13. Intramolecular Addition of Nucleophilic Carbenes to Acceptor-Substituted Alkenyl Groups: Synthesis and Transformation of Homobenzofurans and Synthesis of a Homoindole

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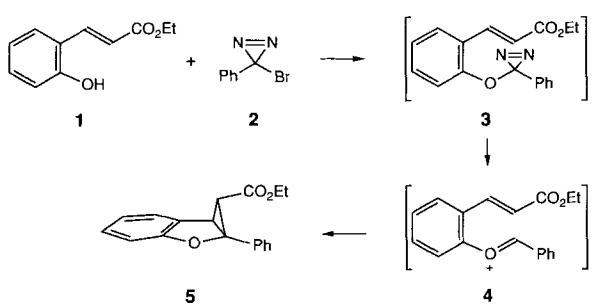
(2.X.92)

The intramolecular addition of unsaturated alkoxycarbenes leads in high yields and diastereoselectively to fused cyclopropanes (*Scheme 1*). Reaction of the halodiazirines **2**, **10**, **11**, and **20** with the unsaturated phenolates **1**, **8**, and **9** yielded intermediate alkoxydiazirines, and hence the homobenzofurans **5**, **12**–**16**, **22**, and **26** (*Scheme 2*). The intermediate alkoxydiazirine **25** was isolated at low temperature (*Scheme 3*). An equilibrium between the cyclopropane derivatives **12** and **27**, and **14** and **28** was established at 120°. At 200°, **12** rearranged to the chromene **29**, by disrotarory opening of the cyclopropane ring, followed by electrocyclization. Hydrogenation of **29** gave the (all-*cis*)-chroman **32** (*Scheme 4*). The homoindole **35** was obtained in good yields, presumably by an $S_{RN}1$ reaction from **34** and **10** (*Scheme 5*).

Introduction. – Little is known about intramolecular reactions of nucleophilic, and particularly of alkoxy-alkyl-carbenes [1][1]). We have reported a method for the synthesis of benzylidene acetals, based upon the intramolecular insertion into O–H bonds of alkoxy-alkyl-carbenes [3], and now describe their intramolecular addition to electron-deficient alkenyl groups [4]. The intermolecular version of this reaction leads to donor-acceptor-substituted cyclopropanes, which are versatile synthetic intermediates [5]. Similarly, the intramolecular process should form two new rings, of which one is a cyclopropane.

To illustrate the intramolecular addition of unsaturated alkoxycarbenes, we have treated the Na salts of *o*-hydroxycinnamates with halodiazirines, expecting the formation of thermally labile alkoxydiazirines [6], which should generate carbenes *in situ* under mild conditions [7]. The intramolecular addition of these carbenes should lead to homobenzofurans. This sequence is illustrated in *Scheme 1* for the reaction of the cinnamate **1** [8] with

Scheme 1



1 **2** **3** **4** **5**

[1]) For intramolecular reactions of electrophilic carbenes, see *e.g.* [2].

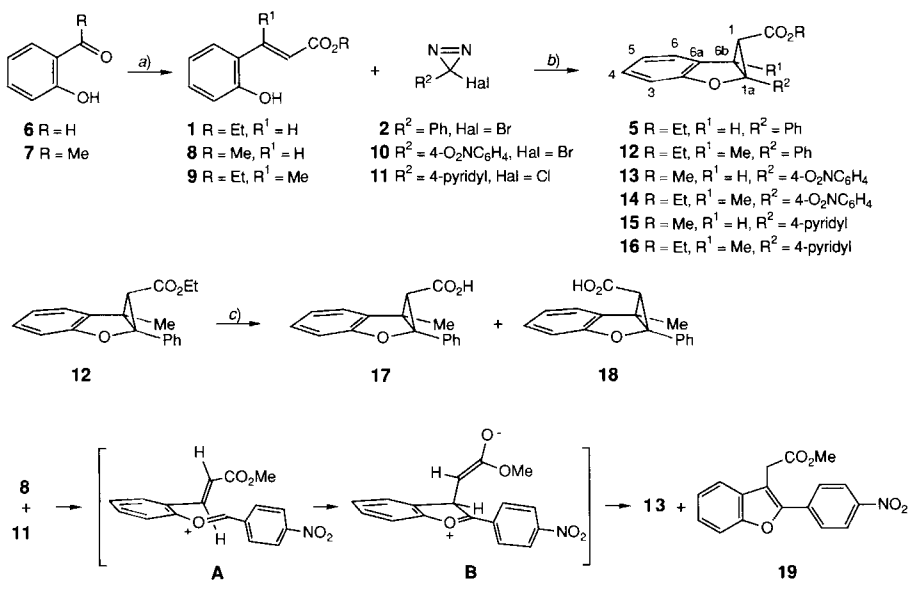
the diazirine **2**, leading *via* **3** and **4** to the homobenzofuran **5**. In similar way, *o*-aminocinnamates may lead to homoindoles with a so far unknown substitution pattern.

Homobenzofurans (= cyclopropa[*b*]benzofurans) have been prepared by the intermolecular addition of thermally generated (chloro)(phenyl)carbene to coumarin in two steps and in an overall yield of 55% [9]. They have also been prepared by intramolecular addition of electrophilic triplet carbenes to alkenyl phenyl ethers [10], while the analogous addition of electrophilic singlet carbenes is difficult on account of the barrier associated with the required rotation around the bond connecting the aryl group and the divalent C-atom [11]. Homoindoles (= cyclopropa[*b*]indoles) have been prepared by the CuCN-catalyzed addition of ethyl diazoacetate to indoles [12]. Both, the yields and the stereoselectivity are poor.

We report here the synthesis of some homobenzofurans, their thermal equilibration, their transformation into chromenes, and the synthesis of a homoindole.

Results and Discussion. – Synthesis of the *o*-hydroxycinnamates **1** [8] and **8** [13] from salicylaldehyde (**6**) was straightforward (*Scheme 2*). *Wittig* olefination of **7**, however, was slow at 65°, and gave 4-methylcoumarin[2]) at 110°. Under reflux in benzene, the desired **9** [8] was obtained in 58% together with 28% of 4-methylcoumarin. The diazirines **2**, **10**,

Scheme 2



a) 7, 1.58 equiv. of Ph_3PCHCO_2Et, C_6H_6, reflux, 6 h; **9** (58%). *b*) *1*) 1 equiv. of the Na salt of **1**, **2**, DMF/hexane 1:1.7, r.t., 12 h; **5** (82%); *2*) 1.1 equiv. of the Na salt of **1**, **2**, DMF/hexane 1:1, r.t., 12 h; **12** (79%); *3*) 1.2 equiv. of the Na salt of **8**, **10**, DMF/hexane 1:1, 0° for 5 min, r.t. for 12 h; **13** (64%), **19** (15%); *4*) 1.2 equiv. of the Na salt of **9**, **10**, DMF/hexane 1:2, −12° for 5 min, r.t. for 12 h; **14** (83%). *5*) 1.5 equiv. of the Na salt of **8**, **11**, 3-Å molecular sieves, DMPU, r.t., 12 h; **15** (68%). *6*) 1 equiv. of the Na salt of **9**, **11**, DMF/hexane 2:3, 0°, 3.5 h; **16** (63%). *c*) 3 equiv. of KOH, EtOH/H_2O 10:1, reflux, 0.5 h; **17** (28%), **18** (69%).

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[2]) The yield of this apparently advantageous procedure [8] was almost quantitative.

11, and **20** were prepared from the corresponding amidines according to *Graham*'s procedure [14]. An improved workup doubled the (poor) yield of 3-bromo-3-(4-nitrophenyl)diazirine (**10**) [15], which was crystallized from hexane at −78°, and characterized by its UV and ^{13}C-NMR spectra (*s* at 36.03 ppm for the diazirine-C-atom).

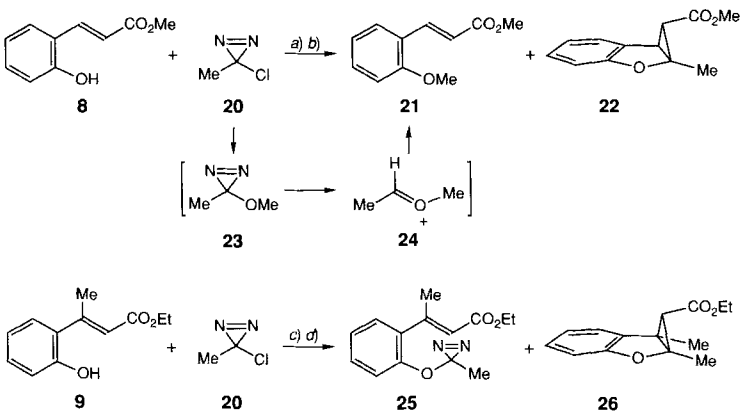
The Na salts derived from **1** and from **9** reacted rapidly with the diazirine **2**, as shown by the disappearance of the yellow color of a DMF solution of the salts. Spontaneous thermolysis of the intermediate *bona fide* diazirines gave the cyclopropanes **5** (82%) and **12** (79%). Saponification of **12** was accompanied by epimerization, and yielded a 29:71 mixture **17**/**18**, evidencing the deprotonation at the α-position of the C=O function [16] under mild conditions. The analogous reaction between the Na salt of **8** [13] and the diazirine **10** gave, in addition to the expected product **13** (64%), a significant amount (15%) of the benzofuran **19** as long, yellow needles. Its formation can be rationalized as follows. Stabilization of the intermediate, donor-acceptor-stabilized carbene **A** requires that the π planes of the 4-nitrophenyl substituent and of the oxycarbenium group must be perpendicular to each other. The intramolecular, nucleophilic addition of the singlet carbene to the π system requires a rotation around the bond connecting the alkenyl moiety to the aromatic ring [10]. The 4-nitrophenyl group in the ensuing zwitterion **B** is oriented perpendicularly to the average plane of the benzofurylium ring, both for kinetic and themodynamic reasons, and thus hinders the approach of the enolate group to the oxycarbenium center, which is required for formation of the cyclopropane ring. Protonation-deprotonation (hydride shift followed by tautomerisation?) leads to the benzofuran **19**. This path is not available to the C(3) Me-substituted zwitterion derived from **9** and **10**, which indeed yield 83% of the cyclopropane **14**.

