(2a-e)** are obtained by condensation of aldehydes ArCHO with indanone and tetralone, respectively, in the presence of *p*-toluenesulfonic acid (APTS) according to ref [24], the methyl *N*-arylideneglycinate were prepared from reaction of aromatic aldehydes Ar'CHO with methyl glycine ester according to reported methods[25-27].

General procedure for the cycloaddition reaction of enones 1 and 2 with azomethine ylide

To a solution of methyl *N*-arylideneglycinate **(3f-i)** (1 mmol) in dry CH_2Cl_2 or CH_3CN (10 mL), triethylamine (1 mmol), enone **(1a-e)** or **(2a-e)** (1mmol) and AgOAc (0.10 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 The combined organic layers was washed with brine, dried ($MgSO_4$) filtered and the solvent evaporated in vacuo. The crude product was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (7 : 3) as the eluent to give analytical pure spiropyrrolidines **4** and **5**.

Preparation of spiropyrrolines 6

To a stirred solution of cycloadducts **4ag**, **4ah** and **4df** (0.75 mmol) in CH_2Cl_2 (2 mL) was added portion wise of *NBS* (0.14 g, 0.82 mmol) at room temperature over 20 min and stirring was continued for 1h. After completion of the reaction as determined by TLC, H_2O (10 mL) was added and the organic layer was washed with further portions of H_2O (2×10 mL) and brine (10 mL), then dried over $MgSO_4$ and evaporated in vacuo. The residue was then triturated with cold EtOH and filtered to provide the title product **6,** which was purified by re-crystallization from EtOH.

4af: methyl 1-oxo-2',4'-diphenyl-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.34 g (88%); white needles, mp: 180°C ± 2, IR (KBr): 1681, 1743, 3447 cm^{-1}, ^1H NMR δ: 2.69-2.84 (AB, 2H, *J* = 18 Hz, H-3), 3.55 (s, br, 1H, NH), 3.79 (s, 3H, OCH_3), 3.90 (d, 1H, *J* = 6 Hz, H-5'), 4.32 (d, 1H, *J* = 6 Hz, H-4'), 4.53 (s, 1H, H-2'), 6.94-7.35 (m, 14H, H_{arom}), ^{13}C NMR δ: 35.4, 52.4, 55.8, 65.5, 67.4, 73.8, 123.3, 125.6, 127.5, 128.1, 128.2, 129.5, 130.1, 131.8, 133.3, 134.9, 134.9, 135.8, 139.0, 142.0, 170.2, 207.2, Anal. Calcd. for $C_{26}H_{23}NO_3$: C, 78.57, H, 5.83, N, 3.52, Found: C,78.56, H, 5.99, N, 3.49.

4ag: methyl 1-oxo-2'-(*p*-methylphenyl)-4'-phenyl-1, 3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.31 g (77%); white crystals, mp: 200 °C ± 2 , IR (KBr): 1683, 1740, 3449 cm^{-1}, ^1H NMR δ: 2.09 (s, 3H, Ar-CH_3), 2.68-2.82 (AB, 2H, *J* = 18 Hz, H-3), 3.52 (s, br, 1H, NH), 3.73 (s, 3H, OCH_3), 3.90 (d, 1H, *J* = 6 Hz, H-5'), 4.31 (d, 1H , *J* = 6 Hz, H-4'), 4.48 (s,1H, H-2'), 6.77-7.33 (m, 13H, H_{arom}) ,^{13}C NMR δ: 21.3, 35.2, 51.4, 55.8, 65.5, 67.4, 72.8 , 113.3, 119.4, 125.6, 127.5, 128.1, 128.2, 129.5, 130.1 ,131.8, 133.3, 134.9, 134.9, 135.8, 139, 152, 170.28, 208.2, Anal. Calcd. for $C_{27}H_{25}NO_3$: C, 78.81, H, 6.12, N, 3.40, Found: C, 78.83, H, 6.12, N, 3.39.

4ah: methyl 1-oxo-2'-(*p*-methoxyphenyl)-4'-phenyl-1, 3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.31 g (74%), white needles, mp: 192 °C ± 2, IR (KBr): 168, 1740, 3449 cm^{-1}, ^1H NMR δ: 2.66-2.81 (AB, 2H, *J* = 18 Hz, H-3), 3.53 (s, br, 1H, NH), 3.58 (s, 3H, Ar-OCH_3), 3.74 (s, 3H, OCH_3), 3.90 (d, 1H, *J* = 6 Hz, H-5'), 4.33 (d, 1H, *J* = 6 Hz, H-4'), 4.49 (s, 1H, H-2'), 6.51-7.34 (m, 13H, H_{arom}), ^{13}C NMR δ: 35.5, 52.4, 52.5, 65.6, 67.4, 73.8, 123.3, 126.6, 127.5, 128.1, 128.1, 129.5, 130.1, 132.8, 133.3, 134.9, 134.9, 135.8, 139.1, 152.0, 173.2, 208.2. Anal. Calcd. for $C_{27}H_{25}NO_4$: C, 75.86, H, 5.89, N, 3.28, Found: C, 75.83, H, 5.86, N, 3.29.

4ai: methyl 1-oxo-2'-(*p*-chlorophenyl)-4'-phenyl-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.31 g (74%), white crystals, mp: 162 °C ± 2, IR (KBr): 1689, 1750, 3449 cm^{-1}, ^1H NMR δ: 2.67-2.85 (AB, 2H, *J* = 18 Hz, H-3), 3.23 (s, br, 1H, NH), 3.77 (s, 3H, OCH_3), 3.92 (d, 1H, *J* = 6 Hz, H-5'), 4.28 (d, 1H, *J* = 6 Hz, H-4'), 4.47 (s, 1H, H-2'), 6.95-7.33 (m, 13H, H_{arom}), ^{13}C NMR δ: 35.4, 52.4, 55.8, 65.6, 67.4, 73.8, 123.3, 125.6, 127.5, 128.1, 128.2, 129.4, 130.1, 132.8, 133.3, 134.9, 134.9, 135.8, 139.1, 152.06, 173.2, 208.2, Anal. Calcd. for $C_{26}H_{22}ClNO_3$: C, 72.30, H, 5.13, N, 3.28; Found: C, 72.32, H, 5.16, N, 3.29.

4bf: methyl 1-oxo-2'-phenyl-4'-(*p*-methylphenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.31 g (77%), white needles, mp: 210 °C ± 2, IR (KBr): 1689, 1750, 3449 cm^{-1}, ^1H NMR δ: 2.29 (s, 3H, Ar-CH_3), 2.75-2.79 (AB, 2H, *J* = 18 Hz, H-3), 3.02 (s, br, 1H, NH), 3.88 (s, 3H, OCH_3), 3.89 (d, 1H, *J* = 6 Hz, H-5'), 4.27 (d, 1H, *J* = 6 Hz, H-4'), 4.49 (s, 1H, H-2'), 6.98-7.23 (m, 13H, H_{arom}), ^{13}C NMR δ: 21.0, 35.4, 52.4, 55.8, 65.6, 67.4, 73.8, 123.3, 125.5, 127.5, 128.3, 128.2, 129.5, 130.2, 132.9, 133.3, 134.9, 134.9, 135.8, 139.1, 152.0, 173.2, 208.2, Anal. Calcd. for $C_{27}H_{25}NO_3$: C, 78.81, H, 6.12, N, 3.40, Found: C, 78.82, H, 6.16, N, 3.42.

