Reaction of *E*-2-Arylidene-1-indanones, *Z*-Aurones, *Z*-1-Thioaurones and *Z*-2-Arylidene-2,3-dihydro-1*H*-indol-3-ones with Diazomethane

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Dedicated to Professor Dr. Károly Lempert on the occasion of his 75th birthday

1,3-Dipolar cycloaddition of *E*-2-arylidene-1-indanones **1a-h** and *Z*-aurones **3a-c** with diazomethane provided *trans*-spiro-1-pyrazolines **2a-h** and **4a-c**, respectively, as sole products. However, the same cycloaddition of *Z*-1-thioaurones **5a-f** afforded a mixture of *Z*-α-methyl-1-thioaurones **6a-f** and *trans*-cyclopropane derivatives **7a-f** as a result of the spontaneous denitrogenation of the initially formed 1-pyrazolines. Similar reaction of *Z*-2-arylidene-2,3-dihydro-1*H*-indol-3-ones **8a,b** and diazomethane yielded *trans*-cyclopropanes **9a,b**. Structure and stereochemistry of the compounds synthesized have been elucidated by nmr spectroscopic measurements.

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Introduction.

Synthesis of pyrazolines by the reaction of α,β-enones and diazomethane has been investigated by several research groups [1-9]. It has turned out that this 1,3-dipolar cycloaddition of chalcones and related α,β-unsaturated ketones with diazomethane yielded 2-pyrazolines as the thermodynamically more stable products of this cycloaddition [5-9]. However, the reaction of exocyclic α,β-unsaturated ketones as a distinct group of the α,β-enones afforded spiro-1-pyrazolines as stable products [10-15].

In our previous papers [11-13] cycloaddition of both *E*-and *Z*-isomers of 2-arylidene-1-tetralones, 3-arylidene-chromanones, -1-thiochromanones and -flavanones with diazomethane has been discussed in details. The reaction proved to be diastereospecific providing such spiro-1-pyrazolines where the stereochemistry of the starting α,β-unsaturated ketones has been retained. In the case of these α,β-unsaturated ketones with six-membered ring system, replacement of the methylene group of the 2-arylidene-1-tetralones at position 4 either by an oxygen or by a sulfur atom was without influence on the course of the reaction and on the stereochemistry and stability of the reaction products, respectively. No substituent effect originating from the *para*-substitution of the arylidene moiety of the starting materials could be detected [11].

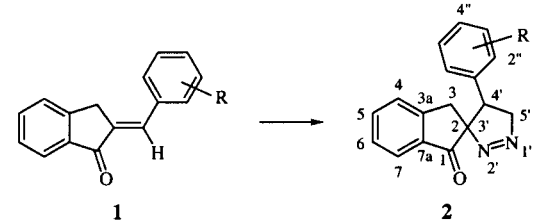
We report here the reaction of *E*-2-arylidene-1-indanones **1a-h**, *Z*-aurones [2-(arylmethylene)benzo[*b*]furan-3(2*H*)-ones] **3a-c**, *Z*-1-thioaurones [2-(arylmethylene)benzo[*b*]-thiophen-3(2*H*)-ones] **5a-f** and *Z*-2-arylidene-2,3-dihydro-1*H*-indol-3-ones **8a,b** with diazomethane and the elucidation of the structure and stereochemistry of the reaction products by nmr spectroscopic measurements.

Results and Discussion.

Formerly we investigated the 1,3-dipolar cycloaddition of diazomethane with exocyclic α,β-unsaturated ketones with six-membered ring system [11-13]. It seemed expedient to perform similar reaction of the homologous exocyclic α,β-enones with five-membered ring system and diazomethane to get informations on the course of this 1,3-dipolar cycloaddition and on the stability of the reaction products. 2-Arylidene-1-indanones **1**, aurones **3**, 1-thioaurones **5**, and 2-arylidene-2,3-dihydro-1*H*-indol-3-ones **8** appeared to be convenient substrates for this purpose. In our present study only those isomers of compounds **1**, **3**, **5** and **8** are included where the carbonyl group and the aryl moiety are on the opposite sides of the double bond (*cf.* Schemes 1-4).

E-2-Arylidene-1-indanones **1a-h** were allowed to react with diazomethane in a mixture of anhydrous ether and

Scheme 1



1 **2**

1a, 2a	R = 4-Me	**1e, 2e**	R = 4-F
1b, 2b	R = 2-MeO	**1f, 2f**	R = 2-Cl
1c, 2c	R = 3-MeO	**1g, 2g**	R = 3-Cl
1d, 2d	R = 4-MeO	**1h, 2h**	R = 4-Cl

acetone to afford spiro-1-pyrazolines **2a-h** in good yields (Scheme 1). The *trans* relative configuration of compounds **2a-h** was unambiguously proven by NOE difference spectroscopy. The fact that the irradiation of proton 3-H_a resulted in NOE enhancement on the aromatic protons (*cf.* Table 1) reveals their spatial proximity. Furthermore, irradiation of proton 4'-H showed similar NOE characteristics corroborating this assumption.

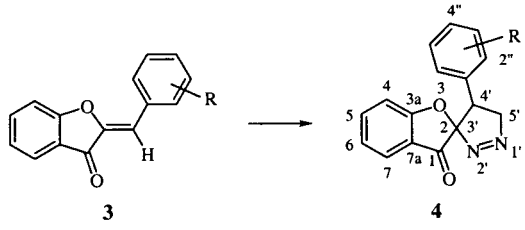
In our previous investigations [11-13] it has been concluded that the substituent present in the *para*-position of the phenyl group is almost without influence either on the course of the reaction or on the stereochemistry of the reaction product.

In the case of *E*-2-arylidene-1-indanones **1** the same electron donor substitituent (methoxy group) or the same electron acceptor substituent (chloro) were introduced systematically

into the *ortho, meta* and *para*-position. It has turned out that such a change in the substitution pattern of the phenyl group may result in the alteration of the envelope conformation of the five-membered 1-pyrazoline ring as reflected in the coupling constant values between the 4'-H and 5'-H protons (see Experimental, compounds **2a-h**), but has no effect on the product stability and on the stereochemistry of the cycloaddition. It is also worth mentioning that compounds **2a-h** are similarly stable substances as spiro-1-pyrazolines obtained by the reaction of the homologous *E*-2-arylidene-1-tetralones with diazomethane [11,12].

Similarly to compounds **1a-h**, *Z*-aurones **3a-c** were allowed to react with diazomethane in a mixture of anhydrous methylene chloride and diethyl ether to obtain spiro-1-pyrazolines **4a-c** as sole isolable products (Scheme 2).