The reaction of the Na salt of **8** with 3-chloro-3-(4-pyridyl)diazirine (**11**) resulted in a complex mixture of products, except in *N*,*N*′-dimethyl-*N*,*N*′-propyleneurea (DMPU), where the pyridyl-cyclopropane **15** was obtained in a yield of 68%. The more highly substituted pyridine derivative **16** had to be prepared from **9** and **11** at lower temperatures and using shorter times (3.5 h) than what was required for the synthesis of **5** and **12**. It was obtained in 63% yield as cubic crystals.

To investigate the synthesis of 2-alkyl-substituted homobenzofurans, we used the explosive 3-chloro-3-methyldiazirine (**20**; *Scheme 3*), which has to be stored and used at low temperatures [17]. The reaction of **20** with the Na salt of **8** (prepared with NaOMe in MeOH, followed by evaporation of MeOH) in DMF at −60 to −15° gave only 10% of **22** besides 42% of the known methyl ether **21** [18]. We assumed that **21** is formed by *O*-methylation with the oxycarbenium ion **24**, which is generated by protonation of (methoxy)-(methyl)carbene. This carbene is formed by low temperature thermolysis of **23**, which results from methoxy-chloride exchange [6] between **20** and NaOMe. The Na salt of **8** was, therefore, prepared by using a very slight excess of dried NaOMe and indeed gave **22** in 53% yield when treated at −50 to −15° with **20** in a 2:1 mixture of DMPU and THF (m.p. of the mixture *ca.* −50°). Similarly, the homobenzofuran **26** was isolated in 65% from the low-temperature treatment of the Na salt of **9** with **20**. When the exchange reaction of **9** with **20** was run for a shorter time (3.5 h) and at lower temperatures (from −70 to −25°), we isolated the postulated alkoxydiazirine **25** (44%) and **26** (13%) by flash chromatography at −25°.

The IR spectrum of **25** shows the presence of the C=C bond (1640 cm^{-1}), while the N=N absorption (1570 cm^{-1}) could only be detected immediately after filling the IR cell

Scheme 3



a) 1.6 equiv. of the Na salt of **8**, **20**, DMF/hexane 1:1, −70° to 10°, 12 h; **21** (42%), **22** (10%). *b*) 1.5 equiv. of the Na salt of **8**, **20**, DMPU/THF 2:1, −60° to −15° for 3.5 h, r.t. for 2 d; **21** (19%), **22** (53%). *c*) Na salt of **9**, 1.3 equiv. of **20**, DMF/hexane 4:1, −70° to −25°, 3.5 h; **25** (44%), **26** (13%). *d*) Na salt of **9**, 2.5 equiv. of **20**, DMF/hexane 7:4, 3-Å molecular sieves, −60° to 10°, 12 h; **26** (65%).

at room temperature. The ^{13}C-NMR spectrum (−40°) showed a *s* for the diazirine moiety at 53.48 ppm. The ^{1}H-NMR spectrum shows a *q* for H−C(2) at 5.78 ppm ($J \approx 1.5$ Hz) and a *d* for the vinylic Me group at 2.37 ppm ($J \approx 1.2$ Hz).

The esters **5**, **12**–**16**, **19**, **21**, **22**, and **26** all exhibit a strong IR band of the C=O group between 1735 and 1710 cm^{-1}. The IR spectra of the carboxylic acids **17** and **18** exhibit COOH absorptions at 3500–2500, and at 1695 and 1710 cm^{-1}, respectively. The small J(1,6b) values (3.8–4.4 Hz, *Table 2*) for **5**, **13**, **15**, and **22** are characteristic for *trans*-couplings in cyclopropanes [19], indicating the *cis*-orientation of the R^2 substituent and the alkoxycarbonyl group. The *cis*-arrangement of Me−C(6b) and Ph−C(1a) in **12** was evidenced by NOE's (*Table 4*). Irradiation of Me−C(6b) gave a 3% enhancement for the Ph−C(1a) signal, while no enhancement was observed for the Me−C(6b) of Ph−C(1a) signals upon irradiation of H−C(1). The ^{1}H-NMR spectra (*Table 1*) show the same chemical shift for the Me−C(6b) signals of **12** and **17** (1.86 ppm), as opposed to the one for **18** (1.48 ppm, $\Delta\delta = 0.40$ ppm), evidencing that **12** and **17** possess the same configuration, where the Me group is exposed to the anisotropic effect of the nearby C=O group. The configurational assignment is confirmed by the chemical shift for H−C(1) in **12** (1.77 ppm) and **17** (1.74 ppm), as opposed to the one for **18** (2.42 ppm, $\Delta\delta = 0.65$ and 0.68 ppm). These chemical-shift values demonstrate the shielding effect of the benzo ring in **12** and **17**. In the ^{13}C-NMR spectra (*Table 3*), the proximity of the COOEt and COOH groups, respectively, to Me−C(6b) (γ effect) is manifested by a 6-ppm upfield shift of the Me signals of **12** (10.55 ppm) and **17** (10.35 ppm), as compared to the chemical shift for **18** (16.02 ppm). The *trans*-arrangement of the COOH and Me groups in **18** is supported by NOE experiments (*Table 4*). Irradiation on H−C(1) produces a significant enhancement of the Ph−C(1a) (11%) and the Me−C(6b) (6%) signals; irradiation on Me−C(8) leads to a similar effect for Ph−C(1a) (13%) and H−C(1) (8%). Similar chemical-shift values (*Tables 1* and *3*) suggest the same configuration for **14**–**16** and **26** as for **12**.

Table 1. *^{1}H-NMR* (400 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of the Homobenzofurans* **5**, **12–18**, **22**, **26–28**, *and the Homoindole* **35**

Compound	H–C(1)	R–C(1a)	H–C(3)	H–C(4)	H–C(5)	H–C(6)	H–C(6b)	Me–C(6b)	MeO *or* EtO
5[a])	1.66	7.55–7.38	6.88	7.18	6.96	[b])	3.82	–	3.82–3.95, 0.98
13	1.87	7.73, 8.26	6.95	7.22	7.00	7.46	3.87	–	3.57
15	1.85	7.46, 8.64	6.95	7.21	6.99	7.45	3.85	–	3.58
22	1.36	1.86	6.85	7.14	6.90	7.33	3.19	–	3.73
35	2.13	7.15, 8.19	7.88	7.31	7.14	7.44	3.49	2.12[c])	4.32–4.22, 1.32
12[d])	1.77	7.44–7.39	6.87	7.18	6.99	7.36	–	1.86	4.15–3.98, 1.17
14[d])	1.85	7.65, 8.29	6.90	7.22	7.04	7.39	–	1.89	4.16–4.03, 1.21
16	1.82	7.40, 8.68	6.91	7.21	7.02	7.37	–	1.90	4.12–4.07, 1.19
17	1.74	7.46–7.42	6.89	7.20	7.02	7.38	–	1.86	–
26[a])[d])	1.26	1.86	6.84	7.16	6.94	7.35	–	1.66	4.13, 1.22
18	2.42	7.45–7.37	6.93	7.23	7.00	7.31	–	1.48	–
27[d])	2.48	7.48–7.37	6.95	7.24	7.00	7.33	–	1.48	3.99–3.89, 1.04
28	2.62	7.64, 8.26	7.01	7.29	7.05	7.34	–	1.52	3.95, 1.04

[a]) In (D_6)acetone. [b]) Hidden by Ph–C(1a). [c]) AcN. [d]) At 300 MHz.

Table 2. *^{1}H-NMR* (400 MHz, $CDCl_3$) *Coupling Constants* [Hz] *of the Homobenzofurans* **5**, **12–18**, **22**, **26–28**, *and the Homoindole* **35**

Compound	J(1,6b)	J(3,4)	J(3,5)	J(4,5)	J(4,6)	J(5,6)	$J(CH_2,CH_3)$
5[a])	4.0	8.1	1.0	7.6	1.4	7.6	7.1
13	4.3	8.2	1.1	7.6	1.3	7.4	–
15	4.4	8.1	0.9	7.8	1.2	7.5	–
22	3.8	8.1	0.9	7.5	1.3	7.5	–
35	4.7	8.3	0.9	8.3	0.6	7.1	7.2
12[b])	–	8.0	0.7	7.6	1.1	7.5	7.2
14	–	8.0	0.7	7.6	1.0	7.6	7.1
16[b])	–	8.0	1.3	7.7	1.2	7.5	7.2
17	–	8.1	0.9	7.4	1.3	7.4	–
26[a])[b])	–	8.0	0.9	7.5	1.2	7.5	–
18	–	8.1	0.9	7.4	1.3	7.4	–
27[b])	–	8.1	0.6	7.4	1.1	7.5	7.1
28	–	8.1	0.8	7.5	1.2	7.4	7.1

[a]) (D_6)Acetone. [b]) At 300 MHz.

The 4-nitrophenyl group of **13**, **14**, and **19** is observed in the IR (1520 cm^{-1}) and the ^{1}H-NMR spectra. The constitution of **19** is suggested by the UV spectrum (λ_{max} 359 nm, ε 26469), evidencing the presence of a longer conjugated system [20], and by the ^{1}H-NMR (s of CH_2–C(3) at 3.93 ppm) and ^{13}C-NMR data (s of C(2) at 150.85 ppm, s of C(3) at 113.68 ppm; 4 additional s of aromatic C). The presence of the 4-pyridyl group in **15** and **16** is evident from the *AA'BB'* system in the aromatic region of the ^{1}H-NMR spectra. In the ^{13}C-NMR spectrum of **16**, the Me–C(6b) signal shows a γ effect, as it was noticed for **12** (*Table 4*), evidencing the synperiplanar arrangement of the COOMe and Me group. The presence of the Me–C(1a) substituent in **22** is evidenced by the NMR spectra,

displaying a *s* (3 H) at 1.86 ppm and a *q* at 13.73 ppm. The NMR spectra of **26** show Me *s* at 1.86 and 1.66 ppm and *q* at 11.32 and 8.69 ppm.

