Synthesis and structural elucidation of novel spiropyrazolines precursors to spiro-*gem*-dimethylcyclopropanes

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1,3-dipolar cycloaddition reaction of 2-diazopropane (DAP) **1** with 2-arylidene-1-tetralone **2a–b** led exclusively to spiro-Δ^1-pyrazolines **3a–b**. When 4-methyl-2-arylidene-1-tetralones **2c–d** was used as starting dipolarophile a mixture of diastereiosomeric cycloadducts **4a–b** and **5a–b** was obtained. The photochemical nitrogen-extrusion studied for spiropyrazolines **3a–b** and **4a–b** led stereospecifically to spiro-gem-dimethylcyclopropanes. In all cases, the reaction regiochemistry and stereochemistry was discussed on the basis of 2D-NMR experiments.

Keywords: 1,3-dipolar cycloaddition, 2-diazopropane, spiropyrazoline, spiro-*gem*-dimethylcyclopropane, 2D-NMR techniques

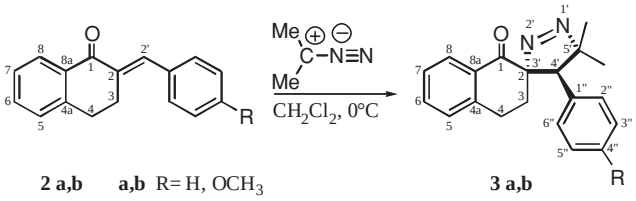
1,3-dipolar cycloaddition of α-β-unsaturated ketones with diazoalkanes represent one of the most useful methods for the synthesis of Δ^1-pyrazoline,[1-3] which have been shown to possess a wide range of biological activities.[4,5] Particularly, spiropyrazolines prepared from 1,3-dipoles and exocyclic α,β-enones drew the interest of several researchers.[6-8]

As a continuation of our studies directed towards the synthesis of new pyrazolinic systems from 2-diazopropane and enones,[9-11] we report here the results we have obtained on reacting 2-diazopropane (DAP) **1** with 2-arylidene-1-tetralone **2a,b** and 2-arylidene-4-methyl-1-tetralones **2c,d**. Photochemical transformations of the obtained cycloadducts gave the corresponding *gem*-dimethylcyclopropanes.

Results and discussion

The 2-arylidene-1-tetralones **2a,b** were allowed to react with excess DAP at 0 °C in dichloromethane, the reaction monitored by thin layer chromatography (CH_2Cl_2/MeOH; 9:1) showed the formation of a single cycloadduct which was assigned, on the basis of its spectroscopic data, as spiro-pyrazolines **3a,b** (Scheme 1). It is worth mentioning here that, contrary to our results previously published concerning the simultaneous addition of two molecules of diazopropane on both C=C and C=O functionalities,[9,10] the regiochemistry was here not affected if temperature was lowered to –78 °C.

According to previous reports, it was expected that dipolarophiles **2a,b** could behave as Michael acceptor towards 2-diazopropane to give the *"normal"* regioisomeric cycloadduct.[12] On the other hand, since the two faces of the enone ring are sterically equivalent, both possible attacks of DAP led to a racemic mixture of enantiomeric pairs for which complete structural assignments were established by mean of usual spectroscopic techniques: IR, mass and ^1H, ^{13}C NMR spectroscopy. Additional support for the assignments was provided by the two-dimensional hetero-nuclear ^1H–^{13}C : HMQC and HMBC spectra. Thus, inspection of the HMBC spectra for compounds **3a,b** showed in both cases that the methyl protons Me_a and Me_b present a unique correlation with tertiary C-4' and quaternary C-5'. Moreover the aromatic protons H-2" and H-6" correlate simultaneously with C-5' which is thereby directly bonded to the aryl group. This consequent [aryl-(C-4')–(C-5')–(Me_a, Me_b)] linkage proofs the proposed regiochemistry of the cycloaddition. On the other hand assignment of methyls Me_a and Me_b was deduced from the NOESY maps. Thus, the nOe cross-peak between both protons H-2" and H-6" with methyl Me_b placed these three units on the same side of the average pyrazole-ring plane. H_4' and Me_a are then on the other side (Fig. 1). We should



Scheme 1

notice that although the compounds investigated exist as racemates, owing to a better understanding of the stereo-chemistry, only enantiomers possessing the (*R*) configuration at C-2:3' are illustrated on Fig. 1.

