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REVIEW

Advancements in Syntheses of Carbazole and Its Dervatives

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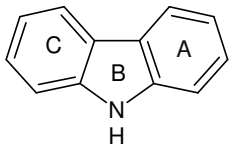
In this review article, we summarize different synthetic routes for the syntheses of carbazole and its derivatives which are known to have important photophysical and biological properties. Moreover, a detailed coverage from year 2001-Feb 2008 of the classical and the non-classical procedures for the total syntheses of biologically active carbazole alkaloids and their derivatives have also been reported.

Key Words: Heterocyclic compounds, Carbazole.

INTRODUCTION

The prevalence of heterocycles in medicinally important compounds continues to derive the need for new methods for their preparation[1]. Carbazole derivatives are known to have important photo physical and biological properties[2]. Carbazole **A** was isolated first from coal tar in 1872 by Graebe and Glazer[3].



A Carbazole

In this review, the authors summarize different synthetic routes for the syntheses of carbazole alkaloids and their derivatives. Moreover, a detailed coverage from year 2001-Feb 2008 of the classical methods and the non-classical procedures for the total syntheses of biologically active carbazole alkaloids and their derivatives have also been reported. The nomenclature used in this review for carbazole alkaloids is that used by Chemical Abstracts. Conventional tricyclic ring systems are denoted by A, B and C and the numbering starts from ring A. The term carbazole used in this review refers to a 9*H*-carbazole. The classification of the carbazoles is based on the substitution pattern of ring A, although ring C may also carry various substituents.

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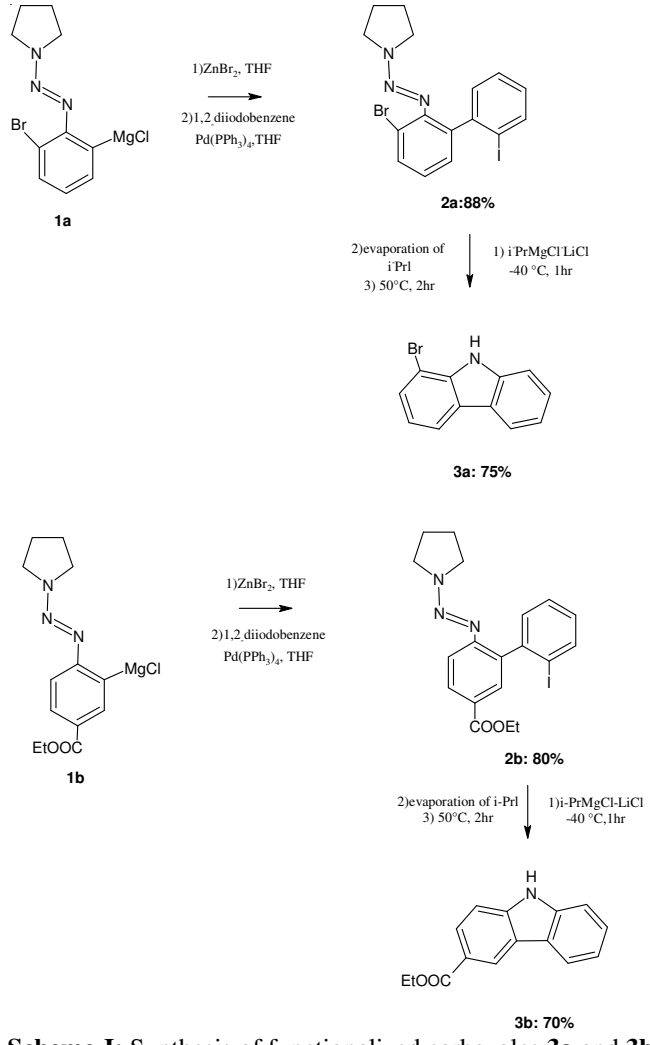
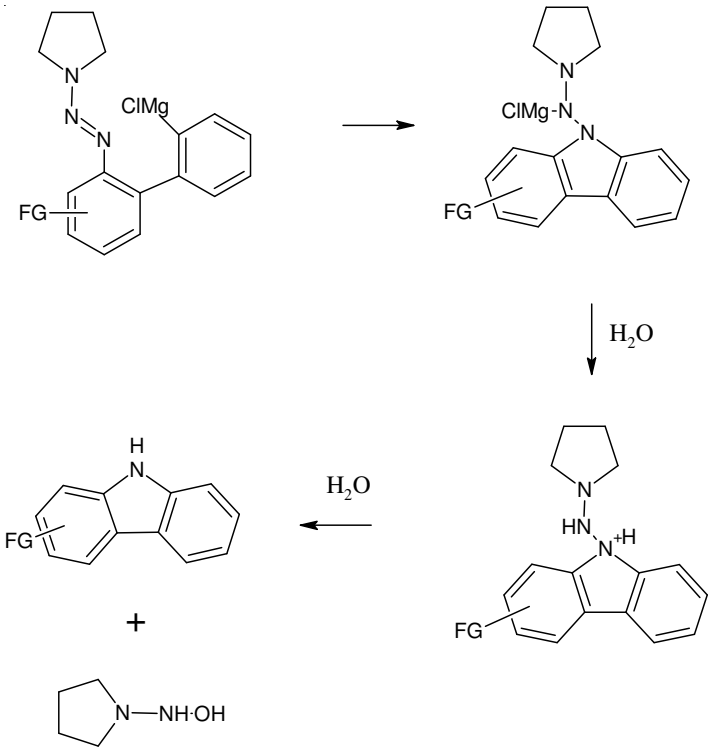
A brief overview of different methods used for syntheses of carbazoles and its derivatives are given in the proceeding sections.

Ching-Yuan Li and co-workers[4] have developed a method for new carbazole synthesis[5] starting from Grignard reagent **1a** and **1b**, they have done a Negishi cross-coupling with 1,2-diiodobenzene resulting in the formation of derived polyfunctional biphenyls **2a** (88 %) and **2b** (80 %). The reaction of the compound type **2a** and **2b** with *i*-PrMgCl-LiCl (1-1 equiv., -40 °C, 1 h) gives the functional carbazoles **3a** (75 %) and **3b** (70 %), respectively. The evaporation of *i*-PrI from the I/Mg-exchange is very important before heating (50 °C, 2 h). Otherwise, unnecessary cross-coupling side products with *i*-PrI are observed (**Scheme-I**). An empirical mechanism of the cyclization in which hydroxylamine derivative is formed as side product of carbazole derivative is shown (**Scheme-II**).

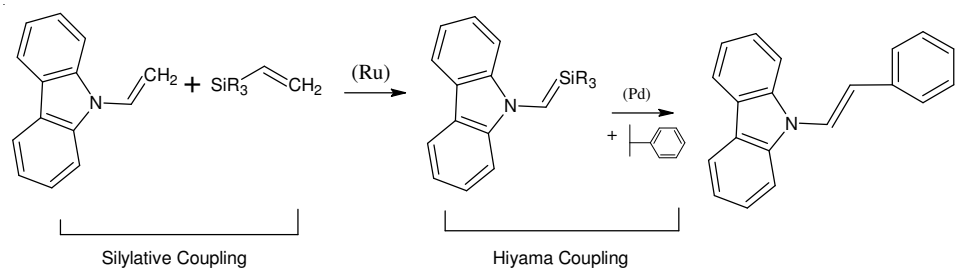


Scheme-I: Synthesis of functionalized carbazoles **3a** and **3b**



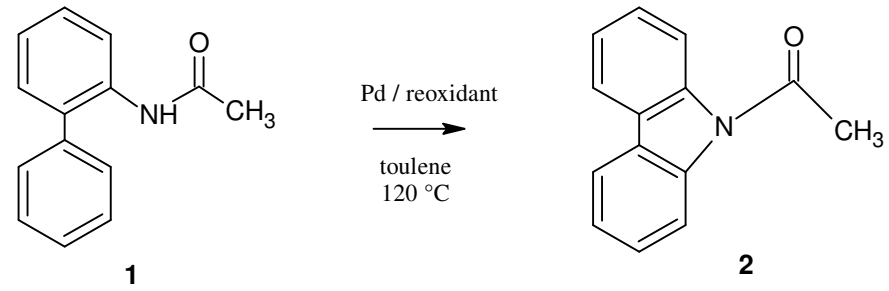
Scheme-II: Plausible mechanism of carbazole formation

Marciniec *et al.*[6] reports the efficient syntheses of (E)-N-(silyl) vinyl carbazole that has been fairly prepared by a new catalytic route, the effective stereoselective silylative coupling of vinyl carbazole with vinyl trisubstituted silanes in the presences of $[RuH(Cl)(CO)(PCy_3)_2]$[7] in comparison with the catalytic activity of $[RuCl_2(PCy_3)(IMeSH_2)(=CHPh)$ and Grubb's catalysts.The synthesized E-N-(silyl)vinyl carbazoles further undergo the effective Hiyama coupling reaction with iodobenzene resulting in the formation of stereoselective (E)-9-[2-(phenyl)ethenyl]-9*H*-carbazole in high yield (**Scheme-III**).



Scheme-III

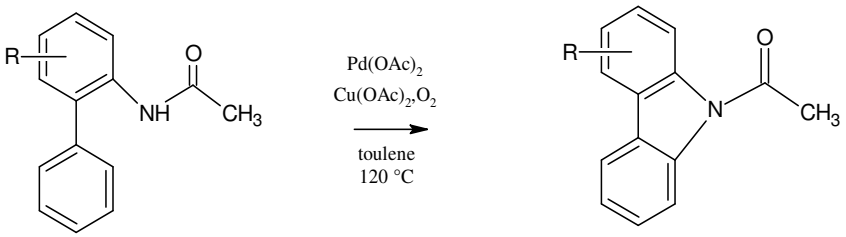
Tsang and co-workers[8] proposed a method which involves the formation of N-acetyl carbazole (**2**) from 2-acetamino phenyl (**1**) using palladium precatalyst and a reoxidant combination. Preliminary results suggests that the use of a combination of 5 % $Pd(OAc)_2$ at 120 °C under an atmosphere of air or oxygen provide a near quantitative yield of **2** in toluene (**Scheme-IV**).

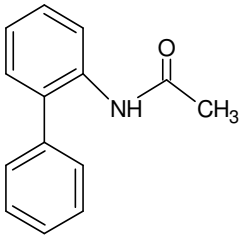
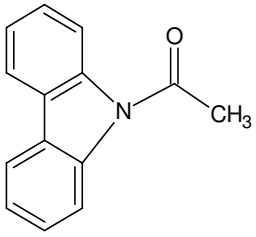


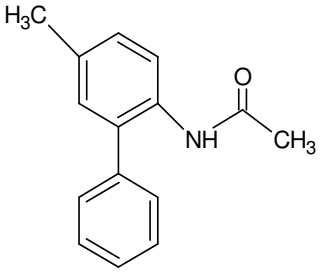
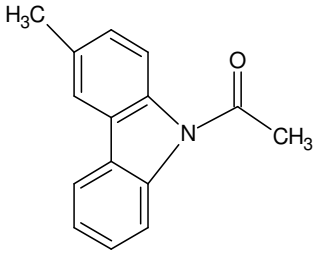
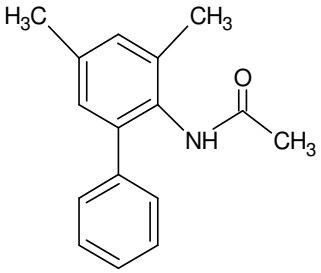
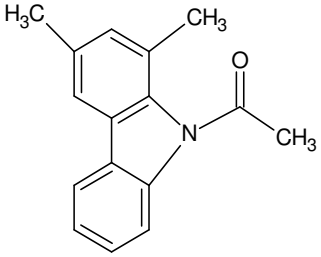
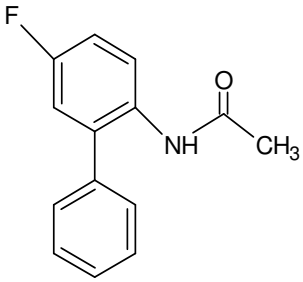
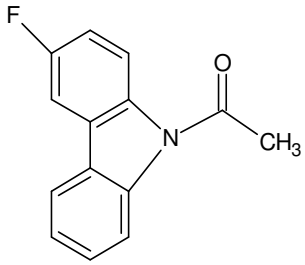
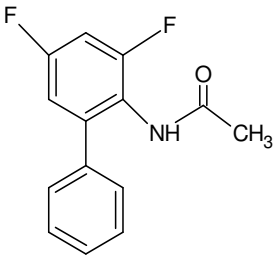
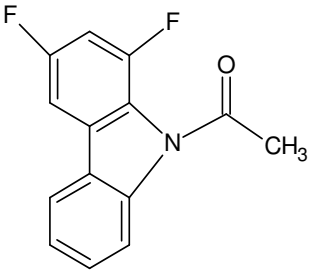
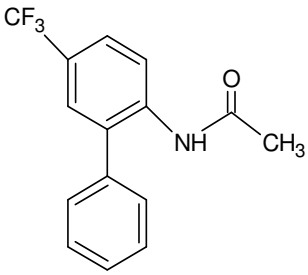
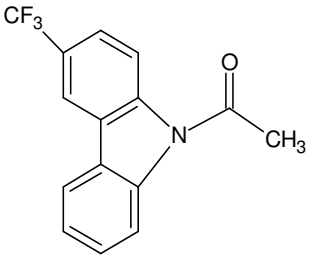
Scheme-IV: Scheme of reaction conditions for carbazole synthesis

With these results in hand they examined the scope and generality of the method. Following a procedure for Suzuki-Miyaura coupling reaction[9], a series of substituted analogues and derivatives of **4a** were prepared by using 2-haloacetamide and the appropriate boric acid. As can be seen from Table-1 the methods fairly bears the substitution on upper aromatic group. This process is compatible with a variety of electron withdrawing and electron donating groups.