Scheme 2



3 **4**

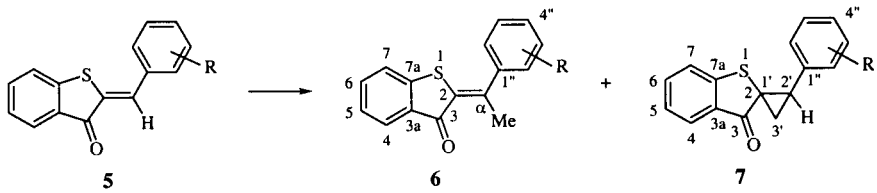
3a, 4a R = H
3b, 4b R = 2-Me
3c, 4c R = 4-MeO

Since there is an oxygen atom next to the spiro carbon atom (position 3) in these molecules, no NOE experiement can be performed to prove the relative spatial arrangement of the phenyl group at position 4' and the carbonyl group. For this reason, in this case one can conclude from the results of analogous reactions [11-13] that spiro-1-pyrazolines **4a-c** should be *trans*-isomers owing to the fact that these compounds were obtained from α,β-enone isomers providing *trans*-products in this concerted 1,3-dipolar cycloaddition. This assumption is corroborated by our observation that chemical shift value of 5'-H_{cis} atom determined by the irradiation of proton 4'-H reveals similar downfield shift if compared to the 5'-H_{trans} one as observed in the case of spiro-1-pyrazolines **2a-h** with fully confirmed stereochemistry. We also mention that spiro-1-pyrazolines **4a-c** almost completely decomposed during several months at ambient temperature which means that they are less stable substances than the analogous spiro-1-pyrazolines **2a-h** (*cf.* Scheme 1) or than the homologous spiro-1-pyrazolines prepared by the reaction of 3-arylidenechromanones and diazomethane [11,13].

When *Z*-1-thioaurones **5a-f** were allowed to react with diazomethane in a mixture of anhydrous methylene chloride and diethyl ether, no traces of the expected spiro-1-pyrazolines could be isolated or even detected by thin-layer chromatography (tlc). Instead, denitrogenated products **6a-f** and **7a-f** were detected in the solution on tlc monitoring. Compositions of the crude reaction mixtures have been determined by ^{1}H nmr spectroscopy. These measurements revealed the presence of approx. 40% α-methyl-1-thioaurones **6a-f** and 60% cyclopropane derivatives **7a-f**. Compounds **6a-f** and **7a-f** have been separated by column chromatography and characterized by ^{1}H and ^{13}C nmr spectroscopy (*cf.* Experimental). It is worth mentioning that the mass balance is about 50% taking into account the yields of the isolated products. This may be a consequence of some decomposition on the chromatographic column reflected in the appearance of brown zones on the column during the separation. Moreover, although compound **7b** could be detected by ^{1}H nmr measurement in the crude reaction mixture, it completely decomposed in the course of the chromatographic separation and, therefore, its physical constants, analytical and spectroscopic data are not included in the experimental section. Stereochemistry of compounds **6a-f** and **7a,c-f** has been elucidated by ^{1}H and ^{13}C nmr measurements.

Relative steric arrangements of the carbonyl group and the methyl group at position α of compounds **6a-f** cannot be determined by NOE experiments. However, in our previous study [16] we managed to prove that in the major products of the thermal decomposition of spiro-1-pyrazolines prepared from exocyclic α,β-enones of similar stereochemistry the carbonyl group and the methyl group are on the same side of the double bond. This is reflected in the downfield shift of the chemical shift value of the methyl group as well. Owing to the fact that the ^{1}H chemical shift values of the methyl groups are very similar to that measured for the major diastereomer of the 2-(α-methylbenzylidene)-1-indanone (2.72 ppm) [16] and are considerably different from that of the minor one (2.25 ppm) [16] the same stereochemistry can be assumed for

Scheme 3



5 **6** **7**

5a, 6a, 7a R = H
5b, 6b, 7b R = 4-MeO
5c, 6c, 7c R = 4-F
5d, 6d, 7d R = Cl
5e, 6e, 7e R = 4-Br
5f, 6f, 7f R = 3,4-Cl_2

compounds **6a-f.** It is worth mentioning that in the crude reaction mixtures a singlet ^1H signal of weak intensity could be detected at 2.45 ppm which may belong to the α-methyl group of a minor *E*-diastereomer with opposite stereochemistry.

Without further information, in the case of cyclopropane derivatives **7a,c-f** (Scheme 3) NOE measurements alone are insufficient to determine the relative stereoposition of the carbonyl group and the aryl moiety at position 2'. However, the 3'-H_{cis} proton shows a characteristic downfield shift in comparison with the 3'-H_{trans} proton as a result of the deshielding effect of the adjacent carbonyl group. When the 2'-H proton was irradiated a great NOE enhancement (Table 1) was measured on this shifted 3'-H_{cis} signal which proves that these hydrogens are located on the same side of the cyclopropane ring. In consequence, the carbonyl and phenyl groups should be on the opposite sides, that is, the relative configuration of the alkene is retained in the product.

Table 1

Results of the NOE Difference Measurements

Compound	Proton irradiated	NOE enhancements (%)
2a	3-H_a	3-H_b (20.9)' 2",6"-H (2.5)' 3",5"-H (2.1)
	4'-H	5'-H_{cis} (4.5)' 2",6"-H (6.4)' 3-H_b (1.8)
2b	4'-H	5'-H_{cis} (6.5)' 5",6"-H (8.0)' 3-H_b (2.3)
2f	4'-H	5'-H_{cis} (6.7)' 6"-H (2.3)' 3-H_b (1.1)
2h	4'-H	5'-H_{cis} (4.4)' 2",6"-H (9.7)' 3-H_b (8.0)
7a	2'-H	3'-H_{cis} (4.7)' 2",6"-H (5.7)
7d	2'-H	3'-H_{cis} (4.3)' 2",6"-H (5.0)
7e	2'-H	3'-H_{cis} (4.0)' 2",6"-H (5.8)
7f	2'-H	3'-H_{cis} (5.2)' 2"-H (4.5)' 6"-H (3.7)
9a	2'-H	3'-H_{cis} (3.0)' 2",6"-H (4.0)
	3'-H_{cis}	2'-H (5.0)' 3'-H_{trans} (12.0)
	3'H_{trans}	3'-H_{cis} (13.0)' 2",6"-H (10.0)

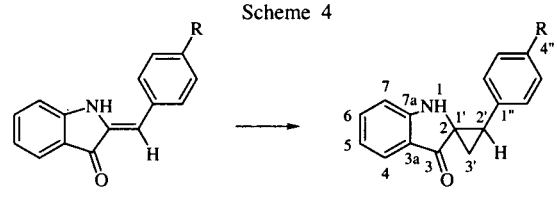
The greater ^3J coupling constant between the 2'-H proton and the 3'-H proton with downfield shift provides a further proof for this assignment since the $^3J_{H,Hcis} > {}^3J_{H,Htrans}$ relationship has been well established for the cyclopropane derivatives [17].