As thermolysis of the acid corresponding to **5** leads to a benzofuranacetic acid, with loss or migration of H–C(6b) [9], one expects a different type of compound from **12** and **14** which possess a Me substituent at C(6b). Prolonged heating of **12** in DMPU at 120°

Table 3. *^{13}C-NMR* (50.6 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of the Homobenzofurans* **5**, **12–18**, **22**, **26–28**, *and the Homoindole* **35**

Compound	C(1)	C(1a)	C(2a)	C(3)	C(4), C(5)	C(6)	C(6a)	C(6b)
5	32.38[a])	77.91	158.93	110.42	124.06, 121.12	128.31	128.55	31.04[a])
13[b])	34.01[a])	78.82	159.60	111.21	125.46, 122.61	129.18	129.66	32.01[a])
15	32.89[a])	77.39	158.49	110.58	124.17, 121.56	128.26	128.26	32.10[a])
22[b])	33.95[a])	74.78	158.79	110.16	123.96, 120.90	127.71	129.63	29.22[a])
35	32.41[a])	57.40	143.27	116.38	124.57, 123.92	128.10	129.16	37.00[a])
12[b])	33.46	81.98	158.79	110.97	123.88, 122.15	128.90	135.37	39.52
14[b])	33.62	80.39	158.64	111.13	123.99, 122.49	129.18	134.82	40.09
16	33.32	78.93	157.53	110.47	122.77, 121.35	128.18	133.72	39.27
17[b])	32.83	82.16	158.79	110.94	123.91, 122.15	128.93	135.33	39.78
26[b])	32.90	77.81	158.76	110.87	123.80, 121.82	128.74	135.23	38.79
18[b])	26.37	81.31	161.38	109.96	125.05, 121.96	128.68	134.93	41.22
27	26.03	80.83	160.69	109.12	123.85, 120.94	127.89	130.44	40.59
28	27.15	79.12	160.06	118.61	123.89, 121.40	128.26	128.01	42.15

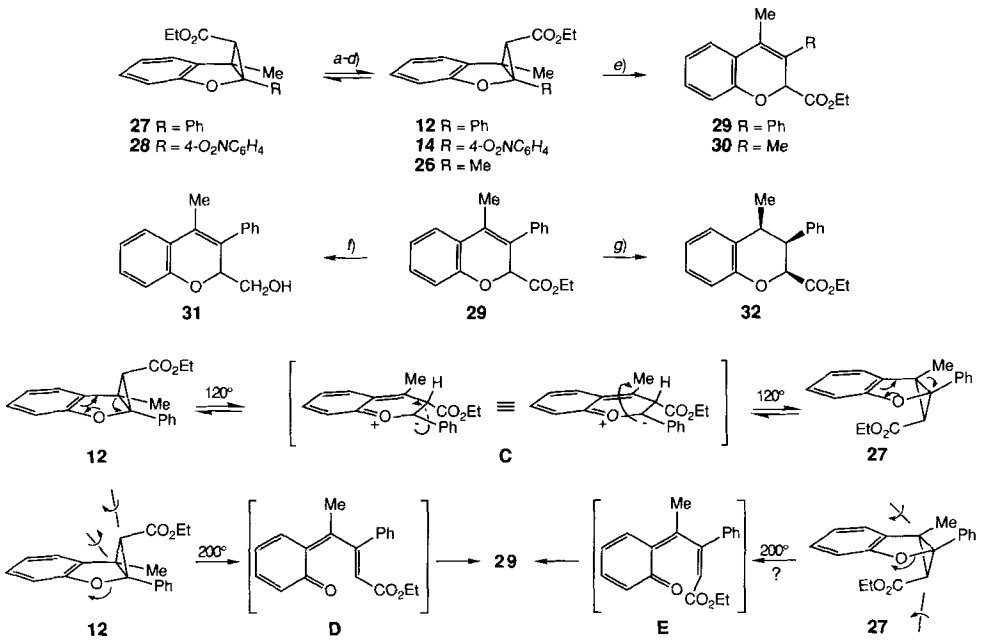
Compound	Me–C(6b)	C=O	MeO *or* EtO	Ph *or* 4-$O_2NC_6H_4$ *or* 4-pyridyl[c])
5	–	170.10	60.78, 13.96	132.24, 128.31, 129.19, 129.10
13[b])	–	170.83	52.70	140.32, 130.93, 124.32, 149.16
15	–	169.78	52.17	141.23, 122.68, 149.68
22[b])	13.73[d])	172.16	51.96	–
35	169.76[a])[e]), 25.74[e])	169.83[a])	61.61, 13.98	141.02, 123.17, 130.84, 147.36
12[b])	10.55	170.84	61.23, 14.55	132.29, 129.55, 131.66, 130.36
14[b])	10.30	170.50	61.60, 14.52	139.17, 132.68, 124.57, 149.50
16	9.85	169.62	60.74, 14.11	140.19, 124.23, 150.03
17[b])	10.35	171.65	–	132.24, 128.93, 129.55, 130.39
26[b])	8.69, 11.32[d])	171.37	61.24, 14.63	
18[b])	16.02	167.77	–	130.04, 128.84, 128.62, 129.81
27	16.10	166.73	60.34, 13.96	133.84, 127.89, 128.54, 128.73
28	15.59	165.77	60.59, 13.80	141.25, 127.63, 123.89, 147.70

[a]) Assignment may be interchanged. [b]) In CD_3CN. [c]) Sequence: *ipso*-C, *ortho*-C, *meta*-C, *para*-C. [d]) Me–C(2). [e]) AcN.

Table 4. *NOE Experiments with* **12**, **18**, *and* **29**

Compound	Irradiation on	Observed NOE, Intensity	
12	H–C(1)	none	
	Me–C(6b)	Ph–C(1a), 3%	H–C(6), 3%
	Ph–C(1a)	Me–C(6b), 1%	
18	H–C(1)	Ph–C(1a), 11%	Me–C(6b), 6%
	Me–C(6b)	Ph–C(1a), 13%	H–C(1), 8%
29	H–C(2)	Ph–C(3), 4%	
	Me–C(4)	H–C(5), 3%	Ph–C(3), 1%
	Ph–C(3)	H–C(2), 2%	Me–C(4), 1%

Scheme 4



a) From **27**: *1*) 120°, DMPU, 24 h; **12** (22%), **27** (48%); *2*) neat **27**, 120°; after 60 h: **12**/**27** 42:58; after 74 h: **12**/**27** 44:56; *3*) cat. NaOEt, DMF, 12 h; **12** (33%), **27** (53%). *b*) From **12**: *1*) 120°, DMPU, 24 h; **12** (40%), **27** (50%); *2*) neat **12**, 120°; after 60 h: **12**/**27** 43:57; after 74 h: **12**/**27** 44:56; *3*) cat. NaOEt, DMF, 12 h; **12** (34%), **27** (48%). *c*) From **28**: 120°, DMPU, 24 h; **14** (14%), **28** (27%). *d*) From **14**: 120°, DMPU, 20 h; **14** (28%), **28** (50%). *e*) *1*) From **12**: DMPU, 195–200°, 8 h; **29** (94%); *2*) from **26**: DMPU, 195–200°, 5 h; **30** (86%). *f*) $LiAlH_4$, Et_2O, 0°, 20 min; 85%. *g*) H_2, Pd/C, AcOEt, r.t., 12 h; > 97%.

leads to a mixture **12**/**27** (90%, 43:57; *Scheme 4*). Small amounts of **29** (*ca.* 5%) were also formed (see below). Similar thermolysis of **27** resulted in a mixture **12**/**27** in a ratio of 31:69 (70%). Parallel thermolysis (74 h at 120°) of neat **12** and **27** showed that an equilibrium was established at a **12**/**27** ratio of *ca.* 43:57. Thermolysis of **12** at 200° produced 94% of the chromene **29**. Reduction of **29** with $LiAlH_4$ yielded the primary alcohol **31** and catalytic hydrogenation of **29** gave quantitatively the (all-*cis*)-chroman **32** [21].

In a similar way, thermolysis at 120° of **14** in DMPU gave a 36:64 mixture **14**/**28**. Approximately the same ratio (33:67) resulted from thermolysis of **28**, again suggesting an equilibration. The dimethyl-substituted homobenzofuran **26**, however, behaved in a different manner. It proved stable at 160°, well above the temperature at which **12**/**27** and **14**/**28** epimerize. After 50 min at 180°, only trace amounts of **30** were detected by TLC. At 200°, **26** rearranged to **30** in 86% yield.

Presumably, the diastereoisomeric cyclopropanes are thermally equilibrated *via* the oxonium ylide **C** [22] and not by β-elimination/β-addition (*cf.* [16], *Scheme 4*). This hypothesis is consistent with the thermal stability of **26**, which would have to equilibrate *via* an oxonium ylide lacking the stabilization by the Ph substituent.

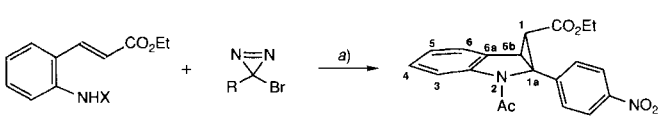
In the ^{1}H-NMR spectrum of **27**, H–C(1) resonates at 2.42 ppm and Me–C(6b) at 1.86 ppm. In the ^{13}C-NMR spectrum, the Me–C(6b) signal at 16.10 ppm is shifted downfield. The chemical shifts of **27** parallel those of **18** and differ from those of **12** (*Tables 1* and *3*), demonstrating that **18** and **27** possess the same configuration. The configuration of **14** and **28** is clear from a comparison of the ^{13}C-NMR data of Me–C(6b) at 10.30 ppm for **14** and at 15.59 ppm for **28** with those for **17** and **18** (*Table 3*).

