

Synthesis of Compounds Containing a Cycloalka[*b*]indole Fragment

R. R. Gataullin

Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences,
pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia
e-mail: gataullin@anrb.ru

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Abstract—The review summarizes recent advances in the field of synthesis of compounds having a cycloalka[*b*]indole skeleton.

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Numerous natural compounds contain a cycloalka[*b*]indole moiety as the base structural fragment [1–49]. Examples are representatives of a large class of nitrogen-containing hexacycles of the Kopsifoline series [8], isolated from *Kopsia officinalis* leaves, and a number of carbazole systems isolated from *Clausena anisata* and called Clausamines (D, E, F, G, etc.) [10]. The latter showed antitumor activity. The same compound family includes alkaloid Siamenol which turned out to be active against HIV [11]. Some alkaloid molecules contain two or even three cycloalka[*b*]indole fragments with different degrees of hydrogenation. These are bis-indole systems Pedunculine and Peduncularidine [14] and the largest among analogous known alkaloids Strychnohexamine, which was isolated from *Strychnos icaja* root [15]. Various structurally related alkaloids are also produced by *Vinca rosea*

Linn. [17, 46]; in particular Vincalokoblastine showed antitumor cytotoxic activity and inhibited replication of tumor cells and lymphocytes. Alkaloid Vindoline having a hexahydrocarbazole skeleton was isolated from leaves of *Vinca rosea* Linn. Plants of the family *Aspidosperma* produce polycyclic compounds with a cyclohexa[*b*]indole skeleton.

Compounds having a cycloalka[*b*]indole skeleton often act as antagonists toward some receptors. In particular, a synthetic heterocyclic compound with a substituted 7-fluorotetrahydrocyclopenta[*b*]indole fragment is prostaglandin D₂ receptor antagonist [50]. Hexahydrocarbazole is the key structural fragment of Pirlindole which is widely used in medicine [51–55]. Therefore, search for new methods for the preparation of cycloalka[*b*]indole derivatives attracts interest of many researchers [56–62]. Up to now, several synthetic routes to cycloalka[*b*]indole systems have been reported.

Synthesis from phenylhydrazones. One of the earliest approaches to indole derivatives having a cycloalkane fragment fused at the [*b*] side is based on the cyclization of cycloalkanone phenylhydrazones. Various substituted cycloalka[*b*]indoles can be synthesized by heating the corresponding cycloalkanone phenylhydrazone [63] with acids (e.g., H₂SO₄ [64–66]), Amberlyst 15 [67], or zeolites [68]. For example, tetrahydrocarbazoles **3** (*n* = 2) were obtained in 63–65% yield by reaction of phenylhydrazines **1** with cyclohexanone **2** (*n* = 2) in the presence of zeolite, the most active being H-Y zeolite [68] (Scheme 1). The Japp–Klingemann condensation of diazonium salts with 2-oxocycloalkanecarboxylic acids, followed by Fischer

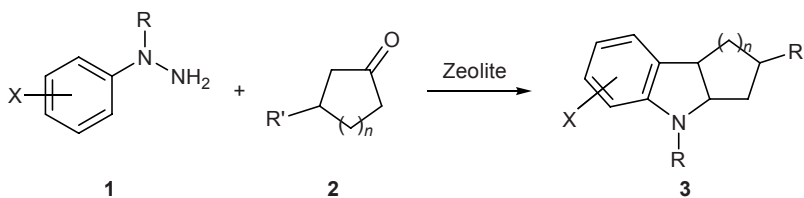


Rail Rafkatovich Gataullin was born in 1959 in Arslanovo village, Kigi region, Bashkir ASSR. In 1985 he graduated from the Faculty of Chemistry, Bashkir State University. R.R. Gataullin worked as shift supervisor at the epoxy resin shop, *Khimprom* Ufa Industrial Association. Candidate of chemical sciences since 1993; doctor of chemical sciences since 2004; Professor since 2006. R.R. Gataullin is now leading research worker at the Institute of Organic Chemistry, Ufa

Research Center, Russian Academy of Sciences. Six candidate dissertations were sustained under his guidance.

Fields of scientific interest: chemistry of dihydropyrans, alkenylanilines, pyrimidine nucleosides, and benzo-fused nitrogen-containing heterocycles.

Scheme 1.



cyclization of the hydrazones thus formed [69], also afforded cycloalka[b]indoles.

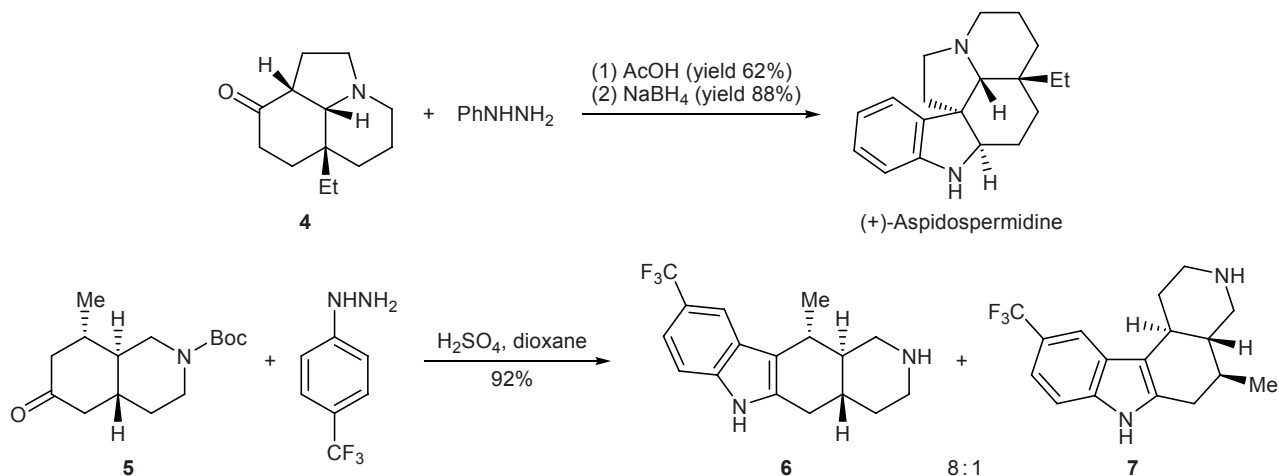
The regioselectivity in the formation of cycloalka[b]indole structures according to Fischer in each particular case is determined by the structure of the ketone component. In the synthesis of (+)-aspidospermidine, the reaction of ketone **4** with phenylhydrazine was performed by heating in acetic acid [70, 71], and the new C–C bond was formed between the *ortho*-carbon atom in the benzene ring and the most substituted carbon atom in ketone **4** (Scheme 2). Analogous reaction of ketone **5** with 4-trifluoromethylphenylhydrazine in dioxane in the presence of H₂SO₄ gave a mixture of linearly and angularly fused indole derivatives **6** and **7** at a ratio of 8:1. The process was also accompanied by hydrolysis of the trifluoromethyl group to carboxy. The optimal temperature was

found to range from 67 to 72°C; in this case, the concentration of the hydrolysis products was minimal (<5%) [72].

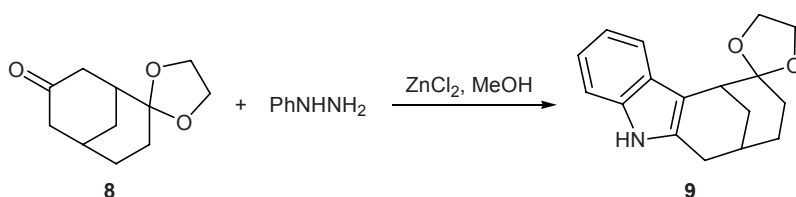
Fischer closure of indole ring in the synthesis of conformationally rigid melatonin analog from ketone **8** and phenylhydrazine in the presence of ZnCl₂ is regioselective, and compound **9** is formed in 53% yield [73]. The use of acetic acid was less advantageous due to incomplete conversion of phenylhydrazone derived from ketone **8** (Scheme 3).

Both acetic acid and zinc chloride were used as catalysts in the synthesis of tetrahydrocarbazole **10** from phenylhydrazine and Rink amide resin-supported substituted cyclohexanone **11**. The procedure for the treatment of the reaction mixture after the key step was fairly complex and time-consuming. Almost all transformations occurred with molecules linked to

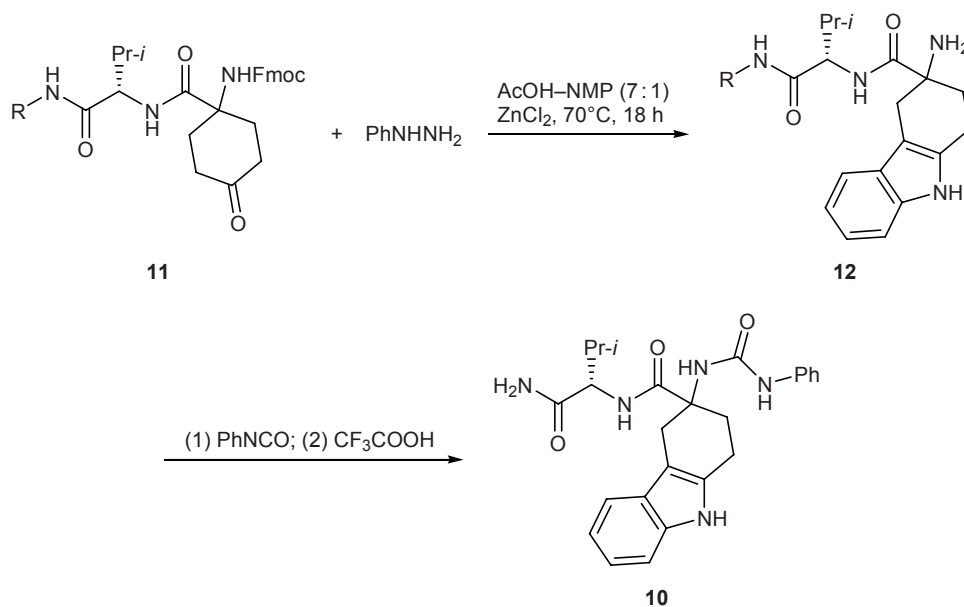
Scheme 2.



Scheme 3.

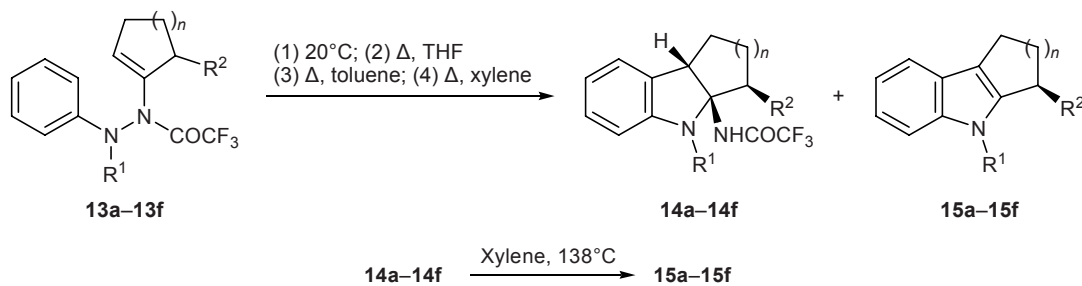


Scheme 4.



Fmoc = Fluoren-9-ylmethoxycarbonyl.

Scheme 5.



$n = 1$, $R^1 = R^2 = \text{H}$ (a); $R^1 = \text{Ph}$, $R^2 = \text{H}$ (b), Me (c), PhSCH_2 (d); $n = 2$, $R^1 = \text{Ph}$, $R^2 = \text{H}$ (e), Me (f).

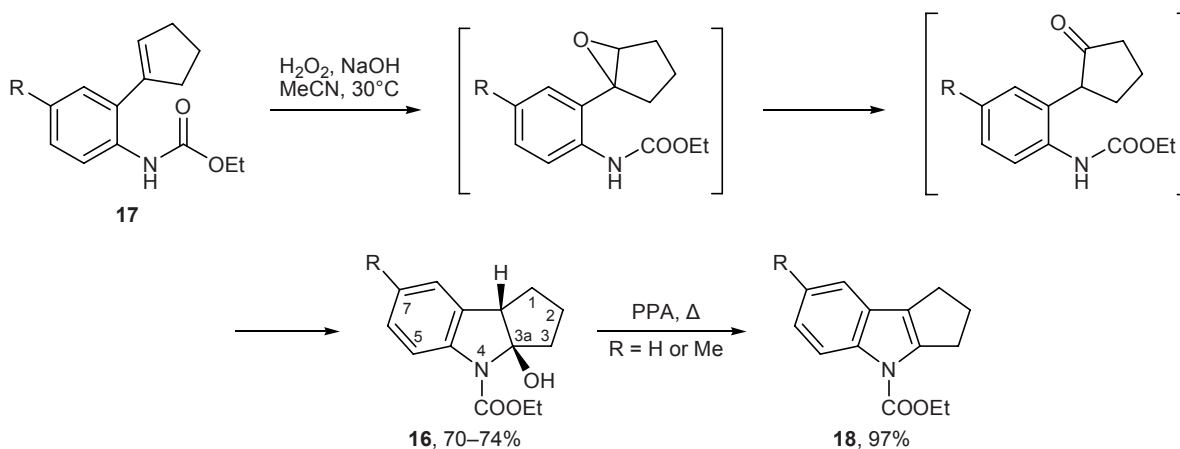
the polymeric support, so that the product can readily be purified from unreacted compounds and by-products by washing with various solvents. After treatment of polymer-supported heterocycle **12** with a solution of phenyl isocyanate, final product **10** was separated from the polymeric support by the action of trifluoroacetic acid, and its overall yield was 34% [74] (Scheme 4).

One more version of the synthesis of cycloalka[*b*]indoles according to Fischer is cyclization of *N*-trifluoroacetylhydrazines **13a–13f**. Thermal instability of the trifluoroacetamido group affects the degree of hydrogenation of the resulting cyclopenta- and cyclohexa[*b*]indoles **14** and **15**. Increased temperature favors formation of compounds **15a–15f** [75] (Scheme 5). Unlike trifluoroacetamido group, the hydroxy group on C^{3a} in cyclopenta[*b*]indoles **16** is stable. Compounds **16** are obtained by oxidation of ethyl carbamates **17**

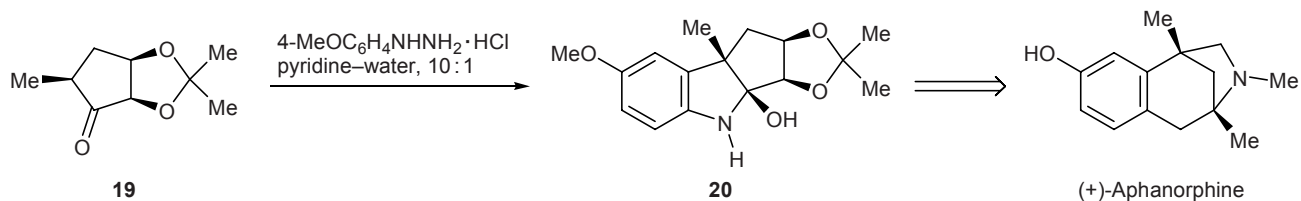
with a 50% solution of hydrogen peroxide [76, 77]. Dehydration of **16** to **18** occurs only on heating in polyphosphoric acid (Scheme 6). 5-Methyl- and 5-methoxy-substituted analogs of **16** cannot be synthesized by oxidation with hydrogen peroxide.

Regio- and stereoselective Fischer reaction of protected dihydroxycyclopentanone **19** with *p*-methoxyphenylhydrazine hydrochloride gave 2,3-isopropylidenedioxyhexahydrocyclopenta[*b*]indole **20** having a stable hydroxy group on C^{3a} . Compound **20** is an intermediate product in the synthesis of alkaloid aphanorphine which possesses analgesic properties [78, 79] (Scheme 7). 2,2-Disubstituted tetrahydrocarbazole **22** was obtained in 15% yield from heptane-2,6-dione (**21**) and 2 equiv of phenylhydrazine [80] (Scheme 8). Phenylhydrazone **26** reacted with diethylaluminum 2,2,6,6-tetramethylpiperide (DATMP) under mild

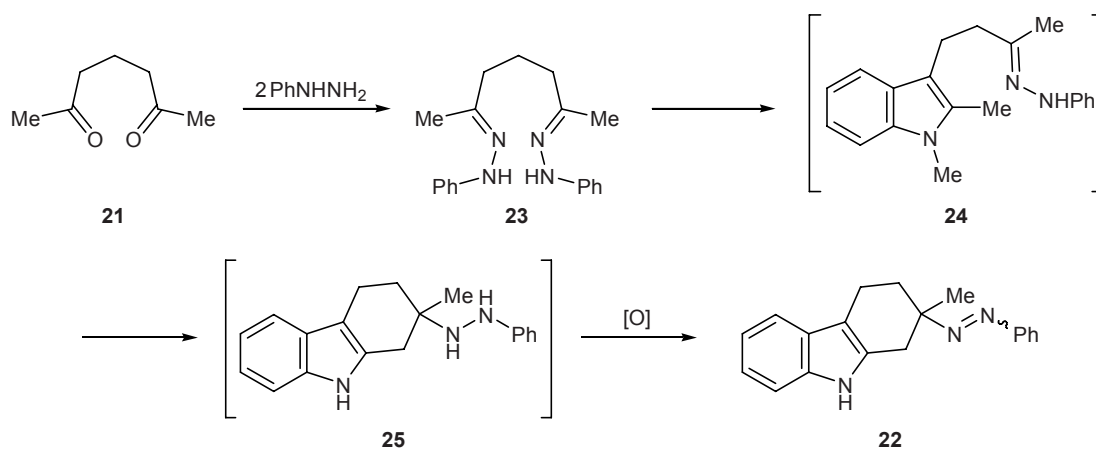
Scheme 6.



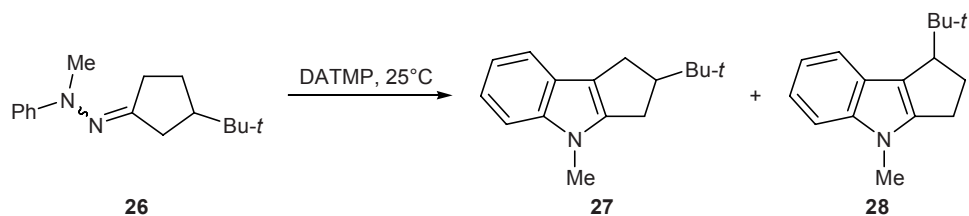
Scheme 7.