In order to study the diastereoselectivity of the reaction when the faces of enone **2** are diastereotopic, we reinvestigated the same reaction using as starting dipolarophile the 4-methyl-2-arylidene-1-tetralones **2c,d**. In this case, the creation of two new centres of chirality may, logically, give rise to the formation of a diastereoisomeric mixture of pyrazolines. Indeed, when reacted with 2-diazopropane, enones **2c,d** led to a mixture of two products which were unambiguously assigned as diastereiosomeric spiro-pyrazolines **4a,b** and **5a,b** resulting from different approaches of the diazoalkane on both faces of the dipolarophile **2c,d** (Scheme 2). The proposed stereochemistry is in agreement with the fact that 2-diazopropane preferentially attacks on the less hindered face leading to the major cycloadduct **4a,b**.

To avoid the accidental equivalence involving overlapped signals of methyl groups in the tetralone ring and those of the pyrazoline, the samples were dissolved in $CDCl_3$ mixed with few drops of C_6D_6. Pyrazolines **4a,b** and **5a,b** in the HMBC spectra exhibited a whole set of linkages confirming the same skeleton for both stereoisomers. Having established the two dimensional structure of compounds **4a,b** and **5a,b**, we have investigate, and discussed their stereochemistry on the basis

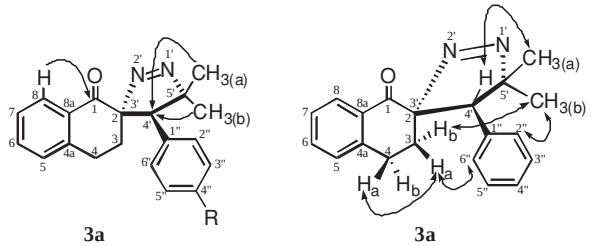


Fig. 1

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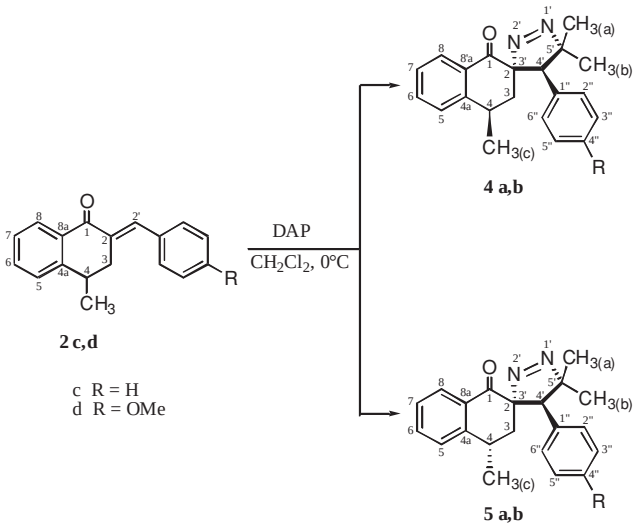


Scheme 2

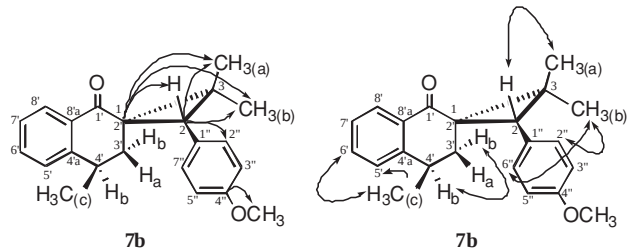
of the NOESY experiments. Thus, the spectrum of products **4a,b** showed a nOe cross-peak between

H-3b and $Me_{(b)}$, H-4 and ($Me_{(c)}$, H-3a). This placed $Me_{(c)}$ and the aryl group on the same side of average tetralone ring plane according to the most favoured approach of the diazoalkane.