The K band (316 nm, ε 10243) in the UV spectrum of **29** suggests a longer conjugated system for **29** than for **12**. The ^{13}C-NMR data (7*d* and 5*s* of sp^2 –C signals and a *d* at 77.79 ppm for C(2)) suggest a Ph-substituted chromene structure. In the ^{1}H-NMR spectrum, there is a long-distance coupling (J = 1.1 Hz) between Me–C(4) and H–C(2). The easy loss of the COOEt group in the MS and the unconjugated ester C=O band in the IR spectrum at 1735 cm^{-1} suggest a conjugated Ph rather than a conjugated ester group. NOE experiments did not provide convincing evidence for the substitution pattern of the Ph and COOEt groups as shown in **29** (only 1% enhancement of Ph–C(3) from the irradiation of Me–C(4), *Table 4*), but the absence of a second *s* between 150 and 160 ppm (compare with **9**) is only consistent with a β,γ-unsaturated ester. The structure is confirmed by the transformation of **29** into the primary alcohol **31**. The OH group of **31** is indicated by the IR and the ^{1}H-NMR spectrum (1.91 ppm, *dd*, J = 3.6, 9.1, exchangeable with D_2O). H–C(2) (5.09 ppm) couples with Me–C(4) (J = 1.3 Hz) and CH_2–C(2). A typical geminal J value (12.2 Hz) is observed for the two protons of CH_2 group. The nearly identical UV absorption pattern of **31** and **29** supports the substitution pattern of **29**. The hypso- and hypochromic effect in the UV spectrum of **30** is due to the change from a Ph to a Me group. The ^{1}H-NMR spectrum of **30** shows that the two Me *s* at 2.00 and at 1.97 ppm are attached to the C=C bond, but do not couple with H–C(2) (*s* at 5.06 ppm). The ^{13}C-NMR spectrum indicates three Me groups appearing at 16.89, 13.97, and 13.01 ppm; C(2) resonates at 77.23 ppm. The small values for $J(2,3) = 3.2$ and $J(3,4) = 6.3$ Hz agree with the expected (all-*cis*)-configuration of **32** and a half chair conformation [23].

The formation of **29** can be rationalized by a disrotatory opening of the cyclopropane ring of **12** (*Scheme 4*), leading to the intermediate **D**, followed by electrocyclization [24]. The disrotatory opening of **27** leading to **E** is unlikey on account of the interaction of the two bulky groups at C(1) and C(8).

The application to the synthesis of homoindoles was examined by treating the *o*-aminocinnamate **33** [25] and its *N*-acetyl derivative **34** with the diazirines **2** and **10**. The amine **33** did not react with **2** in the presence of a weak base such as Et_3N or pyridine. Strong base (BuLi) led to a complex mixture of products. While the *N*-acetyl derivative **34** reacted with **2** in the presence of dimsyl sodium to give at best (as indicated by TLC)

Scheme 5



33 X = H
34 X = Ac

2 R = Ph
10 R = 4-$O_2NC_6H_4$

35

a) 1.2 equiv. of $NaCH_2S(O)CH_3$, **34**, DMSO/THF 1:1, 0° for 10 min, 1.2 equiv. of **10**, 0° for 4 min; 82%.

small amounts of homoindoles, it yielded rapidly 82% of the homoindole **35**, when **2** was replaced by its nitro analogue **10**. The presence of 2 equiv. of 1,3-dinitrobenzene reduced the yields of **35** to 47% only. This is in keeping with an $S_{RN}1$ mechanism, which has been evidenced for the azide-halide exchange of halodiazirines [15], but the weak effect of the single-electron-transfer inhibitor [26] does not permit to exclude a (competitive) S_N2' process.

The structure of **35** is evidenced by the IR spectrum which shows a NO_2 band at 1520 cm^{-1} and C=O absorptions at 1725 and 1680 cm^{-1}. The ^{1}H-NMR spectrum shows the typical *trans*-coupling (J(1,6b) = 4.7 Hz) [19] for the vicinal cyclopropane H-atoms. The ^{13}C-NMR spectrum shows a quaternary C-atom *s* for C(1a) at 57.40 ppm.

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Experimental Part

General. Solvents were distilled before use. DMPU was distilled over CaH_2 and then twice in a *Kugelrohr* apparatus *in vacuo* (*i.v.*). Normal workup means distribution of the crude product between the indicated org. solvent and H_2O, drying of the org. layer ($MgSO_4$), filtration, and evaporation of the filtrate *i.v.* at or below 40° in a *Büchi* rotary evaporator. TLC: *Merck* silica gel *60F-254* plates, detection by heating with 0.02M I_2 and 0.30M KI in 20% of H_2SO_4. Flash chromatography (FC): silica gel *Merck 60* (0.04–0.063 mm). Prep. HPLC: *Spherisorb silica* (5 μm) 250 × 20 mm column, (UV (280 nm) detection, 16 ml/min). M.p.: uncorrected. IR: 3 or 4% $CHCl_3$ soln., unless indicated otherwise. UV: λ_{max} (ε) in nm. ^{1}H- and ^{13}C-NMR: chemical shifts δ in ppm and coupling constants J in Hz. The 4-nitrophenylamidine and 4-pyridylamidine salts were prepared from the corresponding nitriles [27]. Except for 3-chloro-3-(4-pyridyl)diazirine [28], all halodiazirines were prepared by the *Graham* reaction [14].

4-Methylcoumarin [8]. A mixture of **7** (500 mg, 3.67 mmol) and [(ethoxycarbonyl)methylene]triphenylphosphorane (2.10 g, 5.58 mmol) in toluene (10 ml) was heated to reflux overnight. Evaporation of the solvent and FC (hexane/Et_2O 2:1) gave a solid (605 mg), which was crystallized from Et_2O to give pure 4-methylcoumarin (370 mg). The mother liquor was treated with AcOEt and hexane to give another batch of pure 4-methylcoumarin (208 mg). Long, colorless needles (combined yield 98%, [8] 51%). R_f (hexane/AcOEt 2:1) 0.51. M.p. 76–78° ([8]: 82°). IR: 2990*w*, 1700*s*, 1605*s*, 1570*w*, 1450*w*, 1385*m*, 1370*m*, 1320*w*, 1165*w*, 1155*w*, 1140*w*, 1070*m*, 1035*w*, 940*s*, 850*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.62 (*dd*, J = 1.5, 7.8, H–C(5)); 7.54 (*ddd*, J = 1.5, 7.3, 8.5, H–C(7)); 7.36–7.28 (*m*, H–C(6), H–C(8)); 6.31 (*q*, J = 1.2, H–C(3)); 2.45 (*d*, J = 1.3, Me–C(4)).

Ethyl (E)-3-(2-Hydroxyphenyl)but-2-enoate (**9**). A soln. of **7** (4.57 g, 33.60 mmol, recrystallized in hexane at –20° and [(ethoxycarbonyl)methylidene]triphenylphosphorane (20.00 g, 53.14 mmol) in benzene (85 ml) was heated under reflux for 6 h. Evaporation of the solvent and FC (hexane/Et_2O 5:2) gave a fraction (2.01 g) containing 4-methylcoumarin and **9**, from which **9** (0.64 g) was crystallized (Et_2O/hexane). HPLC (hexane/AcOEt 5:2) of the mother liquor (4.70 g) gave pure **9** (3.44 g, 58% combined yield) and 4-methylcoumarin (1.52 g, 28%).

Data of **9**: R_f (hexane/AcOEt 2:1) 0.42. t_R (hexane/AcOEt 5:2) 7.2 min. M.p. 91–93°. UV ($CHCl_3$): 263 (8790), 240 (8204). IR: 3550*m*, 3330*m*, 2990*m*, 1690*s*, 1630*s*, 1440*m*, 1370*w*, 1340*m*, 1275*s*, 1160*s*, 1100*m*, 1035*s*, 880*m*, 830*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.20 (*dt*, J = 1.5, 7.8, H–C(4')); 7.14 (*dd*, J = 1.7, 7.7, H–C(6')); 6.94–6.88 (*m*, H–C(3'), H–C(5')); 6.00 (*q*, J = 1.3, H–C(2)); 5.60 (br. *s*, exchangeable with D_2O, OH); 4.22 (*q*, J = 7.2, CH_3CH_2); 2.53 (*d*, J = 1.4, 3 H–C(4)); 1.31 (*t*, J = 7.1, CH_3CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.55 (*s*, C=O); 154.41 (*s*); 151.90 (*s*); 130.04 (*s*); 129.59 (*d*); 128.34 (*d*); 120.63 (*d*); 119.89 (*d*); 116.16 (*d*); 60.09 (*t*, CH_3CH_2); 20.11 (*q*, C(4)); 14.27 (*q*, CH_3CH_2). CI-MS: 207 (100, $[M + 1]^+$); 161 (30). Anal. calc. for $C_{12}H_{14}O_3$ (206.23): C 69.88, H 6.84; found: C 69.81, H 6.62.

3-Bromo-3-(4-nitrophenyl)diazirine (**10**). A mixture of 4-nitrophenylamidine hydrochloride (11.85 g, 58.78 mmol), LiBr (25 g), and DMSO (250 ml) was stirred, until the solids had dissolved and then pentane (200 ml) was added. A freshly prepared soln. of NaOBr (550 mmol in 420 ml of H_2O) was added, and the temp. was kept between 5° to 20°. Stirring was continued for 1 h at r.t., under gradual formation of an emulsion. The emulsion was filtered through SiO_2, which was washed with Et_2O. Normal workup (pentane, brine) and FC (pentane/Et_2O 100:1.5) of

the residue (5.11 g) gave **10** (2.80–4.05 g, 20–29%). An anal. sample (fine, colorless needles) was obtained by crystallization from hexane at −70°. R_f (hexane/Et_2O 100:1.5) 0.18. UV (CH_2Cl_2): 376 (521), 369 (578), 360 (687), 343 (653), 306 (716). IR (CH_2Cl_2): 3105*w*, 1605*w*, 1580*m*, 1530*s*, 1350*s*, 1320*w*, 1110*w*, 1015*m*, 1000*m*, 880*w*, 870*w*, 840*s*. ^{1}H-NMR (300 MHz, CD_2Cl_2): 8.33–8.22 (*m*, H–C(3'), H–C(5')); 7.35–7.28 (*m*, H–C(2'), H–C(6')). ^{13}C-NMR (50 MHz, CD_2Cl_2): 147.65 (*s*, C(4')); 142.66 (*s*, C(1')); 127.67 (*d*, C(3'), C(5')); 123.44 (*d*, C(2'), C(6')); 36.03 (*s*, C(3)). CI-MS: 244 (8, $[M + 3]^+$), 242 (9, $[M + 1]^+$), 218 (8), 217 (28), 216 (100), 215 (30), 214 (95), 200 (9), 199 (6), 198 (9), 193 (6), 170 (7), 169 (11), 167 (11), 151 (13), 150 (20), 134 (14). Anal. calc. for $C_7H_4BrN_3O_2$ (242.0): C 34.73, H 1.66, N 17.35; found: C 34.63, H 1.47, N 17.40.