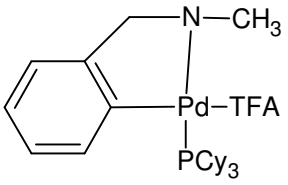
TABLE-1
CYCLIZATION OF 2-PHENYLACETANILIDES



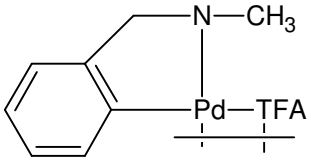
Entry	Substrate	Product	Yield (%)
1			94

Entry	Substrate	Product	Yield (%)
2			92
3			93
4			94
5			90
6			88

Robin.B.Bedford *et al.*[10] explained that the sequential palladium catalyzed amination and C-H activation reactions between 2-chloro-N-alkylated anilines and aryl bromide yields carbazole in one reaction. The catalysts studied for carbazole synthesis were complex **5a**[11]or **5b**[11]



5a

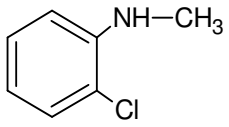
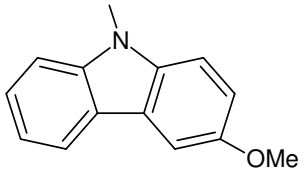
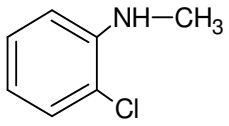
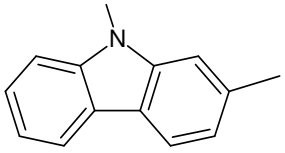
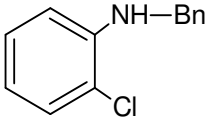
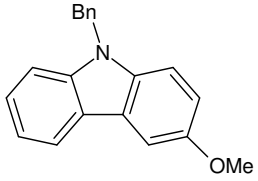
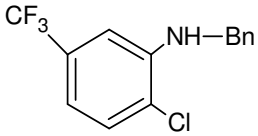
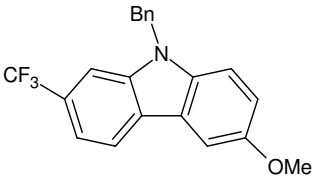


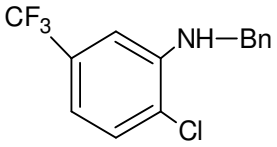
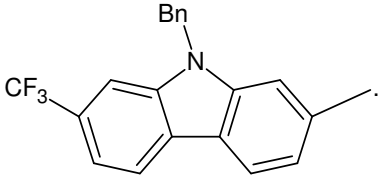
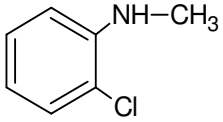
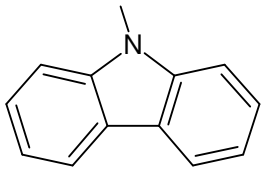
5b

Both **5a** and **5b** have been found to give good activity in aryl chloride coupling reaction to produce carbazole.

These conditions to produce coupled derivatives of carbazole were then used for the rest of catalytic studies and the results are summarized in Table-2.

TABLE-2
CATALYTIC SYNTHESES OF CARBAZOLES FROM 2-CHLOROANILINES AND ARYL BROMIDES, BrC_6H_4R[a]

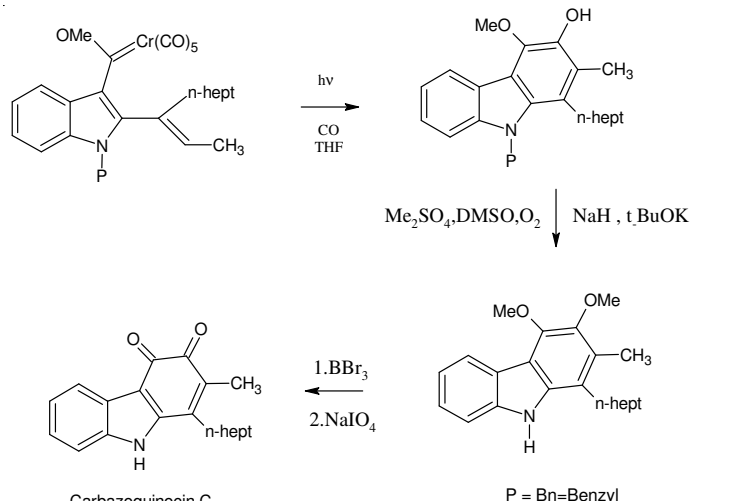
Entry	2-Haloaniline	R	Coupled product	Yield (%)
1		4-OMe		47
2		3-Me		57
3		4-OMe		40
4		4-OMe		27

Entry	2-Haloaniline	R	Coupled product	Yield (%)
5		3-Me		51
6		H		61

[a]Reaction conditions: 2-Haloaniline (1.30 mmol), aryl bromide (1.22 mmol), NaOtBu (6.10 mmol), Pd(OAc) (4-5 mol %), $PtBu_3$ (5-7 mol), toluene (13.0 mL), reflux, 24 h (reaction time not optimized). [b]Non-optimized isolated yields, GC yields given in parentheses.

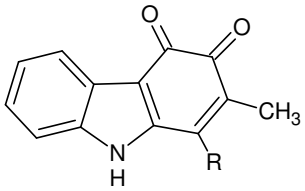
As can seen, the double coupling reaction proceeds smoothly, generating the carbazole products when N-substituted-2-chloroanilines are used as substrates (entry 1-6).

Rawat and Wulf[12] proposed an effective approach to the synthesis of carbazole-3,4-quinone alkaloid in which *o*-quinone unit is constructed through a *o*-benzannulation reaction of a doubly unsaturated Fischer carbine complex. A direct route to carbazole derivative is by photoinduced *o*-benzannulation of 3-(2-vinyl) indolyl carbine complexes and these carbazole derivatives are oxygenated in 3 and 4 position to get carbazoquinocin (**Scheme-V**).



Scheme-V

Another unique synthesis of carbazoquinocin C (Fig: 1D) was also reported by Knolker[13] and Pindur[14].

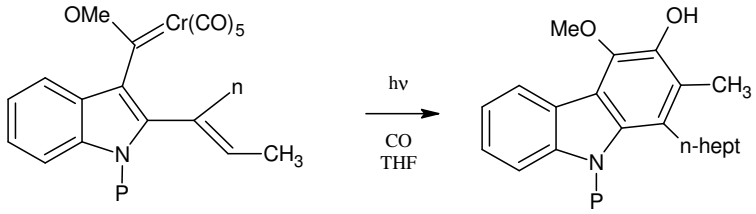


Carbazoquinocin (C)

R= $(CH_2)_6Me$

Fig. 1D

Similarly Merlic *et al.*[15] reports that carbazole (**8**) in (65 %) and **9** in (62 %) yield are obtained by photolysis of 3-indolyl carbine complexes **6** and **7** under an atmosphere of carbon monoxide (**Scheme-VI**).



(6) P= Bn

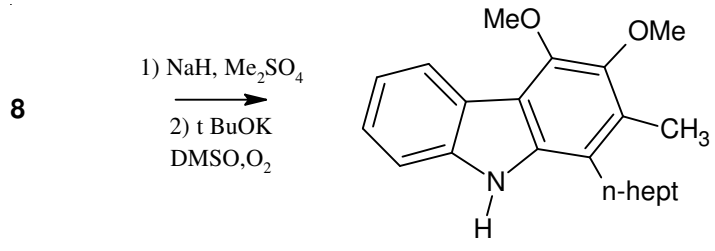
(7) P= PMB

(8) P=Bn 65%

(9) P= PMB 62%

Scheme-VI

The deprotection of **8** to synthesize another derivative of carbazole was only achieved when the phenol function was derivatized as its methyl ether and then benzyl cleavage could be achieved with potassium *tert*-butoxide in DMSO in the presence of oxygen[16] to obtain 10 in 94 % yield for 2 steps (**Scheme-VII**).



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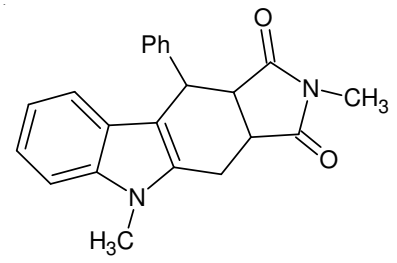
Scheme-VII

In another effort for carbazole syntheses Cochard and co-workers[17], worked on the Yonemitsu condensation between indole, Meldrum's acid and various aldeyhdes. Extending this three-component reaction to 2-substituted indoles **11**[18], carbazole derivatives **12** and **13** were prepared (**Scheme-VIII**).They also reported the synthesis of another carbazole derivative (Diels-Alder adduct) **14** by heating a mixture of 1,2-dimethyl indole, benzaldehyde and N-methyl-malemide under reflux in toluene and the product was obtained in 26 % yield. They explain that if benzene is used instead of toluene there will be no reaction even after 1 day reflux. However, the addition of Meldrums acid and D,L-proline as catalyst to the dienophile containing mixture results in formation of tetrahydrocarbazoles derivatives.



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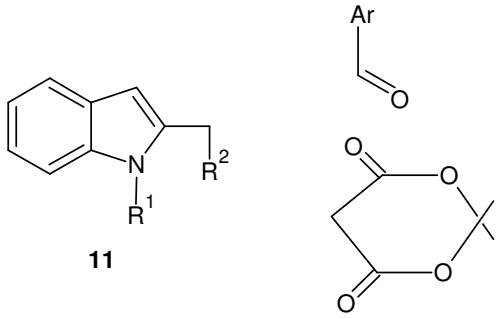

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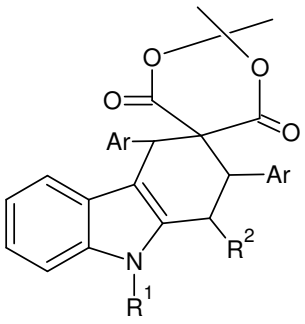

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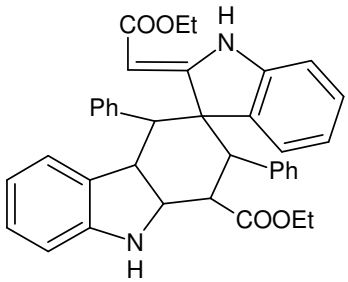

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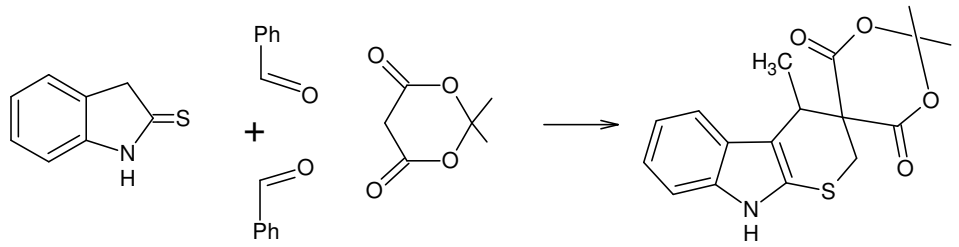
Scheme-VIII

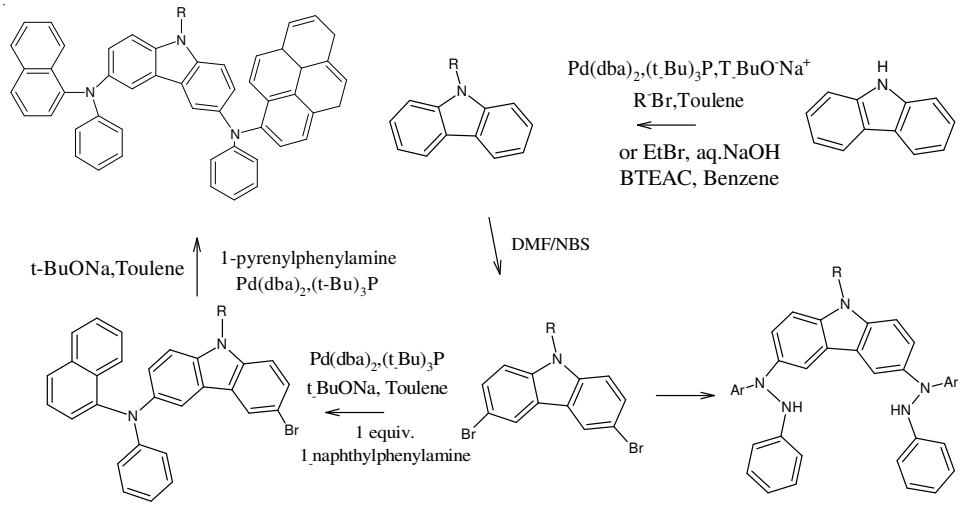
They explain that this condensation is not reserved to 2-carbon substituted indoles, as indole-2-thione reacted smoothly with benzaldehyde and Meldrums acid to yield 67 % tetrahydrocarbazole (**15**) as the single isomer (**Scheme-IX**).



