JOURNAL OF LABELLED COMPOUNDS AND RADIOPHARMACEUTICALS
J Labelled Cpd Radiopharm 2001; **44**: 529–539.
DOI: 10.1002/jlcr.484

Synthesis and deuterium labeling of some 4-phenyl, 3-substituted isochromanes

Anne-Laure Guyard, Alain Valleix, Bernard Rousseau and Jean-Christophe Cintrat*
CEA/Saclay, Service des Molécules Marquées, Bât. 547, Département de Biologie Cellulaire et Moléculaire, 91191 Gif sur Yvette Cedex, France

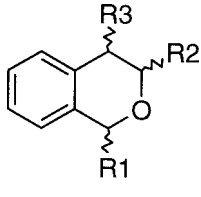
Summary

The preparation of a number of 4-phenyl isochromanes as well as the deuterated analogs is described using a simple strategy starting from easily obtained acetals. The diasteresoselectivity and the enantioselectivity of the adopted approach are both good. The deuterated analogs are prepared using tributyltin deuteride or triethyl deuterosilane. Copyright © 2001 John Wiley & Sons, Ltd.

Key Words: acetal; deuterium; isochromanes; tributyltin deuteride; triethyl deuterosilane

Introduction

Unlike their natural analogues the coumarins, isochromanes (Scheme 1) have received little attention. Nevertheless recently, isochromanes



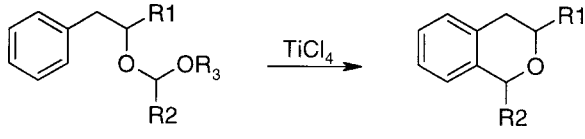
Scheme 1.

*Correspondence to: J.-C. Cintrat, CEA/Saclay, Service des Molécules Marquées, Bât. 547, Département de Biologie Cellulaire et Moléculaire, 91191 Gif sur Yvette Cedex, France. E-mail: jean-christophe.cintrat@cea.fr

Received 7 February 2001
Revised 5 April 2001
Accepted 11 April 2001
Published online ▮▮▮▮

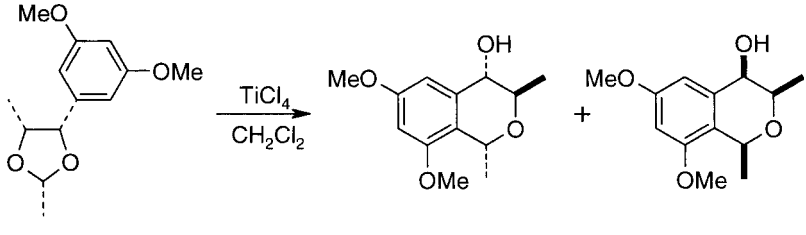
bearing functionalities have been used either as fragrances (musk)[1] or as herbicides.[2] This class of compound has also shown therapeutic activity as potential ligands for the D1 or D4 receptor of dopamine.[3]

The ease of accessing isochromanes is related to their complexity. In fact, the synthesis of the unsubstituted isochromane (3,4-dihydro-1H-2-benzopyrane) is easily achieved starting from 2-(2-hydroxymethylphenyl)ethanol.[4,5] In a related manner, Thibault *et al.* have gained monosubstituted isochromanes starting from α-chloro ethers.[6] Now the most commonly used approach arises from the work of Mohler and Thompson.[7] Their approach deals with the Lewis acid catalyzed cyclization of acyclic acetals derived from phenethylalcohols (Scheme 2). Using this route, enantio-enriched 1,3-substituted isochromanes can be obtained but the starting enantiopure alcohols are usually difficult to obtain.



Scheme 2.