Scheme 8.



Scheme 9.



conditions [81] to give a mixture of isomeric cyclo-penta[*b*]indoles **27** and **28** whose ratio depended on the *E/Z*-isomer ratio in the initial phenylhydrazone (Scheme 9).

Synthesis of cycloalka[*b*]indoles from tryptamine derivatives. Tryptamine derivatives are often used as intermediate products in the synthesis of polycyclic alkaloids having a cyclohexa[*b*]indole fragment [82].

The total synthesis of Vindoline, which is the major alkaloid isolated from *Vinca rosea* Linn. leaves [83], involved acid-catalyzed cyclization of substituted indole **29** (yield 80%) [84]. Judging by the structure of cyclization product **30**, the process may be regarded as intramolecular Diels–Alder reaction between the indole and hydroxy diene fragments in intermediate **31** (Scheme 10).

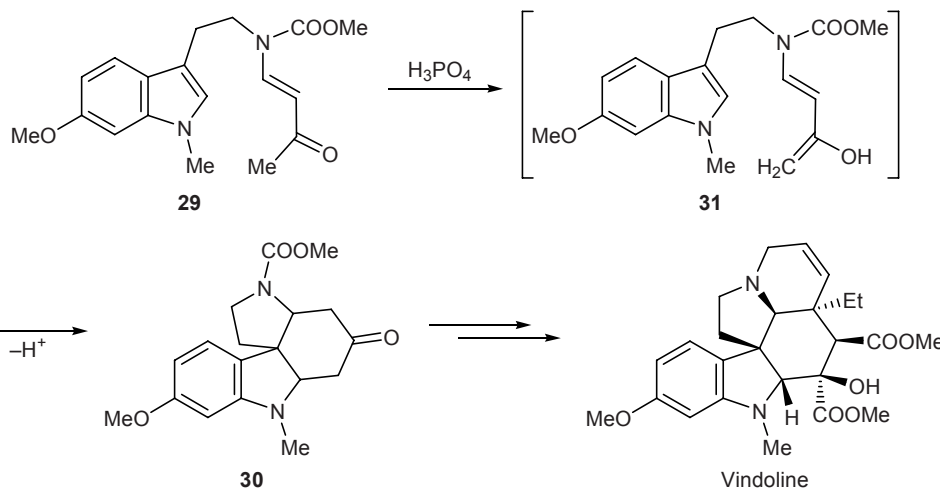
Dehydration [85] of enaminoketone **32**, followed by intramolecular [4+2]-cycloaddition, afforded 15-oxo-vincadifformine **33** which was reduced in regio- and stereoselective fashion to 15 β -hydroxyvincadifformine (Scheme 11); the latter showed antibacterial, antiviral, and anticarcinogenic activity. Alkaloids Vincadifformine and Tabersonine were synthesized starting from azepino[4,5-*b*]indole **34** [86] (Scheme 12). Pre-

sumably, the formation of epimer mixture **35a/35b** is also the result of intramolecular Diels–Alder reaction in the assumed tryptamine intermediate **36** (the fraction of *cis* isomer **35a** is 49%). Both epimers can be used in further steps to obtain Vincadifformine and Tabersonine.

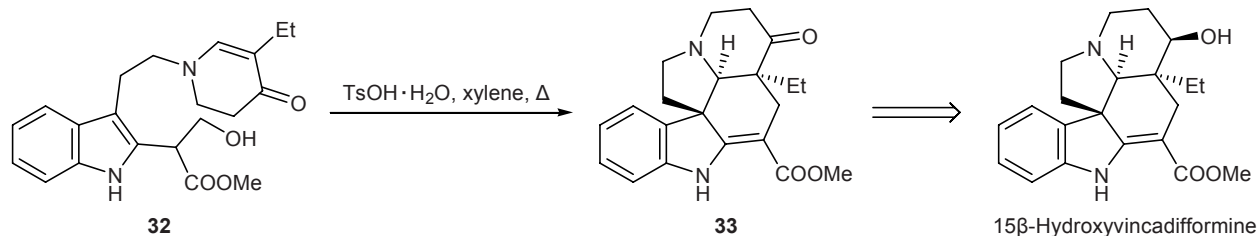
The mechanism of formation of the **C** and **D** rings in tetracyclic compound **37** is analogous to that described above. (\pm)-Ibopphyllidine **37** was synthesized by heating indole **38** with methyl 3-acetoxy-2-methyl-6-oxohexanoate (**39**) in toluene in the presence of *p*-toluenesulfonic acid [87] (Scheme 13).

Heureux et al. [88] proposed a procedure for rapid construction of the tetracyclic core of the *Aspidosperma* and *Strychnos* alkaloid families. The first key step is sequential polycyclization of tryptamine deriva-

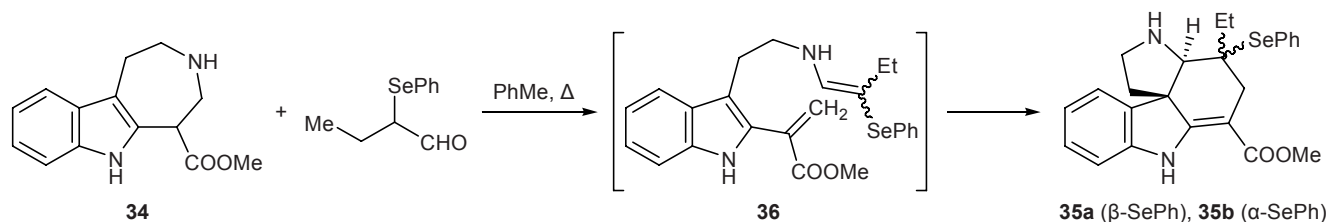
Scheme 10.



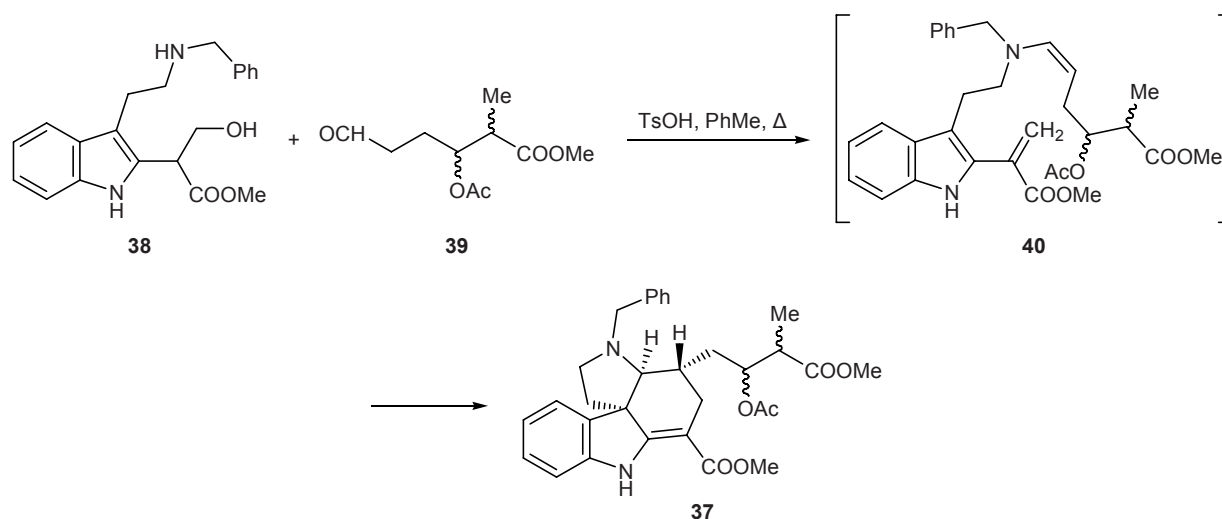
Scheme 11.



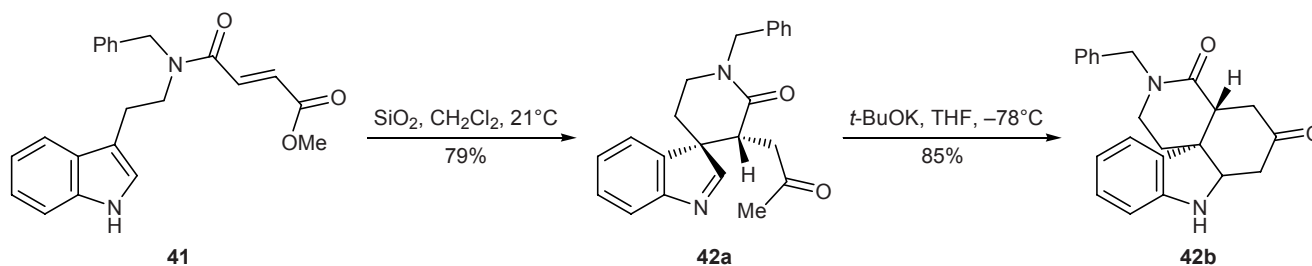
Scheme 12.



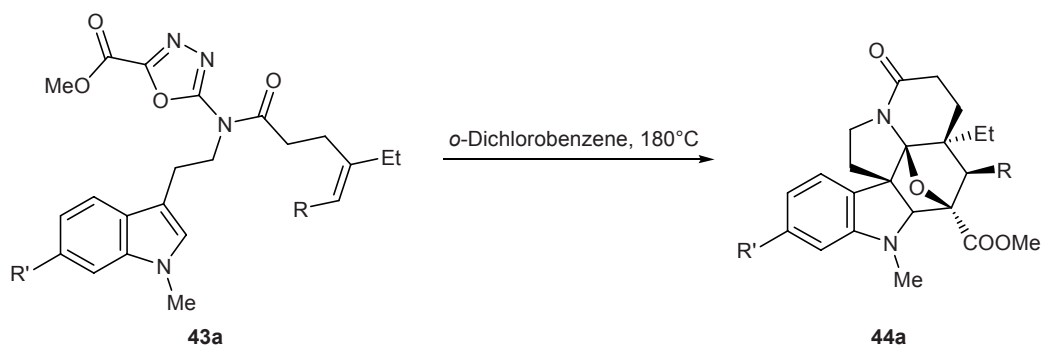
Scheme 13.



Scheme 14.



Scheme 15.

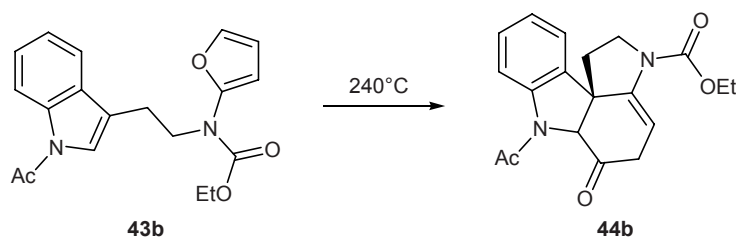


tive **41** to decahydropyridocarbazolone **42b** by the action of potassium *tert*-butoxide in the presence of silica gel. Stirring of **41** in methylene chloride over silica gel gave unstable spiro-fused indole **42a**, and the latter was transformed into tetracyclic compound **42b** by treatment with potassium *tert*-butoxide in THF at low temperature (Scheme 14).

Yuan et al. [89] described efficient and unusually concise total syntheses of both enantiomers of the *Aspidosperma* alkaloids 4-deacetoxy-6,7-dihydrovin-

dorosine and minovine, where one of the key steps was tandem intramolecular Diels–Alder reaction/1,3-dipolar cycloaddition of 1,3,4-oxadiazole **43a** ($\text{R} = \text{H}$). The process gave rise to three new rings, four new C–C bonds, and five chiral centers. Analogous reaction with compound **43a** ($\text{R} = \text{OCH}_2\text{Ph}$) gave other alkaloids of the same series [90] (Scheme 15). An example of another way of formation of polycyclic systems from furyl-containing tryptamine derivatives is heating of ethyl furylcarbamate **43b**. The reaction gives 62%

Scheme 16.



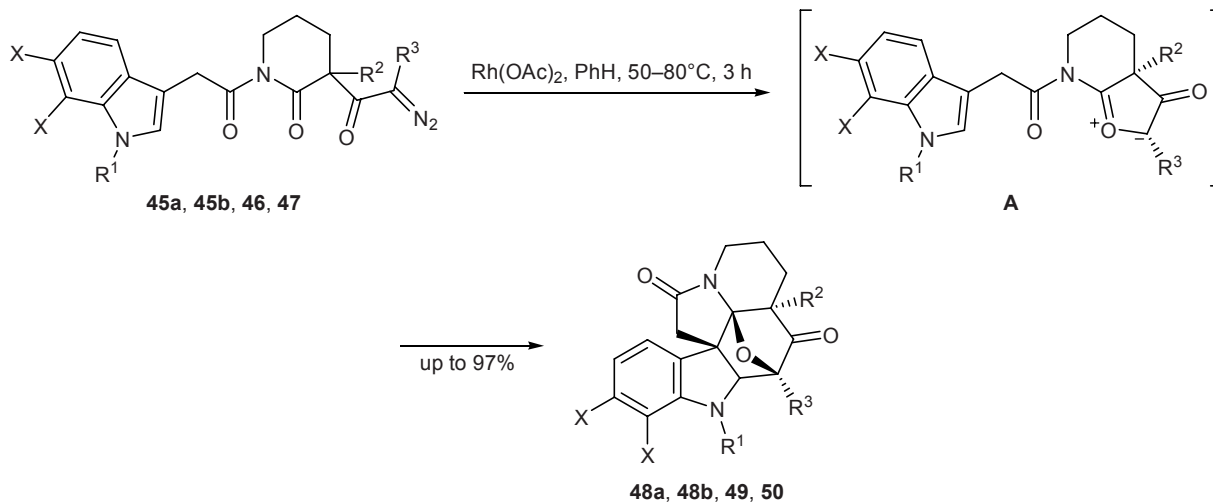
of compound **44b** as a result of intramolecular [4+2]-cycloaddition (Scheme 16). Presumably, carbamate **43b** is more thermally stable than its *tert*-butyl analog which undergoes decomposition on heating to 240°C [91].

Kopsifoline alkaloids were synthesized via multi-step Rh(OAc)₂-catalyzed cyclization of indoles **45–47** on heating to 30–80°C. The resulting indolizino-

indoles **48–50** [92–94] possess an epoxy bridge which is sensitive to acids. The authors presumed that intermediate dipole **A** adds in a stepwise mode at the double carbon–carbon bond in the indole fragment [92, 94] (Scheme 17).

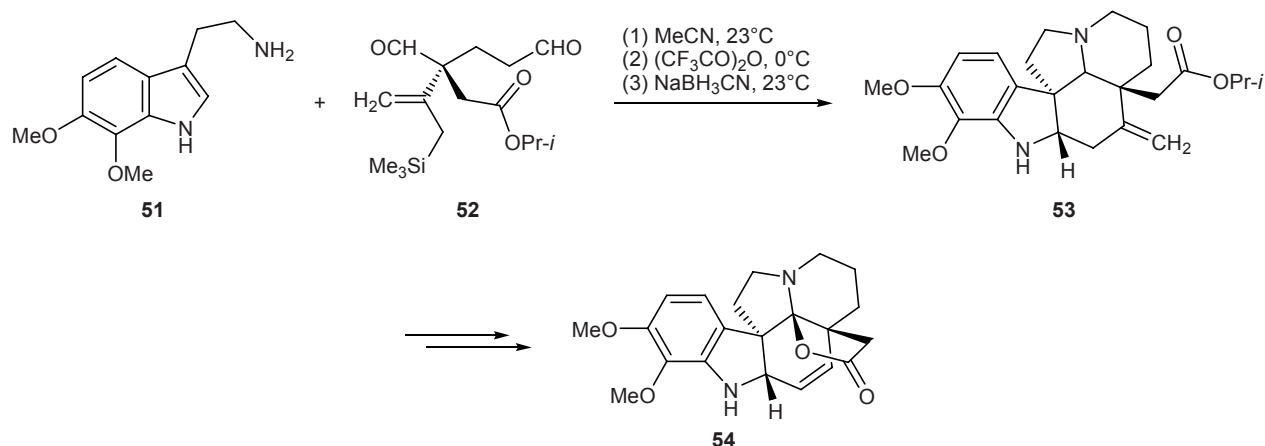
Alkaloid Aspidophytine **54** was synthesized in 86% yield in several steps starting from dimethoxytrypta-

Scheme 17.



45, 48, X = H, R¹ = Me, R² = R³ = EtOCO (**a**), R² = Et, R³ = MeOCO (**b**); **46, 49**, X = H, R¹ = Ts, R² = PhCH₂OCH₂CH₂, R³ = MeOCO; **47, 50**, X = MeO, R¹ = Me, R² = *t*-BuOCOCH₂, R³ = MeOCO.

Scheme 18.

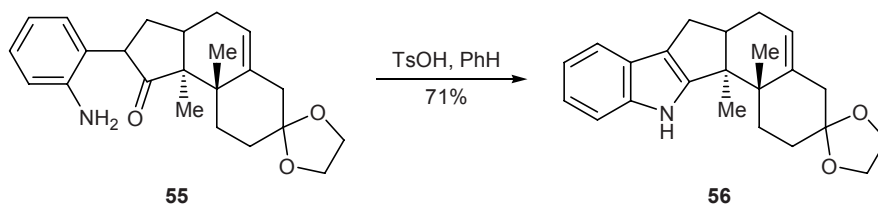


mine **51** and dialdehyde **52** [95] (Scheme 18). Here, intermediate pentacyclic compound **53** was formed in the first step under mild conditions.

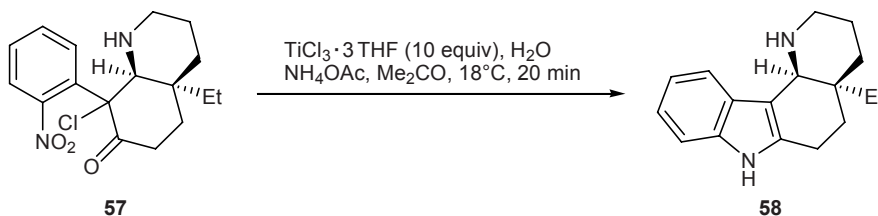
Intramolecular condensation of 2-(2-oxocycloalkyl)- and *N*-(2-oxocycloalkyl)anilines. Natural compounds with a cycloalka[*b*]indole skeleton are often synthesized from intermediate products obtained by intramolecular condensation of 2-(2-oxocycloalkyl)- and *N*-(2-oxocycloalkyl)anilines. For example, intramolecular condensation of amino ketone **55** in benzene in the presence of *p*-toluenesulfonic acid gives 71% of polycyclic compound **56** as intermediate product in the synthesis of (+)-paspalicine and (+)-paspalinine [96] (Scheme 19). In the synthesis of (±)-aspidospermidine, 3-ethoxycyclohexenone was converted in several steps into diastereoisomerically pure perhydroquinoline **57** which was reduced to pyridinocarbazole **58** with $\text{TiCl}_3 \cdot 3 \text{ THF}$ (Scheme 20), and the subsequent three-step sequence afforded the final product [97].