15

Scheme-IX

By means of palladium-catalyzed C-N bond formation very stable carbazole derivatives that contain peripheral diarylamines at the 3- and 6-positions and an ethyl or aryl substituent at the 9-position of the carbazole moiety have been synthesized by Thomas *et al.*[19]. These new carbazole compounds (carbs) are important as they are amorphous with high glass transition temperatures (Tg, 120-194 °C) and high thermal decomposition temperatures (Td > 450 °C). **Scheme-X** outlines the synthesis of all compounds used in their study. The structure of new carbazole-3,6-diamine are illustrated in Fig. 1.



Scheme-X

Fortunately several methods exist for synthesis of carbazoles, often bearing functionality, by either ring contraction or cyclization of suitable precursors[20].

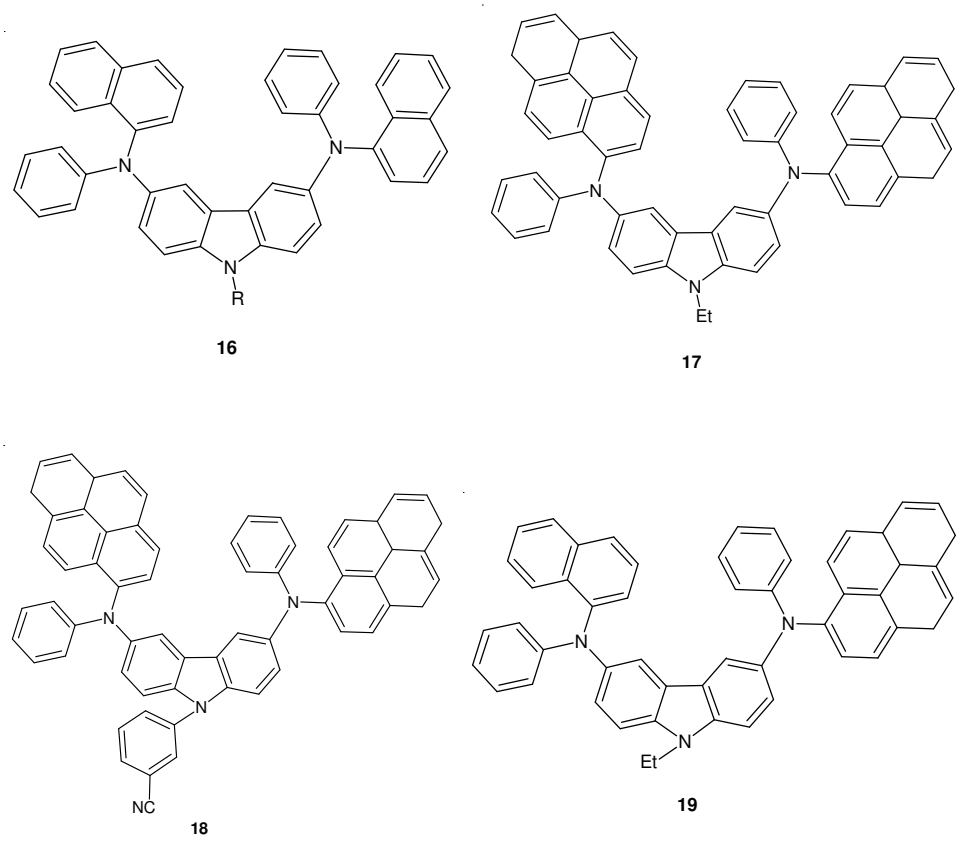


Fig. 1. Structures of carbazole derivatives

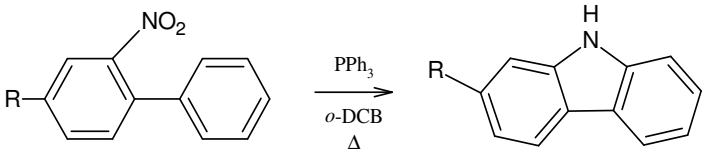
Adam *et al.*[21] reported the methods for preparation of a series of substituted carbazoles from the corresponding 2-nitrobiphenyl derivatives using one of the novel modification of Codagan reaction. The proposed reaction conditions were straight forward and convenient to execute. 2-Nitrobiphenyl derivatives were subjected to reductive cyclization under previously optimized conditions-reflux in *o*-dichlorobenzene (*o*-DCB) in the presence of 2.5 equivalents of PPh_3 until complete consumption of starting material. The results of these experiments are summarized in Table-3.

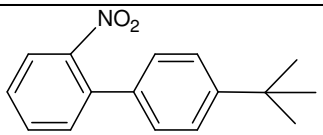
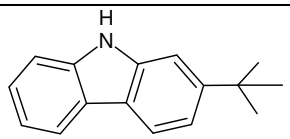
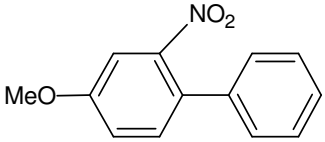
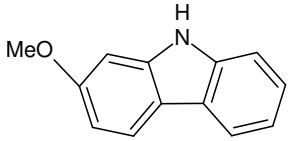
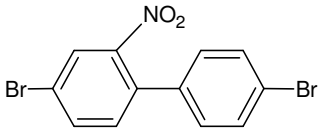
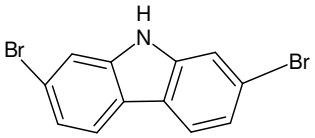
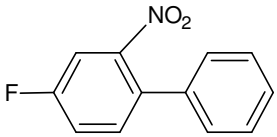
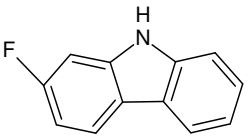
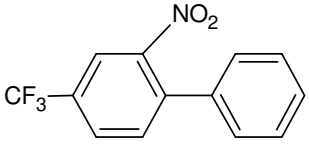
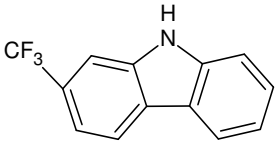
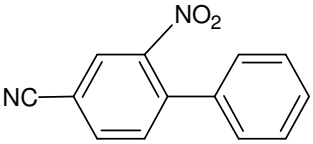
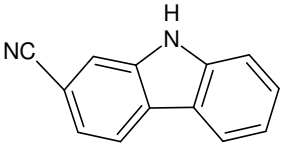
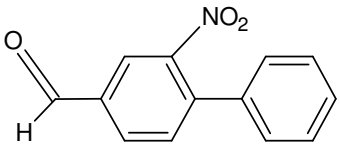
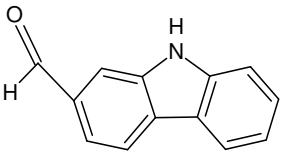
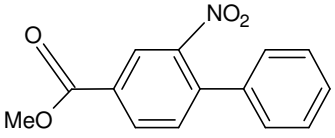
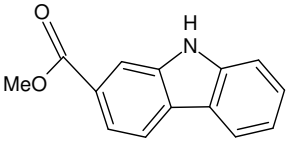
The alternative synthesis of carbazoles derivatives (entry 1, 2, 8) given in Table-3 was also reported in literature[20, 22,23] but the yield was not significant.

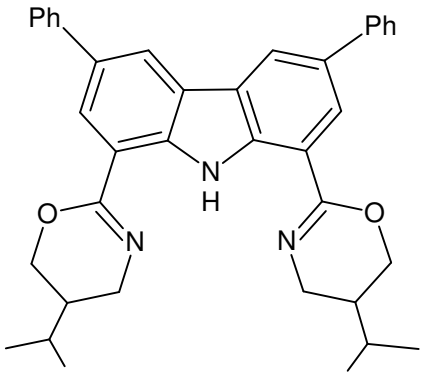
Francois *et al.*[24] synthesized two N-oligo-ether carbazoles monomers, which have been, respectively, electro-polymerized and polymerized by polycondensation.

Another important 17-step scheme for synthesis of carbazole derivative (-) gilbertine in 55 % yield was reported by Jan Jiricek *et al.*[25]. Syntheses of another important C^2-symmetrical tridentate *bis*(oxazolinyl)carbazole[26] derivative ligand **20** is reported.

TABLE-3
CARBAZOLES BY REDUCTIVE CYCLIZATION OF NITROPHENYLS

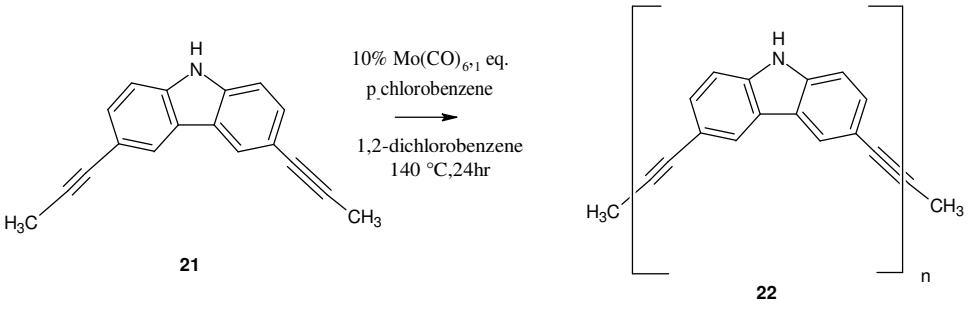


Entry	Nitrophenyl	Carbazole	Reaction time (h)	Yield (%)
1			21	67
2			7	91
3			5	75
4			3.5	91
5			6	85
6			5	75
7			4	78
8			7	90



20

Glen *et al.*[27] describes the metathesis of N-Alkyl-3,6-dipropynyl carbazoles **21** into N-alkyl poly(carbazolylene-ethynylenes) **22** (**Scheme-XI**). Metathesis was performed using the "shake and bake" system, a mixture of $Mo(CO)_6$/*p*-chlorophenol in *o*-dichlorobenzene at 140 °C for 24 h.



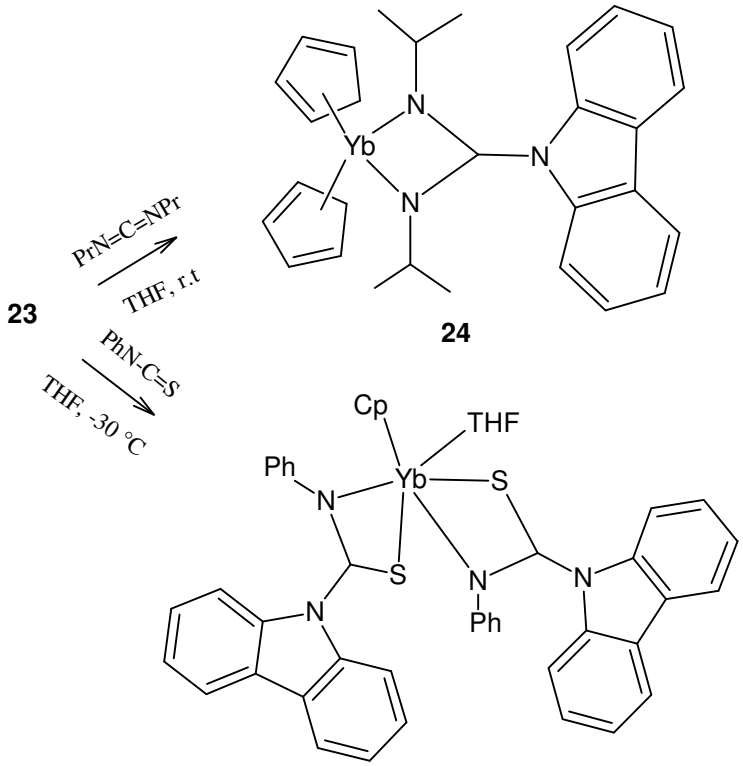
21 **22**

Scheme-XI

Zhang *et al.*[28] proposed a method for synthesis of a ytterbocene derivatives containing aromatic nitrogen ligands, $(C_5H_5)_2$YbCbz(THF) (**23**). Reaction of **23** with N,N´diisopropylcarbodiimide (*i*PrNdCdN*i*Pr) gives monoinzertion of *i*PrNdCdN*i*Pr into the Yb-N(carbazolate) bond, resulting in the formation of ytterbocene guanidinate $(C_5H_5)_2$Yb[*i*PrN.C(Cbz).N*i*Pr] (**24**), while treatment of **23** with 1 equiv of phenyl isothiocyanate (PhNCS) yields the unexpected monocyclo-pentadienylytterbium complex (C_5H_5)Yb[S.C(Cbz).NPh]$_2$(THF) (**25**) (**Scheme-XII**).

By the oxidative coupling reaction N,N′-dimethyl-3-3-bicarbazyl(DEDC)- and N-N′-diphenyl-3,3-bicarbazyl (DPBC) derivatives were synthesized by Kim and co-workers[29].

Using the iron-mediated arylamine cyclization as the key step Kataeva *et al.*[30] have achieved a short and highly efficient access to 2,7-dioxygenated tricyclic carbazole alkaloids.