To obtain the corresponding isochromanes labeled on the pyranyl ring following the previous sequences necessitates the introduction of a deuterium or tritium atom at a very early stage of the synthesis. We were intrigued as to whether we could apply the labeling approach designed by Giles[8] who started from cyclic acetals bearing nucleophilic arylrings (Scheme 3):

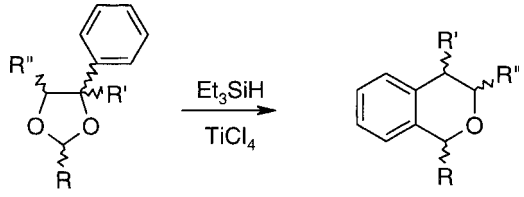


Scheme 3.

Initially, we report our results on the preparation of some isochromanes before reporting the extension of the method to deuterium labeling.

Results and discussion

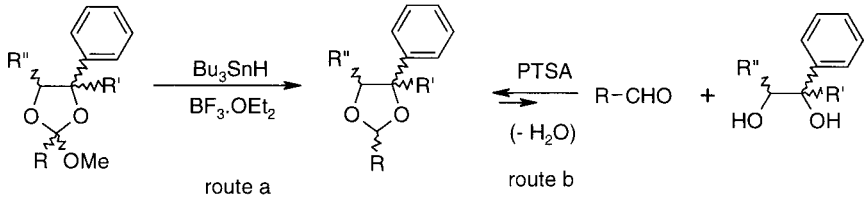
As in the Giles approach, our key step is the conversion of an acetal to the isochromane skeleton (Scheme 4):



2 **3**

Scheme 4.

All the starting acetals **2** have been prepared either from the corresponding cyclic orthoesters[9] **1** by substitution of the methoxy substituent using tributyltin hydride in the presence of boron trifluoride etherate (Scheme 5, route a) or *via* acetalization of an aldehyde (Scheme 5, route b).



1 **2**

Scheme 5.

The results are summarized in Table 1.

The acetals **2** were obtained in fairly good yields, ranging from 65 to 95%. Each was synthesized as a racemic mixture or in an enantiopure form (entries 1–2, 4, 8–9). We were able to obtain acetals bearing an alkyl substituent on C5 (entries 1, 7), a benzyl group (entry 6) or no substituents (entry 3). Most of these acetals bear a phenyl group at C5 (entries 2, 4–5, 8–9). Using either route a or b (Scheme 5), 2-substituted acetals have been synthesized (entries 8 and 9), but using route b gives a diastereomeric mixture of *trans* and *cis* acetals (entry 9).

With these acetals in hand the next step was to convert the dioxolane rings into isochromanes. This was achieved using a combination of

Table 1. Synthesis of acetals[a]

Entry	R	R′	R″	Acetal	Yield (%)	Isochromane	Yield
1	H	Ph	CH_3	**(5*S*)-2a**	95	(3*R*, 4*R*)- **3a**	30%[b]
2	H	Ph	Ph	(±)-and **(5*S*)-2b**	95	(±)-and **(3*R*, 4*S*)-3b**	30%[c]
3	H	H	H	(±)-**2c**	90	—	—
4	H	H	Ph	Meso and **(4*S*, 5*S*)-2d**	89	—	—
5	H	Ph	*p*-CF_3Ph	(±)-**2e**	80	(±)-**3e**	25%[c]
6	H	Ph	Benzyl	(±)-**2f**	65	—	—
7	H	Ph	Isopropyl	(±)-**2g**	95	(±)-**3g**	5%[c]
8	CH_3	Ph	Ph	**(2*R*, 5*S*)-2h**	91	—	—
9	Ph	Ph	Ph	**(5*S*)-2i**	93[a]	—	—

[a] This is the sole acetal synthesized via route b giving a mixture of *trans*/*cis* compounds (*trans*/*cis* = 85/15.
[b] *Trans*/*cis*: 80/20.
[c] *Trans*/*cis* > 95/5 > (based on ^{1}H NMR).