Photolysis of spiropyrazolines **3a,b** *and* **4a,b**

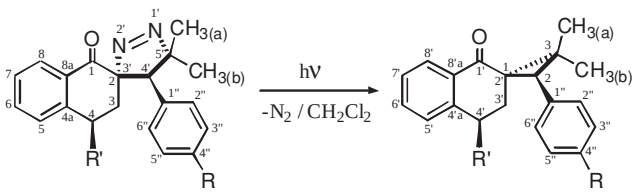
The *gem*-dimethylcyclopropane unit is a key structural feature of many valuable natural products.[13,14] Thus, irradiation of pyrazolines **3a,b** and **4a,b** in dry dichloromethane at room temperature, led exclusively to the formation of the expected spiro-*gem*-dimethylcyclopropanes **6a,b** and **7a,b** (Scheme 3) which mass spectra confirmed the nitrogen extrusion.

Similarly, total assignments of cyclopropanes **6** and **7** have been established by means of 1D and 2D-NMR techniques. So, since the relative stereochemistry of cyclopropanes **7a,b** could be deduced from that of the precursor pyrazolines **4a,b**,[15] nevertheless, additional proofs were recovered by NOESY experiments (Fig. 2).



HMBC correlations NOESY correlations

Fig. 2



Scheme 3

Conclusions

The results obtained in this study show that spiro-Δ^1-pyrazolines can be prepared through 1,3-dipolar cycloaddition of 2-diazopropane to exocyclic α,β–unsaturated ketones. The obtained pyrazolines were transformed by photolysis, into the corresponding *gem*-dimethylecyclopropanes. The relative configuration and stereochemistry of the products have been determined by NMR 1D and 2D spectroscopy.

Experimental

Melting points were taken on a Büchi-500 capillary apparatus. IR spectra (potassium bromide) were run on a BIORAD FTS-6000 IR spectrometer. ^1H and ^{13}C NMR spectra were recorded with AC-300 Bruker spectrometer; 2D experiments were performed at 400 MHz with AMX-400 Bruker machine and using $CDCl_3$ with TMS as an internal standard. The mass spectra were measured using an Nier-Johnson Kratos MS-80 Rf mass spectrometer with L.SIMS (Liquid Secondary Ion Mass Spectrometry) technique (positive mode), Cs^+ as a bombardment ions in a thioglycerol matrix.

Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} plates (Merck) with UV (254 nm) visualisation whereas chromatographic separations were conducted on silica gel Si-60-7734 Merck using water-jacketed coluns. Elemental analyses were performed at the Institut de Chimie des Substances Naturelles. CNRS, 91190 Gif-sur-Yvette, France.

Enones **2a,b** and **2c,d** were obtained respectively by basic aldolic condensation of corresponding aldehydes with 1-tetralone and 4-methyl-1-tetralone.[16,17] 2-Diazopropane **1** was prepared according to the Staudinger[4] method and conserved in etheral solutions at –78°C.

Photolysis of pyrazolines **4** and **5** were realised in dry dichloromethane, and irradiated at 300 nm in a Rayonet apparatus for 30 min.

Cycloaddition of 2-diazopropane with enones **2a,b** *at 0°C*
Preparation of spiro-Δ^1-pyrazolines **3a,b**

To a stirred solution containing 2 g (8.45–7.57 mmol) of enone **2a,b** in 100 ml of anhydrous dichloromethane at 0°C was added in small fractions a 2.8 M ethereal solution of 2-diazopropane prepared at –78°C. The progress of the reaction was monitored by a TLC control (90-10 hexane-ethyl acetate elution) and the reaction was discontinued when enone **2a,'b** had totally reacted. The solvent was evaporated under reduced pressure. The resulting crude oil was purified on a silica gel column using hexane-ethyle acetate as eluent (80: 20), products **3a,b** were obtained in 84–78 % average yield.