4bg: methyl 1-oxo-2', 4'-di (*p*-methylphenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.33 g (78%), white needles, mp: 180°C ± 2, IR (KBr): 1689, 1750, 3449 cm^{-1}, ^1H NMR δ: 2.06 (s, 3H, Ar-CH_3), 2.28 (s, 3H, Ar-CH_3), 2.68-2.83 (AB, 2H, *J* = 18 Hz, H-3), 3.13 (s, br, 1H, NH), 3.76 (s, 3H, OCH_3), 3.85 (d, 1H, *J* = 6 Hz, H-5'), 4.26 (d, 1H, *J* = 6 Hz, H-4'), 4.44 (s, 1H, H-2'), 6.77-7.26 (m, 12H, H_{arom}), ^{13}C NMR δ: 20.9, 21.1, 35.4, 52.4, 55.9, 65.6, 67.6, 73.8, 123.3, 125.4, 127.5, 128.3, 128.2, 129.4, 130.2, 132.9, 133.3, 134.9, 134.9, 135.8, 139.1, 152.0, 173.2, 208.2. Anal. Calcd. for $C_{28}H_{27}NO_3$: C, 79.03, H, 6.40, N, 3.29, Found: C, 79.05, H, 6.43, N, 3.30.

4bh: methyl 1-oxo-2'-(*p*-methoxyphenyl)-4'-(*p*-methylphenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.35 g (80%), white needles, mp: 168°C ± 2, IR (KBr): 1680, 1754, 3450 cm^{-1} , ^1H NMR δ: 2.36 (s, 3H, Ar-CH_3), 2.73-2.90 (AB, 2H, *J* = 18 Hz, H-3), 2.79 (s, br, 1H, NH), 3.76 (s, 3H, Ar-OCH_3), 3.79 (s, 3H, OCH_3), 3.93 (d, 1H, *J* = 6 Hz, H-5'), 4.36 (d, 1H, *J* = 6 Hz, H-4'), 4.53 (s, 1H, H-2'), 6.58-7.36 (m, 12H, H_{arom}), ^{13}C NMR δ: 21.1, 35.4, 52.5, 55.1, 65.4, 67.4, 73.4, 113.5, 123.3, 125.4, 127.5, 128.2, 129.2, 129.4, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.1, 159.2, 173.3, 208.0 Anal. Calcd. for $C_{28}H_{27}NO_4$: C, 76.17, H, 6.16, N, 3.17, Found: C, 76.19, H, 6.13, N, 3.17.

4bi: methyl 1-oxo-2'-(*p*-chlorophenyl)-4'-(*p*-methylphenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.40 g (92%), yellow crystals, mp: 184°C ± 2, IR (KBr): 1682, 1754, 3449 cm^{-1}, ^1H NMR δ: 2.36 (s, 3H, Ar-CH_3), 2.76-2.91 (AB, 2H, *J* = 18 Hz, H-3), 2.82 (s, br, 1H, NH), 3.81 (s, 3H, OCH_3), 3.94 (d, 1H, *J* = 6 Hz, H-5'), 4.35 (d, 1H, *J* = 6 Hz, H-4'), 4.52 (s, 1H, H-2'), 6.85-7.34 (m, 12H, H_{arom}), ^{13}C NMR δ: 21.1, 35.5, 52.4, 55.9, 65.6, 67.5, 73.8, 123.3, 125.39, 127.5, 128.2, 129.2, 129.4, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.1, 152.0, 172.2, 208.2 Anal. Calcd. for $C_{27}H_{24}ClNO_3$: C, 72.72, H, 5.42, N, 3.14, Found: C, 72.72, H, 5.42, N, 3.14.

4cf: methyl 1-oxo-2'-phenyl-4'-(*p*-methoxyphenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.27 g (65%), white needles, mp: 188 °C ± 2, IR (KBr): 1680, 1754, 3439 cm^{-1}, ^1H NMR δ: 2.69-2.85 (AB, 2H, *J* = 18 Hz , H-3), 3.16 (s, br, 1H, NH), 3.73 (s, 3H, Ar-OCH_3), 3.76 (s, 3H, OCH_3), 3.87 (d, 1H, *J* = 6 Hz, H-5'), 4.24 (d, 1H, *J* = 6 Hz, H-4'), 4.46 (s, 1H, H-2'), 6.81-7.23 (m, 13H, H_{arom}), ^{13}C NMR δ: 35.6, 52.4, 55.4, 65.9, 67.7, 74, 114.2, 123.3, 125.6, 127.5, 128.1, 128.2, 129.5, 130.1, 131.8, 133.3, 134.9, 134.9, 135.8, 139.0, 142, 158.7, 173.3, 208.0 Anal. Calcd. for $C_{27}H_{25}NO_4$: C, 75.86, H, 5.89, N, 3.28, Found: C, 75.84, H, 5.86, N, 3.28.

4cg: methyl 1-oxo-2'-(p-methylphenyl)-4'-(*p*-methoxyphenyl)-1,3-dihydrospiro [indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.28 g (65%), white crystals, mp: 142 °C ± 2, IR (KBr): 1680, 1754, 3439 cm^{-1}, ^1H NMR δ: 2.09 (s, 3H, Ar-CH_3), 2.68-2.87 (AB, 2H, *J* = 18 Hz, H-3), 2.74 (s, br, 1H, NH), 3.69 (s, 3H, Ar-OCH_3), 3.73 (s, 3H, OCH_3), 3.84 (d, 1H, *J* = 6 Hz, H-5'), 4.25 (d, 1H, *J* = 6 Hz, H-4'), 4.44 (s, 1H, H-2'), 6.77-7.28 (m, 12H, H_{arom}), ^{13}C NMR δ: 20.9, 35.4, 52.5, 55.4, 65.6, 67.4, 73.6, 114.2, 125.3, 127.5, 128.2, 129.2, 129.4, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.1, 158.7, 173.1, 208.0 Anal. Calcd. for $C_{28}H_{27}NO_4$: C, 76.17, H, 6.16, N, 3.17, Found: C, 76.19, H, 6.13, N, 3.16.

4ch: methyl 1-oxo-2',4'-di(*p*-methoxyphenyl)-1,3-dihydrospiro [indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.29 g (64%), beige crystals, mp: 150 °C ± 2, IR (KBr): 1679, 1754, 3440 cm^{-1}, ^1H NMR δ: 2.67-2.84 (AB, 2H, *J* = 18 Hz, H-3), 2.78 (s, br, 1H, NH), 3.58 (s, 3H, Ar-OCH_3), 3.74 (s, 3H, Ar-OCH_3), 3.77 (s, 3H, OCH_3), 3.83 (d, 1H, *J* = 6 Hz, H-5'), 4.25 (d, 1H, *J* = 6 Hz, H-4'), 4.43 (s, 1H, H-2'), 6.51-7.29 (m, 12H, H_{arom}), ^{13}C NMR δ: 35.4, 52.5, 55.1, 65.6, 67.5, 73.5, 113.4, 123.3, 125.3, 127.5, 128.2, 129.2, 129.4, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.1, 159.1, 173.1, 208.1. Anal. Calcd. for $C_{28}H_{27}NO_5$: C, 73.51, H, 5.95, N, 3.06, Found: C, 73.53, H, 5.94, N, 3.07.