*Ethyl 1a,6b-Dihydro-*c*-1a-phenyl-1*H*-cyclopropa[*b*]benzofuran-*r*-1-carboxylate* (**5**). At r.t., a soln. of NaOEt (1 equiv.) in EtOH (10 ml) was treated with **1** (1.92 g, 10 mmol). After dissolution of **1**, the mixture was taken to dryness. A soln. of **2** (1.96 g, 10 mmol) in dry hexane (17.3 ml) was added in one portion to a soln. of the Na salt of **1** in dry DMF (10 ml) under Ar at r.t. The yellow color of the DMF layer changed to deep red within 30 s and became purple after stirring overnight. Normal workup (Et_2O, 1M cold aq. NaOH) and FC (hexane/Et_2O 10:1.5) of the purple oil (3.78 g) gave **5** (2.28 g, 82%). Colorless oil. R_f (hexane/Et_2O 10:1.5) 0.25. UV ($CHCl_3$): 279 (4739), 240 (3108). IR: 3030*m* (sh), 2980*m*, 1720*s*, 1615*w* (sh), 1595*m*, 1475*s* (sh), 1460*s*, 1450*m* (sh), 1400*m*, 1370*s*, 1330*s*, 1150*m*, 1135*s*, 1100*w*, 1060*m*, 1035*s*, 1025*s*, 1010*m*, 955*s*, 900*m*, 870*m*, 850*w*, 690*w*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3*. CI-MS: 281 (100, $[M + 1]^+$), 207 (14). Anal. calc. for $C_{18}H_{16}O_3$ (280.31): C 77.12, H 5.75; found: C 77.33, H 5.76.

*Ethyl 1a,6b-Dihydro-*c*-6b-methyl-*c*-1a-phenyl-1*H*-cyclopropa[*b*]benzofuran-*r*-1-carboxylate* (**12**). Under Ar, a soln. of **2** (778 mg, 3.97 mmol) in dry hexane (8 ml) was added in one portion to a soln. of the Na salt of **9** (prepared from **9** (900 mg, 4.369 mmol) similarly as described above for **1**) in dry DMF (7 ml) at r.t. Stirring was continued for 12 h. Normal workup (Et_2O, 1M cold. aq. NaOH) and FC (hexane/AcOEt 100:3) gave **12** (895 mg) and an impure fraction of **12** (62 mg). HPLC (hexane/AcOEt 100:3) yielded an additional crop of **12** (20 mg, combined yield 79%). An anal. sample was obtained from Et_2O/pentane at −20°. Cubic crystals. R_f (hexane/AcOEt 100:3) 0.3. t_R (hexane/AcOEt 100:3) 8.2 min. M.p. 54°. UV ($CHCl_3$): 280 (4490), 240 (2858). IR: 3020*w*, 2980*m*, 2940*w*, 1720*s*, 1600*w*, 1450*s*, 1370*m*, 1340*s*, 1280*m*, 1160*s*, 1110*w*, 1090*w*, 1075*w*, 1030*s*, 970*s*, 920*m*, 910*m*, 860*m*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3* CI-MS: 295 (100, $[M + 1]^+$), 263 (3), 221 (21). Anal. calc. for $C_{19}H_{18}O_3$ (294.33): C 77.52, H 6.16; found: C 77.40, H 6.32.

*Methyl 1a,6b-Dihydro-*c*-1a-(4-nitrophenyl)-1*H*-cyclopropa[*b*]benzofuran-*r*-1-carboxylate* (**13**) *and Methyl 2-(4-Nitrophenyl)benzofuran-3-acetate* (**19**). A soln. of **10** (0.60 g, 2.48 mmol) in dry hexane (10 ml) was added in one portion to a soln. of the Na salt of **8** (from 0.51 g (2.90 mmol) of **8**) in dry DMF (10 ml) under Ar at 0°. The cooling bath was removed after 5 min, the mixture was allowed to warm to r.t. overnight. Normal workup (Et_2O, 1M cold aq. NaOH) and FC (hexane/AcOEt 10:3) of the residue (1.20 g) gave a crude product (1.10 g), from which **19** (105 mg) crystallized by addition of Et_2O/hexane as long, yellow needles. The mother liquor was concentrated, filtered through SiO_2 (hexane/Et_2O 5:1), and twice subjected to HPLC (hexane/Et_2O 5:1), producing **13** (493 mg, 64%) and **19** (7 mg, combined yield 15%).

Data of **13**: R_f (hexane/Et_2O 5:1) 0.25. t_R (hexane/Et_2O 5:1) 13.4 min. UV ($CHCl_3$): 277 (14466). IR: 3020*w*, 2980*w*, 2950*w*, 1720*s*, 1600*m*, 1520*s*, 1465*m*, 1440*m*, 1345*s*, 1160*w*, 1140*s*, 1100*w*, 1070*s*, 1040*w*, 1015*m*, 965*m*, 880*w*, 850*s*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3*. EI-MS: 311 (40, M^+), 294 (10), 280 (22), 264 (5), 253 (17), 252 (100, $[M - CO_2Me]^+$), 207 (9), 206 (63), 205 (32), 194 (9), 178 (6), 177 (6), 176 (14), 165 (9), 152 (7), 151 (8), 150 (8), 102 (5), 89 (6), 88 (7), 76 (13), 75 (6), 74 (8). Anal. calc. for $C_{17}H_{13}NO_5$ (311.3): C 65.59, H 4.20, N 4.50; found: C 65.39, H 4.10, N 4.32.

Data of **19**: R_f (hexane/Et_2O 5:1) 0.22. t_R (hexane/Et_2O 5:1) 13.7 min. M.p. 159–161°. UV ($CHCl_3$): 359 (26469), 250 (19091). IR: 3030*w*, 2950*m*, 2825*w*, 1735*s*, 1600*s*, 1510*m*, 1430*w*, 1330*s*, 1095*s*, 1060*m*, 1005*m*, 955*w*, 850*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.36 (*td*, J = 2.4, 9.0, H–C(3'), H–C(5')); 8.07 (*td*, J = 2.3, 9.1, H–C(2'), H–C(6')); 7.68 (*ddd*, J = 0.7, 1.5, 7.7, H–C(4)); 7.55 (*td*, J = 1.0, 8.4, H–C(7)); 7.41 (*ddd*, J = 1.5, 7.4, 8.4, H–C(6)); 7.33 (*dt*, J = 1.1, 7.4, H–C(5)); 3.93 (*s*, CH_2); 3.77 (*s*, Me). ^{13}C-NMR (50 MHz, (D_6)acetone): 171.13 (*s*, C=O); 155.07 (*s*, C(7a)); 150.85 (*s*, C(2)); 137.16 (*s*); 130.61 (*s*); 128.49 (*d*, C(3'), C(5')); 126.91 (*d*); 124.90 (*d*, C(2'), C(6')); 124.18 (*d*); 121.35 (*d*); 113.68 (*s*, C(3)); 112.04 (*d*); 52.54 (*q*, Me); 30.69 (CH_2). EI-MS: 312 (11, $[M + 1]^+$), 311 (69, M^+), 253 (10), 252 (70), 235 (5), 207 (16), 206 (100), 205 (60), 178 (19), 177 (13), 176 (28), 165 (12), 152 (10), 151 (12), 150 (6), 139 (5), 76 (8), 75 (6), 55 (6), 43 (6), 41 (7). Anal. calc. for $C_{17}H_{13}NO_5$ (311.3): C 65.59, H 4.20, N 4.50; found: C 65.50, H 3.91, N 4.30.

*Ethyl 1a,6b-Dihydro-*c*-6b-methyl-*c*-1a-(4-nitrophenyl)cyclopropa[*b*]benzofuran-*r*-1-carboxylate* (**14**). Under Ar, the Na salt of **9** (from 500 mg (2.43 mmol) of **9**) was added to a stirred mixture of **10** (489 mg, 2.02 mmol), hexane (20 ml), and dry DMF (10 ml) in a −12° cooling bath. The cooling bath was removed after 5 min, and the mixture was allowed to warm to r.t. overnight. Normal workup (Et_2O, 1M aq. NaOH) and FC (hexane/AcOEt

20:1) of the residue (0.69 g) gave **14** (0.57 g, 83%). Colorless oil. R_f (hexane/AcOEt 20:1) 0.19. UV ($CHCl_3$): 276 (14678). IR: 3020*w*, 2980*w*, 2940*w*, 1720*s*, 1600*s*, 1520*s*, 1460*s*, 1345*s*, 1280*w*, 1160*s*, 1100*w*, 1090*w*, 1030*s*, 1010*m*, 975*m*, 910*m*, 850*s*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3*. EI-MS: 294 (2, $[M - OEt]^+$), 267 (18), 266 (100, $[M - CO_2Et]^+$), 221 (8), 220 (30, $[M - CO_2Et - NO_2]^+$), 219 (6), 205 (8). Anal. calc. for $C_{19}H_{17}NO_5$ (339.3): C 67.25, H 5.05, N 4.13; found: C 67.30, H 4.92, N 3.91.