Rel-(3R,4'R)-5',5'-dimethyl-4'-phenyl-3,4,4',5'-tetrahydro-1*H*,3*H-spiro(naphthalene-2,3'-pyrazol)-1-one* (**3a**): Compound **3a** formed colourless crystals; m.p. 110°C; yield 72%. ^1H NMR (400 MHz): δ (ppm) = 1.38 (s, 3H, $CH_{3(a)}$), 1.56 (s, 3H, $CH_{3(b)}$), 2.20 (m, 1H, H-3a), 2.55 (m, 1H, H-3b), 2.80 (m, 1H, H-4a), 3.50 (m, 1H, H-4b), 3.80 (m, 1H, H-4'), 7.15 (m, 2H, H-2",6"), 7.25 (m, 1H, H-5), 7.28 (m, 1H, H-4"), 7.30 (m, 2H, H-3",5"), 7.31 (m, 1H, H-7), 7.50 (m, 1H, H-6), 8.06 (m, 1H, H-8). ^{13}C NMR (75 MHz): δ (ppm) = 24.3 ($CH_{3(a)}$), 26.0 (C-4), 27.9 ($CH_{3\ (b)}$), 31.9 (C-3), 51.2 (C-4'), 93.0 (C-5'), 100.7 (C-2:3'), 127.1 (C-7), 127.1 (C-5), 128.0 (C-3",5"), 128.6 (C-8), 128.6 (C-4"), 131.1 (C-2",6"), 131.7 (C-8a), 135.7 (C-1"), 143.8 (C-4a), 192.0 (C-1). IR(KBr), ν_{cm-1}: 1550 (N=N), 1600 (C=C_{arom}), 1682 (C=O), 2962 (C-H). MS (L.SIMS$^+$): *m/z* (int. Rel.%): 305 (MH^+, 47), 277 (MH^+-N_2, 75). Analysis: calculated for $C_{20}H_{20}N_2O$: C 78.92; H 6.62; N 9.20. Found: C 78.74; H 6.81; N 9.07.

Rel-(3R,4'R)-4'-(4-methoxyphenyl)-5',5'-dimethyl-3,4,4',5'-tetrahydro-1*H*,3*H-spiro(naphthalene-2,3'-pyrazol)-1-one* (**3b**): Compound **3b** formed colourless crystals; m.p. 105°C; yield 69%. ^1H NMR (300 MHz): δ (ppm) = 1.40 (s, 3H, $CH_{3(a)}$), 1.60 (s, 3H, $CH_{3(b)}$), 2.20 (m, 1H, H-3a), 2.60 (m, 1H, H-3b), 2.84 (m, 1H, H-4a), 3.52 (m, 1H, H-4b), 3.80 (m, 1H, H-4'), 3.80 (s, 3H, OCH_3), 6.88 (m, 2H, H-3",5"), 7.10 (m, 2H, H-2",6"), 7.28 (m, 1H, H-5), 7.56 (m, 1H, H-6), 7.40 (m, 1H, H-7), 8.10 (m, 1H, H-8). ^{13}C NMR (75 MHz): δ (ppm) = 24.4 ($CH_{3(a)}$), 26.1 (C-4), 28.0 ($CH_{3(b)}$), 31.9 (C-3), 50.7 (C-4'), 55.4 (OCH_3), 93.0 (C-5'), 100.6 (C-2:3'), 113.6 (C-3",5"), 126.9 (C-7), 127.5 (C-1"), 128.7 (C-5), 128.8 (C-8), 131.9 (C-8a), 132.2 (C-2",6"), 134.1 (C-6), 144.0 (C-4a), 158.6 (C-4"), 192.3 (C-1). IR(KBr), ν_{cm-1}: 1600 (N=N), 1530 (C=C_{arom}), 1674 (C=O), 2962 (C-H). MS (L.SIMS$^+$): *m/z* (int. Rel.%): 335 (MH^+, 50), 307 (MH^+-N_2, 80). Analysis: calculated for $C_{21}H_{22}N_2O_2$: C 75.42; H 6.63; N 8.38. Found: C 75.41; H 6.55; N 8.31.