The fact that spiro-1-pyrazolines initially formed by the reaction of *Z*-1-thioaurones with diazomethane even cannot be detected in the crude reaction mixtures, reveals that these substances should be very unstable in comparison with their analogous compounds **2a-h** (*cf.* Scheme 1) and with their homologous spiro-1-pyrazolines synthesized by the reaction of 3-arylidene-1-thiochromanones and diazomethane [11,13]. This pronounced denitrogenation ability may be a consequence of stereoelectronic effect present in the molecule [18] or the alteration of the bond angles as a result of the replacement of the CH_2 moiety by a sulfur atom.

It has been found in many cases that thermal denitrogenation of pyrazolines obtained by the reaction of ethylene derivatives and diazomethane provides cyclopropanes and/or olefins where the stereochemistry of the starting unsaturated compound is retained [16,19-21]. The same feature seems to be valid for the formation of compounds **6a-f** and **7a-f** in our present study.

As a fourth group of exocyclic α,β-enones with five-membered ring system, we also investigated this 1,3-dipolar cycloaddition of *Z*-2-arylidene-2,3-dihydro-1*H*-indol-3-ones **8a,b**. Compounds **8a,b** were allowed to react with diazomethane in a mixture of anhydrous methylene chloride and diethyl ether to afford cyclopropane derivatives **9a,b** as sole products (Scheme 4). In the case of these α,β-unsaturated ketones neither the appropriate spiro-1-pyrazolines nor α-methyl derivatives could be isolated or even detected by tlc in the crude reaction mixtures.

Scheme 4



8a, 9a R = H
8b, 9b R = Me

The *trans* relative configuration of the carbonyl and phenyl groups in the cyclopropane derivative **9a** was deduced in same way that in the case of the sulfur analogues **7a,c-f**. The great NOE enhancement observed on the signal of 3'-H proton with greater downfield shift when the 2'-H proton was irradiated clearly shows their *cis*-position in the cyclopropane ring.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^1H and ^{13}C nmr spectra were recorded on Bruker WP 200 SY and Varian Gemini 200 spectrometers at 200/50 MHz in deuteriochloroform at room temperature using tetramethylsilane as the internal standard. tlc was performed on Kieselgel 60 F_{254} (Merck) layer using hexane-acetone (7:3 v/v) or methylene chloride-hexane (3:2 v/v) as eluents. Starting materials **1a-h, 3a-c, 5a-f** and **8a,b** were synthesized according to known procedures [22-25]. It should be mentioned that in the case of compounds **7** and **9** the H_{cis} proton and the carbonyl group are on the same side, while the H_{trans} proton and carbonyl group are on the opposite sides of the cyclopropane ring.

Synthesis of Spiro-1-pyrazolines **2a-h** by the Reaction of *E*-2-Arylidene-1-indanones **1a-h** with Diazomethane. General Procedure.

A mixture of *E*-2-arylidene-1-indanone (**1a-h**, 5.0 mmoles), diazomethane (15.0 mmoles), anhydrous acetone (50.0 ml) and diethyl ether (30.0 ml) was allowed to stand in refrigerator for 48 hours, then the solvent was evaporated *in vacuo* and the residue

was crystallized from methanol to afford spiro-1-pyrazolines **2a-h** (Scheme 1).

trans-4',5'-Dihydro-4'-(4-methylphenyl)spiro[2*H*-indene-2,3'-[3*H*]pyrazol]-1-(3*H*)-one (**2a**).

This compound was obtained as white crystals in 86% yield, mp 126-127°; ^{1}H nmr: δ 2.32 (s, 3H, 4"-CH_3), 2.86 (d, J = 17.9 Hz, 1H, 3-H_b), 3.48 (d, J = 17.9 Hz, 3-H_a), 3.59 (dd, J = 7.7 and 3.7 Hz, 1H, 4'-H), 5.08 (dd, J = 17.8 and 3.7 Hz, 1H, 5'-H_{trans}), 5.20 (dd, J = 17.8 and 7.7 Hz, 1H, 5'-H_{cis}), 6.75 (d, J = 8.7 Hz, 2H, 2",6"-H), 7.08 (d, J = 8.7 Hz, 2H, 3",5"-H), 7.42 (m, 2H, 4,6-H), 7.62 (ddd, 1H, 5-H), 7.80 (dd, J = 8.3 and 1.0 Hz, 1H, 7-H); ^{13}C nmr: δ 20.3 (4"-CH_3), 33.7 (C-3), 43.9 (C-4'), 86.7 (C-5'), 105.1 (C-3'), 124.9 (C-7), 126.6 (C-4 or C-6), 127.4 (C-2",6"), 128.0 (C-4 or C-6), 129.6 (C-3",5"), 134.8 (C-7a), 135.8 (C-5), 137.1 (C-4"), 137.3 (C-1"), 153.4 (C-3a), 199.9 (C-1).

Anal. Calcd. for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.13. Found: C, 78.10; H, 5.90; N, 10.04.

trans-4',5'-Dihydro-4'-(2-methoxyphenyl)spiro[2*H*-indene-2,3'-[3*H*]pyrazol]-1(3*H*)-one (**2b**).

This compound was prepared as white crystals in 85% yield, mp 118-119°; ^{1}H nmr: δ 2.77 (d, J = 18.0 Hz, 1H, 3-H_b), 3.41 (d, J = 18.0 Hz, 1H, 3-H_a), 3.59 (s, 3H, 2"-OCH_3), 3.88 (dd, J = 8.4 and 5.0 Hz, 1H, 4'-H), 4.99 (dd, J = 17.8 and 5.0 Hz, 1H, 5'-H_{trans}), 5.ll (dd, J = 17.8 and 8.4 Hz, 1H, 5'-H_{cis}), 6.83 (d, J = 8.1 Hz, 1H, 3"-H), 6.90 (m, 2H, 5",6"-H). 7.26 (ddd, 1H, 4"-H), 7.41 (m, 2H, 4,6-H), 7.61 (ddd, 1H, 5-H), 7.82 (d, J = 7.6 Hz, 1H, 7-H); ^{13}C nmr: δ 33.1 (C-3), 39.3 (C-4'), 54.6 (2"-OCH_3), 84.3 (C-5'), 103.9 (C-3'), 110.6 (C-3"), 120.8 (C-5"), 124.9 (C-7), 126.6, 127.9 (C-4,6), 128.1 (C-1"), 128.8, 129.3 (C-2",6"), 135.2 (C-7a), 153.7 (C-3a), 157.2 (C-4"), 201.1 (C-1).