*Methyl 1a,6b-Dihydro-*c*-1a-(4-pyridyl)cyclopropa[*b*]benzofuran-*r*-1-carboxylate* (**15**). Under Ar, a mixture of the Na salt of **8** (from 102 mg (0.575 mmol) of **8**), 3-Å molecular sieves, DMPU (15 ml), and **11** (60 mg, 0.40 mmol) was stirred at r.t. overnight. Normal workup (Et_2O, 1M aq. NaOH) and FC (Et_2O/hexane/Et_3N 30:20:1) of the residue (410 mg) gave **15** (71 mg, 68%). Colorless syrup. R_f (Et_2O/hexane/Et_3N 30:20:1) 0.25. IR: 2960*m*, 1720*s*, 1600*m*, 1460*m*, 1440*m*, 1350*s*, 1140*m*, 1100*w*, 1065*m*, 1040*w*, 1010*m*, 970*w*, 910*m*, 880*w*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3*. CI-MS: 269 (14, $[M + 2]^+$), 268 (100, $[M + 1]^+$), 208 (19, $[M - CO_2Me]^+$). Anal. calc. for $C_{16}H_{13}NO_3$ (267.3): C 71.90, H 4.90, N 5.24; found: C 71.94, H 5.07, N 5.40.

*Ethyl 1a,6b-Dihydro-*c*-6b-methyl-*c*-1a-(4-pyridyl)cyclopropa[*b*]benzofuran-*r*-1-carboxylate* (**16**). Under Ar, a mixture of the Na salt of **9** (from 1.150 g (5.58 mmol) of **9**), **11** (868 mg, 5.66 mmol), hexane (15 ml), and DMF (10 ml) was stirred and cooled in an ice-bath. TLC showed completion of the reaction in 3.5 h. Normal workup (Et_2O, 1M aq. NaOH) and FC (hexane/Et_2O/Et_3N 33:66:2) of the residue (1.50 g) gave a fraction containing traces of impurity which were removed by HPLC (hexane/Et_2O/Et_3N 33:66:2) to give **16** (1.035 g, 63%). R_f (hexane/Et_2O/Et_3N 33:66:2) 0.35. t_R (hexane/Et_2O/Et_3N 33:66:2) 10.6 min. M.p. 66–67° (Et_2O/hexane). UV ($CHCl_3$): 278 (6213), 240 (5540). IR: 2990*s*, 1720*s*, 1600*s*, 1555*w*, 1480*s*, 1465*m*, 1410*m*, 1385*w*, 1370*w*, 1340*s*, 1280*m*, 1158*s*, 1110*w*, 1090*m*, 1070*w*, 1040*s*, 980*w*, 910*m*, 860*m*, 830*w*, 820*m*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3*. EI-MS: 266 (11, $[M - Et]^+$), 223 (17), 222 (100, $[M - CO_2Et]^+$), 220 (8), 115 (7). Anal. calc. for $C_{18}H_{17}NO_3$ (295.33): C 73.20, H 5.80, N 4.74; found: C 73.20, H 6.00, N 4.66.

*1a,6b-Dihydro-*c*-6b-methyl-*c*-1a-phenylcyclopropa[*b*]benzofuran-*r*-1-carboxylic Acid* (**17**) *and 1a,6b-Dihydro-*t*-6b-methyl-*t*-1a-phenylcyclopropa[*b*]benzofuran-*r*-1-carboxylic Acid* (**18**). A soln. of **12** (300 mg, 1.13 mmol) and KOH (172 mg, 3.38 mmol) in abs. EtOH (40 ml) and H_2O (4 ml) was kept at reflux for 0.5 h. The soln. was concentrated *i.v.* at 40° to *ca.* 5 ml and neutralized with dil. HCl. Normal workup (Et_2O, brine) and crystallization (Et_2O/hexane 4:1) of the colorless residue (310 mg) gave **18** (163 mg). Cubic crystals. HPLC (hexane/Et_2O/AcOH 200:100:3) of the mother liquor yielded **17** (75 mg, 28%) and an additional crop of **18** (23 mg, total yield 69%).

Data of **17**: R_f (hexane/Et_2O/AcOH 200:100:3) 0.49. t_R (hexane/Et_2O/AcOH 200:100:3) 5.2 min. M.p. 181° (hexane/CH_2Cl_2). UV ($CHCl_3$): 280 (3447), 241 (5688). IR: 3515*w*, 3500–2500*s* (br.), 1695*s*, 1600*m*, 1480*s*, 1465*m*, 1450*s*, 1380*w*, 1320*w*, 1280*m*, 1170*w*, 1125*w*, 1110*m*, 1085*s*, 1070*m*, 1040*m*, 1010*m*, 980*s*, 920*m*, 900*m*, 860*w*, 820*w*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3*. CI-MS: 267 (100, $[M + 1]^+$). Anal. calc. for $C_{17}H_{14}O_3$ (266.28): C 76.67, H 5.30; found: C 76.69, H 5.50.

Data of **18**: R_f (hexane/Et_2O/AcOH 200:100:3) 0.48. t_R (hexane/Et_2O/AcOH 200:100:3) 6.2 min. M.p. 153° (hexane/Et_2O). UV ($CHCl_3$): 280 (5635), 241 (3737). IR: 3500–2500*m* (br.), 1710*s*, 1600*m*, 1480*s*, 1450*s*, 1280*m*, 1115*m*, 1070*w*, 1025*w*, 1015*w*, 845*w*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3*. CI-MS: 267 (100, $[M + 1]^+$). Anal. calc. for $C_{17}H_{14}O_3$ (266.28): C 76.67, H 5.30; found: C 76.95, H 5.40.

*Methyl (*E*)-3-(2-Methoxyphenyl)prop-2-enoate* (**21**) *and Methyl 1a,6b-Dihydro-*c*-1a-methylcyclopropa[*b*]benzofuran-*r*-1-carboxylate* (**22**). *a*) Under Ar, **20** (0.51 g, 5.67 mmol) and the Na salt of **8** (from 1.85 g (9.25 mmol) of **8**, dried in high vacuum for 12 h) were added in turn to a mixture of hexane (15 ml), DMF (15 ml), and 3-Å molecular sieves at −70° (bath temp.). The mixture was stirred overnight, during which time the temp. rose to 10°. Normal workup (Et_2O, 1M aq. NaOH) and FC (hexane/Et_2O 20:1) of the residue (0.92 g) gave **21** (508 mg, 42%) and **22** (102 mg, 10%) as colorless oils.

b) Under Ar, **20** (0.47 g, 2.35 mmol) was added to a cooled (−60°) soln. of the Na salt of **8** (from 0.322 g (3.558 mmol) of **8**, dried for 24 h in high vacuum) in DMPU (10 ml) and THF (5 ml). The mixture was stirred for 3.5 h at −15° and checked with TLC (only a small amount of **22** had formed). The mixture was kept for 2 d at r.t. Normal workup (Et_2O, brine) and FC (hexane/Et_2O 20:1) of the residue (0.55 g) gave **21** (90 mg, 19%) and **22** (252 mg, 53%).

Data of **21**: R_f (hexane/Et_2O 20:1) 0.14. UV ($CHCl_3$): 322 (6504), 281 (9842). IR (neat): 3080*w*, 3000*w*, 2950*s*, 2920*m*, 2840*m*, 1720*s*, 1630*m*, 1600*m*, 1580*w*, 1490*m*, 1470*m*, 1440*m*, 1320*m*, 1295*m*, 1270*m*, 1240*m*, 1160*m*, 1120*w*, 1110*m*, 1050*m*, 990*m*, 940*w*, 870*m*, 780*m*, 750*s*, 720*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.01 (*d*, *J* = 16.2, H–C(3)); 7.51 (*dd*, *J* = 1.6, 7.7, H–C(6′)); 7.35 (*ddd*, *J* = 1.6, 7.6, 8.5, H–C(4′)); 6.96 (*dd*, *J* = 7.3, 7.8, H–C(5′)); 6.92 (*d*, *J* = 8.3, H–C(3′)); 6.56 (*d*, *J* = 16.2, H–C(2)); 3.89, 3.81 (2*s*, 2 Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.40 (*s*, C=O); 159.34 (*s*, C(2′)); 140.51 (*d*); 132.86 (*d*); 129.62 (*d*); 123.93 (*s*, C(1′)); 121.77 (*d*); 119.16 (*d*); 112.60 (*d*); 56.40, 52.11 (2*q*, 2 Me).

Data of **22**: R_f (hexane/Et_2O 20:1) 0.17. UV ($CHCl_3$): 280 (4327). IR: 2840*w*, 1720*s*, 1600*w*, 1460*m*, 1440*m*, 1375*m*, 1330*s*, 1140*s*, 1100*m*, 1010*w*, 970*m*, 910*w*, 870*w*, 850*m*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table*

3. EI-MS: 204 (6, M^+), 146 (19), 145 (100, $[M - CO_2Me]^+$), 144 (5), 115 (15). Anal. calc. for $C_{12}H_{12}O_3$ (204.22): C 70.57, H 5.92; found: C 70.79, H 6.17.

*Ethyl (*E*)-3-[2-(1-Aziethoxy)phenyl]but-2-enoate* (**25**) *and Ethyl 1a,6b-Dihydro-*c*-1a,6b-dimethylcyclopropa[*b*]benzofuran-*r*-1-carboxylate* (**26**). *a*) Under Ar, **20** (0.40 g, 2.35 mmol) was added to a cooled (−70°) mixture of DMF (20 ml), hexane (5 ml), and the Na salt of **9** (from 0.42 g (1.84 mmol) of **9**). The mixture was stirred for 3.5 h at −25° (bath temp.), diluted with cold Et_2O (−25°) and washed with brine (0°). Dyring ($MgSO_4$), evaporation at r.t. (without water bath), and FC (pentane/Et_2O 100:1, column cooled to −25°, fractions evaporated as above) of the residue gave **25** (210 mg, 44%) and **26** (56 mg, 13%).

b) Under Ar, **20** (1.34 g, 14.8 mmol) was added to a cooled (−60°) mixture of DMF (35 ml), hexane (20 ml), 3-Å molecular sieves, and the Na salt of **9** (from 1.74 g (5.83 mmol) of **9**). The mixture was stirred at −60° (bath temp.) and the temp. was allowed to rise to 10° overnight. Normal workup (Et_2O, 1M aq. NaOH) and FC (pentane/Et_2O 100:1) of the residue (1.36 g) gave **26** (435 mg) and a mixture of **25** and **26** (480 mg) as colorless oils. Storing the mixture for 2 d at −20° converted the remaining **25** into **26** (440 mg, combined yield 65%).