Cycloaddition of 2-diazopropane with enones **2c,d** *at 0°C. Preparation of spiro-*Δ^1*-pyrazolines* (**4,5**)

To a stirred solution containing 2 g (8.06–7.19 mmol) of enone **2c,d** in 100 ml of anhydrous dichloromethane at 0°C was added in small fractions a 2.8 M etheral solution of 2-diazopropane prepared at –78°C. The TLC controls (90-10 hexane-ethyl acetate elution) indicated the apparition of two new products **4** and **5** and the reaction was stopped when enones **2c,d** had totally reacted. The solvent was evaporated under reduced pressure. The resulting crude oil was purified on 150 g of silica gel eluting with hexane progressively enriched, until 10%, with ethyl acetate. Two products were obtained **4a,b** (1.77–1.61 g) and **5a,b** (390–430 mg), yield = 82 and 18%.

Rel-(2R,4R,4'R)-4-methyl-5',5'-dimethyl-4'-phenyl-3,4,4',5'-tetrahydro-1H,3H-spiro(naphthalene-2,3'-pyrazol)-1-one **(4a):** Compound **4a** formed colourless crystals; m.p. 110°C; yield 82%. ^{1}H NMR (400 MHz): δ (ppm) = 1.40 (d, *J* = 6.8 Hz, 3H, $CH_{3(c)}$), 1.42 (s, 3H, $CH_{3(a)}$), 1.60 (s, 3H, $CH_{3(b)}$), 1.82 (m, 1H, H-3a), 2.32 (m, 1H, H-3b), 3.88 (m, 1H, H-4), 4.03 (m, 1H, H-4'), 7.20–7.32 (4H, 2",3",4",5",6"), 7.33 (m, 1H, H-7), 7.46 (m, 1H, H-5), 7.57 (m, 1H, H-6), 8.07 (d, *J* = 8.5 Hz, 1H, H-8). ^{13}C NMR (75 MHz): δ (ppm) = 20.8 ($CH_{3(c)}$), 24.5 ($CH_{3(a)}$), 28.1 ($CH_{3(b)}$), 29.8 (C-4), 41.8 (C-3), 50.7 (C-4'), 93.0 (C-5'), 102.1 (C-2:3'), 126.7 (C-4"), 126.8 (C-7), 127.3 (C-5), 128.3 (C-3",5"), 128.8 (C-8), 131.7 (C-2",6"), 134.4 (C-6), 135.7 (C-1"), 148.3 (C-4a), 191.8 (C-1). IR (KBr), ν_{cm-1}: 1600 (N=N), 1530 (C=C_{arom}), 1680 (C=O), 3000 (C-H). MS (L.SIMS$^+$): *m/z* (int. Rel.%): 319 (MH^+, 35), 291 (MH^+-N_2, 75). Analysis: calculated for $C_{21}H_{22}N_2O$: C 79.21; H 6.96; N 8.80. Found: C 78.67; H 7.04; N 9.03.

Rel-(2R,4R,4'R)-4-methyl-5',5'-dimethyl-4'-(4-methoxyphenyl)-5',5'-dimethyl-3,4,4',5'-tetrahydro-1H,3H-spiro(naphthalene-2,3'-pyrazol)-1-one **(4b):** Compound **4b** formed colourless crystals; m.p. 93°C; yield 82%. ^{1}H NMR (400 MHz): δ (ppm) = 1.39 (d, *J* = 6.5 Hz, 3H, $CH_{3(c)}$), 1.40 (s, 3H, $CH_{3(a)}$), 1.56 (s, 3H, $CH_{3(b)}$), 1.79 (m, 1H, H-3a), 2.26 (m, 1H, H-3b), 3.76 (s, 3H, OCH_3), 3.85 (m, 1H, H-4), 3.95 (m, 1H, H-4'), 6.82 (m, , 2H, H-3",5"), 7.11 (m, 2H, H-2",6"), 7.31 (m, 1H, H-7), 7.44 (m, 1H, H-5), 7.56 (m, 1H, H-6), 8.04 (d, *J* = 7.8 Hz, 1H, H-8). ^{13}C NMR (75 MHz): δ (ppm) = 20.6 ($CH_{3(c)}$), 24.3 ($CH_{3(a)}$), 27.8 ($CH_{3(b)}$), 29.6 (C-4), 41.6 (C-3), 49.7 (C-4'), 55.1 (OCH_3), 92.5 (C-5'), 101.7 (C-2:3'), 113.6 (C-3",5"), 126.5 (C-5), 126.6 (C-7), 127.5 (C-1"), 128.6 (C-8), 131.7 (C-8a), 132.4 (C-2",6"), 134.2 (C-6), 148.0 (C-4a), 158.7 (C-4"), 191.8 (C-1). IR (KBr), ν_{cm-1}: 1600 (N=N), 1530 (C=C_{arom}), 1720 (C=O), 3000 (C-H). MS (L.SIMS$^+$): *m/z* (int. Rel.%): 349 (MH^+, 25), 321 (MH^+-N_2, 100). Analysis: calculated for $C_{22}H_{24}N_2O_2$: C 75.83; H 6.94; N 8.04. Found: C 74.98; H 6.98; N 7.89.