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.84; H, 5.57; N, 9.55.

trans-4',5'-Dihydro-4'-(3-methoxyphenyl)-spiro[2*H*-indene-2,3'-[3*H*]pyrazol]-1(3*H*)-one (**2c**).

This compound was obtained as white crystals in 78% yield, mp 106-107°; ^{1}H nmr: δ 2.88 (d, J = 18.0 Hz, 1H, 3-H_b), 3.51 (d, 18.0 Hz, 1H, 3-H_a), 3.60 (dd, J = 7.1 and 4.3 Hz, 1H, 4'-H), 3.75 (s, 3H, 3"-OCH_3), 5.11 (dd, J = 17.9 and 4.3 Hz, 1H, 5'-H_{trans}), 5.21 (dd, J = 17.9 and 7.1 Hz, 1H, 5'-H_{cis}), 6.40 (dd, 1H, 2"-H), 6.45(ddd, 1H, 4"-H), 6.79 (ddd, 1H, 6"-H), 7.21 (dd, 1H, 5"-H), 7.44 (m, 2H, 4,6-H), 7.64 (ddd, 1H, 5-H), 7.81 (dd, J = 8.1 and 1.0 Hz, 1H, 7-H); ^{13}C nmr: δ 33.6 (C-3), 44.2 (C-4'), 55.1 (3"-OCH_3), 86.5 (C-5'), 105.2 (C-3'), 112.7, 113.5 (C-2",4"), 119.9 (C-6"), 125.1 (C-7), 126.7, 128.2 (C-4,6), 130.2 (C-5"), 135.0 (C-7a), 136.1 (C-5), 142.2 (C-1"), 153.7 (C-3a), 160.2 (C-2"), 200.2 (C-1).

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.86; H, 5.49; N, 9.61.

trans-4',5'-Dihydro-4'-(4-methoxyphenyl)spiro[2*H*-indene-2,3'-[3*H*]pyrazol]-1(3*H*)-one (**2d**).

This compound was obtained as white crystals in 75% yield, mp 113-114°; ^{1}H nmr: δ 2.88 (d, J = 18.0 Hz, 1H, 3-H_b), 3.49 (d, J = 18.0 Hz, 1H, 3-H_a), 3.59 (dd, J = 7.8 and 3.7 Hz, 1H, 4'-H), 3.79 (s, 3H, 4"-OCH_3), 5.08 (dd, J = 17.9 and 3.7 Hz, 1H, 5'-H_{trans}), 5.21 (dd, J = 17.9 and 7.7 Hz, 1H, 5'-H_{cis}), 6.80 (s, 4H, 2",3",5",6"-H), 7.42 (m, 2H, 4,6-H), 7.63 (ddd, 1H, 5-H), 7.79 (dd, J = 8.1 and 1.0 Hz, 1H, 7-H); ^{13}C nmr: δ 33.5 (C-3), 43.6 (C-4'), 55.1 (4"-OCH_3), 86.7 (C-5'), 105.2 (C-3), 114.4 (C-3",5"), 125.1 (C-7), 126.7, 128.1 (C-4,6), 128.7 (C-2",6"), 132.6 (C-1"), 135.0 (C-7a), 136.0 (C-5), 153.6 (C-3a), 159.7 (C-4"), 200.3 (C-1).

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.88, H, 5.50; N, 9,54.

trans-4',5'-Dihydro-4'-(4-fluorophenyl)-spiro[2*H*-indene-2,3'-[3*H*]pyrazol]-1(3*H*)-one (**2e**).

This substance was isolated as pale yellow crystals in 77% yield, mp 117-118°; ^{1}H nmr: δ 2.83 (d, J = 18.0 Hz, 1H, 3-H_b), 3.50 (d, J = 18.0 Hz, 1H, 3-H_a), 3.63 (dd, J = 7.8 and 3.3 Hz, 1H, 4'-H), 5.07 (dd, J = 17.7 and 3.3 Hz, 1H, 5'-H_{trans}), 5.21 (dd, J = 17.7 and 7.8 Hz, 1H, 5'-H_{cis}), 6.81-7.02 (m, 4H, 2",3",5",6"-H), 7.45 (m, 2H, 4,6-H), 7.65 (ddd, 1H, 5-H), 7.80 (d, J = 7.6 Hz, 1H, 7-H); ^{13}C nmr: δ 33.5 (C-3), 43.5 (C-4'), 86.7 (C-5'), 105.1 (C-3'), 115.9 (d, $^2J_{C-F}$ = 21.5 Hz, C-3",5"), 125.1 (C-7), 126.7, 128.2 (C-4,6), 129.2 (d, $^3J_{C-F}$ = 8.1 Hz, C-2",6"), 134.8 (C-7a), 136.1 (C-5), 136.3 (C-1"), 153.4 (C-3a), 162.2 (d, $^1J_{C-F}$ = 246.0 Hz, C-4"), 199.9 (C-1).

Anal. Calcd. for $C_{17}H_{13}FN_2O$: C, 72.85; H, 4.67; N, 9.99. Found: C, 72.80; H, 4.69; N, 9.93.

trans-4'-(2-Chlorophenyl)-4',5'-dihydrospiro[2*H*-indene-2,3'-[3*H*]pyrazol]-1(3*H*)-one (**2f**).

This compound was obtained as pale yellow plates in 81% yield, mp 102-103°; ^{1}H nmr: δ 2.79 (d, J = 17.6 Hz, 1H, 3-H_b), 3.50 (d, J = 17.6, 1H, 3-H_a), 4.23 (dd, J = 7.4 and 3.7 Hz, 1H, 4'-H), 5.15 (dd, J = 18.0 and 7.4 Hz, 1H, 5'-H_{trans}), 5.26 (dd, J = 18.0 and 3.7 Hz, 1H, 5'-H_{cis}), 6.80 (dd, 1H, 6"-H), 7.23 (m, 2H, 3",4"-H), 7.38 (ddd, 1H, 5"-H), 7.47 (m, 2H, 4,6-H), 7.66 (ddd, 1H, 5-H), 7.82 (d, J = 8.0 Hz, 1H, 7-H). ^{13}C nmr: δ 33.4 (C-3), 39.9 (C-4'), 85.6 (C-5'), 105.1 (C-3'), 125.1 (C-7), 126.6, 127.75 (C-4,6), 128.2, 128.4, 128.8, 129.9 (C-3",4",5",6"), 134.1, 134.6 (C-7a,2"), 138.1 (C-1"), 153.5 (C-3a), 199.6 (C-1).