The reaction of 2-chlorocyclohexanone (**59**) with aniline (**60**) gives the best results in high-boiling solvents in the presence of Na_2CO_3 and a small amount of quinoline or pyridine. 2-Phenylaminocyclohexanone (**61**) thus obtained underwent cyclization to tetrahydrocarbazole **62** on heating in 2-ethoxyethanol in the presence of anhydrous MgCl_2 as catalyst [98] (Scheme 21). Potassium *tert*-butoxide catalyzed formation of nitro-substituted cyclopenta[*b*]indoles. Heating of 3-nitroaniline (**63**) with cyclopentanone (**64**) in DMSO in the presence of *t*-BuOK gave compound **65** with an impurity of minor isomer **66** [99] (Scheme 22). The reaction of 4-(phenylsulfonyl)-*N*-(4-tolylsulfonyl)aniline (**67**) with 1-phenylsulfonylcyclohexene (**68**) in the presence of trifluoroacetic anhydride led to hexahydrocarbazole **69** which was oxidized to tetrahydrocarbazole **70** with *m*-chloroperoxybenzoic acid (Scheme 23). The reaction with cyclohexene is not the only reported example; reactions with other olefins were also

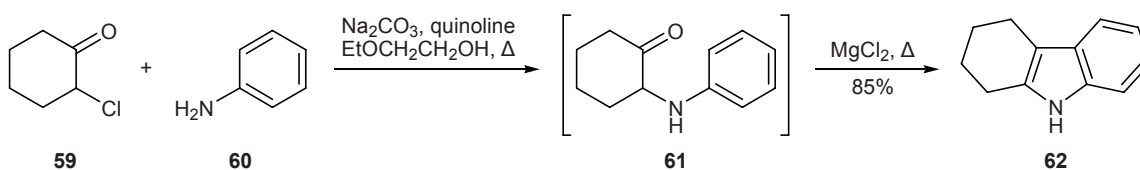
Scheme 19.



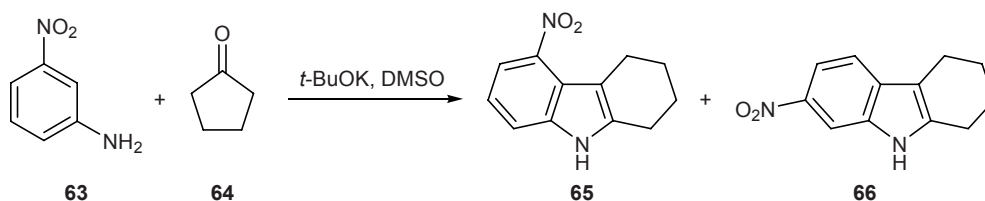
Scheme 20.



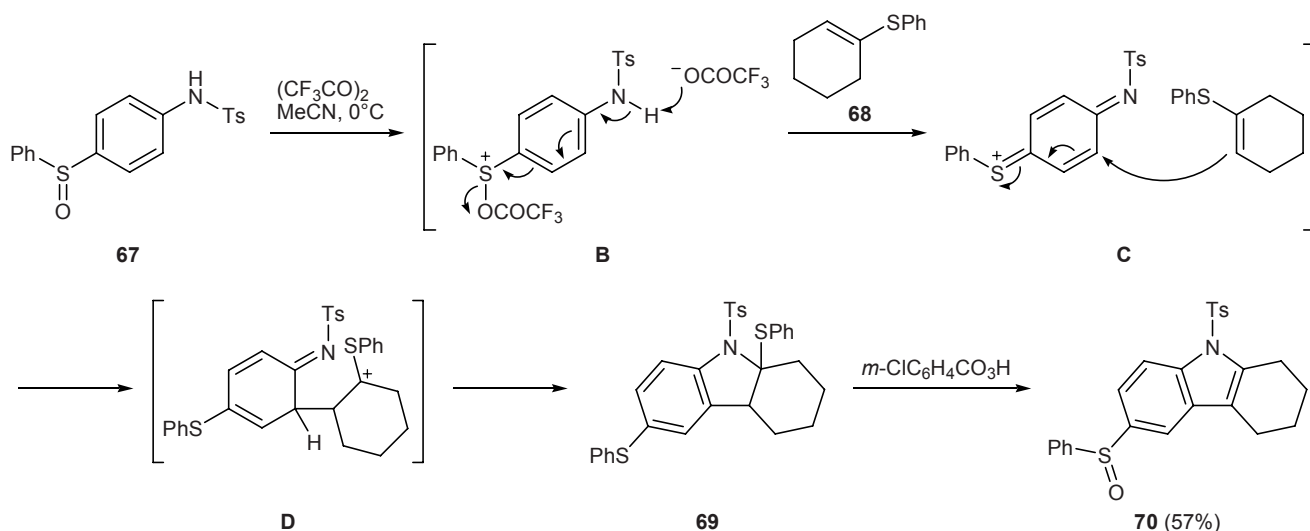
Scheme 21.



Scheme 22.



Scheme 23.



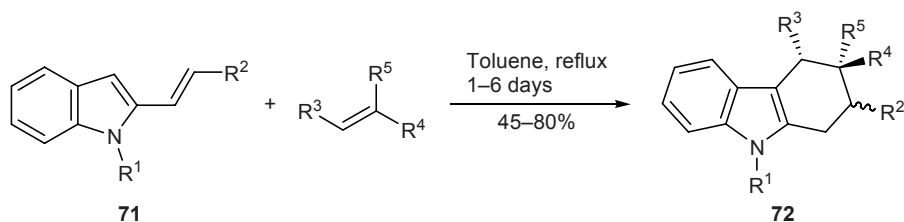
studied. A mechanism involving intermediate formation of quinoid structures **B–D** was proposed [100].

Diels–Alder reactions of 2- and 3-vinylindoles with various dienophiles. In most cases such reactions give rise to partially hydrogenated carbazoles [101]. Stereo- and regioselectivity of some [4+2]-cycloadditions are likely to be determined by structural and electronic factors. Cycloaddition of 2-vinylindoles **71** at the C=C bond of α,β -unsaturated carbonyl compounds stereoselectively yields tetrahydrocarbazoles **72** (Scheme 24). In some cases, the products were formed as mixtures of diastereoisomers [102]. Carbazoles **74** were obtained in 12–73% yield by heating

acetylenedicarboxylic acid esters or *N*-phenylmaleimide with 2-vinylindoles **73** in boiling toluene [103] (Scheme 25).

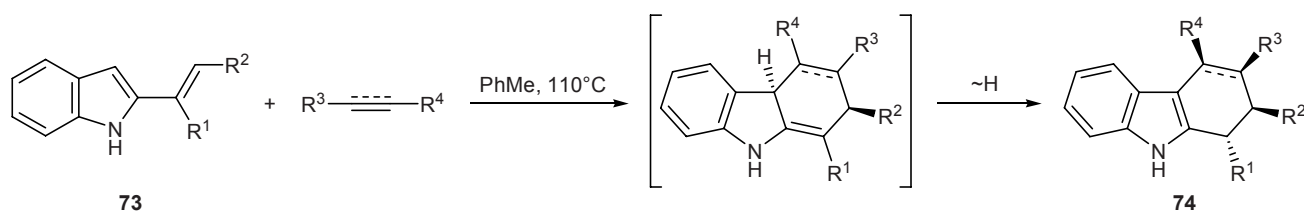
2-Vinylindoles may exist as two stabilized conformers **75** and **76**. Compounds with R = H or R = Me are unstable, and they can readily undergo polymerization. Steric interaction between the *N*-methyl group and substituent R in the vinyl fragment destabilizes cisoid conformation of diene system **76** and inhibits formation of diester **77**. Therefore, the yields of 1,2-dihydrocarbazoles **77** from 2-vinylindoles were poor (8–37%) [104] (Scheme 26). The Diels–Alder reactions of acetimides **78** and **79** with methyl acrylate,

Scheme 24.



$\text{R}^1 = \text{H, EtOCO}$; $\text{R}^2 = \text{H, Me, Bu, Ph}$; $\text{R}^3 = \text{H, Me, Ph}$; $\text{R}^4 = \text{MeOCO, EtOCO, CHO, MeCH}_2\text{C(O)}$; $\text{R}^5 = \text{H, Me}$.

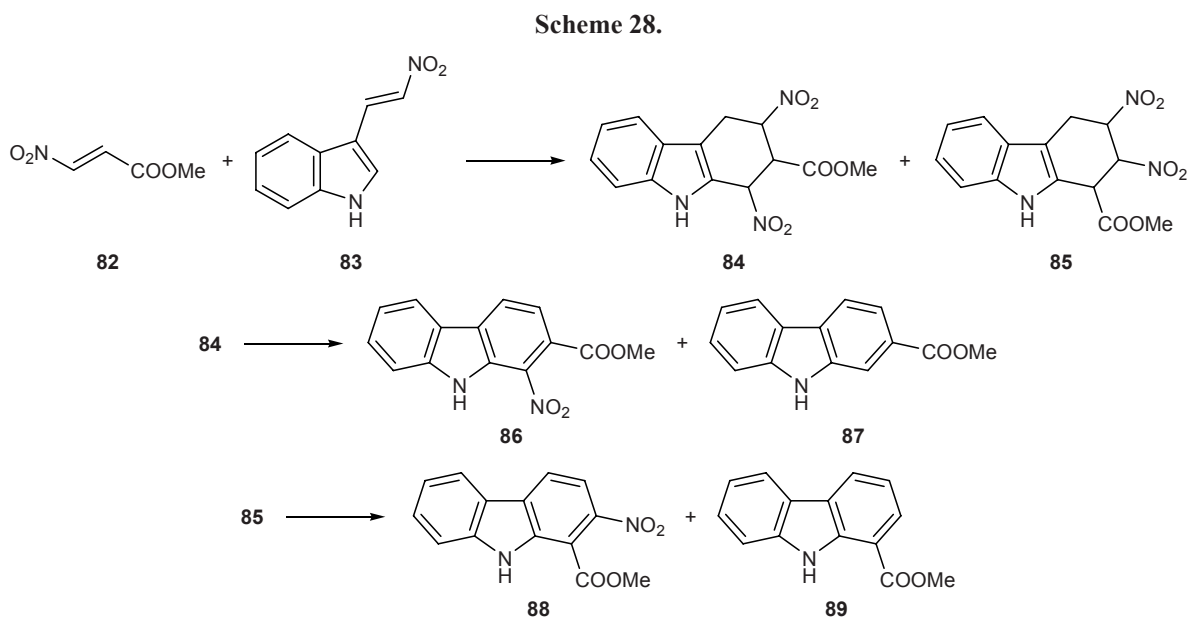
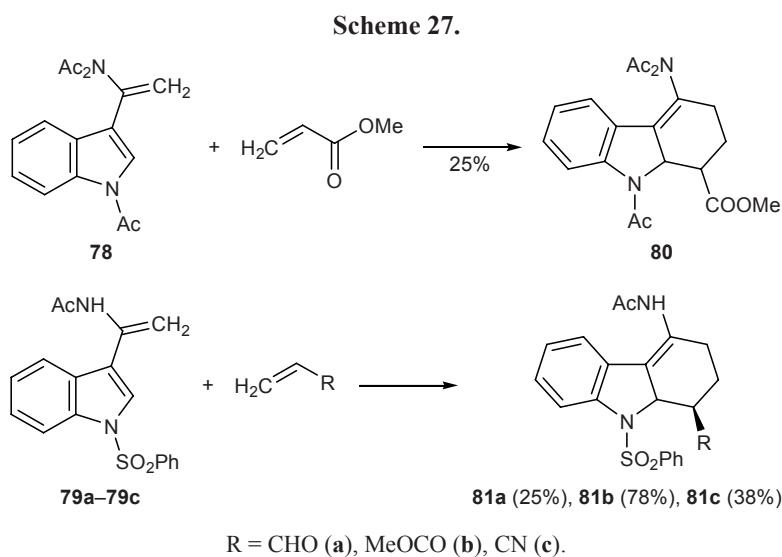
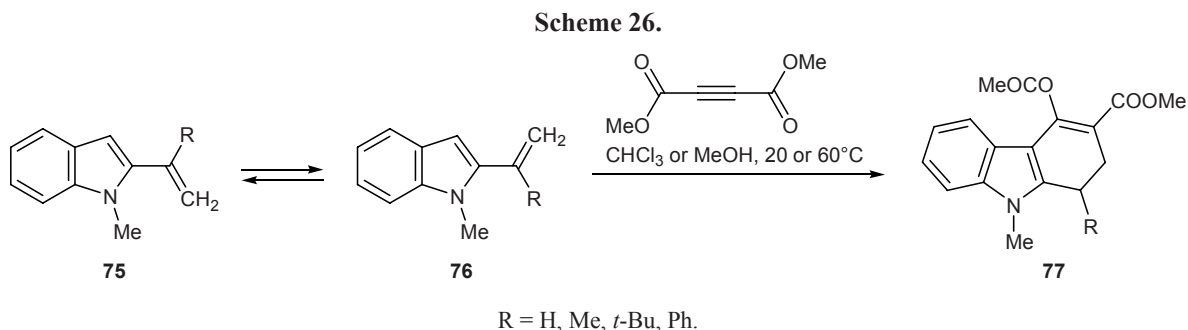
Scheme 25.

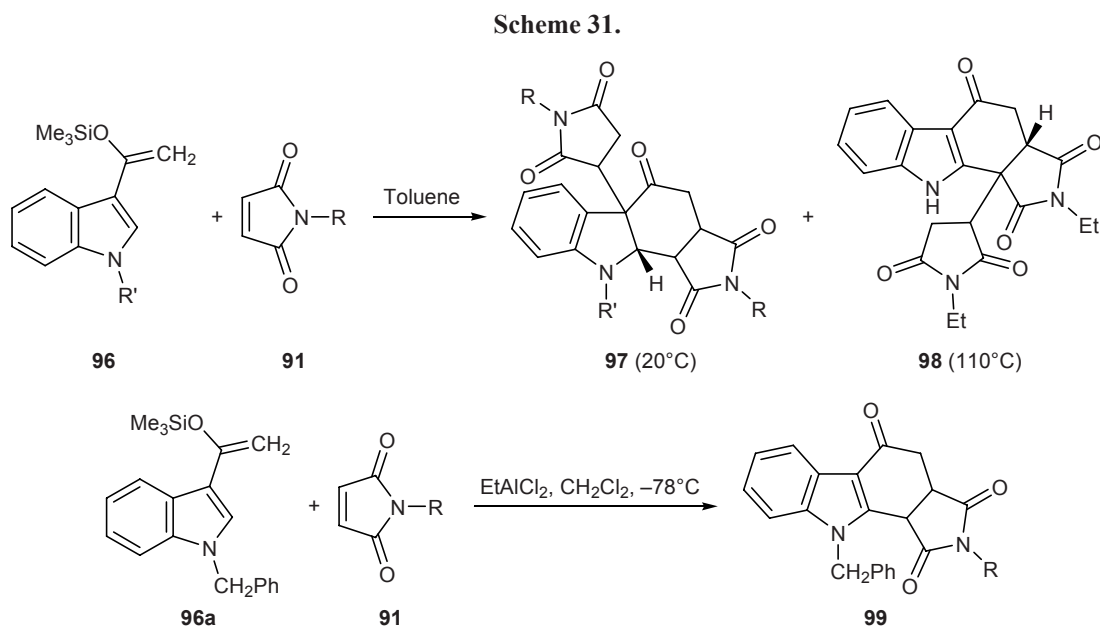
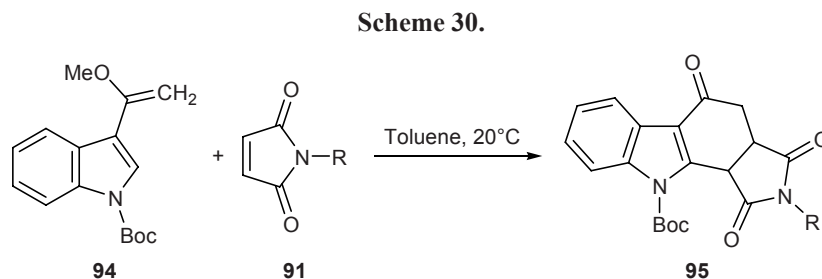
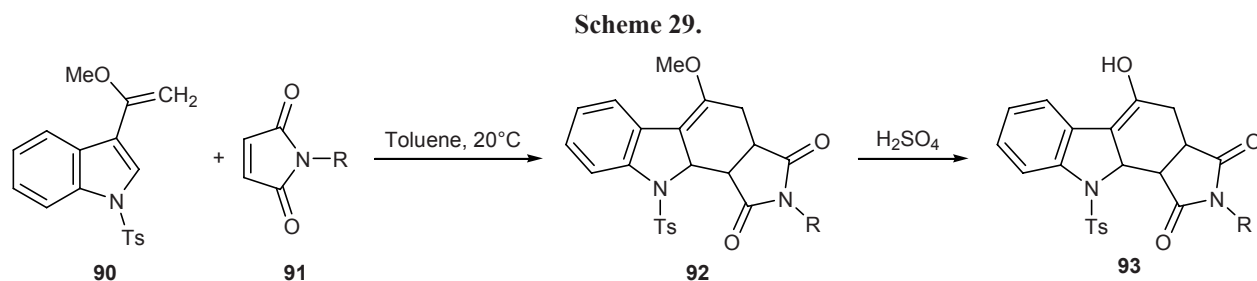


$\text{R}^1, \text{R}^2 = \text{H, Me}$; $\text{R}^3 = \text{R}^4 = \text{MeOCO, PhOCO}$; $\text{R}^3\text{R}^4 = \text{PhN(C=O)}_2$.

acrolein, and acrylonitrile afforded dihydrocarbazoles **80** and **81**. The best yields and high stereoselectivity were obtained in the reactions with *N*-phenylsulfonylindole **79** [105] (Scheme 27).