Rel-(2R,4S,4'R)-4-methyl-5',5'-dimethyl-4'-phenyl-3,4,4',5'-tetrahydro-1H,3H-spiro(naphthalene-2,3'-pyrazol)-1-one **(5a):** Compound **5a** formed colourless crystals; m.p. 98°C; yield 18%. ^{1}H NMR (400 MHz): δ (ppm) = 1.23 (d, *J* = 6.8 Hz, 3H, $CH_{3(c)}$), 1.30 (s, 3H, $CH_{3(a)}$), 1.46 (s, 3H, $CH_{3(b)}$), 2.35–2.52 (m, 2H, H-3a, H-4), 2.65–2.71 (m, 1H, H-3b), 3.20 (m, 1H, H-4'), 6.96 (m, 2H, H-2",6"), 7.22–7.31 (m, 4H, H-5,3",4",5"), 7.33 (m, 1H, H-7), 7.52 (m, 1H, H-6), 8.02 (d, *J* = 7.8 Hz, 1H, H-8). ^{13}C NMR (75 MHz): δ (ppm) = 21.9 ($CH_{3(c)}$), 24.4 ($CH_{3(a)}$), 27.9 ($CH_{3(b)}$), 28.9 (C-4), 37.6 (C-3), 54.0 (C-4'), 93.3 (C-5'), 99.7 (C-2:3'), 126.7 (C-4"), 127.1 (C-7), 127.3 (C-5), 128.0 (C-3",5"), 128.3 (C-8), 130.4 (C-2",6"), 130.6 (C-8a), 134.1 (C-6), 136.2 (C-1"), 147.6 (C-4a), 194.4 (C-1). IR (KBr), ν_{cm-1}: 1600 (N=N), 1530 (C=C_{arom}), 1682 (C=O), 3000 (C-H). MS (L.SIMS$^+$): *m/z* (int. Rel.%): 319 (MH^+, 35), 291 (MH^+-N_2, 75).

Rel-(2R,4S,4'R)-4-methyl-5',5'-dimethyl-4'-(4-methoxyphenyl)-5',5'-dimethyl-3,4,4',5'-tetrahydro-1H,3H-spiro(naphthalene-2,3'-pyrazol)-1-one **(5b):** Compound **5b** formed colourless crystals; m.p. 97°C; yield 18%. ^{1}H NMR (400 MHz): δ (ppm) = 1.25 (d, *J* = 6.5 Hz, 3H, $CH_{3(c)}$), 1.30 (s, 3H, $CH_{3(a)}$), 1.45 (s, 3H, $CH_{3(b)}$), 2.43–2.53 (m, 2H, H-3a,4), 2.65 (m, 1H, H-3b), 3.16 (m, 1H, H-4'), 3.78 (s, 3H, OCH_3), 6.78 (m, , 2H, H-3",5"), 6.87 (m, 2H, H-2",6"), 7.23 (m, 1H, H-5), 7.32 (m, 1H, H-7), 7.52 (m, 1H, H-6), 8.02 (d, *J* = 8.8 Hz, 1H, H-8). ^{13}C NMR (100 MHz): δ (ppm) = 22.3 ($CH_{3(c)}$), 24.6 ($CH_{3(a)}$), 28.2 ($CH_{3(b)}$), 29.1 (C-4), 37.9 (C-3), 53.7 (C-4'), 55.4 (OCH_3), 93.5 (C-5'), 99.8 (C-2:3'), 113.7 (C-3",5"), 126.9 (C-7), 127.3 (C-5), 128.4 (C-1"), 128.6 (C-8), 130.9 (C-8a), 131.3 (C-6), 131.6 (C-2",6"), 148.0 (C-4a), 159.0 (C-4"), 194.8 (C-1). IR (KBr), ν_{cm-1}: 1608 (N=N), 1530 (C=C_{arom}), 1677 (C=O), 3000 (C-H). MS (L.SIMS$^+$): *m/z* (int. Rel.%): 349 (MH^+, 25), 321 (MH^+-N_2, 100). Analysis: calculated for $C_{22}H_{24}N_2O_2$: C 75.83; H 6.94; N 8.04. Found: C 75.81; H 6.68; N 7.64.