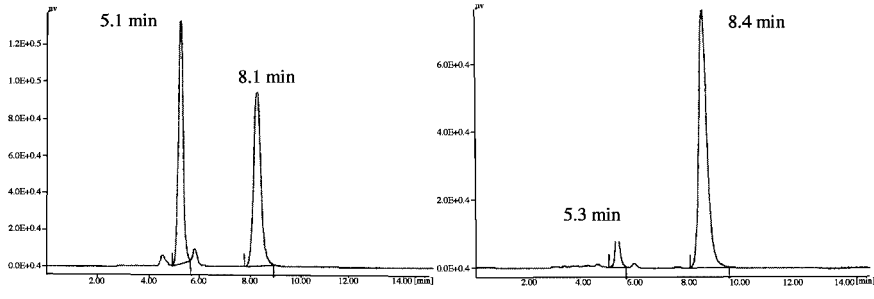
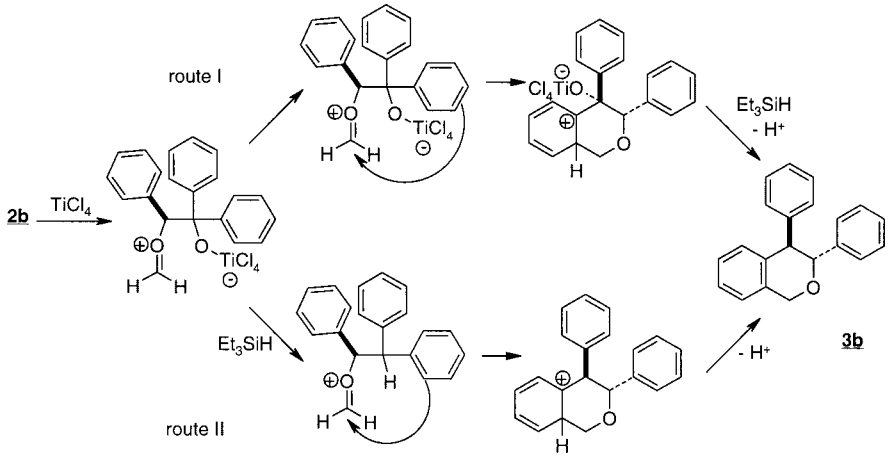


Figure 1. Chiral HPLC analysis of (±)-3b and (3*R*, 4*S*)-3b

triethylsilane and titanium tetrachloride, according to Scheme 4. The first obvious comment to make is that only acetals with two aryl rings at C4 are converted into isochromanes (entries 1–2, 5, 7). When R″ is an aromatic group as well, the diastereoselectivity of the cyclization is excellent since only one single diastereomer was observed in the crude ^{1}H NMR spectrum (entries 2, 5, 7). The *trans* configuration was assigned on the basis of the H3/H4 coupling constant, estimated at about 9 Hz.[10] The enantioselectivity of the reaction, starting from the enantiopure acetal **2b** has also been checked. A chiral HPLC analysis showed no loss of the optical integrity of the starting material (Figure 1).

If R″ is a smaller group, however, the diastereoselectivity decreases and 20% of the *cis* compound is obtained along with the *trans* isomer (entry 1). It is noteworthy that for the bulky isopropyl group a low yield was obtained (entry 7).

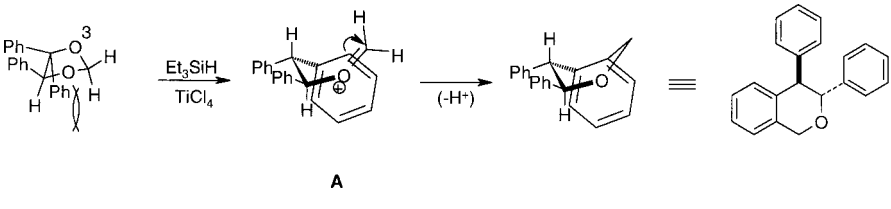
In order to rationalize the use of Et_3SiH, we have run the experiments with acetal **2b** in the absence of the silane. To our great surprise and in contrast with previously described work,[8] no isochromane formation was detectable in the crude NMR spectrum. Thus, we postulate the following mechanism (Scheme 6) for the conversion of the acetals into the isochromanes:



Scheme 6.