4ci: methyl 1-oxo-2'-(*p*-chlorophenyl)-4'-(*p*-methoxyphenyl)-1, 3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.30 g (67%), white crystals, mp: 158°C ± 2, IR (KBr): 1677, 1754, 3449 cm^{-1}, ^1H NMR δ: 2.75-2.95 (AB, 2H, *J* = 18 Hz, H-3), 2.81 (s, br, 1H, NH), 3.81 (s, 3H, Ar-OCH_3), 3.89 (s, 3H, OCH_3), 3.95(d, 1H, *J* = 6 Hz, H-5'), 4.39 (d, 1H, *J* = 6 Hz, H-4'), 4.57 (s, 1H, H-2'), 6.89-7.41 (m, 12H, H_{arom}), ^{13}C NMR δ: 35.4, 52.5, 55.0, 65.5, 67.5, 73.5, 114.3, 123.3, 125.3 ,127.5, 128.2, 129.2, 129.4, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.1, 151.8, 173.1, 207.5, Anal. Calcd. for $C_{27}H_{24}ClNO_4$: C, 70.20, H, 5.24, N, 3.03, Found: C, 70.20, H, 5.26, N, 3.06.

4df: methyl 1-oxo-2'-phenyl-4'-(*p*-chlorophenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.29 g (68%), beige needles, mp: 200 °C ± 2, IR (KBr) : 1677, 1754, 3449 cm^{-1}, ^1H NMR δ: 2.69-2.90 (AB, 2H, *J* = 18 Hz, H-3), 3.06 (s, br, 1H, NH), 3.78 (s, 3H, OCH_3), 4.06 (d, 1H, *J* = 6 Hz, H-5'), 4.28 (d, 1H, *J* = 6 Hz, H-4'), 4.49 (s, 1H, H-2'), 6.98-8.25 (m, 13H, H_{arom}), ^{13}C NMR δ: 35.7, 52.7, 55.2, 65.6, 67.2, 74.4, 123.5, 125.3, 127.5, 128.2, 129.2, 129.4, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.1, 151.1, 172.5, 206.7 Anal. Calcd. for $C_{27}H_{24}ClNO_4$: C, 70.20, H, 5.24, N, 3.03, Found: C, 70.25, H, 5.24, N, 3.03.

4dg: methyl 1-oxo-2'-(*p*-methylphenyl)-4'-(*p*-chlorophenyl)-1, 3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.28 g (63%), brown crystals, mp: 168 °C ± 2, IR (KBr) : 1677, 1754, 3449 cm^{-1}, ^1H NMR δ: 2.17 (s, 3H, Ar-CH_3), 2.77-2.93 (AB, 2H, *J* = 18 Hz, H-3), 2.83 (s, br, 1H, NH), 3.86 (s, 3H, OCH_3), 4.13 (d, 1H, *J* = 6 Hz, H-5'), 4.38 (d, 1H, *J* = 6 Hz, H-4'), 4.55 (s, 1H, H-2'), 6.88-8.26 (m, 12H, H_{arom}), ^{13}C NMR δ: 20.9, 35.6, 52.7, 55.3, 65.5, 66.9, 74.1, 123.5, 125.3 ,127.5, 128.2, 129.2, 129.4, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.1, 151.2, 172.5, 206.9, Anal. Calcd. for $C_{27}H_{24}ClNO_3$: C, 72.72, H, 5.42, N, 3.14, Found : C, 72.66, H, 5.38, N, 3.15.

4dh: methyl 1-oxo-2'-(*p*-methoxyphenyl)-4'-(*p*-chlorophenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.31 g (69%), beige crystals, mp: 152 °C ± 2, IR (KBr): 1679, 1759, 3450 cm^{-1}, ^1H NMR δ: 2.75-2.90 (AB, 2H, *J* = 18 Hz, H-3), 3.17 (s, br, 1H, NH), 3.66 (s, 3H, Ar-OCH_3), 3.68 (s, 3H, OCH_3), 4.13 (d, 1H, *J* = 6 Hz, H-5'), 4.34 (d, 1H, *J* = 6 Hz, H-4'), 4.52 (s, 1H, H-2'), 6.59-8.25 (m, 12H, H_{arom}), ^{13}C NMR δ: 35.6, 52.6, 55.1, 65.4, 67.0, 74.0, 113.5, 125.3, 127.5, 128.3, 129.2, 129.5, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.2, 159.2, 172.6, 207.0. Anal. Calcd. for $C_{27}H_{24}ClNO_4$: C, 70.20, H, 5.24, N, 3.03, Found: C, 69.85, H, 5.14, N, 2.94.

4di: methyl 1-oxo-2', 4'-di(*p*-chlorophenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.33 g (72%), beige crystals, mp: 178°C ± 2, IR (KBr): 1679, 1759, 3450 cm^{-1}, ^1H NMR δ:2.71-2.84 (AB, 2H, *J* = 18 Hz, H-3), 2.78 (s, br, 1H, NH), 3.77 (s, 3H, OCH_3), 4.06 (d, 1H, *J* = 6 Hz, H-5'), 4.28 (d, 1H, *J* = 6 Hz, H-4'), 4.46 (s, 1H, H-2'), 6.96-8.17 (m, 12H, H_{arom}), ^{13}C NMR δ: 35.8, 52.7, 54.9, 65.5, 66.8, 73.6, 123.6, 125.3, 127.5, 128.2, 129.2, 129.4, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.1, 151.0, 172.5, 206.4 Anal. Calcd. for $C_{26}H_{21}Cl_2NO_3$: C, 66.96, H, 4.54, N, 3.00, Found: C, 66.78, H, 4.42, N, 2.87.

4ef: methyl 1-oxo-2'-phenyl-4'-(*p*-nitrophenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.39 g (90%), white needles, mp: 210 °C ± 2, IR (KBr): 1676, 1759, 3449 cm^{-1}, ^1H NMR δ: 2.70-2.82 (AB, 2H, *J* = 18 Hz, H-3), 2.92 (s, br, 1H, NH), 3.77 (s, 3H, OCH_3), 3.90 (d, 1H, *J* = 6 Hz, H-5'), 4.23 (d, 1H, *J* = 6 Hz, H-4'), 4.45 (s, 1H, H-2'), 6.96-7.50 (m, 13H, H_{arom}) , ^{13}C NMR δ: 35.6, 52.5, 55.2, 55.3, 65.6, 67.4, 74.2, 123.3, 125.3, 127.5, 128.3, 129.2, 129.5, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.2, 151.6, 172.9, 207.5 Anal. Calcd. for $C_{26}H_{22}N_2O_5$: C, 72.30, H, 5.13, N, 3.24, Found : C, 72.32, H, 5.11, N, 3.24.

