84. Thermal 1,6-Electrocyclization Reactions of Acceptor-Substituted 2,3-Divinyl-1*H*-indoles Yielding Functionalized Carbazoles

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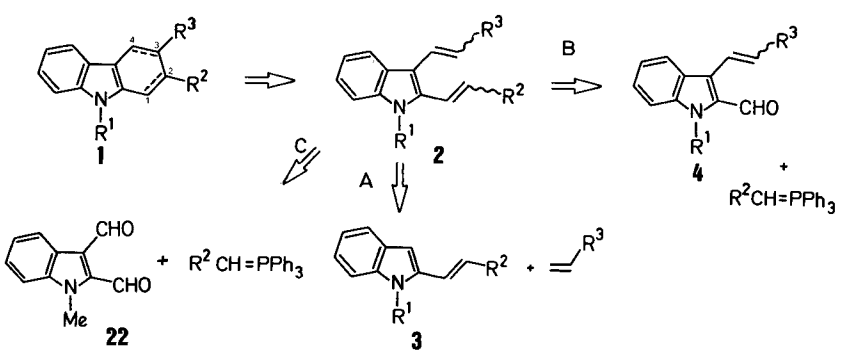
Three new synthetic procedures for and thermal 1,6-electrocyclizations of acceptor-substituted 2,3-divinyl-1*H*-indoles leading to functionalized carbazoles are described. The scope and limitations as well as some mechanistic aspects of the methodologies are discussed. The key strategies employed include Pd(II)-catalyzed coupling and *Wittig* procedures.

Introduction. – Acceptor- and donor-functionalized and/or annellated carbazoles and carbazole alkaloids have now attained considerable interest, since some representatives have been shown to exhibit antifungal, antibiotic, and antitumor activities [1–16]. Hence, there is still a major requirement for short and highly selective syntheses of these classes of heterocyclic compounds starting from readily available substrates. In this context, the *Diels-Alder* reactions of 2- and/or 3-vinyl-1*H*-indoles with C,C-dienophiles have been established as a highly efficient and attractive concept for convergent syntheses [5] [6]. An alternative pericyclic methodology should be provided by the thermally-induced, and also the photochemically-induced, 1,6-electrocyclization reactions of the selectively functionalized 2,3-divinyl-1*H*-indoles **2** to furnish the selectively functionalized carbazole derivatives **1**, as depicted in the retrosynthetic analysis *(Scheme 1)*.

The synthetic potential of this electrocyclization methodology has not yet been evaluated sufficiently (for the first realization of this strategy for the synthesis of hyellazole alkaloids, see [7] [8]). Thus, in continuation of the investigations reported in [9], we now describe the realization of the syntheses of 2,3-divinyl-1*H*-indoles **2** carrying accep-

Scheme 1

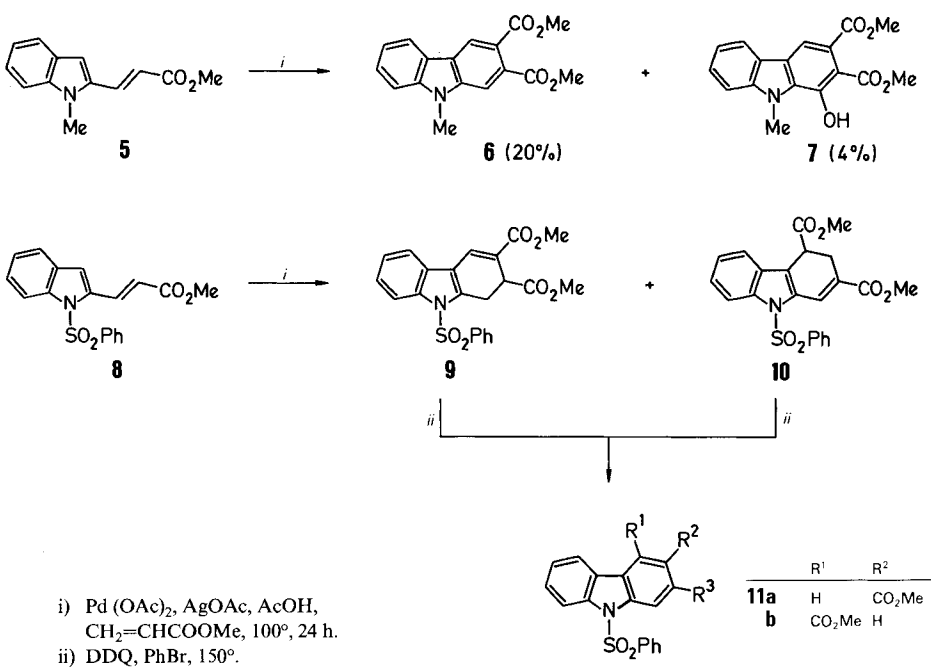


tor groups according *Scheme 1* and their 1,6-electrocyclizations to produce the carbazole derivatives **1**. We also include some further new experimental results and demonstrate the scope and limitations of this concept.

Results and Discussion. – As a consequence of their high-lying HOMO energy together with their high π-donor reactivity, 2,3-divinyl-1*H*-indoles **2** bearing donor groups at the vinyl moiety are not very stable and extremely difficult to purify, as has already been reported [7] [8]. We, therefore, directed our attention to the synthesis of acceptor-substituted derivatives of **2** which should be more stable. The syntheses of the previously unknown starting materials for the carbazoles **1**, namely the acceptor-substituted 2,3-divinyl-1*H*-indoles **2** (R^1 = Me, SO_2Ph, $R^2 = CO_2Me$, COMe, $R^3 = CO_2Me$, CN) were initially attempted by two routes (*Scheme 1*): *A*) the $Pd(OAc)_2$-catalyzed vinylation [10] [11] of 2-vinyl-1*H*-indoles **3** and *B*) the salt-free *Wittig* reaction of 3-vinyl-1*H*-indole-2-carbaldehydes **4** with appropriate ylides. A further alternative (*C*), the tandem *Wittig* reaction of a 1*H*-indole-2,3-dicarbaldehyde **22**, has also been tested, turning out to have only limited synthetic potential. In addition, some 2-phenyl-1*H*-indole-3-acrylates were synthesized to be used as formal 2,3-divinyl-1*H*-indole analogues.

Method A. We have found, however, that the Pd(II)-catalyzed coupling reactions of **5** and **8** with methyl acrylate gave rise to the novel carbazole derivatives **6**/**7** and **9**/**10** (3:1 by ^{1}H-NMR) directly in a one-pot procedure (*Scheme 2*). The product **7** was formed as the result of an auto-oxidation process (*cf.* [12]). The isomeric dihydrocarbazoles **9**/**10** could not be separated preparatively and were, thus, oxidized to **11a** and **11b**, respectively, by reaction with DDQ. According to MNDO calculations on the parent com-

Scheme 2

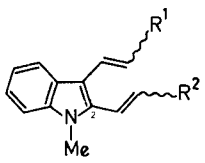


i) Pd $(OAc)_2$, AgOAc, AcOH, CH_2=CHCOOMe, 100°, 24 h.
ii) DDQ, PhBr, 150°.

	R^1	R^2	R^3	Yield [%]
11a	H	CO_2Me	CO_2Me	18
b	CO_2Me	H	CO_2Me	22

pounds, the 1,2-dihydrocarbazole structure is generally thermodynamically more stable than the 3,4-dihydrocarbazole structure (for MO calculations on vinylindoles, see [13]; see also compounds **19b**, **19e**, and **19g**).

Method B. From the *Wittig* reactions of suitable *N*-methylated 1*H*-indole-2-carbaldehydes **4** (*Method B, Scheme 1*) with acceptor-stabilized *Wittig* reagents ($Ph_3P{=}CH{-}CO_2Me$, $Ph_3P{=}CH{-}COMe$), the novel 2,3-divinylindoles **2a–e** were obtained in varying degrees of selectivity (for the selectivity of the *Wittig* reaction, see [14]).