Indeed if the reaction would proceed *via* route I, we should have obtained the 4-hydroxy isochromane after hydrolysis of the reaction mixture but this compound was not detected in the crude ^1H NMR spectrum when we omitted triethylsilane. Thus, since the presence of Et_3SiH is necessary, route I may be ruled out.

The stereochemical outcome of this reaction can also be rationalized by the following transition state (Scheme 7):

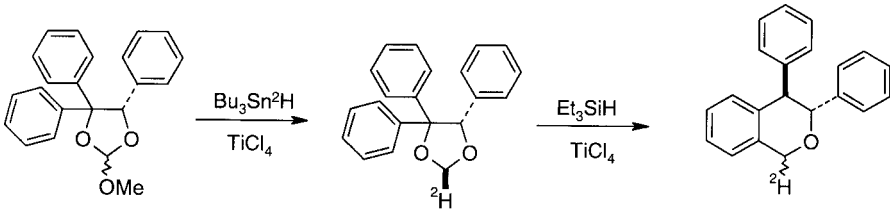


Scheme 7.

First O3 of the acetal can be complexed by the Lewis acid, due to the higher basicity of this oxygen and to a decomplexation of the axial H2 and Ph4 substituents. Then the postulated oxocarbenium intermediate

A adopts a 6-membered transition state (boat like) with all the bulky substituents in a pseudo-equatorial position. Finally, the phenyl ring attacks the oxocarbenium yielding the *trans* isochromane.

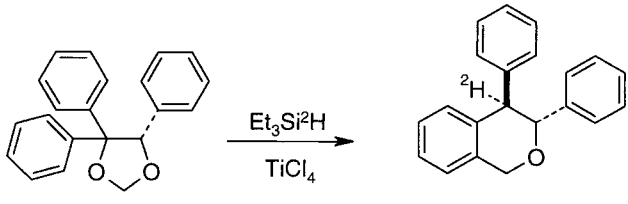
The use of metallic hydrides in our synthetic route to isochromanes allowed us to consider the preparation of deuterated (or tritiated) isochromanes. Therefore, the synthesis was done again with commercially available tributyltin deuteride in the first step to give **[2-^{2}H]- 2b** as a single diastereomer (i.e. > 95% based on MS and ^{1}H NMR). Then reaction of this 2-deutero acetal in the presence of Et_3SiH and $TiCl_4$ gives the corresponding 1-deutero isochromane but with complete epimerization at C1. (Scheme 8)



1b **2-[^{2}H]-2b** **1-[^{2}H]-3b**

Scheme 8.

In a similar vein, reaction of acetal **2b** in the presence of Et_3Si^2H (freshly prepared from Et_3SiCl and $LiAl^2H_4$)[11] and $TiCl_4$ gives the corresponding 4-deutero isochromane **[4-^{2}H]-3b** (i.e. > 95% based on MS and ^{1}H NMR) with excellent diastereoselectivity since only one of the two expected diastereomers (the *trans* isomer) was detectable on the ^{1}H NMR spectrum of the crude reaction mixture (Scheme 9).



2b **4-[^{2}H]-3b**

Scheme 9.

Conclusion

Starting from easily obtainable acetals, we have been able to synthesize a number of 4-phenyl isochromanes. The diastereoselectivity favours the *trans* isomer. The use of tributyltin deuteride or deuterated triethylsilane yields the corresponding 1- or 4-deuterated analogs with excellent isotopic enrichments. Since the introduction of the isotope mainly in the 4 position is achieved in the very last step of the synthesis of the isochromane skeleton, this route would be of interest for the preparation of tritiated isochromane.

Experimental

General methods

Non commercially available diols were prepared according to literature procedures.[12] $CDCl_3$ was from Eurisotop. All other chemicals were commercially available.

^1H and ^{13}C NMR spectra were recorded on a Brüker AC300 spectrometer operating, respectively, at 300.125 and 75.47 MHz. Deuterium incorporation was measured by integration of the respective ^1H NMR signals and by referring to the signal of another proton or group of protons within the molecule as internal standard or *via* MS.