4eg: methyl 1-oxo-2'-(*p*-methylphenyl)-4'-(*p*-nitrophenyl)-1, 3-dihydrospiro [indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.41 g (92%), white crystals, mp: 160 °C ± 2, IR (KBr): 1676, 1759, 3449 cm^{-1}, ^1H NMR δ: 2.11 (s, 3H, Ar-CH_3), 2.69-2.90 (AB, 2H, *J* = 18 Hz , H-3), 3.06 (s, br, 1H, NH), 3.63 (s, 3H, OCH_3), 4.26 (d, 1H, *J* = 6 Hz, H-5'), 4.31 (d, 1H, *J* = 6 Hz, H-4'), 4.54 (s, 1H, H-2'), 6.71-7.57 (m, 12H, H_{arom}), ^{13}C NMR δ: 21.0, 35.7, 52.5, 55.2, 64.2, 67.2, 70.3, 113.6, 123.3, 125.3,127.5, 128.3, 129.2, 129.5, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.2, 142.2, 172.5, 198.6 Anal. Calcd. for C_{27} $H_{24}N_2O_5$: C, 71.04, H, 5.30, N, 6.14, Found : C, 70.98., H, 5.28, N, 6.13.

4eh: methyl 1-oxo-2'-(*p*-methoxyphenyl)-4'-(*p*-nitrophenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.28 g (61%), white needles, mp: 120 °C ± 2, IR (KBr) : 1679, 1760, 3448 cm^{-1}, ^1H NMR δ: 2.68-2.80 (AB, 2H, *J* = 18 Hz, H-3), 3.07 (s, br, 1H, NH), 3.78 (s, 3H, Ar-OCH_3), 3.81 (s, 3H, OCH_3) ,3.85 (d, 1H, *J* = 6 Hz, H-5'), 4.27 (d, 1H, *J* = 6 Hz, H-4'), 4.45 (s, 1H, H-2'), 6.52-7.7 (m, 12H, H_{arom}), ^{13}C NMR δ: 35.4, 52.6, 55.1, 65.3, 67.1, 73.5, 113.5, 125.3 ,127.5, 128.2, 129.2, 129.4, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.1, 139.4, 172.8, 207.7, Anal. Calcd. for $C_{27}H_{24}N_2O_6$: C,68.63, H, 5.12, N, 5.93, Found : C, 68.61, H, 5.02, N, 5.87.

4ei: methyl 1-oxo-2'-(*p*-chlorophenyl)-4'-(*p*-nitrophenyl)-1,3-dihydrospiro[indene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.29 g (61%), white crystals, mp: 130 °C ± 2, IR (KBr): 1680, 1760, 3449 cm^{-1}, ^1H NMR δ: 2.65-2.83 (AB, 2H, *J* = 18 Hz, H-3), 2.64 (s, br, 1H, NH), 3.73 (s, 3H, OCH_3), 3.90 (d, 1H, *J* = 6 Hz ,H-5'), 4.23 (d, 1H, *J* = 6 Hz, H-4'), 4.43 (s, 1H, H-2'), 6.95-7.85 (m, 12H, H_{arom}), ^{13}C NMR δ: 35.6, 52.6, 54.9, 65.5, 67.1, 73.3, 123.5, 125.3, 127.5, 128.4, 129.3, 129.5, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.6, 142.2, 151.4, 172.9, 207.1, Anal. Calcd. for $C_{26}H_{21}ClN_2O_5$: C, 65.48, H, 4.44, N, 5.87, Found : C, 65.56, H, 4.52, N, 5.83.

5af: methyl 1-oxo-2', 4'-diphenyl-3, 4-dihydro-1H-spiro [naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.33 g (82%); white crystals, mp: 168°C ± 2, IR (KBr): 1680, 1743, 3447 cm^{-1}, ^1H NMR: 1.63 (td, *J* = 5 Hz, 12.5 Hz, 1H, H-3), 1.87 (dt, *J* = 3 Hz, 10.5 Hz, 1H, H-4), 2.64 (dt, *J* = 3 Hz, 10.5 Hz, 1H, H-4), 2.69 (s, br, 1H, NH), 3.01 (td, *J* = 5 Hz, 12.5 Hz, 1H, H-3), 3.63 (s, 3H, OCH_3); 4.31(d, *J* = 8.7 Hz, 1H, H-5'), 4.44 (d, *J* = 8.7 Hz, 1H, H-4'), 4.55 (s, 1H, H-2'), 6.8-7.53 (m, 14H, H_{arom}), ^{13}C NMR :25.3, 3.5, 52.4, 55.5, 61.3, 64.2, 70.9, 126.3, 127.1, 127.5, 127.9, 128.0, 128.3, 129.3, 132.8, 133.0, 138.1, 139.1, 142.0, 173.8, 198.5 Anal. Calcd. for $C_{27}H_{25}NO_3$: C, 78.81, H, 6.12, N, 3.4. Found: C, 78.83, H, 6.2, N, 3.38.

5ag: methyl 1-oxo-2'-(*p*-methylphenyl)-4'-phenyl-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.31 g (74%); white crystals mp: 158°C ± 2, IR (KBr): 1681, 1740, 3447 cm^{-1}, ^1H NMR: 1.83 (td, *J* = 5 Hz, 12.5 Hz, 2H, H-3), 1.86 (dt, *J* = 3 Hz, 10.5 Hz, 1H, H-4), 2.09 (s, 3H, Ar-CH_3), 2.65 (dt, *J* = 3 Hz, 10.5 Hz, 1H, H-4), 2.81 (s, br, 1H, NH), 3.02 (td, *J* = 5 Hz, 12.5 Hz, 1H, H-3), 3.67 (s, 3H, CH_3), 4.28 (d, *J* = 8.7 Hz, 1H, H-5'), 4.43 (d, *J* = 8.7 Hz, 1H, H-4'), 4.53 (s, 1H, H-2'), 6.77-7.58 (m, 13H, H_{arom}). ^{13}C NMR: 21.0 25.3 , 30.4 , 52.4 , 55.6 , 61.3 , 64.2 , 70.7,126.3 ,127.0, 127.5, 127.8, 128.0, 128.3, 128.7, 129.3, 132.9, 132.0, 137.5, 138.2,142.1, 142.1, 173.9, 198.65. Anal. Calcd. for $C_{28}H_{27}NO_3$: C, 79.03, H, 6.4, N, 3.29. Found: C, 79.01, H, 6.2, N, 3.28.

5ah: methyl 1-oxo-2'-(*p*-methoxyphenyl)-4'-phenyl-3, 4-dihydro-1H-spiro [naphthalene-2, 3'-pyrrolidine]-5'-carboxylate

Yield 0.22 g (52%); beige crystals, mp: 168°C ± 2, IR (KBr): 1681, 1741, 3449 cm^{-1}; ^1H NMR: 1.65 (td, *J* = 5 Hz, 12.8 Hz, 1H, H-3), 1.79 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 2.66 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 2.74 (s, br, 1H, NH), 2.98 (td, *J* = 5 Hz, 12.8 Hz, 1H, H-3), 3.59 (s, 3H, OCH_3), 3.65 (s, 3H, Ar-OCH_3), 4.29 (d, *J* = 8.7 Hz, 1H, H-5'), 4.42 (d, *J* = 8.7 Hz, 1H, H-4'), 4.49 (s, 1H, H-2'), 6.5-7.2 (m, 13H, H_{arom}),^{13}C NMR : 25.3, 30.4, 52.4, 55.1, 55.5, 61.0, 64.2, 113.3, 126.3, 127.1, 127.5, 128.0, 128.3, 129.1, 129.3, 132.8,133.0, 138.2, 142.1, 173.8, 198.7.Anal.Calcd. for $C_{28}H_{27}NO_4$: C, 76.17, H, 6.16, N, 3.17. Found: C, 76.18, H, 6.1 N, 3.28.