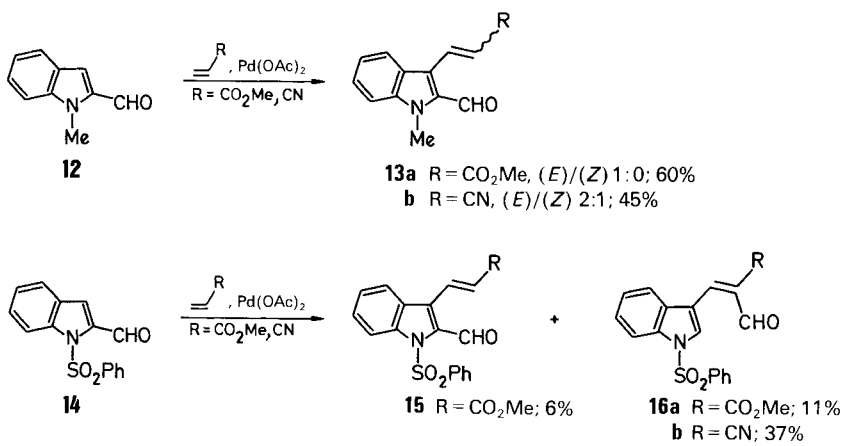


	R^1	R^2	Conf.[a])	Yield [%]
2a	CO_2Me	CO_2Me	(*E,E*)	43
b	CO_2Me	CO_2Me	(*Z,E*)	11
c	CO_2Me	MeCO	(*E,E*)	58
d	CN	CO_2Me	(*E,E*)	87
e	CN	CO_2Me	(*E,Z*)	65

[a]) In all cases, first configurational descriptor refers to the 2-vinyl group on the indole nucleus.

*Pd(II)-Catalyzed Coupling Reactions of 1*H*-Indole-2-carbaldehydes with Electron-Poor Alkenes and Mechanistic Considerations.* Compounds of the type **4** (*Scheme 1*) are readily and conveniently available by the Pd(II)-catalyzed coupling reactions of the appropriate 1*H*-indole-2-carbaldehydes. Thus, the substrates **13a** and **13b** were easily prepared from **12** (*Scheme 3*). However, in the case of the starting indole derivative **14**,

Scheme 3

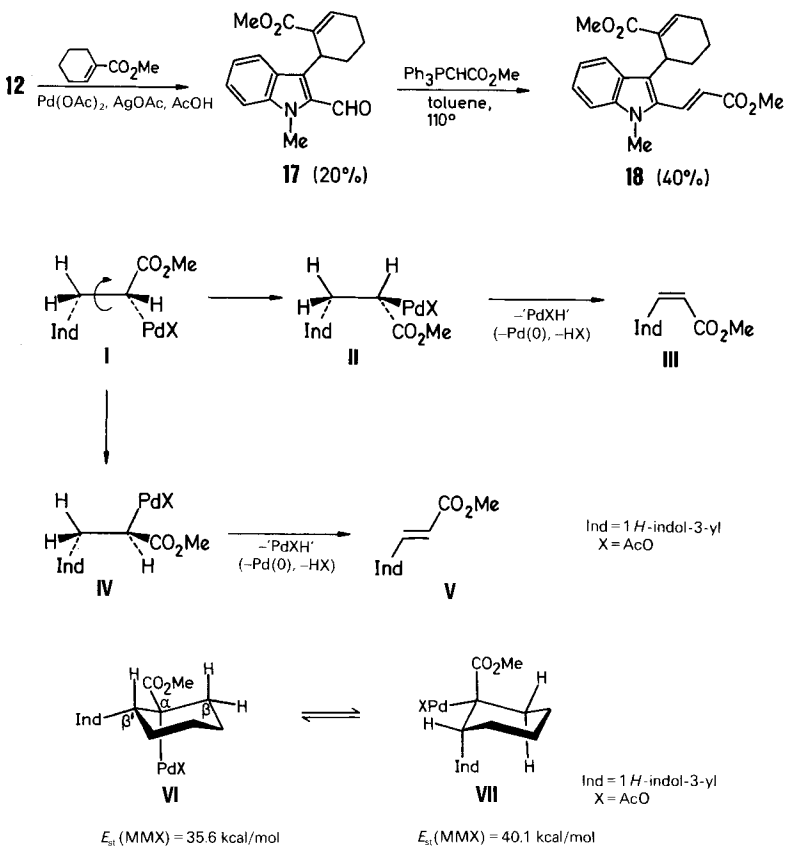


we obtained the unexpected products **16a** and **16b** from the coupling reactions with methyl acrylate and acrylonitrile, respectively (*Scheme 3*); only with methyl acrylate, the expected 'normal' product **15** was formed in addition to **16a**. It has yet not been possible to separate the mixture **15**/**16a** even by use of medium-pressure liquid chromatography (MPLC). These products were, however, characterized unambiguously on the basis of their 400-MHz ^{1}H-NMR spectra. The mechanism responsible for the formation of **16a**, **b**

is assumed to involve a Pd-induced CHO-group transfer to the C(β)-atom of the neighboring side chain.

Furthermore, we were able to extend the coupling methodology to include the reaction of **12** with methyl cyclohex-1-enecarboxylate as an electron-poor alkene *(Scheme 4)*

Scheme 4



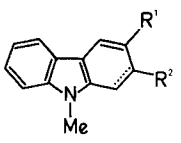
which yielded the product **17** exclusively. The purification of compound **17** was difficult due to its thermal instability. In addition to some diagnostically relevant 400-MHz ^{1}H-NMR spectral data, the assignment of the unexpected constitution of **17** was indirectly but convincingly supported by its conversion to **18** in a stereoselective, salt-free *Wittig* reaction. The position of the double bond in the cyclohexene moiety was then established in the more stable product **18**, principally with the help of ^{1}H-NMR-NOE analysis in conjunction with ^{13}C-NMR-APT techniques and ^{13}C-NMR simulation[1]).

[1]) The ^{13}C-NMR simulator program packet of the 'Visper' series from VCH-Verlagsgesellschaft, Weinheim, was used for the ^{13}C-NMR simulation.

In general, the mechanism of the above-mentioned Pd(II)-catalyzed olefination at C(3) of the indole moiety involves the formation of a new C–C bond *via* 1,2-addition of an (1*H*-indol-3-yl)palladium species to the highly polarized C=C bond of the acceptor-substituted olefin [15]. These assumptions are well established in the chemistry of other 1,2-additions of olefins in the presence of organopalladium reagents (for the mechanism of the Pd(II)-catalyzed coupling reaction and further synthetic applications, see [15]).

In the reactions of acyclic alkenes and indoles *via* the primarily formed indole-PdOAc species, the intermediates **I**, **II**, and **IV** *(Scheme 4)* need to be discussed for the equilibrium [15]. Only the conformers **II** and **IV** are able to undergo the assumed colinear *cis*-β-elimination of Pd/AcOH [15] to form the (*Z*)- and (*E*)-3-vinyl-1*H*-indoles **III** and **V**, respectively. However, in the case of the coupling reaction with the cyclic olefin, two conformers **VI** and **VII** are possible, as can be seen from observations of *Dreiding* models. According to MMX force-field calculations[2]), conformer **VI** is more stable than conformer **VII** ($\Delta E_{steric} = 4.5$ kcal·mol^{-1}); thus, the equilibrium shown in *Scheme 4* should lie on the left side. Moreover, a nearly co-linear 1,2-*cis*-elimination of Pd/AcOH in the α,β'-direction in **VII** is geometrically difficult, whereas the same elimination in the α,β'-direction from **VI** is completely impossible. We, thus, assume that the exclusively formed product **17** results from the energetically more favorable conformer **VI** *via* a 1,2-*cis*-elimination process in the α,β-direction[3]).

*Electrocyclization of 2,3-Divinyl-1*H*-indoles* **2**. In boiling PhBr and, in most cases, in the presence of Pd/C as a dehydrogenation catalyst, the 2,3-divinyl-1*H*-indoles **2a–e** underwent electrocyclization to furnish the functionalized carbazoles **19a–g** in yields of



	R^1	R^2
19a	CO_2Me	CO_2Me
b[a])	CO_2Me	CO_2Me
c	CO_2Me	COMe
d	CO_2Me	H
e[a])	CN	CO_2Me
f	CN	CO_2Me
g[a])	CO_2Me	COMe

[a]) 1,2-Dihydroderivatives.

7–84%. The 2,3-dihydrocarbazoles primarily anticipated from the 1,6-electrocyclization process are stabilized probably by subsequent [1,5]-H shifts and, in all cases, certainly by elimination of H_2. In the case of the electrocyclization of **2c** (R^1=CO_2Me, R_2=MeCO), an additional elimination of CH_3COH took place to produce compound **19d** along with the products **19c** and **19g**. In the cases of the electrocyclizations of **2a**/**2b** (R^1=R^2=CO_2Me), **2c**, and **2d**/**2e** (R^1=CN, R^2=CO_2Me), the more stable 1,2-dihydrocarbazoles **19b**, **19g**, and

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[2]) The MMX molecular-mechanics calculations are performed with the program PCMODEL-pi including pi-VESCF routines (*Serena Software Ltd.*, Bloomington, Indiana, USA). MMX version by *K.E. Gilbert* and *J.J. Gajewski* based on MM2 (*Allinger*, QCPE 395) and MMP1 Pi (*Allinger*, QCPE 318) modified by *K. Steliou*.