Anal. Calcd. for $C_{17}H_{13}ClN_2O$: C, 68.80; H, 4.41; N, 9.43. Found: C, 68.84; H, 4.44; N, 9.46.

trans-4'-(3-Chlorophenyl)-4',5'-dihydrospiro[2*H*-indene-2,3'-[3*H*]pyrazol]-1(3*H*)-one (**2g**).

This compound was isolated as pale yellow crystals in 82% yield, mp 104-105°; ^{1}H nmr: δ 2.84 (d, J = 17.7 Hz, 1H, 3-H_b), 3.51 (d, J = 17.7 Hz, 1H, 3-H_a), 3.60 (dd, J = 7.7 and 3.6 Hz, 1H, 4'-H), 5.13 (dd, J = 17.9 and 3.6 Hz, 1H, 5'-H_{trans}), 5.21 (dd, J = 17.9 and 7.7 Hz, 1H, 5'-H_{cis}), 6.75 (ddd, 1H, 6"-H), 6.89 (brs, 1H, 2"-H), 7.27 (m, 2H, 3",4"-H), 7.44 (m, 2H, 4,6-H), 7.66 (ddd, 1H, 5-H), 7.81 (dd, J = 8.3 and 0.9 Hz, 1H, 7-H); ^{13}C nmr: δ 33.5 (C-3), 43.8 (C-4'), 86.5 (C-5'), 105.1 (C-3'), 125.1 (C-7), 125.8 (C-6"), 126.7, 127.8, 128.3 (C-4,6,2",4"), 130.4 (C-5"), 134.7, 134.9 (C-7a,3"), 136.1 (C-5), 142.6 (C-1"), 199.6 (C-1).

Anal. Calcd. for $C_{17}H_{13}ClN_2O$: C, 68.80; H, 4.41; N, 9.43. Found: C, 68.76; H, 4.39; N, 9.48.

trans-4'-(4-Chlorophenyl)-4',5'-dihydrospiro[2*H*-indene-2,3'-[3*H*]pyrazol]-1(3*H*)-one (**2h**).

This compound was obtained as pale yellow crystals in 74% yield, mp 128-129°; ^{1}H nmr: δ 2.83 (d, J = 17.9 Hz, 1H, 3-H_b), 3.50 (d, J = 17.9 Hz, 1H, 3-H_a), 3.61 (dd, J = 8.0 and 3.4 Hz, 1H, 4'-H), 5.08 (dd, J = 17.8 and 3.4 Hz, 1H, 5'-H_{trans}), 5.22 (dd, J = 17.8 and 8.0 Hz, 1H, 5'-H_{cis}), 6.80 (d, J = 8.2 Hz, 2H, 2",6"-H), 7.26 (d, J = 8.2 Hz, 2H, 3",5"-H), 7.44 (m, 2H, 4,6-H), 7.65 (ddd, 1H, 5-H), 7.80 (dd, J = 8.0 and 1.0 Hz, 1H, 7-H); ^{13}C nmr: δ 33.7 (C-3), 43.7 (C-4'), 86.6 (C-5'), 105.0 (C-3'), 125.1 (C-7), 126.6,

128.2 (C-4,6), 128.9, 129.2 (C-2",3",4",5"), 133.4 (C-1"), 134.7 (C-7a), 136.0 (C-5), 153.2 (C-3a), 199.5 (C-1).

Anal. Calcd. for $C_{17}H_{13}ClN_2O$: C, 68.80; H, 4.41; N, 9.43. Found: C, 68.84; H, 4.48; N, 9.47.

Preparation of Spiro-1-pyrazolines **4a-c** by the Reaction of *Z*-Aurones **3a-c** with Diazomethane. General Procedure.

The appropriate *Z*-aurone (**3a-c**; 5.0 mmoles) and diazomethane (15.0 mmoles) were dissolved in a 1:1 v/v mixture of anhydrous methylene chloride and diethyl ether (80.0 ml). The solution was allowed to stand in refrigerator for 48 hours, the solvent was evaporated under reduced pressure and the residue was crystallized from methanol to obtain spiro-1-pyrazolines **4a-c** (Scheme 2).

trans-4',5'-Dihydro-3-oxa-4'-phenylspiro[2*H*-indene-2,3'[3*H*]-pyrazol]-1-one (**4a**).

This compound was isolated as white crystals in 65% yield, mp 121-122°; ^{1}H nmr: δ 3.68 (dd, J = 7.8 and 4.7 Hz, 1H, 4'-H), 5.10 (dd, J = 18.1 and 4.7 Hz, 1H, 5'-H_{trans}), 5.25 (dd, J = 18.1 and 7.8 Hz, 1H, 5'-H_{cis}), 6.99-7.30 (m, 7H, 5,7-H + Ph), 7.62 (ddd, 1H, 6-H), 7.72 (dd, J = 7.4 and 0.7 Hz, 1H, 4-H); ^{13}C nmr: δ 43.7 (C-4'), 85.4 (C-5'), 113.6 (C-4), 119.6, 119.1 (C-7a,3'), 123.3 (C-6), 125.1 (C-7), 127.7 (C-4"), 128.3, 128.6 (C-2",3",5",6"), 134.7 (C-1"), 138.9 (C-5), 172.0 (C-3a), 194.8 (C-1).

Anal. Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.71; H, 4.58; N, 10.59. Found: C, 72.75; H, 5.61; N, 10.63.

trans-4',5'-Dihydro-4'-(2-methylphenyl)-3-oxaspiro[2*H*-indene-2,3'[3*H*]pyrazol]-1-one (**4b**).

This compound was isolated as colourless plates in 81% yield, mp 111-112°; ^{1}H nmr: δ 2.10 (s, 3H, 2"-CH_3), 3.96 (dd, J = 7.4 and 4.1 Hz, 1H, 4'-H), 5.15 (dd, J = 18.0 and 7.4 Hz, 1H, 5'-H_{trans}), 5.28 (dd, J = 18.0 and 4.1 Hz, 1H, 5'-H_{cis}), 6.91 (m, 1H, 6"-H), 7.04-7.23 (m, 5H, 5,7,3",4",5"-H), 7.64 (ddd, 1H, 6-H), 7.73 (d, J = 7.7 Hz, 1H, 4-H); ^{13}C nmr: δ 19.9 (2"-CH_3), 39.1(C-4'), 85.2 (C-5'), 113.8 (C-4), 120.0, 119.4 (C-7a,3'), 123.5 (C-6), 125.3, 126.5, 127.3, 127.7 (C-7,4",5",6"), 130.5 (C-3"), 133.4 (C-2"), 136.8 (C-1"), 139.2 (C-5), 172.6 (C-3a), 194.3 (C-1).