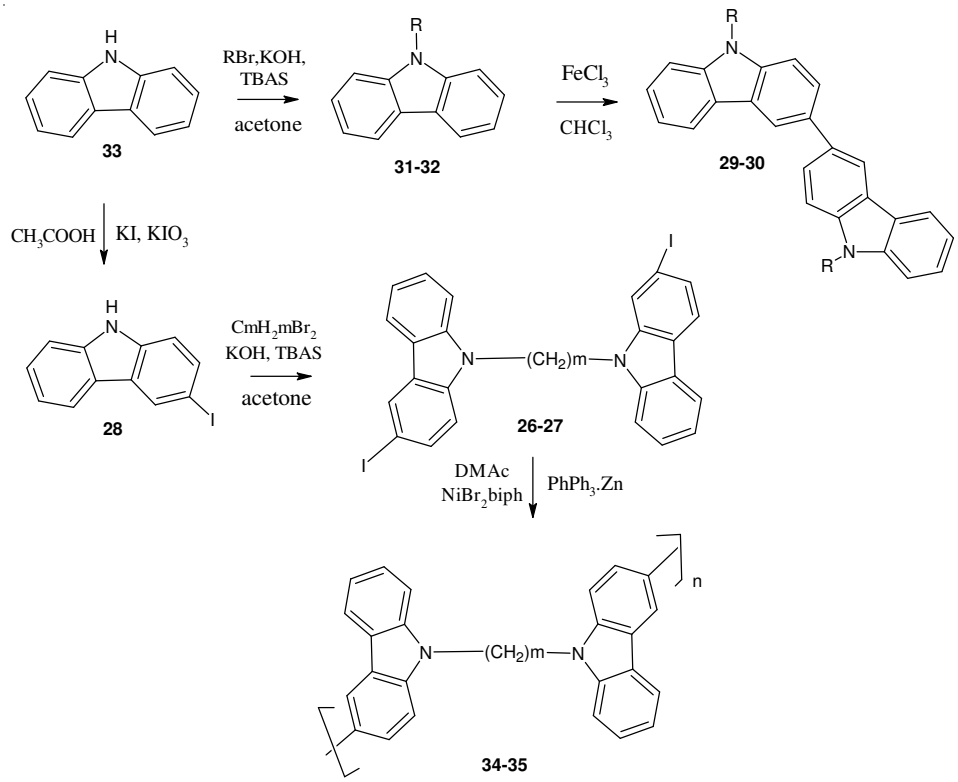
Scheme-XII

Balamurali and co-workers[31] reported the syntheses for a series of new 5,6,11,12-tetrahydroindole[2,3-α]carbazole derivatives.

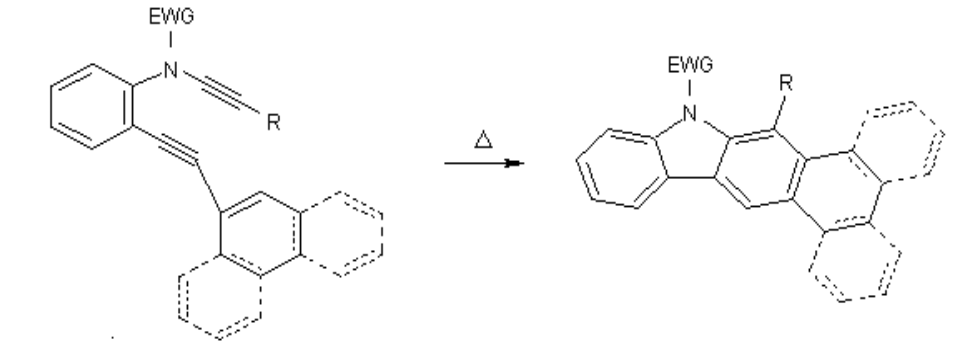
Grigalevicius *et al.*[32] synthesized the polymers containing 3,3-dicarbazyl in main chain **34** and **35** (**Scheme-XIII**) by dehalogenated condensation of 1,6-di-(3-iodo-9-carbazolyl)hexane (**26)** and 1-12-di(3-iodo-9-carbazolyl) dodecane (**27**), respectively which were prepared by alkylation of 3-iodo-9*H*-carbazole (**28**) with dibromoalkanes. The model compounds of the polymers 9,9-diethyl-3-3-dicarbazyl (**29**) and 9,9-diethyl-3,3-dicarbazyl were synthesized by chemical oxidation of corresponding 9-alkyl-carbazoles (**31-32**), which were prepared by alkylation of 9-H carbazole (**33**) in the presence of $FeCl_3$.

By radical copolymerization of monomers NVK and OVDAC carbazole containing amphiphilic novel statistical co-polymers with blue fluorescence and amphiphilic groups were synthesized by Sun *et al.*[33].

In an effort to synthesize carbazoles and benzannulated carbazoles, Maria *et al.*[34] reports a new adaptation of intra molecular dehydro Diels-Alder (IDDA) reaction strategy using substituted ynamides[35-38] (**Scheme-XIV**).

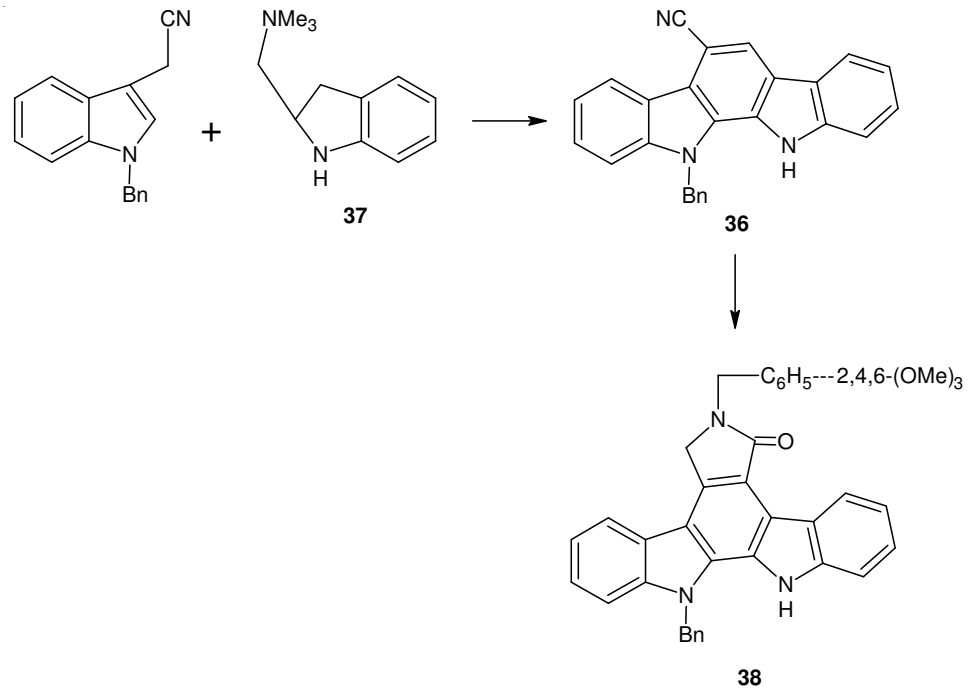


Scheme-XIII



Scheme-XIV: Strategy for synthesis of carbazoles and benzannulated carbazoles by intramolecular Dehydro Diels-Alder reaction of Ynamides

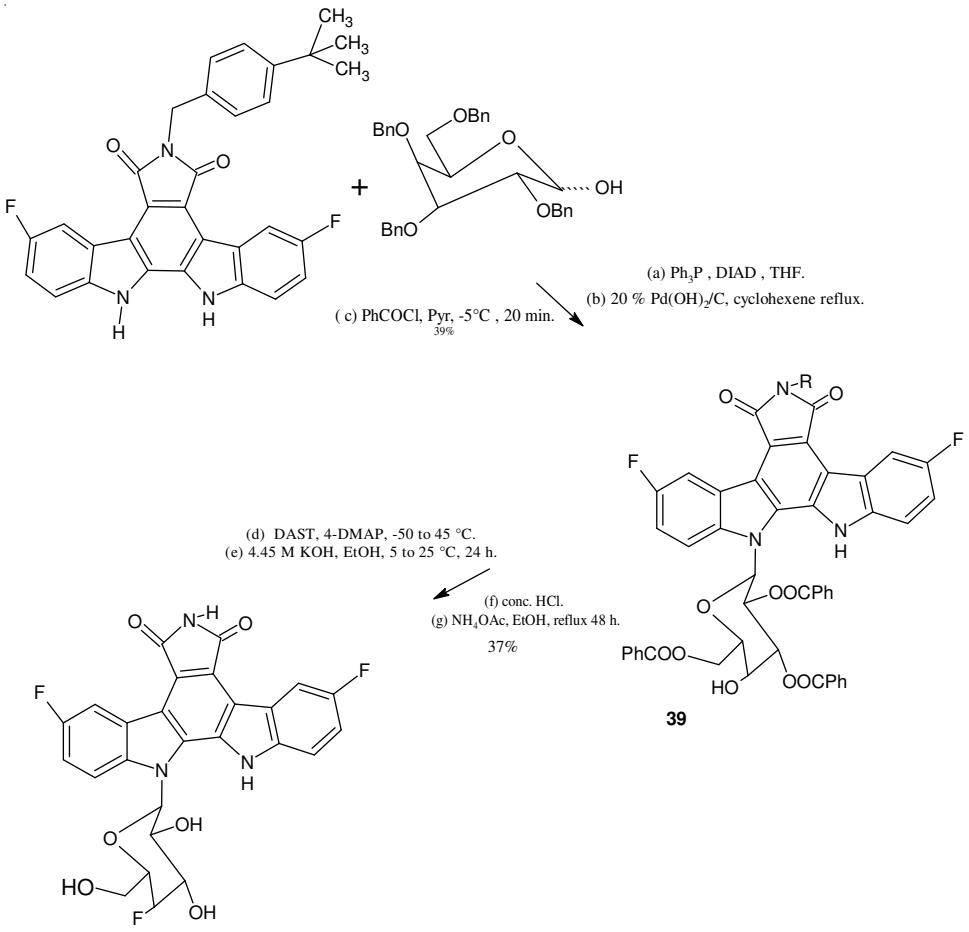
Yasuhiro *et al.*[39] reports synthesis of 12-benzyl-5-cyano-11,12-dihydroindole [2,3-a]carbazole (**36**) using gramine methiodide (**37**) and acetonitrile as starting material and the synthesis of 12-benzyl-6-(2,4,6-trimethoxy benzyl)indole[2,3-a]-pyrrolo[3,4-c]carbazole (**38**) starting from **36** (**Scheme-XV**).



Scheme-XV

Another important synthesis of novel hyperbranched carbazoles/fluorene-based copolymers by one pot Suzuki polycondensation (SPC) were successfully achieved by Chung-Wen *et al.*[40]. Other then this *via* several successful efforts random and alternating fluorene/carbazole copolymers have been designed and synthesized to be used as light-emitting layer in blue light-emitting diodes[41,42].

Mark and coworkers[43] adopted the best possible procedure for the synthesis of 4-fluoro-glycoside analogues (carbazole derivatives) which involves post glycosylative modification of a D-galacto-fluoroindolo carbazole intermediate (**39**) shown in **Scheme-XVI**. Tribenzoate (**39**) is also one of the intermediate for the synthesis of 4,6-difluoro analogue and the 4,4-*gem*-difluoro analogue (**Scheme-XVI**). The synthesis of the indolocarbazole core and its glycocylation are also well described in literature[44]. The structures and dynamical formation of carbazole (Cz) dimer cations in solid states were investigated by Toshiki *et al.*[45].

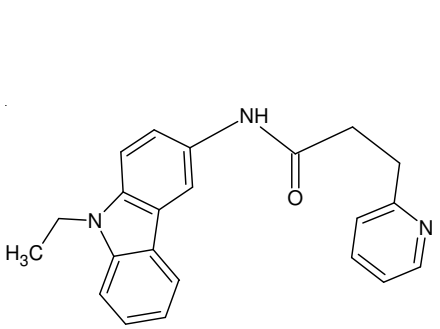


Scheme-XVI: Synthesis of 4-fluoro,4,6-difluoro and 4,4-*gem*-difluoro analogues

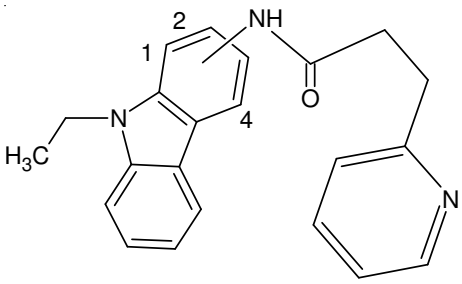
Block and coworkers[46] describes the preparation of pyridyl propionate derivatives and **41a**, the ring-substituted analogues **41b,c,d,g-i** and the isomeric carbazole derivatives (**42-44**) were prepared by condensation of the corresponding aniline with pyridyl propionic acid (Fig. 2).

They also proposed the synthesis of other carbazole derivatives in which the appropriately substituted phenyl hydrazine was condensed with the commercially available ketone **45** to give **46** with unambiguous regiochemistry. Oxidation of the ring and alkylation on nitrogen lead to carbazole ester **47**, whose hydrolysis produces desired aniline derivatives of carbazole (**Scheme-XVII**).