5ai: methyl 1-oxo-2'-(*p*-chlorophenyl)-4'-phenyl-3, 4-dihydro-1H-spiro [naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.19 g (43%); white crystals, mp: 180°C ±2, IR (KBr): 1679, 1735, 3446 cm^{-1}; ^1H NMR: 1.72 (td, *J* = 5 Hz, 12.8 Hz, 1H, H-3), 1.95 (dt, *J* = 3 Hz, 11 Hz, 1H, H-4), 2.76 (dt, *J* = 3 Hz, 11 Hz, 1H, H-4), 2.81 (s, br, 1H, NH), 3.15 (td, *J* = 5 Hz, 12.8 Hz, 1H, H-3), 3.77 (s, 3H, OCH_3), 4.40 (d, *J* = 8.7 Hz, 1H, H-5'), 4.53 (d, *J* = 8.7 Hz, 1H, H-4'), 4.65 (s, 1H, H-2'), 7.04-7.67 (m, 13H, H_{arom}). ^{13}C NMR : 25.3, 30.1, 52.5, 54.9, 61.2, 63.9, 69.6, 126.6, 127.2, 127.6,128.1, 128.3, 129.33, 133.3, 137.7, 141.9, 141.9, 173.8, 198.1. Anal. Calcd. for $C_{27}H_{24}ClNO_3$: C, 27.72, H, 5.42, N, 3.14. Found: C, 27.62; H, 5.41, N, 3.12.

5bf: methyl 1-oxo-2'-phenyl-4'-(*p*-methylphenyl)-3, 4-dihydro-1H-spiro [naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.27 g (65%), white crystals, mp: 138°C ± 2, IR (KBr): 1683, 1735, 3447 cm^{-1}, ^1H NMR: 1.68 (td, *J* = 5 Hz, 12.8 Hz, 1H, H-3), 1.87 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 2.20 (s, 3H, Ar- CH_3), 2.62 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 2.83 (s, br, 1H, NH), 3.05 (td, *J* = 5 Hz, 12,8 Hz, 1H, H-3), 3.69 (s, 3H, CH_3), 4.27 (d, *J* = 8.7 Hz, 1H, H-5'), 4.41 (d, *J* = 8.7 Hz, 1H, H-4'), 3.69 (s, 3H, CH_3), 4.55 (s, 1H, H-2'), 6.89-7.57 (m, 13H, H_{arom}). ^{13}C NMR : 21.0, 25.3, 30.4, 52.4, 55.2, 61.2, 64.3,70.9, 126.3, 127.5, 127.8, 128.0, 128.0, 129.0, 129.1, 132.9, 136.7, 142.1, 173.9, 198.6. Anal. Calcd. for $C_{28}H_{27}NO_3$: C, 79.03, H, 6.4, N, 3.29. Found: C, 79.01, H, 6.2, N, 3.28.

5bg: methyl 1-oxo-2',4'-di(*p*-methylphenyl)-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.32 g (73%); beige crystals, mp: 146°C ± 2, IR (KBr) : 1684, 1749, 3449 cm^{-1}, ^1H NMR : 1.65 (td, *J* = 4.5 Hz, 12.8 Hz, 1H, H-3), 1.84 (dt, *J* = 3 Hz, 10.5 Hz, 1H, H-4), 2.01 (s, 6H, 2Ar-CH_3), 2.65 (dt, *J* = 3 Hz, 10.5 Hz, 1H, H-4), 2.69 (s, br, 1H, NH), 2.94 (td, *J* = 4.5 Hz, 12.8 Hz, 1H, H-3), 3.70 (s, 3H, OCH_3), 4.32 (d, *J* = 8.4 Hz, 1H, H-5'), 4.36 (d, *J* = 8.4 Hz, 1H, H-4'), 4.49 (s, 1H, H-2'), 6.80-7.61 (m, 12H, H_{arom}). ^{13}C NMR: 21.0, 21.0, 25.4, 52.4, 55.3, 61.2, 64.3, 70.7, 126.2, 127.5, 127.8, 128.0, 128.6, 129.0, 129.1, 132.9, 135.1, 136.0, 136.6, 137.4, 142.2, 173.9, 198.7, 207.1. Anal. Calcd. for $C_{29}H_{29}NO_3$: C, 79.24, H, 6.65, N, 3.19. Found: C, 79.23, H, 6.66, N, 3.15.

5bh: methyl 1-oxo-2'-(*p*-methoxyphenyl)-4'-(*p*-methylphenyl)-3, 4-dihydro-1H-spiro [naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.29 g (64%); beige crystals, mp: 138°C ± 2, IR (KBr): 1682, 1745, 3449 cm^{-1}, ^1H NMR : 1.68 (td, *J* = 5 Hz, 12.5 Hz, 1H, H-3), 1.82 (dt, 5.1, *J* = 3.5 Hz, 11.5 Hz, 1H, H-4), 2.23 (s, 3H,Ar- CH_3), 2.61 (dt, *J* = 3.5 Hz, 11.5 Hz, 1H, H-4), 2.77 (s, br, 1H, NH), 3.03 (td, *J* = 5 Hz, 12.5 Hz, 1H, H-3), 3.59 (s, 3H, OCH_3), 3.37 (s, 3H, Ar-OCH_3), 4.23 (d, *J* = 9 Hz, 1H, H-5'), 4.37 (d, *J* = 9 Hz, 1H, H-4'), 4.50 (s, 1H, H-2'), 6.50-7.59 (m, 12H, H_{arom}). ^{13}C NMR :

21.0, 25.4, 30.4, 52.4, 55.3, 61.0, 64.2, 70.4, 113.3, 126.3, 127.5, 128, 129, 129.1, 129.1, 131, 132.9, 132.9, 135.1, 136.6, 142.2, 159, 173.8, 198.8. Anal. Calcd. for $C_{29}H_{29}NO_4$: C, 76.46, H, 6.42, N, 3.07. Found: C, 76.44, H, 6.39, N, 3.07.

5bi: methyl 1-oxo-2'-(*p*-chlorophenyl)-4'-(*p*-methylphenyl)-3,4-dihydro-1H-spiro [naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.43 g (94%); yellow crystals, mp: 184°C ± 2, IR (KBr):1680,1743, 3446 cm^{-1}, ^1H NMR : 1.73 (td, *J* = 4.5 Hz, 12.5 Hz, 1H, H-3), 1.93 (dt, *J* = 3 Hz, 10.5 Hz, 1H, H-4), 2.30 (s, 3H, Ar-CH_3), 2.75 (dt, *J* = 3 Hz, 10.5 Hz, 1H, H-4), 2.87 (s, br, 1H, NH), 3.09 (td, *J* = 4.5 Hz, 12.5 Hz, 1H, H-3), 3.74 (s, 3H, OCH_3), 4.35 (d, *J* = 8.7 Hz, 1H, H-5'), 4.48 (d, *J* = 8.7 Hz, 1H, H-4'), 4.61 (s, 1H, H-2'), 6.97-7.63 (m, 12H, H_{arom}). ^{13}C NMR : 21, 25.3, 30.1, 52.4, 54.6, 61.3, 64, 69.7, 126.5, 127.6, 128.1, 128.1, 129, 129.2, 129.3, 132.8, 133.2, 133.5, 134.6, 136.8, 138,142, 173.8, 198.1. Anal.Calcd. for $C_{28}H_{26}ClNO_3$: C, 73.1, H, 5.7, N, 3.05. Found: C, 73.09, H, 5.5, N, 3.03.