Data of **25**: R_f (hexane/Et_2O 100:1) 0.12. IR: 2980*m*, 2940*m*, 1710*s*, 1640*m*, 1600*w*, 1570*w*, 1485*m* (sh), 1445*m*, 1390*w*, 1375*m*, 1340*m*, 1320*w*, 1170*m*, 1110*m*, 1070*w*, 1040*m*, 1010*w*, 995*w*, 940*m*, 880*w*, 840*m*. ^{1}H-NMR (300 MHz, $CDCl_3$, 233 K): 7.58 (*dd*, J = 0.7, 8.2, H–C(6′)); 7.39 (*ddd*, J = 1.8, 7.5, 8.3, H–C(5′)); 7.15 (*dd*, J = 1.8, 7.6, H–C(3′)); 7.07 (*dt*, J = 0.9, 7.4, H–C(4′)); 5.78 (*q*, J = 1.5, H–C(2)); 4.16 (*q*, J = 7.1, CH_3CH_2); 2.37 (*d*, J = 1.2, 3 H–C(4)); 1.29 (*t*, J = 7.2, CH_3CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$, 233 K): 166.58 (*s*, C=O); 155.85 (*s*, C(2′)); 148.77 (*s*); 133.31 (*s*, C(3)); 129.44 (*d*); 129.39 (*d*); 122.83 (*d*); 119.27 (*d*); 114.99 (*d*); 60.03 (*t*, CH_3CH_2); 53.48 (*s*, CN_2); 19.91, 17.29 (2*q*, 2 Me); 14.11 (*q*, CH_3CH_2).

Data of **26**: R_f (hexane/Et_2O 100:1) 0.22. UV ($CHCl_3$): 281 (4687). IR: 2960*m*, 2930*w*, 2880*w*, 1715*s*, 1615*w*, 1600*w*, 1480*m*, 1460*w*, 1390*w*, 1375*m*, 1345*m*, 1325*m*, 1310*w*, 1280*w*, 1260*m*, 1185*w*, 1160*w*, 1150*w*, 1120*s*, 1045*w*, 1015*w*, 940*m*, 890*w*, 840*w*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3*. EI-MS: 187 (< 5, $[M - OEt]^+$), 160 (11), 159 (100, $[M - CO_2Et]^+$), 115 (7), 91 (5), 29 (6), 27 (3). Anal. calc. for $C_{14}H_{16}O_3$ (232.27): C 72.39, H 6.94; found: C 72.32, H 7.10.

Thermolysis of **12** *in DMPU. a*) Under Ar, a soln. of **12** (730 mg, 2.48 mmol) in DMPU (3 ml) was heated at 120° for 24 h. The mixture was cooled and workup up normally (Et_2O, brine). Filtration of the Et_2O layer through SiO_2 (hexane/Et_2O 5:1) gave an oil (0.90 g). HPLC (hexane/AcOEt 20:1) yielded **12** (279 mg, 40%), **27** (364 mg, 50%), and **29** (39 mg, 5%).

b) A soln. of **12** (600 mg) in DMPU (5 ml) was heated under Ar to 195–200° until disappearence of **12** (8 h). After cooling, normal workup (Et_2O, brine) and FC (hexane/Et_2O 100:3) of the residue (0.85 g) gave **29** (565 mg, 94%).

*Data of Ethyl 1a,6b-Dihydro-*t*-6b-methyl-*t*-1a-phenylcyclopropa[*b*]benzofuran-*r*-1-carboxylate* (**27**): R_f (hexane/Et_2O 10:3.5) 0.44. t_R (hexane/AcOEt 20:1) 6.7 min. UV ($CHCl_3$): 280 (2439), 241 (4183). IR: 2980*m*, 2930*w*, 2870*w*, 1730*s*, 1620*w*, 1600*m*, 1480*s*, 1470*w*, 1450*s*, 1385*w*, 1280*s*, 1160*s*, 1115*w*, 1100*w*, 1080*m*, 1050*w*, 1035*w*, 1020*w*, 1015*m*, 950*w*, 850*w*, 840*m*, 690*m*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3*. EI-MS: 222 (16), 221 (100, $[M - CO_2Et]^+$), 220 (6), 219 (8), 205 (4), 203 (3), 202 (10), 192 (3), 191 (9), 190 (7), 189 (6), 178 (8), 177 (4), 176 (4), 165 (4), 115 (5). Anal. calc. for $C_{19}H_{18}O_3$ (294.33): C 77.52, H 6.16; found: C 77.28, H 6.33.

*Data of Ethyl 4-Methyl-3-phenyl-2*H*-1-benzopyran-2-carboxylate* (**29**). Colorless oil. R_f (hexane/Et_2O 100:3) 0.09. t_R (hexane/AcOEt 20:1) 7.5 min. UV ($CHCl_3$): 316 (10243), 276 (10951), 243 (15737). IR: 2980*m*, 1735*s*, 1600*w*, 1480*m*, 1450*m*, 1370*w*, 1350*w*, 1180*w*, 1110*m*, 1075*m*, 1015*m*, 980*w*, 855*w*. ^{1}H-NMR (400 MHz, (D_6)acetone): 7.45–7.30 (*m*, Ph); 7.32–7.30 (*m*, irrad. at 7.19→*d*, J = 6.9; irrad. at 6.95→br. *s*, H–C(5)); 7.19 (*dt*, $J \approx 1.6$, 7.8, irrad. at 6.95→*dd*, J = 1.0, 7.9, H–C(7)); 6.95 (*dt*, J = 1.1, 7.5, irrad. at 7.19→*dd*, J = 1.0, 7.0, H–C(6)); 6.90 (*dd*, J = 1.1, 8.0, irrad. at 7.19→*d*, J = 0.7; irrad. at 6.95→*d*, $J \approx 6.9$, H–C(8)); 5.52 (*q*, = 1.1, H–C(2)); 3.98–3.88 (*m*, CH_3CH_2); 1.97 (*d*, J = 1.1, Me–C(4)); 0.96 (*t*, J = 7.2, CH_3CH_2). ^{13}C-NMR (50 MHz, (D_6)acetone): 169.70 (*s*, C=O); 153.80 (*s*, C(8a)); 139.25 (*s*); 130.32 (*d*); 129.92 (*d*); 129.49 (*s*); 129.11 (*d*); 128.25 (*d*); 127.71 (*s*); 125.23 (*d*); 124.60 (*s*); 122.34 (*d*); 116.62 (*d*); 77.79 (*d*, C(2)); 61.27 (*t*, CH_3CH_2); 14.85, 14.19 (2*q*, Me–C(4), CH_3CH_2). CI-MS: 297 (20, $[M + 3]^+$), 295 (100, $[M + 1]^+$), 263 (2), 221 (23), 161 (3). Anal. calc. for $C_{19}H_{18}O_3$ (294.33): C 77.52, H 6.16; found: C 77.77, H 6.00.

Thermal Equilibration of **12** *and* **27** *at 120°. a*) Under Ar, a soln. of **27** (27 mg) in DMPU (0.5 ml) was heated to 120° for 24 h. Cooling of the soln., normal workup (Et_2O, brine), and filtration of the Et_2O layer through SiO_2 (hexane/Et_2O 5:1) gave an oil (22 mg), which was analyzed by ^{1}H-NMR (**12**/**27** 37:63). HPLC (hexane/AcOEt 20:1) gave **12** (6 mg, 22%) and **27** (13 mg, 48%).

b) Neat **27** (20 mg) was heated under Ar to 120°. Samples were taken after 60 h and 74 h and analyzed by ^{1}H-NMR showing a **12**/**27** ratio of 43:57 and 44:56, respectively. Similarly, neat **12** (20 mg) was transformed into **12**/**27** (42:58 after 60 h, and 44:56 after 74 h).

Base-Catalyzed Equilibration of **12** *and* **27**. *a*) A soln. of **12** (100 mg) and NaOEt (15 mg) in DMF (5 ml) was stirred for 12 h at r.t. Normal workup (Et_2O, brine) gave crude **12**/**27** (106 mg, 37:63 (^{1}H-NMR)). FC (hexane/Et_2O 20:1) gave **12** (34 mg, 34%) and **27** (48 mg, 48%).

b) A soln. of **27** (30 mg) and NaOEt (5 mg) in DMF (1.5 ml) was stirred at r.t. for 12 h. Normal workup (Et_2O, brine) and prep. TLC (hexane/Et_2O 20:1) of the residue (32 mg) gave **12** (10 mg, 33%) and **27** (16 mg, 53%).

Equilibration of **14** *and* **28**. *a*) A soln. of **14** (285 mg) in DMPU (2.5 ml) was kept under Ar for 48 h at 120°. After cooling, normal workup (Et_2O, brine) and FC (hexane/Et_2O 5:1) of the residue (320 mg) gave **28** (142 mg, 50%) and an impure fraction of **14**. HPLC yielded pure **14** (80 mg, 28%).

b) A soln. of **28** (22 mg) in DMPU (0.5 ml) was kept under Ar for 20 h at 120°. After cooling, normal workup (Et_2O, brine) and filtration of the Et_2O layer through SiO_2 (hexane/Et_2O 5:1) gave crude **14**/**28** (16 mg, 1:2 (^{1}H-NMR)). HPLC (hexane/AcOEt 20:1) gave **14** (3 mg, 14%) and **28** (6 mg, 27%).

*Data of Ethyl 1a,6b-Dihydro-*t*-6b-methyl-*t*-1a-(4-nitrophenyl)cyclopropa[*b*]benzofuran-*r*-1-carboxylate* (**28**): R_f (hexane/Et_2O 5:1) 0.27. t_R (hexane/Et_2O 5:1) 6.2 min. UV ($CHCl_3$): 283 (12945), 239 (5307, sh). IR: 3030*w*, 2990*w*, 2930*w*, 2870*w*, 1730*s*, 1605*s*, 1520*s*, 1480*s*, 1470*w*, 1390*w*, 1350*s*, 1280*m*, 1160*m*, 1130*w*, 1090*w*, 1080*w*, 1050*w*, 1025*w*, 1010*m*, 855*s*, 840*w*. ^{1}H-NMR: see *Tables 1 and 2*. ^{13}C-NMR: see *Table 3*. EI-MS: 294 (< 5, $[M - OEt]^+$), 267 (11), 266 (63, $[M - CO_2Et]^+$), 222 (16), 221 (100, $[M - CO_2Et - NO_2 + 1]^+$), 220 (30, $[M - CO_2Et - NO_2]^+$), 219 (7), 205 (12), 201 (12), 169 (10), 75 (42), 74 (24), 58 (44). Anal. calc. for $C_{19}H_{17}NO_5$ (339.3): C 67.25, H 5.05, N 4.13; found: C 67.53, H 4.99, N 3.93.