[3]) In the Pd(II)-catalyzed coupling reactions with other cyclic alkenes reported in [15], new isomeric coupling products were detected (varying positions of the double bond), thus, demonstrating that cyclic alkenes generally react in other elimination directions. However, in our case, the reaction of **12** with methyl cyclohex-1-enecarboxylate was regiospecific.

19e, respectively, could be isolated additionally. They were readily converted to the (14π)-carbazoles in the presence of Pd/C. Thus, we assume that the dihydro compounds represent the precursors of the fully aromatized carbazoles. On the other hand, we cannot rule out the possibility that the initially formed electrocyclization products can always react directly to the fully aromatic carbazoles.

The subsequent stabilization of the primarily and probably disrotatorily formed 2,3-dihydrocarbazoles from 1,6-electrocyclizations of **2** does not provide any relevant structural information about the stereochemistry for an analysis of a potential HOMO-controlled and, thus, orbital-symmetry-allowed process [16][4]). According to the FMO concept, a *cis*-2,3-disubstituted dihydrocarbazole is to be expected in the first step[4]). MMX force-field calculations[3]) [17] demonstrate that the ground-state (s-*Z*,s-*Z*)-conformation of the prepared (*E*,*E*)-2,3-divinyl-1*H*-indoles **2** is energetically more favored than the (s-*E*,s-*E*)-conformer (ΔE_{st} = 3 kcal·mol^{-1}). The MMX calculation, performed exemplarily for compound **2a**, reveals a transition state of the hexatriene unit which resembles a twisted half-chair conformation (*Fig. 2*; for transition states of electrocylizations, see [18]). Steric effects do not have a significant influence on the reactivity.

*Synthesis of Methyl 2-Phenyl-1*H*-indole-3-acrylates as Formal 2,3-Divinyl-1*H*-indole Analogues.* The 1,6-electrocyclizations of substituted arenes bearing olefinic groups are generally known but become operative above all in the photo-excited state (LUMO control)[5]). Thus, we have synthesized some previously unknown 2-aryl-3-vinyl-1*H*-indoles from 2-aryl-1*H*-indoles *via* the Pd(II)-catalyzed coupling methodology. The starting materials **20a–c** were readily prepared by the conventional *Fischer* method [20]. The $Pd(OAc)_2$-catalyzed reactions of **20a–c** gave rise to the expected products **21a–c** in moderate-to-low yields *(Scheme 5)*. The reaction of the bromo derivative **20b** additionally produced a small amount of a further coupling product **21d** in a side reaction.

However, in spite of several variations of the reaction conditions, the new compounds **21** could not be induced to undergo cyclization to furnish the desired annellated carbazole derivatives under thermal conditions (even at temperatures up to 240° in an autoclave).

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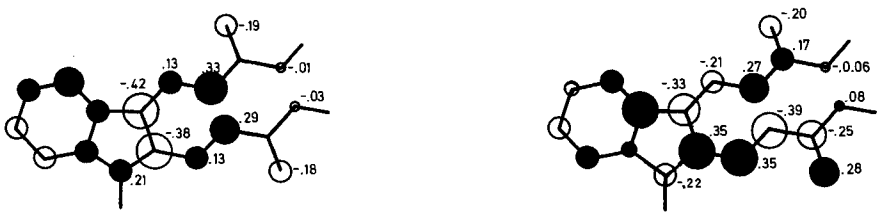
[4]) However, pi-VESCF calculations[2]) [17], exemplarily performed on compound **2a**, reveal a thermal, symmetry-allowed, HOMO-controlled disrotatory electrocyclization of the hexatriene subunit. The frontier molecular orbitals of interest are illustrated in *Fig. 1*.



$E_{HOMO} = -10.55$ eV $E_{LUMO} = -3.16$ eV

Fig. 1. *HOMO and LUMO orbitals with coefficients of* **2a** *according to pi-VESCF calculations*[2]) [17]. The geometry is optimized and a fully coplanar (s-*Z*,s-*Z*)-conformation is calculated throughout.

[5]) For the first photochemically induced electrocyclizations of 2-phenyl-3-vinyl-1*H*-indoles, see [19a]; for a related procedure, see [19b].

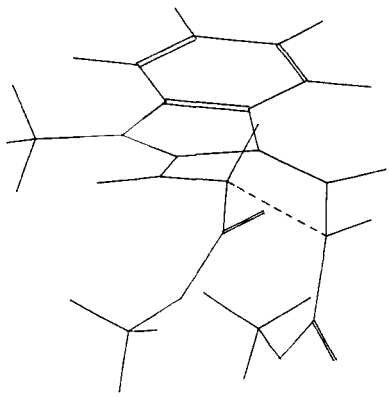
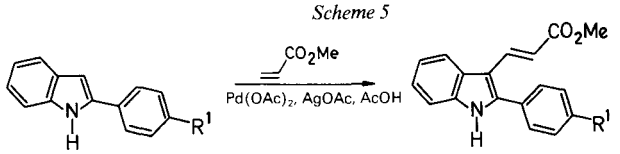


Fig. 2. *MMX Force-field-calculated transition-state geometry of* (E,E)-**2a**[2]). The starting ground-state conformation has (s-*Z*,s-*Z*)-geometry.

Scheme 5



20a R^1 = H
b R^1 = Br
c R^1 = MeO

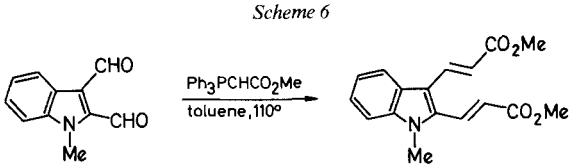
21a R^1 = H; 31%
b R^1 = Br; 31%
c R^1 = MeO; 34%
d R^1 = CH=CHCO$_2$Me (*E*); 2%

Photochemically-induced 1,6-electrocyclizations [19] should prove to be suitable procedures, and the experimental results of this photochemical variation will be reported later.

Method C. We have also repeated the known synthesis [21] of the 1*H*-indole-2,3-dicarbaldehyde **22** as an interesting building block and, under modified workup conditions, isolated the product in 92% yield. An exemplarily performed tandem *Wittig* reaction of **22**, acting as a formal conjugated 1,4-diketone, with [(methoxycarbonyl)methylidene]-(triphenyl)phosphorane furnished the 2,3-divinyl-1*H*-indole **2a** (already prepared as described above) stereoselectively (*Scheme 6*).

In conclusion, the present results illustrate the scope and limitations of the direct access to acceptor-substituted 2,3-divinyl-1*H*-indoles as well as their direct transformation to functionalized carbazoles having substitution patterns that are not easily obtainable by other methods [3] [4]. The Pd(II)-catalyzed, regiospecific vinylation of 3-unsubsti-

Scheme 6



22 **2a** (30%)

tuted 1*H*-indoles was extended, and the experimental results demonstrate that the coupling procedure tolerates the presence of vinyl, formyl, and aryl functions at C(2) of the indole without any problems. Furthermore, the synthesized 9*H*-carbazole derivatives represent highly interesting building blocks for the synthesis of carbazole alkaloids [1] and compounds for medicinal chemistry [2].

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Experimental Part

General. All reactions must be performed in highly pure, anh. solvents under inert atmospheres. Column chromatography (CC): silica gel *60* (*Merck*, 0.063–0.200-mm particle size). Flash chromatography (FC): silica gel *60* (*Merck*, 0.040–0.063-mm particle size). Petroleum ether (40–60°) with varying amounts of AcOEt was used as eluent. M.p.: *Büchi SMP 20*; not corrected. ^{1}H- and ^{13}C-NMR (100.6 MHz) spectra: *Bruker WM 200* and *Bruker WM 400* spectrometers, δ[ppm] scale, coupling constants J in Hz, TMS as internal standard. The constitutions of the compounds **7**, **11a**, **11b**, **16b**, **18**, **19a**, **19b**, and **19g** were unequivocally elucidated with the aid of ^{1}H, ^{1}H-NOE measurements using a 400-MHz NMR spectrometer. EI-MS (70 eV): *Varian MAT 7*, data given as m/z (%). C, H, N Analyses: *Carlo Erba Strumentazione.*