Methyl 3-nitroacrylate (**82**) reacted with 3-(2-nitroethyl)indole (**83**) in boiling toluene in the presence of AlCl_3 to produce regioisomeric methyl dinitrotetrahydrocarbazolecarboxylates **84** and **85** which under-





97, R = Me, Et, Ph; R' = Boc, *t*-BuCO, Ts; 99, R = Ph (2%), Et (2.3%).

went oxidative denitration with formation of compounds **86–89** [106] (Scheme 28). The reaction of indole **90** with *N*-substituted maleimides **91** in toluene at 20°C resulted in the formation of substituted pyrrolo[3,4-*a*]carbazoles **92** [107], and treatment of the latter with dilute sulfuric acid gave enol **93** (Scheme 29). Presumably, the tosyl group stabilizes the double bond in **92** and **93**, whereas the cycloaddition of *N*-Boc-substituted indole **94** to maleimides **91** yields only

ketone **95** (Scheme 30). Trimethylsilyloxyvinyl analogs **96** with various substituents on the nitrogen atom (R' = Ts, *t*-BuCO, PhCH₂) reacted with maleimides **91** to form more complex products, tetra- and hexahydrocarbazole derivatives **97–99**. The product structure depends on the R' substituent, temperature, solvent, and the presence of Lewis acids [108] (Scheme 31).

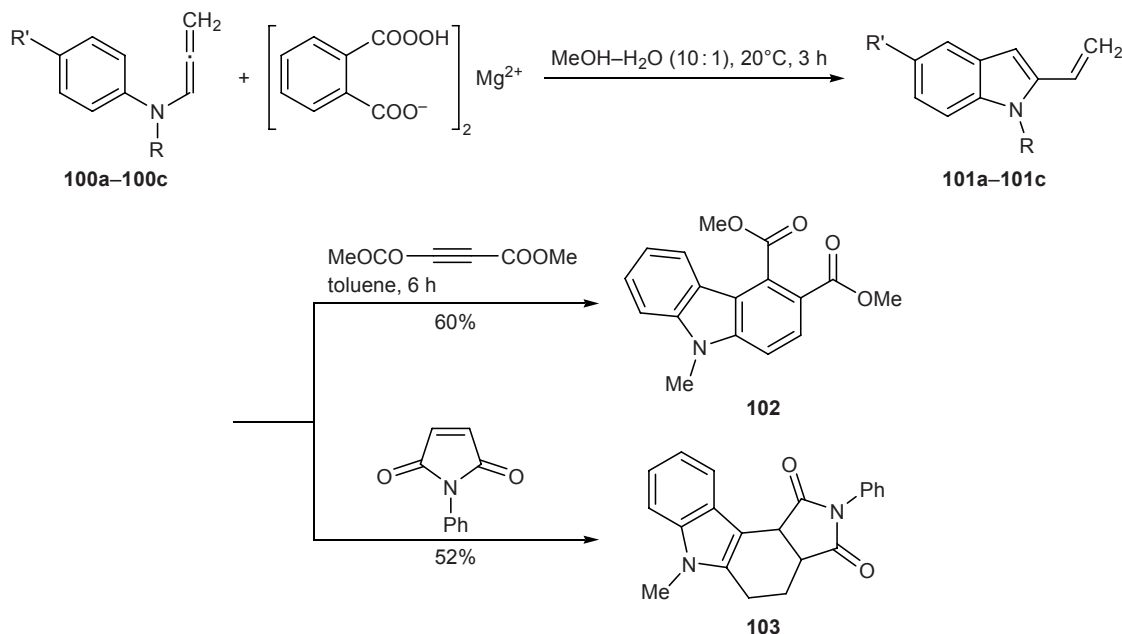
Treatment of *N*-alkyl-*N*-allenylanilines **100a–100c** with a solution of magnesium monoperoxyphthalate in

aqueous methanol at room temperature gave indoles **101a–101c** [109], the yield of *N*-methyl derivative **101a** being 80%. Heating of **101a** with dimethyl acetylenedicarboxylate afforded 60% of carbazole **102**, while pyrrolocarbazole **103** was formed in 52% yield in the reaction of **101a** with *N*-phenylmaleimide under analogous conditions (Scheme 32).

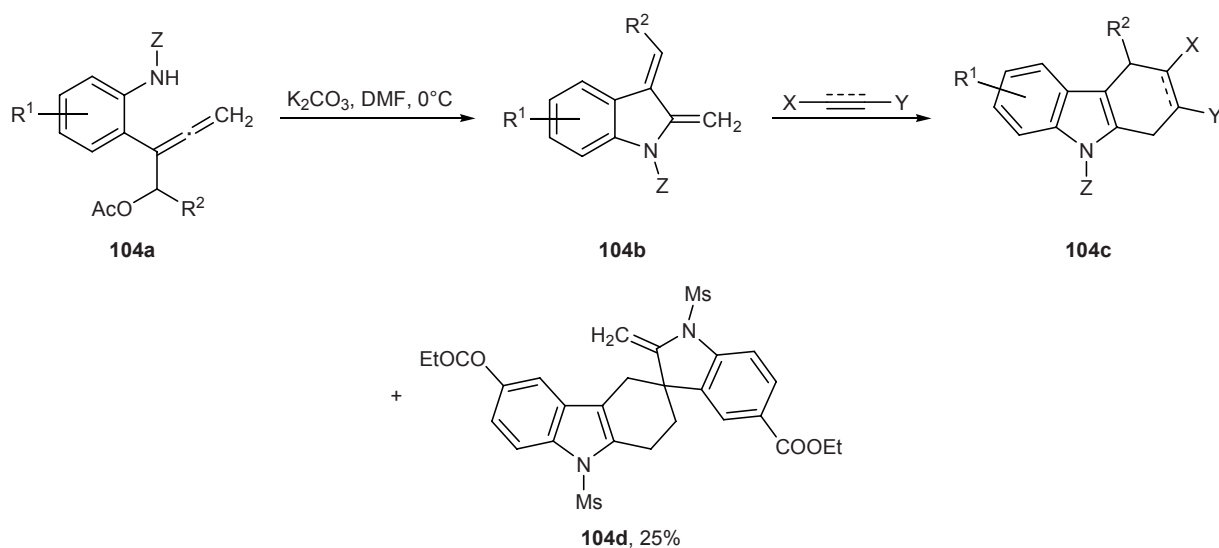
Tetrahydrocarbazoles can also be obtained from indole-2,3-quinodimethane intermediates that are fairly

active in Diels–Alder reactions. Tetrahydrocarbazoles **104c** were thus synthesized in 17–85% yield from *o*-allylaniline **104a** and the corresponding dienophiles in DMF in the presence of K_2CO_3 at $0^\circ C$ through intermediate formation of quinodimethane structure **104b** [110]. The reaction with *N*-methylsulfonyl derivative **104a** having an ethoxycarbonyl group in the *para* position was accompanied by formation of 25% of dimerization product **104d** (Scheme 33).

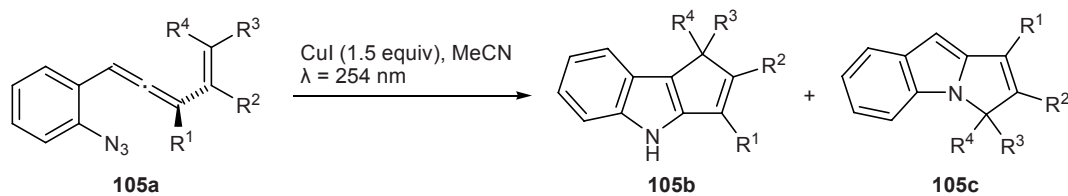
Scheme 32.



Scheme 33.

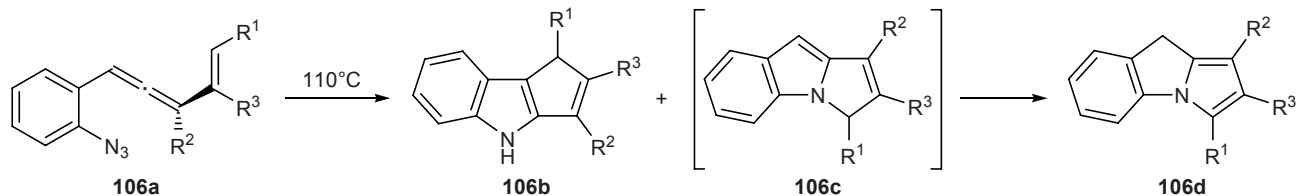


Scheme 34.

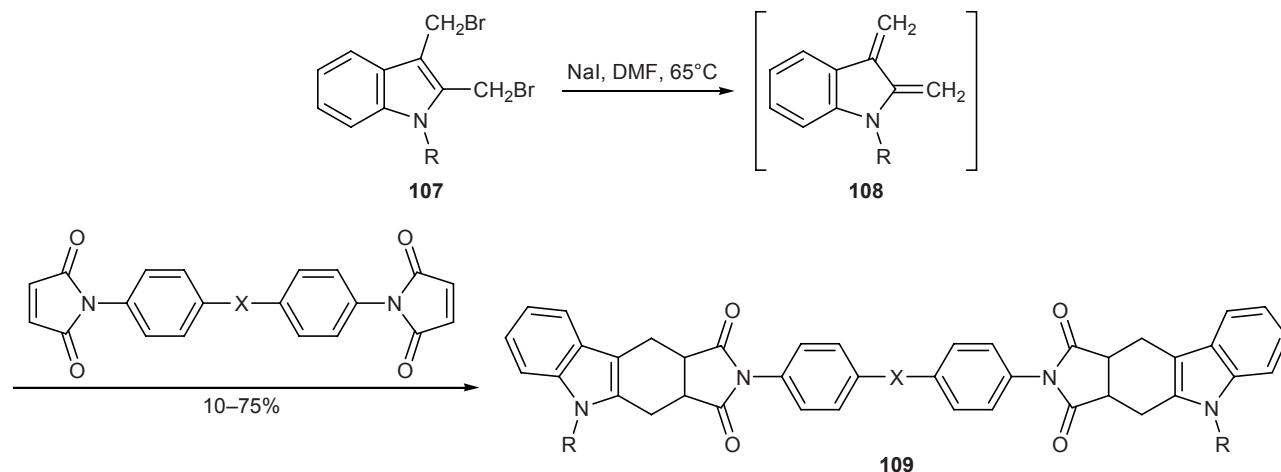


$R^1 = \text{Me, CH}_2\text{OTBS, Ph; } R^2R^3 = (\text{CH}_2)_4; R^2 = \text{H, Me, Ph; } R^3 = \text{H, Ph; } R^4 = \text{H, Ph; TBS} = \text{tributylsilyl.}$

Scheme 35.



Scheme 36.



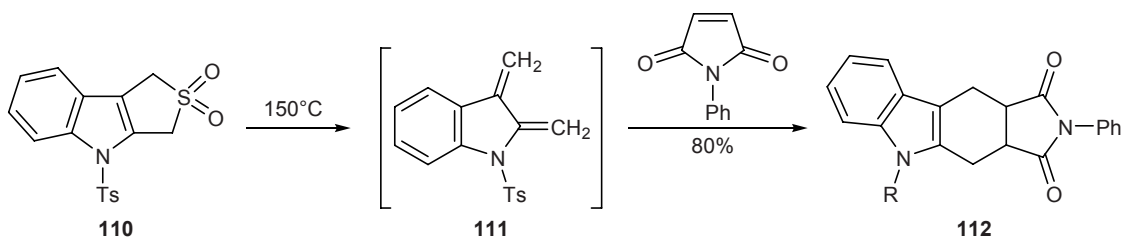
$X = \text{O, NH, (CH}_2)_2, \text{N=N, S-S, OP(=O)(OH)O, 1,3,4\text{-oxadiazole-2,5-diyl, NHC(O)CH}_2\text{CH}_2\text{C(O)NH, etc.}$

Recent studies on the use of allenylbenzene derivatives in the synthesis of polycyclic structures have extended the potential in the preparation of cyclopenta[*b*]indoles. For example, irradiation of azides **105a** in the presence of copper(I) iodide leads to the formation of 53–69% of cyclopenta[*b*]indole and pyrrolo[1,2-*a*]indole derivatives **105b** and **105c** at different ratios [111] (Scheme 34). However, photoinduced cyclizations and thermal decomposition of such azides are not selective. On heating in boiling toluene ($c = 0.1 \text{ M}$), *o*-(alka-1,2,4-trienyl)phenyl azides **106a** give rise to cyclopenta[*b*]indoles **106b–106d** whose ratio depends on the R^1 – R^3 substituents. Compounds **106c** were formed in 35–40% yield only from azides **106a** with $R^1 = \text{Ph, } R^2 = \text{Me, } R^3 = \text{H}$ and $R^1R^3 = (\text{CH}_2)_3, R^2 = \text{Me}$. In the other cases, the products were compounds **106b**

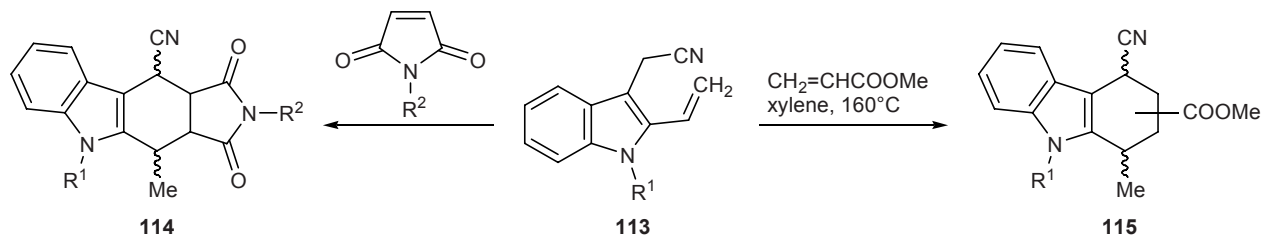
and **106d** at a ratio of 1:1.5 to 2.7:1 (yield 51–96%) [112] (Scheme 35).

Indole-2,3-quinodimethane intermediates **108** were generated from 2,3-bis(bromomethyl)indoles **107** by heating with sodium iodide in DMF. The subsequent reaction with bis-maleimide derivatives gave the corresponding bis-indole Diels–Alder adducts **109** [113] (Scheme 36). The reaction of thienoindole *S,S*-dioxide **110** with *N*-phenylmaleimide at 150°C also involved intermediate formation of bis-methylenecyclopentadiene derivative **111** and led to the formation of pyrrolo[1,2-*a*]indole **112** [114] (Scheme 37). Diels–Alder reactions of 2-vinylindoles **113** with methyl acrylate and maleimides at high temperature (175–210°C) gave mixtures of stereoisomeric tetrahydrocarbazoles **114** and **115** in 3–68% yield [115] (Scheme 38).

Scheme 37.



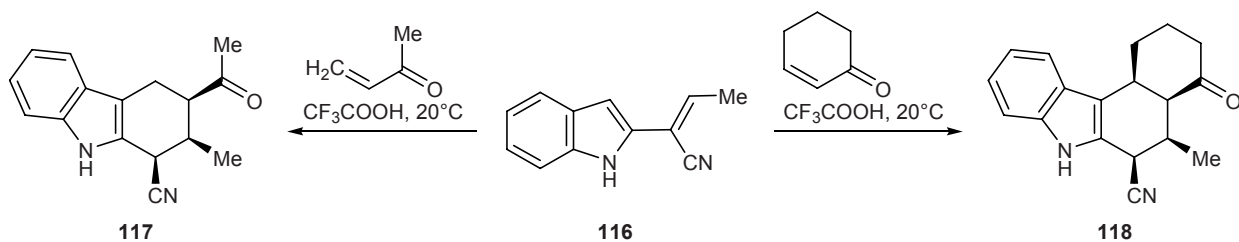
Scheme 38.



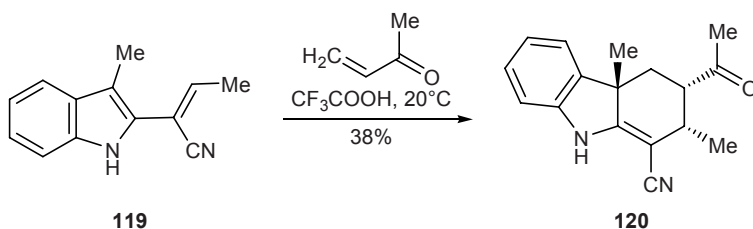
The presence of a cyano group in the vinyl fragment did not affect the Diels–Alder reaction of 2-(1-cyanoprop-1-en-1-yl)indole (**116**) with but-3-en-2-one and cyclohex-2-en-1-one. As a result, partly hydrogenated carbazoles **117** and **118**, respectively, were obtained in 40–58% yield [116] (Scheme 39). Analogous reaction of 2-(1-cyanoprop-1-en-1-yl)-3-methylindole (**119**) was not accompanied by [1,3]-hydride shift in the Diels–Alder adduct, and the product was tetrahydrocarbazole **120** (Scheme 40). Indole itself can act as dienophile in the synthesis of carbazoles. Diels–Alder reactions of 1-methoxy- and 1-dimethylamino-3-trimethylsilyloxybuta-1,3-dienes with 3- and 2-nitroindoles gave 23–73% of 2- and 3-hydroxycarba-

zoles. For instance, 3-nitroindole **121** reacted with 1-methoxy-3-trimethylsilyloxybuta-1,3-diene on heating in toluene, and the subsequent treatment with hydrogen chloride in THF produced a mixture of 35% of 2-hydroxycarbazole **122** and 56% of carbazol-2-one **123** [117] (Scheme 41). 3-Phenylsulfonyl-1,4,4a,9a-tetrahydrocarbazoles **126a** and **126b** were obtained in 42–63% yield by Diels–Alder reaction of sulfonyl-substituted diene **124** with indolylmagnesium iodides **125a** and **125b** generated from equimolar amounts of the corresponding indole and methylmagnesium iodide (Scheme 42). The yield was considerably lower (23%) when the initial indole had a methyl group in the 2-position [118].