Synthesis of cyclopropanes **6** *and* **7**

A solution of the **3** or **4** (250 mg) in dry dichloromethane (150 ml) was irradiated at 300 nm for 20–30 min. After the reaction was completed, the solvent was removed *in vacuo*. In most cases products **6** and **7** remained as colourless oils in analytically pure form. In other cases further purification by column chromatography was necessary (hexane/ethylacetate: 7/3)

Rel-(1R,2S)-2-phenyl-3,3-dimethyl-3',4'-dihydro-1'H-spiro(cyclopropane-1,2'-naphthalen)-1'-one **(6a):** Compound **6a** formed colourless oil; yield 54%. ^{1}H NMR (400 MHz): δ (ppm) = 1.28 (s, 3H, $CH_{3(b)}$), 1.35 (s, 3H, $CH_{3(a)}$), 1.70 (m, 1H, H-3'a), 2.38 (m, 1H, H-3'b), 2.88 (m, 1H, H-4'a), 3.03 (m, 1H, H-4'b), 3.26 (s, 1H, H-2), 7.18 (m, 2H, H-2",6"), 7.25 (m, 1H, H-5'), 7.32 (m, 2H, H-3",5"), 7.24 (m, 1H, H-4"), 7.33 (m, 1H, H-7'), 7.47 (m, 1H, H-6'), 8.16 (d, *J* = 7.8, 1H, H-8'). ^{13}C NMR (100 MHz): δ (ppm) = 19.0 ($CH_{3(b)}$), 22.0 ($CH_{3(a)}$), 26.6 (C-3'), 28.9 (C-4'), 32.6 (C-3), 36.5 (C-2), 40.6 (C-1:2), 126.4 (C-4"), 126.6 (C-7'), 127.5 (C-8'), 128.3 (C-3",5"), 128.7 (C-5'), 130.7 (C-2",6"), 133.0 (C-6'), 133.4 (C-8'a), 136.7 (C-1"), 144.0 (C-4'a), 196.8 (C-1'). MS (IE); *m/z* = (int.rel. %): 276 M^+ (100), 291 (40), 161 (80).

Rel-(1R,2S)-2-(4-methoxyphenyl)-3,3-dimethyl-3',4'-dihydro-1'H-spiro(cyclopropane-1,2'-naphthalen)-1'-one **(6b):** Compound **6b** formed colourless oil; yield 43%. ^{1}H NMR (400 MHz): δ (ppm) = 1.24 (s, 3H, $CH_{3(b)}$), 1.30 (s, 3H, $CH_{3(a)}$), 1.70 (m, 1H, H-3'a), 2.28 (m, 1H, H-4'b), 2.34 (m, 1H, H-3'b), 3.10 (m, 1H, H-4'a), 3.23 (s, 1H, H-2), 3.86 (OCH_3), 6.85 (m, 2H, H-3",5"), 7.09 (m, 2H, H-2",6"), 7.18–7.37 (m, 2H, H-5',7'), 7.45 (m, 1H, H-6'), 8.10 (d, *J* = 8.6, 1H, H-8'). ^{13}C NMR (75 MHz): δ (ppm) = 18.8 ($CH_{3(b)}$), 21.9 ($CH_{3(a)}$), 26.4 (C-3'), 28.8 (C-4'), 32.6 (C-3), 35.8 (C-2), 40.3 (C-1:2'), 55.2 (OCH_3), 113.7 (C-3"-5"), 126.5 (C-7'), 127.5 (C-8'), 128.5 (C-5'), 131.5 (C-2"-6"), 132.9 (C-6'), 133.0 (C-8'a), 143.9 (C-4'a), 157,8 (C-4"), 196.6 (C-1'). MS (IE); *m/z* = (int.rel. %): 306 M^+ (100), 291 (40), 161 (80).