*Dimethyl (*E,E*)- and (*Z,E*)-3,3'-(1-Methyl-1*H*-indole-2,3-diyl)bis[prop-2-enoate]* (**2a** and **2b**, resp). *Method A.* Compound **13a** (see below; 1 g, 4.12 mmol) and [(methoxycarbonyl)methylidene](triphenyl)phosphorane (7.4 g, 22 mmol) were added to toluene (120 ml), and the mixture was heated under reflux for 3 h. The mixture was evaporated under vacuum to a volume of *ca.* 5 ml and the residue separated by CC using petroleum ether/AcOEt 4:1, yielding 665 mg (54%) of **2a**/**2b** 4:1 which could not be separated without decomposition occurring by further chromatographic procedures. Colorless crystals. M.p. of mixture 126–128° (petroleum ether). ^{1}H-NMR (**2a**; 400 MHz, (D_6)DMSO): 3.73 (*s*, CH_3N or CH_3O); 3.79 (*s*, CH_3N or CH_3O); 3.85 (*s*, CH_3N or CH_3O); 6.37 (*d*, J = 16.2, vinyl H); 6.51 (*d*, J = 15.9, vinyl H); 7.24 (*dd*, J = 7.5, 7.5, H–C(5) or H–C(6)); 7.37 (*dd*, J = 8.2, 8.2, H–C(6) or H–C(5)); 7.63 (*d*, J = 8.3, H–(4) or H–C(7)); 7.85 (*d*, J = 15.9, vinyl H); 7.89 (*d*, J = 16.1, vinyl H); 7.95 (*d*, J = 8, H–C(7) or H–C(4)). ^{1}H-NMR (**2b** as mixture with **2a**; 400 MHz, (D_6)DMSO): 3.5 (*s*, CH_3N or CH_3O); 3.75 (*s*, CH_3N or CH_3O); 6.16 (*d*, J = 12, vinyl H); 6.24 (*d*, J = 16, vinyl H); 7.12 (*dd*, J = 7.0, 7.1, H–C(5) or H–C(6)); 7.18 (*d*, J = 12, vinyl H); 7.2–7.3 (*m*, 2 H, H–C(4) or H–C(7), H–C(6) or H–C(5)); 7.56 (*d*, J = 8.3, H–C(7) or H–C(4)); 7.78 (*d*, J = 16, vinyl H). EI-MS: 299 (31, M^+), 286 (8), 240 (58), 208 (77), 182 (100). Anal. calc. for $C_{17}H_{17}NO_4$ (299.12): C 68.22, H 5.72, N 4.68; found: C 68.11, H 5.66, N 4.40.

*Method B. 1-Methyl-1*H*-indole-2,3-dicarbaldehyde* (**22**; 400 mg, 2.1 mmol) and [(methoxycarbonyl)-methylidene](triphenyl)phosphorane (1.2 g, 3.6 mmol) were dissolved in toluene (50 ml), and the soln. was heated under reflux for 2 h. Workup as described under *Method A* gave 190 mg (30%) of isomerically pure **2a**.

*Methyl (*E*)-3-[1-Methyl-2-(3-oxobut-1-enyl)-1*H*-indol-3-yl]prop-2-enoate* (**2c**). Compound **13a** (1 g, 4.12 mmol) and (acetylmethylidene)(triphenyl)phosphorane (2 g, 6.3 mmol) were suspended in toluene (120 ml) and heated under reflux for 2 h. The mixture was then concentrated to 5 ml and the residue separated by CC using petroleum ether/AcOEt 1:1: 680 mg (58%) of **2c**. Colorless crystals. M.p. 129° (hexane). ^{1}H-NMR (400 MHz, (D_6)DMSO): 2.43 (*s*, Ac); 3.72 (*s*, CH_3N or CH_3O); 3.85 (*s*, CH_3O or CH_3N); 6.5 (*d*, J = 16, vinyl H); 6.55 (*d*, J = 16.5, vinyl H); 7.24 (*dd*, J = 7.7, 7.6, H–C(5) or H–C(6)); 7.36 (*dd*, J = 7.3, 8.1, H–C(6) or H–C(5)); 7.62 (*d*, J = 8.3, H–C(4) or H–C(7)); 7.8 (*d*, J = 16.4, vinyl H); 7.87 (*d*, J = 16, vinyl H); 7.93 (*d*, J = 8.1, H–C(7) or H–C(4)). EI-MS: 283 (37, M^+), 240 (74), 208 (86), 182 (100). Anal. calc. for $C_{17}H_{17}NO_3$ (283.12): C 72.12, H 6.05, N 4.94; found: C 72.35, H 5.99, N 4.88.

*Methyl (*E,E*)- and (*E,Z*)-3-[3-(2-Cyanoethenyl)-1-methyl-1*H*-indol-2-yl]prop-2-enoate* (**2d** and **2e**, resp.). Compound **13b** (see below; 2:1 (*E*)/(*Z*)-mixture; 450 mg, 2.14 mmol) and [(methoxycarbonyl)-methylidene](triphenyl)phosphorane (1.8 g, 30 mmol) were suspended in toluene (50 ml) and heated under reflux for 3 h. The mixture was then concentrated to *ca.* 5–10 ml and the residue separated by CC using petroleum ether/AcOEt 3:2 yielding 484 mg (85%) of **2d**/**2e** 8.7:6.5 which could not be separated. Colorless crystals. M.p. of mixture 110–112° (hexane). ^{1}H-NMR (**2d**; 200 MHz, (D_6)DMSO): 3.8 (*s*, CH_3N or CH_3O); 3.83 (*s*, CH_3O or CH_3N); 6.24 (*d*, J = 16.5, vinyl H); 6.42 (*d*, J = 16.1, vinyl H); 7.2–7.4 (*m*, H–C(5), H–C(6)); 7.6–8.0 (*m*, arom. H, vinyl H). ^{1}H-NMR (**2e** as mixture with **2d**; 200 MHz, (D_6)DMSO): 3.78 (*s*, CH_3N or CH_3O); 3.89 (*s*, CH_3O or CH_3N); 5.90 (*d*, J = 11.8, vinyl H); 6.28 (*d*, J = 16, vinyl H); 7.2–7.4 (*m*, 2 H, H–C(5), H–C(6)); 7.6–8.0 (*m*, 4 H, arom. H, vinyl H). EI-MS: 266 (26, M^+), 235 (5), 207 (100), 197 (63). Anal. calc. for $C_{16}H_{14}N_2O_2$ (266.11): C 72.22, H 5.30, N 10.53; found: C 72.19, H 5.22, N 10.49.

Methyl (E)-3-(2-Formyl-1-methyl-1H-indol-3-yl)prop-2-enoate (**13a**). *1-Methyl-1H-indole-2-carbaldehyde* (**12**; 1.2 g, 7.5 mmol), methyl prop-2-enoate (1.95 g, 22.5 mmol), $Pd(OAc)_2$ (200 mg, 0.75 mmol), and AgOAc (2.55 g, 15 mmol) were suspended in AcOH (50 ml) and heated under reflux for 20 h. The mixture was then filtered, the solid washed with CH_2Cl_2, and the org. phase evaporated. The residue was taken up in a small amount of toluene and separated by FC using petroleum ether/AcOEt 7:2: 1.09 g (60%) of **13a**. Yellow crystals. M.p. 112° (AcOEt). ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.75 (*s*, CH_3N or CH_3O); 4.0 (*s*, CH_3O or CH_3N); 6.64 (*d*, J = 16.2, vinyl H); 7.29 (*dd*, J = 7.7, 7.3, H–C(5) or H–C(6)); 7.49 (*dd*, J = 7.9, 7.6, H–C(6) or H–C(5)); 7.68 (*d*, J = 8.5, H–C(4) or H–C(7)); 8.04 (*d*, J = 8.2, H–C(7) or H–C(4)); 8.35 (*d*, J = 16.1, vinyl H); 10.32 (*s*, CHO). EI-MS: 243 (10, M^+), 185 (100), 184 (84), 158 (53). Anal. calc. for $C_{14}H_{13}NO_3$ (243.09): C 69.17, H 5.39, N 5.76; found: C 68.98, H 5.29, N 5.39.