A typical procedure for the preparation of acetals **1** is as follows:

In a Schlenk tube, 127 µL (1.2 mmol) of $BF_3 \cdot OEt_2$ is added to a solution of 1 mmol of C2 epimeric **1** in 20 mL of anhydrous CH_2Cl_2, at −78°C. The resulting solution was stirred for 15 min at −78°C and 295 µL (1.1 mmol) of Bu_3SnH are then added dropwise. The reaction was monitored by TLC, and when no more starting material could be detected (typically after 7/8 h), the reaction mixture was diluted by 20 mL of CH_2Cl_2, quenched with 10 mL of a saturated aqueous solution of NH_4Cl, the aqueous layer was extracted with 2×50 mL of CH_2Cl_2 and the organic phases were combined and dried over Na_2SO_4. After filtration and evaporation of the organic phase, the residue was purified on silica gel (eluent hexane/Et_3N:100/1 then hexane/Et_2O/Et_3N:75/25/1, Rf = 0.3) giving compound **2**.

(5*S*)-5-methyl-4,4-diphenyl-[1,3]-dioxolane 2a

^1H *NMR*: 1.07 (d, $J = 6.7$ Hz, 3H, CH_3); 5.21 (q, $J = 6.7$ Hz, 1H, H_5); 4.93 (s, 1H, H_2 or $H_{2'}$); 5.43 (s, 1H, H_2 or $H_{2'}$);7.22–7.46 (m, 10H, H_{ar}).

^{13}C *NMR*: 17.37 (CH_3); 79.51 (C_5); 86.86 (C_4); 93.30 (C_2); 126.55; 126.94; 127.36; 127.55; 128.14 (CH_{ar}); 141.95; 143.18 ($C_{quat.\ ar}$).

M.S.: 258$[M + NH_4]^+$.

I.R.: 3087; 2981; 2934; 2872; 1599–1584–1493–1448; 1386; 1200–960; 755; 700.

(±)- and (5*S*)-4,4,5-triphenyl-[1,3]-dioxolane 2b

^{1}H *NMR*: 5.12 (s, 1H, H_2); 5.68 (s, 1H, $H_{2'}$); 5.76 (s, 1H, H_5); 7.02–7.68(m, 15H, H_{ar}).

^{13}C *NMR*: 85.18 (C_5); 88.67 (C_4); 93.88 (C_2); 126.52; 126.87; 127.00; 127.20; 127.42; 127.59; 128.17 (CH_{ar}); 127.78; 140.30; 140.66; 142.72 ($C_{quat.\ ar}$).

M.S.: 320 $[M + NH_4]^+$.

I.R.: 3087; 2981; 1599–1492–1448; 1200 to 960; 752; 695

(±)-4-phenyl-[1,3]-dioxolane 2c

^{1}H *NMR*: 3.69 (dd, $J = 7.3$ Hz, $J = 7.9$ Hz, 1H, H_5 or H_5); 4.25 (dd, $J = 6.7$ Hz, $J = 7.9$ Hz, 1H, H_5 or H_5); 5.00 (dd, $J = 6.7$, 7.3 Hz, 1H, H_4); 5.09 (s, 1H, H_2 or $H_{2'}$); 5.27 (s, 1H, H_2 or $H_{2'}$); 7.25–7.36 (m, 5H, H_{ar}).

^{13}C *NMR*: 71.65 (C_5); 77.41 (C_4); 95.82 (C_2); 125.87; 127.91; 128.39 (CH_{ar}); 139.17 ($C_{quat.\ ar}$).

Meso and (4*S*, 5*S*)-4,5-diphenyl-[1,3]-dioxolane 2d

meso- 2d

^{1}H *NMR*: 5.21 (s, 1H, H_2 or $H_{2'}$); 5.29 (s, 2H, H_4 or H_5); 5.68 (s, 1H, H_2 or $H_{2'}$); 6.93–7.25 (m, 10H, H_{ar}).