Rel-(1R,2S,4'R)-2-phenyl-3,3,4'-trimethyl-3',4'-dihydro-1'H-spiro(cyclopropane-1,2'-naphthalene)-1'-one **(7a):** Compound **7a** formed colourless oil; yield 65%. ^{1}H NMR (400 MHz): δ (ppm) = 1.25 (s, 3H, $CH_{3(b)}$), 1.35 (d, *J* = 6.8 Hz, 3H, $CH_{3(c)}$), 1.36 (s, 3H, $CH_{3(a)}$), 1.58 (m, 1H, H-3'b), 2.15 (m, 1H, H-3'a), 3.08 (m, 1H, H-4'), 3.30 (s, 1H, H-2), 7.09–7.39 (m, 7H, H-arom), 7.48 (m, 1H, H-6'), 8.18 (d, *J* = 7.8, 1H, H-8'). ^{13}C NMR (75 MHz): δ (ppm) = 18.9 ($CH_{3(b)}$), 20.0 ($CH_{3(c)}$), 21.8 ($CH_{3(a)}$), 32.1 (C-4'), 32.1 (C-3), 35.5 (C-3'), 36.1 (C-2), 40.7 (C-1:2'), 126.0 (C-5'), 126.2 (C-4"), 126.3 (C-7'), 127.4 (C-8'), 128.2 (C-3",5"), 130.6 (C-2",6"), 132.8 (C-8'a), 133.1 (C-6'), 136.5 (C-1"), 147.8 (C-4'a), 196.8 (C-1'). MS (IE); *m/z* = (int.rel. %): 290 M^+ (100), 275 (40).

Rel-(1R,2S,4'R)-2-(4-methoxyphenyl)-3,3,4'-trimethyl-3',4'-dihydro-1'H-spiro(cyclopropane-1,2'-naphthalene)-1'-one **(7b):** Compound **7b** formed colourless oil; yield 58%. ^{1}H NMR (400 MHz): δ (ppm) = 1.22 (s, 3H, $CH_{3(b)}$), 1.31 (s, 3H, $CH_{3(a)}$), 1.33 (d, *J* = 6.8 Hz, 3H, $CH_{3(c)}$), 1.58 (m, 1H, H-3'b), 2.11 (m, 1H, H-3'a), 3.07 (m, 1H, H-4'), 3.21 (s, 1H, H-2), 3.74 (s, 3H, OCH_3), 6.83 (m, 2H, H-3",5"), 7.05 (m, 2H, H-2"-6"), 7.30 (m, 1H, H-7'), 7.36 (m, 1H, H-5'), 7.48 (m, 1H, H-6'), 8.14 (d, *J* = 7.7, 1H, H-8'). ^{13}C NMR (100 MHz): δ (ppm) = 18.9 ($CH_{3(b)}$), 20.6 ($CH_{3(c)}$), 22.0 ($CH_{3(a)}$), 32.2 (C-4'), 32.7 (C-3), 35.5 (C-3'), 35.5 (C-2), 40.8 (C-1:2'), 55.2 (OCH_3), 113.7 (C-3",5"), 126.1 (C-5'), 126.4 (C-7'), 127.5 (C-8'), 128.5 (C-1"), 131.6 (C-2",6"), 133.0 (C-8'a), 133.2 (C-6'), 148.0 (C-4'a), 158,2 (C-4"), 197.0 (C-1'). MS (IE); *m/z* = (int.rel. %): 320 M^+ (80), 305 (40), 161 (78).

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