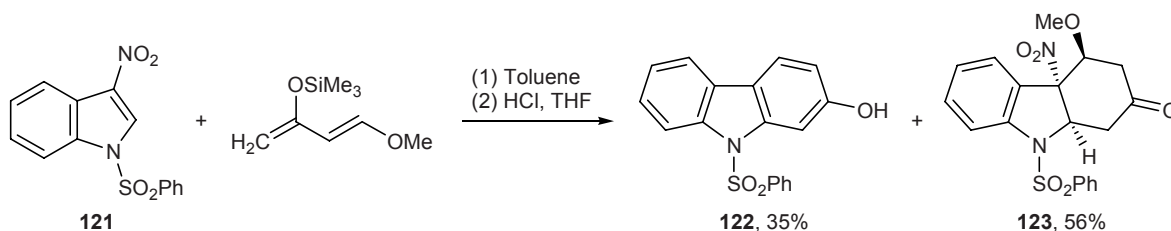
Scheme 39.



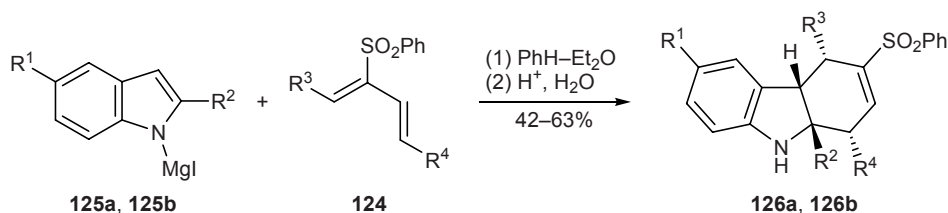
Scheme 40.



Scheme 41.



Scheme 42.



Synthesis of cycloalka[*b*]indoles with the use of heavy metals and their complexes. Wong et al. [119] proposed a one-pot procedure for the synthesis of functionalized tetrahydrocarbazoles and cyclopenta[*b*]indoles **127** [119]. 2-(*o*-Nitrophenyl)cyclohexanone **128** was reduced with triethylammonium formate to the corresponding hydroxylamine, and cyclization of the latter in methanol in the presence of lead gave 94–97% of *N*-hydroxytetrahydrocarbazole or cyclopenta[*b*]indole **127** (Scheme 43).

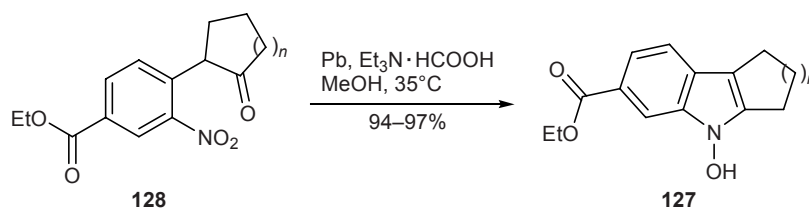
Various alkaloids, such as pyrayaquinones A and B, murrayaquinone A, and koeniginequinone A [120], were synthesized using carbazol-4-ones as intermediate products. Scott and Suderberg [121] reported on a new synthesis of carbazolones via two successive palladium-catalyzed reactions. Following the proposed procedure, 2-iodocyclohex-2-en-1-one (**129**, $n = 2$) reacted with 1-nitro-2-(tributylstannyl)benzene (**130**) in the presence of bis(benzonitrile)palladium(II) chloride, triphenylarsine, and copper iodide in *N*-methylpyrrolidin-2-one to give compound **131** in a good yield, and the latter was converted into 1,2-dihydrocarbazol-4(3*H*)-one **132**. Cyclohexenone derivatives **131** ($n = 2$)

were obtained in almost the same yield by reaction of *o*-bromo- or *o*-iodonitrobenzene with 2-tributylstannylcyclohexan-1-one. The hydrogenation of **131** over Pd/C was accompanied by cyclization with formation of cycloalka[*b*]indoles **133** [122] (Scheme 44).

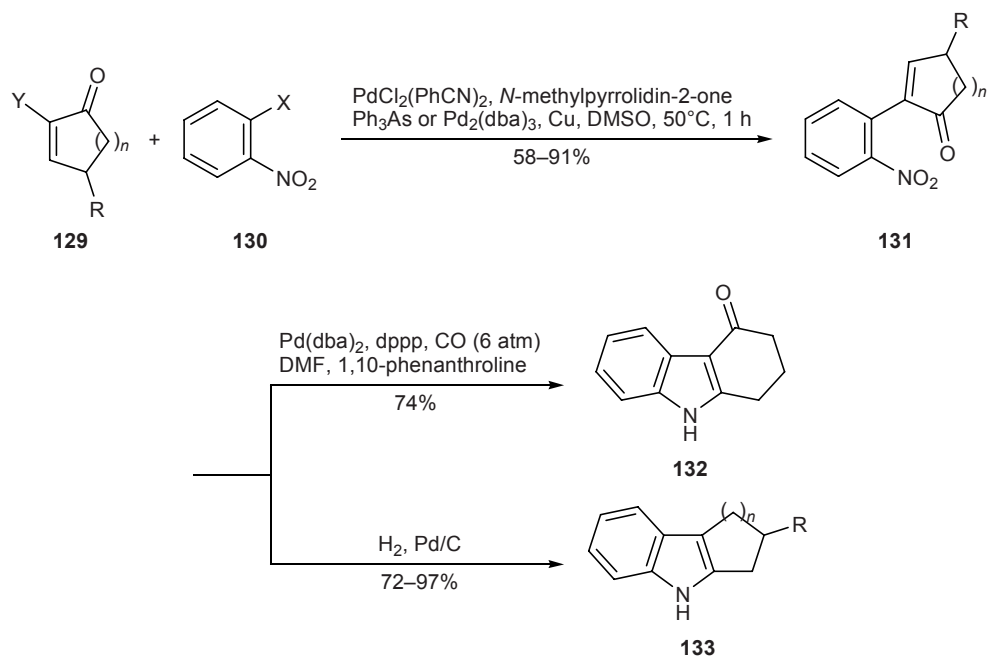
Heterocycles of the carbazole series were also obtained in satisfactory yields from *N*-aryl enamines in the presence of metal-complex catalysts. Palladium(0)-catalyzed intramolecular cyclization of 3-[(2-bromoaryl)amino]cyclohex-2-en-1-ones **134** gave no more than 38% of dihydrocarbazolones **135** [123, 124] (Scheme 45). The total syntheses of murrayaquinone A (**138a**), koeniginequinone A (**138b**), and koeniginequinone B (**138c**) together with the corresponding regioisomers **139a–139c** from isomeric arylaminobenzoquinones **136** and **137** were reported. The reaction was catalyzed by palladium acetate. The use of an equimolar amount of the catalyst somewhat shortened the reaction time, while in the presence of a catalytic amount of Pd(OAc)₂ the yields of the cyclization products were comparable (65–84%) [34] (Scheme 46).

The *Strychnos* alkaloid Minfiensine and its precursor **140** containing a tetrahydrocarbazole fragment

Scheme 43.

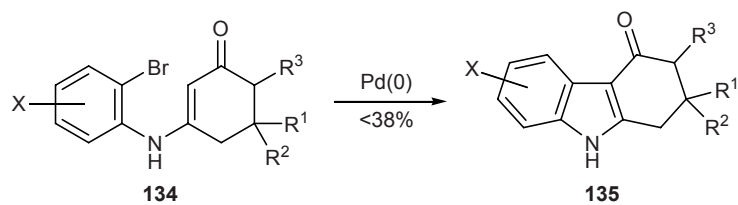


Scheme 44.



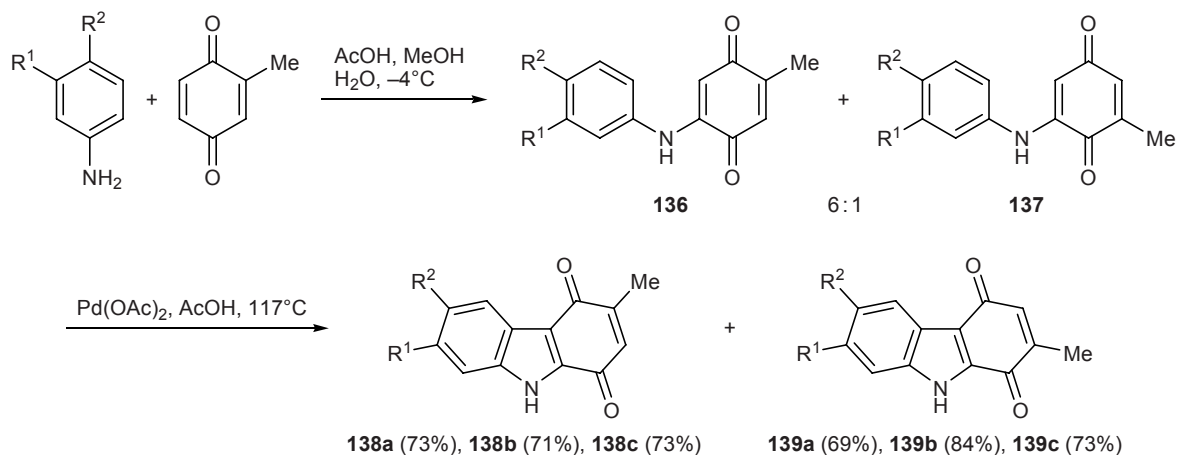
X = Br, I, Bu₃Sn; Y = I, Bu₃Sn; n = 1–3, R = H; n = 1, R = EtOCOCH₂.

Scheme 45.



X = MeO, O₂N; R¹, R², R³ = H, Me.

Scheme 46.



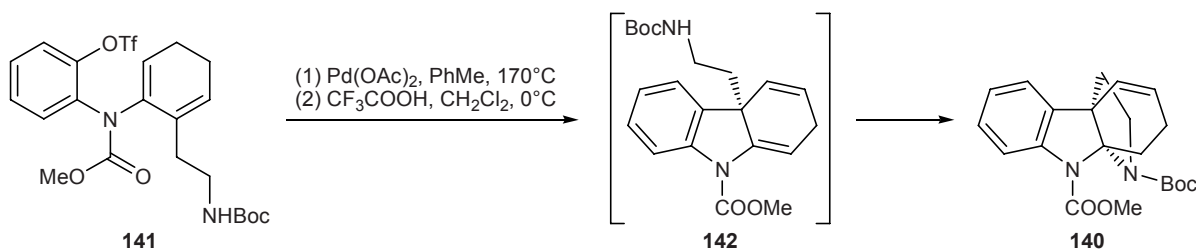
R¹ = R² = H (a); R¹ = MeO, R² = H (b); R¹ = R² = MeO (c).

were synthesized starting from enamine **141** as shown in Scheme 47. The cyclization was catalyzed by palladium acetate and (*S*)-4-*tert*-butyl-2-[2-(diphenylphosphinyl)phenyl]-4,5-dihydrooxazole. The reaction at 170°C in a microwave furnace (reaction time 30 min) gave intermediate product **142** which was treated (without isolation) with trifluoroacetic acid at 0°C. The yield of tetracyclic compound **140** was 75% [125]. (+)-Aspidospermidine was prepared from tetrahydrocarbazol-4-one **144** which was synthesized via successive treatment of enaminone **143** with sodium hydride and copper(I) iodide [126] (Scheme 48). Palladium-catalyzed cross-coupling of 1- or 2-acetoxycyclohexa-1,3-dienes with *N*-(*p*-tolylsulfonyl)aniline (**145**) gave tetrahydrocarbazoles **146** (75%) and **147** (16%) which were then converted into ketones **148** and **149**, respectively [127] (Scheme 49). Compound **148** was also synthesized from tetrahydrocarbazole **150** via oxymere-

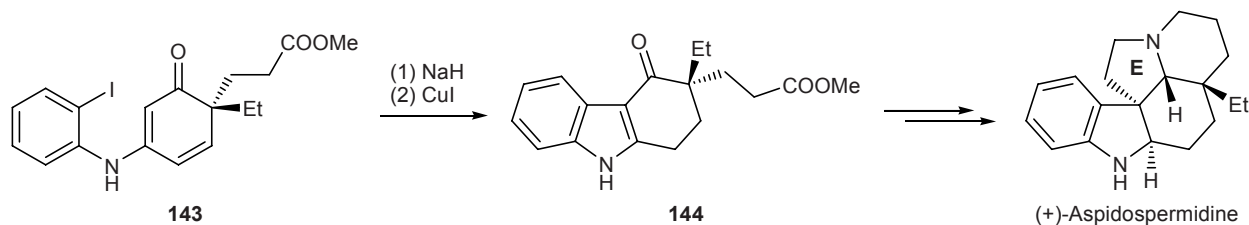
curation–demercuration [128], followed by oxidation of 2-hydroxycarbazole **151** with potassium dichromate in the presence of H₂SO₄ in acetone (Scheme 50). The reaction of macrocyclic allene **154** with *N*-(*p*-tolylsulfonyl)aniline (**145**) in the presence of Pd catalyst afforded cyclotrideca[*b*]indole **155**. Analogous cycloalka[*b*]indoles were obtained from the corresponding cyclic allenes with smaller rings [129] (Scheme 51).

Cyclization of methylsulfonyl derivative **157a** of indole **156a** (R² = CH₂=CH), as well as of compound **157b** (R² = OCH₂Ph; a part of the cyclic skeleton is shown with dashed bonds), by the action of *t*-BuMgCl in the presence of Zn(OTf)₂ resulted in the construction of the main skeleton of (+)-nodulisporic acid F, as well as of the heptacyclic skeleton of (–)-nodulisporic acid D [130, 131] (Scheme 52). (+)-Nodulisporic acid F is the simplest member of a family of novel ectoparasitocidal indole alkaloids. Compound **157c** with

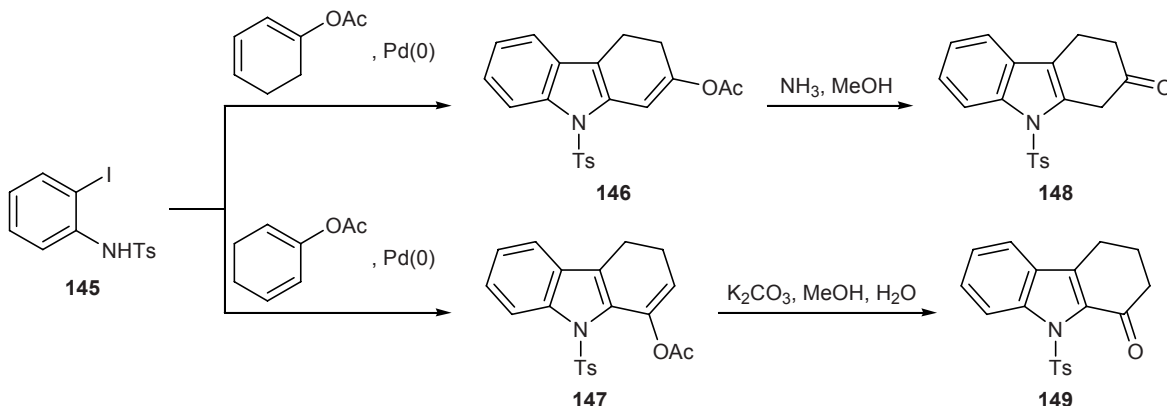
Scheme 47.



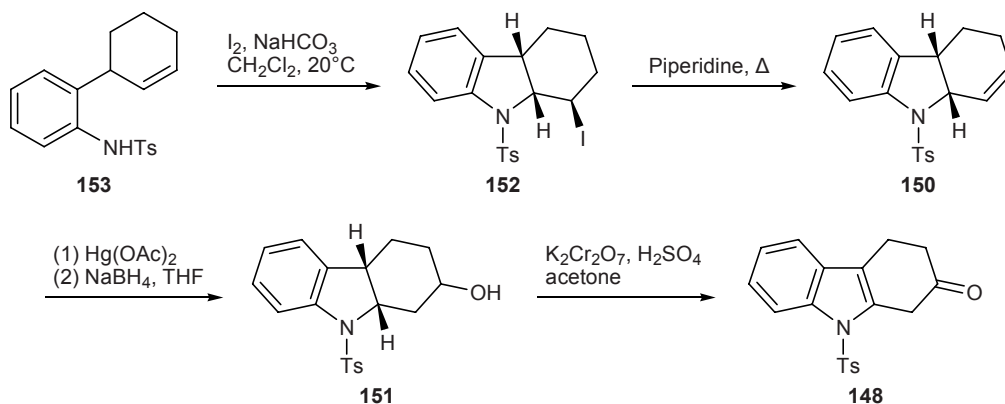
Scheme 48.



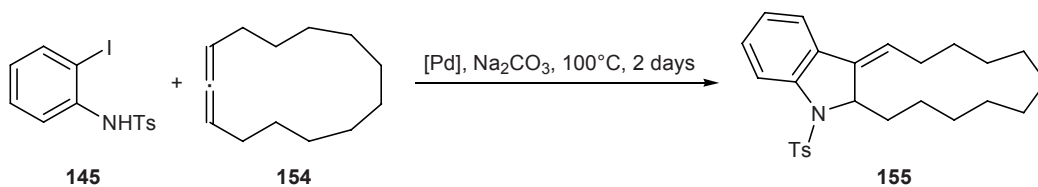
Scheme 49.



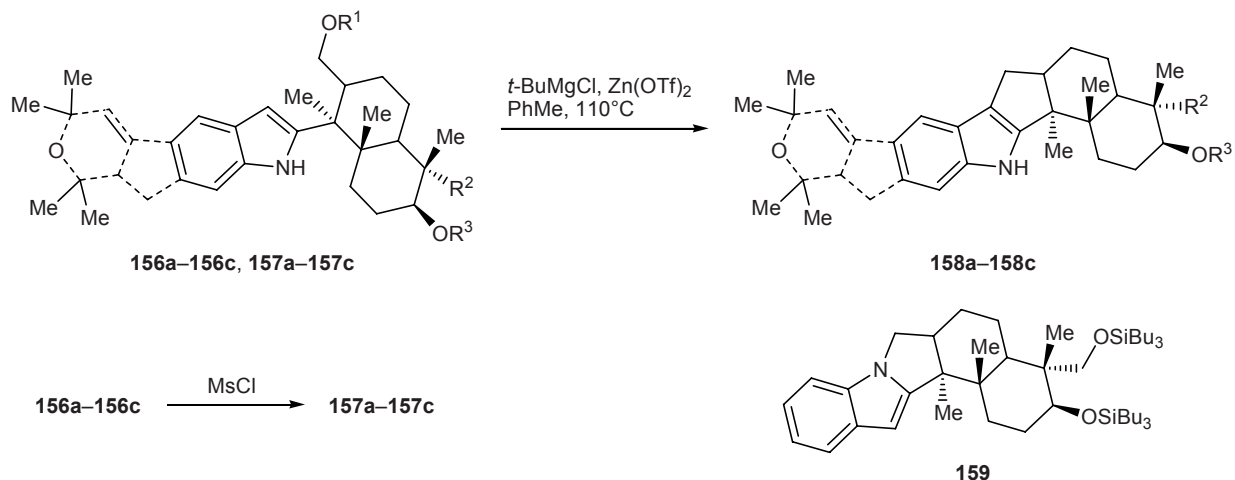
Scheme 50.