^{13}C *NMR*: 81.59 (C_4 and C_5); 95.40 (C_2); 126.52, 127.20, 127.36 (CH_{ar}); 136.64 ($C_{quat.\ ar}$).

(4*S*, 5*S*)-4,5-diphenyl-[1,3]- dioxolane 2d

^{1}H *NMR*: 4.72 (s, 2H, H_2); 5.48 (s, 2H, H_4 and H_5); 7.25-7.40 (m, 10H, H_{ar}).

(±)-4,4-diphenyl-5-(4-trifluoromethyl-phenyl)-[1,3]-dioxolane 2e

^{1}H *NMR*: 5.07 (s, 1H, H_5); 5.67 (s, 1H, H_2 or $H_{2'}$); 5.81 (s, 1H, H_2 or $H_{2'}$); 7.00–7.58 (m, 14H, H_{ar}).

^{13}C *NMR*: 83.88 (C_5); 89.09 (C_4); 93.97 (C_2); 124.18 (q, $J_{3F} = 258$ Hz); 124.22; 126.62, 126.94, 127.65, 127.84, 128.33, 128.52, 128.69, 128.85, 129.04, 129.95, 130.76 (CH_{ar}); 139.04 (q, $^3J_{3F} = 34.3$ Hz); 141.95, 142.27 ($C_{quat.\ ar}$).

(±)-5-benzyl-4,4-diphenyl-[1,3]-dioxolane 2f

^{1}H *NMR*: 2.35 (dd, $J = 14$, 10 Hz, 1H, H_6 or $H_{6'}$); 2.62 (dd, $J = 14$, 2 Hz, 1H, H_6 or $H_{6'}$); 4.76 (dd, $J = 2$, 10 Hz, 1H, H_5); 4.88 (s, 1H, H_2 or $H_{2'}$); 5.47 (s, 1H, H_2 or $H_{2'}$); 7.17-7.33 (m, 15H, H_{ar}).

^{13}C *NMR*: 38.46 (C_6); 84.40 (C_5), 86.93 (C_4); 93.49 (C_2); 126.23, 126.62, 127.07, 127.17, 127.46, 127.65, 128.17, 128.78 (CH_{ar}); 138.36, 141.82, 142.92 ($C_{quat.ar}$).

(±)-5-isopropyl-4,4-diphenyl-[1,3]-dioxolane 2g

^{1}H *NMR*: 0.77 (d, $J = 6.7$ Hz, 3H, CH_3); 0.85 (d, $J = 6.7$ Hz; 3H, CH_3); 1.64 (dsept, $J = 5.5$, 6.7 Hz, 1H, H_6); 4.46 (d, $J = 5.5$ Hz, 1H, H_5); 4.83 (s, 1H, H_2 or $H_{2'}$); 5.37 (s, 1H, H_2 or $H_{2'}$); 7.19–7.29 (m, 10H, H_{ar})

^{13}C *NMR*: 17.43; 18.18 (CH_3); 20.70 (C_6); 87.02 (C_5); 87.12 (C_4); 93.13 (C_2); 126.91, 127.13, 127.33, 127.39, 128.07 (CH_{ar}); 141.53, 143.66 ($C_{quat.ar}$).

(2*R*,5*S*)-2-methyl-4,4,5-triphenyl-[1,3]-dioxolane (100% *trans*) **2h**

^{1}H *NMR*: 1.82 (d, $J = 5$ Hz, 3H, CH_3); 5.38 (q, $J = 5$ Hz, 1H, H_2); 5.86 (s, 1H, H_5); 7.04–7.75 (m, 15H, H_{ar}).

(5*S*)-2,4,4,5-tetraphenyl-[1,3]-dioxolane 2i

^{1}H *NMR*: Major diastereomer (85%): 6.01 (s, 1H, H_5); 6.07 (s, 1H, H_2); 6.74–7.80 (m, 15H, H_{ar}).

Minor diastereomer (15%): 5.65 (s, 1H, H_5); 6.74 (s, 1H, H_2); 6.74–7.80 (m, 15H, H_{ar}).