3-(2-Formyl-1-methyl-1H-indol-3-yl)prop-2-enenitrile (**13b**). Prepared analogously to **13a** from **12** (1.2 g, 7.5 mmol), prop-2-enenitrile (1.5 ml, 30 mmol), $Pd(OAc)_2$ (200 mg, 0.75 mmol), and AgOAc (2.55 g, 15 mmol). The residue obtained was separated by FC (petroleum ether/AcOEt 4:1): 710 mg (45%) of (*E*)-**13b** (separated from the (*Z*)-**13b** by fractional crystallization). Yellow crystals. M.p. 150° (Et_2O). ^{1}H-NMR ((*E*)-**13b**; 200 MHz, (D_6)DMSO): 4.04 (*s*, CH_3N); 6.47 (*d*, J = 16.3, vinyl H); 7.3 (*dd*, J = 7.5, 7.4, H–C(5) or H–C(6)); 7.49 (*dd*, J = 7.9, 7.6, H–C(6) or H–C(5)); 7.68 (*d*, J = 8.5, H–C(4) or H–C(7)); 8.11 (*d*, J = 8.2, H–C(7) or H–C(4)); 8.35 (*d*, J = 16.2, vinyl H); 10.32 (*s*, CHO). ^{1}H-NMR ((*Z*)-**13b** in mixture with the (*E*)-**13b**; 200 MHz, (D_6)DMSO): 4.08 (*s*, CH_3N); 6.11 (*d*, J = 12, vinyl H); 7.3 (*dd*, J = 7.5, 7.4, H–C(5) or H–C(6)); 7.49 (*dd*, J = 7.9, 7.6, H–C(6) or H–C(5)); 7.68 (*d*, J = 8.5, H–C(4) or H–C(7)); 7.83 (*d*, J = 8.7, H–C(7) or H–C(4)); 7.98 (*d*, J = 11.9, vinyl H); 10.15 (*s*, CHO). EI-MS: 210 (83, M^+), 182 (75), 181 (100), 154 (30), 140 (38). Anal. calc. for $C_{13}H_{10}N_2O$ (210.08): C 74.33, H 4.80, N 13.33; found: C 74.10, H 4.79, N 13.55.

Methyl (E)-3-[2-Formyl-1-(phenylsulfonyl)-1H-indol-3-yl]prop-2-enoate (**15**) *and Methyl (E)-2-Formyl-3-[1-(phenylsulfonyl)-1H-indol-3-yl]prop-2-enoate* (**16a**). Prepared as described above for **13a** from *1-(phenylsulfonyl)-1H-indole-2-carbaldehyde* (**14**; 1.14 g, 4 mmol), methyl prop-2-enoate (1.1 g, 12 mmol), $Pd(OAc)_2$ (50 mg, 0.4 mmol), and AgOAc (1.34 g, 8 mmol). The residue obtained was separated by FC (petroleum ether/AcOEt 3:1): 250 mg (17%) of **15**/**16a** 1:2 which could not be separated without decomposition. EI-MS: 369 (100, M^+). Anal. (for mixture) calc. for $C_{19}H_{15}NO_5S$ (369.16): C 61.82, H 4.10, N 3.79; found: C 61.89, H 4.05, N 3.66.

15: ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.75 (*s*, CH_3); 6.77 (*d*, J = 16.5, vinyl H); 7.31 (*dd*, J = 7.7, 7.3, H–C(5) or H–C(6)); 7.44–7.70 (*m*, H_p, H_m of $PhSO_2$); 7.74 (*dd*, J = 7.5, 7.5, H–C(6) or H–C(5)); 7.8 (*d*, J = 7.9, H_o of $PhSO_2$); 7.98 (*d*, J = 16.5, vinyl H); 8.01 (*d*, J = 8.1, H–C(4) or H–C(7)); 8.15 (*d*, J = 8.5, H–C(7) or H–C(4)); 10.52 (*s*, CHO).

16a: ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.74 (*s*, CH_3); 7.15 (*s*, vinyl H); 7.31 (*dd*, J = 7.7, 7.9, H–C(5) or H–C(6)); 7.44–7.70 (*m*, H–C(6) or H–C(5), H_p, H_m of $PhSO_2$); 7.8 (*d*, J = 7.9, H_o of $PhSO_2$); 7.89 (*d*, J = 8.4, H–C(4) or H–C(7)); 8.08 (*d*, J = 8.4, H–C(7) or H–C(4)); 8.3 (*s*, H–C(2)); 9.75 (*s*, CHO).

(Z)-2-Formyl-3-[1-(phenylsulfonyl)-1H-indol-3-yl]prop-2-enenitrile (**16b**). Prepared as described above for **13a** from **14** (1.14 g, 4 mmol), prop-2-enenitrile (673 mg, 12 mmol), $Pd(OAc)_2$ (90 mg, 0.4 mmol), and AgOAc (1.34 g, 8 mmol). The residue obtained was separated by FC (petroleum ether/AcOEt 7:2): 500 mg (37%) of **16b**. Yellow crystals. M.p. 156° (toluene). ^{1}H-NMR (400 MHz, (D_6)DMSO): 7.38 (*dd*, J = 7.9, 7.9 H–C(5) or H–C(6)); 7.53–7.61 (*m*, H_m, H_p of $PhSO_2$); 7.68 (*dd*, J = 7.1, 7.1, H–C(6) or H–C(5)); 7.82 (*d*, J = 7.9, H–C(4)); 7.88 (*d*, J = 8.25, H_o of $PhSO_2$); 8.02 (*s*, vinyl H); 8.17 (*d*, J = 8.8, H–C(7)); 8.96 (*s*, H–C(2)); 9.76 (*s*, CHO). ^{13}C-NMR (100.6 MHz, (D_6)DMSO): 112.85 (quat. C); 114.25 (quat. C); 114.90; 120.15 (CN); 123.67; 125.28; 126.58; 128.74 (quat. C); 129.18; 129.87, 132.20 (quat. C); 135.17; 135.96 (quat. C); 146.94; 157.98; 188.83 (CHO). EI-MS: 336 (30, M^+), 285 (19), 221 (11), 195 (100), 180 (22), 167 (23). Anal. calc. for $C_{18}H_{12}N_2O_3S$ (336.06): C 64.33, H 3.60, N 8.34; found: C 63.99, H 3.48, N 8.03.

Methyl 6-(2′-Formyl-1′-methyl-1′H-indol-3′-yl)cyclohex-1-enecarboxylate (**17**). Prepared as described above for **13a** from **12** (1.2 g, 7.5 mmol), methyl cyclohex-1-enecarboxylate (3.2 g, 22.5 mmol), $Pd(OAc)_2$ (200 mg, 0.75 mmol), and AgOAc (2.55 g, 15 mmol). The residue obtained was separated by FC (petroleum ether/AcOEt 3:1): 450 mg (20%) of **17**. Colorless crystals. M.p. 112° (hexane). ^{1}H-NMR (200 MHz, (D_6)DMSO): 1.66–1.74 (*m*, H_α–C(4), H_β–C(4)); 1.80–1.89 (*m*, H_α–C(5) or H_β–C(5)); 2.0–2.2 (*m*, H_β–C(5) or H_α–C(5)); 2.3–2.5 (*m*, H_α–C(3), H_β–C(3)); 3.4 (*s*, CH_3); 4.0 (*s*, CH_3); 4.66 (br. *s*, H–C(6)); 7.06 (*dd*, J = 7.1, 7.8, H–C(5′) or H–C(6′)); 7.17–7.40 (*m*, H–C(6′) or H–C(5′), H–C(2)); 7.53 (*d*, J = 8.6, H–C(4′) or H–C(7′)); 7.66 (*d*, J = 7.9, H–C(7′) or H–C(4′)); 10.24 (*s*, CHO). EI-MS: 297 (58, M^+), 268 (100), 236 (60), 208 (35), 175 (32). Anal. calc. for $C_{18}H_{19}NO_3$ (297.14): C 72.76, H 6.45, N 4.71; found: C 72.59, H 6.39, N 4.68.

Dimethyl 9-Methyl-9H-carbazole-2,3-dicarboxylate (**6**≡**19a**). *Method A: Methyl 3-(1-methyl-1H-indol-2-yl)prop-2-enoate* (**5**; 1.075 g, 5 mmol), methyl prop-2-enoate (1.3 g, 15 mmol), $Pd(OAc)_2$ (0.12 g, 0.5 mmol), and AgOAc (1.7 g, 10 mmol) were suspended in AcOH (40 ml), and the mixture was heated under reflux for 24 h. After

filtration and washing of the solid with CH_2Cl_2, the residue from the org. phase was separated by FC (petroleum ether/AcOEt 7:2): 300 mg (20%).

Method B: Compound **2a** (400 mg, 1.34 mmol) was dissolved in PhBr (50 ml) containing 10% Pd/C (200 mg), and the mixture was heated under reflux for 6 h. The concentrated residue was then separated by FC (petroleum ether/AcOEt 7:2): 30 mg (7.5%). Colorless crystals. M.p. 138° (AcOEt) [22]. ^{1}H-NMR (200 MHz, (D_6)DMSO): 3.86 (*s*, CH_3O); 3.95 (*s*, CH_3N); 7.30 (*dd*, J = 7.2, 7.6, H–C(6) or H–C(7)); 7.58 (*dd*, J = 7.1, 8.1, H–C(7) or H–C(6)); 7.7 (*d*, J = 8.2, H–C(5) or H–C(8)); 7.9 (*s*, H–C(1) or H–C(4)); 8.34 (*d*, J = 7.8, H–C(8) or H–C(5)); 8.68 (*s*, H–C(4) or H–C(1)). EI-MS: 297 (71, $M^{+\cdot}$), 266 (100), 251 (14). Anal. calc. for $C_{17}H_{15}NO_4$ (297.10): C 68.73, H 5.09, N 4.71; found: C 68.68, H 5.15, N 4.79.