Scheme 51.



Scheme 52.



156, $\text{R}^1 = \text{H}$; 157, $\text{R}^1 = \text{MeSO}_2$; $\text{R}^2 = \text{CH}_2=\text{CH}$, $\text{R}^3 = \text{Et}_3\text{SiO}$ (a); $\text{R}^2 = \text{PhCH}_2\text{O}$, $\text{R}^3 = \text{Et}_3\text{SiO}$ (b); $\text{R}^2 = \text{Bu}_3\text{SiOCH}_2$, $\text{R}^3 = \text{Bu}_3\text{SiO}$ (c).

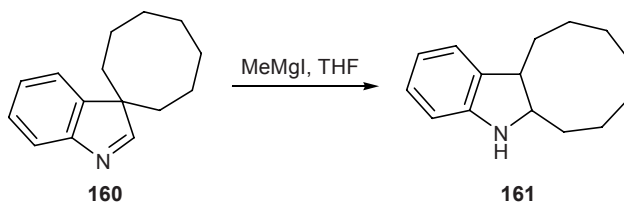
$\text{R}^2 = \text{CH}_2\text{OTBS}$, $\text{R}^3 = \text{OTBS}$ gives rise to a regioisomer of **158c**, cyclization product at the nitrogen atom **159**; the isomer ratio changes from 1.0:1.8 to 9.0:1.0, depending on the reaction conditions [130]. Analogous cyclization of methylsulfonyl derivative with *tert*-butylmagnesium chloride was used in the convergent synthesis of (–)-21-isopentenylpaxilline which is a biologically active tremorgenic alkaloid having a cyclopenta[*b*]indole fragment [132].

Spiro-fused indole **160** reacted with methylmagnesium iodide in THF to produce cyclonona[*b*]indole **161**

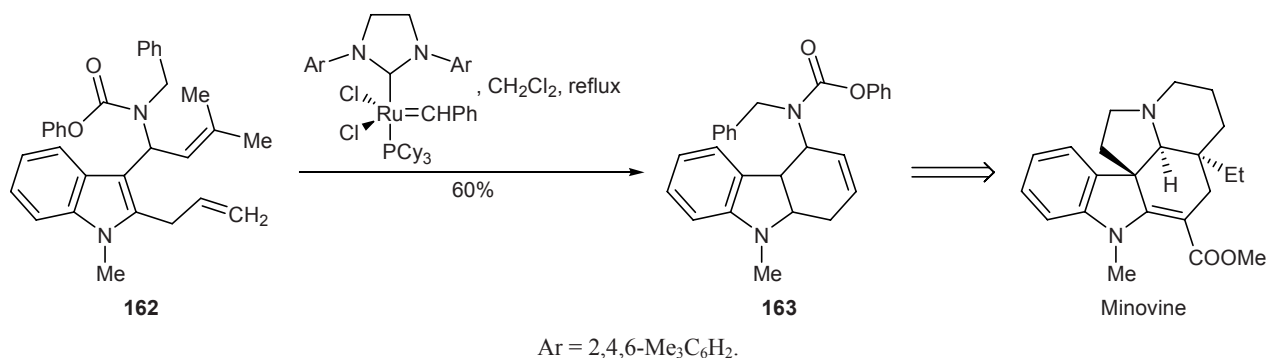
in almost quantitative yield [133] (Scheme 53). Several examples of the formation of cycloalka[*b*]indoles from 2,3-dialkenylindoles were reported [134, 135]. 4-Aminodihydrocarbazole as probable precursor of minovine was synthesized from 2,3-dialkenylindole **162**. Metathesis of **162** in the presence of the second-generation Grubbs ruthenium catalyst in boiling methylene chloride led to the formation of 60% of 1,4-dihydrocarbazole **163** [135] (Scheme 54).

Cycloalka[*b*]indoles **165a** and **166b** were formed in 47–90% yield from 2-(pent-4-en-1-yl)- and 2-(hex-

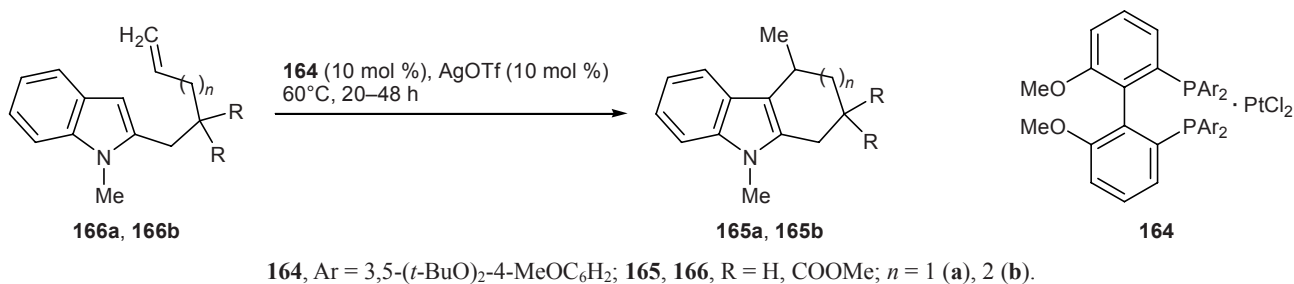
Scheme 53.



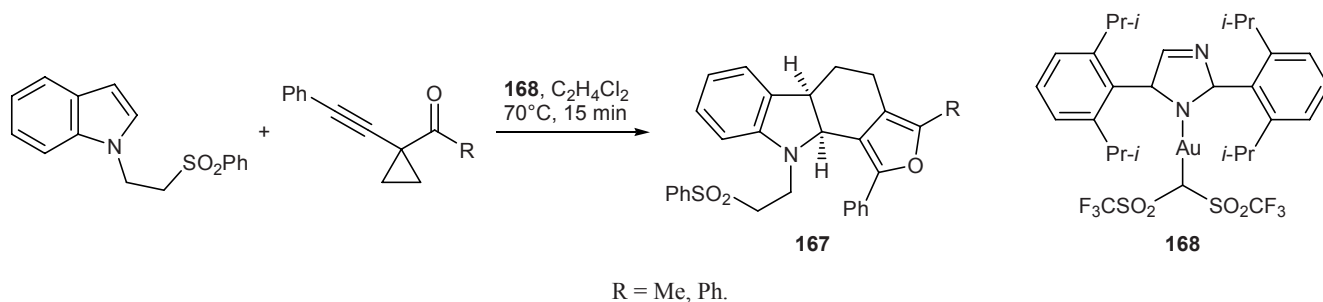
Scheme 54.



Scheme 55.



Scheme 56.

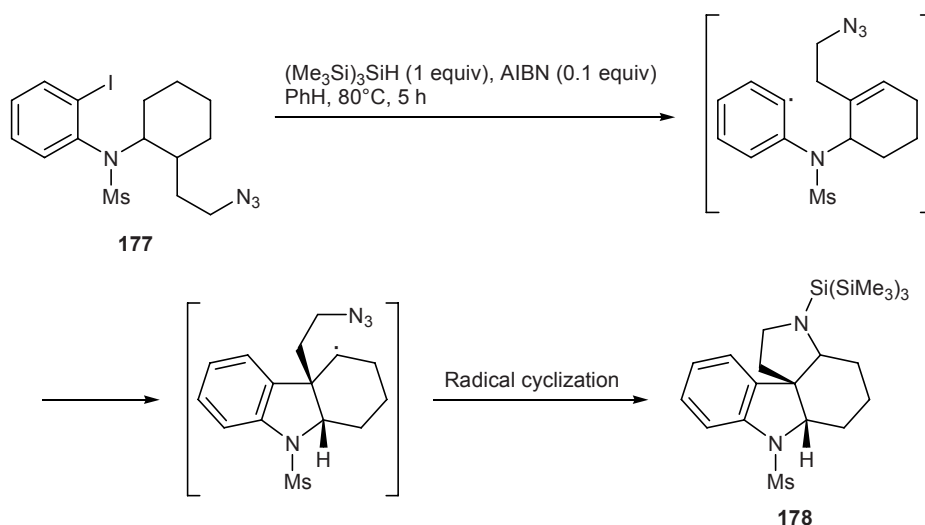


5-en-1-yl)indoles **166a** and **166b** on heating with 10 mol % of platinum complex **164** at 60°C in the presence of silver trifluoromethanesulfonate in different solvents [136] (Scheme 55). The reaction with *N*-methyl-2-(2-ethoxycarbonylpent-4-en-1-yl)indole (R = CO₂Me) gave 94% of diastereoisomeric methyl 4,9-dimethyltetrahydrocarbazole-2-carboxylates with a *cis*-to-*trans* isomer ratio of 9:1. The use of 2 mol % of PtCl₂ and 5 mol % of HCl as catalyst favored

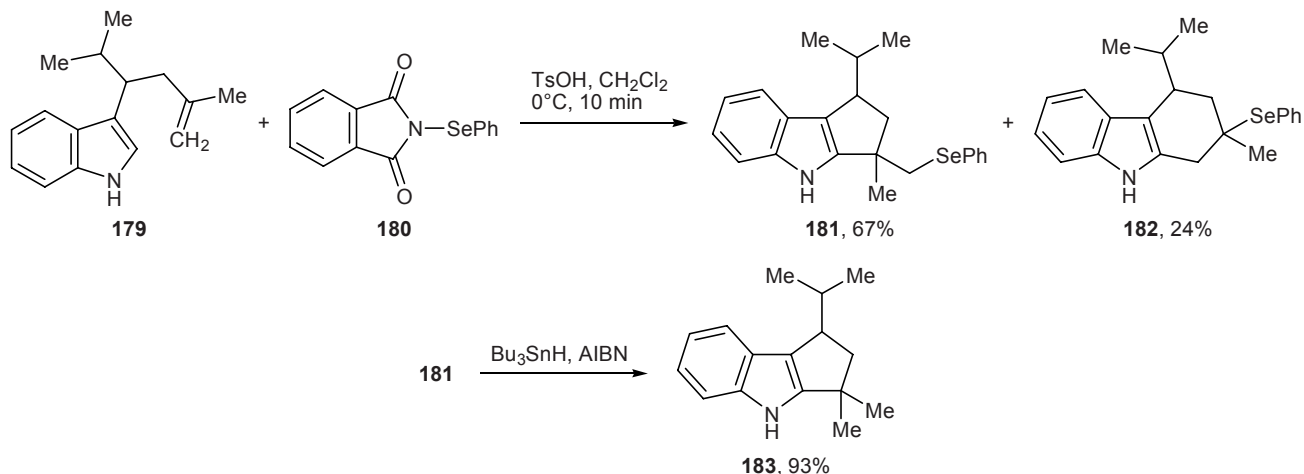
formation of a 1:2 mixture of diastereoisomers with an overall yield of 98% [137].

One more example of the synthesis of cycloalka[*b*]indoles in the presence of metal complexes with a fairly large substituent on the metal atom is the formation of tetrahydrocarbazoles **167** having a fused furan ring in the reaction of cyclopropyl ketones with indole in the presence of 5 mol % of gold catalyst **168**. The yields of carbazoles **167** ranged from 87 to 91%,

Scheme 61.



Scheme 62.



[146] (Scheme 62). Analogous reaction with 2-homoallyl derivative **184** afforded only tetrahydrocarbazole **185** (Scheme 63). The cyclization involves intermediate formation of 3-phenylselanylindole **186** (path *b*) which was isolated and characterized. Reductive deselenation of **185** by the action of Bu_3SnH gave tetrahydrocarbazole **187** in high yield [146].

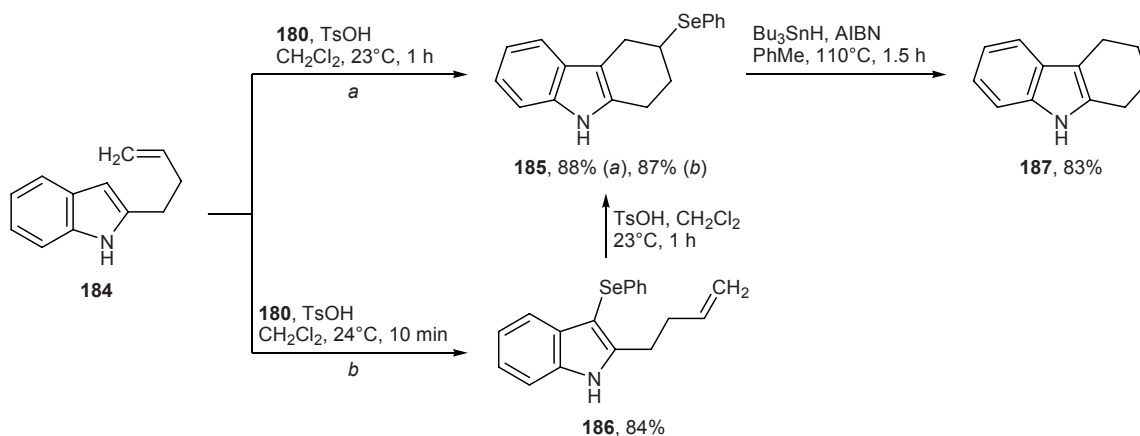
Ondetti and Deulofeu [147] described the total synthesis of alkaloid Guatambuine from methyl 3-(pyridin-3-ylmethyl)indole-2-carboxylate, where one step (among five) was radical cyclization of *Se*-phenyl indole-2-carboselenoate **188** by the action of tributylstannane (Scheme 64). Piperidinocarbazole derivative **189** thus formed was converted without additional purification into the target alkaloid [148].

Compound **190** was reported to react with Bu_3SnH in the presence of azobis(isobutyronitrile) (AIBN) to

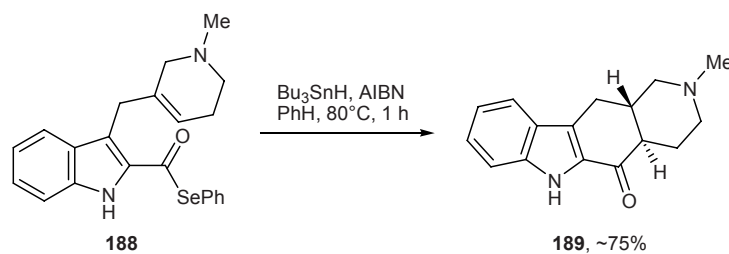
give tetrahydrocyclopenta[*b*]indole **191**. Probable reaction mechanisms were proposed, one of which involved 5-*endo*-trig cyclization of intermediate **192** with formation of radical **194** which is converted into final structure **191** via C–C bond cleavage and elimination of hydrogen atom. Another path is formation of intermediate vinyl radical **195** whose 5-*exo*-trig cyclization yields cyclopenta[*b*]indole **191**. Carbazole radical **192** also gives rise to methyl 3-ethyl-9-methylsulfonyl-3,4,4a,9a-tetrahydrocarbazole-3-carboxylate (**193**) [149] (Scheme 65).

Analogous reaction of *N*-(penta-1,4-dien-3-yl)anilines **196a–196c** leads to a mixture of indoles **197–199** in poor yields (Scheme 66). Under similar conditions, compound **200** was converted into *N*-methylsulfonylhexahydrocyclohepta[*b*]indole **201** in 50% yield. On the other hand, eight-membered analog **202** ($n = 2$)

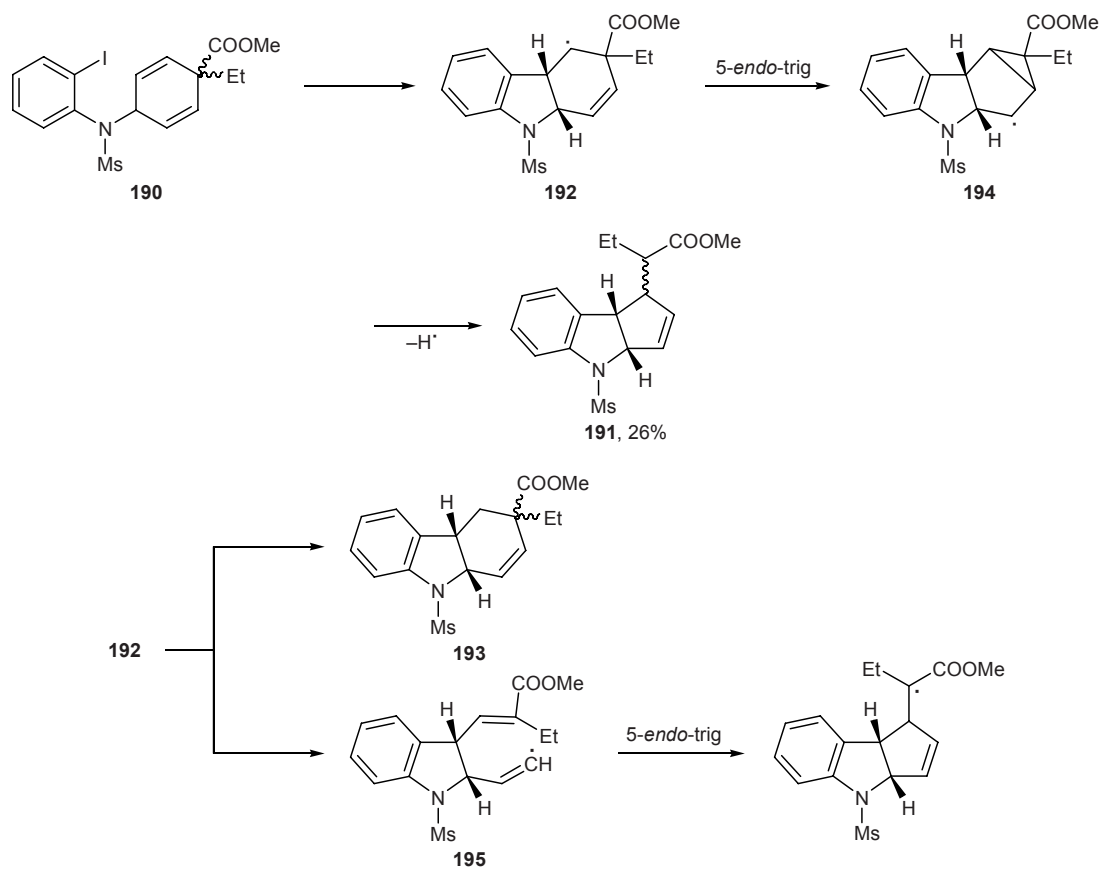
Scheme 63.