*Ethyl 3,4-Dimethyl-3-phenyl-2*H*-1-benzopyran-2-carboxylate* (**30**). Under Ar, a soln. of **26** (116 mg) in DMPU (5 ml) was heated to 195–200°, until **26** had disappeared (5 h). Normal workup (Et_2O, brine) and filtration of the Et_2O layer through SiO_2 (hexane/Et_2O 50:1) gave an oily residue (105 mg). Prep. TLC (hexane/CH_2Cl_2 1:1) gave **30** (90 mg, 86%). R_f (hexane/CH_2Cl_2 100:3) 0.45. UV ($CHCl_3$): 308 (5060), 266 (5081), 241 (9416). IR: 2990*m*, 2920*m*, 2880*w*, 1720*s*, 1600*w*, 1480*m*, 1450*m*, 1360*w*, 1140*w*, 1070*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.18–6.89 (*m*, 4 arom. H); 5.06 (*s*, H–C(2)); 4.18–4.08 (*m*, CH_3CH_2); 2.00, 1.97 (2*s*, Me–C(2), Me–C(3)); 1.20 (*t*, J = 7.1, CH_3CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.81 (*s*, C=O); 152.23 (*s*, C(8a)); 128.24 (*d*); 124.95 (*s*); 123.42 (*s*); 123.25 (*d*); 122.45 (*s*); 121.28 (*d*); 115.53 (*d*); 77.23 (*d*, C(2)); 60.97 (*t*, CH_3CH_2); 16.89, 13.97, 13.01 (3*q*, 3 Me). CI-MS: 234 (14), 233 (100, $[M + 1]^+$), 232 (6), 201 (11), 199 (5), 160 (9), 159 (95, $[M - CO_2Et]^+$). Anal. calc. for $C_{14}H_{16}O_3$ (232.27): C 72.39, H 6.94; found: C 72.66, H 7.12.

*(4-Methyl-3-phenyl-2*H*-1-benzopyran-2-yl)methanol* (**31**). A stirred soln. of **29** (100 mg, 0.34 mmol) in Et_2O (5 ml) was treated at 0° with $LiAlH_4$ (110 mg, 2.9 mmol). Stirring was continued at 0° for 20 min. After slow addition of AcOEt, the mixture was filtered through SiO_2, and eluted with AcOEt. Evaporation of the filtrate and prep. TLC (hexane/Et_2O 100:3) of the residue (88 mg) gave 31 (75 mg, 85%). R_f (hexane/Et_2O 100:3) 0.73. UV ($CHCl_3$): 316 (8599), 276 (8647), 242 (13330). IR: 3600*m*, 3070*w*, 3000*w*, 2960*w*, 2920*w*, 2870*w*, 1640*w*, 1600*m*, 1575*w*, 1485*s*, 1450*m*, 1380*m*, 1320*s*, 1300*w*, 1130*m*, 1110*m*, 1030*m*, 1020*m*, 965*m*, 890*m*, 860*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.43–7.25 (*m*, 6 arom H); 7.19 (*dt*, J = 1.6, 7.7, H–C(7)); 6.98 (*dt*, J = 1.3, 7.6, H–C(6)); 6.93 (*dd*, J = 1.1, 8.0, H–C(8)); 5.09 ('*qdd*', J = 1.3, 2.7, 8.4, H–C(2)); 3.75 (*ddd*, J = 3.3, 8.4, 11.9; after addn. of $D_2O \rightarrow$ *dd*, J = 8.4, 12.2; irrad. at 5.09 → *d*, J = 12.3, CH_a–C(2)); 3.46 (*ddd*, J = 2.7, 9.0, 12.0; after addn. of $D_2O \rightarrow$ *dd*, J = 2.7, 12.2; irrad. at 5.09 → *d*, J = 12.3, CH_b–C(2)); 1.97 (*d*, J = 1.3; irrad. at 5.09 → *s*, Me–C(4)); 1.91 (*dd*, J = 3.6, 9.1, exchangeable with D_2O, OH). ^{13}C-NMR: 151.32 (*s*, C(8a)); 138.09 (*s*); 130.44 (*s*); 128.97 (3*d*); 128.44 (2*d*); 127.42 (*d*); 126.67 (*s*); 124.21 (*s*); 124.05 (*d*); 121.42 (*d*); 116.20 (*d*); 80.06 (*d*, C(2)); 61.97 (*t*, CH_2); 14.53 (*q*, Me – C(4)). CI-MS: 254 (8), 253 (44, $[M + 1]^+$), 252 (5), 251 (6), 236 (18), 235 (100, $[M - OH]^+$), 222 (13), 221 (77, $[M - CO_2Et]^+$), 209 (6). Anal. calc. for $C_{14}H_{16}O_3$ (252.3): C 80.92, H 6.39; found: C 81.19, H 6.50.

*Ethyl c-4-Methyl-c-3-phenyl-2*H*-1-benzopyran-2-carboxylate* (**32**). A mixture of **29** (70 mg, 0.24 mmol) and 10% Pd/C (7 mg) in AcOEt (10 ml) was vigorously stirred under a static H_2 atmosphere at r.t. overnight. Filtration through *Celite* and evaporation of the filtrate gave **32** (71 mg, 100%). Colorless oil. R_f (hexane/Et_2O 10:1) 0.22. IR: 3030*w*, 2990*m*, 2930*m*, 2880*m*, 1760*s*, 1730*s*, 1610*w*, 1580*m*, 1490*s*, 1455*s*, 1450*s*, 1370*m*, 1340*w*, 1310*w*, 1270*s*, 1140*s*, 1105*s*, 1080*w*, 1065*w*, 1030*s*, 950*w*, 940*w*, 865*m*, 835*m*, 695*w*. ^{1}H-NMR (300 MHz, C_6D_6): 7.16–6.80 (*m*, 9 arom. H); 4.72 (*d*, J = 3.1, H–C(2)); 3.83–3.76 (*m*, CH_3CH_2); 3.28 (*dd*, J = 3.0, 6.3, H–C(3)); 3.04 ('*dq*', J = 6.2, 6.8, H–C(4)); 0.91 (*d*, J = 6.9, Me–C(4)); 0.71 (*t*, J = 7.1, CH_3CH_2). ^{13}C-NMR (50 MHz, CD_3CN): 169.65 (*s*, C=O); 154.58 (*s*, C(8a)); 137.59 (*s*); 130.89 (*d*); 128.89 (*d*); 128.68 (*d*); 128.25 (*d*); 128.13 (*d*); 127.24 (*s*); 122.70 (*d*); 116.99 (*d*); 78.06 (*d*, C(2)); 61.66 (*t*, CH_3CH_2); 46.59, 33.78 (2*d*, C(3), C(4)); 17.03 (*q*, Me–C(4)); 14.42 (*q*, CH_3CH_2). EI-MS: 297 (19), 296 (100, M^+), 223 (23, $[M - CO_2Et]^+$), 221 (6), 208 (5), 207 (11), 178 (9), 177 (12), 176 (8), 148 (6), 145 (6), 132 (5), 131 (33), 121 (10), 120 (100), 119 (5), 105 (21), 103 (14), 92 (8), 91 (54), 77 (12). Anal. calc. for $C_{19}H_{20}O_3$ (296.35): C 77.00, H 6.80; found: C 76.78, H 6.90.

*Ethyl 2-Acetyl-1a,6b-dihydro-*c*-1a-(4-nitrophenyl)cyclopropa[*b*]indole-*r*-1-carboxylate* (**35**). A suspension of NaH (172 mg, 60% in oil) in dry DMSO (10 ml) was heated for 1.5 h to 65–75° and cooled to r.t. An aliquot of this mixture (1.2 ml, 0.52 mmol) was added to a cold (0°) soln. of **34** (100 mg, 0.43 mmol) in THF (1.2 ml) under Ar. The

soln. turned yellow within 10 min. After the addition of **10** (124 mg, 0.51 mmol) in one portion, stirring was continued, until the evolution of N_2 had diminished (4 min) and the color of the mixture had turned violet. Pouring the mixture onto ice/Et_2O, normal workup (AcOEt, brine), and FC (CH_2Cl_2/hexane 5:1) of the residue (252 mg) gave **35** (122 mg, 82%). R_f (CH_2Cl_2) 0.3. M.p. 127–130° (Et_2O). IR: 3000*w*, 1725*s*, 1680*s*, 1610*m*, 1520*m*, 1485*m*, 1470*m*, 1375*s*, 1350*s*, 1320*s*, 1300*m*, 1155*m*, 1105*w*, 1050*w*, 1020*m*, 870*w*, 820*m*. ^{1}H-NMR: see *Tables 1* and *2*. ^{13}C-NMR: see *Table 3*. CI-MS: 367 (100, $[M + 1]^+$), 337 (52). Anal. calc. for $C_{20}H_{18}N_2O_5$ (366.38): C 65.56, H 4.95, N 7.65; found: C 65.75, H 5.11, N 7.81.

Inhibition Experiments with 1,3-Dinitrobenzene (DNB). As described above for the preparation of **35**, 3 parallel reactions were performed with a mixture of NaH in DMSO (3.6 ml, 0.17 mmol of NaH), a soln. of **34** (30 mg, 0.13 mmol) in THF (3.6 ml), and **10** (30 mg, 0.17 mmol). The first run (without DNB) gave **35** (37 mg, 78%). In the second run, DNB (10 mg, 0.065 mmol) was added before the addition of **10**. Similar processing of the mixture gave **34** (9 mg, 30%) and **35** (28 mg, 60%). In the third run, DNB (40 mg, 0.27 mmol) was added before the addition of **10**. Workup gave **34** (10 mg, 32%) and **35** (22 mg, 47%).

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