*Dimethyl 1-Hydroxy-9-methyl-9*H*-carbazole-2,3-dicarboxylate* (**7**). Compound **5** (1.08 g, 5 mmol), methyl prop-2-enoate (1.3 g, 15 mmol), $Pd(OAc)_2$ (0.12 g, 0.5 mmol), and AgOAc (1.7 g, 10 mmol) were suspended in AcOH (40 ml), and the mixture was heated under reflux for 24 h. Workup as described above for **13a** gave a residue which was taken up in toluene and separated by FC (petroleum ether/AcOEt 7:2): 63 mg (4%) of **7**. Colorless crystals. M.p. 164° (AcOEt). ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.83 (*s*, CH_3O); 3.84 (*s*, CH_3O); 4.17 (*s*, CH_3N); 7.27 (*dd*, J = 7.3, 7.5, H–C(6) or H–C(7)); 7.54 (*dd*, J = 7.6, 7.7, H–C(7) or H–C(6)); 7.64 (*d*, J = 8.3, H–C(8)); 8.24 (*d*, J = 7.8, H–C(5)); 8.3 (*s*, H–C(4)); 9.98 (*s*, OH, exchangeable with D_2O). EI-MS: 313 (43, $M^{+\cdot}$), 281 (100), 266 (30), 223 (57), 190 (70). Anal. calc. for $C_{17}H_{15}NO_5$ (313.09): C 65.22, H 4.83, N 4.47; found: C 65.48, H 4.56, N 4.38.

*Dimethyl 1,2-Dihydro-9-(phenylsulfonyl)-9*H*-carbazole-2,3-dicarboxylate* (**9**) *and Dimethyl 3,4-Dihyro-9-(phenylsulfonyl)-9*H*-carbazole-2,4-dicarboxylate* (**10**). Prepared as described above for **13a** from **8** (950 mg, 2.8 mmol), methyl prop-2-enoate (720 mg, 8.4 mmol), $Pd(OAc)_2$ (63 mg, 0.28 mmol), and AgOAc (935 mg, 5.6 mmol). The residue obtained was taken up in a small volume of toluene and separated by FC (petroleum ether/AcOEt 3:1): 480 mg (40%) of **9**/**10** 3:1 (by ^{1}H-NMR) which could not be separated. EI-MS: 427 (30), 425 (20, $M^{+\cdot}$), 167 (100). Anal. calc. for $C_{22}H_{19}NO_6S$ (425.09): C 62.16, H 4,51, N 3.29; found: C 62.33, H 4.69, N 3.39.

9: ^{1}H-NMR (400 MHz, C_6D_6): 2.95 (*dd*, J = 18.6, 8.8, H_α–C(1)); 3.08 (*s*, CH_3); 3.53 (*s*, CH_3); 4.1 (*dd*, J = 7.9, 1.0, H_β–C(2)); 4.45 (*dd*, J = 18.6, 1.0, H_β–C(1)); 6.57–6.71 (*m*, H_p,H_m of $PhSO_2$); 6.93 (*dd*, J = 7.4, 7.5, H–C(6) or H–C(7)); 7.04–7.10 (*m*, H–C(5) or H–C(8), H–C(7) or H–C(6)); 7.82 (*s*, H–C(4)); 7.86 (*d*, J = 5.8, H_o of $PhSO_2$); 8.28 (*d*, J = 8.4, H–C(8) or H–C(5)).

*Dimethyl 9-(Phenylsulfonyl)-9*H*-carbazole-2,3-dicarboxylate* (**11a**). The mixture **9**/**10** (425 mg, 1 mmol) was dissolved in PhBr (40 ml). After addition of 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ; 450 mg, 2 mmol), the mixture was heated under reflux for 3 h, filtered through silica gel, evaporated, and the residue separated by FC (petroleum ether/AcOEt 3:1): 50 mg (18%) of **11a**. Colorless crystals. M.p. 176° (AcOEt). ^{1}H-NMR (400 MHz, C_6D_6): 3.58 (*s*, CH_3O); 3.59 (*s*, CH_3O); 6.46 (*dd*, J = 8.1, 6.6, H_m of $PhSO_2$); 6.53–6.57 (*m*, H_p of $PHSO_2$); 6.96 (*dd*, J = 7.5, 7.6, H–C(6) or H–C(7)); 7.19 (*dd*, J = 6.7, 6.8, H–C(7) or H–C(6)); 7.27 (*d*, J = 7.7, H–C(5)); 7.65–7.67 (*m*, H_o of $PhSO_2$); 8.06 (*s*, H–C(4)); 8.42 (*d*, J = 8.5, H–C(8)); 9.09 (*s*, H–C(1)). EI-MS: 423 (91, $M^{+\cdot}$), 392 (19), 283 (78), 251 (100), 205 (17). Anal. calc. for $C_{22}H_{12}NO_6S$ (432.08): C 62.46, H 2.86, N 3.31; found: C 62.35, H 2.79, N 3.26.

*Dimethyl 9-(Phenylsulfonyl)-9*H*-carbazole-2,4-dicarboxylate* (**11b**). Product **11b** was also formed in the preparation of **11a** using the same amounts of reactants and the same workup: 30 mg (22%) of **11b**. Colorless crystals. M.p. 212° (AcOEt). ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.98 (*s*, CH_3O); 3.99 (*s*, CH_3O); 7.46–7.52 (2 H_m, H_o, H_p of $PhSO_2$); 7.64 (*dd*, J = 7.77, 7.06, H–C(6) or H–C(7)); 7.72 (*dd*, J = 7.36, 8.4, H–C(7) or H–C(6)); 7.82 (*d*, J = 8.27, H_o of $PhSO_2$); 8.34 (*d*, J = 8.34, H–C(5) or H–C(8)); 8.42 (*s*, H–C(3)); 8.56 (*d*, J = 7.92, H–C(8) or H–C(5)); 9.14 (*d*, J = 1.1, H–C(1)). EI-MS: 423 (61, $M^{+\cdot}$), 283 (100), 251 (21). Anal. calc. for $C_{22}H_{17}NO_6S$ (423.08): C 62.46, H 2.86, N 3.31; found: C 62.19, H 2.72, N 3.18.

*Methyl (*E*)-3-{1′-Methyl-3′-[2″-(methoxycarbonyl)cyclohex-2″-en-1′-yl]-1′*H*-indol-2′-yl}prop-2-enoate* (**18**). Compound **17** (580 mg, 1.95 mmol) and [(methoxycarbonyl)methylidene](triphenyl)phosphorane (1.2 g, 3.6 mmol) were suspended in toluene (60 ml). The mixture was then heated under reflux for 3 h, evaporated, and the residue separated by CC (petroleum ether/AcOEt 5:1): 275 mg (40%) of **18**. Colorless crystals. M.p. 128–129° (hexane): ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.62–1.65 (*m*, H_α–C(5″), H_β–C(5″)); 1.73–1.76 (*m*, H_α–C(6″) or H_β–C(6″)); 1.93–1.98 (*m*, H_β–C(6″) or H_α–(6″)); 2.35–2.49 (*m*, H_α–C(4″), H_β–C(4″)); 3.4 (*s*, CH_3); 3.76 (*s*, CH_3); 3.80 (*s*, CH_3); 4.2 (*s*, H–C(1″)); 6.38 (*d*, J = 16.3, vinyl H); 6.97 (*dd*, J = 7.3, 7.7, H–C(5′) or H–C(6′)); 7.14 (*s*, H–C(3″)); 7.19 (*dd*, J = 7.4, 7.9, H–C(6′) or H–C(5′)); 7.44 (*d*, J = 8.4, H–C(7′)); 7.52 (*d*, J = 8,1, H–C(4′)); 7.87 (*d*, J = 16.2, vinyl H). ^{13}C-NMR (100.6 MHz, (D_6)DMSO): 19.5, 25.2, 30.9 (C(4″), C(5″), C(6″)); 31.3 (CH_3N); 32.0 (C(1″)); 51.2 (CH_3O); 51.5 (CH_3O); 110.2 (C(3″)); 117.9, 119.3, 120.2, 123.4 (C(4′), C(5′), C(6′) C(7′)); 122.2 (C(3′)); 125.9 (C(3′a)); 130.6 (C(2″)); 132.2 (C(2′)); 132.4 (C(3)); 138.6 (C(7′a)); 140.4 (C(2)); 166.6 (*C*OOCH$_3$);

166.7 ($COOCH_3$). EI-MS: 353 (100, M^+), 294 (32), 289 (30), 281 (32), 262 (55), 234 (67). Anal. calc. for $C_{21}H_{23}NO_4$ (353.16): C 71.42, H 6.56, N 3.97; found: C 71.33, H 6.29, N 3.73.