The 1,4-substituted derivative **48r** was synthesized from 5-bromo-indole by condensation with hexane-2,5-dione to form 1,4-dimethyl-6-bromocarbazole, followed by alkylation, nitration on the 3-position and reduction of the nitro and bromine functionality, as illustrated in (**Scheme-XVIII**).



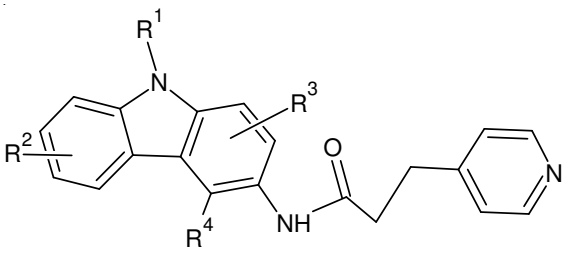
41a



42 1- carbazole

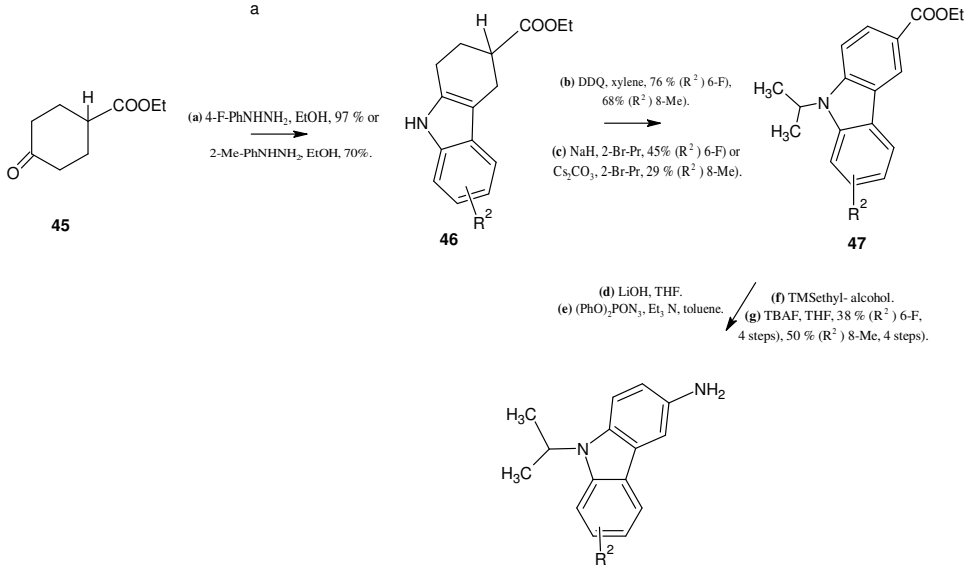
43 2- carbazole

44 4- carbazole

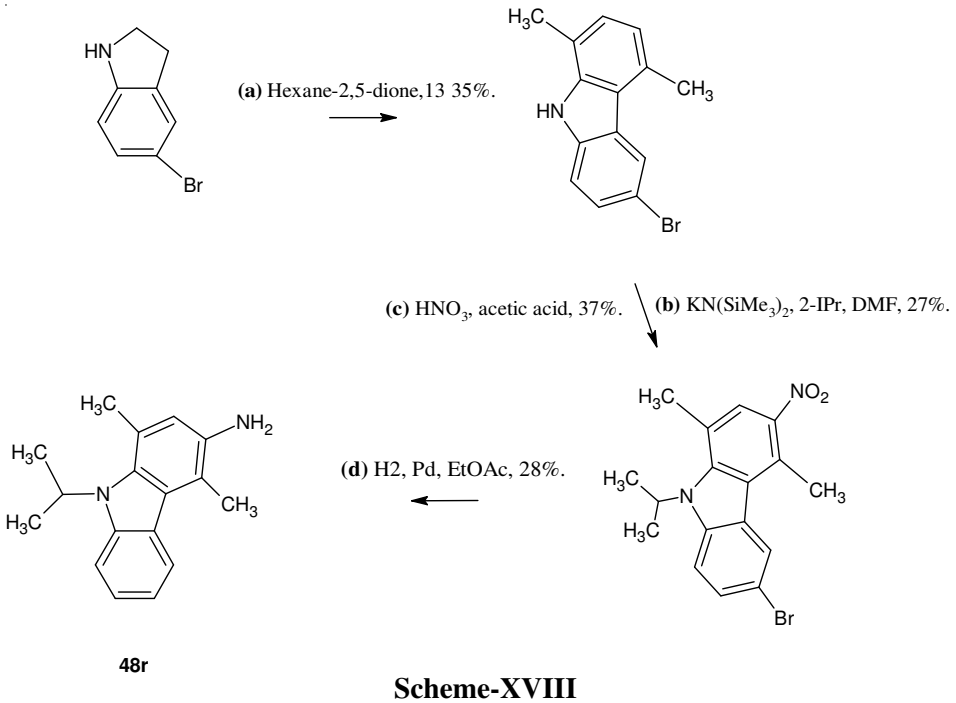


41 a-d,g-i

Fig. 2. Different carbazole derivatives



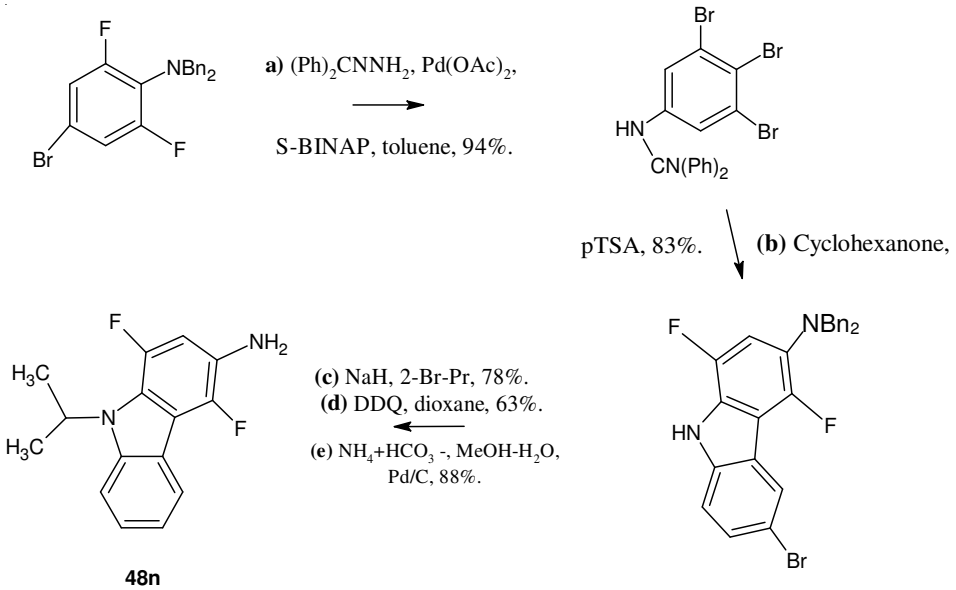
Scheme-XVII



48r

Scheme-XVIII

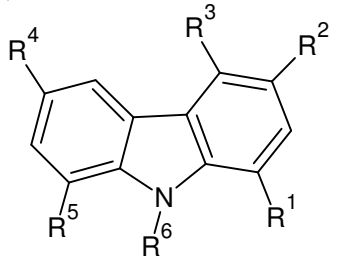
The 2,4 difluoro aniline **48n** was synthesized from 4-bromo-2,6-difluoro-aniline and protected as its dibenzylaminederivative (**49**) as illustrated in (**Scheme-XIX**).



48n

Scheme-XIX

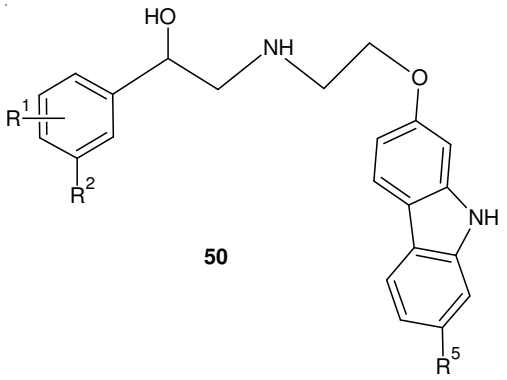
Lao *et al.*[47] reported a one pot synthesis to the carbazole derivative (**49**).



49

Li and co-workers[48] reported the synthesis of 9-aminocarbazole from carbazole and $NaNO_2$ in acetic acid followed by treating 9-nitrosocarbazole with zinc and acetic acid in ethanol.

Tian *et al.*[49] synthesized novel metal chromium containing organic monomer, N-vinyl carbazole chromium tricarbonyl and structural confirmation was done by elemental analysis, IR and NMR spectra. Another important process of preparing 1-[9*H*-carbazol-4-yloxyl]-3-[(2-(2-methoxy phenoxy)ethyl)amino propan-2-ol] as well as acid addition salts of this salt was reported by Ratkei *et al.*[50]. Ikuta *et al.*[51] prepared carbazole derivative **50** which are β_3 agonists and are useful as preventive and therapeutic drugs for diabetes, obesity, hyperlipedemia diseases, *etc*.

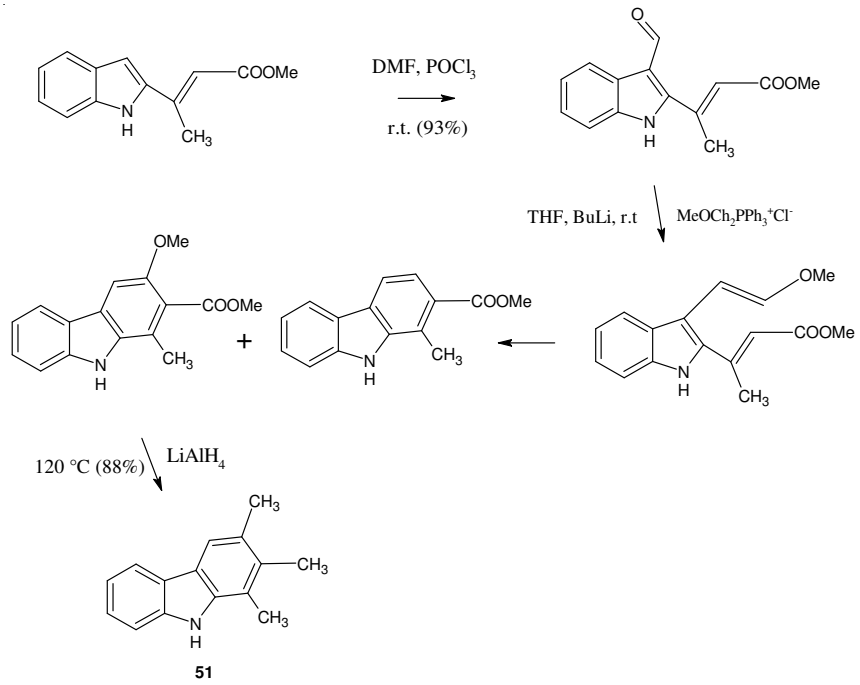


50

Poly [2-(3-nitro carbazolyl)ethyl methacrylate] (poly-(NC2MA)) with controlled molecular weight distribution was successfully synthesized by Cho *et al.*[52] using (methyl methacryloyl) potassium (MMA) as a weak initiator in the presence of diethyl zinc (Et_2Zn) in THF at -78 °C.

Wang *et al.*[53] reported that two new V-Shaped A-π-D-π-A type compounds, N-butyl-3,6-*bis*(E)-2-[5-dimestylboryl)thiophene-2-yl]vinyl)carbazole (BBTC) and N-hexyl-3,6-*bis*[(E)-4-(dimestylboryl)styryl]carbazole (BBSC), with trivalent boron and carbazole as electron acceptor and core of π-conjugated bridged respectively, were synthesized.