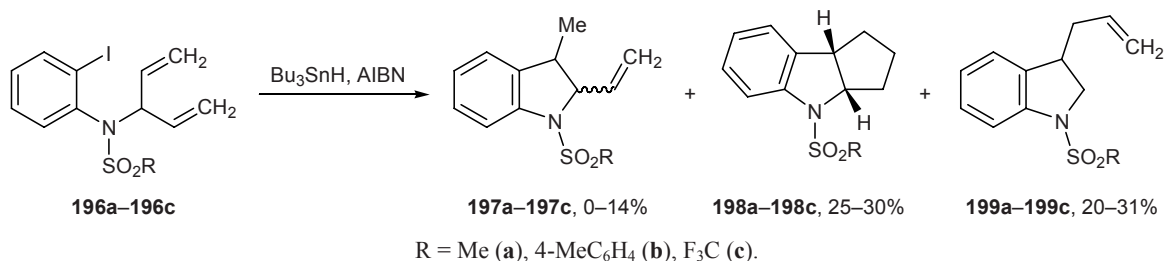
Scheme 64.



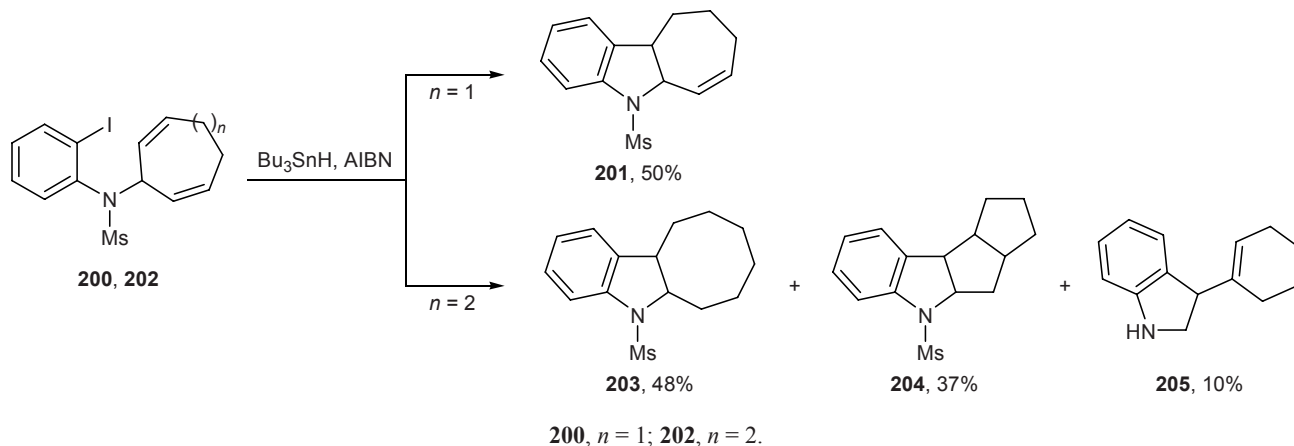
Scheme 65.



Scheme 66.



Scheme 67.



gave rise to tricyclic compound **203** and two more indole derivatives, tetracyclic compound **204**, and 3-(cyclohex-1-en-1-yl)-2,3-dihydro-1*H*-indole **205**, the latter being formed as a result of transannular cyclization (Scheme 67).

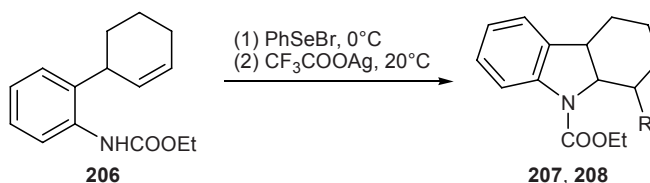
Cyclization of 2-(cycloalk-2-en-1-yl)anilines. The discovery of the aromatic amino-Claisen rearrangement have made *o*-cycloalkenylanilines as accessible as their numerous *o*-alkenyl analogs, and these compounds have found application in the synthesis of various cycloalka[*b*]indoles in the presence of electrophilic reagents. The cyclization of ethyl 2-(cyclohex-2-en-1-yl)phenylcarbamate (**206**) with phenylselenanyl bromide under mild conditions afforded hexahydrocarbazole **207** [150] (Scheme 68).

As a rule, acid-catalyzed intramolecular cyclizations of *o*-cycloalkenylanilines result in the formation

of unfunctionalized partially hydrogenated cycloalka[*b*]indoles [151, 152]. Hexahydrocyclopenta[*b*]indoles **210a–210e** (E = H) were obtained in good yields by heating 2-(cyclopent-2-en-1-yl)anilines **209a–209e** with HCl at 200°C [153–155] (Scheme 69). The kinetic study on the cyclization of cyclopentenylaniline **209a** [155] showed that the substrate consumption conforms to first-order equation. The energy of activation of this process was estimated at 98.1±2.2 kJ/mol, which is consistent with published data [155]. The reactions of anilines **209** with iodine gave 85–91% of 3-iodo-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indoles **210** (E = I) [153].

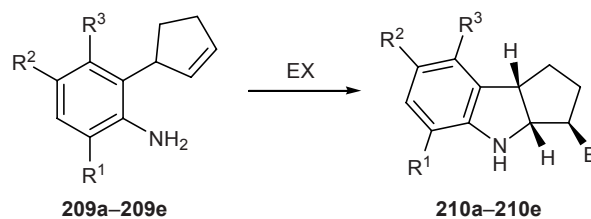
Cyclohexenylanilines **211a–211f** reacted with molecular iodine in carbon tetrachloride to produce cyclohexa[*b*]indoles **212a–212f** which separated from the solution. Compounds **212a–212f** in polar solvents

Scheme 68.



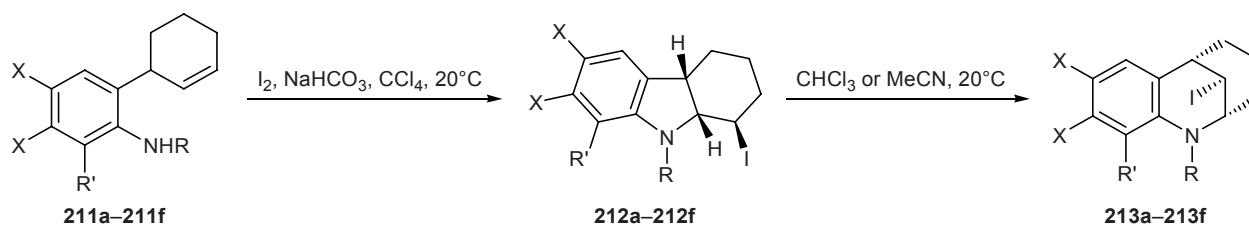
207, R = PhSe; 208, R = H.

Scheme 69.



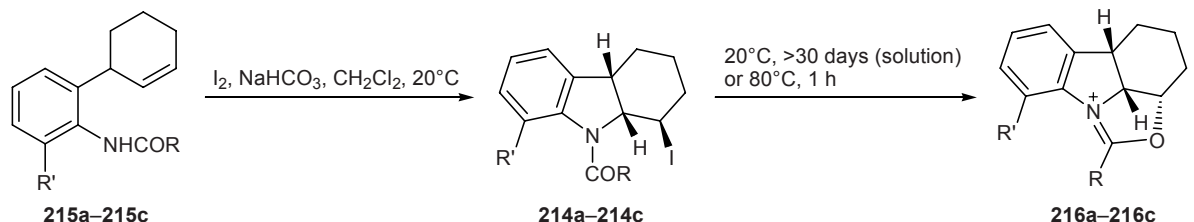
E = H, I; R¹ = Me, R² = R³ = H (a); R¹ = R² = R³ = H (b); R¹ = R² = Me, R³ = H (c); R¹ = MeO, R² = R³ = H (d); R¹ = R³ = Me, R² = H (e).

Scheme 70.



R = R' = X = H (a); R = X = H, R' = MeO (b); R = R' = H, X = F (c); R = Me, R' = X = H (d); R = PhCH₂, R' = X = H (e); R = *i*-Pr, R' = X = H (f).

Scheme 71.

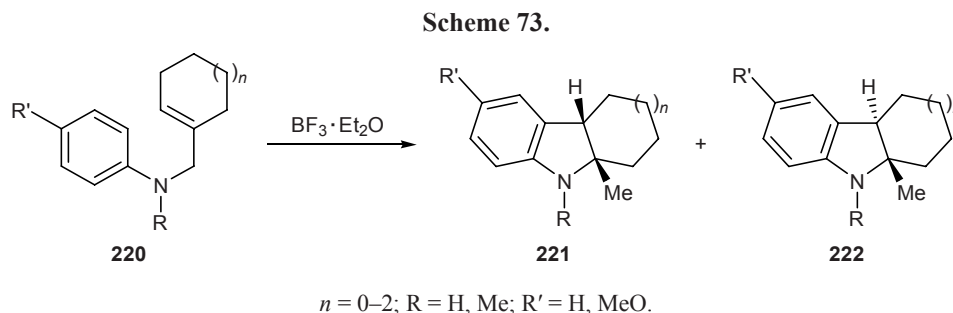
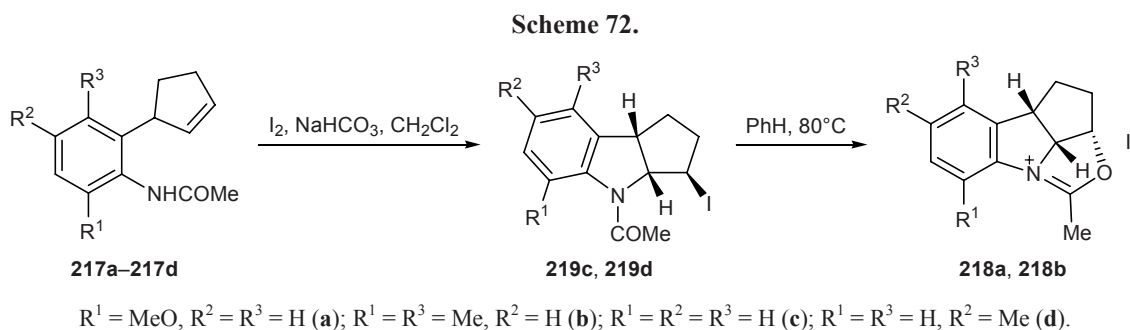


R = Me, R' = H (a); R = Ph, R' = Me (b); R = Ph, R' = H (c).

underwent isomerization to 3,4-benzo-2-azabicyclo[3.3.1]nonanes **213a–213f** (Scheme 70). The isomerization was strongly hindered if the aromatic ring contained two fluorine atoms [156–163]. Bromination and iodination of *N*-methylsulfonyl- and *N*-(*p*-tolylsulfonyl)cyclohexenylanilines led to the formation of 1-halohexahydrocarbazoles which did not undergo isomerization [156, 159]. On the other hand, the presence of an acyl protecting group at the nitrogen atom in 1-iodohexahydrocarbazoles **214a–214c** obtained by cyclization of *N*-acyl-2-cyclohexenylanilines **215a–215c** did not prevent them from undergoing isomerization. The electron density on the amide nitrogen atom in **214** is lower than on the nitrogen atom in analogous sulfonyl derivatives, and this factor is likely to favor isomerization of hexahydrocarbazoles **214a–214c** to oxazolocarbazolium iodides **216a–216c** in nearly quantitative yields [164, 165] (Scheme 71). The reac-

tion outcome in the cyclization of cyclopentenylanilides **217a–217d** was found to depend on the presence of substituent in the other *ortho* position. 2,6-Di-substituted anilines **217a** and **217b** gave rise to oxazolo[5,4,3-*de*]carbazolium salts **218a** and **218b**, respectively, whereas cyclization of **217c** and **217d** (R¹ = H) resulted in the formation of hexahydrocyclopentaindoles **219c** and **219d** which turned out to be stable (no subsequent oxazole ring closure occurred; Scheme 72).

Apart from *o*-cycloalkenylanilines, *N*-cycloalkenylanilines can also be converted into cycloalka[*b*]indoles. An example of such transformations is illustrated by Scheme 73. Heating of *N*-cycloalkenylanilines **220** with boron trifluoride–ether complex gave the corresponding stereoisomeric cycloalka[*b*]indole derivatives **221** and **222** in poor yields. As with allylanilines having no substituent on the α -carbon atom in

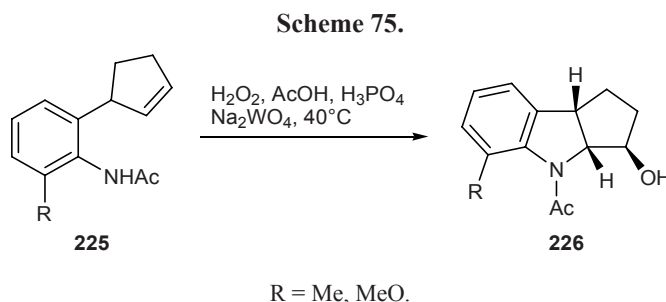
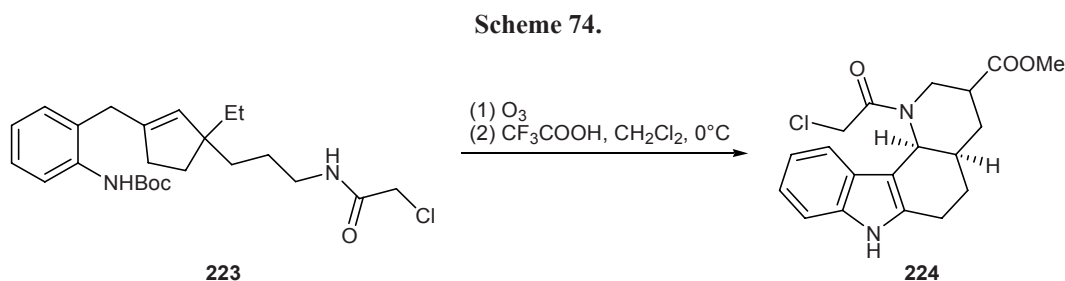


the allyl moiety, the reaction is generally accompanied by side processes, in particular, by isomerization of the product formed as a result of migration of the cycloalkenyl group to the *ortho* position [167].

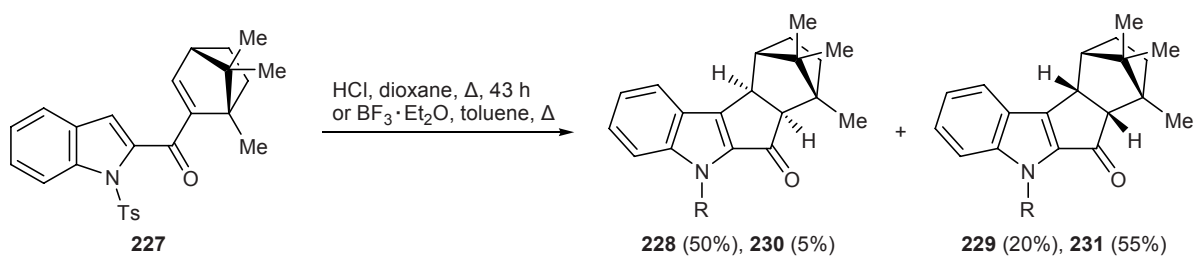
Formation of cycloalka[*b*]indoles in oxidative processes. Only a few data are available in the literature on the synthesis of cycloalka[*b*]indole derivatives by oxidation reactions. Ozonolysis of *o*-alkenylaniline **223**, followed by treatment of the reaction mixture with trifluoroacetic acid in methylene chloride, gave tetracyclic compound **224** as intermediate in the syn-

thesis of (\pm)-aspidospermidine [168] (Scheme 74). Hexahydrocyclopenta[*b*]indoles **225** were synthesized by oxidation of *N*-acetyl-2-cyclopentenylanilines **226** with hydrogen peroxide in acetic acid in the presence of sodium tungstate and phosphoric acid (Scheme 75). From compound **226** ($\text{R} = \text{H}$), only the corresponding double bond epoxidation product was obtained [169, 170].

Synthesis of cycloalka[*b*]indoles from various 2(3)-alkyl(oxoalkyl)indoles. Most initial compounds of this type are commercially unavailable; therefore,

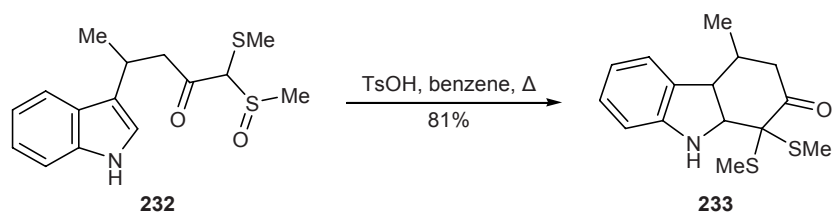


Scheme 76.