*Dimethyl 1,2-Dihydro-9-methyl-9*H*-carbazole-2,3-dicarboxylate* (**19b**). The mixture **2a**/**2b** (400 mg, 1.34 mmol) was dissolved in PhBr (50 ml) containing 10% Pd/C (200 mg) and heated under reflux for 6 h. After filtration and evaporation, the residue was separated by FC (petroleum ether/AcOEt 7:2): 112 mg (28%) of **19b**. When **2a**/**2b** (300 mg, 1 mmol) was heated under reflux in PhBr in the absence of Pd/C for 4 h, 220 mg (77%) of **19b** were obtained. Colorless crystals. M.p. 130° (AcOEt). ^{1}H-NMR (200 MHz, (D_6)DMSO): 3.22 (*dd*, J = 9.2, 17.7, H_α–C(1)); 3.54 (*dd*, J = 2.6, 17.5, H_β–C(1)); 3.55 (*s*, CH_3O or CH_3N); 3.7 (*s*, CH_3N or CH_3O); 4.0 (*dd*, J = 9.1, 2.6, H_β–C(2)); 7.1–7.2 (*m*, H–C(6), H–C(7)); 7.48 (*d*, J = 7.2, H–C(8)); 7.73 (*d*, J = 7.3, H–C(5)); 7.97 (*s*, H–C(4)). EI-MS: 299 (68, M^+), 239 (86), 208 (100), 181 (75). Anal. calc. for $C_{17}H_{17}NO_4$ (299.12): C 68.26, H 5.73, N 4.68; found: C 68.01, H 5,39, N 4.52.

*Methyl 2-Acetyl-9-methyl-9*H*-carbazole-3-carboxylate* (**19c**) *and Methyl 9-Methyl-9*H*-carbazole-3-carboxylate* (**19d**). Compound **2c** (250 mg, 0.88 mmol) was dissolved in PhBr (30 ml) containing 10% Pd/C (120 mg), and the mixture was heated under reflux for 6 h. After filtration and evaporation the residue was separated by FC (petroleum ether/AcOEt 7:2).

19c: 150 mg (61%). Colorless crystals. M.p. 159° (AcOEt). ^{1}H-NMR (200 MHz, (D_6)DMSO): 2.58 (*s*, $COCH_3$); 3.85 (*s*, CH_3O); 3.95 (*s*, CH_3N); 7.3 (*dd*, J = 7.3, 7.5, H–C(6) or H–C(7)); 7.56 (*dd*, J = 7.2, 7.7, H–C(7) or H–C(6)); 7.66 (*d*, J = 8.1, H–C(5) or H–C(8)); 7.81 (*s*, H–C(1) or H–C(4)); 8.32 (*d*, J = 7.7, H–C(8) or H–C(5)); 8.67 (*s*, H–C(4) or H–C(1)). EI-MS: 281 (91, M^+), 266 (100), 250 (24). Anal. calc. for $C_{17}H_{15}NO_3$ (281.10): C 72.64, H 5.38, N 4.98; found: C 72.03, H 5.22, N 4.87.

19d: 15 mg (7%). Colorless crystals. M.p. 128° (CH_2Cl_2). ^{1}H-NMR (400 MHz, CD_2Cl_2): 3.87 (*s*, CH_3N or CH_3O); 3.94 (*s*, CH_3O or CH_3N); 7.30 (*dd*, J = 7.0, 7.8, H–C(6) or H–C(7)); 7.44 (*d*, J = 8.5, H–C(5) or H–C(8)); 7.47 (*d*, J = 8.15, H–C(8) or H–C(5)); 7.53 (*dd*, J = 7.10, 7.0, H–C(7) or H–C(6)); 8.16 (*m*, H–C(1), H–C(2)); 8.81 (*d*, J = 1.7, H–C(4)). EI-MS: 239 (100, M^+), 213 (86), 180 (42). Anal. calc. for $C_{15}H_{13}NO_2$ (239.09): C 75.36, H 5.48, N 5.86; found: C 75.44, H 5.65, N 5.99.

*Methyl 3-Cyano-1,2-dihydro-9-methyl-9*H*-carbazole-2-carboxylate* (**19e**) *and Methyl 3-Cyano-9-methyl-9*H*-carbazole-2-carboxylate* (**19f**). The mixture **2d**/**2e** (400 mg, 1.5 mmol) was dissolved in PhBr (50 ml) containing 10% Pd/C (200 mg), and the mixture was heated under reflux for 6 h. After filtration and evaporation the residue separated by FC (petroleum ether/AcOEt 4:1 and 2:1).

19e: 96 mg (24%). Colorless crystals. M.p. 161° (toluene). ^{1}H-NMR (200 MHz, (D_6)DMSO): 3.25 (*dd*, J = 8.8, 17.6, H_α–C(1)); 3.53 (*dd*, J = 4.4, 17.6, H_β–C(1)); 3.65 (*s*, CH_3N or CH_3O); 3.75 (*s*, CH_3O or CH_3N); 3.91 (*dd*, J = 8.7, 4.3, H_β–C(2)); 7.12–7.22 (*m*, H–C(6), H–C(7)); 7.49 (*dd*, J = 2.1, 6.7, H–C(8)); 7.68 (*dd*, J = 2.1, 6.2, H–C(5)). EI-MS: 266 (37, M^+), 207 (100), 192 (56). Anal. calc. for $C_{16}H_{14}N_2O_2$ (266.11): C 72.22, H 5.30, N 10.53; found: C 72.23, H 5.49, N 10.44.

19f: 44 mg (11%). Colorless crystals. M.p. 241° (toluene). ^{1}H-NMR (400 MHz, CD_2Cl_2): 3.94 (*s*, CH_3N or CH_3O); 4.03 (*s*, CH_3O or CH_3N); 7.37 (*dd*, J = 7.5, 7.6, H–C(6) or H–C(7)); 7.53 (*d*, J = 8.3, H–C(5) or H–C(8)); 7.64 (*dd*, J = 7.3, 7.1, H–C(7) or H–C(6)); 8.15 (*d*, J = 7.9, H–C(8) or H–C(5)). EI-MS: 264 (100, M^+), 233 (67), 205 (50). Anal. calc. for $C_{16}H_{12}N_2O_2$ (264.09): C 72.77, H 4.58, N 10.61; found: C 72.91, H 4.72, N 10.82.

*Methyl 2-Acetyl-1,2-dihydro-9-methyl-9*H*-carbazole-3-carboxylate* (**19g**). Compound **2c** (500 mg, 1.8 mmol) was dissolved in PhBr (40 ml) and heated under reflux for 4 h. The soln. was then evaporated and the residue separated by FC (petroleum ether/AcOEt 7:2): 420 mg (84%) of **19g**. Colorless crystals. M.p. 132° (AcOEt). ^{1}H-NMR (200 MHz, (D_6)DMSO): 2.12 (*s*, Ac); 3.15 (*dd*, J = 9.1, 17.6, H_β–C(1)); 3.53 (*dd*, J = 2.5, 17.6, H_α–C(1)); 3.75 (*s*, CH_3N or CH_3O); 3.76 (*s*, CH_3O or CH_3N); 3.94 (*dd*, J = 9.1, 2.4, H_β–C(2)); 7.1–7.2 (*m*, H–C(6), H–C(7)); 7.47 (*d*, J = 7.5, H–C(8)); 7.7 *dd*, J = 1.8, 6.0, H–C(5)). EI-MS: 283 (25, M^+), 239 (72), 208 (65), 181 (100). Anal. calc. for $C_{17}H_{17}NO_3$ (283.12). C 72.12, H 6.05, N 4.95; found: C 72.11, H 6.31, N 4.88.

*Methyl (*E*)-3-(2′-Phenyl-1′*H*-indol-3′-yl)prop-2-enoate* (**21a**). 2-Phenyl-1*H*-indole (1.0 g, 5 mmol), methyl prop-2-enoate (0.12 g, 0.5 mmol), $Pd(OAc)_2$ (0.12 g, 0.5 mmol), and AgOAc (1.7 g, 10 mmol) were suspended in AcOH (50 ml). The mixture was heated under reflux for 12 h, then filtered, the solid washed with CH_2Cl_2, and the combined org. phases were evaporated. The residue was taken up in a small volume of toluene and separated by FC (petroleum ether/AcOEt 3:1): 430 mg (31%) of **21a**. Colorless amorphous crystals. M.p. 167° (Et_2O). ^{1}H-NMR (200 MHz, (D_6)DMSO): 3.69 (*s*, CH_3O); 6.49 (*d*, J = 16.1, vinyl H); 7.2–7.6 (*m*, arom. H); 7.85 (*d*, J = 15.5, vinyl H); 7.94 (*d*, J = 7.8, H–C(4′) or H–C(7′)); 12.45 (*s*, NH). EI-MS: 277 (50, M^+), 246 (20), 218 (100), 217 (80). Anal. calc. for $C_{18}H_{15}NO_2$ (277.11): C 78.02, H 5.46, N 5.05; found: C 77.98, H 5.51, N 5.12.