A typical procedure for the conversion of acetals **1** into isochromanes **3** is as follows:

In a flame dried Schlenk tube, 150 µL (1.2 mmol) of $TiCl_4$ is first added to a solution of 1 mmol of acetal **2** in 20 mL of anhydrous CH_2Cl_2, at −78°C under nitrogen immediately followed by the addition of 290 µL of Et_3SiH (1.1 mmol). The reaction was monitored by TLC, and when no more starting material could be detected (typically after 7/8 h), the reaction mixture was diluted with 20 mL of CH_2Cl_2, quenched with 10 mL of a saturated aqueous solution of NH_4Cl, the aqueous layer was extracted with 2×50 mL of CH_2Cl_2 and the organic phases were combined and dried over Na_2SO_4. After filtration and evaporation of the organic phase, the residue was purified on silica gel (eluent hexane: 100% then hexane/Et_2O: 95/5, Rf = 0.3) then repurified using semi-preparative HPLC (Zorbax C8 column, 4 mL/min, CH_3CN/H_2O 60/40) giving pure compound **3**.

3-methyl-4-phenyl-isochromane (*trans*/*cis* 80/20) **3a**
^{1}H *NMR*: *Trans* isomer: 1.19 (d, $J = 3.7$ Hz, 3H, CH_3); 3.84 (dq, $J = 3.7$ and 6.1 Hz, 1H, H_3); 3.85 (d, $J = 6.1$ Hz, 1H, H_4); 4.90 and 5.00 (AB system, $J = 15$ Hz, 2H, $H_1 \times 2$); 6.73–7.31 (m, 9H, H_{ar}).

Cis isomer: 1.18 (d, $J = 3.7$ Hz, 3H, CH_3); 3.85 (d, $J = 6.1$ Hz, 1H, H_4); 4.08 (dq, $J = 3.7$, 6.1 Hz, 1H, H_3); 4.95 et 5.03 (AB system, $J = 15$ Hz, 2H, $H_1 \times 2$); 6.73–7.31 (m, 9H, H_{ar}).

^{13}C *NMR*: 19.50 (CH_3); 52.02 (C_4); 68.32 (C_1); 77.22 (C_2); 123.51, 125.81, 126.91, 128.01, 128.49, 129.20, 129.40 (CH_{ar}); 134.35, 137.39, 142.34 ($C_{quat\cdot ar}$)

3,4-diphenyl-isochromane (*trans*/*cis* = 92/8), *trans* isomer data reported[13] **3b**
^{1}H *NMR*: 4.24 (d, $J = 9.8$ Hz, 1H, H_3); 4.68 (d, $J = 9.8$ Hz, 1H, H_4); 5.03 and 5.14 (AB system, $J = 15$ Hz, 2H, $H_1 \times 2$); 6.81–7.21 (m, 14H, H_{ar}).

HPLC: 250 × 4.6 mm, 5μ RP C8 column, eluted with 60/40 CH_3CN/H_2O, UV 254 nm, 1 mL/min, tr = 10.7 min.

The chiral separation was carried out on a Whelk (Pirkle type) (*S*,*S*) column (250 × 4.6 mm) supplied by Regis Technologies. The eluent used was a mixture of iso-octane/iso-propanol 98/2 (0.8 mL/min, 25°C, UV detection 220 nm).

3-(4-trifluoromethyl-phenyl)-4-phenyl-isochromane (*trans*/*cis* > 95/5) **3e**
^{1}H *NMR* (*trans* isomer): 4.18 (d, $J = 9$ Hz, 1H, H_4); 4.75 (d, $J = 9$ Hz, 1H, H_3); 5.07 and 5.17 (AB system, $J = 15$ Hz, 2H, $H_1 \times 2$); 6.82–7.54 (m, 13H, H_{ar}).