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.06. Found: C, 73.41; H, 5.10, N, 10.01.

trans-4',5'-Dihydro-4'-(4-methoxyphenyl)-3-oxaspiro[2*H*-indene-2,3'-[3*H*]pyrazol]-1-one (**4c**).

This compound was isolated as white crystals in 87% yield, mp 88-89°; ^{1}H nmr: δ 3.71 (s, 3H, 4"-OMe), 3.77 (dd, J = 7.8 and 5.3 Hz, 1H, 4'-H), 5.07 (dd, J = 18.4 and 5.3 Hz, 1H, 5'-H_{trans}), 5.21 (dd, J = 18.4 and 7.8 Hz, 1H, 5'-H_{cis}), 6.80 (d, J = 8.5 Hz, 2H, 3",5"-H), 6.96 (d, J = 8.5 Hz, 2H, 2",6"-H), 7.18-7.34 (m, 2H, 4,6-H), 7.73-7.79 (m, 2H, 5,7-H); ^{13}C nmr: δ 42.2 (C-4'), 57.7 (4"-OMe), 84.5 (C-5'), 113.2 (C-4), 113.6 (C-3",5"), 118.3, 119.0 (C-7a,3'), 123.4 (C-6), 124.6 (C-7), 126.2 (C-1"), 129.2 (C-2",6"), 139.3 (C-5), 158.4 (C-4"), 171.1 (C-3a), 194.3 (C-1).

Anal. Calcd. for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.51. Found: C, 69.42; H, 4.75; N, 9.55.

General Procedure for the Reaction of *Z*-1-Thioaurones **5a-f** with Diazomethane.

The appropriate *Z*-1-thioaurone (**5a-f**, 5.0 mmoles) was dissolved in anhydrous methylene chloride (50.0 ml) and diazomethane (15.0 mmoles) dissolved in anhydrous diethyl ether (30.0 ml) was added. The solution was allowed to stand in refrigerator for 48 hours. The solvent was evaporated *in vacuo* and the two reaction products formed were separated on silica gel (Merck) column by using methylene chloride-hexane (3:2 v/v) as eluent to afford compounds **6a-f** and **7a-f** (Scheme 3).

2-(1-Phenylethylidene)benzo[*b*]thiophen-3(2*H*)-one (**6a**).

This compound was isolataed as yellow crystals in 20% yield, mp 85-86°; ^{1}H nmr: δ 2.83 (s, 3H, CH_3), 7.22 (ddd, 1H, 5-H), 7.31 (d, J = 7.4 Hz, 1H, 7-H), 7.45 (m, 6H, 6-H+Ph), 7.89 (d, J = 8.2 Hz, 1H, 4-H); ^{13}C nmr: δ 21.6 (CH_3), 123.3, 124.8, 126.8 (C-4,5,7), 127.3, 128.7 (C-2',3',5',6'), 128.9 (C-4'), 130.2 (C-2 or C_α), 132.8 (C-3a), 134.6 (C-6), 143.8 (C-1'), 146.1 (C-2 or C_α), 151.3 (C-7a), 188.8 (C-3).

Anal. Calcd. for $C_{16}H_{12}OS$: C, 76.17; H, 4.79. Found: C, 76.11; H, 4.76.

2-[1-(4-Methoxyphenyl)ethylidene]benzo[*b*]thiophen-3(2*H*)-one (**6b**).

This compound was isolated as yellow crystals in 38% yield, mp 124-125°; ^{1}H nmr: δ 2.82 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.96 (d, J = 8.3 Hz, 2H, 3',5'-H), 7.22 (ddd, 1H, 5-H), 7.33 (d, J = 7.9 Hz, 1H, 7-H), 7.45 (d, J = 8.3 Hz, 2H, 2',6'-H), 7.48 (ddd, 1H, 6-H), 7.88 (d, J = 8.0 Hz, 1H, 4-H); ^{13}C nmr: δ 21.6 (CH_3), 55.3 (OCH_3), 114.0 (C-3',5'), 123.3, 124.8, 126.8 (C-4,5,7), 129.3 (C-2',6'), 129.5 (C-2 or C_α), 132.9 (C-3a), 134.4 (C-6), 136.0 (C-1'), 146.0 (C-2 or C_α), 151.4 (C-7a), 160.3 (C-4'), 188.7 (C-3).

Anal. Calcd. for $C_{17}H_{14}O_2S$: C, 72.33; H, 4.99. Found: C, 72.38; H, 4.96.

2-[1-(Fluorophenyl)ethylidene]benzo[*b*]thiophen-3(2*H*)-one (**6c**).

This compound was prepared as yellow crystals in 23% yield, mp 109-110°; ^{1}H nmr: δ (deuteriochloroform): 2.81 (s, 3H, CH_3), 7.10-7.56 (m, 7H, 5,6,7,2',3',5',6'-H), 7.89 (d, J = 7.8 Hz, 1H, 4-H); ^{13}C nmr: δ 21.6 (CH_3), 115.8 (d, $^2J_{C\text{-}F}$ = 21.7 Hz, C-3',5'), 123.3, 124.9, 126.9 (C-4,5,7), 129.5 (d, $^3J_{C\text{-}F}$ = 8.4 Hz, C-2'6'), 130.4 (C-2 or C_α), 132.7 (C-3a), 134.7 (C-6), 139.7 (C-1'), 145.8 (C-2 or C_α), 162.9 (d, $^1J_{C\text{-}F}$ = 248.9 Hz, C-4'), 188.8 (C-3).

Anal. Calcd. for $C_{16}H_{11}FOS$: C, 71.10; H, 4.10. Found: C, 71.16; H, 4.07.

2-[1-(4-Chlorophenyl)ethylidene]benzo[*b*]thiophen-3(2*H*)-one (**6d**).

This substance was prepared as yellow crystals in 18% yield, mp 112-113°; ^{1}H nmr: δ 2.80 (s, 3H, CH_3), 7.26 (ddd, 1H, 5-H), 7.33 (d, J = 7.2, 1H, 7-H), 7.41 (s, 4H, 2",3",5",6"-H), 7.51 (ddd, 1H, 6-H), 7.89 (d, J = 8.1 Hz, 1H, 4-H). ^{13}C nmr: δ 21.4 (CH_3), 123.3, 125.0, 126.9 (C-4,5,7), 128.9, 129.0 (C-2',3',5',6'), 130.5 (C-2 or C_α), 132.6 (C-3a), 134.8 (C-6), 134.9 (C-4'), 142.1 (C-1'), 145.7 (C-2 or C_α), 149.6 (C-7a), 188.8 (C-3).