*Methyl (*E*)-3-[2′-(4″-Bromophenyl)-1′*H*-indol-3′-yl]prop-2-enoate* (**21b**) *and Methyl (*E,E*)-3-{2′-{4″-[2-(methoxycarbonyl)ethenyl]phenyl}-1′*H*-indol-3′-yl}prop-2-enoate* (**21d**). Prepared as described above for **21a**

from 2-(4-bromophenyl)-1*H*-indole (1.36 g, 5 mmol), methyl prop-2-enoate (1.3 g, 15 mmol), $Pd(OAc)_2$ (0.12 g, 0.5 mmol), and AgOAc (1.7 g, 10 mmol).

21b: 560 mg (31%). Colorless amorphous crystals. M.p. 215° (AcOEt). ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.34 (*s*, CH_3); 6.48 (*d*, *J* = 15.9, vinyl H); 7.21 (*dd*, *J* = 7.1, 6.9, H–C(5′) or H–C(6′)); 7.27 (*dd*, *J* = 7.1, 7.3, H–C(6′) or H–C(5′)); 7.48 (*d*, *J* = 7.9, H–C(4′) or H–C(7)); 7.54 (*d*, *J* = 8.5, H_m or H_o of Ph); 7.78 (*d*, *J* = 15.9, vinyl H); 7.81 (*d*, *J* = 8.42, H_o or H_m of Ph); 7.93 (*d*, *J* = 7.9, H–C(7′) or H–C(4′)); 12.18 (*s*, NH). EI-MS: 357 (56, M^+), 355 (58), 297 (38), 295 (40), 217 (100). Anal. calc. for $C_{18}H_{14}BrNO_2$ (356.01): C 60.73, H 3.97, N 3.93; found: C 60.21, H 4.03, N 4.21

21d: 40 mg (2%). Colorless crystals. M.p. 211° (toluene). ^{1}H-NMR (400 MHz, CD_2Cl_2): 3.78 (*s*, CH_3); 3.81 (*s*, CH_3); 6.52 (*d*, *J* = 16.0, vinyl H); 6.58 (*d*, *J* = 16.0, vinyl H); 7.25–7.33 (*m*, H–C(5′), H–C(6′)); 7.49 (*d*, *J* = 7.2, H–C(4′) or H–C(7′)); 7.60 (*d*, *J* = 8.3, H_m or H_o of Ph); 7.67 (*d*, *J* = 8.3, H_o or H_m of Ph); 7.70 (*d*, *J* = 16.1, vinyl H); 7.94 (*d*, *J* = 16.0, vinyl H); 7.96 (*d*, *J* = 7.7, H–C(7′) or H–C(4′)); 8.86 (*s*, NH). EI-MS: 361 (100, M^+), 330 (20), 301 (33), 270 (60), 242 (40). Anal. calc. for $C_{22}H_{19}NO_4$ (361.13): C 73.17, H 5.30, N 3.88; found: C 73.02, H 5.12, N 3.44.

*Methyl (*E*)-3-[2′-(4″-Methoxyphenyl)-1′*H*-indol-3′-yl]prop-2-enoate* (**21c**). Prepared as described above for **21a** from 2-(4-methoxyphenyl)-1*H*-indole (1.17 g, 5 mmol), methyl prop-2-enoate (1.3 g, 15 mmol), $Pd(OAc)_2$ (0.12 g, 0.5 mmol), and AgOAc (1.7 g, 10 mmol): 520 mg (34%) of **21c**. Colorless crystals. M.p. 156° (toluene). ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.67 (*s*, CH_3); 3.85 (*s*, CH_3); 6.44 (*d*, *J* = 15.9, vinyl H); 7.1–7.25 (*m*, H_o or H_m of Ph, H–C(5′), H–C(6′)); 7.46 (*d*, *J* = 7.9, H–C(4′) or H–C(7′)); 7.53 (*d*, *J* = 8.6, H_m or H_o of Ph); 7.82 (*d*, *J* = 15.9, vinyl H); 7.90 (*d*, *J* = 7.7, H–C(7′) or H–C(4′)); 12.04 (*s*, NH). EI-MS: 307 (95, M^+), 276 (30), 248 (100), 204 (50). Anal. calc. for $C_{19}H_{17}NO_3$ (307.12): C 74.31, H 5.58, N 4.56; found: C 74.22, H 5.69, N 4.21.

REFERENCES

[1] U. Pindur, *Chimia* 1990, in press, and ref. cit. therein.
[2] P. Bhattacharrya, D.P. Chakraborty, *Prog. Chem. Org. Nat. Prod.* **1987,** *52,* 160.
[3] A. Brossi, 'The Alkaloids', Academic Press, New York, 1985, Vol. 26, p. 1.
[4] J.A. Joule, in 'Adv. Heterocyclic Chem.' Ed. A.R. Katritzky, Academic Press, New York, 1984, Vol. 35, p. 83.
[5] U. Pindur, *Heterocycles* **1988,** *27,* 1253.
[6] U. Pindur, L. Pfeuffer, *Tetrahedron Lett.* **1987,** *28,* 3079.
[7] S. Kano, E. Sugino, S. Shibuya, S. Hibino, *J. Org. Chem.* **1981,** *46,* 3856.
[8] S. Kano, E. Sugino, S. Shibuya, S. Hibino, *J. Chem. Soc., Chem. Commun.* **1980,** 1241; S. Hibino, S. Kano, N. Mochizuki, E. Sugino, *J. Org. Chem.* **1984,** *49,* 5006; R.A. Jones, P.M. Fresneda, T. Aznar Saliente, J. Sepulveda-Arques, *Tetrahedron* **1984,** *40,* 4837; P. Van Doren, D. Vanderzande, S.S. Toppet, G. Hoornaert, *ibid.* **1989,** *45,* 6761.
[9] U. Pindur, R. Adam, *Heterocycles,* in press.
[10] T. Itahara, K. Kawasaki, F. Ouseto, *Synthesis* **1984,** 236.
[11] T. Itahara, M. Ikeda, T. Sakakibara, *J. Chem. Soc., Perkin Trans. 1* **1983,** 1361; E. Akgün, U. Pindur, *J. Heterocycl. Chem.* **1985,** *22,* 585.
[12] U. Pindur, M. Eitel, *Heterocycles* **1988,** *27,* 863.
[13] U. Pindur, L. Pfeuffer, *Monatsh. Chem.* **1989,** *120,* 27; U. Pindur, R. Adam, unpublished results.
[14] B.E. Maryanoff, A.B. Reitz, *Chem. Rev.* **1989,** *89,* 863.
[15] Y. Fujiwara, P. Maruyama, M. Yoshidomi, H. Taniguchi, *J. Org. Chem.* **1981,** *46,* 851; G.D. Davis, Jr., A. Hallberg, *Chem. Rev.* **1989,** *89,* 1433.
[16] I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions', John Wiley & Sons, New York, 1976.
[17] T. Clark, 'Computational Chemistry', Wiley-Interscience, New York, 1987.
[18] E.N. Marvell, 'Thermal Electrocyclic Reactions', Academic Press, New York, 1980; J.C. Jutz, *Topics Curr. Chem.* **1978,** *73,* 125.
[19] a) C. Galvez, I. Fernandez, J. Vasquez, *J. Chem. Res., Synop.* **1987,** 16; b) A.V. Metelitsa, N.V. Volbushko, O.T. Lyashik, E.A. Medyantseva, A.P. Knyazev, M.I. Knyazhanskii, V.I. Minkin, *Khim. Geterotsikl. Soedin* **1989,** 705.
[20] B. Robinson, 'The Fischer Indole Synthesis', John Wiley & Sons, New York, 1982; K. Kaji, H. Nagashima, *J. Pharm. Soc. Jpn.* **1952,** *72,* 1589.
[21] G. Dupas, J. Duflos, G. Queguiner, *J. Heterocycl. Chem.* **1980,** *17,* 93.
[22] G. Dupas, J. Duflos, G. Queguiner, *J. Heterocycl. Chem.* **1983,** *20,* 967.