3-(4-trifluoromethyl-phenyl)-4-phenyl-isochromane (*trans*/*cis* > 95/5) **3g**
^{1}H *NMR* (*trans* isomer): 0.96 (d, $J = 7$ Hz, 3H, CH_3); 0.99 (d, $J = 7$ Hz, 3H, CH_3); 1.66 (sept, $J = 7$ Hz, 1H, H_5); 3.62 (dd, $J = 7$, 9 Hz, 1H, H_3); 4.12 (d, $J = 9$ Hz, 1H, H_4); 5.07 and 5.17 (AB system, $J = 15$ Hz 2H, $H_1 \times 2$); 7.02–7.34 (m, 9H, H_{ar}).

(2*R*,5*S*)-2-deuterio-4,4,5-triphenyl-[1,3]-dioxolane (2*R*,5*S*)-2-[^{2}H]-2b (i.e. = 92%)
^{1}H *NMR*: 5.63 (s, 1H, H_5); 5.72 (s, 1H, H_2); 7.01–7.63 (m, 15H, H_{ar}).

1-deutero-3,4-diphenyl-isochromane(±)-, epi-2, 2-[^{2}H]-3b (i.e. = 92%)
^{1}H *NMR*: 4.44 (d, $J = 9.$ Hz, 1H, H_3); 4.94 (d, $J = 9$ Hz, 1H, H_4); 5.31 (s, 0.4H, H_1); 5.42 (d, 0.6H, H_1); 7.35–7.71 (m, 14H, H_{ar}).

^{13}C *NMR*: 52.21 (C_4); 68.65 (t, $J_D = 26$ Hz, C_1); 84.34 (C_3); 123.81, 126.20, 126.62, 126.75, 126.95, 127.66, 127.98, 128.18, 129.53, 129.86 (CH_{ar}); 134.58, 137.69, 140.34, 141.51 ($C_{quat.ar}$)

4-deutero-3,4-diphenyl-isochromane (100% *trans*, i.e. > 95%) **(±)-, 4-[^{2}H]- 3b**

^1H *NMR*: 4.74 (s, 1H, H_3); 5.07 and 5.18 (AB system, $J = 15$ Hz, 2H, $H_1 \times 2$); 6.86–7.26 (m, 14H, H_{ar}).

References

1. Frater G, Mueller U, Petrzilka M. *Eur Pat Appl* 1995 EP 677521 A1 19951018, application: EP 95-102462 19950222.
2. Cutler HG, Majetich G, Tian X, Spearing P. U.S., 1999, US 5922889 A 19990713, *Pat Appl*: US 96-667749 19960621.
3. Deninno MP, Schoenleber R, Perner RJ, et al. *J Med Chem* 1991; **34**: 2561–2569; Tenbrick RE, Bergh CL, Ducan JN, et al. *J Med Chem* 1996 **39**: 2435–2437.
4. Warnell JL, Shriner RL. *J Am Chem Soc* 1957; **79**: 3165–3167.
5. Siegel S, Coburn S. *J Am Chem Soc* 1951; **73**: 5494–5495.
6. Thibault J *Ann Chim* 1971; **6**: 263–274.
7. Mohler DL, Thompson DW. *Tetrahedron Lett* 1987; **28**: 2567–2570.
8. Giles RGF, Rickards RW, Senanayake BS. *J Chem Soc Perkin Trans 1* 1996; 2241–2248; Giles RGF, Rickards RW, Senanayake BS. *J Chem Soc Perkin Trans* 1 1997; 3361–3370.
9. Ando M, Ohhara H, Takase K. *Chem Lett* 1986; 879–882.
10. Randall JC, Vaulx RL, Hobbes ME, Hauser CR. *J Org Chem* 1965; **30**: 2035–2037.
11. Brookhart M, Grant BE. *J Am Chem Soc* 1993; **115**: 2151–2156.
12. Braun H, Graf S, Herzog S. *Org Synth* 1993; **72**: 32–37.
13. Mc Cullough KJ, Masuyama A, Morgan KM, *et al*. *J Chem Soc Perkin Trans 1* 1998; 2353–2362.