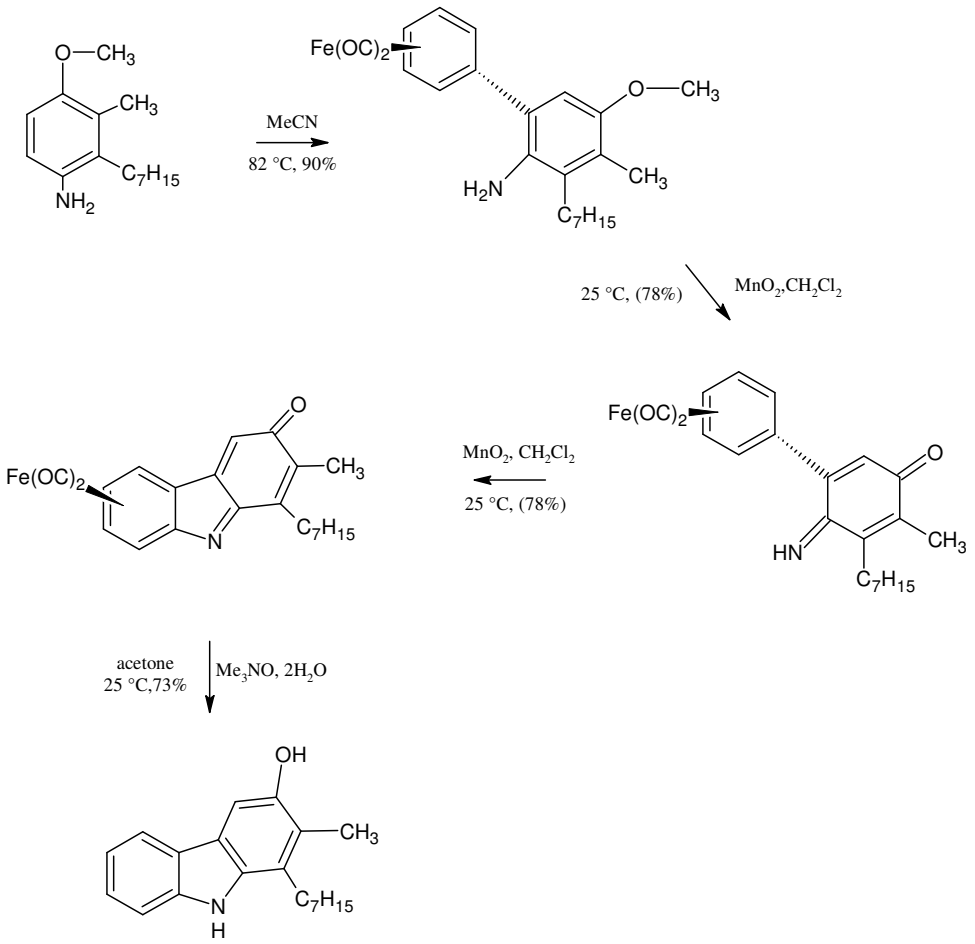
Chowdhury *et al.*[54] developed 2 routes to the synthesis of 4-deoxycarbazomycin B (**51**) by a Fischer-Borsche synthesis and a Pd(II)-mediated oxidative cyclization, respectively. They also described the significant inhibitory activity of 4-deoxycarbazomycin B (**51**) against various Gram-positive and negative bacteria (**Scheme-XX**).



Scheme-XX

Another synthesis to carbazole[55] (**56**) is also reported in literature (**Scheme-XXI**).

Hibino *et al.*[56] reported a formal synthesis of murrayaquinone A from 2-chloro-3-formylindole **62** by an electrocyclization involving an intermediate allene, a 2-vinyl substituent and the indole 2,3-bond. The 2-ethenyl-3-propargyl indole, a precursor of the intermediate hexatriene system for the electrocyclization, was prepared from 2-chloro-3-formylindole in five steps (**Scheme-XXII**). The keystep in this sequence is the palladium (0)-catalyzed cross-coupling reaction of the N-benzyloxymethyl-indole with tributylvinyl tin to give the 3-formyl-2-vinylindole (**57**). Addition of ethynyl magnesium bromide to compound **57**, followed by treatment with benzyl-oxymethyl chloride (BOMCl), afforded the 2-ethenyl-3-propargylindole (**58**).The thermal electrocyclization of compound **58** in the presence of potassium *t*-butoxide (KO*t*-Bu) at 90 °C provided the 3-methyl-4-oxycarbazole (**59**) in 81 % yield. Deprotection of **59** under Birch reaction conditions gave a mixture of N-hydroxymethyl-4-hydroxy-3-methylcarbazole (**60**) and 4-hydroxy-3-methylcar-bazole (**61**) in 75 and 22 % yield, respectively. However, **60** was transformed to **61** with Triton B in a yield of 71 % (**Scheme-XXII**)[56].



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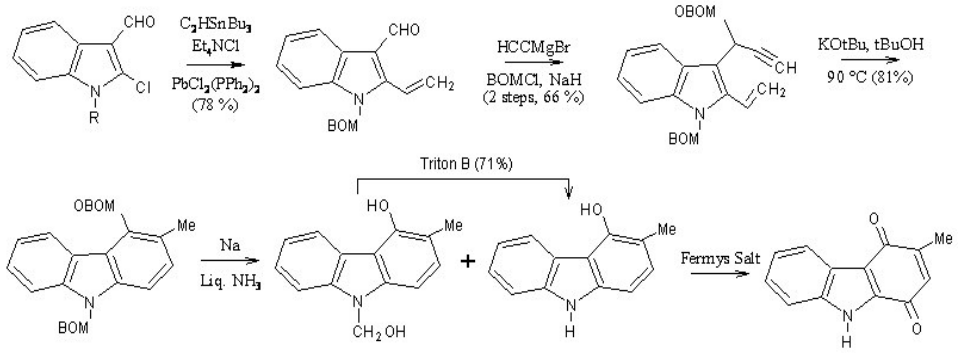
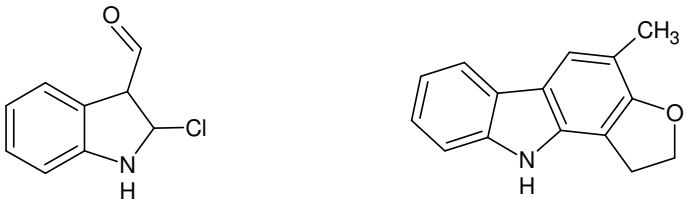
Scheme-XXI



Scheme-XXII

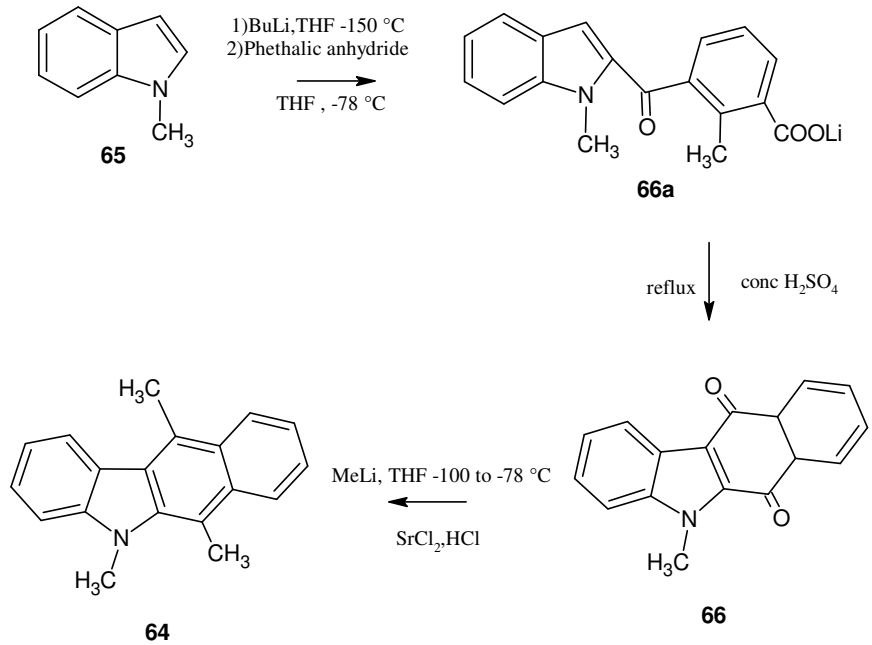
Hibino *et al.*[56] also describes the total synthesis of furostifolie (carbazole derivatives) **62** from 2-chloro-3-formylindole (**63**) in which they use electrocyclic reaction of intermediate allene with the 2,3-double bonds of indole and furan as the key step (Fig. 4).



63 **62**

Fig. 4

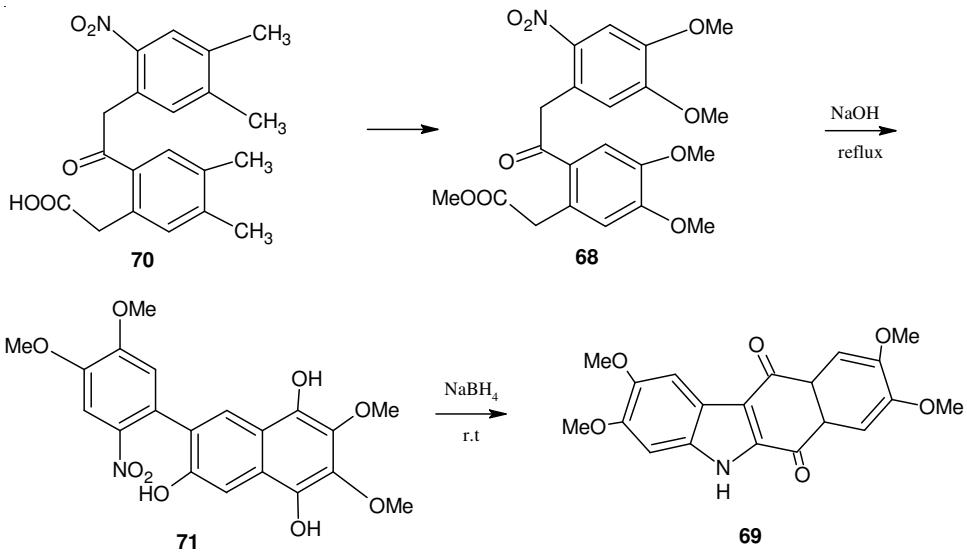
Koomen *et al.*[57] reported the synthesis of the trimethylbenzo[b]carbazole (**64**) starting from 1-methylindole (**65**). Selective deprotonation of 1-methylindole (**65**) at C-2 with BuLi and addition of phthalic anhydride afforded the intermediate lithium salt **65**, which was cyclized to the quinone **66** using strongly acidic conditions. Double methylation of the quinone **66** with methyllithium followed *in situ* by reduction with tin(II) chloride provided directly 5,6,11-trimethyl-5*H*-benzo[b]carbazole (**64**) (**Scheme-XXIII**).



65 **66a** **66** **64**

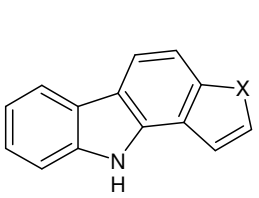
Scheme-XXIII

Using a Claisen condensation as the key step Castedo *et al.*[58] reported a simple synthesis of 2,3,8,9-tetramethoxy-5*H*-benzo[b]carbazole-6,11-dione **69** from the nitro keto ester **68**. The nitro keto acid **70** was prepared by nitration of the corresponding keto acid. Esterification of **70** led to the nitro keto ester **68**. Treatment of the nitro keto ester **68** with sodium hydroxide in refluxing methanol afforded the nitroquinone **71** *via* a Claisen condensation and subsequent oxidation in the air. The reduction of the nitro group in compound **71** with sodium borohydride in 2-propanol was followed by a cyclization to afford 2,3,8,9-tetramethoxy-5*H*-benzo[b]carbazole-6,11-dione **69** in 92 % yield (**Scheme-XXIV**). More recently, Estevez *et al.*[58,59] described further applications of the same approach. An application of the same precursor to the synthesis of benzo[a]carbazoles is described.



Scheme-XXIV

Over the past years, the rapidly growing class of heteroaryl-condensed carbazoles began to attract increasing interest because of their broad spectrum of useful biological activities[60]. To provide an overview on the hetaryl-annulated carbazole derivatives, these compounds are classified into [a]-annulated (**72**), [b]-annulated (**73**) and [c]-annulated (**74**) furo-, thieno- and pyrrolo carbazoles, respectively. This classification is solely based on the position at which the heteroaromatic ring is fused to the carbazole nucleus, either at bond a, b, or c (**Scheme-XXV**). In **Scheme-XXV**, only the structures with a [3,2]-annulated heteroaromatic 5-membered ring are shown. Moreover, the mode of fusion of the annulated heteroaromatic ring itself can vary, which leads to an even broader variety of heterocyclic ring systems.



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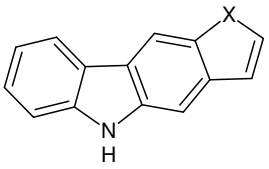

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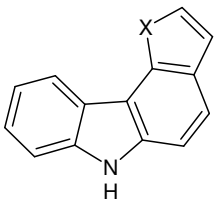
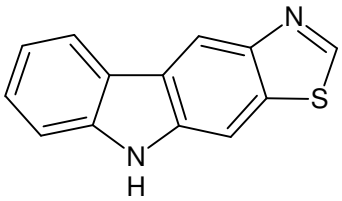


74

X=O,S,NH

Scheme-XXV

Govindaraji and co-workers[61] reported another very important on carbazole containing monomers from the monobenzyl ester of L-glutamic acid and triamine using Clauson-kass and amide coupling reaction. Besson and co-workers[62] recently described a simple synthesis of thiazolo[5,4 b]carbazoles **75** from the corresponding 3-aminocarbazoles (**Scheme-XXVI**). Achab *et al.*[63] obtained imidazo[4,5-c]carbazoles (**76**) by electrocyclization of an appropriate 3-(imidazol-5-yl)-2-vinylindole.