Anal. Calcd. for $C_{16}H_{11}ClOS$: C, 67.02; H, 3.87. Found: C, 67.08; H, 3.84.

2-[1-(4-Bromophenyl)ethylidene]benzo[*b*]thiophen-3(2*H*)-one (**6e**).

This compound was isolated as yellow crystals in 20% yield, mp 104-105°; ^{1}H nmr: δ 2.80 (s, 3H, CH_3), 7.26 (ddd, 1H, 5-H), 7.33 (m, 3H, 7,2',6'-H), 7.52 (ddd, 1H, 6-H), 7.59 (d, J = 7.7 Hz, 2H, 3',5'-H), 7.89 (d, J = 7.6 Hz, 1H, 4-H); ^{13}C nmr: δ 21.4 (CH_3), 123.2 (C-4'), 123.4 125.0, 126.9 (C-4,5,7), 129.2 (C-3',5'), 130.5 (C-2 or C_α), 132.0 (C-2',6'), 132.6 (C-3a), 134.8 (C-6), 142.5 (C-1'), 145.7 (C-2 or C_α), 149.6 (C-7a), 188.8 (C-3).

Anal. Calcd. for $C_{16}H_{11}BrOS$: C, 58.02; H, 3.35. Found: C, 58.08; H, 3.37.

2-[1-(3,4-Dichlorophenyl)ethylidene]benzo[*b*]thiophen-3(2*H*)-one (**6f**).

This compound was obtained as yellow crystals in 16% yield, mp 143-144°; ^{1}H nmr: δ 2.77 (s, 3H, CH_3), 7.22-7.37 (m, 3H, 6,2',5'-H), 7.49-7.57 (m, 3H, 5,7,6'-H), 7.88 (d, J = 8.1 Hz, 1H, 4-H); ^{13}C nmr: δ 21.2 (CH_3), 123.4, 125.1, 126.8, 126.9 (C-4,5,7,6'), 129.5, 130.8 (C-2',5'), 130.8 (C-2 or C_α), 132.4 (C-3a), 133.1 (C-3',4'), 134.9 (C-6), 143.4 (C-1'), 145.4 (C-2 or C_α), 147.6 (C-7a), 188.7 (C-3).

Anal. Calcd. for $C_{16}H_{10}Cl_2OS$: C, 59.83; H, 3.14. Found: C, 59.78; H, 3.16.

2'-Phenylspiro[benzo[*b*]thiophen-2(3*H*),1'-cyclopropan]-3-one (**7a**).

This compound was obtained as white crystals in 31% yield, mp 94-95°; ^{1}H nmr: δ 2.12 (dd, J = 8.0 and 5.3 Hz, 1H, 3'-H_{trans}), 2.25 dd, J = 9.5 and 8.3 Hz, 1H, 3'-H_{cis}), 3.18 (dd, J = 9.5 and 8.0 Hz, 1H, 2'-H), 7.15-7.38 (m, 7H, 5,7-H + Ph), 7.50 (ddd, 1H, 6-H), 7.82 (dd, J = 7.8 and 1.1 Hz, 1H, 4-H); ^{13}C nmr: δ 22.4 (C-3'), 35.8 (C-2'), 46.4 (C-1'), 124.2, 124.8, 126.2 (C-4,5,7), 127.7 (C-4"), 128.1, 128.6 (C-2",6",3",5"), 130.5 (C-3a), 134.7 (C-6), 136.6 (C-1"), 152.4 (C-7a), 199.0 (C-3).

Anal. Calcd. for $C_{16}H_{12}OS$: C, 76.17; H, 4.79. Found: C, 76.11; H, 4.76.

2'-(4-Fluorophenyl)spiro[benzo[*b*]thiophen-2(3*H*),1'-cyclopropan]-3-one (**7c**).

This compound was isolated as colourless plates in 32% yield, mp 116-117°; ^{1}H nmr: δ 2.05 (dd, J = 8.0 and 5.4 Hz, 1H, 3'-H_{trans}), 2.25 (dd, J = 9.5 and 5.4 Hz, 1H, 3'-H_{cis}), 3.14 (dd, J = 9.5 and 8.0 Hz, 1H, 2'-H), 6.98-7.29 (m, 5H, 5,2",3",5",6"-H), 7.38 (dd, J = 7.4 and 0.9 Hz, 1H, 7-H), 7.52 (ddd, 1H, 6-H), 7.83 (d, J = 8.2 Hz, 1H, 4-H); ^{13}C nmr: δ 22.5 (C-3'), 34.9 (C-2'), 46.1 (C-1'), 115.5 (d, $^2J_{C\text{-}F}$ = 21.8 Hz, C-3",5"), 124.2, 124.9, 126.3 (C-4,5,7), 129.9 (d, $^3J_{C\text{-}F}$ = 8.1 Hz, C-2",6"), 130.4 (C-3a), 132.4 (C-1"), 134.8 (C-6), 152.2 (C-7a), 162.4 (d, $^1J_{C\text{-}F}$ = 246.2 Hz, C-4"), 198.9 (C-3).

Anal. Calcd. for $C_{16}H_{11}FOS$: C, 71.10; H, 4.10. Found: C, 71.14; H, 4.07.

2'-(4-Chlorophenyl)spiro[benzo[*b*]thiophen-2(3*H*),1'-cyclopropan]-3-one (**7d**).

This compound was isolated as pale yellow crystals in 26% yield, mp 137-138°; ^{1}H nmr: δ 2.05 (dd, J = 8.1 and 5.5 Hz, 3'-H_{trans}), 2.25 (dd, J = 9.5 and 5.5 Hz, 1H, 3'-H_{cis}), 3.12 (dd, J = 9.5 and 8.1 Hz, 1H, 2'-H), 7.12 (d, J = 8.4 Hz, 2H, 2",6"-H), 7.26 (ddd, 1H, 5-H), 7.35 (d, J = 8.4 Hz, 2H, 3",5"-H), 7.40 (d, J = 7.2 Hz, 1H, 7-H), 7.53 (ddd, 1H, 6-H), 7.83 (d, J = 8.0 Hz, 1H, 4-H); ^{13}C nmr: δ 22.3 (C-3'), 34.9 (C-2'), 46.0 (C-1'), 124.2, 124.9, 126.3 (C-4,5,7), 128.8, 129.5 (C-2",3",5",6"), 130.4 (C-3a), 133.6 (C-4"), 134.8 (C-6), 135.2 (C-1"), 152.1 (C-7a), 198.8 (C-3).