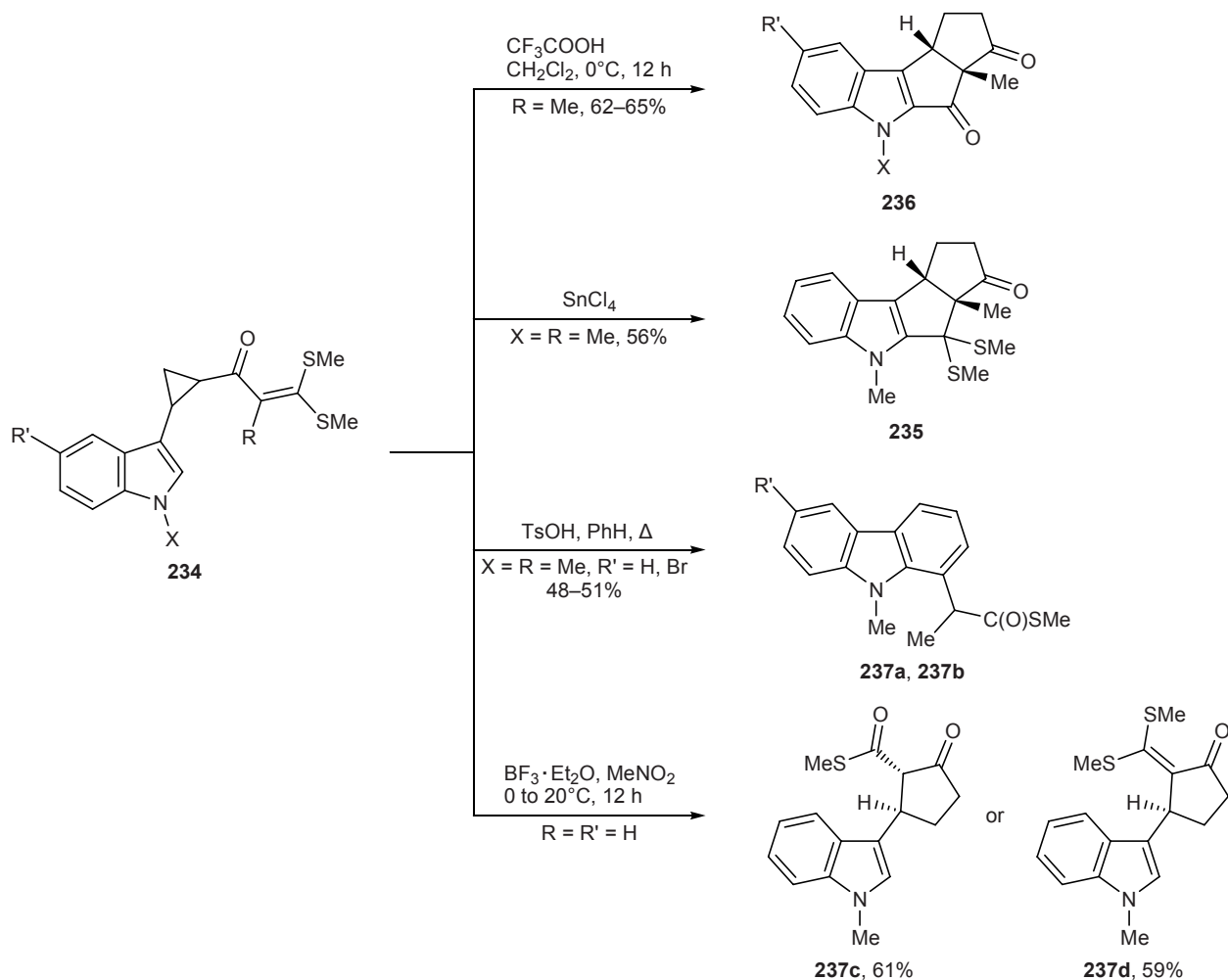


228, 229, R = Ts; 230, 231, R = H.

Scheme 77.



Scheme 78.

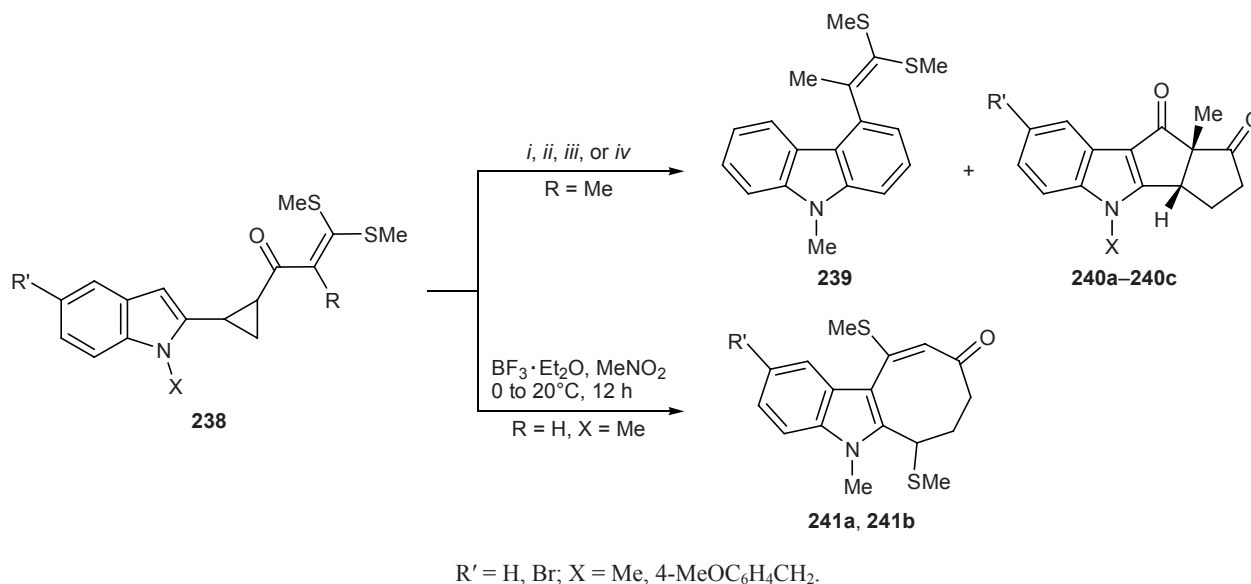


the corresponding procedures are fairly tedious. Cheng et al. [171–173] performed the total synthesis of analogs of alkaloid (\pm)-Yuehchukene [174] isolated from *Murraya paniculata*. Here, the starting compounds were 2- or 3-substituted indoles. A procedure was proposed for the synthesis of compounds having a cyclopenta[*b*]indole skeleton from accessible (1*S*)-(–)- or (1*R*)-(+)-camphor derivatives. The cyclization of 2-substituted *N*-(*p*-tolylsulfonyl)indole **227** in boiling dioxane containing concentrated hydrochloric acid gave a mixture of stereoisomeric cyclopenta[*b*]indoles **228** and **229** with a fused bicyclo[2.2.2]heptane fragment. Treatment of **228** and **229** with boron trifluoride in toluene on heating resulted in removal of the tosyl group with formation of NH derivatives **230** and **231** [173] (Scheme 76).

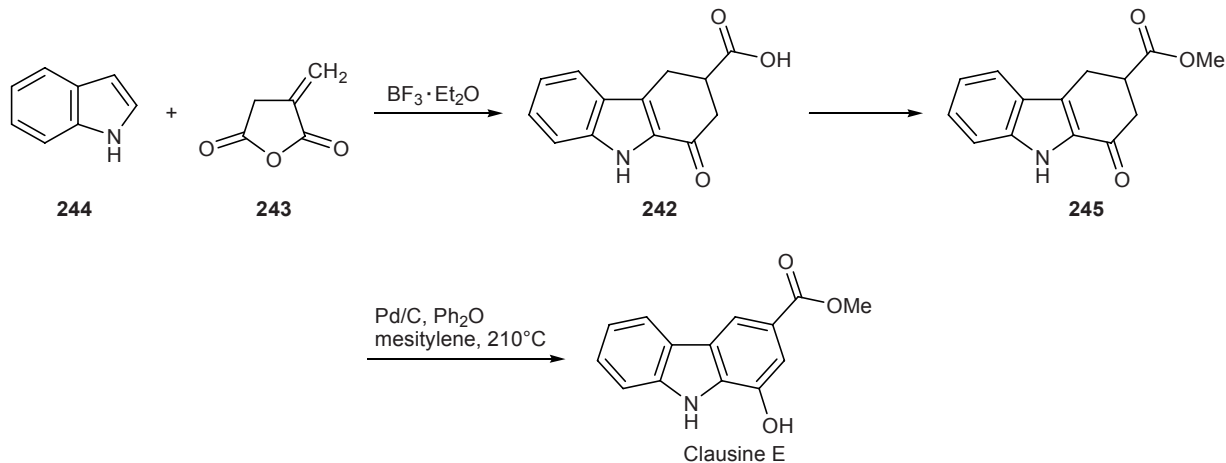
4-Methyl-1,1-bis(methylsulfonyl)-1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-2-one (**233**) was synthesized in 81% yield by cyclization of sulfur-containing 3-substituted indole **232** on heating in benzene in the presence of *p*-toluenesulfonic acid [175] (Scheme 77). Dithio acetals like **233** mediate some cyclizations of dithio derivatives of 2- and 3-cyclopropyl-substituted indoles in the presence of various Lewis and Brønsted acids. Probable mechanisms of these cyclizations were proposed.

The transformation of 3-cyclopropylindole **234**, catalyzed by SnCl₄, gave 56% of dithio acetal **235**, and the latter was isolated as individual substance (Scheme 78). In the other cases, dithio acetals were assumed to be formed as intermediates. The reactions catalyzed by H₃PO₄ or CF₃COOH afforded tetracyclic

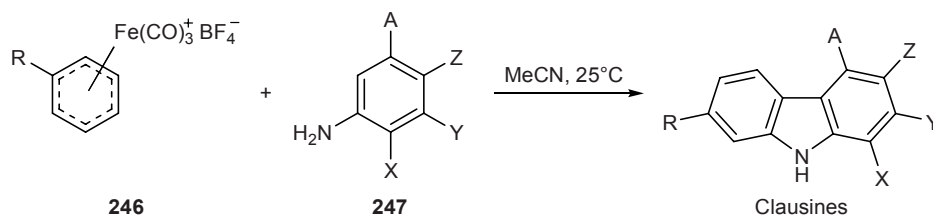
Scheme 79.



Scheme 80.



Scheme 81.



R = H (Clausines H and K), MeO (Clausine O).

diketones **236** (yield 56–63%) [176]. Carbazoles **237a** and **237b** were formed in 48–51% yield by prolonged heating of indole derivatives **234** (R' = H, Br; X = Me) in boiling benzene in the presence of *p*-toluenesulfonic acid. Compound **234** (R = R' = H) in the presence of boron trifluoride–ether complex underwent intramolecular cyclization involving the alkenoylcyclopropyl fragment with formation of 3-(indol-3-yl)cyclopentanone **237c**. Analogous reaction catalyzed by SnCl₄ led to bis(methylsulfanyl)methylidenecyclopentanone **237d** (Scheme 78).

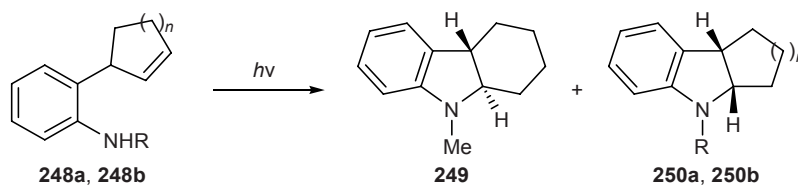
2-Cyclopropylindole **238** in the presence of SnCl₄ or TsOH (*i*) was converted into carbazole **239** (yield 25–65%) (Scheme 79), whereas 53–69% of diketone **240a** was obtained in the reactions catalyzed by BF₃·Et₂O (*ii*), CF₃COOH (*iii*), and MeSO₂H (*iv*). Indole **238** (R = H) in the presence of BF₃·Et₂O gave rise to cycloocta[*b*]indoles **241a** and **241b**. If R = Me, the products were diketones **240b** and **240c** (R' = H, Br; X = Me, 4-methoxybenzyl) [176].

Heterocyclic compound **242** is an intermediate product in the synthesis of alkaloid Clausine E. It was obtained by Michael addition of itaconic anhydride (**243**) to 1*H*-indole (**244**) in the presence of a catalytic

amount of a Lewis acid. 1-Oxo-1,2,3,4-9*H*-carbazole-3-carboxylic acid (**242**) was esterified with methanol, and ester **245** was subjected to dehydrogenation under severe conditions to isolate the target alkaloid in 38% yield [177] (Scheme 80). Insofar as the yield was not high, a one-step procedure for the synthesis of such carbazoles is more attractive. According to this procedure, some structurally related carbazole alkaloids, such as Carquinostatin A [178], Furostifoline [179, 180], and Clausines H, K, and O [181], were synthesized by electrophilic substitution in anilines **247** by tricarbonyliron complex **246** (Scheme 81).

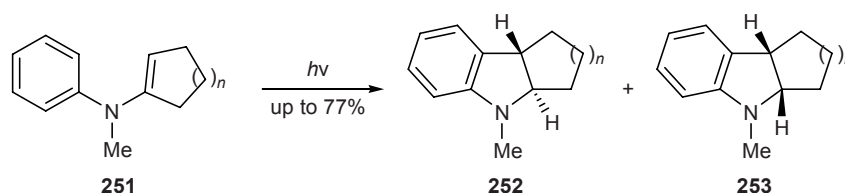
Photocyclizations. Photochemical cyclizations make it possible to obtain *N*-alkyl-substituted cycloalka[*b*]indoles. No cyclization occurs with compounds lacking an alkyl group on the nitrogen atom. UV irradiation promotes the transformation of 2-(cyclohex-2-en-1-yl)-*N*-methylaniline (**248a**) into a mixture of carbazoles **249** and **250a** with an overall yield of 97% (*trans*–*cis* isomer ratio 2:1) [182] (Scheme 82). Photochemical cyclization of 2-(cyclopent-2-en-1-yl)-*N*-ethylaniline (**248b**) gives 32% of *N*-ethylhexahydrocyclopenta[*b*]indole **250b**. Photocyclization of *N*-cycloalkenylanilines **251** is characterized by higher

Scheme 82.

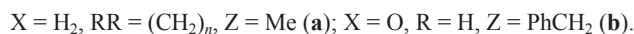
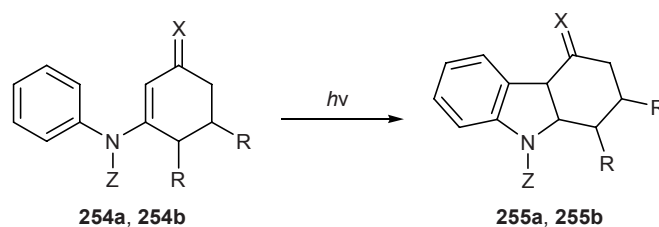


$n = 2$, R = Me (**a**); $n = 1$, R = Et (**b**).

Scheme 83.



Scheme 84.

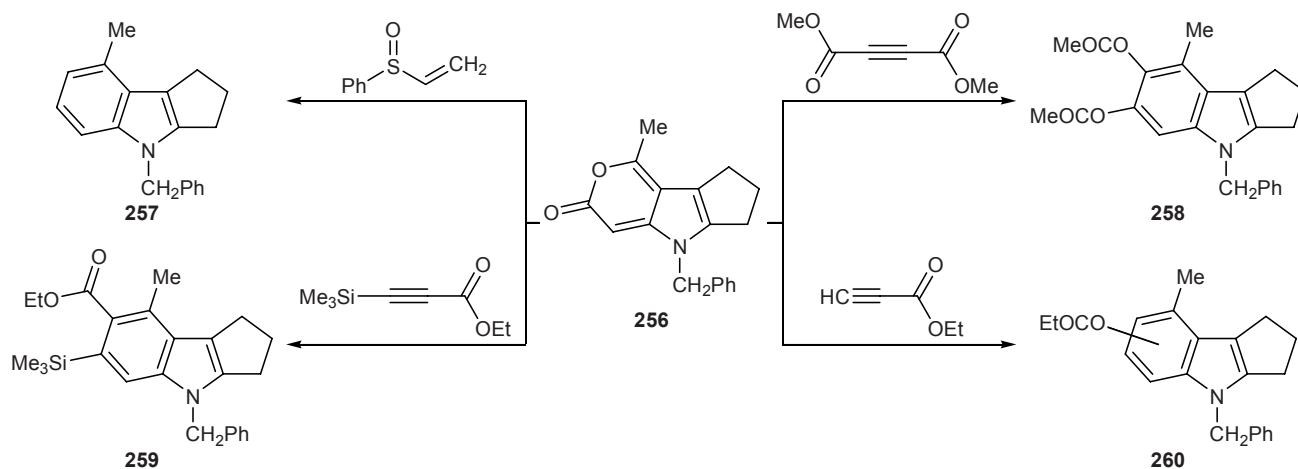


yields of products **252** and **253** (up to 77%) [183, 184] (Scheme 83). Amines **254a** and **254b** having more complex cyclohexenyl fragments underwent photochemical cyclization to give tetracyclic compound **255a** [185] and carbazol-4-one **255b**, respectively [186, 187] (Scheme 84).

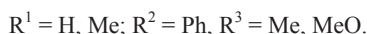
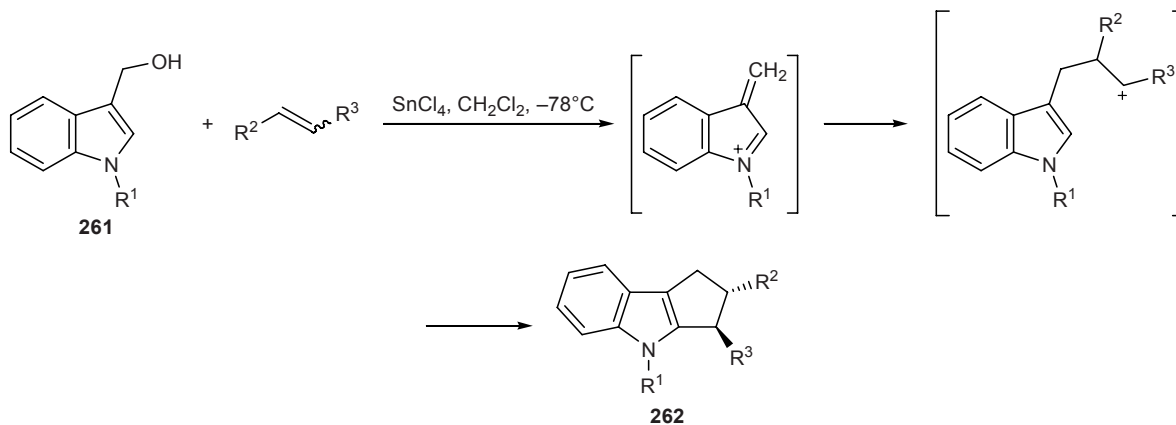
Syntheses of cyclopenta[b]indoles from cyclopentapyranopyrrole and indol-3-ylmethanol. The

Diels–Alder reactions of cyclopentapyranopyrrole **256** with phenyl vinyl sulfone and acetylenic compounds may be regarded as nontrivial method for the synthesis of cycloalka[b]indole derivatives. In such a way, compounds **257–260** having various substituents in the aromatic ring were synthesized in 47–89% yield [188] (Scheme 85). Likewise, indol-3-ylmethanol **261** reacted under mild conditions with olefinic compounds to

Scheme 85.



Scheme 86.



give cyclo-penta[b]indoles **262** with various substituents in the saturated fragment [189]. In the reactions with phenylpropene the yields attained 55–63%, whereas in the condensations with other alkenes the yields of **262** did not exceed 17–27% (Scheme 86).

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