5cf: methyl 1-oxo-2'-phenyl-4'-(*p*-methoxyphenyl)-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.30 g (69%); beige crystals, mp: 152°C ±2, IR (KBr):1680,1743, 3449 cm^{-1}, ^1H NMR : 1.63 (td, *J* = 5 Hz, 13.8 Hz, 1H, H-3), 1.85 (dt, *J* = 3 Hz, 12.5 Hz, 1H, H-4), 2.09 (dt, *J* = 3 Hz, 12.5 Hz, 1H, H-4), 2.49 (s, br, 1H, NH), 3.01 (td, *J* = 5 Hz, 13.8 Hz, 1H, H-3), 3.70 (s, 6H, 2Ar-OCH_3), 4.31 (d, *J* = 8.7 Hz, 1H, H-5'), 4.39 (d, *J* = 8.7 Hz, 1H, H-4'), 4.57 (s, 1H, H-2'), 6.76-7.52 (m, 13H, H_{arom}). ^{13}C NMR : 30.1, 31, 52.5, 54.6, 55.2, 61.1, 66.4, 170.4, 113.7, 126.4, 127.5, 127.9, 128, 129.7, 130.3, 132.8, 133.1, 142.1, 158.6, 172.6, 198.5. Anal. Calcd. for $C_{28}H_{27}NO_4$: C, 76.17, H, 6.16, N, 3.17. Found: C, 76.18; H, 6.1; N, 3.28.

5cg: methyl 1-oxo-2'-(*p*-methylphenyl)-4'-(*p*-methoxyphenyl)-3,4-dihydro-1H-spiro [naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.26 g (59%); white crystals, mp: 140°C ± 2, IR (KBr): 1680, 1743, 3449 cm^{-1}; 1H NMR: 1.65 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 1.83 (dt, *J* = 3 Hz, 12.5 Hz, 1H, H-4), 2.81 (dt, *J* = 3 Hz, 12.5 Hz, 1H, H-4), 2.99 (s, br, 1H, NH), 3.39 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 3.62 (s, 3H, Ar-CH_3), 3.68 (s, 3H, CH_3), 4.20 (d, *J* = 8.7 Hz, 1H, H-5'), 4.37 (d, *J* = 8.7 Hz, 1H, H-4'), 4.49 (s, 1H, H-2'), 6.5-7.57 (m, 12H, H_{arom}). ^{13}C NMR: 15.3, 20.9, 35.5, 52.5, 55.3, 65.5, 65.9, 67.3, 123.4, 125.5, 126.6, 127.2, 128.7, 129, 130.1, 133, 133.1, 134.6, 135.9, 137.6, 139.5, 151.7, 173.0, 207.6. Anal. Calcd. for $C_{29}H_{29}NO_4$: C, 76.46, H, 6.42, N, 3.07. Found: C, 76.44, H, 6.39, N, 3.07.

5ch: methyl 1-oxo-2', 4'-di (*p*-methoxyphenyl)-3, 4-dihydro-1H-spiro [naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.28 g (61%); yellow crystals, mp: 151°C ± 2, IR (KBr): 1681, 1745, 3397 cm^{-1}, ^1H NMR : 1.15 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 1.33 (dt, *J* = 3 Hz, 12 Hz, 1H, H-4), 2.07 (s, 6H, 2 Ar-OCH_3), 2.97 (s, br, 1H, NH), 3.02 (dt, *J* = 3 Hz, 12 Hz, 1H, H-4), 3.43 (td, 5 Hz, 13.5 Hz, 1H, H-3), 3.76 (s, 3H, OCH_3), 4.21 (d, *J* = 9 Hz, 1H, H-5'), 4.23 (d, *J* = 9 Hz, 1H, H-4'), 4.41 (s, 1H, H-2'), 6.77-7.28 (m, 12H, H_{arom}). ^{13}C NMR : 25.3, 26.9, 30.4, 52.5, 55.1, 61.8, 70.2, 113.3, 113.6, 126.3, 127.5, 128, 129, 130, 130.2, 131.4, 132.9, 132.9, 142.1, 174, 198.7. Anal. Calcd. for $C_{29}H_{29}NO_3$: C, 73.87, H, 6.20, N, 2.97. Found C, 73.77, H, 6.30, N, 2.97.

5ci: methyl 1-oxo-2'-(*p*-chlorophenyl)-4'-(*p*-methoxyphenyl)-3,4-dihydro-1H-spiro [naphthalene-2, 3'-pyrrolidine]-5'-carboxylate

Yield 0.38 g (80%); yellow crystals, mp: 160°C ± 2, IR (KBr):1680, 1743, 3446 cm^{-1}, ^1H NMR: 1.71 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 1.89 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 2.68 (s, br, 1H, NH), 2.69 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 3.01 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 3.68

(2s, 6H, OCH_3), 4.25 (d, *J* = 9.3 Hz, 1H, H-5'), 4.38 (d, *J* = 9.3 Hz, 1H, H-4'), 4.53 (s, 1H, H-2'), 6.74-7.55 (m, 12H, H_{arom}). ^{13}C NMR : 25.3, 30, 52.4, 61.3, 63.9, 69.3, 67.3, 113.6, 126.5, 127.6, 128.1, 128.2, 129.2, 129.3, 130.3, 132.8, 133.2, 133.4, 138.2, 141.9, 158.6, 173.9, 198 .Anal. Calcd. for $C_{28}H_{26}ClNO_4$: C, 70.66, H, 5.51, N, 2.94. Found: C, 70.66, H, 5.51, N, 2.94.

5df: methyl 1-oxo-4'-(*p*-chlorophenyl)-2'-phenyl-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.32 g (74%); white crystals, mp: 182°C ±2, IR (KBr): 1675,1744, 3447 cm^{-1},^1H NMR : 1.71 (td, *J* = 5 Hz, 13.8 Hz, 1H, H-3), 2.01 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 2.58 (s, br, 1H, NH), 2.72 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 3.23 (td, *J* = 5 Hz, 13.8 Hz, 1H, H-3), 3.72 (s, 3H, CH_3), 3.91 (d, *J* = 9 Hz, 1H, H-5'), 4.25 (d, *J* = 9 Hz, 1H, H-4'), 4.40 (s, 1H, H-2'), 7.02-8.20 (m, 13H, H_{arom}). ^{13}C NMR: 25.3, 35.5, 52.5, 55.3, 65.5, 65.9, 67.3, 123.4, 123.5, 126.5, 131, 133, 137.8, 141.9, 151.7, 173, 198. Anal. Calcd. for $C_{27}H_{24}ClNO_3$: C, 27.72, H, 5.42, N, 3.14. Found: C, 27.62, H, 5.41, N, 3.12.