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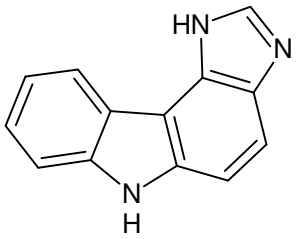


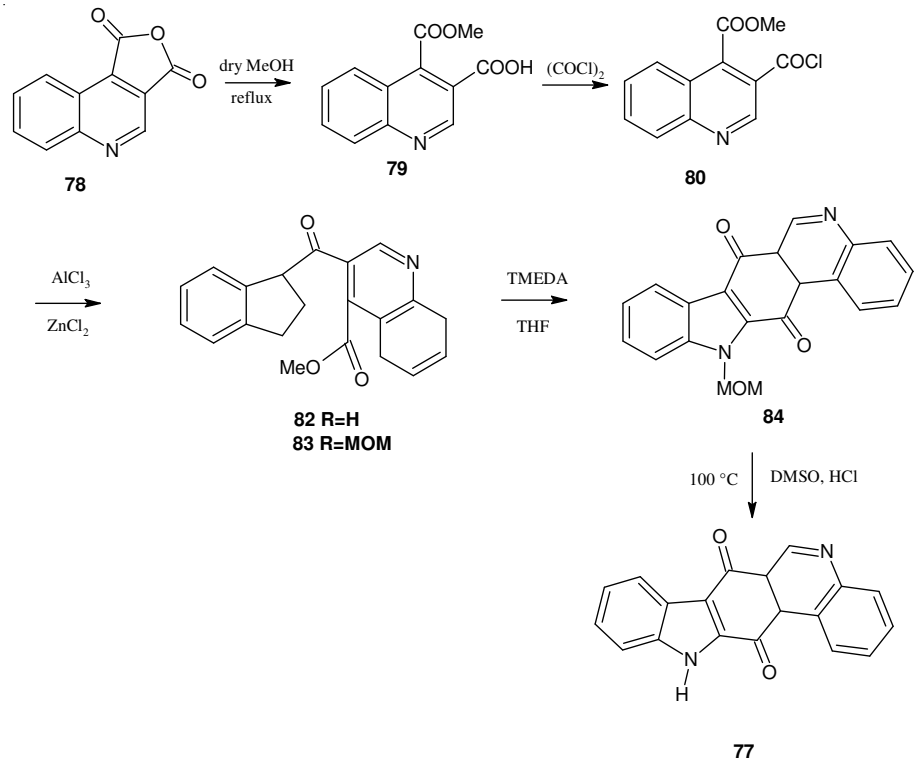
76

Scheme-XXVI

The diverse synthetic approaches to the isomeric indolocarbazole ring systems were also summarized by Bergman and co-workers[64]. Further synthesis of various indolo[2,3-a]carbazoles[65] from indigo were described. Faul[66] and Sullivan introduced phenyliodine(III)*bis*(trifluoroacetate)(PIFA) as an oxidant for the conversion of 2,3-*bis*(indol-3-yl)maleimides to indolo[2,3-a]carbazoles.

Another important synthetic route to carbazole derivative by an alternative route to calothrixin B (**77**) was described more recently by Chai *et al.*[67] starting from quinoline-3,4-anhydride (**78**). A completely regioselective ring opening of quinoline-3,4-anhydride (**78**) by refluxing in superdry methanol afforded quinoline-3-carboxylic acid 4-methyl ester (**79**), which was transformed to the corresponding acid chloride **80**. Friedel-Crafts acylation of indole **81** with the acid chloride **80** provided the diaryl ketone **82** in 80 % yields. Compound **82** was protected as the N-MOM derivative **83**. Lithiation at the 2-position of the indole ring with lithium

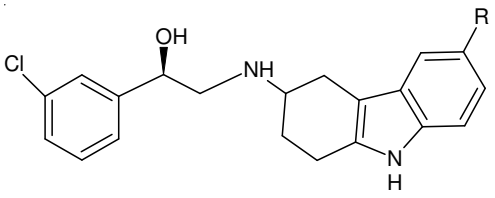
hexamethyldisilazide (LHMDS) in the presence of tetramethyl-ethylenediamine (TMEDA) followed by cyclization afforded N-MOM-calothrixin B (**84**) in 54 % yield. Cleavage of the N-MOM group provided calothrixin B (**77**) (**Scheme-XXVII**)[67]. This synthesis afforded calothrixin B (**77**) in 6 steps and 25 % overall yield based on quinoline-3,4-anhydride **78** (**Scheme-XXVII**).



Scheme-XXVII

Shi *et al.*[68] prepared carbazole-based bi-functional photo refractive polymers with controlled azo groups content *via* a post azo-coupling reaction.

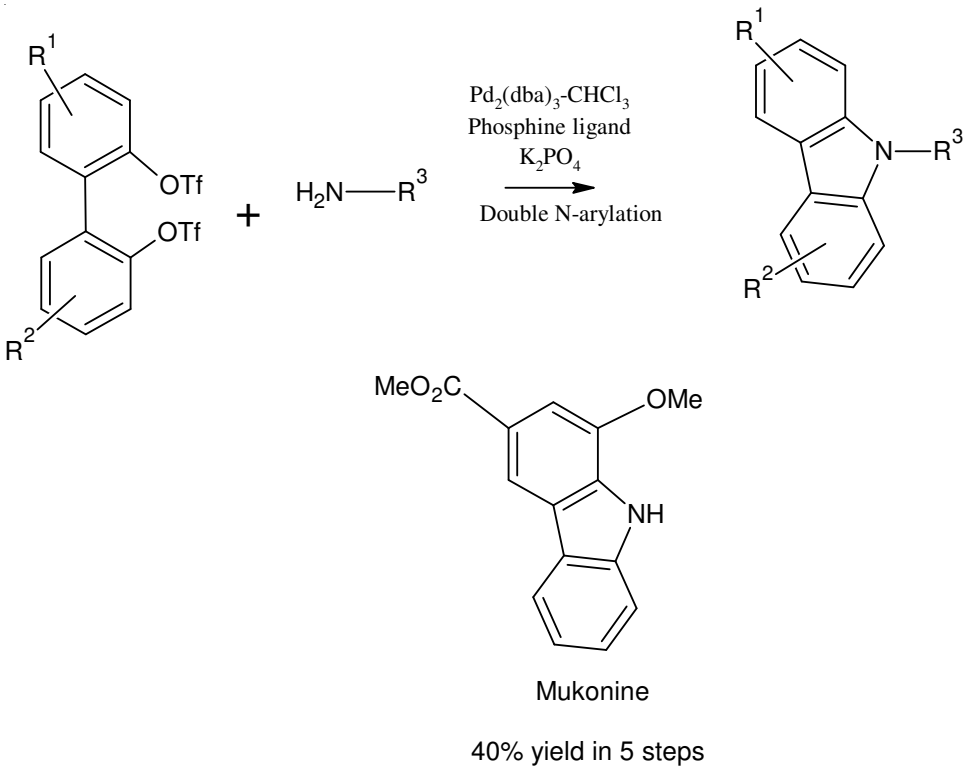
A series of 2-(3-chlorophenyl)-2-hydroxyethylamine derivatives (**85**) containing a tetrahydrocarbazole linker were prepared and evaluated for their β3-adrenoceptor agonistic activity by Ha *et al.*[69].



85

Treatment of 1-aminobiphenyl and diphenylamine with catalytic amount of Pt/C in hydrothermal water (250 °C, 4 MPa) affords 9*H*-carbazole[70] in good yield. Here, water works as reoxidizing reagent for platinum catalyst. Fullerene adducts carrying oligocarbazole moieties were successfully prepared by the Bingel reactions by Yosuke *et al.*[71].

The double N-arylation of primary amines with 2,2'-biphenylylene ditriflates was investigated for the synthesis of multisubstituted carbazoles by Atsushi and co-workers[72]. For the reaction the excellent catalysts were palladium complexes supported by 2-dicyclohexylphosphino-2'-methylbiphenyl or Xantphos [4,5-*bis*(diphenylphosphino)-9,9-dimethylxanthene]. The catalysts allow the use of anilines with an electron-donating or electron-withdrawing substituent and multi-substituted 2,2'-biphenylylene ditriflates as substrates. Ammonia equivalents, such as *o*-*t*-butyl carbamate, are also used as a nitrogen source to give the N-protected carbazoles which can easily give the corresponding N-unsubstituted carbazoles after deprotection. By using this route, a carbazole alkaloid, mukonine, is synthesized in 40 % yield for 5 steps, in comparable efficiency to the recent precedents (**Scheme-XXVIII**).



Scheme-XXVIII

Su *et al.*[73] reported the synthesis and self-assembly of a new conjugated dichalcone substituted carbazole-based low molecular mass organogelator.

Sapiyanskaite[74] reported the synthesis of derivatives of 1-(9-alkyl-9*H*-carbazol-3-yl)-4-carboxy-2-pyrrolidinones (methyl esters, hydrazides). They studied the condensation of the synthesized hydrazides with aromatic aldehydes, acetylacetone and acetoacetic ester. Structural analysis of the obtained compound was done by IR and NMR spectroscopy. Rajasekaran and Thampi[75] synthesized twelve different derivatives of substituted-{5-[2-(1,2,3,4-tetrahydrocarbazol-9-yl)ethyl]tetrazol-1-yl}alkanones (**3-14**) by reacting 9-[2-(1*H*-tetrazol-5-yl)-ethyl]-2,3,4,9-tetrahydro-1*H*-carbazole and the appropriate acid chlorides. 9-[2-(1*H*-tetrazol-5-yl)ethyl]-2,3,4,9-tetrahydro-1*H*-carbazole was synthesized by them by reacting 3-(1,2,3,4-tetrahydrocarbazol-9-yl) propionitrile with sodium azide and ammonium chloride.

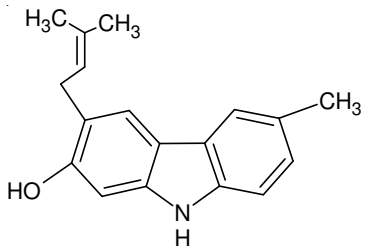
The syntheses of a series of carbazole derivatives and their SAR at the NPY Y1 receptor is described is recently described in literature by Leslie *et al.*[76].

Martin and Prasad[77] explains that the reaction of 1-oxo-1,2,3,4 tetrahydrocarbazoles with formaldehyde and ethylenediamine yielded N,N'-*bis*(1,2,3,4-tetrahydrocarbazol-1-ylidene)ethane-1,2-diamines (a carbazole derivative). A novel class of HCV NS5B RNA dependent RNA polymerase inhibitors containing 2,3,4,9-tetrahydro-1*H*-carbazole[78] and 1,2,3,4-tetrahydro-cyclopenta[b]indole scaffolds were also designed and synthesized. Jasztold-Howorko and co-workers[79] starting from 2-(6-methoxy-1-methyl-9*H*-carbazol-2-yl)ethylamine and mixed anhydrides of 4-nitrobenzoic acid or 4-methoxybenzoic acid, obtained the corresponding 5,6-dimethyl-9-methoxy-1-(4-substituted phenyl)-6*H*-pyrido[4,3-b]carbazoles, 5,6-dimethyl-9-hydroxy-1-(4-substituted phenyl)-6*H*-pyrido[4,3-b]carbazoles and their quaternary salts.

Roy *et al.*[80] reported the synthesis of two indolo-carbazoles and evaluated biologically as novel ChK_1 inhibitors (**Scheme-XXIX**).

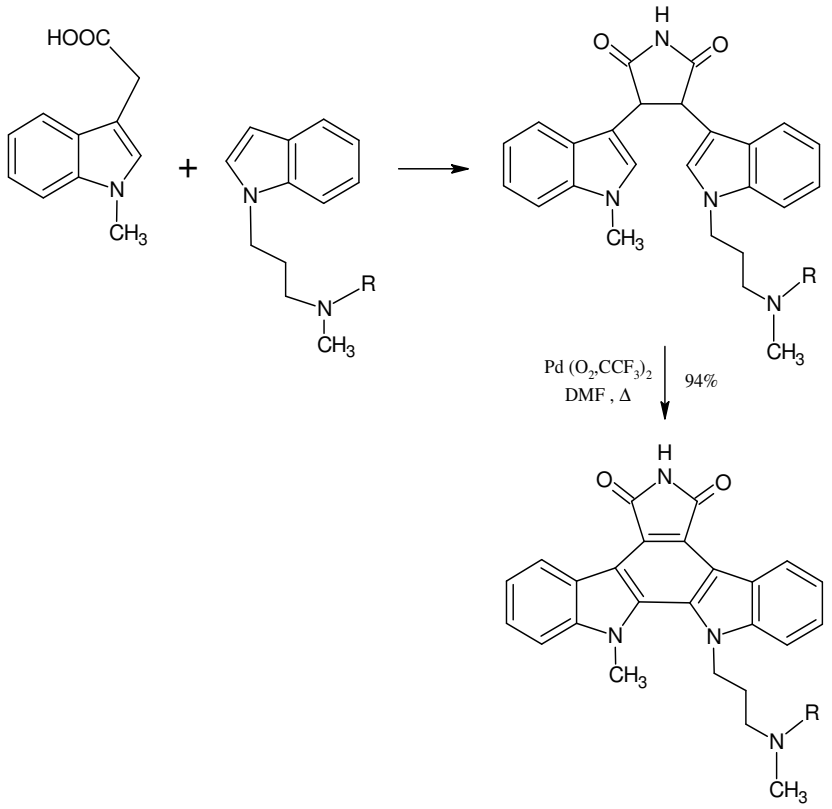
Synthesis and activity of carbazole derivatives against mycobacterium tuberculosis is reported by Choi and co-workers[81].

Using a convergent palladium-catalyzed construction of the carbazole frame work as the key step, Krahl *et al.*[82] have achieved a short synthesis of 7-oxygenated carbazole alkaloids clauszoline-k, 3-formyl-7-hydroxycarbazole, Clausine C (clauszoline-L), Clausine M, Clausine N and anti HIV active siamenol (**86**).