Anal. Calcd. for $C_{16}H_{11}ClOS$: C, 67.02; H, 3.87. Found: C, 67.06; H, 3.84.

2'-(4-Bromophenyl)spiro[benzo[*b*]thiophen-2(3*H*),1'-cyclopropan]-3-one (**7e**).

This compound was prepared as colourless plates in 35% yield, mp 143-144°; ^{1}H nmr: δ 2.05 (dd, J = 8.0 and 5.4 Hz, 1H, 3'-H_{trans}), 2.25 (dd, J = 9.4 and 5.4 Hz, 1H, 3'-H_{cis}), 3.10 (dd, J = 9.4 and 8.0 Hz, 1H, 2'-H), 7.07 (d, J = 8.4 Hz, 2H, 2",6"-H), 7.25 (ddd, 1-H, 5-H), 7.38 (d, J = 8.3 Hz, 1H, 7-H), 7.47 (d, J = 8.4 Hz, 2H, 3",5"-H), 7.51 (ddd, 1H, 6-H), 7.83 (d, J = 7.8 Hz, 1H, 4-H); ^{13}C nmr: δ 22.2 (C-3'), 35.0 (C-2'), 45.9 (C-1'), 121.6 (C-4"), 124.2, 124.9, 126.3 (C-4,5,7), 129.8 (C-2",6"), 130.3 (C-3a), 131.7 (C-3",5"), 134.8 (C-6), 135.7 (C-1"), 152.1 (C-7a), 198.7 (C-3).

Anal. Calcd. for $C_{16}H_{11}BrOS$: C, 58.02; H, 3.35. Found: C, 58.08; H, 3.32.

2'-(3,4-Dichlorophenyl)spiro[benzo[*b*]thiophen-2(3*H*),1'-cyclopropan]-3-one (**7f**).

This copound was isolated as pale yellow plates in 32% yield, mp 131-132°; ^{1}H nmr: δ 2.02 (dd, J = 7.9 and 5.5 Hz, 1H, 3'-H_{trans}), 2.24 (dd, J = 9.4 and 5.5 Hz), 1H, 3'-H_{cis}), 3.08 (dd, J = 9.4 and 7.9 Hz, 1H, 2'-H), 7.02 (dd, J = 8.3 and 1.9 Hz, 6"-H), 7.25 (ddd, 1H, 5-H), 7.27 (d, J = 1.9 Hz, 1H, 2"-H), 7.37 (d, J = 8.0 Hz, 1H, 7-H), 7.38 (d, J = 8.3 Hz, 1H, 5"-H), 7.52 (ddd, 1H, 6-H), 7.88 (d, J = 7.7 Hz, 1H, 4-H); ^{13}C nmr: δ 22.1 (C-3'), 34.3 (C-2'), 45.7 (C-1'), 124.2, 125.0, 126.4 (C-4,5,7), 127.5 (C-6"), 130.2, 130.5 (C-2",5"), 131.8, 132.8 (C-3a, 3",4"), 135.0 (C-6), 136.9 (C-1"), 151.9 (C-7a), 198.5 (C-3).

Anal. Calcd. for $C_{16}H_{10}Cl_2OS$: C, 59.83; H, 3.14. Found: C, 59.78; H, 3.16.

Reaction of *Z*-2-Arylidene-2,3-dihydro-1*H*-indol-3-ones **8a,b** with Diazomethane

A mixture of *Z*-2-arylidene-2,3-dihydro-1*H*-indol-3-one (**8a,b**; 2.5 mmoles), diazomethane (7.5 mmoles), anhydrous methylene chloride (50.0 ml) and diethyl ether (30.0 ml) was allowed to stand in refrigerator for 48 hours. The solvent was evaporated under reduced pressure and the residue was crystallized from methanol to yield **9a,b** (Scheme 4).

2'-Phenylspiro[1*H*-indol-2(3*H*),1'-cyclopropan]-3-one (**9a**).

This compound was isolated as white crystals in 78% yield, mp 142-143°; ^{1}H nmr: δ 1.89 (dd, J = 8.1 and 5.5 Hz, 1H, 3'-H_{trans}), 1.98 (dd, J = 9.5 and 5.5 Hz, 1H, 3'-H_{cis}), 2.98 (dd, J = 9.5 and 8.1 Hz, 1H, 2'-H), 4.35 (brs, 1H, NH), 6.80 (d, J = 8.3 Hz, 1H, 7-H), 6.85 (ddd, 1H, 5-H), 7.12-7.30 (m, 5H, Ph), 7.33 (ddd, 1H, 6-H), 7.62 (d, J = 7.8 Hz, 1H, 4-H); ^{13}C nmr: δ 19.8 (C-3'), 33.6 (C-2'), 54.2 (C-1'), 113.5 (C-7), 119.8 (C-5), 122.1 (C-3a), 123.9 (C-4), 127.6 (C-4"), 128.4, 129.0 (C-2",3",5",6"), 135.6 (C-1"), 135.7 (C-6), 160.0 (C-7a), 198.8 (C-3).

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.72; H, 5.54; N, 5.99.

2'-(4-Methoxyphenyl)spiro[1*H*-indol-2(3*H*),1'-cyclopropan]-3-one (**9b**).

This compound was obtained as white crystals in 76% yield, mp 158-159°; ^{1}H nmr: δ 1.87 (dd, J = 8.1 and 5.5 Hz, 1H, 3'-H_{trans}), 1.96 (dd, J = 9.5 and 5.5 Hz, 1H, 3'-H_{cis}), 2.28 (s, 3H, 4"-CH_3), 2.94 (dd, J = 9.5 and 8.1 Hz, 1H, 2'-H), 4.35 (brs, 1H, NH), 6.80 (d, J = 8.1 Hz, 1H, 7-H), 6.84 (ddd, 1H, 5-H), 7.02, 7.10 (A_2B_2, J = 8.2 Hz, 4H, 2",3",5",6"-H), 7.34 (ddd, 1H, 6-H), 7.61 (d, J = 7.8 Hz, 1H, 4-H); ^{13}C nmr: δ 19.8 (C-3'), 33.4 (C-2'), 54.2 (C-1'), 113.5 (C-7), 119.7 (C-5), 122.1 (C-3a), 123.9 (C-4), 128.3, 129.7 (C-2",3",5",6"), 132.4 (C-1"), 135.6 (C-6), 137.4 (C-4"), 160.0 (C-7a), 198.9 (C-3).

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.61. Found: C, 81.86; H, 6.09; N, 5.63.

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