5dg: methyl 1-oxo-4'-(*p*-chlorophenyl)-2'-(*p*-methylphenyl)-3, 4-dihydro-1H-spiro[naphthalene-2, 3'-pyrrolidine]-5'-carboxylate

Yield 0.22 g (50%), white crystals, mp: 170°C ±2, IR (KBr):1676, 1745, 3447 cm^{-1}, ^1H NMR : 1.74 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 1.99 (dt, *J* = 3 Hz, 12 Hz, 1H, H-4), 2.17 (s, 3H, Ar-CH3), 2.75 (dt, *J* = 3 Hz, 12 Hz, 1H, H-4), 2.84 (s, br, 1H, NH), 3.15 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 3.73(s, 3H, CH_3), 4.31 (d, *J* = 9.3 Hz, 1H, H-5'), 4.52 (d, *J* = 9.3 Hz, 1H, H-4'), 4.61 (s, 1H, H-2'), 6.84-7.60 (m, 12H, H_{arom}). ^{13}C NMR : 21, 25.3, 30.3, 52.4, 54.5, 61.5, 63.7, 70.1, 126.3, 127.6, 127.7, 128.7, 130.7, 132.9, 132.9, 133, 136.3, 136.4, 137.5, 141.9, 173.6, 197.9 . Anal. Calcd. for $C_{28}H_{26}ClNO_3$: C, 73.11, H, 5.7, N, 3.05. Found: C, 73.09, H, 5.5, N, 3.03.

5dh: methyl 1-oxo-4'-(*p*-chlorophenyl)-2'-(*p*-methoxyphenyl)-3,4-dihydro-1H-spiro[naphthalene-2, 3'-pyrrolidine]-5'-carboxylate

Yield 0.28 g (60%), white crystals, mp: 172°C ±2, IR (KBr):1677, 1745, 3447 cm^{-1}, ^1H NMR : 1.64 (td, *J* = 5 Hz, 13.8 Hz, 1H, H-3), 1.72 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 2.82 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 2.87 (s, br, 1H, NH), 3.28 (td, *J* = 5 Hz, 13.8 Hz, 1H, H-3), 3.69 (2s, 6H, OCH_3), 4.28 (d, *J* = 9.3 Hz, 1H, H-5'), 4.52 (d, *J* = 9.3 Hz, 1H, H-4'), 4.59 (s, 1H, H-2'), 6.57-7.61 (m, 12H, H_{arom}). ^{13}C NMR: 25.3, 30.4, 52.4, 54.4, 55.2, 61.2, 69.8, 113.4, 126.4, 127.6, 128.1, 128.4, 129, 130.6, 131.3, 132.9, 132.9, 133, 136.4, 141.9, 159.1, 159.1, 173.6, 198.1. Anal. Calcd. for $C_{28}H_{26}ClNO_4$: C, 70.66, H, 5.51, N, 2.94. Found: C, 70.66, H, 5.51, N, 2.94.

5di: methyl 1-oxo-2',4'-di(*p*-chlorophenyl)-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.38 g (68%), white crystals, mp: 188°C ± 2. IR (KBr):1675, 1744, 3447 cm^{-1},^1H NMR : 1.87 (td, *J* = 4.5 Hz, 13.5 Hz, 1H, H-3), 1.93 (dt, *J* = 3 Hz, 12 Hz, 1H, H-4), 2.76 (dt, *J* = 3 Hz, 12 Hz, 1H, H-4), 2.79 (s, br, 1H, NH), 3.03 (td, *J* = 4.5 Hz, 13.5 Hz, 1H, H-3), 3.59 (s, 3H, OCH_3), 4.25 (d, *J* = 9.6 Hz, 1H, H-5'), 4.46 (d, *J* = 9.6 Hz, 1H, H-4'), 4.56 (s, 1H, H-2'), 6.94-7.52 (m, 12H, H_{arom}). ^{13}C NMR: 25.2, 29.7, 52.5, 53.7, 61.4, 63.3, 68.9, 126.6, 127.6, 128.1, 128.2, 128.4, 129.2, 130.6, 132.6, 133.0, 133.4, 133.5, 135.7, 138.2, 141.7, 173.5, 197.4. Anal. Calcd. for $C_{27}H_{23}Cl_2NO_3$: C, 67.51, H, 4.83, N, 2.92. Found: C, 67.49, H, 4.85, N, 2.92.

5ef: methyl 1-oxo-2'-phenyl-4'-(*p*-nitrophenyl)-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.37 g (83%), beige crystals, mp: 168°C ± 2, IR (KBr): 1673, 1731, 3446 cm^{-1}, ^1H NMR: 1.79 (td, *J* = 4.5 Hz, 13.5 Hz, 1H, H-3), 1.99 (dt, *J* = 3 Hz, 12.5 Hz, 1H, H-4), 2.55 (dt, *J* = 3 Hz, 12.5 Hz, 1H, H-4), 2.67 (s, br, 1H, NH), 3.11 (td, *J* = 4.5 Hz, 13.5 Hz, 1H, H-3), 3.62 (s, 3H, OCH_3), 4.39 (d, *J* = 9 Hz, 1H, H-5'), 4.45 (d, *J* = 9 Hz, 1H, H-4') ,4.56 (s, 1H, H-2'), 6.79-7.67 (m, 13H, H_{arom}). ^{13}C NMR: 25.3, 30.5, 52.4, 55.5, 61.3, 64.2, 70.9, 126.3, 127.4, 127.5, 128.1, 130.3, 131.5, 137.6, 141.4, 173.8, 198.5. Anal. Calcd. for $C_{27}H_{24}N_2O_5$: C, 71.04, H, 5.30, N, 6.14. Found: C, 71.06, H, 5.29, N, 6.14.

5eg: methyl 1-oxo-2'-(*p*-methylphenyl)-4'-(*p*-nitrophenyl)-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.23 g (51%), yellow crystals, mp: 168°C ± 2, IR (KBr): 1677, 1735, 3446 cm^{-1}, ^1H NMR: 1.58 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 1.75 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 2.23 (s, 3H, Ar-CH_3), 2.65 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 2.84 (s, br, 1H, NH), 2.96 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 3.72 (s, 3H, OCH_3), 4.33 (d, *J* = 9 Hz, 1H, H-5'), 4.39 (d, J = 9 Hz, 1H, H-4'), 4.45 (s, 1H, H-2'), 6.72-7.82 (m, 12H, H_{arom}). ^{13}C NMR:25.2, 30.4 , 52.4 , 54.2 , 56.3 , 61.2 , 64.23, 126.5, 127.5, 127.6, 128.1, 128.7, 130.3, 132.6, 123, 133.2, 137.7, 141.6 ,145.2 ,173.6 , 198.7. Anal. Calcd. for $C_{28}H_{26}N_2O_5$: C, 71.47, H, 5.57, N, 5.95. Found: C, 71.47, H, 5.57, N, 5.95.