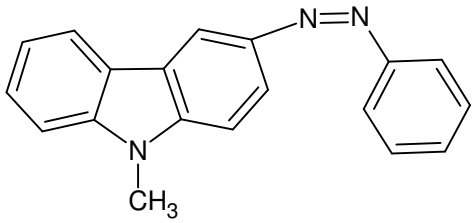
Siamenol

86



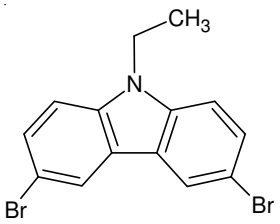
Scheme-XXIX

Lu *et al.*[83] reported the synthesis of a noval series of multi-triarylamine-substituted carbazole based dendrimers with an oligothiophene core. Another important synthesis of 9-methyl-3-phenyldiazenyl-9*H*-carbazole, $C_{19}H_{15}N_3$ (**87**) by condensation of 3-nitrosocarbazole and anilne with subsequent methylation is reported by Kyziol and co-workers[84].



87

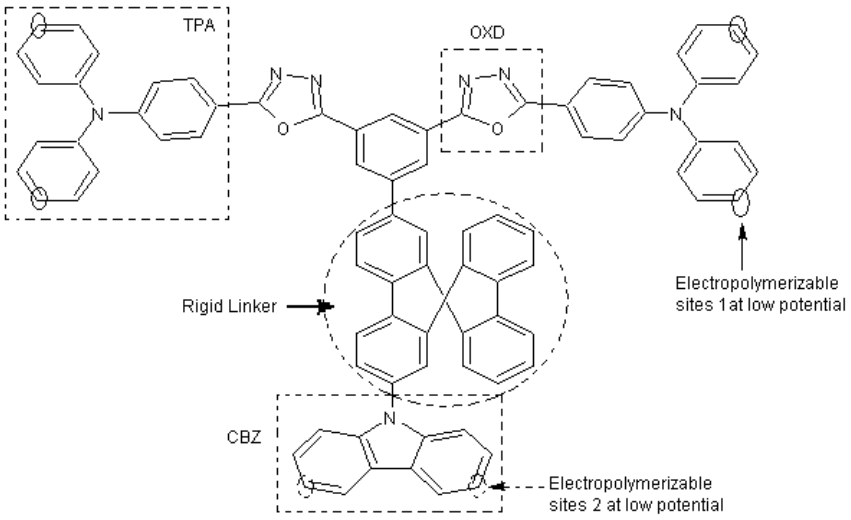
Huang[85] reported the synthesis of another very important carbazole derivative, 3,6-dibromo-9-ethyl-9*H*-carbazole (**88**), by N-alkylation of bromoethane with 3,6-dibromo-9*H*-carbazole.



88

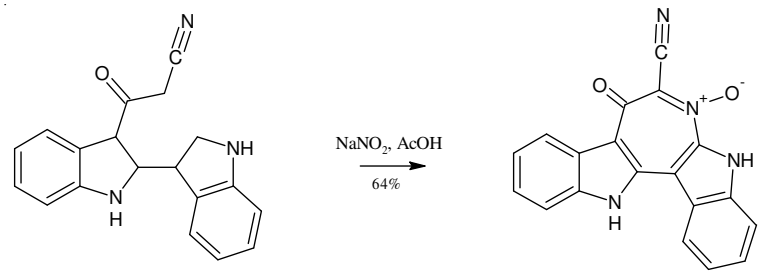
Synthesis and alkylation of indolo [3,2-b] carbazoles is also reported by Yundina *et al.*[86]. One and two-dimensional (1D & 2D) carbazole based hemicyanines, where methyl pyridium, methyl indolium and methyl benzothiazolium, were prepared by Knoevenagel condensation by Gu and co-workers[87]. Another novel thermally stable and hole-transporting amorphous molecules, 9,9-*bis*(4-[*bis*-(4´-carbazol-9-yl-biphenyl-4-yl)-amino]-phenyl)flourene has been synthesized in two step reactions by Nomura *et al.* [88]. Oliveria *et al.*[89] explained the synthesis of 3 new benzopyranocarbazoles from hydroxyl benzo[a]carbazole.

Two monodisperse fluorene-centered, ethynylene-linked carbazole oligomers were prepared and structurally characterized. They were highly fluorescent and emitted bright blue in solutions and in films by Zhao *et al.*[90]. One of the interesting and novel carbazole derivative 9,9'-spirobifluorene-cored donor-acceptor (D-A) bichromophore system was successfully synthesized by Natera *et al.*[91]. They synthesized a novel 9,9'-spirobifluorene-cored donor-acceptor (D-A) bichromophore system (**89**) in which triphenylamine (TPA) and carbazole (CBZ) groups are used as electron-donating moieties and the 1,3,4-oxadiazole (OXD) groups are electron-withdrawing moieties.



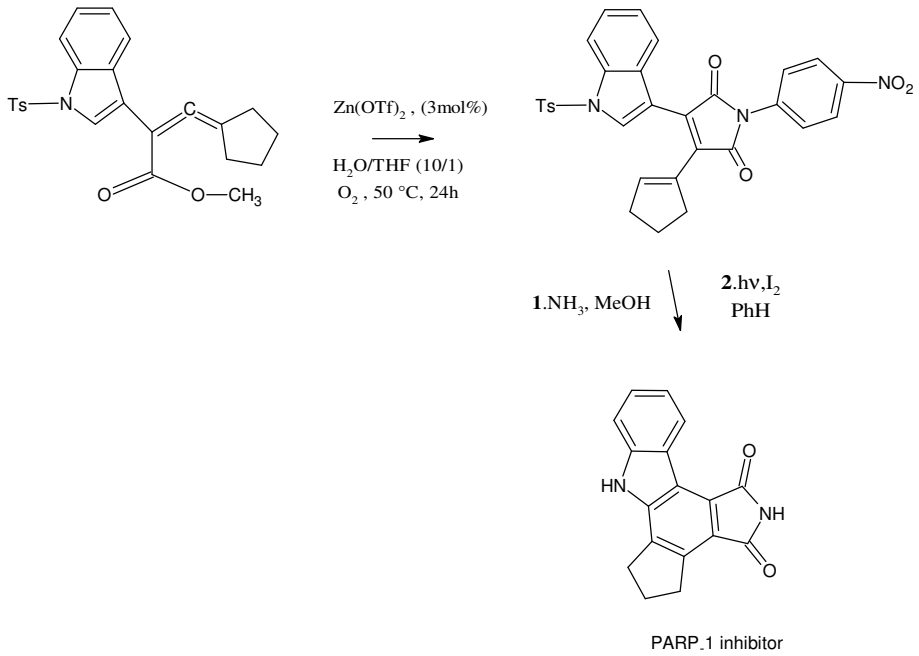
9,9'-spirobifluorene-cored donor-acceptor (D-A) bichromophore system (89)

Wahlström and co-workers[92] reports 3-cyclization reactions involving cyanoacetylated bisindoles which provides access to various novel cyclohepta[2,1-b:3,4-b']-diindole derivatives as well as some related fused pentacyclic systems. Treatment of 3-cyanoacetyl-2,3'-diindolylmethane with methanesulfonic acid gave 6-(cyanomethyl)indolo[3,2-b]carbazole in a good yield.



Scheme-XXX

The synthesis, characterization and field-effect transistor (FET) properties of new indolo [3,2-b]carbazoles are described by Boudreault *et al.*[93]. Li *et al.*[94] reports Lewis acid $Zn(OTf)_2$-catalyzed tandem annulations of isonitriles and allenic esters which lead to efficient and flexible syntheses of a range of biologically significant maleimides and carbazoles and related compounds (**Scheme-XXXI**). A mechanistic rationale is proposed to account for the observed reactivity.



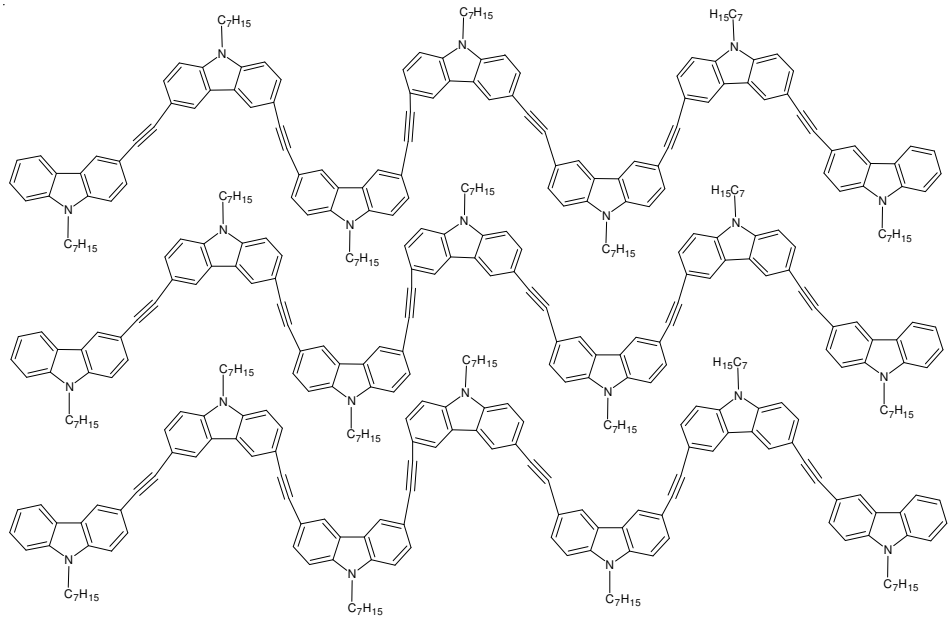
PARP_1 inhibitor

Scheme-XXXI

Yoon and coworkers[95] report the synthetic route of a novel oligomer (oligo-(2-{2-but-1-enyl-6-[2-(9-decyl-6-formyl-9*H*-carbazol-3-yl)-vinyl]-pyran-4-ylidene}-malononitrile)) (Olg(Cz-Pyr-CN)) with an average degree of polymerization. The molecule was synthesized by Knovenagel condensation reaction.

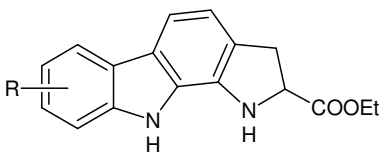
Two polycarbazoles with tetrathiafulvalene (TTF) were synthesized first by Yamamoto coupling reaction using Ni(1,5-cyclooctadiene)$_2$ (Ni(COD)$_2$) as the catalyst by Liu *et al.*[96]. One-pot synthesis of carbazole from two aromatic rings was accomplished by a Suzuki-Miyaura and amination reaction by Kitamura *et al.*[97].

Zhao *et al.*[98] synthesized a series of monodisperse, pyrene-modified oligocarbazoles. Carbazoles were linked by ethynylene through the 3- and 6-positions, having a stable zigzag molecular backbone (**Scheme-XXXII**).



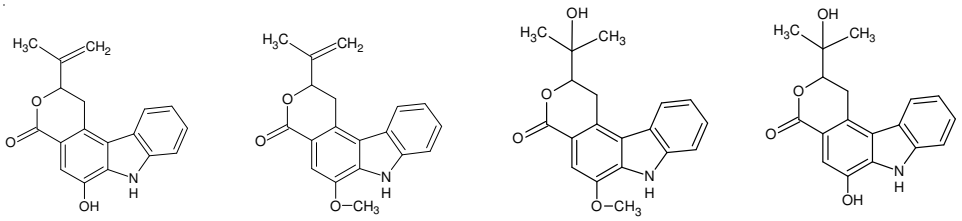
Scheme-XXXII

Using the methodology of laser flash photolysis both in polar and non-polar solvents photoinduced intramolecular events of newly synthesized *bis*(carbazole trimer)-C_{60} adducts have been systematically studied by Konno *et al.*[99]. Pyrrolo[2,3-a]-carbazole derivatives (**90**) were synthesized and were evaluated for their effects on CDK1/cyclinB activity were evaluated by Fousteris *et al.*[100].



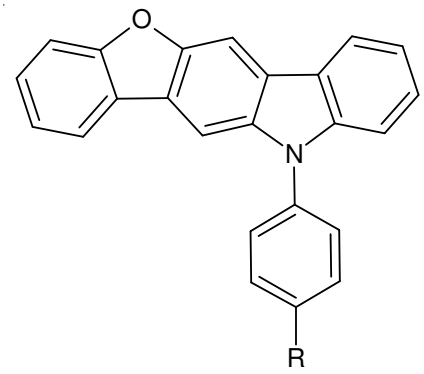
90

The first total syntheses of clausamines A-C and clausevatine D (**Scheme-XXXIII**) is reported by Lebold *et al.*[101]. In the main reaction, the carbazole core is constructed regiospecifically making use of Diels-Alder reaction between an imine quinone and cyclic diene.



Scheme-XXXIII

Making use of unsymmetrical heteroacenes palladium-catalyzed double N-arylation of arylamines, 11-phenylbenzofuro[3,2-b]carbazole (Ph-BFC) (**91**) and its alkoxylated derivatives were readily prepared by Kawaguchi *et al.*[102]. These derivatized carbazoles were able to form antiparallel co facial π-stacking arrangements due to their unsymmetrical structures. Their physical properties show that they have potential to act as active layers in organic field-effect transistors.



91

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