5eh: methyl 1-oxo-2'-(*p*-methoxyphenyl)-4'-(*p*-nitrophenyl)-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.39 g (81%), yellow crystals, mp: 170°C ± 2, IR (KBr): 1675, 1729, 3445 cm^{-1}, ^1H NMR: 1.57 (td, *J* = 4.5 Hz, 13 Hz, 1H, H-3), 1.81 (dt, *J* = 3 Hz, 11 Hz, 1H, H-4), 2.53 (dt, *J* = 3 Hz, 11 Hz, 1H, H-4), 2.79 (s, br, 1H, NH), 2.98 (td, *J* = 4.5 Hz, 13 Hz, 1H, H-3), 3.59 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 4.31 (d, *J* = 9.8 Hz, 1H, H-5'), 4.42 (d, *J* = 9.8 Hz, 1H, H-4') , 4.50 (s,1H, H-2'), 6.78-7.02 (m, 12H, H_{arom}). ^{13}C NMR: 24.9, 29.2, 35.4, 51.9, 55.7, 59.3, 64.1, 67.6, 120.9, 121.1, 124.1, 124.5, 125.9, 128.1, 128.6, 129.1, 129.1, 129.2, 129.2, 132.8, 133.0, 134.3, 139.9, 145.4, 145.6, 157.9, 171.6, 198.4. Anal. Calcd. for $C_{28}H_{26}N_2O_6$: C, 69.12, H, 5.51, N, 2.94. Found: C, 69.11, H, 5.51, N, 2.84.

5ei: methyl 1-oxo-2'-(*p*-chlorophenyl)-4'-(*p*-nitrophenyl)-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidine]-5'-carboxylate

Yield 0.37 g (77%), beige crystals, mp: 171°C ±2, IR (KBr): 1680, 1743, 3445 cm^{-1}, ^1H NMR :1.57 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 2.02 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 3.21 (dt, *J* = 3 Hz, 11.5 Hz, 1H, H-4), 3.23 (s, br, 1H, NH), 3.56 (td, *J* = 5 Hz, 13.5 Hz, 1H, H-3), 3.52 (s, 3H, OCH_3), 4.40 (d, *J* =9.5 Hz, 1H, H-5'), 4.62 (d, *J* =9. Hz, 1H, H-4'), 4.68 (s, 1H, H-2'), 6.93-7.97 (m, 12H, H_{arom}). ^{13}C NMR: 25.2, 29.8, 52.5, 52.7, 61.3, 62.3, 67.8, 124.6, 125.5, 126.3, 126.9, 127.3, 127.8, 131.0, 131.8, 132.1, 136.5, 142.5, 173.2, 197.2. Anal. Calcd. for $C_{27}H_{23}ClN_2O_5$: C, 66.06, H, 4.72, N, 5.71. Found: C, 69.10, H, 5.52, N, 2.82.

6ag: methyl 1-oxo-4'-phenyl-2'-(*p*-methylphenyl)-1,3,4',5'-tetrahydrospiro[indene-2, 3'-pyrrole]-5'-carboxylate

Yield 0.19 g (60%), white needles, mp: 176°C ± 2, IR (KBr) : 1639, 1680, 1740 cm^{-1}, ^1H NMR: 2.09 (s, 3H, Ar-CH_3), 2.94-3.12 (AB, 2H, *J* = 18 Hz, H-3), 3.73 (s, 3H, CH_3), 4.10 (d, 1H, *J* = 6 Hz, H-5'), 4.91(d, 1H, *J* = 6 Hz, H-4'), 6.77-7.33 (m, 13H, H_{arom}), ^{13}C NMR: 21.3, 35.2, 51.4, 55.8, 65.5, 67.4, 72.8, 113.3, 119.4, 125.6, 127.5, 128.1, 128.2, 129.5, 130.1, 131.8, 133.3, 134.9, 134.9, 135.8, 139, 151, 170.2, 175.2, 208.2. Anal. Calcd. for: $C_{27}H_{23}NO_3$: C 79.20, H, 5.66, N; 3.42, Found: C, 79.22, H, 5.66, N, 3.40.

6ah: methyl 1-oxo-4'-phenyl-2'-(*p*-methoxyphenyl)-1,3,4',5'-tetrahydrospiro[indene-2,3'-pyrrole]-5'-carboxylate

Yield 0.24 g (75%); white crystals, mp: 178°C ± 2, IR (KBr): 1642, 1677, 1735 cm^{-1}, ^1H NMR: 3.72 (s, 3H, Ar-CH_3), 2.95-3.28 (AB, 2H, *J* = 18 Hz, H-3), 3.73 (s, 3H, OCH_3), 4.2 (d, 1H, *J* = 6 Hz, H-5'), 5.16 (d, 1H, *J* = 6 Hz, H-4'), 6.51-7.34(m, 13H, H_{arom}), ^{13}C NMR: 21.3 , 35.2, 52.4, 57.8, 69.9, 67.4, 75.3, 124.6, 127.5, 128.1, 128.2, 129.5, 130.1, 131.8, 133.3, 134.9, 134.9, 135.8, 139, 152.1, 171.5, 175.3, 205.2. Anal. Calcd. for $C_{27}H_{23}NO_4$: C, 76.22, H, 5.45, N, 3.29, Found: C, 76.24, H, 5.47, N, 3.27.

6df: methyl 1-oxo-4'-(*p*-chlorophenyl)-2'-phenyl-1,3,4',5'-tetrahydrospiro[indene-2,3'-pyrrole]-5'-carboxylate

Yield 0.19 g (65%); white needles, mp: 160°C ± 2, IR (KBr): 1642, 1677, 1735 cm^{-1}, ^1H NMR: 2.90-3.02 (AB, 2H, *J* = 18 Hz, H-3), 3.8 (s, 3H, OCH_3), 4.3 (d, 1H, *J* = 6 Hz, H-5'), 5.15 (d, 1H, *J* = 6 Hz, H-4'), 6.96-7.50 (m, 13H, H_{arom}),^{13}C NMR: 32.6, 52.5, 55.1, 55.3, 65.6, 70.4, 75.6, 123.3, 125.3, 127.5, 128.3, 129.2, 129.5, 130.5, 132.9, 133.5, 134.9, 134.9, 135.8, 139.2, 151.6, 171.4, 175.5, 207.5, Anal. Calcd. for $C_{26}H_{20}ClNO_3$: C, 72.64, H, 4.69, N, 3.26, Found: C, 72.62, H, 4.66, N, 3.23.

X-ray crystallography

Colourless crystals of **4bg**, **4ci** and **5bi** have been mounted on a Nonius Kappa Apex II diffractometer and the intensity data have been collected at 115 K with Mo K_α radiation of $\lambda = 0.71073$ Å. These data were further treated with the suite of SAINT V8.27B (Bruker AXS Inc., 2012) programs and within the OLEX2 frame[34]. The models of the structures have been solved by direct methods with SUPERFLIP[35] (**4bg** and **4ci**) or with SHELXS-97[30] (**5bi**) and refined with SHELXL-97[36]. There is a slight disorder of the OMe group in **5bi** with statistic occupancies of 0.56 and 0.44 for O, C and H atoms of this group. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogens bound to N atoms were located from difference-Fourier maps and isotropically refined for **4bg** and **4ci** but included in a riding model for **5bi**. All other H atoms were placed in calculated positions and refined as riding on the heavy atoms bearing them.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre: deposition numbers CCDC 1029334 (**4bg**), CCDC 1029335 (**4ci**) and CCDC 1029336 (**5bi**) contain detailed crystallographic data for this publication. These data may be obtained free of charge from the Cambridge Crystallographic Data Center through www.ccdc.cam.ac.uk/data_request/cif.

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